

Electronic Supporting Information (ESI)

A Chemo- and Regioselective Pd(0)-Catalyzed Three-Component Spiroannulation

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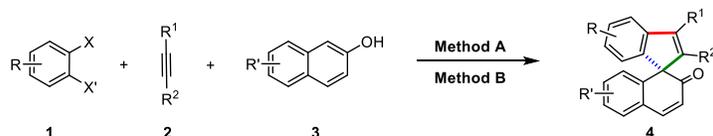
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A. General information:

All reactions were carried out under an argon atmosphere using standard Schlenk-Lines or glovebox (Innovative Technology). All reagents were used as received unless otherwise noted. DMF was dried over CaH₂, 1,4-dioxane and THF were dried over sodium. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F₂₅₄); visualization of the developed chromatogram was performed by fluorescence. Flash chromatography was performed with silica gel (300-400 mesh). Proton nuclear magnetic resonance (¹H NMR) data were acquired on Bruker Ascend 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (¹³C NMR) data were acquired at 100 MHz on Bruker Ascend 400 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.16 ppm for CDCl₃. Fluorine nuclear magnetic resonance (¹⁹F NMR) data were acquired at 376 MHz on a Bruker Ascend 400 (400 MHz) spectrometer and all ¹⁹F NMR spectra in this manuscript are proton-decoupled. Infrared (IR) data were recorded as films on potassium bromide

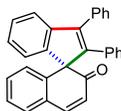
plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. Single crystal structures were measured on a Bruker SMART APEX II CCD diffractometer with a graphite monochromated Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$, at 296(2) K) or a Bruker D8 VENTURE PHOTON II diffractometer with a graphite monochromated Ga $K\alpha$ ($\lambda = 1.34138 \text{ \AA}$, at 175(2) K) radiation. 1,2-Dihalobenzenes **1a-m**, **1o** and **1a^{I-V}** were purchased from Innochem (China); **1n^I** was prepared according to the literature methods. Alkynes **2a**, **2m**, **2o**, **2r** and **2s** were purchased from Innochem (China); **2b-i**,² **2j**,³ **2k**,² **2l**,⁴ **2n**,⁵ **2p**,⁶ **2q**⁷ and **2t**⁸ were prepared according to the literature methods. 2-Naphthols **3b**, **3g-o** and **3q** were purchased from Innochem (China); **3c**,⁹ **3d**,¹⁰ **3e**,¹¹ **3f**¹² and **3p**¹³ were prepared according to the literature methods.

B. Catalytic results:



Method A: In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $\text{Pd}(\text{OAc})_2$ (2.2 mg, 0.01 mmol), dppp (5.0 mg, 0.012 mmol), K_3PO_4 (84.9 mg, 0.40 mmol), 1,2-dihalobenzene **1** (0.30 mmol), alkyne **2** (0.30 mmol) and 2-naphthol **3** (0.20 mmol), followed by sequential addition of 1,4-dioxane (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO_4 , filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product **4**.

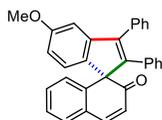
Method B: In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $\text{Pd}(\text{OAc})_2$ (2.2 mg, 0.01 mmol), K_3PO_4 (84.9 mg, 0.40 mmol), 1,2-dihalobenzene **1** (0.30 mmol), alkyne **2** (0.30 mmol) and 2-naphthol **3** (0.20 mmol), followed by sequential addition of 1,4-dioxane (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO_4 , filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product **4**.



2,3-Diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**4a**)

White solid (71.4 mg, 90% yield for **1a** (A)); 65.0 mg, 82% yield for **1a** (B); 58.7 mg, 74% yield for **1a^I** (A); 61.8 mg, 78% yield for **1a^I** (B); 34.1 mg, 43% yield for **1a^{II}** (A); 34.9 mg, 44% yield for **1a^{II}** (B); 46.0 mg, 58% yield for **1a^{III}** (A); 32.3 mg, 47% yield for **1a^{III}** (B); 31.7 mg, 40% yield for **1a^{IV}** (A); 6.3

mg, 8% yield for **1a^{IV}** (B); 0% yield for **1a^V**). PE/EA = 10:1, $R_f = 0.33$. m.p.: 176.7-177.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, $J = 9.9$ Hz, 1H), 7.54 (d, $J = 7.0$ Hz, 2H), 7.50-7.38 (m, 4H), 7.34-7.21 (m, 3H), 7.17 (t, $J = 7.3$ Hz, 1H), 7.07 (t, $J = 7.2$ Hz, 1H), 7.04-6.93(m, 5H), 6.86 (d, $J = 6.5$ Hz, 2H), 6.41 (d, $J = 9.9$ Hz, 1H). The ¹H NMR data is consistent with that reported in the literature.¹⁴



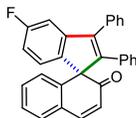
5-Methoxy-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4b)

Yellow solid (69.1 mg, 81% yield (A); 68.2 mg, 80% yield (B)). PE/EA = 10:1, $R_f = 0.22$. m.p.: 79.6-80.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, $J = 9.8$ Hz, 1H), 7.58-7.37 (m, 6H), 7.26 (d, $J = 14.0$ Hz, 1H), 7.17 (t, $J = 7.3$ Hz, 1H), 7.04-6.88 (m, 5H), 6.83 (s, 3H), 6.61 (d, $J = 8.0$ Hz, 1H), 6.38 (d, $J = 9.9$ Hz, 1H), 3.74 (s, 3H). The ¹H NMR data is consistent with that reported in the literature.¹⁵



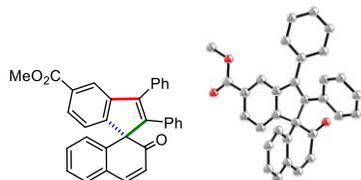
5-Methyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4c)

Yellow solid (42.7 mg, 52% yield (A); 59.9 mg, 73% yield (B)). PE/EA = 10:1, $R_f = 0.35$. m.p.: 100.3-100.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, $J = 9.9$ Hz, 1H), 7.56-7.39 (m, 6H), 7.25 (d, $J = 7.8$ Hz, 1H), 7.16 (t, $J = 7.3$ Hz, 1H), 7.08 (s, 1H), 7.03-6.94 (m, 4H), 6.91-6.80 (m, 4H), 6.39 (d, $J = 9.9$ Hz, 1H), 2.30 (s, 3H). The ¹H NMR data is consistent with that reported in the literature.¹⁶



5-Fluoro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4d)

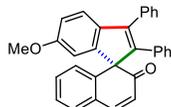
Yellow solid (28.2 mg, 34% yield (A); 62.2 mg, 75% yield (B)). PE/EA = 10:1, $R_f = 0.31$. m.p.: 89.9-90.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, $J = 9.8$ Hz, 1H), 7.55-7.38 (m, 6H), 7.29 (t, $J = 7.8$ Hz, 1H), 7.19 (t, $J = 7.3$ Hz, 1H), 7.08-6.91 (m, 6H), 6.83 (d, $J = 6.9$ Hz, 2H), 6.75 (t, $J = 8.4$ Hz, 1H), 6.39 (d, $J = 9.9$ Hz, 1H). The ¹H NMR data is consistent with that reported in the literature.¹⁵



(CCDC: 1978474)

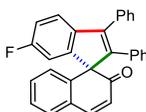
Methyl 2'-oxo-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalene]-5-carboxylate (4e)

Yellow solid (62.7 mg, 69% yield (A); <5% (B)). PE/EA = 5:1, $R_f = 0.28$. m.p.: 277.7-278.1 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.94 (s, 1H), 7.79 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.69 (d, $J = 9.9$ Hz, 1H), 7.56-7.39 (m, 6H), 7.30 (t, $J = 7.2$ Hz, 1H), 7.19 (t, $J = 7.3$ Hz, 1H), 7.10-6.92 (m, 5H), 6.84 (d, $J = 6.9$ Hz, 2H), 6.41 (d, $J = 9.9$ Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.9, 167.1, 152.5, 146.5, 146.4, 146.1, 144.2, 140.2, 134.7, 134.1, 130.9, 130.3, 130.1, 129.8, 129.6, 129.2, 129.1, 128.3, 128.2, 128.1, 128.0, 127.5, 127.0, 126.6, 122.9, 121.8, 71.8, 52.2. IR (KBr): 3057, 2951, 1720, 1665, 1437, 1286, 1242, 1199, 1099, 742, 699 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{22}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 477.1467, found 477.1467.



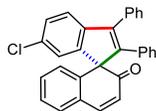
6-Methoxy-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4f)

White solid (32.4 mg, 38% yield (A); 67.4 mg, 79% yield (B)). PE/EA = 10:1, $R_f = 0.20$. m.p.: 238.2-238.6 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.66 (d, $J = 9.9$ Hz, 1H), 7.53 (d, $J = 6.9$ Hz, 2H), 7.43 (t, $J = 15.1$ Hz, 4H), 7.27 (t, $J = 6.4$ Hz, 1H), 7.19 (t, $J = 8.6$ Hz, 2H), 6.98 (s, 4H), 6.85-6.75 (m, 3H), 6.59 (s, 1H), 6.39 (d, $J = 9.9$ Hz, 1H), 3.70 (s, 3H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



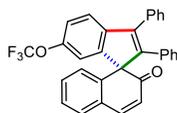
6-Fluoro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4g)

White solid (59.7 mg, 72% yield (A); <5% (B)). PE/EA = 10:1, $R_f = 0.28$. m.p.: 53.7-54.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, $J = 9.9$ Hz, 1H), 7.54-7.38 (m, 6H), 7.34-7.17 (m, 3H), 7.03-6.91 (m, 5H), 6.82 (d, $J = 6.7$ Hz, 2H), 6.73 (d, $J = 8.0$ Hz, 1H), 6.40 (d, $J = 9.9$ Hz, 1H). The ^1H NMR data is consistent with that reported in the literature.¹⁶



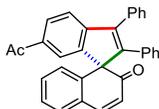
6-Chloro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4h)

Yellow solid (63.8 mg, 74% yield (A); 20.7 mg, 24% yield (B)). PE/EA = 10:1, $R_f = 0.33$. m.p.: 252.1-252.6 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.57 (d, $J = 9.9$ Hz, 1H), 7.43-7.27 (m, 6H), 7.21-7.16 (m, 1H), 7.15-7.06 (m, 3H), 6.93-6.84 (m, 5H), 6.73 (dd, $J = 7.9, 1.4$ Hz, 2H), 6.30 (d, $J = 9.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.0, 149.1, 146.5, 145.7, 144.2, 143.9, 140.3, 134.8, 134.1, 132.0, 130.9, 130.3, 129.7, 129.5, 129.2, 129.0, 128.2, 128.1, 128.0, 127.9, 127.4, 127.0, 126.5, 122.8, 122.3, 71.5. IR (KBr): 3057, 2924, 1665, 1589, 1453, 1233, 1200, 827, 741, 698 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{19}\text{ClO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 453.1022, found 453.1023.



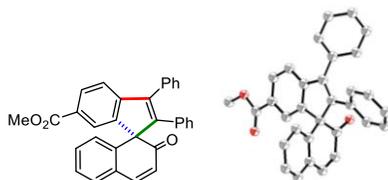
2,3-Diphenyl-6-(trifluoromethoxy)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4i)

White solid (67.3 mg, 70% yield (A); 29.8 mg, 31% yield (B)). PE/EA = 20:1, R_f = 0.25. m.p.: 203.8-204.3 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.69 (d, J = 9.9 Hz, 1H), 7.56-7.37 (m, 6H), 7.35-7.25 (m, 2H), 7.20 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 7.05-6.93 (m, 4H), 6.88-6.81 (m, 3H), 6.41 (d, J = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.9, 149.1, 147.7, 147.6, 146.6, 146.4, 144.3, 143.7, 140.1, 134.8, 134.0, 131.0, 130.3, 129.7, 129.5, 129.2, 129.1, 128.2, 128.1, 127.5, 127.1, 126.5, 122.6, 120.6, 120.4 (q, J = 257.2 Hz), 115.3, 71.6. ^{19}F NMR (376 MHz, CDCl_3): δ -57.88. IR (KBr): 3058, 2924, 1667, 1604, 1476, 1259, 1221, 1166, 750, 698 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{19}\text{F}_3\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 503.1235, found 503.1236.



6-Acetyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4j)

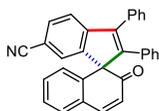
White solid (77.2 mg, 88% yield (A); 8.8 mg, 10% yield (B)). PE/EA = 5:1, R_f = 0.30. m.p.: 260.2-260.7 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 9.8 Hz, 1H), 7.58 (s, 1H), 7.54-7.40 (m, 6H), 7.38-7.25 (m, 2H), 7.17 (t, J = 7.3 Hz, 1H), 7.06-6.97 (m, 3H), 6.91 (d, J = 7.6 Hz, 1H), 6.84 (d, J = 7.0 Hz, 2H), 6.41 (d, J = 9.8 Hz, 1H), 2.49 (s, 3H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



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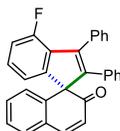
Methyl 2'-oxo-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalene]-6-carboxylate (4k)

Yellow solid (76.4 mg, 84% yield (A); 17.3 mg, 19% yield (B)). PE/EA = 5:1, R_f = 0.28. m.p.: 258.7-259.1 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 9.9 Hz, 1H), 7.58 (s, 1H), 7.49-7.34 (m, 6H), 7.31-7.19 (m, 2H), 7.11 (t, J = 7.6 Hz, 1H), 7.03-6.90 (m, 3H), 6.86 (d, J = 7.7 Hz, 1H), 6.79 (d, J = 7.5 Hz, 2H), 6.35 (d, J = 9.9 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.0, 167.0, 150.5, 148.7, 147.9, 146.7, 144.2, 140.1, 134.7, 134.0, 130.9, 130.4, 130.0, 129.9, 129.6, 129.3, 129.1, 128.3, 128.2, 128.0, 127.7, 127.0, 126.6, 122.9, 121.6, 71.6, 52.1. IR (KBr): 3057, 2924, 1718, 1665, 1603, 1439, 1285, 1233, 1117, 758, 698 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{22}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 477.1467, found 477.1468.



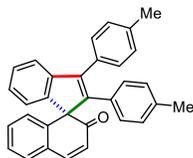
2'-Oxo-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalene]-6-carbonitrile (4l)

White solid (56.5 mg, 67% yield (A); <5% (B)). PE/EA = 10:1, $R_f = 0.24$. m.p.: 272.9-273.3 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.73 (d, $J = 9.8$ Hz, 1H), 7.57-7.42 (m, 7H), 7.34 (t, $J = 7.6$ Hz, 2H), 7.26-7.17 (m, 2H), 7.09-6.97 (m, 3H), 6.93-6.81 (m, 3H), 6.42 (d, $J = 9.9$ Hz, 1H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



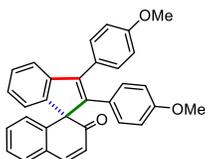
4-Fluoro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4m)

White solid (43.1 mg, 52% yield (A); 46.4 mg, 56% yield (A)). PE/EA = 10:1, $R_f = 0.26$. m.p.: 232.2-232.6 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, $J = 9.8$ Hz, 1H), 7.52 (d, $J = 5.1$ Hz, 2H), 7.45-7.33 (m, 4H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.21 (t, $J = 7.3$ Hz, 1H), 7.05-6.89 (m, 6H), 6.77 (t, $J = 10.3$ Hz, 3H), 6.37 (d, $J = 9.9$ Hz, 1H). The ^1H NMR data is consistent with that reported in the literature.¹⁷



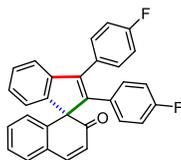
2,3-Di-p-tolyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4a')

Yellow solid (62.8 mg, 74% yield (A); 59.4 mg, 70% yield (B)). PE/EA = 10:1, $R_f = 0.33$. m.p.: 109.8-110.4 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.68 (d, $J = 9.8$ Hz, 1H), 7.43 (d, $J = 7.2$ Hz, 3H), 7.32-7.13 (m, 6H), 7.09-6.95 (m, 3H), 6.86-6.73 (m, 4H), 6.41 (d, $J = 9.8$ Hz, 1H), 2.44 (s, 3H), 2.17 (s, 3H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



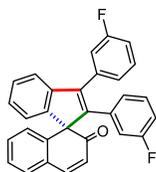
2,3-Bis(4-methoxyphenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4b')

Yellow solid (38.3 mg, 42% yield (A); 61.2 mg, 67% yield (B)). PE/EA = 5:1, $R_f = 0.28$. m.p.: 114.7-115.1 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.68 (d, $J = 9.9$ Hz, 1H), 7.50-7.40 (m, 3H), 7.31-7.14 (m, 4H), 7.06-6.93 (m, 5H), 6.80 (d, $J = 8.2$ Hz, 2H), 6.54 (d, $J = 8.2$ Hz, 2H), 6.40 (d, $J = 9.9$ Hz, 1H), 3.88 (s, 3H), 3.66 (s, 3H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



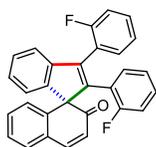
2,3-Bis(4-fluorophenyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4c')

Yellow solid (74.4 mg, 86% yield (A); 75.2 mg, 87% yield (B)). PE/EA = 10:1, R_f = 0.31. m.p.: 184.8-185.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, J = 9.9 Hz, 1H), 7.52-7.41 (m, 3H), 7.33-7.25 (m, 3H), 7.22-7.06 (m, 4H), 7.01 (d, J = 7.3 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 6.84-6.67 (m, 4H), 6.38 (d, J = 9.9 Hz, 1H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



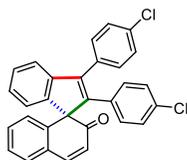
2,3-Bis(3-fluorophenyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4d')

Yellow solid (55.4 mg, 64% yield (A); 53.6 mg, 62% yield (A)). PE/EA = 10:1, R_f = 0.30. m.p.: 158.3-158.7 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.69 (d, J = 9.9 Hz, 1H), 7.45 (t, J = 7.3 Hz, 2H), 7.34-7.17 (m, 6H), 7.15-7.07 (m, 2H), 7.06-6.90 (m, 3H), 6.75 (t, J = 8.2 Hz, 1H), 6.62 (d, J = 7.6 Hz, 1H), 6.54 (d, J = 10.6 Hz, 1H), 6.40 (d, J = 9.9 Hz, 1H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



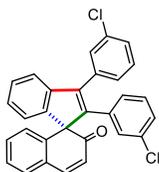
2,3-Bis(2-fluorophenyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4e')

White solid (67.5 mg, 78% yield (A); 0% yield (B)). PE/EA = 10:1, R_f = 0.21. m.p.: 70.6-71.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.57 (d, J = 9.8 Hz, 1H), 7.41-7.23 (m, 6H), 7.22-7.09 (m, 4H), 7.08-6.93 (m, 4H), 6.84 (t, J = 7.2 Hz, 1H), 6.75 (t, J = 9.2 Hz, 1H), 6.38 (d, J = 9.8 Hz, 1H). The ^1H NMR data is consistent with that reported in the literature.¹⁶



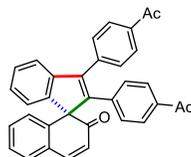
2,3-Bis(4-chlorophenyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4f')

Yellow solid (86.6 mg, 93% yield (A); 80.9 mg, 87% yield (B)). PE/EA = 10:1, $R_f = 0.33$. m.p.: 108.9-109.4 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.68 (d, $J = 9.8$ Hz, 1H), 7.45 (s, 5H), 7.34-7.16 (m, 4H), 7.13-6.96 (m, 4H), 6.90 (d, $J = 7.5$ Hz, 1H), 6.76 (d, $J = 7.9$ Hz, 2H), 6.39 (d, $J = 9.9$ Hz, 1H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



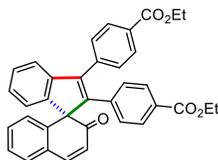
2,3-Bis(3-chlorophenyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4g')

White solid (75.4 mg, 81% yield (A); 73.5 mg, 79% yield (B)). PE/EA = 10:1, $R_f = 0.31$. m.p.: 92.8-93.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, $J = 9.9$ Hz, 1H), 7.51 (s, 1H), 7.43-7.32 (m, 4H), 7.29-7.20 (m, 3H), 7.18-7.12 (m, 1H), 7.09-7.04 (m, 1H), 7.00-6.97 (m, 2H), 6.94-6.85 (m, 2H), 6.79 (t, $J = 1.8$ Hz, 1H), 6.71-6.67 (m, 1H), 6.36 (d, $J = 9.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.2, 147.8, 146.5, 144.6, 144.5, 140.3, 136.5, 136.0, 134.9, 134.0, 130.9, 130.4, 130.3, 129.8, 129.4, 129.3, 128.9, 128.5, 128.1, 128.0, 127.9, 127.6, 127.5, 127.1, 127.0, 126.5, 122.0, 121.9, 71.9. IR (KBr): 3061, 2924, 1638, 1592, 1562, 1461, 1394, 1270, 1209, 752 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{18}\text{Cl}_2\text{ONa}$ $[\text{M}+\text{Na}]^+$ 487.0632, found 487.0635.



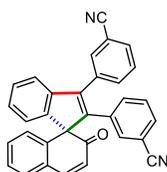
1,1'-((2'-Oxo-2'*H*-spiro[indene-1,1'-naphthalene]-2,3-diyl)bis(4,1-phenylene))bis(ethan-1-one) (4h')

Yellow solid (72.1 mg, 75% yield (A); 32.7 mg, 34% yield (B)). PE/EA = 10:1, $R_f = 0.24$. m.p.: 117.6-118.1 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.06 (d, $J = 8.3$ Hz, 2H), 7.71 (d, $J = 9.9$ Hz, 1H), 7.61 (dd, $J = 18.8, 8.4$ Hz, 4H), 7.46 (d, $J = 7.5$ Hz, 1H), 7.33-7.26 (m, 3H), 7.21-7.16 (m, 1H), 7.15-7.08 (m, 1H), 7.04 (d, $J = 7.5$ Hz, 1H), 6.93-6.88 (m, 3H), 6.41 (d, $J = 9.9$ Hz, 1H), 2.67 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.8, 197.5, 196.1, 147.9, 146.6, 145.9, 145.2, 144.4, 140.3, 140.0, 139.0, 136.9, 135.7, 131.0, 130.4, 129.9, 129.8, 129.3, 129.2, 128.3, 128.2, 128.1, 127.3, 127.0, 126.6, 122.2, 122.1, 72.0, 26.8, 26.6. IR (KBr): 3060, 2923, 1680, 1603, 1401, 1358, 1268, 1192, 824, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{34}\text{H}_{24}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 503.1623, found 503.1621.



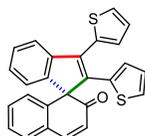
Diethyl 4,4'-((2'-oxo-2'*H*-spiro[indene-1,1'-naphthalene]-2,3-diyl)dibenzoate (4i')

White solid (56.2 mg, 52% yield (A); 96.2 mg, 89% yield (B)). PE/EA = 5:1, $R_f = 0.21$. m.p.: 142.4-142.7 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, $J = 8.1$ Hz, 2H), 7.76-7.57 (m, 5H), 7.46 (d, $J = 7.5$ Hz, 1H), 7.37-7.26 (m, 3H), 7.22-7.03 (m, 3H), 6.92 (t, $J = 8.8$ Hz, 3H), 6.42 (d, $J = 9.9$ Hz, 1H), 4.44 (q, $J = 7.0$ Hz, 2H), 4.28 (q, $J = 7.0$ Hz, 2H), 1.44 (t, $J = 7.1$ Hz, 3H), 1.31 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.1, 166.4, 166.2, 147.9, 146.5, 145.7, 145.3, 144.5, 140.3, 139.6, 138.7, 130.9, 130.4, 130.3, 129.8, 129.6, 129.4, 129.0, 128.1, 128.0, 127.2, 127.0, 126.5, 122.1, 122.0, 72.0, 61.2, 60.9, 14.5, 14.4. IR (KBr): 3061, 2983, 1716, 1666, 1607, 1275, 1180, 1107, 1021, 757 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{36}\text{H}_{28}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 563.1834, found 563.1833.



3,3'-(2'-Oxo-2'H-spiro[indene-1,1'-naphthalene]-2,3-diyl)dibenzonitrile (4j')

White solid (38.4 mg, 43% yield (A); <5% (B)). PE/EA = 10:1, $R_f = 0.23$. m.p.: 259.2-259.7 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.80 (s, 1H), 7.72 (t, $J = 9.4$ Hz, 3H), 7.59 (t, $J = 7.6$ Hz, 1H), 7.48 (d, $J = 7.3$ Hz, 1H), 7.40-7.20 (m, 5H), 7.16 (t, $J = 7.2$ Hz, 2H), 7.05 (d, $J = 7.3$ Hz, 3H), 6.89 (d, $J = 7.5$ Hz, 1H), 6.39 (d, $J = 9.9$ Hz, 1H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



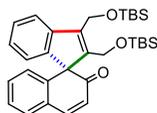
2,3-Di(thiophen-2-yl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4k')

Yellow solid (31.9 mg, 39% yield (A); 25.3 mg, 31% yield (A)). PE/EA = 10:1, $R_f = 0.23$. m.p.: 82.9-83.3 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.73 (d, $J = 9.8$ Hz, 1H), 7.61-7.45 (m, 2H), 7.36-7.17 (m, 6H), 7.10-6.93 (m, 4H), 6.72 (s, 1H), 6.50-6.37 (m, 2H). The ^1H NMR data is consistent with that reported in the literature.¹⁶



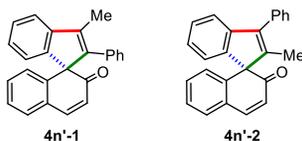
2,3-Dipropyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4l')

Yellow solid (62.4 mg, 95% yield (A); 57.8 mg, 88% yield (B)). PE/EA = 20:1, $R_f = 0.27$. m.p.: 88.5-89.1 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.63 (d, $J = 9.9$ Hz, 1H), 7.42-7.38 (m, 1H), 7.31-7.21 (m, 3H), 7.18-7.12 (m, 1H), 7.01-6.94 (m, 1H), 6.83 (d, $J = 7.4$ Hz, 1H), 6.65 (d, $J = 7.8$ Hz, 1H), 6.35 (d, $J = 9.9$ Hz, 1H), 2.63 (t, $J = 7.6$ Hz, 2H), 2.29-2.20 (m, 1H), 2.09-1.99 (m, 1H), 1.82-1.65 (m, 2H), 1.20-1.09 (m, 2H), 1.05 (t, $J = 7.4$ Hz, 3H), 0.76 (t, $J = 7.3$ Hz, 3H). The ^1H NMR data is consistent with that reported in the literature.¹⁶



2,3-Bis((*tert*-butyldimethylsilyloxy)methyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**4m'**)

White solid (43.7 mg, 41% yield (A); 92.7 mg, 87% yield (B)). PE/EA = 20:1, $R_f = 0.36$. m.p.: 196.7-197.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.57 (d, $J = 9.9$ Hz, 1H), 7.38 (dd, $J = 10.9, 7.9$ Hz, 2H), 7.25-7.09 (m, 3H), 6.96 (t, $J = 7.4$ Hz, 1H), 6.88 (d, $J = 7.4$ Hz, 1H), 6.78 (d, $J = 7.7$ Hz, 1H), 6.31 (d, $J = 9.9$ Hz, 1H), 4.83 (s, 2H), 4.70 (d, $J = 14.4$ Hz, 1H), 4.48 (d, $J = 14.4$ Hz, 1H), 0.94 (s, 9H), 0.66 (s, 9H), 0.16 (s, 6H), -0.24 (d, $J = 15.3$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.3, 147.9, 147.1, 145.4, 144.5, 141.2, 140.2, 130.1, 129.8, 129.6, 127.4, 127.1, 126.9, 126.4, 125.7, 121.4, 121.1, 69.9, 59.0, 58.4, 26.1, 25.9, 18.5, 18.4, -5.1, -5.2, -5.8, -5.9. IR (KBr): 3059, 2946, 2857, 1660, 1462, 1398, 1252, 1080, 838, 762 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{44}\text{O}_3\text{Si}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 555.2727, found 555.2730.



Method A: The regioisomeric mixture of **4n'** (rr = 2:1) was purified by silica gel column chromatography with PE/EA (20/1), affording **4n'-1** and **4n'-2** in 61% (40.8 mg) and 30% (20.1 mg) yield, respectively.

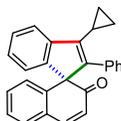
Method B: The regioisomeric mixture of **4n'** (rr = 2:1) was purified by silica gel column chromatography with PE/EA (20/1), affording **4n'-1** and **4n'-2** in 60% (40.7 mg) and 30% (20.1 mg) yield, respectively.

3-Methyl-2-phenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**4n'-1**)

White solid. m.p.: 130.4-130.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.59 (d, $J = 9.9$ Hz, 1H), 7.45-7.28 (m, 3H), 7.25-7.11 (m, 5H), 7.06 (q, $J = 7.2$ Hz, 3H), 6.95 (d, $J = 7.4$ Hz, 1H), 6.82 (d, $J = 7.7$ Hz, 1H), 6.33 (d, $J = 9.9$ Hz, 1H), 2.40 (s, 3H). The ^1H NMR data is consistent with that reported in the literature.¹⁴

2-Methyl-3-phenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**4n'-2**)

White solid. m.p.: 127.3-127.9 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.69 (d, $J = 9.9$ Hz, 1H), 7.62-7.49 (m, 4H), 7.48-7.41 (m, 2H), 7.36-7.22 (m, 4H), 7.07-7.01 (m, 2H), 6.82 (d, $J = 7.7$ Hz, 1H), 6.40 (d, $J = 9.9$ Hz, 1H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 198.0, 147.6, 146.2, 145.9, 144.4, 142.6, 140.7, 134.4, 130.7, 130.5, 129.9, 129.4, 128.6, 127.9, 127.8, 127.7, 126.9, 126.8, 125.6, 122.3, 120.8, 72.0, 12.4. IR (KBr): 3060, 2921, 1663, 1618, 1450, 1392, 1235, 1197, 745, 702 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{25}\text{H}_{18}\text{ONa}$ $[\text{M}+\text{Na}]^+$ 357.1255, found 357.1255.

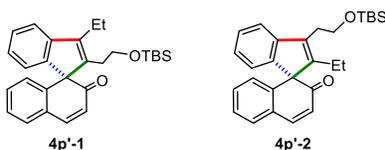


Method A: The regioisomeric mixture of **4o'** (rr = 2:1) was purified by silica gel column chromatography with PE/EA (20/1), affording the major isomer **4o'** in 48% yield (34.6 mg).

Method B: The regioisomeric mixture of **4o'** (rr = 2:1) was purified by silica gel column chromatography with PE/EA (20/1), affording the major isomer **4o'** in 50% yield (36.0 mg).

3-Cyclopropyl-2-phenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**4o'**)

White solid. PE/EA = 10:1, R_f = 0.34. m.p.: 158.4-158.7 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.59 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 7.2 Hz, 1H), 7.33-7.22 (m, 2H), 7.21-7.11 (m, 6H), 7.04 (t, J = 7.2 Hz, 1H), 6.92 (d, J = 7.4 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.31 (d, J = 9.9 Hz, 1H), 2.08-1.98 (m, 1H), 0.98 (d, J = 8.1 Hz, 2H), 0.68 (s, 2H). The ^1H NMR data is consistent with that reported in the literature.¹⁶



Method A: The regioisomeric mixture of **4p'** (rr = 1.5:1) was purified by silica gel column chromatography with PE/EA (10/1), affording **4p'-1** and **4p'-2** in 48% (41.3 mg) and 32% (27.6 mg) yield, respectively.

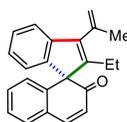
Method B: The regioisomeric mixture of **4p'** (rr = 1.5:1) was purified by silica gel column chromatography with PE/EA (10/1), affording **4p'-1** and **4p'-2** in 50% (43.1 mg) and 34% (29.3 mg) yield, respectively.

2-(2-((*Tert*-butyldimethylsilyloxy)ethyl)-3-ethyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**4p'-1**)

White solid. m.p.: 107.6-108.0 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, J = 9.9 Hz, 1H), 7.40 (dd, J = 7.6, 1.0 Hz, 1H), 7.34-7.23 (m, 3H), 7.19-7.13 (m, 1H), 7.05-6.96 (m, 1H), 6.86 (d, J = 7.4 Hz, 1H), 6.64 (d, J = 7.7 Hz, 1H), 6.35 (d, J = 9.9 Hz, 1H), 3.42-3.22 (m, 2H), 2.68 (q, J = 7.6 Hz, 2H), 2.52-2.33 (m, 2H), 1.29 (t, J = 7.6 Hz, 3H), 0.80 (s, 9H), -0.09 (d, J = 3.8 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.9, 148.9, 146.1, 145.8, 145.7, 142.2, 140.8, 130.4, 130.2, 129.8, 127.7, 127.6, 127.4, 127.0, 125.7, 122.0, 119.9, 71.2, 62.2, 31.5, 26.1, 19.2, 18.4, 13.9, -5.2. IR (KBr): 3061, 2957, 2863, 1658, 1462, 1394, 1243, 1086, 834, 749 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{28}\text{H}_{35}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 431.2406, found 431.2405.

