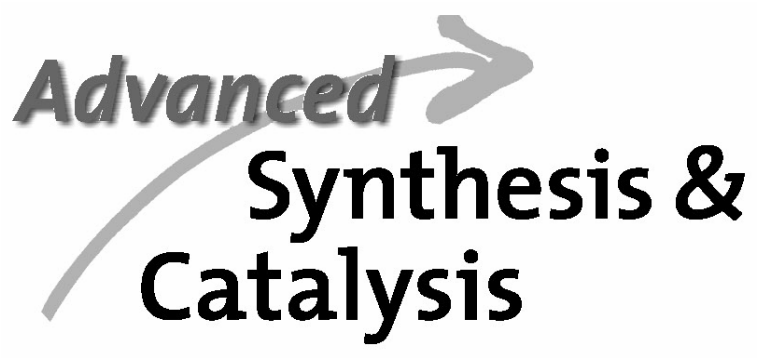

Supporting Information

Supporting Information for

Brønsted Acid-Catalyzed Highly Efficient Cycloisomerizations of Alkynes Bearing Bis(acetoxy) Groups to Indenyl Ketones

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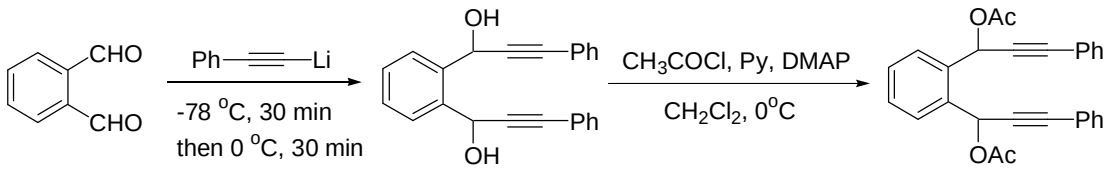
Experimental section

All reactions were carried out under nitrogen. The solvent of THF was distilled from sodium/benzophenone and CH_2Cl_2 was distilled from P_2O_5. Alkynes such as 1-hexyne or phenylacetylene were purchased from Acros Co. Ltd. Trifluoromethanesulfonic acid was

purchased from Acros Co. Ltd. All commercial reagents were used without further purification.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Varian XL-300 MHz spectrometer at 300, 75.4 and 282.3MHz, respectively, and in $CDCl_3$ (containing 0.03% TMS) solutions. ^{1}H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ= 77.00 ppm) as internal reference, and ^{19}F NMR spectra was referenced to $CFCl_3$. NMR yields were determined using dibromomethane as an internal standard. 2D NMR experiments of HMQC, gCOSY and HMBC spectra were recorded in $CDCl_3$ solutions on Varian XL-300 MHz spectrometer. Mass spectra and high-resolution mass spectra were obtained by using HP5989A, IonSpec 4.7 Tesla FTMS, Waters Micromass GCT, and APEXIII 7.0 TESLA FTMS mass spectrometers. Elemental analyses were performed on an Italian Carlo-Erba 1106 analyzer. Single crystal X-ray diffraction data were collected on Bruker SMART APEX diffractiometers with molybdenum cathodes.

A typical procedure for the preparation of diester 1a.[1, 2]



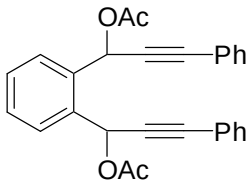
1a

To a solution of phenylacetylene (2.4 mL, 22 mmol) in dry THF (40 mL) was added n-BuLi (13.1 ml, 21 mmol, 1.6M in hexanes) slowly at –78 °C, and the mixture was stirred for 30 minutes at the same reaction temperature. *o*-Phthalaldehyde (1.34g, 10 mmol) was added and stirred for another 30 minutes at –78 °C, then the mixture was warmed up to 0 °C and stirred for 30 minutes. The reaction was quenched with a saturated aquous solution of NH_4Cl and extracted with EtOAc. The extract was washed with brine and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was used directly for the next step.

To a solution of the above residue, pyridine (20 equiv.) and catalytic amount of DMAP in anhydrous CH_2Cl_2 was slowly added acetyl chloride (4 equiv.) at 0 °C. The reaction was stirred at the same temperature for 30 min before being diluted with hexanes. The solid precipitates

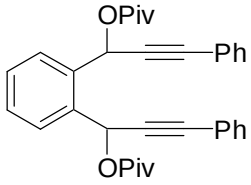
were filtered off and the filtrate obtained was concentrated. The residue was purified through silica gel flash column chromatography (hexanes/ethyl acetate = 20/1) to yield the desired acetate.

The diesters of **2a**, **1f**, **5** and **8** were prepared according to above procedures.



1a

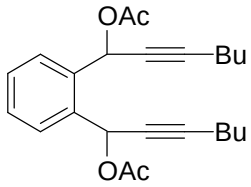
Acetic acid 1-[2-(1-acetoxy-3-phenyl-prop-2-ynyl)-phenyl]-3-phenyl-prop-2-ynyl ester (1a). This is a known compound.[3] Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 20:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.4:1 as a sticky liquid in 83% combined yield (two steps from *o*-phthalaldehyde). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers, d 2.02 (s, 6H), 2.05 (s, 6H), 7.15-7.23 (m), 7.39-7.41 (m), 7.73-7.80 (m). ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers, 20.46, 20.49, 63.07, 63.33, 85.36, 85.43, 86.78, 87.28, 121.49, 121.51, 127.87, 127.89, 128.46, 128.50, 128.93, 129.04, 129.15, 131.43, 131.51, 134.89, 135.04, 168.92, 168.98. LRMS (ESI) for $C_{28}H_{22}O_4Na$ $[M+Na]^+$: calcd 445.1, found 445.1.



2a

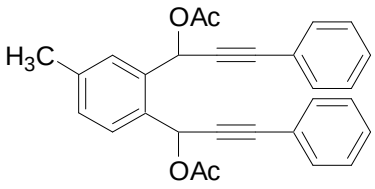
2,2-Dimethyl-propionic acid 1-{2-[1-(2,2-dimethyl-propionyloxy)-3-phenyl- prop-2-ynyl] -phenyl}-3-phenyl-prop-2-ynyl ester (2a). Ester was formed by using 2,2-dimethyl-propionyl chloride instead of acetyl chloride. Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 20:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.2:1 as a sticky liquid in 94% combined yield (two steps from *o*-phthalaldehyde). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers, d

1.15 (s), 7.02 (s), 7.05 (s), 7.11-7.18 (m), 7.25-7.35 (m), 7.60-7.64 (m), 7.70-7.73 (m). ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers, d 26.73, 26.75, 38.53, 63.22, 63.43, 85.75, 85.93, 86.52, 87.21, 121.87, 121.91, 127.89, 127.93, 128.41, 128.44, 128.94, 128.97, 129.09, 131.59, 131.64, 135.30, 135.31, 176.43, 176.52. LRMS (ESI) for $C_{34}H_{34}O_4Na$ $[M+Na]^+$: calcd 529.2, found 529.3.



1f

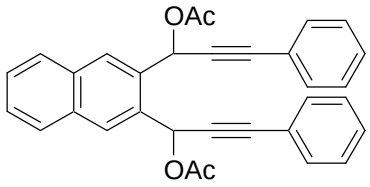
Acetic acid 1-[2-(1-acetoxy-hept-2-ynyl)-phenyl]-hept-2-ynyl ester (1f). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 20:1) afforded the title compound as a mixture of two diastereomers with a ratio of 3.21:1 as a sticky liquid in 85% combined yield (two steps from *o*-phthalaldehyde). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers, d 0.86-0.92 (m), 1.30-1.54 (m), 2.06 (s), 2.10 (s), 2.18-2.28 (m), 6.74 (s), 6.75 (s), 7.36-7.40 (m), 7.61-7.70 (m). ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers, d 13.49, 18.48, 18.52, 20.97, 21.87, 30.31, 30.36, 63.09, 63.53, 76.57, 88.31, 88.68, 128.47, 128.93, 128.98, 129.03, 135.44, 135.59, 169.41. HRMS (ESI) for $C_{24}H_{30}O_4Na$ $[M+Na]^+$: calcd 405.2042, found 405.2032.



5

Acetic acid 1-[2-(1-acetoxy-3-phenyl-prop-2-ynyl)-4-methyl-phenyl]-3-phenyl-prop-2-ynyl ester (5). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1:1 as a colorless liquid in 80% combined yield (two steps from aldehyde). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: d 2.05 (s), 2.07 (s), 2.08 (s), 2.09 (s), 2.38 (s),

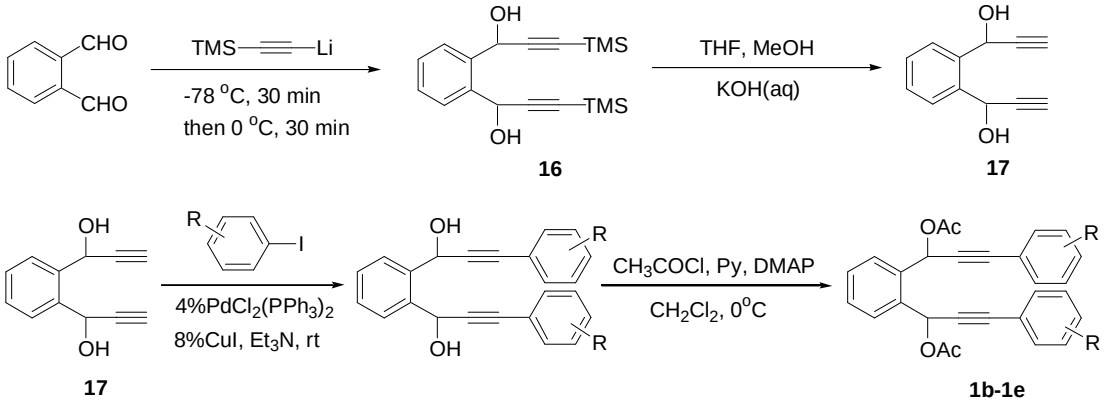
7.05-7.06 (m), 7.19-7.26 (m), 7.40-7.42 (m), 7.53-7.67 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: d 20.89, 21.10, 63.28, 63.40, 63.52, 63.67, 85.60, 85.65, 85.69, 85.73, 86.78, 86.87, 87.30, 87.39, 121.89, 121.91, 128.04, 128.07, 128.59, 128.61, 128.93, 129.28, 129.37, 129.80, 129.99, 130.06, 131.71, 131.80, 131.82, 132.22, 132.38, 134.88, 135.03, 139.29, 139.40, 169.29, 169.32, 169.36, 169.39; IR (neat): 3055, 2228, 1744, 1598, 1490, 1443, 1369, 1224, 1015, 996, 966, 757, 691 cm^{-1}; HRMS (MALDI/DHB) for $C_{29}H_{24}O_4Na$ $[M+Na]^+$: calcd 459.1567, found 459.1566.



8

Acetic acid 1-[3-(1-acetoxy-3-phenyl-prop-2-ynyl)-naphthalen-2-yl]-3-phenyl -prop-2-ynyl ester (8). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.5:1 as a light yellow liquid in 61% combined yield (two steps from aldehyde) . ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: d 2.11 (s), 2.13 (s), 7.22-7.27 (m), 7.42-7.47 (m), 7.49-7.52 (m), 7.87-7.90, (m), 8.23 (s), 8.27(s); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: d 20.95, 63.74, 64.01, 85.59, 85.69, 87.21, 87.72, 121.84, 121.87, 127.05, 127.12, 127.85, 127.88, 128.09, 128.11, 128.67, 128.71, 129.25, 131.76, 131.85, 132.55, 132.61, 132.99, 133.01, 169.39, 169.43; IR (neat): 3057, 2228, 1745, 1598, 1490, 1443, 1369, 1224, 1015, 958, 889, 756, 691 cm^{-1}; HRMS (MALDI/DHB) for $C_{32}H_{24}O_4K$ $[M+K]^+$: calcd 511.1306, found 511.1306.

General procedure for the preparation of diester 1b-1f.[1,2]



1,1'-(1,2-Phenylene)bis(3-(trimethylsilyl)prop-2-yn-1-ol) 16: To a solution of trimethlysilylacetylene (3.13 mL, 22 mmol) in dry THF (40 mL) was added n-BuLi (13.1 ml, 21 mmol, 1.6M in hexanes) slowly at –78 °C, and the mixture was stirred for 30 minutes at the same reaction temperature. *o*-Phthalaldehyde (1.34g, 10 mmol) was added and stirred for another 30 minutes at –78 °C, then the mixture was warmed up to 0 °C and stirred for 30 minutes. The reaction was quenched with a saturated aquous solution of NH_4Cl and extracted with EtOAc. The extract was washed with brine (2 x 50 mL) and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was used directly for the next step.

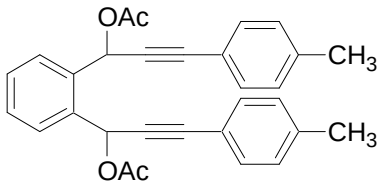
1-[2-(1-Hydroxy-prop-2-ynyl)-phenyl]-prop-2-yn-1-ol 17:[1] To a solution of the above residue containing **16** (ca. 10 mmol) in THF (20 mL) and MeOH (20 mL) was added KOH (aq) (160 mg, 2.86 mmol; in 8 mL of water) at 0 °C. After stirring for 1 hour, the volatiles were removed and the residue was dissolved in EtOAc and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude residue was purified by column chromatography on silica gel to yield **17** (1.78 g, 96%, two steps from *o*-phthalaldehyde) as a brown liquid. NMR spectra show that it is a mixture of two diastereomers with a ratio of 2.27:1. Major isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.68-2.71 (m), 4.32 (d, J = 2.4 Hz, 2H), 5.74 (bs, 2H), 731-7.39 (m), 7.77-7.81 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 61.19, 75.99, 82.24, 127.79, 129.07, 136.97. Minor isomer: ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.68-2.71 (m), 4.74 (d, J = 4.2 Hz, 2H), 5.91 (bs, 2H), 7.31-7.39 (m), 7.58-7.62 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si) d 62.71, 75.69, 82.50, 128.99, 137.46. One peak was overlapped with the signals of the major isomer.

General procedure for the synthesis of diacetate 1b-1e.

Terminal alkyne **17** (1.0 mmol), $PdCl_2(PPh_3)_2$ (0.04 mmol) and CuI (0.08 mmol) were

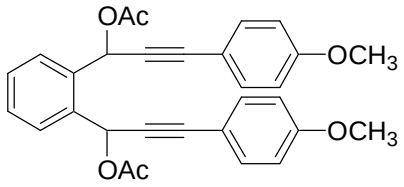
added in a dry Schlenk tube. To the mixture were added Et_3N (5 mL) and the aryl iodide (2.2 mmol). The resulting mixture was stirred at room temperature until the reaction was completed as monitored by thin-layer chromatography. The reaction was quenched with a saturated NH_4Cl solution and extracted with ether. The combined organic layers were washed with brine and dried over Na_2SO_4. The product was then purified by flash column chromatography or used directly for the next step.

To a solution of the above diol (1.0 mmol), pyridine (1.62 mL, 20.0 mmol) and a catalytic amount of DMAP in anhydrous CH_2Cl_2 (4.0 mL) at 0 ^oC, was slowly added acetyl chloride (0.29 mL, 4.0 mmol).[2] The reaction mixture was stirred at 0 ^oC for 30 minutes before being diluted with hexanes (30 mL). The solid precipitates were filtered off and the filtrate obtained was concentrated. The residue was purified by flash chromatography on silica gel to give the desired diacetate . NMR spectra show that it is a mixture of two diastereomers.



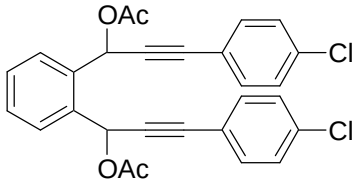
1b

Acetic acid 1-[2-(1-acetoxy-3-*p*-tolyl-prop-2-ynyl)-phenyl]-3-*p*-tolyl-prop-2-ynyl ester (1b). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.5:1 as a white solid in 80% combined yield (two steps from diol **17**). ^1H NMR ($CDCl_3$, Me_4Si) two isomers: d 2.08 (s), 2.09 (s), 2.31 (s), 7.03-7.07 (m), 7.29-7.33 (m), 7.41-7.45 (m), 7.71-7.79 (m); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) two isomers: d 20.95, 21.41, 63.49, 63.71, 84.80, 84.90, 87.22, 87.73, 118.82, 118.85, 128.81, 128.85, 128.87, 129.16, 129.21, 129.31, 131.70, 131.81, 135.25, 135.37, 138.82, 138.83, 169.39, 169.45; IR (KBr): ?/cm^{-1} 3031, 2923, 2229, 1742, 1510, 1451, 1369, 1221, 1015, 952, 912, 818, 765; Anal. Calcd for $C_{30}H_{26}O_4$: C, 79.73; H, 5.83. Found: C, 79.98; H, 5.82.



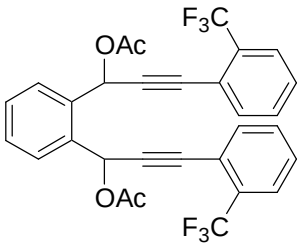
1c

Acetic acid 1-{2-[1-acetoxy-3-(4-methoxy-phenyl)-prop-2-ynyl]-phenyl}-3-(4-methoxy-phenyl)-prop-2-ynyl ester (1c). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.59:1 as a brown solid in 76% combined yield (two steps from diol **17**). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: d 2.07 (s), 2.08 (s), 3.70 (s), 3.71 (s), 6.73-6.77 (m), 7.08 (s), 7.33-7.38 (m), 7.39-7.43 (m), 7.71-7.79 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: d 20.74, 54.91, 63.36, 63.61, 84.13, 84.16, 86.92, 87.43, 113.58, 113.70, 128.56, 128.97, 129.05, 129.16, 133.16, 133.25, 135.16, 135.28, 159.69, 169.21, 169.27. HRMS (EI) for $C_{28}H_{23}O_4$ $[M\text{-}CH_3COO]^+$: calcd 423.1596, found 423.1589.



1d

Acetic acid 1-{2-[1-acetoxy-3-(4-chloro-phenyl)-prop-2-ynyl]-phenyl}-3-(4-chloro-phenyl)-prop-2-ynyl ester (1d). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 5:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.03:1 in 37% combined yield (two steps from diol **17**). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers, d 2.08 (s), 2.10 (s), 7.08 (s), 7.09 (s), 7.17-7.28 (m), 7.31-7.33 (m), 7.41-7.445 (m), 7.71-7.77 (m). ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers, d 20.70, 63.09, 63.40, 85.72, 86.26, 86.42, 120.14, 128.31, 128.35, 128.63, 129.08, 129.26, 129.36, 132.87, 134.65, 134.81, 134.99, 169.09, 169.13. HRMS (MALDI/DHB) for $C_{28}H_{20}Cl_2O_4Na$ $[M+Na]^+$: calcd: 513.0631, found 51.3.0642.

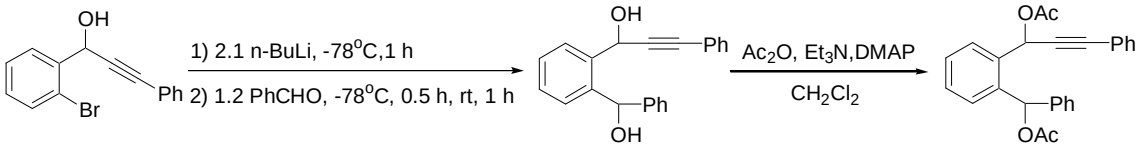


1e

Acetic acid 1-{2-[1-acetoxy-3-(2-trifluoromethyl-phenyl)-prop-2-ynyl]-phenyl}-3-(2-trifluoromethyl-phenyl)-prop-2-ynyl ester (1e). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 1.6:1 as a colorless liquid in 62% combined yield (two steps from diol **17**) . ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: d 2.08 (d, J = 5.7 Hz, 3H), 2.11 (d, J = 6.0 Hz, 3H), 7.10 (s, 1H), 7.11 (s, 1H), 7.33-7.48 (m), 7.53-7.60 (m), 7.80-7.87 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: d 20.51, 62.89, 63.35, 82.97, 83.31, 90.81, 90.91, 119.90, 123.20 (q, J_{C-F} = 271.9Hz), 125.57 (q, J_{C-F} = 5.0Hz), 128.51, 128.86, 129.38, 129.41, 129.52, 131.25, 131.47 (q, J_{C-F} = 33.2Hz), 133.89, 134.02, 134.33, 134.55, 169.23; ^{19}F NMR ($CDCl_3$, Me_4Si) d -62.59, -62.51; IR (neat): 3074, 3038, 3005, 2234, 1747, 1603, 1574, 1492, 1452, 1371, 1319, 1225, 1173, 1131, 1016, 956, 765 cm^{-1}; HRMS (ESI) for $C_{30}H_{20}O_4F_6Na$ $[M+Na]^+$: calcd 581.1158, found 581.1155.

Preparation of the diesters of 1g, 1j, 1k, 1l, 1m and 1o.

A typical procedure for the preparation of diester 1g.

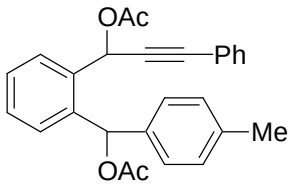


1g

To a stirring solution of 1-(2-bromophenyl)-3-phenylprop-2-yn-1-ol [4](1 mmol) in THF (4 mL) was slowly added n-BuLi (1.31 mL, 2.1 mmol, 1.6 mol/L) at -78 ^{o}C. The resulting solution was stirred at this temperature for 1 h. Then benzaldehyde (1.2 mmol) was added and stirred at -78 ^{o}C for 0.5 h and at room temperature for 1 h. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated by

rotary evaporation to yield the diol which was used directly without further purification.

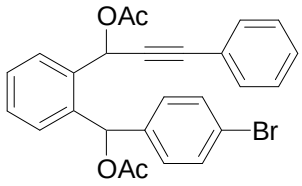
To a solution of the crude diol in dichloromethane were added DMAP (0.2 mmol), Ac_2O (4 mmol), triethylamine (6 mmol), and the reaction mixture was stirred for 0.5 h. After addition of an appropriate volume of aqueous saturated $NaHCO_3$ solution to adjust the pH of the aqueous phase at 9–10, the mixture was extracted with EtOAc, dried over Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by flash chromatography on silica gel (ethyl acetate / petroleum ether 1:8) to give the desired diester of **acetic acid [2-(1-acetoxy-3-phenyl-prop-2-ynyl)-phenyl]- phenyl-methyl ester (1g)** in 58% yield as yellow oil. ^{1}H NMR shows that it is a mixture of two diastereomers with a ratio of 3.3:1. ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: d 1.84 (s), 1.96 (s), 2.13 (s), 2.13 (s), 6.85 (s), 6.95 (s), 7.24-7.36 (m), 7.37-7.46 (m), 7.55-7.58 (m), 7.75-7.78 (m), 7.81-7.85 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: d 20.48, 20.54, 20.96, 20.99, 63.28, 63.43, 73.02, 73.24, 85.18, 85.23, 87.03, 87.45, 121.79, 121.81, 127.34, 127.36, 127.80, 127.84, 128.03, 128.12, 128.25, 128.28, 128.33, 128.40, 128.45, 128.53, 128.59, 128.76, 128.83, 129.06, 129.10, 131.69, 134.57, 134.77, 137.51, 137.61, 139.12, 139.36, 169.14, 169.38, 169.53, 169.56; HRMS (ESI) for $C_{26}H_{22}O_4Na$ $[M+Na]^+$: calcd: 421.1410, found 421.1408.



1j

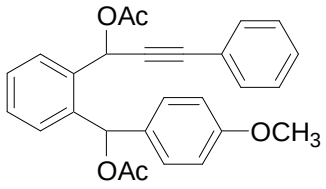
Acetic acid [2-(1-acetoxy-3-phenyl-prop-2-ynyl)-phenyl]-*p*-tolyl-methyl ester (1j). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=8:1) afforded the desired product in 57% yield as a yellow liquid. ^{1}H NMR shows that it is a mixture of two diastereomers with a ratio of 4.2:1. ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: d 1.84 (s), 1.98 (s), 2.11 (s), 2.28 (s), 6.86 (s), 6.95 (s), 7.08-7.31 (m), 7.35-7.47 (m), 7.56-7.59 (m), 7.75-7.83 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: d 20.22, 20.29, 20.69, 20.71, 62.99, 63.25, 72.84, 85.13, 87.22, 121.61, 127.15, 127.34, 127.57, 127.86, 128.11, 128.20, 128.28, 128.41, 128.51, 128.75, 128.89, 130.14, 131.47, 134.21, 134.59,

136.03, 136.24, 137.30, 137.44, 137.62, 168.87, 169.28, 169.34; HRMS (ESI) for $C_{27}H_{24}O_4Na$ $[M+Na]^+$: calcd: 435.1567, found 435.1546.



1k

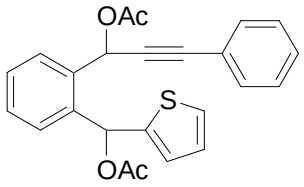
Acetic acid 1-{2-[acetoxy-(4-bromo-phenyl)-methyl]-phenyl}-3-phenyl- prop-2-ynyl ester (1k). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=8:1) afforded the desired product in 63% yield as a yellow oil. ^{1}H NMR shows that it is a mixture of two diastereomers with a ratio of 2.2:1. ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: d 1.91 (s), 1.97 (s), 2.10 (s), 2.11 (s), 6.87 (s), 6.94 (s), 7.15-7.26 (m), 7.30-7.42 (m), 7.52-7.55 (m), 7.74-7.81 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: d 20.55, 20.90, 63.08, 63.56, 72.48, 72.52, 85.05, 85.09, 87.11, 87.58, 121.60, 121.83, 121.94, 127.91, 128.04, 128.60, 128.63, 128.66, 128.69, 128.74, 128.93, 128.98, 129.11, 129.17, 129.19, 131.31, 131.40, 131.59, 131.62, 134.57, 134.94, 136.92, 137.06, 138.36, 138.49, 169.10, 169.27, 169.37, 169.41; HRMS (ESI) for $C_{26}H_{21}O_4BrNa$ $[M+Na]^+$: calcd: 499.0515, found 499.0492.



1l

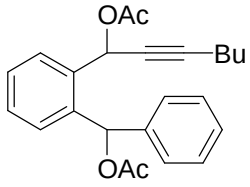
Acetic acid [2-(1-acetoxy-3-phenyl-prop-2-ynyl)-phenyl]-(4-methoxy-phenyl)-methyl ester (1l). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate= 5:1) afforded the desired product in 70% yield as a yellow liquid. ^{1}H NMR shows that it is a mixture of two diastereomers with a ratio of 2.4:1. ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: d 1.81 (s), 1.97 (s), 2.07 (s), 3.65 (s), 3.66 (s), 6.81 (d, J = 8.7 Hz), 6.87 (s), 6.97 (s), 7.19-7.26 (m), 7.30-7.40 (m), 7.47-7.50 (m), 7.59-7.62 (m), 7.76-7.84 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: d 20.31, 20.42, 20.83, 20.85, 54.82, 62.99, 63.22,

72.75, 85.04, 85.12, 86.88, 87.26, 113.46, 113.58, 121.64, 121.67, 127.25, 127.91, 128.02, 128.10, 128.21, 128.46, 128.55, 128.59, 128.75, 128.93, 129.00, 130.99, 131.25, 131.52, 134.10, 134.46, 137.68, 159.03, 159.10, 168.95, 169.30, 169.38, 169.46; HRMS (ESI) for $C_{27}H_{24}O_5Na$ $[M+Na]^+$: calcd: 451.1516, found 451.1529.



1m

Acetic acid 1-[2-(acetoxy-thien-2-yl-methyl)-phenyl]-3-phenyl-prop-2-ynyl ester (1m). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=8:1) afforded the desired product in 62% yield as a yellow liquid. ^{1}H NMR shows that it is a mixture of two diastereomers with a ratio of 3.7:1. ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: d 1.85 (s), 1.90 (s), 2.06 (s), 6.85-6.87 (m), 7.00 (s), 7.19-7.28 (m), 7.34-7.47 (m), 7.60-7.64 (m), 7.68-7.74 (m), 7.81-7.84 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: d 20.29, 20.36, 20.80, 20.82, 63.40, 63.47, 68.79, 69.00, 84.84, 87.11, 87.57, 121.61, 126.25, 126.34, 126.37, 127.20, 127.22, 127.36, 127.79, 127.93, 127.94, 128.53, 128.61, 128.66, 129.09, 129.16, 131.57, 131.59, 134.09, 137.35, 137.43, 142.53, 142.96, 169.03, 169.25, 169.28, 169.31; HRMS (ESI) for $C_{24}H_{20}O_4SNa$ $[M+Na]^+$: calcd: 427.0975, found 427.0954.

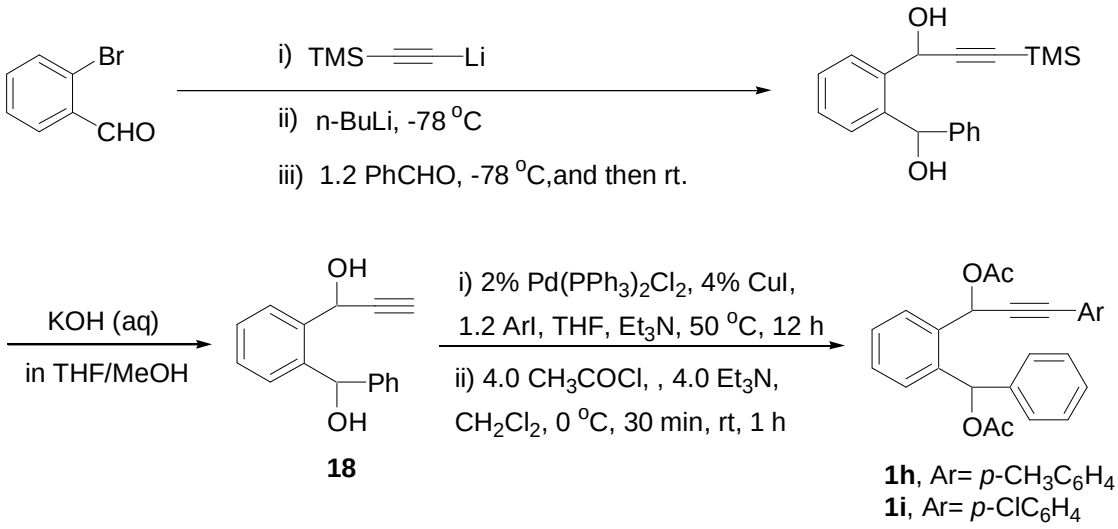


1o

Acetic acid [2-(1-acetoxy-hept-2-ynyl)-phenyl]-phenyl-methyl ester (1o). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=8:1) afforded the desired product in 75% yield as a colorless liquid. ^{1}H NMR shows that it is a mixture of two diastereomers with a ratio of 1.6:1. ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers: d 0.86 (t, J = 6.9 Hz), 0.88 (t, J = 7.2 Hz), 1.32-1.48 (m), 1.78 (s), 1.93 (s), 2.12-2.19 (m), 6.61 (t,

J = 1.8 Hz), 6.70 (t, *J* = 1.8 Hz), 7.23-7.34 (m), 7.36-7.42 (m), 7.52-7.55 (m), 7.67-7.70 (m), 7.74-7.77 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers: d 13.50, 18.43, 20.61, 20.73, 21.09, 21.13, 21.87, 30.24, 30.28, 63.24, 63.56, 73.03, 73.16, 76.30, 76.33, 88.56, 89.00, 127.48, 127.50, 127.81, 127.85, 127.98, 128.25, 128.33, 128.34, 128.41, 128.71, 128.80, 128.90, 128.97, 135.12, 135.28, 137.48, 137.61, 139.31, 139.47, 169.34, 169.59, 169.64; HRMS (ESI) for $C_{24}H_{26}O_4Na$ $[M+Na]^+$: calcd: 401.1723, found 401.1739.

General procedure for the preparation of diesters 1h and 1i.



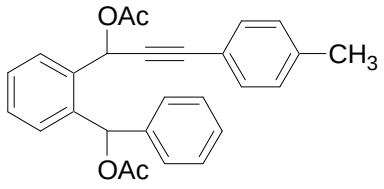
n-BuLi (1.6 M in hexane, 3.13 mL, 5.0 mmol) was slowly added to a solution of trimethylsilylacetylene (0.74 mL, 5.25 mmol) in dry THF (10 mL) cooled at -78 °C, and the mixture was stirred for 30 minutes before 2-bromobenzaldehyde (0.59 mL, 5.0 mmol) was slowly added. The reaction mixture was then warmed up to room temperature and stirred for 1 h. The mixture was cooled down again to -78 °C and n-BuLi (3.44 mL. 5.5 mmol) was slowly added. After stirring for 1.5 h, benzaldehyde (0.608 mL, 6.0 mmol) was added and stirred for 0.5 h at -78 °C. The reaction mixture was warmed up to room temperature and stirred for 2 h, then it was quenched with saturated NH_4Cl, diluted with ethyl acetate. The organic layer was separated, washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, filtered and concentrated.

To a solution of the above crude residue in THF (10 mL) and MeOH (10 mL) was added KOH (aq) (40 mg, 0.72 mmol, in 4 mL of water) at 0 °C. After stirring for 2 hours, volatiles were removed and the residue was dissolved in ethyl acetate (50 mL). The organic layer was

separated, washed with brine (2 x 30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by column chromatography on silica-gel using petroleum ether / ethyl acetate 2:1 as eluent to yield **1-[2-(Hydroxy-phenyl-methyl)-phenyl]-prop-2-yn-1-ol (18)** as a mixture of two diastereomers with a ratio of 9:1 in 69% yield (overall yield from 2-bromobenzaldehyde). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers, d 2.52 (d, *J* = 2.4 Hz), 2.58 (d, *J* = 2.4 Hz), 4.60 (s), 4.76 (s), 5.38 (s), 5.65 (s), 6.02 (s), 6.17 (s), 7.00 (dd, *J*= 7.6, 1.2 Hz), 7.07-7.12 (m), 7.17-7.27 (m), 7.55-7.58 (m), 7.75 (dd); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers, d 61.25, 62.51, 71.44, 73.50, 75.34, 75.59, 82.79, 126.10, 126.72, 127.13, 127.36, 127.55, 128.06, 128.16, 128.22, 128.64, 128.72, 129.71, 137.32, 137.69, 140.94, 141.15, 141.89, 142.20. HRMS (EI) for $C_{16}H_{14}O_2$: calcd: 238.0994, found 238.0995.

To a solution of **18** (238.3 mg, 1.0 mmol) in THF (4 mL) and Et_3N (1 mL) were added 1-iodo-4-methylbenzene (262 mg, 1.2 mmol), CuI (8 mg, 0.04 mmol) and $Pd(PPh_3)_2Cl_2$ (15 mg, 0.02 mmol). The mixture was stirred at 50 ^{o}C for 12 h, then quenched with saturated NH_4Cl at room temperature, diluted with ethyl acetate. The organic layer was separated, washed with saturated $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, filtered and concentrated.

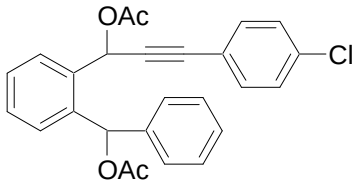
To a solution of the above residue in dry CH_2Cl_2 (4 mL) and Et_3N (0.58 mL, 4.0 mmol) was added acetyl chloride (0.292 mL, 4.0 mmol) slowly at 0 ^{o}C. After stirring for 0.5 h, the mixture was warmed up to room temperature and stirred for 1 h. The reaction mixture was then quenched with saturated $NaHCO_3$, diluted with ethyl acetate. The organic layer was separated, washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica-gel to afford the desired acetate (**1h**).



1h

Acetic acid [2-(1-acetoxy-3-*p*-tolyl-prop-2-ynyl)-phenyl]-phenyl-methyl ester (1h).

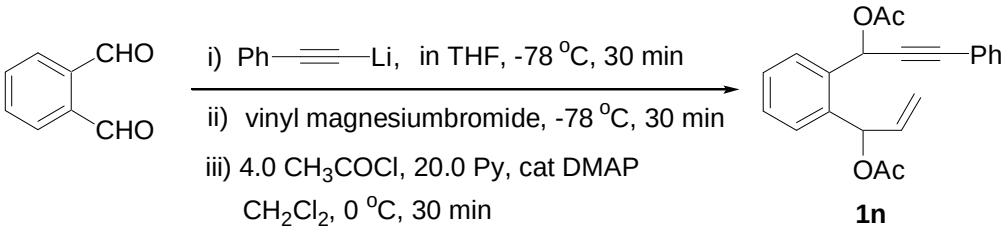
Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 10:1) afforded the title compound as a mixture of two diastereomers with a ratio of 9:1 as yellow oil in 76% yield (overall yield from diol **18**). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers, d 1.81 (s), 1.93 (s), 2.10 (s), 2.28 (s), 6.87 (s), 6.97 (s), 7.05 (d, *J* = 8.4 Hz), 7.19-7.44 (m), 7.53-7.57 (m), 7.75-7.78 (m), 7.82-7.86 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers, d 20.47, 20.55, 20.95, 20.98, 21.30, 63.35, 63.52, 72.99, 73.22, 84.50, 84.54, 87.23, 87.66, 118.76, 127.35, 127.78, 127.83, 128.10, 128.24, 128.32, 128.38, 128.43, 128.51, 128.76, 128.79, 128.83, 129.02, 129.05, 131.62, 134.68, 134.92, 137.51, 137.60, 138.73, 139.15, 139.39, 169.16, 169.41, 169.55. HRMS (ESI) for $C_{27}H_{24}O_4Na$ $[M+Na]^+$: calcd: 435.1567, found 435.1581.



1i

Acetic acid {2-[1-acetoxy-3-(4-chloro-phenyl)-prop-2-ynyl]-phenyl}-phenyl- methyl ester (1i). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate = 8:1) afforded the title compound as a mixture of two diastereomers with a ratio of 9:1 as yellow oil in 63% yield (overall yield from diol **18**). ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers, d 1.84 (s), 1.91 (s), 2.11 (s), 6.86 (s), 6.96 (s), 7.20-7.47 (m), 7.56-7.59 (m), 7.71-7.74 (m), 7.77-7.81 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers, d 20.45, 20.95, 20.98, 63.28, 63.36, 73.00, 73.19, 86.19, 86.26, 120.29, 127.34, 127.41, 127.82, 128.18, 128.25, 128.32, 128.35, 128.47, 128.57, 128.70, 128.77, 129.18, 132.94, 132.96, 134.35, 134.55, 134.61, 137.51, 137.62, 139.08, 139.37, 169.10, 169.30, 169.51, 169.55. HRMS (ESI) for $C_{26}H_{21}ClO_4Na$ $[M+Na]^+$: calcd: 455.1021, found 455.1043.

Preparation of diester 1n.



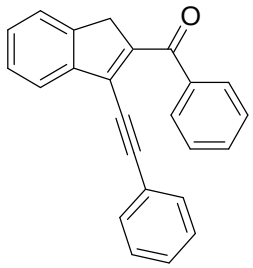
1n

n-BuLi (1.6 M in hexane, 1.38 mL, 2.2 mmol) was slowly added to a solution of phenylacetylene (0.26 mL, 2.4 mmol) in dry THF (5 mL) cooled at -78 ^{o}C, and the mixture was stirred for 30 minutes before adding to a cooled solution of *o*-phthalaldehyde (0.27 g, 2.0 mmol) in THF (5 mL). After 30 minutes a solution of the vinylmagnesium bromide (4 mmol) was added via cannula. The reaction mixture was stirred for 30 minutes at -78 ^{o}C, then quenched with brine (30 mL) and 3M HCl (10 mL), diluted with ethyl acetate (30 mL). The organic layer was separated, washed with brine (2 x 15), dried over anhydrous Na_2SO_4, filtered and concentrated.

To a solution of the above residue, pyridine (3.30 mL, 40.0 mmol) and catalytic amount of DMAP in anhydrous CH_2Cl_2 (12 mL) at 0 ^{o}C was slowly added acetyl chloride (0.58 mL, 8.0 mmol). The reaction was stirred at the same temperature for 30 min before being diluted with hexanes (15 mL). The solid precipitates were filtered off and the filtrate obtained was concentrated. The residue was purified through silica gel flash column chromatography (petroleum ether/ethyl acetate = 5:1) to yield the desired acetate in 73% yield (overall yield from *o*-phthalaldehyde). ^{1}H NMR show that it is a mixture of two diastereomers with a ratio of 1.6:1. **Acetic acid 1-[2-(1-acetoxy-3-phenyl-prop-2-ynyl)-phenyl]-allyl ester (1n)**. ^{1}H NMR ($CDCl_3$, Me_4Si) two isomers, d 2.05 (s), 2.06 (s), 2.10 (s), 2.11 (s), 5.22-5.28 (m), 5.97-6.12 (m), 6.68-6.70 (m), 6.98 (s), 7.03 (s), 7.25-7.26 (m), 7.35-7.48 (m), 7.73-7.80 (m). ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers, d 20.70, 20.73, 20.78, 20.81, 62.96, 63.48, 72.36, 72.67, 85.39, 85.43, 86.83, 87.29, 116.82, 117.10, 121.70, 121.76, 128.00, 128.30, 128.37, 128.41, 128.45, 128.55, 128.73, 129.02, 129.10, 131.57, 134.58, 134.78, 135.67, 135.79, 136.53, 136.69, 169.10, 169.30, 169.31. HRMS (MALDI/DHB) for $C_{22}H_{20}O_4Na$ $[M+Na]^+$: calcd: 371.1254, found 371.1272.

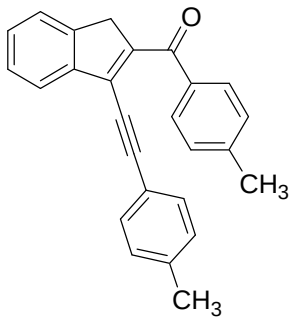
General procedure for the determination of NMR yields listed in Table 1.

To a solution of diacetate **1a or 2a** (0.4 mmol, in 4 mL dry CH_2Cl_2) was added Lewis acids or Brønsted Acids as shown in Table 1. The mixture was kept at room temperature and the reaction was monitored by TLC. After the reaction completed, water (4 mL) and saturated $NaHCO_3$ solution (8 mL) were added to the mixture. Then the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4. The solvent was evaporated in vacuo at room temperature and the residue was taken into a NMR detection using CH_2Br_2 as an internal standard.



3a

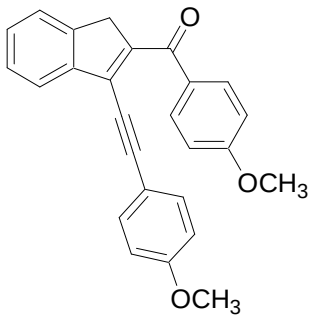
Phenyl-(3-phenylethynyl-1*H*-inden-2-yl)-methanone (3a). Purification of the crude product by flash column chromatography on silica-gel (petroleum ether/ethyl acetate = 5:1) followed by recrystallization in petroleum ether/CH_2Cl_2 afforded the title compound in 65% yield (104 mg, 0.5 mmol scale) as a yellow solid. M.p.116-118 ^oC. ^1H NMR ($CDCl_3$, Me_4Si) d 4.05 (s, 2H), 7.03-7.06 (m, 2H), 7.21-7.30 (m, 3H), 7.42-7.51 (m, 4H), 7.55-7.58 (m, 2H), 7.75-7.77 (m, 1H), 7.91-7.94 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si) d 39.66, 82.88, 101.68, 121.99, 122.47, 124.20, 127.13, 128.04, 128.17, 128.38, 129.09, 129.60, 131.92, 132.20, 132.40, 138.76, 142.86, 143.43, 145.53, 193.73. HRMS (EI) for $C_{24}H_{26}O$: calcd: 320.1201, found 320.1209.



3b

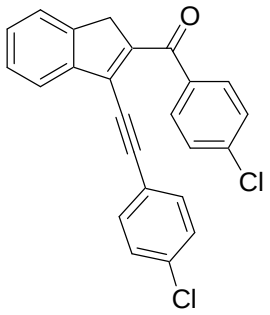
***p*-Tolyl-(3-*p*-tolylethynyl-*1H*-inden-2-yl)-methanone (3b).** Purification of the crude product

by flash column chromatography on silica-gel (petroleum ether/ethyl acetate=3:1) followed by washing with ether afforded the title compound in 70% yield (85 mg, 0.35 mmol scale) as a red brown solid. M.p. 185-187 ^{o}C; ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.32 (s, 3H), 2.42 (s, 3H), 4.03 (s, 2H), 6.92 (d, *J* = 7.2 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.39-7.46 (m, 2H), 7.53-7.56 (m, 1H), 7.73-7.58 (m, 1H), 7.83 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 21.53, 21.58, 39.63, 82.60, 101.78, 119.06, 122.41, 124.15, 127.05, 128.20, 128.65, 128.93, 129.83, 131.83, 132.22, 136.16, 139.39, 142.75, 142.85, 143.49, 145.56, 193.57; IR (neat): 2208, 1628, 1604, 1545, 1371, 1279, 769, 747 cm^{-1}; HRMS (EI) for $C_{26}H_{20}O$ $[M]^+$: calcd 348.1514, found 348.1500.



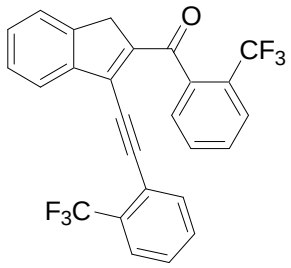
3c

(4-Methoxy-phenyl)-[3-(4-methoxy-phenylethynyl)-1*H*-inden-2-yl]-methanone (3c). Purification of the crude product by flash column chromatography on silica-gel (petroleum ether/ethyl acetate=3:1) followed by recrystallization in petroleum ether/CH_2Cl_2 afforded the title compound in 76% yield (70 mg, 0.4 mmol scale) as a red brown solid. M.p. 171-176 ^{o}C; ^{1}H NMR ($CDCl_3$, Me_4Si) d 3.79 (s, 3H), 3.85 (s, 3H), 4.02 (s, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 7.40-7.44 (m, 2H), 7.53-7.56 (m, 1H), 7.73-7.76 (m, 1H), 7.96 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 39.78, 55.27, 55.44, 82.28, 101.45, 113.20, 113.84, 114.25, 122.27, 124.12, 127.01, 128.02, 131.32, 131.56, 132.17, 133.47, 142.80, 143.53, 145.37, 160.20, 163.08, 192.44; IR (neat): 3002, 2931, 2835, 1600, 1573, 1509, 1459, 1251, 1169, 1029, 833, 758 cm^{-1}; HRMS (EI) for $C_{26}H_{20}O_3$ $[M]^+$: calcd 380.1412, found 380.1394.



