Supporting Information

Dual rhodium/copper catalysis: Synthesis of benzo[*b*]fluorenes and 2-naphthalenylmethanones *via* de-diazotized cycloadditions

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Context

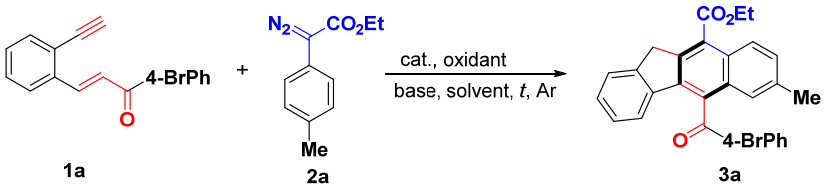
Experimental

General Information

^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ (DMSO-d_6) with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

Condition optimization

Table 1. Optimization of the Reaction Conditions for Forming **3a**[a]



entry	[Rh] (mol %)	[Cu] (mol %)	oxidant (equiv.)	*t*/ °C	solvent	base (equiv.)	yield[b] (%)
1	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	-	60	CH_3CN	TIBA (4.0) [c]	28
2	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	-	60	CH_3CN	TIBA (3.0)	17
3	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	-	60	CH_3CN	TBA (4.0) [d]	trace
4	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	-	60	CH_3CN	Et_3N (4.0)	trace
5	$[Cp^*RhCl_2]_2$ (1.5)	-	-	60	CH_3CN	TIBA (4.0)	trace
6	-	CuI (10)	-	60	CH_3CN	TIBA (4.0)	trace
7	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	-	60	DCE	TIBA (4.0)	ND
8	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	-	60	DMSO	TIBA (4.0)	ND
9	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	-	60	THF	TIBA (4.0)	ND
10	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	-	60	DMF	TIBA (4.0)	38
11	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	-	70	DMF	TIBA (4.0)	33
12	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	-	50	DMF	TIBA (4.0)	27
13	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	$PhI(OAc)_2$ (1.0)	60	DMF	TIBA (4.0)	60
14	$[Cp^*RhCl_2]_2$ (1.5)	CuBr(10)	$PhI(OAc)_2$ (1.0)	60	DMF	TIBA (4.0)	trace
15	$[Cp^*RhCl_2]_2$ (1.5)	CuCl(10)	$PhI(OAc)_2$ (1.0)	60	DMF	TIBA (4.0)	trace
16	Rh_2Cl_4 (1.5)	CuI (10)	$PhI(OAc)_2$ (1.0)	60	DMF	TIBA (4.0)	40
17	$Rh_2(OAc)_4$(1.5)	CuI (10)	$PhI(OAc)_2$ (1.0)	60	DMF	TIBA (4.0)	43
18	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	$PhI(OAc)_2$ (0.5)	60	DMF	TIBA (4.0)	45
19	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	O_2	60	DMF	TIBA (4.0)	ND
20	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	BQ (1.0)	60	DMF	TIBA (4.0)	ND
21	$[Cp^*RhCl_2]_2$ (1.5)	CuI (10)	$PhI(O_2CCF_3)_2$ (1.0)	60	DMF	TIBA (4.0)	ND

[a]Reactions conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), catalyst (x mol %), base (y mmol), and dry solvent (2 mL) under Ar conditions. [b]Isolated yield base on **1a**. [c]Triisobutylamine (TIBA). [d]Tributylamine (TBA).

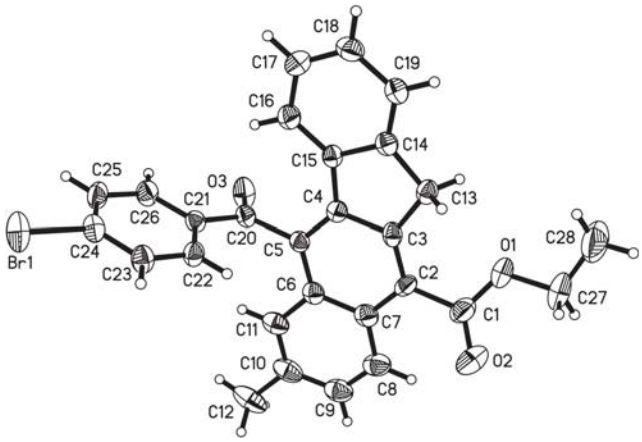


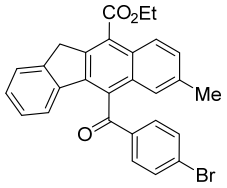
Figure 1 The ORTEP Drawing of **3a** (Thermal ellipsoids are set at 30% probability level)

General Procedure for the Synthesis of Products 3

Example for the synthesis of **3a**:

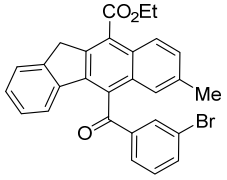
Typical procedure: Under argon conditions, 1-(4-bromophenyl)-3-(2-ethynylphenyl)prop-2-en-1-one (62 mg, 0.2 mmol), CuI (3.8 mg, 10 mol %), $[Cp^*RhCl_2]_2$ (1.8 mg, 1.5 mol %), triisobutylamine (148 mg, 0.8 mmol), and dry DMF (0.75 ml) were added into a dry 10-mL Shrek tube. The mixture was stirred at 60 ºC for 10 min. Then ethyl 2-diazo-2-(*p*-tolyl)acetate (81.6 mg, 0.4 mmol) in 1.25 mL of dry MDF was added to the suspension at 60 ºC over 1.5 hours *via* a syringe pump. After completion of the addition, the reaction mixture was stirred at 60 ºC for an additional 10.5 hours. After the completion of reaction (monitored by TLC), the residue was quenched with saturated NH_4Cl solution, washed with water (20 mL) and extracted with ethyl acetate to provide organic phase, which was dried over Na_2SO_4 and then concentrated under the reduced pressure to give brown oil. Eventually, the resulting oil was further purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 45:1) to give pure yellow solid product **3a**.

Ethyl 5-(4-bromobenzoyl)-7-methyl-11H-benzo[b]fluorene-10-carboxylate (3a)



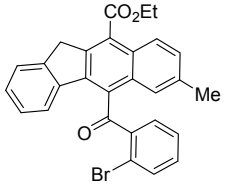
Yellow solid, mp 225-226 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.26 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.56-7.41 (m, 3H), 7.32 (d, J = 1.2 Hz, 1H), 7.29-7.15 (m, 3H), 7.14-7.01 (m, 1H), 4.39 (q, J = 7.2 Hz, 2H), 4.22 (s, 2H), 2.32 (s, 3H), 1.48 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.6, 168.0, 144.0, 141.3, 138.2, 136.7, 136.3, 135.7, 132.5, 131.4, 130.7, 130.0, 129.5, 128.3, 127.8, 127.2, 126.6, 125.5, 125.1, 124.4, 123.2, 61.5, 37.2, 21.7, 14.6; IR (KBr, v) 3087, 3026, 2981, 1712, 1663, 1565, 1477, 1396, 1296 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{22}BrO_3$, 485.0752 $[M+H]^+$, found 485.0736.

Ethyl 5-(3-bromobenzoyl)-7-methyl-11H-benzo[b]fluorene-10-carboxylate (3b)



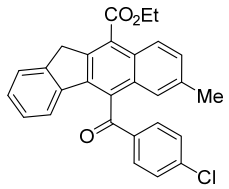
Yellow solid, mp 163-164 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.34 (d, J = 8.8 Hz, 1H), 8.18 (s, 1H), 7.81-7.67 (m, 2H), 7.56 (d, J = 7.6 Hz, 1H), 7.44-7.38 (m, 1H), 7.33-7.29 (m, 3H), 7.27 (s, 1H), 7.17 (s, 1H), 4.64 (q, J = 7.2 Hz, 2H), 4.30 (s, 2H), 2.41 (s, 3H), 1.56 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.3, 168.0, 144.1, 141.3, 138.6, 138.2, 137.3, 136.7, 136.3,132.2, 131.6, 130.7, 129.5, 129.0, 127.8, 127.2, 126.7, 125.5, 125.1, 124.3, 61.5, 37.2, 21.7, 14.5; IR (KBr, v) 2963, 2923, 1705, 1670, 1565, 1423, 1368, 1261,1184 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{22}BrO_3$, 485.0752 $[M+H]^+$, found 485.0781.

Ethyl 5-(2-bromobenzoyl)-7-methyl-11H-benzo[b]fluorene-10-carboxylate (3c)



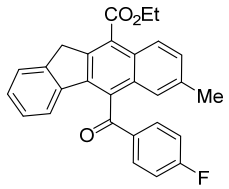
Yellow solid, mp 156-157 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.23 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.53-7.43 (m, 2H), 7.43-7.22 (m, 5H), 7.16 (s, 1H), 7.12-7.03 (m, 1H), 4.55 (q, J = 7.2 Hz, 2H), 4.22 (s, 2H), 2.35 (s, 3H), 1.59 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.3, 168.0, 144.0, 141.3, 138.4, 136.7, 135.8, 133.9, 130.9, 129.4, 128.3, 127.6, 127.2, 125.4, 125.0, 124.4, 123.4, 61.5, 37.2, 21.8, 14.5; IR (KBr, v) 3077, 3013, 2976, 2903, 1713, 1660, 1565, 1480, 1389, 1299 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{22}BrO_3$, 485.0752 $[M+H]^+$, found 485.0759.

Ethyl 5-(4-chlorobenzoyl)-7-methyl-11H-benzo[b]fluorene-10-carboxylate (3d)



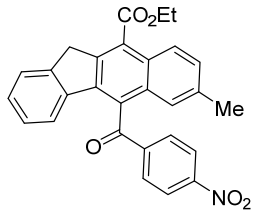
Yellow solid, mp 213-214 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.33 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 8.8 Hz, 3H), 7.37-7.27 (m, 3H), 7.22-7.10 (m, 1H), 4.47 (q, J = 7.2 Hz, 2H), 4.29 (s, 2H), 2.40 (s, 3H), 1.62 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.4, 168.0, 144.0, 141.3, 141.0, 138.2, 136.6, 135.3, 131.9, 131.3, 130.7, 129.5, 129.4, 128.3, 127.8, 127.2, 126.6, 125.5, 125.1, 124.4, 123.2, 61.5, 37.2, 21.7, 14.6; IR (KBr, v) 3094, 2961, 2918, 1711, 1664, 1569, 1466, 1367, 1284, 1167 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{22}ClO_3$, 441.1257 $[M+H]^+$, found 441.1266.

Ethyl 5-(4-chlorobenzoyl)-7-methyl-11H-benzo[b]fluorene-10-carboxylate (3e)



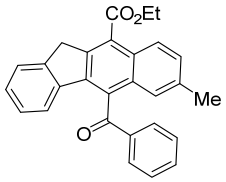
Yellow solid, mp 190-191 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.34 (d, J = 8.8 Hz, 1H), 8.07-7.87 (m, 2H), 7.55 (d, J = 7.2 Hz, 1H), 7.48-7.27 (m, 4H), 7.23-7.01 (m, 3H), 4.63 (q, J = 7.2 Hz, 2H), 4.30 (s, 2H), 2.40 (s, 3H), 1.60 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.0, 168.0, 166.5 (J_{CF} = 255.5 Hz), 142.7, 138,3, 136.6, 136,2, 133.5, 132.8 (J_{CF} = 9.7 Hz), 132.1, 130.7, 129.4, 128.0 (J_{CF} = 3.8 Hz), 127.1, 126.5, 125.5, 125.1, 124.4, 123.2, 116.4 (J_{CF} = 22.0 Hz), 61.5, 37.2, 21.7, 14.6; IR (KBr, v) 3075, 2979, 2904, 1711, 1667, 1503, 1474, 1369, 1234, 1154, 1101 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{22}FO_3$, 425.1553 $[M+H]^+$, found 425.1532.

Ethyl 7-methyl-5-(4-nitrobenzoyl)-11H-benzo[b]fluorene-10-carboxylate (3f)



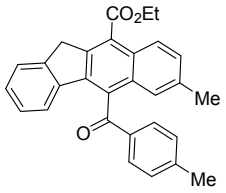
Yellow solid, mp 221-222 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.35 (d, J = 8.8 Hz, 1H), 8.27 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 7.2 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 7.37-7.27 (m, 3H), 7.21-7.09 (m, 1H), 4.64 (q, J = 7.2 Hz, 2H), 4.31 (s, 2H), 2.40 (s, 3H), 1.60 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.1, 167.9, 151.0, 144.2, 141.2, 141.0, 138.0, 137.0, 136.5, 130.9, 130.8, 130.5, 130.0, 128.5, 127.2, 127.1, 125.7, 125.3, 124.0, 123.0, 61.6, 37.2, 21.8, 14.5; IR (KBr, v) 3105, 2976, 2920, 1712, 1672, 1524, 1346, 1233, 1182 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{22}NO_5$, 451.1420 $[M+H]^+$, found 452.1466.

Ethyl 5-benzoyl-7-methyl-11H-benzo[b]fluorene-10-carboxylate (3g)



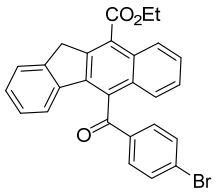
Yellow solid, mp 188-189 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.34 (d, J = 9.2 Hz, 1H), 7.94 (d, J = 7.2 Hz, 2H), 7.66-7.51 (m, 2H), 7.49-7.32 (m, 5H), 7.28 (d, J = 9.2 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 4.63 (q, J = 8.8 Hz, 2H), 4.30 (s, 2H), 2.39 (s, 3H), 1.57 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 199.6, 168.1, 144.0, 141.4, 138.4, 137.0, 36.4, 136.2, 134.4, 132.6, 130.9, 130.0, 129.4, 129.1, 128.1, 127.8, 127.1, 126.3, 125.4, 125.0, 124.6, 123.4, 61.5, 37.2, 21.7, 14.6; IR (KBr, v) 2964, 2918, 1711, 1667, 1578, 1448, 1368, 1231, 1117 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{23}O_3$, 407.1647 $[M+H]^+$, found 407.1634.

Ethyl 7-methyl-5-(4-methylbenzoyl)-11H-benzo[b]fluorene-10-carboxylate (3h)



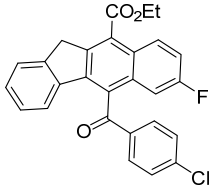
Yellow solid, mp 259-260 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.36 (d, J = 9.6 Hz, 1H), 7.86 (d, J = 7.2 Hz, 2H), 7.55 (d, J = 7.2 Hz, 1H), 7.47-7.37 (m, 3H), 7.30 (d, J = 7.6 Hz,1H), 7.25 (d, J = 8.0 Hz, 2H), 7.21-7.13 (m, 1H), 4.65 (q, J = 8.8 Hz, 2H), 4.32 (s, 2H), 2.42 (s, 3H), 2.41 (s, 3H), 1.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 199.2, 168.2, 145.5, 144.0, 141.4, 138.5, 136.4, 134.6, 132.9, 130.9, 130.1, 129.8, 129.3, 127.9, 127.1, 125.4, 124.9, 124.7, 123.4, 61.5, 37.2, 21.9, 21.7, 14.6; IR (KBr, v) 2963, 2918, 1718, 1665, 1367, 1258, 1172 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{25}O_3$, 421.1804 $[M+H]^+$, found 421.1800.

Ethyl 5-(4-bromobenzoyl)-11H-benzo[b]fluorene-10-carboxylate (3i)



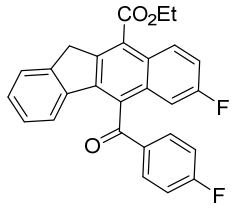
Yellow solid, mp 137-138 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.42 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.64-7.53 (m, 5H), 7.51-7.41 (m, 1H), 7.39-7.29 (m, 2H), 7.23-7.13 (m, 1H), 4.63 (q, J = 5.6 Hz, 2H), 4.32 (s, 2H), 1.60 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.3, 167.9, 144.0, 142.2, 138.1, 135.6, 132.5, 131.3, 128.4, 127.2, 127.1, 126.7, 125.7, 125.4, 125.1, 123.2, 61.6, 37.2, 14.5; IR (KBr, v) 3086, 2962, 2924, 1706, 1664, 1506, 1446, 1370, 1216, 1169 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{19}BrO_3$, 471.0596 $[M+H]^+$, found 471.0556.

Ethyl 5-(4-chlorobenzoyl)-7-fluoro-11H-benzo[b]fluorene-10-carboxylate (3j)



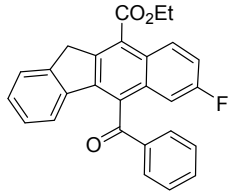
Yellow solid, mp 173-174 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.54-8.40 (m, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 7.8 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.37-7.30 (m, 3H), 7.25-7.11 (m, 2H), 4.66 (q, J = 7.2 Hz, 2H), 4.31 (s, 2H), 1.58 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.5, 166.4 (J_{CF} = 258.6 Hz), 142.7, 136.4, 131.3 (J_{CF} = 9.2 Hz), 129.6, 128.4 (J_{CF} = 8.8 Hz), 126.2, 123.5 (J_{CF} = 2.7 Hz), 117.2 (J_{CF} = 24.3 Hz), 109.1 (J_{CF} = 21.6 Hz), 61.8, 37.2, 29.7, 14.5; IR (KBr, ν) 3048, 2989, 2913, 1701, 1656, 1574, 1459, 1359, 1243, 1154 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{19}ClFO_3$, 445.1007 $[M+H]^+$, found 445.0994.

Ethyl 7-fluoro-5-(4-fluorobenzoyl)-11H-benzo[b]fluorene-10-carboxylate (3k)



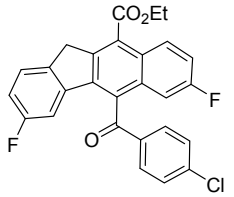
Yellow solid, mp 172-173 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.55-8.42 (m, 1H), 8.09-7.86 (m, 2H), 7.57 (d, J = 7.6 Hz, 1H), 7.41-7.30 (m, 3H), 7.25-7.06 (m, 4H), 4.73 (q, J = 7.2 Hz, 2H), 4.31 (s, 2H), 1.62 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.0, 166.5 (J_{CF} = 241.1 Hz), 16(J_{CF} = 256.7 Hz)4.0 151.9, 144.2, 143.9, 137.5 (J_{CF} = 2.4 Hz), 136.7, 132.7 (J_{CF} = 8.9 Hz), 131.5 (J_{CF} = 9.0 Hz), 128.6, 128.3, 127.3 (J_{CF} = 3.2 Hz), 126.7, 126.4, 125.1 (J_{CF} = 5.3 Hz), 124.7, 123.5 (J_{CF} = 5.4 Hz), 121.6, 117.3, 116.5 (J_{CF} = 22.1 Hz), 112.8, 109.1 (J_{CF} = 21.5 Hz), 98.0, 61.7, 48.9, 37.3, 21.0, 14.5, 10.5; IR (KBr, ν) 3033, 2991, 2912, 1700, 1664, 1577, 1444, 1366, 1288, 1143 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{19}F_2O_3$, 429.1302 $[M+H]^+$, found 429.1303.

Ethyl 5-benzoyl-7-fluoro-11H-benzo[b]fluorene-10-carboxylate (3l)



Yellow solid, mp 182-183 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.67-8.40 (m, 1H), 7.93 (d, J = 7.6 Hz, 2H), 7.72-7.52 (m, 2H), 7.52-7.41 (m, 2H), 7.40-7.29 (m, 3H), 7.23 (s, 1H), 7.16 (s, 1H), 4.79 (q, J = 7.2 Hz, 2H), 4.31 (s, 2H), 1.63 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.7, 167.8, 160.7 (J_{CF} = 246.5 Hz), 143.0, 141.7 (J_{CF} = 9.4 Hz), 138.0, 137.5, 136.5, 134.6, 131.6, 130.0, 128.5, 128.3 (J_{CF} = 8.8 Hz), 126.5 (J_{CF} = 4.3 Hz), 123.6, 117.1 (J_{CF} = 24.6 Hz), 109.3 (J_{CF} = 21.7 Hz), 61.7, 37.3, 14.5; IR (KBr, ν) 3068, 2994, 2924, 1704, 1666, 1578, 1465, 1369, 1251, 1169 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{20}FO_3$, 411.1396 $[M+H]^+$, found 411.1327.

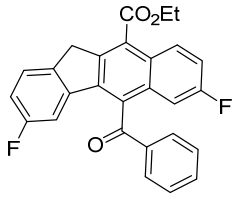
Ethyl 5-benzoyl-7-fluoro-11H-benzo[b]fluorene-10-carboxylate (3m)



Yellow solid, mp 226-227 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.58-8.44 (m, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.58-7.47 (m, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.41-7.31 (m, 1H), 7.24-7.16 (m, 1H), 7.11-6.93 (m, 2H), 4.75 (q, J = 7.2 Hz, 2H), 4.26 (s, 2H), 1.60 (t, J = 14.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.0, 167.5, 162.2 (J_{CF}

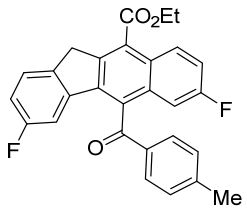
= 242.8 Hz), 159.8 (J_{CF} = 247.7 Hz), 142.3 (J_{CF} = 2.6 Hz), 141.6, 139.6, 139.4 (J_{CF} = 8.8 Hz), 136.7 (J_{CF} = 3.2 Hz), 134.7, 131.4 (J_{CF} = 9.0 Hz), 129.8, 128.5 (J_{CF} = 9.0 Hz), 127.0, 126.9, 126.7, 126.1 (J_{CF} = 8.9 Hz), 117.6 (J_{CF} = 24.7 Hz), 116.0 (J_{CF} = 23.0 Hz), 110.3 (J_{CF} =23.9 Hz), 109.2 (J_{CF} = 22.0 Hz), 61.8, 36.6, 14.5; IR (KBr, *v*) 3091, 2962, 2906, 1712, 1663, 1568, 1434, 1349, 1262, 1156 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{18}ClF_2O_3$, 463.0913 $[M+H]^+$, found 463.0910.

Ethyl 5-benzoyl-3,7-difluoro-11H-benzo[b]fluorene-10-carboxylate (3n)



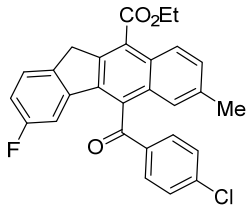
Yellow solid, mp 187-188 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.77-8.24 (m, 1H), 7.91 (d, J = 7.2 Hz,2H), 7.72-7.57 (m, 1H), 7.56-7.41 (m, 3H), 7.39-7.32 (m, 1H), 7.25-7.21 (m, 1H), 7.09-6.95 (m, 2H), 4.32 (q, J = 6.8 Hz, 2H), 4.26 (s, 2H), 1.60 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.2, 167.6, 162.2 (J_{CF} = 242.5 Hz), 1660.8 (J_{CF} = 247.1 Hz), 142.3 (J_{CF} = 2.6 Hz), 139.6 (J_{CF} = 9.0 Hz), 139.5, 136.6 (J_{CF} = 3.2 Hz), 134.9, 133.0, 131.6 (J_{CF} = 9.0 Hz), 129.3, 128.4 (J_{CF} = 9.0 Hz), 126.7, 126.5 (J_{CF} = 8.9 Hz), 125.9, 117.5 (J_{CF} = 24.7 Hz), 115.8 (J_{CF} = 22.9 Hz), 110.4 (J_{CF} = 24.0 Hz), 109.4 (J_{CF} = 21.9 Hz), 61.8, 36.7, 14.5; IR (KBr, *v*) 3063, 2962, 2926, 1715, 1669, 1579, 1449, 1368, 1247, 1158 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{19}F_2O_3$, 429.1302 $[M+H]^+$, found 429.1315.

Ethyl 3,7-difluoro-5-(4-methylbenzoyl)-11H-benzo[b]fluorene-10-carboxylate (3o)



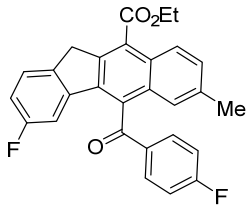
Yellow solid, mp 238-239 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.58-8.38 (m, 1H), 7.79 (d, J = 7.2, 2H), 7.54-7.41 (m, 1H), 7.39-7.30 (m, 1H), 7.23 (d, J = 2.8 Hz, 3H), 7.12-6.66 (m, 2H), 4.66 (q, J = 8.4 Hz, 2H), 4.26 (s, 2H), 2.41 (s, 3H), 1.61 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.8, 167.6, 162.2 (J_{CF} = 244.1 Hz), 160.7 (J_{CF} = 247.0 Hz), 146.1, 142.4, 139.5 (J_{CF} = 2.3 Hz), 136.5 (J_{CF} = 3.3 Hz)132.8 ,131.6 (J_{CF} = 9.0 Hz) 130.1 (J_{CF} = 7.8 Hz), 128.3 (J_{CF} = 8.9 Hz), 126.7, 126.0, 125.9 (J_{CF} = 8.9 Hz), 117.5 (J_{CF} = 24.6 Hz), 115.7 (J_{CF} = 23.1 Hz), 110.5 (J_{CF} = 24.1 Hz), 109.5 (J_{CF} = 22.6 Hz), 61.7, 36.7, 22.0, 14.5; IR (KBr, *v*) 2963, 2921, 1720, 1663, 1510, 1434, 1366, 1261, 1180 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{21}F_2O_3$, 443.1459 $[M+H]^+$, found 443.1436.

Ethyl 5-(4-chlorobenzoyl)-3-fluoro-7-methyl-11H-benzo[b]fluorene-10-carboxylate (3p)



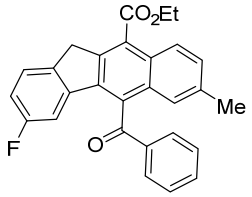
Yellow solid, mp 238-239 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.34 (d, J = 8.8 Hz, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.56-7.38 (m, 4H), 7.34 (s, 1H), 7.11-6.87 (m, 2H), 4.65 (q, J = 8.4 Hz, 2H), 4.25 (s, 2H), 2.40 (s, 3H), 1.65 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.9, 167.8, 162.2 (J_{CF} = 242.4 Hz), 141.9, 141.3, 139.9 (J_{CF} = 8.9 Hz), 139.4, 136.9, 135.4 (J_{CF} = 3.2 Hz), 133.7, 131.3, 130.7, 129.7, 128.0, 126.7, 126.0 (J_{CF} = 8.9 Hz), 125.6, 124.5, 115.4 (J_{CF} = 22.9 Hz), 110.1 (J_{CF} = 23.9 Hz),61.6, 3 6.5, 21.7, 14.5; IR (KBr, v) 3097, 2980, 2920, 1728, 1664, 1583, 1484, 1334, 1221, 1189 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{21}ClFO_3$, 459.1163 $[M+H]^+$, found 459.1167.

Ethyl 3-fluoro-5-(4-fluorobenzoyl)-7-methyl-11H-benzo[b]fluorene-10-carboxylate (3q)



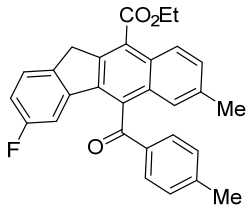
Yellow solid, mp 201-202 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.34 (d, J = 8.8 Hz, 1H), 8.07-7.87 (m, 2H), 7.58-7.32 (m, 3H), 7.18-7.06 (m, 2H), 7.05-6.94 (m, 2H), 4.66 (q, J = 8.4 Hz, 2H), 4.25 (s, 2H), 2.40 (s, 3H), 1.60 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.5, 166.6 (J_{CF} = 249.3 Hz), 162.2 (J_{CF} = 242.1 Hz), 161.0, 141.9, 140.0 (J_{CF} = 8.8 Hz), 138.1, 135.3 (J_{CF} = 3.2 Hz), 134.3, 133.3 (J_{CF} = 2.9 Hz)132.8 (J_{CF} = 9.3 Hz), 132.7, 130.7, 129.8, 128.0, 126.6, 126.0 (J_{CF} = 8.9 Hz), 125.9, 125.5, 124.6, 116.5 (J_{CF} = 22.0 Hz), 115.4 (J_{CF} = 22.9 Hz), 110.1 (J_{CF} = 24.0 Hz), 61.6, 38.5, 21.7, 14.5; IR (KBr, v) 2990, 2959, 1709, 1669, 1501, 1446, 1349, 1221, 1165 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{21}F_2O_3$, 443.1459 $[M+H]^+$, found 443.1428.

Ethyl 5-benzoyl-7-methyl-11H-benzo[b]fluorene-10-carboxylate (3r)



Yellow solid, mp 223-224 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.34 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 7.6 Hz, 2H), 7.73-7.58 (m, 1H), 7.53-7.33 (m, 5H), 7.12-6.93 (m, 2H), 4.67 (q, J = 8.0 Hz, 2H), 4.25 (s, 2H), 2.39 (s, 3H), 1.57 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 199.2, 167.9, 162.2 (J_{CF} = 242.0 Hz), 141.9, 140.1, 139.4, 136.7 (J_{CF} = 8.2 Hz), 135.3 (J_{CF} = 3.2 Hz), 134.6, 132.0, 129.9 , 129.2, 128.0, 126.5, 125.9 (J_{CF} = 8.9 Hz), 124.7, 115.2 (J_{CF} = 23.0 Hz), 110.2 (J_{CF} = 23.9 Hz), 61.5, 36.6, 21.7, 14.5; IR (KBr, v) 2975, 2926, 1712, 1666, 1578, 1448, 1349, 1245, 1160 cm^{-1}; HRMS (ESI) *m/z* calcd for $[M+H]^+$ Chemical Formula: $C_{28}H_{21}FO_3$ 424.1475, found 425.1523. HRMS (ESI) *m/z* calcd for $C_{28}H_{22}FO_3$, 425.1553 $[M+H]^+$, found 425.1523.

Ethyl 3-fluoro-7-methyl-5-(4-methylbenzoyl)-11H-benzo[b]fluorene-10-carboxylate (3s)



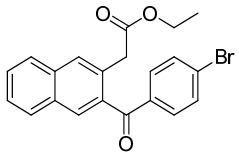
Yellow solid, mp 239-240 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.34 (d, J = 9.2 Hz, 1H), 7.82 (d, J = 7.2 Hz, 2H), 7.51-7.36 (m, 3H), 7.31-7.20 (m, 2H), 7.11-6.86 (m, 2H), 4.75 (q, J = 7.2 Hz, 2H), 4.24 (s, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 1.58 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.7, 168.0, 162.2 (J_{CF} = 241.9 Hz), 145.8, 141.9, 140.2 (J_{CF} = 9.0 Hz), 139.3, 136.6, 135.2 (J_{CF} = 3.2 Hz), 134.4, 132.2, 130.0, 129.8, 128.1, 126.3, 125.8 (J_{CF} = 8.9 Hz), 125.4, 124.8, 115.2 (J_{CF} = 22.9 Hz), 110.2 (J_{CF} = 24.0 Hz), 61.5, 36.6, 21.9, 21.7, 14.6; IR (KBr, ν) 3028, 2981, 2918, 1720, 1663, 1483, 1367, 1247, 1191 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{29}H_{24}FO_3$, 439.1709 $[M+H]^+$, found 439.1653.

General Procedure for the Synthesis of Products 4a-l

Example for the synthesis of **4a**:

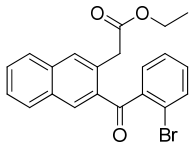
Typical procedure: Under argon conditions, 1-(4-bromophenyl)-3-(2-ethynylphenyl)prop-2-en-1-one (62 mg, 0.2 mmol), CuI (3.8 mg, 10 mol %), $[Cp^*RhCl_2]_2$ (1.8 mg, 1.5 mol %) triisobutylamine (148 mg, 0.8 mmol), and dry CH_3CN (1.0 ml) were continuously added into a dry 10-mL Shrek tube. The mixture was stirred at 90 °C for 10 min. Then ethyl diazoacetate (**2d**, 45.6 mg, 0.4 mmol) in 1.0 mL of dry acetonitrile was added to the suspension at 90 °C over 1.5 hours *via* a syringe pump. After completion of the addition, the reaction mixture was stirred at 90 °C for an additional 10.5 hours. After the completion of reaction (monitored by TLC), the residue was quenched with saturated NH_4Cl solution, washed with water (20 mL) and extracted with ethyl acetate to provide organic phase, which was dried over Na_2SO_4 and then concentrated under the reduced pressure to give brown oil. Eventually, the resulting oil was further purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 45:1) to give pure pale yellow solid product **4a**.

Ethyl 2-(3-(4-bromobenzoyl)naphthalen-2-yl)acetate (4a)



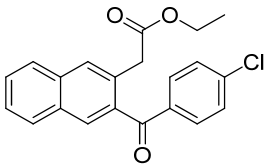
Pale yellow solid, mp 72-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.96-7.75 (m, 5H, ArH), 7.74-7.50 (m, 4H, ArH), 4.14 (s, 2H), 4.05 (q, J = 7.2 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.9, 171.6, 136.9, 135.5, 134.3, 132.1, 131.6, 131.2, 131.1, 131.0, 130.8, 128.5, 128.3, 128.0, 127.5, 126.9, 60.9, 39.1, 14.1; IR (KBr, ν) 3064, 3021, 1733, 1651, 1445, 1342, 1209, 1185 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{18}BrO_3$, 397.0439 $[M+H]^+$, found 397.0441.

Ethyl 2-(3-(2-bromobenzoyl)naphthalen-2-yl)acetate (4b)



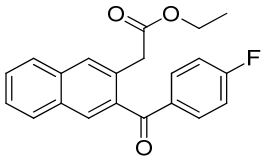
Pale yellow solid, mp 137-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.36 (d, J = 8.8 Hz, 2H, ArH), 8.08 (d, J = 8.4 Hz, 2H, ArH), 7.92-7.79 (m, 4H, ArH), 7.67-7.54 (m, 2H, ArH), 4.20 (s, 2H), 4.07 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.2, 171.7, 150.1, 1443, .143.3, 134.9, 134.5, 131.9, 131.4, 131.3, 131.1, 130.8, 130.5, 129.5, 128.7, 128.6, 127.5, 127.1, 126.6, 123.9, 123.5, 83.9, 61.0, 39.0, 14.2; IR (KBr, ν) 3103, 3069, 3048, 3000, 1732, 1664, 1518, 1402, 1317, 1211, 1191 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{18}BrO_3$, 397.0439 $[M+H]^+$, found 397.0421.

Ethyl 2-(3-(4-chlorobenzoyl)naphthalen-2-yl)acetate (4c)



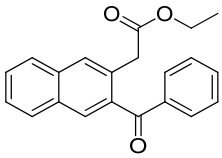
Pale yellow solid, mp 79-80 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.93-7.76 (m, 6H, ArH), 7.70-7.52 (m, 4H, ArH), 4.14 (s, 2H), 4.05 (q, J = 7.2 Hz, 2H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.7, 171.5, 139.3, 136.4, 134.3, 131.9, 131.2, 131.1, 131.0, 130.8, 128.6, 128.5, 128.2, 127.5, 126.8, 60.9, 39.1, 14.1; IR (KBr, v) 3055, 1683, 1651, 1462, 1359, 1172 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{18}ClO_3$, 353.0944 $[M+H]^+$, found 353.0932.

Ethyl 2-(3-(4-fluorobenzoyl)naphthalen-2-yl)acetate (4d)



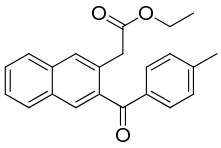
Pale yellow solid, mp 85-86 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.03-7.77 (m, 6H, ArH), 7.65-7.50 (m, 2H, ArH), 7.23-7.07 (m, 2H, ArH), 4.13 (s, 2H), 4.05 (q, J = 7.2 Hz, 2H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.4, 171.6, 165.7 (J_{CF} = 253.1 Hz), 135.8, 134.4 (J_{CF} = 2.9 Hz), 134.2, 133.2, 131.1, 131.0 (J_{CF} = 7.2 Hz), 129.6, 128.1, 127.5, 126.8, 115.5 (J_{CF} = 21.8 Hz), 60.9, 39.1, 14.1; IR (KBr, v) 3061, 3002, 1725, 1659, 1505, 1464, 1371, 1228, 1152 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{18}FO_3$, 337.1240 $[M+H]^+$, found 337.1234.

