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SUPPORTING INFORMATION

Title: Synthesis of 3-Alkynylselenophene Derivatives by a Copper-Free Sonogashira Cross-Coupling Reaction
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Ref. No.: O200700707

Materials and Methods

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 200 MHz on a DPX-200 NMR spectrometer or at 400 MHz on DPX-400 NMR spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained either at 50 MHz on a DPX-200 NMR spectrometer or at 100 MHz on a DPX-400 NMR spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet) and m (multiplet). High resolution mass spectra were recorded on a MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. Column chromatography was performed using Silica Gel (230-400 mesh) following the methods described by Still.[1] Thin layer chromatography (TLC) was performed using Silica Gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapour, or acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry argon. Reagents and solvents were handled using standard syringe techniques. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a Variac controller.

General procedure for the cross-coupling reaction: To a Schlenck tube, under argon, containing an appropriate 3-iodoselenophene (0.50 mmol) in DMF (2.5 mL) was added to $Pd(PPh_3)_2Cl_2$ (0.035g, 0.05 mmol). The resulting solution was stirred for 5 minutes at room temperature. After this time, appropriate terminal alkyne (1.5 mmol) dissolved in 1 mL of Et_3N was then added dropwise, and the reaction mixture was allowed to stir at room temperature for 12 hours. After this the mixture was diluted with dichloromethane

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[1] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem*. **1978**, *43,* 2923-2925.

(20 mL), and washed with brine (3x20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent. Selected spectral and analytical data for **4-(2,5-Diphenyl-selenophen-3-yl)-2-methyl-but-3-yn-2-ol (3a):** Yield: 0.166g (91%). H^1 NMR ($CDCl_3$, 400 MHz): δ 7.83-7.81 (m, 2H), 7.54-7.50 (m, 3H), 7.42-7.29 (m, 6H), 2.11 (s, 1H), 1.60 (s, 6H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 151.79, 147.42, 135.50, 135.41, 129.59, 128.95, 128.45, 128.12, 128.05, 127.97, 125.99, 119.94, 94.66, 79.44, 65.67, 31.20. MS (relative intensity) *m*/*z*: 347 (100), 305 (77), 281 (61), 128 (50), 77 (21). HRMS calcd for $C_{21}H_{18}OSe$: 366.0523. Found: 366.0529.

1-(2,5-Diphenyl-selenophen-3-yl)-3-methyl-pent-1-yn-3-ol (3b). Yield: 0.183g (97%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.83-7.78 (m, 2H), 7.56-7.50 (m, 3H), 7.44-7.29 (m, 6H), 2.07 (s, 1H), 1.76 (quart, J = 7.50 Hz, 2H), 1.54 (s, 3H), 1.05 (t, J = 7.50 Hz, 3H). C^{13} NMR ($CDCl_3$, 100 MHz) δ (ppm): 151.69, 147.39, 135.48, 135.40, 129.72, 128.95, 128.44, 128.11, 128.01, 127.95, 125.99, 120.05, 93.66, 80.47, 69.22, 36.43, 29.10, 9.03. MS (relative intensity) *m*/*z*: 361 (100), 332 (53), 317 (22), 281 (71), 206 (44), 129 (56), 77 (35). HRMS calcd for $C_{22}H_{20}OSe$: 380.0679. Found: 380.0683.

1-(2,5-Diphenyl-selenophen-3-ylethynyl)-cyclohexanol (3c). Yield: 0.174g (86%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.84-7.79 (m, 2H), 7.56-7.51 (m, 3H), 7.43-7.29 (m, 6H), 2.12 (s, 1H), 1.72-1.52 (m, 8H), 1.36-1.17 (m, 2H). C^{13} NMR ($CDCl_3$, 50 MHz) δ (ppm): 151.65, 147.43, 135.55, 135.47, 129.79, 128.96, 128.44, 128.12, 128.09, 127.95, 126.02, 120.23, 93.78, 81.34, 69.28, 39.89, 25.17, 23.29. MS (relative intensity) *m*/*z*: 387 (100), 305 (32), 281 (65), 206 (47), 129 (63), 77 (41). HRMS calcd for $C_{24}H_{22}OSe$: 406.0836. Found: 406.0831.

1-(2,5-Diphenyl-selenophen-3-yl)-pent-1-yn-3-ol (3d). Yield: 0.166g (91%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.83-7.78 (m, 2H), 7.55-7.50 (m, 3H), 7.44-7.29 (m, 6H), 4.54-4.49 (m, 1H), 2.00 (s, 1H), 1.87-1.73 (m, 2H), 1.04 (t, J = 7.42 Hz, 3H). C^{13} NMR ($CDCl_3$, 50 MHz) δ (ppm): 151.96, 147.52, 135.48, 135.42, 129.73, 128.97, 128.52, 128.16, 128.04, 127.99, 126.02, 119.96, 90.98, 82.00, 64.29, 30.82, 9.42. MS (relative intensity) *m*/*z*: 347 (100), 318 (21), 281 (69), 206 (52), 129 (73), 77 (35). HRMS calcd for $C_{21}H_{18}OSe$: 366.0523. Found: 366.0528.

3-(2,5-Diphenyl-selenophen-3-yl)-prop-2-yn-1-ol (3e). Yield: 0.128g (74%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.82-7.77 (m, 2H), 7.55-7.29 (m, 9H), 4.46 (s, 2H), 1.78 (s, 1H). C^{13} NMR ($CDCl_3$, 100 MHz) δ (ppm): 152.18, 147.56, 135.40, 135.31, 129.67, 128.94, 128.58, 128.16, 127.98, 127.96, 125.97, 119.78, 88.16, 82.75, 51.62. MS (relative intensity) *m*/*z*: 319 (100), 281 (55), 206 (47), 129 (63), 77 (40). HRMS calcd for $C_{19}H_{14}OSe$: 338.0210. Found: 338.0207.

3-(3-Ethoxy-prop-1-ynyl)-2,5-diphenyl-selenophene (3f). Yield: 0.122g (67%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.83-7.78 (m, 2H), 7.55-7.50 (m, 3H), 7.44-7.29 (m, 6H), 4.34 (s, 2H), 2.61 (quart, J = 6.98 Hz, 2H), 1.24 (t, J = 6.98 Hz, 3H). C^{13} NMR ($CDCl_3$, 100 MHz) δ (ppm): 152.08, 147.46, 135.50, 135.42, 129.82, 128.97, 128.53, 128.13, 128.03, 127.98, 126.02, 120.02, 86.48, 83.07, 65.40, 58.59, 15.03. MS (relative intensity) *m*/*z*: 365 (100), 320 (73), 281 (41), 206 (61), 129 (55), 77 (47). HRMS calcd for $C_{21}H_{18}OSe$: 366.0523. Found: 366.0518.

2,5-diphenyl-3-(phenylethynyl)-selenophene (3g). Yield: 0.180g (94%). H^1 NMR ($CDCl_3$, 400 MHz): δ 7.92-7.89 (m, 2H), 7.61 (s, 1H), 7.58-7.56 (m, 2H), 7.49-7.29 (m,

11H). C^{13} NMR ($CDCl_3$, 100 MHz): δ 151.76, 147.47, 135.71, 135.50, 131.41, 129.61, 129.00, 128.59, 128.36, 128.16, 128.15, 128.14, 128.00, 126.08, 123.37, 120.57, 90.34, 86.86. MS (relative intensity) *m*/*z*: 383 (100), 306 (56), 282 (77), 204 (38), 128 (51), 101 (19), 77 (28). HRMS calcd for $C_{24}H_{16}Se$: 384.0417. Found: 384.0411.

3-Cyclohex-1-enylethynyl-2,5-diphenyl-selenophene (3h). Yield: 0.180g (93%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.88-7.83 (m, 2H), 7.57-7.25 (m, 9H), 6.19-6.14 (m, 1H), 2.22-2.12 (m, 4H), 1.68-1.59 (m, 4H). C^{13} NMR ($CDCl_3$, 100 MHz) δ (ppm): 150.55, 147.02, 135.80, 135.57, 135.06, 129.81, 128.95, 128.45, 127.99, 127.90, 127.88, 126.02, 121.03, 120.82, 92.40, 84.22, 28.90, 25.79, 22.29, 21.50. MS (relative intensity) *m*/*z*: 387 (100), 306 (65), 281 (56), 206 (42), 129 (39), 77 (62). HRMS calcd for $C_{24}H_{20}Se$: 388.0730. Found: 388.0734.

3-Hept-1-ynyl-2,5-diphenyl-selenophene (3i). Yield: 0.182g (97%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.87-7.83 (m, 2H), 7.56-7.49 (m, 3H), 7.41-7.28 (m, 6H), 2.39 (t, *J* = 7.13 Hz, 2H), 1.67-1.49 (m, 2H), 1.46-1.28 (m, 4H), 0.91 (t, *J* = 7.13 Hz, 3H). C^{13} NMR ($CDCl_3$, 100 MHz) δ (ppm): 150.27, 146.94, 135.82, 135.63, 130.18, 128.93, 128.44, 127.95, 127.86, 127.83, 126.00, 121.29, 91.73, 77.71, 31.14, 28.24, 22.24, 19.55, 14.00. MS (relative intensity) *m*/*z*: 377 (100), 362 (73), 348 (33), 334 (30), 320 (26), 281 (56), 206 (58), 129 (61), 77 (53). HRMS calcd for $C_{23}H_{22}Se$: 378.0887. Found: 378.0882.

3-(3,3-Dimethyl-but-1-ynyl)-2,5-diphenyl-selenophene (3j). Yield: 0.127g (70%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.89-7.85 (m, 2H), 7.56-7.48 (m, 3H), 7.44-7.27 (m, 6H), 1.31 (s, 9H). C^{13} NMR ($CDCl_3$, 50 MHz) δ (ppm): 150.18, 146.83, 135.83, 135.63, 130.10, 128.90, 128.29, 127.91, 127.81, 127.79, 126.00, 121.19, 99.64, 76.46, 30.76, 28.16. MS (relative intensity) *m*/*z*: 363 (100), 318 (63), 281 (68), 206 (42), 129 (58), 77 (39). HRMS calcd for $C_{22}H_{20}Se$: 364.0730. Found: 364.0733.

4-(2,5-Dibutyl-selenophen-3-yl)-2-methyl-but-3-yn-2-ol (3k). Yield: 0.134g (83%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 6.76 (s, 1H), 2.89 (t, *J* = 7.79 Hz, 2H), 2.75 (t, *J* = 7.57 Hz, 2H), 2.07 (s, 1H), 1.70-1.56 (m, 10H), 1.49-1.28 (m, 4H), 0.97-0.88 (m, 6H). C^{13} NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.05, 148.49, 128.04, 119.64, 94.58, 78.48, 65.69, 34.34, 34.25, 32.15, 31.60, 31.07, 22.12, 22.02, 13.80, 13.77. MS (relative intensity) *m*/*z*: 307 (100), 278 (34), 242 (77), 211 (63), 183 (52), 155 (39), 129 (32). HRMS calcd for $C_{17}H_{26}OSe$: 326.1149. Found: 326.1153.

2,5-Dibutyl-3-phenyletynyl-selenophene (3l). Yield: 0.161g (94%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.55-7.45 (m, 2H), 7.36-7.28 (m, 3H), 6.88 (s, 1H), 3.00 (t, *J* = 7.79 Hz, 2H), 2.78 (t, *J* = 7.50 Hz, 2H), 1.76-1.30 (m, 8H), 0.99-0.89 (m, 6H). C^{13} NMR ($CDCl_3$, 100 MHz) δ (ppm): 155.16, 148.55, 131.30, 128.25, 128.06, 127.76, 123.79, 120.30, 90.08, 85.88, 34.48, 34.27, 32.21, 31.28, 22.18, 22.06, 13.85, 13.79. MS (relative intensity) *m*/*z*: 343 (100), 266 (72), 242 (70), 211 (51), 183 (62), 155 (44), 129 (47). HRMS calcd for $C_{20}H_{24}Se$: 344.1043. Found: 344.1048.