3d

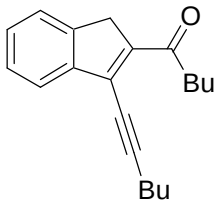
(4-Chloro-phenyl)-[3-(4-chloro-phenylethynyl)-1*H*-inden-2-yl]-methanone (3d). Purification of the crude product by flash column chromatography on silica-gel (petroleum ether/ethyl acetate = 5:1) followed by washing with petroleum ether/ether afforded the title compound in 61% yield (95 mg, 0.4 mmol scale) as a white solid. M.p. 199-201 ^{o}C; ^{1}H NMR ($CDCl_3$, Me_4Si) d 4.04 (s, 2H), 6.97-7.00 (m, 2H), 7.26-7.30 (m, 2H), 7.44-7.47 (m, 4H), 7.56-7.59 (m, 1H), 7.72-7.75 (m, 1H), 7.84-7.87 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si) d 39.60, 83.71, 100.91, 120.26, 122.54, 124.34, 127.28, 128.34, 128.73, 128.82, 131.07, 132.61, 133.02, 135.53, 137.20, 138.52, 142.90, 143.11, 145.57, 192.30. HRMS (EI) for $C_{24}H_{14}Cl_2O$: calcd: 388.0422, found 388.0418.



3e

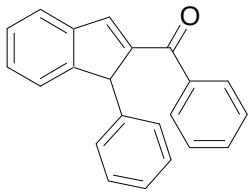
(2-Trifluoromethyl-phenyl)-[3-(2-trifluoromethyl-phenylethynyl)-1*H*-inden-2-yl]-methanone (3e). Purification of the crude product by flash column chromatography on silica-gel (petroleum ether/ethyl acetate=10:1) afforded the title compound in 32% yield (59 mg, 0.4 mmol scale) as a red brown crystal. M.p. 127-129 ^{o}C; ^{1}H NMR ($CDCl_3$, Me_4Si) d 4.04 (s, 2H), 6.88-6.91 (m, 1H), 7.40-7.54 (m, 5H), 7.57-7.64 (m, 4H), 7.72-7.78 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 38.55, 87.01, 98.31, 119.80, 123.14 (q, J_{C-F} = 272.0Hz), 123.28, 123.74 (q, J_{C-F} = 270.2Hz), 124.32, 125.79 (q, J_{C-F} = 5.2Hz), 126.54 (q, J_{C-F} = 4.6Hz), 127.48, 127.76 (q, J_{C-F} = 31.9Hz), 128.23, 128.99, 129.33, 129.57, 131.05, 131.26 (q, J_{C-F} = 30.9Hz), 131.68,

134.45, 135.38, 139.67, 143.11, 143.44, 145.51, 191.58; ^{19}F NMR ($CDCl_3$, Me_4Si) d -62.20, -58.66; IR (neat): 2208, 1627, 1605, 1548, 1371, 1318, 1165, 1135, 1111, 774, 766, 759, 658 cm^{-1}; HRMS (MALDI/DHB) for $C_{26}H_{15}OF_6$ $[M+H]^+$: calcd 457.1022, found 457.1041; Anal. Calcd. for $C_{26}H_{15}OF_6$: C, 68.40, H, 3.11; Found: C, 68.43; H, 3.09.



3f

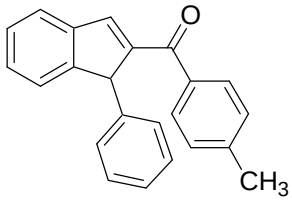
1-(3-Hex-1-ynyl-1*H*-inden-2-yl)-pentan-1-one (3f). Purification of the crude product by flash column chromatography on silica-gel (petroleum ether : CH_2Cl_2 = 2:3) followed by recrystallization in petroleum ether afforded the title compound in 51% yield (143 mg, 1 mmol scale) as a white solid. M.p. 43-45 ^oC; ^{1}H NMR ($CDCl_3$, Me_4Si) d 0.97 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H), 1.39-1.46 (m, 2H), 1.51-1.59 (m, 2H), 1.61-1.85 (m, 4H), 2.61 (t, *J* = 6.9 Hz, 2H), 3.13 (t, *J* = 7.5 Hz, 2H), 3.75 (s, 2H), 7.35-7.40 (m, 2H), 7.44-7.47 (m, 1H), 7.63-7.66 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si) d 13.54, 13.96, 19.69, 22.08, 22.58, 26.64, 30.51, 38.12, 40.96, 75.29, 104.59, 122.50, 124.01, 126.82, 128.23, 132.13, 142.72, 144.20, 145.17, 198.31. HRMS (EI) for $C_{20}H_{24}O$: calcd: 280.1827, found 280.1829.



4g

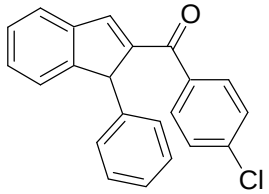
Phenyl(1-phenyl-1*H*-inden-2-yl)methanone (4g). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=10:1) afforded the desired product in 81% yield (72 mg, 0.3 mmol scale) as a yellow solid. M.p. 145-147 ^oC;. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) d 5.18 (s, 1H), 7.15-7.25 (m, 5H), 7.29-7.36 (m, 3H), 7.41-7.56 (m, 5H), 7.80-7.83 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 55.77, 123.82, 124.68, 126.87, 127.44, 127.89, 128.27, 128.57, 128.64, 128.99, 132.10, 138.17, 138.57, 141.57,

142.72, 149.40, 150.30, 191.82; HRMS (EI) for $C_{22}H_{16}O$: calcd: 296.1201, found 296.1204.



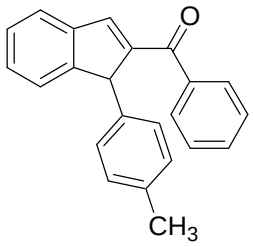
4h

(1-Phenyl-1*H*-inden-2-yl)-*p*-tolyl-methanone (4h). Purification of the crude product by flash column chromatography on silica-gel (petroleum ether/ethyl acetate = 8:1) afforded the title compound in 36% yield (52 mg, 0.46 mmol scale). M.p. 105-106 ^{o}C; ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.40 (s, 3H), 5.19 (d, *J* = 1.5 Hz, 1H), 7.13-7.36 (m, 10H), 7.46 (d, *J* = 2.1 Hz, 1H), 7.51-7.54 (m, 1H), 7.74 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 21.56, 55.87, 123.72, 124.68, 126.86, 127.41, 127.92, 128.50, 128.57, 128.98, 129.22, 135.94, 138.24, 141.69, 142.07, 142.88, 149.63, 150.23, 191.59. HRMS (EI) for $C_{23}H_{18}O$: calcd: 310.1358, found 310.1361.



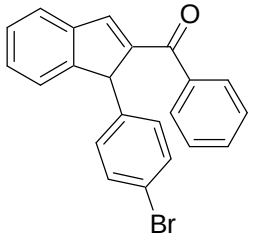
4i

(4-Chloro-phenyl)-(1-phenyl-1*H*-inden-2-yl)-methanone (4i). Purification of the crude product by flash column chromatography on silica-gel (petroleum ether/ethyl acetate = 5:1) afforded the title compound in 91% yield (126 mg, 0.42 mmol scale) as a yellow solid. M.p. 134-135 ^{o}C; ^{1}H NMR ($CDCl_3$, Me_4Si) d 5.16 (s, 1H), 7.14-7.55 (m, 12H), 7.75 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si) d 55.79, 123.91, 124.71, 126.96, 127.52, 127.86, 128.58, 128.61, 128.83, 130.37, 136.86, 137.99, 138.43, 141.40, 142.78, 149.11, 150.28, 190.47. HRMS (EI) for $C_{22}H_{15}ClO$: calcd: 330.0811, found 330.0808.



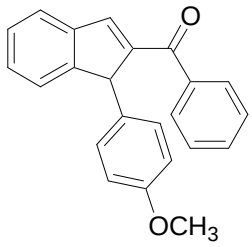
4j

Phenyl(1-p-tolyl-1H-inden-2-yl)methanone (4j). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=10:1) afforded the desired product in 86% yield (80 mg, 0.3 mmol scale) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) d 2.22 (s, 3H), 5.14 (s, 1H), 7.00-7.08 (m, 4H), 7.26-7.32 (m, 3H), 7.38-7.43 (m, 3H), 7.47-7.50 (m, 2H), 7.79-7.81 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) d 20.97, 55.41, 123.73, 124.57, 127.31, 127.69, 128.18, 128.54, 128.95, 129.24, 132.01, 134.97, 136.30, 138.56, 141.51, 142.48, 149.45, 150.39, 191.77; HRMS (EI) for $C_{23}H_{18}O$: calcd: 310.1358, found 310.1351.



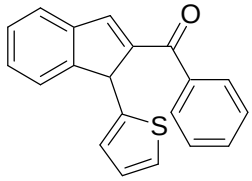
4k

(1-(4-Bromophenyl)-1H-inden-2-yl)(phenyl)methanone (4k). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=10:1) afforded the desired product in 85% yield (95 mg, 0.3 mmol scale) as a yellow solid. M.p. 146-149 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 5.11 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.21-7.37 (m, 5H), 7.40-7.56 (m, 5H), 7.78-7.80 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 55.02, 120.64, 123.99, 124.58, 127.66, 128.30, 128.81, 128.90, 129.67, 131.63, 132.20, 137.36, 138.39, 141.56, 142.98, 148.85, 149.65, 191.60; HRMS (EI) for $C_{22}H_{15}BrO$: calcd: 374.0306, found 374.0315.



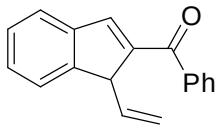
4l

(1-(4-Methoxyphenyl)-1H-inden-2-yl)(phenyl)methanone (4l). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=5:1) afforded the desired product in 95% yield (93 mg, 0.3 mmol scale) as a yellow solid. M.p. 122-124 ^{o}C. ^{1}H NMR ($CDCl_3$, Me_4Si) d 3.67 (s, 3H), 5.14 (d, *J* = 1.5 Hz, 1H), 6.74-6.77 (m, 2H), 7.08-7.11 (m, 2H), 7.27-7.31 (m, 3H), 7.38-7.43 (m, 3H), 7.47-7.51 (m, 2H), 7.79-7.82 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 54.97, 54.98, 113.93, 123.73, 124.56, 127.30, 128.18, 128.52, 128.82, 128.92, 129.86, 132.02, 138.52, 141.45, 142.30, 149.49, 150.43, 158.35, 191.80; HRMS (EI) for $C_{23}H_{18}O_2$: calcd: 326.1307, found 326.1310.



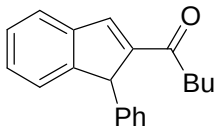
4m

Phenyl(1-(thiophen-2-yl)-1H-inden-2-yl)methanone (4m). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=10:1) afforded the desired product as a mixture of two isomers (the another isomer was suggested to be double bond isomer of phenyl-(3-thiophen-2-yl-1H-inden-2-yl)- methanone, the ratio of two isomers is 8.0:1, **4m** is the major isomer) in 78% combined yield (70 mg, 0.3 mmol scale) as a yellow oil. ^{1}H NMR ($CDCl_3$, Me_4Si) major isomer: d 5.53 (s, 1H), 6.86-6.89 (m, 1H), 7.02-7.08 (m, 2H), 7.31-7.56 (m, 8H), 7.85 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) major isomer: d 50.28, 123.70, 123.97, 124.67, 125.80, 126.72, 127.80, 128.28, 128.67, 129.06, 138.33, 139.96, 140.90, 142.23, 148.59, 148.85, 191.68, one signal was overlapped with other signals; HRMS (EI) for $C_{20}H_{14}OS$: calcd: 302.0765, found 302.0757.



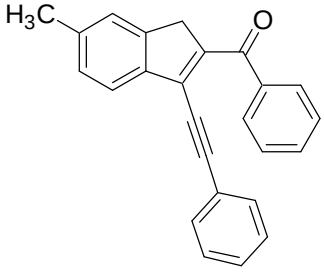
4n

Phenyl-(1-vinyl-1*H*-inden-2-yl)-methanone (4n). Purification of the crude product by flash column chromatography on silica-gel (petroleum ether/ethyl acetate = 5:1) afforded the title compound in 43% yield (42 mg, 0.4 mmol scale) as a liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) d 4.67 (d, *J* = 8.1Hz, 1H), 5.21 (d, *J* = 8.1Hz, 1H), 5.42 (d, *J* = 17.1Hz, 1H),5.73-5.84 (m, 1H), 7.33-7.41 (m, 3H), 7.45-7.59 (m, 5H), 7.83-7.86 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si) d 54.10, 117.60, 123.92, 124.74, 127.53, 128.28, 128.36, 128.99, 132.06, 134.10, 138.76, 141.73, 142.81, 147.50, 147.63, 192.20. HRMS (EI) for $C_{18}H_{14}O$: calcd: 246.1045, found 246.1036.



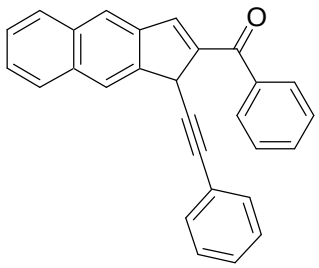
4o

1-(1-Phenyl-1H-inden-2-yl)pentan-1-one (4o). Purification of the crude product by column chromatography on silica-gel (petroleum ether/ethyl acetate=10:1) afforded the desired product in 75% yield (62 mg, 0.3 mmol scale) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) d 0.86 (t, *J* = 7.5 Hz, 3H), 1.21-1.33 (m, 2H), 1.52-1.62 (m, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 4.89 (s, 1H), 7.04-7.07 (m, 2H), 7.15-7.33 (m, 6H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.68-7.69 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) d 13.79, 22.26, 26.50, 39.10, 55.06, 123.65, 124.56, 126.67, 127.28, 127.64, 128.47, 128.54, 138.59, 140.08, 141.26, 149.80, 150.50, 197.39; HRMS (MALDI/DHB) for $C_{20}H_{20}O$: calcd: 276.1514, found 276.1515.



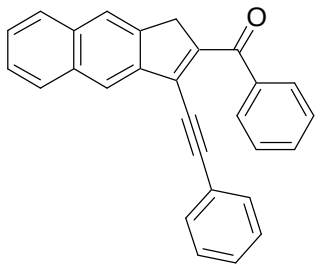
6

(6-Methyl-3-phenylethynyl-1*H*-inden-2-yl)-phenyl-methanone (6). Purification of the crude product by flash column chromatography on silica-gel (petroleum ether/ethyl acetate=5:1) afforded the title compound in 73% yield (51 mg, 0.2 mmol scale) as a red orange solid. M.p. 115-117 ^{o}C; ^{1}H NMR ($CDCl_3$, Me_4Si) d 2.47 (s, 3H), 4.01 (s, 2H), 7.02-7.06 (m, 2H), 7.21-7.32 (m, 4H), 7.38 (s, 1H), 7.45-7.50 (m, 2H), 7.54-7.57 (m, 1H), 7.60-7.64 (m, 1H), 7.89-7.92 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 21.72, 39.32, 83.05, 101.54, 122.00, 122.15, 124.90, 127.95, 128.03, 128.10, 129.01, 129.50, 131.89, 131.98, 132.56, 138.73, 138.95, 140.94, 143.18, 144.63, 193.60; IR (neat): 3058, 3026, 2920, 2207, 1713, 1630 1598, 1546, 1488, 1445, 1367, 1281, 1223, 757, 713, 691 cm^{-1};HRMS (EI) for $C_{25}H_{18}O$ $[M]^+$: calcd 334.1358, found 334.1350.



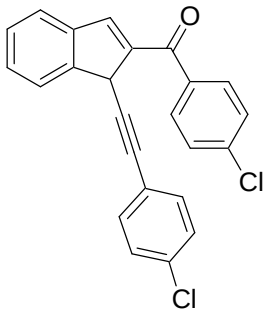
9

Phenyl-(1-phenylethynyl-1*H*-cyclopenta[*b*]naphthalen-2-yl)-methanone (9). To the reaction mixture was added water. The organic layer was separated and washed with water, dried with Na_2SO_4. Evaporation of the solvent afforded the title compound in 99% yield (74 mg, 0.2 mmol scale) as a brown solid. ^{1}H NMR ($CDCl_3$, Me_4Si) d 5.23 (s, 1H), 7.20-7.22 (m, 3H), 7.37-7.40 (m, 2H), 7.48-7.52 (m, 5H), 7.57-7.61 (m, 1H), 7.86-7.94 (m, 5H), 8.13 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 40.42, 82.05, 85.22, 123.19, 123.45, 126.11, 126.70, 127.86, 127.99, 128.21, 128.42, 128.47, 129.11, 131.80, 132.37, 133.30, 133.86, 138.39, 139.82, 142.20, 142.24, 145.98, 191.53; IR (neat): 3056, 3025, 2333,1645, 1597, 1578, 1549, 1520, 1493, 1447, 1431, 1342, 1329, 1247, 1227, 749, 698 cm^{-1}; HRMS (EI) for $C_{28}H_{18}O$ $[M]^+$: calcd 370.1358, found 370.1361.



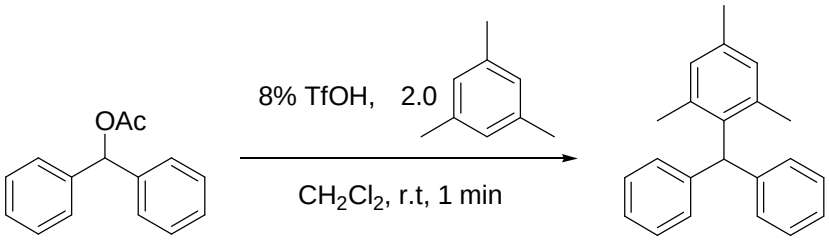
10

Phenyl-(3-phenylethynyl-1*H*-cyclopenta[*b*]naphthalen-2-yl)-methanone (10). Purification of the crude product by flash column chromatography on silica-gel (petroleum ether/ethyl acetate=10:1) afforded the title compound in 61% yield (45 mg, 0.2 mmol scale) as a red brown solid. M.p. 100-102 ^{o}C; ^{1}H NMR ($CDCl_3$, Me_4Si) d 4.13 (s, 2H), 7.08-7.11 (m, 2H), 7.23-7.31 (m, 3H), 7.46-7.61 (m, 5H), 7.86-7.98 (m, 5H), 8.15 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 38.78, 82.77, 101.75, 121.42, 121.98, 122.78, 125.64, 126.33, 127.91, 128.08, 128.18, 128.51, 129.14, 129.62, 131.96, 132.31, 132.79, 133.66, 138.64, 139.26, 142.37, 146.39, 193.89; IR (neat): 3049, 2202 1616, 1597, 1544, 1487, 1443, 1368, 1284, 752, 703 cm^{-1}; HRMS (EI) for $C_{28}H_{18}O$ $[M]^+$: calcd 370.1358, found 370.1353.



4d

(4-Chloro-phenyl)-[1-(4-chloro-phenylethynyl)-1*H*-inden-2-yl]-methanone (4d). NMR yield: 94%. ^{1}H NMR ($CDCl_3$, Me_4Si) d 5.05 (s, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.39-7.49 (m, 5H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) d 41.05, 81.21, 85.11, 121.54, 124.29, 124.46, 128.26, 128.29, 128.71, 129.47, 130.47, 132.97, 133.83, 136.50, 138.75, 140.88, 143.25, 144.78, 145.64, 190.08. LRMS (EI) *m/z* 389 (M^+), 388, 353, 139 (100).

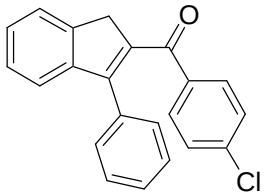


99%

2-Diphenylmethyl-1,3,5-trimethylbenzene. This is a known compound.[5] ^{1}H NMR ($CDCl_3$, Me_4Si) d 1.99 (s, 6H), 2.26 (s, 3H), 5.99 (s, 1H), 6.84 (s, 2H), 7.07-7.10 (m, 4H), 7.16-7.26 (m, 6H). ^{13}C NMR ($CDCl_3$, Me_4Si) d 20.79, 21.96, 50.95, 125.86, 128.12, 129.27, 130.09, 135.95, 137.03, 137.53, 142.47. HRMS (EI) for $C_{22}H_{22}O$: calcd 286.1722, found 286.1723.

Isomerization of 4i to 2,3-disubstituted indene 3i.

4i (50 mg in 4 mL CH_2Cl_2) was added to a 25 mL round-bottomed flask. Then silica gel (1 g) was added and the solvent was evaporated *in vacuo*. the mixture was stirred at 100 ^{o}C for 20 hours. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to afford the desired indenyl ketone **3i** in 72% yield.



3i

(4-Chloro-phenyl)-(3-phenyl-1H-inden-2-yl)-methanone (3i). ^{1}H NMR ($CDCl_3$, Me_4Si) d 4.03 (s, 2H), 7.04-7.07 (m, 2H), 7.18-7.25 (m, 5H), 7.37-7.52 (m, 5H), 7.62 (d, *J* = 6.9Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si) d 40.40, 122.66, 124.38, 126.92, 127.68, 127.89, 128.20, 128.30, 129.27, 130.55, 133.77, 136.18, 137.95, 139.80, 143.65, 143.96, 150.39, 194.27. HRMS (EI) for $C_{22}H_{15}OCl$: calcd 330.0811, found 330.0800.

References:

(1) Rodríguez, D.; Castedo, L.; Domínguez, D.; Saá, C. *Org. Lett.* **2003**, *5*, 3119.

(2) Wang, S.; Zhang, L. *Org. Lett.* **2006**, *8*, 4585-4587.

(3) Sugimoto, Y.; Hanamoto, T.; Inanaga, J. *Appl. Organomet. Chem.* **1995**, *9*, 369.

(4) Bradley, J. C.; Durst, T. *J. Org. Chem.* **1991**, *5*6, 5459

(5) Kessler, H.; Moosmayer, A.; Rieker, A. *Tetrahedron* **1969**, 25, 287.

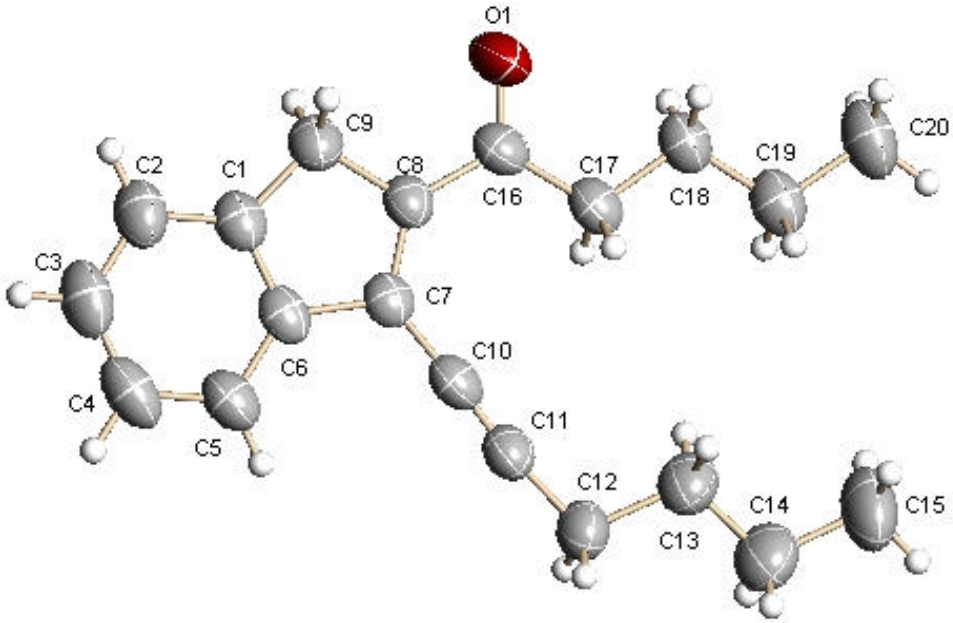


Figure 1, The X-ray crystal structure of compound **3f**.

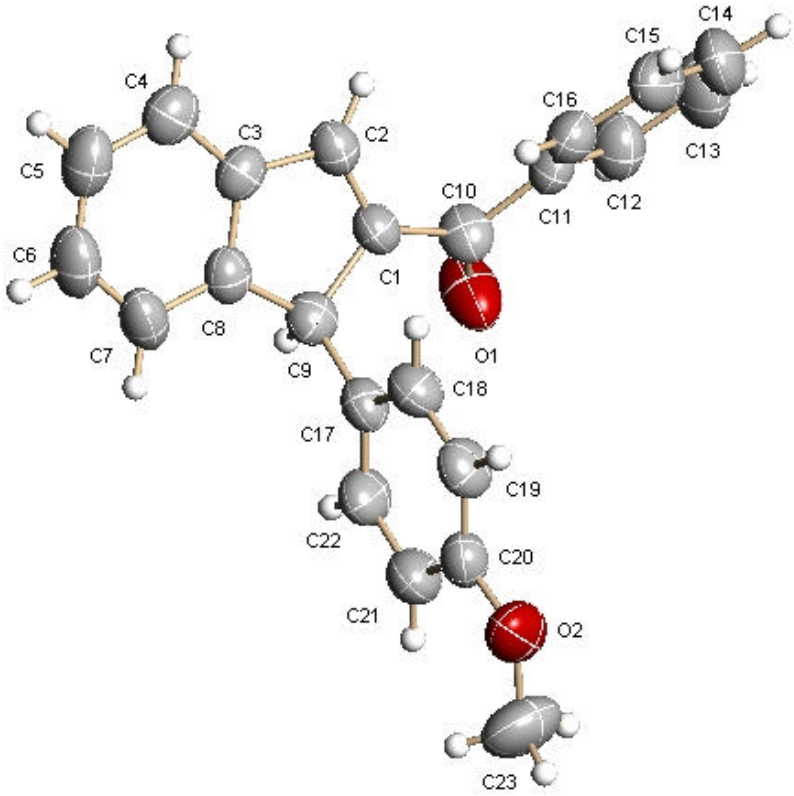
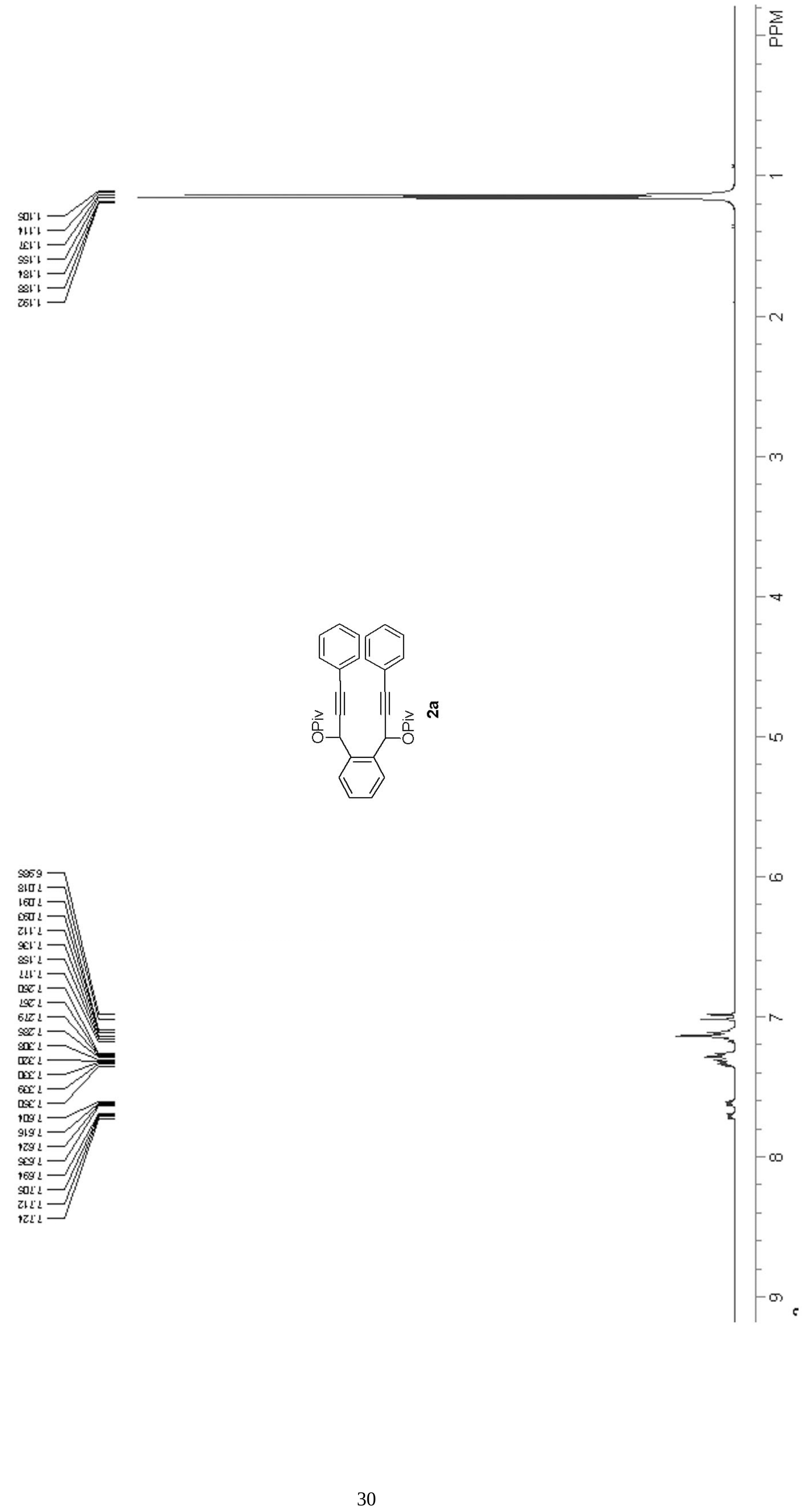
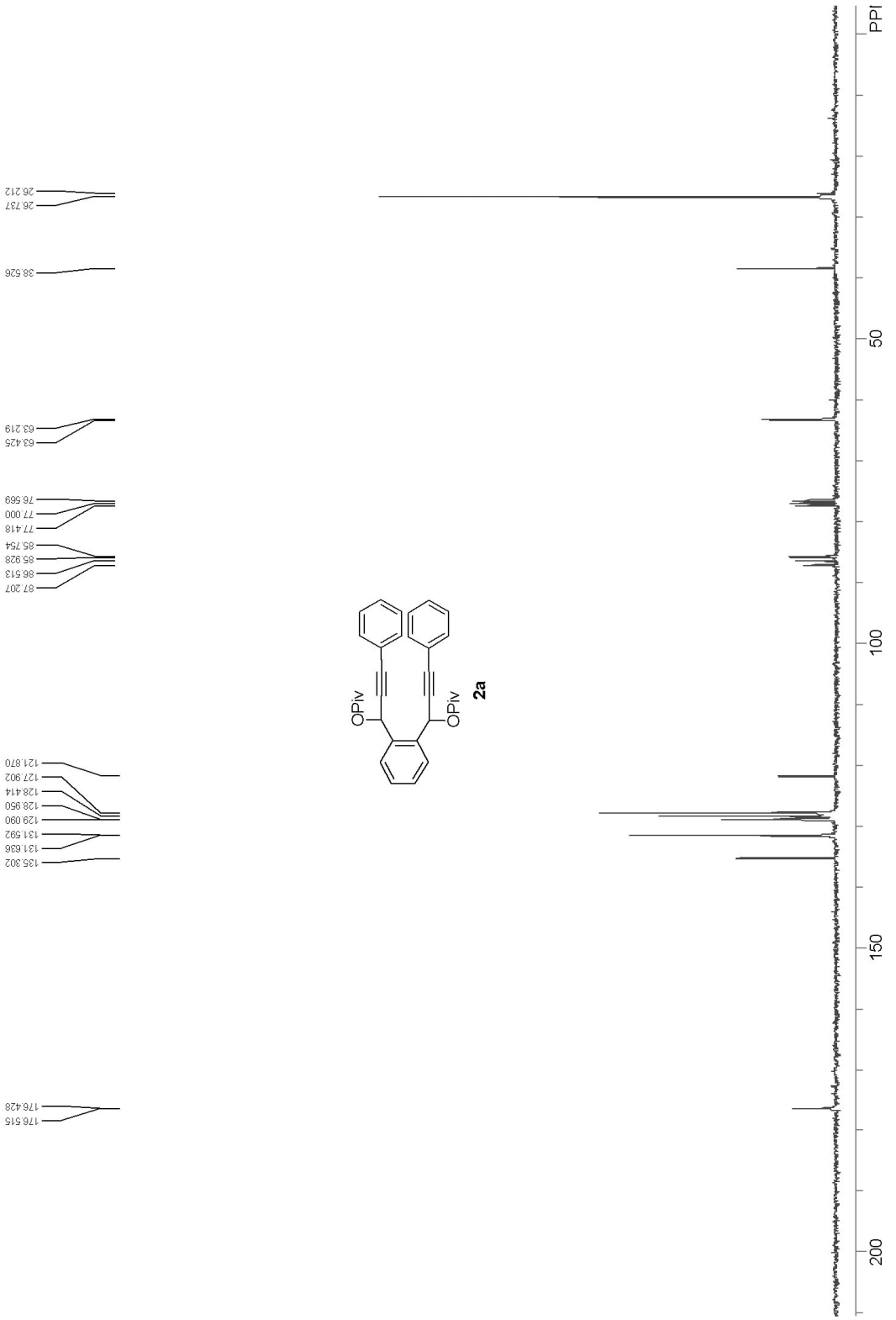


Figure 2, The X-ray crystal structure of compound **4l**.


OPiv
OPiv
2a
PPM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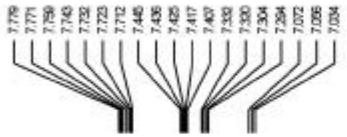
38.526
63.219
63.425
76.569
77.000
77.418
85.754
85.928
86.513
87.207
121.870
127.902
128.414
128.950
129.090
131.592
131.636
135.302
176.428
176.515
OPiv
OPiv
2a
PPM
200
150
100
50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7.771
7.759
7.740
7.732
7.723
7.712
7.445
7.436
7.429
7.417
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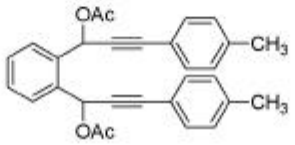
7.072
7.066
7.034


2.306
2.084
2.079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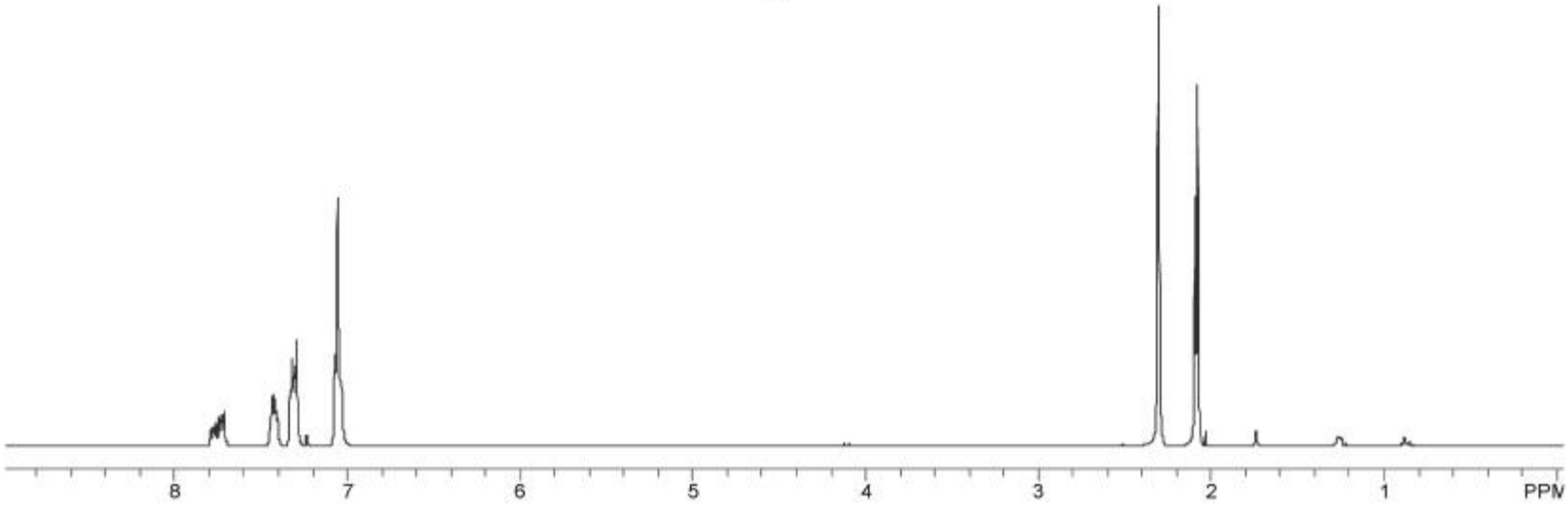
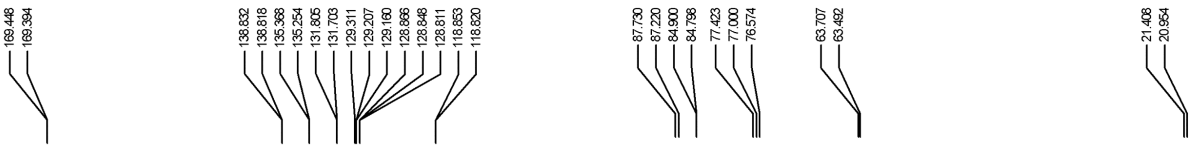
CH3
CH3
OAc

1b


8
7
6
5
4
3
2
1
PPM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129.207
129.160
128.866
128.848
128.811
118.853
118.820
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87.220
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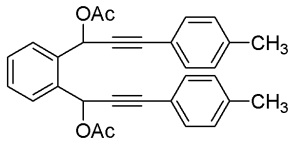
76.574
63.707
63.492
21.406
20.954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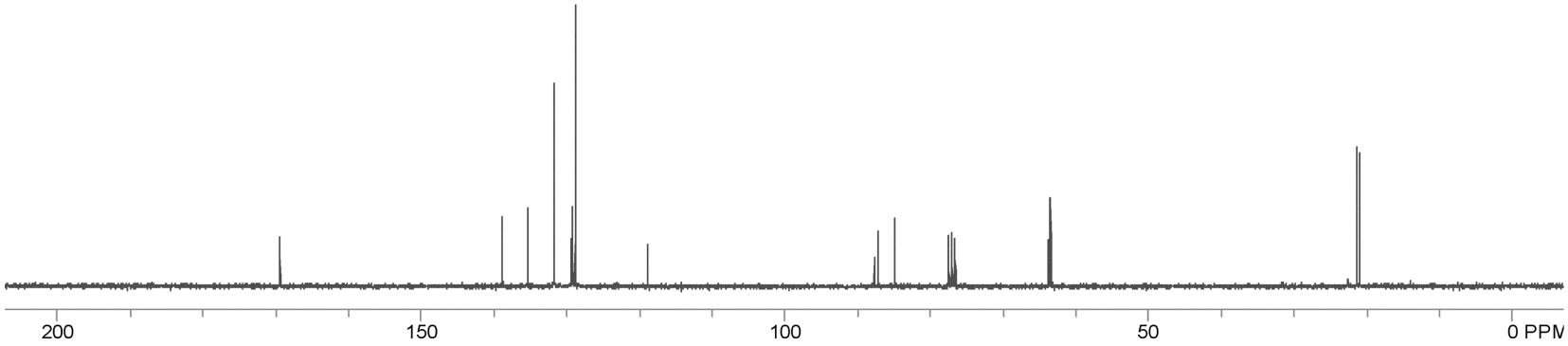
CH3
CH3
OAc

