Supplementary Information

Design Strategy and preliminary antiproliferative investigation of modified lignan skeleton derived from aryne and statin

Yu Lei, Yinshan Wen, Xiaoliang Xu, Qiong Hu, Meng Chang, Ruihua Qiang, and Yimin Hu*

School of Chemistry and Materials Science, Anhui Normal University,

Wuhu, Anhui 241002, China

E-mail: yiminhu@ahnu.edu.cn

Contents

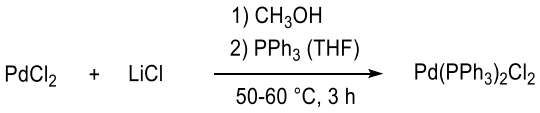
1. General experimental procedures

All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. The chemicals were purchased from Adamas-beta, Macklin reagent, TCI chemicals, and Bidepharm. All solvents and materials were pre-dried, redistilled or recrystallized before use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300/400/500 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 and $CDCl_3$ resonance in the ^{13}C spectra as 77.16 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. High-resolution mass spectra were recorded on an Agilent model G6220 mass spectrometer (APCI).

X-ray structure analysis. Crystal of compounds **3h** suitable for X-ray analysis were obtained via the slow diffusion of petroleum ether into their ethyl acetate solution. The vial containing this solution was placed, loosely capped, to promote the crystallization. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were collected using a Bruker APEX-II CCD diffractometer operating at T = 293 K. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ) at 0.71073 Å. The total number of runs and images was based on the strategy calculation from the program APEX2 (Bruker). The structure was solved by the structure solution program Olex2 (Dolomanov et al., 2009), and the model was refined with version 2014/7 of ShelXL (Sheldrick, 2015) using full matrix least squares on F^2 minimization.

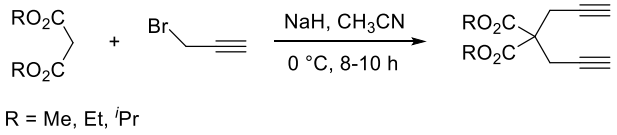
General procedure for preparation of tetraynes

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 h. After reaction solution cooled, filtered and washed with anhydrous ethanol, yellow solid $Pd(PPh_3)_2Cl_2$ catalyst was obtained finally.

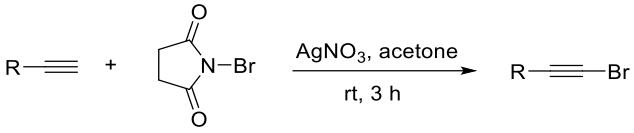
Preparation of diyne substrates



R = Me, Et, ^{i}Pr

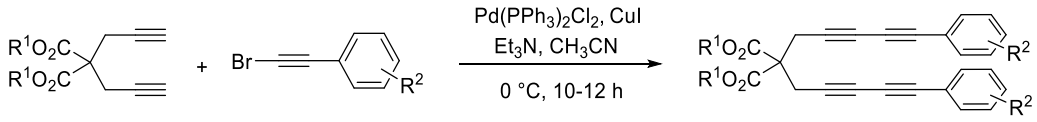
10 g NaH (60%) and 200-300 mL acetonitrile were added in 500 mL three-necked flask with magnetic stirring. 100 mmol malonate and 30 g 3-bromopropyne (98%) were added in the above 500 mL three-necked flask dropwise in turn by separatory funnel, magnetically stirred for 8-10 h under ice-water bath. The 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 substrates



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

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.

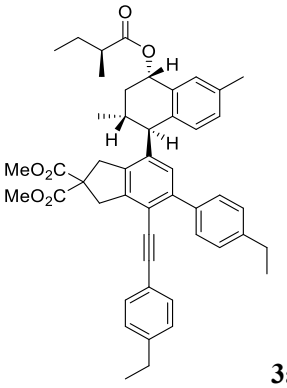
General procedure for preparation of compounds 3a-m, 4a-i, and 5a-f.

Tetrayne (0.2 mmol) and statin (1.2 equiv.) were mixed in a Teflon-lined cap sealed tube equipped with a magnetic stir bar and heated in a 110 ºC oil bath in toluene (4 mL) for 8 hours. Then the reaction mixture was cooled to room temperature, quenched with saturated NaCl, and extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc : petroleum ether = 1: 20-40) to yield the product.

General procedure for preparation of compounds 6a-c.

Tetrayne (1.0 mmol) and ethyl abietate **2d** (1.2 equiv) were mixed in an oven-dried Schlenk tube equipped with a magnetic stir bar and heated in a 90 ºC oil bath in toluene (6 mL) for 8 hours. Then the reaction mixture was cooled to room temperature, quenched with saturated NaCl, and extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc : petroleum ether = 1: 20-40) to yield the product.

2. Characterization data for new compounds

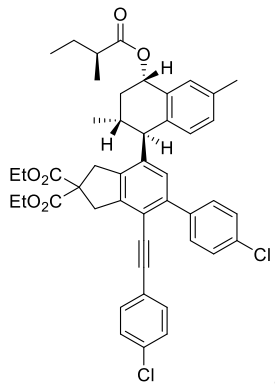


3a

Dimethyl 7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (107 mg, 74% yield); TLC (petroleum ether/EtOAc = 15 : 1) : R_f = 0.26.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.03 (s, 1H), 6.93 (s, 1H), 6.90 (d, J = 7.9 Hz, 1H), 6.61 (d, J = 8.0 Hz, 1H), 6.18 (dd, J = 10.2, 5.8 Hz, 1H), 3.86 (d, J = 17.2 Hz, 1H), 3.79 (d, J = 6.7 Hz, 1H), 3.78 (s, 3H), 3.74 (d, J = 10.6 Hz, 1H), 3.69 (s, 3H), 3.54 (d, J = 15.9 Hz, 1H), 3.20 (s, 1H), 2.69 (q, J = 7.6 Hz, 2H), 2.64 (q, J = 7.6 Hz, 2H), 2.54-2.47 (m, 1H), 2.37-2.33 (m, 1H), 2.29 (s, 3H), 2.23-2.15 (m, 1H), 1.83-1.77 (m, 1H), 1.67-1.63 (m, 1H), 1.60-1.54 (m, 1H), 1.27 (t, J = 7.7 Hz, 3H), 1.24 (d, J = 7.0 Hz, 3H), 1.22 (t, J = 7.6 Hz, 3H), 1.01 (t, J = 7.4 Hz, 3H), 0.98 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.9, 172.2, 172.0, 144.7, 143.8, 143.5, 142.9, 141.2, 137.8, 136.6, 135.9, 135.6, 131.5, 129.4, 128.8, 128.0, 127.5, 126.8, 121.0, 116.3, 96.2, 86.8, 71.0, 59.9, 53.2, 53.0, 41.7, 41.2, 40.0, 37.7, 29.0, 28.8, 26.9, 21.2, 20.5, 16.9, 15.7, 15.5, 11.9. **FT-IR** (KBr): v 2966, 2936, 2337, 2314, 1727, 1518, 1426, 1368, 1213, 1084, 803 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{48}H_{52}O_6$ $[M+H]^+$ 725.3837, found 725.3828.



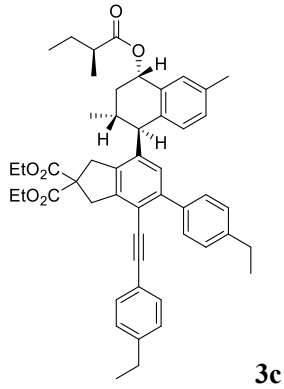
3b

Diethyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (131 mg, 86% yield); TLC (petroleum ether/EtOAc = 15 : 1) : R_f = 0.30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.26 (s, 4H), 7.04 (s, 1H), 6.90 (d, J = 9.1 Hz, 2H), 6.58 (d, J = 7.9 Hz, 1H), 6.18 (dd, J = 10.3, 5.7 Hz, 1H), 4.28-4.14 (m, 4H), 3.84-3.72 (m, 3H), 3.57 (d, J = 16.4 Hz, 1H), 3.25 (s, 1H), 2.54-2.47 (m, 1H), 2.40-2.31 (m, 1H), 2.28 (s, 3H), 2.23-2.14 (m, 1H), 1.83-1.76 (m, 1H), 1.68-1.63 (m, 1H), 1.60-1.57 (m, 1H), 1.28 (d, J = 5.9 Hz, 3H), 1.25 (t, J = 6.3 Hz, 3H), 1.22 (t, J = 7.4 Hz, 3H), 1.01 (t, J = 7.5 Hz, 3H), 0.98 (d, J = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 176.8, 171.6, 171.5, 141.8, 138.8, 136.4, 136.0, 135.7, 134.4, 133.58, 132.7, 130.8, 129.3, 128.8, 128.2, 126.8, 121.9, 115.8, 95.0, 88.0, 70.9, 62.1, 62.0, 59.9, 41.7, 41.0, 39.9, 37.7, 31.6, 30.3, 26.9, 21.2, 20.5, 16.9, 14.2, 14.1, 11.9. **FT-IR** (KBr): ν 2964, 2925, 2331, 2326, 1712, 1522, 1407, 1328, 1217, 1084, 792 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{46}H_{46}Cl_2O_6$ $[M+H]^+$ 765.2744, found 765.2735.



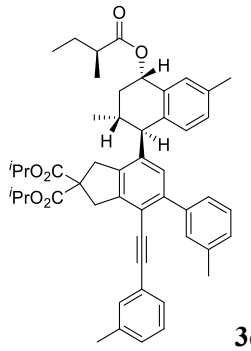
3c

Diethyl 7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (111 mg, 74% yield); TLC (petroleum ether/EtOAc = 15 : 1) : R_f = 0.32.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.03 (s, 1H), 6.92-6.88 (m, 2H), 6.61 (d, J = 8.0 Hz, 1H), 6.18 (dd, J = 10.3, 5.9 Hz, 1H), 4.26-4.14

(m, 4H), 3.85 (d, J = 17.3 Hz, 1H), 3.78-3.74 (m, 2H), 3.56 (d, J = 16.2 Hz, 1H), 3.24 (s, 1H), 2.69 (q, J = 7.6 Hz, 2H), 2.64 (q, J = 7.7 Hz, 2H), 2.50 (dd, J = 13.9, 6.9 Hz, 1H), 2.37-2.34 (m, 1H), 2.28 (s, 3H), 2.23-2.17 (m, 1H), 1.83-1.77 (m, 1H), 1.65-1.63 (m, 1H), 1.58-1.56 (m, 1H), 1.28 (d, J = 6.9 Hz, 3H), 1.27-1.26 (m, 3H), 1.25-1.24 (m, 3H), 1.23-1.22 (m, 3H), 1.22-1.20 (m, 3H), 1.01 (t, J = 7.5 Hz, 3H), 0.98 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.9, 171.8, 171.7, 144.7, 144.0, 143.5, 142.9, 141.2, 138.0, 137.9, 136.7, 135.8, 135.6, 131.5, 129.5, 129.4, 128.8, 128.0, 127.5, 126.8, 121.0, 116.3, 96.1, 86.9, 71.0, 62.0, 61.9, 59.9, 41.7, 41.1, 39.9, 37.7, 29.0, 28.8, 26.9, 21.2, 20.5, 16.9, 15.7, 15.5, 14.2, 14.1, 11.9. **FT-IR** (KBr): v 2966, 2925, 2324, 2328, 1717, 1532, 1417, 1338, 1207, 1094, 832 cm^{-1}. **HRMS** (APCI): m/z calcd for $C_{50}H_{56}O_6$ $[M+H]^+$ 753.4150, found 753.4142.

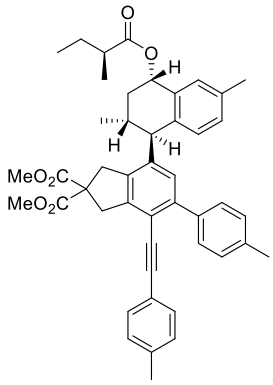


3d

Diisopropyl7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(*m*-tolyl)-4-(*m*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (132 mg, 72% yield); TLC (petroleum ether/EtOAc = 20 : 1) : R_f = 0.28.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.18-7.15 (m, 4H), 7.10 (d, J = 6.8 Hz, 1H), 7.03 (s, 1H), 6.91-6.89 (m, 2H), 6.62 (d, J = 8.0 Hz, 1H), 6.19 (dd, J = 10.4, 5.7 Hz, 1H), 5.12-5.07 (m, 1H), 5.05-5.00 (m, 1H), 3.83 (d, J = 17.3 Hz, 1H), 3.77-3.74 (m, 2H), 3.57 (d, J = 16.5 Hz, 1H), 3.29-3.19 (m, 1H), 2.52-2.48 (m, 1H), 2.40 (s, 3H), 2.37-2.33 (m, 1H), 2.32 (s, 3H), 2.27 (s, 3H), 2.24-2.20 (m, 1H), 1.83-1.77 (m, 1H), 1.68-1.63 (m, 1H), 1.60-1.56 (m, 1H), 1.26-1.24 (m, 12H), 1.18 (d, J = 6.2 Hz, 3H), 1.01 (t, J = 7.6 Hz, 3H), 0.99 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.8, 171.3, 171.2, 144.1, 143.2, 141.3, 140.5, 138.3, 138.0, 137.4, 136.7, 135.9, 135.6, 132.1, 130.2, 129.5, 129.1, 128.9, 128.6, 128.3, 128.2, 127.9, 126.8, 126.6, 123.7, 116.2, 96.1, 87.2, 71.0, 69.4, 69.4, 59.8, 41.7, 41.1, 39.9, 37.8, 34.7, 29.8, 26.9, 21.7, 21.6, 21.6, 21.3, 21.2, 20.5, 16.9, 11.9. **FT-IR** (KBr): v 2964, 2928, 2363, 2326, 1716, 1503, 1441, 1371, 1260, 1102, 807 cm^{-1}. **HRMS** (APCI): m/z calcd for $C_{50}H_{56}O_6$ $[M+H]^+$ 753.4150, found 753.4143.

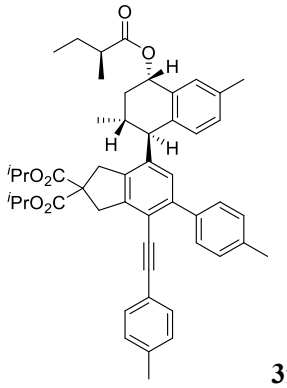


3e

Dimethyl 7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (98 mg, 70% yield); TLC (petroleum ether/EtOAc =10 : 1) : R_f = 0.30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 7.03 (s, 1H), 6.93-6.89 (m, 2H), 6.60 (d, J = 8.0 Hz, 1H), 6.18 (dd, J = 10.4, 5.6 Hz, 1H), 3.86 (d, J = 17.3 Hz, 2H), 3.78 (s, 3H), 3.74 (d, J = 10.1 Hz, 1H), 3.69 (s, 3H), 3.54 (d, J = 15.8 Hz, 1H), 3.26-3.15 (m, 1H), 2.52-2.48 (m, 1H), 2.39 (s, 3H), 2.37-2.36 (m, 1H), 2.35 (s, 3H), 2.29 (s, 3H), 2.23-2.17 (m, 1H), 1.83-1.77 (m, 1H), 1.63-1.60 (m, 1H), 1.59-1.54 (m, 1H), 1.24 (d, J = 7.1 Hz, 3H), 1.01 (t, J = 7.4 Hz, 3H), 0.98 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.9, 172.2, 172.0, 143.9, 142.9, 141.2, 138.4, 137.8, 137.6, 137.2, 136.6, 135.9, 135.6, 131.4, 129.5, 129.3, 129.2, 128.8, 128.7, 126.8, 120.7, 116.3, 96.1, 86.8, 71.0, 59.9, 53.2, 53.0, 41.7, 41.2, 40.0, 37.7, 34.5, 29.8, 26.9, 21.6, 21.4, 21.2, 20.5, 16.9. **FT-IR** (KBr): v 2967, 2939, 2363, 2314, 1737, 1512, 1436, 1388, 1220, 1064, 808 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{46}H_{48}O_6$ $[M+H]^+$ 697.3524, found 697.3517.



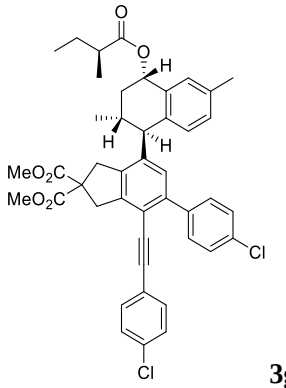
3f

Diisopropyl 7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (112 mg, 74% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.30.

^{1}H NMR (500 MHz， $CDCl_3$): **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.50 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 7.02 (s, 1H), 6.89 (d, J = 6.1 Hz, 2H), 6.62 (d, J = 8.0 Hz, 1H),

6.18 (dd, *J* = 10.3, 5.8 Hz, 1H), 5.11-5.06 (m, 1H), 5.04-4.99 (m, 1H), 3.81 (d, *J* = 17.3 Hz, 1H), 3.76-3.72 (m, 2H), 3.56 (d, *J* = 16.5 Hz, 1H), 3.28-3.17 (m, 1H), 2.52-2.46 (m, 1H), 2.38 (s, 3H), 2.37-2.36 (m, 1H), 2.35 (s, 3H), 2.27 (s, 3H), 2.22-2.17 (m, 1H), 1.83-1.77 (m, 1H), 1.65-1.63 (m, 1H), 1.58-1.55 (m, 1H), 1.27-1.24 (m, 12H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.98 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 176.8, 171.3, 171.2, 144.1, 142.9, 141.2, 138.3, 138.1, 137.7, 137.1, 136.7, 135.9, 135.6, 131.4, 129.5, 129.4, 129.1, 128.9, 128.7, 126.8, 120.9, 116.2, 96.0, 86.9, 71.0, 69.4, 69.3, 59.8, 41.7, 41.1, 39.9, 37.7, 34.7, 29.9, 26.9, 21.7, 21.6, 21.6, 21.4, 21.2, 20.5, 16.9, 11.9. **FT-IR** (KBr): *ν* 2960, 2922, 2366, 2324, 1728, 1510, 1446, 1384, 1263, 1107, 810 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{50}H_{56}O_6$ $[M+H]^+$ 753.4150, found 753.4142.

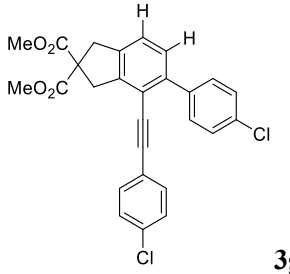


3g

Dimethyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (122 mg, 83% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.20.

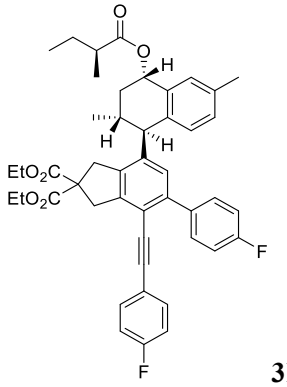
^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.51 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.29 (s, 4H), 7.05 (s, 1H), 6.91 (d, *J* = 5.9 Hz, 2H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.18 (dd, *J* = 10.4, 5.8 Hz, 1H), 3.84 (d, *J* = 17.3 Hz, 1H), 3.78 (s, 3H), 3.77-3.73 (m, 2H), 3.69 (s, 3H), 3.55 (d, *J* = 16.5 Hz, 1H), 3.25-3.19 (m, 1H), 2.54-2.47 (m, 1H), 2.38-2.34 (m, 1H), 2.29 (s, 3H), 2.22-2.16 (m, 1H), 1.83-1.77 (m, 1H), 1.68-1.63 (m, 1H), 1.57-1.55 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.98 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 176.9, 172.0, 141.9, 138.8, 136.3, 136.0, 135.7, 134.5, 133.7, 132.7, 130.8, 129.3, 128.9, 128.2, 126.9, 121.9, 115.8, 95.1, 87.9, 70.9, 59.9, 53.3, 53.1, 41.7, 41.1, 39.9, 37.7, 26.9, 21.3, 20.5, 16.9, 11.9. **FT-IR** (KBr): *ν* 2965, 2941, 2363, 2318, 1739, 1522, 1426, 1378, 1230, 1064, 1027, 818 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{44}H_{42}Cl_2O_6$ $[M+H]^+$ 737.2431, found 737.2423.



3g'

Dimethyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.29 (s, 4H), 7.23 (s, 2H), 3.81 (s, 2H), 3.79 (s, 6H), 3.69 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.1, 143.6, 141.5, 139.4, 139.0, 134.6, 133.6, 132.8, 130.8, 128.9, 128.6, 128.2, 124.5, 121.8, 117.7, 95.3, 87.8, 59.8, 53.3, 41.1, 41.0.

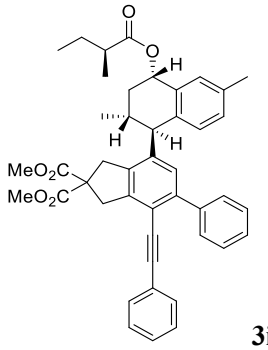


3h

Diethyl 7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

White solid; (120 mg, 82% yield); m.p. 126-128°C, TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.30.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.35-7.30 (m, 2H), 7.11-6.97 (m, 5H), 6.91-6.89 (d, J = 7.7 Hz, 2H), 6.59 (d, J = 7.9 Hz, 1H), 6.19 (dd, J = 9.9, 5.9 Hz, 1H), 4.26-4.14 (m, 4H), 3.87-3.71 (m, 3H), 3.57 (d, J = 16.5 Hz, 1H), 3.23 (d, J = 16.4 Hz, 1H), 2.56-2.45 (m, 1H), 2.38-2.33 (m, 1H), 2.29 (s, 3H), 2.24-2.16 (m, 1H), 1.85-1.76 (m, 1H), 1.70-1.62 (m, 1H), 1.57 (s, 1H), 1.30-1.20 (m, 9H), 1.04-0.97 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.9, 171.7, 171.5, 163.5 (d, $J_{C\text{-}F}$ = 18.9 Hz), 161.6 (d, $J_{C\text{-}F}$ = 15.6 Hz), 144.1, 142.1, 141.6, 138.5, 136.5, 136.0, 135.7, 133.3 (d, $J_{C\text{-}F}$ = 8.3 Hz), 131.1 (d, $J_{C\text{-}F}$ = 7.9 Hz), 129.4, 128.8, 126.8, 119.6, 116.0, 115.8 (d, $J_{C\text{-}F}$ = 22.0 Hz), 114.8 (d, $J_{C\text{-}F}$ = 21.2 Hz), 94.9, 86.8, 70.9, 62.0 (d, $J_{C\text{-}F}$ = 14.1 Hz), 59.9, 41.7, 41.0, 39.9, 37.7, 34.6, 26.9, 21.3, 20.5, 16.9, 14.2, 14.1, 11.9. **FT-IR** (KBr): ν 2968, 2944, 2333, 2324, 1737, 1532, 1426, 1348, 1217, 1084, 803 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{46}H_{46}F_2O_6$ $[M+H]^+$ 733.3335, found 733.3326.



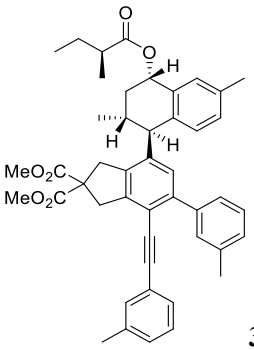
3i

Dimethyl 7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (97 mg, 73% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.26.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 7.4 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.36-7.34 (m, 3H), 7.29-7.28 (m,

3H), 7.04 (s, 1H), 6.95 (s, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.19 (dd, *J* = 10.3, 5.8 Hz, 1H), 3.87 (d, *J* = 17.2 Hz, 1H), 3.80 (d, *J* = 3.6 Hz, 1H), 3.78 (s, 3H), 3.76 (d, *J* = 9.5 Hz, 1H), 3.70 (s, 3H), 3.56 (d, *J* = 16.5 Hz, 1H), 3.28-3.17 (m, 1H), 2.52-2.48 (m, 1H), 2.38-2.34 (m, 1H), 2.29 (s, 3H), 2.23-2.18 (m, 1H), 1.83-1.77 (m, 1H), 1.68-1.66 (m, 1H), 1.59-1.55 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.7 Hz, 3H), 0.99 (d, *J* = 7.0, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.9, 172.1, 143.2, 141.4, 140.5, 136.5, 135.9, 135.7, 131.5, 129.5, 129.4, 128.8, 128.4, 128.3, 128.0, 127.5, 126.9, 123.7, 116.2, 96.0, 87.3, 71.0, 59.9, 53.2, 53.0, 41.7, 41.2, 40.0, 37.8, 34.5, 26.9, 21.2, 20.5, 16.9, 11.9. **FT-IR** (KBr): *v* 2960, 2934, 2343, 2314, 1717, 1532, 1416, 1358, 1227, 1074, 823 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{44}H_{44}O_6$ $[M+H]^+$ 669.3211, found 669.3202.

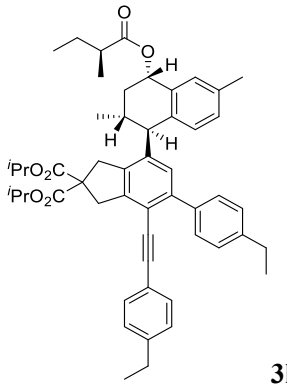


3j

Dimethyl 7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(*m*-tolyl)-4-(*m*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (92 mg, 66% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.26.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.20-7.16 (m, 4H), 7.10 (d, *J* = 6.8 Hz, 1H), 7.04 (s, 1H), 6.95 (s, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.19 (dd, *J* = 10.3, 5.7 Hz, 1H), 3.87 (d, *J* = 17.2 Hz, 1H), 3.79 (s, 1H), 3.78 (s, 3H), 3.75 (d, *J* = 10.5 Hz, 1H), 3.69 (s, 3H), 3.55 (d, *J* = 16.7 Hz, 1H), 3.26-3.17 (m, 1H), 2.52-2.49 (m, 1H), 2.40 (s, 3H), 2.38-2.35 (m, 1H), 2.32 (s, 3H), 2.29 (s, 3H), 2.24-2.17 (m, 1H), 1.83-1.77 (m, 1H), 1.69-1.65 (d, *J* = 12.1 Hz, 1H), 1.57-1.56 (m, 1H), 1.25 (d, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.99 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.9, 172.1, 172.0, 143.9, 143.2, 141.3, 140.4, 138.1, 137.4, 136.6, 135.9, 135.6, 132.1, 130.2, 129.4, 129.2, 128.8, 128.6, 128.3, 128.2, 127.9, 126.8, 126.6, 123.6, 116.3, 96.2, 87.1, 71.0, 59.9, 53.2, 53.0, 41.7, 41.2, 40.0, 37.8, 34.5, 29.9, 26.9, 21.7, 21.4, 21.2, 20.5, 16.9, 11.9. **FT-IR** (KBr): *v* 2960, 2934, 2343, 2314, 1717, 1532, 1416, 1358, 1227, 1074, 823 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{46}H_{48}O_6$ $[M+H]^+$ 697.3524, found 697.3516.

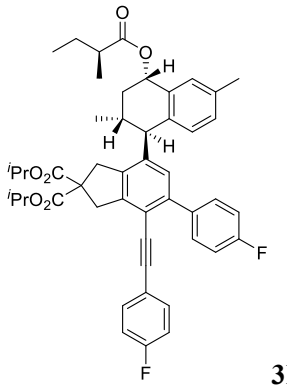


3k

Diisopropyl 7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-1*H*-indene-2,2(3*H*)dicarboxylate

colourless oil; (112 mg, 72% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, J = 8.1 Hz, 2H), 7.30-7.28 (m, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.02 (s, 1H), 6.89 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 7.9 Hz, 1H), 6.18 (dd, J = 10.3, 5.9 Hz, 1H), 5.11-5.06 (m, 1H), 5.04-4.99 (m, 1H), 3.83-3.72 (m, 3H), 3.56 (d, J = 16.5 Hz, 1H), 3.28-3.17 (m, 1H), 2.68 (q, J = 7.8 Hz, 2H), 2.64 (q, J = 7.7 Hz, 2H), 2.53-2.46 (m, 1H), 2.37-2.33 (m, 1H), 2.27 (s, 3H), 2.23-2.17 (m, 1H), 1.83-1.77 (m, 1H), 1.68-1.63 (m, 1H), 1.57-1.54 (m, 1H), 1.28-1.24 (m, 12H), 1.23-1.21 (m, 6H), 1.17 (d, J = 6.3 Hz, 3H), 1.01 (t, J = 7.5 Hz, 3H), 0.98 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.9, 171.3, 171.2, 144.6, 143.4, 142.9, 141.1, 138.1, 137.9, 136.7, 135.8, 135.6, 131.5, 129.5, 129.4, 128.8, 127.9, 127.4, 126.7, 121.1, 116.2, 96.0, 86.9, 71.0, 69.4, 69.3, 59.8, 51.6, 41.7, 41.0, 39.9, 37.7, 29.0, 28.7, 26.9, 21.7, 21.6, 21.6, 21.2, 20.5, 16.9, 15.7, 15.5, 11.9. **FT-IR** (KBr):*v* 2964, 2926, 2360, 2322, 1718, 1503, 1451, 1381, 1267, 1112, 804 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{52}H_{60}O_6$ $[M+H]^+$ 781.4463, found 781.4455.



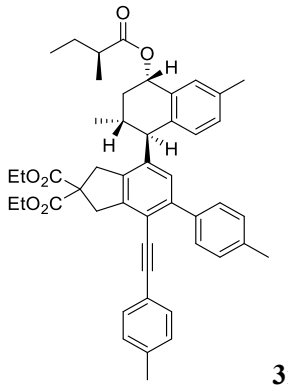
3l

Diisopropyl 7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (130 mg, 85% yield); TLC (petroleum ether/EtOAc = 15 : 1) : R_f = 0.28.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55-7.52 (m, 2H), 7.33-7.30 (m, 2H), 7.08 (t, J = 8.7 Hz, 2H), 7.04 (s, 1H), 7.00 (t,

J = 8.7 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.87 (s, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 6.18 (dd, *J* = 10.5, 5.7 Hz, 1H), 5.11-5.06 (m, 1H), 5.05-5.00 (m, 1H), 3.82-3.71 (m, 3H), 3.57 (d, *J* = 16.6 Hz, 1H), 3.29-3.16 (m, 1H), 2.54-2.47 (m, 1H), 2.38-2.34 (m, 1H), 2.28 (s, 3H), 2.23-2.15 (m, 1H), 1.84-1.76 (m, 1H), 1.68-1.63 (m, 1H), 1.61-1.57 (m, 1H), 1.27-1.24 (m, 12H), 1.18 (d, *J* = 6.3 Hz, 3H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.98 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 176.9, 171.2, 171.1, 163.5 (d, J_{C-F} = 18.9 Hz), 161.6 (d, J_{C-F} = 15.4 Hz), 144.1, 142.1, 141.6, 138.7, 136.5, 136.0, 135.7, 133.3 ((d, J_{C-F} = 8.3 Hz)), 131.1 (d, J_{C-F} = 8.0 Hz), 129.4, 128.9, 126.8, 119.7, 116.0, 115.8 (d, J_{C-F} = 21.9 Hz), 114.8 (d, J_{C-F} = 21.3 Hz), 94.9, 86.9, 71.0, 69.5 (d, J_{C-F} = 8.3 Hz), 59.8, 51.5, 41.7, 41.0, 39.9, 37.7, 34.7, 29.9, 26.9, 21.7, 21.6, 21.6, 21.2, 20.5, 16.9, 11.9. **FT-IR** (KBr): *ν* 2964, 2928, 2360, 2324, 1725, 1507, 1456, 1384, 1260, 1113, 809 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{48}H_{50}F_2O_6$ $[M+H]^+$ 761.3648, found 761.3639.

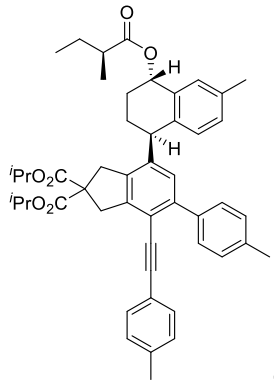


3m

Diethyl 7-((1*R*,2*R*,4*S*)-2,6-dimethyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(p-tolyl)-4-(p-tolylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate

colourless oil; (98 mg, 68% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.34.

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.51 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.03 (s, 1H), 6.94-6.86 (m, 2H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.18 (dd, *J* = 10.1, 5.8 Hz, 1H), 4.28-4.11 (m, 4H), 3.85 (d, *J* = 17.3 Hz, 1H), 3.80-3.72 (m, 2H), 3.56 (d, *J* = 16.4 Hz, 1H), 3.29-3.14 (m, 1H), 2.53-2.47 (m, 1H), 2.38 (s, 3H), 2.37-2.35 (m, 1H), 2.34 (s, 3H), 2.28 (s, 3H), 2.24-2.18 (m, 1H), 1.83-1.76 (m, 1H), 1.68-1.62 (m, 1H), 1.58-1.54 (m, 1H), 1.27-1.25 (m, 6H), 1.21 (d, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 176.9, 171.8, 171.6, 144.0, 142.8, 141.2, 138.3, 138.0, 137.6, 137.1, 136.6, 135.8, 135.6, 131.4, 129.5, 129.3, 129.1, 128.8, 128.7, 126.8, 120.8, 116.2, 96.0, 86.9, 71.0, 62.0, 61.9, 59.9, 51.7, 41.7, 41.1, 39.9, 37.7, 34.6, 29.9, 26.9, 21.6, 21.4, 21.2, 20.5, 16.9, 14.2, 14.1, 11.9. **FT-IR** (KBr): *ν* 2964, 2926, 2326, 2320, 1730, 1512, 1426, 1328, 1218, 1072, 810 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{48}H_{52}O_6$ $[M+H]^+$ 725.3837, found 725.3831.

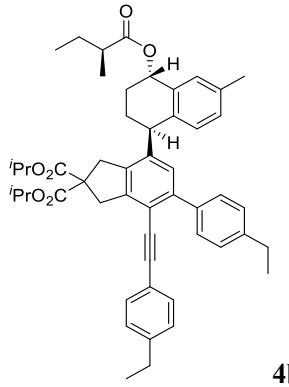


4a

Diisopropyl 7-((1*R*,4*S*)-6-methyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (104 mg, 70% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.07 (s, 1H), 6.97 (d, J = 7.9 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.66 (s, 1H), 6.08 (t, J = 5.5 Hz, 1H), 5.12-5.08 (m, 1H), 5.07-5.03 (m, 1H), 4.26 (t, J = 6.2 Hz, 1H), 3.79 (s, 2H), 3.61 (d, J = 16.5 Hz, 1H), 3.44 (d, J = 16.5 Hz, 1H), 2.45-2.41 (m, 1H), 2.37 (s, 3H), 2.34 (s, 3H), 2.32-2.31 (m, 1H), 2.29 (s, 3H), 2.24-2.18 (m, 1H), 1.92-1.82 (m, 2H), 1.77-1.72 (m, 1H), 1.53-1.49 (m, 1H), 1.28-1.22 (m, 12H), 1.19 (d, J = 7.1 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.6, 171.3, 144.0, 142.7, 142.1, 138.3, 137.8, 137.3, 137.1, 136.3, 136.1, 135.5, 131.4, 129.9, 129.4, 129.1, 128.9, 128.8, 128.6, 120.8, 116.2, 95.9, 86.9, 70.1, 69.4, 69.4, 59.9, 42.4, 41.6, 41.1, 39.6, 27.1, 27.1, 26.9, 21.7, 21.7, 21.6, 21.3, 21.2, 16.9, 11.8. **FT-IR** (KBr): v 2964, 2932, 2347, 2334, 1718, 1532, 1431, 1327, 1241, 1074, 809 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{49}H_{54}O_6$ $[M+H]^+$ 739.3993, found 739.3985.



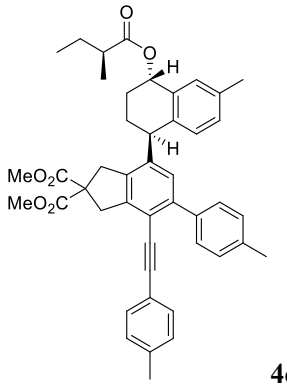
4b

Diisopropyl 5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-7-((1*R*,4*S*)-6-methyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (104 mg, 68% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, J = 7.3 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 7.7 Hz, 2H), 7.12 (d, J = 7.7 Hz, 2H), 7.07 (s, 1H), 6.97 (d, J = 7.8 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.67 (s, 1H), 6.08 (t, J = 5.4 Hz, 1H),

5.12-5.03 (m, 2H), 4.26 (t, J = 5.9 Hz, 1H), 3.79 (s, 2H), 3.61 (d, J = 16.5 Hz, 1H), 3.45 (d, J = 16.2 Hz, 1H), 2.67 (q, J = 7.4 Hz, 2H), 2.63 (q, J = 7.3 Hz, 2H), 2.46-2.41 (m, 1H), 2.35-2.31 (m, 1H), 2.29 (s, 3H), 2.23-2.18 (m, 1H), 1.93-1.72 (m, 2H), 1.77-1.72 (m, 1H), 1.54-1.48 (m, 1H), 1.28-1.25 (m, 12H), 1.23-1.20 (m, 6H), 1.19 (d, J = 7.2 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.7, 171.3, 144.6, 143.9, 143.4, 142.8, 142.0, 138.0, 137.3, 136.3, 136.1, 135.5, 131.5, 129.9, 129.4, 129.3, 128.9, 128.8, 127.9, 127.4, 121.1, 116.2, 95.9, 86.9, 70.1, 69.4, 69.4, 59.9, 42.4, 41.6, 41.1, 39.6, 29.0, 28.7, 27.1, 27.0, 26.9, 21.7, 21.7, 21.7, 21.2, 16.9, 15.7, 15.5, 11.8. **FT-IR** (KBr): ν 2960, 2931, 2357, 2324, 1734, 1509, 1456, 1385, 1246, 1154, 1074, 1021, 831 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{51}H_{58}O_6$ $[M+H]^+$ 767.4306, found 767.4297.

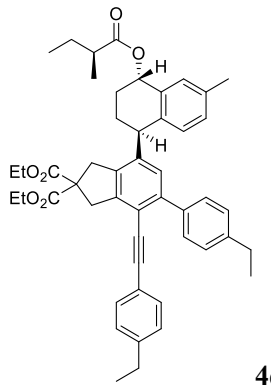


4c

Dimethyl 7-((1*R*,4*S*)-6-methyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

Colourless oil; (90 mg, 66% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.24.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 7.07 (s, 1H), 6.98 (d, J = 7.8 Hz, 1H), 6.79 (d, J = 7.9 Hz, 1H), 6.69 (s, 1H), 6.08 (t, J = 5.5 Hz, 1H), 4.25 (t, J = 6.2 Hz, 1H), 3.84 (s, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 3.64 (d, J = 16.4 Hz, 1H), 3.46 (d, J = 16.5 Hz, 1H), 2.46-2.42 (m, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H), 2.29-2.26 (m, 1H), 2.23-2.18 (m, 1H), 1.93-1.82 (m, 2H), 1.78-1.72 (m, 1H), 1.55-1.49 (m, 1H), 1.20 (d, J = 7.0 Hz, 3H), 0.96 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.7, 172.2, 172.2, 147.2, 143.7, 142.8, 142.1, 138.4, 137.6, 137.1, 136.3, 136.0, 135.6, 131.4, 129.8, 129.3, 129.1, 129.0, 128.9, 128.7, 124.6, 124.1, 120.7, 119.3, 116.2, 96.1, 86.8, 70.1, 59.8, 53.2, 53.2, 42.6, 41.6, 41.3, 39.8, 35.0, 34.7, 31.6, 30.4, 29.8, 27.1, 26.9, 21.6, 21.3, 21.2, 16.9, 11.8. **FT-IR** (KBr): ν 2966, 2929, 2342, 2334, 1718, 1542, 1446, 1355, 1236, 1154, 1094, 1021, 821 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{45}H_{46}O_6$ $[M+H]^+$ 683.3367, found 683.3356.

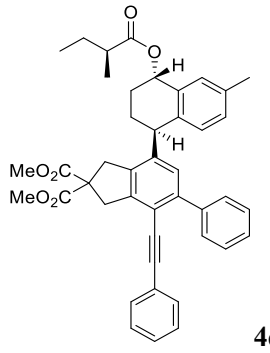


4d

Diethyl 5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-7-((1*R*,4*S*)-6-methyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (99 mg, 67% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.32.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 7.07 (s, 1H), 6.97 (d, J = 7.8 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.69 (s, 1H), 6.08 (t, J = 5.6 Hz, 1H), 4.29-4.22 (m, 4H), 4.20 (d, J = 7.1 Hz, 1H), 3.83 (s, 2H), 3.64 (d, J = 16.5 Hz, 1H), 3.47 (d, J = 16.5 Hz, 1H), 2.68 (q, J = 7.6 Hz, 2H), 2.63 (q, J = 7.6 Hz, 2H), 2.46-2.42 (m, 1H), 2.36-2.32 (m, 1H), 2.29 (s, 3H), 2.23-2.19 (m, 1H), 1.93-1.82 (m, 2H), 1.78-1.72 (m, 1H), 1.54-1.49 (m, 1H), 1.30 (d, J = 7.1 Hz, 3H), 1.26-1.23 (m, 6H), 1.20 (t, J = 7.0 Hz, 6H), 0.95 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.7, 171.8, 171.8, 144.6, 143.8, 143.4, 142.8, 142.0, 137.9, 137.2, 136.3, 136.0, 135.5, 131.5, 129.9, 129.4, 129.3, 128.9, 128.8, 127.9, 127.4, 121.0, 116.2, 96.0, 86.9, 70.0, 62.0, 61.9, 59.8, 42.4, 41.5, 41.1, 39.6, 29.8, 29.0, 28.7, 27.0, 26.8, 21.2, 16.9, 15.7, 15.5, 14.2, 14.2, 11.8. **FT-IR** (KBr): ν 2960, 2931, 2357, 2324, 1734, 1508, 1456, 1387, 1242, 1158, 1074, 1024, 831 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{49}H_{54}O_6$ $[M+H]^+$ 739.3993, found 739.3987.