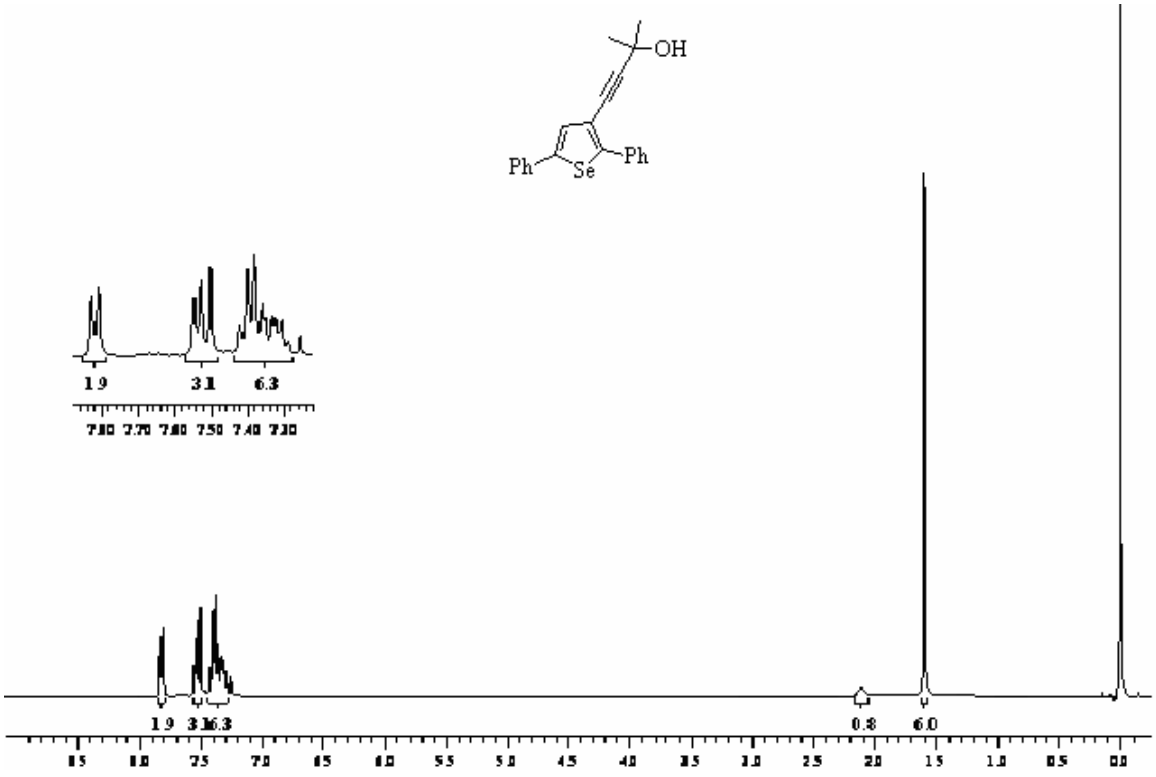
4-(2,5-Di-*p*-methylphenyl-selenophen-3-yl)-2-methyl-but-3-yn-2-ol (3m). Yield: 0.184g (94%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.71 (d, *J* = 8.31, 2H), 7.44-7.40 (m, 3H), 7.22-7.15 (m, 4H), 2.38-2.36 (m, 6H), 1.99 (s, 1H), 1.60 (s, 6H). C^{13} NMR ($CDCl_3$, 100 MHz) δ (ppm): 151.54, 147.04, 138.09, 137.90, 132.83, 132.78, 129.62, 129.16, 129.04, 127.82, 125.89, 119.37, 94.47, 79.71, 65.74, 31.26, 21.26, 21.18. MS (relative intensity) *m*/*z*: 375 (100), 345 (47), 309 (78), 128 (58), 91 (57). HRMS calcd for $C_{23}H_{22}OSe$: 394.0836. Found: 394.0840.

4-(2-Butyl-5-phenyl-selenophen-3-yl)-2-methyl-but-3-yn-2-ol (3n). Yield: 0.134g (78%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.77-7.72 (m, 2H), 7.40-7.25 (m, 3H), 6.96 (s, 1H), 2.81 (t, J = 7.49 Hz, 2H), 2.02 (s, 1H), 1.73-1.56 (m, 8H), 1.41 (sex, J = 7.49 Hz, 2H), 0.94 (t, J = 7.49 Hz, 3H). C^{13} NMR ($CDCl_3$, 50 MHz) δ (ppm): 150.61, 150.37, 135.95, 130.75, 128.34, 127.93, 127.70, 118.38, 94.17, 79.80, 65.72, 34.20, 32.17, 31.25, 22.06, 13.79. MS (relative intensity) *m*/*z*: 327 (100), 297 (52), 261 (56), 246 (33), 232 (21), 155 (45), 128 (42), 77 (34). HRMS calcd for $C_{19}H_{22}OSe$: 346.0836. Found: 346.0831.

4-[5-(1-Hydroxy-1-methyl-ethyl)-2-phenyl-selenophen-3-yl]-2-methyl-but-3-yn-2-ol (3o). Yield: 0.156g (90%). H^1 NMR ($CDCl_3$, 200 MHz), δ (ppm): 7.76-7.71 (m, 2H), 7.40-7.25 (m, 3H), 7.05 (s, 1H), 2.61 (s, 1H), 2.46 (s, 1H), 1.62 (s, 6H), 1.55 (s, 6H). C^{13} NMR ($CDCl_3$, 100 MHz) δ (ppm): 159.58, 151.15, 135.67, 128.35, 127.95, 127.94, 127.88, 118.43, 94.10, 79.65, 72.71, 65.61, 31.99, 31.16. MS (relative intensity) *m*/*z*: 311 (100), 281 (72), 245 (45), 206 (31), 128 (56), 77 (21). HRMS calcd for $C_{18}H_{20}O_2Se$: 348.0629. Found: 348.0624.

General Procedure for the Preparation of (*Z*)-vinylic telluride 4. Powered NaOH (0.044g; 1.1 mmol) was added to a two-neck round bottomed flask equipped with a reflux condenser, containing a solution of alkynylselenophene **3a** (0.365g, 1.0 mmol) in dry toluene (2 mL) under argon atmosphere. The mixture was slowly heated to reach reflux temperature, at this time the reaction mixture became dark brown and was refluxed for 4 hours. The solution of the ethynylselenophene obtained was cooled to room temperature and then a solution of dibutylditelluride (0.185g; 0.5 mmol) in 95% ethanol (10 mL) was added. $NaBH_4$ (0.092g; 2.5 mmol) was added under vigorous stirring and gas evolution was observed during addition. The reaction mixture was stirred under reflux for 6h, allowed to reach room temperature, diluted with ethyl acetate (60 mL) and washed with brine (3x30 mL) and water (3x30 mL). After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using hexane as the eluent. Selected spectral and analytical data for **3-(2-Butyltellanyl-vinyl)-2,5-diphenyl-selenophene (4)**. Yield: 0.335g (68%). H^1 NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.80 (s, 1H), 7.59-7.57 (m, 2H), 7.48-7.23 (m, 9H), 6.91 (d, J = 10.85 Hz, 1H), 2.76 (t, J = 7.44 Hz, 2H), 1.83 (quint, J = 7.44 Hz, 2H), 1.42 (sex, J = 7.44 Hz, 2H), 0.94 (t, J = 7.44 Hz, 3H). C^{13} NMR ($CDCl_3$, 100 MHz) δ (ppm):148.12, 138.65, 136.13, 132.96, 129.59, 129.37, 128.91, 128.49, 127.67, 127.62, 126.06, 125.28, 124.16, 105.08, 34.04, 24.99, 13.43, 8.41. MS (relative intensity) *m*/*z*: 495 (100), 438 (25), 311 (86), 282 (70), 210 (62), 204 (38), 184 (75), 128 (51), 77 (25). HRMS calcd for $C_{22}H_{22}SeTe$: 495.9949. Found: 495.9954.