1b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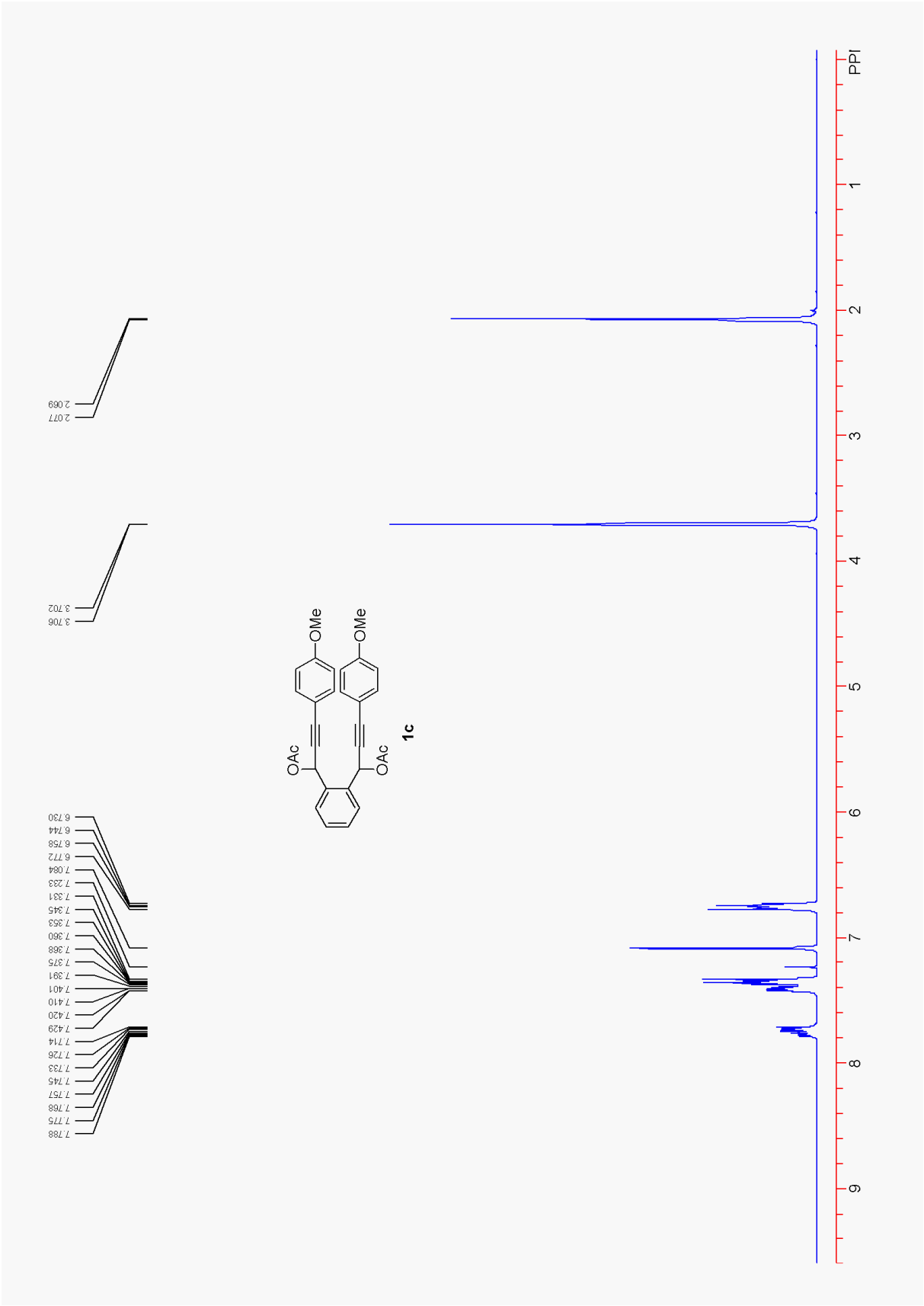
150
100
50
0 PPM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7.768
7.757
7.745
7.733
7.726
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7.410
7.401
7.391
7.375
7.368
7.360
7.353
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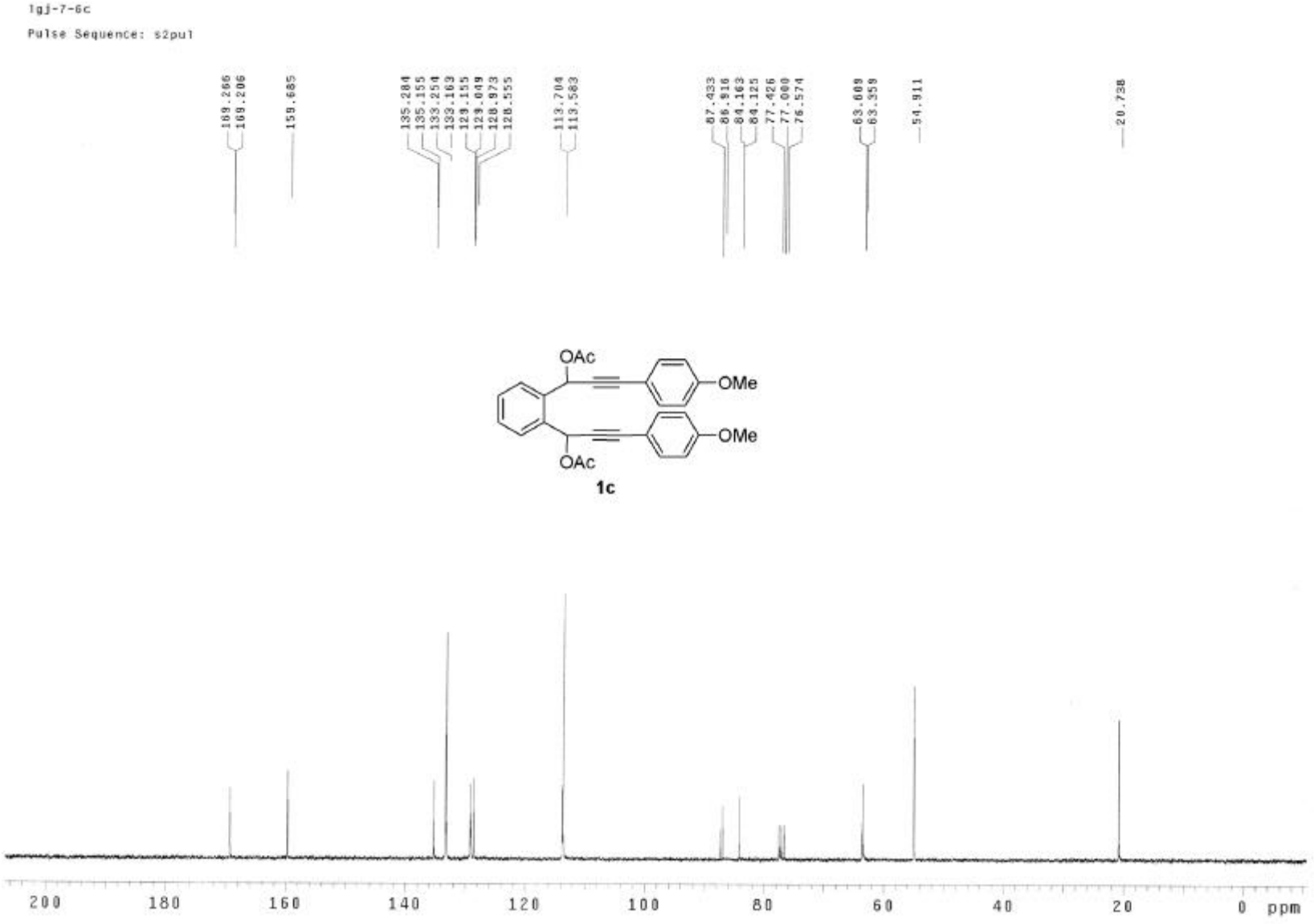
6.730
OMe
OMe
OAc
OAc
1c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86.916
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84.125
77.426
77.000
76.574
63.609
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54.911
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OMe
OMe
OAc
1c
200
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160
140
120
100
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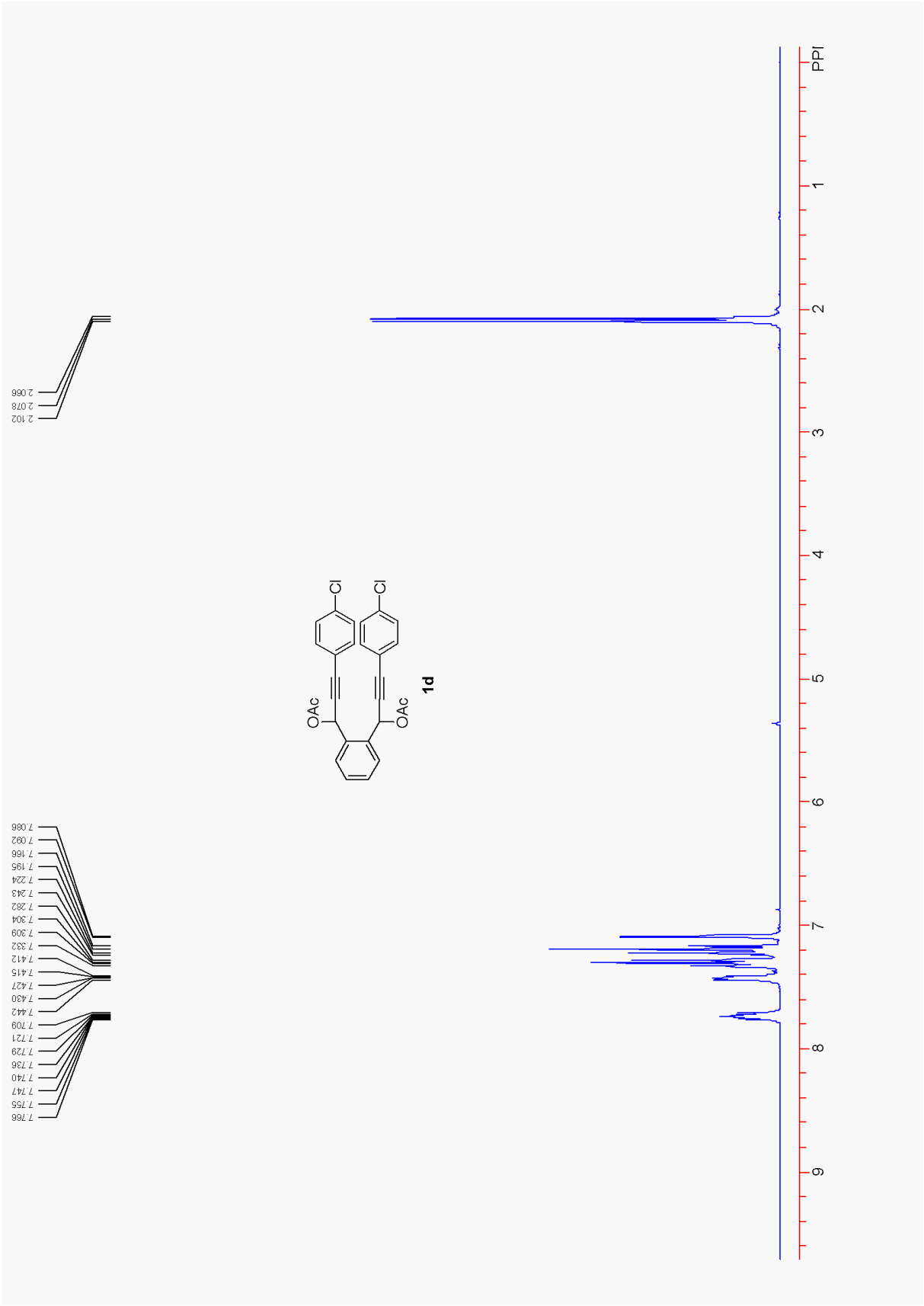
60
40
20
0
ppm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7.243
7.262
7.304
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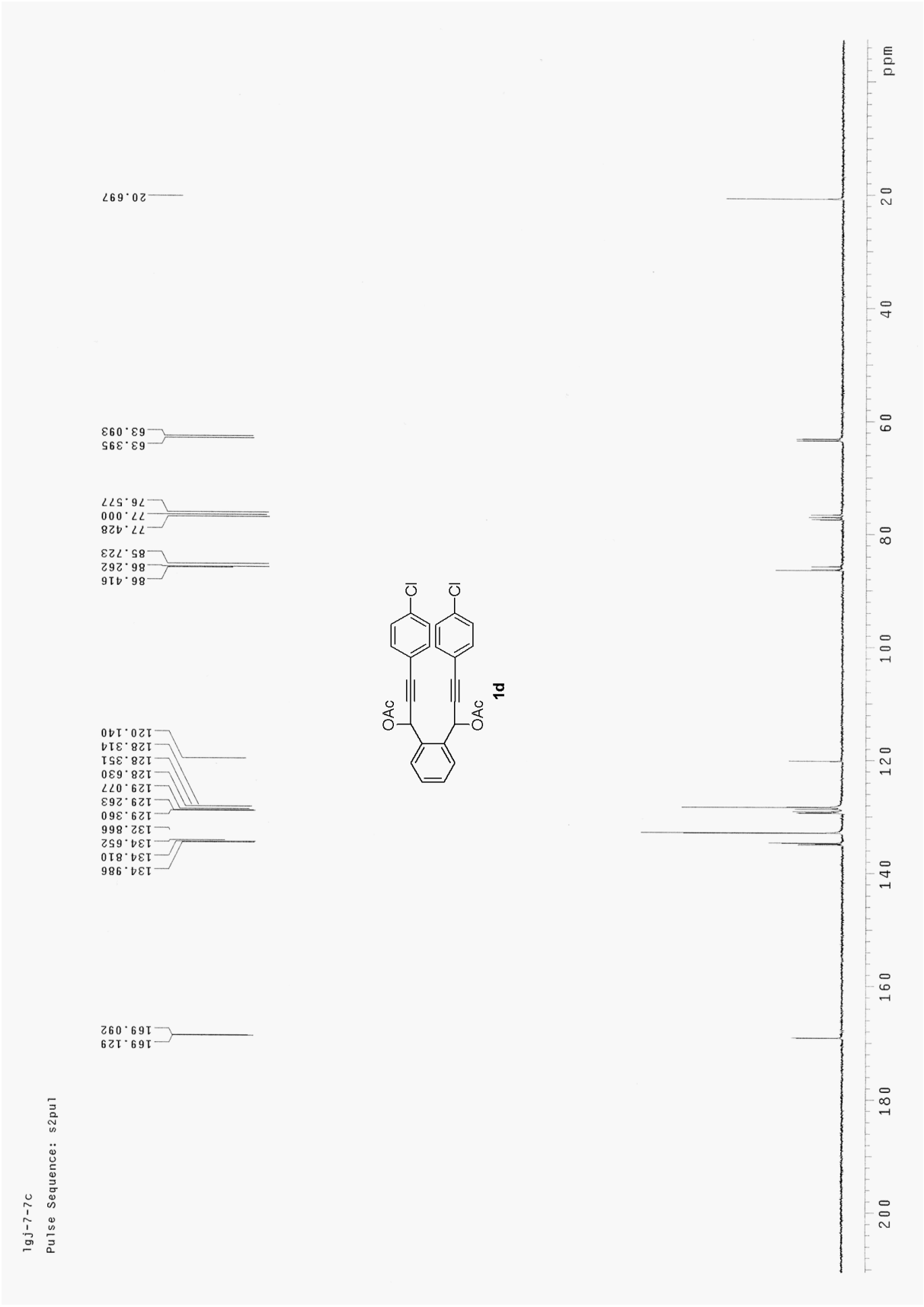
Cl
OAc
OAc
1d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128.351
128.314
120.140
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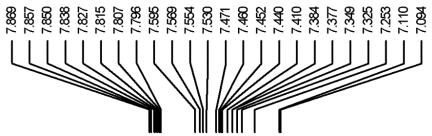
86.262
85.723
77.428
77.000
76.577
63.395
63.093
20.697
OAc
OAc
Cl
Cl
1d
ppm
200
180
160
140
120
100
80
60
40
20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7.530
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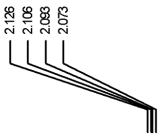
7.094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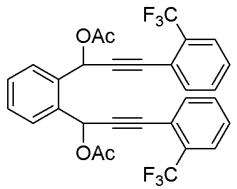
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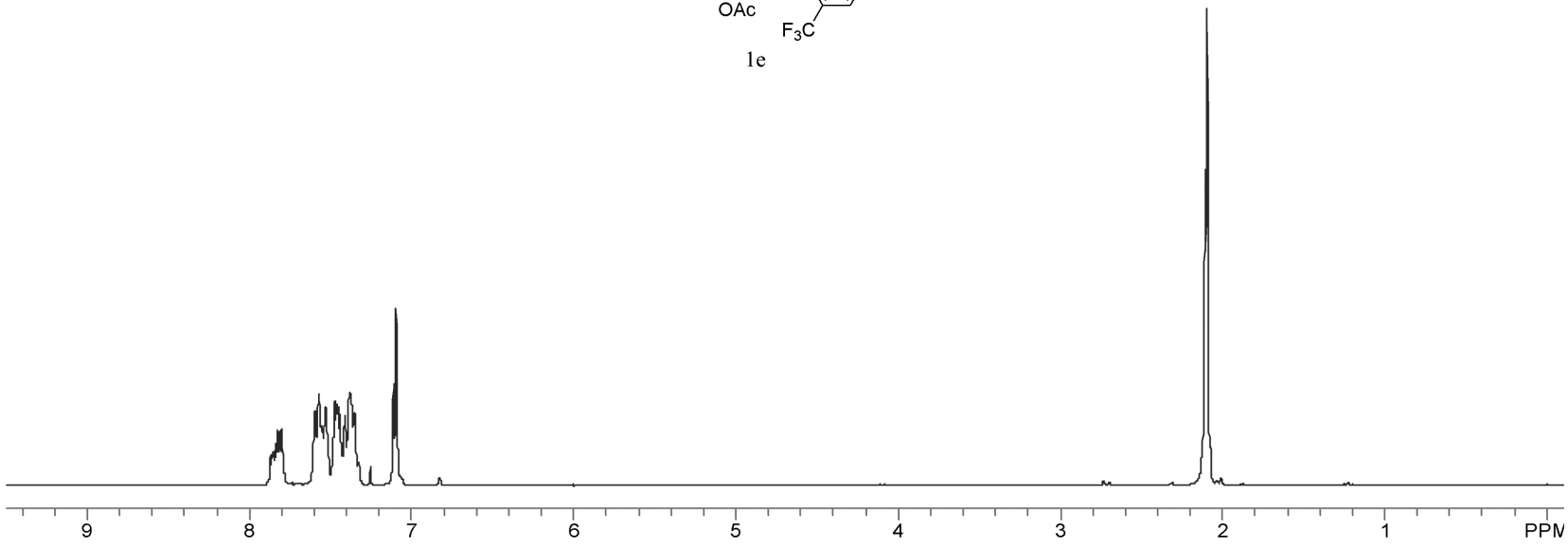
OAc
OAc
F3C

1e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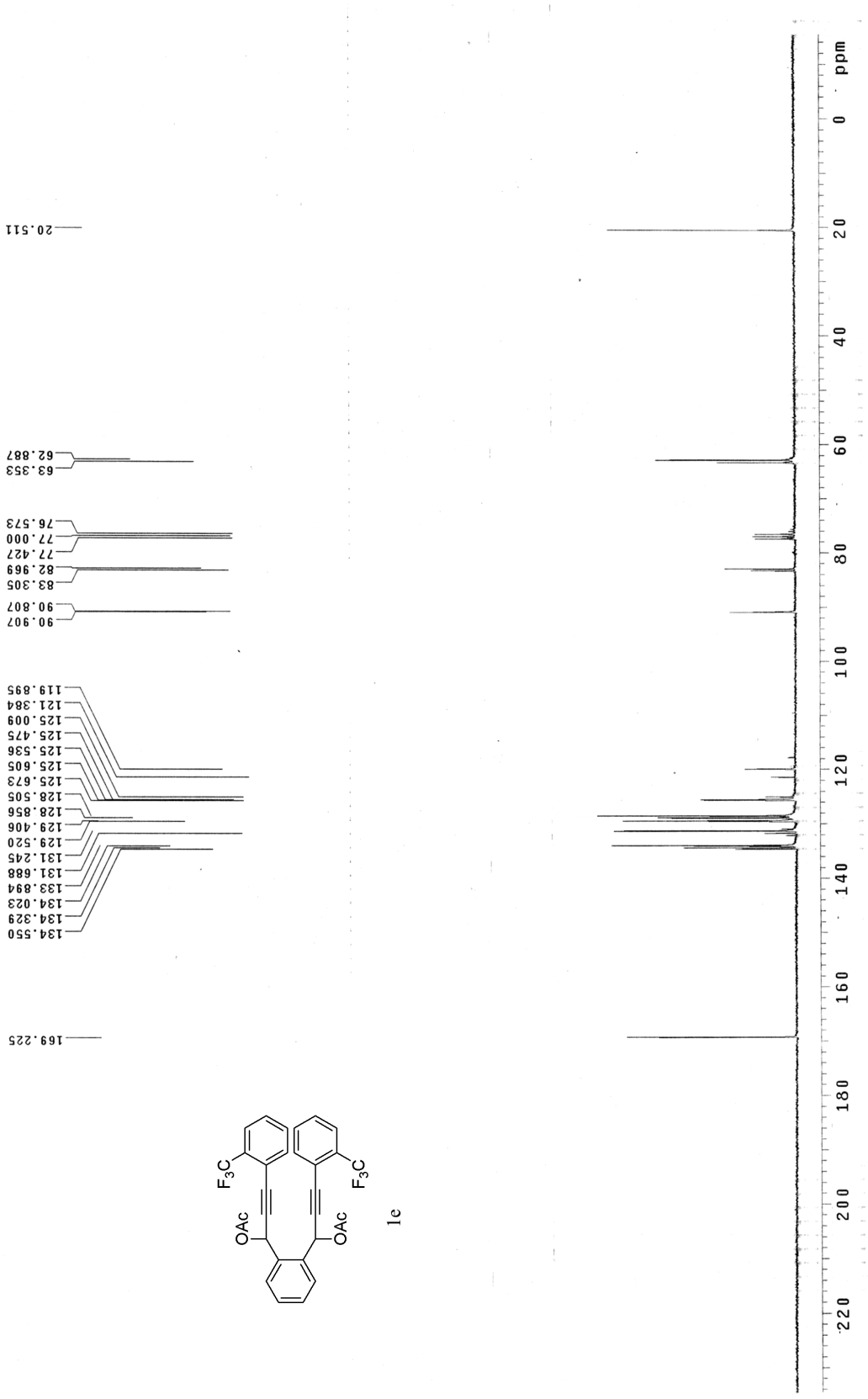
8
7
6
5
4
3
2
1
PPM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129.520
131.245
131.688
133.894
134.023
134.329
134.550
169.225
F3C
OAc
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F3C
1e
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100
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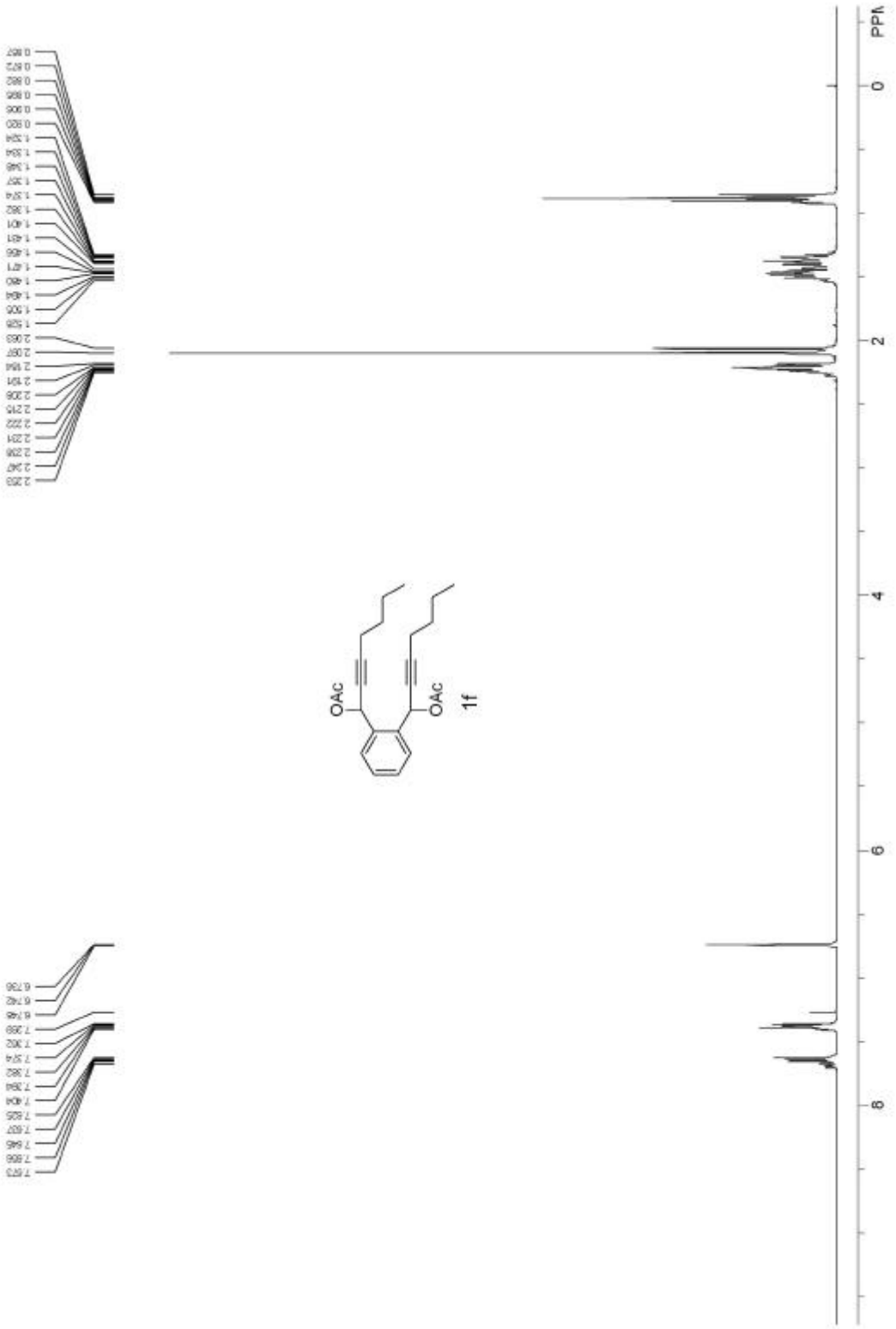
180
200
220
ppm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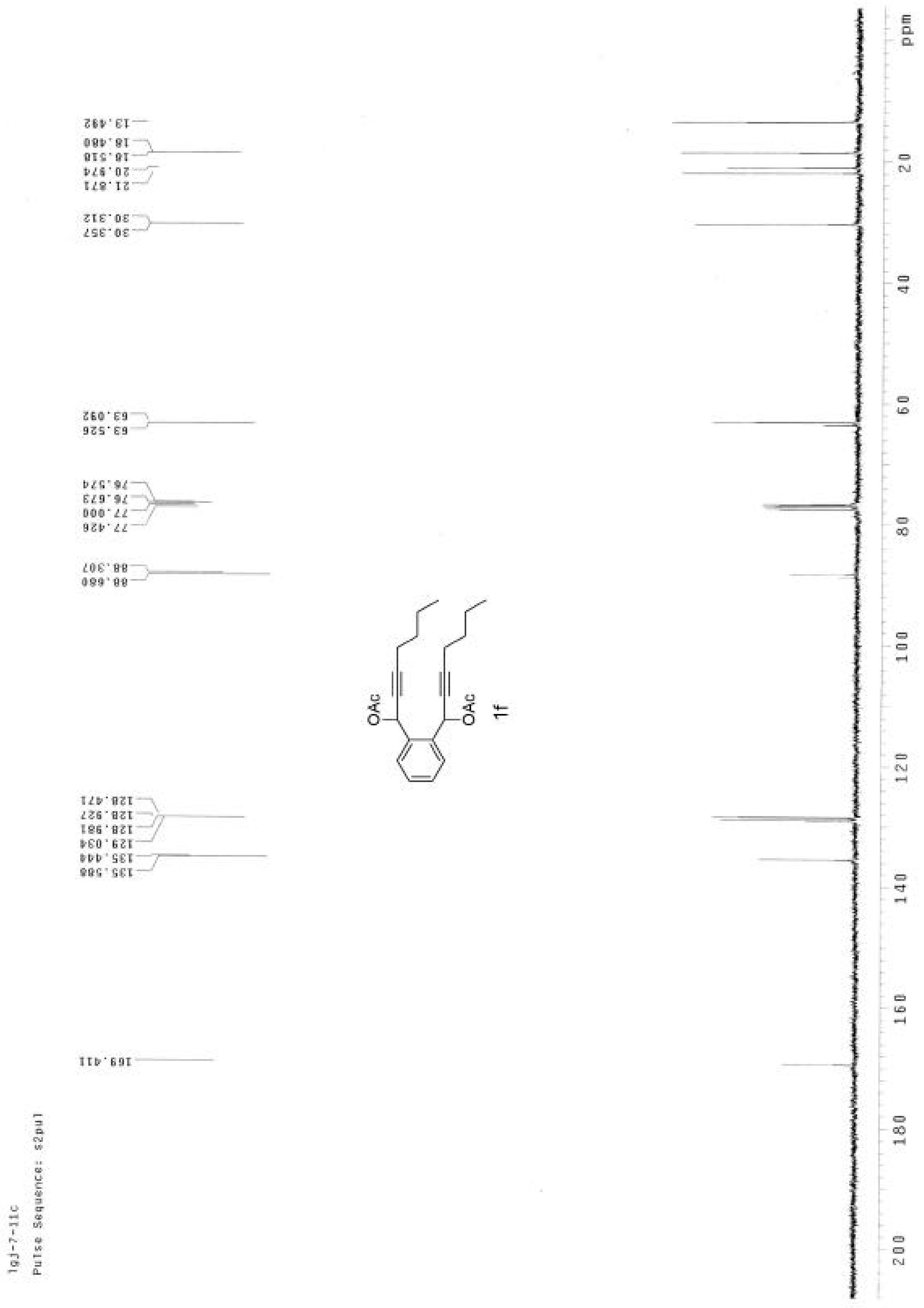
OAc
1f
PPM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1f
ppm
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60
80
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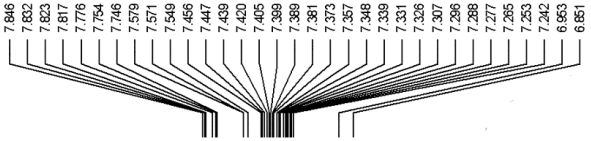
140
160
180
200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7.439
7.420
7.405
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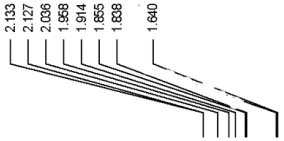
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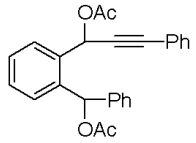
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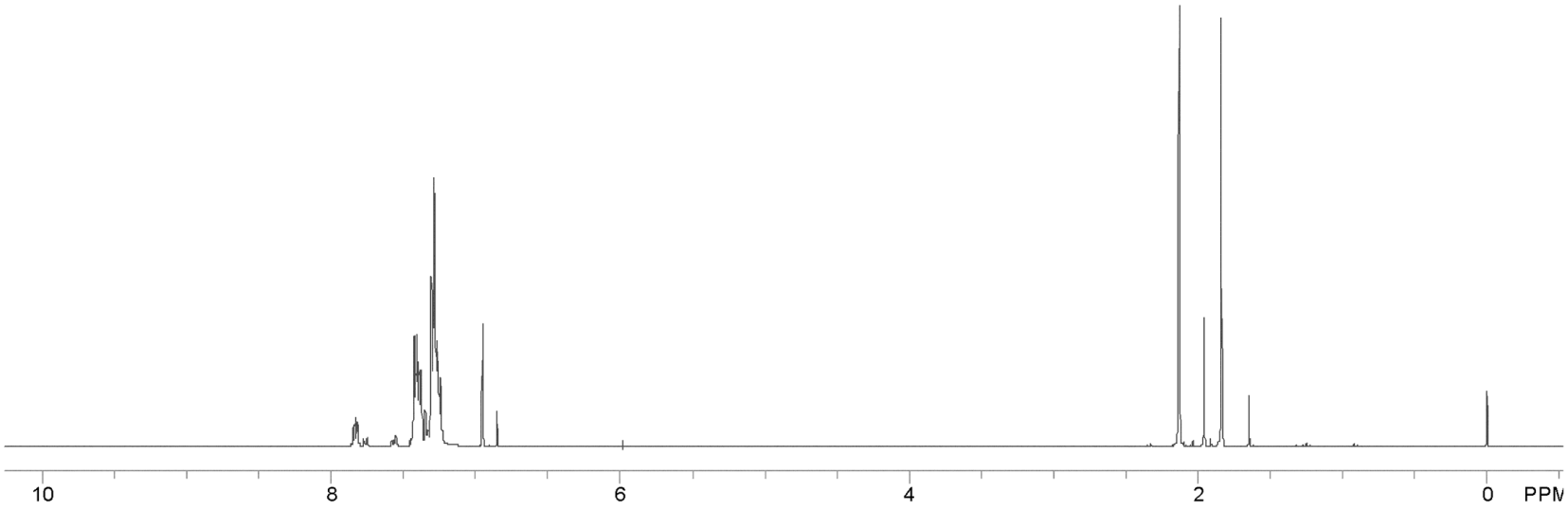
Ph
Ph
OAc

1g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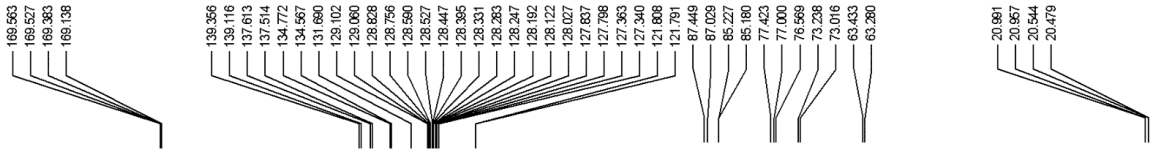
8
6
4
2
0
PPM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128.283
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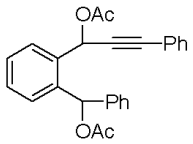
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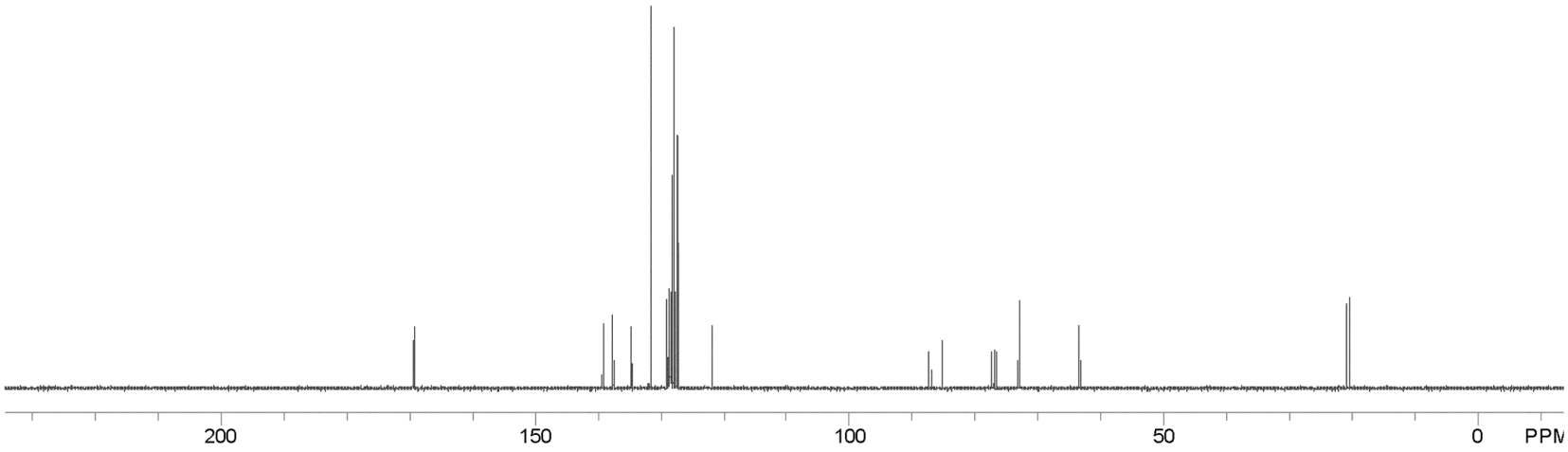
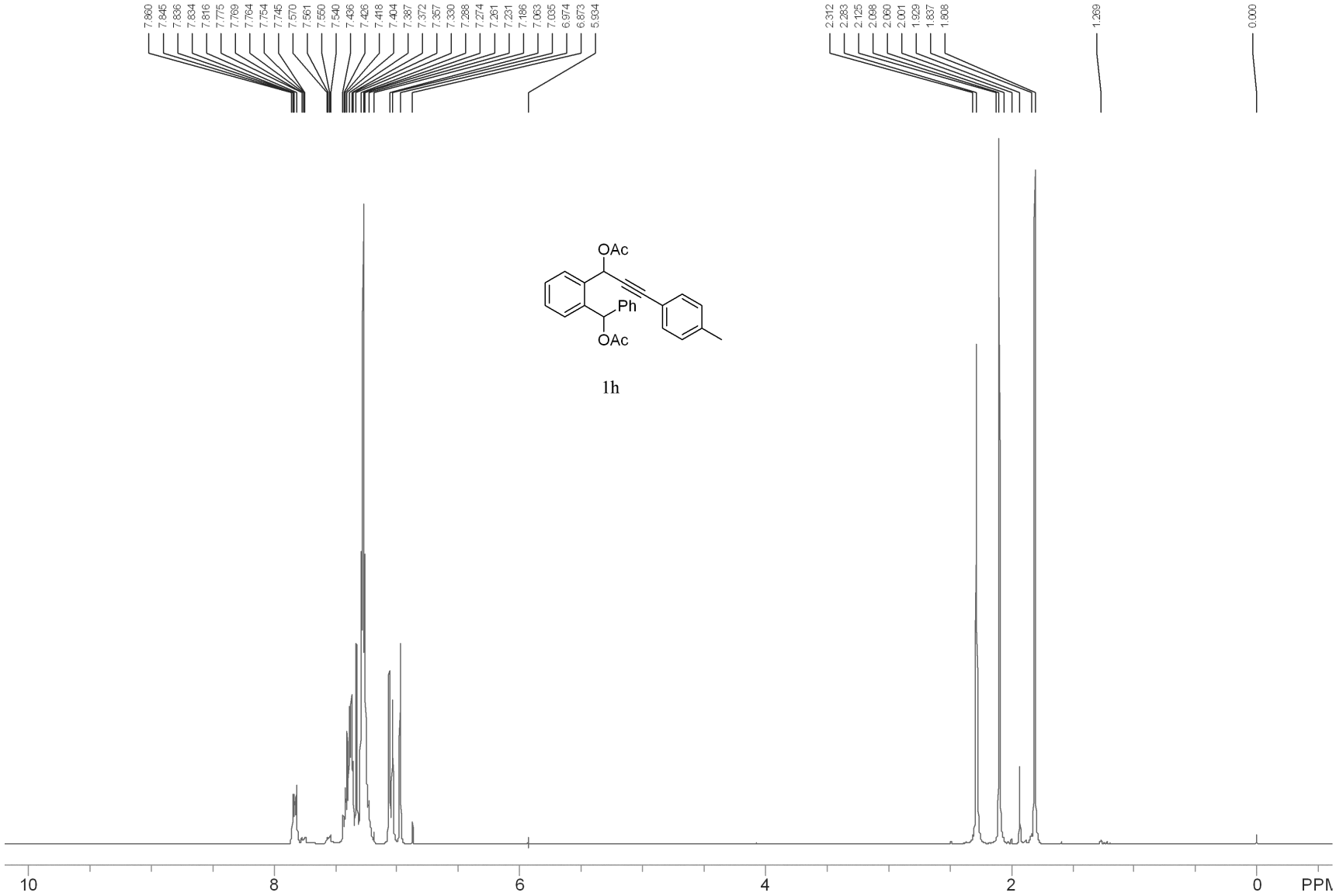
Ph
Ph
OAc

1g


200
150
100
50
0
PPM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7.418
7.404
7.387
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7.231
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7.063
7.035
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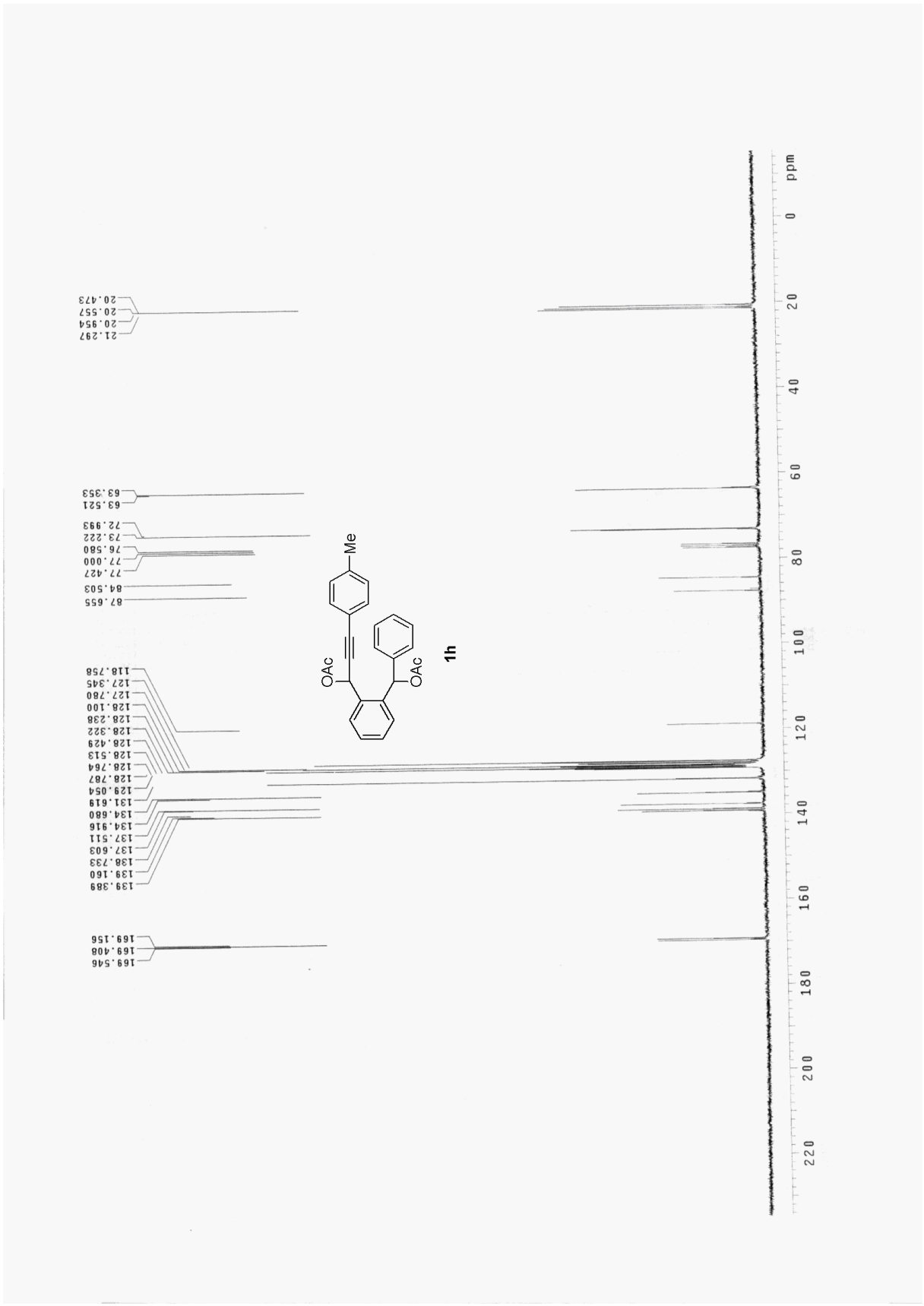
Ph
OAc
10
8
6
4
2
0
PPM