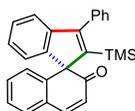
3-(2-((*Tert*-butyldimethylsilyloxy)ethyl)-2-ethyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**4p'-2**)

White solid. m.p.: 111.2-111.7 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.64 (d, J = 9.9 Hz, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.32-7.21 (m, 3H), 7.16-7.13 (m, 1H), 6.97 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 7.4 Hz, 1H), 6.69 (d, J = 7.8 Hz, 1H), 6.36 (d, J = 9.9 Hz, 1H), 3.90 (t, J = 7.3 Hz, 2H), 2.98-2.85 (m, 2H), 2.44-2.36 (m, 1H), 2.19-2.12 (m, 1H), 0.91 (s, 9H), 0.79 (t, J = 7.7 Hz, 3H), 0.09 (d, J = 3.5 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.9, 150.1, 148.6, 146.3, 146.0, 141.0, 138.7, 130.3, 130.1, 129.7, 127.6, 127.5, 127.4, 126.9, 125.4, 121.7, 119.8, 71.2, 62.2, 29.9, 26.1, 20.6, 18.5, 13.8, -5.1. IR (KBr): 3061, 2927, 1723, 1658, 1459, 1391, 1236, 1204, 1046, 823, 750 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{28}\text{H}_{34}\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 453.2226, found 453.2227.



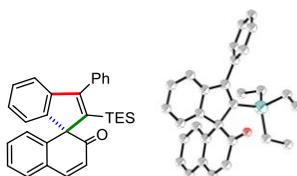
3-Ethyl-2-(prop-1-en-2-yl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4q')

Yellow solid (13.7 mg, 22% yield (A); 33.7 mg, 54% yield (B)). PE/EA = 10:1, R_f = 0.31. m.p.: 63.1-63.5 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.61 (d, J = 9.9 Hz, 1H), 7.38 (d, J = 6.9 Hz, 1H), 7.30-7.11 (m, 4H), 7.01-6.91 (m, 1H), 6.83 (d, J = 7.5 Hz, 1H), 6.68 (d, J = 7.6 Hz, 1H), 6.34 (d, J = 9.9 Hz, 1H), 5.39-5.29 (m, 1H), 5.16-5.06 (m, 1H), 2.38-2.27 (m, 1H), 2.22-2.02 (m, 4H), 0.77 (t, J = 7.6 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 197.5, 148.6, 148.5, 145.9, 145.8, 145.2, 140.9, 139.3, 130.4, 130.2, 129.8, 127.7, 127.6, 127.4, 126.9, 125.5, 121.9, 120.6, 116.4, 71.0, 23.1, 21.1, 13.8. IR (KBr): 3066, 2969, 1662, 1457, 1385, 1269, 1233, 1203, 903, 818, 755 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{21}\text{O}$ $[\text{M}+\text{H}]^+$ 313.1592, found 313.1594.



3-Phenyl-2-(trimethylsilyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4r')

Yellow solid (19.6 mg, 25% yield (A); 49.5 mg, 63% yield (B)). PE/EA = 20:1, R_f = 0.38. m.p.: 155.3-155.9 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.67 (d, J = 9.9 Hz, 1H), 7.57-7.41 (m, 6H), 7.30 (t, J = 7.4 Hz, 1H), 7.22 (t, J = 7.1 Hz, 1H), 7.19-7.13 (m, 1H), 7.02-6.96 (m, 4H), 6.41 (d, J = 9.9 Hz, 1H), -0.23 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 197.6, 159.2, 149.8, 148.3, 146.3, 145.9, 141.4, 136.9, 130.3, 130.1, 129.7, 129.4, 128.4, 128.0, 127.7, 127.6, 127.1, 126.7, 126.3, 121.7, 121.2, 74.0, 0.3. IR (KBr): 3062, 2957, 1663, 1558, 1451, 1395, 1243, 1202, 859, 749, 700 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{24}\text{OSiNa}$ $[\text{M}+\text{Na}]^+$ 415.1494, found 415.1499.



(CCDC: 1978475)

3-Phenyl-2-(triethylsilyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4s')

Yellow solid (7.0 mg, 11% yield (A); 51.3 mg, 59% yield (B)). PE/EA = 20:1, R_f = 0.39. m.p.: 87.2-87.7 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.68 (d, J = 9.9 Hz, 1H), 7.57-7.42 (m, 6H), 7.32-7.28 (m, 1H), 7.21 (m, 1H), 7.17-7.12 (m, 1H), 7.02-6.87 (m, 4H), 6.42 (d, J = 9.9 Hz, 1H), 0.70 (t, J = 7.9 Hz, 9H), 0.39-0.12 (m, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 196.9, 159.7, 150.7, 147.2, 146.4, 145.9, 141.3, 137.0, 130.2, 130.0, 129.7, 129.3, 128.3, 128.0, 127.7, 127.6, 127.3, 127.1, 126.4, 121.7, 121.2, 73.8, 7.6, 4.4. IR (KBr): 3061, 2953, 2877, 1662, 1455, 1234, 1201, 1013, 737, 702 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{30}\text{OSiNa}$ $[\text{M}+\text{Na}]^+$ 457.1964, found 457.1964.



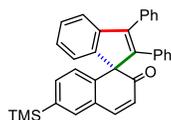
6'-Methoxy-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4a'')

Yellow solid (67.4 mg, 79% yield (A); <5% (B)). PE/EA = 10:1, $R_f = 0.20$. m.p.: 115.8-116.3 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, $J = 9.9$ Hz, 1H), 7.55 (d, $J = 7.3$ Hz, 2H), 7.51-7.38 (m, 3H), 7.37-7.21 (m, 2H), 7.16-6.99 (m, 5H), 6.96 (d, $J = 2.4$ Hz, 1H), 6.89 (t, $J = 6.9$ Hz, 3H), 6.76 (dd, $J = 8.6, 2.5$ Hz, 1H), 6.43 (d, $J = 9.9$ Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.1, 158.9, 148.1, 146.1, 145.5, 145.3, 144.6, 135.3, 134.5, 132.8, 130.8, 129.6, 129.2, 128.9, 128.3, 128.0, 127.9, 127.8, 127.2, 127.1, 126.4, 121.9, 121.8, 116.8, 114.6, 71.3, 55.5. IR (KBr): 3059, 2931, 1662, 1563, 1495, 1455, 1269, 1167, 1034, 742, 698 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{22}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 449.1517, found 449.1517.



6'-((*Tert*-butyldimethylsilyl)oxy)-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4b'')

Yellow solid (57.9 mg, 55% yield (A); 0% yield (B)). PE/EA = 20:1, $R_f = 0.27$. m.p.: 98.7-99.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.58-7.50 (m, 3H), 7.46-7.36 (m, 3H), 7.32-7.22 (m, 2H), 7.08 (t, $J = 7.5$ Hz, 1H), 7.04-6.96 (m, 4H), 6.89 (d, $J = 2.4$ Hz, 1H), 6.87-6.76 (m, 3H), 6.67 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.36 (d, $J = 9.9$ Hz, 1H), 0.98 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.2, 155.1, 148.2, 146.0, 145.6, 144.4, 135.3, 134.6, 133.4, 131.0, 129.7, 129.3, 128.9, 128.3, 128.0, 127.9, 127.8, 127.1, 127.0, 126.4, 122.6, 121.9, 121.8, 120.9, 71.5, 25.8, 18.3, -4.2, -4.3. IR (KBr): 3059, 2932, 2857, 1665, 1494, 1275, 1169, 973, 846, 751, 696 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{36}\text{H}_{34}\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 549.2226, found 549.2223.



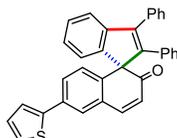
2,3-Diphenyl-6'-(trimethylsilyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4c'')

Yellow solid (78.7 mg, 84% yield (A); 37.5 mg, 40% yield (B)). PE/EA = 10:1, $R_f = 0.22$. m.p.: 105.1-105.6 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, $J = 9.8$ Hz, 1H), 7.53 (s, 3H), 7.49-7.37 (m, 3H), 7.33-7.19 (m, 3H), 7.08-6.92 (m, 6H), 6.85 (d, $J = 6.1$ Hz, 2H), 6.40 (d, $J = 9.8$ Hz, 1H), 0.25 (s, 9H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



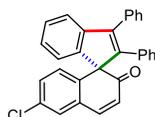
2,3,6'-Triphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4d'')

Yellow solid (73.7 mg, 78% yield (A); 71.8 mg, 76% yield (B)). PE/EA = 10:1, R_f = 0.21. m.p.: 141.8-142.4 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, J = 9.9 Hz, 1H), 7.65 (d, J = 1.4 Hz, 1H), 7.60-7.51 (m, 4H), 7.50-7.22 (m, 9H), 7.12-6.98 (m, 6H), 6.90 (dd, J = 7.5, 1.7 Hz, 2H), 6.46 (d, J = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.7, 147.8, 146.2, 145.6, 145.2, 144.9, 140.6, 140.1, 139.9, 135.3, 134.5, 130.2, 129.7, 129.4, 129.3, 129.1, 129.0, 128.6, 128.1, 128.0, 127.9, 127.8, 127.5, 127.2, 127.1, 127.0, 126.5, 122.0, 121.8, 71.7. IR (KBr): 3058, 2923, 1664, 1487, 1452, 1267, 1226, 1186, 752, 698 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{36}\text{H}_{24}\text{ONa}$ $[\text{M}+\text{Na}]^+$ 495.1725, found 495.1724.



2,3-Diphenyl-6'-(thiophen-2-yl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4e'')

Yellow solid (67.0 mg, 70% yield (A); 20.1 mg, 21% yield (B)). PE/EA = 5:1, R_f = 0.33. m.p.: 155.2-155.7 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.72 (d, J = 9.9 Hz, 1H), 7.65 (d, J = 1.2 Hz, 1H), 7.55 (d, J = 7.1 Hz, 2H), 7.50-7.35 (m, 7H), 7.33-7.23 (m, 2H), 7.13-6.98 (m, 6H), 6.91-6.87 (m, 2H), 6.45 (d, J = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.8, 147.7, 146.2, 145.5, 145.0, 144.9, 141.0, 139.8, 135.3, 135.2, 134.4, 130.2, 129.6, 129.2, 129.0, 128.7, 128.1, 128.0, 127.9, 127.8, 127.5, 127.2, 127.1, 126.8, 126.5, 126.1, 122.0, 121.8, 120.9, 71.6. IR (KBr): 3058, 2924, 1663, 1561, 1490, 1453, 1268, 1223, 744, 697 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{34}\text{H}_{22}\text{OSNa}$ $[\text{M}+\text{Na}]^+$ 501.1289, found 501.1289.



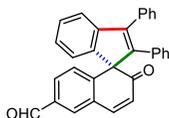
6'-Chloro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4f'')

White solid (37.9 mg, 44% yield (A); 70.7 mg, 82% yield (B)). PE/EA = 10:1, R_f = 0.34. m.p.: 123.2-123.7 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, J = 10.0 Hz, 1H), 7.55 (d, J = 7.2 Hz, 2H), 7.52-7.39 (m, 4H), 7.34-7.28 (m, 2H), 7.19-6.99 (m, 6H), 6.96-6.83 (m, 3H), 6.47 (d, J = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.1, 147.3, 145.5, 145.1, 144.8, 144.6, 139.5, 135.0, 134.2, 133.4, 131.4, 130.6, 129.6, 129.5, 129.1, 129.0, 128.5, 128.2, 128.1, 128.0, 127.9, 127.3, 126.6, 122.1, 121.7, 71.4. IR (KBr): 3059, 2923, 1666, 1486, 1452, 1231, 1196, 881, 749, 697 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{19}\text{ClONa}$ $[\text{M}+\text{Na}]^+$ 453.1022, found 453.1022.



6'-Bromo-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (4g'')

Yellow solid (75.1 mg, 79% yield (A); 76.1 mg, 80% yield (B)). PE/EA = 10:1, R_f = 0.35. m.p.: 124.9-125.4 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.64-7.59 (m, 2H), 7.55 (d, J = 6.9 Hz, 2H), 7.51-7.39 (m, 3H), 7.35-7.24 (m, 3H), 7.12-7.01 (m, 5H), 6.91-6.81 (m, 3H), 6.47 (d, J = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.0, 147.1, 145.4, 145.1, 144.7, 144.6, 140.0, 135.0, 134.1, 133.5, 132.5, 131.6, 129.6, 129.1, 129.0, 128.7, 128.2, 128.1, 128.0, 127.8, 127.3, 126.6, 122.2, 121.7, 121.3, 71.4. IR (KBr): 3058, 2923, 1666, 1485, 1452, 1270, 1231, 1194, 748, 698 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{19}\text{BrONa}$ $[\text{M}+\text{Na}]^+$ 497.0517, found 497.0517.



2'-Oxo-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalene]-6'-carbaldehyde (4h'')

Yellow solid (51.8 mg, 61% yield (A); 26.3 mg, 31% yield (B)). PE/EA = 10:1, R_f = 0.23. m.p.: 107.7-108.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.97 (s, 1H), 7.95 (s, 1H), 7.76 (d, J = 10.1 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.57-7.39 (m, 5H), 7.30 (t, J = 8.3 Hz, 2H), 7.15-6.95 (m, 6H), 6.82 (d, J = 7.3 Hz, 2H), 6.51 (d, J = 10.0 Hz, 1H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



6'-Acetyl-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4i'')

Yellow solid (66.7 mg, 76% yield (A); 43.9 mg, 50% yield (B)). PE/EA = 5:1, R_f = 0.28. m.p.: 132.6-133.1 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, J = 1.5 Hz, 1H), 7.66-7.57 (m, 2H), 7.41 (d, J = 7.0 Hz, 2H), 7.38-7.25 (m, 3H), 7.22-7.10 (m, 2H), 6.99-6.81 (m, 6H), 6.72 (dd, J = 7.9, 1.5 Hz, 2H), 6.36 (d, J = 9.9 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.0, 195.8, 147.0, 146.5, 145.6, 145.4, 145.3, 144.6, 136.6, 135.0, 134.1, 130.4, 130.1, 129.7, 129.6, 129.1, 129.0, 128.3, 128.2, 128.1, 127.7, 127.4, 127.3, 126.6, 122.2, 121.7, 71.8, 26.6. IR (KBr): 3058, 2923, 1681, 1618, 1453, 1374, 1273, 1222, 756, 697 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{32}\text{H}_{22}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 461.1517, found 461.1513.



Ethyl-2'-oxo-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalene]-6'-carboxylate (4j'')

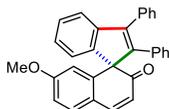
Yellow solid (73.1 mg, 78% yield (A); 72.2 mg, 77% yield (B)). PE/EA = 10:1, R_f = 0.21. m.p.: 130.9-131.5 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.01 (s, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 10.0 Hz, 1H), 7.46-7.39 (m, 2H), 7.37-7.26 (m, 3H), 7.23-7.08 (m, 2H), 6.98-6.83 (m, 6H), 6.77-6.68 (m, 2H), 6.36 (d, J = 9.9 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.9,

165.7, 147.1, 146.2, 145.6, 145.3, 145.2, 144.7, 135.0, 134.2, 131.4, 131.1, 130.1, 129.9, 129.6, 129.1, 129.0, 128.2, 128.1, 127.5, 127.3, 127.2, 126.6, 122.2, 121.7, 71.9, 61.3, 14.4. IR (KBr): 3059, 2983, 1717, 1668, 1453, 1373, 1285, 1222, 1114, 1022, 756, 698 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{33}\text{H}_{24}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 491.1623, found 491.1623.



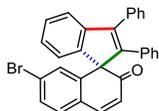
2'-Oxo-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalene]-6'-carbonitrile (4k'')

White solid (59.9 mg, 71% yield (A); 10.1 mg, 12% yield (A)). PE/EA = 5:1, R_f = 0.31. m.p.: 146.3-147.0 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.59 (d, J = 1.5 Hz, 1H), 7.53 (d, J = 10.0 Hz, 1H), 7.45-7.24 (m, 6H), 7.23-7.11 (m, 2H), 7.00-6.83 (m, 6H), 6.74-6.63 (m, 2H), 6.41 (d, J = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.1, 146.5, 146.4, 145.6, 145.5, 144.2, 143.7, 134.7, 133.9, 133.5, 133.2, 130.8, 129.5, 129.1, 129.0, 128.7, 128.5, 128.3, 128.2, 128.0, 127.5, 126.8, 122.4, 121.7, 118.0, 111.9, 71.7. IR (KBr): 3059, 2923, 2230, 1668, 1623, 1451, 1265, 1210, 754, 695 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{19}\text{NONa}$ $[\text{M}+\text{Na}]^+$ 444.1364, found 444.1364.



7'-Methoxy-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4l'')

Yellow solid (74.2 mg, 87% yield (A); 55.4 mg, 65% yield (B)). PE/EA = 10:1, R_f = 0.21. m.p.: 210.2-210.8 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, J = 9.8 Hz, 1H), 7.54 (d, J = 7.1 Hz, 2H), 7.50-7.35 (m, 4H), 7.31-7.21 (m, 2H), 7.11-6.97 (m, 5H), 6.90 (d, J = 5.7 Hz, 2H), 6.79 (d, J = 8.4 Hz, 1H), 6.52 (s, 1H), 6.29 (d, J = 9.8 Hz, 1H), 3.64 (s, 3H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



7'-Bromo-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4m'')

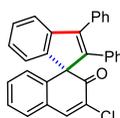
Yellow solid (80.8 mg, 85% yield (A); 48.5 mg, 51% yield (B)). PE/EA = 10:1, R_f = 0.25. m.p.: 215.7-216.3 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, J = 9.9 Hz, 1H), 7.46-7.41 (m, 2H), 7.37-7.24 (m, 4H), 7.22-7.12 (m, 3H), 6.99-6.87 (m, 6H), 6.78-6.71 (m, 2H), 6.30 (d, J = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.7, 147.1, 145.4, 145.2, 145.1, 144.5, 143.2, 134.9, 134.1, 131.2, 131.0, 130.0, 129.6, 129.1, 129.0, 128.7, 128.2, 128.1, 127.3, 127.0, 126.6, 125.4, 122.2, 121.7, 71.4. IR (KBr): 3058, 2924,

1663, 1583, 1490, 1451, 1266, 841, 755, 698 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{19}\text{BrONa}$ $[\text{M}+\text{Na}]^+$ 497.0517, found 497.0517.



3'-Methoxy-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4n'')

Yellow solid (65.7 mg, 77% yield (A); <5% (B)). PE/EA = 10:1, R_f = 0.21. m.p.: 129.4-129.9 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.51 (d, J = 6.9 Hz, 2H), 7.47-7.36 (m, 3H), 7.34-7.19 (m, 4H), 7.09-6.95 (m, 6H), 6.90 (d, J = 7.6 Hz, 1H), 6.83 (d, J = 6.6 Hz, 2H), 6.74 (s, 1H), 3.85 (s, 3H). The ^1H NMR data is consistent with that reported in the literature.¹⁵



3'-Chloro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one (4o'')

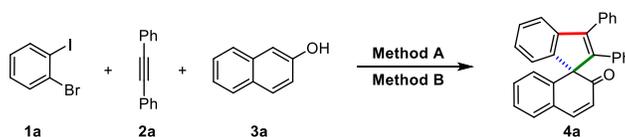
Yellow solid (46.5 mg, 54% yield (A); 64.6 mg, 75% yield (B)). PE/EA = 20:1, R_f = 0.35. m.p.: 131.1-131.6 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.89 (s, 1H), 7.54 (d, J = 7.1 Hz, 2H), 7.50-7.39 (m, 4H), 7.34-7.27 (m, 3H), 7.20 (t, J = 7.4 Hz, 1H), 7.11 (t, J = 7.1 Hz, 1H), 7.06-6.99 (m, 5H), 6.84 (d, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 189.6, 147.0, 145.4, 145.0, 144.5, 143.5, 140.1, 134.9, 134.0, 130.9, 130.8, 129.7, 129.6, 129.5, 129.1, 129.0, 128.3, 128.2, 128.1, 128.0, 127.3, 127.0, 126.7, 122.2, 121.8, 72.9. IR (KBr): 3059, 2923, 1677, 1603, 1492, 1451, 1267, 1229, 754, 697 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{19}\text{ClONa}$ $[\text{M}+\text{Na}]^+$ 453.1022, found 453.1023.



2,3-Diphenyl-6'H-spiro[indene-1,5'-quinolin]-6'-one (4p'')

White solid (31.0 mg, 39% yield (A); 31.8 mg, 40% yield (B)). PE/EA = 5:1, R_f = 0.27. m.p.: 104.7-105.2 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 8.55 (d, J = 3.7 Hz, 1H), 7.87 (d, J = 10.1 Hz, 1H), 7.55-7.38 (m, 5H), 7.33-7.24 (m, 2H), 7.20 (dd, J = 7.9, 1.3 Hz, 1H), 7.13-6.97 (m, 6H), 6.82 (dd, J = 8.0, 1.5 Hz, 2H), 6.65 (d, J = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.6, 149.3, 148.9, 147.2, 146.7, 145.6, 145.5, 144.2, 134.9, 134.6, 134.0, 130.7, 129.6, 129.1, 129.0, 128.4, 128.3, 128.2, 127.5, 126.7, 124.5, 122.3, 121.9, 71.1. IR (KBr): 3055, 2924, 1670, 1493, 1447, 1227, 1113, 795, 750, 698 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{29}\text{H}_{19}\text{NONa}$ $[\text{M}+\text{Na}]^+$ 420.1364, found 420.1361.

Large-scale reaction (1.0 mmol):

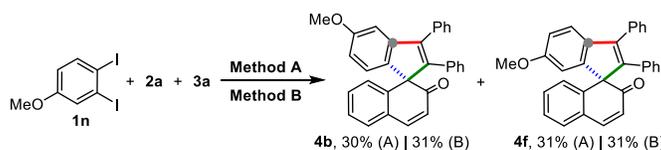


Method A: In a glovebox, a 25.0 mL vial equipped with a stirring bar was charged with Pd(OAc)₂ (11.0 mg, 0.05 mmol), dppp (25.0 mg, 0.06 mmol), K₃PO₄ (424.5 mg, 2.00 mmol), 1-bromo-2-iodobenzene **1a** (424.4 mg, 1.50 mmol), 1,2-diphenylethyne **2a** (267.5 mg, 1.50 mmol) and 2-naphthol **3a** (144.0 mg, 1.00 mmol), followed by sequential addition of 1,4-dioxane (10.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO₄, filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product **4a** (325.2 mg, 82% yield).

Method B: In a glovebox, a 25.0 mL vial equipped with a stirring bar was charged with Pd(OAc)₂ (11.0 mg, 0.05 mmol), K₃PO₄ (424.5 mg, 2.00 mmol), 1-bromo-2-iodobenzene **1a** (424.4 mg, 1.50 mmol), 1,2-diphenylethyne **2a** (267.5 mg, 1.50 mmol) and 2-naphthol **3a** (144.0 mg, 1.00 mmol), followed by sequential addition of 1,4-dioxane (10.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO₄, filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product **4a** (309.3 mg, 78% yield).

C. Mechanistic studies:

a)

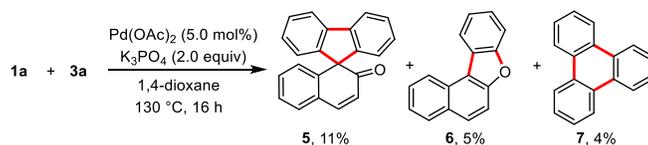


Method A: In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with Pd(OAc)₂ (2.2 mg, 0.01 mmol), dppp (5.0 mg, 0.012 mmol), K₃PO₄ (84.9 mg, 0.40 mmol), 1,2-diiodo-4-methoxybenzene **1n** (108.0 mg, 0.30 mmol), 1,2-diphenylethyne **2a** (53.5 mg, 0.30 mmol) and 2-naphthol **3a** (28.8 mg, 0.20 mmol), followed by sequential addition of 1,4-dioxane (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO₄, filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product **4b** (25.6 mg, 30% yield) and **4f** (26.4 mg, 31% yield).

Method B: In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with Pd(OAc)₂ (2.2 mg, 0.01 mmol), K₃PO₄ (84.9 mg, 0.40 mmol), 1,2-diiodo-4-methoxybenzene **1n** (108.0 mg, 0.30 mmol), 1,2-diphenylethyne **2a** (53.5 mg, 0.30 mmol) and 2-naphthol **3a** (28.8 mg, 0.20 mmol), followed by sequential addition of 1,4-dioxane (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO₄, filtered, and concentrated *in vacuo*. The residue

was then purified on silica gel to afford the desired product **4b** (26.4 mg, 31% yield) and **4f** (26.4 mg, 31% yield).

b)



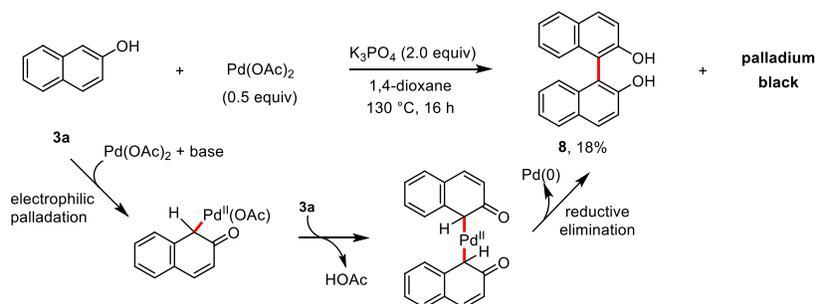
In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with Pd(OAc)₂ (4.4 mg, 0.02 mmol), K₃PO₄ (169.8 mg, 0.80 mmol), 1-bromo-2-iodobenzene **1a** (169.7 mg, 0.60 mmol) and 2-naphthol **3a** (57.6 mg, 0.40 mmol), followed by sequential addition of 1,4-dioxane (4.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO₄, filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product **5** (13.0 mg, 11% yield), **6** (4.4 mg, 5% yield) and **7** (1.8 mg, 4% yield).

5: Yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.80 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.72 (d, *J* = 9.9 Hz, 1H), 7.45 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.40 (td, *J* = 7.5, 1.1 Hz, 2H), 7.29 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.22 (td, *J* = 7.5, 1.2 Hz, 2H), 7.15-7.07 (m, 3H), 6.54-6.47 (m, 1H), 6.36 (d, *J* = 9.9 Hz, 1H). The ¹H NMR data is consistent with that reported in the literature.¹⁸

6: White solid. ¹H NMR (400 MHz, CDCl₃): δ 8.63 (d, *J* = 8.3 Hz, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 1H), 7.83-7.66 (m, 3H), 7.61-7.40 (m, 3H). The ¹H NMR data is consistent with that reported in the literature.¹⁹

7: White solid. ¹H NMR (400 MHz, CDCl₃): δ 8.72-8.62 (m, *J* = 6.2, 3.4 Hz, 6H), 7.75-7.60 (m, *J* = 6.3, 3.3 Hz, 6H). The ¹H NMR data is consistent with that reported in the literature.²⁰

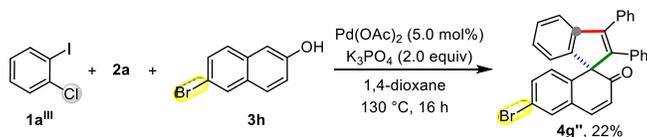
c)



In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with Pd(OAc)₂ (22.4 mg, 0.1 mmol), K₃PO₄ (84.9 mg, 0.40 mmol) and 2-naphthol **3** (0.20 mmol), followed by sequential addition of 1,4-dioxane (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO₄, filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product

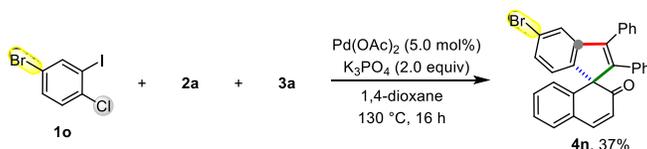
8 (5.2 mg, 18% yield, PE/EA = 10:1, $R_f = 0.23$). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.97 (d, $J = 8.9$ Hz, 2H), 7.89 (dd, $J = 8.6, 1.1$ Hz, 2H), 7.41-7.33 (m, 4H), 7.34-7.27 (m, 2H), 7.16 (d, $J = 1.1$ Hz, 2H), 5.04 (s, 1H). The $^1\text{H NMR}$ data is consistent with that reported in the literature.²¹

d)



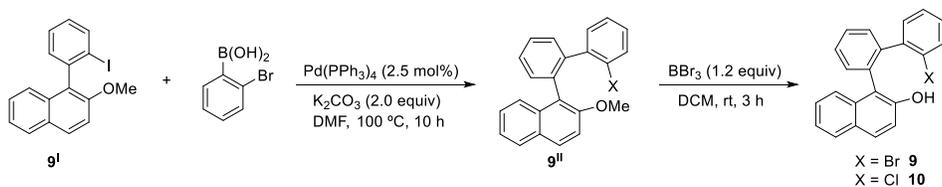
In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $\text{Pd}(\text{OAc})_2$ (2.2 mg, 0.01 mmol), K_3PO_4 (84.9 mg, 0.40 mmol), 1-chloro-2-iodobenzene **1a'''** (71.5 mg, 0.30 mmol), 1,2-diphenylethyne **2a** (53.5 mg, 0.30 mmol) and 6-bromonaphthalen-2-ol **3h** (44.6 mg, 0.20 mmol), followed by sequential addition of 1,4-dioxane (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO_4 , filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product **4g''** (20.9 mg, 22% yield).

e)



In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $\text{Pd}(\text{OAc})_2$ (2.2 mg, 0.01 mmol), K_3PO_4 (84.9 mg, 0.40 mmol), 4-bromo-1-chloro-2-iodobenzene **1o** (95.2 mg, 0.30 mmol), 1,2-diphenylethyne **2a** (53.5 mg, 0.30 mmol) and 2-naphthol **3a** (28.8 mg, 0.20 mmol), followed by sequential addition of 1,4-dioxane (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO_4 , filtered, and concentrated *in vacuo*. The residue was then purified on silica gel (PE/EA = 10:1, $R_f = 0.28$) to afford the desired product **4n** (35.2 mg, 37% yield).

f)



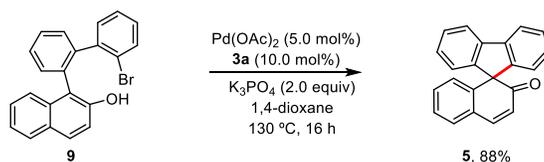
A 100 mL round bottom flask with a stir bar was fitted with a rubber septum and flame dried under high vacuum. The flask was purged with argon and charged with $\text{Pd}(\text{PPh}_3)_4$ (86.7 mg, 0.075 mmol), K_2CO_3 (0.83 g, 6.0 mmol), 1-(2-iodophenyl)-2-methoxynaphthalene²² **9^I** (1.08 g, 3.0 mmol), (2-bromophenyl)boronic acid (0.72 g, 3.6 mmol), 15.0 mL deoxygenated DMF. The mixture was stirred at 80 °C until the reaction was judged to be completed by TLC analysis. Water was added and extracted with

EtOAc. The organic phase was dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the **9^H**.

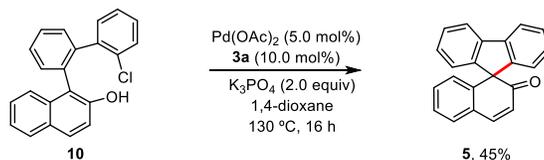
A solution of BBr_3 (1.2 equiv.) in CH_2Cl_2 was slowly added to a solution of the above product in CH_2Cl_2 (15.0 mL) at 0 °C and the mixture was stirred for 3 h at room temperature. After cooled to 0 °C, the reaction was quenched with ice cold H_2O and extracted with CH_2Cl_2 . The organic layer was dried over MgSO_4 , filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel to afford the inseparable mixture of isomers product.

9 (0.47 g, 42%). ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 8.1$ Hz, 1H), 7.69-7.63 (m, 2.5 H), 7.63-7.58 (m, 4H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.51-7.39 (m, 4H), 7.37-7.31 (m, 1.5H), 7.29-7.24 (m, 0.5H), 7.23-7.15 (m, 1H), 7.07 (d, $J = 7.7$ Hz, 0.5H), 7.02 (d, $J = 8.9$ Hz, 1H), 6.98-6.87 (m, 1.5H), 6.87-6.72 (m, 2.5H), 5.18 (s, 0.5H), 5.10 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.7, 150.6, 142.6, 142.3, 140.5, 140.4, 134.2, 133.1, 132.9, 132.8, 132.7, 132.4, 131.8, 131.0, 130.8, 129.6, 129.6, 129.1, 129.0, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 127.6, 126.6, 126.4, 126.1, 125.6, 124.9, 123.4, 123.2, 123.1, 123.0, 120.3, 119.5, 117.5, 116.9. IR (KBr): 3057, 1620, 1599, 1516, 1424, 1216, 1146, 817, 749 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{15}\text{BrONa}$ $[\text{M}+\text{Na}]^+$ 397.0204, found 397.0203.

