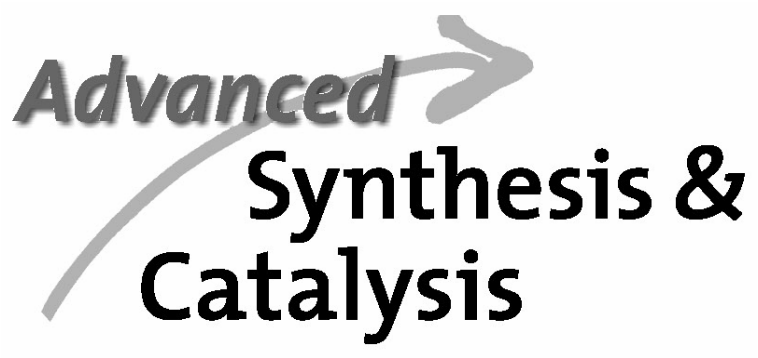

Supporting Information

Supporting Information:

Palladium-Catalyzed Efficient and One-Pot Synthesis of Diarylacetylenes from the Reaction of Aryl Chlorides with 2-Methyl-3-butyn-2-ol

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List of Contents Pages

1. Experimental section and characterization data of products

(1) General method

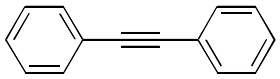
All organic starting materials are analytically pure and used without further purification. $PdCl_2(PCy_3)_2$ was prepared by literature method.[10] ^1H and ^{13}C NMR spectra were recorded on JOEL JNM-ECA300 spectrometers at 300 MHz and 75 MHz, respectively. ^1H chemical shifts (δ) were referenced to TMS, and ^{13}C NMR chemical shifts (δ) were referenced to internal solvent resonance. GC analyses of organic compounds were performed on an Agilent Technologies 1790 GC (with a TC-WAX capillary 25m column) instrument. Mass spectra were obtained on a HEWLETT 5890 PACKARD SERIES II GC/MS spectrometer with a PEG-25M column. High-resolution mass spectra were obtained with a ZAB-HS mass spectrometer from the Department of Chemistry of Beijing University. Element analyses were obtained with a Flash EA 1112 Element Analyzer in the Institute of Chemistry, Chinese Academy of Sciences.

(2) A Typical Experimental Procedure for the Reaction of Chlorobenzene (1a) with 2-Methyl-3-butyn-2-ol Affording Diphenylacetylene (2a) (Table 1, entry 6): A mixture of **1a** (4.0 mmol, 450.0 mg), 2-methyl-3-butyn-2-ol (1.0 mmol, 84.0 mg), Cs_2CO_3 (3.0 mmol, 978.0 mg), piperidine (0.1 mmol, *ca*. 10μL), and $PdCl_2(PCy_3)_2$ (0.05 mmol, 36.8 mg,) in DMSO (3.0 mL) under nitrogen in a sealed tube was heated with stirring at 120 ^oC for 12 h. After cooling, the reaction mixture was diluted with CH_2Cl_2 to 5.0 mL and octadecane (0.2 mmol, 50.0 mg) was added as internal standard for GC analysis. After GC and GCMS analyses, removing the solvents and volatiles under vacuum, the residue was then subjected to preparative TLC isolation (silica, eluted with cyclohexane). **2a** was obtained in 153.0 mg (0.86 mmol, 86 %) as white solid. The results of GC analysis of the reaction mixture revealed that **2a** was formed in 90 % yield.

(3) A Typical Experimental Procedure for the Reaction of 4-Chlorotoluene (1b), Methyl 3-Chlorobenzoate (1h) with 2-Methyl-3-butyn-2-ol Affording Methyl 3-Phenylethynylbenzoate (3b) (Table 3, entry 2): A mixture of **1b** (2.0 mmol, 253.0 mg), **1h** (2.0 mmol, 341.2 mg), 2-methyl-3-butyn-2-ol (1.0 mmol, 84.0 mg), Cs_2CO_3 (3.0 mmol, 978.0 mg), piperidine (0.1 mmol), and $PdCl_2(PCy_3)_2$ (0.05 mmol, 36.8 mg,)

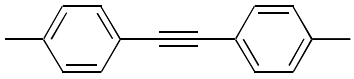
in DMSO (3.0 mL) under nitrogen in a sealed tube was heated with stirring at 120 ^{o}C for 12 h. After treatment as described above and twice careful preparative TLC isolation, **3b** was obtained in 80.0 mg (0.32 mmol, 32 %) as yellow solid, and **2h** was also isolated in 64.6 mg (0.22 mmol, 22 %).

(4). Characterization data of products



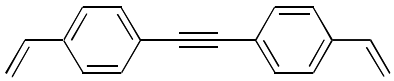
2a

Diphenylacetylene **2a:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.50 (m, 4H), 7.37-7.28 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.7, 128.4, 128.3, 123.3, 89.4; GCMS *m*/*z* (% rel. inten.) 178 (M^+, 100), 152 (21), 126 (8), 113 (2), 98 (6), 77 (3).



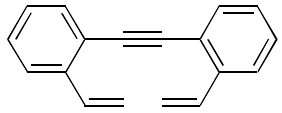
2b

Di-*p*-tolylacetylene **2b**[1]**:** White solid, mp 137-138 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, 4H, *J* = 8.2 Hz), 7.14 (d, 4H, *J* = 8.2 Hz), 2.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 131.5, 129.1, 120.4, 88.9, 21.5; GCMS *m*/*z* (% rel. inten.) 206 (M^+, 100), 191 (28), 165 (11), 139 (9), 115 (8), 98 (3), 89 (5).



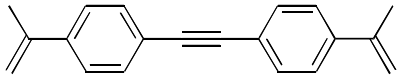
2c

1,2-Bis(4-vinylphenyl)acetylene **2c**[2]**:** Pale-yellow solid, mp 137-139 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, 4H, *J* = 8.0 Hz), 7.38 (d, 4H, *J* = 8.0 Hz), 6.70 (dd, 2H, *J* = 17.5, 11.0 Hz), 5.78 (d，2H, *J* = 17.5 Hz), 5.30 (d，2H, *J* = 11.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 136.2, 131.8, 126.1, 122.5, 114.7, 90.1; GCMS *m*/*z* (% rel. inten.) 230 (M^+, 100), 202 (40), 189 (9), 163 (8), 77(6).