1h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OAc
1h
ppm
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40
60
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100
120
140
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180
200
220
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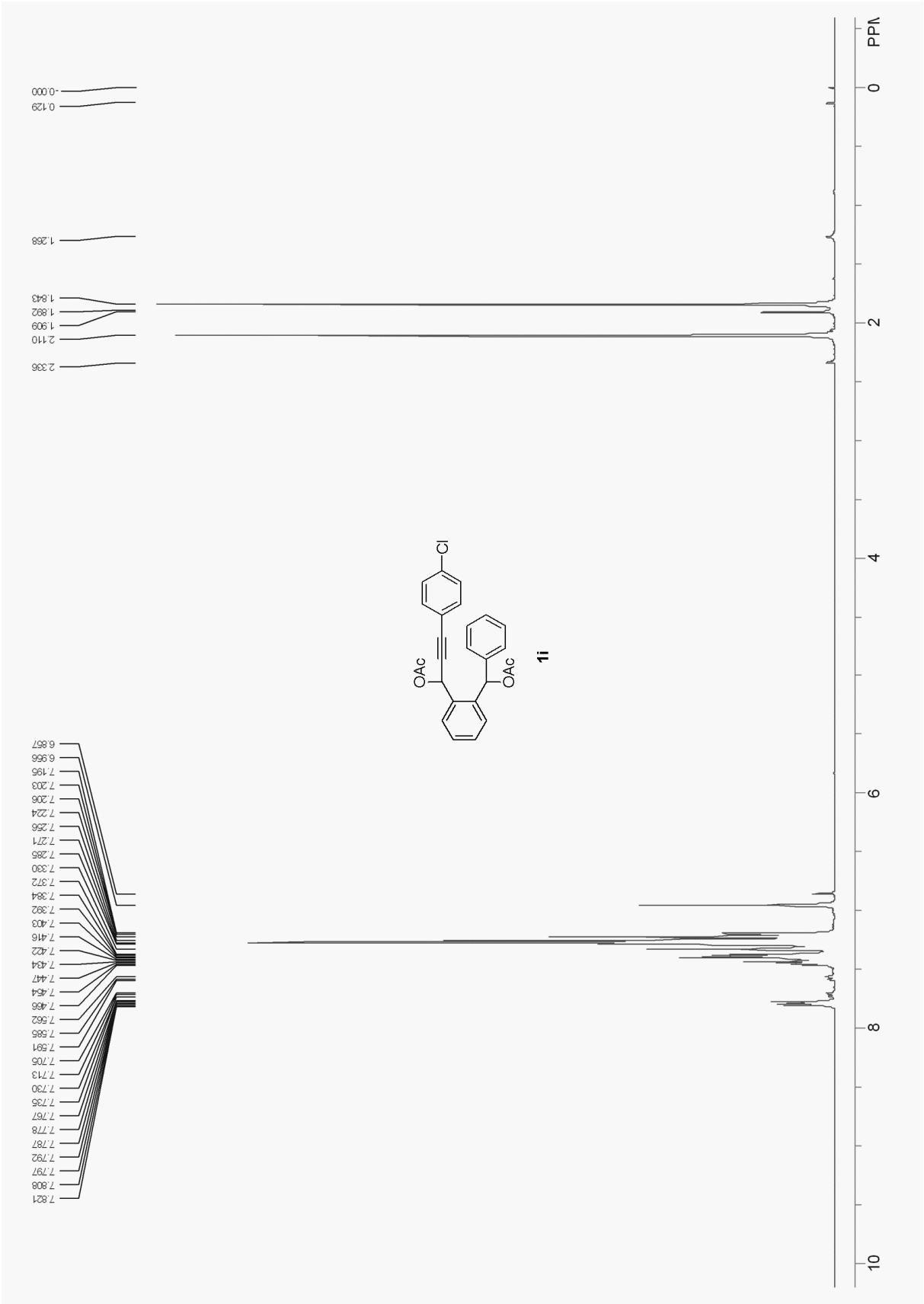
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7.256
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7.285
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7.821
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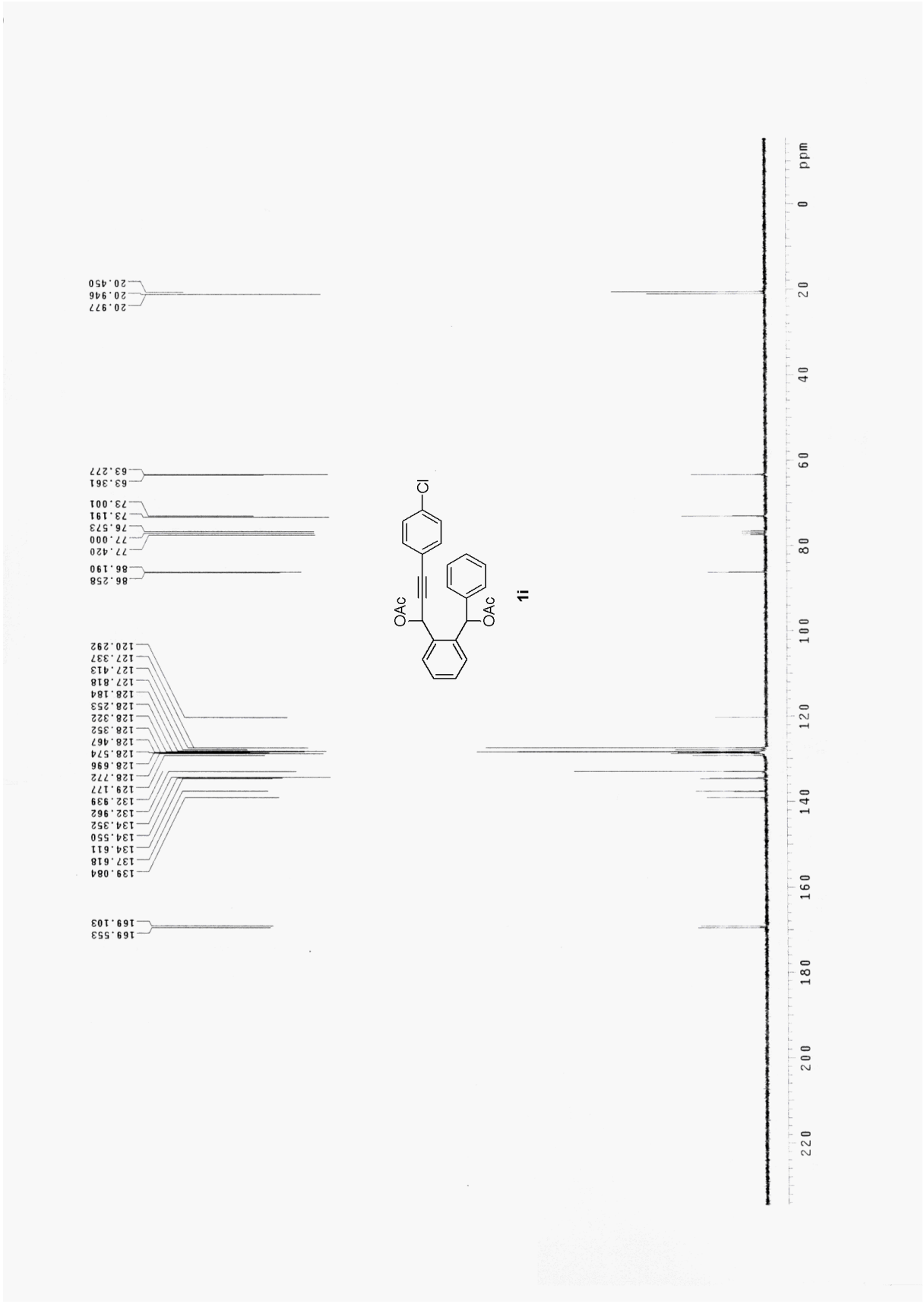
OAc
Cl
1i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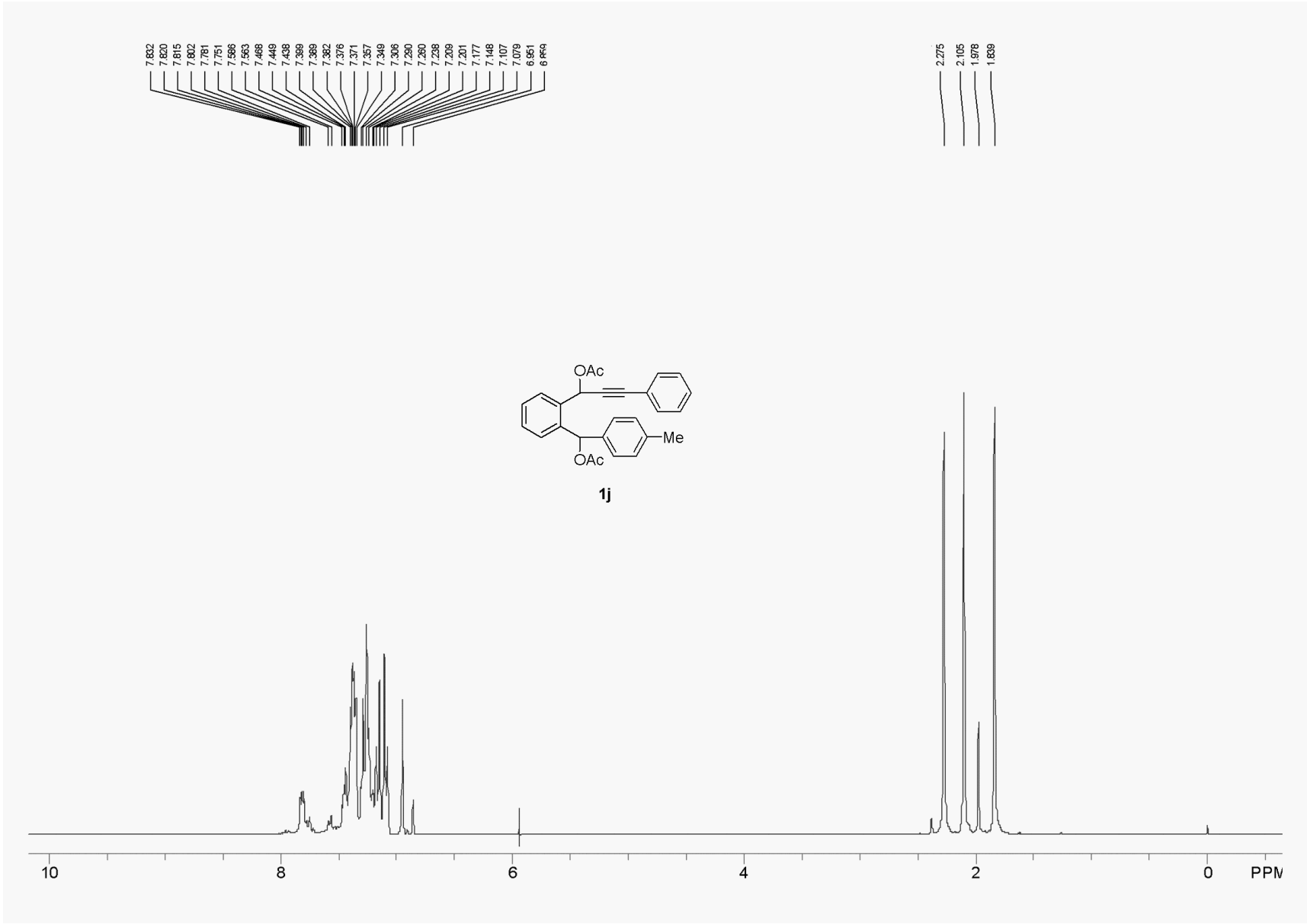
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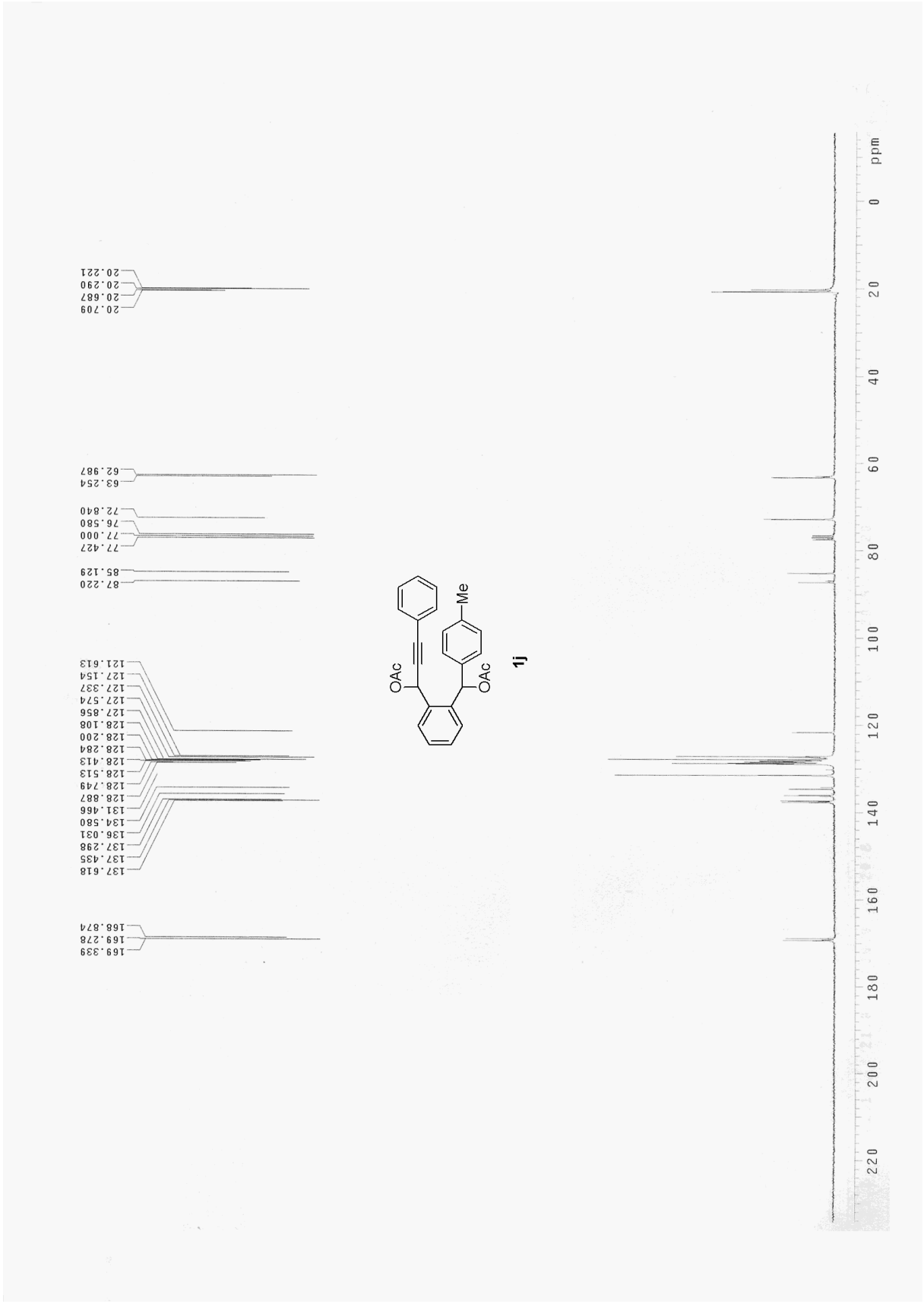
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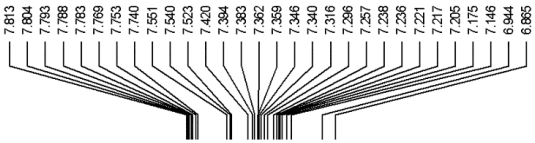
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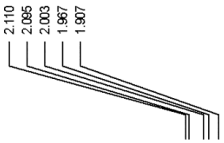
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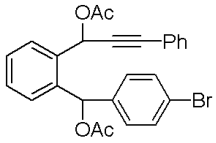
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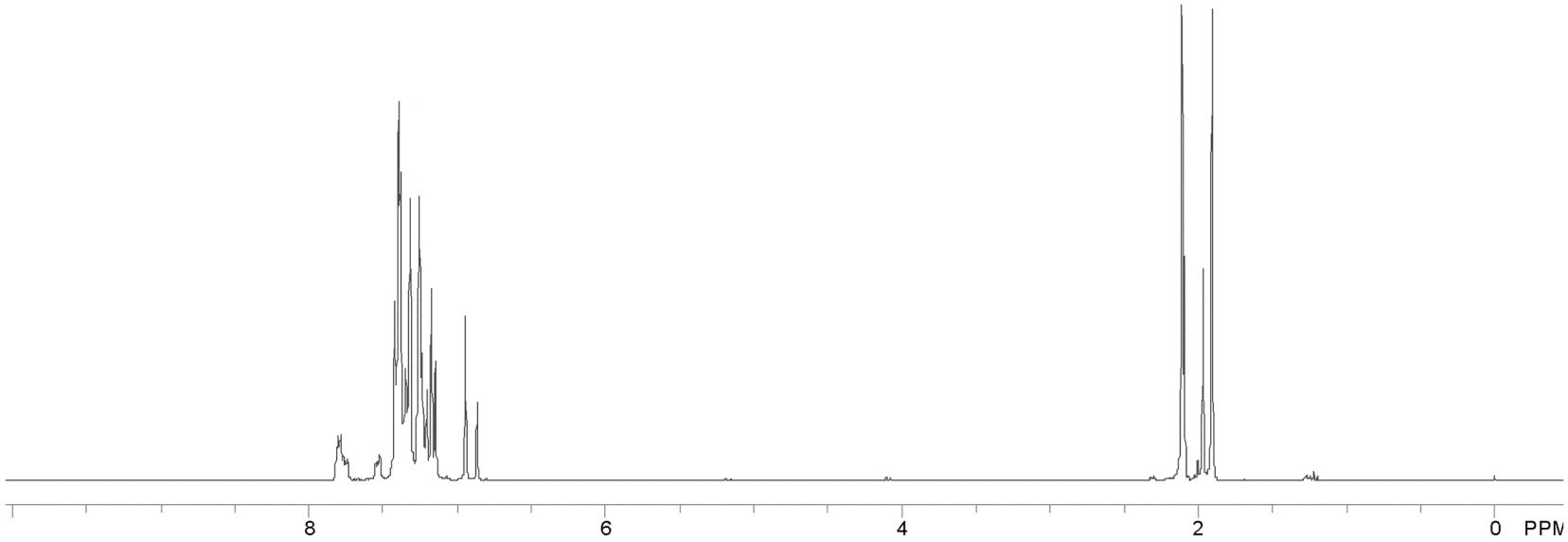
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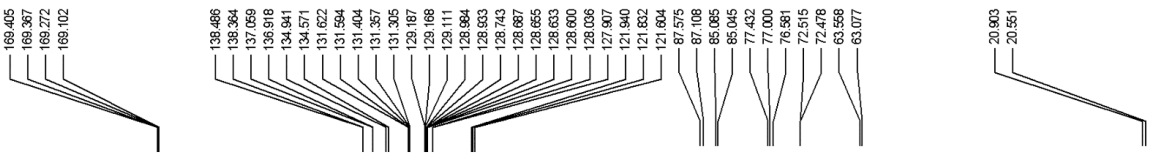
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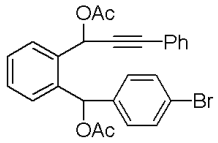
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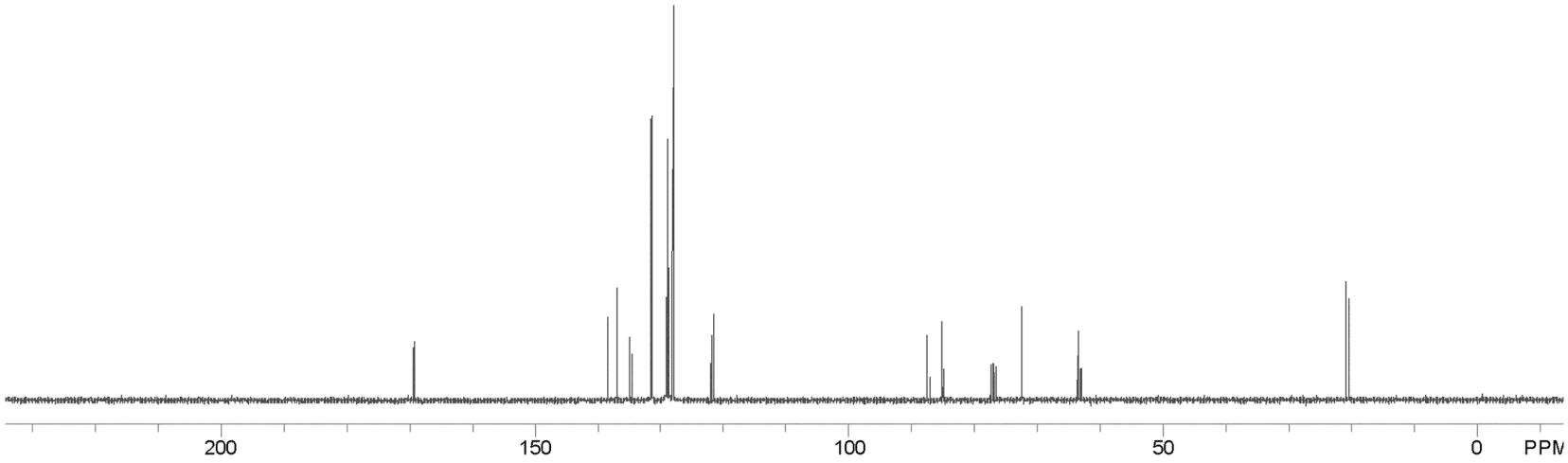
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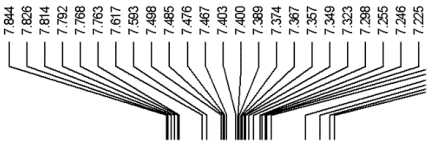
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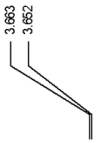
7.225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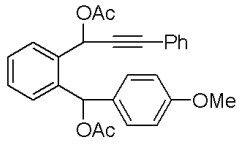
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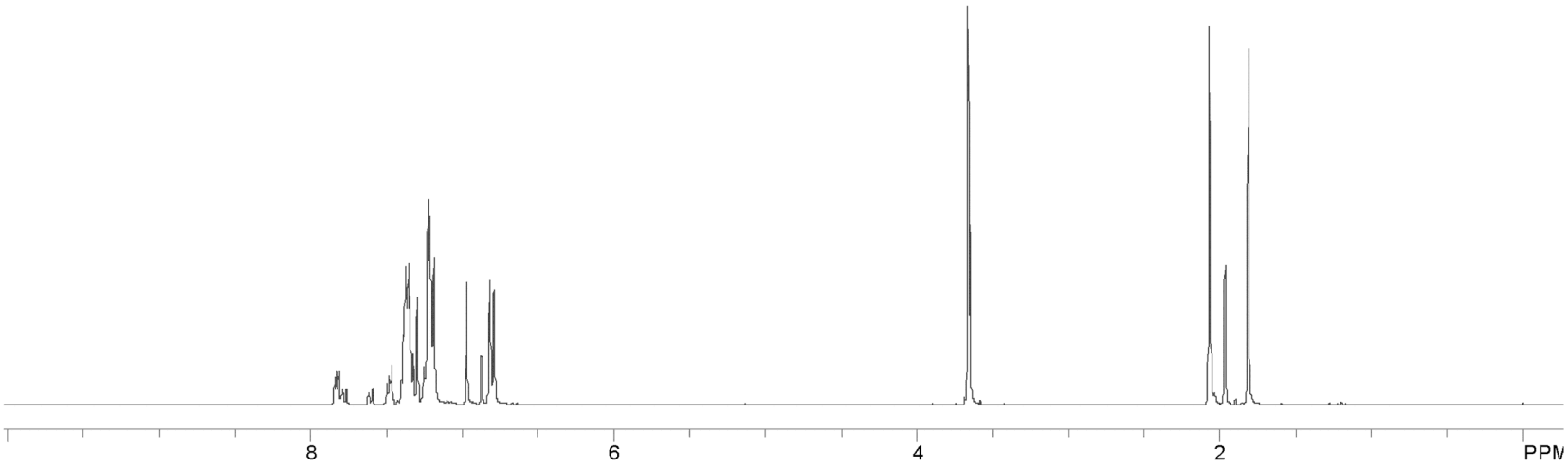
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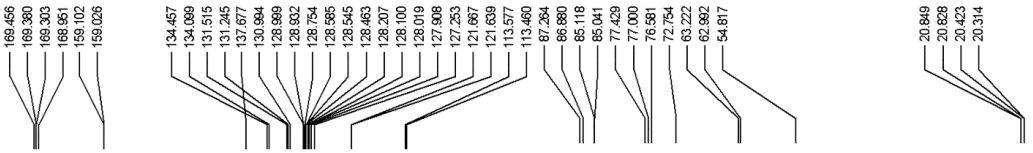
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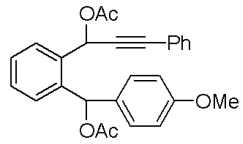
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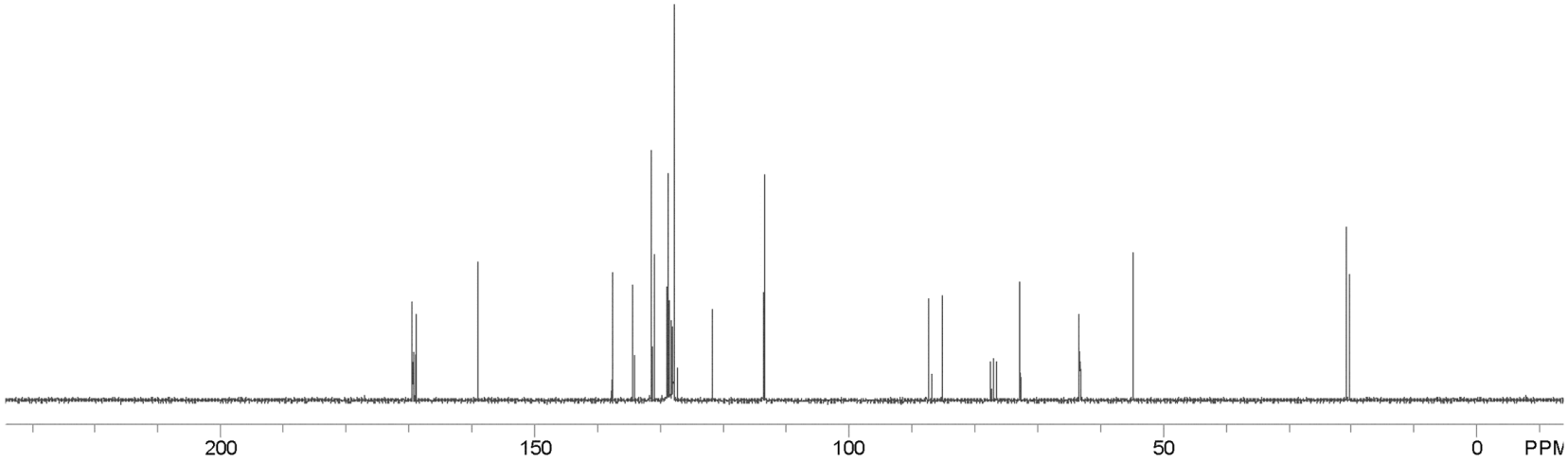
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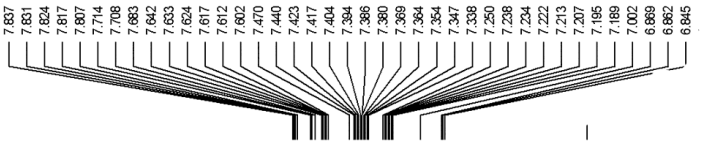
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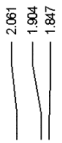
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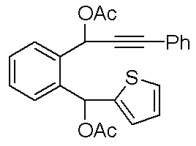
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Ph
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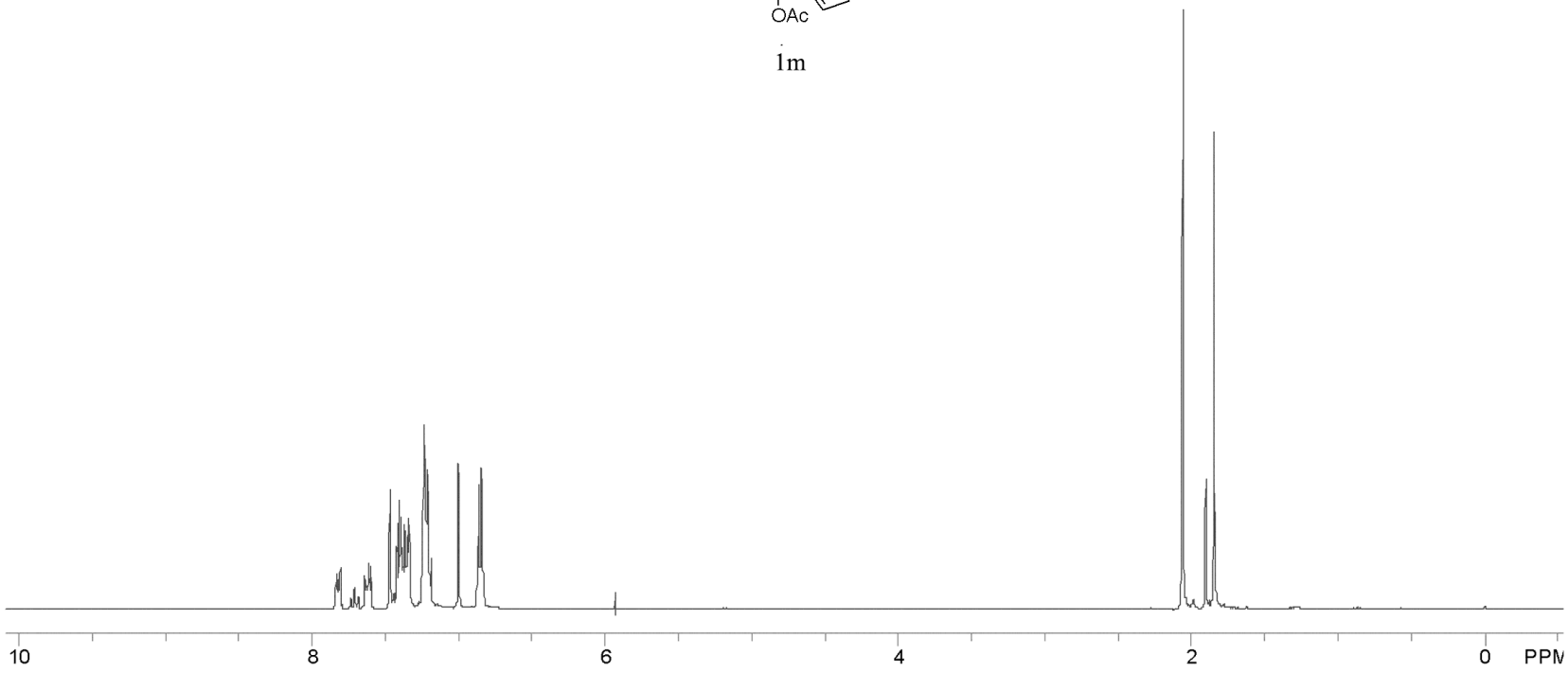
1m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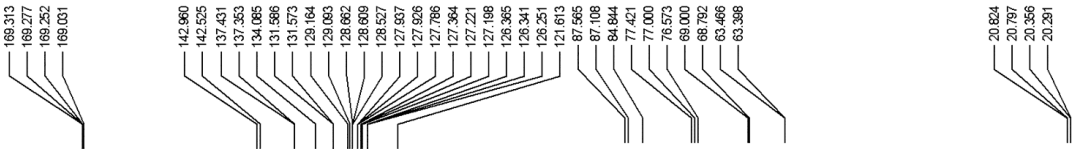
PPM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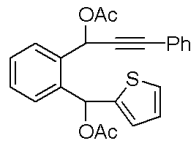
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S
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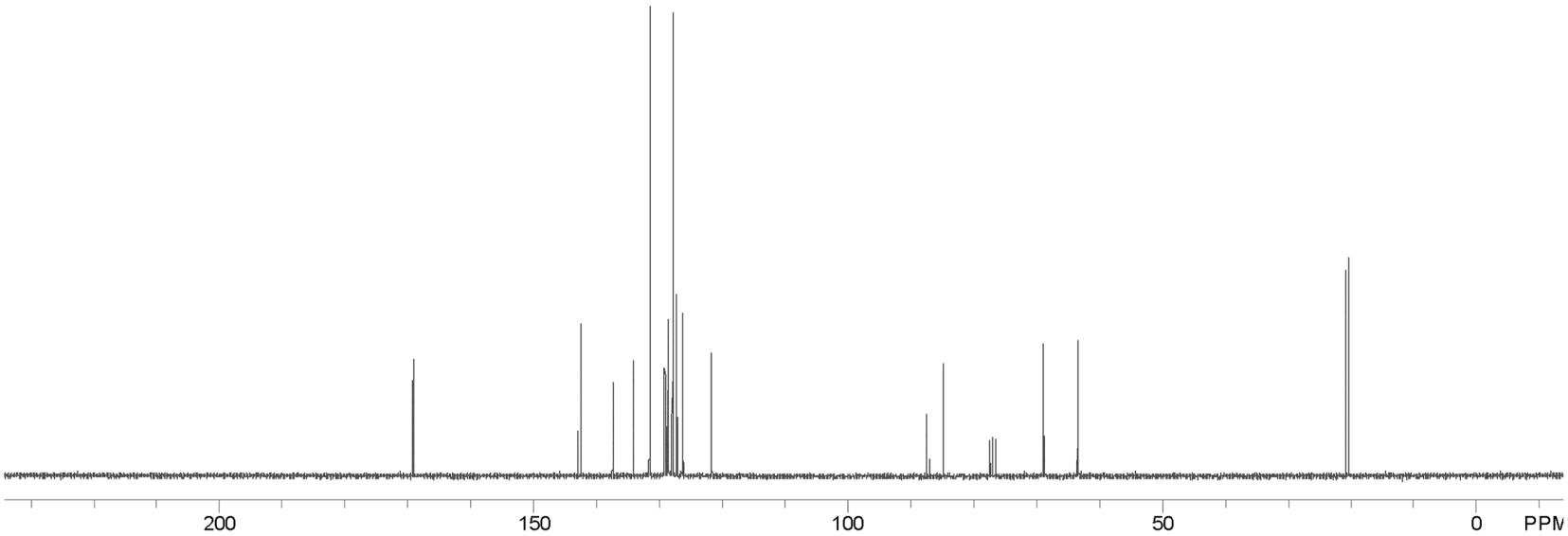
1m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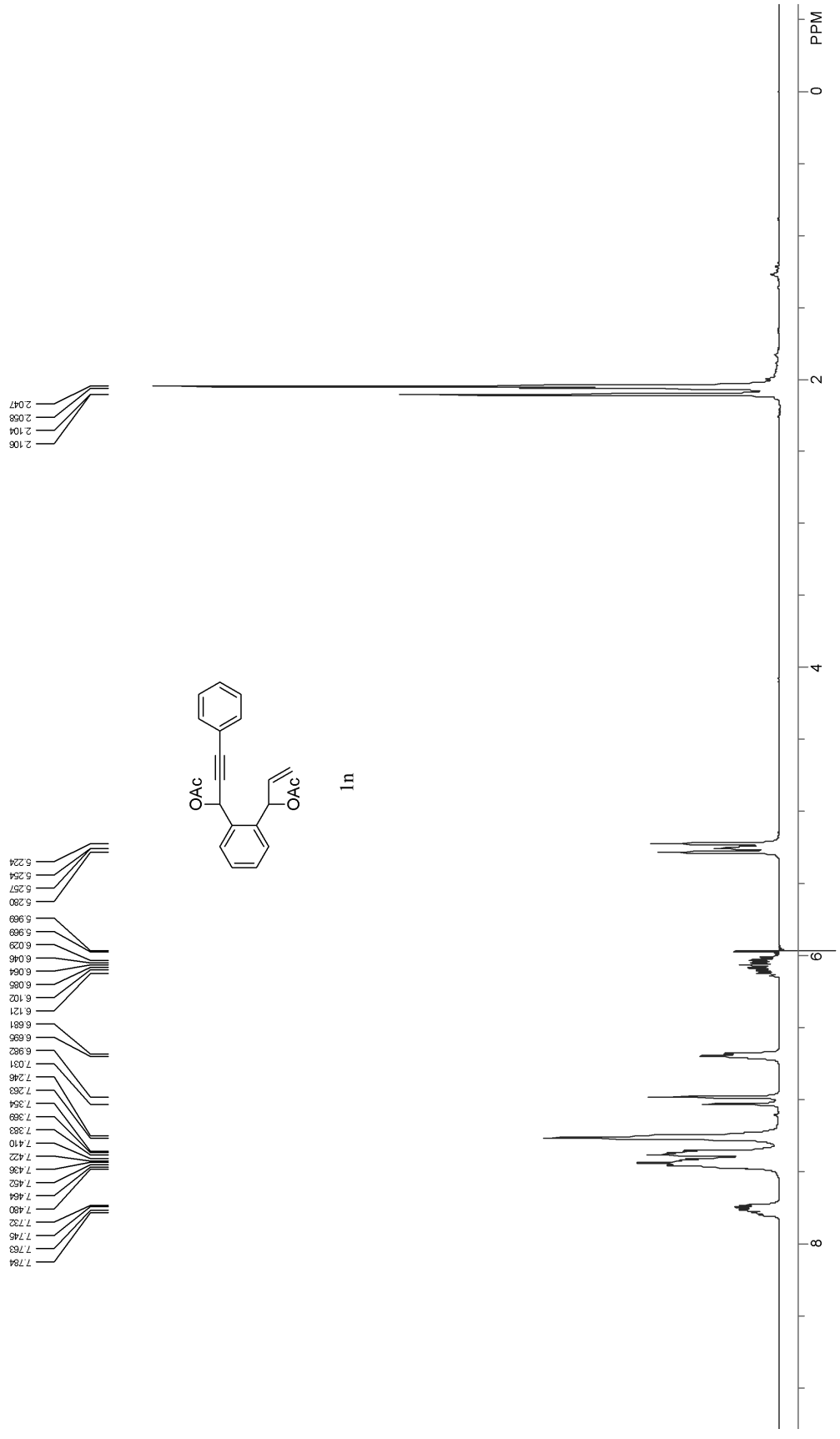
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OAc
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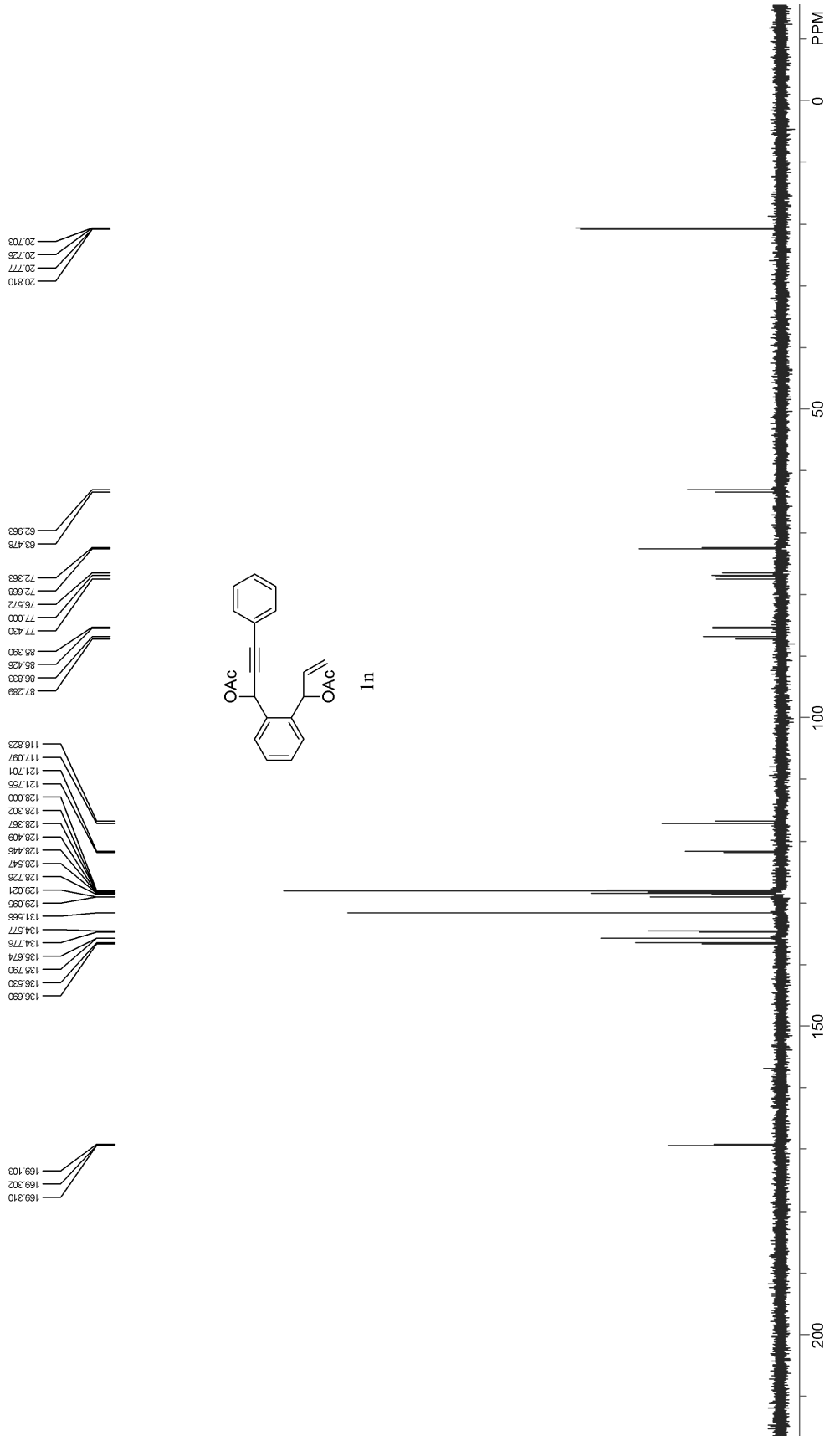
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1n
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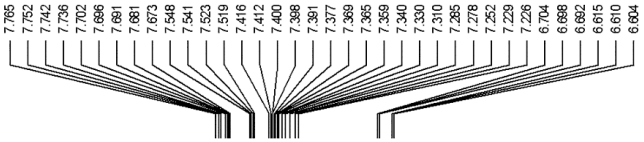
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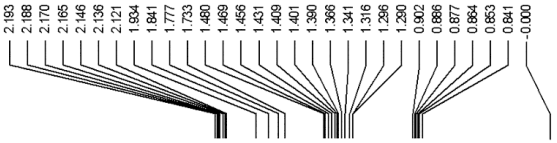
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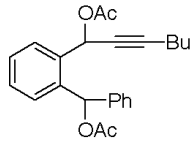
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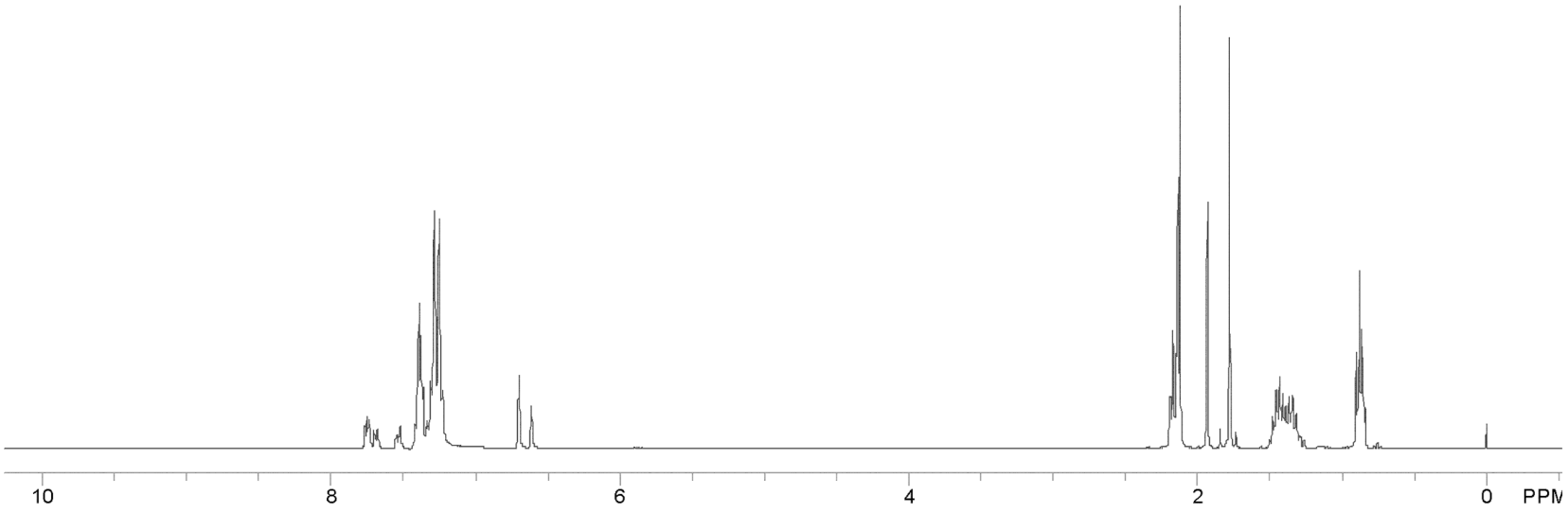
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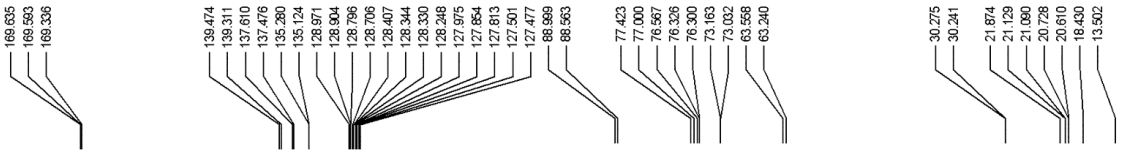
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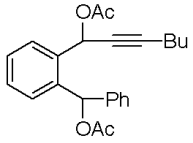
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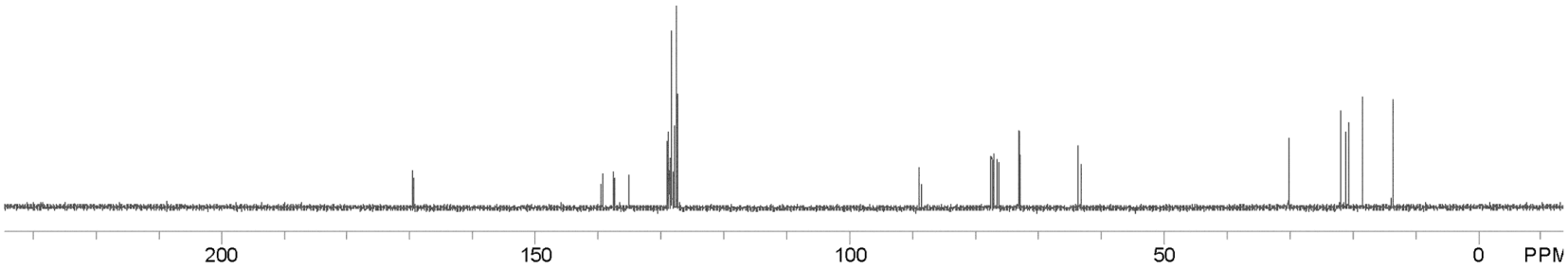
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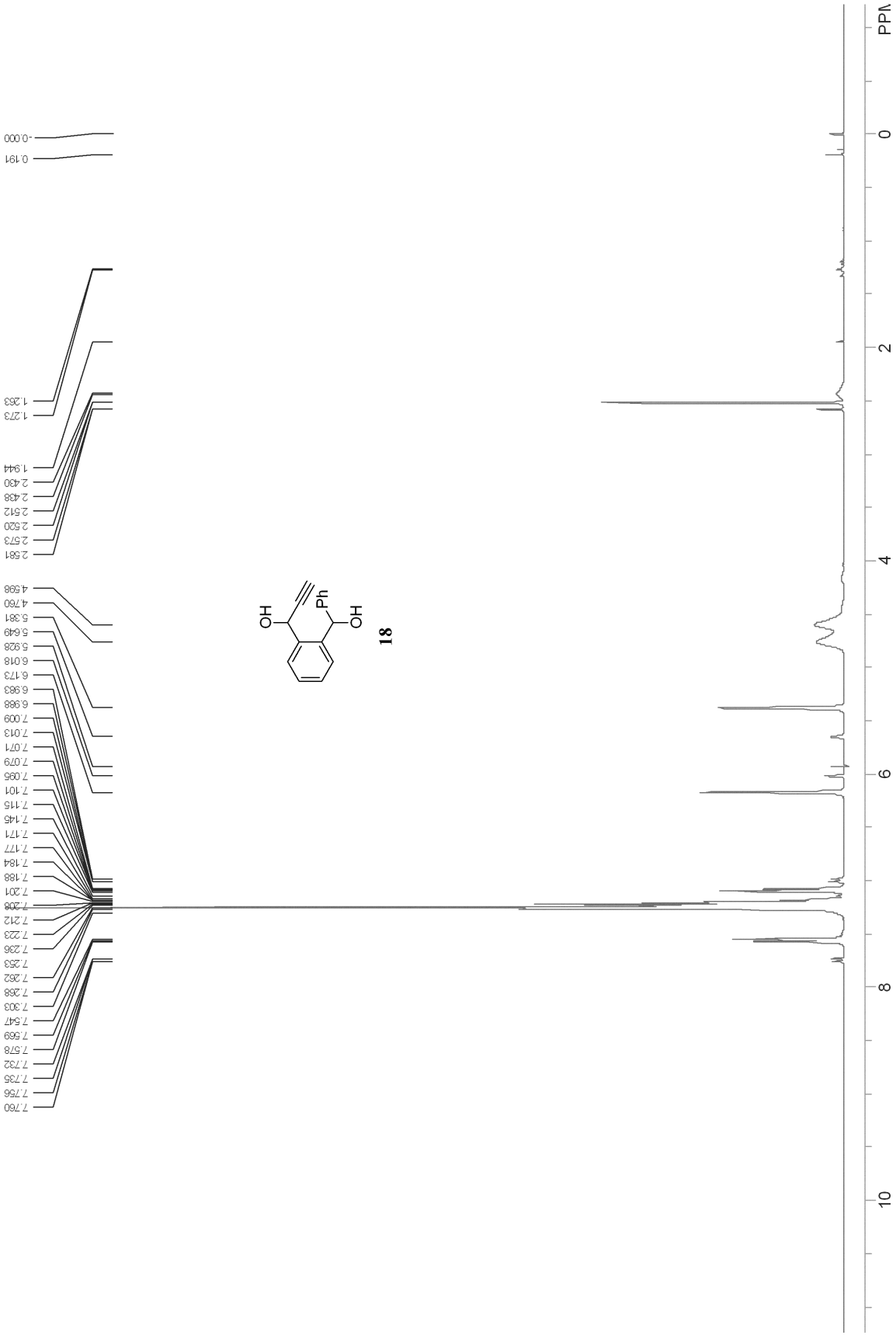
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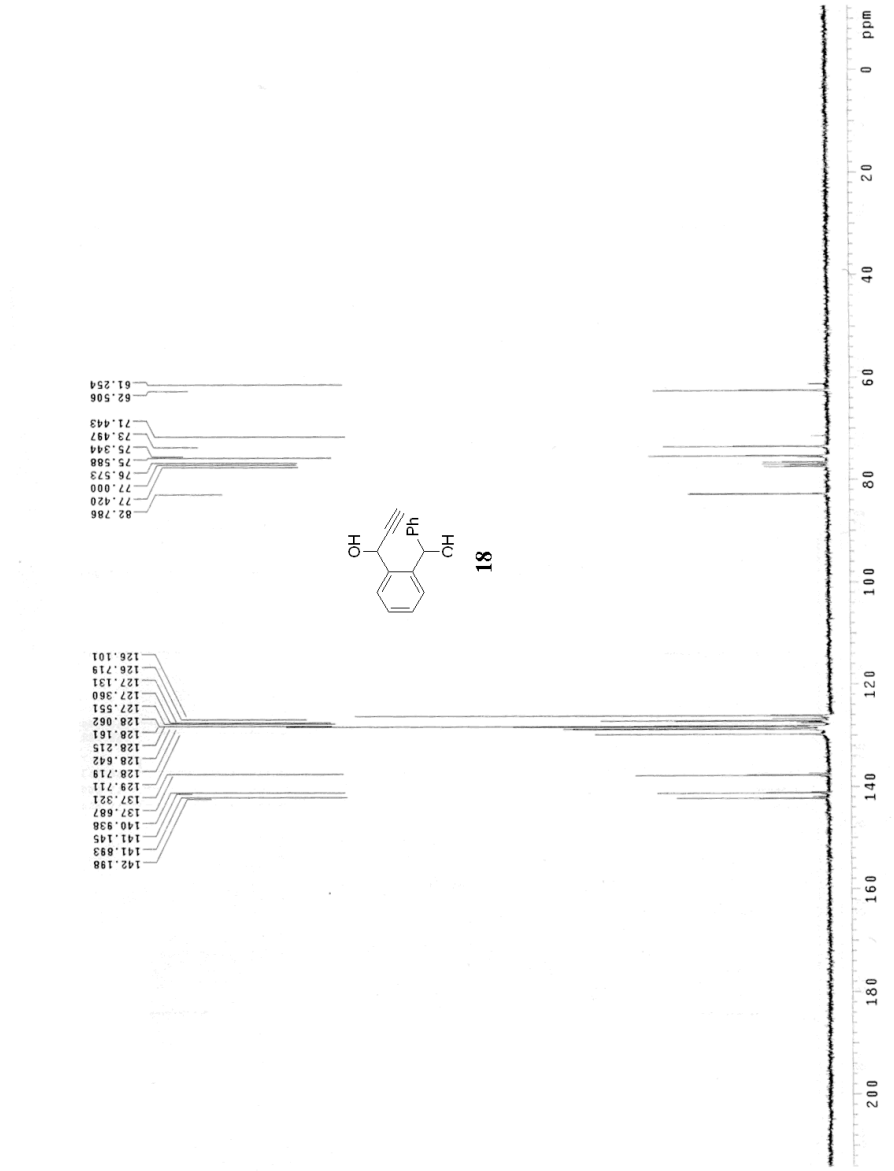
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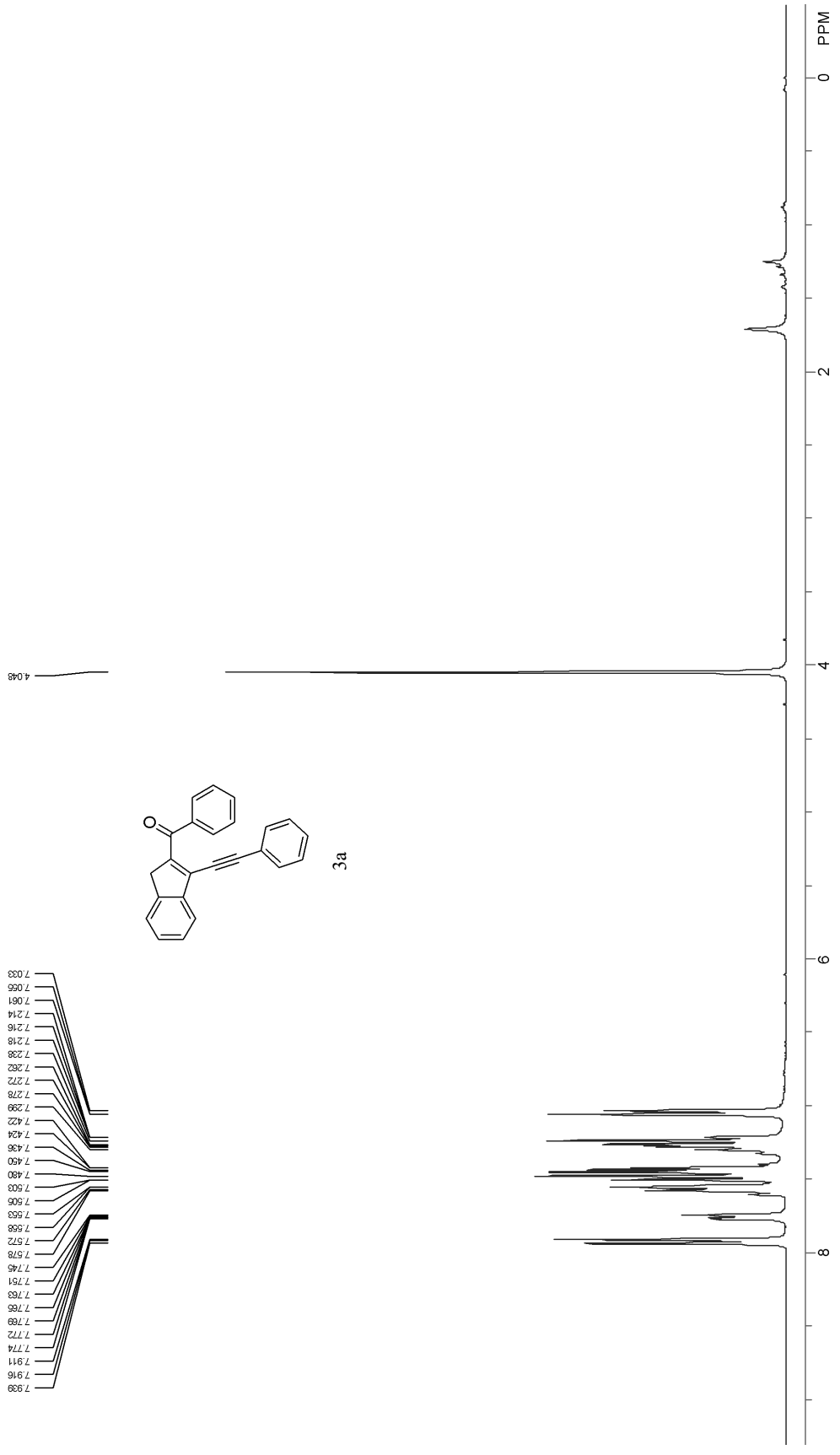
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7.299
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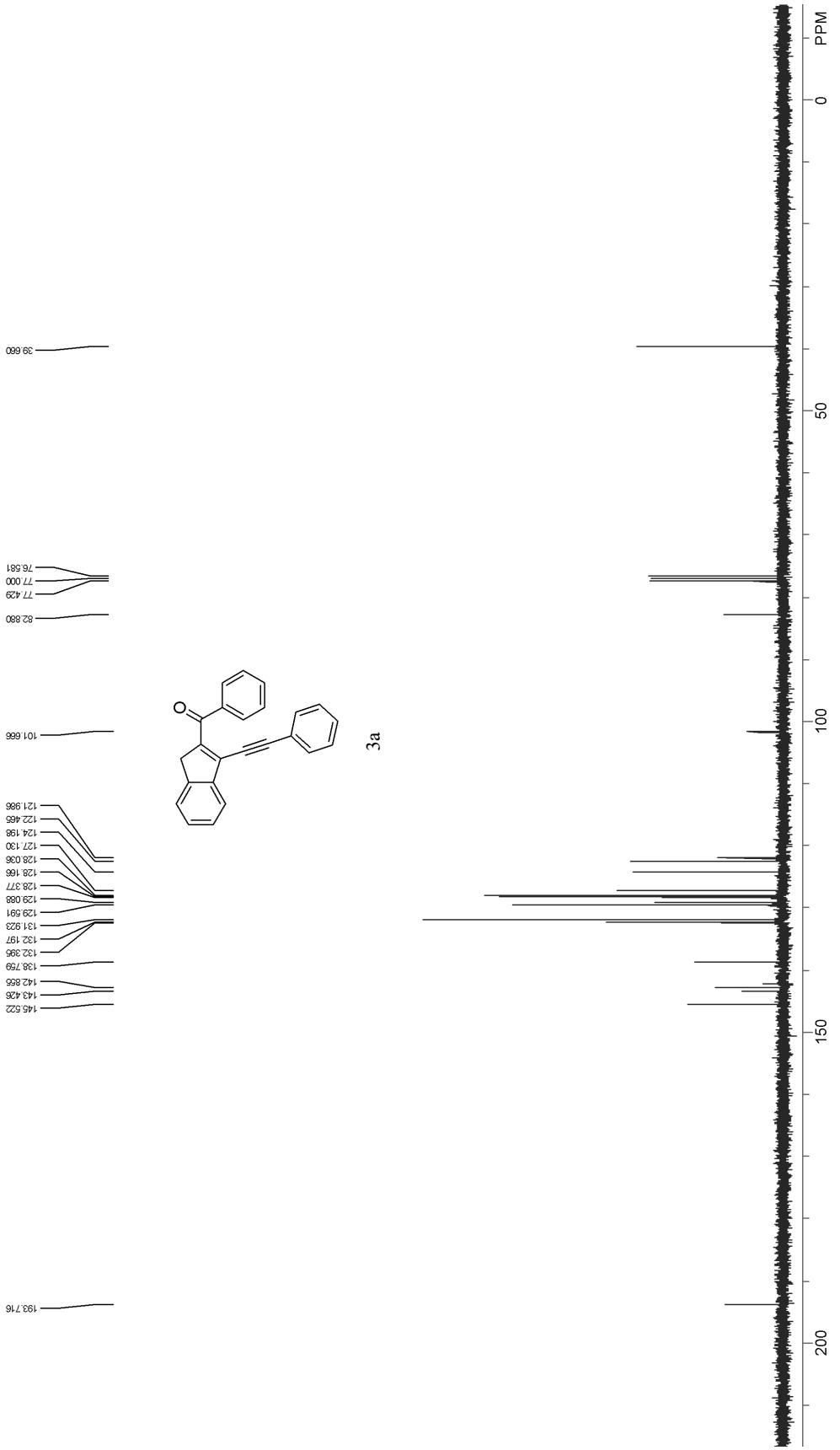
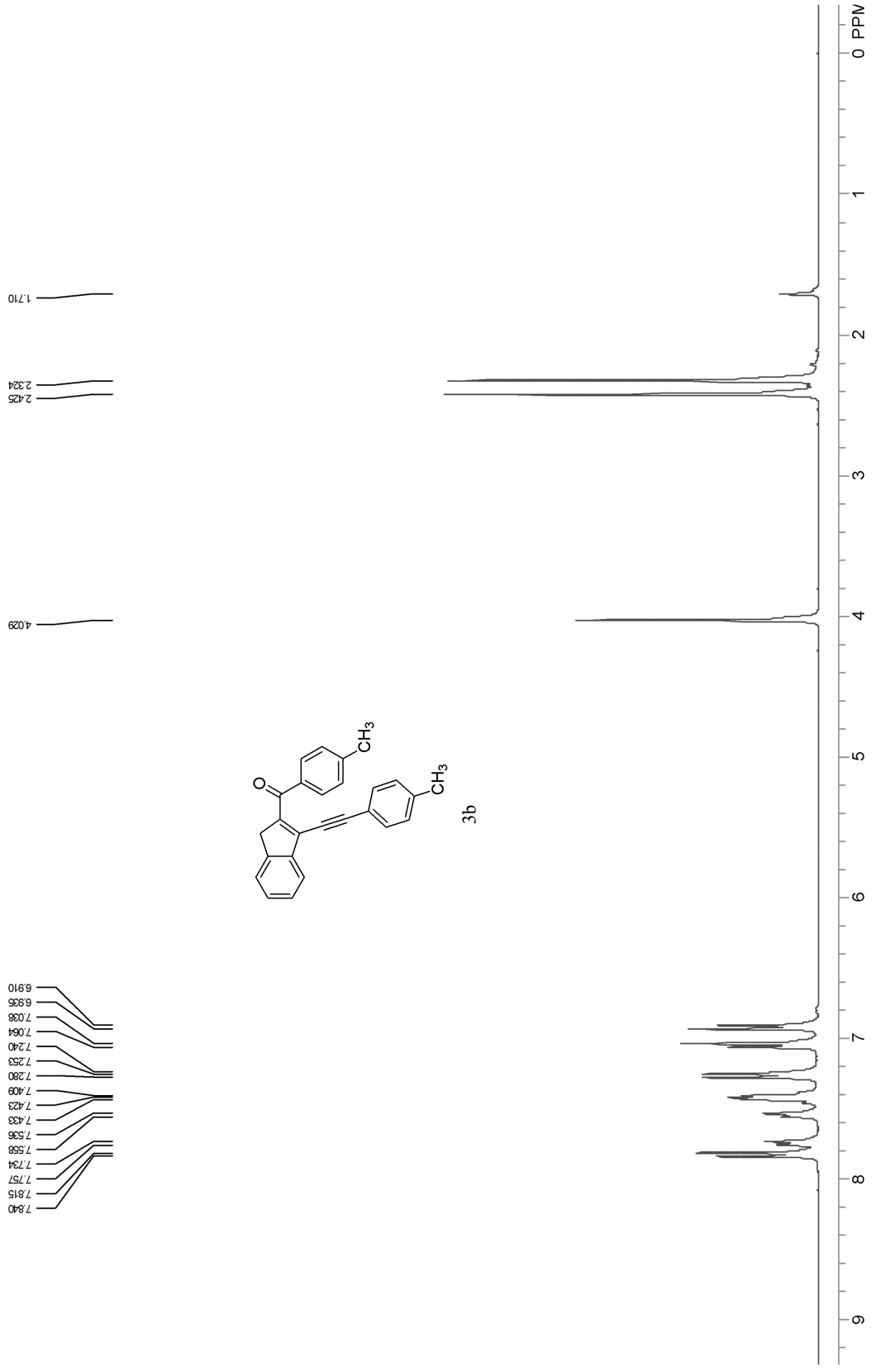
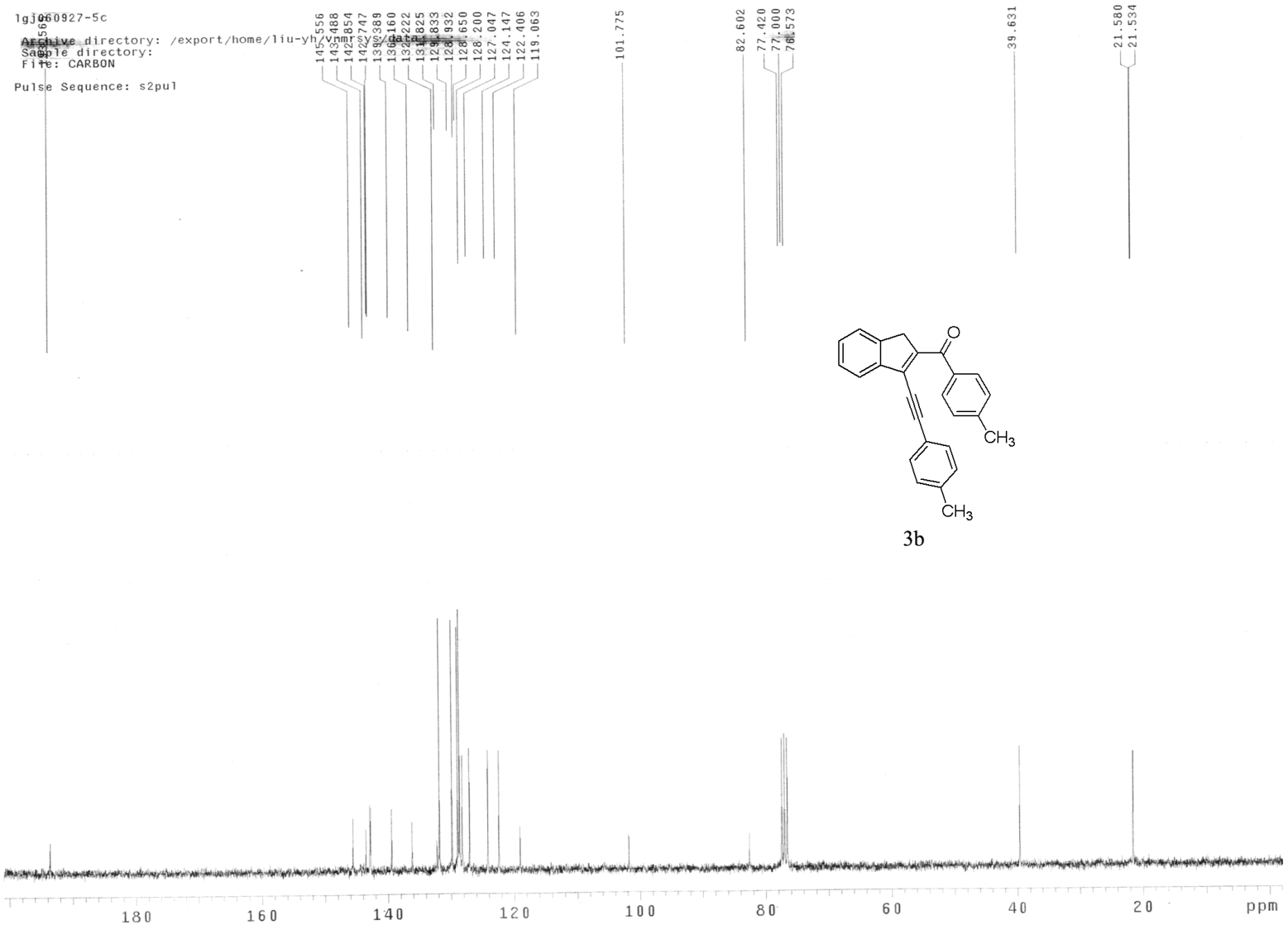
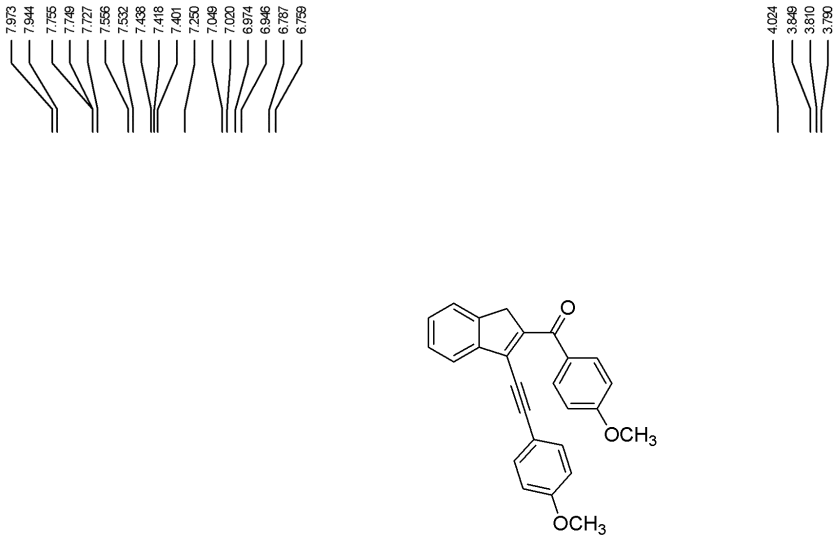
7.272
7.262
7.238
7.218
7.216
7.214
7.061
7.055
7.033
O
3a


