Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Transition-Metal-Free Approaches to 2,3-Diarylated Indenones from 2-Alkynylbenzaldehydes and Phenols with Tunable Selectivity

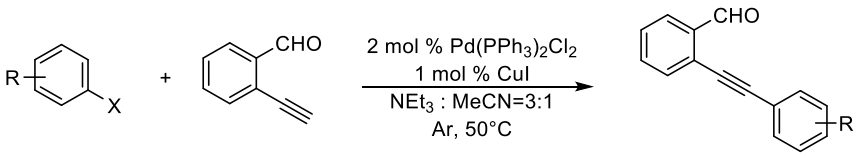
CONTENTS

1. General Information.

NMR spectra were recorded on a Bruker AM 400 MHz or 600 MHz spectrometer and calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$ (^1H): δ = 7.26 ppm; $CDCl_3$ (^{13}C): δ = 77.23 ppm. High-resolution mass analysis was performed using a Thermo Scientific™ Q Exactive™ Hybrid Quadrupole-Orbitrap Mass Spectrometer. Melting points were determined on a Stanford Research Systems OptiMelt apparatus. The infrared (IR) spectra were acquired as thin films using a universal ATR sampling accessory on a Bruker Vertex 80 FT-IR spectrometer and the absorption frequencies are reported in cm^{-1}. Flash chromatography separations were carried out using silica gel columns. All new compounds were characterized by ^1H NMR, ^{13}C NMR, HRMS, and IR. The structure of known compounds was confirmed by comparing their ^1H NMR data with those of literature. All reagents and solvents were used as received from commercial sources without further purification. Compounds **1a**,[1] **2a**,[2] **3a**,[2] **4a**,[3] **5a**,[4] **6a**,[5] **7a**,[6] **22a'**,[7] **26a**,[8] **29a**,[9] **30a**,[10] **31a**,[11] **32a**,[12] **33a**,[12] **33a'**,[12] **34a**,[12] **35a**,[12] and **35a'**[12] were prepared by following the literature procedure.

2. General Procedure for the Synthesis of 2-Alkynylbenzaldehydes.

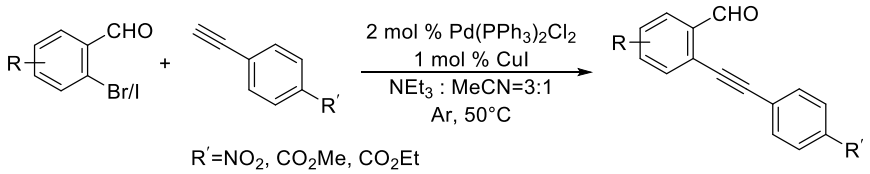
2.1 Typical Procedure A for the Synthesis of 2-Alkynylbenzaldehydes.



To a solution of aryl halide (1.0 mmol, 1.0 equiv.) and $PdCl_2(PPh_3)_2$ (0.02 mmol, 0.02 equiv.) in Et_3N/MeCN (3:1, 4.0 mL) were added 2-ethynylbenzaldehyde (1.5 mmol, 1.5 equiv.) and CuI (0.01 mmol, 0.01 equiv.). The reaction mixture was heated in an oil bath at 50 °C under argon. The progress of the reaction was monitored by TLC analysis to establish its completion. After cooling to room temperature, the reaction was diluted

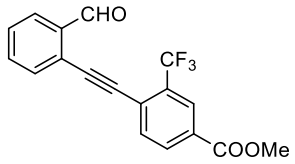
with ethyl acetate (30 mL), washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate).

2.2 Typical Procedure B for the Synthesis of 2-Alkynylbenzaldehydes.



To a solution of *o*-halobenzaldehydes (1.0 mmol, 1.0 equiv.) and $PdCl_2(PPh_3)_2$ (0.02 mmol, 0.02 equiv.) in Et_3N/MeCN (3:1, 4.0 mL) were added terminal alkyne (1.5 mmol, 1.5 equiv.) and CuI (0.01 mmol, 0.01 equiv.). The reaction mixture was heated in an oil bath at 50 °C under argon. The progress of the reaction was monitored by TLC analysis to establish its completion. After cooling to room temperature, the reaction was diluted with ethyl acetate (30 mL), washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate).

Synthesis of methyl 4-((2-formylphenyl)ethynyl)-3-(trifluoromethyl)benzoate (8a).

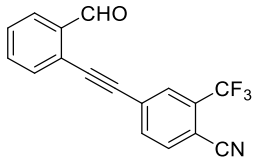


8a

This compound was prepared according to typical procedure A at 50 °C for 12 h by using methyl 4-bromo-3-(trifluoromethyl)benzoate (0.283 g, 1.0 mmol) and 2-ethynylbenzaldehyde (0.195 g, 1.5 mmol). After flash column chromatography (PE/EtOAc = 10:1), **8a** was obtained as an amorphous yellow solid (0.226 g, 68%). R_f = 0.28 (PE/EtOAc = 10:1); m.p. 101-103°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 8.38 (s, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.63 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.53 (dd, *J* = 7.5, 7.5 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 165.4, 136.5, 134.4, 134.1, 133.9, 132.7, 132.0 (q, *J* = 31.3 Hz), 130.4, 130.0, 127.8, 127.5 (q, *J* = 5.0 Hz), 125.5,

125.1, 123.3 (q, J = 274.7 Hz), 93.6, 91.2, 52.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.40; IR (neat): 1726, 1606, 1436, 1259, 1127, 739 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{12}F_3O_3$ 333.07331; found 333.07336.

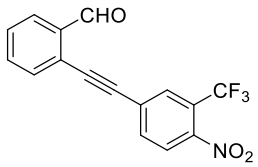
Synthesis of 4-((2-formylphenyl)ethynyl)-2-(trifluoromethyl)benzonitrile (9a).



9a

This compound was prepared according to typical procedure A at 50 °C for 12 h by using 4-iodo-2-(trifluoromethyl)benzonitrile (0.297 g, 1.0 mmol) and 2-ethynylbenzaldehyde (0.195 g, 1.5 mmol). After flash column chromatography (PE/EtOAc = 20:1), **9a** was obtained as an amorphous yellow solid (0.288 g, 96 %). R_f =0.42 (PE/EtOAc = 5:1); m.p. 132-133℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 8.01 – 7.92 (m, 2H), 7.89 – 7.81 (m, 2H), 7.69 (d, J = 7.5 Hz, 1H), 7.65 (dd, J = 7.4, 7.4 Hz, 1H), 7.57 (dd, J = 7.3, 7.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 136.4, 135.04, 135.02, 134.1, 133.9, 133.5 (q, J = 32.3 Hz), 130.2, 129.8 (q, J = 4.0 Hz), 128.5, 128.0, 124.6, 122.1 (q, J = 275.7 Hz), 115.2, 109.8, 92.7, 91.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.17; IR (neat): 1697, 1603, 1332, 1292, 1127, 760 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{17}H_9F_3NO$ 300.06307; found 300.06305.

Synthesis of 2-((4-nitro-3-(trifluoromethyl)phenyl)ethynyl)benzaldehyde (10a).

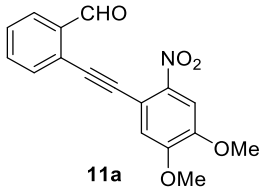


10a

This compound was prepared according to typical procedure A at 50 °C for 5 h by using 4-bromo-1-nitro-2-(trifluoromethyl)benzene (0.270 g, 1.0 mmol) and 2-ethynylbenzaldehyde (0.195 g, 1.5 mmol). After flash column chromatography (PE/EtOAc = 20:1), **10a** was obtained as an amorphous yellow solid (0.280 g, 88%). R_f =0.28 (PE/EtOAc = 10:1); m.p. 105-107℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 8.02 –7.97 (m, 2H), 7.95 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.70 (d, J

= 7.5 Hz, 1H), 7.65 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.57 (dd, *J* = 7.4, 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 147.3, 136.4, 135.9, 134.2, 133.9, 131.2 (q, *J* = 4.0 Hz), 130.2, 128.6, 128.1, 125.8, 124.7 (q, *J* = 34.3 Hz), 124.6, 121.7 (q, *J* = 274.7 Hz), 92.3, 90.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -60.09; IR (neat): 1779, 1535, 1402, 1266, 1043, 908 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_9F_3NO_3$ 320.05290; found 320.05380.

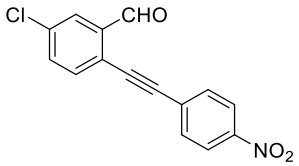
Synthesis of 2-((4,5-dimethoxy-2-nitrophenyl)ethynyl)benzaldehyde (11a).



11a

This compound was prepared according to typical procedure A at 50 °C for 6 h by using 1-iodo-4,5-dimethoxy-2-nitrobenzene (0.309 g, 1.0 mmol) and 2-ethynylbenzaldehyde (0.195 g, 1.5 mmol). After a flash column chromatography (PE / EtOAc = 10:1), **11a** was obtained as an amorphous yellow solid (0.221 g, 71%). R_f =0.22 (PE/EtOAc = 5:1); m.p. 185-187℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.74 –7.67 (m, 2H), 7.60 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.49 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.09 (s, 1H), 4.01 (s, 3H), 3.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 153.1, 149.6, 142.8, 136.5, 134.0, 133.9, 129.5, 127.7, 126.2, 115.3, 112.1, 107.9, 92.2, 91.5, 56.9, 56.7; IR (neat): 1729, 1574, 1395, 1254, 1052, 764 cm^{-1}; HRMS(ESI) m/z : $[M+H]^+$ calculated for $C_{17}H_{14}NO_5$ 312.08665; found 312.08630.

Synthesis of 5-chloro-2-((4-nitrophenyl)ethynyl)benzaldehyde (20a).

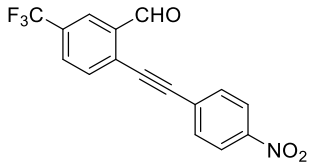


20a

This compound was prepared according to typical procedure B at 50 °C for 4 h by using 2-bromo-5-chlorobenzaldehyde (0.219 g, 1.0 mmol) and 1-ethynyl-4-nitrobenzene (0.221 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 10:1), **20a** was obtained as an amorphous yellow solid (0.241 g, 84%). R_f =0.45

(PE/EtOAc = 10:1); m.p. 172-173℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.26 (d, *J* = 8.2 Hz, 2H), 7.94 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.56 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 147.8, 137.3, 136.5, 134.9, 134.2, 132.7, 129.0, 128.1, 124.1, 123.7, 94.9, 89.0; IR (neat) :1691, 1509, 1182, 1104, 897 cm^{-1}; HRMS(ESI) m/z : $[M+H]^+$ calculated for $C_{15}H_9ClNO_3$ 286.02655; found 286.02649.

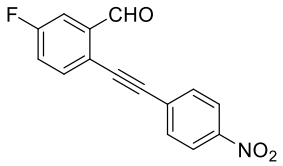
Synthesis of 2-((4-nitrophenyl)ethynyl)-5-(trifluoromethyl)benzaldehyde (21a).



21a

This compound was prepared according to typical procedure B at 50 °C for 4 h by using 2-bromo-5-(trifluoromethyl)benzaldehyde (0.253 g, 1.0 mmol) and 1-ethynyl-4-nitrobenzene (0.221 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 10:1), **21a** was obtained as an amorphous yellow solid (0.146 g, 46%). R_f =0.38 (PE/EtOAc = 10:1); m.p. 123-124℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.27 (d, *J* = 8.5 Hz, 2H), 8.22 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 148.1, 136.5, 134.3, 132.9, 131.8 (q, *J* = 34.3 Hz), 130.3 (q, *J* = 3.0 Hz), 128.6, 128.5, 125.2 (q, *J* = 3.0 Hz), 124.1, 123.3 (q, *J* = 273.7 Hz), 96.2, 88.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.14; IR (neat) : 1697, 1518, 1402, 1263, 1177, 854 cm^{-1}; HRMS(ESI) m/z : $[M+H]^+$ calculated for $C_{16}H_9F_3NO_3$ 320.05290; found 320.05292.

Synthesis of 5-fluoro-2-((4-nitrophenyl)ethynyl)benzaldehyde (22a).

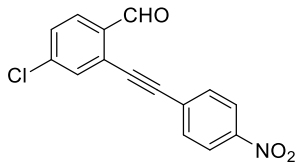


22a

This compound was prepared according to typical procedure B at 50 °C for 11 h by using 2-bromo-5-fluorobenzaldehyde (0.203 g, 1.0 mmol) and 1-ethynyl-4-nitrobenzene (0.221 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 10:1), **22a** was obtained as an amorphous yellow solid (0.166 g, 62%). R_f =0.37

(PE/EtOAc = 10:1); m.p. 156-157°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.53 (d, *J* = 2.9 Hz, 1H), 8.24 (d, *J* = 8.7 Hz, 2H), 7.71 – 7.66 (m, 3H), 7.63 (dd, *J* = 8.4, 2.7 Hz, 1H), 7.33 (td, *J* = 8.2, 2.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 189.9, 163.2 (d, *J* = 253.7 Hz), 147.8, 138.4 (d, *J* = 6.0 Hz), 135.8 (d, *J* = 7.6 Hz), 132.6, 129.1, 124.0, 121.7 (d, *J* = 22.7 Hz), 121.6 (d, *J* = 4.5 Hz), 114.6 (d, *J* = 19.6 Hz), 93.8, 89.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -106.91; IR (neat) :1691, 1506, 1339, 1145, 1097, 745 cm^{-1}; HRMS(ESI) m/z : $[M+H]^+$ calculated for $C_{15}H_9FNO_3$ 270.05610; found 270.05612 .

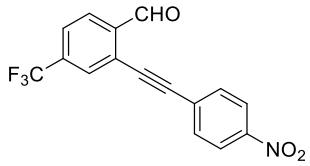
Synthesis of 4-chloro-2-((4-nitrophenyl)ethynyl)benzaldehyde (20a').



20a'

This compound was prepared according to typical procedure B at 50 °C for 4 h by using 2-bromo-4-chlorobenzaldehyde (0.219 g, 1.0 mmol) and 1-ethynyl-4-nitrobenzene (0.221 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 20:1), **20a'** was obtained as an amorphous yellow solid (274.0 mg, 96%). R_f = 0.22 (PE/EtOAc = 20:1); m.p. 166-167°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 8.27 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.67 (s, 1H), 7.50 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1, 147.1, 139.8, 133.8, 132.6, 132.0, 129.5, 128.7, 128.0, 126.0, 123.3, 94.2, 87.8; IR (neat) : 1692, 1515, 1400, 1271, 1105, 891 cm^{-1}; HRMS(ESI) m/z : $[M+H]^+$ calculated for $C_{15}H_9ClNO_3$ 286.02655; found 286.02612.

Synthesis of 2-((4-nitrophenyl)ethynyl)-4-(trifluoromethyl)benzaldehyde (21a').

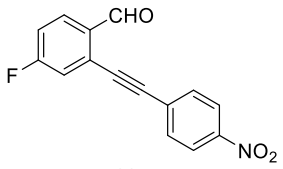


21a'

This compound was prepared according to typical procedure B at 50 °C for 12 h by using 2-iodo-4-(trifluoromethyl)benzaldehyde (0.300 g, 1.0 mmol) and 1-ethynyl-4-nitrobenzene (0.221 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc =

10:1), **21a'** was obtained as an amorphous yellow solid (0.248 g, 78%). R_f = 0.38 (PE/EtOAc = 10:1); m.p. 173-174℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 8.28 (d, *J* = 8.3 Hz, 2H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.96 (s, 1H), 7.80 – 7.72 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 148.1, 138.3, 135.7 (q, *J* = 33.3 Hz), 132.9, 130.8 (q, *J* = 3.0 Hz), 128.8, 128.6, 126.4 (q, *J* = 3.0 Hz), 126.0, 124.1, 123.2 (q, *J* = 274.7 Hz), 95.4, 88.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.39; IR (neat) :1697, 1587, 1338, 1280, 1123, 904 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_9F_3NO_3$ 320.05290; found 320.05292.

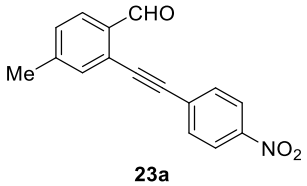
Synthesis of 4-fluoro-2-((4-nitrophenyl)ethynyl)benzaldehyde (22a').



22a'

This compound was prepared according to typical procedure B at 50 °C for 12 h by using 2-bromo-4-fluorobenzaldehyde (0.203 g, 1.0 mmol) and 1-ethynyl-4-nitrobenzene (0.221 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 10:1), **22a'** was obtained as an amorphous yellow solid (0.172 g, 64%). R_f =0.35 (PE/EtOAc = 10:1); m.p. 155-156℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.27 (d, *J* = 8.6 Hz, 2H), 8.01 (dd, *J* = 8.6, 5.9 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.36 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.27 – 7.20 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 165.8 (d, *J* = 258.6 Hz), 148.0, 133.1 (d, *J* = 3.0 Hz), 132.8, 131.0 (d, *J* = 10.1 Hz), 128.8, 127.9 (d, *J* = 11.1 Hz), 124.1, 120.3 (d, *J* = 23.2 Hz), 117.7 (d, *J* = 22.2 Hz), 94.9, 88.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.53; IR (neat) :1691, 1597, 1513, 1343, 1214, 856 cm^{-1}; HRMS(ESI) m/z : $[M+H]^+$ calculated for $C_{15}H_9FNO_3$ 270.05610; found 270.05609.

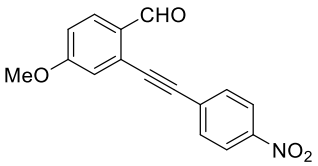
Synthesis of 4-methyl-2-((4-nitrophenyl)ethynyl)benzaldehyde (23a).



23a

This compound was prepared according to typical procedure B at 50 °C for 10 h by using 2-bromo-4-methylbenzaldehyde (0.199 g, 1.0 mmol) and 1-ethynyl-4-nitrobenzene (0.221 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 10:1), **23a** was obtained as an amorphous yellow solid (0.136 g, 51%). R_f =0.33 (PE/EtOAc = 10:1); m.p. 151-153℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 8.25 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.50 (s, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 147.7, 145.3, 134.2, 134.1, 132.6, 130.9, 129.5, 128.3, 125.4, 124.0, 93.5, 90.5, 21.8; IR (neat) :1688, 1595, 1510, 1341, 1264, 743 cm^{-1}; HRMS(ESI) m/z : $[M+H]^+$ calculated for $C_{16}H_{12}NO_3$ 266.08117; found 266.08054.

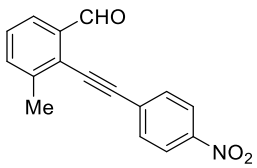
Synthesis of 4-methoxy-2-((4-nitrophenyl)ethynyl)benzaldehyde (24a).



24a

This compound was prepared according to typical procedure B at 50 °C for 8 h by using 2-bromo-4-methoxybenzaldehyde (0.215 g, 1.0 mmol) and 1-ethynyl-4-nitrobenzene (0.221 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 10:1), **24a** was obtained as an amorphous yellow solid (0.145 g, 52%). R_f =0.20 (PE/EtOAc = 10:1); m.p. 140-141℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 8.25 (d, *J* = 7.9 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.12 (s, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 164.0, 147.7, 132.7, 130.4, 130.0, 129.3, 127.4, 124.0, 117.8, 116.5, 93.7, 90.1, 56.0; IR (neat): 1687, 1515, 1395, 1236, 1093, 745 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{12}NO_4$ 282.07608; found 282.07620.

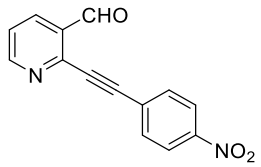
Synthesis of 3-methyl-2-((4-nitrophenyl)ethynyl)benzaldehyde (25a).



25a

This compound was prepared according to typical procedure B at 50 °C for 4 h by using 2-iodo-3-methylbenzaldehyde (0.246 g, 1.0 mmol) and 1-ethynyl-4-nitrobenzene (0.221 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 10:1), **25a** was obtained as an amorphous yellow solid (0.240 g, 90%). R_f = 0.42 (PE/EtOAc = 10:1); m.p. 140-142℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 147.7, 142.3, 136.6, 135.3, 132.5, 129.6, 129.4, 125.6, 125.1, 124.0, 98.5, 89.0, 20.7; IR (neat): 1690, 1514, 1387, 1242, 1170, 853 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{12}NO_3$ 266.08117; found 266.08118.

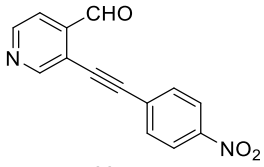
Synthesis of 2-((4-nitrophenyl)ethynyl)nicotinaldehyde (27a).



27a

This compound was prepared according to typical procedure B at 50 °C for 3 h by using 2-bromonicotinaldehyde (0.186 g, 1.0 mmol) and 1-ethynyl-4-nitrobenzene (0.221 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 2:1), **27a** was obtained as an amorphous yellow solid (0.241 g, 95%). R_f = 0.38 (PE/EtOAc = 2:1); m.p. 194-195℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 8.86 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.30 – 8.23 (m, 3H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.49 (dd, *J* = 7.7, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 154.8, 148.2, 145.0, 135.4, 133.2, 132.5, 128.2, 124.3, 124.1, 93.2, 89.1; IR (neat) : 1694, 1511, 1397, 1346, 1260, 751 cm^{-1}; HRMS(ESI) m/z : $[M+H]^+$ calculated for $C_{14}H_9N_2O_3$ 253.06077; found 253.06105.

Synthesis of 3-((4-nitrophenyl)ethynyl)isonicotinaldehyde (28a).

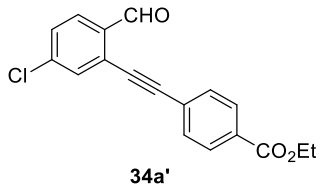


28a

This compound was prepared according to typical procedure B at 50 °C for 3 h by

using 3-bromoisonicotinaldehyde (0.186 g, 1.0 mmol) and 1-ethynyl-4-nitrobenzene (0.221 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 2:1), **28a** was obtained as an amorphous yellow solid (0.217 g, 86%). R_f = 0.40 (PE/EtOAc = 2:1); m.p. 204-205℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 9.00 (s, 1H), 8.81 (d, *J* = 4.3 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 2H), 7.79 – 7.72 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 154.9, 150.6, 148.1, 141.0, 132.9, 128.6, 124.1, 120.1, 112.0, 96.6, 86.9; IR (neat): 1693, 1588, 1512, 1341, 1209, 846 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{14}H_9N_2O_3$ 253.06077; found 253.06144.

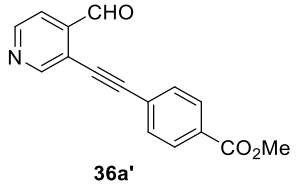
Synthesis of ethyl 4-((5-chloro-2-formylphenyl)ethynyl)benzoate (34a').



34a'

This compound was prepared according to typical procedure B at 50 °C for 3 h by using 2-bromo-4-chlorobenzaldehyde (0.219 g, 1.0 mmol) and ethyl 4-ethynylbenzoate (0.261 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 20:1), **34a'** was obtained as an amorphous white solid (0.207 g, 66%). R_f = 0.47 (PE/EtOAc = 10:1); m.p. 139-141℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.64 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 166.0, 140.5, 134.5, 133.2, 131.9, 131.2, 129.9, 129.8, 129.1, 127.7, 126.4, 96.6, 86.4, 61.5, 14.5; IR (neat): 1713, 1588,1467, 1396, 1190, 1111, 758 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{18}H_{14}ClO_3$ 313.06260; found 313.06317.

Synthesis of methyl 4-((4-formylpyridin-3-yl)ethynyl)benzoate (36a').

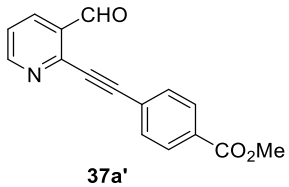


36a'

This compound was prepared according to typical procedure B at 50 °C for 4 h by using 3-bromoisonicotinaldehyde (0.186 g, 1.0 mmol) and methyl 4-ethynylbenzoate

(0.240 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 5:1), **36a'** was obtained as an amorphous white solid (0.237 g, 89%). R_f = 0.23 (PE/EtOAc = 3:1); m.p. 141-142℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.97 (s, 1H), 8.75 (d, *J* = 4.6 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 4.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 166.4, 154.8, 150.1, 140.8, 132.0, 130.9, 129.9, 126.3, 120.8, 119.7, 98.0, 84.7, 52.6; IR (neat): 1778, 1400, 1273, 1205, 1103, 841 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{12}NO_3$ 266.08117; found 266.08151.

Synthesis of methyl 4-((3-formylpyridin-2-yl)ethynyl)benzoate (37a').

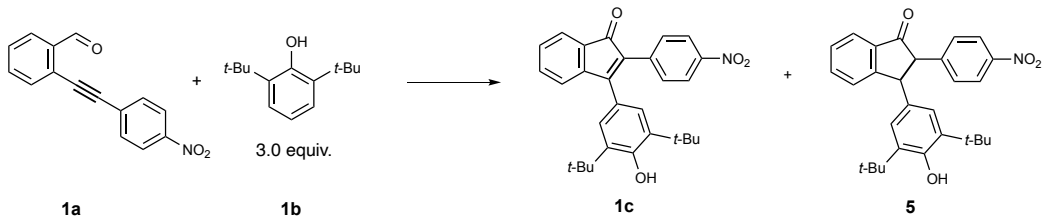


37a'

This compound was prepared according to typical procedure B at 50 °C for 4 h by using 2-bromonicotinaldehyde (0.186 g, 1.0 mmol) and methyl 4-ethynylbenzoate (0.240 g, 1.5 mmol). After a flash column chromatography (PE/EtOAc = 5:1), **37a'** was obtained as an amorphous white solid (0.238 g, 90%). R_f = 0.20 (PE/EtOAc = 3:1); m.p. 146-148℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 8.86 – 8.80 (m, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.47 – 7.41 (m, 1H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 166.4, 154.8, 145.7, 135.2, 132.3, 132.2, 131.2, 129.9, 126.0, 123.9, 94.9, 87.2, 52.6; IR (neat): 1714, 1565, 1432, 1279, 1182, 761 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{16}H_{12}NO_3$ 266.08117; found 266.08145.

3. Optimization of Reaction Conditions

3.1 Optimization of annulation of 2-alkynylbenzaldehydes with phenols



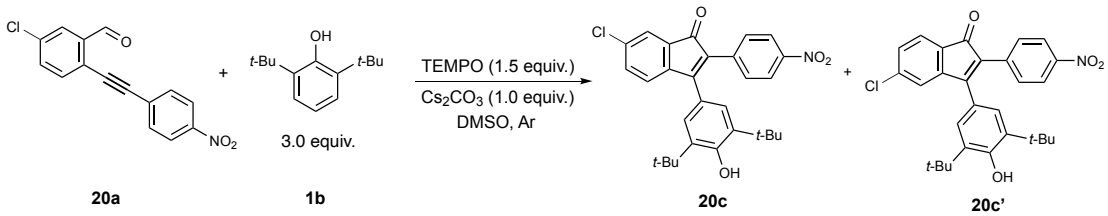
1a **1b** **1c** **5**

Entry	Base	Solvent	Additive	Temp.	Time	% Yield[b]

1	Cs_2CO_3 (1.0)	dioxane	-	50 ℃	46 h	n.r.
2	Cs_2CO_3 (1.0)	DMF	-	50 ℃	46 h	40 + 27
3	Cs_2CO_3 (1.0)	DMSO	-	50 ℃	46 h	42 + 38
4[c]	Cs_2CO_3 (1.0)	DMSO	-	50 ℃	46 h	38 + 38
5	Cs_2CO_3 (1.0)	DMSO	-	70 ℃	23 h	25 + 26
6	Cs_2CO_3 (1.0)	DMSO	-	rt	46 h	45 + 0
7	Cs_2CO_3 (1.0)	DMSO	TEMPO (3.0)	50 ℃	23 h	95 + 0
8	Cs_2CO_3 (1.0)	DMSO	TEMPO (2.0)	50 ℃	23 h	97 + 0
9	Cs_2CO_3 (1.0)	DMSO	TEMPO (1.5)	50 ℃	23 h	96 + 0
10	Cs_2CO_3 (1.0)	DMSO	TEMPO (1.0)	50 ℃	46 h	72 + 0
11	Cs_2CO_3 (1.0)	DMSO	air	50 ℃	46 h	54 + 0
12	Cs_2CO_3 (1.0)	DMSO	O_2	50 ℃	23 h	51 + 0
13	Cs_2CO_3 (1.0)	DMSO	MnO_2 (1.5)	50 ℃	23 h	86 + 0
14	KOH (1.0)	DMSO	TEMPO (1.5)	50 ℃	23 h	77 + 0
15	Na_2CO_3 (1.0)	DMSO	TEMPO (1.5)	50 ℃	46 h	14 + 0
16	$NaHCO_3$ (1.0)	DMSO	TEMPO (1.5)	50 ℃	46 h	19 + 0
17[d]	K_2CO_3 (1.0)	DMSO	TEMPO (1.5)	50 ℃	46 h	54 + 0
18	DBU (1.0)	DMSO	TEMPO (1.5)	50 ℃	46 h	36 + 0
19	Cs_2CO_3 (0.5)	DMSO	TEMPO (1.5)	50 ℃	27 h	79 + 0
20[e]	Cs_2CO_3 (1.0)	DMSO	TEMPO (1.5)	50 ℃	27 h	79 + 0

[a]Reactions were performed with **1a** (0.15 mmol), **1b** (3.0 equiv.), additive and base in solvent (3.0 mL) under Ar. [b]Yield of isolated product. [c]Reaction was set up in a glove box. [d]24% of **1a** recovered. [e]**1b** (2.0 equiv.) was used.

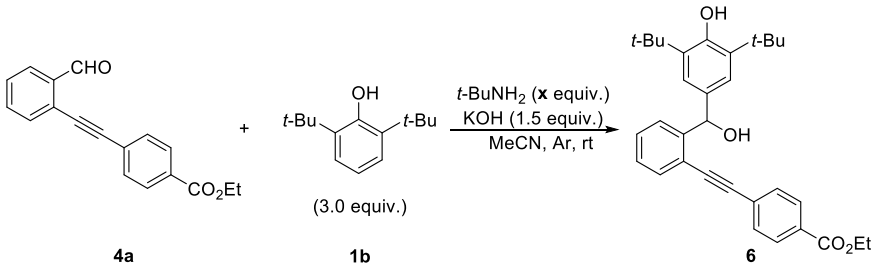
3.2 Optimization of selectivity in synthesis of "non-rearranged" indenones



Entry	Temp.	% Yield	Ratio of **20c**:**20c'**
1	50 ℃	88	70:30
2	23 ℃	80	88:12
3	0 ℃	83	97:3

[a]Reaction conditions: **20a** (0.15 mmol), **1b** (5.0 equiv.), TEMPO (1.5 equiv.) and Cs_2CO_3 (1.0 equiv.) in DMF (3.0 mL) at temperature indicated under Ar for 12 h. All yields are isolated yields. Ratios of **c**:**c'** were determined by HPLC analysis at 254 nm.

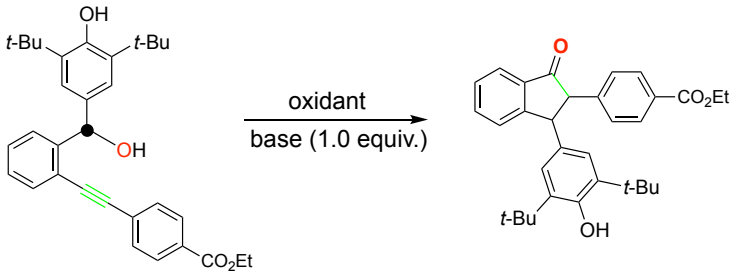
3.3 Optimization of generation benzhydryl alcohol intermediate



Entry	Amine	Time	% Yield[b]
1	none	22 h	trace
2	1.5 equiv.	22 h	32
3	3.0 equiv.	10 h	53
4	3.0 equiv.	14 h	68
5	3.0 equiv.	18 h	78

[a]Reactions were performed with **4a** (0.15 mmol), **1b** (3.0 equiv.), *t*-BuNH$_2$ and KOH (1.5 equiv.) in MeCN (3.0 mL) at room temperature under Ar. [b]Yield of isolated product.

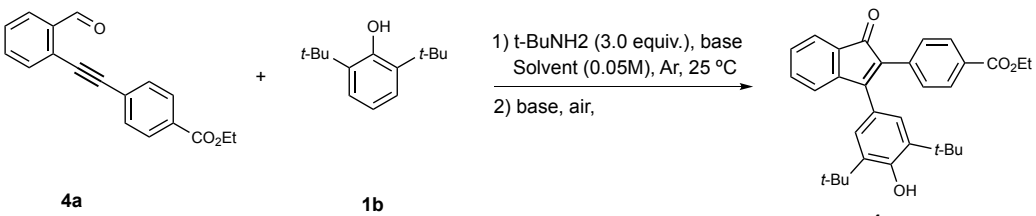
3.4 Optimization of conversion benzhydryl alcohol intermediate to indenones



Entry	Oxidant	Base	Solvent	Temp.	Time	% Yield[b]
1	TEMPO (1.5 equiv.)	Cs_2CO_3	DMSO	50 °C	17 h	22
2[c]	TEMPO (1.5 equiv.)	Cs_2CO_3	DMSO	50 °C	7 h	57
3[d]	air	Cs_2CO_3	DMF	50 °C	17 h	51
4[d]	air	Cs_2CO_3	DMA	50 °C	17 h	45
5[d]	air	Cs_2CO_3	DMSO	rt	23 h	54
6[d]	air	KOH	DMSO	50 °C	5 h	31
7[e]	air	KOH	MeCN	50 °C	5 h	61

[a]Reactions were performed with **6** (0.10 mmol), base (1.0 equiv.) and oxidant in solvent (3.0 mL) under Ar. [b]Yield of isolated product. [c]The reaction mixture was stirred at 50 °C under Argon for 5 h, before addition of TEMPO (1.5 equiv.) and heating for another 2 h. [d]The reaction mixture was stirred at RT under Ar for 15 h, before heating under air for 2 h. [e]The reaction mixture was stirred at 50 °C under Ar for 9 h, before heating under air for another 2 h.

3.5 Optimization for one-pot, two-step synthesis of indenones



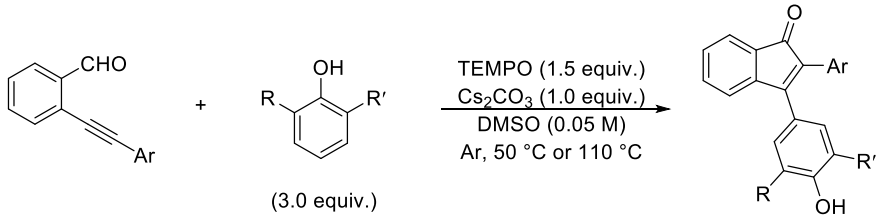
4a **1b** **4c**

Entry	Base	Solvent	Temp.	% Yield
1	KOH (1.5)	MeCN	50 ℃	79
1	KOH (1.5)	MeCN	25 ℃	trace
2	KOH (1.5)	DMF	50 ℃	70
3	KOH (1.5)	DMSO	50 ℃	74
4	KOH (1.5)	dioxane	50 ℃	Trace[b]
5	Cs_2CO_3 (1.5)	MeCN	50 ℃	trace[b]
6	K_2CO_3 (1.5)	MeCN	50 ℃	trace[b]
8[c,d]	-	MeCN	50 ℃	25

[a]Reaction conditions: 4**a** (0.15 mmol), **1b** (3.0 equiv.), *t*-$BuNH_2$ (3.0 equiv.) and base (1.5 equiv.) in solvent (3.0 mL) 25 ℃ under Ar for 23 h, then at 50 °C under air (balloon) with an additional base (1.5 equiv.) for 5h. All yields are isolated yields. [b]**4a** was recovered. [c]Heated at 50 °C under air (balloon) without additional KOH. [d]52% of benzhydryl alcohol intermediate was isolated.

4 General Procedure for the Synthesis of Indenones.

4.1 Typical Procedure A for the Synthesis of Indenones.

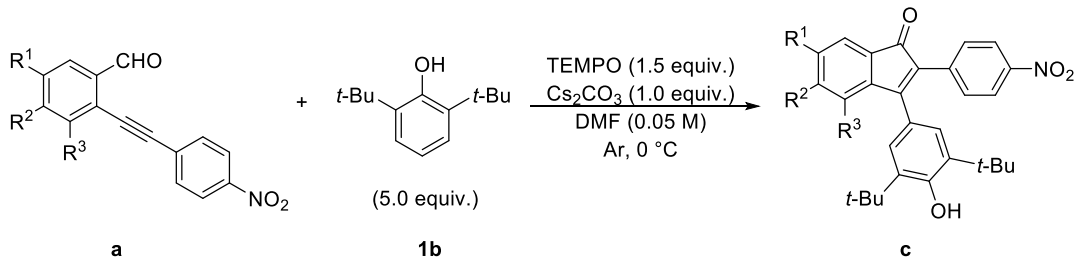


a **b** **c**

To a Schlenk tube was added 2-alkynylbenzaldehyde **a** (0.15 mmol), phenol **b** (0.45 mmol, 3.0 equiv.), Cs_2CO_3 (0.15 mmol, 1.0 equiv.) and TEMPO (0.225 mmol, 1.5 equiv.). The tube was evacuated and refilled with argon. Then the degassed DMSO (3.0 mL) was added to the tube, and the mixture was heated in an oil bath at 50 °C for 22 h (unless other noted). The progress of the reaction was monitored by TLC analysis to establish its completion. After cooling to room temperature, the reaction was diluted with ethyl acetate (15 mL) and washed with brine (15 mL x 2). The aqueous layer was back-extracted with EtOAc (15 mL x 2). The combined organic layers were dried over

$MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate).

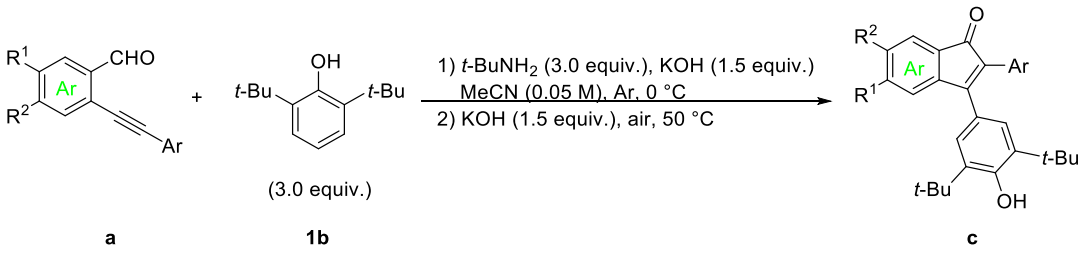
4.2 Typical Procedure B for the Synthesis of "Non-Rearranged" Indenones.



a **1b** **c**

To a Schlenk tube was added 2-alkynylbenzaldehyde **a** (0.15 mmol), **1b** (0.75 mmol, 5.0 equiv.), Cs_2CO_3 (0.15 mmol, 1.0 equiv.) and TEMPO (0.225 mmol, 1.5 equiv.). The tube was evacuated and refilled with argon. The degassed DMF (3.0 mL) was added to the tube, and the mixture was stirred at 0 °C for 12 h (unless other noted). The progress of the reaction was monitored by TLC analysis to establish its completion. After cooling to room temperature, the reaction was diluted with ethyl acetate (15 mL) and washed with water (15 mL x 3). The aqueous layer was back-extracted with EtOAc (15 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate).

4.3 Typical Procedure C for the Synthesis of "Rearranged" Indenones.

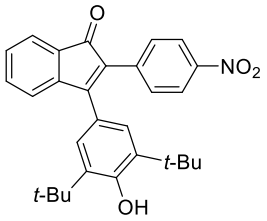


a **1b** **c**

To a solution of 2-alkynylbenzaldehyde **a** (0.15 mmol) and **1b** (0.45 mmol, 3.0 equiv.) in degassed MeCN (3.0 mL) were added KOH (0.225 mmol, 1.5 equiv.) and *t*-$BuNH_2$ (0.45 mmol, 3.0 equiv.) under argon at 0 °C. The resulting solution was stirred at 0 °C for 7 h (unless other noted). KOH (0.225 mmol, 1.5 equiv.) was added and the reaction mixture was heated in an oil bath at 50 °C under air (balloon) for 4 h. The progress of

the reaction was monitored by TLC analysis to establish its completion. After cooling to room temperature, the reaction was diluted with ethyl acetate (15 mL) and washed with water (15 mL x 2). The aqueous layer was back-extracted with EtOAc (15 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate).

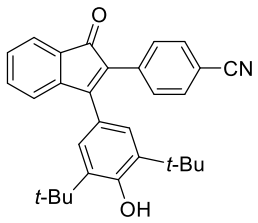
Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-nitrophenyl)-1*H*-inden-1-one (1c).



1c

This compound was prepared according to typical procedure A at 50 °C for 22 h by using 2-((4-nitro-phenyl)ethynyl)benzaldehyde (37. 6 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.7 mg, 0.45 mmol). After a flash column chromatography (PE/EtOAc = 20:1), the product **1c** was obtained as an amorphous red solid (66.1 mg, 97%). R_f = 0.42 (PE/EtOAc = 10:1); m.p. 241-243℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 7.0 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.37 – 7.29 (m, 2H), 7.20 (s, 2H), 5.53 (s, 1H), 1.34 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 159.6, 156.1, 146.8, 144.6, 139.3, 136.8, 133.7, 131.6, 131.1, 129.9, 129.1, 126.3, 123.3, 122.8, 122.4, 34.7, 30.4 (one carbon missing due to overlap); IR (neat): 3619, 2960, 1696, 1513, 1245, 745 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{30}NO_4$ 456.21693; found 456.21683.

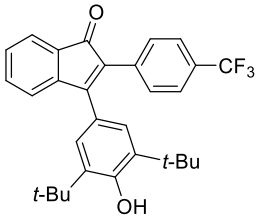
Synthesis of 4-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-oxo-1*H*-inden-2-yl)benzonitrile (2c).



2c

This compound was prepared according to typical procedure A at 23 °C for 25 h by using 4-((2-formyl-phenyl)ethynyl)benzonitrile (34.7 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.7 mg, 0.45 mmol). After a flash column chromatography (PE/EtOAc = 20:1), the product **2c** was obtained as an amorphous red solid (46.7 mg, 71%). R_f = 0.28 (PE/EtOAc = 10:1); m.p. 242-244; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.0 Hz, 1H), 7.55 (d, J = 8.4 Hz, 2H), 7.44 – 7.40 (m, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.18 (s, 2H), 5.54 (s, 1H), 1.33 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 159.0, 156.0, 144.5, 137.2, 136.5, 133.6, 131.9, 131.5, 131.0, 129.7, 129.3, 126.4, 123.3, 122.6, 122.2, 119.3, 110.7, 34.6, 30.3; IR (neat): 3620, 2956, 1601, 1353, 1119, 737 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{30}NO_2$ 436.22711; found 436.22711.

Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-(trifluoromethyl)phenyl)-1*H*-inden-1-one (3c).

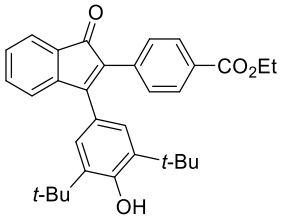


3c

This compound was prepared according to typical procedure C from 2-((4-(trifluoromethyl)phenyl)ethynyl) -benzaldehyde (41.1 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.7 mg, 0.45 mmol) by stirring at 23 °C for 24 h and at 50 °C for 4 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **3c** was obtained as an amorphous red solid (49.3 mg, 69%). R_f = 0.38 (PE/EtOAc = 20:1); m.p. 219-220°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 6.6 Hz, 1H), 7.55 (d, J = 7.8 Hz, 2H), 7.47 – 7.30 (m, 5H), 7.20 (s, 2H), 5.53 (s, 1H), 1.34 (s, 18H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 196.0, 158.4, 155.8, 144.7, 136.4, 136.0, 133.5, 131.6, 130.6, 130.2, 129.5, 129.4 (q, J = 32.3 Hz), 126.5, 125.1 (q, J = 3.0 Hz), 124.4 (q, J = 273.7 Hz), 123.1, 122.8, 122.0, 34.5, 30.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.66; IR (neat): 3624, 2956, 1696, 1321, 1115, 842 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{30}F_3O_2$ 479.21924; found 479.21887.

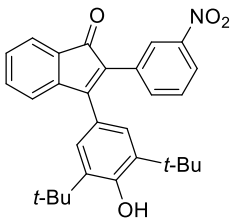
Synthesis of ethyl 4-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-oxo-1*H*-inden-2-yl)benzoate (4c).



4c

This compound was prepared according to typical procedure C from ethyl 4-((2-formylphenyl)ethynyl)-benzoate (41.8 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.7 mg, 0.45 mmol) by stirring at 23 °C for 24 h and at 50 °C for 5 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **4c** was obtained as an amorphous red solid (57.4 mg, 79%). R_f = 0.17 (PE/EtOAc = 20:1); m.p. 237-239℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 6.7 Hz, 1H), 7.42 (t, J = 7.1 Hz, 1H), 7.38-7.29 (m, 4H), 7.22 (s, 2H), 5.51 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H), 1.34 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 166.7, 158.1, 155.7, 144.9, 136.8, 136.4, 133.4, 131.7, 130.5, 130.2, 129.4, 129.3, 129.2, 126.4, 123.1, 122.0, 61.1, 34.6, 30.3, 14.5 (one carbon missing due to overlap); IR (neat): 3739, 2956, 1701, 1273, 1107, 703 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{32}H_{35}O_4$ 483.25299; found 483.25275.

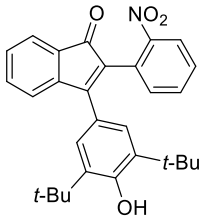
Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3-nitrophenyl)-1*H*-inden-1-one (5c).



5c

This compound was prepared according to typical procedure A from 2-((3-nitrophenyl)ethynyl)benzal-dehyde (37.7 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.7 mg, 0.45 mmol) by stirring at 23 °C for 40 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **5c** was obtained as an amorphous red solid (42.0 mg, 61%). R_f = 0.37 (PE/EtOAc = 10:1); m.p. 200-202℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.09 – 8.06 (m, 1H), 7.64 – 7.58 (m, 2H), 7.47 – 7.40 (m, 2H), 7.36 – 7.29 (m, 2H), 7.20 (s, 2H), 5.53 (s, 1H), 1.32 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 158.9, 156.0, 148.3, 144.6, 136.7, 136.3, 133.9, 133.6, 131.4, 129.7, 129.1, 128.9, 126.2, 125.2, 123.3, 122.6, 122.3, 122.2, 34.6, 30.3; IR (neat): 3619, 2960, 1701, 1528, 1249, 739 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{30}NO_4$ 456.21693; found 456.21646.

Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(2-nitrophenyl)-1*H*-inden-1-one (6c).

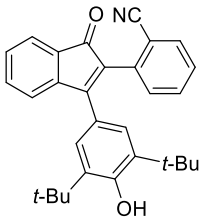


6c

This compound was prepared according to typical procedure A from 2-((2-nitrophenyl)ethynyl)benzaldehyde (37.7 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.7 mg, 0.45 mmol) by stirring at 23 °C for 24 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **6c** was obtained as an amorphous red solid (34.8 mg, 51%). R_f = 0.28 (PE/EtOAc = 10:1); m.p. 143-144℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 6.9 Hz, 1H), 7.51 – 7.36 (m, 4H), 7.32 (t, J = 7.2 Hz, 1H), 7.23 (s, 2H), 7.12 (d, J = 7.3 Hz, 1H), 5.49 (s, 1H), 1.31 (s,

18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 156.7, 155.8, 149.9, 144.9, 136.3, 133.4, 133.0, 132.9, 131.9, 130.1, 129.3, 128.6, 128.5, 126.5, 124.8, 123.5, 122.6, 122.1, 34.5, 30.3; IR (neat): 3617, 2960, 1703, 1526, 1352, 739 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{30}NO_4$ 456.21693; found 456.21683 .

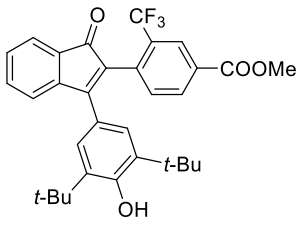
Synthesis of 2-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-oxo-1*H*-inden-2-yl)benzonitrile (7c).



7c

This compound was prepared according to typical procedure A from 2-((2-formylphenyl)ethynyl)benzonitrile (34.7 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.7 mg, 0.45 mmol) by stirring at 23 °C for 24 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **7c** was obtained as an amorphous red solid (39.9 mg, 61%). R_f = 0.27 (PE/EtOAc = 10:1); m.p. 201-202℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 7.7 Hz, 1H), 7.47 – 7.33 (m, 5H), 7.17 (s, 2H), 5.53 (s, 1H), 1.31 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 160.2, 156.0, 144.2, 136.9, 136.3, 133.4, 133.3, 132.6, 131.9, 131.8, 129.7, 129.2, 128.0, 126.7, 123.4, 122.8, 122.4, 118.0, 113.9, 34.5, 30.2; IR (neat): 3619, 2959, 1710, 1354, 1249, 737 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{30}NO_2$ 436.22711; found 436.22717.

Synthesis of methyl 4-(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-oxo-1*H*-inden-2-yl)-3-(trifluoromethyl)benzoate (8c).

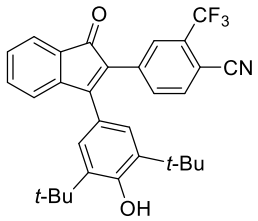


8c

This compound was prepared according to typical procedure A from methyl 4-((2-

formylphenyl)ethynyl)-3-(trifluoromethyl)benzoate (49.8 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.7 mg, 0.45 mmol) by stirring at 50 °C for 22 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **8c** was obtained as an amorphous red solid (60.5 mg, 75%). R_f = 0.23 (PE/EtOAc = 10:1); m.p. 207-208℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 6.9 Hz, 1H), 7.49 – 7.39 (m, 2H), 7.35 (t, *J* = 7.1 Hz, 1H), 7.27 (d, *J* = 6.7 Hz, 1H), 7.18 (s, 2H), 5.48 (s, 1H), 3.96 (s, 3H), 1.29 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 165.9, 158.4, 155.8, 144.5, 137.3, 136.2, 133.3, 133.2, 132.6, 131.9, 131.2 (q, *J* = 30.3 Hz), 130.6, 130.1, 129.5, 128.2 (q, *J* = 5.1 Hz), 126.4, 123.7 (q, *J* = 275.7 Hz), 123.4, 122.8, 122.5, 52.7, 34.5, 30.3. ^{19}F NMR (377 MHz, $CDCl_3$) δ -60.15; IR (neat): 3624, 2960, 1715, 1440, 1259, 893 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{32}H_{32}F_3O_4$ 537.22472; found 537.22577.

Synthesis of 4-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-oxo-1*H*-inden-2-yl)-2-(trifluoromethyl)benzonitrile (9c).

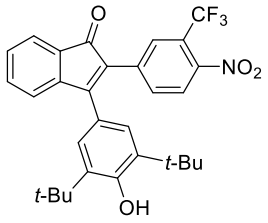


9c

This compound was prepared according to typical procedure A from 4-((2-formylphenyl)ethynyl)-2-(trifluoromethyl)benzonitrile (44.9 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.7 mg, 0.45 mmol) by stirring at 50 °C for 22 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **9c** was obtained as an amorphous red solid (46.6 mg, 62%). R_f = 0.22 (PE/EtOAc = 20:1); m.p. 231-232℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.65-7.58 (m, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.1 Hz, 1H), 7.33 (d, *J* = 7.0 Hz, 1H), 7.19 (s, 2H), 5.61 (s, 1H), 1.36 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 160.7, 156.4, 144.2, 137.6, 137.2, 134.5, 133.9, 133.6, 132.4 (q, *J* = 32.3 Hz), 131.3, 130.2, 128.2 (q, *J* = 4.0 Hz), 127.7, 126.0, 123.5, 122.6, 122.4 (q, *J* = 275.7 Hz), 122.3, 115.9, 107.8, 34.6, 30.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.12; IR (neat): 3538, 2962, 1694, 1305, 1131, 735 cm^{-1}.

HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{31}H_{29}F_3NO_2$ 504.21449; found 504.21515.

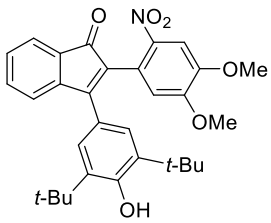
Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-nitro-3-(trifluoromethyl)-phenyl)-1*H*-inden-1-one (10c).



10c

This compound was prepared according to typical procedure A from 2-((4-nitro-3-(trifluoromethyl)-phenyl)ethynyl)benzaldehyde (47.9 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.7 mg, 0.45 mmol) by stirring at 50 °C for 22 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **10c** was obtained as an amorphous red solid (65 mg, 83 %). R_f = 0.17 (PE/EtOAc = 20:1); m.p. 223-225℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.47 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.33 (d, J = 7.0 Hz, 1H), 7.20 (s, 2H), 5.62 (s, 1H), 1.37 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1, 160.8, 156.4, 146.2, 144.3, 137.6, 137.2, 134.3, 133.9, 131.3, 130.3, 129.5 (q, J = 4.0 Hz), 127.4, 125.9, 125.3, 123.6 (q, J = 34.3 Hz), 123.5, 122.6, 122.3, 122.0 (q, J = 274.7 Hz), 34.6, 30.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -60.03; IR (neat): 3537, 2962, 1698, 1354, 1145, 738 cm^{-1}. HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{29}F_3NO_4$ 524.20432; found 524.20496.

Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4,5-dimethoxy-2-nitrophen-yl)-1*H*-inden-1-one (11c).

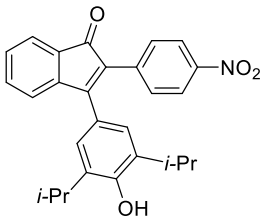


11c

This compound was prepared according to typical procedure A from 2-((4,5-dimethoxy-2-nitrophenyl)-ethynyl)benzaldehyde (46.7 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.7 mg, 0.45 mmol) by stirring at 50 °C for 22 h. After a flash column

chromatography (PE/EtOAc = 5:1), the product **11c** was obtained as an amorphous red solid (40.5 mg, 52%). R_f = 0.27 (PE/EtOAc = 5:1); m.p. 171-172℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.57 (d, *J* = 6.7 Hz, 1H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 7.1 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.24 (s, 2H), 6.38 (s, 1H), 5.49 (s, 1H), 3.96 (s, 3H), 3.59 (s, 3H), 1.33 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 156.1, 155.6, 152.7, 148.6, 145.0, 142.6, 136.5, 133.4, 131.9, 131.1, 129.3, 126.2, 123.5, 123.0, 122.5, 121.9, 113.9, 108.0, 56.7, 56.2, 34.5, 30.3; IR (neat): 3619, 2958, 1705, 1590, 1266, 734 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{31}H_{34}NO_6$ 516.23806; found 516.23785.

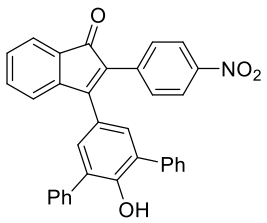
Synthesis of 3-(4-hydroxy-3,5-diisopropylphenyl)-2-(4-nitrophenyl)-1*H*-inden-1-one (12c).



12c

This compound was prepared according to typical procedure A from 2-((4-nitrophenyl)ethyn-yl)benzaldehyde (37.7 mg, 0.15 mmol) and 2,6-di-isopropylphenol (80.2 mg, 0.45 mmol) by stirring at 110 °C for 5 h. After a flash column chromatography (PE/EtOAc = 10:1), the product **12c** was obtained as an amorphous red solid (46.0 mg, 72%). R_f = 0.22 (PE/EtOAc = 10:1); m.p. 253-255℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 6.9 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.36 (t, *J* = 6.9 Hz, 1H), 7.29 (d, *J* = 6.7 Hz, 1H), 7.08 (s, 2H), 5.14 (s, 1H), 3.21 – 3.07 (m, 2H), 1.16 (d, *J* = 6.4 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 159.4, 152.1, 146.7, 144.6, 139.1, 134.6, 133.7, 131.4, 131.0, 129.9, 129.1, 124.7, 123.8, 123.4, 123.4, 122.3, 27.2, 22.8; IR (neat): 3433, 2959, 1687, 1338, 1267, 758 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{27}H_{26}NO_4$ 428.18563; found 428.18539.

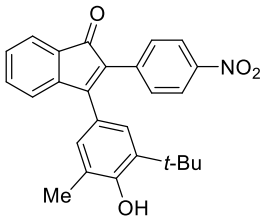
Synthesis of 3-(2'-hydroxy-[1,1':3',1''-terphenyl]-5'-yl)-2-(4-nitrophenyl)-1*H*-inden-1-one (13c).



13c

This compound was prepared according to typical procedure A from 2-((4-nitrophenyl)ethynyl)benzaldehyde (37.7 mg, 0.15 mmol) and [1,1':3',1''-terphenyl]-2'-ol (110.8 mg, 0.45 mmol) by stirred at 110 °C for 5 h. After a flash column chromatography (PE/EtOAc = 5:1), the product **13c** was obtained as an amorphous red solid (44.8 mg, 60%). R_f = 0.32 (PE/EtOAc = 5:1); m.p. 253-254°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 7.0 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.32 (m, 13H), 7.30 (s, 2H), 5.71 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 158.0, 151.4, 147.0, 144.5, 138.5, 136.5, 133.9, 131.0, 130.4, 130.1, 129.9, 129.7, 129.4, 129.3, 128.5, 124.4, 123.6, 123.5, 122.3 (one carbon missing due to overlap); IR (neat): 3515, 2924, 1702, 1341, 1229, 843 cm^{-1}. HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{33}H_{22}NO_4$ 496.15433; found 496.15536.

Synthesis of 3-(3-(*tert*-butyl)-4-hydroxy-5-methylphenyl)-2-(4-nitrophenyl)-1*H*-inden-1-one (14c).

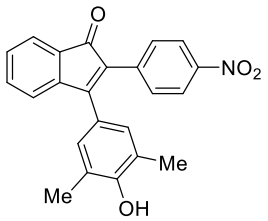


14c

This compound was prepared according to typical procedure A from 2-((4-nitrophenyl)ethynyl)benzaldehyde (37.7 mg, 0.15 mmol) and 2-(*tert*-butyl)-6-methylphenol (73.9 mg, 0.45 mmol) by stirring at 110 °C for 5 h. After a flash column chromatography (PE/EtOAc = 10:1), the product **14c** was obtained as an amorphous red solid (48.3 mg, 78%). R_f = 0.35 (PE/EtOAc = 5:1); m.p. 226-228°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 6.7 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.14 – 7.08 (m, 2H), 2.27 (s, 3H),

1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 159.1, 154.9, 146.8, 144.6, 139.0, 136.6, 133.7, 131.3, 131.0, 129.9, 129.1, 128.8, 126.8, 124.0, 123.4, 123.33, 123.27, 122.3, 34.8, 29.7, 16.3; IR (neat): 3464, 2947, 1593, 1344, 1197, 737 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{26}H_{24}NO_4$ 414.16998; found 414.16956.

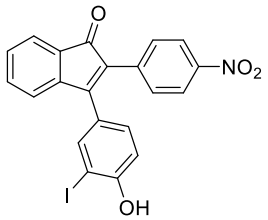
Synthesis of 3-(4-hydroxy-3,5-dimethylphenyl)-2-(4-nitrophenyl)-1*H*-inden-1-one (15c).



15c

This compound was prepared according to typical procedure A from 2-((4-nitrophenyl)ethynyl)benzaldehyde (37.7 mg, 0.15 mmol) and 2,6-dimethylphenol (55.1 mg, 0.45 mmol) by stirring at 110 °C for 5 h. After a flash column chromatography (PE/EtOAc = 5:1), the product **15c** was obtained as an amorphous red solid (43.2 mg, 78%). R_f = 0.10 (PE/EtOAc = 10:1); m.p. 239-240℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 7.0 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.3 Hz, 1H), 7.28 –7.22 (m, 1H), 7.01 (s, 2H), 5.01 (s, 1H), 2.24 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 158.9, 154.3, 146.9, 144.8, 138.7, 133.8, 131.1, 130.9, 129.9, 129.1, 124.2, 123.8, 123.4, 123.3, 122.3, 16.2 (one carbon missing due to overlap); IR (neat): 3447, 2942, 1693, 1264, 1197, 848 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{23}H_{18}NO_4$ 372.12303; found 372.12262.

Synthesis of 3-(4-hydroxy-3-iodophenyl)-2-(4-nitrophenyl)-1*H*-inden-1-one (16c).

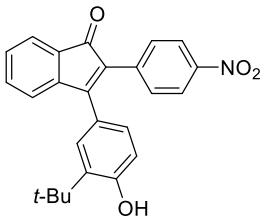


16c

This compound was prepared according to typical procedure A from 2-((4-nitrophenyl)ethynyl)benzaldehyde (37.7 mg, 0.15 mmol) and 2-iodophenol (99.0 mg,

0.45 mmol) by stirring at 110 °C for 5 h. After a flash column chromatography (PE/EtOAc = 2:1), the product **16c** was obtained as an amorphous red solid (37.0 mg, 53%). R_f = 0.13 (PE/EtOAc = 5:1); m.p. 215-216℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.75 (s, 1H), 7.62 (d, *J* = 6.9 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.04 (d, *J* = 8.3 Hz, 1H), 5.71 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 156.6, 156.3, 147.1, 144.3, 138.3, 137.8, 134.1, 131.0, 130.9, 130.7, 130.2, 130.1, 126.2, 123.7, 123.7, 122.0, 116.0, 86.4; IR (neat): 3428, 2930, 1702, 1341, 1184, 739 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{13}INO_4$ 469.98838; found 469.98849.

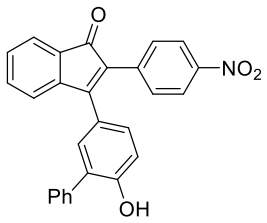
Synthesis of 3-(3-(*tert*-butyl)-4-hydroxyphenyl)-2-(4-nitrophenyl)-1*H*-inden-1-one (17c).



17c

This compound was prepared according to typical procedure A from 2-((4-nitrophenyl)ethynyl)benzaldehyde (37.7 mg, 0.15 mmol) and 2-(*tert*-butyl)phenol (67.6 mg, 0.45 mmol) by stirring at 110 °C for 5 h. After a flash column chromatography (PE/EtOAc = 5:1), the product **17c** was obtained as an amorphous red solid (41.3 mg, 69%). R_f = 0.25 (PE/EtOAc = 5:1); m.p. 254-255℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 6.6 Hz, 1H), 7.49 – 7.40 (m, 3H), 7.36 (t, *J* = 6.9 Hz, 1H), 7.32 – 7.23 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.35 (s, 1H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 158.9, 156.4, 146.8, 144.5, 138.9, 137.2, 133.8, 131.3, 131.0, 130.0, 129.3, 128.7, 127.8, 123.9, 123.5, 123.4, 122.3, 117.4, 34.9, 29.6; IR (neat): 3742, 2957, 1689, 1339, 1195, 644 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{25}H_{22}NO_4$ 400.15433; found 400.15414.

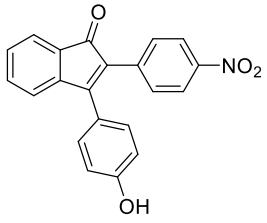
Synthesis of 3-(6-hydroxy-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenyl)-1*H*-inden-1-one (18c).