SELECTED SPECTRA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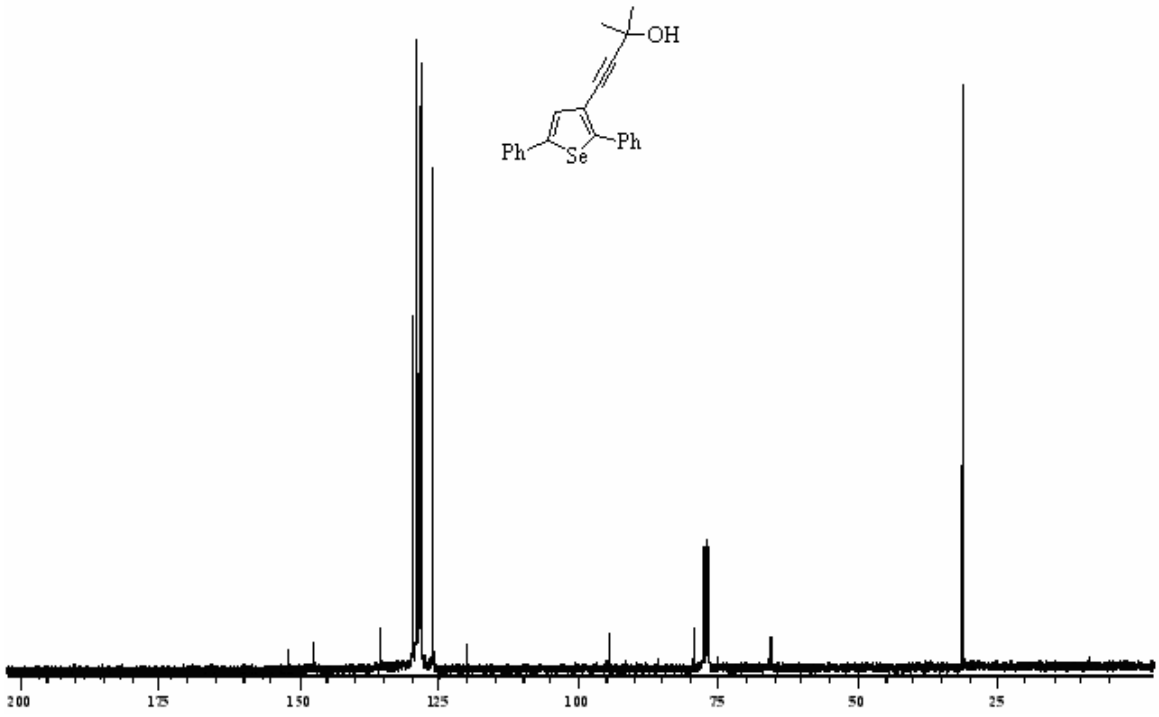
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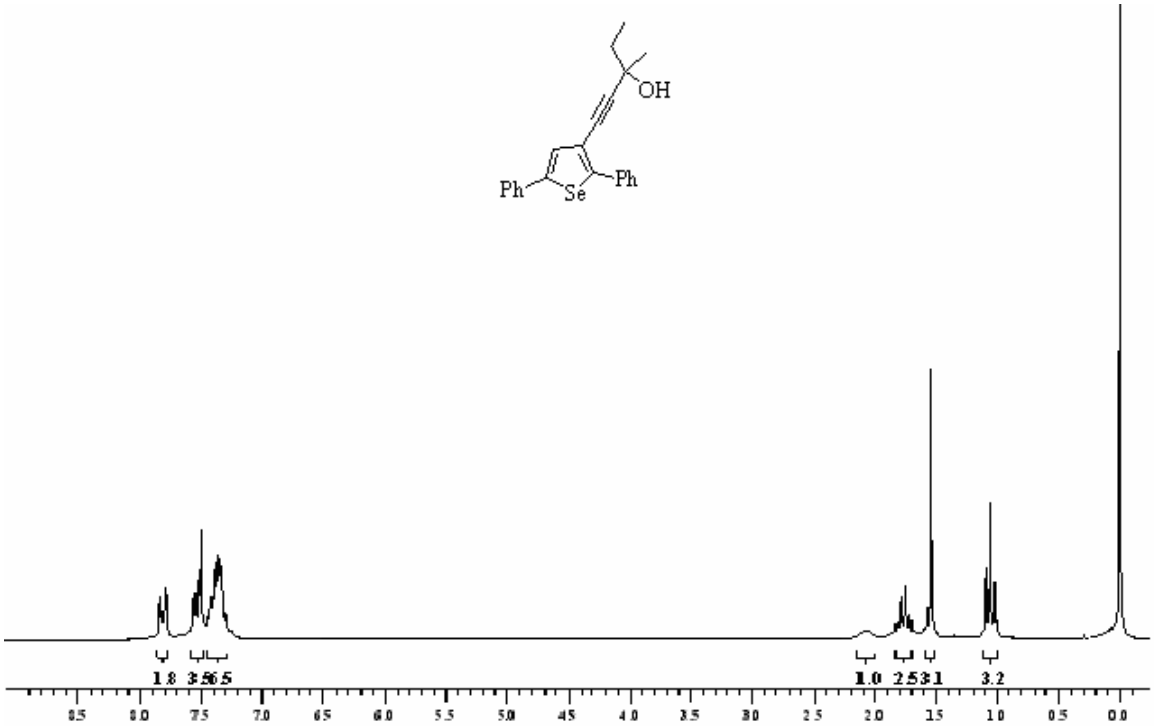
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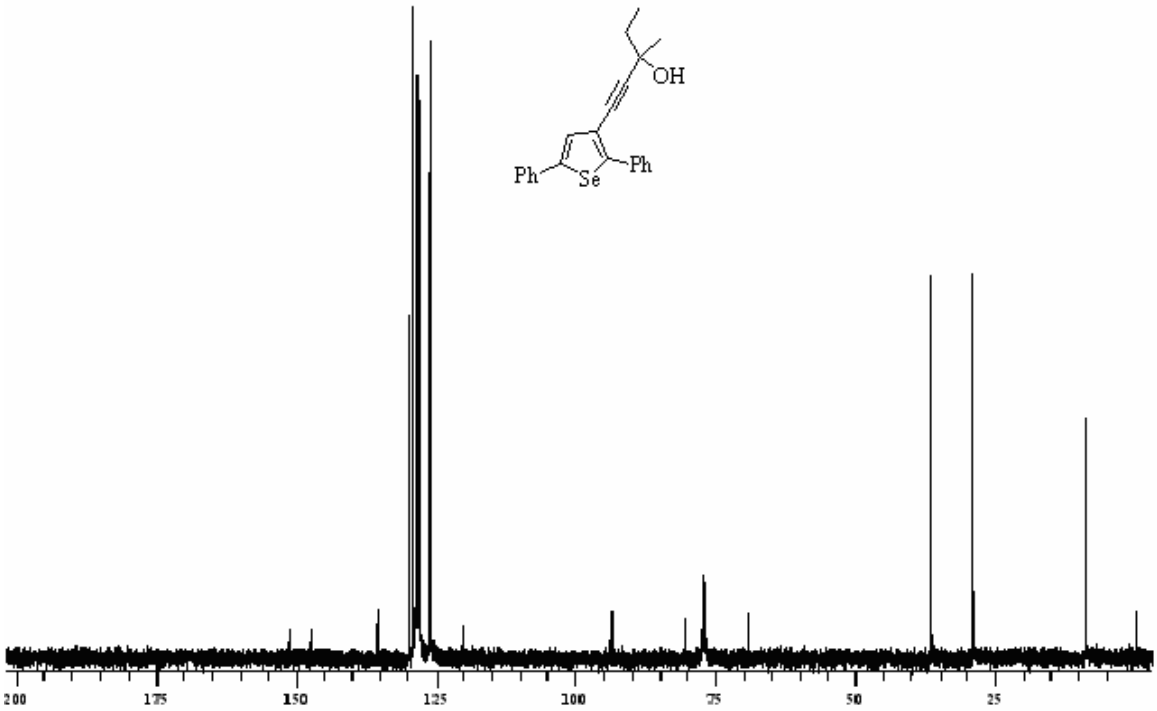
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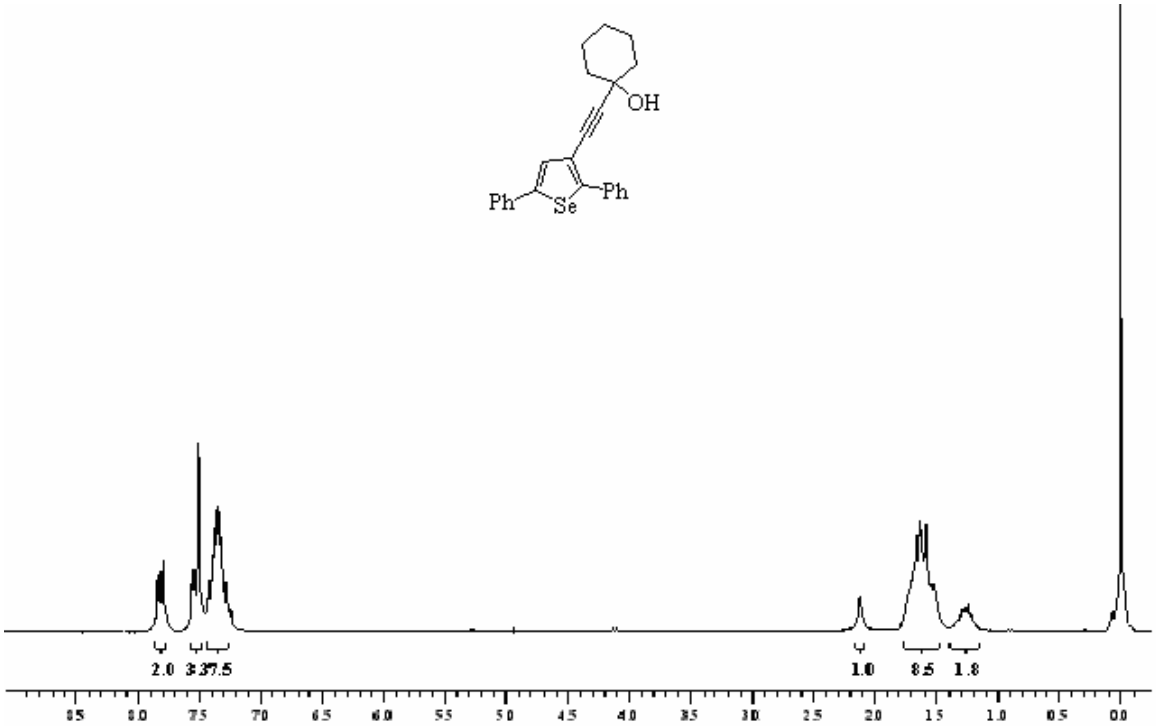
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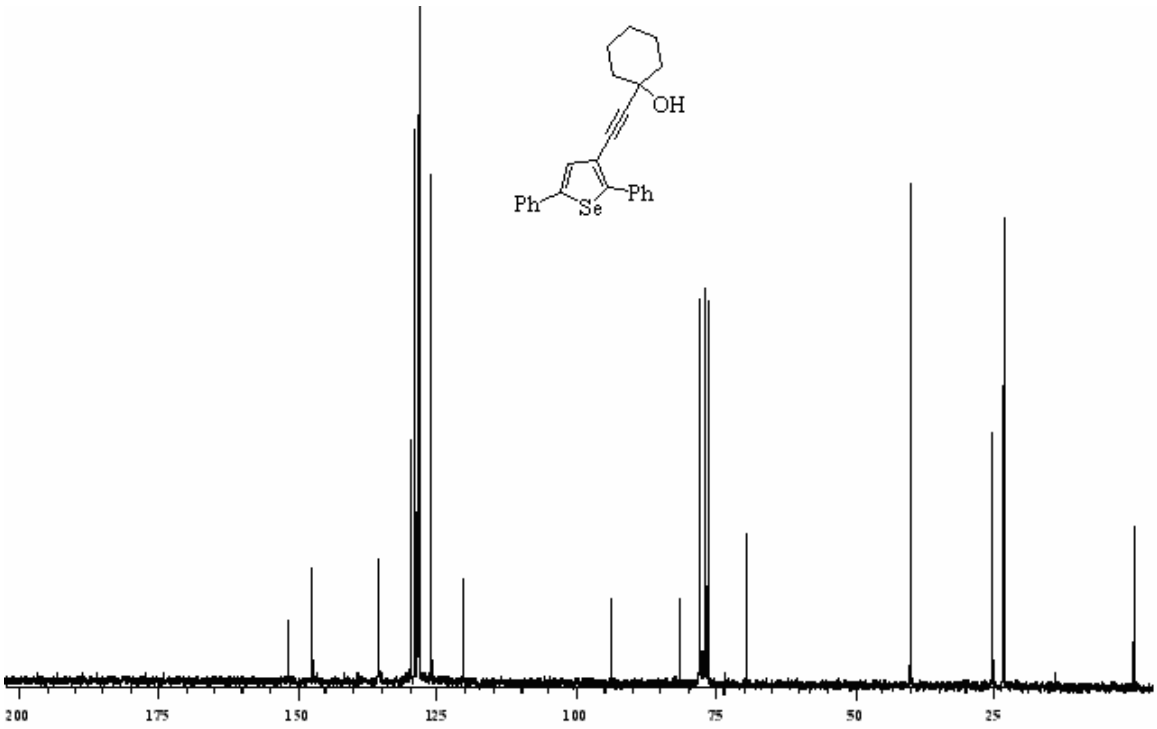
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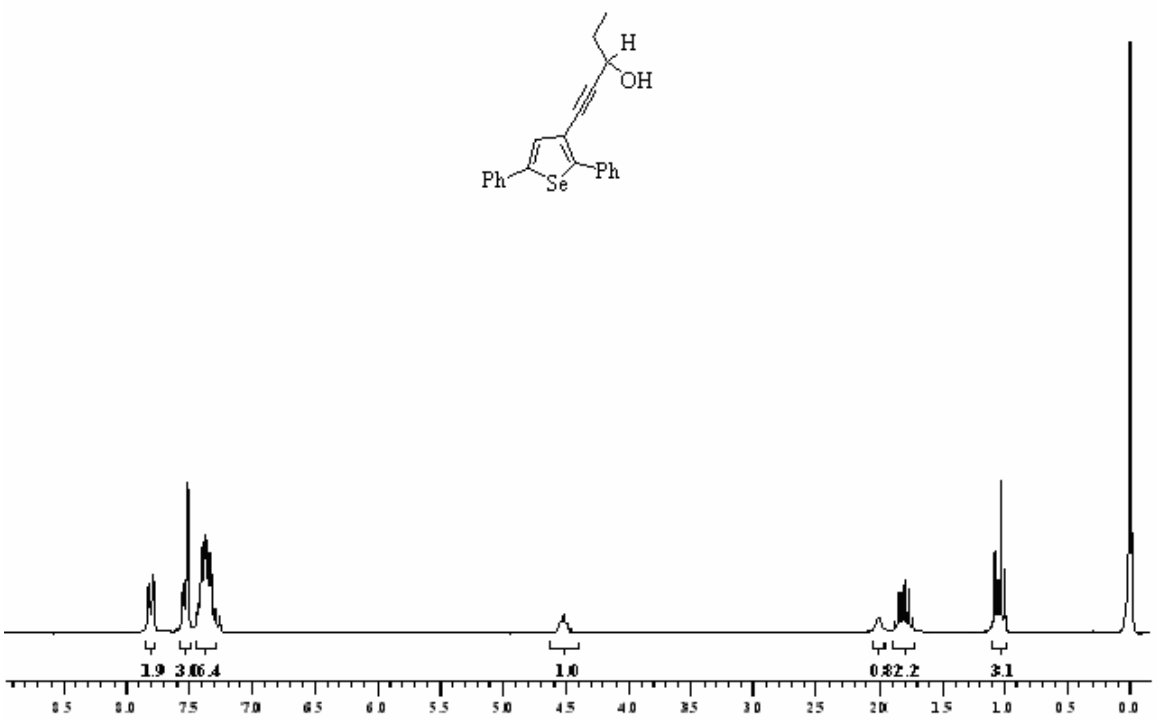
