Ligand-Free Iron-Catalyzed Carbon(sp^2)−Carbon(sp^2) Oxidative Homo-Coupling of Alkenyllithiums

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1. General Information

All reactions were carried out under an atmosphere of dry argon with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox unless otherwise specified. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) on MERCK silica gel 60 F254 coated on aluminum plates. Visualization was accomplished by irradiation with UV light at 254 nm followed by staining with ceric ammonium molybdate (CAM). Organic solvents were concentrated under reduced pressure at appropriate temperature on a rotary evaporator unless otherwise stated. Column chromatography was performed on silica gel (300-400 mesh). Preparative thin-layer chromatography (PTLC) was performed on glass plates (20 × 20 cm) impregnated with silica gel 60 F254 (0.3-0.4 mm thickness). Pentane, diethyl ether, THF and toluene for reactions were dried over sodium wire and distilled under an atmosphere of dry Ar. CH_2Cl_2 was dried over calcium hydride and distilled under an atmosphere of dry Ar. NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C, 377 MHz for ^{19}F) or Bruker Ascend 500 NMR spectrometer (500 MHz for ^{1}H, 126 MHz for ^{13}C, 471 MHz for ^{19}F). Chemical shifts of ^{1}H NMR and ^{13}C NMR spectra were reported as parts per million in δ scale using residual solvent signal as internal standard (note: $CDCl_3$ referenced at δ 7.26 in ^{1}H and δ 77.0 for central line of the triplet in ^{13}C; CD_2Cl_2 referenced at δ 5.32 in ^{1}H and δ 54.0 for central line of the quintet in ^{13}C). Chemical shifts of ^{19}F NMR spectra were reported as parts per million in δ scale using CF_3CO_2H (-76.55 ppm) as internal standard. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constant (*J*, Hz). High resolution mass spectra (HRMS) were obtained on a Thermo Finnigan MAT95XL Mass Spectrometer or a Thermo Scientific Q Exactive Focus Mass Spectrometer. Melting points were measured on a STUART Melting Point Apparatus SMP40 and were uncorrected. GC-MS analyses were performed on an Agilent 7890B system with an Agilent 5977B MSD.

2. Experimental Section

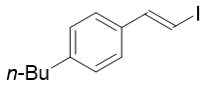
2.1. Preparation of Vinyl Iodides 1

Vinyl iodides **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m** and **1n** were prepared in accordance with a previously reported procedure.[1] The spectral data are in full accordance with the literature report respectively.[1-4]

Vinyl iodide **1o** was prepared in accordance with a previously reported procedure.[5] The spectral data is in full accordance with the literature reported.[6]

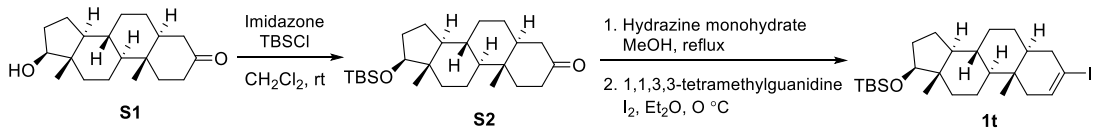
Vinyl iodide **1p** was prepared in accordance with a previously reported procedure.[7] The spectral data is in full accordance with the literature reported.[7]

Vinyl iodides **1q**, **1r** and **1s** were prepared in accordance with a previously reported procedure.[8] The spectral data of **1q**, **1r** and **1s** are in full accordance with the literature reported respectively.[8-10.]



1i

(E)-1-butyl-4-(2-iodovinyl)benzene (1i): 498mg; Yield 87%. Yellow oil. A solution of CH_2I_2 (242 μL, 3.0 mmol) in THF (0.8 mL) was added dropwise to a solution of NaHMDS (1.10 g, 6.0 mmol) in THF (4 mL) and ether (4 mL) at –78 °C (dry ice/acetone bath) in the dark. After 20 min, a solution of the 1-(bromomethyl)-4-butylbenzene (454 mg, 2.0 mmol) in THF (1.5 mL) was added dropwise. The reaction mixture was stirred for 90 min then removed from the cold bath to warm to rt. After 30 min, DBU (298 μL, 2.0 mmol) was added dropwise and the solution stirred for 1 h before ether (25 mL) was added. The mixture was filtered through a plug of celite/silica (approximately 3 cm celite over 3 cm silica) and the solvent removed under reduced pressure. The residue was purified by column chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.40 (d, *J* = 14.9 Hz, 1H), 7.22-7.18 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 14.9 Hz, 1H), 2.61-2.56 (m, 2H), 1.62-1.55 (m, 3H), 1.35 (dd, *J* = 15.0, 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.9, 143.4, 135.2, 128.7, 125.9, 75.3, 35.4, 33.4, 22.3, 13.9 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{12}H_{16}I$ $[M+H]^+$: 287.0291; found: 287.0294.

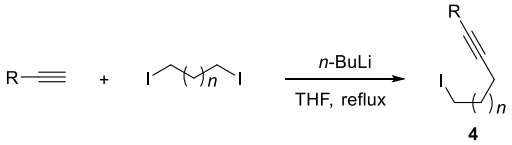


S1 **S2** **1t**

tert-butyl(((5S,8R,9S,10S,13S,14S,17S)-3-iodo-10,13-dimethyl-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)oxy)dimethylsilane (1t): 3.29 g; Yield 64% for 3 steps. Yellow solid. Stanolone (**S1**, 2.91 g, 10 mmol), Imidazone (1.02 g, 15 mmol) and TBSCl

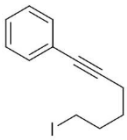
(2.26g, 15 mmol) were added to a 100 mL round bottom flask with CH_2Cl_2 (20 mL) and stirred at rt for 2 h to produce **S2**. Crude hadrazone was synthesized by combining **S2** (4.04g, 10 mmol), hydrazine monohydrate (1.0 mL, 20 mmol) and methanol (25mL) and refluxed for 6 hours. Later iodine (5.0 g, 20 mmol) and ether (15 mL) was added to a flame dried 250 mL 2-neck round bottom flask equipped with a stir bar and a pressure equalized addition funnel, and the mixture was stirred in an ice bath. 1,1,3,3-tetramethylguanidine (24 mL, 20 mmol) was then added to the addition funnel along with ether (15 mL). The guanidine solution was added to the iodine solution dropwise. After the guanidine solution was added the mixture was stirred in the ice bath. After 15 mins, Crude hydrazone (4.2 g) was added slowly to the reaction mixture and was allowed to stir for 45 minutes in the ice bath after addition was complete. After the addition was complete, stirring continued for 45 minutes, after which 10 % HCl (20 mL) was added to quench the reaction. The contents of the reaction flask were poured into a separatory funnel. The organic layer was washed with water, then saturated sodium thiosulfate, then twice 10 % HCl. The organic layer was dried with magnesium sulphate and concentrated. The residue was purified by column chromatography using a mixture of hexane and EA [20:1 to 10:1(v/v)] to get **1t**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.11 (dd, *J* = 3.2, 1.6 Hz, 1H), 3.59-3.51 (m, 1H), 2.12 (ddd, *J* = 14.9, 6.3, 3.2 Hz, 1H), 1.91 (ddd, *J* = 14.9, 11.3, 1.6 Hz, 1H), 1.72-1.62 (m, 4H), 1.58 (d, *J* = 8.0 Hz, 2H), 1.45 (ddd, *J* = 9.2, 7.0, 4.4 Hz, 3H), 1.37-1.31 (m, 2H), 1.28 (ddd, *J* = 10.4, 7.7, 2.5 Hz, 2H), 1.21-1.14 (m, 1H), 1.12-1.05 (m, 1H), 0.95 (ddd, *J* = 13.8, 10.7, 4.9 Hz, 2H), 0.88 (s, 9H), 0.82 (s, 3H), 0.71 (s, 3H), 0.70-0.65 (m, 1H), 0.05 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 137.5, 112.9, 72.1, 54.8, 54.8, 50.1, 45.2, 38.6, 37.0, 36.3, 35.7, 34.6, 33.7, 31.9, 31.6, 28.6, 26.0, 21.1, 18.3, 15.3, 12.3, –4.6 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{25}H_{44}IOSi$ $[M+H]^+$: 515.2200; found: 515.2201. M.p. 176-178 °C.

2.2. General Procedure for Acetylenic Alkyl Iodides 4



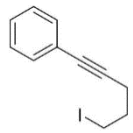
4

To a two- neck flask equipped with a reflux condenser, a gas inlet tube and a magnetic stirring bar, were added the terminal alkyne (3.0 mmol) and dry THF (15 mL, 0.2 M), and the resulting solution was cooled to –78 °C in an acetone-dry ice bath. Then, *n*-BuLi (2.0 mL, 1.6 M) was slowly added via an argon-flushed syringe. The reaction mixture was stirred for 30 min at –78 °C and then warmed up to room temperature. The appropriate diiodide (4.5 mmol) was added and the reaction mixture was heated to reflux overnight. After cooling down to room temperature, the reaction mixture was quenched by saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layers were dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and purified by column chromatography to deliver the corresponding alkyl iodide.



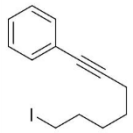
4a

(6-iodohex-1-yn-1-yl)benzene (4a): 680 mg; Yield 80%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.42-7.36 (m, 2H), 7.31-7.27 (m, 3H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.46 (t, *J* = 6.9 Hz, 2H), 2.06-1.98 (m, 2H), 1.77-1.69 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 131.5, 128.2, 127.6, 123.7, 89.2, 81.2, 32.5, 29.4, 18.4, 6.2 ppm. Data was in accordance with that reported in the literature.[11]



4b

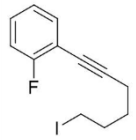
(5-iodopent-1-yn-1-yl)benzene (4b): 608 mg; Yield 75%. Orange oil. Purified by column chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.44-7.36 (m, 2H), 7.33-7.27 (m, 3H), 3.37 (t, *J* = 6.8 Hz, 2H), 2.56 (t, *J* = 6.7 Hz, 2H), 2.14-2.05 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 131.6, 128.2, 127.8, 123.5, 87.8, 81.7, 32.2, 20.5, 5.4 ppm. Data was in accordance with that reported in the literature.[12]



4c

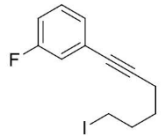
(7-iodohept-1-yn-1-yl)benzene (4c) : 645 mg; Yield 72%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 (dd, *J* = 6.6, 3.2 Hz, 2H),

7.31-7.26 (m, 3H), 3.22 (t, *J* = 7.0 Hz, 2H), 2.43 (t, *J* = 6.7 Hz, 2H), 1.94-1.84 (m, 2H), 1.68-1.54 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 131.5, 128.2, 127.6, 123.9, 89.7, 80.9, 33.0, 29.7, 27.6, 19.2, 6.7 ppm. Data was in accordance with that reported in the literature.[13]



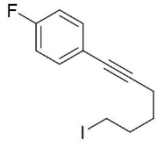
4d

1-fluoro-2-(6-iodohex-1-yn-1-yl)benzene (4d): 613 mg; Yield 68%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.40 (td, *J* = 7.4, 1.7 Hz, 1H), 7.33-7.22 (m, 1H), 7.17-7.01 (m, 2H), 3.27 (t, *J* = 6.9 Hz, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.06-1.96 (m, 2H), 1.78-1.68 (m, 2H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 163.3 (d, *J* = 249.4 Hz), 134.0 (d, *J* = 1.2 Hz), 129.9 (d, *J* = 7.9 Hz), 124.5 (d, *J* = 3.7 Hz), 115.8 (d, *J* = 21.1 Hz), 112.7 (d, *J* = 15.8 Hz), 95.5 (d, *J* = 3.2 Hz), 74.8, 33.1, 29.8, 19.0, 6.9 ppm. **^{19}F NMR** (377 MHz, CD_2Cl_2) δ = –112.30 (ddd, *J* = 9.6, 7.1, 5.5 Hz) ppm. **HRMS** *m/z* (APCI) calcd. for $C_{13}H_{17}FIO$ $[M+H+CH_3OH]^+$: 335.0303; found: 335.0300.



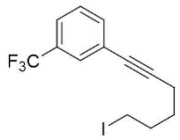
4e

1-fluoro-3-(6-iodohex-1-yn-1-yl)benzene (4e): 617 mg; Yield 68%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.31-7.23 (m, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 9.7 Hz, 1H), 7.00 (td, *J* = 8.7, 2.3 Hz, 1H), 3.26 (t, *J* = 6.9 Hz, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.05-1.93 (m, 2H), 1.77-1.66 (m, 2H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 162.9 (d, *J* = 245.3 Hz), 130.4 (d, *J* = 8.8 Hz), 128.0 (d, *J* = 2.9 Hz), 126.3 (d, *J* = 9.6 Hz), 118.7 (d, *J* = 22.6 Hz), 115.4 (d, *J* = 21.2 Hz), 91.2, 80.3 (d, *J* = 3.4 Hz), 33.1, 29.8, 18.8, 6.9 ppm. **^{19}F NMR** (377 MHz, CD_2Cl_2) δ = –114.36 (td, *J* = 9.2, 6.1 Hz) ppm. **HRMS** *m/z* (APCI) calcd. for $C_{13}H_{17}FIO$ $[M+H+CH_3OH]^+$: 335.0303; found: 335.0297.



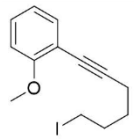
4f

1-fluoro-4-(6-iodohex-1-yn-1-yl)benzene (4f): 620 mg; Yield 68%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.41-7.32 (m, 2H), 7.03-6.93 (m, 2H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 2.04-1.96 (m, 2H), 1.76-1.67 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.1 (d, *J* = 248.4 Hz), 133.3 (d, *J* = 8.2 Hz), 119.8 (d, *J* = 3.4 Hz), 115.4 (d, *J* = 21.9 Hz), 88.8 (d, *J* = 1.3 Hz), 80.1, 32.5, 29.3, 18.3, 6.2 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = –112.96 (tt, *J* = 8.6, 5.4 Hz) ppm. **HRMS** *m/z* (APCI) calcd. for $C_{11}H_{13}FIO$ $[M+H+H_2O]^+$: 306.9990; found: 306.9989.



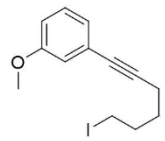
4g

1-(6-iodohex-1-yn-1-yl)-3-(trifluoromethyl)benzene (4g): 710 mg; Yield 67%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 7.66 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 3.27 (t, *J* = 6.9 Hz, 2H), 2.47 (t, *J* = 7.0 Hz, 2H), 2.04-1.96 (m, 2H), 1.76-1.69 (m, 2H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 135.3, 131.1 (q, *J* = 32.4 Hz), 129.4, 128.8 (q, *J* = 3.8 Hz), 125.4, 124.7 (q, *J* = 3.8 Hz), 122.5 (q, *J* = 272.3 Hz), 91.9, 80.1, 33.2, 29.8, 18.8, 6.8 ppm. **^{19}F NMR** (471 MHz, CD_2Cl_2) δ = –63.62 (s) ppm. **HRMS** *m/z* (EI) calcd. for $C_{13}H_{12}F_3I$ $[M]^+$: 351.9930; found: 351.9928.



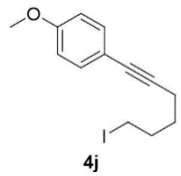
4h

1-(6-iodohex-1-yn-1-yl)-2-methoxybenzene (4h): 660 mg; Yield 70%. Colorless oil. Purified by column chromatography using a mixture of hexane and EA [50:1 to 20:1(v/v)]. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 7.34 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.30-7.21 (m, 1H), 6.92-6.85 (m, 2H), 3.85 (s, 3H), 3.28 (t, *J* = 7.0 Hz, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 2.07-1.99 (m, 2H), 1.75-1.67 (m, 2H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 160.5, 133.9, 129.6, 120.8, 113.4, 111.2, 93.9, 77.8, 56.2, 33.2, 30.1, 19.2, 7.1 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{14}H_{20}IO_2$ $[M+H+CH_3OH]^+$: 347.0502; found: 347.0506.



4i

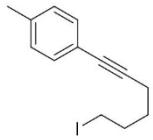
1-(6-iodohex-1-yn-1-yl)-3-methoxybenzene (4i): 650 mg; Yield 69%. Colorless oil. Purified by column chromatography using a mixture of hexane and EA [50:1 to 20:1(v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.19 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.93 (s, 1H), 6.84 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.79 (s, 3H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 2.06-1.97 (m, 2H), 1.76-1.67 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 159.2, 129.2, 124.7, 124.1, 116.4, 114.2, 89.1, 81.1, 55.2, 32.5, 29.3, 18.4, 6.2 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{13}H_{16}IO$ $[M+H]^+$: 315.0240; found: 315.0244.



4j

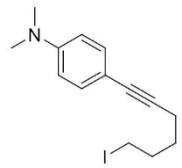
1-(6-iodohex-1-yn-1-yl)-4-methoxybenzene (4j): 670 mg; Yield 71%. Colorless oil. Purified by column chromatography using a mixture of hexane and EA [50:1 to 20:1(v/v)]. **^{1}H NMR** (500 MHz,

$CDCl_3$) δ = 7.33 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 3.80 (s, 3H), 3.25 (t, *J* = 6.8 Hz, 2H), 2.43 (t, *J* = 6.7 Hz, 2H), 2.07-1.96 (m, 2H), 1.76-1.66 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 159.1, 132.9, 115.9, 113.8, 87.6, 80.9, 55.3, 32.5, 29.5, 18.4, 6.3 ppm. Data was in accordance with that reported in the literature.[11]



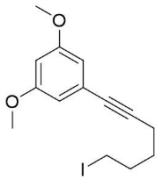
4k

1-(6-iodohex-1-yn-1-yl)-4-methylbenzene (4k): 650 mg; Yield 73%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.44 (t, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 2.06-1.96 (m, 2H), 1.77-1.67 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 137.6, 131.4, 129.0, 120.6, 88.4, 81.2, 32.5, 29.4, 21.4, 18.4, 6.3 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{14}H_{20}IO$ $[M+H+CH_3OH]^+$: 331.0553; found: 331.0551.



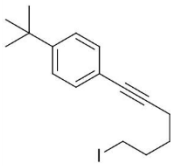
4l

4-(6-iodohex-1-yn-1-yl)-*N*,*N*-dimethylaniline (4l): 661 mg; Yield 67%. Brown oil. Purified by column chromatography using a mixture of hexane and EA [20:1 to 10:1(v/v)]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.96 (s, 6H), 2.44 (t, *J* = 6.9 Hz, 2H), 2.06-1.96 (m, 2H), 1.76-1.65 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 149.7, 132.5, 111.9, 110.8, 86.5, 81.7, 40.3, 32.5, 29.6, 18.5, 6.5 ppm. Data was in accordance with that reported in the literature.[11]



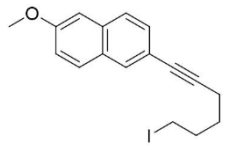
4m

1-(6-iodohex-1-yn-1-yl)-3,5-dimethoxybenzene (4m): 700 mg; Yield 68%. Colorless oil. Purified by column chromatography using a mixture of hexane and EA [50:1 to 20:1(v/v)]. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 6.54 (d, *J* = 2.0 Hz, 2H), 6.40 (s, 1H), 3.76 (s, 6H), 3.27 (t, *J* = 6.9 Hz, 2H), 2.44 (t, *J* = 7.0 Hz, 2H), 2.04-1.94 (m, 2H), 1.75-1.66 (m, 2H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 161.1, 125.7, 109.8, 101.4, 89.6, 81.4, 55.9, 33.2, 30.0, 18.8, 7.0 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{14}H_{18}IO_2$ $[M+H]^+$: 345.0346; found: 345.0340.



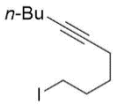
4n

1-(tert-butyl)-4-(6-iodohex-1-yn-1-yl)benzene (4n): 735 mg; Yield 72%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38-7.28 (m, 4H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 2.07-1.97 (m, 2H), 1.77-1.67 (m, 2H), 1.31 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 150.8, 131.2, 125.2, 120.7, 88.4, 81.2, 34.6, 32.4, 31.2, 29.4, 18.4, 6.3 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{16}H_{22}I$ $[M+H]^+$: 341.0761; found: 341.0762.



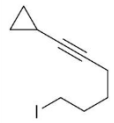
4o

2-(6-iodohex-1-yn-1-yl)-6-methoxynaphthalene (4o): 710 mg; Yield 65%. Yellow solid. Purified by column chromatography using a mixture of hexane and EA [50:1 to 20:1(v/v)]. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.83 (s, 1H), 7.72-7.62 (m, 2H), 7.42 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.19-7.10 (m, 2H), 3.91 (s, 3H), 3.29 (t, *J* = 6.9 Hz, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.08-1.99 (m, 2H), 1.80-1.70 (m, 2H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 158.7, 134.4, 131.3, 129.7, 129.6, 129.0, 127.2, 119.8, 119.3, 106.3, 89.5, 81.8, 55.9, 33.2, 30.1, 19.0, 7.0 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{17}H_{18}IO$ $[M+H]^+$: 365.0397; found: 365.0393. M.p. 75-77 °C.



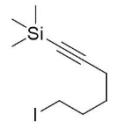
4p

1-iododec-5-yne (4p): 572 mg; Yield 72%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.21 (t, *J* = 7.0 Hz, 2H), 2.23-2.09 (m, 4H), 1.98-1.89 (m, 2H), 1.63-1.54 (m, 2H), 1.51-1.33 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 81.0, 79.1, 32.5, 31.2, 29.7, 21.9, 18.4, 17.7, 13.6, 6.4 ppm. Data was in accordance with that reported in the literature.[13]



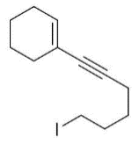
4q

(6-iodohex-1-yn-1-yl)cyclopropane (4q): 500 mg; Yield 67%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 3.19 (t, *J* = 7.0 Hz, 2H), 2.15 (td, *J* = 7.0, 1.9 Hz, 2H), 1.95-1.85 (m, 2H), 1.61-1.52 (m, 2H), 1.24-1.13 (m, 1H), 0.75-0.65 (m, 2H), 0.63-0.56 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 83.9, 74.6, 32.4, 29.6, 17.7, 7.9, 6.4, –0.5 ppm. Data was in accordance with that reported in the literature.[14]



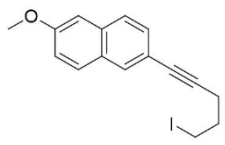
4r

(6-iodohex-1-yn-1-yl)trimethylsilane (4r): 565 mg; Yield 67%. Yellow oil. Purified by column chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 3.22 (t, *J* = 6.9 Hz, 2H), 2.26 (t, *J* = 7.0 Hz, 2H), 1.98-1.90 (m, 2H), 1.67-1.59 (m, 2H), 0.15 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 106.4, 85.2, 32.4, 29.2, 18.8, 6.2, 0.1 ppm. Data was in accordance with that reported in the literature.[15]



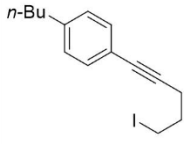
4s

1-(6-iodohex-1-yn-1-yl)cyclohex-1-ene (4s): 591 mg; Yield 68%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.01 (s, 1H), 3.21 (t, *J* = 6.9 Hz, 2H), 2.33 (t, *J* = 6.9 Hz, 2H), 2.12-2.03 (m, 4H), 1.99-1.90 (m, 2H), 1.67-1.52 (m, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 133.5, 120.8, 86.2, 83.0, 32.5, 29.5, 25.5, 22.3, 21.5, 18.2, 6.4 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{13}H_{22}IO$ $[M+H+CH_3OH]^+$: 321.0710; found: 321.0709.



4t

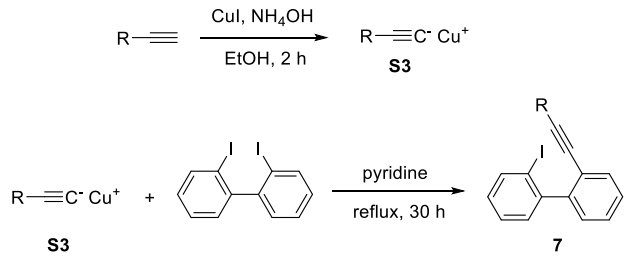
2-(5-iodopent-1-yn-1-yl)-6-methoxynaphthalene (4t): 685 mg; Yield 65%. White solid. Purified by column chromatography using a mixture of hexane and EA [20:1 to 10:1(v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.84 (s, 1H), 7.66 (dd, *J* = 12.3, 8.8 Hz, 2H), 7.42 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.14 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 3.92 (s, 3H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.60 (t, *J* = 6.7 Hz, 2H), 2.16-2.09 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 158.1, 133.8, 131.0, 129.2, 129.1, 128.5, 126.7, 119.3, 118.4, 105.7, 87.3, 82.1, 55.3, 32.3, 20.6, 5.5 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{17}H_{20}IO_2$ $[M+H+CH_3OH]^+$: 383.0502; found: 383.0500. M.p. 71-73 °C.



4u

1-butyl-4-(5-iodopent-1-yn-1-yl)benzene (4u): 688 mg; Yield 70%. Colorless oil. Purified by column chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 3.36 (t, *J* = 6.8 Hz, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.55 (t, *J* = 6.7 Hz, 2H), 2.13-2.04 (m, 2H), 1.62-1.55 (m, 2H), 1.38-1.29 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 142.8, 131.4, 128.3, 120.6, 86.9, 81.8, 35.5, 33.4, 32.2, 22.3, 20.5, 13.9, 5.4 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{16}H_{24}IO$ $[M+H+CH_3OH]^+$: 359.0866; found: 359.0867.

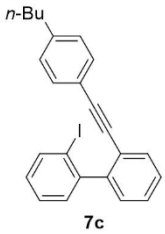
2.3. General Procedure for Acetylenic Phenyl Iodides 7



A solution of cuprous iodide (10 mmol) in aqueous ammoniacal (20 mL) was poured into a solution of terminal alkyne (10 mmol) in ethanol (40 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The bright chartreuse precipitate was filtered off and washed three times with water, ethanol, and ethyl acetate. The bright canary yellow solid was dried at 50 °C under reduced pressure with oil pump. The crude copper(I) reagent **S3** was used without further purification.

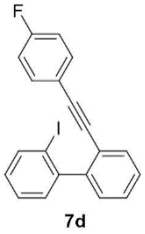
To a 25 mL two necked flask were added copper(I) reagent **S3** (2 mmol), 2,2'-diiodo-1,1'-biphenyl (2 mmol) and pyridine (15 mL). After degassing 30 min with argon, the mixture was refluxed for 30 h under argon atmosphere. The solvent was removed under reduced pressure. Purification by silica gel chromatography afforded the corresponding acetylenic phenyl iodide.

7a and **7b** were prepared following the reported literature protocols.[16]



7c

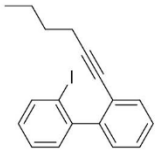
2-((4-butylphenyl)ethynyl)-2'-iodo-1,1'-biphenyl (7c): 348 mg; Yield 40%. Yellow oil. Purified by column chromatography using hexane. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 8.01 (d, *J* = 8.0 Hz, 1H), 7.66-7.60 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 4.4 Hz, 2H), 7.37 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.31-7.27 (m, 1H), 7.14-7.10 (m, 1H), 7.10-7.06 (m, 4H), 2.58 (t, *J* = 7.7, 2H), 1.60-1.52 (m, 2H), 1.38-1.29 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 147.3, 146.4, 144.2, 139.4, 132.1, 131.7, 131.0, 130.0, 129.6, 129.0, 128.5, 128.4, 128.4, 123.5, 120.7, 99.9, 93.8, 88.2, 36.0, 34.0, 22.8, 14.2 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{24}H_{22}I$ $[M+H]^+$: 437.0761; found: 437.0764.



7d

2-((4-fluorophenyl)ethynyl)-2'-iodo-1,1'-biphenyl (7d): 360 mg; Yield 45%. Yellow solid. Purified by column chromatography using hexane. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 8.02 (d, *J* = 8.0 Hz, 1H), 7.67-7.61 (m, 1H), 7.49-7.42 (m, 3H), 7.37 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.32-7.27 (m, 1H), 7.19-7.10 (m, 3H), 6.98 (t, *J* = 8.8 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 163.0 (d, *J* = 249.0 Hz), 147.3,

146.3, 139.4, 133.7 (d, *J* = 8.4 Hz), 132.1, 130.9, 130.1, 129.7, 128.7, 128.5, 128.4, 123.1, 119.8 (d, *J* = 3.5 Hz), 116.0 (d, *J* = 22.2 Hz), 99.9, 92.4, 88.6 ppm. **^{19}F NMR** (377 MHz, CD_2Cl_2) δ = –111.85 (tt, *J* = 8.7, 5.5 Hz) ppm. **HRMS** *m/z* (APCI) calcd. for $C_{20}H_{13}FI$ $[M+H]^+$: 399.0040; found: 399.0040. M.p. 90-92 °C.

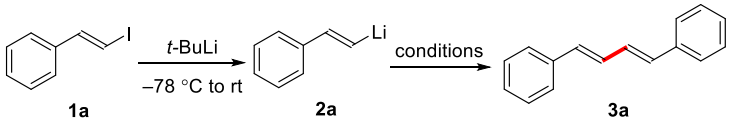


7e

2-(hex-1-yn-1-yl)-2'-iodo-1,1'-biphenyl (7e): 270 mg; Yield 38%. Yellow oil. Purified by column chromatography using hexane. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 7.93 (d, *J* = 7.9 Hz, 1H), 7.50-7.43 (m, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.37-7.30 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.22-7.16 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 2.26-2.12 (m, 2H), 1.32-1.25 (m, 2H), 1.18-1.10 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 147.2, 146.7, 139.3, 132.3, 130.7, 129.9, 129.4, 128.3, 128.2, 127.7, 124.1, 99.9, 94.8, 79.7, 31.0, 22.1, 19.4, 13.9 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{18}H_{18}I$ $[M+H]^+$: 361.0448; found: 361.0447.

2.4. Reaction Conditions Optimization

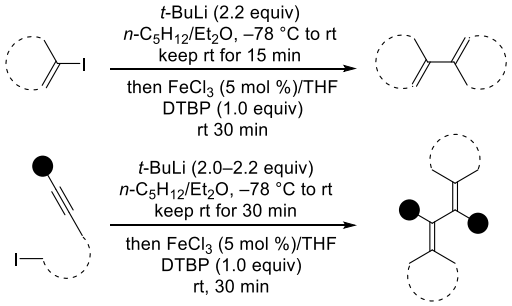
Table S1. Optimization of the Reaction Conditions.[a]



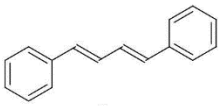
entry	iron salt (mol %)	additive	solvent	*T* (°C)	time (min)	yield (%)[b]
1	$FeCl_3$ (100)	none	THF	rt	60	86
2	FeF_3 (100)	none	THF	rt	60	56
3	$FeBr_3$ (100)	none	THF	rt	60	52
4	$Fe(acac)_3$ (100)	none	THF	rt	60	70
5	FeF_2 (100)	none	THF	rt	60	25
6	$FeCl_2$ (100)	none	THF	rt	60	82
7	$FeBr_2$ (100)	none	THF	rt	60	38
8	$FeCl_3$ (10)	none	THF	rt	60	29
9	$FeCl_3$ (10)	O_2 (balloon)	THF	rt	60	41
10	$FeCl_3$ (10)	DCE (1.0 equiv)	THF	rt	60	84
11	$FeCl_3$ (10)	DTBP (1.0 equiv)	THF	rt	60	86
12	$FeCl_2$ (10)	Et_3N (1.0 equiv)	THF	rt	60	33
13	$FeCl_3$ (10)	DTBP (1.0 equiv)	toluene	rt	60	80
14	$FeCl_3$ (10)	DTBP (1.0 equiv)	Et_2O	rt	60	70
15	$FeCl_3$ (10)	DTBP (1.0 equiv)	THF	0	60	77
16	$FeCl_3$ (10)	DTBP (1.0 equiv)	THF	40	60	81
17	$FeCl_3$ (5)	DTBP (1.0 equiv)	THF	rt	30	86
18[c]	$FeCl_3$ (5)	DTBP (1.0 equiv)	THF	rt	30	94

[a]Reaction condition: a solution of vinyllithium (0.2 mmol) was added to a mixture of iron salt, additive (if applicable) in THF (1.0 mL) at rt. [b]GC–MS analysis. [c]To a solution of vinyllithium (0.2 mmol) were added a solution of $FeCl_3$ in THF (0.1 mL) and additive.

2.5. Optimized Procedure for Butadienes

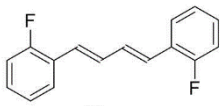


To a Schlenk tube charged with acetylenic iodide (0.2 mmol), were added 1.2 mL *n*-pentane and 0.8 mL diethyl ether via argon-flushed syringes, and the resulting solution was cooled to –78 °C in an acetone-dry ice bath. Then *t*-BuLi (2.0-2.2 equiv) in pentane was added dropwise via an argon-flushed syringe, and the mixture was stirred at –78 °C for an additional 8 min. After removing the cooling bath and stirring for a period of time (15 min for substrates **1**, 30 min for substrates **4** and **7**), a solution of $FeCl_3$ (0.01 mmol) in THF (0.1 mL) was added via an argon-flushed syringe, followed by adding DTBP (0.2 mmol) via an argon-flushed microsyringe. After stirring for 30 min at rt, the reaction mixture was quenched by MeOH and passed through a short silica pad using DCM as an eluent. After concentration, the residue was purified by column chromatography or preparative thin-layer chromatography.



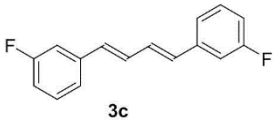
3a

(1E,3E)-1,4-diphenylbuta-1,3-diene (3a): 18.7 mg; Yield 91%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 7.5 Hz, 4H), 7.34 (t, *J* = 7.5 Hz, 4H), 7.24 (t, *J* = 6.0 Hz, 2H), 6.99-6.93 (m, 2H), 6.71-6.65 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 137.3, 132.8, 129.2, 128.6, 127.6, 126.4 ppm. Data was in accordance with that reported in the literature.[17]



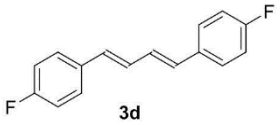
3b

(1E,3E)-1,4-bis(2-fluorophenyl)buta-1,3-diene (3b): 12.3 mg; Yield 51%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 7.57 (td, *J* = 7.7, 1.6 Hz, 2H), 7.27-7.21 (m, 2H), 7.14 (t, *J* = 7.5 Hz, 2H), 7.16-7.05 (m, 4H), 6.92-6.82 (m, 2H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 161.9, 159.9, 132.3 (d, *J* = 5.2 Hz), 129.5 (d, *J* = 8.4 Hz), 127.7 (d, *J* = 3.6 Hz), 126.1 (d, *J* = 3.4 Hz), 125.6 (d, *J* = 12.0 Hz), 124.8 (d, *J* = 3.5 Hz), 116.4, 116.2 ppm. **^{19}F NMR** (471 MHz, CD_2Cl_2) δ = –116.47 (ddd, *J* = 11.3, 7.7, 5.3 Hz) ppm. Data was in accordance with that reported in the literature.[18]



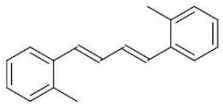
3c

(1E,3E)-1,4-bis(3-fluorophenyl)buta-1,3-diene (3c): 11.9 mg; Yield 49%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, CH_2Cl_2) δ = 7.37-7.26 (m, 2H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.17 (dd, *J* = 10.3, 1.3 Hz, 2H), 7.01-6.87 (m, 4H), 6.74-6.61 (m, 2H) ppm. **^{13}C NMR** (126 MHz, CH_2Cl_2) δ = 164.7, 162.8, 140.2 (d, *J* = 7.7 Hz), 132.9 (d, *J* = 2.7 Hz), 130.8-130.6 (m), 123.0 (d, *J* = 2.6 Hz), 115.0 (d, *J* = 21.4 Hz), 113.1 (d, *J* = 22.0 Hz) ppm. **^{19}F NMR** (471 MHz, CH_2Cl_2) δ = –114.84 - –115.35 (m) ppm. Data was in accordance with that reported in the literature.[19]



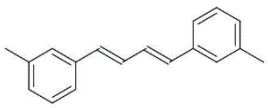
3d

(1E,3E)-1,4-bis(4-fluorophenyl)buta-1,3-diene (3d): 14.0 mg; Yield 58%. Purified by preparative thin-layer chromatography using hexane. White solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.44-7.36 (m, 4H), 7.02 (t, *J* = 8.7 Hz, 4H), 6.88-6.80 (m, 2H), 6.66-6.57 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.3 (d, *J* = 248.2 Hz), 133.5 (d, *J* = 3.4 Hz), 131.5, 128.8 (d, *J* = 1.4 Hz), 127.8 (d, *J* = 8.0 Hz), 115.6 (d, *J* = 21.4 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = –114.92 (dd, *J* = 8.5, 5.6 Hz) ppm. Data was in accordance with that reported in the literature.[17]



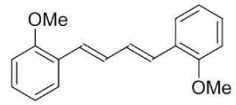
3e

(1E,3E)-1,4-di-o-tolylbuta-1,3-diene (3e): 16.4 mg; Yield 70%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 7.5 Hz, 2H), 7.22-7.15 (m, 6H), 6.92 (t, *J* = 7.4 Hz, 4H), 2.40 (s, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 136.2, 135.6, 130.7, 130.5, 130.3, 127.4, 126.1, 125.0, 19.9 ppm. Data was in accordance with that reported in the literature.[20]



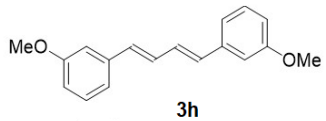
3f

(1E,3E)-1,4-di-m-tolylbuta-1,3-diene (3f): 15.0 mg; Yield 64%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 7.30–7.20 (m, 6H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.01-6.93 (m, 2H), 6.70-6.61 (m, 2H), 2.36 (s, 6H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 138.9, 137.9, 133.3, 129.7, 129.1, 128.9, 127.6, 124.0, 21.7 ppm. Data was in accordance with that reported in the literature.[17]



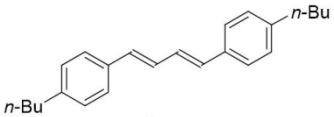
3g

(1E,3E)-1,4-bis(2-methoxyphenyl)buta-1,3-diene (3g): 18.6 mg; Yield 70%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 7.52 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.22 (ddd, *J* = 8.3, 7.5, 1.7 Hz, 2H), 7.07-6.96 (m, 4H), 6.93 (ddd, *J* = 14.6, 10.6, 4.6 Hz, 4H), 3.87 (s, 6H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 157.4, 131.2, 129.0, 127.6, 126.9, 126.8, 121.2, 111.5, 56.0 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{18}H_{19}O_2$ $[M+H]^+$: 267.1380; found: 267.1378. M.p. 80-82 °C.



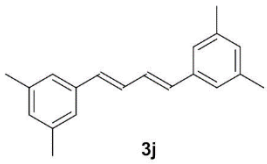
3h

(1E,3E)-1,4-bis(3-methoxyphenyl)buta-1,3-diene (3h): 19.4 mg; Yield 73%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.27 (s, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 2H), 7.00-6.90 (m, 4H), 6.83-6.78 (m, 2H), 6.65 (dd, *J* = 11.8, 2.9 Hz, 2H), 3.84 (s, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 159.8, 138.8, 132.9, 129.6, 129.5, 119.2, 113.3, 111.5, 55.2 ppm. **MS** *m/z* (relative intensity): 266.1 (22.1%), 207.0 (31.3%), 193.1 (52.7%), 137.0 (81.9%), 73.1 (100%). M.p. 91-93 °C.



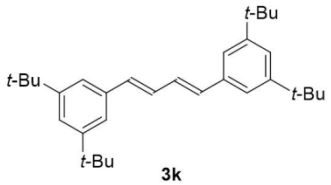
3i

(1E,3E)-1,4-bis(4-butylphenyl)buta-1,3-diene (3i): 20.7 mg; Yield 65%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 8.1 Hz, 4H), 7.16 (d, *J* = 8.1 Hz, 4H), 6.97-6.89 (m, 2H), 6.68-6.61 (m, 2H), 2.62-2.58 (m, 4H), 1.62-1.56 (m, 4H), 1.36 (dd, *J* = 14.9, 7.4 Hz, 4H), 0.93 (dd, *J* = 9.2, 5.5 Hz, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 143.2, 135.4, 132.8, 129.3, 129.0, 126.7, 35.9, 34.2, 22.9, 14.3 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{24}H_{31}$ $[M+H]^+$: 319.2420; found: 319.2416.



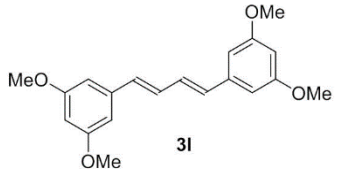
3j

(1E,3E)-1,4-bis(3,5-dimethylphenyl)buta-1,3-diene (3j): 20.7 mg; Yield 79%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.08 (s, 4H), 6.94 (dd, *J* = 11.9, 2.8 Hz, 2H), 6.90 (s, 2H), 6.65-6.57 (m, 2H), 2.34 (s, 12H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 138.0, 137.3, 132.7, 129.3, 129.1, 124.2, 21.3 ppm. Data was in accordance with that reported in the literature.[20]



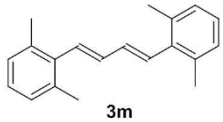
3k

(1E,3E)-1,4-bis(3,5-di-tert-butylphenyl)buta-1,3-diene (3k): 25.4 mg; Yield 59%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 13.7 Hz, 6H), 6.96 (dd, *J* = 12.2, 9.7 Hz, 2H), 6.73 (dd, *J* = 16.7, 4.7 Hz, 2H), 1.35 (s, 36H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.9, 136.6, 133.4, 128.9, 122.0, 120.6, 34.8, 31.4 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{32}H_{47}$ $[M+H]^+$: 431.3672; found: 431.3677.

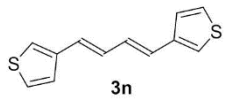


3l

(1E,3E)-1,4-bis(3,5-dimethoxyphenyl)buta-1,3-diene (3l): 25.1 mg; Yield 77%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.95-6.87 (m, 2H), 6.61 (t, *J* = 7.7 Hz, 6H), 6.38 (t, *J* = 2.1 Hz, 2H), 3.82 (s, 12H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 160.9, 139.3, 133.1, 129.5, 104.4, 100.0, 55.3 ppm. Data was in accordance with that reported in the literature.[18]

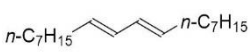

3m

(1E,3E)-1,4-bis(2,6-dimethylphenyl)buta-1,3-diene (3m): 16.2 mg; Yield 62%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.07 (s, 6H), 6.67-6.60 (m, 2H), 6.53-6.47 (m, 2H), 2.38 (s, 12H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) = 136.6, 136.1, 135.0, 130.2, 127.9, 126.6, 21.2 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{20}H_{23}$ $[M+H]^+$: 263.1794; found: 263.1796. M.p. 104-106 °C.



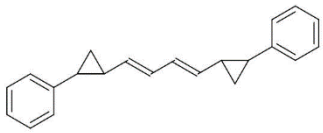
3n

(1E,3E)-1,4-di(thiophen-3-yl)buta-1,3-diene (3n): 14.2 mg; Yield 65%. White solid. Purified by preparative thin-layer chromatography using a mixture of hexane and EA [20:1 (v/v)]. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 7.31 (ddd, *J* = 6.3, 5.1, 2.1 Hz, 4H), 7.22 (dd, *J* = 2.8, 1.2 Hz, 2H), 6.81-6.73 (m, 2H), 6.71-6.64 (m, 2H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 140.8, 129.8, 126.9, 126.8, 125.4, 122.6 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{12}H_{11}S_2$ $[M+H]^+$: 219.0297; found: 219.0295. M.p. 123-125 °C.



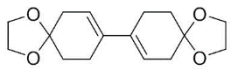
3o

(8E,10E)-octadeca-8,10-diene (3o): 24.5 mg; Yield 98%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.03-5.95 (m, 2H), 5.61-5.52 (m, 2H), 2.06 (d, *J* = 6.9 Hz, 4H), 1.26 (s, 20H), 0.88 (s, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 132.4, 130.3, 32.6, 31.8, 29.7, 29.4, 29.2, 22.7, 14.1 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{18}H_{35}$ $[M+H]^+$: 251.2733; found: 251.2734.



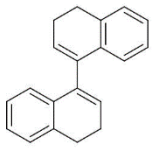
3p

(1E,3E)-1,4-bis(2-phenylcyclopropyl)buta-1,3-diene (3p): 21.7 mg; Yield 76%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.25 (t, *J* = 7.5 Hz, 4H), 7.15 (d, *J* = 7.3 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 4H), 6.13 (dd, *J* = 11.5, 2.8 Hz, 2H), 1.99-1.88 (m, 2H), 1.73-1.60 (m, 2H), 1.28-1.20 (m, 2H), 1.11 (dt, *J* = 8.9, 5.3 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 143.0, 134.5, 129.0, 128.8, 126.1, 27.6, 26.2 26.2, 17.6 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{22}H_{23}$ $[M+H]^+$: 287.1794; found: 287.1792.



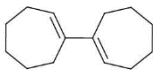
3q

1,1',4,4'-tetraoxa-8,8'-bispiro[4.5]decane-7,7'-diene (3q): 13.1 mg; Yield 47%. Colorless oil. Purified by preparative thin-layer chromatography using a mixture of hexane and EA [20:1 (v/v)]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.68 (s, 2H), 3.97 (s, 8H), 2.43 (t, *J* = 6.1 Hz, 4H), 2.37 (s, 4H), 1.79 (t, *J* = 6.6 Hz, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 135.4, 119.3, 107.9, 64.4, 64.4, 35.9, 31.1, 24.8 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{16}H_{23}O_4$ $[M+H]^+$: 279.1580; found: 279.1598.



3r

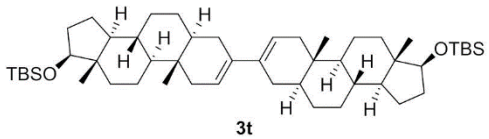
3,3',4,4'-tetrahydro-1,1'-binaphthalene (3r): 19.9 mg; Yield 77%. White Solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.17 (d, *J* = 7.0 Hz, 2H), 7.10 (td, *J* = 7.3, 1.2 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 7.5 Hz, 2H), 6.09 (t, *J* = 4.5 Hz, 2H), 2.91 (t, *J* = 7.8 Hz, 4H), 2.41 (td, *J* = 8.0, 4.6 Hz, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 138.3, 135.8, 134.7, 128.0, 127.4, 126.8, 126.3, 125.1, 28.2, 23.3 ppm. Data was in accordance with that reported in the literature.[21]



3s

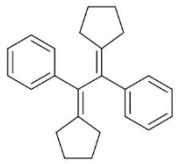
[1,1'-bi(cycloheptane)]-1,1'-diene (3s): 12.2 mg; Yield 64%. White Solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 5.77 (t, *J* = 6.8 Hz, 1H), 2.30-2.22 (m, 2H), 2.14 (dd, *J* = 11.2, 6.7 Hz, 2H), 1.78-1.72 (m, 2H), 1.46 (ddd, *J* = 10.8, 8.0, 5.2 Hz,

4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 148.0, 125.7, 32.8, 30.5, 28.5, 27.0, 26.9 ppm. Data was in accordance with that reported in the literature.[22]



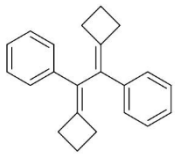
3t

Compound (**3t**): 58.1 mg; Yield 75%. White Solid. Purified by column chromatography using a mixture of hexane and EA [20:1 to 10:1(v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 5.68 (s, 2H), 3.60-3.53 (m, 2H), 2.14 (ddd, *J* = 15.2, 6.2, 3.1 Hz, 2H), 2.04 (dd, *J* = 8.7, 2.7 Hz, 2H), 1.90 (s, 2H), 1.74-1.65 (m, 6H), 1.63-1.59 (m, 2H), 1.52-1.41 (m, 6H), 1.41-1.35 (m, 4H), 1.31-1.26 (m, 8H), 1.14-1.06 (m, 2H), 1.03-0.94 (m, 4H), 0.91 (s, 24H), 0.85 (s, 6H), 0.74-0.66 (m, 2H), 0.07 (s, 12H). **13C NMR** (126 MHz, $CDCl_3$) δ = 149.6, 124.1, 72.2, 56.7, 54.8, 47.5, 45.3, 38.7, 37.0, 35.9, 35.7, 33.9, 32.0, 32.0, 31.6, 28.8, 26.0, 21.4, 18.3, 16.2, 12.4, –4.6 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{50}H_{87}Si_2O_2$ $[M+H]^+$: 775.6239; found: 775.6253. M.p. 240-242 °C.



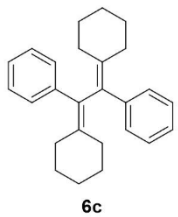
6a

1,2-dicyclopentylidene-1,2-diphenylethane (6a): 24.5 mg; Yield 78%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.32-7.17 (m, 8H), 7.12 (t, *J* = 7.0 Hz, 2H), 2.47 (m, 4H), 2.33 (m, 4H), 1.74-1.64 (m, 8H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 143.6, 142.1, 134.0, 128.9, 128.3, 126.3, 33.5, 32.9, 27.7, 26.6 ppm. **HRMS** *m/z* (ESI) calcd. for $C_{24}H_{26}Na$ $[M+Na]^+$: 337.1924; found: 337.1927.



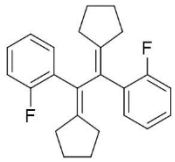
6b

1,2-dicyclobutylidene-1,2-diphenylethane (6b): 21.0 mg; Yield 73%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 7.31 (d, *J* = 7.5 Hz, 4H), 7.24 (t, *J* = 7.7 Hz, 4H), 7.12 (t, *J* = 7.3 Hz, 2H), 3.13-3.05 (m, 4H), 2.73-2.66 (m, 4H), 2.09-1.99 (m, 4H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 142.5, 139.8, 130.2, 128.6, 127.6, 126.4, 33.3, 32.6, 18.0 ppm. **HRMS** *m/z* (ESI) calcd. for $C_{22}H_{22}Na$ $[M+Na]^+$: 309.1614; found: 309.1610. M.p. 72-74 °C.



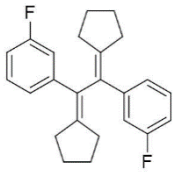
6c

1,2-dicyclohexylidene-1,2-diphenylethane (6c): 13.7 mg; Yield 40%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18-7.12 (m, 4H), 7.12-7.06 (m, 2H), 6.92 (d, *J* = 7.1 Hz, 4H), 2.58-2.47 (m, 2H), 2.41-2.32 (m, 2H), 2.25-2.16 (m, 2H), 2.11-2.02 (m, 2H), 1.77-1.69 (m, 2H), 1.68-1.59 (m, 6H), 1.59-1.49 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 141.6, 137.0, 133.9, 129.4, 127.5, 125.7, 32.3, 31.3, 28.3, 28.0, 26.9 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{26}H_{31}$ $[M+H]^+$: 343.2420; found: 343.2422.



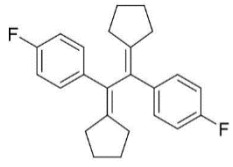
6d

1,2-dicyclopentylidene-1,2-bis(2-fluorophenyl)ethane (6d): 19.5 mg; Yield 56%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.17-7.08 (m, 2H), 7.02-6.88 (m, 6H), 2.38 (t, *J* = 7.1 Hz, 4H), 2.12 (t, *J* = 7.2 Hz, 4H), 1.78-1.68 (m, 4H), 1.68-1.59 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.8 (d, *J* = 245.5 Hz), 145.8, 130.8 (d, *J* = 4.5 Hz), 129.5 (d, *J* = 17.1 Hz), 127.8 (d, *J* = 8.2 Hz), 126.5, 123.4 (d, *J* = 3.5 Hz), 115.3 (d, *J* = 23.3 Hz), 32.3 (d, *J* = 1.6 Hz), 31.6 (d, *J* = 3.3 Hz), 26.6, 26.3 ppm. **^{19}F NMR** (377 MHz, $CDCl_3$) δ = –114.58 (m) ppm. **HRMS** *m/z* (APCI) calcd. for $C_{24}H_{25}F_2$ $[M+H]^+$: 351.1919; found: 351.1916.



6e

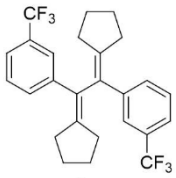
1,2-dicyclopentylidene-1,2-bis(3-fluorophenyl)ethane (6e): 16.8 mg; Yield 48%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.25-7.18 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 7.01-6.94 (m, 2H), 6.93-6.74 (m, 2H), 2.52-2.45 (m, 4H), 2.36-2.28 (m, 4H), 1.74-1.64 (m, 8H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 163.2 (d, *J* = 243.6 Hz), 145.6, 144.2 (d, *J* = 7.3 Hz), 132.6 (d, *J* = 2.1 Hz), 129.7 (d, *J* = 8.5 Hz), 124.7 (d, *J* = 2.6 Hz), 115.4 (d, *J* = 21.4 Hz), 113.2 (d, *J* = 21.2 Hz), 33.7, 33.1, 27.7, 26.5 ppm. **^{19}F NMR** (377 MHz, CD_2Cl_2) δ = –115.07 (ddd, *J* = 10.8, 8.7, 6.5 Hz) ppm. **HRMS** *m/z* (APCI) calcd. for $C_{24}H_{25}F_2$ $[M+H]^+$: 351.1919; found: 351.1914.



6f

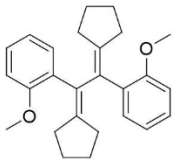
1,2-dicyclopentylidene-1,2-bis(4-fluorophenyl)ethane (6f): 16.0 mg; Yield 46%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.23-7.16 (m, 4H), 6.98-6.86 (m, 4H), 2.47-2.38 (m, 4H), 2.32-2.25 (m, 4H), 1.72-1.63 (m, 8H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 161.0 (d, *J* = 245.0 Hz), 143.0, 137.4 (d, *J* = 3.2 Hz), 132.5, 129.7 (d,

J = 7.6 Hz), 114.6 (d, *J* = 21.1 Hz), 32.9, 32.4, 27.1, 26.0 ppm. **^{19}F NMR** (377 MHz, $CDCl_3$) δ = –117.70 (tt, *J* = 8.7, 5.5 Hz) ppm. Data was in accordance with that reported in the literature.[23]



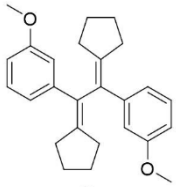
6g

1,2-dicyclopentylidene-1,2-bis(3-(trifluoromethyl)phenyl)ethane (6g): 13.5 mg; Yield 30%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 7.50 (s, 2H), 7.46-7.33 (m, 6H), 2.51-2.42 (m, 4H), 2.36-2.30 (m, 4H), 1.75-1.65 (m, 8H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 146.4, 142.6, 132.3, 132.2, 130.5 (q, *J* = 31.7 Hz), 129.0, 125.4 (q, *J* = 3.8 Hz), 125.0 (q, *J* = 272.2 Hz), 123.2 (q, *J* = 3.7 Hz), 33.8, 33.0, 27.6, 26.5 ppm. **^{19}F NMR** (471 MHz, CD_2Cl_2) δ = –63.20 (s) ppm. **HRMS** *m/z* (APCI) calcd. for $C_{26}H_{25}F_6$ $[M+H]^+$: 451.1855; found: 451.1838.