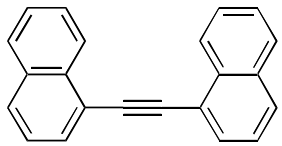
2d

1,2-Bis(2-vinylphenyl)acetylene **2d**[3]**:** Pale yellow solid, mp 42-45 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65-7.25 (m, 10H), 5.86 (d, 2H, *J* = 17.5 Hz), 5.40 (d, 2H, *J* = 11.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 135.1, 132.6, 128.6, 127.6, 124.8, 122.1, 115.8, 92.4; GCMS *m*/*z* (% rel. inten.) 230 (M^+, 42), 202 (21), 189 (6), 163 (4), 115 (100), 77 (6).



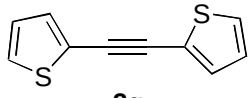
2e

1,2-Bis[4-(2-propenyl)phenyl]acetylene (2e): Pale-yellow solid, mp 140-142 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, 4H, *J* = 8.4 Hz), 7.44 (d, 4H, *J* = 8.4 Hz), 5.42 (d, 2H, *J* = 0.7 Hz), 5.13 (d, 2H, *J* = 0.7 Hz), 2.15 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 140.9, 131.5, 125.4, 122.4, 113.2, 89.9, 21.6; GCMS *m*/*z* (% rel. inten.) 258 (M^+, 100), 243 (18), 202 (37), 189 (8), 115 (16), 91 (6); Anal. Calcd for $C_{20}H_{18}$: C, 93.02; H, 6.98. Found: C, 94.02; H, 7.01. HRMS (M^+) *m*/*z* calcd for $C_{20}H_{18}$ 258.1408, found 258.1402.



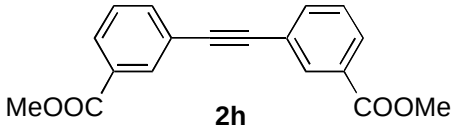
2f

Bis(1-naphthyl)acetylene **2f**[4]**:** Pale-yellow solid, mp 127-128 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60-7.45 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.4, 130.6, 129.0, 128.4, 127.0, 126.5, 126.4, 125.4, 121.2, 92.5; GCMS *m*/*z* (% rel. inten.) 278 (M^+, 100), 276 (53), 250 (5), 138 (6), 125 (4).



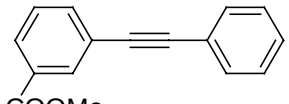
2g

Bis(2-thiophenyl)acetylene **2g**[5]**:** Pale-yellow solid, mp 99-100 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.25 (m, 4H), 7.04-7.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.1, 127.6, 127.2, 123.0, 86.2; GCMS *m*/*z* (% rel. inten.) 190 (M^+, 100), 158 (9), 145 (23), 132 (12), 114 (11), 93 (17), 86 (12).



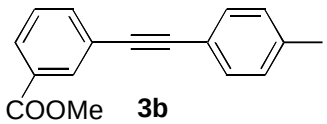
2h

Bis(3-methoxycarbonyl-phenyl)acetylene (2h): Pale-yellow solid, mp 169-171 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (s, 2H), 8.01 (d, 2H, *J* = 7.7 Hz), 7.70 (d, 2H, *J* = 7.7 Hz), 7.45 (virtual t, 2H, *J* = 7.7 Hz), 3.94 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 135.8, 132.9, 130.6, 129.5, 128.6, 123.4, 89.2, 52.3; GCMS *m*/*z* (% rel. inten.) 294 (M^+, 100), 263 (75), 235 (15), 189 (17), 176 (48), 150 (16), 102 (8); Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.45; H, 4.76. Found: C, 72.79; H, 4.64; HRMS (M^+) *m*/*z* calcd for $C_{18}H_{14}O_4$ 294.0892, found 294.0889.



3a

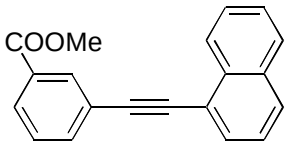
Methyl 3-phenylethynylbenzoate **3a**[6]**:** yellow solid, mp 68~70 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (m, 1H), 8.02 (d, 1H, *J* = 7.9 Hz), 7.70 (d, 1H, *J* = 7.9 Hz), 7.53~7.56 (m, 2H), 7.34~7.43 (m, 4H), 3.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 135.7, 132.7, 131.7, 130.5, 129.2, 128.6, 128.5, 128.4, 123.8, 122.9, 90.3, 88.3, 52.3; GCMS *m*/*z* (% rel. inten.) 236 (M^+, 100), 205 (55), 176 (44), 151 (15), 103 (9), 88 (18), 77 (5).



3b

Methyl 3-(*p*-tolylethynyl)benzoate (3b): pale-yellow solid, mp 127~129 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (m, 1H), 7.98 (d, 1H, *J* = 7.8 Hz), 7.68 (d, 1H, *J* = 7.8

Hz), 7.41~7.46 (m, 3H), 7.15~7.17 (d, 2H, *J* = 8.2 Hz), 3.93 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 138.7, 135.6, 132.7, 131.6, 130.4, 129.2, 129.0, 128.5, 124.0, 119.8, 90.5, 87.7, 52.3, 21.5; GCMS *m*/*z* (% rel. inten.) 250 (M^+, 100), 219 (34), 189 (29), 176 (9), 139 (5), 109 (9), 95 (7), 82 (5); HRMS (M^+) *m*/*z* calcd for $C_{17}H_{14}O_2$ 250.0994, found 250.0991.



3c

Methyl 3-(1-naphthylethynyl)benzoate (3c): viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, 1H, *J* = 8.5 Hz), 8.31 (m, 1H), 8.01 (d, 1H, *J* = 7.6 Hz), 7.75~7.85 (m, 4H), 7.41~7.60 (m, 4H), 3.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 135.7, 133.2, 132.7, 130.6, 130.5, 129.7, 129.3, 129.1, 128.6, 128.4, 126.9, 126.5, 126.1, 125.3, 123.9, 120.5, 93.2, 88.5, 52.3; GCMS *m*/*z* (% rel. inten.) 286 (M^+, 100), 255 (12), 226 (49), 200 (5), 127 (8), 113 (20), 100 (5); HRMS (M^+) *m*/*z* calcd for $C_{20}H_{14}O_2$ 286.0994, found 286.0992.

