Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper-mediated radical alkylarylation of unactivated alkenes with acetonitrile leading to fluorenes and pyrroloindoles

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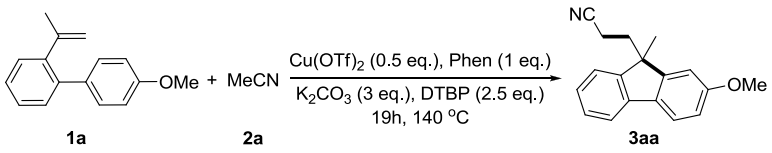
Experimental Section:

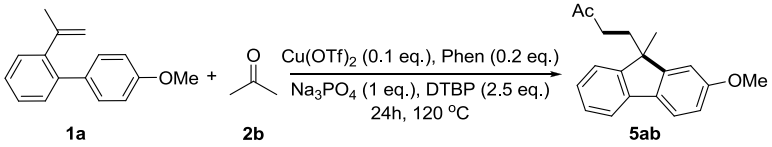
General

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in air and using undistilled solvent, without need of precautions to exclude air and moisture unless otherwise noted. Melting points were recorded on an Electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^{1}H, ^{13}C NMR spectra were recorded in $CDCl_3$ on 400 MHz spectometers. Tetramethylsilane (TMS) served as internal standard for ^{1}H NMR and ^{13}C NMR. High resolution mass spectra were obtained using a commercial apparatus (ESI or EI Source).

General procedure for rapid assembly of fluorene and pyrroloindole derivatives

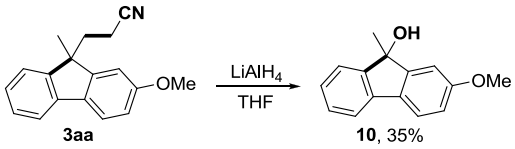


Alkene **1a** (0.2 mmol), acetonitrile **2a** (2 mL), $Cu(OTf)_2$ (0.1 mmol), 1,10-phenanthroline (0.2 mmol), K_2CO_3 (0.6 mmol) and di-*tert*-butyl peroxide (0.5 mmol) was stirred at 140 °C under air in a pressure-tight tube. Upon completion of the reaction (indicated by TLC), solvent was removed in vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as eluent, affording pure product **3aa**.



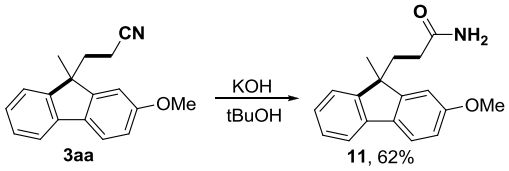
Alkene **1a** (0.3 mmol), acetone **2a** (2 mL), $Cu(OTf)_2$ (0.03 mmol), 1,10-phenanthroline (0.06 mmol), Na_3PO_4 (0.3 mmol) and di-*tert*-butyl peroxide (0.75 mmol) was stirred at 120 °C under air in a pressure-tight tube. Upon completion of the reaction (indicated by TLC), solvent was removed in vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as eluent, affording pure product **5ab**.

General procedure for the synthesis of compound 10



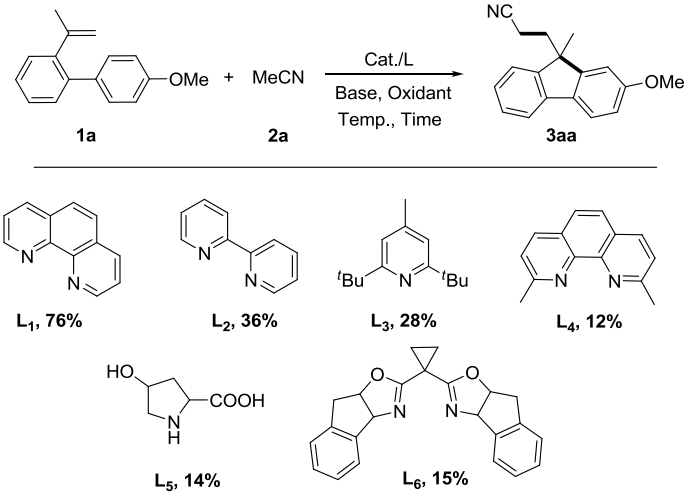
0.25 mmol of 3-(2-methoxy-9-methyl-9*H*-fluoren-9-yl)propanenitrile **3aa** was dissolved in 2.0 mL dry THF. Then 1 mmol of $LiAlH_4$ was added slowly at 0 °C. After 10 minutes, the cold bath was removed and the reaction mixture was stirred at room temperature for 3 h. The desired product 2-methoxy-9-methyl-9*H*-fluoren-9-ol **10** was obtained after purification by flash chromatography on silica gel (white solid, 35%).

General procedure for the synthesis of compound 11



0.5 mmol of 3-(2-methoxy-9-methyl-9*H*-fluoren-9-yl)propanenitrile **3aa** and 2 mmol of KOH was dissolved in 2.0 mL of 2-methyl-2-propanol. The reaction mixture was stirred at 80 °C for 48 h. The desired product 3-(2-methoxy-9-methyl-9*H*-fluoren-9-yl)propanamide **11** was obtained after purification by flash chromatography on silica gel (white solid, 62%).

Table S1: Optimization of the reaction conditions[a]



Entry	Catalyst (equiv)	Ligand (equiv)	Oxidant (x equiv)	Base (x equiv)	Time (h)	Temp. (°C)	GC-Yeild[b]	
							3aa	1a[c]
1	$Cu(OTf)_2$(0.5)	L_1(1)	DTBP(2.5)	K_3PO_4(3)	19	140	76	0
2	$Cu(OTf)_2$(0.5)	L_2(1)	DTBP(2.5)	K_3PO_4(3)	19	140	36	42
3	$Cu(OTf)_2$(0.5)	L_3(1)	DTBP(2.5)	K_3PO_4(3)	19	140	28	20
4	$Cu(OTf)_2$(0.5)	L_4(1)	DTBP(2.5)	K_3PO_4(3)	19	140	12	43
5	$Cu(OTf)_2$(0.5)	L_5(1)	DTBP(2.5)	K_3PO_4(3)	19	140	14	50
6	$Cu(OTf)_2$(0.5)	L_6(1)	DTBP(2.5)	K_3PO_4(3)	19	140	15	88
7	$Cu(OTf)_2$(0.5)	--	DTBP(2.5)	K_3PO_4(3)	19	140	0	--
8	$Cu(OTf)_2$(0.2)	L_1(0.4)	DTBP(2.5)	K_3PO_4(3)	19	140	10	38
9	$Cu(OTf)_2$(0.5)	L_1(0.5)	DTBP(2.5)	K_3PO_4(3)	19	140	20	28
10	$Cu(OTf)_2$(0.2)	L_1(0.2)	DTBP(2.5)	K_3PO_4(3)	19	140	24	31
11	**$Cu(OTf)_2$(0.5)**	**L_1(1)**	**DTBP(2.5)**	**K_2CO_3(3)**	**19**	**140**	**96(78)[d]**	**0**
12	$Cu(OTf)_2$(0.5)	L_1(1)	DTBP(2.5)	CS_2CO_3(3)	19	140	36	40
13	$Cu(OTf)_2$(0.5)	L_1(1)	DTBP(2.5)	NaOAc(3)	19	140	49	0
14	$Cu(OTf)_2$(0.5)	L_1(1)	DTBP(2.5)	ButOK(3)	19	140	67	trace
15	$Cu(OTf)_2$(0.5)	L_1(1)	DTBP(2.5)	KOH(3)	19	140	48	18
16	$Cu(OTf)_2$(0.5)	L_1(1)	DTBP(2.5)	--	19	140	trace	78
17	$Cu(OAc)_2$(0.5)	L_1(1)	DTBP(2.5)	K_2CO_3(3)	19	140	61	0
18	CuOAc(0.5)	L_1(1)	DTBP(2.5)	K_2CO_3(3)	19	140	56	trace
19	Cu_2O(0.5)	L_1(1)	DTBP(2.5)	K_2CO_3(3)	19	140	33	9
20	$Cu(NO_3)_2$(0.5)	L_1(1)	DTBP(2.5)	K_2CO_3(3)	19	140	83	trace
21	--	L_1(1)	DTBP(2.5)	K_2CO_3(3)	19	140	0	--
22	$Cu(OTf)_2$(0.5)	L_1(1)	DCP(2.5)	K_2CO_3(3)	19	140	62	trace
23	$Cu(OTf)_2$(0.5)	L_1(1)	TBPB(2.5)	K_2CO_3(3)	19	140	51	0
24	$Cu(OTf)_2$(0.5)	L_1(1)	BPO(2.5)	K_2CO_3(3)	19	140	23	17
25	$Cu(OTf)_2$(0.5)	L_1(1)	DTBP(2.5)	K_2CO_3(3)	19	130	87	0
26	$Cu(OTf)_2$(0.5)	L_1(1)	DTBP(2.5)	K_2CO_3(3)	12	140	79	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (2 mL), catalyst (0.5 equiv), ligand (1 equiv), base (3 equiv) and oxidant (2.5 equiv) at 140 °C under air; DTBP = di-*tert*-butyl peroxide; DCP = dicumyl peroxide; TBPB = *tert*-butylperoxybenzoate; BPO = benzoyl peroxide. [b]Yields were determined by GC with an internal standard (biphenyl) on the basis of the ratio between the formed products and the initial amount of limiting reactant. [c]The recovery of **1a**. [d]Isolated yields.

Figure S1: The fluorescence spectra of prepared polycyclic **3va**, **3ta**, **5ba** and **5fa**

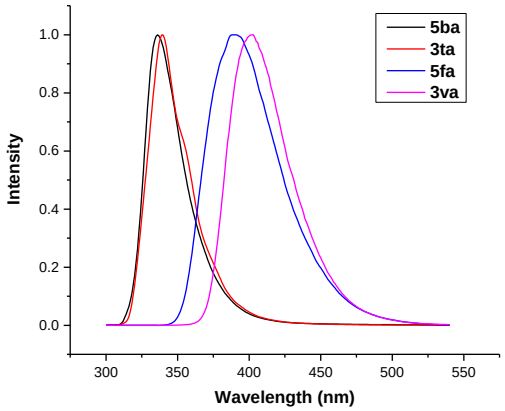
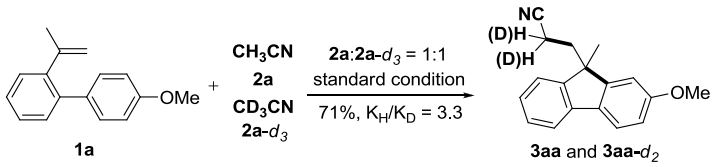
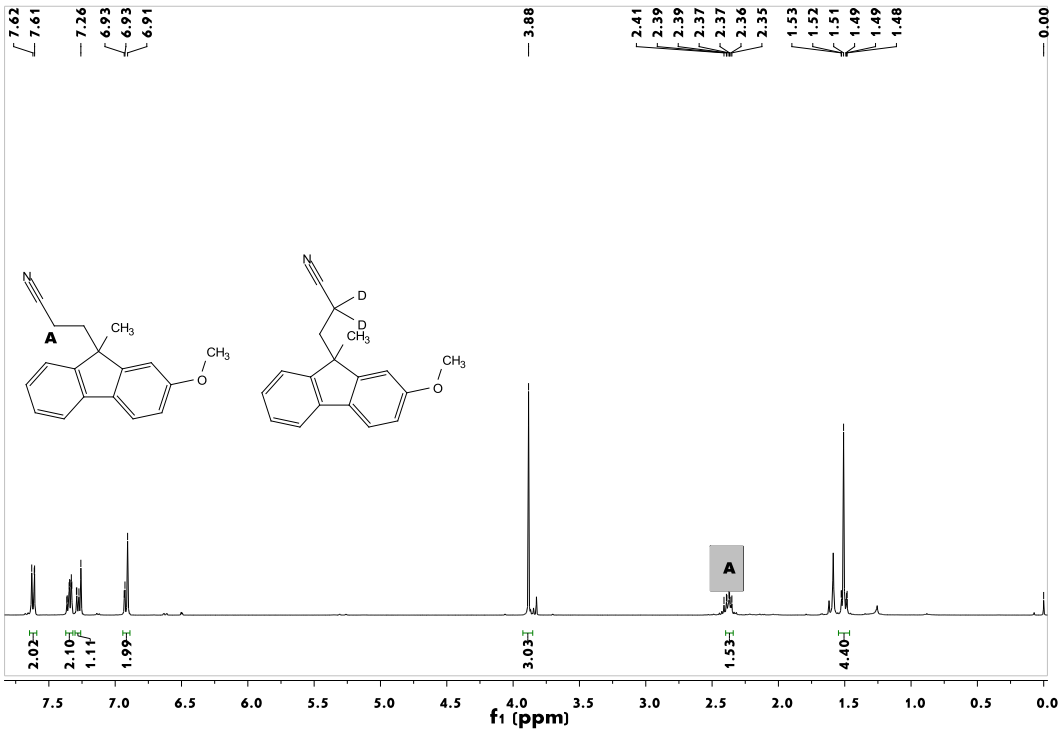


Figure S2: Kinetic isotope effects (KIE) experiment





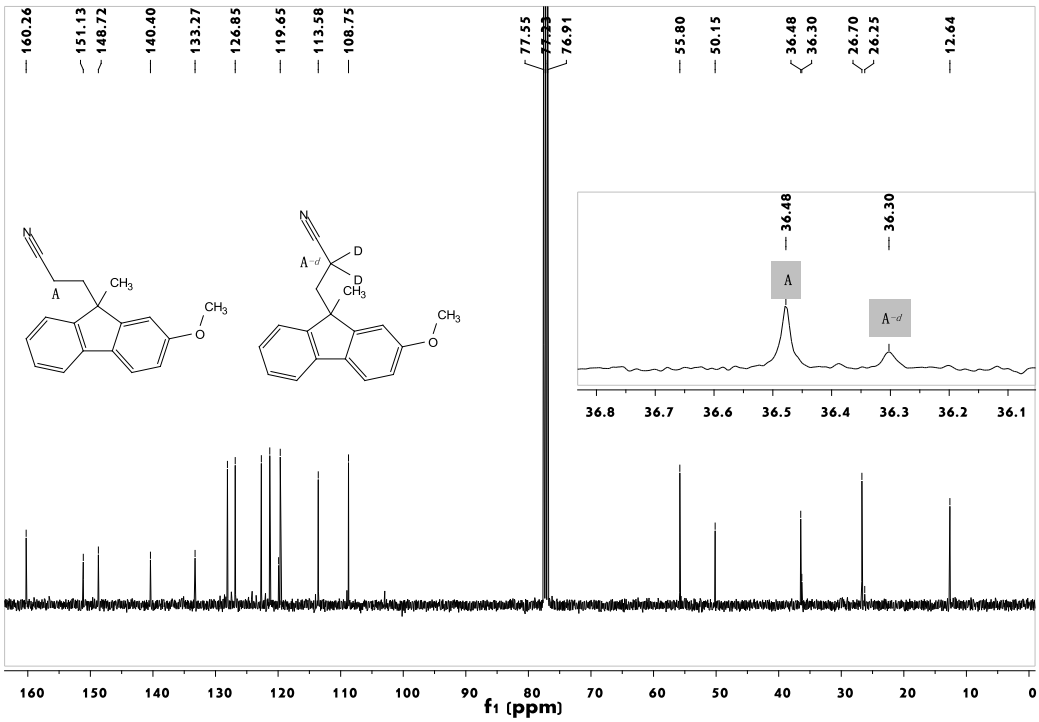
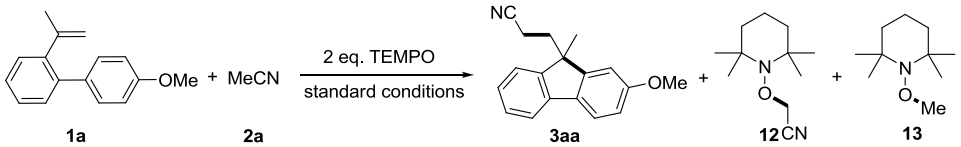
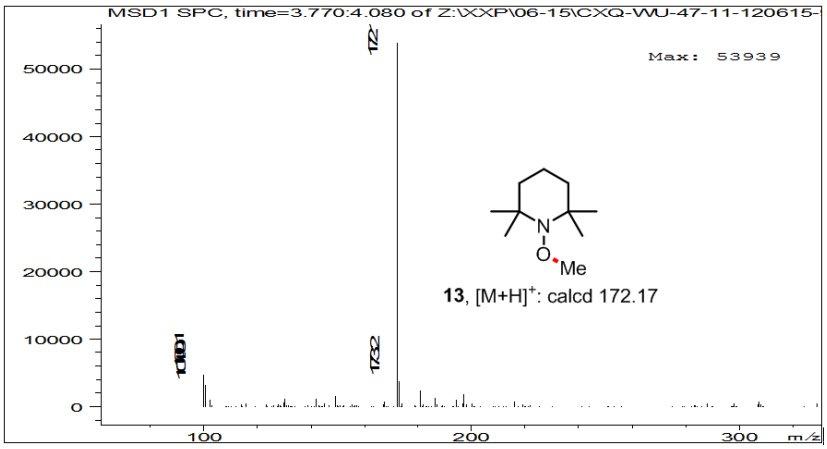
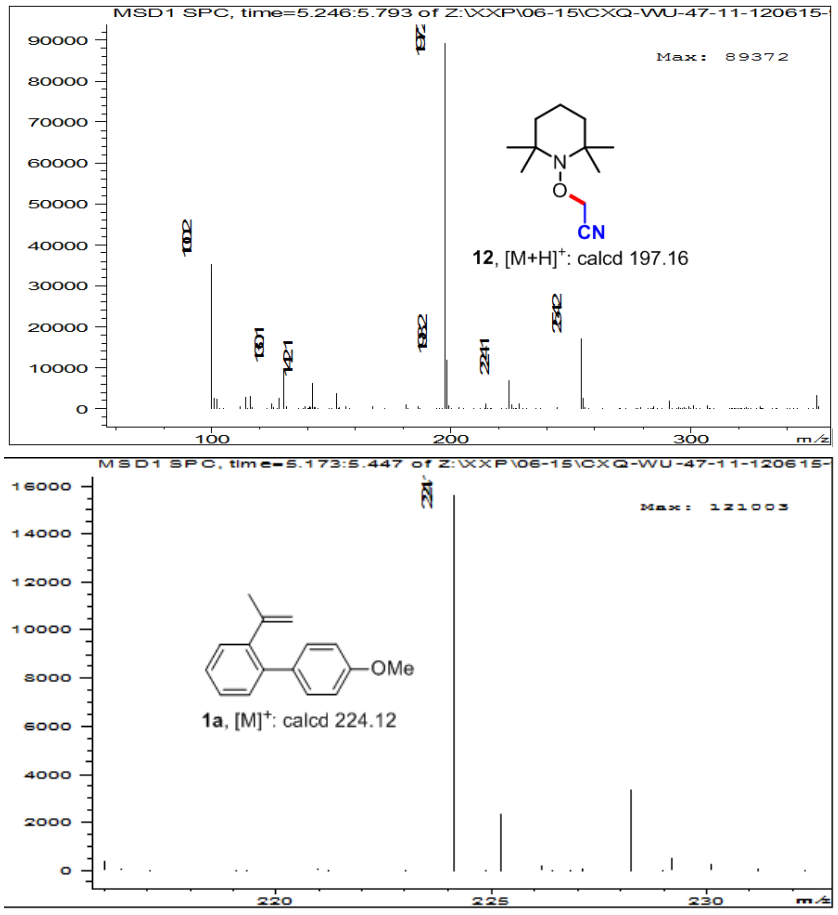


Figure S3: Trapping experiment with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO).

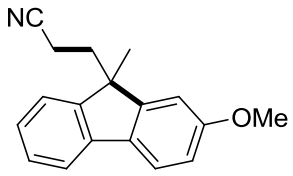


1a, $[M]^+$: calcd 224.12
3aa, not detected
12, $[M+H]^+$: calcd 197.16
13, $[M+H]^+$: calcd 172.17

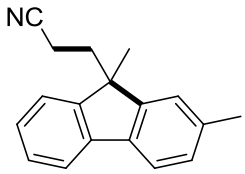




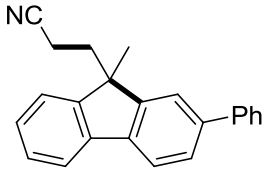
Analytical and spectral data of products:



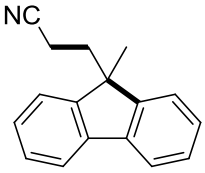
3-(2-Methoxy-9-methyl-9*H*-fluoren-9-yl)propanenitrile (3aa): Yield = 78%. Colourless oil. IR (KBr) ν = 2960, 2925, 2866, 2246, 1610, 1459, 1280, 1253, 1036, 822, 736 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.59 (m, 2H), 7.37–7.31 (m, 2H), 7.29–7.25 (m, 1H), 6.94–6.89 (m, 2H), 3.88 (s, 3H), 2.45–2.31 (m, 2H), 1.51 (s, 3H), 1.50–1.47 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 151.1, 148.7, 140.4, 133.3, 128.1, 126.8, 122.7, 121.3, 119.9, 119.6, 113.6, 108.8, 55.8, 50.2, 36.5, 26.7, 12.6 ppm. HRMS m/z: calcd for $C_{18}H_{17}NNaO$ $[M+Na]^+$ 286.1202, found: 286.1205.



3-(2,9-Dimethyl-9*H*-fluoren-9-yl)propanenitrile (3ba): Yield = 72%. Colourless oil. IR (KBr) ν = 2959, 2923, 2863, 2245, 1446, 1214, 823, 778, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (dd, *J* = 5.5, 2.7 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.38–7.28 (m, 3H), 7.18 (d, *J* = 6.7 Hz, 2H), 2.44 (s, 3H), 2.42–2.36 (m, 2H), 1.51 (s, 3H), 1.51–1.46 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.4, 149.1, 140.5, 138.1, 137.8, 128.9, 128.0, 127.5, 123.5, 122.8, 120.2, 120.2, 120.0, 50.0, 36.4, 26.7, 22.0, 12.7 ppm. HRMS m/z: calcd for $C_{18}H_{17}NNa$ $[M+Na]^+$ 270.1253, found: 270.1262.

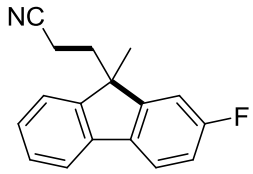


3-(9-methyl-2-phenyl-9*H*-fluoren-9-yl)propanenitrile (3ca): Yield = 50%. White solid. M.p. 108.2–109.3 °C. IR (KBr) ν = 2987, 2972, 2246, 1435, 1407, 1251, 1075, 895, 760, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.72 (m, 2H), 7.67–7.60 (m, 3H), 7.59 (d, *J* = 1.1 Hz, 1H), 7.51–7.45 (m, 2H), 7.43–7.33 (m, 4H), 2.50–2.41 (m, 2H), 1.58 (s, 3H), 1.57–1.53 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.9, 149.5, 141.3, 140.1, 139.6, 129.1, 128.2, 128.1, 127.7, 127.4, 127.3, 122.9, 121.5, 120.8, 120.6, 119.8, 50.3, 36.4, 26.7, 12.7 ppm. HRMS m/z: calcd for $C_{23}H_{19}NNa$ $[M+Na]^+$ 332.1410, found: 332.1407.

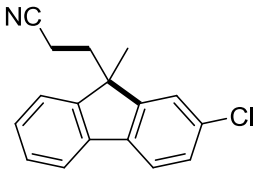


3-(9-methyl-9*H*-fluoren-9-yl)propanenitrile (3da): Yield = 59%. White solid. M.p. 72.2–74.5 °C. IR (KBr) ν = 2955, 2920, 2852, 2242, 1443, 1260, 1076, 1025, 799, 731 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 6.1, 2.7 Hz, 2H), 7.40–7.33 (m, 6H), 2.47–2.37 (m, 2H), 1.53 (s, 3H), 1.51–1.45 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 140.4, 128.1, 128.0, 122.8, 120.5, 119.9, 50.2, 36.4, 26.6, 12.7 ppm. HRMS m/z: calcd for $C_{17}H_{15}NNa$ $[M+Na]^+$ 256.1097,

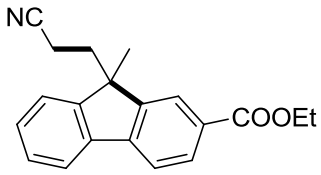
found: 256.1090.



3-(2-fluoro-9-methyl-9*H*-fluoren-9-yl)propanenitrile (3ea): Yield = 74%. White solid. M.p. 60.1–61.7 °C. IR (KBr) ν = 2957, 2922, 2862, 2246, 1613, 1444, 1265, 1186, 898, 821, 776, 734 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.71–7.63 (m, 2H), 7.41–7.30 (m, 3H), 7.11–7.05 (m, 2H), 2.46–2.33 (m, 2H), 1.56–1.50 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 162.0, 151.6, 151.6, 149.0, 149.0, 139.6, 136.4, 136.3, 128.3, 127.7, 122.8, 121.7, 121.6, 120.2, 119.6, 115.4, 115.2, 110.5, 110.3, 50.4, 50.4, 36.3, 26.5, 12.7 ppm. HRMS m/z: calcd for $C_{17}H_{14}FNNa$ $[M+Na]^+$ 274.1002, found: 274.1008.

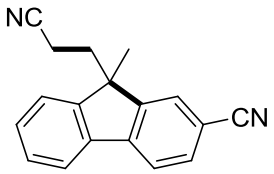


3-(2-chloro-9-methyl-9*H*-fluoren-9-yl)propanenitrile (3fa): Yield = 53%. Colourless oil. IR (KBr) ν = 2959, 2920, 2850, 2245, 1632, 1443, 1263, 1083, 825, 789, 735 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.71–7.66 (m, 1H), 7.66–7.61 (m, 1H), 7.41–7.34 (m, 5H), 2.47–2.33 (m, 2H), 1.56–1.48 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 149.0, 139.3, 139.0, 133.8, 128.4, 128.3, 123.4, 122.9, 121.5, 120.6, 119.49, 50.4, 36.2, 26.5, 12.7 ppm. HRMS m/z: calcd for $C_{17}H_{14}ClNNa$ $[M+Na]^+$ 290.0707, found: 290.0711.

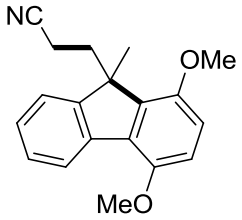


ethyl 9-(2-cyanoethyl)-9-methyl-9*H*-fluorene-2-carboxylate (3ga): Yield = 61%. White solid. M.p. 134.9–136.6 °C. IR (KBr) ν = 2977, 2965, 2928, 2243, 1707, 1446, 1289, 1257, 1220, 1099, 1026, 860, 757, 740 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.11 (dd, J = 8.0, 1.5 Hz, 1H), 8.07–8.05 (m, 1H), 7.80–7.85 (m, 2H), 7.42 (d, J = 2.8 Hz, 3H), 4.46–4.39 (m, 2H), 2.55–2.40 (m, 2H), 1.57 (s, 3H), 1.53–1.47 (m, 2H), 1.47–1.40 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =

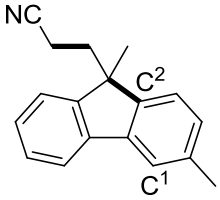
166.8, 150.3, 149.3, 144.9, 139.3, 130.1, 129.9, 129.2, 128.4, 124.0, 123.1, 121.4, 120.2, 119.5, 61.4, 50.3, 36.1, 26.5, 14.6, 12.7 ppm. HRMS m/z: calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$ 306.1489, found: 306.1499.



9-(2-cyanoethyl)-9-methyl-9*H*-fluorene-2-carbonitrile (3ha): Yield = 59%. Colourless oil. IR (KBr) ν = 2961, 2922, 2850, 2223, 1609, 1447, 1184, 837, 783, 738 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.85–7.77 (m, 2H), 7.73–7.66 (m, 2H), 7.48–7.42 (m, 3H), 2.45 (dd, *J* = 8.8, 7.4 Hz, 2H), 1.56 (s, 3H), 1.55–1.49 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 149.8, 144.9, 138.5, 132.6, 129.9, 128.7, 126.6, 123.2, 121.7, 121.1, 119.3, 119.0, 111.0, 50.5, 35.8, 26.4, 12.7 ppm. HRMS m/z: calcd for $C_{18}H_{15}N_2$ $[M+H]^+$ 259.1230, found: 259.1231.

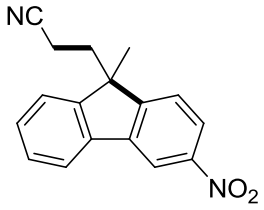


3-(1,4-dimethoxy-9-methyl-9*H*-fluoren-9-yl)propanenitrile (3ia): Yield = 65%. Colourless oil. IR (KBr) ν = 2965, 2923, 2245, 1503, 1456, 1248, 1051, 1017, 756, 745, 668 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.10–8.04 (m, 1H), 7.37–7.29 (m, 3H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 3.94 (s, 3H), 3.86 (s, 3H), 2.95–2.85 (m, 1H), 2.30–2.20 (m, 1H), 1.57 (s, 3H), 1.55–1.45 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.0, 150.5, 149.6, 139.6, 136.4, 129.7, 127.9, 127.2, 124.4, 121.7, 120.3, 110.9, 110.2, 55.9, 55.8, 51.3, 33.4, 24.3, 12.9 ppm. HRMS m/z: calcd for $C_{19}H_{19}NNaO_2$ $[M+Na]^+$ 316.1308, found: 316.1311.

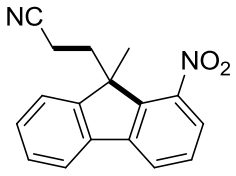


3-(3,9-dimethyl-9*H*-fluoren-9-yl)propanenitrile (3ja) and 3-(1,9-dimethyl-9*H*-fluoren-9-yl)propanenitrile (3ja'): Yield = 55% (C^1/C^2 isomers, **3ja**/**3ja'** =

1:1). IR (KBr) ν = 2962, 2925, 2866, 2242, 1582, 1453, 1279, 1027, 821, 766, 741 cm^{-1}. The ^{1}H NMR spectrum of the isolated product showed a 1:1 mixture of **3ja** and its isomer **3ja'**. ^{1}H NMR (400MHz, $CDCl_3$) **3ja** and its isomer **3ja'**: δ = 7.72–7.66 (m, 1H), 7.60–7.51 (m, 1H), 7.39–7.30 (m, 3H), 7.27–7.24 (m, 1H), 7.16 (d, *J* = 7.6 Hz, 0.5H), 7.08 (d, *J* = 7.5 Hz, 0.5H), 2.80–2.70 (m, 0.5H), 2.52 (s, 1.5H), 2.44 (s, 1.5H), 2.42–2.33 (m, 1.5H), 1.62 (s, 1.5H), 1.56–1.42 (m, 3.5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) **3ja** and its isomer **3ja'**: δ = 149.9, 149.6, 146.3, 145.4, 141.0, 140.5, 140.5, 140.3, 137.9, 134.5, 130.6, 128.9, 128.2, 128.0, 128.0, 127.9, 122.8, 122.5, 122.3, 121.1, 120.4, 120.2, 120.0, 119.9, 118.2, 51.5, 49.8, 36.4, 34.0, 26.7, 24.5, 21.7, 19.2, 12.7, 12.6 ppm. HRMS m/z: calcd for $C_{18}H_{17}NNa$ $[M+Na]^+$ 270.1253, found: 270.1256.

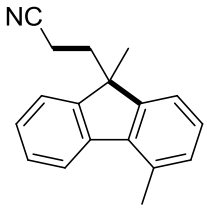


3-(9-methyl-3-nitro-9*H*-fluoren-9-yl)propanenitrile (3ka): Yield = 23%. Yellow oil. IR (KBr) ν = 2961, 2923, 2851, 2245, 1519, 1343, 1090, 1025, 782, 728 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.55 (d, *J* = 2.0 Hz, 1H), 8.25 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.87–7.79 (m, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.50–7.42 (m, 3H), 2.48 (t, *J* = 8.1 Hz, 2H), 1.65–1.55 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 149.4, 148.7, 142.1, 138.2, 129.7, 128.8, 123.6, 123.2, 123.1, 121.4, 119.1, 115.6, 50.7, 35.9, 26.5, 12.7 ppm. HRMS m/z: $C_{17}H_{14}N_2NaO_2$ $[M+Na]^+$ 301.0947, found: 301.0941.