10 (0.33 g, 33%). ^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 8.1$ Hz, 2H), 7.70-7.55 (m, 7H), 7.54-7.44 (m, 2.5H), 7.43-7.30 (m, 3.5H), 7.24-7.12 (m, 1.5H), 7.10-6.97 (m, 2.5H), 6.97-6.84 (m, 1H), 6.83-6.69 (m, 2H), 5.15 (s, 0.5H), 5.09 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.6, 140.6, 138.6, 134.0, 133.0, 131.9, 131.0, 130.0, 129.4, 129.0, 128.6, 128.5, 128.1, 127.6, 126.5, 125.9, 125.2, 124.8, 123.5, 120.1, 119.5, 117.4, 116.8, 115.6. IR (KBr): 3058, 1620, 1597, 1517, 1428, 1217, 1147, 817, 750 cm^{-1} . HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{15}\text{ClONa}$ $[\text{M}+\text{Na}]^+$ 353.0709, found 353.0709.



In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $\text{Pd}(\text{OAc})_2$ (2.2 mg, 0.01 mmol), **3a** (2.9 mg, 0.02 mmol), K_3PO_4 (84.9 mg, 0.40 mmol) and 1-(2'-bromo-[1,1'-biphenyl]-2-yl)naphthalen-2-ol **9** (75.0 mg, 0.20 mmol), followed by sequential addition of 1,4-dioxane (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO_4 , filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product **5** (51.8 mg, 88% yield).

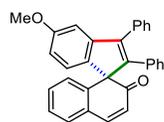


In a glovebox, a 5.0 mL vial equipped with a stirring bar was charged with $\text{Pd}(\text{OAc})_2$ (2.2 mg, 0.01 mmol), **3a** (2.9 mg, 0.02 mmol), K_3PO_4 (84.9 mg, 0.40 mmol) and 1-(2'-chloro-[1,1'-biphenyl]-2-

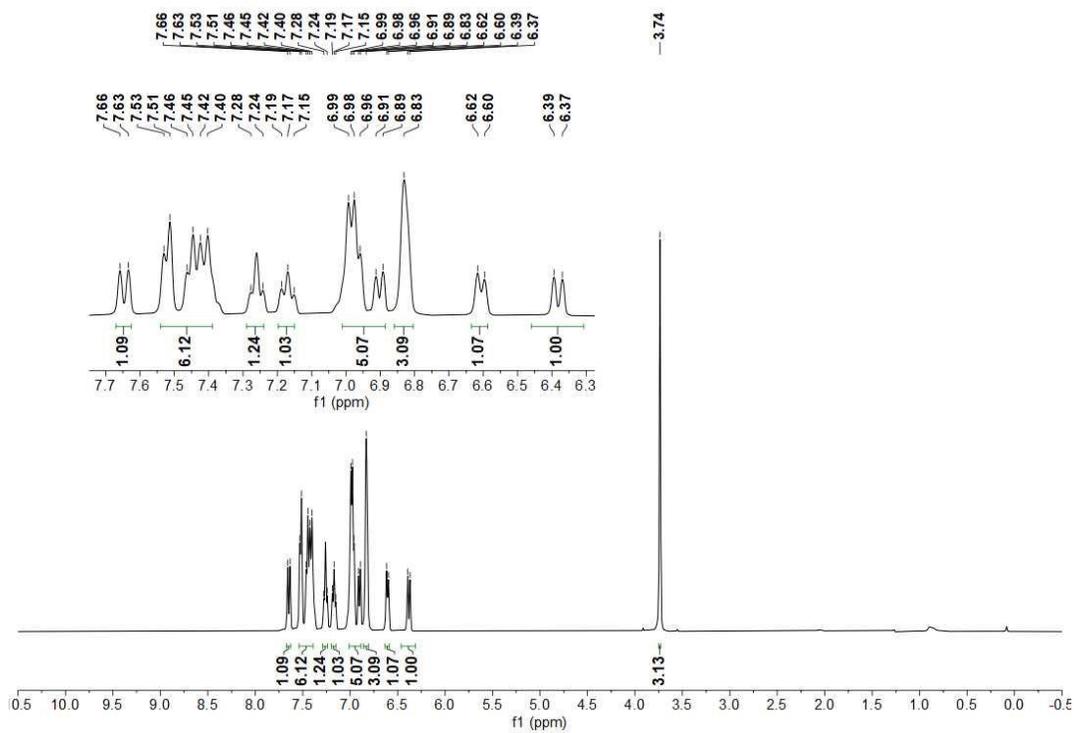
yl)naphthalen-2-ol **10** (66.0 mg, 0.20 mmol), followed by sequential addition of 1,4-dioxane (2.0 mL). The vial was sealed with a Teflon screw cap and then the reaction mixture was heated at 130 °C for 16 h. After the reaction vessel was cooled to room temperature, the mixture was extracted with EtOAc, dried over MgSO₄, filtered, and concentrated *in vacuo*. The residue was then purified on silica gel to afford the desired product **5** (26.5 mg, 45% yield).

D. References:

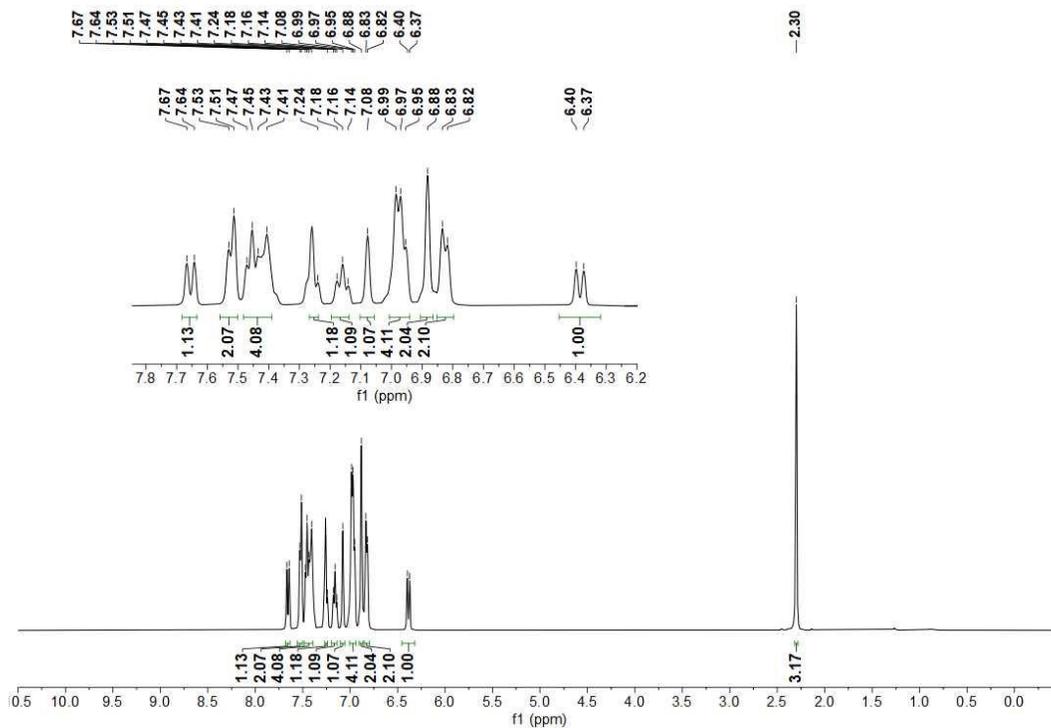
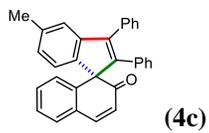
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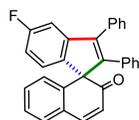
(4b)



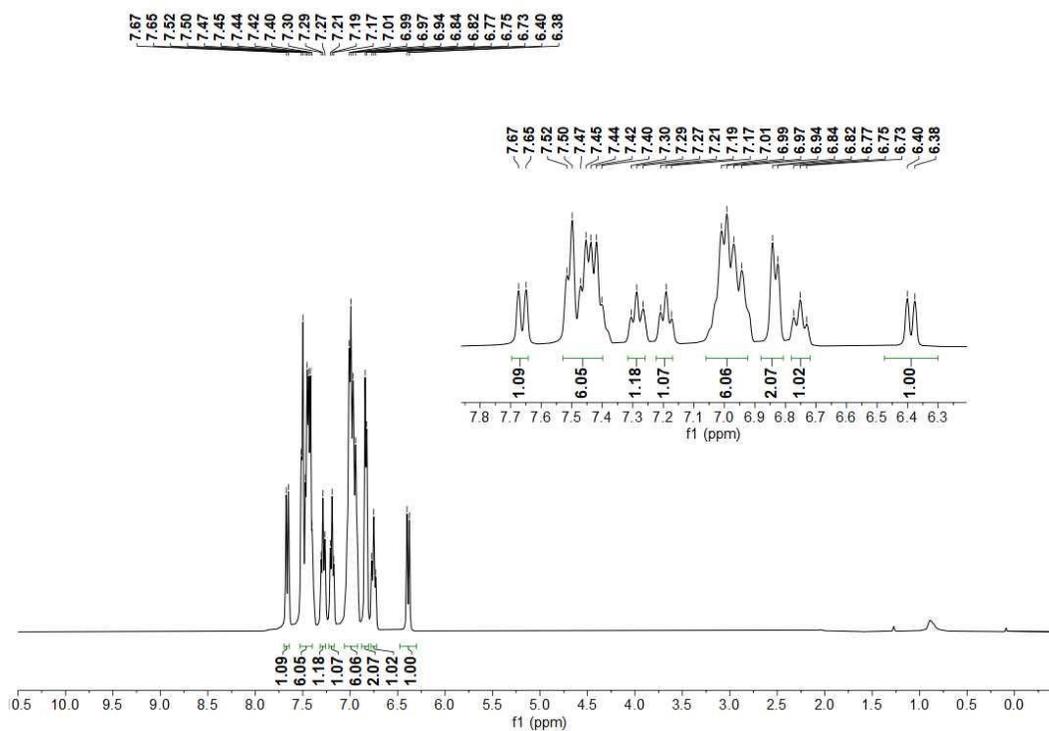
The ^1H NMR data is consistent with that reported in the literature.¹⁵



The ^1H NMR data is consistent with that reported in the literature.¹⁶



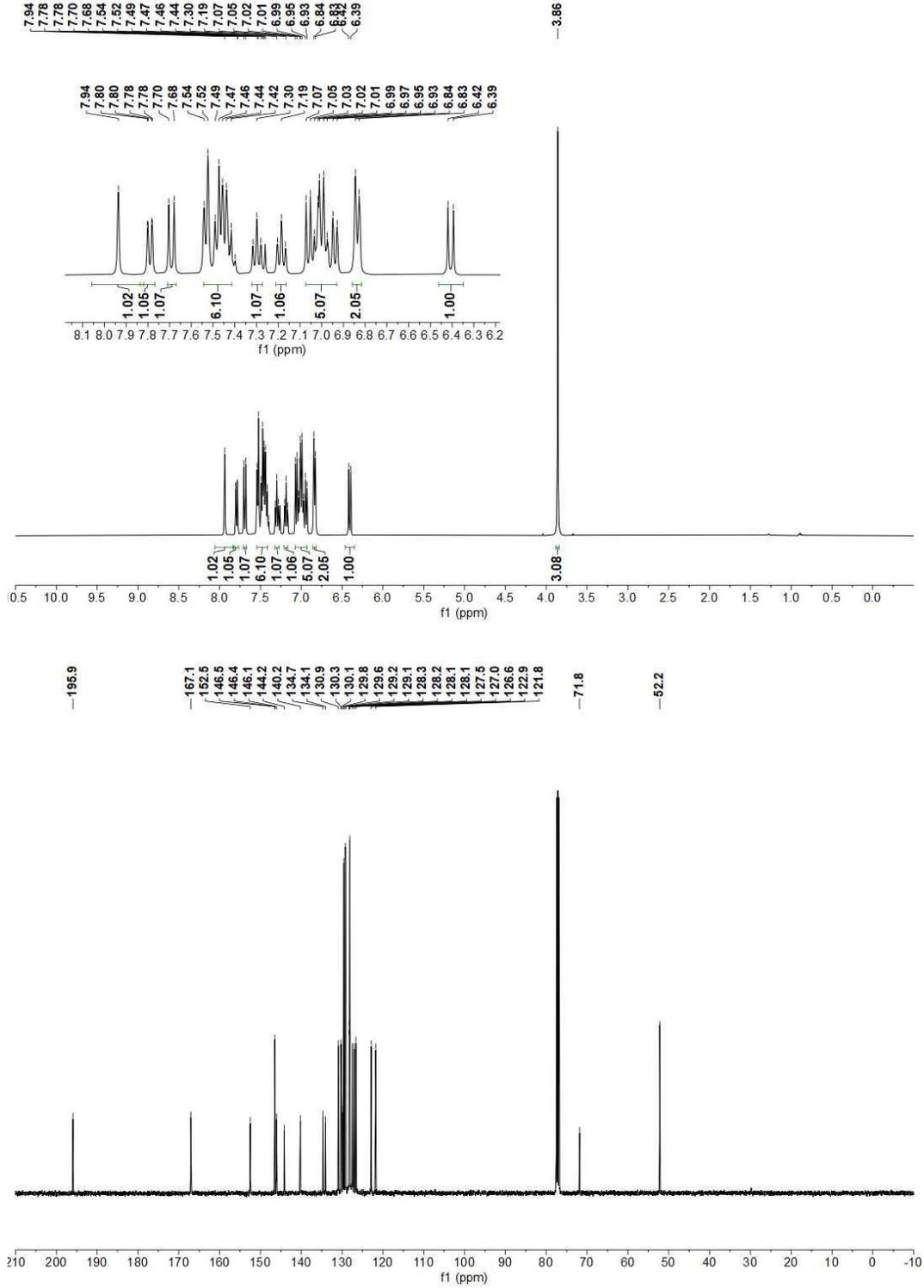
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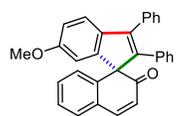


The ^1H NMR data is consistent with that reported in the literature.¹⁵

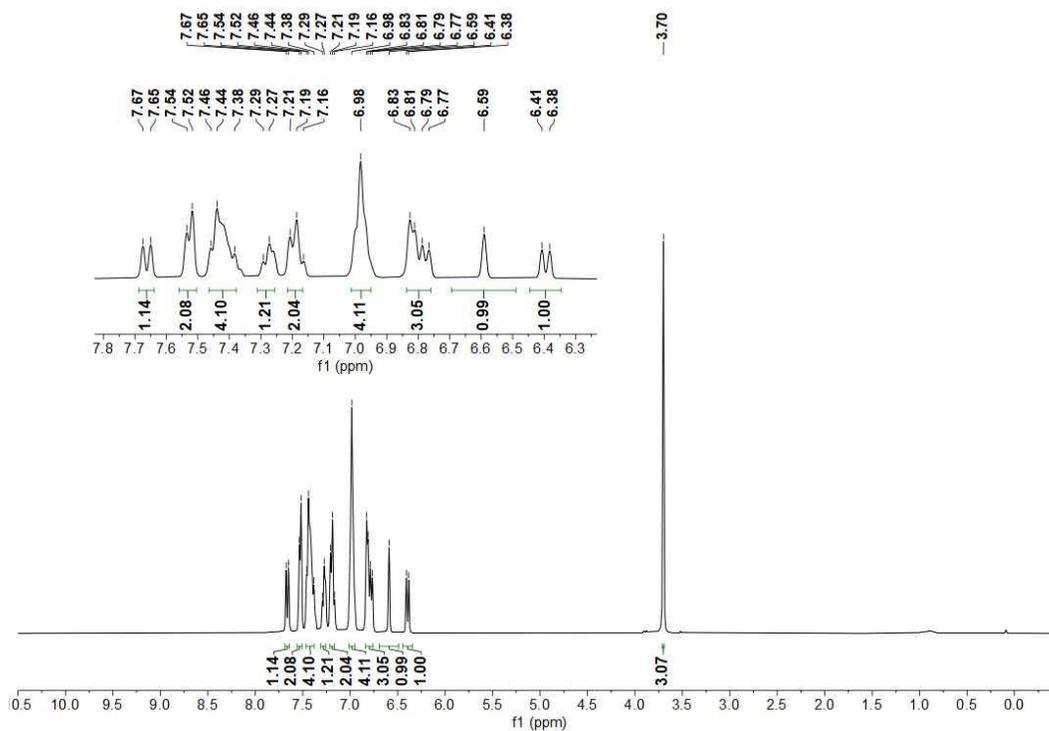


(4e)

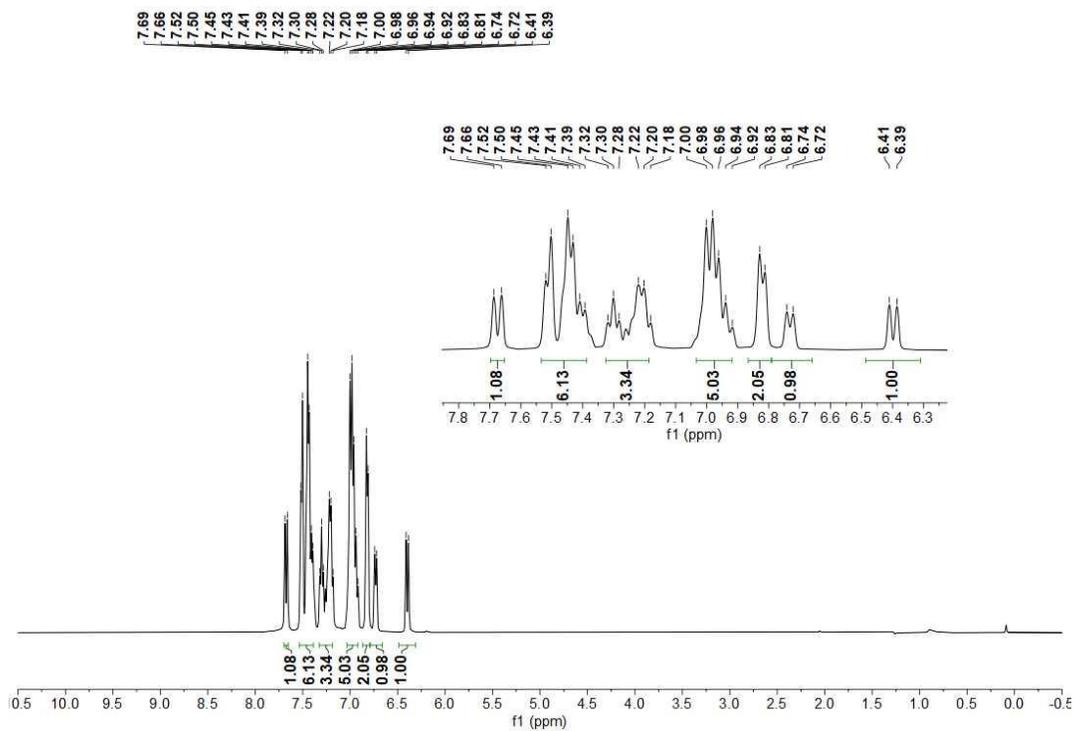
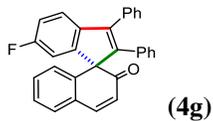




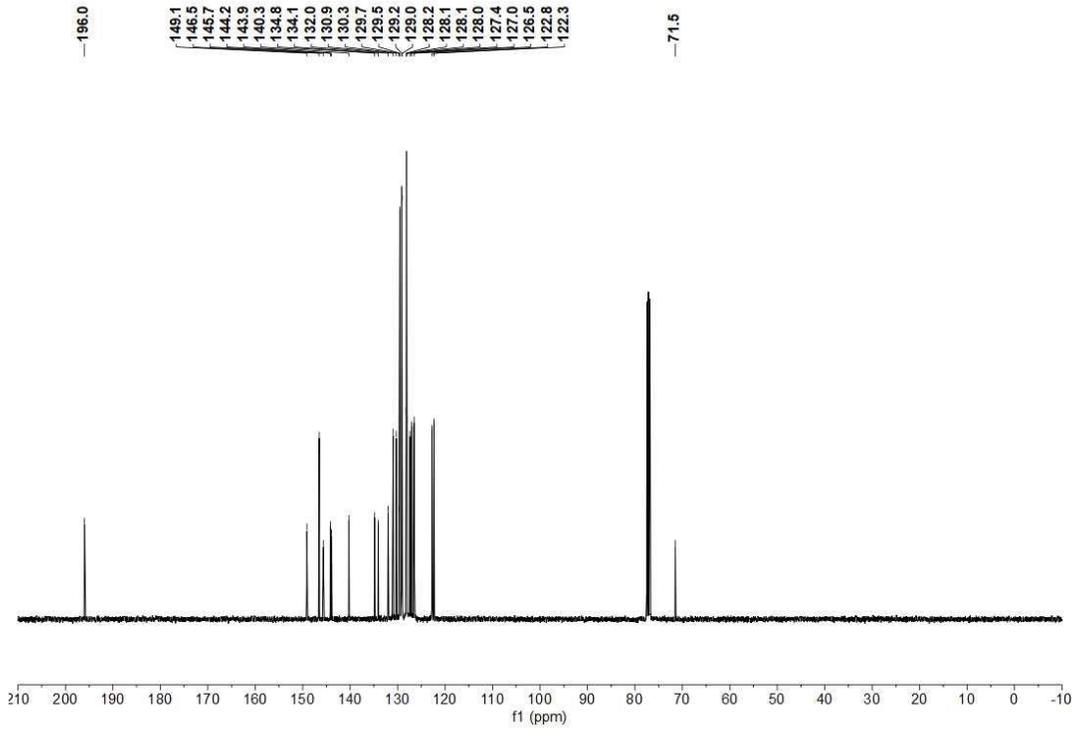
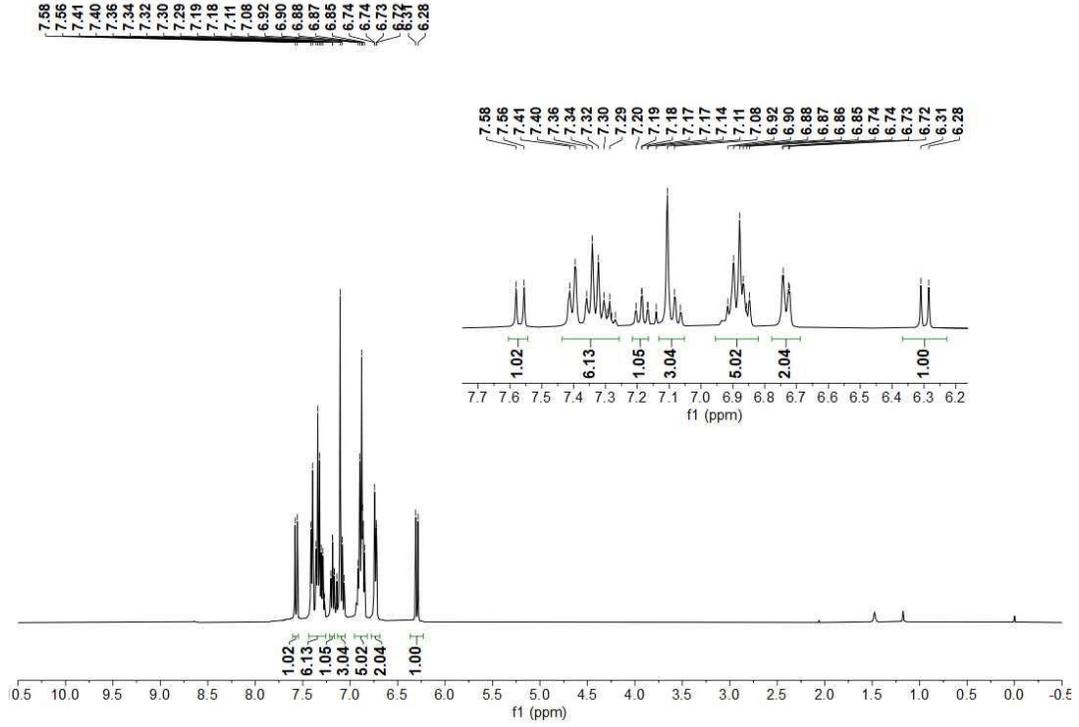
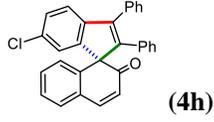
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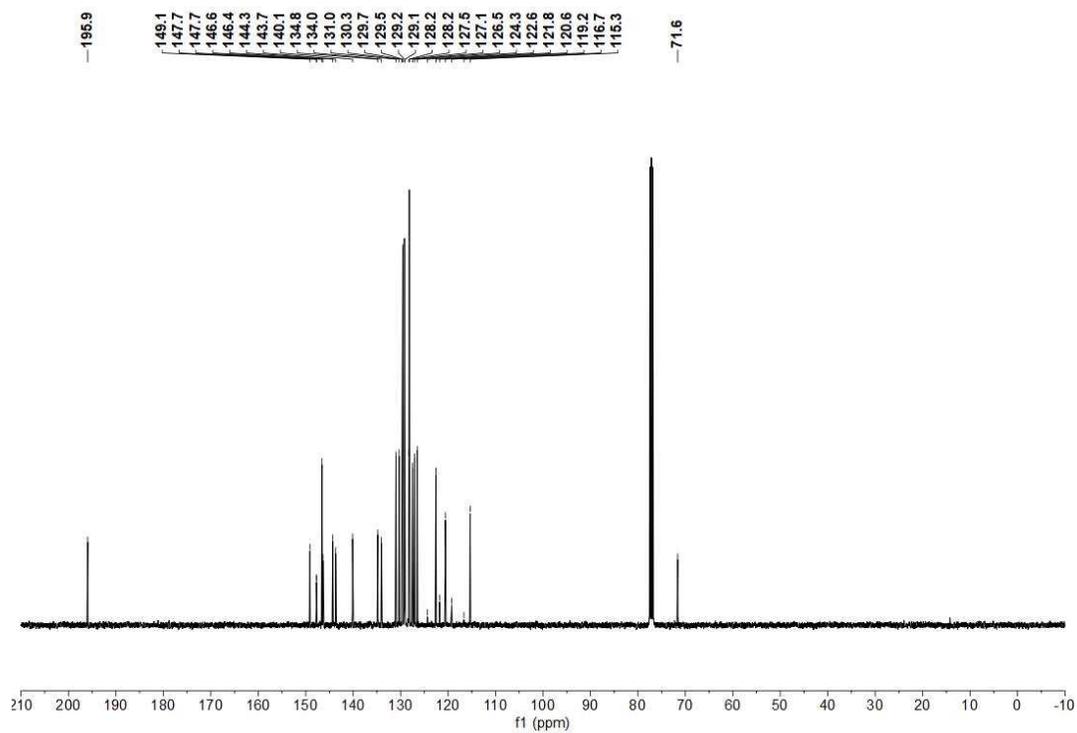
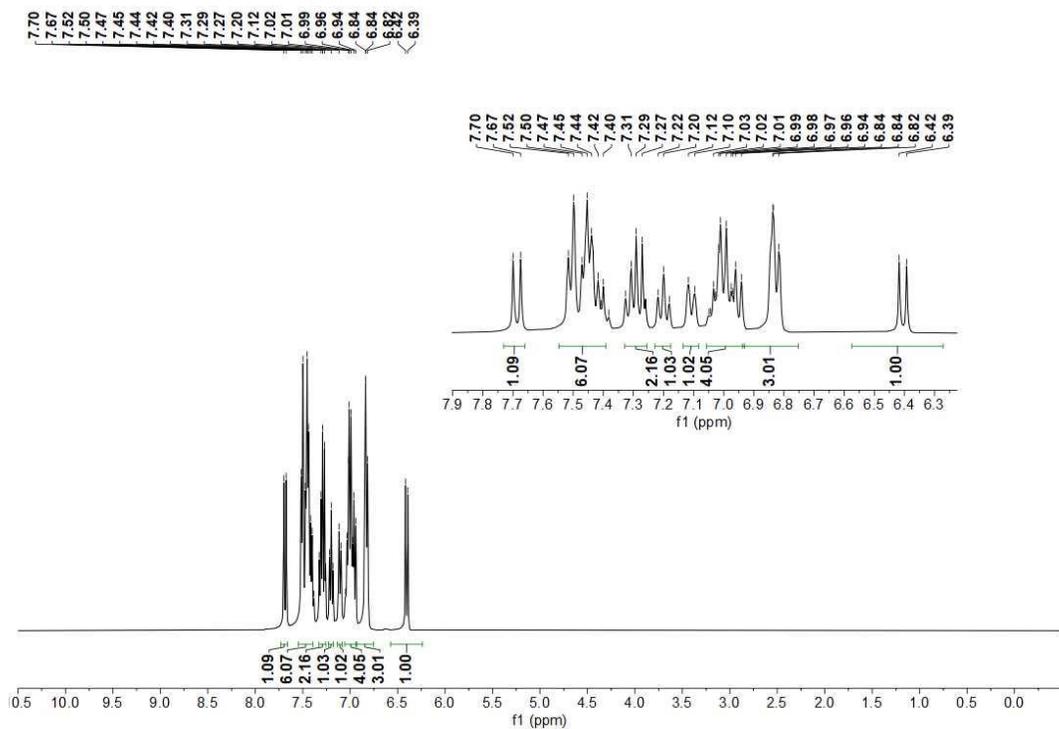
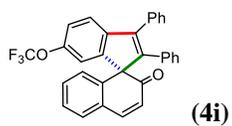


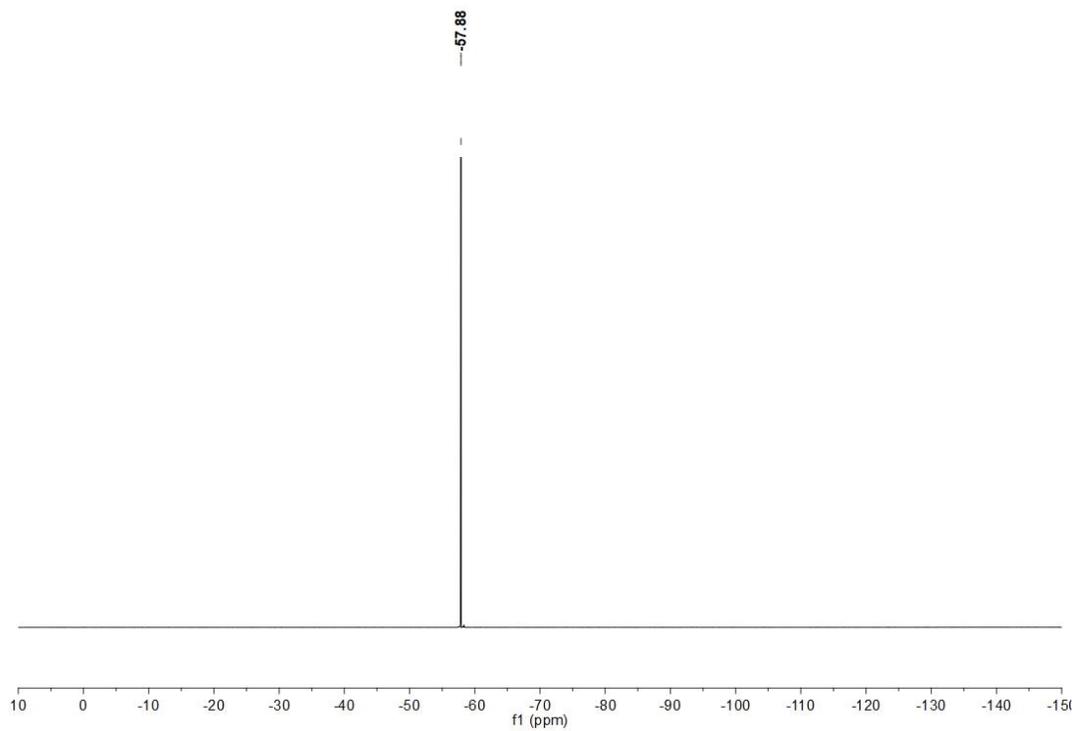
The ^1H NMR data is consistent with that reported in the literature.¹⁵

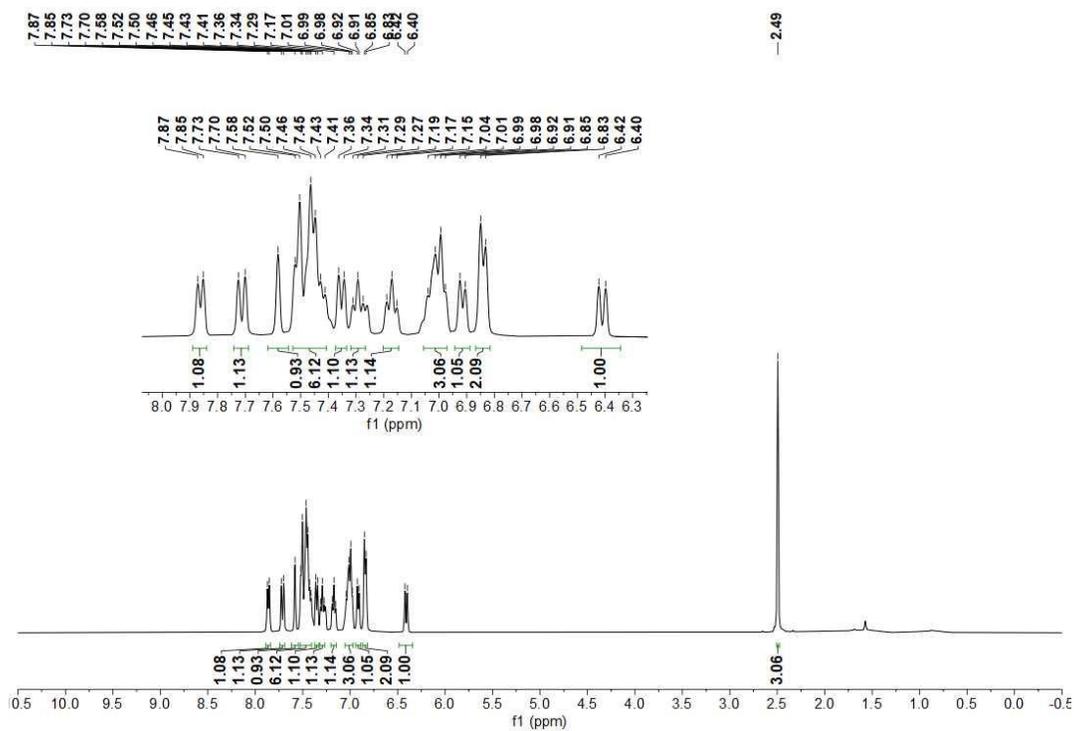
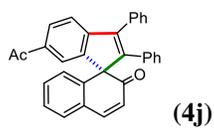


