Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Fused Diethynylbenzenes and Phenanthrenes via Arynes with Alkynylsilanes

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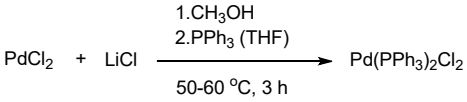
Contents

1. General experimental procedures

All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. The chemicals were purchased from Alfa Aesar, TCI and Acros Chemicals. All solvents and materials were pre-dried, redistilled or recrystallized before use. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on a Bruker Avance 400 spectrometer with $CDCl_3$ as the solvent. Chemical shifts are reported in ppm by assigning TMS resonance in the ^{1}H NMR spectra as 0.00 ppm, $CDCl_3$ resonance in the ^{13}C spectra as 77.2 ppm. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Data for ^{13}C NMR are recorded with broad-band proton decoupling technique and are reported in terms of chemical shift. Column chromatography was performed on silica gel 300–400 mesh. Thin-layer chromatography (TLC) was performed on silica gel plates (HSGF 254). Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. The FT-IR spectra were recorded from KBr pellets or thin film from $CHCl_3$ on the NaCl window in the 4000-400 cm^{-1} ranges on a Nicolet 5DX spectrometer. All HRMS spectra were record using EI at 70 eV. X-ray Crystallography diffraction data of **3l, 3o, 6c and 8g** were collected at room temperature with a Bruker SMART Apex CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) with a graphite monochromator using the ω-scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically.

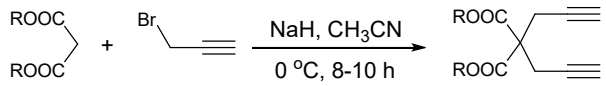
(1) General procedure for preparation of tetraynes [1]:

Preparation of catalyst $Pd(PPh_3)_2Cl_2$



3.54 g $PdCl_2$ and 4 g LiCl were mixed in a 500 mL three-necked flask with 150-200 mL methanol as solvent, magnetically stirred and heated in oil bath at 50-60 °C. After the solid was dissolved, 25 mL of THF (removed water with sodium wire) containing 13.1 g PPh_3 were added in the above three-necked flask, and the color of the solution changed from brown to yellow, reflux reaction for 3 hours. After reaction solution cooled, filtered and washed with anhydrous ethanol, yellow solid $Pd(PPh_3)_2Cl_2$ catalyst was obtained finally.

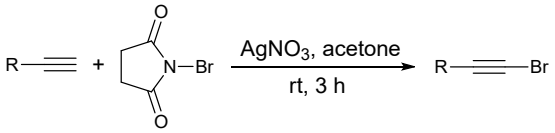
Preparation of diyne substrates



R = Me, Et, ^{i}Pr

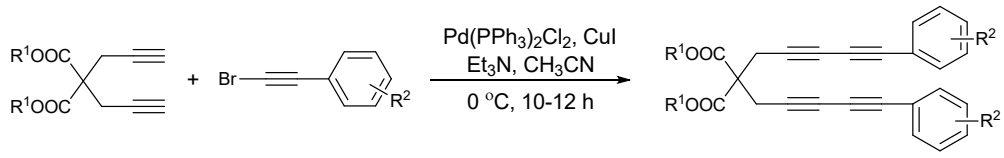
10 g NaH (60%) and 200-300 mL acetonitrile were added in 500 mL three-necked flask with magnetic stirring. 100 mmol malonate and 30 g 3-bromopropyne (98%) were added in the above 500 mL three-necked flask dropwise in turn by separatory funnel, magnetically stirred for 8-10 h under ice-water bath. The organic phase was extracted with ethyl acetate and dried with anhydrous $MgSO_4$. The solvent was evaporated in vacuo and diyne substrates as white solid were obtained finally.

Preparation of brominated alkynes



10.68 g 1-bromopyrrolidine-2,5-dione (NBS), 0.43 g $AgNO_3$, and 50 mmol phenylacetylene or substituted phenylacetylene or alkyl alkyne were added in 250 mL three-necked flask in turn, 100 mL acetone as a solvent, magnetically stirred at room temperature for 3 h. The organic phase was extracted with *n*-hexane and dried with anhydrous $MgSO_4$. The solvent was evaporated in vacuo and brominated alkynes compound as brown solid were obtained finally.

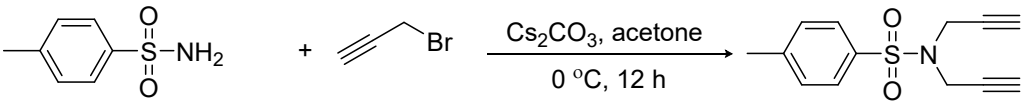
*Preparation of tetrayne substrate*s



R^1 = Me, Et, ^{i}Pr
R^2 = H, *p*-Me, *m*-Me, *p*-Et, *p*-Cl, *p*-F

0.3 g $Pd(PPh_3)_2Cl_2$, 0.25 g CuI and 20 mmol diyne substrate were added in 500 mL three-necked flask, protected with anhydrous anaerobic conditions under argon. After 0.5 h, 200-300 mL acetonitrile, 8.08 g Et_3N and 50 mmol brominated aryl alkyne were added in turn, magnetically stirred for 10-12 h under ice-water bath. The organic phase was extracted with ethyl acetate and dried with anhydrous $MgSO_4$. It was separated by column chromatography on silica gel to obtain tetrayne substrate as yellow solid finally.

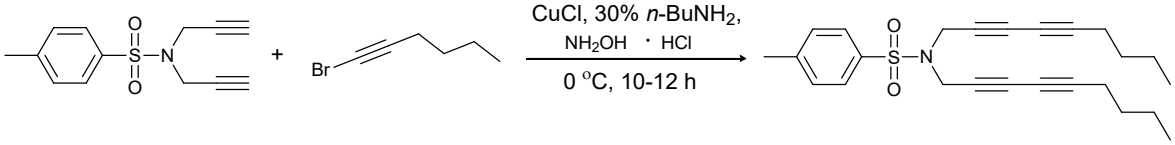
Preparation of 4-methyl-N, N-di (prop-2-yn-1-yl) benzenesulfonamide



40 mmol *p*-toluenesulfonamide, 120 mmol Cs_2CO_3, 200 mL acetone as solvent were added in 500 mL three-necked flask, protected with anhydrous anaerobic conditions under argon. After 0.5 h, 120 mmol 3-bromopropyne were added dropwise by constant pressure funnel in turn, magnetically stirred under ice-water bath, reaction for 24 hours. The organic phase was extracted with ethyl acetate and dried with

anhydrous $MgSO_4$. It was separated by column chromatography on silica gel to obtain the product as yellow solid finally.

Preparation of 4-methyl-N, N-di (nona-2,4-diyn-1-yl) benzenesulfonamide



0.7 g CuCl, 0.28 g NH_2OH•HCl and 20 mmol 4-methyl-*N*, *N*-di (prop-2-yn-1-yl) benzenesulfonamide were added in 500 mL three-necked flask, protected with anhydrous anaerobic conditions under argon. After 0.5 h, 90 mL 30% *n*-$BuNH_2$ aqueous solution (27 g *n*-$BuNH_2$ + 64 mL water) and 60 mmol 1-bromide hexyne (freshly prepared) was added dropwise by the constant pressure funnel in turn, 100-150 mL CH_2Cl_2 as solvent, magnetically stirred under ice-water bath, reaction for 10-12 h. The organic phase was extracted with ethyl acetate and dried with anhydrous $MgSO_4$. It was separated by column chromatography on silica gel to obtain the product as yellow oil finally.

(2) General procedure for the reaction of 1,4-bis(trimethylsilyl)-1,3-butadiyne and HDDA-derived benzynes:

Tetrayne (1.0 mmol), 1,4-bis(trimethylsilyl)-1,3-butadiyne (1.4 equiv), are mixed in an oven-dried Schlenk tube (50 mL) equipped with a magnetic stir bar and heated in a 105-110 °C oil bath in 4 mL toluene for 20 hours under air. The reaction mixture was cooled to room temperature, and the solvent was evaporated in vacuo. Followed by preparative thin-layer chromatography (TLC) on silica gel with the appropriate mixture of petroleum ether and ethyl acetate, Butadiynylation products are separated and purified by using column chromatography on silica gel. The eluent is EtOAc: petroleum ether = 1: 200.

(3) General procedure for the reaction of trimethyl(phenylethynyl)silane and HDDA-derived benzynes:

Tetrayne (1.0 mmol), trimethyl(phenylethynyl)silane (1.4 equiv), are mixed in an oven-dried Schlenk tube (50 mL) equipped with a magnetic stir bar and heated in a 110-115 °C oil bath in 4 mL CH_3CN for 24 hours under air. The reaction mixture was cooled to room temperature, and the solvent was evaporated in vacuo. Followed by preparative thin-layer chromatography (TLC) on silica gel with the appropriate mixture of petroleum ether and ethyl acetate, Butadiynylation products are separated and purified by using column chromatography on silica gel. The eluent is EtOAc: petroleum ether = 1: 80.

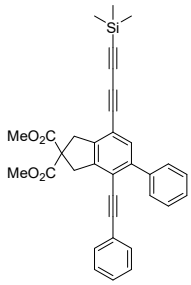
(4) General procedure for the base promoted reaction of trimethyl(phenylethynyl)silane and HDDA-derived benzynes:

Tetrayne (1.0 mmol), trimethyl(phenylethynyl)silane (1.2 equiv), and Cs_2CO_3 (1.0 equiv), are mixed in an oven-dried Schlenk tube (50 mL) equipped with a magnetic stir bar and heated in a 100-105 °C oil bath in 4 mL CH_3CN for 12 hours under air. The reaction mixture was cooled to room temperature, and the solvent was evaporated in vacuo. Followed by preparative thin-layer chromatography (TLC) on silica gel with the appropriate mixture of petroleum ether and ethyl acetate, Butadiynylation products are separated and purified by using column chromatography on silica gel. The eluent is EtOAc: petroleum ether = 1: 100.

References:

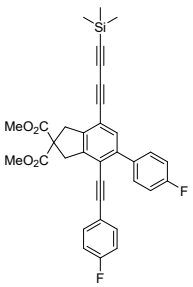
1. (*a*) J. Chen, V. Palani and T. R. Hoye, *J. Am. Chem. Soc.*, 2016, **138**, 4318−4321; (*b*) N.-K. Lee, S. Y. Yun, P. Mamidipalli, R. M. Salzman, D. Lee, T. Zhou and Y. Xia, *J. Am. Chem. Soc.*, 2014, **136**, 4363−4368; (*c*) B. Liu, C. Mao, Q. Hu, L. Yao and Y. Hu, *Org. Chem. Front.*, 2019, 6, 2788−2791; (*d*) X. Zheng, B. Liu, F. Yang, Q. Hu, L. Yao and Y. Hu, *Org. Lett.*, 2020, **22**, 956–959.

2. Characterization Data for the New Compounds



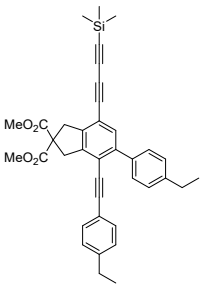
Dimethyl 5-phenyl-4-(phenylethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3a)

White solid; (387 mg, 73% yield); m. p. 137-142 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.47. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 6.8 Hz, 2H; Ar-H), 7.44 (t, J = 6.9 Hz, 2H; Ar-H), 7.40-7.37 (m, 2H; Ar-H), 7.35-7.33 (m, 2H; Ar-H), 7.30-7.28 (m, 3H; Ar-H), 3.84 (s, 2H; $C(COOMe)_2$-CH_2), 3.80 (s, 6H; -$C(COOCH_3)_2$), 3.79(s, 2H; $C(COOMe)_2$-CH_2), 0.25 (s, 9H; -C≡C-$Si(CH_3)_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.84, 143.48, 142.95, 142.53, 139.39, 132.36, 131.54, 129.27, 128.63, 128.36, 128.02, 127.78, 123.02, 119.19, 117.21, 98.32, 92.60, 87.69, 86.87, 78.75, 74.42, 59.00, 53.25, 41.31, 40.71, 1.05, -0.39. **FT-IR** (KBr): ν = 2962, 2200, 1734, 1600, 1492, 1437, 1260, 1159, 1078, 1025, 849, 698 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{34}H_{30}O_4Si$ $[M+Na]^+$: 553.1806, found 553.1807.



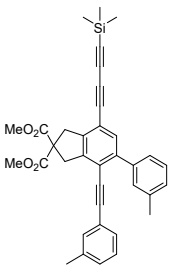
Dimethyl 5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3b)

White solid; (430 mg, 76% yield); m. p. 186-188 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.58. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (t, J = 6.8 Hz, 2H; Ar-H), 7.37-7.30 (m, 3H; Ar-H), 7.13 (t, J = 8.5 Hz, 2H; Ar-H), 7.01 (t, J = 8.5 Hz, 2H; Ar-H), 3.80 (s, 8H; $C(COOMe)_2$-CH_2 & -$C(COOCH_3)_2$), 3.78 (s, 2H; $C(COOMe)_2$-CH_2), 0.25 (s, 9H; -C≡C-Si$(CH_3)_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.77, 162.77(d, $J_{C\text{-}F}$ = 251.5 Hz), 143.49, 142.69, 141.85, 135.39 (d, J = 3.0 Hz), 133.44 (d, J = 8.1 Hz), 132.24, 130.92 (d, J = 8.1 Hz), 118.96, 118.92, 117.36, 115.91, 115.69, 115.08, 114.87, 97.34, 92.80, 87.59, 86.35, 78.94, 74.18, 58.97, 53.27, 41.25, 40.66, 1.05, -0.41. **FT-IR** (KBr): v = 2963, 2199, 1736, 1600, 1508, 1230, 1098, 1021, 801, 481 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{34}H_{28}F_2O_4Si$ $[M+Na]^+$: 589.1617, found 589.1620.



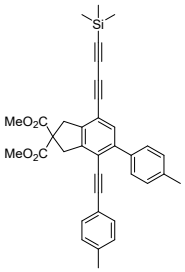
Dimethyl 5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3c)

White solid; (406 mg, 71% yield); m. p. 127-131 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.65. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.1 Hz, 2H; Ar-H), 7.38 (s, 1H; Ar-H), 7.29-7.26 (m, 4H; Ar-H), 7.14 (d, J = 8.2 Hz, 2H; Ar-H), 3.82 (s, 2H; $C(COOMe)_2$-CH_2), 3.80 (s, 6H; $C(COOCH_3)_2$), 3.78 (s, 2H; $C(COOMe)_2$-CH_2), 2.72 (q, J = 7.6 Hz, 2H; Ar-CH_2), 2.64 (q, J = 7.6 Hz, 2H; Ar-CH_2), 1.30 (t, J = 7.6 Hz, 3H; -CH_3), 1.22 (t, J = 7.6 Hz, 3H; -CH_3), 0.25 (s, 9H; -C≡C-Si$(CH_3)_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.90, 145.14, 143.83, 143.35, 142.74, 142.21, 136.73, 132.30, 131.55, 129.19, 127.93, 127.51, 120.29, 119.38, 116.89, 98.61, 92.42, 87.75, 86.49, 78.53, 75.21, 58.97, 52.59, 41.34, 40.70, 29.67, 28.66, 15.61, 15.42, -0.38. **FT-IR** (KBr): v = 2962, 2199, 1736, 1511, 1434, 1252, 1199, 1072, 923, 850 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{38}H_{38}O_4Si$ $[M+Na]^+$: 609.2432, found 609.2435.



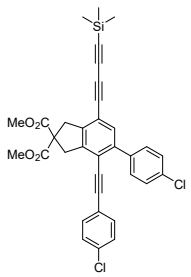
Dimethyl 5-(m-tolyl)-4-(m-tolylethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3d)

White solid; (402 mg, 72% yield); m. p. 102-105 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.62. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 3H; Ar-H), 7.33 (t, J = 7.6 Hz, 1H; Ar-H), 7.21-7.11 (m, 5H; Ar-H), 3.83 (s, 2H; $C(COOMe)_2$-CH_2), 3.80 (s, 6H; -$C(COOCH_3)_2$), 3.78 (s, 2H; $C(COOMe)_2$-CH_2), 2.42 (s, 3H; Ar-CH_3), 2.32 (s, 3H; Ar-CH_3), 0.25 (s, 9H; -C≡C-Si$(CH_3)_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.87, 143.41, 142.94, 142.37, 139.28, 138.04, 137.51, 132.37, 132.10, 130.02, 129.52, 128.62, 128.49, 128.25, 127.92, 126.36, 122.87, 119.23, 117.06, 98.61, 92.51, 87.71, 86.64, 78.63, 74.50, 59.00, 53.25, 41.32, 40.69, 21.57, 21.24, 0.02, -0.39. **FT-IR** (KBr): v = 2954, 2198, 1729, 1601, 1434, 1363, 1250, 1072, 845, 786, 689, 498 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{36}H_{34}O_4Si$ $[M+Na]^+$: 581.2119, found 581.2122.



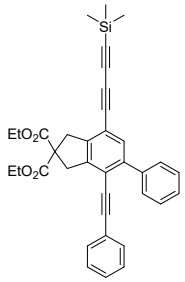
Dimethyl 5-(p-tolyl)-4-(p-tolylethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3e)

White solid; (396 mg, 71% yield); m. p. 160-162 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.68. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.1 Hz, 2H; Ar-H), 7.38 (s, 1H; Ar-H),7.26 (t, J = 8.4 Hz, 4H; Ar-H), 7.12 (d, J = 8.0 Hz, 2H; Ar-H), 3.83 (s, 2H; $C(COOMe)_2$-CH_2), 3.80 (s, 6H; -$C(COOCH_3)_2$), 3.78 (s, 2H; $C(COOMe)_2$-CH_2), 2.42 (s, 3H; Ar-CH_3), 2.35 (s, 3H; Ar-CH_3), 0.25 (s, 9H; -C≡C-Si$(CH_3)_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.89, 143.41, 142.66, 142.20, 138.84, 137.51, 136.49, 132.33, 131.45, 129.11, 128.73, 120.04, 119.32, 116.92, 98.58, 92.44, 87.75, 86.43, 78.55, 74.58, 58.98, 53.22, 41.34, 40.70, 21.59, 21.31, 0.02, -0.38. **FT-IR** (KBr): v = 2854, 2196, 1732, 1605, 1511, 1251, 1169, 1076, 850, 818, 637 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{36}H_{34}O_4Si$ $[M+Na]^+$: 581.2119, found 581.2124.



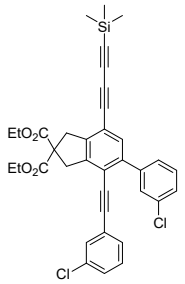
Dimethyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3f)

White solid; (468 mg, 78% yield); m. p. 110-113 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.59. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H; Ar-H), 7.43-7.40 (m, 2H; Ar-H), 7.34 (s, 1H; Ar-H), 7.31-7.27 (m, 4H; Ar-H), 3.80 (s, 8H; $C(COOMe)_2$-CH_2 & -$C(COOCH_3)_2$), 3.78 (s, 2H; $C(COOMe)_2$-CH_2), 0.25 (s, 9H; -C≡C-$Si(CH_3)_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.74, 143.70, 142.94, 141.66, 137.75, 134.86, 133.93, 132.71, 132.21, 130.54, 128.82, 128.26, 121.23, 118.66, 117.64, 114.79, 97.35, 92.97, 87.47 (d, J = 10.1 Hz), 79.10, 74.05, 58.95, 53.30, 41.24, 40.66, 0.02, -0.41. **FT-IR** (KBr): ν = 2955, 2200, 1740, 1596, 1491, 1435, 1248, 1158, 1091, 1014, 845 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{34}H_{28}Cl_2O_4Si$ $[M+Na]^+$: 621.1026, found 621.1033.



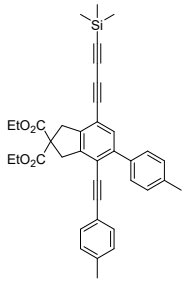
Diethyl 5-phenyl-4-(phenylethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3g)

White solid; (402 mg, 72% yield); m. p. 116-118 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.51. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2H; Ar-H),7.46-7.42 (m, 2H; Ar-H), 7.40-7.36 (m, 2H; Ar-H), 7.35-7.32 (m, 2H; Ar-H), 7.31-7.28 (m, 3H; Ar-H), 4.26 (q, J = 6.3 Hz, 4H; -$C(COOCH_2)_2$), 3.82 (s, 2H; $C(COOEt)_2$-CH_2), 3.77 (s, 2H; $C(COOEt)_2$-CH_2), 1.30 (t, J = 8.0 Hz, 6H; -CH_3), 0.25 (s, 9H; -C≡C-$Si(CH_3)_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.42, 143.64, 142.90, 142.67, 139.44, 132.36, 131.53, 129.28, 128.59,128.34,128.00,127.75, 123.07, 119.18, 117.18, 98.23, 92.49, 87.74, 86.92, 78.66, 74.51, 62.04, 59.08, 41.18, 40.60, 14.09, 1.05, 0.02, -0.39. **FT-IR** (KBr): ν = 2980, 2197, 1736, 1599, 1438, 1249, 1176, 1047, 921, 851, 759 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{36}H_{34}O_4Si$ $[M+Na]^+$: 581.2119, found 581.2122.



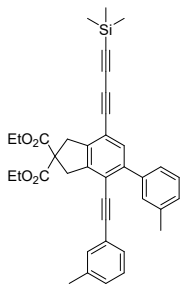
Diethyl 5-(3-chlorophenyl)-4-((3-chlorophenyl)ethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3h)

White solid; (458 mg, 73% yield); m. p. 125-126 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.76. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 1H; Ar-H), 7.44-7.40 (m, 1H; Ar-H), 7.39-7.37 (m, 4H; Ar-H), 7.31-7.28 (m, 1H; Ar-H), 7.26-7.24 (m, 2H; Ar-H), 4.26 (q, J = 7.1 Hz, 4H; -C($COOCH_2$)$_2$), 3.80 (s, 2H; C($COOEt$)$_2$-CH_2), 3.77 (s, 2H; C($COOEt$)$_2$-CH_2), 1.31 (t, J = 7.1 Hz, 6H; -CH_3), 0.25 (s, 9H; -C≡C-Si(CH_3)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.28, 143.96, 143.35, 141.47, 140.97, 134.26, 133.85, 132.18, 131.35, 129.68 (d, J = 5.1 Hz), 129.40 (d, J = 4.0 Hz), 128.99, 127.96, 127.39, 124.47, 118.48, 117.84, 97.12, 92.96, 87.53 (d, J = 3.0 Hz), 79.17, 74.06, 62.12, 59.06, 41.09, 40.58, 14.09, 0.02, -0.41. **FT-IR** (KBr): v = 2961, 2201, 1726, 1594, 1366, 1252, 1159, 1077, 929, 846, 700 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{36}H_{32}Cl_2O_4Si$ [M+Na]$^+$: 649.1339, found 649.1345.



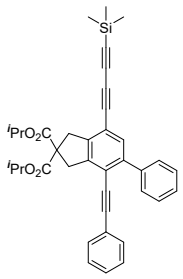
Diethyl 5-(p-tolyl)-4-(p-tolylethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3i)

White solid; (399 mg, 68% yield); m. p. 118-120 °C; TLC (petroleum ether/EtOAc = 8:1), R_f = 0.78. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.50 (d, J = 8.1, 2H; Ar-H), 7.37 (s, 1H; Ar-H), 7.25 (t, J = 8.2 Hz, 4H; Ar-H), 7.11 (d, J = 7.8 Hz, 2H; Ar-H), 4.25 (q, J = 7.1 Hz, 4H; -C($COOCH_2$)$_2$)), 3.81 (s, 2H; C($COOEt$)$_2$-CH_2), 3.76 (s, 2H; C($COOEt$)$_2$-CH_2), 2.41 (s, 3H; Ar-CH_3), 2.35 (s, 3H; Ar-CH_3), 1.29 (t, J = 7.1 Hz, 6H; -CH_3), 0.25 (s, 9H; -C≡C-Si(CH_3)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.47, 143.58, 142.61, 142.35, 138.80, 137.48, 136.54, 133.33, 131.45, 129.12, 128.72, 120.09, 119.32, 116.90, 98.50, 92.35, 87.81, 86.49, 78.47, 74.68, 62.03, 59.07, 41.22, 40.60, 21.45 (d, J = 30.3 Hz), 14.10, -0.37. **FT-IR** (KBr): v = 2963, 2197, 1736, 1606, 1462, 1366, 1248, 1185, 1075, 851, 813 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{38}H_{38}O_4Si$ [M+Na]$^+$: 609.2432, found 609.2438.



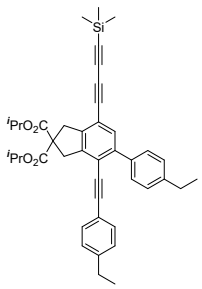
Diethyl 5-(m-tolyl)-4-(m-tolylethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3j)

White solid; (393 mg, 67% yield); m. p. 80-83 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.74. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 3H; Ar-H), 7.33 (t, J = 7.5 Hz, 1H; Ar-H), 7.21-7.11 (m, 5H; Ar-H), 4.26 (q, J = 7.1 Hz, 4H; -C($COOCH_2$)$_2$)), 3.82 (s, 2H; C($COOEt$)$_2$-CH_2), 3.77 (s, 2H; C($COOEt$)$_2$-CH_2), 2.42 (s, 3H; Ar-CH_3), 2.32 (s, 3H; Ar-CH_3), 1.30 (t, J = 7.1 Hz, 6H; -CH_3), 0.25 (s, 9H; -C≡C-Si(CH_3)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.45, 143.58, 142.89, 142.51, 139.33, 138.03, 137.49, 132.37, 132.10, 130.02, 129.48, 128.61, 128.46, 128.24, 127.91, 126.37, 122.92, 119.22, 117.04, 98.53, 92.41, 87.76, 86.70, 78.55, 74.60, 62.04, 59.08, 41.19, 40.59, 21.41 (d, J = 30.3 Hz), 14.09, 0.02, -0.38. **FT-IR** (KBr): v = 2979, 2196, 1735, 1603, 1463, 1366, 1244, 1183, 1076, 847, 789 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{38}H_{38}O_4Si$ [M+Na]$^+$: 609.2432, found 609.2439.



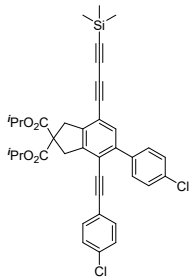
Diisopropyl 5-phenyl-4-(phenylethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3k)

White solid; (439 mg, 75% yield); m. p. 145-148 °C; TLC (petroleum ether/EtOAc = 8:1), R_f = 0.58. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, J = 6.8 Hz, 2H; Ar-H), 7.44 (t, J = 6.9 Hz, 2H; Ar-H), 7.40-7.38 (m, 2H; Ar-H), 7.34-7.28 (m, 5H; Ar-H), 5.14-5.04 (m, 2H; -C($COOCH$)$_2$)), 3.79 (s, 2H; C(COO^iPr)$_2$-CH_2), 3.73 (s, 2H; C($COOEt$)$_2$-CH_2), 1.29 (m, 12H; -CH_3), 0.25 (s, 9H; -C≡C-Si(CH_3)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.97, 143.77, 142.87, 142.75, 139.48, 132.41, 131.53, 129.29, 128.56, 128.35, 128.00, 127.73, 123.13, 119.19, 117.17, 98.19, 92.41, 87.81, 86.96, 78.59, 74.59, 69.54, 59.14, 41.14, 40.56, 21.61, 21.58, -0.38. **FT-IR** (KBr): v = 2982, 2199, 1723, 1600, 1365, 1253, 1197, 1103, 849, 775, 702 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{38}H_{38}O_4Si$ [M+Na]$^+$: 609.2432, found 609.2441.



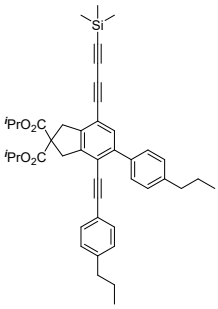
Diisopropyl 5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3l)

White solid; (469 mg, 73% yield); m. p. 116-118 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.85. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.5 (d, J = 8.2, 2H; Ar-H), 7.39 (s, 1H; Ar-H), 7.29-7.26 (m, 4H; Ar-H), 7.14 (d, J = 8.1, 2H; Ar-H), 5.14-5.05 (m, 2H; -C(COOCH)$_2$)), 3.79 (s, 2H; C(COO^{i}Pr)$_2$-CH$_2$), 3.73 (s, 2H; C(COO^{i}Pr)$_2$-CH$_2$), 2.72 (q, J = 7.6 Hz, 2H; Ar-CH$_2$), 2.64 (q, J = 7.6 Hz, 2H; Ar-CH$_2$), 1.32-1.28 (m, 12H; -CH$_3$), 1.27-1.20 (m, 6H; -CH$_3$), 0.25 (s, 9H; -C≡C-Si(CH$_3$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.02, 145.06, 143.70 (d, J = 12.1 Hz), 142.66, 142.44, 136.82, 132.35, 131.54, 129.21, 127.92, 127.50, 120.40, 119.37, 116.85, 98.45, 92.23, 87.86, 86.56, 78.35, 74.76, 69.50, 59.10, 41.15, 40.54, 28.79 (d, J = 23.2 Hz), 21.61, 21.59, 15.53 (d, J = 10.1 Hz), 0.04, -0.36. **FT-IR** (KBr): v = 2965, 2202, 1727, 1607, 1512, 1373, 1258, 1198, 1104, 802 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{42}H_{46}O_4Si$ $[M+Na]^+$: 665.3058, found 665.3061.



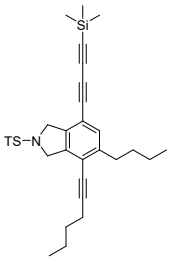
Diisopropyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3m)

White solid; (518 mg, 79% yield); m. p. 209-212 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.79. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H; Ar-H), 7.42-7.38 (m, 2H; Ar-H), 7.34 (s, 1H; Ar-H), 7.31-7.29 (m, 3H; Ar-H), 7.26-7.25 (m, 1H; Ar-H), 5.14-5.04 (m, 2H; -C(COOCH)$_2$)), 3.76 (s, 2H; C(COO^{i}Pr)$_2$-CH$_2$), 3.72 (s, 2H; C(COO^{i}Pr)$_2$-CH$_2$), 1.29 (m, 12H; -CH$_3$), 0.25 (s, 9H; -C≡C-Si(CH$_3$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.88, 143.99, 143.16, 141.57, 137.84, 134.79, 133.83 (d, J = 8.1 Hz), 132.70, 132.25, 130.56, 128.81, 128.23, 121.32, 118.65, 117.59, 97.21, 92.78, 87.63, 87.50, 78.93, 74.21, 69.87, 69.63, 59.09, 41.06, 40.52, 21.60, 21.58, 21.51, 1.05, -0.4. **FT-IR** (KBr): v = 2981, 2102, 1729, 1608, 1493, 1365, 1254, 1194, 1100, 927, 858 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{38}H_{36}Cl_2O_4Si$ $[M+Na]^+$: 677.1652, found 677.1651.



Diisopropyl 5-(4-propylphenyl)-4-((4-propylphenyl)ethynyl)-7-((trimethylsilyl)buta-1,3-diyn-1-yl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3n)

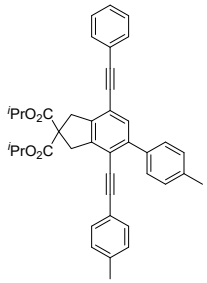
White solid; (470mg, 70% yield); m. p. 120-124 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.84. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.8 Hz, 2H; Ar-H), 7.38 (s, 1H; Ar-H), 7.26 (s, 1H; Ar-H), 7.24 (d, J = 6.2 Hz, 3H; Ar-H), 7.11 (d, J = 8.0 Hz, 2H; Ar-H), 5.13-5.04 (m, 2H; -C(COOCH)$_2$)), 3.78 (s, 2H; C(COO^{i}Pr)$_2$-CH$_2$), 3.72 (s, 2H; C(COO^{i}Pr)$_2$-CH$_2$), 2.65 (t, J = 7.6 Hz, 2H; -CH$_2$), 2.57 (t, J = 7.6 Hz, 2H; -CH$_2$), 1.75-1.67 (m, 2H; -CH$_2$-), 1.67-1.57 (m, 2H; -CH$_2$-), 1.29-1.27 (m, 12H; -CH$_3$), 0.99 (t, J = 7.3 Hz, 3H; -CH$_3$), 0.92 (t, J = 7.3 Hz, 3H; -CH$_3$), 0.25 (s, 9H; -C≡C-Si(CH$_3$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.01, 143.54 (d, J = 5.1 Hz), 142.73, 142.43, 142.19, 136.84, 132.33, 131.43, 129.12, 128.51, 128.08, 120.40, 119.39, 116.83, 98.45, 92.21, 87.86, 86.62, 78.35, 74.76, 71.57, 71.44, 69.81, 69.48, 59.11, 41.14, 40.54, 37.92 (d, J = 18.2 Hz), 31.46, 30.20, 29.73, 24.49 (d, J = 18.2 Hz), 21.59 (d, J = 2.0 Hz), 21.52, 13.90, 13.77, 1.05, -0.37. **FT-IR** (KBr): v = 2963, 2197, 1728, 1609, 1461, 1372, 1261, 1194, 1101, 801 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{44}H_{50}O_4Si$ [M+Na]$^+$: 693.3371, found 693.3384.