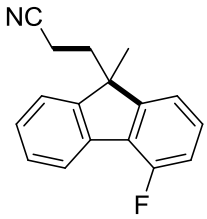


3-(9-methyl-1-nitro-9*H*-fluoren-9-yl)propanenitrile (3ka'): Yield = 40%. Yellow oil. IR (KBr) ν = 2970, 2921, 2245, 1528, 1458, 1346, 1066, 762, 728 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.02 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.96 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.81–7.73 (m, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.51–7.41 (m, 3H), 3.27–3.17 (m, 1H), 2.42–2.32 (m, 1H), 1.63 (s, 3H), 1.61–1.49 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5, 148.4, 144.6, 141.1, 137.6, 129.8, 129.7, 128.5, 125.3, 123.8, 122.7, 120.6, 119.1, 77.6, 77.2, 76.9, 53.2, 34.5, 23.9, 13.0 ppm. HRMS m/z: calcd

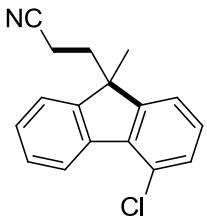
for: $C_{17}H_{14}N_2NaO_2$ $[M+Na]^+$ 301.0947, found: 301.0938.



3-(4,9-dimethyl-9*H*-fluoren-9-yl)propanenitrile (3la): Yield = 57%. Colourless oil. IR (KBr) ν = 2958, 2924, 2862, 2246, 1453, 1376, 1031, 792, 734 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.86 (d, *J* = 7.5 Hz, 1H), 7.42–7.33 (m, 3H), 7.28–7.23 (m, 2H), 7.15 (dd, *J* = 6.5, 1.4 Hz, 1H), 2.70 (s, 3H), 2.44–2.37 (m, 2H), 1.50 (s, 3H), 1.49–1.43 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.6, 141.4, 138.4, 133.7, 130.4, 128.0, 127.7, 127.3, 123.6, 122.7, 120.2, 119.9, 49.7, 36.5, 27.0, 21.2, 12.6 ppm. HRMS m/z: calcd for $C_{18}H_{17}NNa$ $[M+Na]^+$ 270.1253, found: 270.1245.

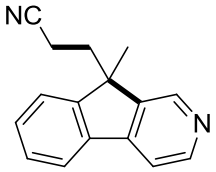


3-(4-fluoro-9-methyl-9*H*-fluoren-9-yl)propanenitrile (3ma): Yield = 76%. Colourless oil. IR (KBr) ν = 2961, 2921, 2850, 2246, 1580, 1454, 1243, 1223, 951, 795, 729 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.92 (d, *J* = 6.8 Hz, 1H), 7.43–7.36 (m, 3H), 7.34–7.28 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.10–7.04 (m, 1H), 2.45–2.39 (m, 2H), 1.53 (s, 3H), 1.53–1.48 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 157.4, 152.2, 148.6, 137.5, 137.5, 129.3, 129.3, 128.5, 128.2, 124.1, 124.0, 122.6, 119.6, 118.5, 118.5, 115.3, 115.1, 50.9, 36.4, 26.7, 12.7 ppm. HRMS m/z: calcd for $C_{17}H_{14}FNNa$ $[M+Na]^+$ 274.1002, found: 274.1009.

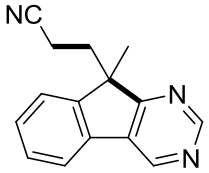


3-(4-chloro-9-methyl-9*H*-fluoren-9-yl)propanenitrile (3na): Yield = 49%. Colourless oil. IR (KBr) ν = 2961, 2925, 2864, 2246, 1570, 1443, 1424, 1128, 797, 730 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.43–8.37 (m, 1H), 7.45–7.38 (m, 3H), 7.35 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.31–7.26 (m,

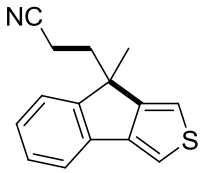
2H), 2.44–2.39 (m, 2H), 1.52 (s, 3H), 1.51–1.46 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8, 149.3, 139.1, 137.2, 129.7, 129.5, 128.6, 128.6, 128.2, 124.4, 122.5, 121.1, 119.6, 50.3, 36.4, 26.9, 12.6 ppm. HRMS m/z: calcd for $C_{17}H_{14}ClNNa$ $[M+Na]^+$ 290.0707, found: 290.0716.



3-(9-methyl-9*H*-indeno[2,1-*c*]pyridin-9-yl)propanenitrile (3oa): Yield = 56%. White solid. M.p. 93.2–94.7 °C. IR (KBr) ν = 2987, 2971, 2901, 2237, 1600, 1407, 1251, 1075, 742 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.69 (s, 1H), 8.65 (d, J = 4.8 Hz, 1H), 7.83–7.79 (m, 1H), 7.63 (d, J = 4.9 Hz, 1H), 7.55–7.43 (m, 3H), 2.58–2.42 (m, 2H), 1.61 (s, 3H), 1.59–1.49 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 149.5, 148.2, 145.0, 143.9, 138.0, 130.6, 128.6, 123.2, 122.2, 119.2, 115.3, 49.9, 35.9, 26.3, 12.8 ppm. HRMS m/z: calcd for $C_{16}H_{14}N_2Na$ $[M+Na]^+$ 257.1049, found: 257.1050.

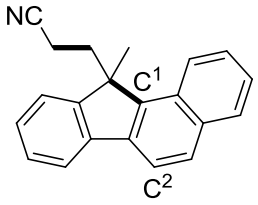


3-(9-methyl-9*H*-indeno[2,1-*d*]pyrimidin-9-yl)propanenitrile (3pa): Yield = 68%. White solid. M.p. 89.3–90.7 °C. IR (KBr) ν = 2967, 2927, 2867, 2246, 1585, 1557, 1396, 1292, 1123, 1000, 809, 755 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 9.16 (s, 1H), 9.04 (s, 1H), 7.85–7.79 (m, 1H), 7.53–7.44 (m, 3H), 2.70–2.60 (m, 1H), 2.34–2.24 (m, 1H), 1.88–1.75 (m, 2H), 1.56 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.3, 157.2, 148.4, 147.6, 134.9, 132.2, 130.0, 128.8, 123.5, 122.0, 119.0, 50.8, 34.0, 24.3, 12.9 ppm. HRMS m/z: calcd for $C_{15}H_{14}N_3$ $[M+H]^+$ 236.1182, found: 236.1192.

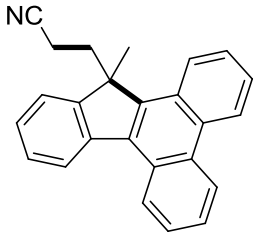


3-(8-methyl-8*H*-indeno[1,2-*c*]thiophen-8-yl)propanenitrile (3qa): Yield = 37%. White solid. M.p. 62.4–64.3 °C. IR (KBr) ν = 2955, 2922, 2853, 2242, 1605, 1447, 1277, 1117, 1019, 751, 715

cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.50–7.45 (m, 1H), 7.40 (d, J = 4.9 Hz, 1H), 7.34–9.29 (m, 2H), 7.25–7.20 (m, 2H), 2.46–2.31 (m, 2H), 1.75–1.62 (m, 2H), 1.57 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 151.3, 145.4, 138.2, 129.6, 128.0, 125.7, 122.5, 119.8, 119.7, 119.2, 50.0, 36.6, 26.8, 12.8 ppm. HRMS m/z: calcd for $C_{15}H_{13}NNaS$ $[M+Na]^+$ 262.0661, found: 262.0669.

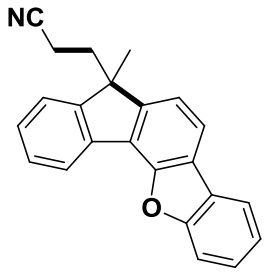


3-(11-methyl-11*H*-benzo[*a*]fluoren-11-yl)propanenitrile (3ra) and 3-(11-methyl-11H-benzo[b]fluoren-11-yl)propanenitrile (3ra'): Yield = 81% (C^1/C^2 isomers, **3ra**/**3ra'** = 4:1). White solid. IR (KBr) ν = 2965, 2924, 2851, 2244, 1455, 1255, 1021, 824, 752 cm^{-1}. The ^1H NMR spectrum of the isolated product showed a 4:1 mixture of **3ra** and its isomer **3ra'**. ^1H NMR (400MHz, $CDCl_3$) **3ra** and its isomer **3ra'**: δ = 8.16–8.07 (m, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.93–7.84 (m, 2H), 7.80 (d, J = 6.7 Hz, 1H), 7.64–7.56 (m, 1H), 7.54–7.40 (m, 2H), 7.45–7.36 (m, 2H), 3.01–2.91 (m, 0.8H), 2.68–2.55 (m, 0.8H), 2.53–2.45 (m, 0.4H), 1.77 (s, 2.4H), 1.61 (s, 0.6H), 1.58–1.50 (m, 0.4H), 1.37–1.31 (m, 1.6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) **3ra** and its isomer **3ra'**: δ = 151.1, 149.6, 147.5, 142.6, 140.5, 139.8, 138.9, 138.4, 134.2, 133.8, 133.6, 130.2, 129.9, 129.7, 128.8, 128.4, 128.4, 128.2, 128.1, 127.8, 127.1, 126.2, 126.1, 125.5, 123.2, 123.1, 122.2, 121.6, 121.1, 120.2, 119.8, 119.8, 118.9, 118.7, 52.0, 49.8, 37.2, 35.6, 27.7, 26.0, 12.8, 12.7 ppm. HRMS m/z: calcd for $C_{21}H_{17}NNa$ $[M+Na]^+$ 306.1253, found: 306.1251.

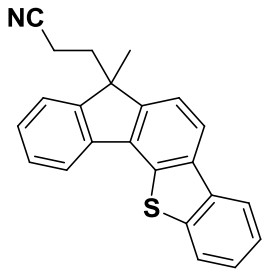


3-(13-methyl-13*H*-indeno[1,2-*l*]phenanthren-13-yl)propanenitrile (3sa): Yield = 76%. Coless oil. IR (KBr) ν = 2987, 2971, 2243, 1732, 1455, 1374, 1241, 1066, 885, 776, 749 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.70–8.63 (m, 2H), 8.38 (s, 1H), 8.33–8.27 (m, 1H), 7.98–7.92 (m, 1H), 7.79–7.73 (m, 2H), 7.66–7.59 (m, 3H), 7.47–7.40 (m, 2H), 2.64–2.44 (m, 2H), 1.86 (s, 3H), 1.75–1.58 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7, 139.1, 132.1, 131.9, 130.7, 130.5, 129.1, 129.1, 127.7, 127.4, 127.4, 127.2, 127.1, 126.9, 126.8, 124.6, 123.6, 123.0, 121.9, 120.6, 119.9, 43.8,

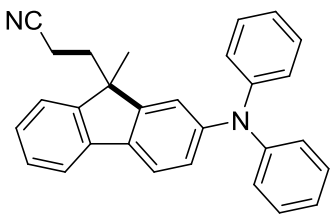
42.4, 34.5, 13.4 ppm. HRMS m/z: calcd for $C_{25}H_{19}NNa$ $[M+Na]^+$ 356.1410, found: 356.1405.



3-(7-methyl-7*H*-benzo[*d*]fluoreno[4,3-*b*]furan-7-yl)propanenitrile (3ta): Yield = 82%. White solid. M.p. 45–47 °C. IR (KBr) ν = 2987, 2971, 2901, 2244, 1579, 1442, 1184, 1075, 826, 731 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.27 (d, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 7.3 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.53–7.48 (m, 2H), 7.47–7.37 (m, 4H), 2.54–2.47 (m, 2H), 1.62 (s, 3H), 1.55–1.49 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 151.1, 149.3, 149.0, 138.1, 128.5, 127.9, 127.4, 124.8, 124.6, 124.2, 123.8, 123.3, 122.6, 120.8, 120.0, 119.8, 117.2, 112.2, 51.3, 36.6, 26.9, 12.7 ppm. HRMS m/z: calcd for $C_{23}H_{17}NNaO$ $[M+Na]^+$ 346.1202, found: 346.1210.

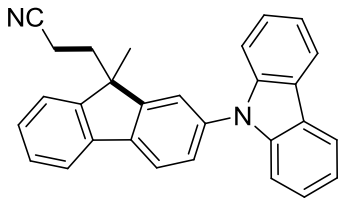


3-(7-methyl-7*H*-benzo[*d*]fluoreno[4,3-*b*]thiophen-7-yl)propanenitrile (3ua): Yield = 70%. White solid. M.p. 45–47 °C. IR (KBr) ν = 2967, 2923, 2245, 1473, 1396, 1021, 1022, 824, 767, 736 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.26–8.18 (m, 2H), 8.00–7.94 (m, 2H), 7.58–7.41 (m, 6H), 2.58–2.49 (m, 2H), 1.62 (s, 3H), 1.54–1.49 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8, 148.2, 139.7, 139.7, 136.6, 135.2, 134.5, 132.7, 128.4, 128.0, 127.1, 125.0, 123.3, 122.7, 122.7, 121.9, 121.2, 119.8, 119.0, 50.9, 36.4, 26.8, 12.7 ppm. HRMS m/z: calcd for $C_{23}H_{17}NNaS$ $[M+Na]^+$ 362.0974, found: 362.0985.

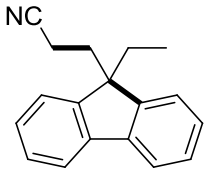


3-(2-(diphenylamino)-9-methyl-9*H*-fluoren-9-yl)propanenitrile (3va): Yield = 63%. White

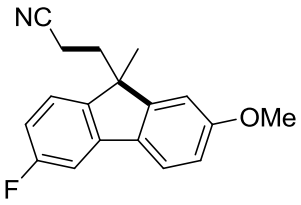
solid. M.p. 120.0–121.5 °C. IR (KBr) ν = 2956, 2923, 2244, 1584, 1486 ,1446, 1273, 1024, 756, 739, 696 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.62 (d, J = 7.4 Hz, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.37–7.26 (m, 7H), 7.16–7.10 (m, 5H), 7.08–7.02 (m, 3H), 2.37–2.20 (m, 2H), 1.59–1.55 (m, 2H), 1.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 149.1, 148.3, 148.0, 140.3, 134.8, 129.6, 128.1, 127.1, 124.6, 123.8, 123.3, 122.7, 121.1, 119.9, 119.8, 118.1, 50.1, 36.2, 26.5, 12.7 ppm. HRMS m/z: calcd for $C_{29}H_{24}N_2Na$ $[M+Na]^+$ 423.1832, found: 423.1817.



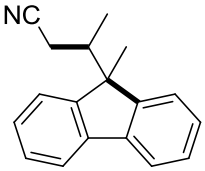
3-(2-(9*H*-carbazol-9-yl)-9-methyl-9*H*-fluoren-9-yl)propanenitrile (3wa): Yield = 77%. White solid. M.p. 62.0–63.5 °C. IR (KBr) ν = 2989, 2953, 2244, 1595, 1495, 1450, 1334, 1229, 833, 749, 739, 723 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 8.16 (d, J = 7.8 Hz, 2H), 7.95–7.89 (m, 1H), 7.79 (d, J = 7.1 Hz, 1H), 7.61–7.56 (m, 2H), 7.47–7.39 (m, 7H), 7.33–7.28 (m, 2H), 2.48–2.36 (m, 2H), 1.69–1.63 (m, 2H), 1.58 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.2, 149.4, 141.1, 139.7, 139.6, 137.4, 128.4, 128.4, 127.1, 126.3, 123.7, 123.0, 121.7, 121.7, 120.7, 120.6, 120.3, 119.5, 109.9, 50.5, 36.2, 26.6, 12.8 ppm. HRMS m/z: calcd for $C_{29}H_{22}N_2Na$ $[M+Na]^+$ 421.1675, found: 421.1680.



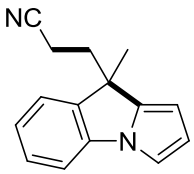
3-(9-ethyl-9*H*-fluoren-9-yl)propanenitrile (4aa): Yield = 46%. White solid. M.p. 78.2–80.1 °C. IR (KBr) ν = 2964, 2924, 2853, 2245, 1448, 1363, 1169, 1081, 1021, 760, 733 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.74–7.69 (m, 2H), 7.40–7.33 (m, 6H), 2.45–2.38 (m, 2H), 2.06 (q, J = 7.4 Hz, 2H), 1.55–1.46 (m, 2H), 0.33 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.4, 141.6, 128.0, 127.9, 122.9, 120.3, 120.0, 55.0, 35.8, 33.0, 12.4, 8.4 ppm. HRMS m/z: calcd for $C_{18}H_{17}NNa$ $[M+Na]^+$ 270.1253, found: 270.1250.



3-(6-fluoro-2-methoxy-9-methyl-9*H*-fluoren-9-yl)propanenitrile (4ca): Yield = 66%. Colourless oil. IR (KBr) ν = 2988, 2963, 2926, 2245, 1614, 1584, 1487, 1431, 1284, 1172, 1037, 871, 823, 743 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.3 Hz, 1H), 7.30–7.26 (m, 2H), 6.99–6.88 (m, 3H), 3.89 (s, 3H), 2.40–2.33 (m, 2H), 1.53–1.51 (m, 1H), 1.50 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 162.2, 160.7, 151.9, 144.1, 144.0, 142.5, 142.4, 132.3, 123.8, 123.7, 121.7, 119.7, 113.8, 113.6, 113.4, 108.8, 107.0, 106.7, 55.8, 49.8, 36.4, 26.8, 12.6 ppm. HRMS m/z: calcd for $C_{18}H_{16}FNNaO$ $[M+Na]^+$ 304.1108, found: 304.1111.

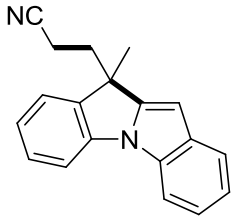


3-(9-methyl-9*H*-fluoren-9-yl)butanenitrile (4da): Yield = 57%. IR (KBr) ν = 2965, 2925, 2245, 1446, 1383, 1296, 1026, 940, 765, 735 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.76–7.68 (m, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.41–7.29 (m, 5H), 2.56–2.47 (m, 1H), 1.81 (dd, *J* = 16.7, 3.4 Hz, 1H), 1.55 (s, 3H), 1.52–1.46 (m, 1H), 1.33 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.7, 140.7, 140.3, 128.1, 128.1, 128.0, 127.6, 124.5, 122.7, 120.5, 120.3, 119.7, 52.9, 40.1, 23.9, 20.4, 15.5 ppm. HRMS m/z: calcd for $C_{18}H_{17}NNa$ $[M+Na]^+$ 270.1253, found: 270.1262.

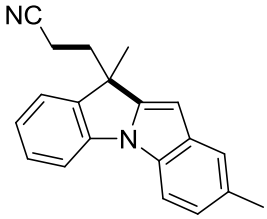


3-(9-methyl-9*H*-pyrrolo[1,2-*a*]indol-9-yl)propanenitrile (5aa): Yield = 35%. Colourless oil. IR (KBr) ν = 2969, 2922, 2245, 1712, 1614, 1491, 1379, 1258, 1066, 750, 708 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.35–7.27 (m, 2H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.16–7.12 (m, 1H), 7.02 (dd, *J* = 2.8, 0.9 Hz, 1H), 6.37 (t, *J* = 3.1 Hz, 1H), 6.04 (dd, *J* = 3.3, 0.9 Hz, 1H), 2.32–2.24 (m, 2H), 1.92–1.84 (m, 1H), 1.76–1.69 (m, 1H), 1.55 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8, 141.5, 140.2, 128.6, 124.1, 123.6, 119.7, 113.8, 110.5, 110.2, 101.3, 77.6, 77.2, 76.9, 44.9, 37.0, 26.7, 13.2 ppm.

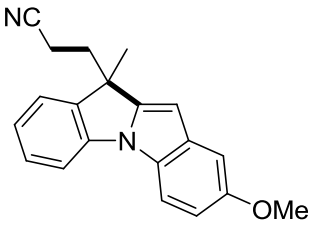
HRMS m/z: calcd for $C_{15}H_{15}N_2$ $[M+H]^+$ 223.1230, found: 223.1235.



3-(10-methyl-10*H*-indolo[1,2-*a*]indol-10-yl)propanenitrile (5ba): Yield = 60%. Colourless oil. IR (KBr) ν = 2963, 2924, 2865, 2245, 1601, 1489, 1453, 1180, 1010, 785, 744, 694 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.77–7.72 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.44–7.38 (m, 1H), 7.35–7.29 (m, 2H), 7.23–7.14 (m, 2H), 6.43 (s, 1H), 2.41–2.35 (m, 2H), 1.96–1.86 (m, 1H), 1.79–1.73 (m, 1H), 1.63 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5, 140.5, 140.3, 133.4, 131.0, 129.1, 123.6, 123.4, 122.6, 121.6, 121.1, 119.5, 111.1, 110.8, 95.9, 44.7, 37.2, 27.3, 13.3 ppm. HRMS m/z: calcd for $C_{19}H_{16}N_2Na$ $[M+Na]^+$ 295.1206, found: 295.1210.

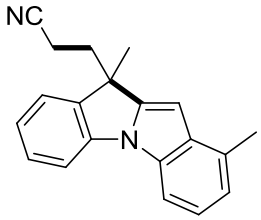


3-(2,10-dimethyl-10*H*-indolo[1,2-*a*]indol-10-yl)propanenitrile (5ca): Yield = 61%. Colourless oil. IR (KBr) ν = 2962, 2922, 2855, 2246, 1608, 1572, 1486, 1300, 1019, 790, 746, 693 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.45–7.36 (m, 2H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.17–7.10 (m, 2H), 6.34 (s, 1H), 2.48 (s, 3H), 2.40–2.33 (m, 2H), 1.94–1.84 (m, 1H), 1.77–1.72 (m, 1H), 1.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.6, 140.6, 140.2, 133.7, 130.5, 129.2, 129.0, 124.0, 123.5, 123.1, 121.4, 119.5, 110.7, 110.6, 95.4, 44.7, 37.2, 27.3, 21.7, 13.3 ppm. HRMS m/z: calcd for $C_{20}H_{18}N_2Na$ $[M+Na]^+$ 309.1362, found: 309.1374.

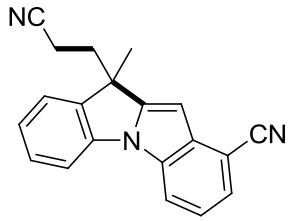


3-(2-methoxy-10-methyl-10*H*-indolo[1,2-*a*]indol-10-yl)propanenitrile (5da): Yield = 60%. White solid. M.p. 91.4–93.0 °C. IR (KBr) ν = 2958, 2928, 2243, 1573, 1485, 1186, 1039, 875, 776,

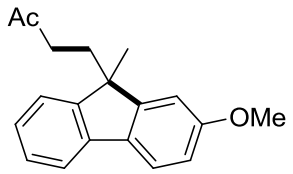
732 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.63 (d, J = 8.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.42–7.37 (m, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.17–7.10 (m, 2H), 6.95 (dd, J = 8.8, 2.5 Hz, 1H), 6.36 (s, 1H), 3.88 (s, 3H), 2.40–2.33 (m, 2H), 1.95–1.85 (m, 1H), 1.79–1.73 (m, 1H), 1.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 149.2, 140.5, 140.1, 134.1, 129.0, 126.1, 123.5, 123.1, 119.5, 112.2, 111.6, 110.3, 103.9, 95.6, 56.1, 44.8, 37.1, 27.2, 13.3 ppm. HRMS m/z: calcd for $C_{20}H_{18}N_2NaO$ $[M+Na]^+$ 325.1311, found: 325.1318.



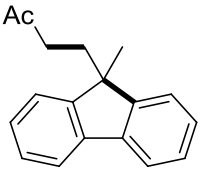
3-(1,10-dimethyl-10*H*-indolo[1,2-*a*]indol-10-yl)propanenitrile (5ea): Yield = 65%. Colourless oil. IR (KBr) ν = 2968, 2922, 2245, 1598, 1499, 1476, 1225, 1076, 1046, 761, 693 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.61–7.54 (m, 2H), 7.44–7.38 (m, 1H), 7.34 (d, J = 7.4 Hz, 1H), 7.24–7.19 (m, 1H), 7.18–7.13 (m, 1H), 7.04–6.99 (m, 1H), 6.45 (d, J = 0.5 Hz, 1H), 2.58 (s, 3H), 2.43–2.34 (m, 2H), 1.96–1.86 (m, 1H), 1.78–1.72 (m, 1H), 1.64 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.9, 140.6, 140.3, 133.1, 131.1, 130.6, 129.0, 123.6, 123.4, 122.7, 121.4, 119.6, 110.8, 108.7, 94.3, 77.6, 77.2, 76.9, 44.8, 37.2, 27.4, 19.0, 13.4 ppm. HRMS m/z: calcd for $C_{20}H_{18}N_2Na$ $[M+Na]^+$ 309.1362, found: 309.1373.



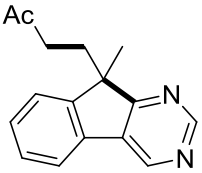
10-(2-cyanoethyl)-10-methyl-10*H*-indolo[1,2-*a*]indole-1-carbonitrile (5fa): Yield = 61%. Colourless oil. IR (KBr) ν = 2987, 2971, 2901, 2218, 1617, 1493, 1227, 1074, 774, 748 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ = 7.97 (d, J = 8.3 Hz, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.57–7.53 (m, 1H), 7.50–7.44 (m, 1H), 7.42–7.34 (m, 2H), 7.26–7.23 (m, 1H), 6.70 (d, J = 0.5 Hz, 1H), 2.49–2.39 (m, 2H), 1.98–1.90 (m, 1H), 1.84–1.76 (m, 1H), 1.68 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4, 140.2, 139.7, 134.7, 130.6, 129.3, 126.0, 124.6, 124.0, 122.3, 118.9, 118.4, 115.5, 111.2, 104.1, 95.0, 45.2, 36.8, 27.1, 13.4 ppm. HRMS m/z: calcd for $C_{20}H_{16}N_3$ $[M+H]^+$ 298.1339, found: 298.1343.



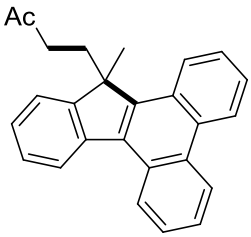
4-(2-methoxy-9-methyl-9*H*-fluoren-9-yl)butan-2-one (5ab): Yield = 46%. Colourless oil. IR (KBr) ν = 1712, 1456, 1253, 1036, 823, 736 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.63 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.35–7.30 (m, 2H), 7.23 (dd, *J* = 7.4, 0.8 Hz, 1H), 6.90 (dd, *J* = 7.3, 2.1 Hz, 2H), 3.87 (s, 3H), 2.34–2.24 (m, 2H), 1.79 (s, 3H), 1.66 (d, *J* = 8.1 Hz, 2H), 1.48 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.2, 160.0, 153.0, 150.5, 140.4, 133.3, 127.5, 126.5, 122.9, 121.0, 119.3, 113.2, 108.8, 55.8, 50.1, 38.9, 34.0, 30.1, 27.2 ppm. HRMS m/z: calcd for $C_{19}H_{21}O_2$ $[M+H]^+$ 281.1536, found: 281.1539.



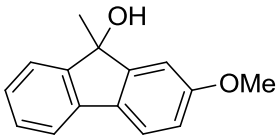
4-(9-methyl-9*H*-fluoren-9-yl)butan-2-one (5db): Yield = 50%. Colourless oil. IR (KBr) ν = 1713, 1444, 1359, 1158, 765, 735 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.73 (dd, *J* = 6.8, 1.8 Hz, 2H), 7.39–7.37 (m, 1H), 7.36 (s, 2H), 7.34–7.29 (m, 3H), 2.37–2.30 (m, 2H), 1.77 (s, 3H), 1.66–1.61 (m, 2H), 1.50 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.1, 151.0, 140.4, 127.6, 127.5, 123.0, 120.1, 50.1, 38.8, 33.9, 30.1, 27.1 ppm. HRMS m/z: calcd for $C_{18}H_{19}O$ $[M+H]^+$ 251.1430, found: 251.1430.



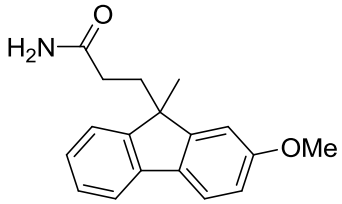
4-(9-methyl-9*H*-indeno[2,1-*d*]pyrimidin-9-yl)butan-2-one (5pb): Yield = 47%. Colourless oil. IR (KBr) ν = 1711, 1585, 1556, 1395, 1161, 809, 754 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 9.15 (s, 1H), 9.03 (s, 1H), 7.81 (dd, *J* = 5.3, 2.4 Hz, 1H), 7.51–7.41 (m, 3H), 2.52–2.42 (m, 1H), 2.34–2.25 (m, 1H), 1.89 (s, 3H), 1.84–1.78 (m, 2H), 1.54 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.9, 178.8, 157.0, 149.2, 148.0, 134.8, 132.2, 129.7, 128.2, 123.7, 121.6, 50.8, 38.6, 32.1, 30.0, 24.5 ppm. HRMS m/z: calcd for $C_{16}H_{17}N_2O$ $[M+H]^+$ 253.1335, found: 253.1344.



4-(13-methyl-13*H*-indeno[1,2-*l*]phenanthren-13-yl)butan-2-one (5sb): Yield = 54%. Colourless oil. IR (KBr) ν = 1710, 1455, 1159, 776, 750 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.67–8.61 (m, 2H), 8.38 (s, 1H), 8.34–8.25 (m, 1H), 7.95 (dd, *J* = 5.9, 3.3 Hz, 1H), 7.74 (dd, *J* = 8.5, 6.6 Hz, 2H), 7.65–7.57 (m, 3H), 7.42–7.36 (m, 2H), 2.56–2.48 (m, 1H), 2.46–2.37 (m, 1H), 1.90–1.82 (m, 1H), 1.82 (d, *J* = 4.4 Hz, 3H), 1.80–1.75 (m, 1H), 1.74 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.1, 141.5, 140.9, 132.1, 131.7, 130.5, 130.5, 129.0, 128.8, 127.8, 127.2, 127.2, 127.1, 126.8, 124.7, 123.3, 123.0, 121.2, 120.1, 42.0, 41.3, 39.9, 35.4, 30.1 ppm. HRMS m/z: calcd for $C_{26}H_{23}O$ $[M+H]^+$ 351.1743, found: 351.1736.



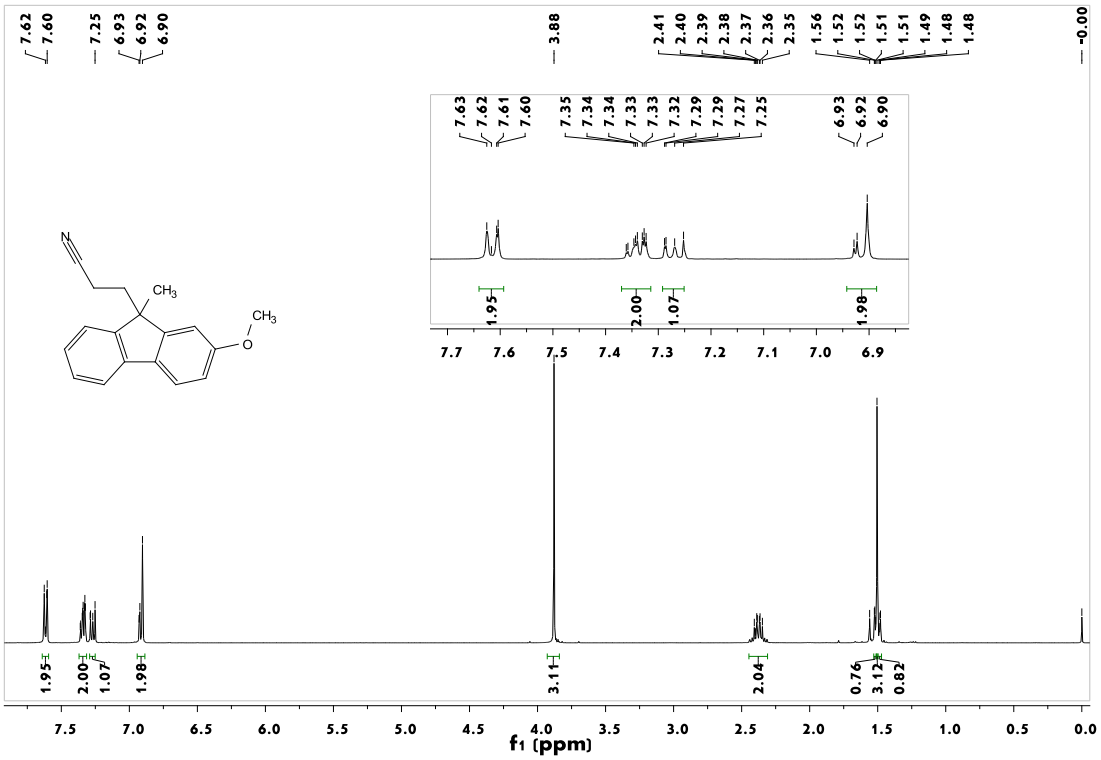
2-methoxy-9-methyl-9*H*-fluoren-9-ol (10): Yield = 35%. White solid. M.p. 121.2–123.0 °C. IR (KBr) ν = 3314, 2922, 2852, 1609, 1459, 1261, 1092, 1033, 803, 735 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 8.3, 2.6 Hz, 3H), 7.36–7.30 (m, 1H), 7.26–7.22 (m, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 6.92–6.88 (m, 1H), 3.87 (s, 3H), 1.98 (s, 1H), 1.73 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5, 152.0, 149.7, 139.1, 131.6, 129.2, 127.1, 123.3, 121.2, 119.5, 114.9, 109.1, 76.9, 55.8, 26.5 ppm. HRMS m/z: calcd for $C_{15}H_{13}O$ $[M–OH]^+$ 209.0961, found: 209.0959.