The ^1H NMR data is consistent with that reported in the literature.¹⁶

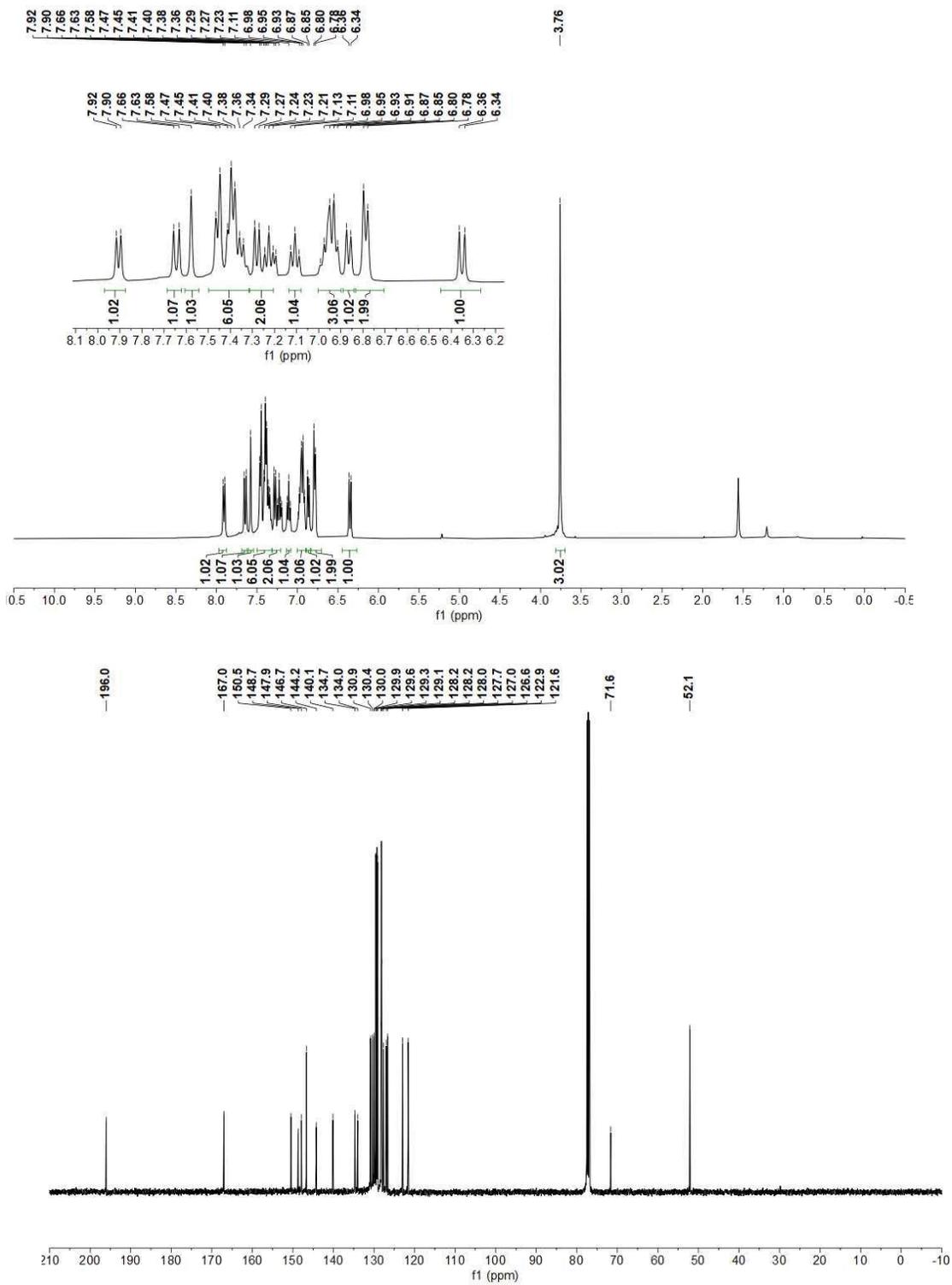
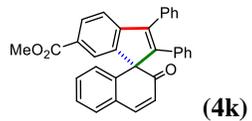


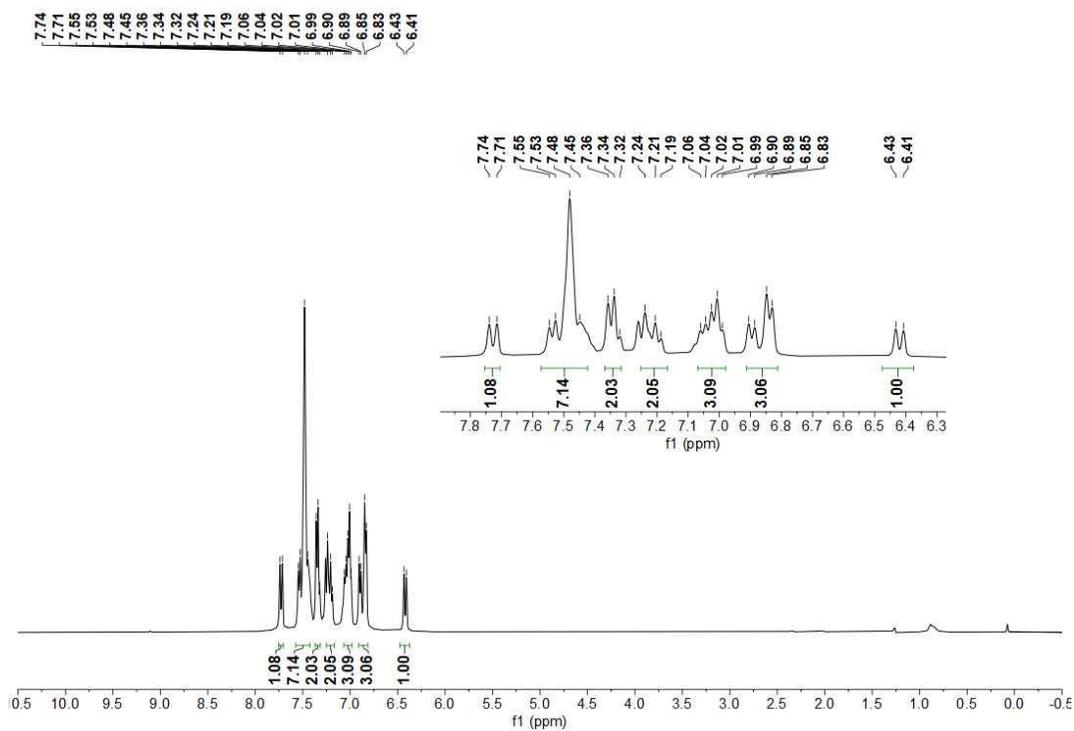
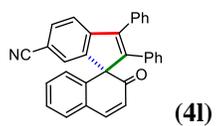




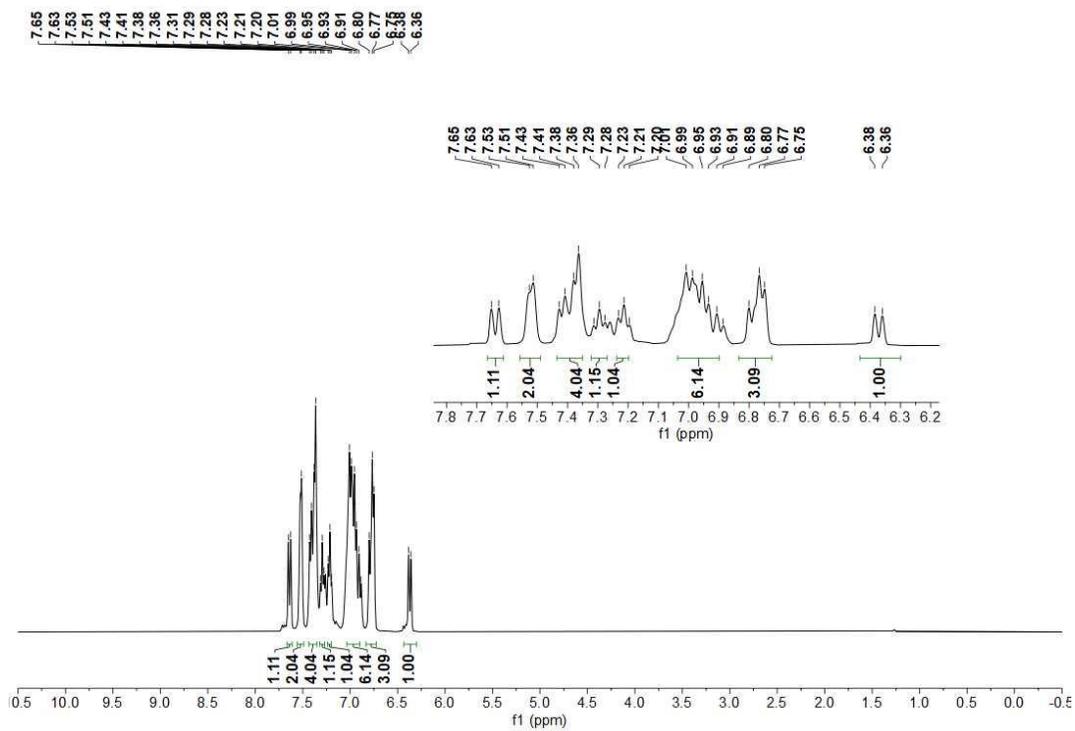
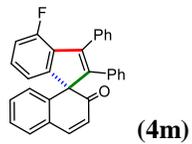


The ¹H NMR data is consistent with that reported in the literature.¹⁵

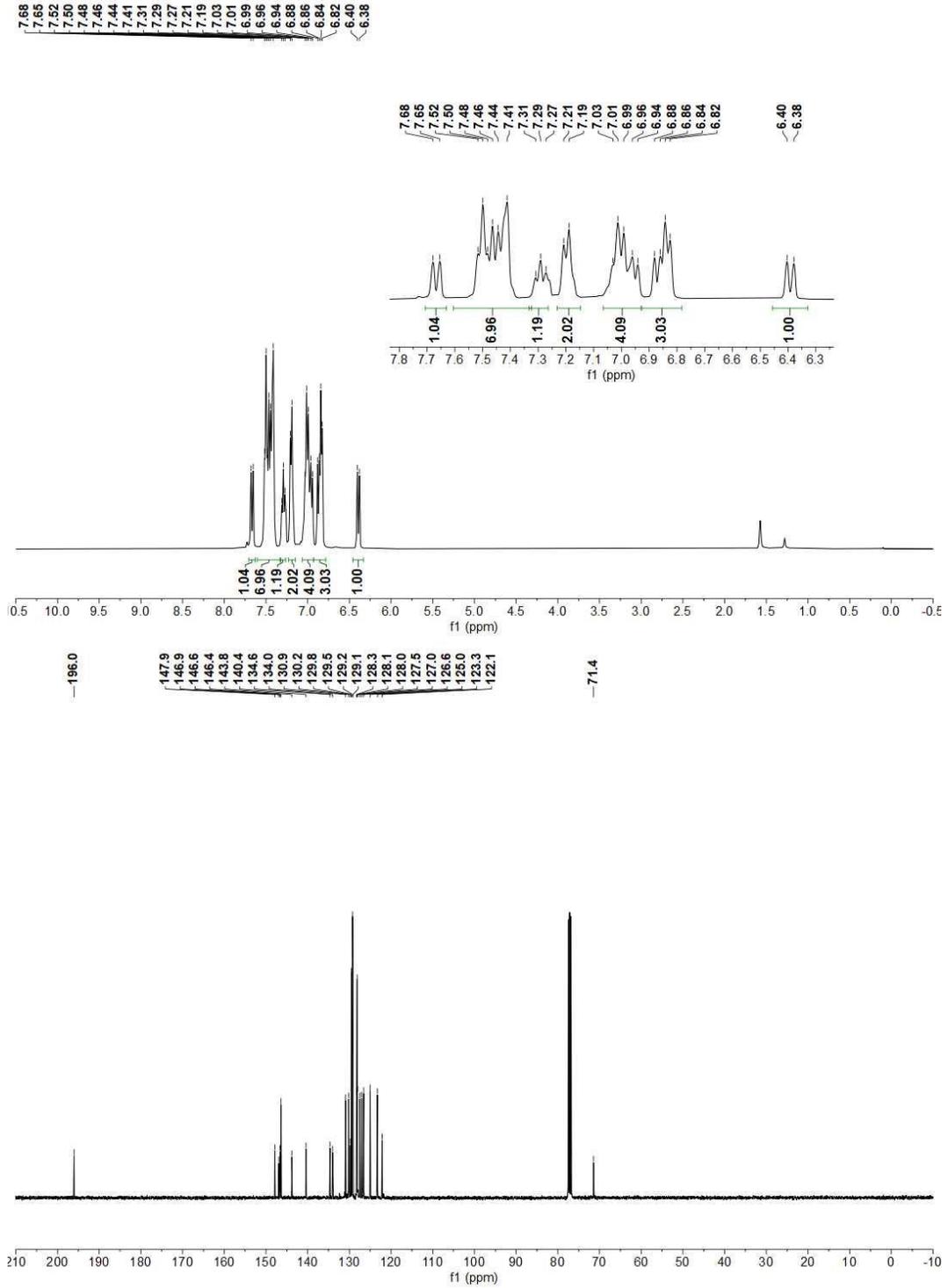
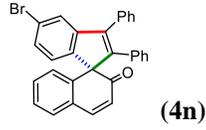


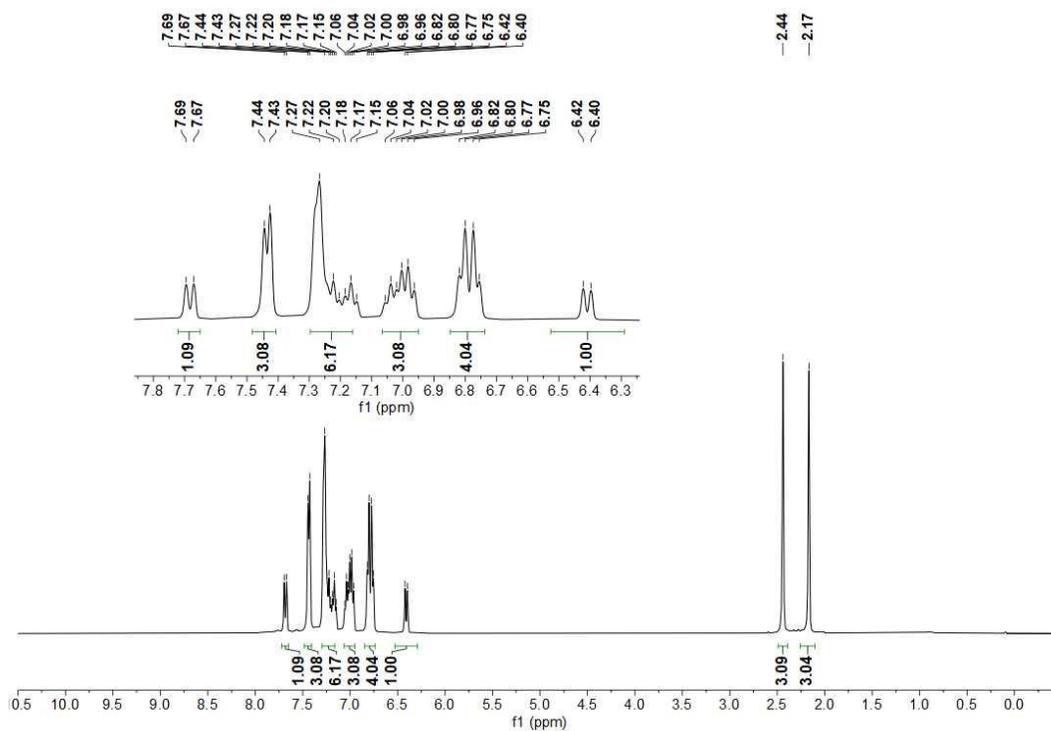
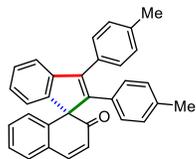


The ¹H NMR data is consistent with that reported in the literature.¹⁵

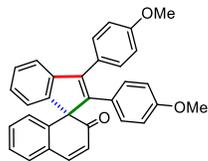


The ^1H NMR data is consistent with that reported in the literature.¹⁷

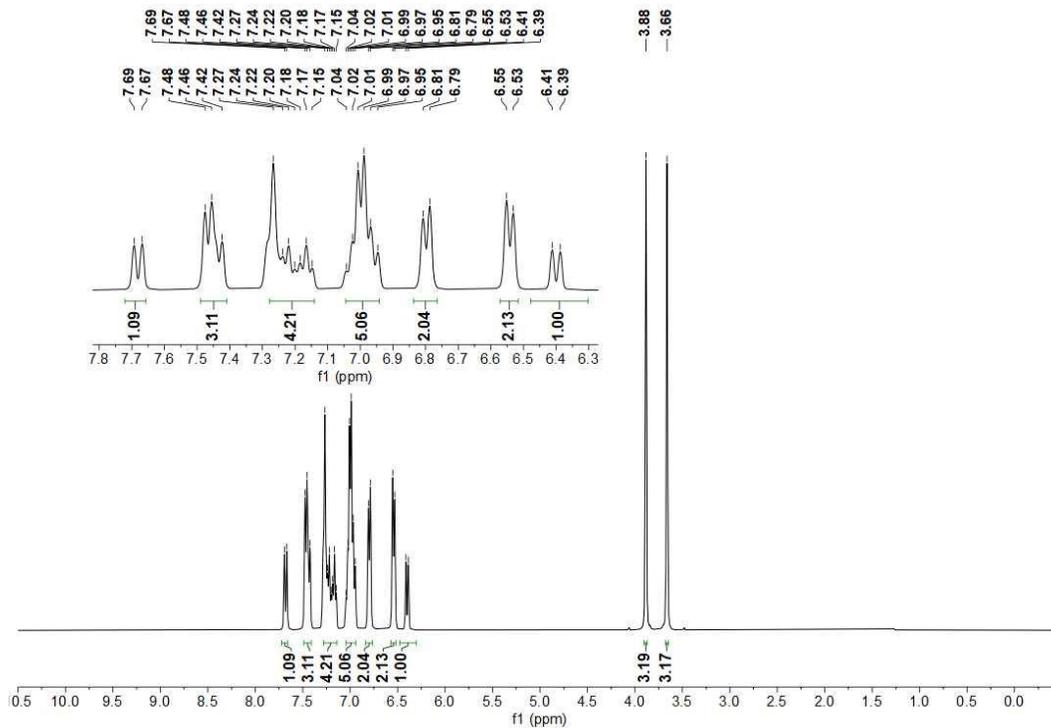




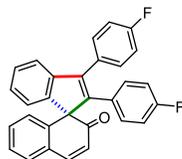
The ^1H NMR data is consistent with that reported in the literature.¹⁵



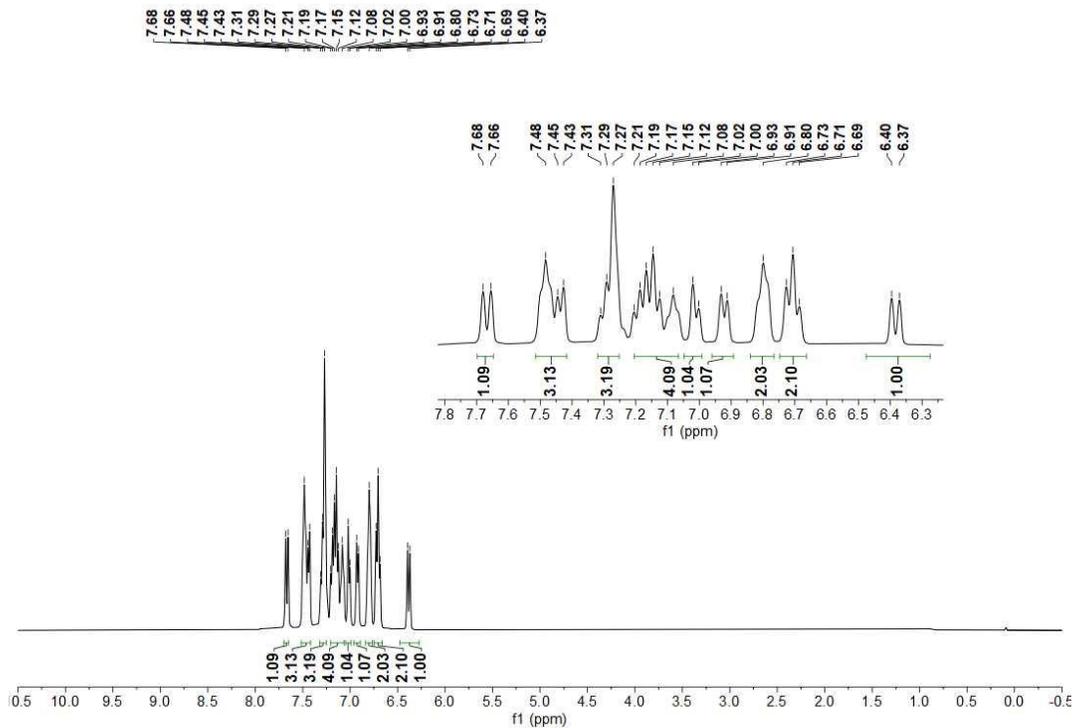
(4b')



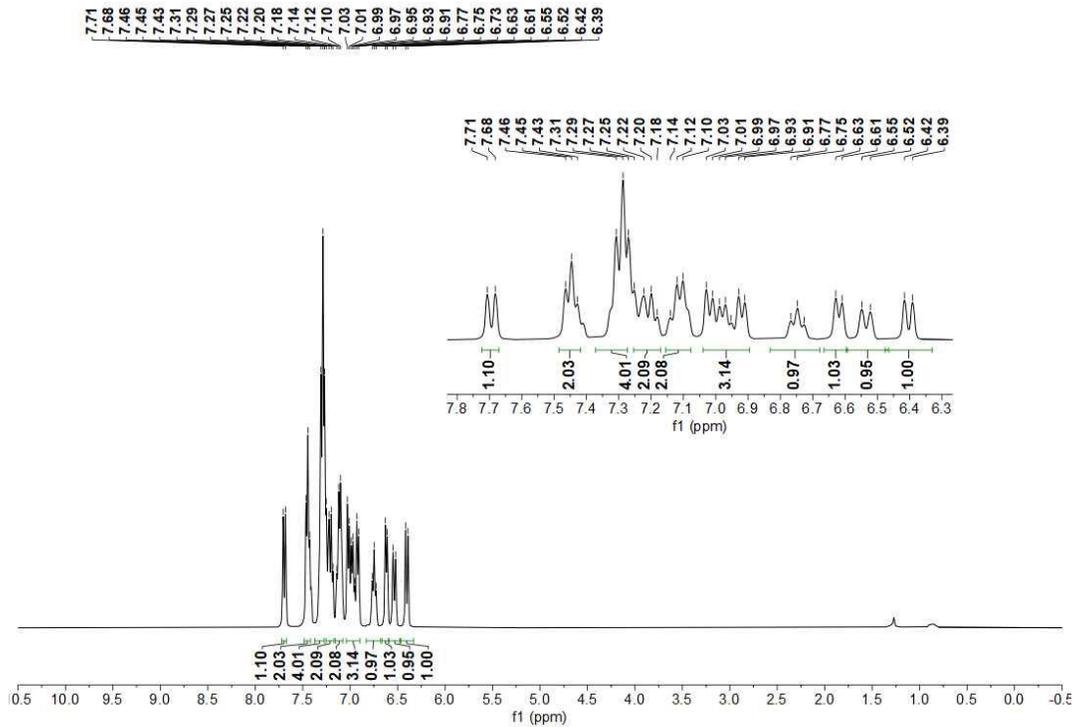
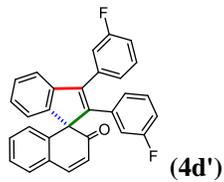
The ^1H NMR data is consistent with that reported in the literature.¹⁵



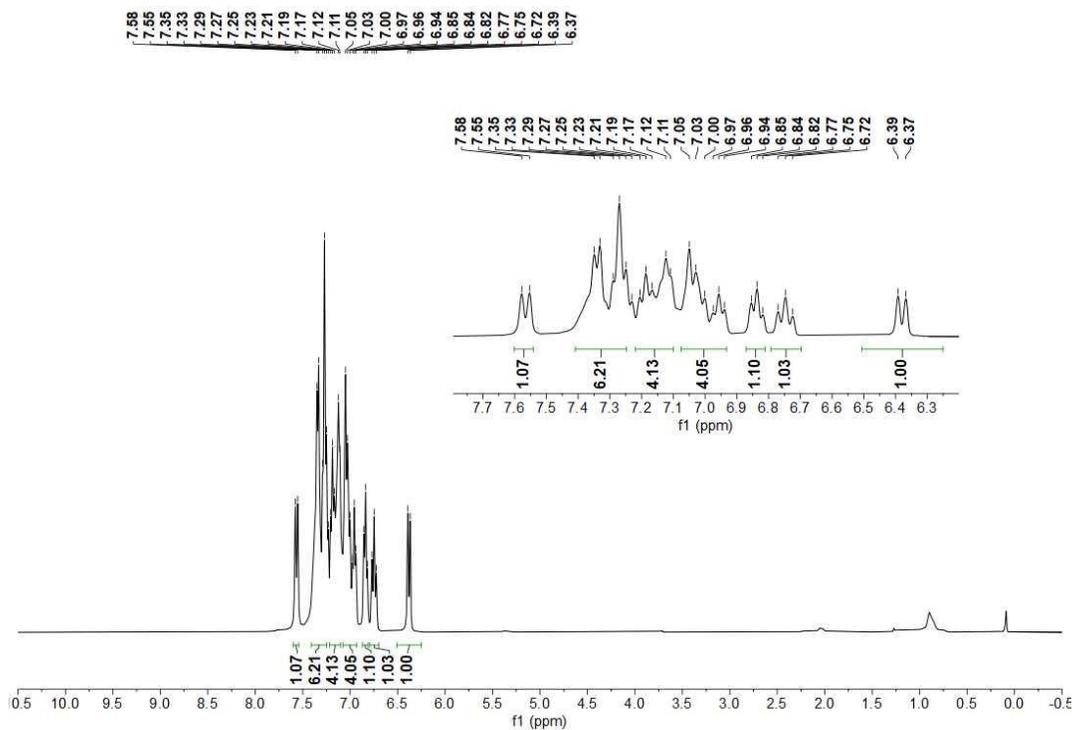
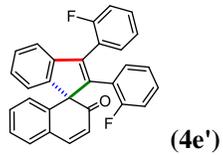
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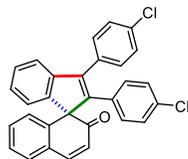
The ^1H NMR data is consistent with that reported in the literature.¹⁵



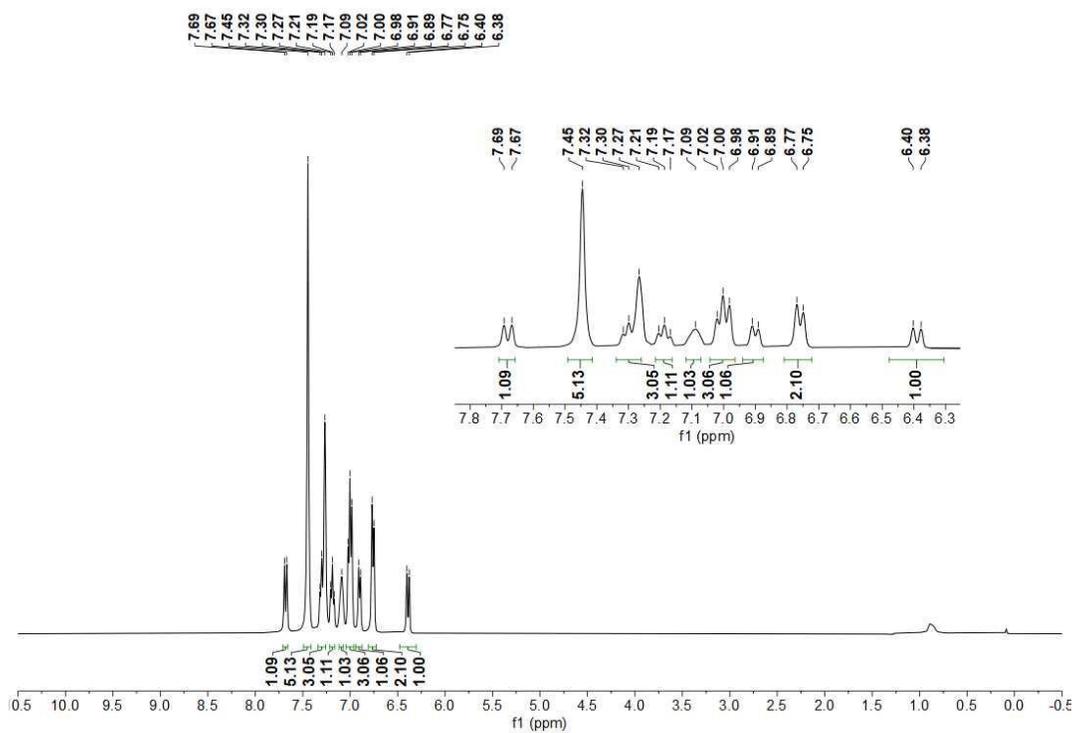
The ¹H NMR data is consistent with that reported in the literature.¹⁵



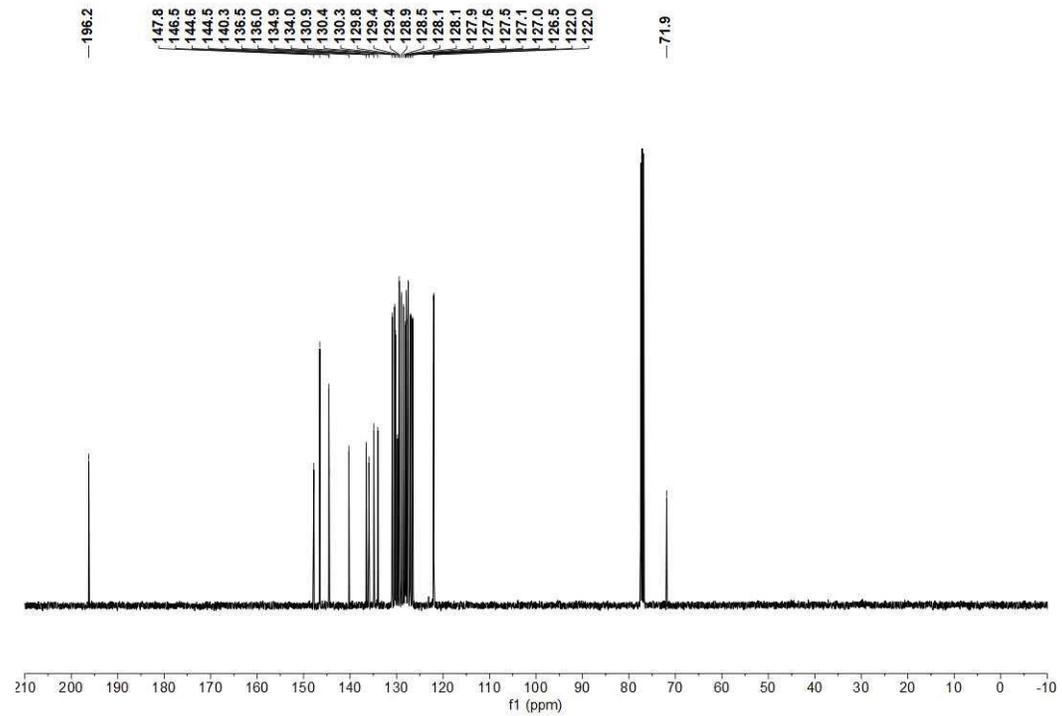
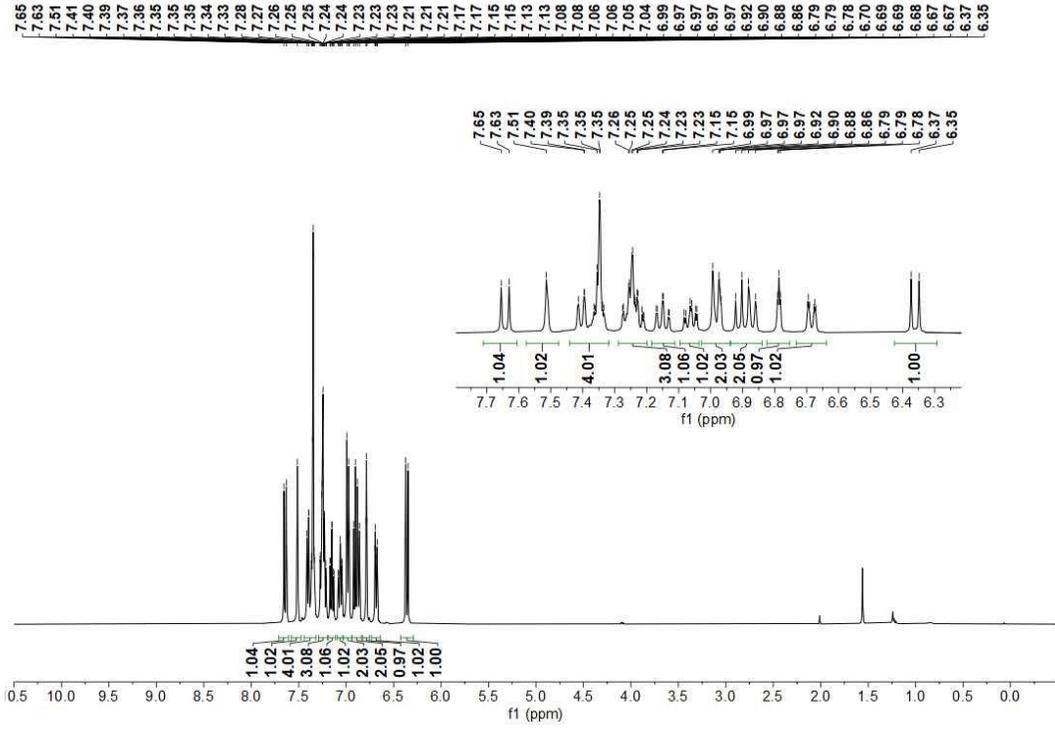
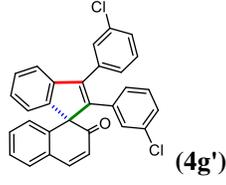
The ^1H NMR data is consistent with that reported in the literature.¹⁶