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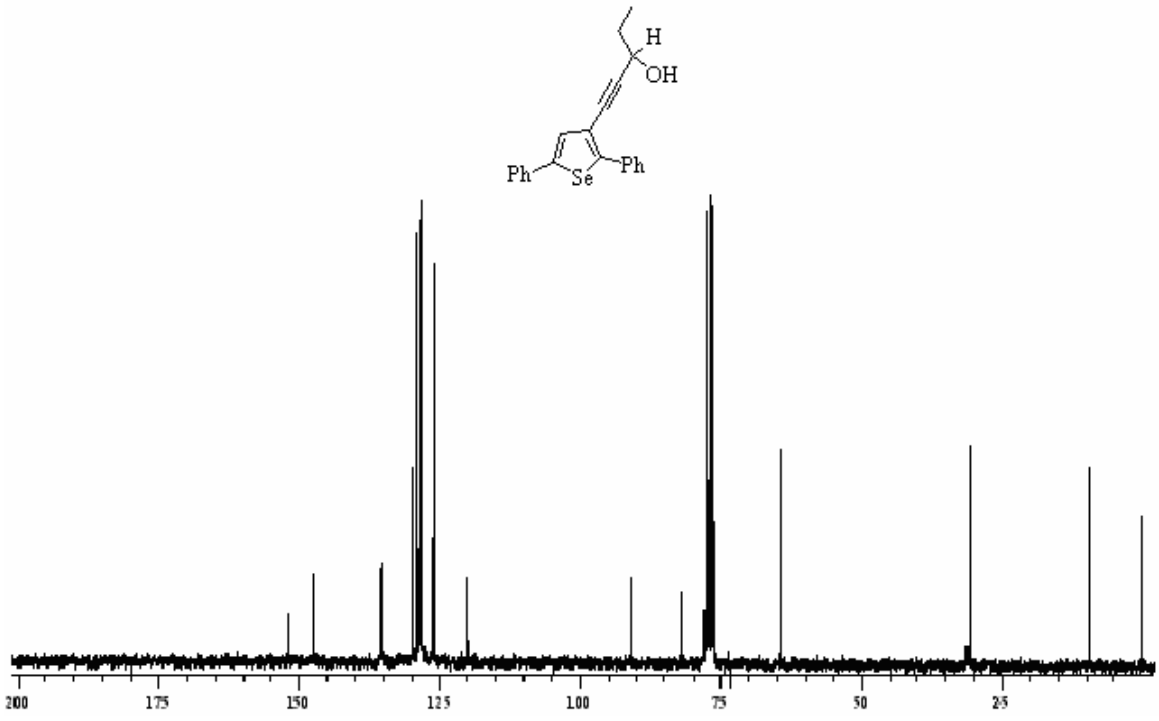
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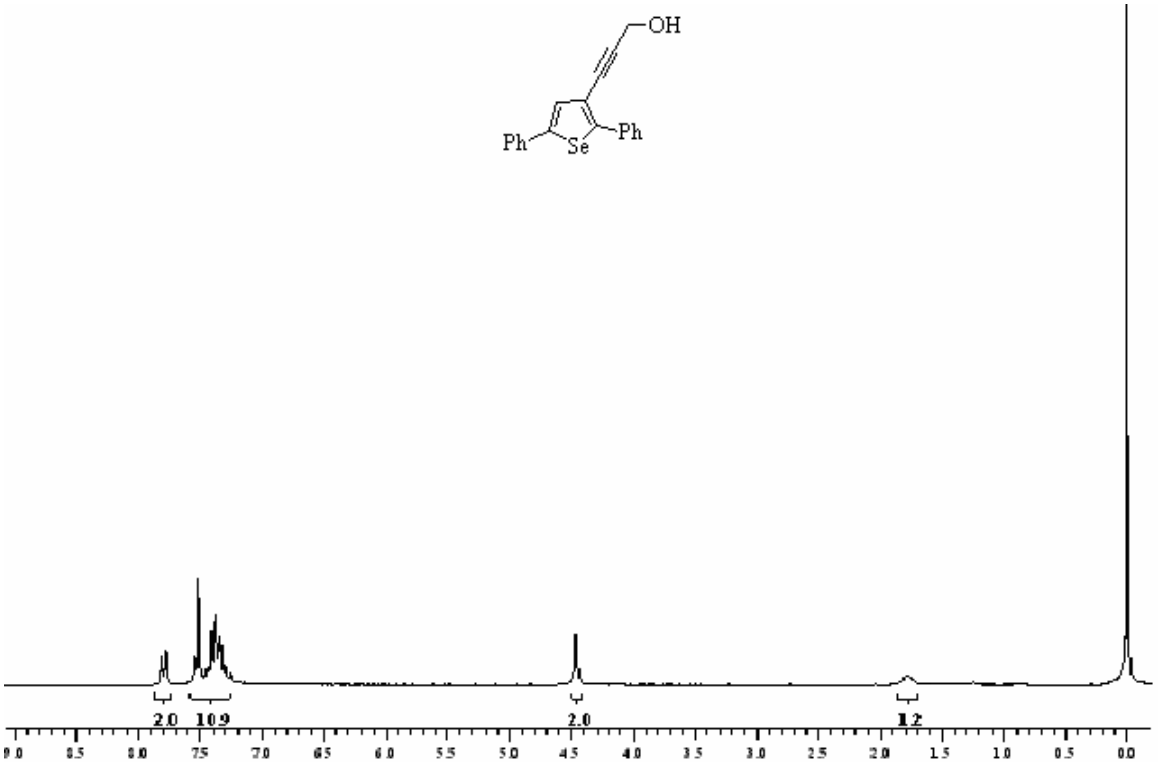
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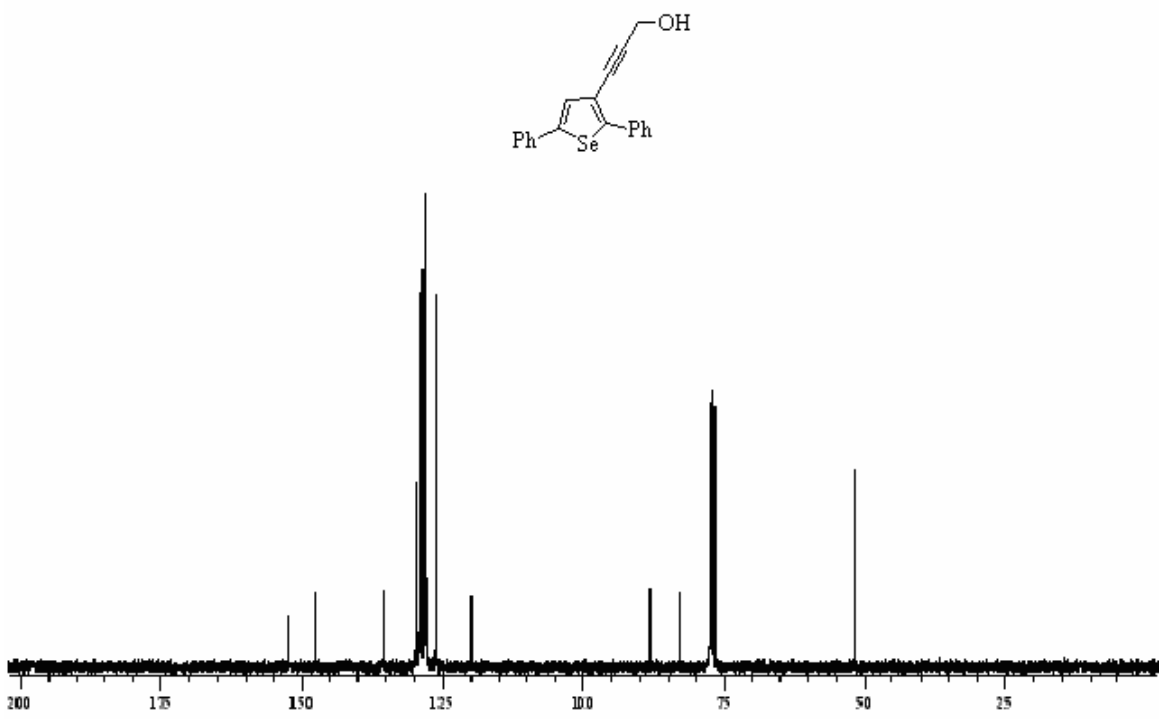
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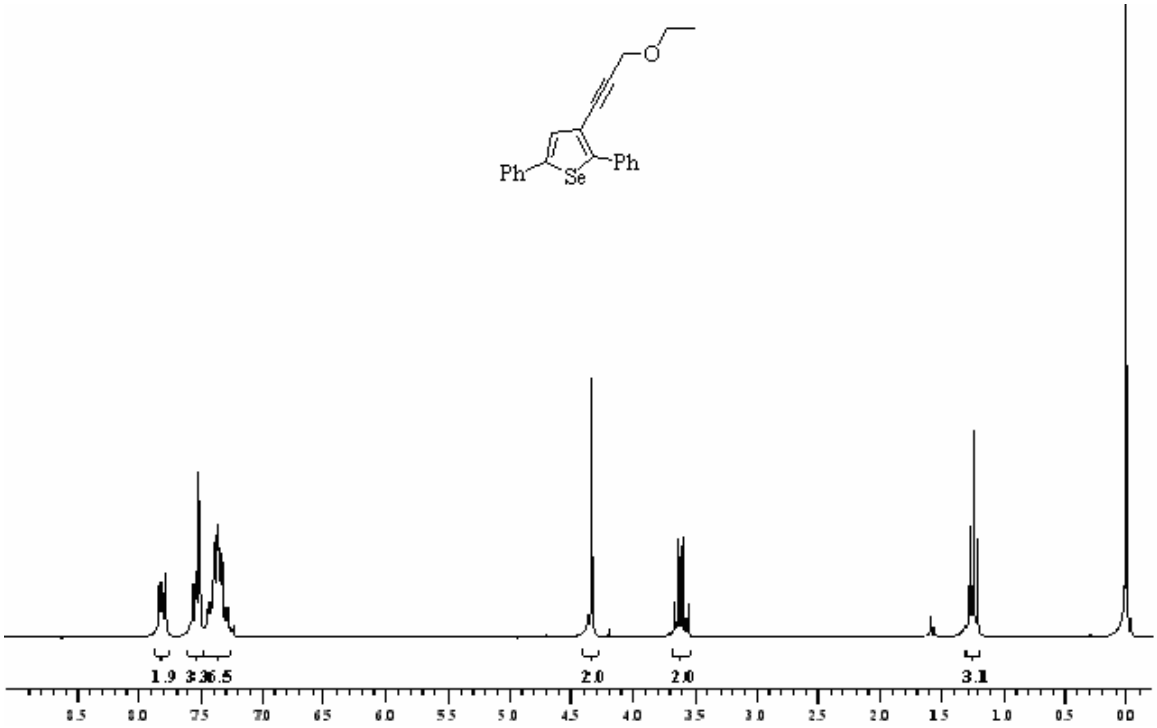
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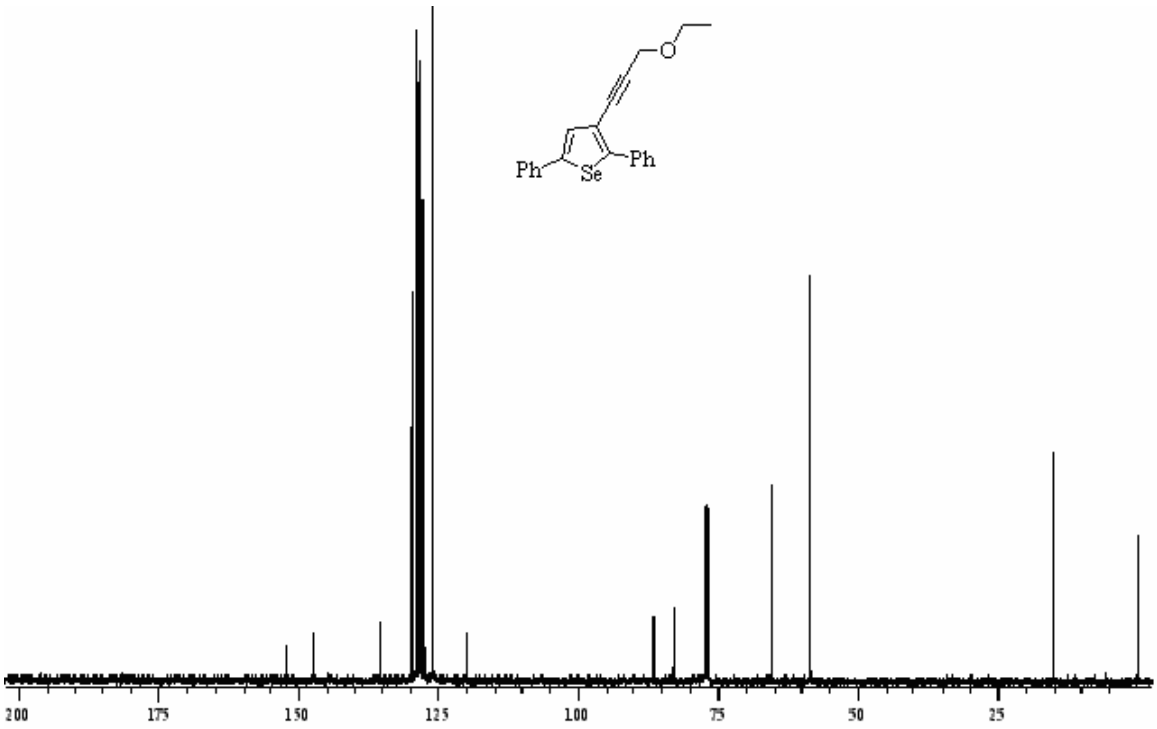
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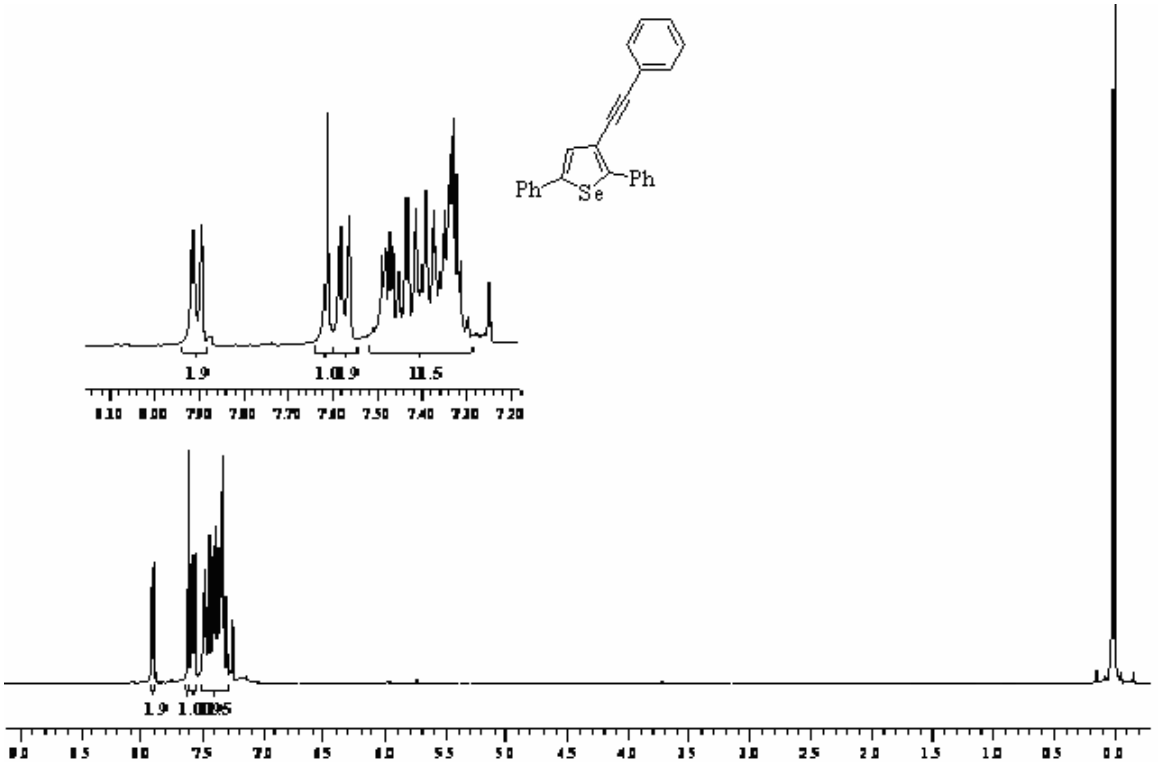