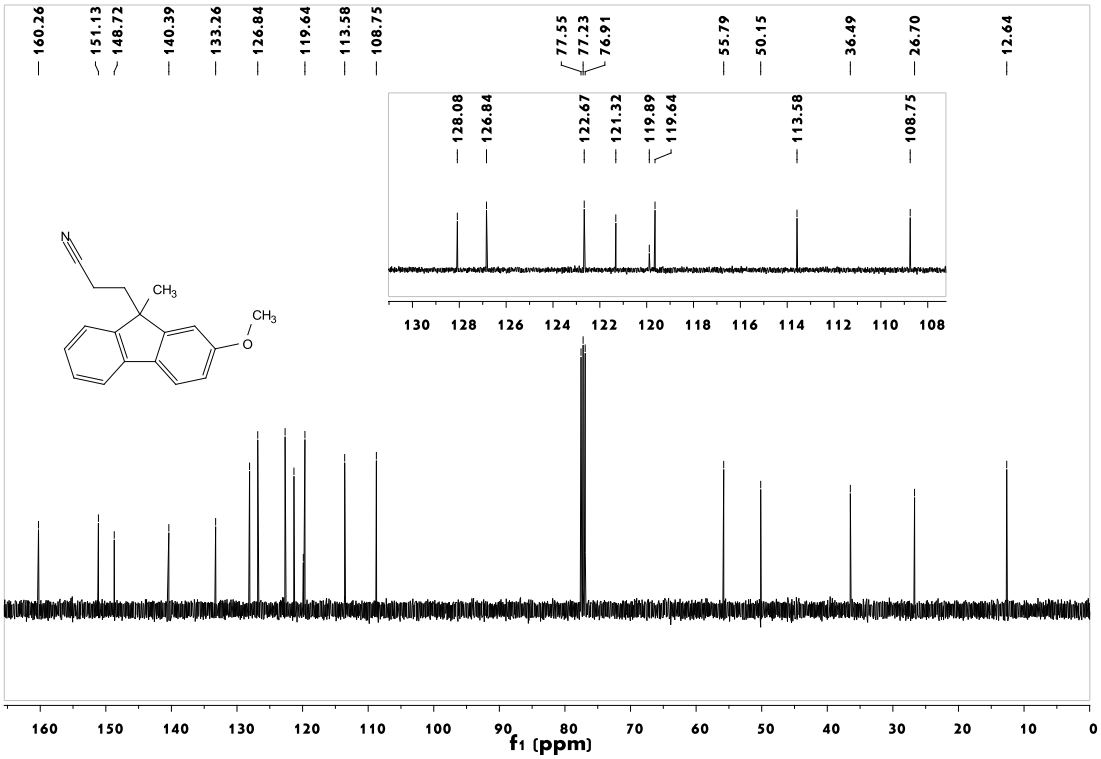


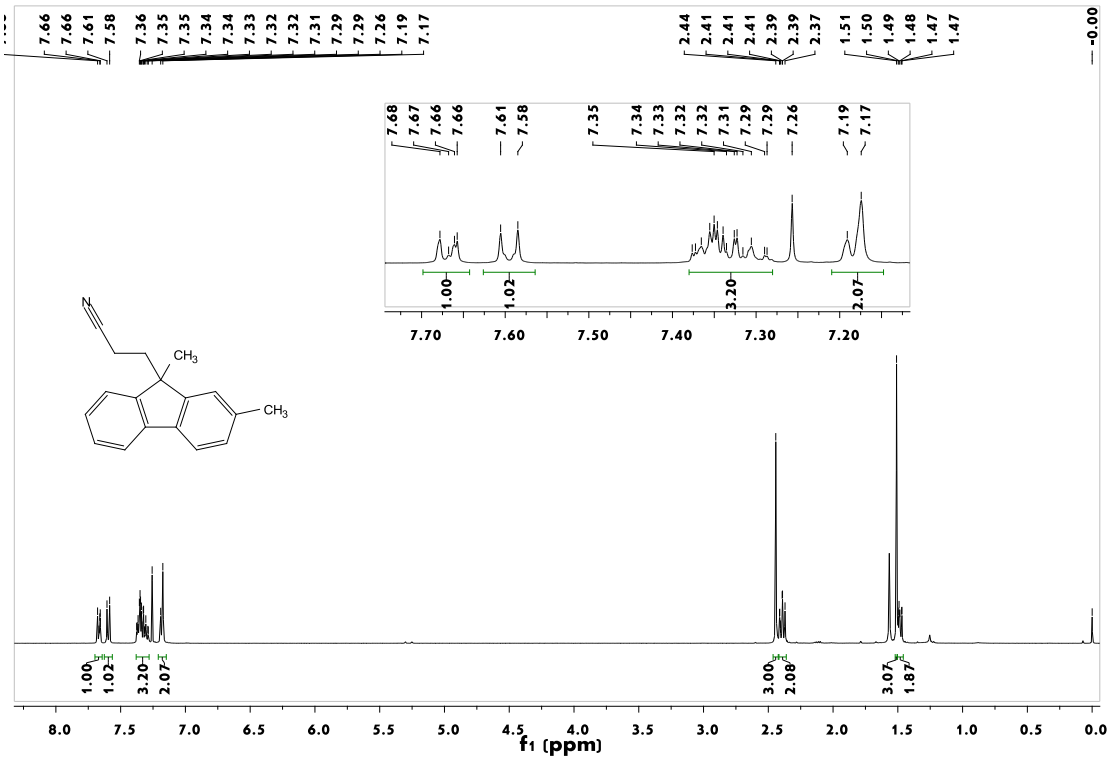
3-(2-methoxy-9-methyl-9*H*-fluoren-9-yl)propanamide (11): Yield = 62%. Colourless oil. IR (KBr) ν = 3449, 3334, 3189, 2956, 2923, 2854, 1660, 1611, 1458, 1272, 1036, 776, 736 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.3 Hz, 2H), 7.39–7.29 (m, 2H), 7.26–7.22 (m, 1H), 6.97–6.86 (m, 2H), 5.08 (d, *J* = 99.6 Hz, 2H), 3.87 (s, 3H), 2.44–2.31 (m, 2H), 1.50 (s, 3H), 1.47–1.39 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.5, 160.1, 152.9, 150.4, 140.3, 133.2, 127.5,

126.6, 122.9, 120.9, 119.3, 113.3, 108.8, 55.8, 50.3, 35.6, 30.7, 27.1 ppm. HRMS m/z: calcd for $C_{18}H_{19}NNaO_2$ $[M+Na]^+$ 304.1308, found: 304.1317.

The ^{1}H , ^{13}C spectra of compounds:



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2.44 2.41 2.41 2.41 2.39 2.39 2.37 1.51 1.50 1.49 1.48 1.47 1.47
-0.00
7.68 7.67 7.66 7.66 7.61 7.58 7.35 7.34 7.33 7.32 7.32 7.31 7.29 7.29 7.26 7.19 7.17
1.00 1.02 3.20 2.07
7.70 7.60 7.50 7.40 7.30 7.20
CH3
CH3
1.00 1.02 3.20 2.07 3.00 2.08 3.07 1.87
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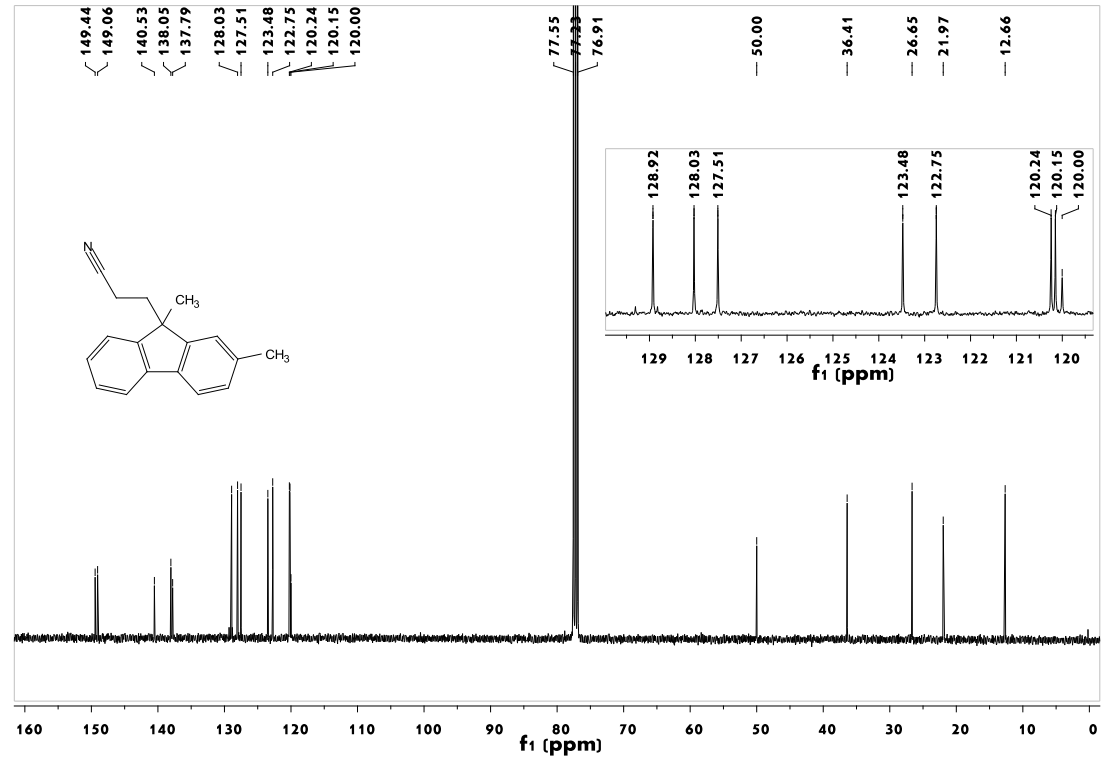
f1 (ppm)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77.55 77.33 76.91
50.00 36.41 26.65 21.97 12.66
128.92 128.03 127.51 123.48 122.75 120.24 120.15 120.00
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f1 (ppm)
CH3
CH3
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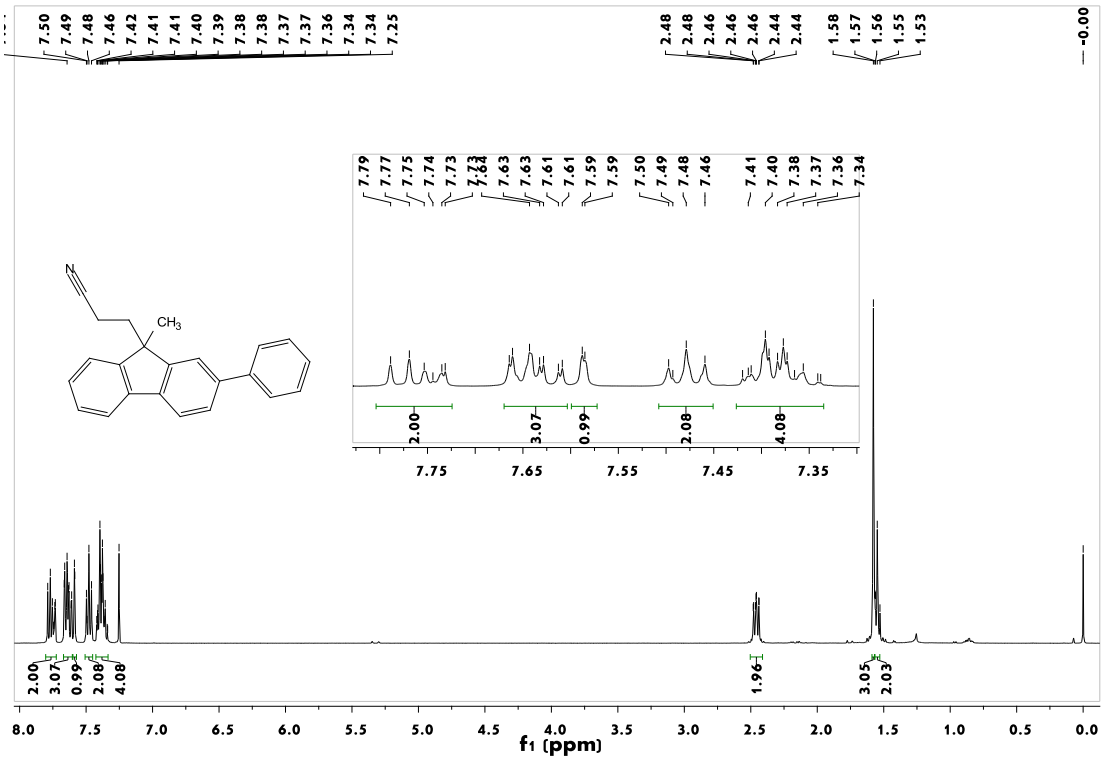
f1 (ppm)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2.48 2.48 2.46 2.46 2.46 2.44 2.44
1.58 1.57 1.56 1.55 1.53
-0.00
7.79 7.77 7.75 7.74 7.73 7.64 7.63 7.63 7.61 7.61 7.59 7.59 7.50 7.49 7.48 7.46 7.41 7.40 7.38 7.37 7.36 7.34
N
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1.96
3.05 2.03
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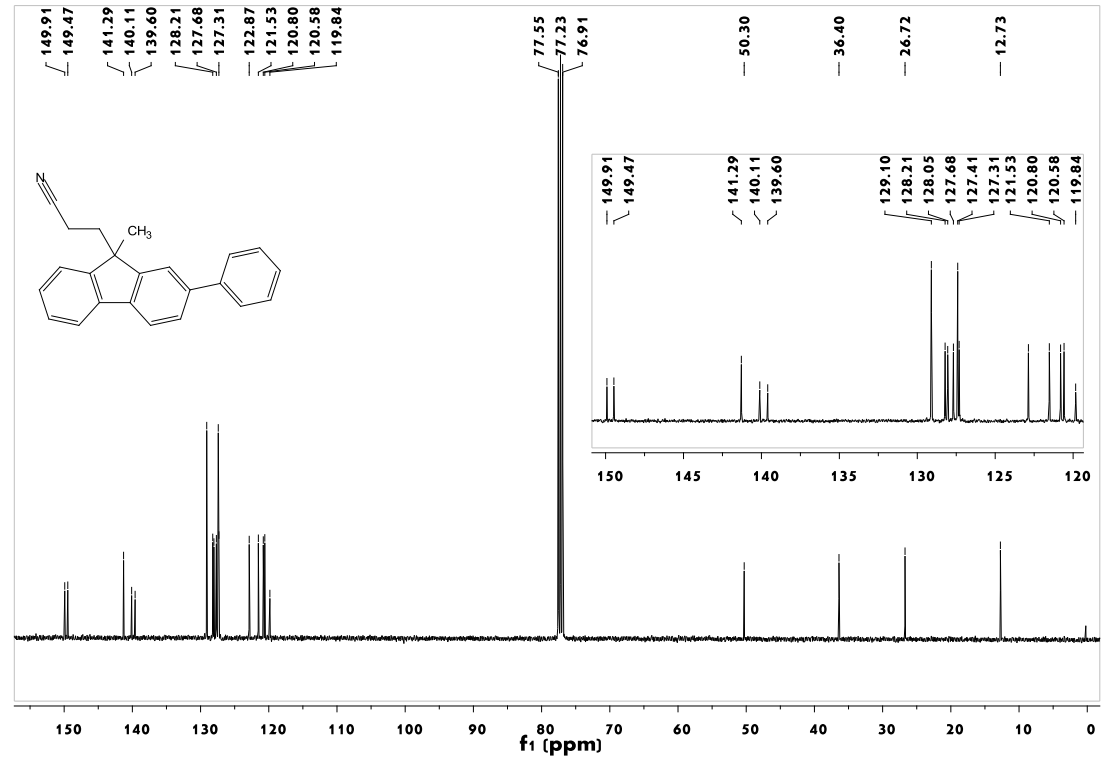
f1 (ppm)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12.73
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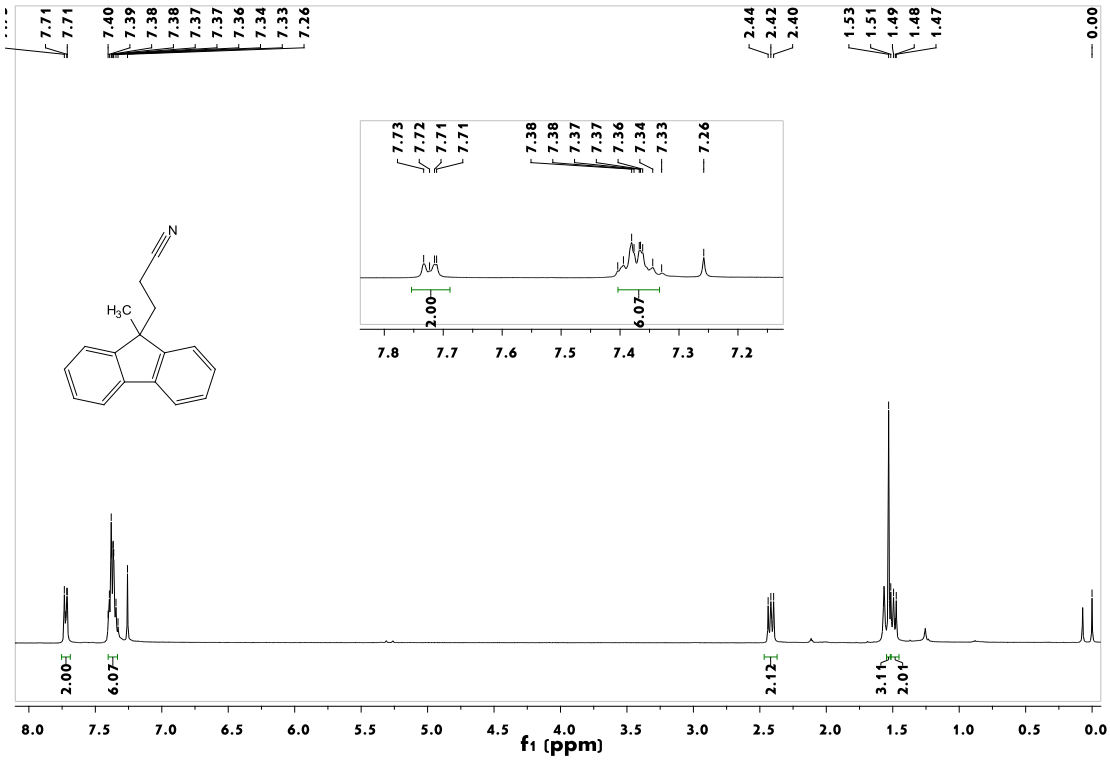
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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1.51
1.49
1.48
1.47
0.00
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7.72
7.71
7.71
7.38
7.38
7.37
7.37
7.36
7.34
7.33
7.26
2.00
6.07
7.8
7.7
7.6
7.5
7.4
7.3
7.2
N
H3C
2.00
6.07
2.12
3.11
2.01
8.0
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7.0
6.5
6.0
5.5
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2.5
2.0
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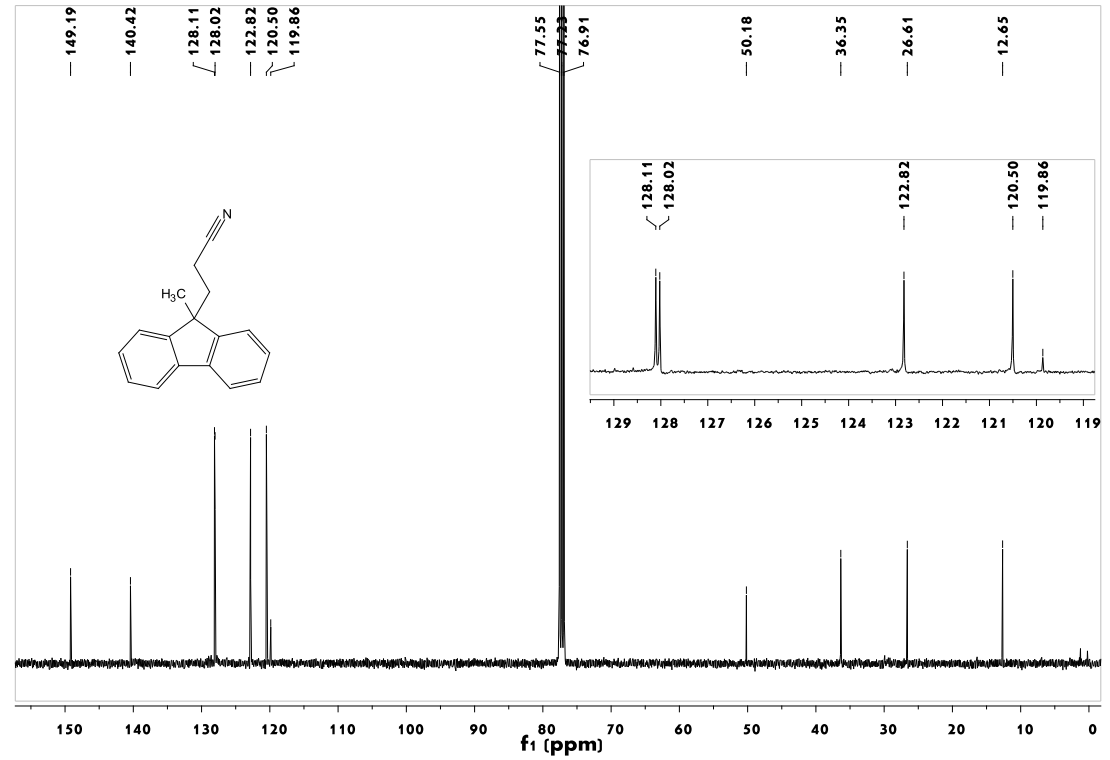
f1 (ppm)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121
120
119
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50
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30
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10
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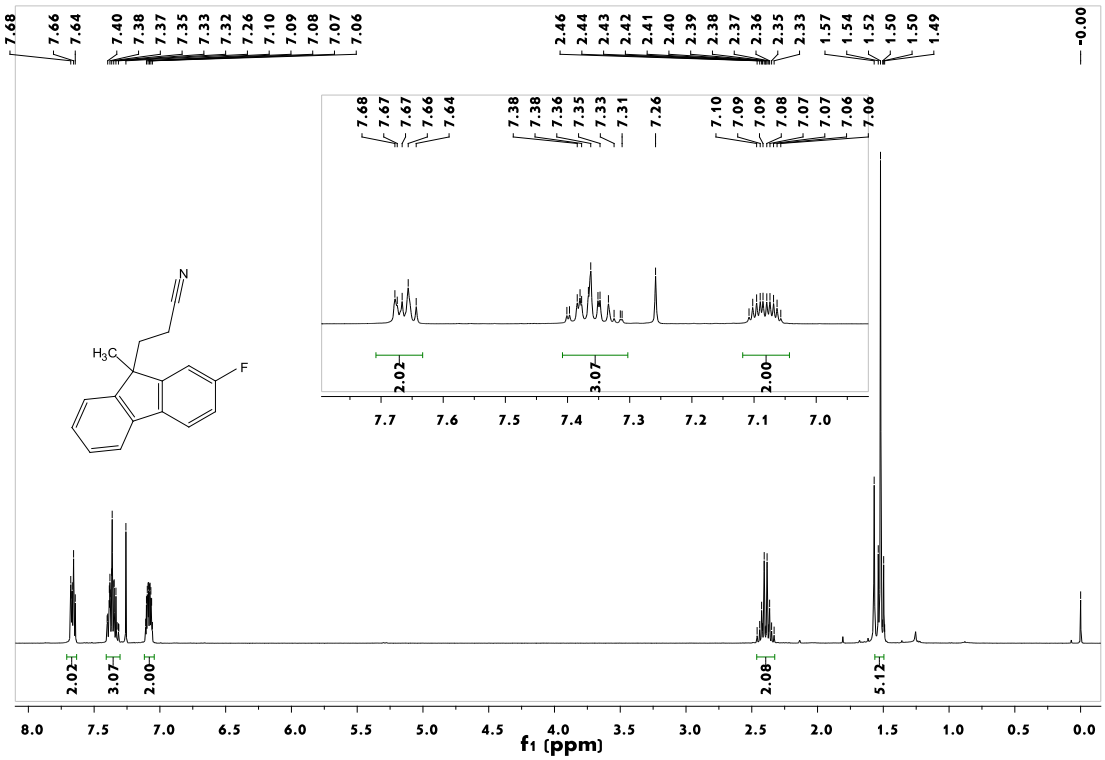
f1 (ppm)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2.46 2.44 2.43 2.42 2.41 2.40 2.39 2.38 2.37 2.36 2.35 2.33 1.57 1.54 1.52 1.50 1.50 1.49
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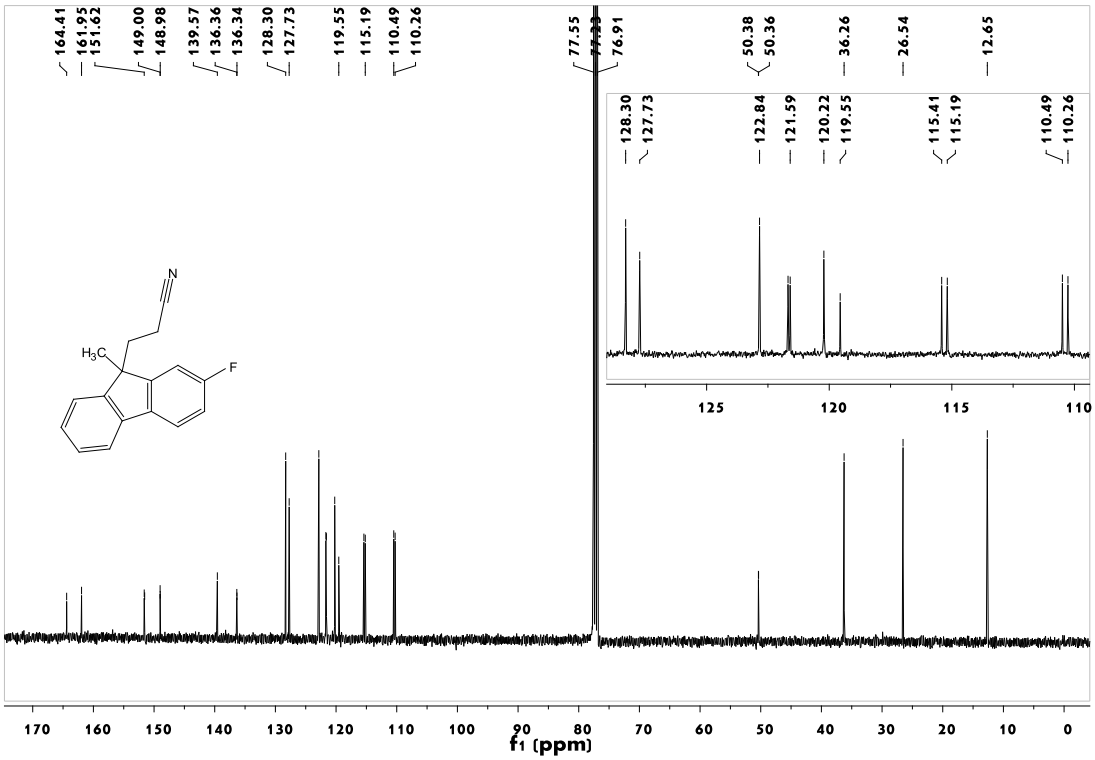
f1 (ppm)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77.55 76.91
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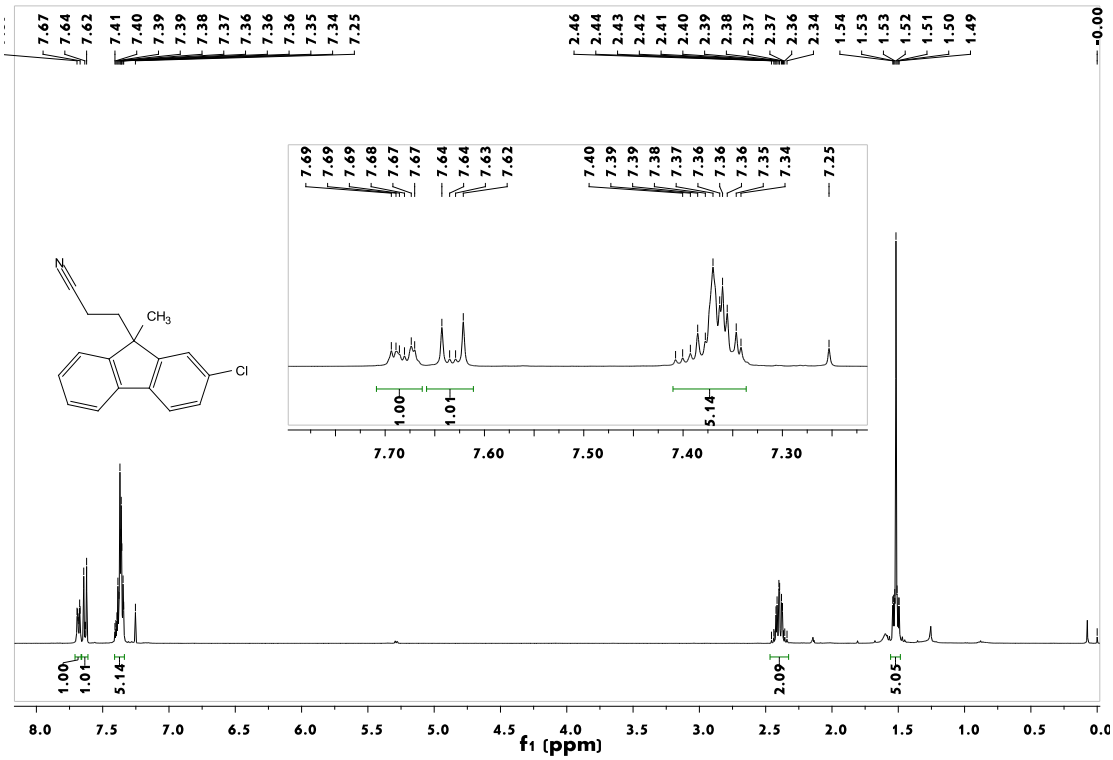
f1 (ppm)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2.46 2.44 2.43 2.42 2.41 2.40 2.39 2.38 2.37 2.37 2.36 2.34
1.54 1.53 1.53 1.52 1.51 1.50 1.49
-0.00
7.69 7.69 7.69 7.68 7.67 7.67 7.64 7.64 7.63 7.62
7.40 7.39 7.39 7.38 7.37 7.36 7.36 7.36 7.35 7.34 7.25
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7.70 7.60 7.50 7.40 7.30
N
CH3
Cl
1.00 1.01 5.14 2.09 5.05
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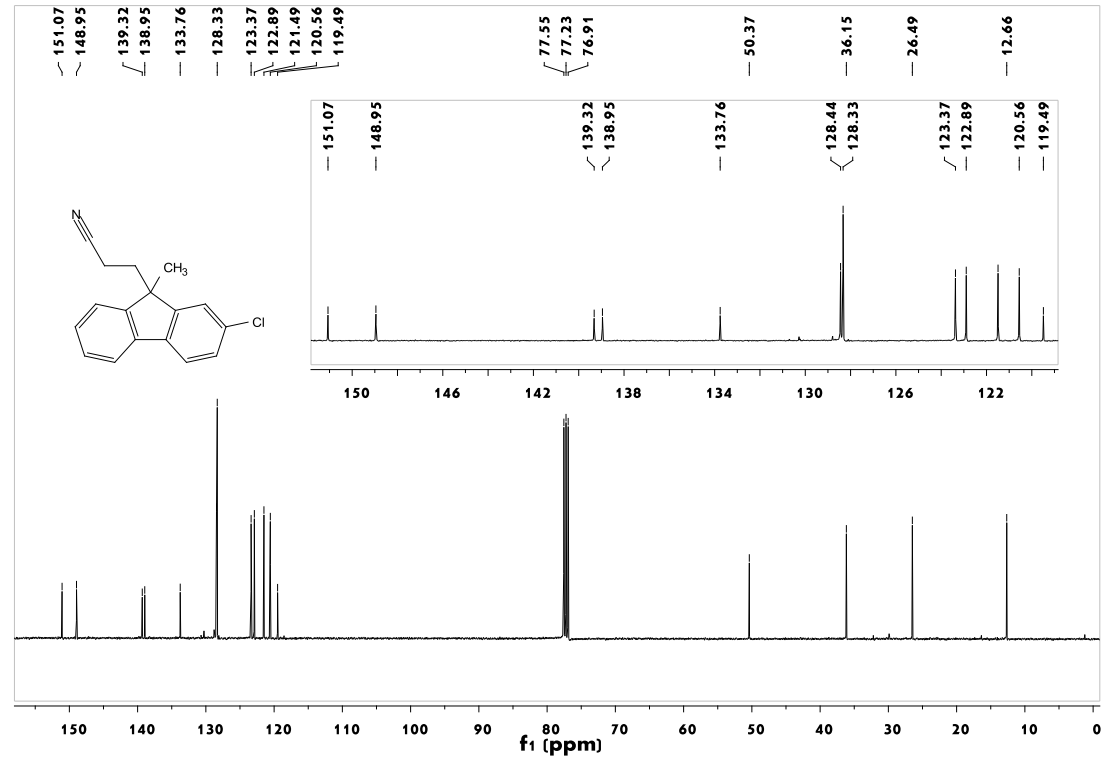
f1 (ppm)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CH3
Cl
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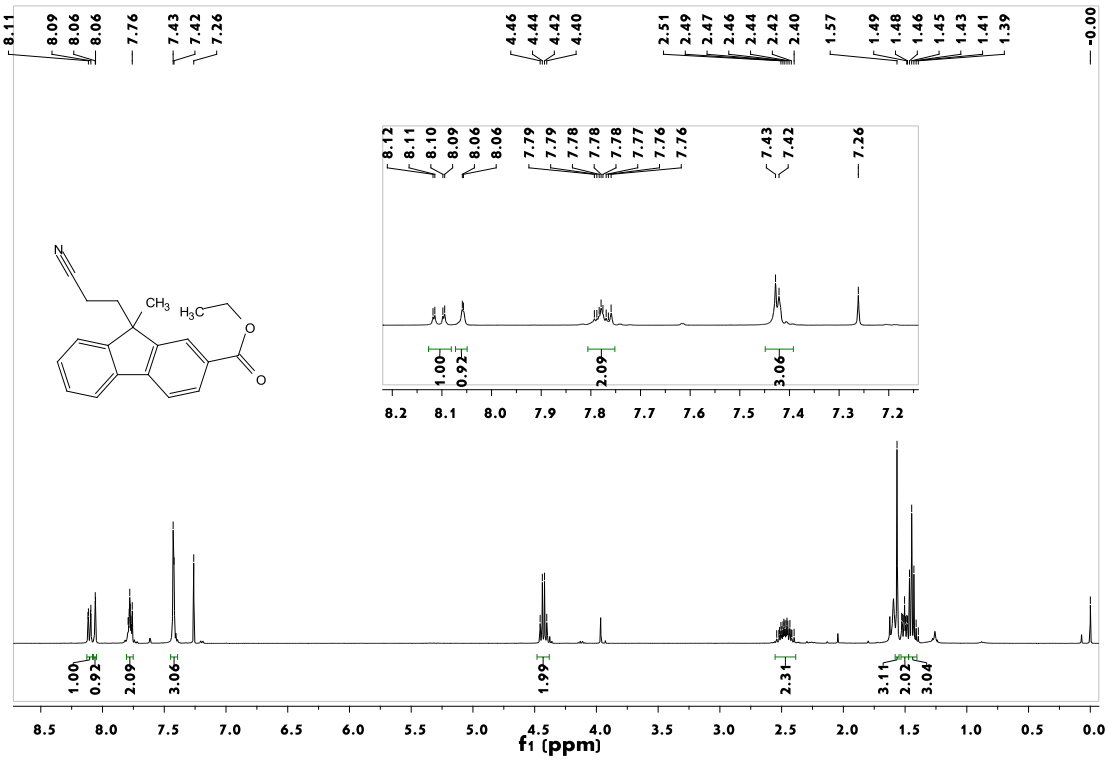
f1 (ppm)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1.48
1.46
1.45
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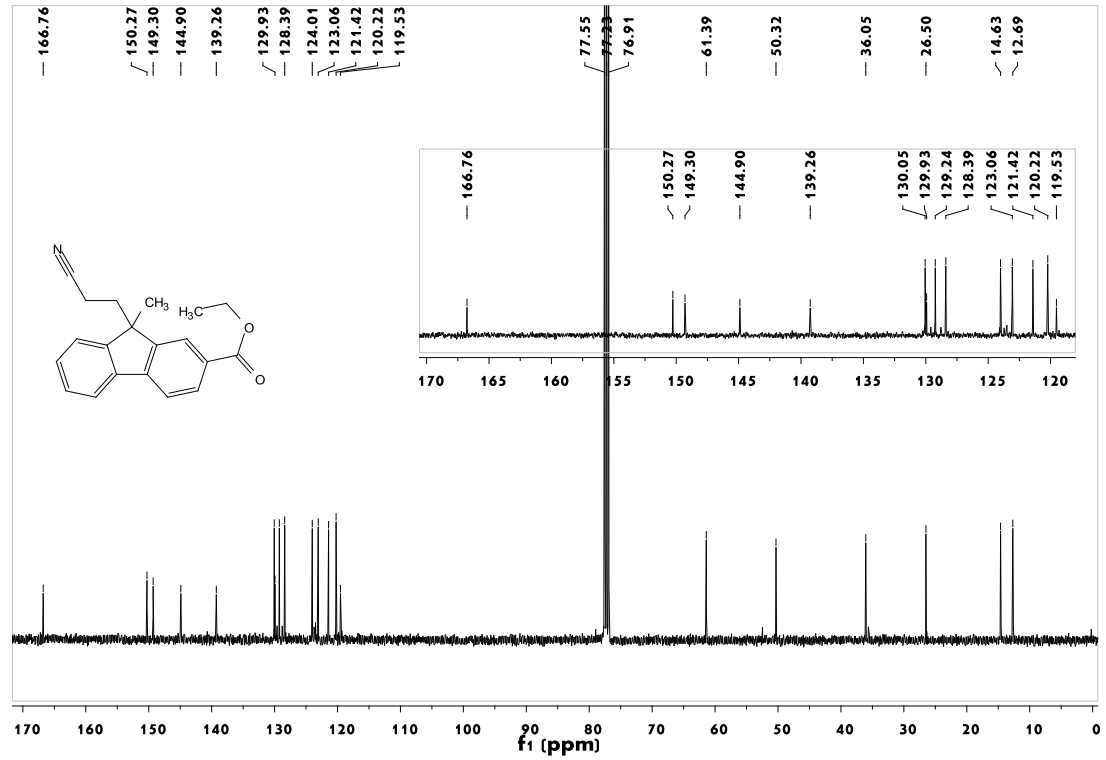
3.04
f1 (ppm)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12.69
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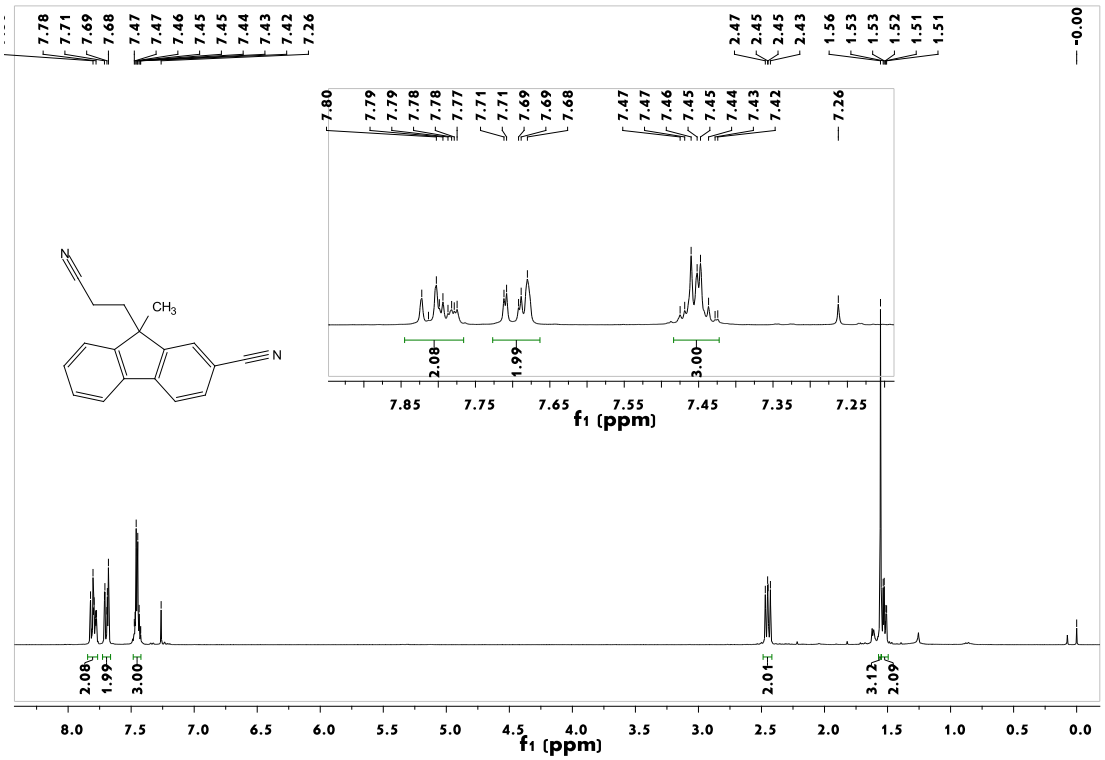
129.24
f1 (ppm)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2.47 2.45 2.45 2.43 1.56 1.53 1.53 1.52 1.51 1.51
-0.00
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2.08 1.99 3.00
7.85 7.75 7.65 7.55 7.45 7.35 7.25
f1 (ppm)
CH3
N
2.08 1.99 3.00 2.01 3.12 2.09
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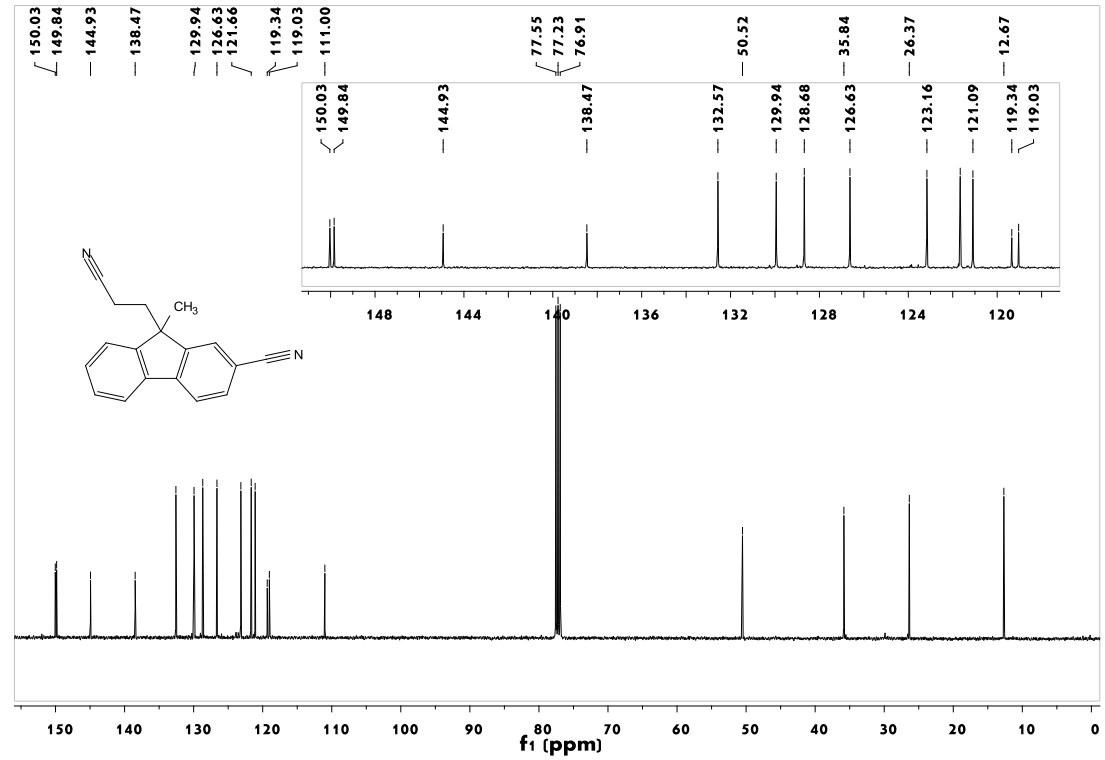
f1 (ppm)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CH3
N
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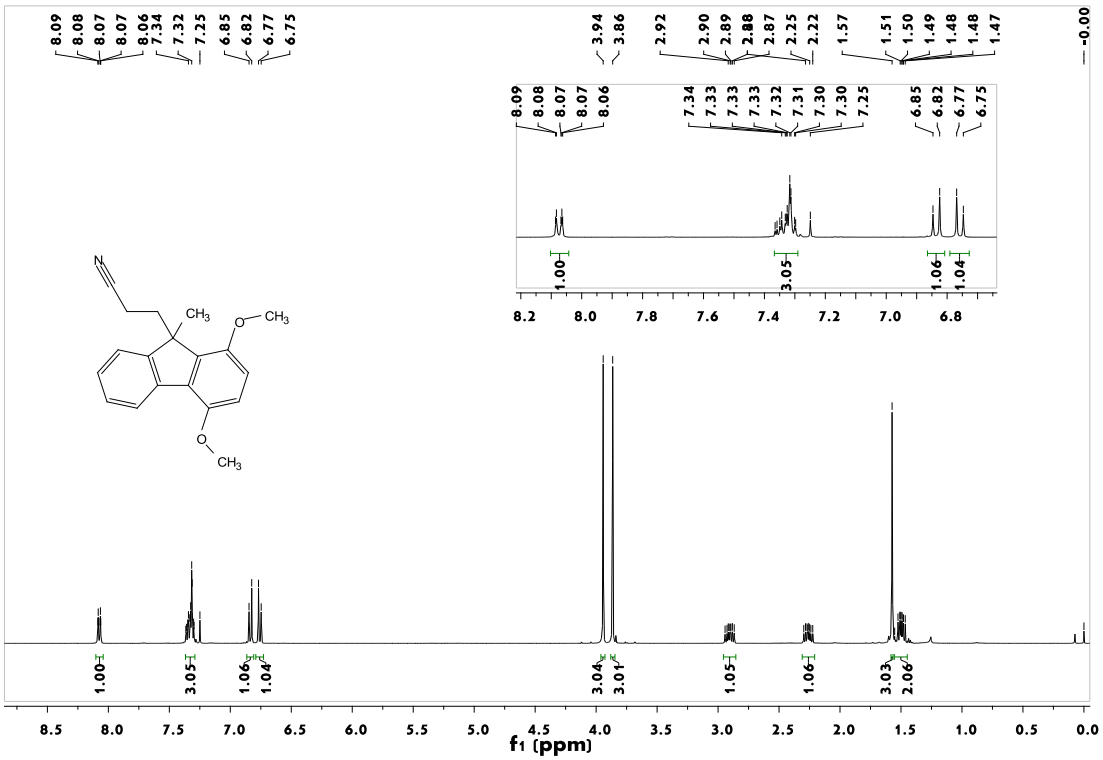
f1 (ppm)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3.94 3.86 2.92 2.90 2.89 2.87 2.25 2.22 1.57 1.51 1.50 1.49 1.48 1.47 0.00
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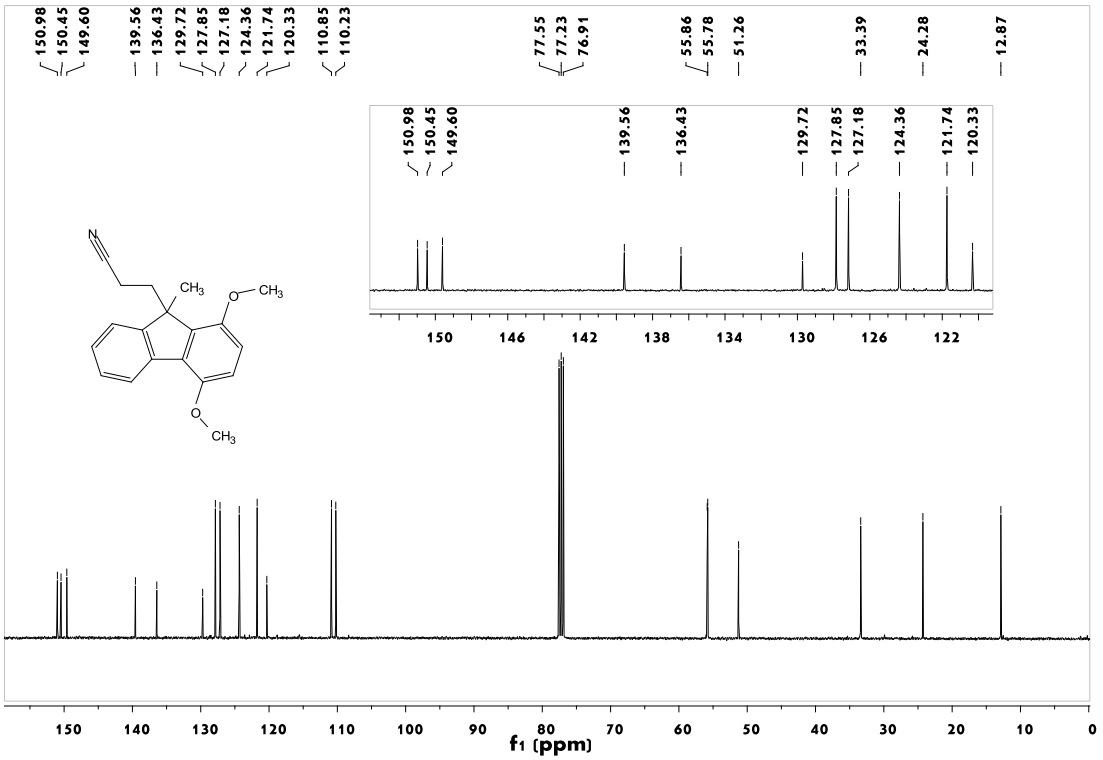
f1 (ppm)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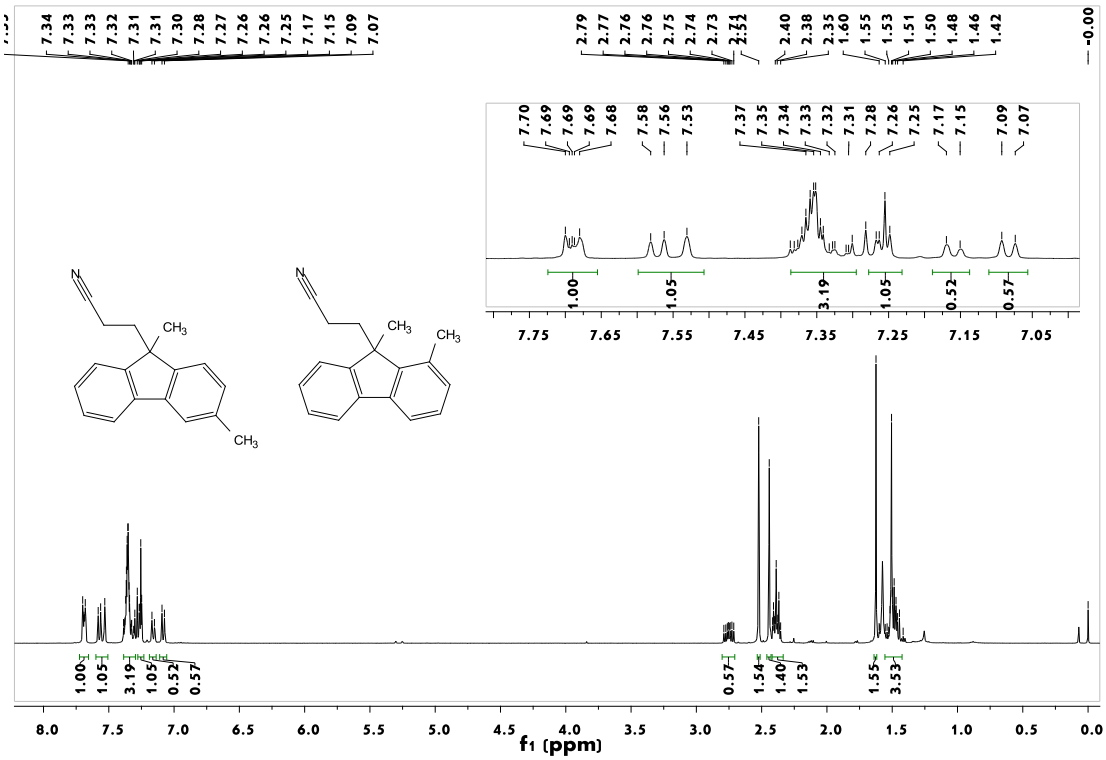
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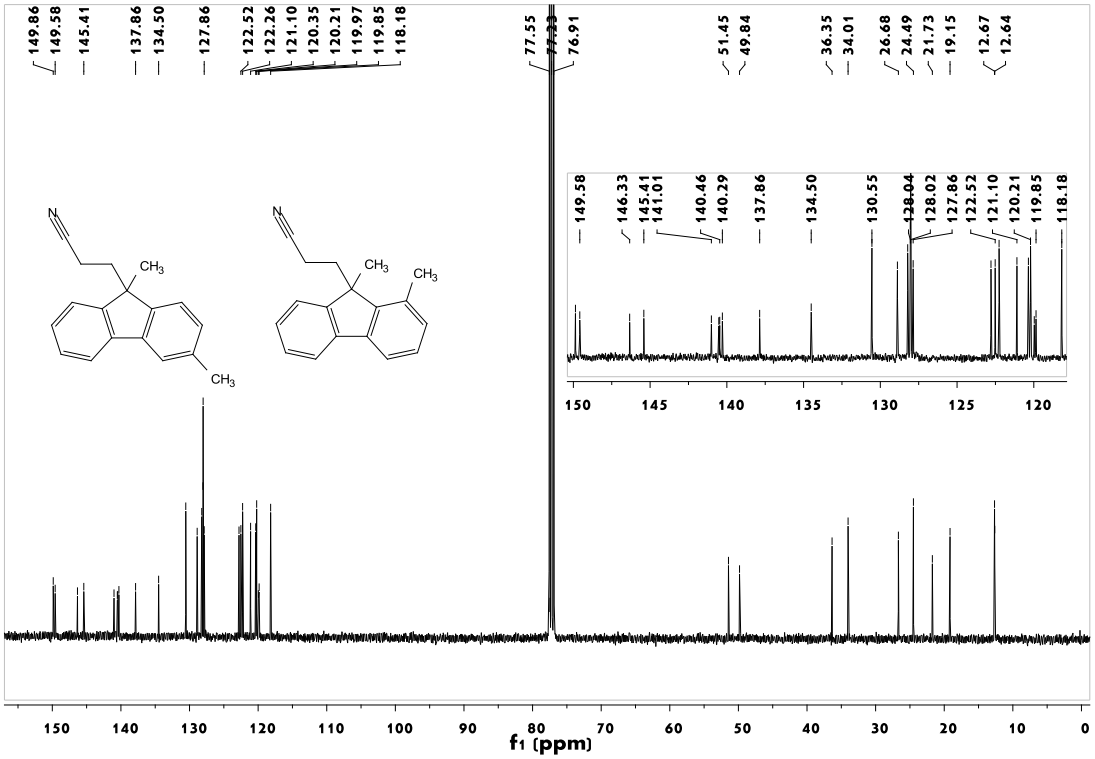
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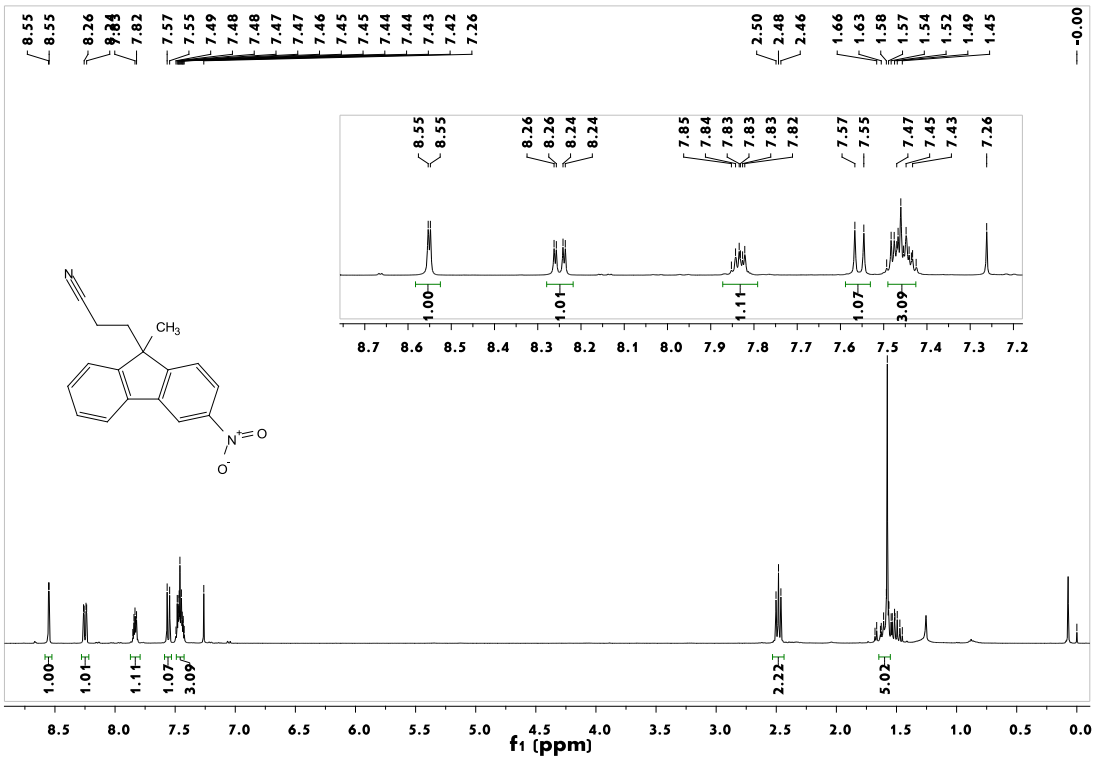
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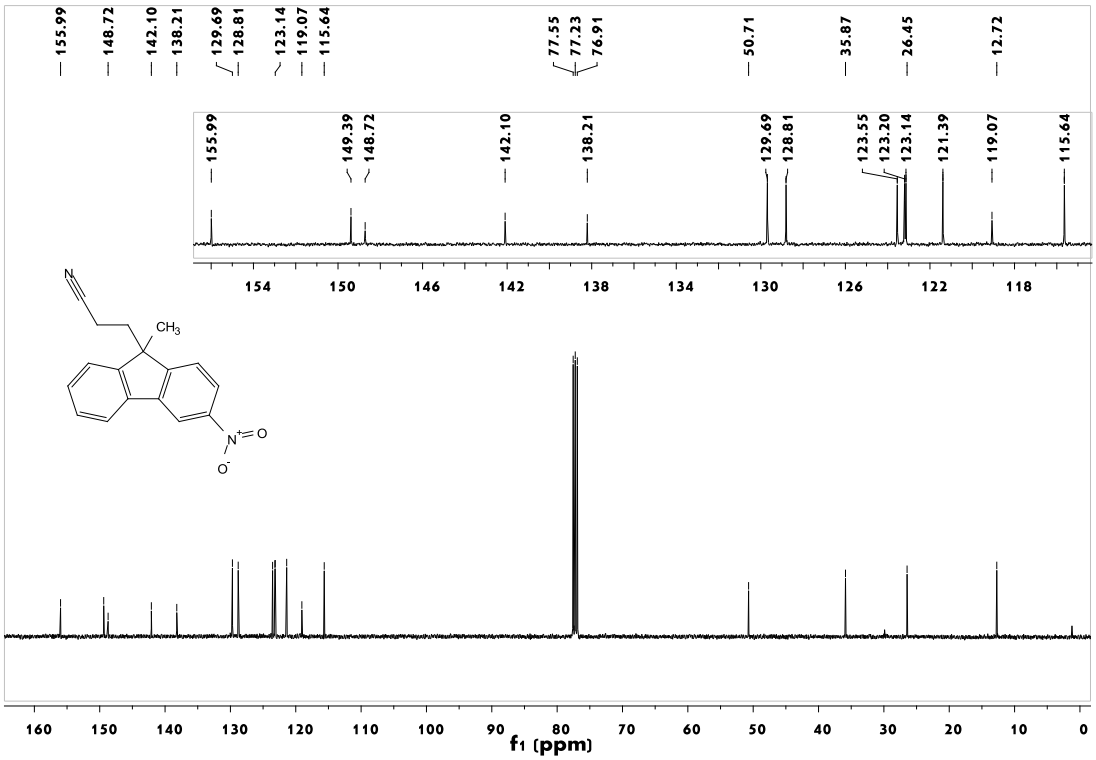
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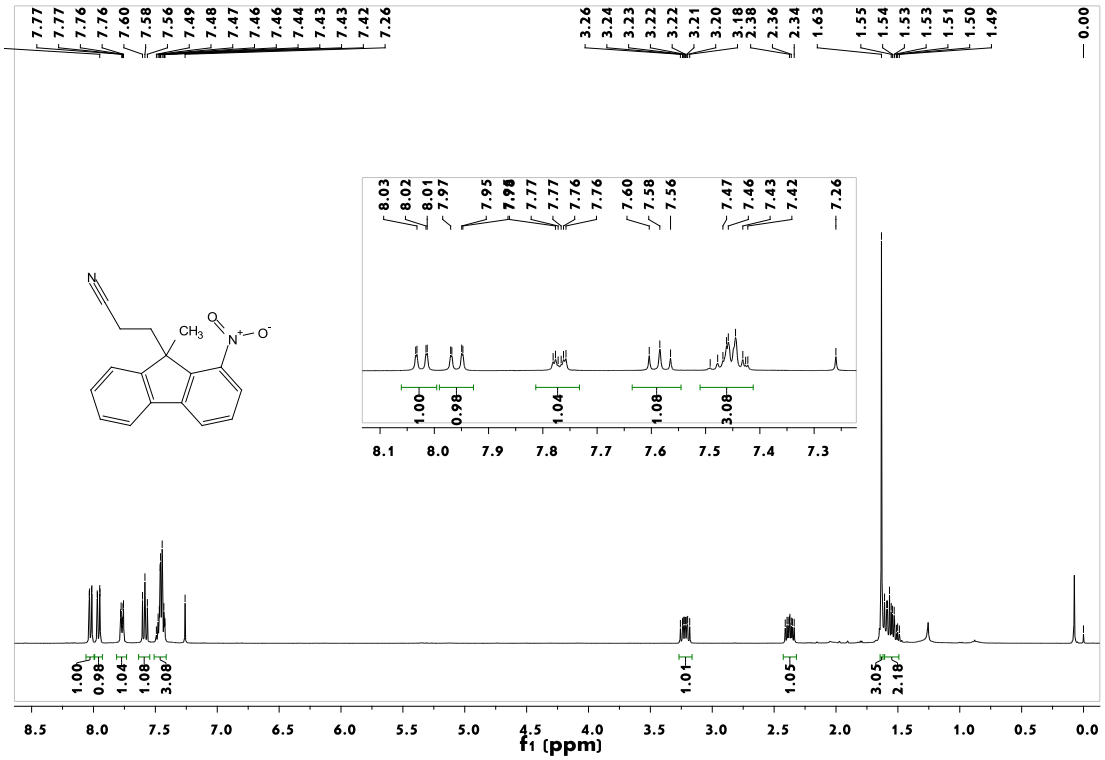
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8.03 8.02 8.01 7.97 7.95 7.77 7.77 7.76 7.76 7.60 7.58 7.56 7.47 7.46 7.43 7.42 7.26
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8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
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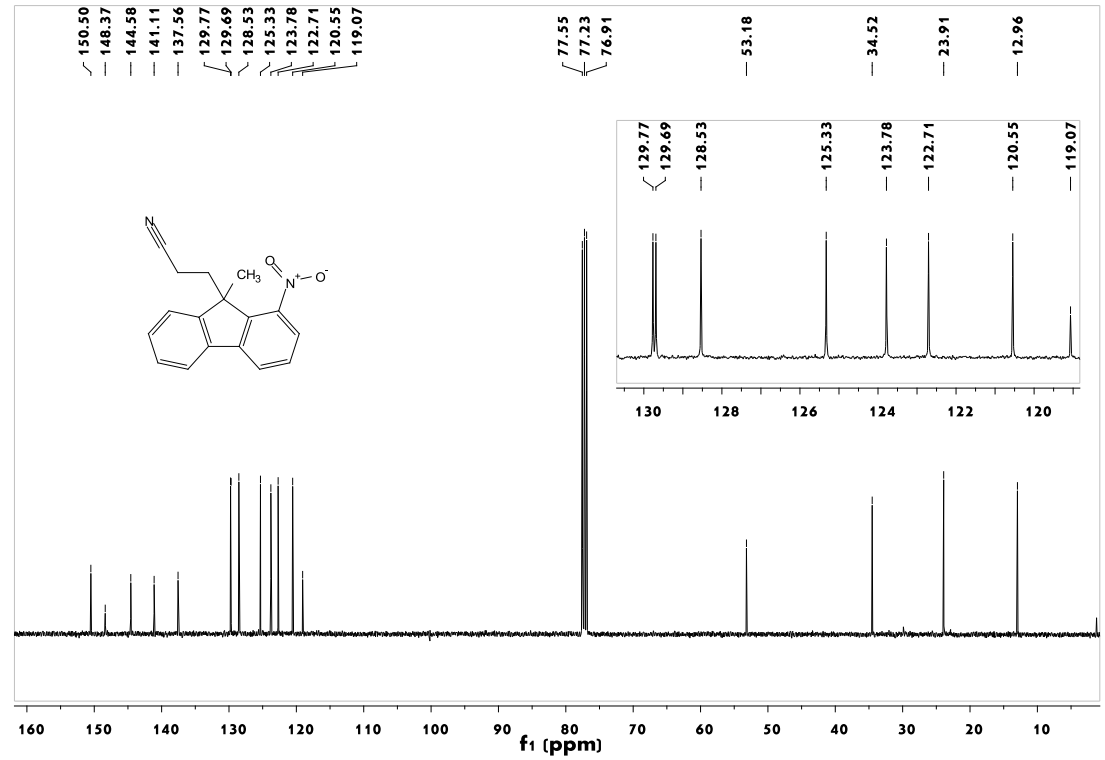
f1 (ppm)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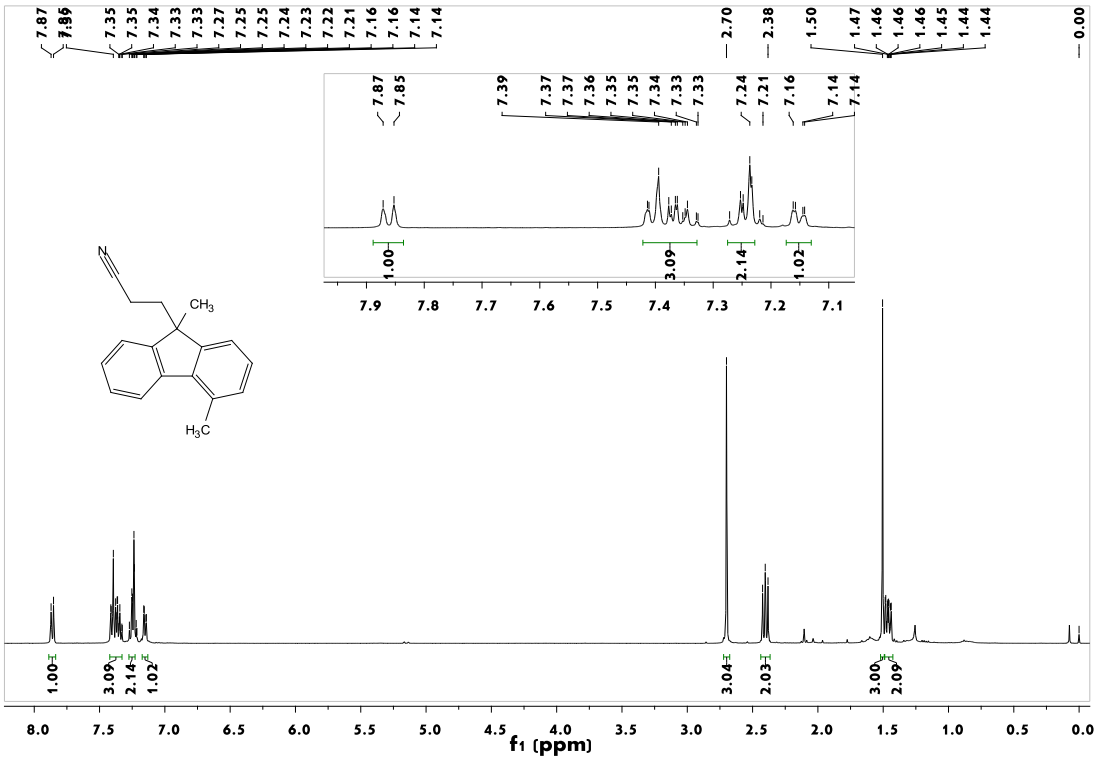
f1 (ppm)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2.70 2.38 1.50 1.47 1.46 1.46 1.46 1.45 1.44 1.44 0.00
7.87 7.85 7.39 7.37 7.37 7.36 7.35 7.35 7.34 7.33 7.33 7.24 7.21 7.16 7.14 7.14
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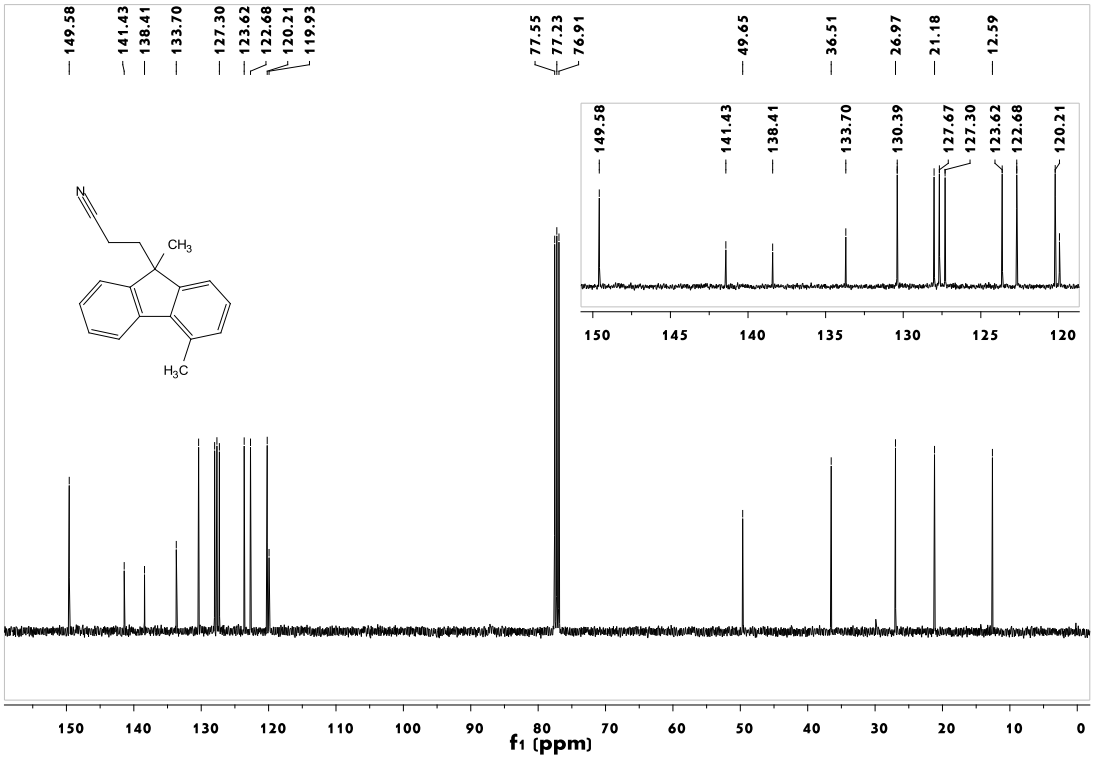
CH3
H3C
1.00 3.09 2.14 1.02 3.04 2.03 3.00 2.09
f1 (ppm)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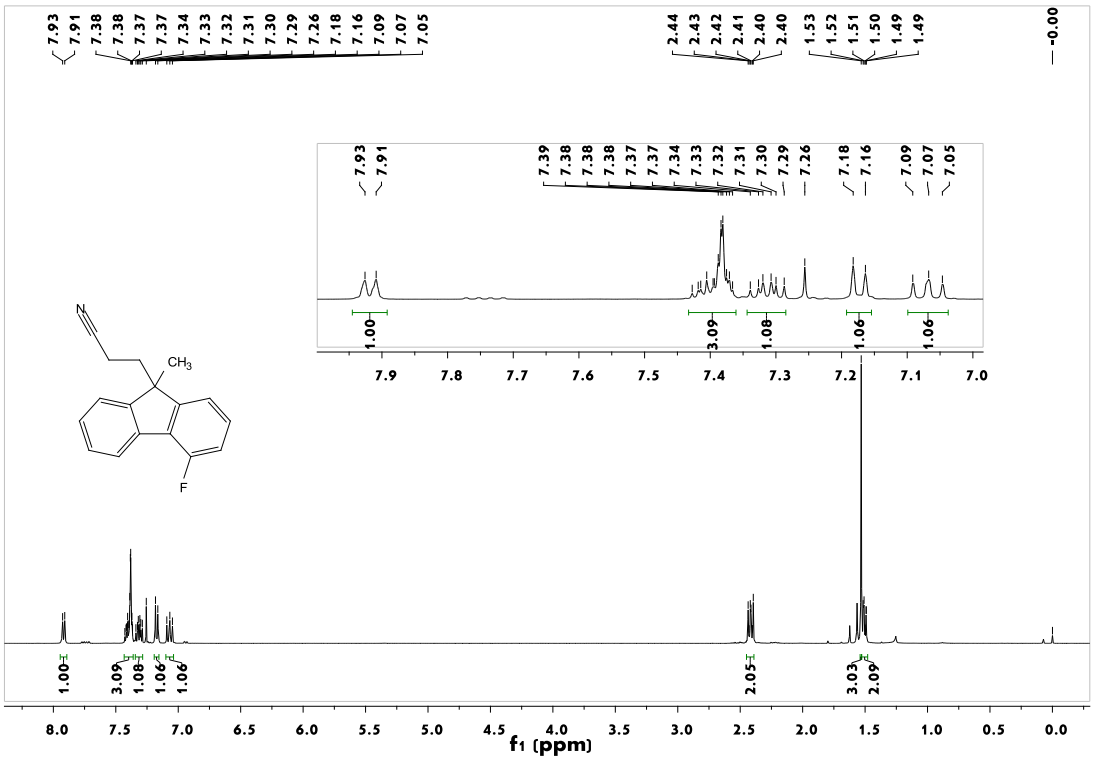
CH3
H3C
f1 (ppm)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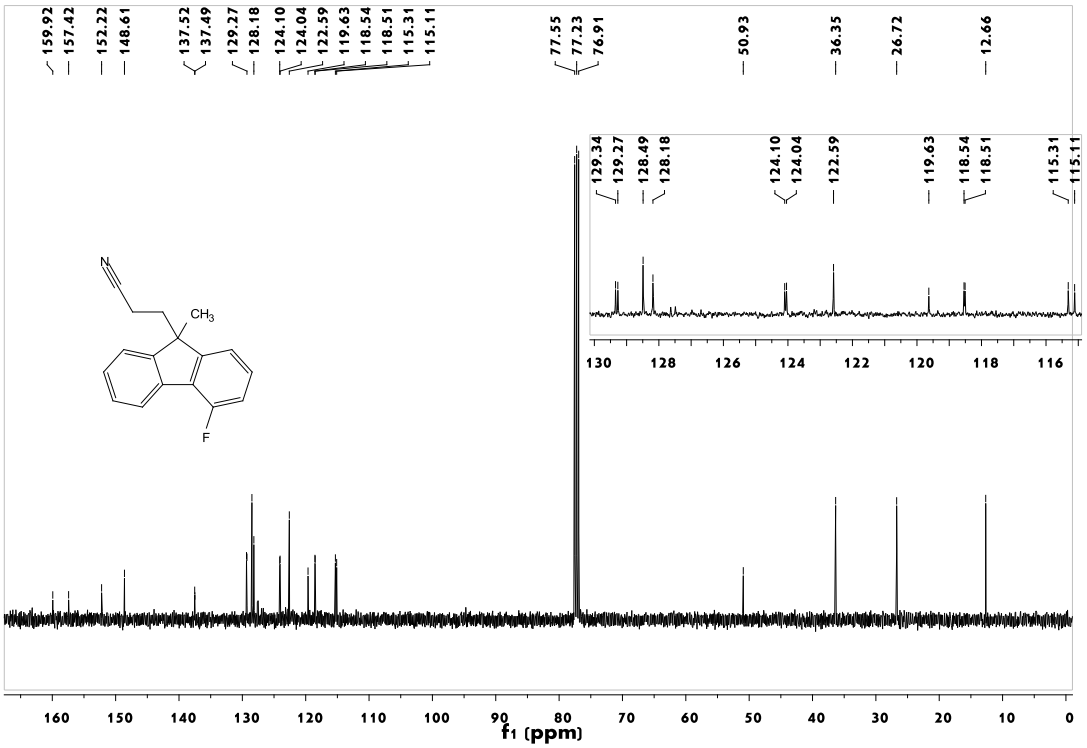
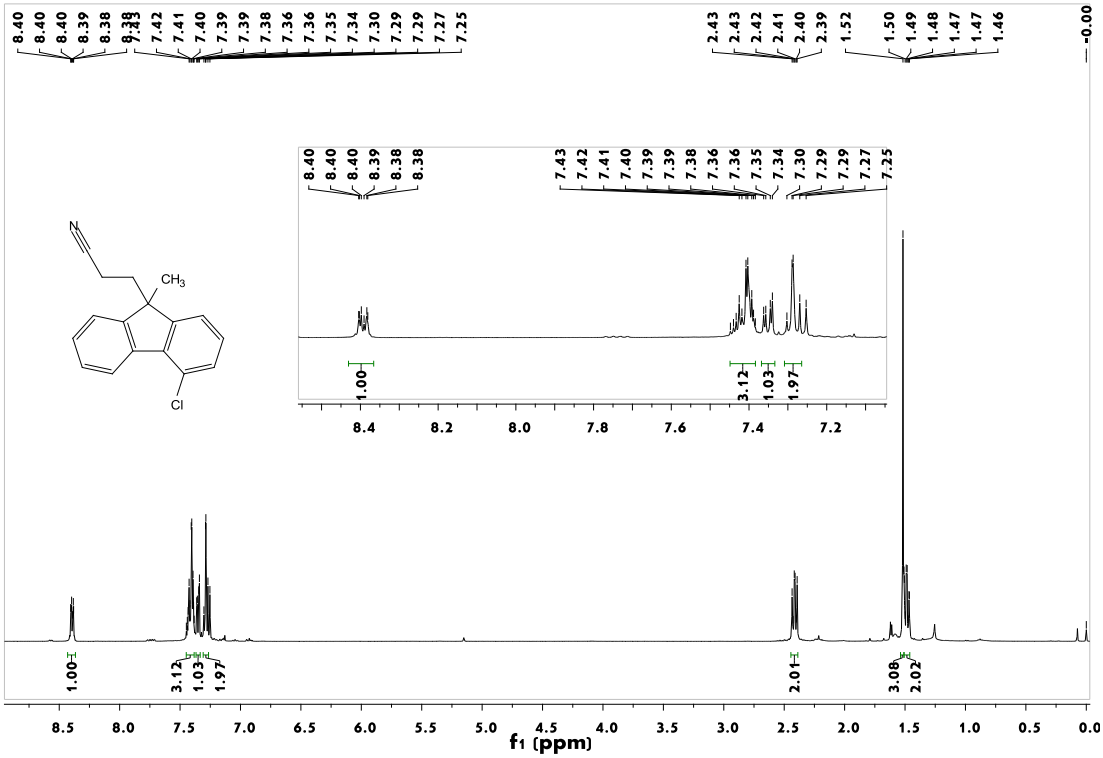
2.44 2.43 2.42 2.41 2.40 2.40 1.53 1.52 1.51 1.50 1.49 1.49
-0.00
1.00 3.09 1.08 1.06 1.06 2.05 3.03 2.09
f1 (ppm)