18c

This compound was prepared according to typical procedure A from 2-((4-nitrophenyl)ethynyl)benzaldehyde (37.7 mg, 0.15 mmol) and [1,1'-biphenyl]-2-ol (76.6 mg, 0.45 mmol) by stirring at 110 °C for 5 h. After a flash column chromatography (PE/EtOAc = 5:1), the product **18c** was obtained as an amorphous red solid (39.4 mg, 63%). R_f = 0.15 (PE/EtOAc = 5:1); m.p. 231-232℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 6.6 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 6.9 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.30 – 7.22 (m, 3H), 7.04 (d, *J* = 7.9 Hz, 1H), 5.66 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 158.2, 154.5, 154.1, 146.9, 144.5, 138.5, 136.0, 133.9, 131.0, 130.8, 130.1, 129.9, 129.8, 129.5, 129.2, 129.1, 128.7, 124.4, 123.6, 123.5, 122.3, 117.0; IR (neat): 3439, 2933, 1700, 1402, 1265, 829 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{27}H_{18}NO_4$ 420.12303; found 420.12311.

Synthesis of 3-(4-hydroxyphenyl)-2-(4-nitrophenyl)-1*H*-inden-1-one (19c).

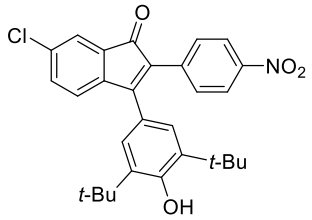


19c

This compound was prepared according to typical procedure A from 2-((4-nitrophenyl)ethynyl)benzaldehyde (37.7 mg, 0.15 mmol) and phenol (42.4 mg, 0.45 mmol) by stirring at 110 °C for 5 h. After a flash column chromatography (PE/EtOAc = 2:1), the product **19c** was isolated as an amorphous red solid (18.8 mg, 37 %). R_f = 0.13 (PE/EtOAc = 5:1); m.p. 242-243℃; ^{1}H NMR (400 MHz, DMSO) δ 10.14 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 2H), 7.58 –7.51(m, 2H), 7.59 – 7.40 (m, 3H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (101 MHz, DMSO)

δ 194.6, 159.5, 158.1, 146.3, 143.8, 138.5, 134.1, 130.9, 130.5, 130.4, 130.0, 128.4, 123.2, 122.7, 122.3, 121.6, 116.0; IR (neat): 3746, 2924, 1792, 1341, 1265, 636 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{21}H_{14}NO_4$ 344.09173; found 344.09122.

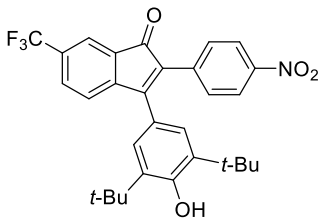
Synthesis of 6-chloro-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-nitrophenyl)-1*H*-inden-1-one (20c).



20c

This compound was prepared according to typical procedure B from 5-chloro-2-((4-nitrophenyl)ethynyl)benzaldehyde (42.9 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring at 0 °C for 12 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **20c** was isolated as an amorphous red solid (60.9 mg, 83%). R_f = 0.27 (PE/EtOAc = 20:1); m.p. 269-270℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.57 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.19 (s, 2H), 5.61 (s, 1H), 1.34 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 159.3, 156.4, 146.9, 142.6, 138.8, 137.0, 136.1, 133.2, 132.9, 131.1, 129.2, 126.3, 123.9, 123.4, 123.2, 122.4, 34.7, 30.4; IR (neat): 3572, 2927, 1692, 1335, 1264, 739 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{29}ClNO_4$ 490.17796; found 490.17725.

Synthesis of 3-(3,5-di-*t*ert-butyl-4-hydroxyphenyl)-2-(4-nitrophenyl)-6-(trifluoro-omethyl)-1*H*-inden-1-one (21c).

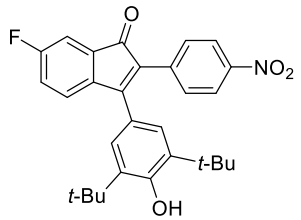


21c

This compound was prepared according to typical procedure B from 2-((4-nitrophenyl)ethynyl)-5-(trifluoromethyl)benzaldehyde (47.9 mg, 0.15 mmol) and 2,6-

di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring at 0 °C for 12 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **21c** was isolated as an amorphous red solid (41.8 mg, 53%). R_f = 0.23 (PE/EtOAc = 20:1); m.p. 246-248℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.85 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.51–7.44 (m, 3H), 7.21 (s, 2H), 5.63 (s, 1H), 1.35 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 158.5, 156.5, 147.9, 147.2, 138.5, 137.1, 132.12 (q, *J* = 33.3 Hz), 132.10, 131.2, 130.9 (q, *J* = 4.0 Hz), 130.8, 126.3, 123.9 (q, *J* = 274.7 Hz), 123.5, 122.2, 122.1, 120.0 (q, *J* = 4.0 Hz), 34.7, 30.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.75. IR (neat): 3578, 2955, 1742, 1516, 1258, 742 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{29}F_3NO_4$ 524.20432; found 524.20392.

Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-fluoro-2-(4-nitrophenyl)-1*H*-inden-1-one (22c).

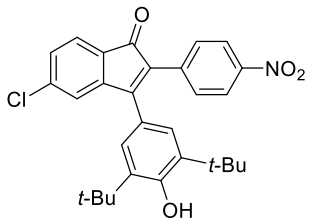


22c

This compound was prepared according to typical procedure B from 5-fluoro-2-((4-nitrophenyl)ethyn-yl)benzaldehyde (40.4 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring at 0 °C for 12 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **22c** was obtained as a crystalline red solid (61.4 mg, 86%). R_f = 0.22 (PE/EtOAc = 20:1); m.p. 241-242℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.44 (s, 2H), 7.34 – 7.27 (m, 2H), 7.20 (s, 2H), 7.10 (t, *J* = 9.6 Hz, 1H), 5.60 (s, 1H), 1.35 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 164.2 (d, *J* = 252.5 Hz), 159.6, 156.4, 146.8, 139.9 (d, *J* = 3.0 Hz), 138.9, 136.8, 134.1 (d, *J* = 7.1 Hz), 131.0, 129.2 (d, *J* = 5.1 Hz), 126.3, 123.6 (d, *J* = 7.1 Hz), 123.4, 122.4, 118.9 (d, *J* = 23.2 Hz), 111.9 (d, *J* = 25.3 Hz), 34.6, 30.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.01; IR (neat): 3616, 2960, 1703, 1517, 1257, 741 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{29}FNO_4$ 474.20751; found 474.20715.

Synthesis of 5-chloro-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-nitrophenyl)-1*H*-

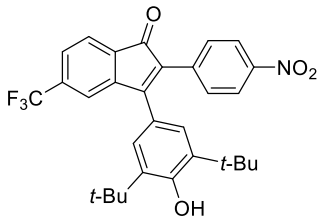
inden-1-one (20c').



20c'

This compound was prepared according to typical procedure B from 4-chloro-2-((4-nitrophenyl)ethynyl)benzaldehyde (42.9 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring at 0 °C for 12 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **20c'** was obtained as a crystalline red solid (47.4 mg, 64%). R_f = 0.38 (PE/EtOAc = 20:1); m.p. 262-263°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.31 (s, 1H), 7.18 (s, 2H), 5.61 (s, 1H), 1.35 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 158.2, 156.4, 146.9, 146.5, 139.9, 138.7, 136.9, 131.1, 123.0, 129.6, 129.4, 126.2, 124.2, 123.4, 123.2, 122.1, 34.6, 30.3; IR (neat): 3617, 2960, 1705, 1402, 1071, 738 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{29}ClNO_4$ 490.17796; found 490.17856.

Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-nitrophenyl)-5-(trifluoromethyl)-1*H*-inden-1-one (21c').

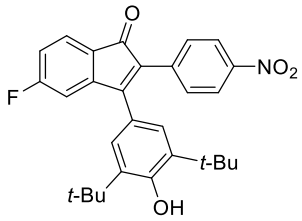


21c'

This compound was prepared according to typical procedure B from 2-((4-nitrophenyl)ethynyl)-4-(trifluoromethyl)benzaldehyde (47.9 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring at 0 °C for 12 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **21c'** was obtained as a crystalline red solid (49.1 mg, 63%). R_f = 0.27 (PE/EtOAc = 20:1); m.p. 263-264°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.67 (d,

J = 7.5 Hz, 1H), 7.60 (s, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.23 (s, 2H), 5.65 (s, 1H), 1.35 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 158.5, 156.6, 147.0, 145.3, 138.5, 137.0, 135.2 (q, *J* = 32.3 Hz), 134.2, 131.1, 130.0, 127.3 (q, *J* = 4.0 Hz), 126.4, 123.7(q, *J* = 273.7 Hz), 123.5, 123.2, 121.9, 119.0 (q, *J* = 3.0 Hz), 34.7, 30.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.21; IR (neat): 3456, 2935, 1706, 1408, 1262, 765 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{29}F_3NO_4$ 524.20432; found 524.20386.

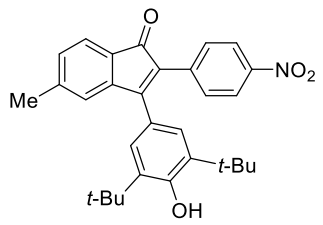
Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-fluoro-2-(4-nitrophenyl)-1*H*-inden-1-one (22c').



22c'

This compound was prepared according to typical procedure B from 4-fluoro-2-((4-nitrophenyl)-ethynyl)benzaldehyde (40.4 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring at 0 °C for 12 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **22c'** was obtained as an amorphous red solid (31.3 mg, 44%). R_f = 0.23 (PE/EtOAc = 20:1); m.p. 262-263 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.7 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.18 (s, 2H), 7.06 – 6.95 (m, 2H), 5.59 (s, 1H), 1.35 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 166.5 (d, *J* = 256.5 Hz), 157.3, 156.3, 147.8 (d, *J* = 10.1 Hz), 146.9, 138.8, 136.9, 131.1, 130.2, 127.2 (d, *J* = 3.0 Hz), 126.2, 125.1 (d, *J* = 10.1 Hz), 123.4, 122.2, 115.4 (d, *J* = 22.2 Hz), 111.2 (d, *J* = 26.3 Hz), 34.6, 30.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.46; IR (neat): 3619, 2959, 1705, 1343, 1205, 742 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{29}FNO_4$ 474.20751; found 474.20731.

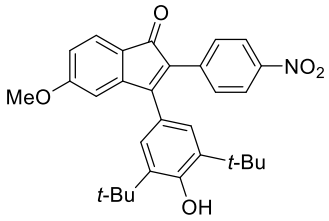
Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-methyl-2-(4-nitrophenyl)-1*H*-inden-1-one (23c).



23c

This compound was prepared according to typical procedure B from 4-methyl-2-((4-nitrophenyl)ethynyl)benzaldehyde (39.8 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring at 23 °C for 48 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **23c** was obtained as an amorphous red solid (15.7 mg, 22%). R_f = 0.17 (PE/EtOAc = 20:1); m.p. 256-257°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.20 (s, 2H), 7.17 – 7.12 (m, 2H), 5.56 (s, 1H), 2.40 (s, 3H), 1.35 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 159.1, 156.0, 146.7, 144.9, 144.6, 139.4, 136.7, 131.1, 129.9, 129.4, 129.1, 126.3, 123.8, 123.4, 123.3, 122.7, 34.6, 30.4, 22.5; IR (neat): 3604, 2957, 1697, 1513, 1245, 740 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{32}NO_4$ 470.23258; found 470.23224.

Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-methoxy-2-(4-nitrophenyl)-1*H*-inden-1-one (24c).

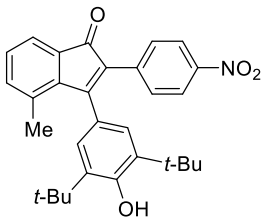


24c

This compound was prepared according to typical procedure B from 4-methoxy-2-((4-nitrophenyl)-ethynyl)benzaldehyde (42.2 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring at 23 °C for 48 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **24c** was obtained as an amorphous red solid (10.7 mg, 15%). R_f = 0.25 (PE/EtOAc = 10:1); m.p. 272-274°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.19 (s, 2H), 6.89 (s, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 5.55 (s, 1H), 3.87 (s, 3H), 1.35

(s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 164.6, 157.3, 156.0, 147.1, 146.7, 139.3, 136.7, 131.1, 130.4, 126.3, 125.2, 124.1, 123.3, 122.6, 111.5, 111.4, 56.0, 34.6, 30.4; IR (neat): 3413, 2958, 1698, 1516, 1343, 746 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{32}NO_5$ 486.22750; found 486.22739.

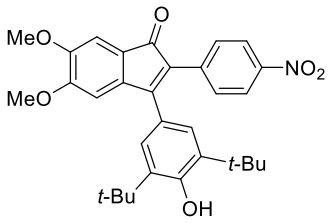
Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4-methyl-2-(4-nitrophenyl)-1*H*-inden-1-one (25c).



25c

This compound was prepared according to typical procedure B from 3-methyl-2-((4-nitrophenyl)-ethynyl)benzaldehyde (39.8 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring at 23 °C for 48 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **25c** was obtained as a crystalline red solid (13.2 mg, 19%). R_f = 0.25 (PE/EtOAc = 20:1); m.p. 206-207℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 6.6 Hz, 1H), 7.32 (d, J = 8.3 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.15 (d, J = 7.7 Hz, 1H), 7.05 (s, 2H), 5.43 (s, 1H), 1.96 (s, 3H), 1.37 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 163.1, 155.1, 146.5, 141.6, 138.8, 138.4, 137.0, 134.2, 131.6, 131.2, 130.8, 129.8, 125.4, 124.9, 123.1, 121.3, 34.7, 30.5, 20.1; IR (neat): 3622, 2960, 1702, 1343, 1239, 748 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{32}NO_4$ 470.23258; found 470.23199.

Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5,6-dimethoxy-2-(4-nitrophenyl)-1*H*-inden-1-one (26c).

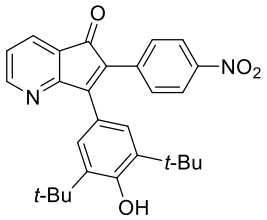


26c

This compound was prepared according to typical procedure A from 4,5-dimethoxy-

2-((4-nitrophenyl)-ethynyl)benzaldehyde (46.6 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.9 mg, 0.45 mmol) by stirring at 70 °C for 22 h. After a flash column chromatography (PE/EtOAc = 10:1), the product **26c** was obtained as an amorphous red solid (49.2 mg, 64%). R_f = 0.30 (PE/EtOAc = 5:1); m.p. 229-231°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.22 (s, 3H), 6.92 (s, 1H), 5.57 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 1.35 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1, 158.3, 156.1, 152.7, 149.9, 146.5, 139.4, 138.6, 136.7, 130.9, 127.6, 126.2, 124.0, 123.3, 122.8, 107.6, 106.9, 56.7, 56.4, 34.6, 30.4; IR (neat): 3618, 2956, 1691, 1338, 1011, 738 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{31}H_{34}NO_6$ 516.23806; found 516.23798.

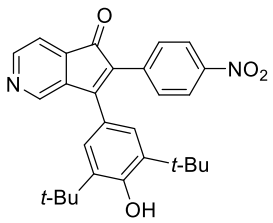
Synthesis of 7-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-(4-nitrophenyl)-5*H*-cyclopenta[*b*]pyridin-5-one (27c).



27c

This compound was prepared according to typical procedure B from 2-((4-nitrophenyl)ethynyl)-nicotinaldehyde (37.8 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring in DMSO (3.0 mL) at 23 °C for 5 h. After a flash column chromatography (PE/EtOAc =5:1), the product **27c** was obtained as an amorphous red solid (45.9 mg, 67%). R_f = 0.47 (PE/EtOAc = 5:1); m.p. 254-255°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 3.6 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 7.0 Hz, 1H), 7.65 (s, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.20 (m, 1H), 5.64 (s, 1H), 1.33 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 166.4, 157.1, 156.4, 152.3, 147.1, 139.0, 136.1, 131.3, 130.9, 129.5, 128.7, 126.0, 123.6, 123.1, 120.9, 34.6, 30.3; IR (neat): 3613, 2959, 1704, 1518, 1252, 750 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{28}H_{29}N_2O_4$ 457.21218; found 457.21170.

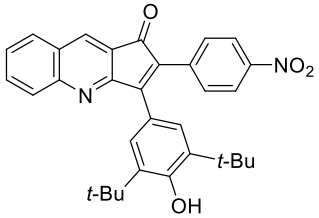
Synthesis of 7-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-(4-nitrophenyl)-5*H*-cyclopenta[*c*]pyridin-5-one (28c).



28c

This compound was prepared according to typical procedure B from 3-((4-nitrophenyl)ethynyl)-isonicotinaldehyde (37.8 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring at 0 °C for 12 h. After a flash column chromatography (PE/EtOAc = 10:1), the product **28c** was obtained as an amorphous red solid (44.1 mg, 64%). R_f = 0.17 (PE/EtOAc = 5:1); m.p. 263-264°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 – 8.76 (m, 1H), 8.69 (s, 1H), 8.16 (d, J = 8.3 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.26 (s, 2H), 5.68 (s, 1H), 1.33 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 160.1, 156.9, 153.3, 147.1, 142.2, 138.5, 138.3, 137.6, 137.0, 131.2, 129.4, 126.6, 123.5, 121.9, 116.4, 34.6, 30.3; IR (neat): 3614, 2960, 1706, 1519, 1257, 845 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{28}H_{29}N_2O_4$ 457.21218; found 457.21152.

Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-nitrophenyl)-1*H*-cyclopenta[*b*]quinolin-1-one (29c).

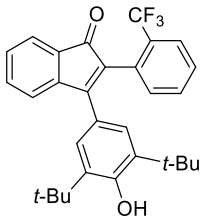


29c

This compound was prepared according to typical procedure B from 2-((4-nitrophenyl)ethynyl)quinoline-3-carbaldehyde (45.3 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (154.8 mg, 0.75 mmol) by stirring at 0 °C for 12 h. After a flash column chromatography (PE/EtOAc = 5:1), the product **29c** was obtained as an amorphous red solid (50.6 mg, 67%). R_f = 0.27 (PE/EtOAc = 10:1); m.p. > 269°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.22 (m, 3H), 8.12 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.81 (s, 2H), 7.76 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 5.67 (s, 1H), 1.36 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 163.8, 157.2, 156.5, 149.7,

147.3, 139.2, 136.2, 136.1, 131.7, 131.4, 131.0, 130.3, 130.2, 129.2, 127.9, 127.4, 125.0, 123.6, 120.9, 34.7, 30.3; IR (neat): 3755, 2958, 1700, 1399, 1265, 751 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{32}H_{31}N_2O_4$ 507.22783; found 507.22757.

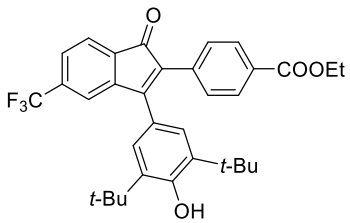
Synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(2-(trifluoromethyl) phenyl) -1*H*-inden-1-one (30c').



30c'

This compound was prepared according to typical procedure C from 2-((2-(trifluoromethyl)phenyl)-ethynyl)benzaldehyde (41.1 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.9 mg, 0.45 mmol) by stirring at 23 °C for 24 h and at 50 °C for 4 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **30c'** was obtained as an amorphous red solid (63.3 mg, 88%). R_f = 0.38 (PE/EtOAc = 10:1); m.p. 198-199°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 7.0 Hz, 1H), 7.53 – 7.38 (m, 4H), 7.33 (t, J = 7.0 Hz, 1H), 7.19 (s, 2H), 7.17 (d, J = 7.4 Hz, 1H), 5.44 (s, 1H), 1.29 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6, 157.8, 155.6, 144.8, 136.0, 133.1, 132.6, 132.2, 132.0, 131.8, 131.6, 130.6 (q, J = 30.3 Hz), 129.2, 128.2, 126.9 (q, J = 5.1 Hz), 126.4, 124.2 (q, J = 274.7 Hz), 123.2, 123.1, 122.3, 34.5, 30.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ-59.99; IR (neat): 3625, 2960, 1729, 1352, 1122, 736 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{30}F_3O_2$ 479.21924; found 479.21967.

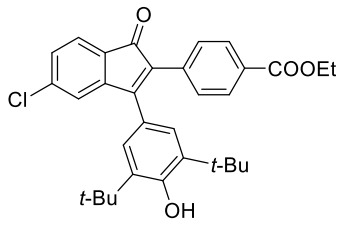
Synthesis of ethyl 4-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-oxo-5-(trifluoromethyl)-1*H*-inden-2-yl)benzoate (33c).



33c

This compound was prepared according to typical procedure C from ethyl 4-((2-formyl-4-(trifluoromethyl)phenyl)ethynyl)benzoate (52.0 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.9 mg, 0.45 mmol) by stirring at 0 °C for 7 h and at 50 °C for 4 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **33c** was obtained as a crystalline red solid (75.5 mg, 91%). R_f = 0.20 (PE/EtOAc = 20:1); m.p. 192-194℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.58 (s, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.24 (s, 2H), 5.60 (s, 1H), 4.38 (q, *J* = 6.8 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.34 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 166.6, 157.2, 156.2, 145.7, 136.7, 136.1, 134.9 (q, *J* = 32.3 Hz), 134.3, 131.4, 130.2, 129.6, 129.5, 126.9 (q, *J* = 4.0 Hz), 126.4, 123.8 (q, *J* = 273.7 Hz), 122.9, 122.3, 118.6 (q, *J* = 3.0 Hz), 61.2, 34.6, 30.3, 14.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.17; IR (neat): 3632, 2960, 1603, 1312, 1122, 743 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{33}H_{34}F_3O_4$ 551.24037; found 551.24005.

Synthesis of ethyl 4-(5-chloro-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-oxo-1*H*-inden-2-yl)benzoate (34c).

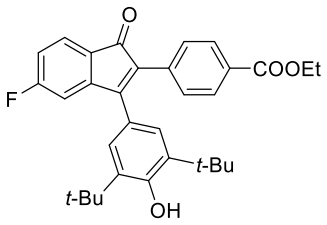


34c

This compound was prepared according to typical procedure C from ethyl 4-((4-chloro-2-formylphenyl)-ethynyl)benzoate (46.9 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.9 mg, 0.45 mmol) by stirring at 0 °C for 8 h and at 50 °C for 5 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **34c** was obtained as a crystalline red solid (64.8 mg, 84%). R_f = 0.20 (PE/EtOAc = 20:1); m.p. 235-236℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.19 (s, 2H), 5.55 (s, 1H), 4.37 (q, *J* = 7.0 Hz, 2H), 1.38 (t, *J* = 7.3 Hz, 3H), 1.34 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 166.6, 156.8, 155.9, 146.9, 139.6, 136.6, 136.3, 131.5, 130.2, 129.7, 129.5, 129.4, 128.9, 126.3, 123.9, 122.8, 122.6, 61.1, 34.6, 30.3, 14.5; IR (neat): 3626, 2961, 1602, 1273, 1109,

744 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{32}H_{34}ClO_4$ 517.21401; found 517.21381.

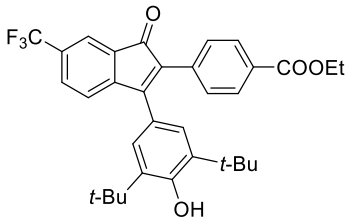
Synthesis of ethyl 4-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-fluoro-1-oxo-1*H*-inden-2-yl)benzoate (35c).



35c

This compound was prepared according to typical procedure C from ethyl 4-((4-fluoro-2-formylphenyl)ethynyl)benzoate (44.4 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.9 mg, 0.45 mmol) by stirring at 0 °C for 8 h and at 50 °C for 21 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **35c** was obtained as a crystalline red solid (44.7 mg, 60 %). R_f = 0.38 (PE/EtOAc = 10:1); m.p. 235-236℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.58 (s, 1H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.19 (s, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.96 (t, *J* = 8.2 Hz, 1H), 5.53 (s, 1H), 4.37 (q, *J* = 6.8 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 3H), 1.34 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 166.7, 166.4 (d, *J* = 255.5 Hz), 155.9, 148.2 (d, *J* = 9.1 Hz), 136.6, 136.4, 131.7, 130.2, 129. 44, 129.38, 128.1, 127.4 (d, *J* = 3.0 Hz), 126.2, 124.8 (d, *J* = 10.1 Hz), 122.6, 114.9 (d, *J* = 22.2 Hz), 110.9 (d, *J* = 26.3 Hz), 61.1, 34.6, 30.3, 14.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -104.09; IR (neat): 3619, 2959, 1704, 1272, 1107, 747 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{32}H_{34}FO_4$ 501.24356; found 501.24335.

Synthesis of ethyl 4-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-oxo-6-(trifluoromethyl)-1*H*-inden-2-yl)benzoate (33c').

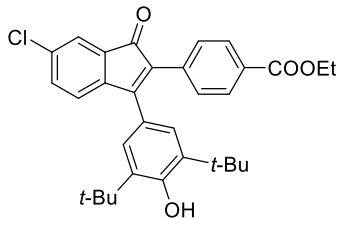


33c'

This compound was prepared according to typical procedure C from ethyl 4-((2-

formyl-5-(trifluoromethyl)phenyl)ethynyl)benzoate (52.0 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.9 mg, 0.45 mmol) by stirring at 0 °C for 7 h and at 50 °C for 4 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **33c'** was obtained as an amorphous red solid (65.9 mg, 80%). R_f = 0.23 (PE/EtOAc = 20:1); m.p. 229-230℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 2H), 7.82 (s, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.22 (s, 2H), 5.57 (s, 1H), 4.37 (q, *J* = 6.8 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.34 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 166.6, 157.1, 156.1, 148.3, 136.6, 136.1, 132.2, 131.5 (q, *J* = 33.3 Hz), 130.7 (q, *J* = 3.0 Hz), 130.2, 129.7, 129.5, 126.4, 124.0 (q, *J* = 272.7 Hz), 122.4, 121.8, 119.8 (q, *J* = 3.0 Hz), 61.2, 34.6, 30.3, 14.5 (one carbon missing due to overlap); ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.69. IR (neat): 3548, 2959, 1599, 1352, 1122, 736 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{33}H_{34}F_3O_4$ 551.24037; found 551.24017.

Synthesis of ethyl 4-(6-chloro-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-oxo-1*H*-inden-2-yl)benzoate (34c').

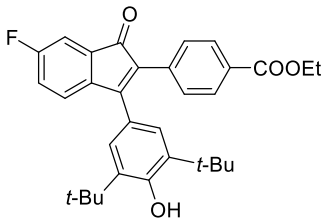


34c'

This compound was prepared according to typical procedure C from ethyl 4-((5-chloro-2-formylphenyl)ethynyl)benzoate (46.9 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.9 mg, 0.45 mmol) by stirring at 0 °C for 7 h, at 23 °C for 16 h, and at 50 °C for 4 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **34c'** was obtained as an amorphous red solid (63.7 mg, 82%). R_f = 0.25 (PE/EtOAc = 20:1); m.p. 209-210℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.54 (s, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 8.9 Hz, 1H), 7.20 (s, 2H), 5.55 (s, 1H), 4.37 (q, *J* = 6.9 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.34 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 166.6, 157.9, 156.0, 142.9, 136.5, 136.4, 135.5, 133.3, 132.6, 130.6, 130.1, 129.4, 126.3, 123.6, 122.8, 122.7, 61.1, 34.6, 30.3, 14.5 (one

carbon missing due to overlap); IR (neat): 3543, 2959, 1705, 1603, 1271, 737 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{32}H_{34}ClO_4$ 517.21401; found 517.21478.

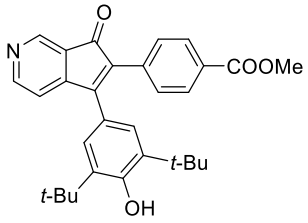
Synthesis of ethyl 4-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-fluoro-1-oxo-1*H*-inden-2-yl)benzoate (35c').



35c'

This compound was prepared according to typical procedure C from ethyl 4-((5-fluoro-2-formylphenyl)-ethynyl)benzoate (44.4 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.9 mg, 0.45 mmol) by stirring at 0 °C for 7 h, at 23 °C for 36 h, and at 50 °C for 4 h. After a flash column chromatography (PE/EtOAc = 20:1), the product **35c'** was obtained as an amorphous red solid (52.4 mg, 70%). R_f = 0.42 (PE/EtOAc = 10:1); m.p. 231-232℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 2H), 7.37 – 7.24 (m, 4H), 7.21 (s, 2H), 7.07 (t, J = 8.3 Hz, 1H), 5.54 (s, 1H), 4.37 (q, J = 7.0 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H), 1.33 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 166.7, 163.9 (d, J = 251.5 Hz), 158.2, 155.9, 140.2 (d, J = 4.0 Hz), 136.52, 136.45, 134.2 (d, J = 8.1 Hz), 130.7, 130.1, 129.4, 129.3, 126.4, 123.1 (d, J = 7.1 Hz), 122.8, 118.6 (d, J = 23.2 Hz), 111.6 (d, J = 25.3 Hz), 61.1, 34.6, 30.3, 14.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.00; IR (neat): 3625, 2977, 1709, 1429, 1266, 895 cm^{-1}. HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{32}H_{34}FO_4$ 501.24356; found 501.24442.

Synthesis of methyl 4-(5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-7-oxo-7*H*-cyclopenta[*c*]pyridin-6-yl)benzoate (36c').

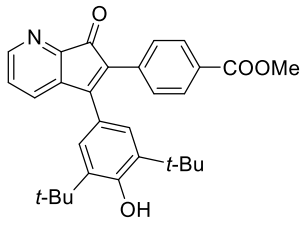


36c'

This compound was prepared according to typical procedure C from methyl 4-((4-

formylpyridin-3-yl)ethynyl)benzoate (39.8 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.9 mg, 0.45 mmol) by stirring at 0 °C for 7 h and at 50 °C for 4 h. After a flash column chromatography (PE/EtOAc = 5:1), the product **36c'** was obtained as an amorphous red solid (26.6 mg, 57%). R_f = 0.20 (PE/EtOAc = 3:1); m.p. 260-262℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 2H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.32 (s, 1H), 7.21 (s, 2H), 5.60 (s, 1H), 3.92 (s, 3H), 1.34 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 167.0, 156.2, 155.8, 155.4, 153.1, 142.8, 136.7, 136.0, 132.2, 130.4, 129.6, 126.4, 125.3, 122.1, 116.7, 52.4, 34.6, 30.3 (one carbon missing due to overlap); IR (neat): 3563, 2958, 1599, 1275, 1112, 739 cm^{-1}; HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{32}NO_4$ 470.23258; found 470.23346.

Synthesis of methyl 4-(5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-7-oxo-7*H*-cyclopenta[*b*]pyridin-6-yl)benzoate (37c').

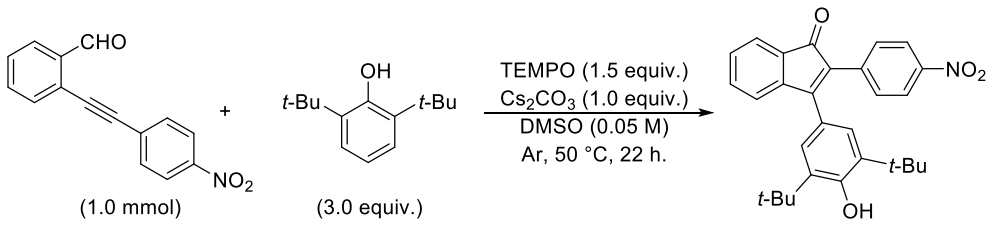


37c'

This compound was prepared according to typical procedure C from methyl 4-((3-formylpyridin-2-yl)ethynyl)benzoate (39.8 mg, 0.15 mmol) and 2,6-di-*tert*-butylphenol (92.9 mg, 0.45 mmol) by stirring at 0 °C for 7 h and at 50 °C for 4 h. After a flash column chromatography (PE/EtOAc = 5:1), the product **37c'** was obtained as an amorphous red solid (32.9 mg, 70%). R_f = 0.22 (PE/EtOAc = 3:1); m.p. 265-266℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.3 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 2H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.23 (s, 2H), 5.60 (s, 1H), 3.92 (s, 3H), 1.33 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 167.1, 156.3, 156.1, 151.9, 149.7, 140.2, 136.7, 136.2, 130.3, 129.9, 129.5, 129.3, 128.3, 126.4, 125.8, 122.3, 52.4, 34.6, 30.3. IR (neat): 3619, 2958, 1602, 1273, 1112, 737 cm^{-1}. HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{30}H_{32}NO_4$ 470.23258; found 470.23251.

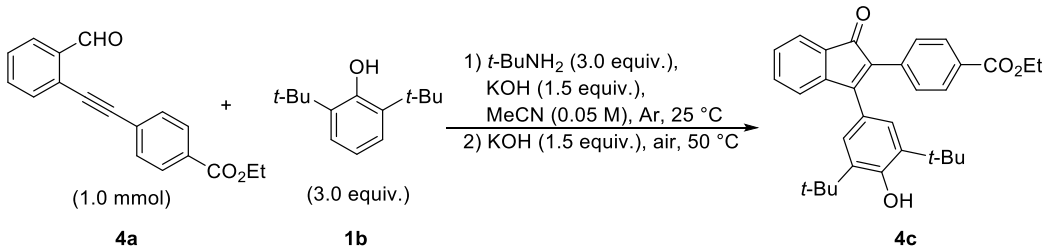
5. Scale-up Reactions and Synthetic Transformations.

5.1. Scale-up of indenone 1c.



To a 50 mL round-bottom flask was added **1a** (0.251 g, 1.0 mmol), **1b** (0.619 g, 3.0 mmol), Cs_2CO_3 (0.326 g, 1.0 mmol) and TEMPO (0.234 g, 1.5 mmol). The flask was evacuated and refilled with argon three times. The degassed DMSO (20.0 mL) was added and the resulting mixture was heated in an oil bath at 50 °C for 22 h. Upon completion, the mixture was cooled to room temperature, diluted with ethyl acetate (40 mL) and washed with brine (50 mL x 2). The combined aqueous layers were back-extracted with EtOAc (30 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate/dichloromethane = 20/1/2) to afford indenone **1c** as an amorphous red solid (0.403 g, 88%).

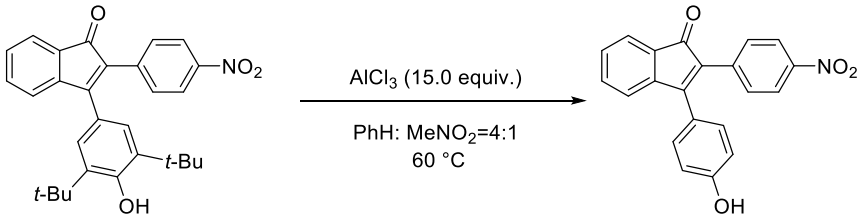
5.2 Scale-up of indenone 4c.



To a solution of **4a** (0.278 g, 1.0 mmol) and **1b** (0.619 g, 3.0 mmol) in degassed MeCN (20.0 mL) were added KOH (0.084 g, 1.5 mmol) and *t*-$BuNH_2$ (0.219 g, 3.0 mmol) under argon at 25 °C. The mixture was stirred at the same temperature for 24 h. An additional KOH (0.084 g, 1.5 mmol) was added and the mixture was heated in an oil bath at 50 °C under air (balloon) for 23 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (40 mL) and washed with water (40 mL). The aqueous layer was back-extracted with EtOAc (30 mL x 2). The combined organic

layers were dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (Silica Gel, petroleum ether/ethyl acetate = 20/1) to afford Indenone **4c** as an amorphous red solid (0.310 g, 64%).

5.3 Synthetic Transformation of 1c.

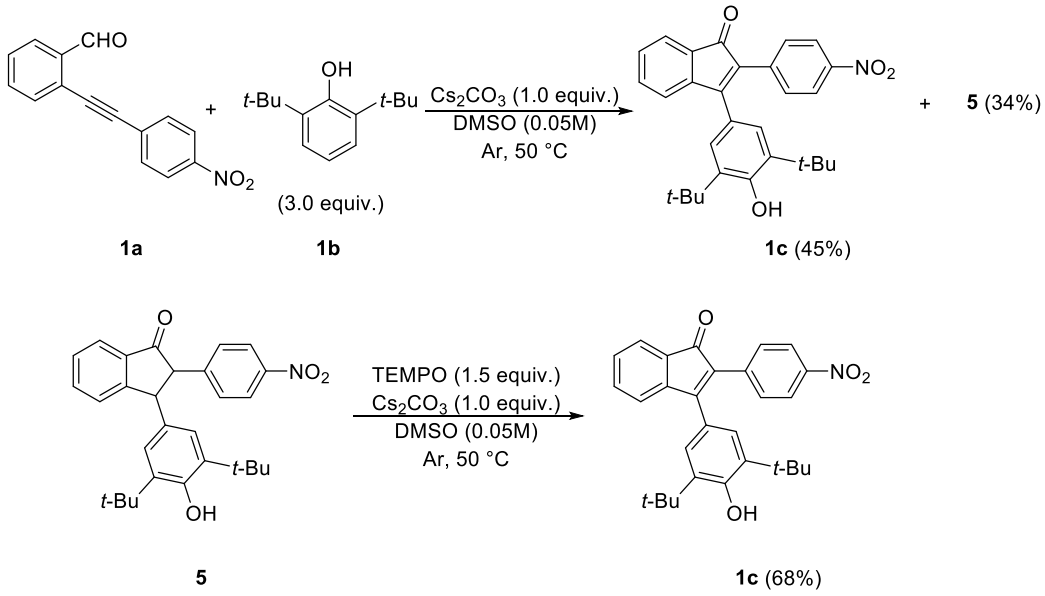


1c **19c**

To a solution of **1c** (0.0683 g, 0.15 mmol) in PhH (4.0 mL) was added $AlCl_3$ (0.300 g, 2.25 mmol) and $MeNO_2$ (1.0 mL). The resulting mixture was heated in an oil bath at 60 °C for 23 h. The progress of the reaction was monitored by TLC analysis to establish its completion. After cooling to room temperature, the reaction mixture was quenched by 1M HCl (10 mL) and extracted with EtOAc (15 mL). The aqueous layer was back-extracted with EtOAc (15 mL x 2). The combined organic layers were washed with saturated $NaHCO_3$ (15 mL x 2), dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (Silica Gel, PE/EtOAc = 10:1) to afford indenone **19c** as an amorphous red solid (0.035 g, 68%), and recover starting material **1c** (0.020 g, 30%).

6. Control Experiments.

6.1 Isolation of indanone intermediate 5.

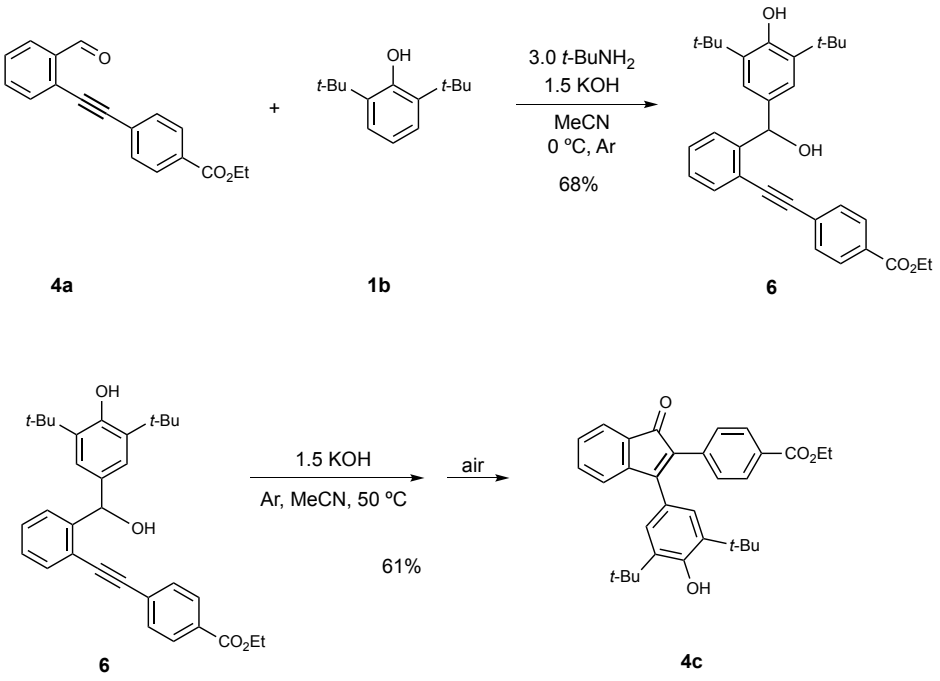


To a solution of 2-((4-nitrophenyl)ethynyl)benzaldehyde **1a** (0.050 g, 0.2 mmol) and 2,6-di-*tert*-butylphenol (0.124 g, 0.6 mmol) in degassed DMSO (4.0 mL) was added Cs_2CO_3 (0.066 g, 0.2 mmol) under argon. The resulting mixture was heated in an oil bath at 50 °C under argon for 22 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (15 mL) and washed twice brine (15 mL x 2). The combined aqueous layers were back-extracted with EtOAc (15 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (Silica Gel, PE/EtOAc = 20:1) to afford indanone **5** as a yellow oil (0.031 g, 34%), along with indenone **1c** (0.040 g, 45%). R_f = 0.22 (PE/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.7 Hz, 2H), 7.89 (d, J = 7.7 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.32 (d, J = 8.7 Hz, 2H), 6.82 (s, 2H), 5.18 (s, 1H), 4.50 (d, J = 4.9 Hz, 1H), 3.89 (d, J = 5.0 Hz, 1H), 1.37 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 156.3, 153.3, 147.3, 146.5, 136.8, 136.0, 135.9, 132.3, 129.7, 128.7, 127.1, 124.4, 124.3, 124.2, 64.5, 54.7, 34.6, 30.5. IR (neat): 3445, 2997, 1657, 1423, 1033, 702 cm^{-1}. HRMS(ESI) m/z: $[M+H]^+$ calculated for $C_{29}H_{32}NO_4$ 458.23258; found 458.23328.

A solution of **5** (0.046 g, 0.1 mmol), Cs_2CO_3 (0.033 g, 0.1 mmol) and TEMPO (0.023 g, 0.15 mmol) in degassed DMSO (2.0 mL) was heated in an oil bath at 50 °C for 4 h under argon. The progress of the reaction was monitored by TLC analysis to establish

its completion. After cooling to room temperature, the mixture was diluted with ethyl acetate (15 mL) and washed with brine (15 mL x 2). The combined aqueous layers were back-extracted with EtOAc (15 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (Silica Gel, PE/EtOAc = 20:1) to afford indenone **1c** as an amorphous red solid (0.029 g, 64%).

6.2 Synthesis of ethyl 4-((2-((3,5-di-*t*ert-butyl-4-hydroxyphenyl)(hydroxy)-methyl)phenyl)ethynyl)benzoate (6).



To a solution of ethyl 4-((2-formylphenyl)ethynyl)benzoate (**4a**) (0.200 g, 0.72 mmol) and **1b** (0.445 g, 2.16 mmol) in degassed MeCN (15.0 mL) were added KOH (0.061 g, 1.08 mmol) and *t*-$BuNH_2$ (0.158 g, 2.16 mmol) under argon at room temperature. The resulting solution was stirred at the same temperature for 14 h. The completed reaction was diluted with ethyl acetate (15 mL) and washed with brine (15 mL x 2). The combined aqueous layers were back-extracted with EtOAc (20 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography (Silica Gel, PE/EtOAc = 10:1) to afford product **6** as a yellow solid (0.235 g, 68%). R_f = 0.47 (PE/EtOAc = 5:1); m.p. 150-152°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 7.8 Hz, 1H), 7.55 –

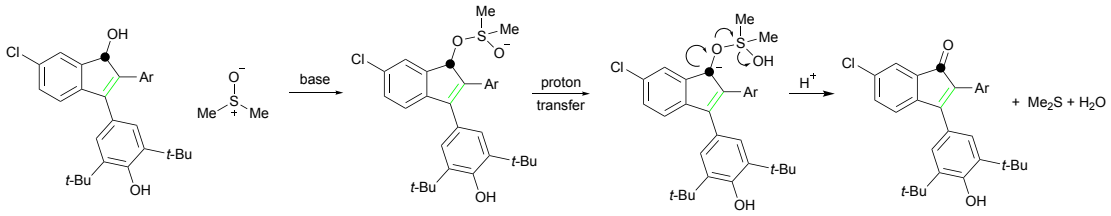
7.47 (m, 3H), 7.42 (t, J = 7.5 Hz, 1H), 7.30 – 7.24 (m, 3H), 6.31 (s, 1H), 5.16 (s, 1H), 4.39 (q, J = 7.1 Hz, 2H), 2.38 (s, 1H), 1.41 (t, J = 7.1 Hz, 3H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 153.5, 146.6, 136.0, 134.0, 132.6, 131.5, 130.2, 129.7, 129.5, 127.9, 127.4, 126.2, 123.8, 120.7, 94.0, 90.9, 74.7, 61.4, 34.6, 30.4, 14.5. IR (neat): 3632, 2962, 1711, 1273, 1109, 743 cm^{-1}. HRMS(ESI) m/z: $[M-H_2O]^+$ calculated for $C_{32}H_{35}O_3$ 467.25807; found 467.25861.

To a solution of **6** (0.048 g, 0.10 mmol) in degassed MeCN (3.0 mL) was added KOH (0.0084g, 0.15 mmol, 1.5 equiv.) and the resulting mixture was stirred at 50 °C under Argon for 2h. Then the mixture was heated at the same temperature under air (balloon) for another 5h. After a flash column chromatography (PE/EtOAc = 20:1), the product **4c** was obtained as an amorphous red solid (30.0 mg, 61%).

7. Proposed Mechanism for Oxidation of Dihydroindenone and Inden-1-ol

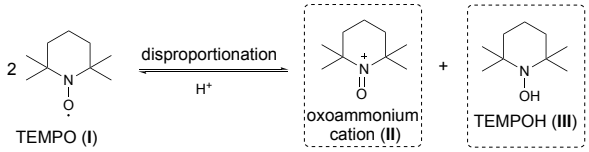
7.1 Proposed mechanism for oxidation of inden-1-ol by DMSO

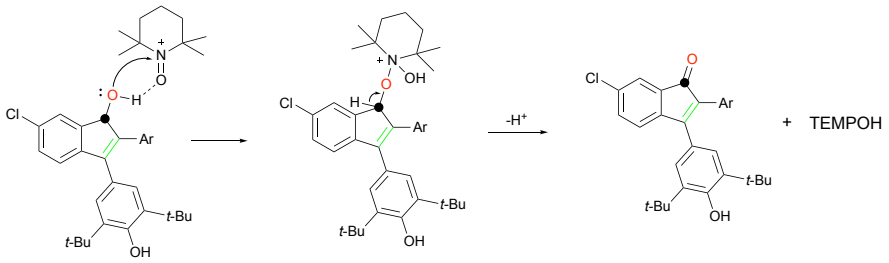
This mechanism was proposed based on oxidation of benzhydrols by DMSO reported by Ravikumar etc.[13]



7.2 Proposed mechanism for oxidation of inden-1-ol by TEMPO

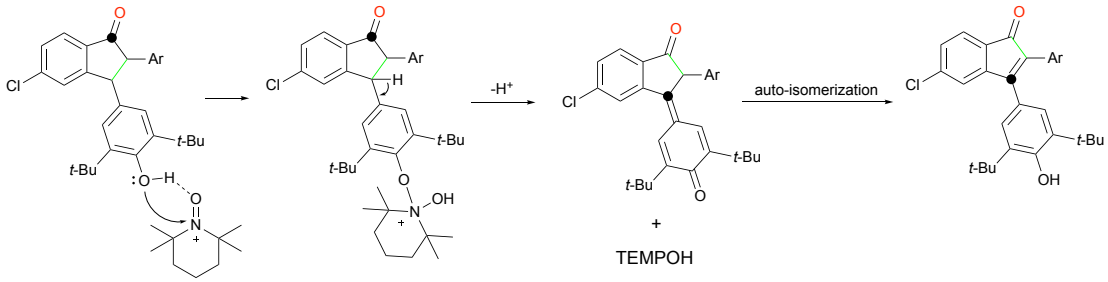
This mechanism was proposed based on oxidation of alcohol by TEMPO reported by Hong etc.[14]





7.3 Proposed mechanism for oxidation of dihydroindenone by TEMPO

This mechanism was proposed based on oxidation of alcohol by TEMPO reported by Hong etc.[14]



8. References

[1] Korich, A. L.; Hughes, T. S. *Org. Lett.* **2008**, *10*, 5405-5408.

[2] Kaiser, R. P.; Mosinger, J.; Cisarova, I.; Kotora, M. *Org. Biomol. Chem.* **2017**, *15*, 6913-6920.

[3] Allen, C. P.; Benkovics, T.; Turek, A. K.; Yoon, T. P. *J. Am. Chem. Soc.* **2009**, *131*, 12560-12561.

[4] Bucher, J.; Stoesser, T.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2015**, *54*, 1666-1670.

[5] Saifuddin, M.; Samala, S.; Krishna, D. G. V.; Kundu, B. *Syn.* **2013**, *45*, 1553-1563.

[6] Mukherjee, A.; Liu, R. S. *Org. Lett.* **2011**, *13*, 660-663.

[7] Chen, J. Y.; Liu, B.; Chen, Y. H.; He, Q.; Yang, C. H. *RSC Adv.* **2014**, *4*, 11168-11175.

[8] Pagire, S. K.; Kreitmeier, P.; Reiser, O. *Angew. Chem., Int. Ed.* **2017**, *56*, 10928-10932.

[9] Verma, A. K.; Kotla, S. K. R.; Choudhary, D.; Patel, M.; Tiwari, R. K. *J. Org. Chem.* **2013**, *78*, 4386-4401.

[10] Mariaule, G.; Newsome, G.; Toullec, P. Y.; Belmont, P.; Michelet, V. *Org. Lett.* **2014**, *16*, 4570-4573.

[11] Alfonsi, M.; Dell'Acqua, M.; Facoetti, D.; Arcadi, A.; Abbiati, G.; Rossi, E. *Eur. J.*

Org. Chem. **2009**, 2852-2862.
[12] Guo, Z.; Liu, T.; Liang, X.; Wu, Y. Yao, T. *Adv. Synth. Catal.* **2020**, *362*, 1053-1057.
[13] R. Chebolu, A. Bahuguna, R. Sharma, V. K. Mishra, P. C. Ravikumar, *Chem. Commun.,* 2015, **51**, 15438.
[14] M. Hong, J. Min, S. Wu, H. Cui, Y. Zhao, J. Li, S. Wang, *ACS Omega*, 2019, **4**, 7054.

9. Single Crystal X-ray Structures of 20c', 21c', 22c, 25c, 33c, 34c and 35c.

The data was collected at Rigaku XtaLAB Synergy four-circle diffractometer under MoKα radiation (λ = 0.71073), with the CrysAlisPro software (version 1.171.39.34b) for data reduction and analysis. The structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. All non-hydrogen atoms in the structure were refined with anisotropic models. All hydrogen atoms were generated geometrically.

9.1 X-ray Crystal of 20c'.

The crystal was obtained by recrystallization in ethyl acetate and petroleum ether. Crystal data and structure refinement for **20c'** were with thermal ellipsoids at 50% probability.

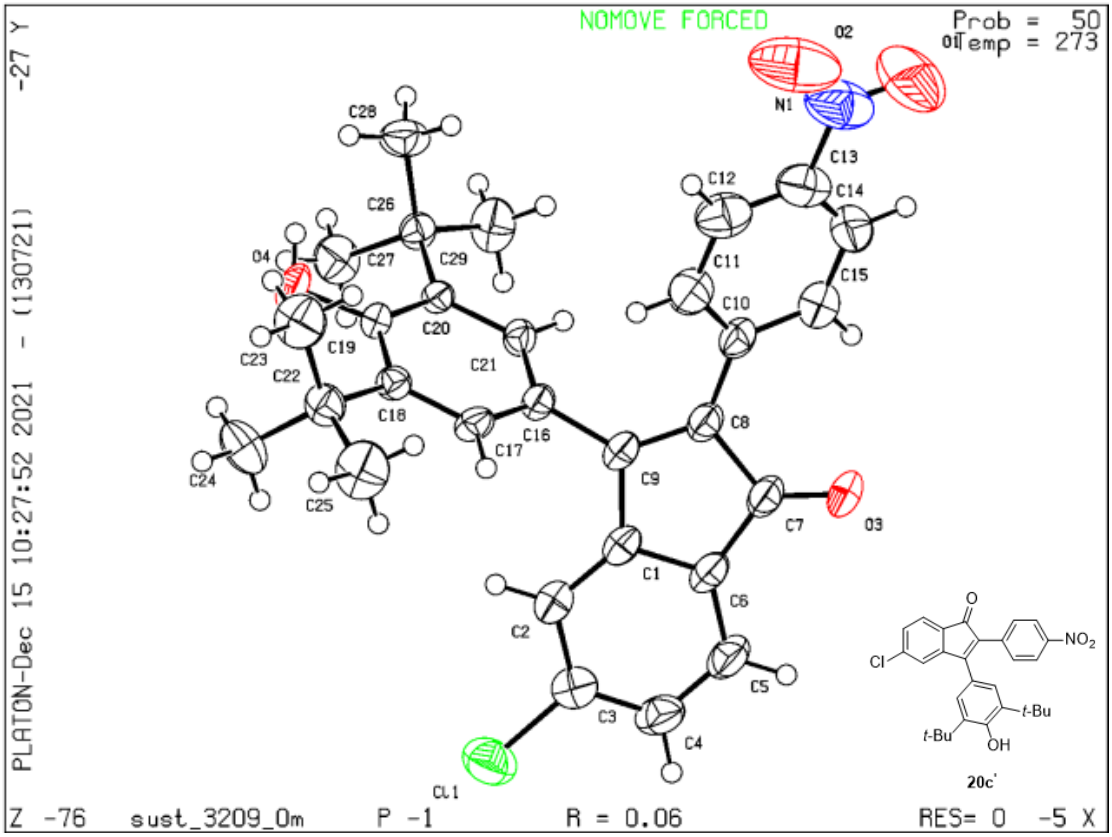


Table S1. Crystal Data and Structure Refinement for **20c'**

Identification code	**20c'**
Empirical formula	$C_{29}H_{28}ClNO_4$
Formula weight	489.97
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
a/Å	10.0582(6)
b/Å	11.3137(7)
c/Å	11.3744(7)
α/°	85.422(2)
β/°	89.974(2)
γ/°	77.443(2)
Volume/Å^3	1259.17(13)
Z	2
ρcalcg/cm^3	1.292
μ/mm^{-1}	0.187

F(000)	516.0
Crystal size/mm^3	0.21 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.92 to 50
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13
Reflections collected	42032
Independent reflections	4436 [R_{int} = 0.0741, R_{sigma} = 0.0422]
Data/restraints/parameters	4436/2/323
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0597, wR_2 = 0.1249
Final R indexes [all data]	R_1 = 0.0879, wR_2 = 0.1338
Largest diff. peak/hole / e Å^{-3}	0.27/-0.25

9.2 X-ray Crystal of 21c'.

The crystal was obtained by recrystallization in ethyl acetate and petroleum ether. Crystal data and structure refinement for **21c'** were with thermal ellipsoids at 50% probability.

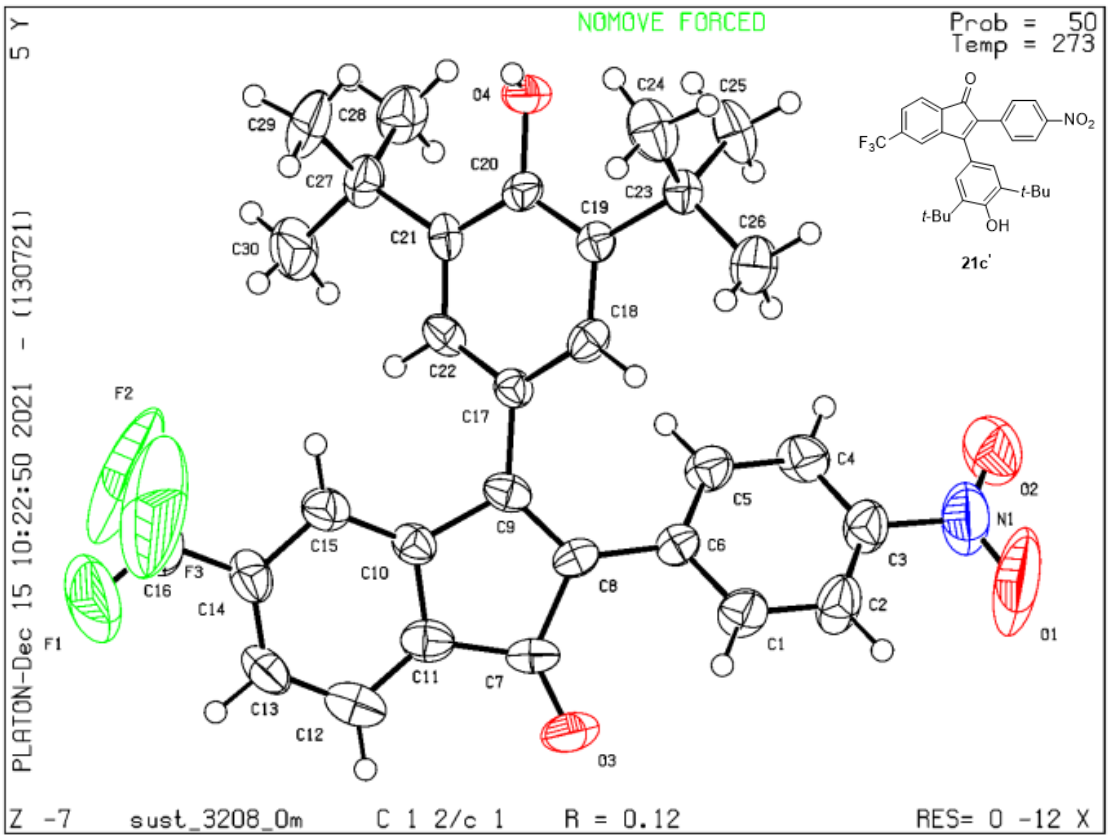


Table S2. Crystal Data and Structure Refinement for **21c'**

Identification code	**21c'**
Empirical formula	$C_{30}H_{28}F_3NO_4$
Formula weight	523.53
Temperature/K	273.15
Crystal system	monoclinic
Space group	C2/c
a/Å	25.520(8)
b/Å	11.215(3)
c/Å	20.049(7)
α/°	90.00
β/°	112.806(9)
γ/°	90.00
Volume/Å^3	5290(3)
Z	8
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	0.101

F(000)	2192.0
Crystal size/mm^3	0.2 × 0.18 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.02 to 49.98
Index ranges	-30 ≤ h ≤ 30, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23
Reflections collected	38214
Independent reflections	4667 [R_{int} = 0.0919, R_{sigma} = 0.0620]
Data/restraints/parameters	4667/12/350
Goodness-of-fit on F^2	1.100
Final R indexes [I>=2σ (I)]	R_1 = 0.1225, wR_2 = 0.2644
Final R indexes [all data]	R_1 = 0.1691, wR_2 = 0.2859
Largest diff. peak/hole / e Å^{-3}	0.61/-0.49

9.3 X-ray Crystal of 22c.

The crystal was obtained by recrystallization in ethyl acetate and petroleum ether. Crystal data and structure refinement for **22c** were with thermal ellipsoids at 50% probability.

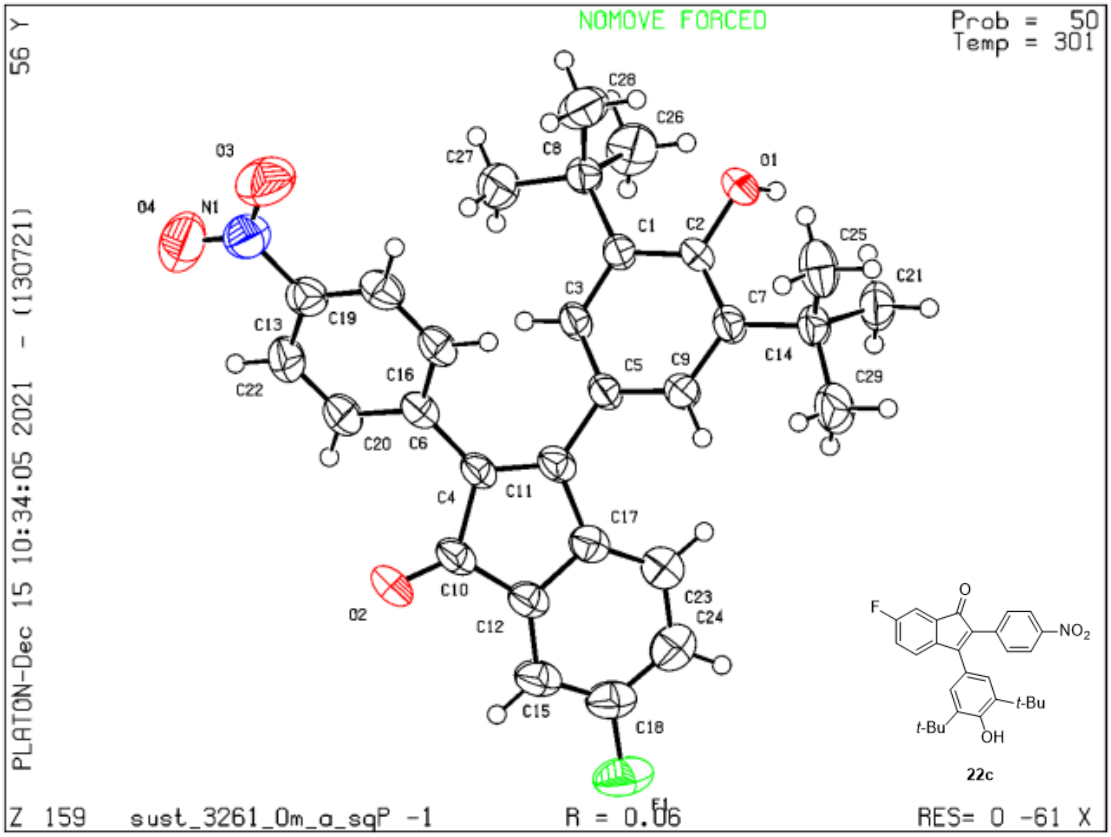


Table S3. Crystal Data and Structure Refinement for **22c**

Identification code	**22c**
Empirical formula	$C_{29}H_{28}FNO_4$
Formula weight	473.52
Temperature/K	301.0
Crystal system	triclinic
Space group	P-1
a/Å	9.4344(4)
b/Å	10.4959(5)
c/Å	14.3304(6)
α/°	96.736(2)
β/°	104.101(2)
γ/°	94.205(2)
Volume/Å^3	1359.10(10)
Z	2
ρ_{calc}g/cm^3	1.157
μ/mm^{-1}	0.081

F(000)	500.0
Crystal size/mm^3	0.21 × 0.19 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.476 to 49.998
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17
Reflections collected	40874
Independent reflections	4795 [R_{int} = 0.0536, R_{sigma} = 0.0329]
Data/restraints/parameters	4795/1/323
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0573, wR_2 = 0.1697
Final R indexes [all data]	R_1 = 0.0851, wR_2 = 0.1845
Largest diff. peak/hole / e Å^{-3}	0.26/-0.39

9.4 X-ray Crystal of 25C.

The crystal was obtained by recrystallization in ethyl acetate and petroleum ether. Crystal data and structure refinement for **25c** were with thermal ellipsoids at 50% probability.