39.660
76.681
77.000
77.429
82.880
101.666
121.986
122.466
124.198
127.130
128.036
128.166
128.377
129.088
129.691
131.923
132.197
132.396
138.759
142.866
143.426
145.522
193.716
O
3a
PPM
0
50
100
150
200


1.710
2.324
2.425
4.029
6.910
6.935
7.038
7.064
7.240
7.253
7.280
7.409
7.423
7.433
7.536
7.558
7.734
7.757
7.815
7.840
O
CH3
CH3
3b
0 PPM
1
2
3
4
5
6
7
8
9


lgj060927-5c
Archive directory: /export/home/liu-yh/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
145.556
143.488
142.854
142.747
130.389
130.160
129.222
128.825
128.833
128.932
128.650
128.200
127.047
124.147
122.406
119.063
101.775
82.602
77.420
77.000
76.573
39.631
21.580
21.534
CH3
CH3
180
160
140
120
100
80
60
40
20
ppm

3b


7.973
7.944
7.755
7.749
7.727
7.556
7.532
7.438
7.418
7.401
7.250
7.049
7.020
6.974
6.946
6.787
6.759
4.024
3.849
3.810
3.790
O
OCH3
OCH3
8
7
6
5
4
3
2
1
PPM

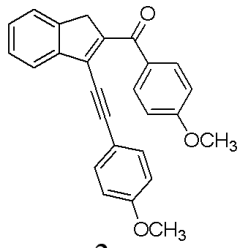
3c

lgj060926-1c

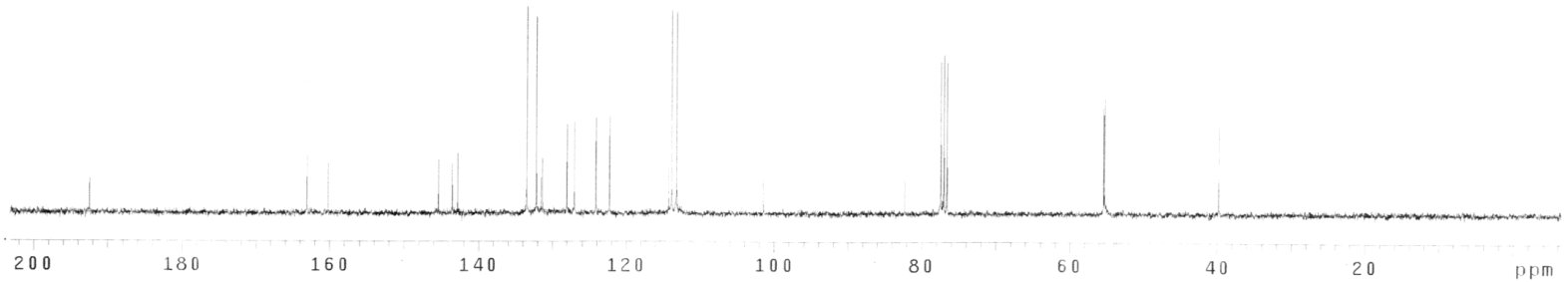
Archive directory: /export/home/liu-yh/vnmrsys/data
Sample directory:
File: CARBON

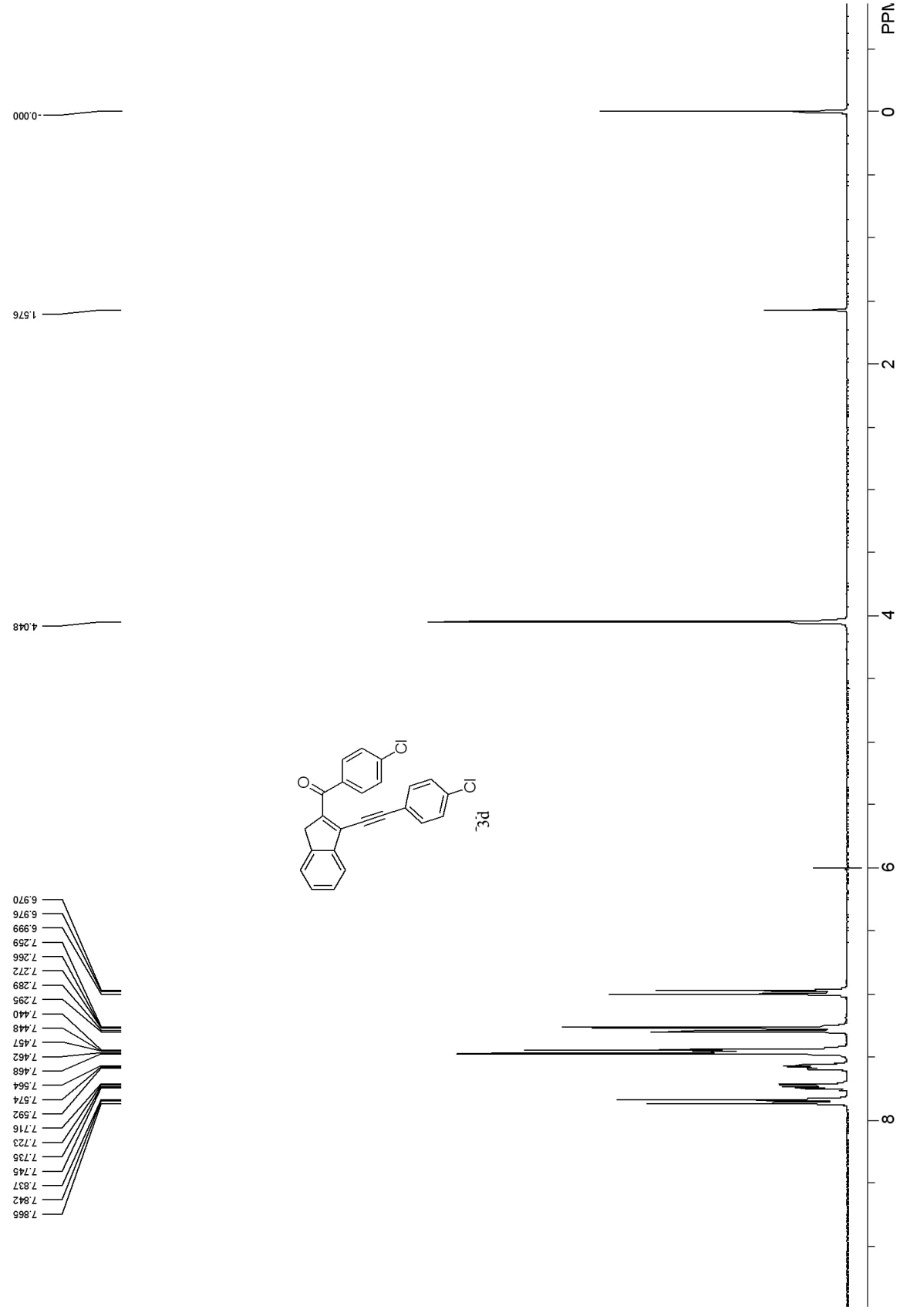
Pulse Sequence: s2pul

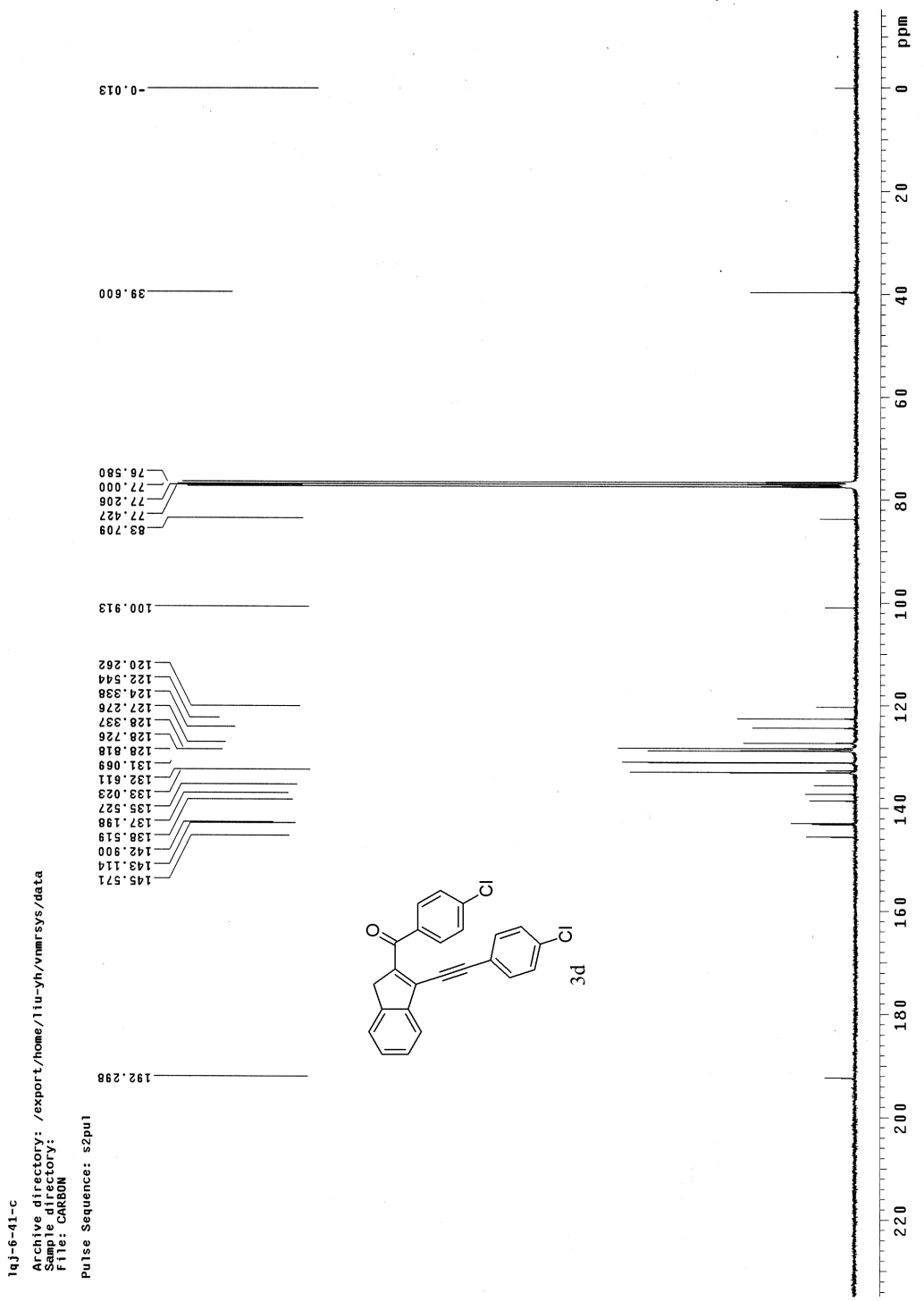
192.443
163.081
160.203
145.365
143.534
142.801
133.474
132.169
131.558
131.321
128.016
127.009
124.116
122.269
114.247
113.843
113.202
101.447
82.282
77.427
77.000
76.580
55.438
55.270
39.776

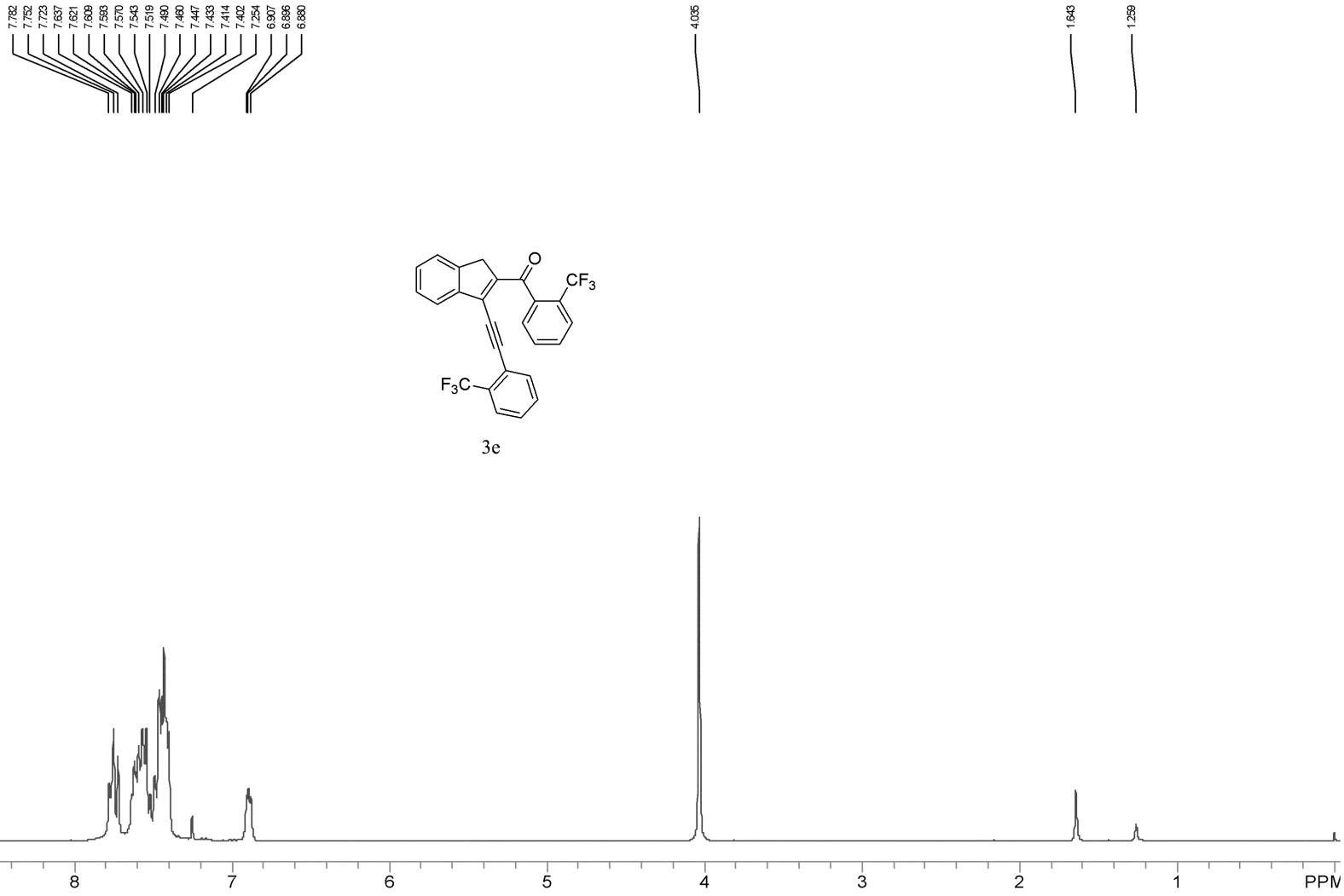


3c

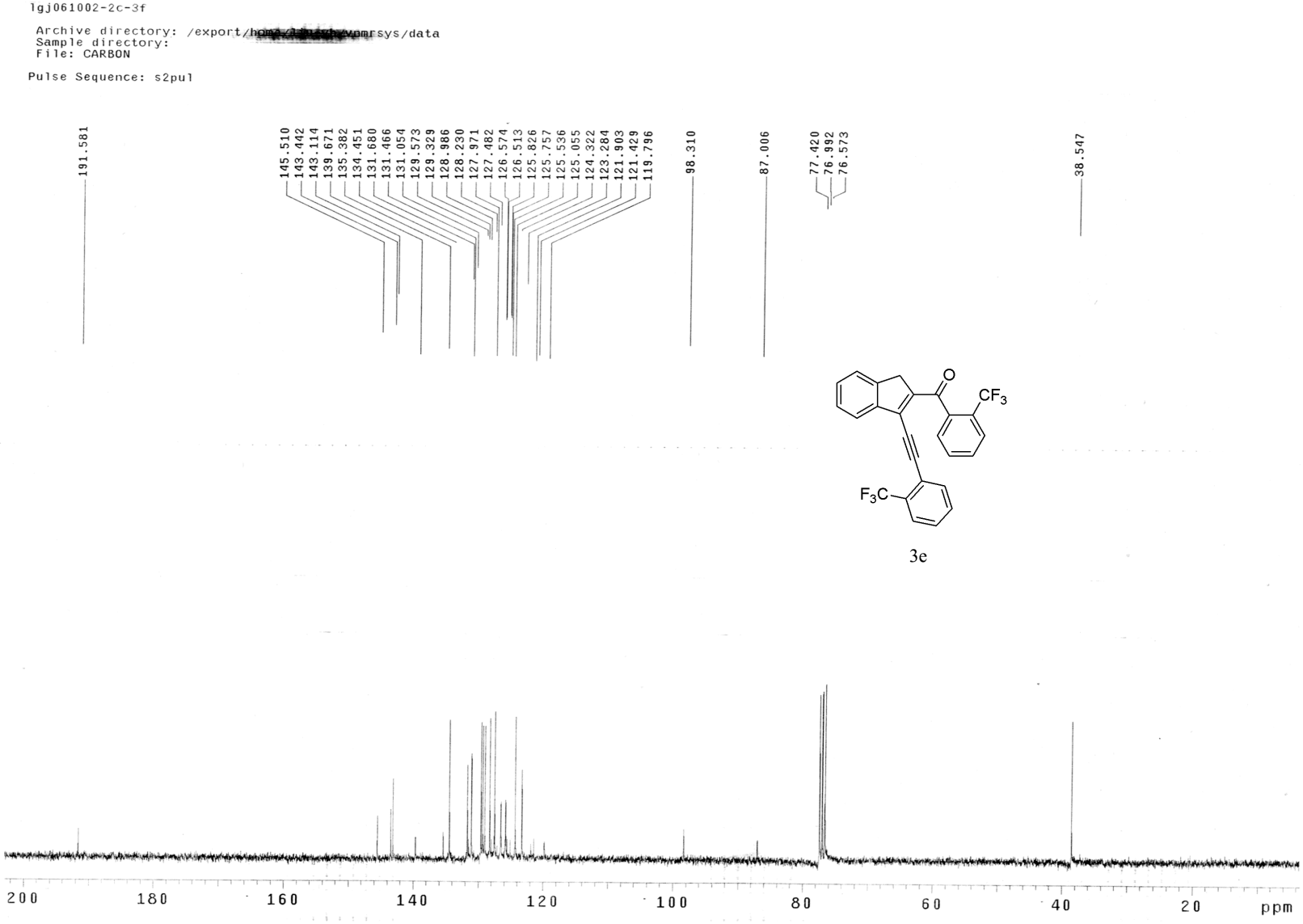



PPM
0
2
4
6
8
0.000
1.576
4.048
6.970
6.976
6.999
7.259
7.266
7.272
7.289
7.295
7.440
7.448
7.457
7.462
7.468
7.564
7.574
7.592
7.716
7.723
7.735
7.745
7.837
7.842
7.865
O
Cl
Cl
3d

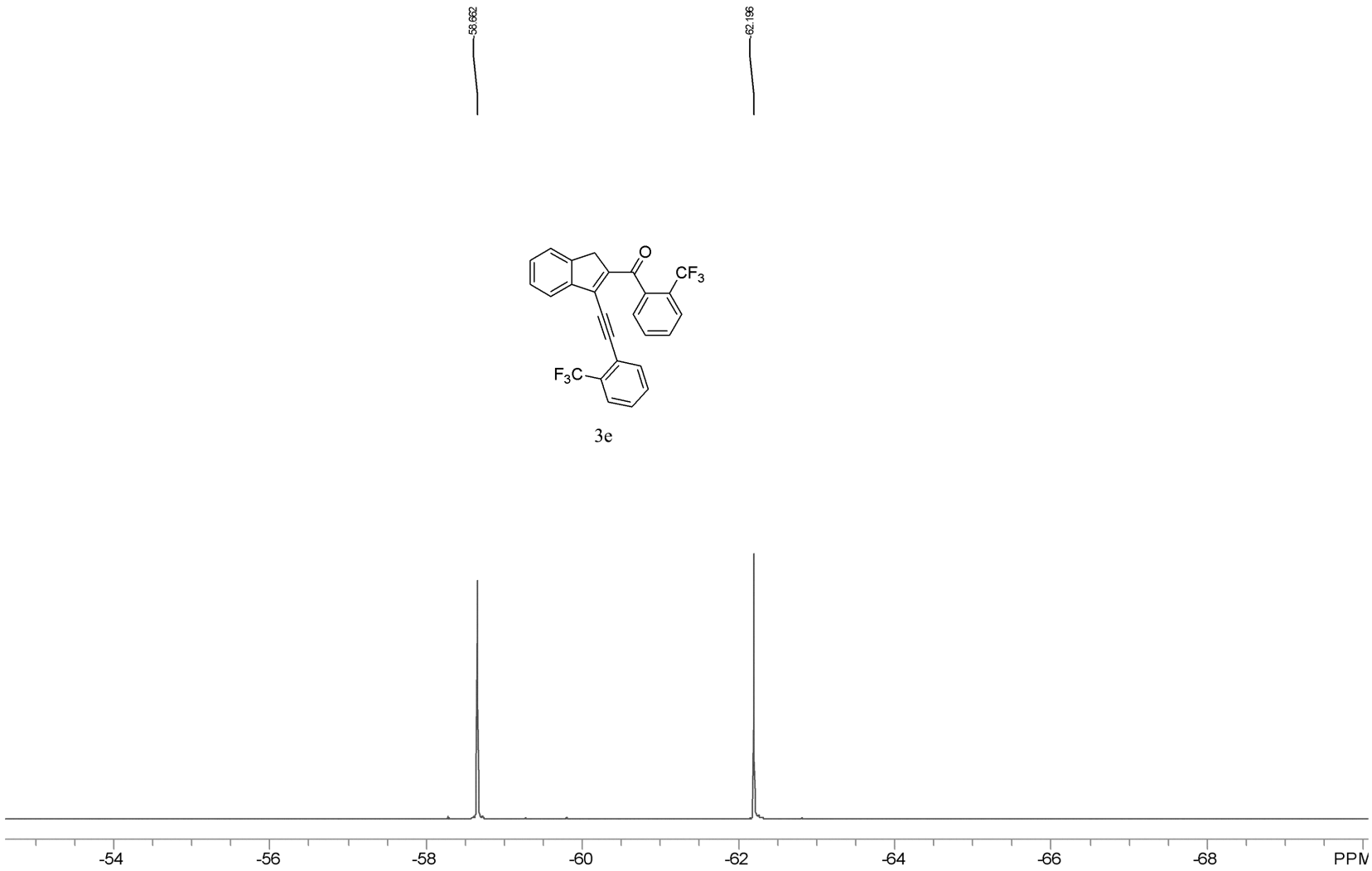

lqj-6-41-c
Archive directory: /export/home/liu-yh/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
-0.013
39.600
76.580
77.000
77.206
77.427
83.709
100.913
120.262
122.544
124.338
127.276
128.337
128.726
128.818
131.069
132.611
133.023
135.527
137.198
138.519
142.900
143.114
145.571
192.298
Cl
O
Cl
3d
ppm


7.782
7.752
7.723
7.637
7.621
7.609
7.593
7.570
7.543
7.519
7.490
7.480
7.447
7.433
7.414
7.402
7.254
6.907
6.896
6.880
4.035
1.643
1.259
O
CF3
F3C
8
7
6
5
4
3
2
1
PPM

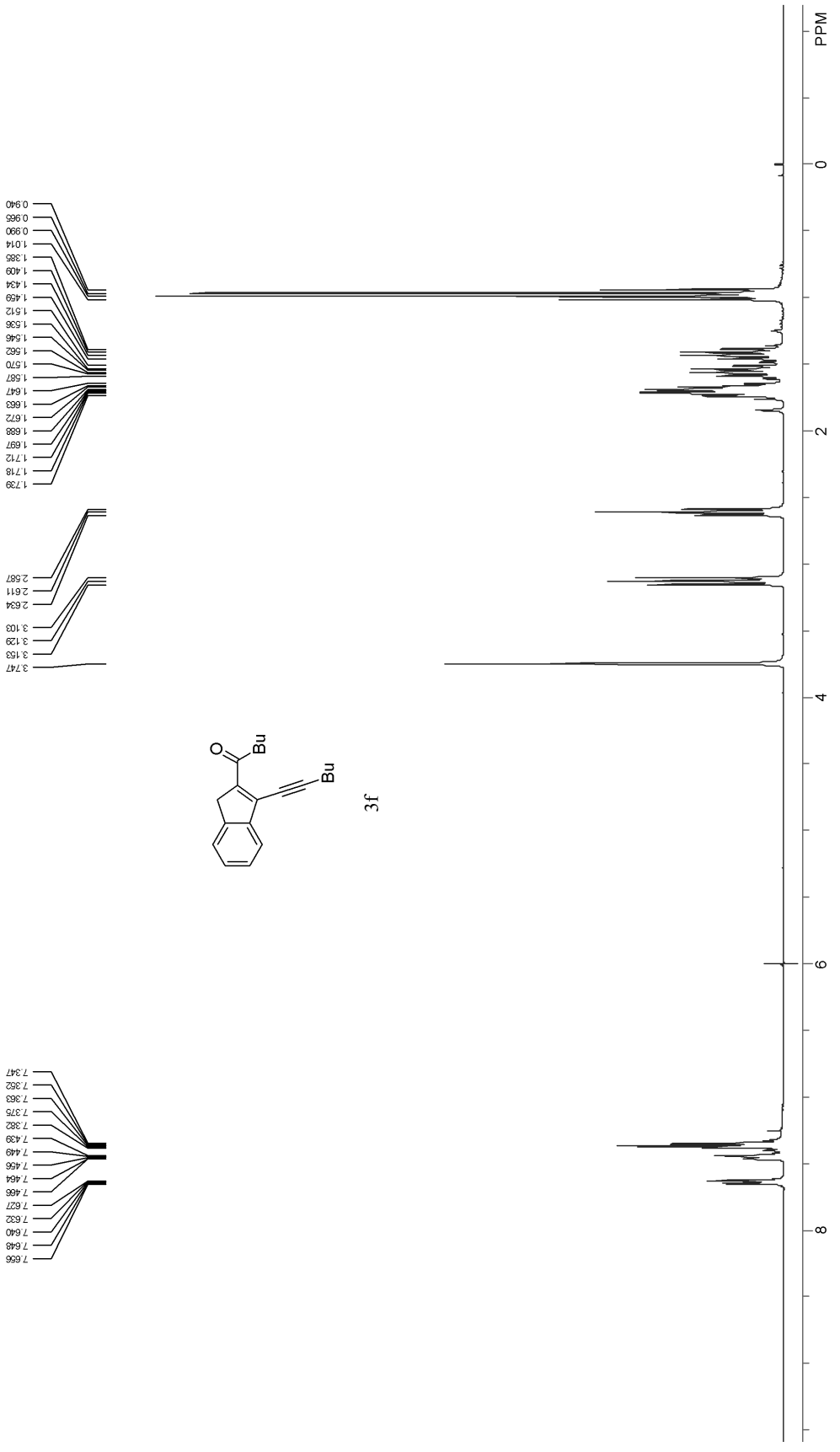
3e

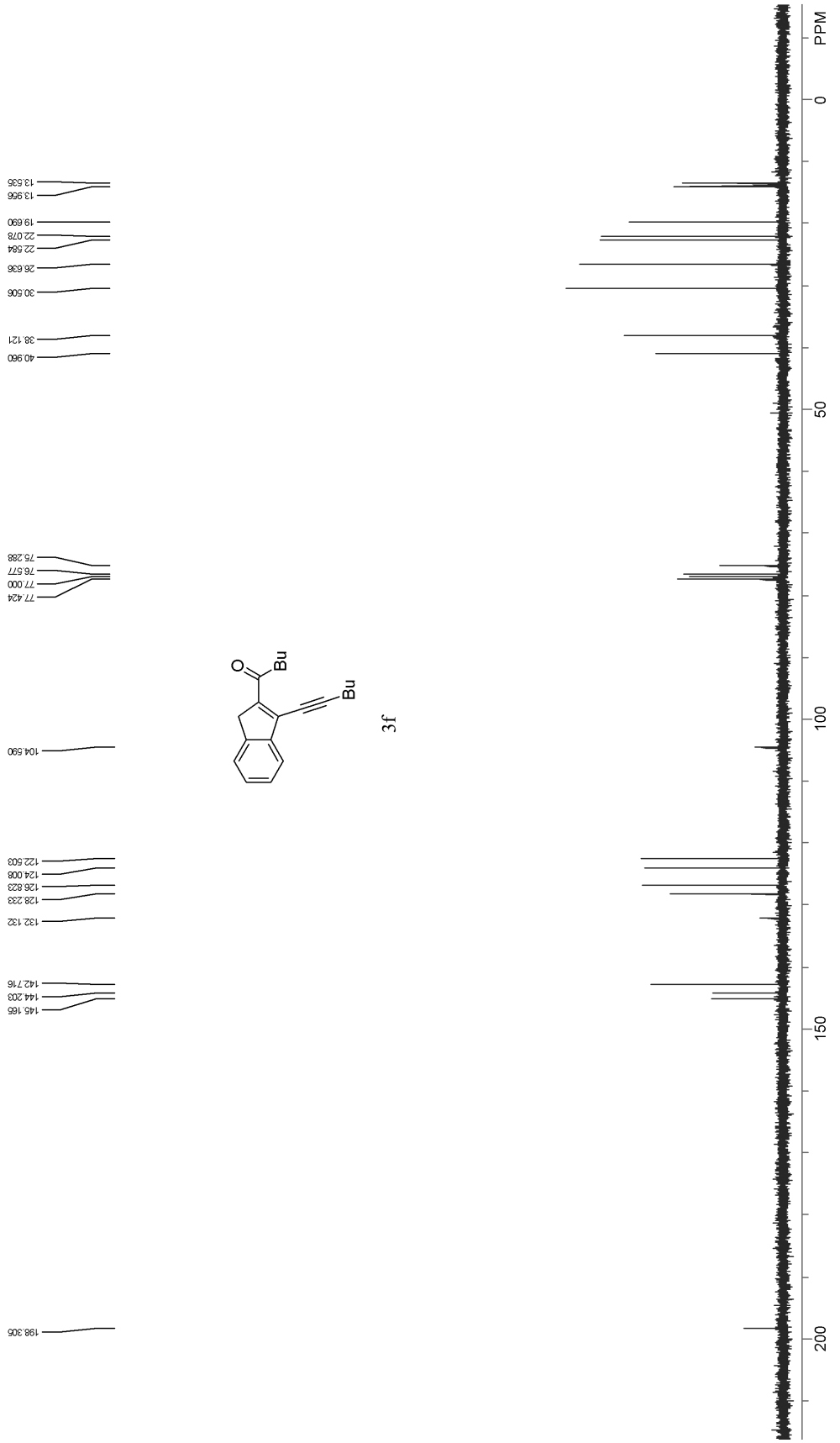

lgj061002-2c-3f
Archive directory: /export/[redacted]vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
191.581
145.510
143.442
143.114
139.671
135.382
134.451
131.680
131.466
131.054
129.573
129.329
128.986
128.230
127.971
127.482
126.574
126.513
125.826
125.757
125.536
125.055
124.322
123.284
121.903
121.429
119.796
98.310
87.006
77.420
76.992
76.573
38.547
O
CF3
F3C
200
180
160
140
120
100
80
60
40
20
ppm