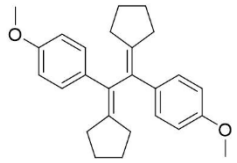
6h

1,2-dicyclopentylidene-1,2-bis(2-methoxyphenyl)ethane (6h): 16.0 mg; Yield 43%. White solid. Purified by preparative thin-layer chromatography using a mixture of hexane and EA [20:1 (v/v)]. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 7.09 (t, *J* = 7.7 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 4H), 6.72 (t, *J* = 7.3 Hz, 2H), 3.60 (s, 6H), 2.35 (t, *J* = 6.9 Hz, 4H), 1.97 (t, *J* = 7.2 Hz, 4H), 1.72-1.65 (m, 4H), 1.61-1.55 (m, 4H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 157.1, 142.9, 132.0, 130.5, 129.7, 127.0, 119.8, 110.9, 55.3, 32.1, 31.4, 26.9, 26.2 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{26}H_{31}O_2$ $[M+H]^+$: 375.2319; found: 375.2325. M.p. 67-69 °C.



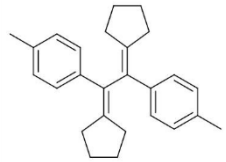
6i

1,2-dicyclopentylidene-1,2-bis(3-methoxyphenyl)ethane (6i): 26.6 mg; Yield 71%. Colorless oil. Purified by preparative thin-layer chromatography using a mixture of hexane and EA [20:1 (v/v)]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.16 (t, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.85-6.80 (m, 2H), 6.70 (dd, *J* = 8.0, 2.2 Hz, 2H), 3.73 (s, 6H), 2.53-2.45 (m, 4H), 2.35-2.25 (t, *J* = 5.9 Hz, 4H), 1.72-1.63 (m, 8H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.0, 143.2, 143.0, 133.2, 128.6, 121.0, 114.2, 111.0, 55.0, 33.0, 32.6, 27.2, 26.0 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{26}H_{31}O_2$ $[M+H]^+$: 375.2319; found: 375.2323.



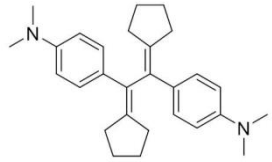
6j

1,2-dicyclopentylidene-1,2-bis(4-methoxyphenyl)ethane (6j): 27.4 mg; Yield 73%. Colorless oil. Purified by preparative thin-layer chromatography using a mixture of hexane and EA [20:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.21 (d, *J* = 8.7 Hz, 4H), 6.79 (d, *J* = 8.8 Hz, 4H), 3.78 (s, 6H), 2.47 (t, *J* = 6.2 Hz, 4H), 2.27 (t, *J* = 6.4 Hz, 4H), 1.71-1.61 (m, 8H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 157.5, 141.2, 134.2, 133.0, 129.3, 113.1, 55.1, 32.8, 32.5, 27.3, 26.1 ppm. **HRMS** *m/z* (ESI) calcd. for $C_{26}H_{30}O_2Na$ $[M+Na]^+$: 397.2138; found: 397.2136.



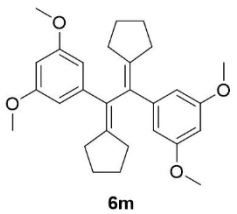
6k

1,2-dicyclopentylidene-1,2-di-p-tolylethane (6k): 26.0 mg; Yield 76%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.17 (d, *J* = 8.1 Hz, 4H), 7.04 (d, *J* = 8.0 Hz, 4H), 2.50-2.45 (m, 4H), 2.29 (s, 6H), 2.27 (t, *J* = 6.4 Hz, 4H), 1.69-1.60 (m, 8H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 142.1, 138.7, 135.2, 133.3, 128.4, 128.2, 32.9, 32.6, 27.2, 26.0, 21.1 ppm. Data was in accordance with that reported in the literature.[23]



6l

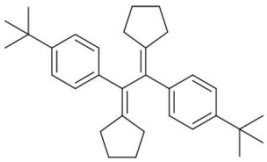
4,4'-(1,2-dicyclopentylideneethane-1,2-diyl)bis(*N*,*N*-dimethylaniline) (6l): 24.8 mg; Yield 62%. Brown oil. Purified by preparative thin-layer chromatography using a mixture of hexane and EA [10:1 (v/v)]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.8 Hz, 4H), 6.64 (d, *J* = 8.9 Hz, 4H), 2.91 (s, 12H), 2.53 (t, *J* = 6.6 Hz, 4H), 2.25 (t, *J* = 6.8 Hz, 4H), 1.71-1.59 (m, 8H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 148.5, 139.6, 133.3, 130.3, 129.0, 112.0, 40.6, 32.8, 32.6, 27.4, 26.0 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{28}H_{37}N_2$ $[M+H]^+$: 401.2951; found: 401.2952.



6m

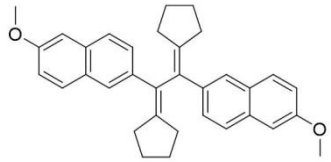
1,2-dicyclopentylidene-1,2-bis(3,5-dimethoxyphenyl)ethane (6m): 26.0 mg; Yield 60%. Colorless oil. Purified by preparative thin-layer chromatography using a mixture of hexane and EA [20:1 (v/v)]. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 6.42 (d, *J* = 2.3 Hz, 4H), 6.27 (t, *J* = 2.3 Hz, 2H), 3.70 (s, 12H),

2.52-2.43 (m, 4H), 2.38-2.29 (m, 4H), 1.73-1.64 (m, 8H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 160.9, 144.1, 143.9, 133.8, 107.2, 98.3, 55.7, 33.5, 33.0, 27.7, 26.5 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{28}H_{35}O_4$ $[M+H]^+$: 435.2530; found: 435.2526.



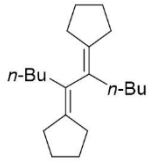
6n

1,2-bis(4-(tert-butyl)phenyl)-1,2-dicyclopentylideneethane (6n): 30.8 mg; Yield 72%. White solid. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.36-7.17 (m, 8H), 2.53 (t, *J* = 6.6 Hz, 4H), 2.34 (t, *J* = 6.5 Hz, 4H), 1.75-1.64 (m, 8H), 1.29 (s, 18H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 149.2, 142.9, 138.7, 133.5, 128.4, 125.2, 34.8, 33.6, 33.1, 31.6, 27.8, 26.5 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{32}H_{43}$ $[M+H]^+$: 427.3359; found: 427.3365. M.p. 110-112 °C.



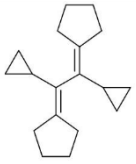
6o

1,2-dicyclopentylidene-1,2-bis(6-methoxynaphthalen-2-yl)ethane (6o): 30.0 mg; Yield 63%. Colorless oil. Purified by preparative thin-layer chromatography using a mixture of hexane and EA [20:1 (v/v)]. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 7.69 (s, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.44 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.14-7.02 (m, 4H), 3.88 (s, 6H), 2.59 (br s, 4H), 2.42 (br s, 4H), 1.79-1.66 (m, 8H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 158.0, 143.7, 137.7, 134.1, 133.5, 129.9, 129.3, 128.2, 127.3, 126.4, 118.9, 106.0, 55.8, 33.7, 33.1, 27.8, 26.7 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{34}H_{35}O_2$ $[M+H]^+$: 475.2632; found: 475.2628.



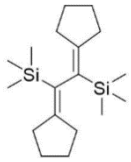
6p

decane-5,6-diylidenedicyclopentane (6p): 12.3 mg; Yield 45%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.26-2.16 (m, 4H), 2.14 -1.85 (m, 8H), 1.72-1.44 (m, 8H), 1.39-1.29 (m, 4H), 0.97-0.79 (m, 10H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 137.5, 132.3, 32.3, 32.1, 30.3, 29.4, 26.7, 26.4, 23.2, 14.1 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{20}H_{35}$ $[M+H]^+$: 275.2733; found: 275.2733.



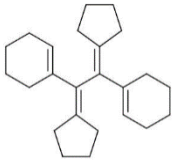
6q

1,2-dicyclopentylidene-1,2-dicyclopropylethane (6q): 7.3 mg; Yield 30%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.38-2.24 (m, 4H), 2.04-1.86 (m, 4H), 1.73-1.61 (m, 4H), 1.55-1.46 (m, 4H), 1.39-1.31 (m, 2H), 0.59-0.38 (m, 6H), 0.25-0.15 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.2, 129.2, 32.2, 29.4, 26.7, 26.5, 13.9, 5.0, 4.7 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{18}H_{27}$ $[M+H]^+$: 243.2107; found: 243.2106.



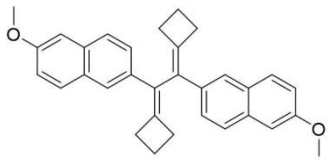
6r

1,2-dicyclopentylidene-1,2-bis(trimethylsilyl)ethane (6r): 9.2 mg; Yield 30%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 2.29 (td, *J* = 7.1, 1.4 Hz, 4H), 2.06-1.95 (m, 4H), 1.68-1.62 (m, 4H), 1.57-1.51 (m, 4H), 0.07 (s, 18H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.9, 135.8, 33.3, 32.4, 27.3, 25.8, 0.3 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{18}H_{35}Si_2$ $[M+H]^+$: 307.2272; found: 307.2276.



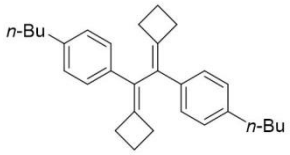
6s

1,2-di(cyclohex-1-en-1-yl)-1,2-dicyclopentylideneethane (6s): 10.0 mg; Yield 31%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 5.50-5.37 (m, 2H), 2.29 (t, *J* = 6.7 Hz, 4H), 2.10 (t, *J* = 6.6 Hz, 4H), 2.05-2.01 (m, 4H), 2.00-1.94 (m, 4H), 1.63-1.56 (m, 10H), 1.55-1.50 (m, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 138.6, 138.2, 135.7, 124.1, 32.0, 31.4, 27.7, 26.8, 26.2, 25.6, 23.3, 22.6 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{24}H_{35}$ $[M+H]^+$: 323.2733; found: 323.2738.



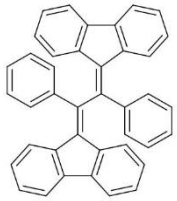
6t

1,2-dicyclobutylidene-1,2-bis(6-methoxynaphthalen-2-yl)ethane (6t): 24.5 mg; Yield 55%. Yellow oil. Purified by preparative thin-layer chromatography using a mixture of hexane and EA [20:1 (v/v)]. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.69 (s, 2H), 7.65-7.60 (m, 4H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.10-7.04 (m, 4H), 3.89 (s, 6H), 3.19 (t, *J* = 6.9 Hz, 4H), 2.68 (t, *J* = 7.0 Hz, 4H), 2.09-2.00 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 157.3, 141.6, 135.0, 132.9, 130.1, 129.5, 129.0, 126.4, 126.3, 125.4, 118.5, 105.5, 55.3, 33.0, 32.2, 17.6 ppm. **HRMS** *m/z* (ESI) calcd. for $C_{32}H_{30}O_2Na$ $[M+Na]^+$: 469.2138; found: 469.2138.



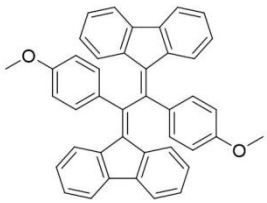
6u

1,2-bis(4-butylphenyl)-1,2-dicyclobutylideneethane (6u): 28.0 mg; Yield 70%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.2 Hz, 4H), 7.05 (d, *J* = 8.3 Hz, 4H), 3.12-3.04 (m, 4H), 2.68-2.62 (m, 4H), 2.54 (t, *J* = 7.8 Hz, 4H), 2.05-1.97 (m, 4H), 1.60-1.53 (m, 4H), 1.39-1.30 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 140.6, 140.3, 136.7, 129.7, 128.1, 126.9, 35.3, 33.5, 32.8, 32.0, 22.4, 17.5, 14.0 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{30}H_{39}$ $[M+H]^+$: 399.3046; found: 399.3048.



8a

1,2-di(9*H*-fluoren-9-ylidene)-1,2-diphenylethane (8a): 40.5 mg; Yield 80%. Yellow solid. Purified by column chromatography using a mixture of hexane and DCM [10:1 to 3:1(v/v)]. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 8.20 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 6.9 Hz, 4H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.33 (dd, *J* = 11.8, 4.3 Hz, 2H), 7.29 (td, *J* = 7.5, 0.7 Hz, 2H), 7.25 (td, *J* = 7.5, 0.7 Hz, 2H), 7.19-7.14 (m, 2H), 7.00-6.93 (m, 6H), 6.74 (d, *J* = 7.9 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 144.2, 141.4, 141.1, 140.1, 139.0, 138.3, 136.1, 132.3, 129.5, 129.0, 129.0, 128.9, 128.1, 127.9, 127.1, 126.0, 124.4, 120.0, 119.9 ppm. M.p. 292-294 °C. Data was in accordance with that reported in the literature.[24]

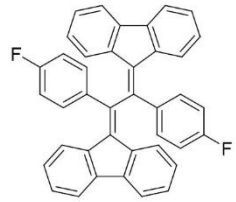


8b

1,2-di(9*H*-fluoren-9-ylidene)-1,2-bis(4-methoxyphenyl)ethane (8b): 48.1 mg; Yield 85%. Yellow solid. Purified by column chromatography using a mixture of hexane and DCM [10:1 to 3:1(v/v)]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.30-7.26 (m, 2H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.04-6.99 (m, 2H), 6.99-6.91 (m, 6H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.70 (d, *J* = 8.2 Hz, 2H), 3.80 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.6, 144.0, 140.8, 140.3, 138.6, 138.0, 135.1, 133.3, 131.7, 129.1, 128.0, 127.4, 126.4, 125.4, 124.0, 119.3, 119.3, 114.0, 55.1 ppm. M.p. 298-300 °C. Data was in accordance with that reported in the literature.[25]

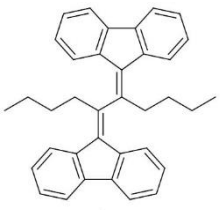
8c

1,2-bis(4-butylphenyl)-1,2-di(9*H*-fluoren-9-ylidene)ethane (8c): 44.5 mg; Yield 72%. Yellow solid. Purified by column chromatography using a mixture of hexane and DCM [10:1 to 3:1(v/v)]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 7.9 Hz, 2H), 7.69 (t, *J* = 8.4 Hz, 4H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 6.99-6.92 (m, 6H), 6.83 (d, *J* = 7.7 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 4H), 1.64-1.55 (m, 4H), 1.38-1.27 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.1, 143.0, 140.8, 140.4, 138.5, 138.0, 136.8, 134.8, 131.6, 128.7, 128.4, 128.1, 128.0, 127.4, 127.3, 126.3, 125.5, 124.1, 119.2, 35.4, 33.3, 22.1, 14.0 ppm. M.p. 206-208 °C. Data was in accordance with that reported in the literature.[25]



8d

1,2-di(9*H*-fluoren-9-ylidene)-1,2-bis(4-fluorophenyl)ethane (8d): 27.0 mg; Yield 50%. Yellow solid. Purified by column chromatography using a mixture of hexane and DCM [50:1 to 5:1(v/v)]. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 8.15 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 7.3 Hz, 4H), 7.60 (t, *J* = 6.0 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.10 (td, *J* = 8.6, 2.3 Hz, 2H), 7.05-6.94 (m, 6H), 6.90 (td, *J* = 8.6, 2.3 Hz, 2H), 6.79 (d, *J* = 7.9 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 163.4 (d, *J* = 247.7 Hz), 142.7, 141.4 (d, *J* = 27.4 Hz), 138.8, 138.1, 136.6, 136.0 (d, *J* = 3.5 Hz), 134.2 (d, *J* = 8.0 Hz), 130.0 (d, *J* = 8.3 Hz), 129.2, 129.1, 128.0, 127.2, 126.0, 124.3, 120.1 (d, *J* = 4.7 Hz), 116.5 (d, *J* = 21.8 Hz), 116.2 (d, *J* = 21.3 Hz) ppm. **^{19}F NMR** (377 MHz, CD_2Cl_2) δ = –113.65 (tt, *J* = 8.7, 5.6 Hz) ppm. **HRMS** *m/z* (APCI) calcd. for $C_{40}H_{25}F_2$ $[M+H]^+$: 543.1919; found: 543.1918. M.p. 296-298 °C.

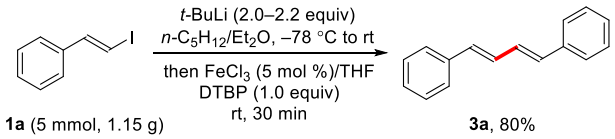


8e

9,9'-(decane-5,6-diylidene)bis(9*H*-fluorene) (8e): 28.0 mg; Yield 60%. Yellow solid. Purified by column chromatography using a mixture of hexane and DCM [50:1 to 10:1(v/v)]. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ = 8.05-7.95 (m, 2H), 7.88-7.80 (m, 2H), 7.69 (dd, *J* = 12.8, 7.7 Hz, 4H), 7.50-7.40 (m, 4H), 7.20 (td, *J* = 7.5, 0.7 Hz, 2H), 7.01-6.91 (m, 2H), 3.35-3.08 (m, 4H), 1.86-1.72 (m, 4H), 1.55-1.44 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, CD_2Cl_2) δ = 148.7, 141.1, 140.1, 138.7, 138.3,

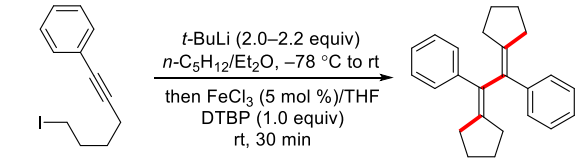
132.7, 128.1, 127.8, 127.7, 127.6, 126.2, 124.9, 120.2, 119.6, 37.6, 30.1, 24.0, 14.2 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{36}H_{35}$ $[M+H]^+$: 467.2733; found: 467.2732. M.p. 156-158 °C.

2.6. Scale-up Syntheses of Butadienes 3a and 6a



1a (5 mmol, 1.15 g) **3a**, 80%

To a Schlenk tube charged with acetylenic iodide **1a** (5 mmol, 1.15 g), were added 30 mL *n*-pentane and 20 mL diethyl ether via argon-flushed syringes, and the resulting solution was cooled to –78 °C in an acetone-dry ice bath. Then *t*-BuLi (8.5 mL, 1.3M) in pentane was added dropwise via an argon-flushed syringe, and the mixture was stirred at –78 °C for an additional 8 min. After removing the cooling bath and stirring for 15 min, a solution of $FeCl_3$ (40.5 mg, 0.25 mmol) in THF (2.5 mL) was added via an argon-flushed syringe, followed by adding DTBP (0.91 mL, 5.0 mmol) via an argon-flushed microsyringe. After stirring for 30 min at rt, the reaction mixture was quenched by MeOH and passed through a short silica pad using DCM as an eluent. After concentration, the residue was purified by column chromatography to get 412 mg butadiene **3a** (yield 80%).

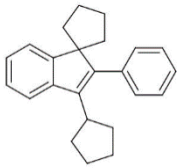


4a (5 mmol, 1.42 g) **6a**, 64%

To a Schlenk tube charged with acetylenic iodide **4a** (5 mmol, 1.42 g), were added 30 mL *n*-pentane and 20 mL diethyl ether via argon-flushed syringes, and the resulting solution was cooled to –78 °C in an acetone-dry ice bath. Then *t*-BuLi (8.5 mL, 1.3M) in pentane was added dropwise via an argon-flushed syringe, and the mixture was stirred at –78 °C for an additional 8 min. After removing the cooling bath and stirring for 30 min, a solution of $FeCl_3$ (40.5 mg, 0.25 mmol) in THF (2.5 mL) was added via an argon-flushed syringe, followed by adding DTBP (0.91 mL, 5.0 mmol) via an argon-flushed microsyringe. After stirring for 30 min at rt, the reaction mixture was quenched by MeOH and passed through a short silica pad using DCM as an eluent. After concentration, the residue was purified by column chromatography to get 502 mg butadiene **6a** (yield 64%).

2.7. Procedure for Indene 9a

To a solution of 1,3-butadiene **6a** (0.1 mmol) in CH_2Cl_2 (2 mL) was added $BF_3{\cdot}OEt_2$ (0.1 mmol) under an argon atmosphere. The reaction mixture was heated to 40 °C. After the reaction solution was stirred for 9 h under an argon atmosphere, the reaction mixture was quenched by the addition of 1 mL of water and then extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated. Purification by silica gel chromatography afforded the indene **9a**.[26]



9a

3'-cyclopentyl-2'-phenylspiro[cyclopentane-1,1'-indene] (9a): 18.8 mg; Yield 60%. Colorless oil. Purified by preparative thin-layer chromatography using hexane. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ = 7.45-7.36 (m, 4H), 7.36-7.31 (m, 1H), 7.23-7.14 (m, 4H), 2.82-2.71 (m, 1H), 2.05-1.98 (m, 2H), 1.96-1.84 (m, 4H), 1.82-1.74 (m, 4H), 1.74-1.67 (m, 2H), 1.63-1.56 (m, 4H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2) δ = 156.1, 150.8, 142.3, 140.1, 138.5, 130.6, 128.5, 127.3, 126.1, 125.3, 122.3, 121.0, 61.8, 39.3, 35.5, 31.6, 27.1, 26.9 ppm. **HRMS** *m/z* (APCI) calcd. for $C_{24}H_{27}$ $[M+H]^+$: 315.2107; found: 315.2104.

3. X-ray Structure Determination

X-ray data of **6b** (CCDC 1860059), **6n** (1860060) and **8b** (1866387) were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-Kα radiation. CCDC 1860059 (**6b**), 1860060 (**6n**) and 1866387 (**8b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

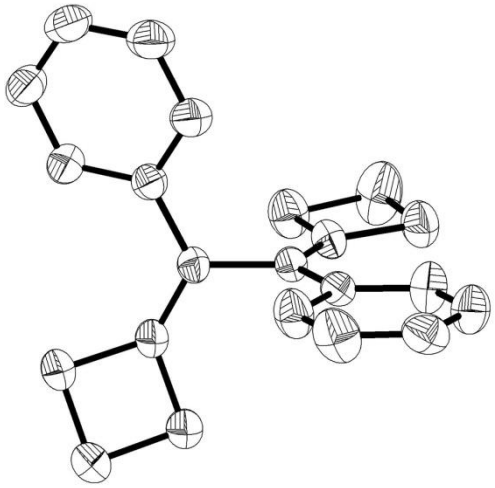


Figure S1: X-ray crystallographic structure of compound **6b** (CCDC 1860059). Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are omitted for clarity.

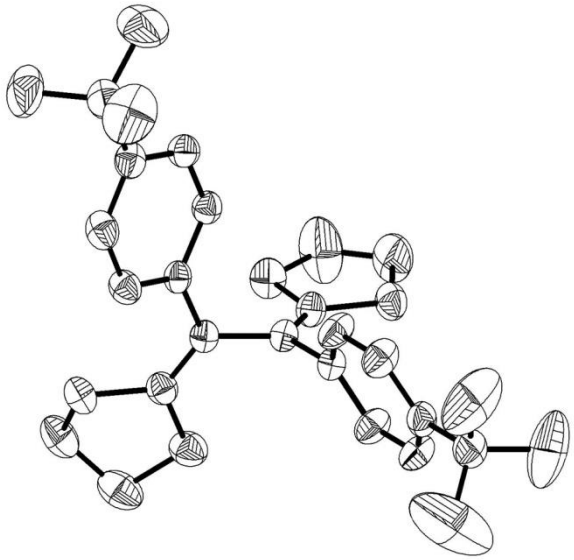


Figure S2: X-ray crystallographic structure of compound **6n** (CCDC 1860060). Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are omitted for clarity.

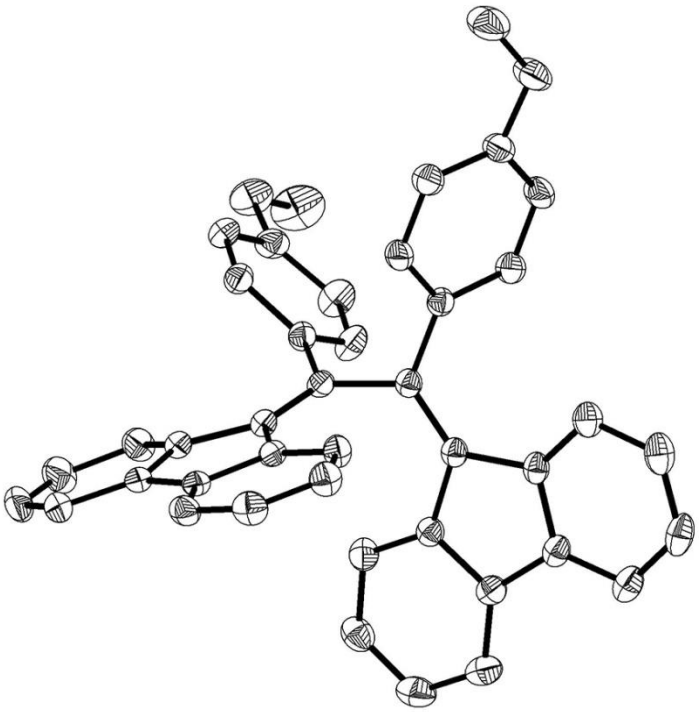
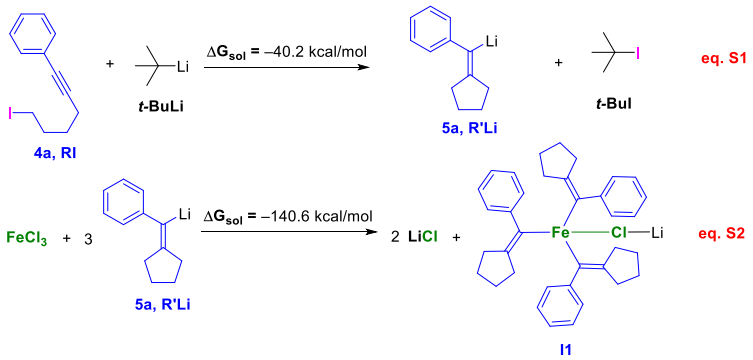


Figure S3: X-ray crystallographic structure of compound **8b** (CCDC 1866387). Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are omitted for clarity.

4. Computational Results

The ωB97X-D[27] functional was used for all calculations, which were carried out with the Gaussian 09 program.[28] Two different basis sets were used. Basis set I was used for geometry optimizations and frequency calculations. The effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LANL2DZ) were employed for Fe,[29-32] supplemented with polarization shells with the following exponents: Fe (f = 2.462),[33-34] and the all-electron 6-31G(d) basis set was used in describing all other atoms.[35-37] All stationary points were confirmed as minima (no imaginary frequency) or transition state structures (only one imaginary frequency). The latter were confirmed to connect appropriate intermediates, reactants, or products by intrinsic reaction coordinate (IRC) calculations.[38-39] All the iron species were optimized along the sexlet-state and the geometric structures of all species in this paper were optimized in the gas phase. Based on the gas phase optimized geometries, the solvation effect of THF was simulated by the SMD solvent model with a larger basis set II , which consisted of LANL2DZ for Fe and 6-311++G(d,p) for other atoms. The solution phase Gibbs free energies are calculated by adding solvation energies on the gas phase relative Gibbs free energies. The same methodology has been widely used in many recent theoretical works.[40-46] Our calculations show that the formation of the exocyclic vinyllithium **5a** (eq. S1) and the Fe(III) active species **I1** (eq. S2) are all facile with exothermic free energy of -40.2 and -140.6 kcal/mol. Fe(III) active species **I1** then undergoes reductive elimination process to give the homo-coupling product **6a** and Fe(I) intermediate **I2**, the free energy barrier for this step is 19.7 kcal/mol (Figure S4) and this is the rate determining step for the whole reaction. Subsequently, the oxidation of **I2** by DTBP occurs fluently to give a very stable Fe(III) intermediate **I4**. At last, active species **I1** is regenerated very quickly with two more molecules of exocyclic vinyllithium **5a** (Figure S4), thus finishing the catalytic cycle (Scheme 5). The theoretical calculated results are consistent with our experimental observation.



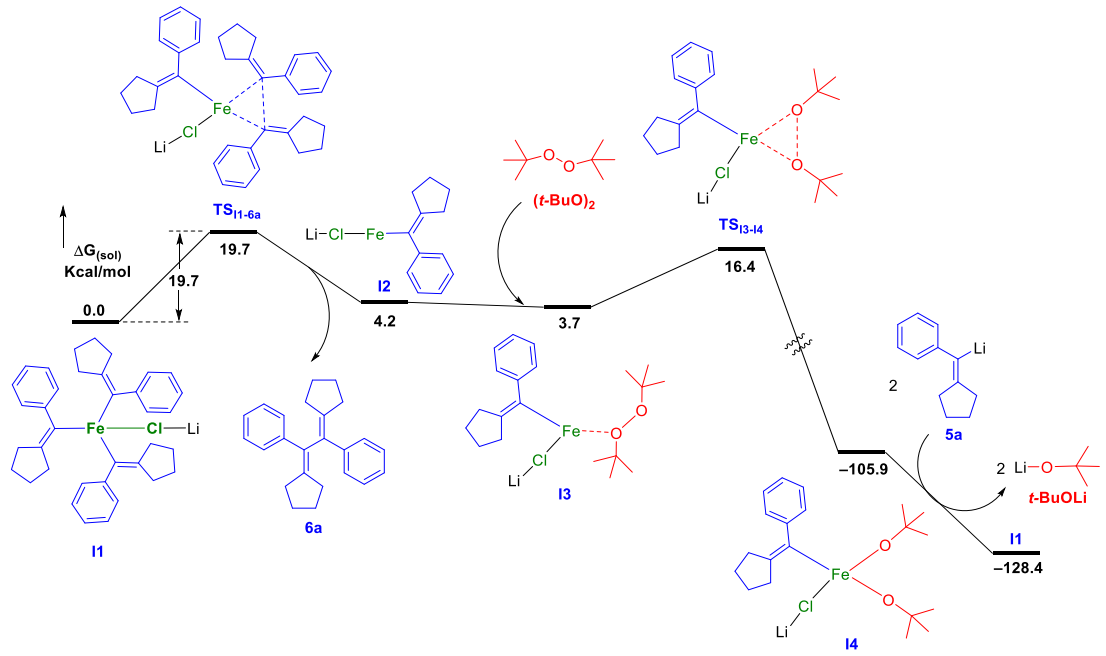


Figure S4: The free energy profile for Fe(III) catalyzed oxidative homo-coupling reaction.

5. EPR Experiments

To a Schlenk tube charged with acetylenic iodide **4a** (0.2 mmol, 56.8 mg), were added 1.2 mL *n*-pentane and 0.8 mL diethyl ether via argon-flushed syringes, and the resulting solution was cooled to –78 °C in an acetone-dry ice bath. Then *t*-BuLi (0.34 mL, 1.3M) in pentane was added dropwise via an argon-flushed syringe, and the mixture was stirred at –78 °C for an additional 8 min. After removing the cooling bath, the mixture was stirred for 30 min to generate vinyllithium **5a**. Then a solution of $FeCl_3$ (1.6 mg, 0.01 mmol) in THF (0.1 mL) was added via an argon-flushed syringe. After stirring for 5 min at rt, an aliquot of 0.2 mL of the solution was transferred to an EPR tube with an argon-flushed syringe under argon flow. The sample solution was immediately frozen in liquid nitrogen. X-Band EPR spectra were recorded with a Bruker EMX EPR spectrometer equipped with a variable-temperature helium flow cryostat system (Oxford Instruments). Instrument settings: microwave frequency, 9.390 GHz; microwave power, 1 mW; modulation amplitude, 3 G; modulation frequency, 100 kHz; time constant, 2.56 ms; conversion time, 40.96 ms. Resonance signals, which may be attributed to a Fe(I) species, were observed at g~1.9-2.0 (Figure S5). No resonance signal due to the presence of $FeCl_3$ or other high-spin Fe(III) species was observed in the lower field region (500-2000 Gauss) of the spectrum (Figure S6).

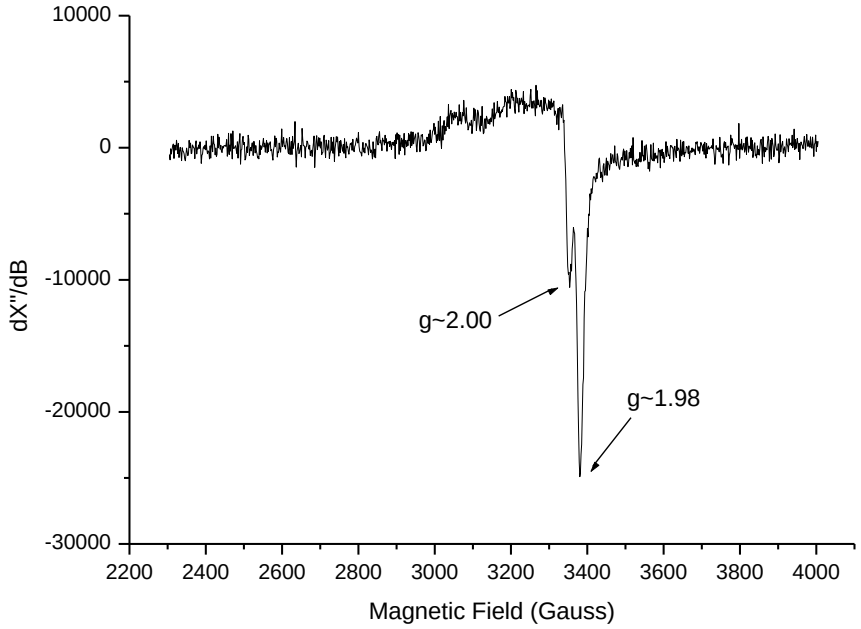


Figure S5: X-Band EPR spectrum of a solution containing **5a** and $FeCl_3$ in pentane/Et_2O/THF at 10K.

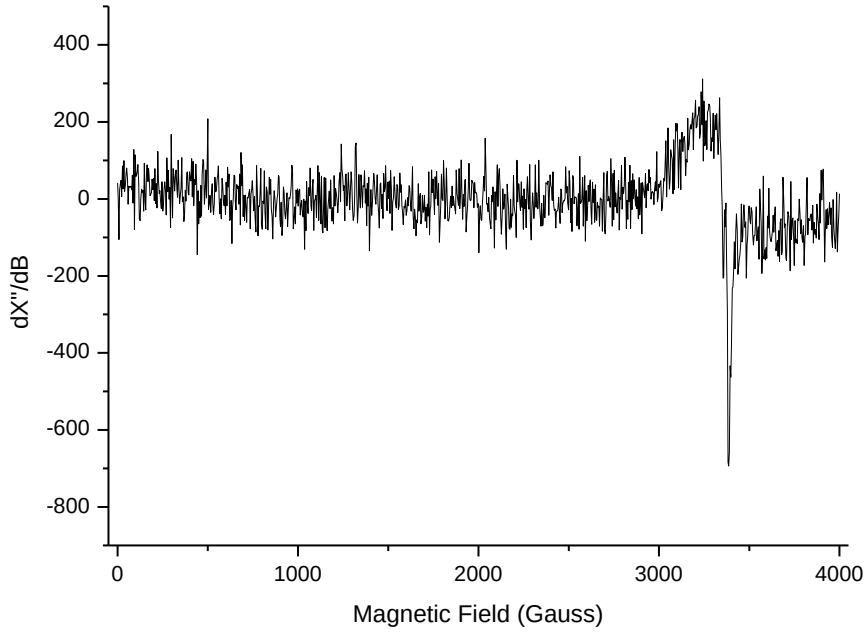


Figure S6: A full EPR spectrum (0-4000 Gauss) of the solution containing **5a** and $FeCl_3$ at 10K. No resonance signal due to the presence of $FeCl_3$ or other high-spin Fe(III) species was observed in the lower field region of 500-2000 Gauss.

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7. Copies of ^{1}H NMR, ^{13}C NMR Spectra

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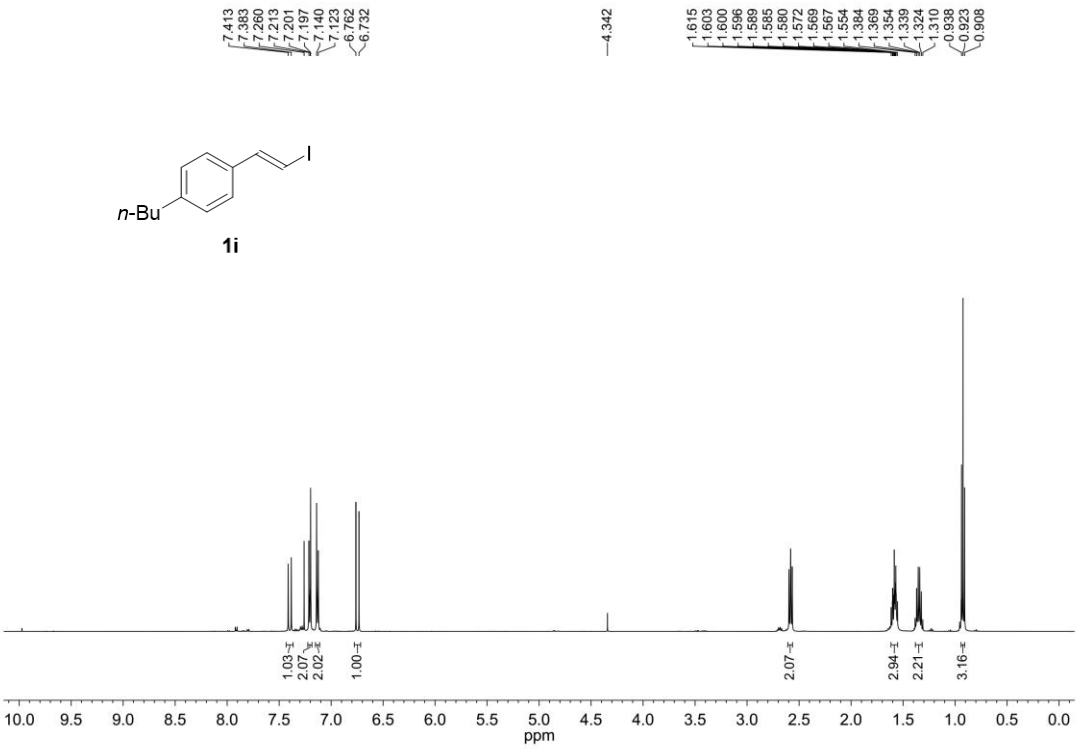

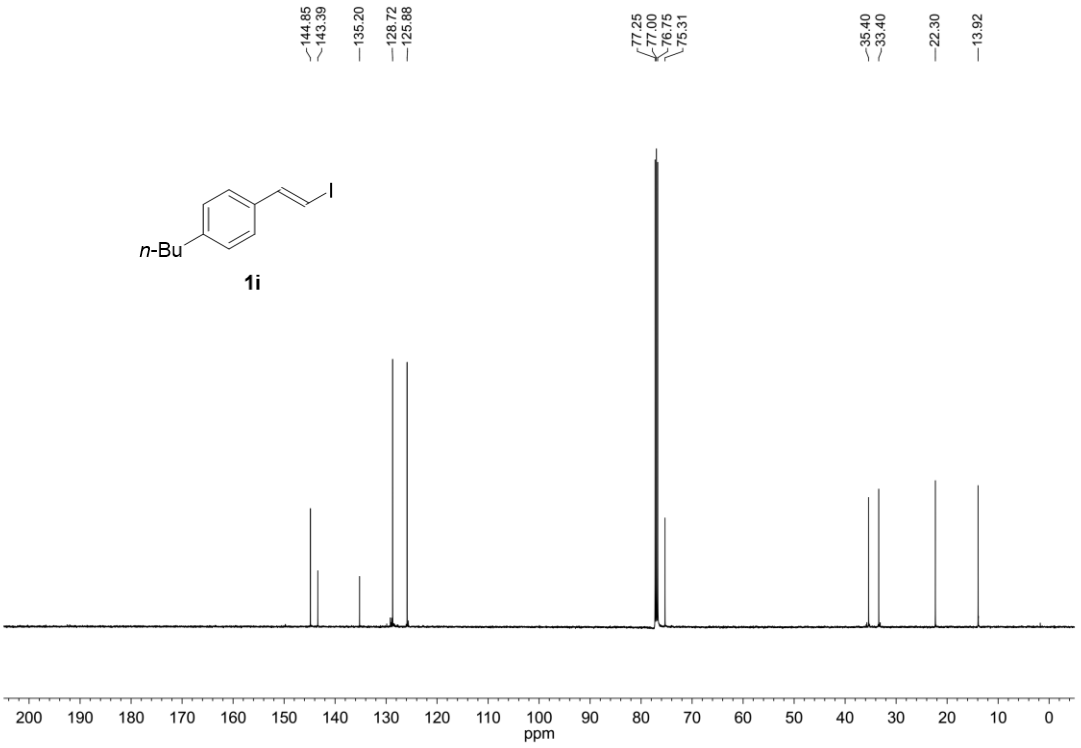

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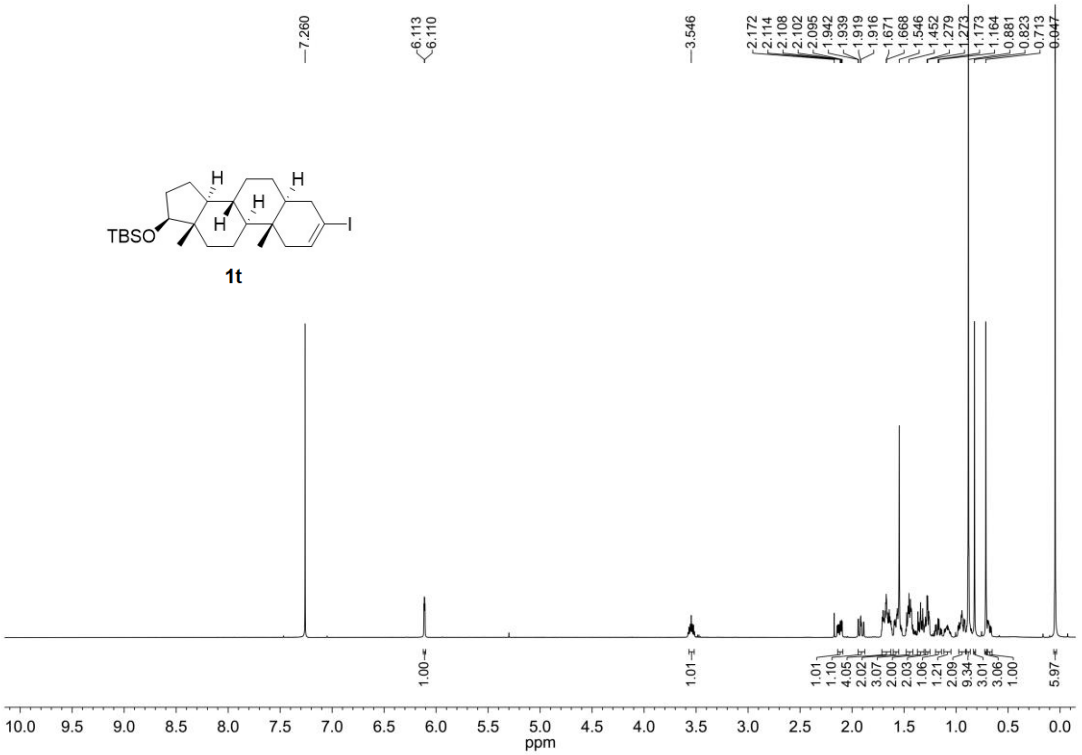

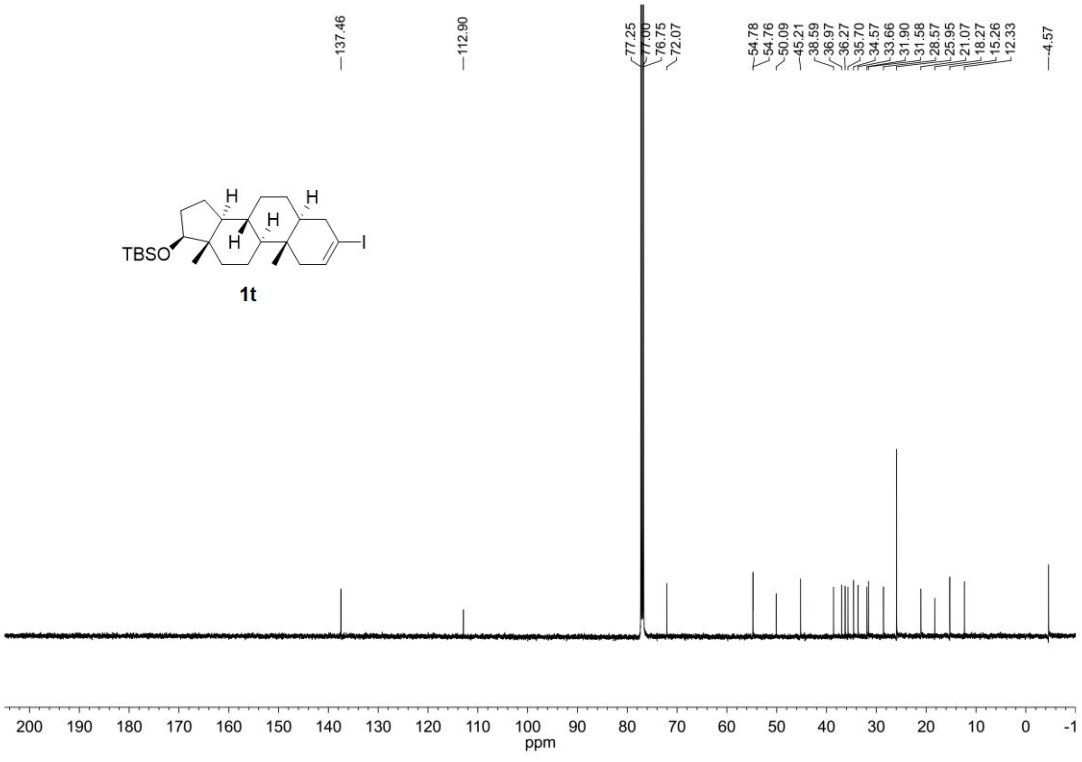

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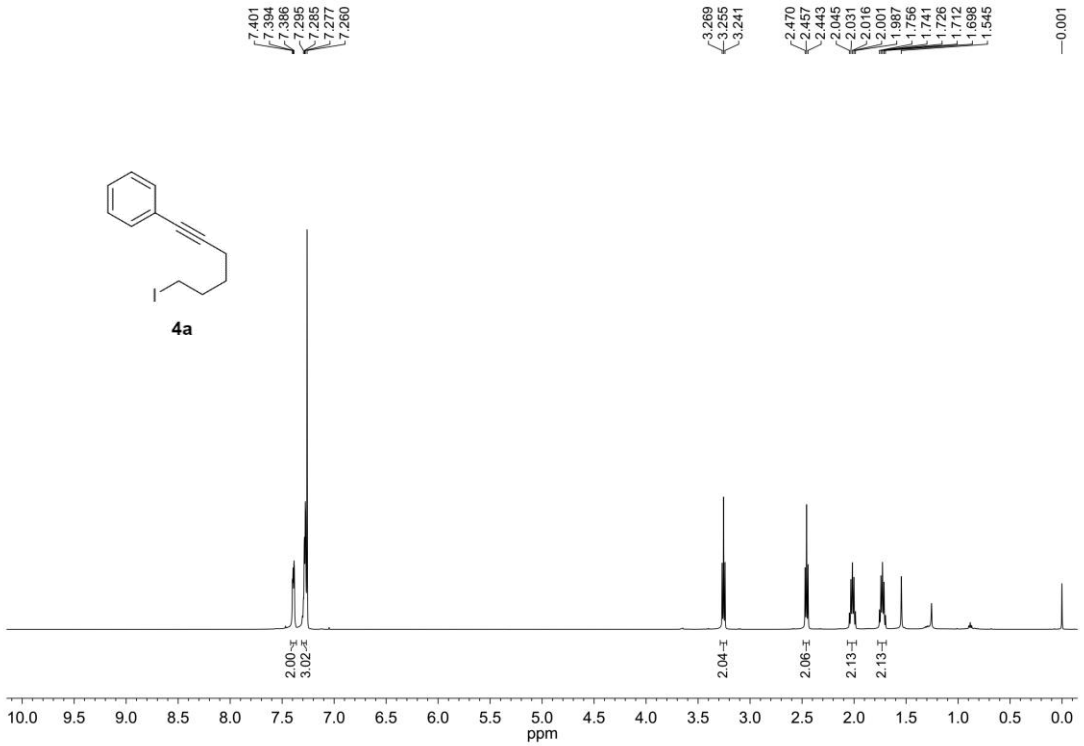

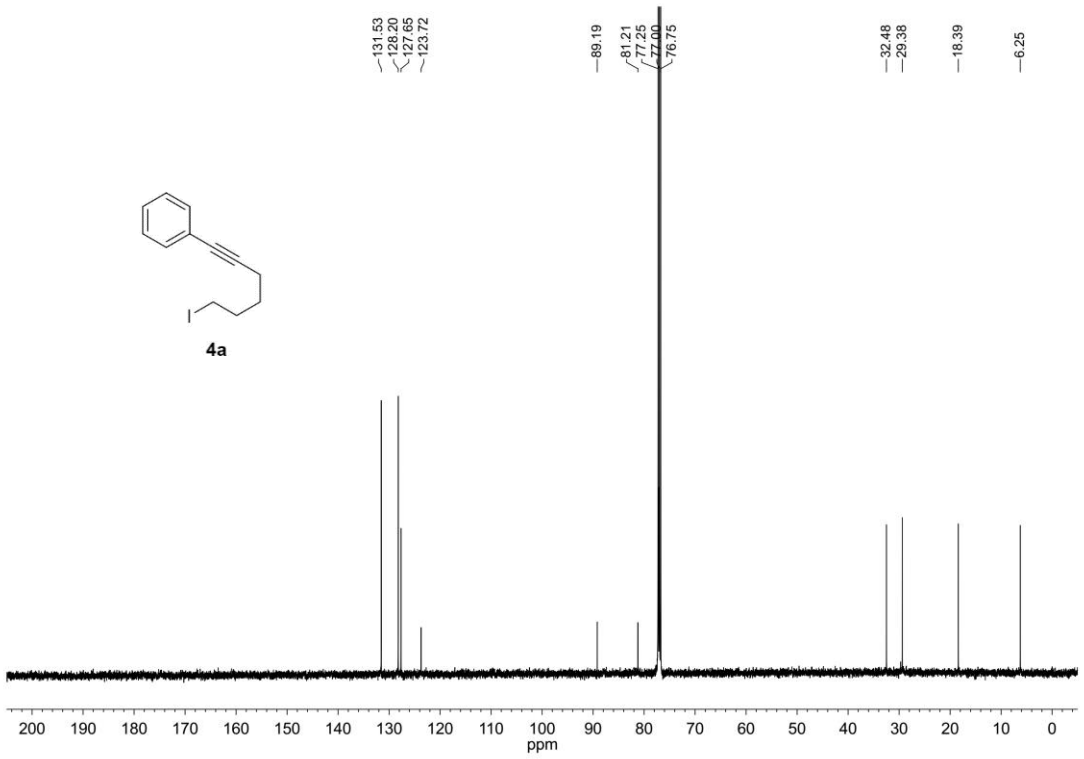

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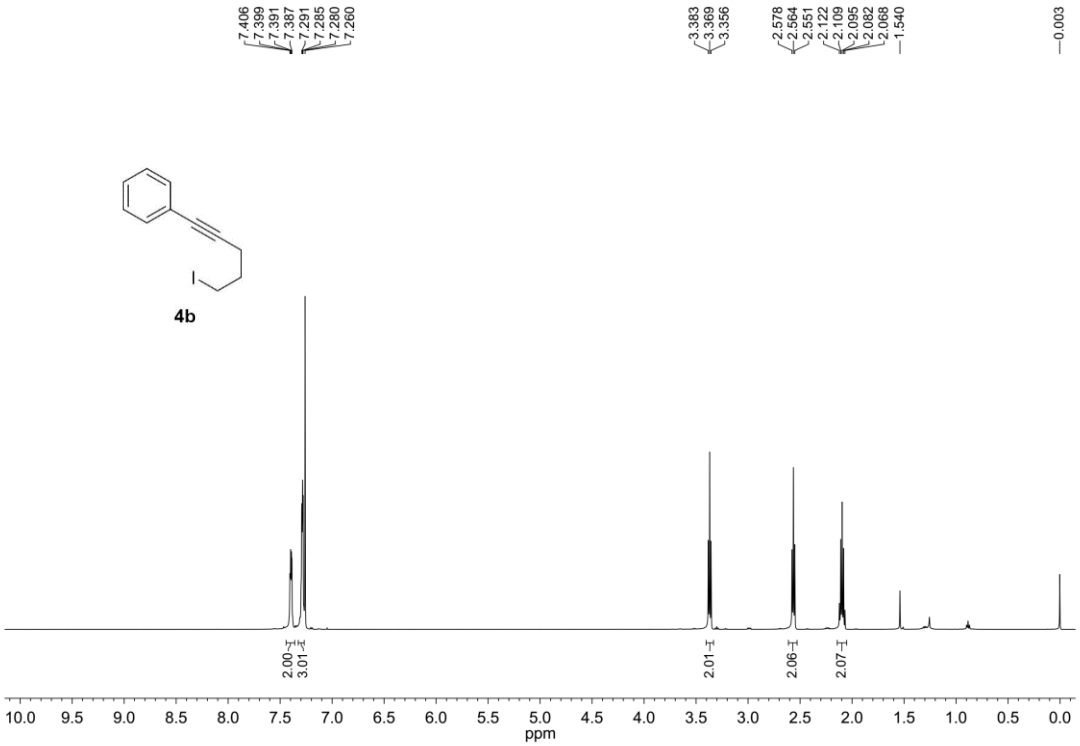