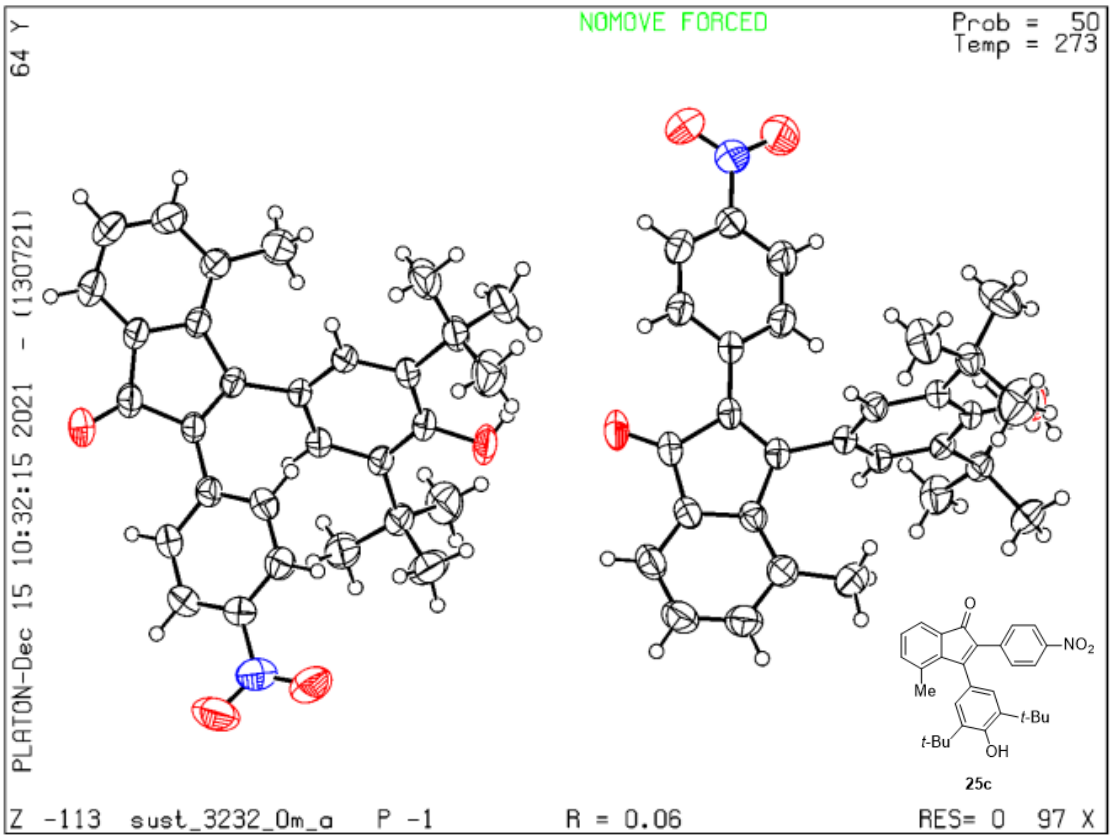


Table S4. Crystal Data and Structure Refinement for **25c**

Identification code	**25c**
Empirical formula	$C_{30}H_{31}NO_4$
Formula weight	469.56
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
a/Å	11.4176(5)
b/Å	11.6040(5)
c/Å	22.5633(10)
α/°	98.223(2)
β/°	92.734(2)
γ/°	119.2730(10)
Volume/Å^3	2556.78(19)
Z	4
ρ_{calc}g/cm^3	1.220
μ/mm^{-1}	0.080

F(000)	1000.0
Crystal size/mm^3	0.21 × 0.21 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.1 to 50
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -26 ≤ l ≤ 26
Reflections collected	79313
Independent reflections	9021 [R_{int} = 0.0882, R_{sigma} = 0.0527]
Data/restraints/parameters	9021/10/647
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0553, wR_2 = 0.1344
Final R indexes [all data]	R_1 = 0.1102, wR_2 = 0.1613
Largest diff. peak/hole / e Å^{-3}	0.36/-0.34

9.5 X-ray Crystal of 33C.

The crystal was obtained by recrystallization in ethyl acetate and petroleum ether. Crystal data and structure refinement for **33c** were with thermal ellipsoids at 50% probability.

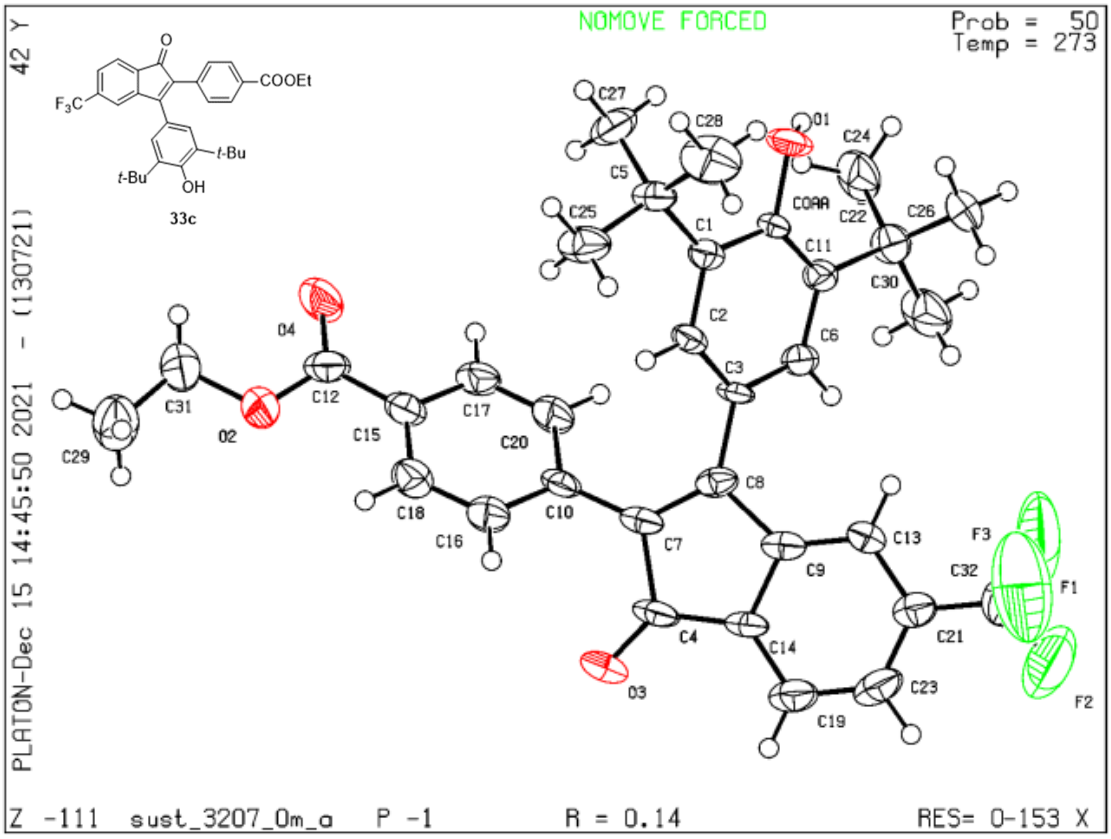


Table S5. Crystal Data and Structure Refinement for **33c**

Identification code	**33c**
Empirical formula	$C_{32}H_{33}F_3NO_4$
Formula weight	552.59
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
a/Å	9.1533(13)
b/Å	12.2143(16)
c/Å	13.953(2)
α/°	96.106(5)
β/°	106.461(5)
γ/°	90.549(5)
Volume/Å^3	1486.3(4)
Z	2
ρ_{calc}g/cm^3	1.235
μ/mm^{-1}	0.093

F(000)	582.0
Crystal size/mm^3	0.18 × 0.17 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.28 to 50
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	42190
Independent reflections	5232 [R_{int} = 0.1761, R_{sigma} = 0.1155]
Data/restraints/parameters	5232/4/369
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.1379, wR_2 = 0.2837
Final R indexes [all data]	R_1 = 0.2196, wR_2 = 0.3238
Largest diff. peak/hole / e Å^{-3}	0.60/-0.55

9.6 X-ray Crystal of 34C.

The crystal was obtained by recrystallization in ethyl acetate and petroleum ether. Crystal data and structure refinement for **34c** were with thermal ellipsoids at 50% probability.

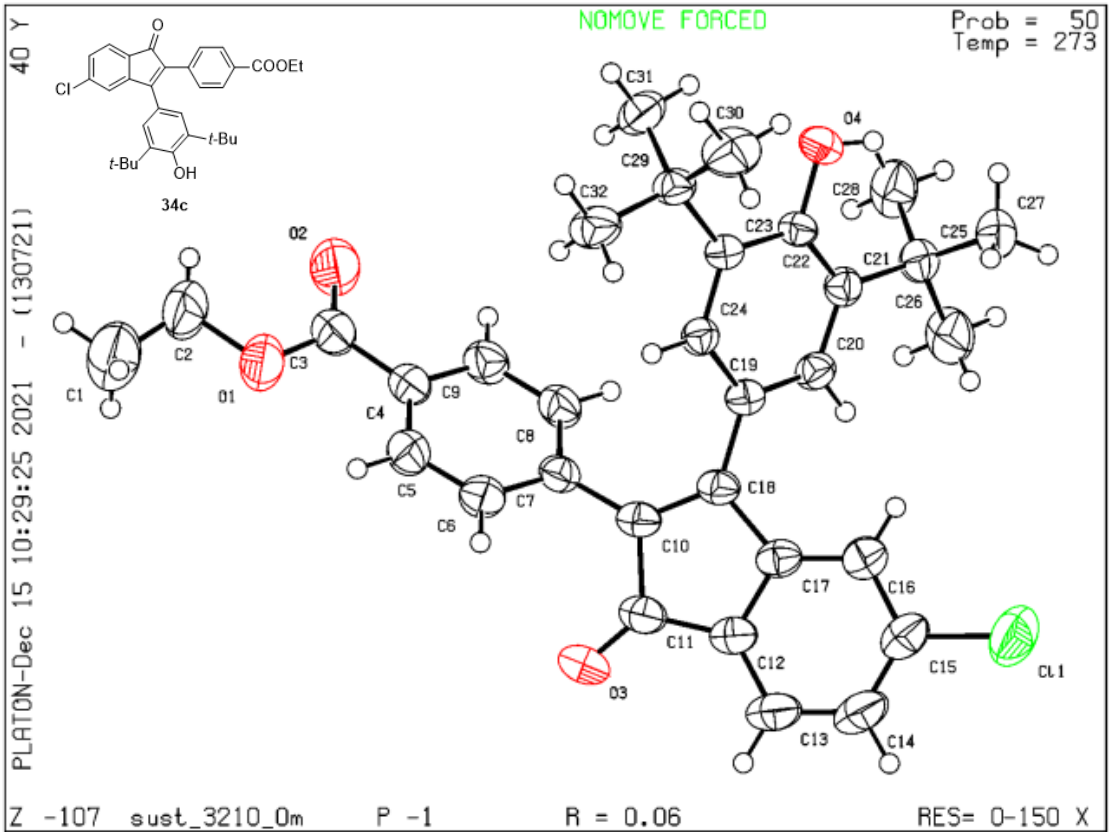


Table S6. Crystal Data and Structure Refinement for **34c**

Identification code	**34c**
Empirical formula	$C_{32}H_{33}ClO_4$
Formula weight	517.03
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
a/Å	9.1084(5)
b/Å	11.8341(7)
c/Å	13.8157(8)
α/°	94.809(2)
β/°	107.322(2)
γ/°	91.397(2)
Volume/Å^3	1414.74(14)
Z	2
ρ_{calc}g/cm^3	1.214
μ/mm^{-1}	0.169

F(000)	548.0
Crystal size/mm^3	0.2 × 0.19 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.42 to 50
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	42560
Independent reflections	4972 [R_{int} = 0.0675, R_{sigma} = 0.0411]
Data/restraints/parameters	4972/2/342
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0601, wR_2 = 0.1536
Final R indexes [all data]	R_1 = 0.0995, wR_2 = 0.1699
Largest diff. peak/hole / e Å^{-3}	0.44/-0.31

9.7 X-ray Crystal of 35C.

The crystal was obtained by recrystallization in ethyl acetate and petroleum ether. Crystal data and structure refinement for **35c** were with thermal ellipsoids at 50% probability.

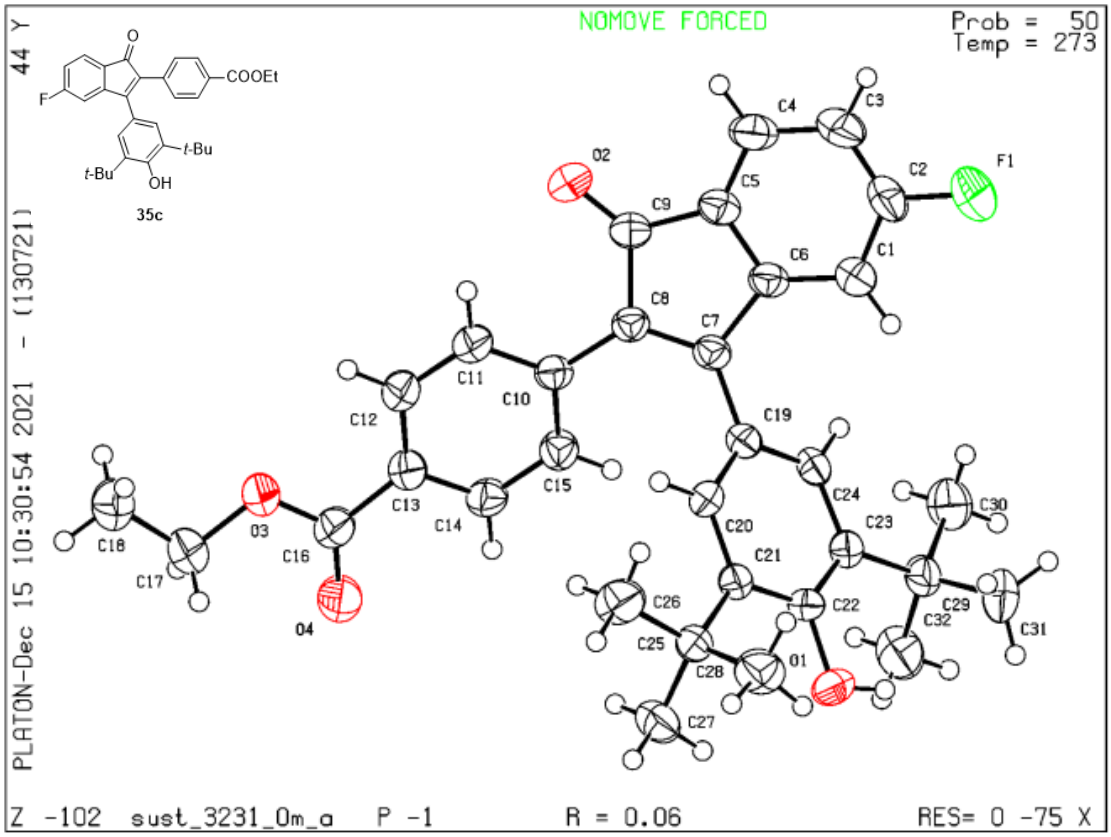


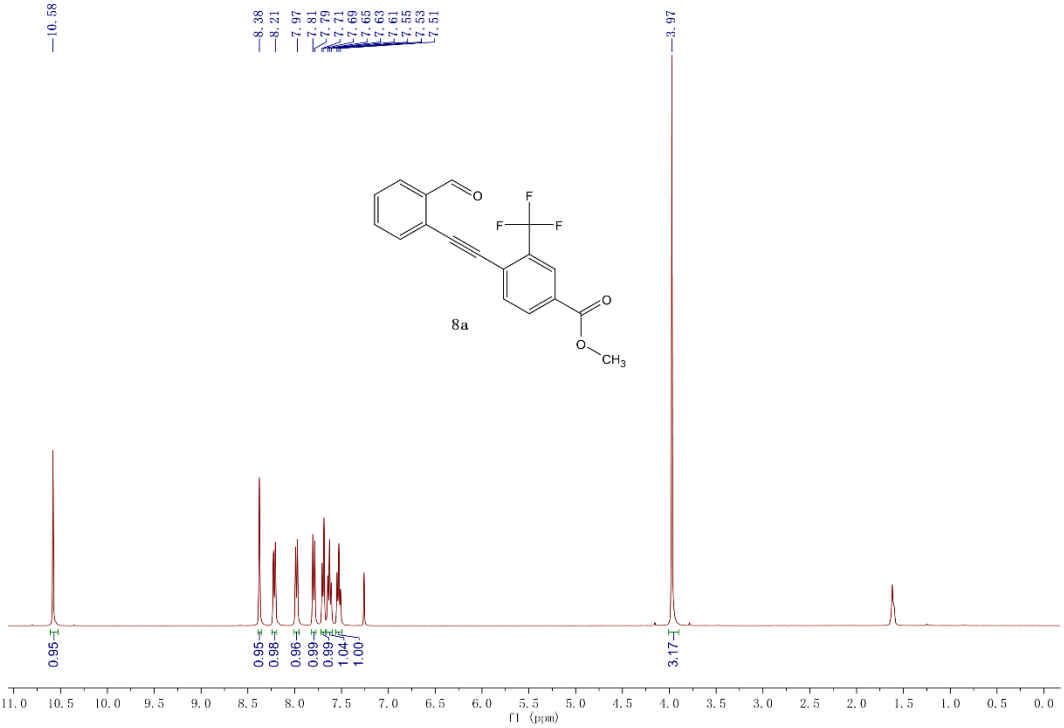
Table S7. Crystal Data and Structure Refinement for **35c**

Identification code	**35c**
Empirical formula	$C_{32}H_{33}FO_4$
Formula weight	500.58
Temperature/K	273.15
Crystal system	triclinic
Space group	P-1
a/Å	10.7537(13)
b/Å	11.4253(14)
c/Å	11.8372(15)
α/°	83.875(4)
β/°	77.861(4)
γ/°	68.433(4)
Volume/Å^3	1321.6(3)
Z	2
ρ_{calc}g/cm^3	1.258
μ/mm^{-1}	0.086

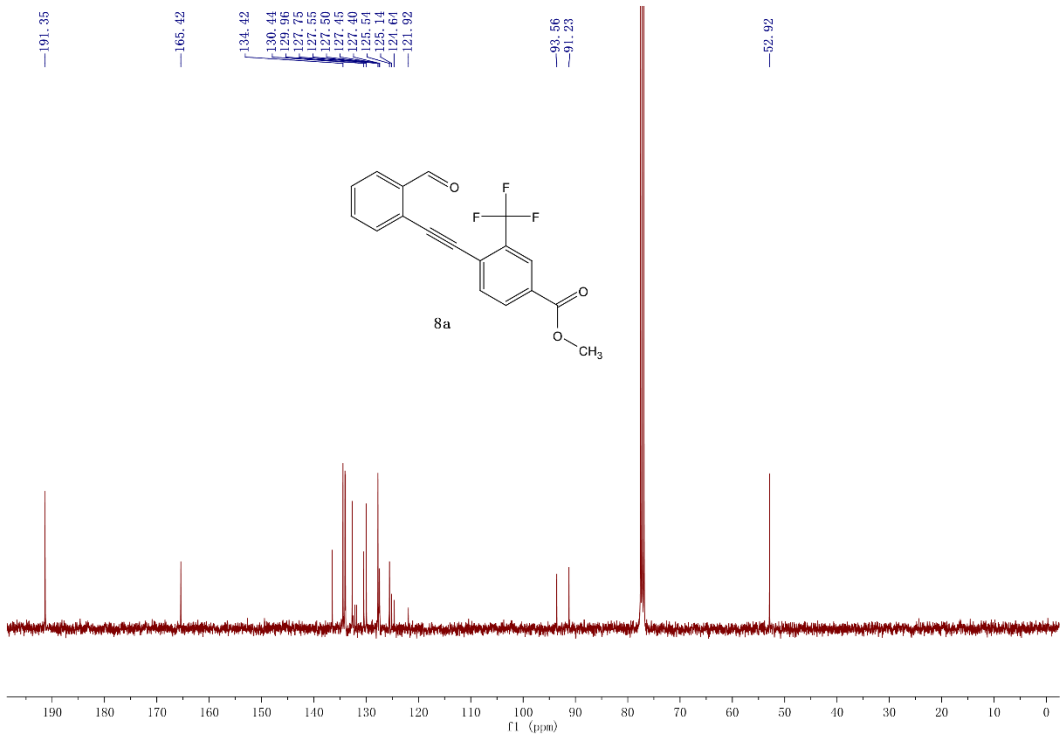
F(000)	532.0
Crystal size/mm^3	0.21 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.14 to 49.98
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	39970
Independent reflections	4645 [R_{int} = 0.1147, R_{sigma} = 0.0742]
Data/restraints/parameters	4645/2/342
Goodness-of-fit on F^2	1.005
Final R indexes [I>=2σ (I)]	R_1 = 0.0618, wR_2 = 0.1492
Final R indexes [all data]	R_1 = 0.1410, wR_2 = 0.1799
Largest diff. peak/hole / e Å^{-3}	0.31/-0.31

10. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectral Copies.

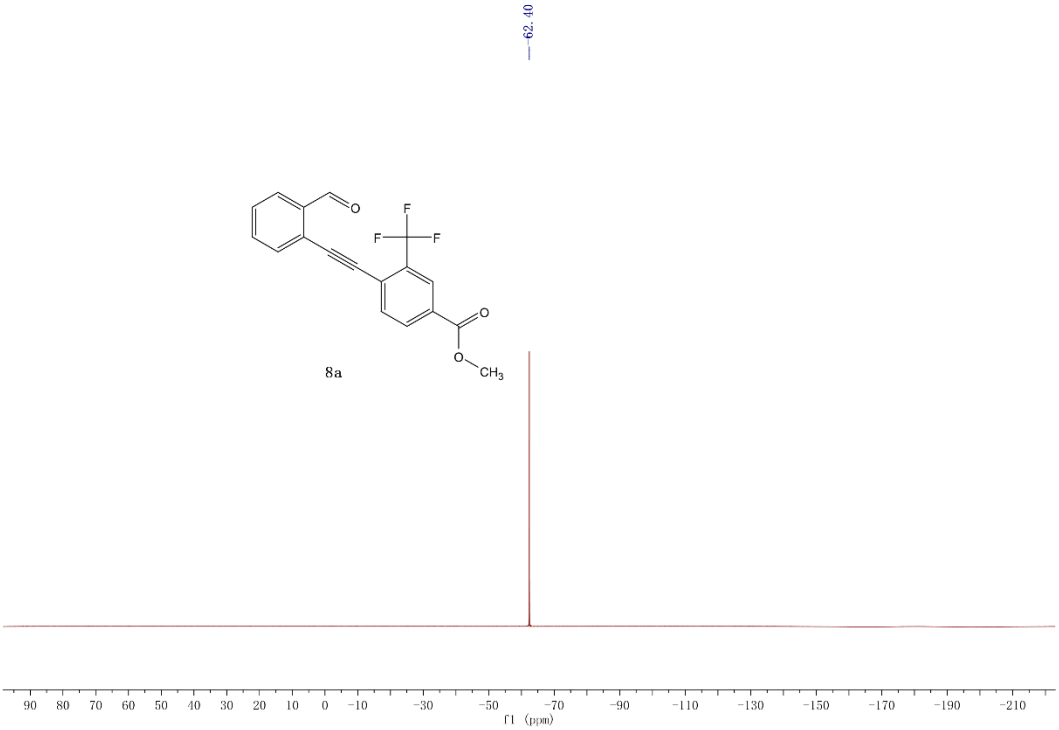
^{1}H NMR (400MHz, $CDCl_3$) for **8a.**



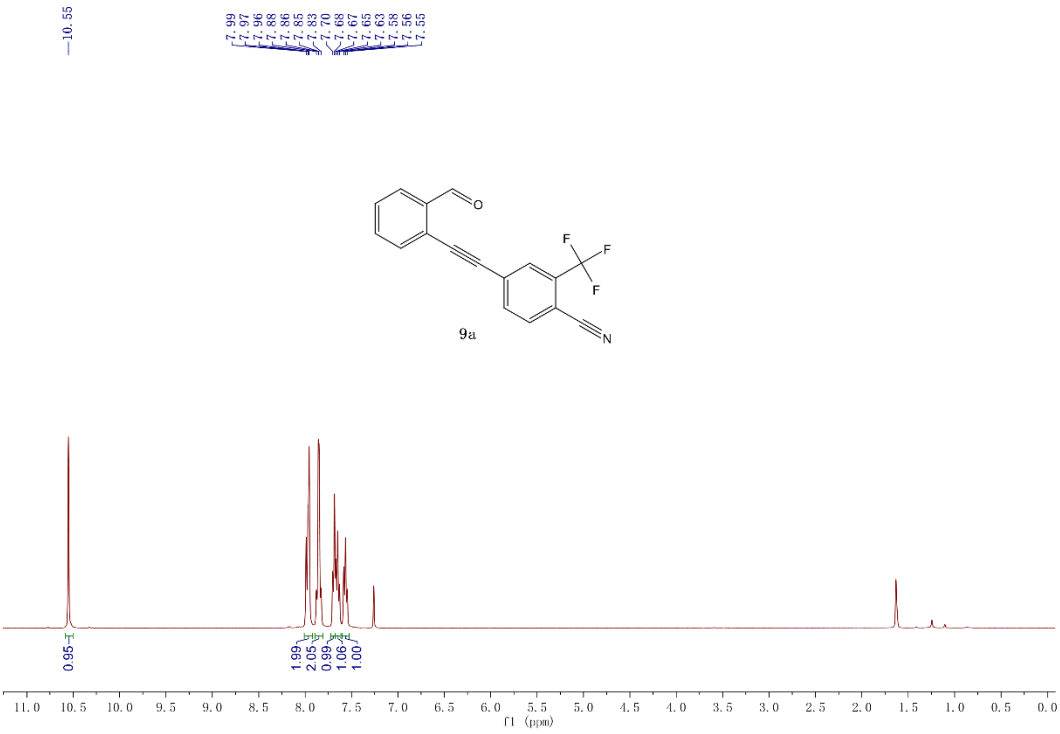
^{13}C NMR (101 MHz, $CDCl_3$) for **8a**.



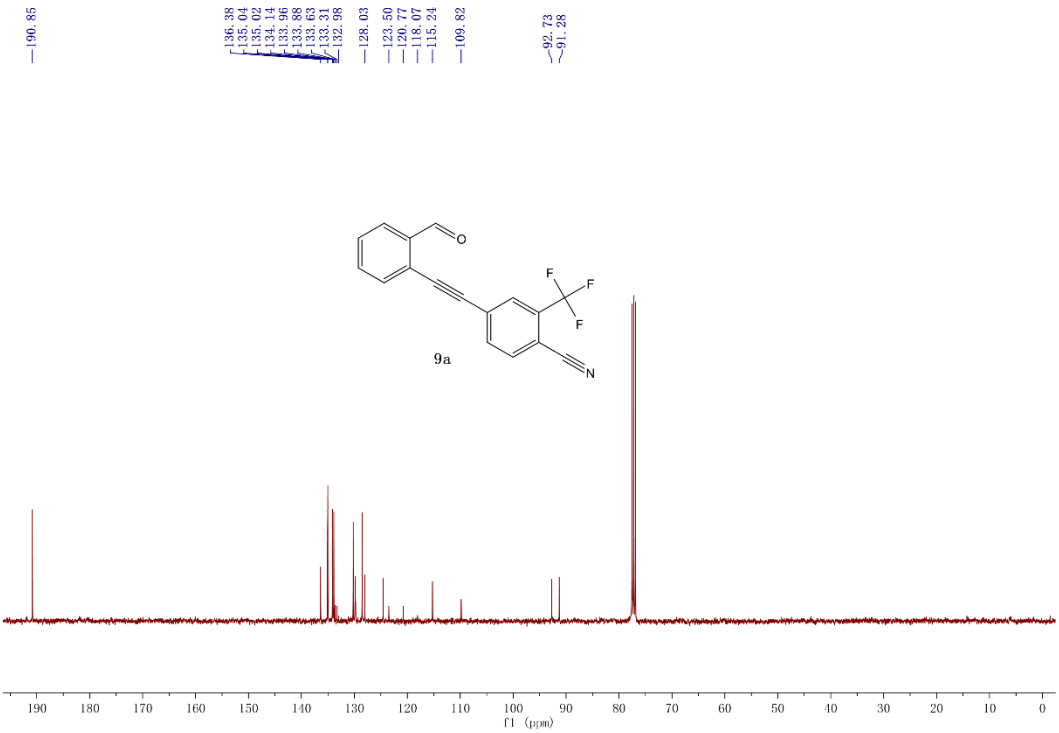
^{19}F NMR (377 MHz, $CDCl_3$) for **8a**.



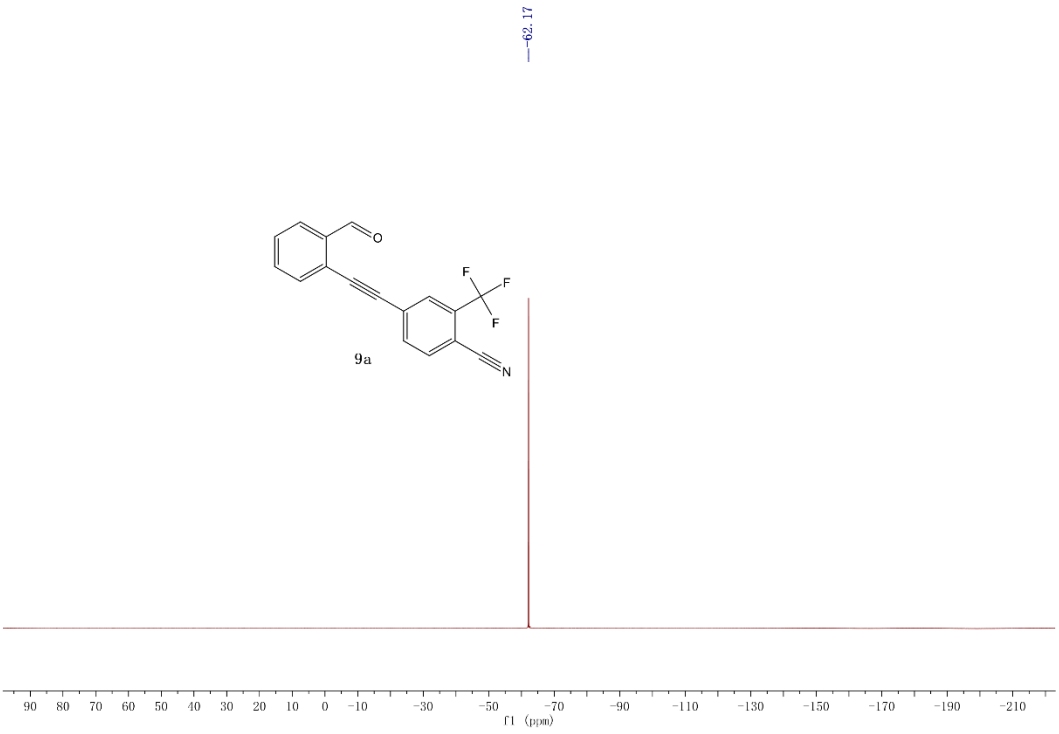
^{1}H NMR (400MHz, $CDCl_3$) for **9a.**



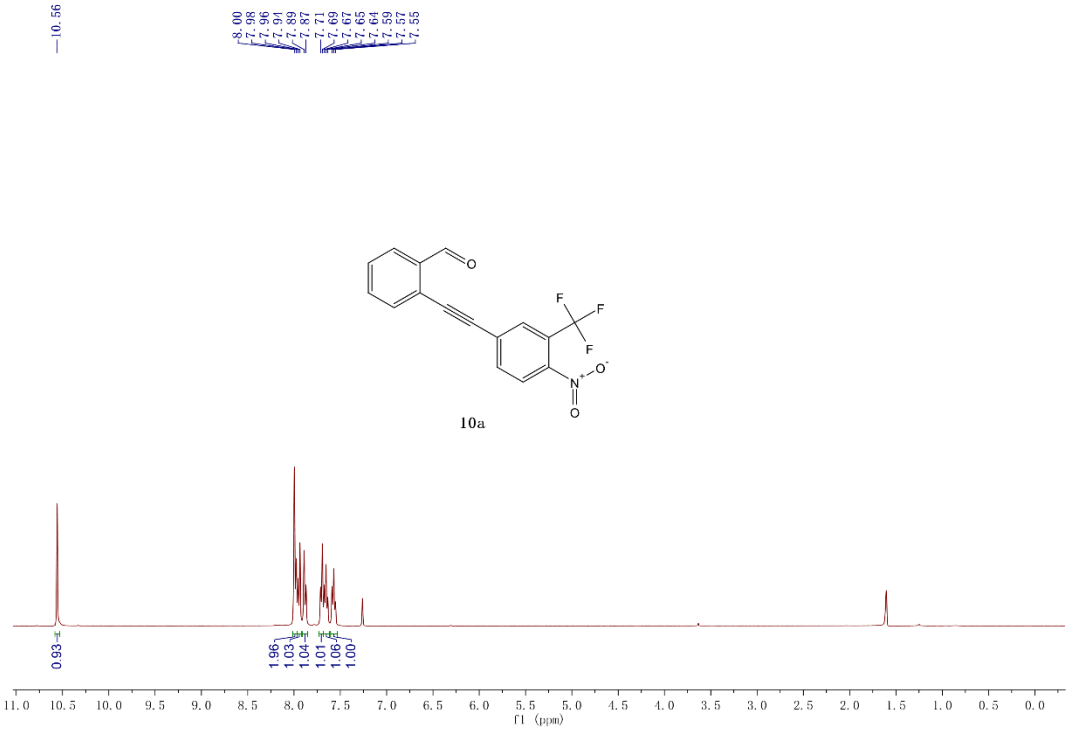
^{13}C NMR (101 MHz, $CDCl_3$) for **9a**.



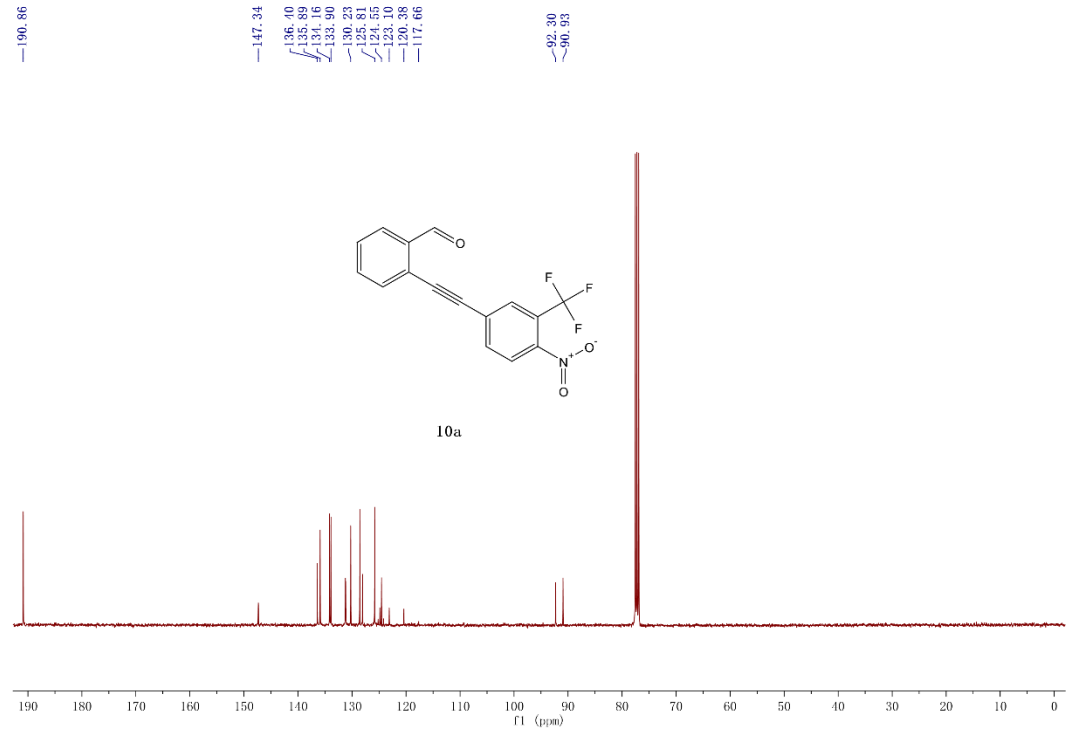
^{19}F NMR (377 MHz, $CDCl_3$) for **9a**.



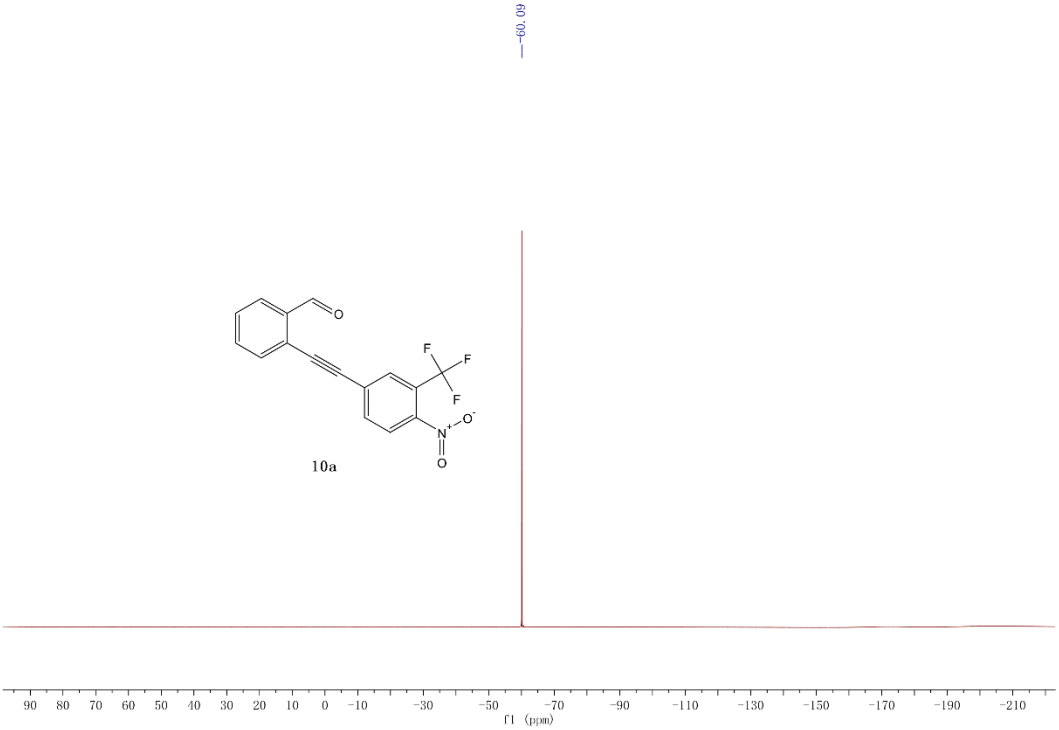
^{1}H NMR (400MHz, $CDCl_3$) for **10a**



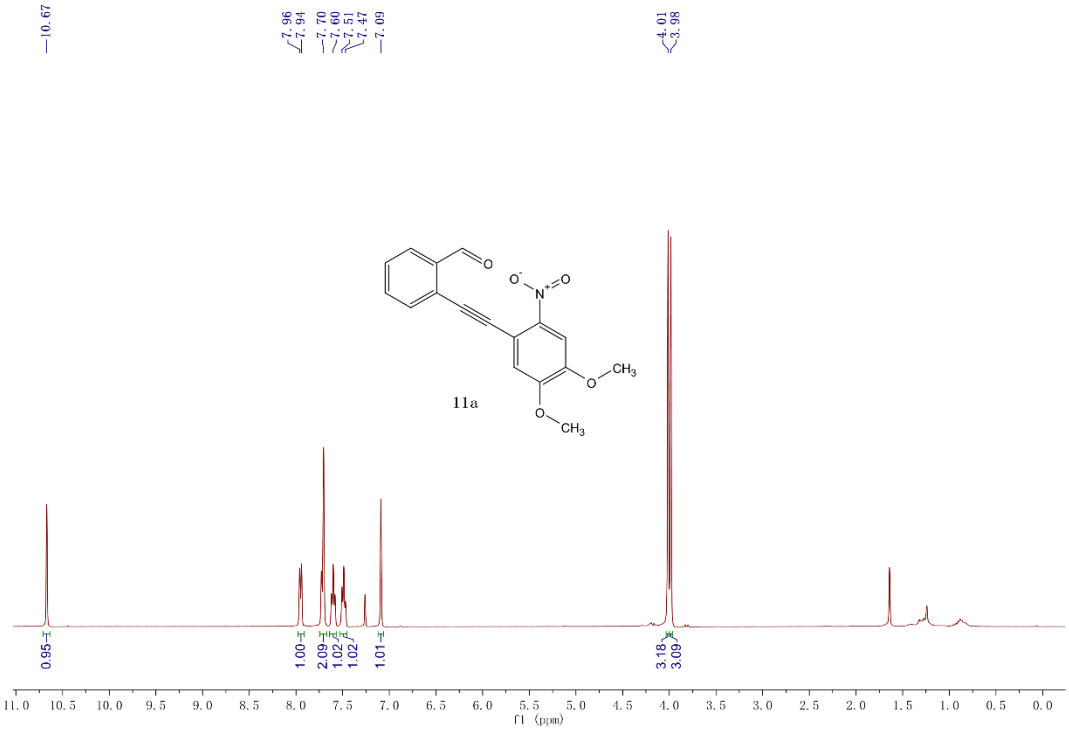
^{13}C NMR (101 MHz, $CDCl_3$) for **10a**.



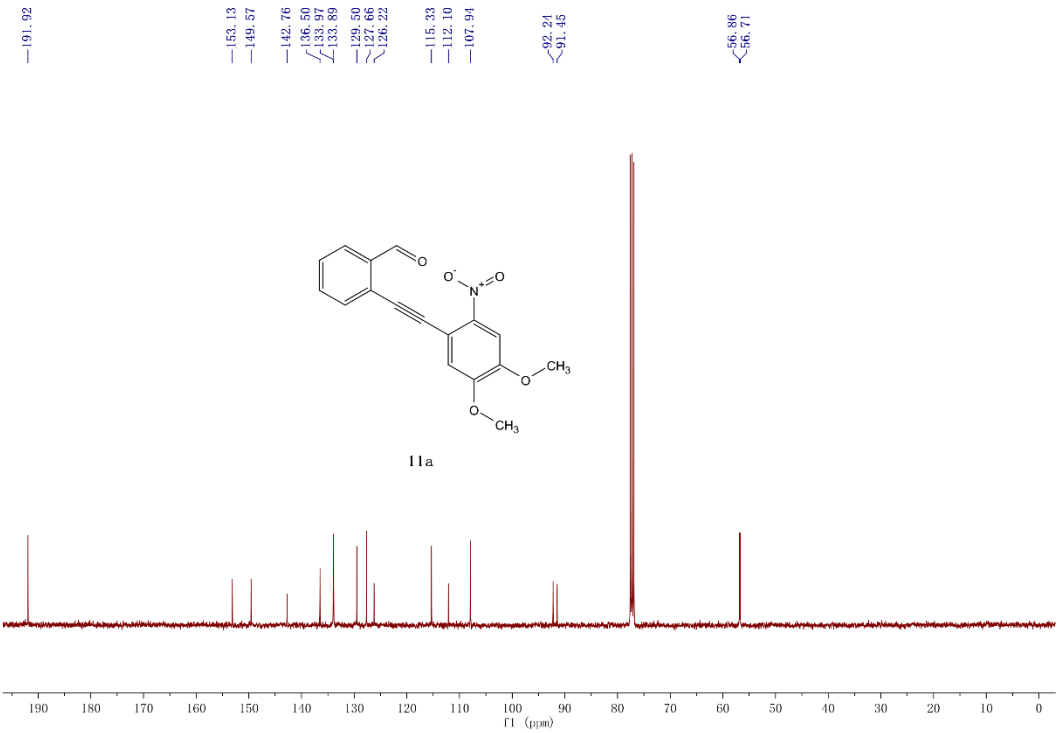
^{19}F NMR (377 MHz, $CDCl_3$) for **10a**.



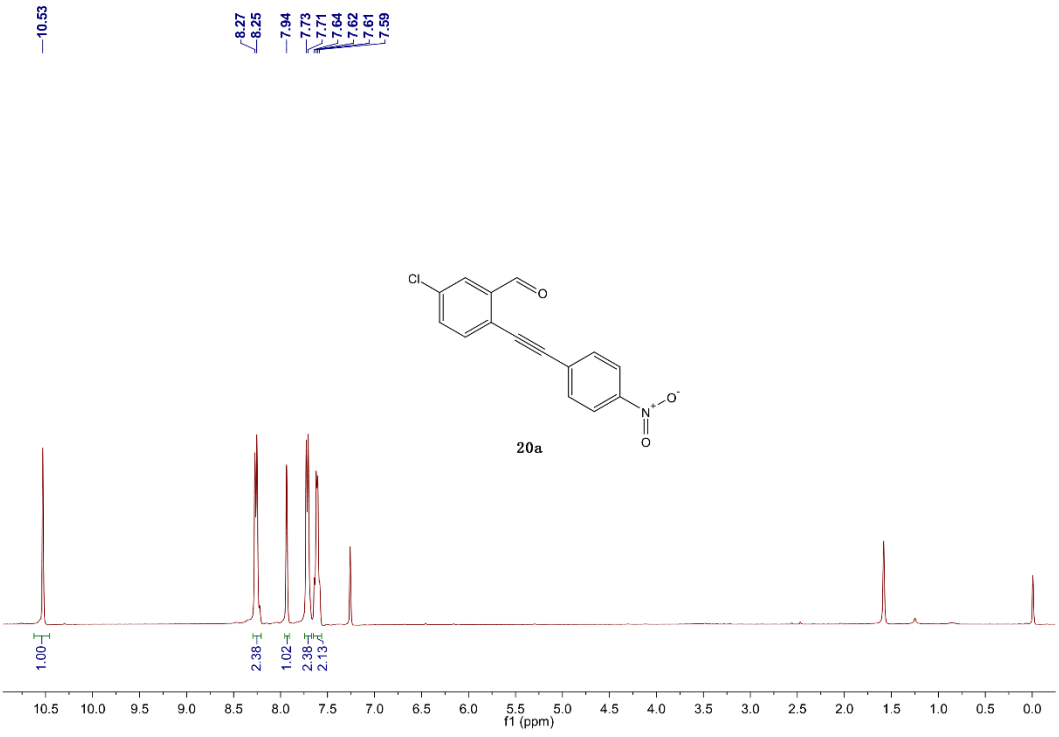
^{1}H NMR (400MHz, $CDCl_3$) for **11a**



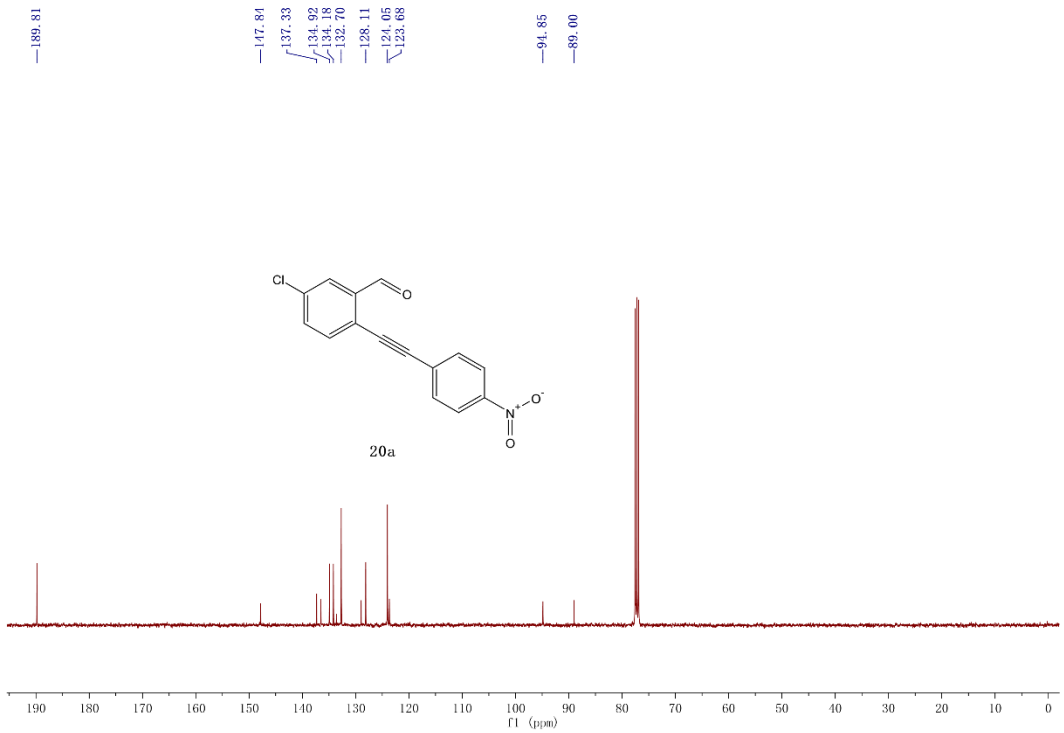
^{13}C NMR (101 MHz, $CDCl_3$) for **11a**.



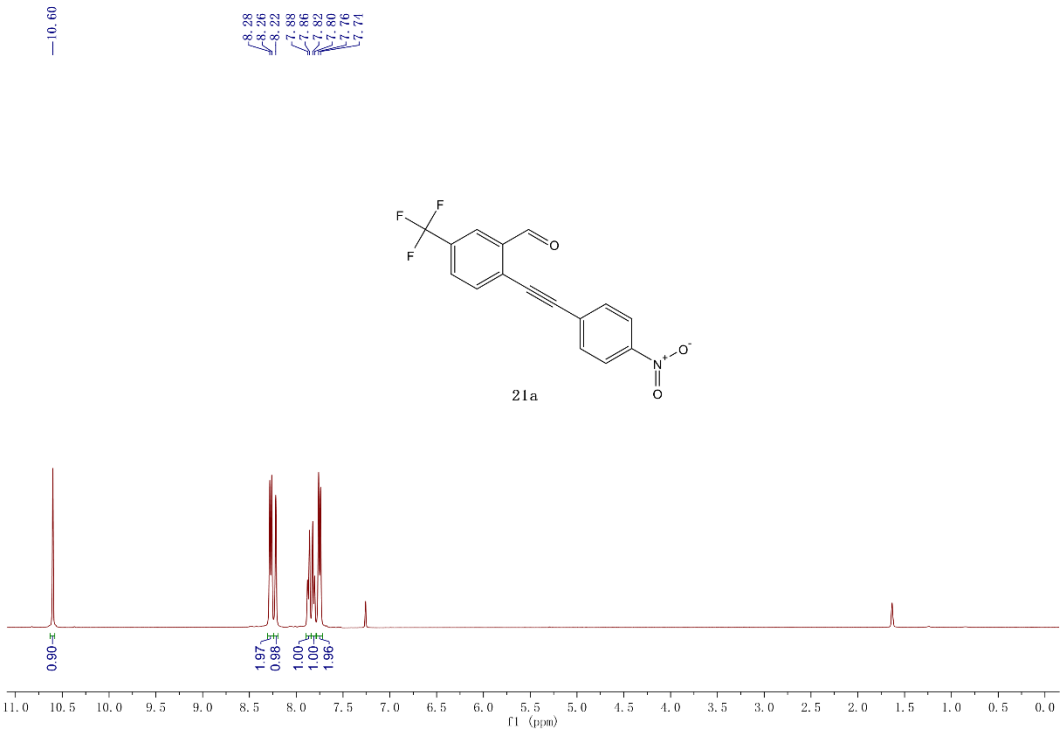
^{1}H NMR (400MHz, $CDCl_3$) for **20a**



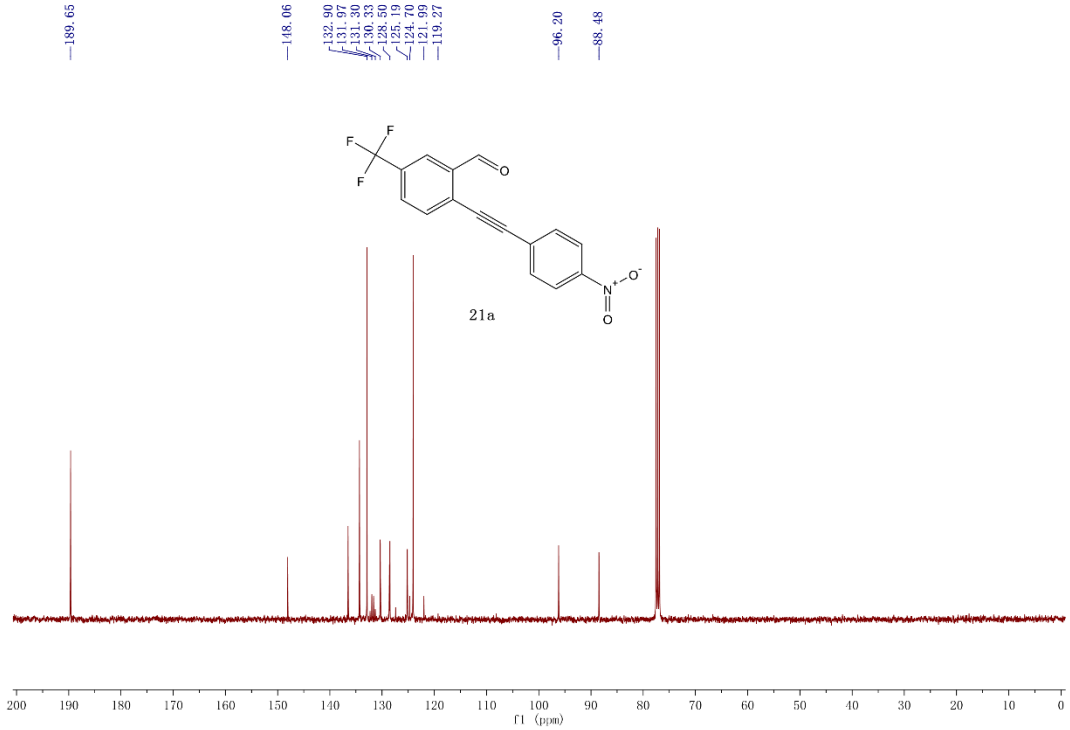
^{13}C NMR (101 MHz, $CDCl_3$) for **20a**.



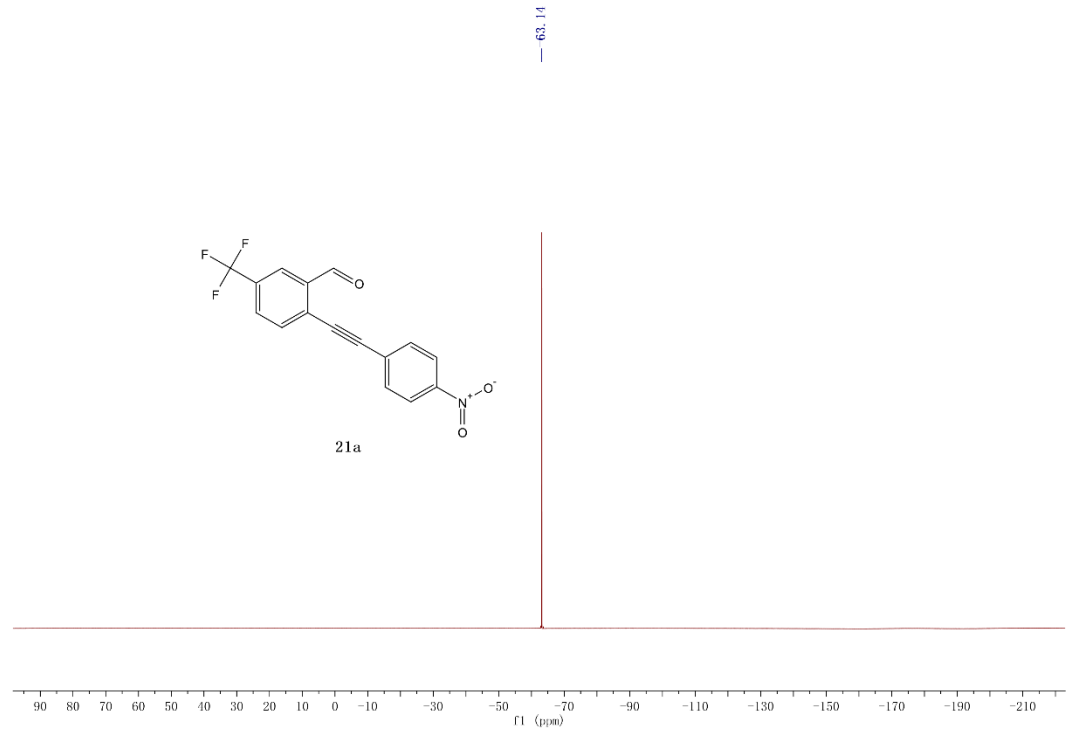
^{1}H NMR (400MHz, $CDCl_3$) for **21a**.



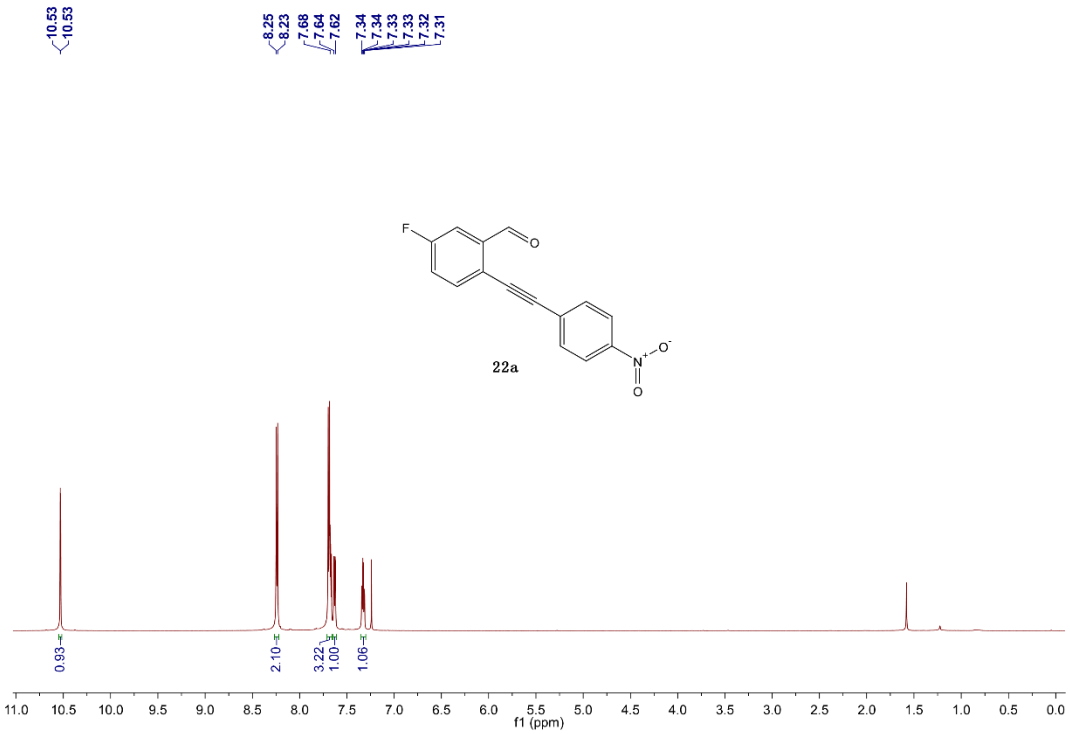
^{13}C NMR (101 MHz, $CDCl_3$) for **21a**.



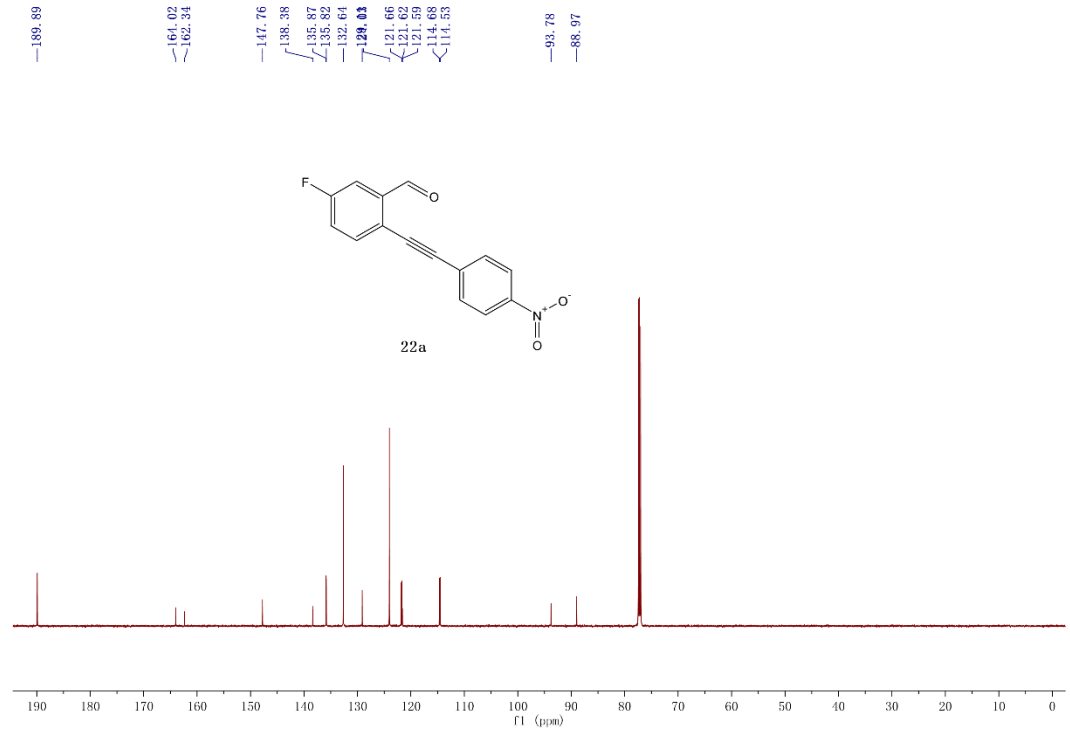
^{19}F NMR (377 MHz, $CDCl_3$) for **21a**.



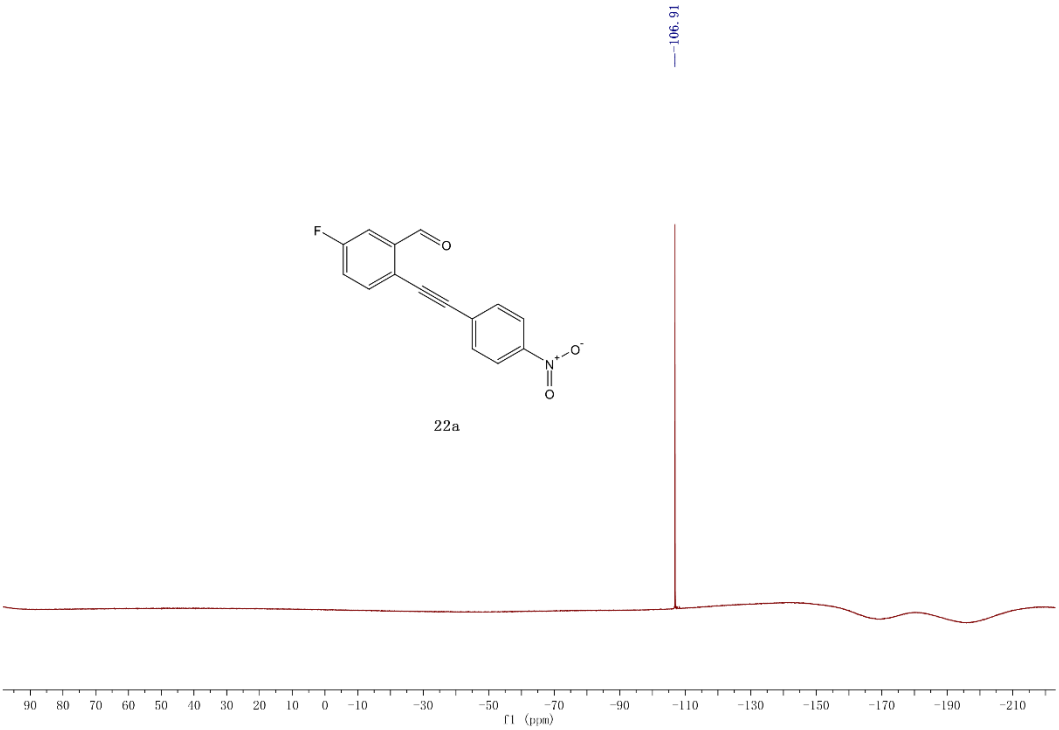
^{1}H NMR (600MHz, $CDCl_3$) for **22a**.