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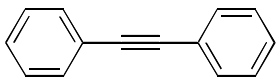
2. The copies of ^{1}H and ^{13}C-NMR charts of all the products



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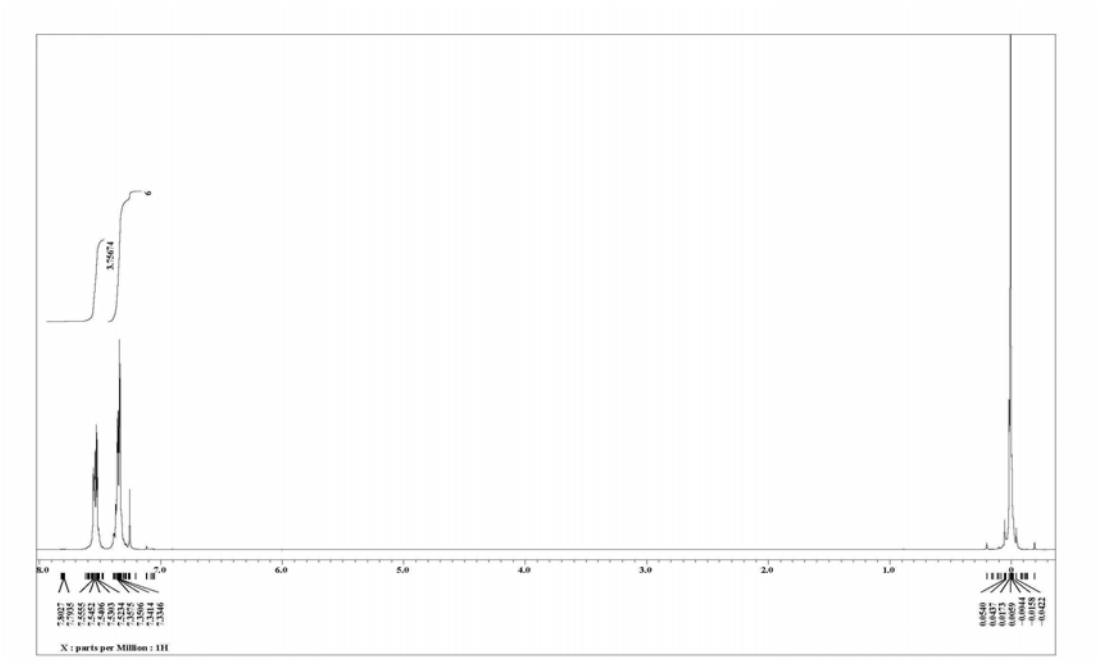

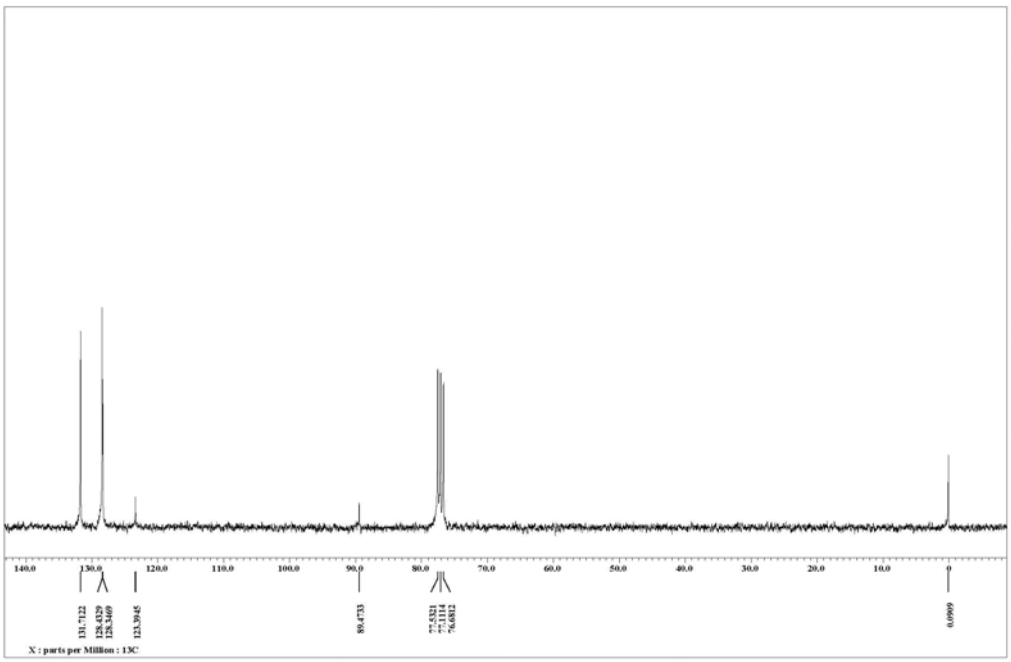

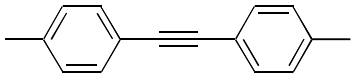

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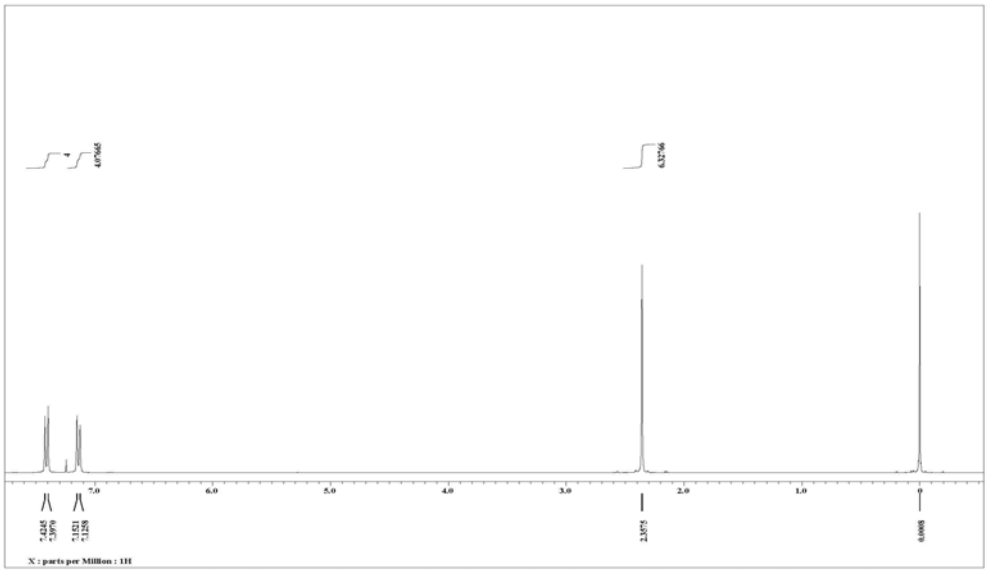
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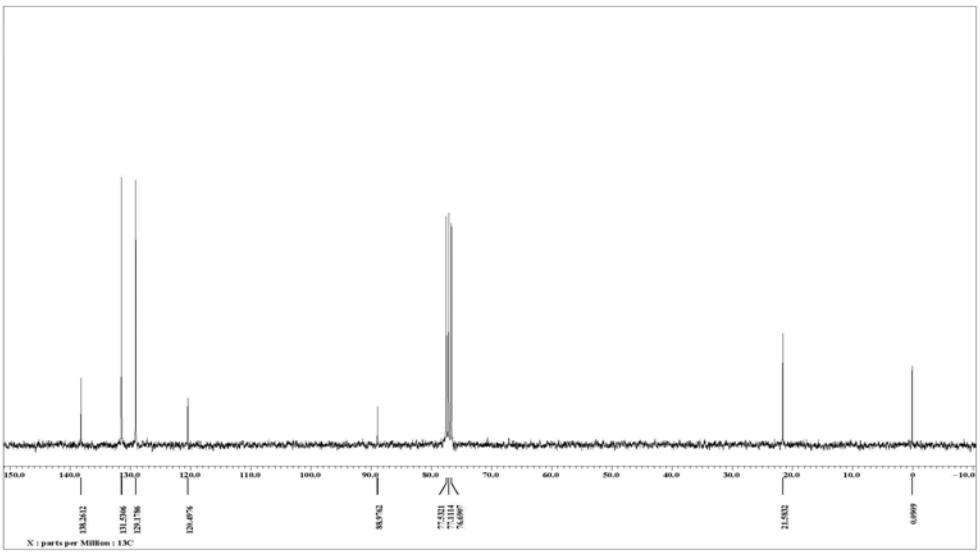
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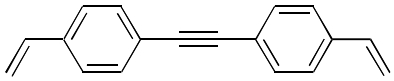