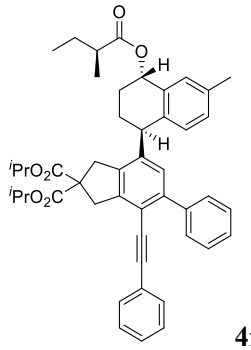
4e

Dimethyl 7-((1*R*,4*S*)-6-methyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (90 mg, 69% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.27.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 7.3 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.35-7.33 (m, 3H), 7.29-7.28 (m, 3H), 7.08 (s, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.72 (s, 1H), 6.09 (t, J = 5.7 Hz, 1H), 4.26 (t, J

= 6.3 Hz, 1H), 3.85 (s, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 3.65 (d, *J* = 16.5 Hz, 1H), 3.47 (d, *J* = 16.6 Hz, 1H), 2.47-2.42 (m, 1H), 2.30 (s, 3H), 2.30-2.27 (m, 1H), 2.24-2.19 (m, 1H), 1.94-1.83 (m, 2H), 1.78-1.72 (m, 1H), 1.54-1.48 (m, 1H), 1.20 (d, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 176.7, 172.2, 143.8, 143.1, 142.4, 140.5, 137.4, 136.4, 136.0, 135.6, 131.5, 129.8, 129.5, 129.3, 129.0, 128.9, 128.4, 128.3, 128.0, 127.5, 123.7, 116.2, 95.9, 87.3, 70.1, 59.8, 53.3, 53.2, 42.6, 41.6, 41.2, 39.8, 27.2, 26.9, 21.2, 16.9, 11.8. **FT-IR** (KBr): *v* 2967, 2931, 2348, 2329, 1734, 1568, 1458, 1347, 1242, 1128, 1084, 1028, 812 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{43}H_{42}O_6$ $[M+H]^+$ 655.3054, found 655.3045.

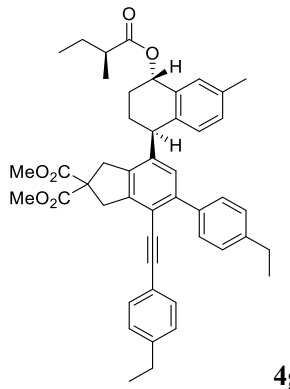


4f

Diethyl 7-((1*R*,4*S*)-6-methyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(4-propylphenyl)-4-((4-propylphenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (109 mg, 77% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.32.

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.52 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.34-7.31 (m, 3H), 7.29-7.27 (m, 3H), 7.07 (s, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.70 (s, 1H), 6.09 (t, *J* = 5.6 Hz, 1H), 5.13-5.04 (m, 2H), 4.27 (t, *J* = 6.3 Hz, 1H), 3.80 (s, 2H), 3.62 (d, *J* = 16.6 Hz, 1H), 3.45 (d, *J* = 16.5 Hz, 1H), 2.47-2.41 (m, 1H), 2.35-2.31 (m, 1H), 2.29 (s, 3H), 2.26-2.19 (m, 1H), 1.94-1.82 (m, 2H), 1.78-1.72 (m, 1H), 1.55-1.49 (m, 1H), 1.29-1.22 (m, 12H), 1.20 (d, *J* = 7.0 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 176.6, 171.3, 144.1, 143.0, 142.3, 140.6, 137.7, 136.4, 136.0, 135.6, 131.5, 129.9, 129.5, 129.3, 128.9, 128.8, 128.4, 128.2, 127.9, 127.4, 123.8, 116.1, 95.7, 87.4, 71.8, 70.1, 69.5, 69.4, 62.2, 59.9, 42.5, 41.6, 41.0, 39.6, 29.9, 27.2, 27.1, 26.9, 22.7, 21.7, 21.7, 21.7, 21.2, 16.9, 14.1, 11.8. **FT-IR** (KBr): *v* 2964, 2933, 2342, 2327, 1724, 1578, 1468, 1357, 1252, 1138, 1074, 1024, 823 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{47}H_{50}O_6$ $[M+H]^+$ 711.3680, found 711.3689.

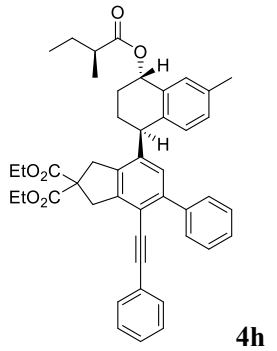


4g

Dimethyl 5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-7-((1*R*,4*S*)-6-methyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (91 mg, 64 % yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.26.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 7.07 (s, 1H), 6.98 (d, J = 7.9 Hz, 1H), 6.79 (d, J = 7.9 Hz, 1H), 6.71 (s, 1H), 6.08 (t, J = 5.4 Hz, 1H), 4.25 (t, J = 6.0 Hz, 1H), 3.84 (s, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 3.65 (d, J = 16.5 Hz, 1H), 3.47 (d, J = 16.4 Hz, 1H), 2.68 (q, J = 7.7 Hz, 2H), 2.63 (q, J = 7.7 Hz, 2H), 2.46-2.41 (m, 1H), 2.30 (s, 3H), 2.29-2.26 (m, 1H), 2.24-2.19 (m, 1H), 1.92-1.83 (m, 2H), 1.78-1.72 (m, 1H), 1.55-1.49 (m, 1H), 1.26 (t, J = 7.6 Hz, 3H), 1.23-1.19 (m, 6H), 0.96 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.7, 172.2, 172.2, 144.7, 143.7, 143.5, 142.9, 142.1, 137.9, 137.1, 136.3, 136.0, 135.6, 131.5, 129.8, 129.4, 129.3, 129.0, 128.9, 128.0, 127.4, 121.0, 116.3, 96.1, 86.8, 70.1, 59.8, 53.2, 53.2, 42.6, 41.6, 41.3, 39.8, 29.8, 29.0, 28.7, 27.1, 26.9, 21.2, 16.9, 15.7, 15.5, 11.8. **FT-IR** (KBr): ν 2964, 2924, 2356, 2336, 1716, 1548, 1448, 1353, 1236, 1134, 1098, 1022, 818 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{47}H_{50}O_6$ $[M+H]^+$ 711.3680, found 711.3687.



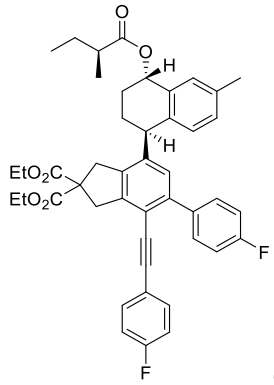
4h

Diethyl 7-((1*R*,4*S*)-6-methyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (97 mg, 71 % yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.35.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, J = 7.2 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.35-7.32 (m, 3H), 7.29-7.27 (m, 3H), 7.07 (s, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.71 (s, 1H), 6.09 (t, J = 5.7 Hz, 1H), 4.30-4.23

(m, 4H), 4.21 (d, J = 7.0 Hz, 1H), 3.84 (s, 2H), 3.65 (d, J = 16.5 Hz, 1H), 3.47 (d, J = 16.4 Hz, 1H), 2.46-2.41 (m, 1H), 2.34-2.31 (m, 1H), 2.30 (s, 3H), 2.25-2.20 (m, 1H), 1.95-1.82 (m, 2H), 1.78-1.72 (m, 1H), 1.55-1.49 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.20 (d, J = 7.1 Hz, 3H), 0.96 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.7, 171.8, 144.0, 143.0, 142.3, 140.6, 137.6, 136.4, 136.0, 135.6, 131.5, 129.8, 129.5, 129.3, 128.9, 128.4, 128.2, 127.9, 127.4, 123.7, 116.1, 95.8, 87.4, 70.1, 62.1, 62.0, 59.8, 42.5, 41.6, 41.1, 39.7, 27.1, 26.9, 21.2, 16.9, 14.2, 14.2, 11.8. **FT-IR** (KBr): ν 2964, 2933, 2356, 2327, 1724, 1538, 1476, 1377, 1232, 1168, 1068, 1020, 825 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{45}H_{46}O_6$ $[M+H]^+$ 683.3367, found 683.3359.

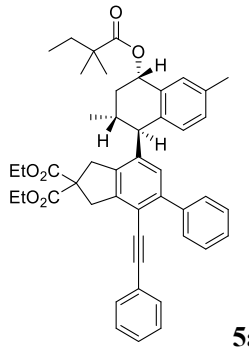


4i

Diethyl 5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-7-((1*R*,4*S*)-6-methyl-4-(((*S*)-2-methylbutanoyl)oxy)-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (122 mg, 85% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.35.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48-7.45 (m, 2H), 7.32-7.29 (m, 2H), 7.08-7.04 (m, 3H), 6.99 (t, J = 8.8 Hz, 3H), 6.78 (d, J = 7.9 Hz, 1H), 6.67 (s, 1H), 6.09 (t, J = 5.8 Hz, 1H), 4.30-4.23 (m, 4H), 4.20 (d, J = 7.1 Hz, 1H), 3.81 (s, 2H), 3.64 (d, J = 16.5 Hz, 1H), 3.45 (d, J = 16.5 Hz, 1H), 2.47-2.43 (m, 1H), 2.30 (s, 3H), 2.29-2.26 (m, 1H), 2.24-2.18 (m, 1H), 1.92-1.83 (m, 2H), 1.78-1.72 (m, 1H), 1.55-1.49 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.20 (d, J = 7.0 Hz, 3H), 0.96 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 176.7, 171.7, 163.5 (d, $J_{C\text{-}F}$ = 23.3 Hz), 161.6 (d, $J_{C\text{-}F}$ = 19.9 Hz), 144.0, 142.5, 142.0, 137.8, 136.4, 135.9, 135.6, 133.3 (d, $J_{C\text{-}F}$ = 8.2 Hz), 131.1 (d, $J_{C\text{-}F}$ = 7.9 Hz), 129.7, 129.3, 128.8 (d, $J_{C\text{-}F}$ = 8.2 Hz), 116.0, 115.8 (d, $J_{C\text{-}F}$ = 21.9 Hz), 114.8 (d, $J_{C\text{-}F}$ = 21.2 Hz), 94.9, 86.8, 70.1, 62.1 (d, $J_{C\text{-}F}$ = 7.8 Hz), 59.9, 42.6, 41.6, 41.1, 39.7, 27.3, 26.9, 21.2, 16.9, 14.2, 14.2, 11.8. **FT-IR** (KBr): ν 2967, 2941, 2346, 2329, 1718, 1536, 1458, 1362, 1241, 1172, 1065, 1023, 805 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{45}H_{44}F_2O_6$ $[M+H]^+$ 719.3179, found 719.3186.

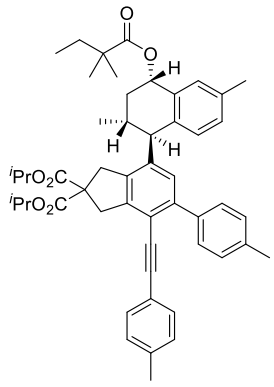


5a

Diethyl 7-((1*R*,2*R*,4*S*)-4-((2,2-dimethylbutanoyl)oxy)-2,6-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (101 mg, 71% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.29.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 7.3 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.37-7.34 (m, 3H), 7.30-7.28 (m, 3H), 7.03 (s, 1H), 6.94 (s, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 6.16 (dd, J = 10.3, 5.8 Hz, 1H), 4.28-4.16 (m, 4H), 3.86 (d, J = 17.2 Hz, 1H), 3.80-3.76 (m, 2H), 3.57 (d, J = 16.5 Hz, 1H), 3.30-3.20 (m, 1H), 2.37-2.34 (m, 1H), 2.28 (s, 3H), 2.23-2.19 (m, 1H), 1.68-1.64 (m, 3H), 1.28-1.24 (m, 12H), 0.99 (d, J = 6.5 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 178.1, 171.7, 171.6, 144.1, 143.1, 141.4, 140.5, 138.3, 136.5, 135.9, 135.8, 131.5, 129.5, 129.4, 128.8, 128.4, 128.2, 128.0, 127.5, 126.8, 123.7, 116.2, 95.9, 87.4, 71.0, 62.0, 61.9, 59.9, 51.7, 43.0, 41.1, 39.9, 37.6, 34.6, 33.4, 29.8, 25.0, 24.8, 21.2, 20.5, 14.2, 14.1, 9.5. **FT-IR** (KBr): ν 2964, 2935, 2314, 2330, 1722, 1542, 1432, 1313, 1207, 1074, 802 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{47}H_{50}O_6$ $[M+H]^+$ 711.3680, found 711.3672.



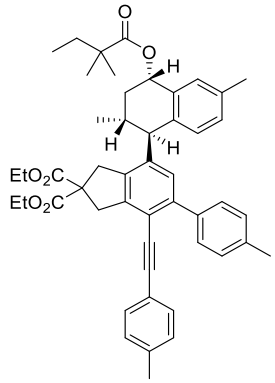
5b

Diisopropyl 7-((1*R*,2*R*,4*S*)-4-((2,2-dimethylbutanoyl)oxy)-2,6-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

White solid; (106 mg, 69% yield); m.p. 130-132 ℃, TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.28.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 7.02 (s, 1H), 6.89 (d, J = 4.3 Hz, 2H), 6.62 (d, J = 8.0 Hz, 1H), 6.15 (dd, J = 10.3, 5.8 Hz, 1H), 5.11-5.06 (m, 1H), 5.04-5.00 (m, 1H), 3.81 (d, J = 17.3 Hz, 1H), 3.77-3.72 (m, 2H), 3.56 (d, J = 16.5 Hz, 1H), 3.33-3.10

(m, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 2.33-2.29 (m, 1H), 2.27 (s, 3H), 2.25-2.18 (m, 1H), 1.69-1.62 (m, 3H), 1.28-1.24 (m, 12H), 1.23 (s, 3H), 1.17 (d, J = 6.2 Hz, 3H), 0.98 (d, J = 6.5 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 178.1, 171.3, 171.2, 138.3, 137.1, 135.8, 131.4, 129.5, 129.4, 129.1, 128.8, 128.7, 126.8, 120.8, 116.2, 86.9, 71.0, 69.4, 69.3, 59.8, 43.0, 41.1, 39.9, 37.6, 33.4, 25.0, 24.8, 21.7, 21.6, 21.6, 21.4, 21.2, 20.6, 9.5. **FT-IR** (KBr): v 2956, 2937, 2342, 2347, 1732, 1532, 1425, 1327, 1232, 1064, 801 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{51}H_{58}O_6$ $[M+H]^+$ 767.4306, found 767.4301.

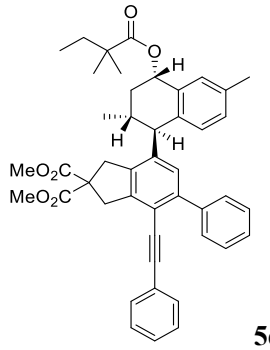


5c

Diethyl 7-((1*R*,2*R*,4*S*)-4-((2,2-dimethylbutanoyl)oxy)-2,6-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (99 mg, 67% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.28.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 7.02 (s, 1H), 6.90 (d, J = 10.6 Hz, 2H), 6.61 (d, J = 8.0 Hz, 1H), 6.15 (dd, J = 10.3, 5.7 Hz, 1H), 4.28-4.14 (m, 4H), 3.85 (d, J = 17.3 Hz, 1H), 3.78-3.74 (m, 2H), 3.56 (d, J = 16.2 Hz, 1H), 3.27-3.18 (m, 1H), 2.39 (s, 3H), 2.35 (s, 3H), 2.33-2.31 (m, 1H), 2.28 (s, 3H), 2.23-2.17 (m, 1H), 1.67-1.62 (m, 3H), 1.27-1.26 (m, 6H), 1.24-1.20 (m, 6H), 0.98 (d, J = 6.5 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 178.1, 171.8, 171.7, 144.0, 142.8, 141.2, 138.3, 137.6, 137.1, 136.6, 135.8, 131.4, 129.5, 129.4, 129.2, 128.7, 128.7, 126.8, 120.8, 116.2, 96.0, 86.9, 71.0, 62.0, 61.9, 59.9, 43.0, 41.1, 39.9, 37.6, 34.5, 33.4, 25.0, 24.8, 21.6, 21.4, 21.3, 20.5, 14.2, 14.1, 9.5. **FT-IR** (KBr): v 2971, 2945, 2324, 2343, 1732, 1532, 1422, 1323, 1227, 1084, 808 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{49}H_{54}O_6$ $[M+H]^+$ 739.3993, found 739.3985.

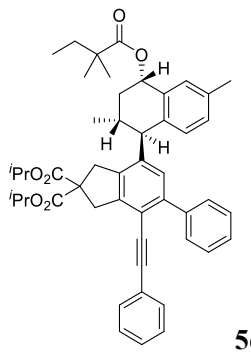


5d

Dimethyl 7-((1*R*,2*R*,4*S*)-4-((2,2-dimethylbutanoyl)oxy)-2,6-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (96 mg, 70% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.24.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 7.4 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.36-7.34 (m, 3H), 7.30-7.28 (m, 3H), 7.03 (s, 1H), 6.95 (s, 1H), 6.91 (d, J = 8.1 Hz, 1H), 6.61 (d, J = 8.0 Hz, 1H), 6.15 (dd, J = 10.2, 5.8 Hz, 1H), 3.89-3.80 (m, 2H), 3.78 (s, 3H), 3.76-3.73 (m, 1H), 3.70 (s, 3H), 3.56 (d, J = 16.1 Hz, 1H), 3.29-3.17 (m, 1H), 2.36-2.33 (m, 1H), 2.29 (s, 3H), 2.24-2.18 (m, 1H), 1.68-1.62 (m, 3H), 1.26 (s, 3H), 1.24 (s, 3H), 0.99 (d, J = 6.5 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 178.1, 172.1, 172.0, 143.1, 141.5, 140.4, 138.2, 136.5, 135.9, 135.9, 131.5, 129.5, 129.4, 128.7, 128.4, 128.3, 128.0, 127.5, 126.8, 123.7, 116.2, 95.9, 87.3, 71.0, 59.9, 53.2, 53.1, 43.0, 41.2, 39.9, 37.6, 34.5, 33.4, 29.8, 25.0, 24.8, 21.3, 20.5, 9.5. **FT-IR** (KBr): v 2963, 2932, 2337, 2328, 1715, 1516, 1432, 1317, 1218, 1064, 808 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{45}H_{46}O_6$ $[M+H]^+$ 683.3367, found 683.3359.

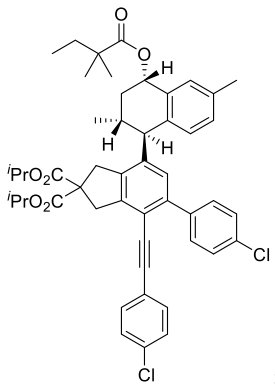


5e

Diisopropyl 7-((1*R*,2*R*,4*S*)-4-((2,2-dimethylbutanoyl)oxy)-2,6-dimethyl-1,2,3,4-tetra-hydronaphthalen-1-yl)-5-phenyl-4-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate

White solid; (112 mg, 76% yield); m.p. 132-134 ℃; TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.24.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, J = 7.2 Hz, 2H), 7.42-7.33 (m, 5H), 7.31-7.28 (m, 3H), 7.02 (s, 1H), 6.90 (d, J = 8.2 Hz, 2H), 6.62 (d, J = 7.9 Hz, 1H), 6.15 (dd, J = 9.9, 5.3 Hz, 1H), 5.13-4.98 (m, 2H), 3.80-3.72 (m, 3H), 3.57 (d, J = 16.4 Hz, 1H), 3.25 (d, J = 16.7 Hz, 1H), 2.37-2.32 (m, 1H), 2.27 (s, 3H), 2.22-2.16 (m, 1H), 1.69-1.59 (m, 3H), 1.28-1.24 (m, 12H), 1.23-1.15 (m, 6H), 0.99 (d, J = 6.4 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 178.1, 171.3, 171.2, 143.1, 141.4, 140.5, 136.6, 135.9, 131.5, 129.5, 128.8, 128.4, 128.2, 127.9, 127.4, 126.8, 123.8, 116.1, 95.8, 87.4, 71.0, 69.5, 69.4, 59.8, 43.0, 41.0, 39.9, 37.6, 33.4, 25.0, 24.8, 21.7, 21.7, 21.6, 21.3, 20.6, 9.5. **FT-IR** (KBr): v 2963, 2937, 2342, 2335, 1718, 1524, 1435, 1343, 1241, 1088, 821 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{49}H_{54}O_6$ $[M+H]^+$ 739.3993, found 739.3985.

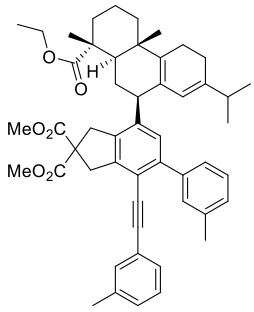


5f

Diisopropyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-7-((1*R*,2*R*,4*S*)-4-((2,2-dimethylbutanoyl)oxy)-2,6-dimethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-indene-2,2(3*H*)-dicarboxylate

colourless oil; (136 mg, 84% yield); TLC (petroleum ether/EtOAc =15 : 1) : R_f = 0.30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.30-7.27 (m, 4H), 7.03 (s, 1H), 6.90 (d, J = 8.1 Hz, 1H), 6.87 (s, 1H), 6.59 (d, J = 8.0 Hz, 1H), 6.17-6.13 (m, 1H), 5.11-5.06 (m, 1H), 5.05-5.00 (m, 1H), 3.82-3.70 (m, 3H), 3.57 (d, J = 16.6 Hz, 1H), 3.31-3.19 (m, 1H), 2.36-2.32 (m, 1H), 2.28 (s, 3H), 2.22-2.16 (m, 1H), 1.68-1.62 (m, 3H), 1.29-1.24 (m, 12H), 1.24 (s, 3H), 1.18 (d, J = 6.3 Hz, 3H), 0.98 (d, J = 6.5 Hz, 3H), 0.94 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.0, 163.7, 163.6, 161.7, 156.5, 155.1, 148.5, 145.6, 143.3, 136.1, 134.1, 133.4, 133.3, 131.7, 131.1, 131.1, 124.8, 122.0, 120.9, 119.5, 116.8, 115.9, 115.7, 115.1, 114.9, 114.8, 112.9, 102.8, 94.8, 86.5, 59.6, 53.3, 41.5, 39.2, 39.1, 23.4. **FT-IR** (KBr): v 2963, 2942, 2337, 2332, 1716, 1542, 1441, 1337, 1251, 1084, 821 cm^{-1}. **HRMS** (APCI): m/z calcd for $C_{49}H_{52}Cl_2O_6$ $[M+H]^+$ 807.3214, found 807.3205.



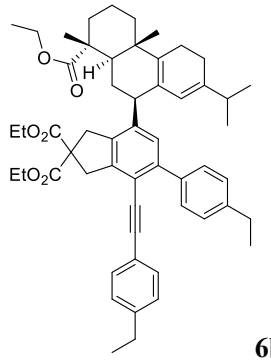
6a

Dimethyl 7-(1-(ethoxycarbonyl)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,5,6,9,10,10a-decahydrophenanthren-9-yl)-5-(m-tolyl)-4-(m-tolylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (1f)

White solid; (606 mg, 79% yield); m. p. 112-113 °C; TLC (petroleum ether/EtOAc = 30 : 1): R_f = 0.26.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, J = 7.3 Hz, 2H), 7.34 (t, J = 7.7 Hz, 1H), 7.21-7.17 (m, 4H), 7.10 (d, J = 6.7 Hz, 1H), 6.99 (s, 1H), 5.14 (s, 1H), 3.87 (t, J = 14.4 Hz, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.74-3.71 (m, 2H), 3.58 (d, J = 16.5 Hz, 1H), 3.44 (d, J = 3.7 Hz, 1H), 3.15-3.09 (m, 1H), 2.42 (s, 3H), 2.32 (s, 3H), 2.29-2.21 (m, 2H), 2.18-2.13 (m, 2H), 2.09-2.05 (m, 2H), 1.91 (d, J = 13.1 Hz, 1H), 1.72-1.60 (m, 4H), 1.45 (d, J = 11.4 Hz, 1H), 1.26-1.21

(m, 2H), 1.15 (s, 3H), 1.10 (s, 3H), 0.99 (d, J = 2.8 Hz, 3H), 0.97 (d, J = 2.7 Hz, 3H), 0.65 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 177.9, 172.3, 172.2, 144.1, 143.3, 142.1, 141.4, 141.1, 141.1, 138.1, 137.7, 137.4, 132.1, 130.6, 129.2, 129.1, 128.6, 128.3, 128.0, 127.9, 126.7, 125.4, 123.7, 120.8, 115.5, 95.8, 87.3, 77.2, 60.3, 59.9, 53.4, 53.2, 47.5, 41.7, 41.3, 40.6, 39.4, 37.7, 36.1, 35.9, 34.6, 27.9, 26.1, 22.6, 21.7, 21.3, 20.4, 18.6, 16.7, 13.5. **FT-IR** (KBr): v 2360, 1734, 1717, 1655, 1558, 1458, 1381, 1241, 1175, 785, 668, 468, 422 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{51}H_{58}O_6$ $[M+H]^+$ 767.4306, found 767.4313.

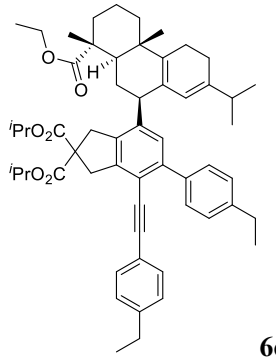


6b

Diethyl 7-(1-(ethoxycarbonyl)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,5,6,9,10,10a-decahydrophenanthren-9-yl)-5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (1i)

White solid; (650 mg, 79% yield); m. p. 91-92 ℃; TLC (petroleum ether/EtOAc = 30 : 1): R_f = 0.34.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 8.0 Hz, 2H), 7.31-7.26 (m, 4H), 7.14 (d, J = 8.0 Hz, 2H), 6.98 (s, 1H), 5.14 (s, 1H), 4.29-4.22 (m, 4H), 3.86 (d, J = 17.2 Hz, 1H), 3.76-3.66 (m, 3H), 3.56 (d, J = 16.5 Hz, 1H), 3.44 (s, 1H), 3.17-3.10 (m, 1H), 2.73 (q, J = 7.6 Hz, 2H), 2.64 (q, J = 7.6 Hz, 2H), 2.28-2.23 (m, 1H), 2.19-2.14 (m, 2H), 2.11-2.05 (m, 4H), 1.91 (d, J = 13.0 Hz, 1H), 1.71-1.58 (m, 4H), 1.44 (d, J = 11.0 Hz, 1H), 1.33 (s, 1H), 1.30-1.27 (m, 6H), 1.26-1.18 (m, 6H), 1.15 (s, 3H), 1.10 (s, 3H), 0.97 (d, J = 3.3 Hz, 3H), 0.96 (d, J = 3.2 Hz, 3H), 0.63 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 177.9, 171.9, 171.6, 144.6, 144.0, 143.3, 143.2, 141.7, 141.2, 140.9, 138.6, 137.6, 131.5, 129.6, 129.0, 128.0, 127.4, 125.4, 121.1, 120.7, 115.5, 95.6, 87.1, 62.1, 62.0, 60.4, 59.9, 47.5, 41.7, 41.1, 40.5, 39.3, 37.6, 36.1, 35.7, 34.5, 29.0, 28.7, 27.9, 26.2, 22.6, 21.3, 20.4, 18.5, 16.7, 15.7, 15.6, 14.2, 13.5. **FT-IR** (KBr): v 2960, 2360, 1732, 1653, 1558, 1458, 1381, 1238, 1108, 1067, 860, 831, 666, 476 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{55}H_{66}O_6$ $[M+H]^+$ 823.4932, found 823.4937.



6c

Diisopropyl 7-(1-(ethoxycarbonyl)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,5,6,9,10,10a-decahydrophenanthren-9-yl)-5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (1o)

White solid; (655 mg, 77% yield); m. p. 90-91 ℃; TLC (petroleum ether/EtOAc = 30 : 1): R_f = 0.45.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 8.0 Hz, 2H), 7.31-7.27 (m, 4H), 7.14 (d, J = 8.0 Hz, 2H), 6.97 (s, 1H), 5.13 (s, 1H), 5.12-5.06 (m, 2H), 3.81 (d, J = 17.2 Hz, 1H), 3.74-3.62 (m, 3H), 3.53 (d, J = 16.6 Hz, 1H), 3.45 (d, J = 5.4 Hz, 1H), 3.20-3.13 (m, 1H), 2.73 (q, J = 7.6 Hz, 2H), 2.64 (q, J = 7.6 Hz, 2H), 2.29-2.21 (m, 1H), 2.21-2.09 (m, 4H), 2.08-2.04 (m, 2H), 1.90 (d, J = 12.8 Hz, 1H), 1.73-1.64 (m, 2H), 1.64-1.55 (m, 2H), 1.46-1.42 (m, 1H), 1.33 (s, 1H), 1.32-1.26 (m, 12H), 1.25-1.21 (m, 6H), 1.15 (s, 3H), 1.10 (s, 3H), 0.97 (d, J = 3.3 Hz, 3H), 0.96 (d, J = 3.2 Hz, 3H), 0.62 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 177.9, 171.4, 171.1, 144.5, 143.9, 143.4, 143.1, 141.7, 141.2, 140.9, 138.6, 137.7, 131.5, 129.6, 128.9, 127.9, 127.4, 125.4, 121.2, 120.7, 115.5, 95.5, 87.2, 69.4, 69.3, 60.4, 59.9, 47.5, 41.6, 40.9, 40.5, 39.2, 37.6, 36.2, 35.7, 34.5, 29.0, 28.7, 28.0, 26.2, 22.6, 21.7, 21.7, 21.3, 20.5, 18.5, 16.7, 15.7, 15.6, 13.5. **FT-R** (KBr): ν 2960, 2341, 1724, 1655, 1558, 1456, 1372, 1246, 1106, 1062, 832, 668, 474, 418 cm^{-1}. **HRMS** (APCI): *m/z* calcd for $C_{57}H_{70}O_6$ $[M+H]^+$ 851.5245, found 851.5241.

3. X-ray crystallographic data of 3h.

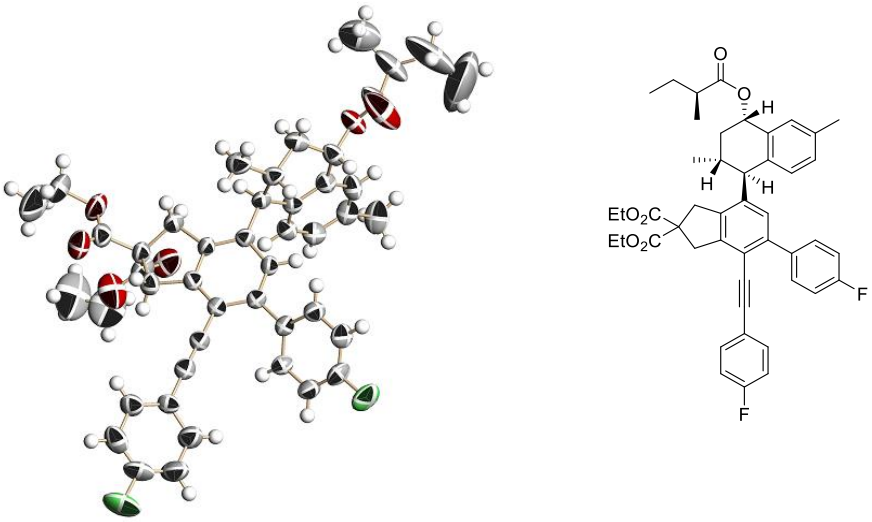


Figure S1. Molecular structure of **3h** (CCDC 2342007) showing thermal ellipsoid at the 30% probability level

```
Bond precision:   C-C = 0.0080 A          Wavelength=0.71073

Cell:             a=12.1596(8)     b=12.2452(8)       c=27.3069(18)
                  alpha=90         beta=95.673(1)     gamma=90
Temperature:      293 K

                 Calculated                Reported
Volume           4046.0(5)                 4046.0(5)
Space group      P 21                      P 1 21 1
Hall group       P 2yb                     P 2yb
Moiety formula   C46 H46 F2 O6             C46 H46 F2 O6
Sum formula      C46 H46 F2 O6             C46 H46 F2 O6
Mr               732.83                    732.83
Dx,g cm-3        1.203                     1.203
Z                4                         4
Mu (mm-1)        0.085                     0.085
F000             1552.0                    1552.0
F000'            1552.82
h,k,lmax         14,14,32                  14,14,32
Nref             14878[ 7816]              14703
Tmin,Tmax        0.980,0.983               0.684,0.745
Tmin'            0.980

Correction method= # Reported T Limits: Tmin=0.684 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 1.88/0.99        Theta(max)= 25.386

R(reflections)= 0.0612( 8612)                wR2(reflections)=
                                             0.1907( 14703)
S = 1.028                  Npar= 1210
```

4. Cell proliferation assay

Cell culture

HeLa cells were cultured in culture media (DMEM, supplemented with 10% FBS and 1% penicillin/streptomycin solution) at 37 °C in an atmosphere of 5% CO_2 and 95% humidified atmosphere.

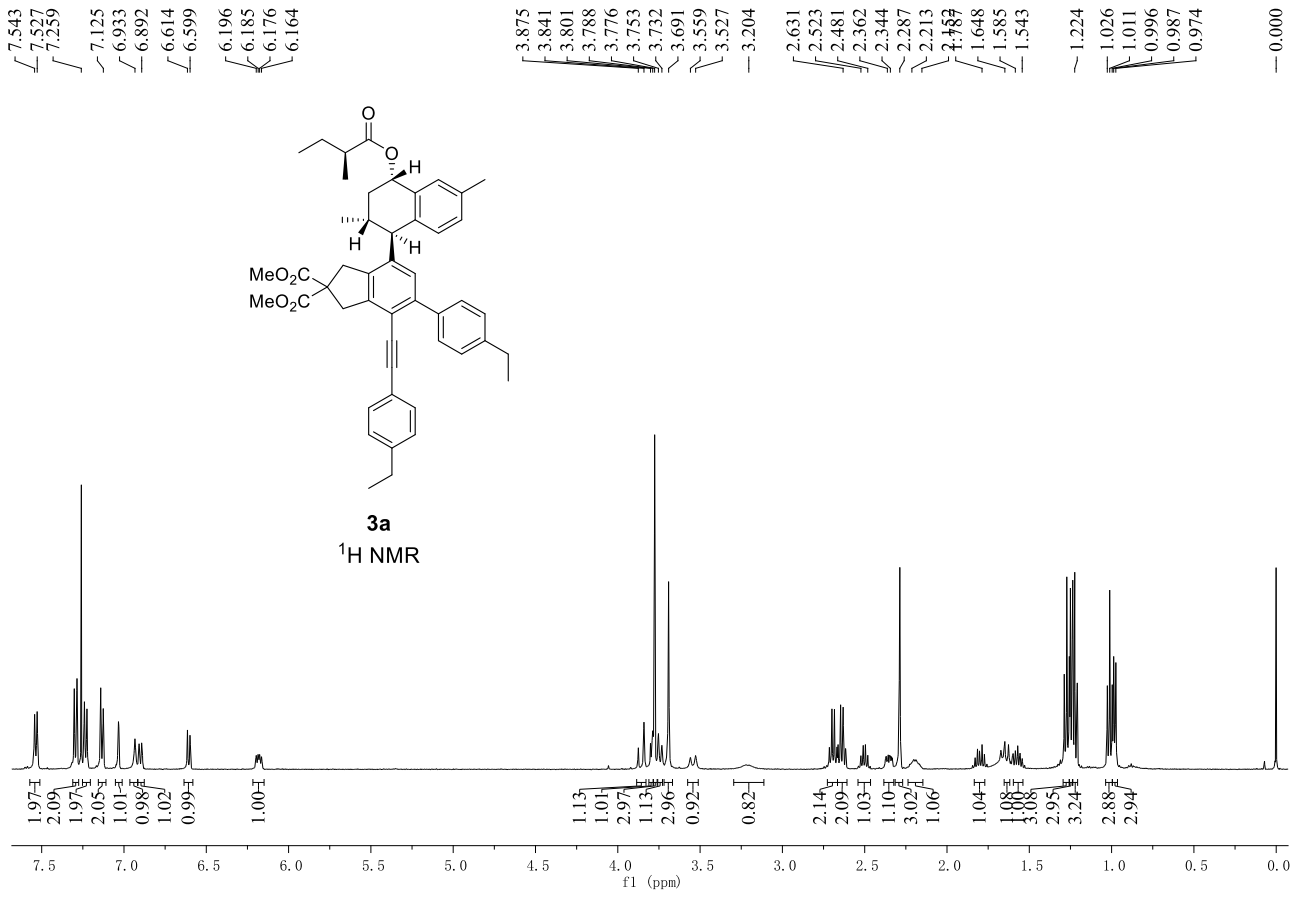
RPMI-8226 cells were cultured in culture media (IMDM, supplemented with 10% FBS and 1% penicillin/streptomycin solution) at 37 °C in an atmosphere of 5% CO_2 and 95% humidified atmosphere.