5-Butyl-4-(hex-1-yn-1-yl)-2-tosyl-7-((trimethylsilyl)buta-1,3-diyn-1-yl)isoindoline (3o)

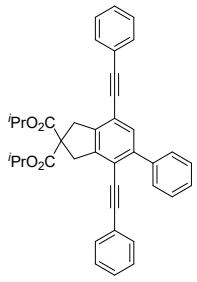
Yellow solid; (355 mg, 67% yield); m. p. 114-120 °C; TLC (petroleum ether/EtOAc = 8:1): R_f =0.61. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79(d, J = 8.0, 2H; Ar-H), 7.33 (d, J = 8.0 Hz, 2H; Ar-H), 7.14 (s, 1H; Ar-H), 4.63 (d, J = 6.4, 4H; Ts-N(CH$_2$)$_2$), 2.65 (t, J = 7.7, 2H; Ar-CH$_2$), 2.47 (t, J = 6.9, 2H; -C≡C-CH$_2$), 2.41 (s, 3H; Ar-CH$_3$), 1.63-1.56 (m, 4H; -CH$_2$), 1.53-1.44 (m, 4H; -CH$_2$), 1.36-1.27 (m, 2H; -CH$_2$), 0.96 (t, J = 7.3 Hz, 3H; -CH$_3$), 0.90 (t, J = 7.3 Hz, 3H; -CH$_3$), 0.25 (s, 9H; -C≡C-Si(CH$_3$)$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.99, 144.19, 139.38, 137.54 (d, J = 9.1 Hz), 134.12, 132.51 (d, J = 18.2 Hz), 130.38, 128.06, 120.15, 114.94 (d, J = 33.3 Hz), 101.88, 87.69, 76.22, 73.83, 73.60, 71.44, 68.10, 54.80 (d, J = 40.4 Hz), 34.06, 33.04 (d, J = 3.0 Hz), 31.14, 22.84, 22.42, 21.99, 19.87, 14.19 (d, J = 29.3Hz), 1.47, 0.45. **FT-IR**

(KBr): v = 2961, 1603, 1359, 1165, 1096, 813, 667, 546 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{32}H_{39}NO_2SSi$ $[M+Na]^+$: 552.2363, found 552.2369.



Diisopropyl 7-(phenylethynyl)-5-(p-tolyl)-4-(p-tolylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (6a)

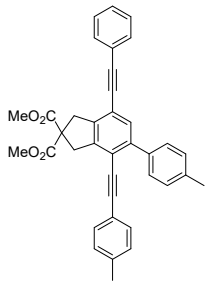
White solid; (446 mg, 75% yield); m. p. 141-149 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.38. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 2H; Ar-H), 7.54 (d, J = 8.0 Hz, 1H; Ar-H), 7.45 (s, 1H; Ar-H), 7.40-7.38 (m, 2H; Ar-H), 7.32-7.29 (m, 2H; Ar-H), 7.27-7.24 (m, 3H; Ar-H), 7.20 (d, J = 8.1 Hz, 1H; Ar-H), 7.16-7.10 (m, 2H; Ar-H), 5.16-5.09 (m, 2H; -C(COOCH)$_2$), 3.86-3.68 (m, 4H; C(COO^{i}Pr)$_2$-CH_2), 2.46 (d, J =10.1 Hz, 3H; Ar-CH_3), 2.37 (d, J = 7.8 Hz, 3H; Ar-CH_3), 1.31 (t, J = 5.7 Hz, 12H; -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.13 (d, J = 12.1 Hz), 144.89, 143.50, 142.61, 140.84, 138.89, 138.55, 137.25, 137.00 (d, J = 4.0 Hz), 131.74, 131.37 (d, J = 4.0 Hz), 130.44, 129.21, 129.10, 129.01, 128.47 (d, J = 8.1 Hz), 128.20, 128.01, 123.54, 123.19, 120.36 (d, J = 6.1 Hz), 119.74, 119.00, 118.11, 89.56, 87.42, 86.75, 86.29, 69.42 (d, J = 5.1 Hz), 59.78, 59.20, 41.32, 40.96, 40.63 (d, J = 7.1 Hz), 21.57 (d, J = 6.1 Hz), 21.39 (d, J = 15.2 Hz). **FT-IR** (KBr): v = 2980, 1728, 1599, 1511, 1465, 1373, 1245, 1181, 1103, 815, 754 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{41}H_{38}O_4$ $[M+Na]^+$: 617.2662, found 617.2665.



Diisopropyl 5-phenyl-4,7-bis(phenylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (6b)

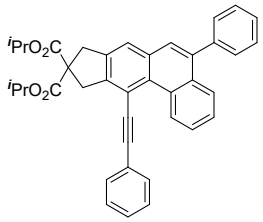
Light yellow liquid; (431 mg, 76% yield); TLC (petroleum ether/EtOAc = 8:1): R_f = 0.42. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.55 (m, 3H; Ar-H), 7.50-7.44 (m, 4H; Ar-H), 7.36 (s, 1H; Ar-H), 7.30-7.26 (m, 2H; Ar-H), 7.25-7.23 (m, 4H; Ar-H), 7.18 (s, 2H; Ar-H), 5.12-5.08 (m, 2H; -C(COOCH)$_2$), 3.85-3.66 (m, 4H; C(COO^{i}Pr)$_2$-CH_2), 1.30-1.27 (m, 12H; -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.06 (d, J = 12.1 Hz), 145.16, 143.42, 141.11, 139.11 (d, J = 8.1 Hz), 131.71, 131.44, 131.30, 130.49, 129.34, 128.40, 128.36, 128.27 (d, J = 3.0 Hz), 128.19 (d, J = 4.0 Hz), 128.01, 127.91, 127.45 (d, J = 6.1 Hz), 127.34, 123.29 (d,

J = 12.1 Hz), 121.93, 119.49, 96.40, 92.21, 89.25, 86.69, 69.44, 69.40, 59.75, 40.70 (d, *J* = 30.3 Hz), 21.56. **FT-IR** (KBr): *v* = 2979, 1727, 1597, 1492, 1442, 1280, 1196, 1104, 901, 756, 690 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{39}H_{34}O_4$ $[M+Na]^+$: 589.2349, found 589.2354.



Dimethyl 7-(phenylethynyl)-5-(p-tolyl)-4-(p-tolylethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (6c)

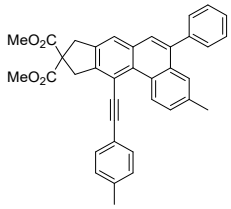
White solid; (380 mg, 71% yield); m. p. 159-162°C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.37. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.50 (d, *J* = 8.0 Hz, 2H; Ar-H), 7.43 (s, 1H; Ar-H), 7.27-7.20 (m, 7H; Ar-H), 7.16 (d, *J* = 8.2 Hz, 2H; Ar-H), 7.08 (d, *J* = 7.7 Hz, 2H; Ar-H), 3.82 (s, 2H; $C(COOMe)_2$-CH_2), 3.79 (s, 6H; -$C(COOCH_3)_2$), 3.68 (s, 2H; $C(COOMe)_2$-CH_2), 2.44 (s, 3H; Ar-CH_3), 2.33 (s, 3H; Ar-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 171.93, 144.91, 143.13, 138.53 (d, *J* = 12.1 Hz), 137.05, 135.89, 131.34 (d, *J* = 3.0 Hz), 130.37, 128.99, 128.17, 128.00, 127.44, 123.45, 122.02, 120.20 (d, *J* = 6.1 Hz), 119.73, 96.67, 92.06, 89.41, 86.17, 59.67, 53.16, 40.90 (d, *J* = 45.5 Hz), 21.48 (d, *J* = 9.1 Hz). **FT-IR** (KBr): *v* = 2953, 1736, 1599, 1511, 1440, 1364, 1240, 1154, 1070, 817, 759 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{37}H_{30}O_4$ $[M+Na]^+$: 561.2036, found 561.2045.



Diisopropyl 5-phenyl-11-(phenylethynyl)-8,10-dihydro-9H-cyclopenta[b]phenanthrene-9,9-dicarboxylate (8b)

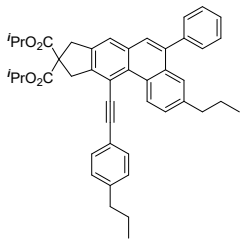
White solid; (442 mg, 78% yield); m. p. 142-143 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.29. **^{1}H NMR** (400 MHz, $CDCl_3$): 10.46 (d, *J* = 8.6 Hz, 1H; Ar-H), 7.91 (d, *J* = 8.2 Hz, 1H; Ar-H), 7.73-7.69 (m, 3H; Ar-H), 7.68-7.65 (m, 1H; Ar-H), 7.61 (s, 1H; Ar-H), 7.57-7.50 (m, 5H; Ar-H), 7.48-7.46 (m, 2H; Ar-H), 7.45-7.40 (m, 2H; Ar-H), 5.15-5.06 (m, 2H; -$C(COOCH)_2$), 4.03 (s, 2H; $C(COO^iPr)_2$-CH_2), 3.83 (s, 2H; $C(COO^iPr)_2$-CH_2), 1.43-1.26 (m, 12H; -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 171.14, 145.80, 140.74, 138.70 (d, *J* = 13.1 Hz), 132.36, 131.86, 131.45, 131.20, 130.06, 128.59 (d, *J* = 4.0 Hz), 128.36, 128.07, 127.40, 126.55 (d, *J* = 8.1 Hz), 126.21, 125.62, 124.47, 123.79, 114.83, 99.67, 89.96, 77.37, 77.05, 76.73,

69.35, 59.86, 41.79, 40.77, 29.74, 21.60. **FT-IR** (KBr): v = 2984, 1726, 1599, 1361, 1253, 1193, 1104, 1067, 897, 772 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{39}H_{34}O_4$ $[M+Na]^+$: 589.2349, found 589.2353.



Dimethyl 3-methyl-5-phenyl-11-(p-tolylethynyl)-8,10-dihydro-9H-cyclopenta[b]phenanthrene-9,9-dicarboxylate (8c)

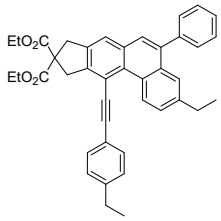
White solid; (388 mg, 72% yield); m. p. 158-160 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.22. **^{1}H NMR** (400 MHz, $CDCl_3$): 10.35 (d, J = 8.7 Hz, 1H; Ar-H), 7.66 (s, 2H; Ar-H), 7.60 (d, J = 7.6 Hz, 2H; Ar-H), 7.56 (s, 1H; Ar-H), 7.53-7.46 (m, 6H; Ar-H), 7.26 (d, J = 8.0 Hz, 2H; Ar-H), 4.04 (s, 2H; $C(COOMe)_2$-CH_2), 3.84 (s, 2H; $C(COOMe)_2$-CH_2), 3.79 (s, 6H; -$C(COOCH_3)_2$), 2.44 (d, J = 12.9 Hz, 6H; Ar-CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.14, 145.13, 140.90, 138.81, 138.55, 137.78, 136.35, 132.04, 132.00, 131.34, 130.02 (d, J = 4.0 Hz), 129.37, 129.08, 128.68, 128.24 (d, J = 22.2 Hz), 127.34, 126.11, 124.26, 120.68, 114.83, 99.98, 89.37, 59.75, 53.17, 41.95, 40.91, 21.65. **FT-IR** (KBr): v = 2952, 1729, 1600, 1362, 1266, 1162, 1072, 967, 821, 774, 701 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{37}H_{30}O_4$ $[M+Na]^+$: 561.2036, found 561.2039.



Diisopropyl 5-phenyl-3-propyl-11-((4-propylphenyl)ethynyl)-8,10-dihydro-9H-cyclopenta[b]phenanthrene-9,9-dicarboxylate (8d)

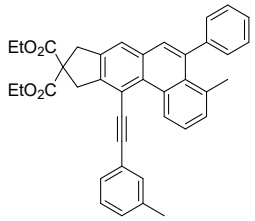
White solid; (482 mg, 74% yield); m. p. 151-153 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.33. **^{1}H NMR** (400 MHz, $CDCl_3$): 10.40 (d, J = 8.7 Hz, 1H; Ar-H), 7.68-7.61 (m, 4H; Ar-H), 7.56-7.48 (m, 6H; Ar-H), 7.46-7.42 (m, 1H; Ar-H), 7.26 (d, J = 7.8 Hz, 2H; Ar-H), 5.13-5.04 (m, 2H; -$C(COOCH)_2$), 4.01 (s, 2H; $C(COO^iPr)_2$-CH_2), 3.80 (s, 2H; $C(COO^iPr)_2$-CH_2), 2.71-2.63 (m, 4H; Ar-CH_2), 1.73-1.62 (m, 4H ; -CH_2-), 1.27 (d, J = 6.4 Hz, 12H; -CH_3), 1.00-0.92 (m, 6H; -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.22, 145.59, 143.52, 141.03, 138.58, 138.15, 132.06 (d, J = 15.2 Hz), 131.37, 130.08, 129.43, 128.74 (d, J = 13.1 Hz), 128.29 (d, J = 15.2 Hz), 127.32, 126.63, 126.20, 125.67, 124.29, 121.13, 114.81, 99.93, 89.55, 69.32, 59.91, 41.85, 40.82, 38.13 (d, J = 4.0 Hz), 24.58 (d, J = 15.2 Hz), 21.62, 13.93 (d, J = 10.1 Hz).

FT-IR (KBr): v = 2959, 1729, 1603, 1510, 1368, 1254, 1190, 1104, 775 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{45}H_{46}O_4$ $[M+Na]^+$: 673.3288, found 673.3293.



Diethyl 3-ethyl-11-((4-ethylphenyl)ethynyl)-5-phenyl-8,10-dihydro-9H-cyclopenta[b]phenanthrene-9,9-dicarboxylate (8e)

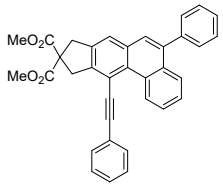
White solid; (451 mg, 76% yield); m. p. 125-128 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.28. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.39 (d, J = 8.8 Hz, 1H; Ar-H), 7.69 (s, 1H; Ar-H), 7.66 (s, 1H; Ar-H), 7.63 (d, J = 8.2 Hz, 2H; Ar-H), 7.57 (s, 1H; Ar-H), 7.54-7.52 (m, 5H; Ar-H), 7.50-7.46 (m, 1H; Ar-H), 7.29 (d, J = 8.1 Hz, 2H; Ar-H), 4.25 (q, J = 7.1 Hz, 4H; -C($COOCH_2$)$_2$), 4.03 (s, 2H; C($COOEt$)$_2$-CH_2), 3.84 (s, 2H; C($COOEt$)$_2$-CH_2), 2.79-2.70 (m, 4H; Ar-CH_2), 1.31-1.24 (m, 12H; -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.68, 145.37, 145.06, 142.54, 140.94, 138.59, 137.96, 132.01 (d, J = 7.1 Hz), 131.44, 130.03, 129.33, 128.65, 128.23 (d, J = 15.2 Hz), 127.29, 126.16 (d, J = 18.2 Hz), 124.96, 124.24, 121.00, 114.79, 99.91, 89.40, 77.35, 77.03, 76.71, 61.88, 59.81, 41.85, 40.82, 28.94, 15.55 (d, J = 14.1 Hz), 14.07. **FT-IR** (KBr): v = 2963, 1730, 1600, 1366, 1247, 1186, 1150, 1071, 832, 774, 704 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{41}H_{38}O_4$ $[M+Na]^+$: 617.2662, found 617.2666.



Diethyl 4-methyl-5-phenyl-11-(m-tolylethynyl)-8,10-dihydro-9H-cyclopenta[b]phenanthrene-9,9-dicarboxylate (8f)

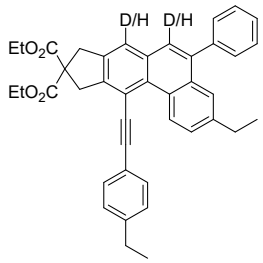
White solid; (414 mg, 73% yield); m. p. 120-123 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.29. **^{1}H NMR** (400 MHz, $CDCl_3$): 10.32 (t, J = 8.6 Hz, 1H; Ar-H), 7.64 (d, J = 21.52 Hz, 1H; Ar-H), 7.57-7.49 (m, 5H; Ar-H), 7.46-7.36 (m, 5H; Ar-H), 7.35-7.31 (m, 1H; Ar-H), 7.22 (d, J = 7.6 Hz, 1H; Ar-H), 4.29-4.23 (m, 4H; -C($COOCH_2$)$_2$), 4.05 (d, J = 6.2 Hz, 2H; C($COOEt$)$_2$-CH_2), 3.84 (d, J = 5.0 Hz, 2H; C($COOMe$)$_2$-CH_2), 2.63 (s, 1H; Ar-CH_3), 2.43 (s, 3H; Ar-CH_3), 2.05 (s, 2H; Ar-CH_3), 1.31-1.25 (m, 6H; -CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.68, 145.65, 145.17, 140.88, 138.53, 138.31 (d, J = 5.1 Hz), 135.40, 132.35, 131.99 (d, J = 4.0 Hz), 131.59, 130.86, 130.64 (d, J = 9.1 Hz), 130.03, 129.40 (d, J = 9.1 Hz), 129.20, 128.52 (d, J = 10.1 Hz), 128.32, 127.91, 127.34, 126.77, 126.45, 126.15, 125.06, 124.74,

123.83, 123.61, 114.96 (d, J = 14.1 Hz), 99.92 (d, J = 5.1 Hz), 89.75 (d, J = 12.1 Hz), 61.93, 59.82 (d, J = 4.0 Hz), 41.91 (d, J = 11.1 Hz), 40.81 (d, J = 4.0 Hz), 25.73, 22.24, 21.38, 14.10, 1.05. **FT-IR** (KBr): v = 2980, 1730, 1596, 1446, 1365, 1252, 1190, 1073, 776, 705 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{39}H_{34}O_4$ $[M+Na]^+$: 589.2349, found 589.2351.



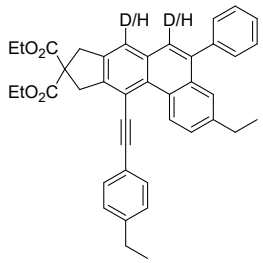
Dimethyl 5-phenyl-11-(phenylethynyl)-8,10-dihydro-9H-cyclopenta[b]phenanthrene-9,9-dicarboxylate (8g)

White solid; (419 mg, 82% yield); m. p. 167-170 °C; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.32. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.45 (d, J = 8.6 Hz, 1H; Ar-H), 7.90 (d, J = 8.2 Hz, 1H; Ar-H), 7.73-7.68 (m, 3H; Ar-H), 7.67-7.64 (m, 1H; Ar-H), 7.60 (s, 1H; Ar-H), 7.56-7.49 (m, 5H; Ar-H), 7.48-7.42 (m, 4H; Ar-H), 4.06 (s, 2H; $C(COOMe)_2$-CH_2), 3.86 (s, 2H; $C(COOMe)_2$-CH_2), 3.80 (s, 6H; -$C(COOCH_3)_2$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ172.08, 145.42, 140.69, 138.90, 138.30, 132.42, 131.89, 131.48, 131.18, 130.05, 128.64 (d, J = 4.0 Hz), 128.36, 128.00, 127.43, 126.60 (d, J = 5.1 Hz), 126.19, 125.67, 124.50, 123.68, 114.91, 99.88, 89.87, 59.75, 53.18, 41.97, 40.92. **FT-IR** (KBr): v = 2951, 1737, 1599, 1434, 1364, 1252, 1152, 1071, 774, 697 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{35}H_{26}O_4$ $[M+Na]^+$: 533.1723, found 533.1726.



8e+CD_3CN

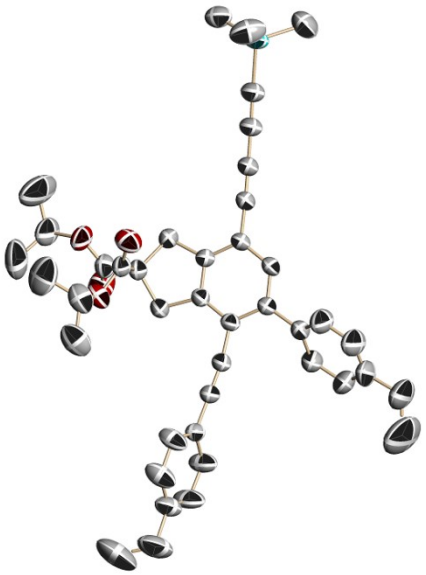
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (d, J = 8.8 Hz, 1H; Ar-H), 7.69 (s, 1H; Ar-H), 7.66 (s, 0.47H; Ar-H), 7.63 (d, J = 8.2 Hz, 2H; Ar-H), 7.57 (s, 0.24H; Ar-H), 7.54-7.52 (m, 5H; Ar-H), 7.50-7.46 (m, 1H; Ar-H), 7.29 (d, J = 8.1 Hz, 2H; Ar-H), 4.25 (q, J = 7.0 Hz, 4H; -$C(COOCH_2)_2$), 4.03 (s, 2H; $C(COOEt)_2$-CH_2), 3.84 (s, 2H; $C(COOEt)_2$-CH_2), 2.79-2.70 (m, 4H; Ar-CH_2), 1.32-1.24 (m, 12H; -CH_3).



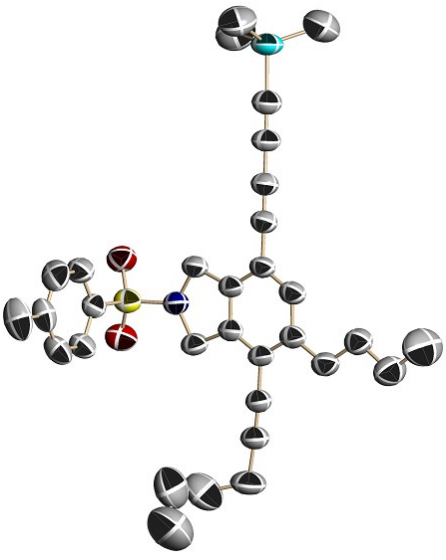
8e+D_2O

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (d, J = 8.7 Hz, 1H; Ar-H), 7.69 (s, 1H; Ar-H), 7.66 (s, 0.6H; Ar-H), 7.63 (d, J = 7.9 Hz, 2H; Ar-H), 7.57 (s, 0.36H; Ar-H), 7.54-7.52 (m, 5H; Ar-H), 7.50-7.46 (m, 1H; Ar-H), 7.29 (d, J = 7.9 Hz, 2H; Ar-H), 4.25 (q, J = 7.1 Hz, 4H; -C($COOCH_2$)$_2$), 4.03 (s, 2H; C($COOEt$)$_2$-CH_2), 3.84 (s, 2H; C($COOEt$)$_2$-CH_2), 2.79-2.70 (m, 4H; Ar-CH_2), 1.31-1.24 (m, 12H; -CH_3).

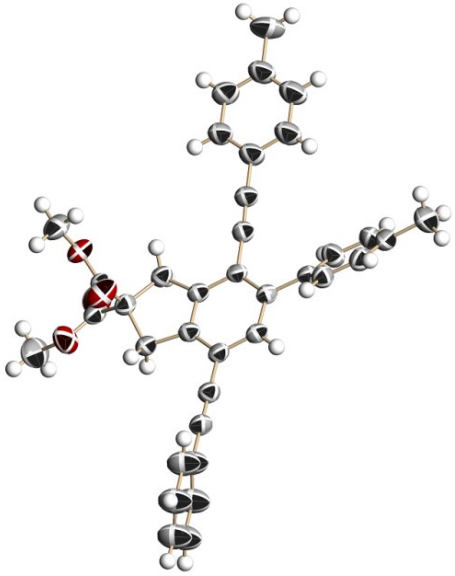
3. X-Ray Structure for 3l, 3o, 6c and 8g



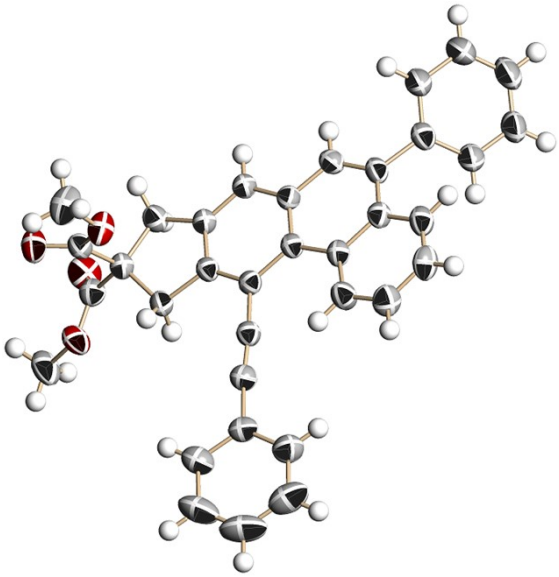
3l



3o



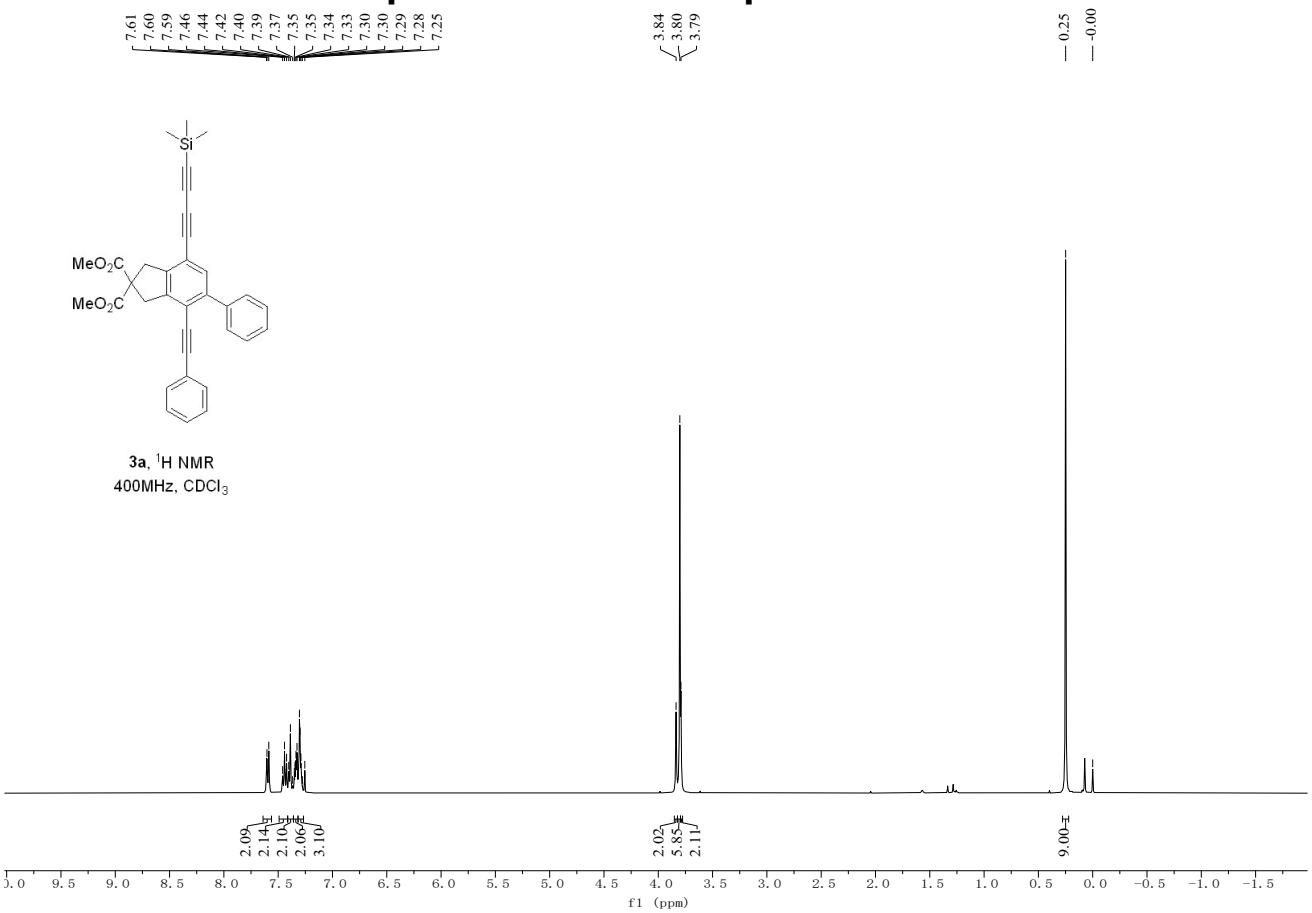
6c



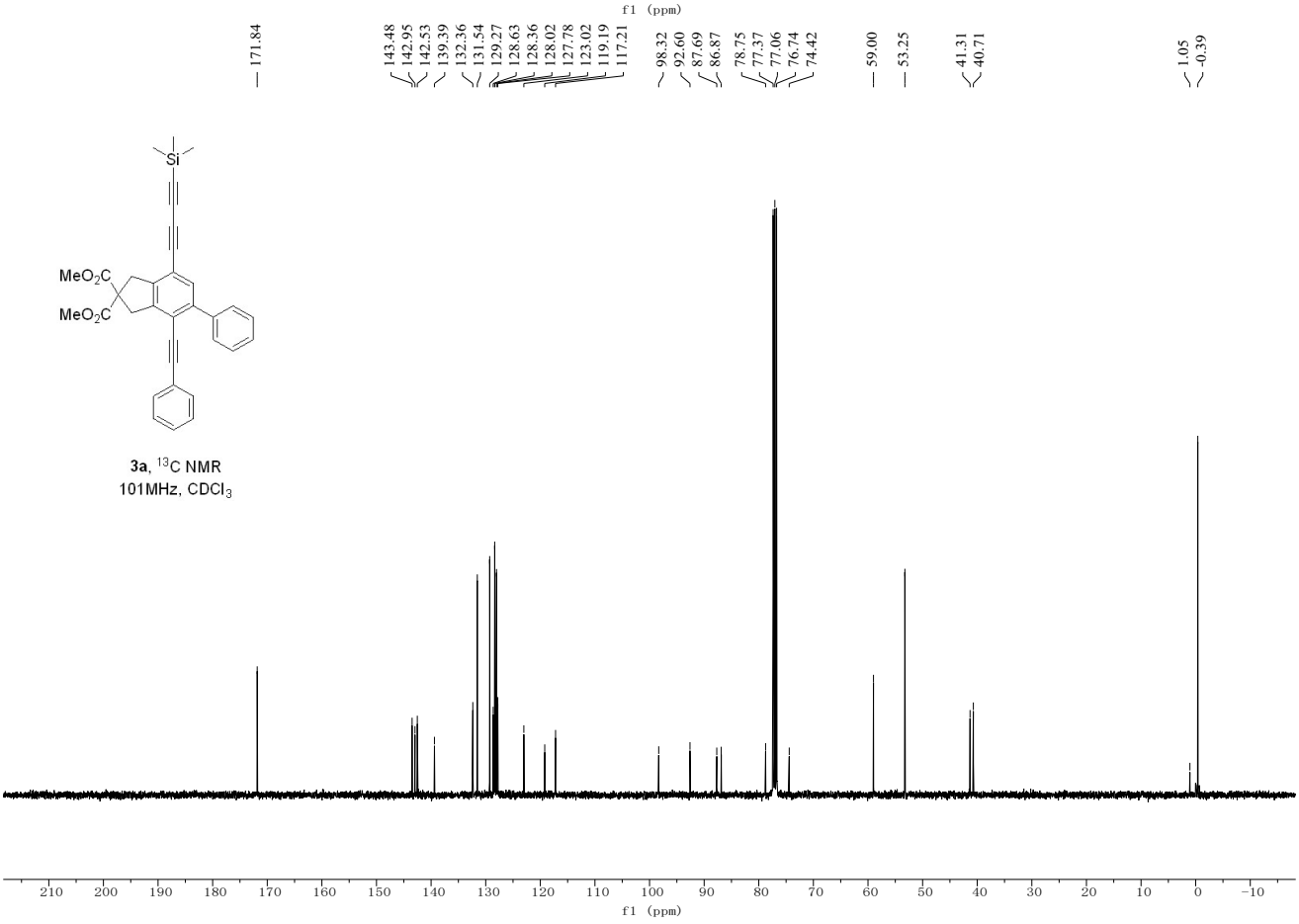
8g

All X-Ray structures were tested at room temperature. The low quality of X-ray diffraction data which led to high R values and low bond precision.