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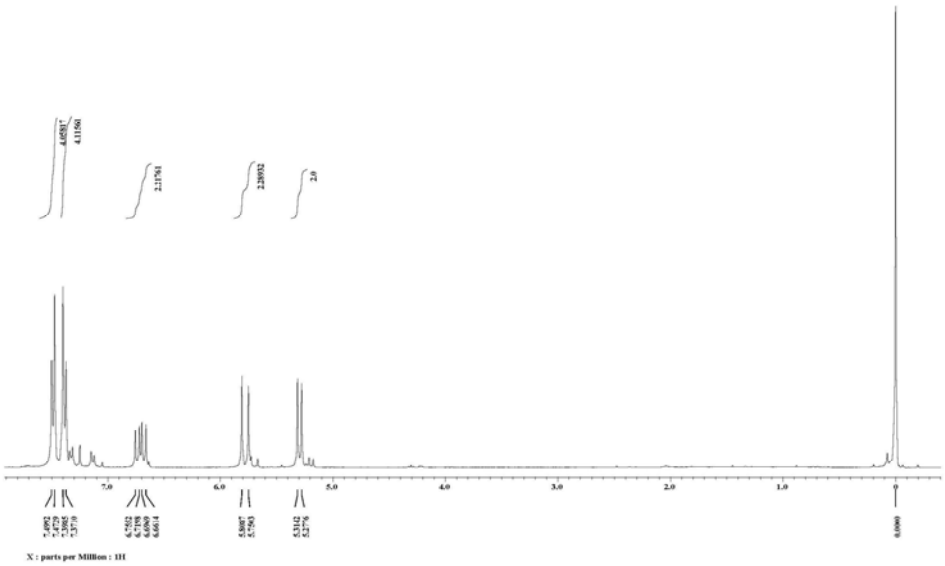
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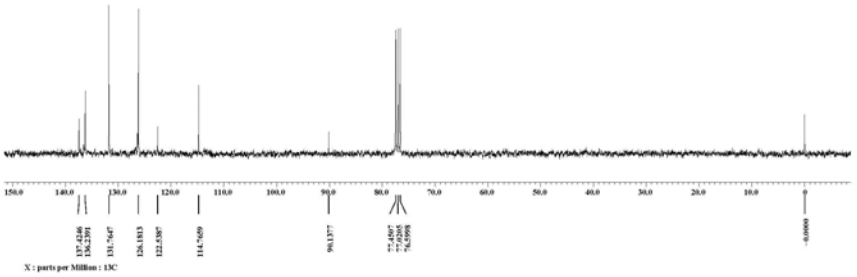
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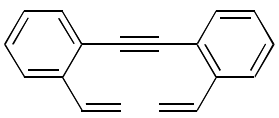

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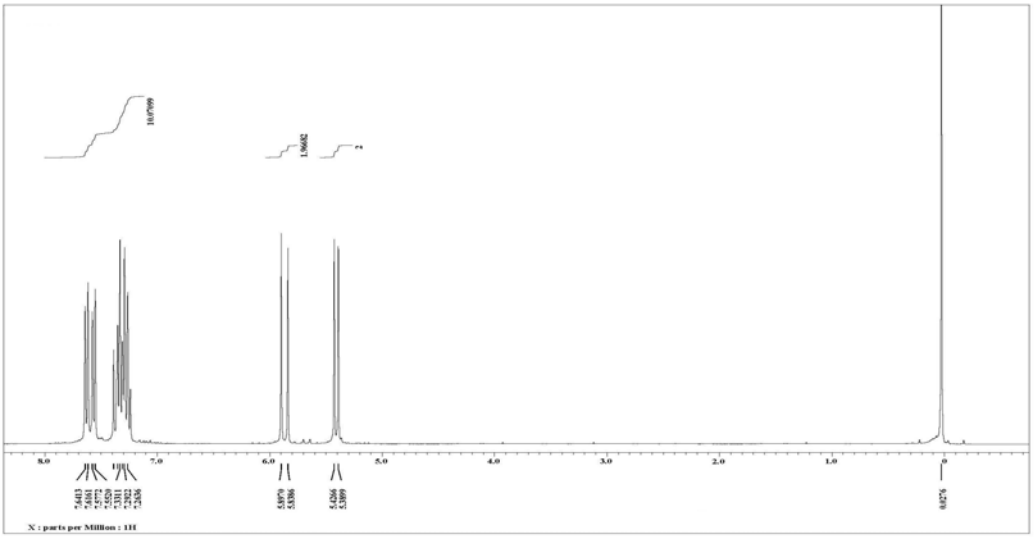