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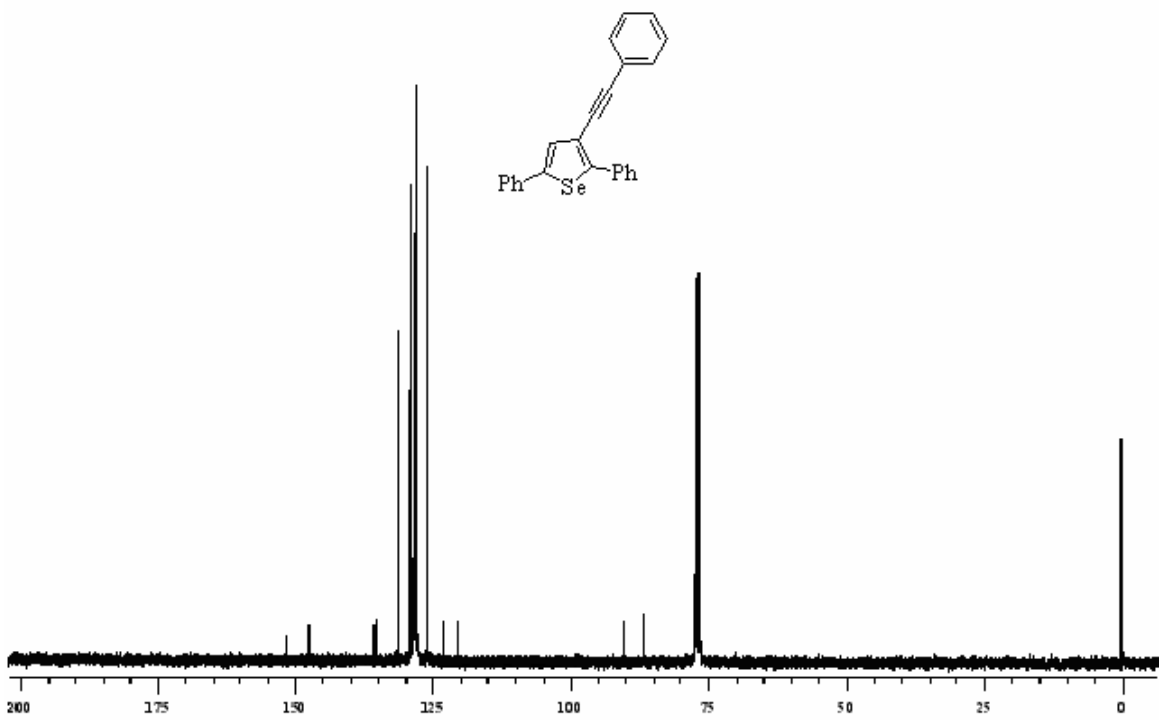
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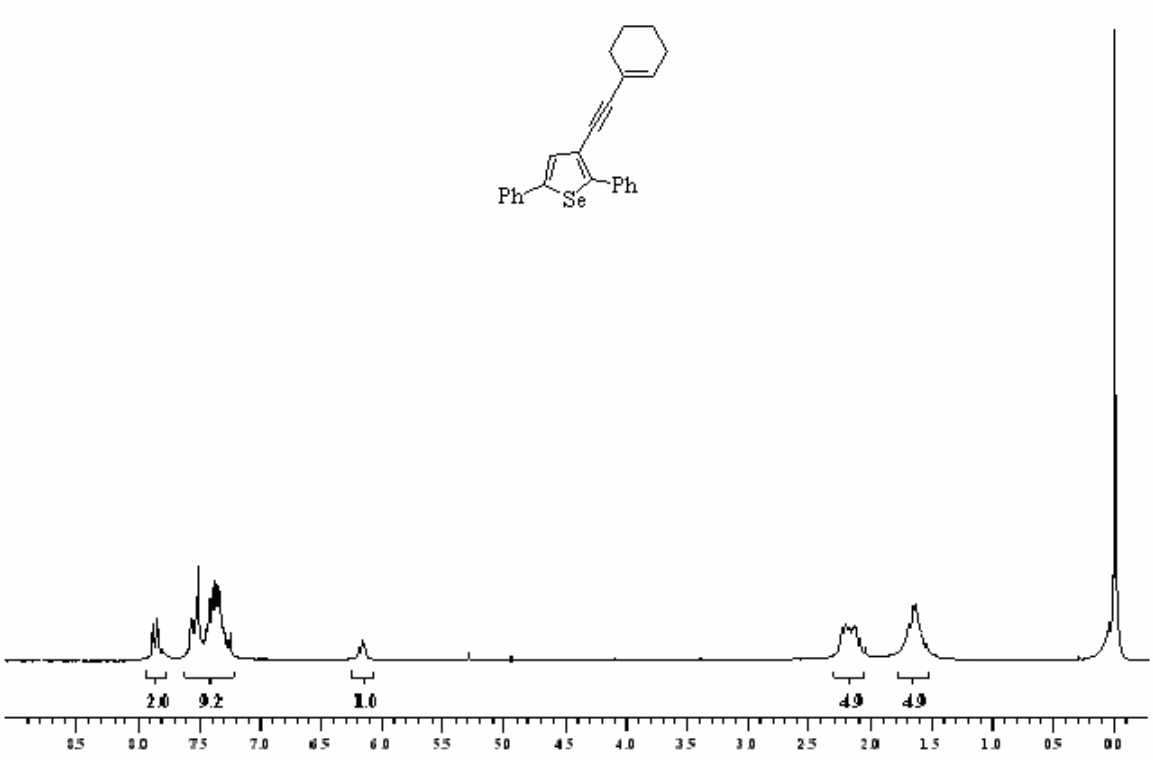
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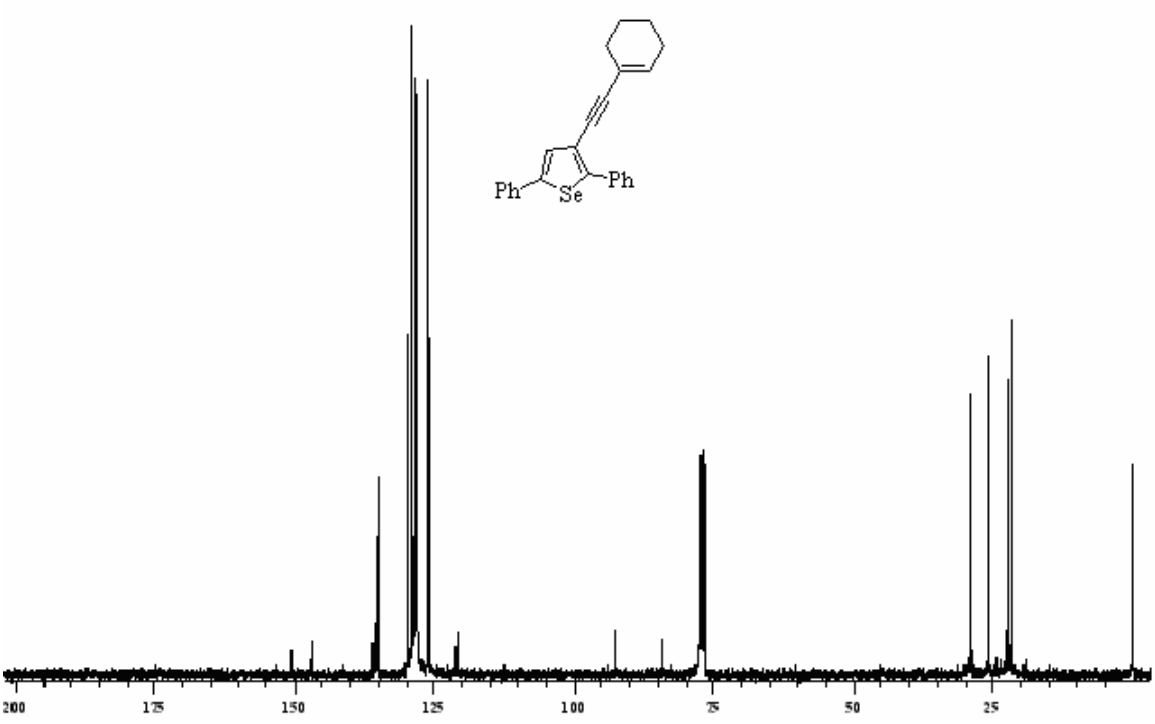
4.9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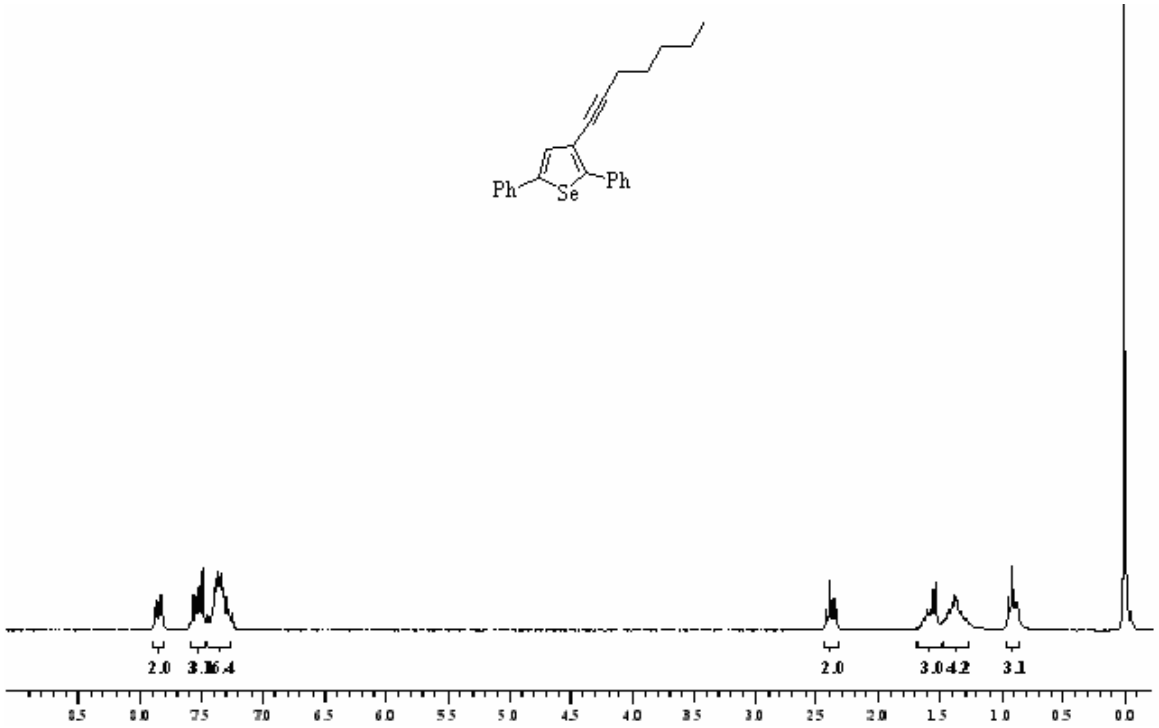
Ph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2.0
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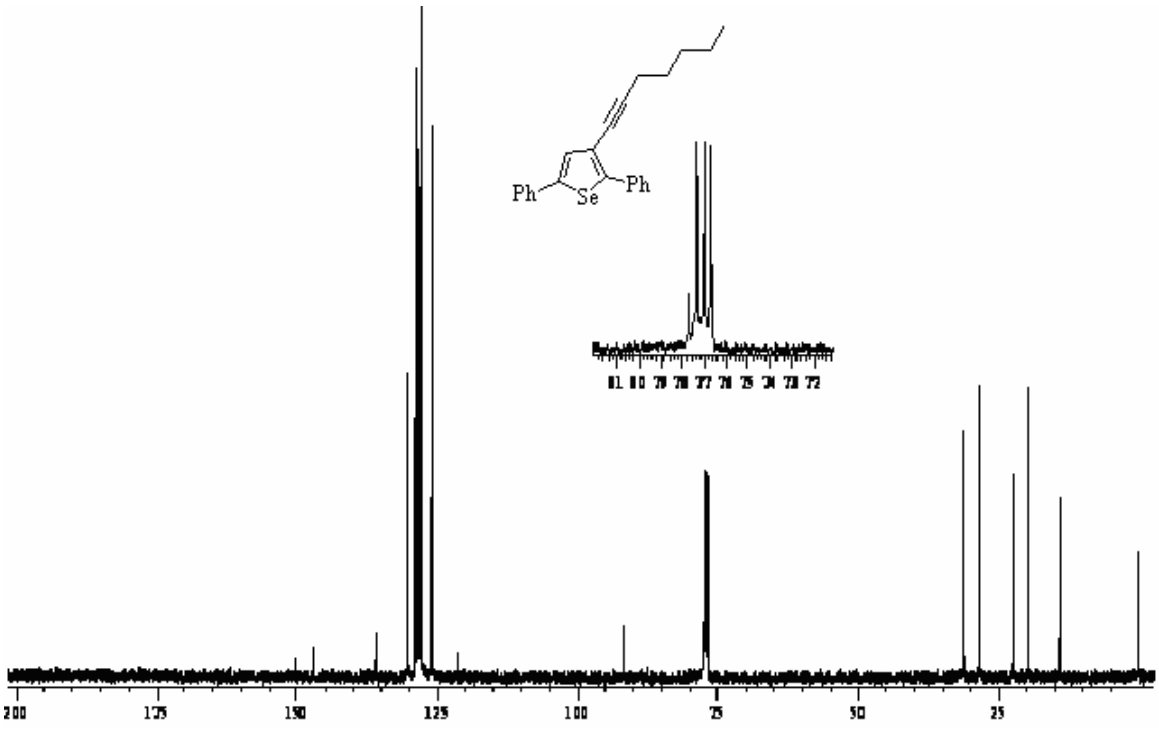