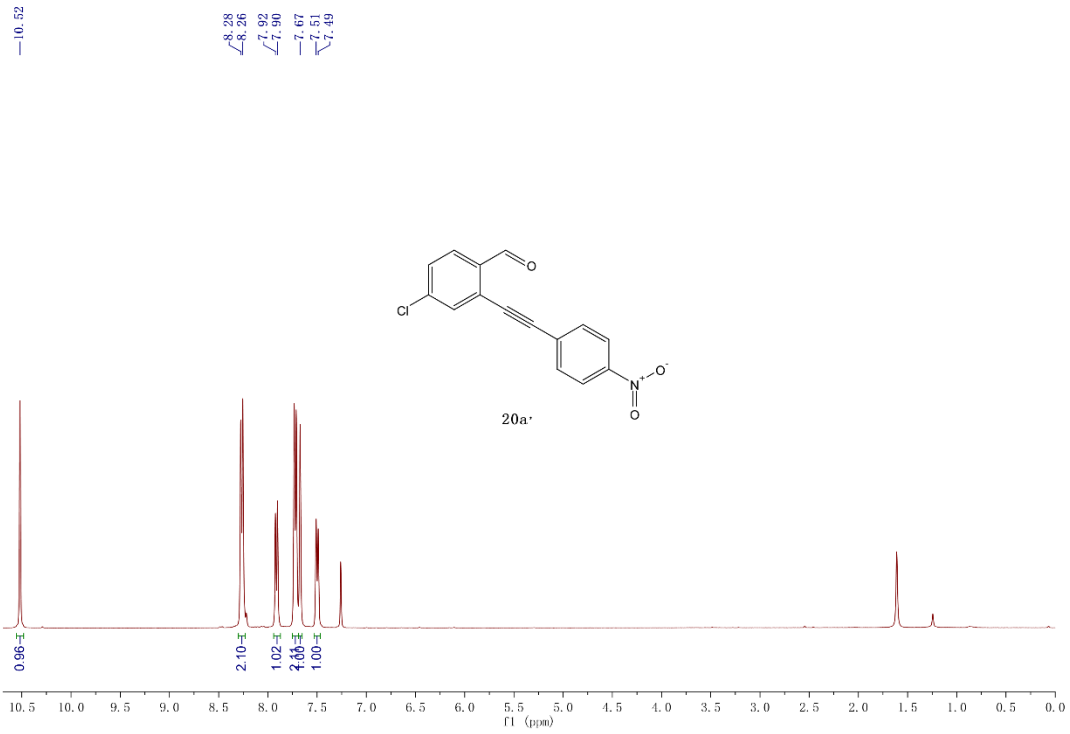
^{13}C NMR (151 MHz, $CDCl_3$) for **22a**.



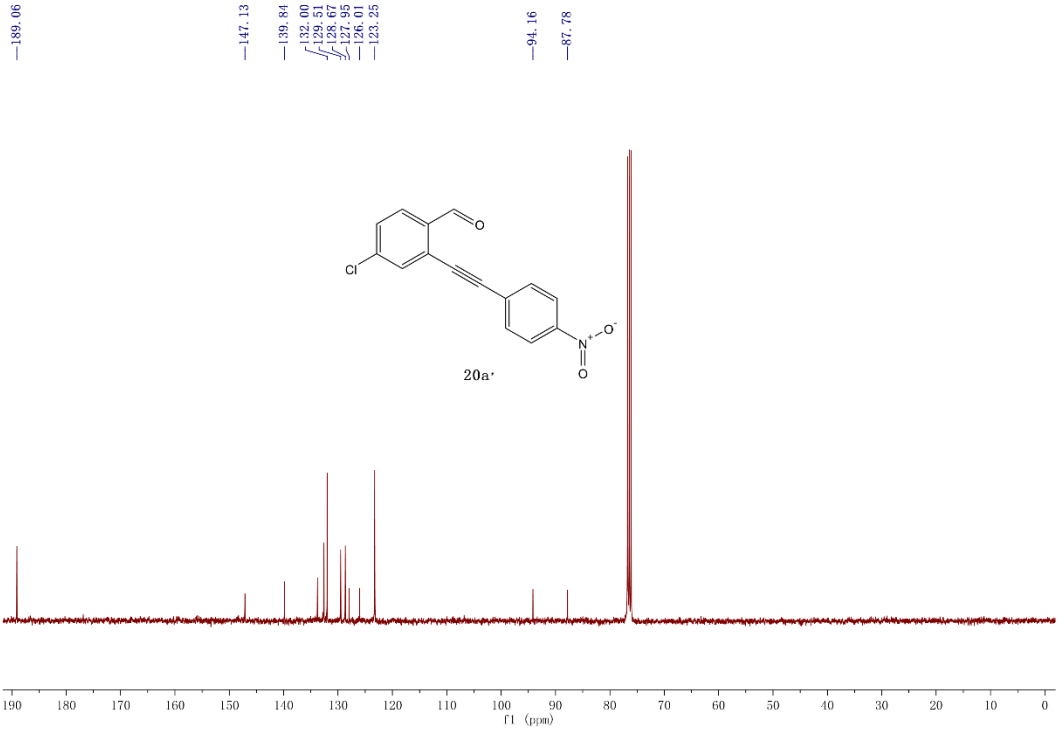
^{19}F NMR (377 MHz, $CDCl_3$) for **22a**.



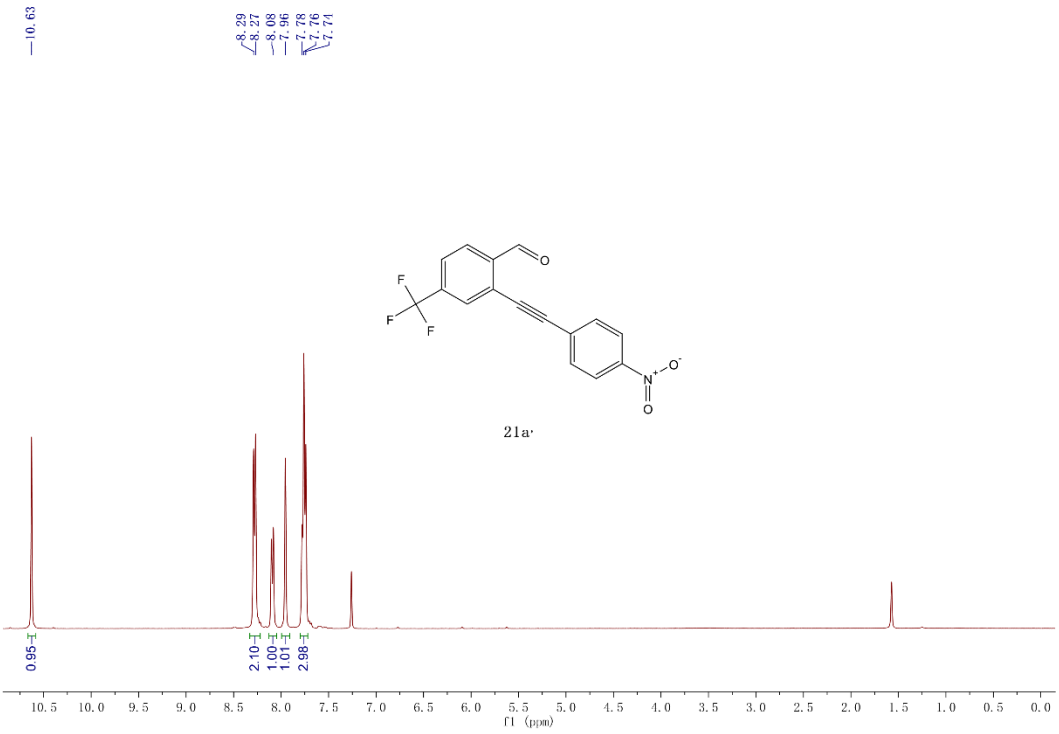
^{1}H NMR (400MHz, $CDCl_3$) for **20a'**.



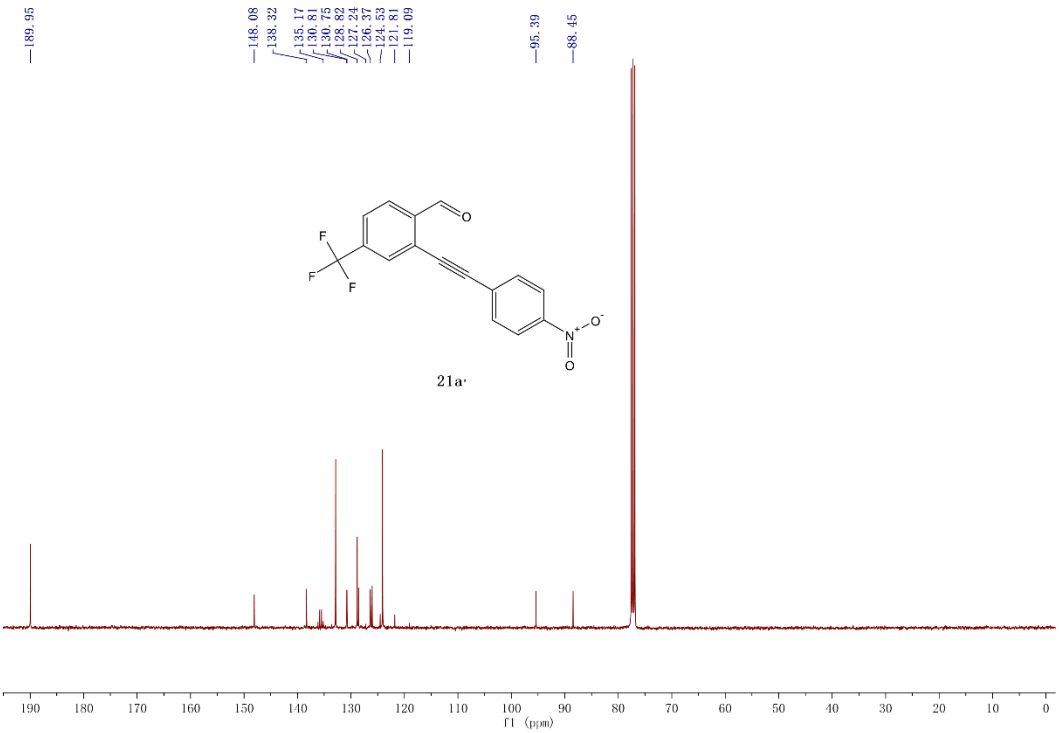
^{13}C NMR (101 MHz, $CDCl_3$) for **20a'**.



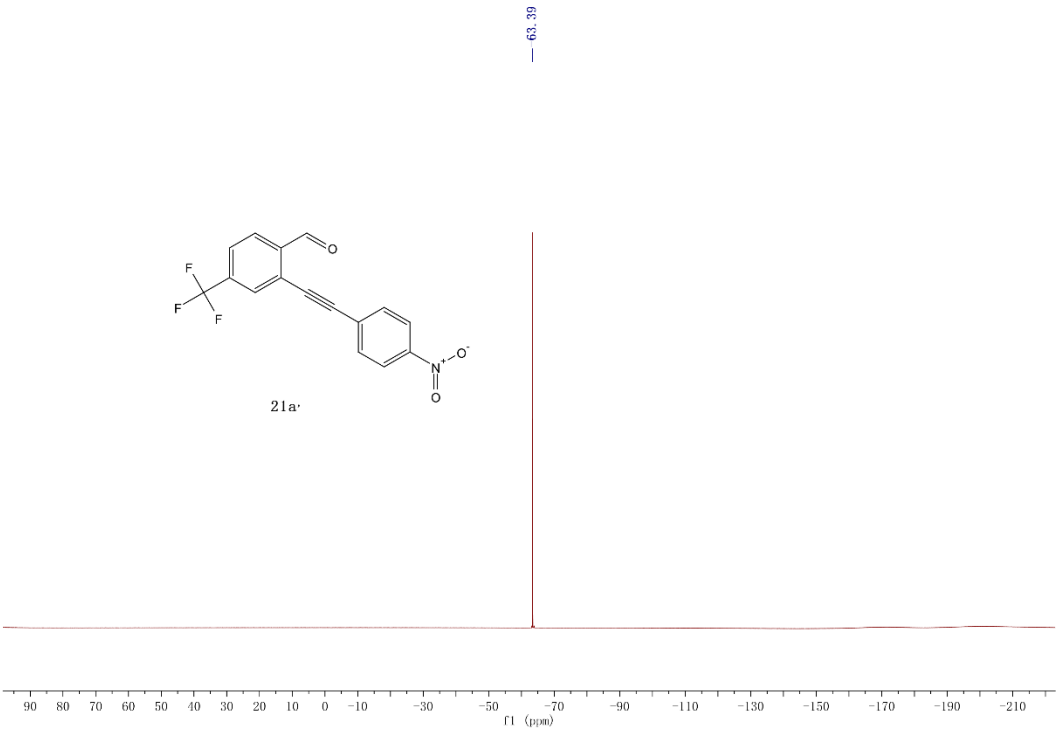
^{1}H NMR (400MHz, $CDCl_3$) for **21a'**.



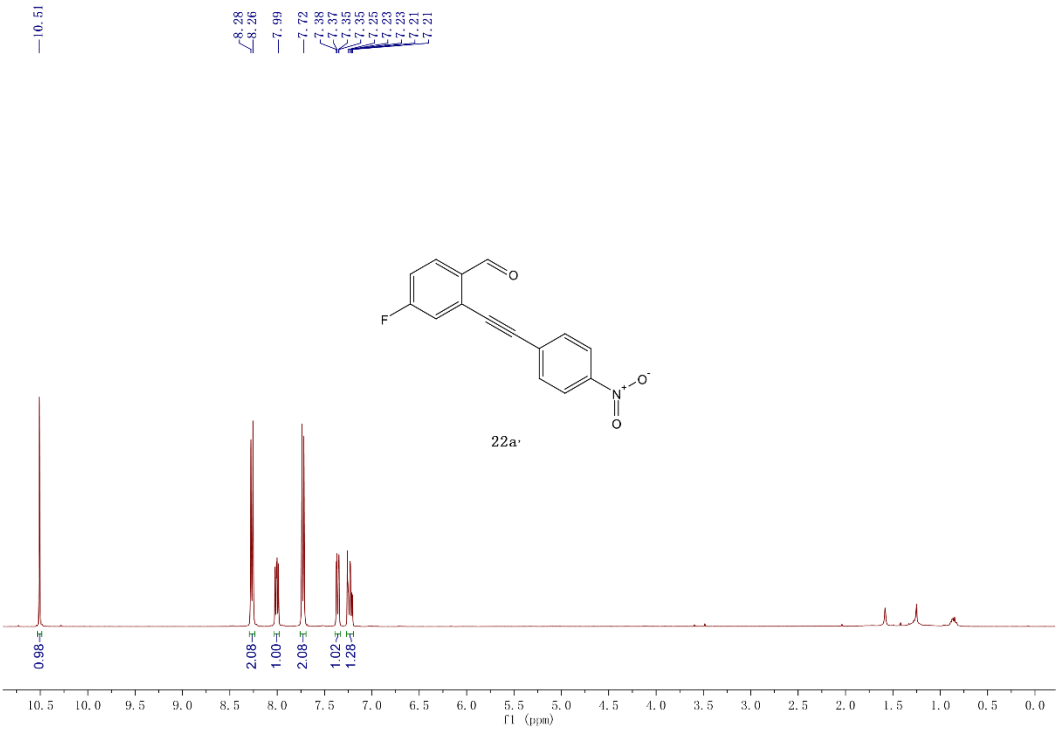
^{13}C NMR (101 MHz, $CDCl_3$) for **21a'**.



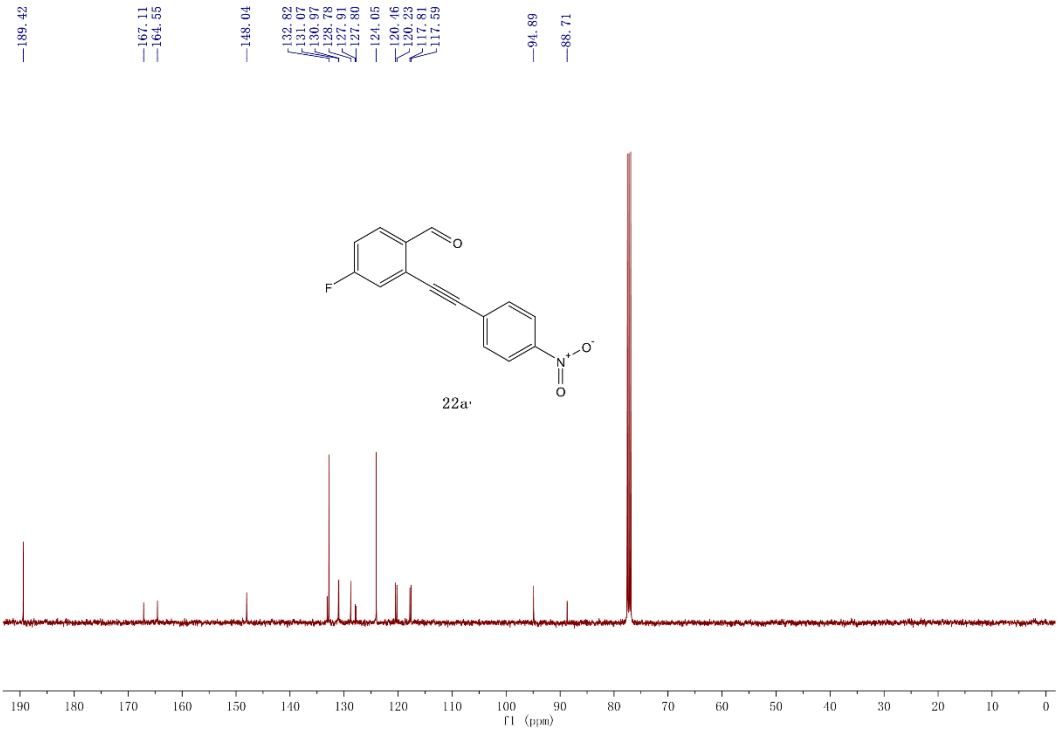
^{19}F NMR (377 MHz, $CDCl_3$) for **21a'**.



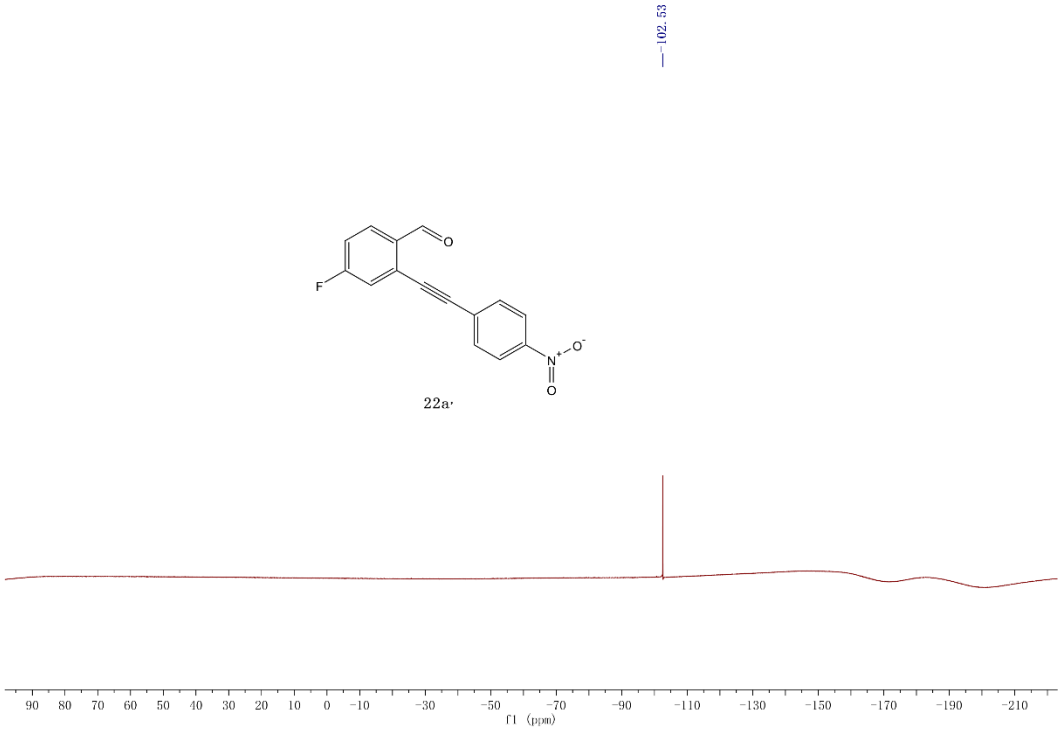
^{1}H NMR (400MHz, $CDCl_3$) for **22a'**.



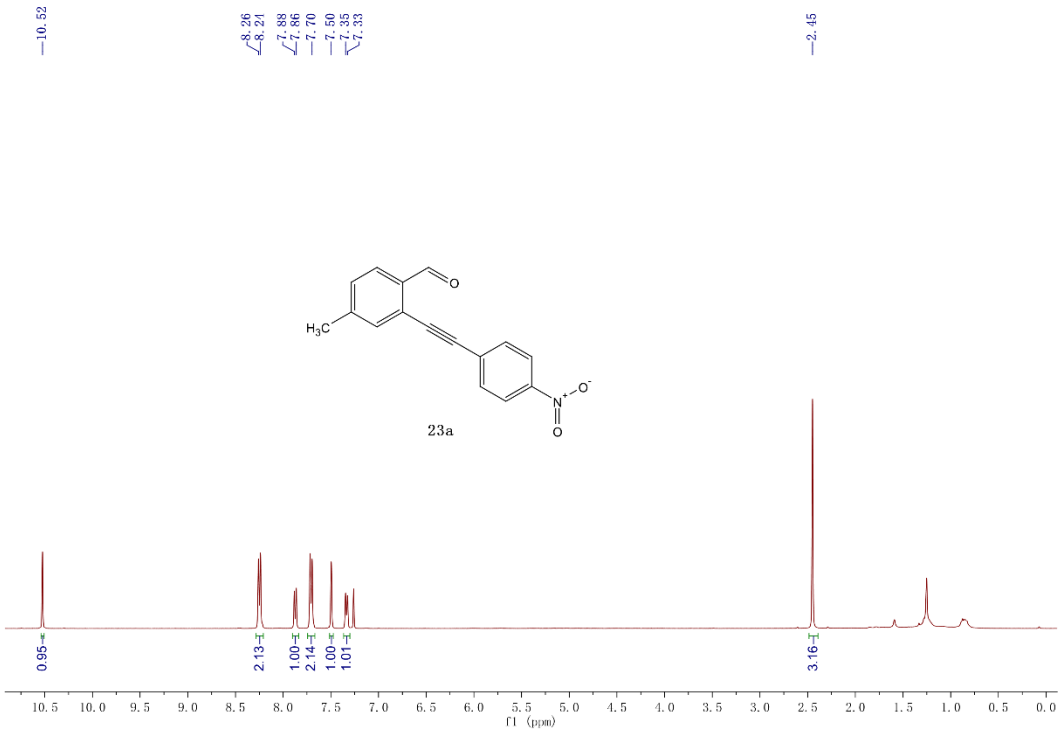
^{13}C NMR (101 MHz, $CDCl_3$) for **22a'**.



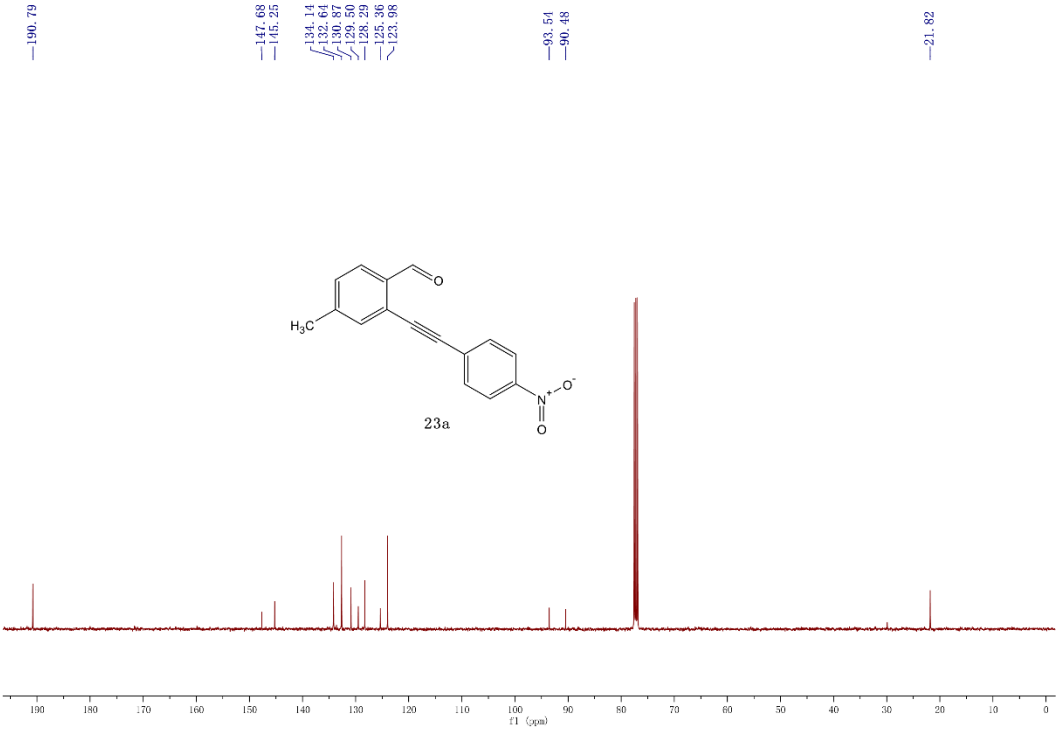
^{19}F NMR (377 MHz, $CDCl_3$) for **22a'**.



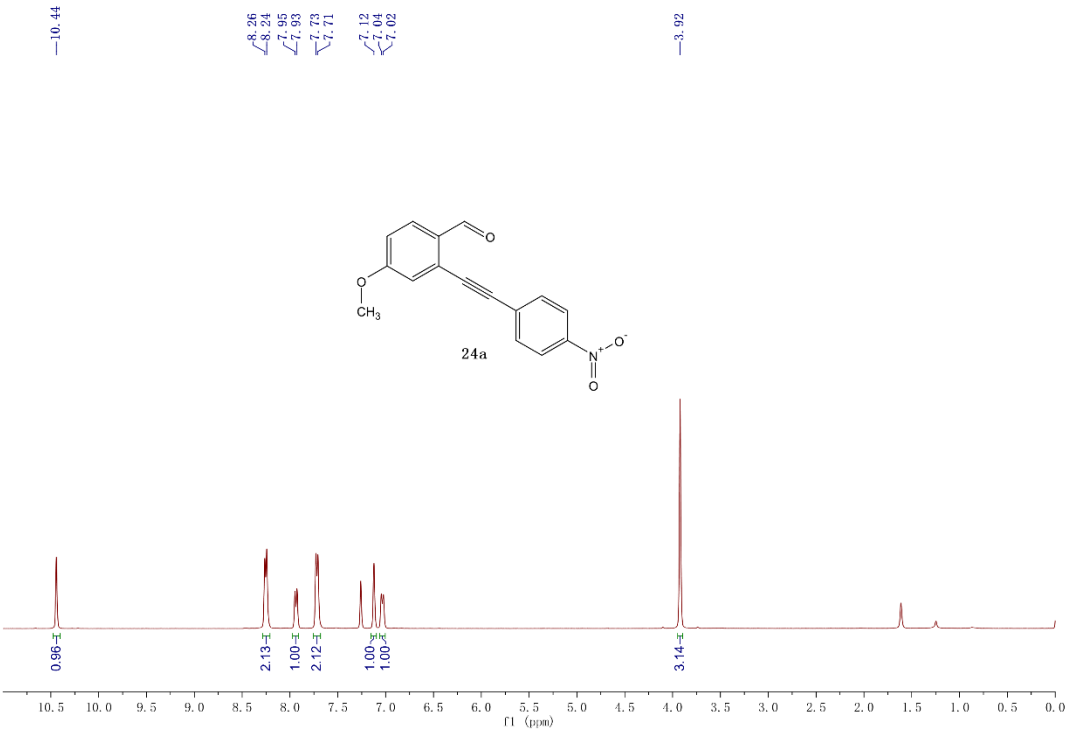
^{1}H NMR (400MHz, $CDCl_3$) for **23a**.



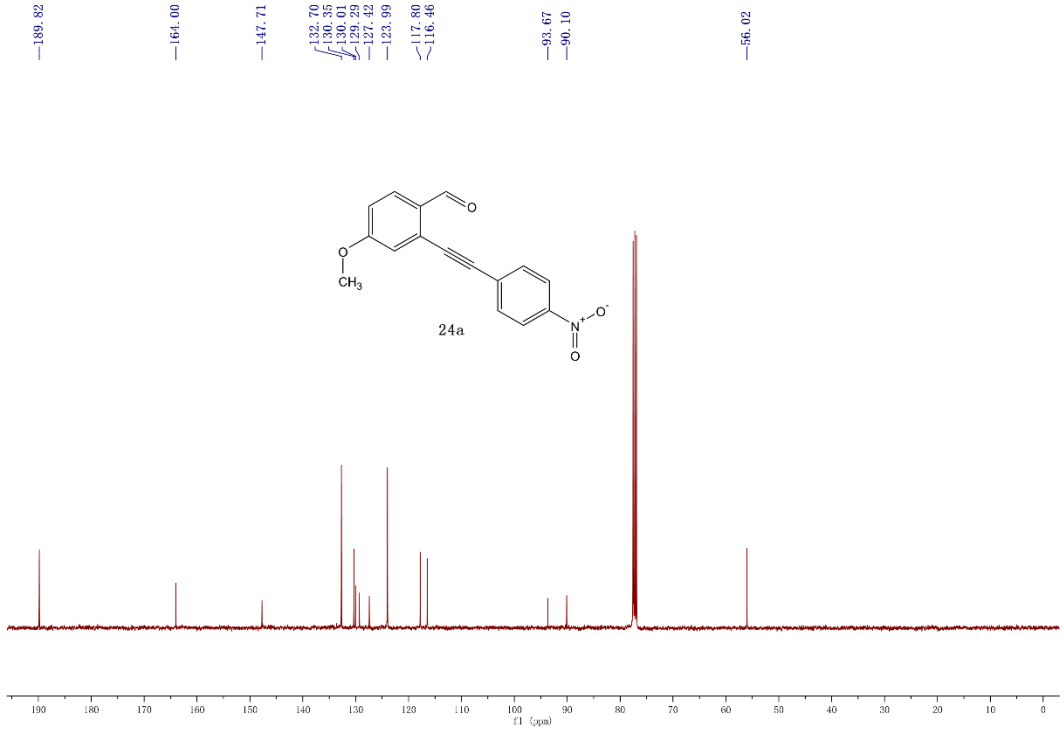
^{13}C NMR (101 MHz, $CDCl_3$) for **23a**.



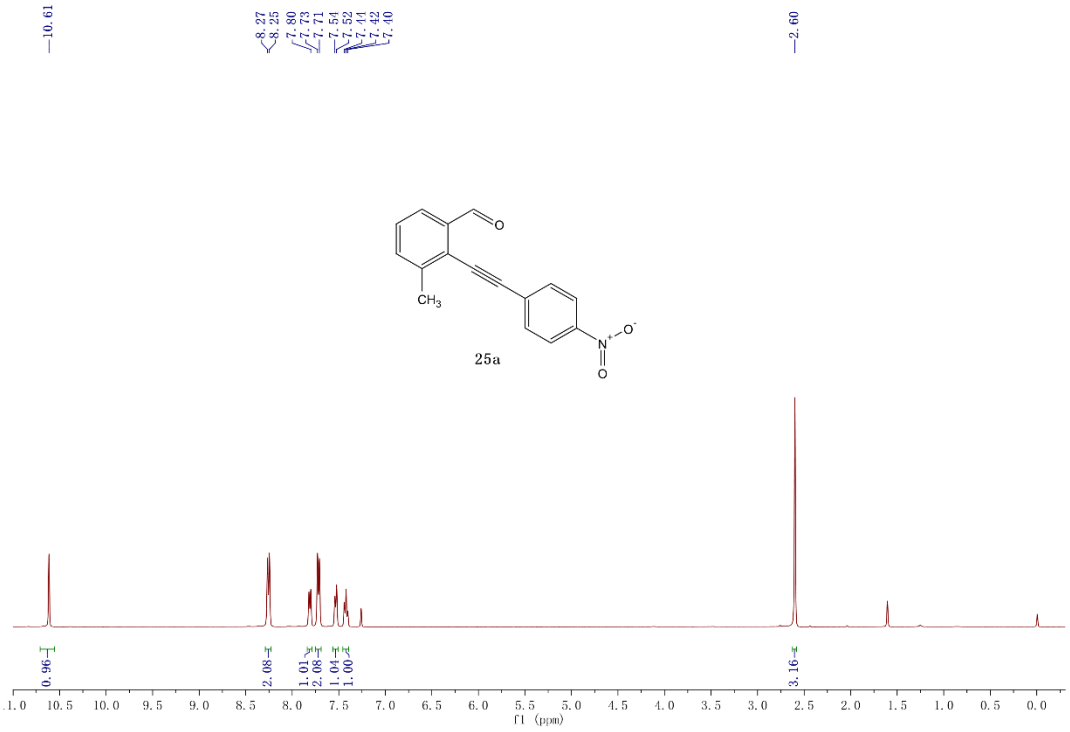
^{1}H NMR (400MHz, $CDCl_3$) for **24a**.



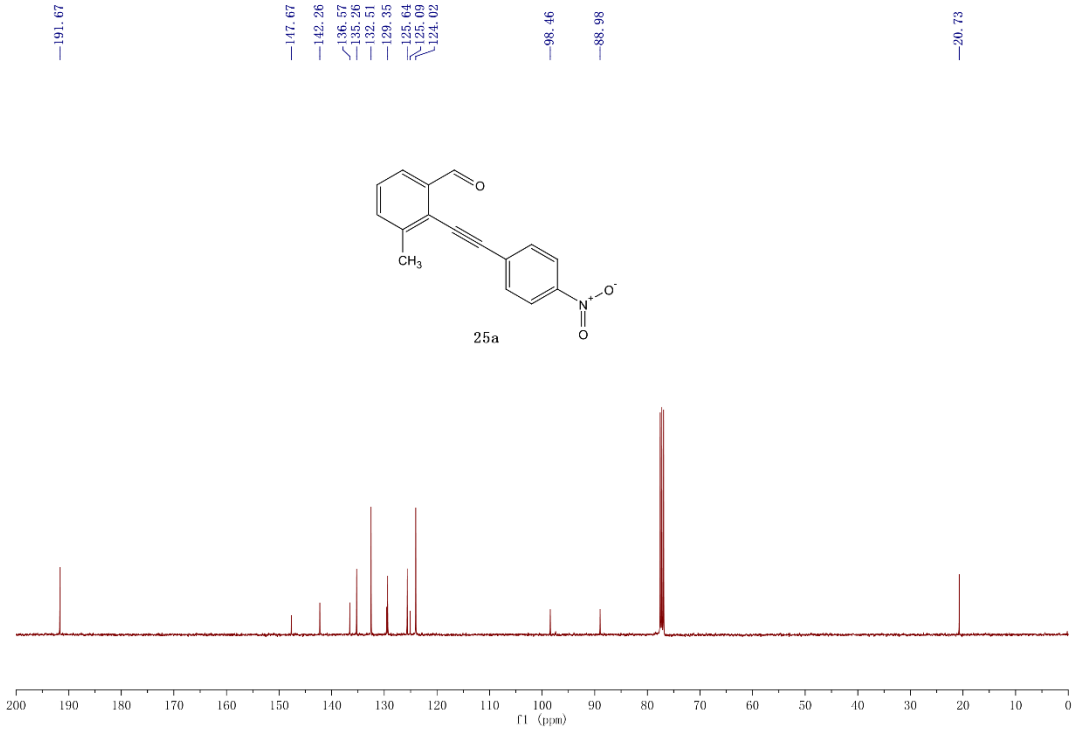
^{13}C NMR (101 MHz, $CDCl_3$) for **24a**.



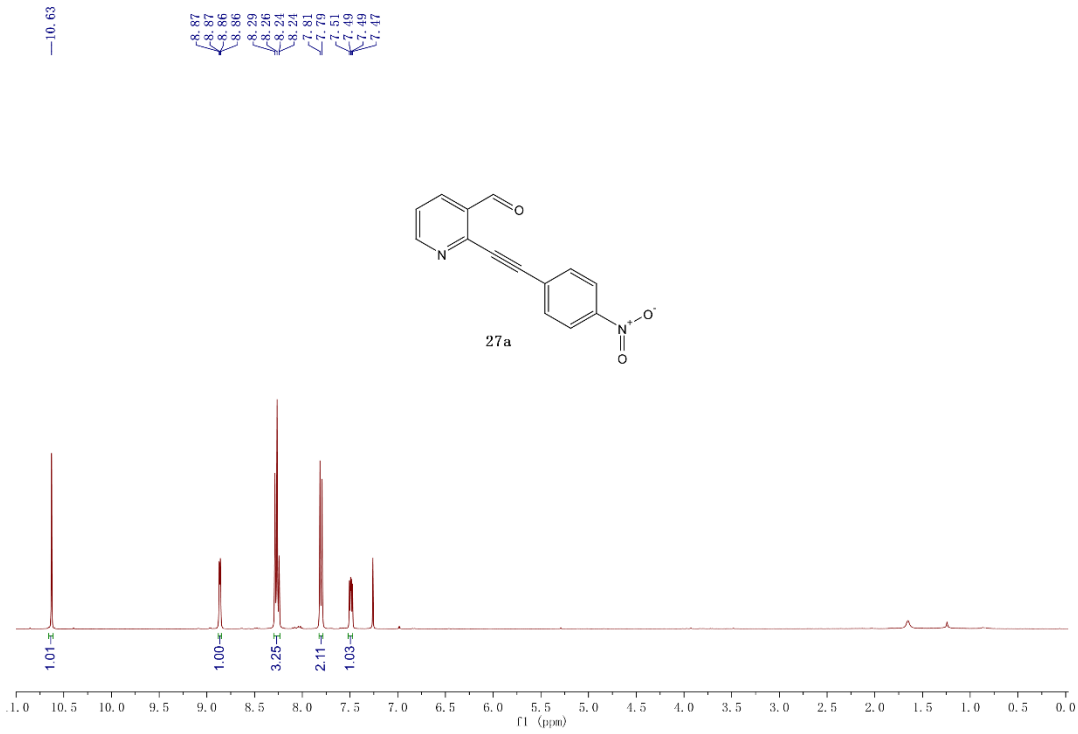
^{1}H NMR (400MHz, $CDCl_3$) for **25a**.



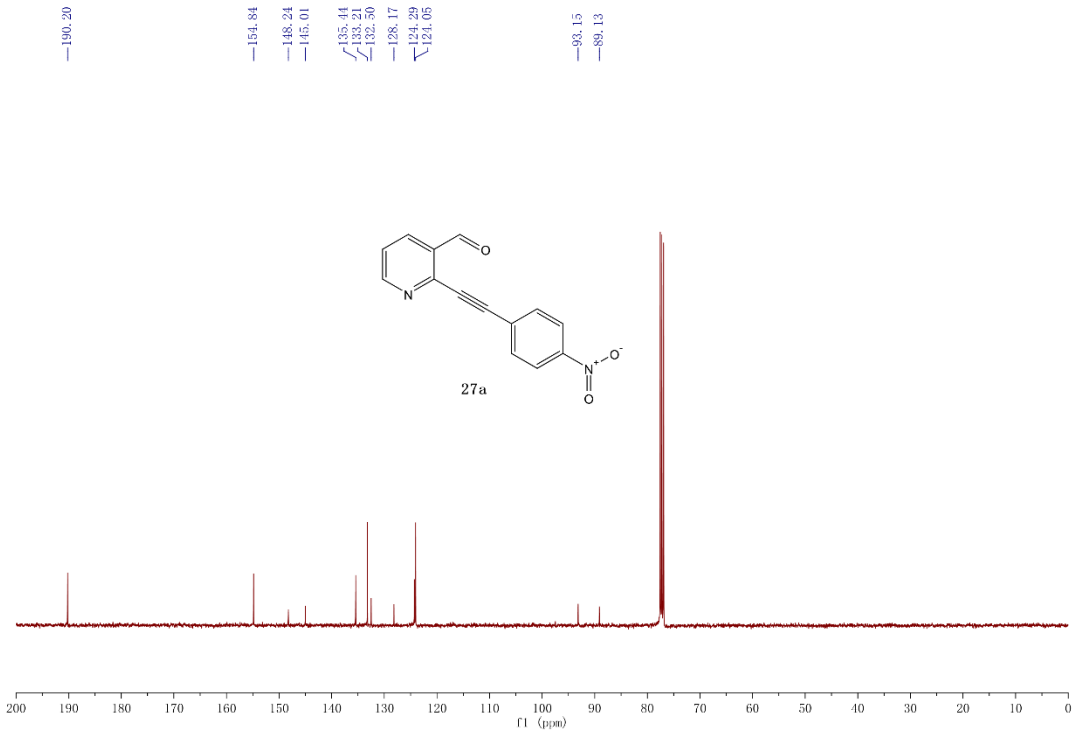
^{13}C NMR (101 MHz, $CDCl_3$) for **25a**.



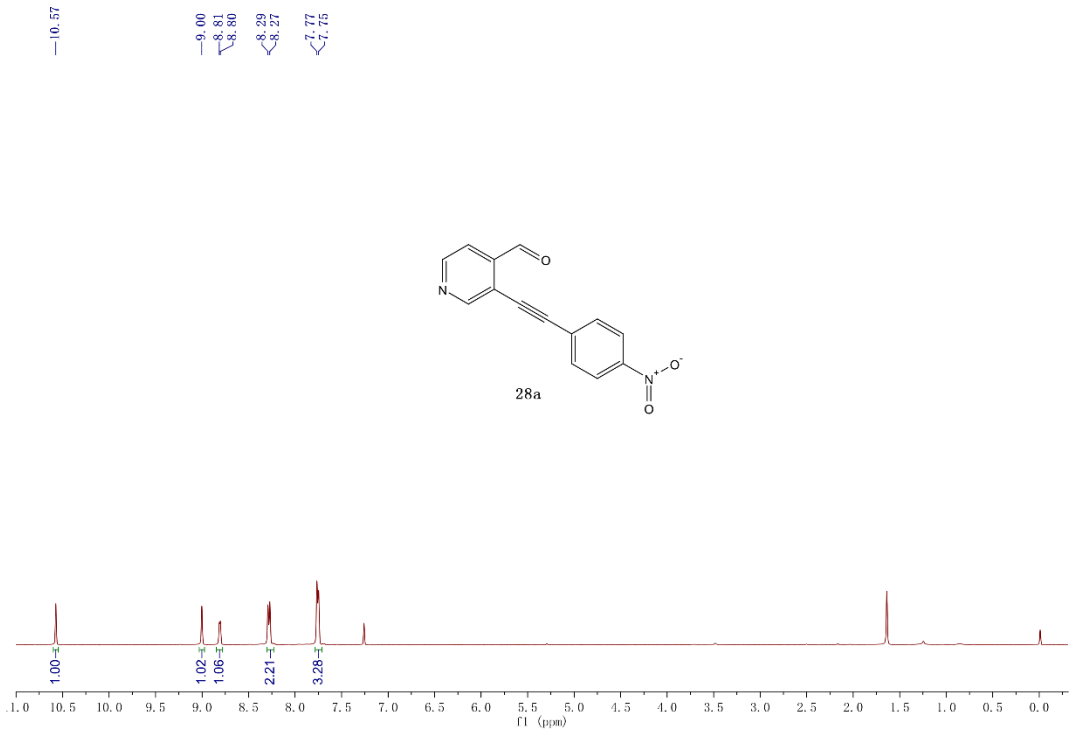
^{1}H NMR (400MHz, $CDCl_3$) for **27a**.



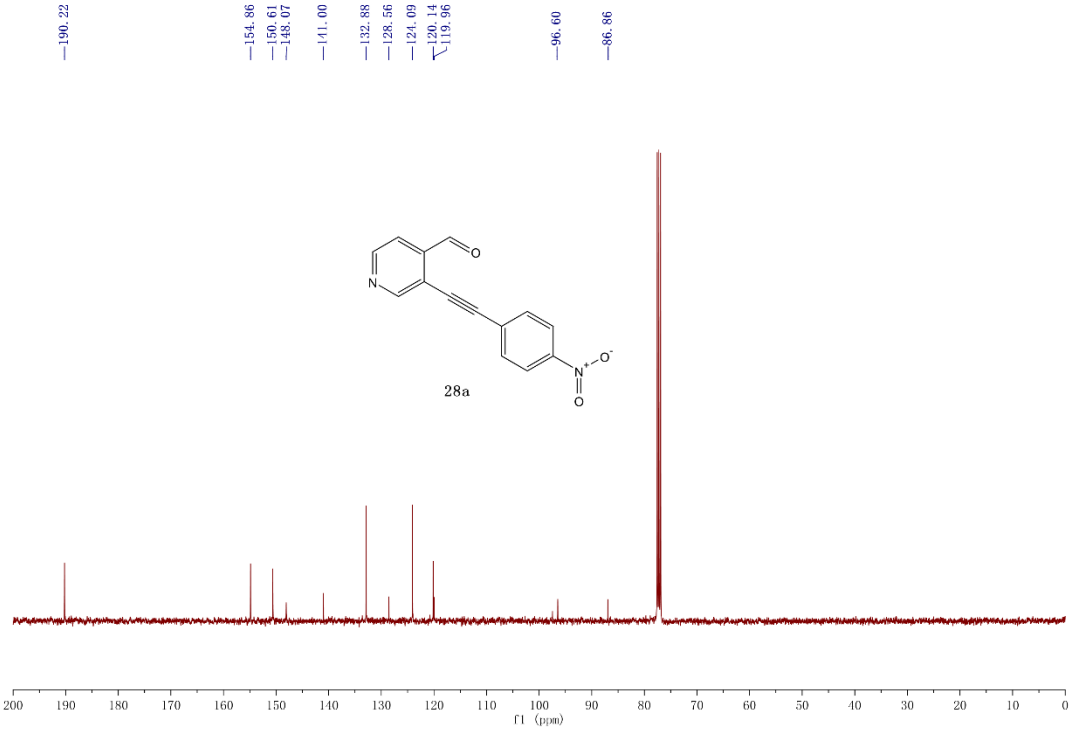
^{13}C NMR (101 MHz, $CDCl_3$) for **27a**.



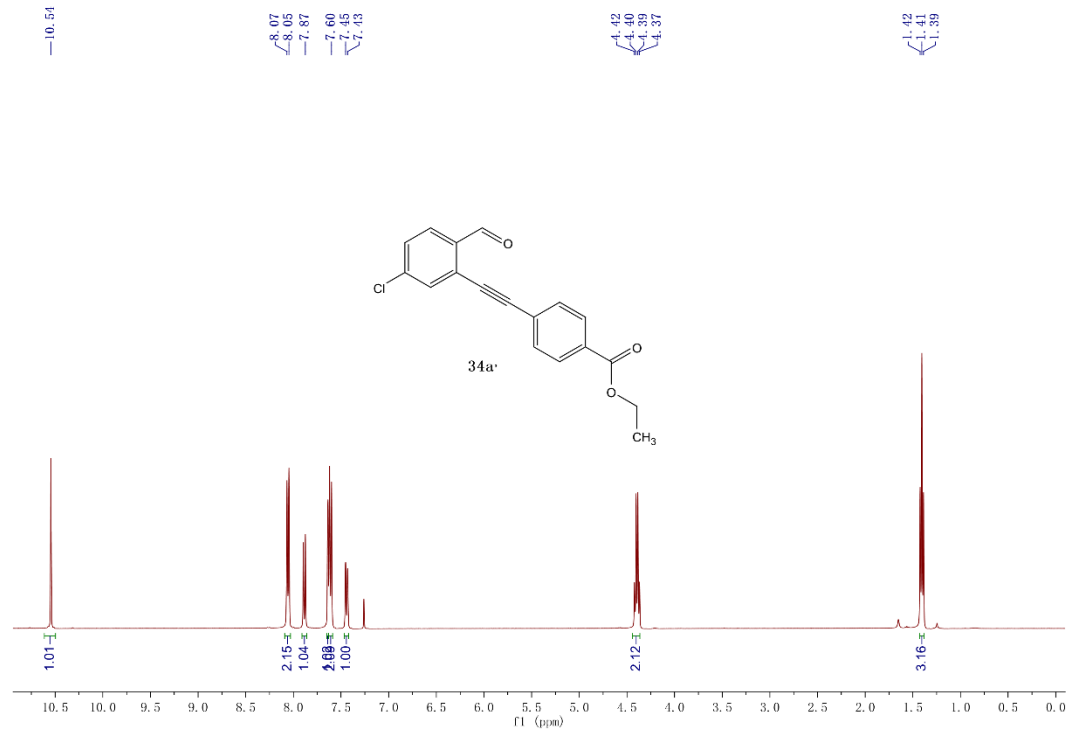
^{1}H NMR (400MHz, $CDCl_3$) for **28a**.



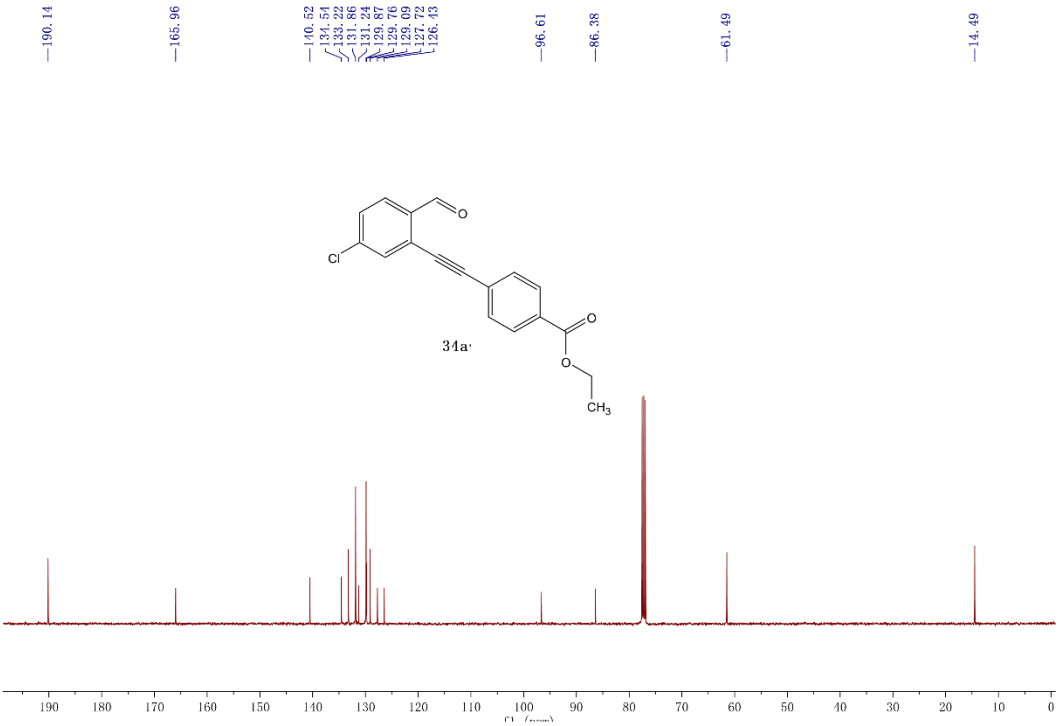
^{13}C NMR (101 MHz, $CDCl_3$) for **28a**.



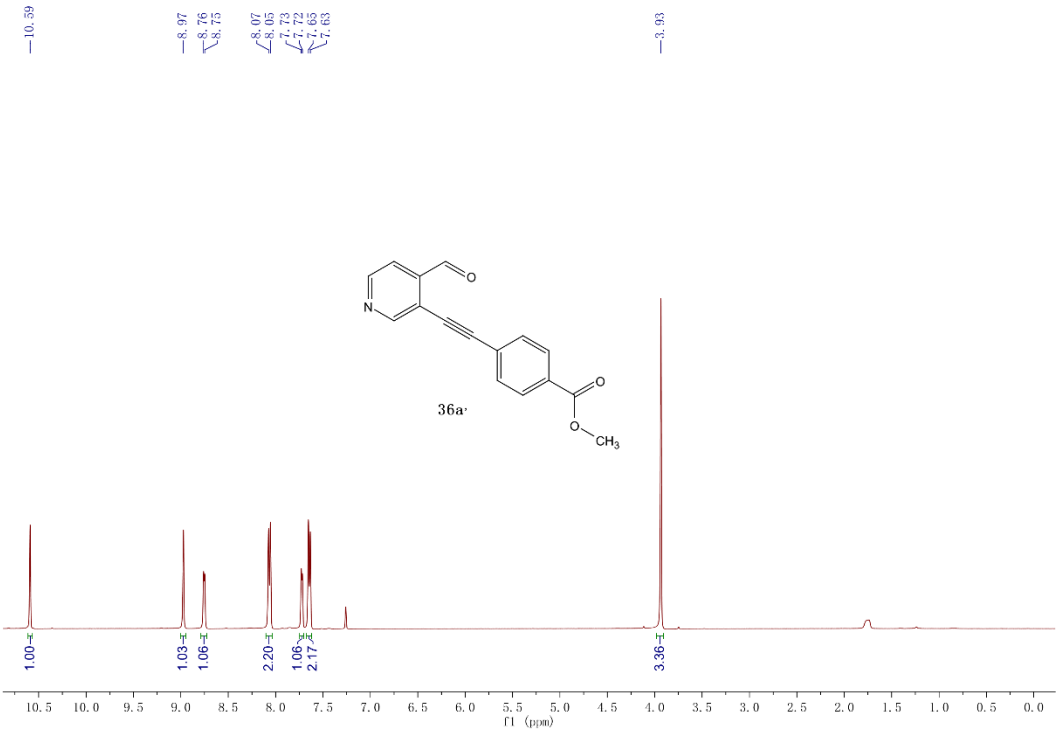
^{1}H NMR (400MHz, $CDCl_3$) for **34a'**.



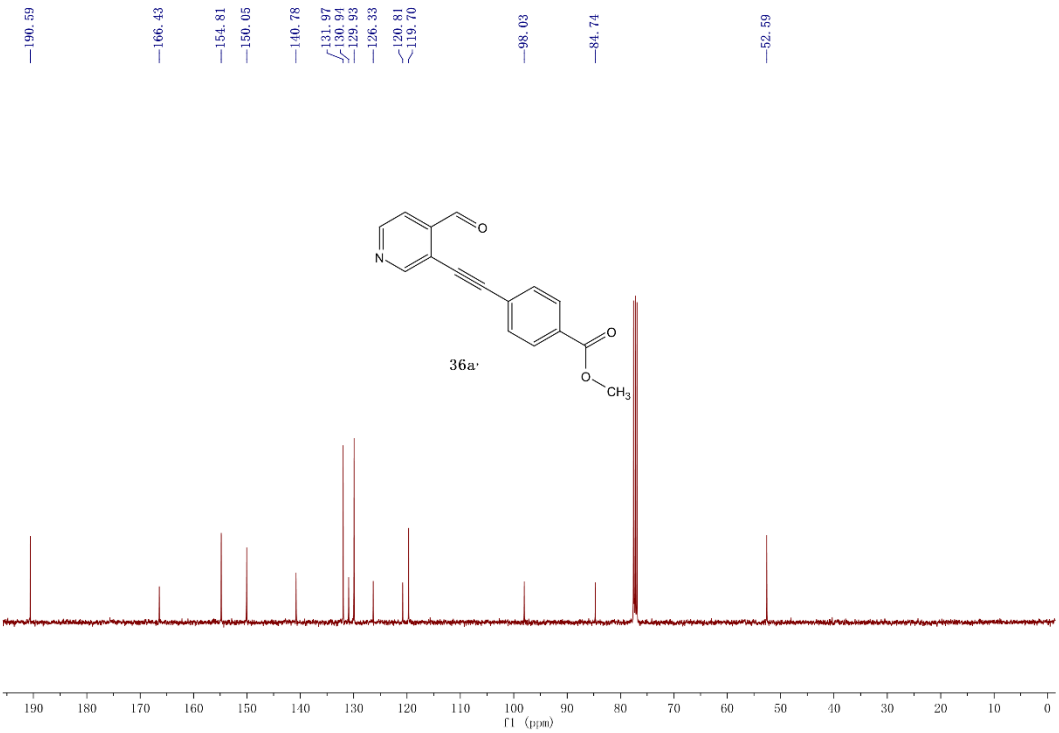
^{13}C NMR (101 MHz, $CDCl_3$) for **34a'**.



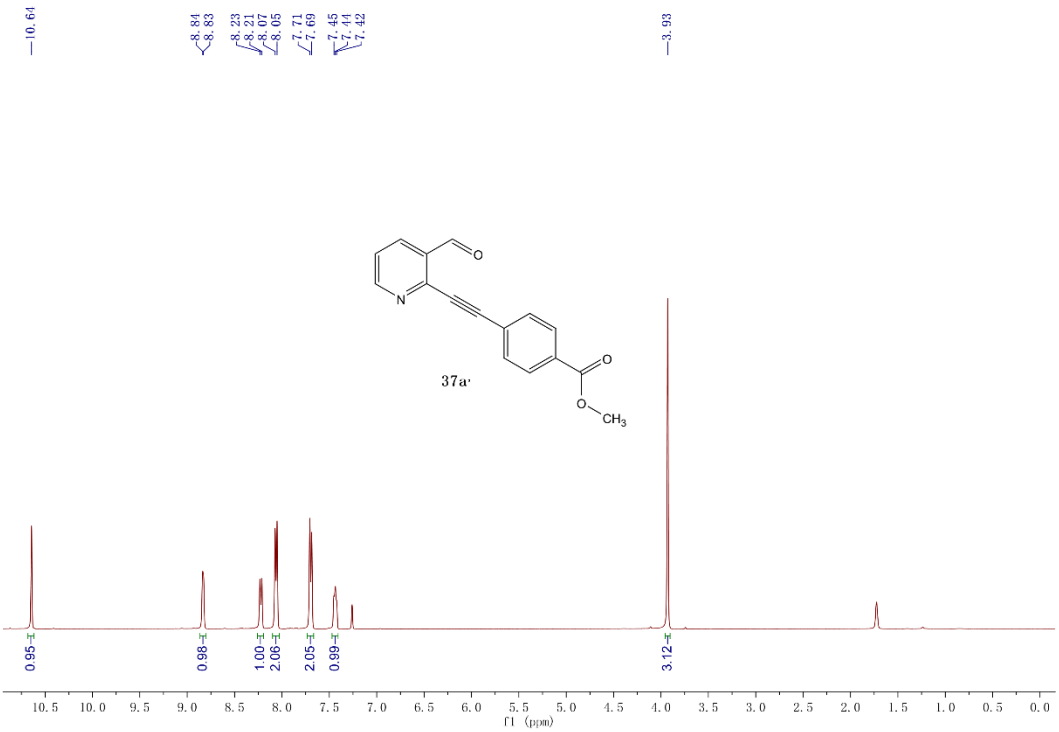
^{1}H NMR (400MHz, $CDCl_3$) for **36a'**.



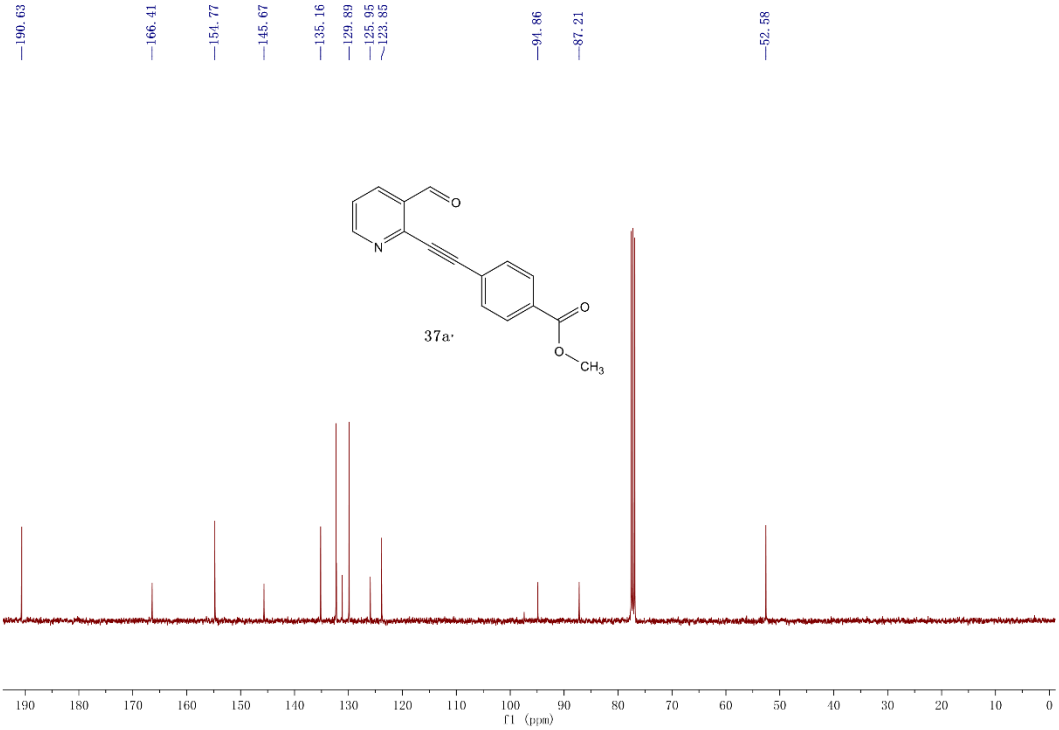
^{13}C NMR (101 MHz, $CDCl_3$) for **36a'**.