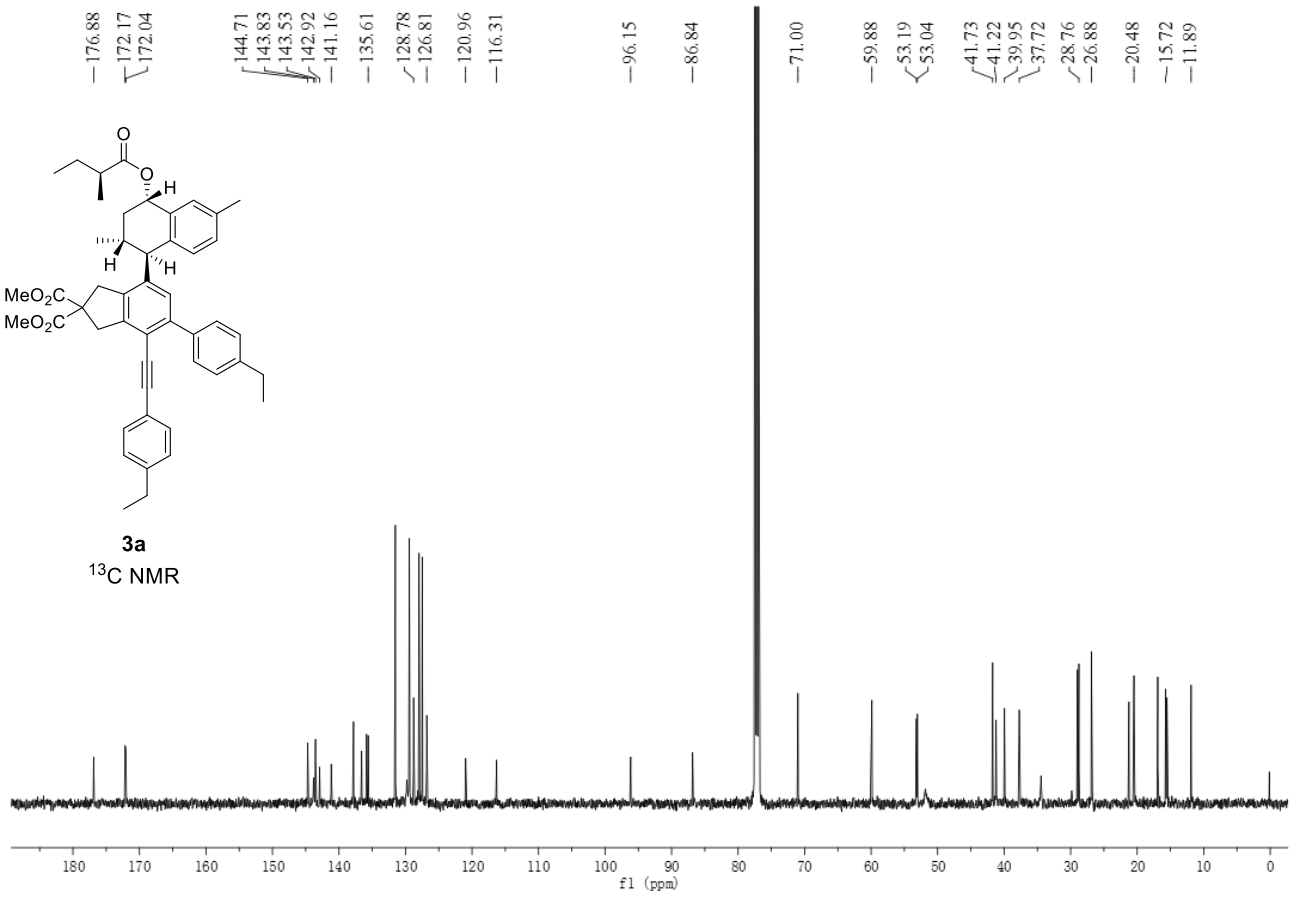
Cytotoxicity determined by the CCK-8 assay

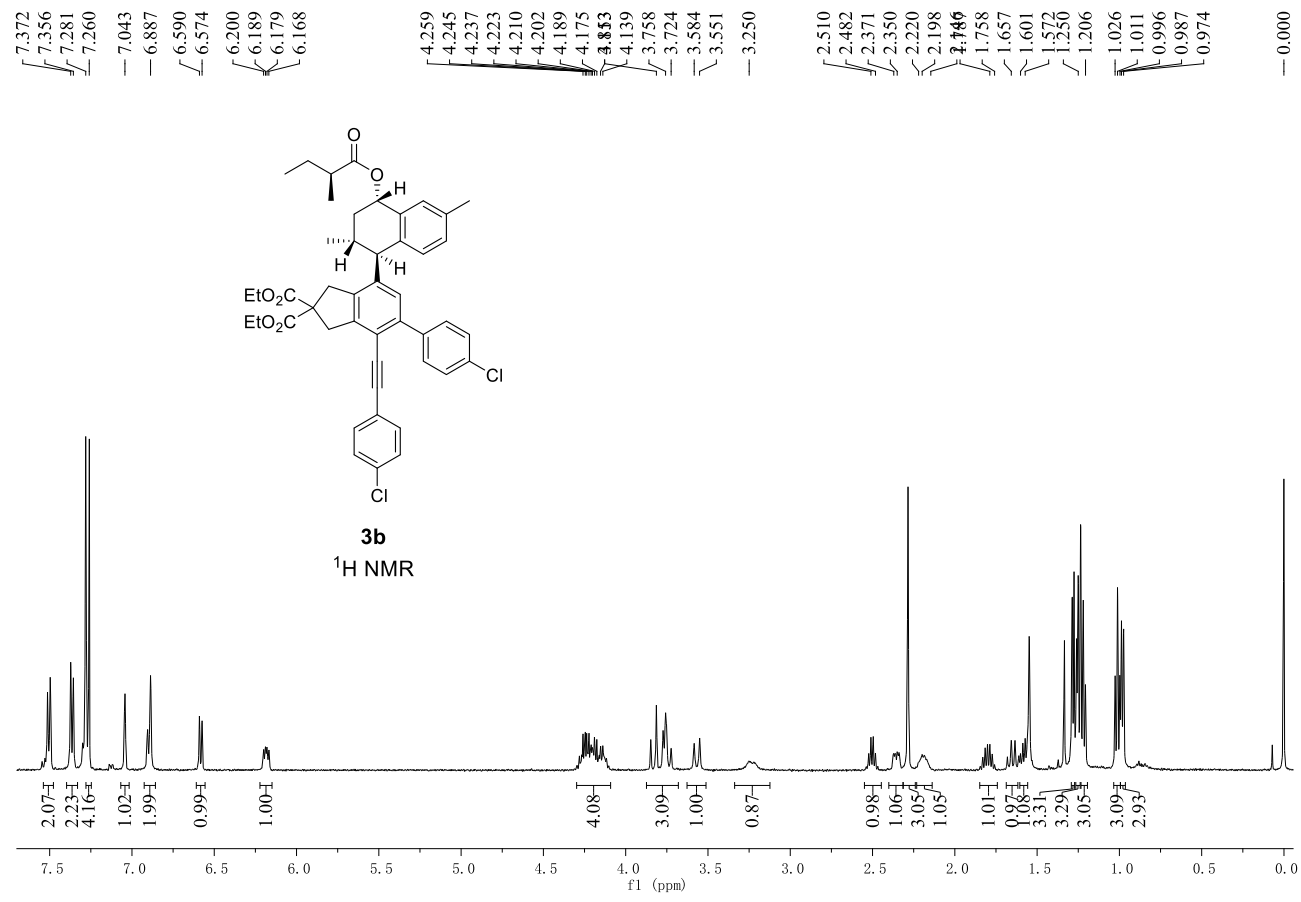
After the completion of cell culture, the medium in the culture bottle were removed, and washed once with PBS buffer, added 0.25% trypsin to digest the cells. Then removed the trypsin, detached the cells with complete culture medium (supplemented with 10% FBS), transferred into the sample channel and mixed uniformly. Count with a cell counting plate and diluted with complete culture medium. The HeLa or RPMI-8226 cells (5000/well/100μL) were seeded on 96-well plates and incubated in DMEM/IMDM medium for 24 h at 37 °C. Then, a gradient concentration of compounds **2a**/**2b**/**4h** from 0 to 30 μM (compound **3b** from 0 to 60 μM) in a fresh medium were added into the

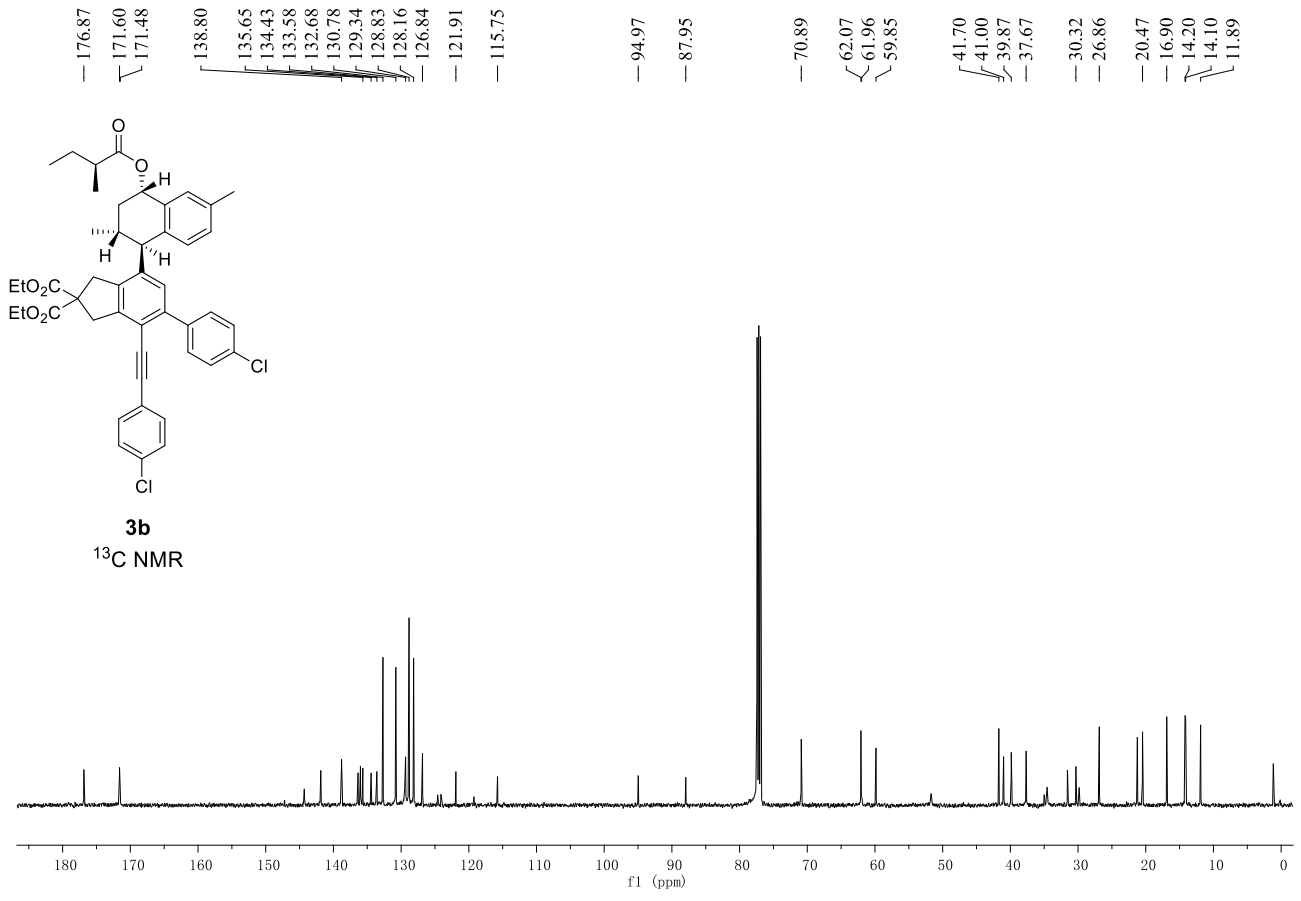
96-well plate, and the cells with the samples were incubated at 37 °C for 24 h. Next, the working solutions were then removed, and the cells were washed three times with PBS buffer cautiously (RPMI-8226 are suspended cells and this step was not performed). After that, 200 μL fresh medium and 20 μL CCK-8 (Cell Counting Kit-8, MCE) were added into each well successively, and the cells were further incubated at 37 °C for 2 h in a 5% CO_2 humidified atmosphere. The plate was shaken for 5 min, and the absorbance was measured at 450 nm using a microplate reader (Biotek).

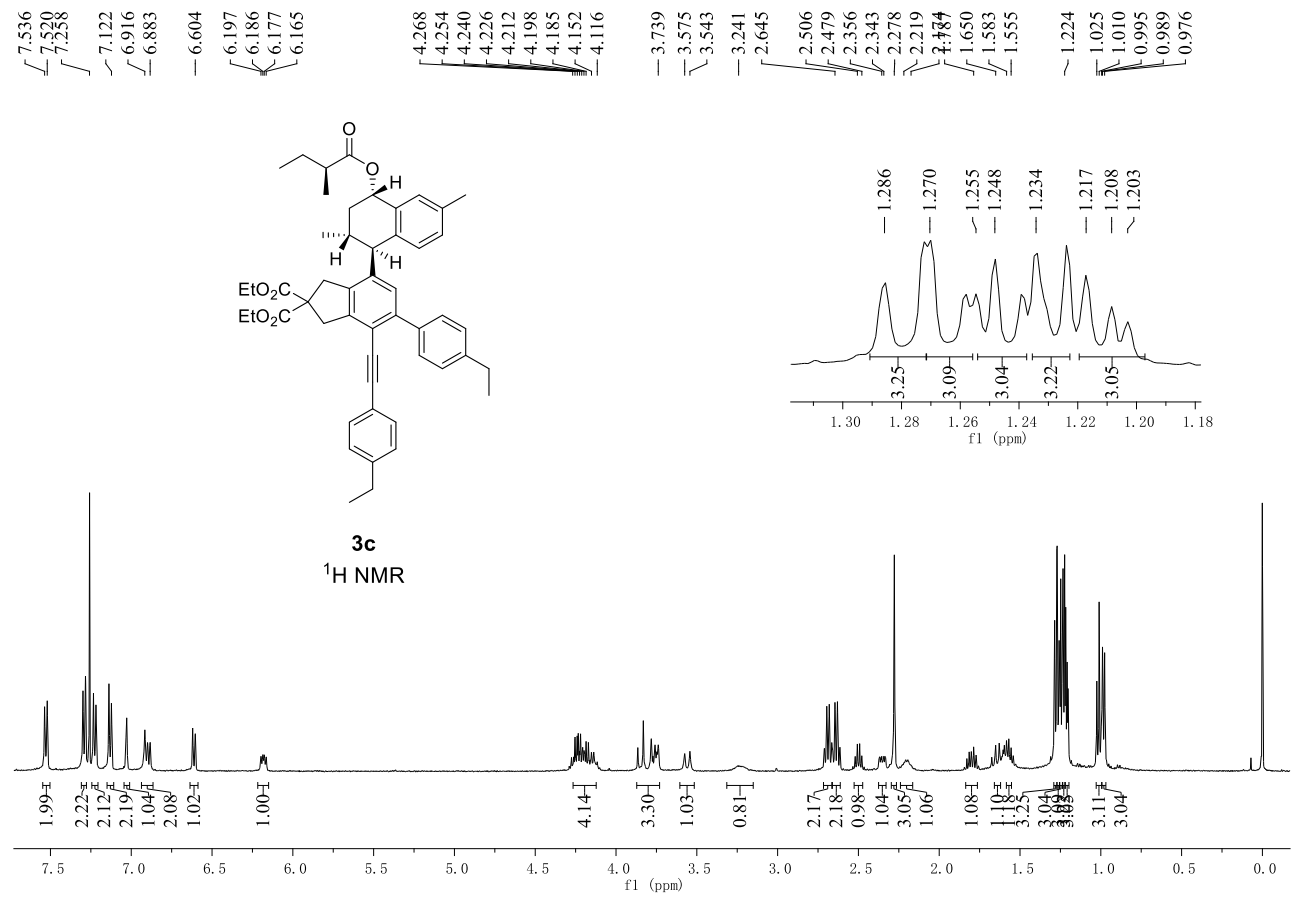
5. ^{1}H and ^{13}C spectra for new compounds

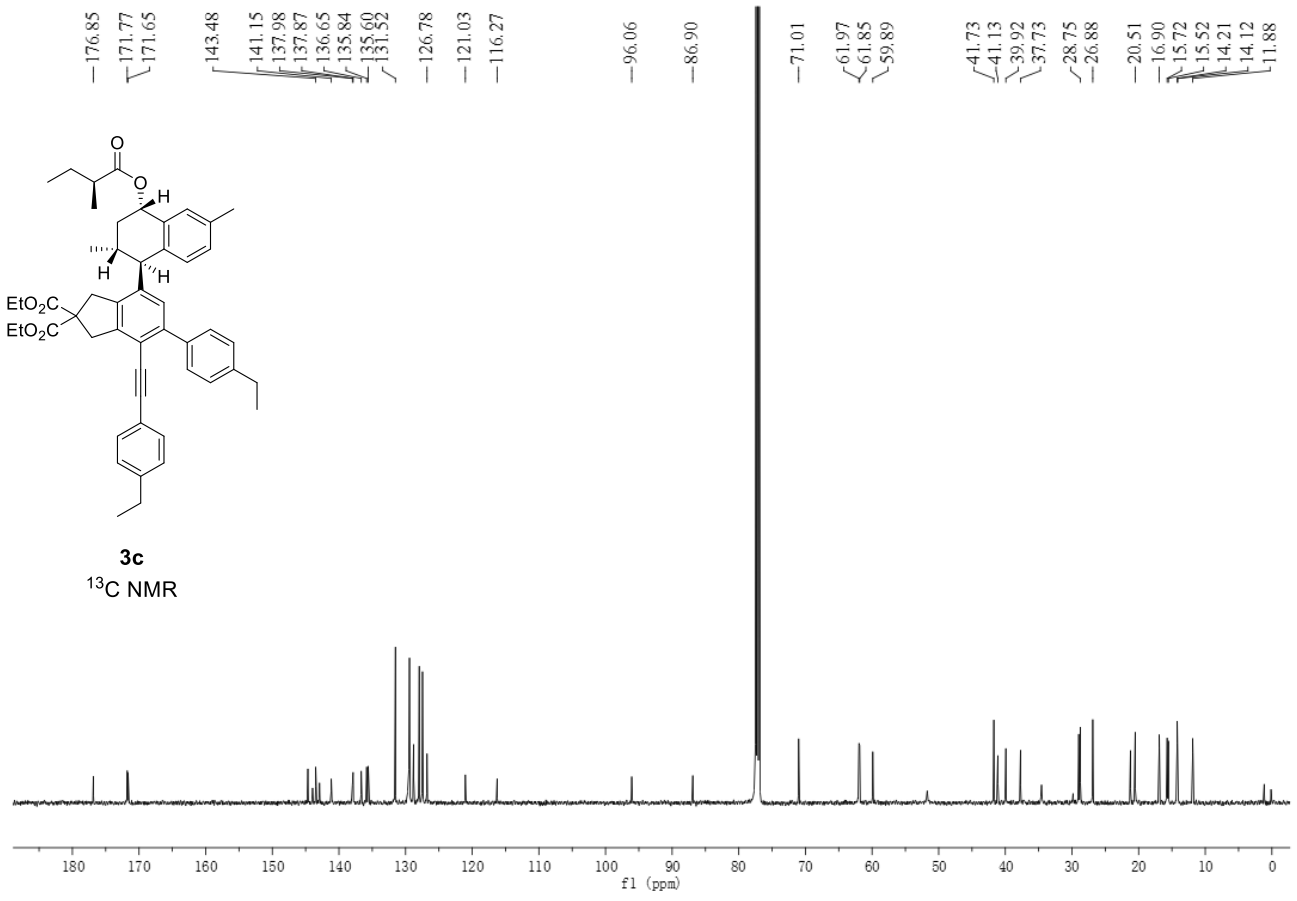

7.543
7.527
7.259
7.125
6.933
6.892
6.614
6.599
6.196
6.185
6.176
6.164
3.875
3.841
3.801
3.788
3.776
3.753
3.732
3.691
3.559
3.527
3.204
2.631
2.523
2.481
2.362
2.344
2.287
2.213
1.648
1.585
1.543
1.224
1.026
1.011
0.996
0.987
0.974
0.000
MeO2C
MeO2C
3a
1H NMR
f1 (ppm)

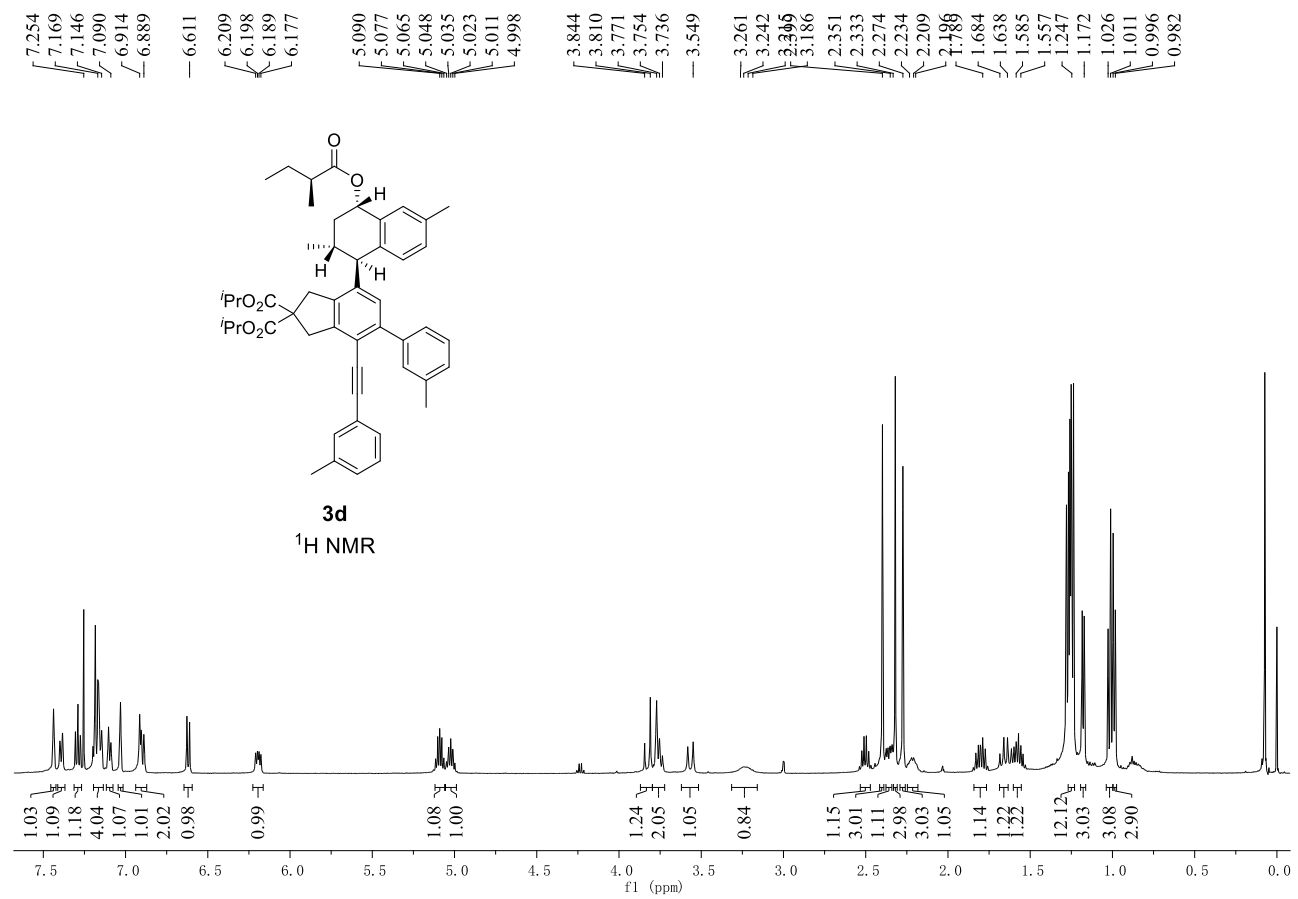

176.88
172.17
172.04
144.71
143.83
143.53
142.92
141.16
135.61
128.78
126.81
120.96
116.31
96.15
86.84
71.00
59.88
53.19
53.04
41.73
41.22
39.95
37.72
28.76
26.88
20.48
15.72
11.89
MeO2C
MeO2C
3a
13C NMR
f1 (ppm)

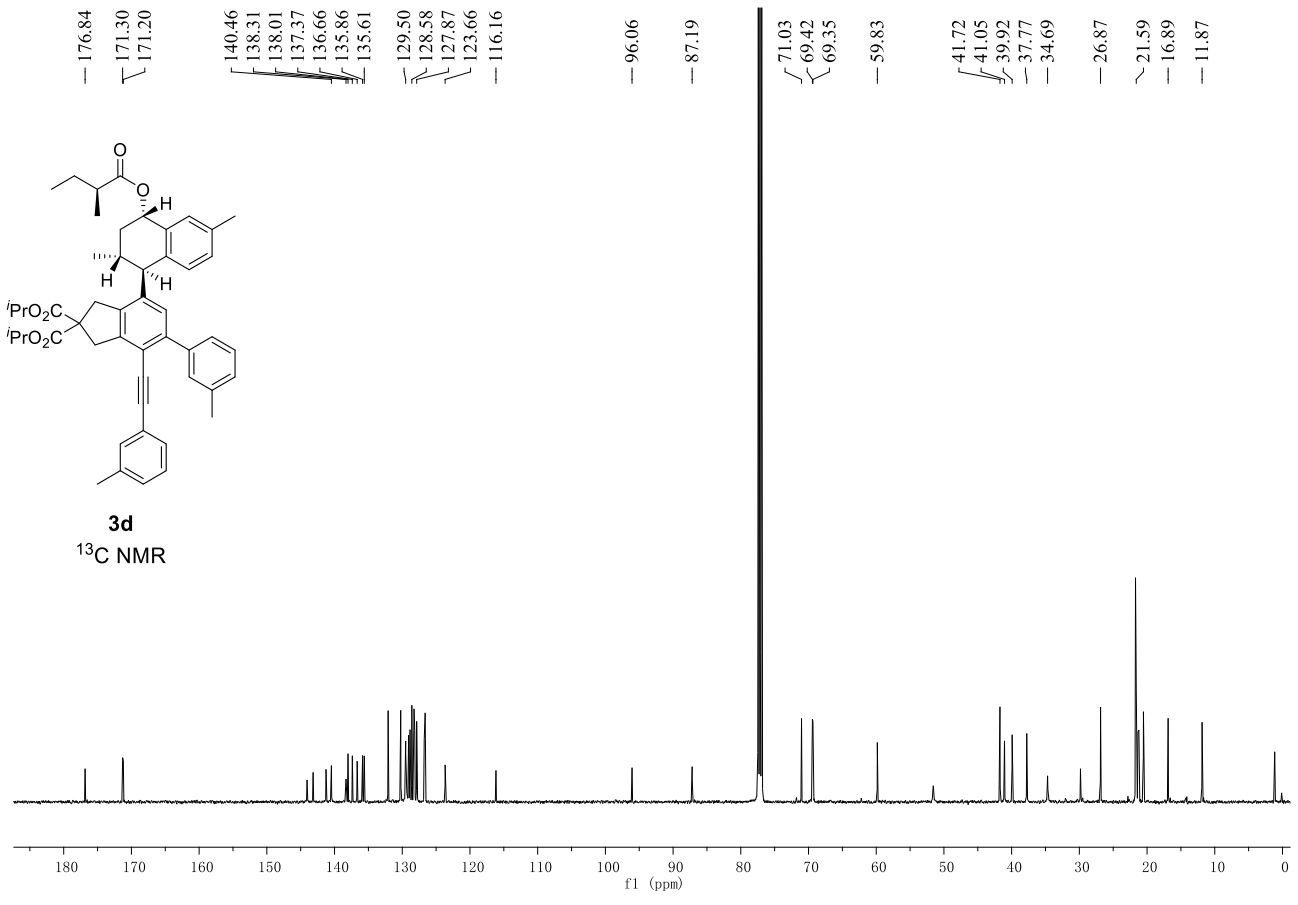

7.372
7.356
7.281
7.260
7.043
6.887
6.590
6.574
6.200
6.189
6.179
6.168
4.259
4.245
4.237
4.223
4.210
4.202
4.189
4.175
4.139
3.758
3.724
3.584
3.551
3.250
2.510
2.482
2.371
2.350
2.220
2.198
1.758
1.657
1.601
1.572
1.250
1.206
1.026
1.011
0.996
0.987
0.974
0.000
EtO2C
EtO2C
Cl
Cl
3b
1H NMR
2.07
2.23
4.16
1.02
1.99
0.99
1.00
4.08
3.09
1.00
0.87
0.98
1.06
3.05
1.05
1.01
0.97
1.08
3.31
3.29
3.05
3.09
2.93
f1 (ppm)

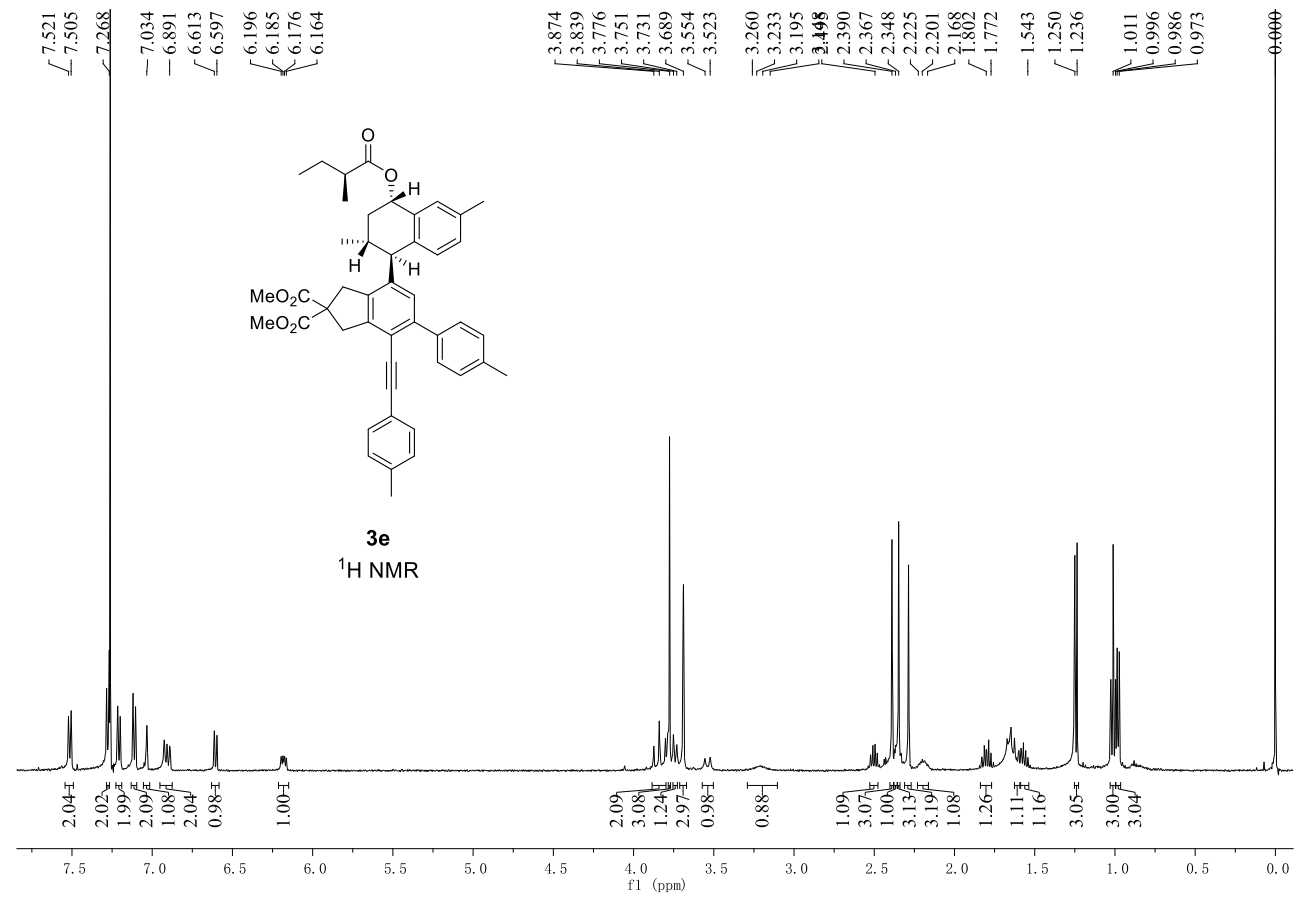

176.87
171.60
171.48
138.80
135.65
134.43
133.58
132.68
130.78
129.34
128.83
128.16
126.84
121.91
115.75
94.97
87.95
70.89
62.07
61.96
59.85
41.70
41.00
39.87
37.67
30.32
26.86
20.47
16.90
14.20
14.10
11.89
EtO2C
EtO2C
Cl
Cl
3b
13C NMR
f1 (ppm)

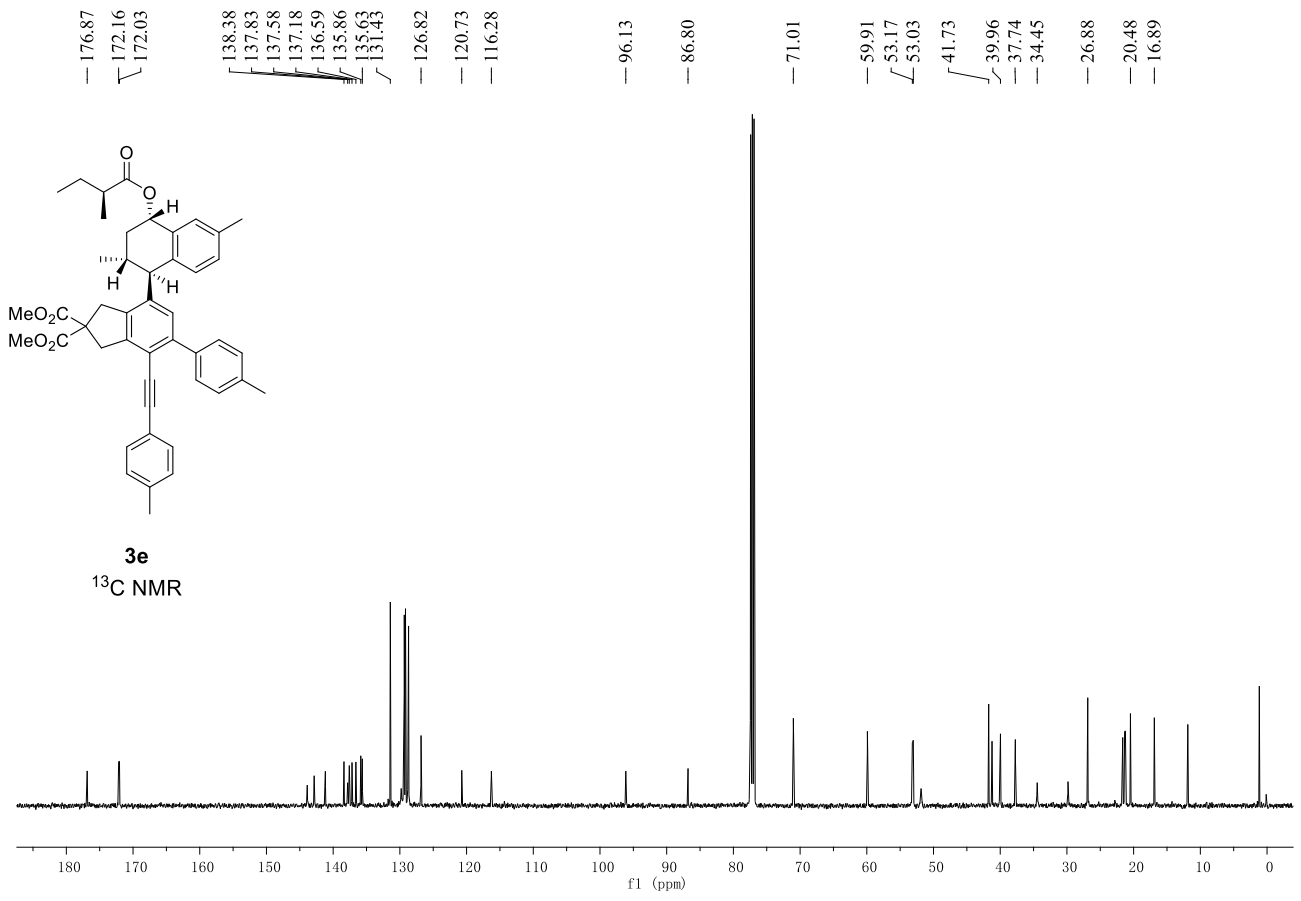

7.536
7.520
7.258
7.122
6.916
6.883
6.604
6.197
6.186
6.177
6.165
4.268
4.254
4.240
4.226
4.212
4.198
4.185
4.152
4.116
3.739
3.575
3.543
3.241
2.645
2.506
2.479
2.356
2.343
2.278
2.219
1.650
1.583
1.555
1.224
1.025
1.010
0.995
0.989
0.976
EtO2C
EtO2C
3c
1H NMR
1.286
1.270
1.255
1.248
1.234
1.217
1.208
1.203
3.25
3.09
3.04
3.22
3.05
f1 (ppm)
1.99
2.22
2.12
2.19
1.04
2.08
1.02
1.00
4.14
3.30
1.03
0.81
2.17
2.18
0.98
1.04
3.05
1.06
1.08
3.11
3.04
f1 (ppm)

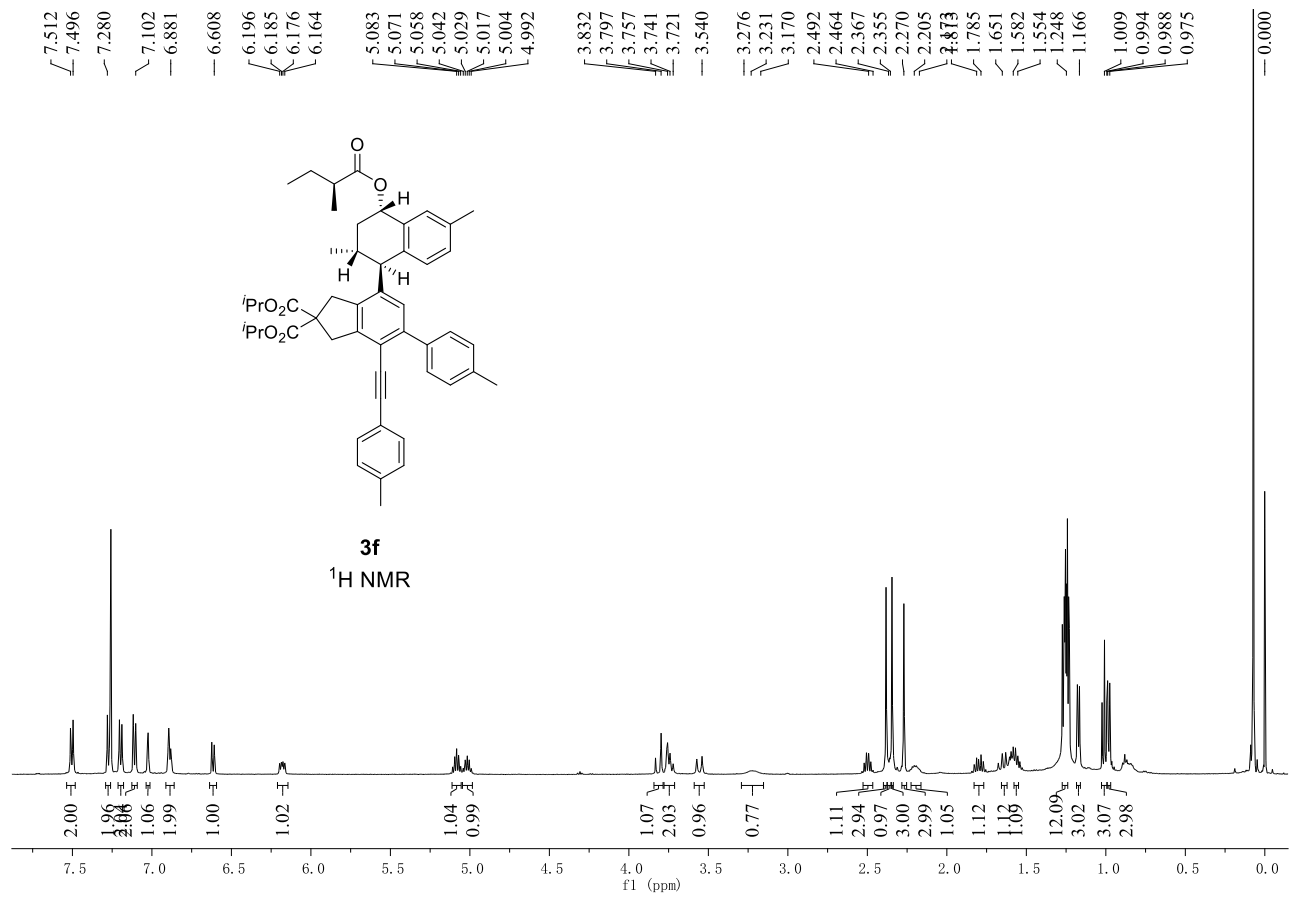

176.85
171.77
171.65
143.48
141.15
137.98
137.87
136.65
135.84
135.60
131.52
126.78
121.03
116.27
96.06
86.90
71.01
61.97
61.85
59.89
41.73
41.13
39.92
37.73
28.75
26.88
20.51
16.90
15.72
15.52
14.21
14.12
11.88
EtO2C
EtO2C
3c
13C NMR
f1 (ppm)


7.254
7.169
7.146
7.090
6.914
6.889
6.611
6.209
6.198
6.189
6.177
5.090
5.077
5.065
5.048
5.035
5.023
5.011
4.998
3.844
3.810
3.771
3.754
3.736
3.549
3.261
3.242
3.186
2.351
2.333
2.274
2.234
2.209
1.684
1.638
1.585
1.557
1.247
1.172
1.026
1.011
0.996
0.982
O
O
H
H
H
iPrO2C
iPrO2C
3d
1H NMR
1.03
1.09
1.18
4.04
1.07
1.01
2.02
0.98
0.99
1.08
1.00
1.24
2.05
1.05
0.84
1.15
3.01
1.11
2.98
3.03
1.05
1.14
12.12
3.03
3.08
2.90
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
f1 (ppm)


176.84
171.30
171.20
140.46
138.31
138.01
137.37
136.66
135.86
135.61
129.50
128.58
127.87
123.66
116.16
96.06
87.19
71.03
69.42
69.35
59.83
41.72
41.05
39.92
37.77
34.69
26.87
21.59
16.89
11.87
O
O
H
H
H
iPrO2C
iPrO2C
3d
13C NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