159.92 157.42 152.22 148.61 137.52 137.49 129.27 128.18 124.10 124.04 122.59 119.63 118.54 118.51 115.31 115.11
77.55 77.23 76.91
50.93 36.35 26.72 12.66
f1 (ppm)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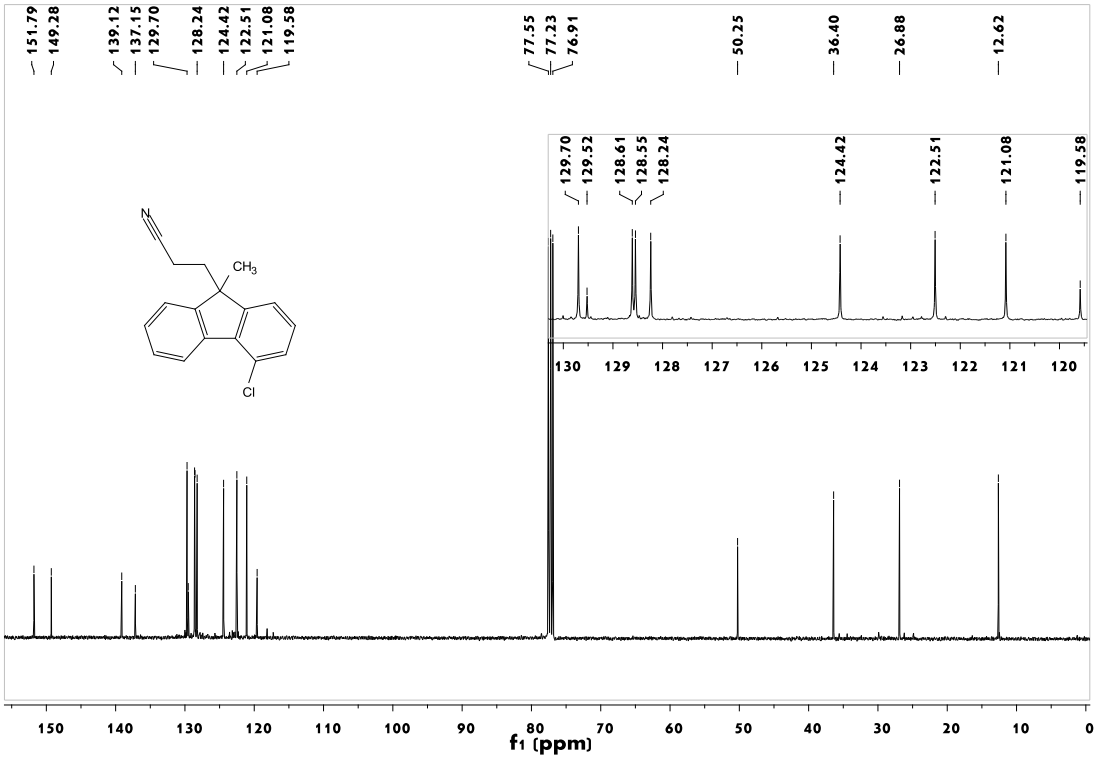
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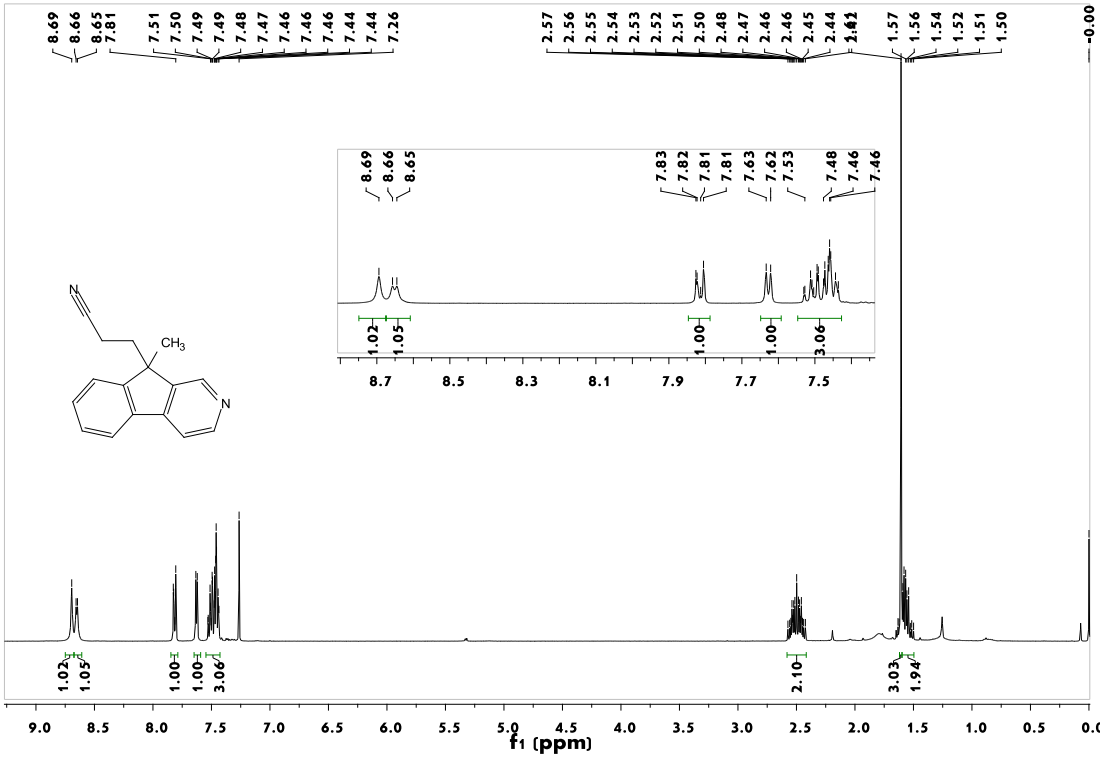
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7.49
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7.47
7.46
7.46
7.46
7.44
7.44
7.26
2.57
2.56
2.55
2.54
2.53
2.52
2.51
2.50
2.48
2.47
2.46
2.46
2.45
2.44
1.57
1.56
1.54
1.52
1.51
1.50
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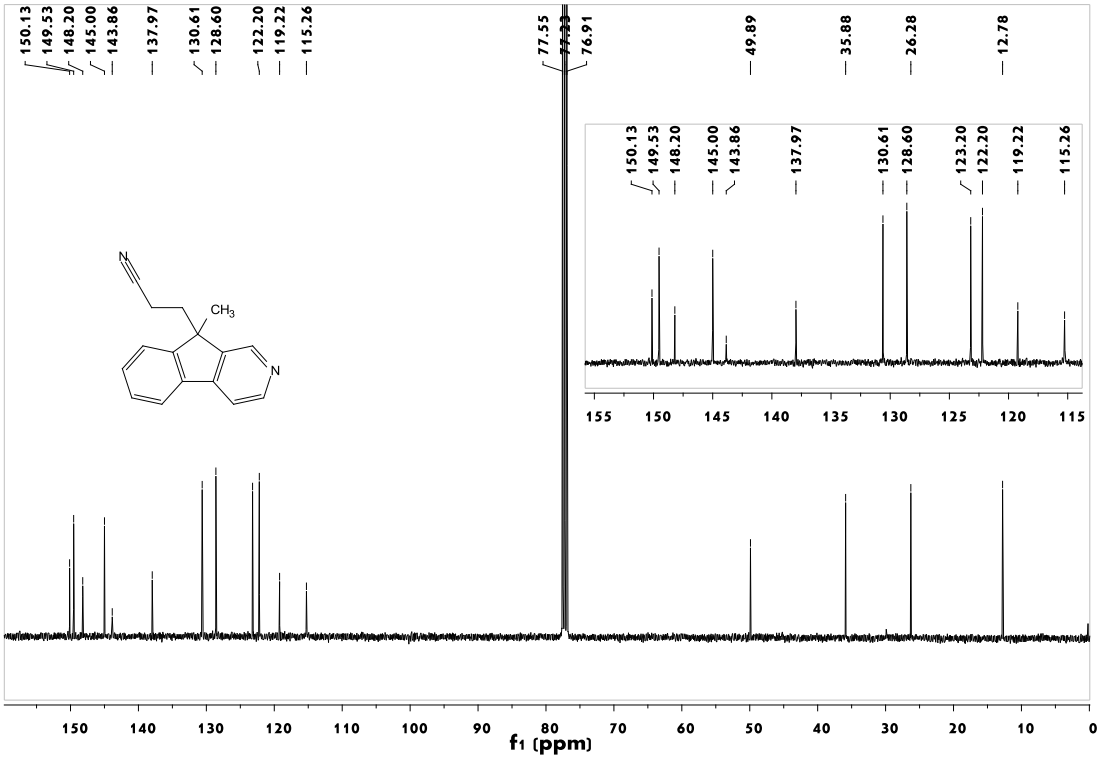
1.02
1.05
1.00
1.00
3.06
2.10
3.03
1.94
f1 (ppm)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149.53
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145.00
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137.97
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128.60
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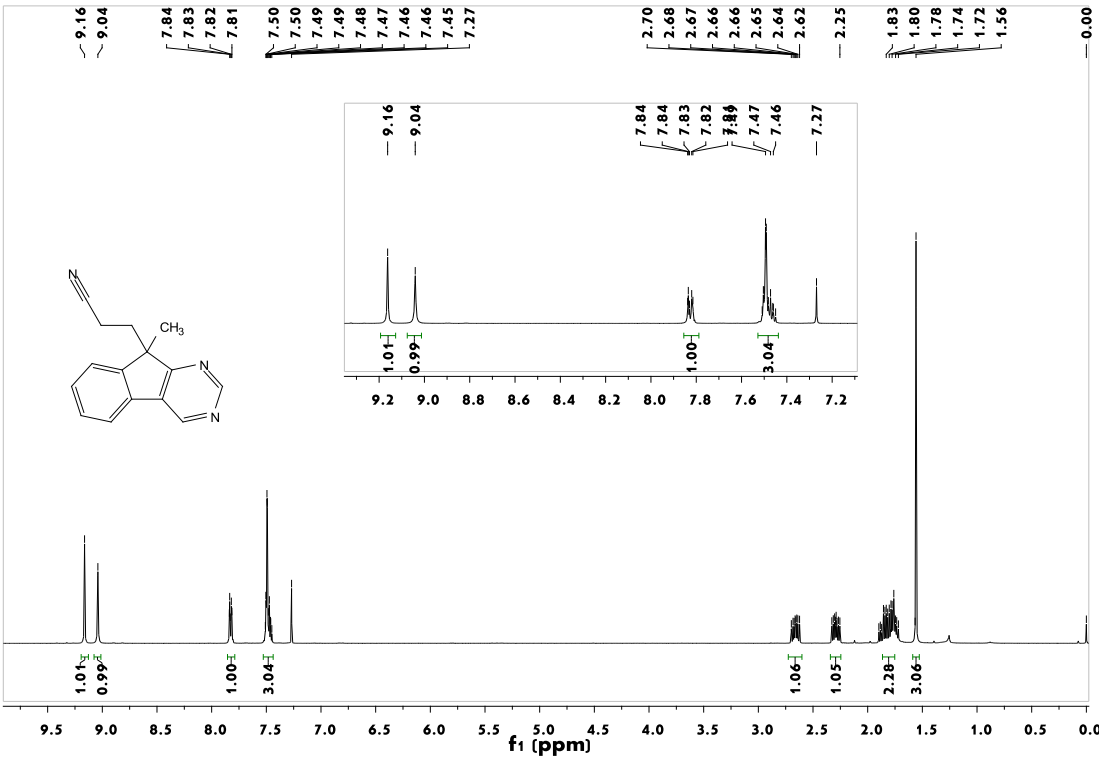
115.26
77.55
76.91
49.89
35.88
26.28
12.78
f1 (ppm)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9.04
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7.83
7.82
7.81
7.50
7.49
7.48
7.47
7.46
7.45
7.27
2.70
2.68
2.67
2.66
2.65
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2.62
2.25
1.83
1.80
1.78
1.74
1.72
1.56
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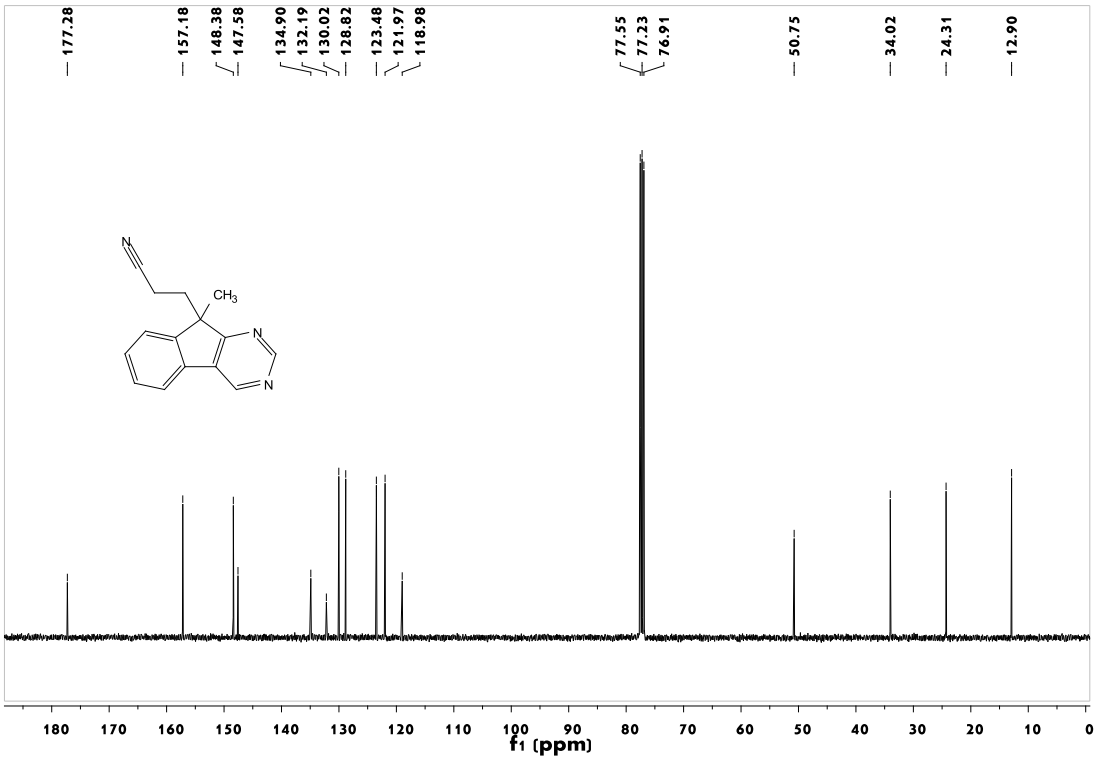
3.04
1.06
1.05
2.28
3.06
f1 (ppm)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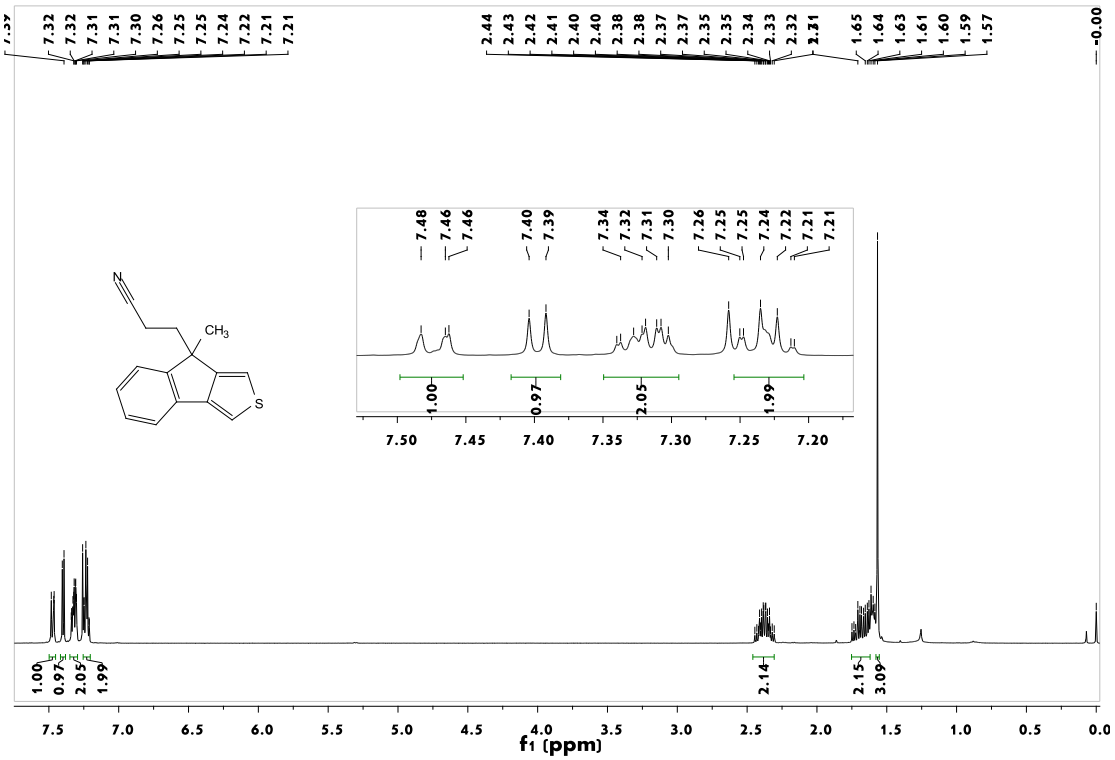
134.90
132.19
130.02
128.82
123.48
121.97
118.98
77.55
77.23
76.91
50.75
34.02
24.31
12.90
CH3
N
N
f1 (ppm)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7.25
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7.22
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7.21
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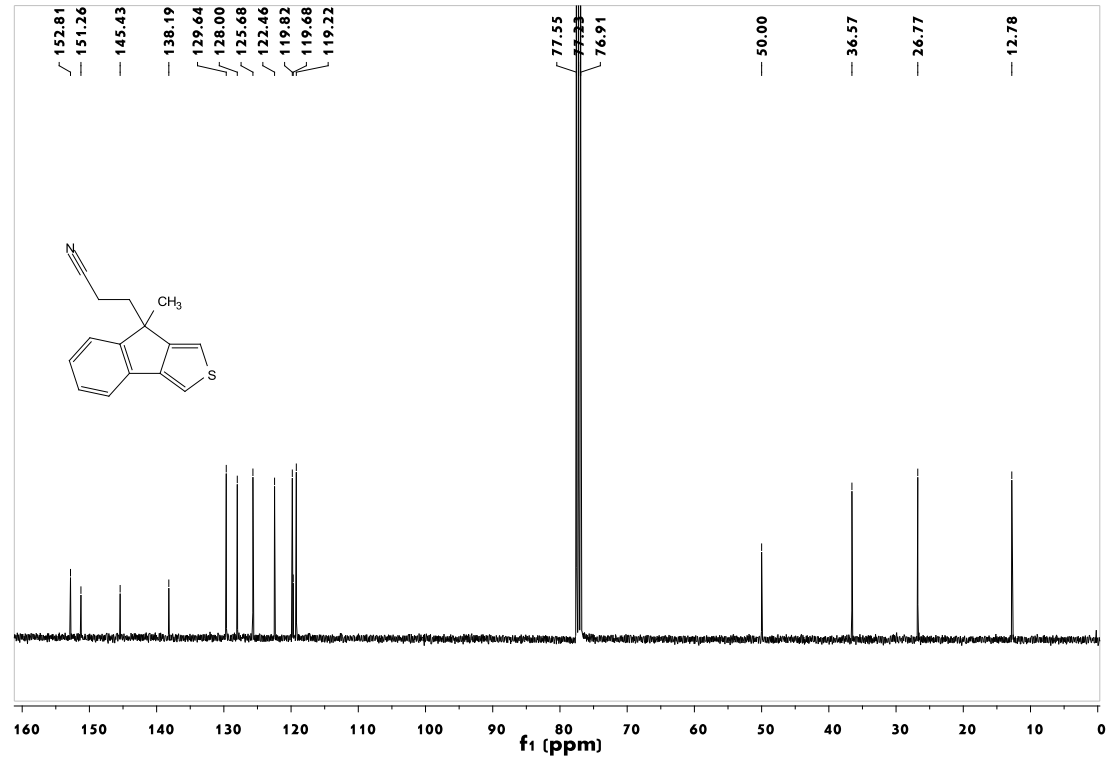
2.42
2.41
2.40
2.40
2.38
2.38
2.37
2.37
2.35
2.35
2.34
2.33
2.32
1.65
1.64
1.63
1.61
1.60
1.59
1.57
0.00
7.48
7.46
7.46
7.40
7.39
7.34
7.32
7.31
7.30
7.26
7.25
7.25
7.24
7.22
7.21
7.21
N
CH3
S
1.00
0.97
2.05
1.99
7.50
7.45
7.40
7.35
7.30
7.25
7.20
1.00
0.97
2.05
1.99
2.14
2.15
3.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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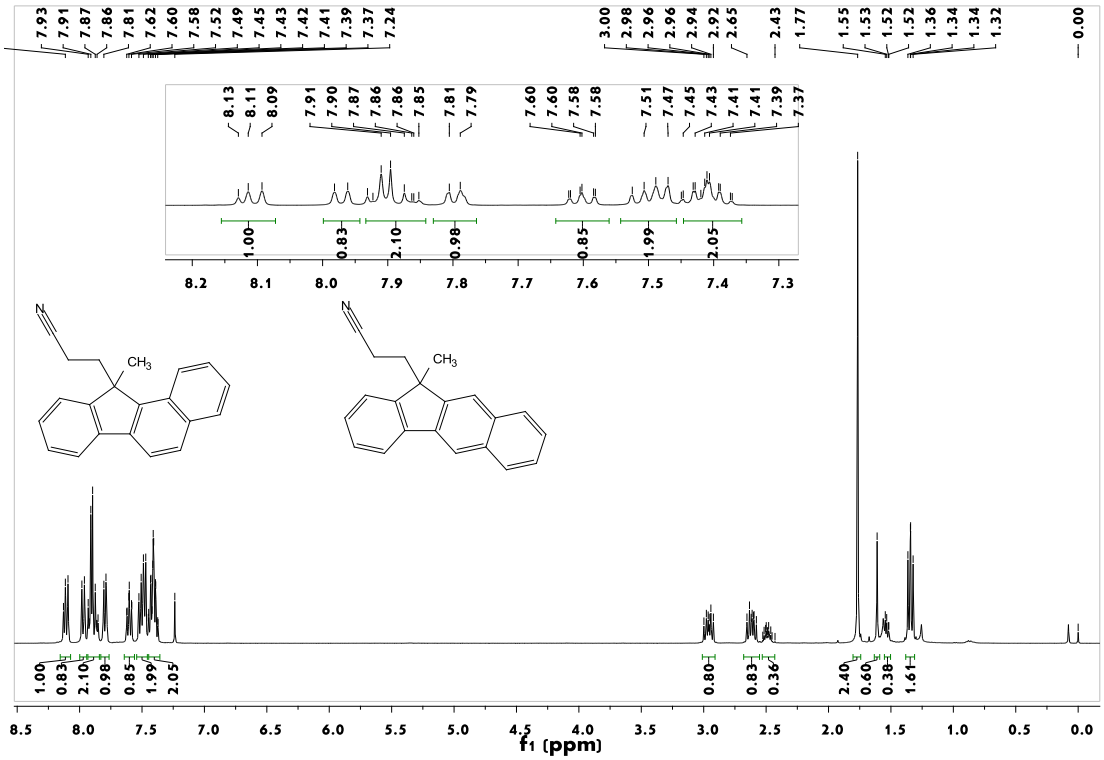
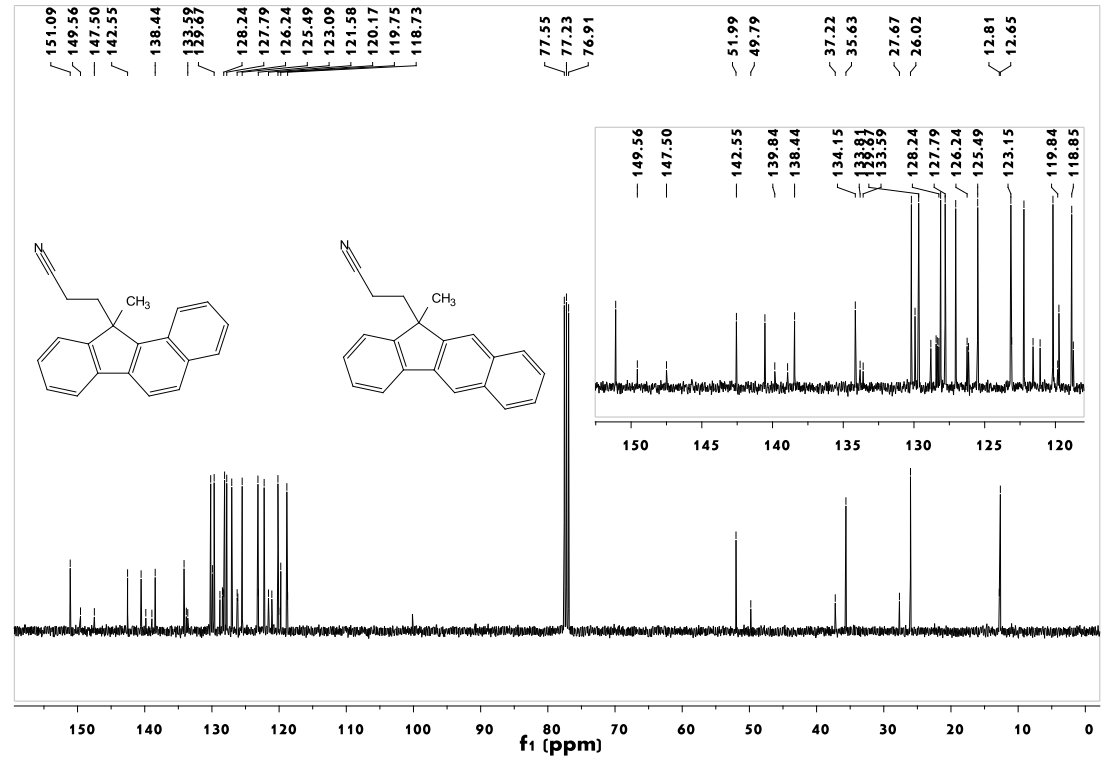
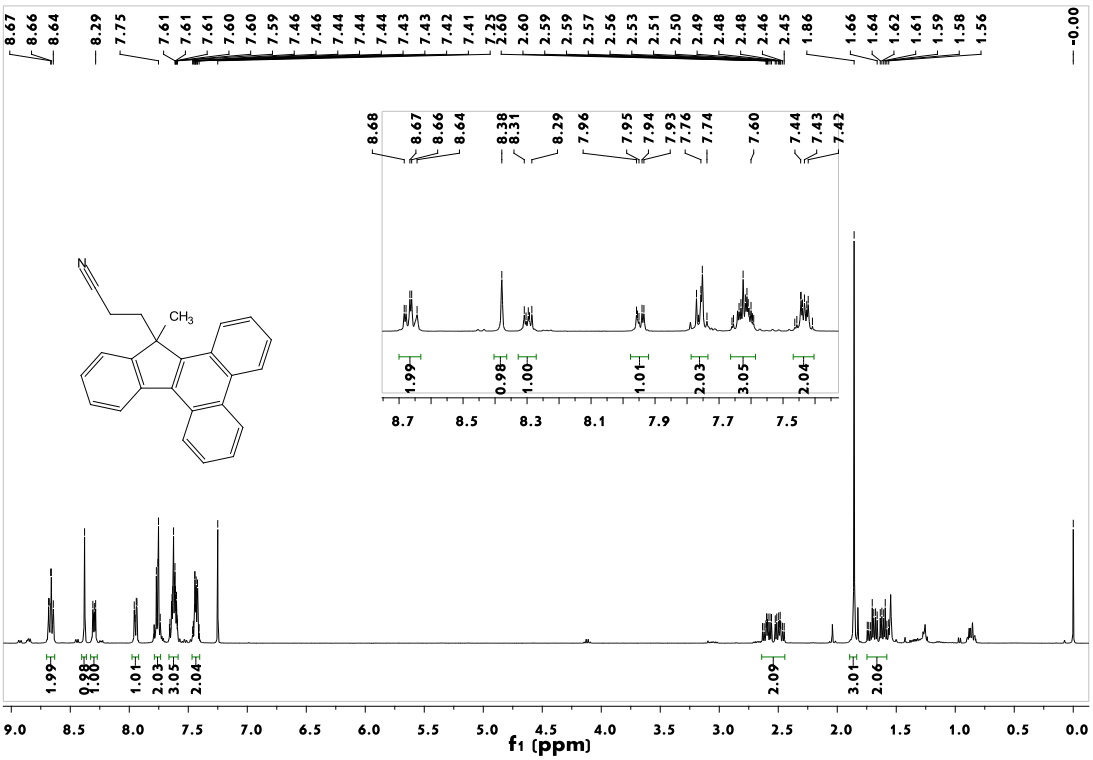
151.26
145.43
138.19
129.64
128.00
125.68
122.46
119.82
119.68
119.22
77.55
77.33
76.91
50.00
36.57
26.77
12.78
N
CH3
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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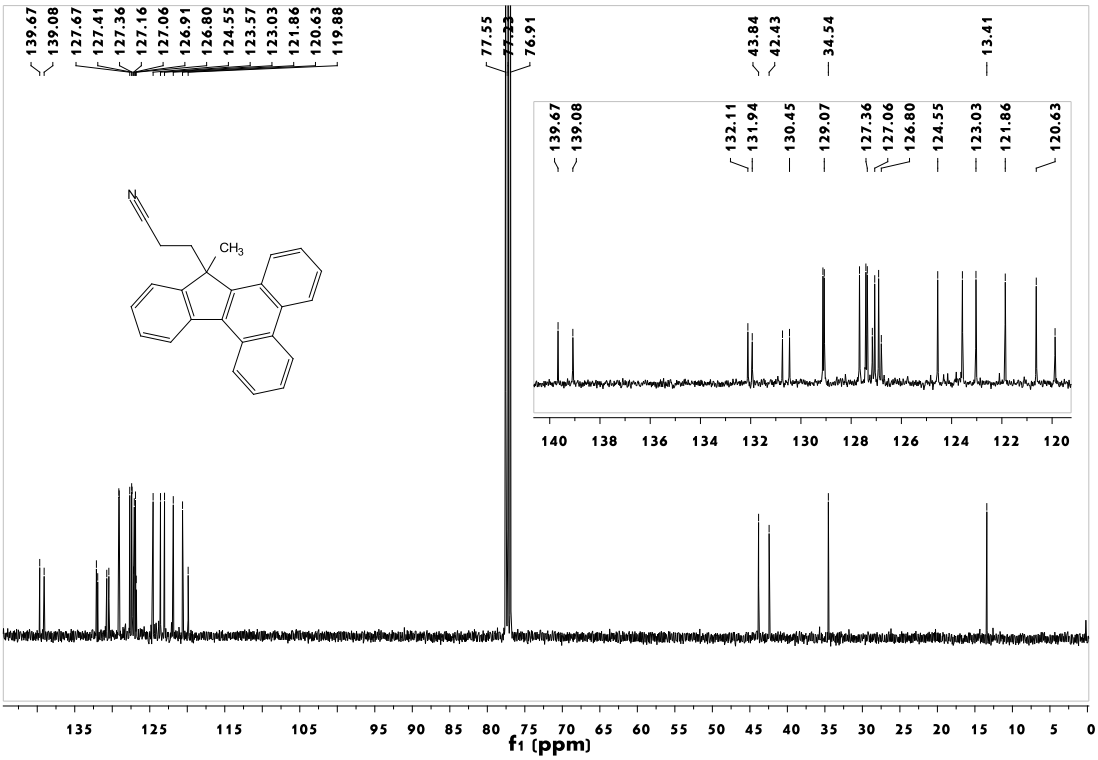
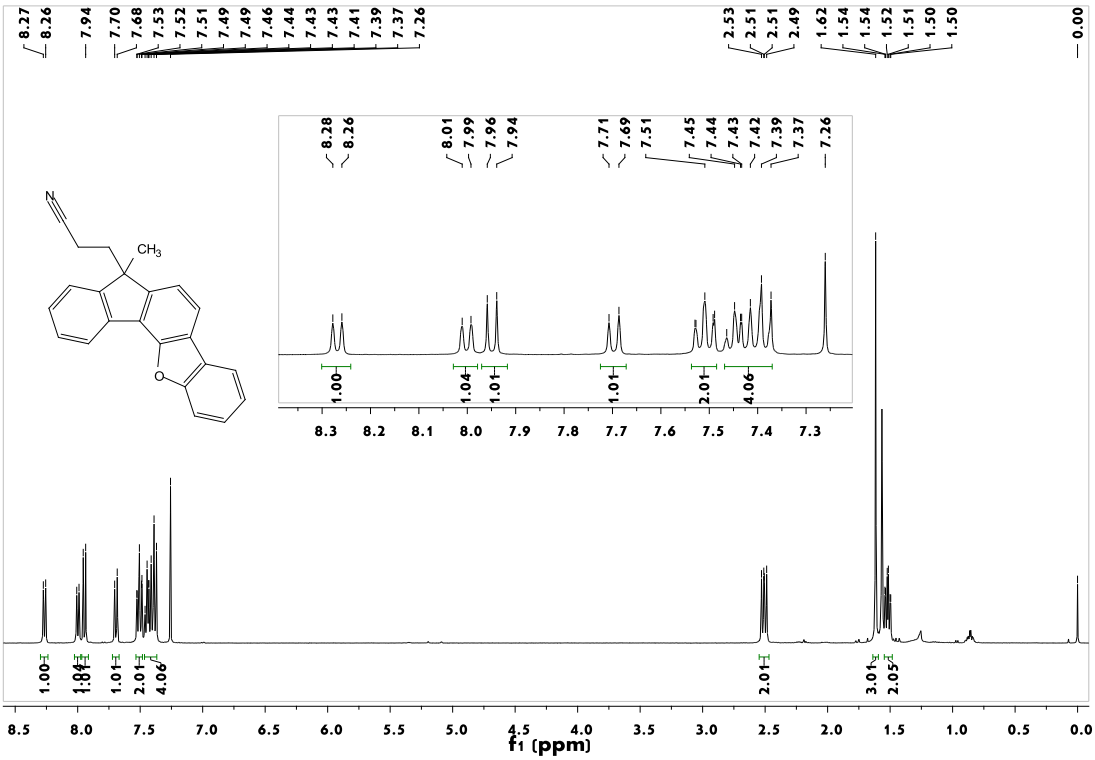
8.68 8.67 8.66 8.64 8.38 8.31 8.29 7.96 7.95 7.94 7.93 7.76 7.74 7.60 7.44 7.43 7.42
1.99 0.98 1.00 1.01 2.03 3.05 2.04
8.7 8.5 8.3 8.1 7.9 7.7 7.5
CH3
1.99 0.98 1.00 1.01 2.03 3.05 2.04 2.09 3.01 2.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