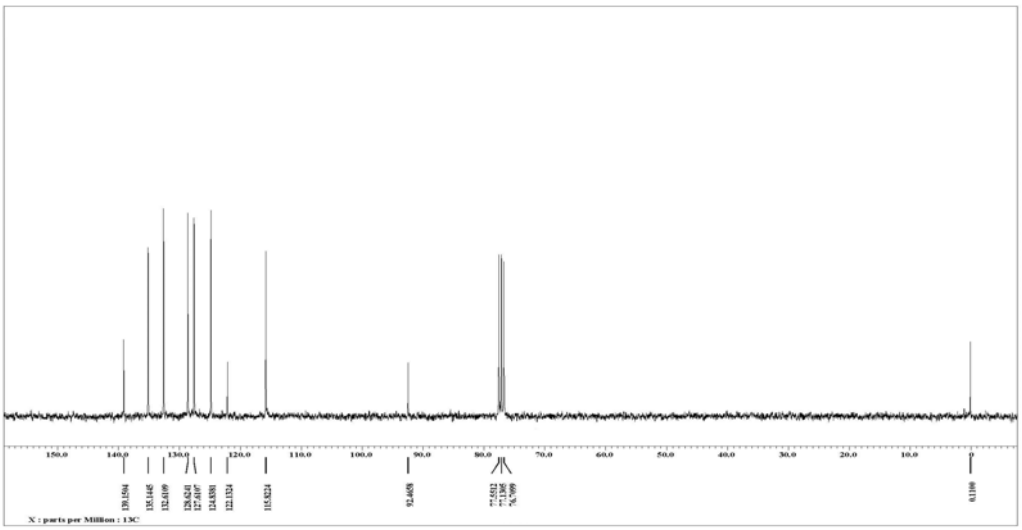

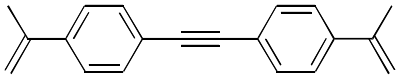

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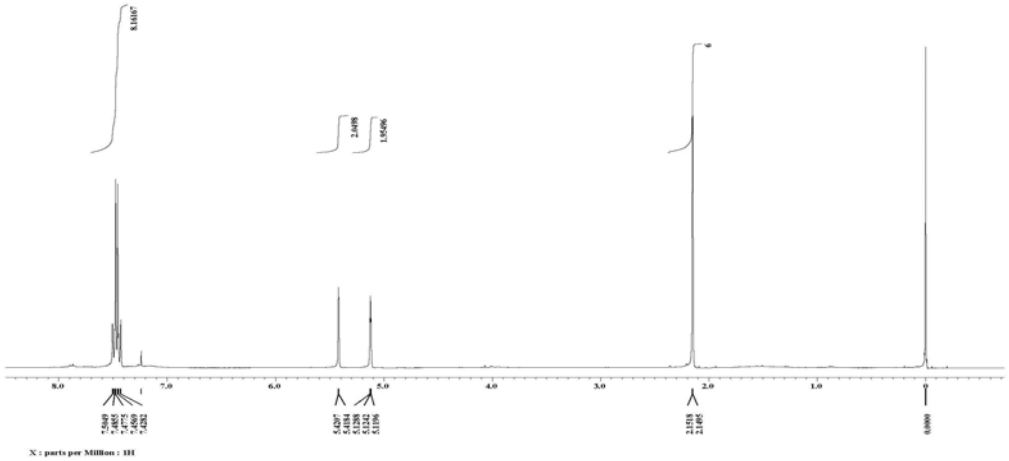