Ethyl 2-(3-benzoylnaphthalen-2-yl)acetate (4e)



Pale yellow solid, mp 98-99 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.99-7.80 (m, 6H, ArH), 7.66-7.48 (m, 5H, ArH), 4.13 (s, 2H), 4.05 (q, J = 7.2 Hz, 2H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.9, 171.6, 138.1, 135.9, 134.2, 132.8, 131.4, 131.2, 130.9, 130.8, 130.6, 128.5, 128.3, 128.1, 127.5, 126.7, 60.9, 39.2, 14.1; IR (KBr, v) 3060, 1718, 1652, 1580, 1448, 1370, 1247, 1186 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{19}O_3$, 319.1334 $[M+H]^+$, found 319.1300.

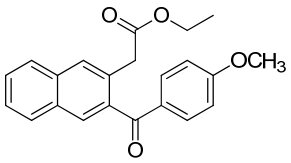
Ethyl 2-(3-(4-methylbenzoyl)naphthalen-2-yl)acetate (4f)



Pale yellow solid, mp 67-68 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.00-7.76 (m, 6H, ArH), 7.56 (d, J = 26.4 Hz, 2H, ArH), 7.31 (d, J = 7 Hz, 2H, ArH), 4.11 (s, 2H), 4.04 (q, J = 7.2 Hz, 2H), 2.48 (s, 3H), 1.18 (t, J = 14.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.6, 171.6, 143.7, 136.2, 135.4, 134.1, 131.2, 131.0, 130.9,

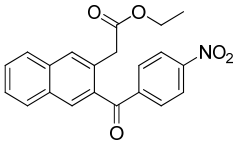
130.8, 130.7, 129.0, 128.4, 128.0, 127.5, 126.7, 60.8, 39.2, 21.7, 14.1; IR (KBr, *v*) 3055, 1732, 1665, 1605, 1549, 1406, 1369, 1287, 1183 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}O_3$, 333.1491 $[M+H]^+$, found 333.1466.

Ethyl 2-(3-(4-methoxybenzoyl)naphthalen-2-yl)acetate (4g)



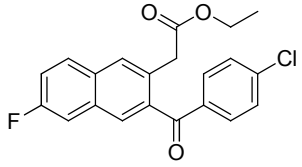
Pale yellow solid, mp 64-65 ºC; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.97-7.80 (m, 6H, ArH), 7.59 (s, 2H, ArH), 7.05-6.94 (m, 2H, ArH), 4.10 (s, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.91 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.6, 171.5, 163.5, 136.5, 134.0, 133.0, 131.2, 130.8, 130.7, 130.5, 128.4, 127.8, 127.5, 126.7, 113.6, 100.0, 60.8, 55.5, 39.1, 29.7, 14.1; IR (KBr, *v*) 3052, 3011, 1726, 1647, 1508, 1406, 1369, 1291, 1108 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}O_4$, 349.1440 $[M+H]^+$, found 349.1421.

Ethyl 2-(3-(4-nitrobenzoyl)naphthalen-2-yl)acetate (4h)



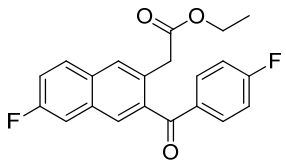
Pale yellow solid, mp 136-137 ºC; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.36 (d, *J* = 8.8 Hz, 2H, ArH), 8.09 (d, *J* = 8.8 Hz, 2H), 7.91-7.80 (m, 4H, ArH), 7.62-7.56 (m, 2H, ArH), 4.20 (s, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.2, 171.7, 150.1, 143.3, 134.9, 134.5, 131.9, 131.4, 131.3, 131.1, 130.8, 129.6, 128.7, 128.6, 127.5, 127.1, 123.9, 123.5, 61.0, 39.0, 14.2; IR (KBr, *v*) 3103, 3031, 3000, 1733, 1664, 1518, 1467, 1350, 1211, 1176 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{18}NO_5$, 364.1185 $[M+H]^+$, found 364.1184.

Ethyl 2-(3-(4-chlorobenzoyl)-7-fluoronaphthalen-2-yl)acetate (4i)



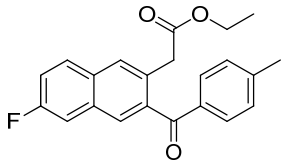
Pale yellow solid, mp 76-77 ºC; ^1H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.96-7.75 (m, 5H, ArH), 7.60-7.35 (m, 4H, ArH), 4.10 (s, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.5, 171.5, 161.1 (J_{CF} = 246.3 Hz), 139.5, 136.7, 136.1, 132.0, 131.9 (J_{CF} = 5.7 Hz), 131.0, 130.1 (J_{CF} = 2.7 Hz), 130.0, 129.9 (J_{CF} = 8..9 Hz), 128.7, 118.5 (J_{CF} = 25.4 Hz), 111.6 (J_{CF} = 20.6 Hz), 61.0, 38.9, 14.1; IR (KBr, *v*) 3023, 1731, 1659, 1586, 1466, 1399, 1277, 1183 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{17}ClFO_3$, 371.0850 $[M+H]^+$, found 371.0798.

Ethyl 2-(7-fluoro-3-(4-fluorobenzoyl)naphthalen-2-yl)acetate (4j)



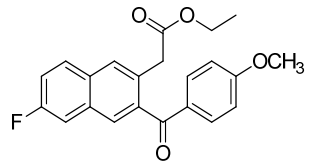
Pale yellow solid, mp 87-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.99-7.79 (m, 5H, ArH), 7.48-7.35 (m, 2H, ArH), 7.25-7.13 (m, 2H, ArH), 4.10 (s, 2H), 4.04 (q, J = 7.2 Hz, 2H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.2, 171.5, 165.8 (J_{CF} = 253.6 Hz), 163.4, 161.0 (J_{CF} = 246.2 Hz), 136.9, 134.1 (J_{CF} = 3.0 Hz), 133.2 (J_{CF} = 9.3 Hz), 131.9 (J_{CF} = 9.4 Hz), 131.0, 130.1 (J_{CF} = 2.8 Hz), 130.0 (J_{CF} = 8.9 Hz), 129.8, 118.4 (J_{CF} = 25.2 Hz), 115.5 (J_{CF} = 21.7 Hz), 111.5 (J_{CF} = 20.6 Hz), 60.9, 38.9, 14.1; IR (KBr, *v*) 3087, 3048, 3022, 1690, 1659, 1503, 1482, 1359, 1236, 1198 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{17}F_2O_3$, 355.1146 $[M+H]^+$, found 355.1142.

Ethyl 2-(7-fluoro-3-(4-methylbenzoyl)naphthalen-2-yl)acetate (4k)



Pale yellow solid, mp 81-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.93-7.75 (m, 5H, ArH), 7.49-7.29 (m, 4H, ArH), 4.08 (s, 2H), 4.04 (q, J = 7.2 Hz, 2H), 2.48 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.4, 171.5, 161.0 (J_{CF} = 245.9 Hz), 144.0, 136.2, 132.0 (J_{CF} = 9.3 Hz), 131.0, 130.7 (J_{CF} = 6.6 Hz), 130.6, 130.1 (J_{CF} = 2.7 Hz), 130.0, 129.9, 129.1, 118.2 (J_{CF} = 25.2 Hz), 111.6, 111.5 (J_{CF} = 20.6 Hz), 60.9, 39.0, 21.8, 14.1; IR (KBr, *v*) 3057, 1728, 1689, 1576, 1465, 1395, 1210, 1130 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{20}FO_3$, 351.1396 $[M+H]^+$, found 351.1386.

Ethyl 2-(7-fluoro-3-(4-methoxybenzoyl)naphthalen-2-yl)acetate (4l)



Pale yellow solid, mp 77-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.95-7.78 (m, 5H, ArH), 7.48-7.31 (m, 2H, ArH), 6.99 (d, J = 9.2 Hz, 2H, ArH), 4.06 (s, 2H), 4.03 (q, J = 7.2 Hz, 2H), 3.91 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 196.3, 171.5, 163.7, 161.0 (J_{CF} = 245.8 Hz), 137.6, 132.9, 132.0 (J_{CF} = 9.3 Hz), 130.9, 130.6, 130.5, 130.1 (J_{CF} = 2.8 Hz), 130.0 (J_{CF} = 9.0 Hz), 129.4, 129.3, 118.1 (J_{CF} = 23.2 Hz), 112.6, 111.4 (J_{CF} = 20.6 Hz), 60.9, 55.5, 38.9, 14.1; IR (KBr, *v*) 3072, 3016, 1724, 1651, 1505, 1442, 1333, 1262, 1149 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{20}FO_4$, 367.1346 $[M+H]^+$, found 367.1372.

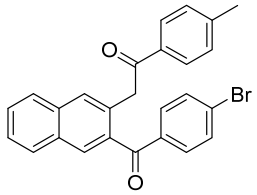
General Procedure for the Synthesis of Products 4m-r

Example for the synthesis of **4m**:

Typical procedure: Under argon conditions, 1-(4-bromophenyl)-3-(2-ethynylphenyl)prop-2-en-1-one (62 mg, 0.2 mmol), CuI (3.8 mg, 10 mol %), $[Cp^*RhCl_2]_2$ (1.8 mg, 1.5 mol %), triisobutylamine (148 mg, 0.8 mmol), and dry CH_3CN (1.0 ml) were continuously added into a dry 10-mL Shrek tube. The mixture was stirred at 40 °C for 10 min. Then 2-diazo-1-(*p*-tolyl)ethanone (**2e**, 64 mg, 0.4 mmol) in 1.0 mL of dry acetonitrile was added to the

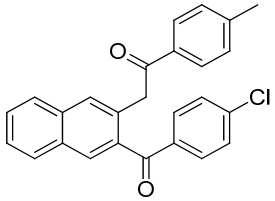
suspension at 40 ºC over 1.5 hours via a syringe pump. After completion of the addition, the reaction mixture was stirred at 40 ºC for an additional 10.5 hours. After the completion of reaction (monitored by TLC), the residue was quenched with saturated NH_4Cl solution, washed with water (20 mL) and extracted with ethyl acetate to provide organic phase, which was dried over Na_2SO_4 and then concentrated under the reduced pressure to give brown oil. Eventually, the resulting oil was further purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 45:1) to give pure pale yellow solid product **4m**.

2-(3-(4-Bromobenzoyl)naphthalen-2-yl)-1-(p-tolyl)ethanone (4m)



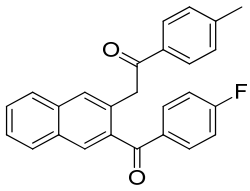
Pale yellow solid, mp 122-123 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.98-7.77 (m, 8H, ArH), 7.64 (d, J = 8.4 Hz, 4H, ArH), 7.29-7.25 (m, 2H, ArH), 4.84 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.2, 197.1, 144.0, 136.9, 136.0, 134.4, 134.3, 132.1, 131.6, 131.1, 131.0, 129.3, 128.5, 128.3, 128.1, 127.9, 127.5, 126.7, 43.3, 21.7; IR (KBr, *v*) 3056, 3028, 1718, 1679, 1584, 1463, 1304, 1286, 1183 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{20}BrO_2$, 443.0647 $[M+H]^+$, found 443.0641.

2-(3-(4-Chlorobenzoyl)naphthalen-2-yl)-1-(p-tolyl)ethanone (4n)



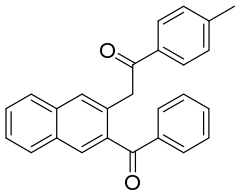
Pale yellow solid, mp 108-109 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.10-7.69 (m, 8H, ArH), 7.47 (d, J = 8.8 Hz, 4H, ArH), 7.29-7.25 (m, 2H, ArH), 4.83 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.2, 197.0, 144.0, 139.2, 136.5, 136.1, 134.4, 132.0, 131.5, 131.1, 131.0, 129.3, 128.6, 128.5, 128.3, 128.1, 127.5, 126.7, 43.3, 21.7; IR (KBr, *v*) 3056, 1683, 1653, 1588, 1457, 1398, 1286, 1179 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{20}ClO_2$, 399.1152 $[M+H]^+$, found 399.1137.

2-(3-(4-Fluorobenzoyl)naphthalen-2-yl)-1-(p-tolyl)ethano (4o)



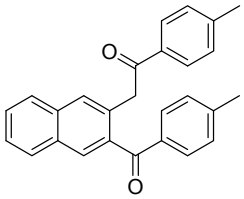
Pale yellow solid, mp 100-101 ºC; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.01-7.95 (m, 2H, ArH), 7.95-7.81 (m, 5H, ArH), 7.79 (s, 1H, ArH), 7.64-7.51 (m, 2H, ArH), 7.29-7.24 (m, 2H, ArH), 7.22-7.13 (m, 2H, ArH), 4.83 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.2, 196.8, 165.6 (J_{CF} = 246.7 Hz), 143.9, 136.3, 134.4 (J_{CF} = 3.0 Hz), 134.3, 133.2, 131.5, 131.1 ,131.0 (J_{CF} = 8.0 Hz), 129.3, 128.5, 128.3, 128.0, 127.5, 126.6, 115.4 (J_{CF} = 21.7 Hz), 43.3, 21.7; IR (KBr, *v*) 3059, 1733, 1654, 1588, 1464, 1341, 1287, 1162 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{20}FO_2$, 383.1447 $[M+H]^+$, found 383.1429.

2-(3-Benzoylnaphthalen-2-yl)-1-(p-tolyl)ethanone (4p)



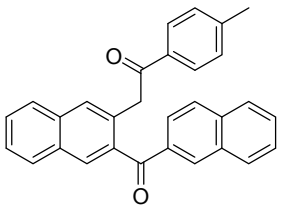
Pale yellow solid, mp 93-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.01-7.89 (m, 5H, ArH), 7.89-7.82 (m, 2H, ArH), 7.79 (s, 1H, ArH), 7.51 (d, *J* = 8.0 Hz, 5H, ArH), 7.29-7.24 (m, 2H, ArH), 4.83 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.3, 197.2, 143.8, 138.2, 136.3, 134.4, 134.3, 132.7, 131.7, 131.4, 131.1, 131.0, 130.6, 129.2, 128.5, 128.4, 128.3, 128.0, 127.5, 126.5, 100.0, 43.4, 21.7; IR (KBr, *v*) 3054, 3026, 1675, 1651, 1577, 1449, 1315, 1246, 1178 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{21}O_2$, 365.1542 $[M+H]^+$, found 365.1521.

2-(3-(4-Methylbenzoyl)naphthalen-2-yl)-1-(p-tolyl)ethanone (4q)



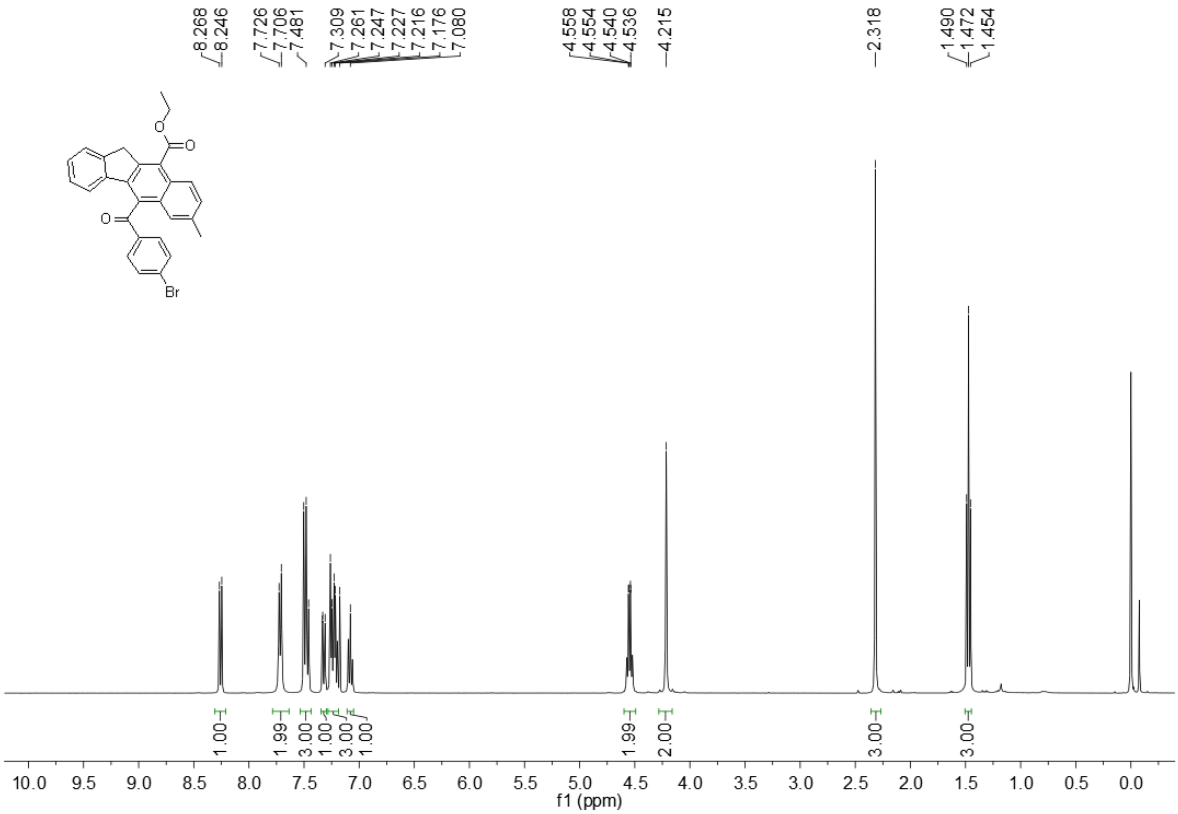
Pale yellow solid, mp 112-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.24-7.65 (m, 8H, ArH), 7.64-7.44 (m, 2H, ArH), 7.30 (d, *J* = 8.8 Hz, 2H, ArH), 7.24 (d, *J* = 8.0 Hz, 2H, ArH), 4.79 (s, 2H), 2.44 (d, *J* = 22.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 197.9, 197.2, 143.8, 143.6, 136.5, 135.5, 134.4, 134.2, 131.6, 131.1, 131.0, 130.9, 130.8, 129.2, 129.0, 128.5, 128.4, 127.8, 127.5, 126.5, 43.3, 29.7, 21.7, 21.6; IR (KBr, *v*) 3057, 1733, 1681, 1572, 1463, 1375, 1284, 1178 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{23}O_2$, 379.1698 $[M+H]^+$, found 379.1688.

2-(3-(4-Methylbenzoyl)naphthalen-2-yl)-1-(naphthalen-2-yl)ethanone (4r)

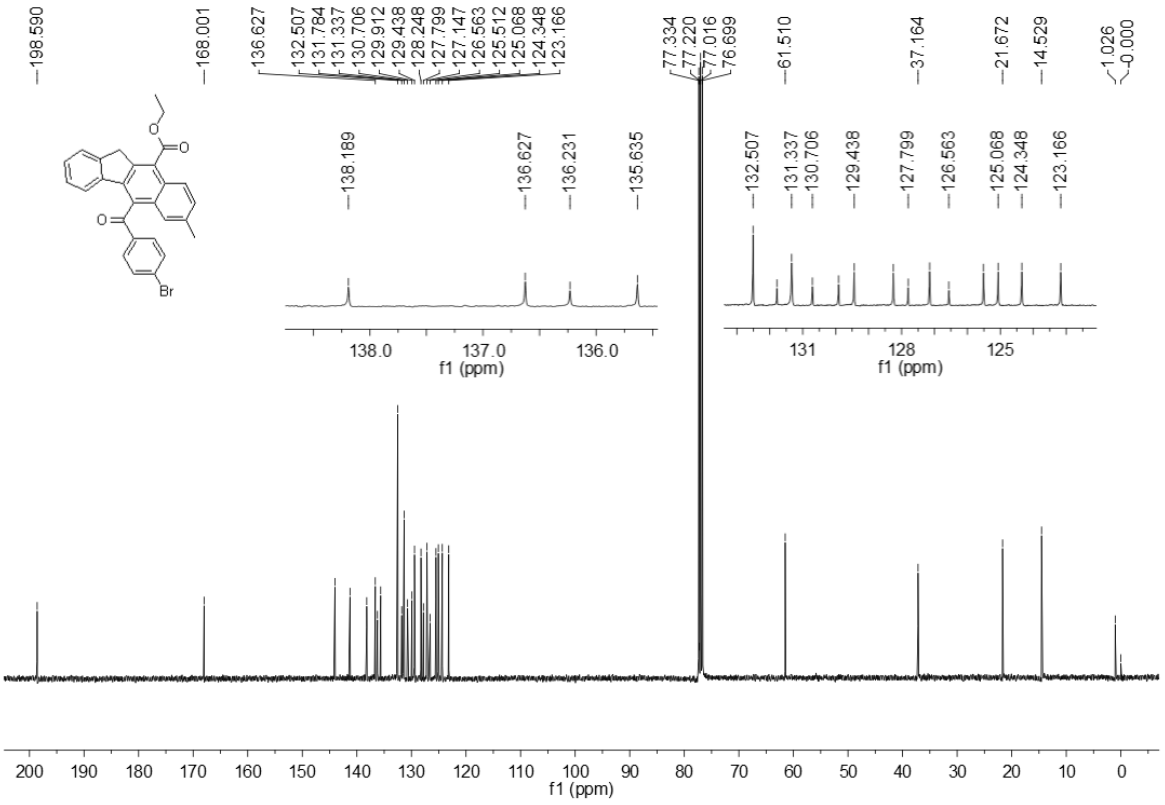


Pale yellow solid, mp 139-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.56 (s, 1H, ArH)), 8.09-7.82 (m, 10H, ArH)), 7.67-7.51 (m, 4H, ArH)), 7.30-7.27 (m, 2H, ArH)), 4.96 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 198.0, 197.6, 143.7, 136.5, 135.6, 135.5, 134.3, 134.2, 132.5, 131.5, 131.2, 131.1, 130.9, 130.8, 130.0, 129.6, 129.0, 128.3, 127.9, 127.7, 127.5, 126.6, 126.5, 124.1, 43.5, 21.7; IR (KBr, *v*) 3055, 1683, 1651, 1462, 1359, 1172 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{30}H_{23}O_2$, 415.1698 $[M+H]^+$, found 415.1669.

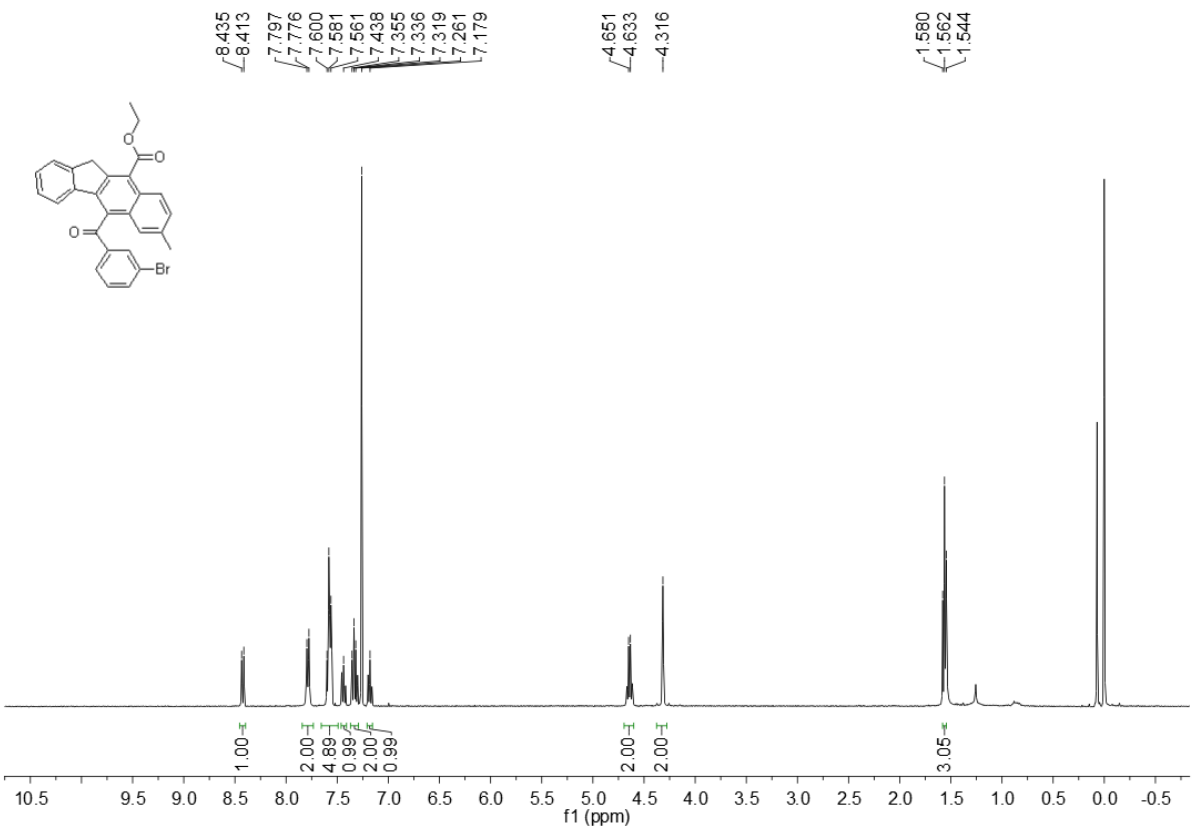
Copies of ^{1}H NMR and ^{13}C NMR of Compounds 3 and 4