3.0
4.2
3.1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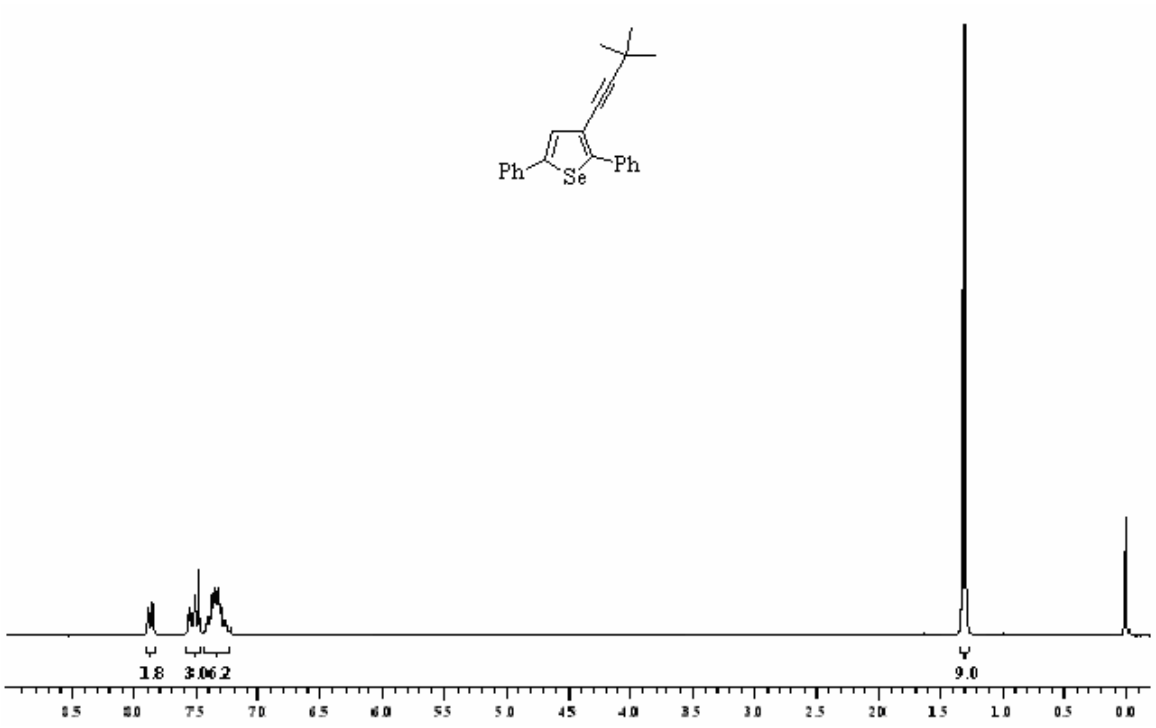
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Se
Ph
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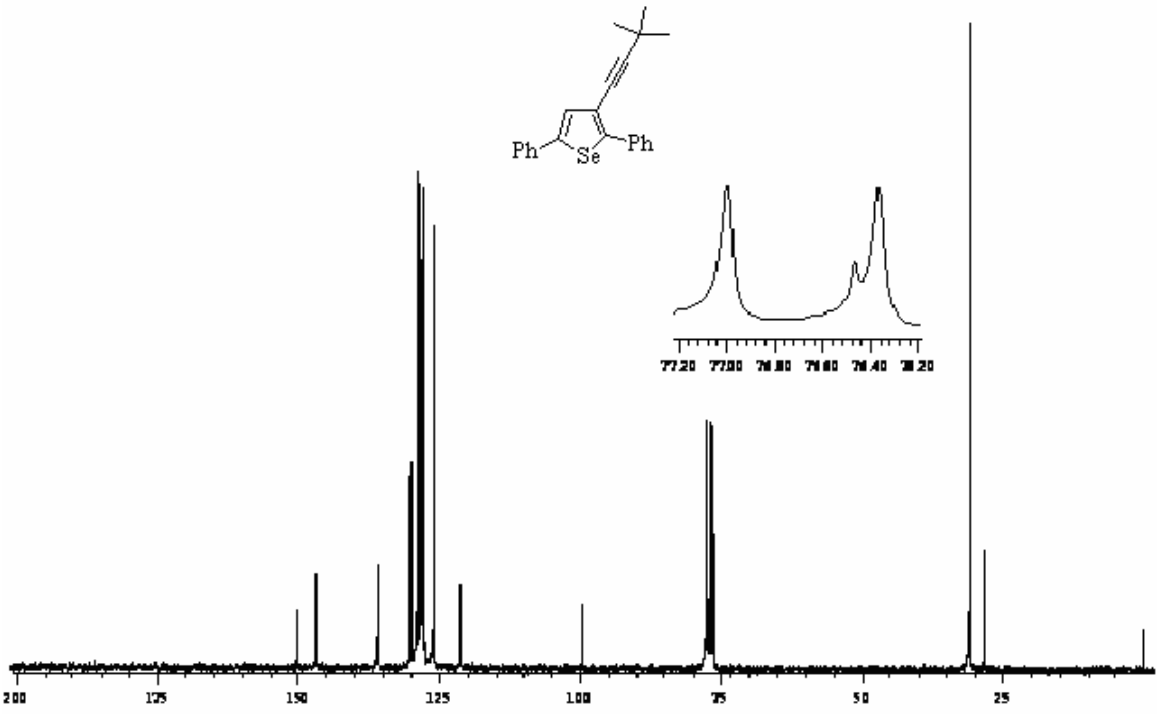
3.06
2
9.0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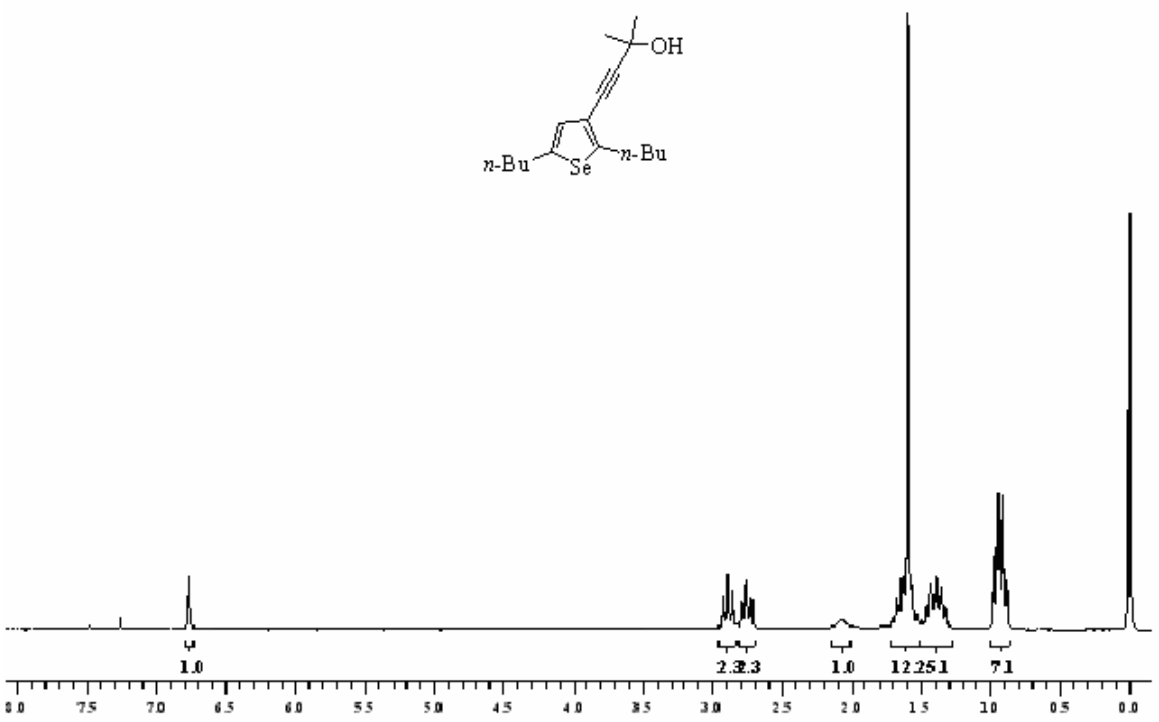
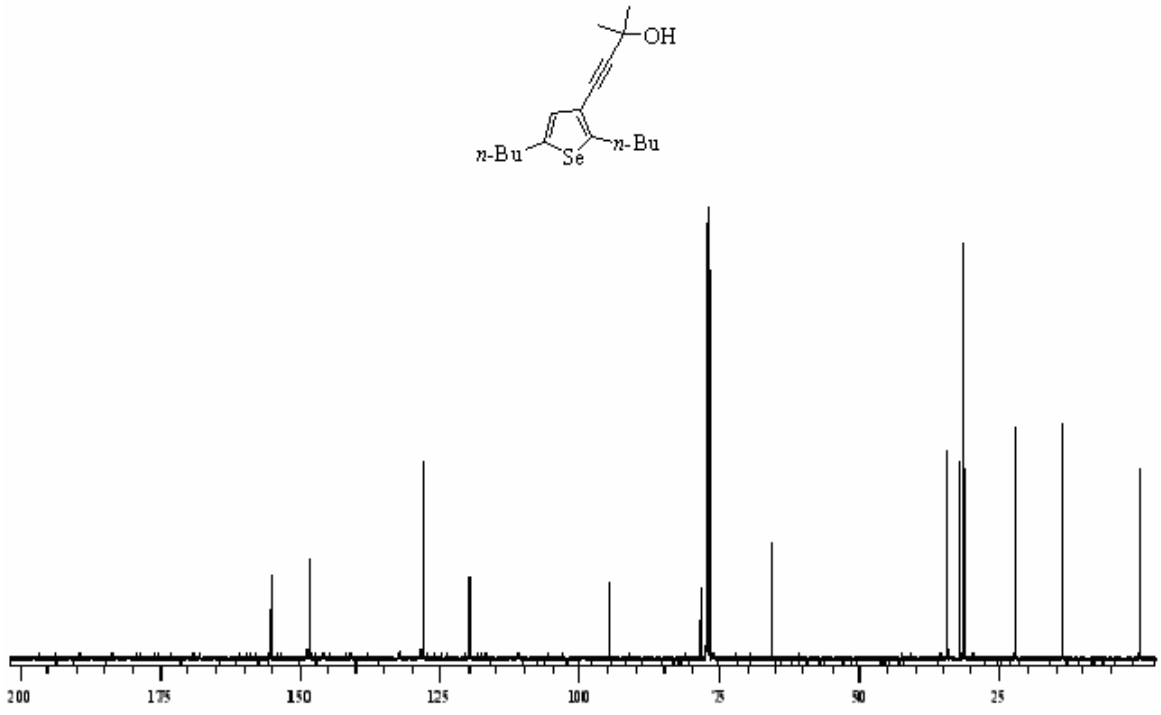
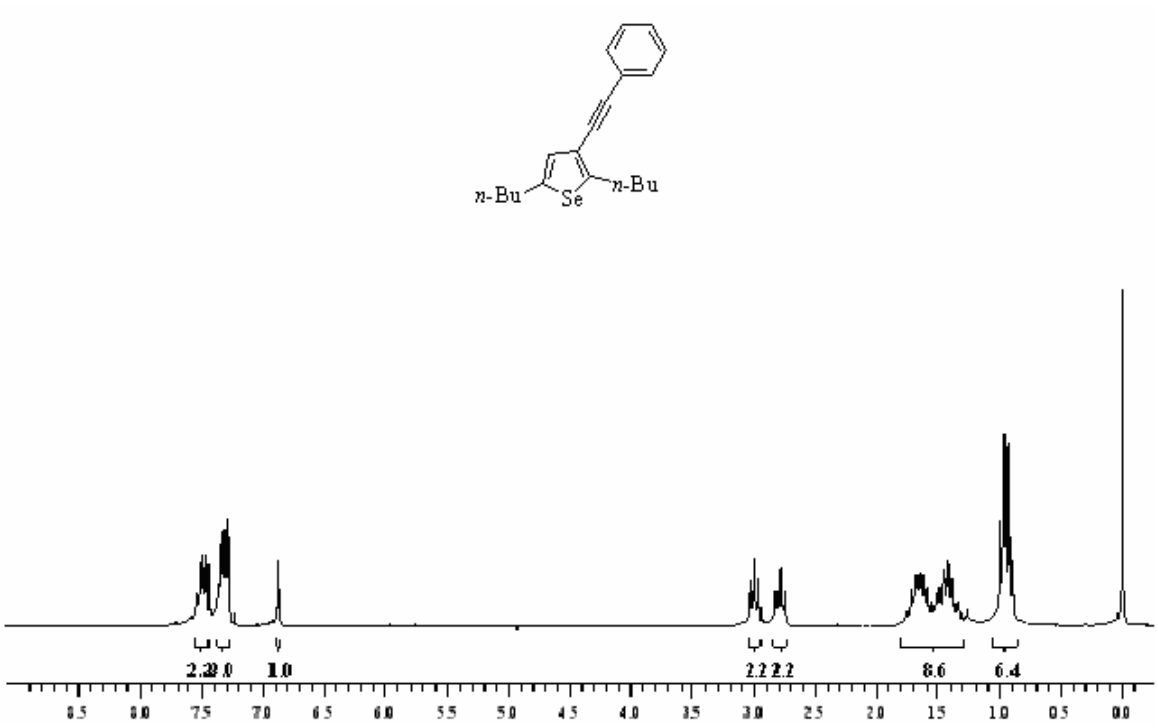
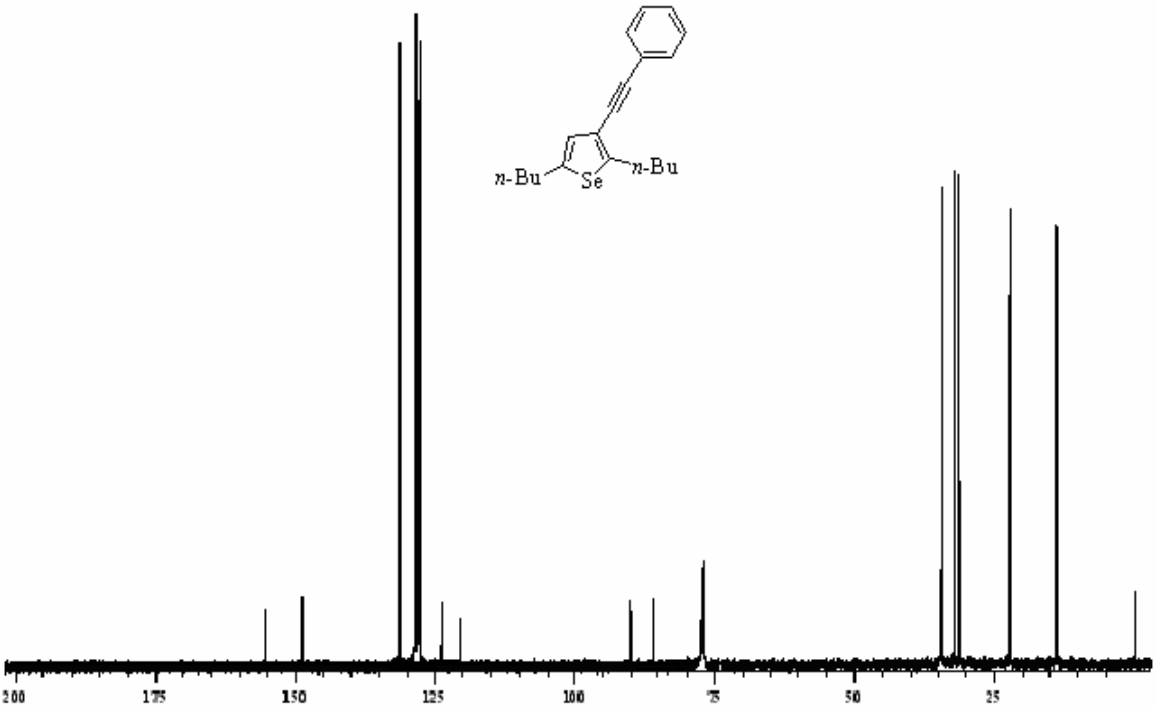
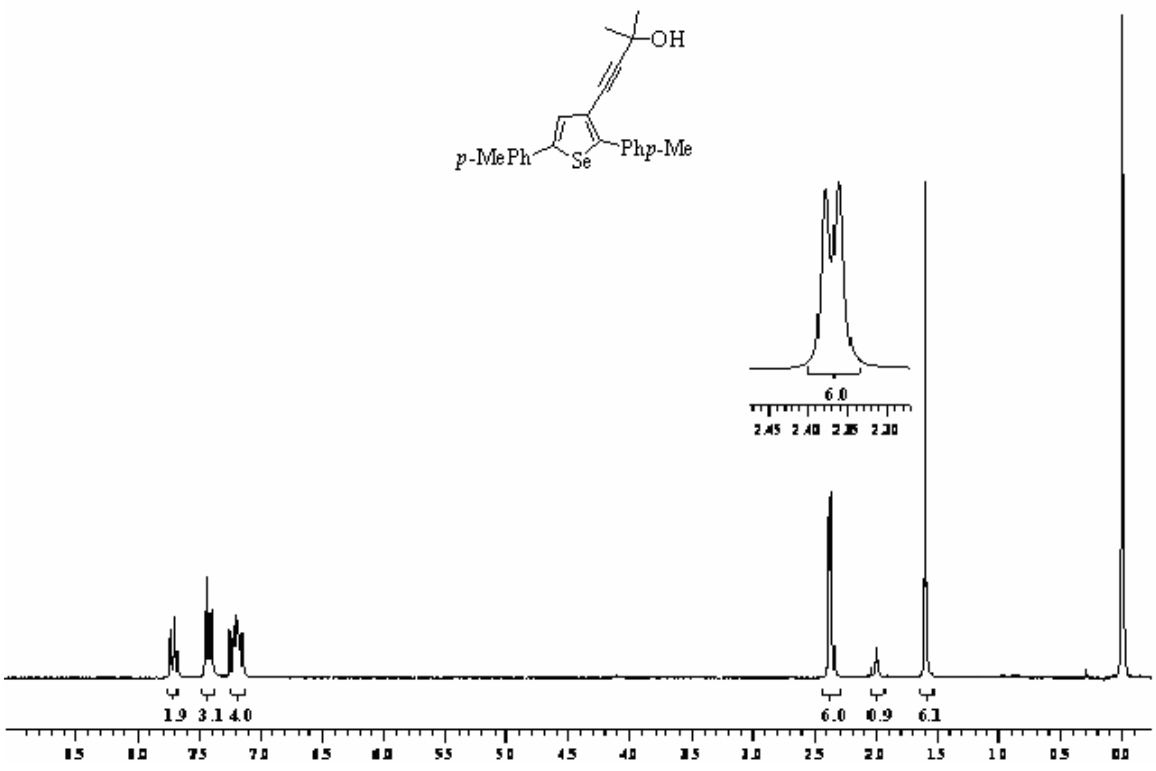
Se
Ph