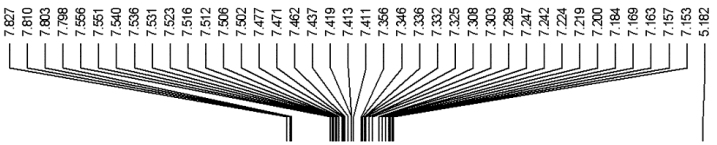
3e



3e


PPM
0
2
4
6
8
O
Bu
Bu
3f
0.940
0.965
0.990
1.014
1.385
1.409
1.434
1.459
1.512
1.536
1.546
1.562
1.570
1.587
1.647
1.663
1.672
1.688
1.697
1.712
1.718
1.739
2.587
2.611
2.634
3.103
3.129
3.153
3.747
7.347
7.362
7.363
7.375
7.382
7.439
7.449
7.456
7.464
7.466
7.627
7.632
7.640
7.648
7.666


13.536
13.956
19.690
22.078
22.584
26.636
30.506
38.121
40.960
75.288
76.577
77.000
77.424
104.590
122.503
124.008
126.823
128.233
132.132
142.716
144.203
145.166
198.306
O
Bu
Bu
3f
PPM
0
50
100
150
200


7.827
7.810
7.803
7.798
7.556
7.551
7.540
7.536
7.531
7.523
7.516
7.512
7.506
7.502
7.477
7.471
7.462
7.437
7.419
7.413
7.411
7.356
7.346
7.336
7.332
7.325
7.308
7.303
7.289
7.247
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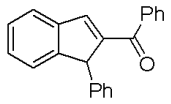
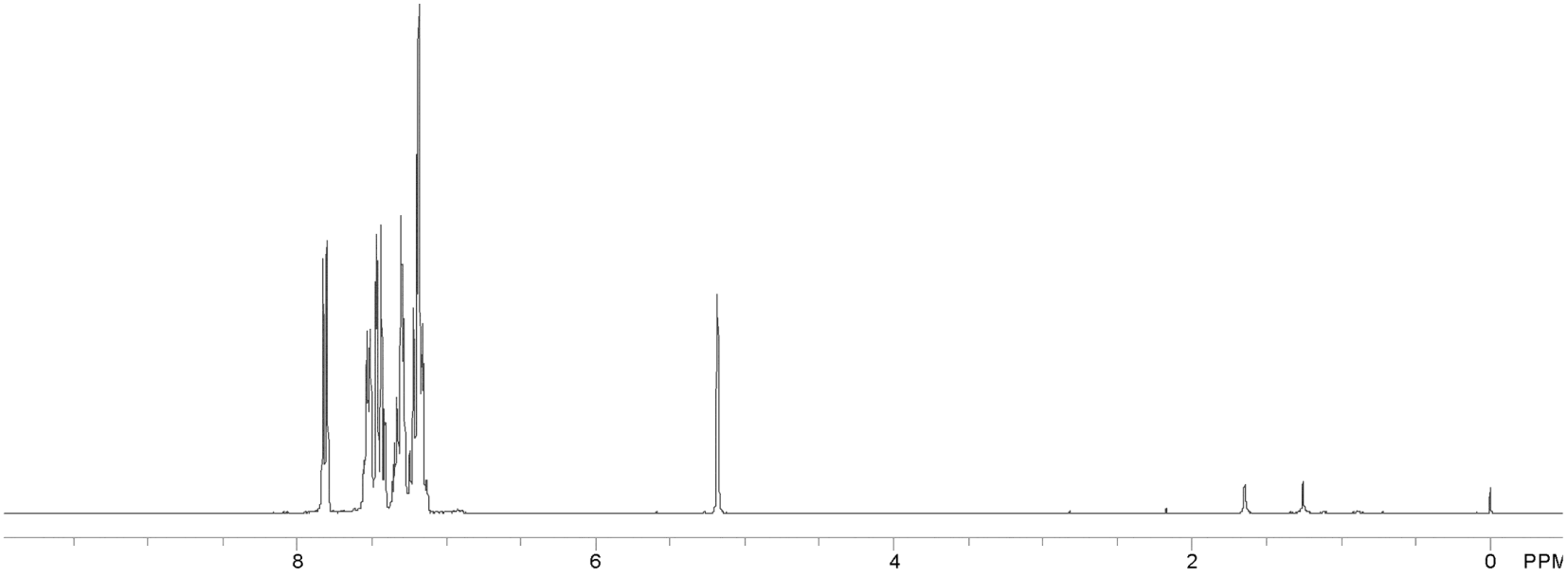
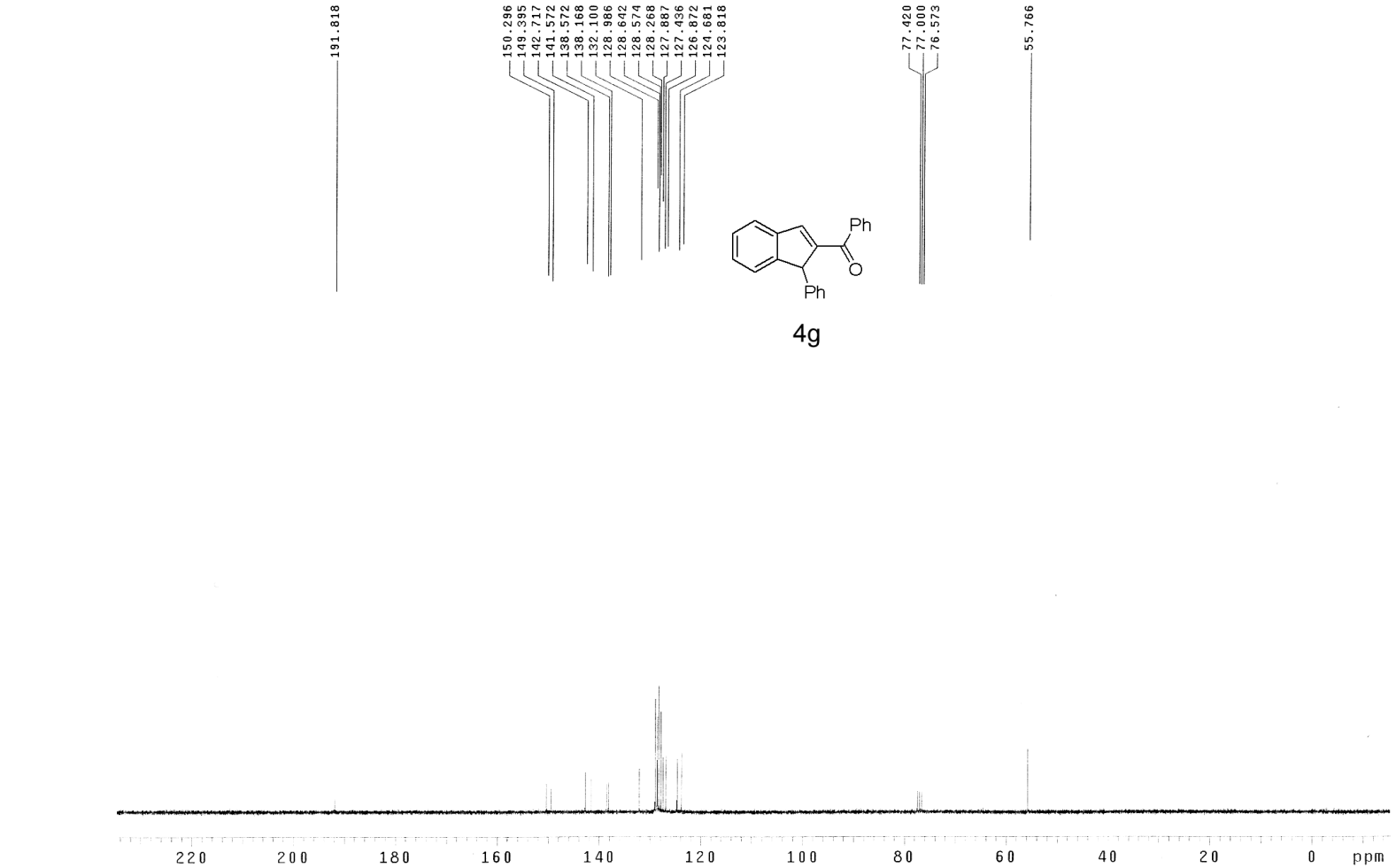
7.224
7.219
7.200
7.184
7.169
7.163
7.157
7.153
5.182

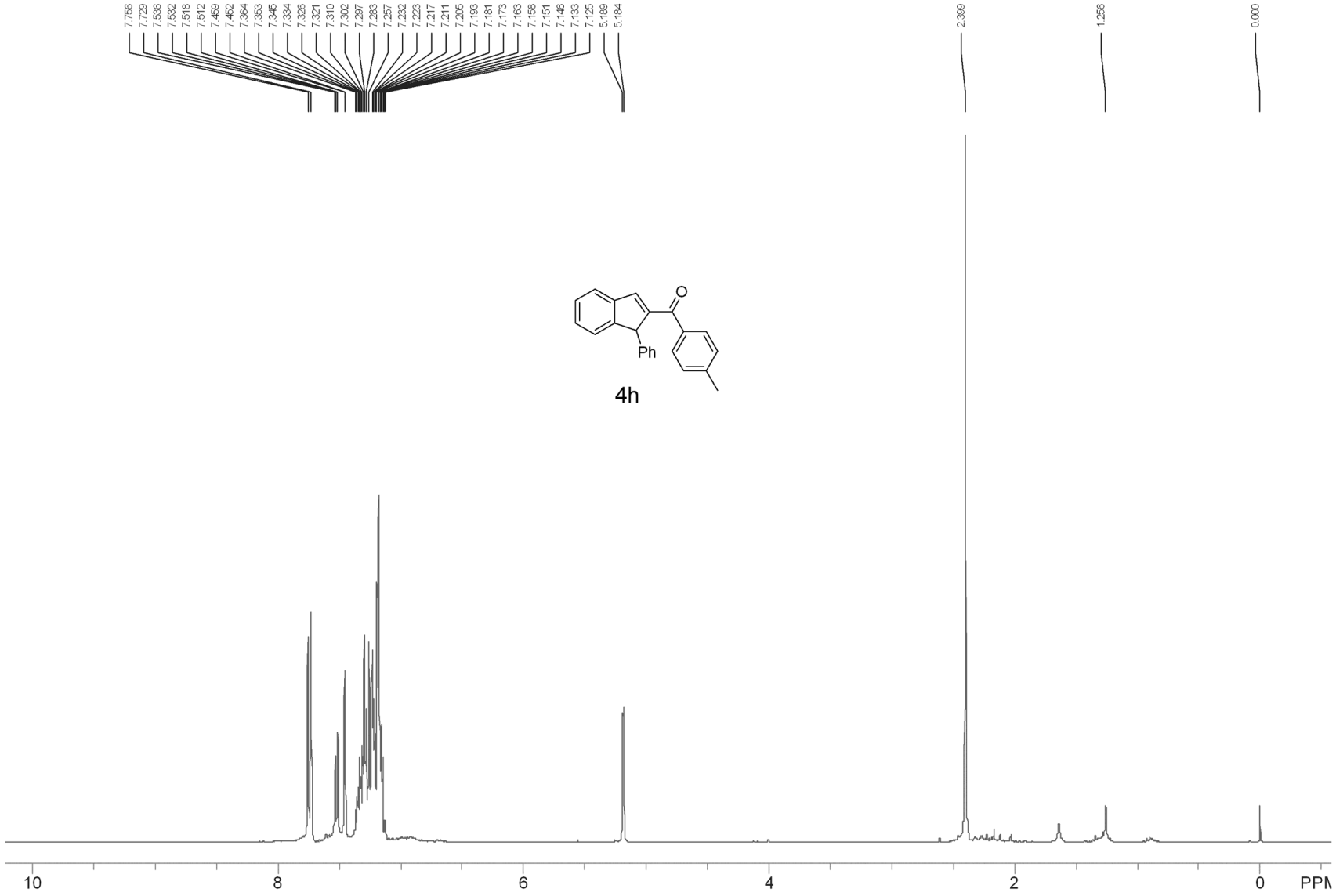

Ph
O
Ph

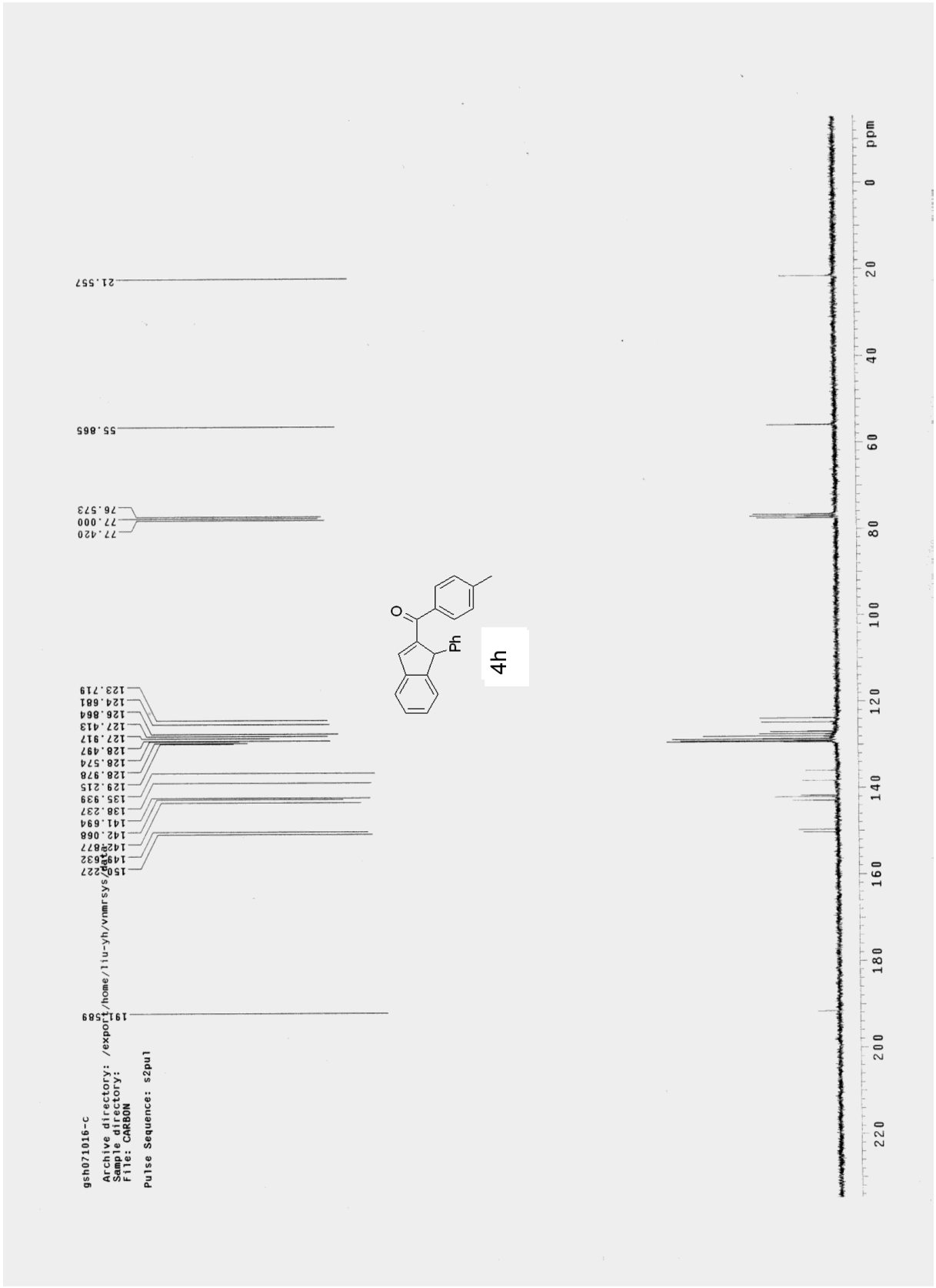
4g

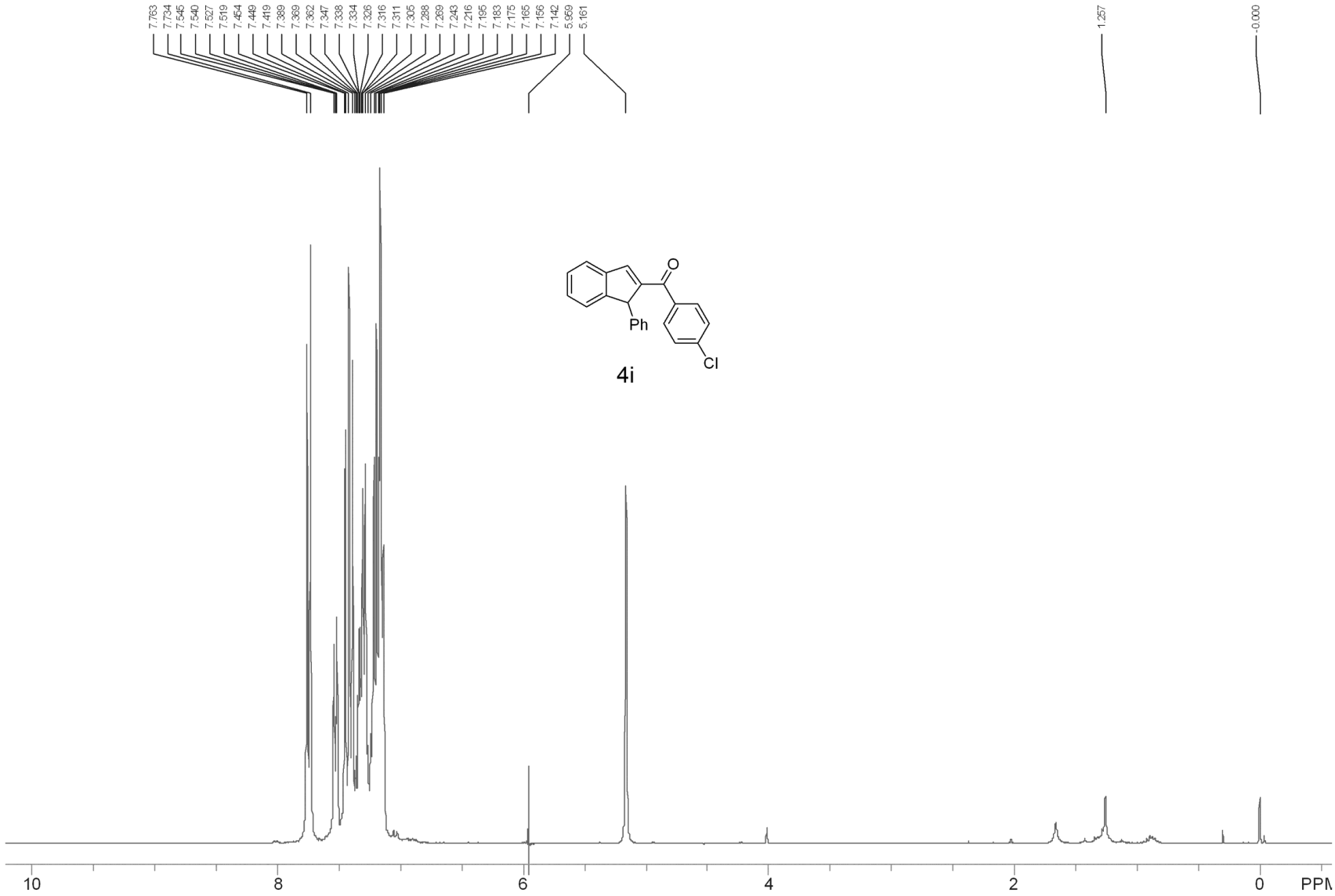

8
6
4
2
0
PPM

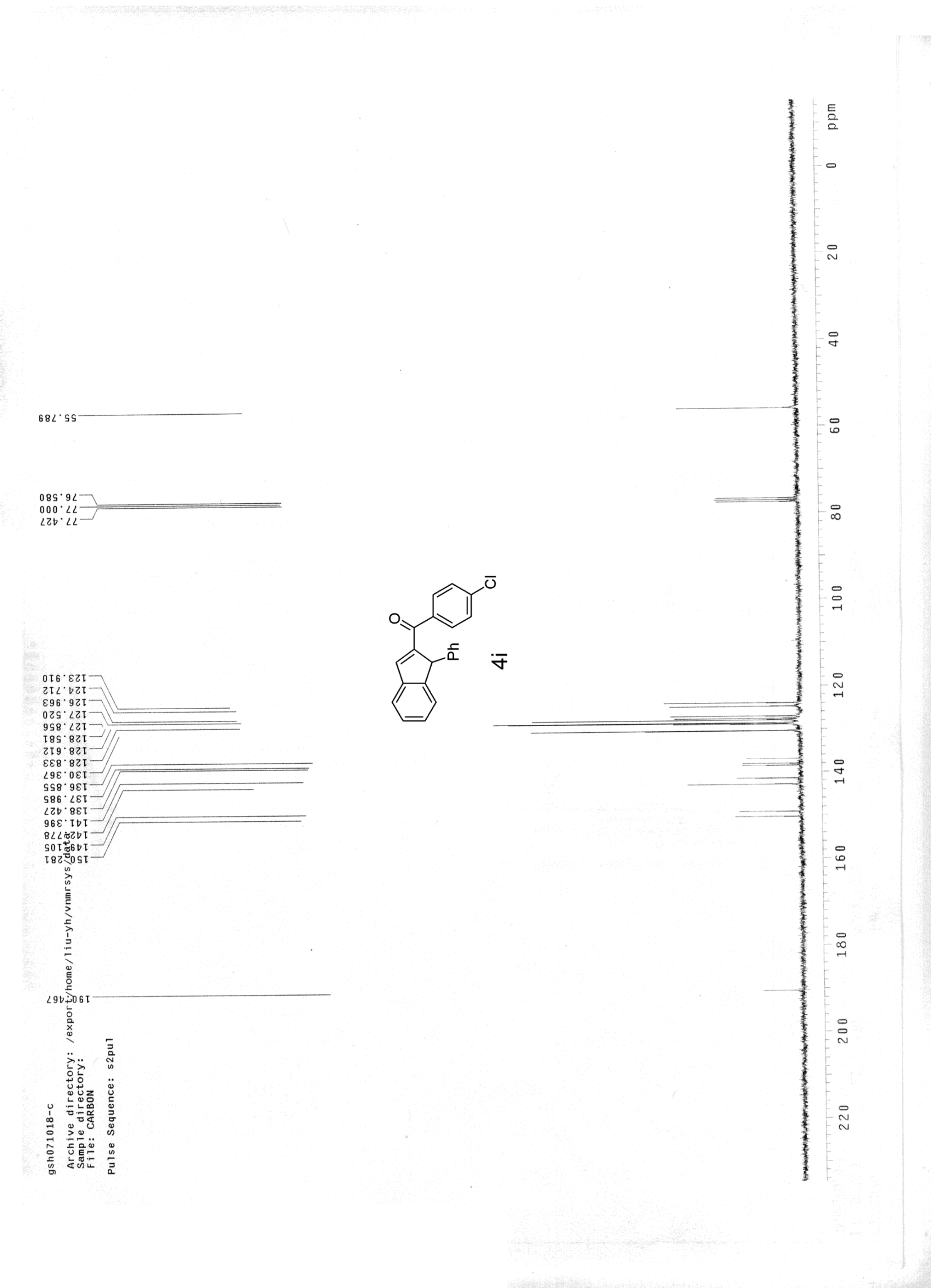

191.818
150.296
149.395
142.717
141.572
138.572
138.168
132.100
128.986
128.642
128.574
128.268
127.887
127.436
126.872
124.681
123.818
77.420
77.000
76.573
55.766
Ph
O
Ph
220
200
180
160
140
120
100
80
60
40
20
0
ppm

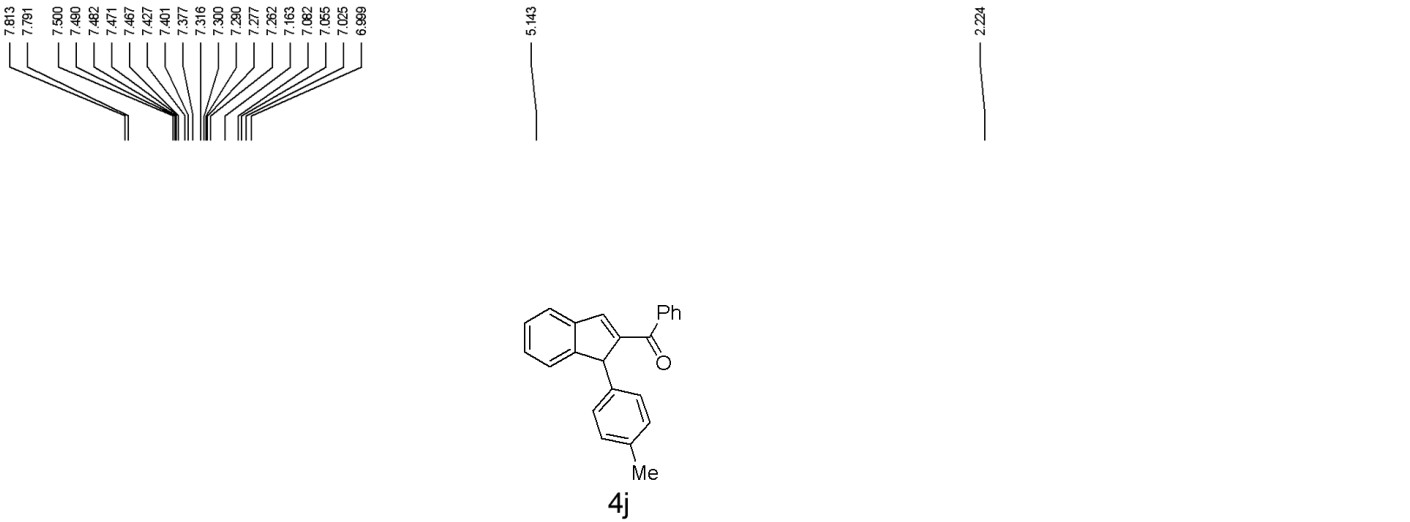
4g

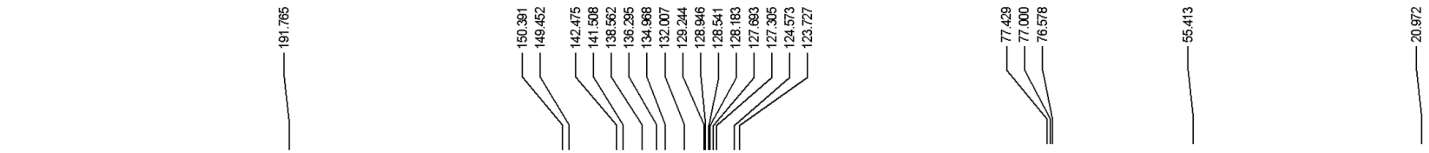

7.756
7.729
7.536
7.532
7.518
7.512
7.459
7.452
7.364
7.353
7.345
7.334
7.326
7.321
7.310
7.302
7.297
7.283
7.257
7.232
7.223
7.217
7.211
7.205
7.193
7.181
7.173
7.163
7.158
7.151
7.146
7.133
7.125
5.189
5.184
2.399
1.256
0.000
O
Ph
4h
10
8
6
4
2
0
PPM


gsh071016-c
Archive directory: /export/home/liu-yh/vnmrsys/
Sample directory:
File: CARBON
Pulse Sequence: s2pul
191.589
150.227
149.632
142.877
142.068
141.694
138.237
135.939
129.215
128.978
128.574
128.497
127.917
127.413
126.864
124.681
123.719
77.420
77.000
76.573
55.865
21.557
O
Ph
4h
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.763
7.734
7.545
7.540
7.527
7.519
7.454
7.449
7.419
7.389
7.369
7.362
7.347
7.338
7.334
7.326
7.316
7.311
7.305
7.288
7.269
7.243
7.216
7.195
7.183
7.175
7.165
7.156
7.142
5.969
5.161
1.257
0.000
O
Ph
Cl
4i
10
8
6
4
2
0
PPM


gsh071018-c
Archive directory: /export/home/liu-yh/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
190.467
150.281
149.105
142.778
141.396
138.427
137.985
136.855
130.367
128.833
128.612
128.581
127.856
127.520
126.963
124.712
123.910
77.427
77.000
76.580
55.789
O
Cl
Ph
4i
ppm


7.813
7.791
7.500
7.490
7.482
7.471
7.467
7.427
7.401
7.377
7.316
7.300
7.290
7.277
7.262
7.163
7.082
7.055
7.025
6.899
5.143
2.224
Ph
O
Me
4j
10
8
6
4
2
0
PPM


191.765
150.391
149.452
142.475
141.508
138.562
136.295
134.988
132.007
129.244
128.946
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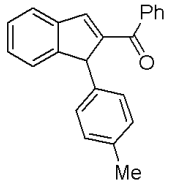
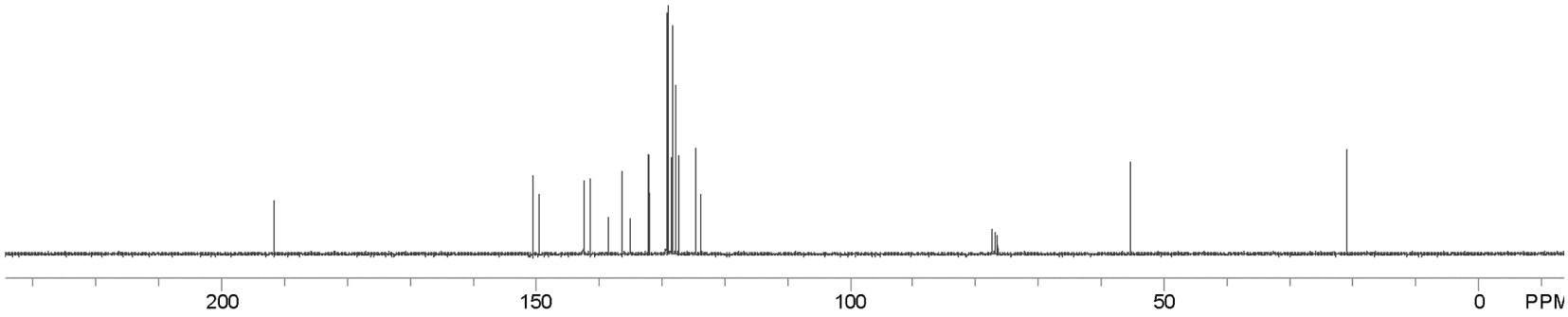
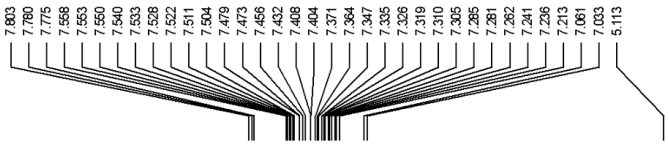
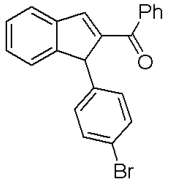
127.305
124.573
123.727
77.429
77.000
76.578
55.413
20.972


Ph
O
Me

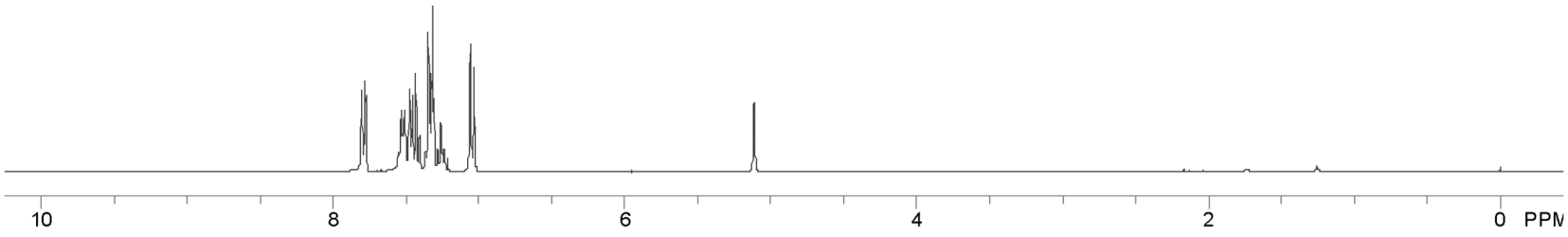
4j

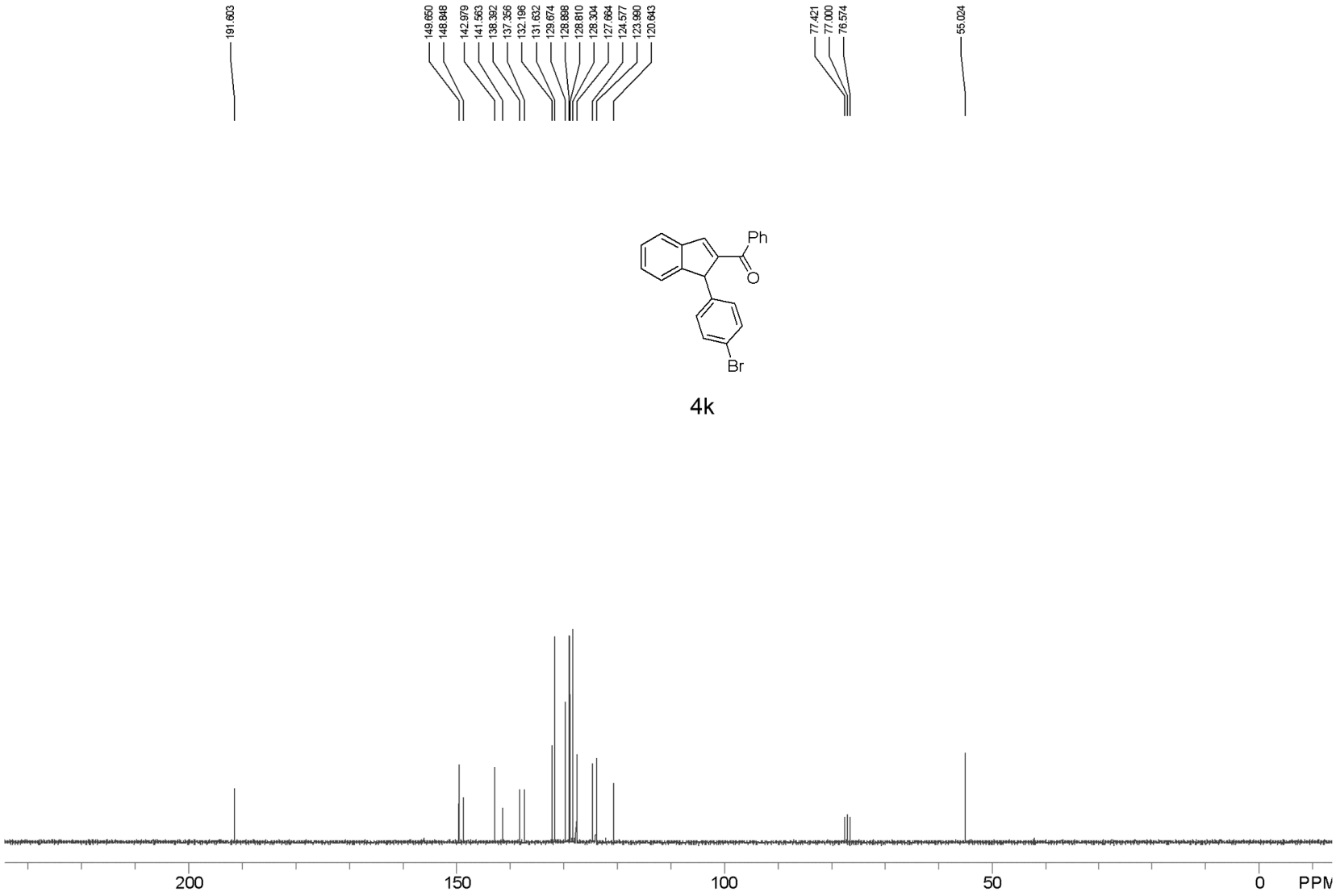

200
150
100
50
0
PPM


7.803
7.780
7.775
7.558
7.553
7.550
7.540
7.533
7.528
7.522
7.511
7.504
7.479
7.473
7.456
7.432
7.408
7.404
7.371
7.364
7.347
7.335
7.326
7.319
7.310
7.305
7.285
7.281
7.262
7.241
7.236
7.213
7.061
7.033
5.113

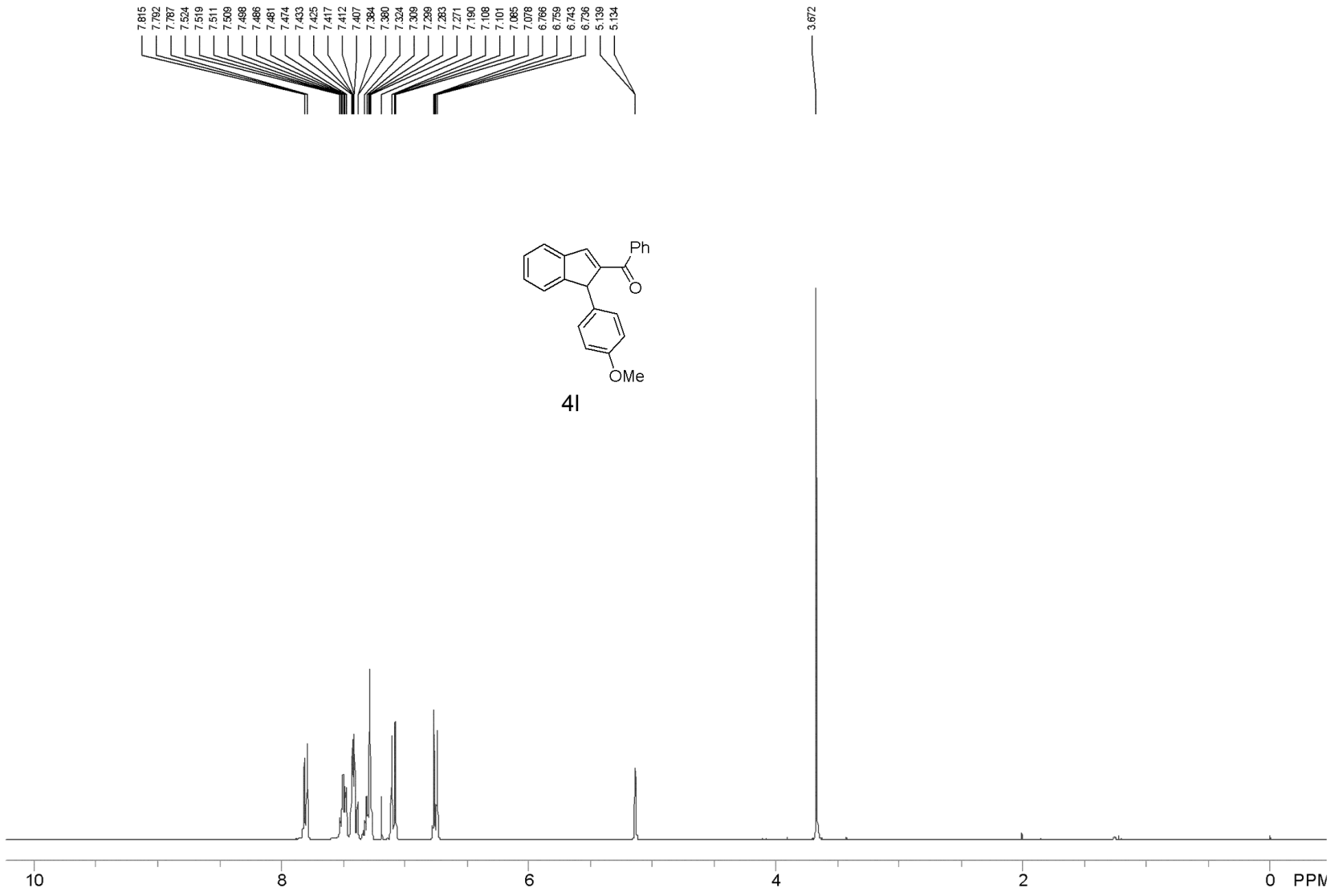

Ph
O
Br

4k

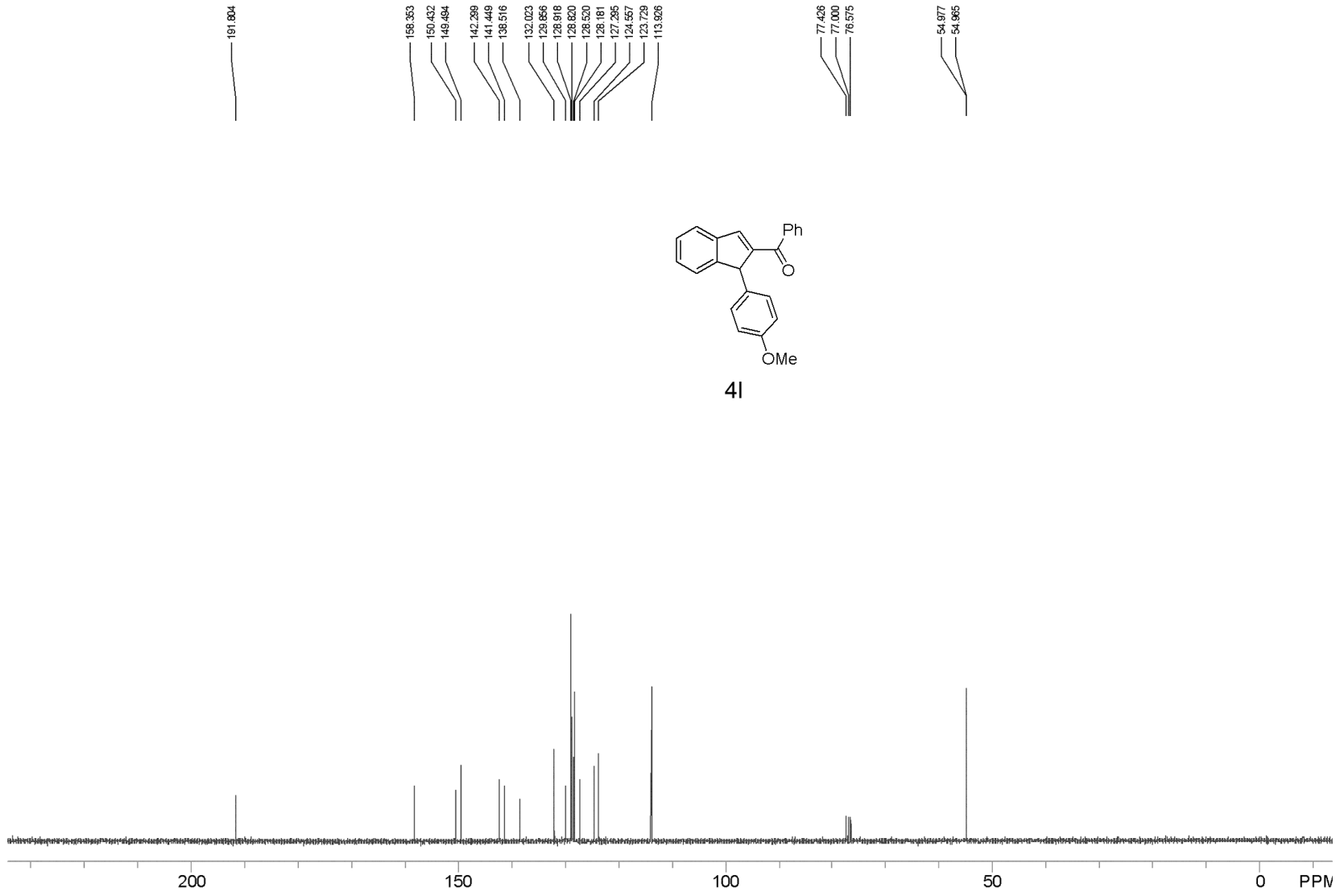

10
8
6
4
2
0
PPM


191.603
149.650
148.848
142.979
141.563
138.392
137.356
132.196
131.632
129.674
128.888
128.810
128.304
127.664
124.577
123.990
120.843
77.421
77.000
76.574
55.024
Ph
O
Br
200
150
100
50
0
PPM