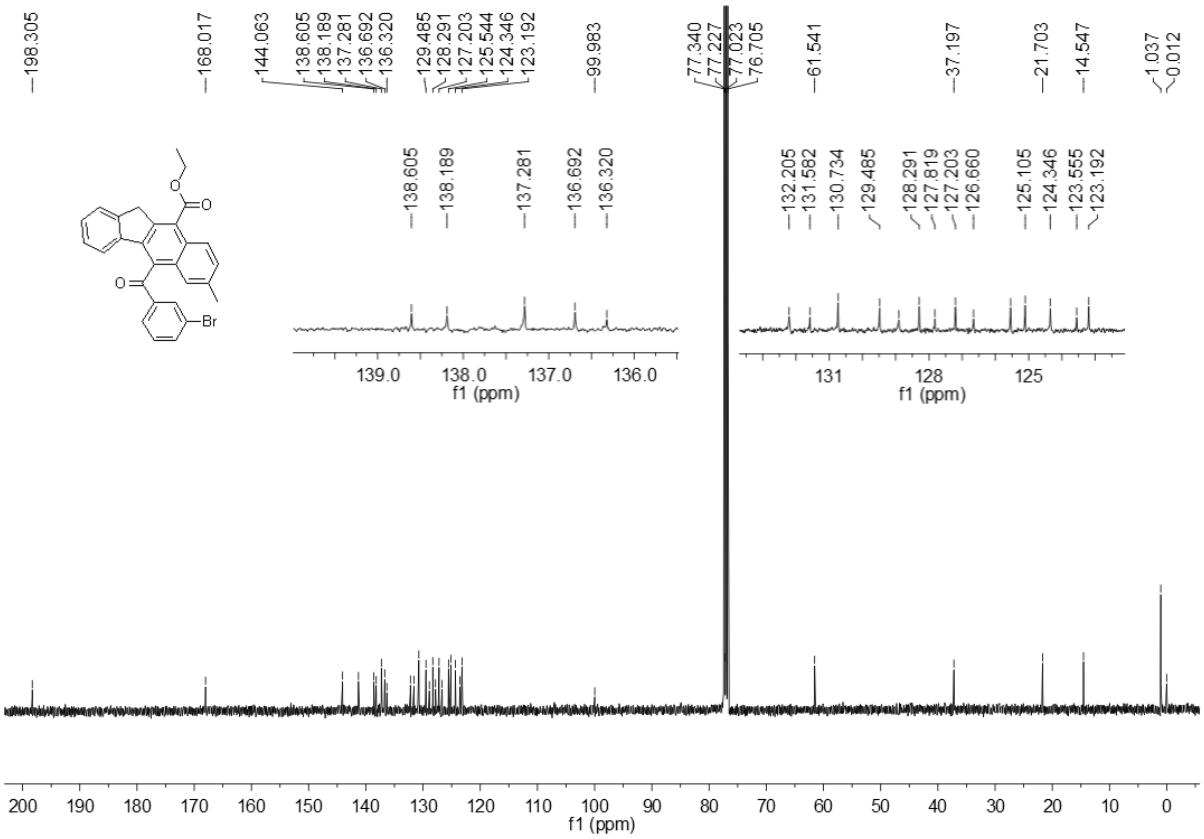
^{1}H NMR Spectrum of Compound 3a



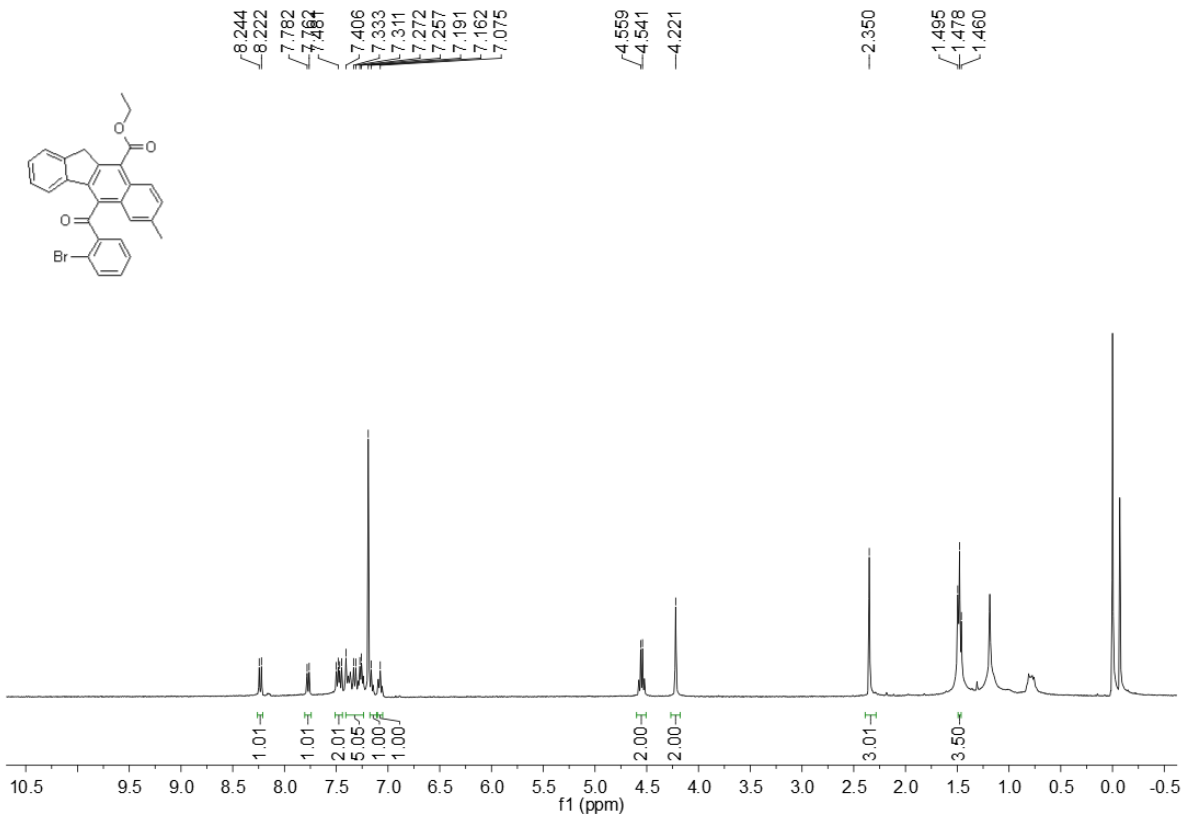
^{13}C NMR Spectrum of Compound 3a



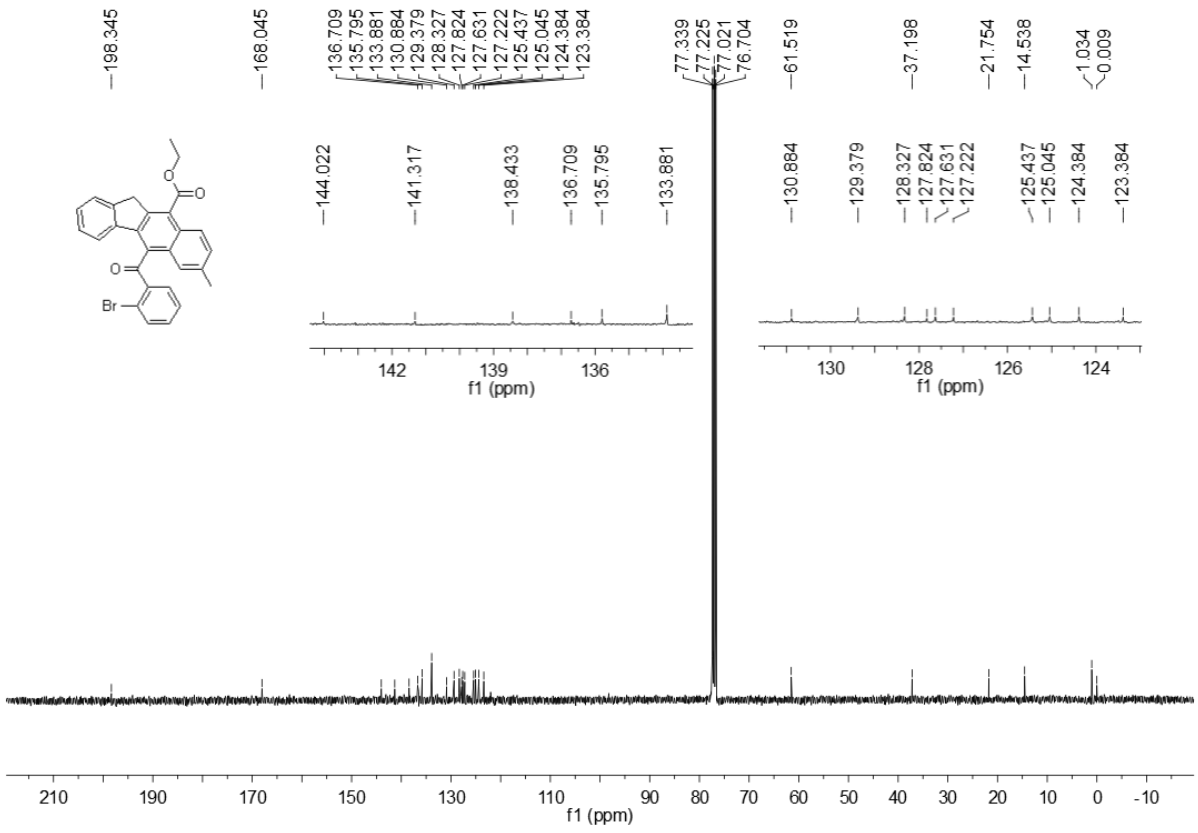
^{1}H NMR Spectrum of Compound 3b



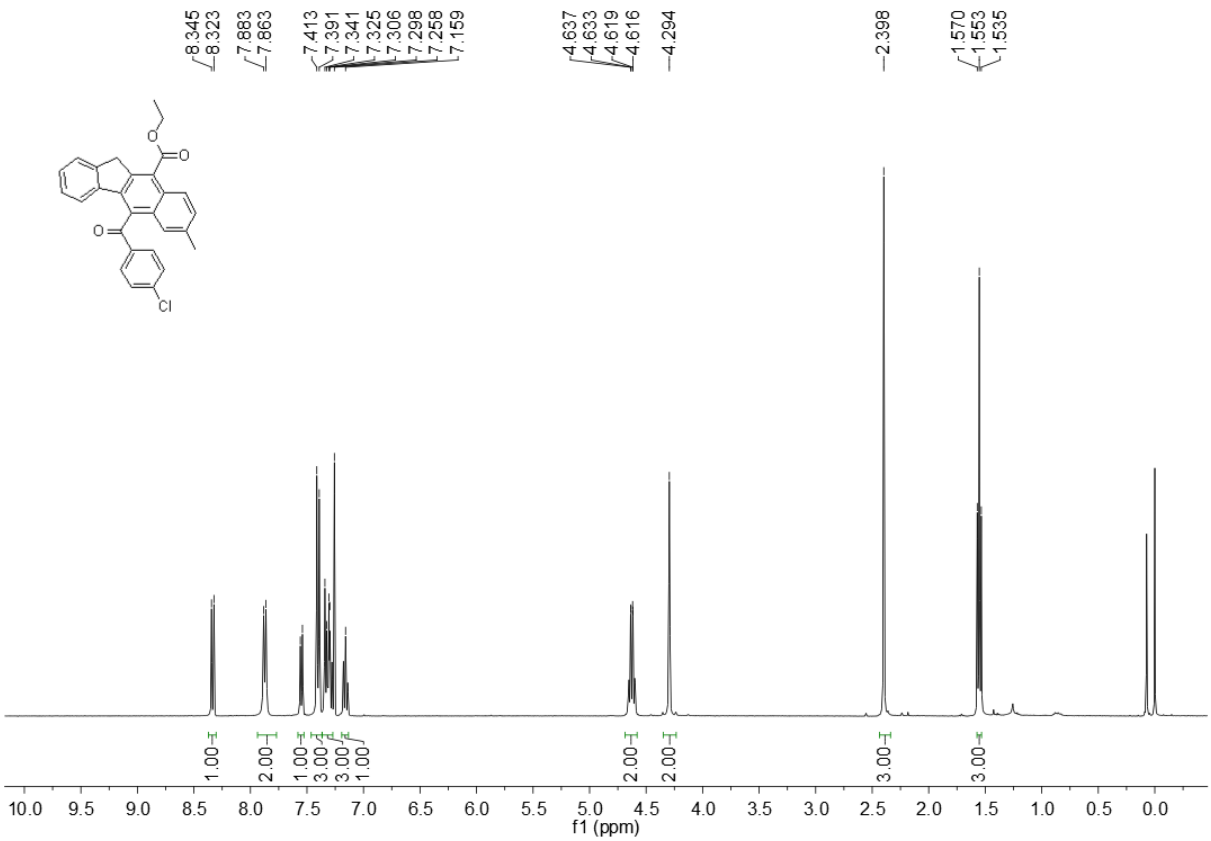
^{13}C NMR Spectrum of Compound 3b



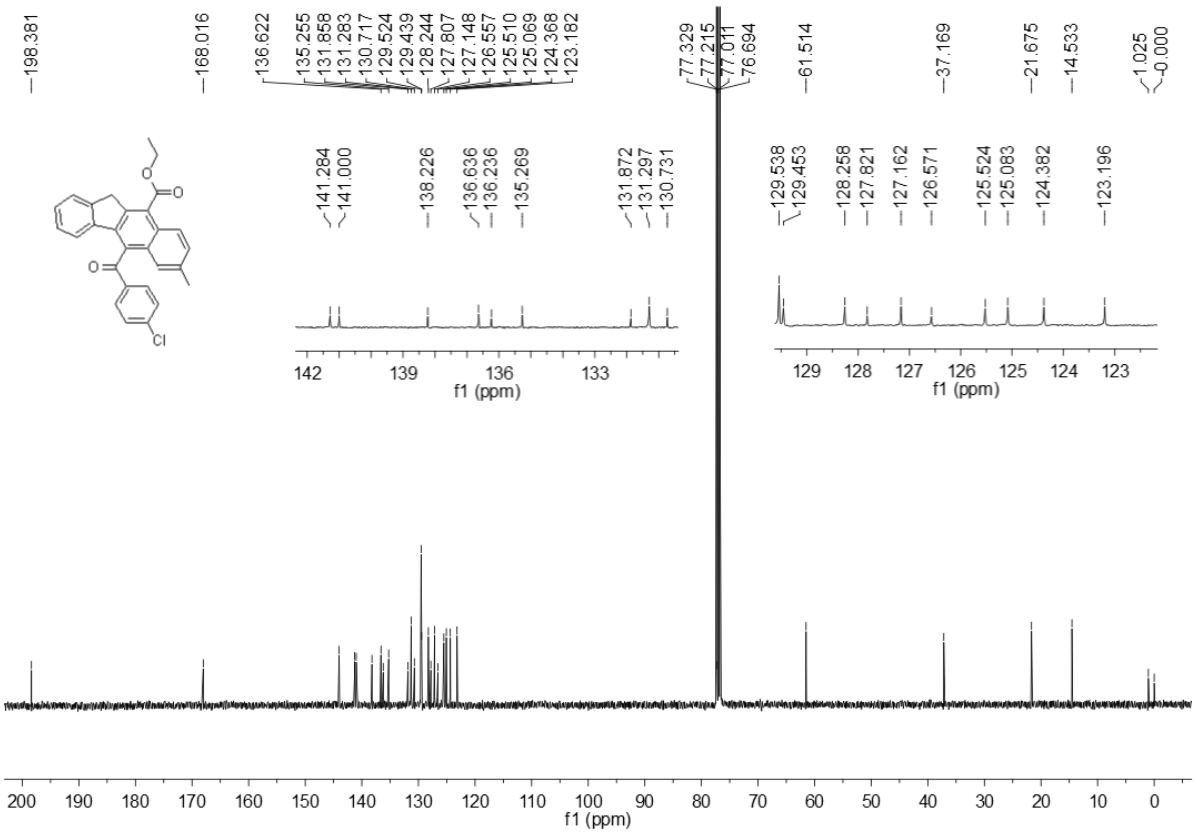
^{1}H NMR Spectrum of Compound 3c



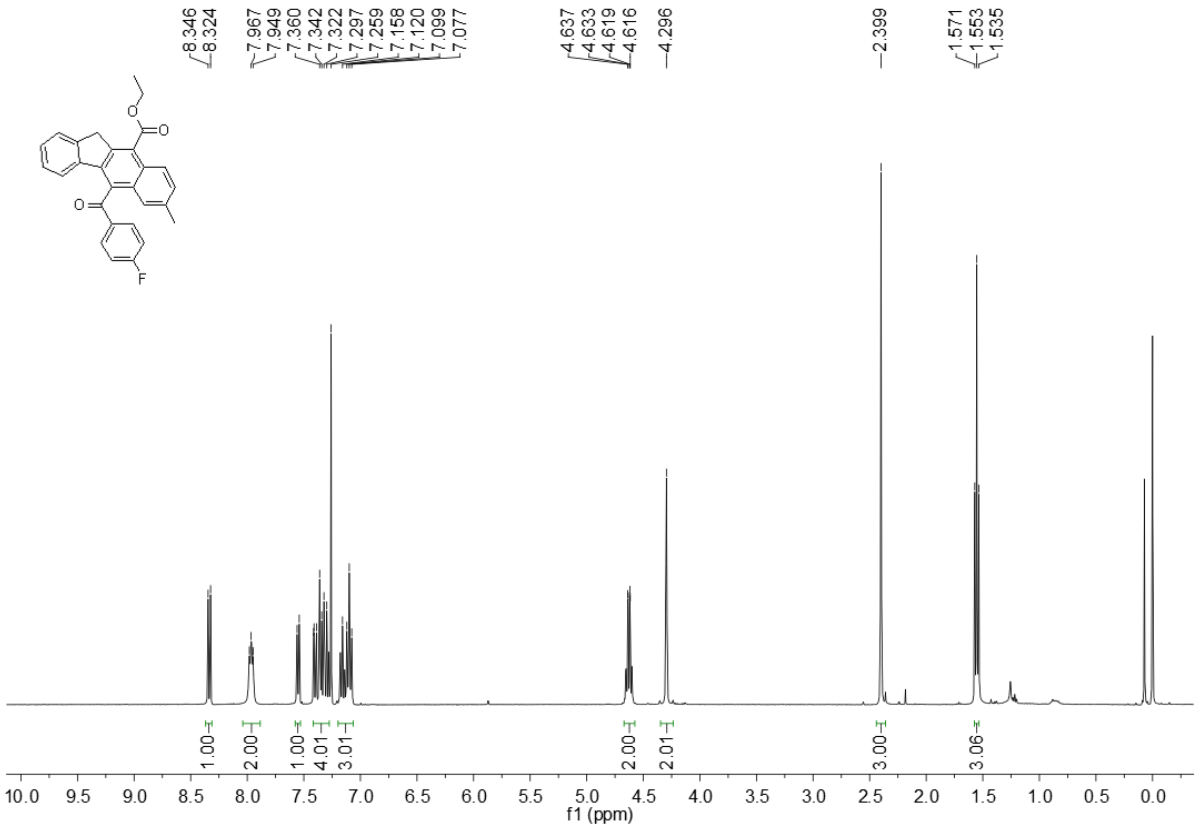
^{13}C NMR Spectrum of Compound 3d



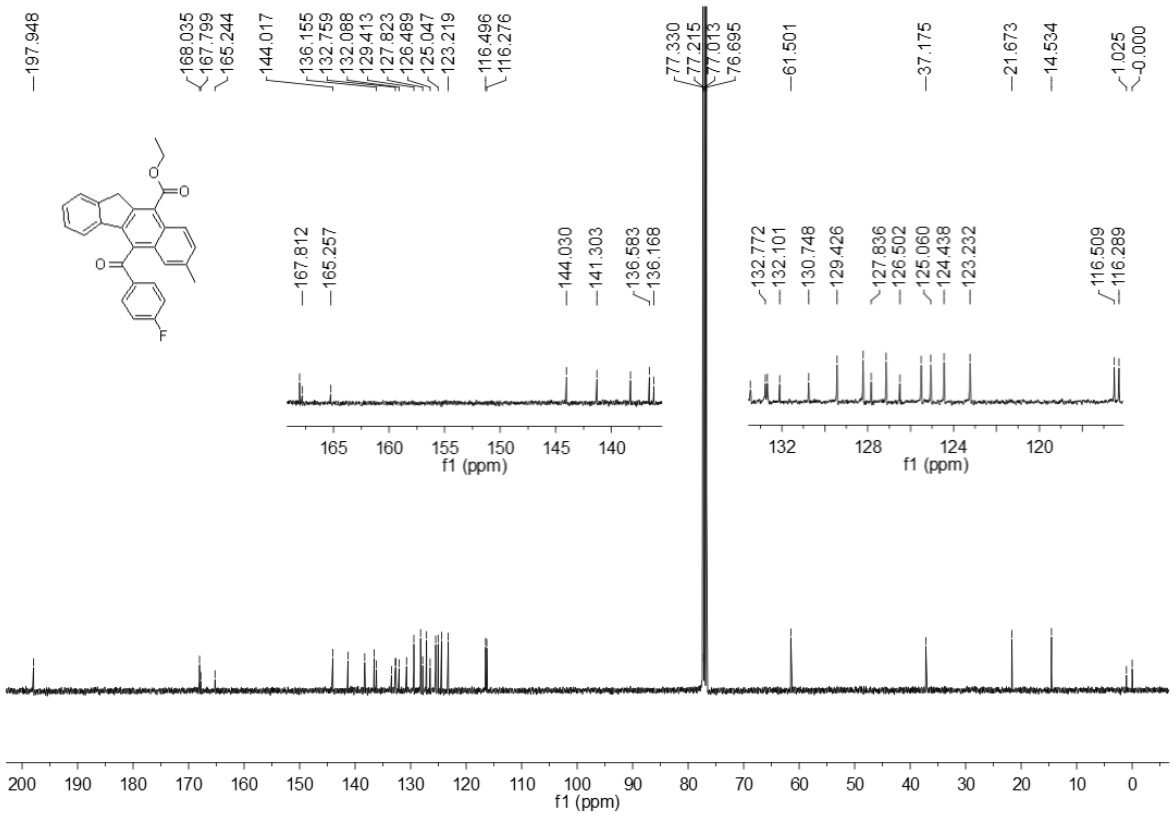
^{1}H NMR Spectrum of Compound 3d



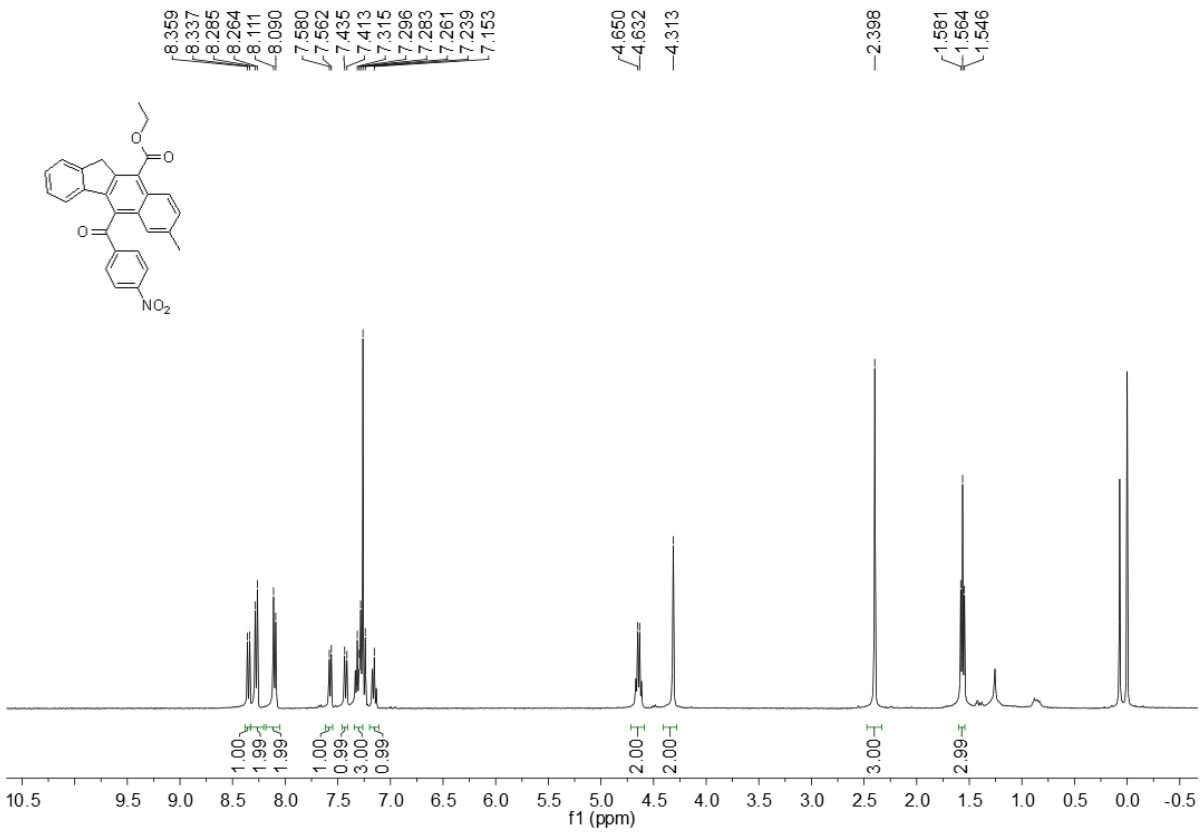
^{13}C NMR Spectrum of Compound 3d



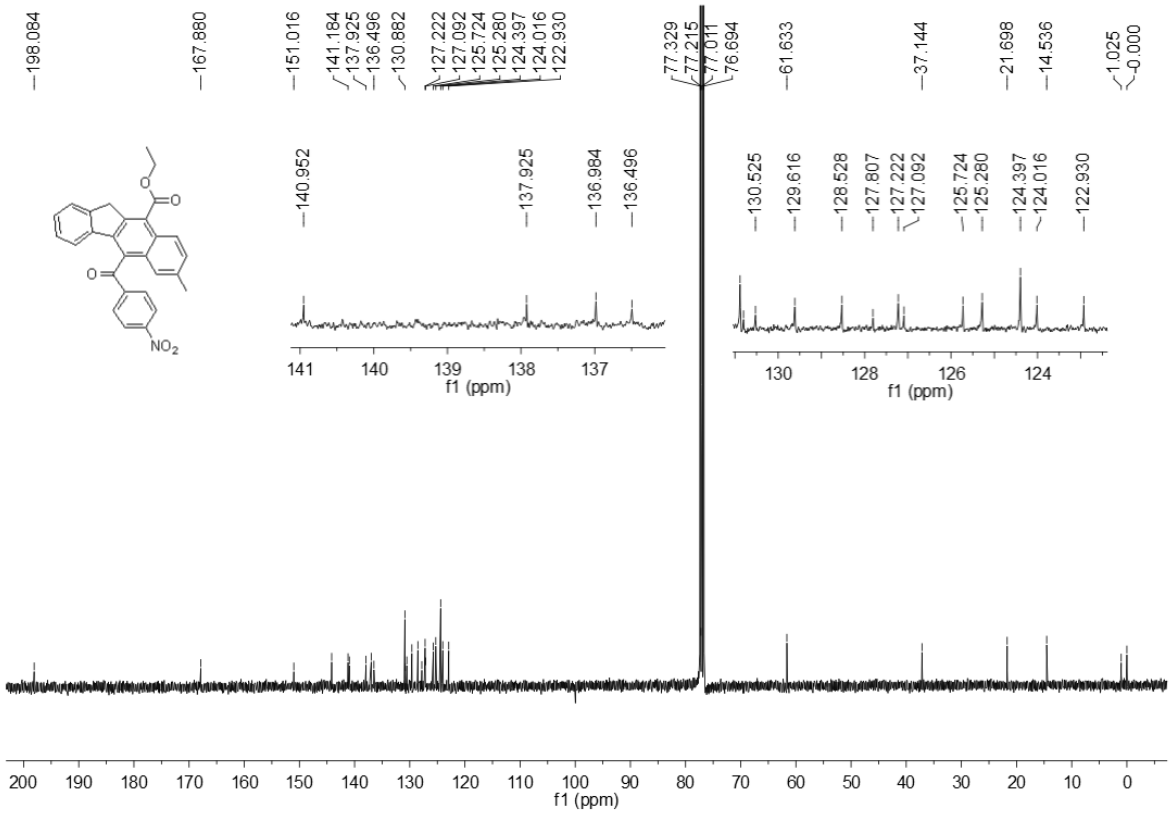
^{1}H NMR Spectrum of Compound 3e



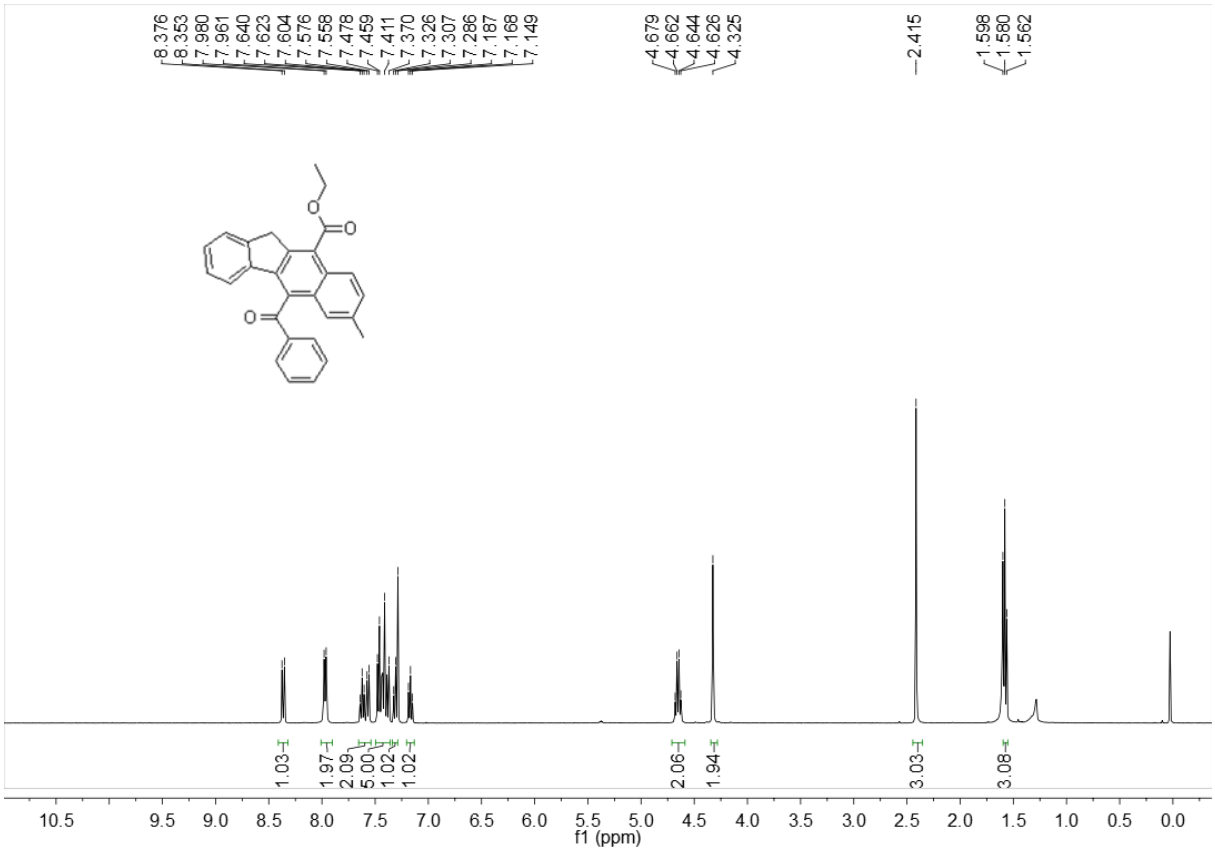
^{13}C NMR Spectrum of Compound 3e



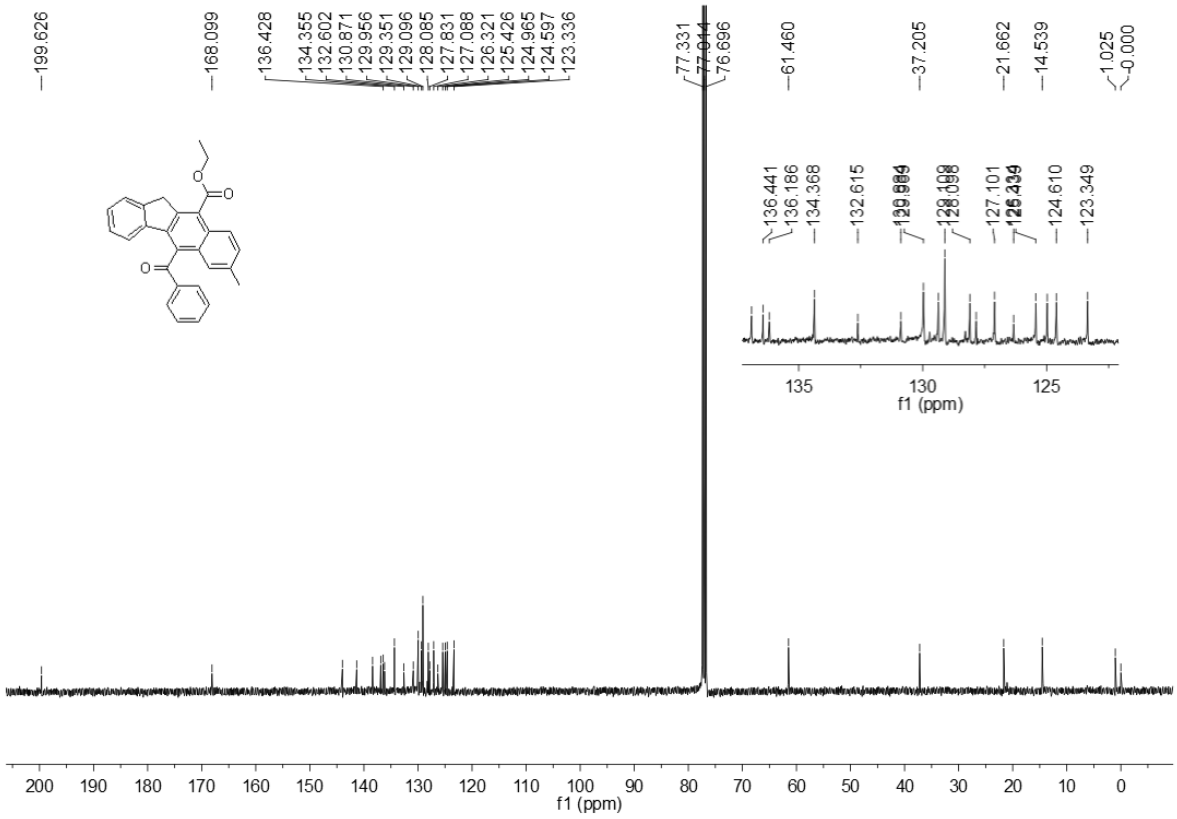
^{1}H NMR Spectrum of Compound 3f



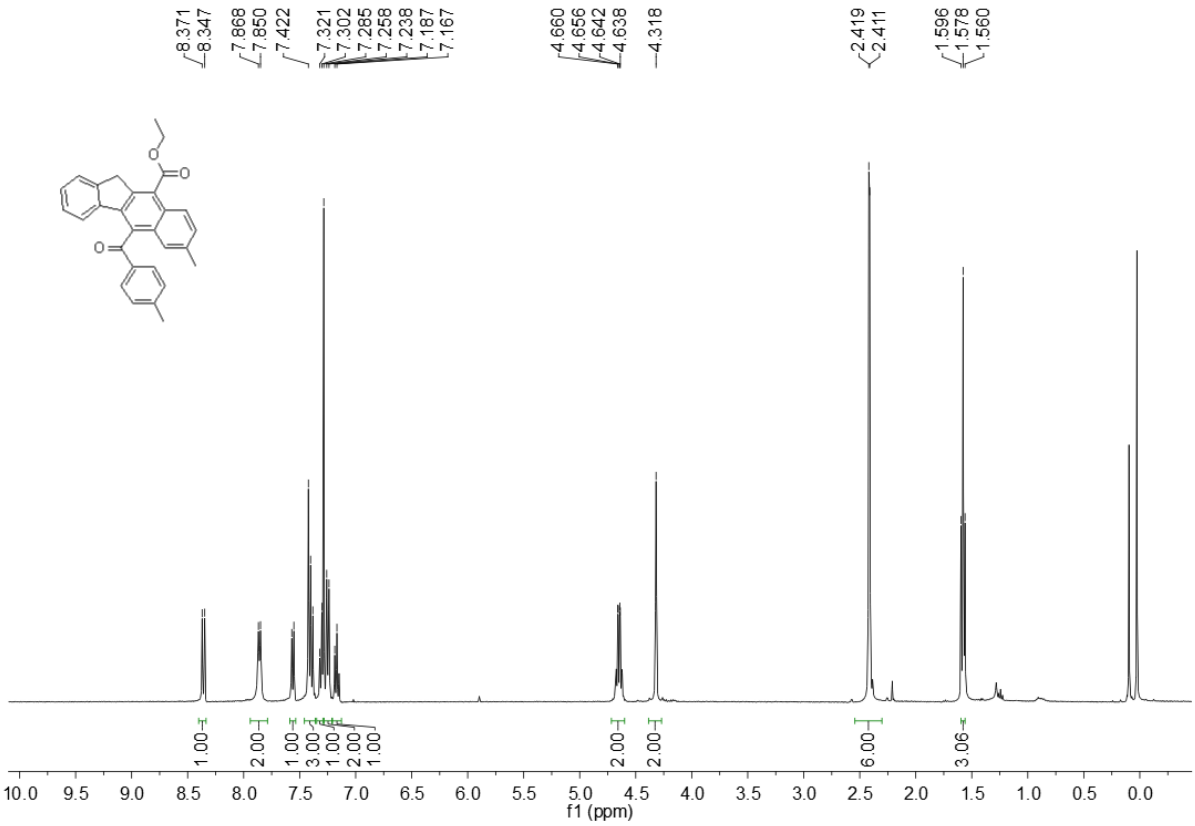
^{13}C NMR Spectrum of Compound 3f