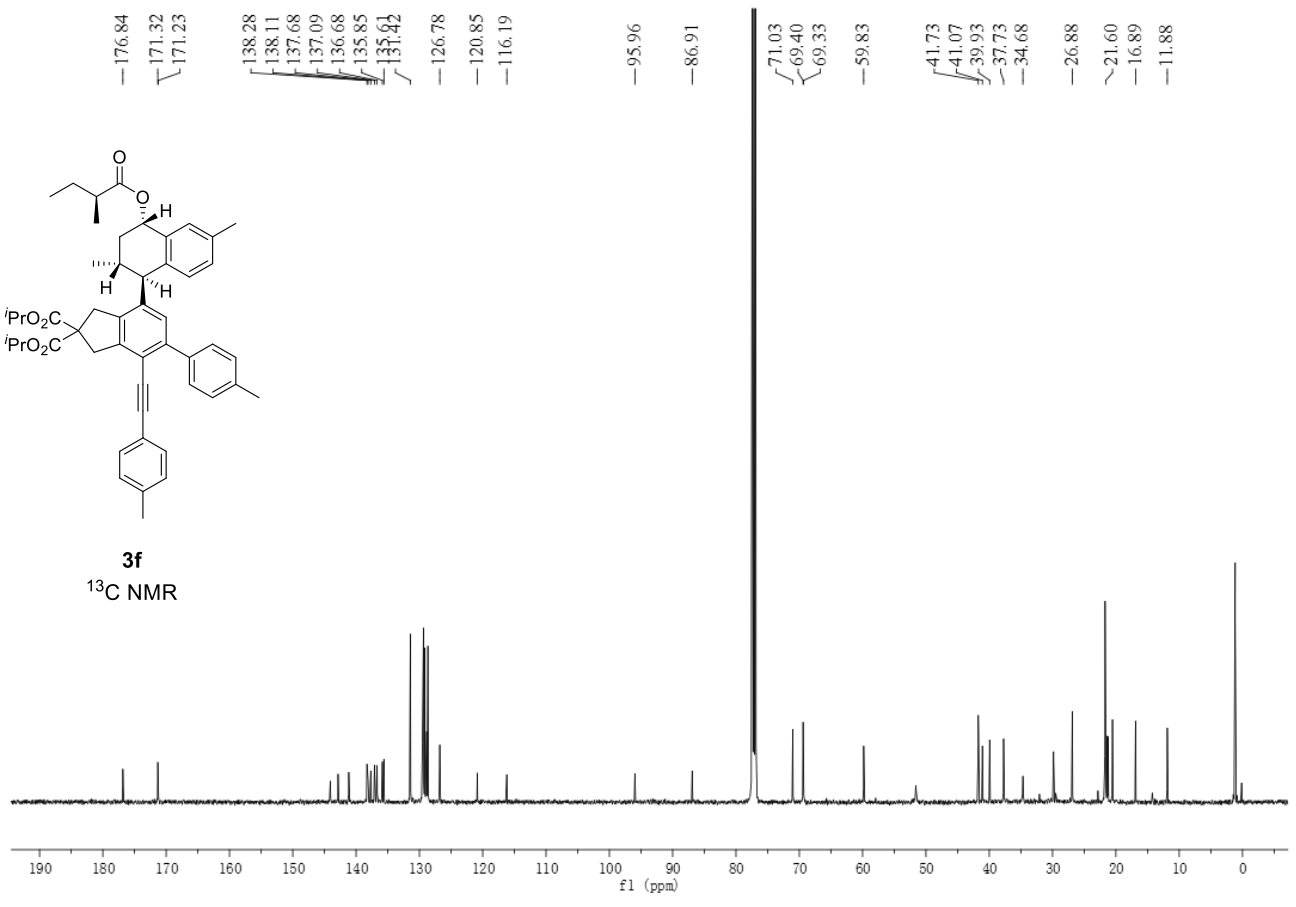

7.521
7.505
7.268
7.034
6.891
6.613
6.597
6.196
6.185
6.176
6.164
3.874
3.839
3.776
3.751
3.731
3.689
3.554
3.523
3.260
3.233
3.195
2.390
2.367
2.348
2.225
2.201
2.168
1.802
1.772
1.543
1.250
1.236
1.011
0.996
0.986
0.973
0.000
MeO2C
MeO2C
3e
1H NMR
f1 (ppm)


176.87
172.16
172.03
138.38
137.83
137.58
137.18
136.59
135.86
135.63
131.43
126.82
120.73
116.28
96.13
86.80
71.01
59.91
53.17
53.03
41.73
39.96
37.74
34.45
26.88
20.48
16.89
MeO2C
MeO2C
3e
13C NMR
f1 (ppm)



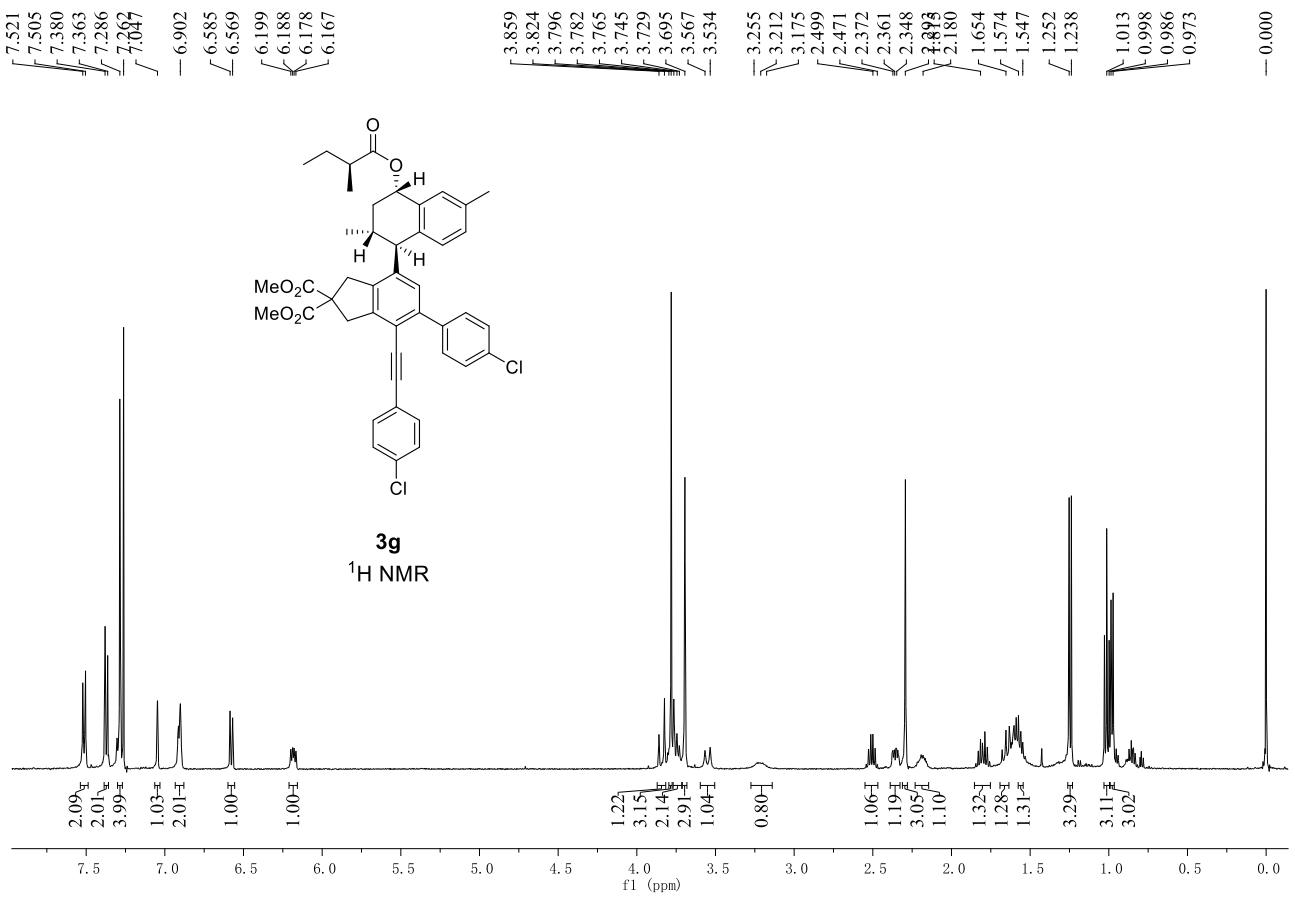
3f

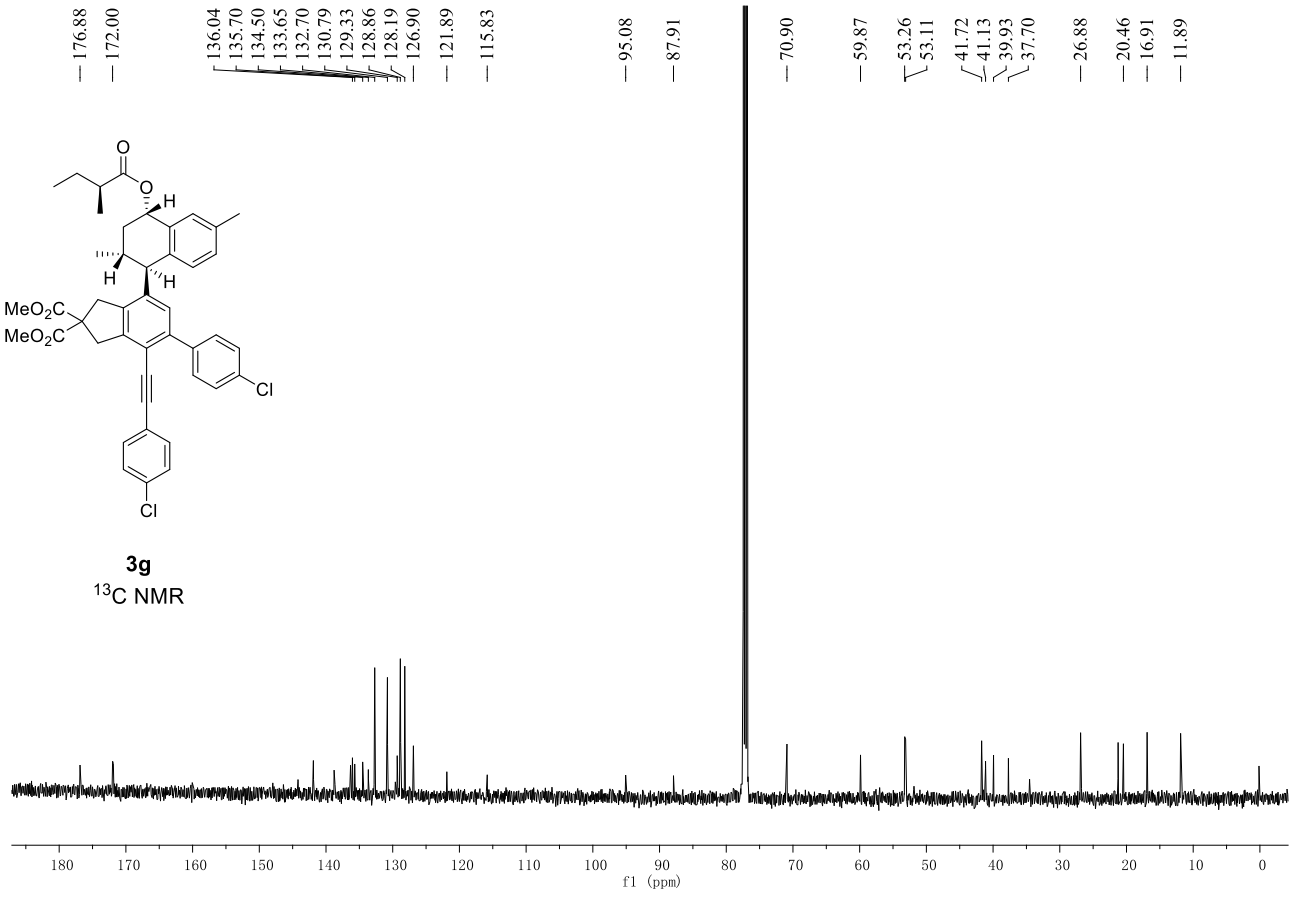
^{1}H NMR

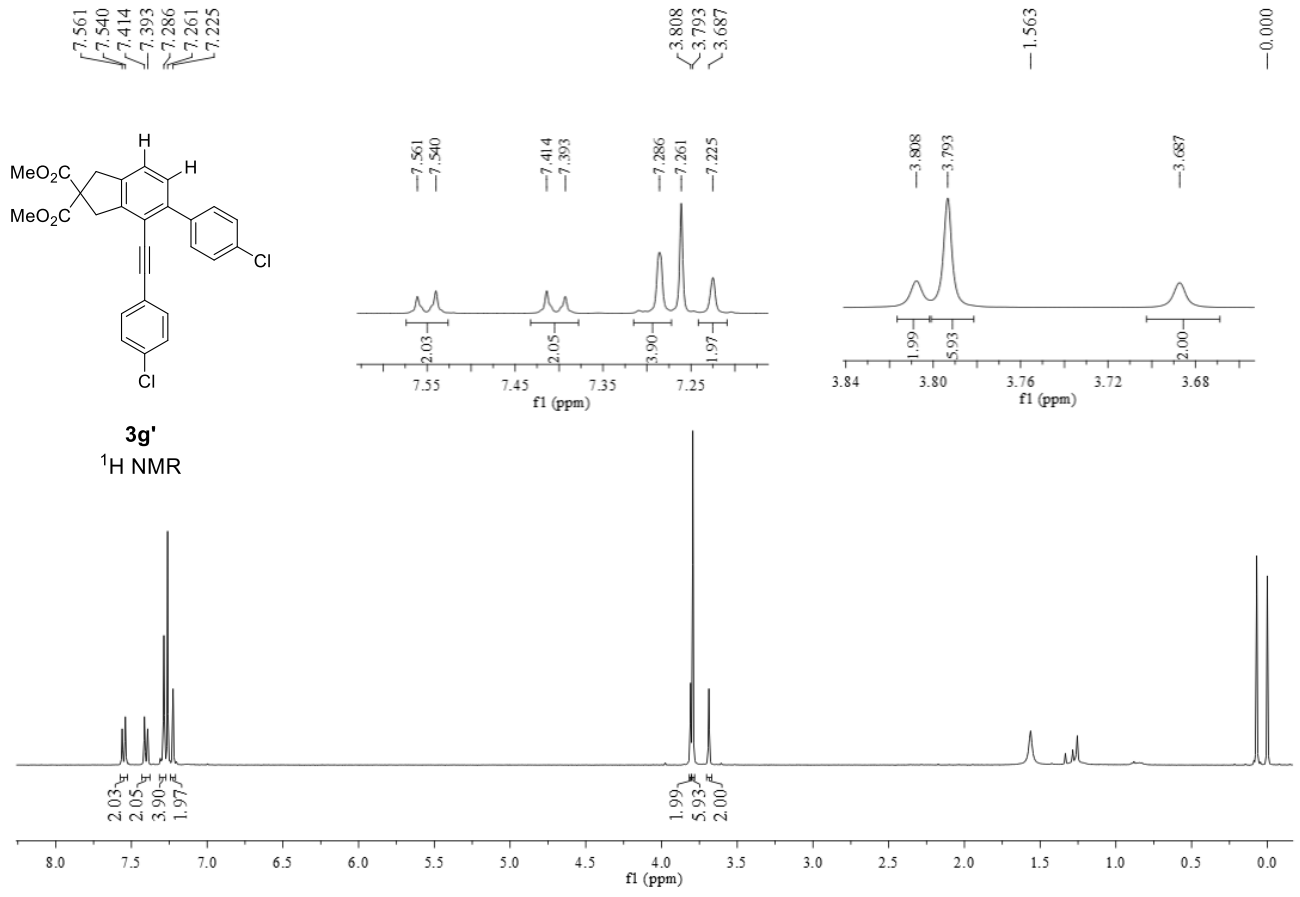


3f

^{13}C NMR

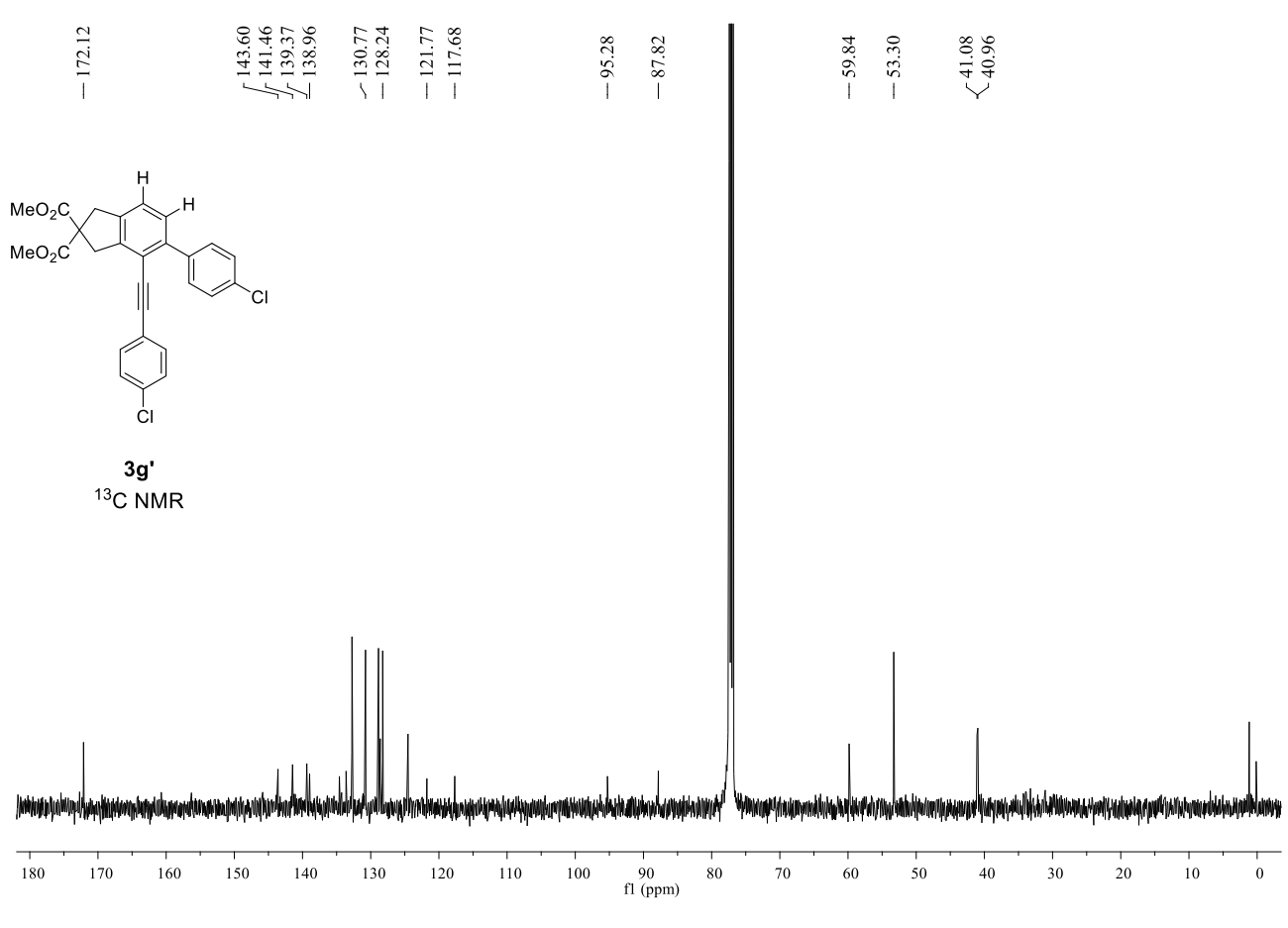

7.521
7.505
7.380
7.363
7.286
7.262
7.047
6.902
6.585
6.569
6.199
6.188
6.178
6.167
3.859
3.824
3.796
3.782
3.765
3.745
3.729
3.695
3.567
3.534
3.255
3.212
3.175
2.499
2.471
2.372
2.361
2.348
2.180
1.654
1.574
1.547
1.252
1.238
1.013
0.998
0.986
0.973
0.000
MeO2C
MeO2C
Cl
Cl
3g
1H NMR
2.09
2.01
3.99
1.03
2.01
1.00
1.00
1.22
3.15
2.14
2.91
1.04
0.80
1.06
1.19
3.05
1.10
1.32
1.28
1.31
3.29
3.11
3.02
f1 (ppm)


176.88
172.00
136.04
135.70
134.50
133.65
132.70
130.79
129.33
128.86
128.19
126.90
121.89
115.83
95.08
87.91
70.90
59.87
53.26
53.11
41.72
41.13
39.93
37.70
26.88
20.46
16.91
11.89
MeO2C
MeO2C
Cl
Cl
3g
13C NMR
f1 (ppm)



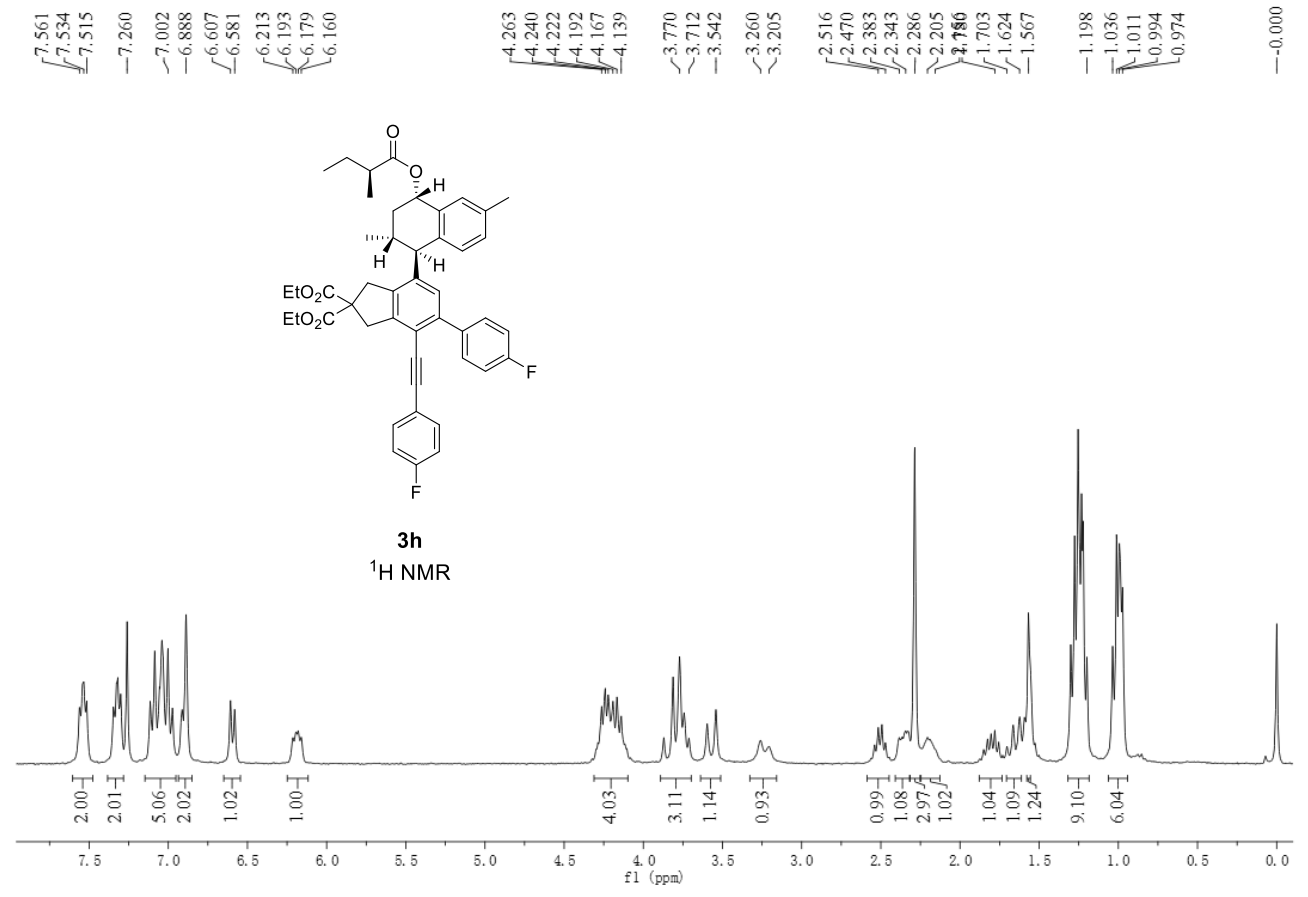
3g'

^{1}H NMR



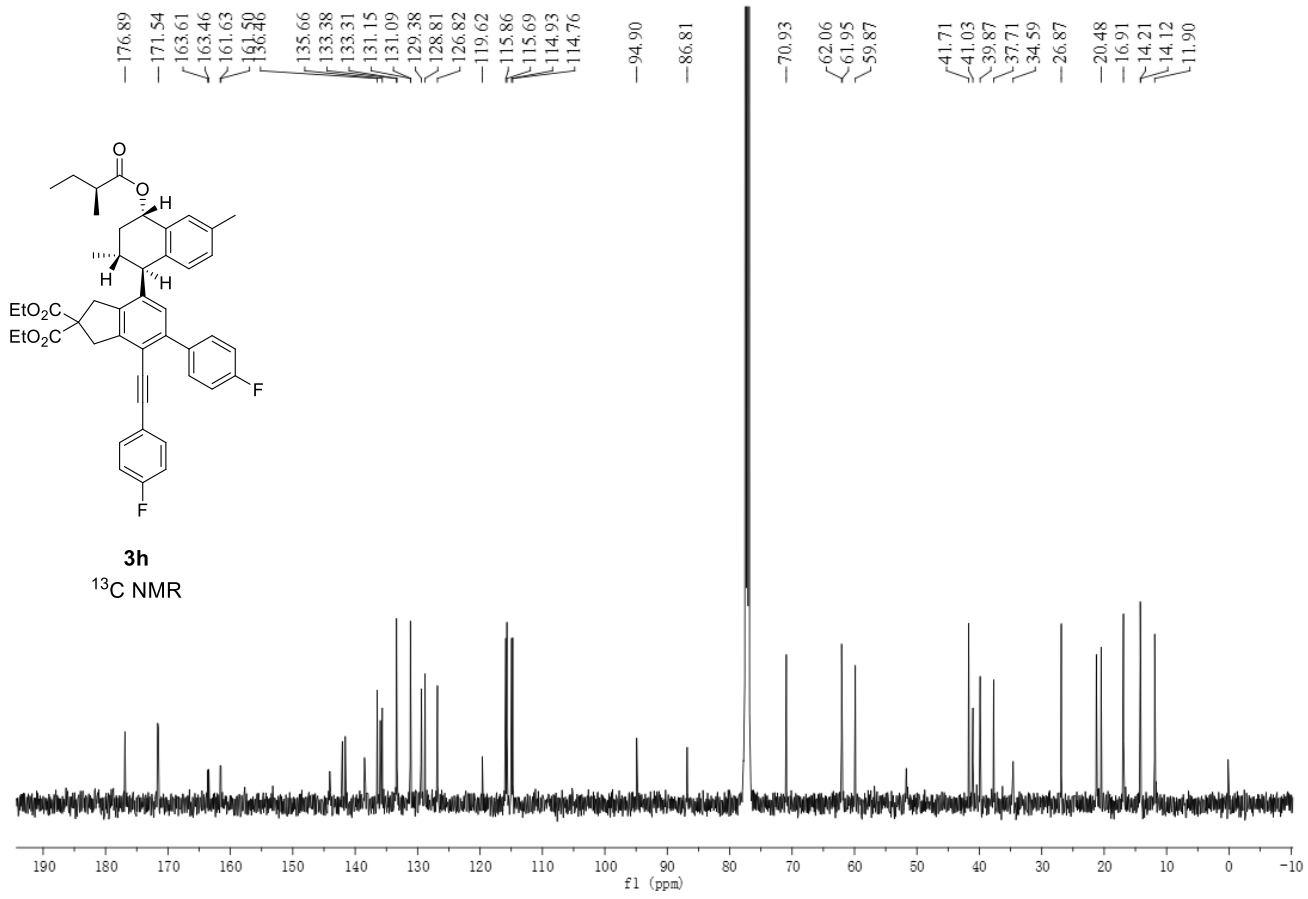
3g'

^{13}C NMR



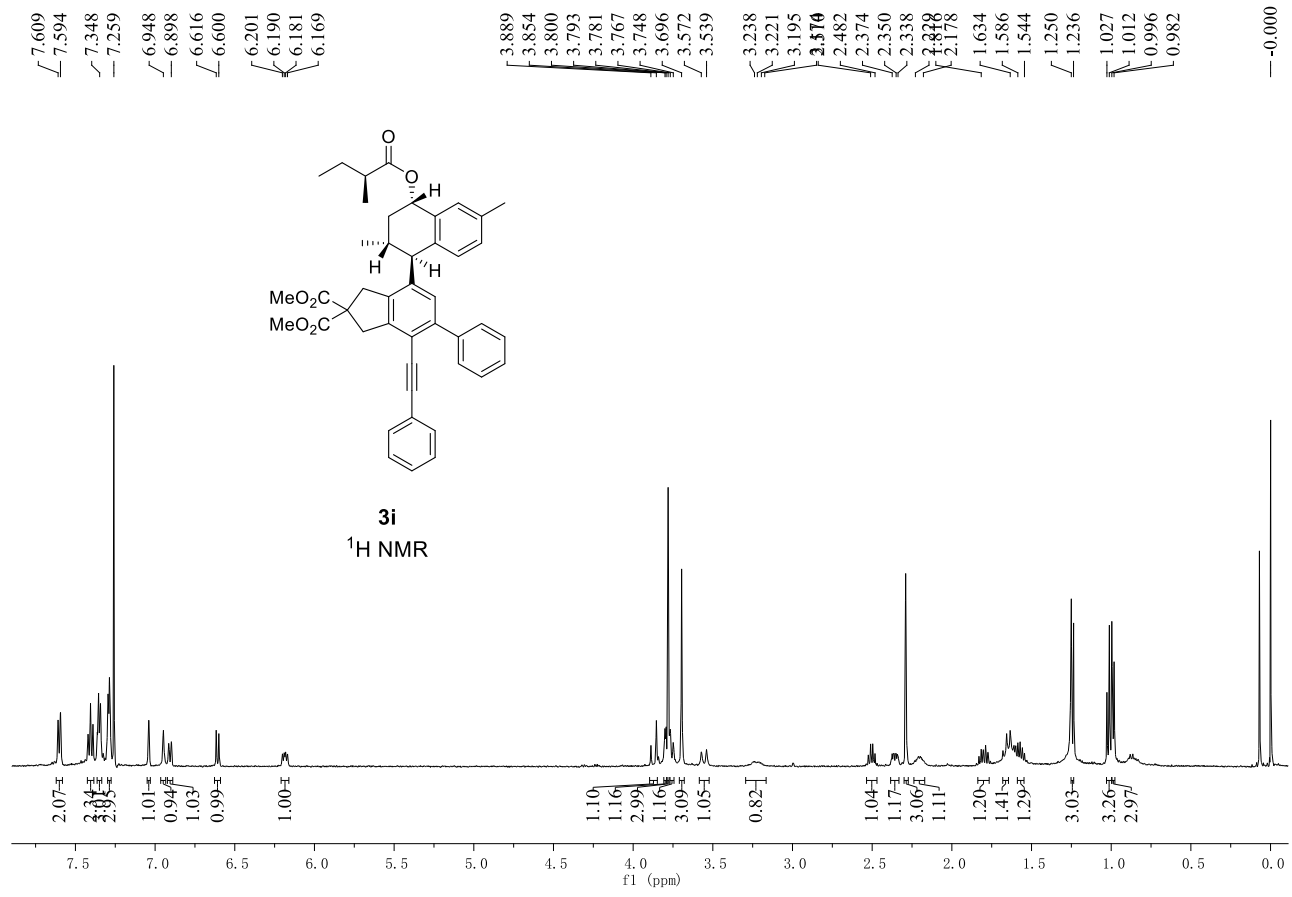
3h

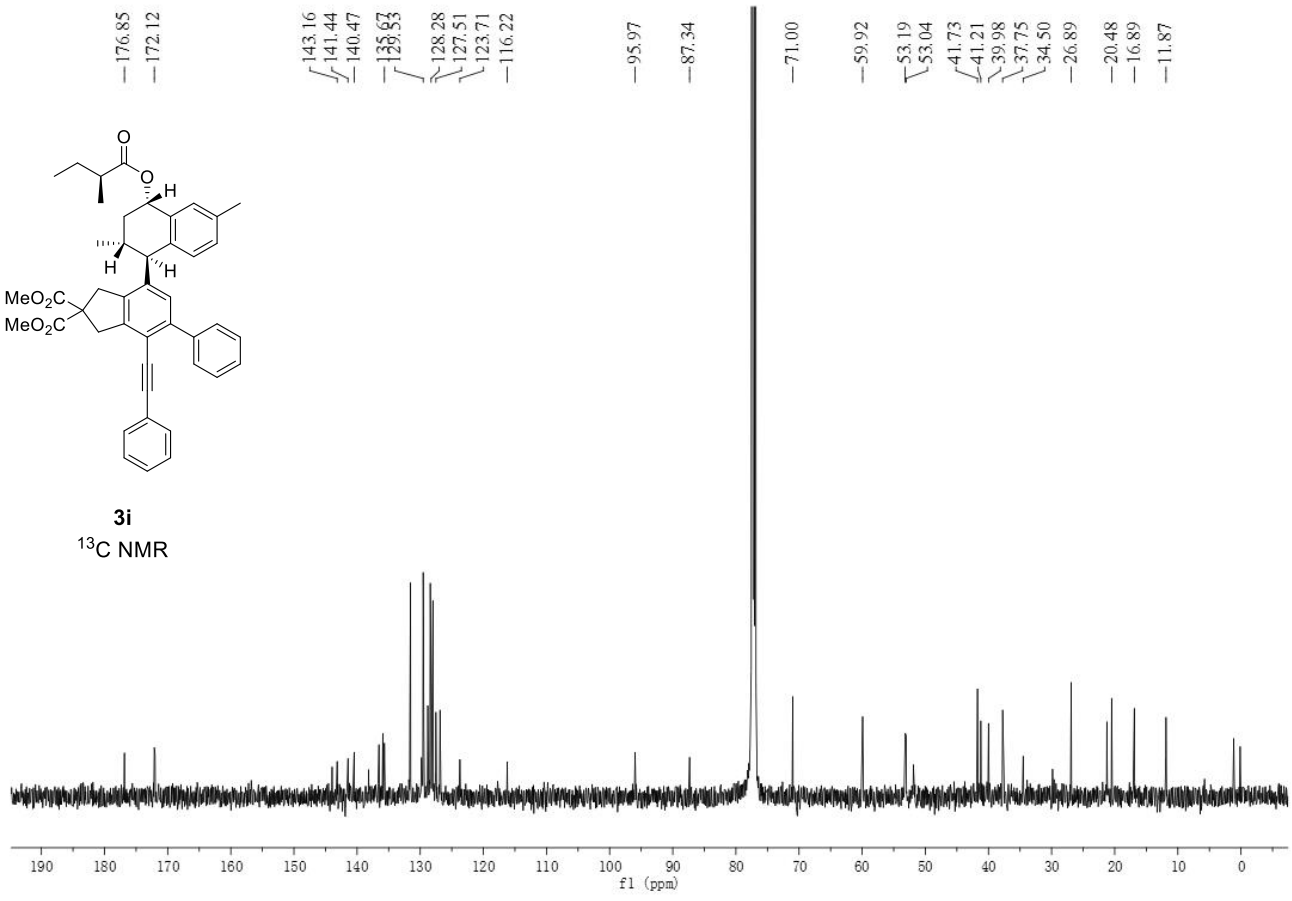
^{1}H NMR

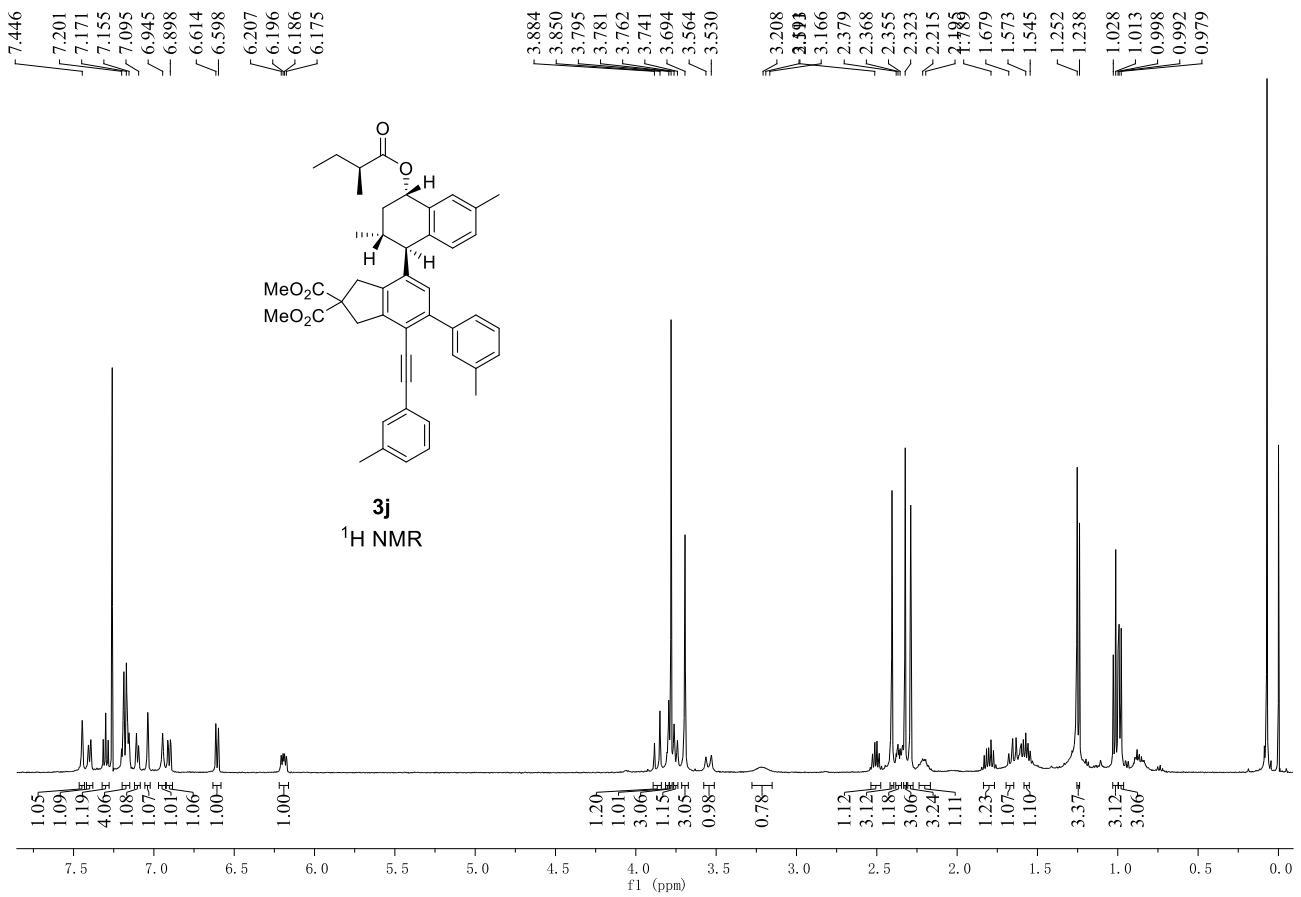


3h

^{13}C NMR

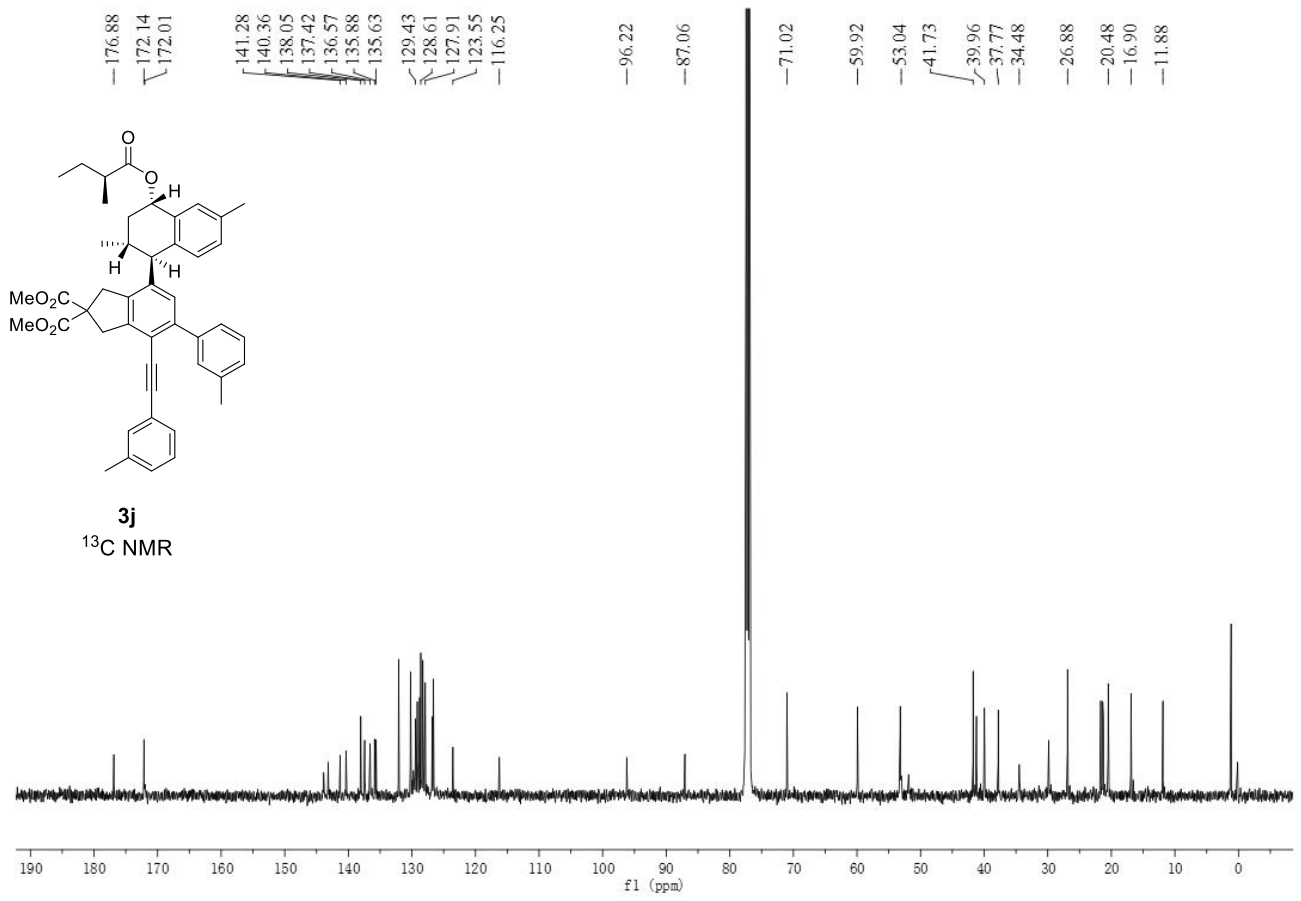

7.609
7.594
7.348
7.259
6.948
6.898
6.616
6.600
6.201
6.190
6.181
6.169
3.889
3.854
3.800
3.793
3.781
3.767
3.748
3.696
3.572
3.539
3.238
3.221
3.195
2.482
2.374
2.350
2.338
2.178
1.634
1.586
1.544
1.250
1.236
1.027
1.012
0.996
0.982
-0.000
MeO2C
MeO2C
3i
1H NMR
f1 (ppm)