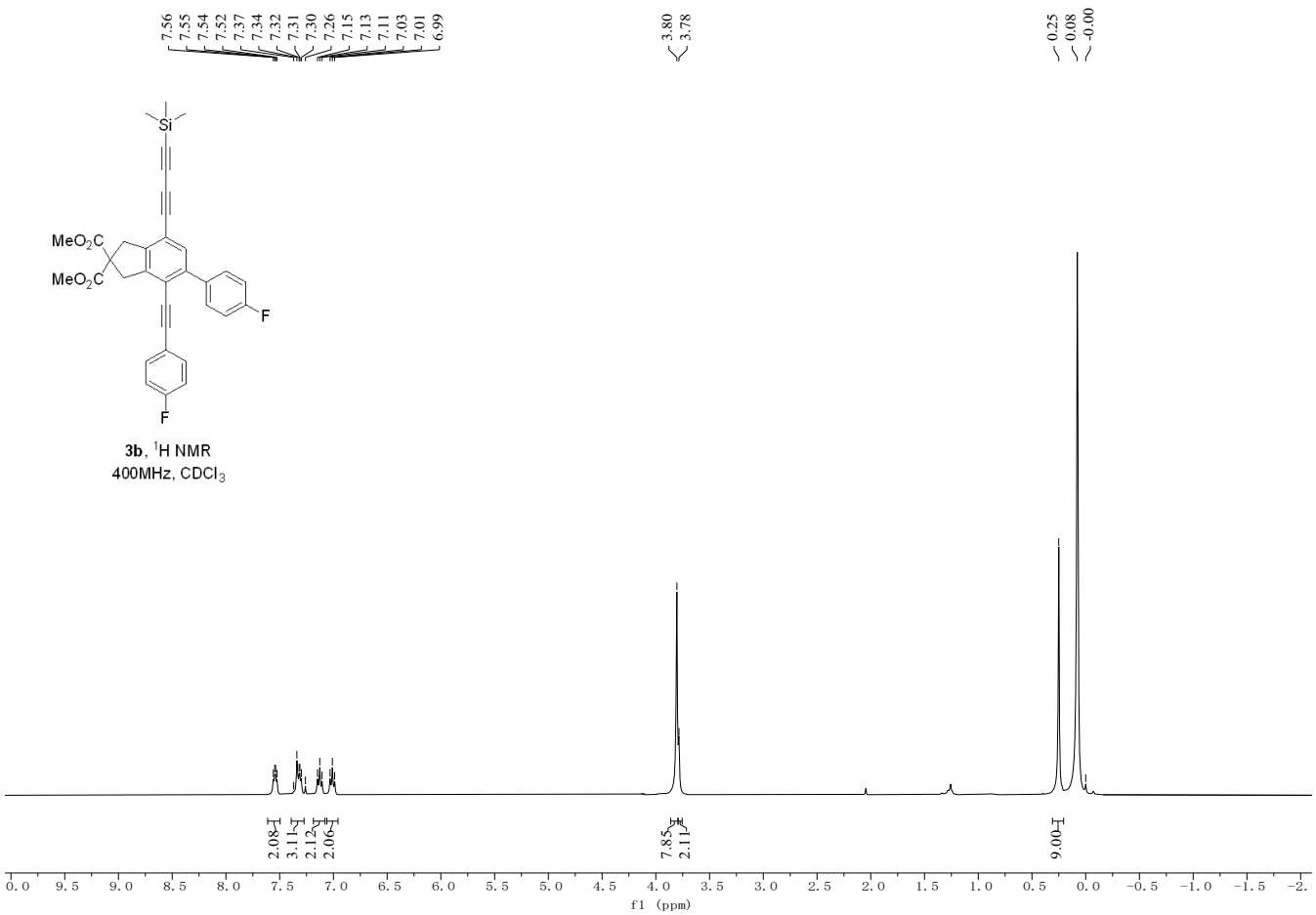
4. ^{1}H NMR & ^{13}C NMR Spectra for New Compounds