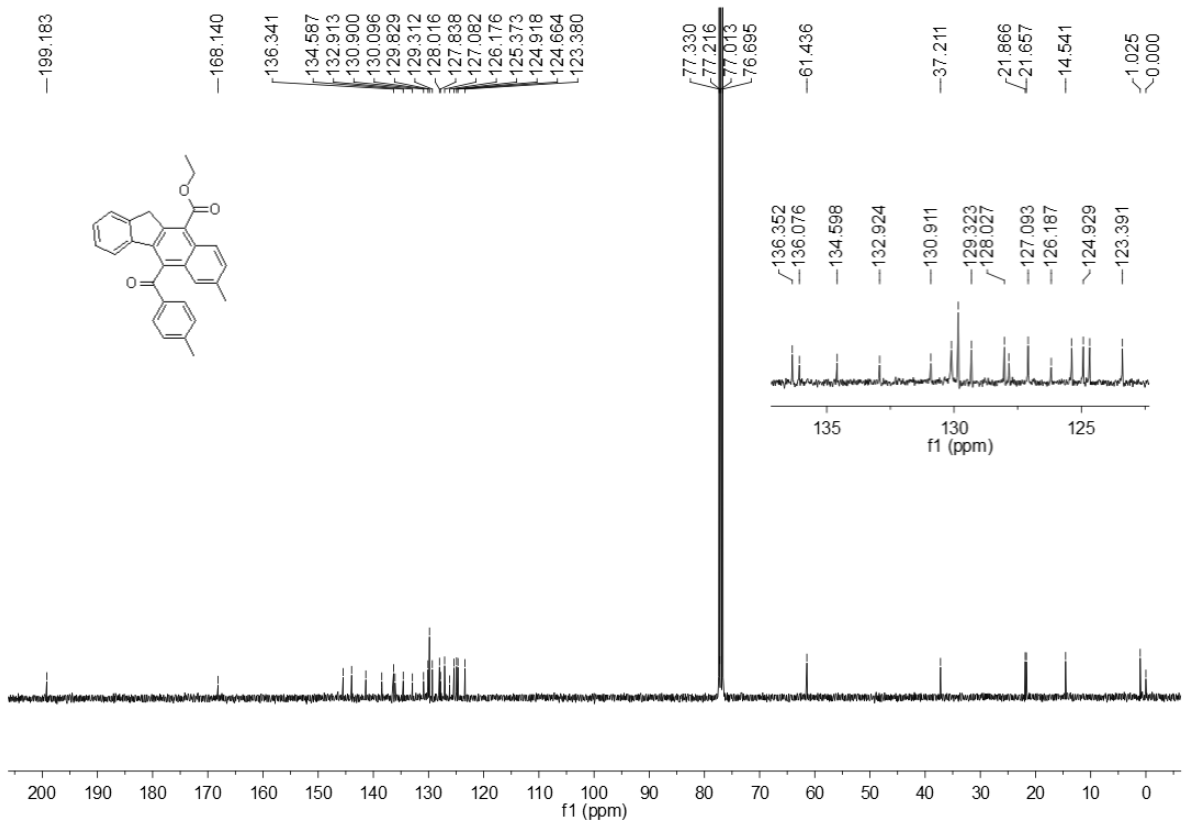
^{1}H NMR Spectrum of Compound 3g



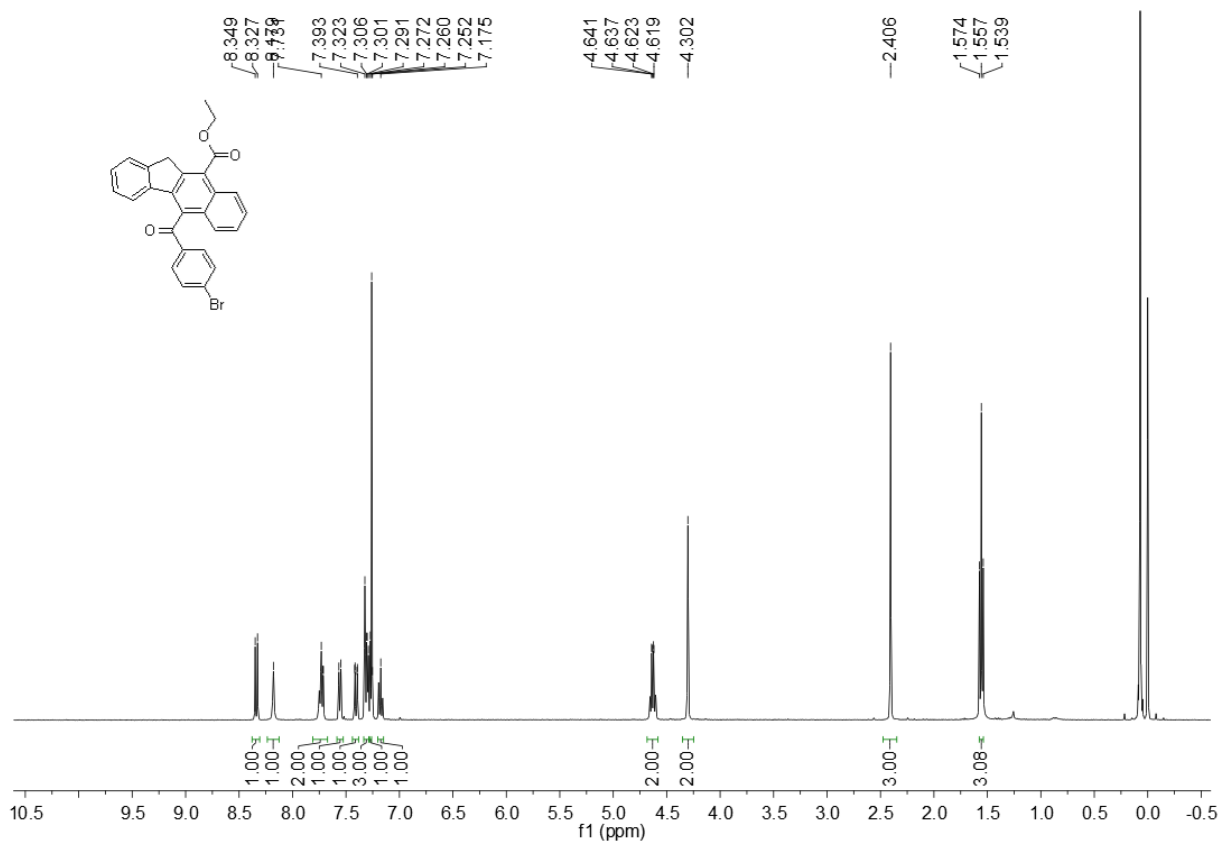
^{13}C NMR Spectrum of Compound 3g



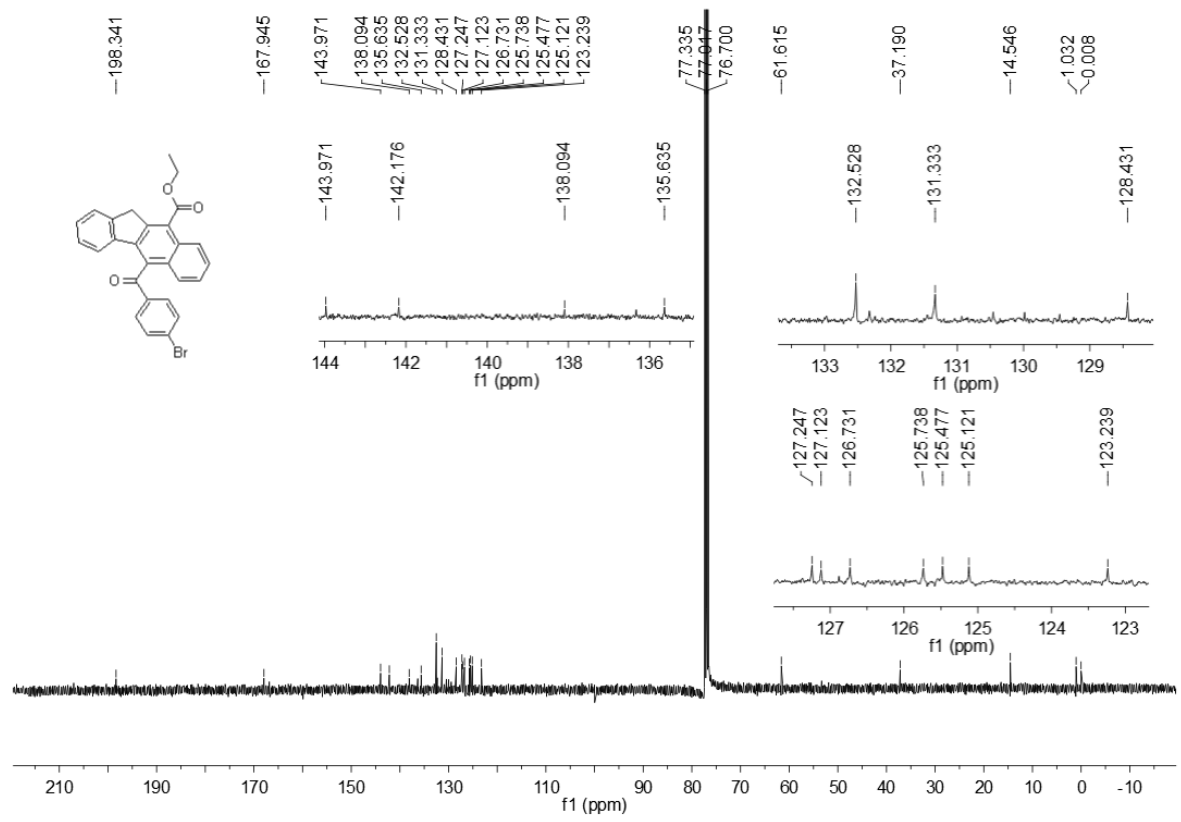
^{1}H NMR Spectrum of Compound 3h



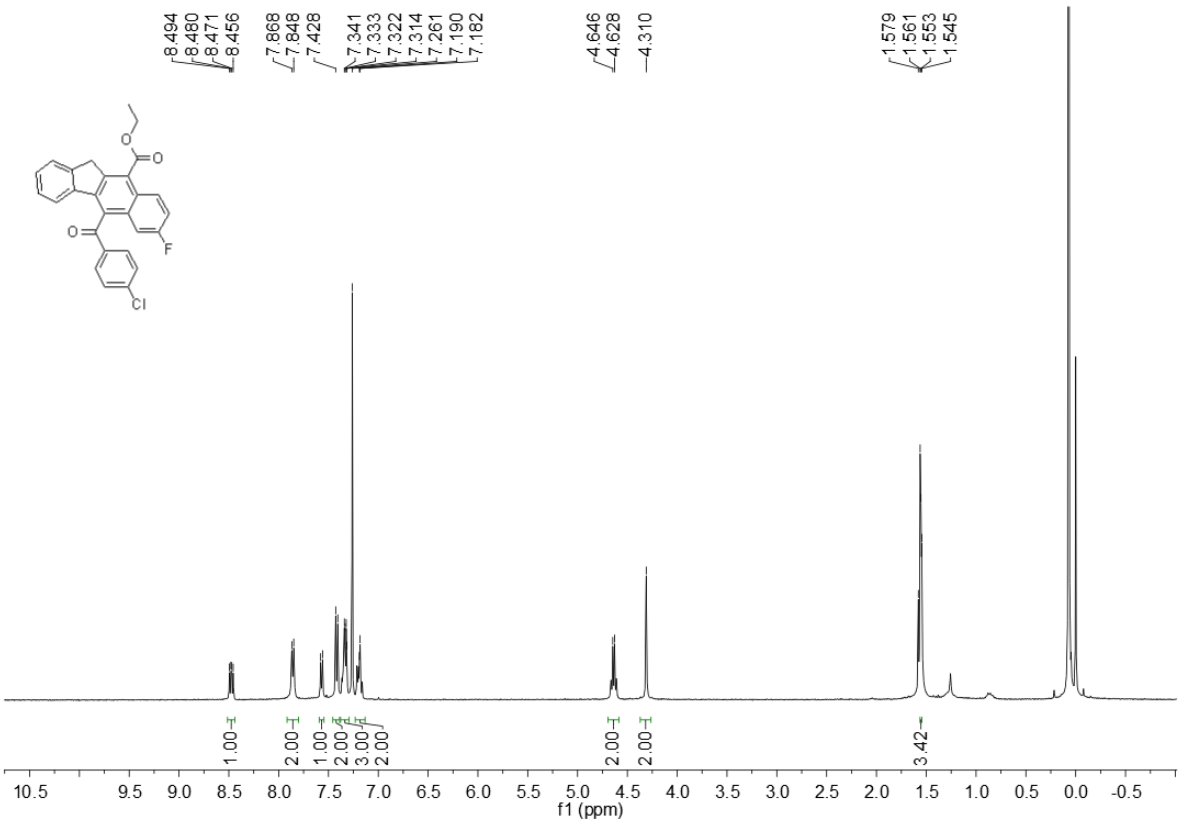
^{1}H NMR Spectrum of Compound 3h



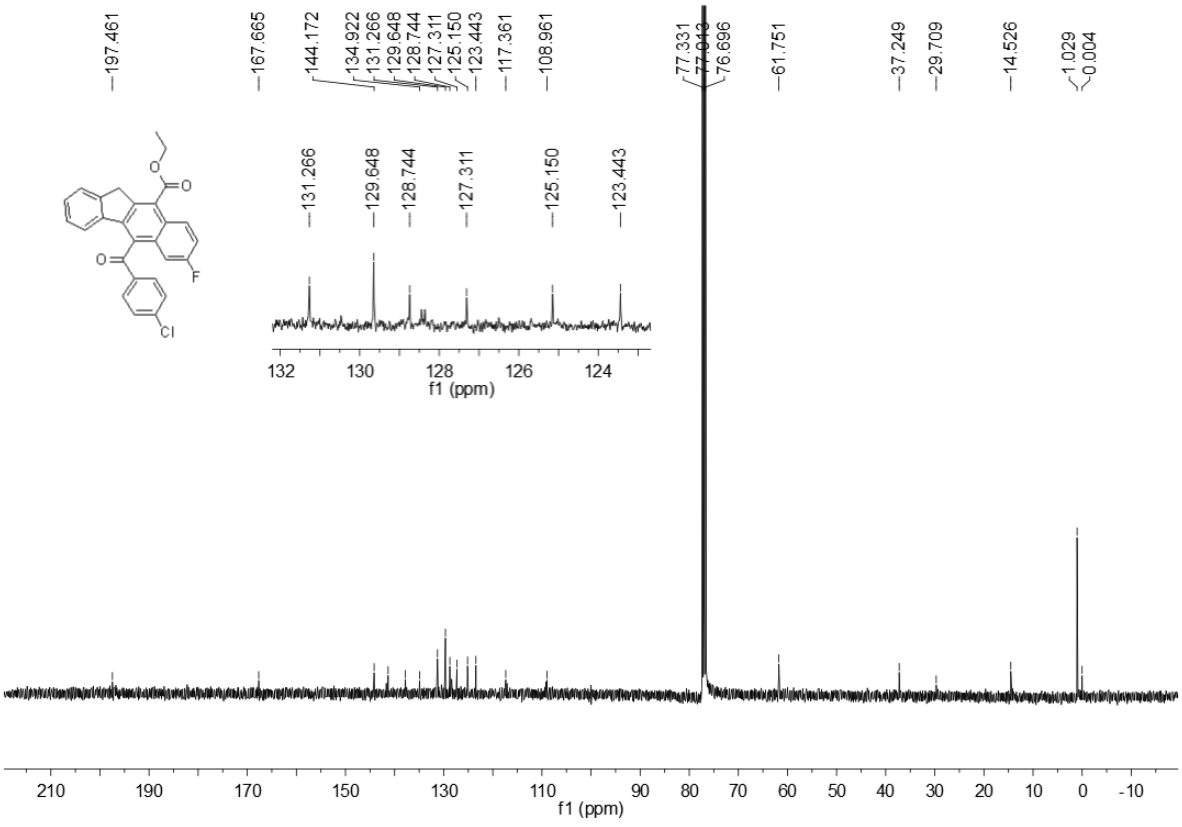
^{1}H NMR Spectrum of Compound 3i



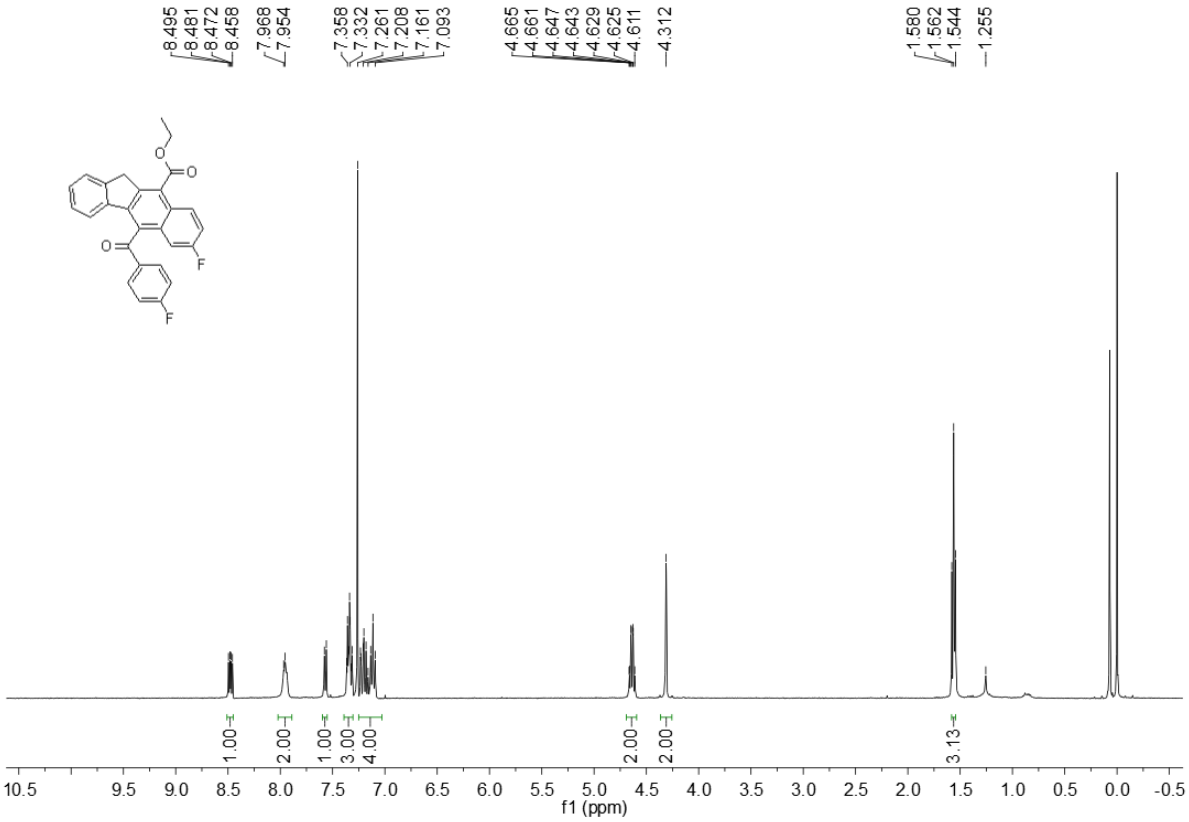
^{13}C NMR Spectrum of Compound 3i



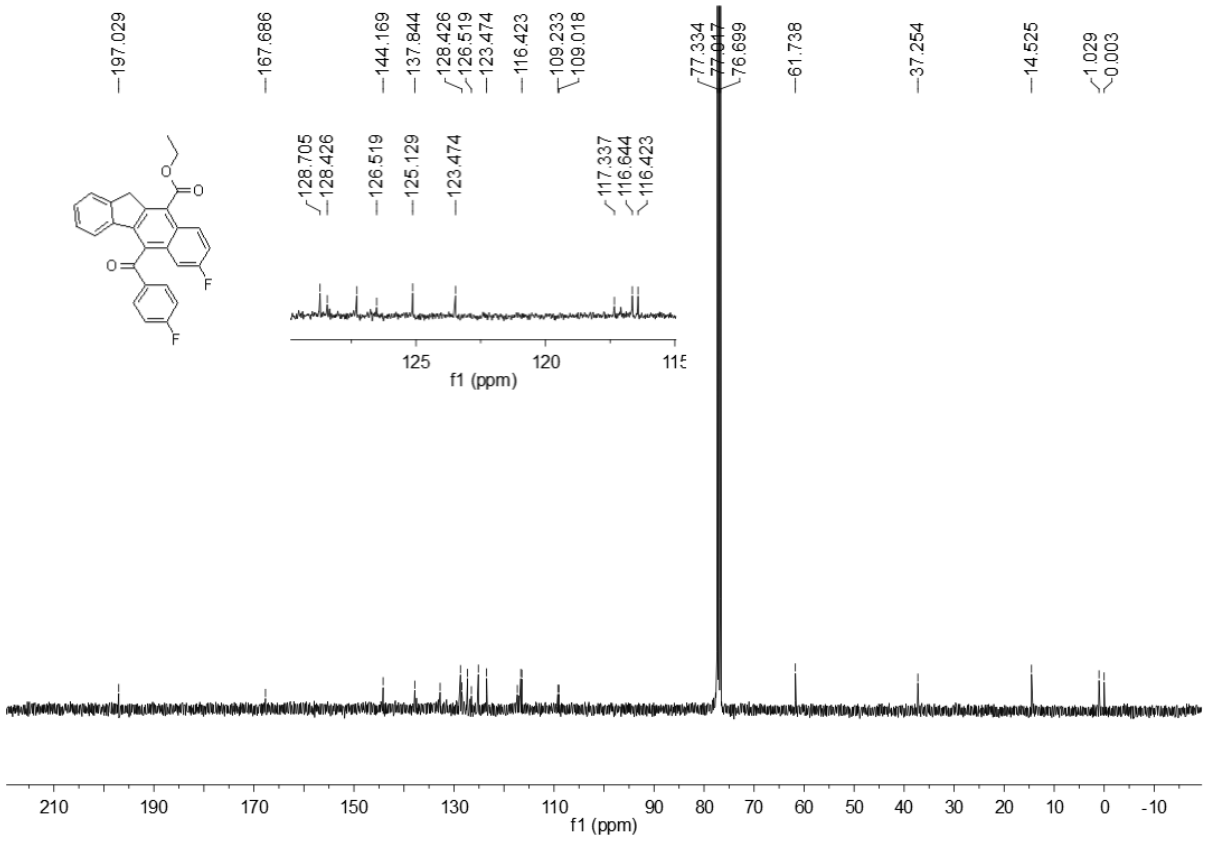
^{1}H NMR Spectrum of Compound 3j



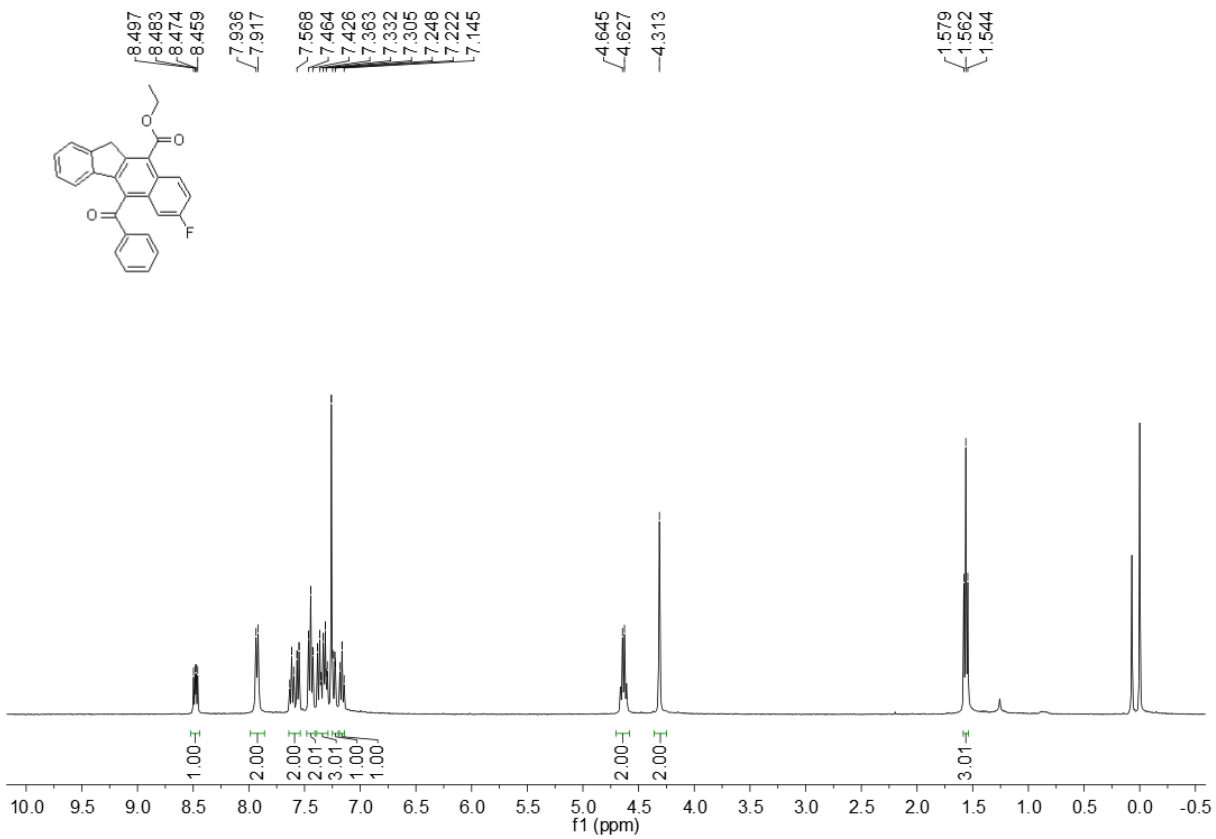
^{13}C NMR Spectrum of Compound 3j



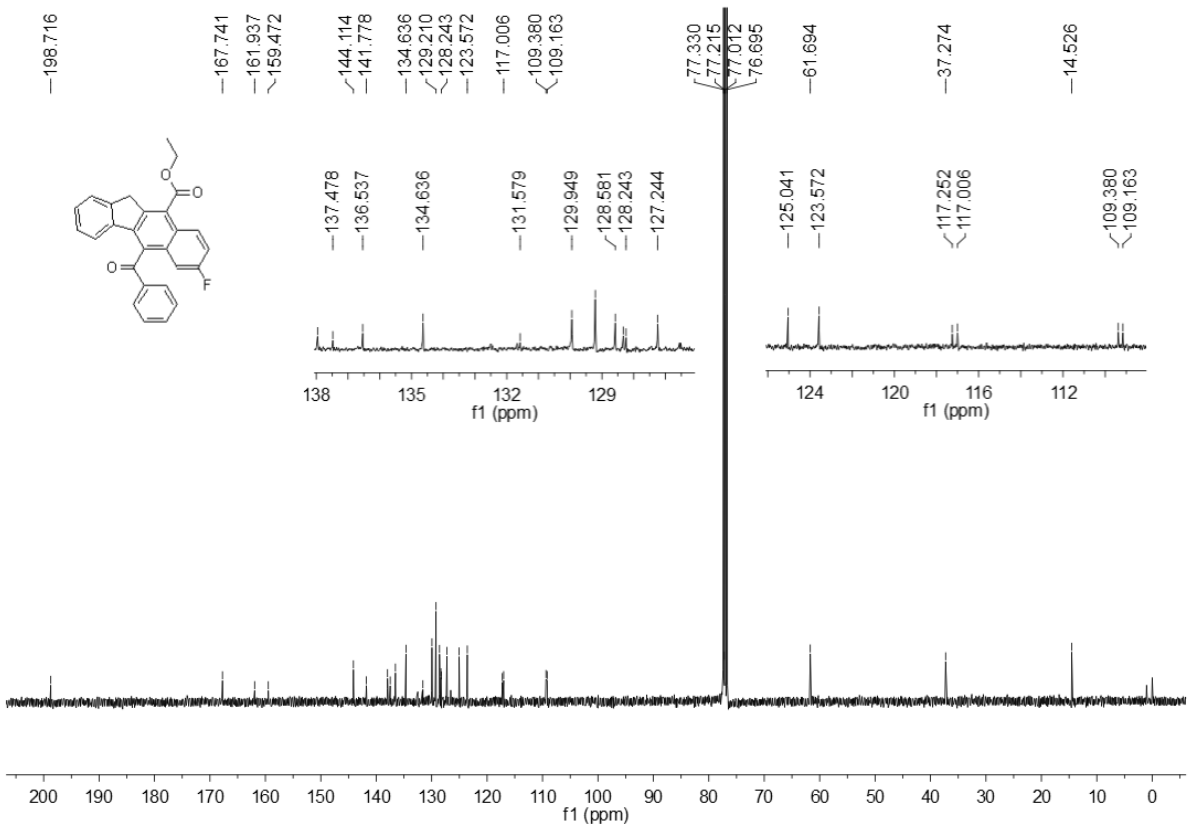
^{1}H NMR Spectrum of Compound 3k



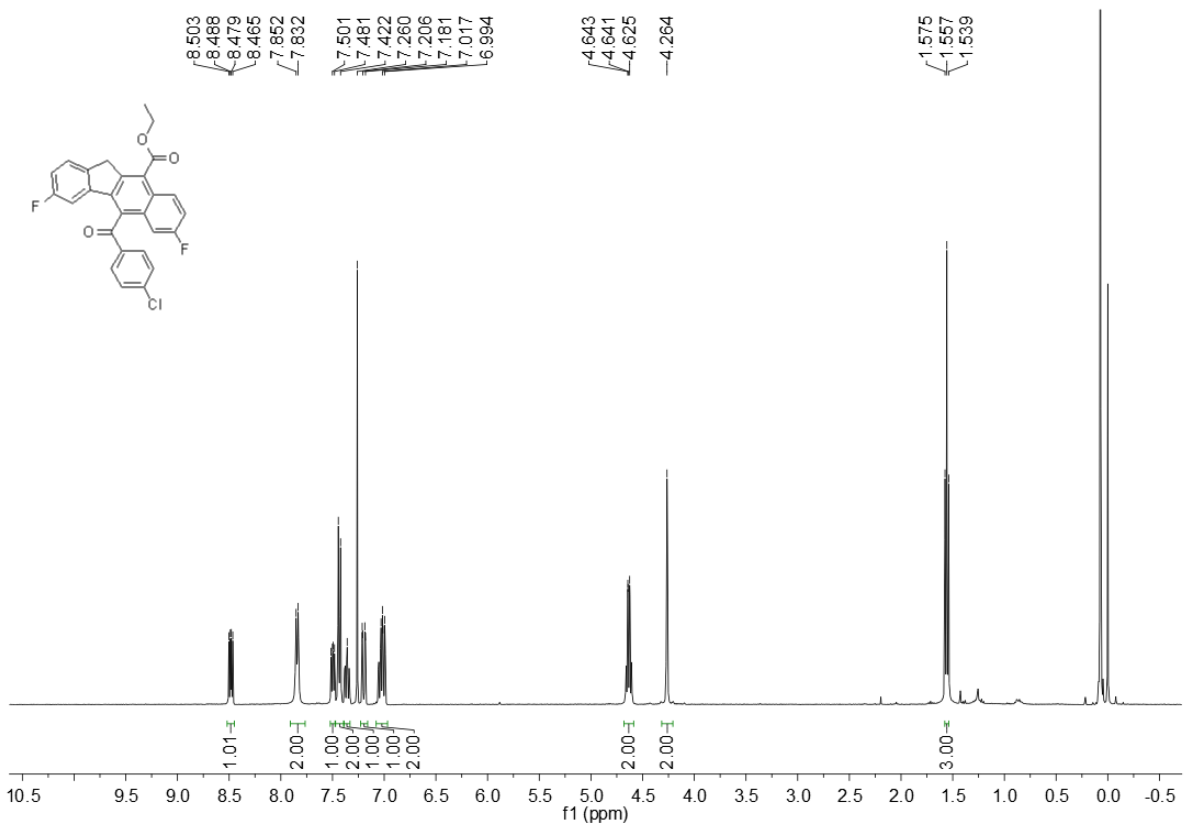
^{13}C NMR Spectrum of Compound 3k



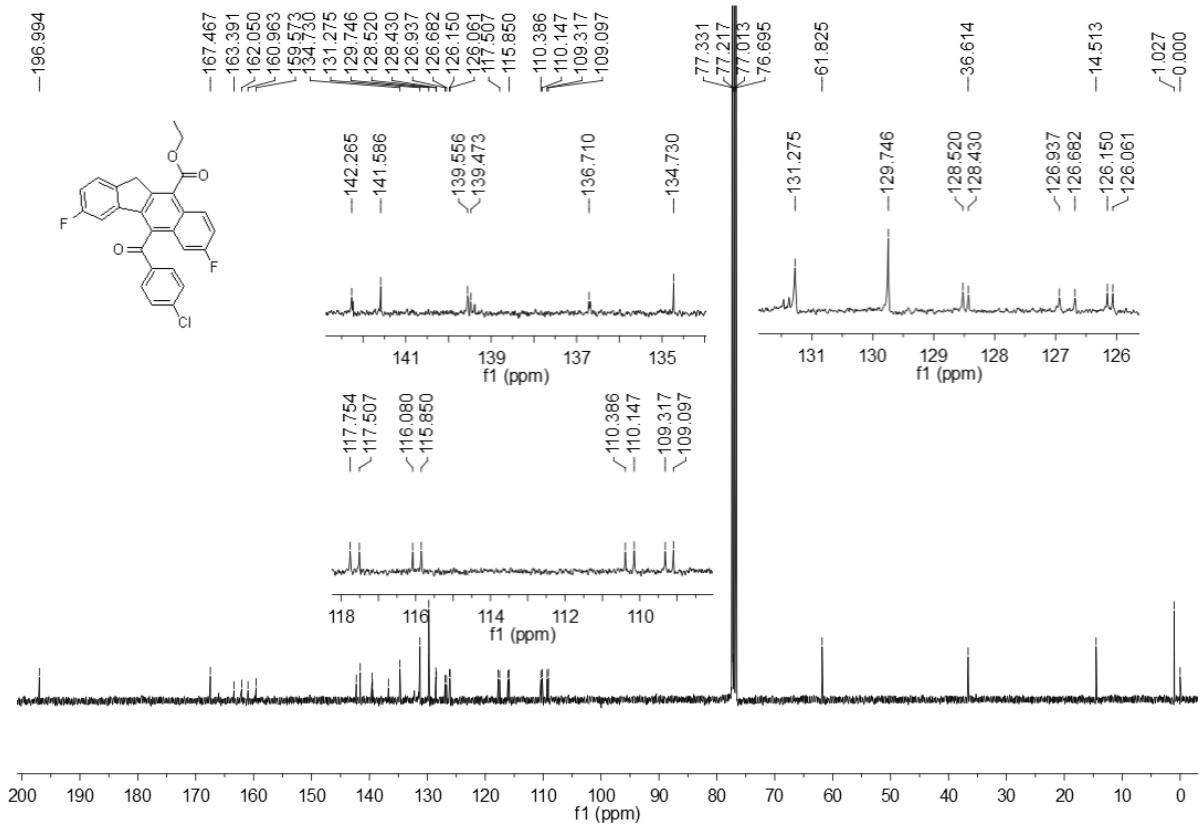
^{1}H NMR Spectrum of Compound 3l



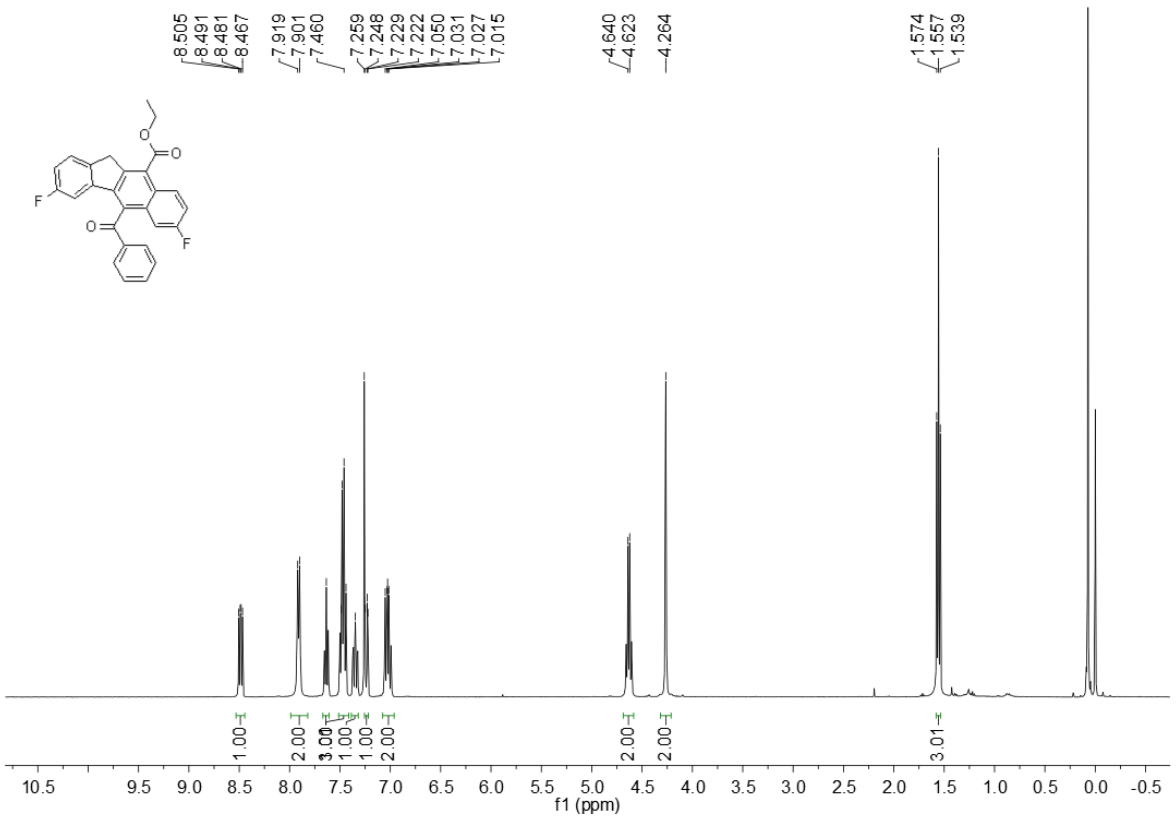
^{13}C NMR Spectrum of Compound 3l