OH
n-Bu
Se
n-Bu
1.0
2.3
2.3
1.0
1.2
2.5
1.1
7.1


OH
n-Bu
Se
n-Bu


n-Bu
Se
n-Bu
2.2
2.0
1.0
2.2
2.2
8.6
6.4


n-Bu
Se
n-Bu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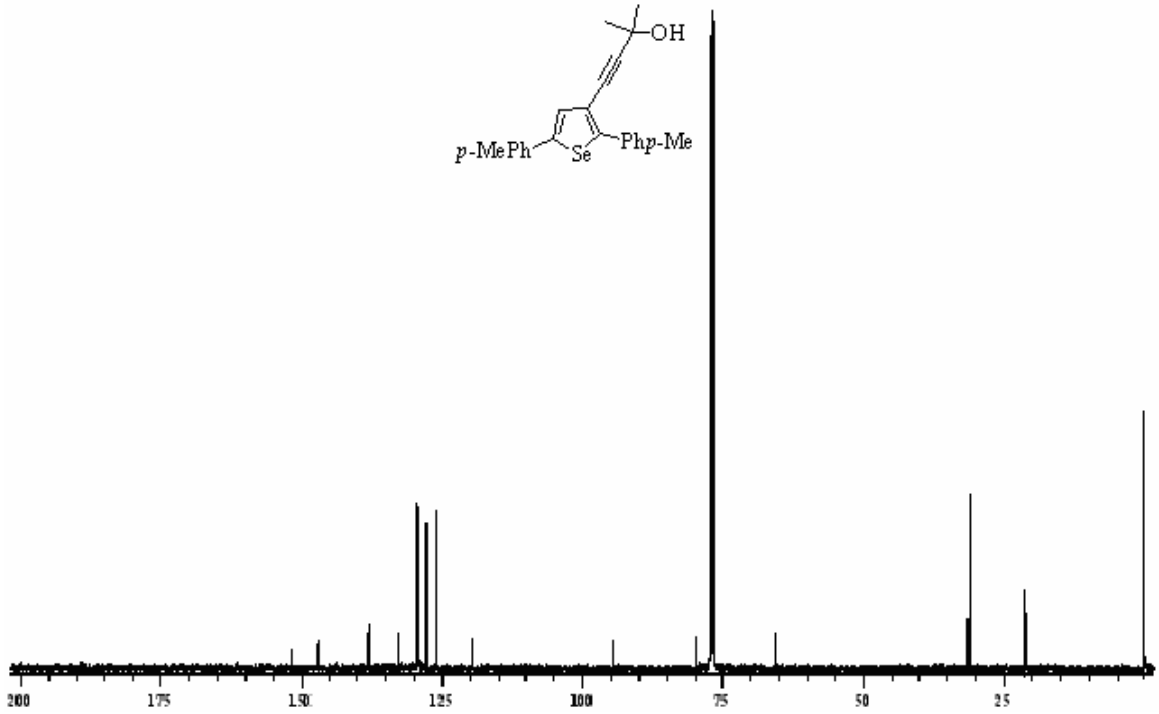
p-MePh
Se
Php-Me
6.0
1.9
3.1
4.0
6.0
0.9
6.1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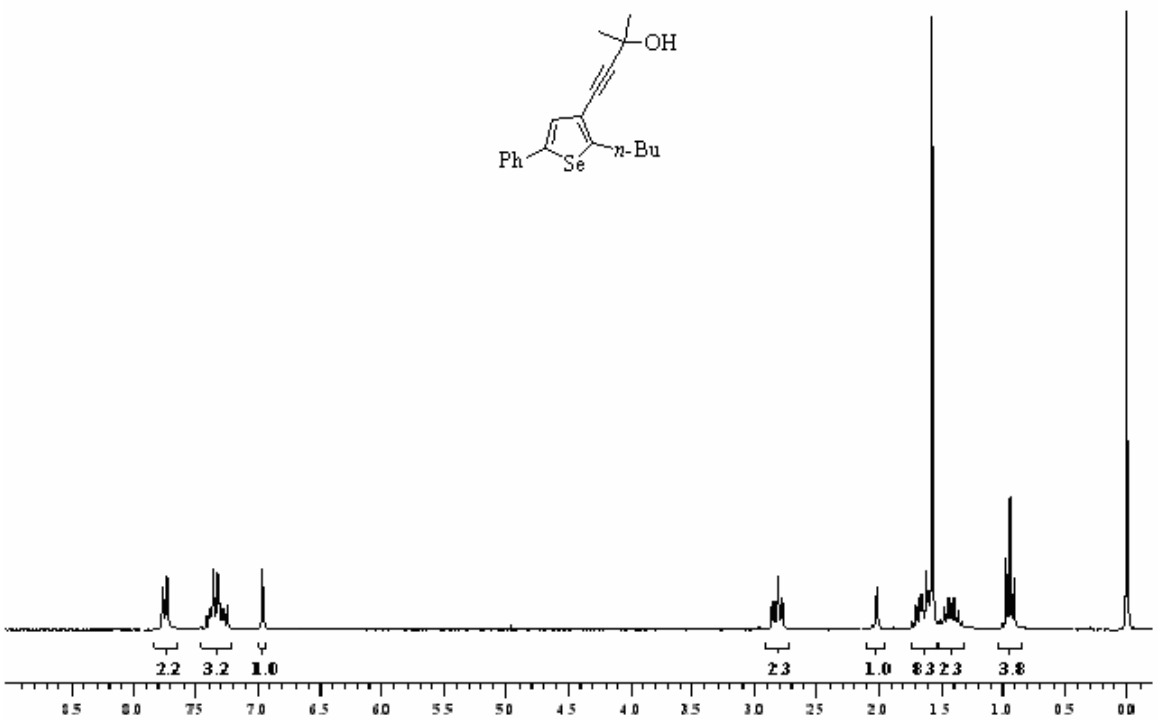
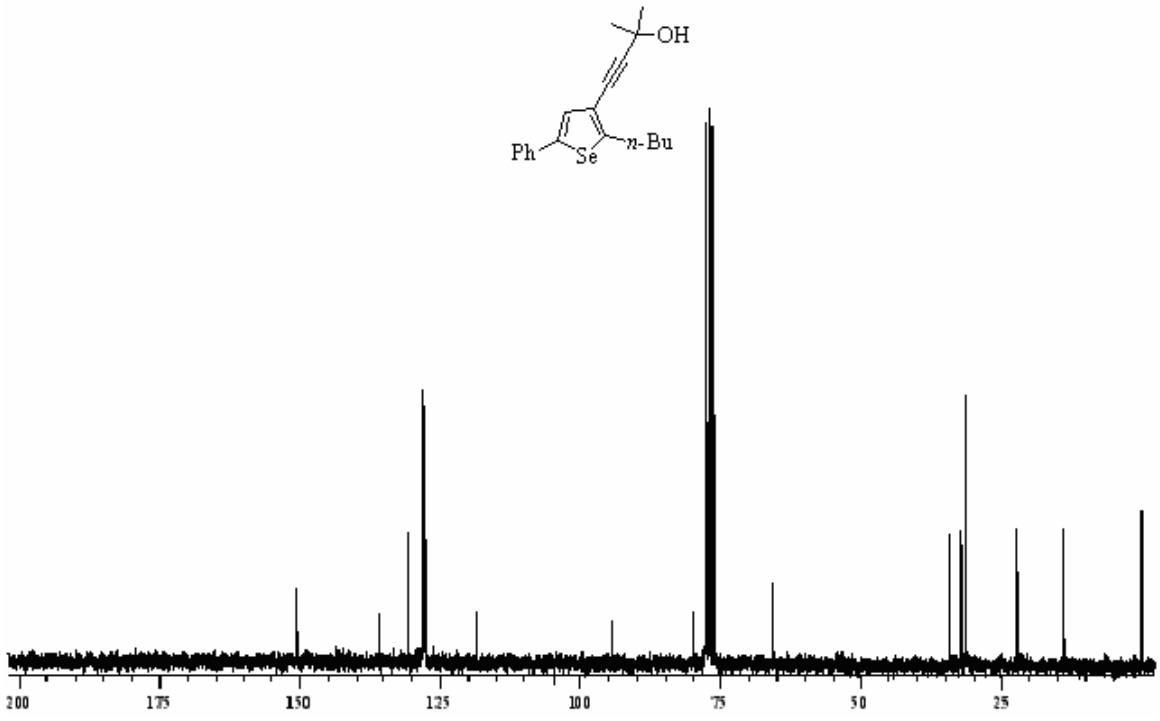
p-MePh
Se
Php-Me