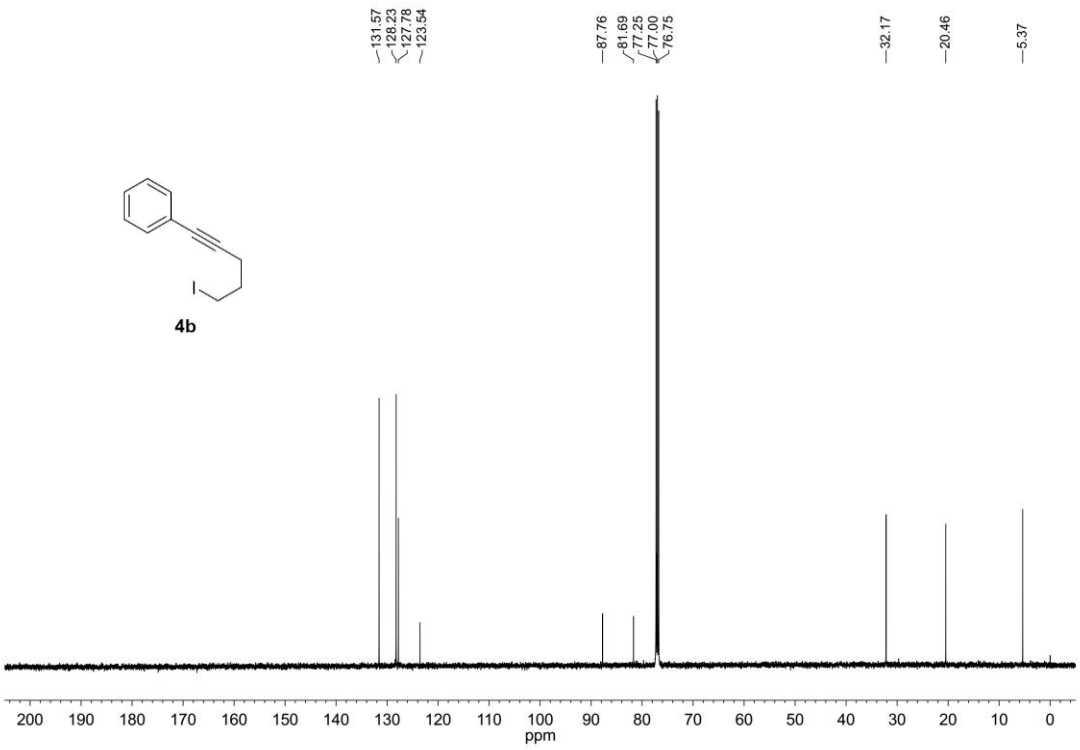

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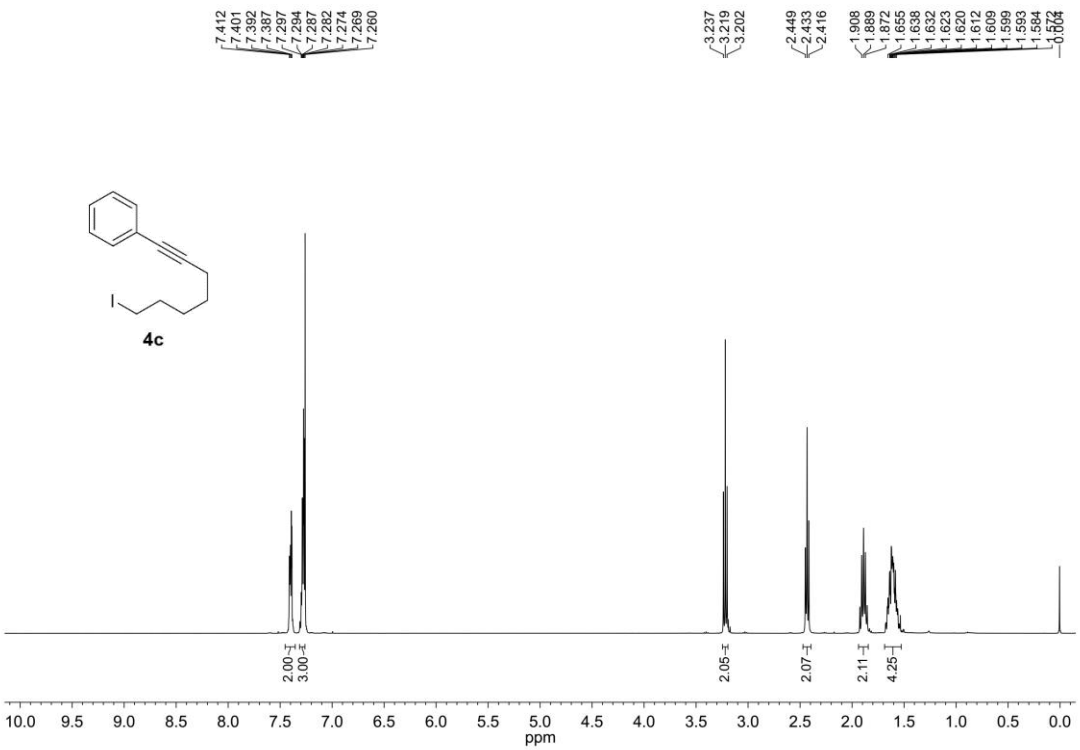

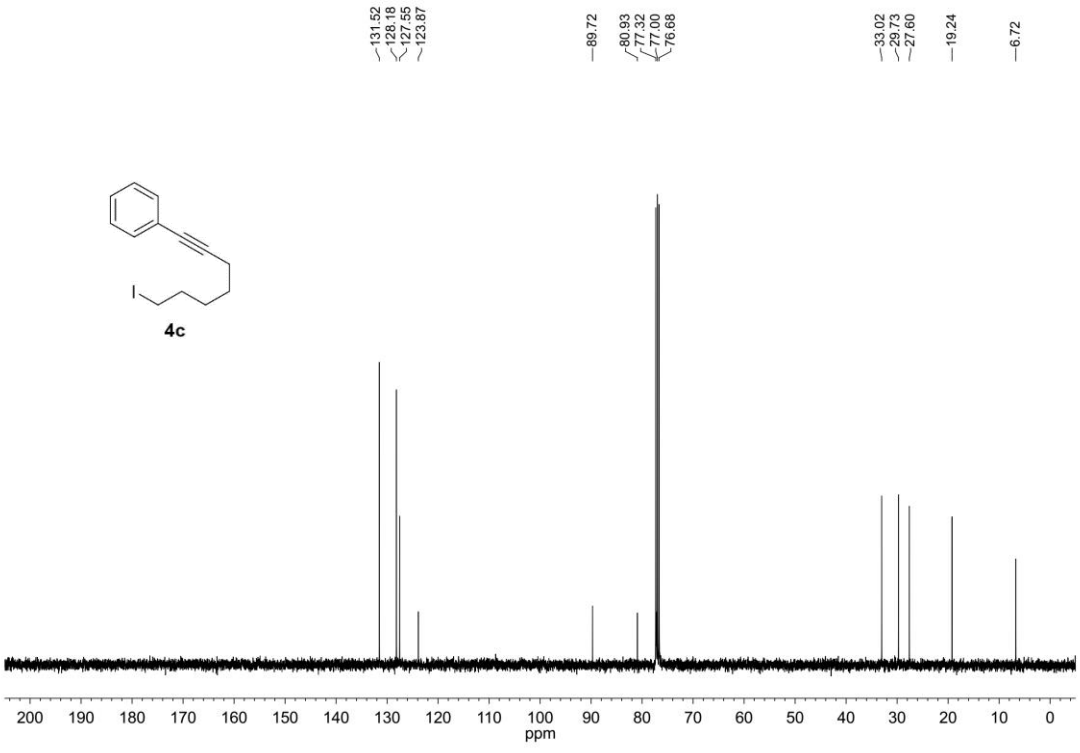

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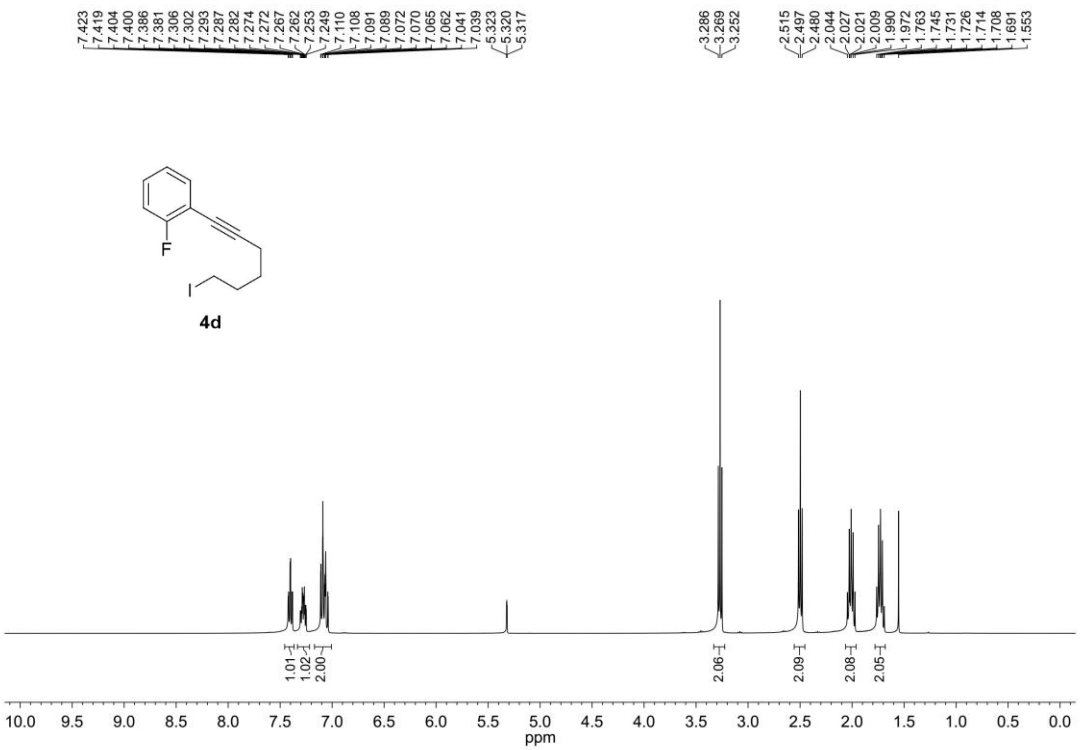

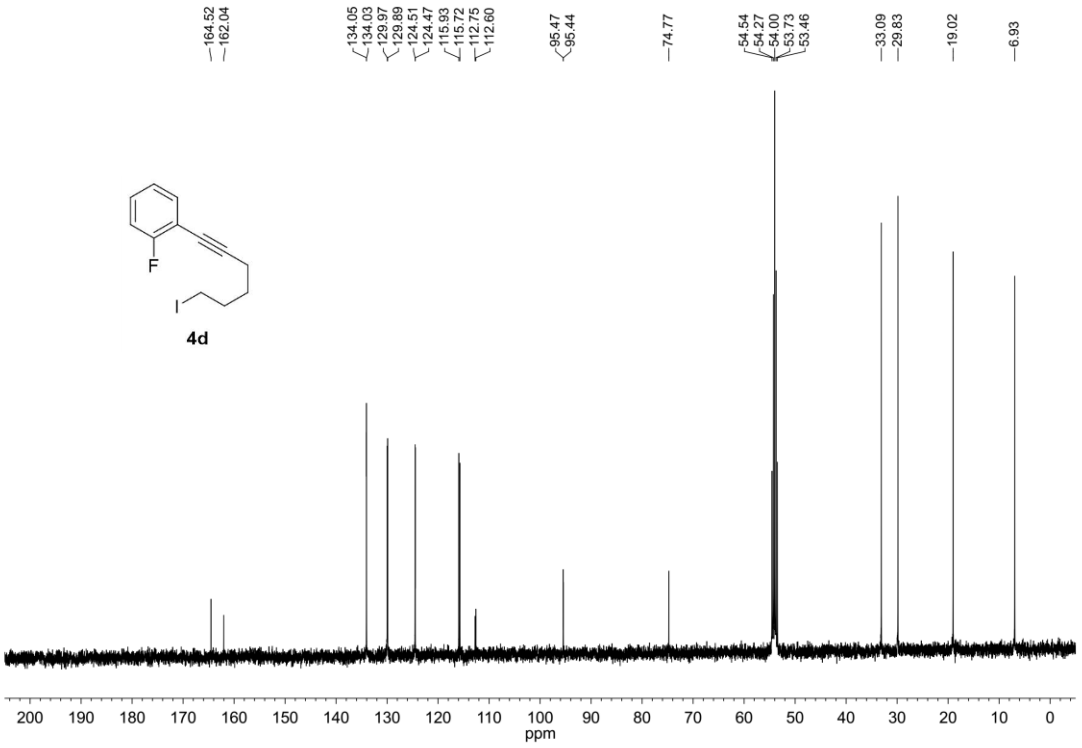

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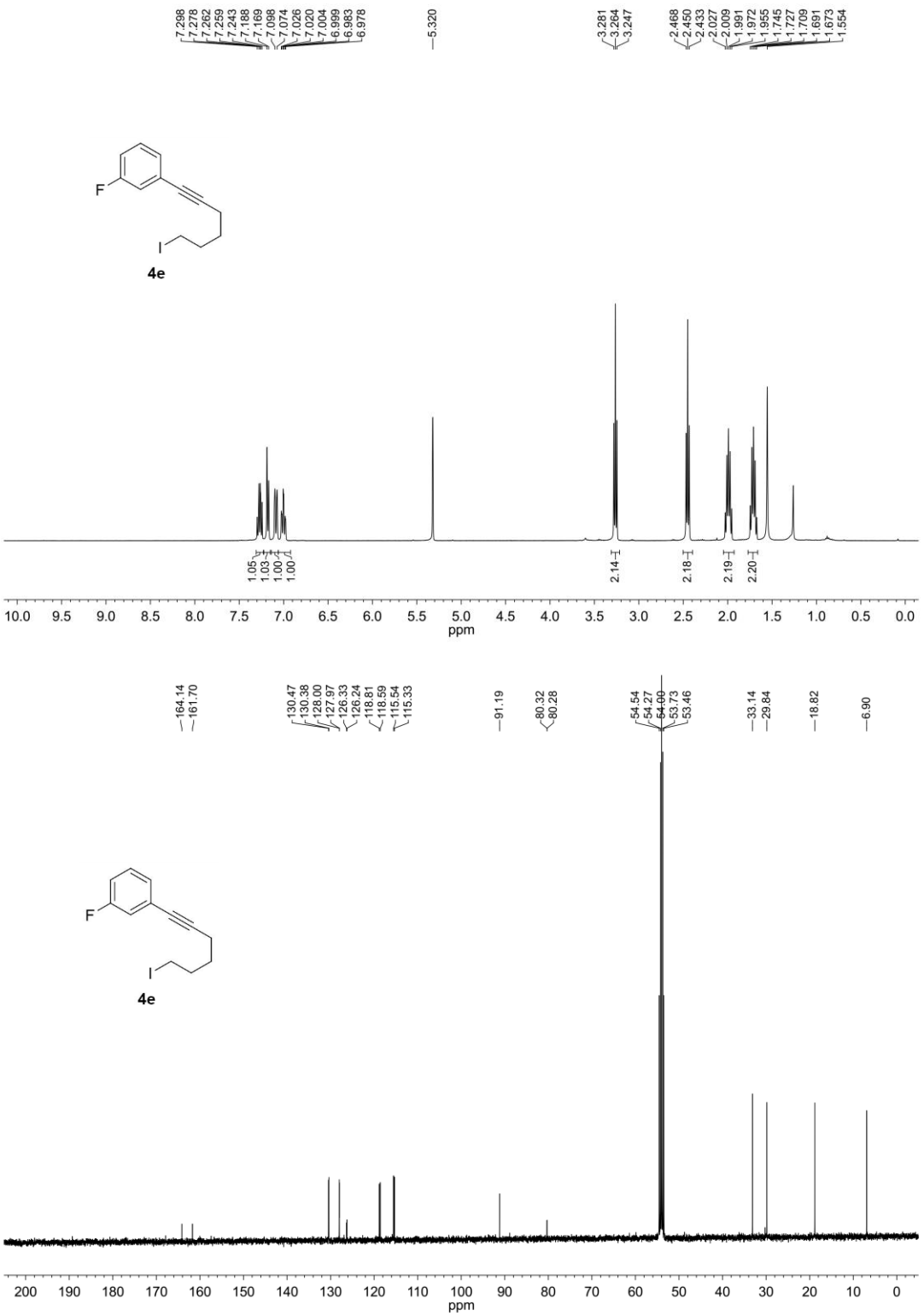

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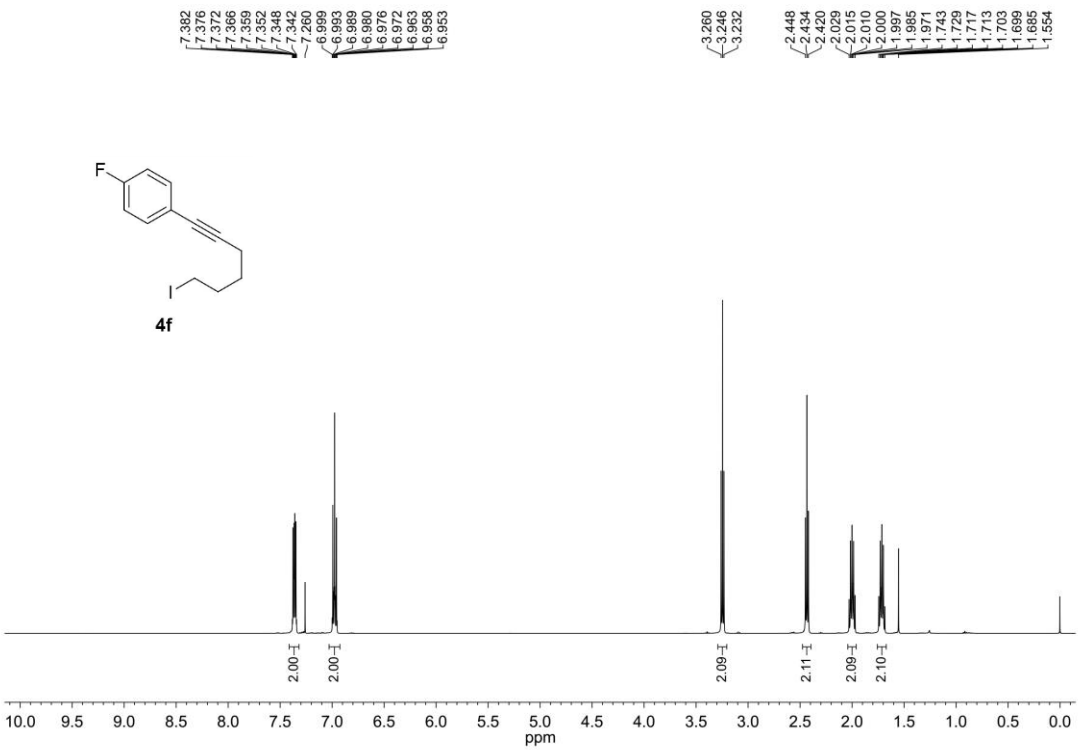

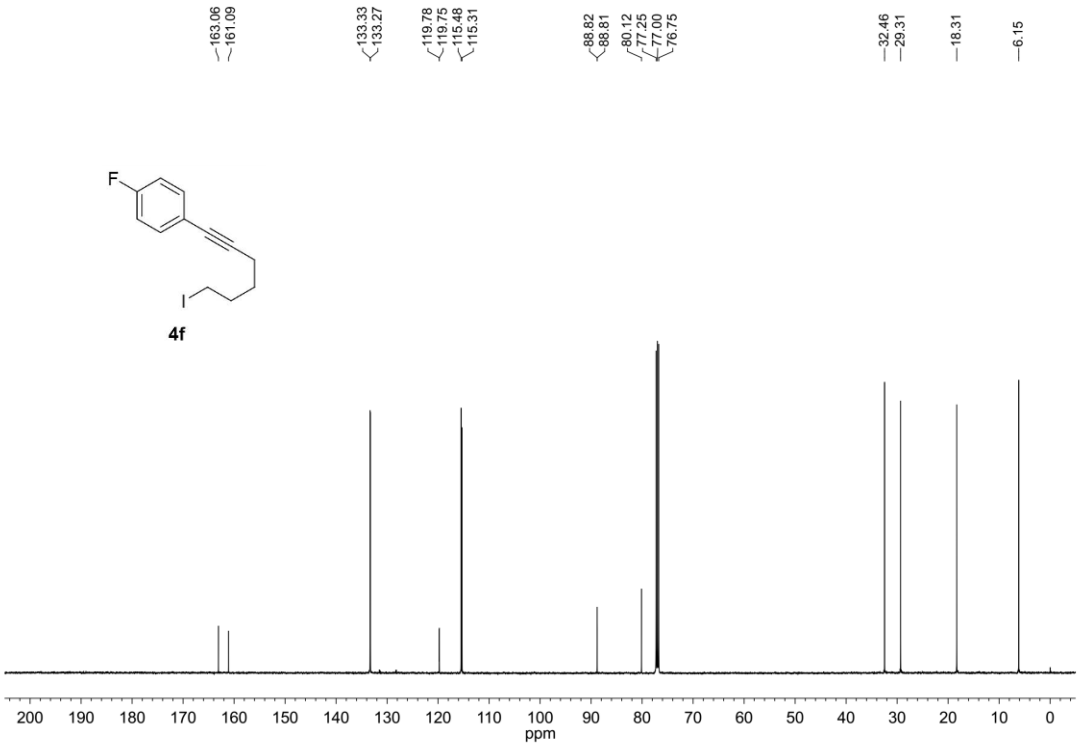

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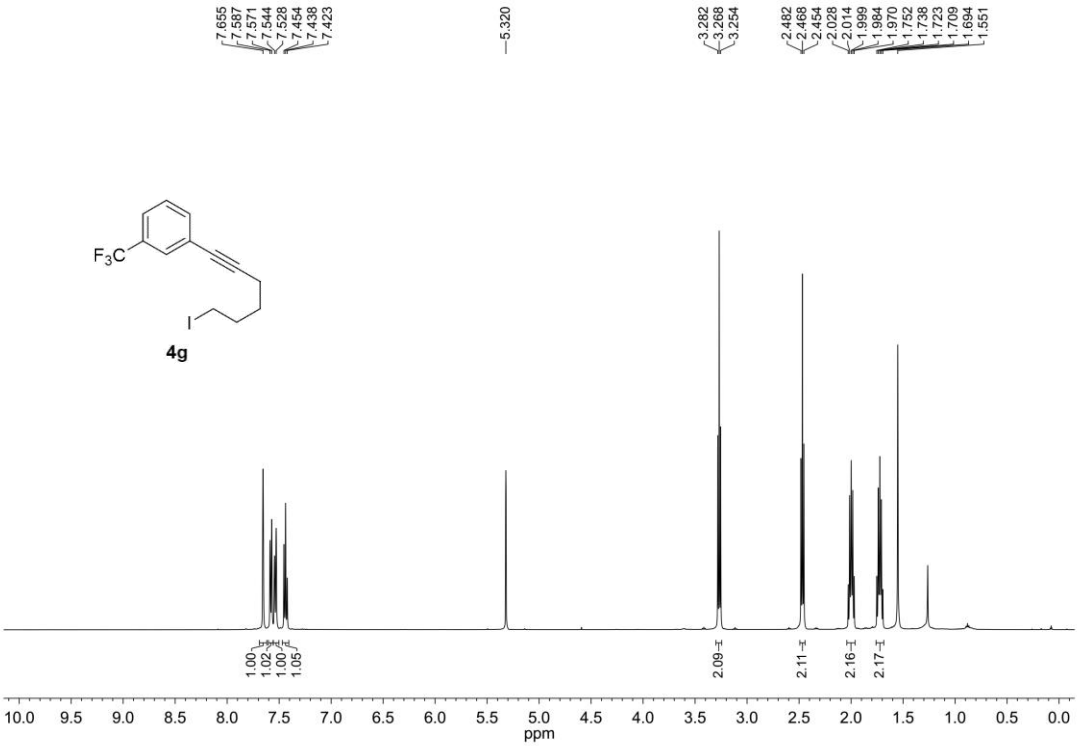

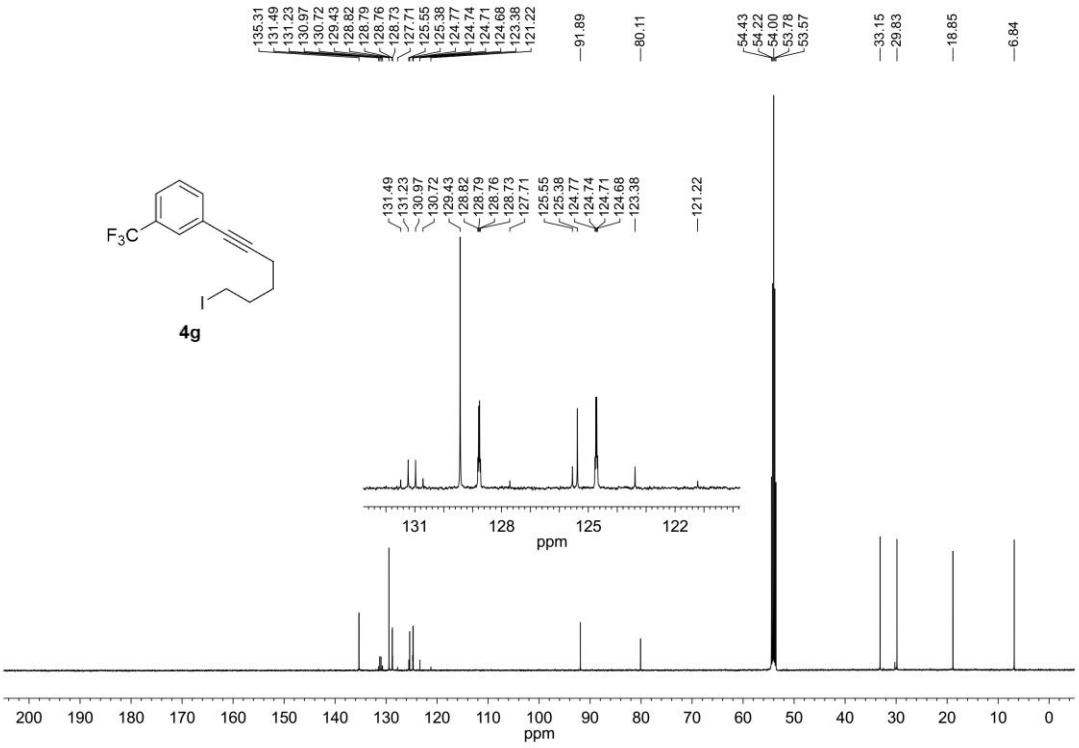

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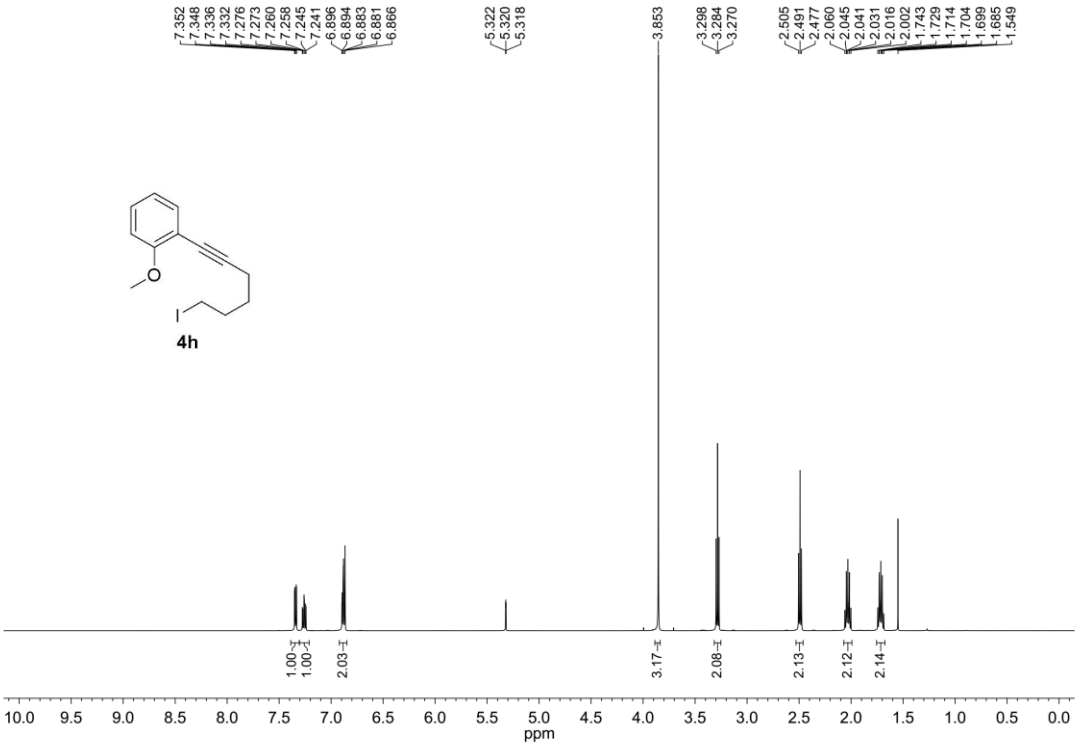

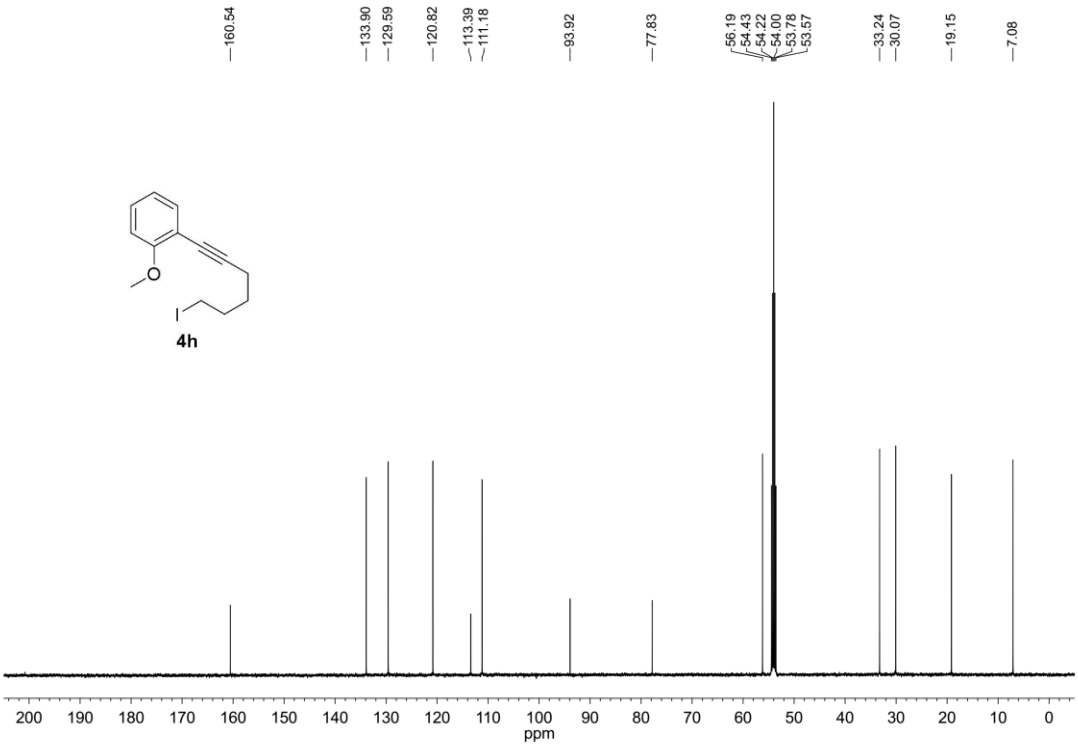

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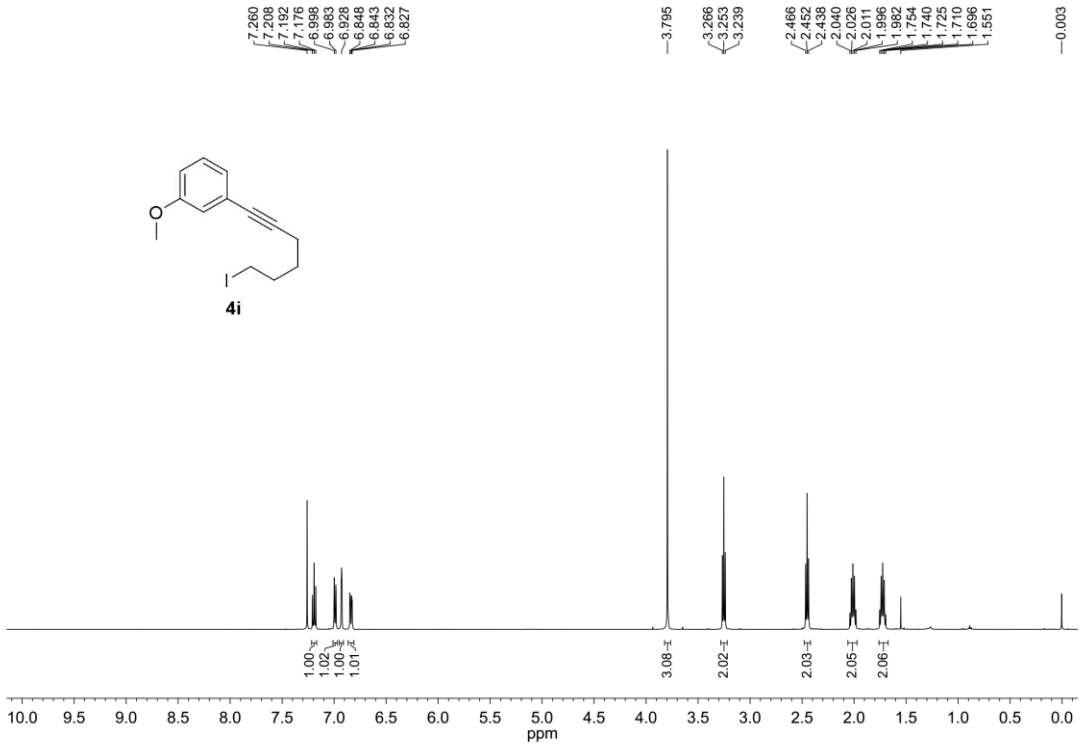

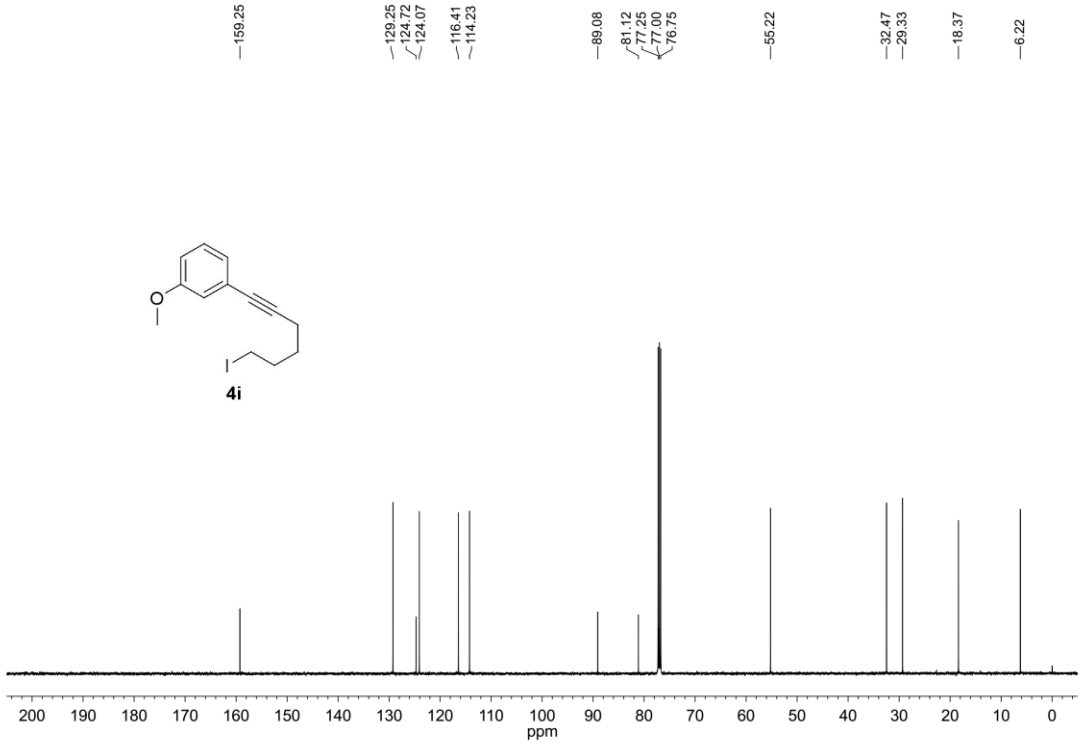

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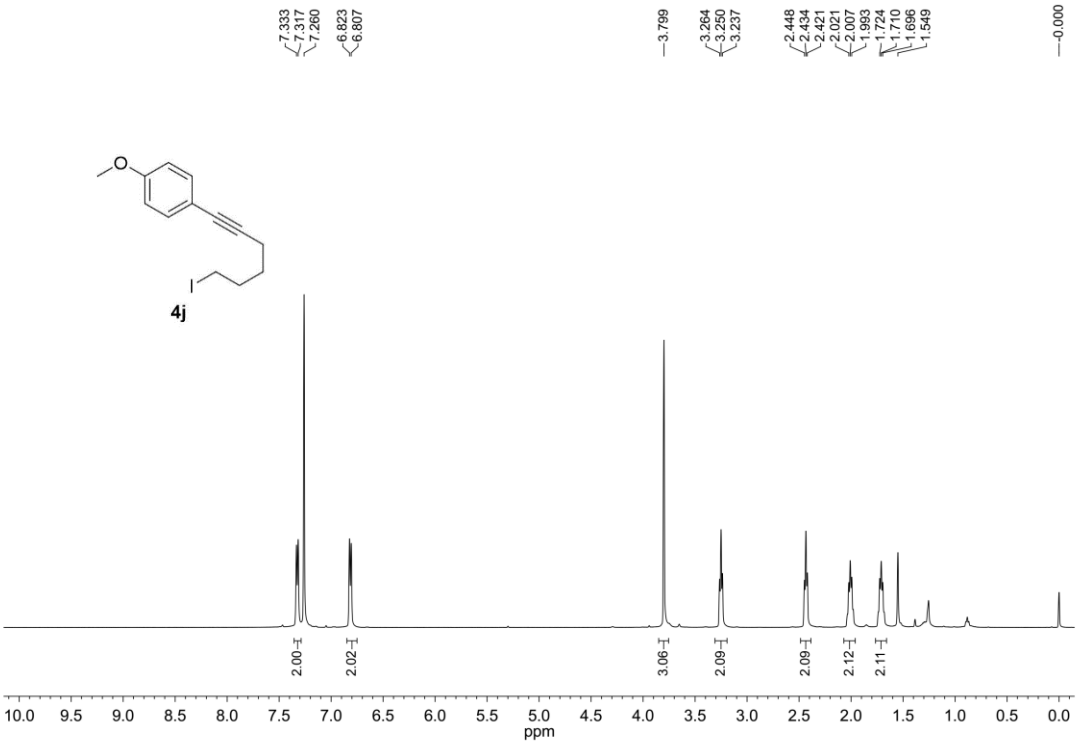

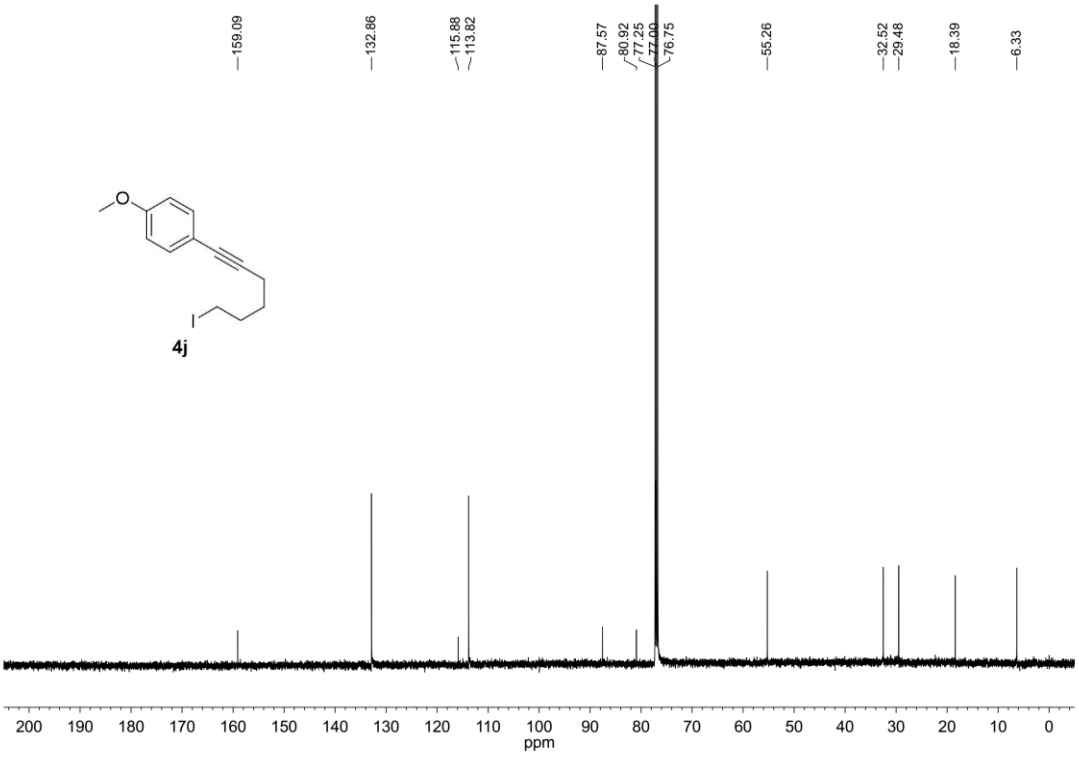

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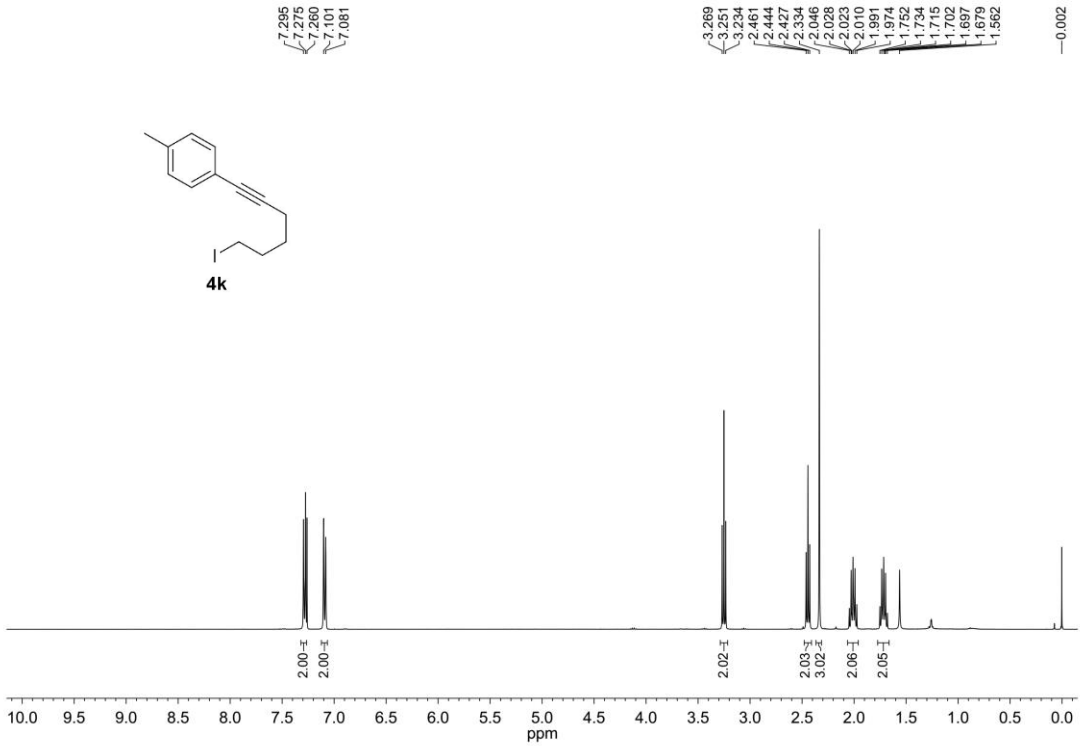

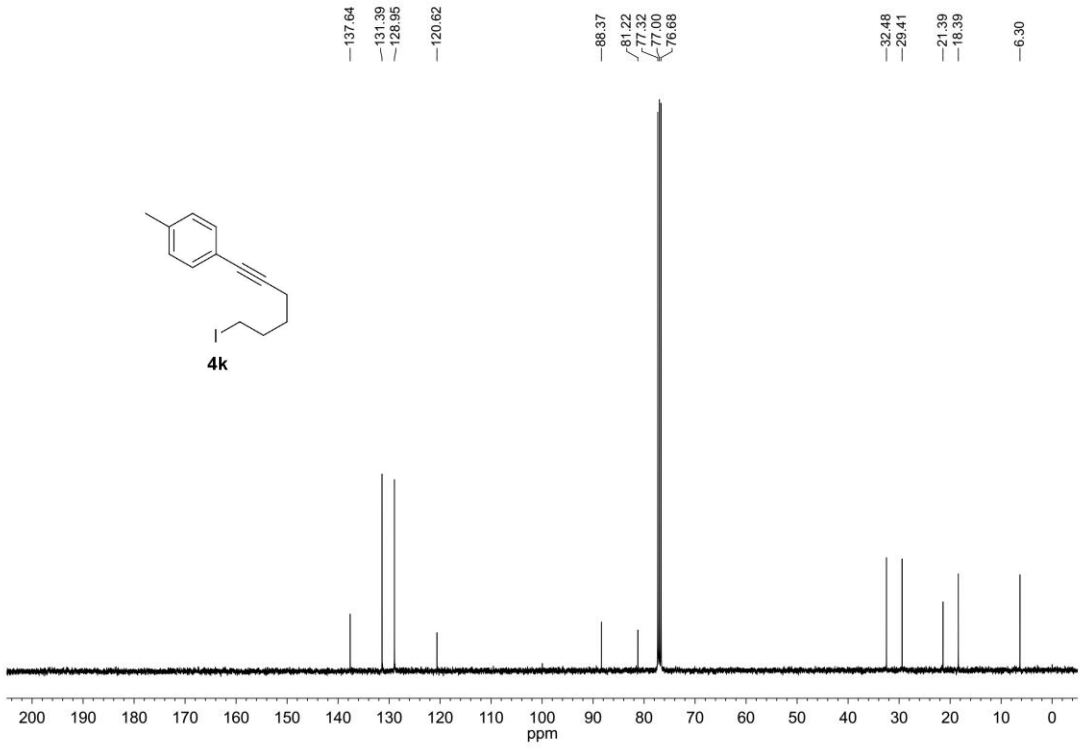

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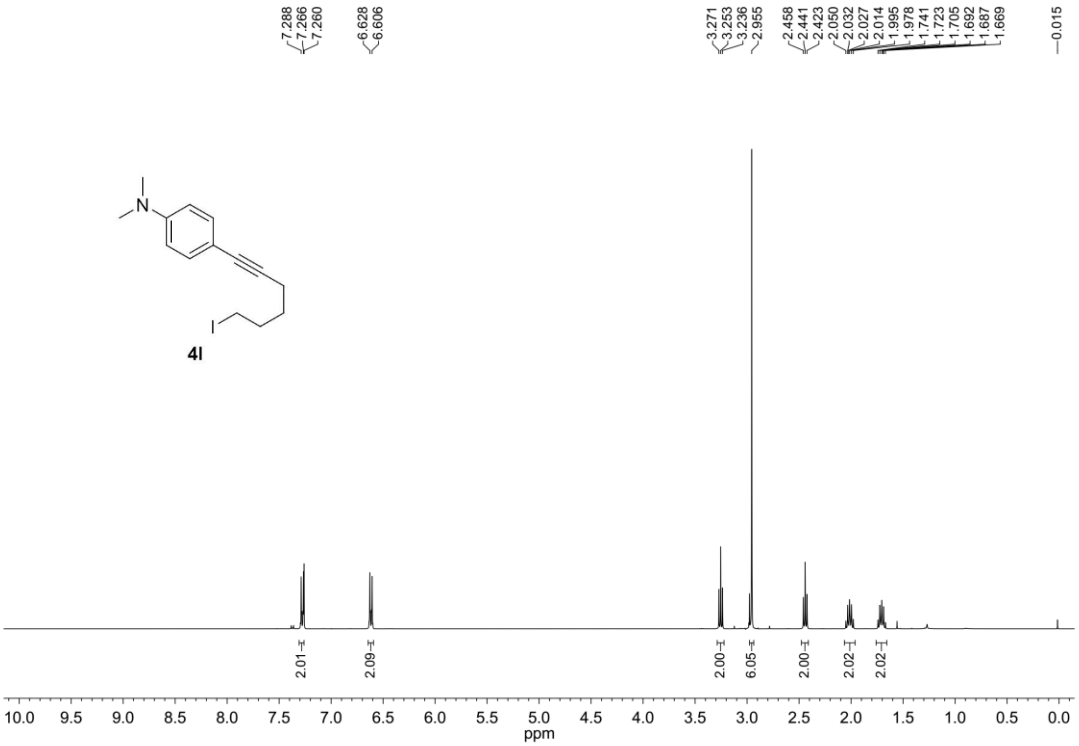

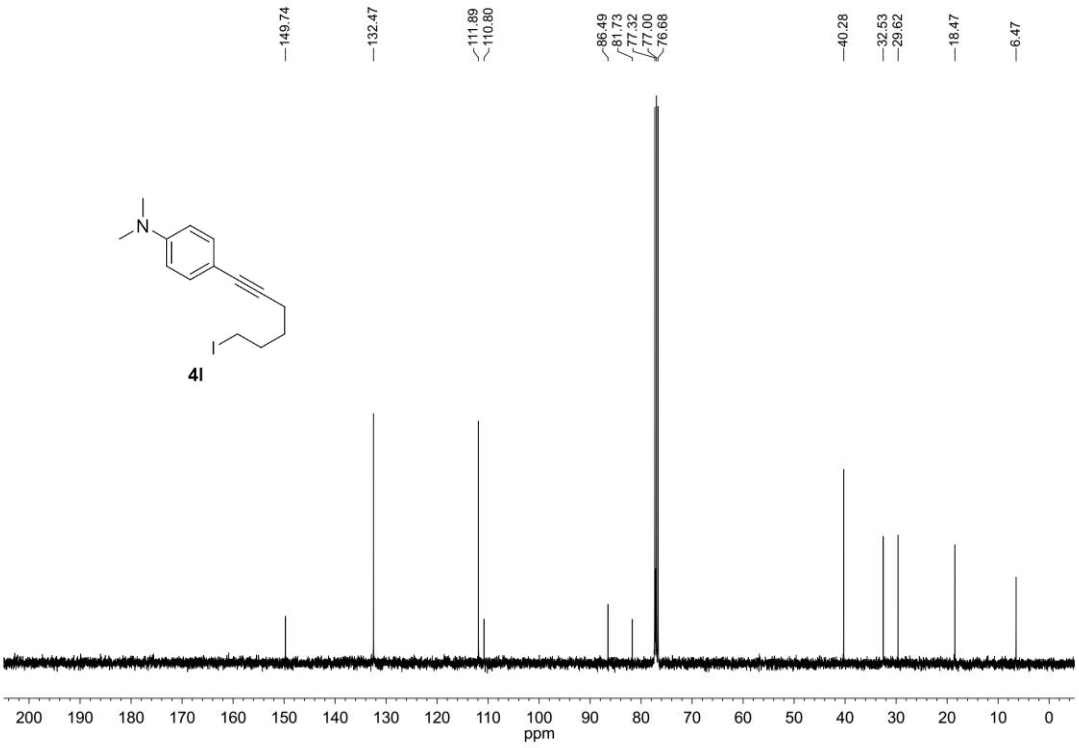

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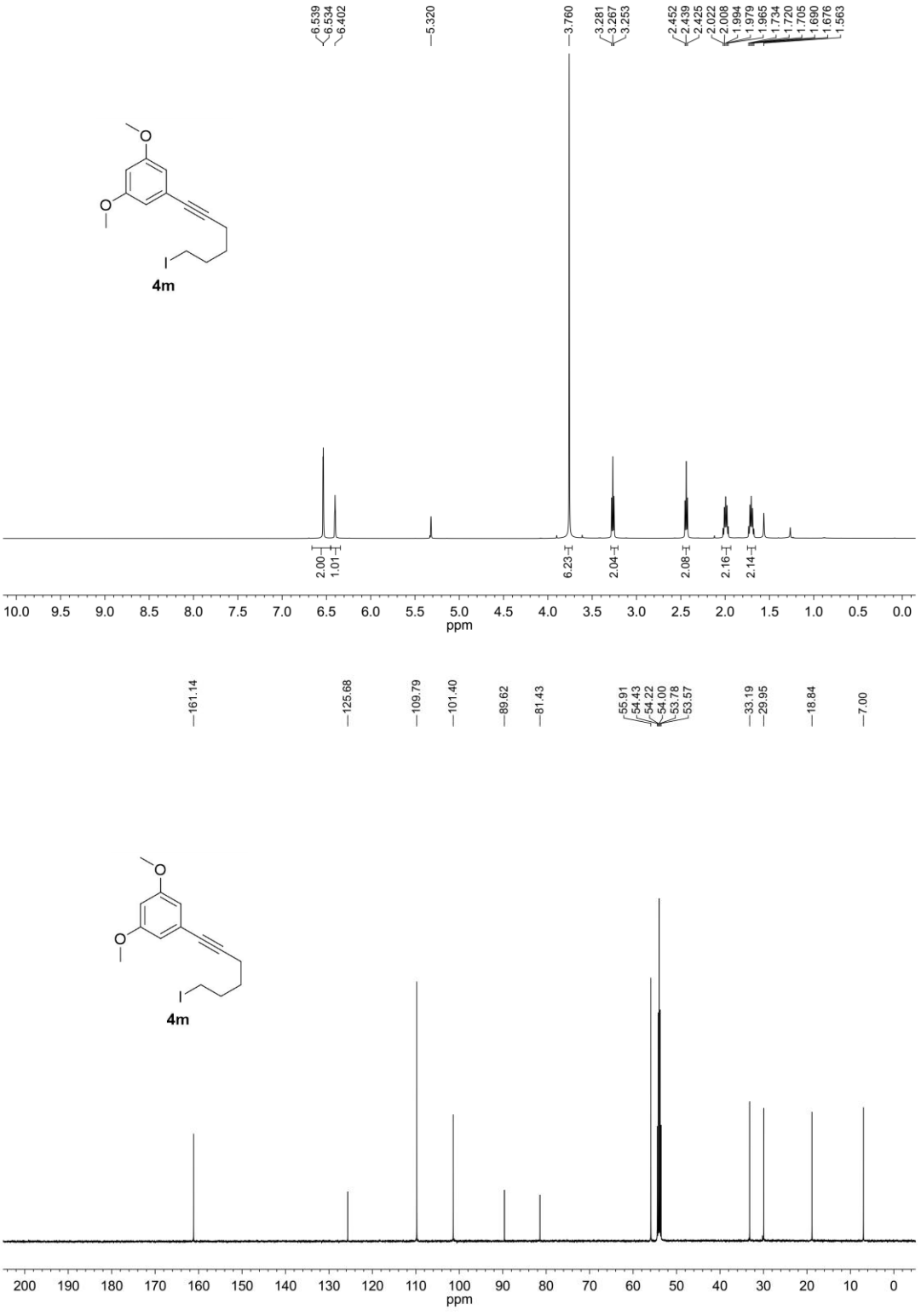