176.85
172.12
143.16
141.44
140.47
135.67
129.53
128.28
127.51
123.71
116.22
95.97
87.34
71.00
59.92
53.19
53.04
41.73
41.21
39.98
37.75
34.50
26.89
20.48
16.89
11.87
MeO2C
MeO2C
3i
13C NMR
f1 (ppm)



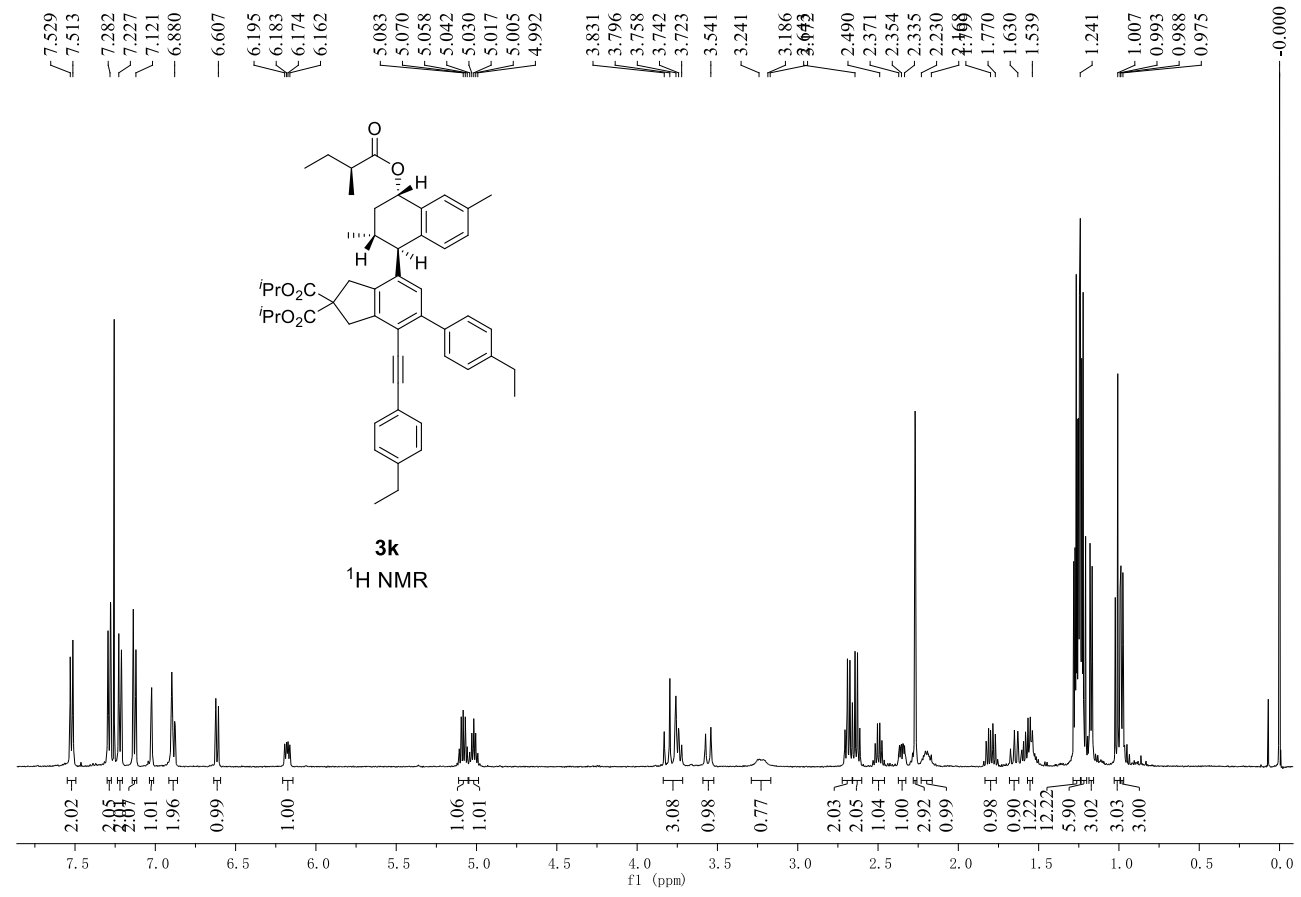
3j

^{1}H NMR



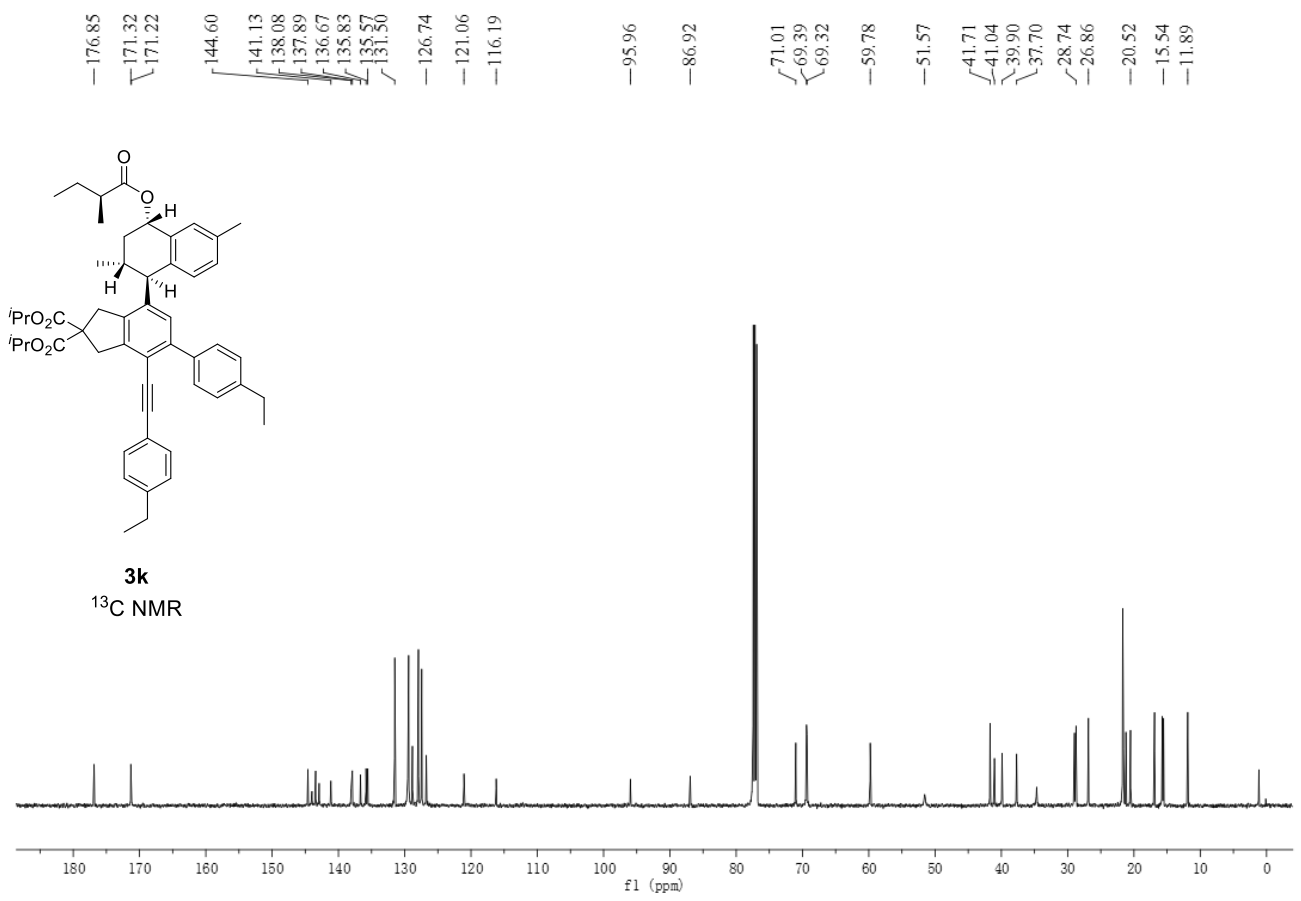
3j

^{13}C NMR



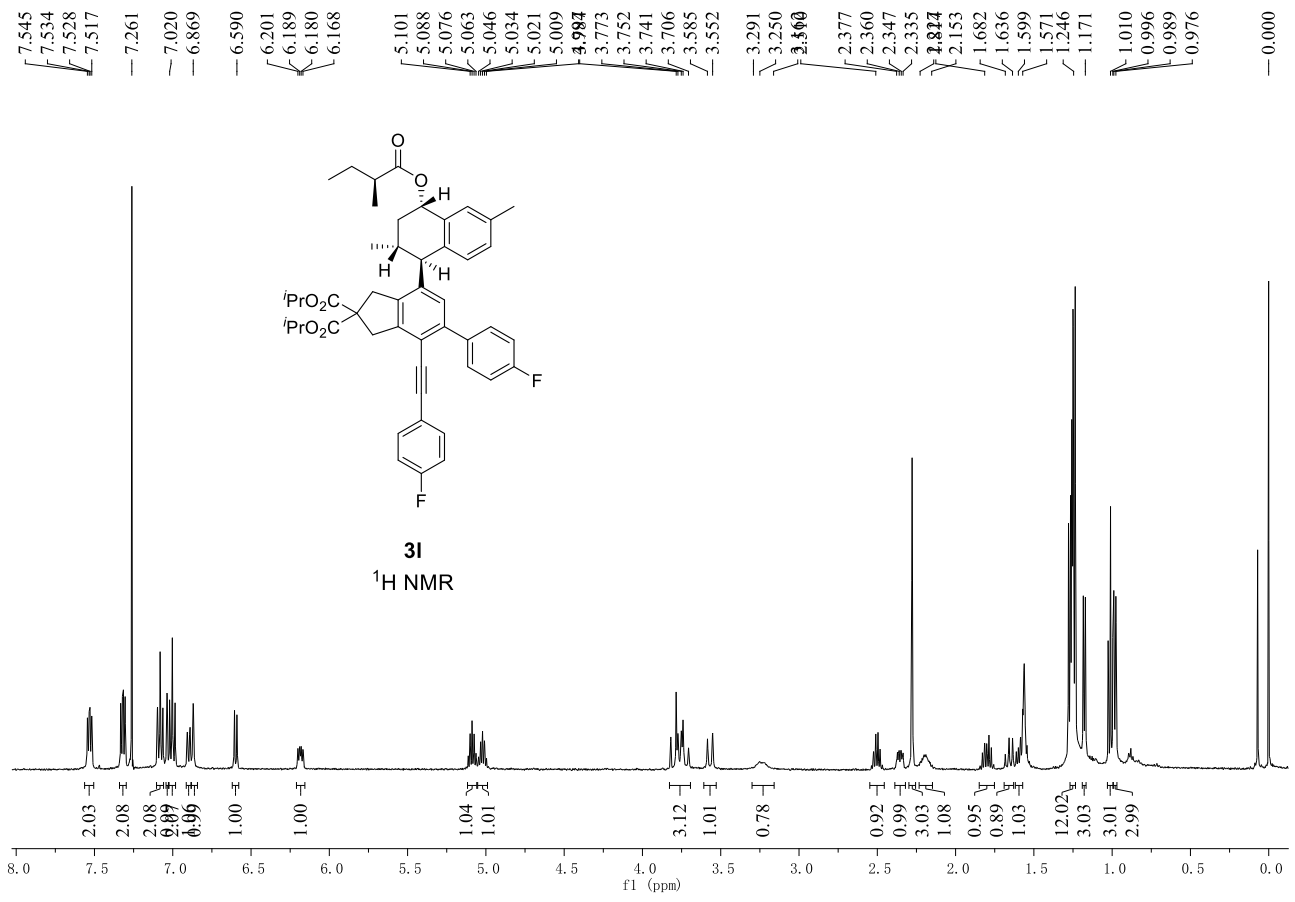
3k

^{1}H NMR



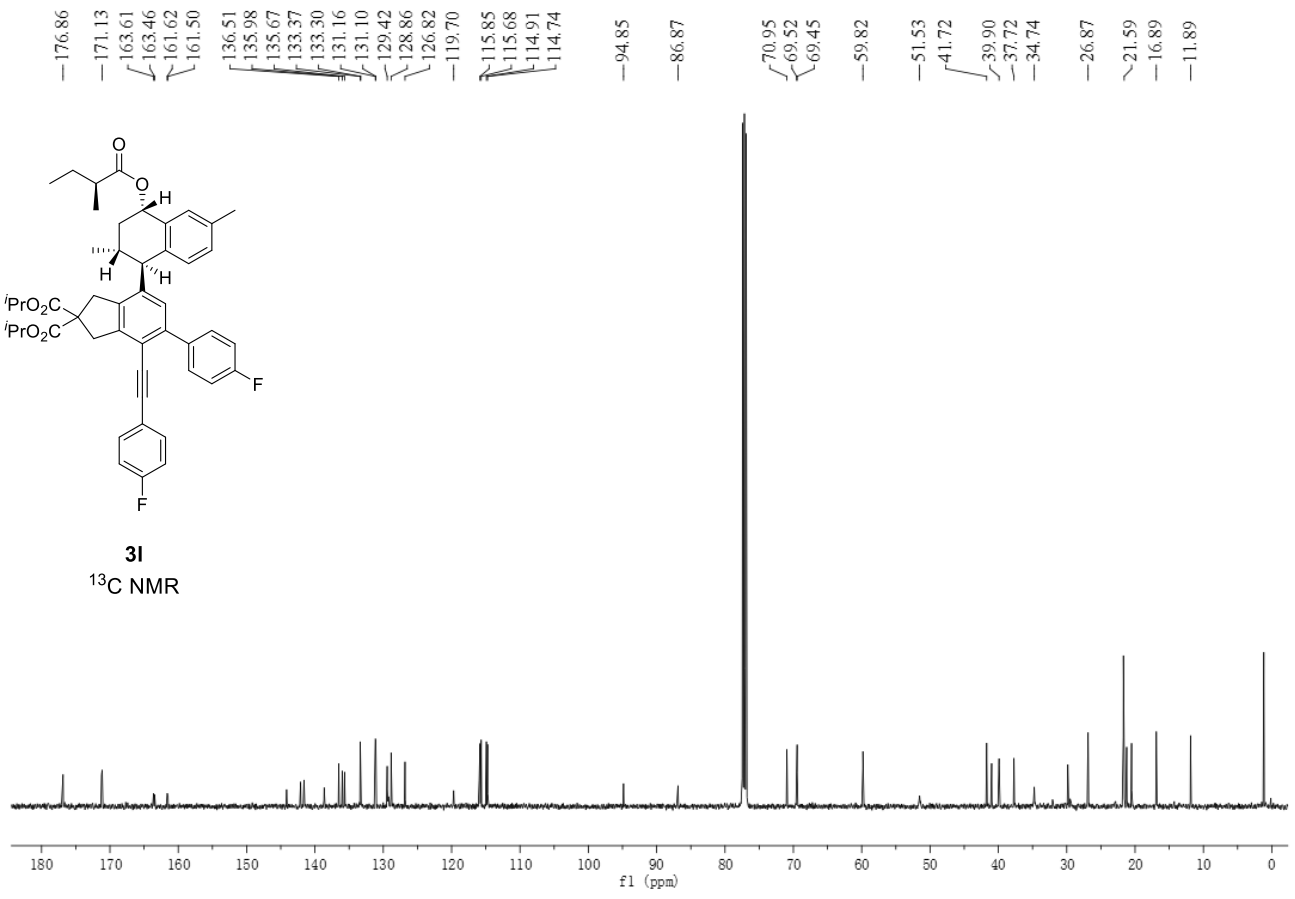
3k

^{13}C NMR



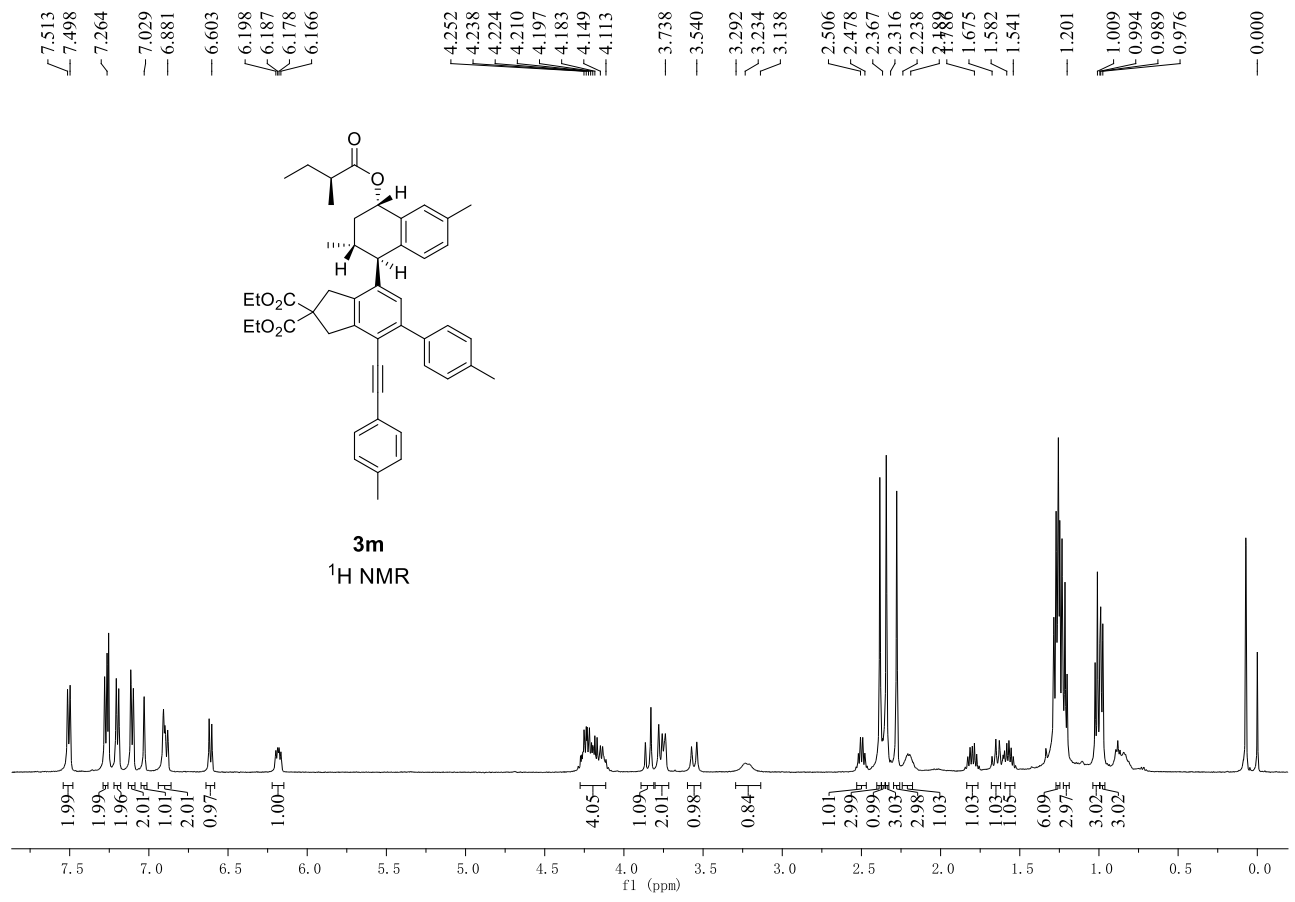
3l

^{1}H NMR



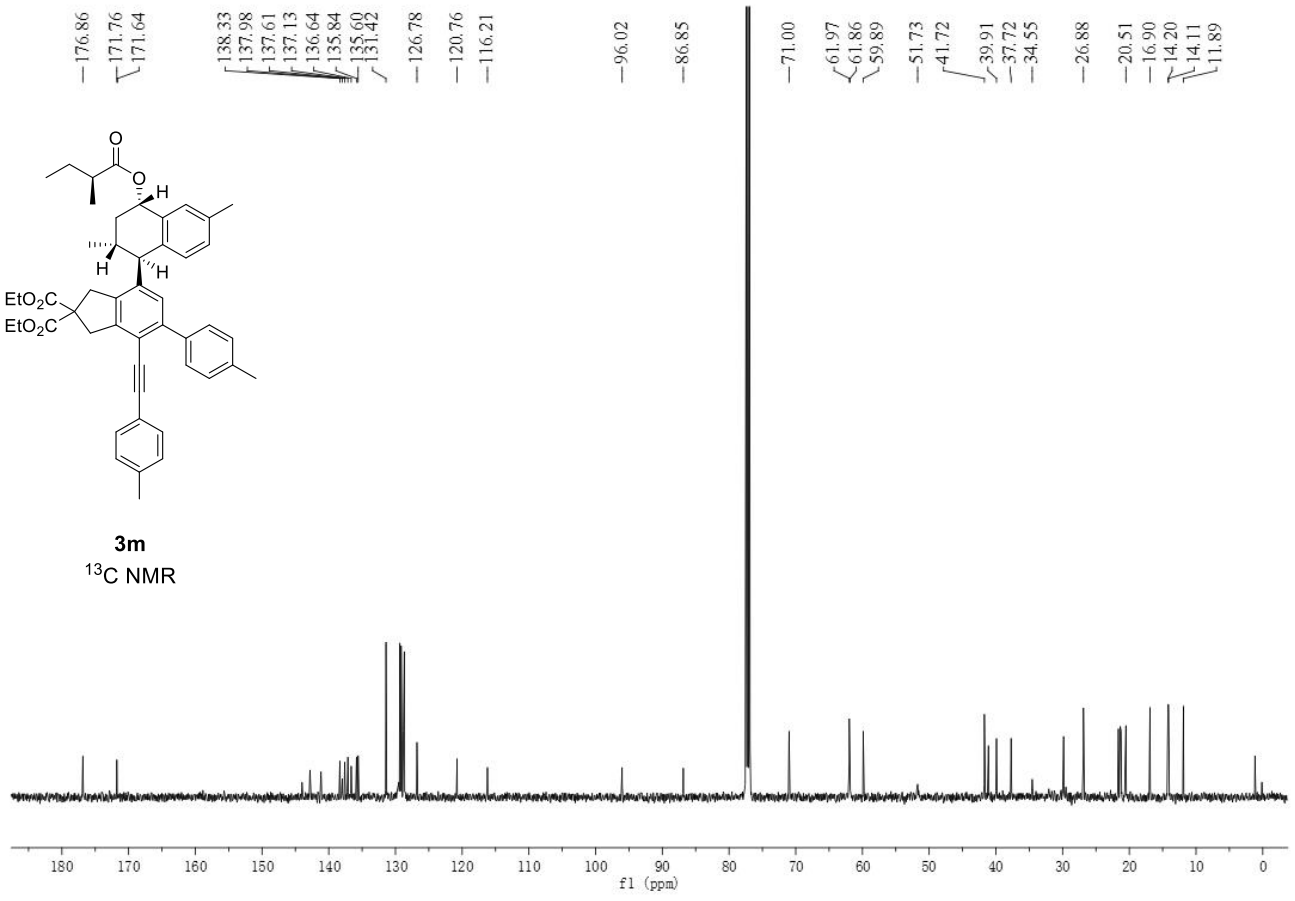
3l

^{13}C NMR



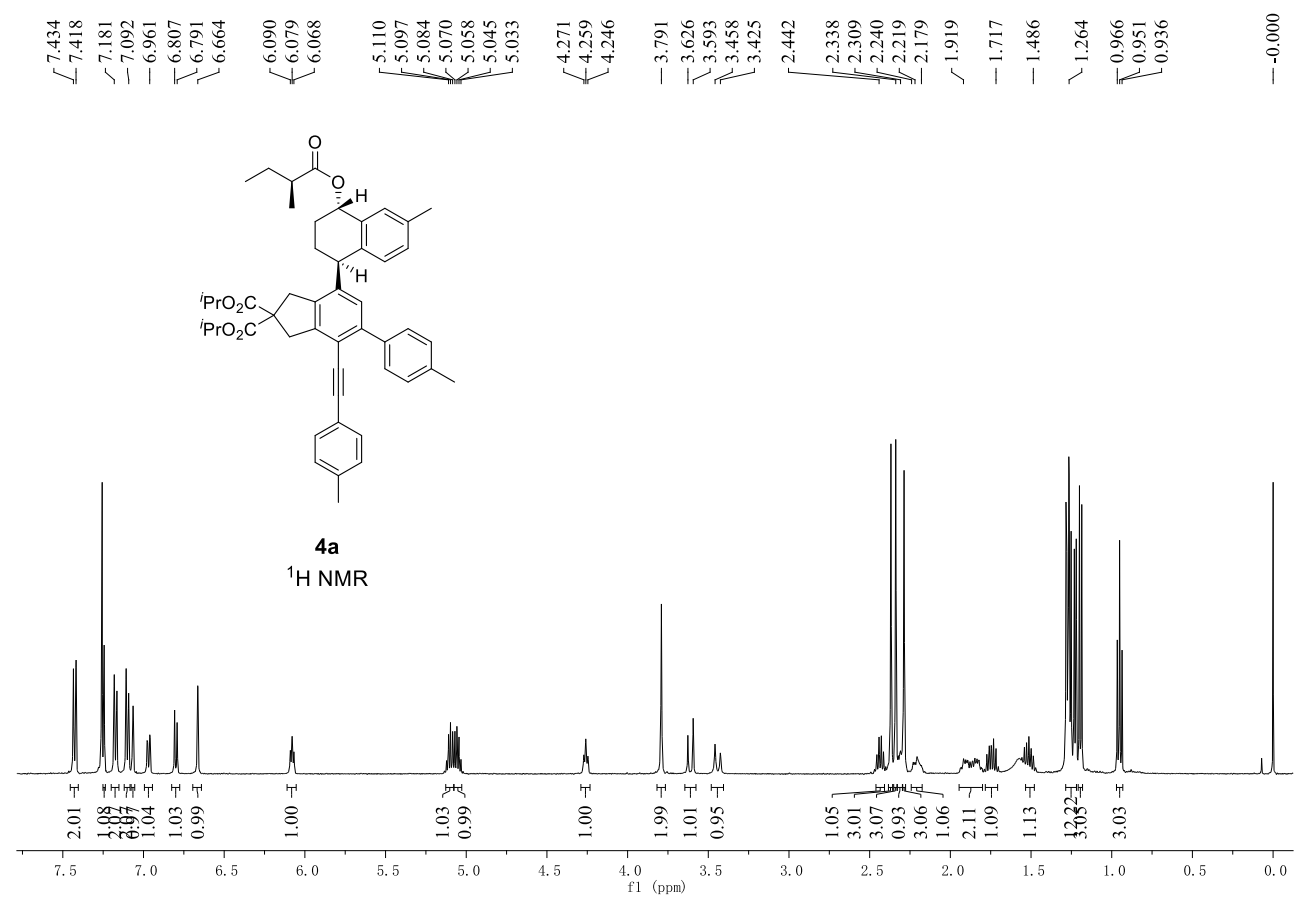
3m

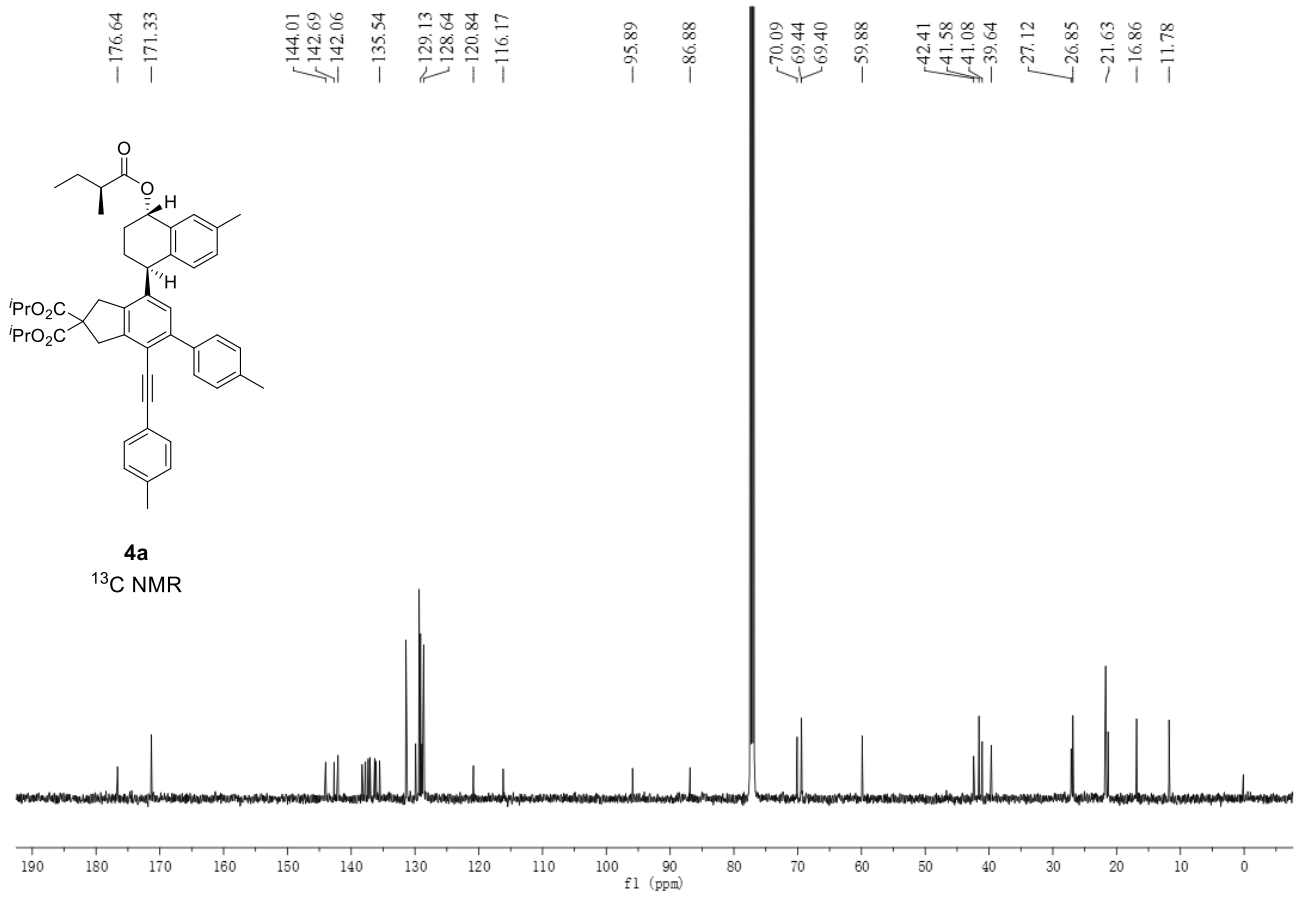
^{1}H NMR

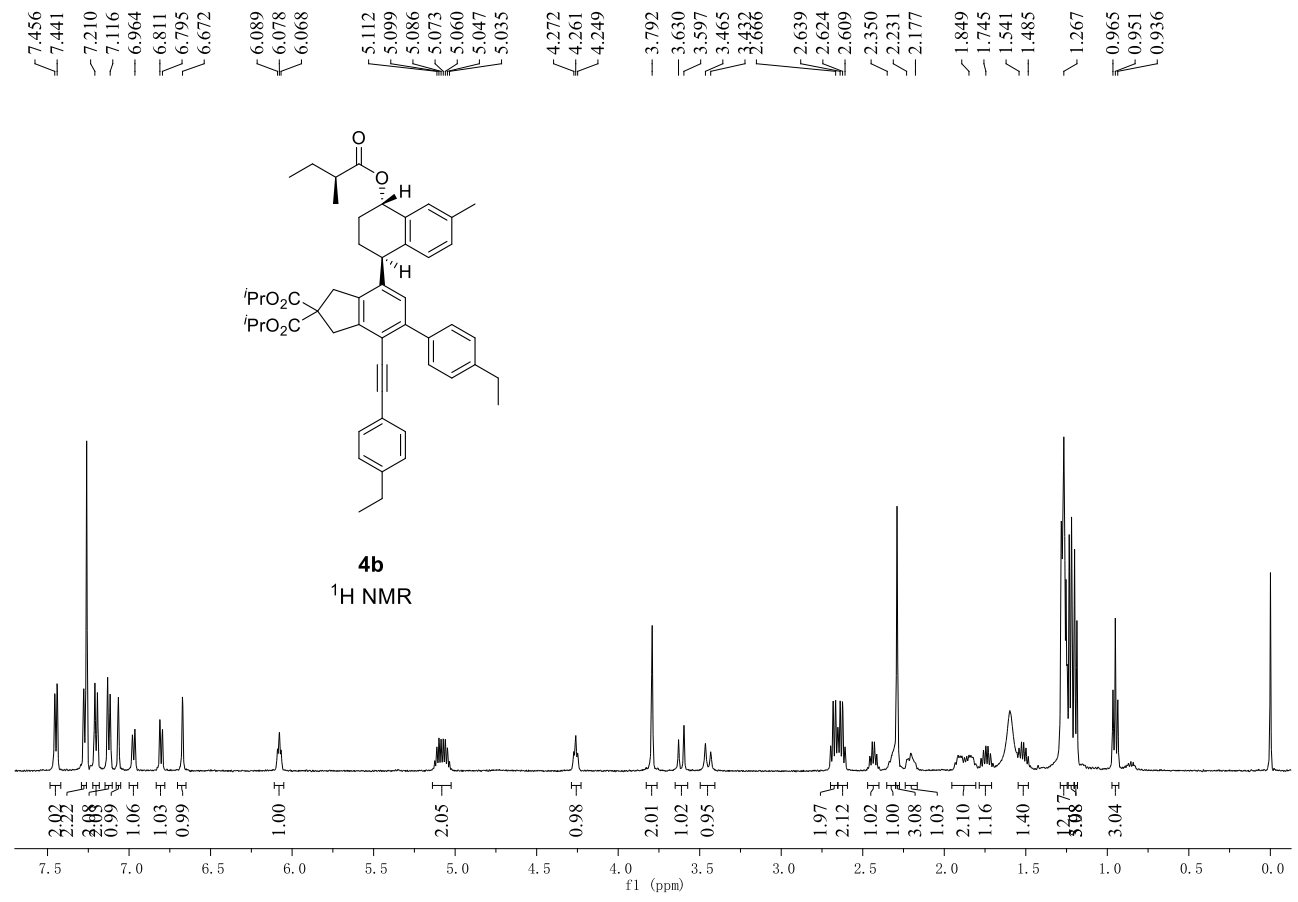


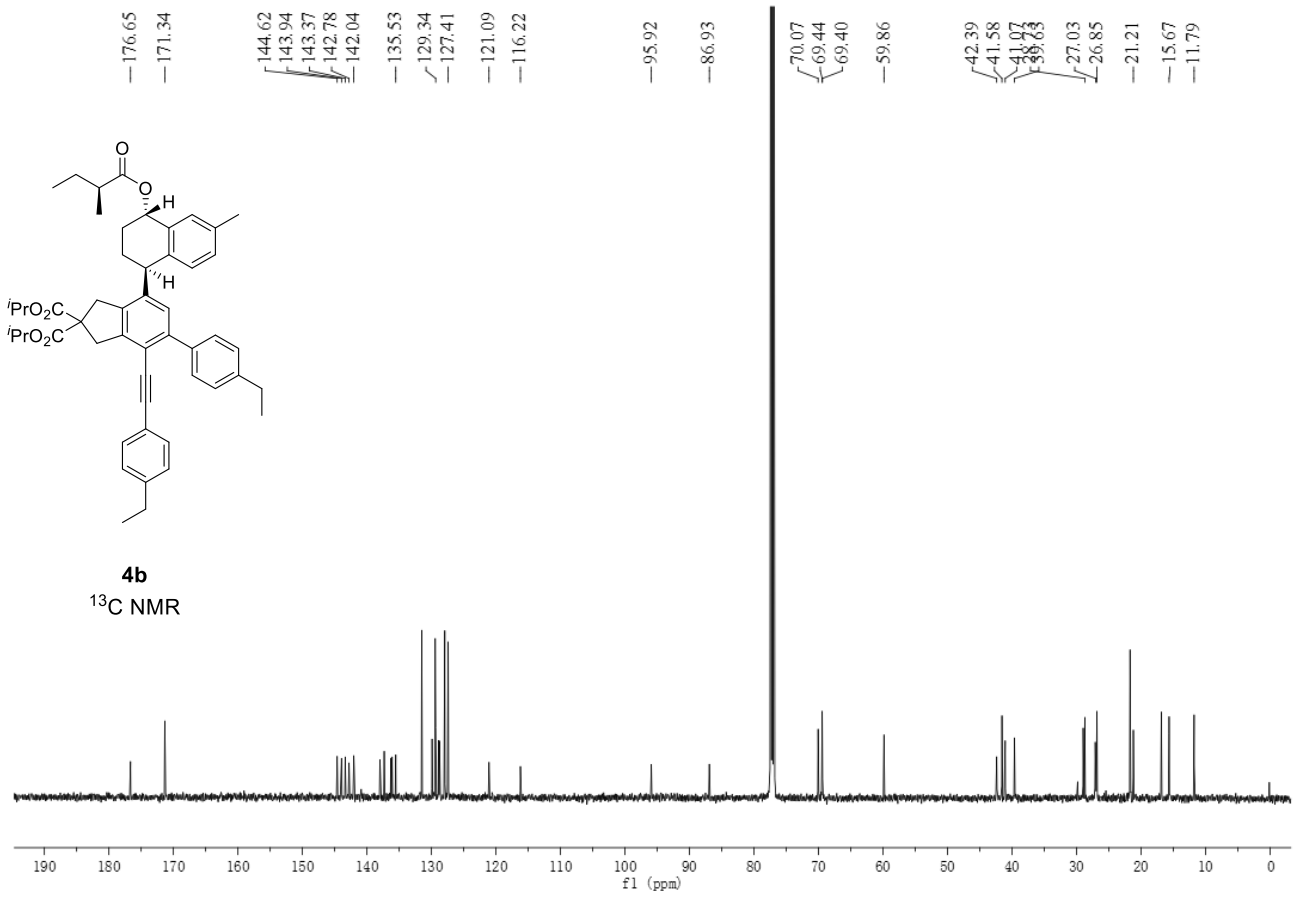
3m

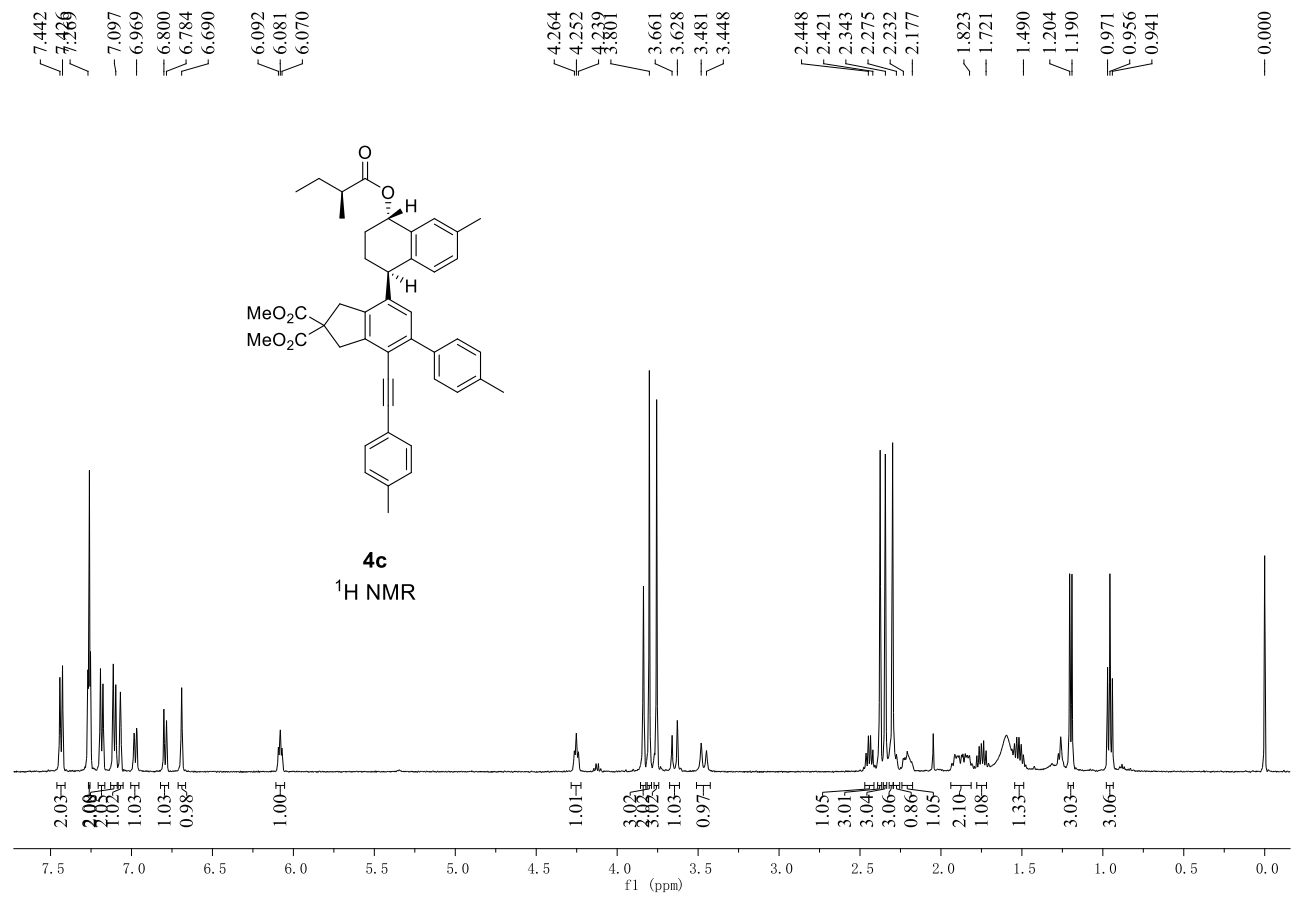
^{13}C NMR

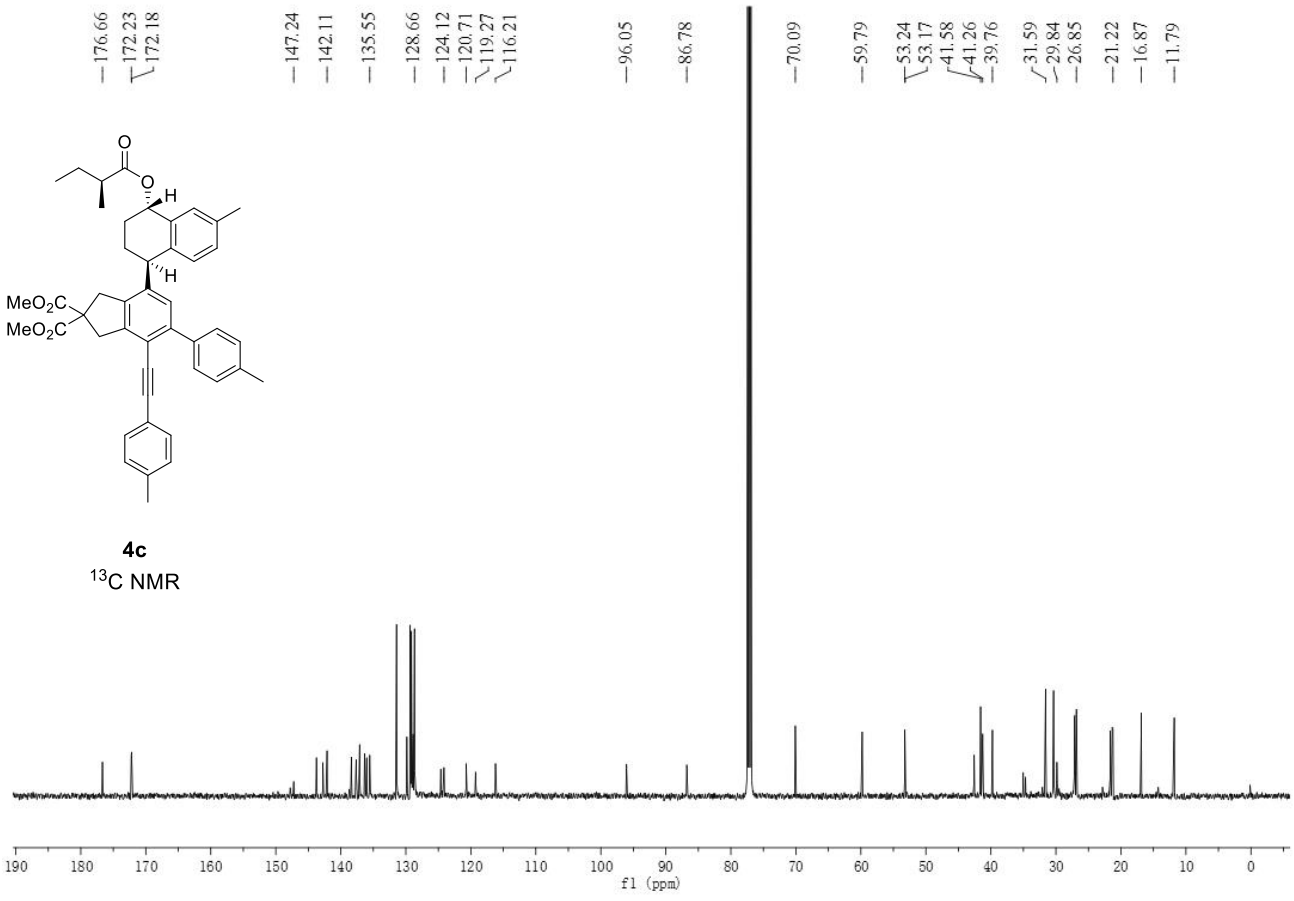

7.434
7.418
7.181
7.092
6.961
6.807
6.791
6.664
6.090
6.079
6.068
5.110
5.097
5.084
5.070
5.058
5.045
5.033
4.271
4.259
4.246
3.791
3.626
3.593
3.458
3.425
2.442
2.338
2.309
2.240
2.219
2.179
1.919
1.717
1.486
1.264
0.966
0.951
0.936
-0.000
2.01
1.08
2.07
1.04
1.03
0.99
1.00
1.03
0.99
1.00
1.99
1.01
0.95
1.05
3.01
0.93
3.06
1.06
2.11
1.09
1.13
3.03
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
f1 (ppm)
4a
1H NMR

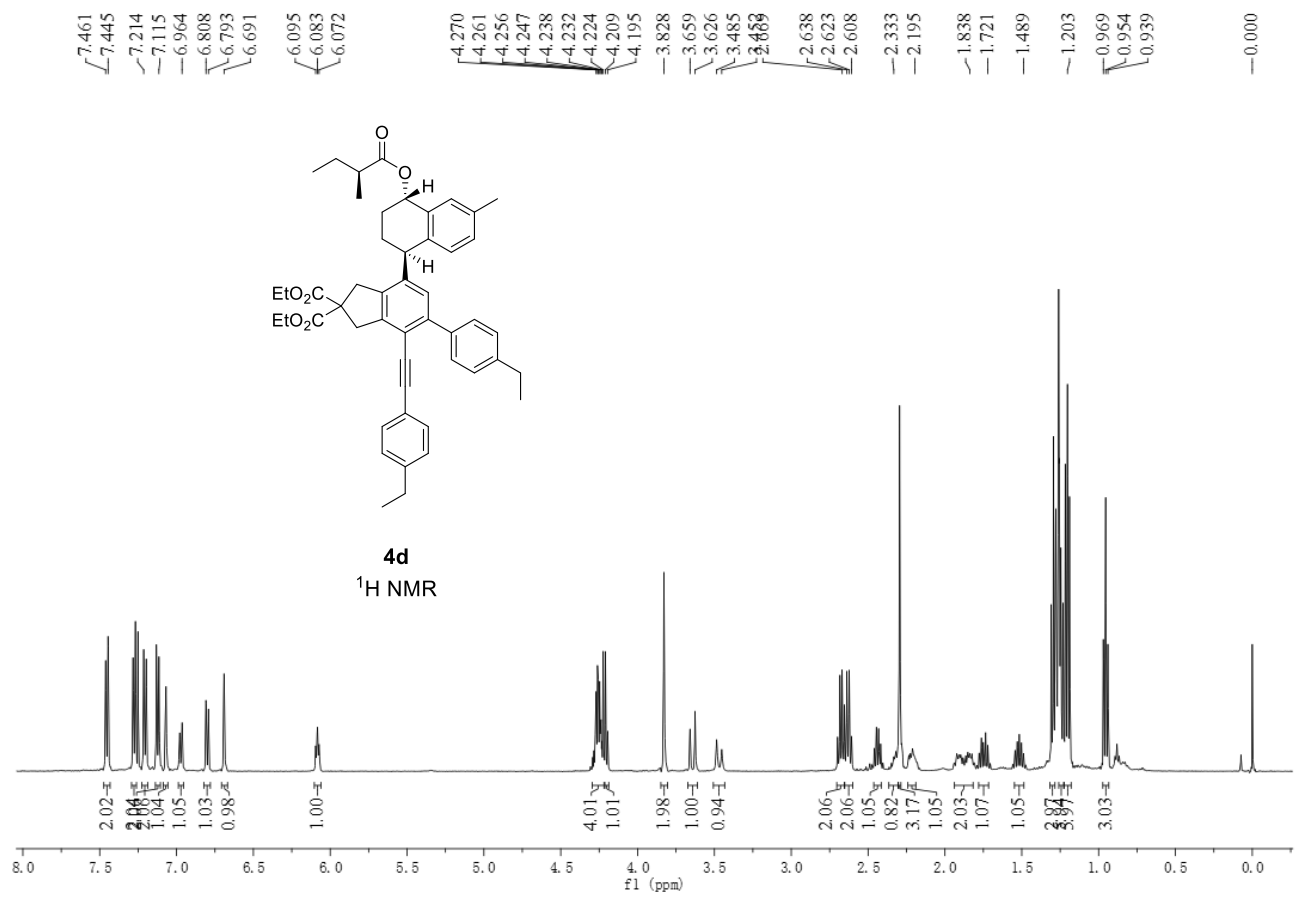

176.64
171.33
144.01
142.69
142.06
135.54
129.13
128.64
120.84
116.17
95.89
86.88
70.09
69.44
69.40
59.88
42.41
41.58
41.08
39.64
27.12
26.85
21.63
16.86
11.78
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
4a
13C NMR

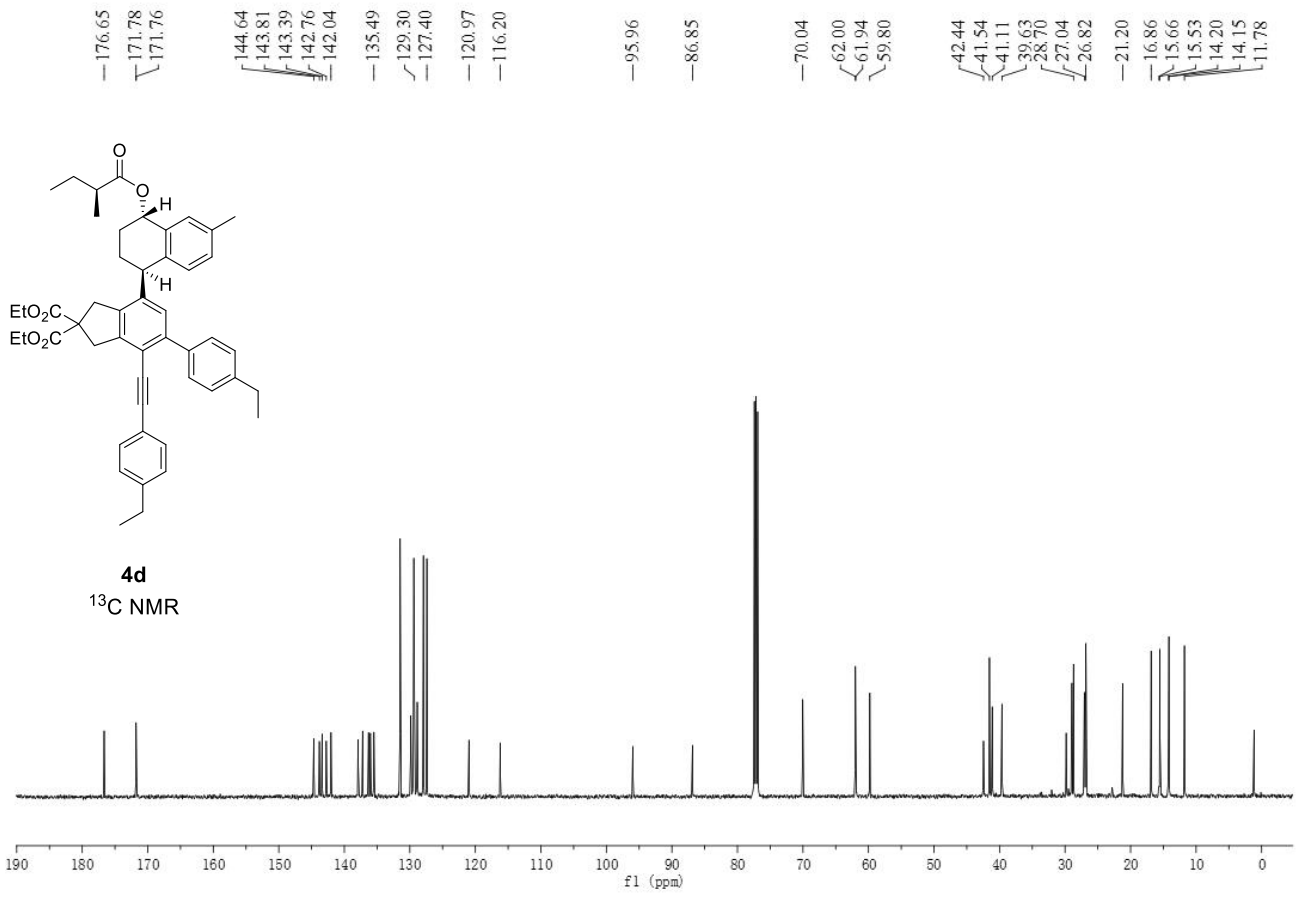

7.456
7.441
7.210
7.116
6.964
6.811
6.795
6.672
6.089
6.078
6.068
5.112
5.099
5.086
5.073
5.060
5.047
5.035
4.272
4.261
4.249
3.792
3.630
3.597
3.465
3.432
2.666
2.639
2.624
2.609
2.350
2.231
2.177
1.849
1.745
1.541
1.485
1.267
0.965
0.951
0.936
O
O
H
H
iPrO2C
iPrO2C
4b
1H NMR
2.02
2.22
2.08
0.99
1.06
1.03
0.99
1.00
2.05
0.98
2.01
1.02
0.95
1.97
2.12
1.02
1.00
3.08
1.03
2.10
1.16
1.40
12.17
3.04