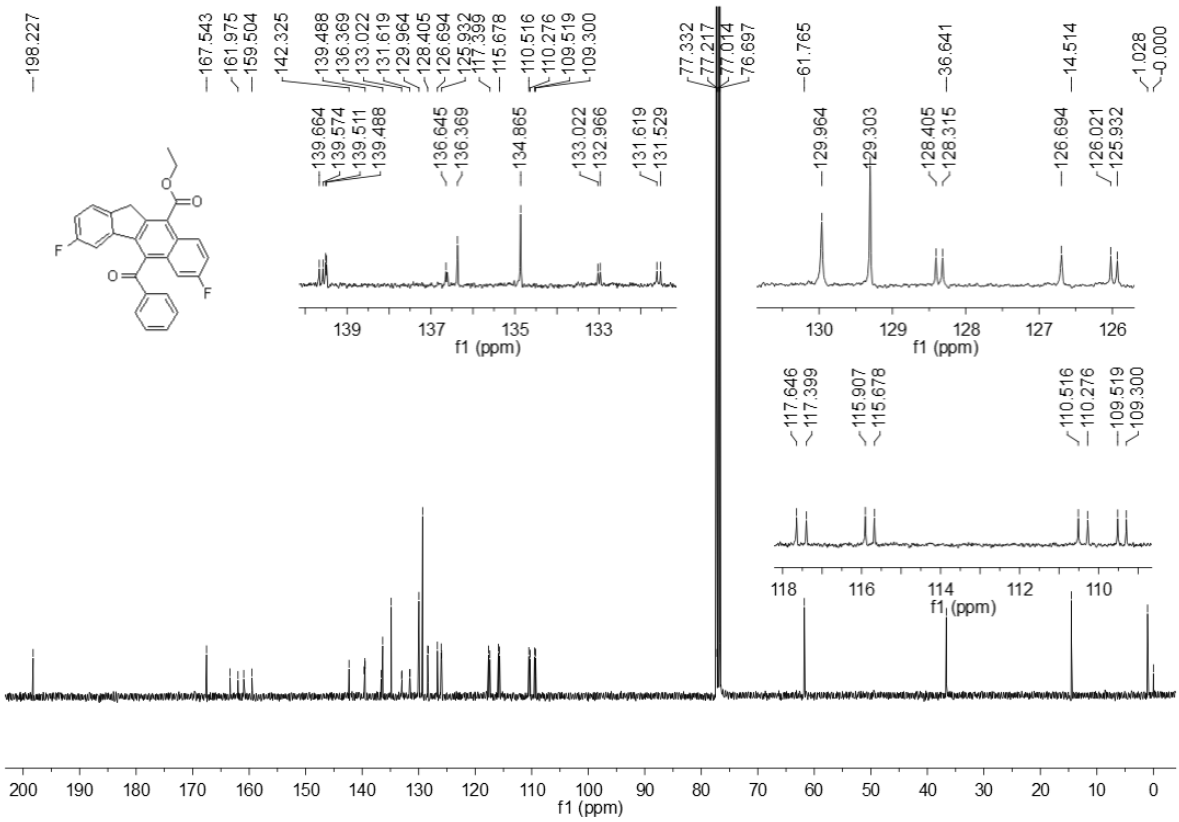
^{1}H NMR Spectrum of Compound 3m



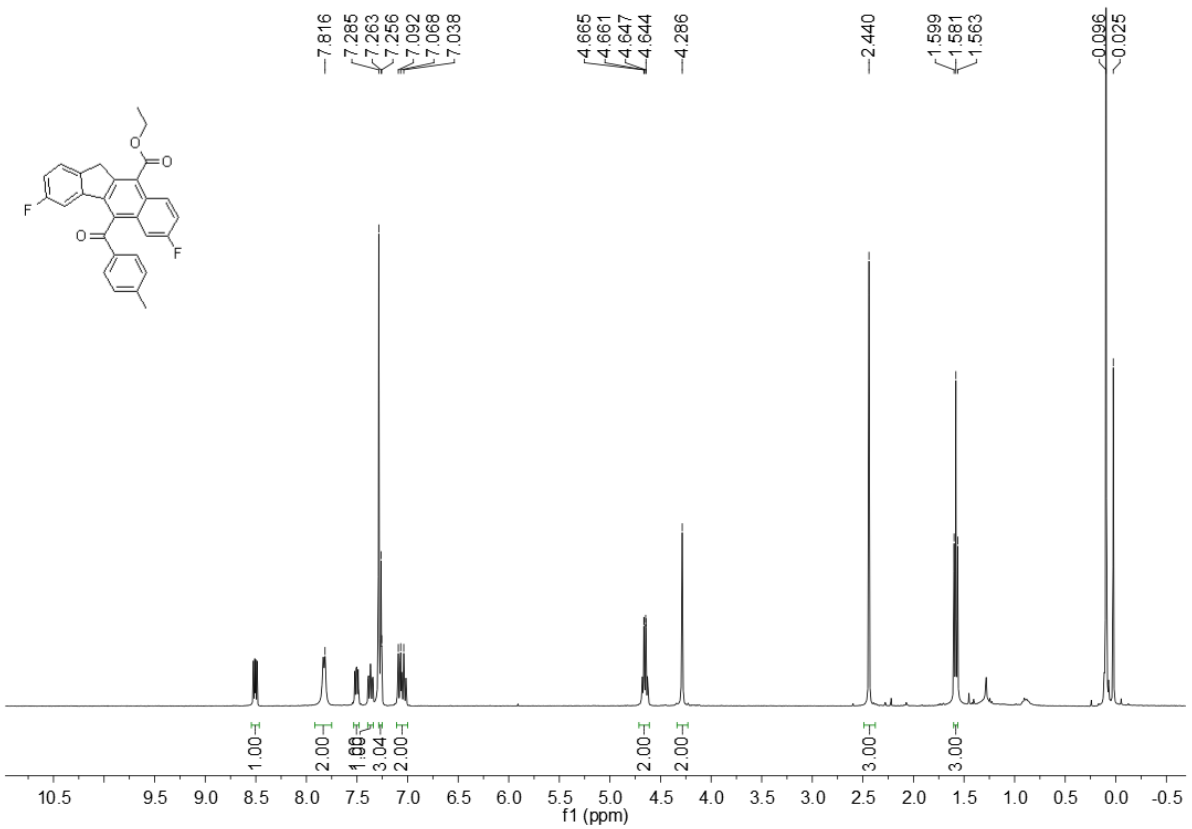
^{13}C NMR Spectrum of Compound 3m



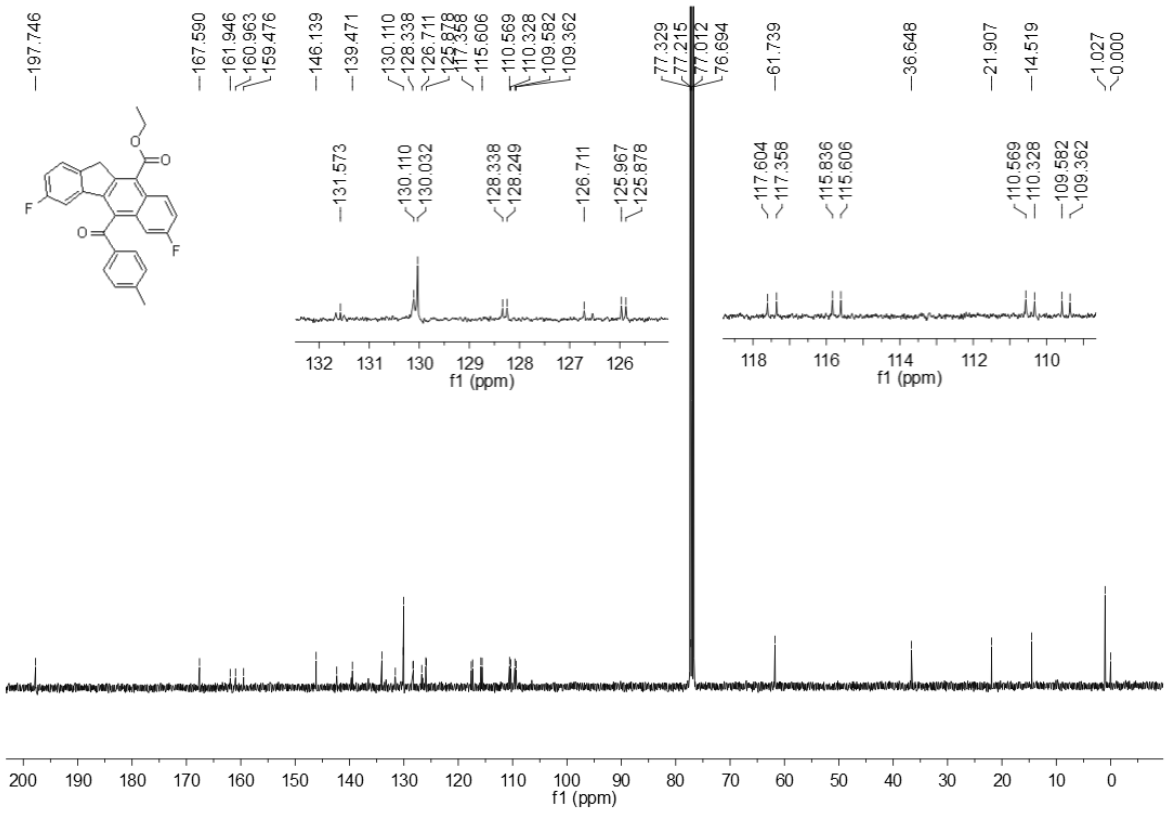
[1]H NMR Spectrum of Compound 3n



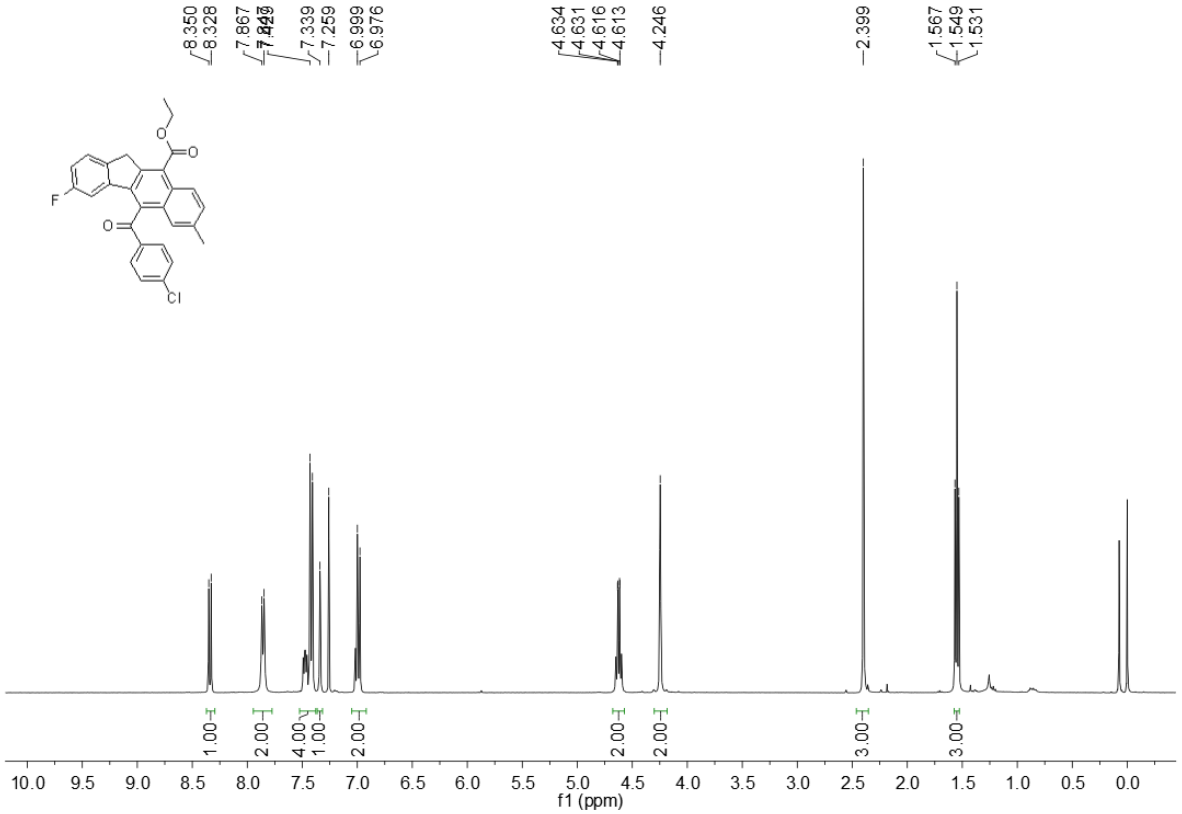
[13]C NMR Spectrum of Compound 3n



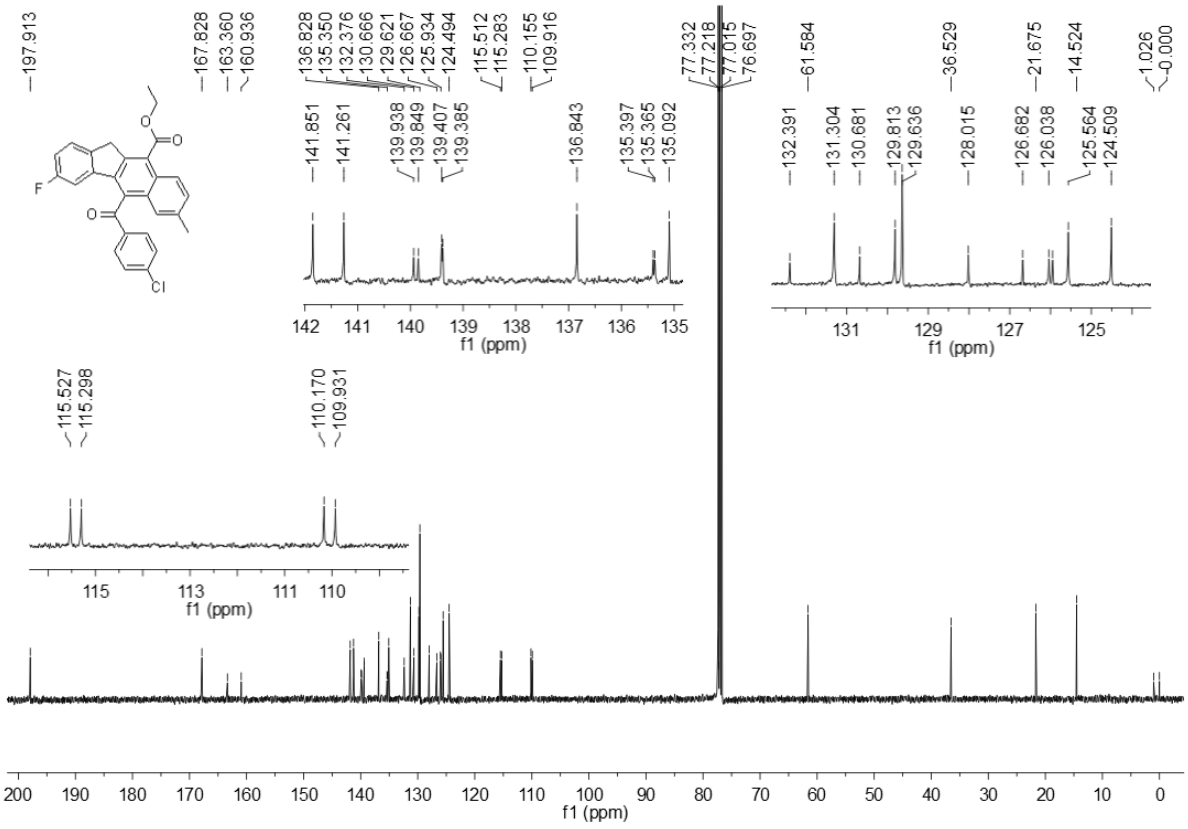
^{1}H NMR Spectrum of Compound 3o



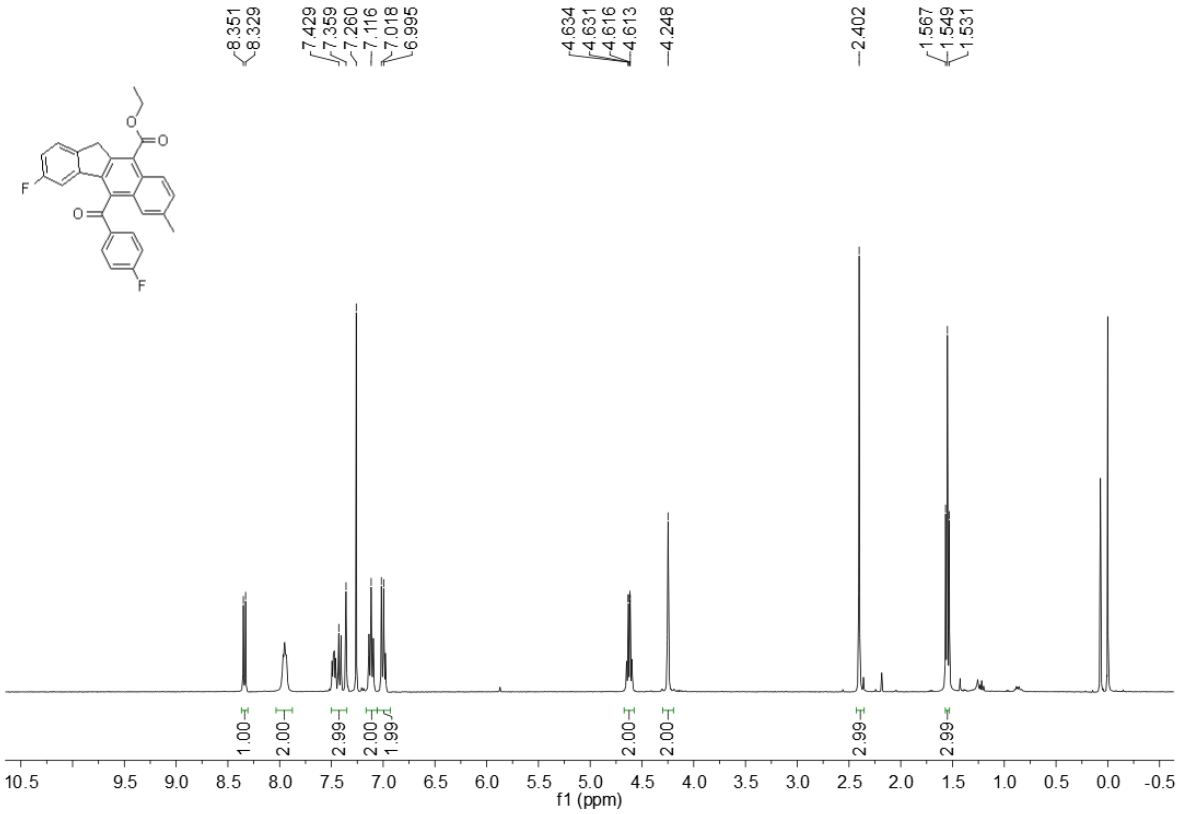
^{13}C NMR Spectrum of Compound 3o



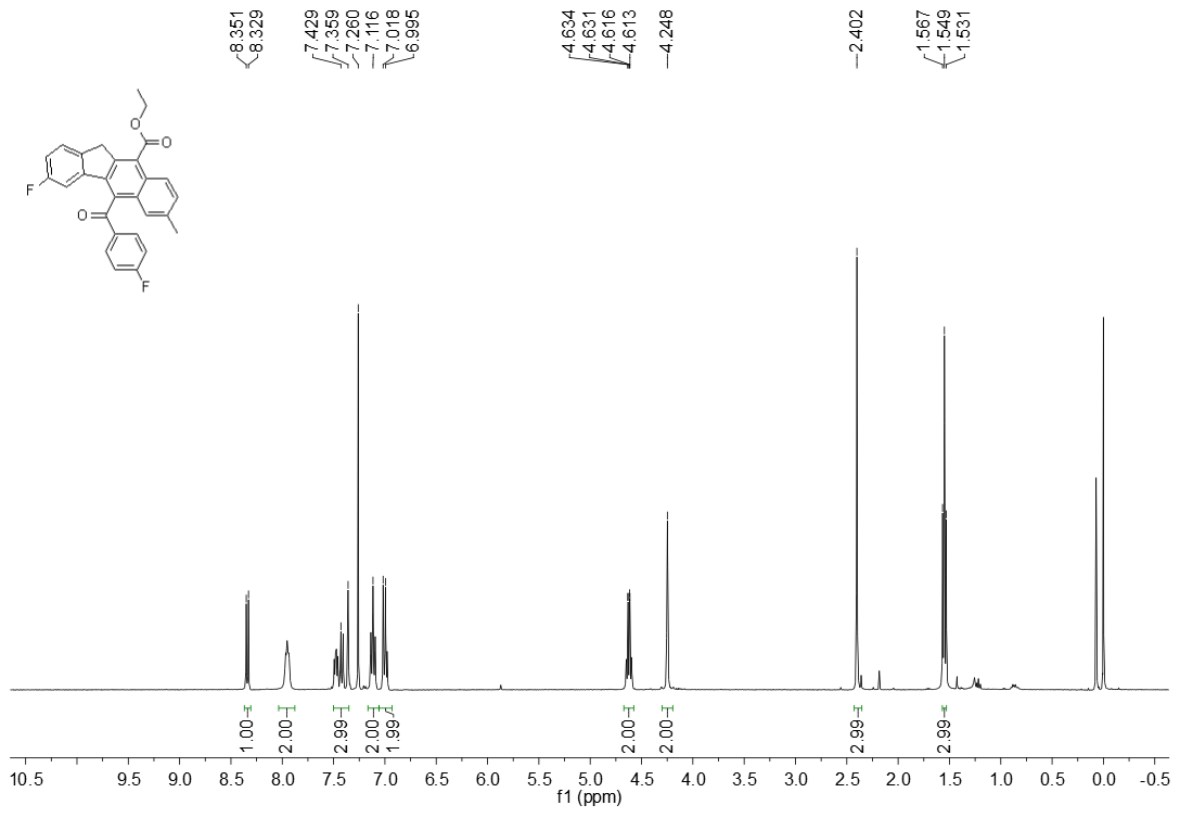
^{1}H NMR Spectrum of Compound 3p



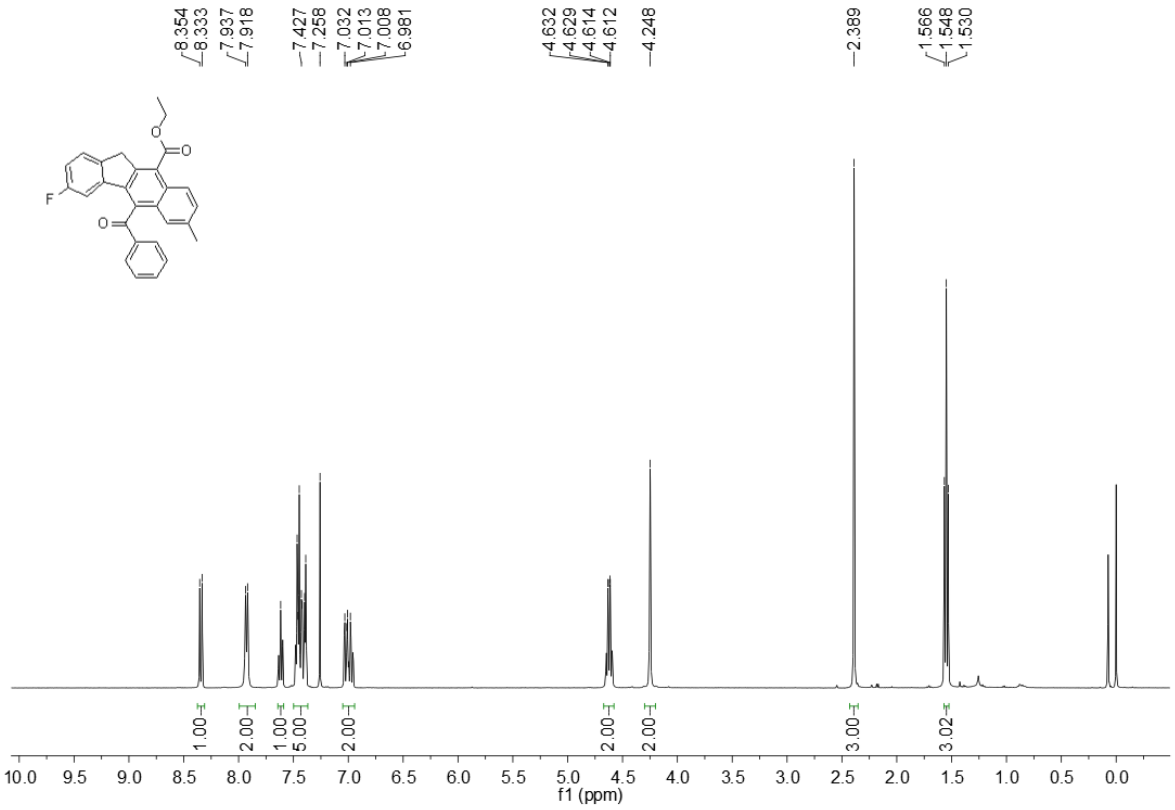
^{13}C NMR Spectrum of Compound 3p



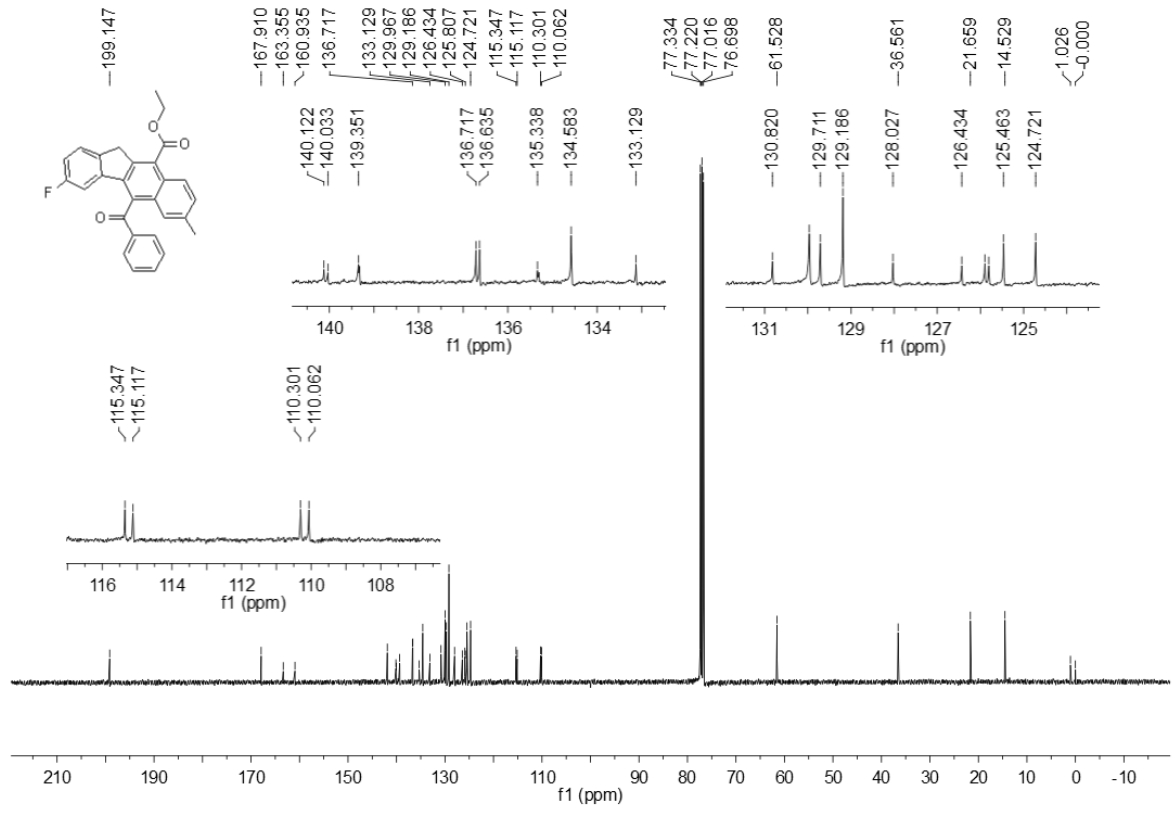
^{1}H NMR Spectrum of Compound 3q



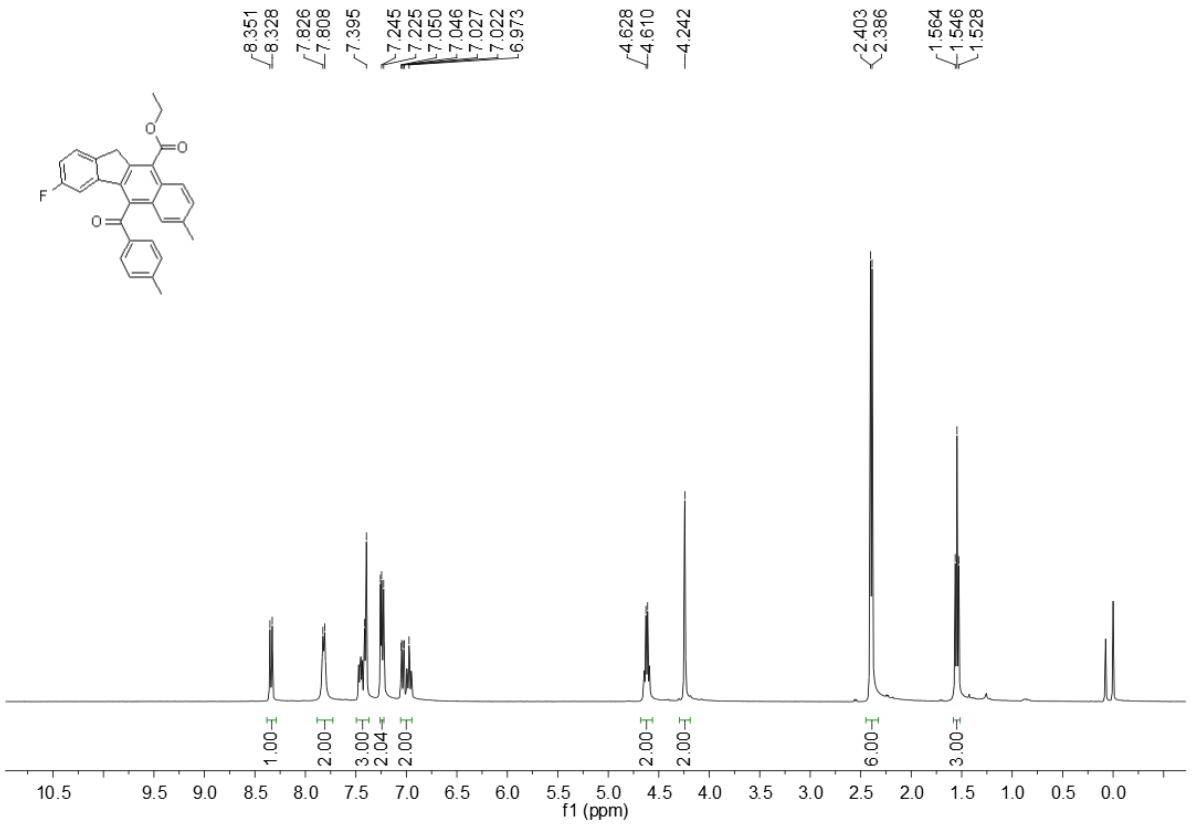
^{1}H NMR Spectrum of Compound 3q



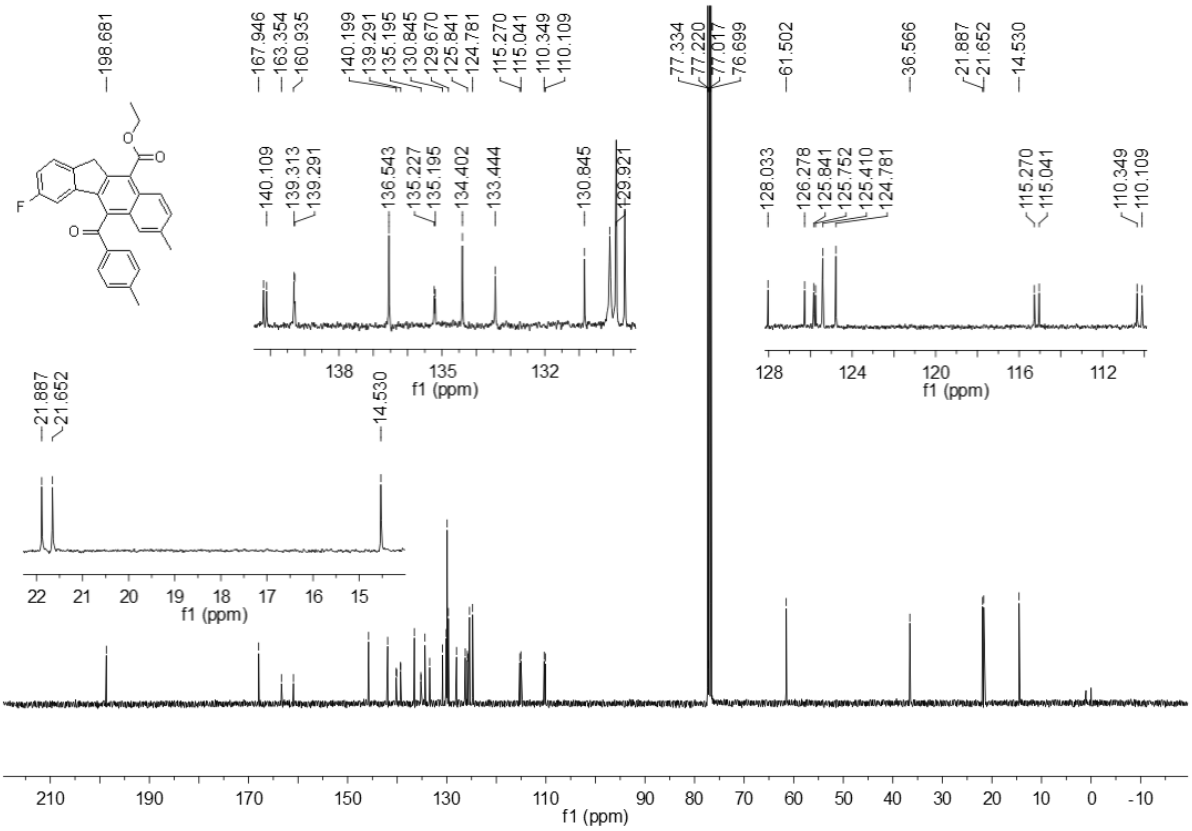
^{1}H NMR Spectrum of Compound 3r



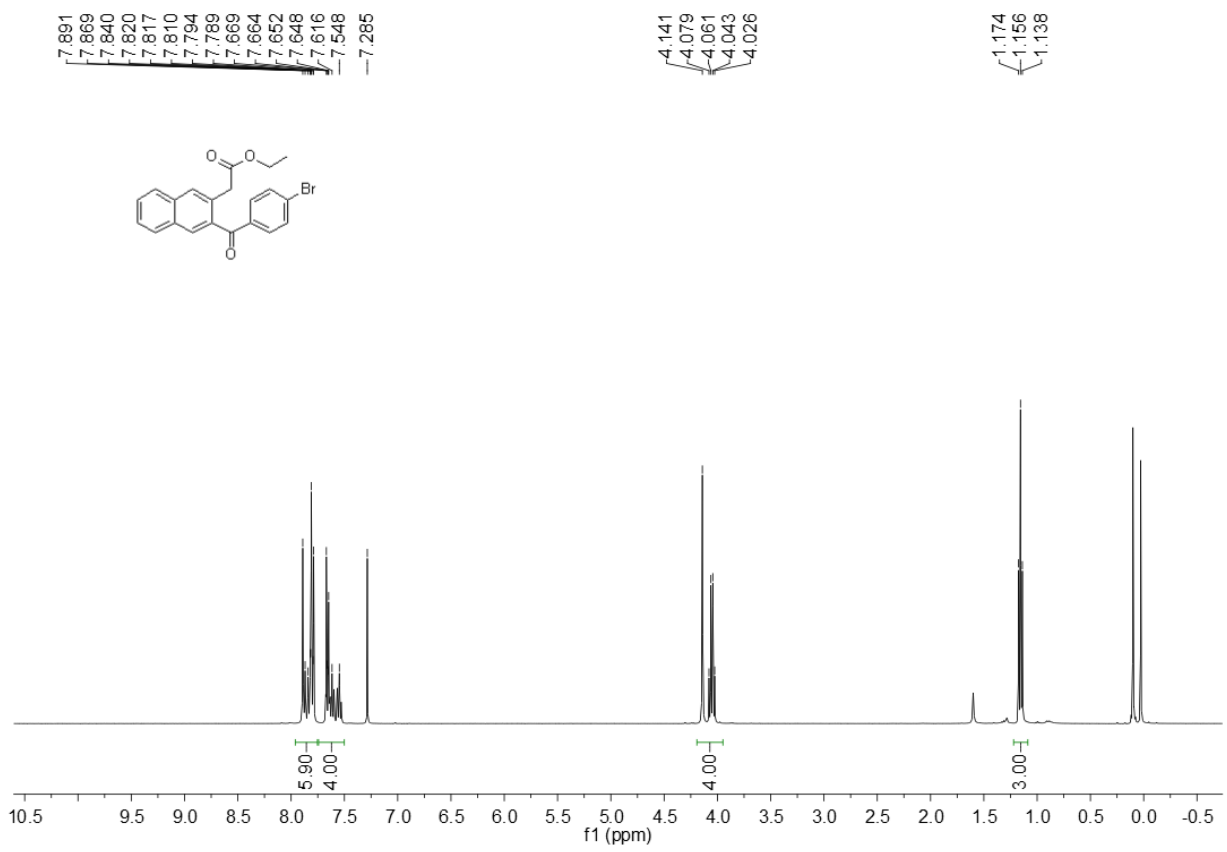
^{13}C NMR Spectrum of Compound 3r