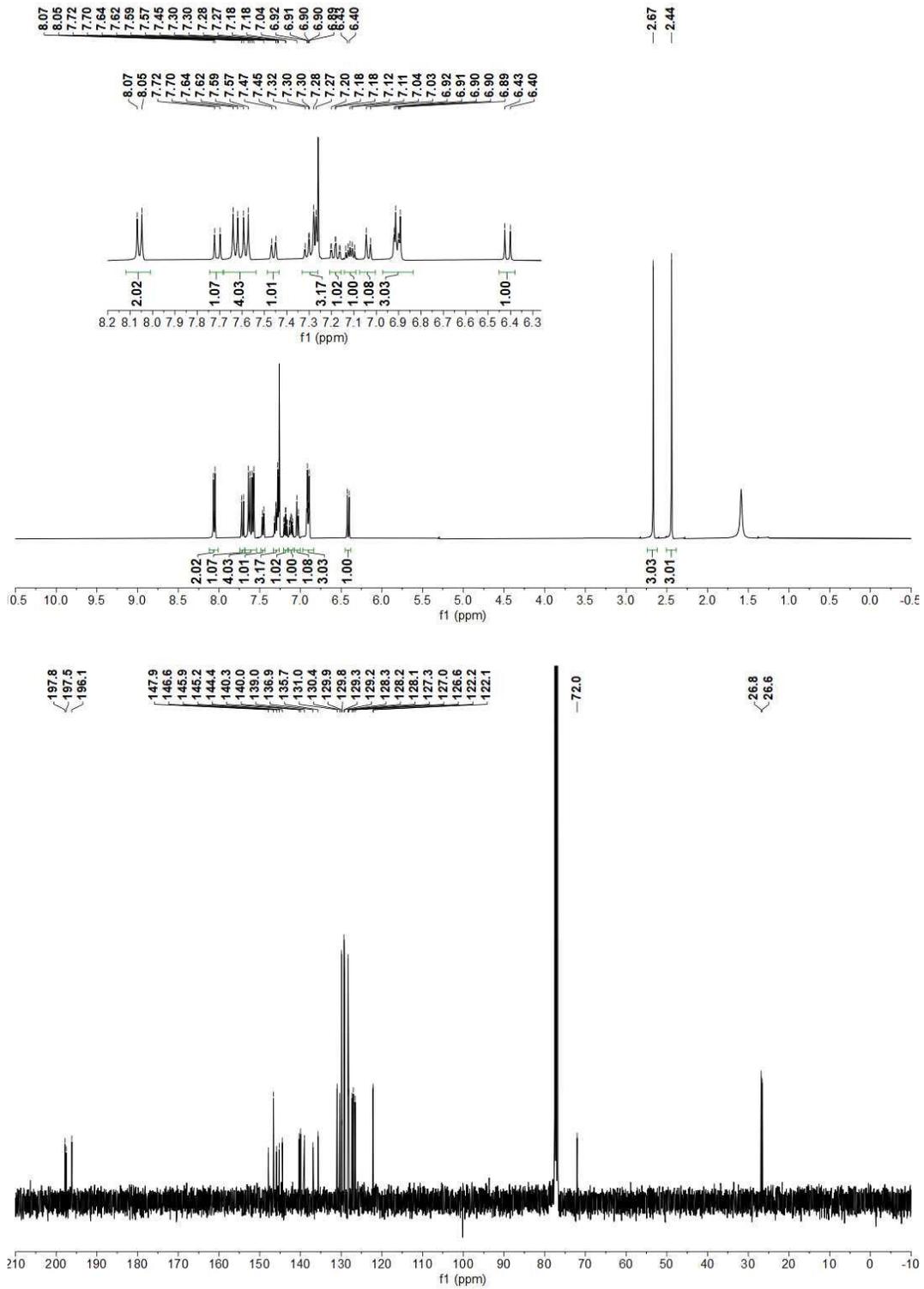
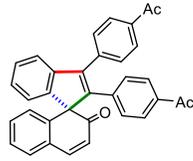


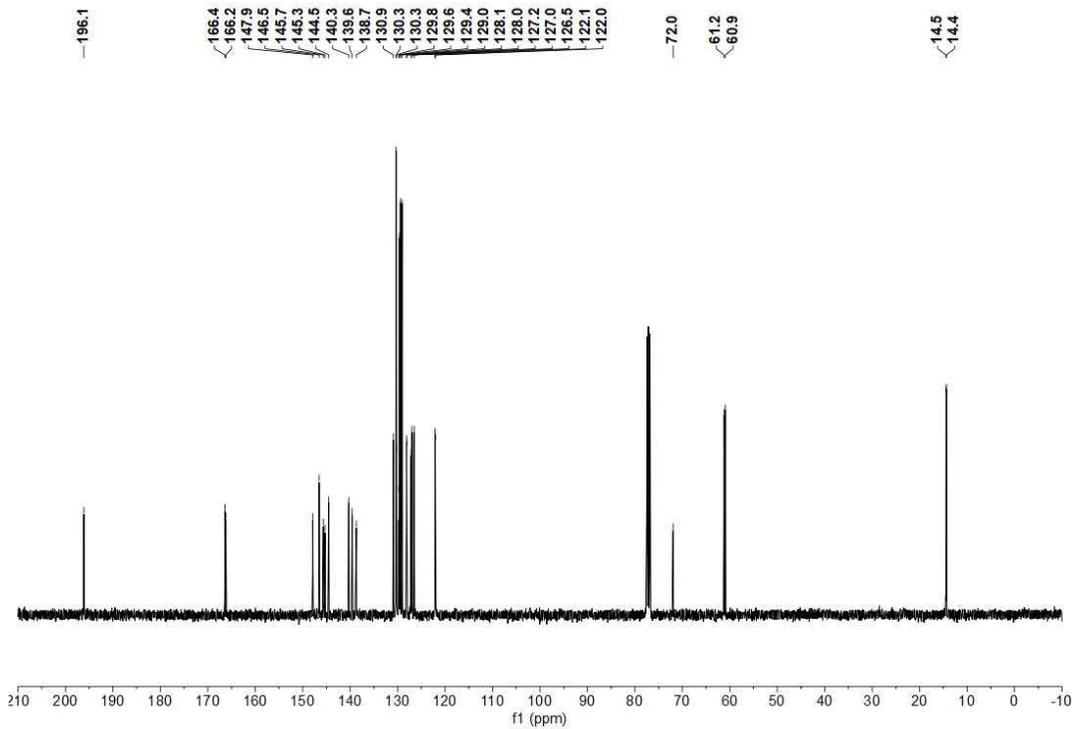
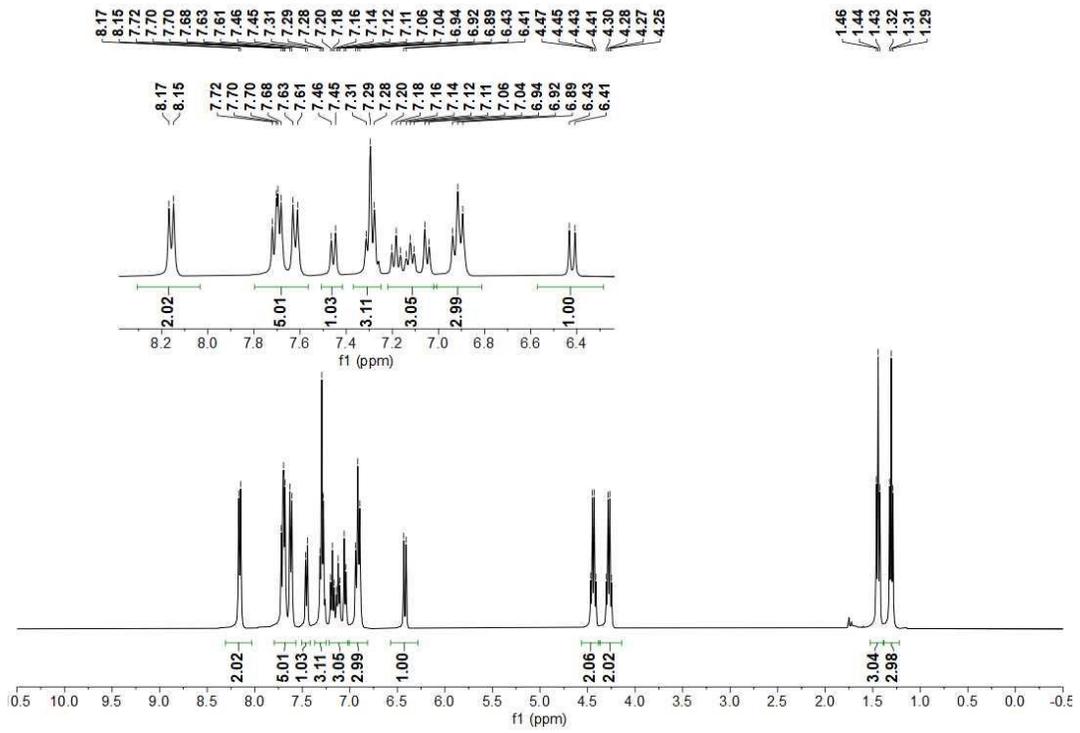
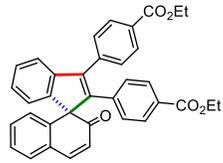
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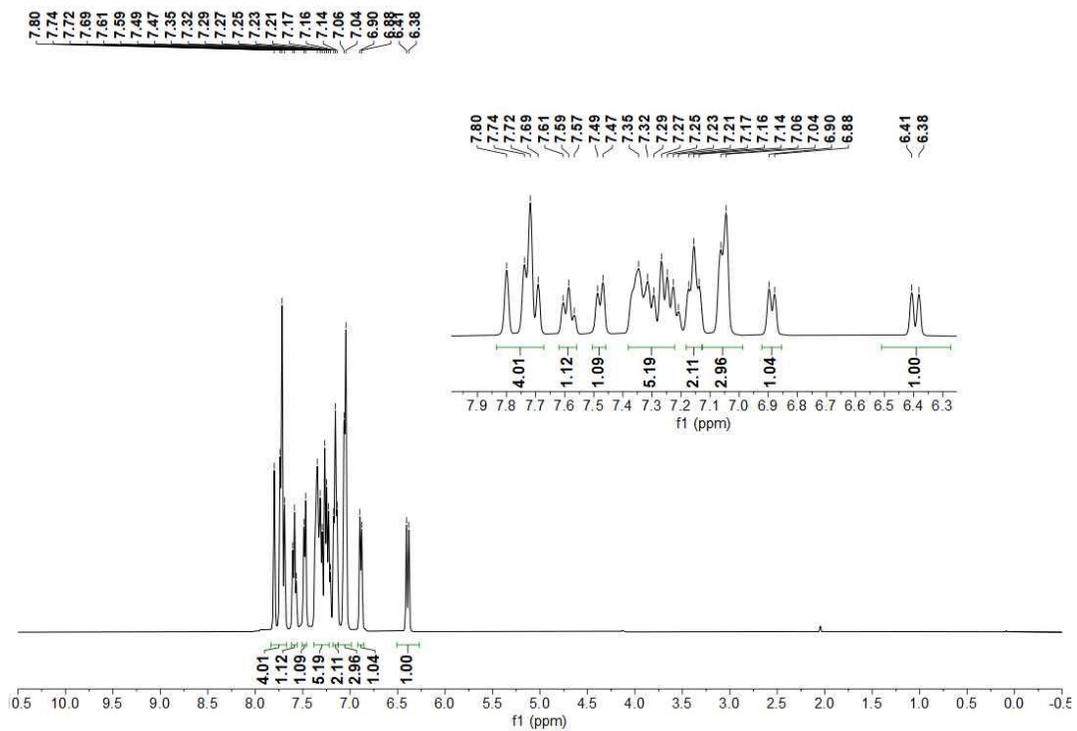
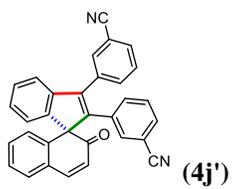


The ¹H NMR data is consistent with that reported in the literature.¹⁵

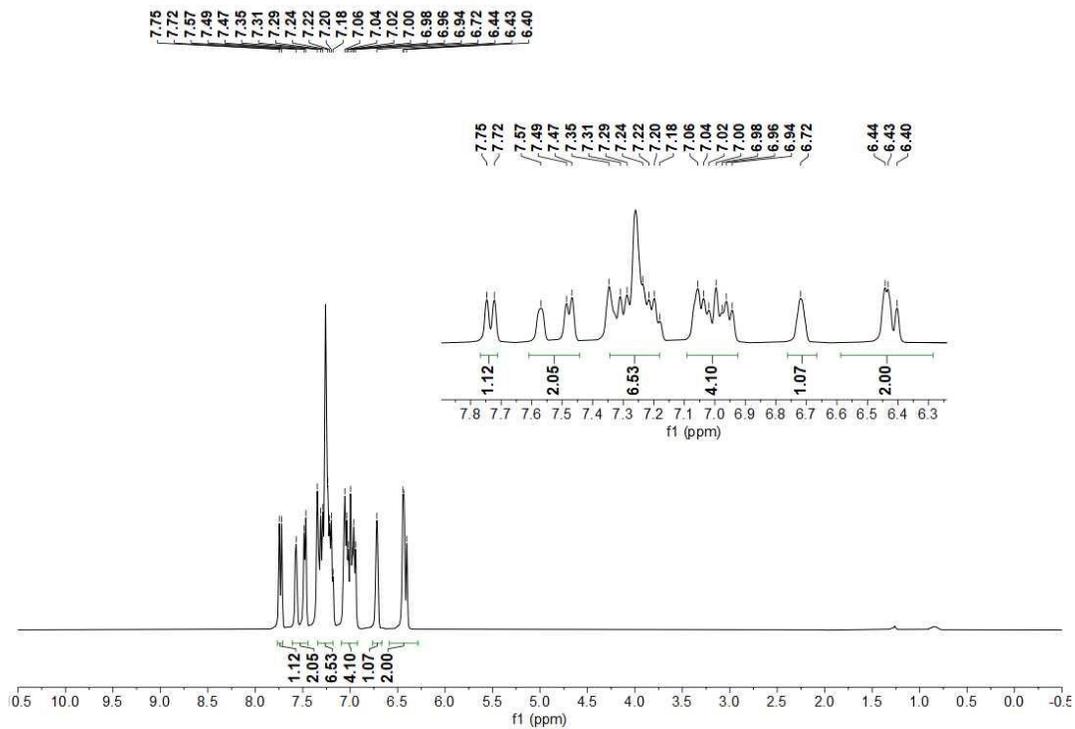
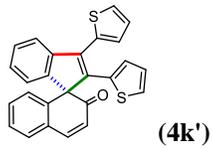




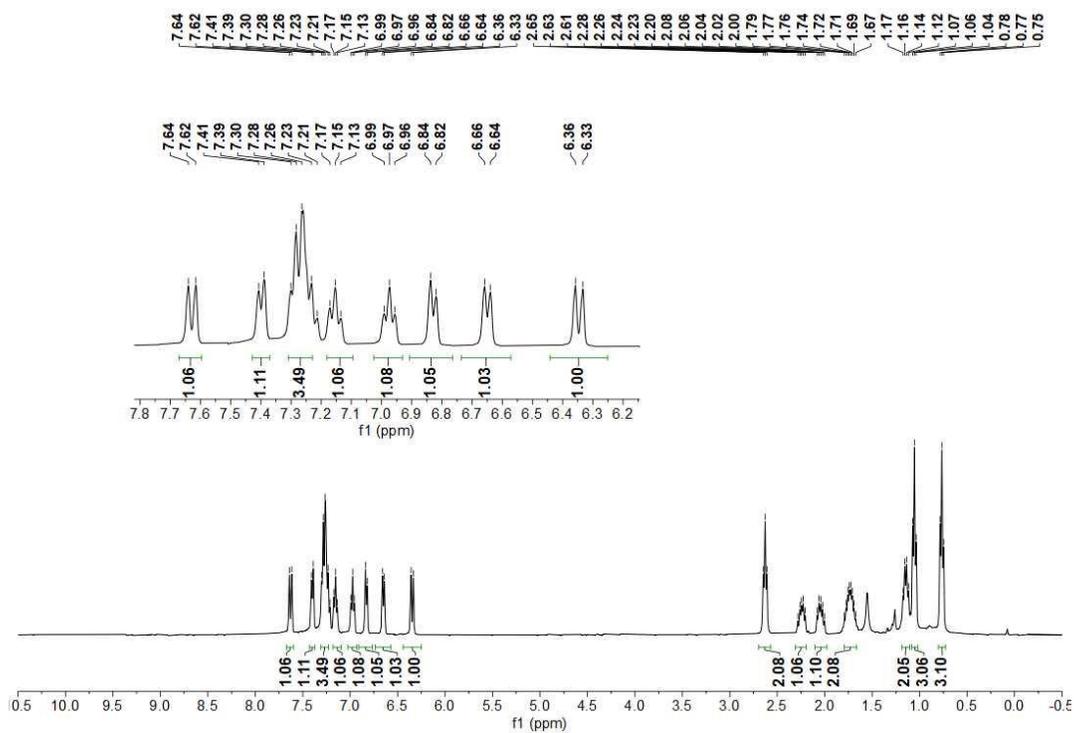
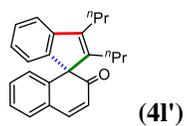




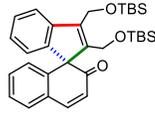
The ^1H NMR data is consistent with that reported in the literature.¹⁵



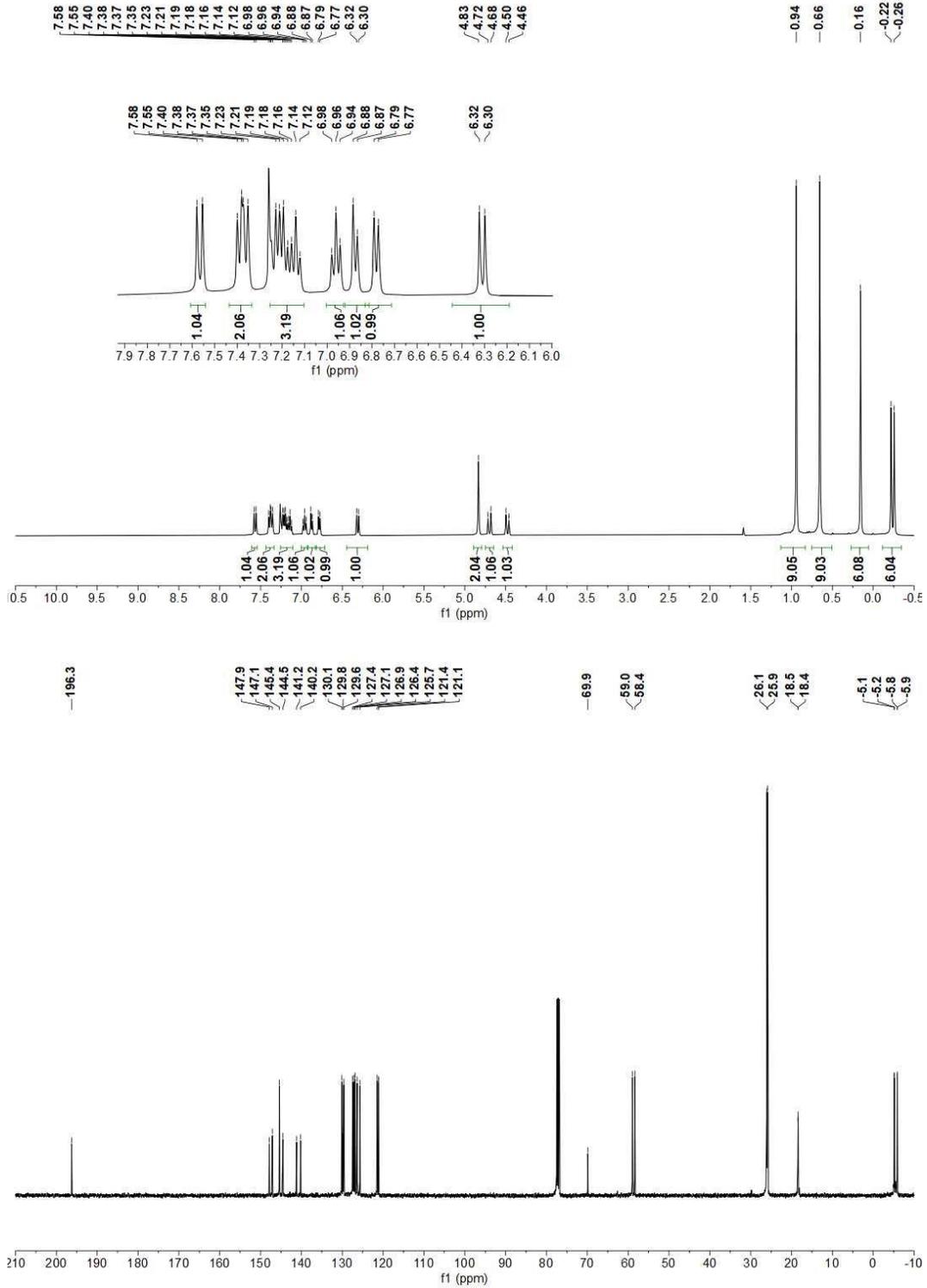
The ^1H NMR data is consistent with that reported in the literature.¹⁶

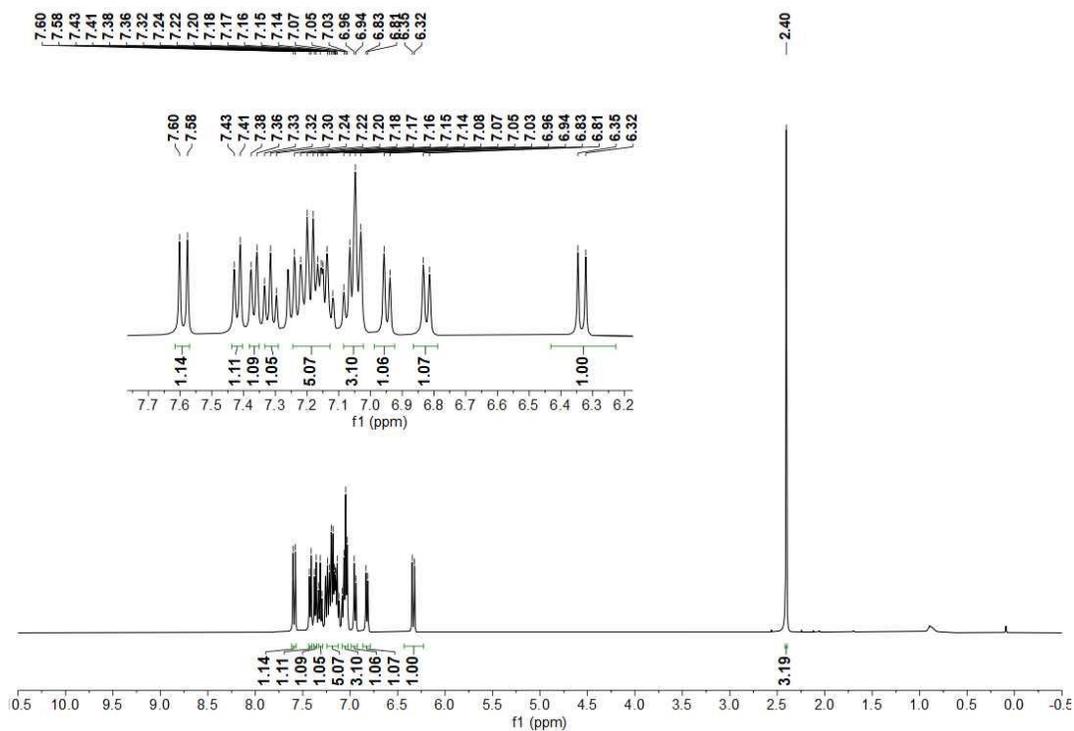
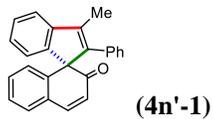


The ¹H NMR data is consistent with that reported in the literature.¹⁶

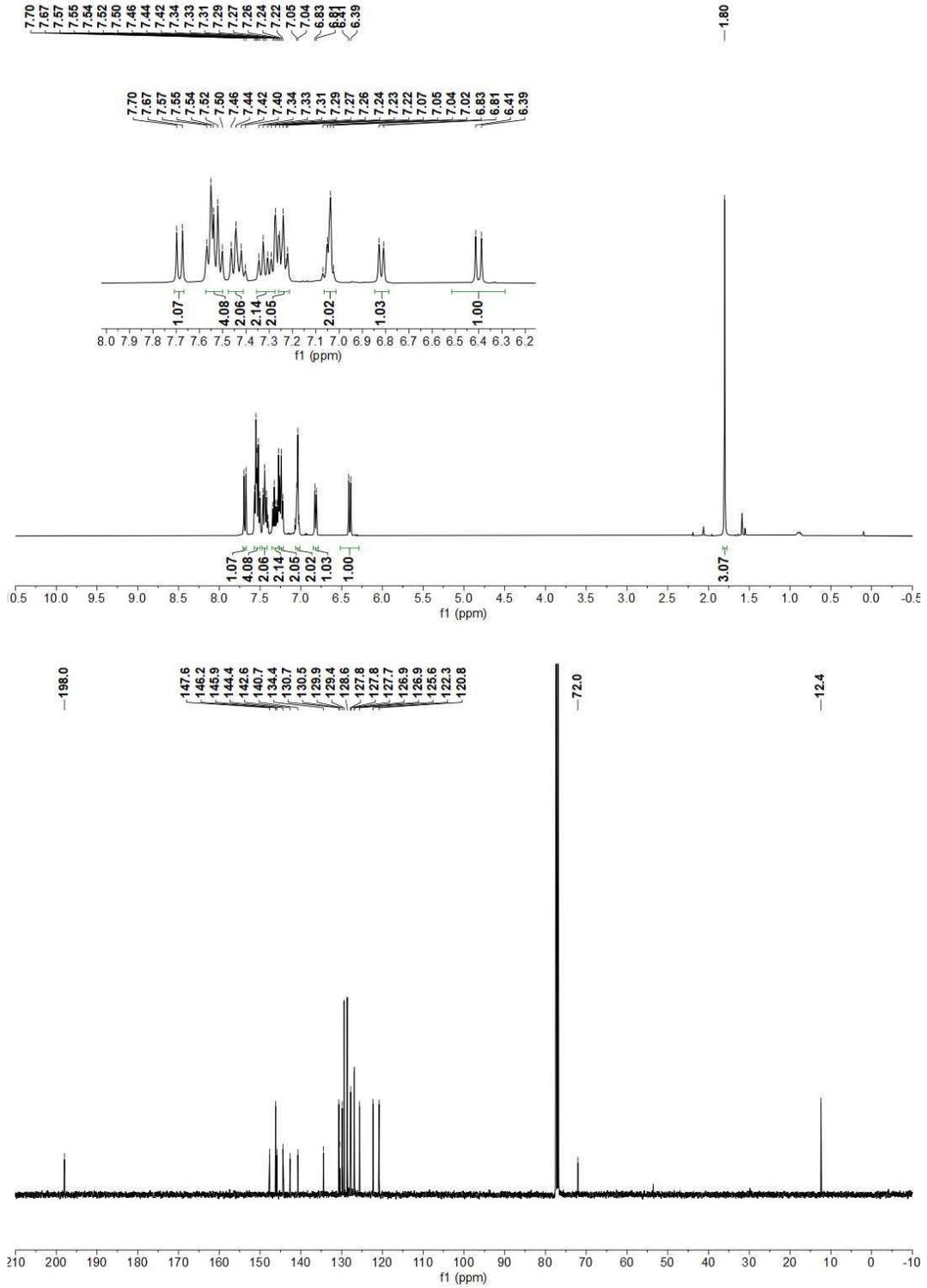
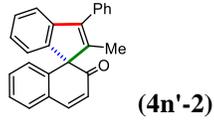


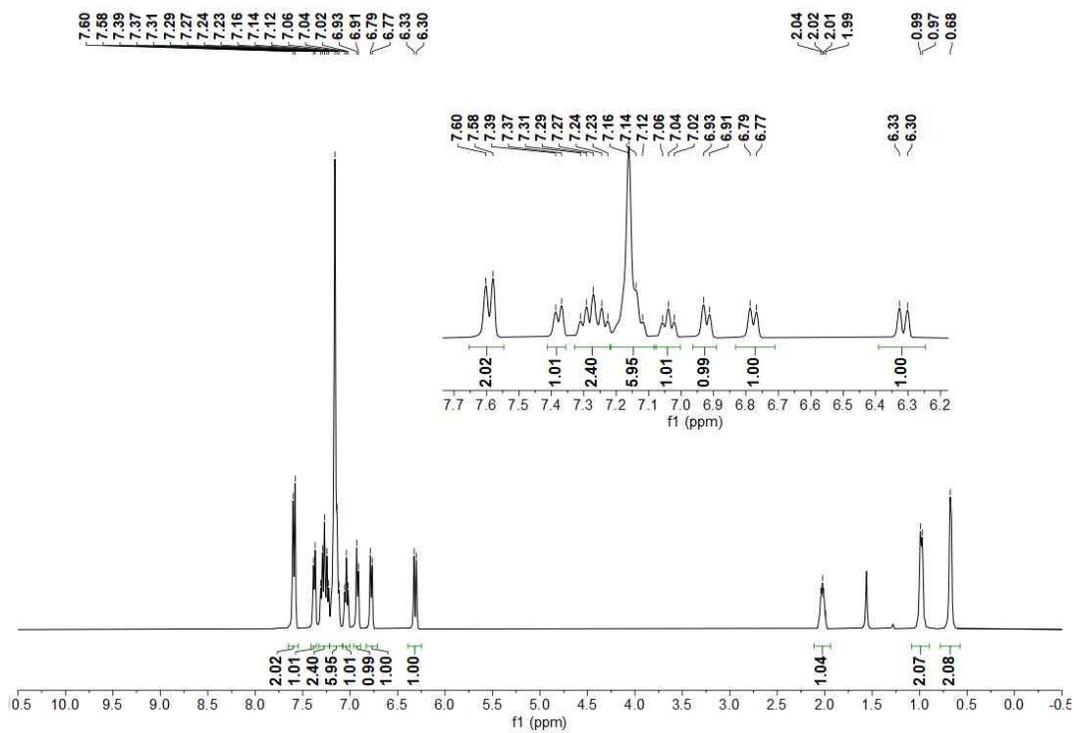
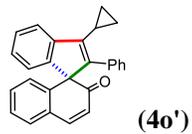
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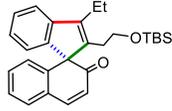