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
f1 (ppm)

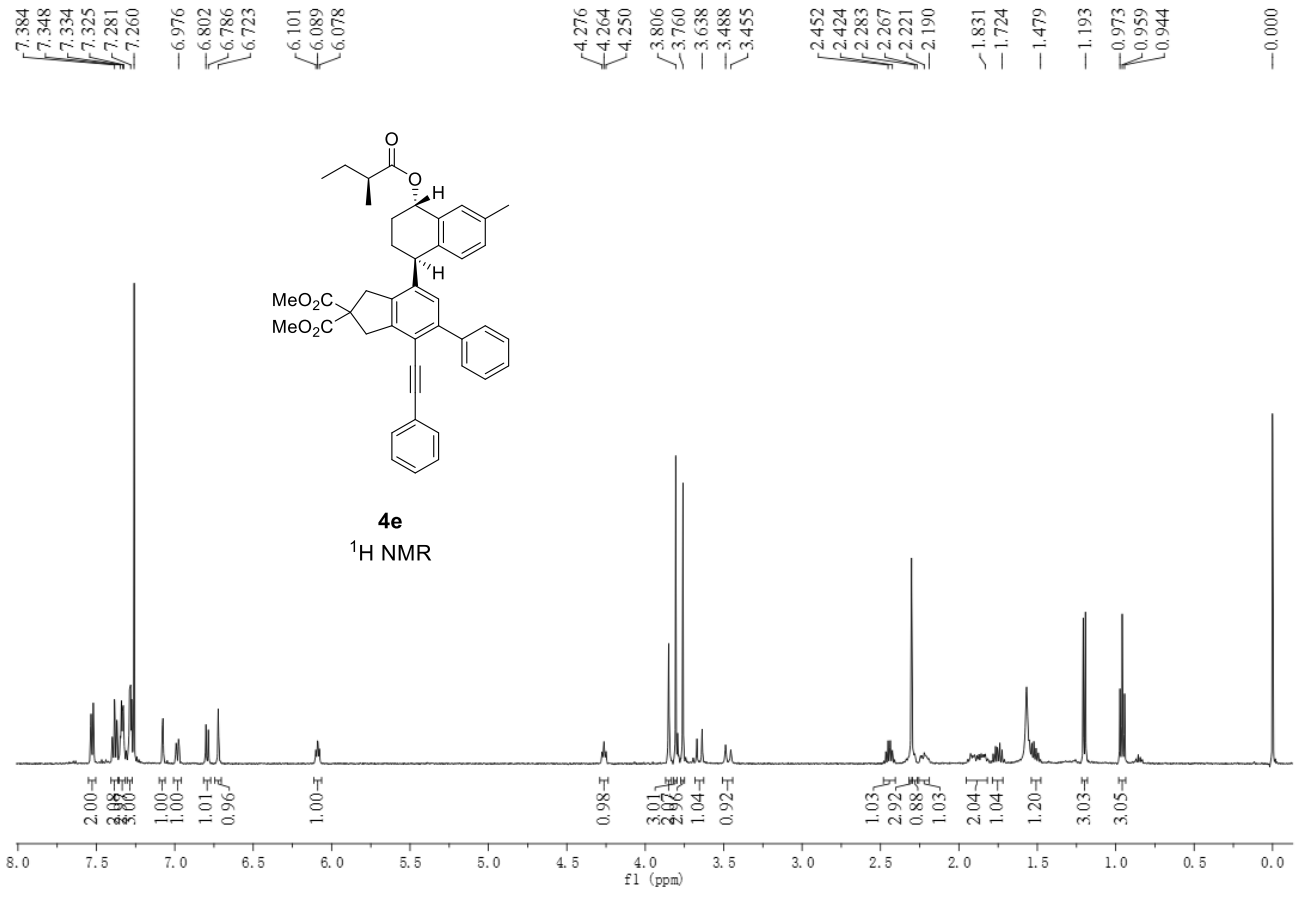

176.65
171.34
144.62
143.94
143.37
142.78
142.04
135.53
129.34
127.41
121.09
116.22
95.92
86.93
70.07
69.44
69.40
59.86
42.39
41.58
41.07
27.03
26.85
21.21
15.67
11.79
O
O
H
H
iPrO2C
iPrO2C
4b
13C NMR
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

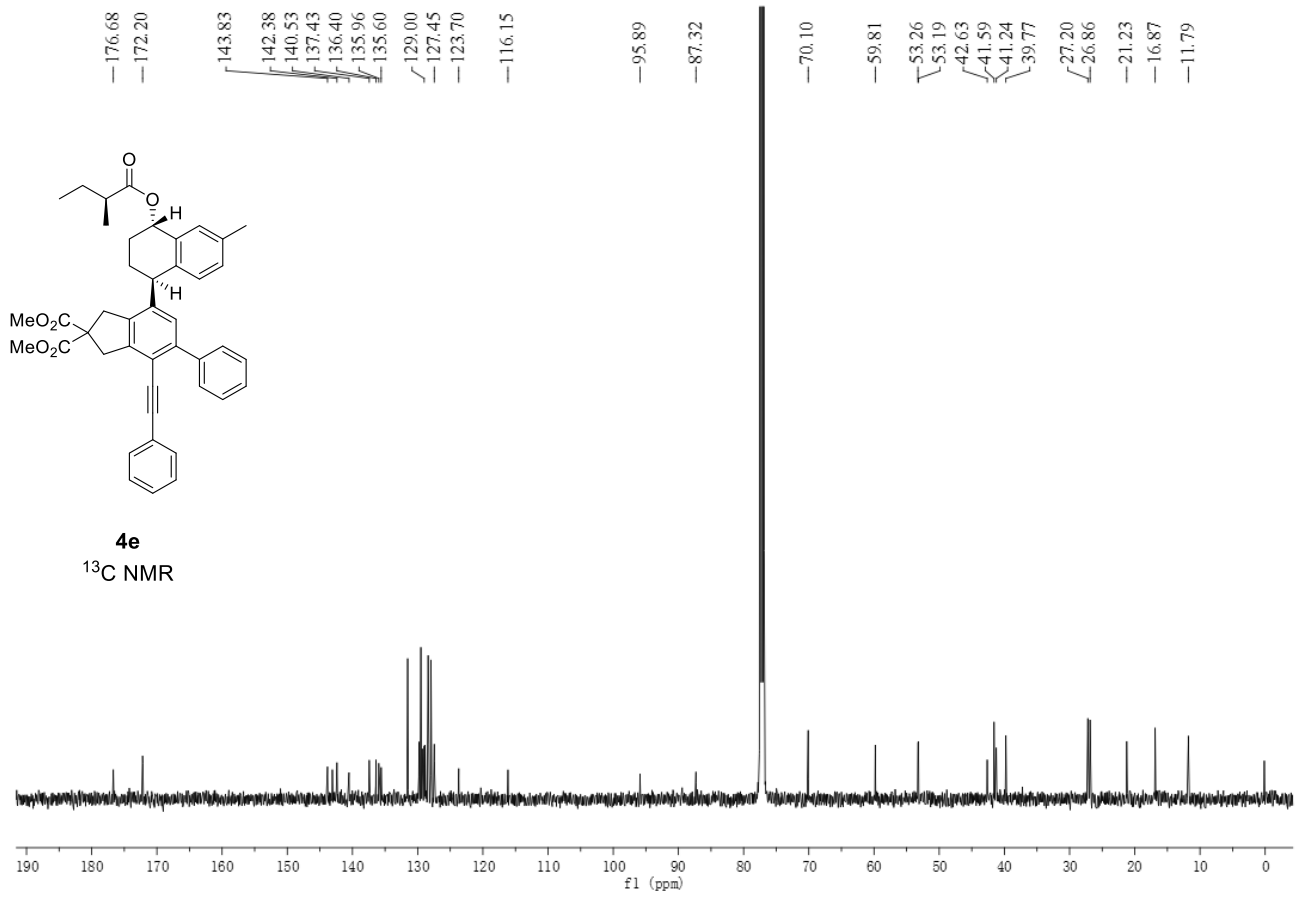

7.442
7.426
7.269
7.097
6.969
6.800
6.784
6.690
6.092
6.081
6.070
4.264
4.252
4.239
3.801
3.661
3.628
3.481
3.448
2.448
2.421
2.343
2.275
2.232
2.177
1.823
1.721
1.490
1.204
1.190
0.971
0.956
0.941
0.000
MeO2C
MeO2C
4c
1H NMR
f1 (ppm)

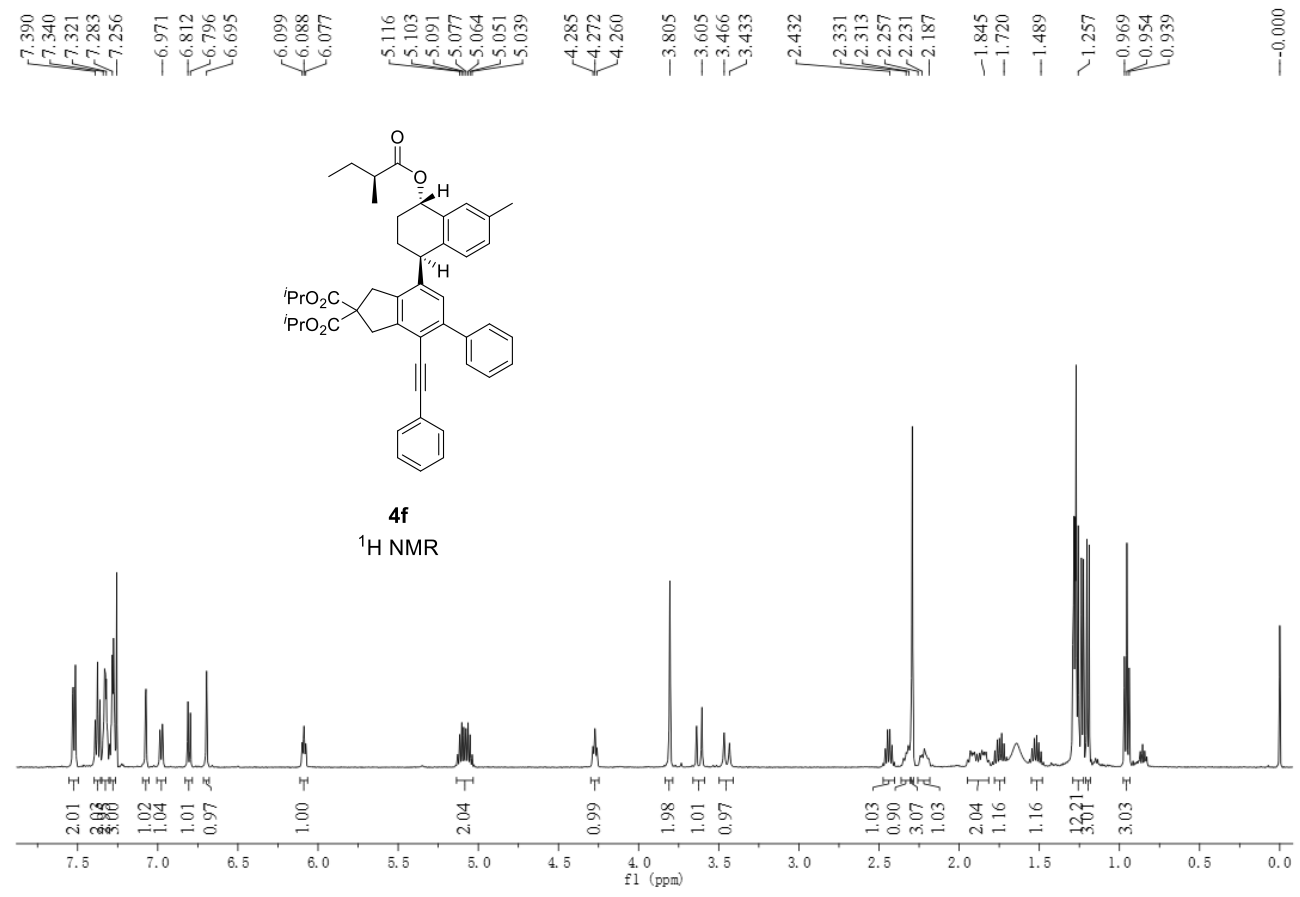

176.66
172.23
172.18
147.24
142.11
135.55
128.66
124.12
120.71
119.27
116.21
96.05
86.78
70.09
59.79
53.24
53.17
41.58
41.26
39.76
31.59
29.84
26.85
21.22
16.87
11.79
MeO2C
MeO2C
4c
13C NMR
f1 (ppm)


7.461
7.445
7.214
7.115
6.964
6.808
6.793
6.691
6.095
6.083
6.072
4.270
4.261
4.256
4.247
4.238
4.232
4.224
4.209
4.195
3.828
3.659
3.626
3.485
2.638
2.623
2.608
2.333
2.195
1.838
1.721
1.489
1.203
0.969
0.954
0.939
0.000
EtO2C
EtO2C
4d
1H NMR
2.02
1.05
1.03
0.98
1.00
4.01
1.01
1.98
1.00
0.94
2.06
2.06
1.05
0.82
3.17
1.05
2.03
1.07
1.05
3.03
f1 (ppm)


176.65
171.78
171.76
144.64
143.81
143.39
142.76
142.04
135.49
129.30
127.40
120.97
116.20
95.96
86.85
70.04
62.00
61.94
59.80
42.44
41.54
41.11
39.63
28.70
27.04
26.82
21.20
16.86
15.66
15.53
14.20
14.15
11.78
EtO2C
EtO2C
4d
13C NMR
f1 (ppm)

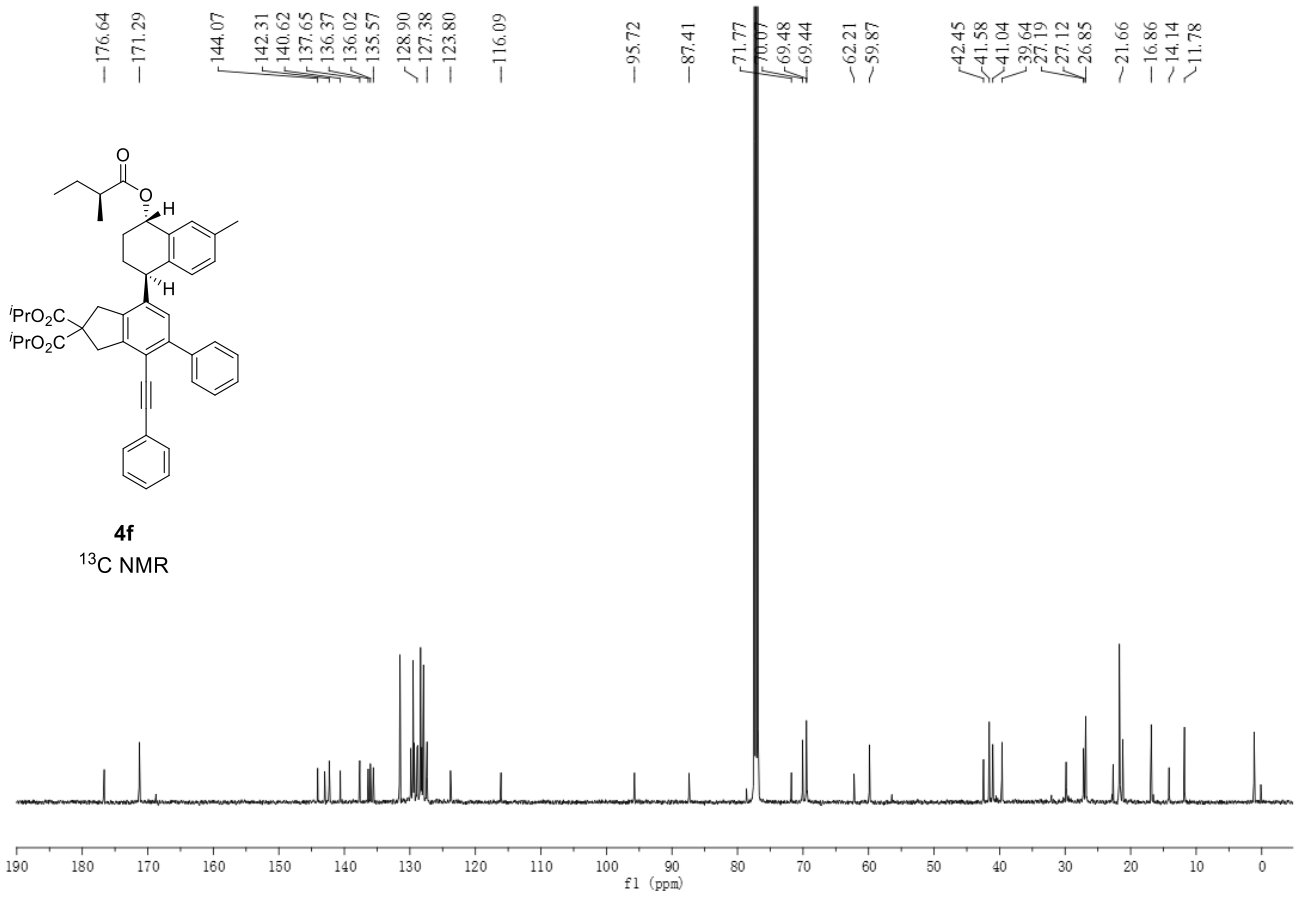

7.384
7.348
7.334
7.325
7.281
7.260
6.976
6.802
6.786
6.723
6.101
6.089
6.078
4.276
4.264
4.250
3.806
3.760
3.638
3.488
3.455
2.452
2.424
2.283
2.267
2.221
2.190
1.831
1.724
1.479
1.193
0.973
0.959
0.944
0.000
MeO2C
MeO2C
4e
1H NMR
f1 (ppm)


176.68
172.20
143.83
142.38
140.53
137.43
136.40
135.96
135.60
129.00
127.45
123.70
116.15
95.89
87.32
70.10
59.81
53.26
53.19
42.63
41.59
41.24
39.77
27.20
26.86
21.23
16.87
11.79
MeO2C
MeO2C
4e
13C NMR
f1 (ppm)