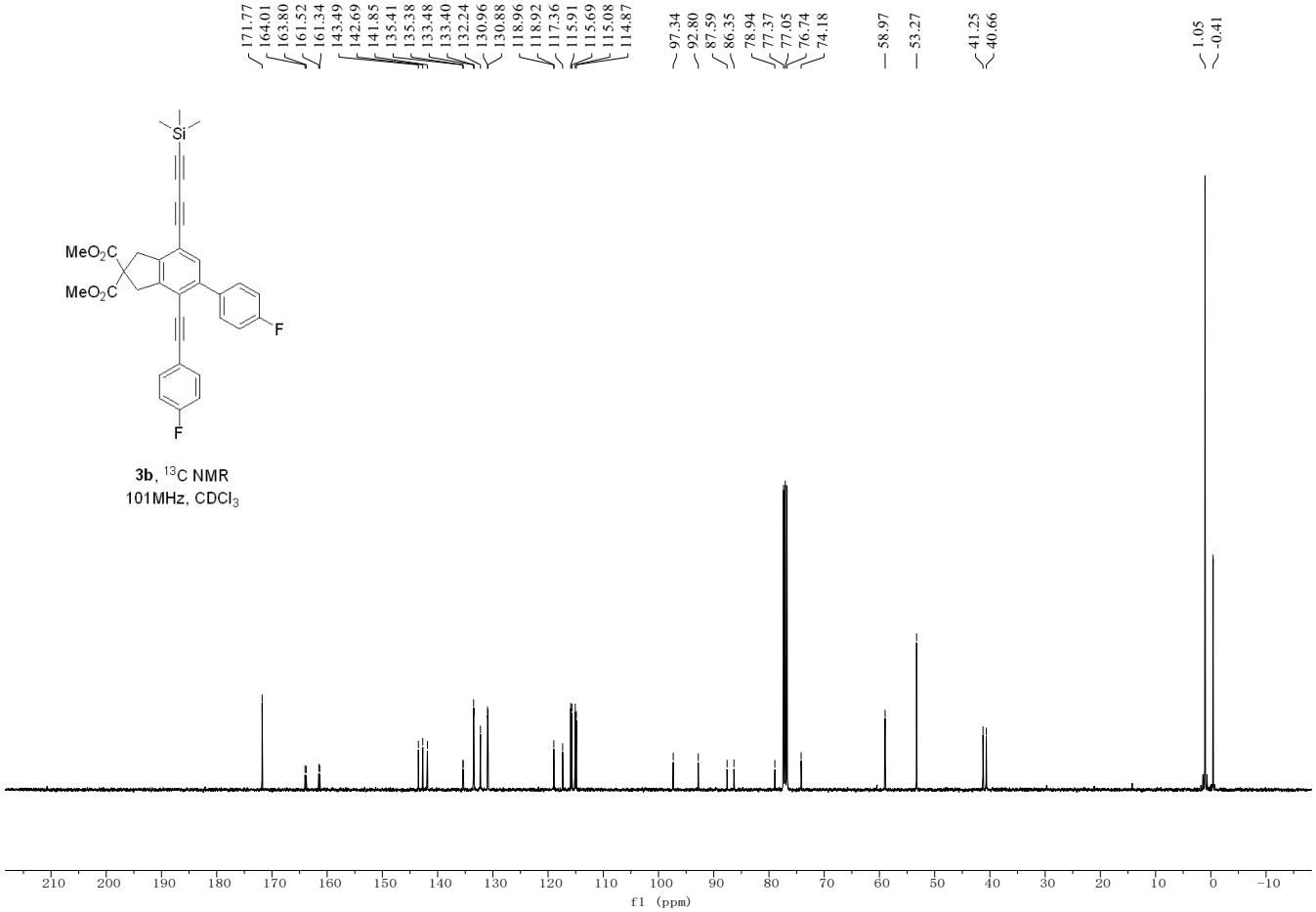
3a, ^{1}H NMR
400MHz, $CDCl_3$



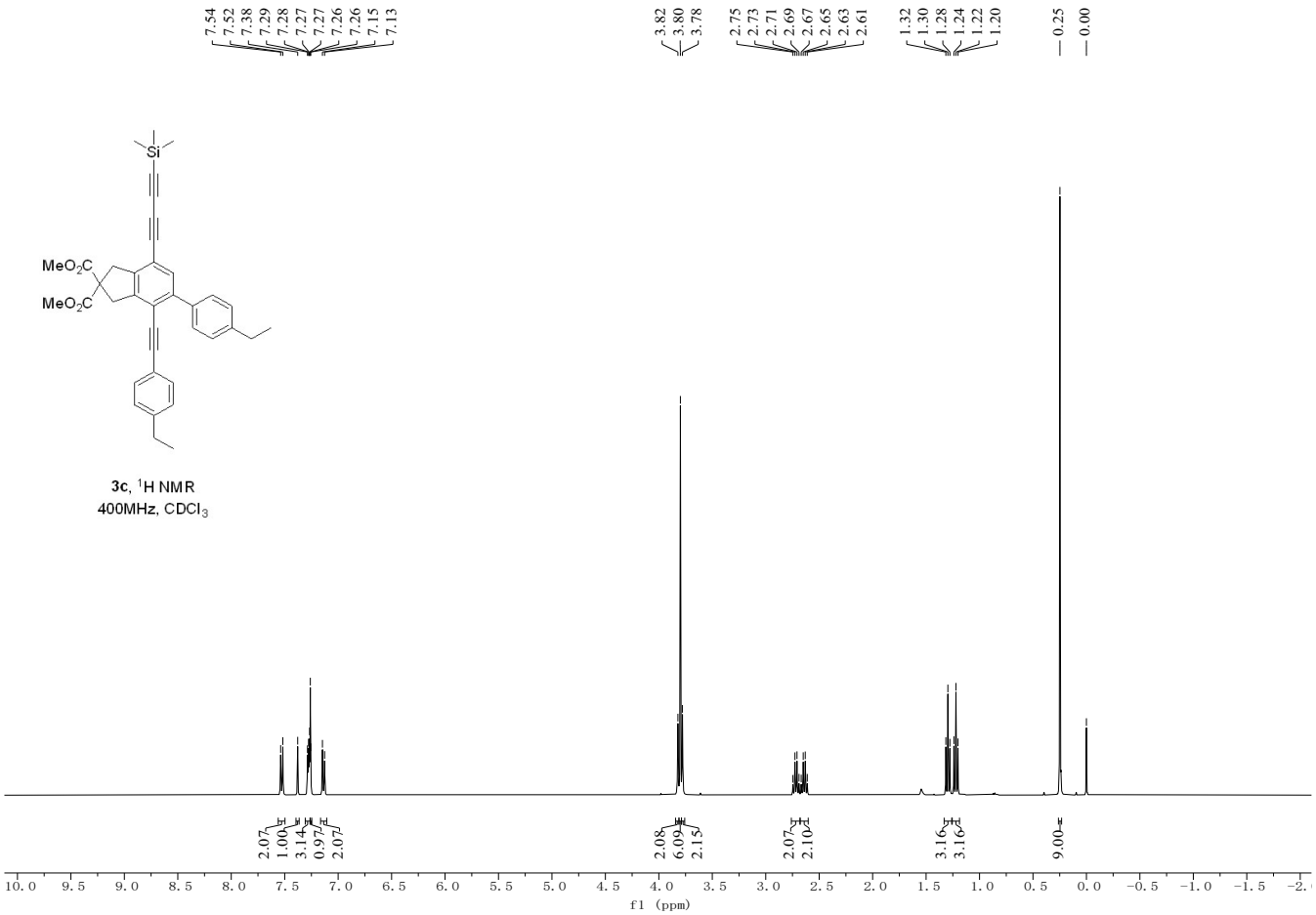
3a, ^{13}C NMR
101MHz, $CDCl_3$



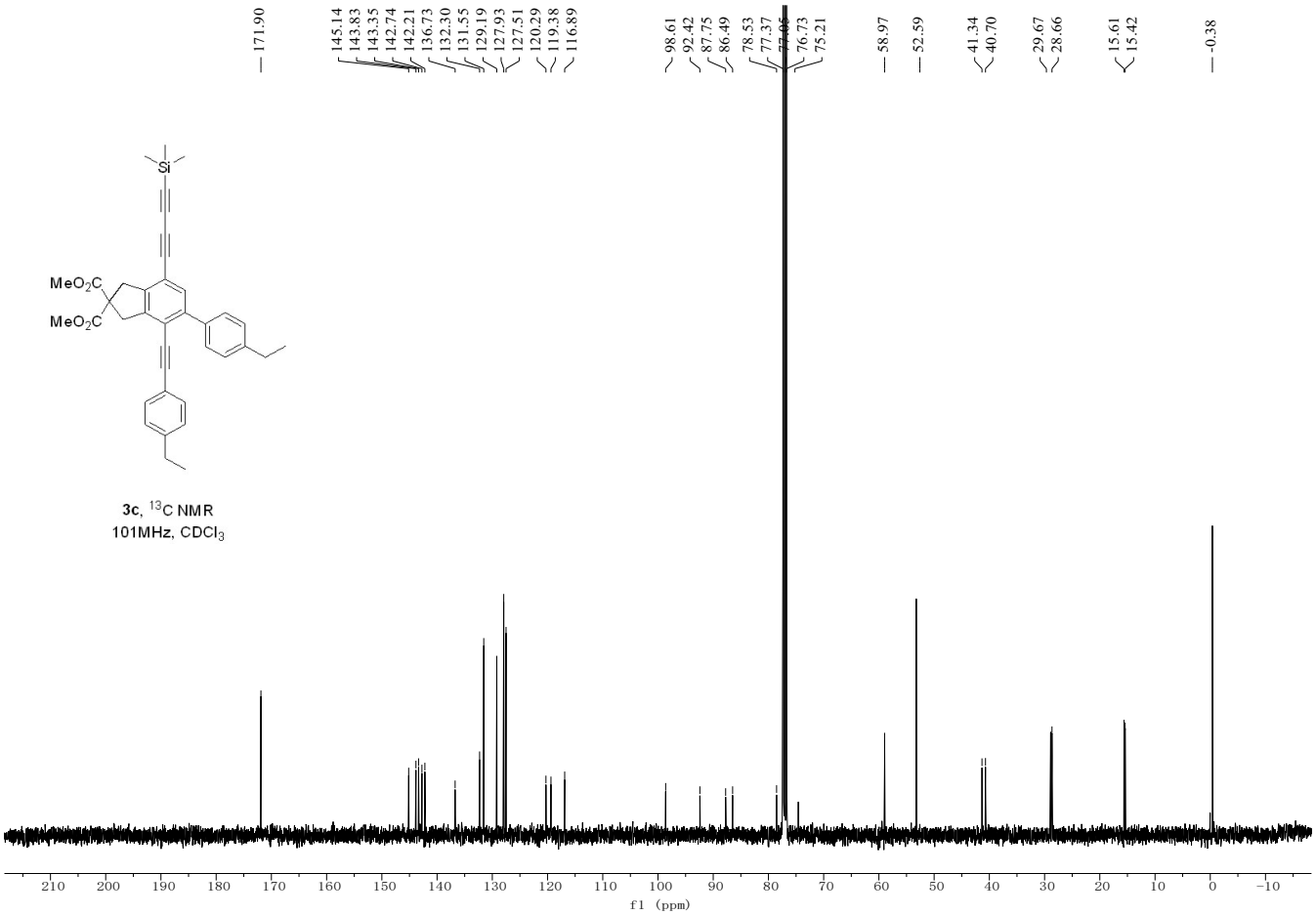
3b, ^{1}H NMR
400MHz, $CDCl_3$



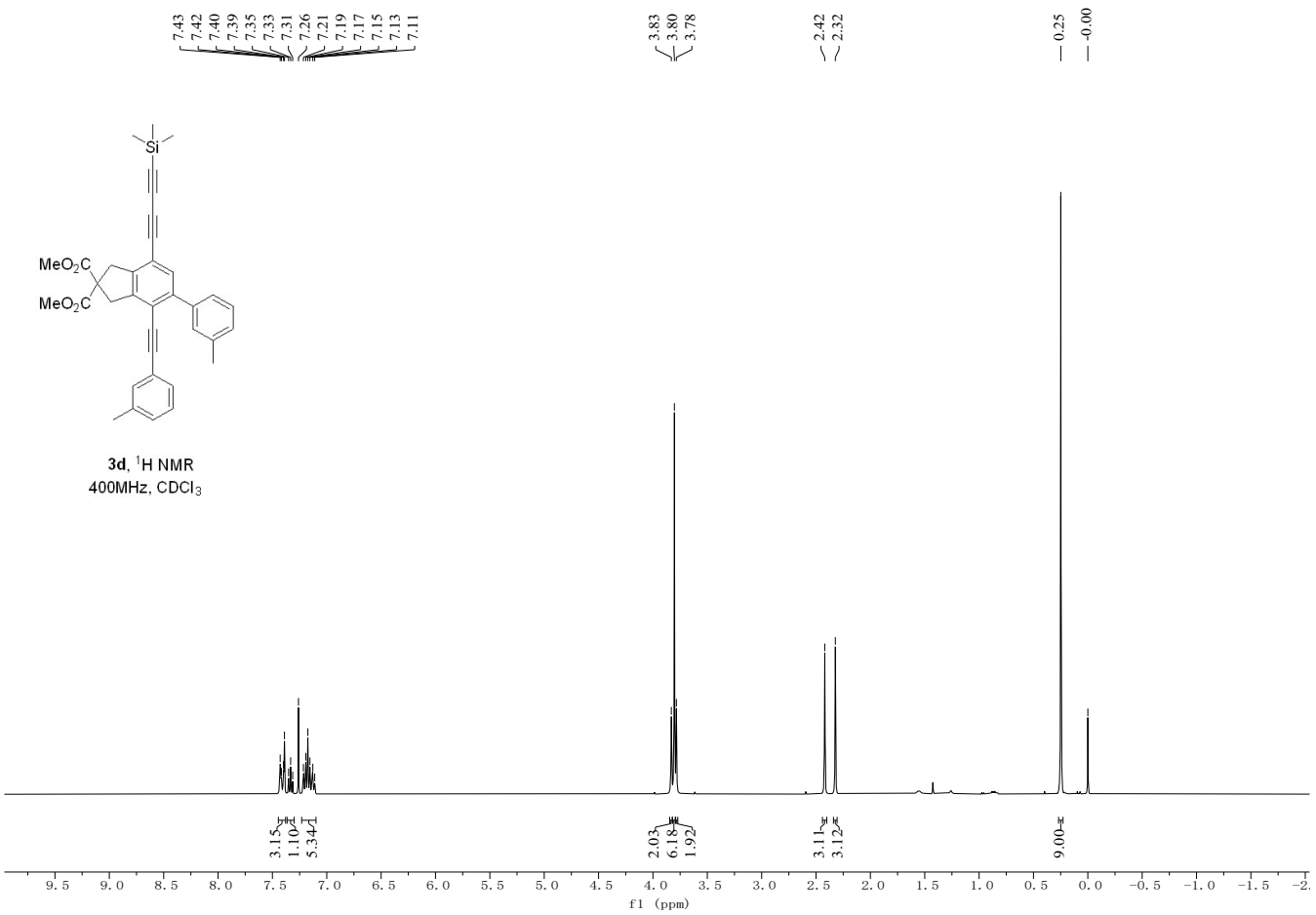
3b, ^{13}C NMR
101MHz, $CDCl_3$



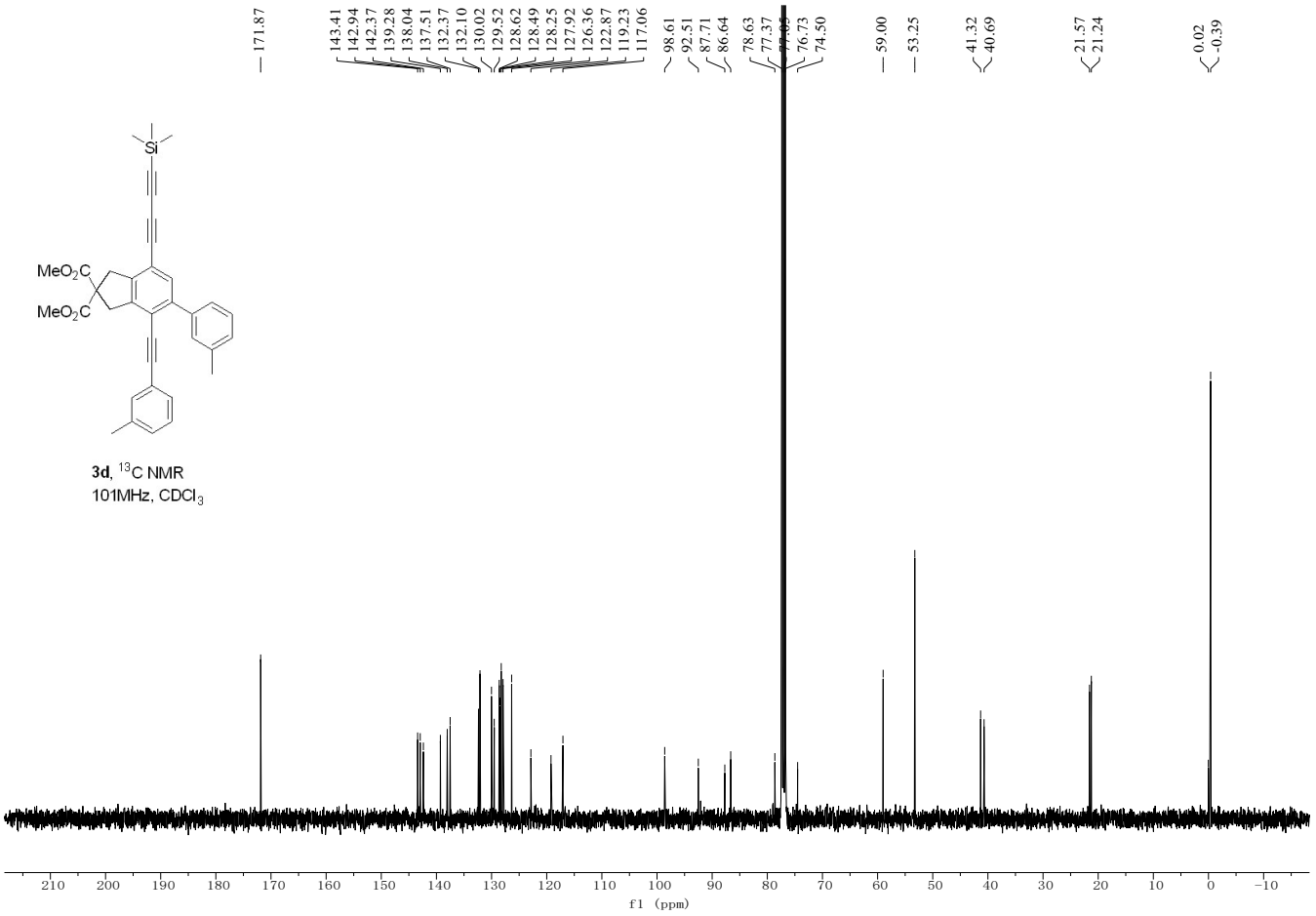
3c, ^{1}H NMR
400MHz, $CDCl_3$



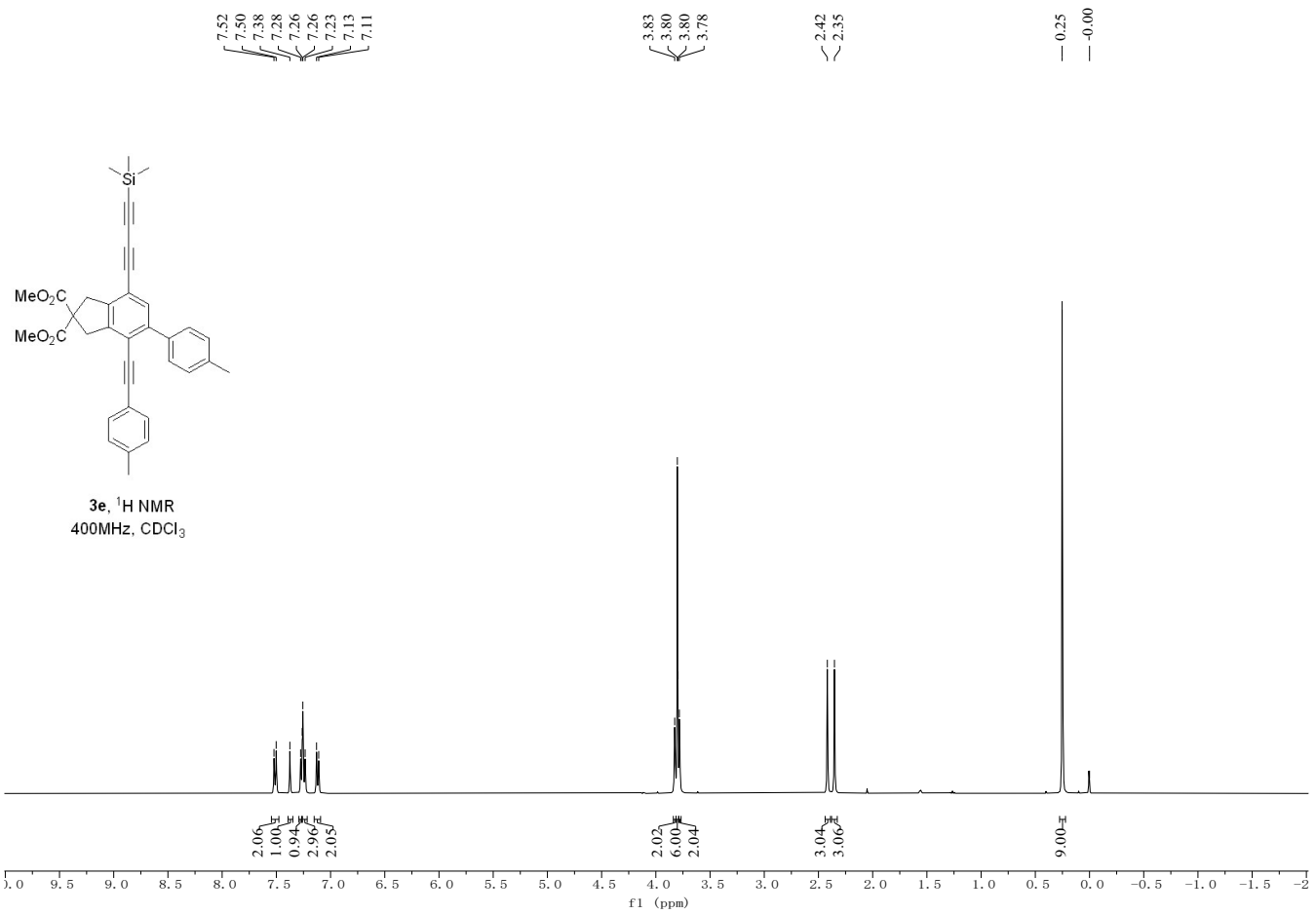
3c, ^{13}C NMR
101MHz, $CDCl_3$



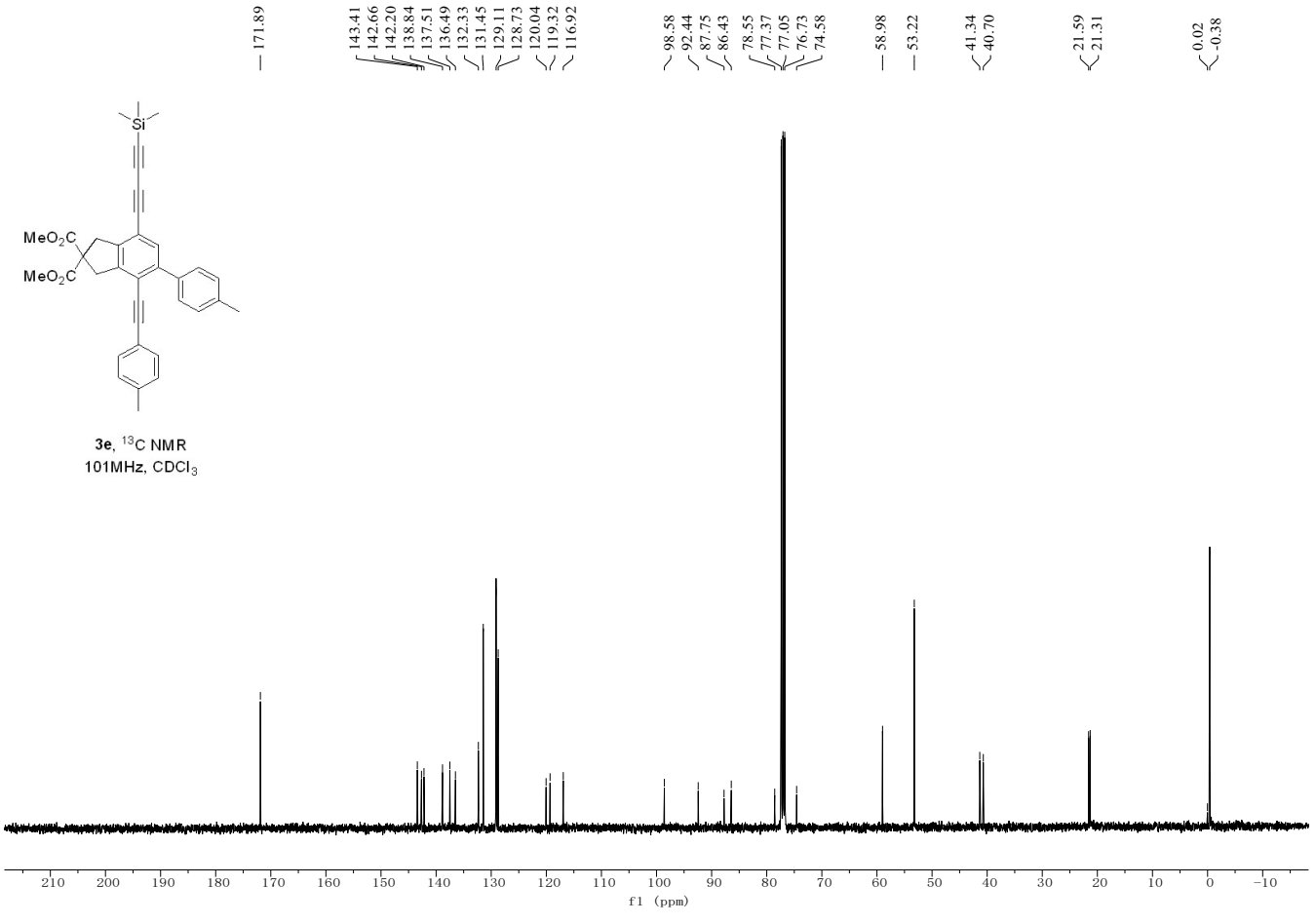
3d, ^{1}H NMR
400MHz, $CDCl_3$



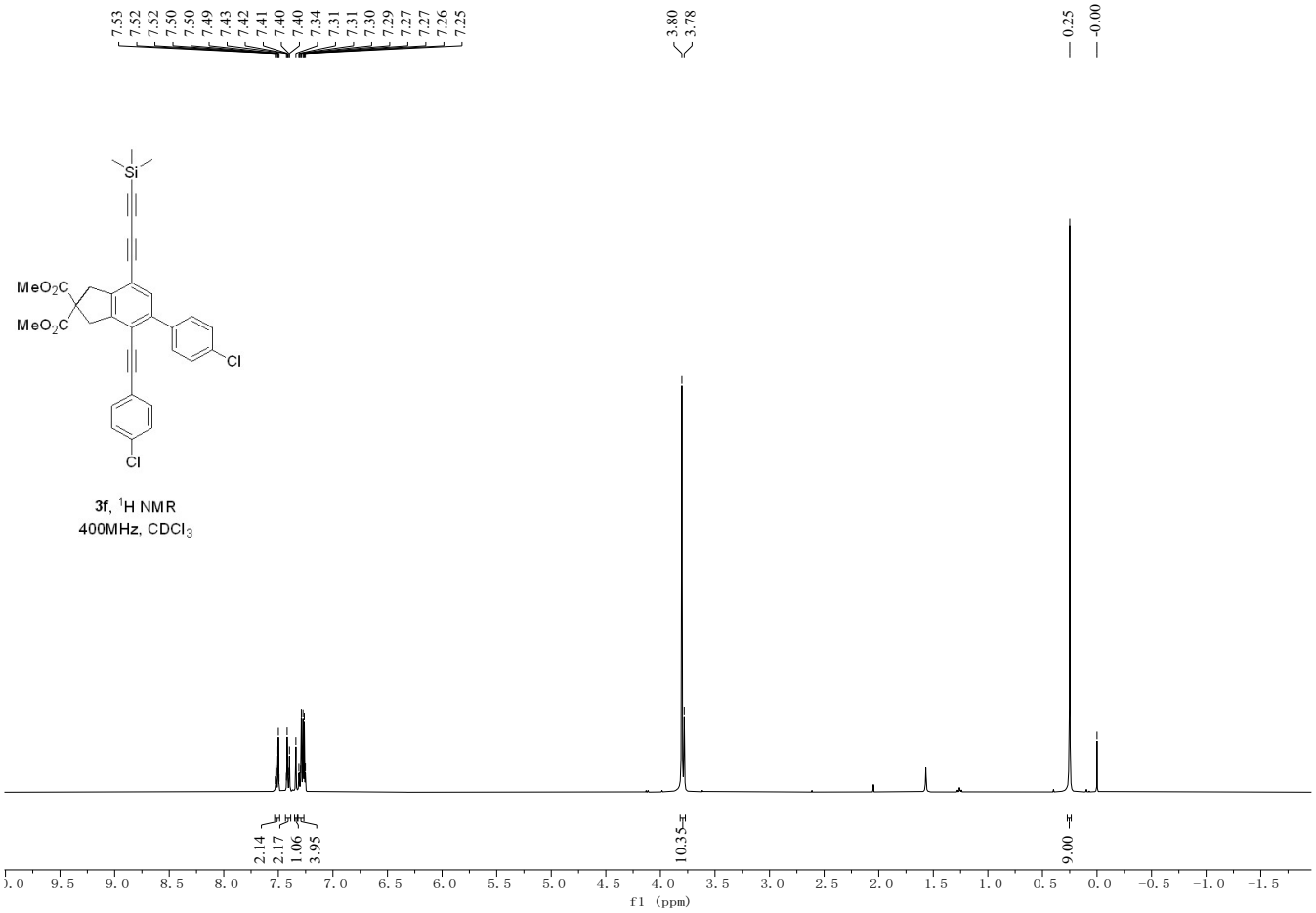
3d, ^{13}C NMR
101MHz, $CDCl_3$



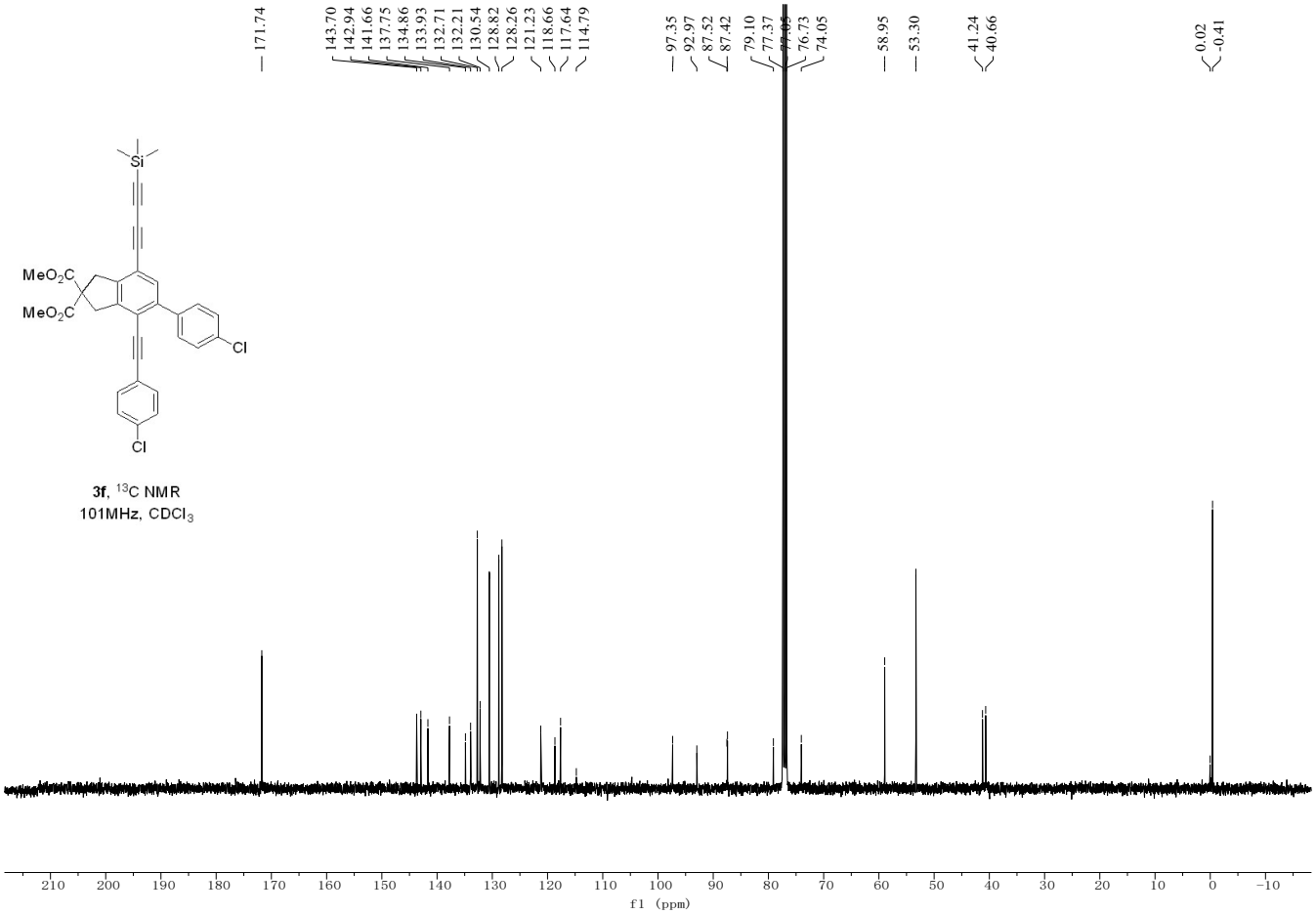
3e, ^{1}H NMR
400MHz, $CDCl_3$



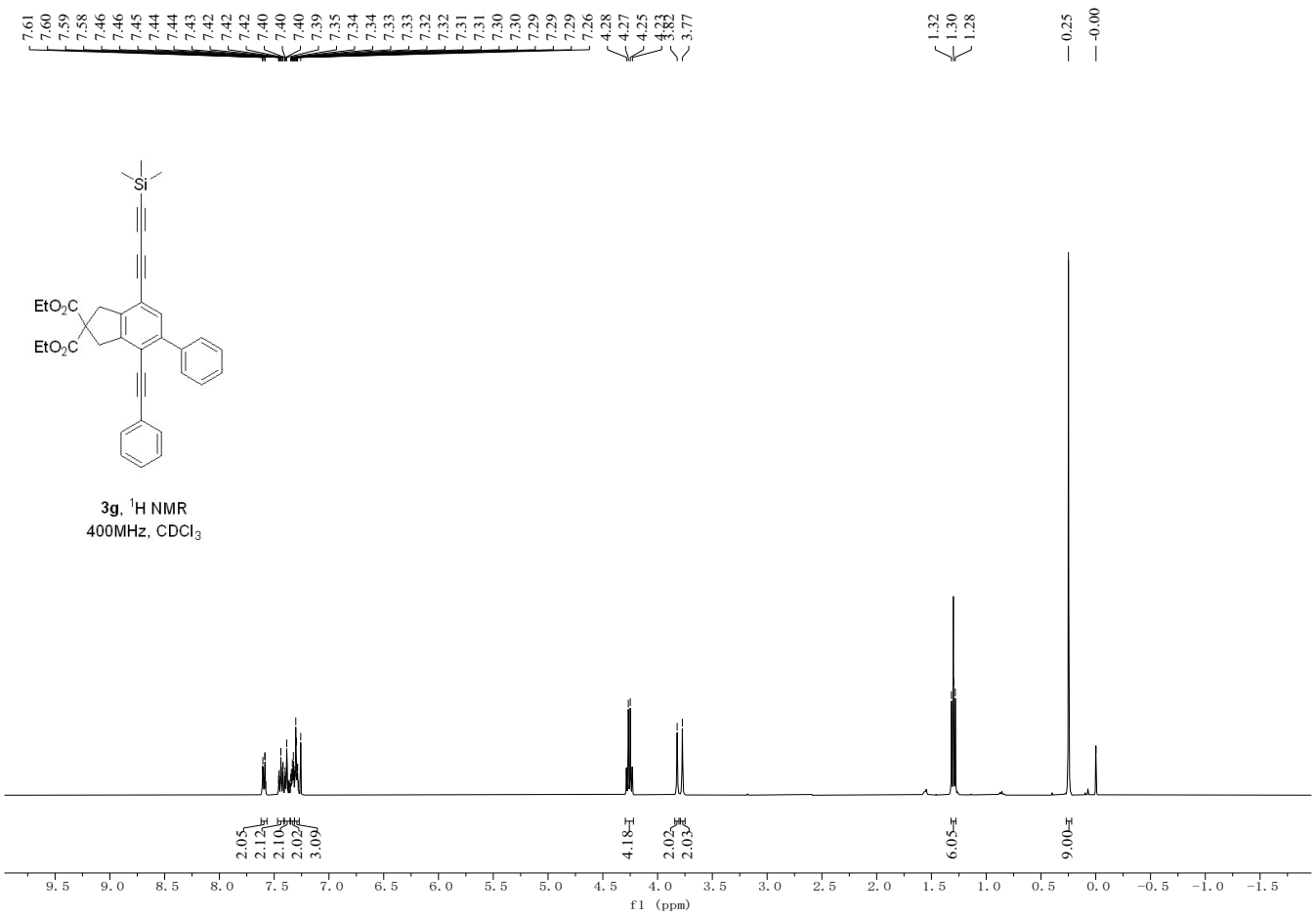
3e, ^{13}C NMR
101MHz, $CDCl_3$

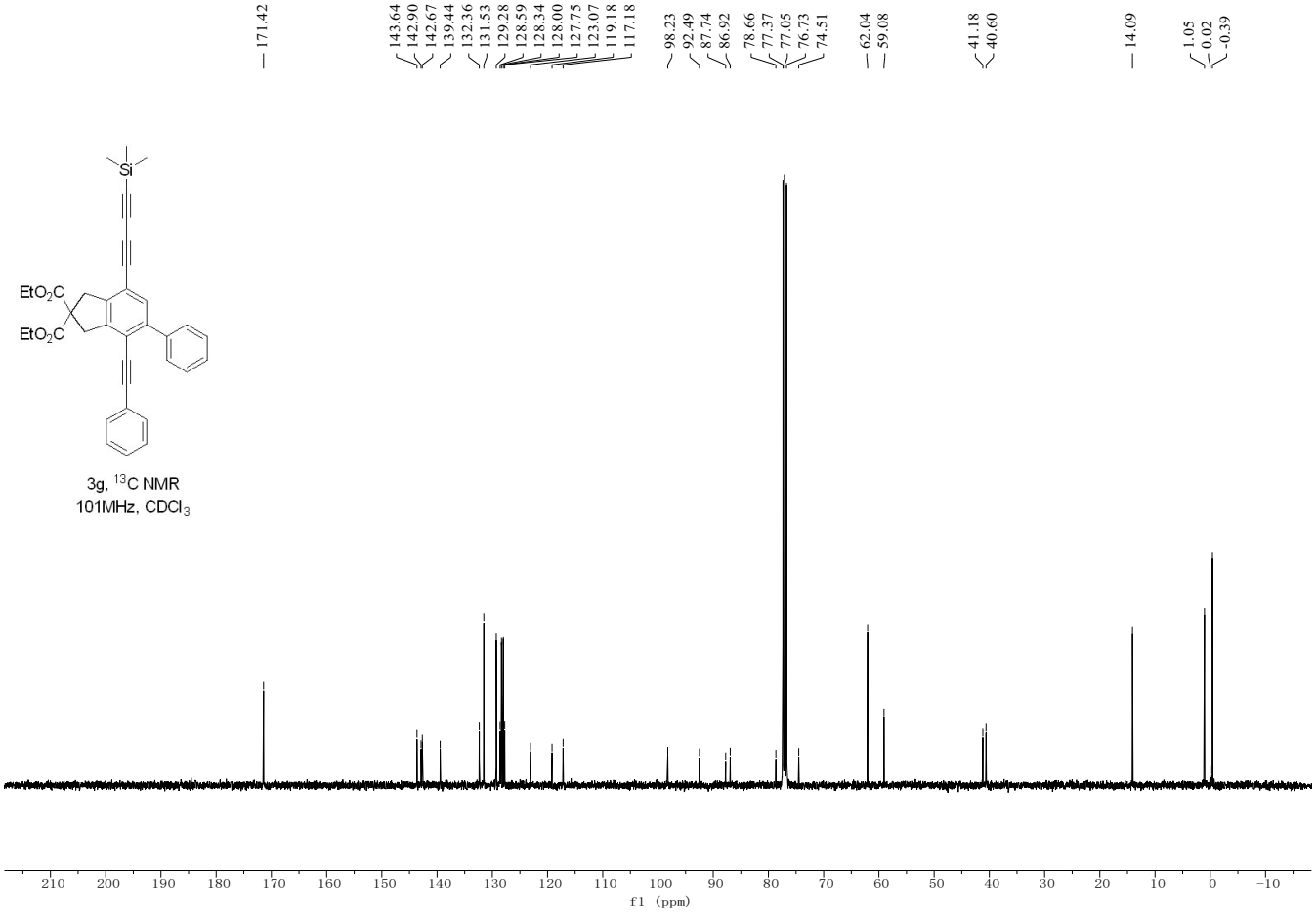


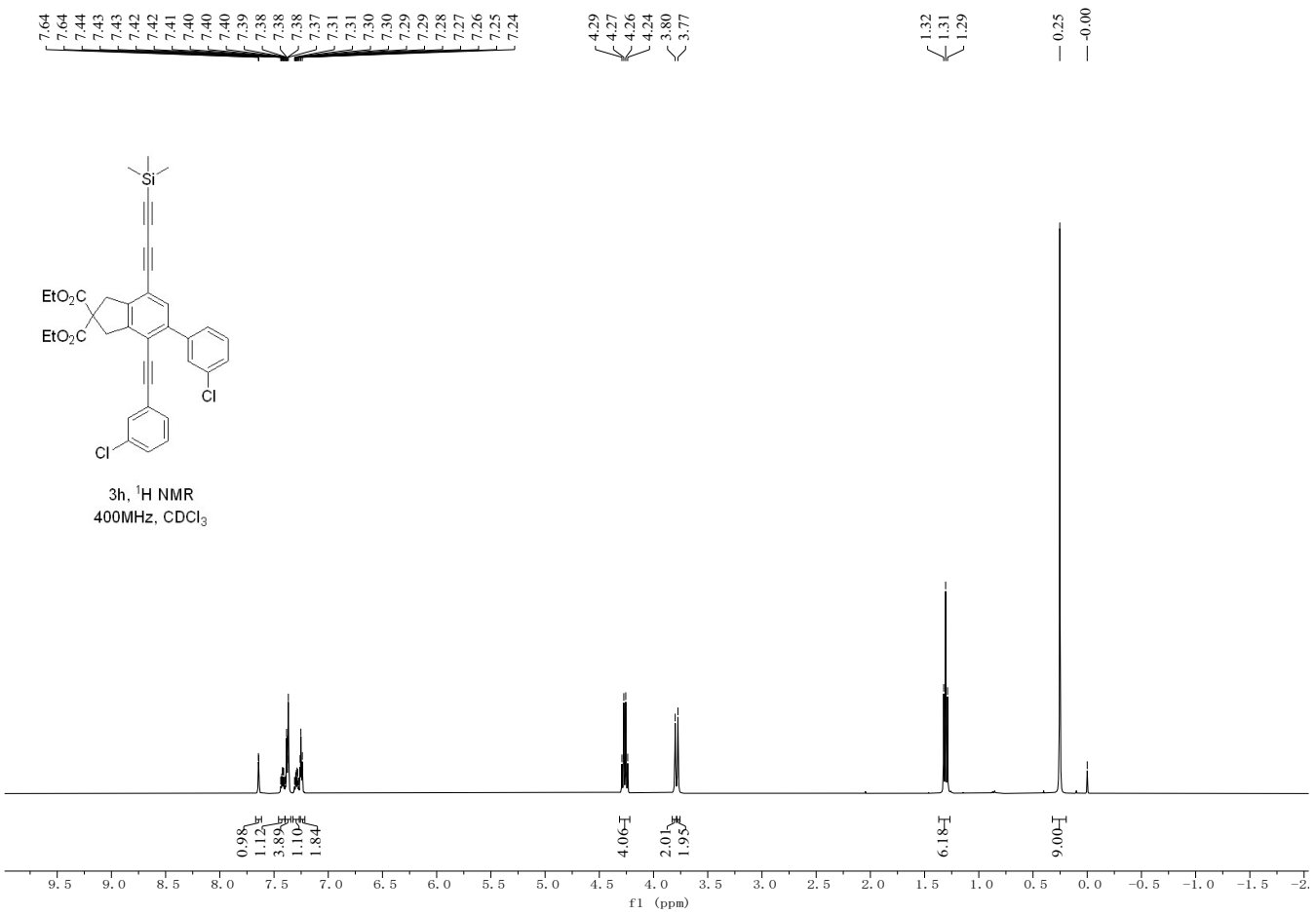
3f, ^{1}H NMR
400MHz, $CDCl_3$

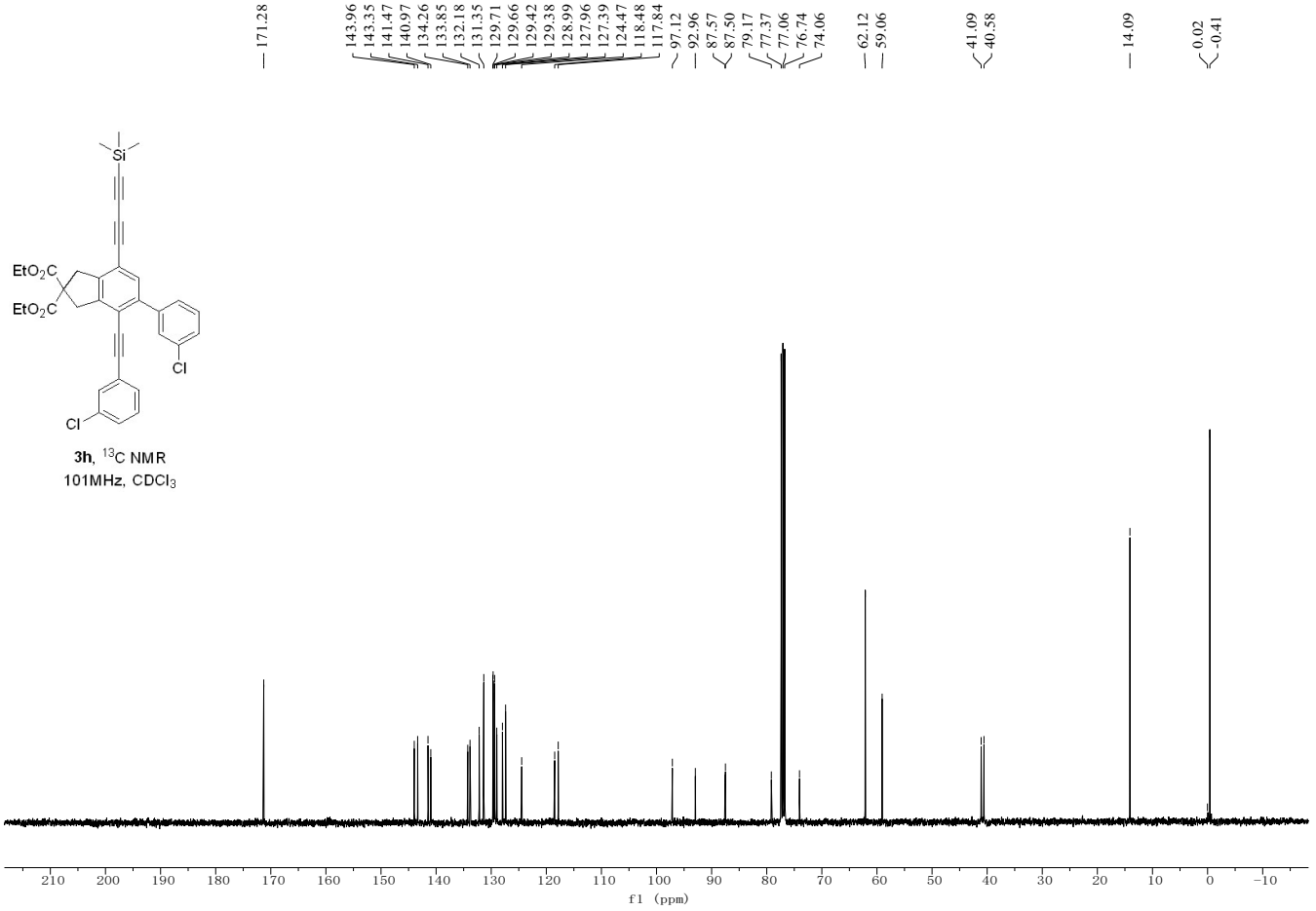


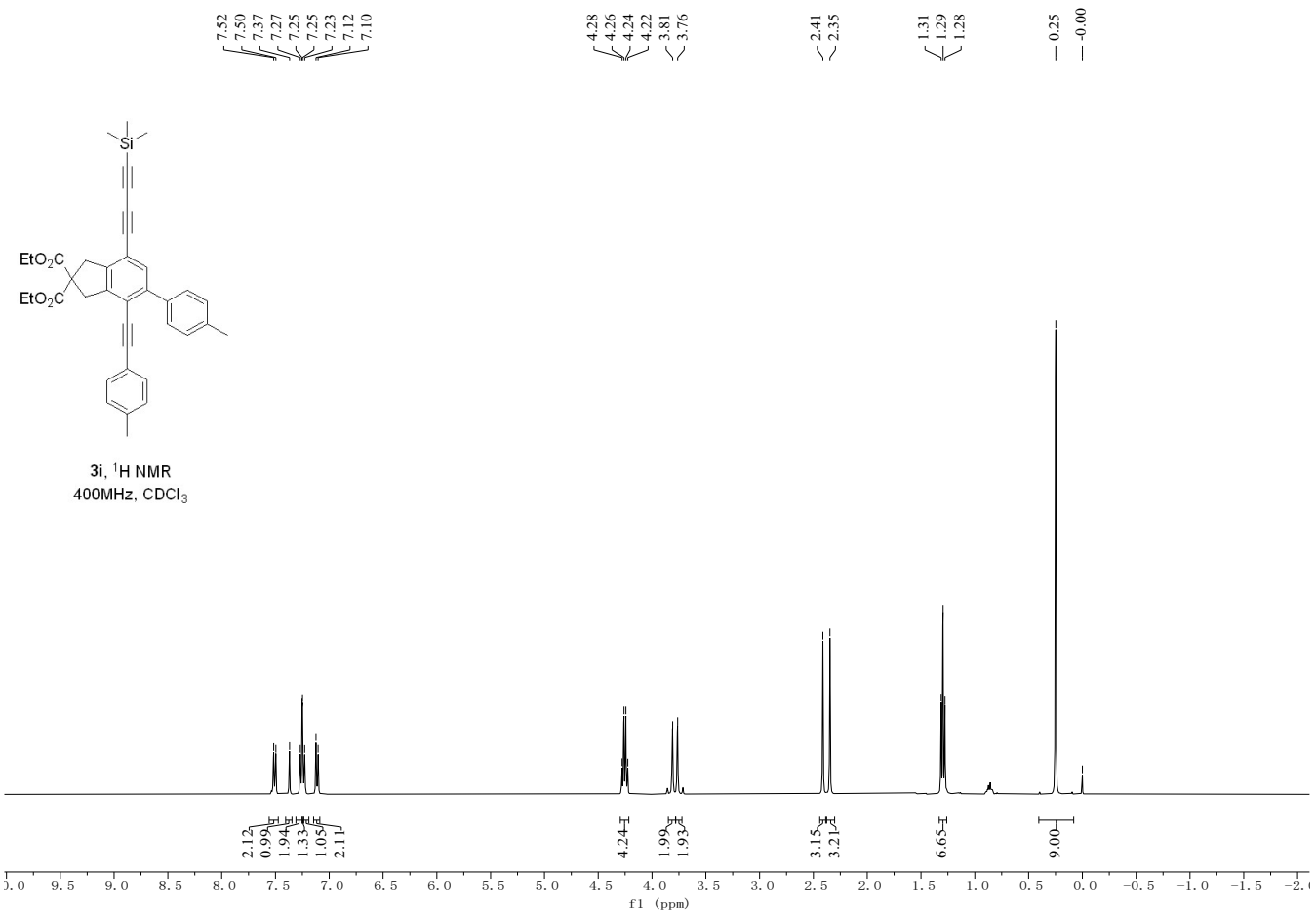
3f, ^{13}C NMR
101MHz, $CDCl_3$


Si
EtO2C
EtO2C
3g, 1H NMR
400MHz, CDCl3
f1 (ppm)

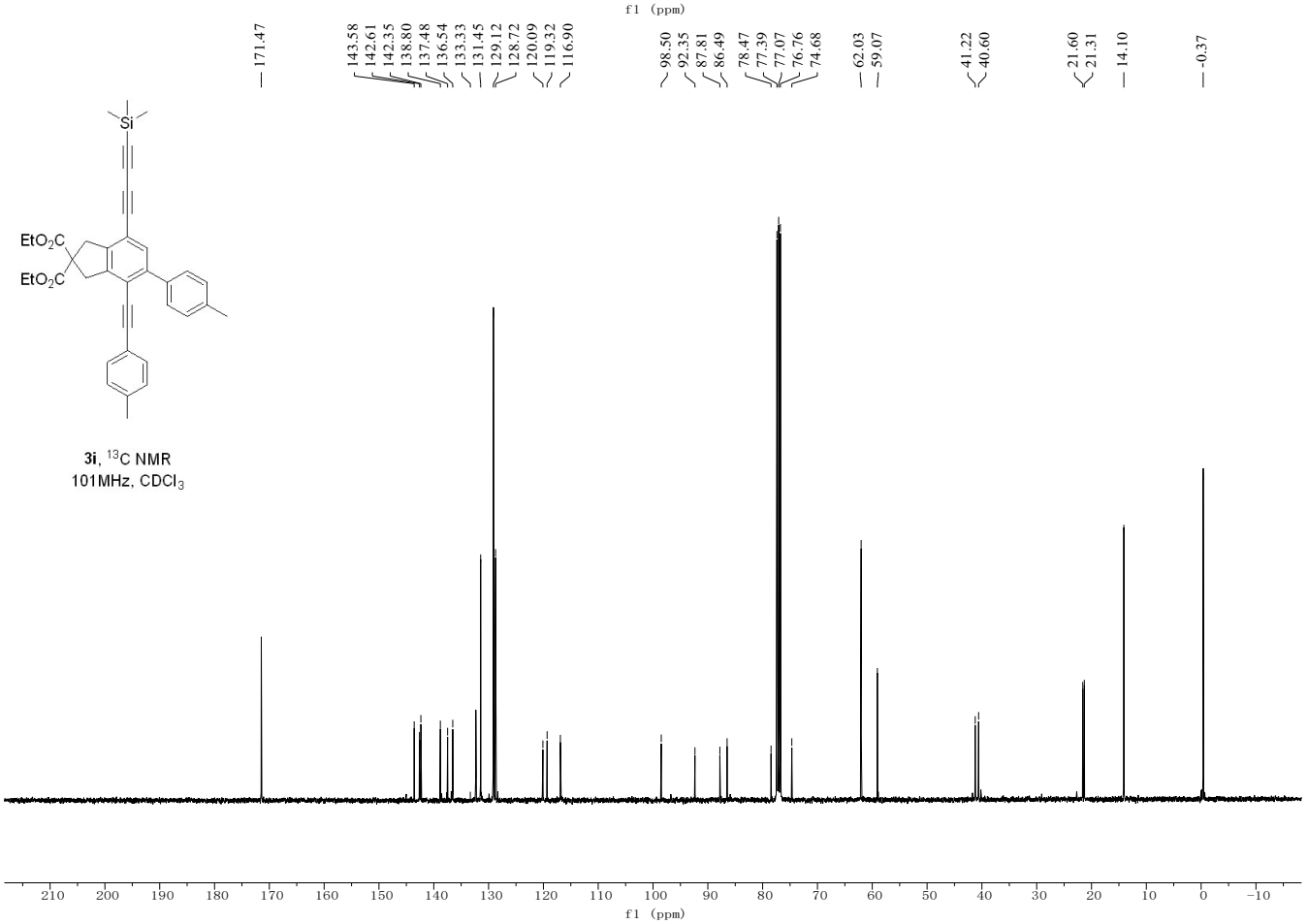

Si
EtO2C
EtO2C
3g, 13C NMR
101MHz, CDCl3
f1 (ppm)


7.64 7.64 7.44 7.43 7.43 7.42 7.42 7.41 7.40 7.40 7.40 7.39 7.38 7.38 7.38 7.37 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.26 7.25 7.24
4.29 4.27 4.26 4.24 3.80 3.77
1.32 1.31 1.29
0.25 -0.00
Si
EtO2C
EtO2C
Cl
Cl
3h, 1H NMR
400MHz, CDCl3
0.98 1.12 3.89 1.10 1.84 4.06 2.01 1.95 6.18 9.00
f1 (ppm)