The ^1H NMR data is consistent with that reported in the literature.¹⁴

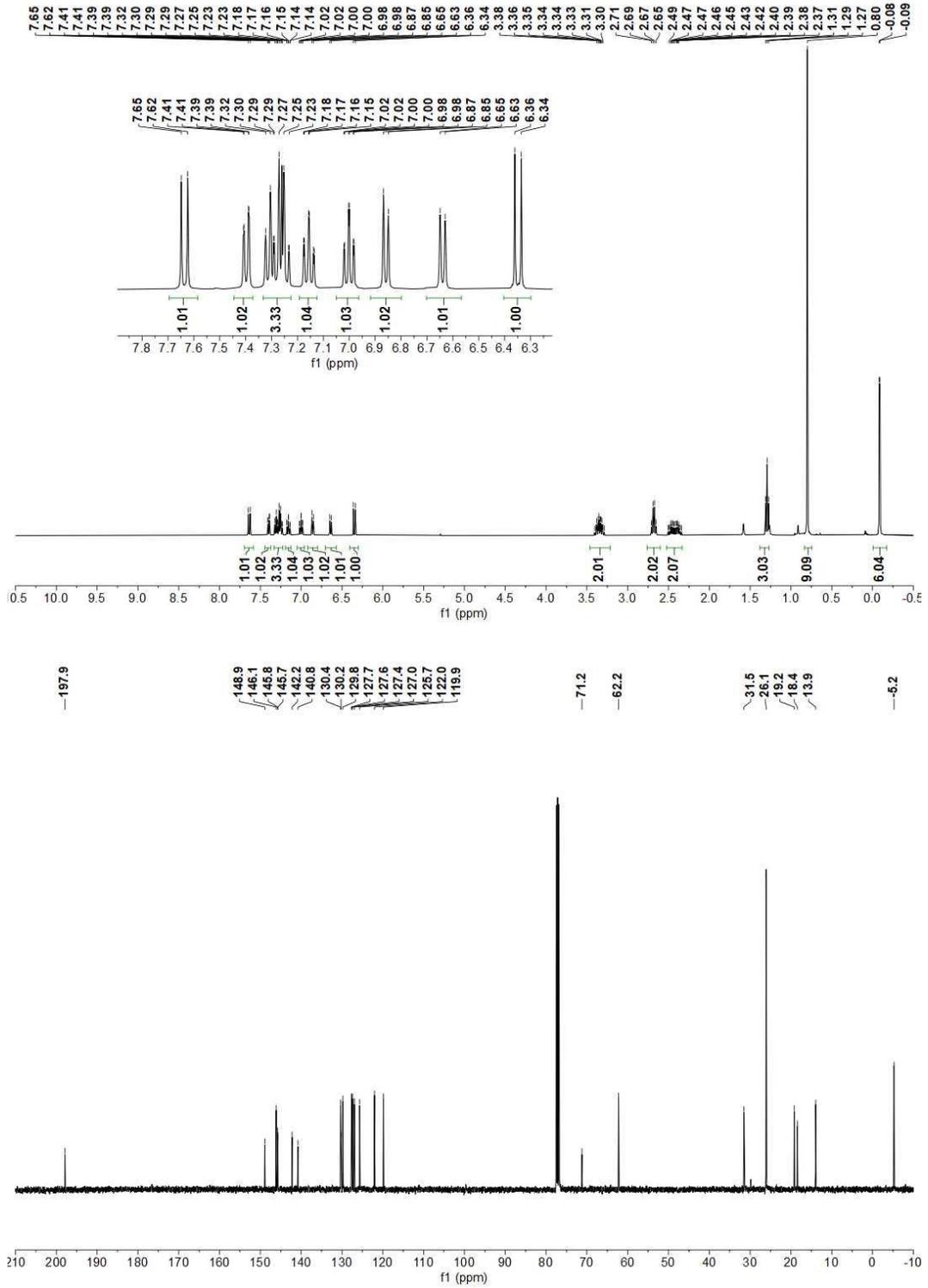


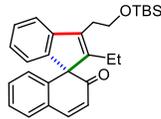


The ¹H NMR data is consistent with that reported in the literature.¹⁶

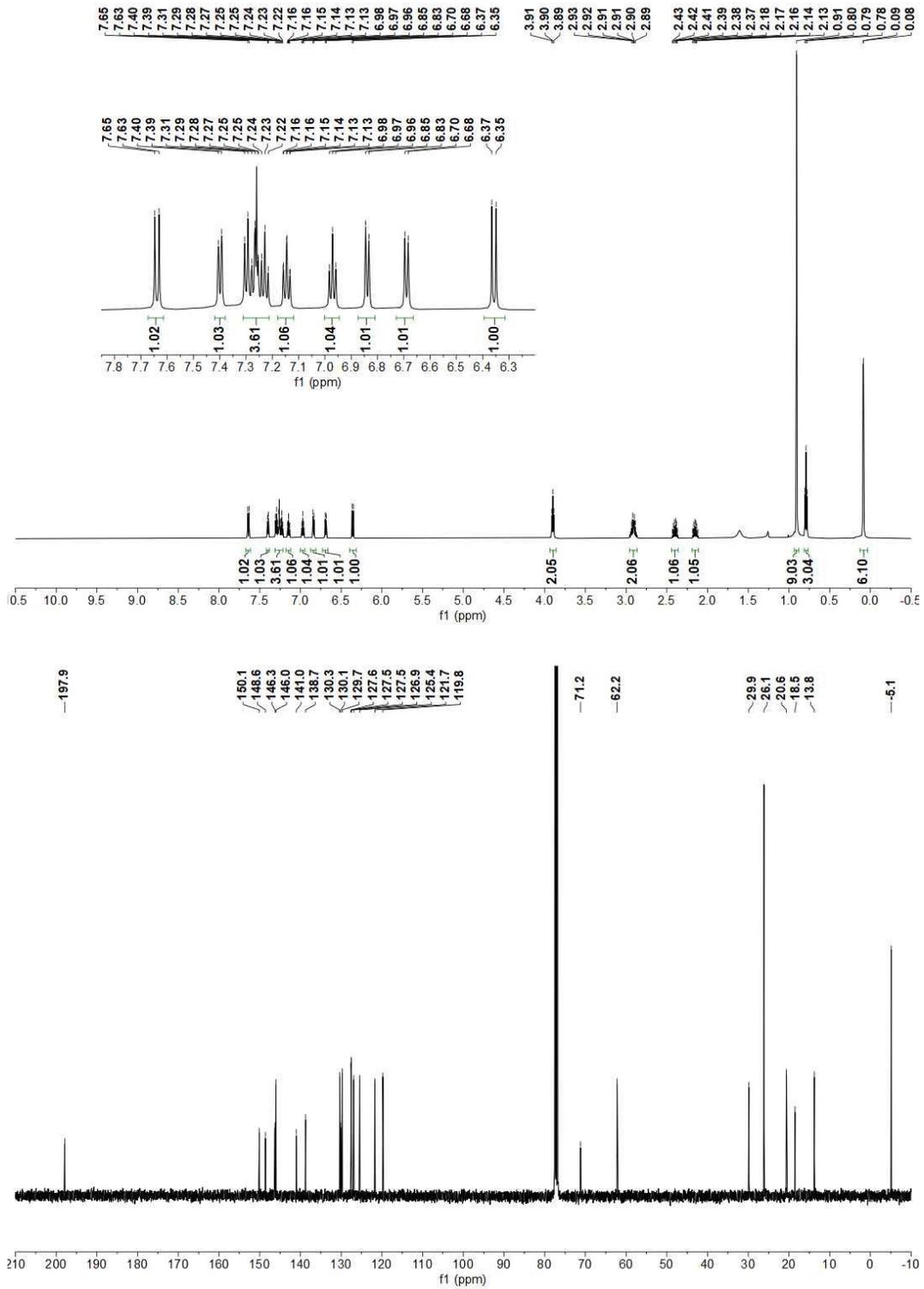


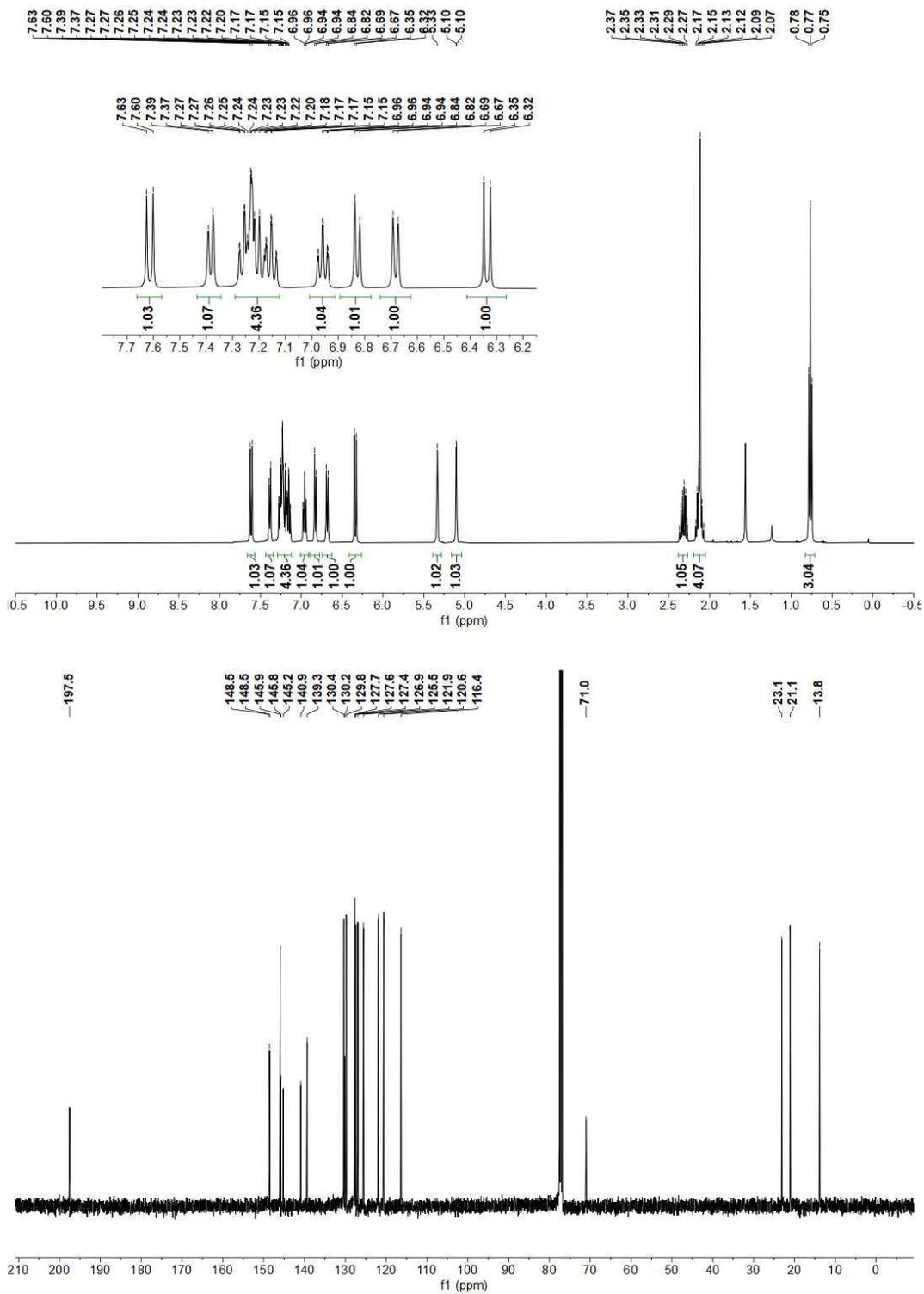
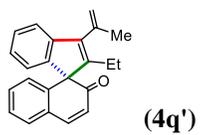
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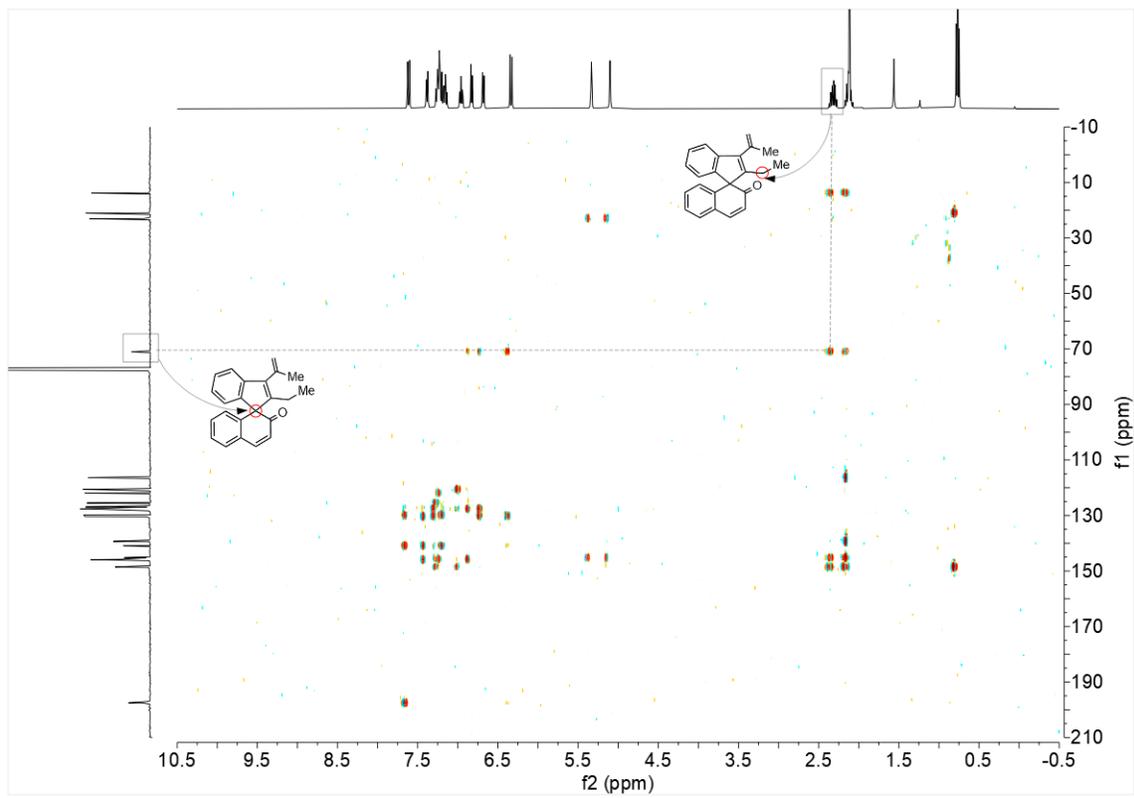


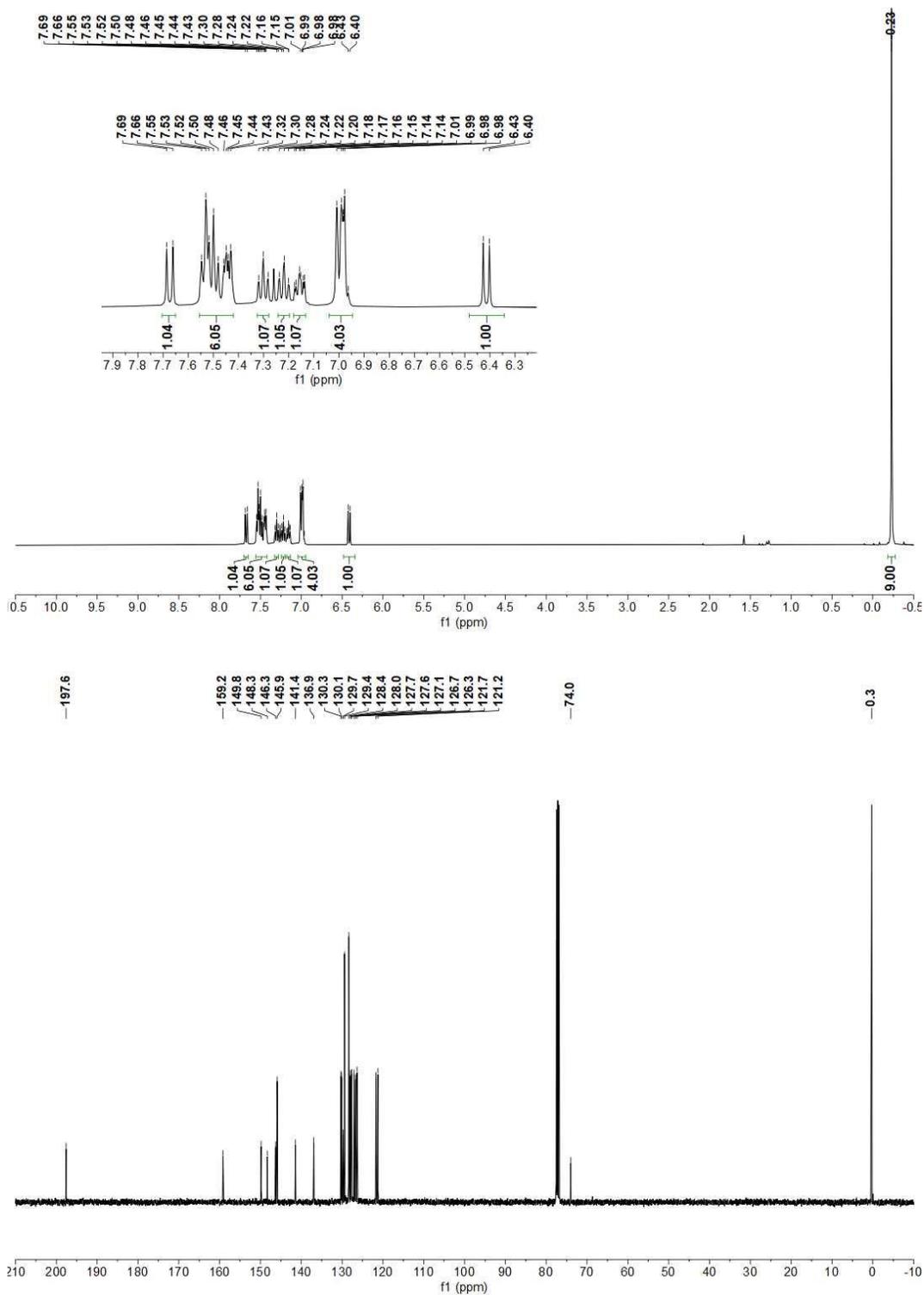
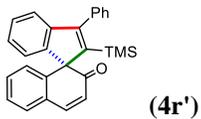
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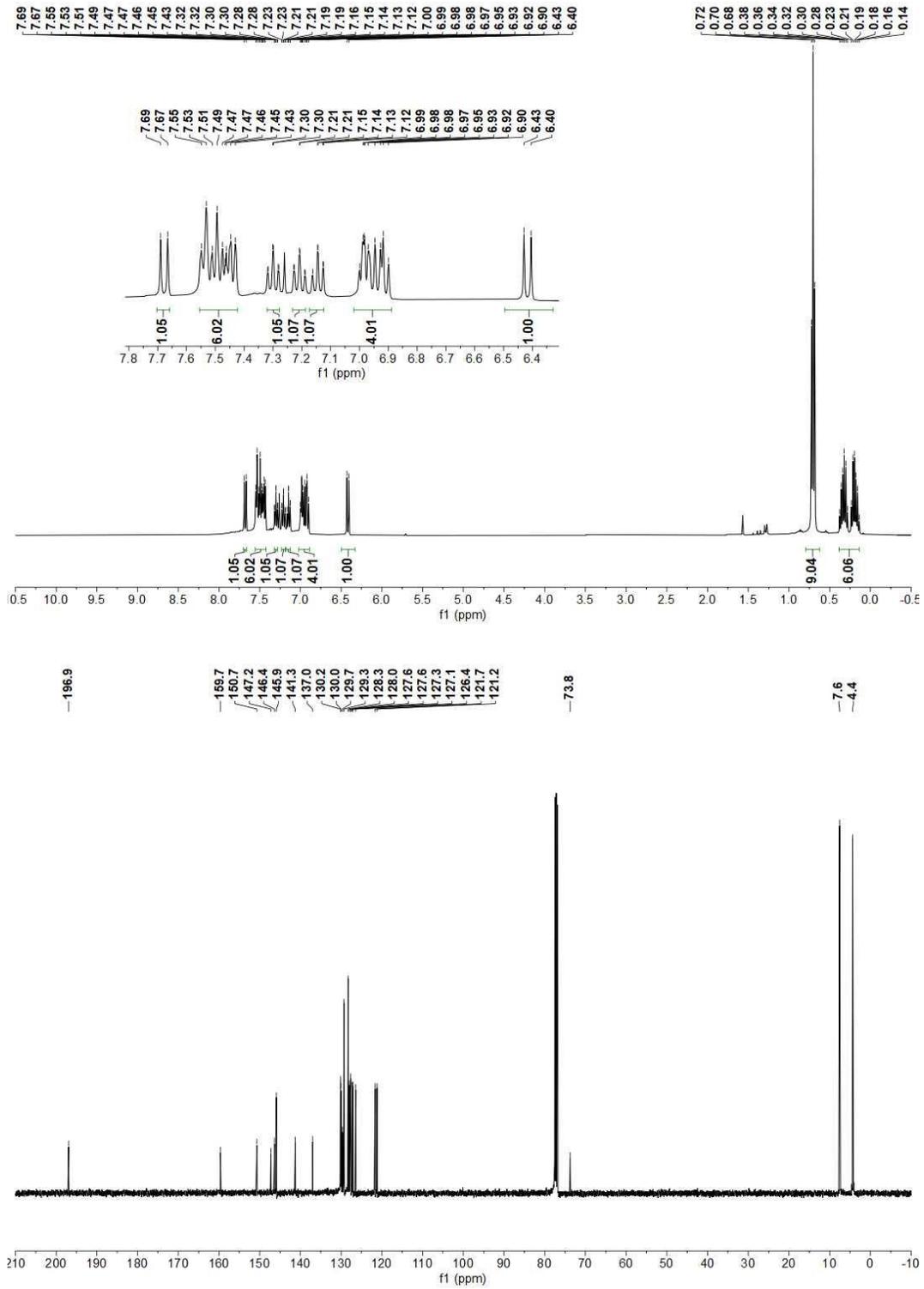
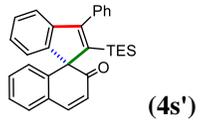


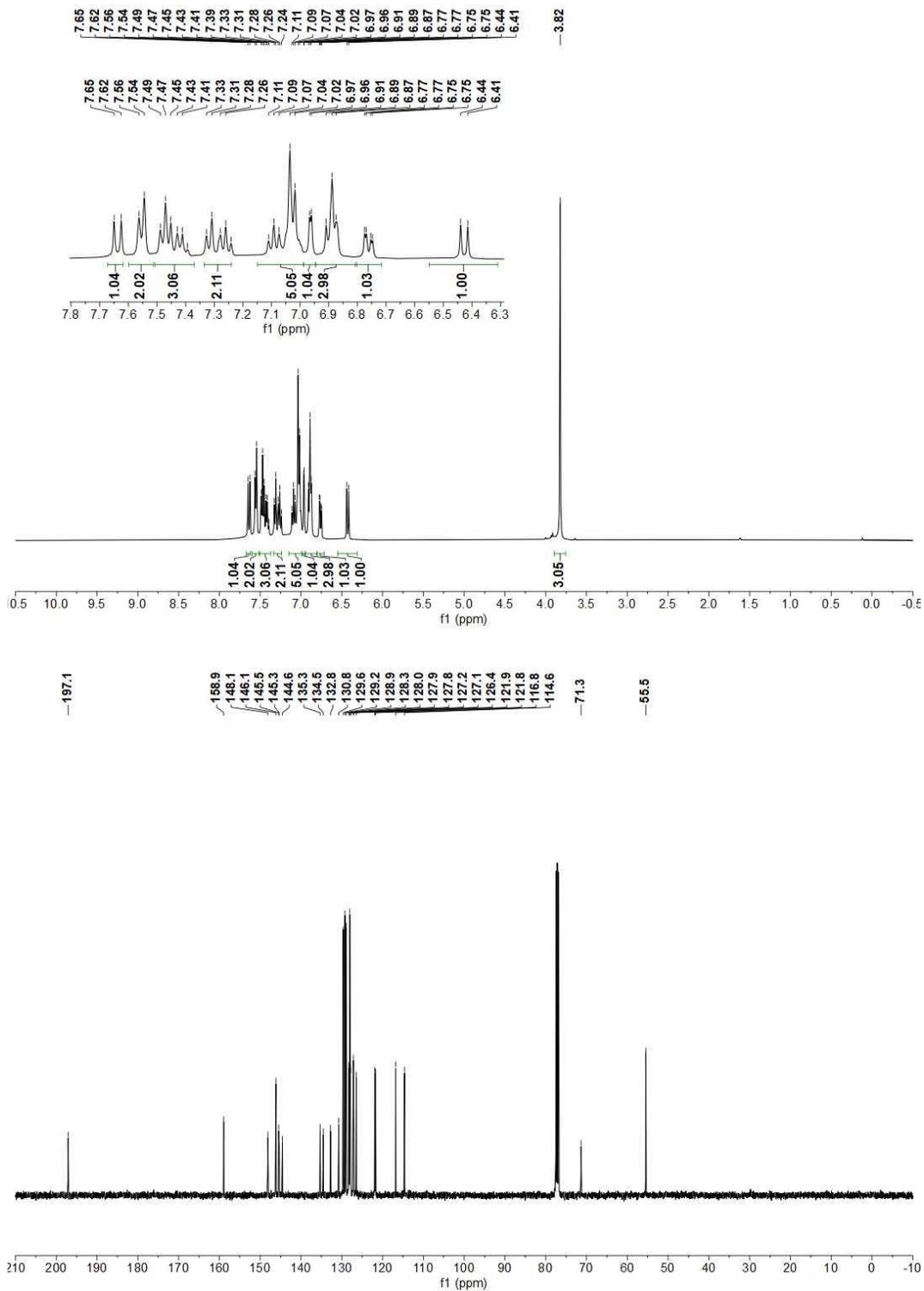
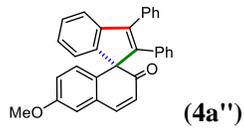


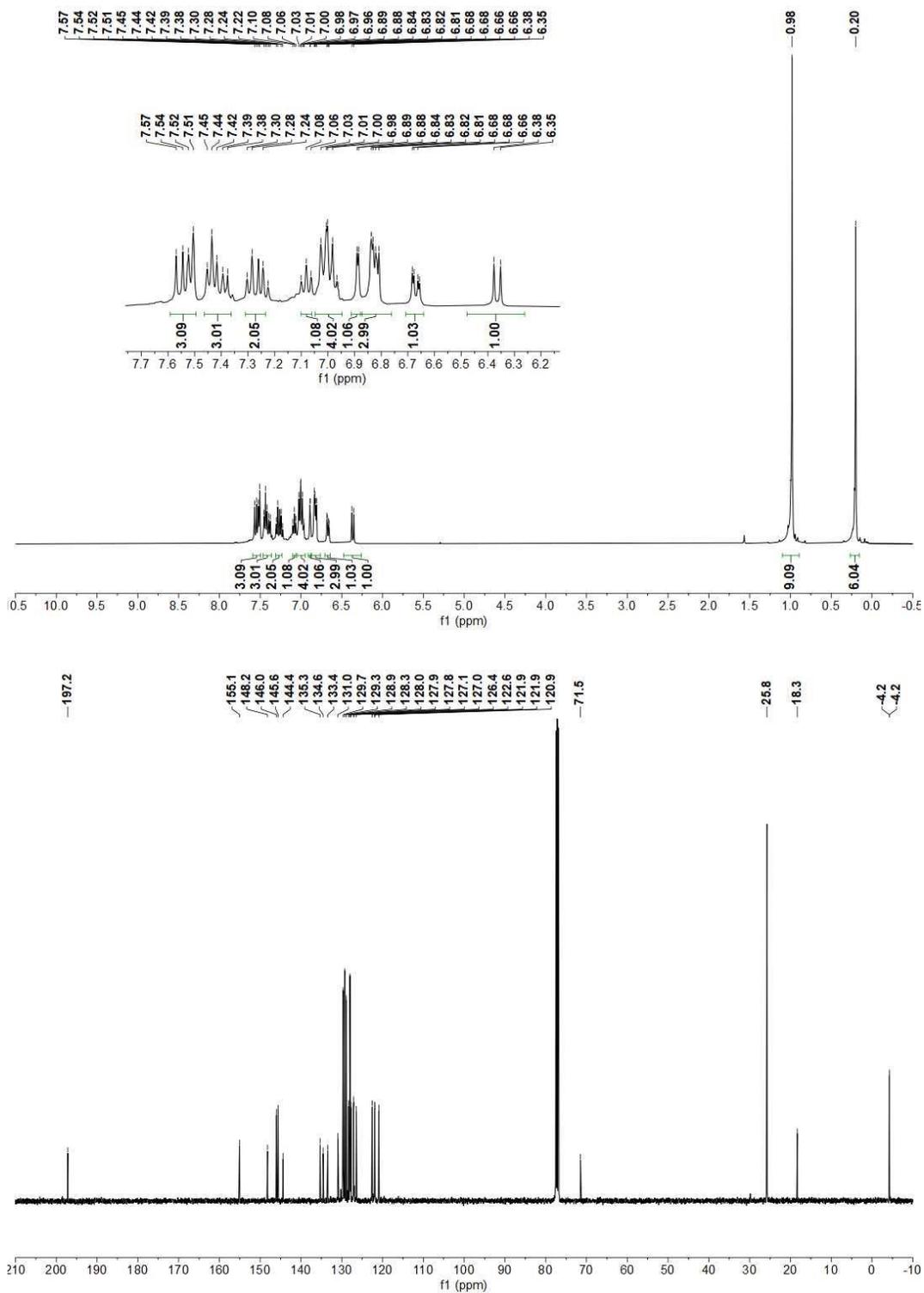
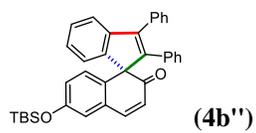
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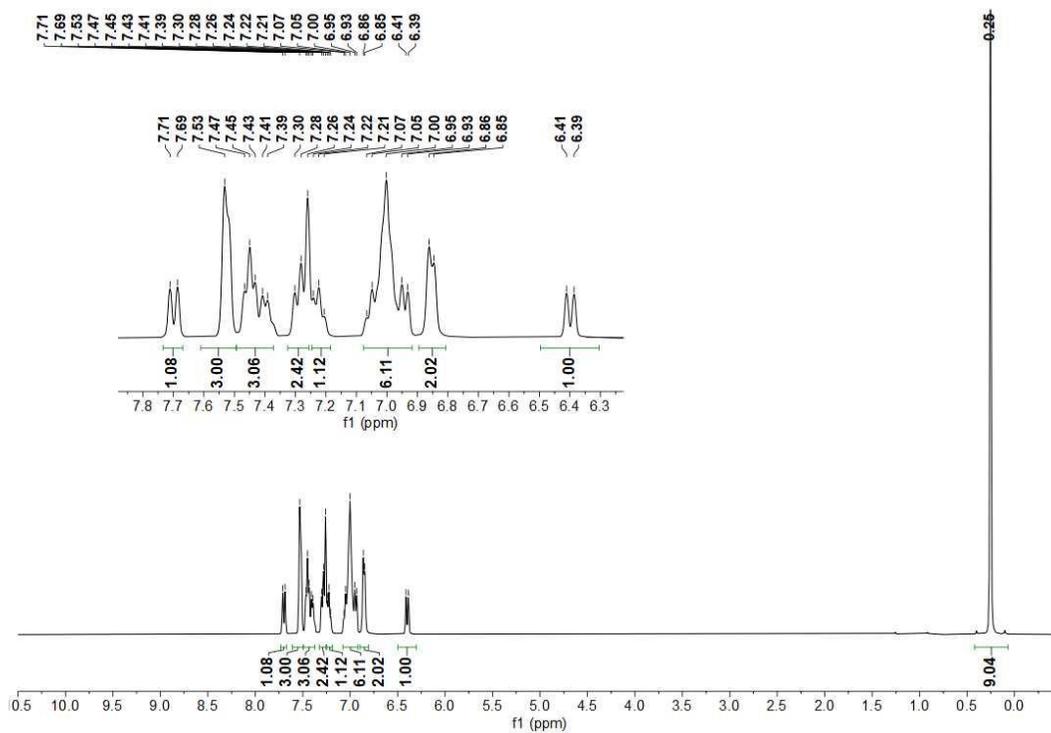
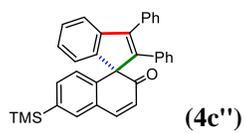