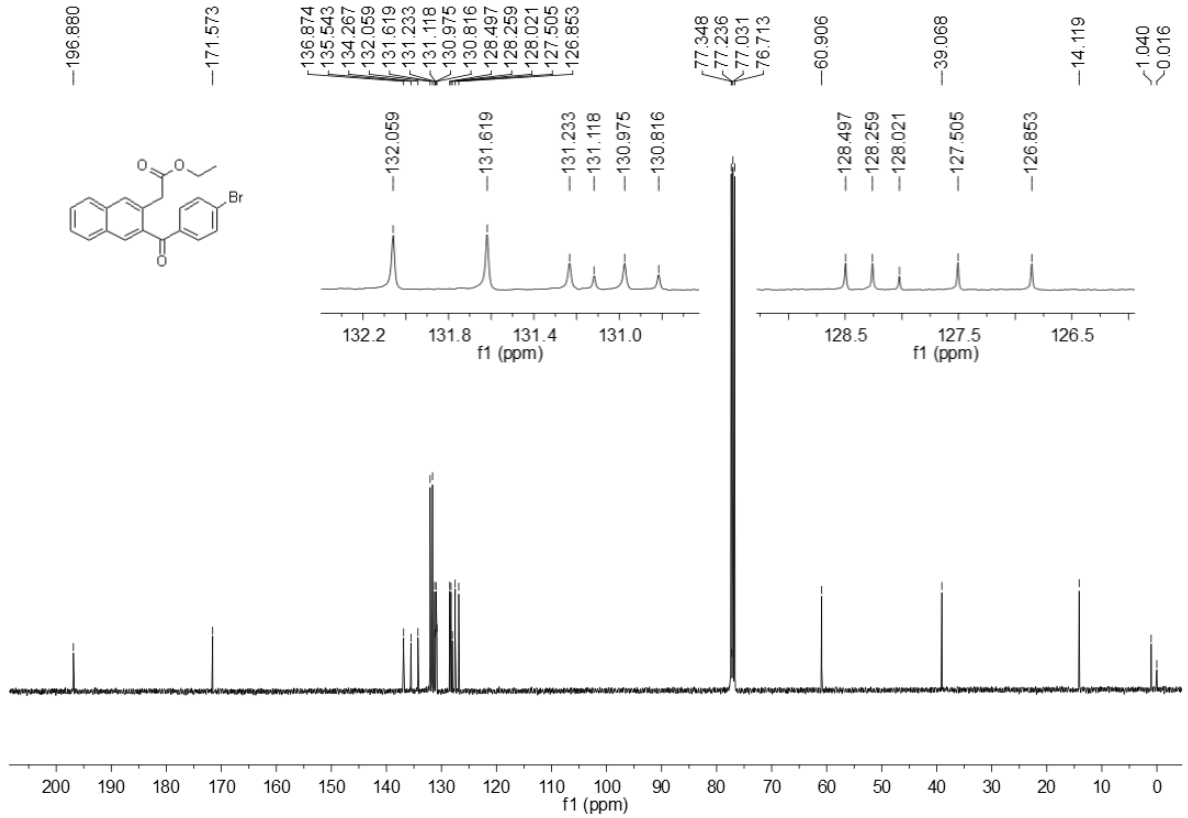
^{1}H NMR Spectrum of Compound 3s



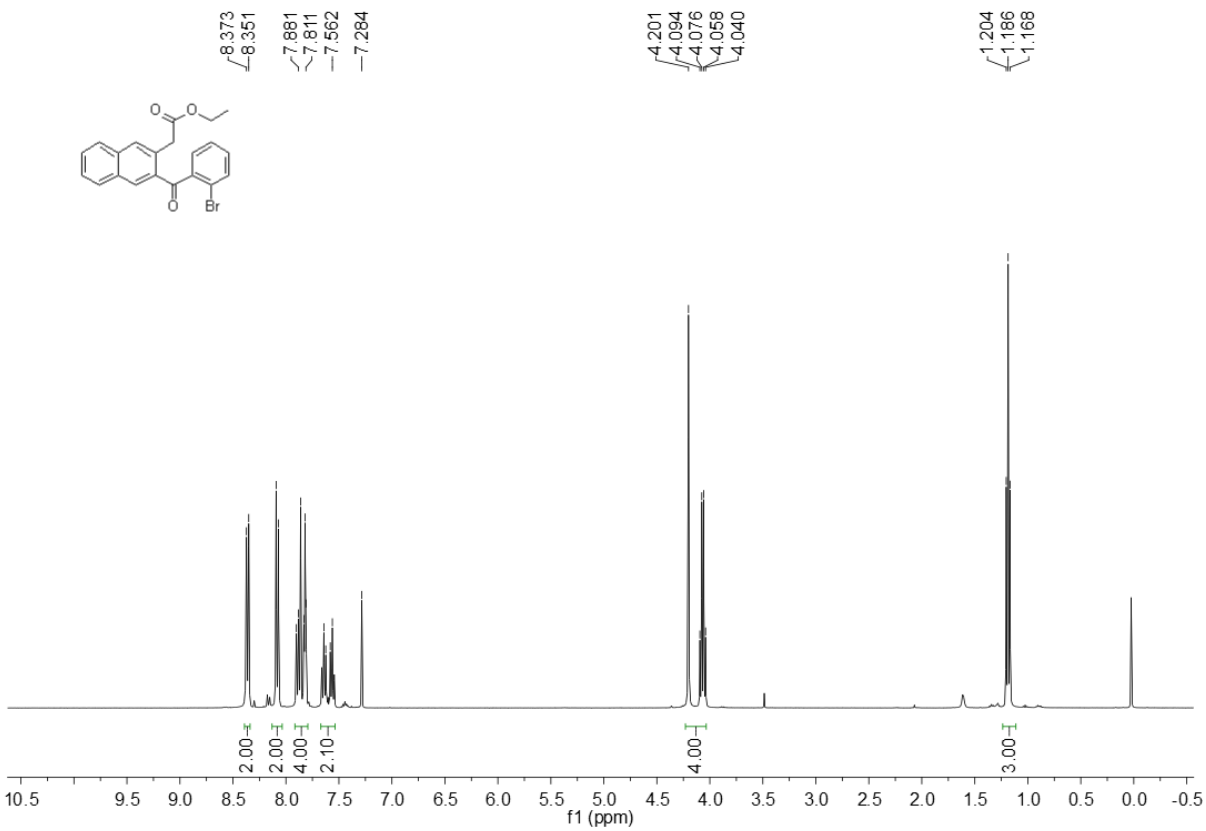
^{13}C NMR Spectrum of Compound 3s



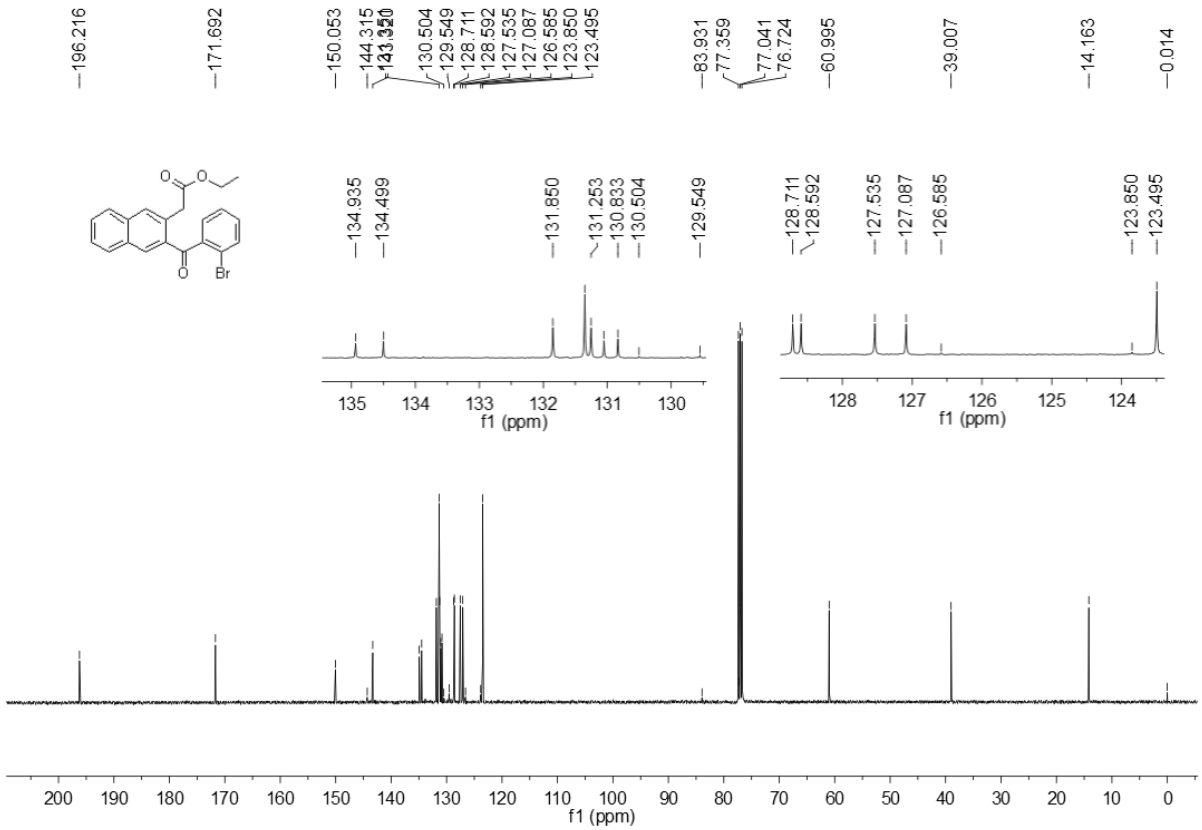
[1]H NMR Spectrum of Compound 4a



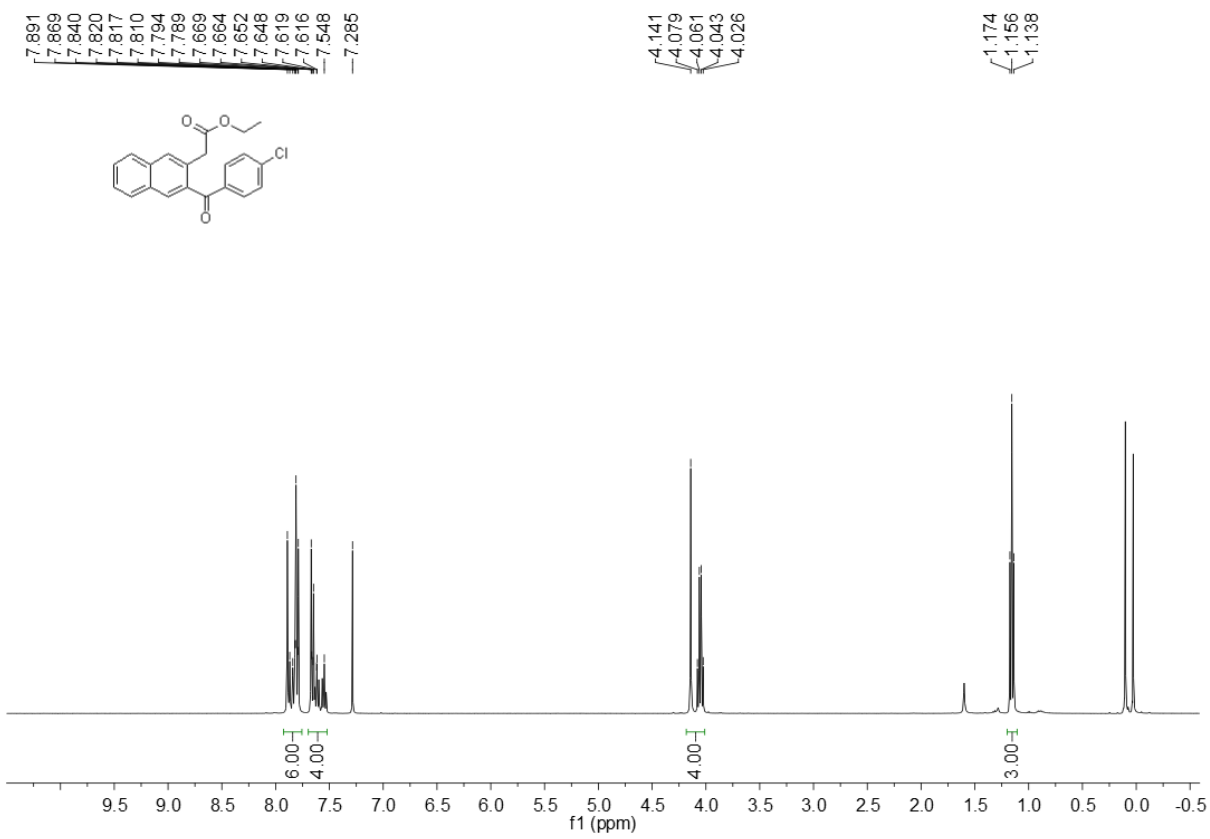
[13]C NMR Spectrum of Compound 4a



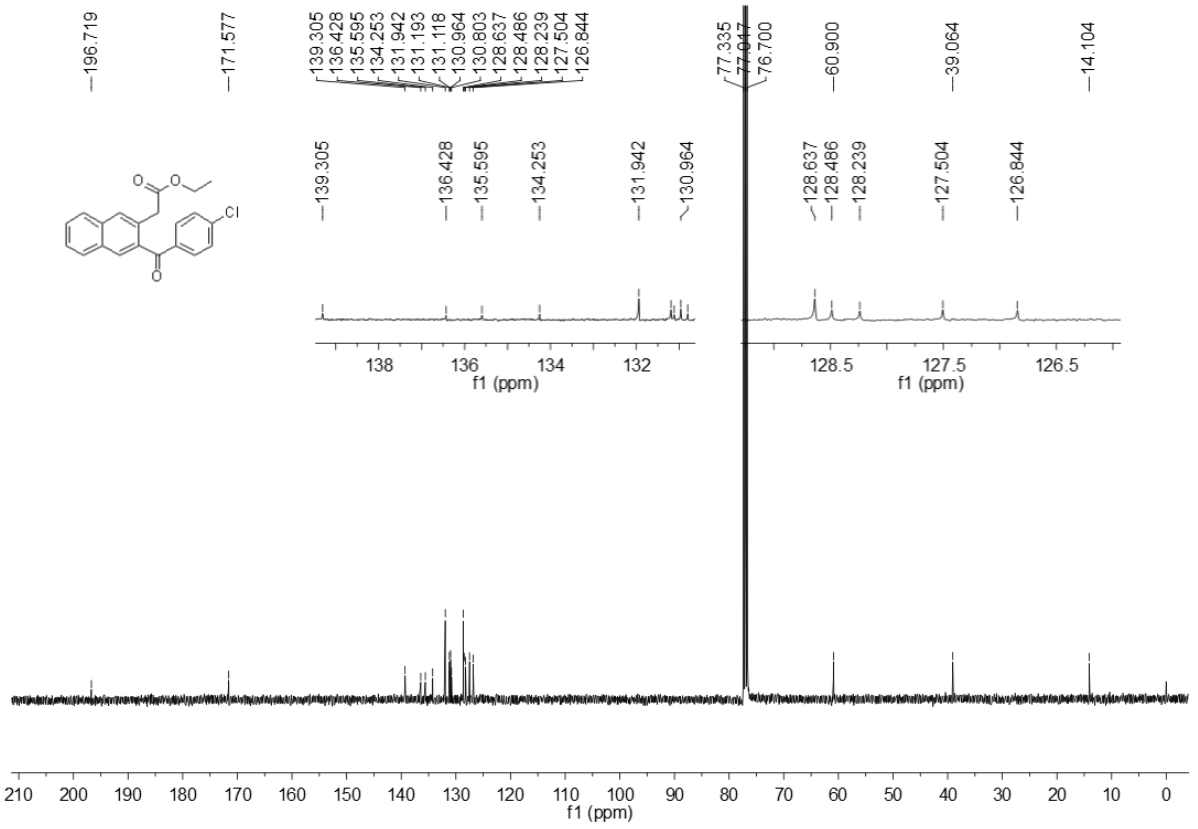
^{1}H NMR Spectrum of Compound 4b



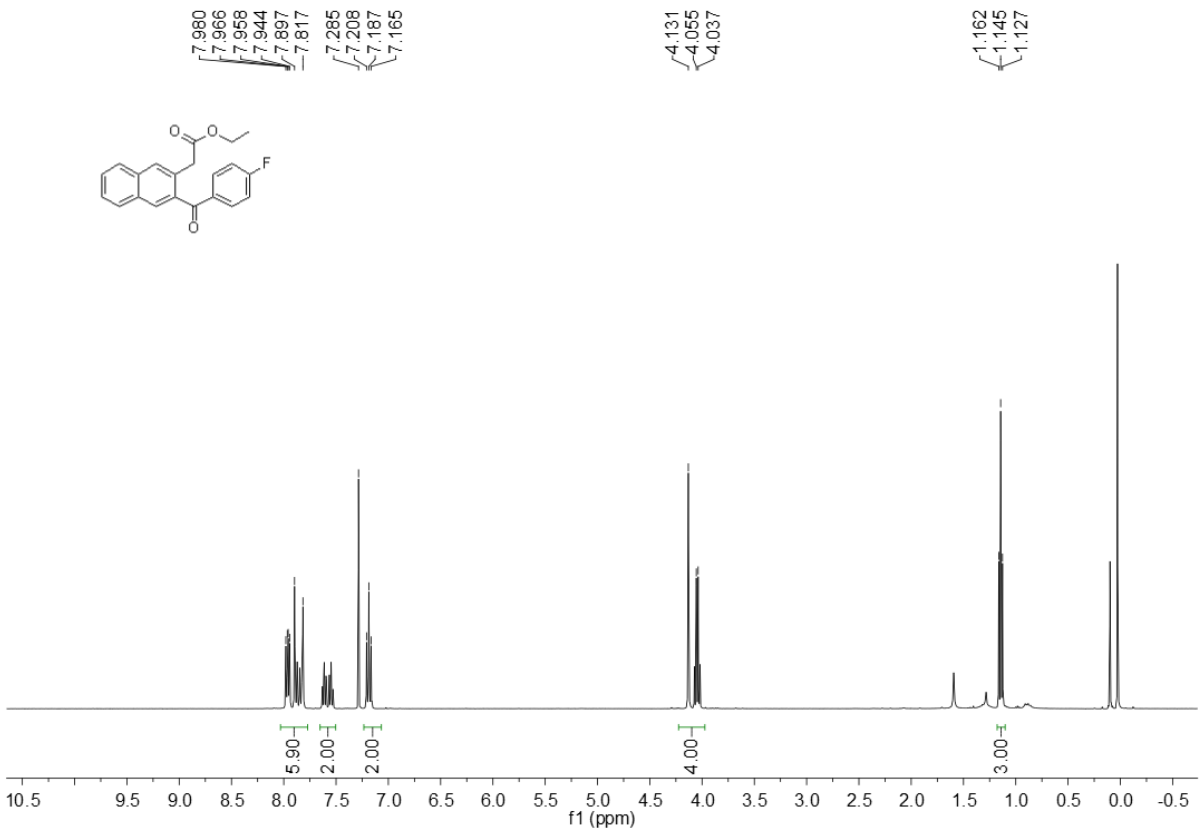
^{13}C NMR Spectrum of Compound 4b



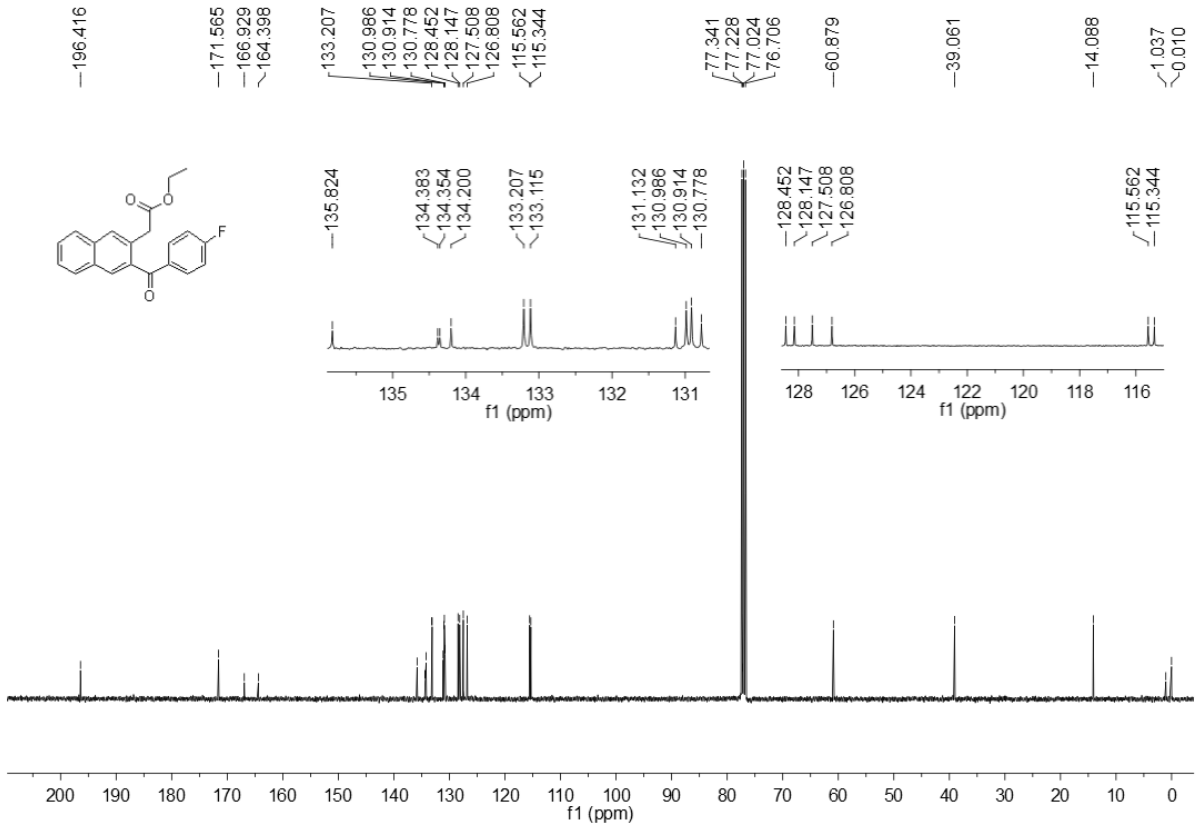
^{1}H NMR Spectrum of Compound 4c



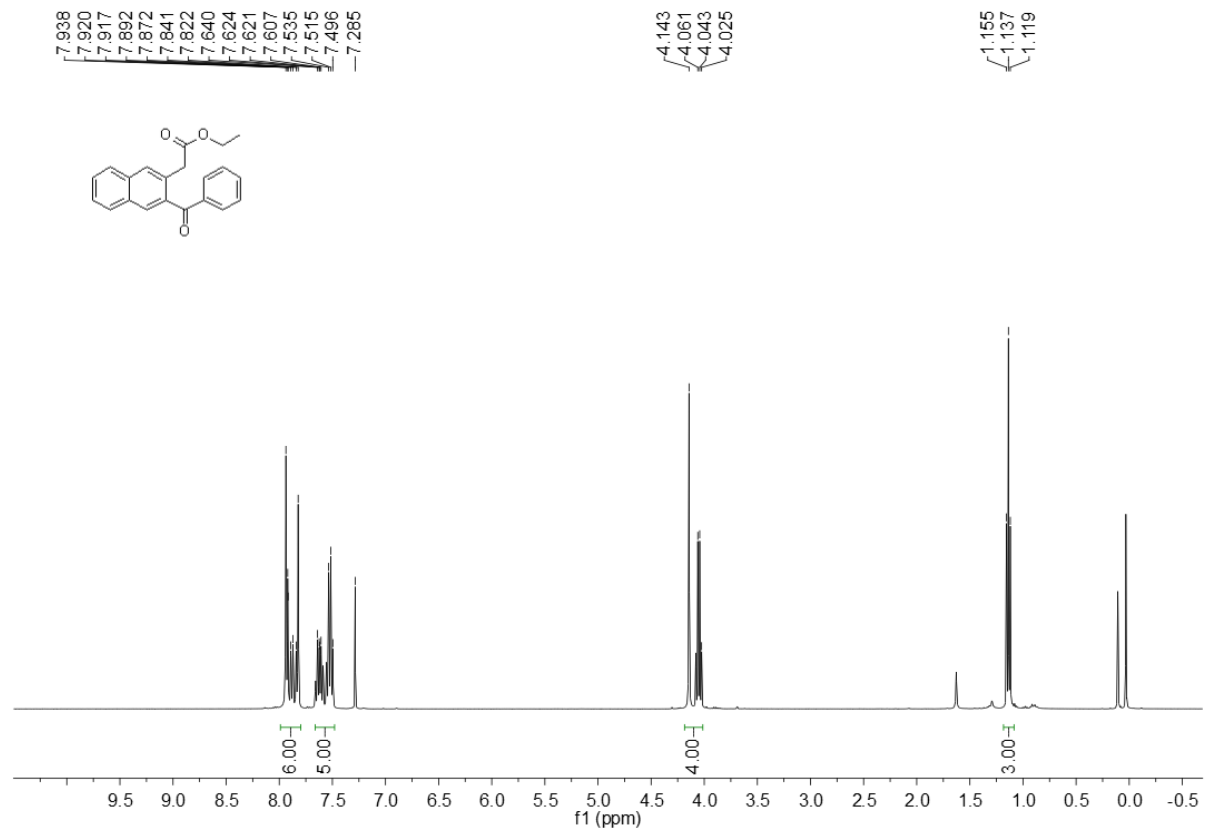
^{13}C NMR Spectrum of Compound 4c



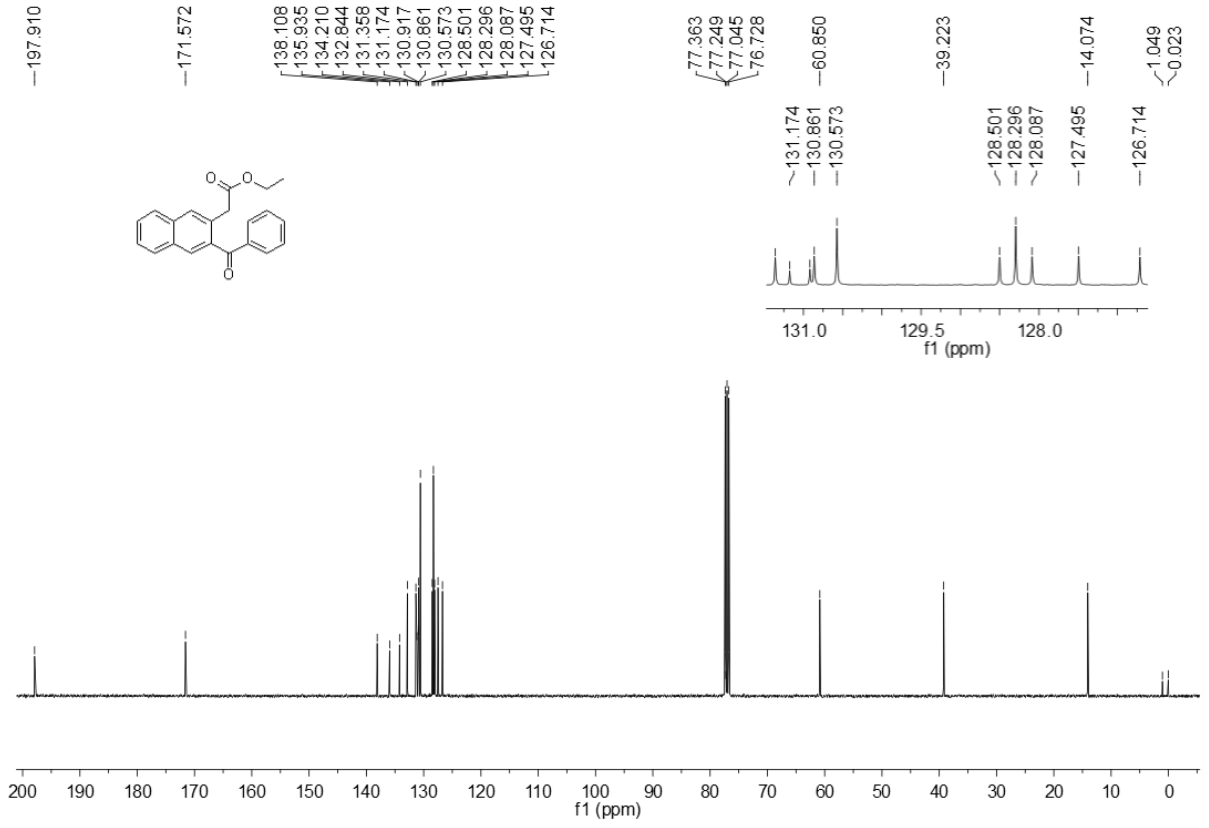
^{1}H NMR Spectrum of Compound 4d



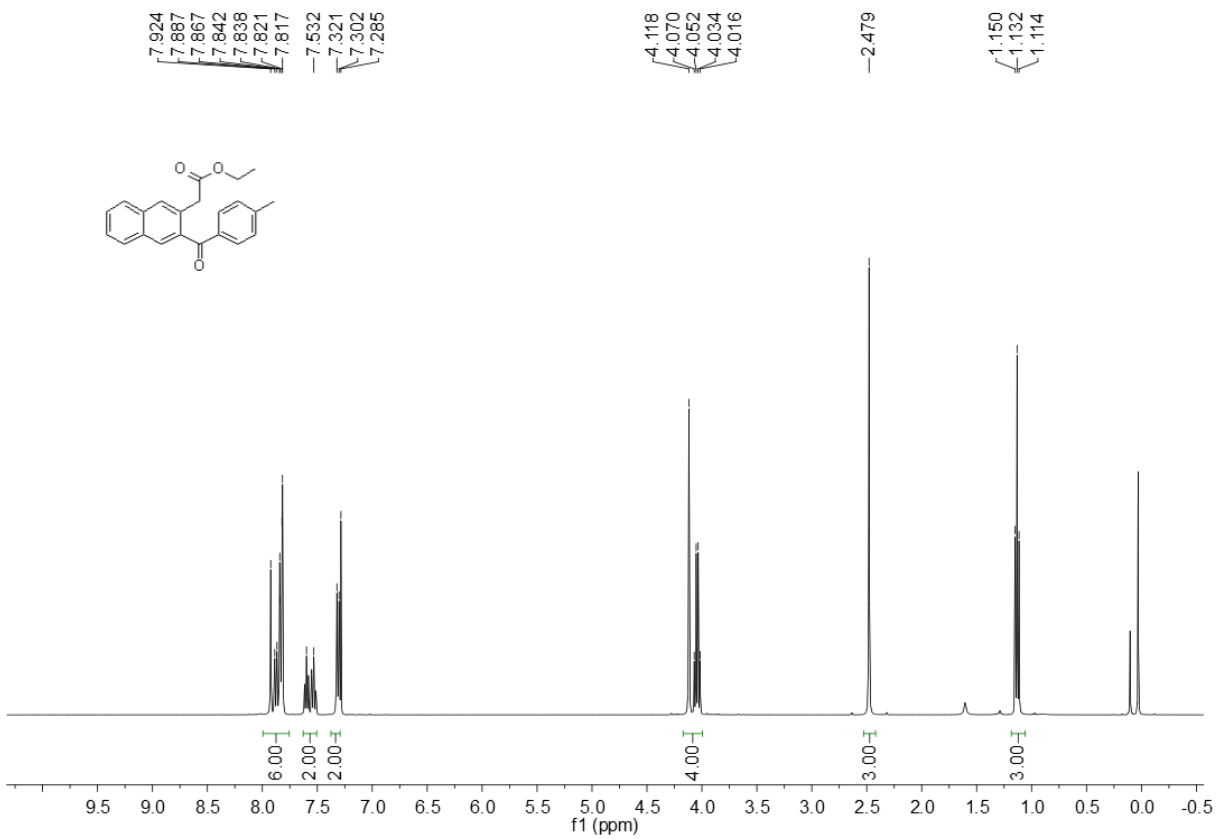
^{13}C NMR Spectrum of Compound 4d



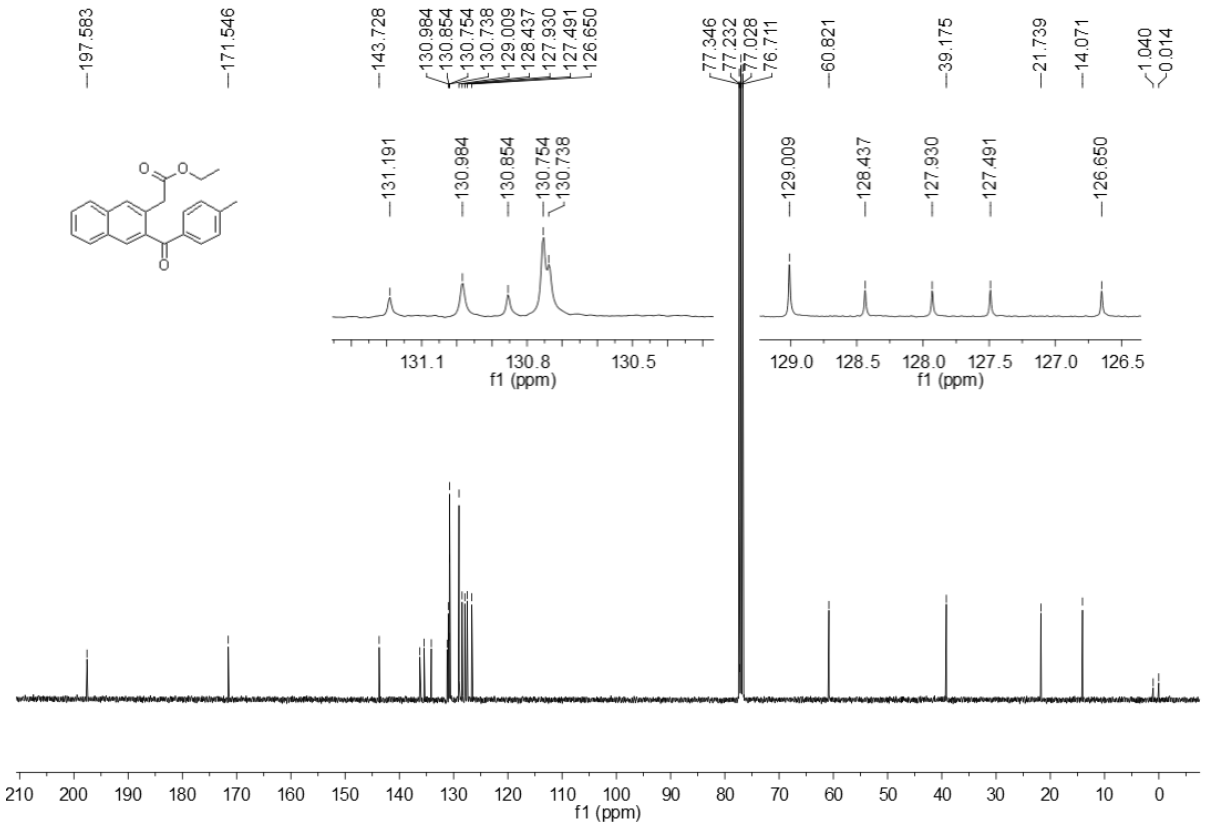
^{1}H NMR Spectrum of Compound 4e



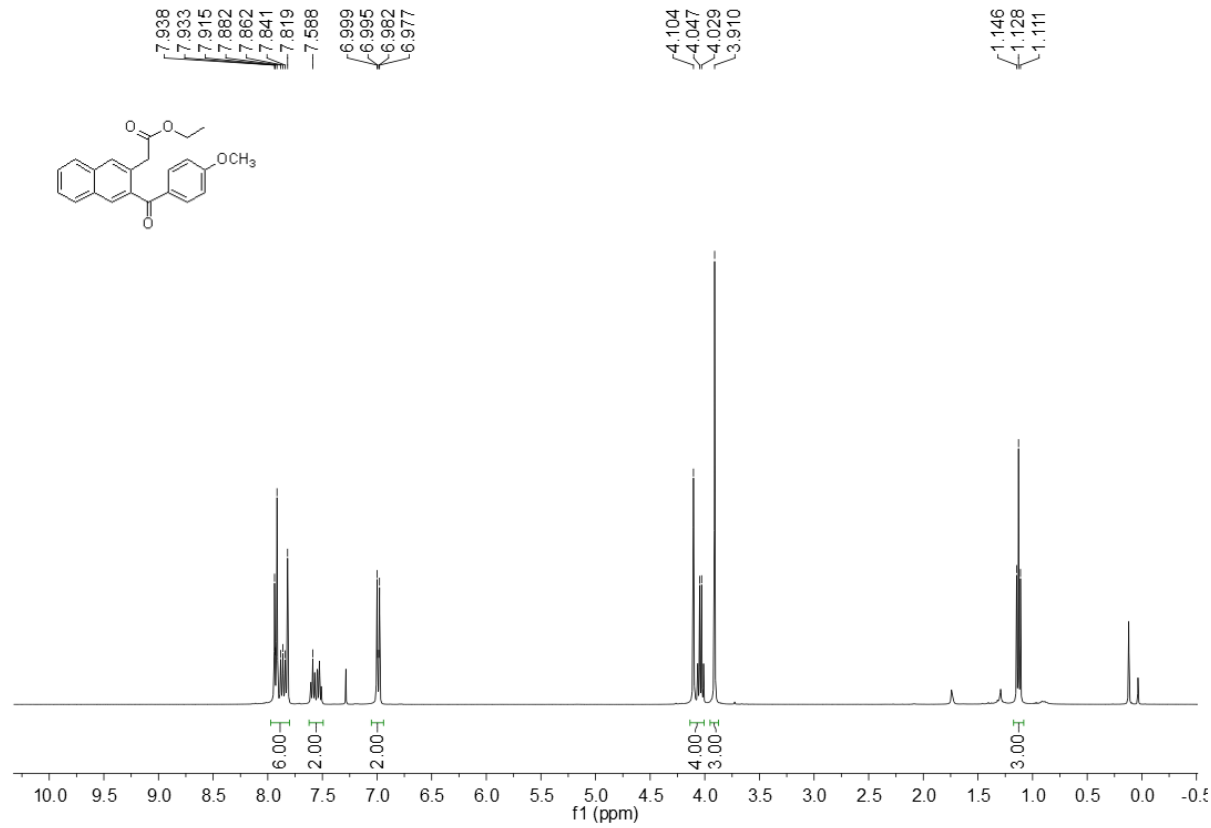
^{13}C NMR Spectrum of Compound 4e