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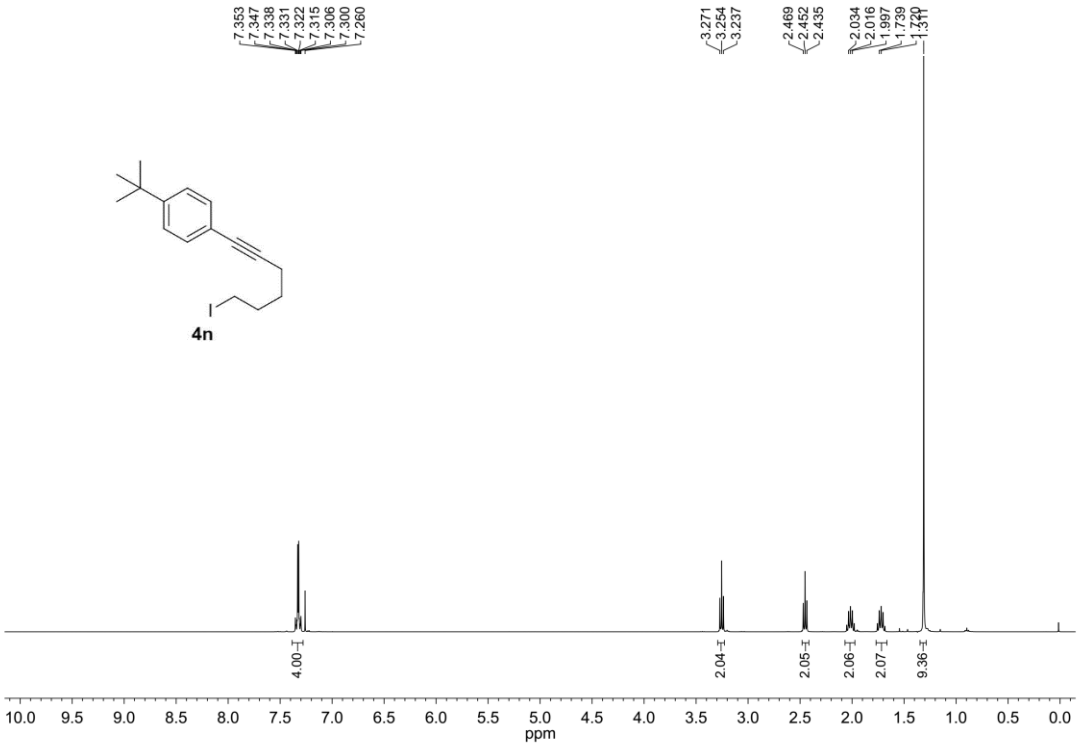
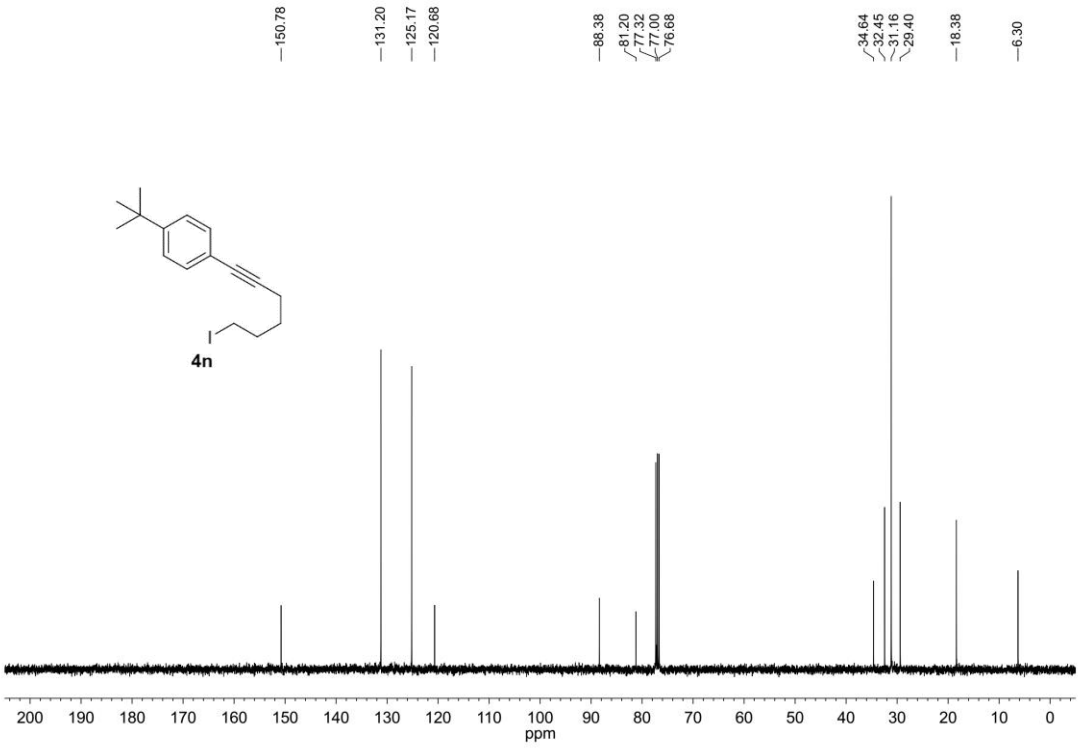
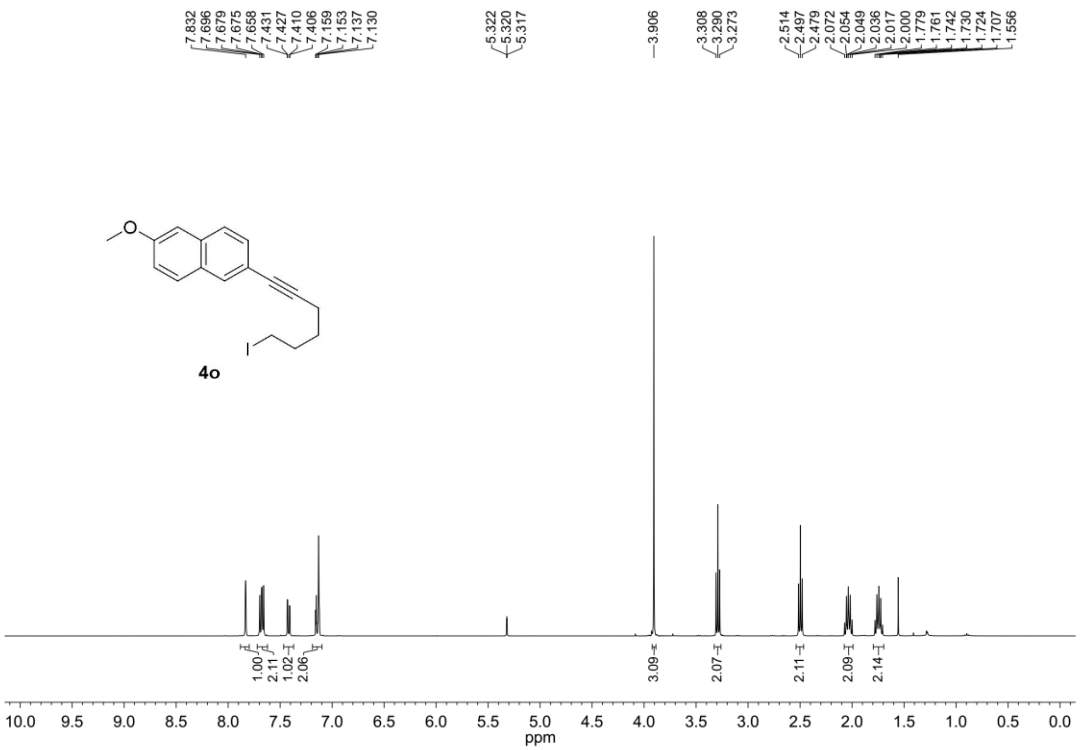
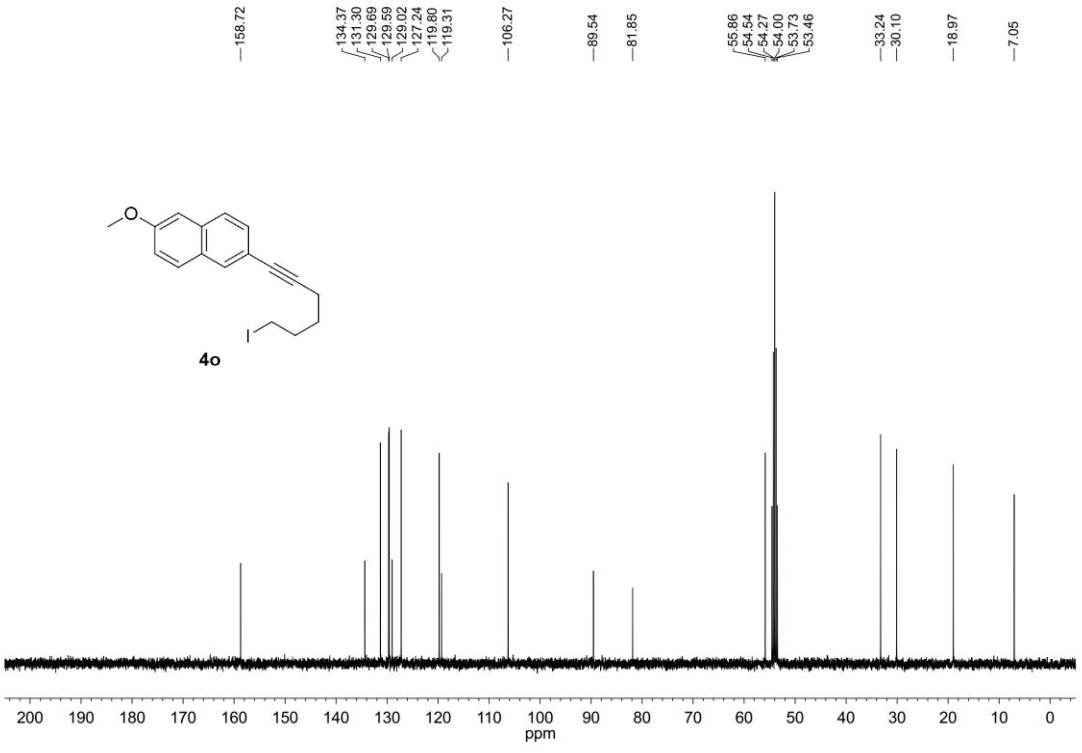


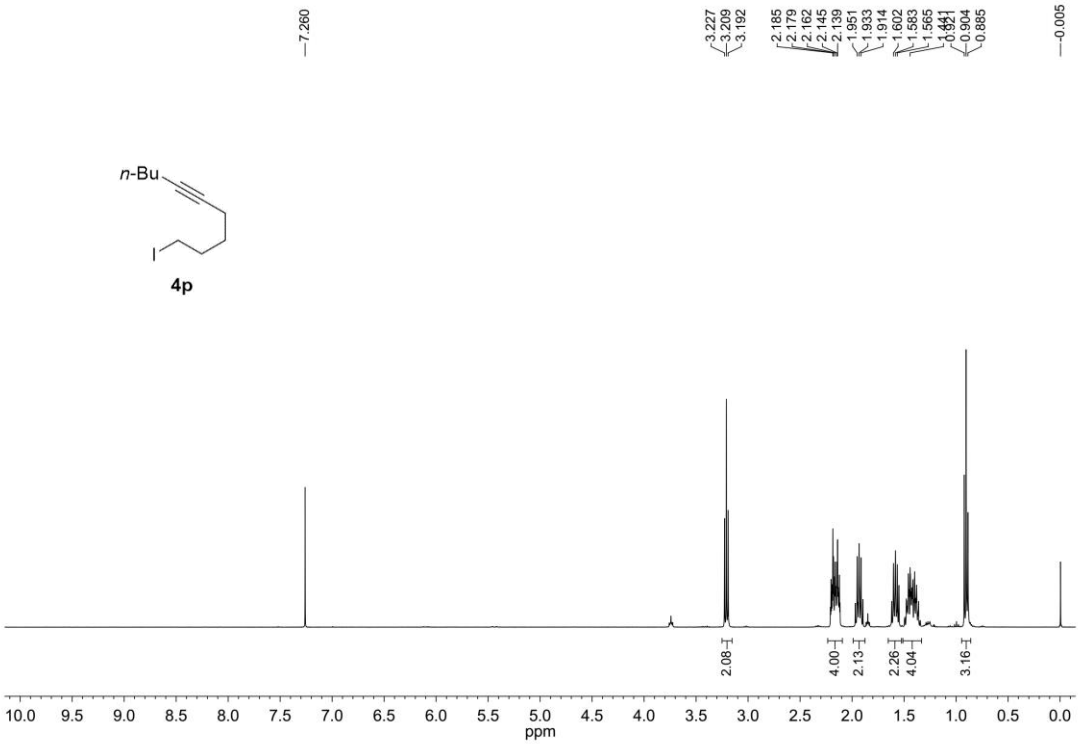


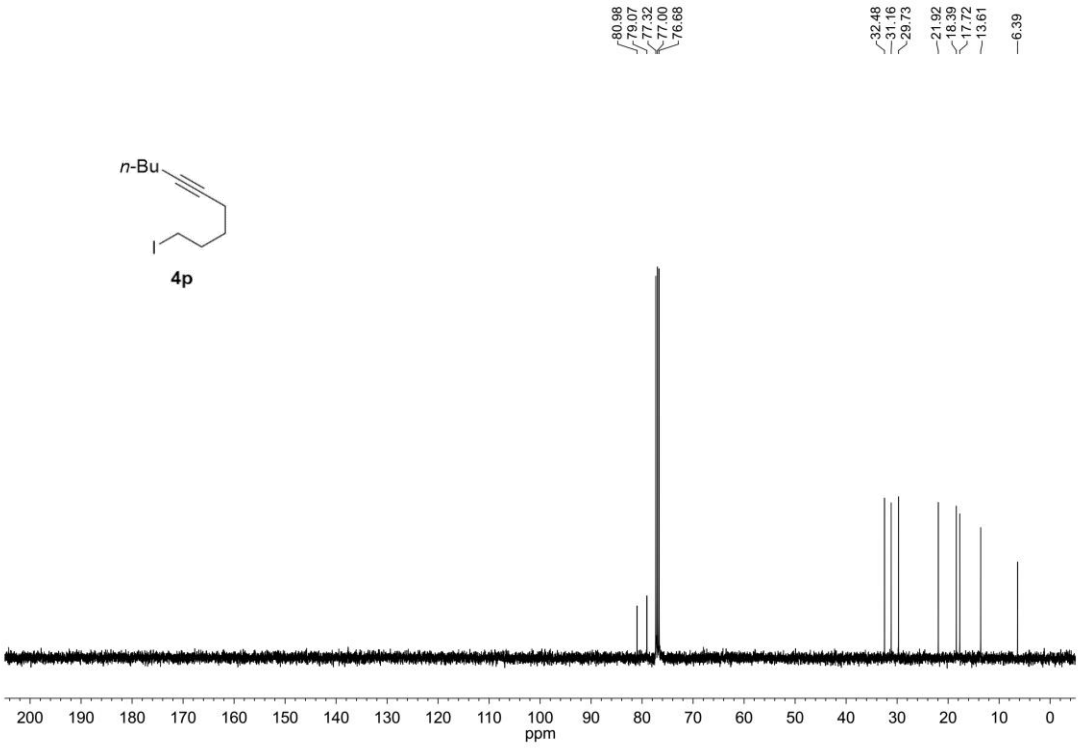
^{1}H NMR (400 MHz, CD_2Cl_2) and **^{13}C NMR** (101 MHz, CD_2Cl_2) Spectra of Compound **4o**



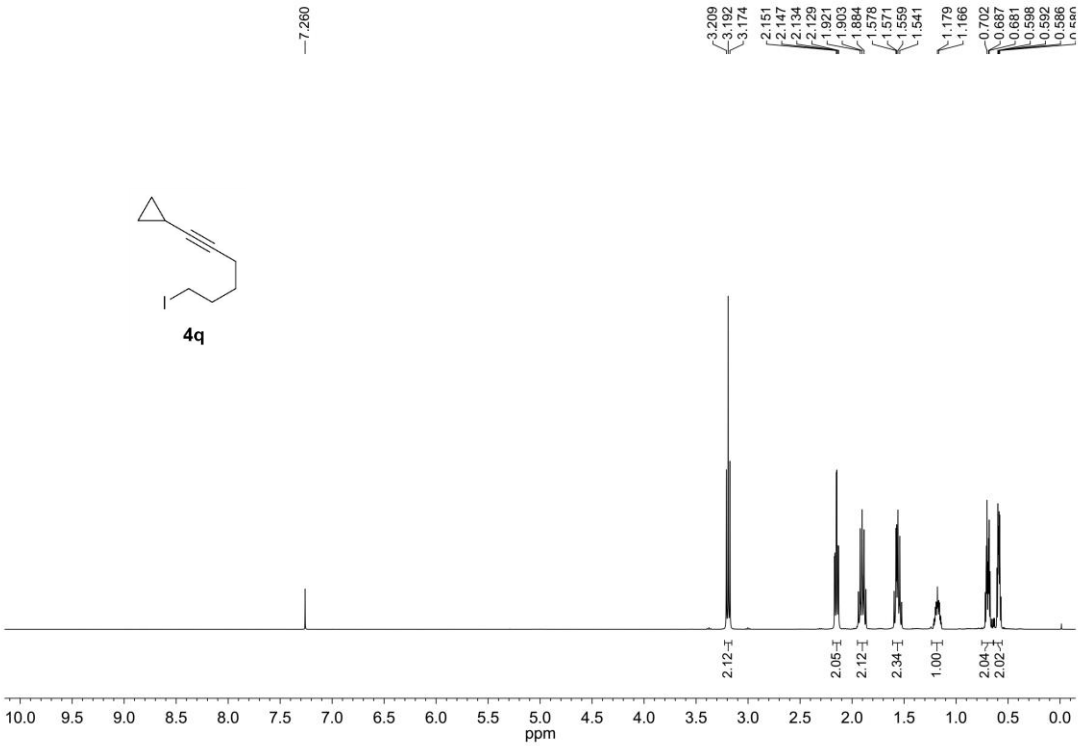


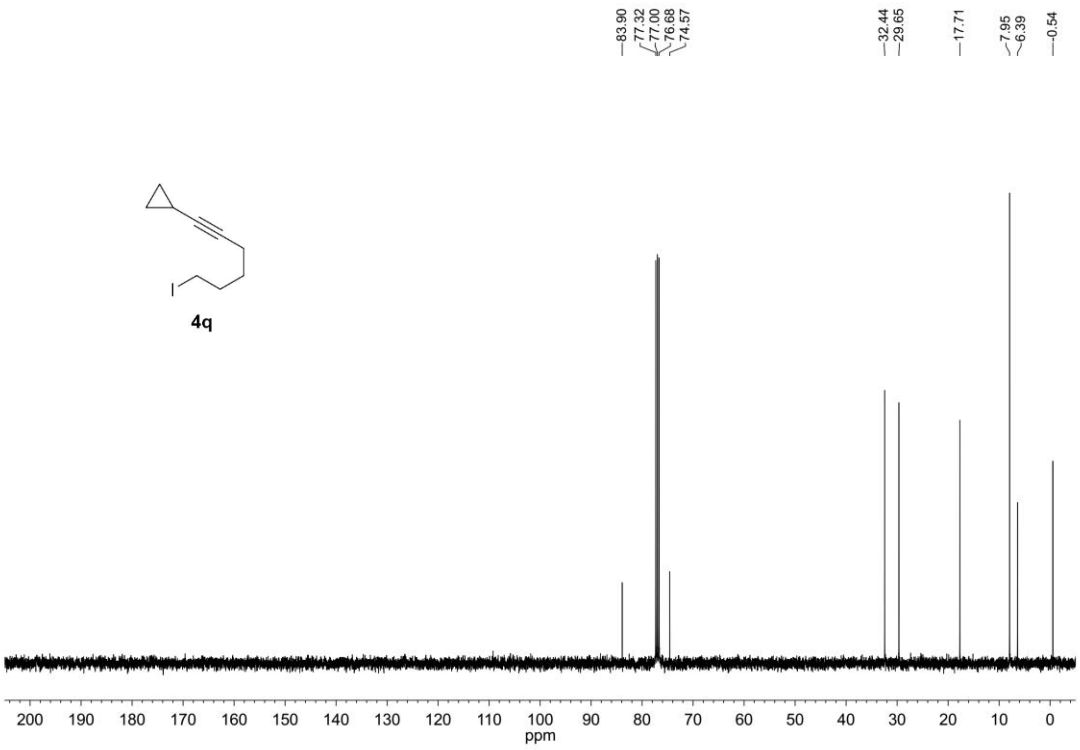
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **4p**



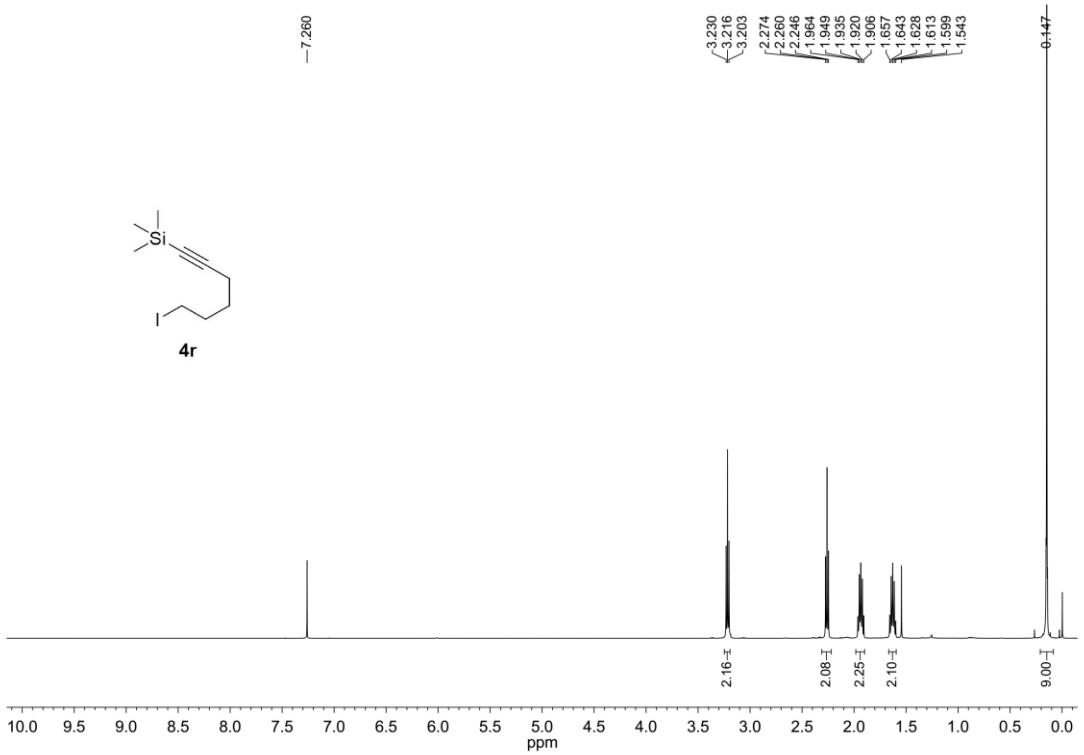


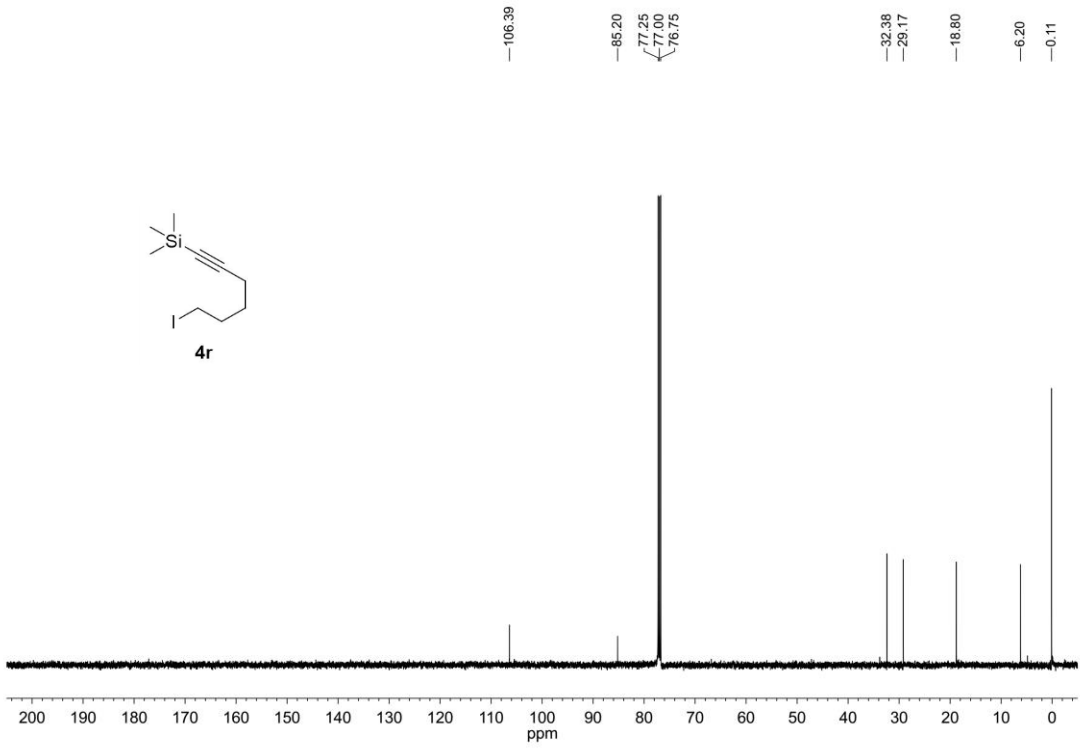
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **4q**



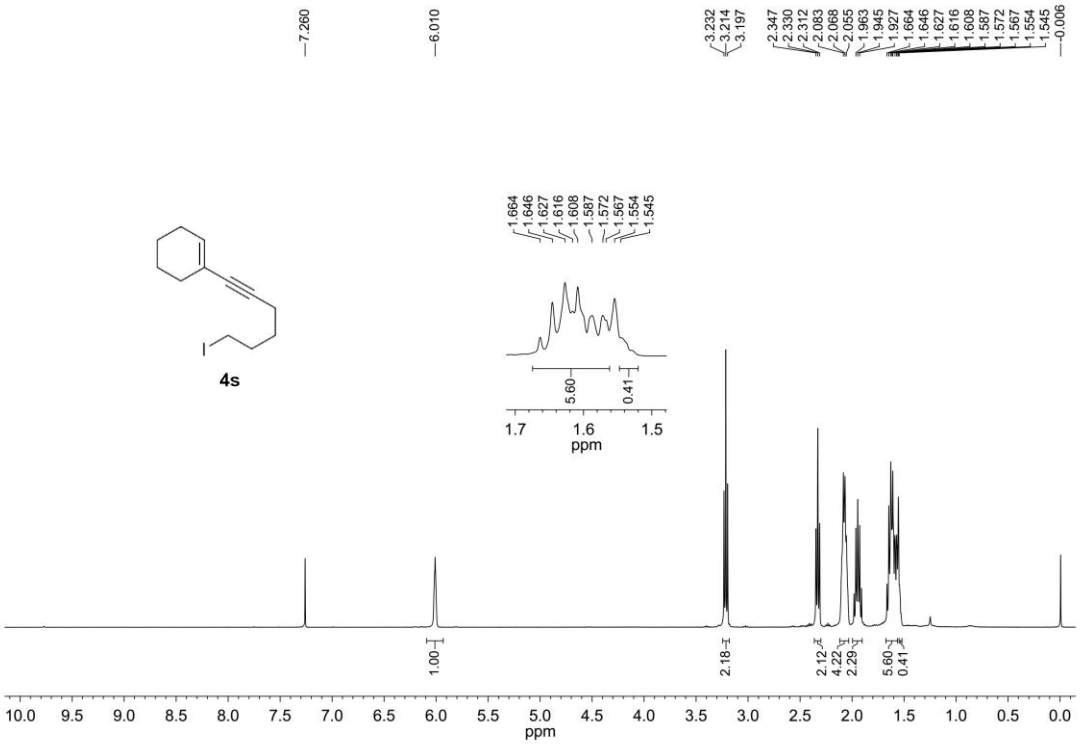


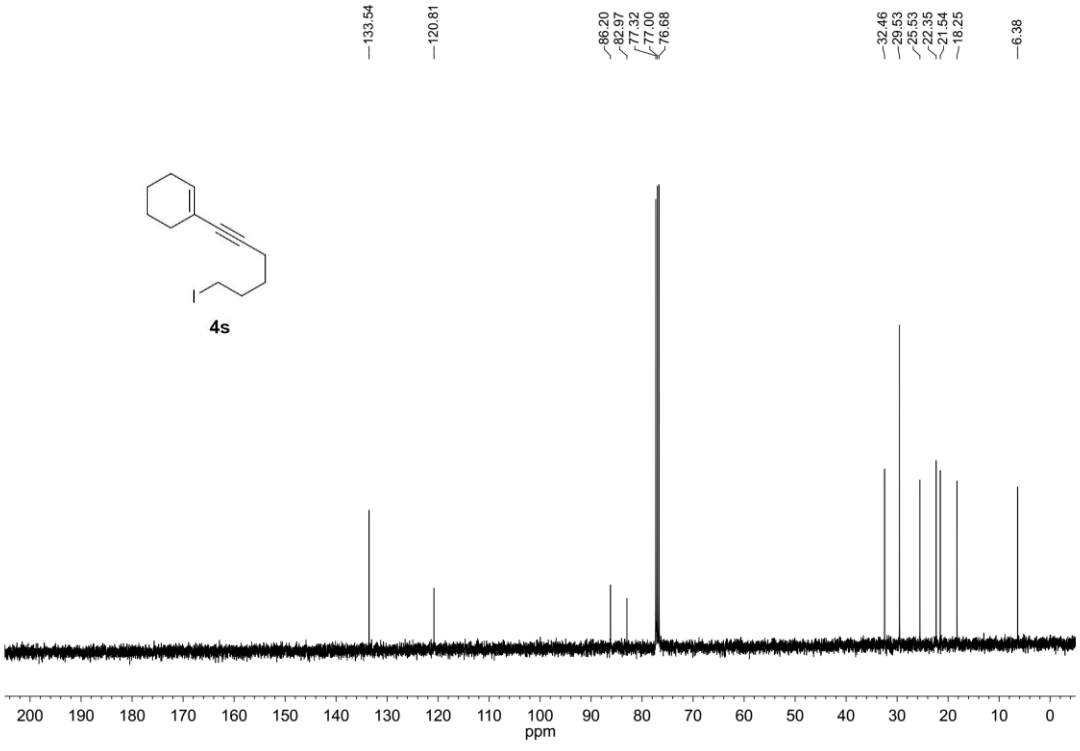
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **4r**



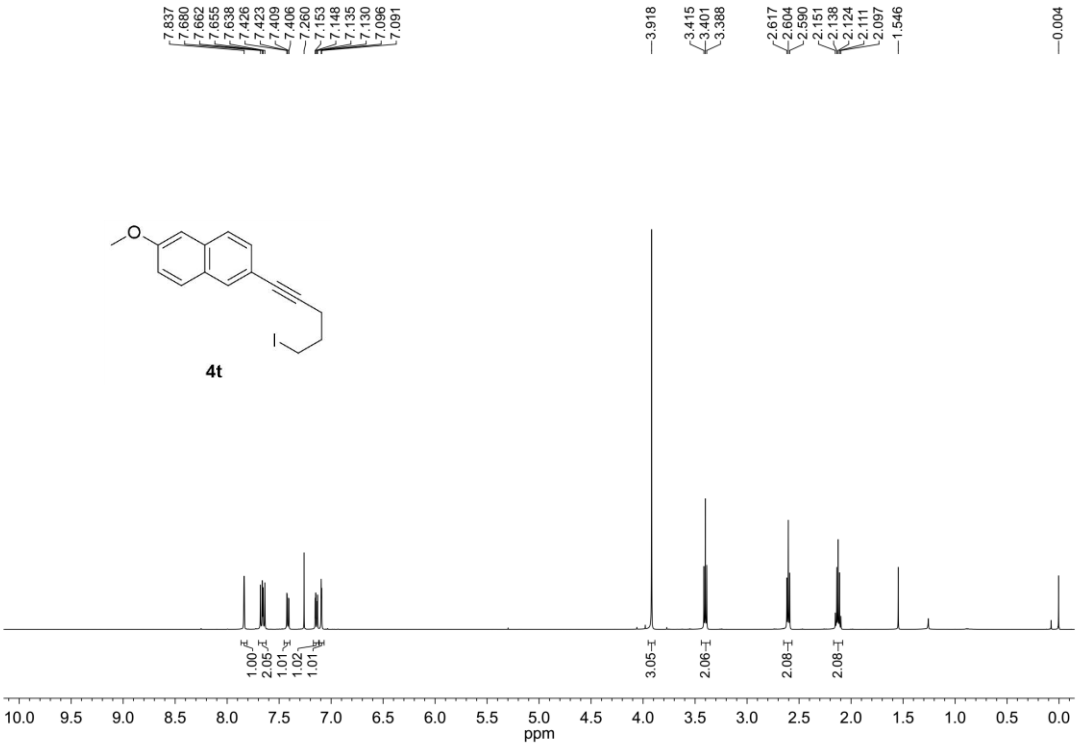


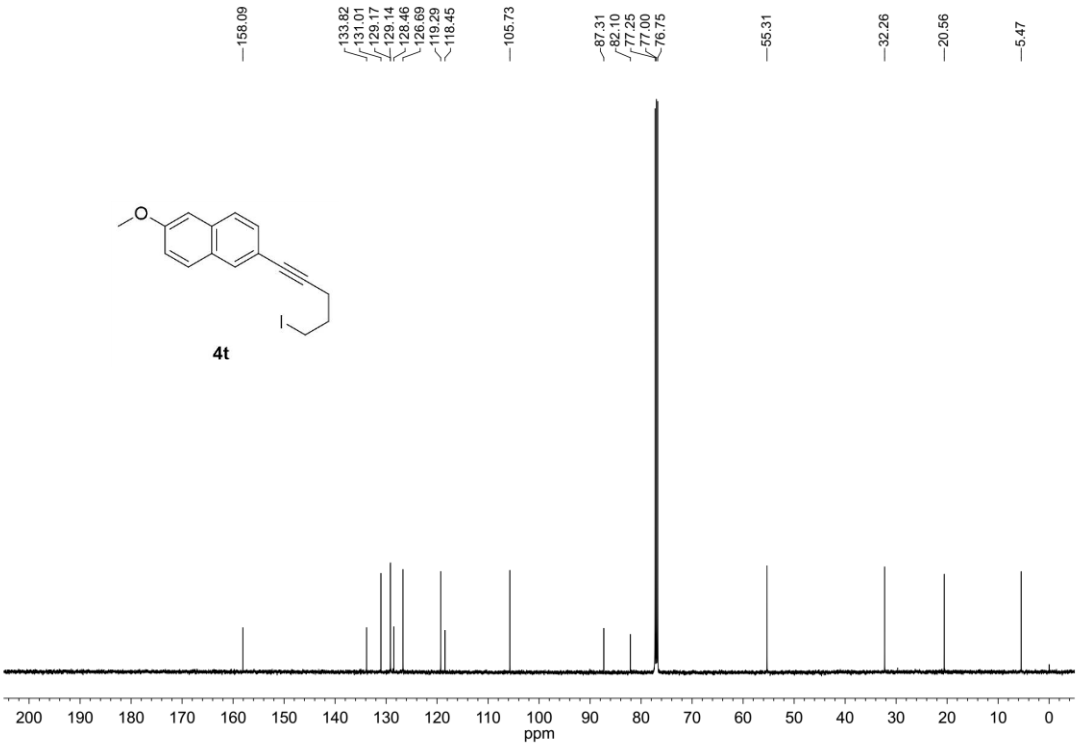
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **4s**



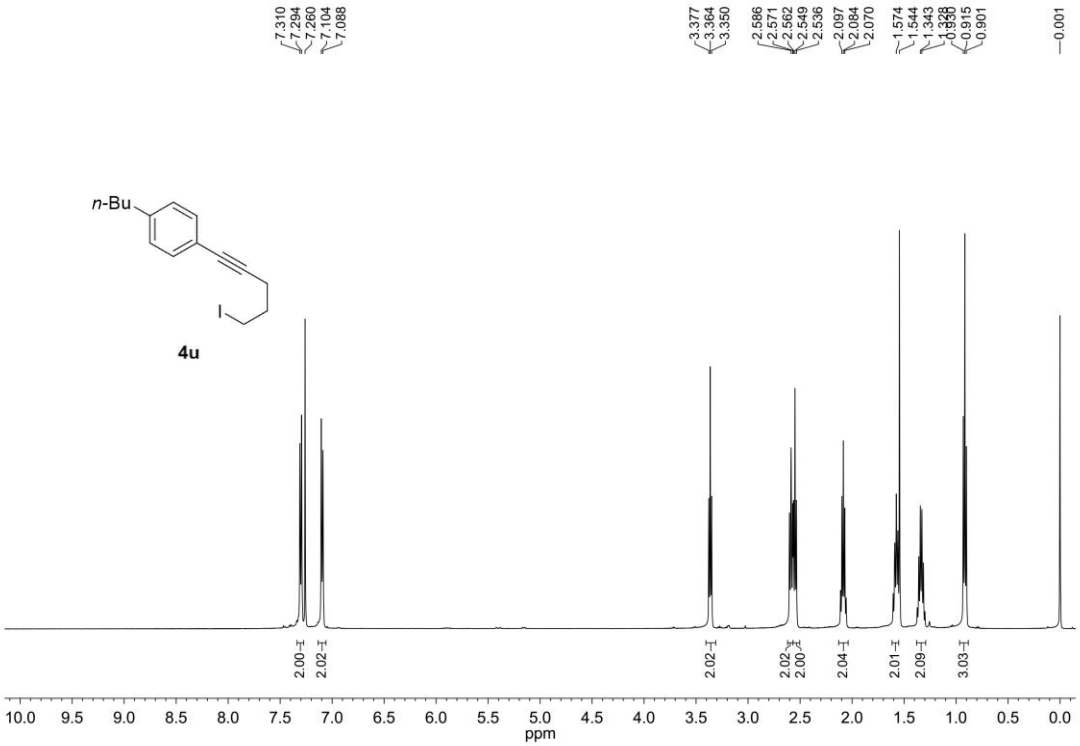


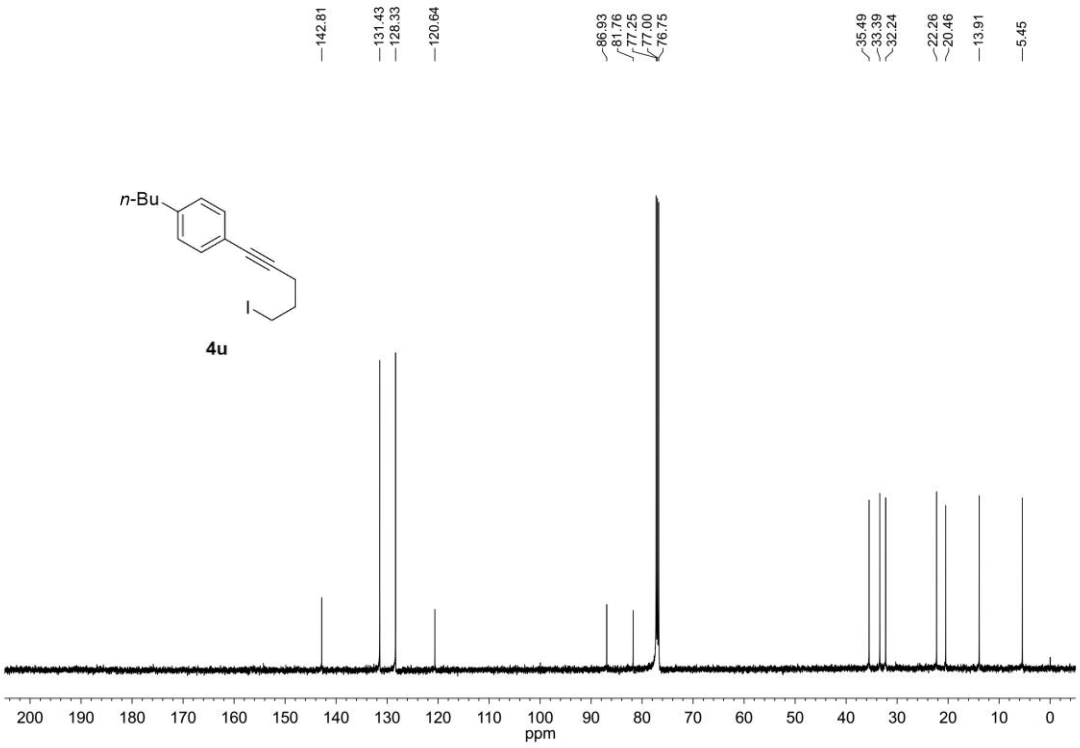
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **4t**



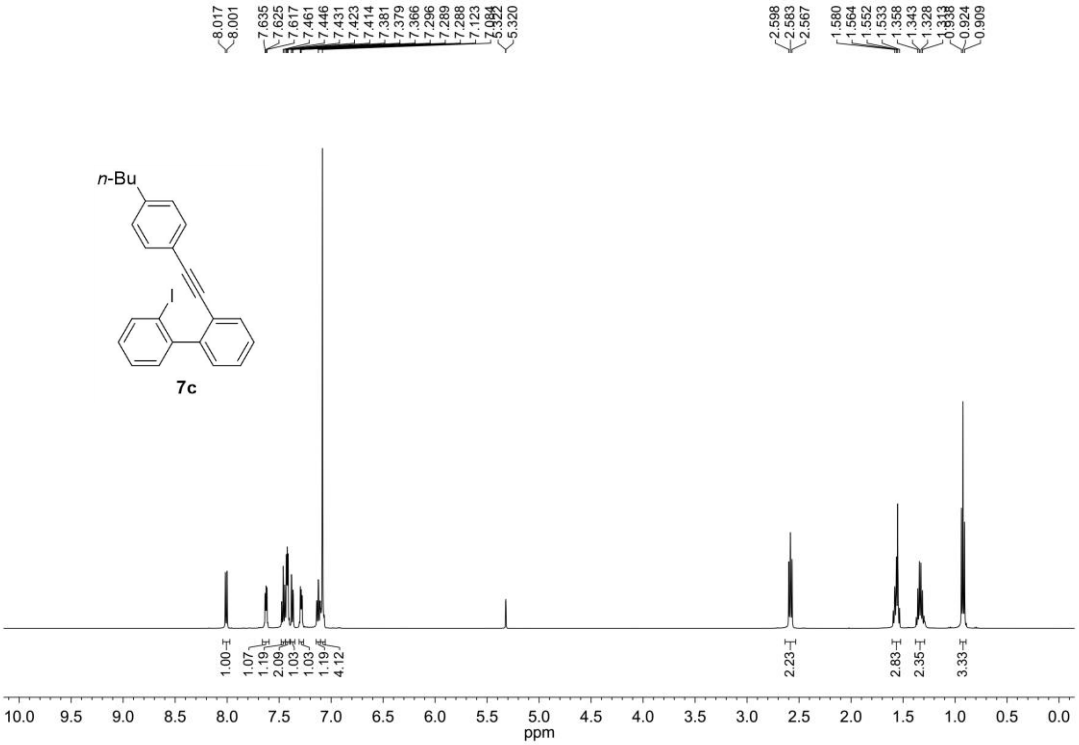


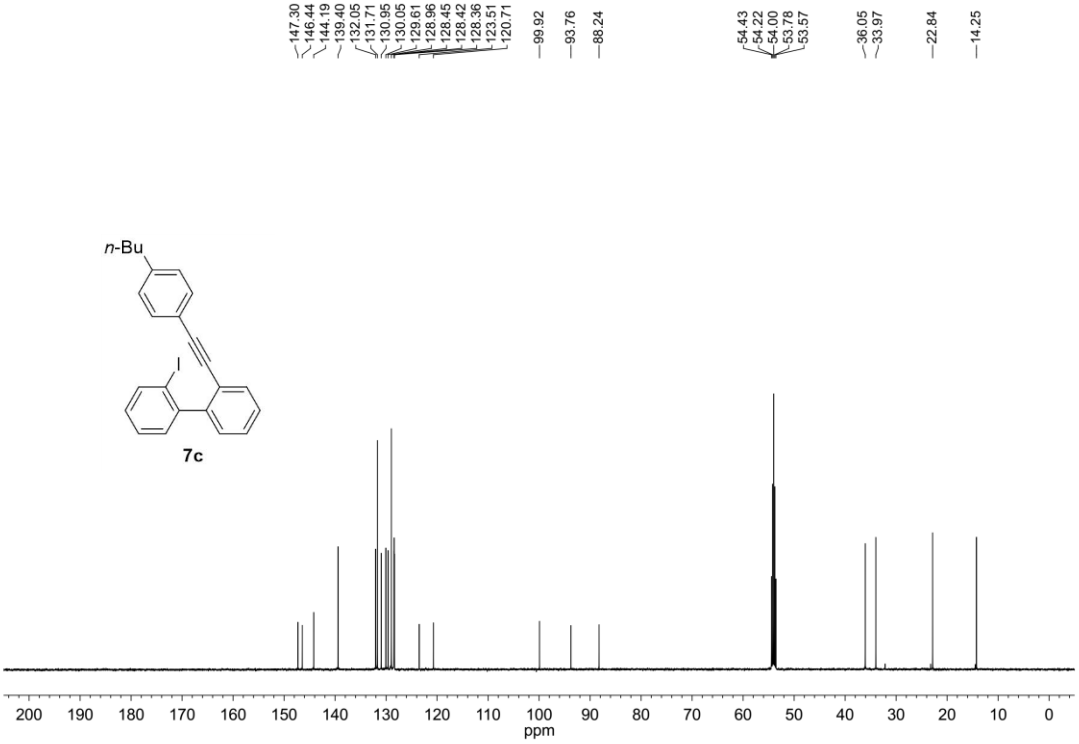
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **4u**



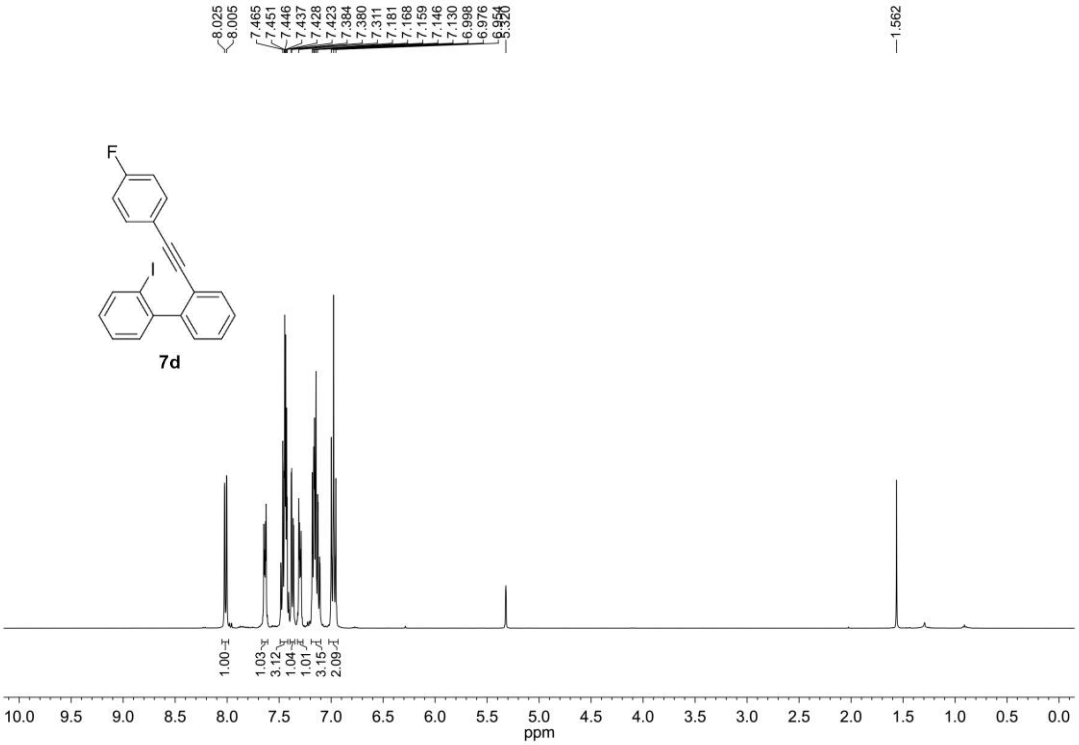


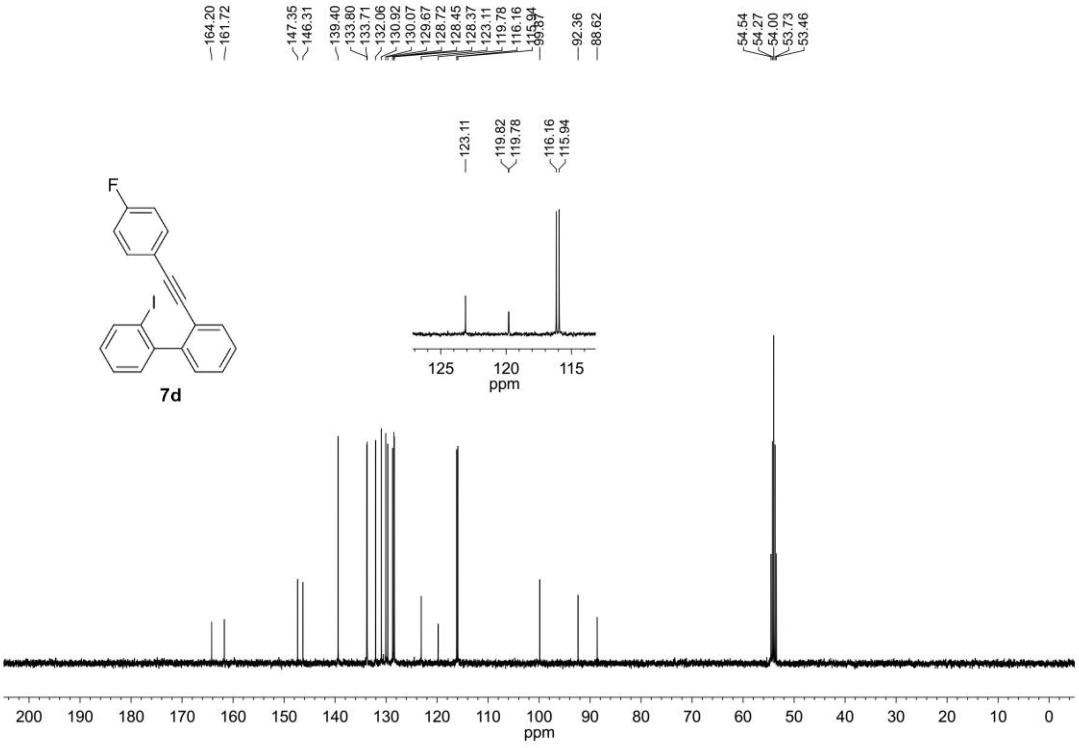
^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **7c**



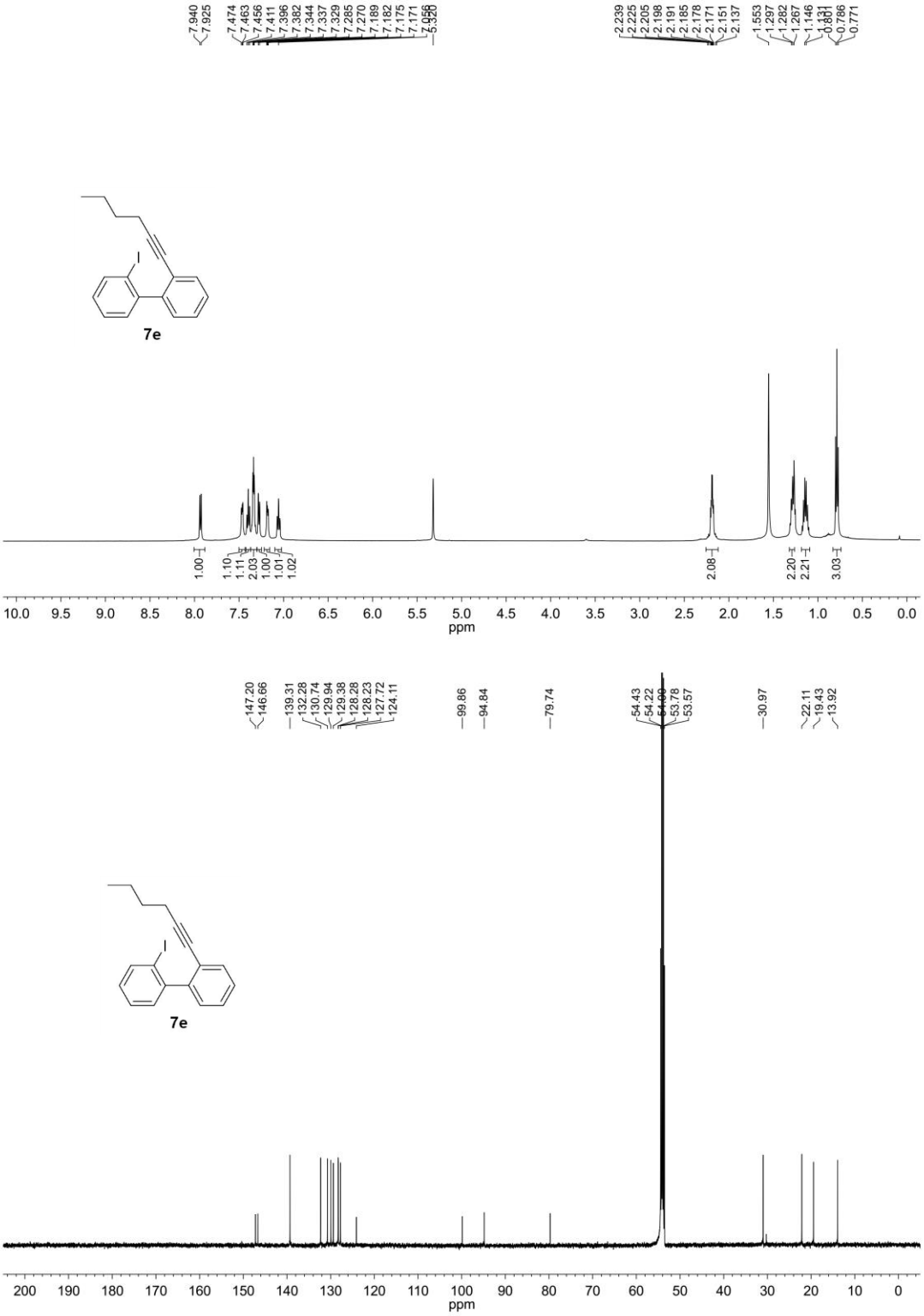


^{1}H NMR (400 MHz, CD_2Cl_2) and **^{13}C NMR** (101 MHz, CD_2Cl_2) Spectra of Compound **7d**