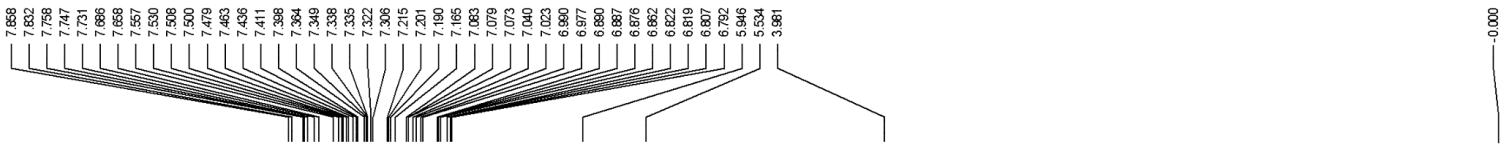
4k

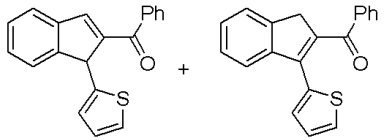

7.815
7.792
7.787
7.524
7.519
7.511
7.509
7.498
7.486
7.481
7.474
7.433
7.425
7.417
7.412
7.407
7.384
7.380
7.324
7.309
7.289
7.283
7.271
7.190
7.108
7.101
7.085
7.078
6.766
6.759
6.743
6.736
5.139
5.134
3.672
Ph
O
OMe
10
8
6
4
2
0
PPM

4l

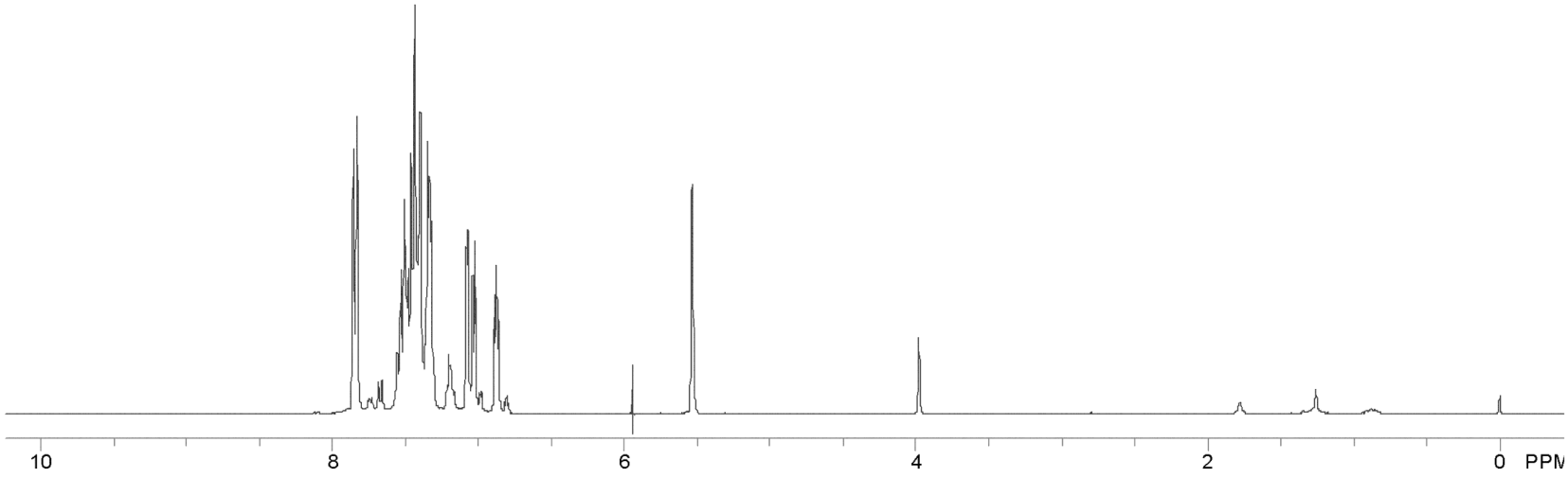

191.804
158.353
150.432
149.494
142.299
141.449
138.516
132.023
129.856
128.918
128.820
128.520
128.181
127.295
124.557
123.729
113.926
77.426
77.000
76.575
54.977
54.965
Ph
O
OMe
200
150
100
50
0
PPM

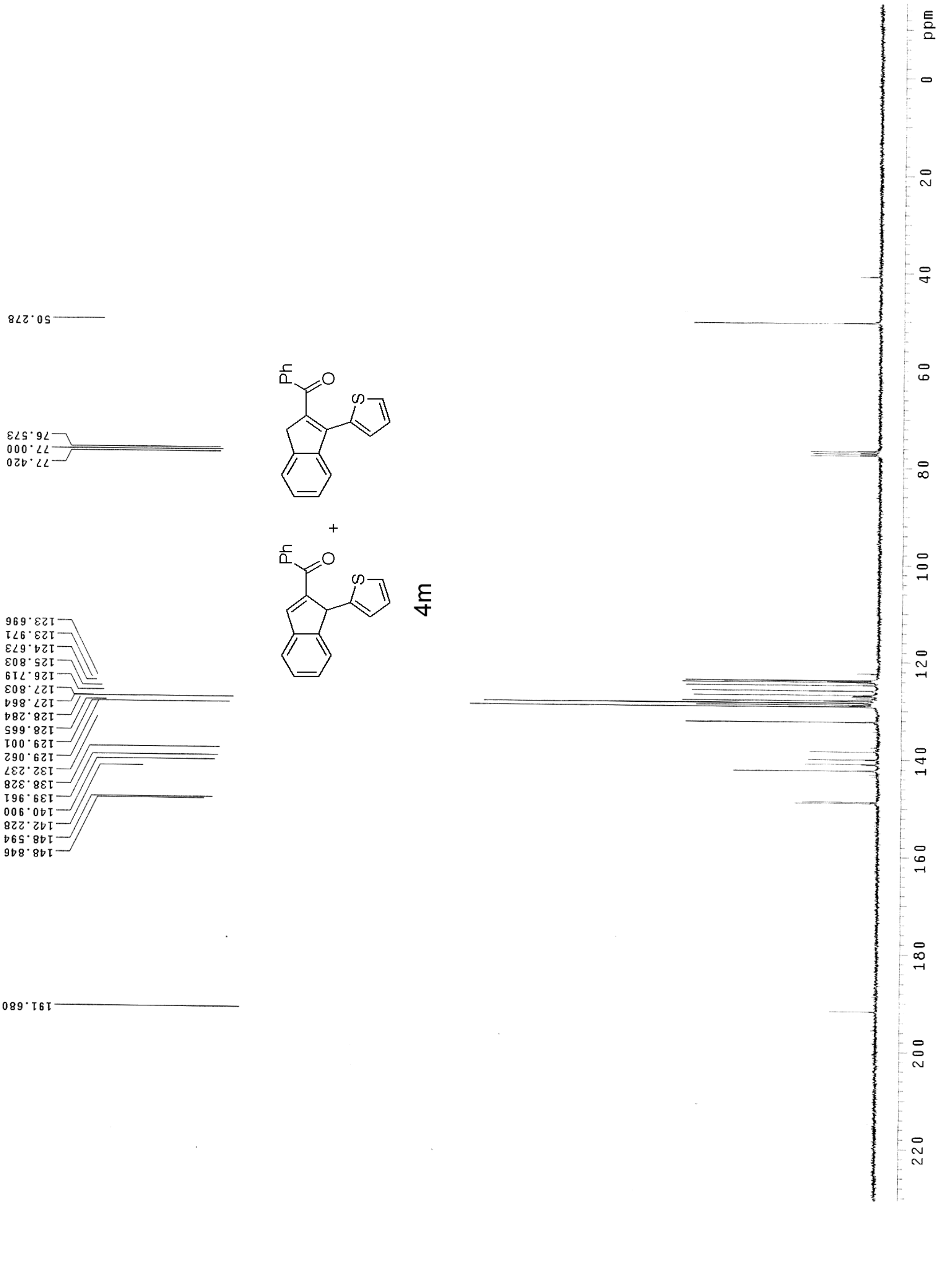
4l

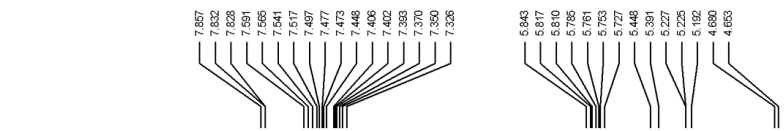

7.858
7.832
7.758
7.747
7.731
7.686
7.658
7.557
7.530
7.508
7.500
7.479
7.463
7.436
7.411
7.398
7.364
7.349
7.338
7.335
7.322
7.306
7.215
7.201
7.190
7.165
7.083
7.079
7.073
7.040
7.023
6.990
6.977
6.880
6.887
6.876
6.862
6.822
6.819
6.807
6.792
5.946
5.534
3.981
-0.000

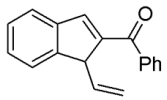

Ph
O
S
+
Ph
O
S

4m

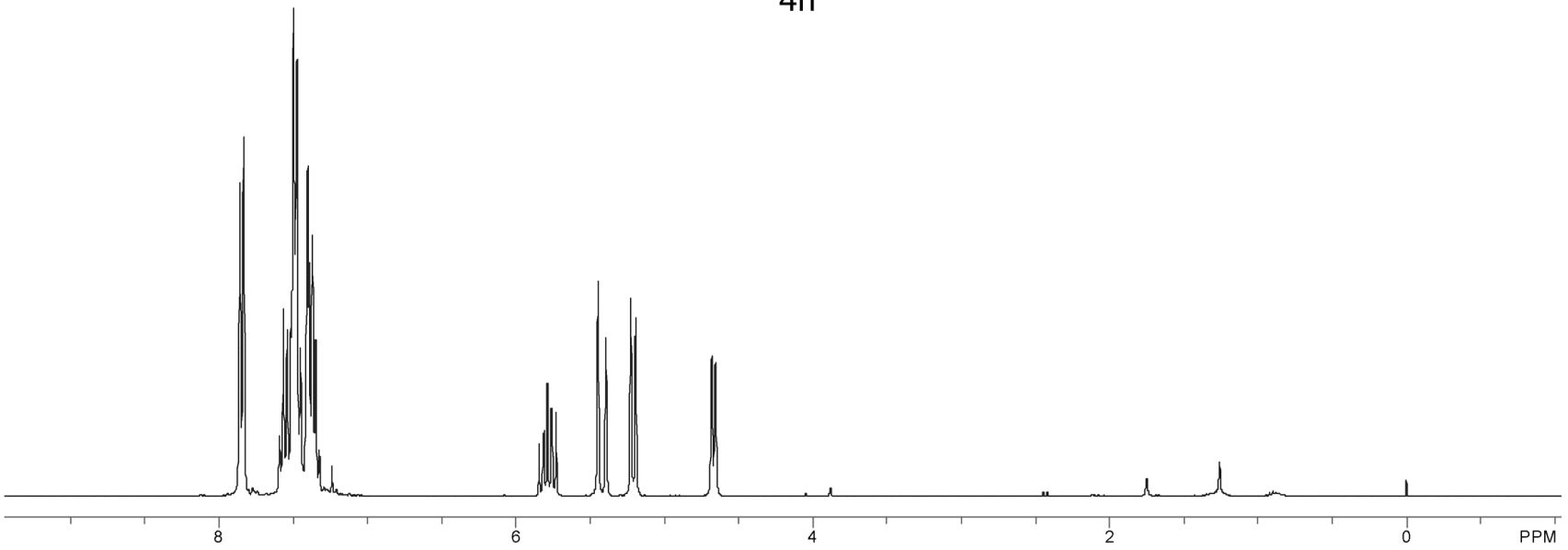

10
8
6
4
2
0
PPM

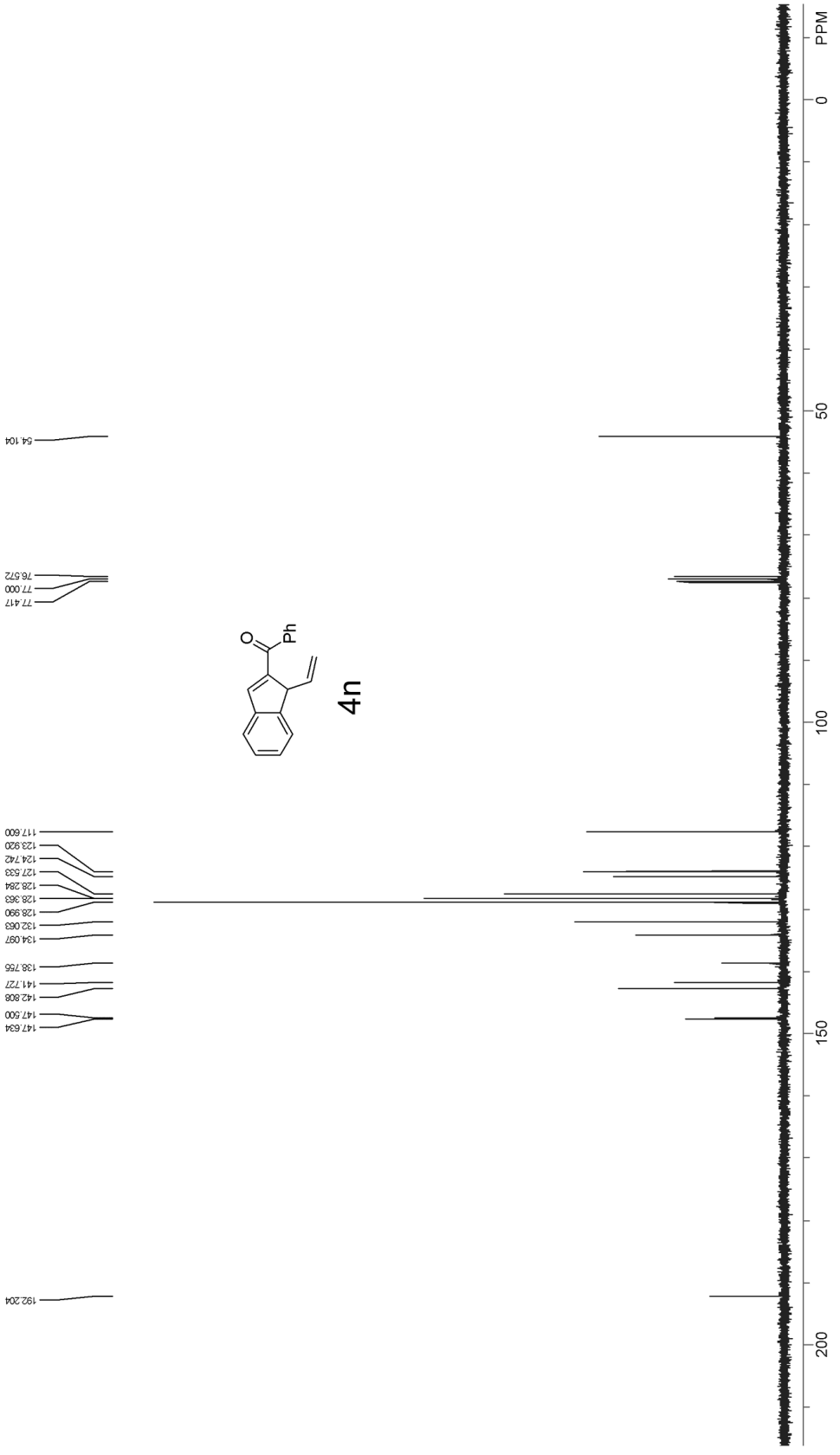

50.278
76.573
77.000
77.420
123.696
123.971
124.673
125.803
126.719
127.803
127.864
128.284
128.665
129.001
129.062
132.237
138.328
139.961
140.900
142.228
148.594
148.846
191.680
Ph
O
S
+
4m
ppm
0
20
40
60
80
100
120
140
160
180
200
220


7.857
7.832
7.828
7.591
7.566
7.541
7.517
7.497
7.477
7.473
7.448
7.406
7.402
7.393
7.370
7.350
7.326
5.843
5.817
5.810
5.786
5.761
5.753
5.727
5.448
5.391
5.227
5.225
5.192
4.680
4.653

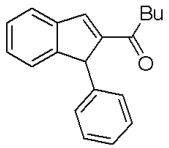

O
Ph

4n

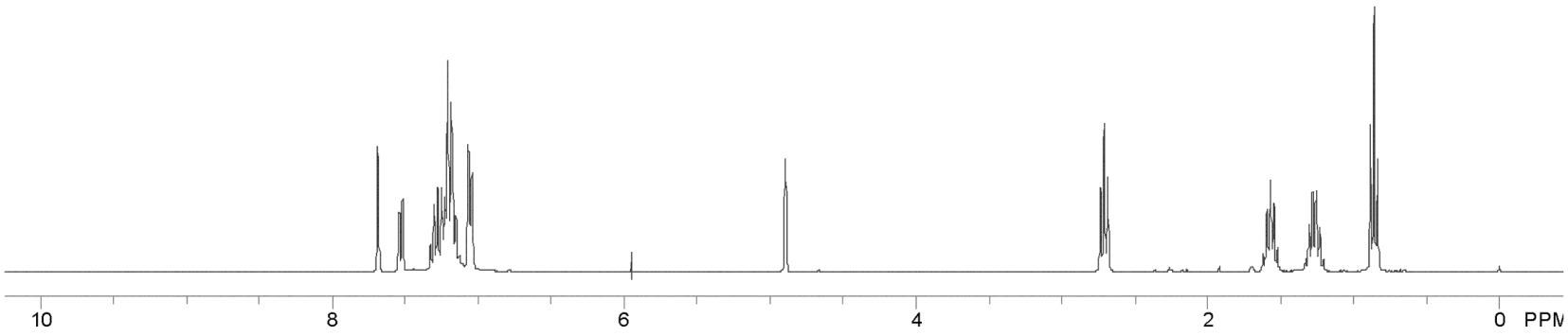

8
6
4
2
0
PPM

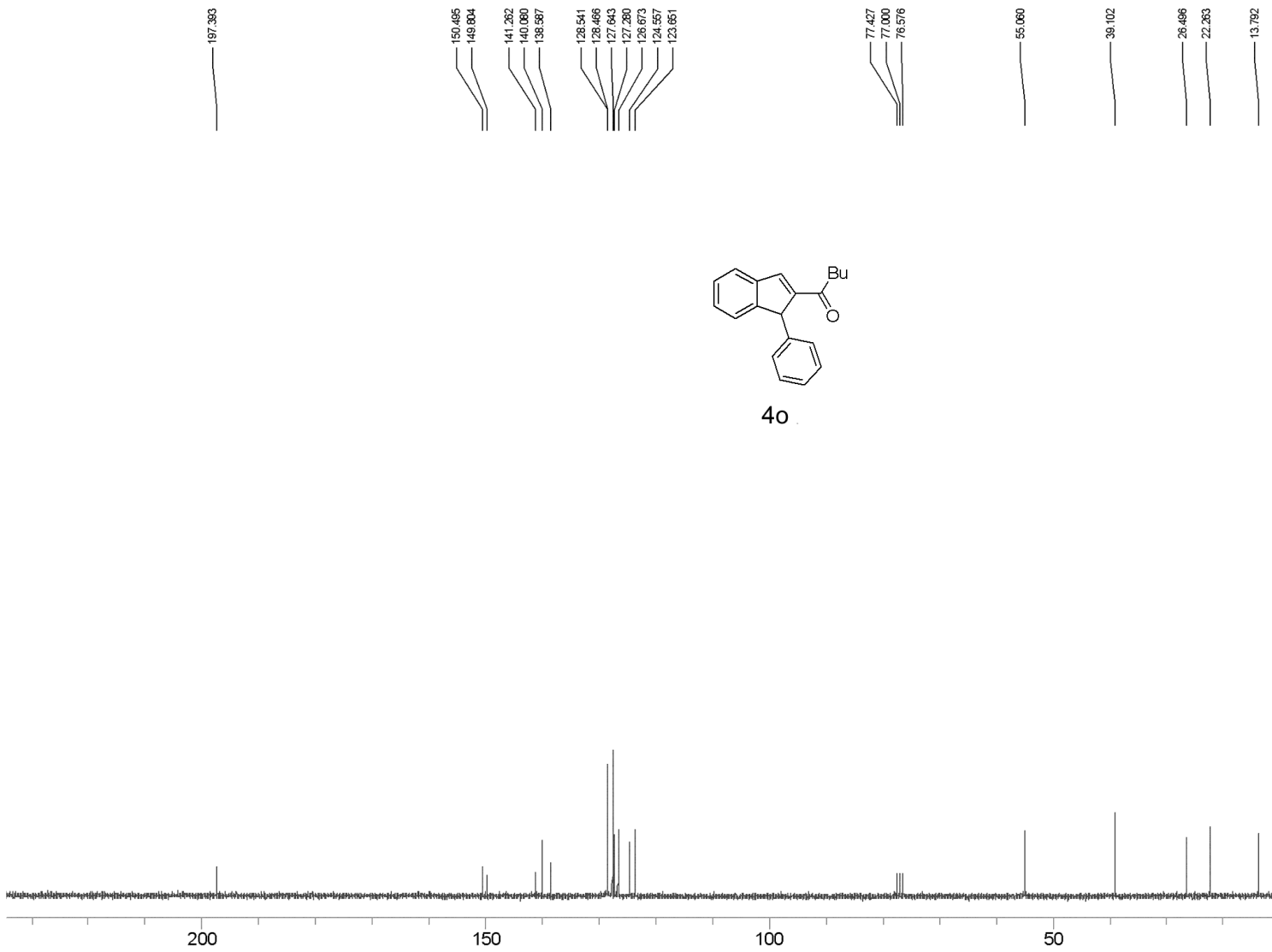

PPM
0
50
100
150
200
192.204
147.600
147.634
142.808
141.727
138.756
134.097
132.063
128.990
128.363
128.284
127.533
124.742
123.920
117.600
77.417
77.000
76.572
54.104
O
Ph
4n


7.689
7.683
7.542
7.518
7.329
7.324
7.305
7.300
7.277
7.252
7.248
7.230
7.224
7.210
7.185
7.175
7.151
7.136
7.131
7.127
7.070
7.043
4.894
2.733
2.708
2.683
1.618
1.593
1.569
1.545
1.520
1.329
1.305
1.280
1.254
1.230
1.206
0.883
0.859
0.834

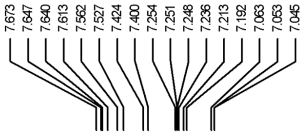

Bu
O

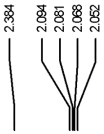
4o

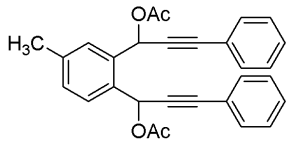

10
8
6
4
2
0
PPM


197.393
150.495
149.804
141.262
140.080
138.587
128.541
128.466
127.643
127.280
126.673
124.557
123.651
77.427
77.000
76.576
55.060
39.102
26.496
22.263
13.792
Bu
O
200
150
100
50
0
PPM

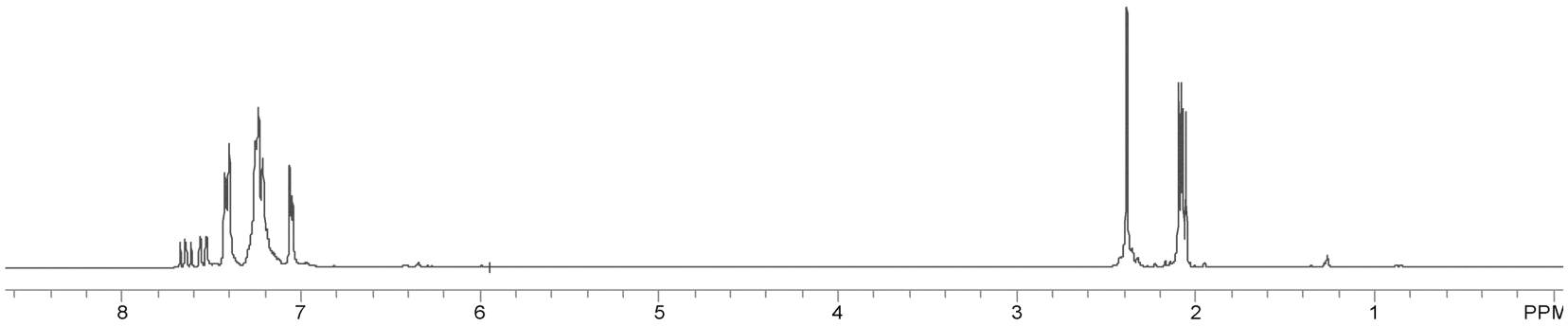
4o

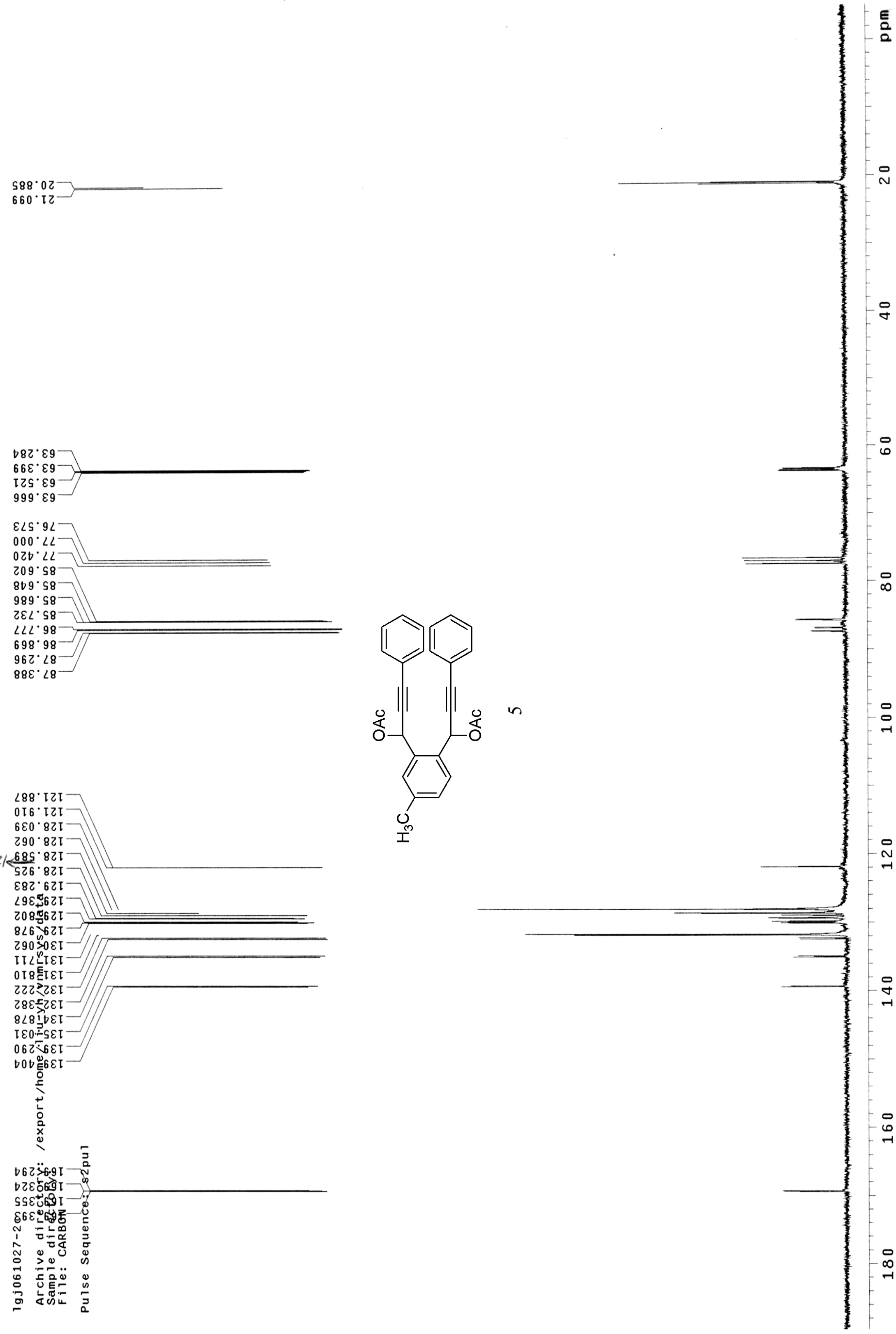

7.673
7.647
7.640
7.613
7.562
7.527
7.424
7.400
7.254
7.251
7.248
7.236
7.213
7.192
7.063
7.053
7.045

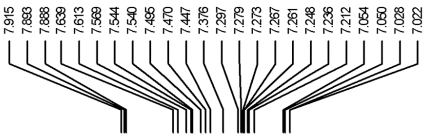

2.384
2.094
2.081
2.068
2.052


OAc
H3C
OAc

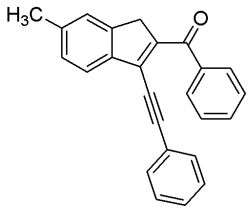
5


8
7
6
5
4
3
2
1
PPM

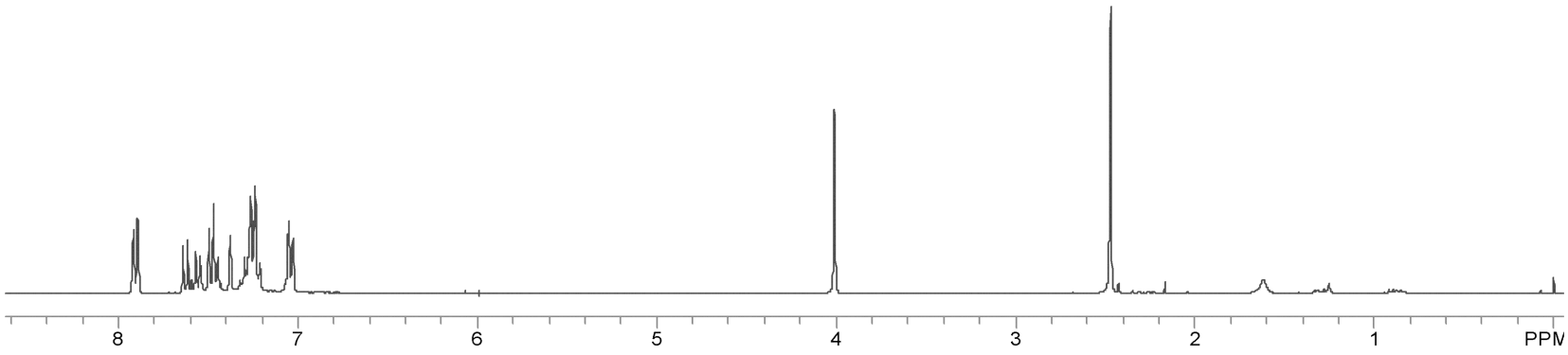

20.885
21.099
63.284
63.399
63.521
63.666
76.573
77.000
77.420
85.602
85.648
85.686
85.732
86.777
86.869
87.296
87.388
121.887
121.910
128.039
128.062
128.589
128.925
129.283
129.367
129.802
129.978
130.062
131.711
131.810
132.222
132.382
134.878
135.031
139.290
139.404
169.294
169.324
169.355
File: CARBON
Pulse Sequence: s2pul
OAc
OAc
H_3C
5
ppm
20
40
60
80
100
120
140
160
180

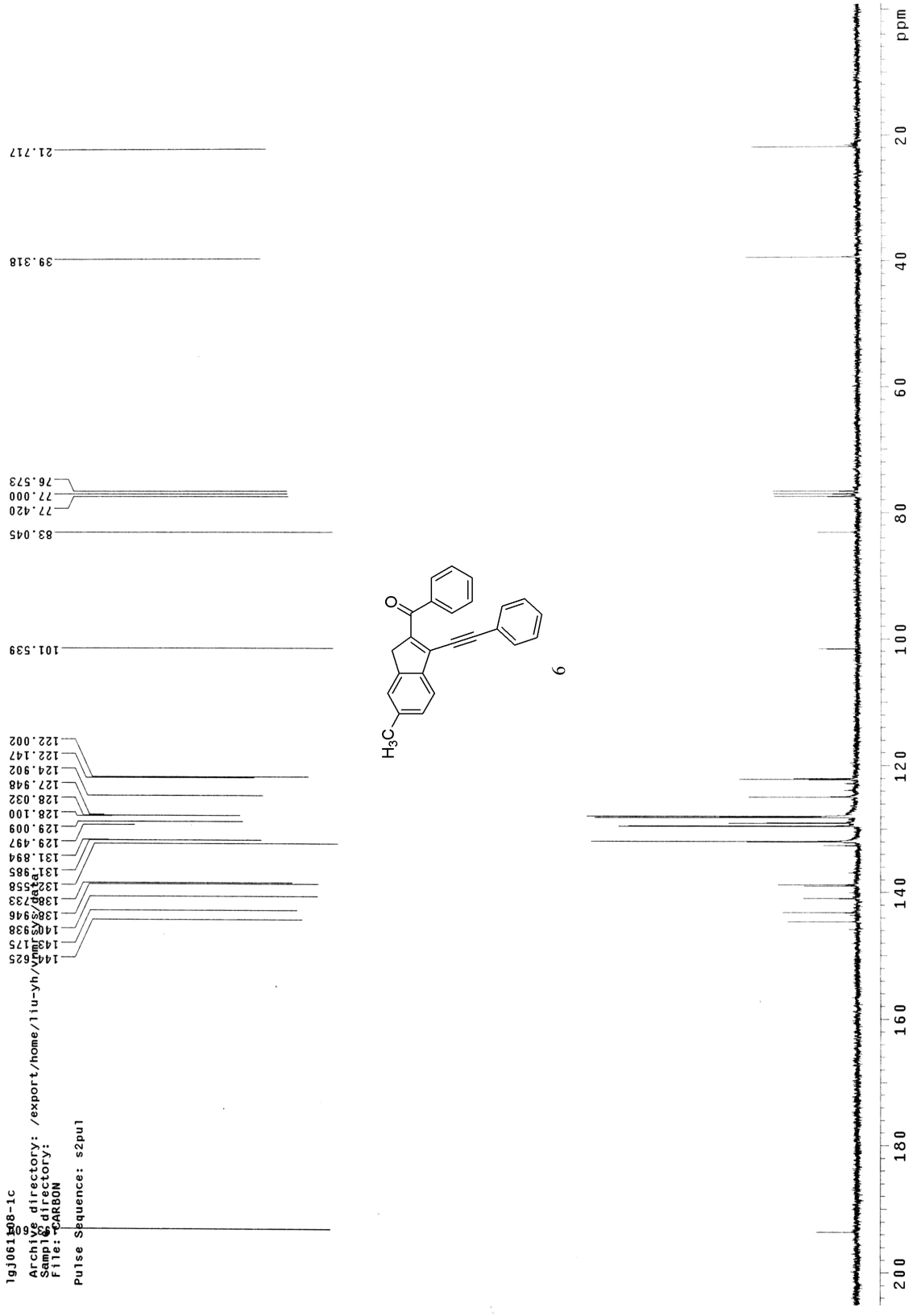

7.915
7.893
7.888
7.639
7.613
7.569
7.544
7.540
7.495
7.470
7.447
7.376
7.297
7.279
7.273
7.267
7.261
7.248
7.236
7.212
7.054
7.050
7.028
7.022

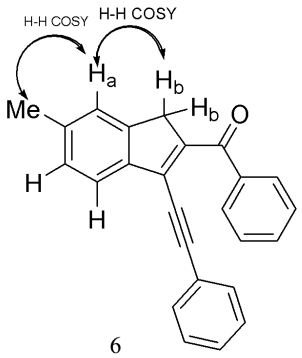

4.009
2.469


H3C
O

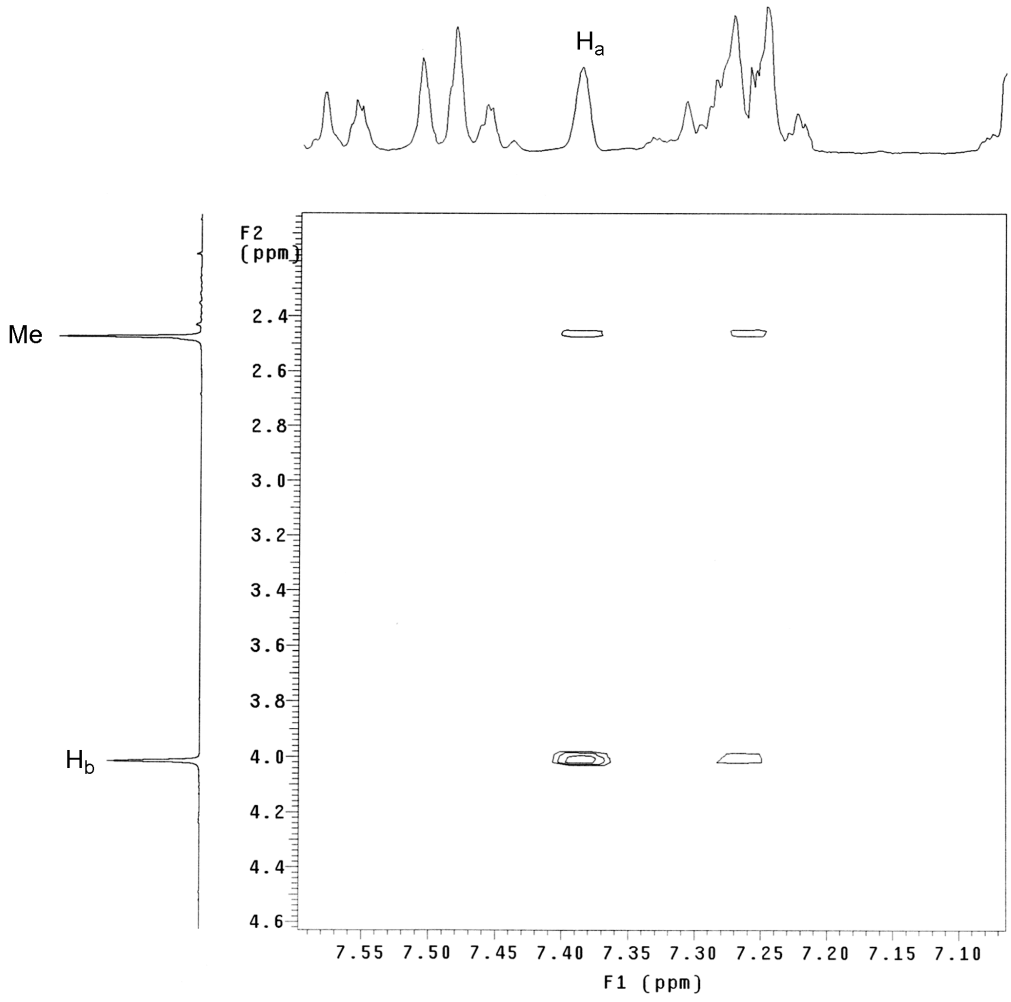
6

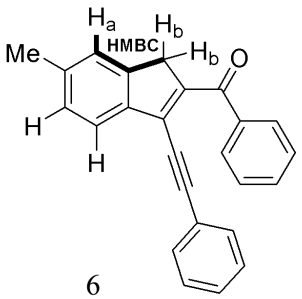

8
7
6
5
4
3
2
1
PPM


lgj061108-1c
Archive directory: /export/home/liu-yh/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
21.717
39.318
76.573
77.000
77.420
83.045
101.539
122.002
122.147
124.902
127.948
128.032
128.100
129.009
129.497
131.894
131.985
132.558
138.733
138.946
140.938
143.175
144.625
H3C
O
6
ppm

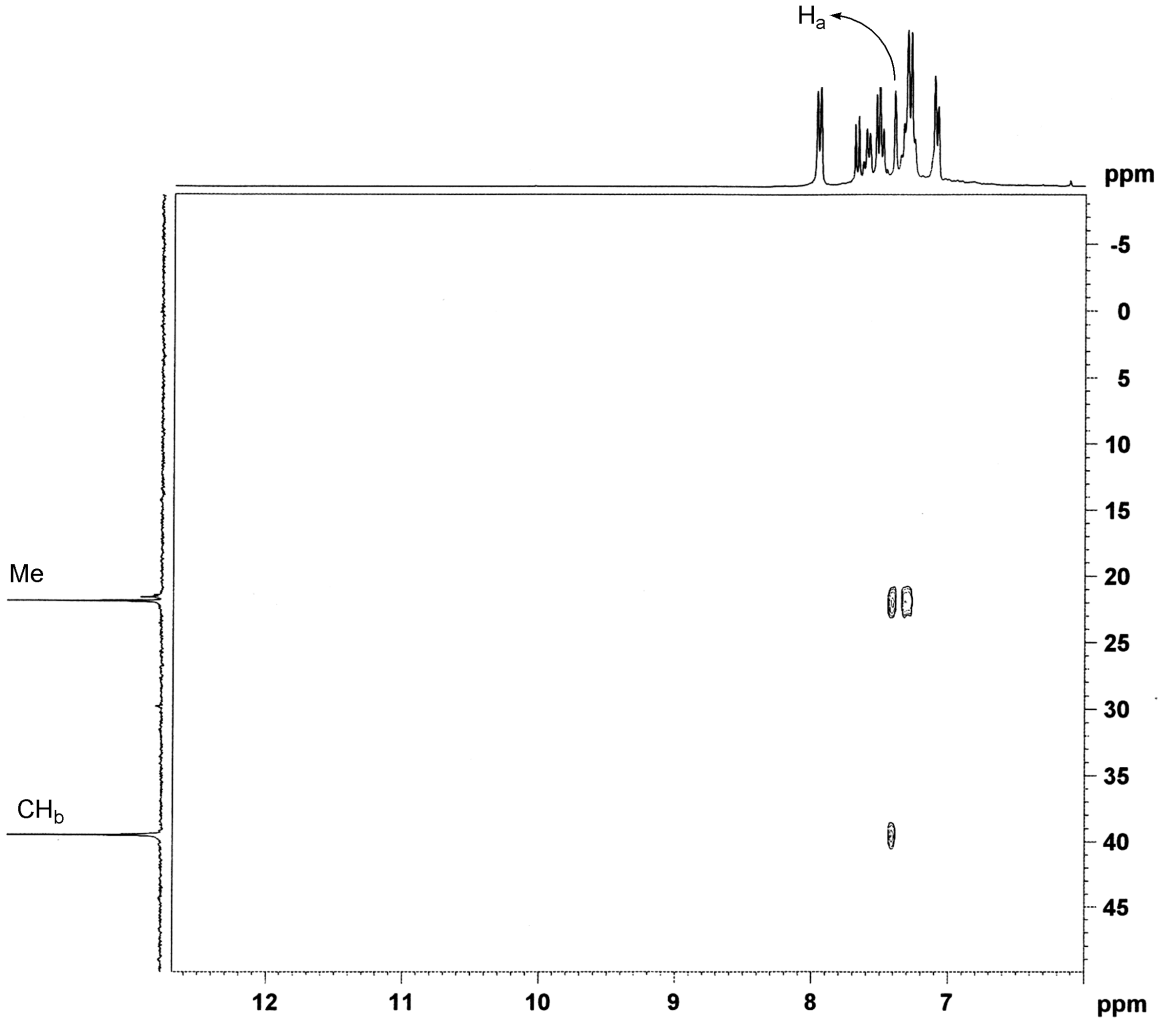

H-H COSY
H-H COSY
Ha
Hb
Me
Hb
O
H
H

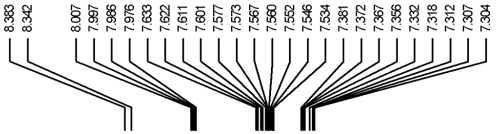
6

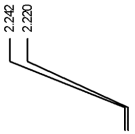

Ha
Me
Hb
F2 (ppm)
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
F1 (ppm)