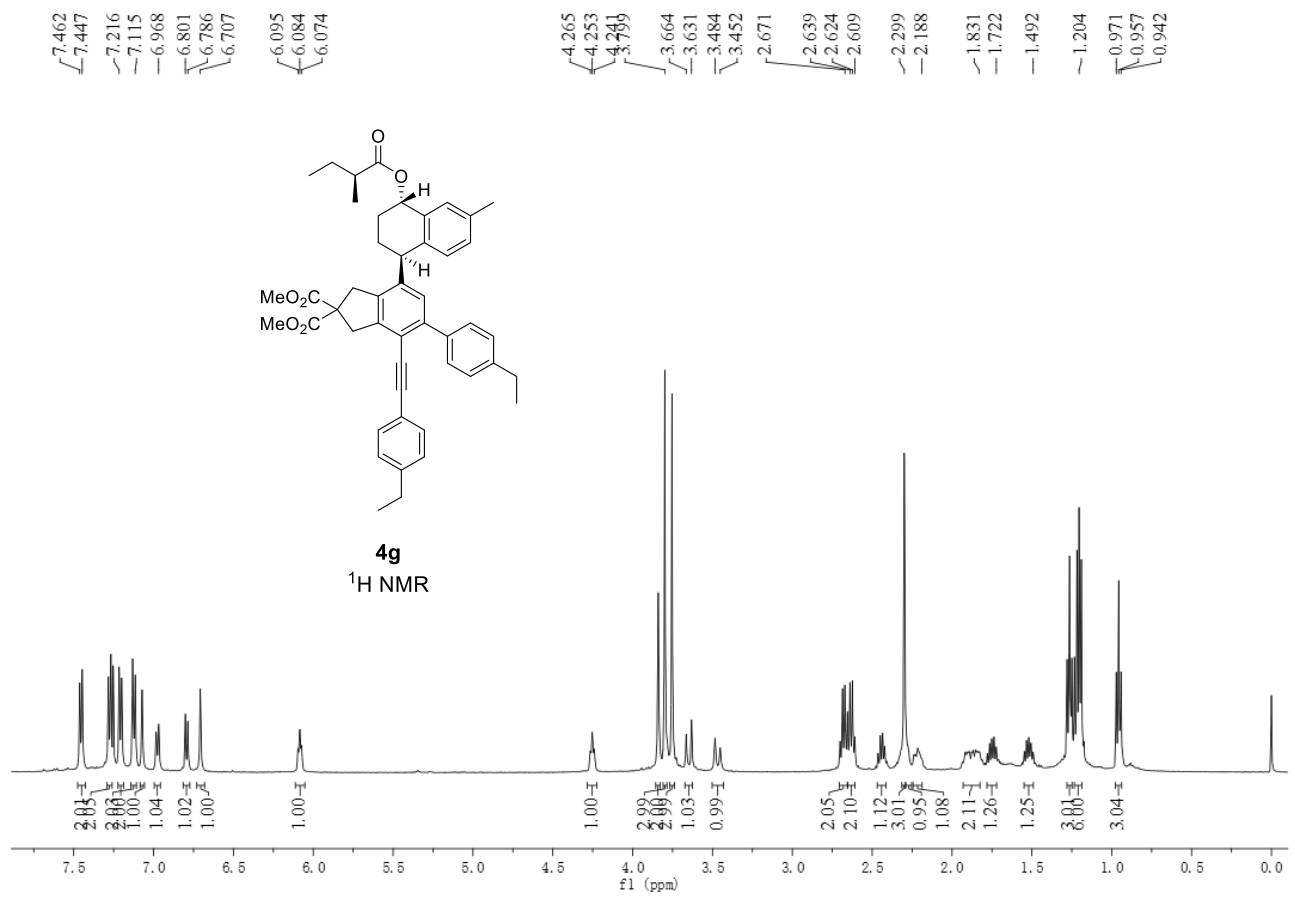
4f

^{1}H NMR



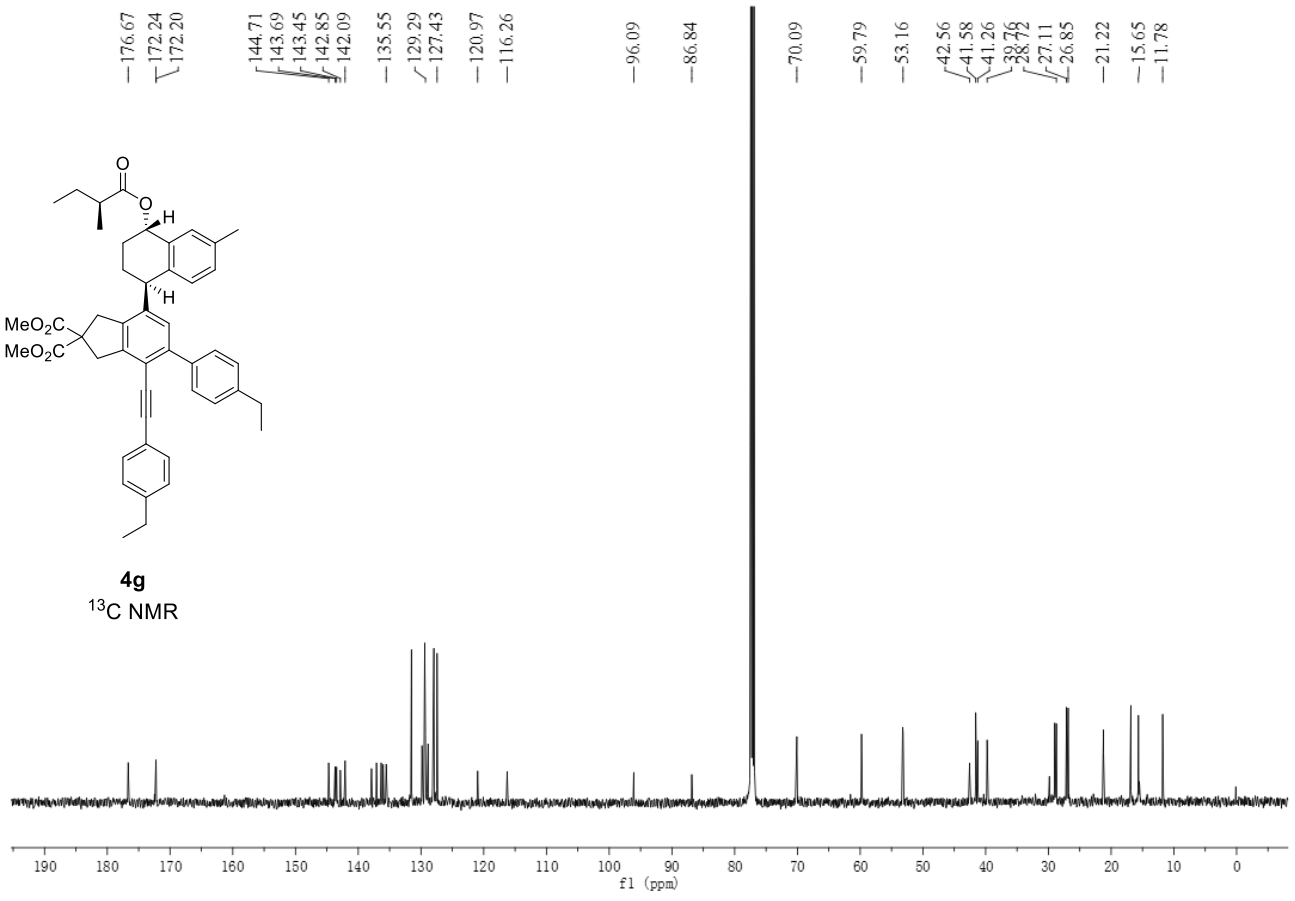
4f

^{13}C NMR



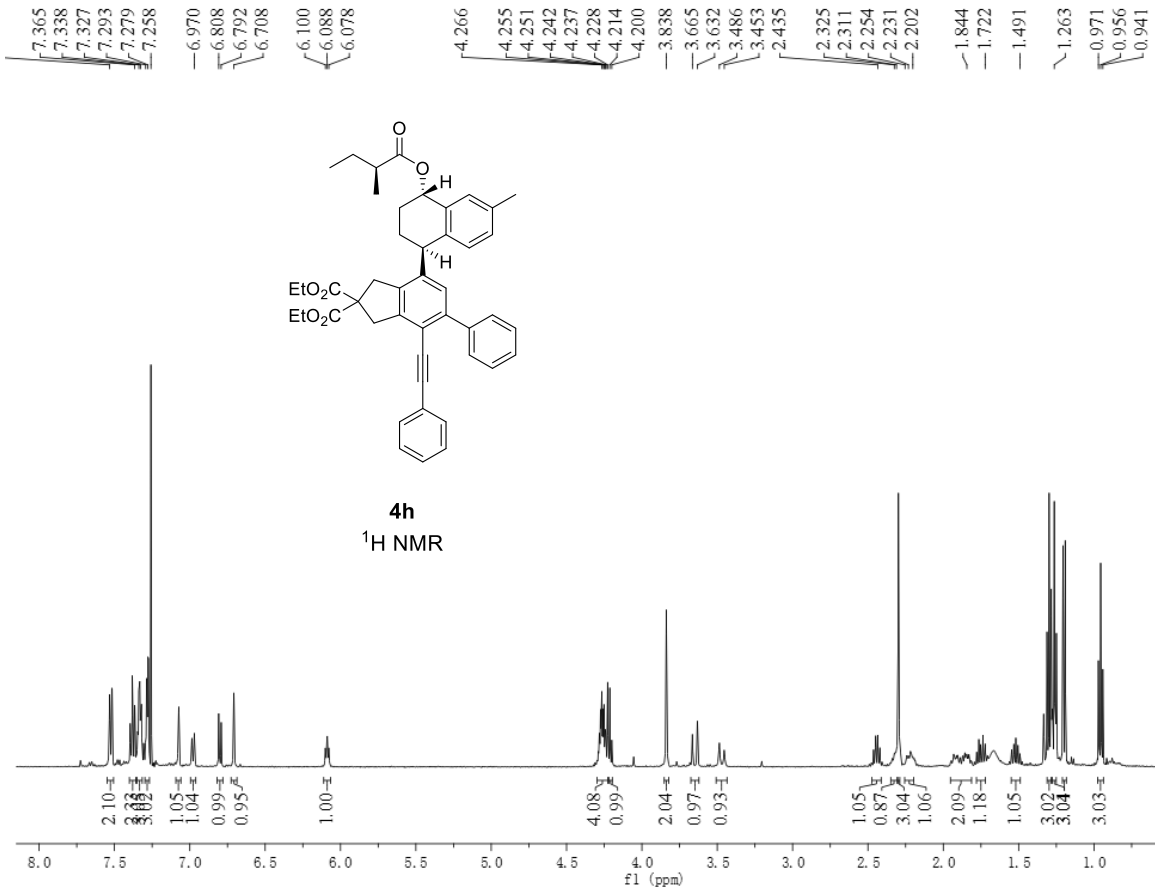
4g

^{1}H NMR



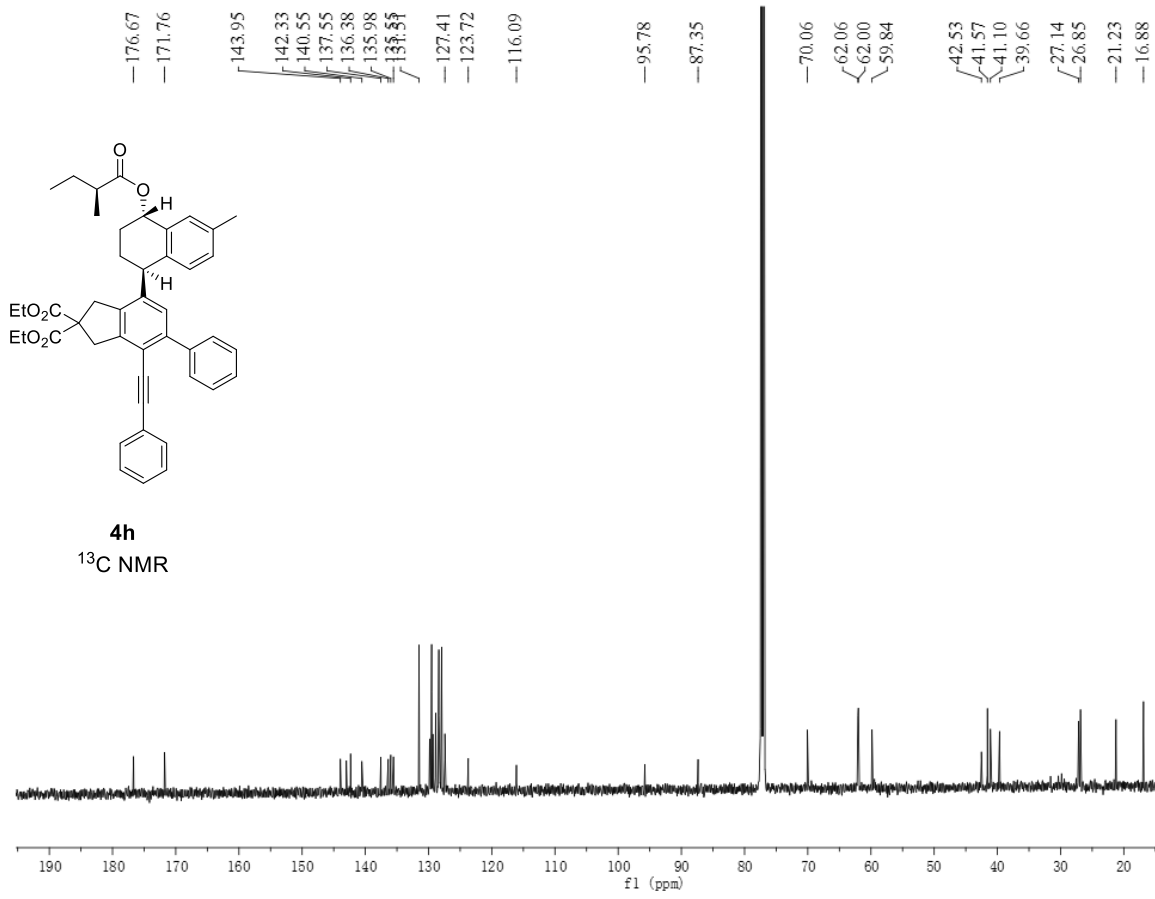
4g

^{13}C NMR



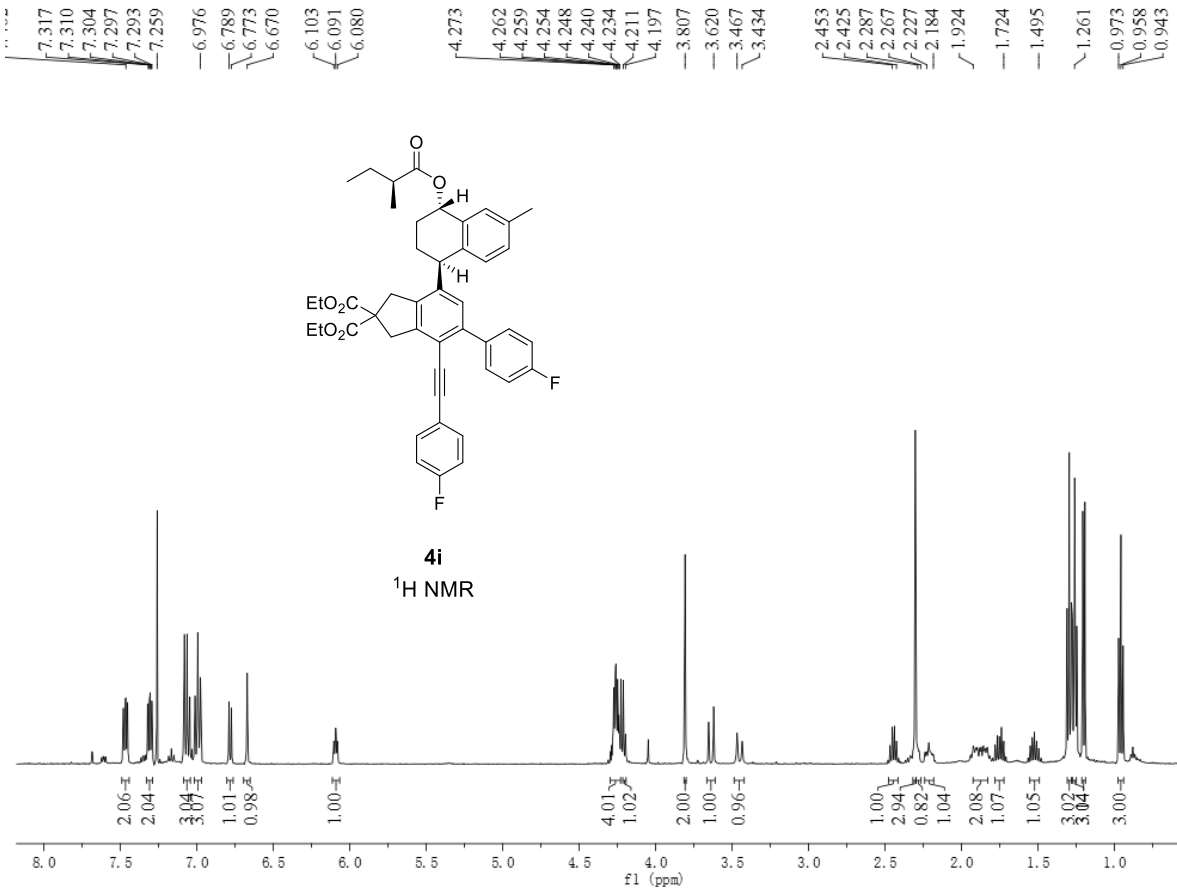
4h

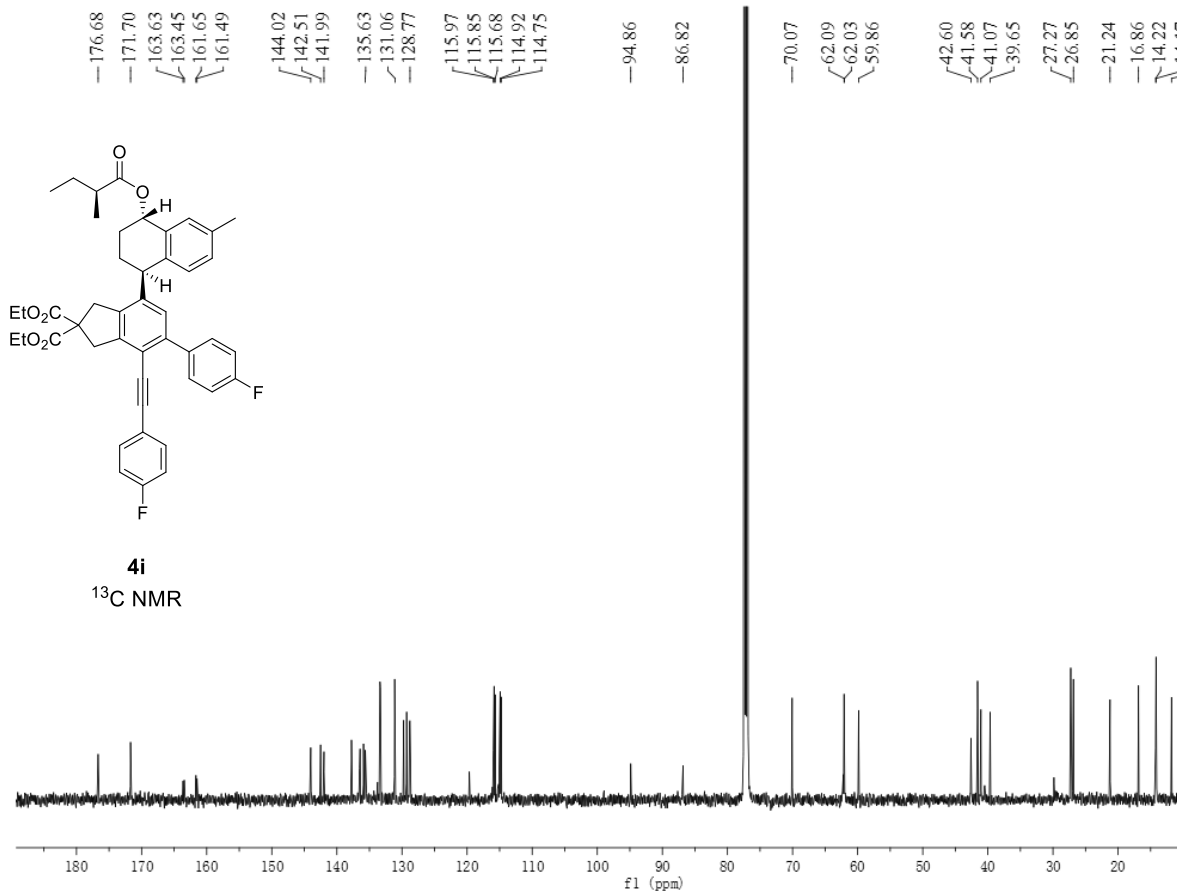
^{1}H NMR

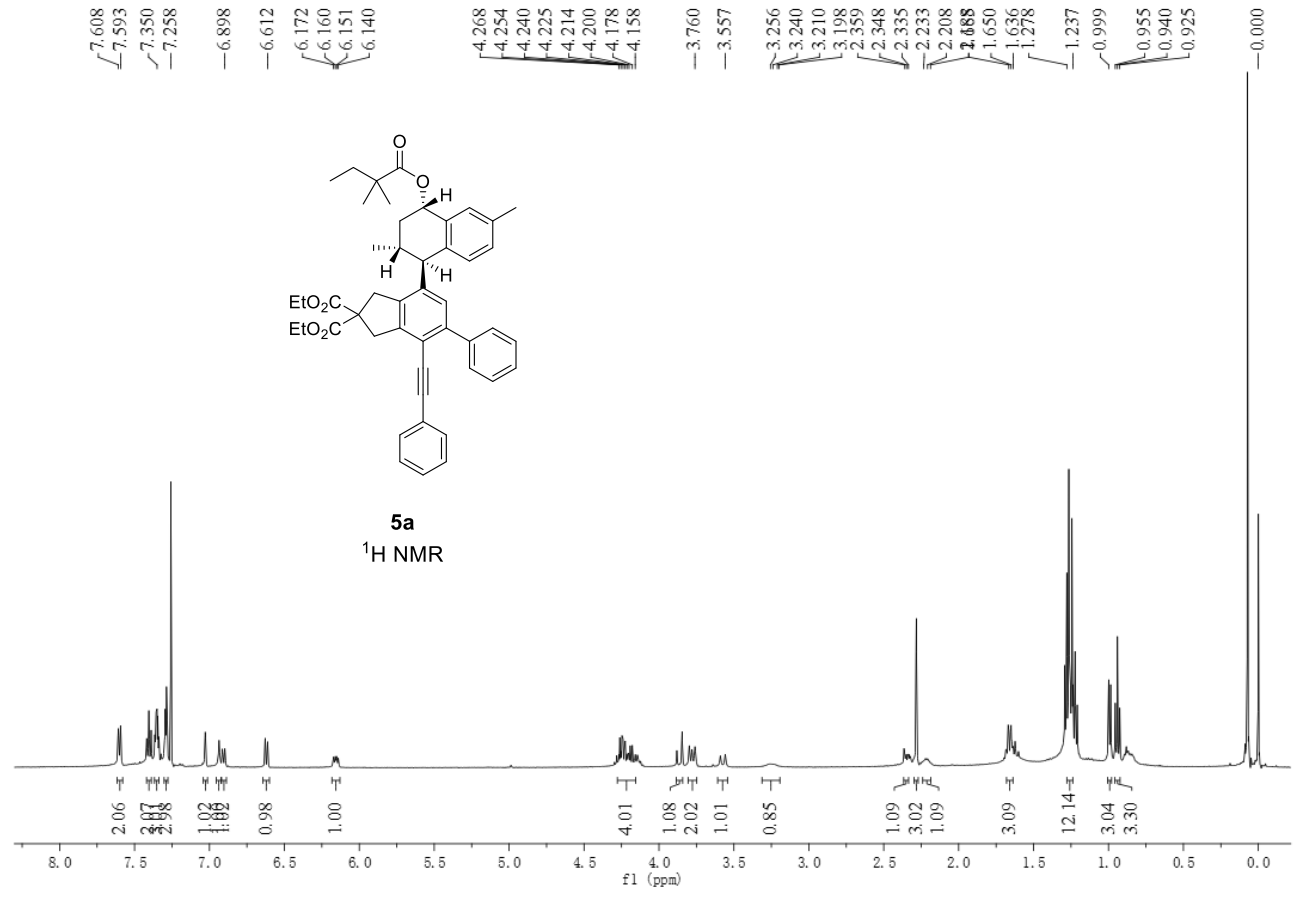


4h

^{13}C NMR

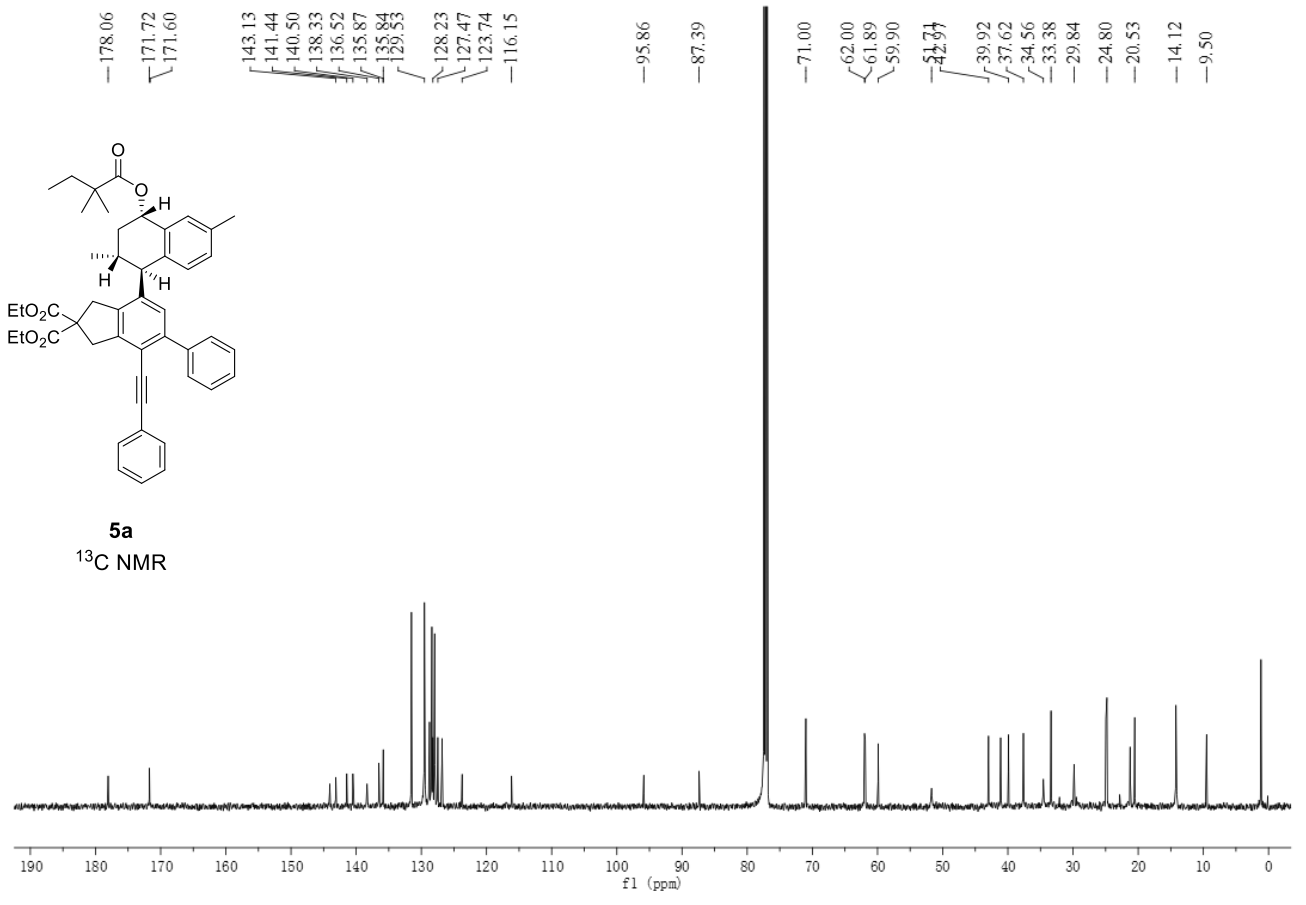

7.317
7.310
7.304
7.297
7.293
7.259
6.976
6.789
6.773
6.670
6.103
6.091
6.080
4.273
4.262
4.259
4.254
4.248
4.240
4.234
4.211
4.197
3.807
3.620
3.467
3.434
2.453
2.425
2.287
2.267
2.227
2.184
1.924
1.724
1.495
1.261
0.973
0.958
0.943
EtO2C
EtO2C
F
F
4i
1H NMR
f1 (ppm)


176.68
171.70
163.63
163.45
161.65
161.49
144.02
142.51
141.99
135.63
131.06
128.77
115.97
115.85
115.68
114.92
114.75
94.86
86.82
70.07
62.09
62.03
59.86
42.60
41.58
41.07
39.65
27.27
26.85
21.24
16.86
14.22
14.17
11.79
EtO2C
EtO2C
F
F
4i
13C NMR
f1 (ppm)



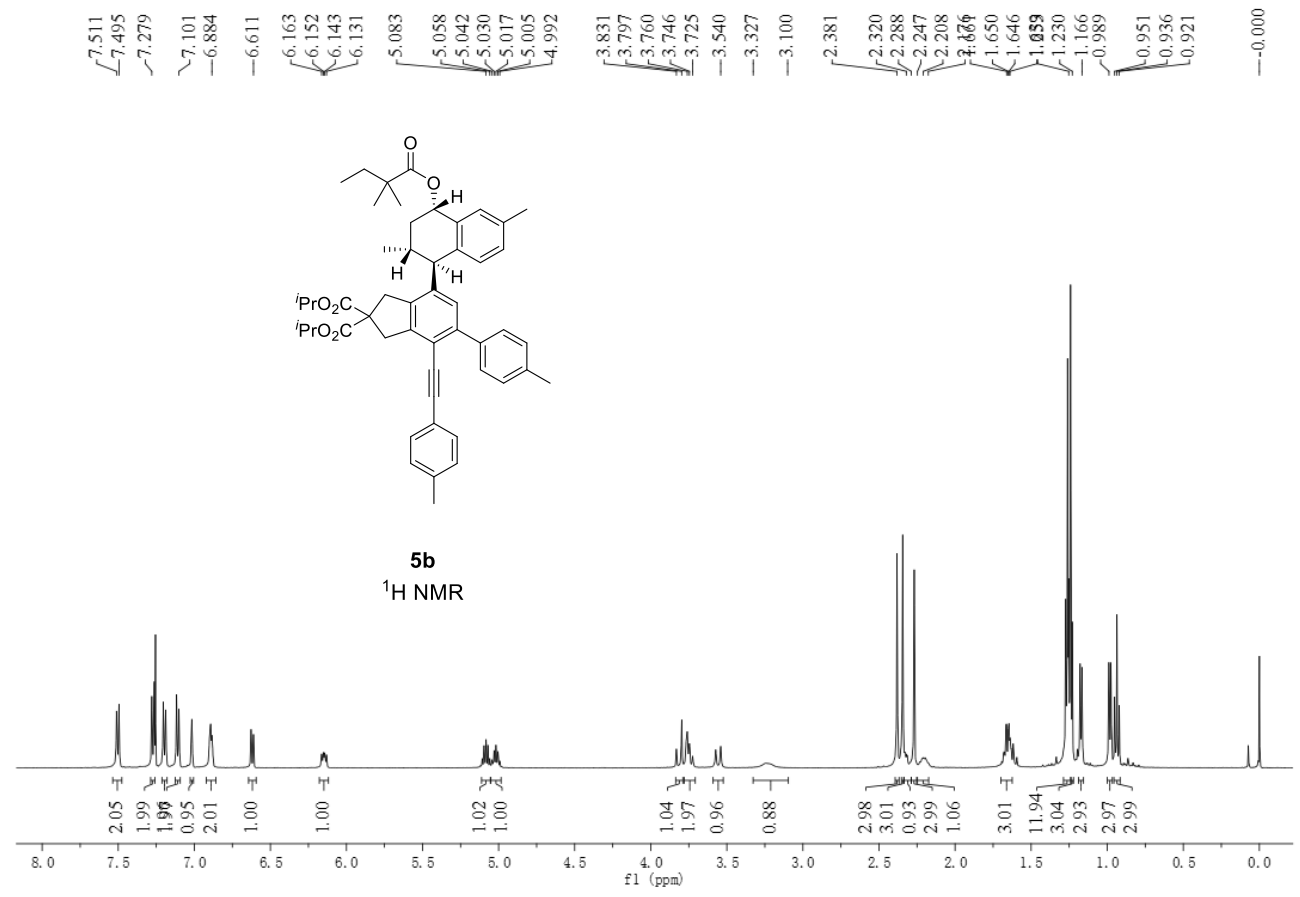
5a

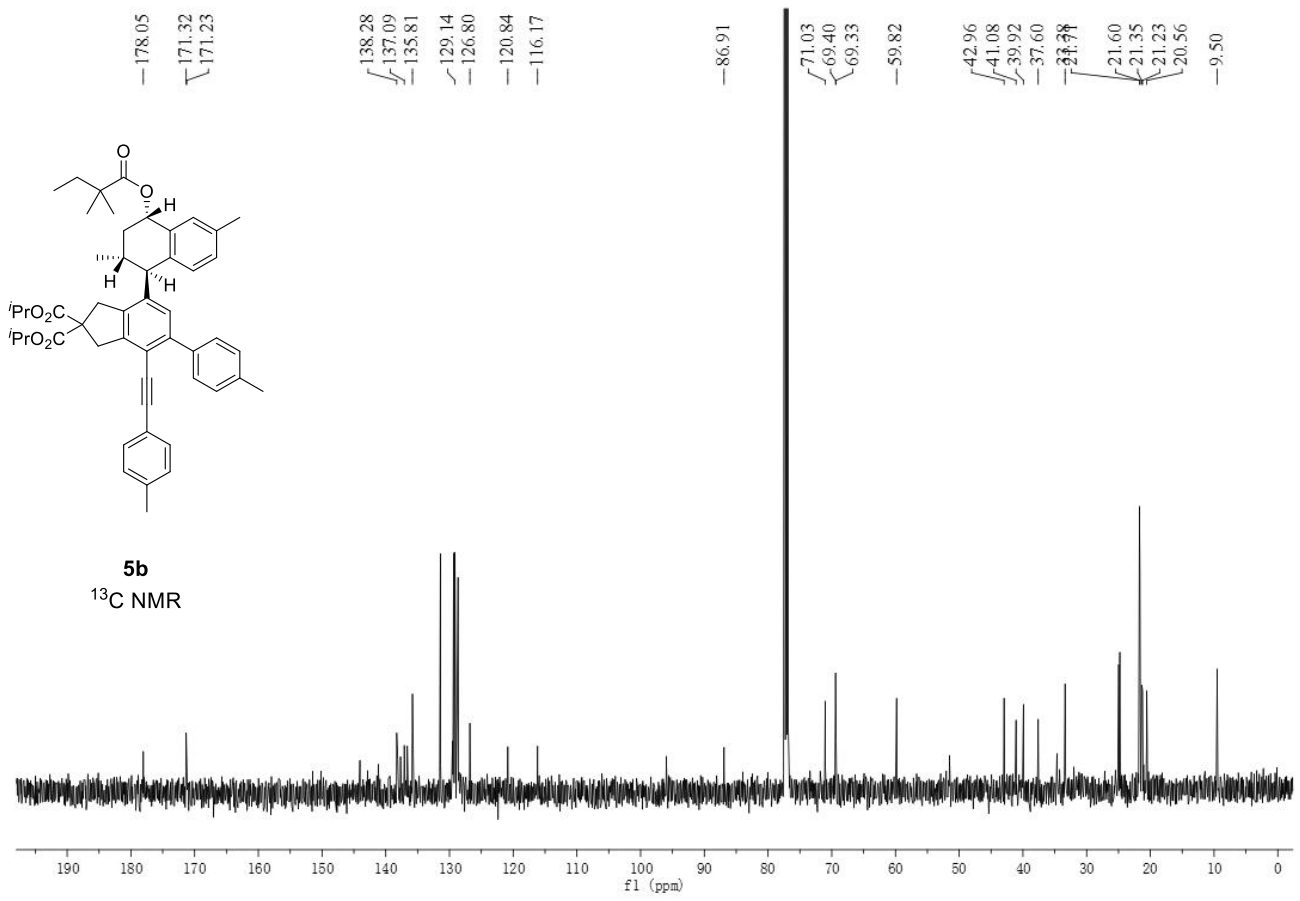
^{1}H NMR

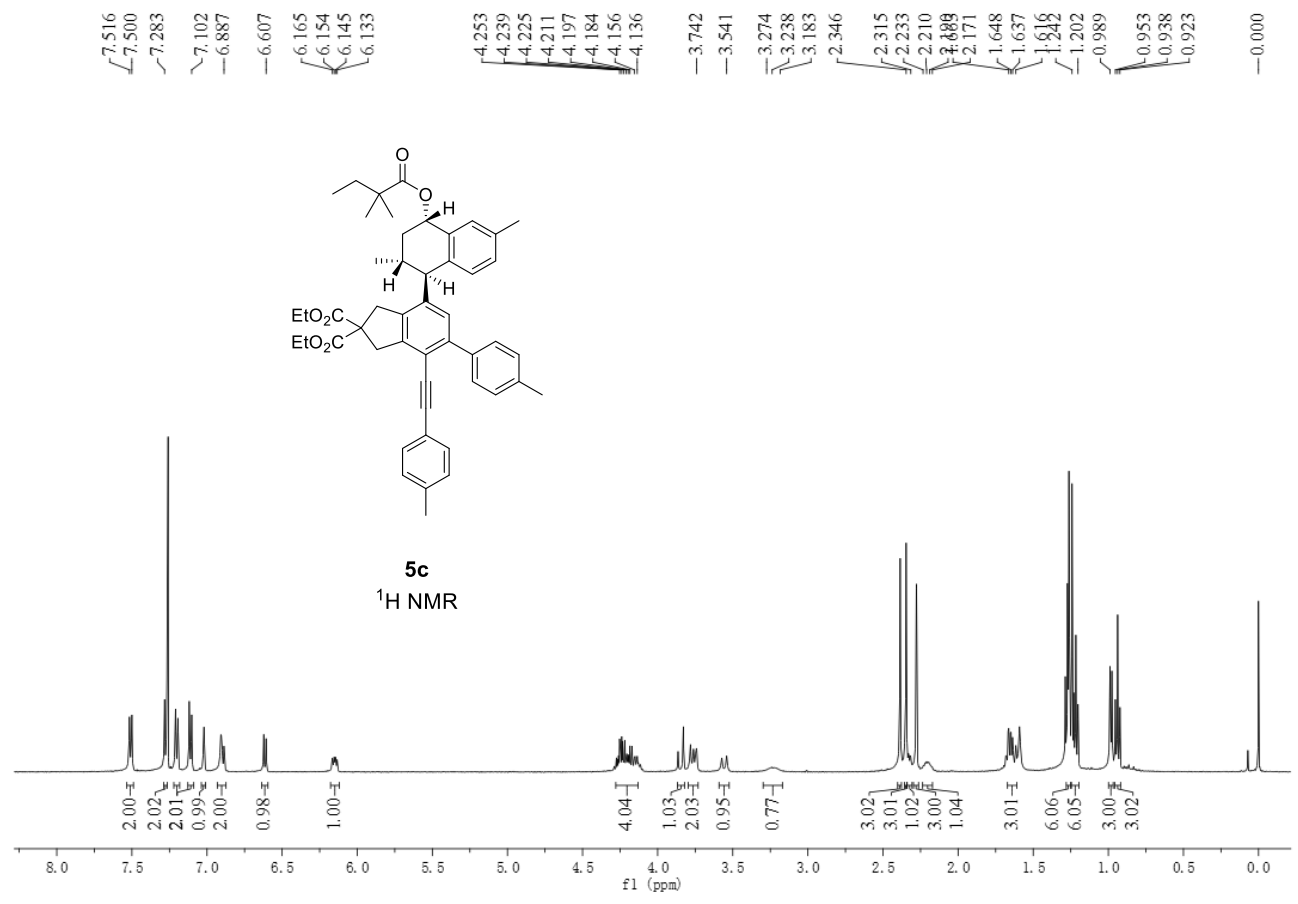


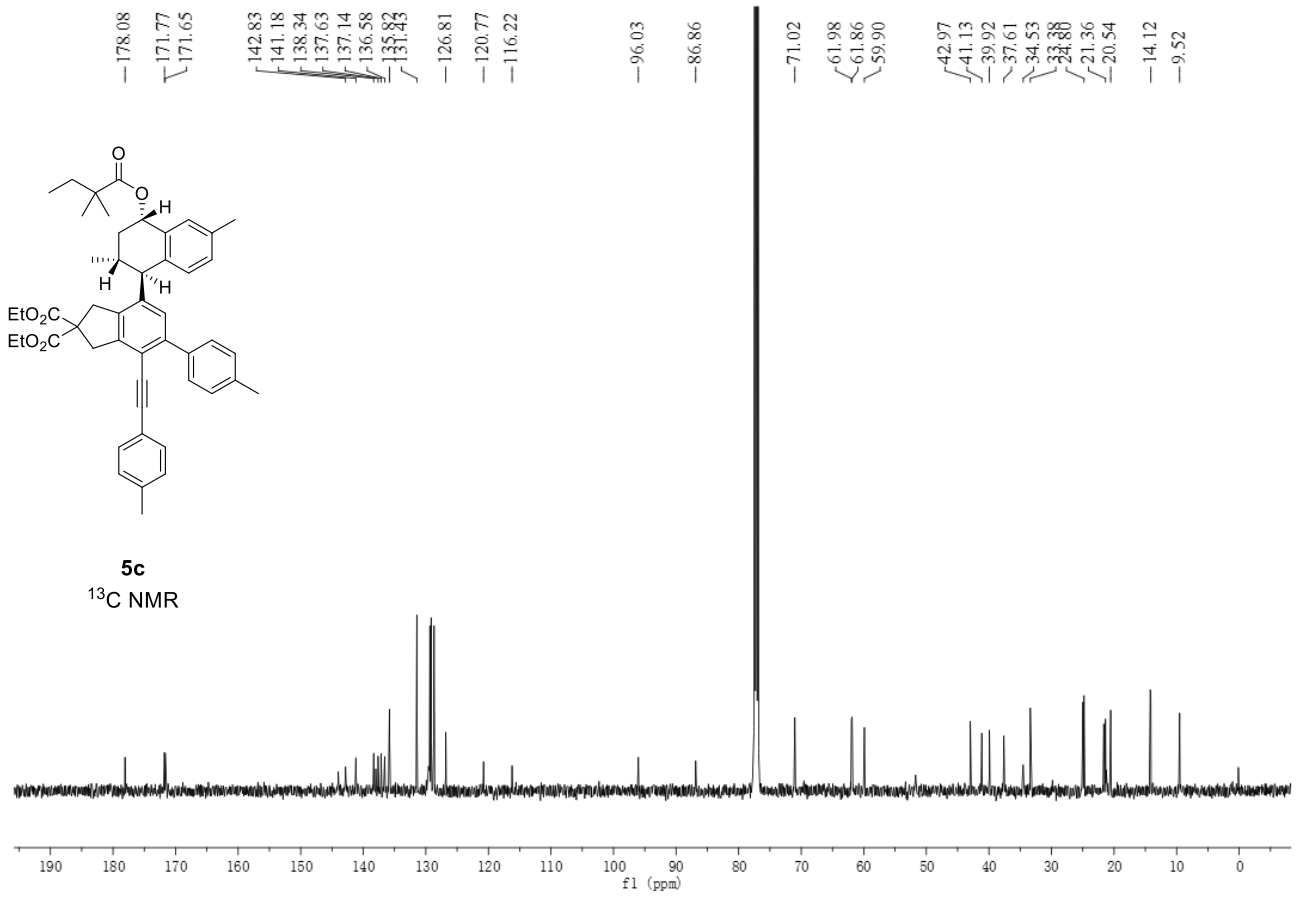
5a

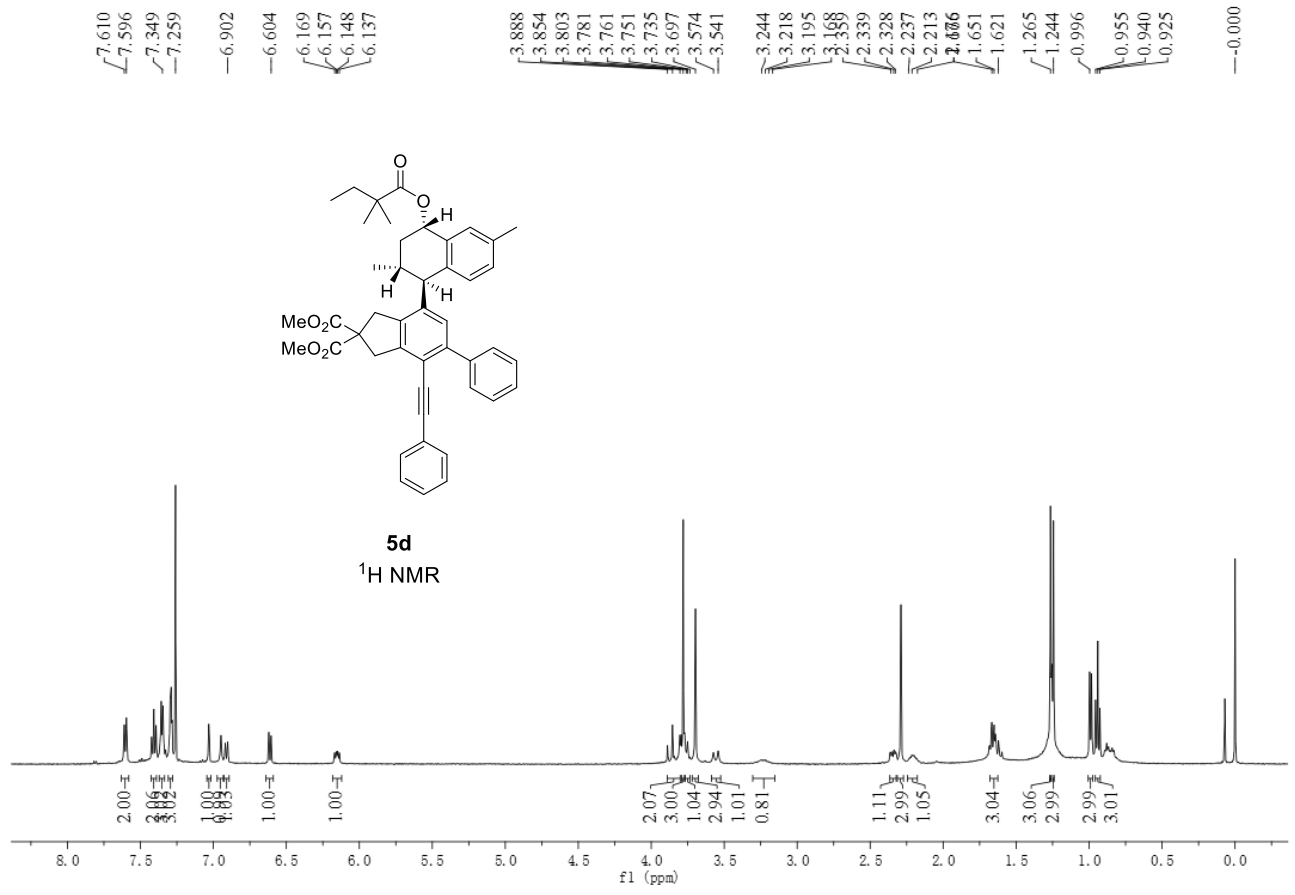
^{13}C NMR

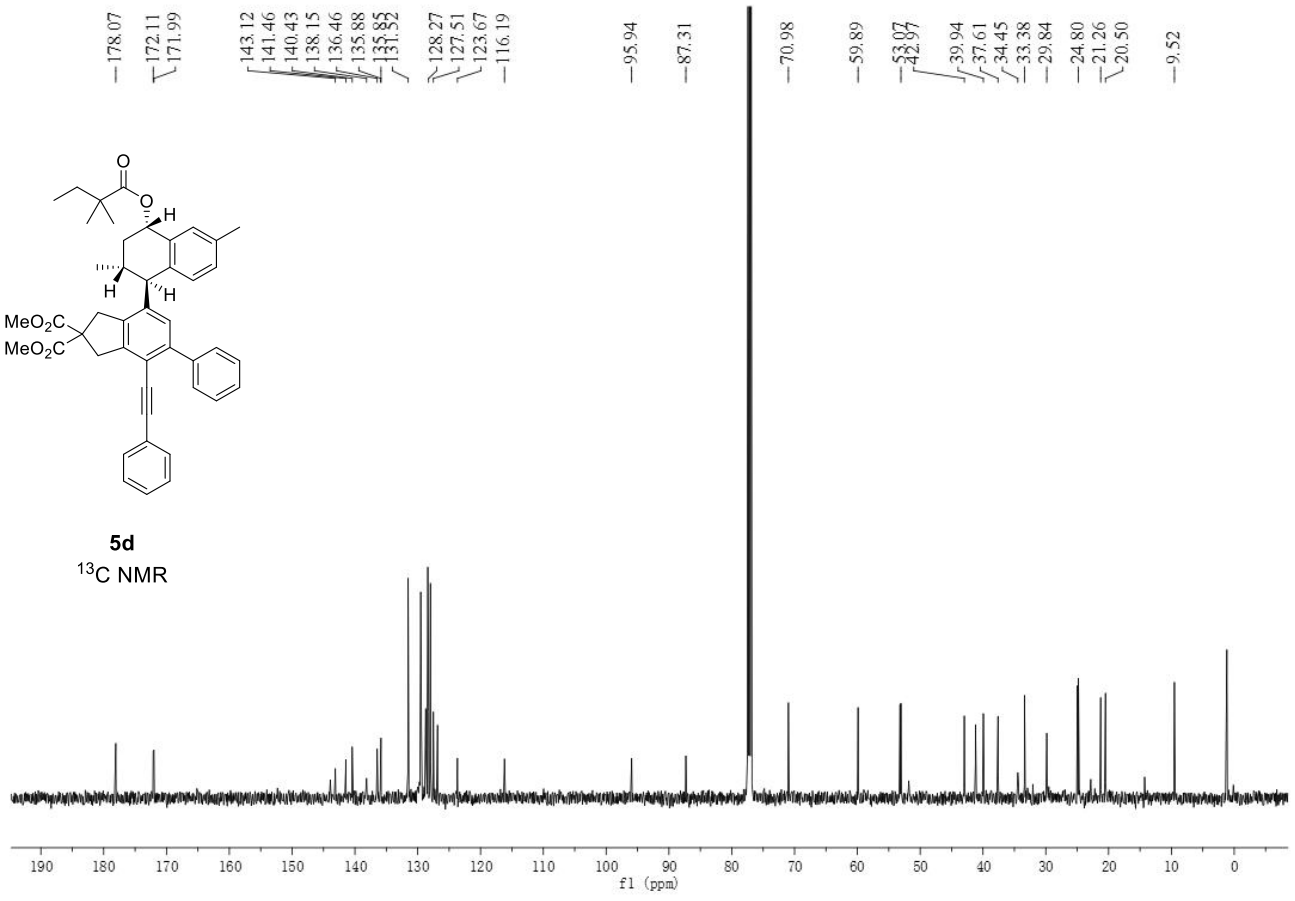

7.511
7.495
7.279
7.101
6.884
6.611
6.163
6.152
6.143
6.131
5.083
5.058
5.042
5.030
5.017
5.005
4.992
3.831
3.797
3.760
3.746
3.725
3.540
3.327
3.100
2.381
2.320
2.288
2.247
2.208
1.650
1.230
1.166
0.989
0.951
0.936
0.921
-0.000
O
O
H
H
H
$^{i}PrO_2C$
$^{i}PrO_2C$
5b
^{1}H NMR
2.05
1.99
0.95
2.01
1.00
1.00
1.02
1.00
1.04
1.97
0.96
0.88
2.98
3.01
0.93
2.99
1.06
3.01
11.94
3.04
2.93
2.97
2.99
f1 (ppm)