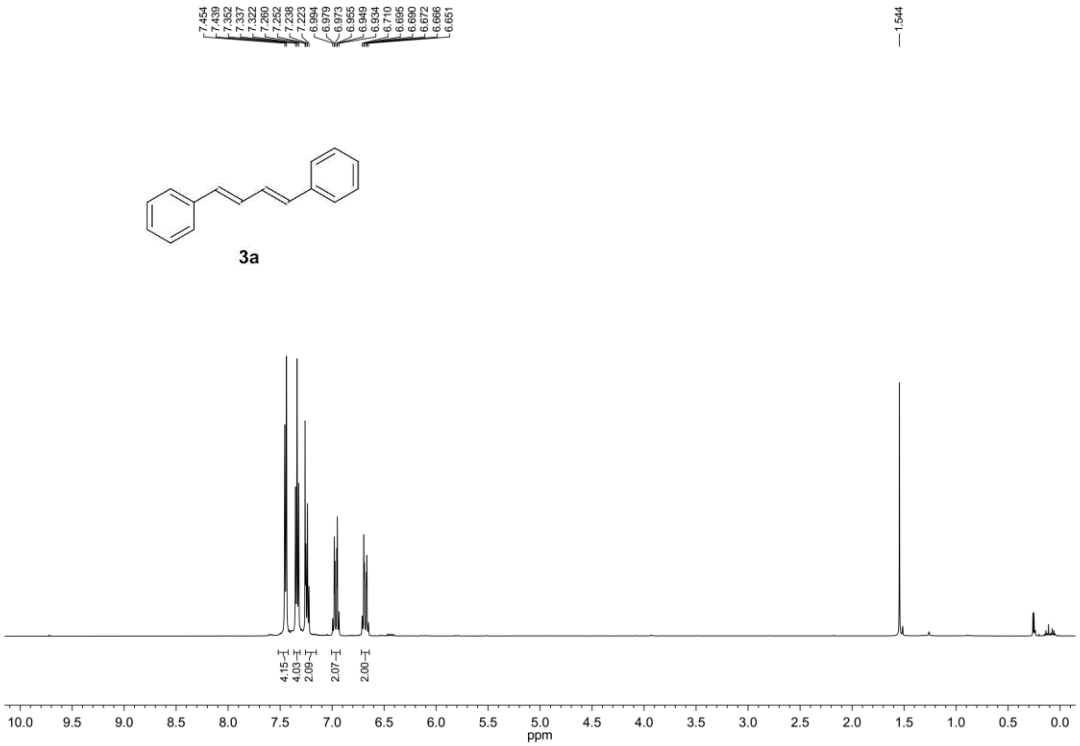


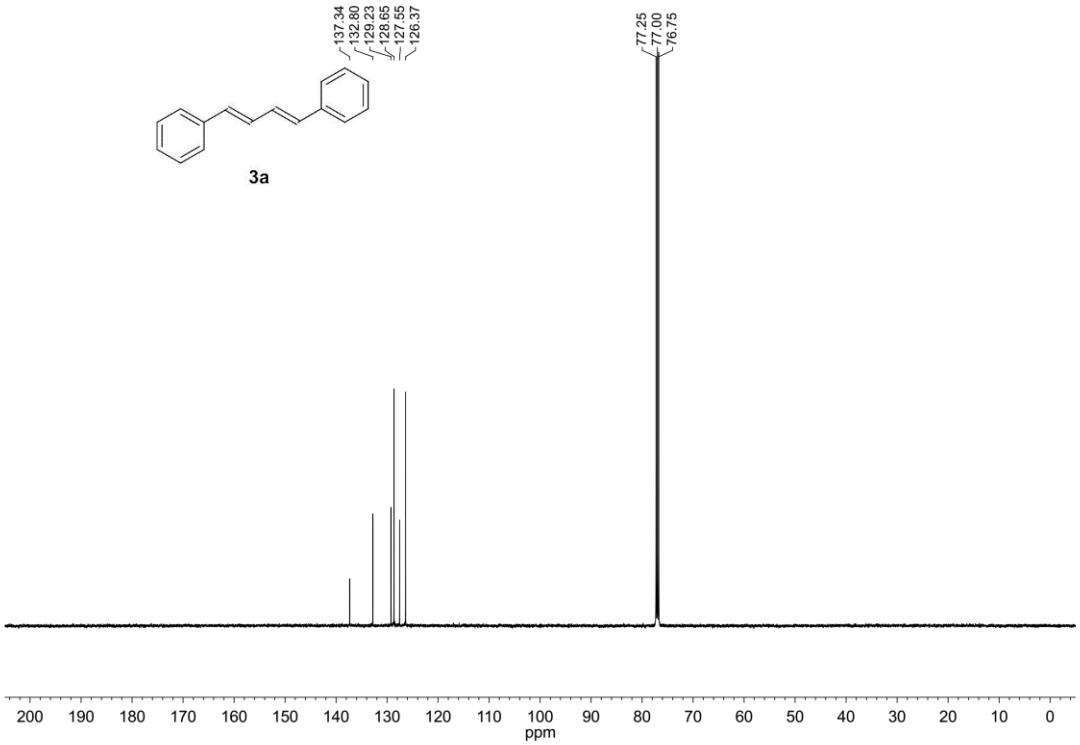


^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **7e**

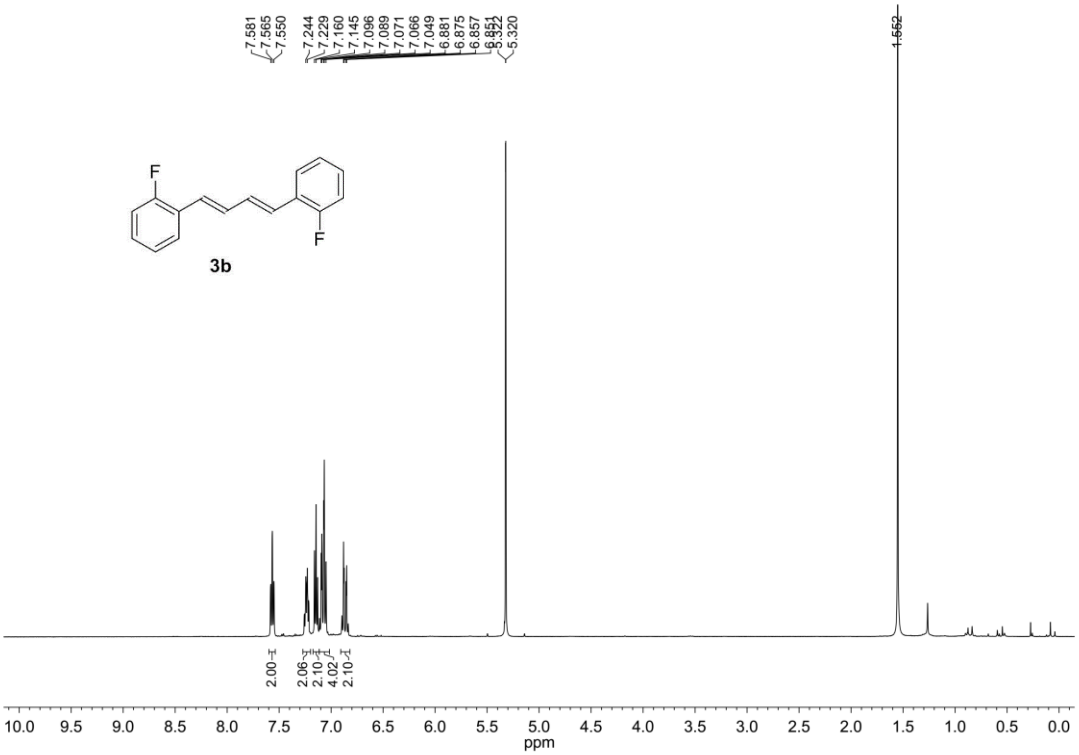


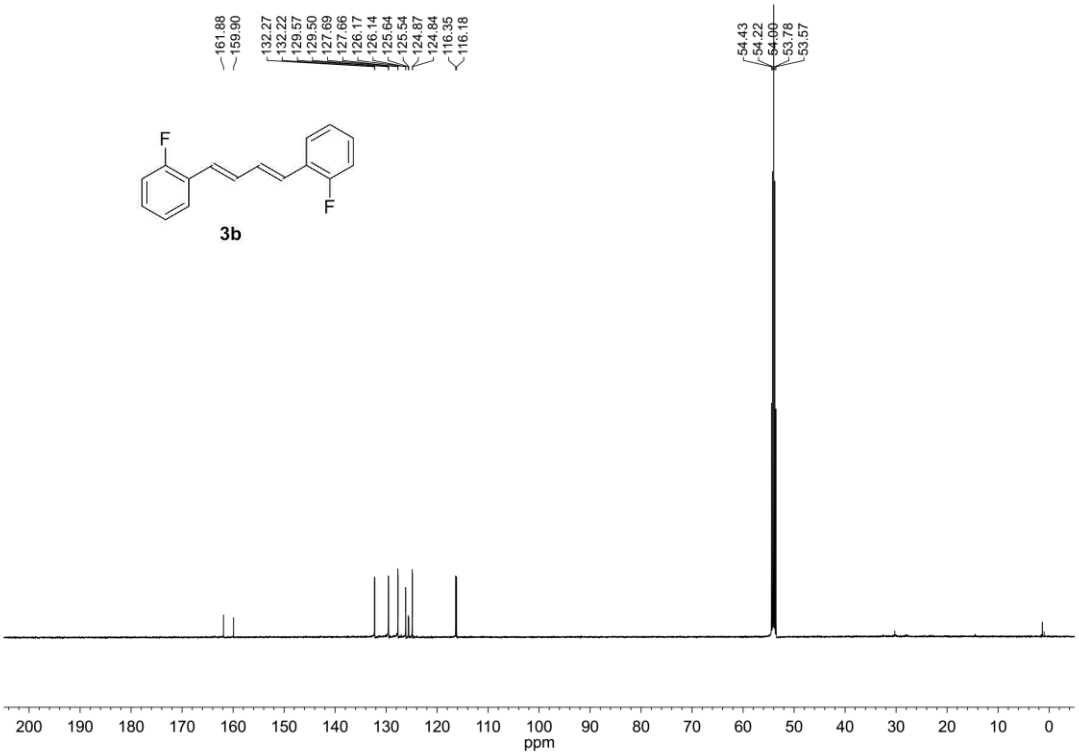
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **3a**



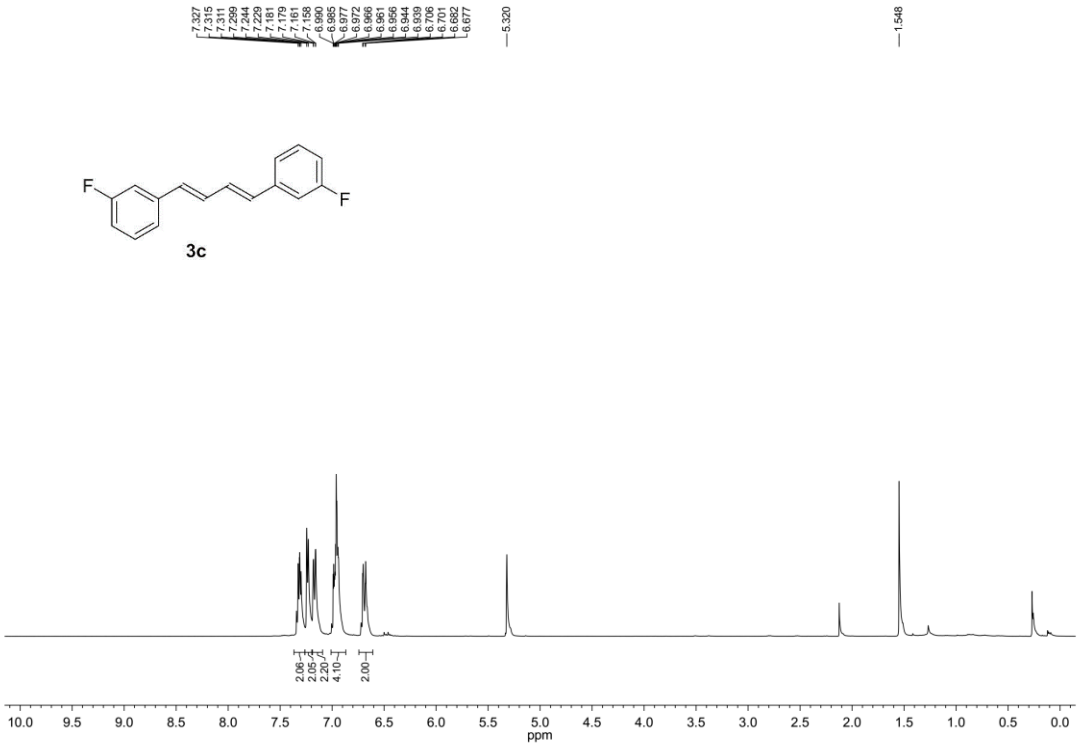


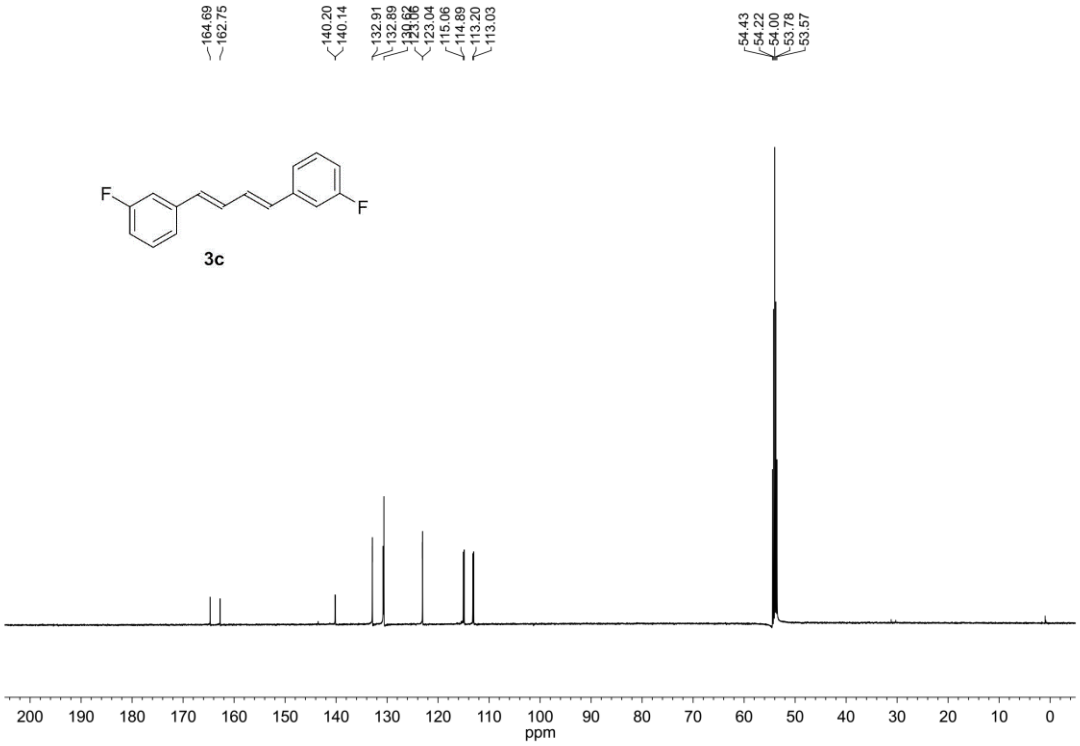
^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **3b**



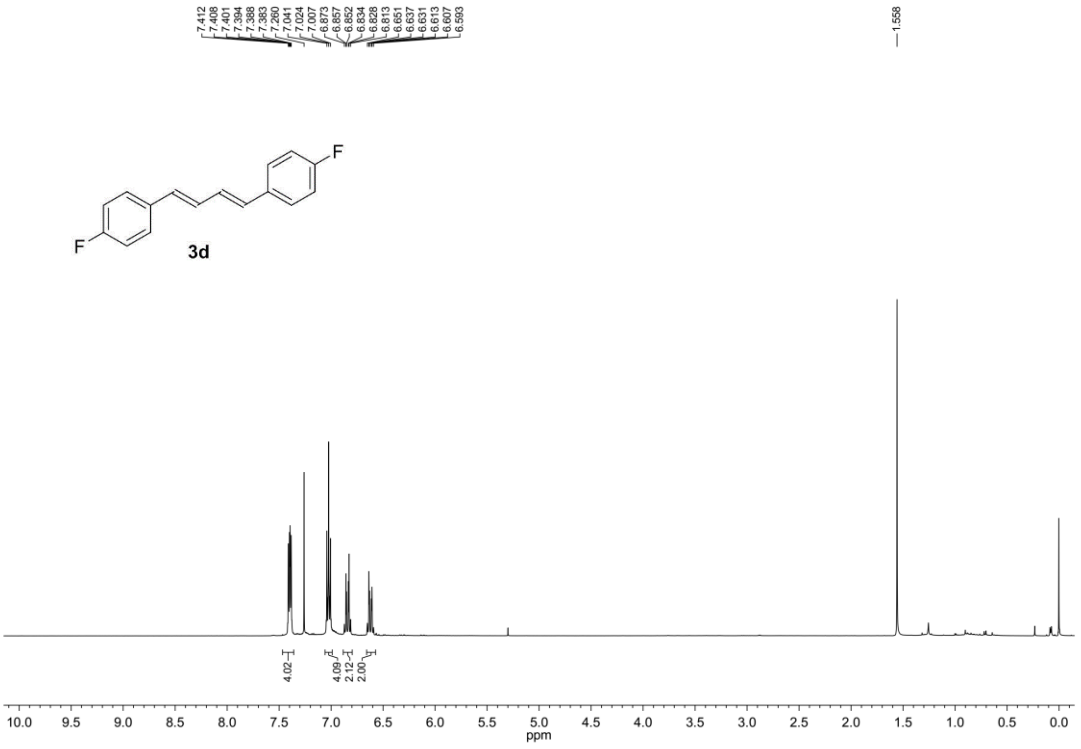


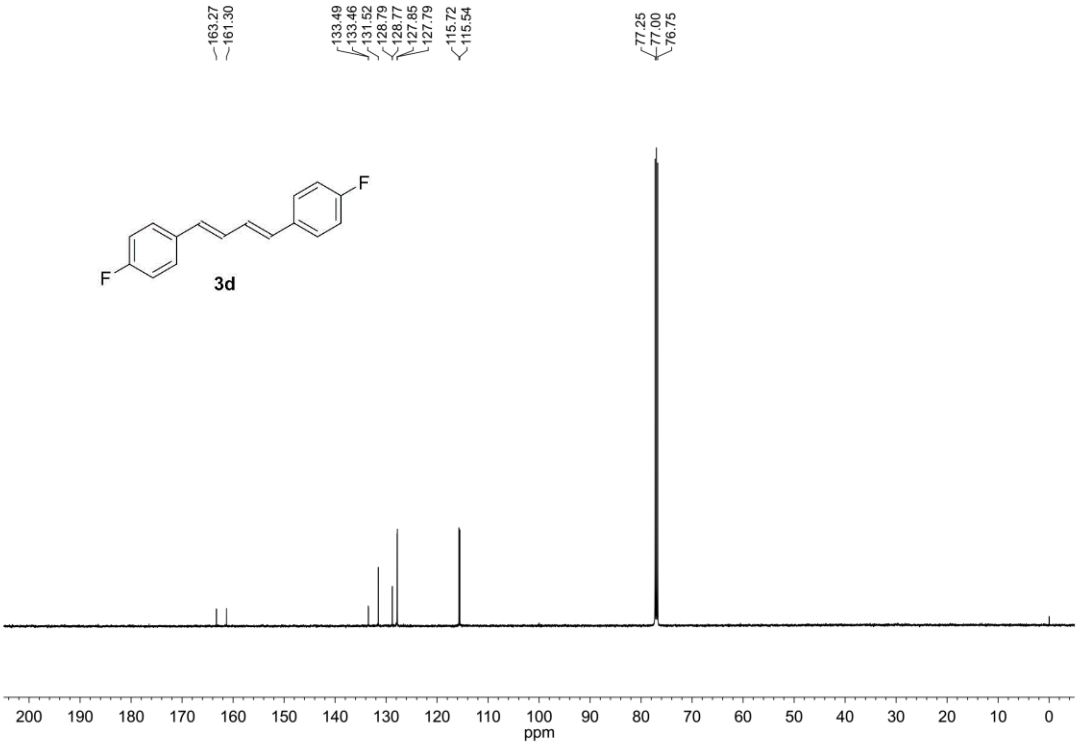
^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **3c**



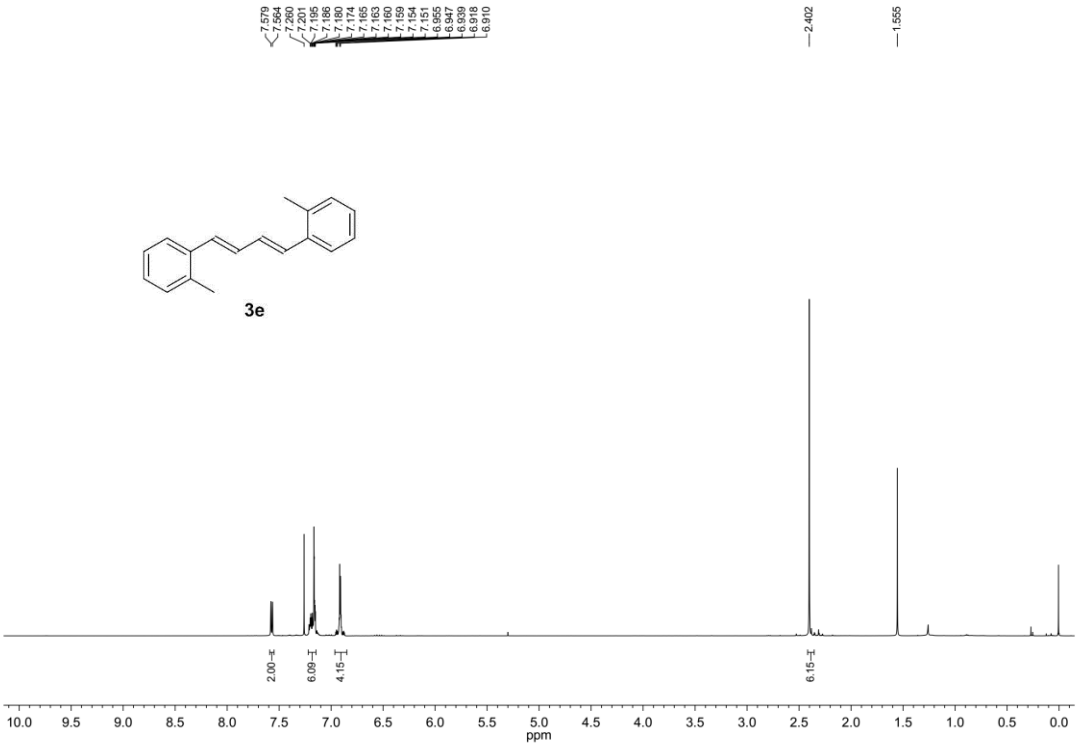


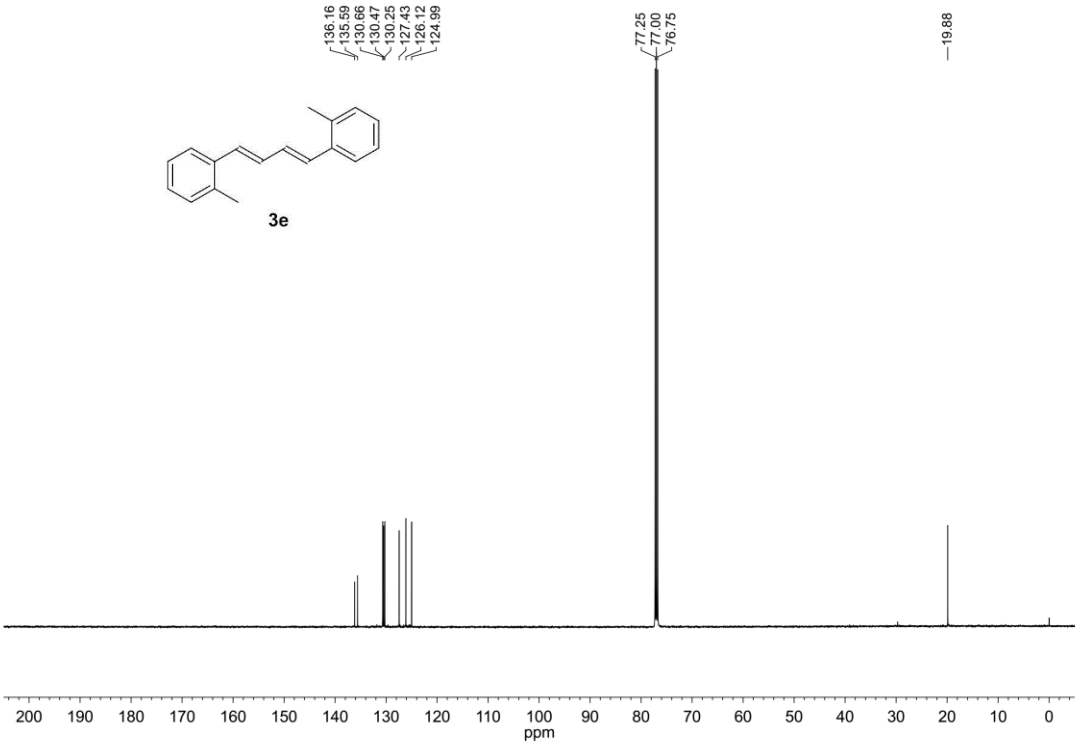
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **3d**



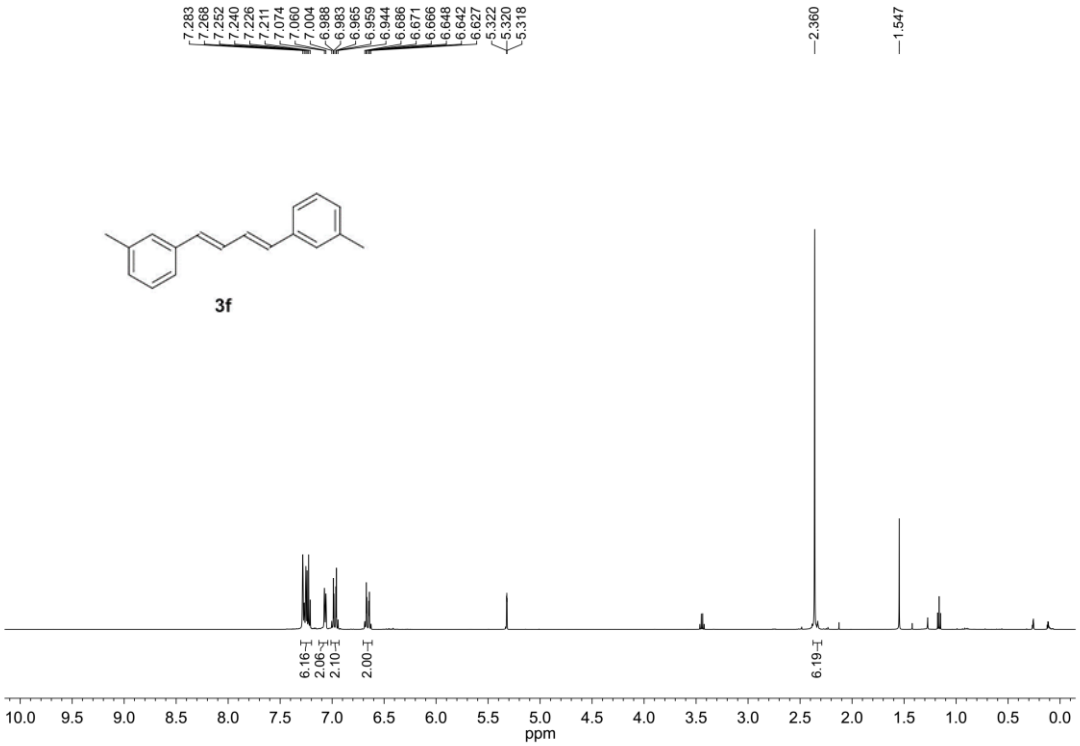


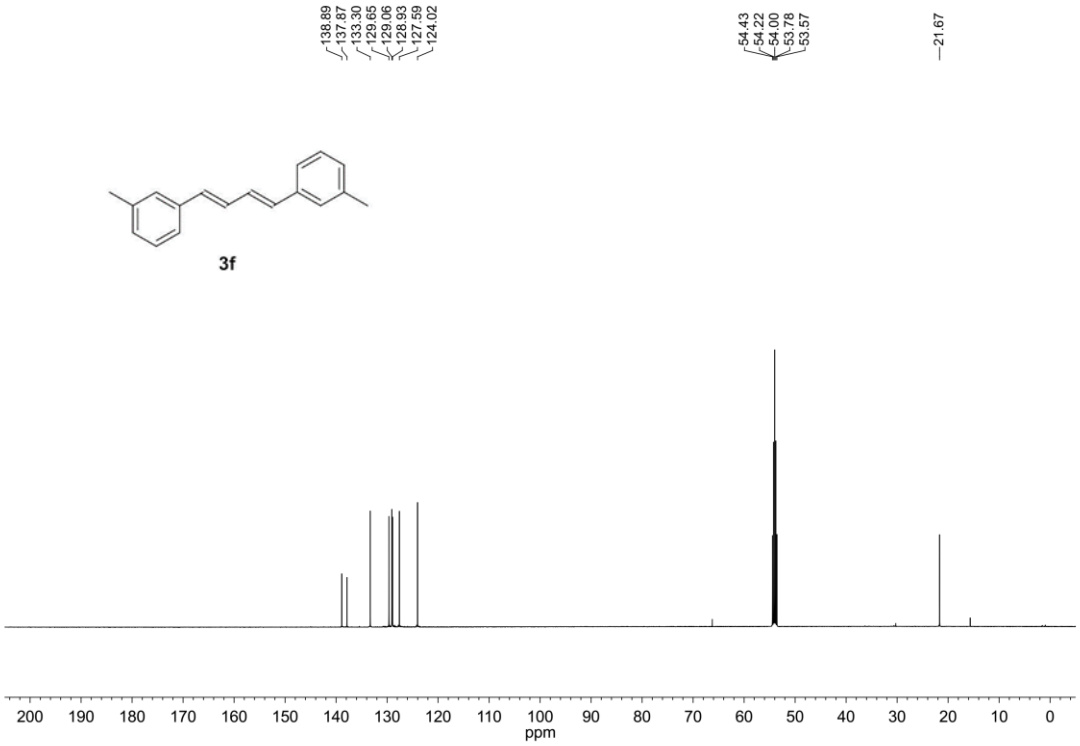
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **3e**



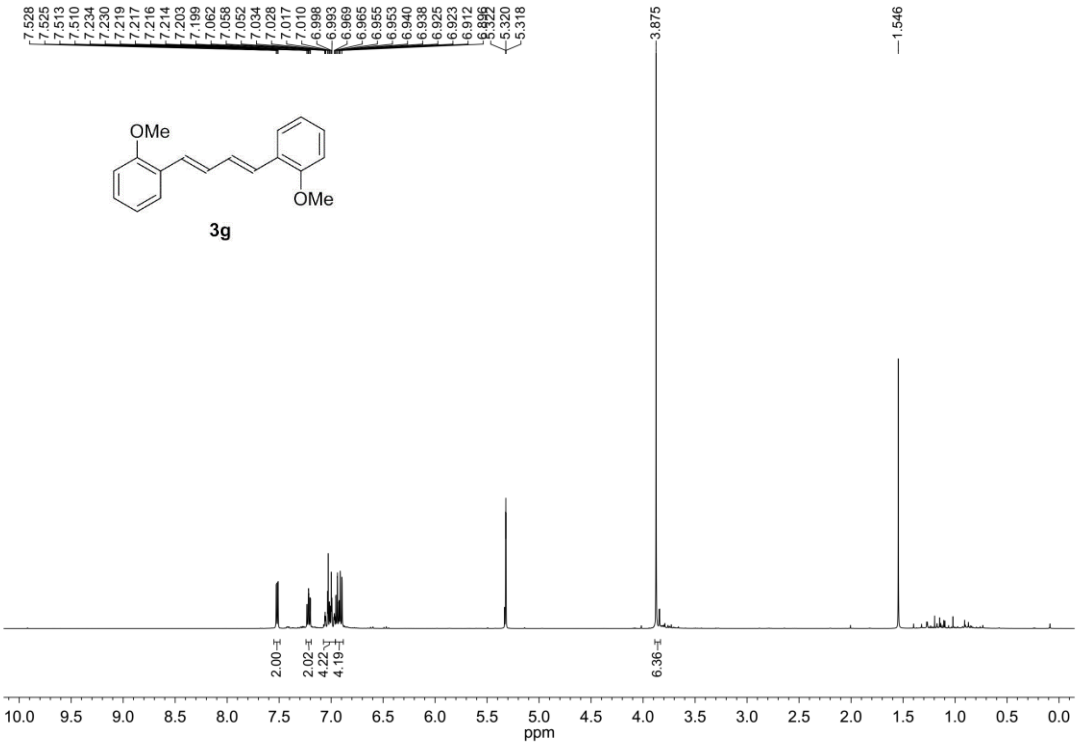


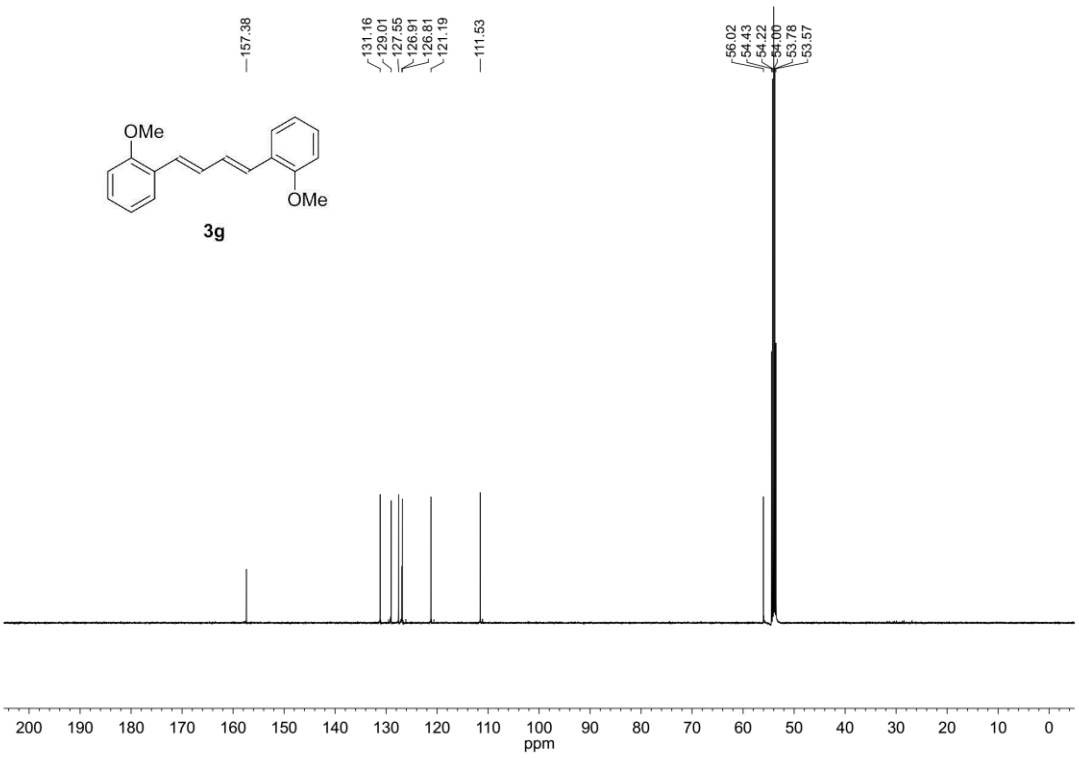
^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **3f**



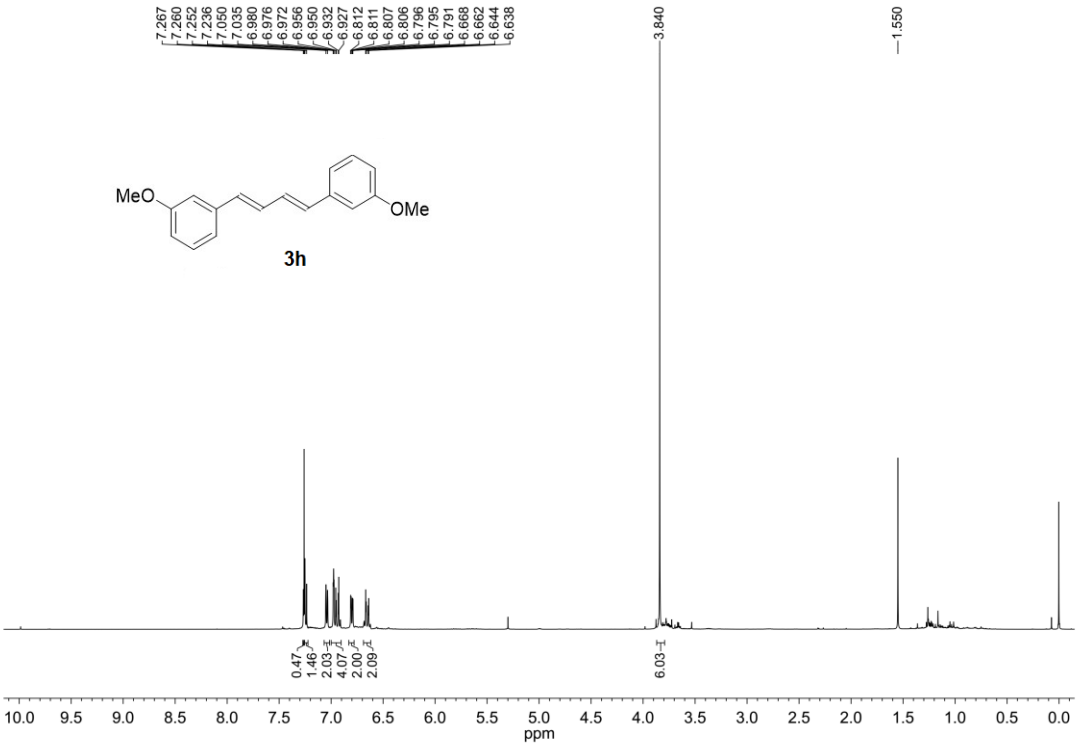


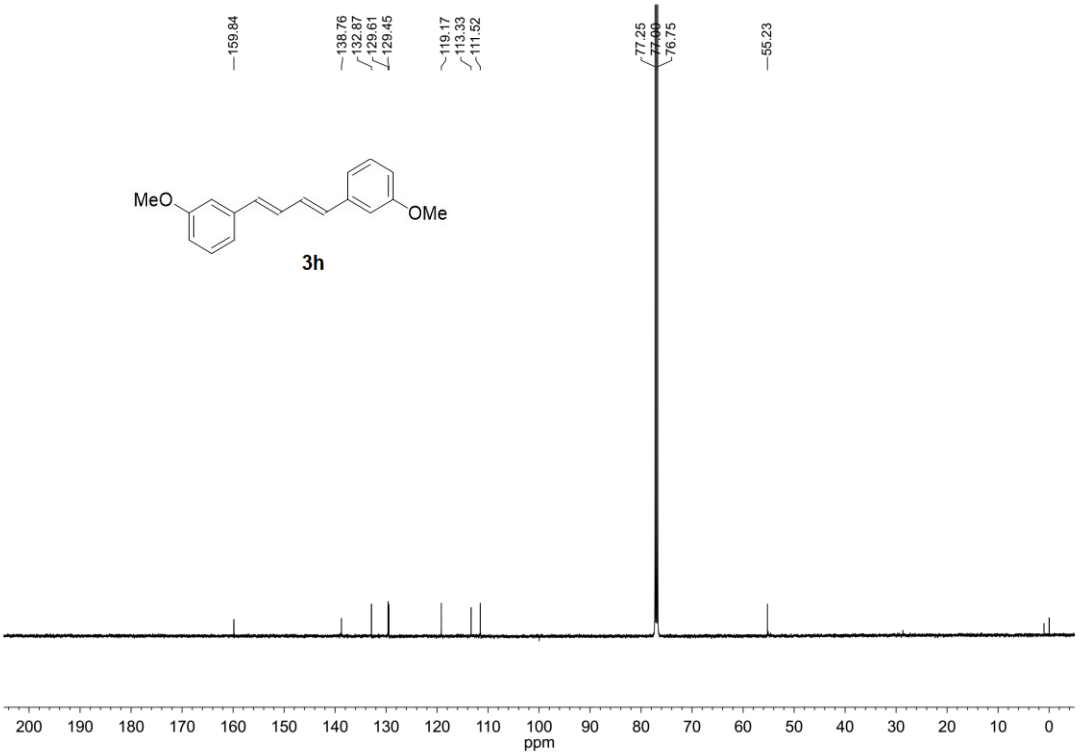
^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **3g**



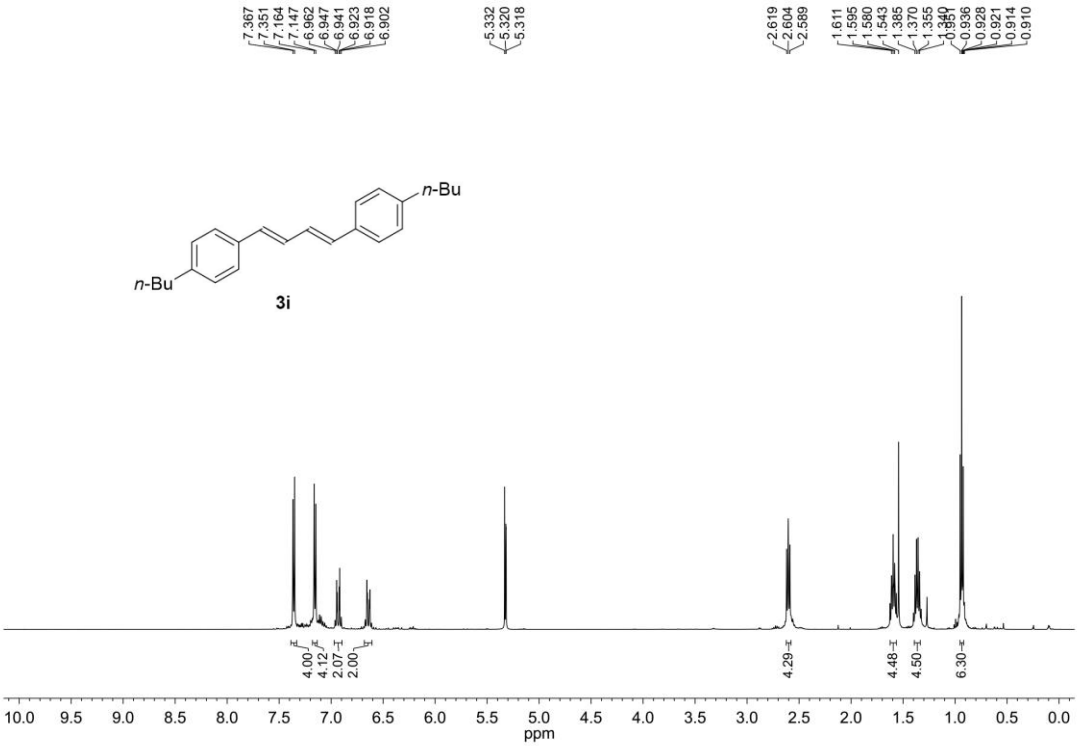


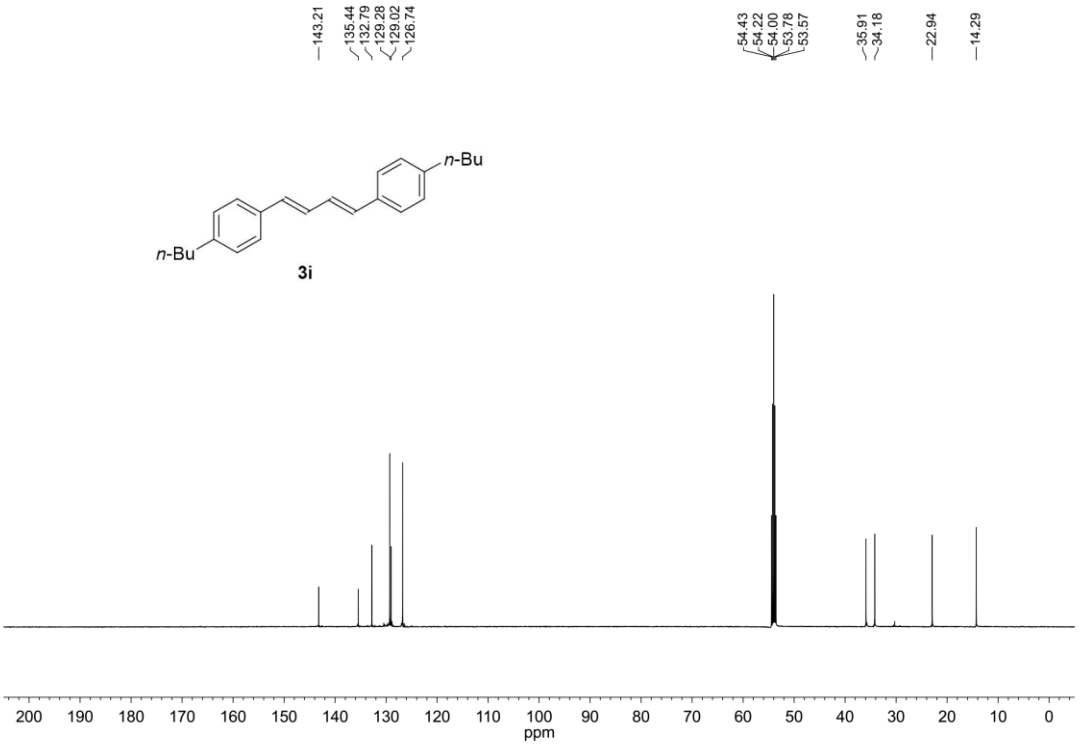
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **3h**



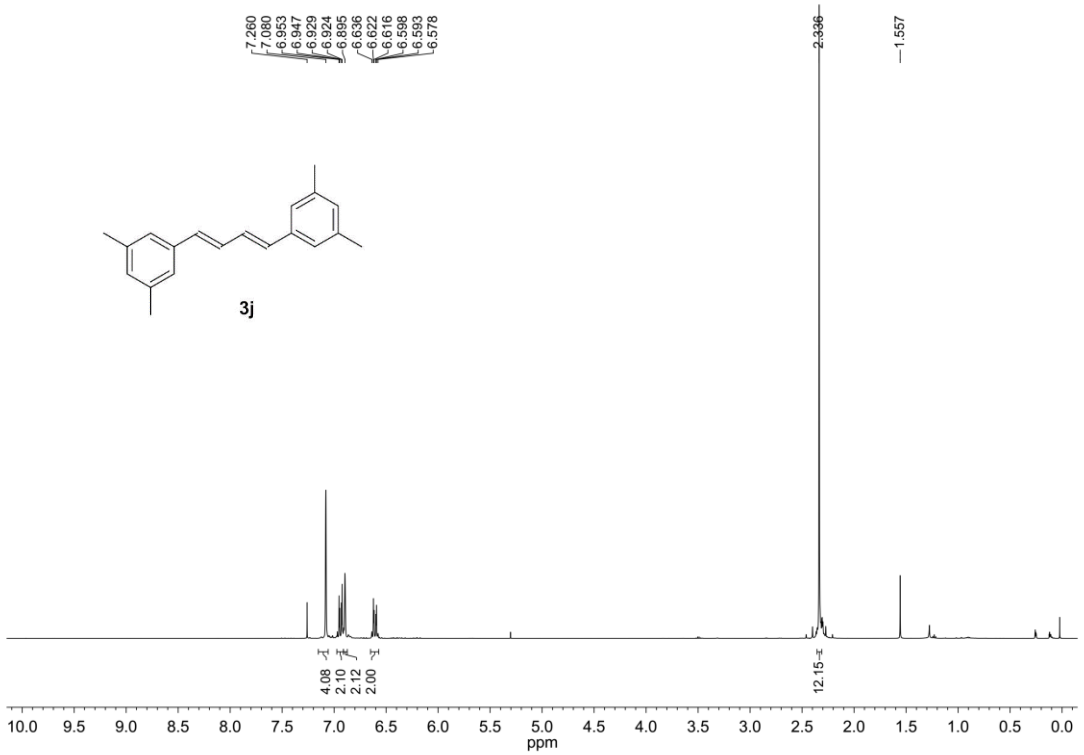


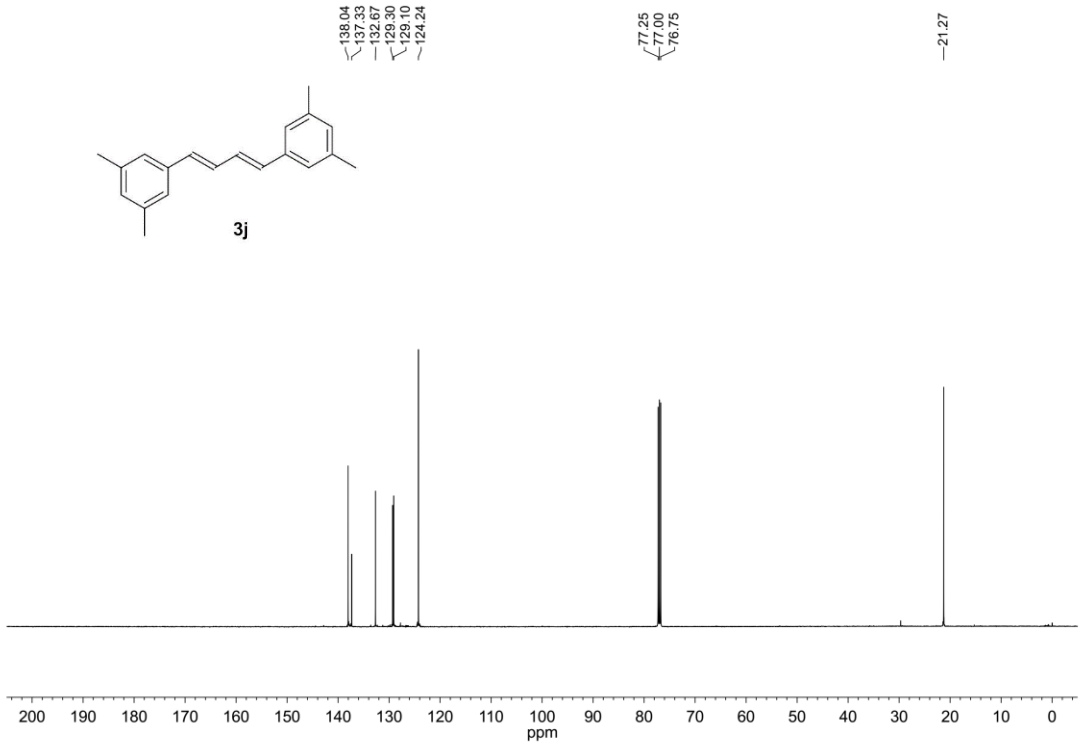
^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **3i**



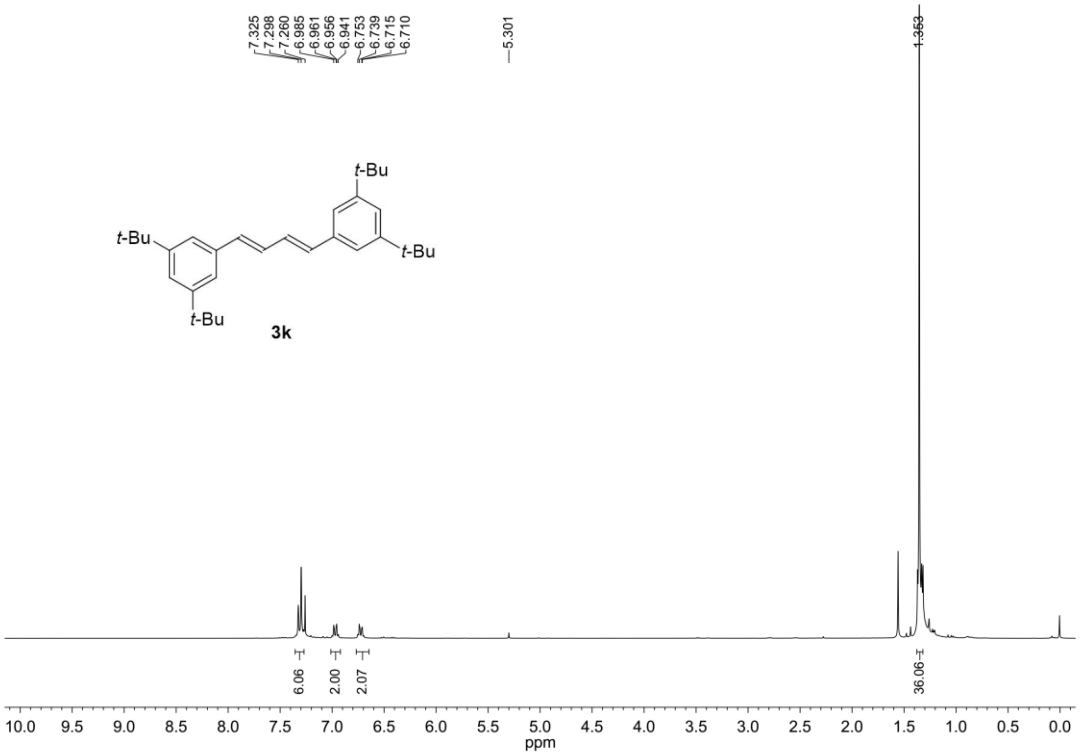


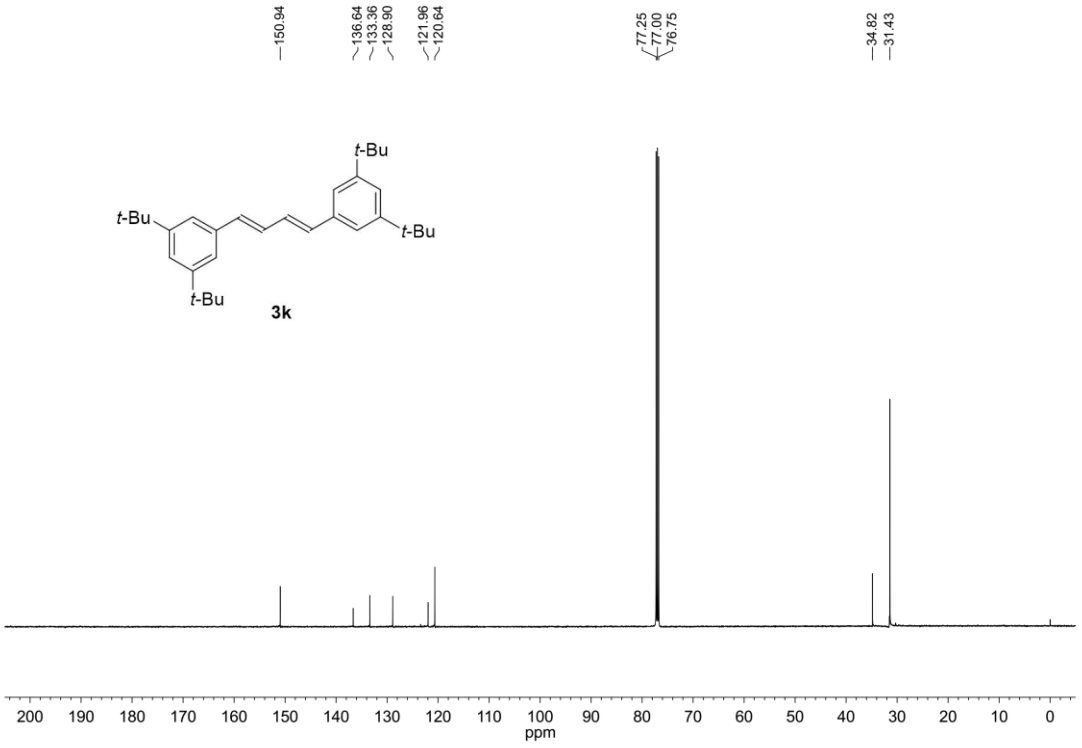
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **3j**