139.67 139.08 127.67 127.41 127.36 127.16 127.06 126.91 126.80 124.55 123.57 123.03 121.86 120.63 119.88
77.55 77.33 76.91
43.84 42.43 34.54 13.41
139.67 139.08 132.11 131.94 130.45 129.07 127.36 127.06 126.80 124.55 123.03 121.86 120.63
140 138 136 134 132 130 128 126 124 122 120
CH3
135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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7.49
7.49
7.46
7.44
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7.39
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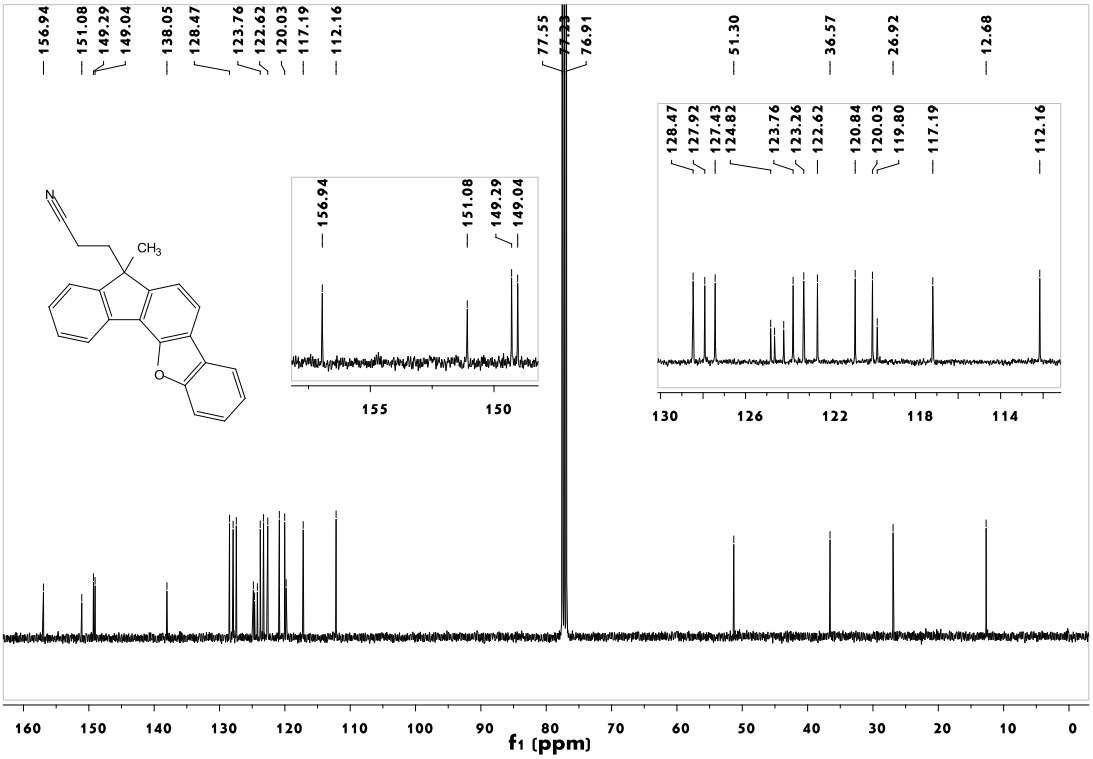
7.26
2.53
2.51
2.51
2.49
1.62
1.54
1.54
1.52
1.51
1.50
1.50
0.00
CH3
1.00
1.04
1.01
2.01
4.06
3.01
2.05
f1 (ppm)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149.04
138.05
128.47
123.76
122.62
120.03
117.19
112.16
77.55
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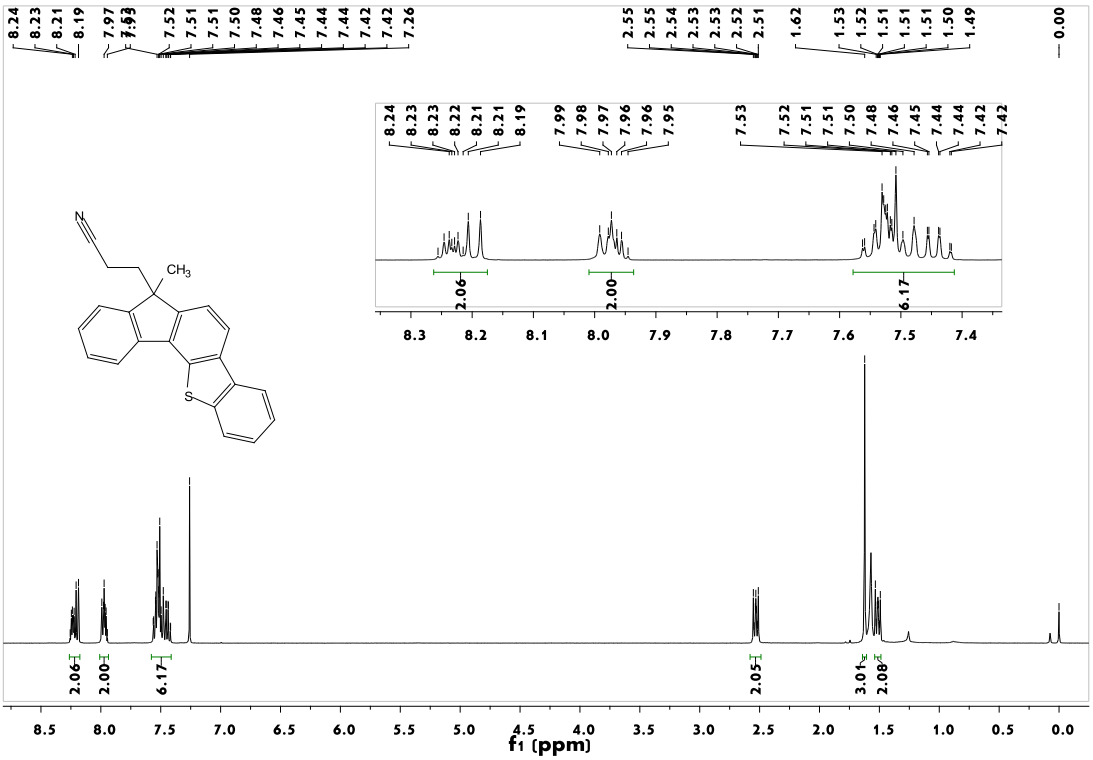
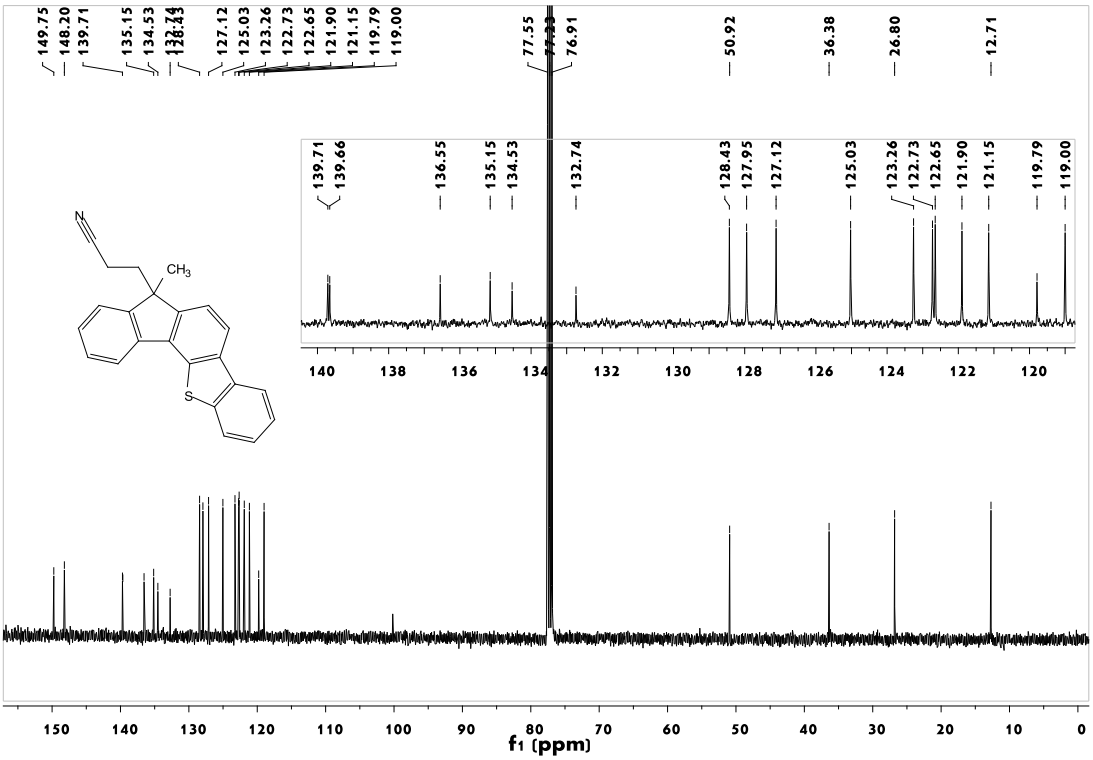
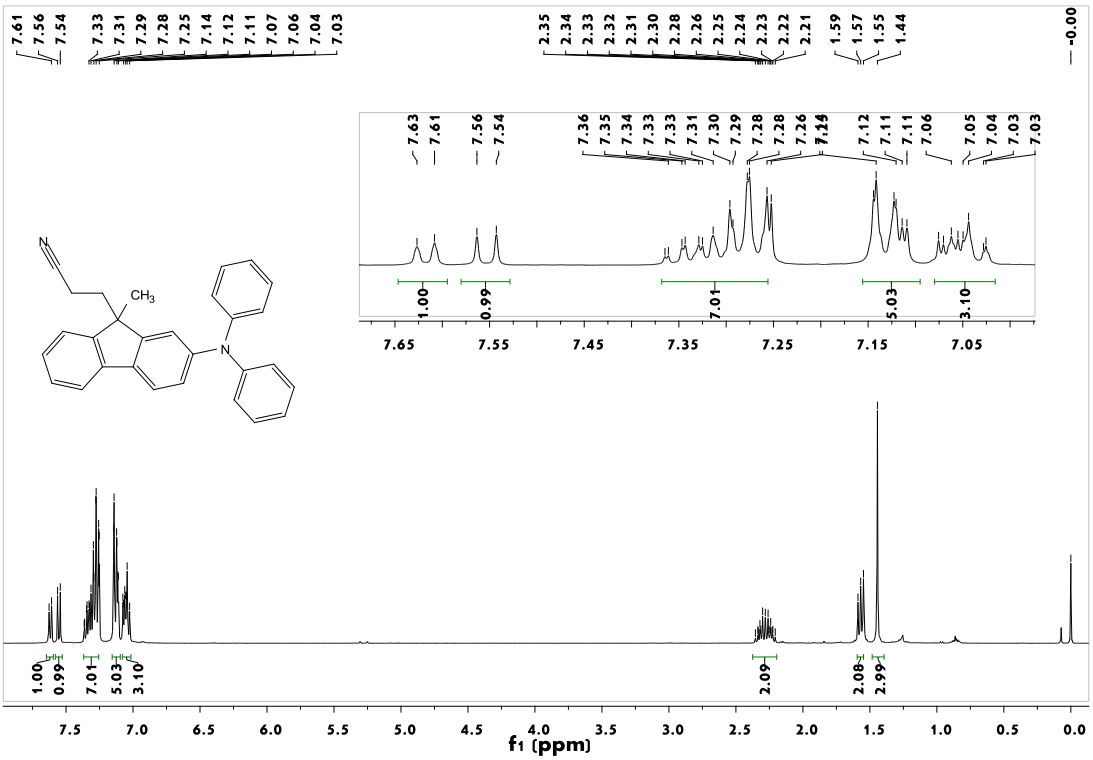
36.57
26.92
12.68
CH3
f1 (ppm)