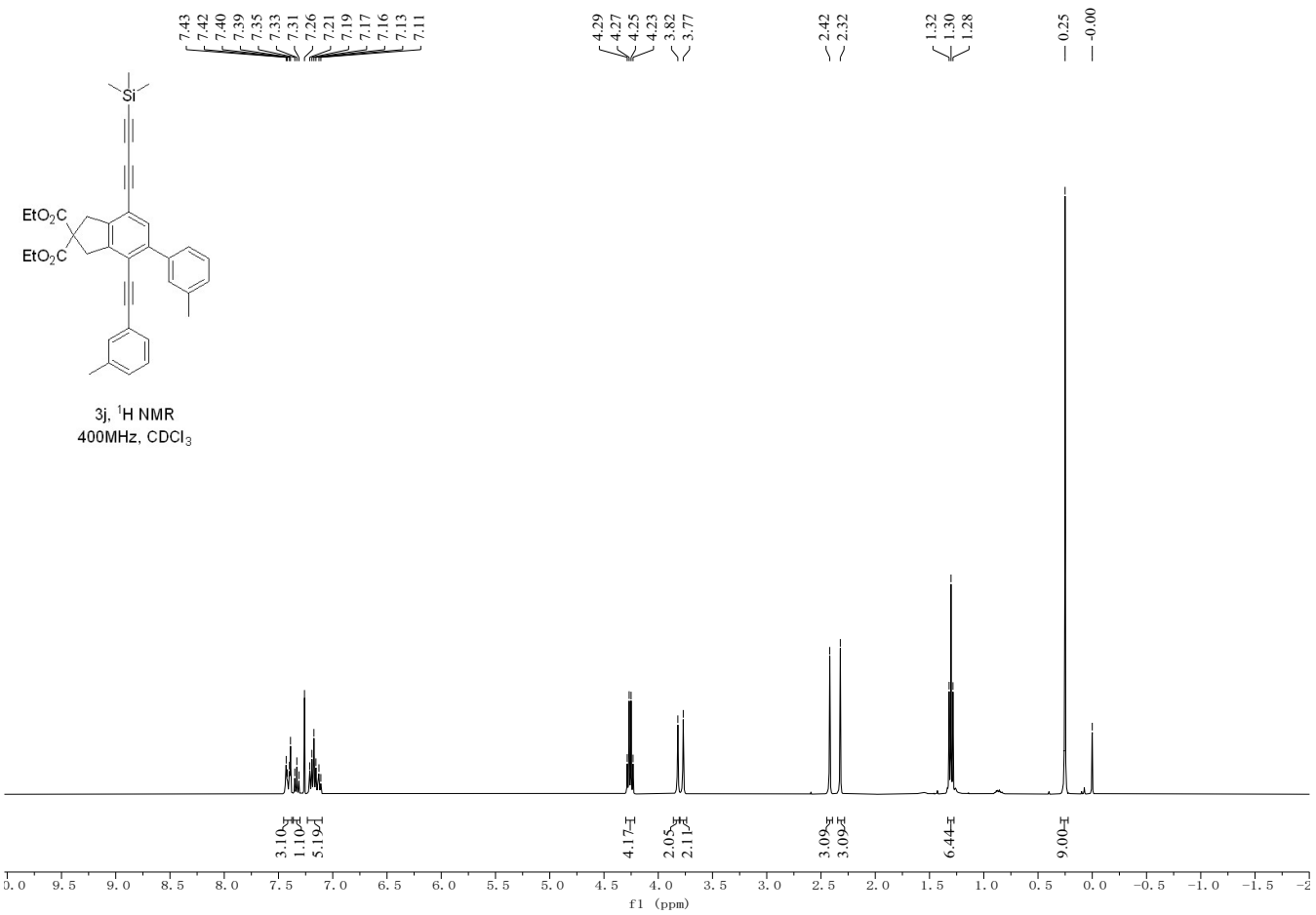

171.28
143.96 143.35 141.47 140.97 134.26 133.85 132.18 131.35 129.71 129.66 129.42 129.38 128.99 127.96 127.39 124.47 118.48 117.84
97.12 92.96 87.57 87.50 79.17 77.37 77.06 76.74 74.06
62.12 59.06
41.09 40.58
14.09
0.02 -0.41
Si
EtO2C
EtO2C
Cl
Cl
3h, 13C NMR
101MHz, CDCl3
f1 (ppm)