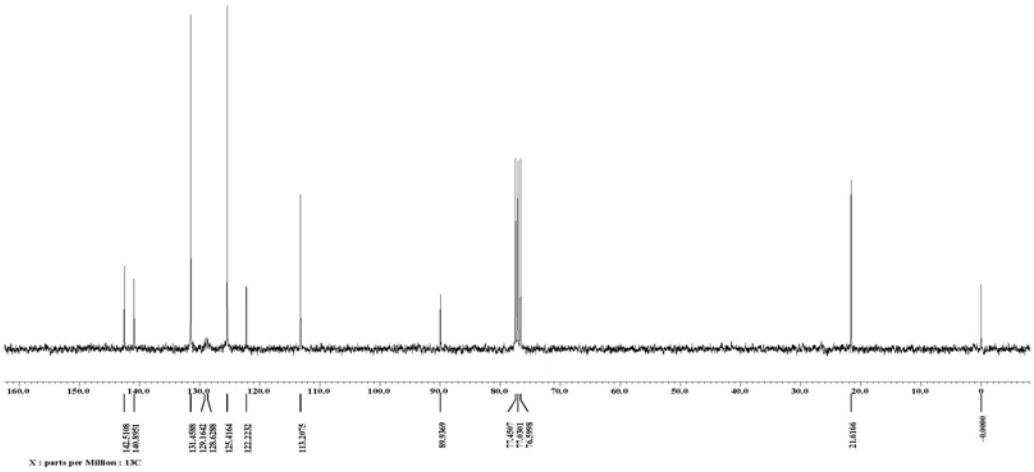

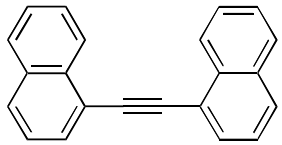

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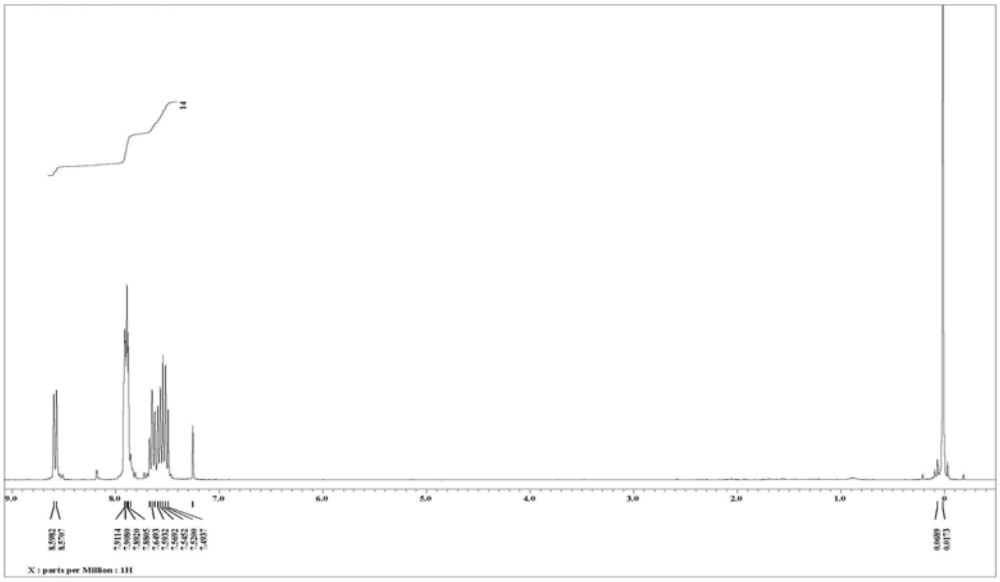
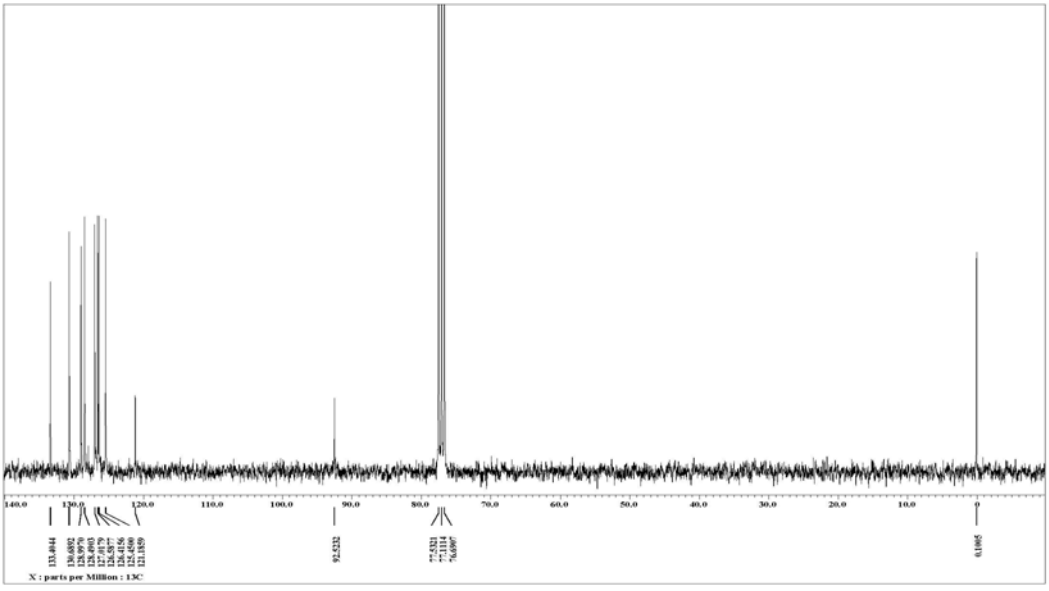
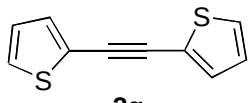
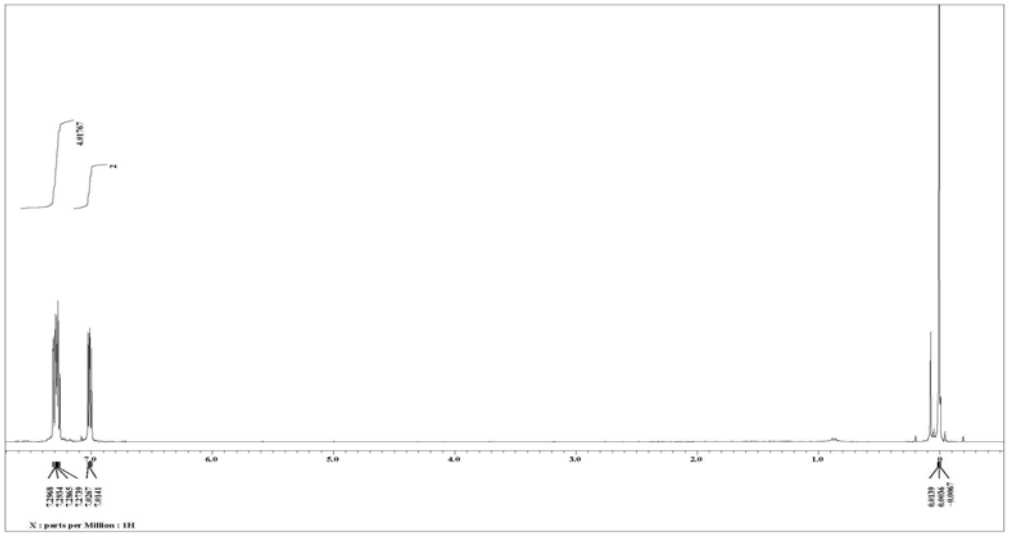
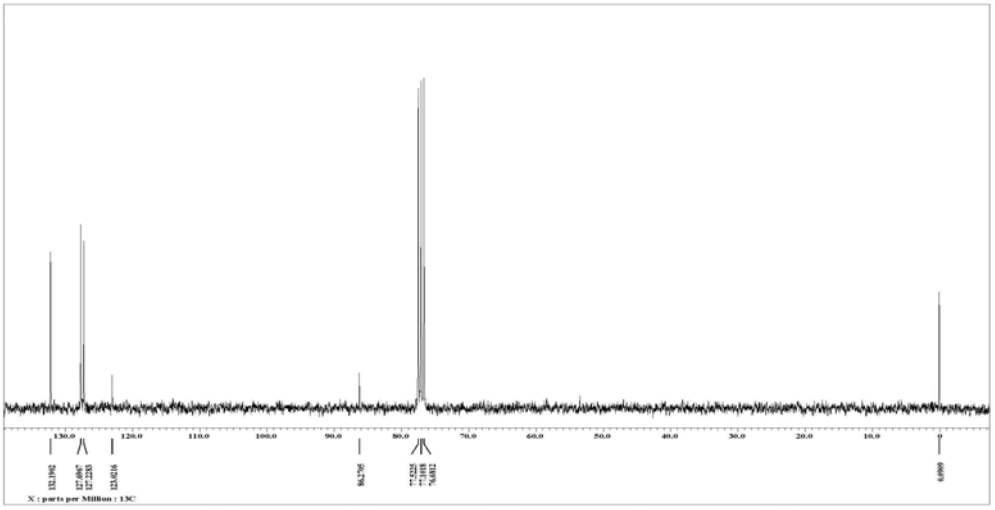