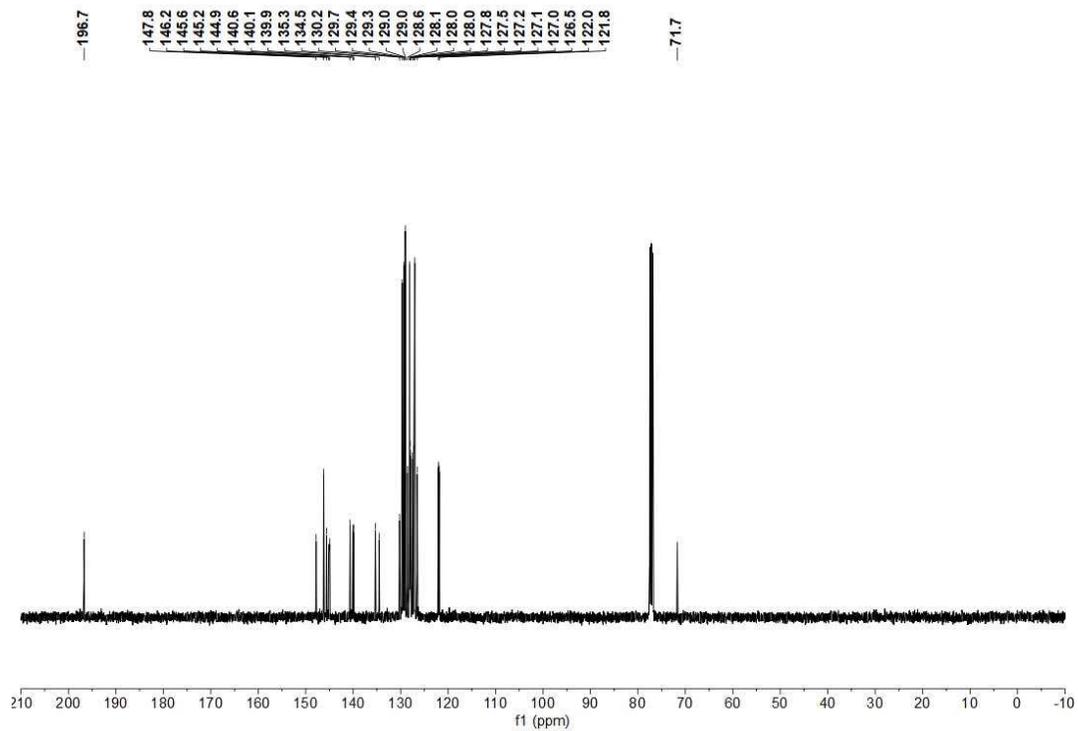
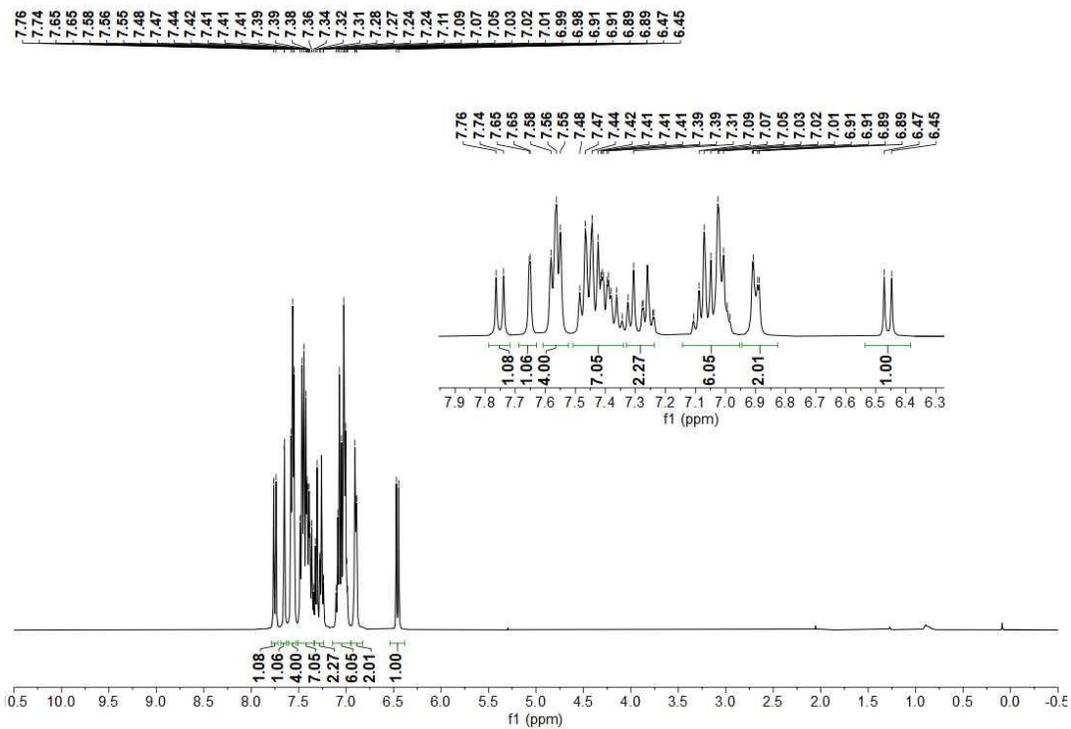
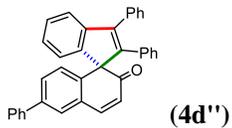


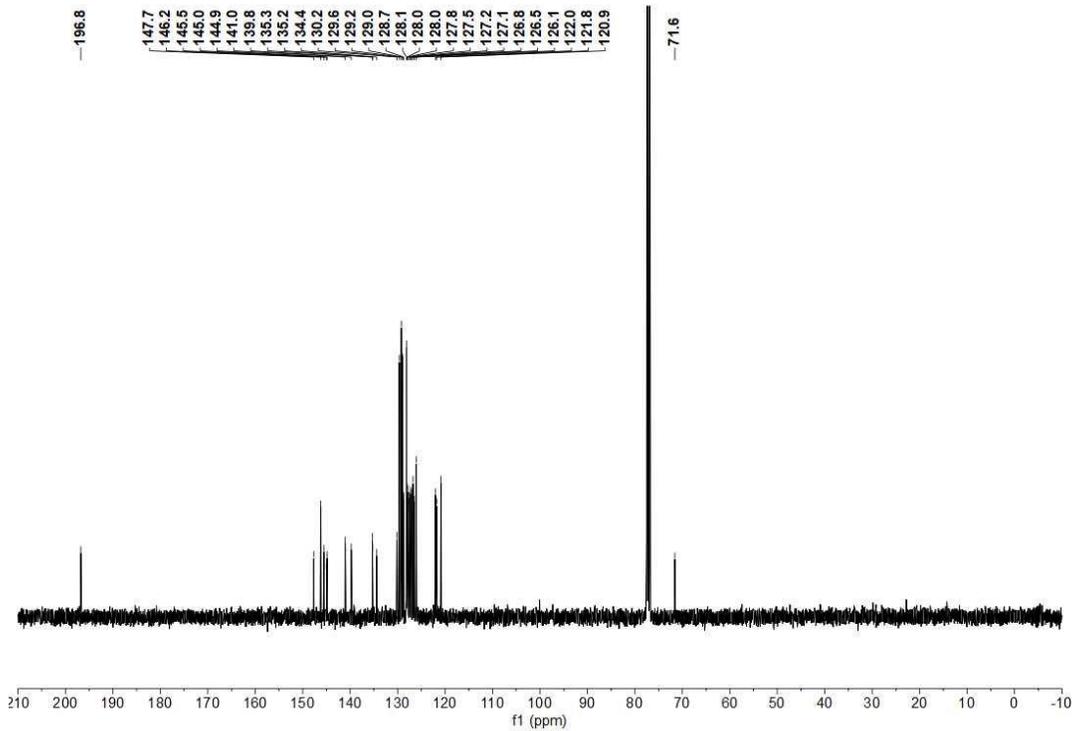
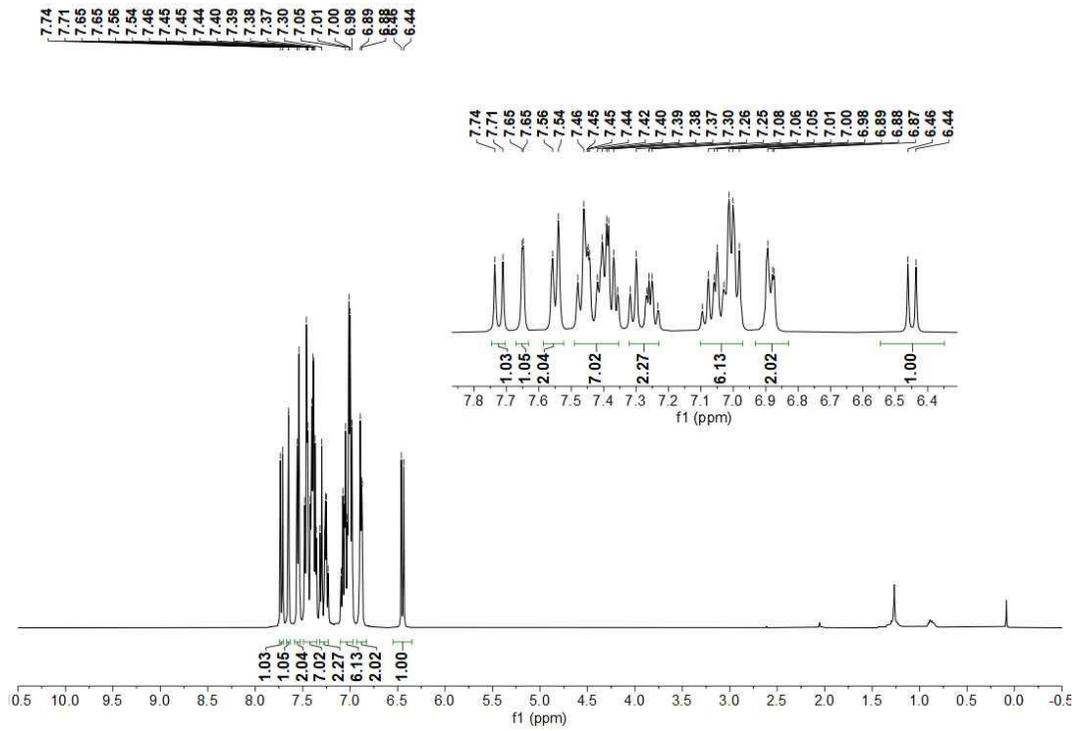
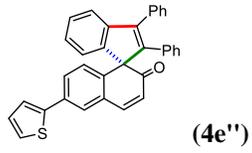


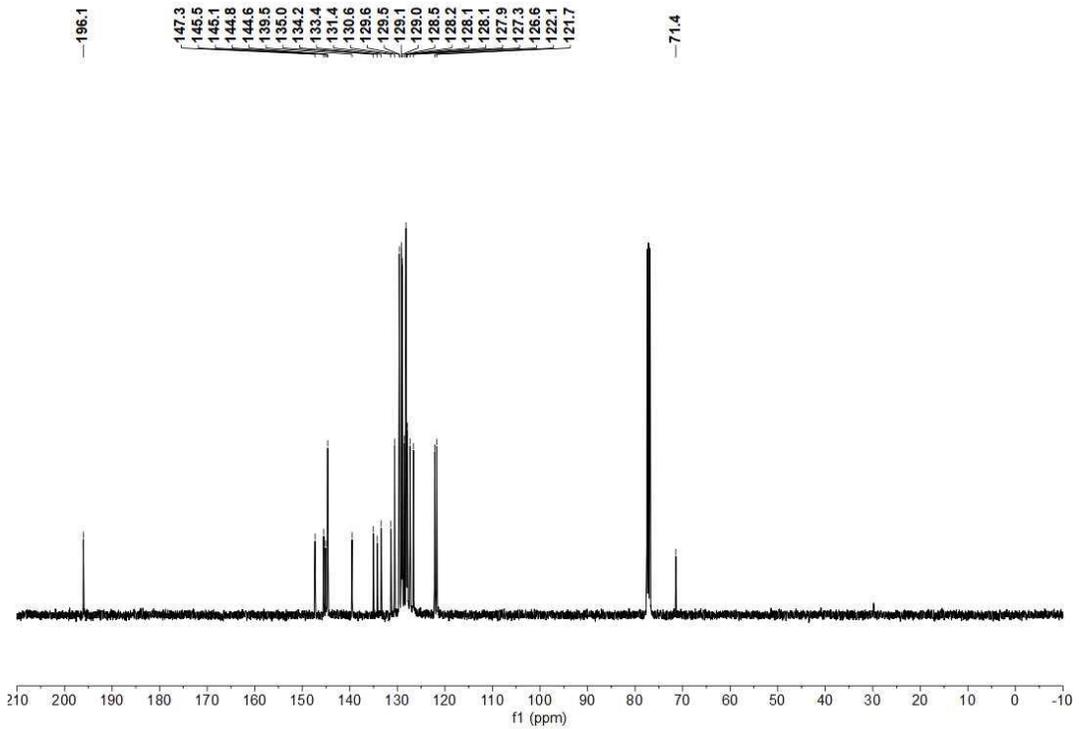
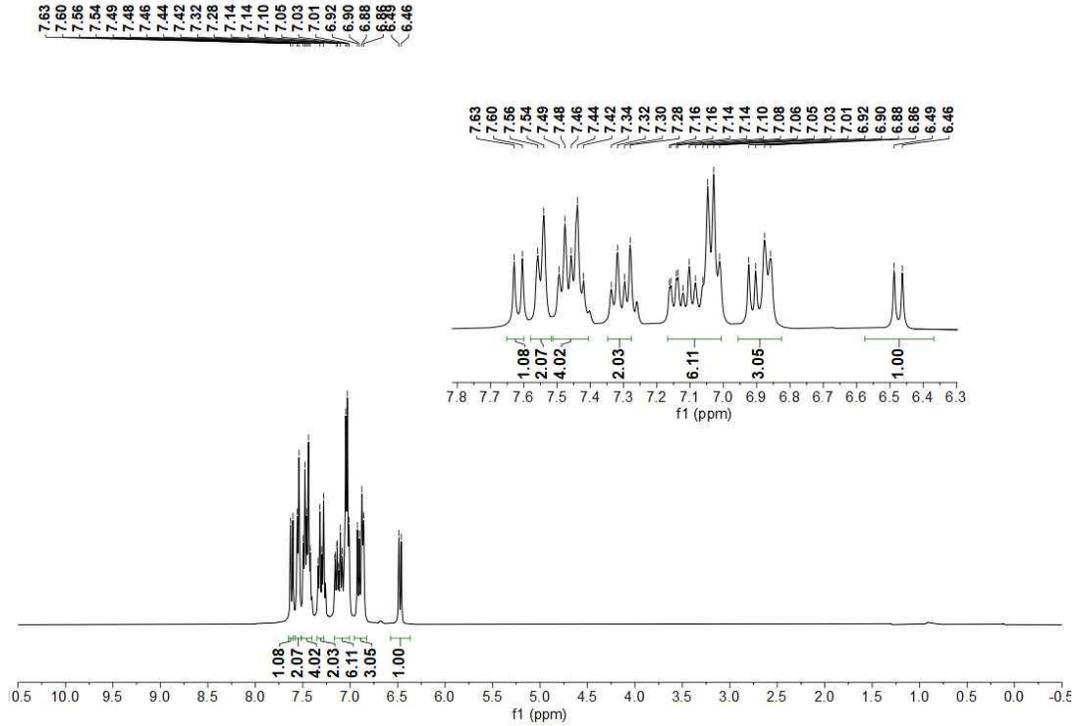
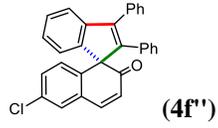


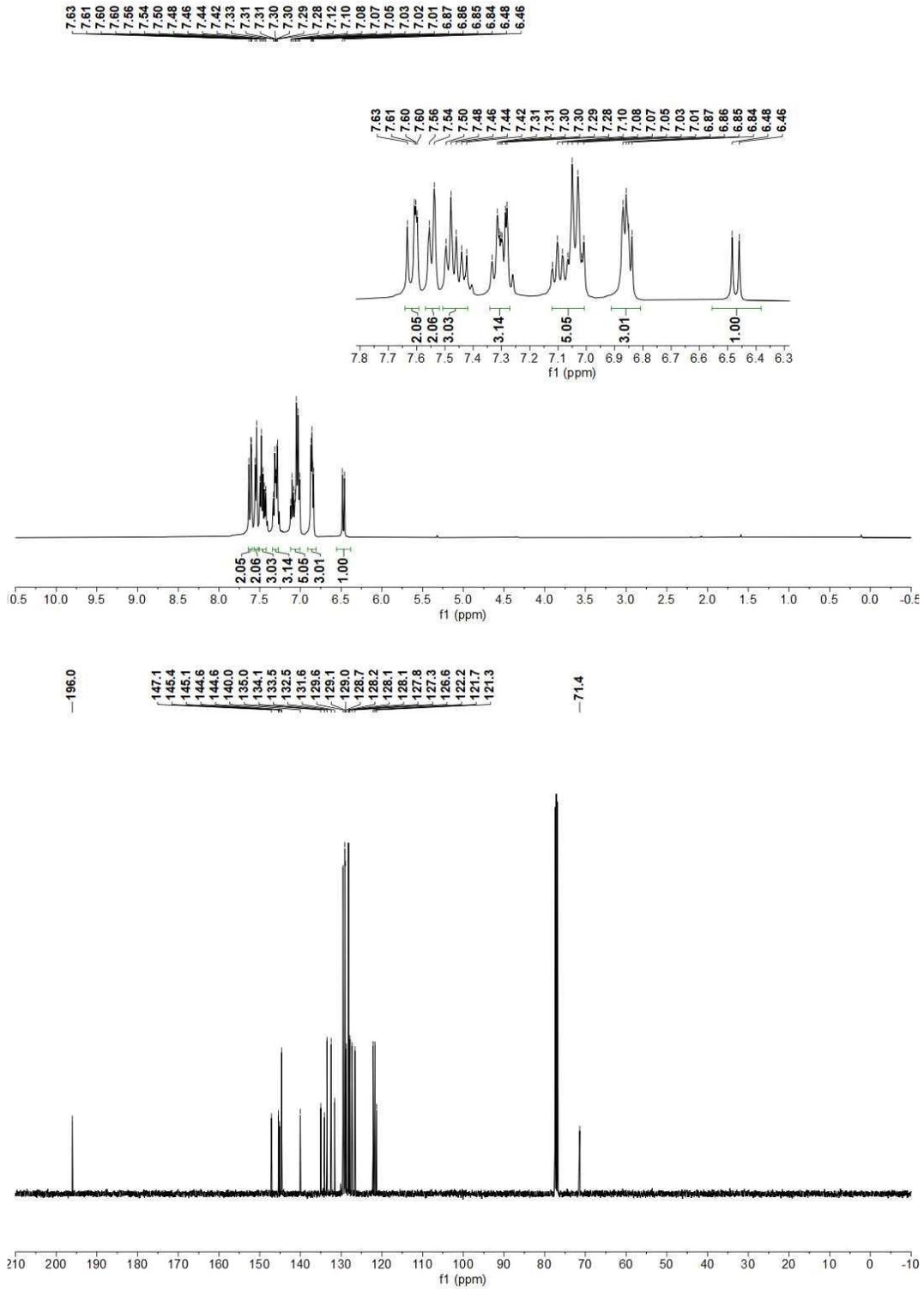
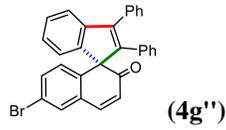


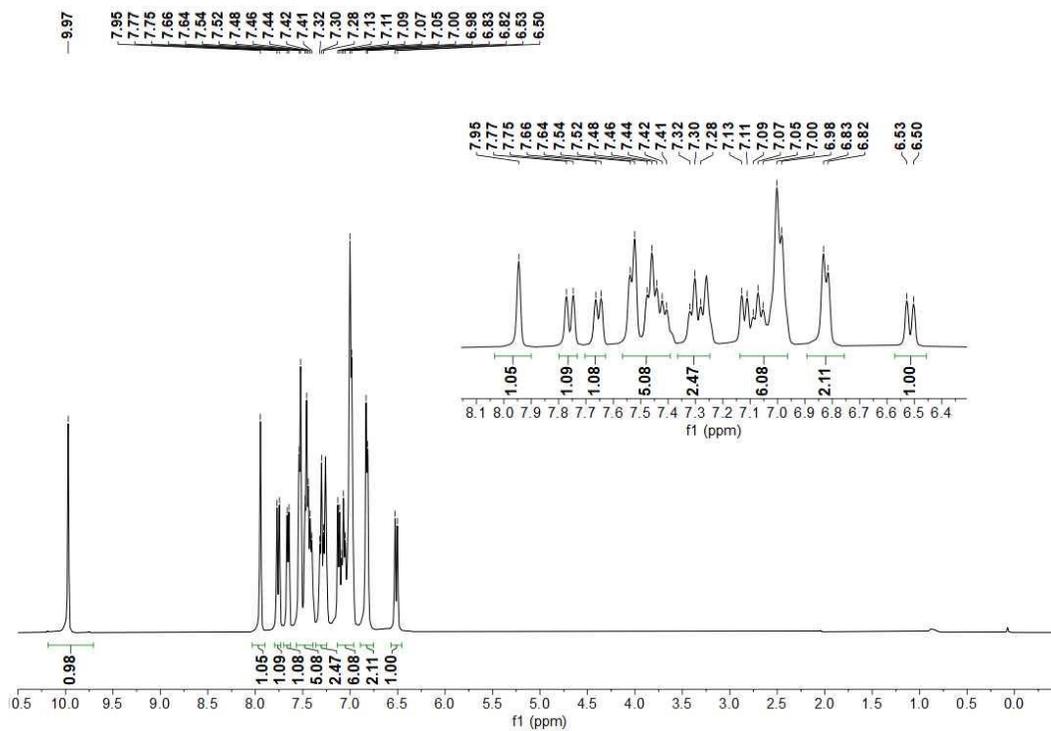
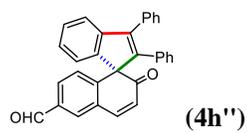
The ^1H NMR data is consistent with that reported in the literature.¹⁵



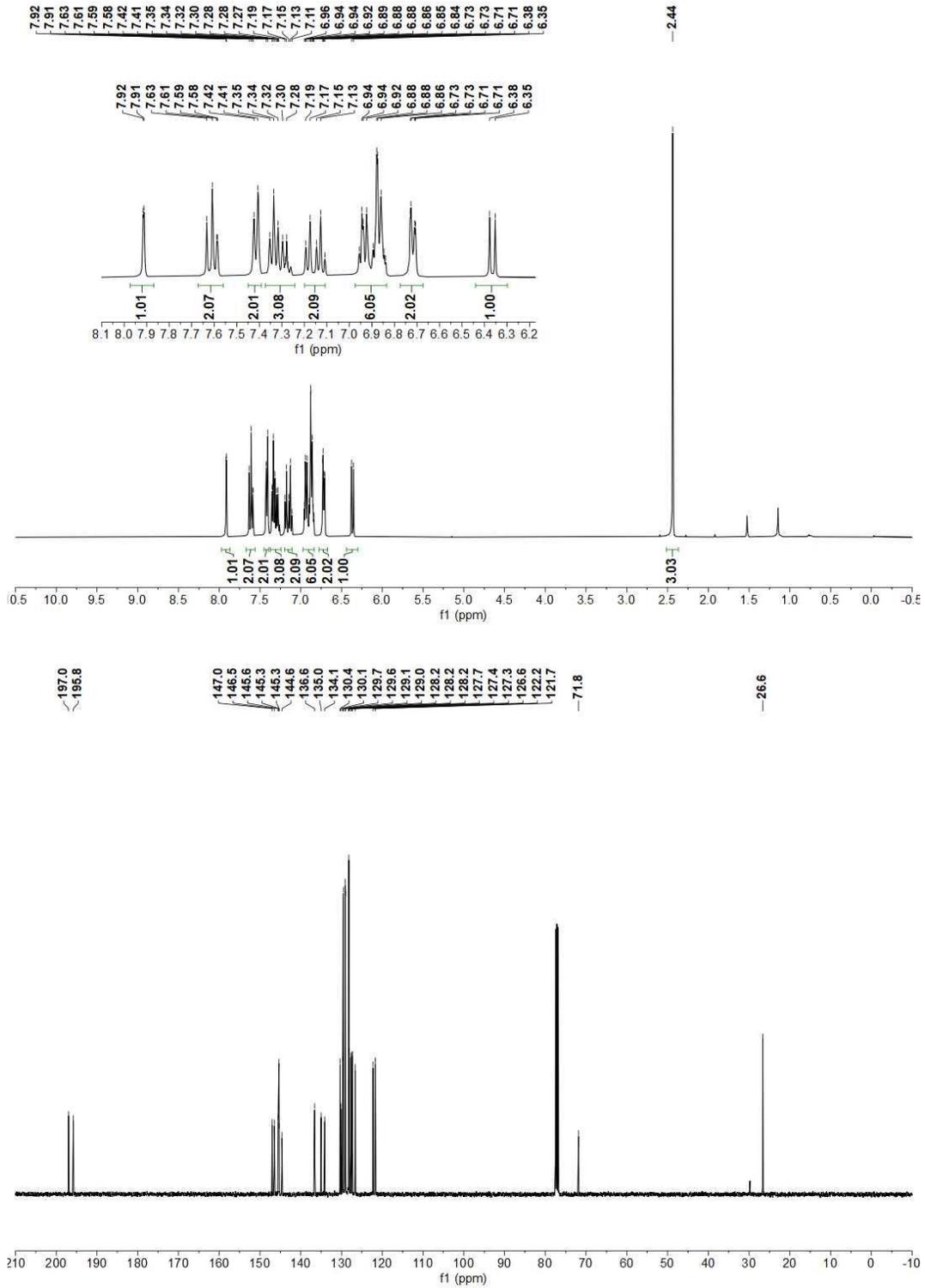
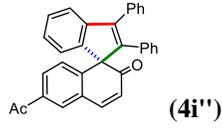


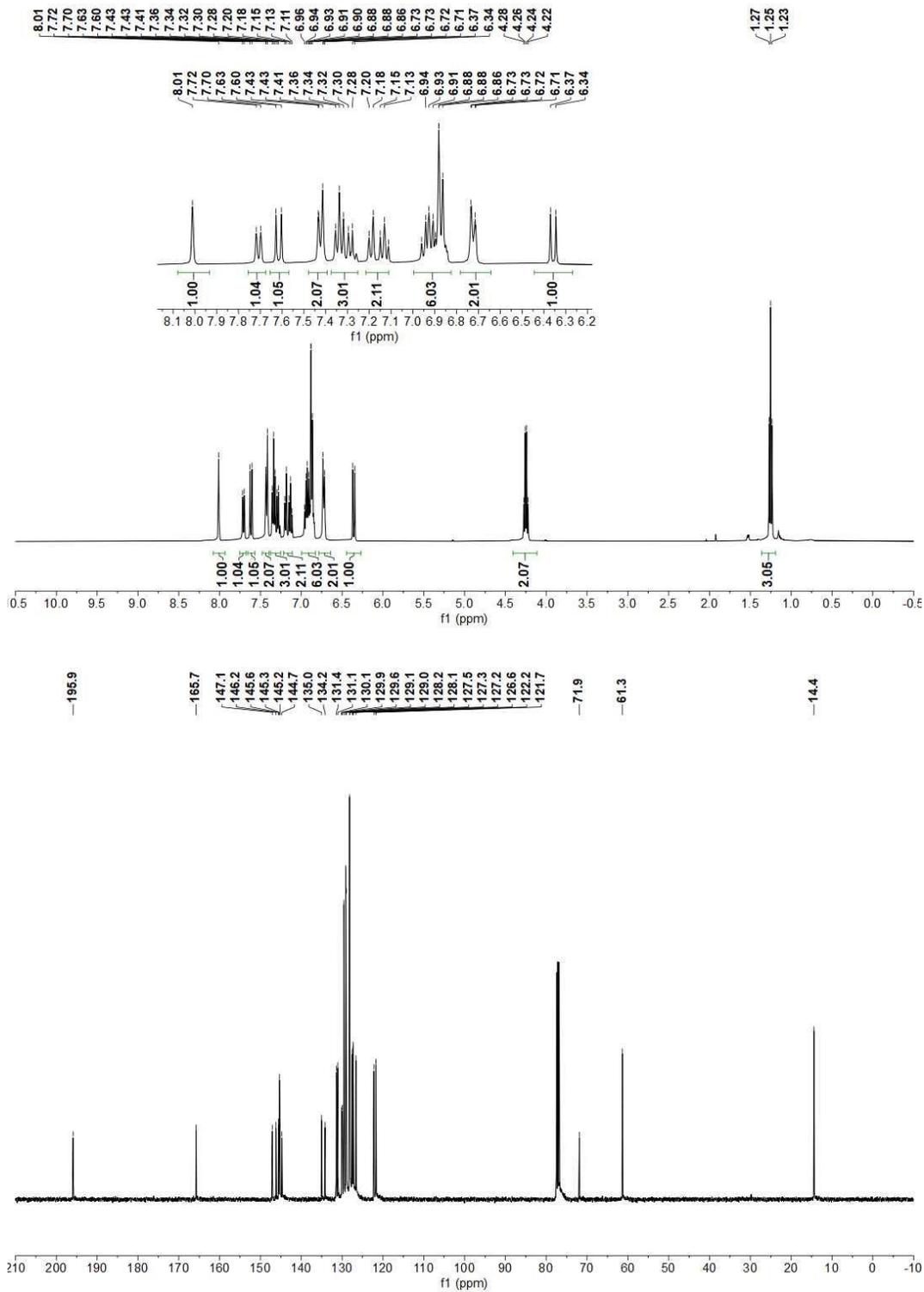
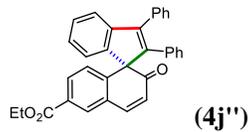


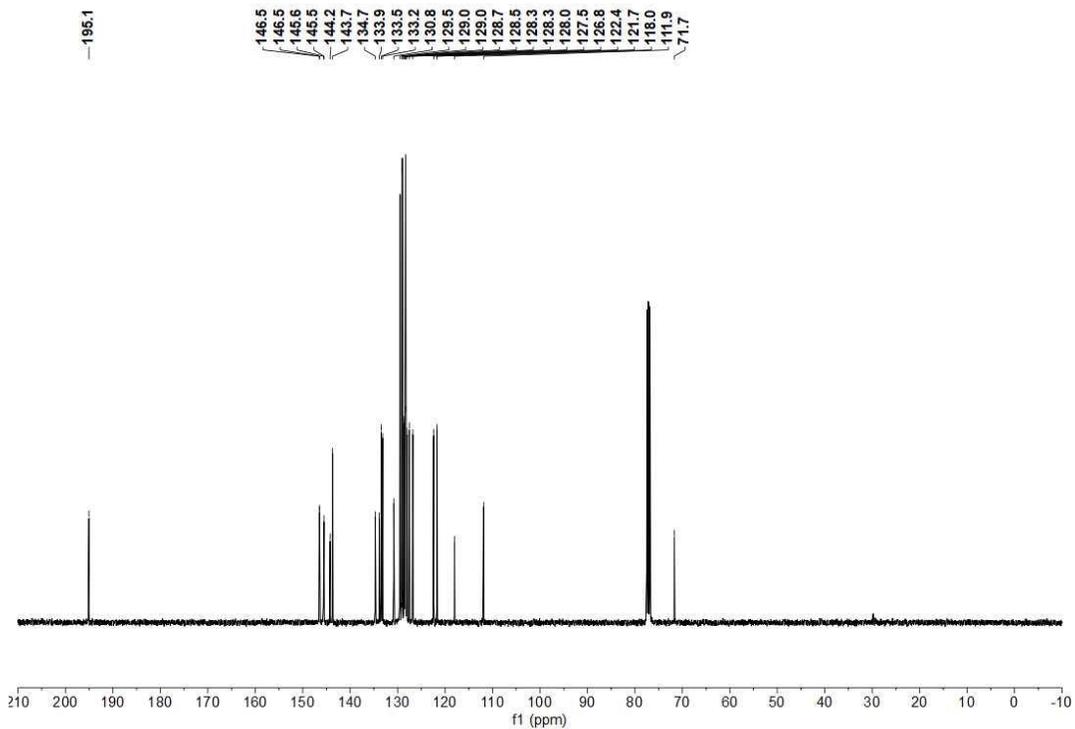
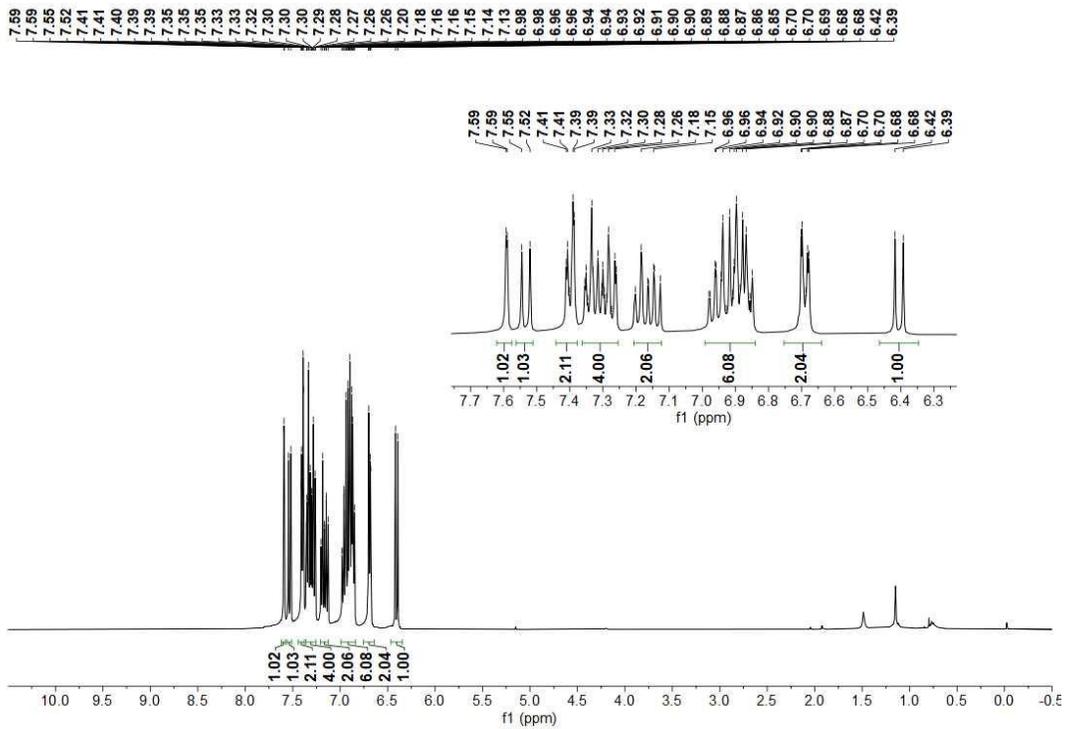
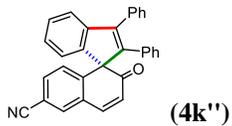