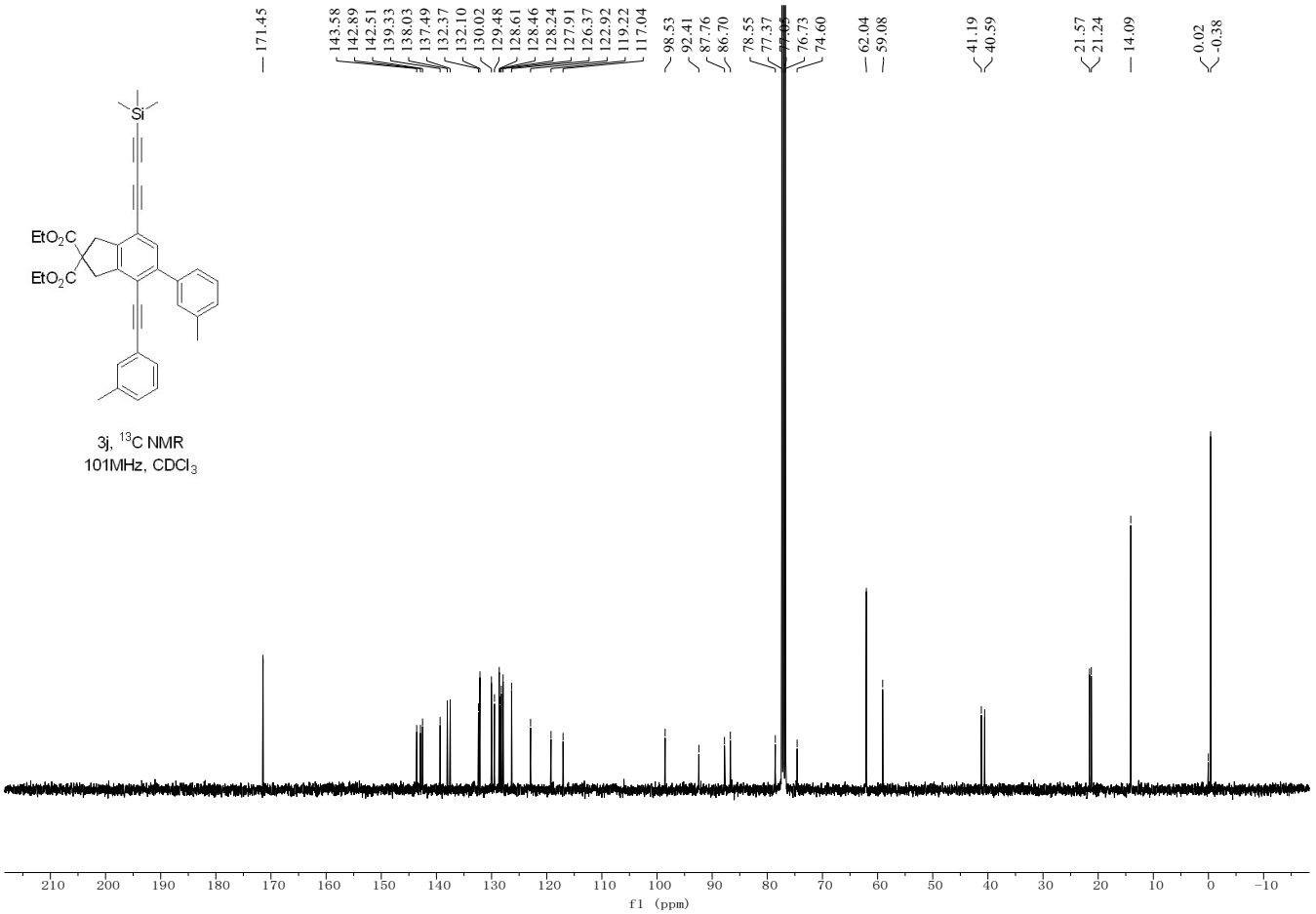
3i, ^{1}H NMR
400MHz, $CDCl_3$



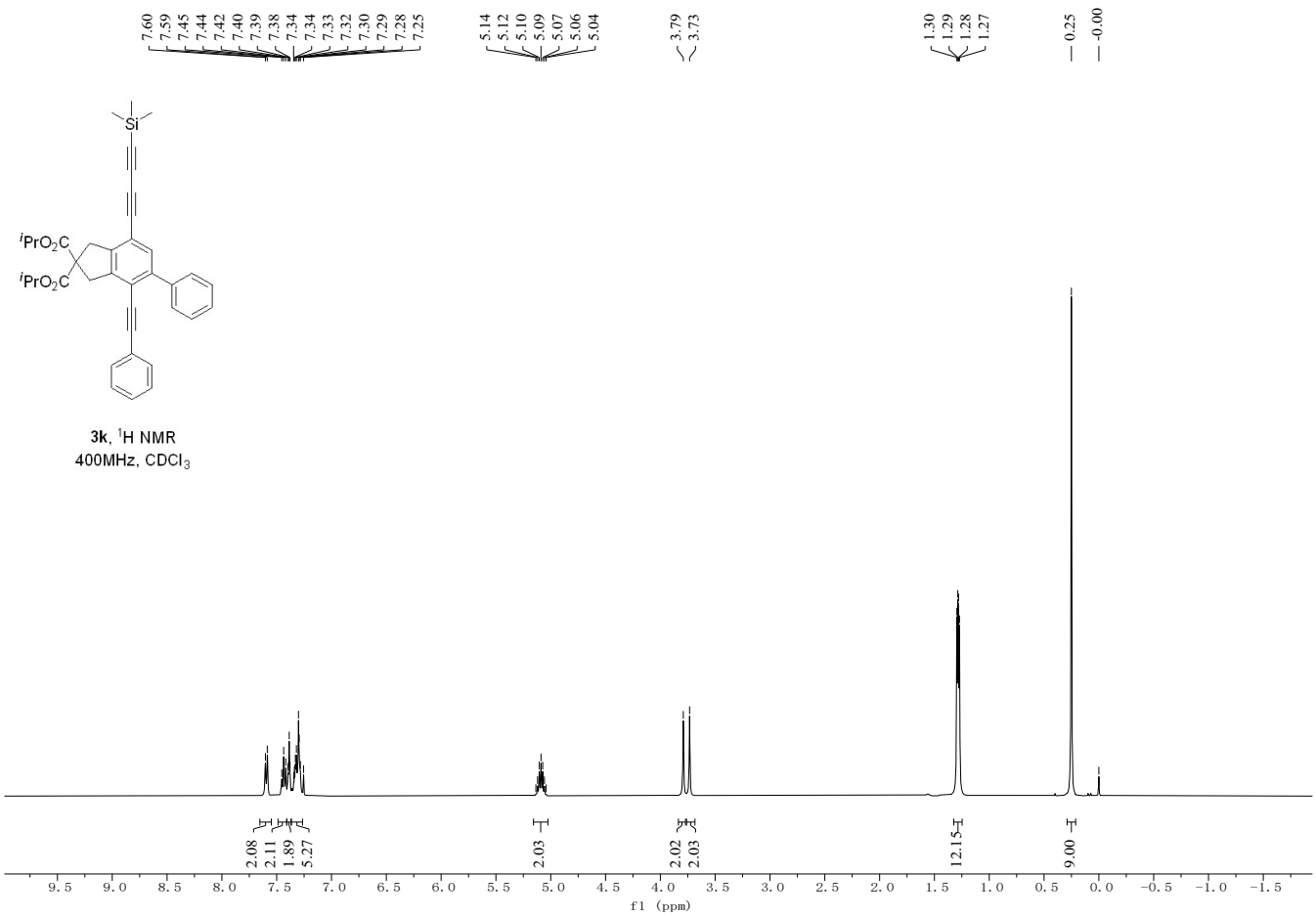
3i, ^{13}C NMR
101MHz, $CDCl_3$



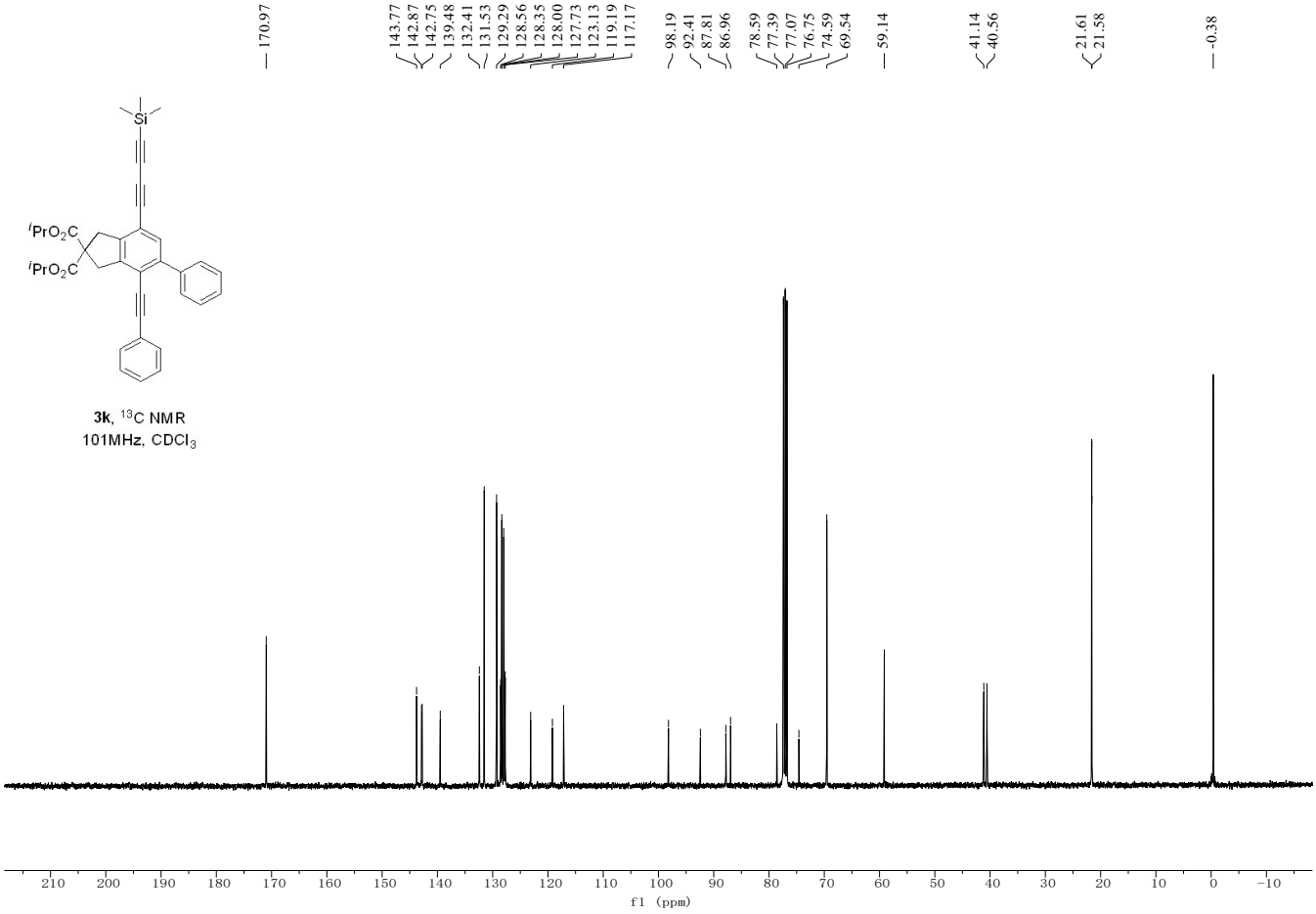
3j, ^{1}H NMR
400MHz, $CDCl_3$



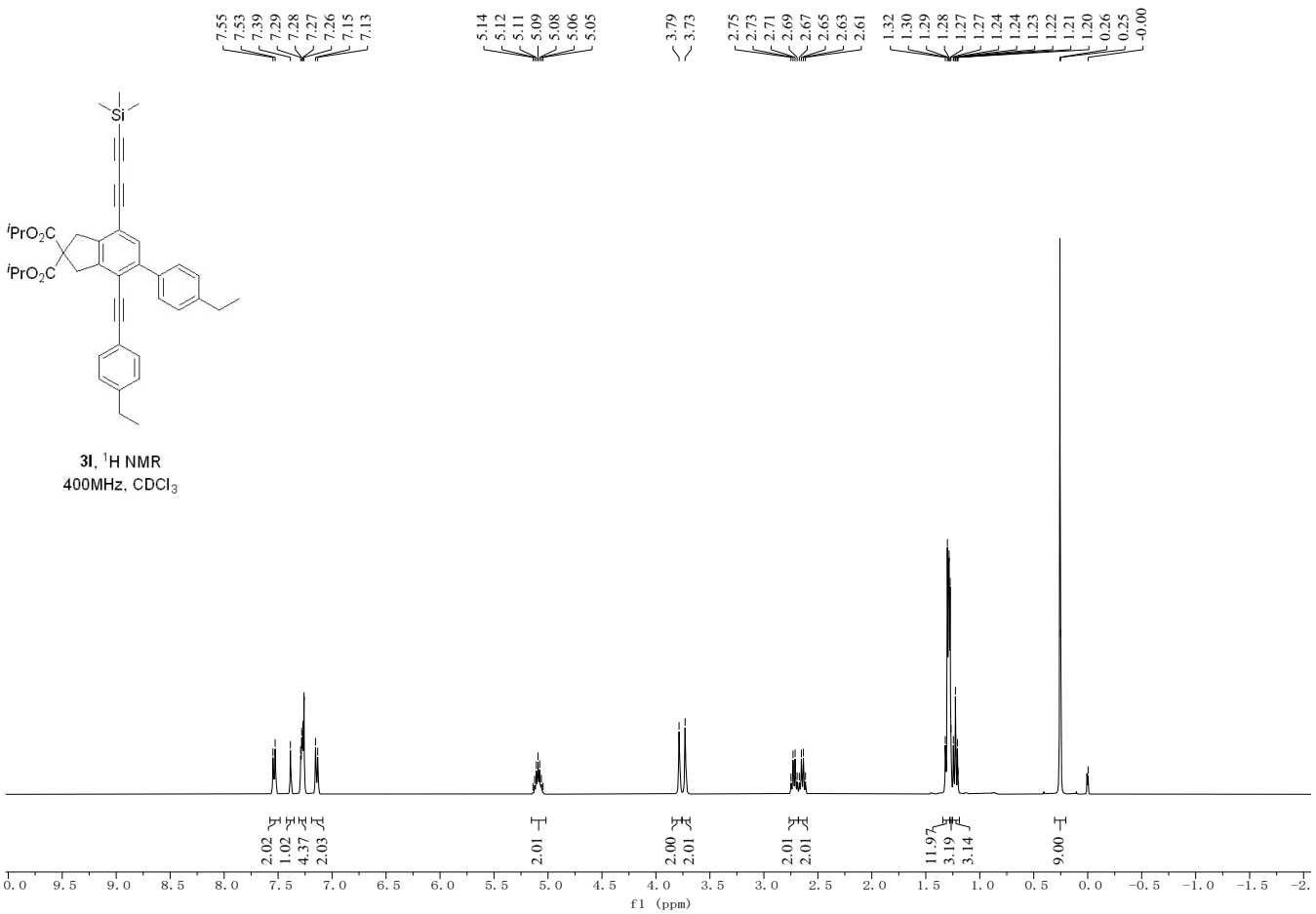
3j, ^{13}C NMR
101MHz, $CDCl_3$



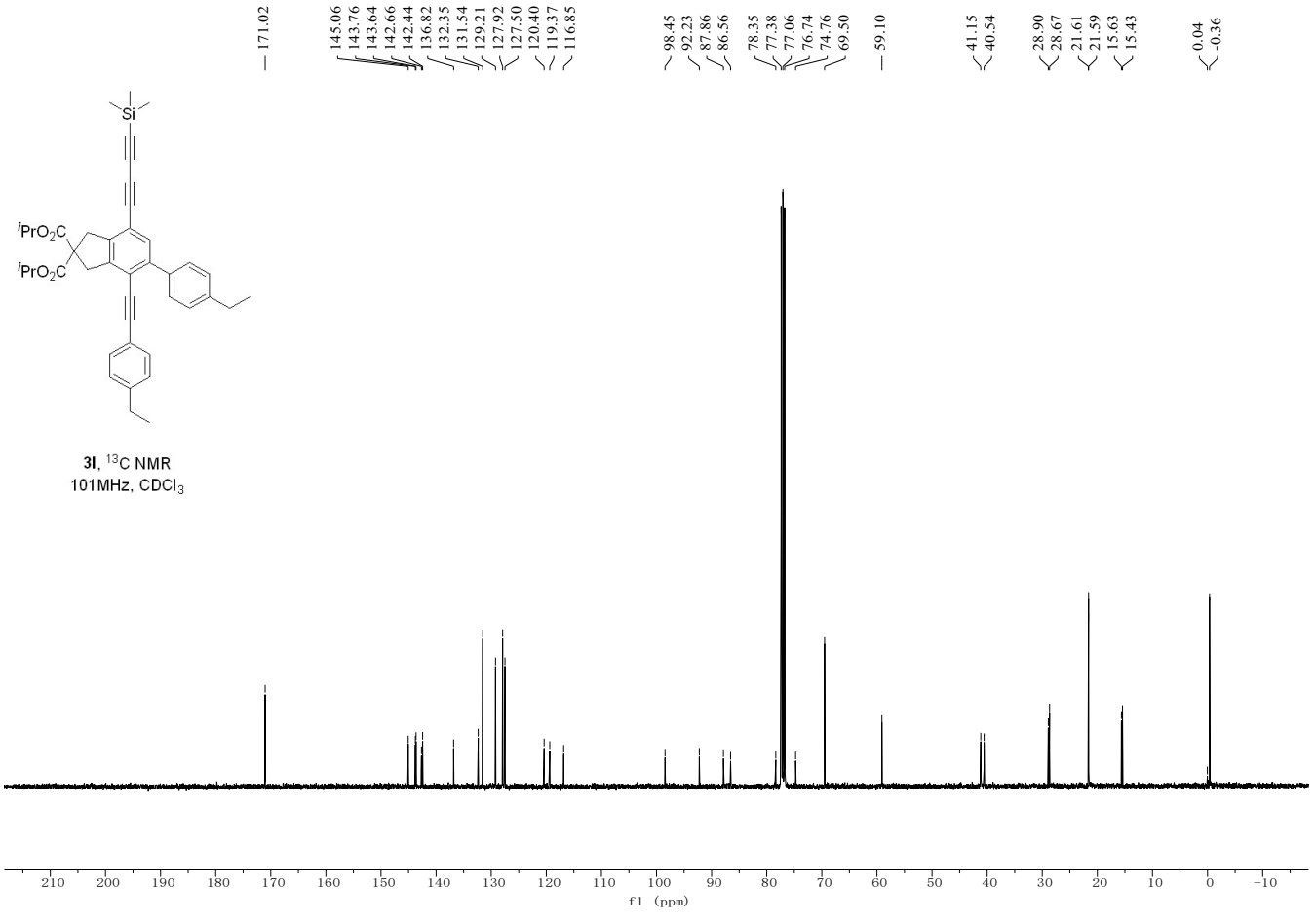
3k, ^{1}H NMR
400MHz, $CDCl_3$



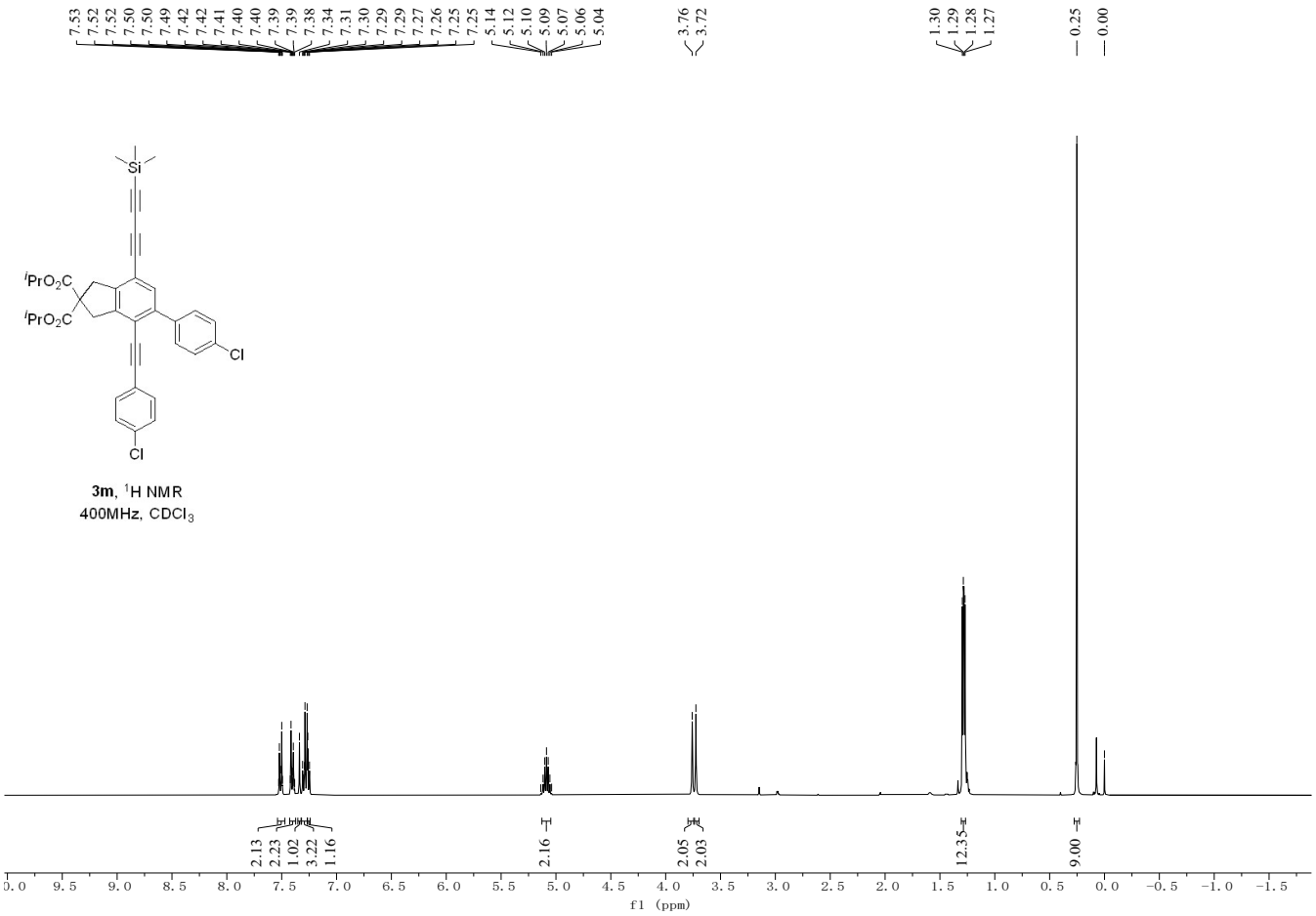
3k, ^{13}C NMR
101MHz, $CDCl_3$



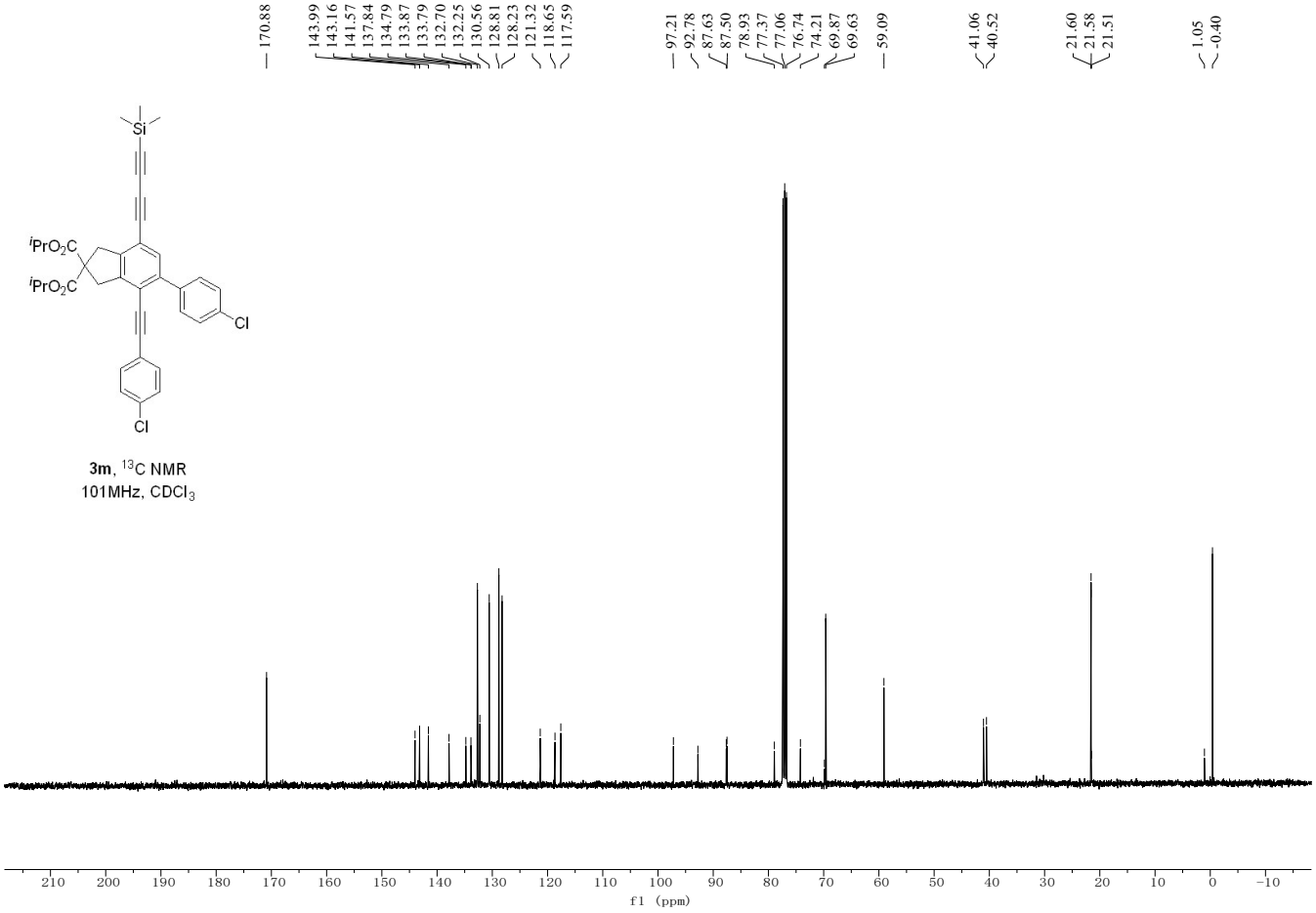
3l, ^{1}H NMR
400MHz, $CDCl_3$



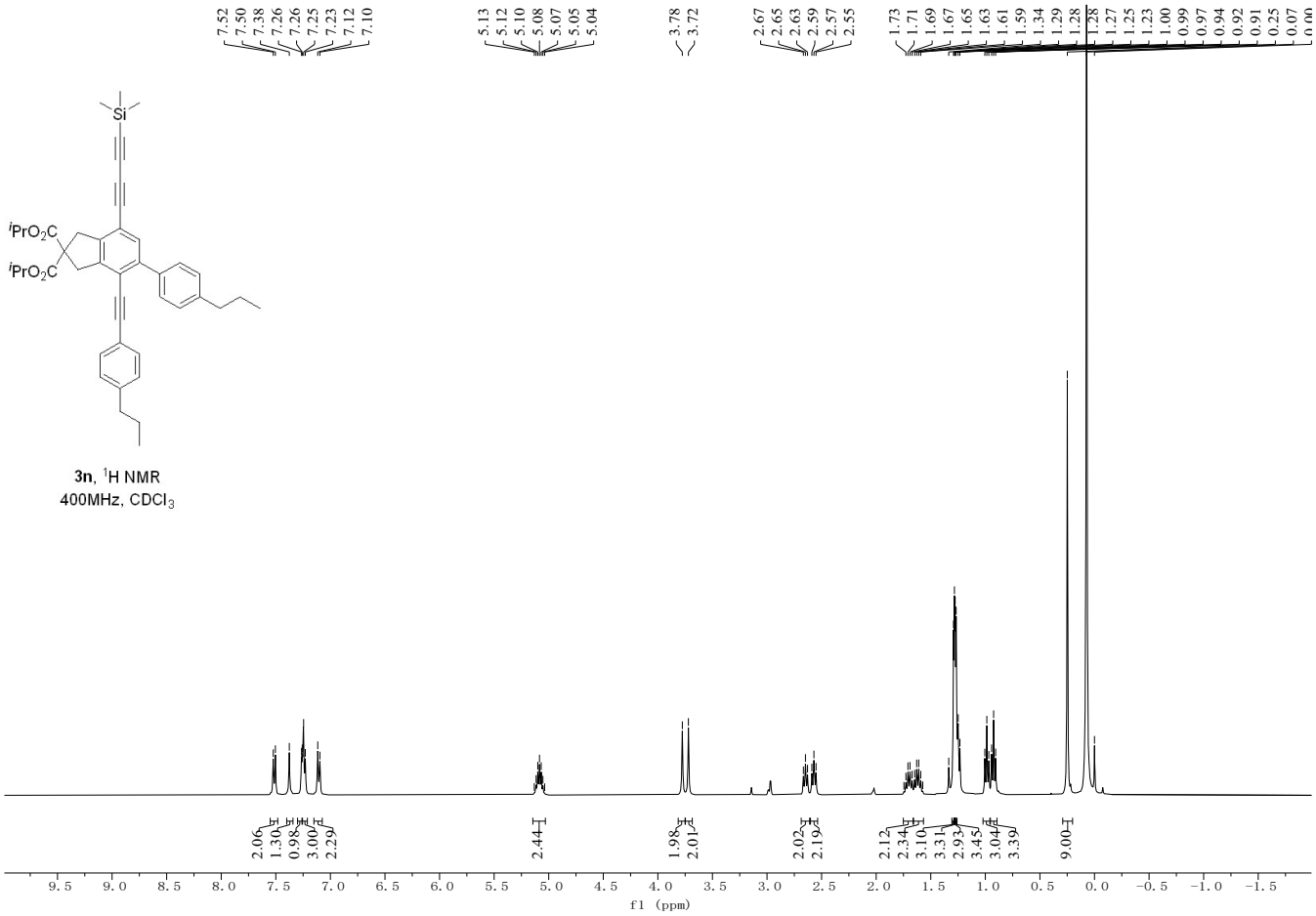
3l, ^{13}C NMR
101MHz, $CDCl_3$



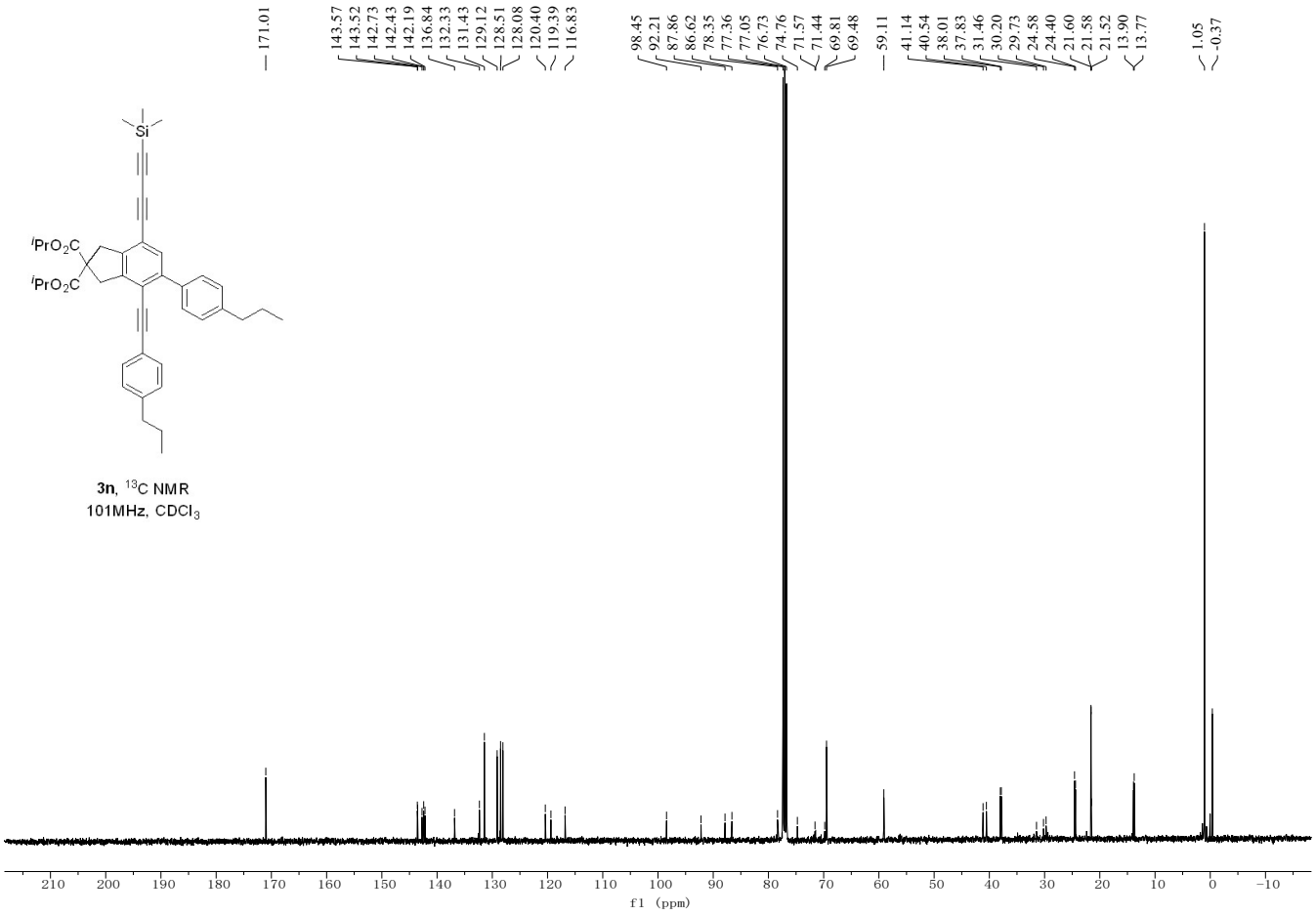
3m, ^{1}H NMR
400MHz, $CDCl_3$



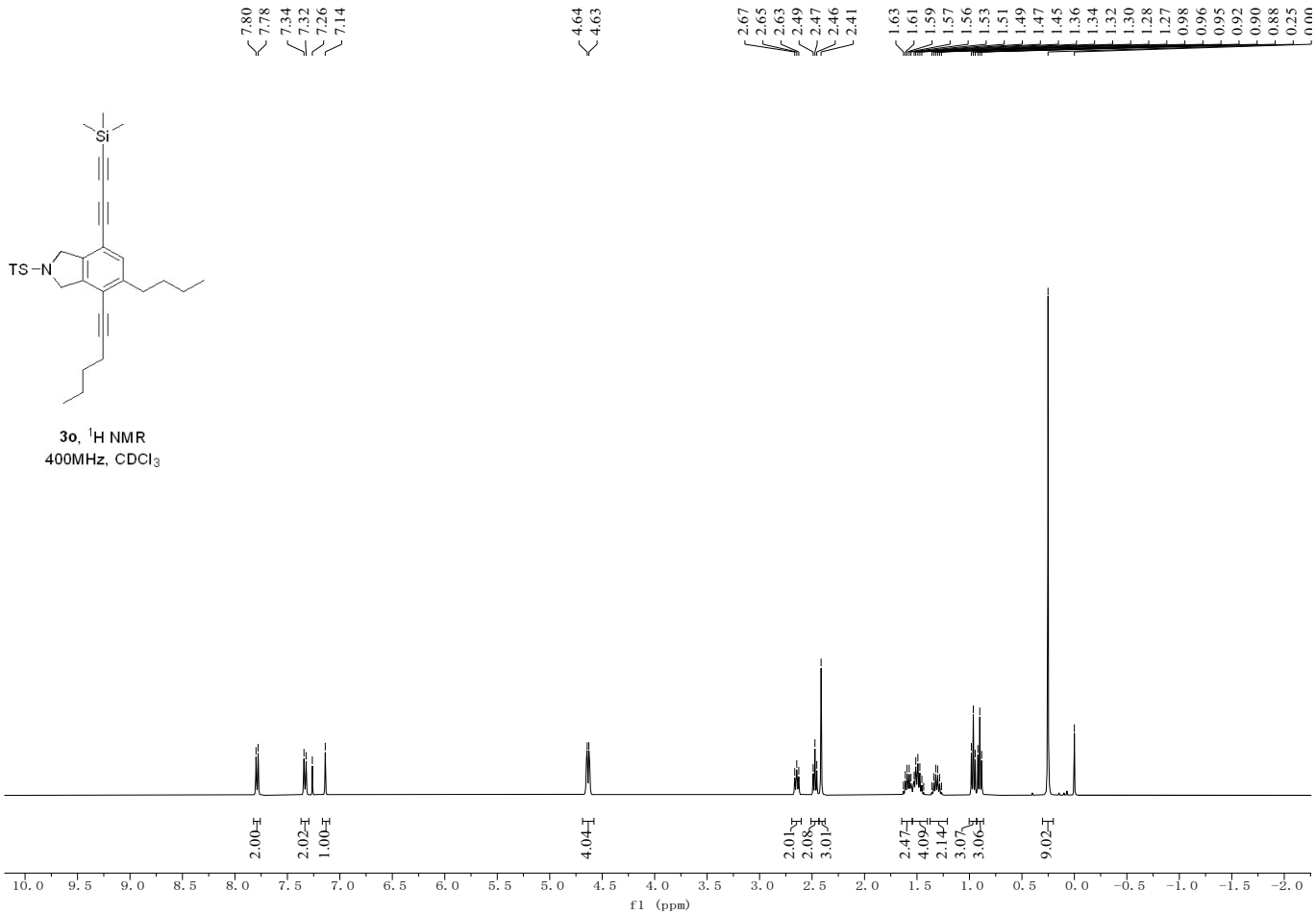
3m, ^{13}C NMR
101MHz, $CDCl_3$



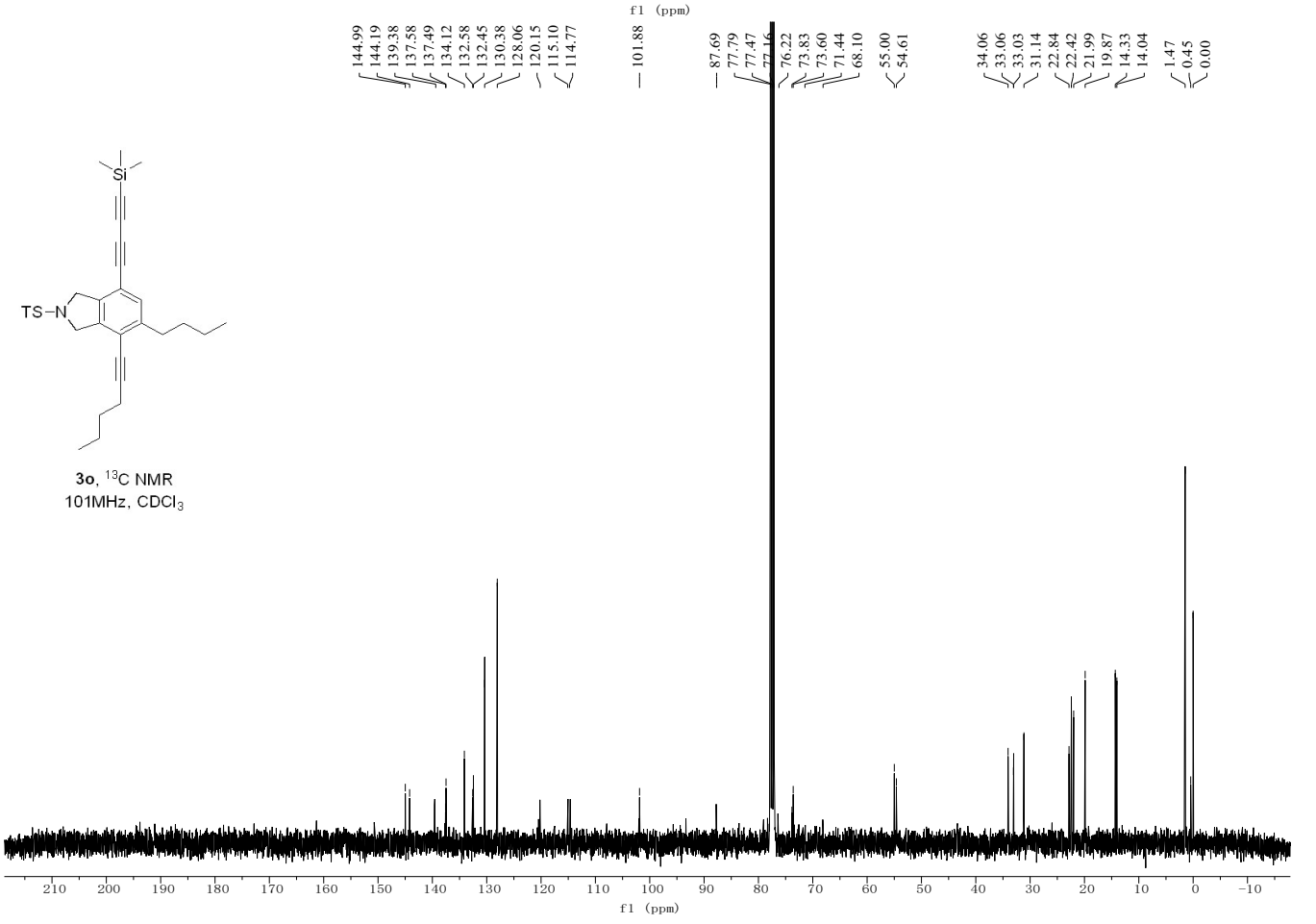
3n, ^{1}H NMR
400MHz, $CDCl_3$



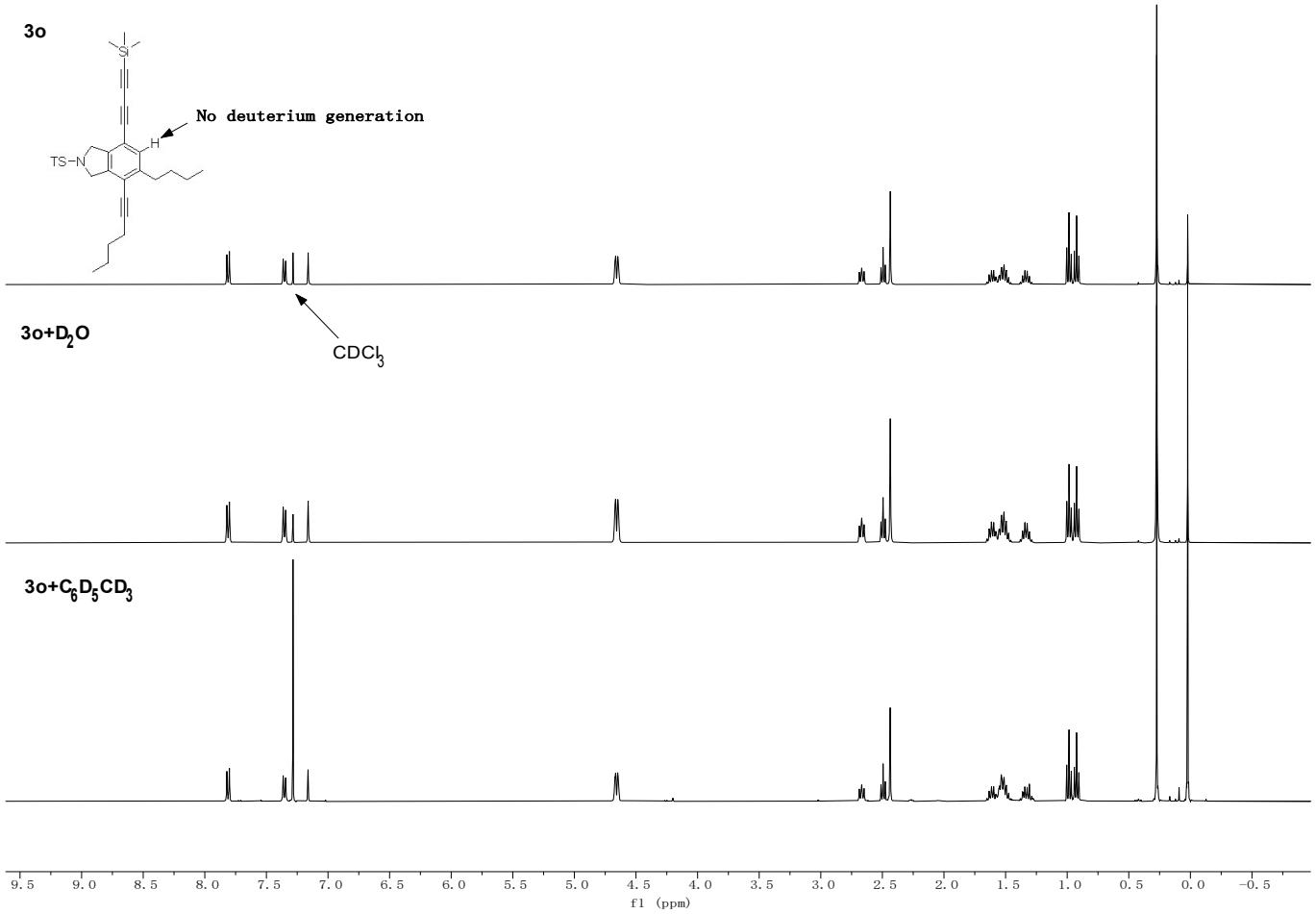
3n, ^{13}C NMR
101MHz, $CDCl_3$

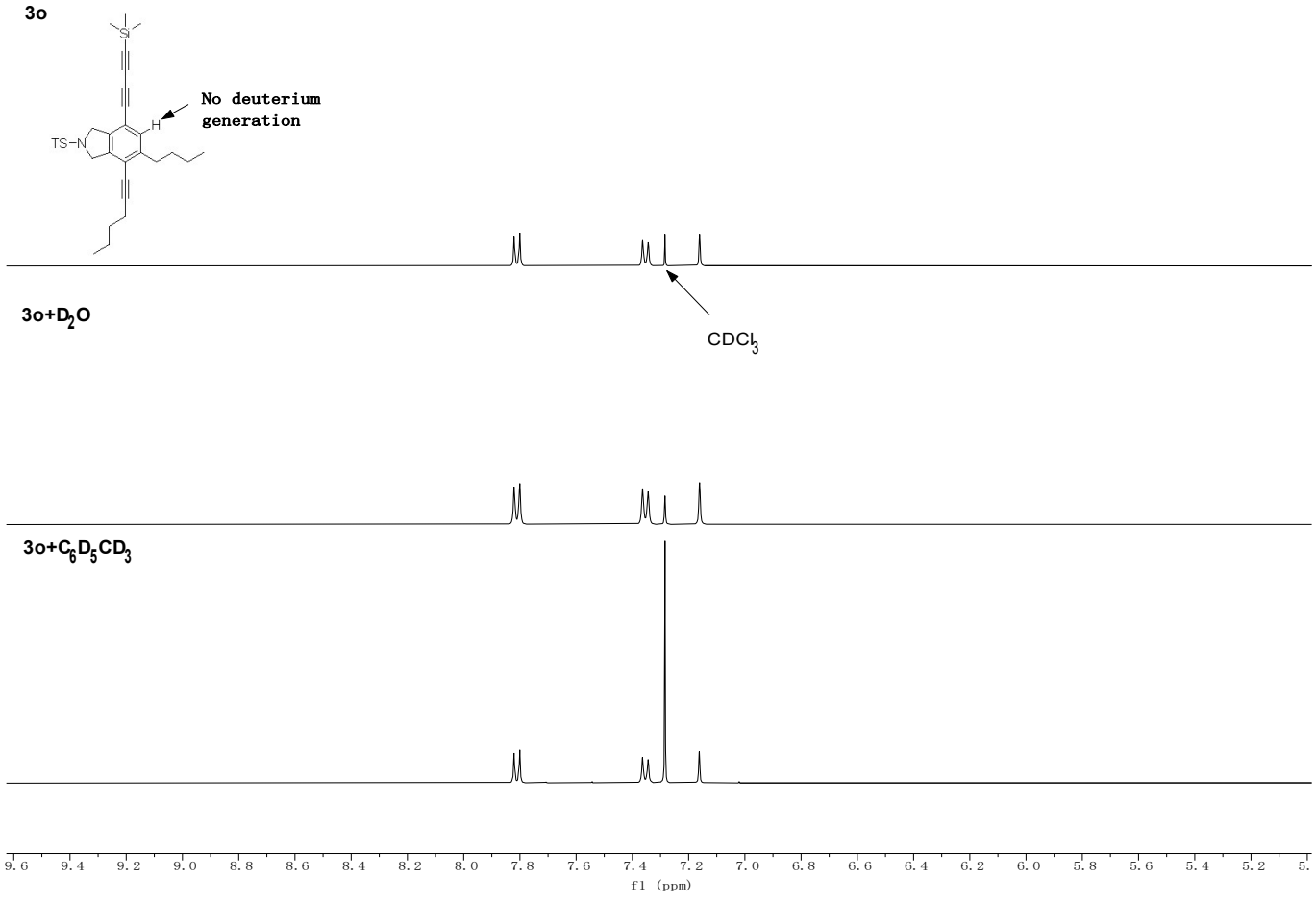


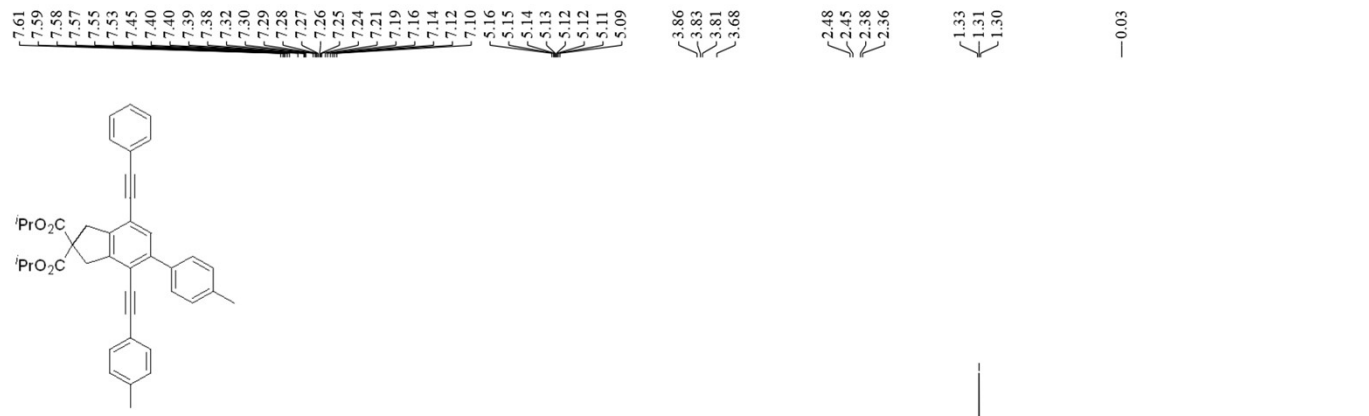
3o, ^{1}H NMR
400MHz, $CDCl_3$



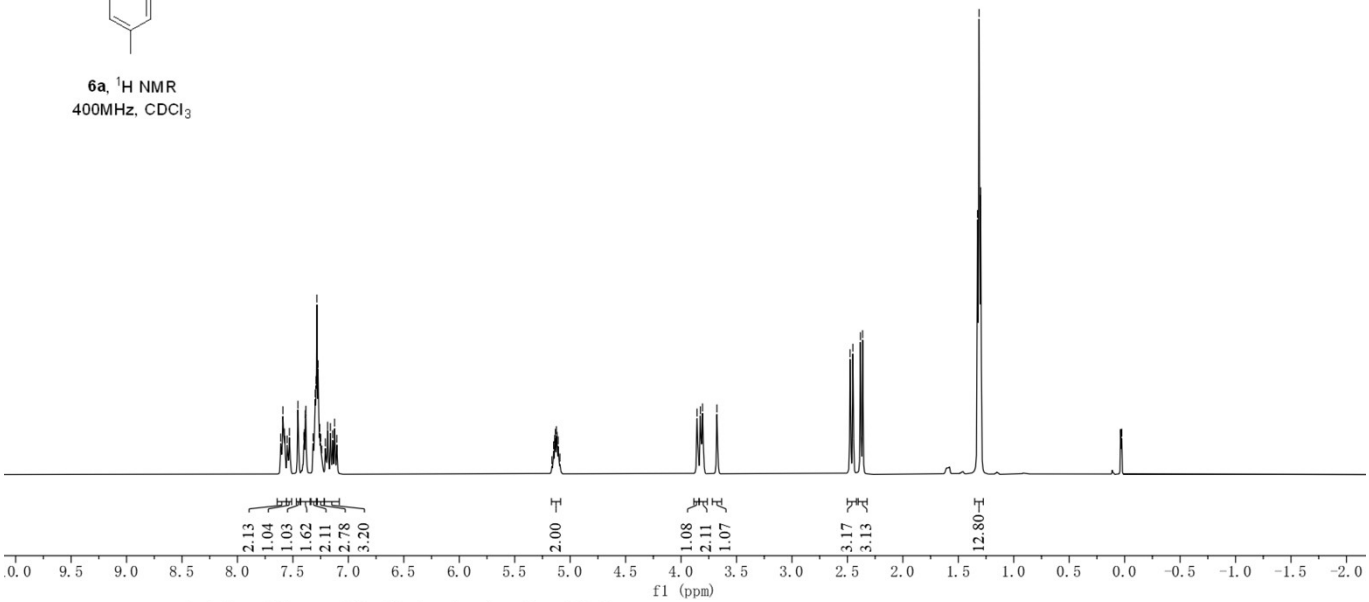
3o, ^{13}C NMR
101MHz, $CDCl_3$

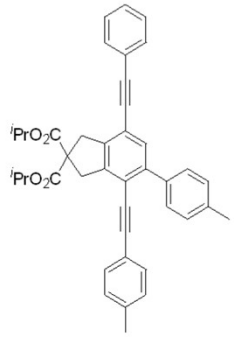

3o
Si
No deuterium generation
H
TS-N
3o+D2O
CDCl3
3o+C6D5CD3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


3o
Si
No deuterium generation
H
TS-N
3o+D2O
CDCl3
3o+C6D5CD3
9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.
f1 (ppm)