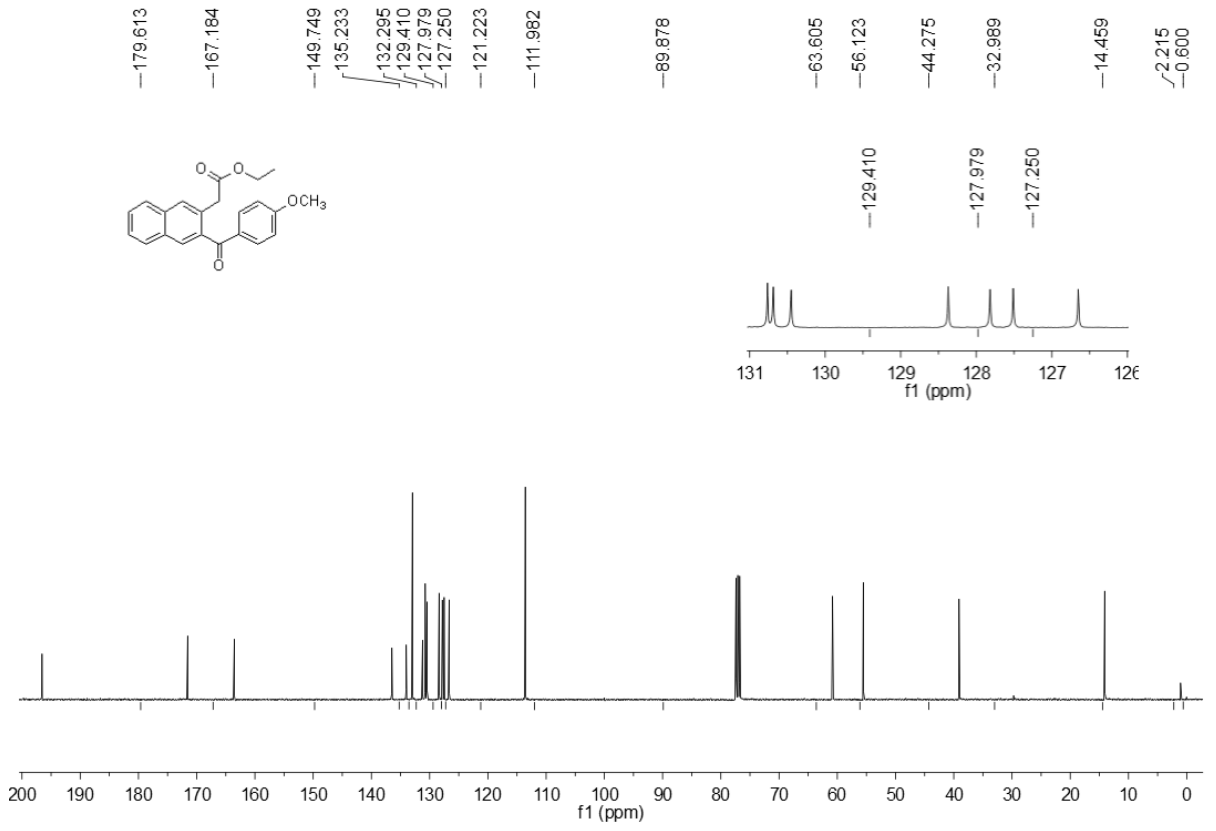
[1]H NMR Spectrum of Compound 4f



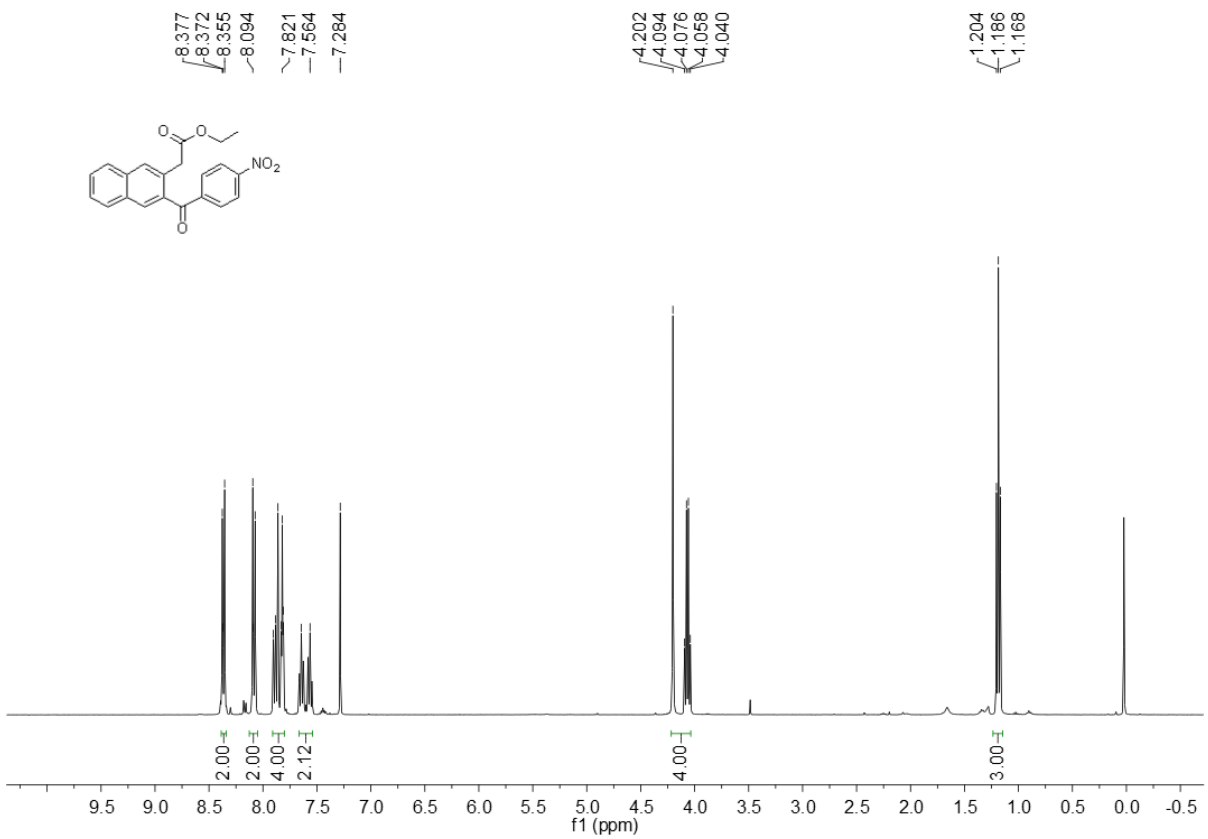
[13]C NMR Spectrum of Compound 4f



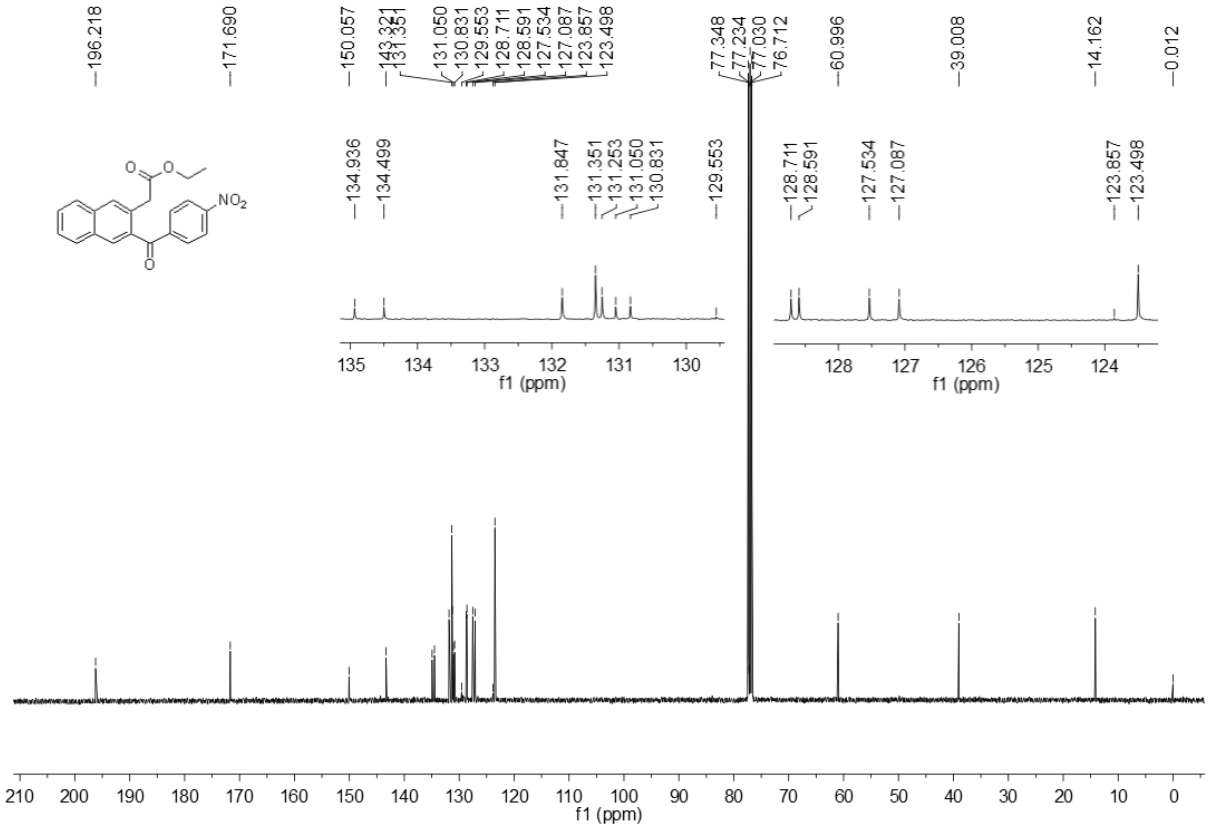
^{1}H NMR Spectrum of Compound 4g



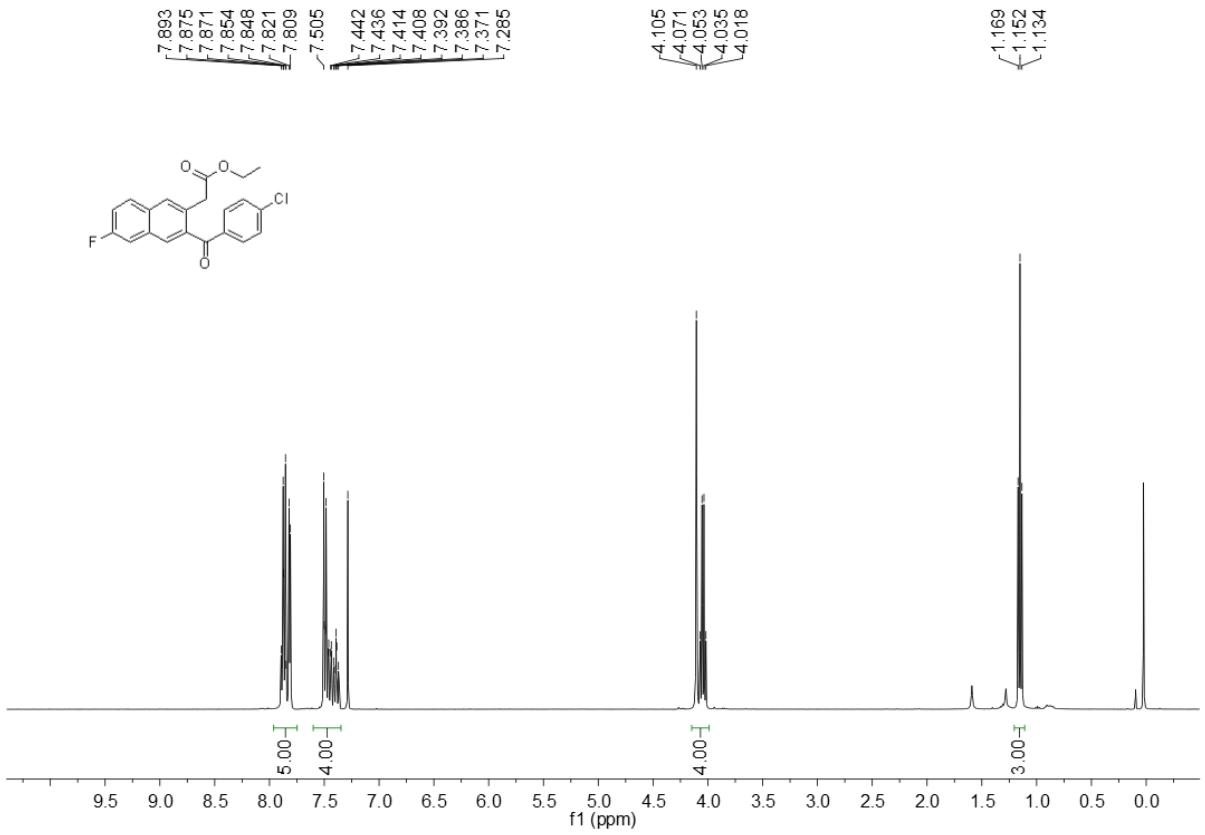
^{13}C NMR Spectrum of Compound 4g



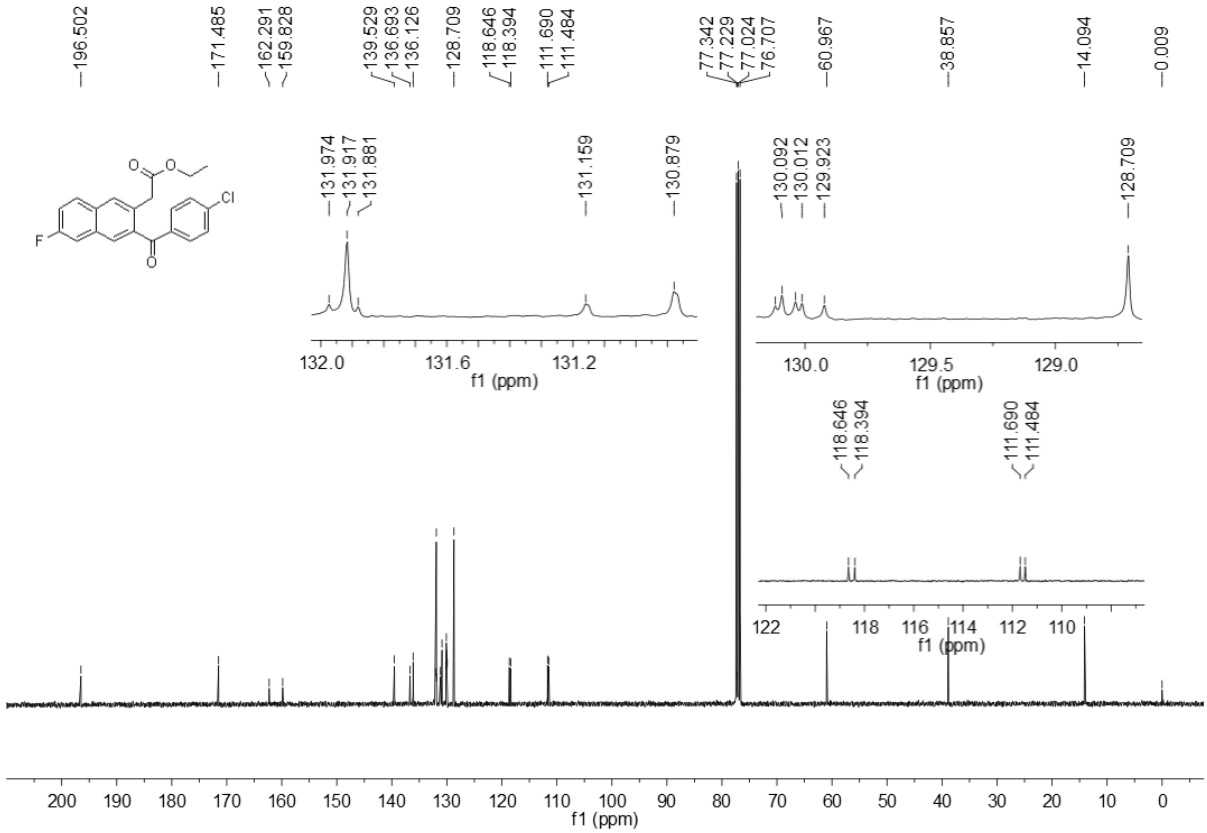
^{1}H NMR Spectrum of Compound 4h



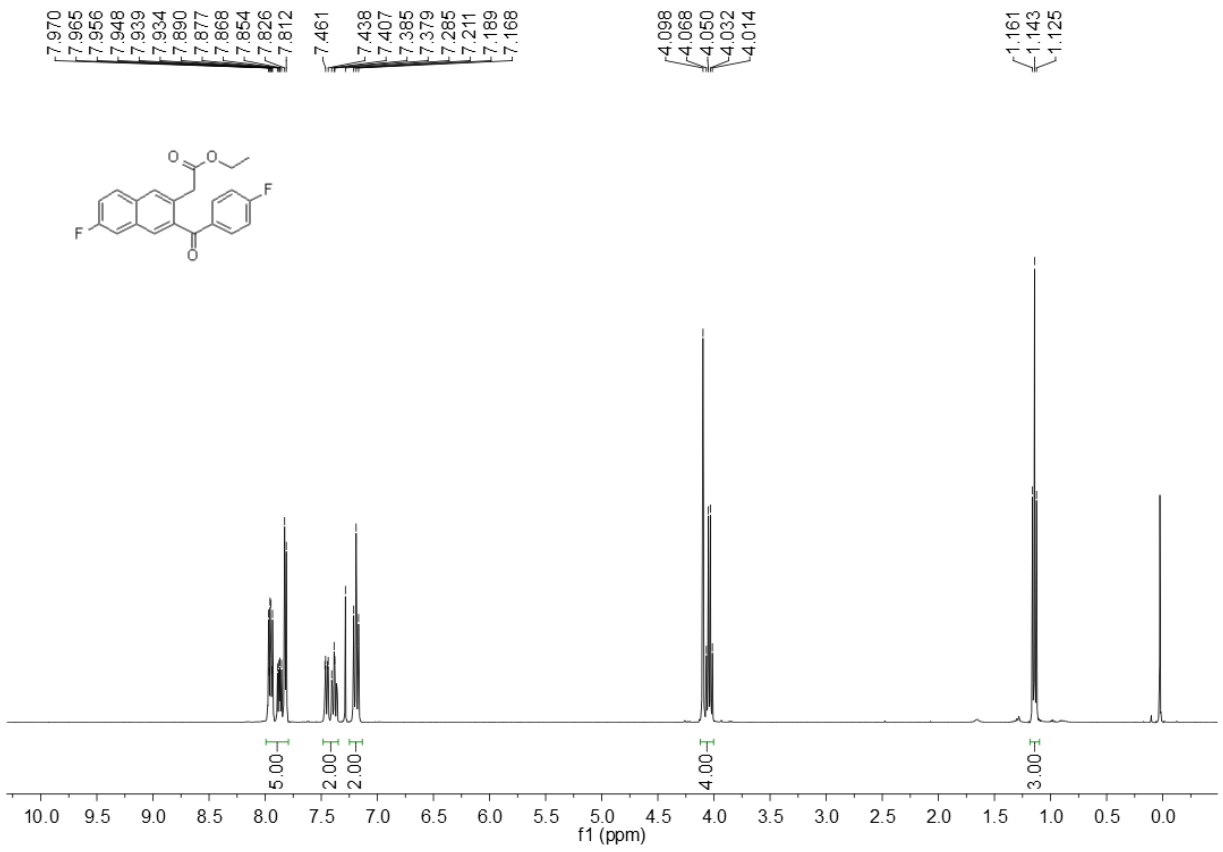
^{1}H NMR Spectrum of Compound 4h



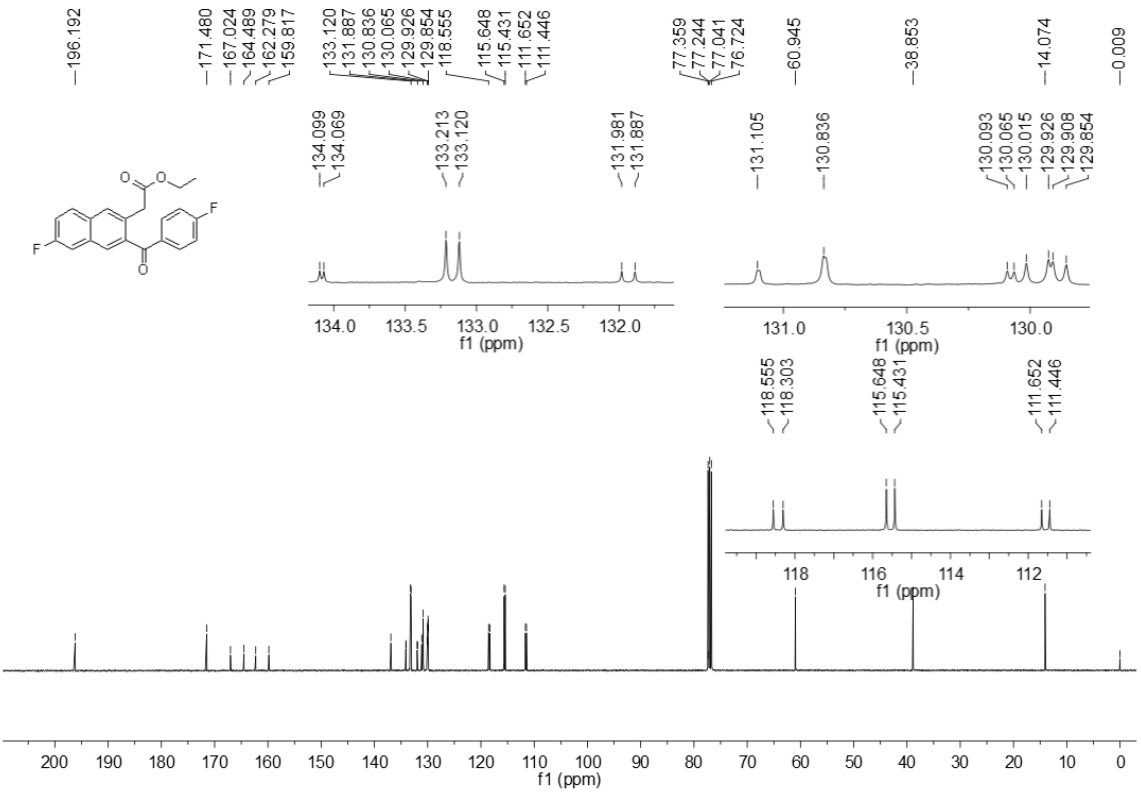
^{1}H NMR Spectrum of Compound 4i



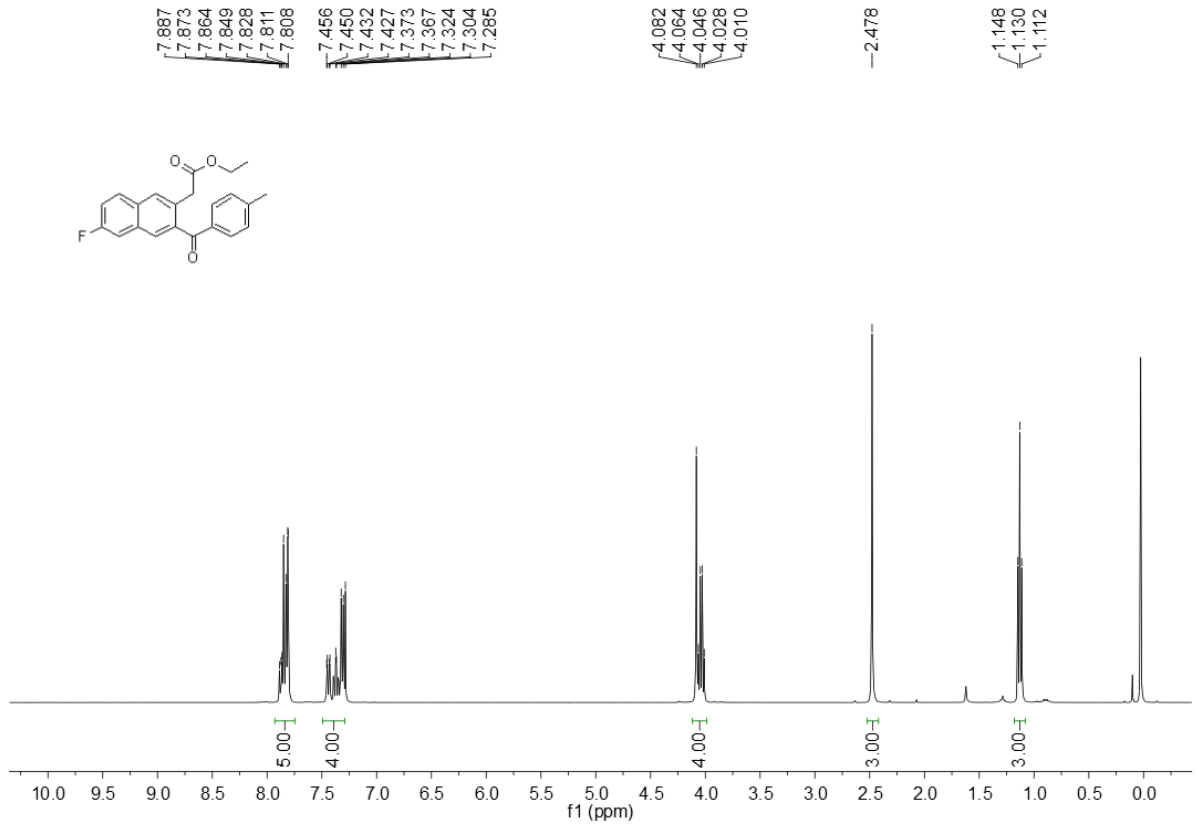
^{1}H NMR Spectrum of Compound 4i



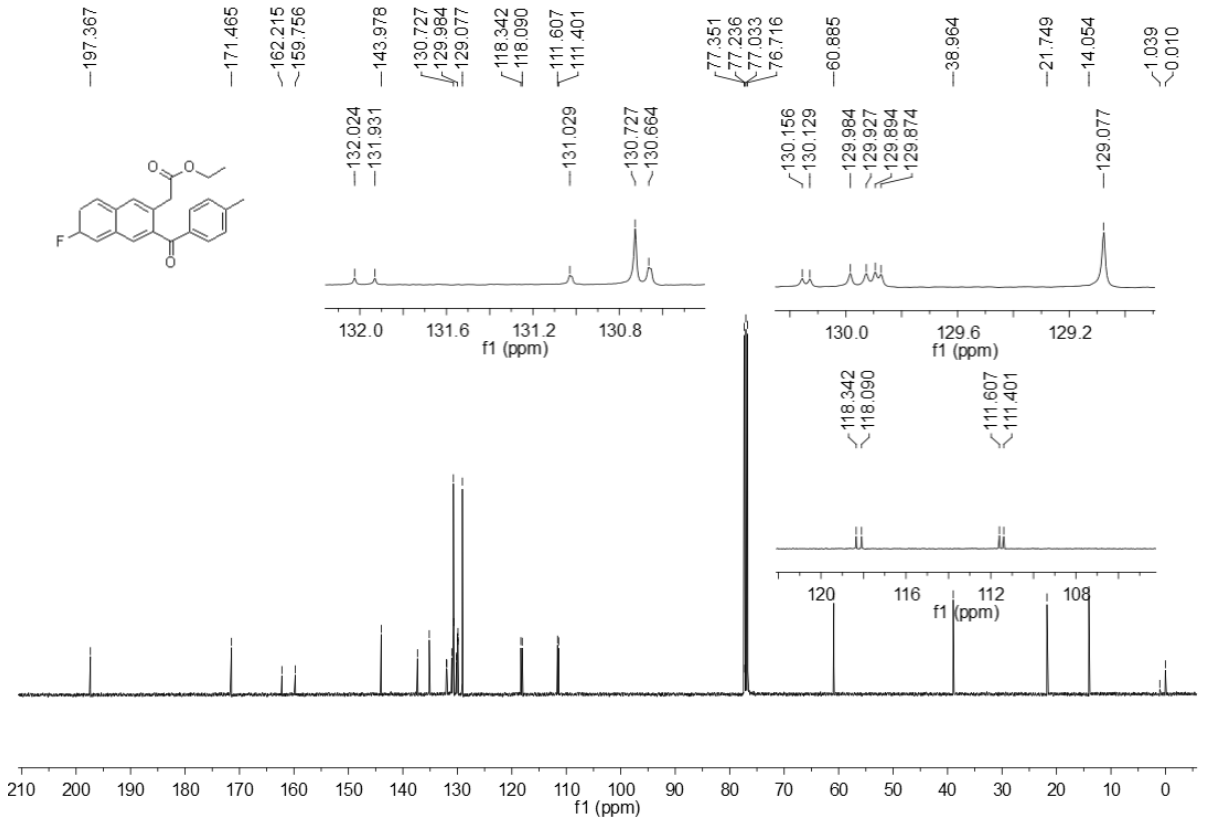
^{1}H NMR Spectrum of Compound 4j



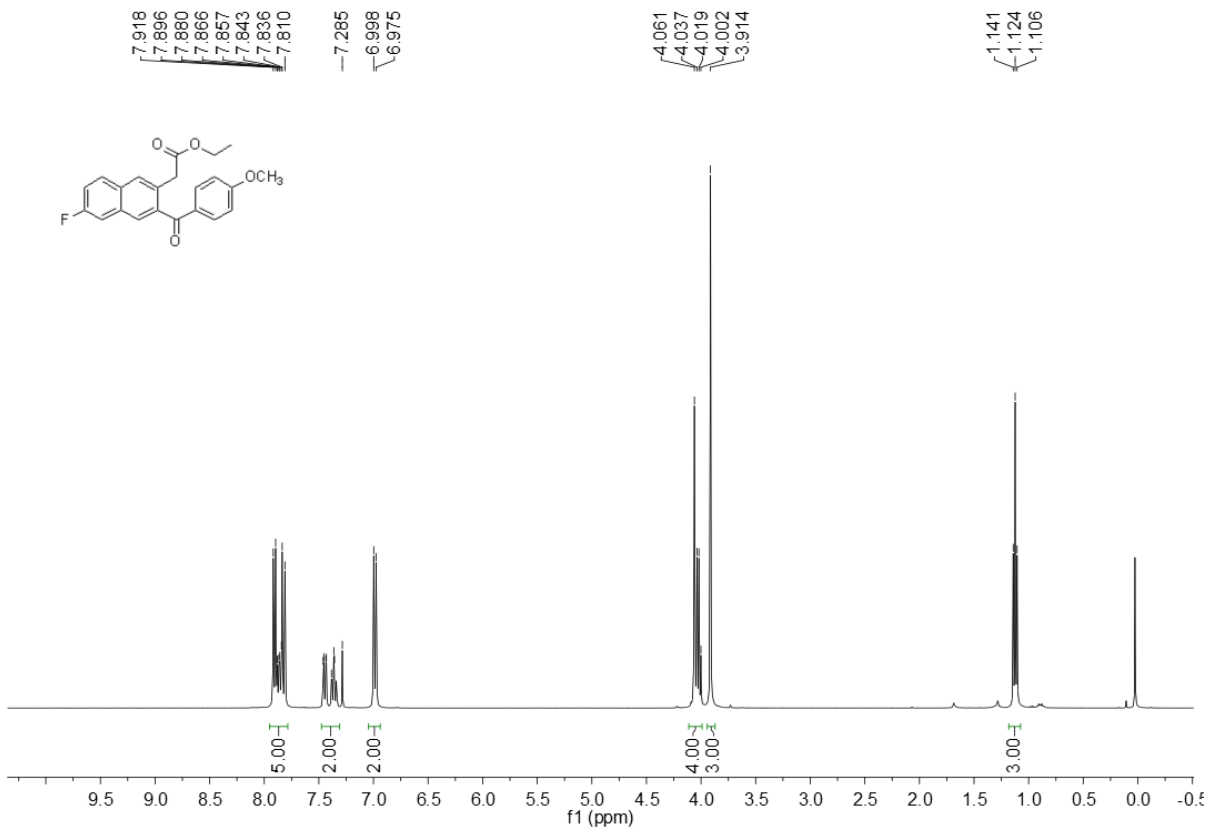
^{13}C NMR Spectrum of Compound 4j



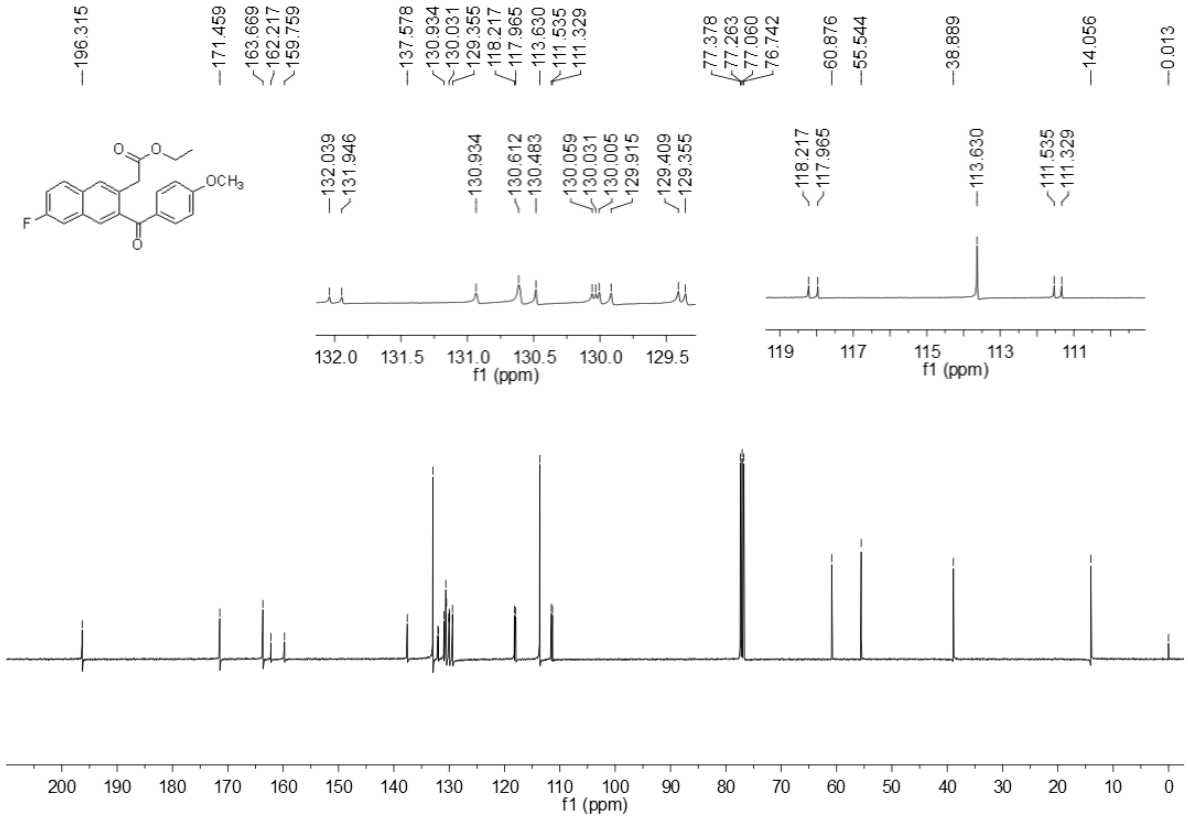
[1]H NMR Spectrum of Compound 4k



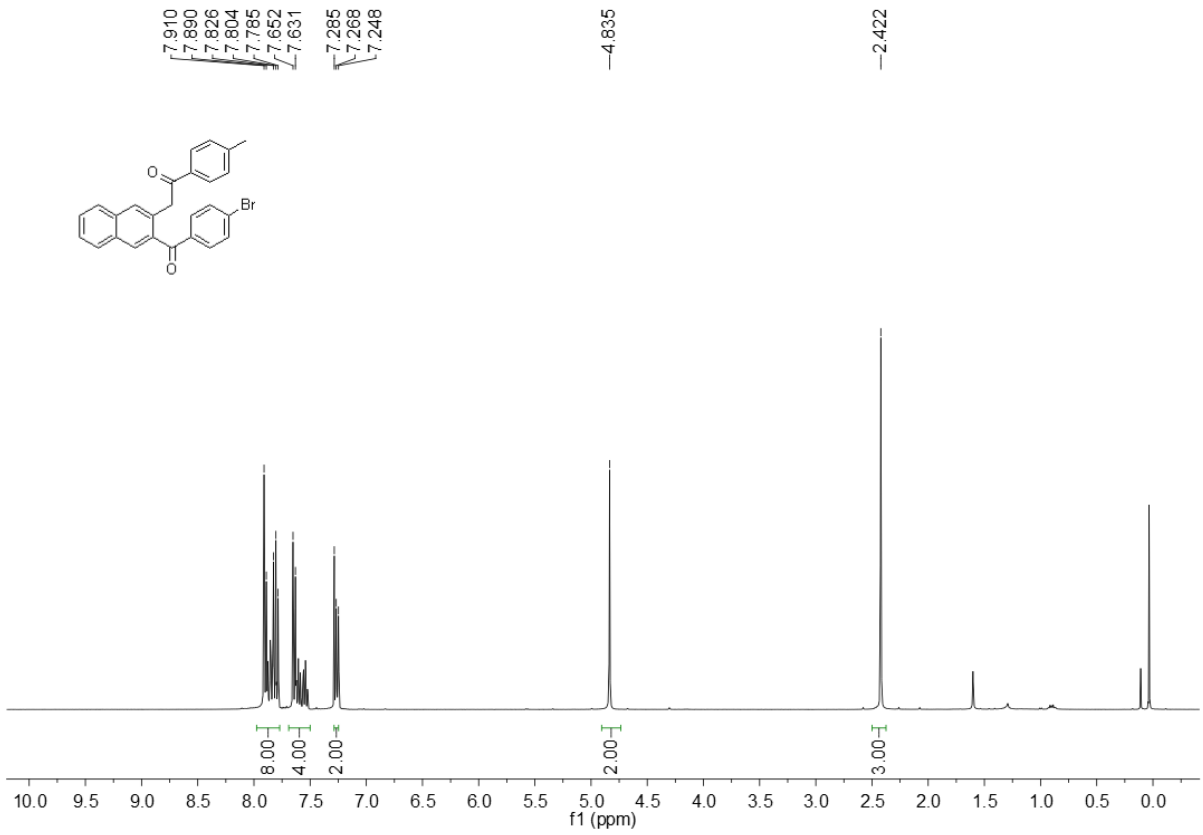
[1]H NMR Spectrum of Compound 4k



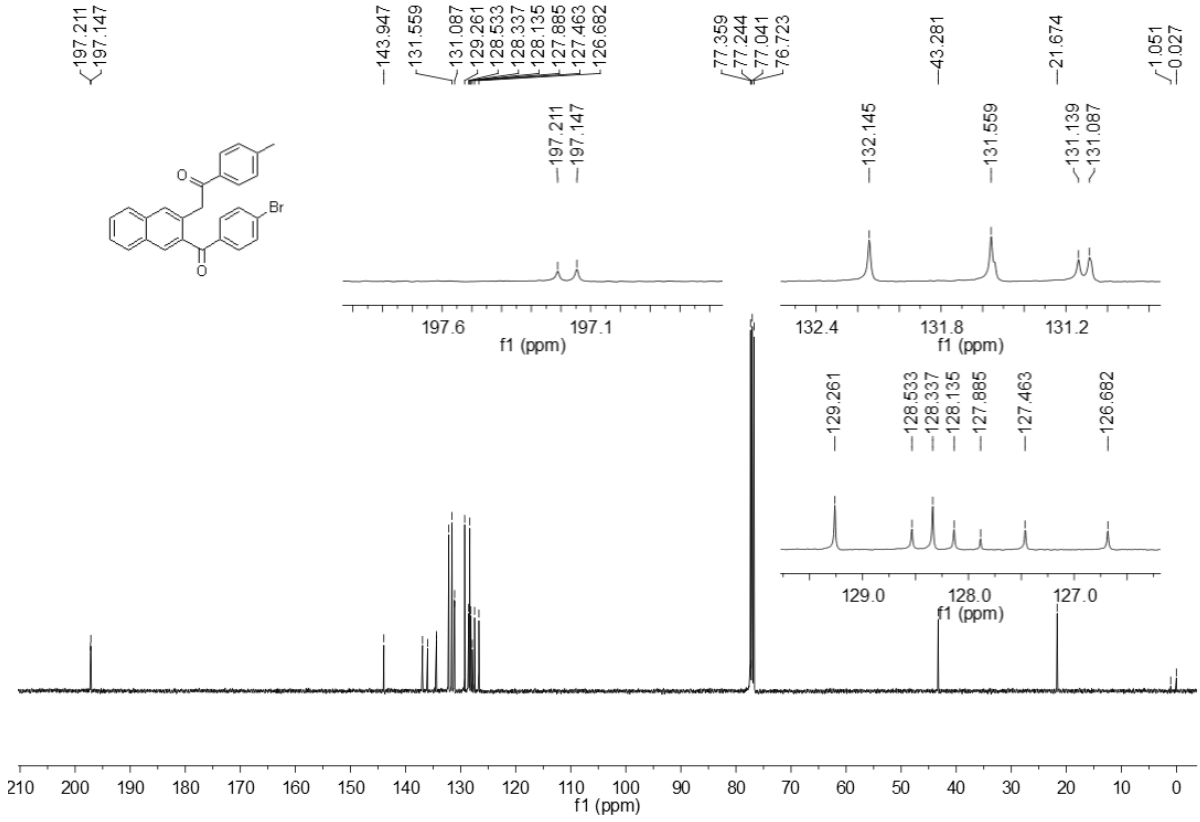