8.24 8.23 8.21 8.19 7.97 7.52 7.51 7.51 7.50 7.48 7.46 7.45 7.44 7.44 7.42 7.42 7.26
2.55 2.55 2.54 2.53 2.53 2.52 2.51 1.62 1.53 1.52 1.51 1.51 1.51 1.50 1.49 0.00
8.24 8.23 8.23 8.22 8.21 8.21 8.19 7.99 7.98 7.97 7.96 7.96 7.95 7.53 7.52 7.51 7.51 7.50 7.48 7.46 7.45 7.44 7.44 7.42 7.42
2.06 2.00 6.17
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4
N
CH3
S
2.06 2.00 6.17 2.05 3.01 2.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.75 148.20 139.71 135.15 134.53 132.74 128.43 127.12 125.03 123.26 122.73 122.65 121.90 121.15 119.79 119.00
77.55 76.91 50.92 36.38 26.80 12.71
139.71 139.66 136.55 135.15 134.53 132.74 128.43 127.95 127.12 125.03 123.26 122.73 122.65 121.90 121.15 119.79 119.00
140 138 136 134 132 130 128 126 124 122 120
N
CH3
S
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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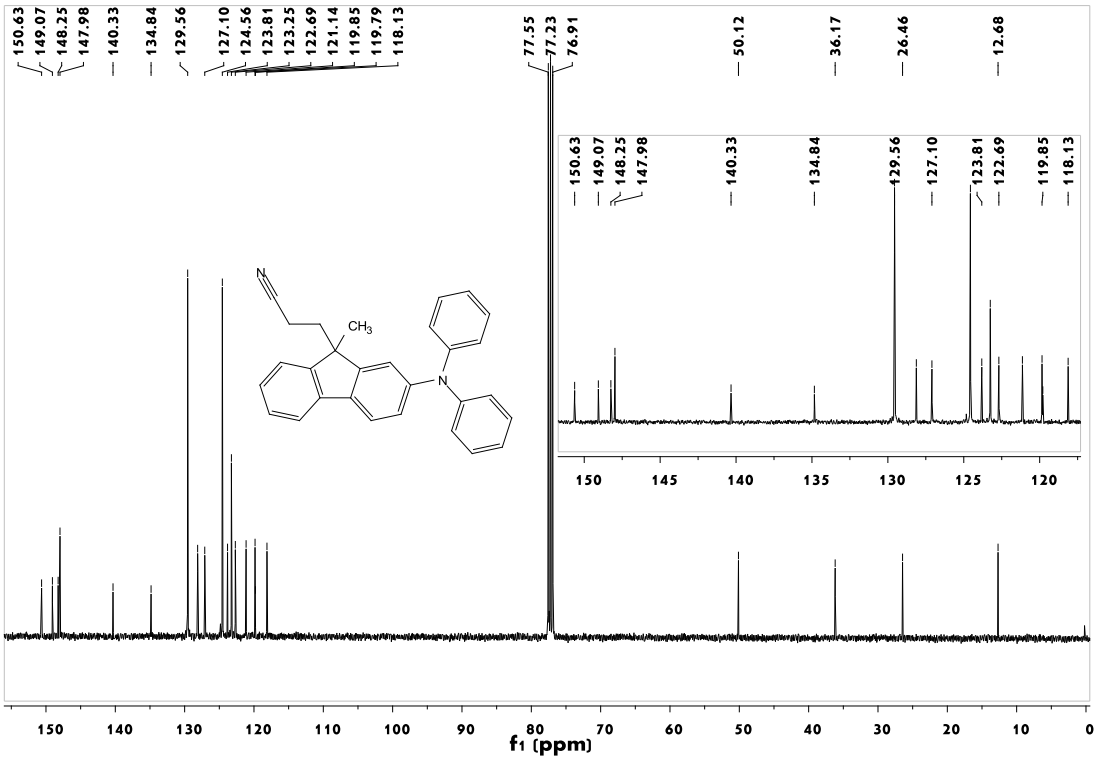
2.35 2.34 2.33 2.32 2.31 2.30 2.28 2.26 2.25 2.24 2.23 2.22 2.21 1.59 1.57 1.55 1.44
-0.00
7.63 7.61 7.56 7.54 7.36 7.35 7.34 7.33 7.33 7.31 7.30 7.29 7.28 7.28 7.26 7.12 7.11 7.11 7.06 7.05 7.04 7.03 7.03
1.00 0.99 7.01 5.03 3.10
7.65 7.55 7.45 7.35 7.25 7.15 7.05
1.00 0.99 7.01 5.03 3.10 2.09 2.08 2.99
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
N
CH3
N


150.63 149.07 148.25 147.98 140.33 134.84 129.56 127.10 124.56 123.81 123.25 122.69 121.14 119.85 119.79 118.13
77.55 77.23 76.91
50.12 36.17 26.46 12.68
150.63 149.07 148.25 147.98 140.33 134.84 129.56 127.10 123.81 122.69 119.85 118.13
150 145 140 135 130 125 120
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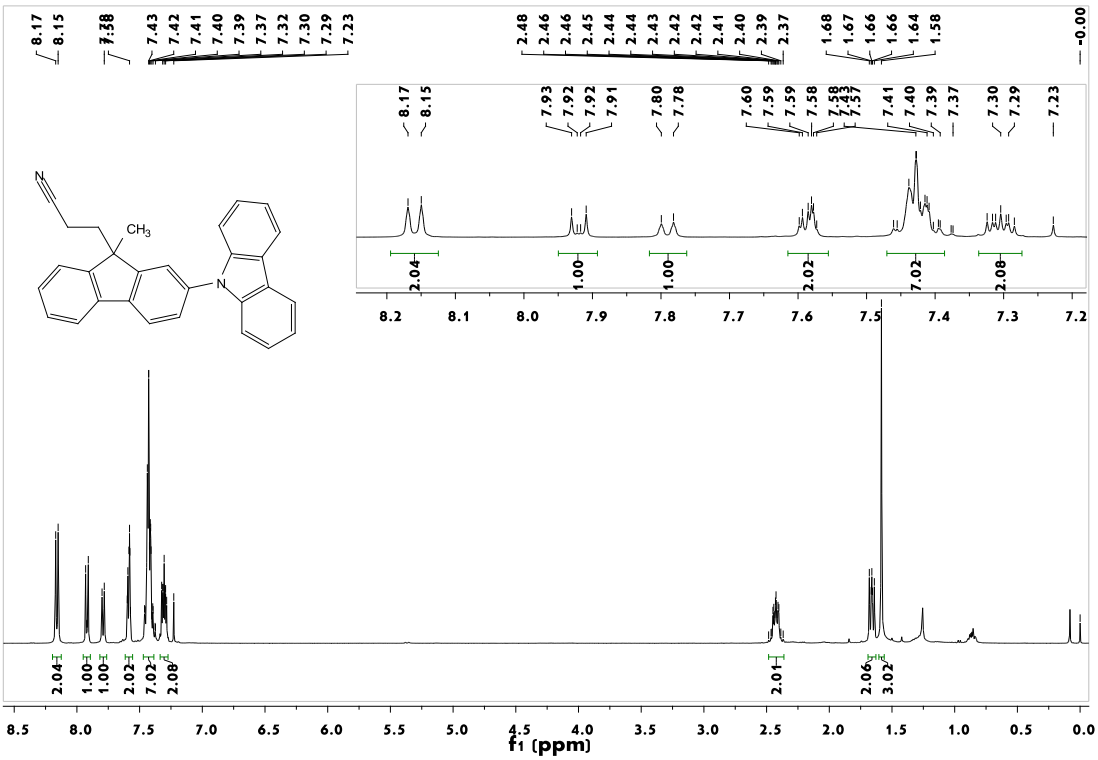
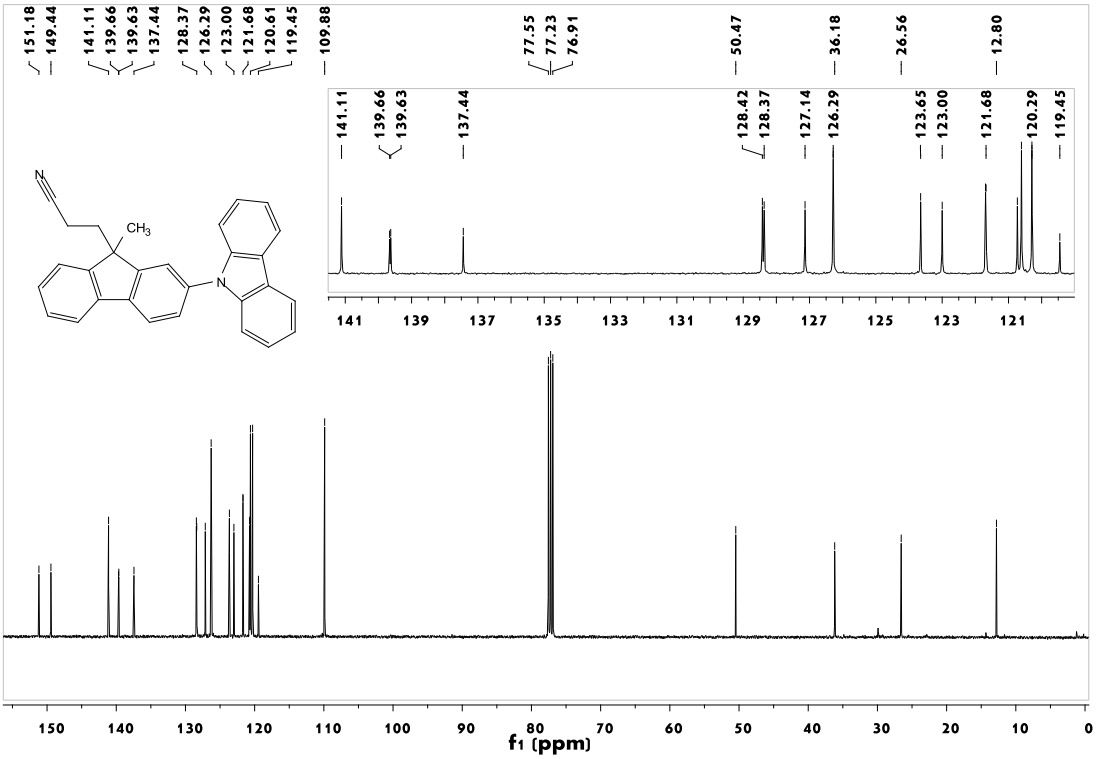
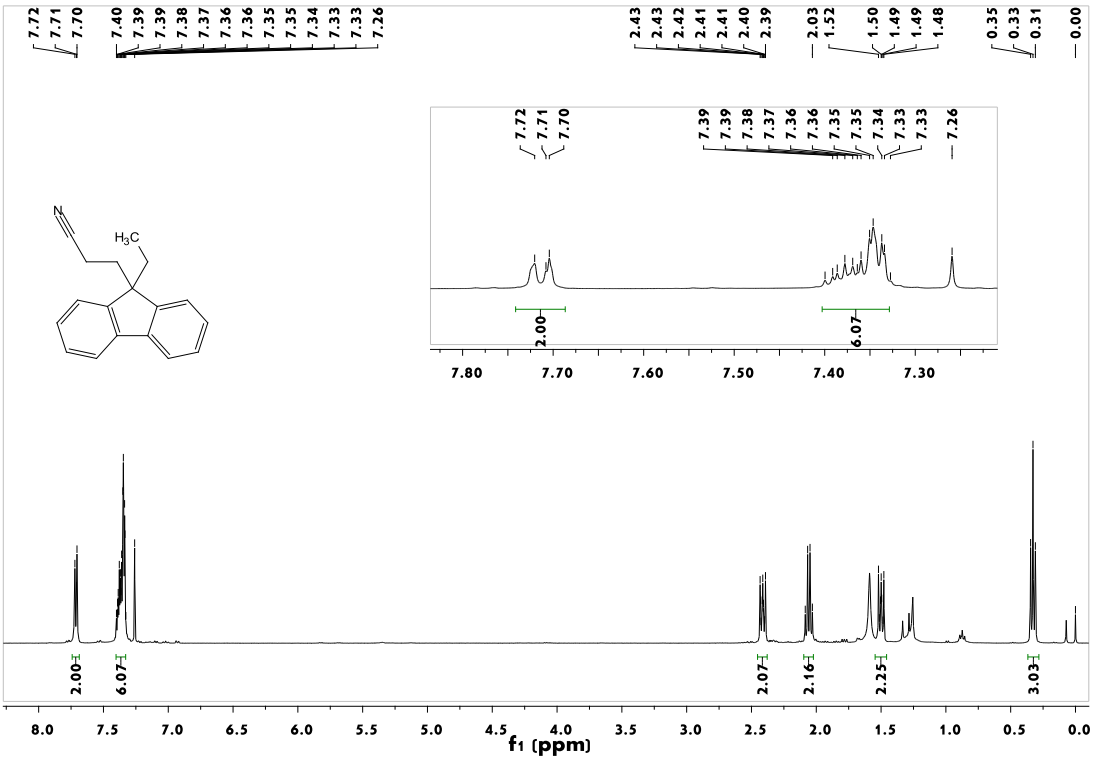
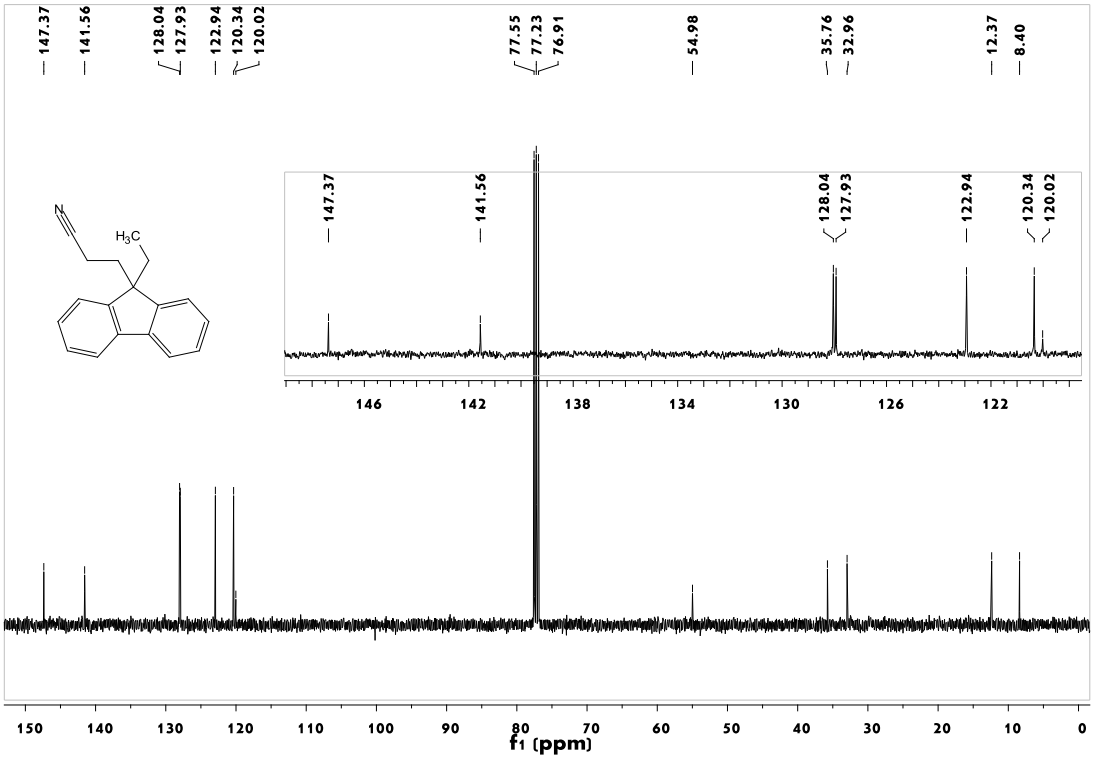
f1 (ppm)
N
CH3
N


f1 (ppm)


f1 (ppm)


7.72 7.71 7.70 7.40 7.39 7.39 7.38 7.37 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.26
2.43 2.43 2.42 2.41 2.41 2.40 2.39 2.03 1.52 1.50 1.49 1.49 1.48 0.35 0.33 0.31 0.00
N
H3C
2.00
6.07
2.00 6.07 2.07 2.16 2.25 3.03
f1 (ppm)


147.37 141.56 128.04 127.93 122.94 120.34 120.02 77.55 77.23 76.91 54.98 35.76 32.96 12.37 8.40
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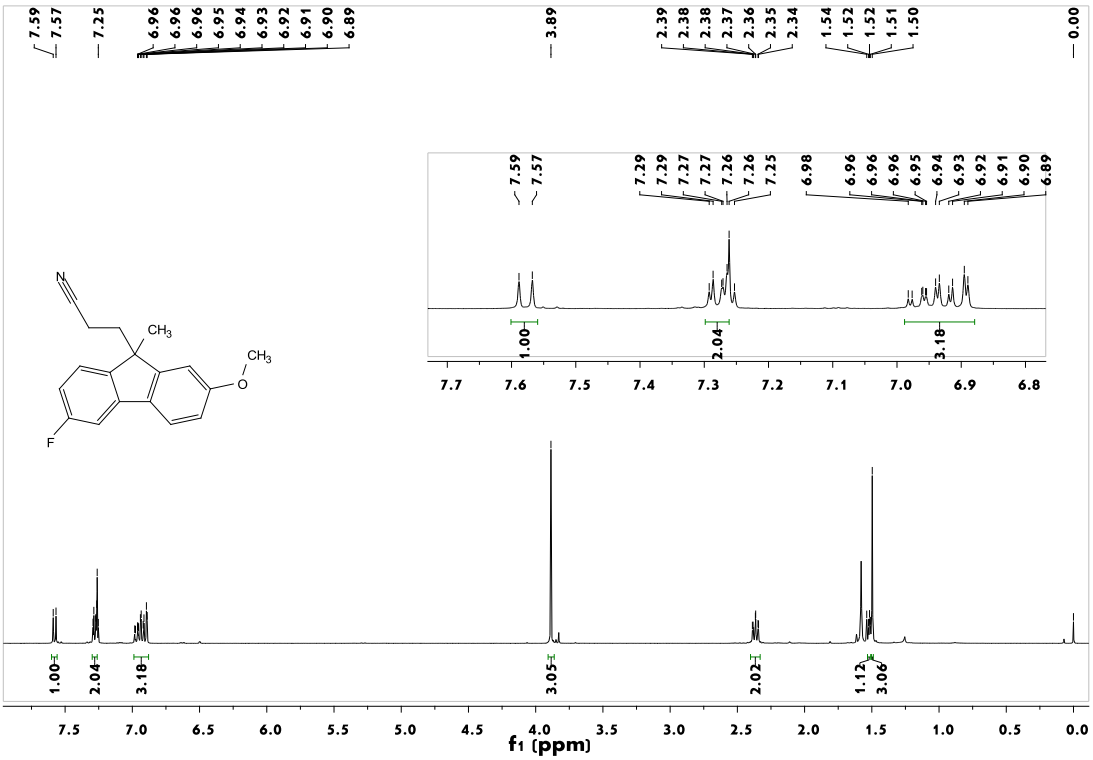
H3C
f1 (ppm)


7.59 7.57 7.25 6.96 6.96 6.96 6.95 6.94 6.93 6.92 6.91 6.90 6.89
3.89
2.39 2.38 2.38 2.37 2.36 2.35 2.34
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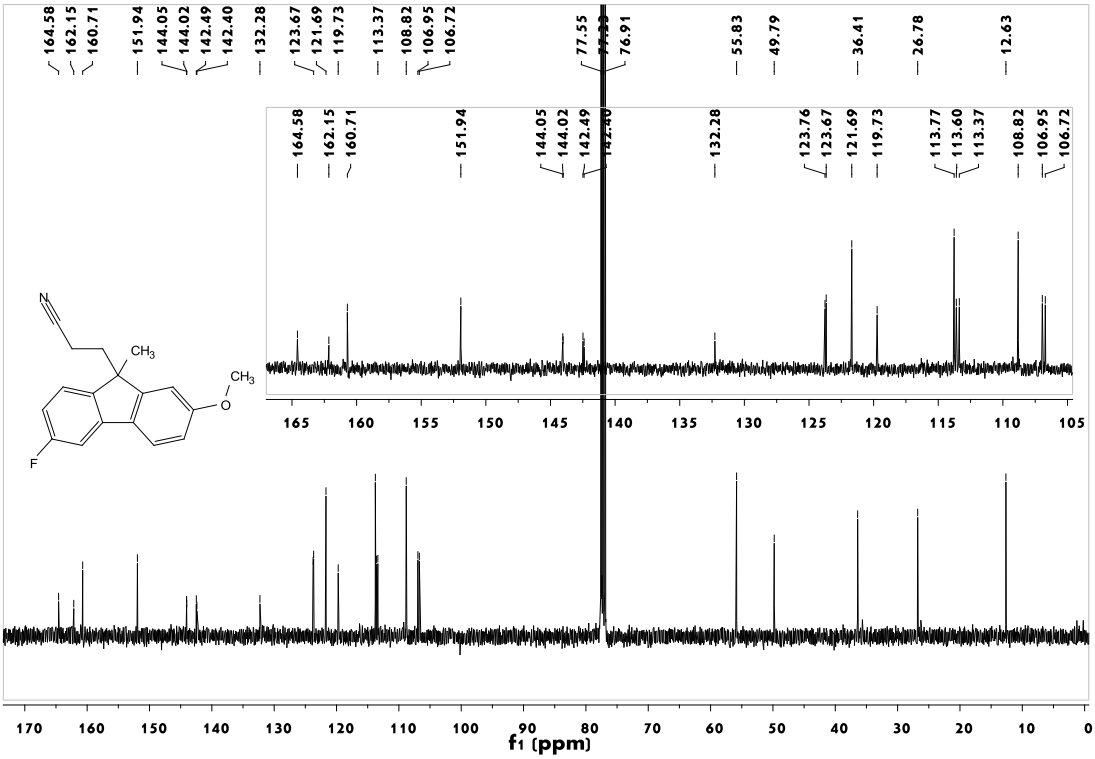
0.00
1.00 2.04 3.18 3.05 2.02 1.12 3.06
f1 (ppm)


164.58 162.15 160.71 151.94 144.05 144.02 142.49 142.40 132.28 123.67 121.69 119.73 113.37 108.82 106.95 106.72
77.55 76.91
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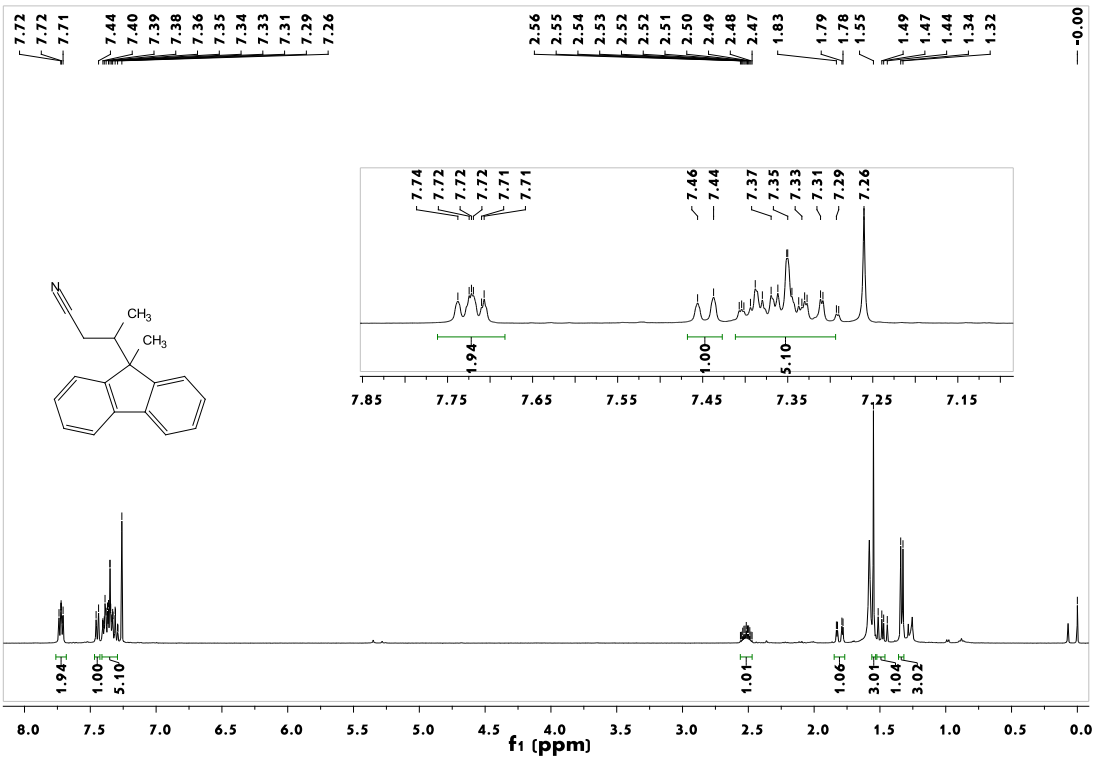
49.79
36.41
26.78
12.63
f1 (ppm)


7.72 7.72 7.71 7.44 7.40 7.39 7.38 7.36 7.35 7.34 7.33 7.31 7.29 7.26
2.56 2.55 2.54 2.53 2.52 2.52 2.51 2.50 2.49 2.48 2.47 1.83 1.79 1.78 1.55 1.49 1.47 1.44 1.34 1.32 -0.00
7.74 7.72 7.72 7.72 7.71 7.71 7.46 7.44 7.37 7.35 7.33 7.31 7.29 7.26
1.94 1.00 5.10
7.85 7.75 7.65 7.55 7.45 7.35 7.25 7.15
CH3 CH3
1.94 1.00 5.10 1.01 1.06 3.01 1.04 3.02
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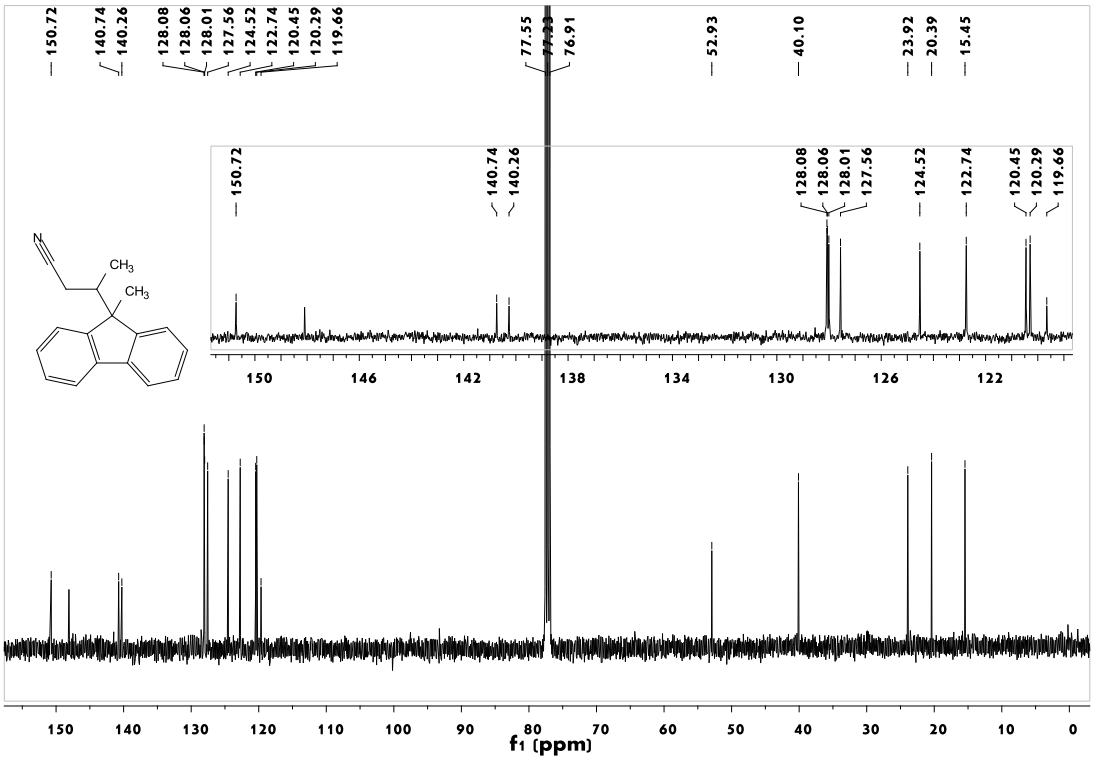
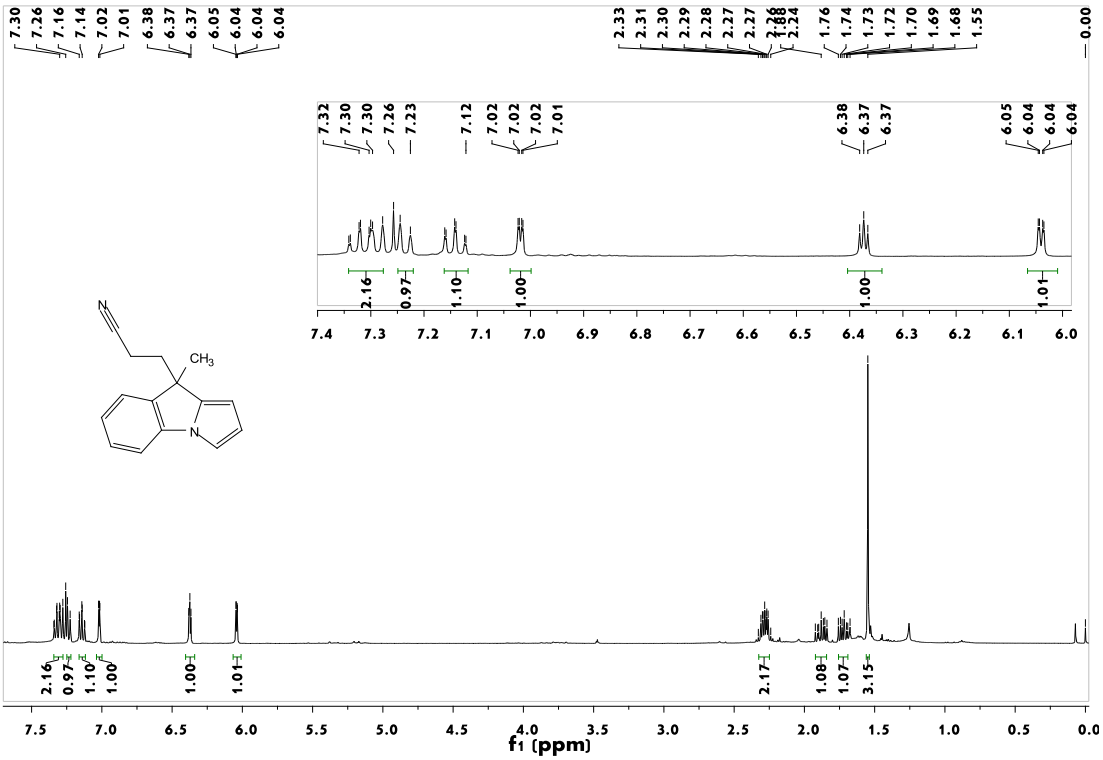
f1 (ppm)