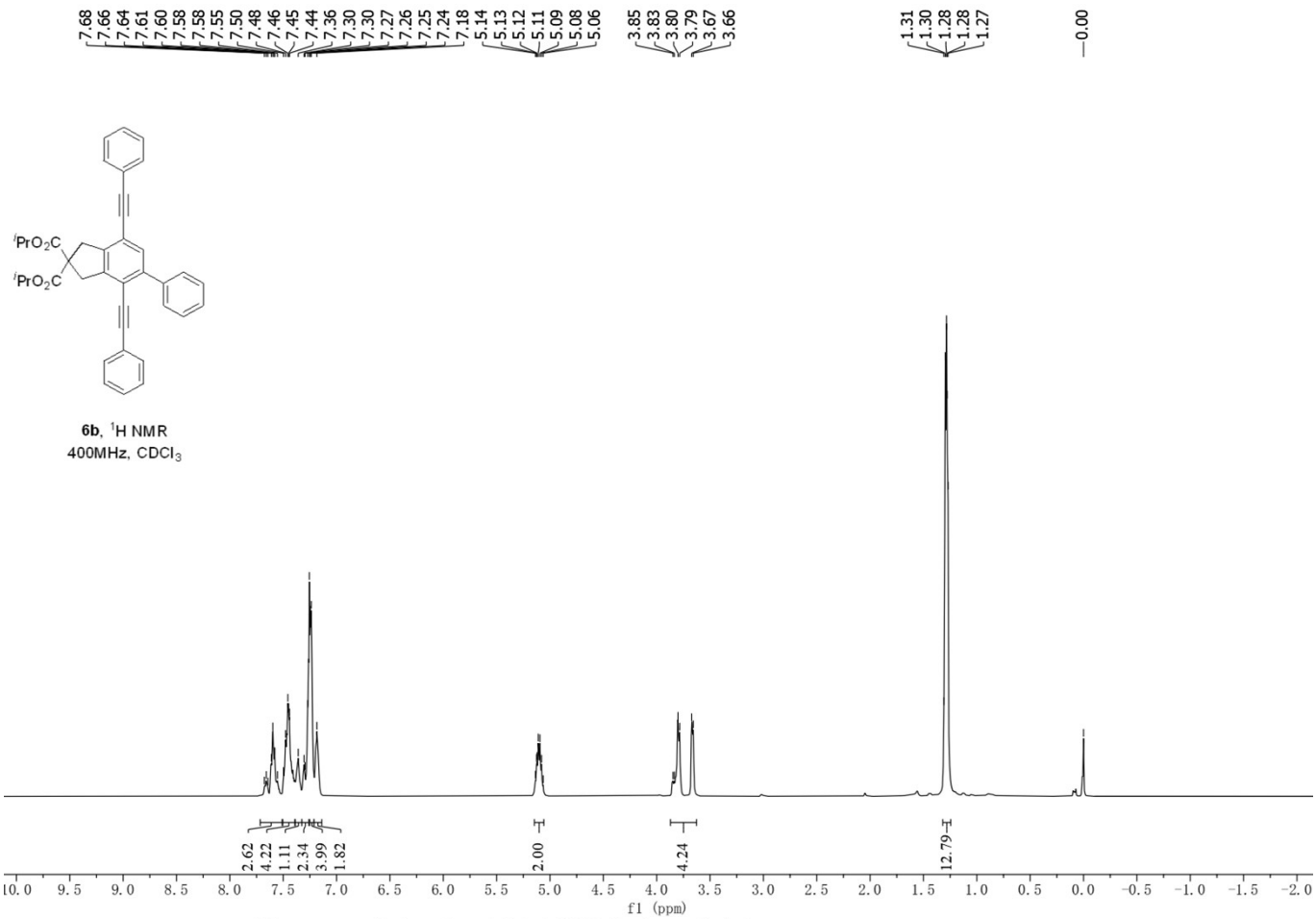


6a, ^{1}H NMR
400MHz, $CDCl_3$

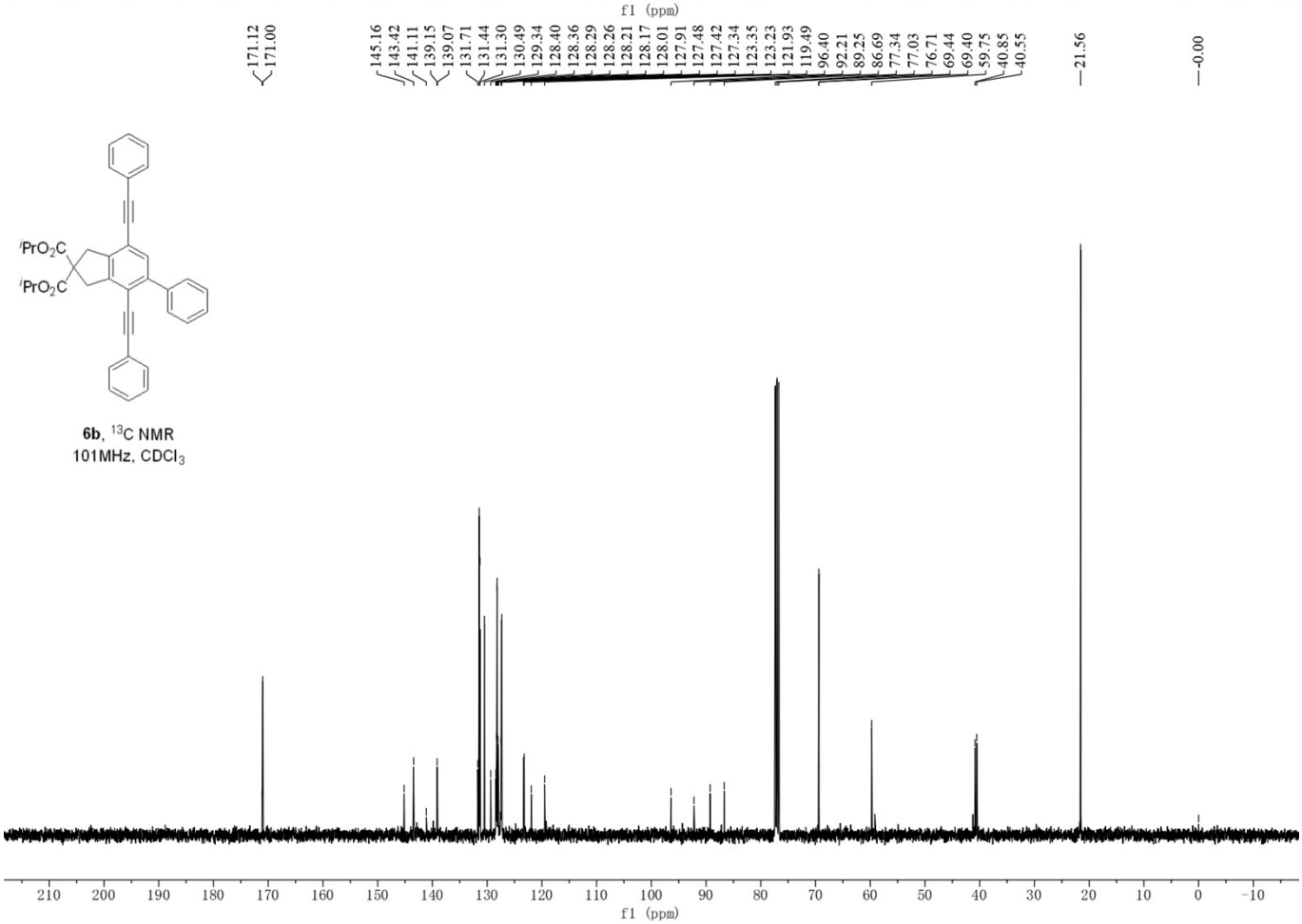




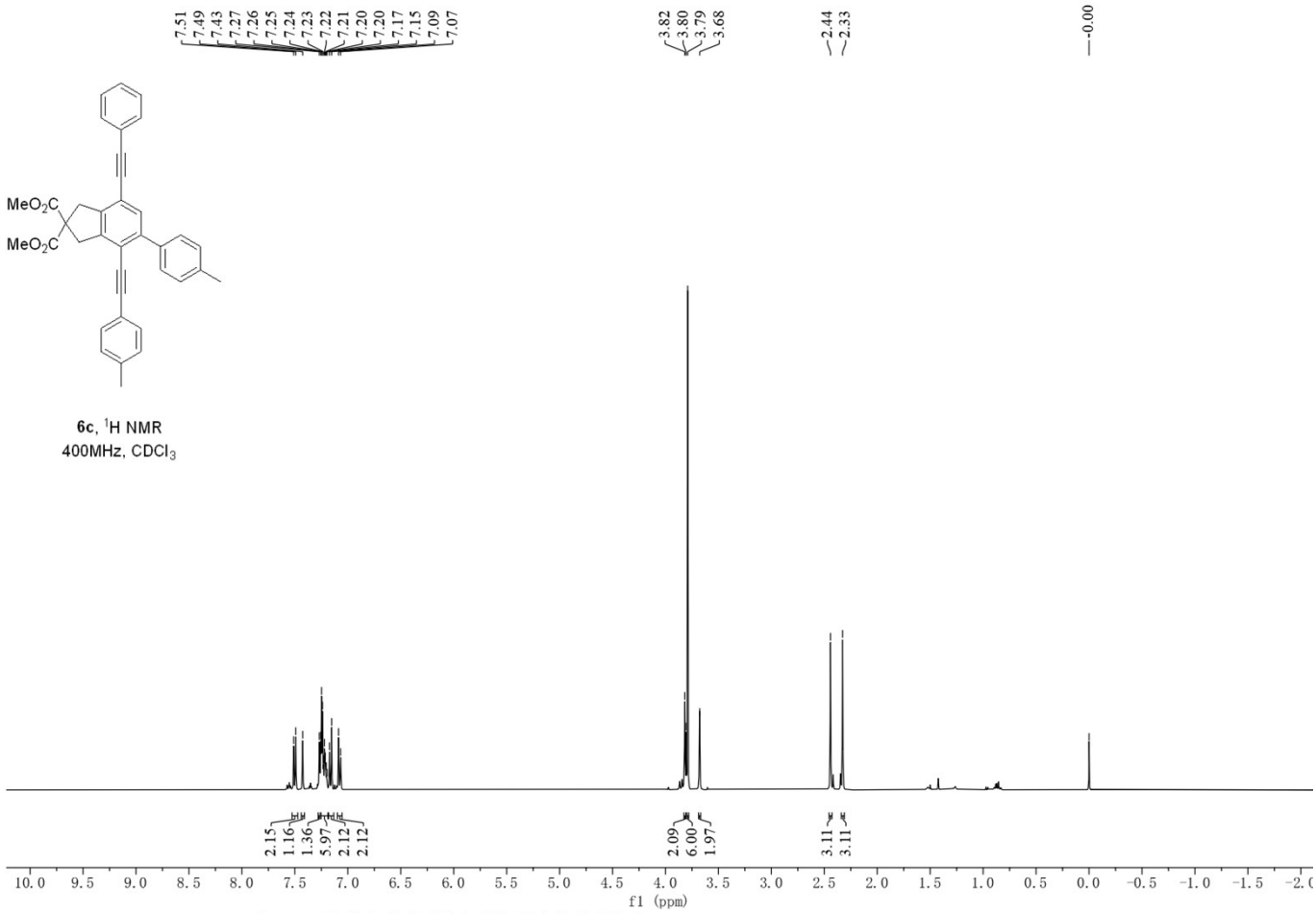
6a, ^{13}C NMR
101MHz, $CDCl_3$



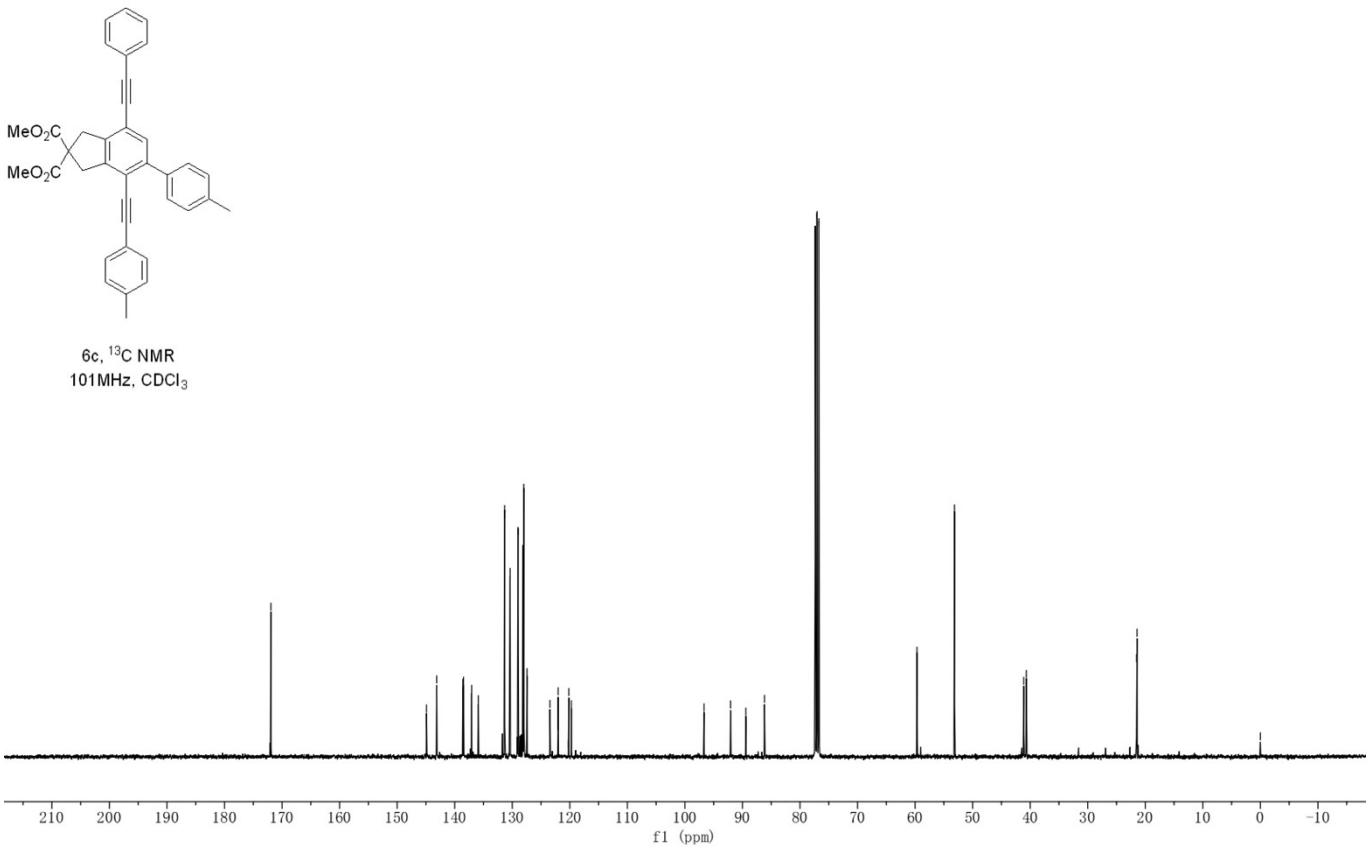
6b, ^{1}H NMR
400MHz, $CDCl_3$



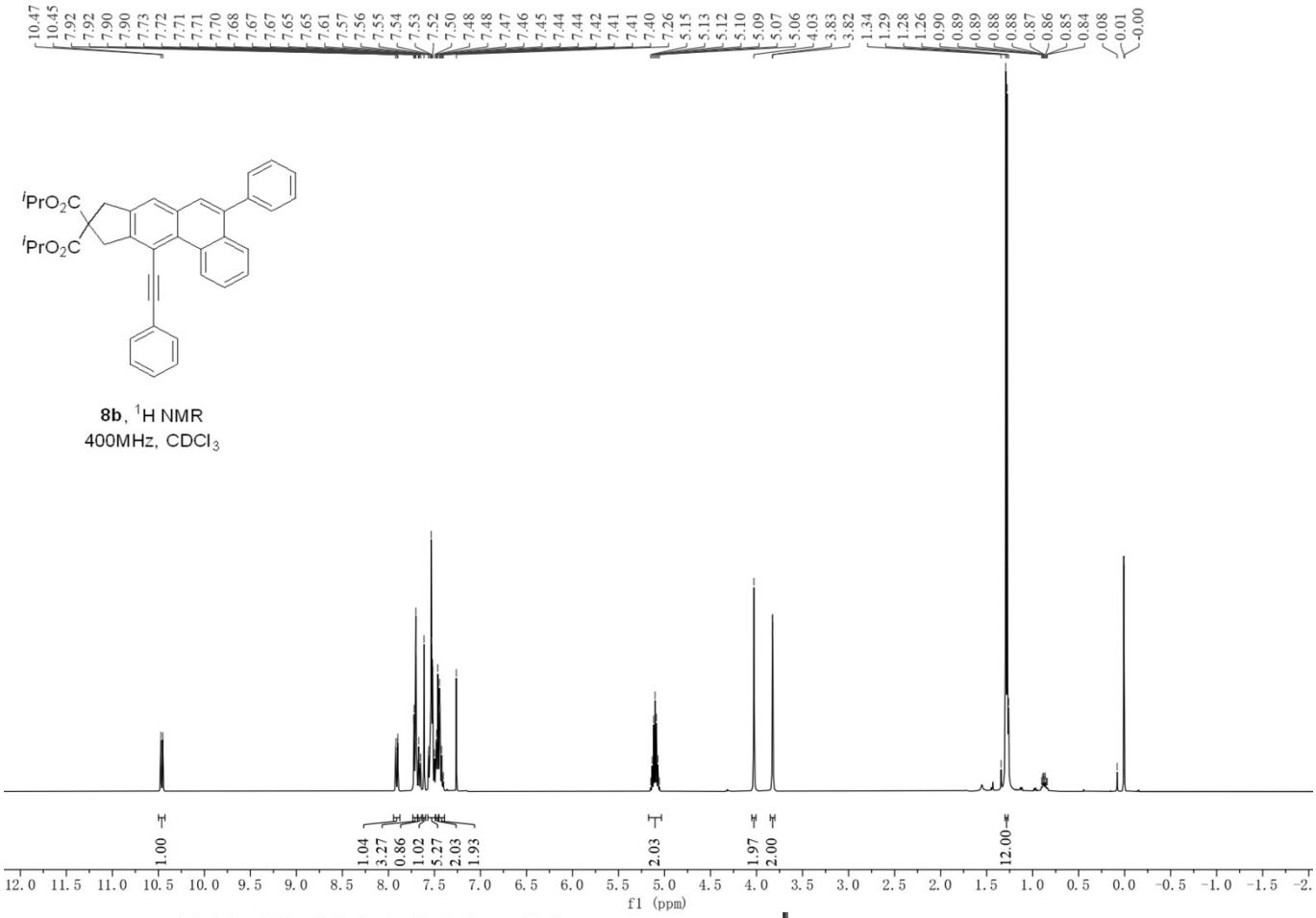
6b, ^{13}C NMR
101MHz, $CDCl_3$



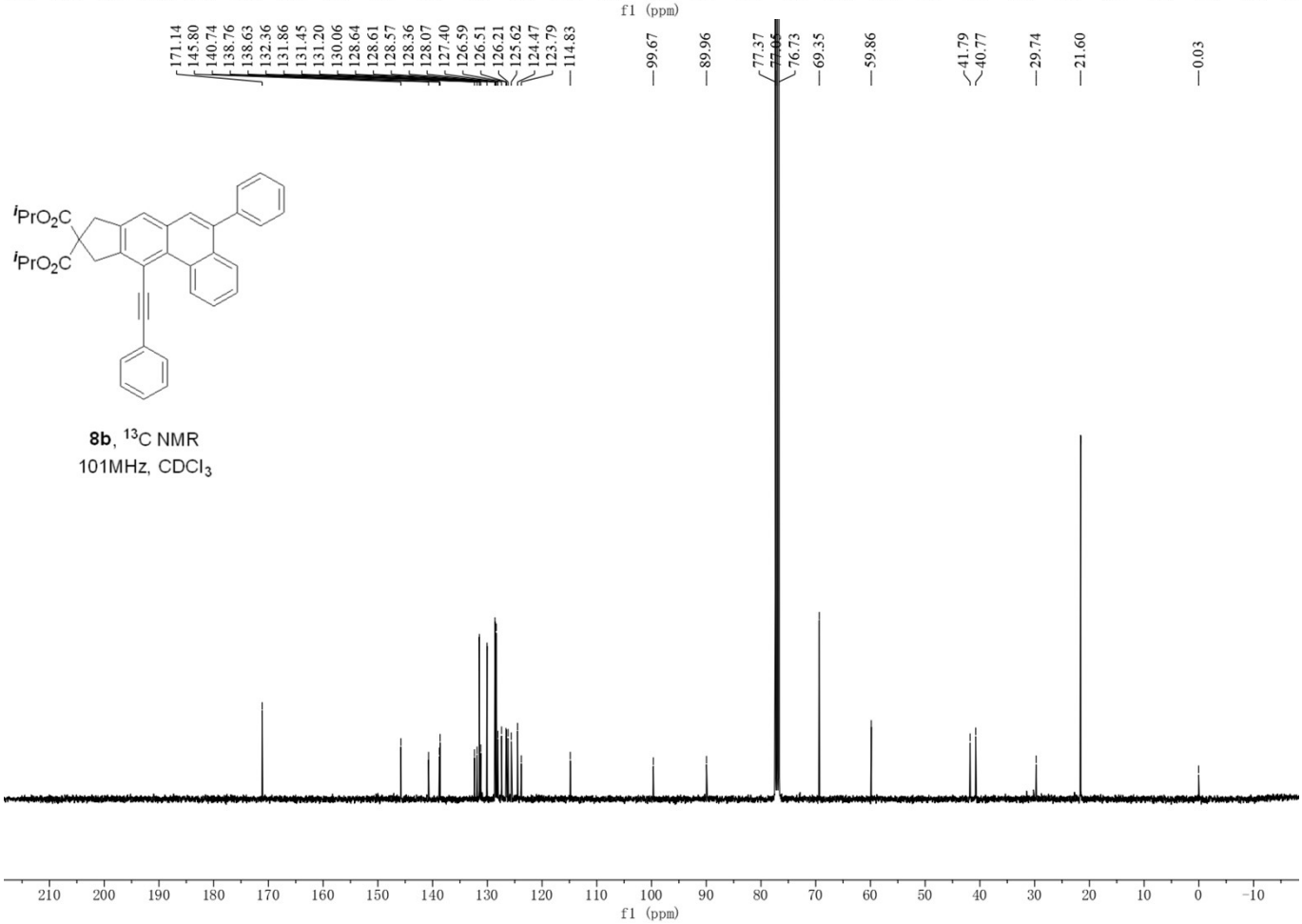
6c, ^{1}H NMR
400MHz, $CDCl_3$



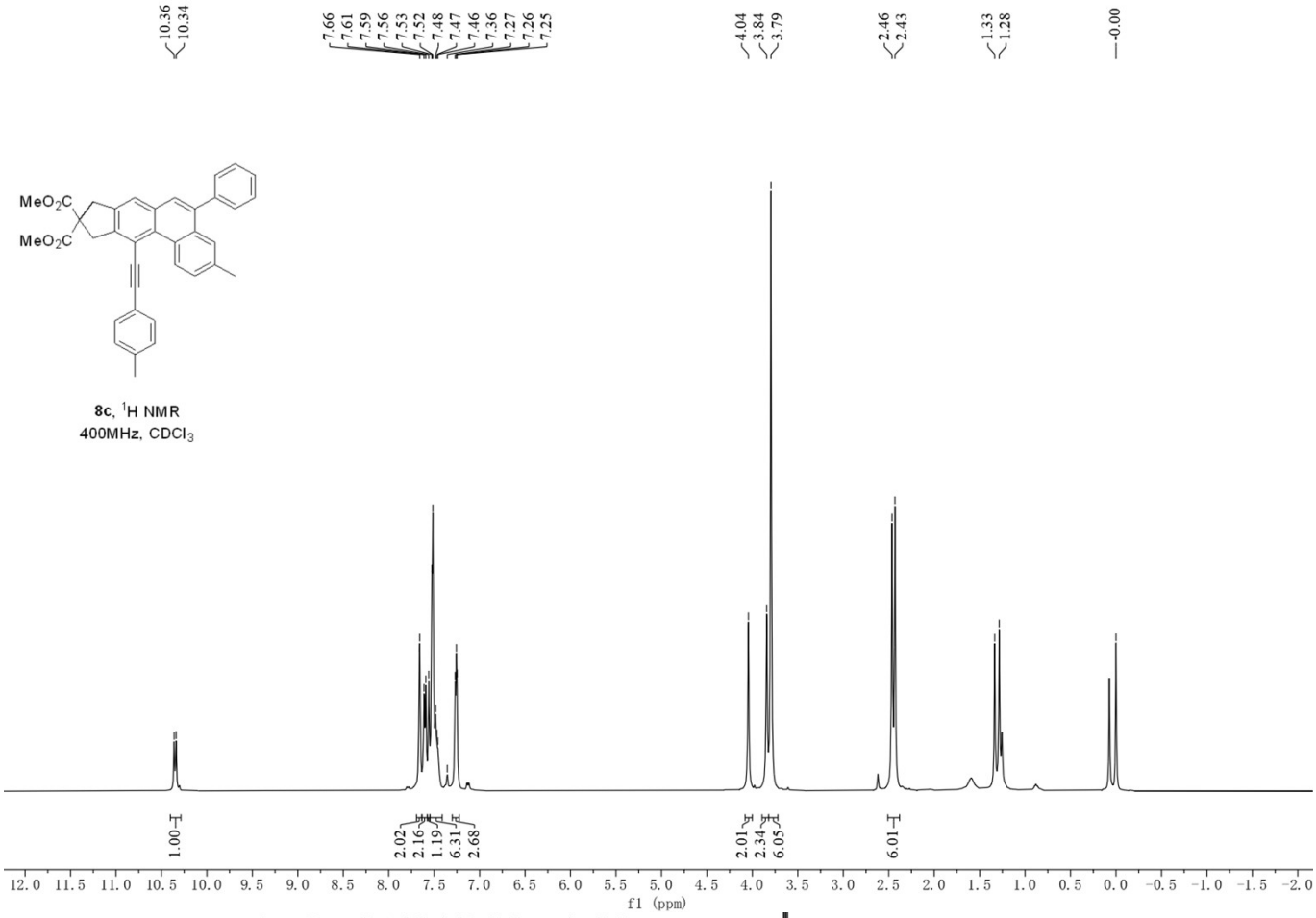
6c, ^{13}C NMR
101MHz, $CDCl_3$



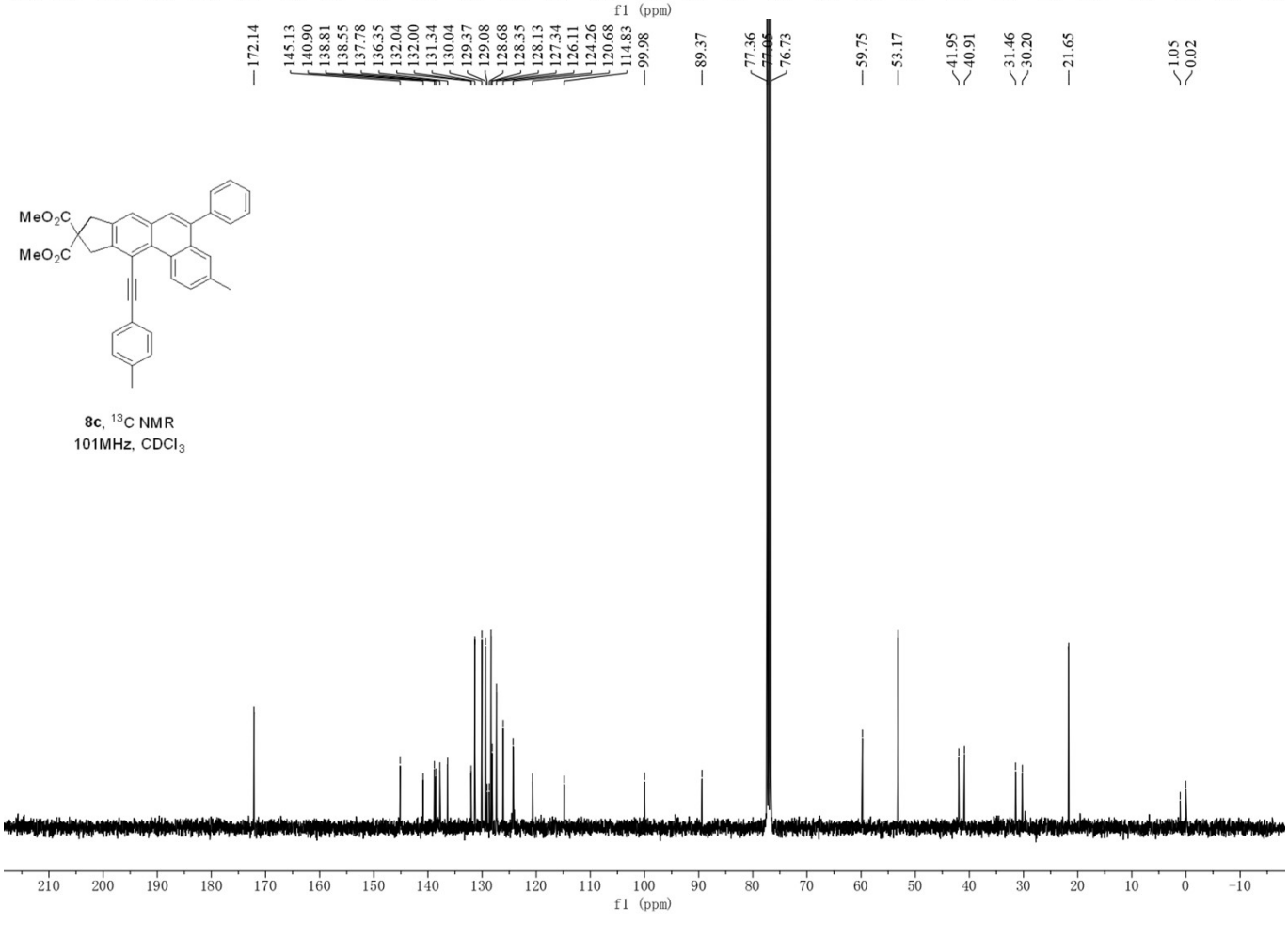
8b, ^{1}H NMR
400MHz, $CDCl_3$



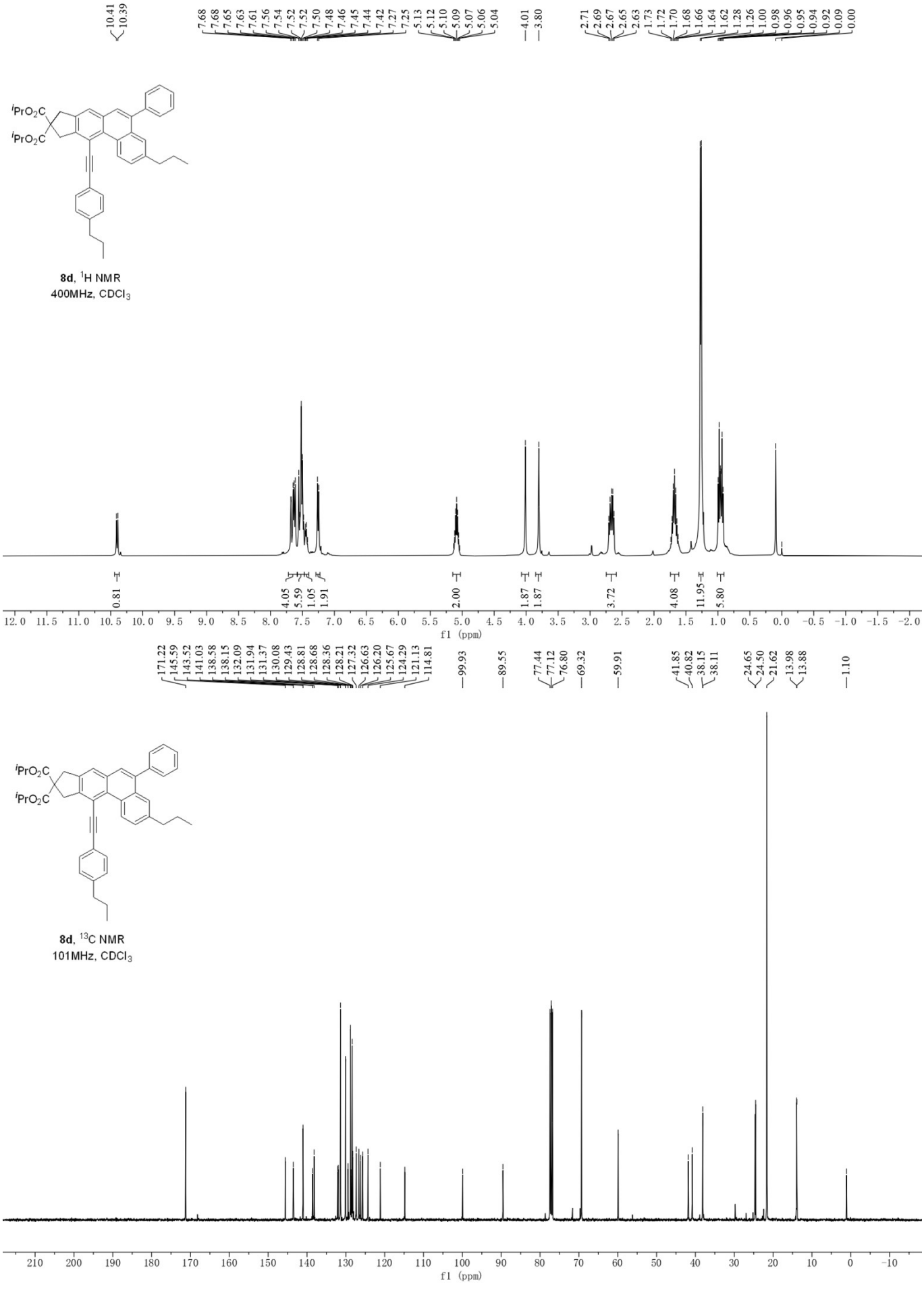
8b, ^{13}C NMR
101MHz, $CDCl_3$

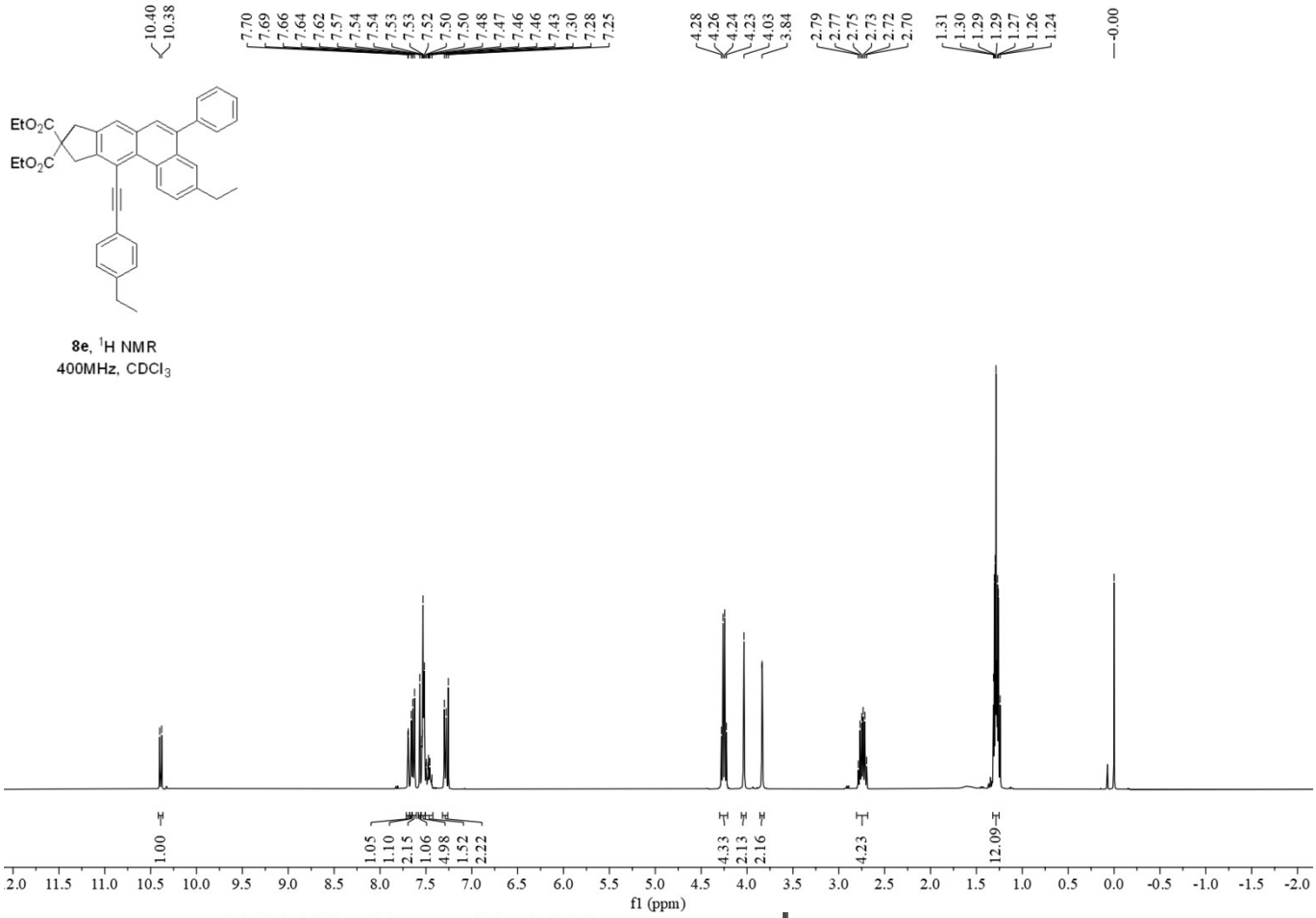


8c, ^{1}H NMR
400MHz, $CDCl_3$

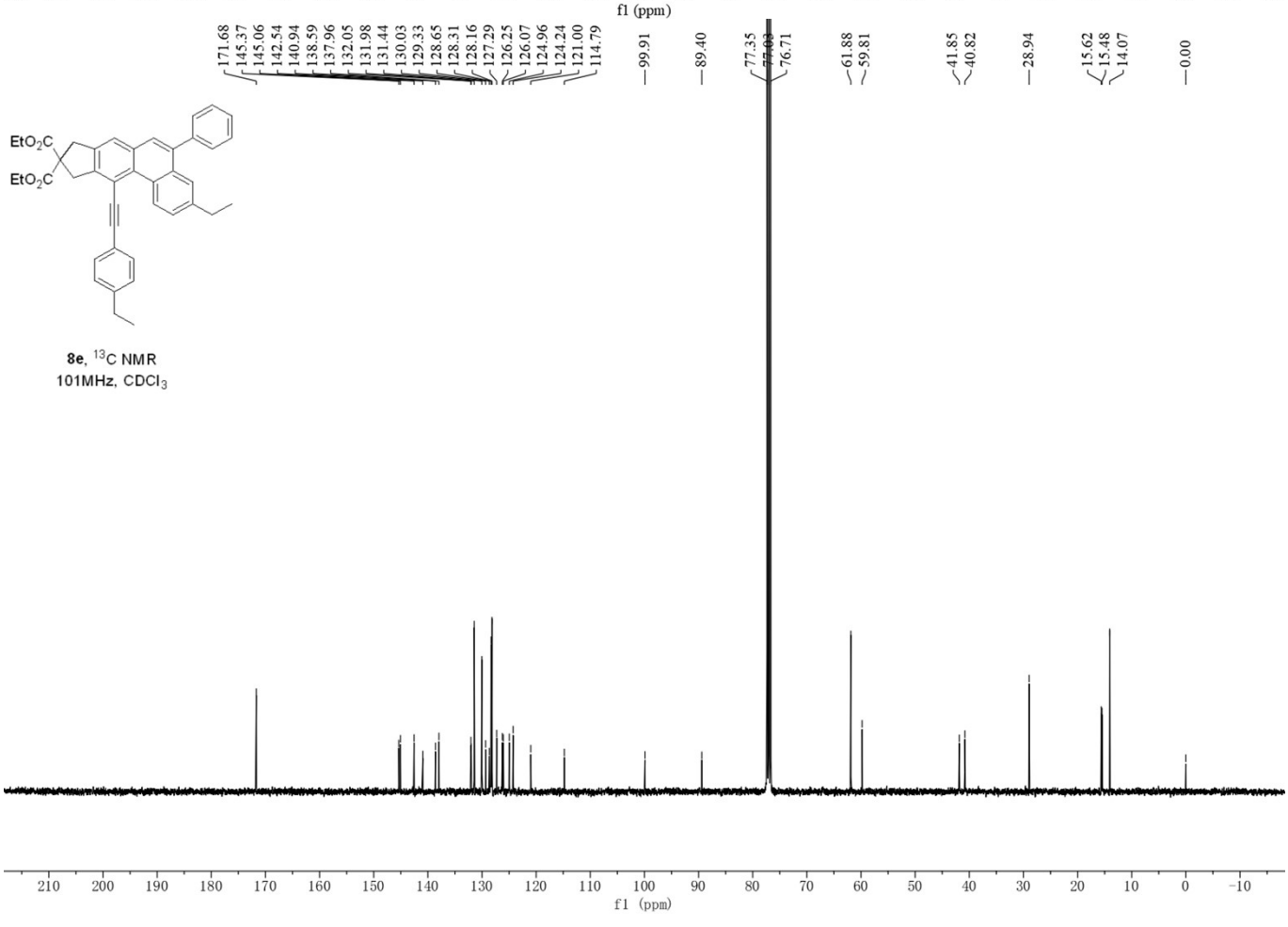


8c, ^{13}C NMR
101MHz, $CDCl_3$

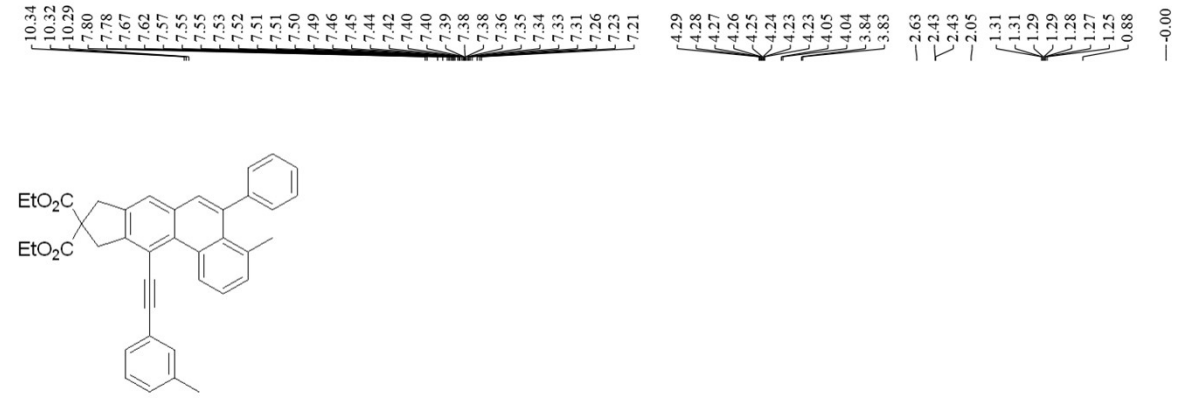

10.41
10.39
7.68
7.68
7.65
7.63
7.61
7.56
7.54
7.52
7.52
7.50
7.48
7.46
7.45
7.44
7.42
7.27
7.25
5.13
5.12
5.10
5.09
5.07
5.06
5.04
4.01
3.80
2.71
2.69
2.67
2.65
2.63
1.73
1.72
1.70
1.68
1.66
1.64
1.62
1.28
1.26
1.00
0.98
0.96
0.95
0.94
0.92
0.09
0.00
iPrO2C
iPrO2C
8d, 1H NMR
400MHz, CDCl3
0.81
4.05
5.59
1.05
1.91
2.00
1.87
1.87
3.72
4.08
11.95
5.80
f1 (ppm)
171.22
145.59