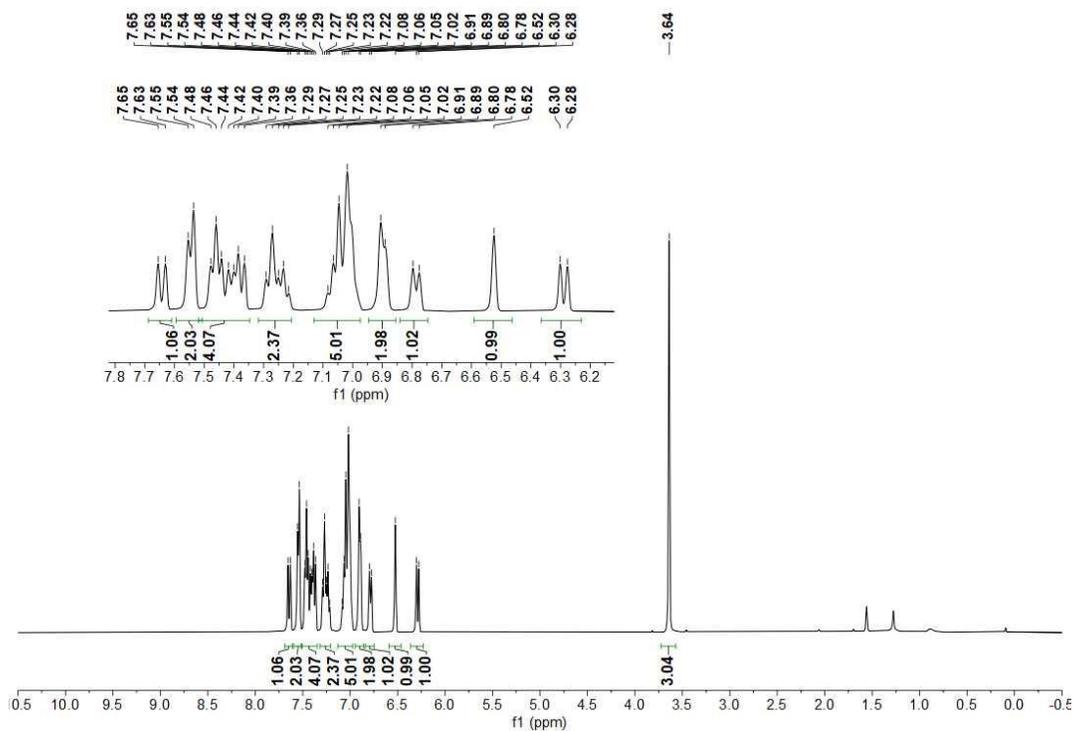
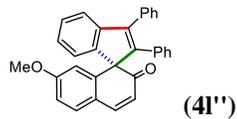


The ^1H NMR data is consistent with that reported in the literature.¹⁵

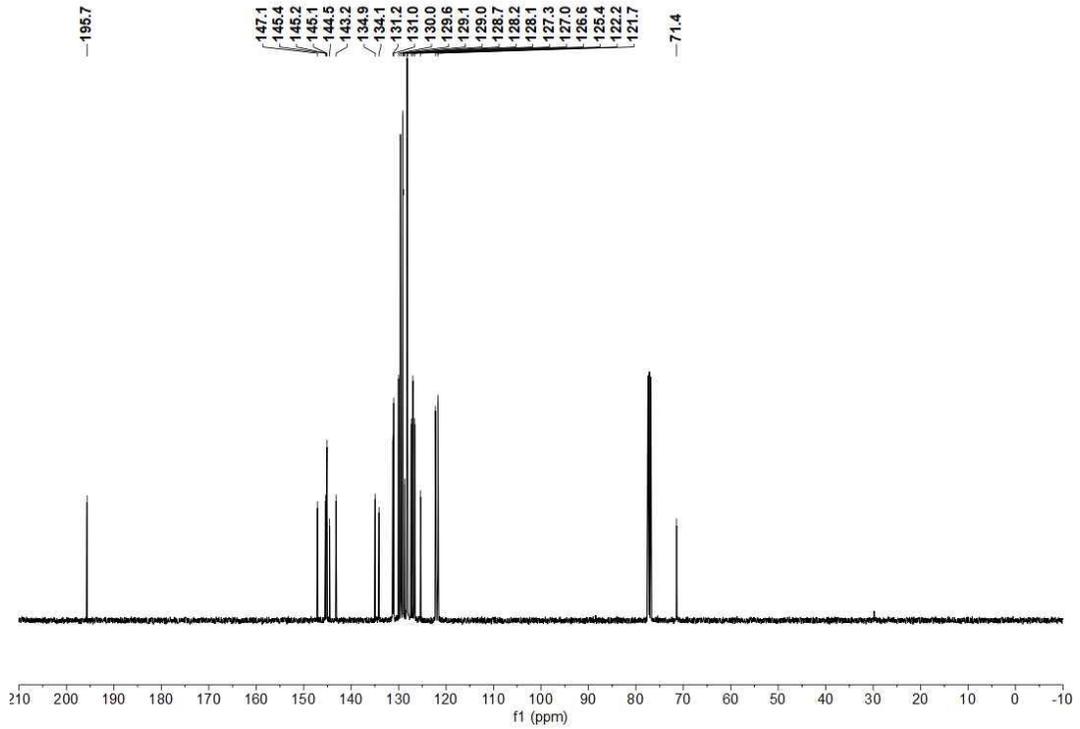
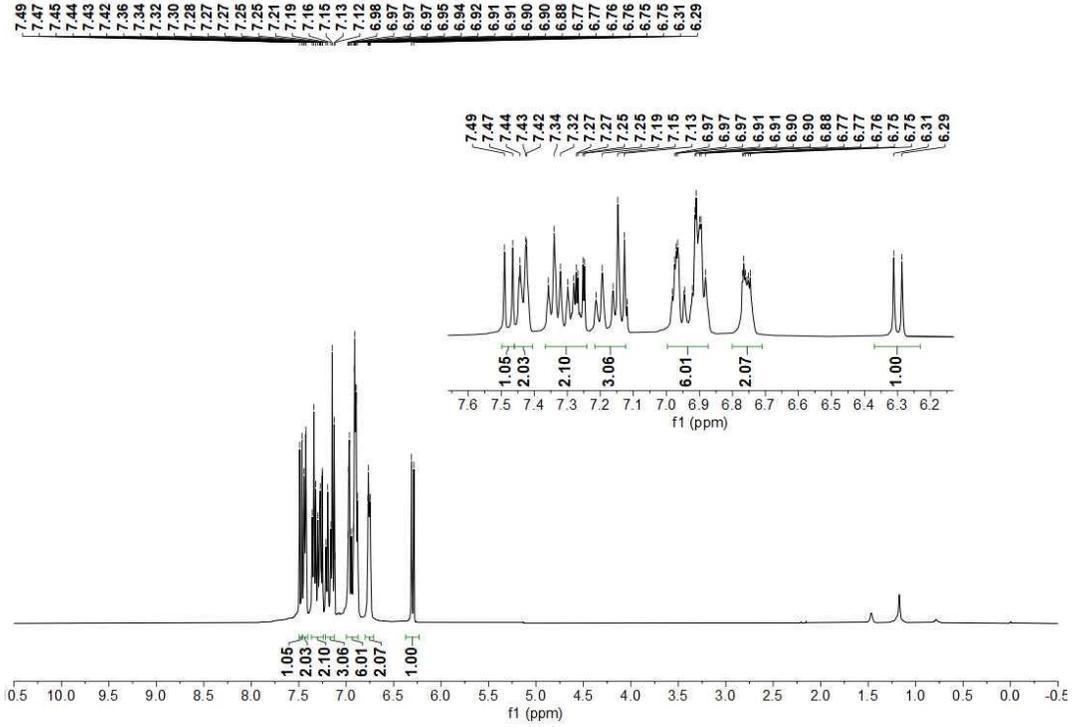
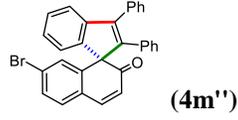


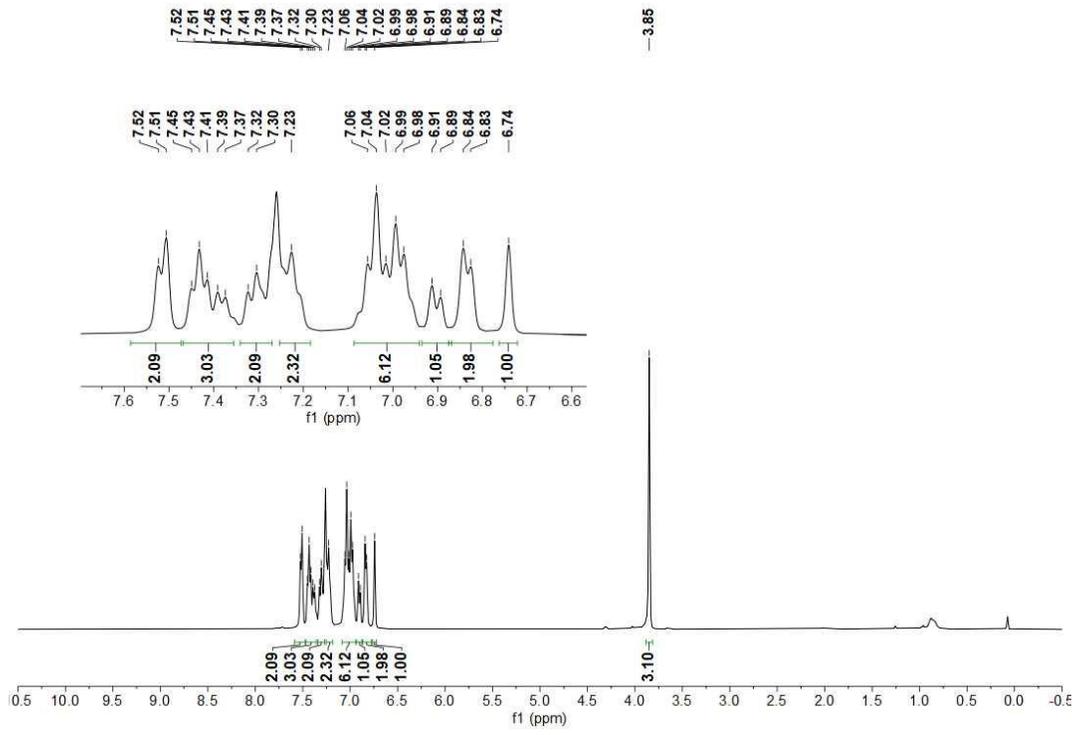
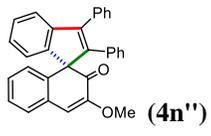




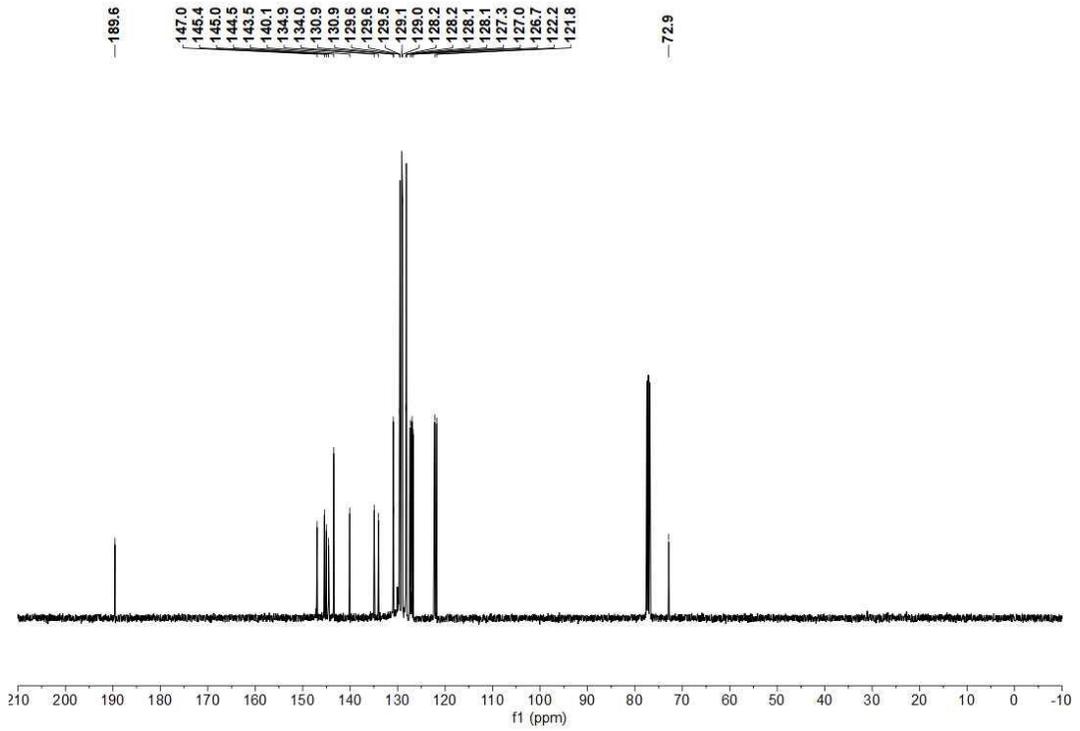
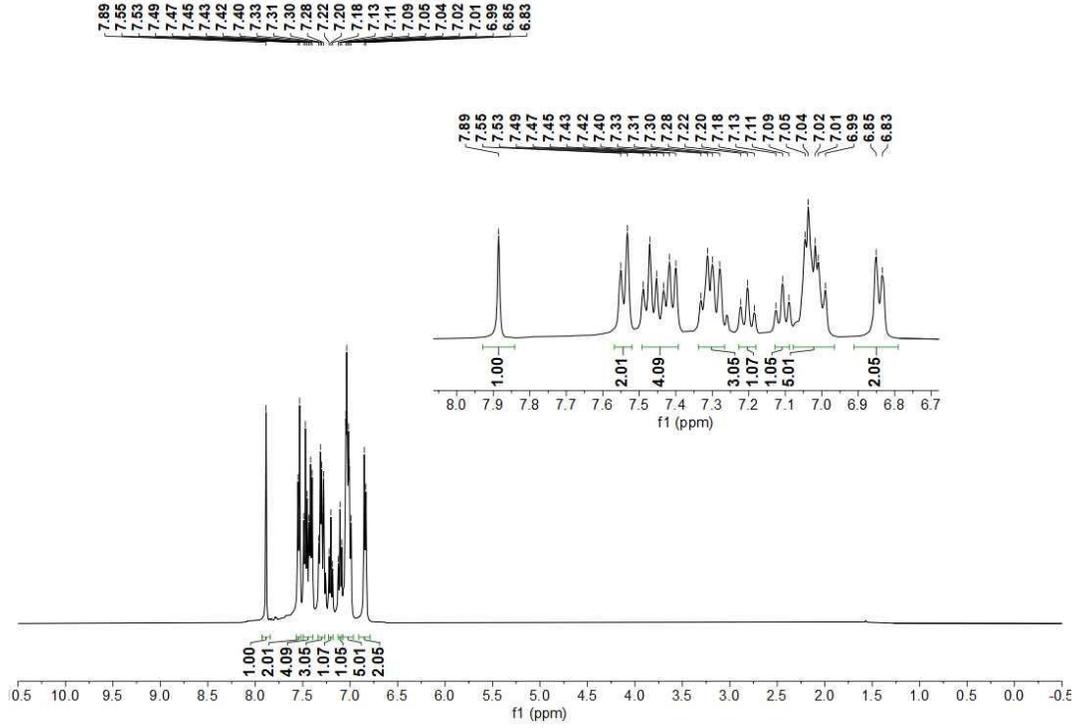
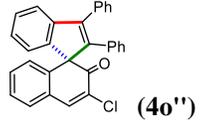


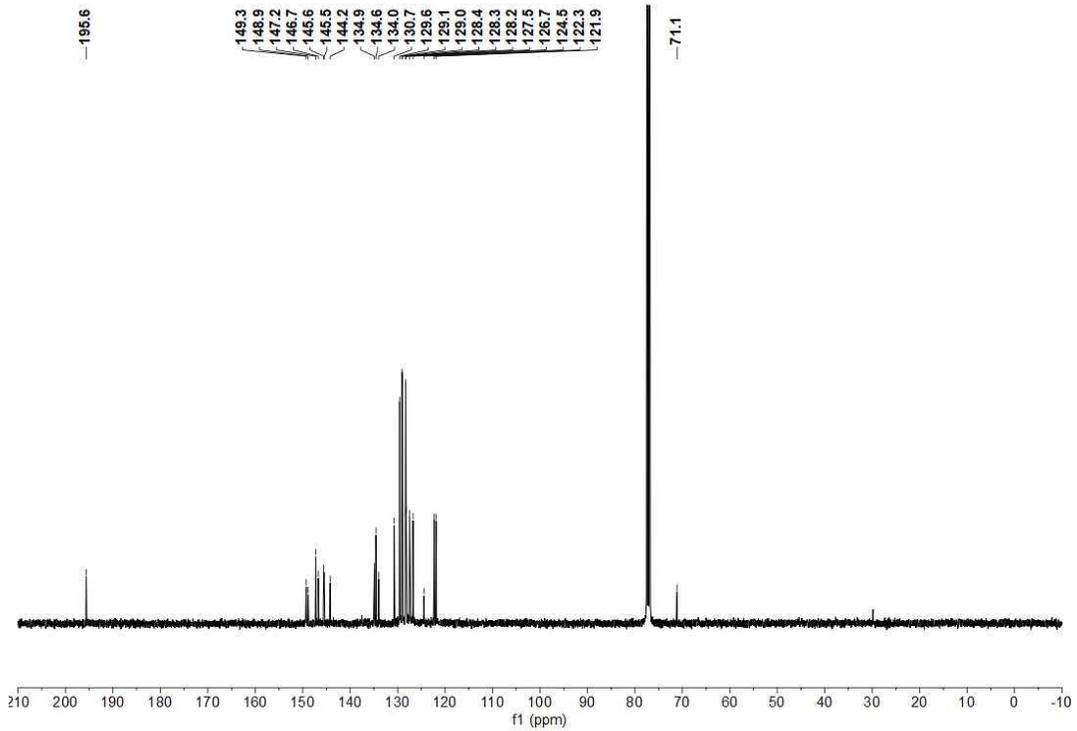
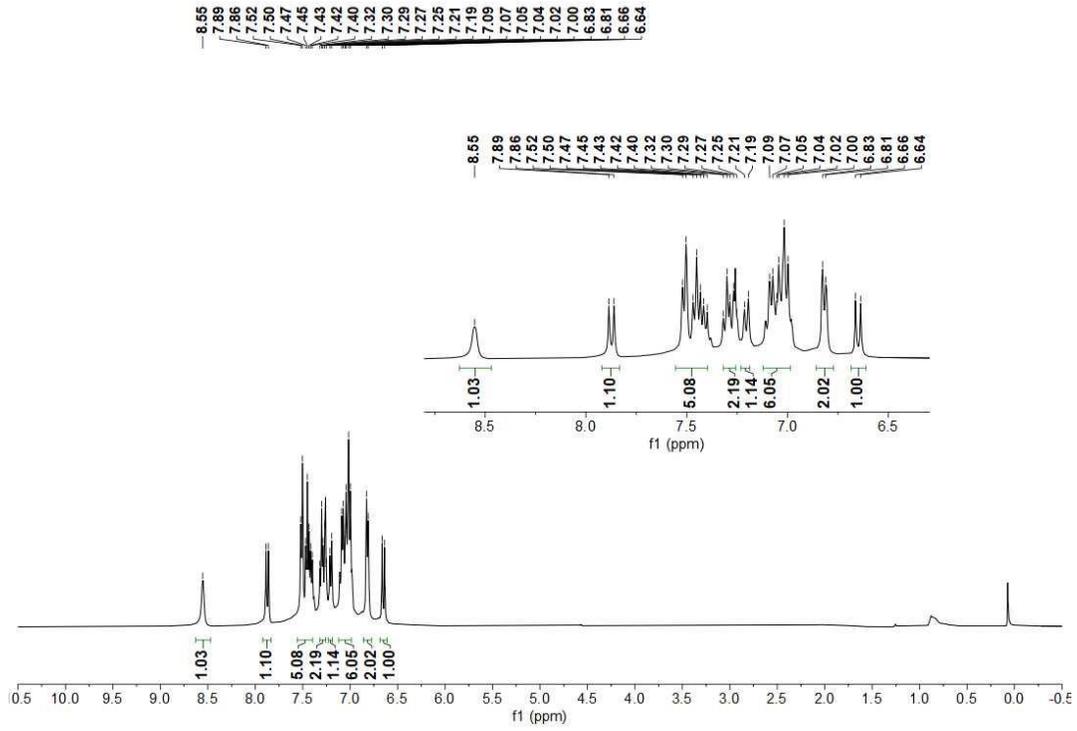
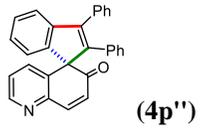
The ¹H NMR data is consistent with that reported in the literature.¹⁵

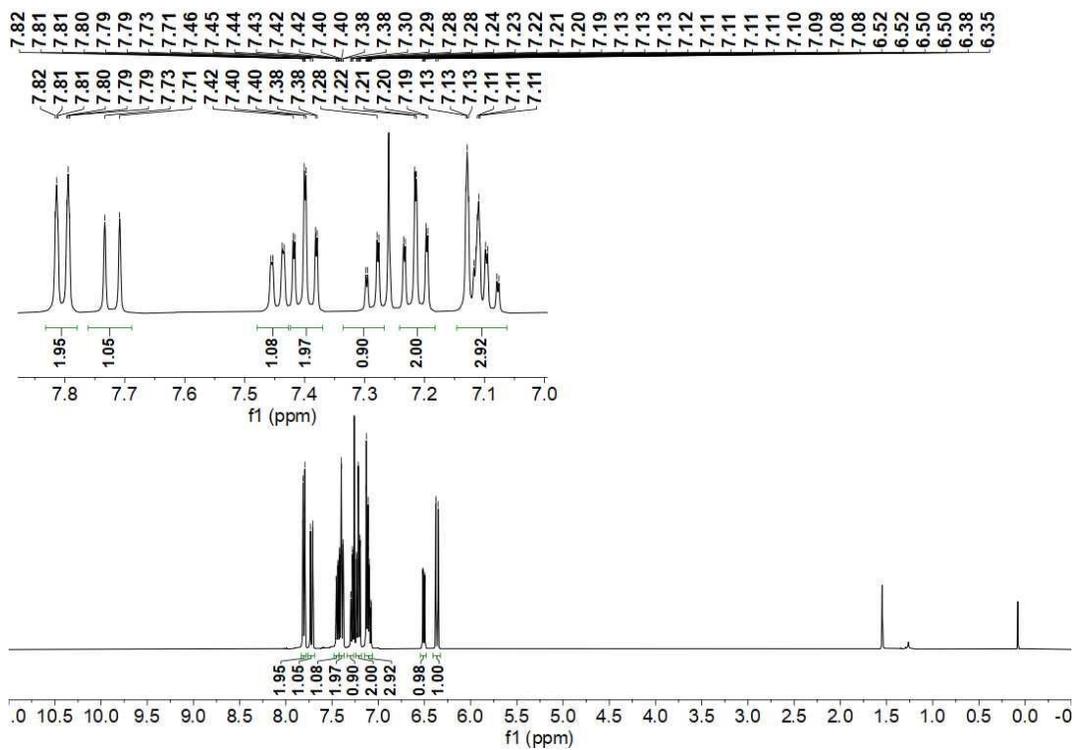
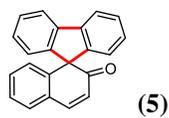




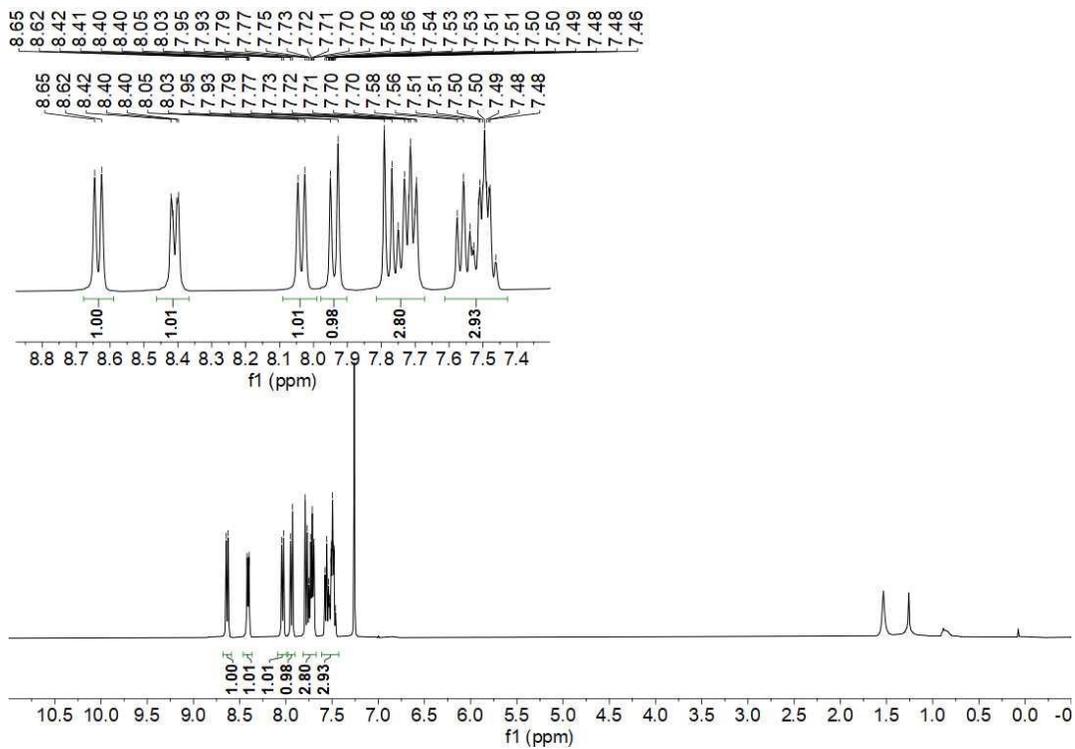
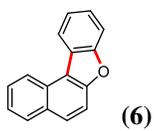
The ¹H NMR data is consistent with that reported in the literature.¹⁵



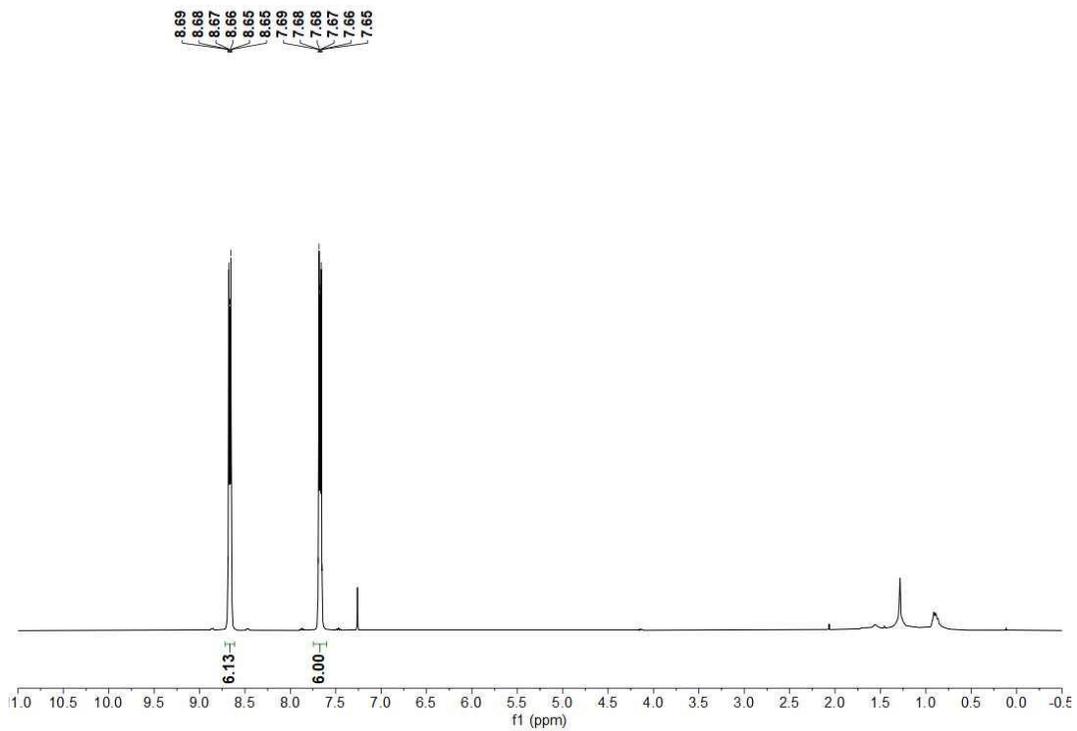
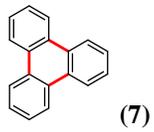




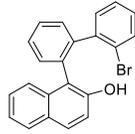
The ¹H NMR data is consistent with that reported in the literature.¹⁸



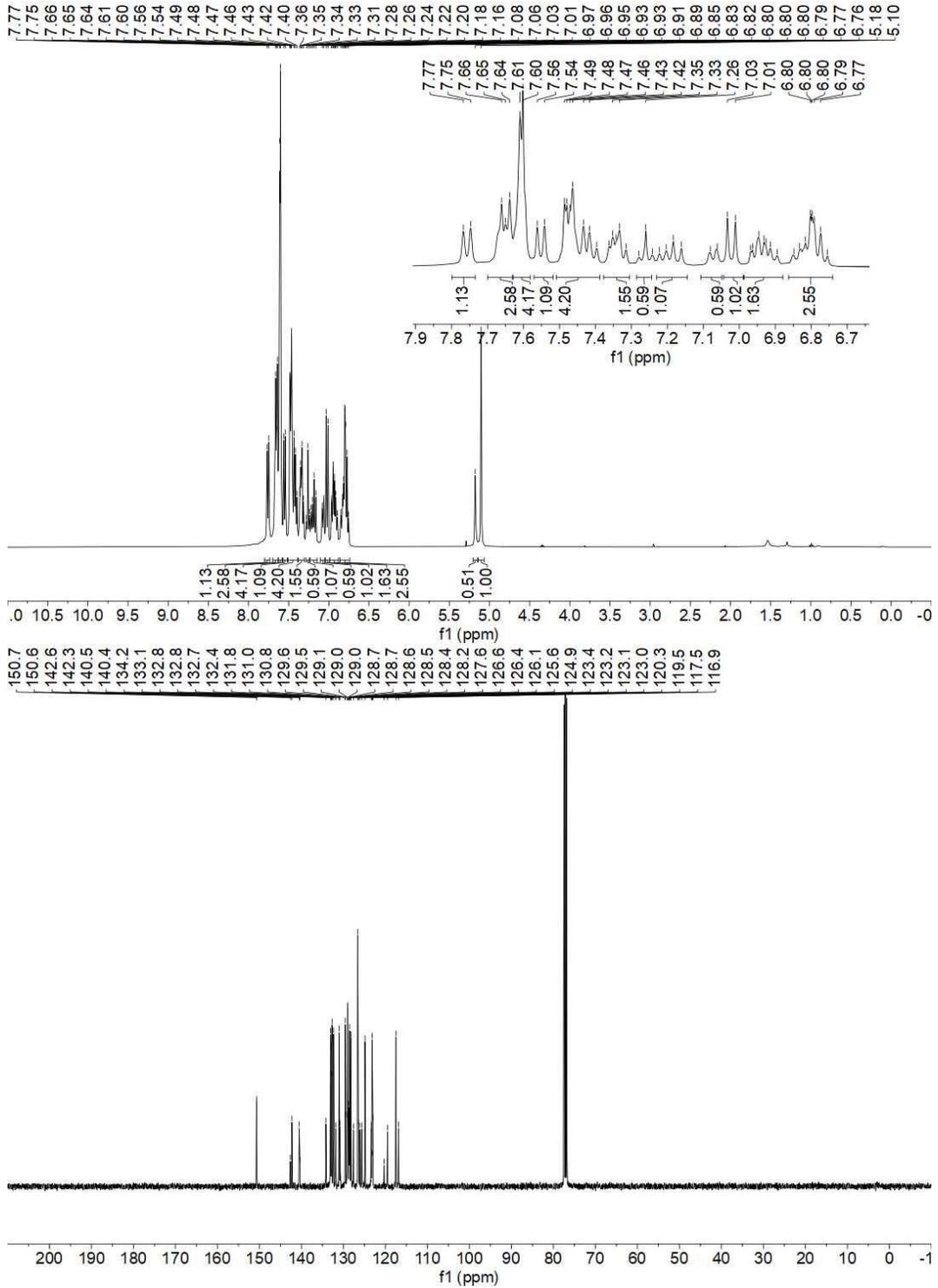
The ^1H NMR data is consistent with that reported in the literature.¹⁹

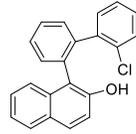


The ¹H NMR data is consistent with that reported in the literature.²⁰



(9)





(10)