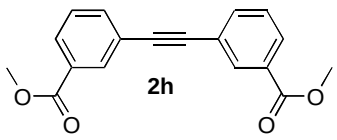




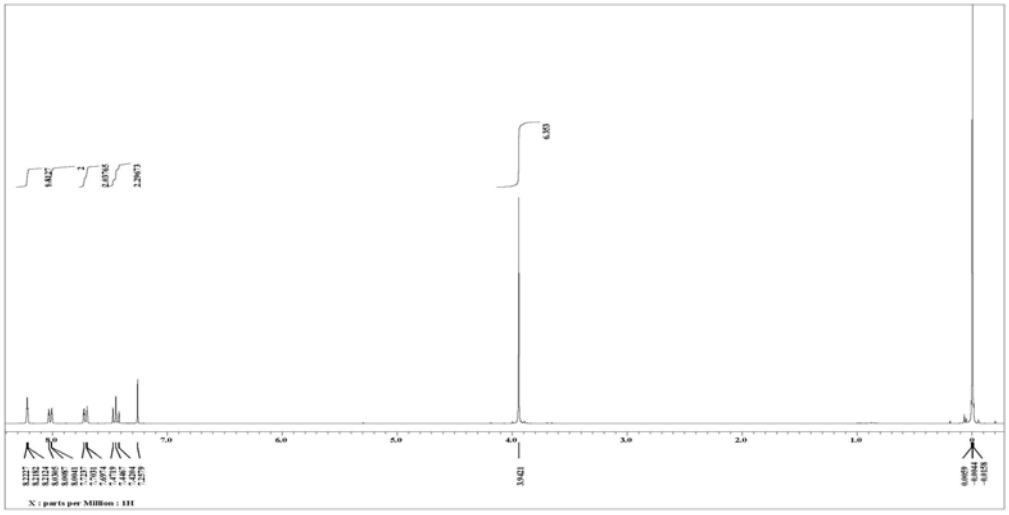
2g

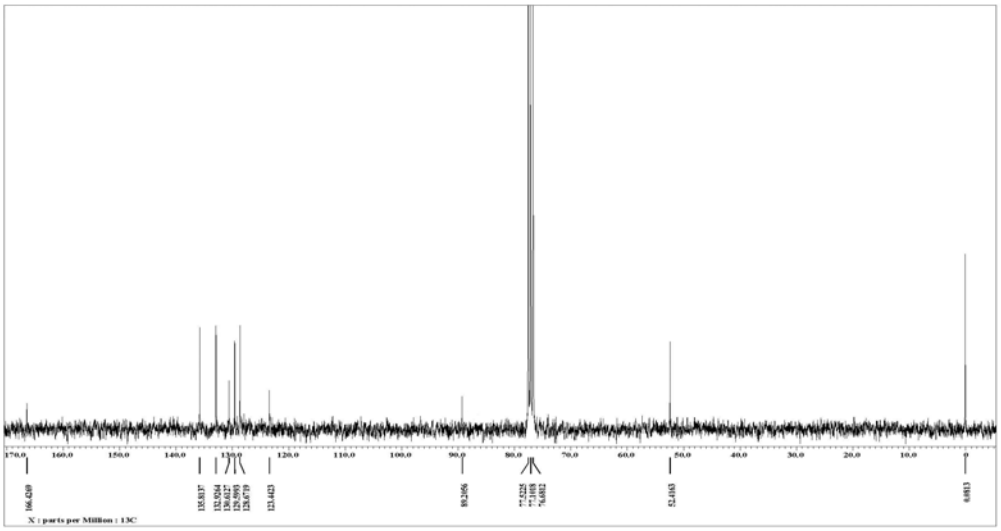


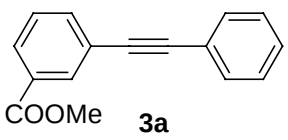




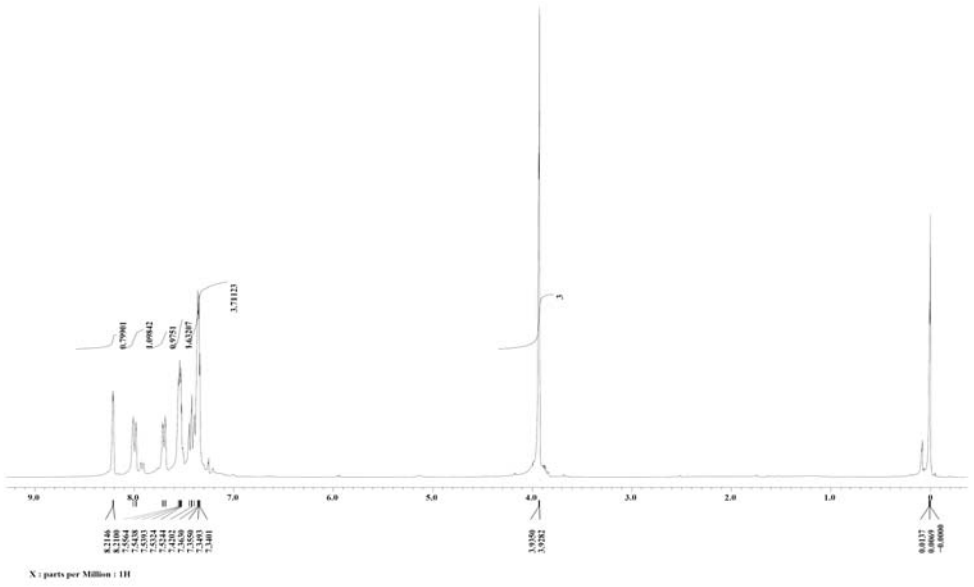
2h

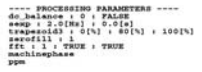




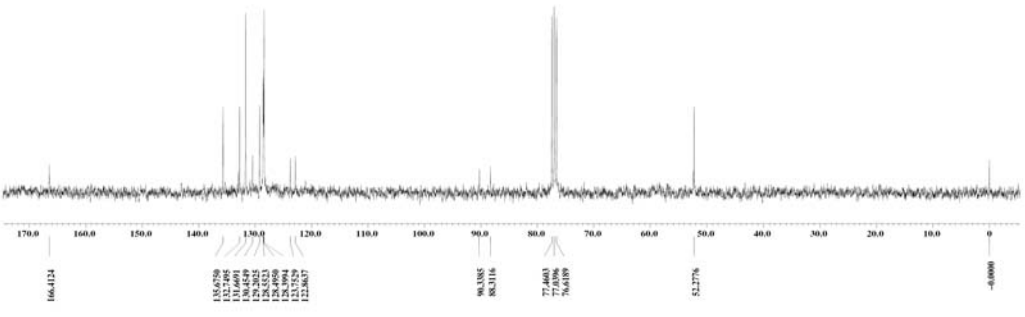

COOMe

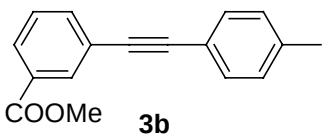
3a


0.79901
1.09842
0.9751
1.63207
3.73123
3
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.2146
8.1988
7.5564
7.5438
7.5301
7.5324
7.5191
7.5430
7.3550
7.3401
3.3550
3.3282
0.0137
0.0069
-0.0000
X : parts per Million : 1H