143.52
141.03
138.58
138.15
132.09
131.94
131.37
130.08
129.43
128.81
128.68
128.36
128.21
127.32
126.63
126.20
125.67
124.29
121.13
114.81
99.93
89.55
77.44
77.12
76.80
69.32
59.91
41.85
40.82
38.15
38.11
24.65
24.50
21.62
13.98
13.88
1.10
iPrO2C
iPrO2C
8d, 13C NMR
101MHz, CDCl3
f1 (ppm)



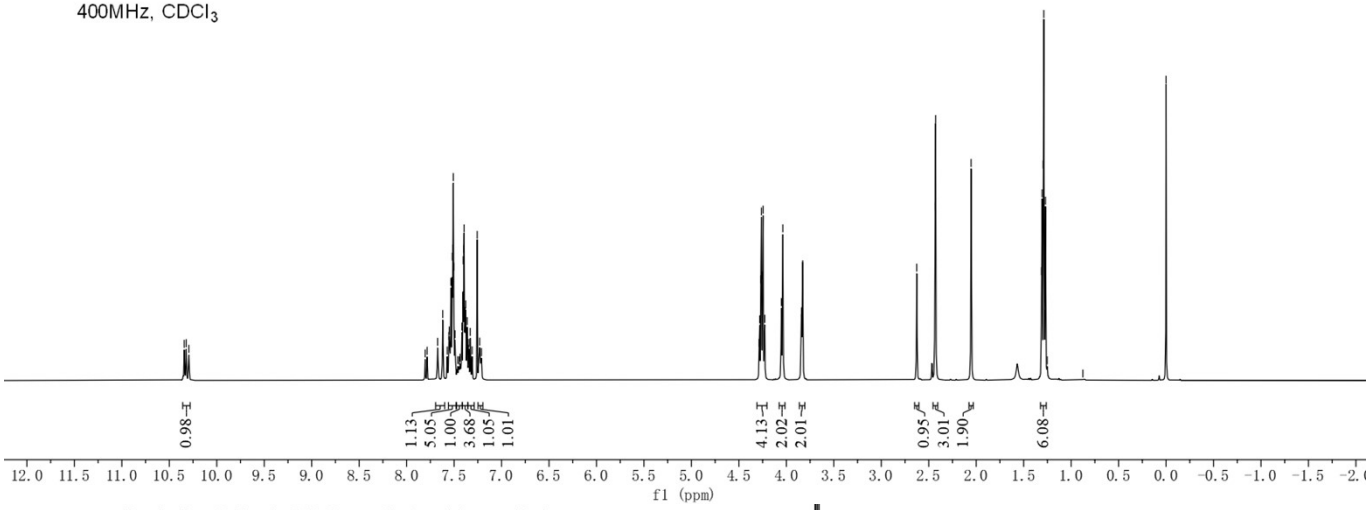
8e, ^{1}H NMR
400MHz, $CDCl_3$

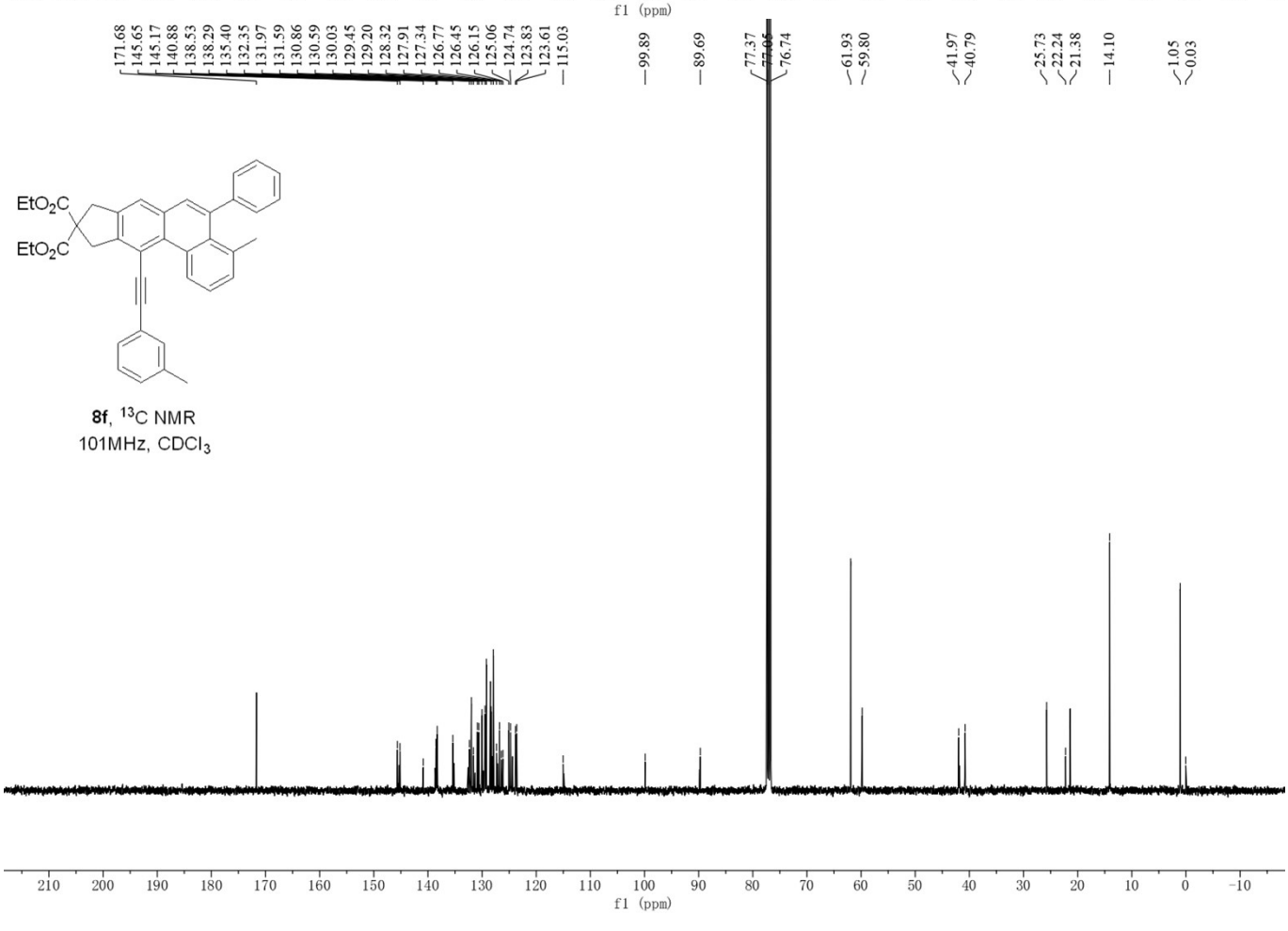


8e, ^{13}C NMR
101MHz, $CDCl_3$

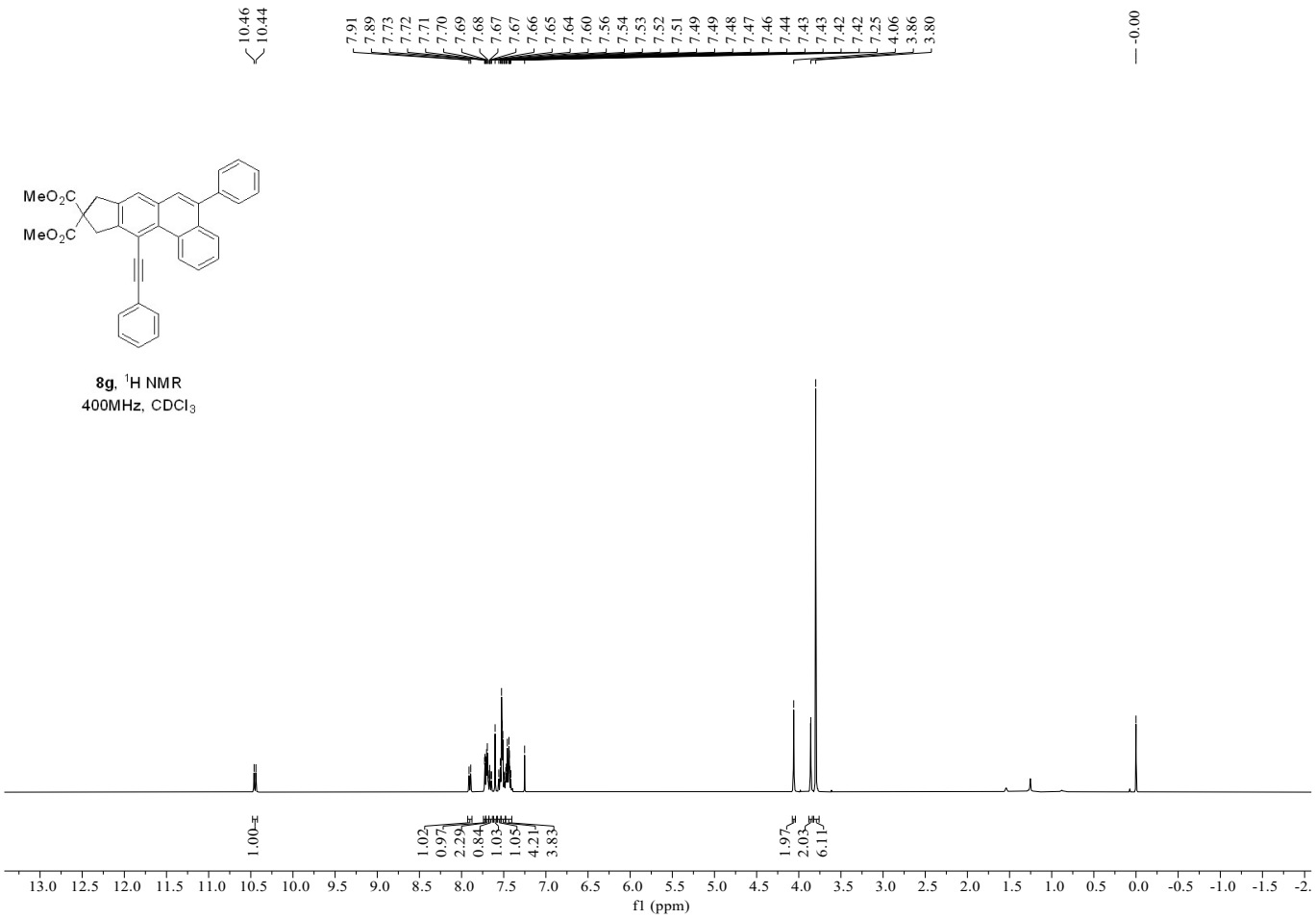


8f, ^{1}H NMR
400MHz, $CDCl_3$

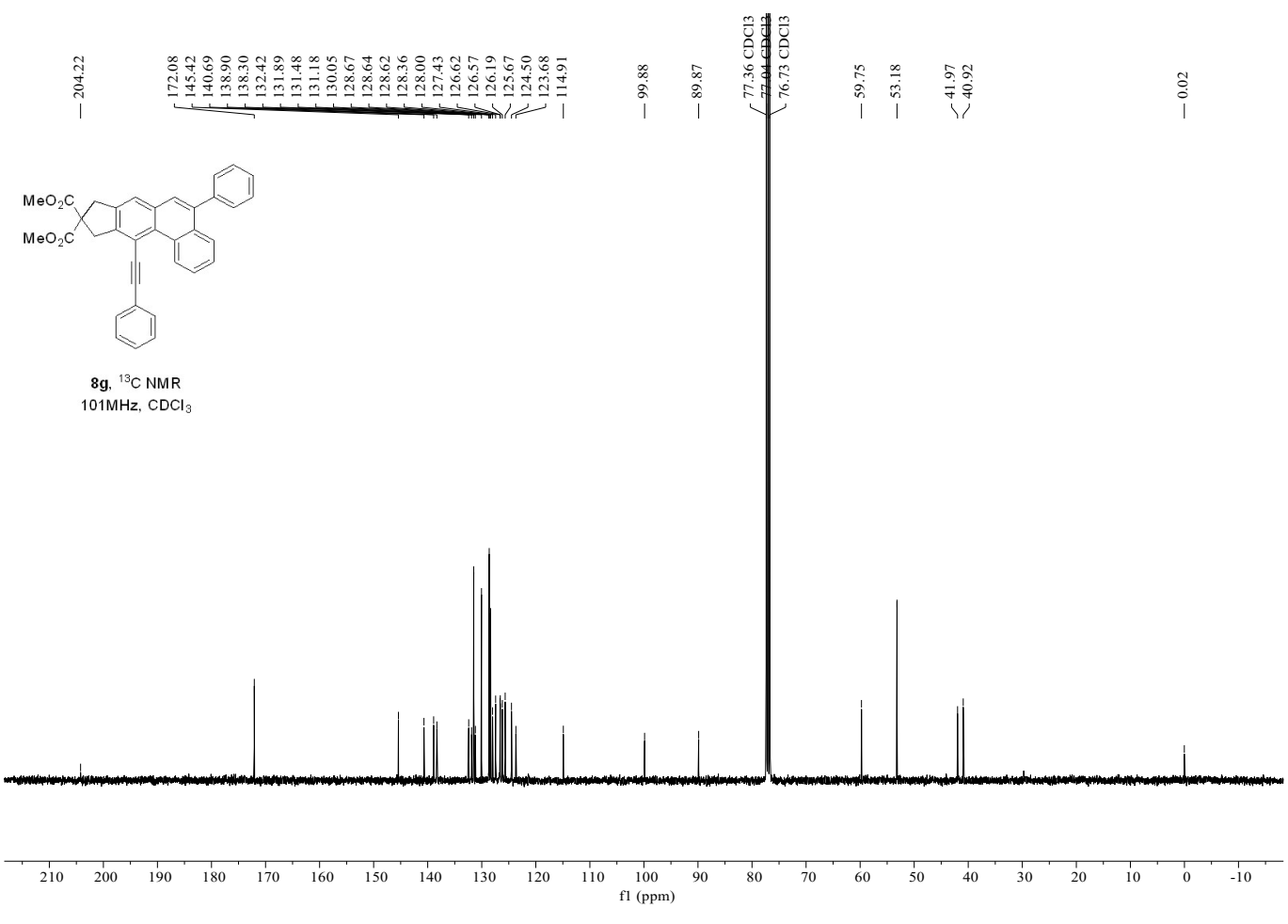




8f, ^{13}C NMR
101MHz, $CDCl_3$

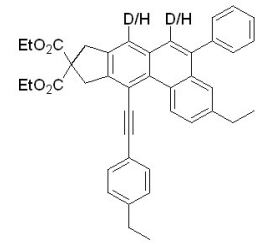


8g, ^{1}H NMR
400MHz, $CDCl_3$

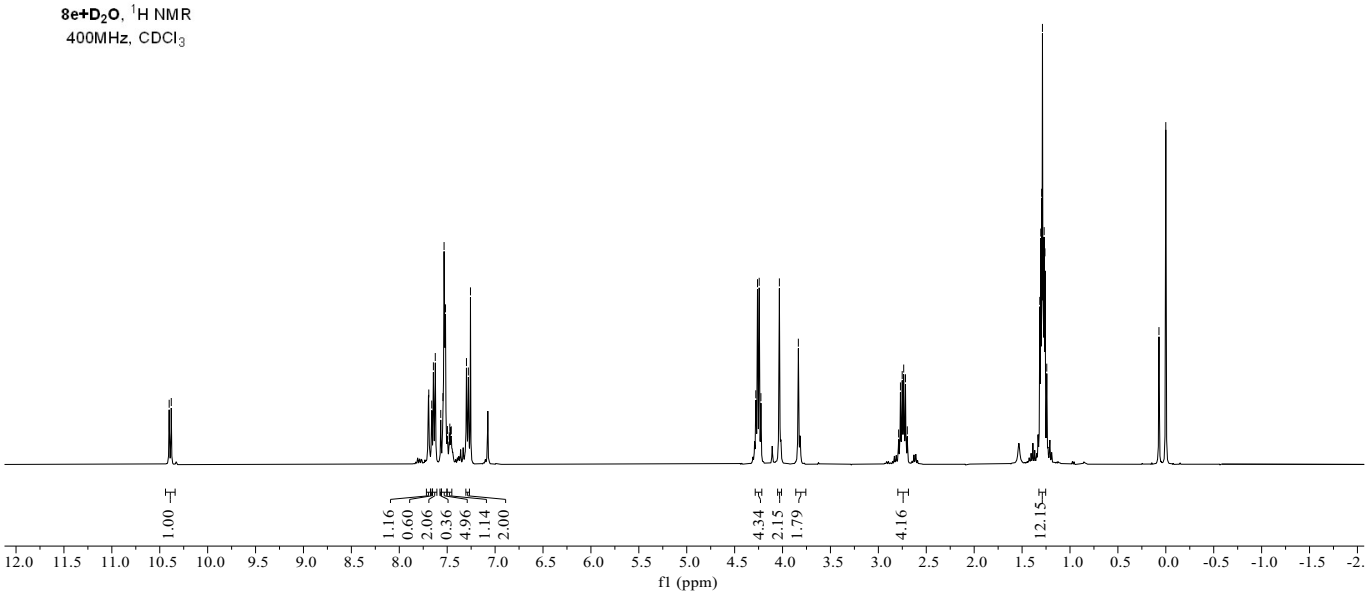


8g, ^{13}C NMR
101MHz, $CDCl_3$

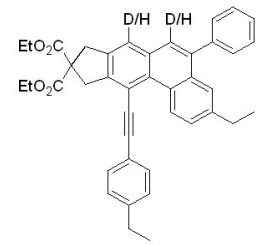
8e+D2O



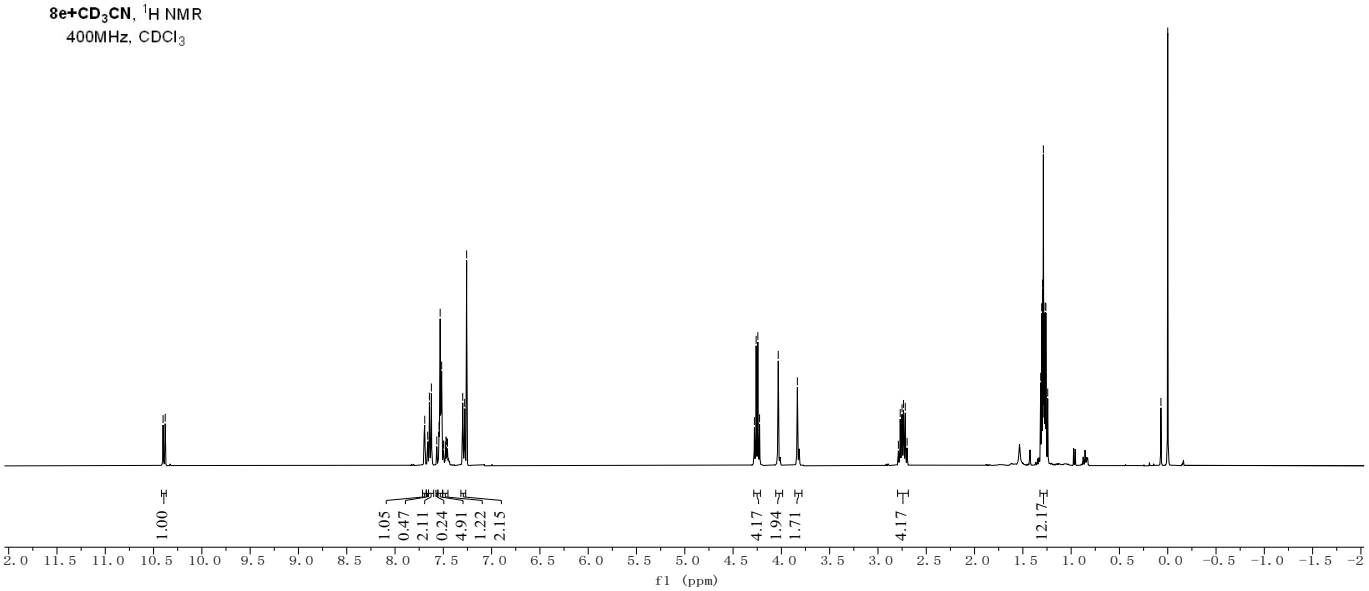
8e+D_2O, ^{1}H NMR
400MHz, $CDCl_3$

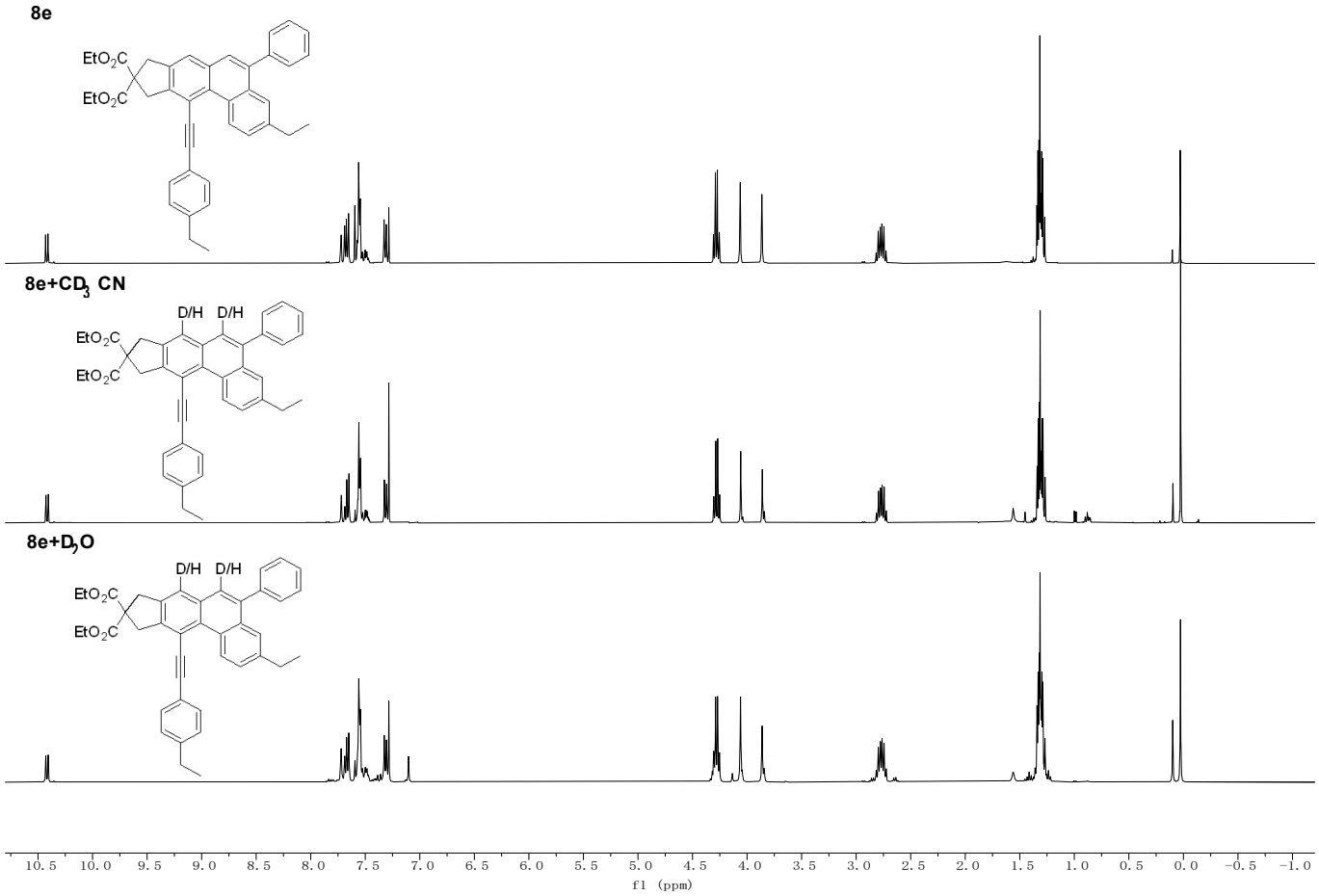


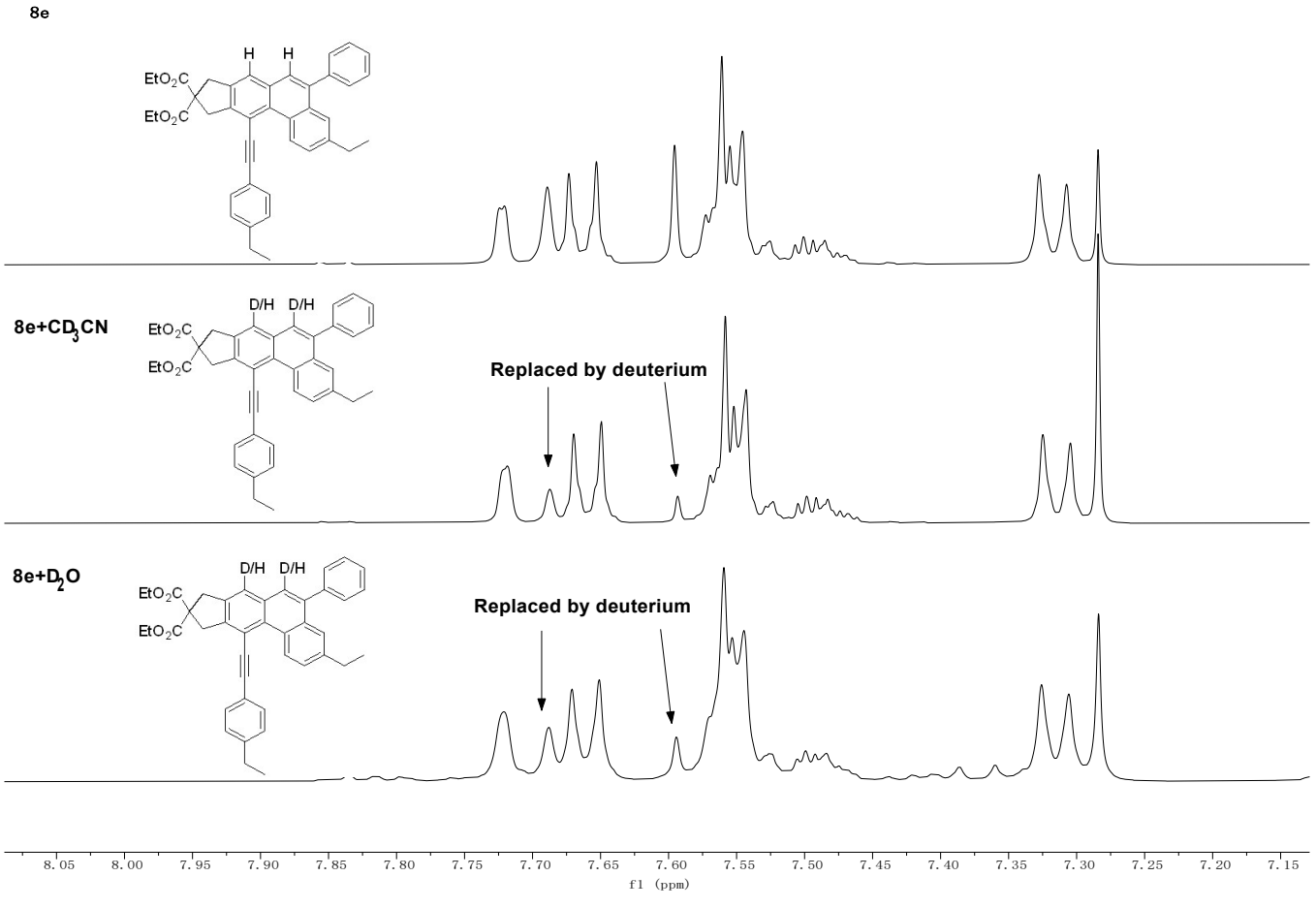
8e+CD3CN



8e+CD_3CN, ^{1}H NMR
400MHz, $CDCl_3$




8e
EtO2C
EtO2C
8e+CD3 CN
D/H D/H
8e+D2O
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


8e
H H
8e+CD3CN
Replaced by deuterium
8e+D2O
8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)