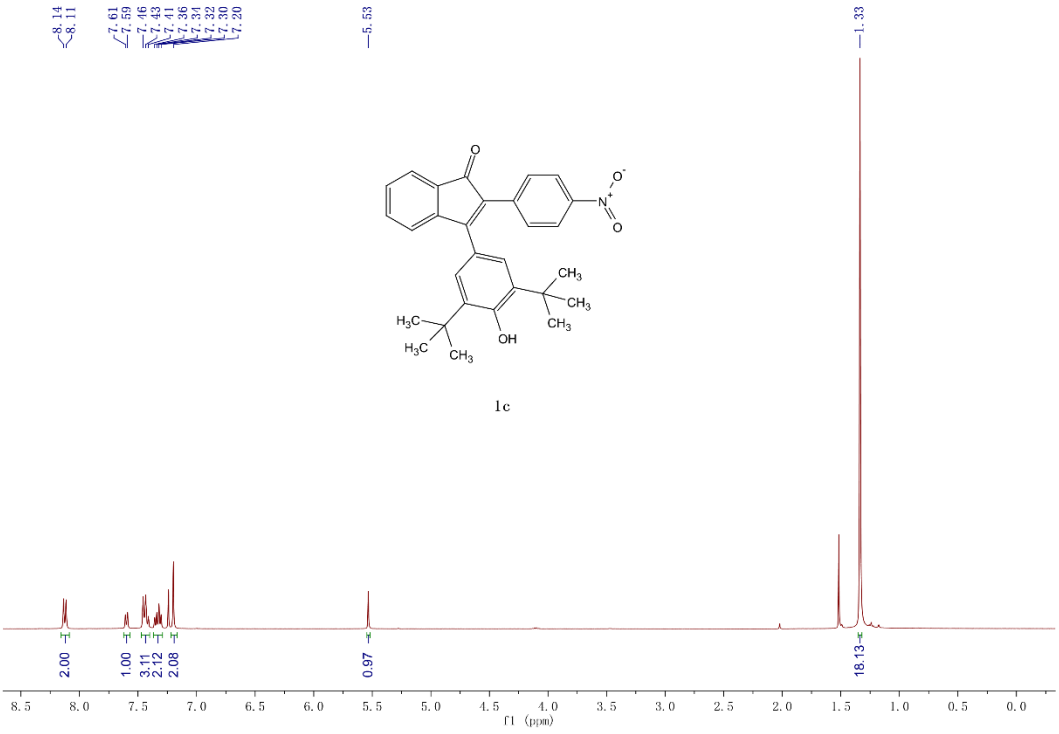
^{1}H NMR (400MHz, $CDCl_3$) for **37a'**.



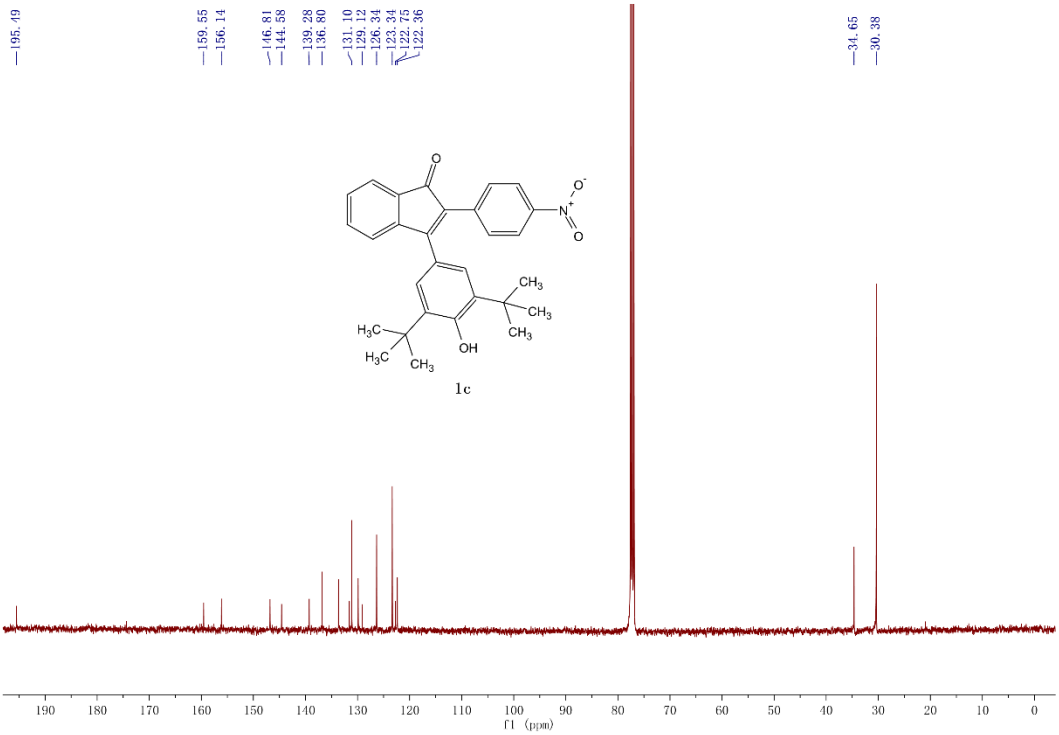
^{13}C NMR (101 MHz, $CDCl_3$) for **37a'**.



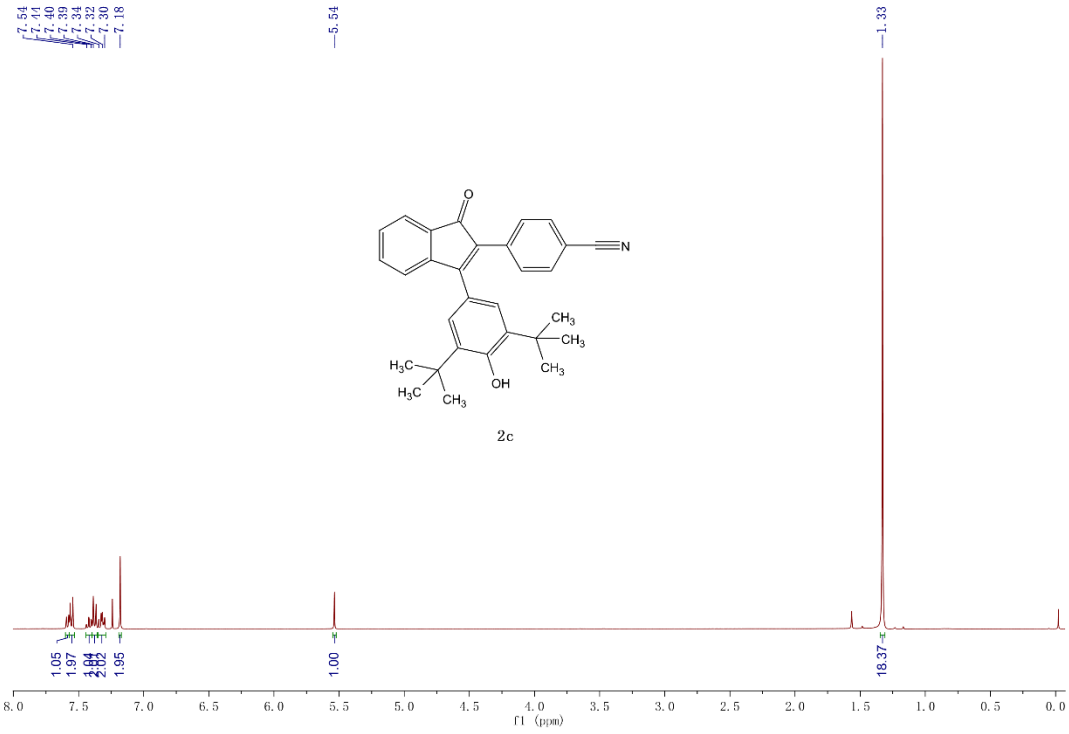
^{1}H NMR (400MHz, $CDCl_3$) for **1c**.



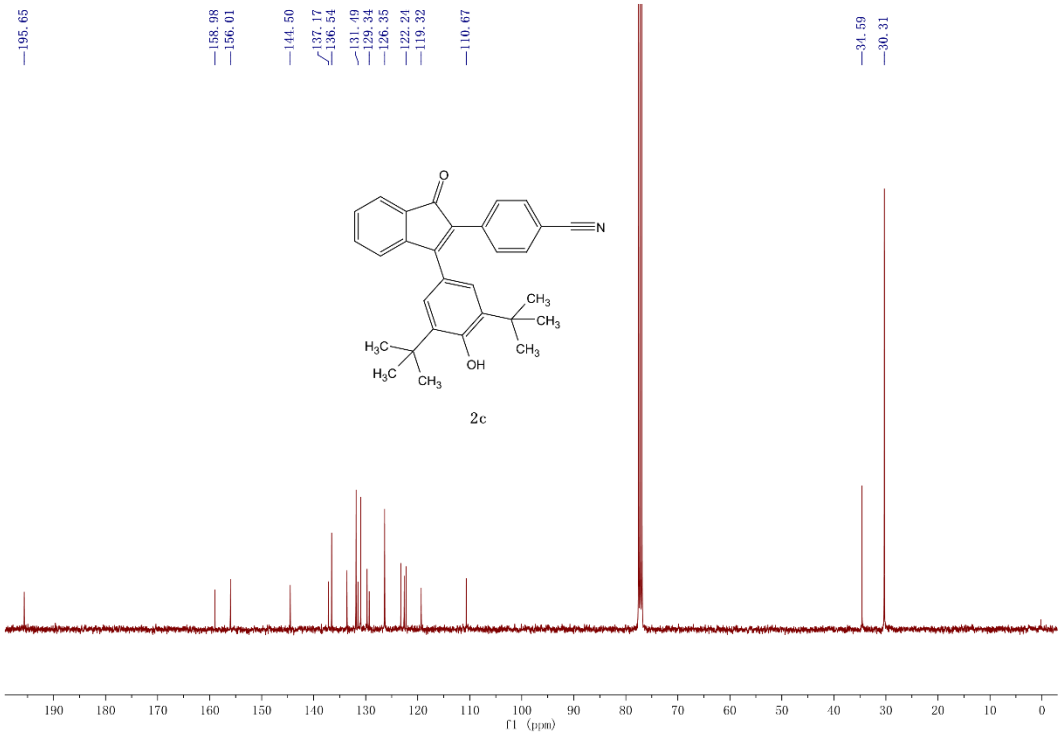
^{13}C NMR (101 MHz, $CDCl_3$) for **1c**.



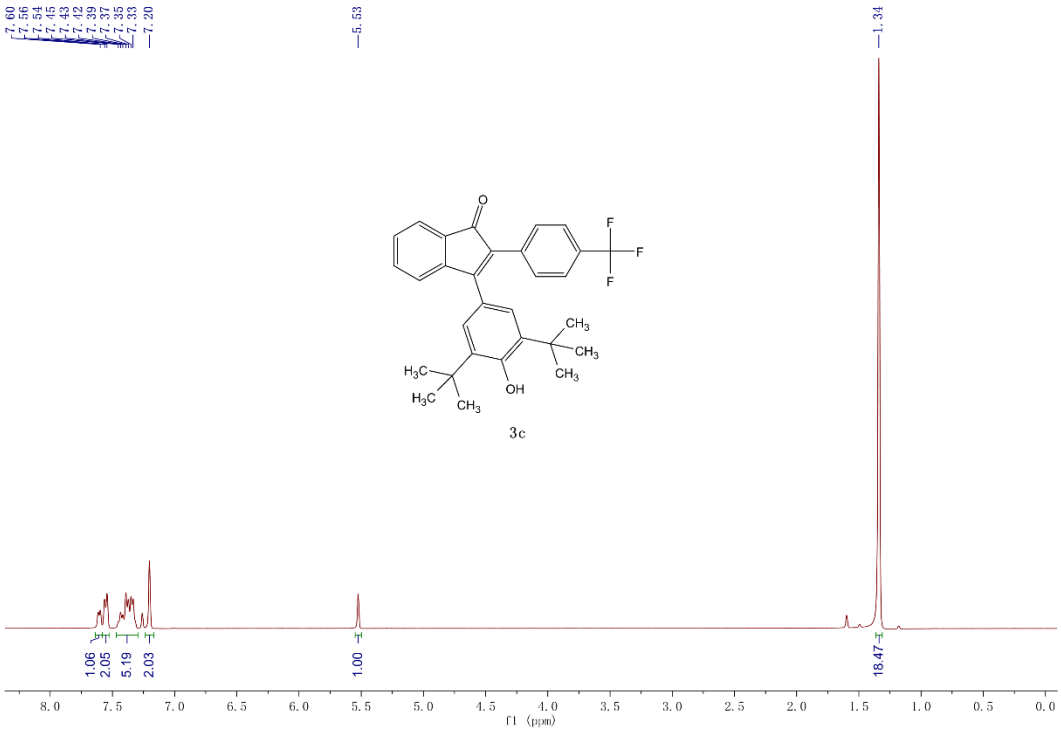
^{1}H NMR (400MHz, $CDCl_3$) for **2c**.



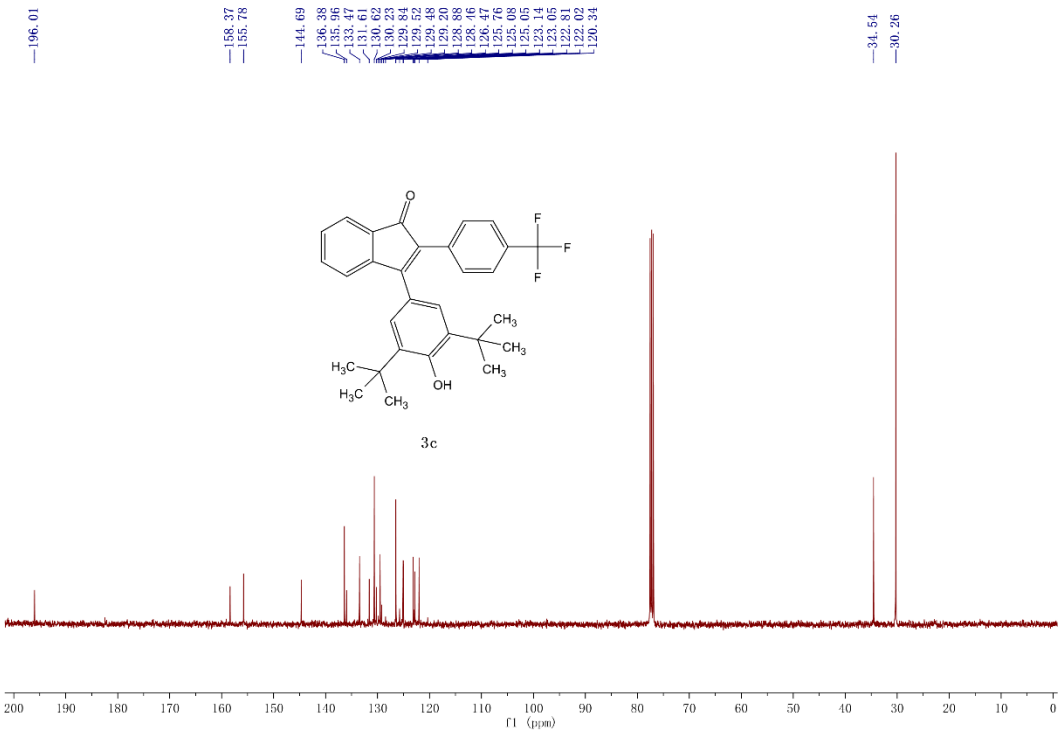
^{13}C NMR (101 MHz, $CDCl_3$) for **2c**.



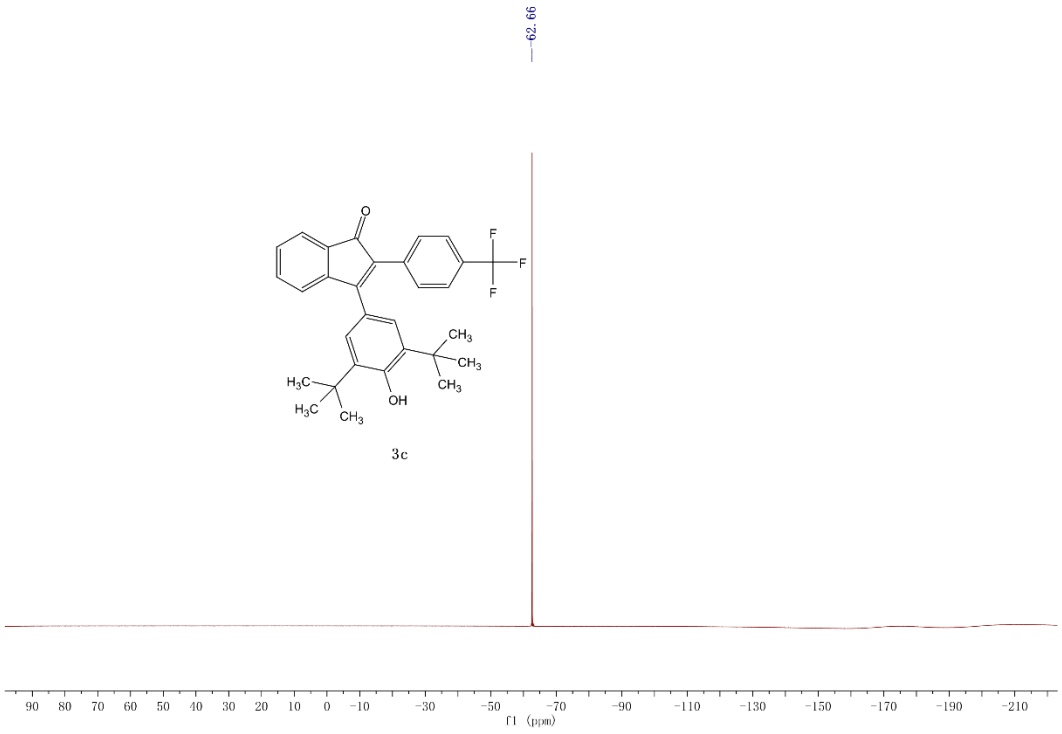
^{1}H NMR (400MHz, $CDCl_3$) for **3c**.



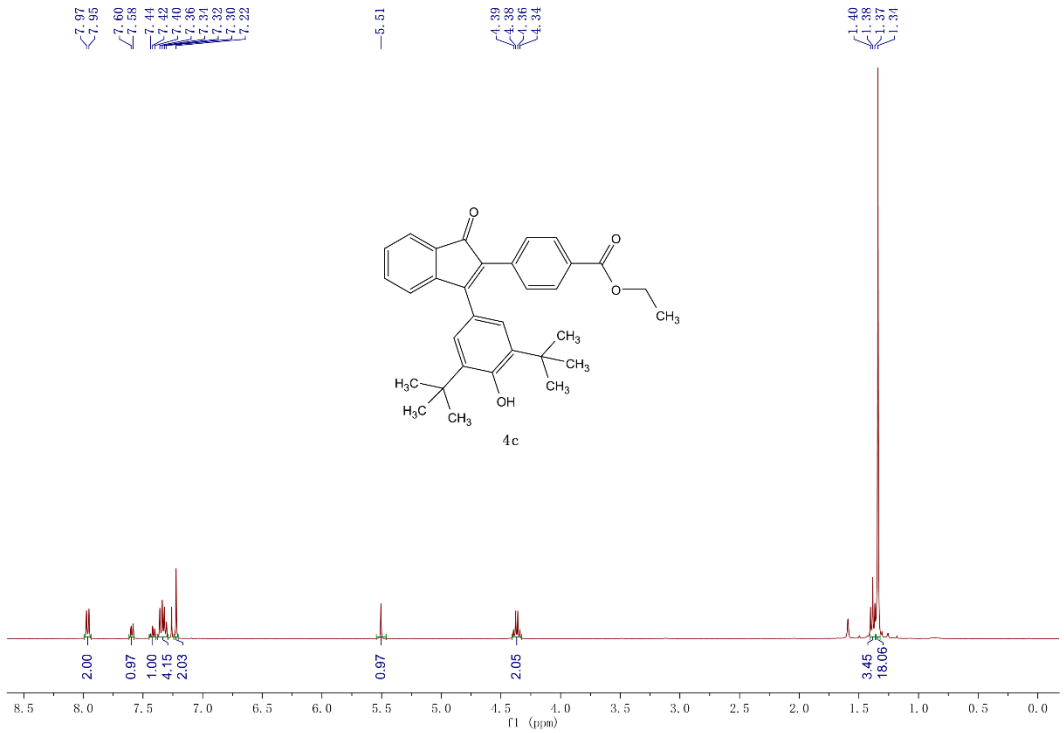
^{13}C NMR (101 MHz, $CDCl_3$) for **3c**.



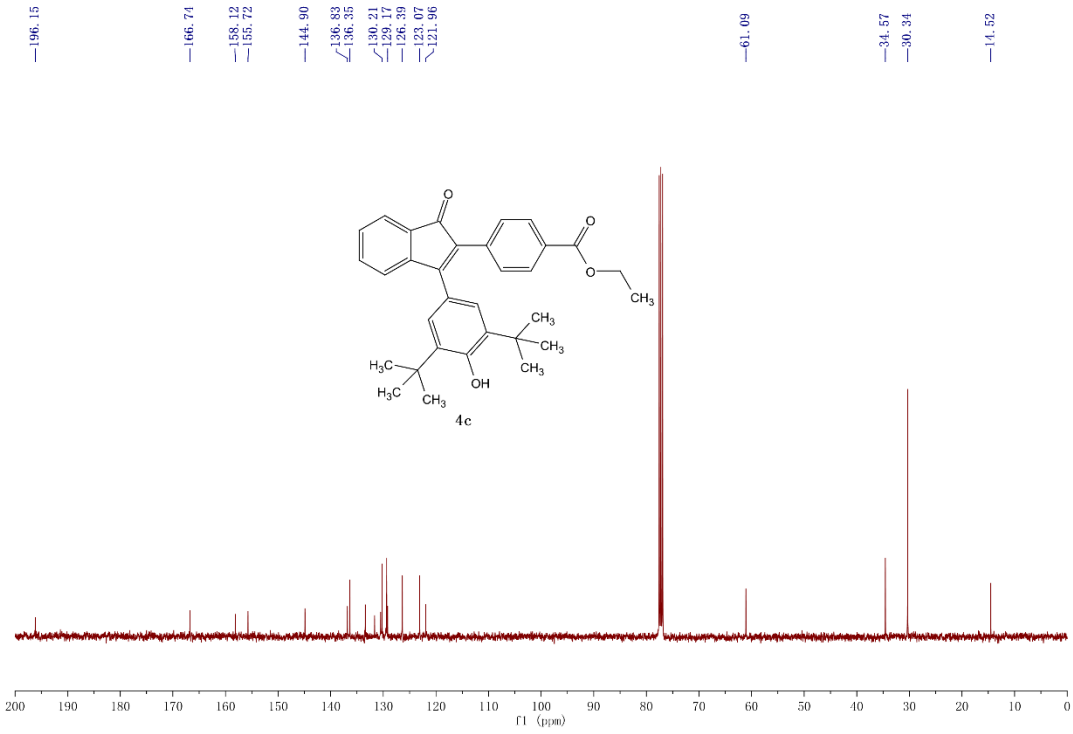
^{19}F NMR (377 MHz, $CDCl_3$) for **3c**.



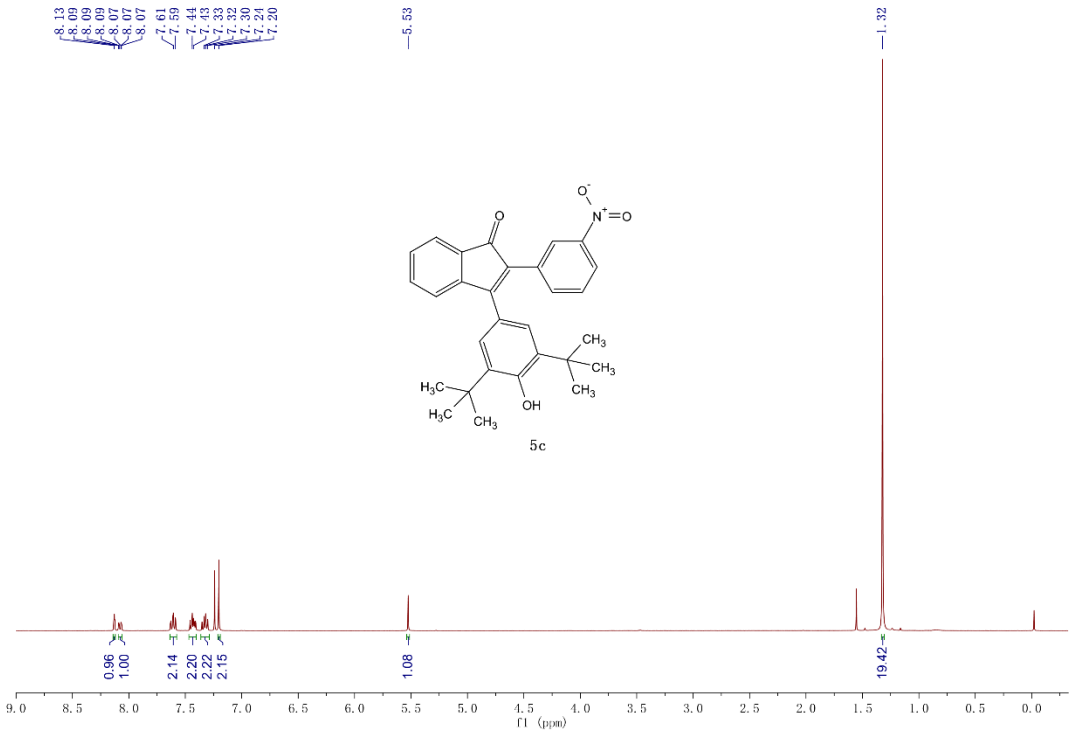
^{1}H NMR (400MHz, $CDCl_3$) for **4c**.



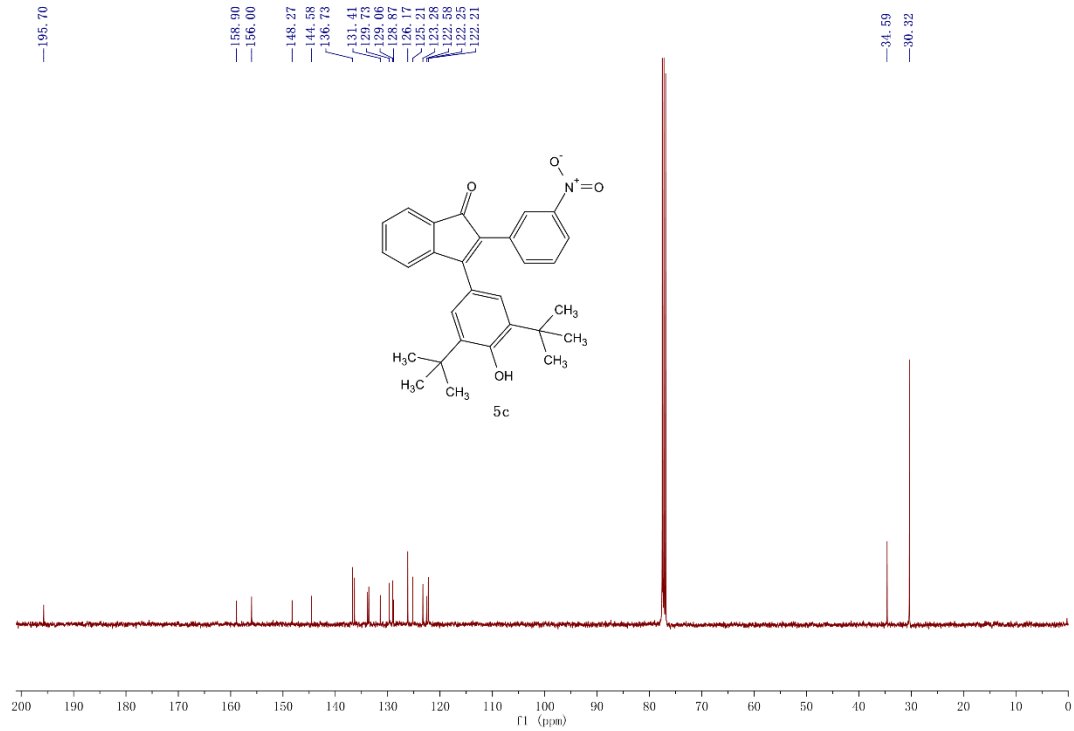
^{13}C NMR (101 MHz, $CDCl_3$) for **4c**.



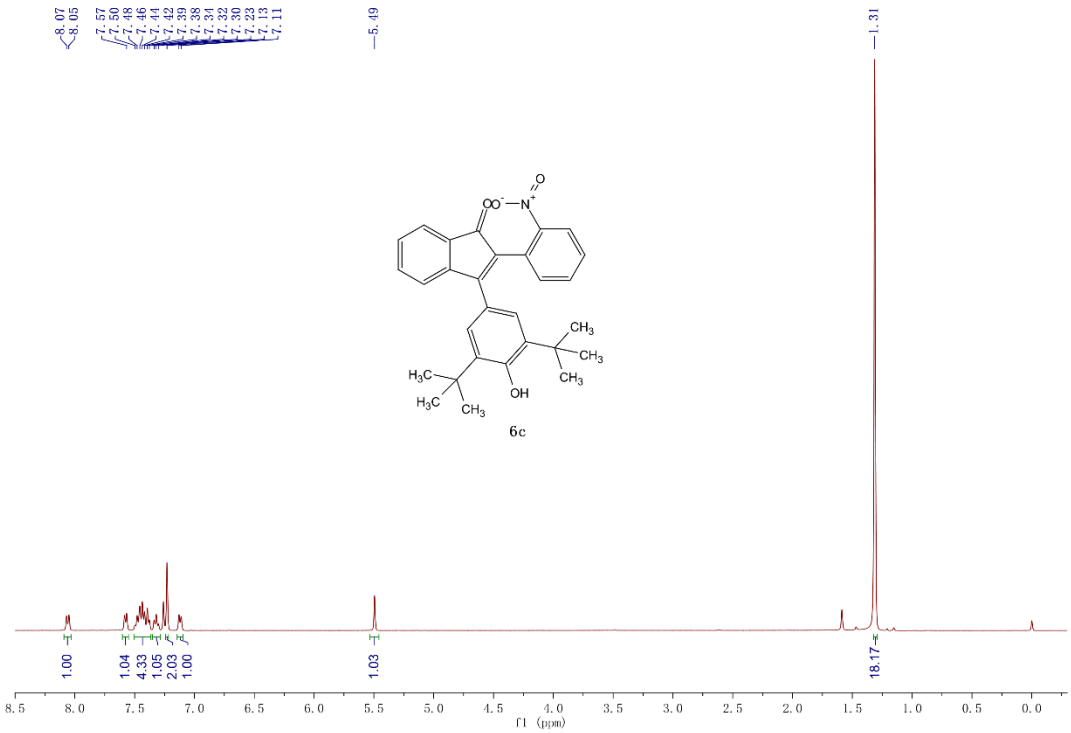
^{1}H NMR (400MHz, $CDCl_3$) for **5c**.



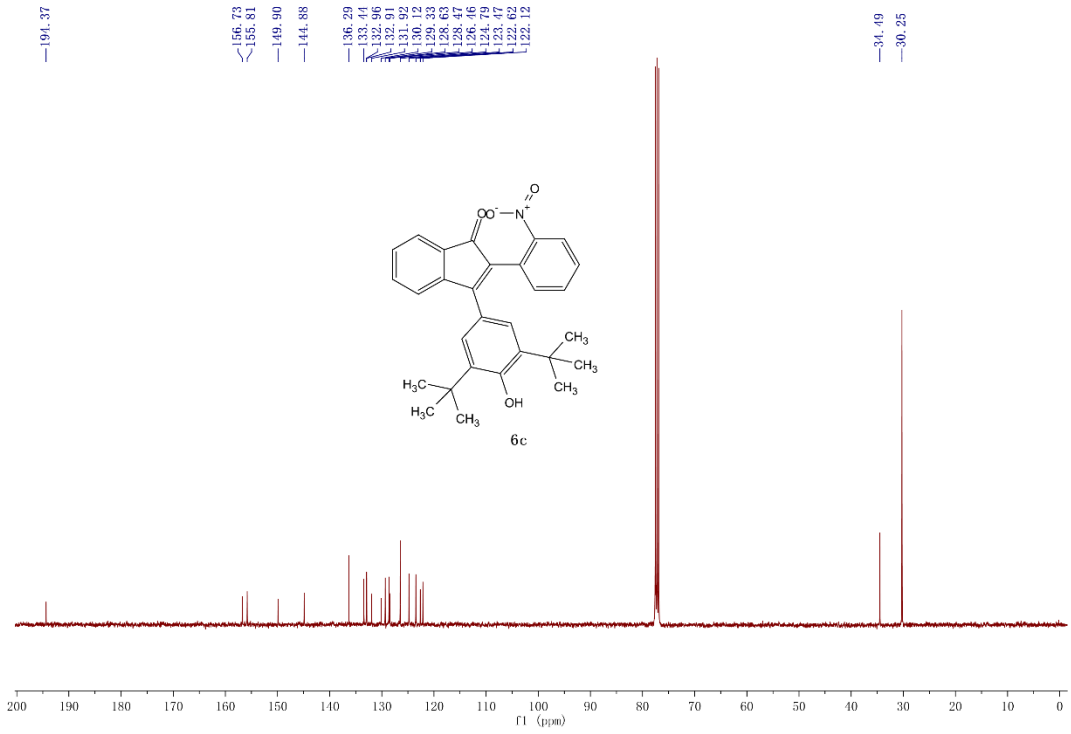
^{13}C NMR (101 MHz, $CDCl_3$) for **5c**.



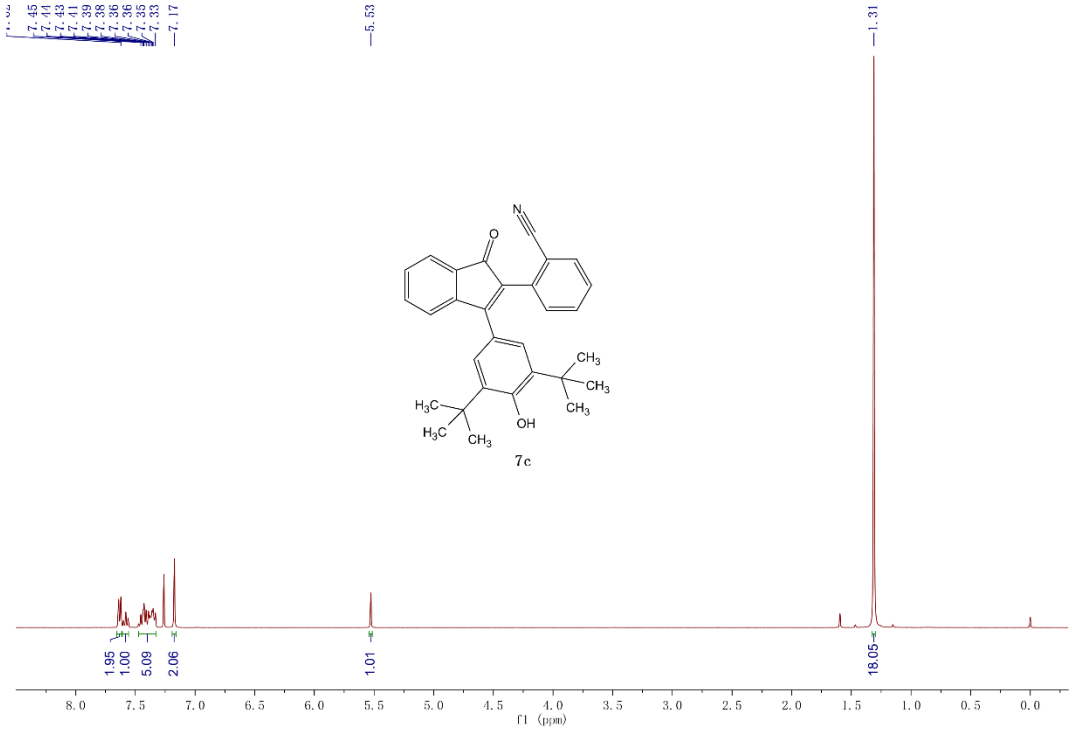
^{1}H NMR (400MHz, $CDCl_3$) for **6c**.



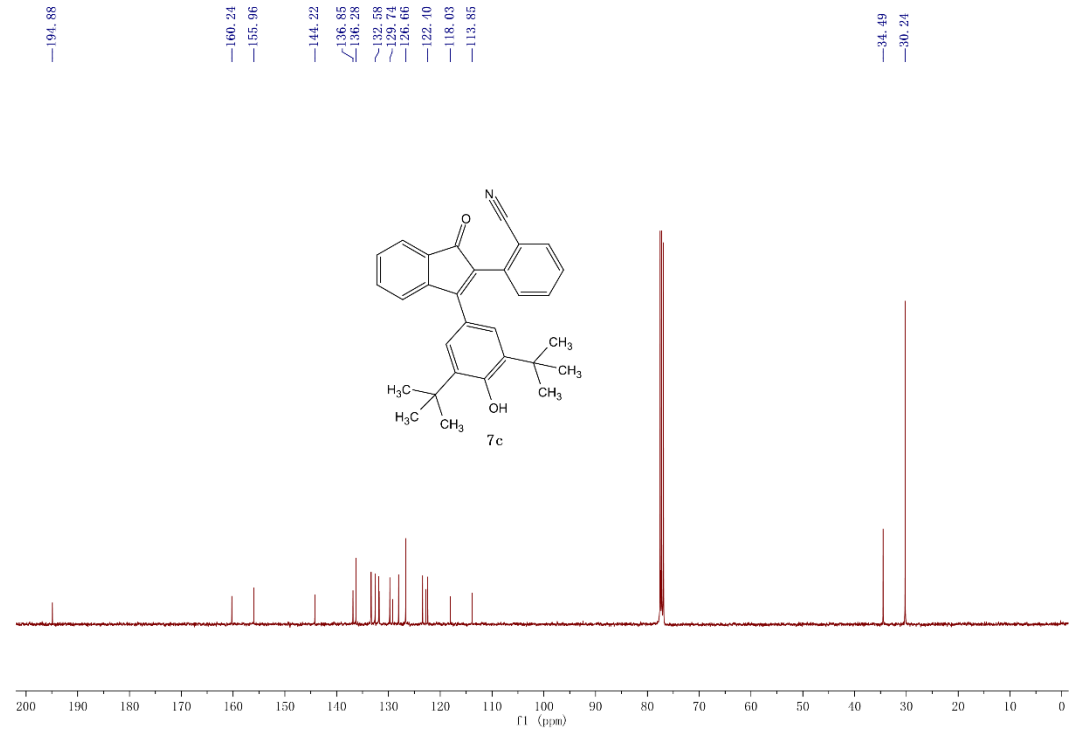
^{13}C NMR (101 MHz, $CDCl_3$) for **6c**.



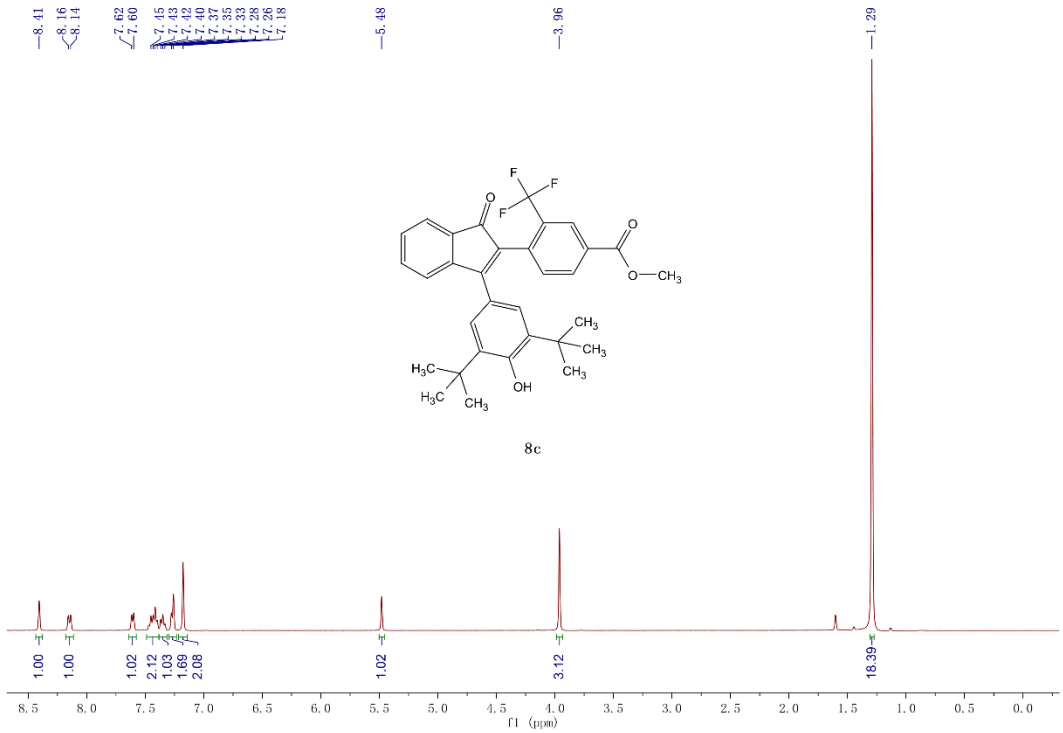
^{1}H NMR (400MHz, $CDCl_3$) for **7c**.



^{13}C NMR (101 MHz, $CDCl_3$) for **7c**.

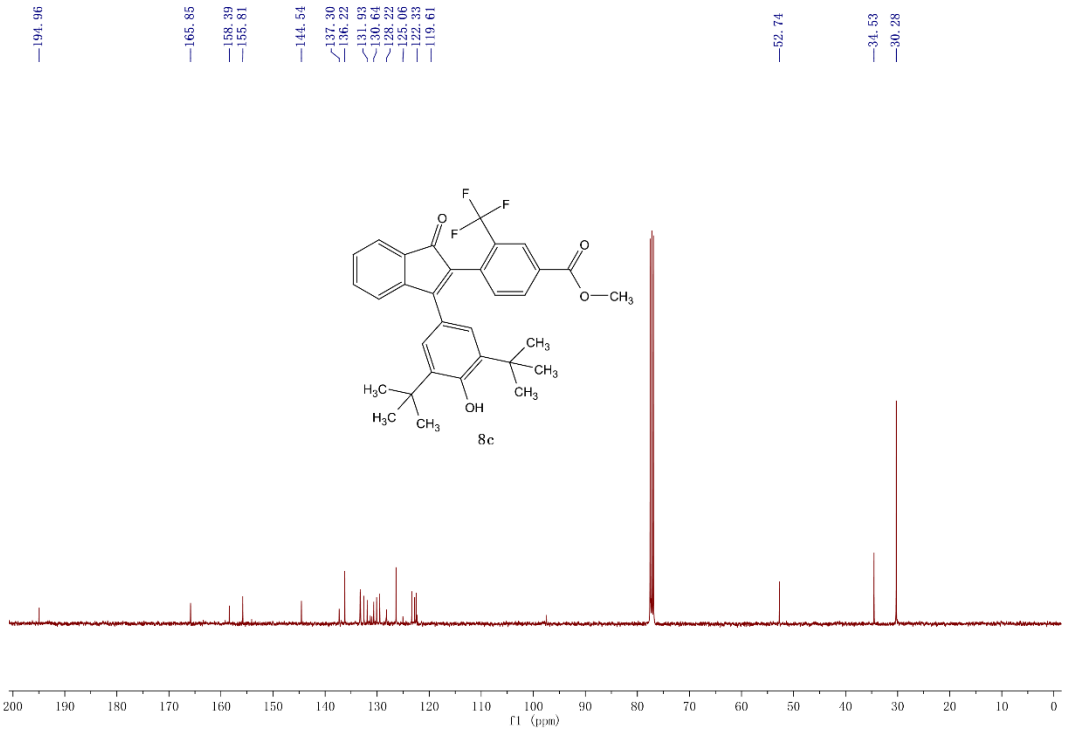


^{1}H NMR (400MHz, $CDCl_3$) for **8c**.



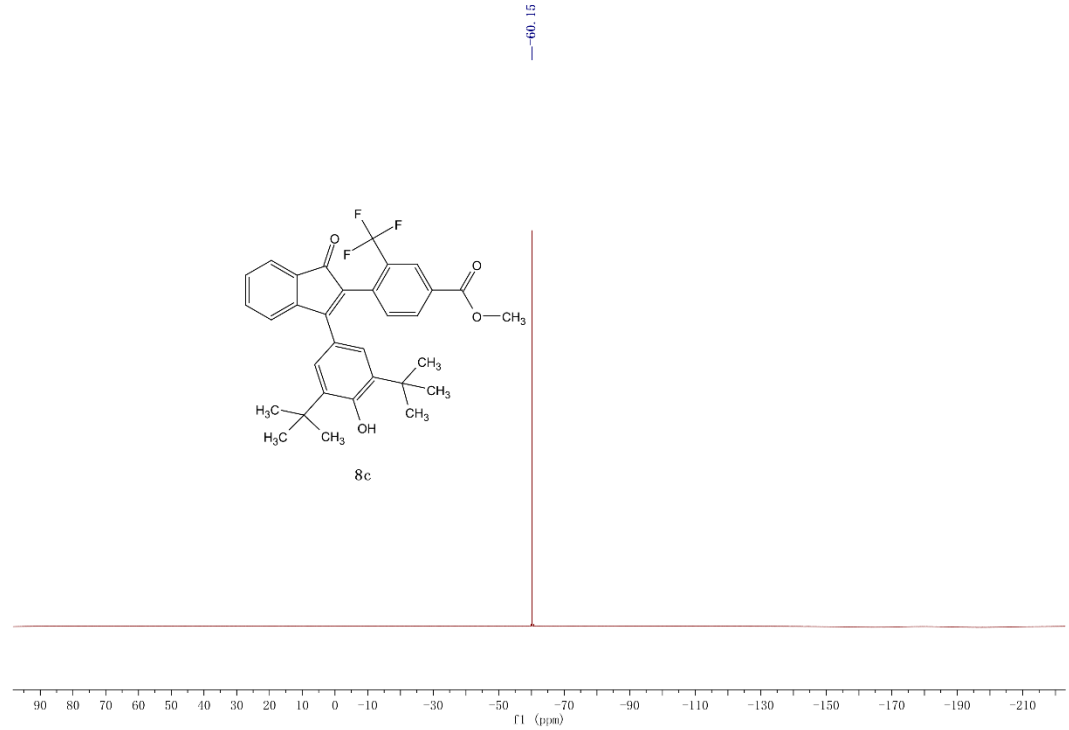
8c

^{13}C NMR (101 MHz, $CDCl_3$) for **8c**.

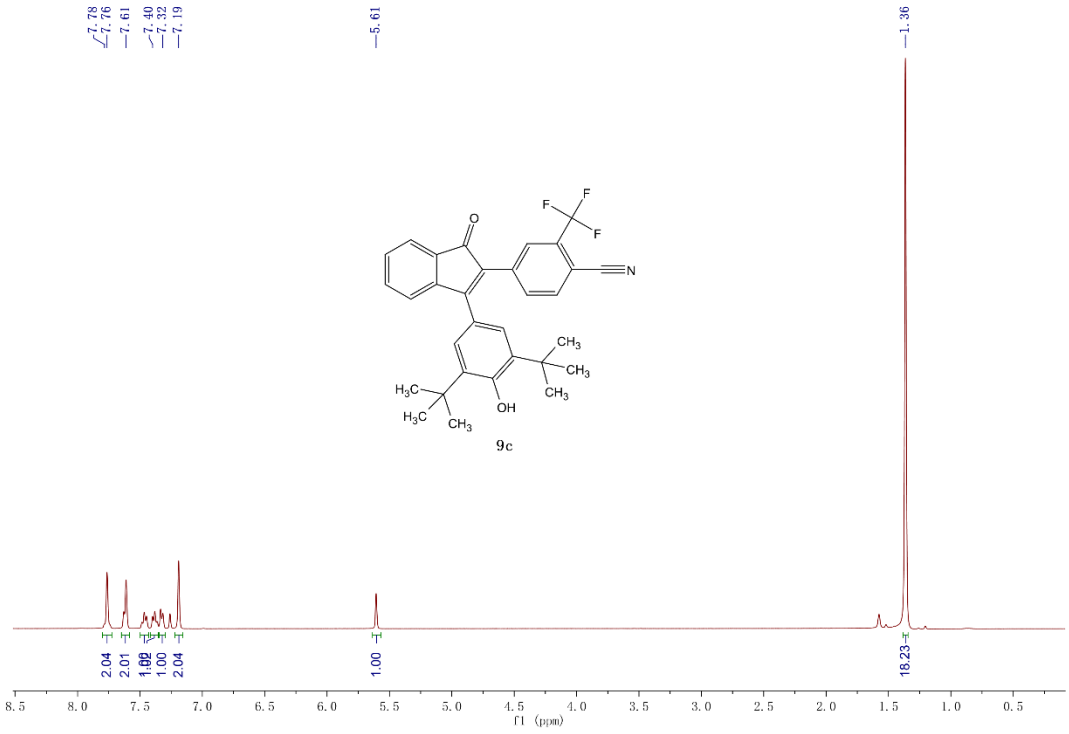


8c

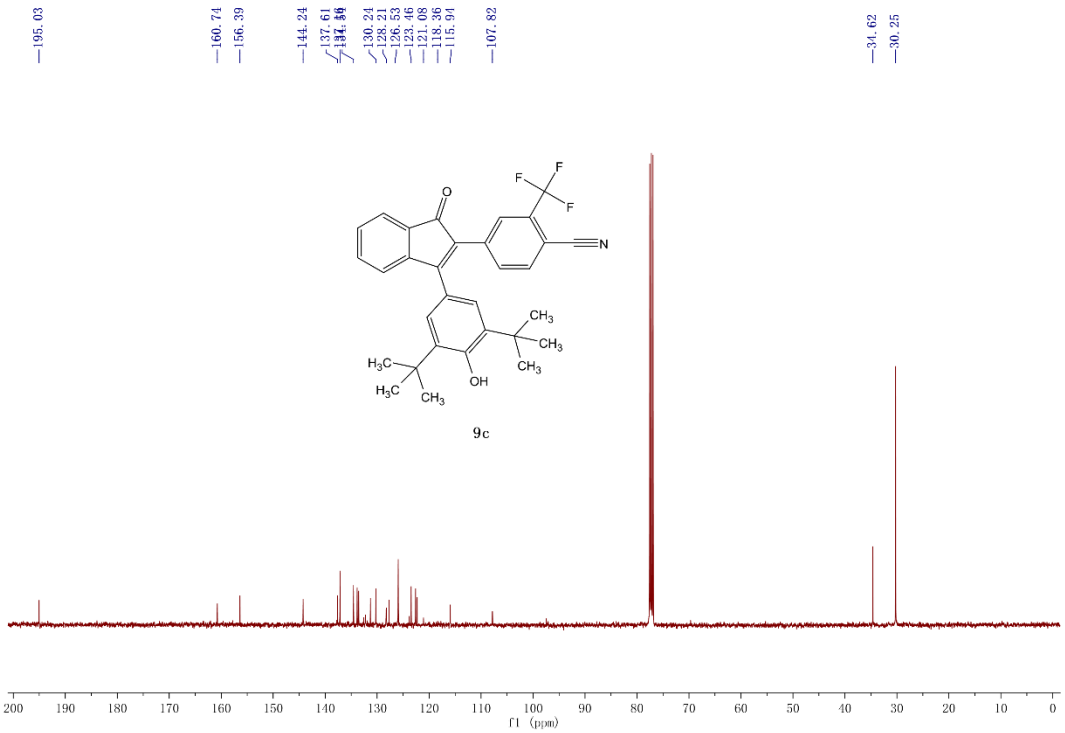
^{19}F NMR (377 MHz, $CDCl_3$) for **8c**.



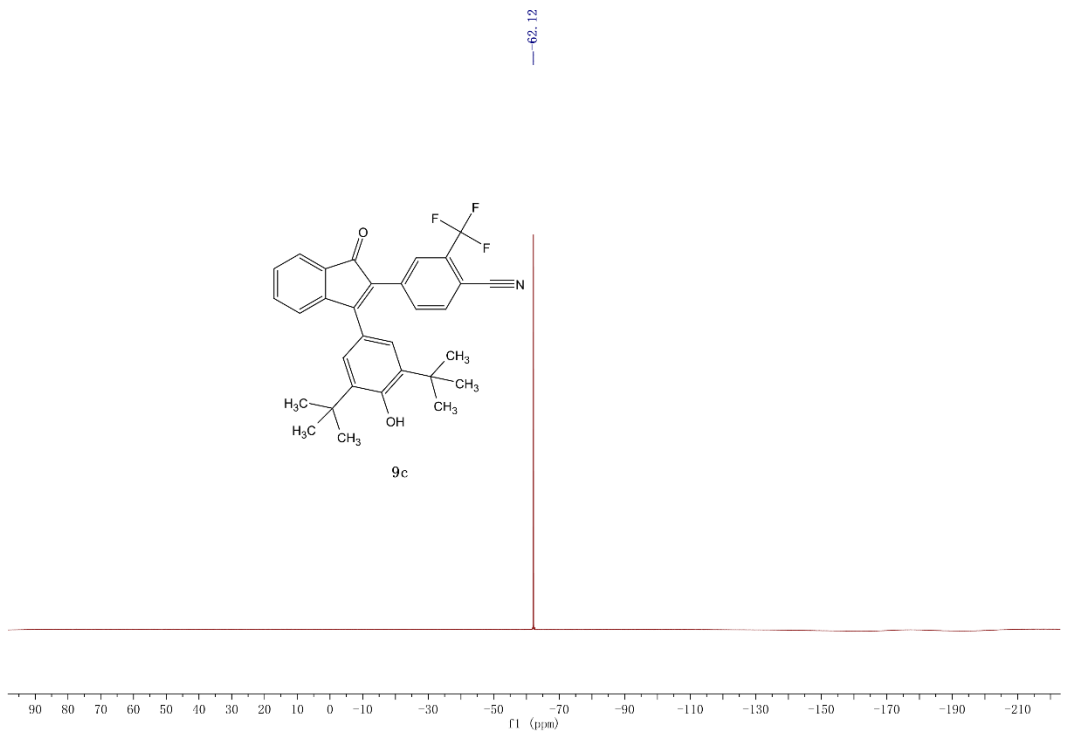
^{1}H NMR (400MHz, $CDCl_3$) for **9c**.



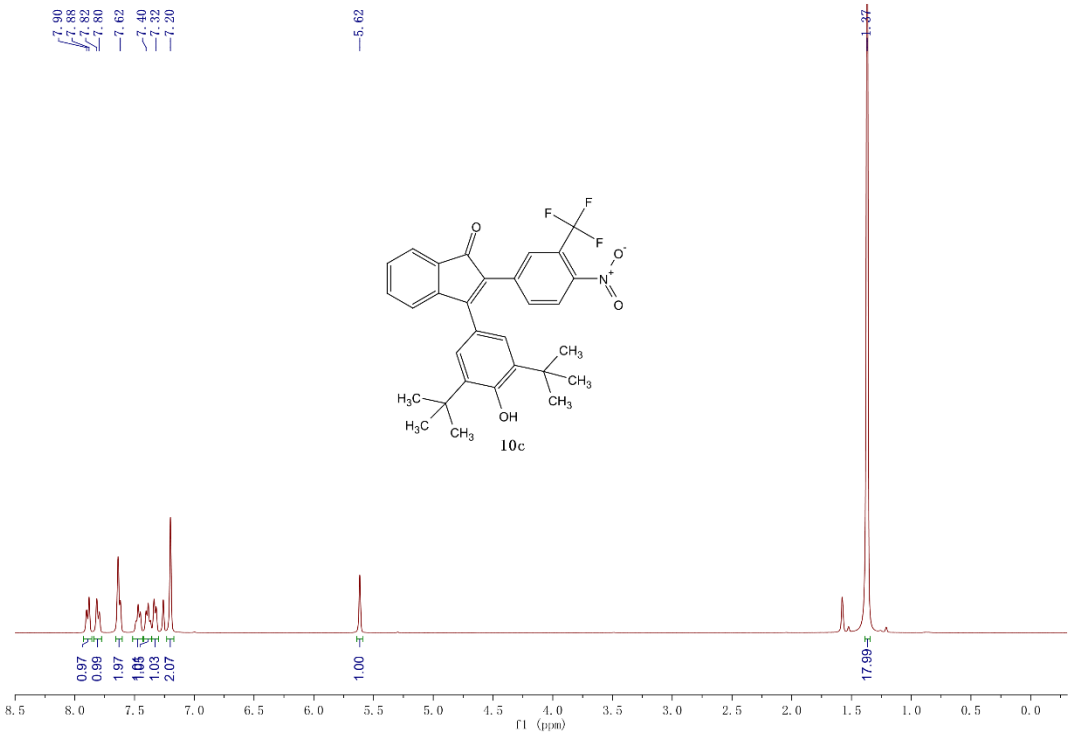
^{13}C NMR (101 MHz, $CDCl_3$) for **9c**.



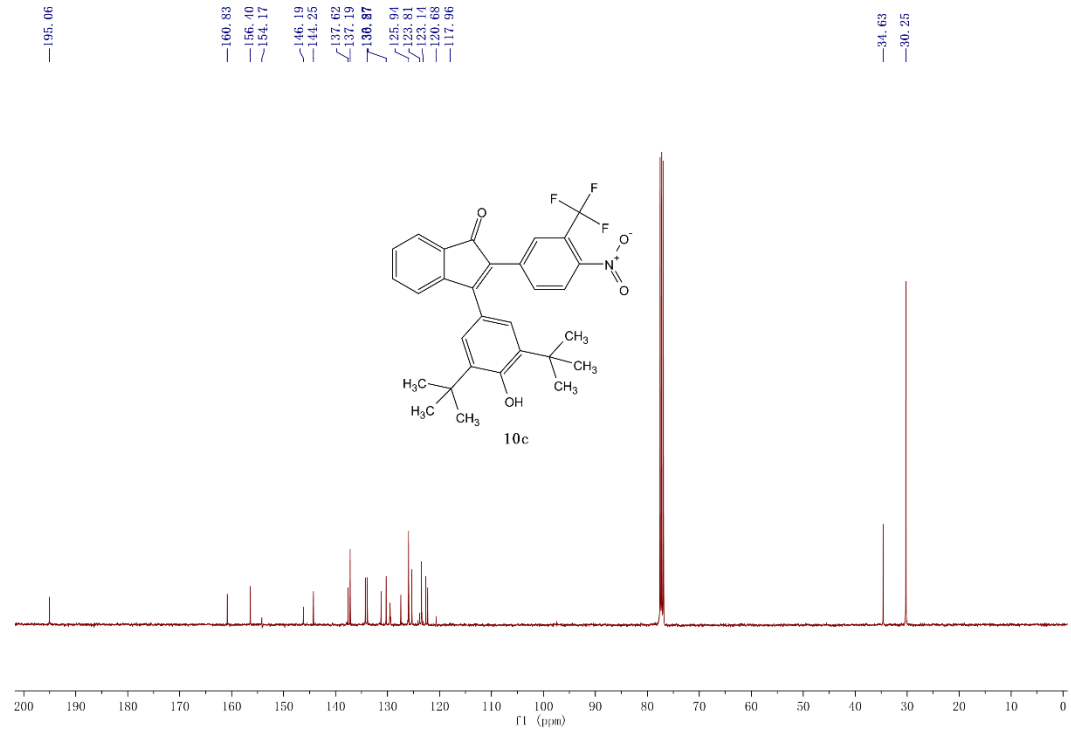
^{19}F NMR (377 MHz, $CDCl_3$) for **9c**.



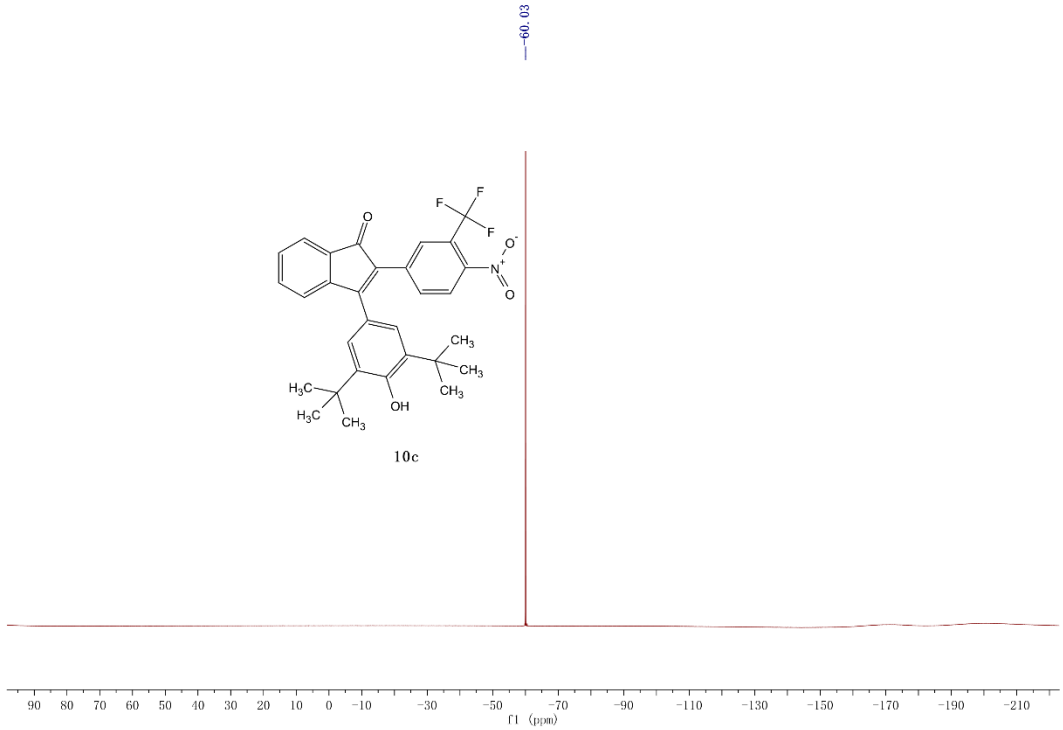
^{1}H NMR (400MHz, $CDCl_3$) for **10c**.



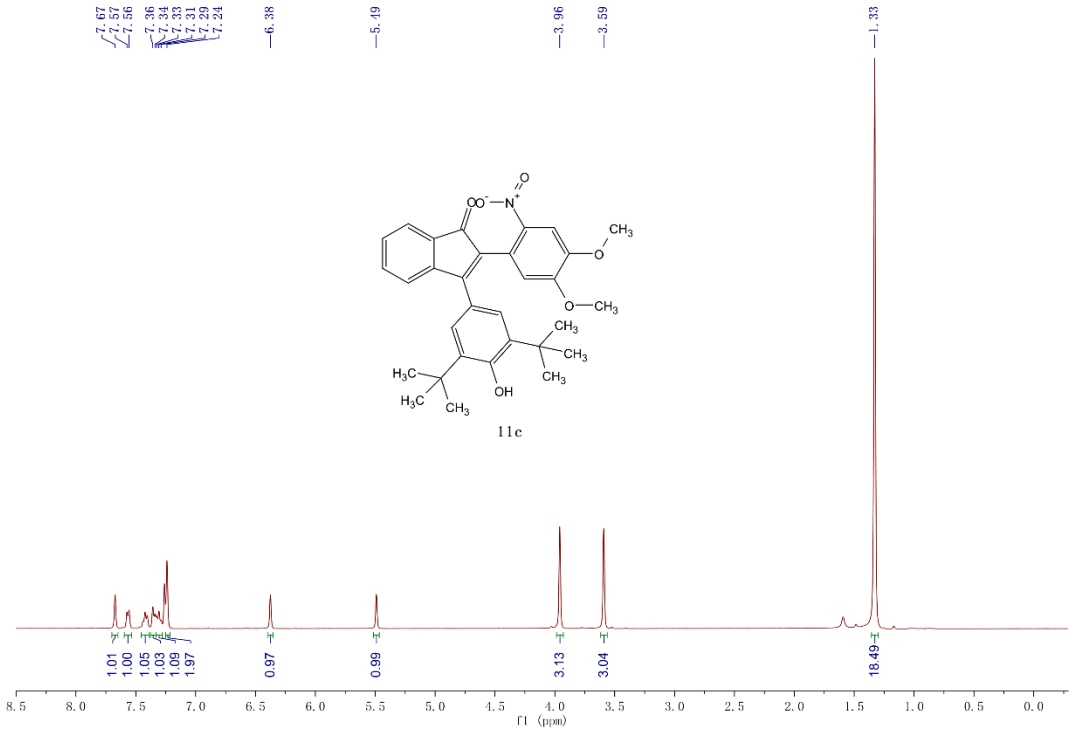
^{13}C NMR (101 MHz, $CDCl_3$) for **10c**.