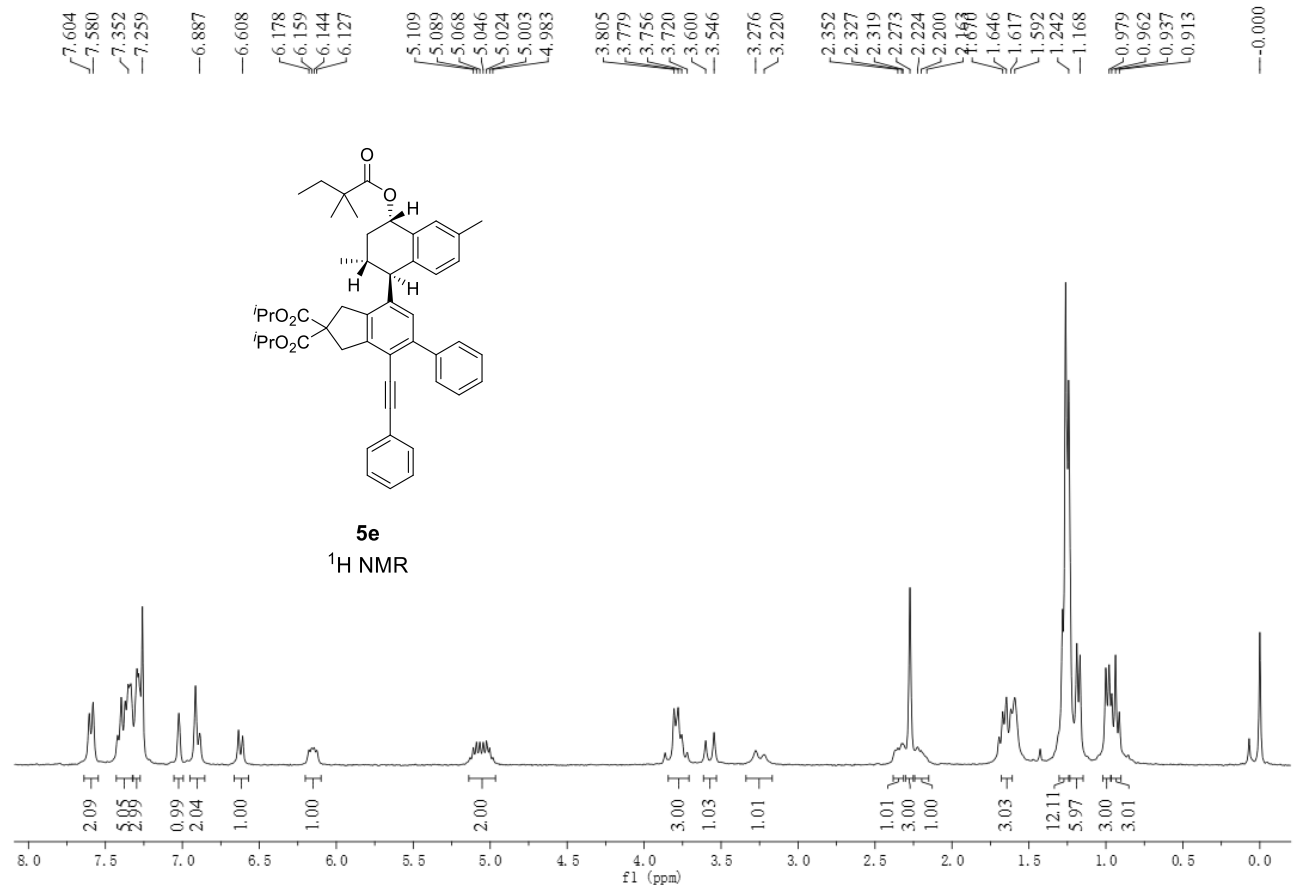

178.05
171.32
171.23
138.28
137.09
135.81
129.14
126.80
120.84
116.17
86.91
71.03
69.40
69.33
59.82
42.96
41.08
39.92
37.60
21.60
21.35
21.23
20.56
9.50
O
O
H
H
H
$^{i}PrO_2C$
$^{i}PrO_2C$
5b
^{13}C NMR
f1 (ppm)


7.516
7.500
7.283
7.102
6.887
6.607
6.165
6.154
6.145
6.133
4.253
4.239
4.225
4.211
4.197
4.184
4.156
4.136
3.742
3.541
3.274
3.238
3.183
2.346
2.315
2.233
2.210
2.171
1.648
1.637
1.242
1.202
0.989
0.953
0.938
0.923
0.000
EtO2C
EtO2C
5c
1H NMR
2.00
2.02
2.01
0.99
2.00
0.98
1.00
4.04
1.03
2.03
0.95
0.77
3.02
3.01
1.02
3.00
1.04
3.01
6.06
6.05
3.00
3.02
f1 (ppm)


178.08
171.77
171.65
142.83
141.18
138.34
137.63
137.14
136.58
126.81
120.77
116.22
96.03
86.86
71.02
61.98
61.86
59.90
42.97
41.13
39.92
37.61
34.53
21.36
20.54
14.12
9.52
EtO2C
EtO2C
5c
13C NMR
f1 (ppm)

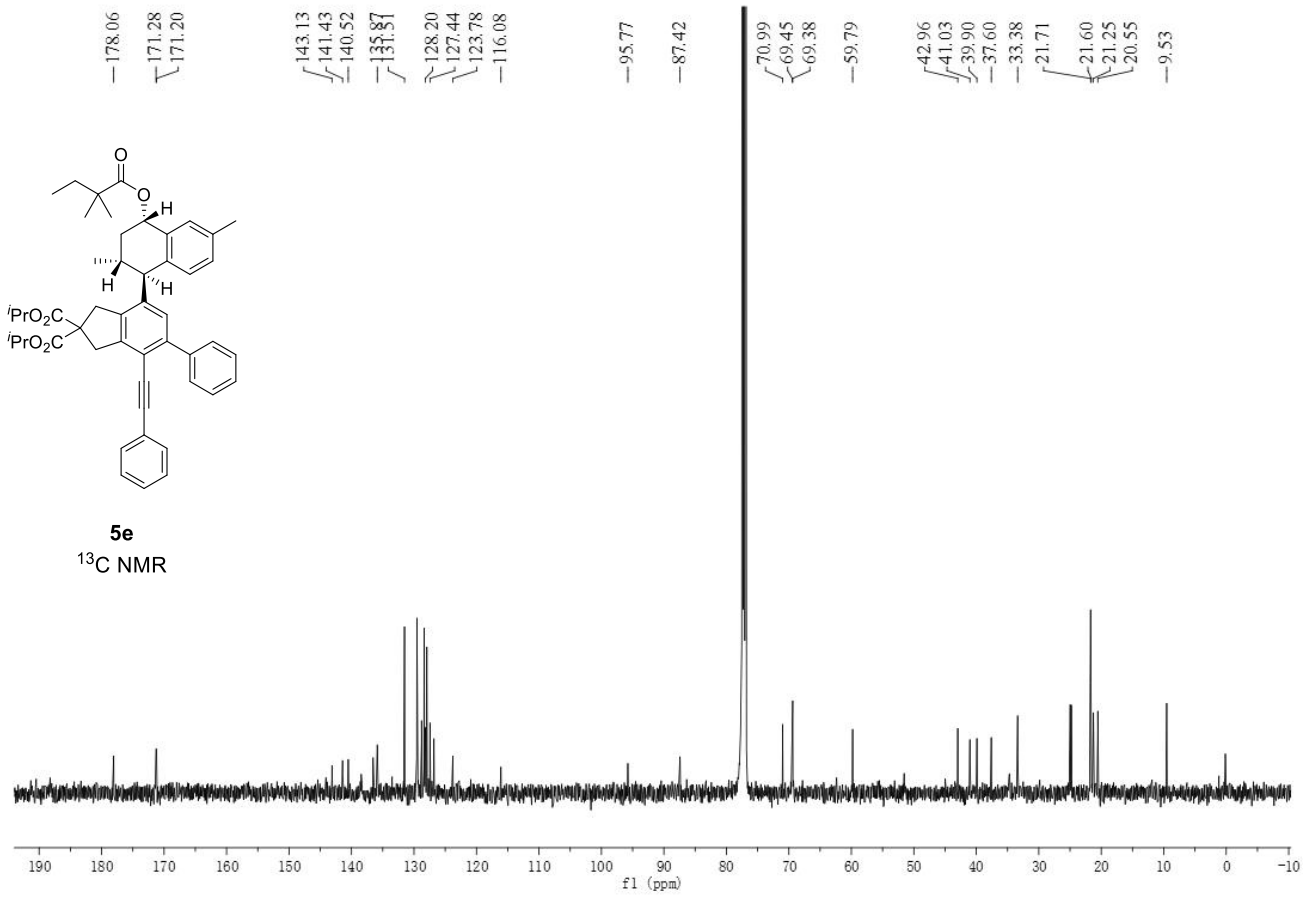

7.610
7.596
7.349
7.259
6.902
6.604
6.169
6.157
6.148
6.137
3.888
3.854
3.803
3.781
3.761
3.751
3.735
3.697
3.574
3.541
3.244
3.218
3.195
2.339
2.328
2.237
2.213
1.651
1.621
1.265
1.244
0.996
0.955
0.940
0.925
-0.000
MeO2C
MeO2C
5d
1H NMR
f1 (ppm)


178.07
172.11
171.99
143.12
141.46
140.43
138.15
136.46
135.88
131.52
128.27
127.51
123.67
116.19
95.94
87.31
70.98
59.89
53.07
42.97
39.94
37.61
34.45
33.38
29.84
24.80
21.26
20.50
9.52
MeO2C
MeO2C
5d
13C NMR
f1 (ppm)



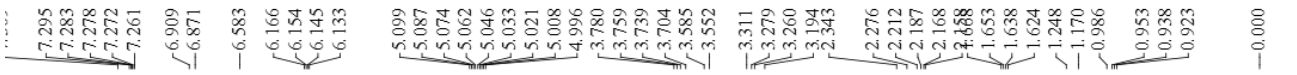
5e

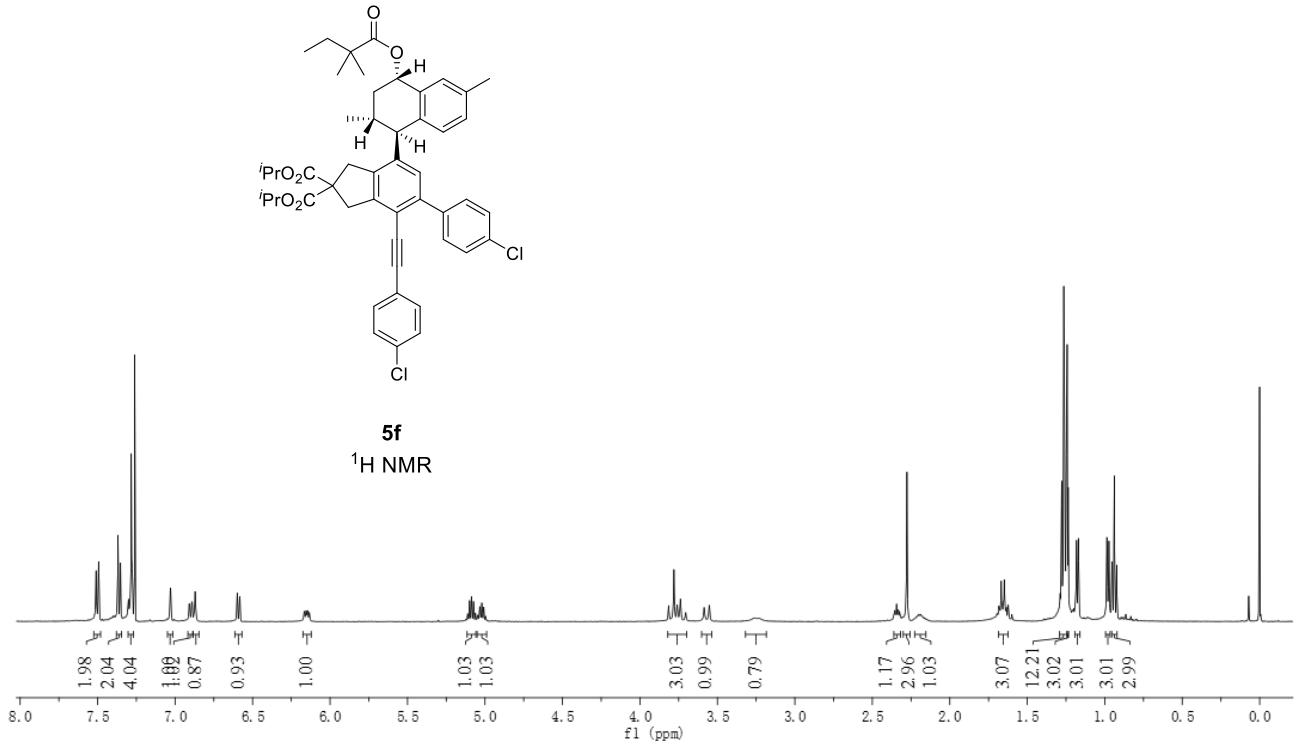
^{1}H NMR



5e

^{13}C NMR



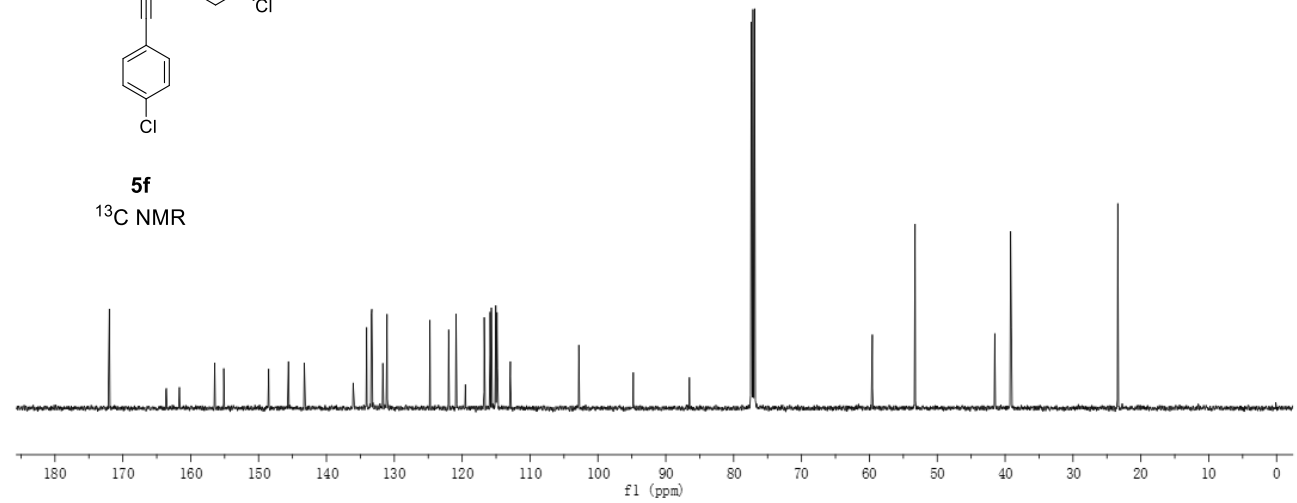


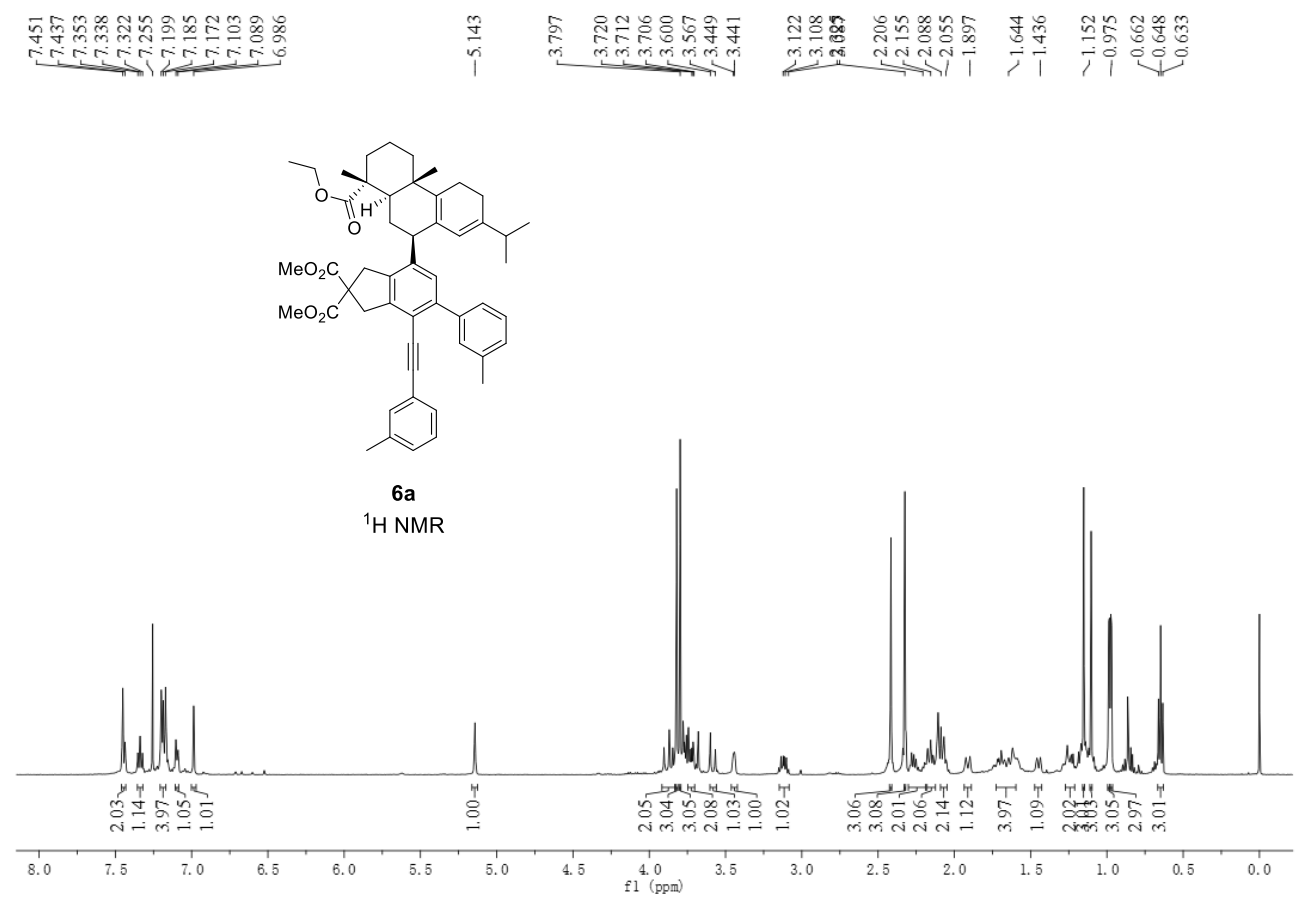
5f

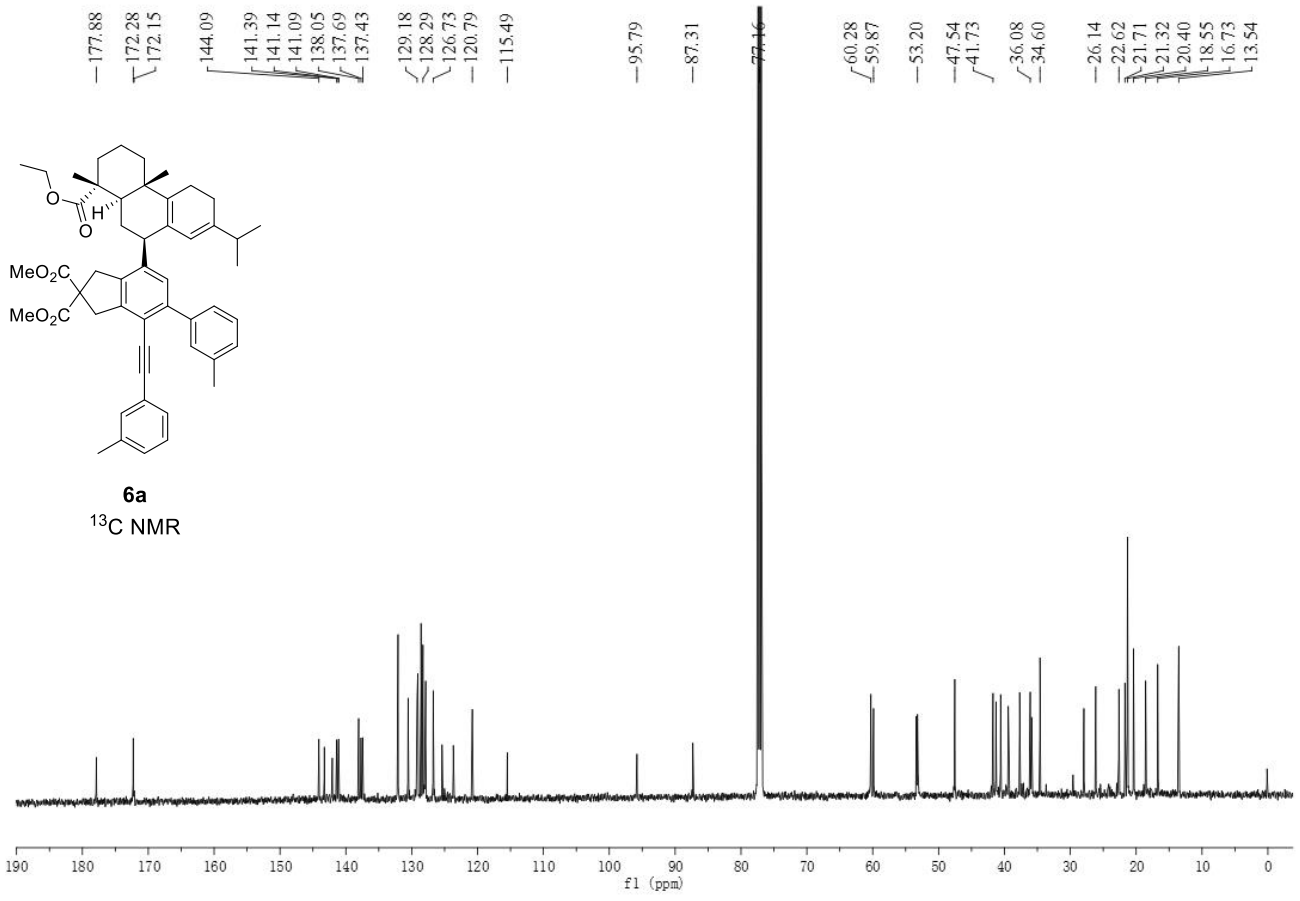
^{1}H NMR

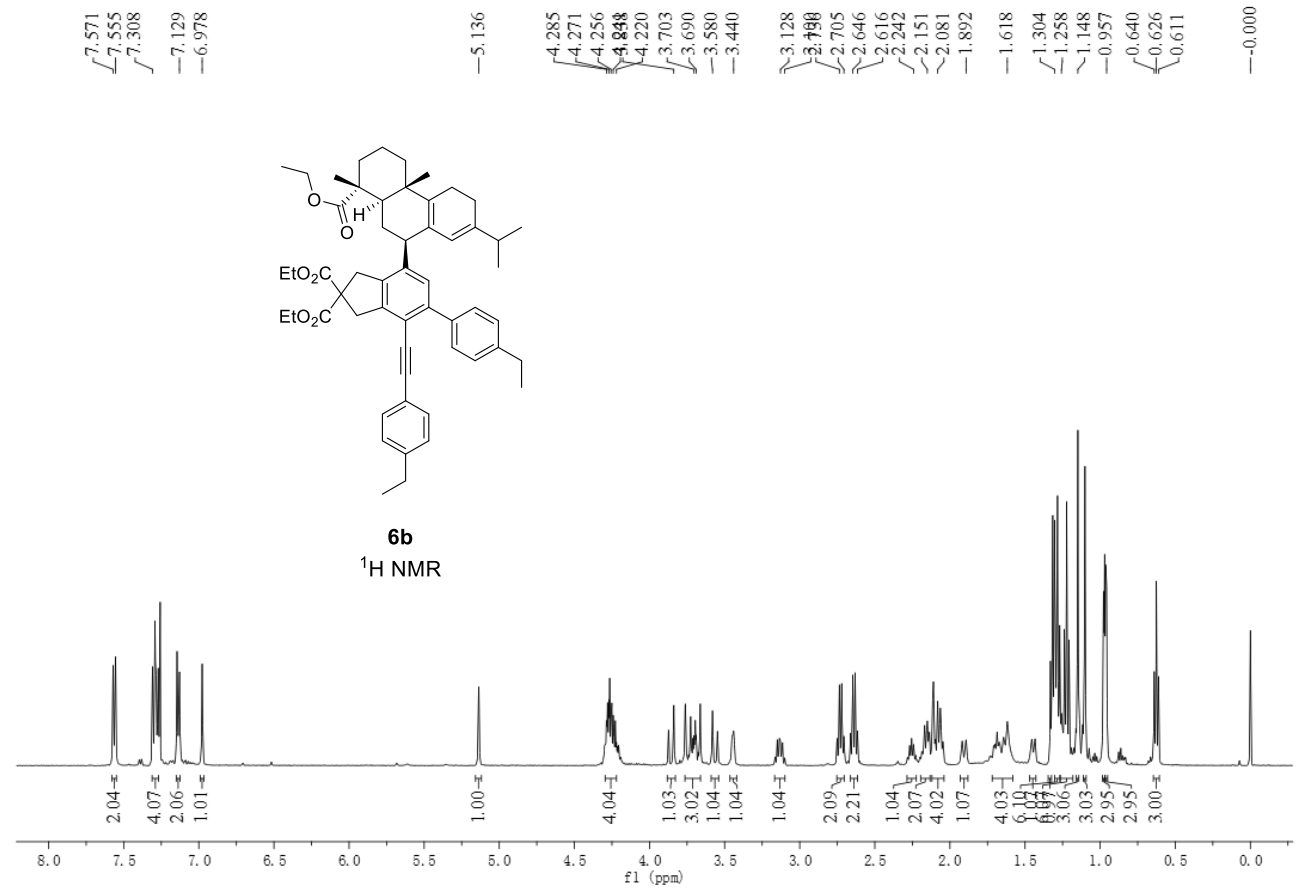
5f

^{13}C NMR



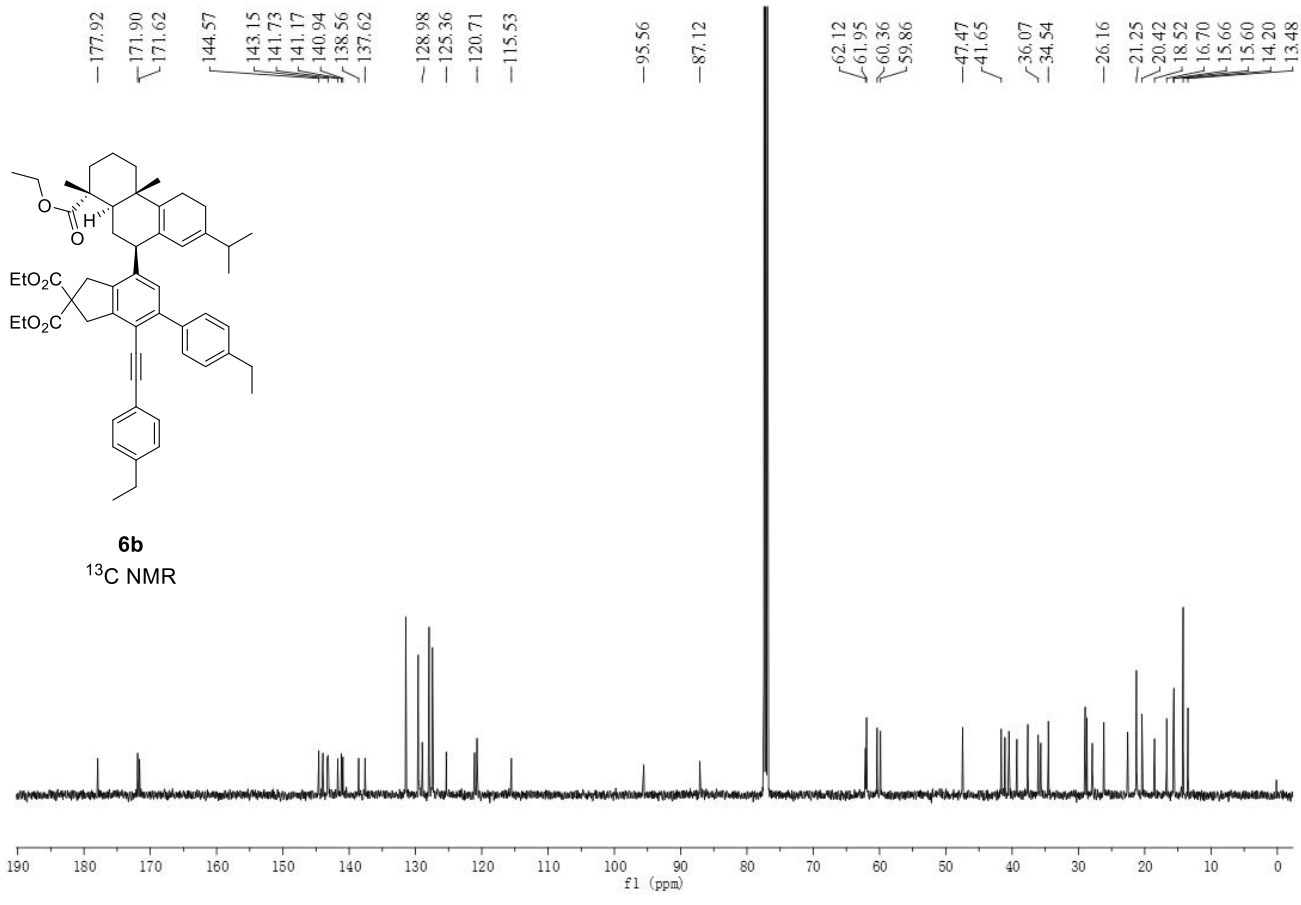

7.451
7.437
7.353
7.338
7.322
7.255
7.199
7.185
7.172
7.103
7.089
6.986
5.143
3.797
3.720
3.712
3.706
3.600
3.567
3.449
3.441
3.122
3.108
2.206
2.155
2.088
2.055
1.897
1.644
1.436
1.152
0.975
0.662
0.648
0.633
MeO2C
MeO2C
6a
1H NMR
f1 (ppm)


177.88
172.28
172.15
144.09
141.39
141.14
141.09
138.05
137.69
137.43
129.18
128.29
126.73
120.79
115.49
95.79
87.31
77.16
60.28
59.87
53.20
47.54
41.73
36.08
34.60
26.14
22.62
21.71
21.32
20.40
18.55
16.73
13.54
MeO2C
MeO2C
6a
13C NMR
f1 (ppm)



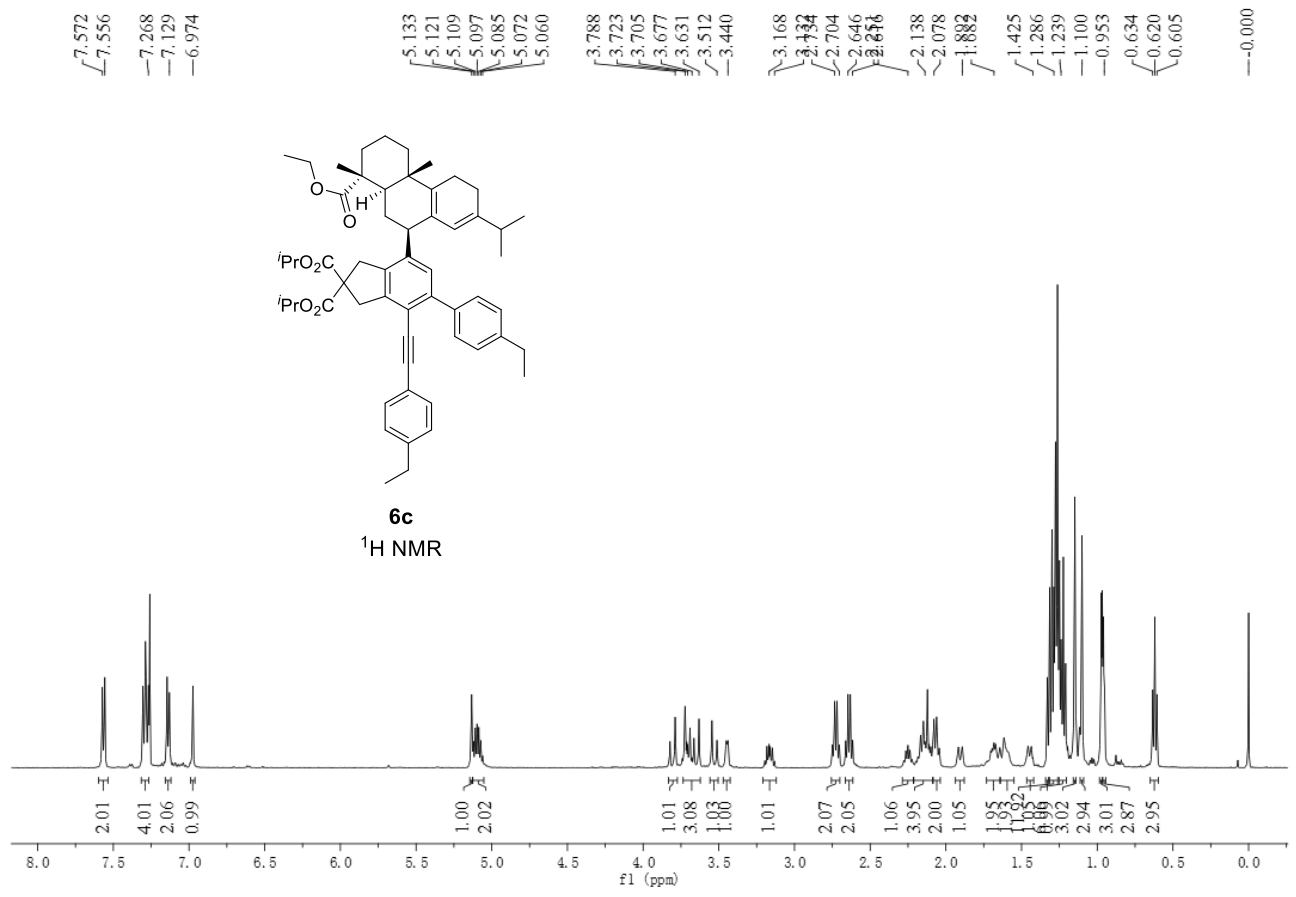
6b

^{1}H NMR



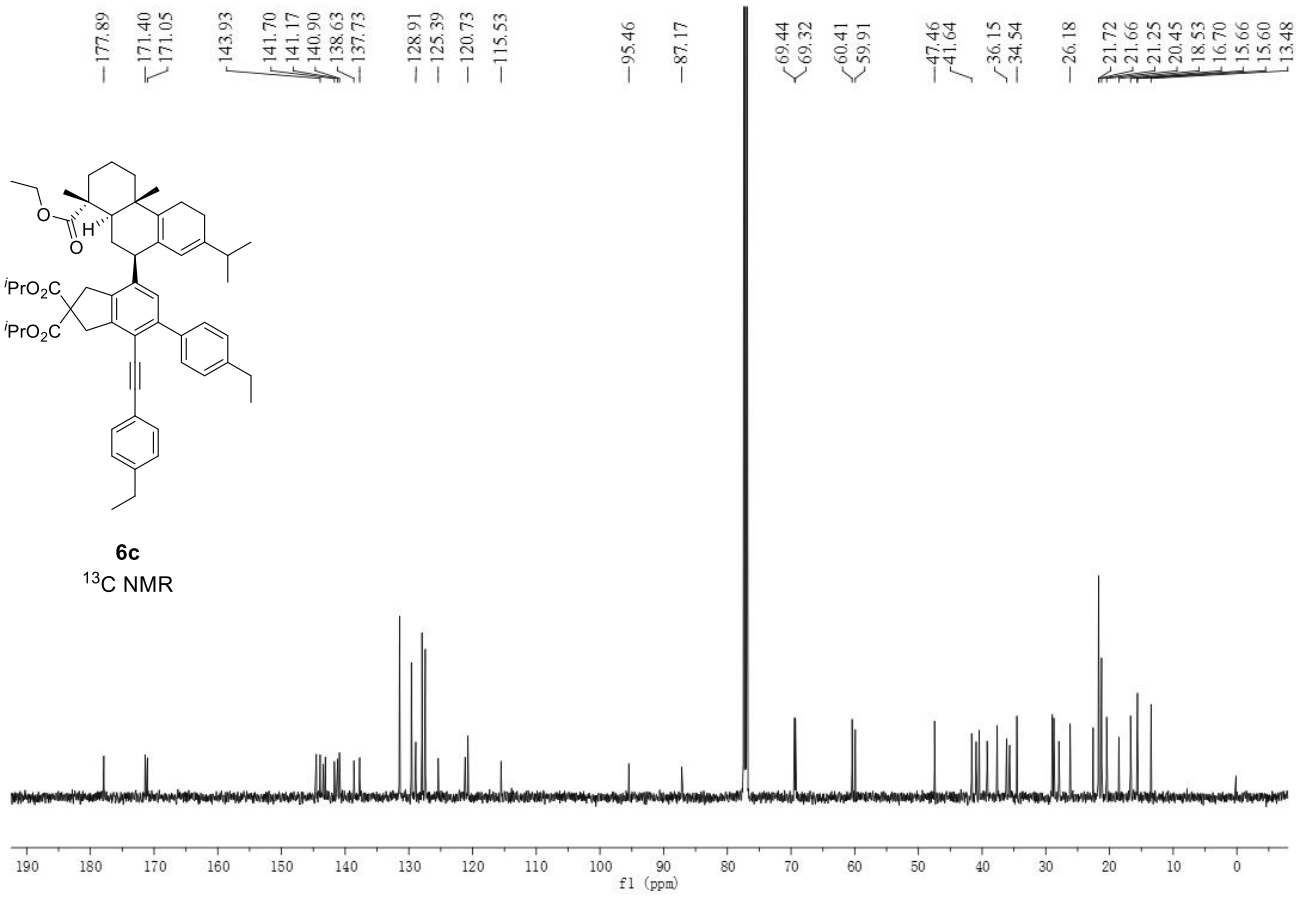
6b

^{13}C NMR



6c

^{1}H NMR



6c

^{13}C NMR