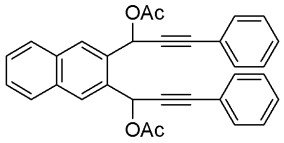

Ha
Hb
HMBC
Me
Hb
O
H
H

6

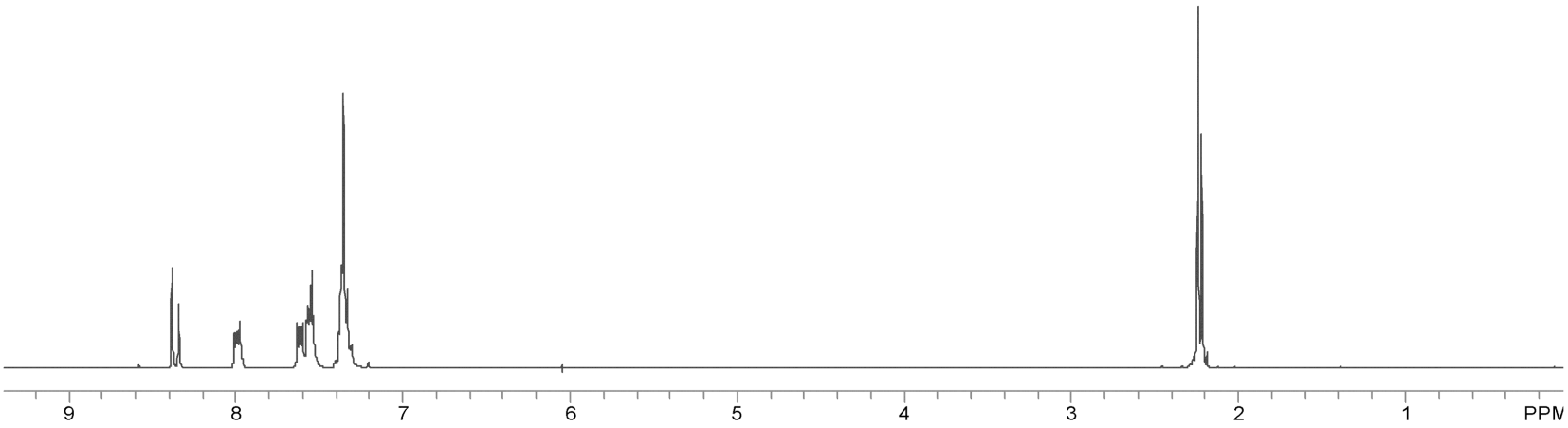

Ha
ppm
-5
0
5
10
15
20
25
30
35
40
45
Me
CHb
12
11
10
9
8
7
ppm

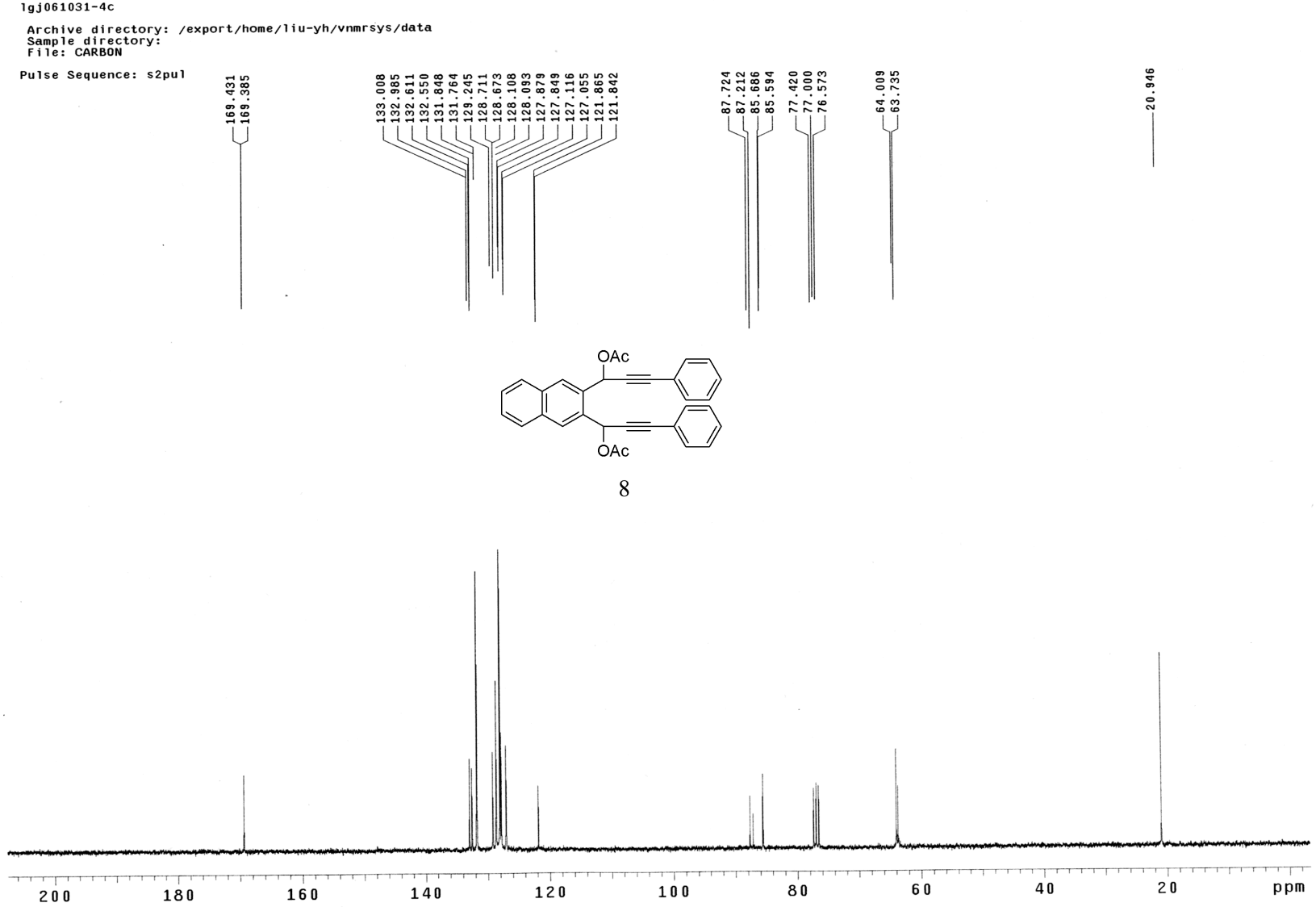

8.383
8.342
8.007
7.997
7.986
7.976
7.633
7.622
7.611
7.601
7.577
7.573
7.567
7.560
7.552
7.546
7.534
7.381
7.372
7.367
7.356
7.332
7.318
7.312
7.307
7.304


2.242
2.220

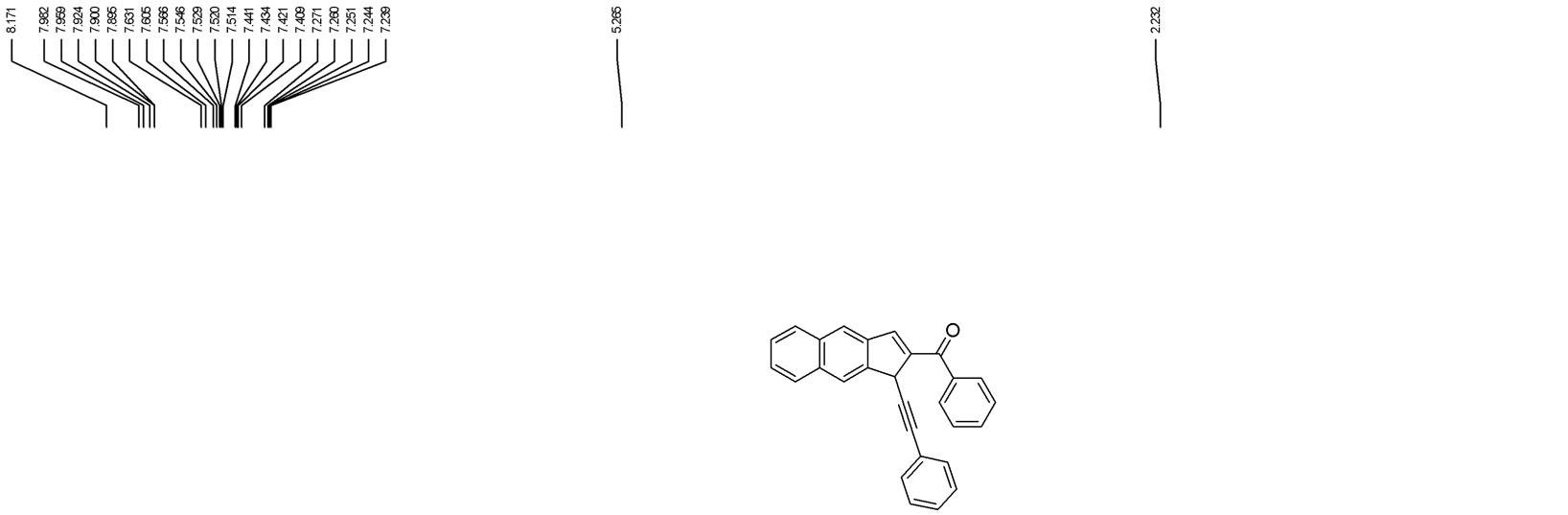

OAc
OAc

8


9
8
7
6
5
4
3
2
1
PPM


lgj061031-4c
Archive directory: /export/home/liu-yh/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
169.431
169.385
133.008
132.985
132.611
132.550
131.848
131.764
129.245
128.711
128.673
128.108
128.093
127.879
127.849
127.116
127.055
121.865
121.842
87.724
87.212
85.686
85.594
77.420
77.000
76.573
64.009
63.735
20.946
OAc
OAc
200
180
160
140
120
100
80
60
40
20
ppm

8

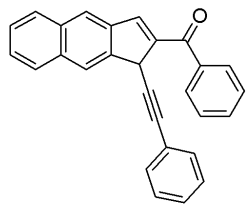

8.171
7.982
7.959
7.924
7.900
7.895
7.631
7.605
7.566
7.546
7.529
7.520
7.514
7.441
7.434
7.421
7.409
7.271
7.260
7.251
7.244
7.239
5.265
2.232
O
9
5.14
5.21
3.06
2.04
1.00
1.22
0.72
CH3COOH
8
7
6
5
4
3
2
1
PPM

lgj061102-1c

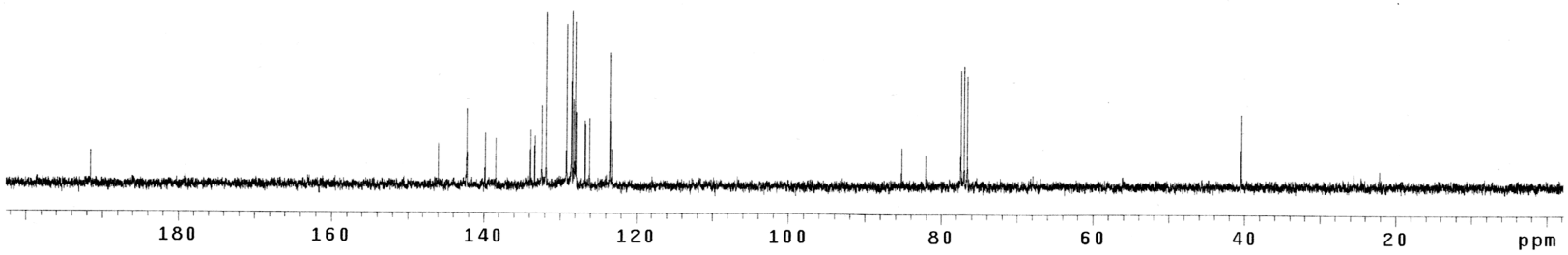
Archive directory: /export/home/liu-yh/vnmrsys/data
Sample directory:
File: CARBON

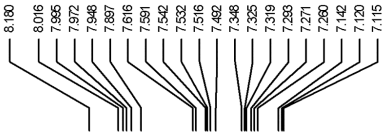
Pulse Sequence: s2pul

191.522
145.976
142.244
142.198
139.824
138.389
133.855
133.298
132.367
131.802
129.108
128.467
128.421
128.207
127.994
127.856
126.704
126.108
123.452
123.185
85.220
82.053
77.427
77.000
76.573
40.417



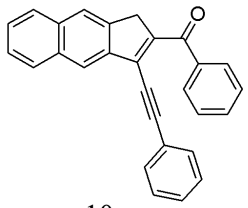
9



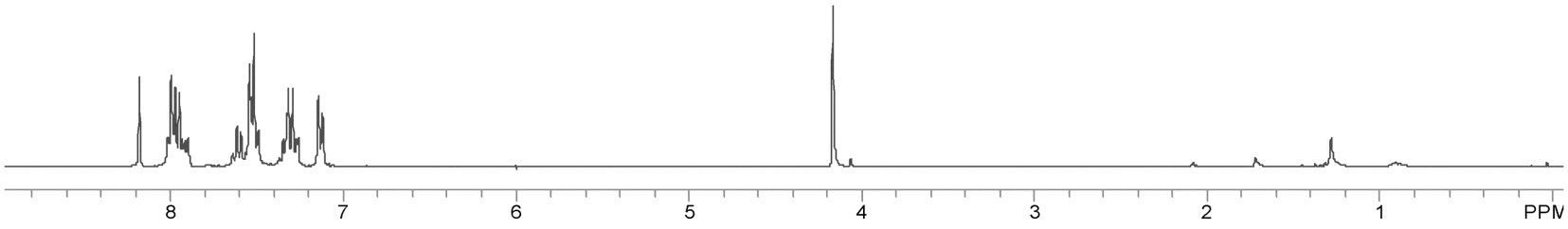

8.180
8.016
7.995
7.972
7.948
7.897
7.616
7.591
7.542
7.532
7.516
7.482
7.348
7.325
7.319
7.293
7.271
7.260
7.142
7.120
7.115

4.166

1.281


O

10

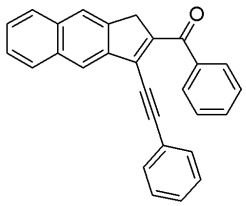

8
7
6
5
4
3
2
1
PPM

lgj061103-1c

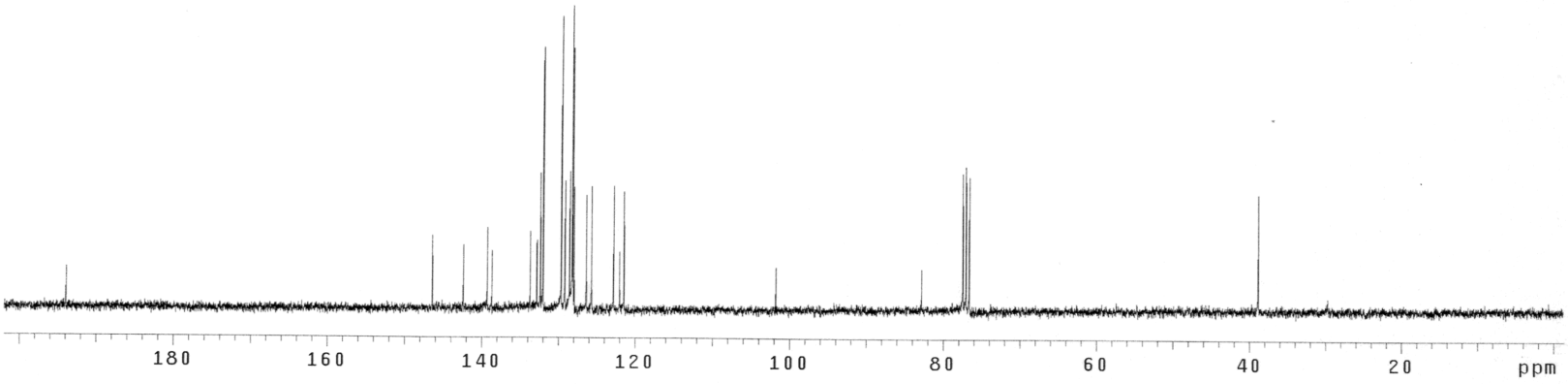
Archive directory: /export/home/liu-yh/vnmrsys/data
Sample directory:
File: CARBON

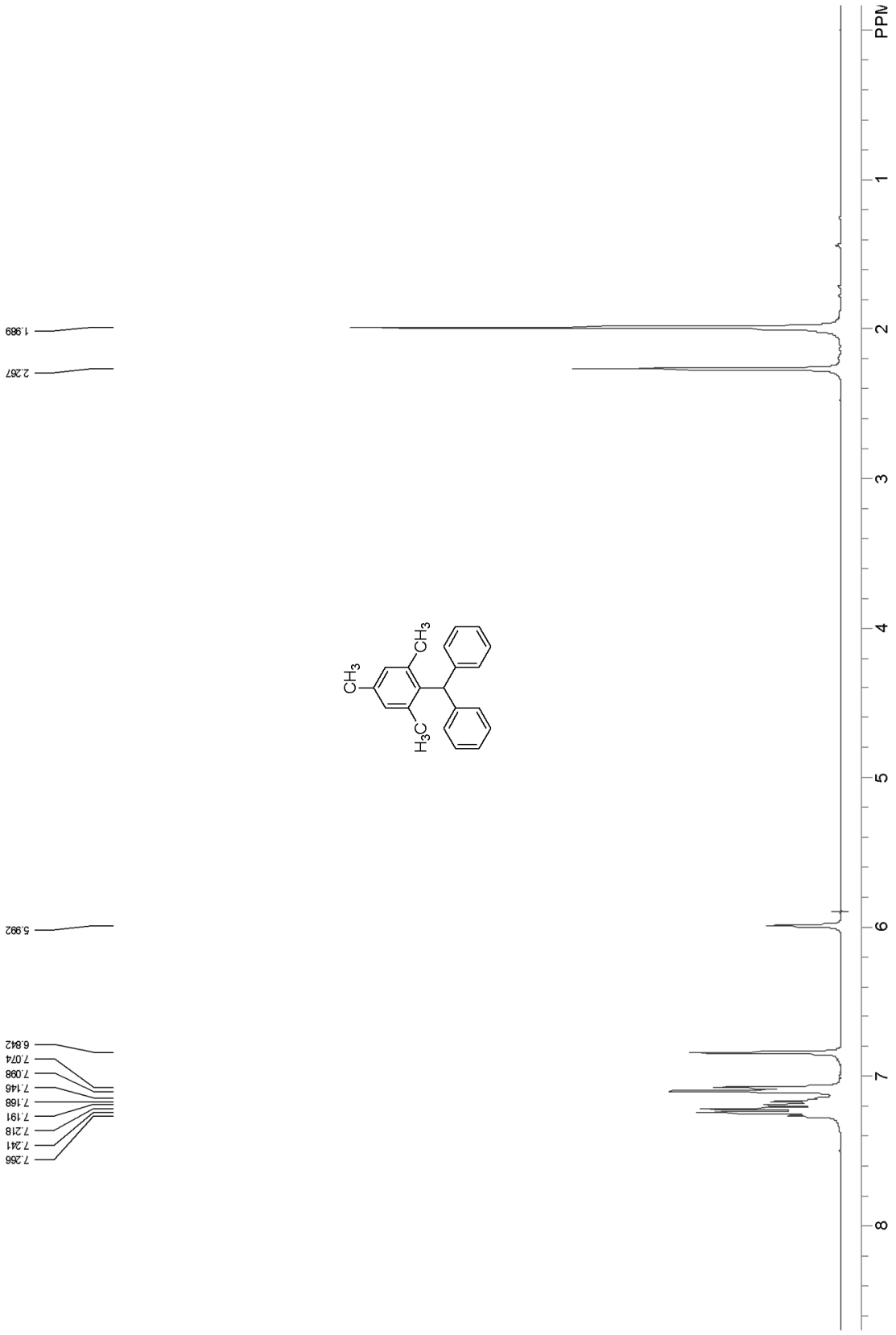
Pulse Sequence: s2pul

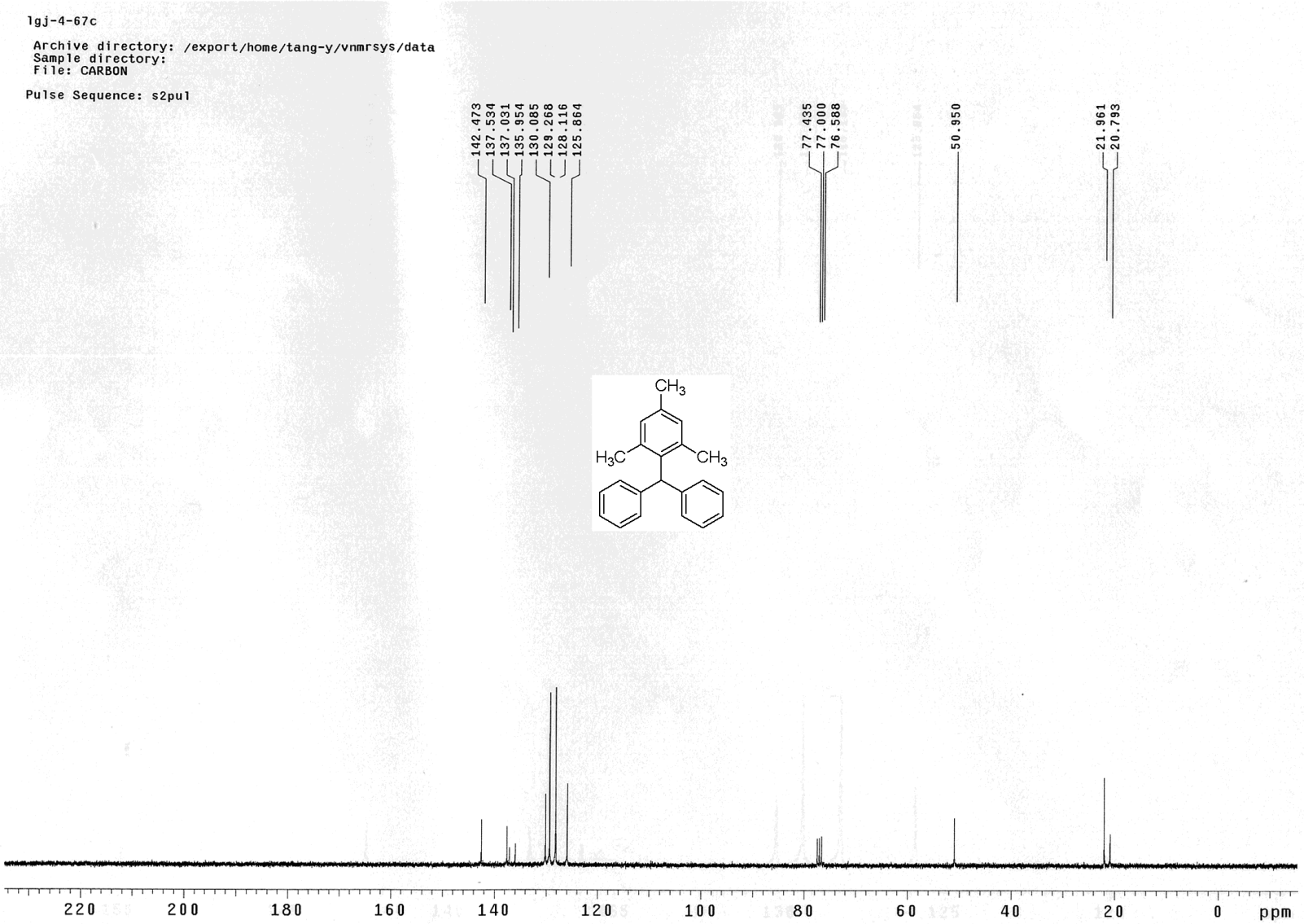
193.886
146.388
142.366
139.259
138.641
133.657
132.787
132.314
131.963
129.619
129.138
128.513
128.184
128.077
127.910
126.330
125.643
122.780
121.979
121.422
101.745
82.770
77.420
77.000
76.573
38.776

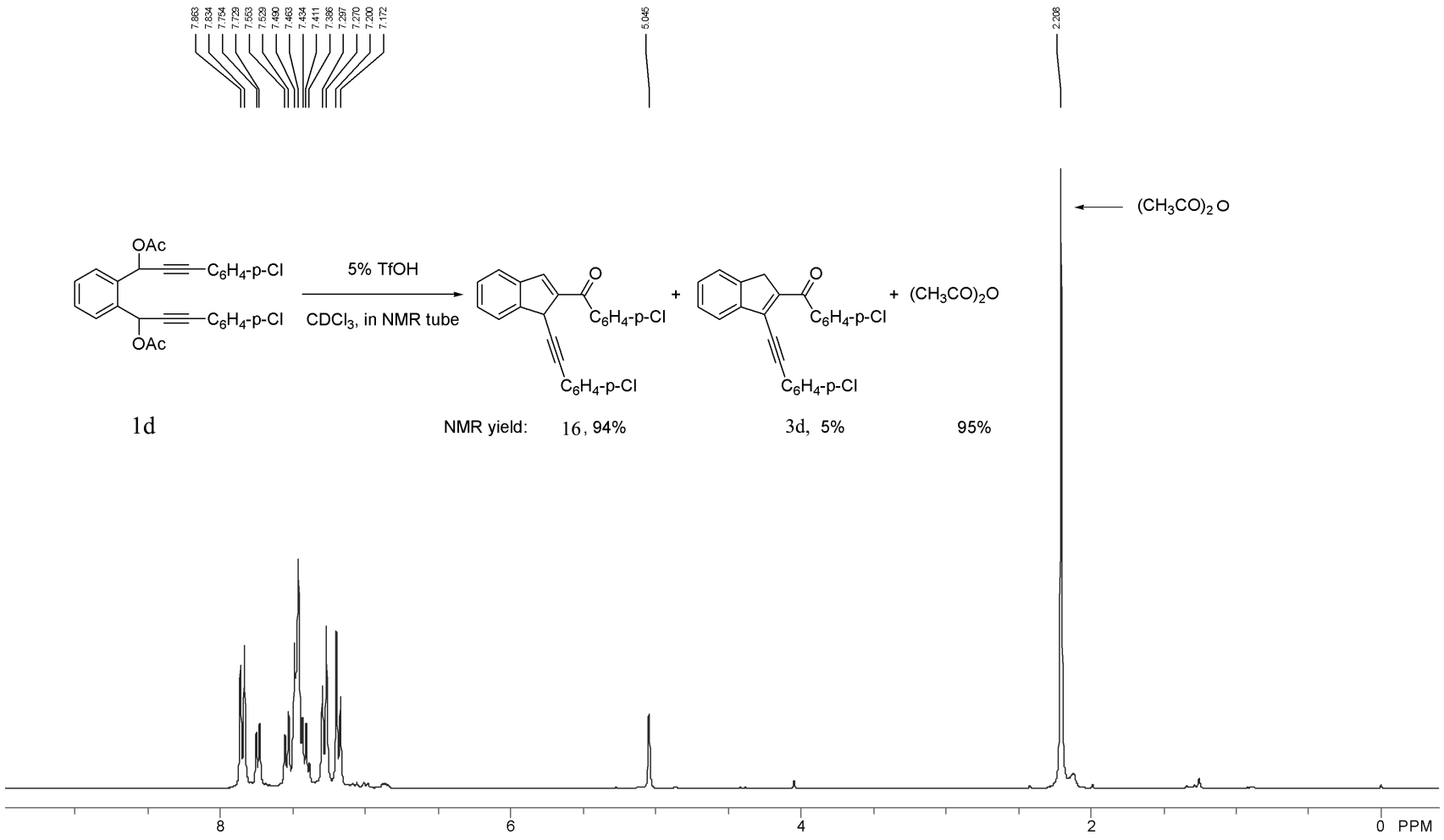


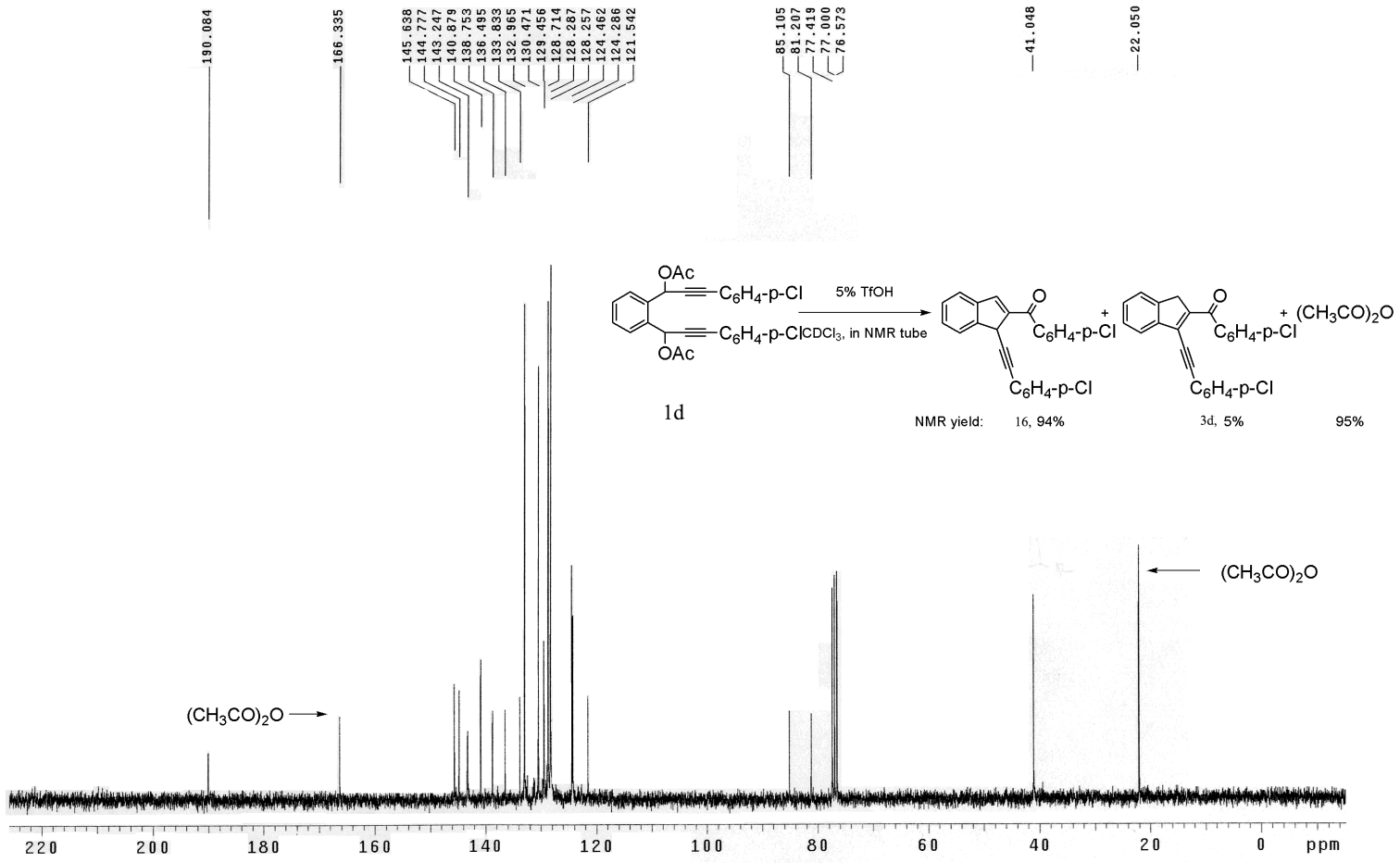
10

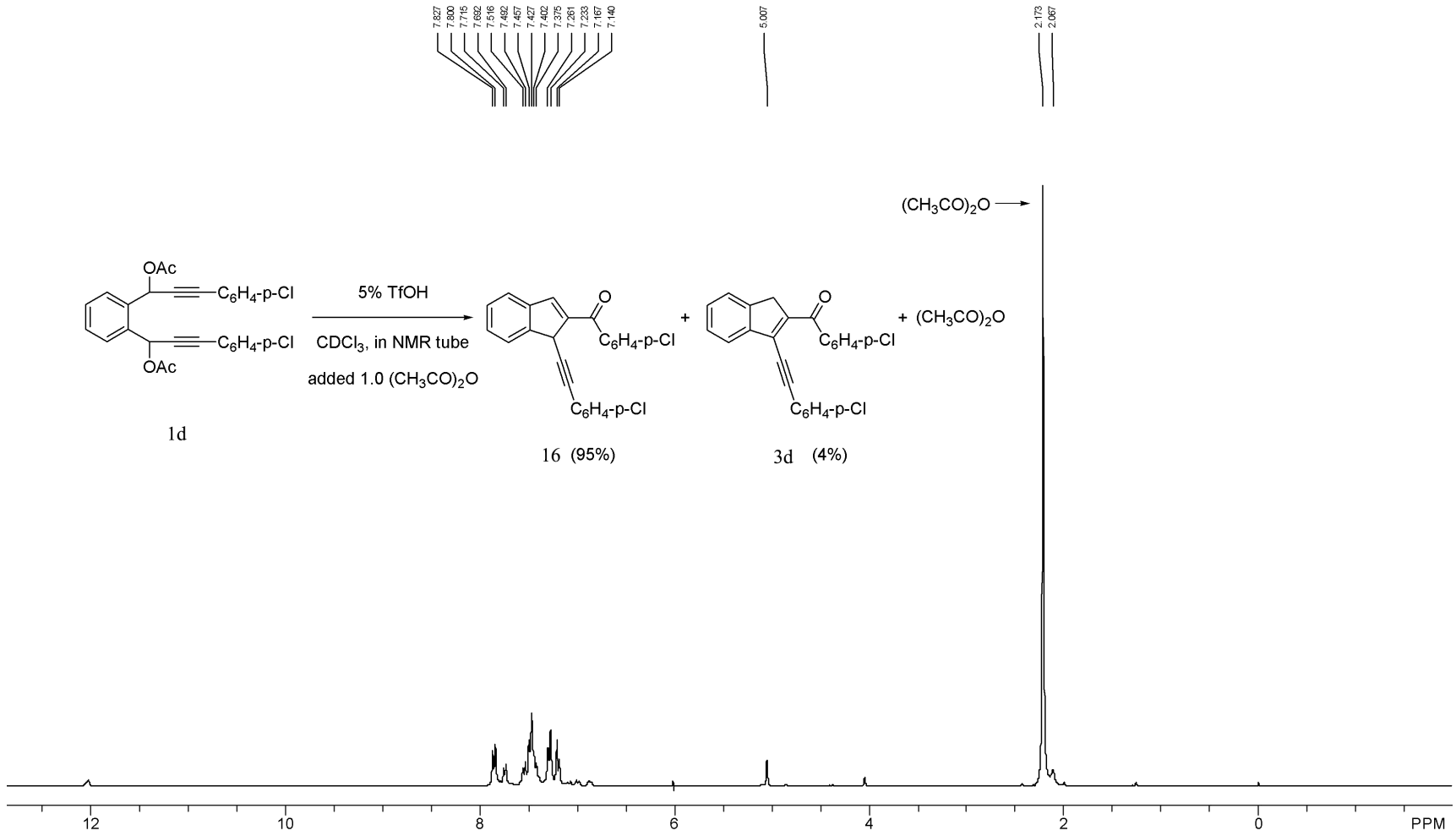



1.989
2.267
5.992
6.942
7.074
7.098
7.146
7.168
7.191
7.218
7.241
7.266
CH3
CH3
H3C
PPM
1
2
3
4
5
6
7
8


lgj-4-67c
Archive directory: /export/home/tang-y/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
142.473
137.534
137.031
135.954
130.085
129.268
128.116
125.864
77.435
77.000
76.588
50.950
21.961
20.793
CH3
H3C
CH3
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.863
7.834
7.754
7.723
7.553
7.529
7.490
7.463
7.434
7.411
7.386
7.297
7.270
7.200
7.172
5.045
2.208
(CH3CO)2O
OAc
C6H4-p-Cl
C6H4-p-Cl
OAc
5% TfOH
CDCl3, in NMR tube
C6H4-p-Cl
C6H4-p-Cl
+
C6H4-p-Cl
C6H4-p-Cl
+ (CH3CO)2O
1d
NMR yield: 16, 94%
3d, 5%
95%
8
6
4
2
0 PPM

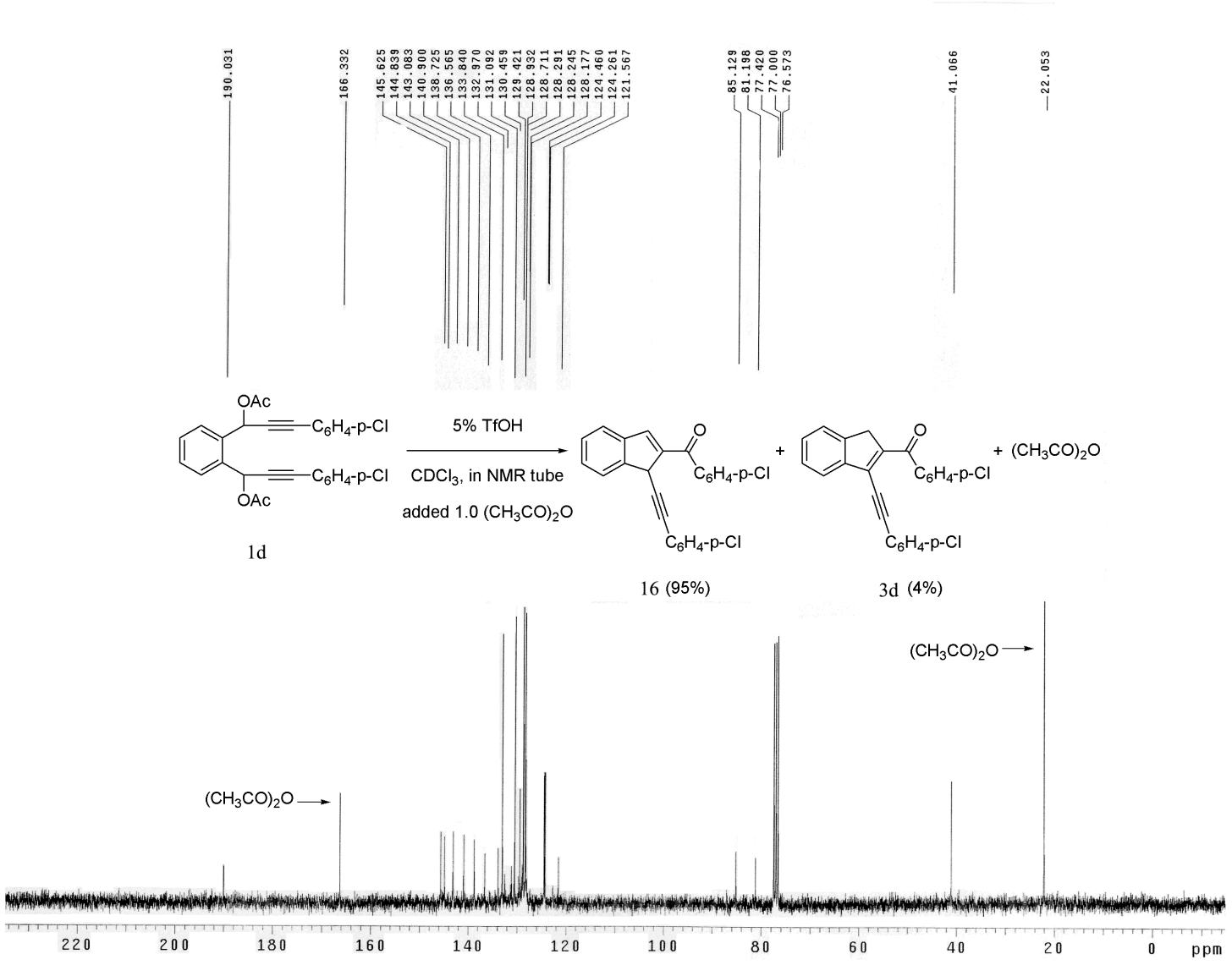

190.084
166.335
145.638
144.777
143.247
140.879
138.753
136.495
133.833
132.965
130.471
128.456
128.714
128.287
128.257
124.462
124.286
121.542
85.105
81.207
77.419
77.000
76.573
41.048
22.050
OAc
C6H4-p-Cl
C6H4-p-Cl
OAc
5% TfOH
CDCl3, in NMR tube
1d
C6H4-p-Cl
C6H4-p-Cl
+
C6H4-p-Cl
+ (CH3CO)2O
C6H4-p-Cl
NMR yield: 16, 94%
3d, 5%
95%
(CH3CO)2O
(CH3CO)2O
220
200
180
160
140
120
100
80
60
40
20
0
ppm

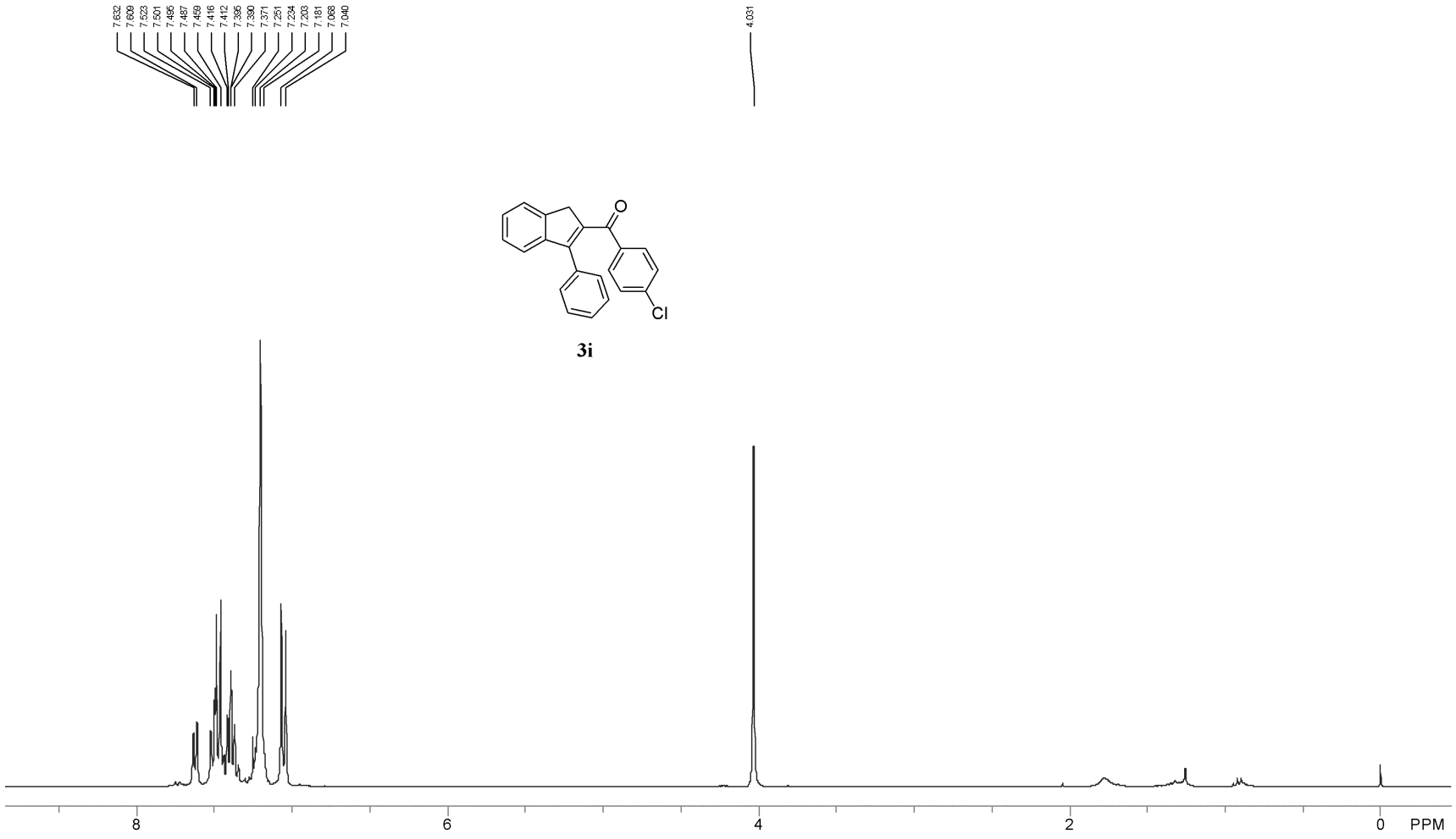

7.827
7.800
7.715
7.682
7.516
7.492
7.457
7.427
7.402
7.375
7.261
7.233
7.167
7.140
5.007
2.173
2.067
(CH3CO)2O
OAc
C6H4-p-Cl
C6H4-p-Cl
OAc
5% TfOH
CDCl3, in NMR tube
added 1.0 (CH3CO)2O
O
C6H4-p-Cl
C6H4-p-Cl
+
O
C6H4-p-Cl
C6H4-p-Cl
+ (CH3CO)2O
12
10
8
6
4
2
0
PPM

1d

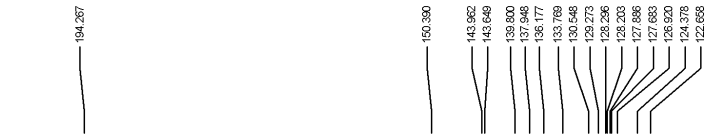
16 (95%)

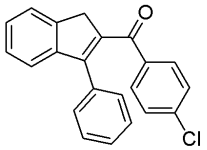
3d (4%)


190.031
166.332
145.625
144.839
143.083
140.900
138.725
136.565
133.840
132.970
131.092
130.459
129.421
128.932
128.711
128.291
128.245
128.177
124.460
124.261
121.567
85.129
81.198
77.420
77.000
76.573
41.066
22.053
OAc
C6H4-p-Cl
C6H4-p-Cl
OAc
5% TfOH
CDCl3, in NMR tube
added 1.0 (CH3CO)2O
C6H4-p-Cl
C6H4-p-Cl
+
C6H4-p-Cl
C6H4-p-Cl
+ (CH3CO)2O
1d
16 (95%)
3d (4%)
(CH3CO)2O
(CH3CO)2O
220
200
180
160
140
120
100
80
60
40
20
0
ppm

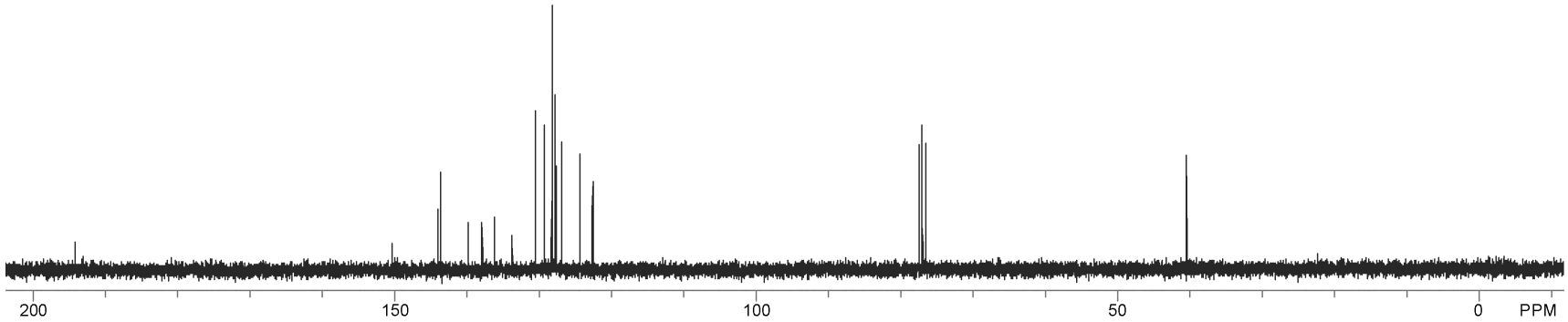

7.632
7.609
7.523
7.501
7.495
7.487
7.459
7.416
7.412
7.395
7.390
7.371
7.251
7.234
7.203
7.181
7.068
7.040
4.031
O
Cl
8
6
4
2
0
PPM

3i


194.267
150.390
143.962
143.649
139.800
137.948
136.177
133.789
130.548
129.273
128.296
128.203
127.886
127.683
126.920
124.378
122.638
77.415
77.000
76.567
40.399


O
Cl

3i


200
150
100
50
0
PPM