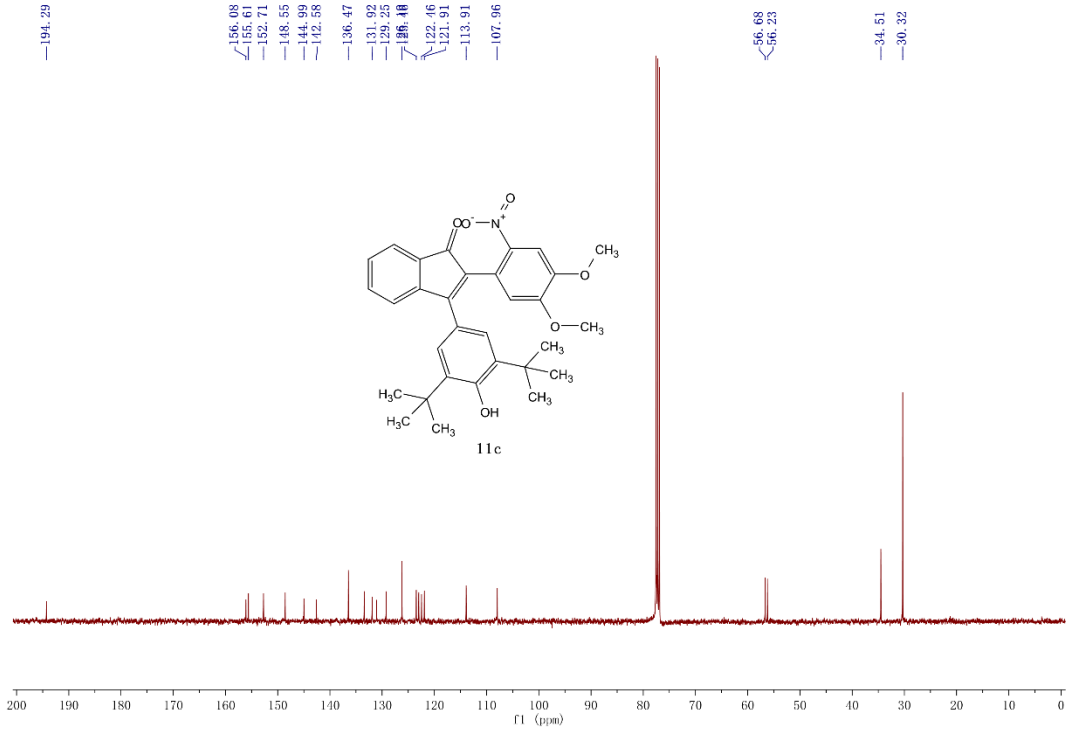
^{19}F NMR (377 MHz, $CDCl_3$) for **10c**.



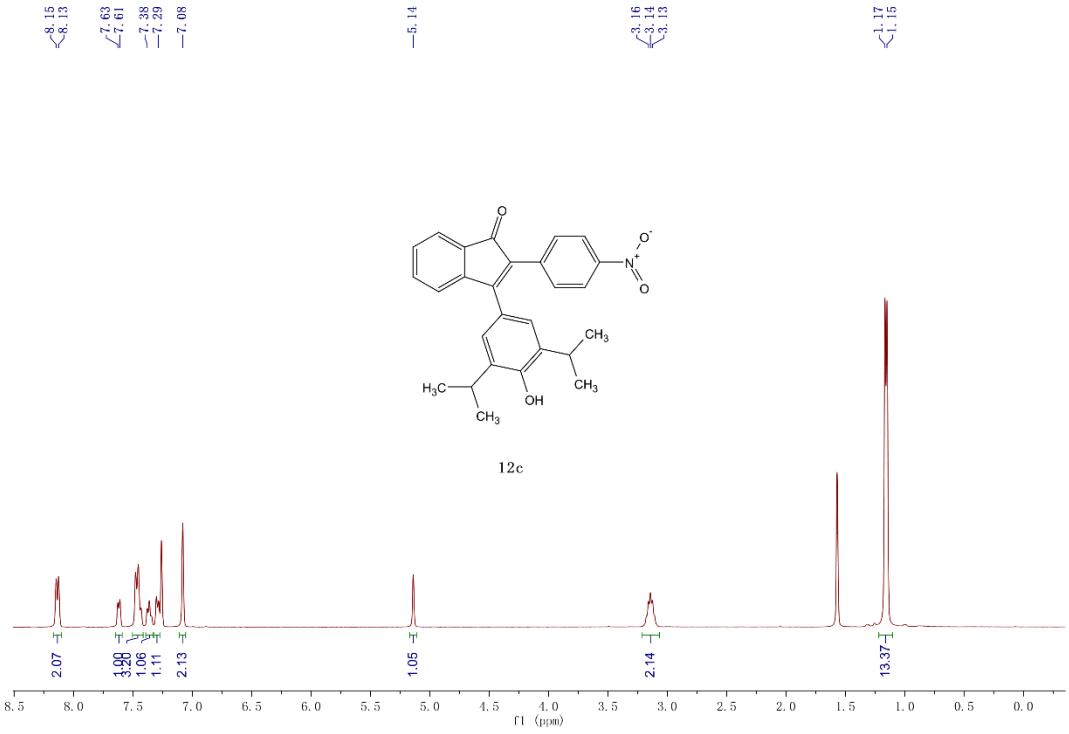
^{1}H NMR (400MHz, $CDCl_3$) for **11c**.



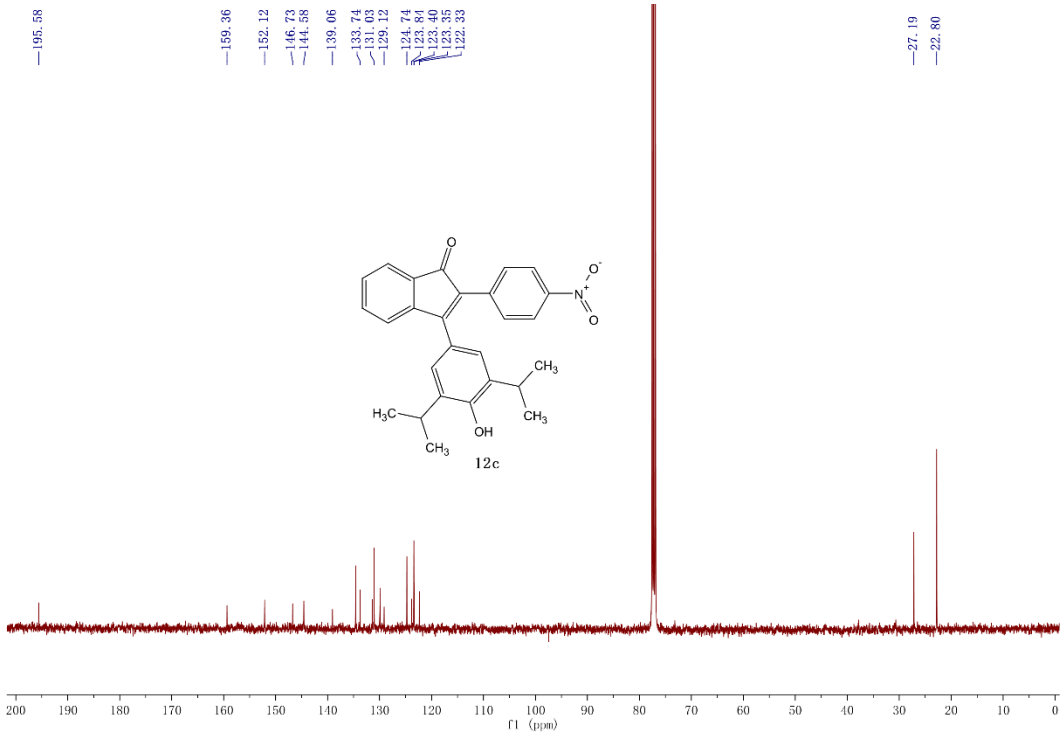
^{13}C NMR (101 MHz, $CDCl_3$) for **11c**.



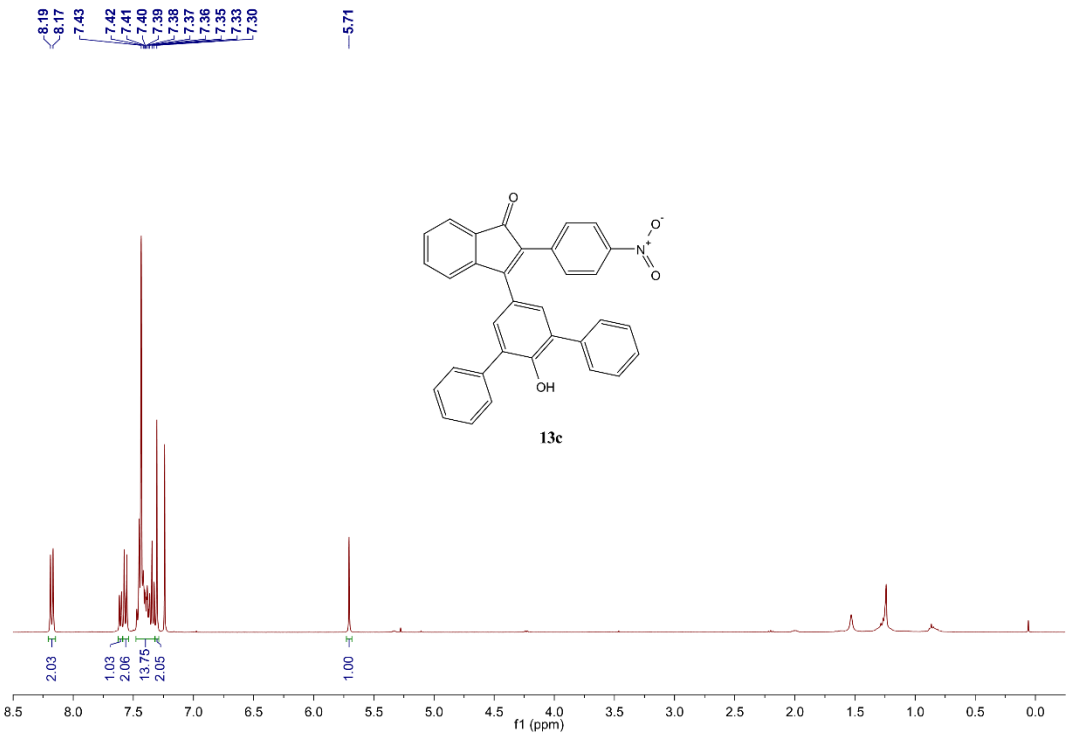
^{1}H NMR (400MHz, $CDCl_3$) for **12c**.



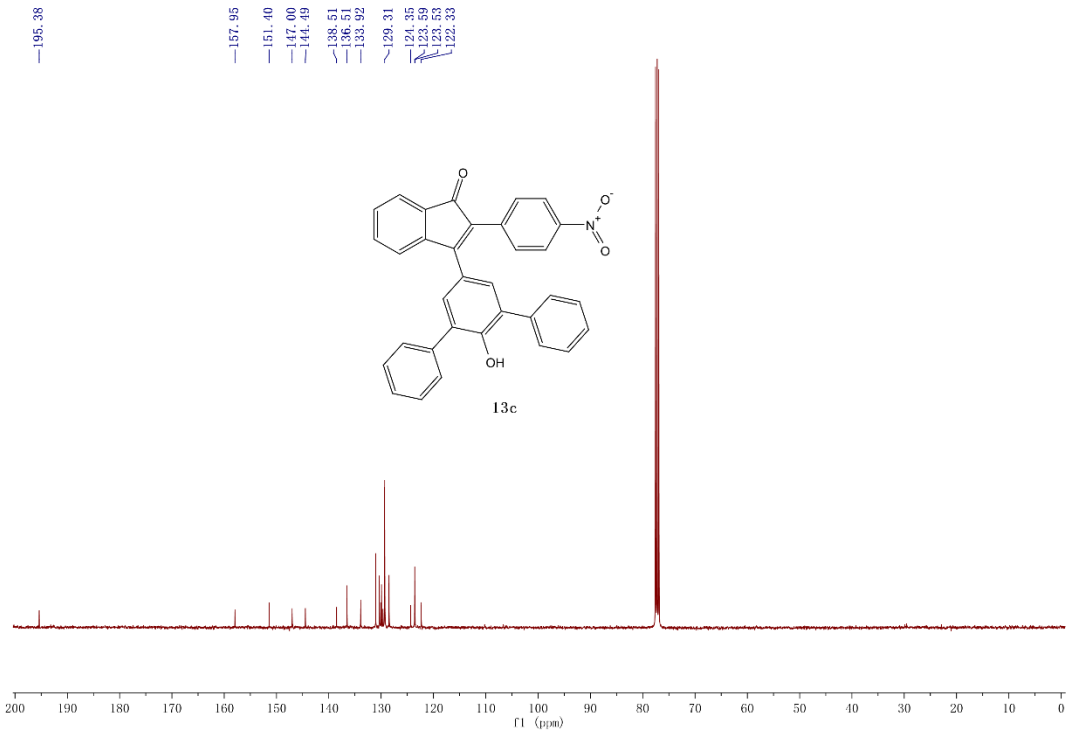
^{13}C NMR (101 MHz, $CDCl_3$) for **12c**.



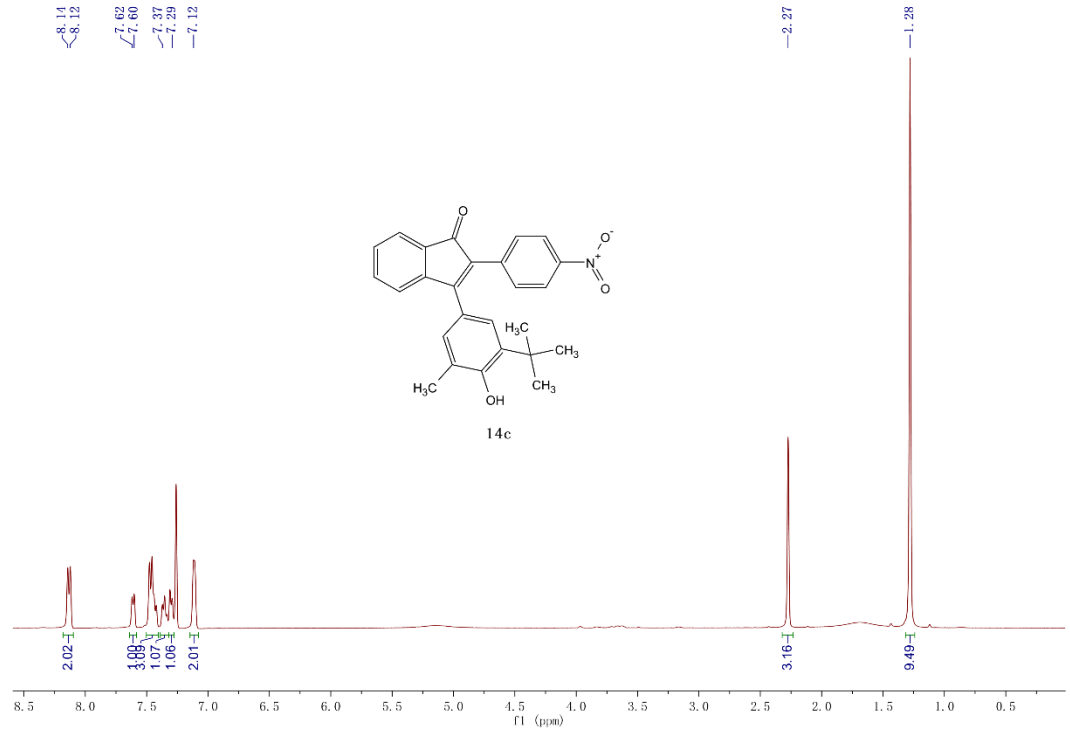
^{1}H NMR (400MHz, $CDCl_3$) for **13c**.



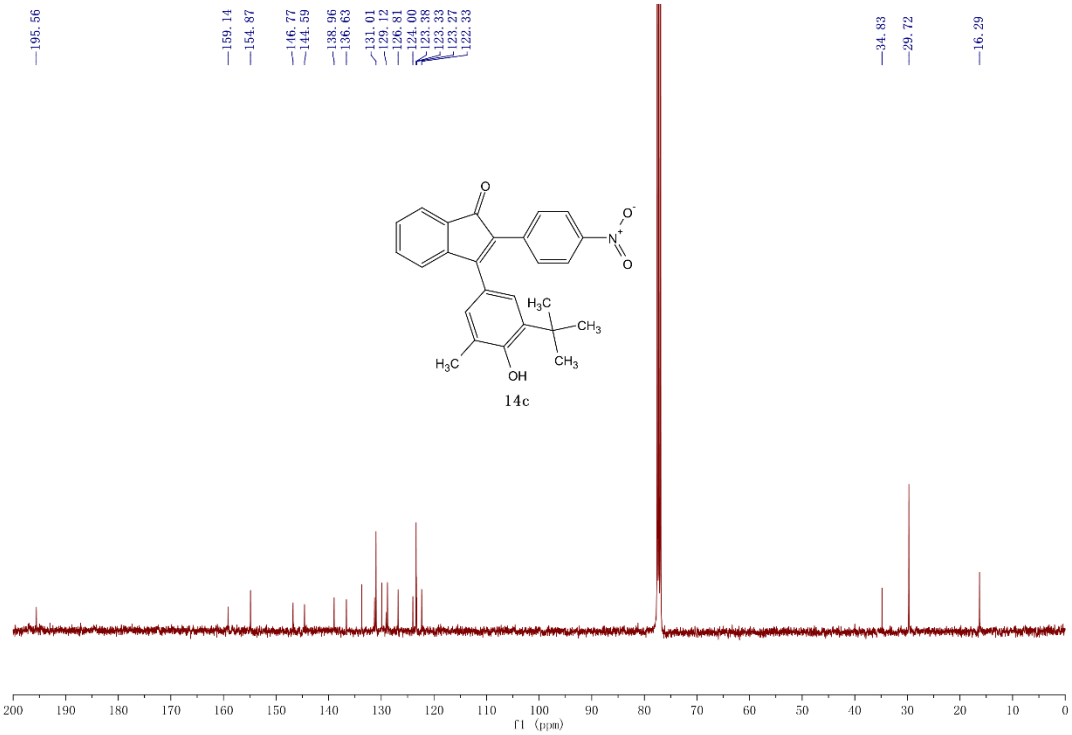
^{13}C NMR (101 MHz, $CDCl_3$) for **13c**.



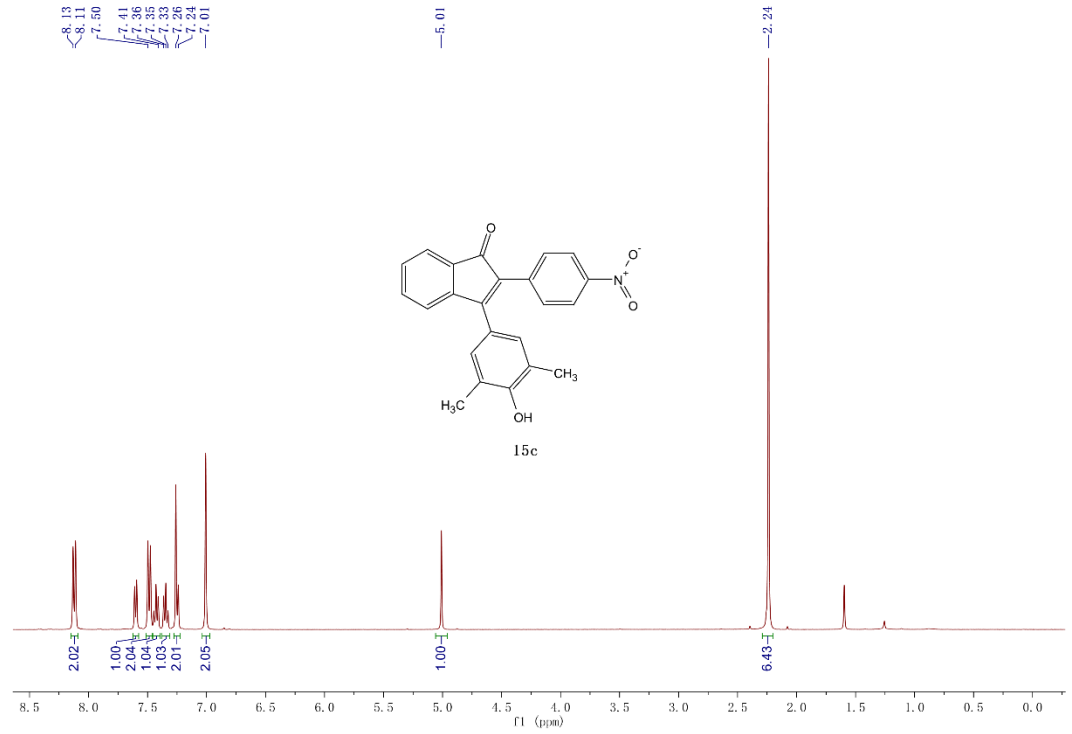
^{1}H NMR (400MHz, $CDCl_3$) for **14c**.



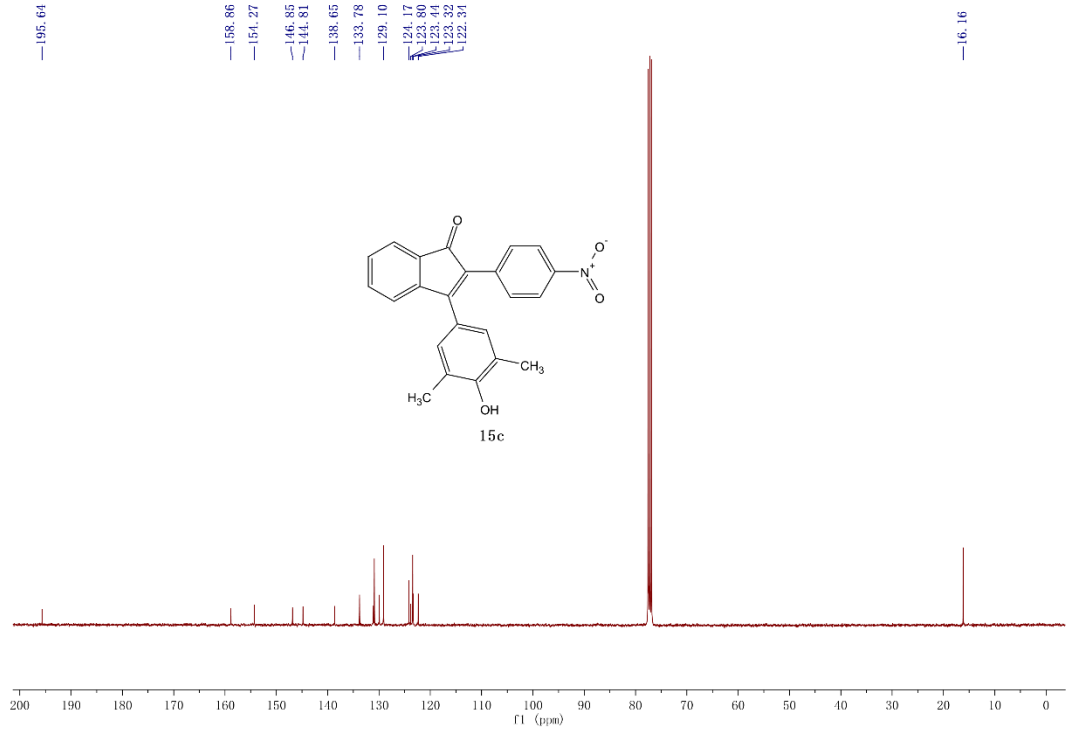
^{13}C NMR (101 MHz, $CDCl_3$) for **14c**.



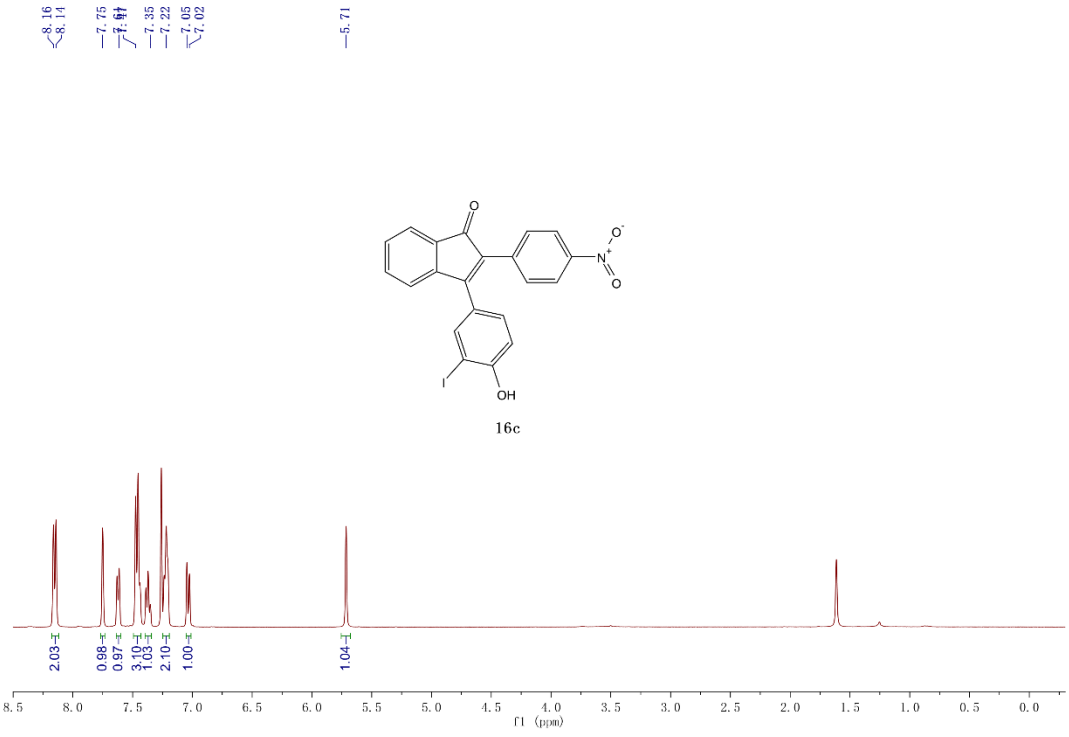
^{1}H NMR (400MHz, $CDCl_3$) for **15c**.



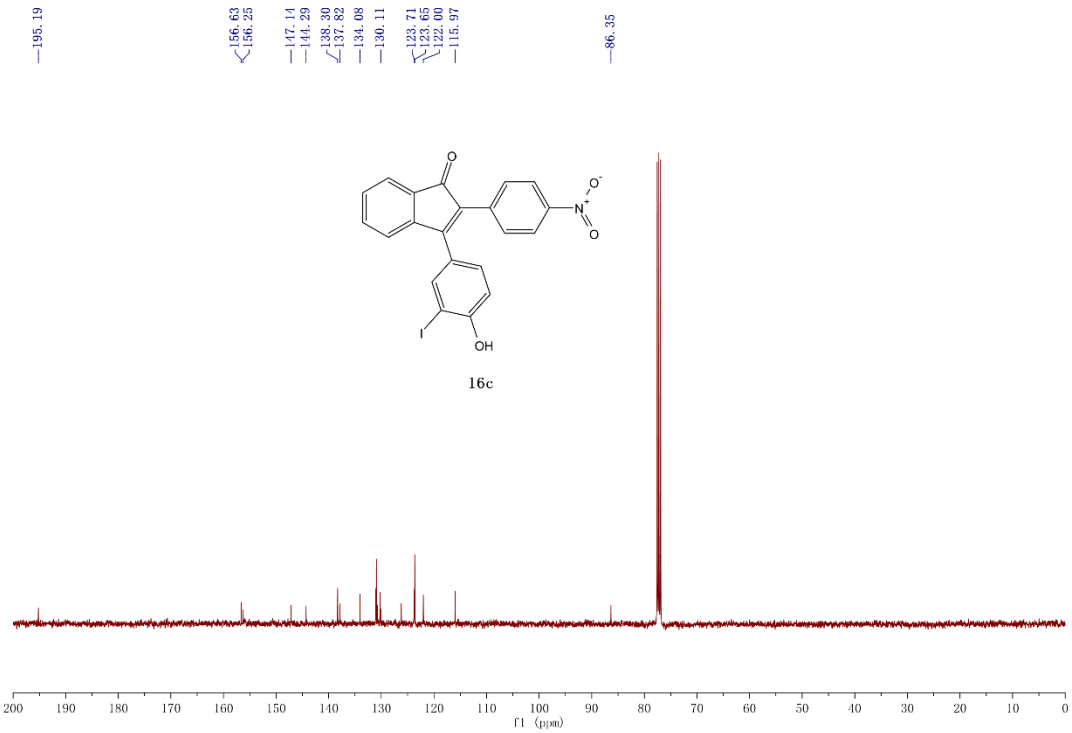
^{13}C NMR (101 MHz, $CDCl_3$) for **15c**.



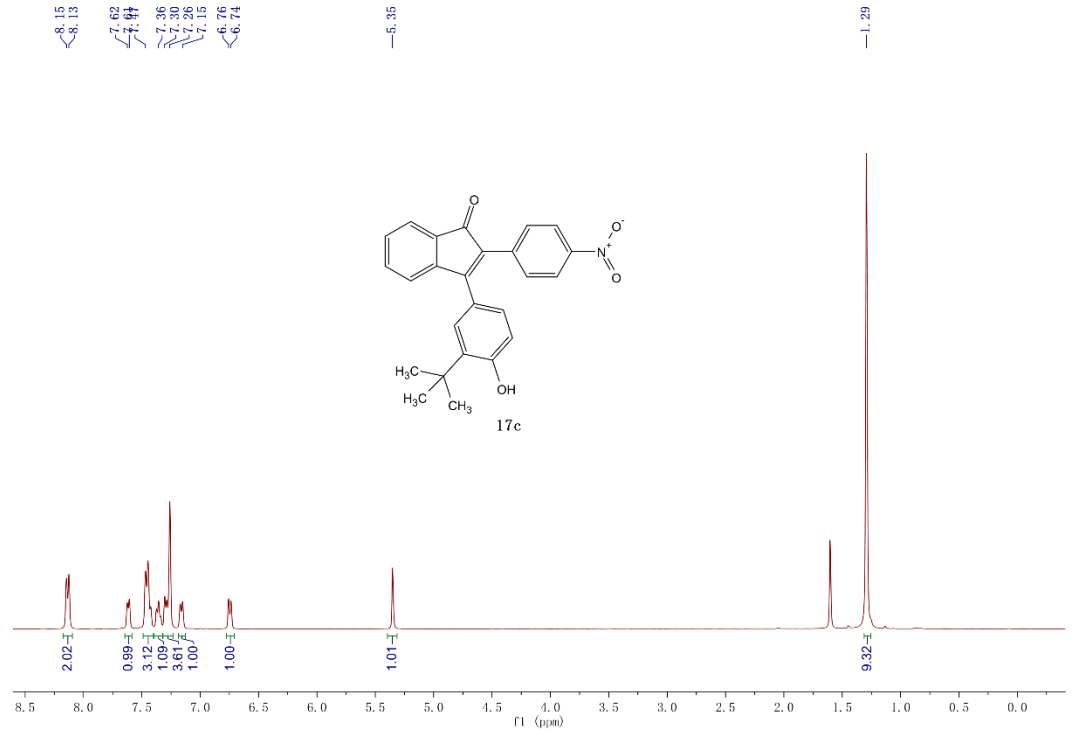
^{1}H NMR (400MHz, $CDCl_3$) for **16c**.



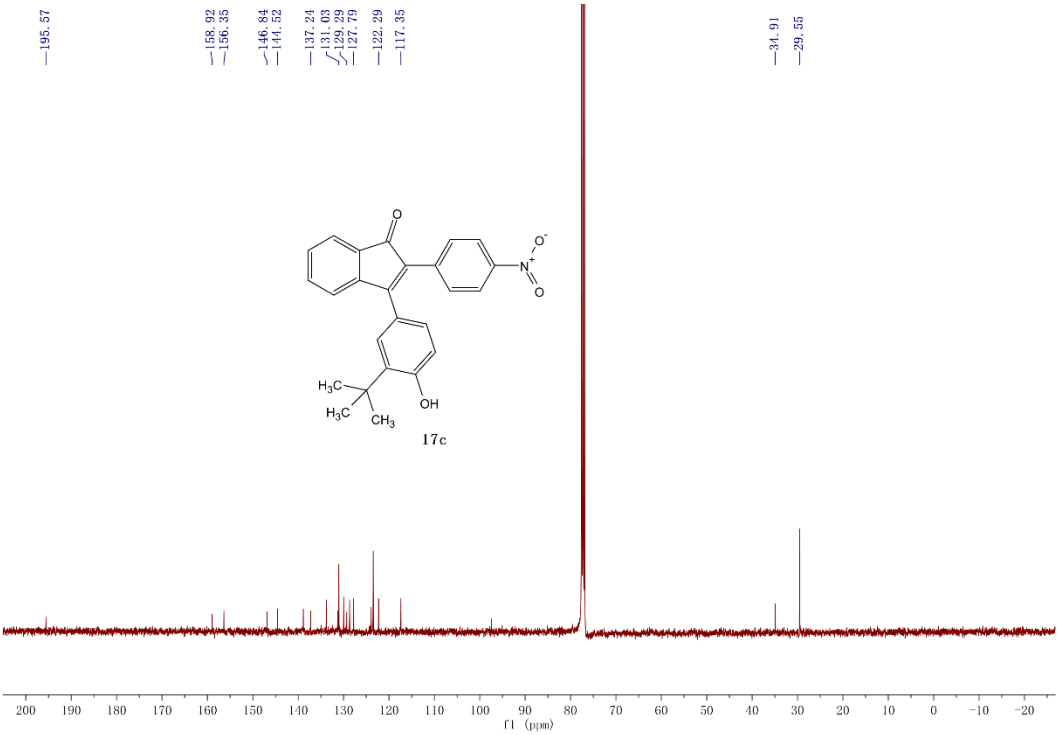
^{13}C NMR (101 MHz, $CDCl_3$) for **16c**.



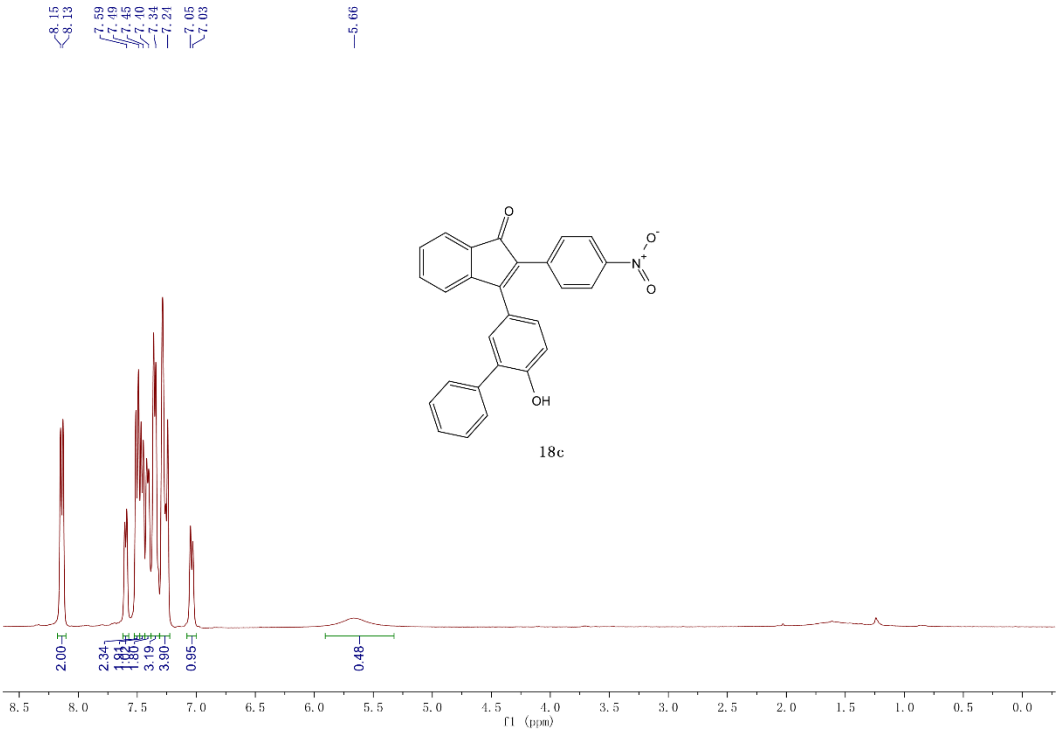
^{1}H NMR (400MHz, $CDCl_3$) for **17c**.



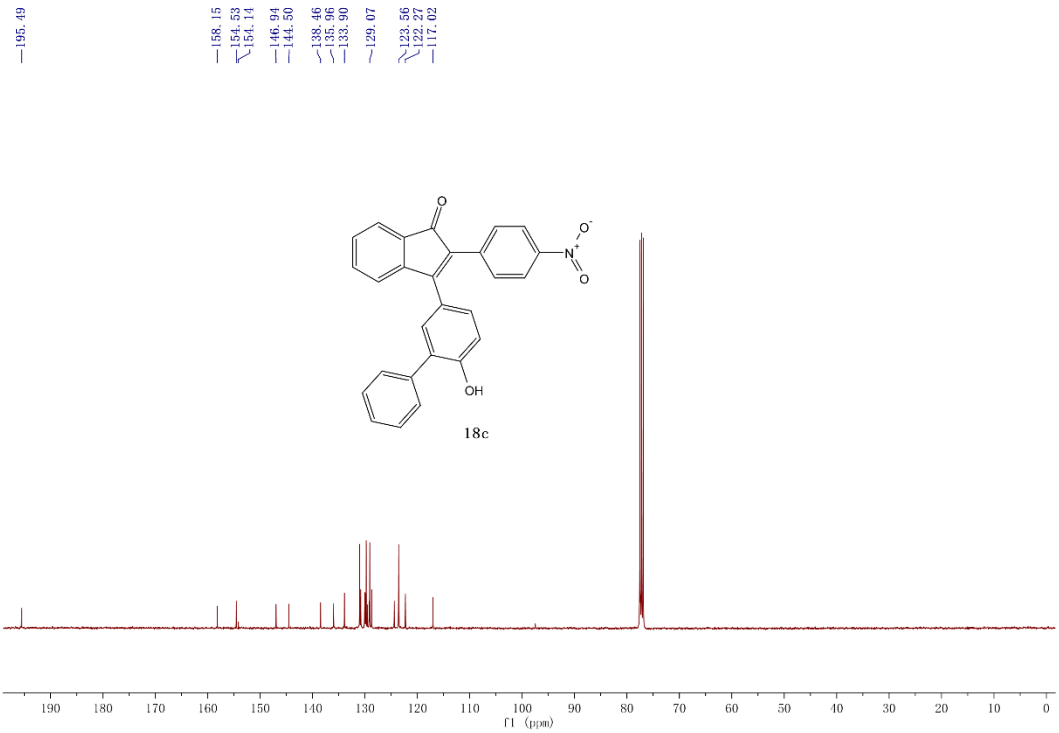
^{13}C NMR (101 MHz, $CDCl_3$) for **17c**.



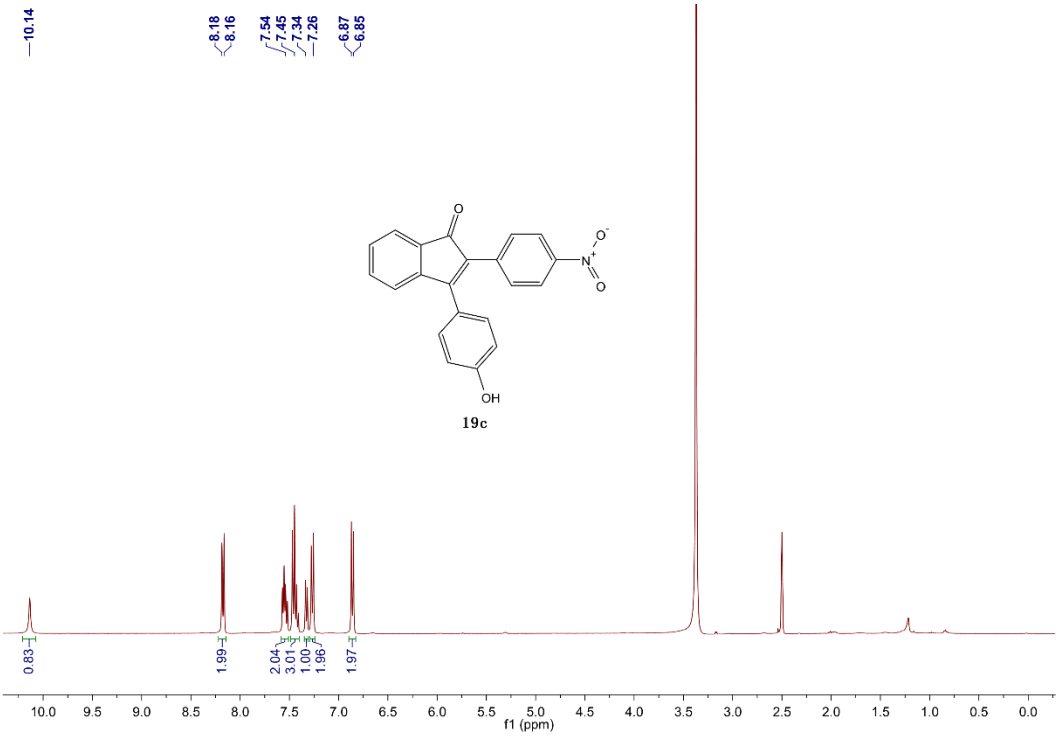
^{1}H NMR (400MHz, $CDCl_3$) for **18c**.



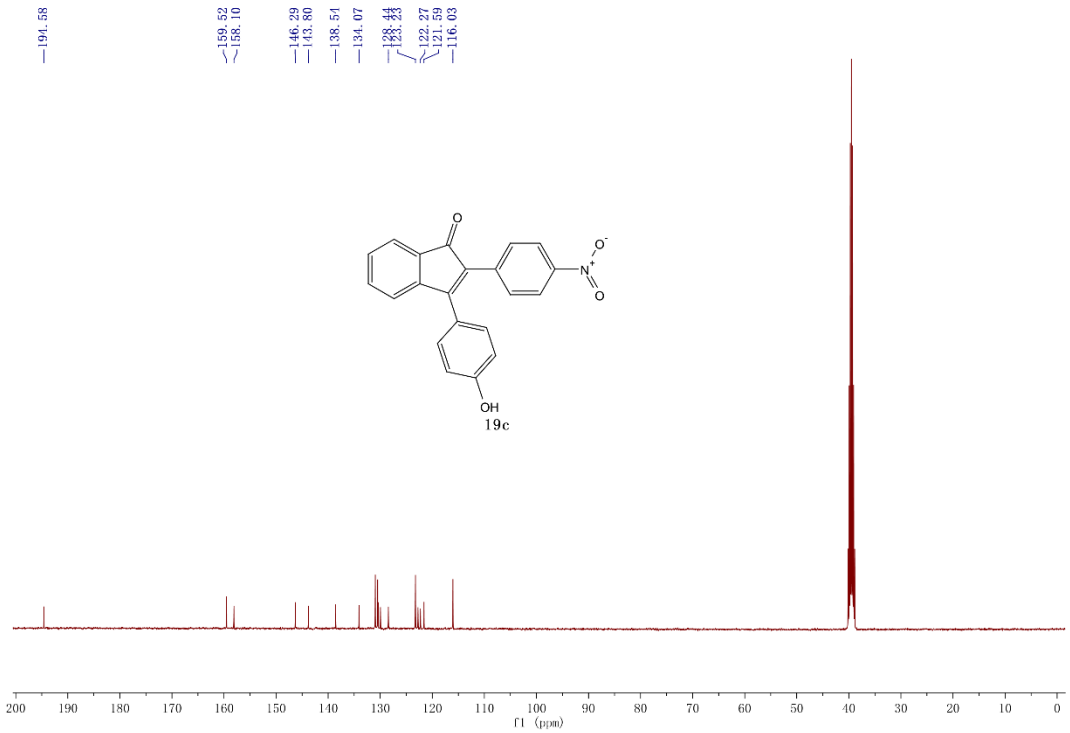
^{13}C NMR (101 MHz, $CDCl_3$) for **18c**.



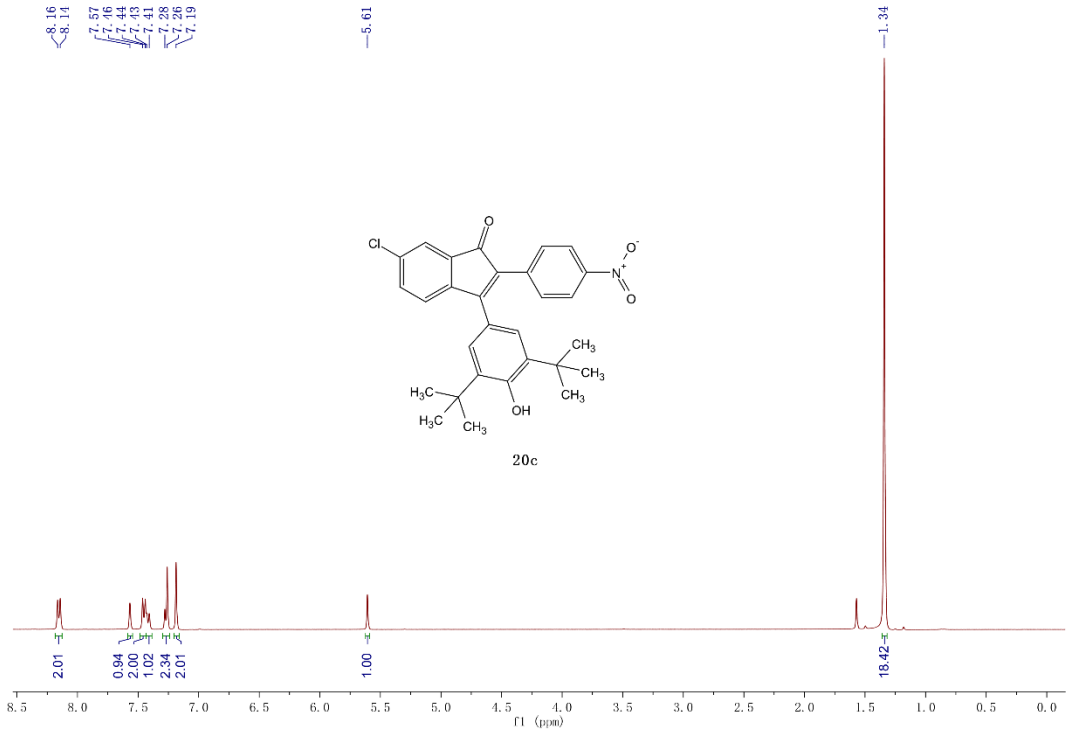
^{1}H NMR (400MHz, DMSO-d_6) for **19c**.



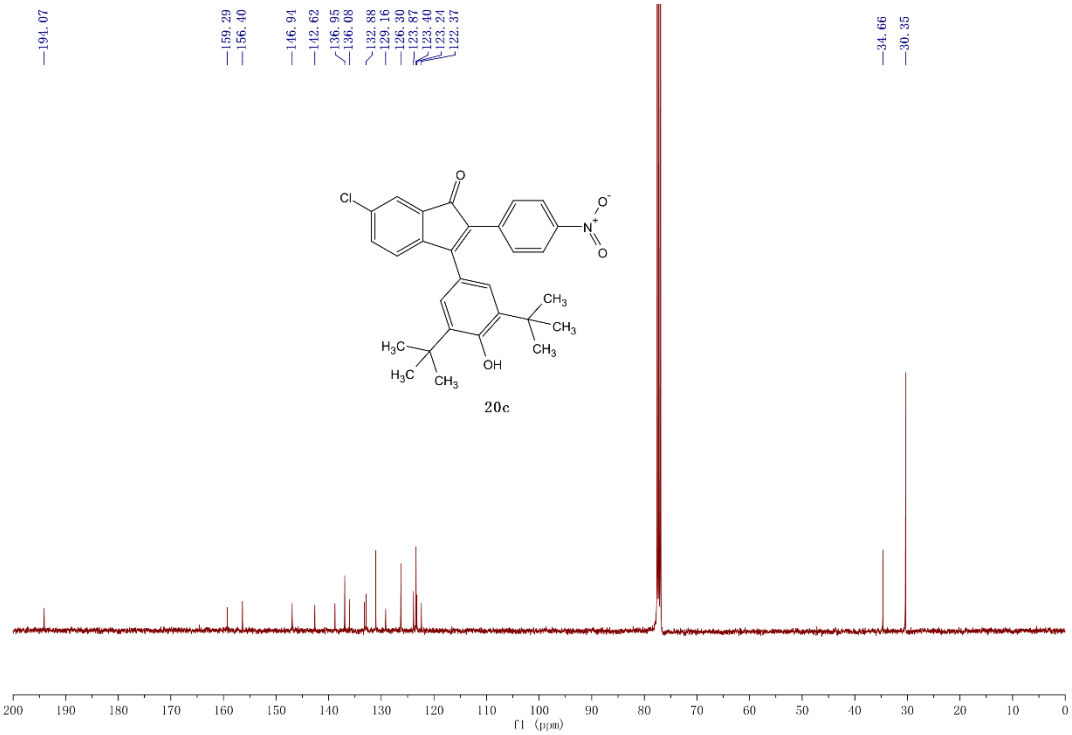
^{13}C NMR (101 MHz, DMSO-d_6) for **19c**.



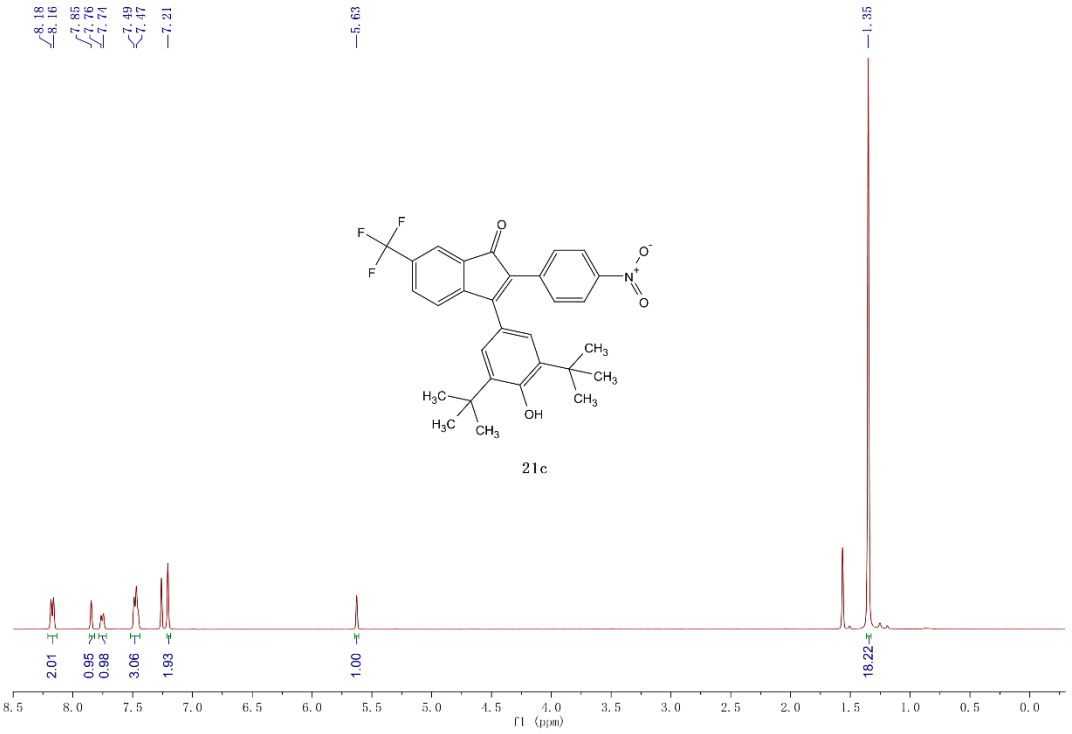
^{1}H NMR (400MHz, $CDCl_3$) for **20c**.



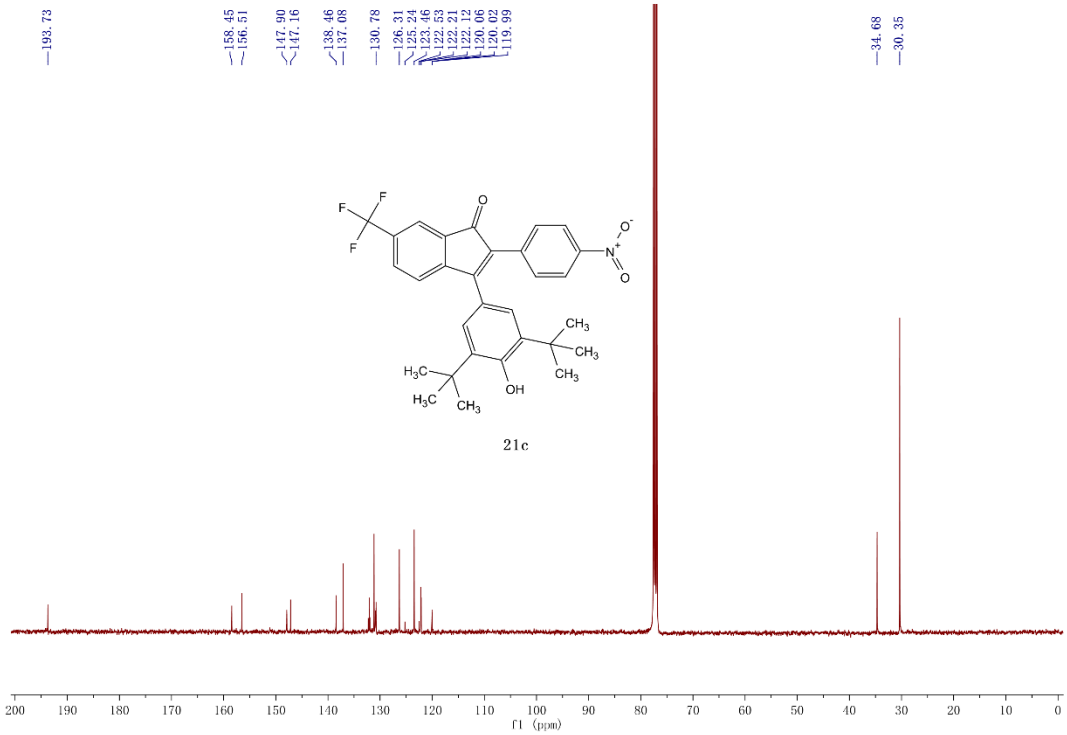
^{13}C NMR (101 MHz, $CDCl_3$) for **20c**.



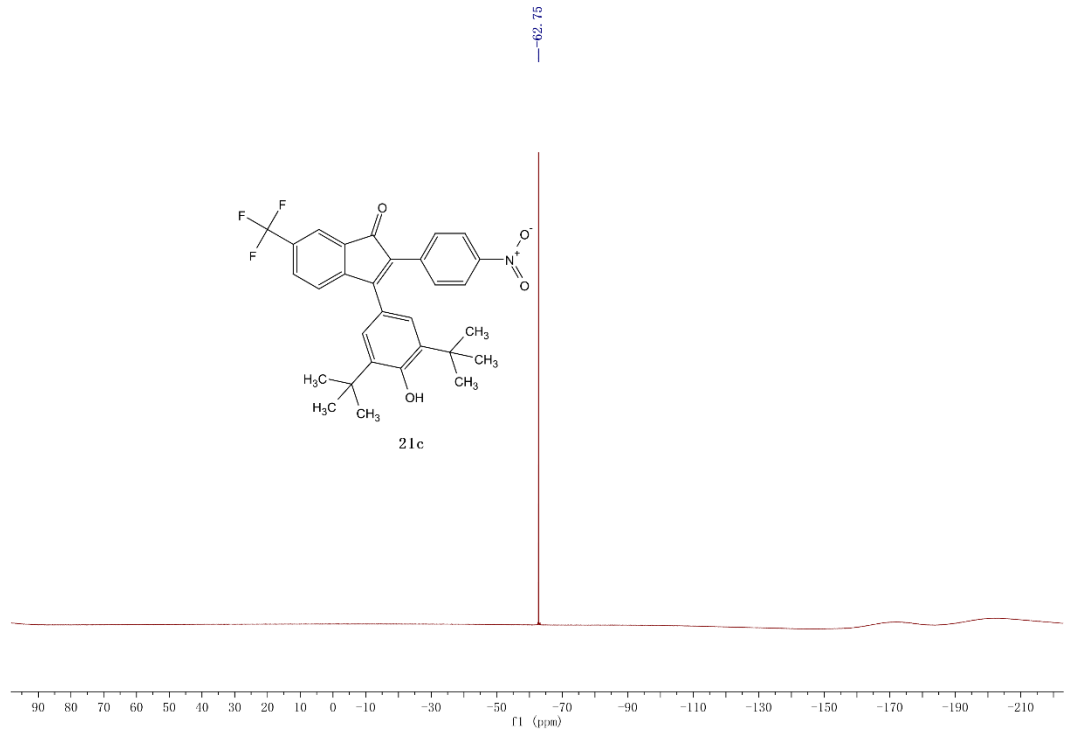
^{1}H NMR (400MHz, $CDCl_3$) for **21c**.



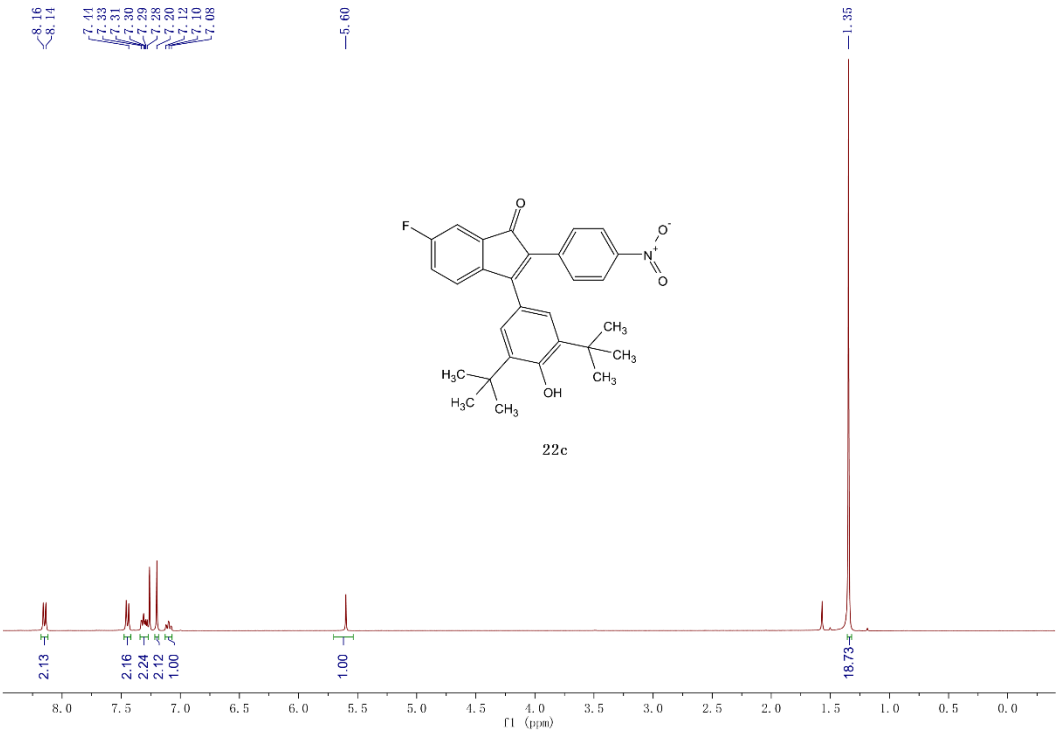
^{13}C NMR (101 MHz, $CDCl_3$) for **21c**.



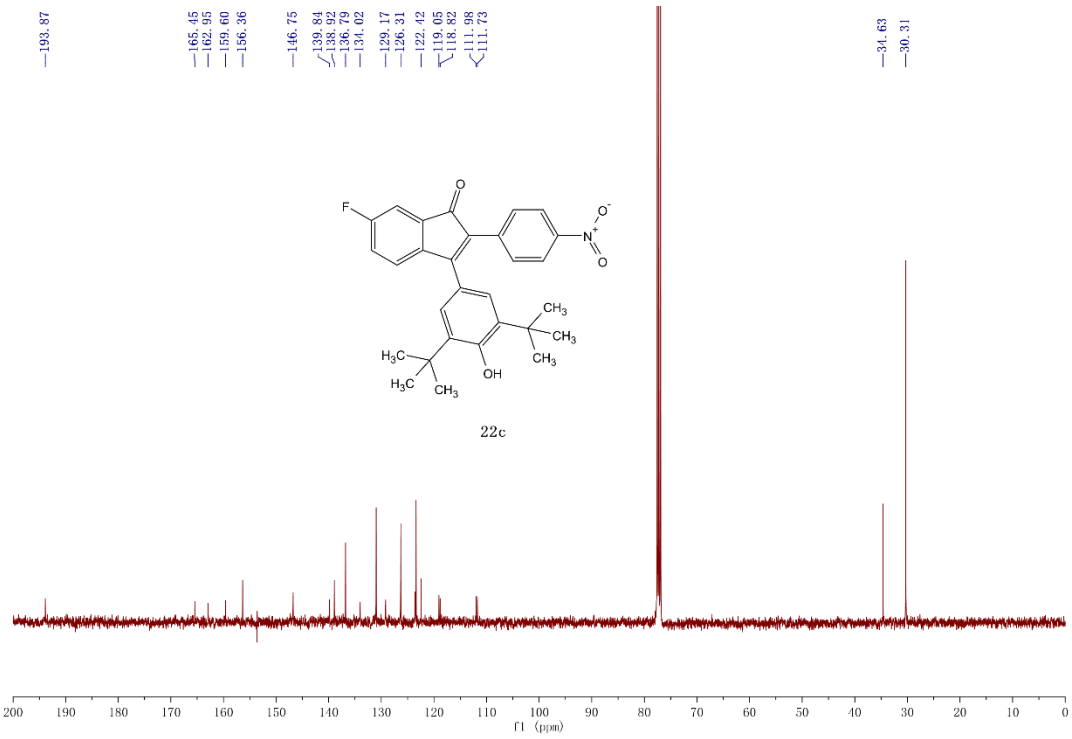
^{19}F NMR (377 MHz, $CDCl_3$) for **21c**.