---- PROCESSING PARAMETERS ----
do_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

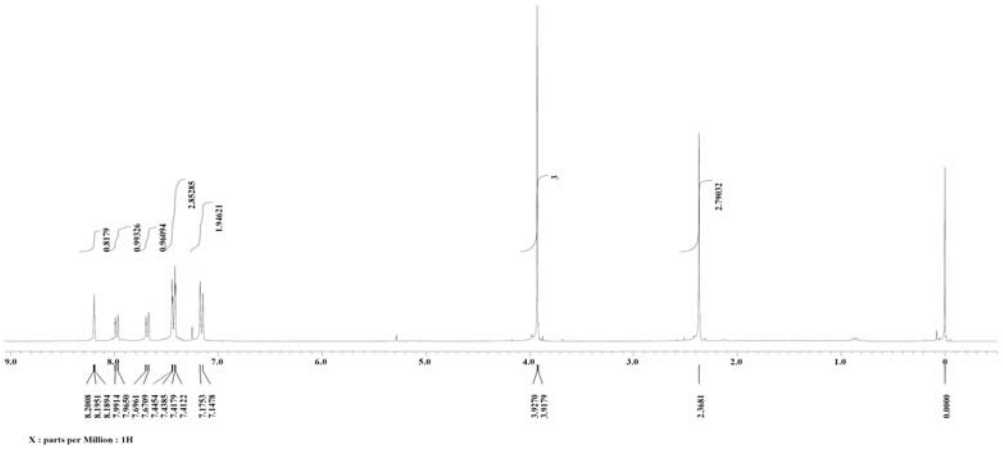
z185(1)--C--single_pulse_dec--X.jdf


170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
166.4124
135.6750
132.2495
131.6401
130.4549
129.2025
128.7413
128.4950
128.3594
123.3378
122.8637
90.3385
88.3316
77.4683
77.0396
76.6189
52.2776
-0.0000
X : parts per Million : 13C



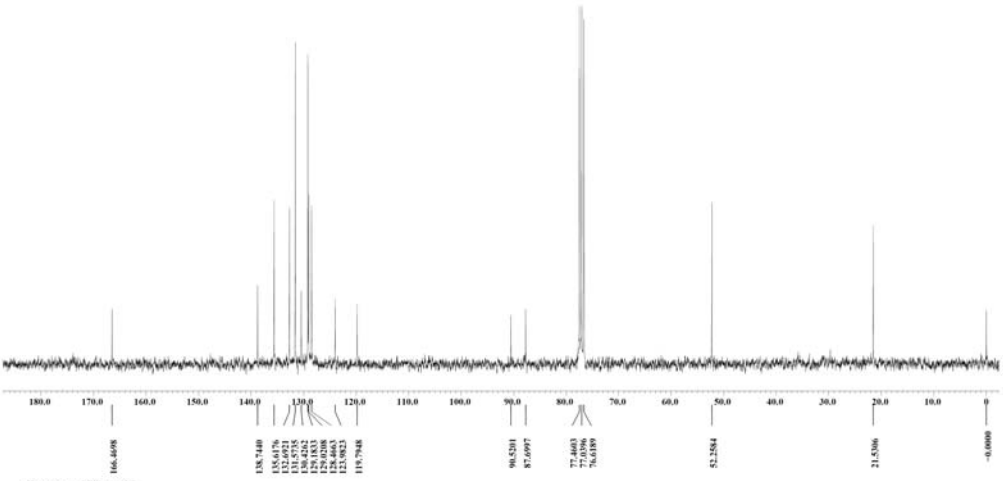
3b

z188(3)~H~single_pulse~2.jdf
single_pulse

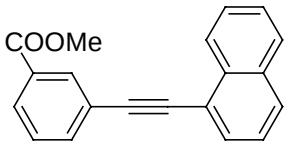


X : parts per Million : 1H

z188(3)~C~single_pulse_dec~2.jdf
single pulse decoupled gated NOE

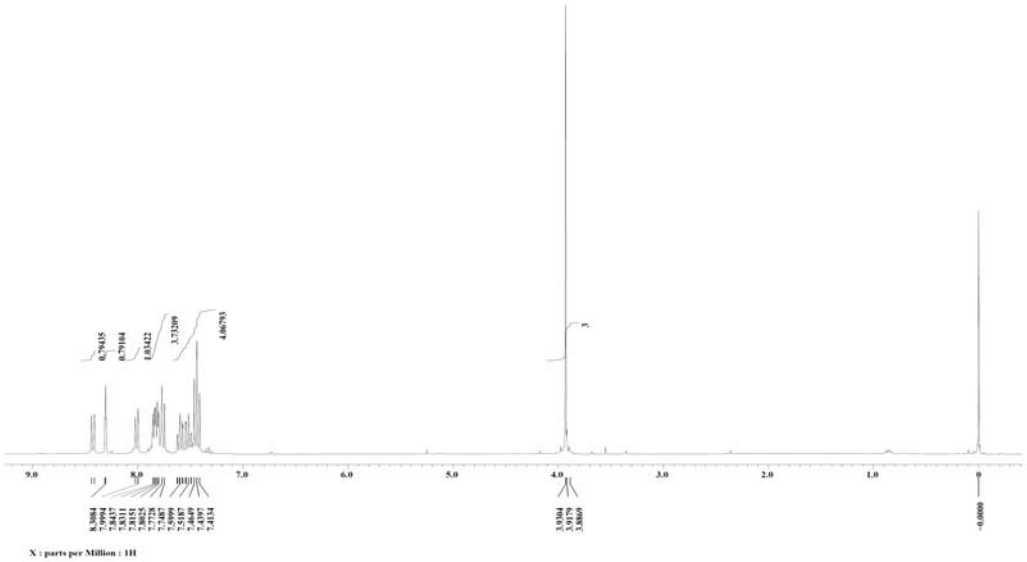


X : parts per Million : 13C



3c

z191(2)~H~single_pulse~2.jdf
single_pulse



---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

z191(2)~C~single_pulse_dec~3.jdf