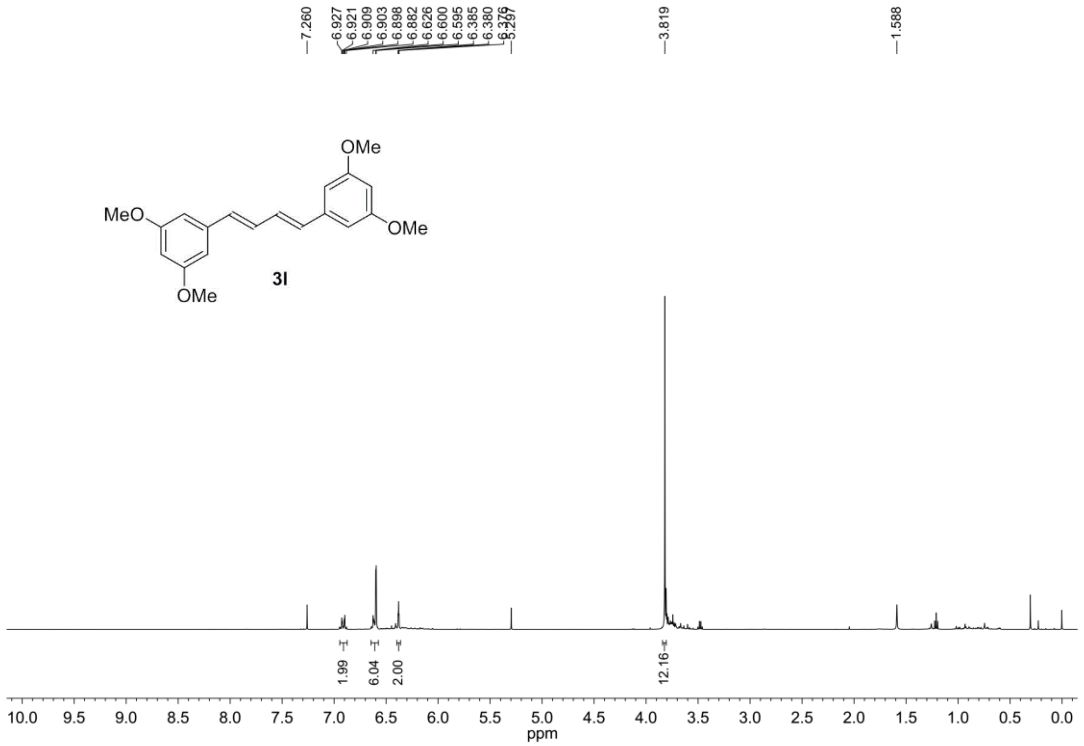


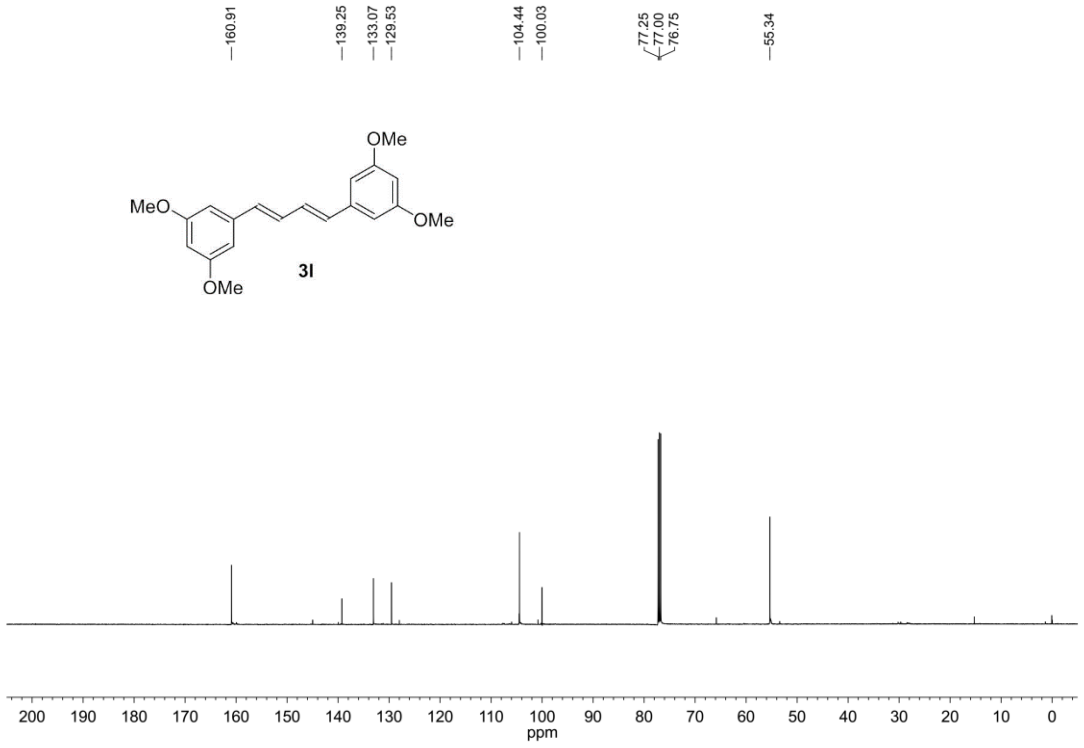
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **3k**



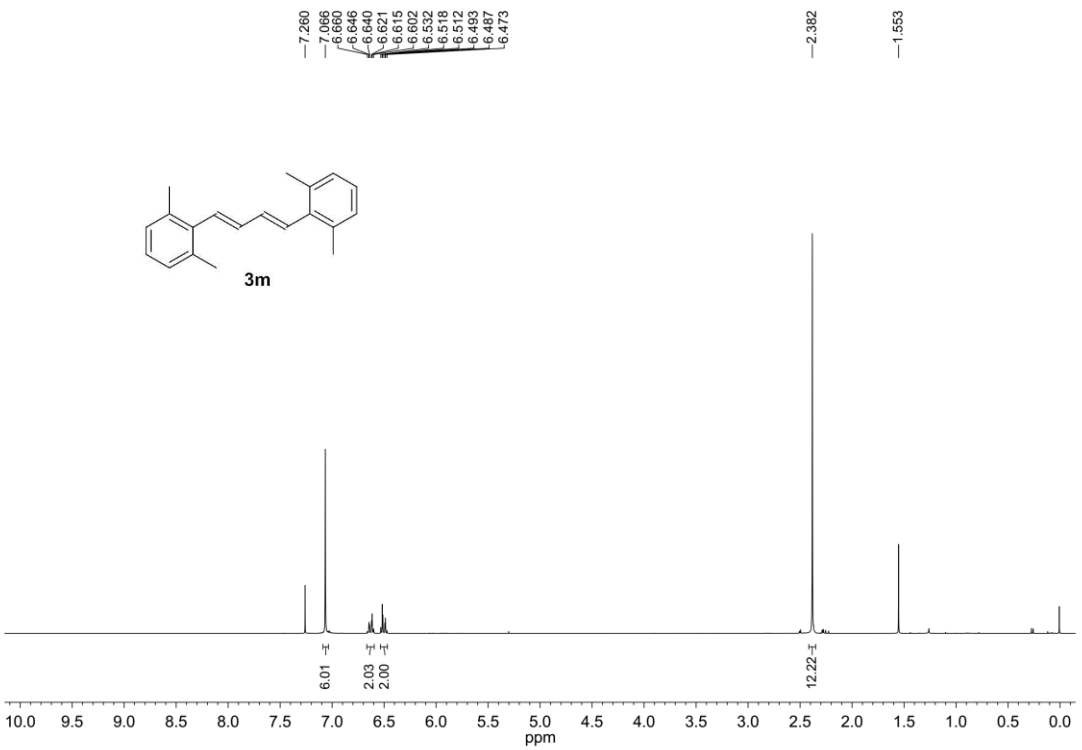


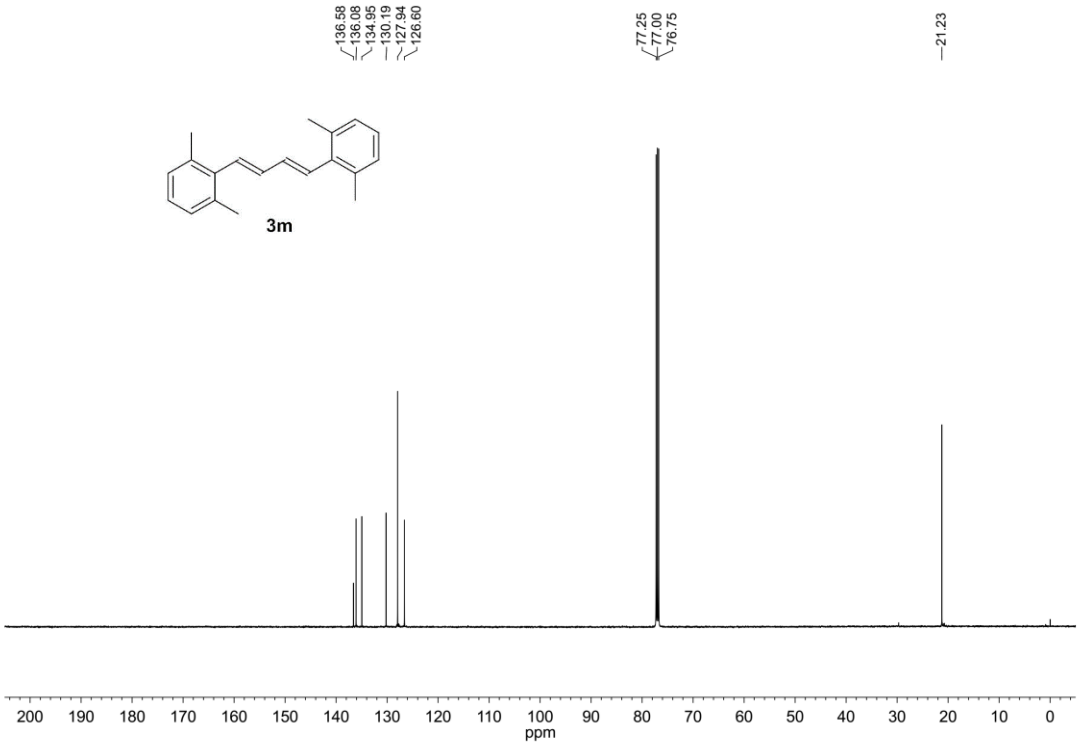
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **3l**



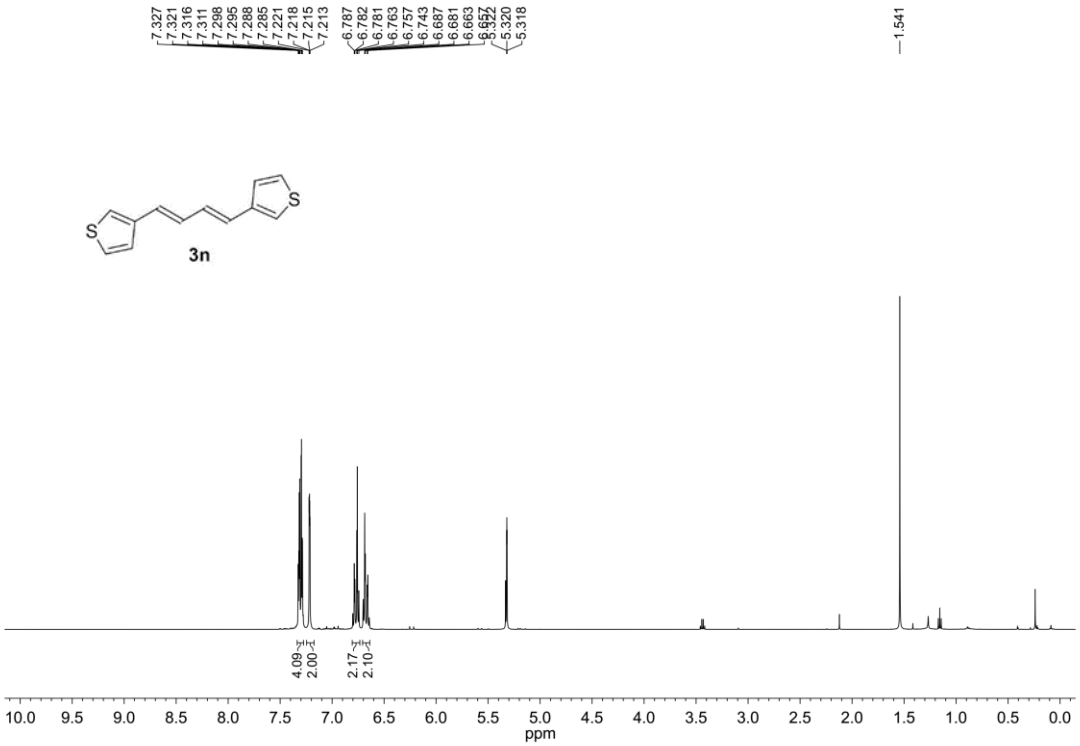


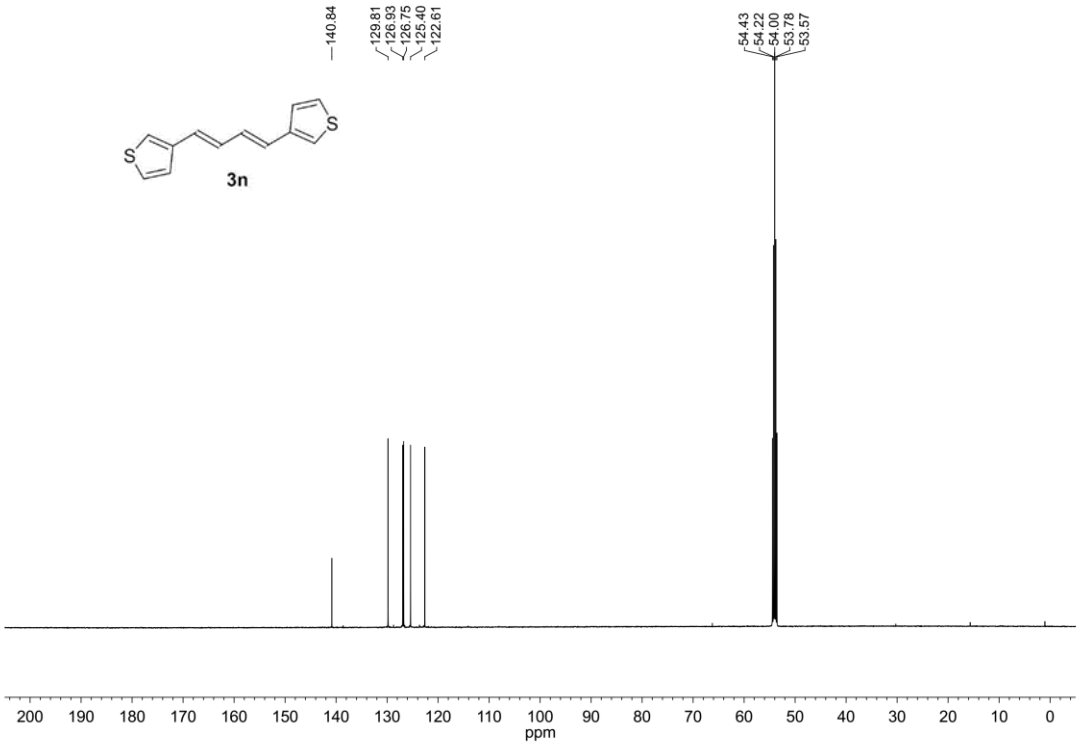
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **3m**



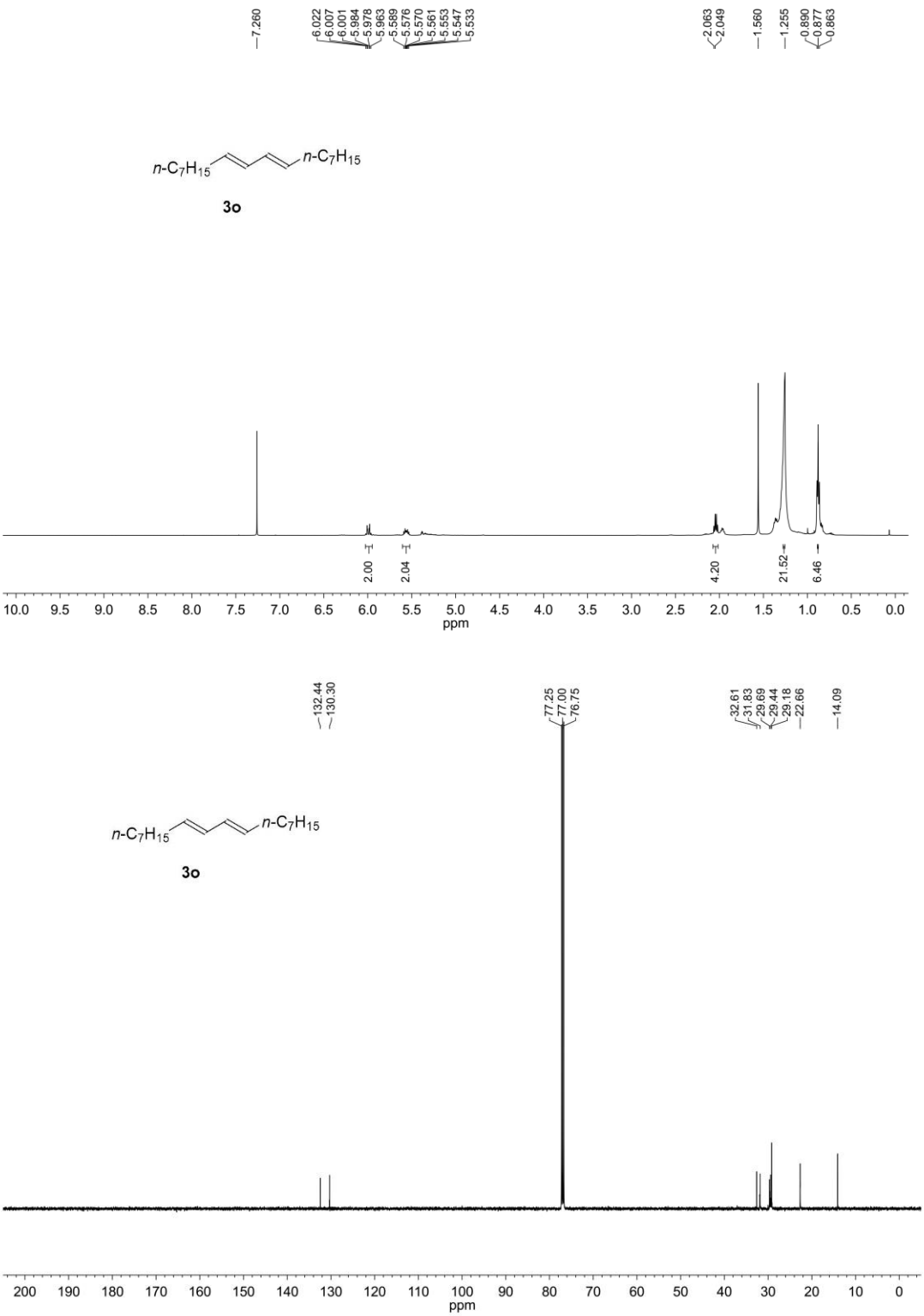


^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **3n**

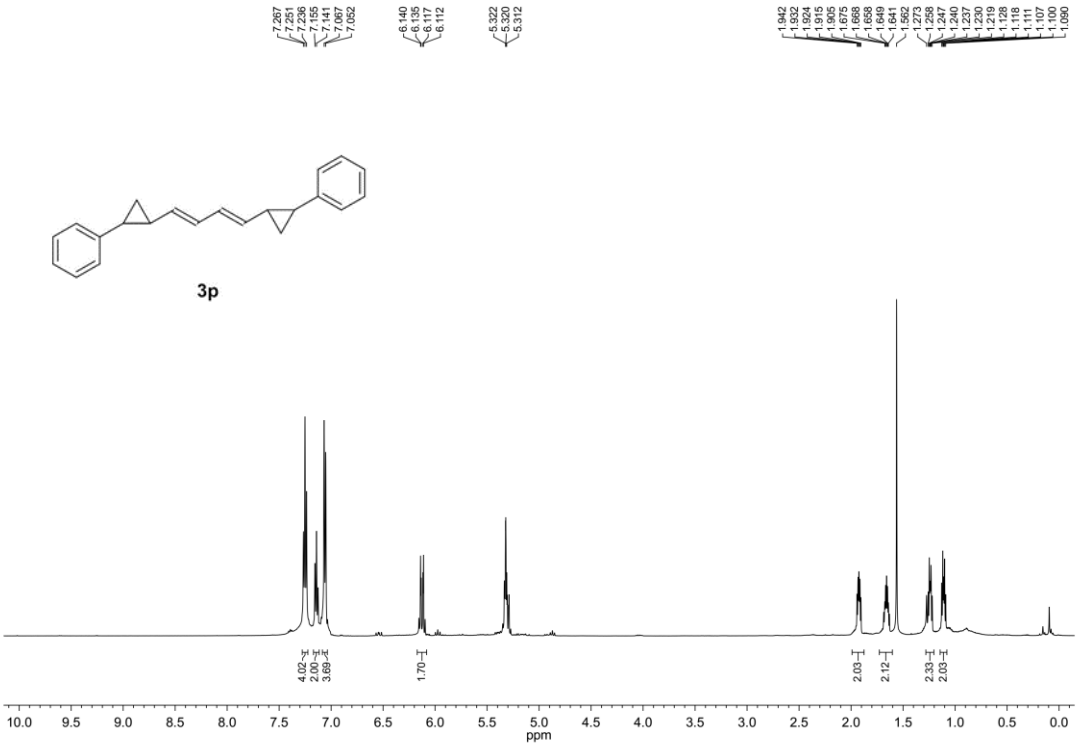


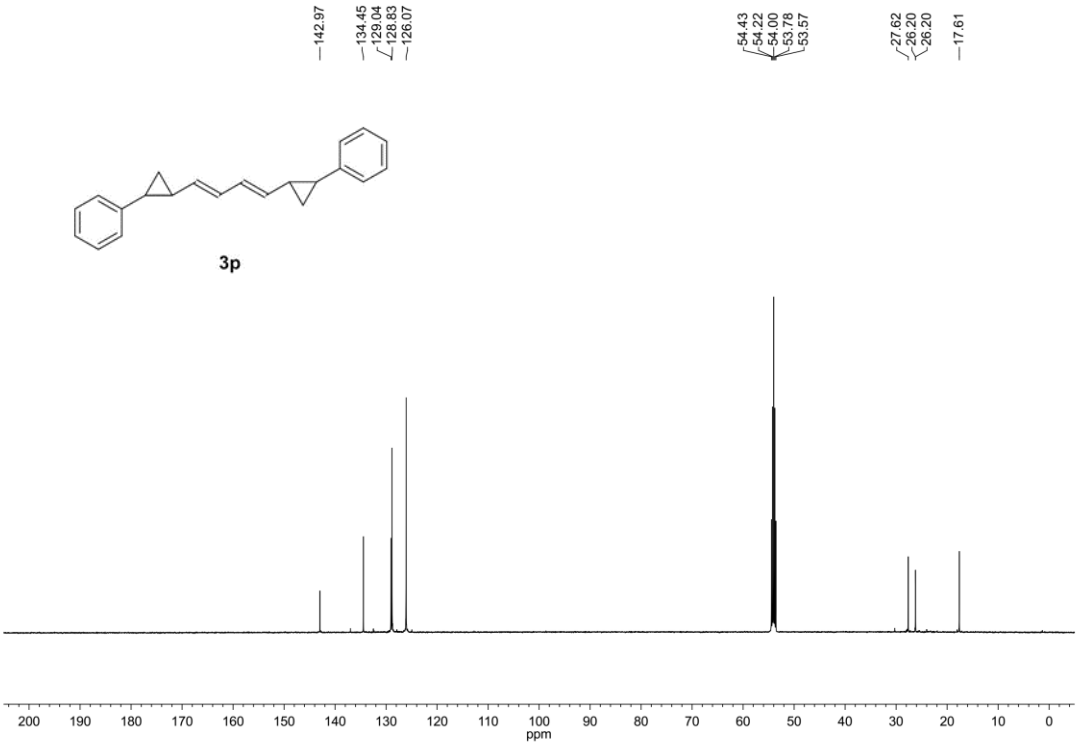


^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **3o**

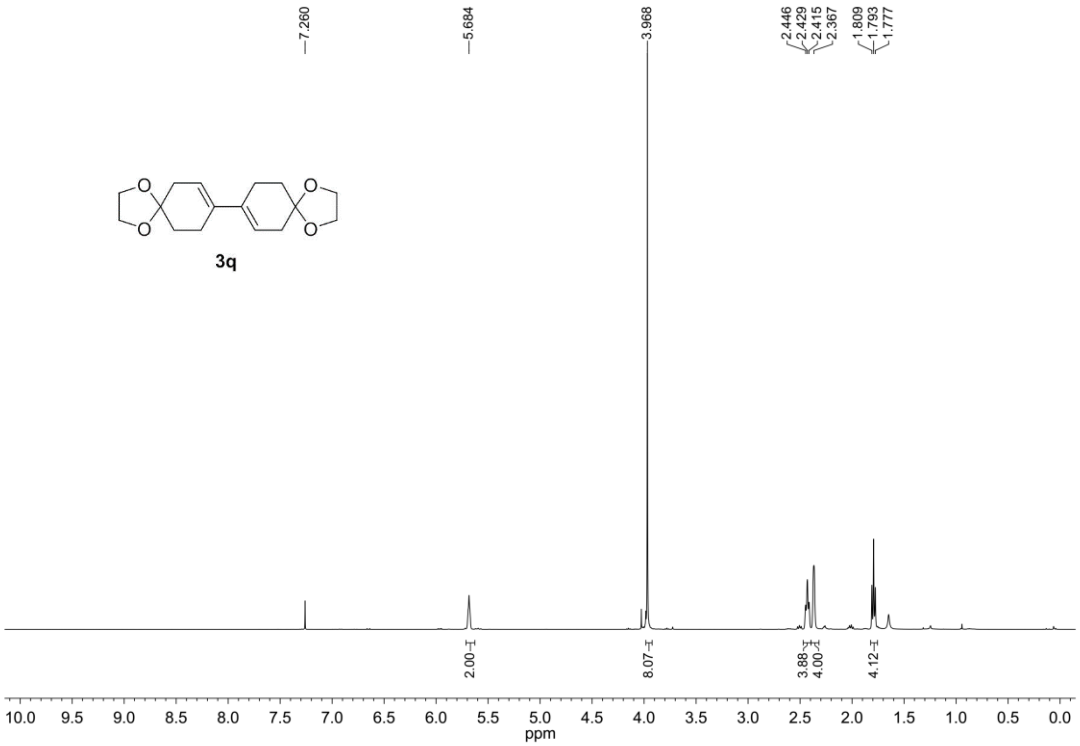


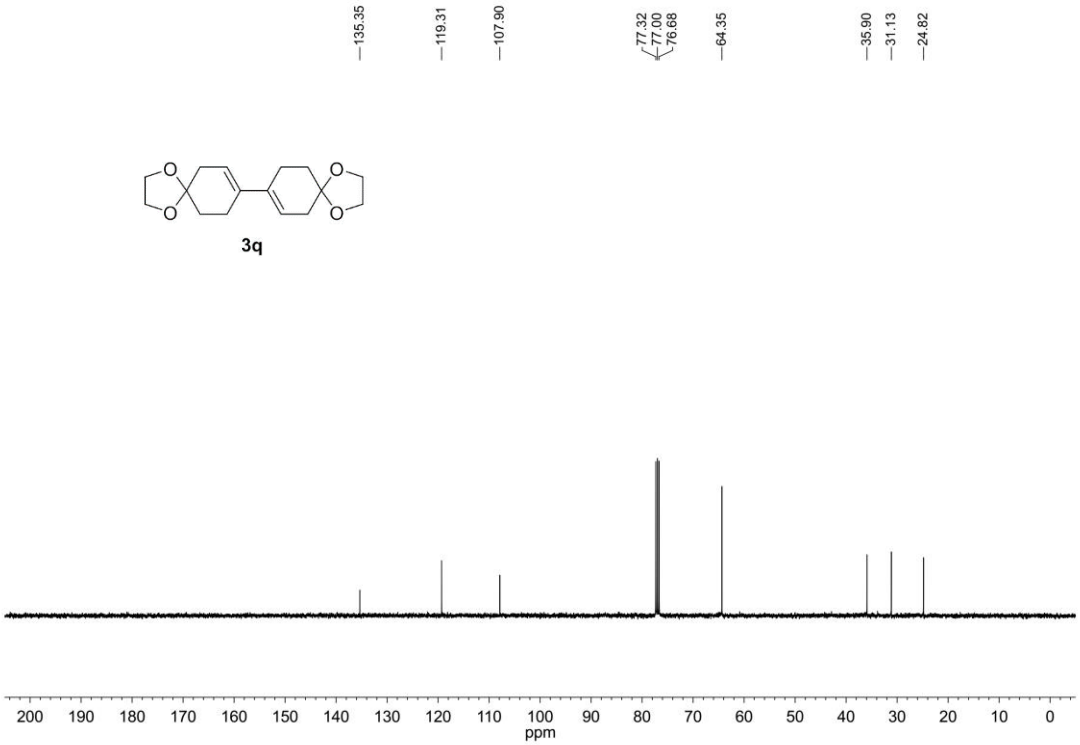
^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **3p**



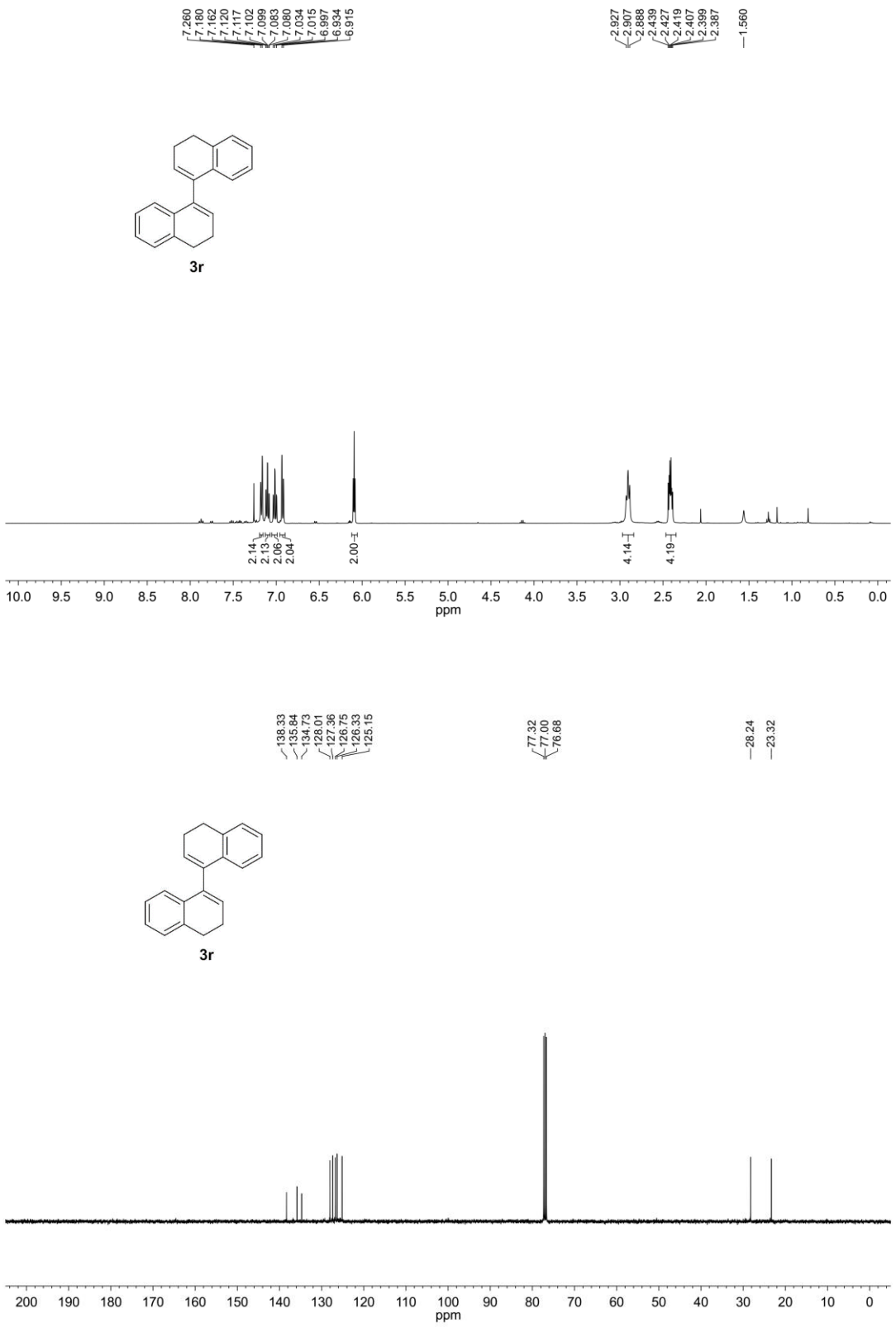


^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **3q**

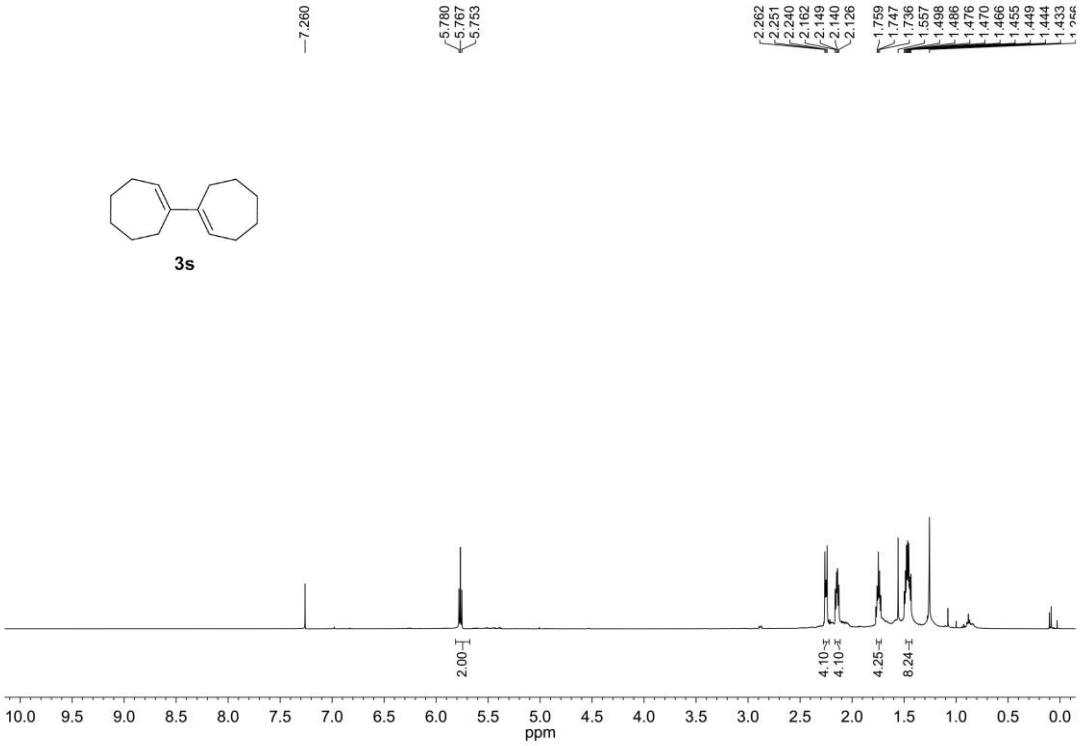


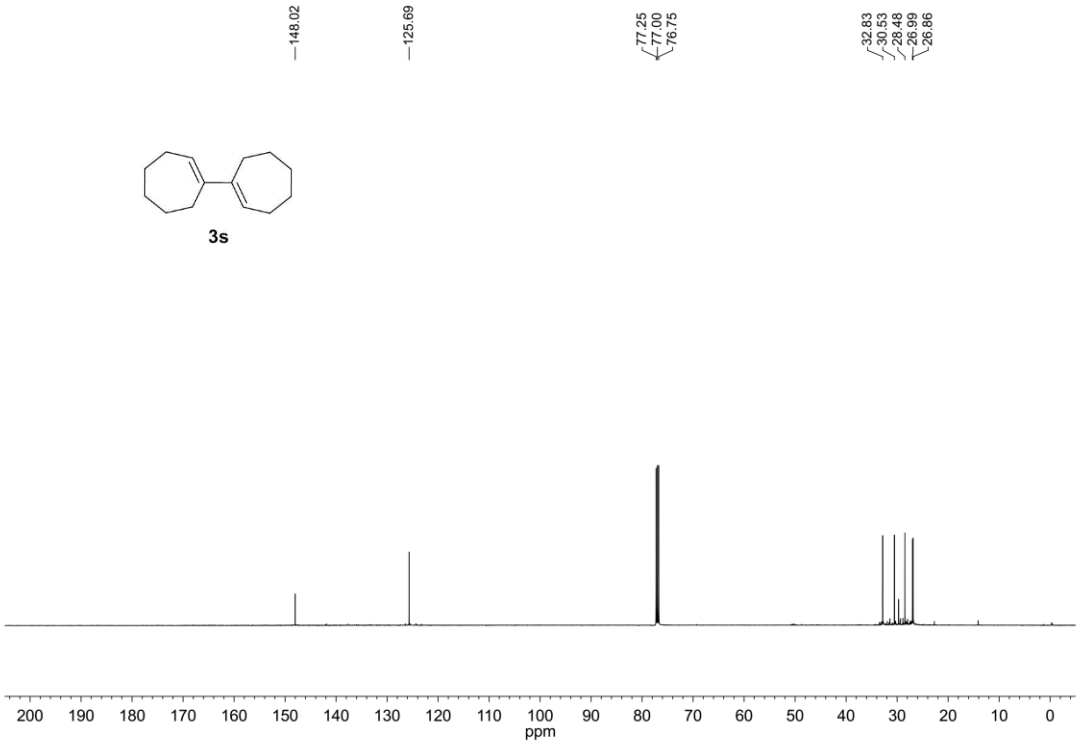


^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **3r**

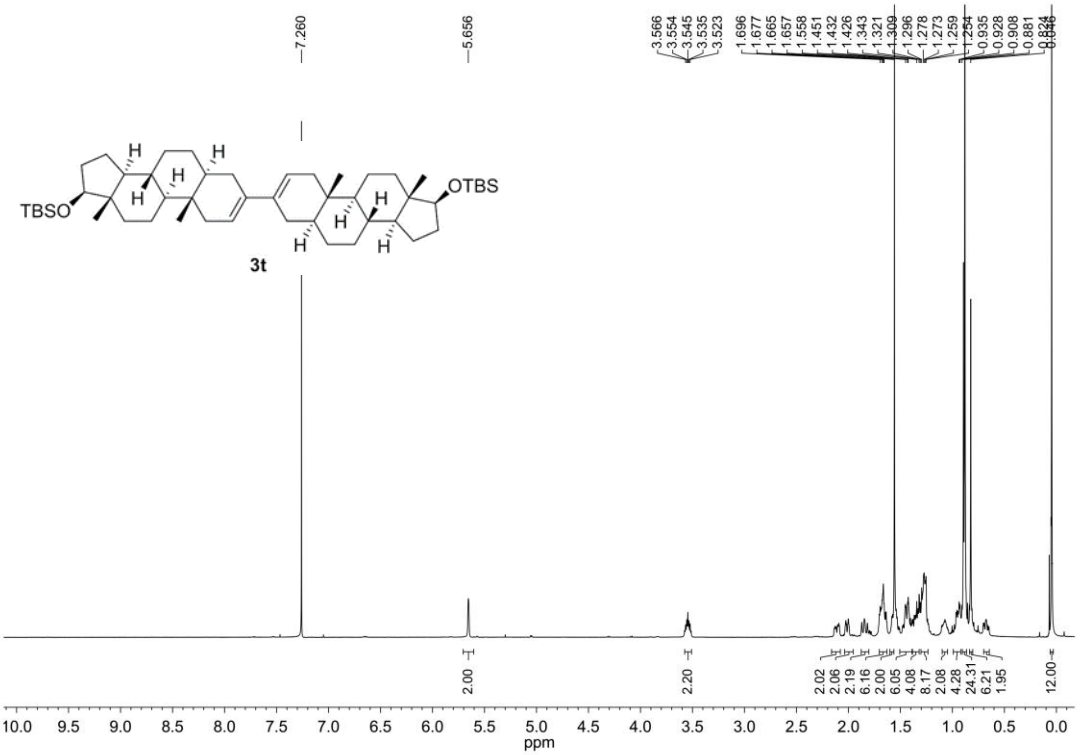


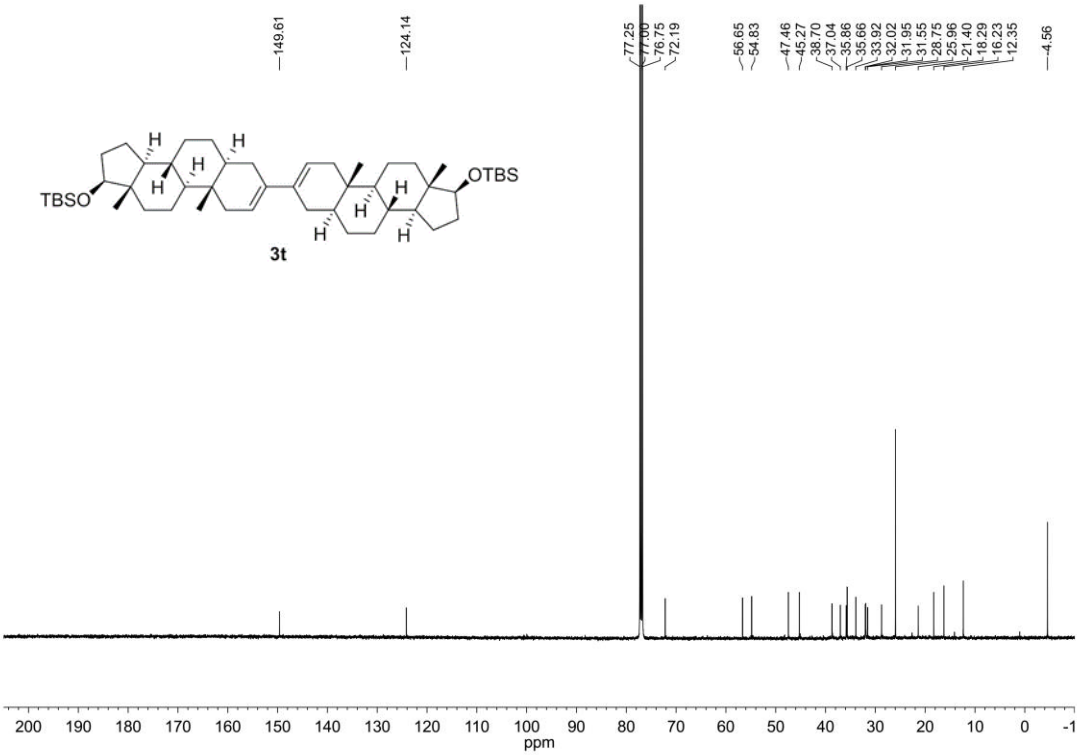
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **3s**



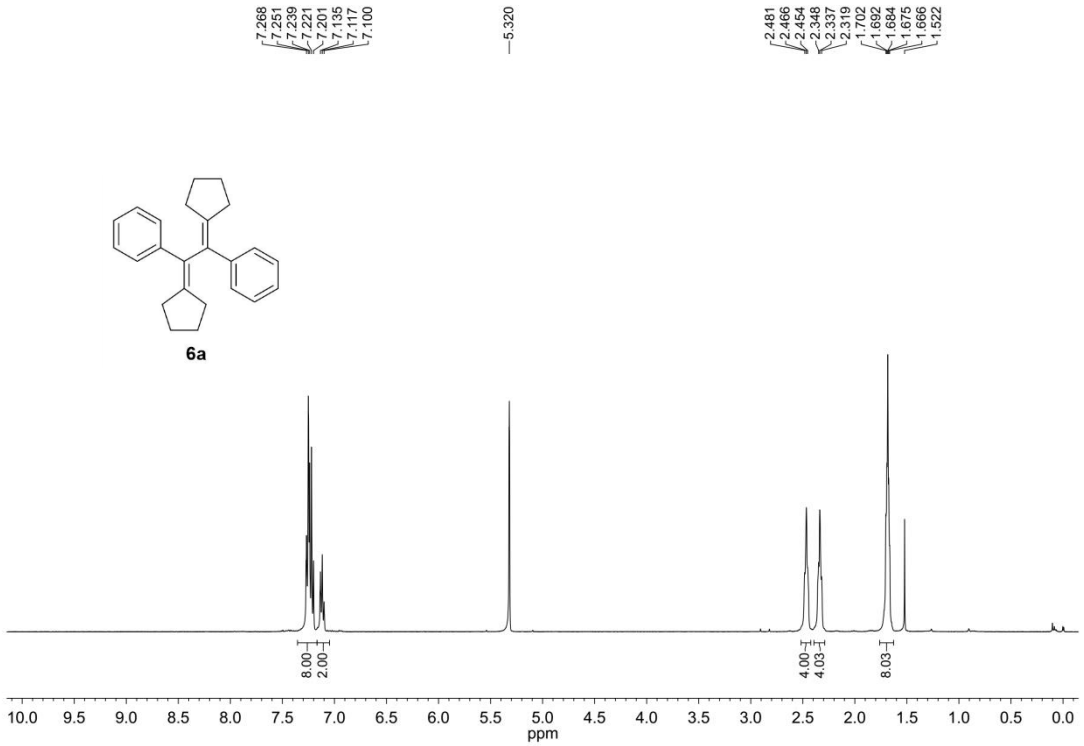


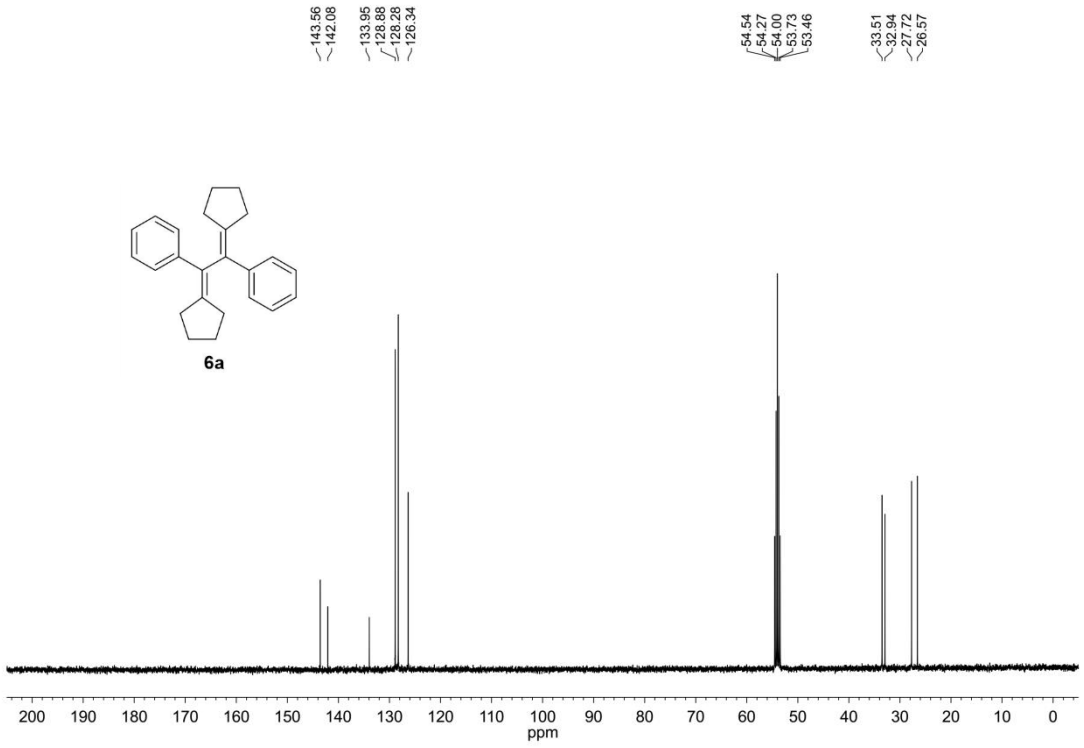
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **3t**



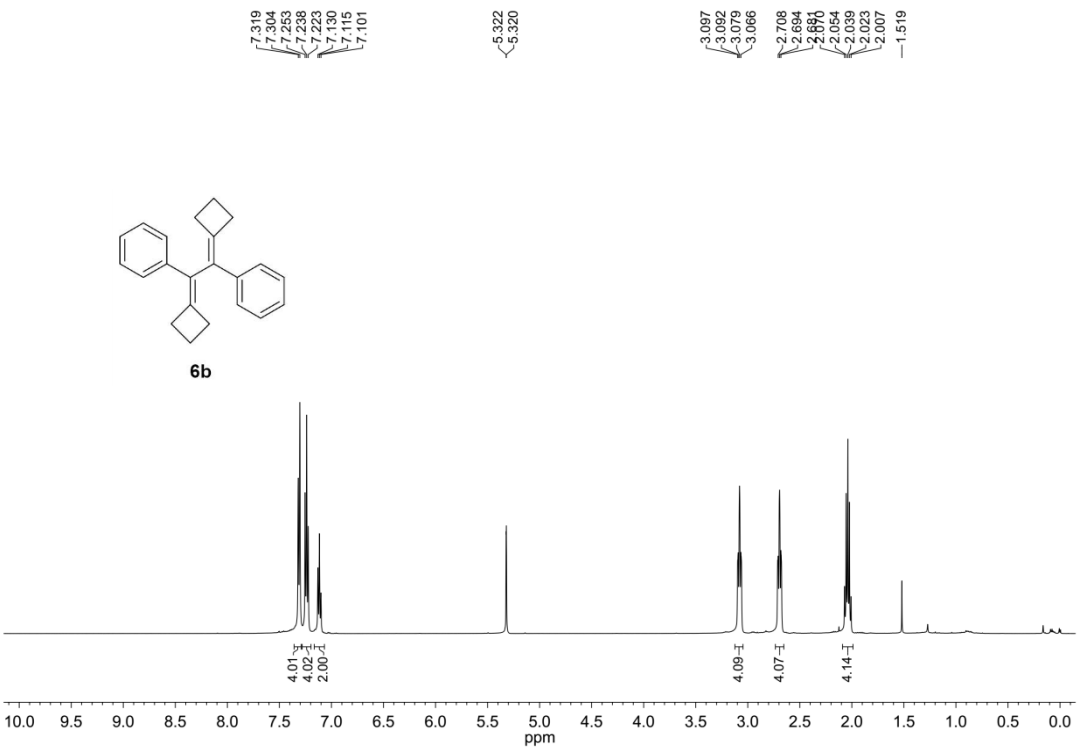


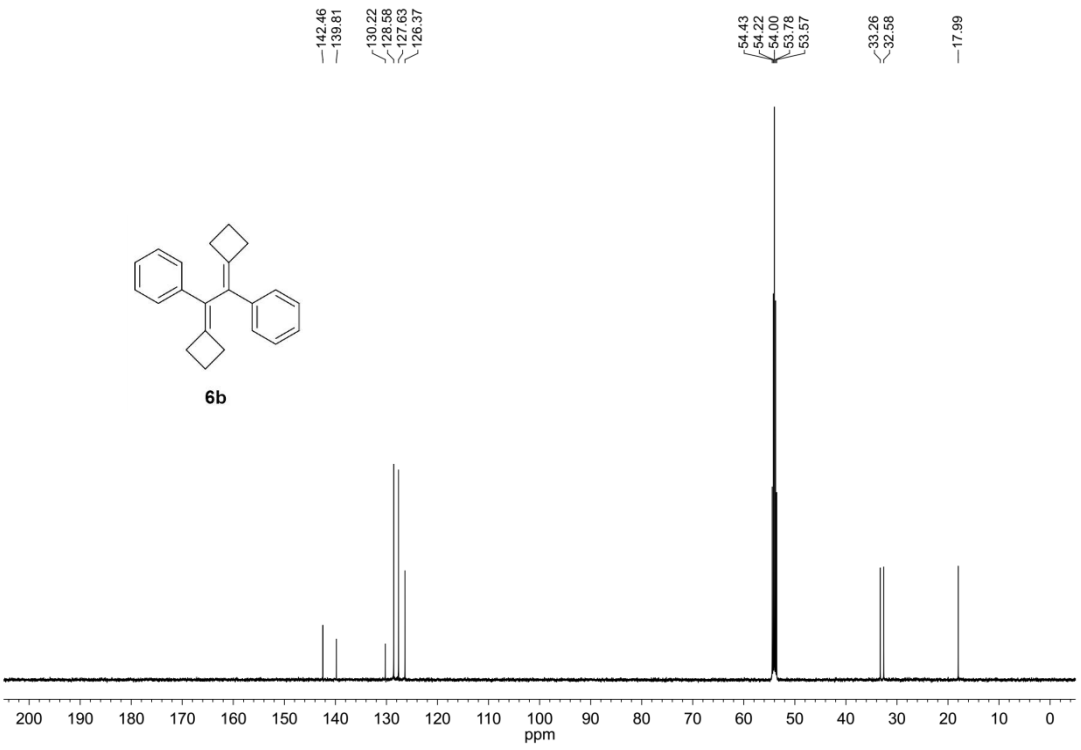
^{1}H NMR (400 MHz, CD_2Cl_2) and **^{13}C NMR** (101 MHz, CD_2Cl_2) Spectra of Compound **6a**



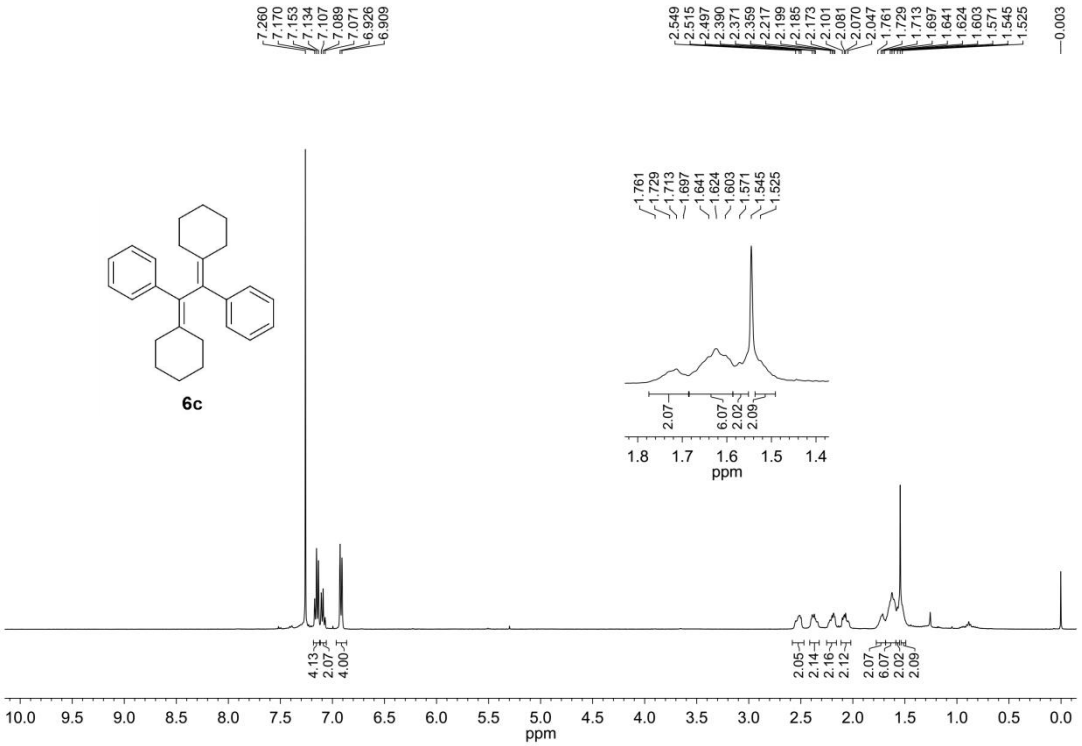


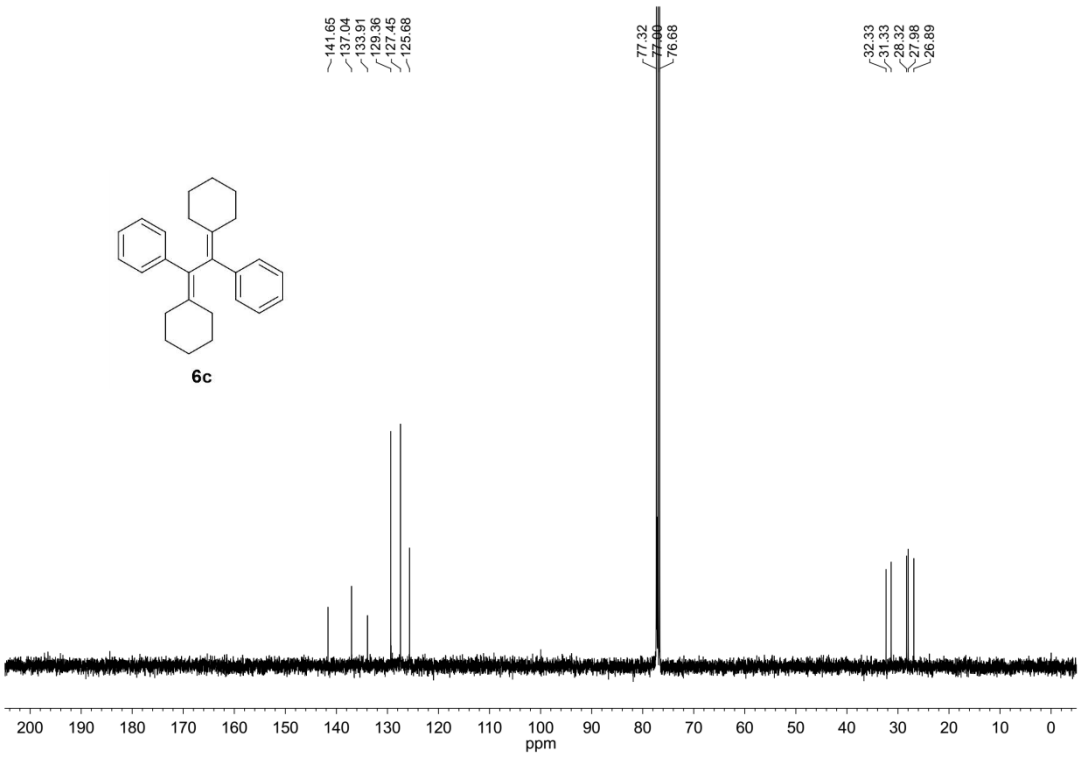
^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **6b**