^{1}H NMR Spectrum of Compound 4l



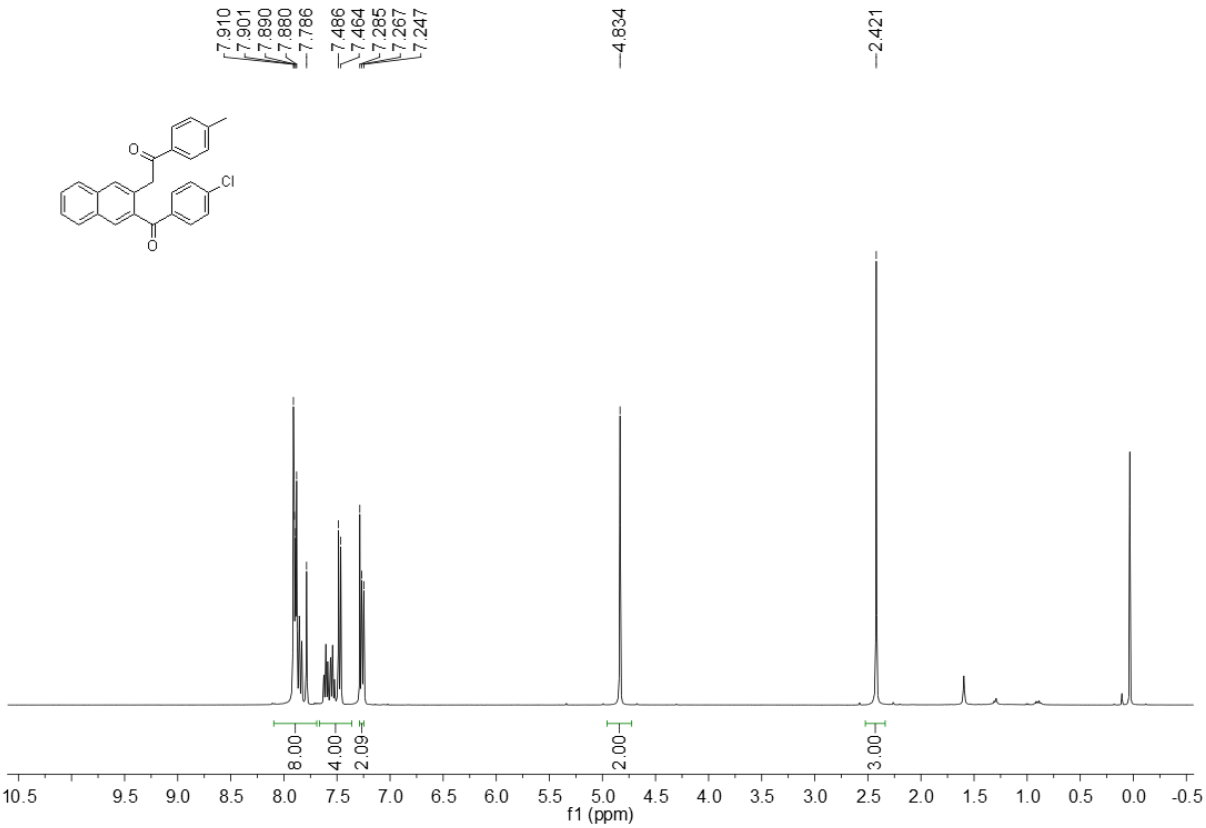
^{13}C NMR Spectrum of Compound 4l



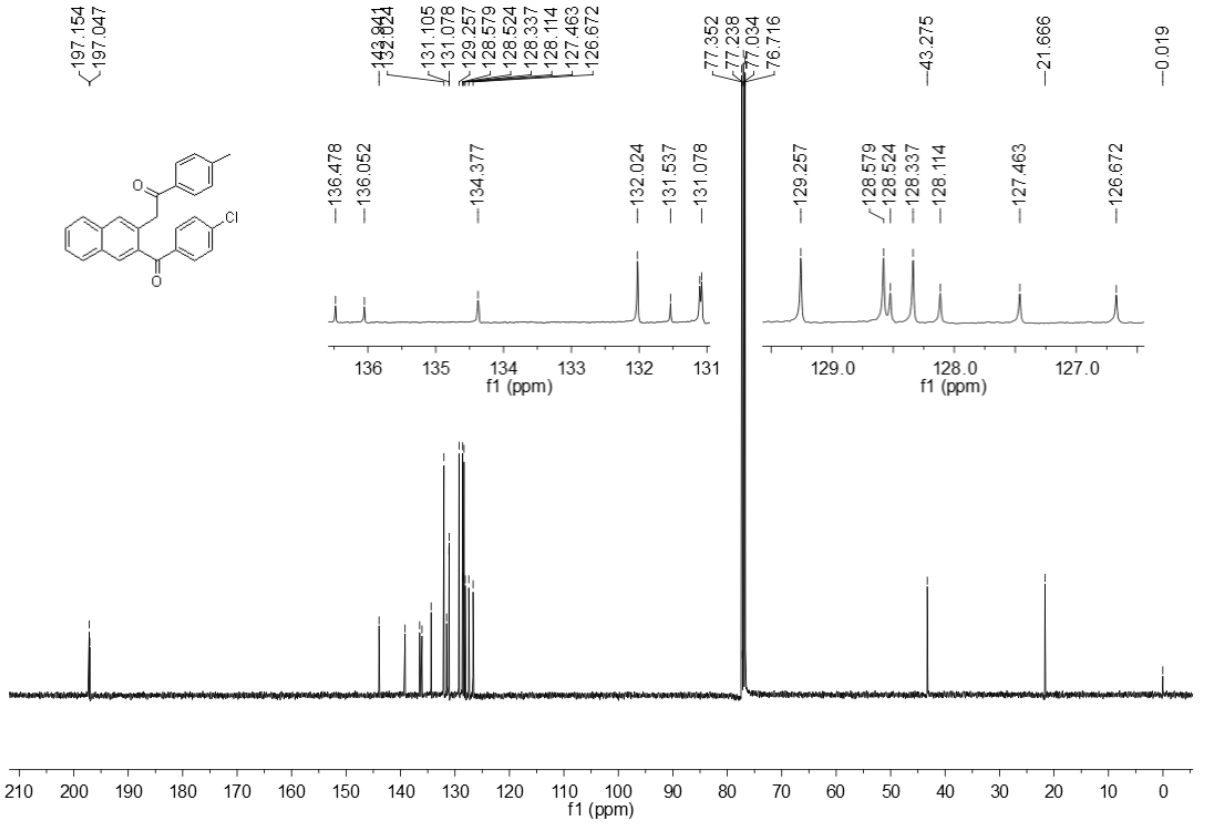
^{1}H NMR Spectrum of Compound 4m



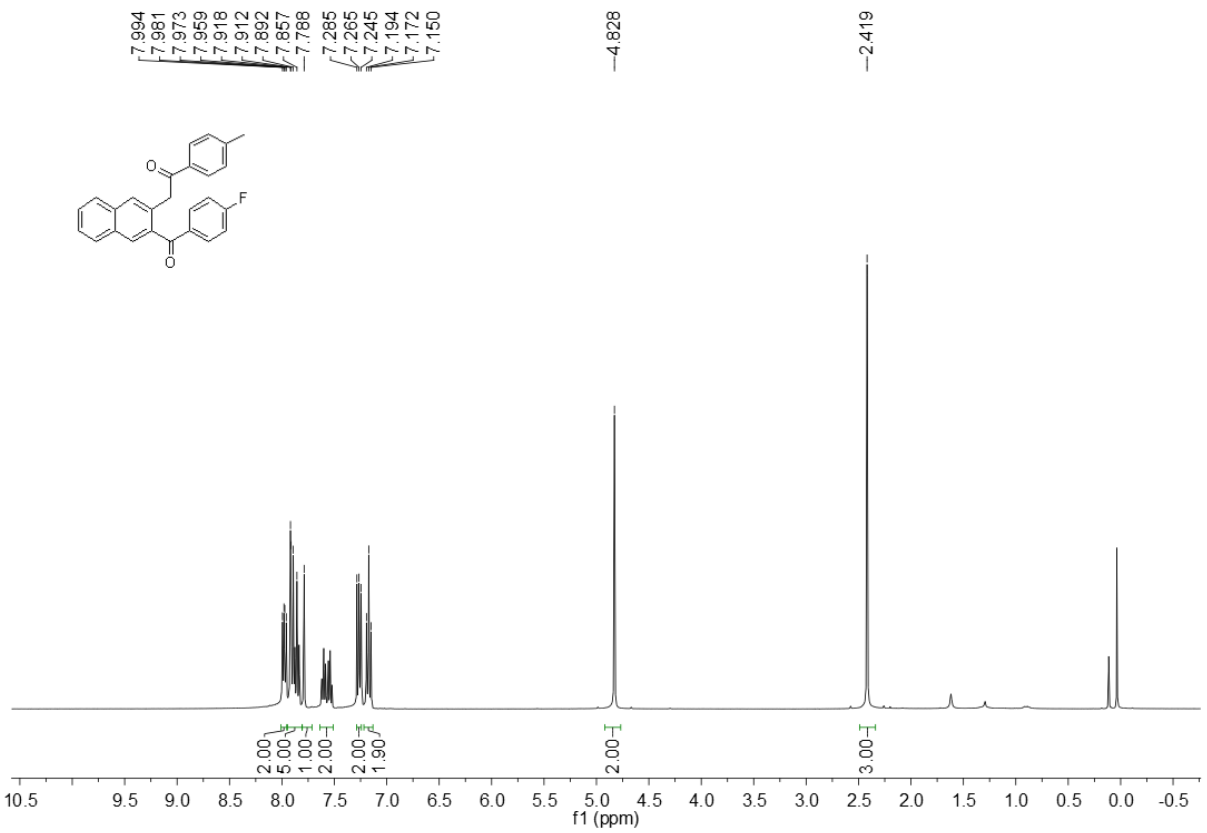
^{13}C NMR Spectrum of Compound 4m



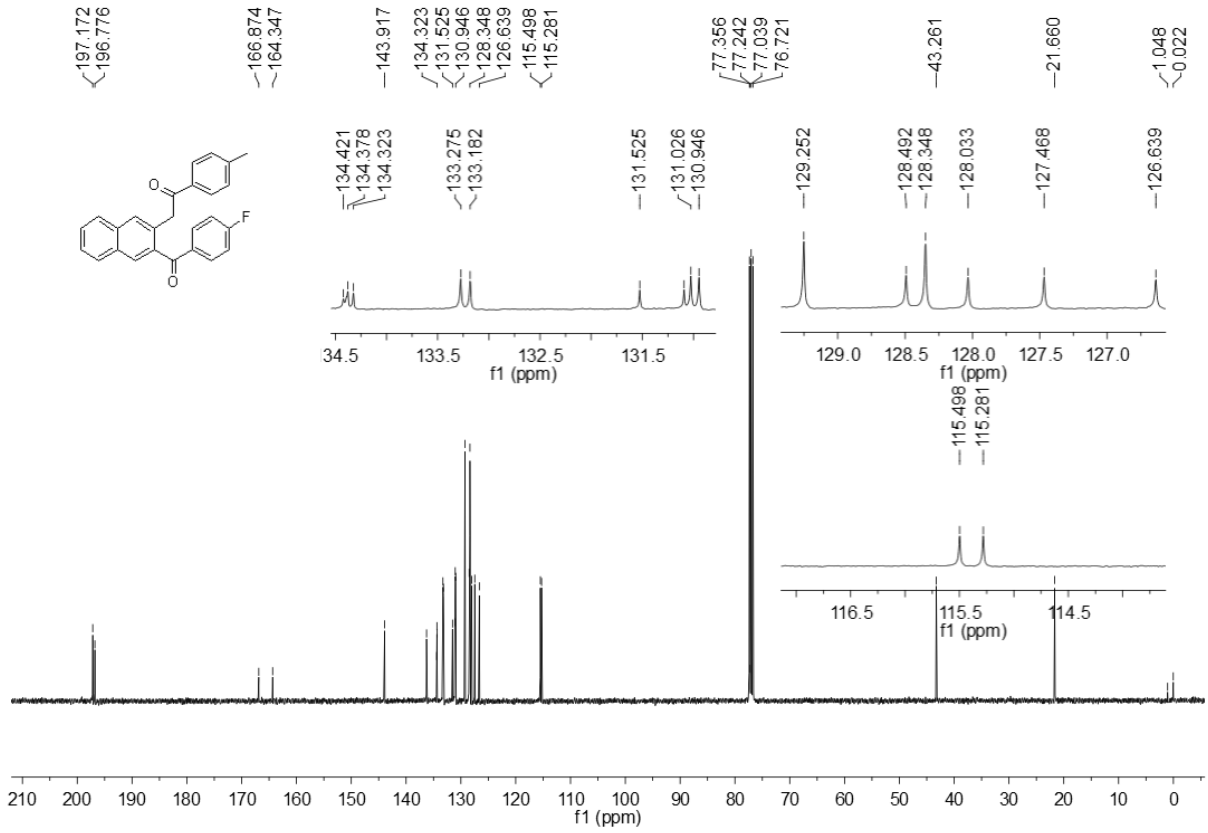
^{1}H NMR Spectrum of Compound 4n



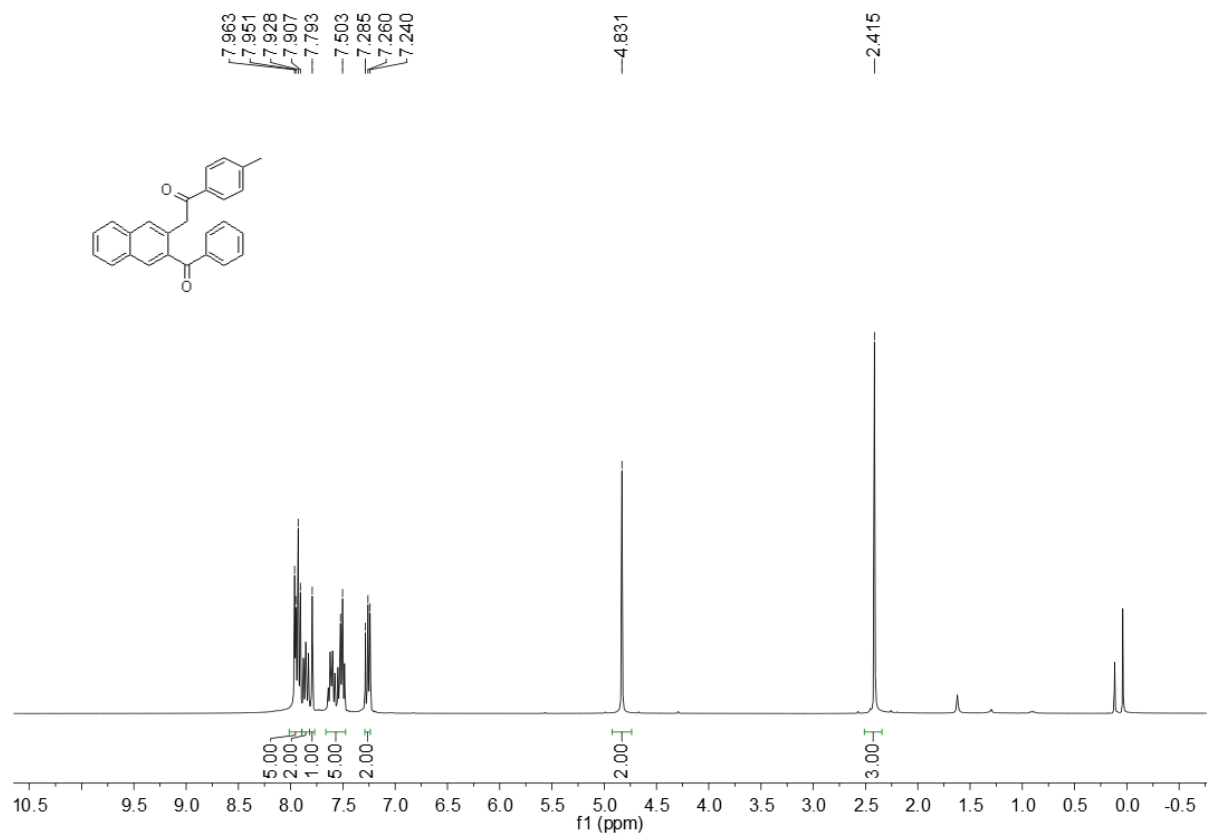
^{13}C NMR Spectrum of Compound 4n



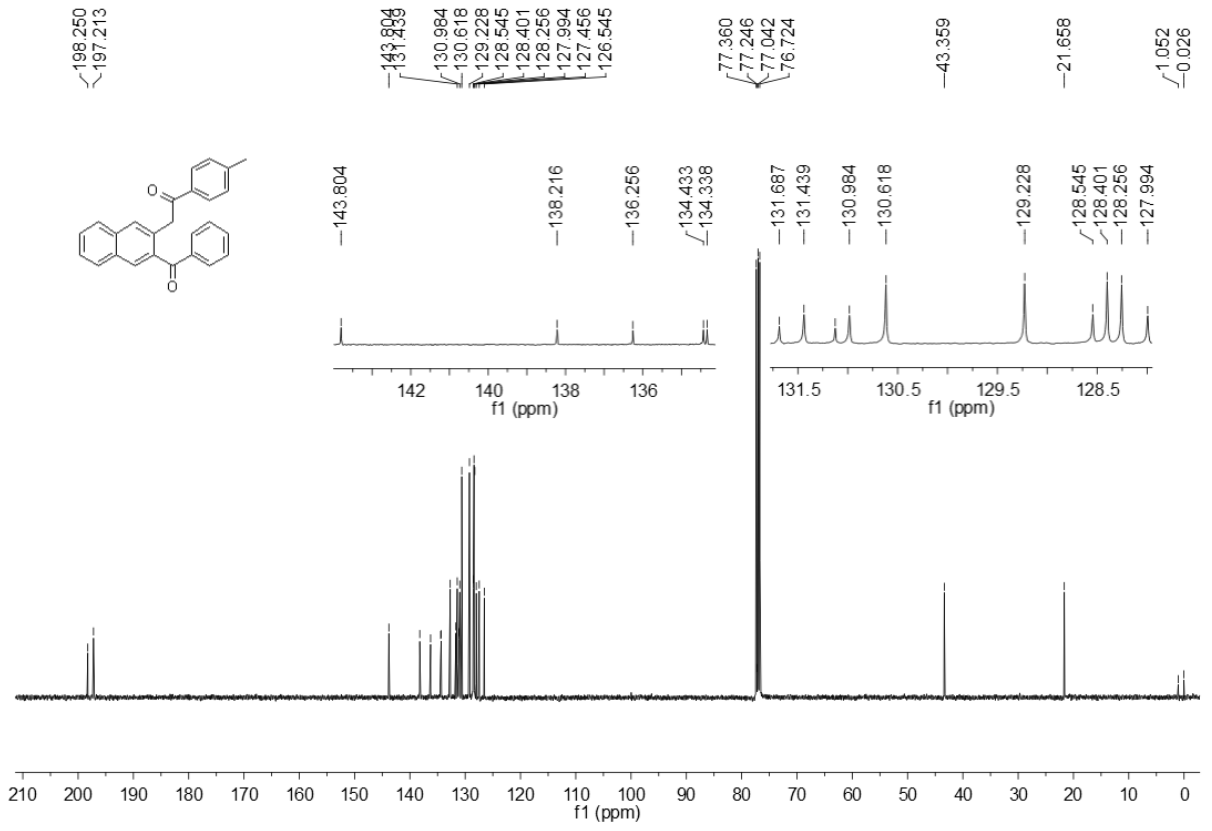
^{1}H NMR Spectrum of Compound 4o



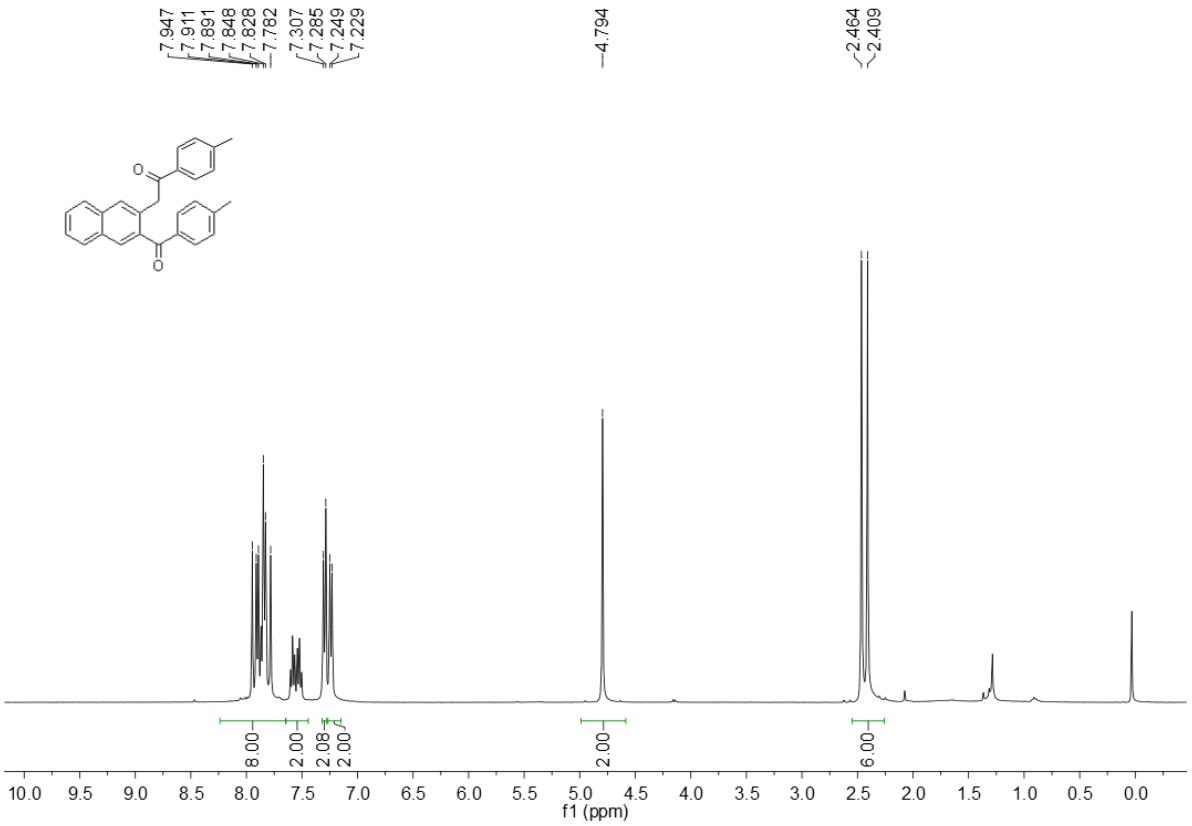
^{1}H NMR Spectrum of Compound 4o



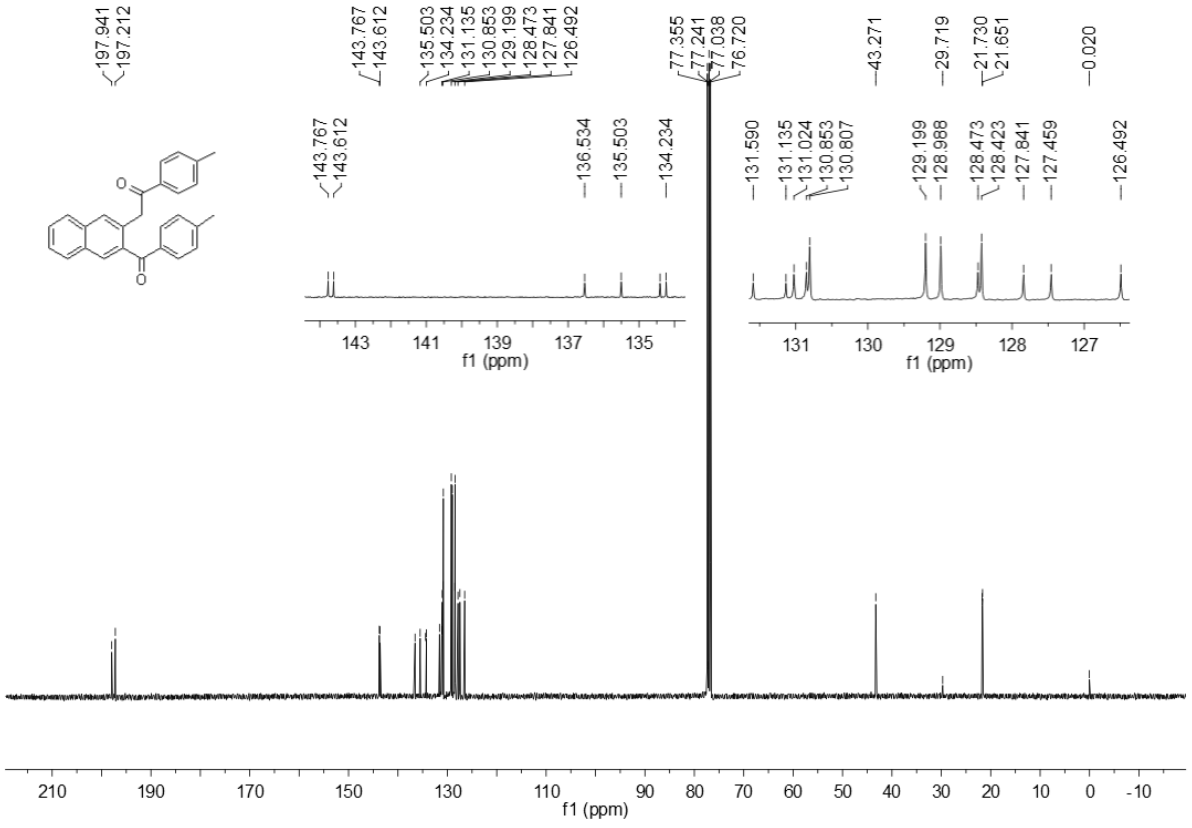
^{1}H NMR Spectrum of Compound 4p



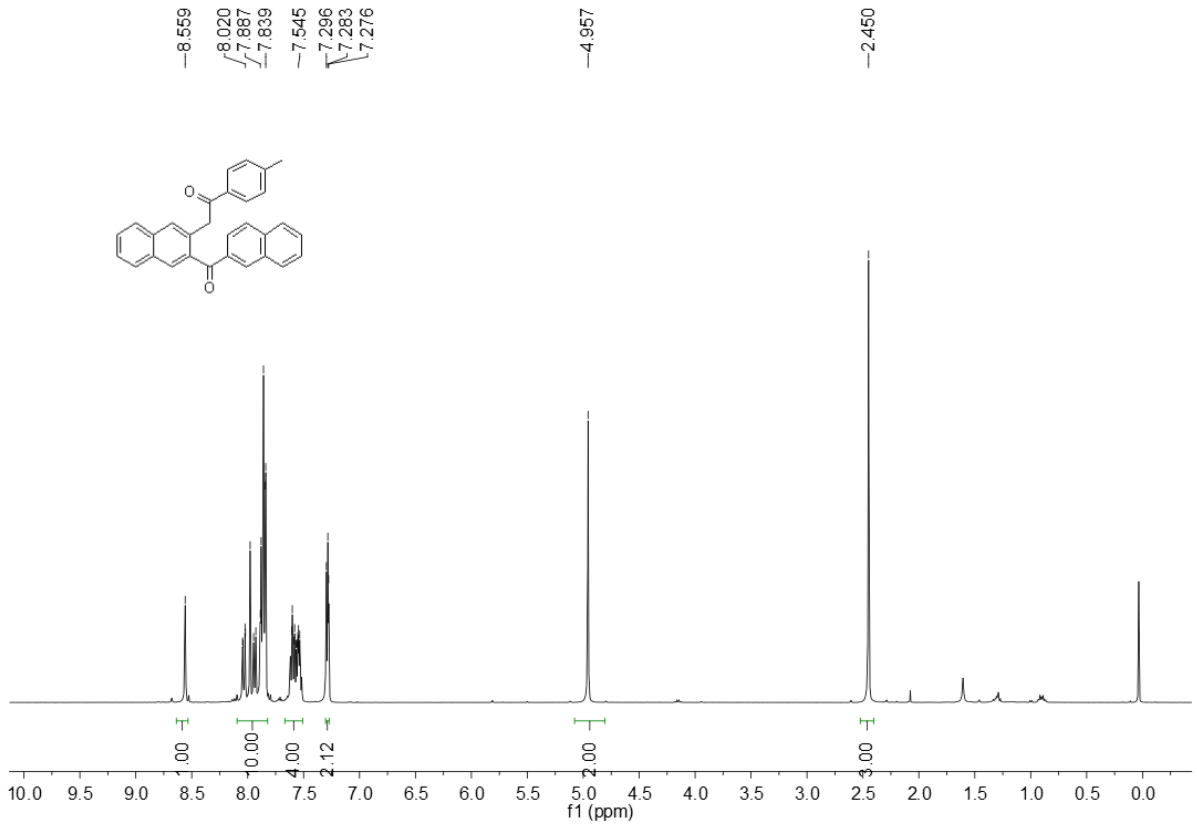
^{1}H NMR Spectrum of Compound 4p



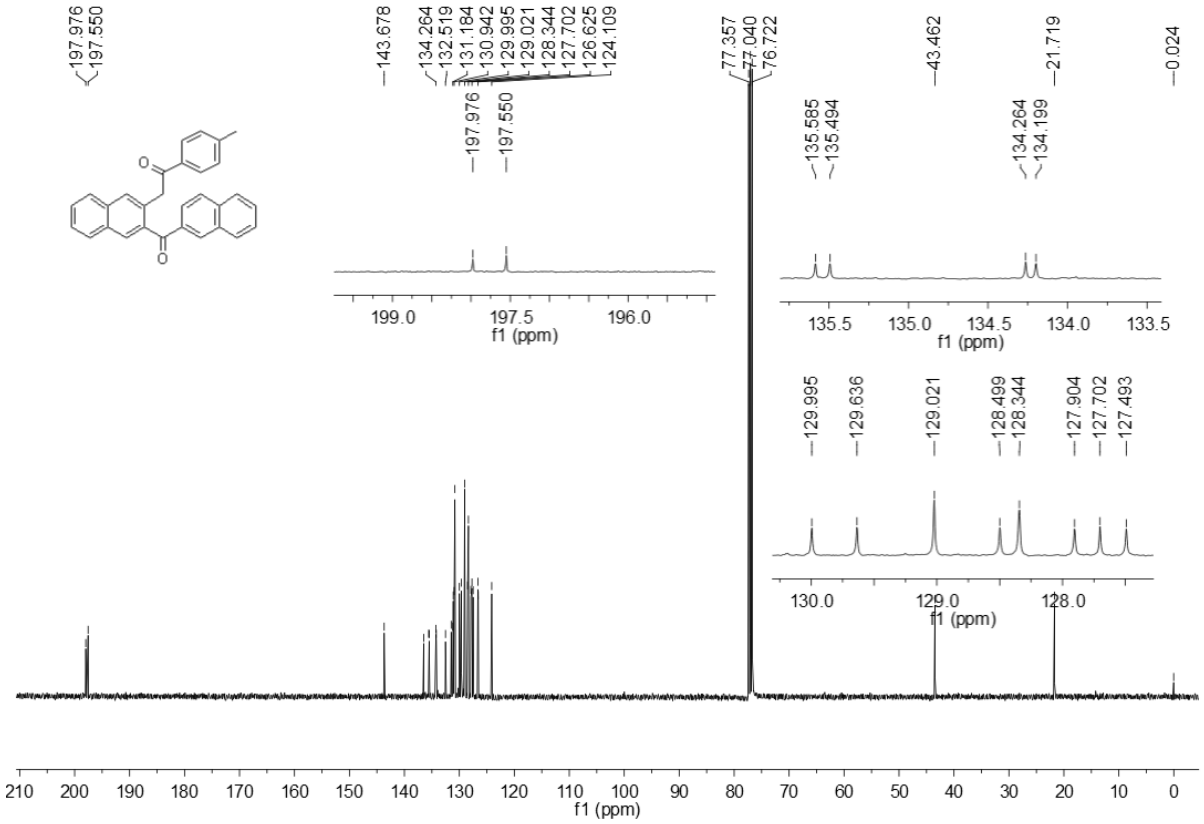
^{1}H NMR Spectrum of Compound 4q



^{1}H NMR Spectrum of Compound 4q



^{1}H NMR Spectrum of Compound 4r



^{1}H NMR Spectrum of Compound 4r