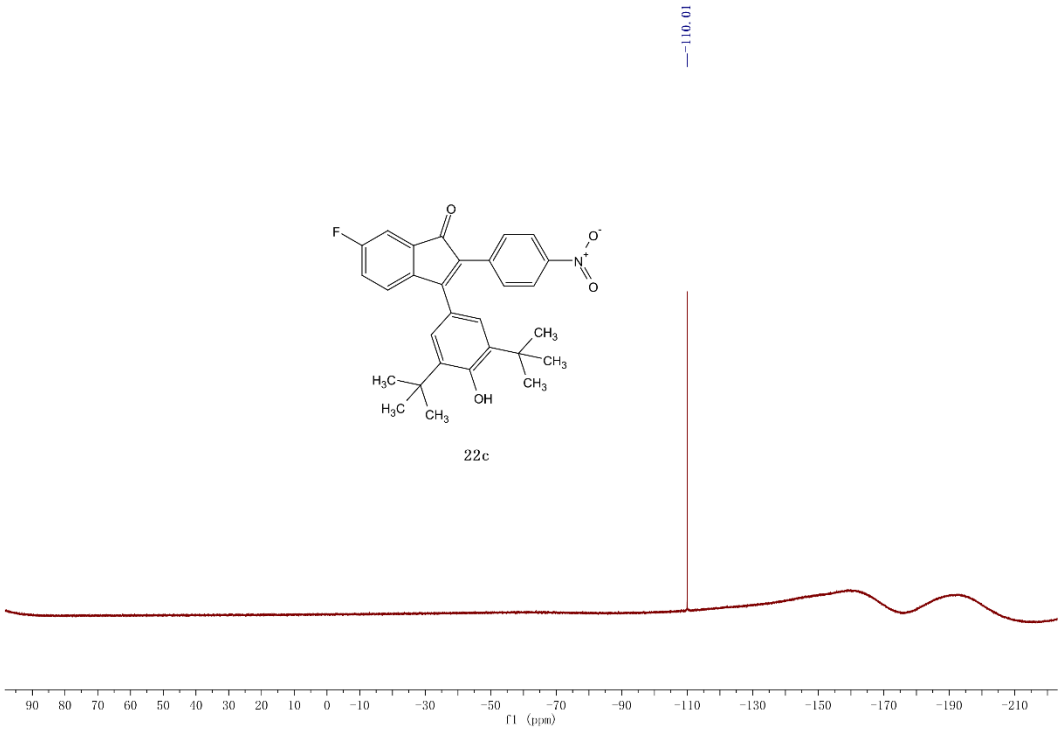
^{1}H NMR (400MHz, $CDCl_3$) for **22c**.



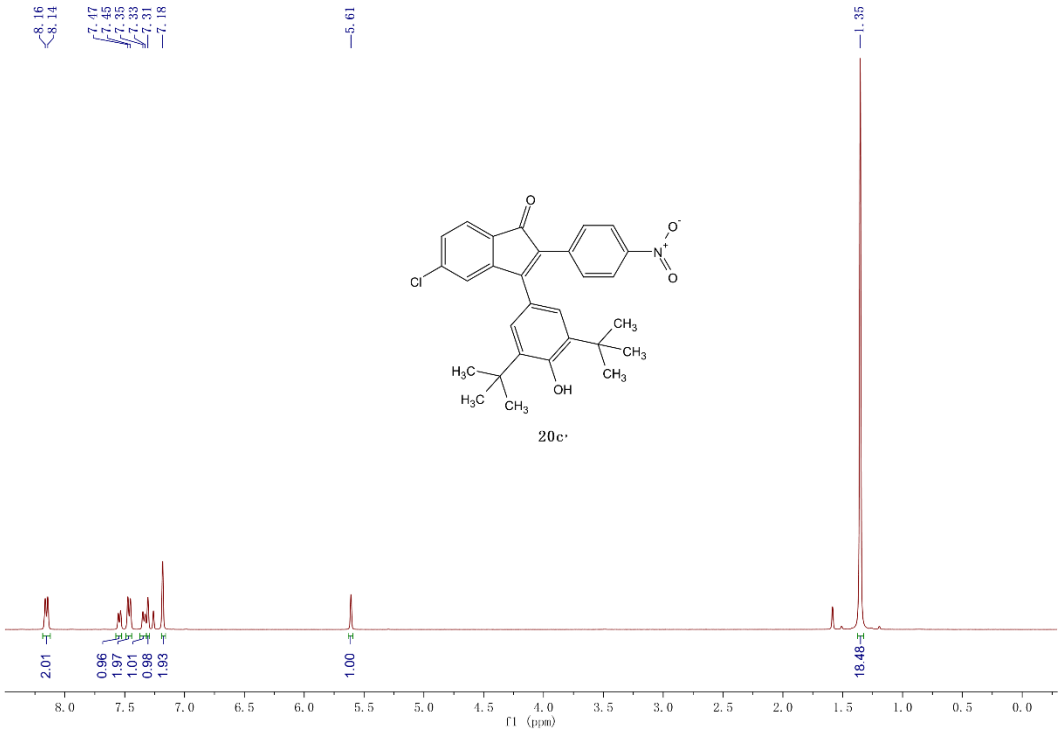
^{13}C NMR (101 MHz, $CDCl_3$) for **22c**.



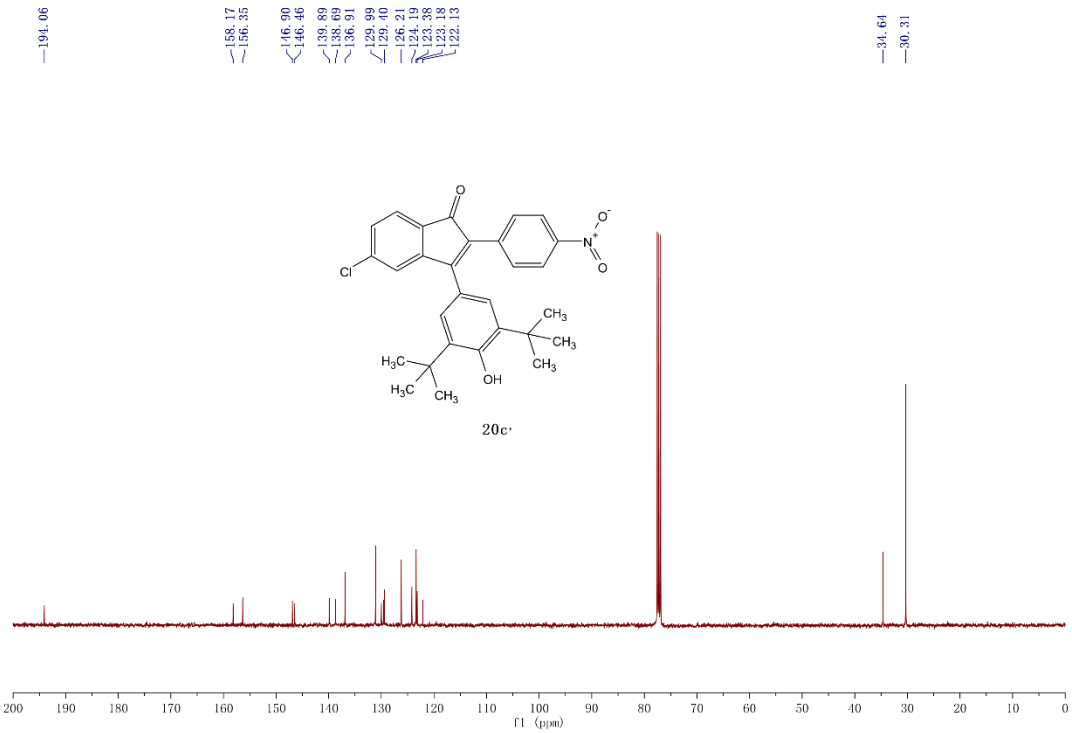
^{19}F NMR (377 MHz, $CDCl_3$) for **22c**.



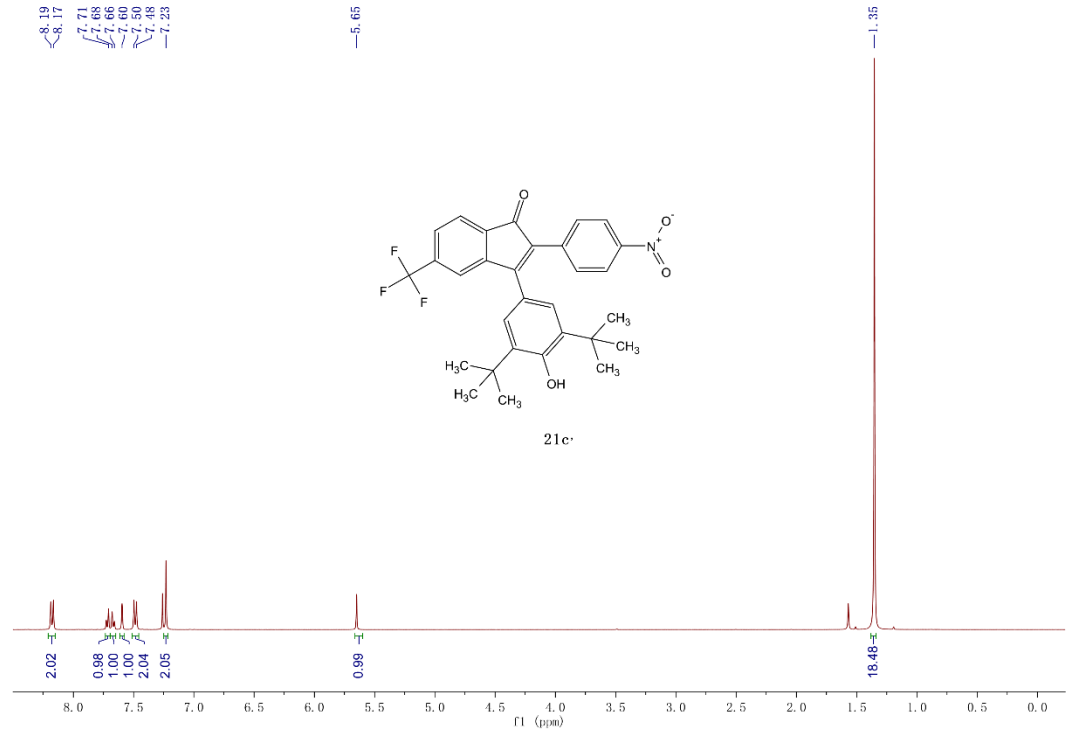
^{1}H NMR (400MHz, $CDCl_3$) for **20c'**.



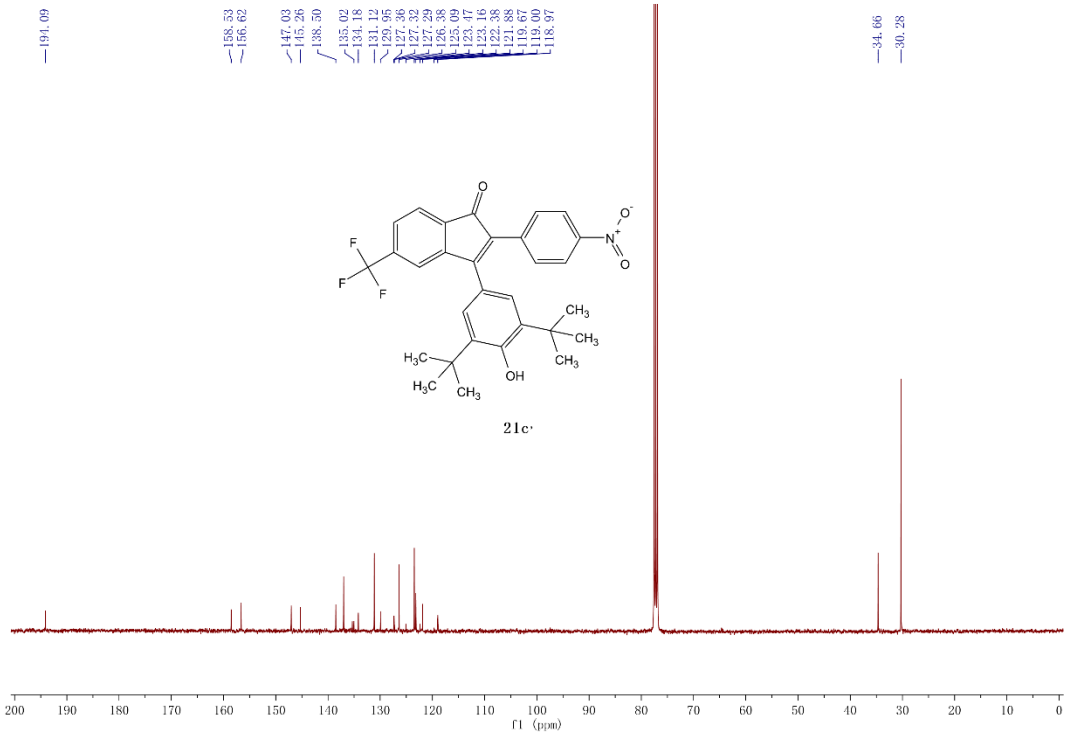
^{13}C NMR (101 MHz, $CDCl_3$) for **20c'**.



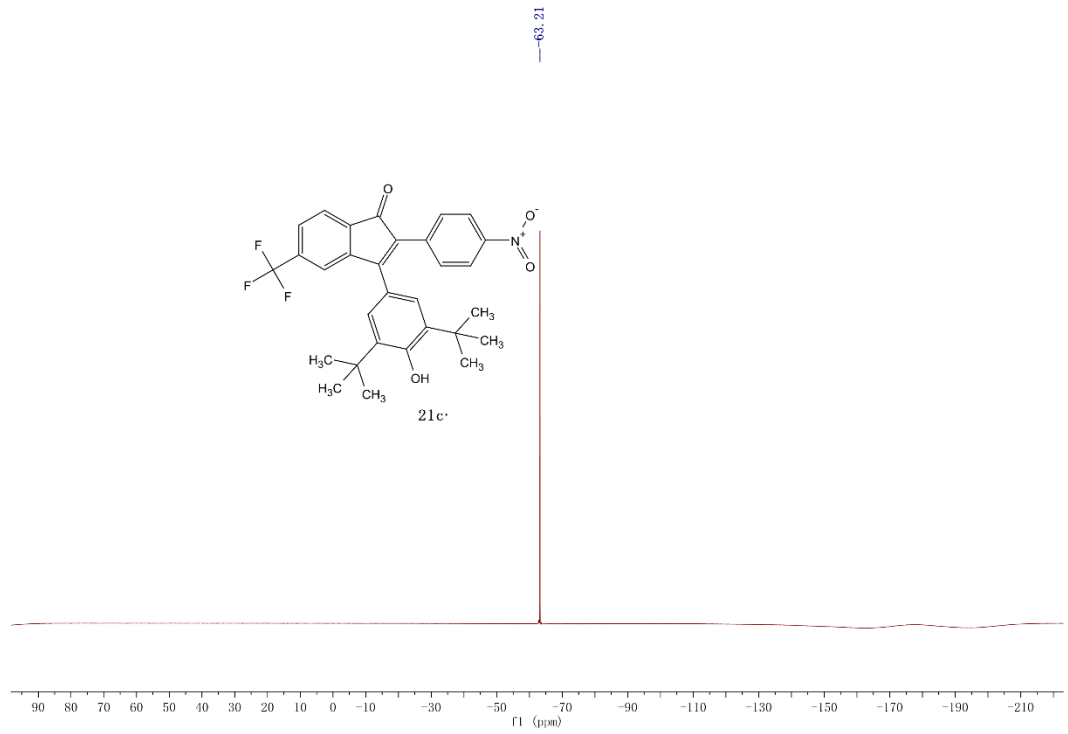
^{1}H NMR (400MHz, $CDCl_3$) for **21c'**.



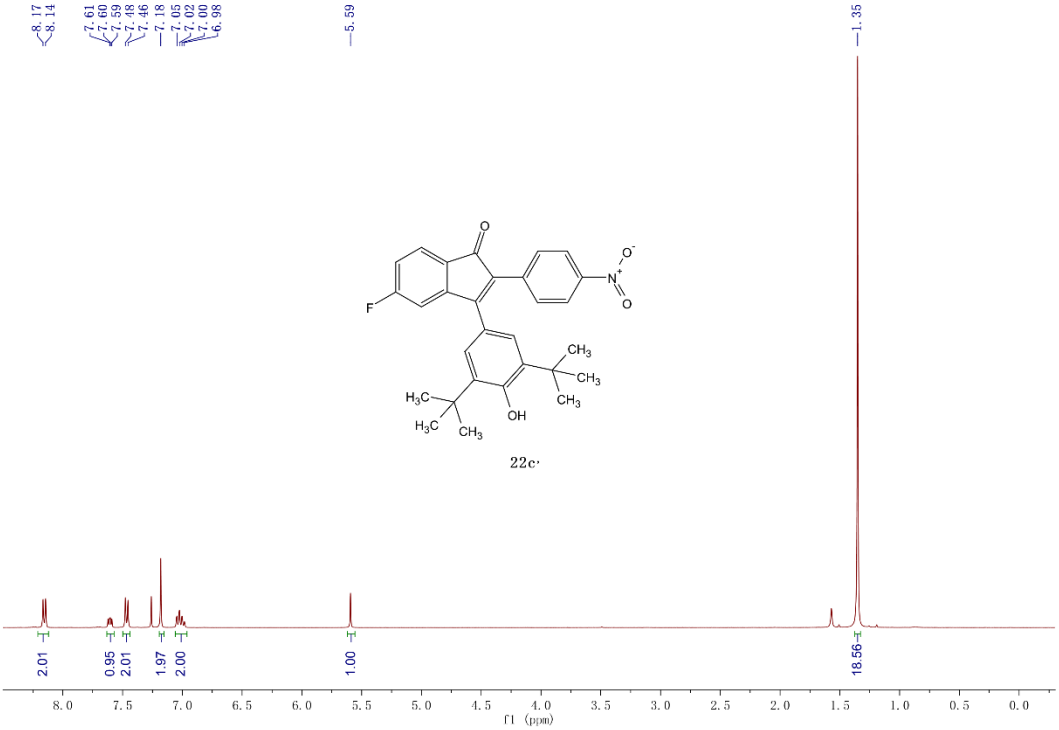
^{13}C NMR (101 MHz, $CDCl_3$) for **21c'**.



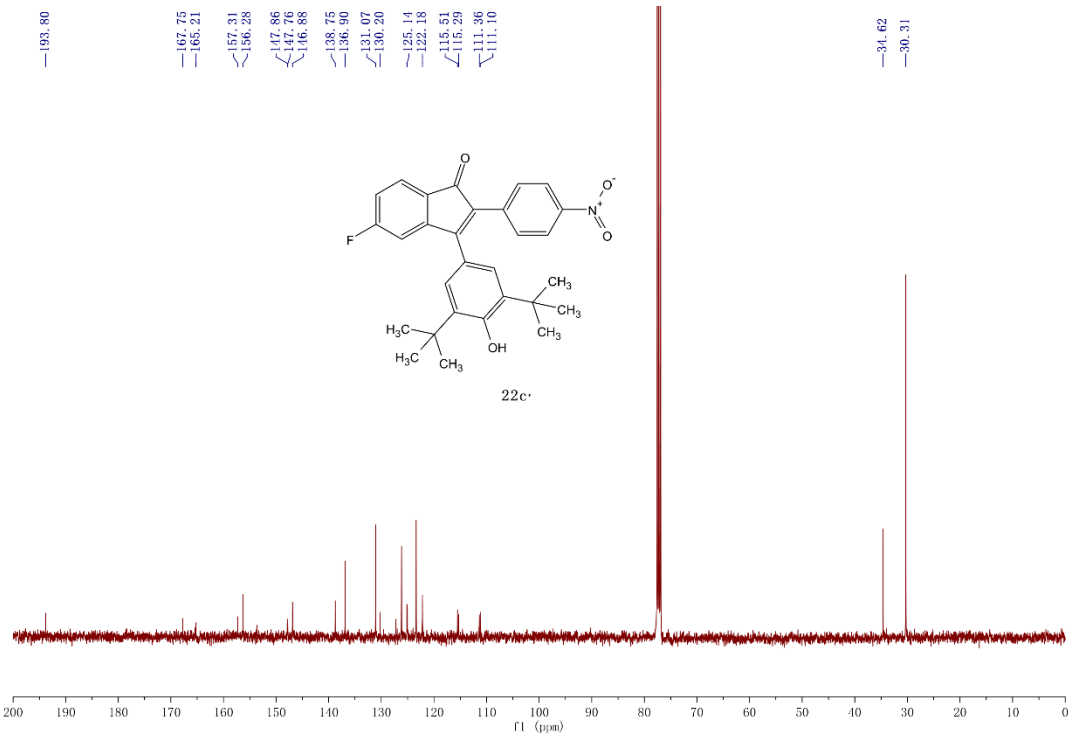
^{19}F NMR (377 MHz, $CDCl_3$) for **21c'**.



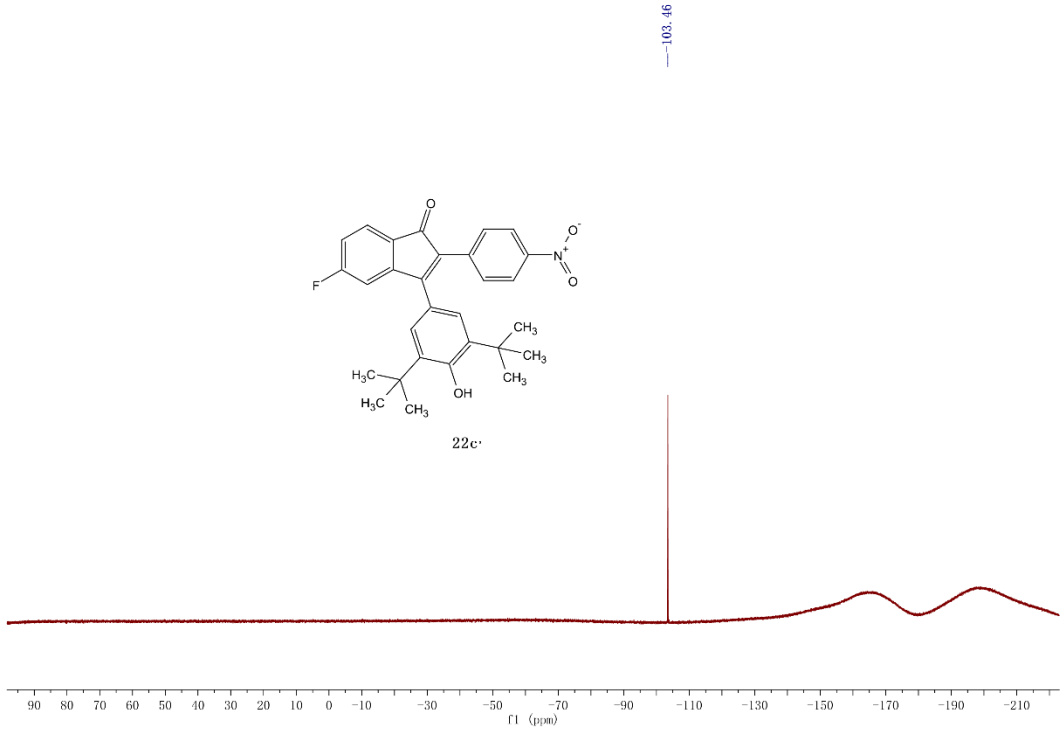
^{1}H NMR (400MHz, $CDCl_3$) for **22c'**.



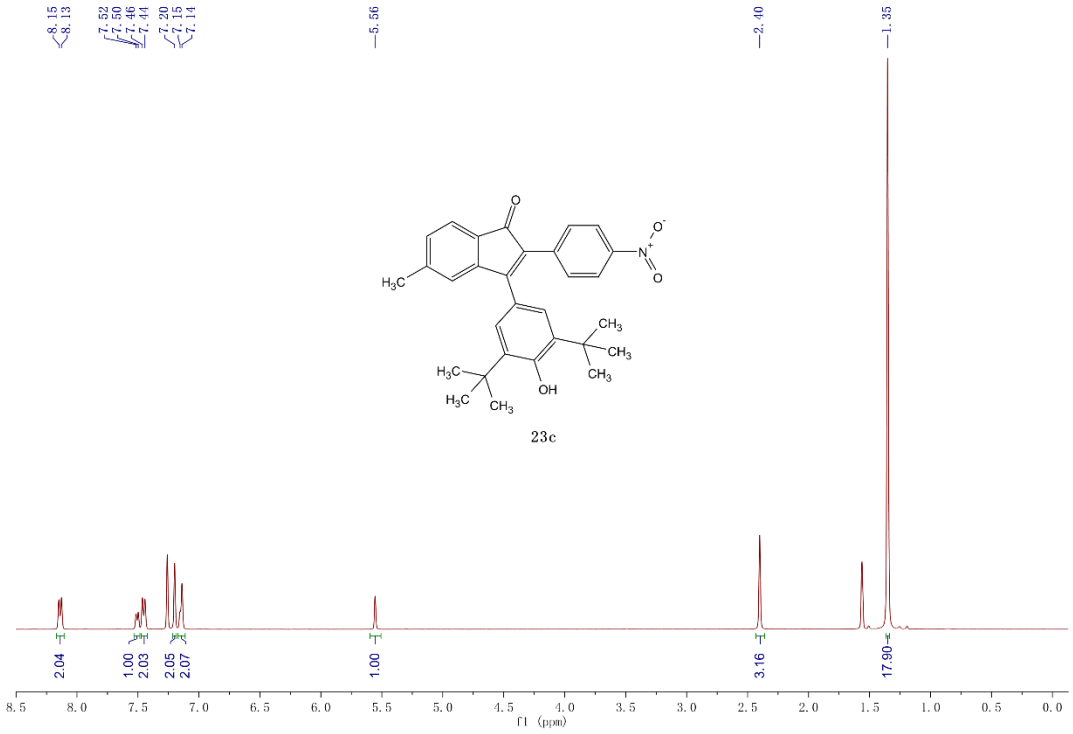
^{13}C NMR (101 MHz, $CDCl_3$) for **22c'**.



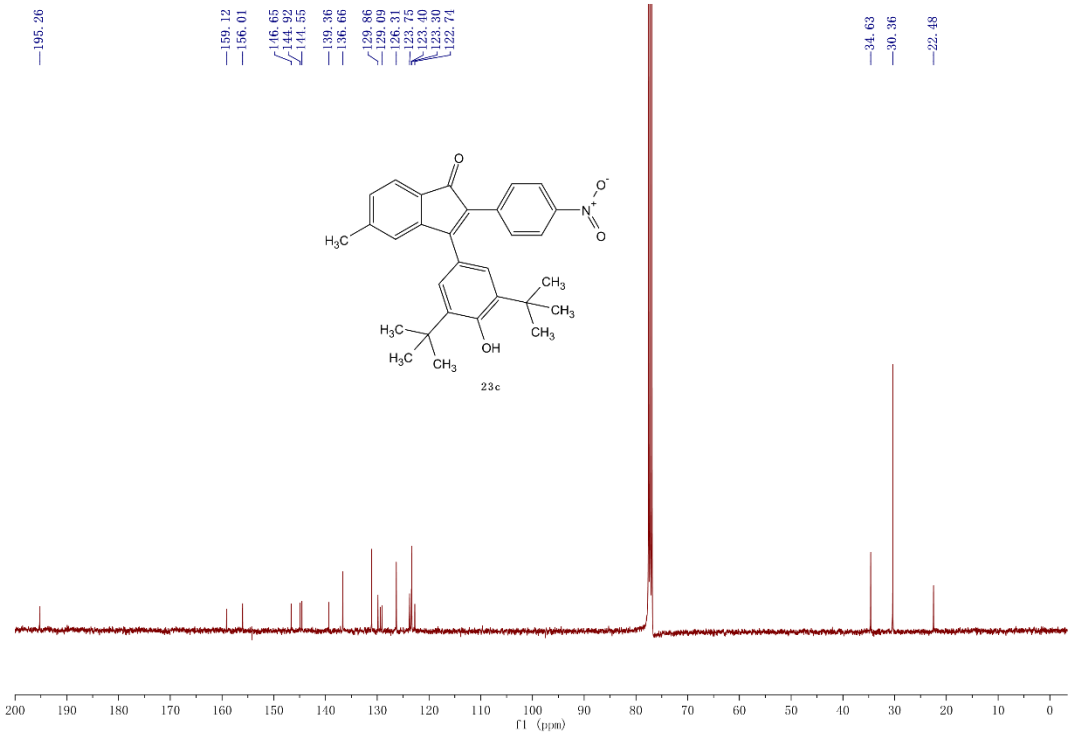
^{19}F NMR (377 MHz, $CDCl_3$) for **22c'**.



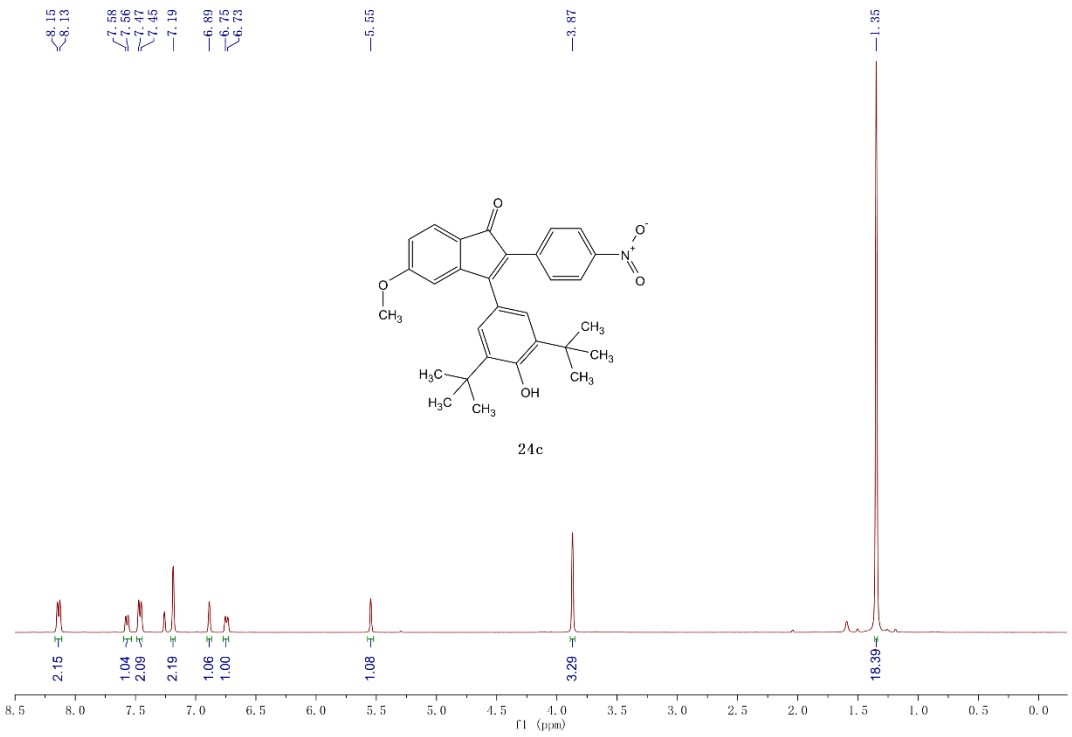
^{1}H NMR (400MHz, $CDCl_3$) for **23c**.



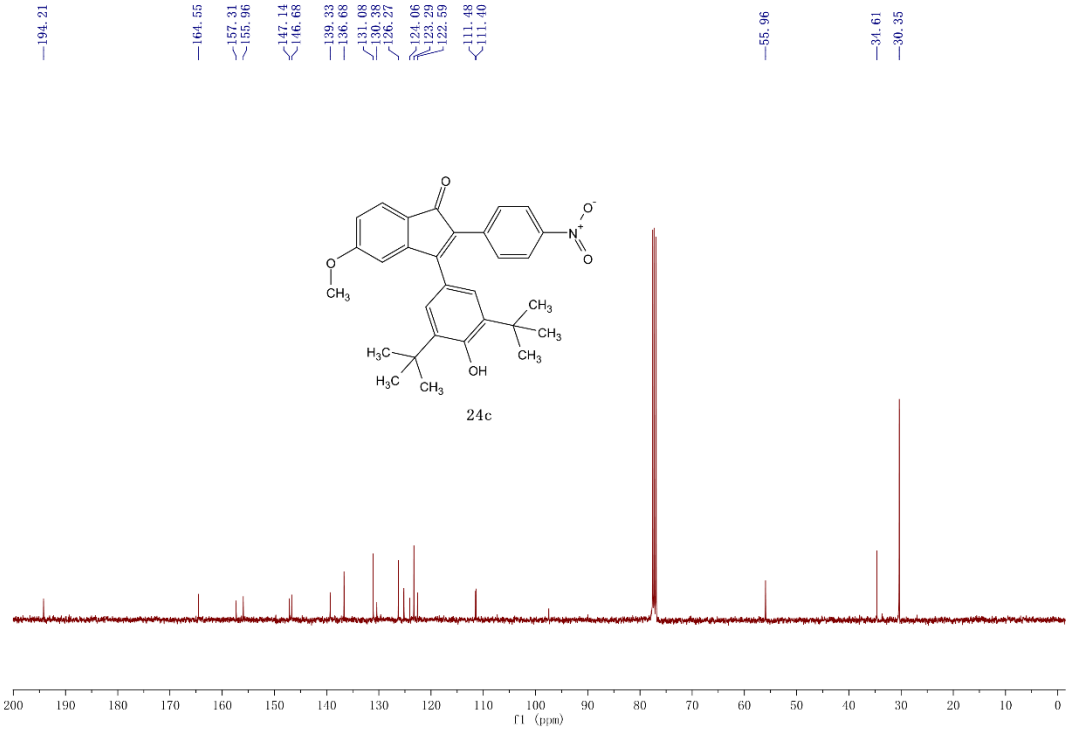
^{13}C NMR (101 MHz, $CDCl_3$) for **23c**.



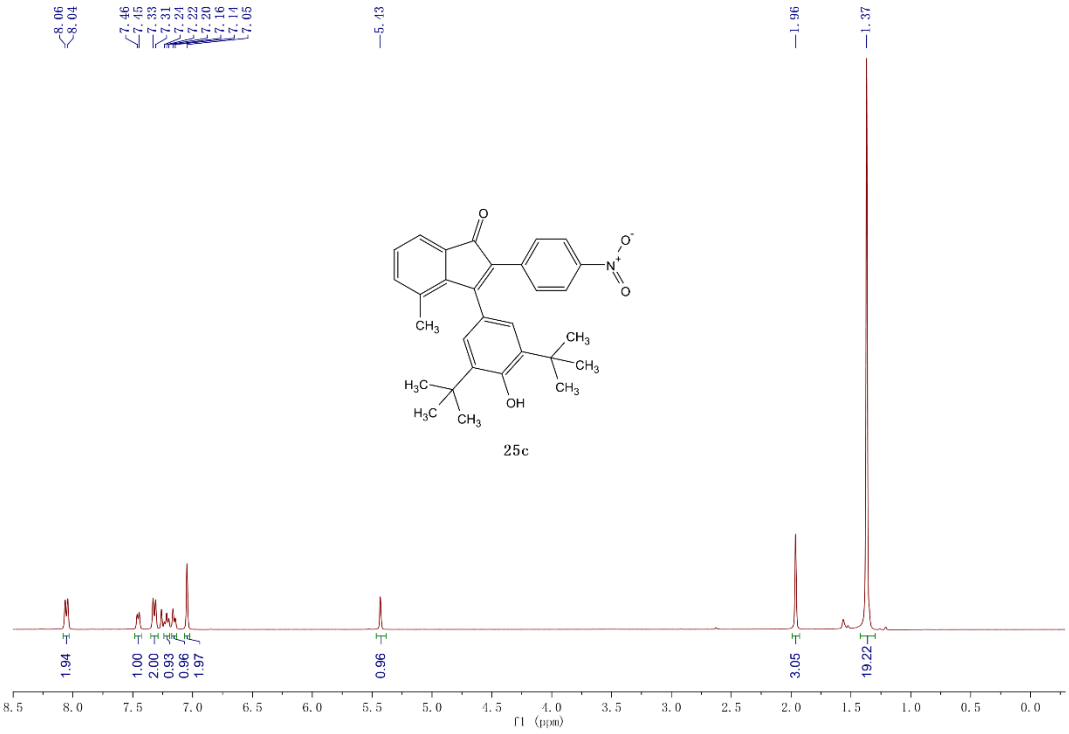
^{1}H NMR (400MHz, $CDCl_3$) for **24c**.



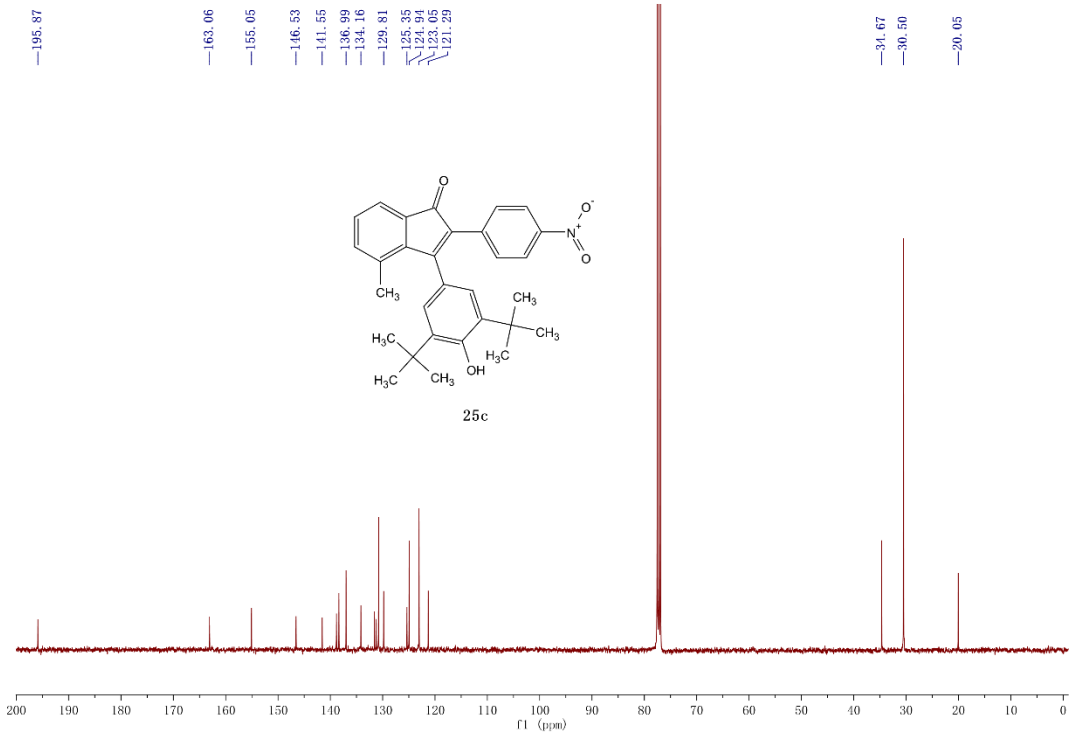
^{13}C NMR (101 MHz, $CDCl_3$) for **24c**.



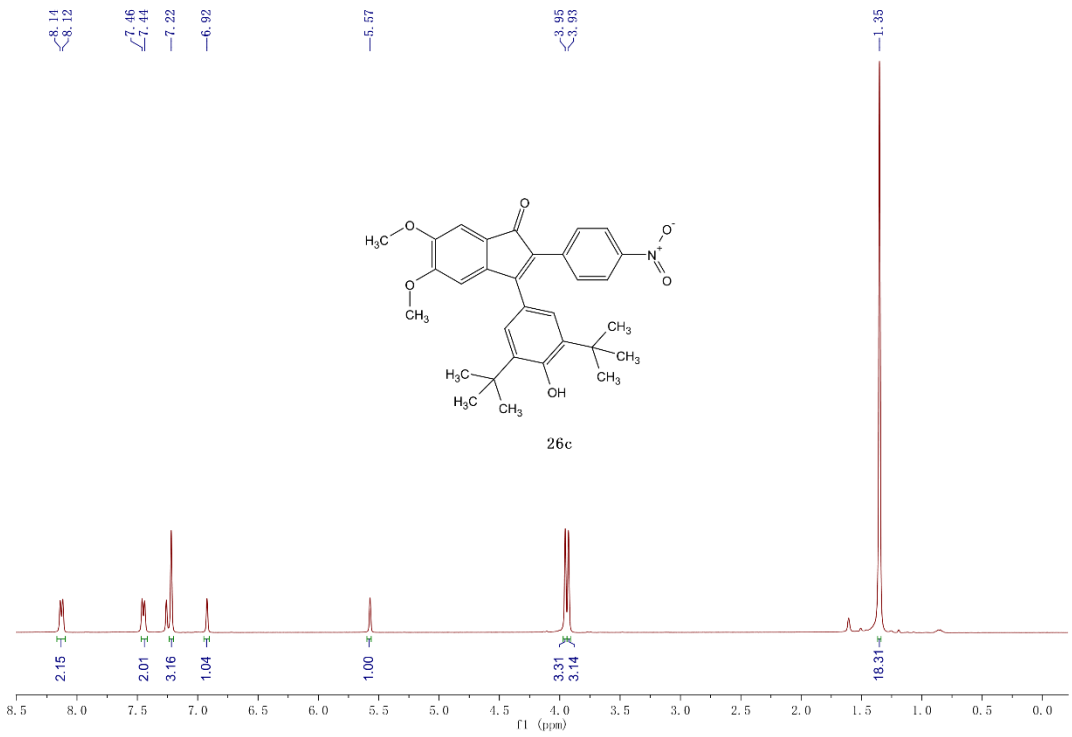
^{1}H NMR (400MHz, $CDCl_3$) for **25c**.



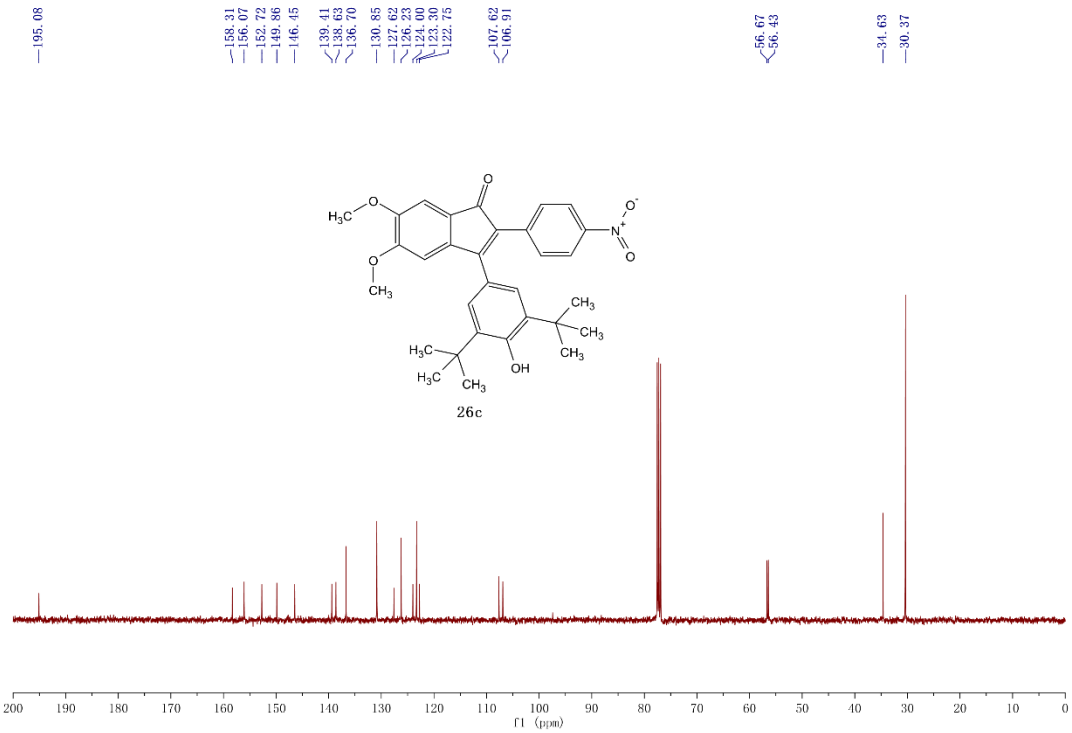
^{13}C NMR (101 MHz, $CDCl_3$) for **25c**.



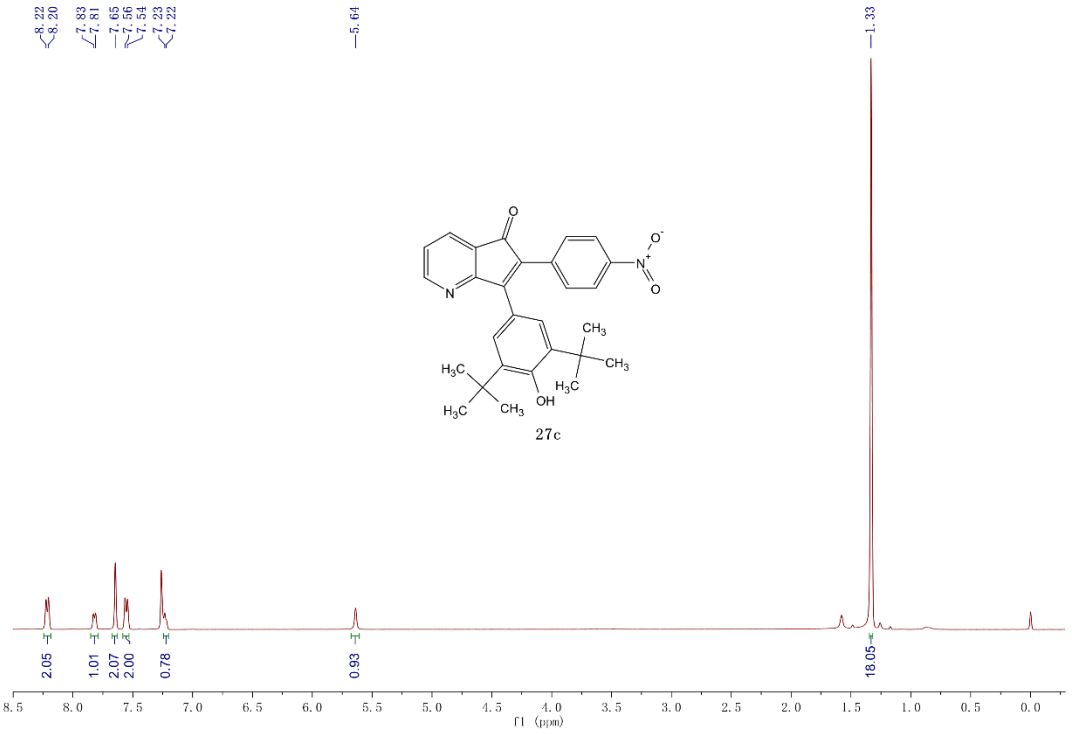
^{1}H NMR (400MHz, $CDCl_3$) for **26c**.



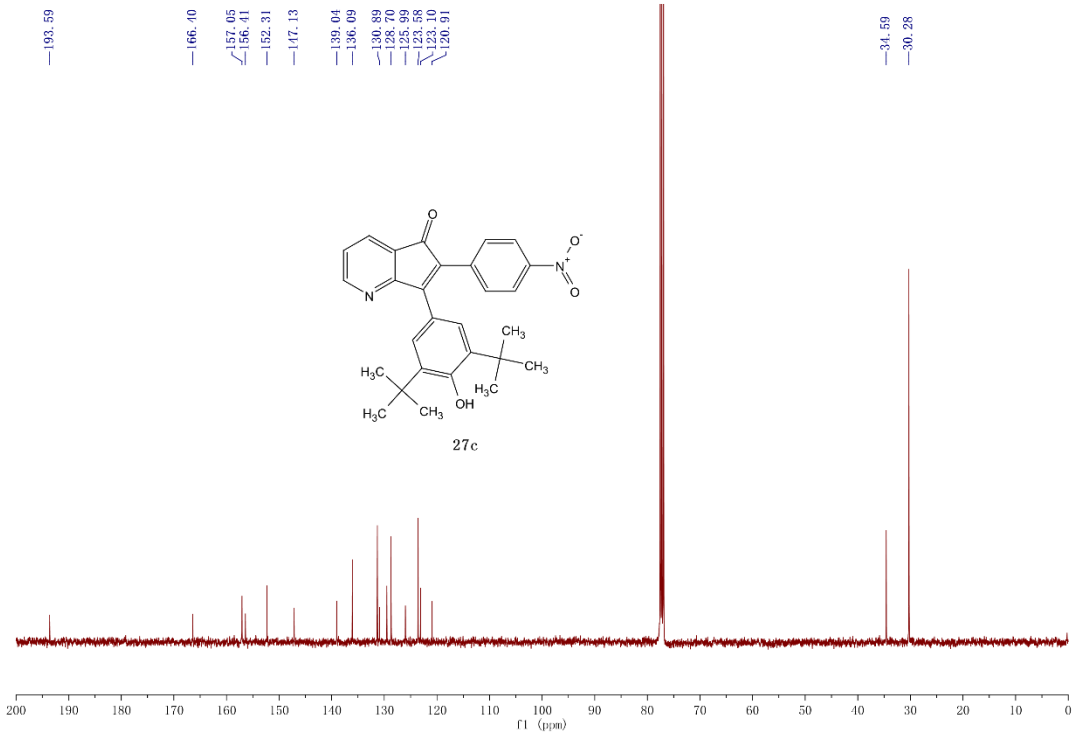
^{13}C NMR (101 MHz, $CDCl_3$) for **26c**.



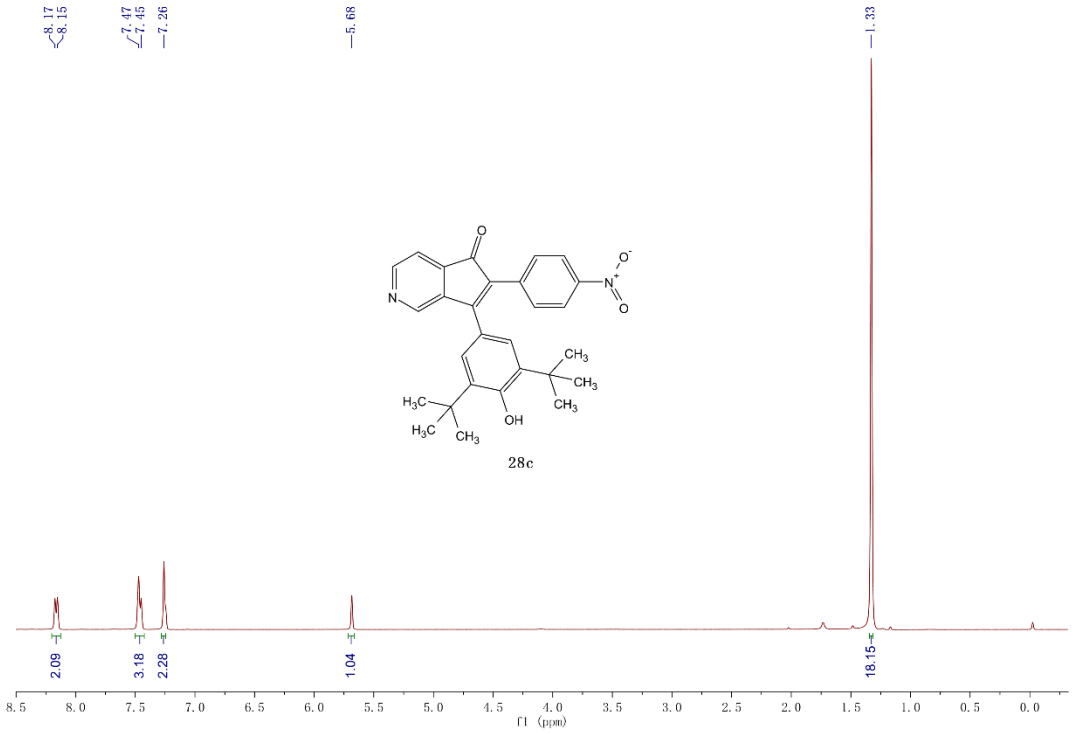
^{1}H NMR (400MHz, $CDCl_3$) for **27c**.



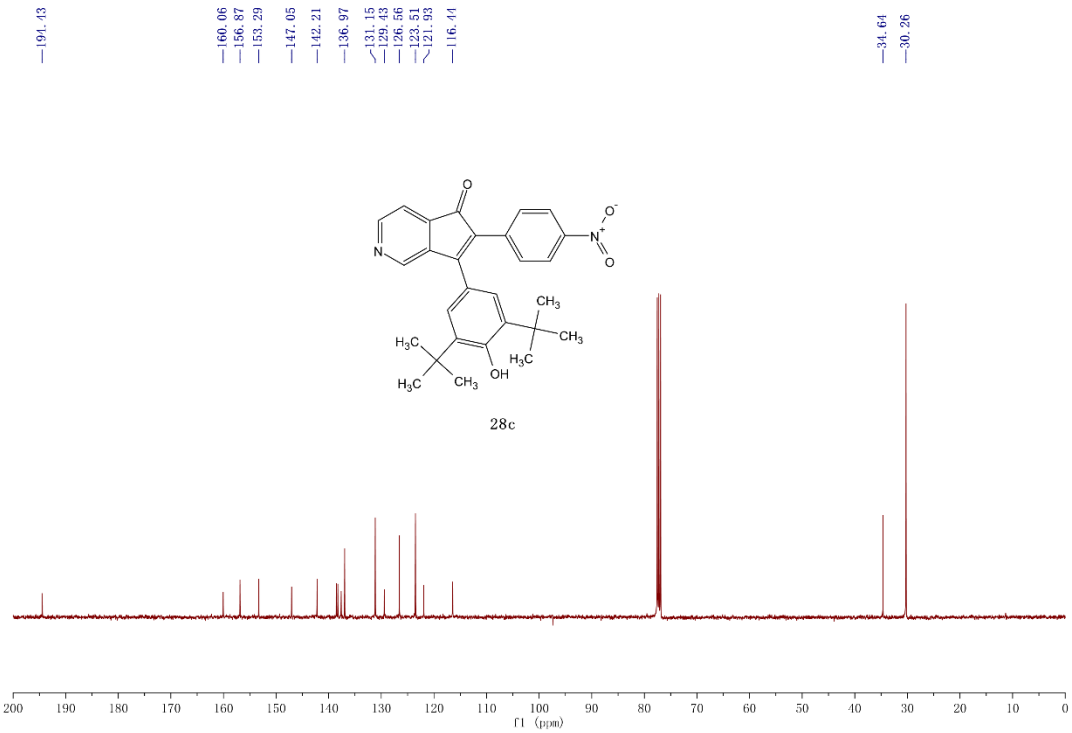
^{13}C NMR (101 MHz, $CDCl_3$) for **27c**.



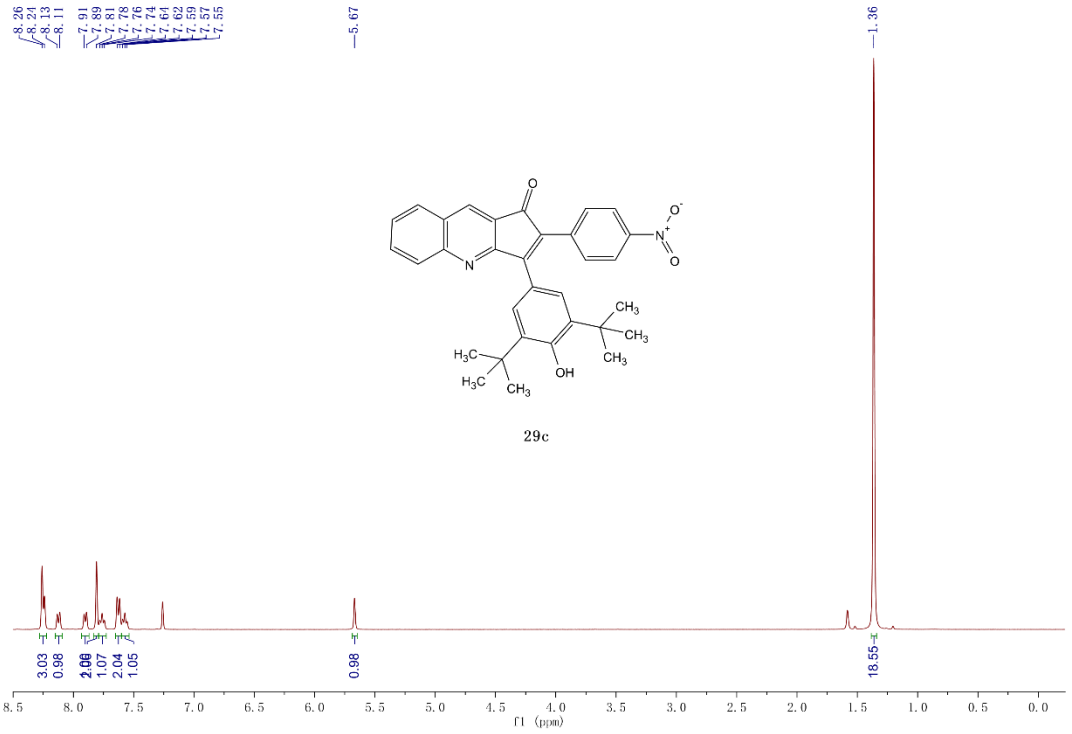
^{1}H NMR (400MHz, $CDCl_3$) for **28c**.



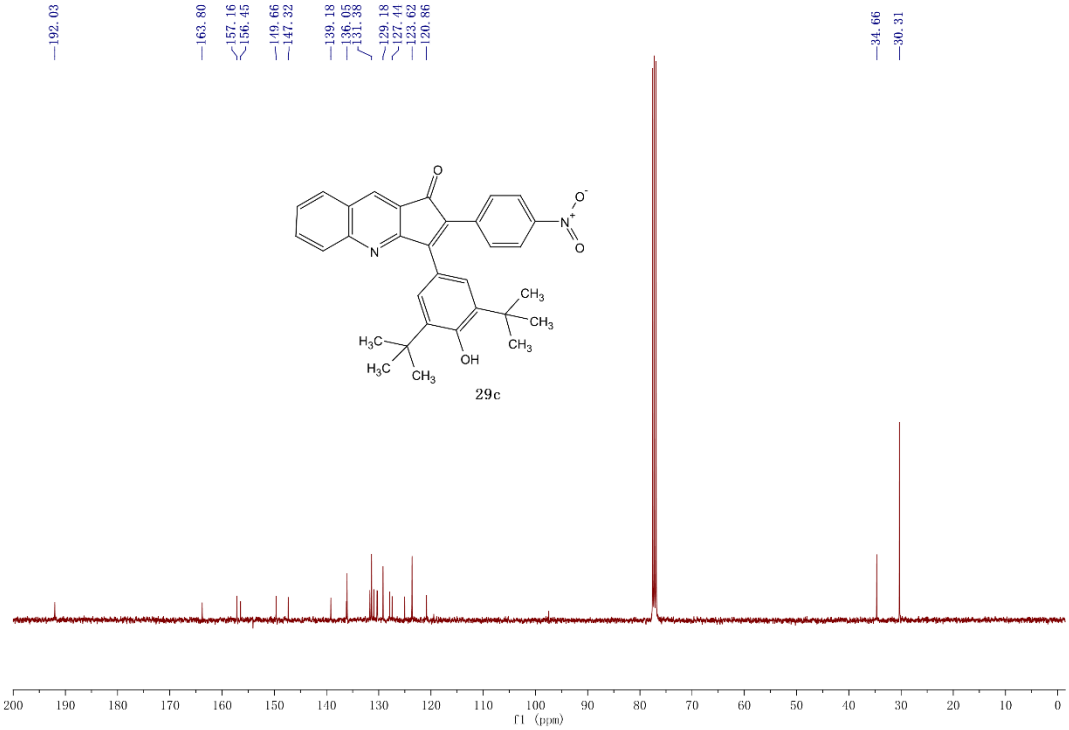
^{13}C NMR (101 MHz, $CDCl_3$) for **28c**.



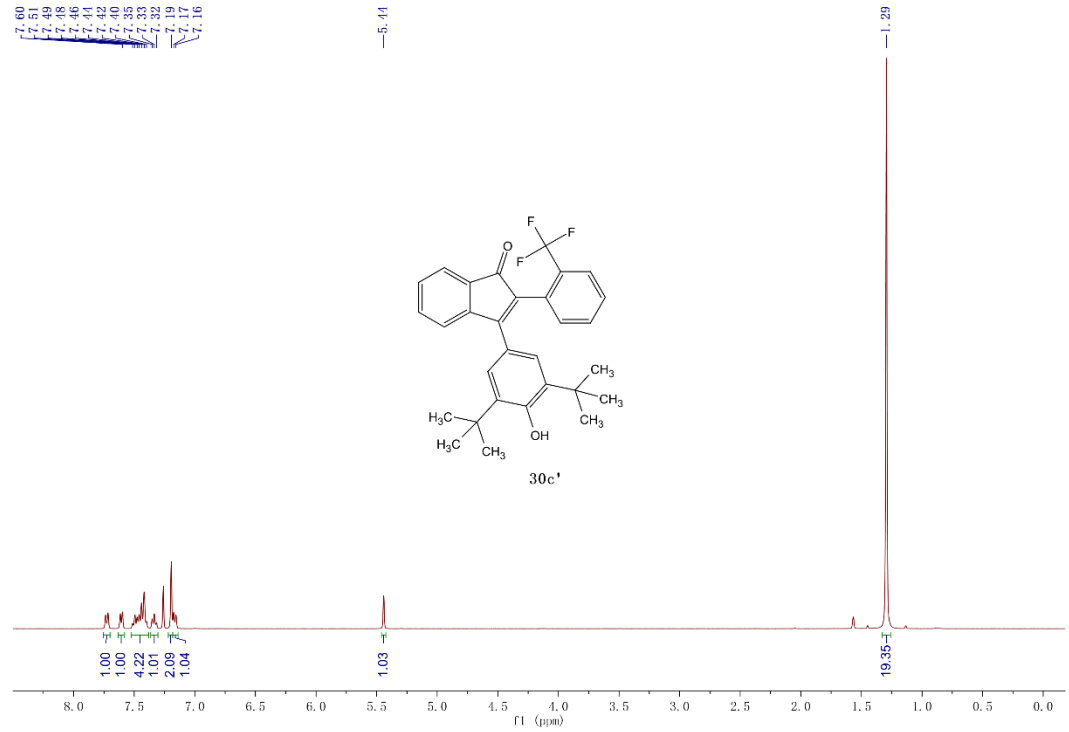
^{1}H NMR (400MHz, $CDCl_3$) for **29c**.



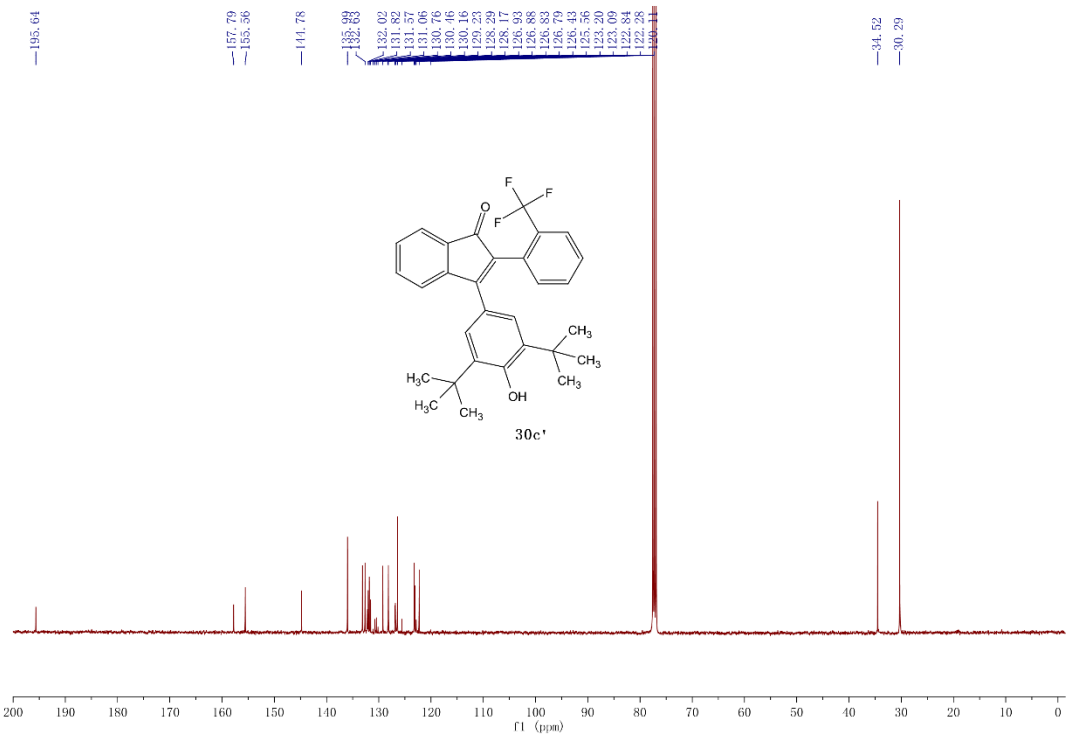
^{13}C NMR (101 MHz, $CDCl_3$) for **29c**.