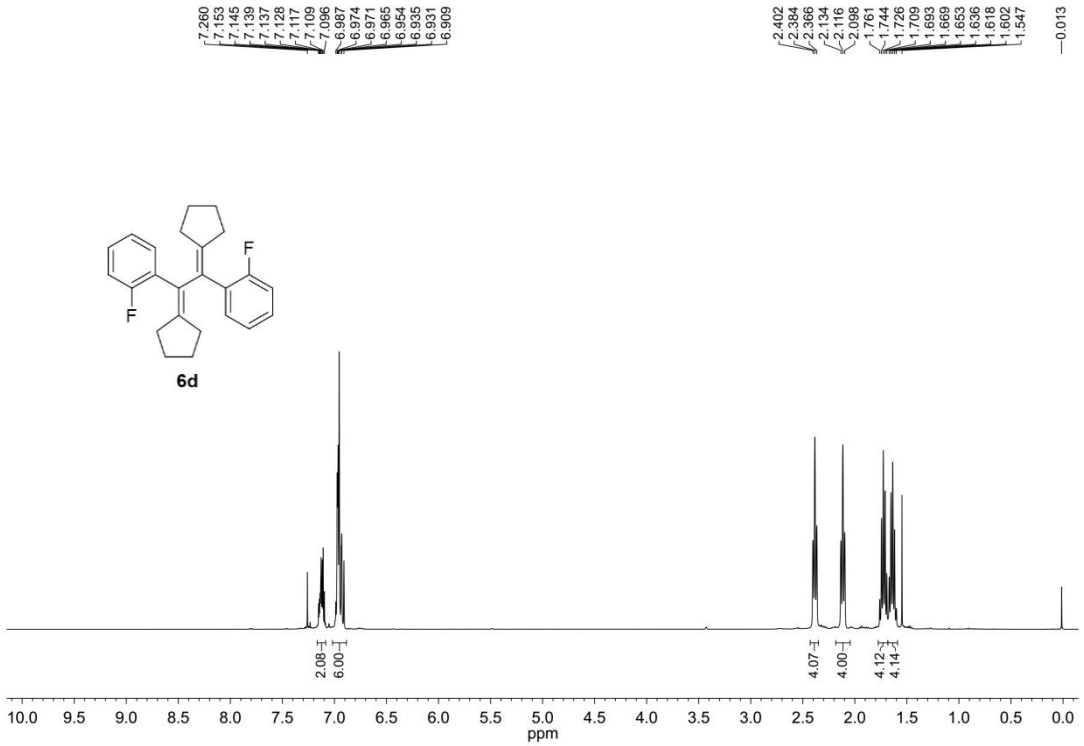


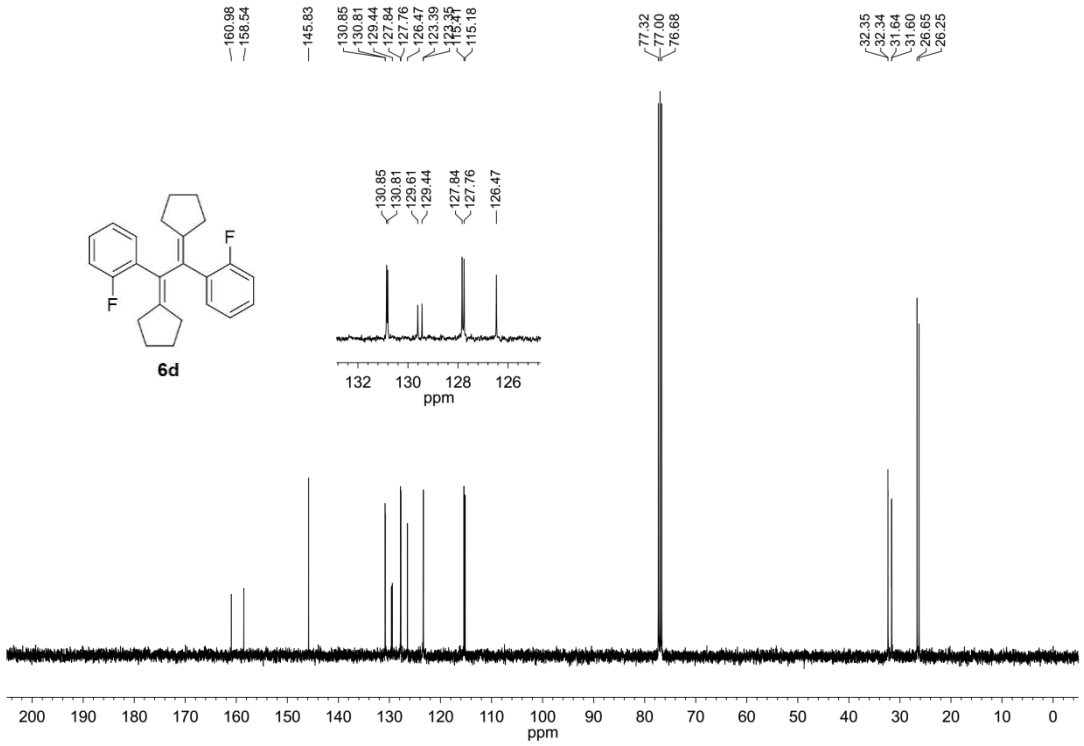
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **6c**



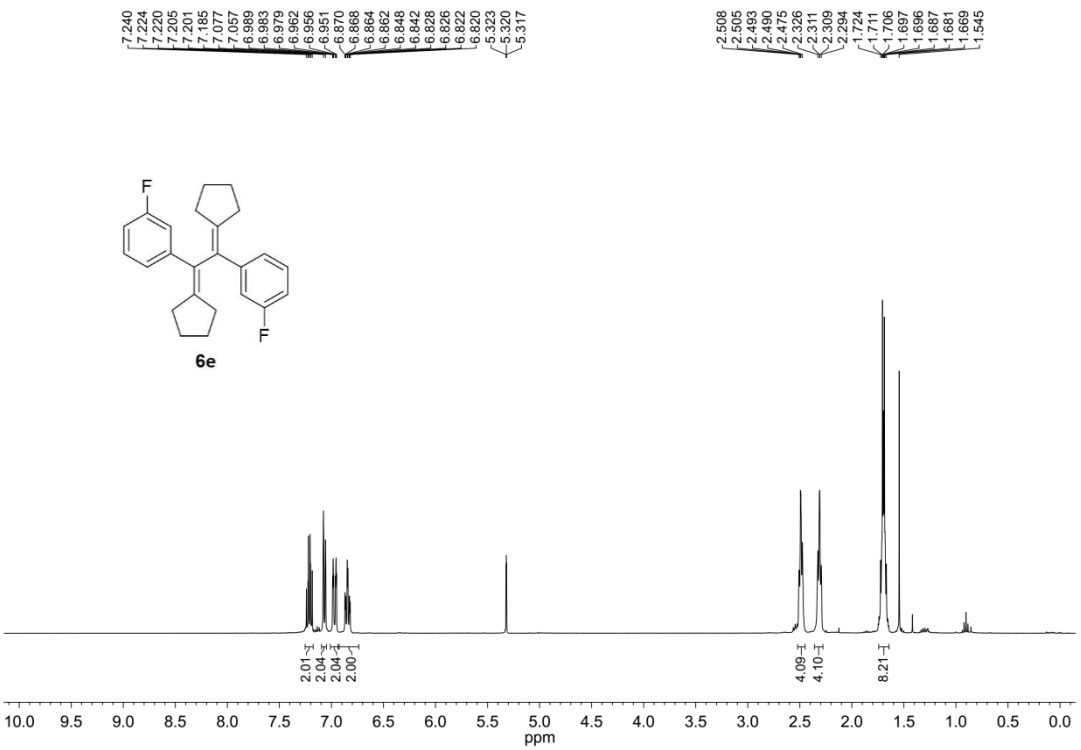


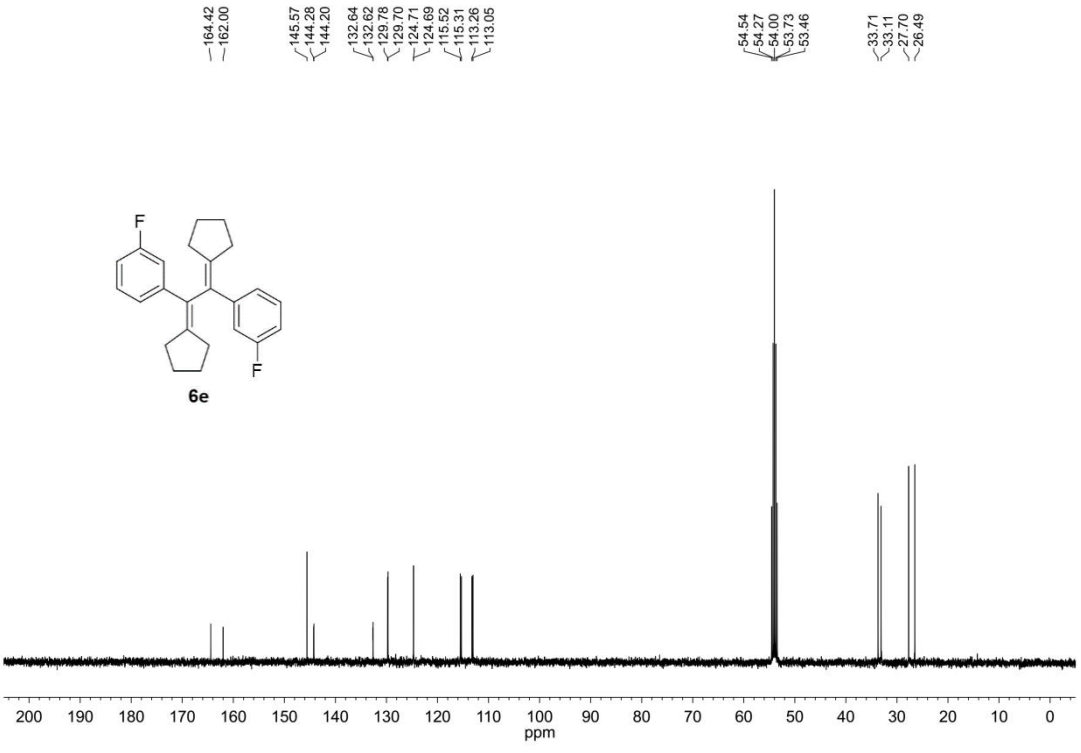
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **6d**



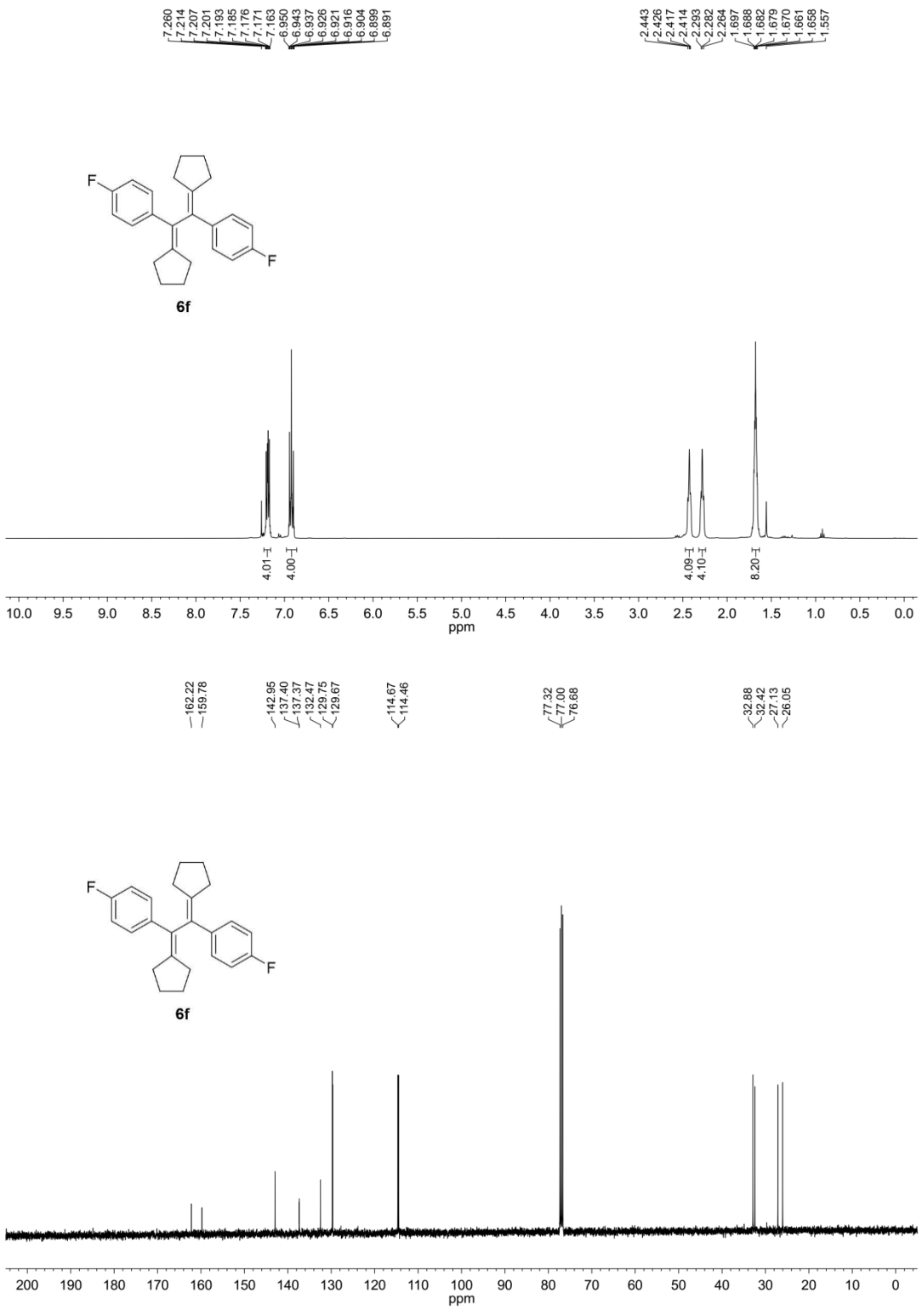


^{1}H NMR (400 MHz, CD_2Cl_2) and **^{13}C NMR** (101 MHz, CD_2Cl_2) Spectra of Compound **6e**

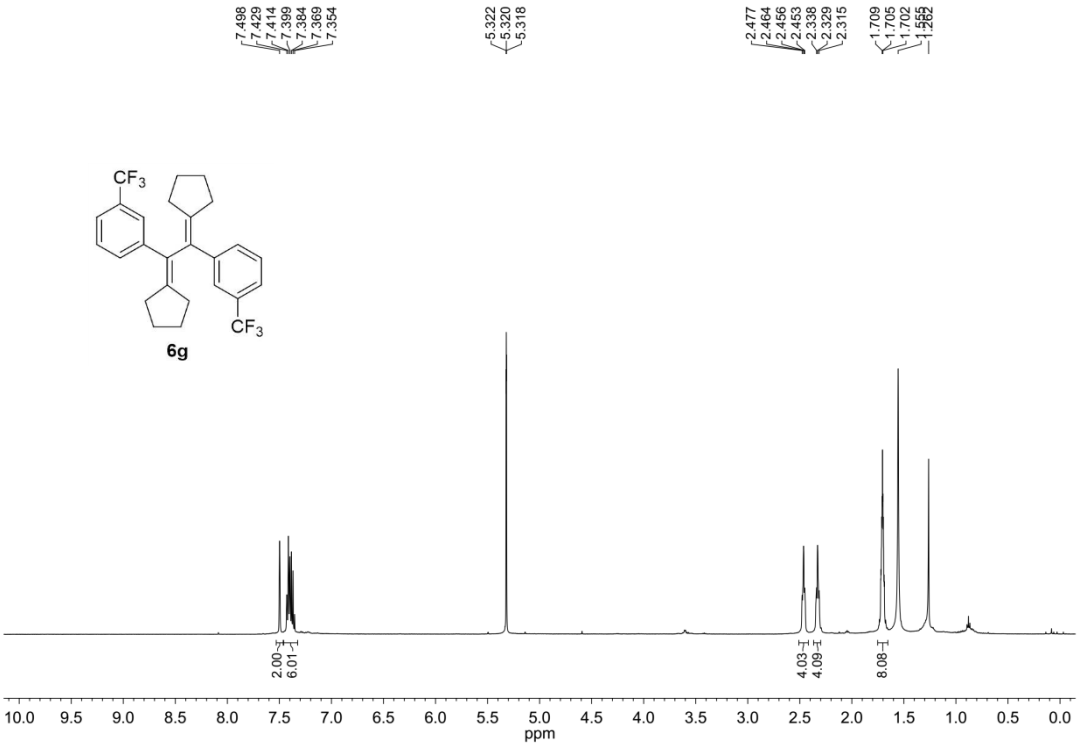


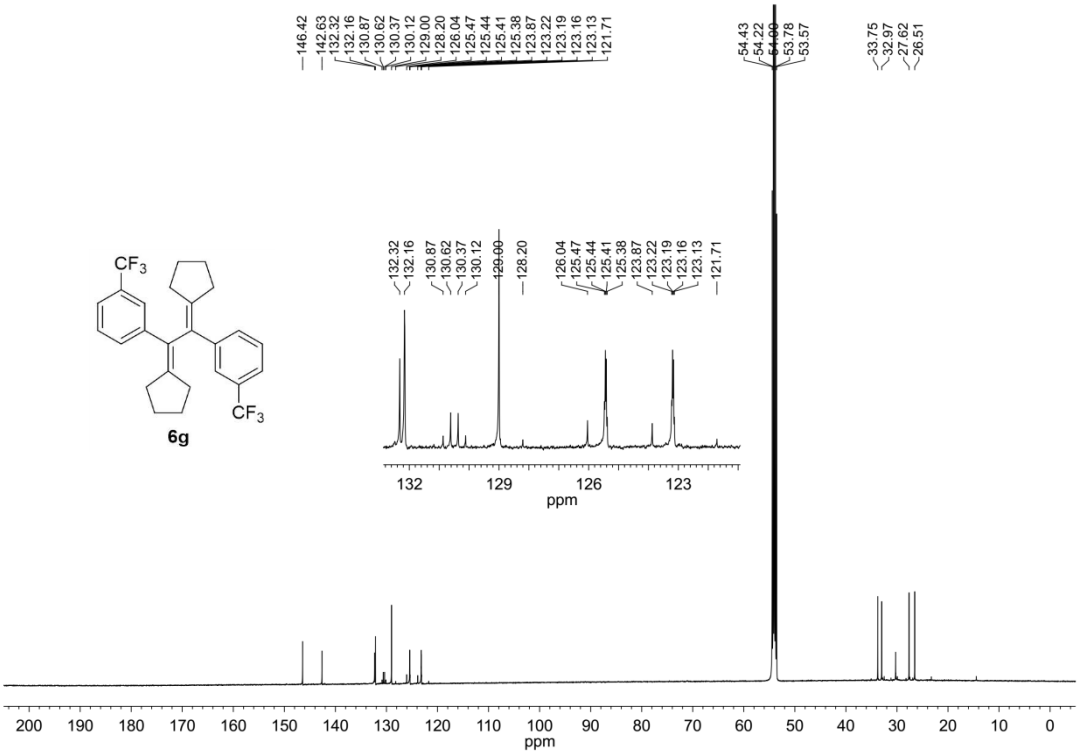


^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **6f**

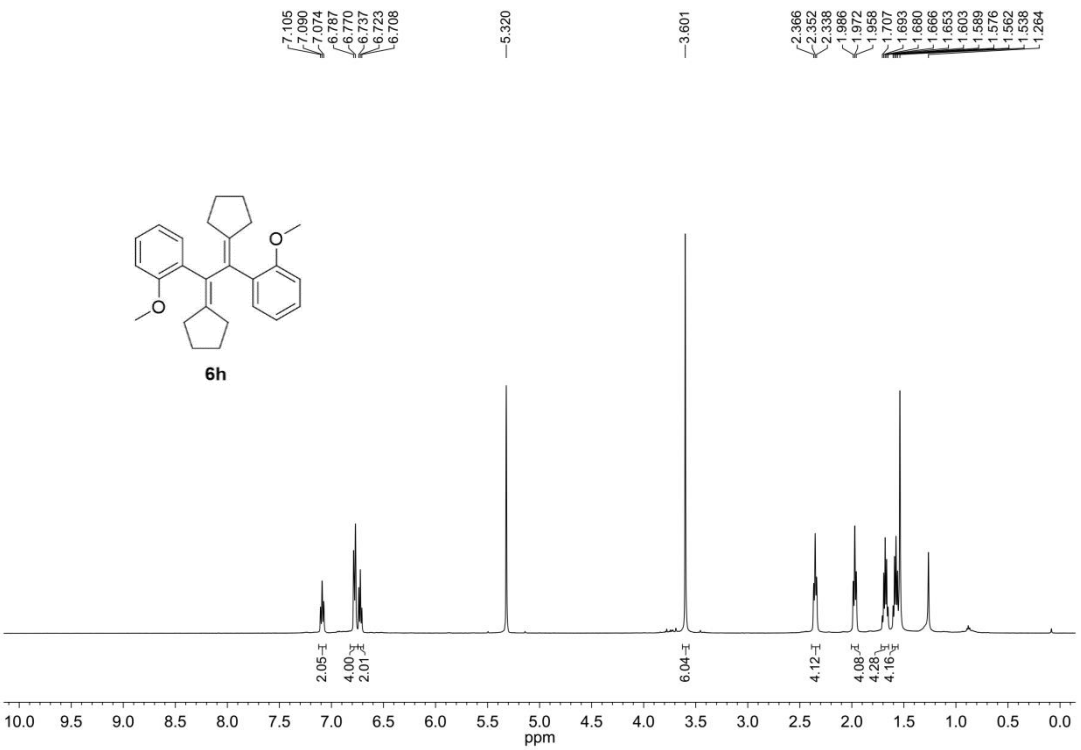


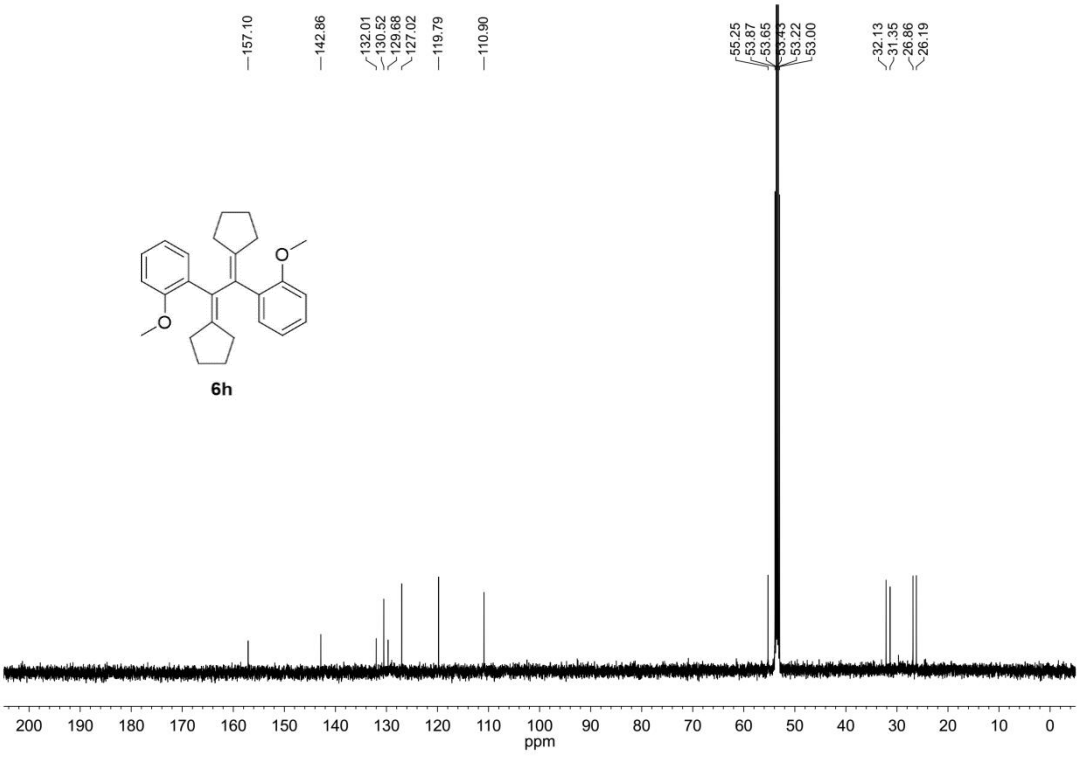
^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **6g**



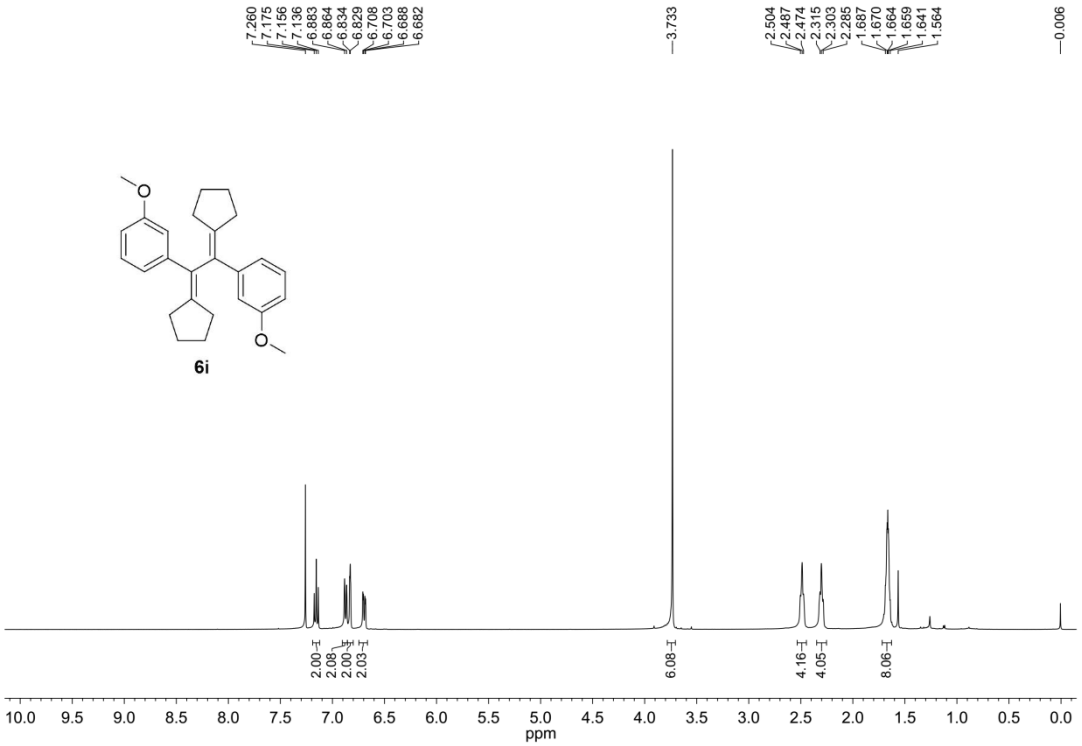


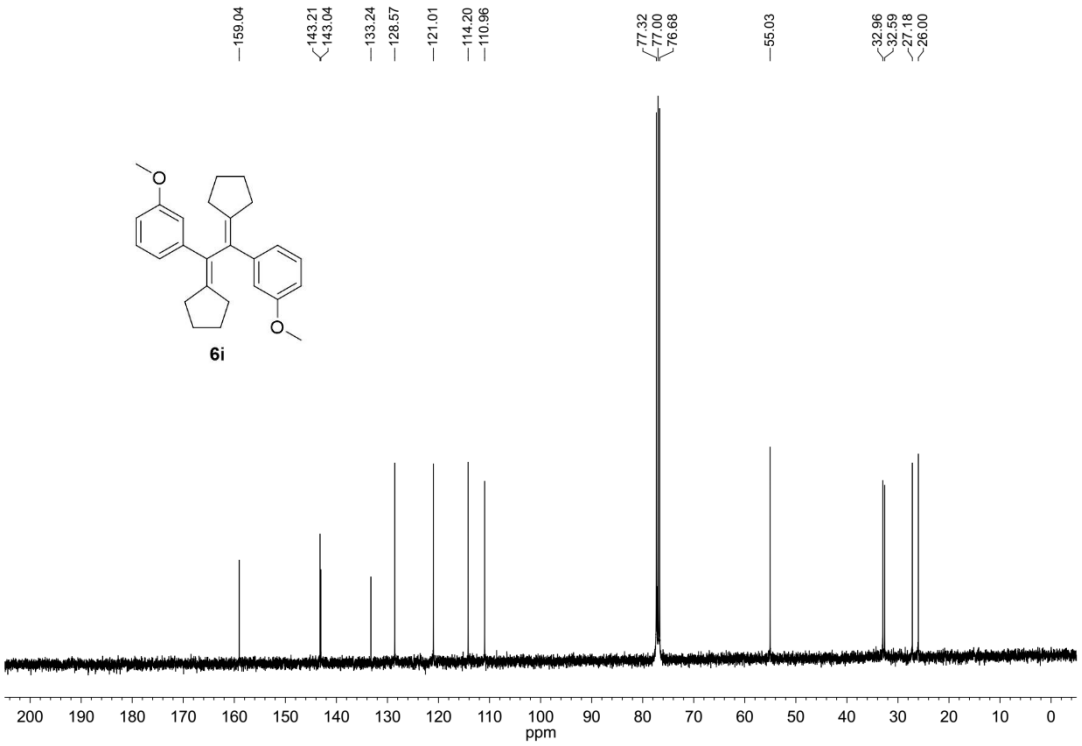
^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **6h**



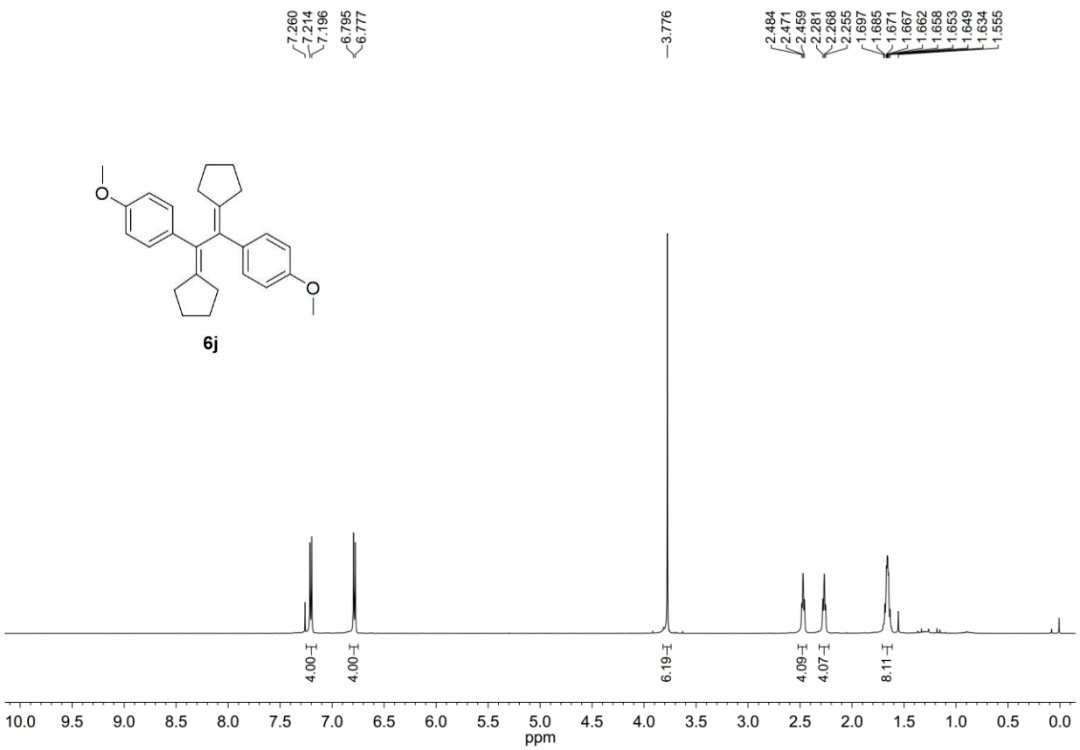


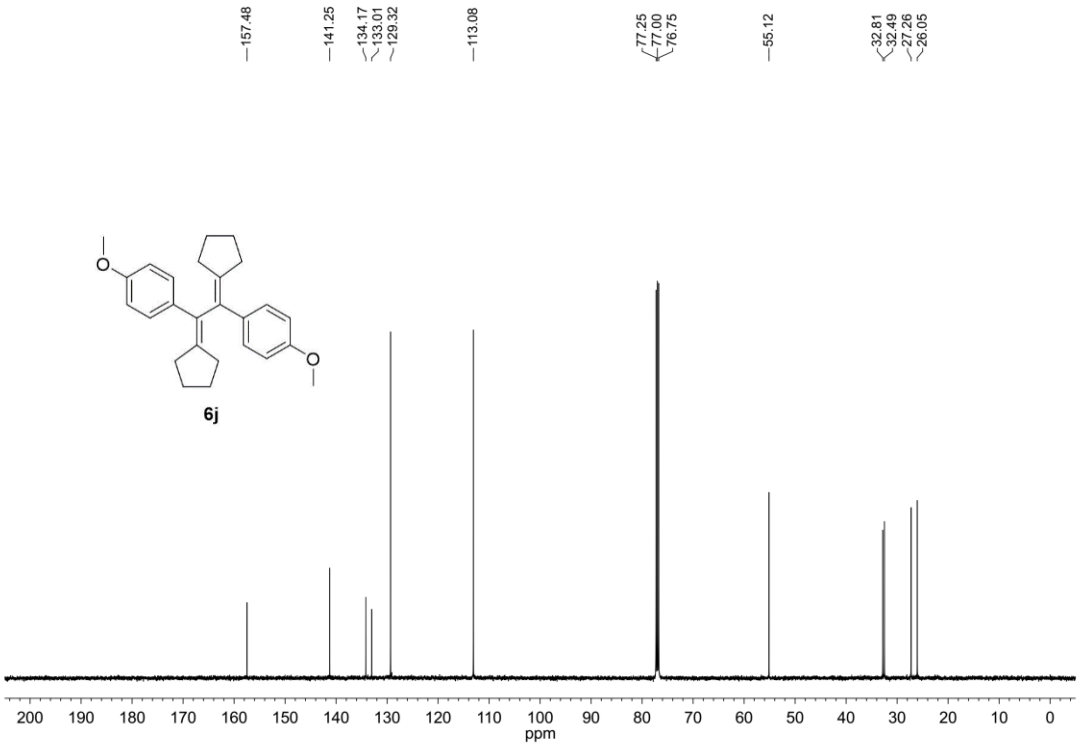
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **6i**



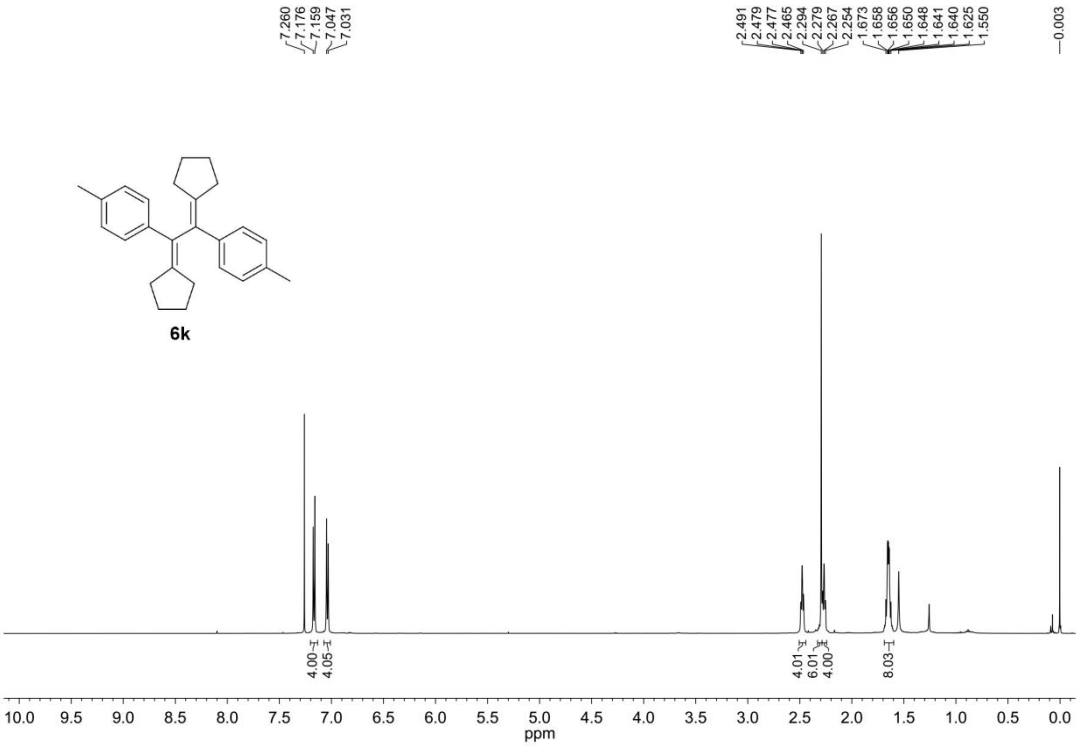


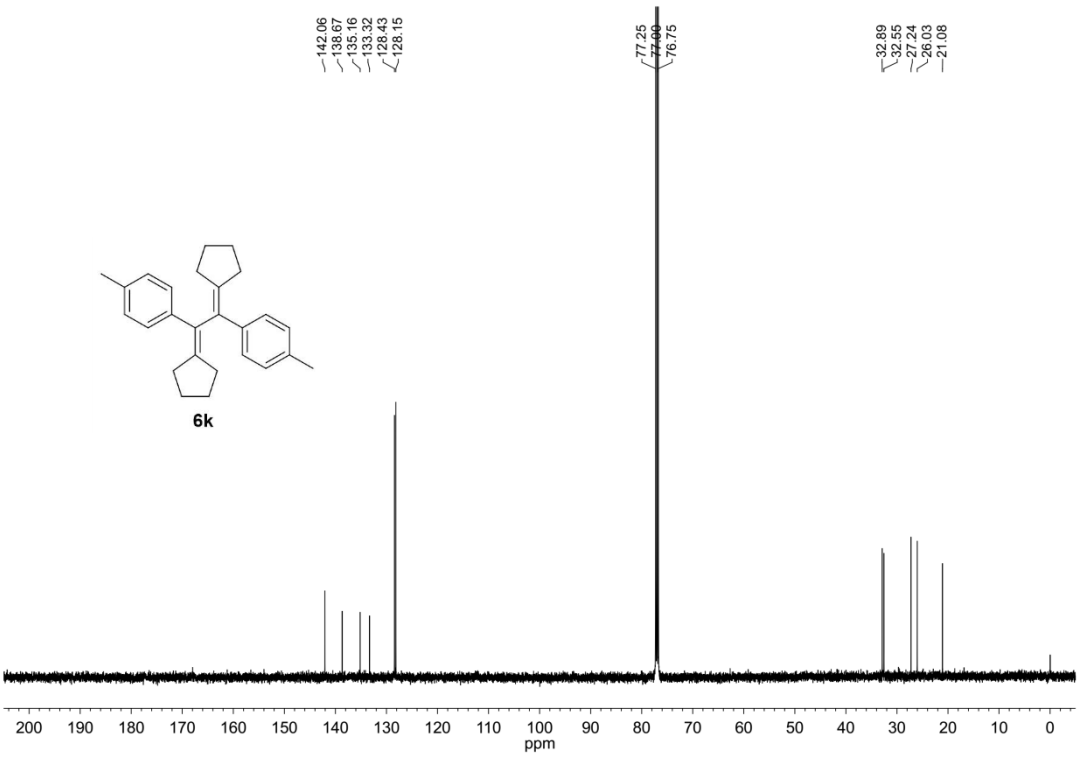
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **6j**



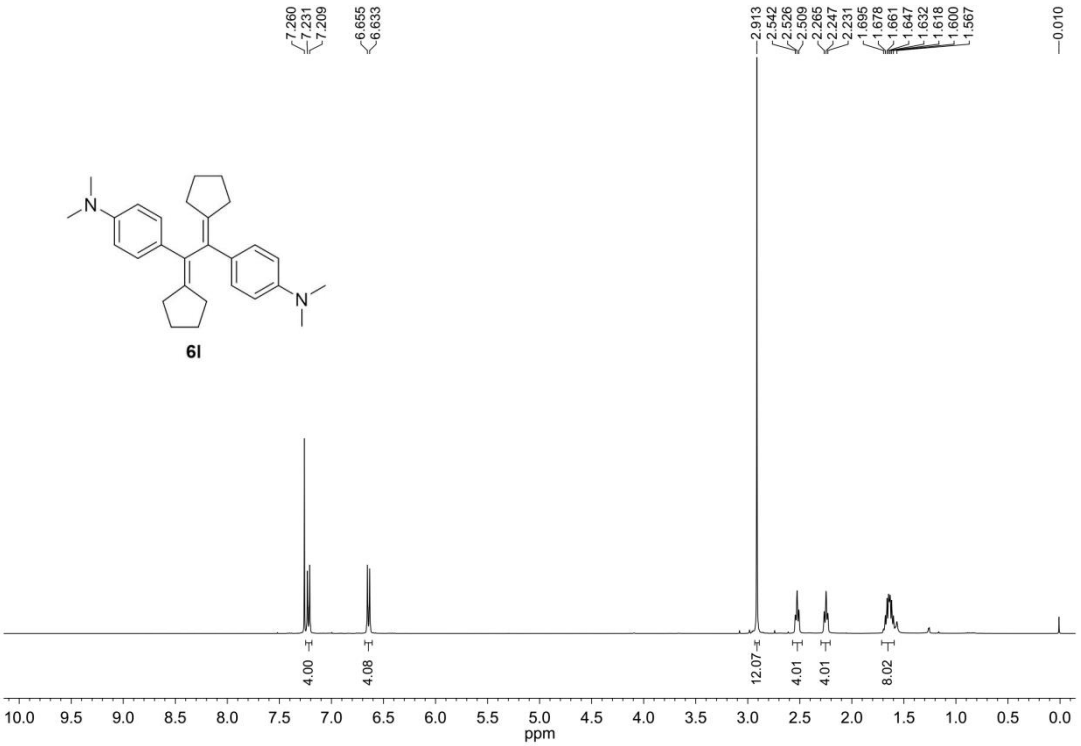


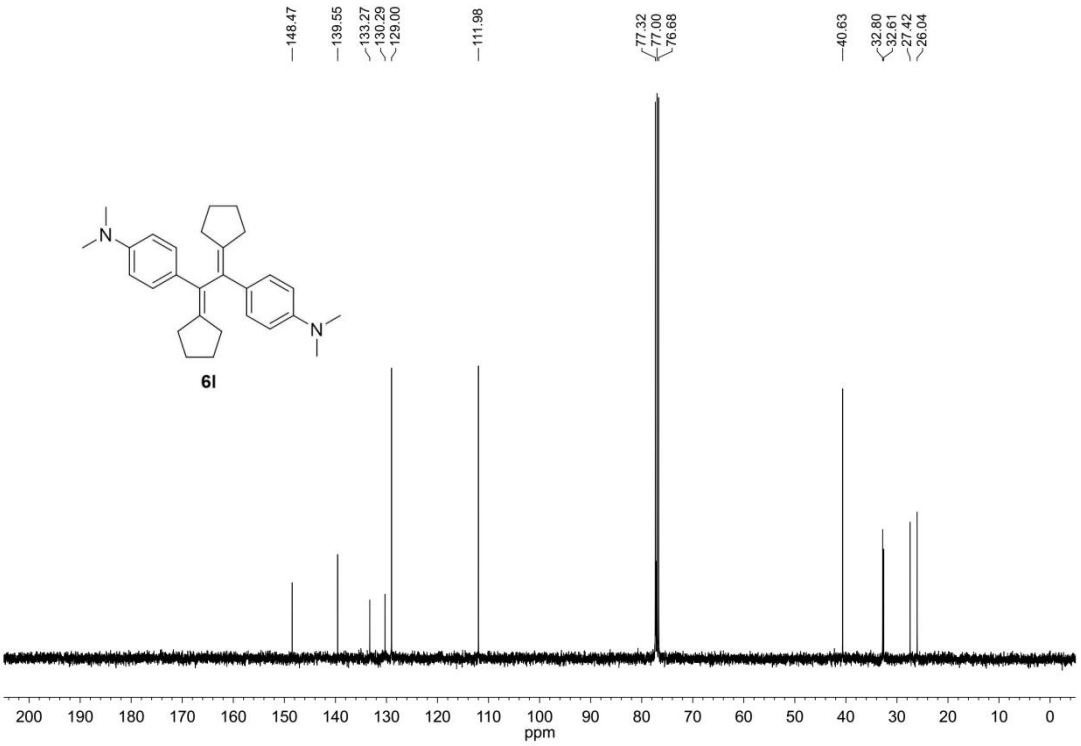
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **6k**



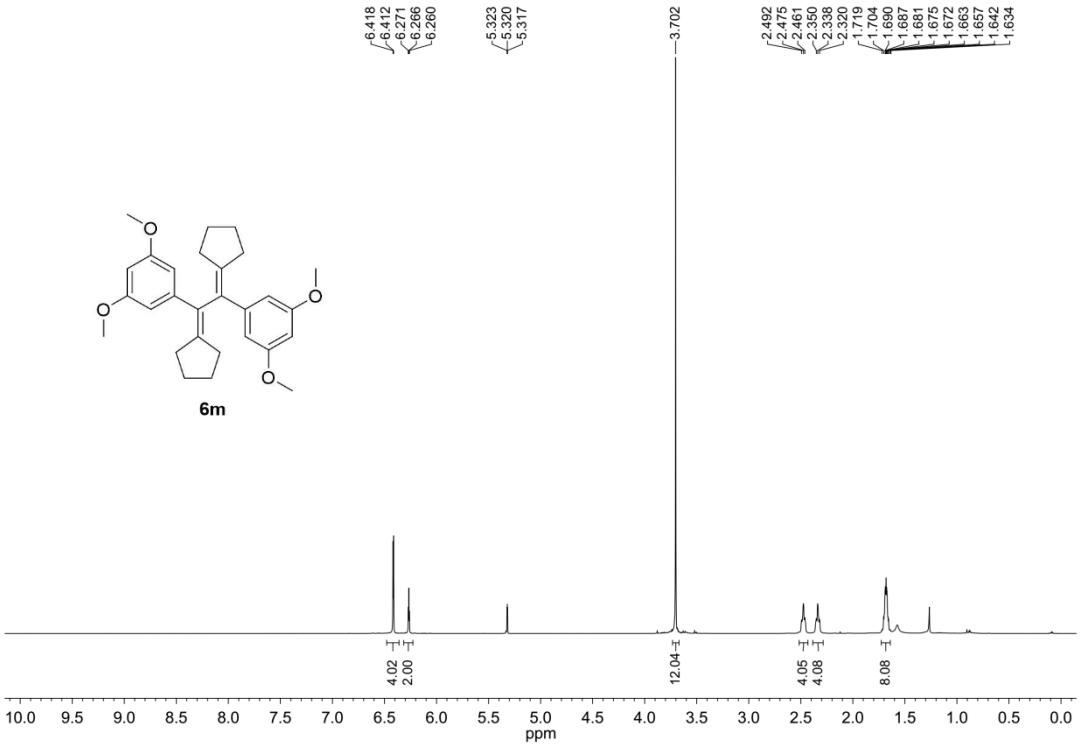


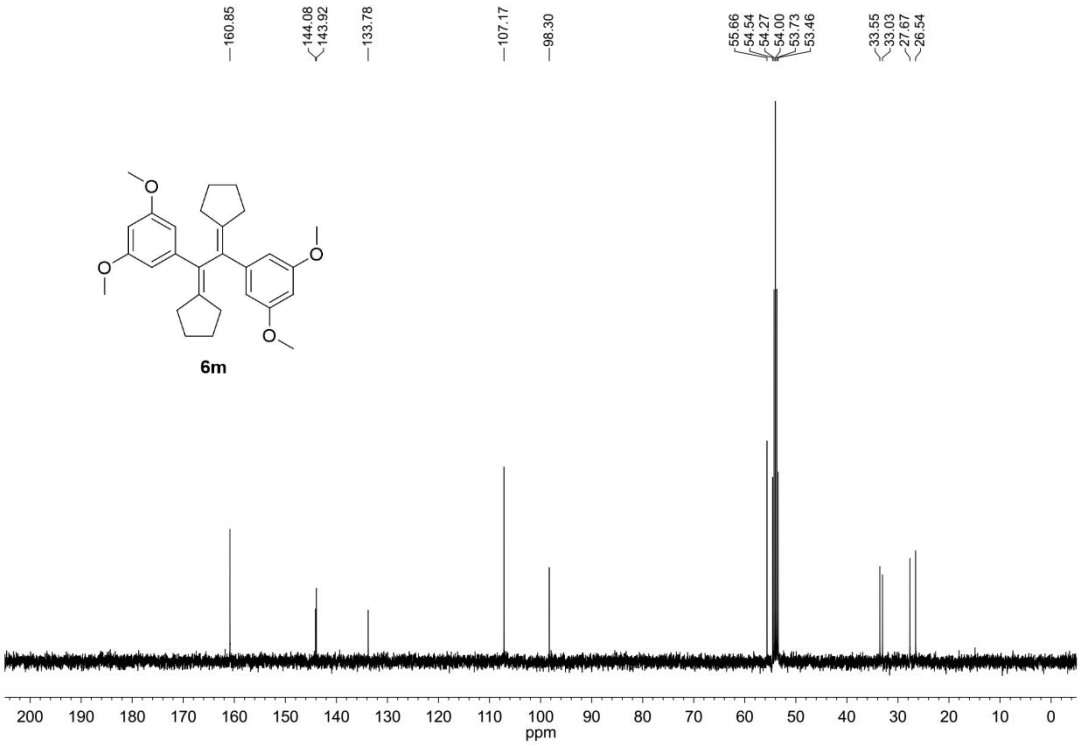
^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **6l**



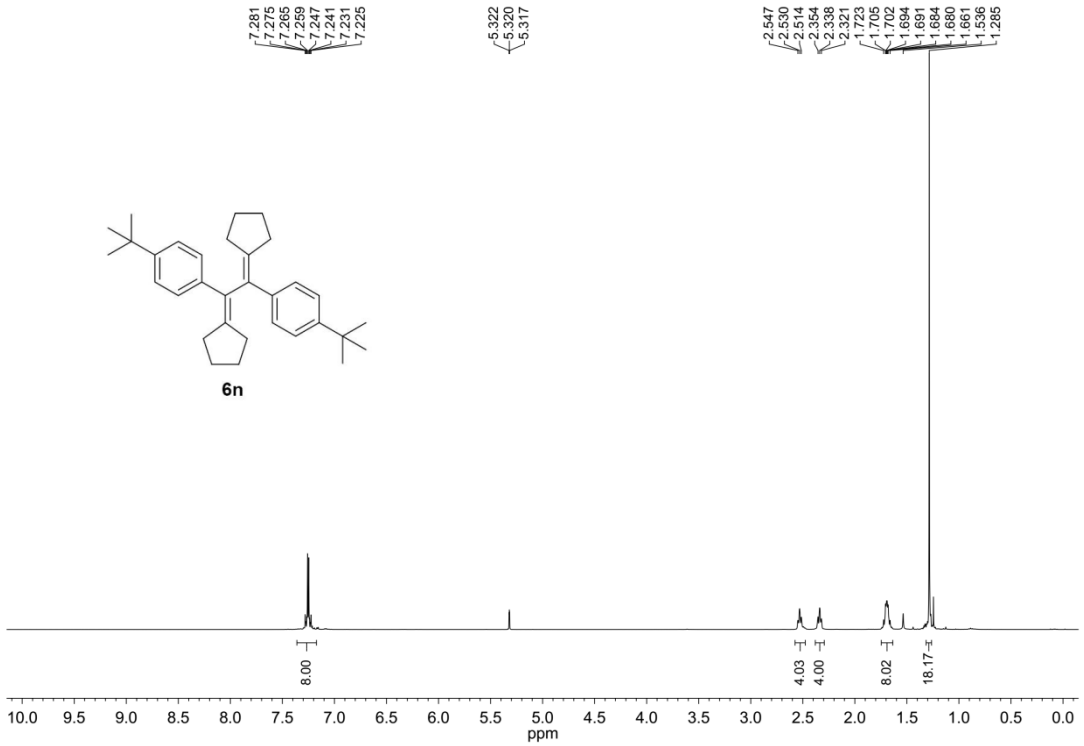


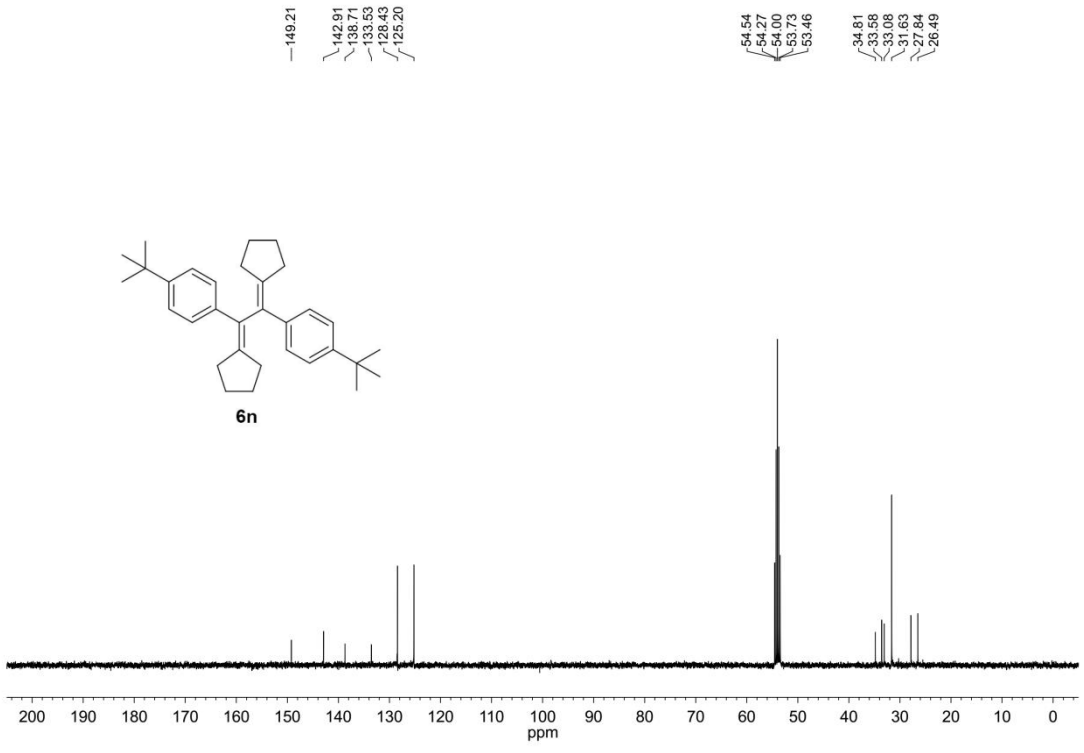
^{1}H NMR (400 MHz, CD_2Cl_2) and **^{13}C NMR** (101 MHz, CD_2Cl_2) Spectra of Compound **6m**