OH
Ph
Se
n-Bu
2.2
3.2
1.0
2.3
1.0
8.3
2.3
3.8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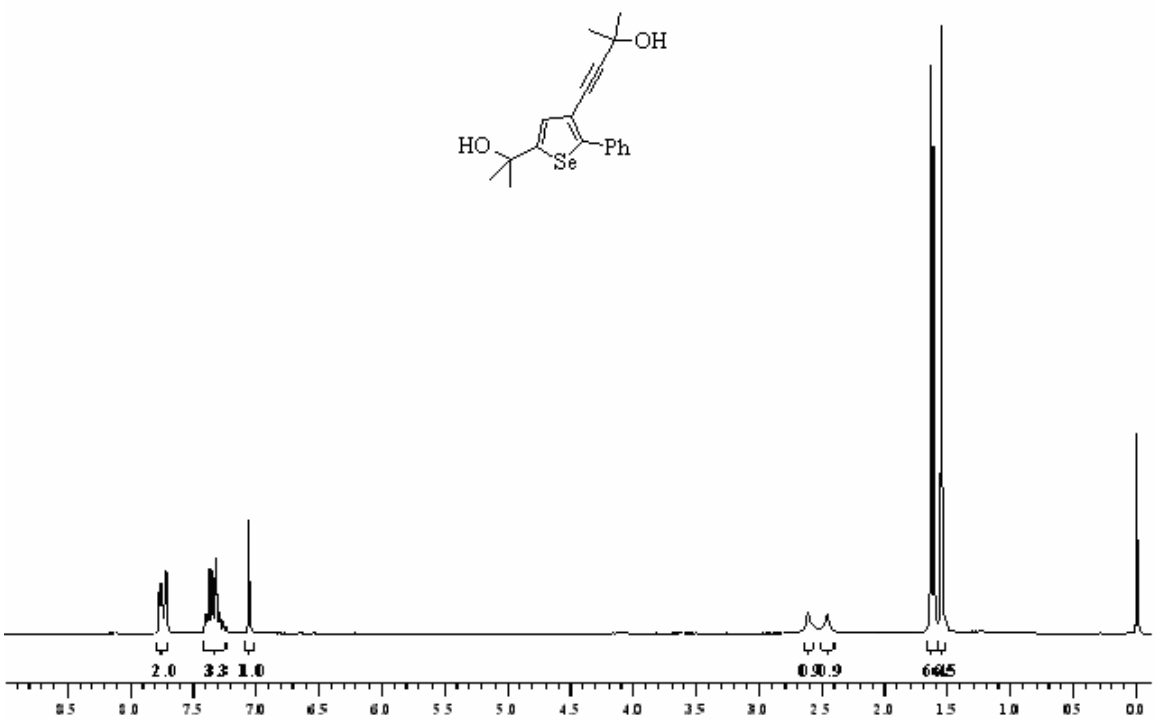
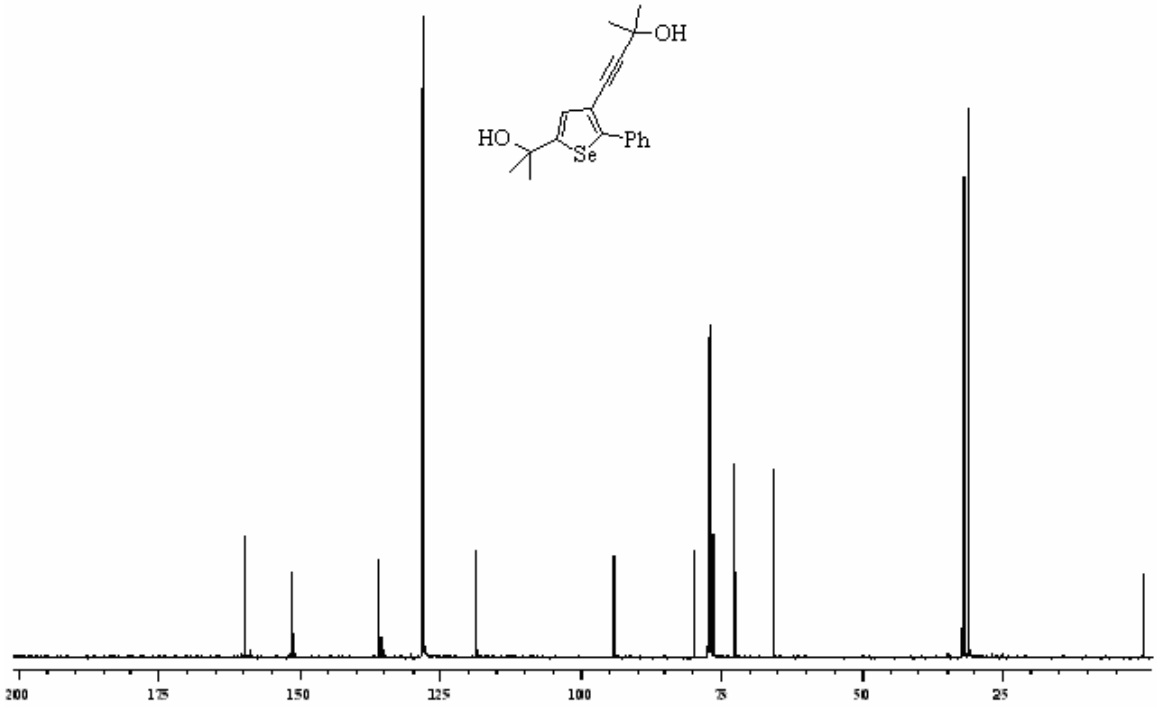
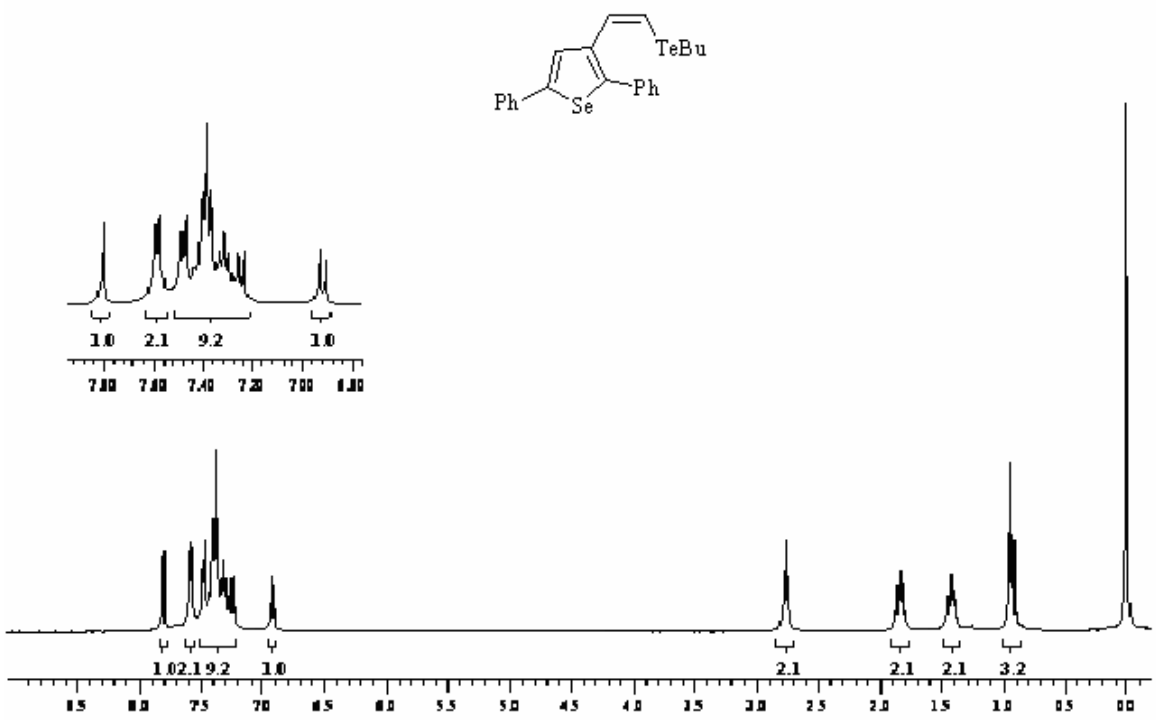
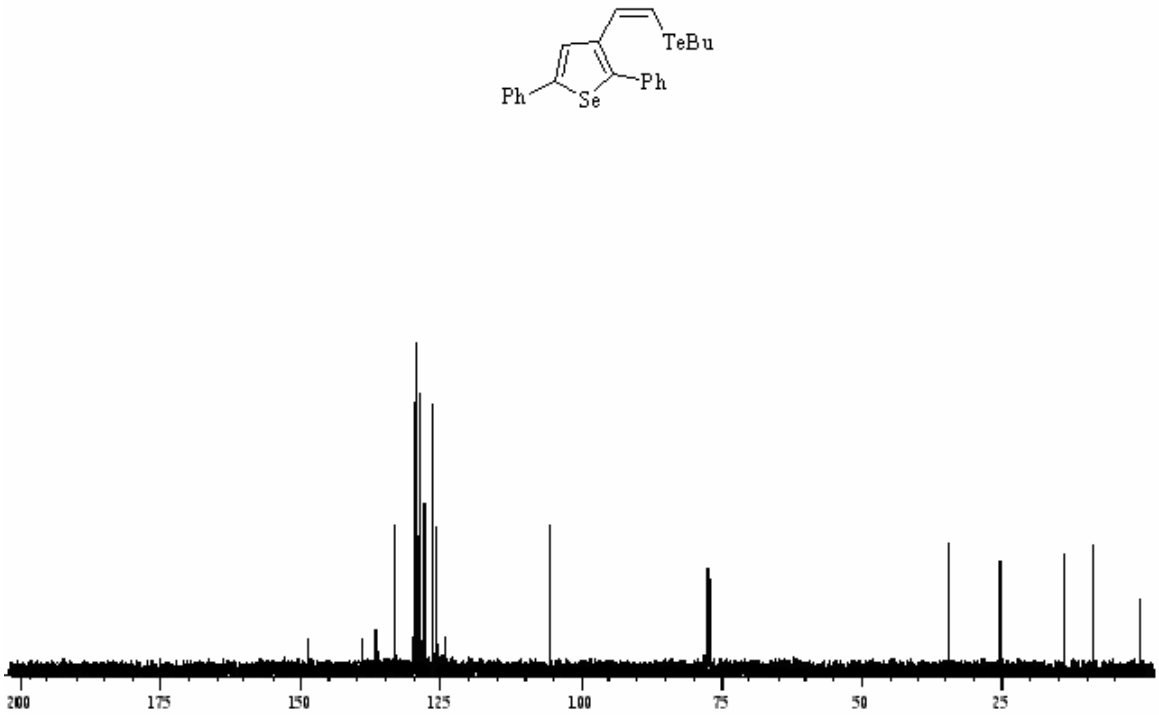
Ph
Se
n-Bu


OH
HO
Se
Ph
2.0
3.3
1.0
0.9
0.9
6.6
6.5


OH
HO
Se
Ph
200
175
150
125
100
75
50
25


TeBu
Ph
Se
Ph
1.0
2.1
9.2
1.0
1.0
2.1
9.2
1.0
2.1
2.1
2.1
3.2


TeBu
Ph
Se
Ph
200
175
150
125
100
75
50
25