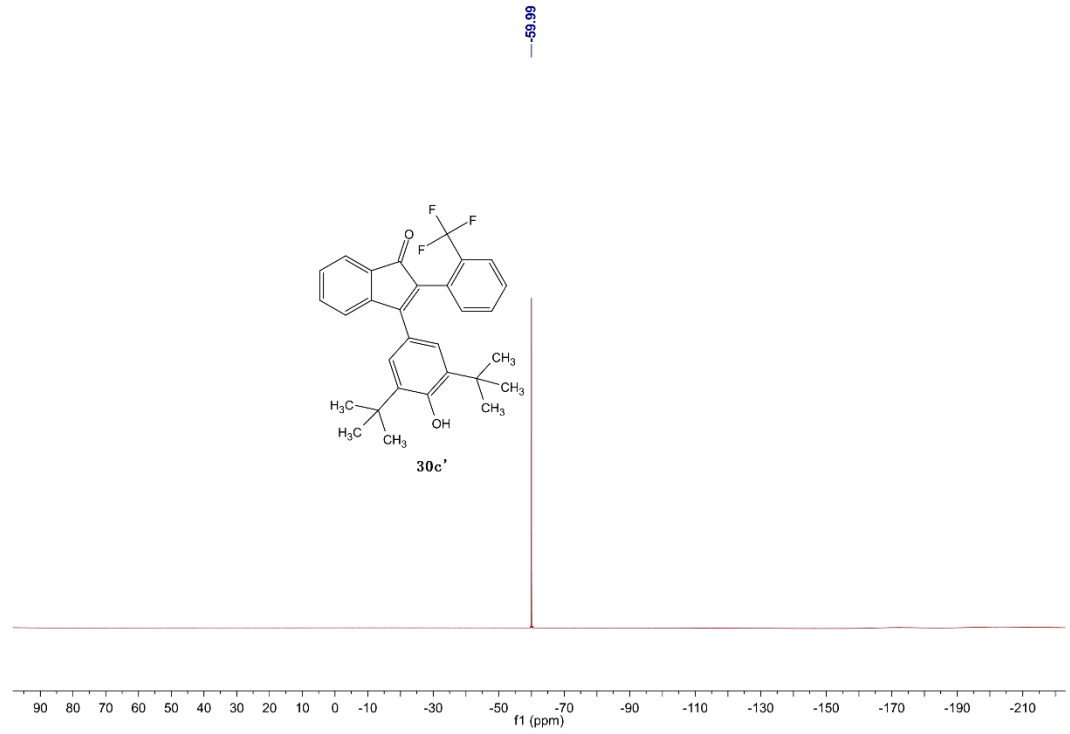
^{1}H NMR (400MHz, $CDCl_3$) for **30c'**.



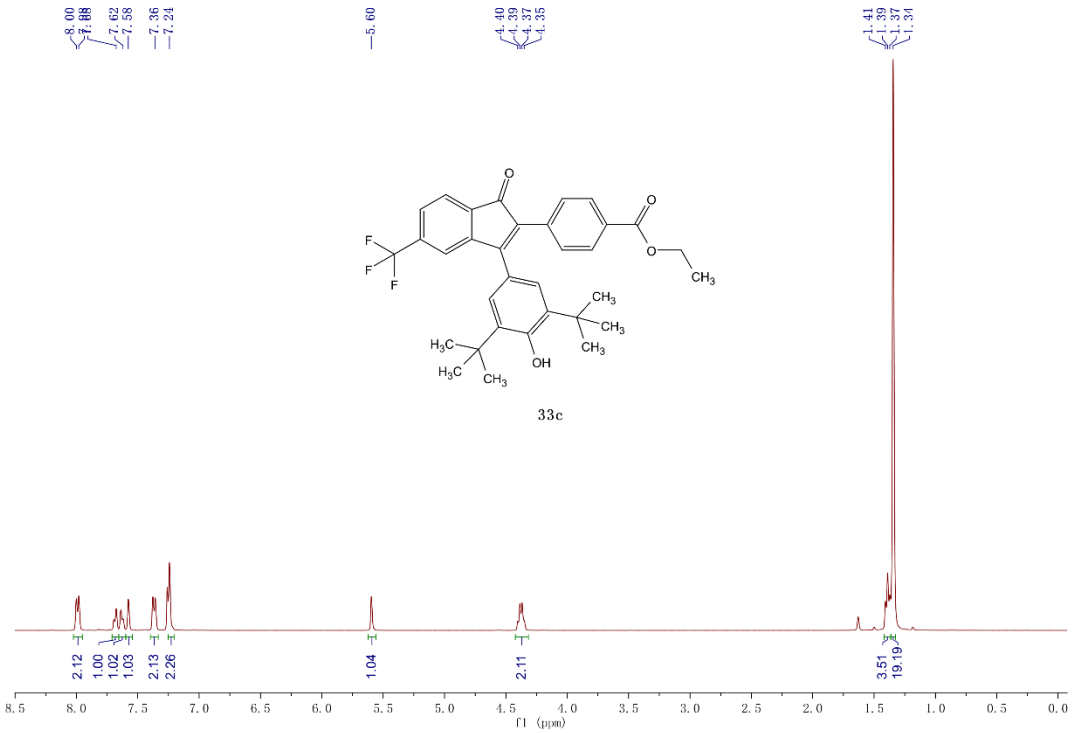
^{13}C NMR (101 MHz, $CDCl_3$) for **30c'**.



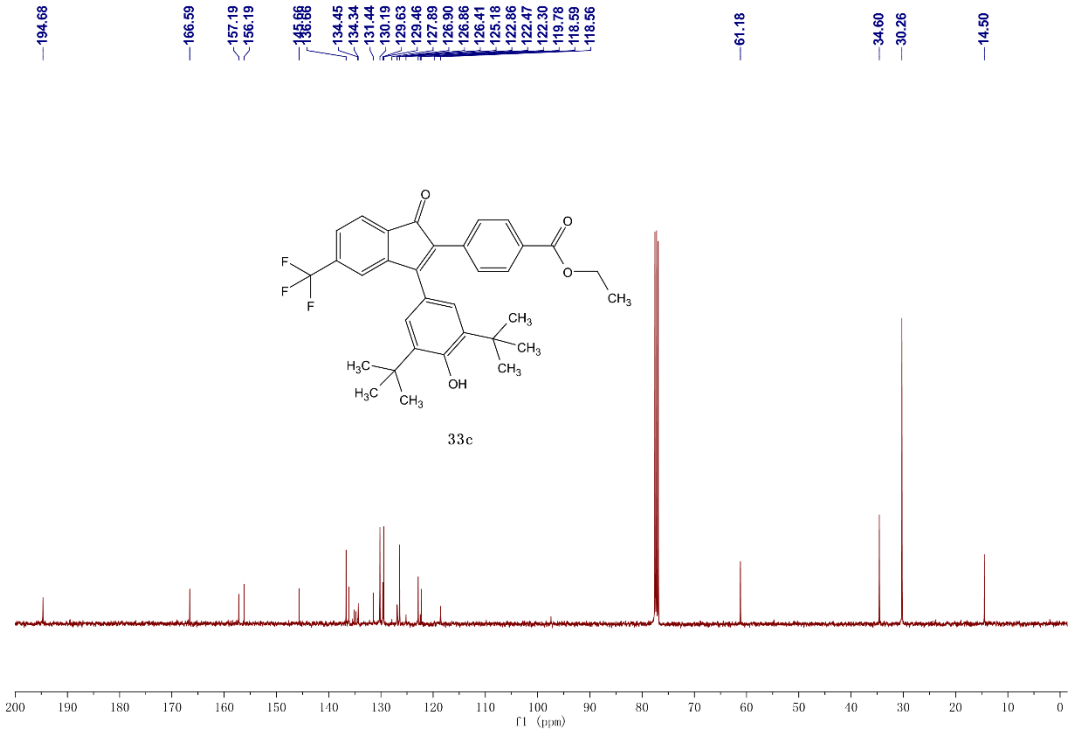
^{19}F NMR (377 MHz, $CDCl_3$) for **30c'**.



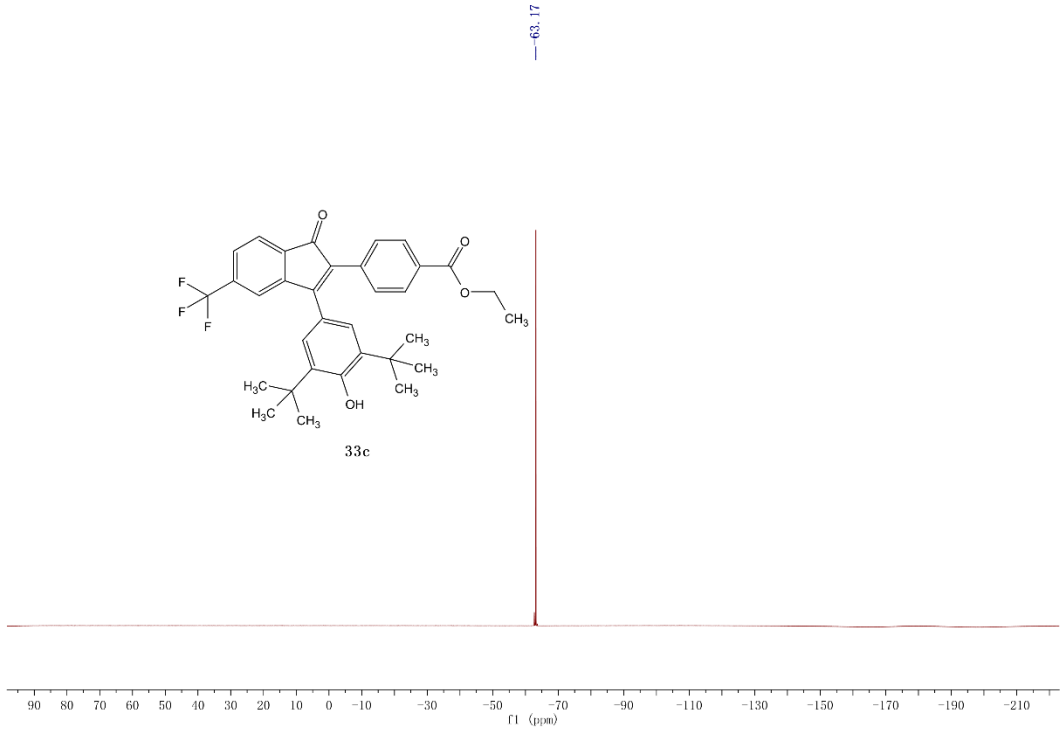
^{1}H NMR (400MHz, $CDCl_3$) for **33c**.



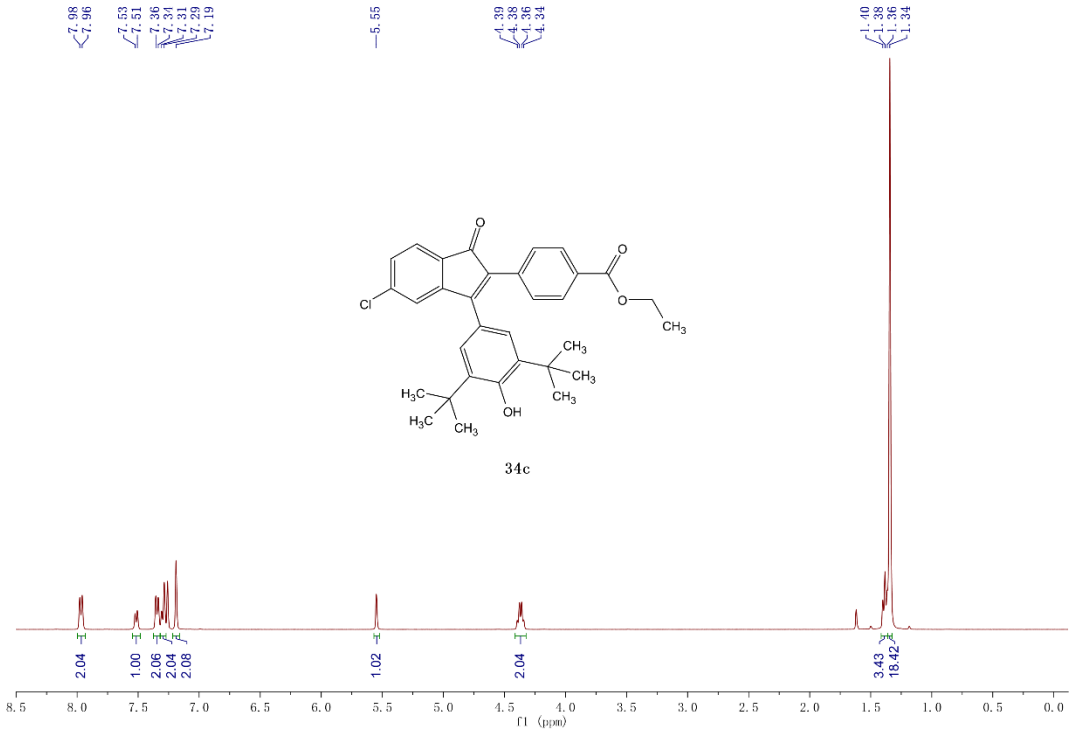
^{13}C NMR (101 MHz, $CDCl_3$) for **33c**.



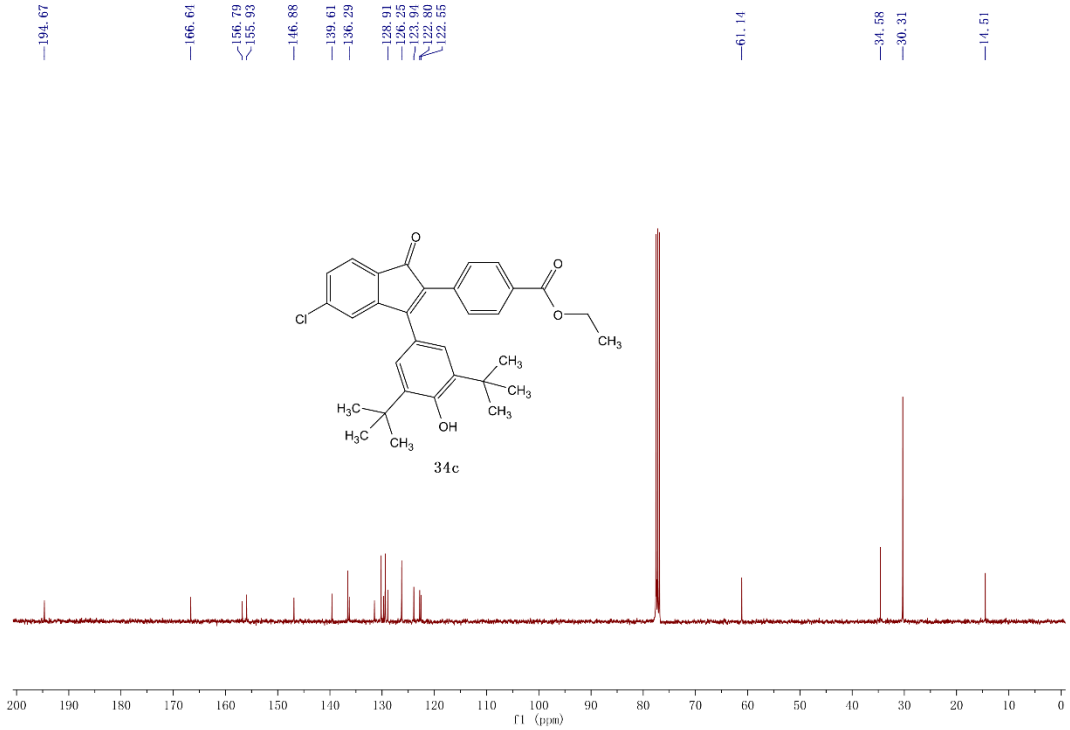
^{19}F NMR (377 MHz, $CDCl_3$) for **33c**.



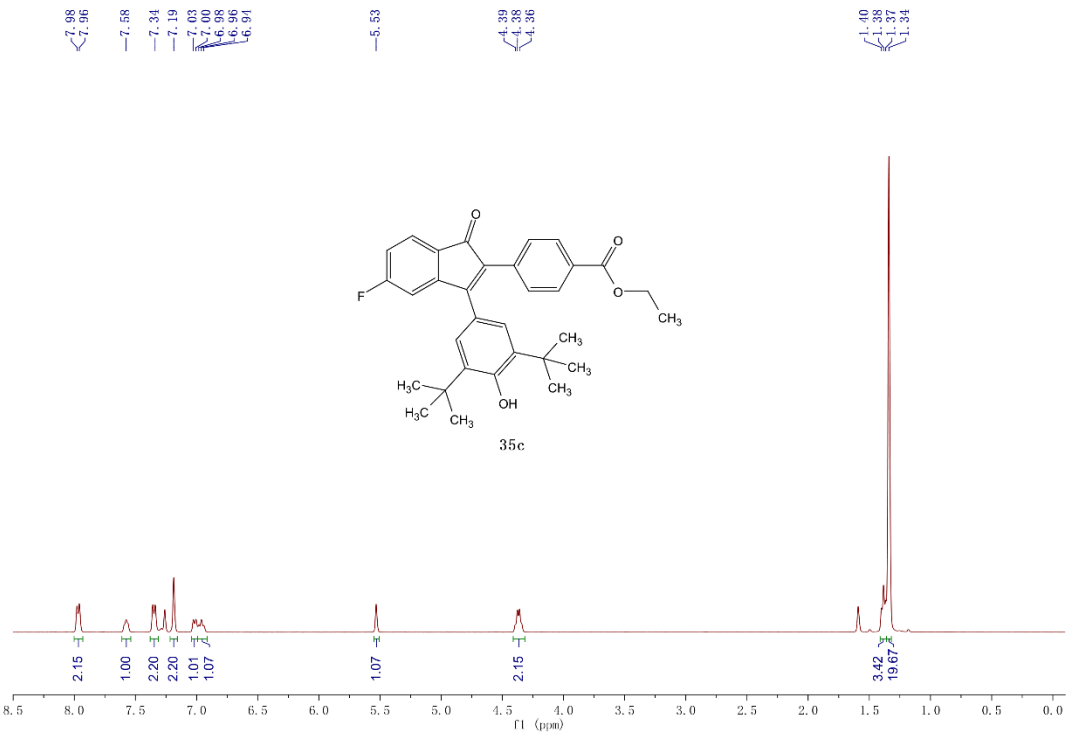
^{1}H NMR (400MHz, $CDCl_3$) for **34c**.



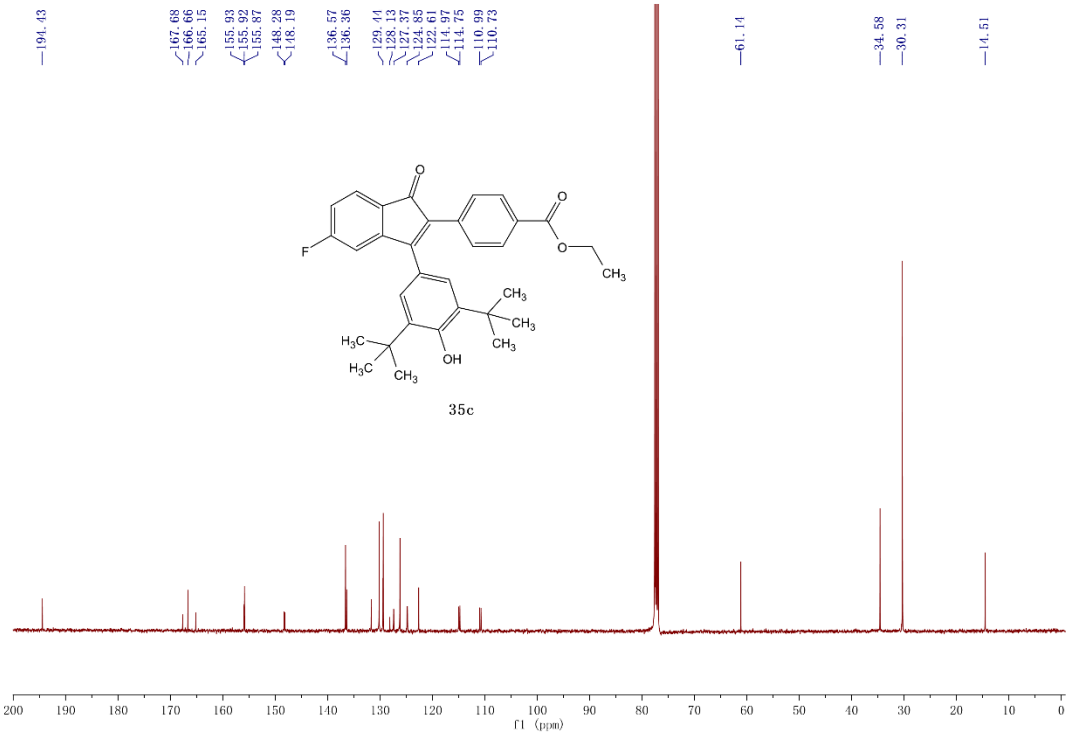
^{13}C NMR (101 MHz, $CDCl_3$) for **34c**.



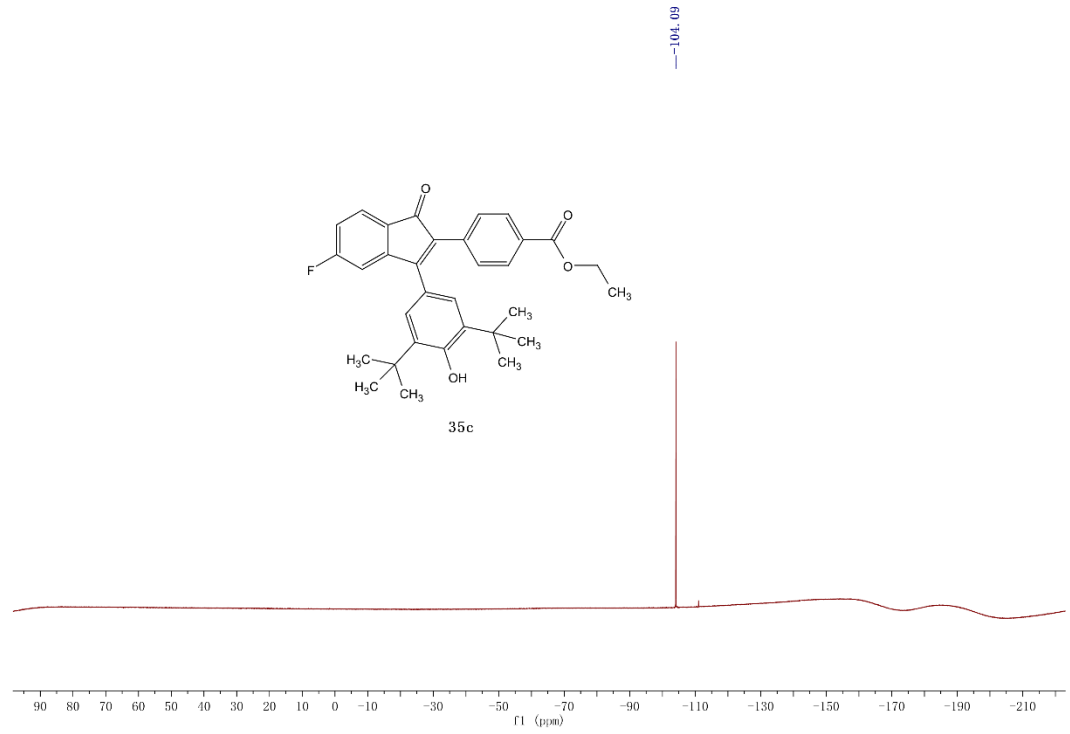
^{1}H NMR (400MHz, $CDCl_3$) for **35c**.



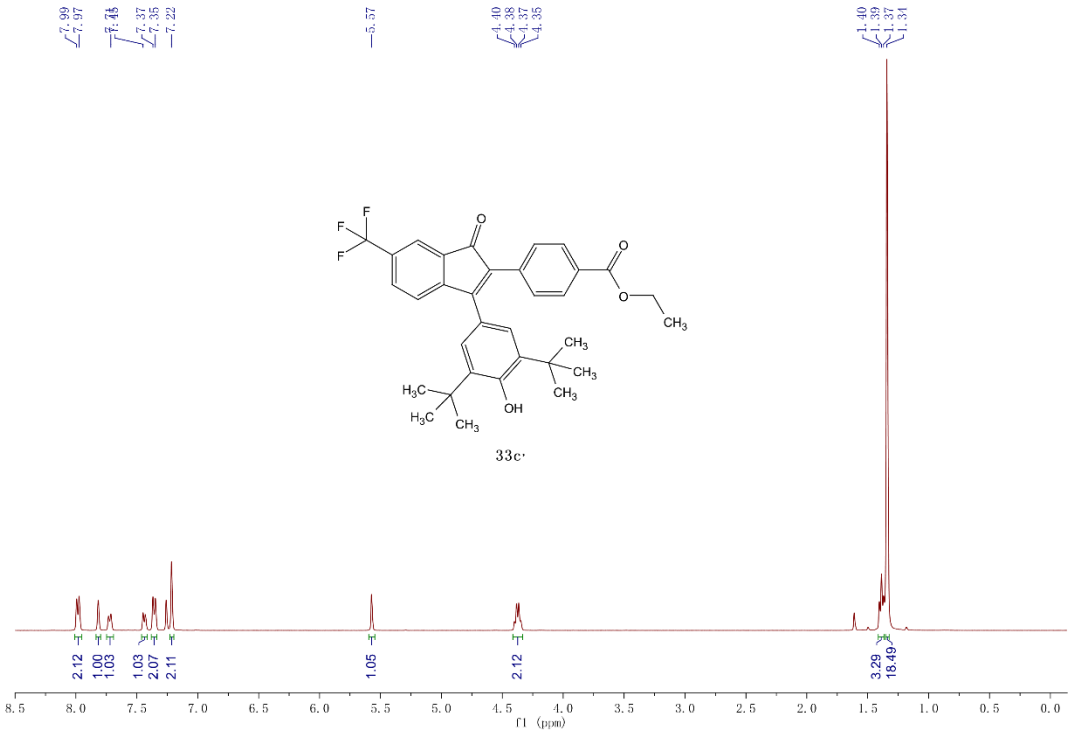
^{13}C NMR (101 MHz, $CDCl_3$) for **35c**.



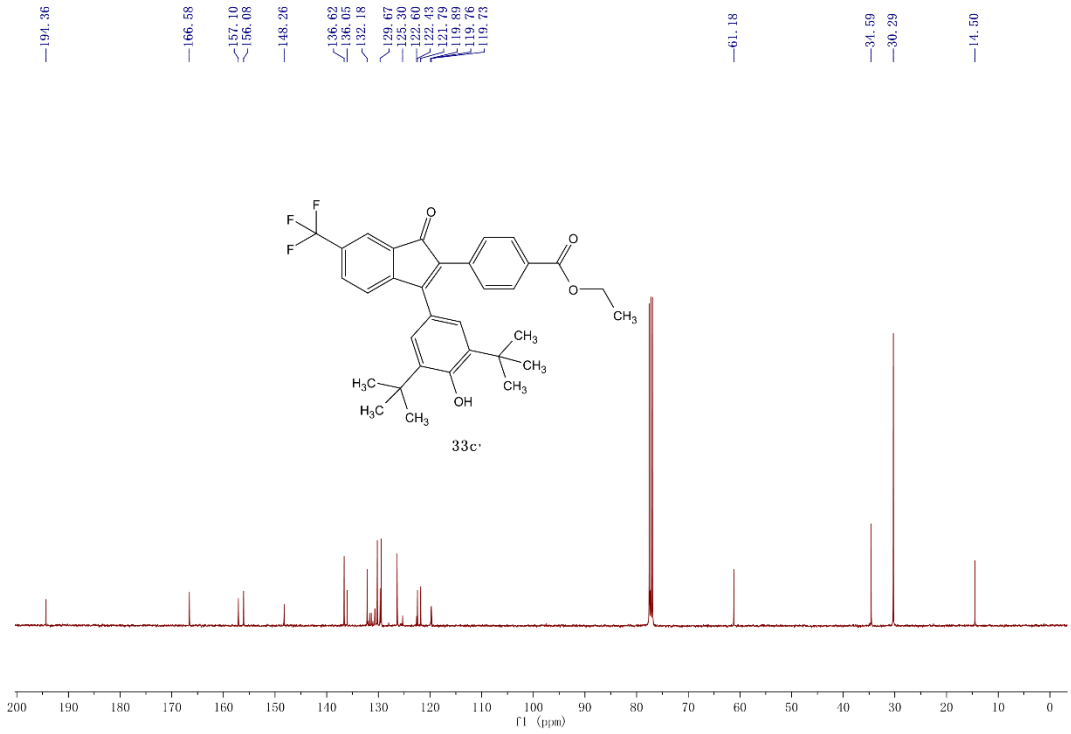
^{19}F NMR (377 MHz, $CDCl_3$) for **35c**.



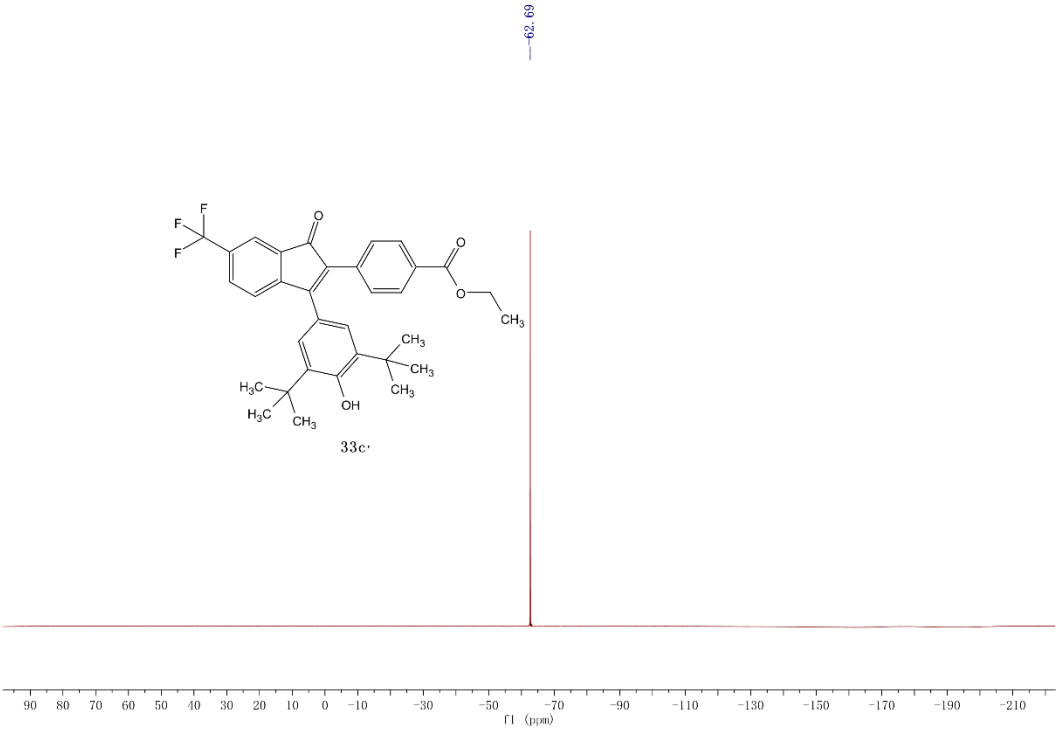
^{1}H NMR (400MHz, $CDCl_3$) for **33c'**.



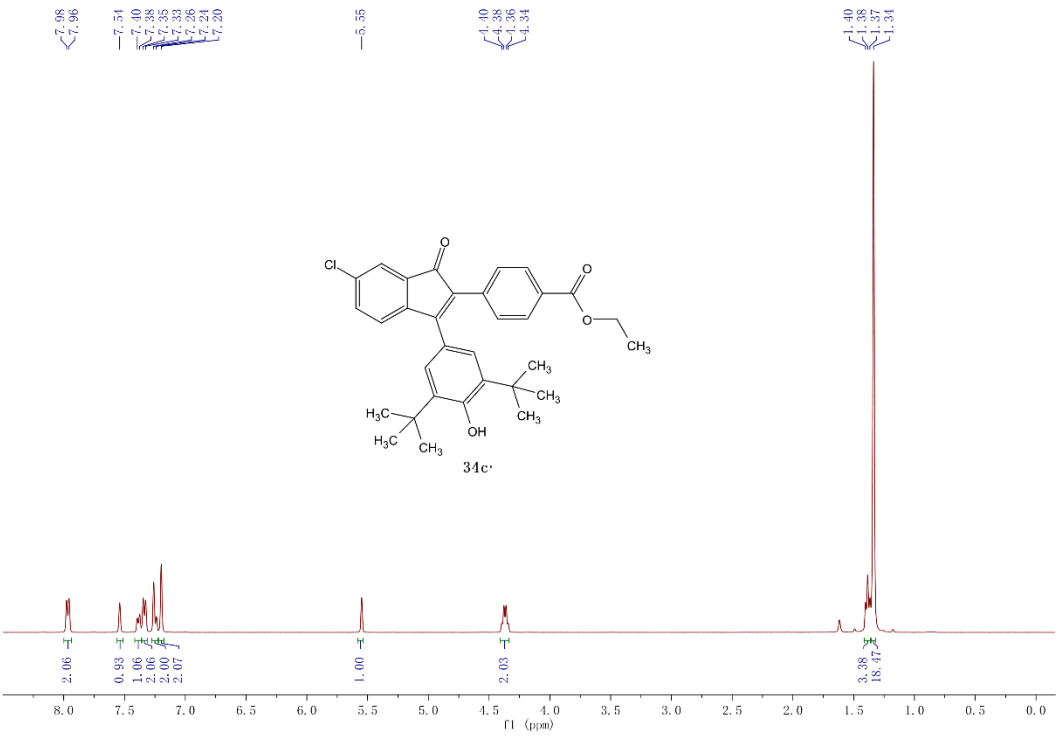
^{13}C NMR (101 MHz, $CDCl_3$) for **33c'**.



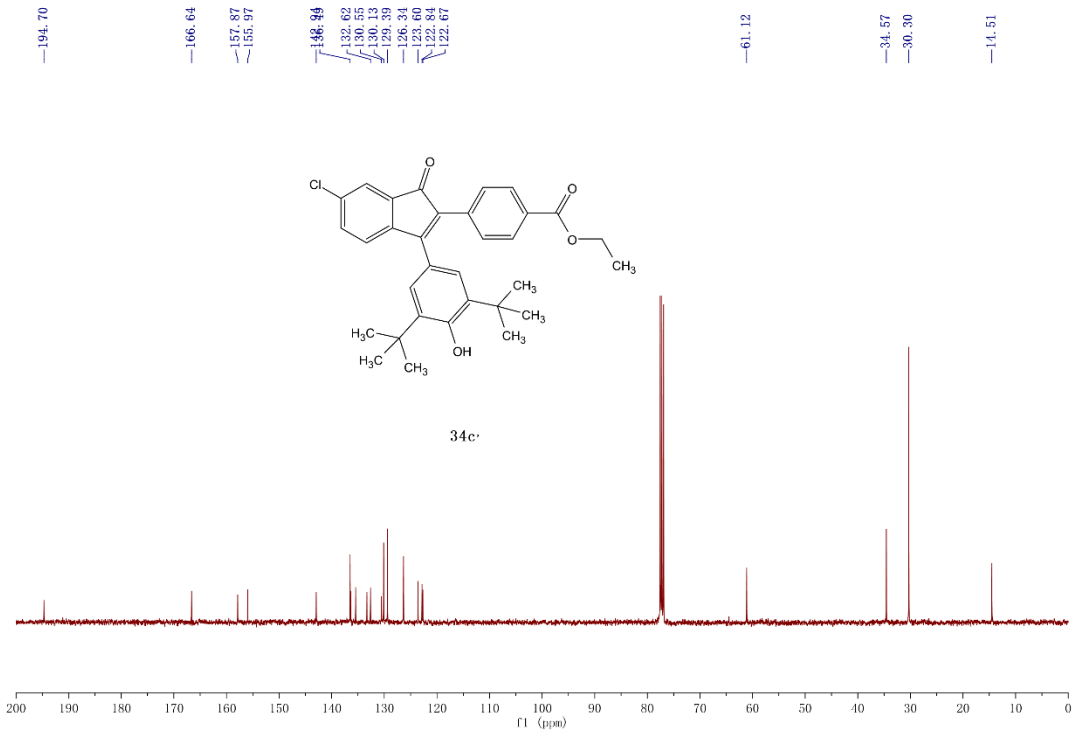
^{19}F NMR (377 MHz, $CDCl_3$) for **33c'**.



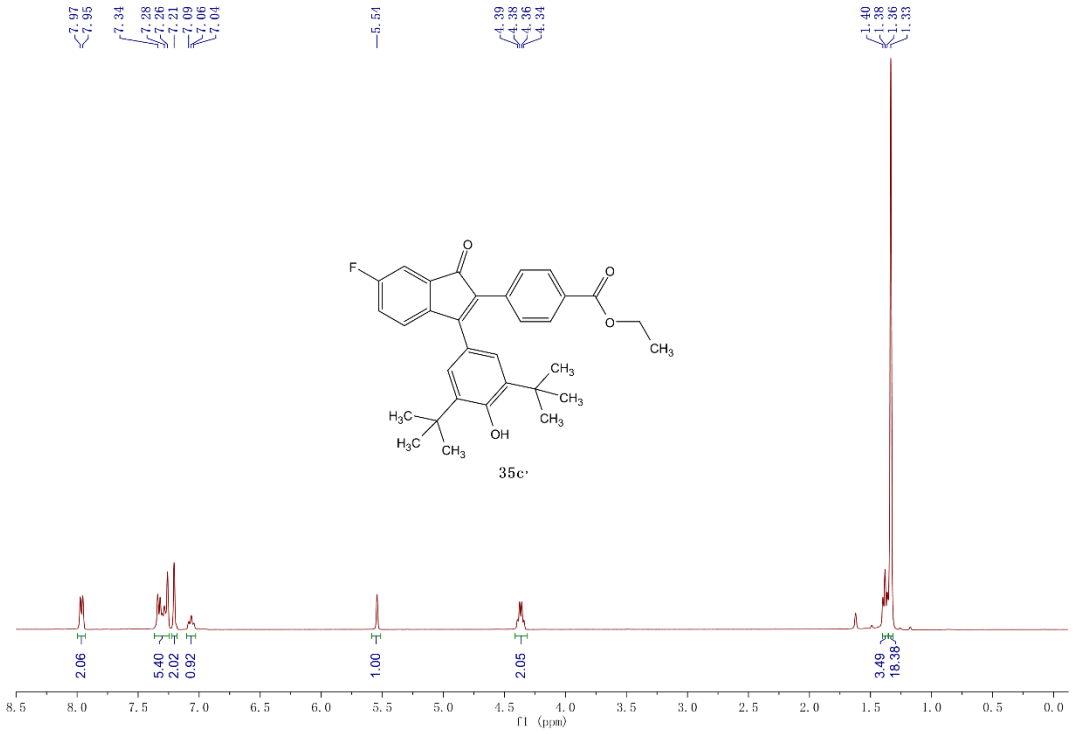
^{1}H NMR (400MHz, $CDCl_3$) for **34c'**.



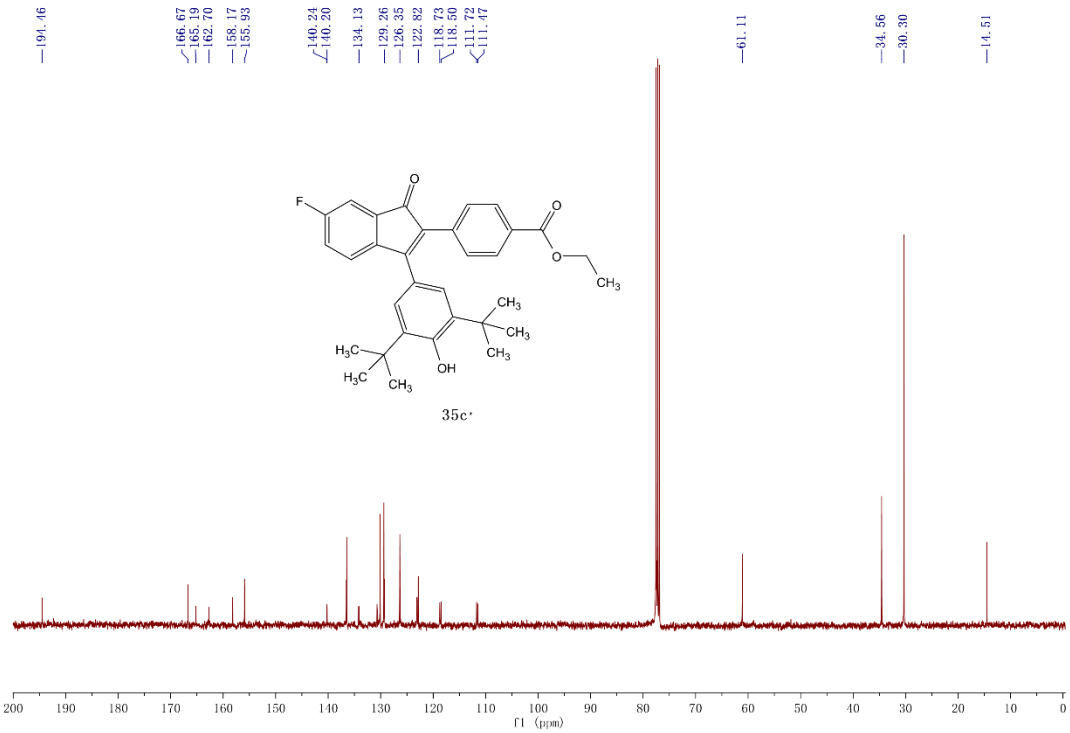
^{13}C NMR (101 MHz, $CDCl_3$) for **34c'**.



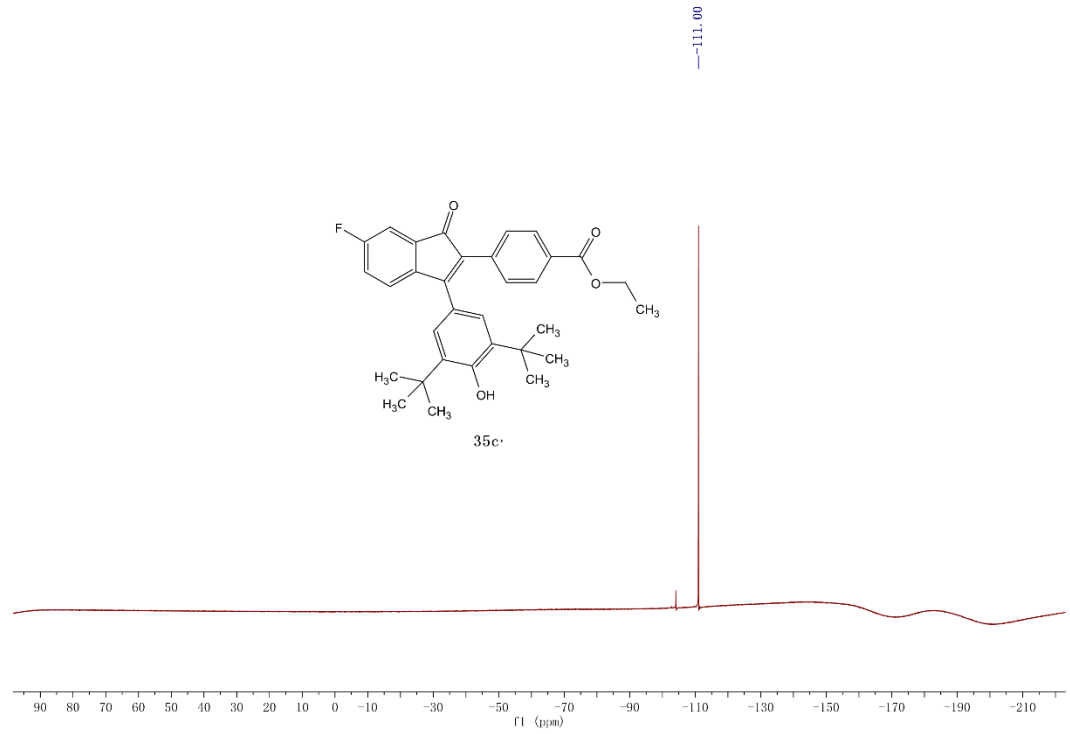
^{1}H NMR (400MHz, $CDCl_3$) for **35c'**.



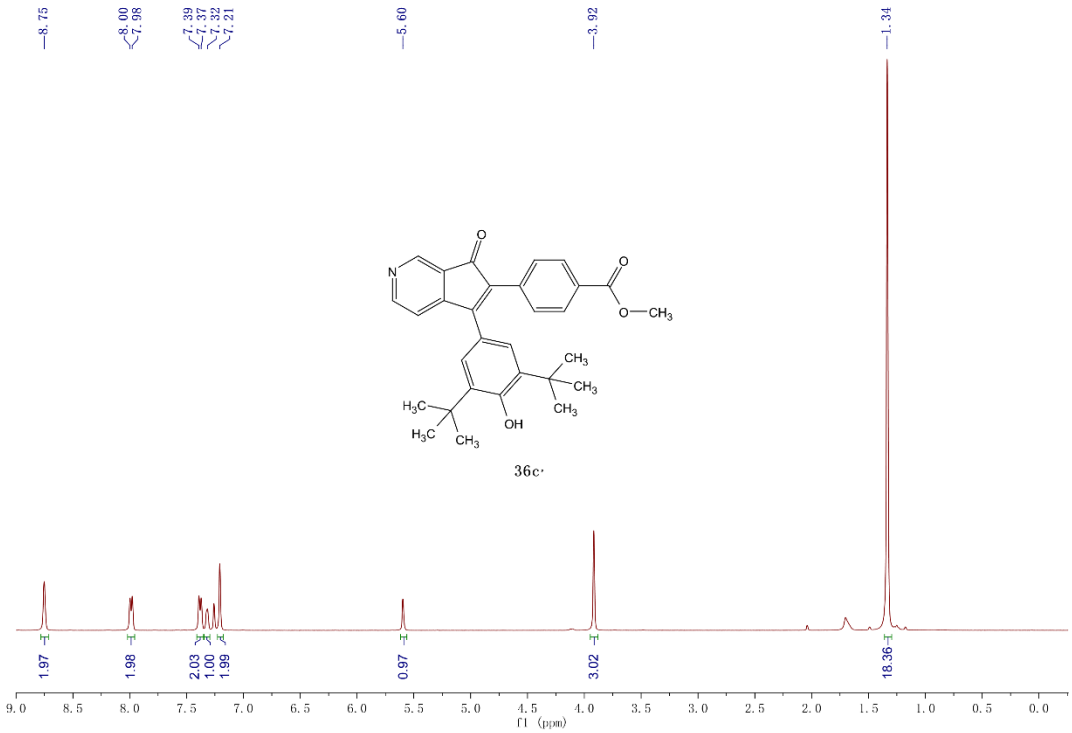
^{13}C NMR (101 MHz, $CDCl_3$) for **35c'**.



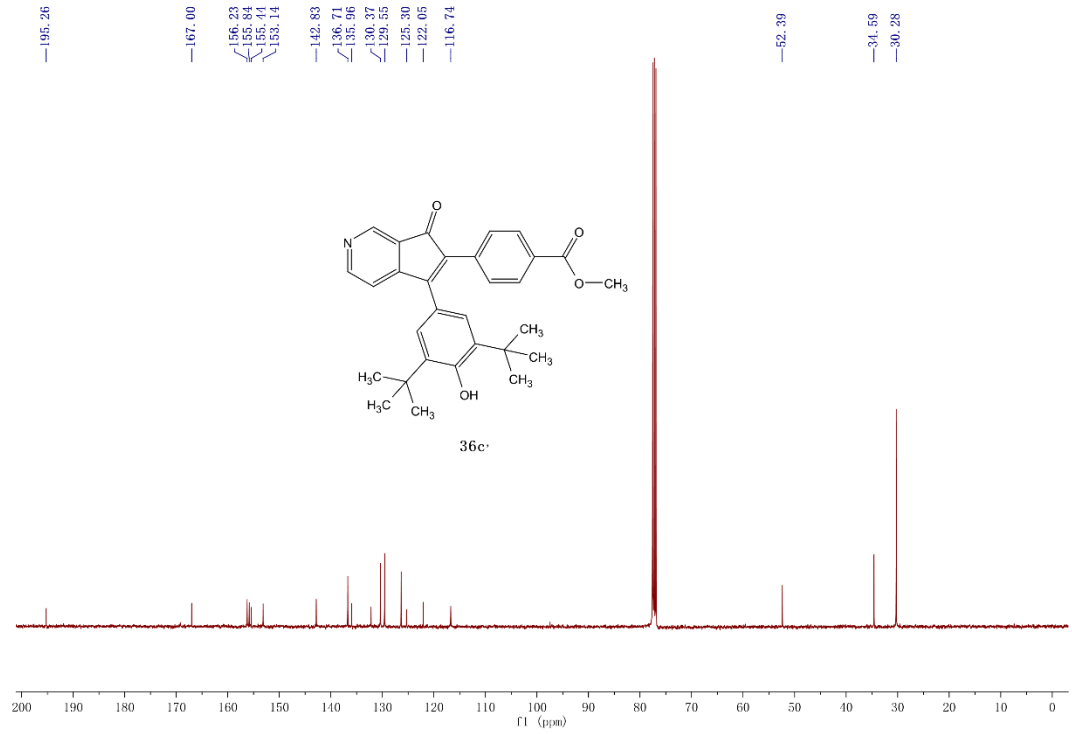
^{19}F NMR (377 MHz, $CDCl_3$) for **35c'**.



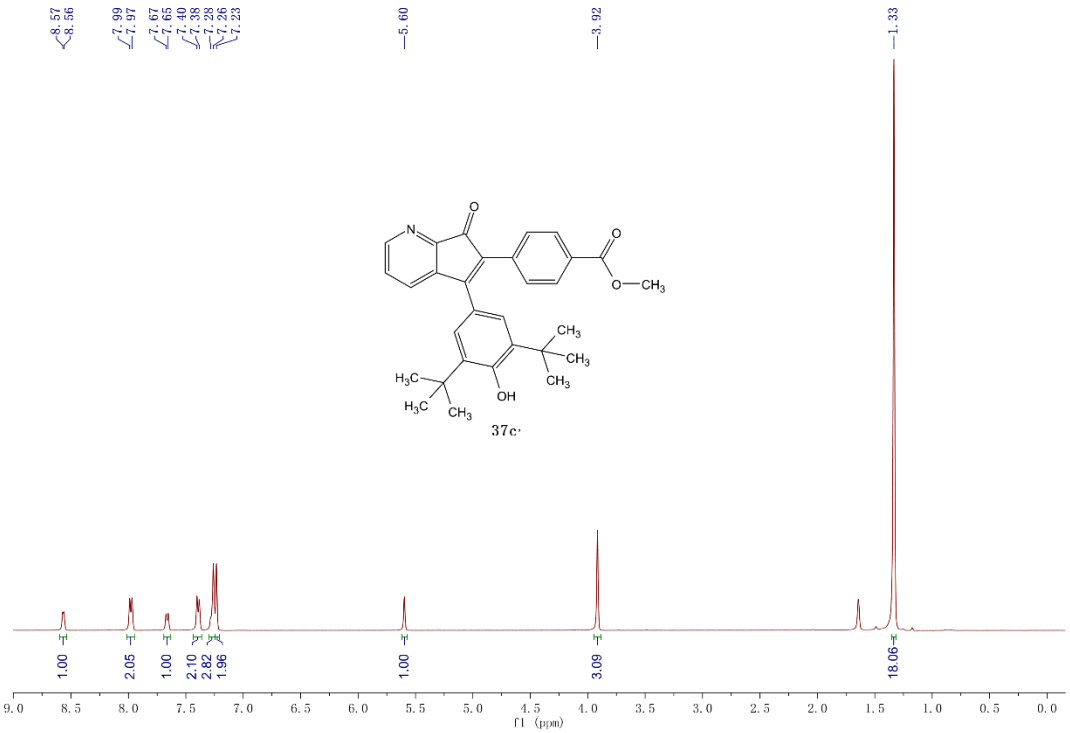
^{1}H NMR (400MHz, $CDCl_3$) for **36c'**.



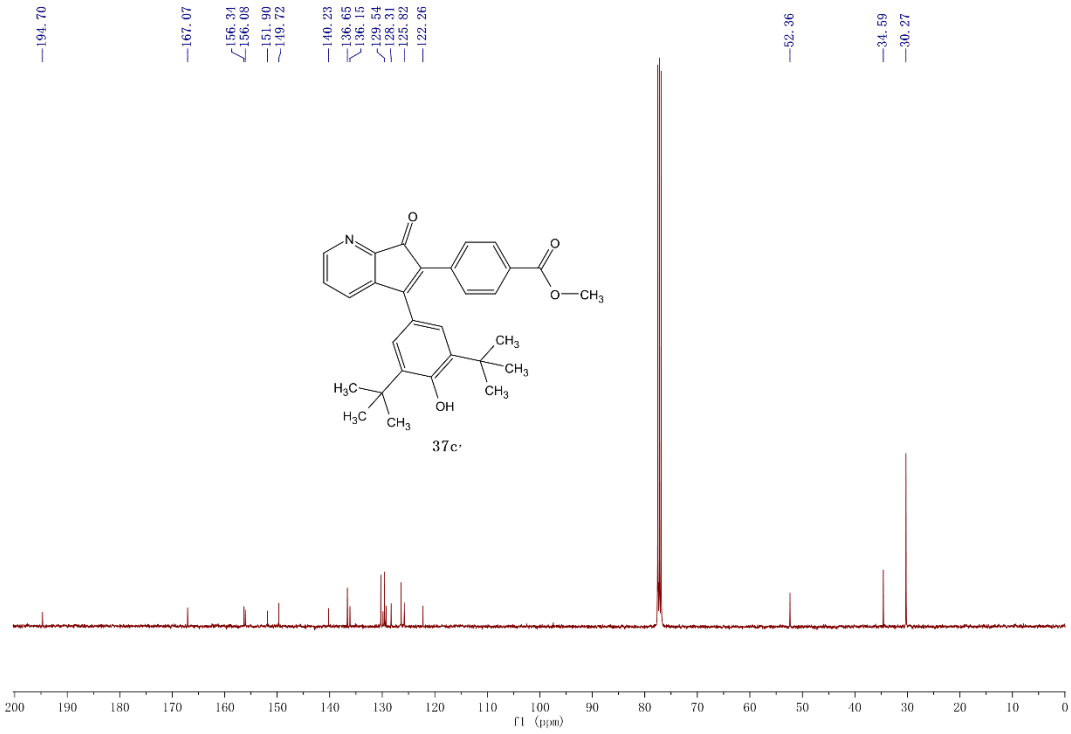
^{13}C NMR (101 MHz, $CDCl_3$) for **36c'**.



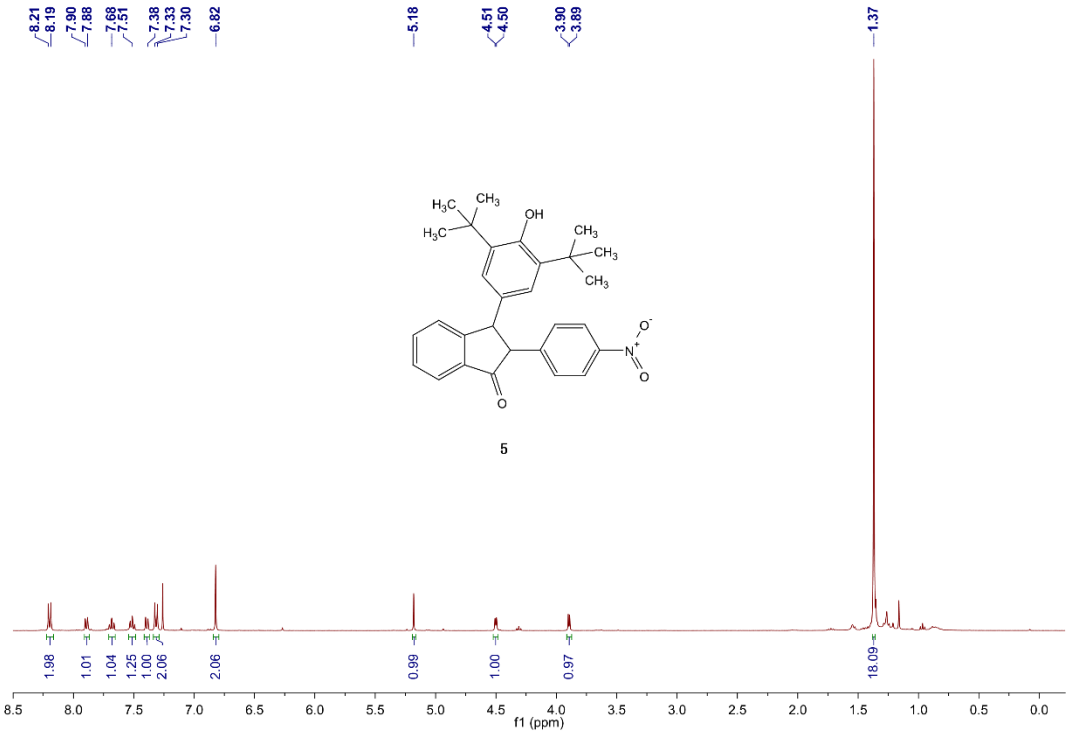
^{1}H NMR (400MHz, $CDCl_3$) for **37c'**.



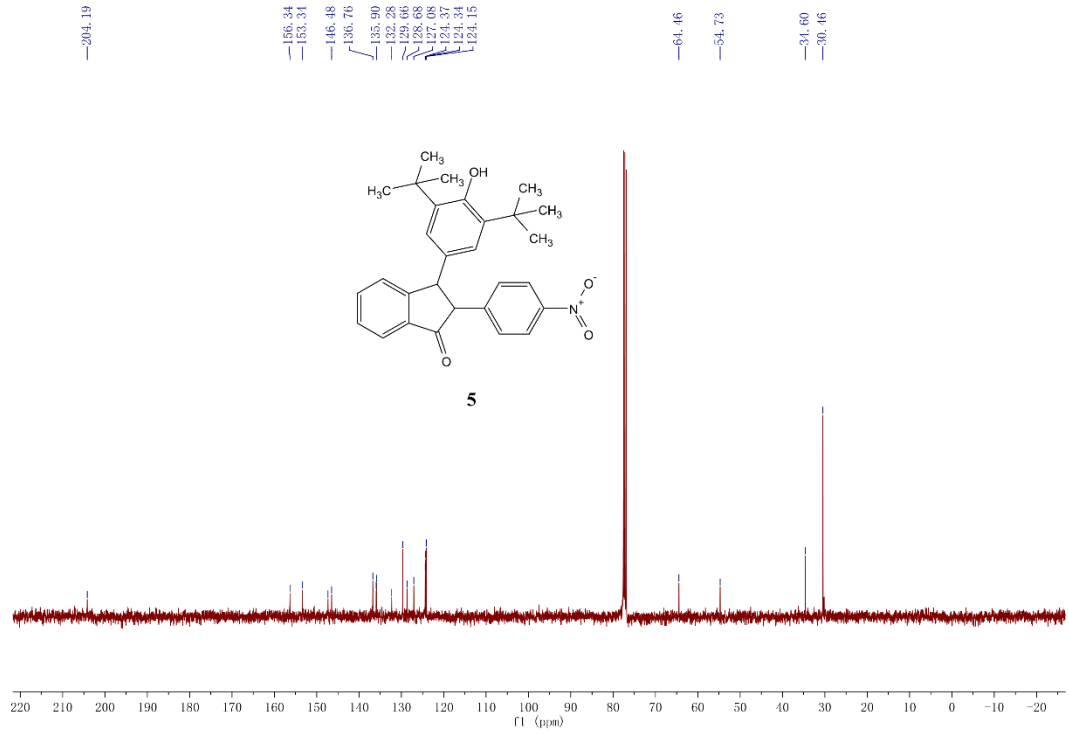
^{13}C NMR (101 MHz, $CDCl_3$) for **37c'**.



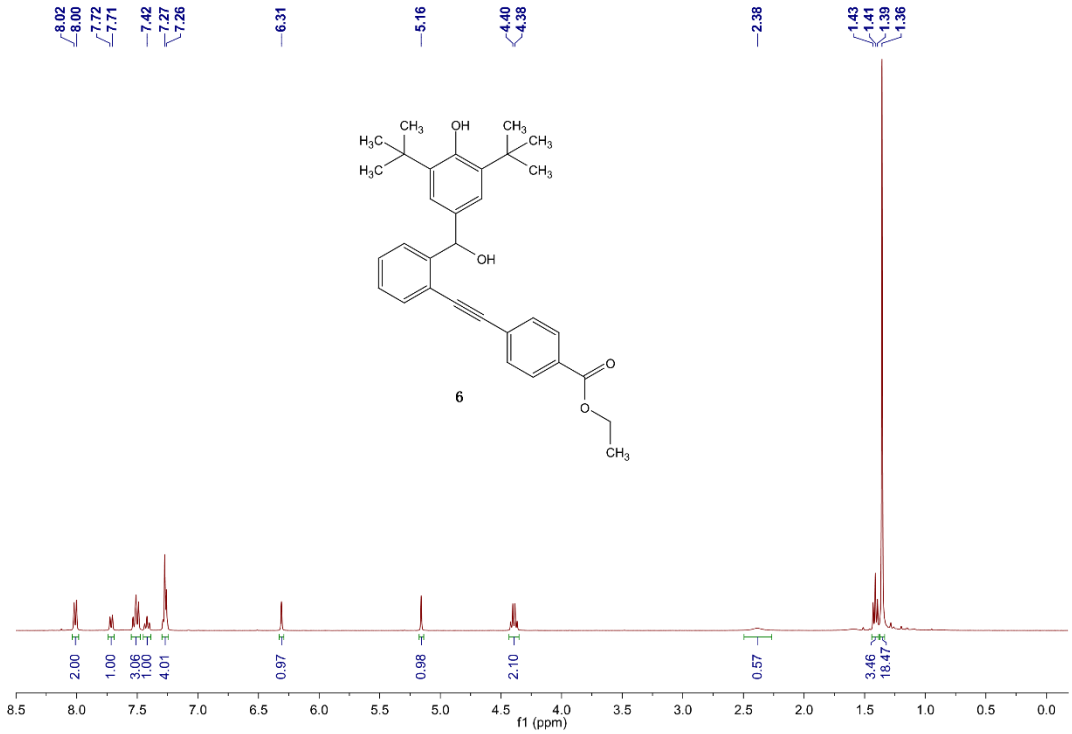
^{1}H NMR (400MHz, $CDCl_3$) for **5**.



^{13}C NMR (101 MHz, $CDCl_3$) for **5**.



^{1}H NMR (400MHz, $CDCl_3$) for **6**.



^{13}C NMR (101 MHz, $CDCl_3$) for **6**.