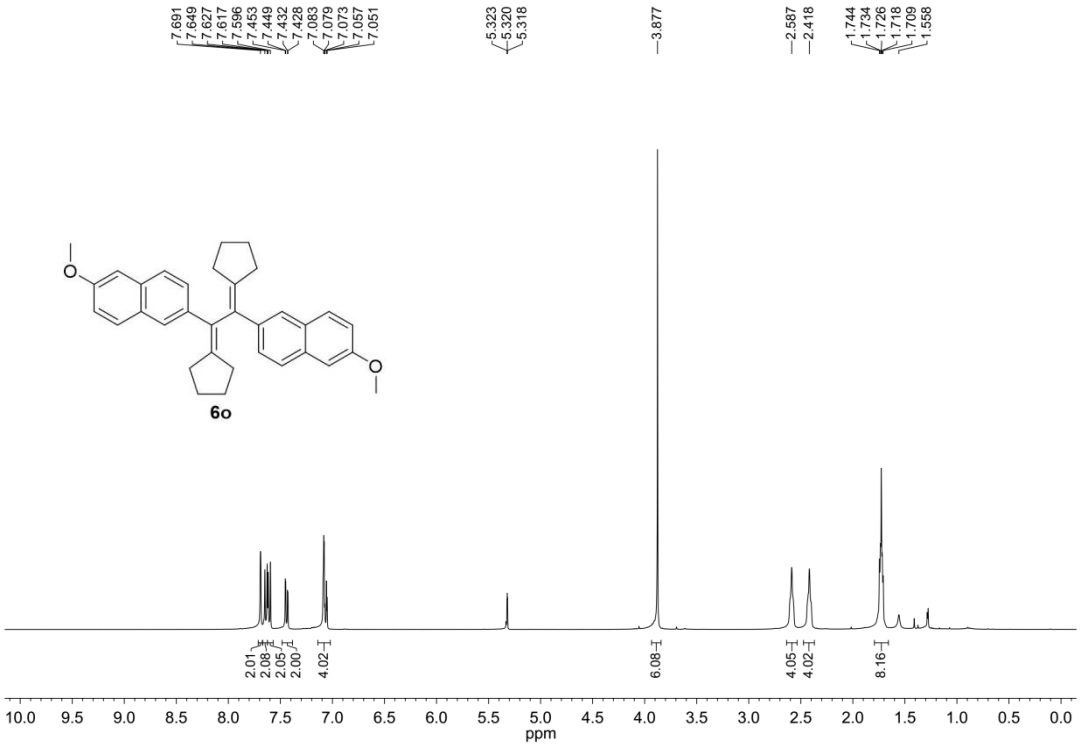


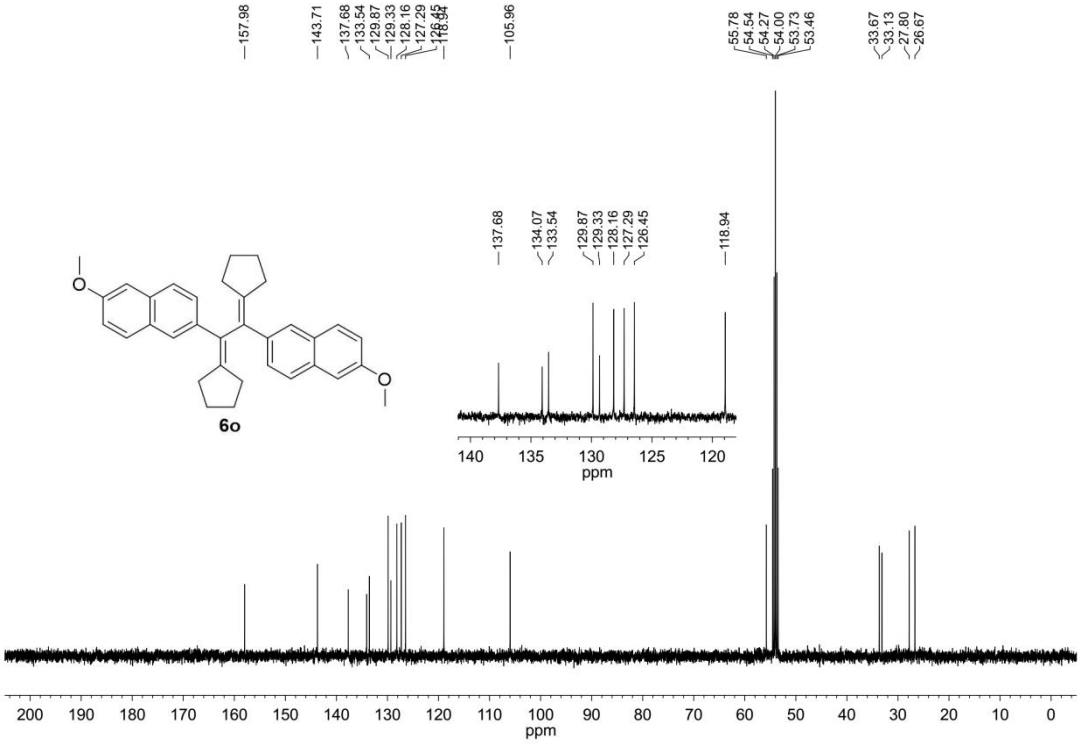
^{1}H NMR (400 MHz, CD_2Cl_2) and **^{13}C NMR** (101 MHz, CD_2Cl_2) Spectra of Compound **6n**



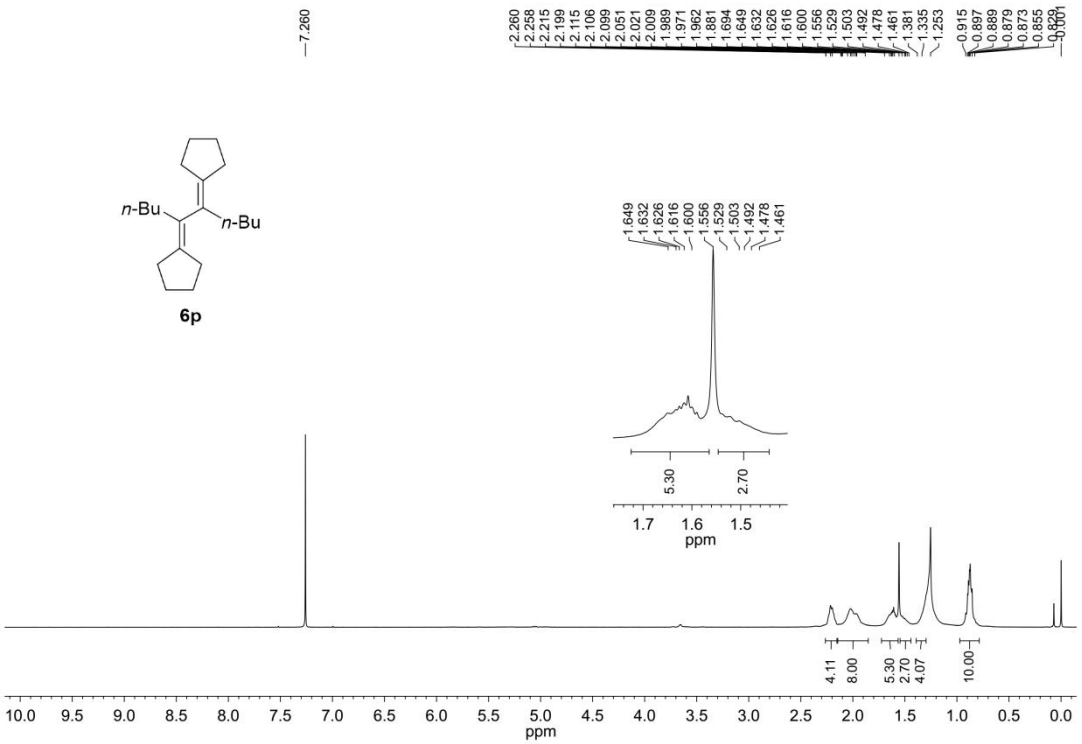


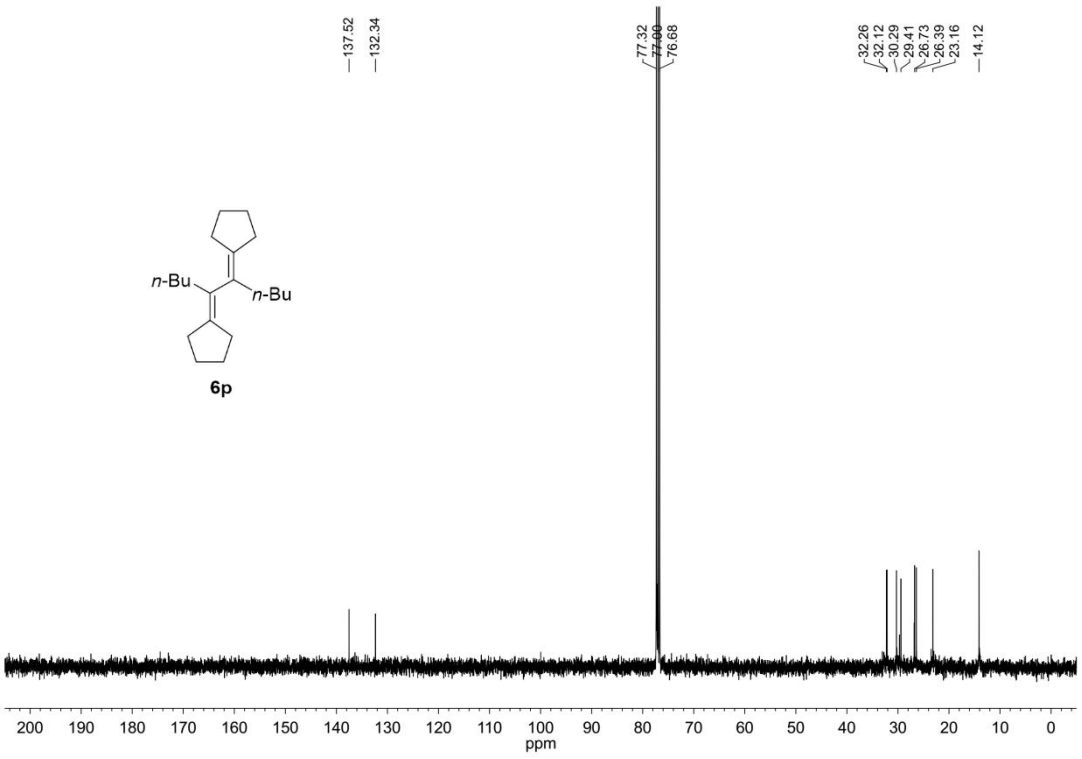
^{1}H NMR (400 MHz, CD_2Cl_2) and **^{13}C NMR** (101 MHz, CD_2Cl_2) Spectra of Compound **6o**



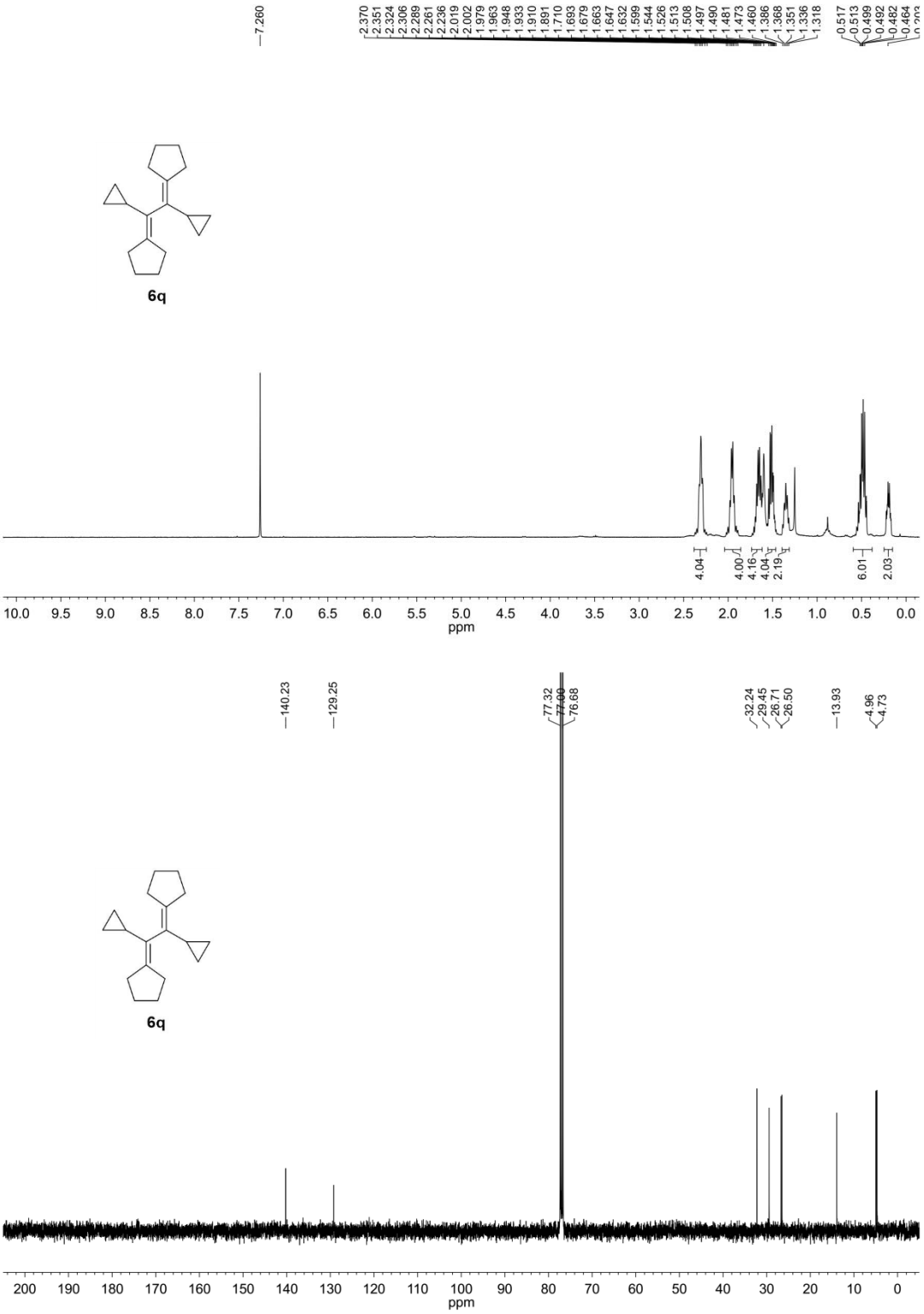


^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **6p**

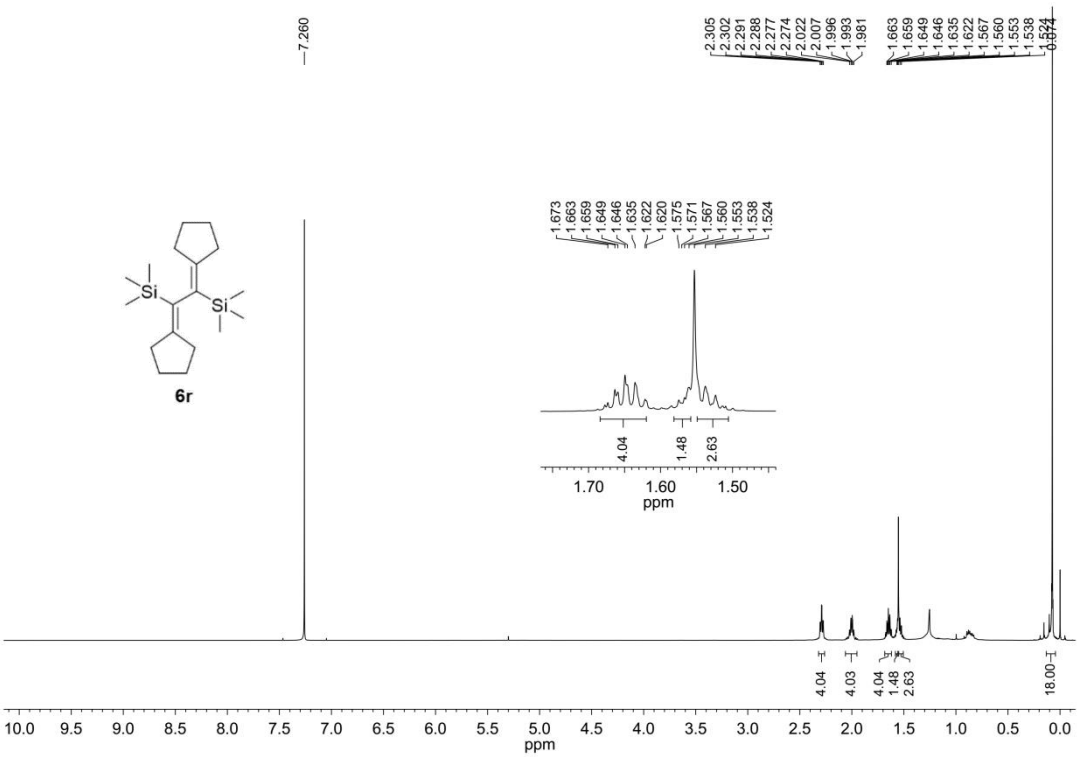


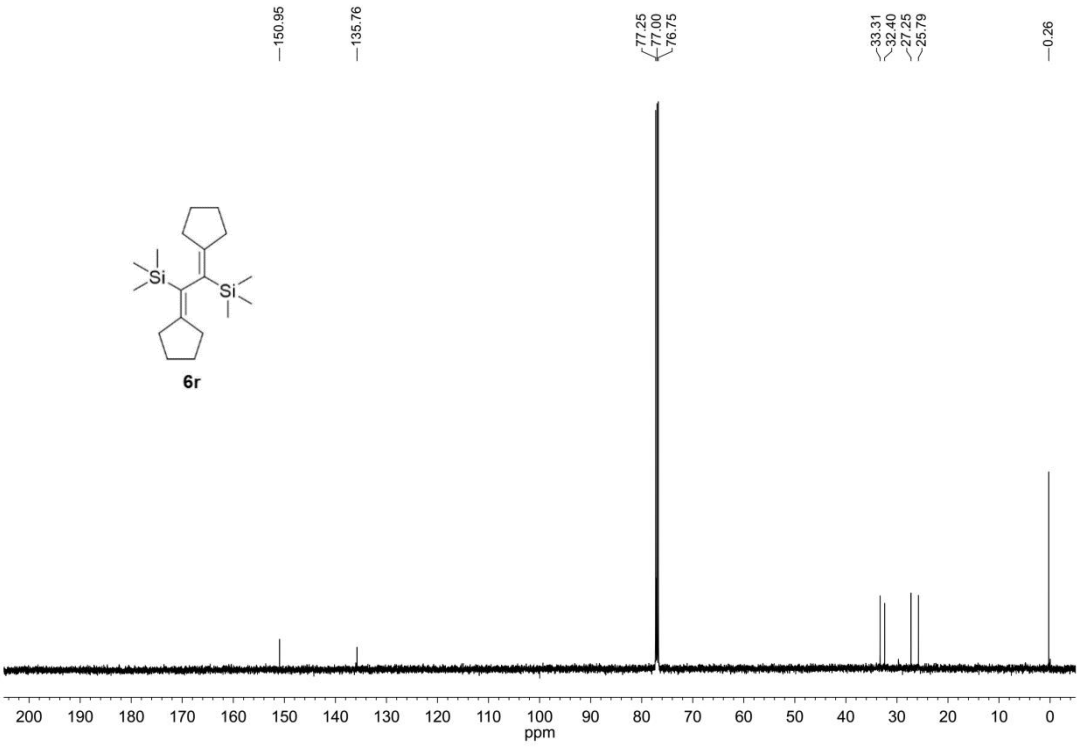


^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **6q**

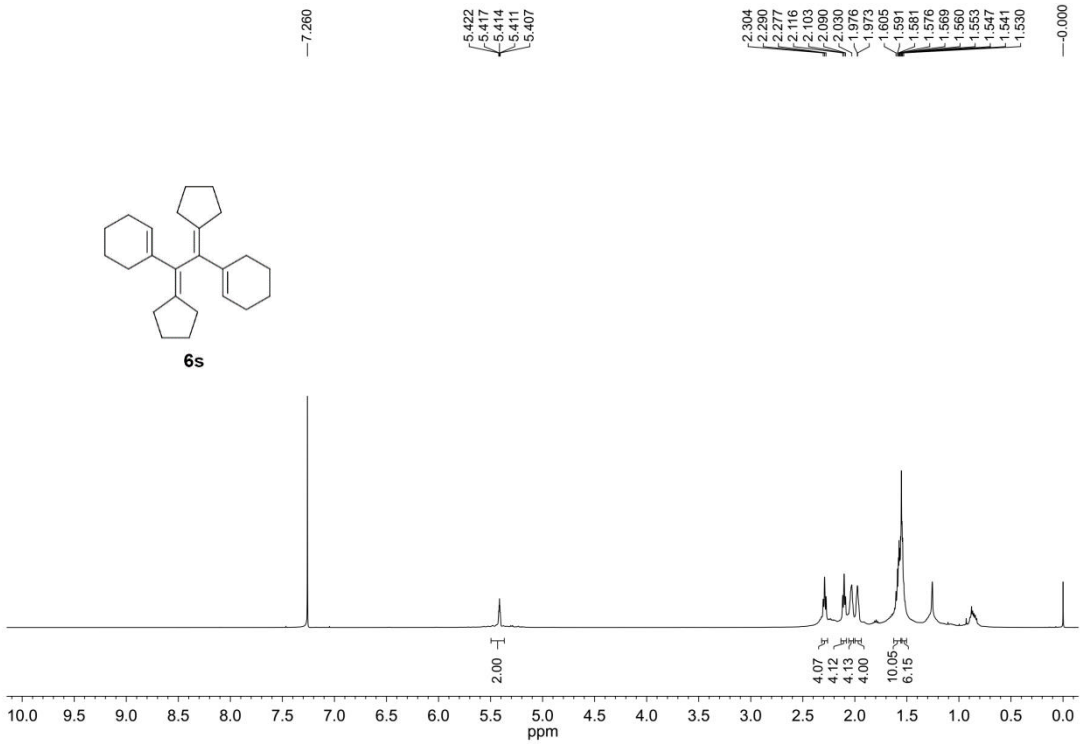


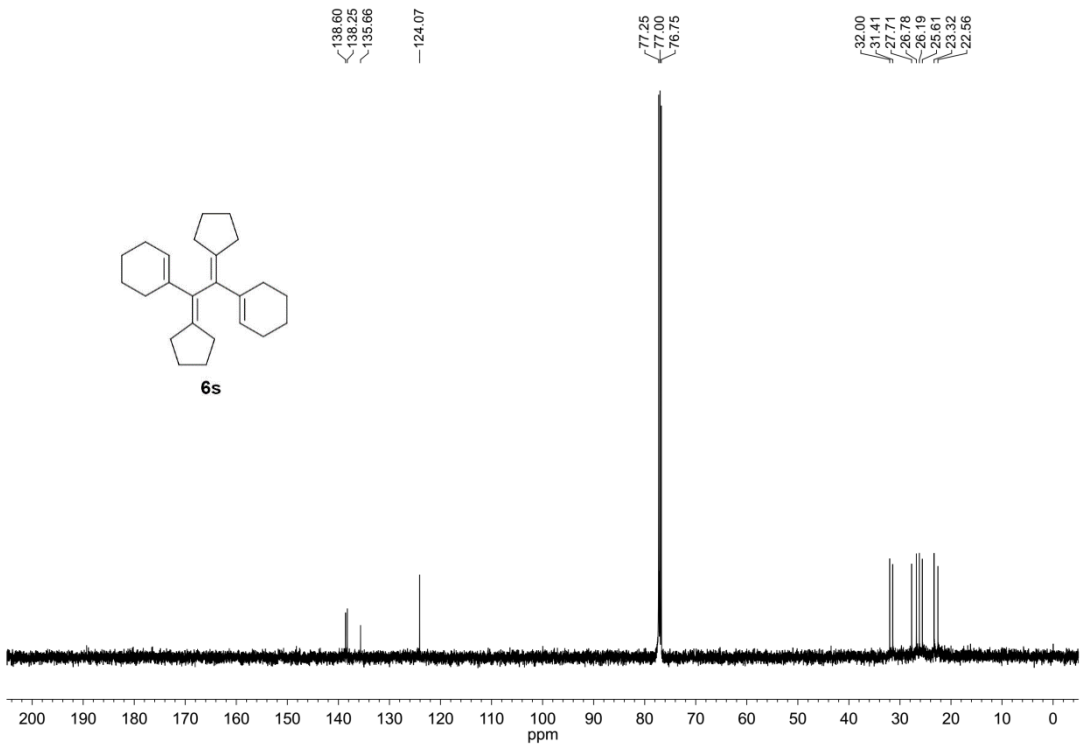
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **6r**



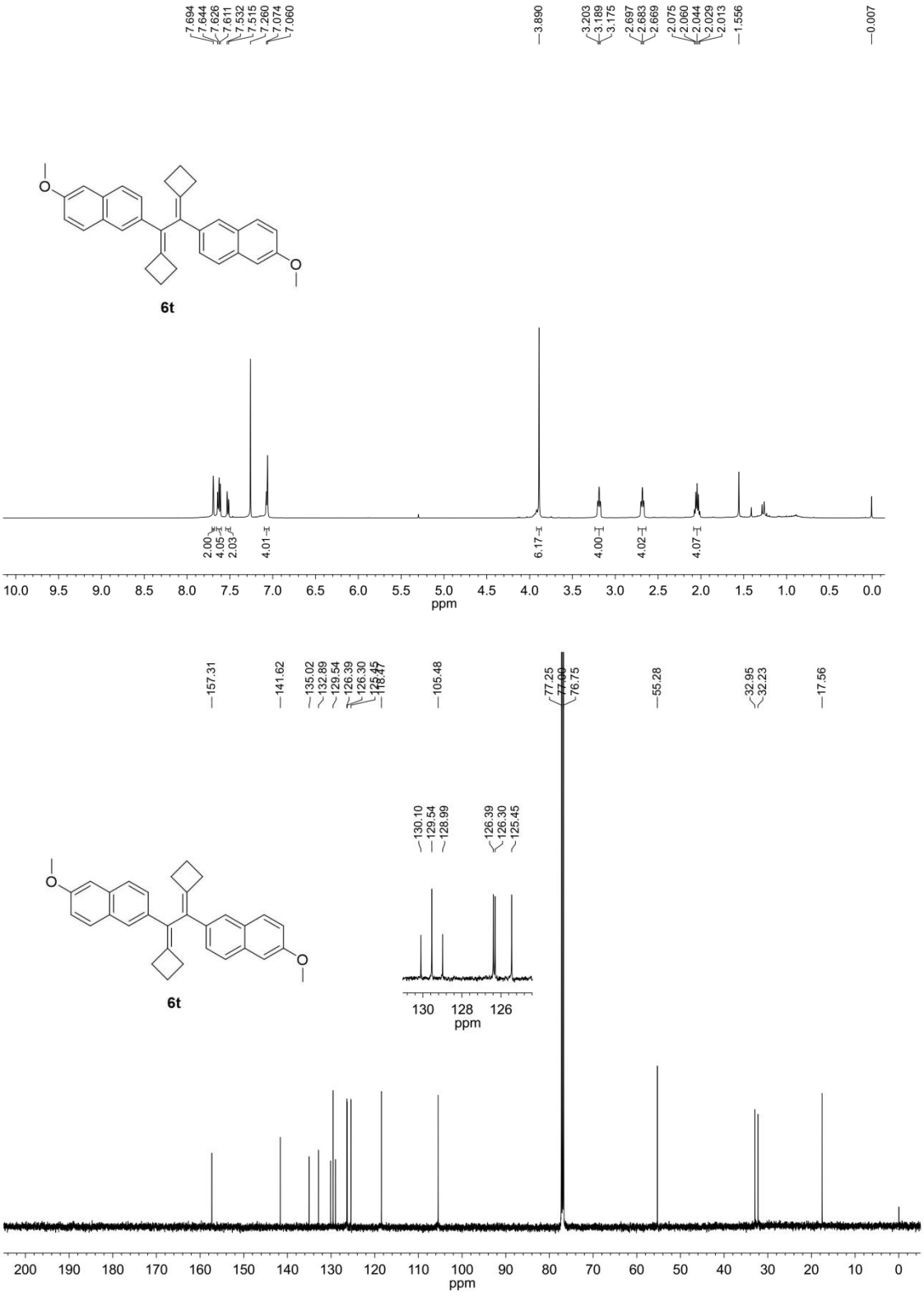


^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **6s**

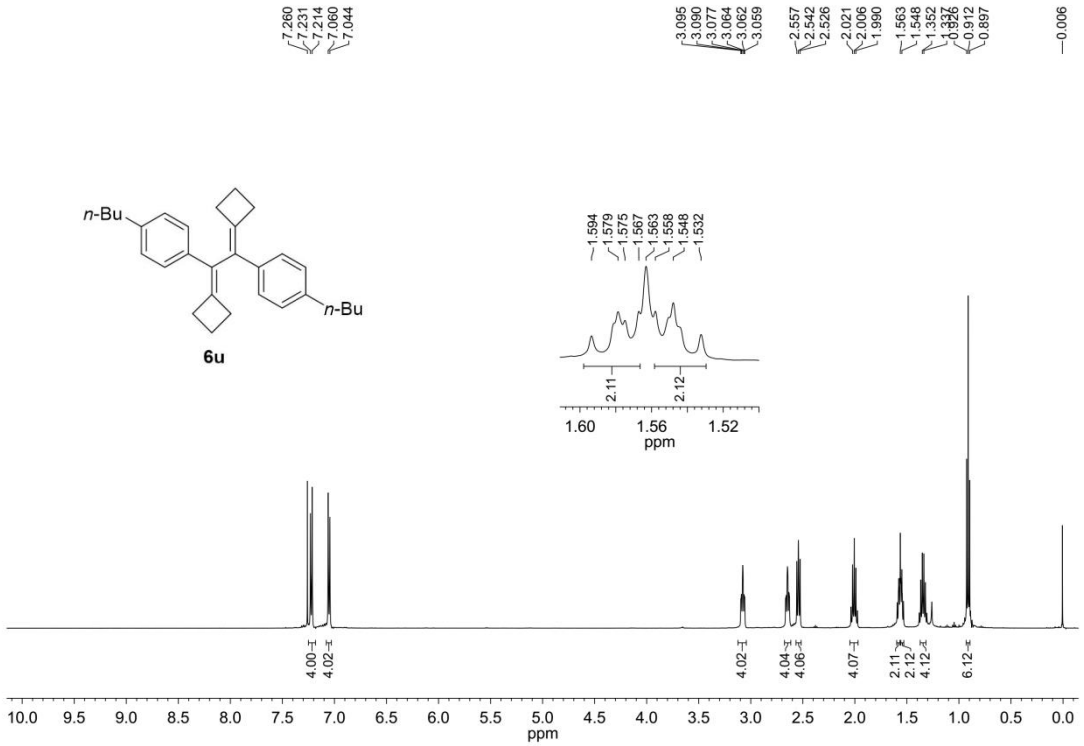


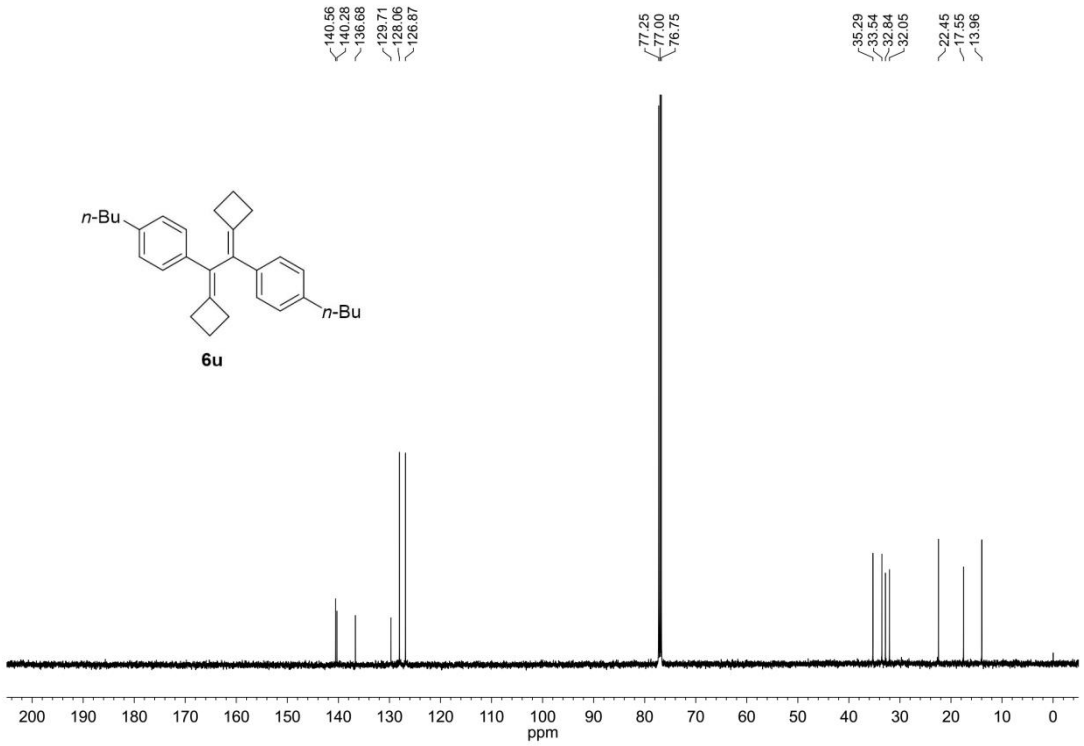


^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **6t**

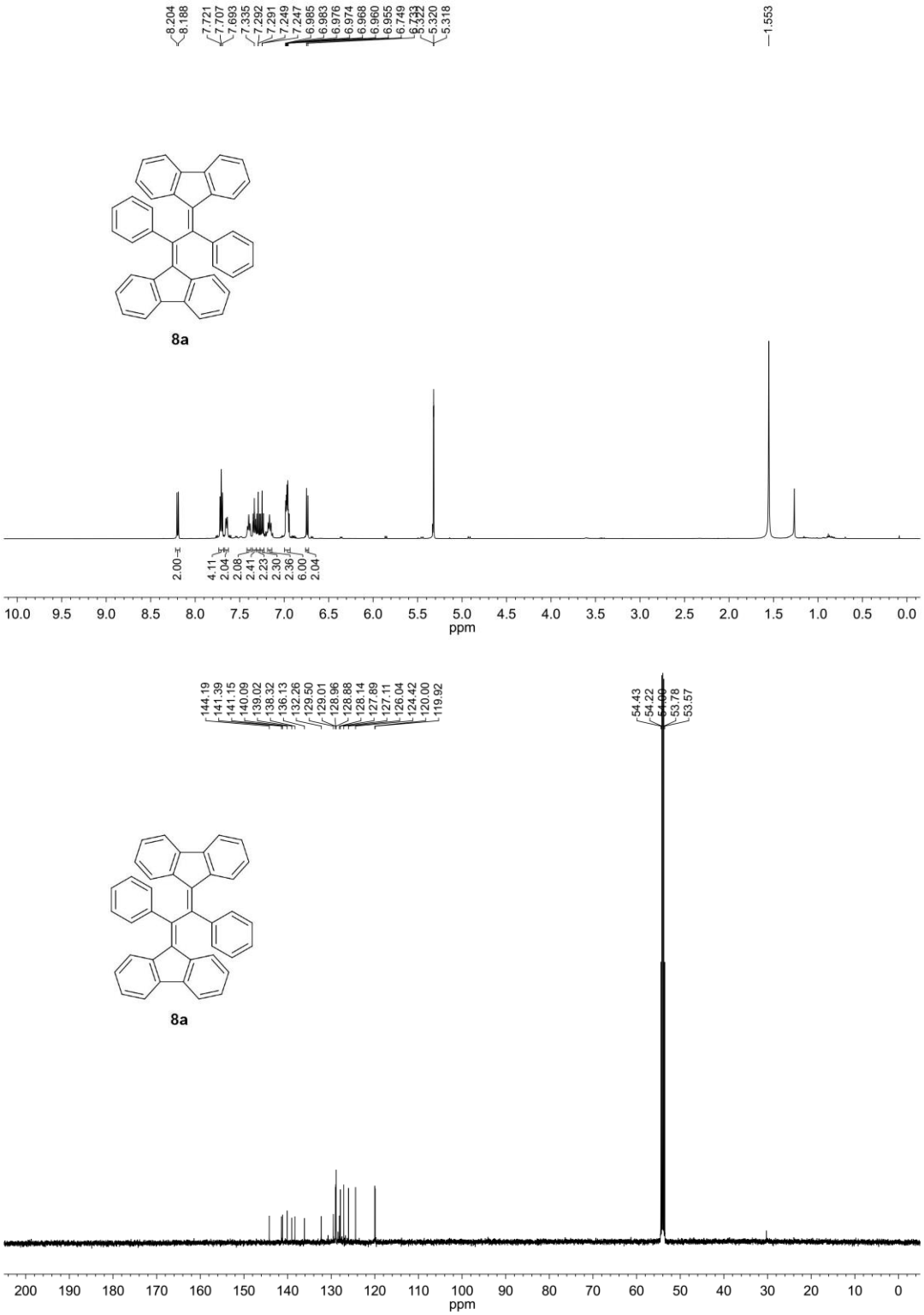


^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR** (126 MHz, $CDCl_3$) Spectra of Compound **6u**

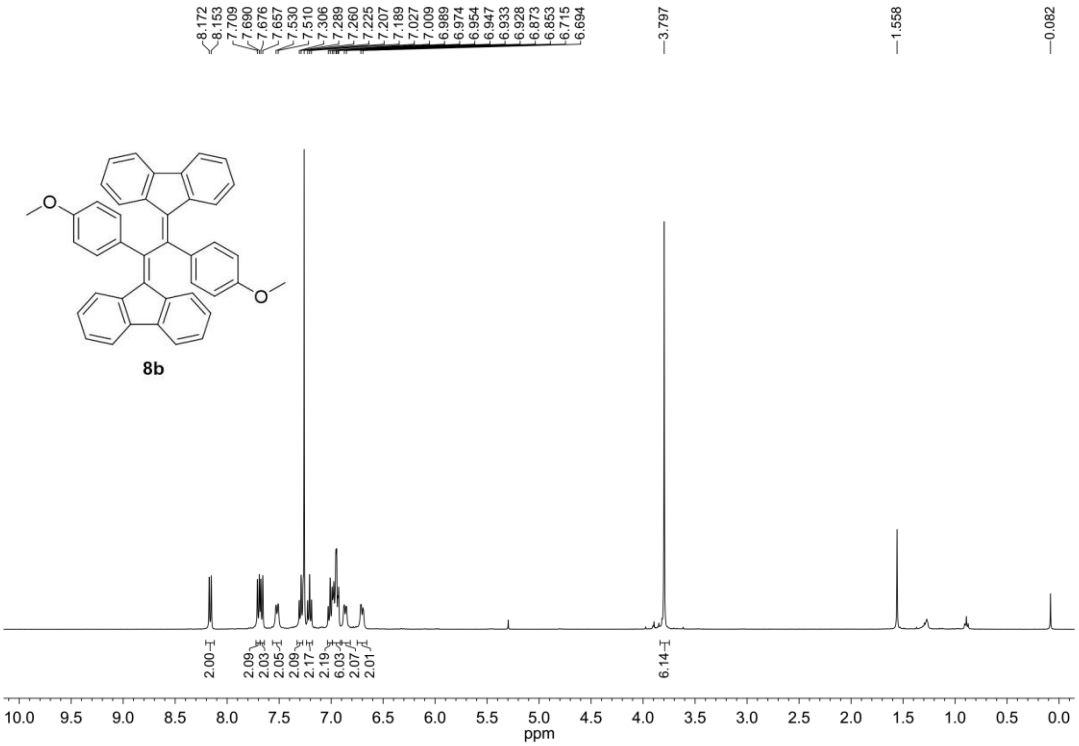


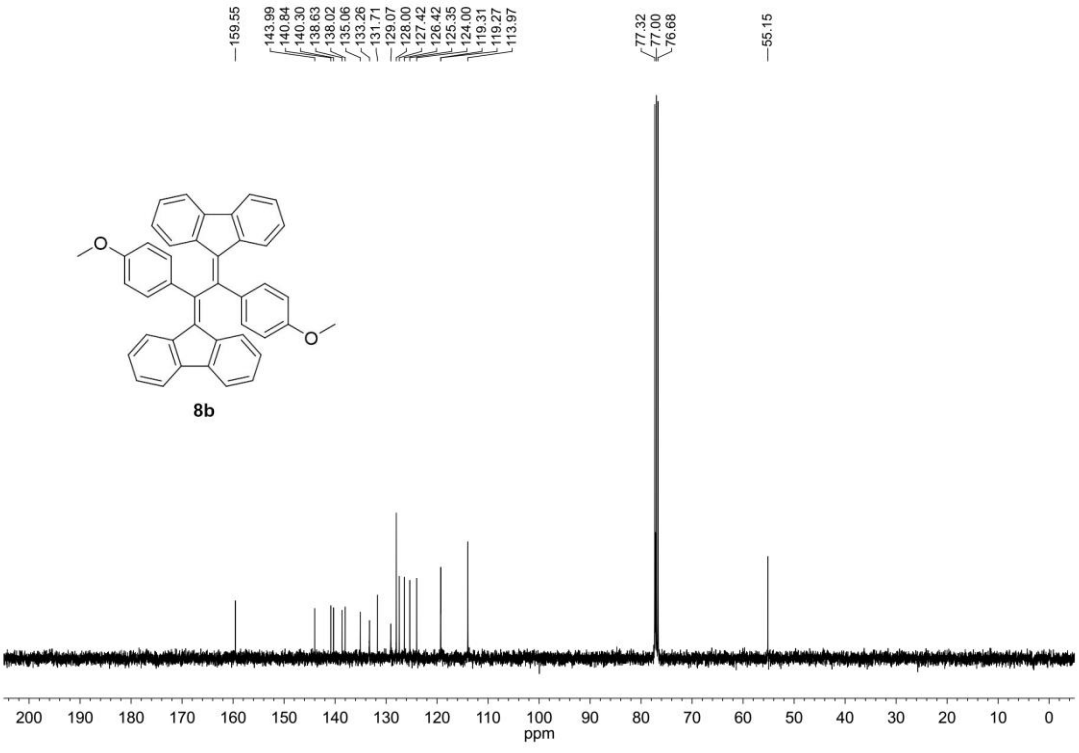


^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **8a**

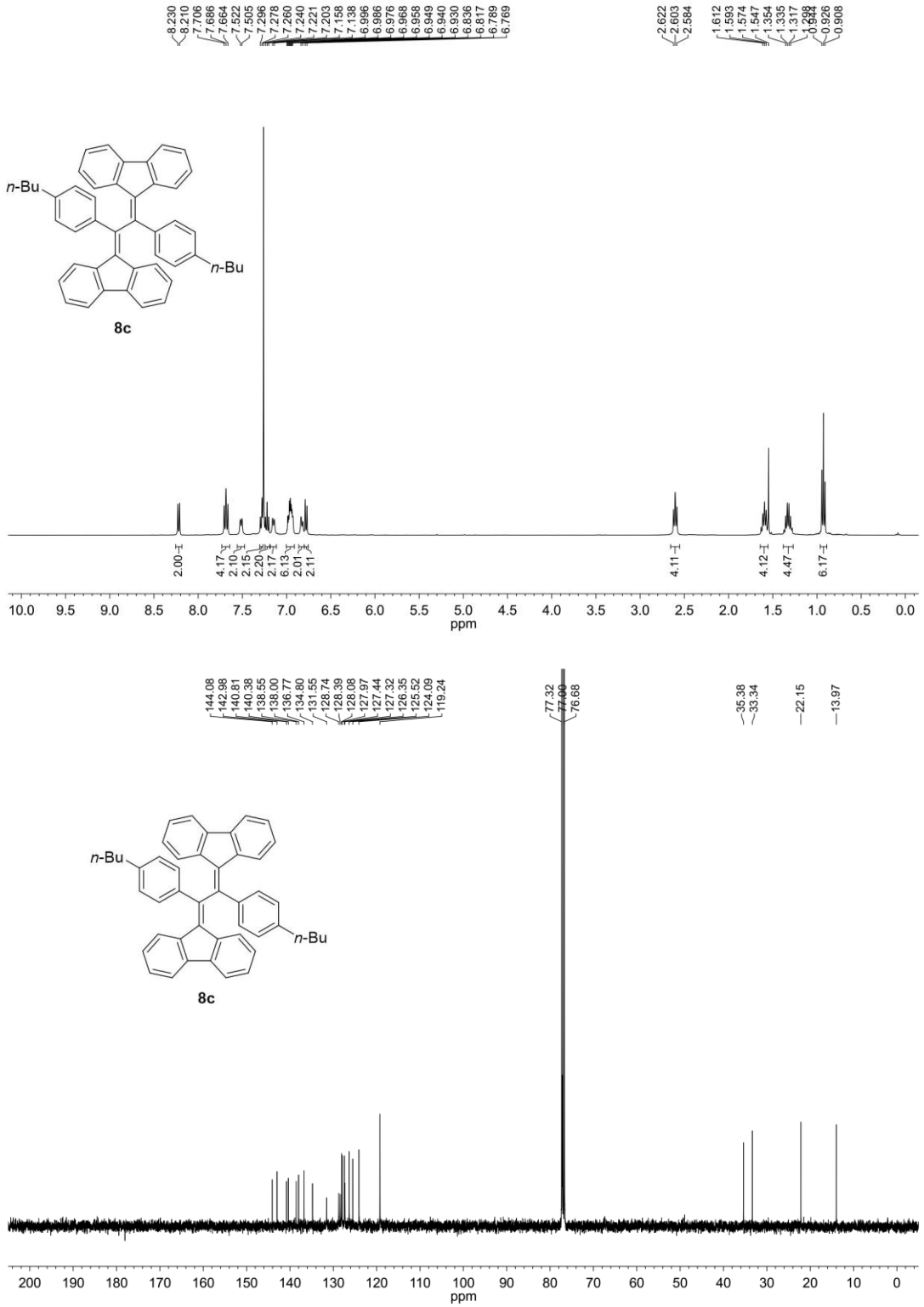


^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **8b**

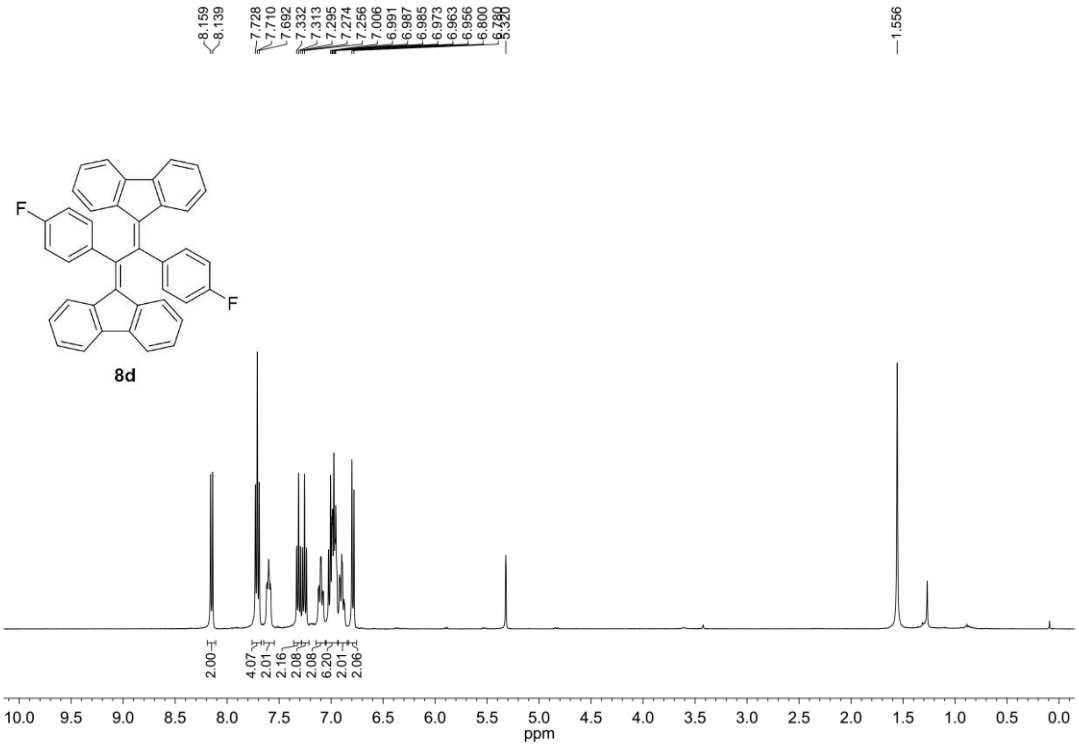


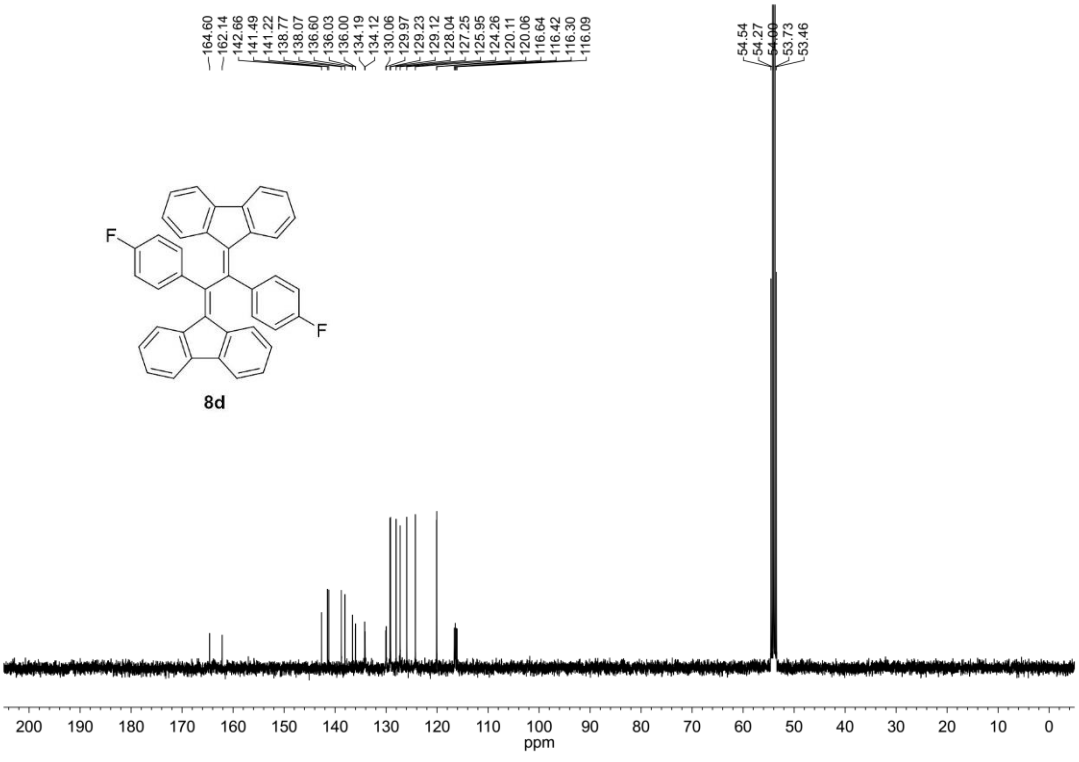


^{1}H NMR (400 MHz, $CDCl_3$) and **^{13}C NMR** (101 MHz, $CDCl_3$) Spectra of Compound **8c**

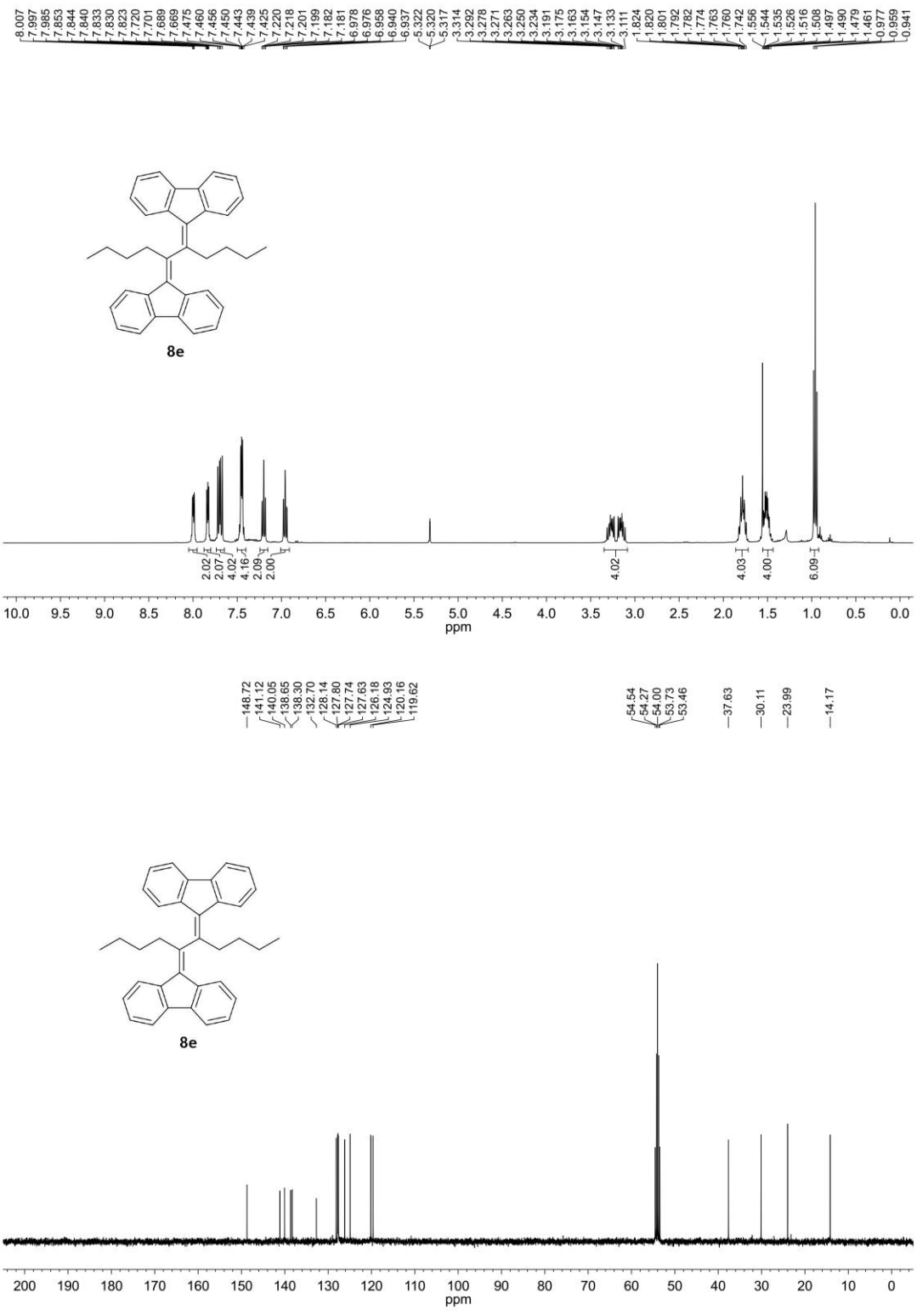


^{1}H NMR (400 MHz, CD_2Cl_2) and **^{13}C NMR** (101 MHz, CD_2Cl_2) Spectra of Compound **8d**





^{1}H NMR (400 MHz, CD_2Cl_2) and **^{13}C NMR** (101 MHz, CD_2Cl_2) Spectra of Compound **8e**



^{1}H NMR (500 MHz, CD_2Cl_2) and **^{13}C NMR** (126 MHz, CD_2Cl_2) Spectra of Compound **9a**