150.72 140.74 140.26 128.08 128.06 128.01 127.56 124.52 122.74 120.45 120.29 119.66
77.55 77.33 76.91 52.93 40.10 23.92 20.39 15.45
150.72 140.74 140.26 128.08 128.06 128.01 127.56 124.52 122.74 120.45 120.29 119.66
150 146 142 138 134 130 126 122
CH3 CH3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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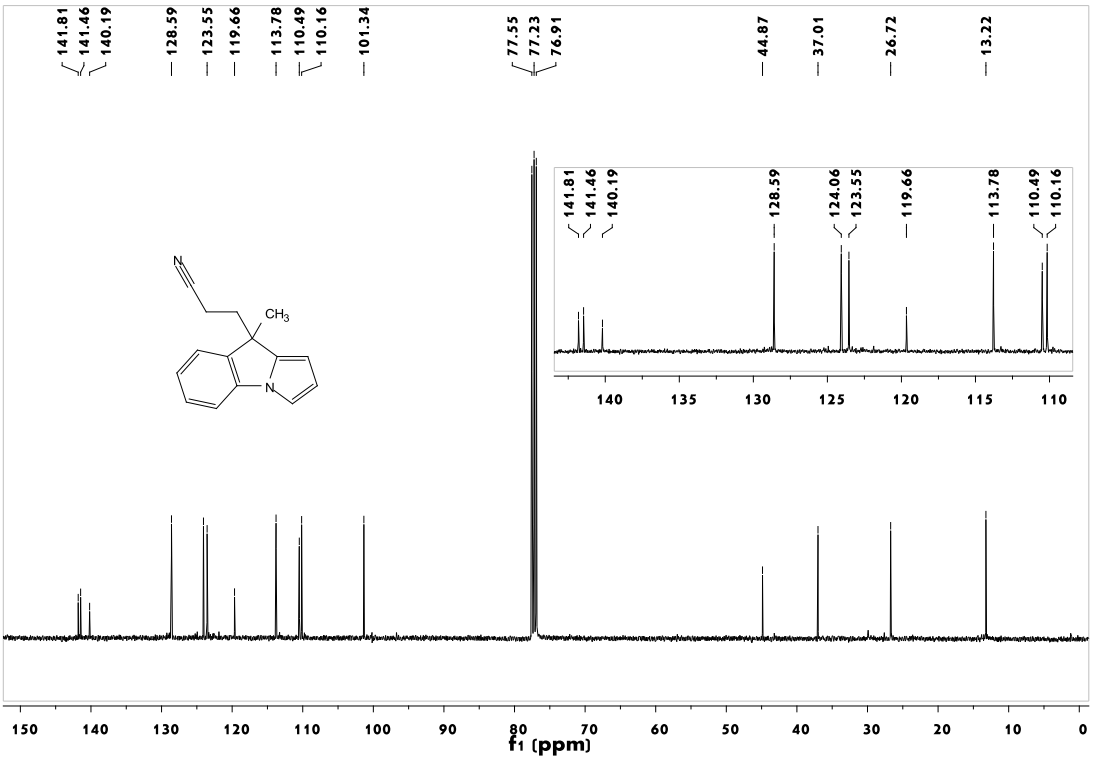
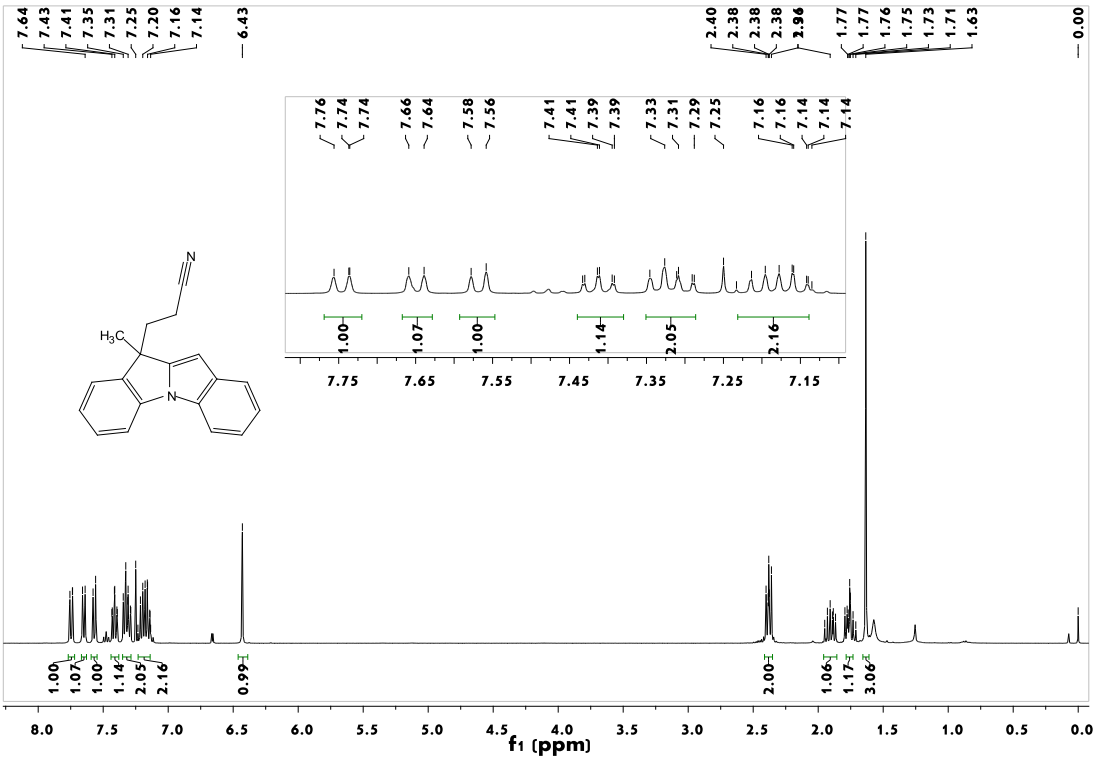
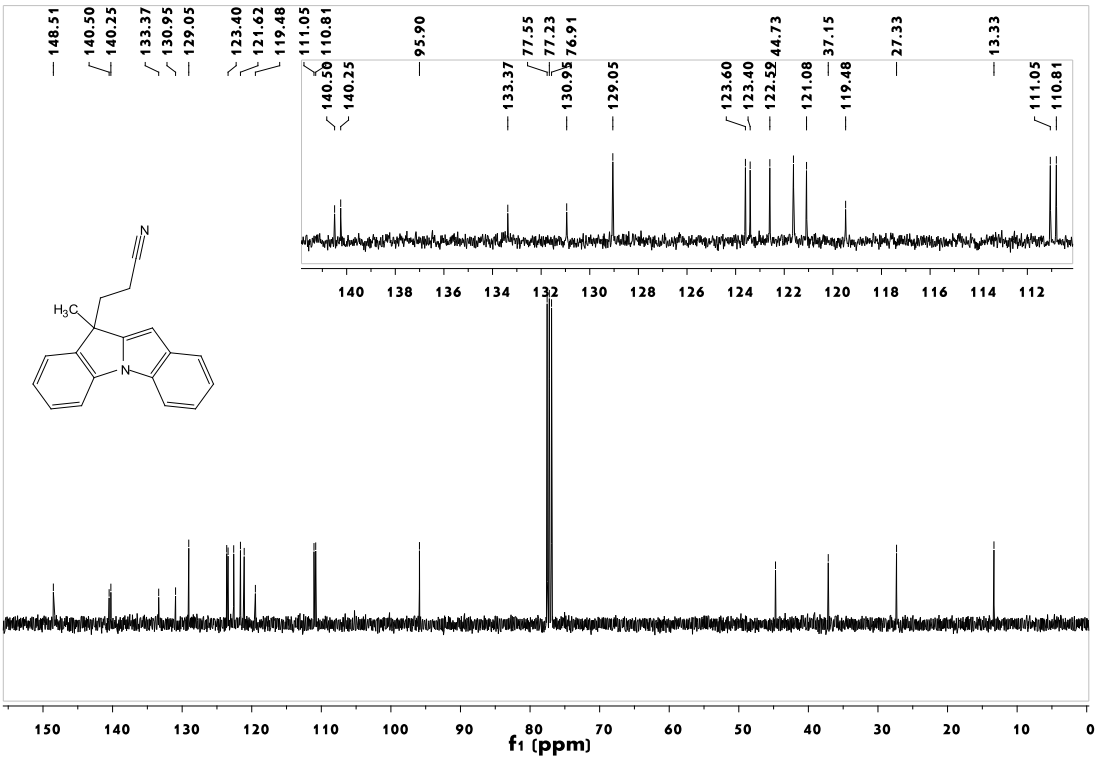
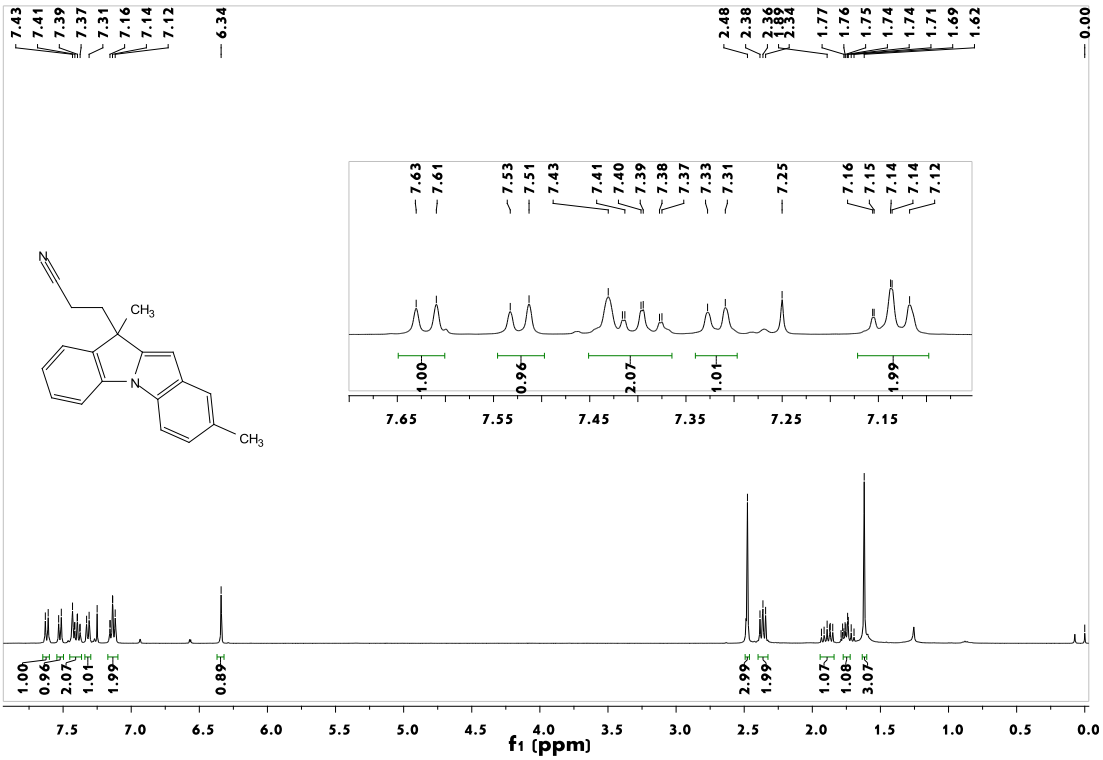
7.32 7.30 7.30 7.26 7.23 7.12 7.02 7.02 7.02 7.01 6.38 6.37 6.37 6.05 6.04 6.04 6.04
2.16 0.97 1.10 1.00 1.00 1.01
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0
CH3
N
2.16 0.97 1.10 1.00 1.00 1.01 2.17 1.08 1.07 3.15
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


141.81 141.46 140.19 128.59 123.55 119.66 113.78 110.49 110.16 101.34 77.55 77.23 76.91 44.87 37.01 26.72 13.22
141.81 141.46 140.19 128.59 124.06 123.55 119.66 113.78 110.49 110.16
140 135 130 125 120 115 110
CH3
N
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.64 7.43 7.41 7.35 7.31 7.25 7.20 7.16 7.14 6.43
2.40 2.38 2.38 2.38 1.77 1.77 1.76 1.75 1.73 1.71 1.63 0.00
7.76 7.74 7.74 7.66 7.64 7.58 7.56 7.41 7.41 7.39 7.39 7.33 7.31 7.29 7.25 7.16 7.16 7.14 7.14 7.14
1.00 1.07 1.00 1.14 2.05 2.16
7.75 7.65 7.55 7.45 7.35 7.25 7.15
1.00 1.07 1.00 1.14 2.05 2.16 0.99 2.00 1.06 1.17 3.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


148.51 140.50 140.25 133.37 130.95 129.05 123.40 121.62 119.48 111.05 110.81 95.90 77.55 77.23 76.91 44.73 37.15 27.33 13.33
140.50 140.25 133.37 130.95 129.05 123.60 123.40 122.59 121.08 119.48 111.05 110.81
140 138 136 134 132 130 128 126 124 122 120 118 116 114 112
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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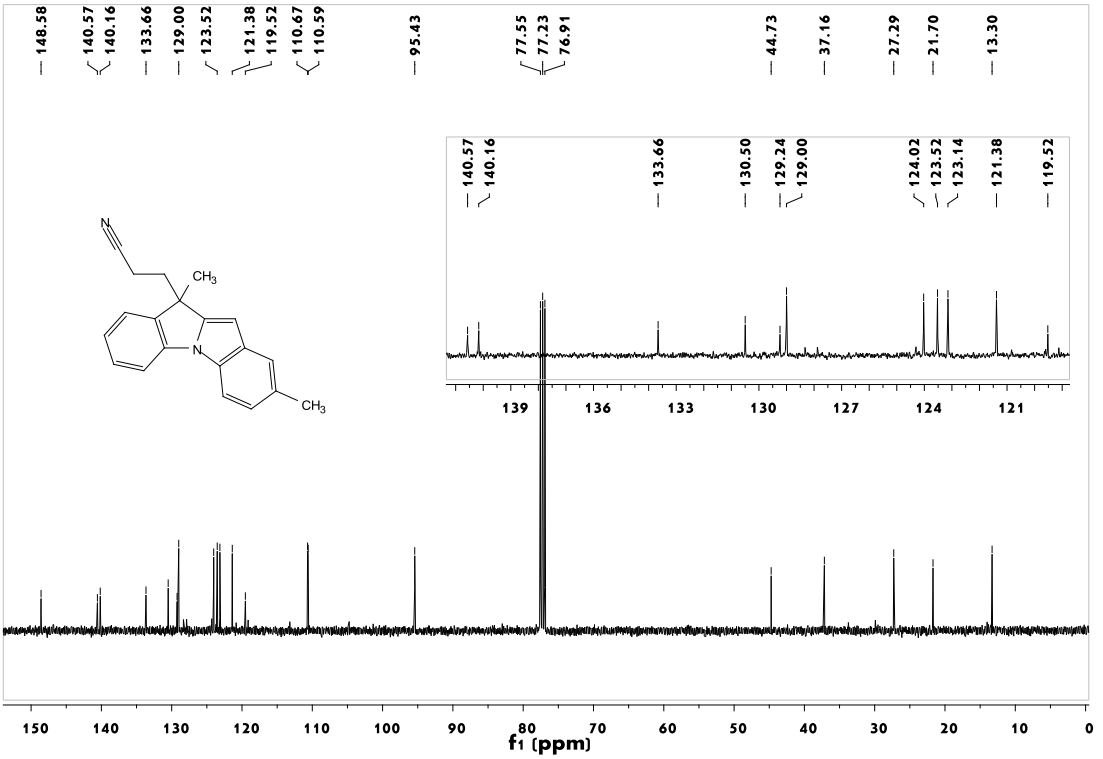
7.14
7.12
6.34
2.48
2.38
2.36
2.34
1.77
1.76
1.75
1.74
1.74
1.71
1.69
1.62
0.00
7.63
7.61
7.53
7.51
7.43
7.41
7.40
7.39
7.38
7.37
7.33
7.31
7.25
7.16
7.15
7.14
7.14
7.12
1.00
0.96
2.07
1.01
1.99
0.89
2.99
1.99
1.07
1.08
3.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
7.65
7.55
7.45
7.35
7.25
7.15
N
CH3
CH3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140.57
140.16
133.66
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123.52
121.38
119.52
110.67
110.59
95.43
77.55
77.23
76.91
44.73
37.16
27.29
21.70
13.30
140.57
140.16
133.66
130.50
129.24
129.00
124.02
123.52
123.14
121.38
119.52
139
136
133
130
127
124
121
150
140
130
120
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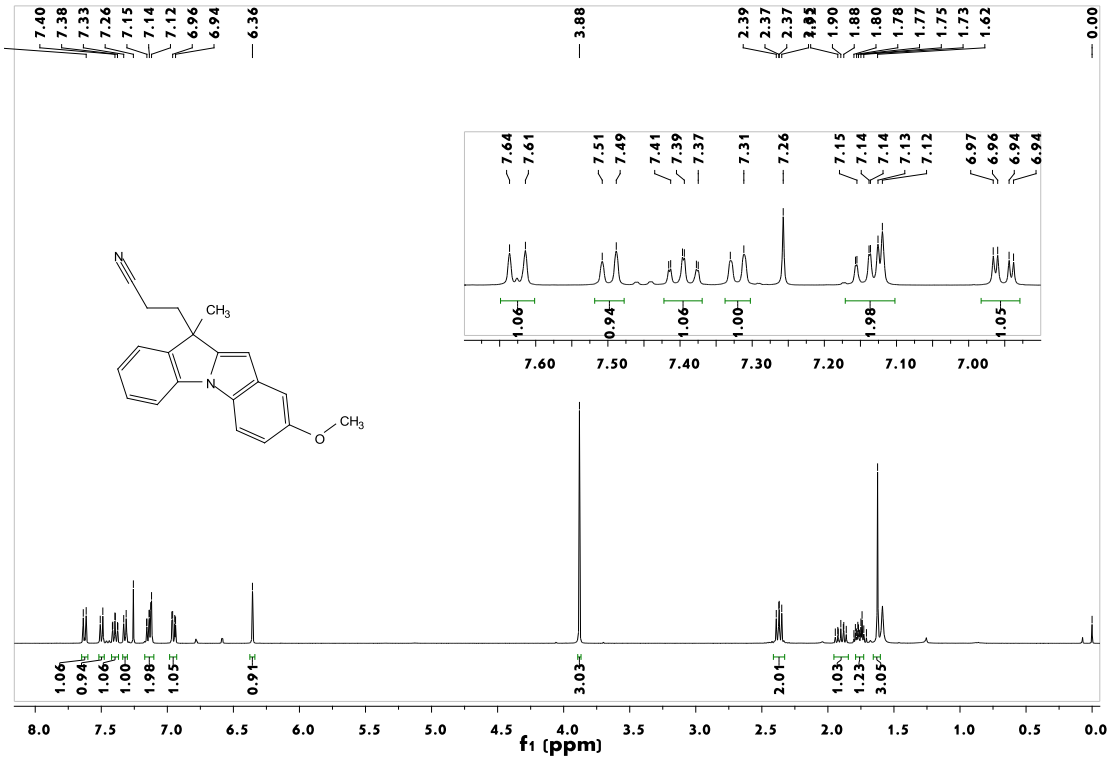
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
N
CH3
CH3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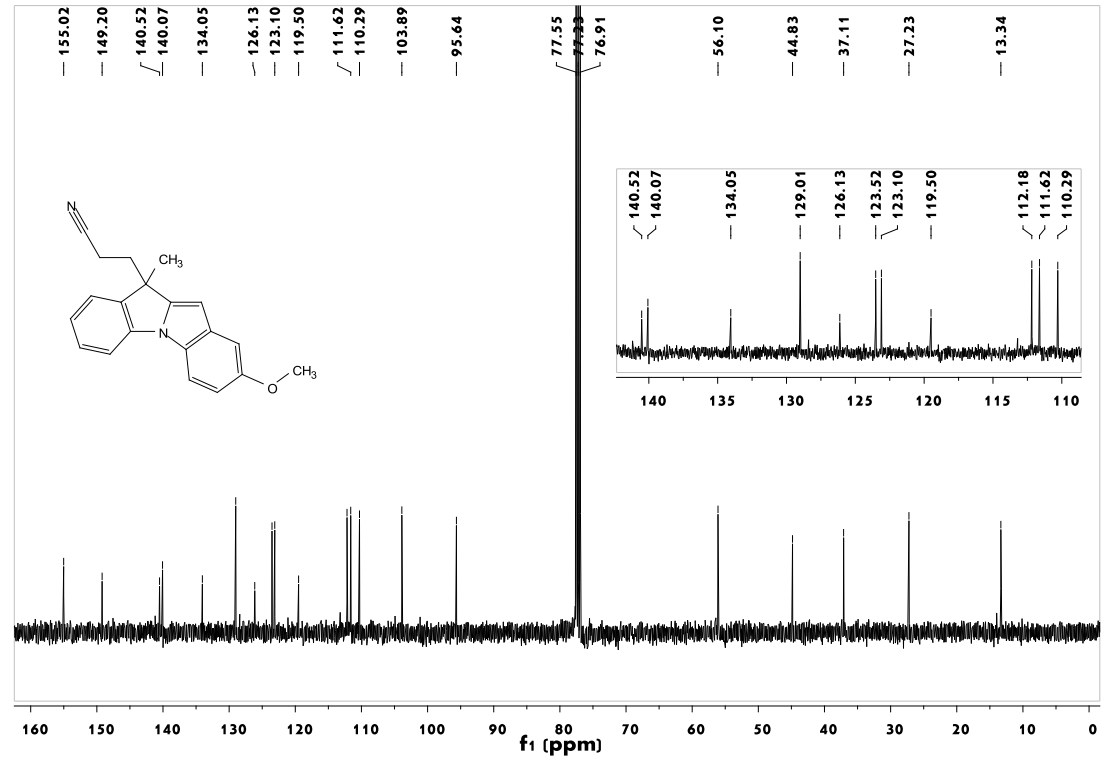
7.38
7.33
7.26
7.15
7.14
7.12
6.96
6.94
6.36
3.88
2.39
2.37
2.37
1.90
1.88
1.80
1.78
1.77
1.75
1.73
1.62
0.00
7.64
7.61
7.51
7.49
7.41
7.39
7.37
7.31
7.26
7.15
7.14
7.14
7.13
7.12
6.97
6.96
6.94
6.94
1.06
0.94
1.06
1.00
1.98
1.05
7.60
7.50
7.40
7.30
7.20
7.10
7.00
CH3
N
O
CH3
1.06
0.94
1.06
1.00
1.98
1.05
0.91
3.03
2.01
1.03
1.23
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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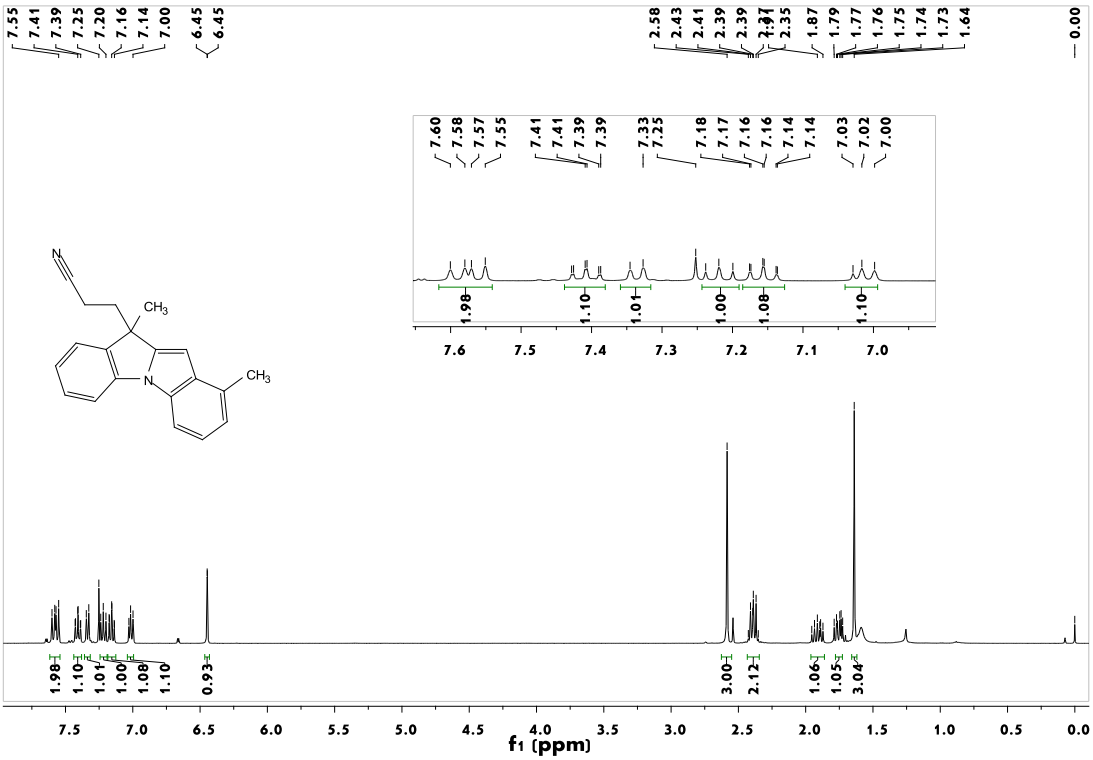
149.20
140.52
140.07
134.05
126.13
123.10
119.50
111.62
110.29
103.89
95.64
77.55
76.91
56.10
44.83
37.11
27.23
13.34
140.52
140.07
134.05
129.01
126.13
123.52
123.10
119.50
112.18
111.62
110.29
140
135
130
125
120
115
110
CH3
N
O
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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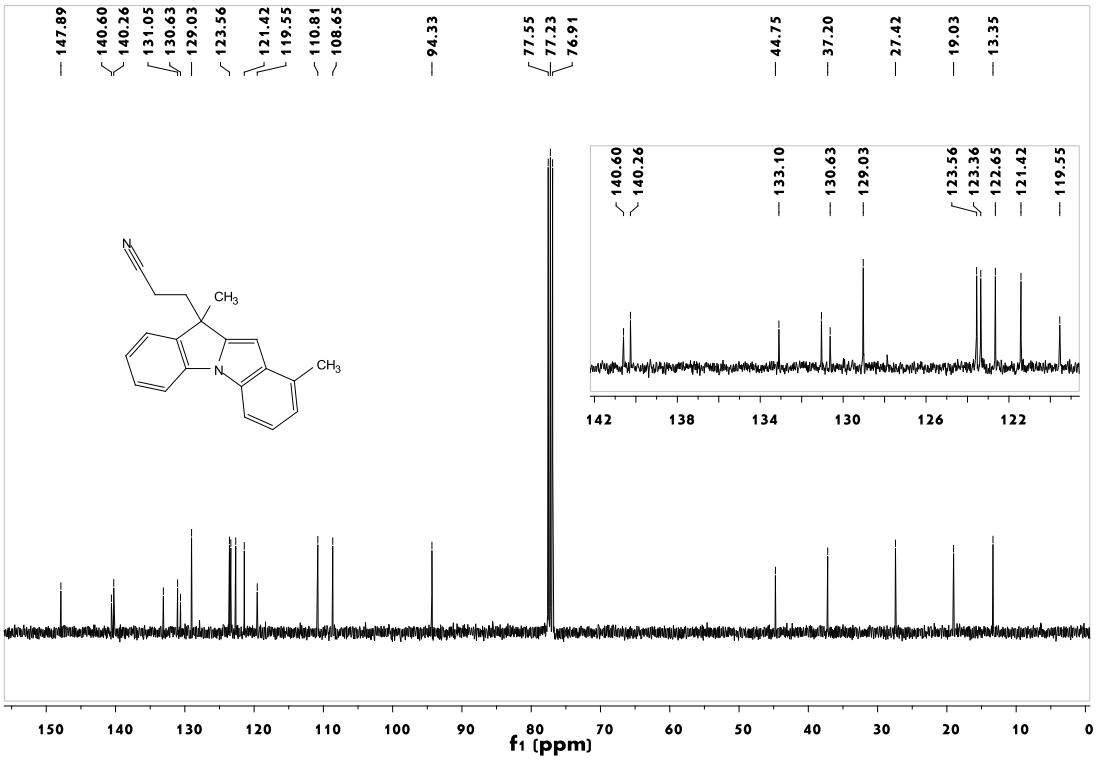
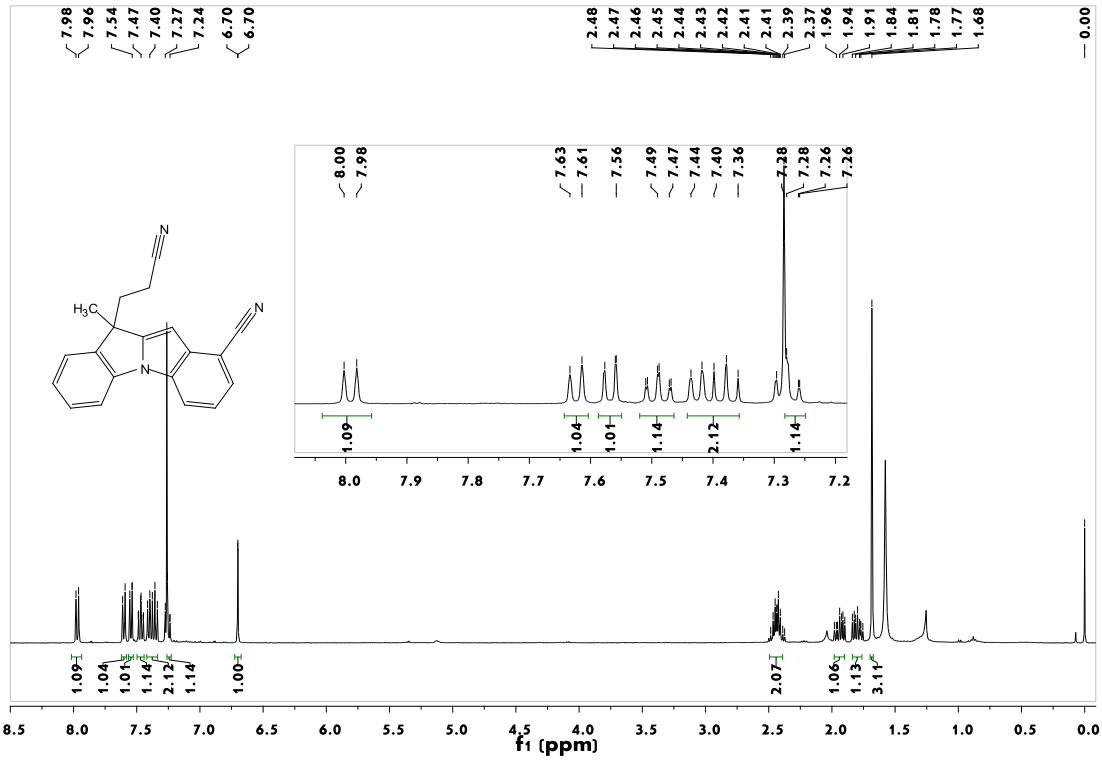
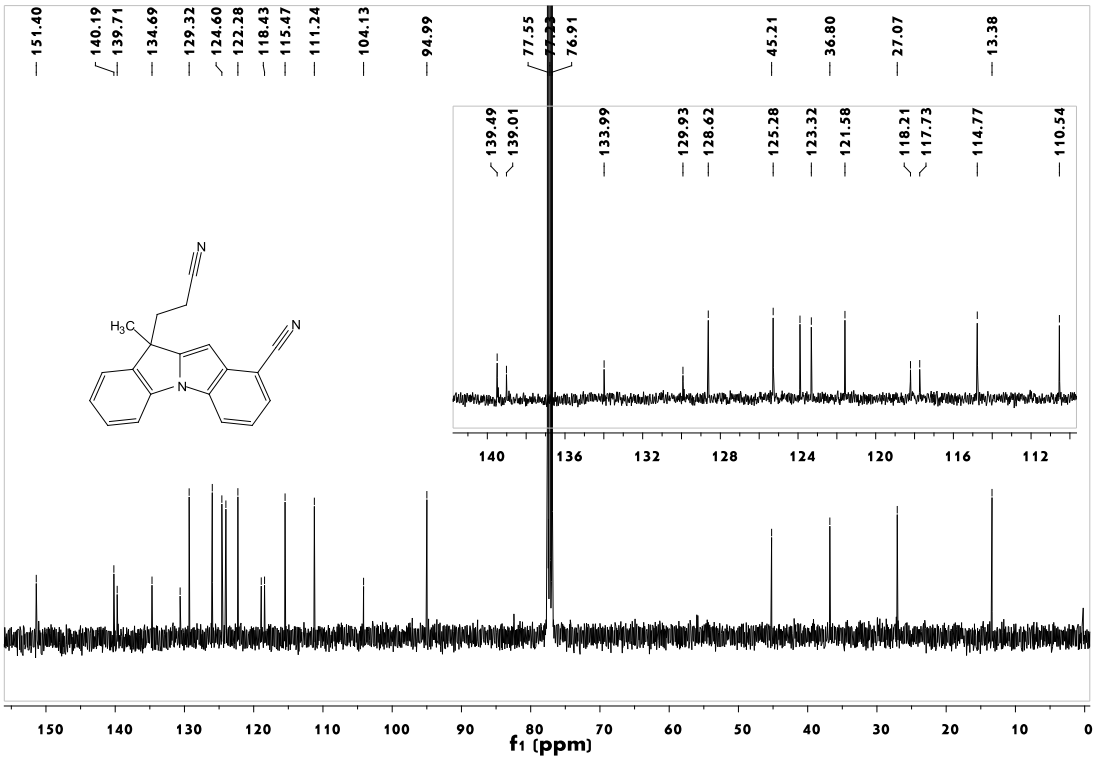
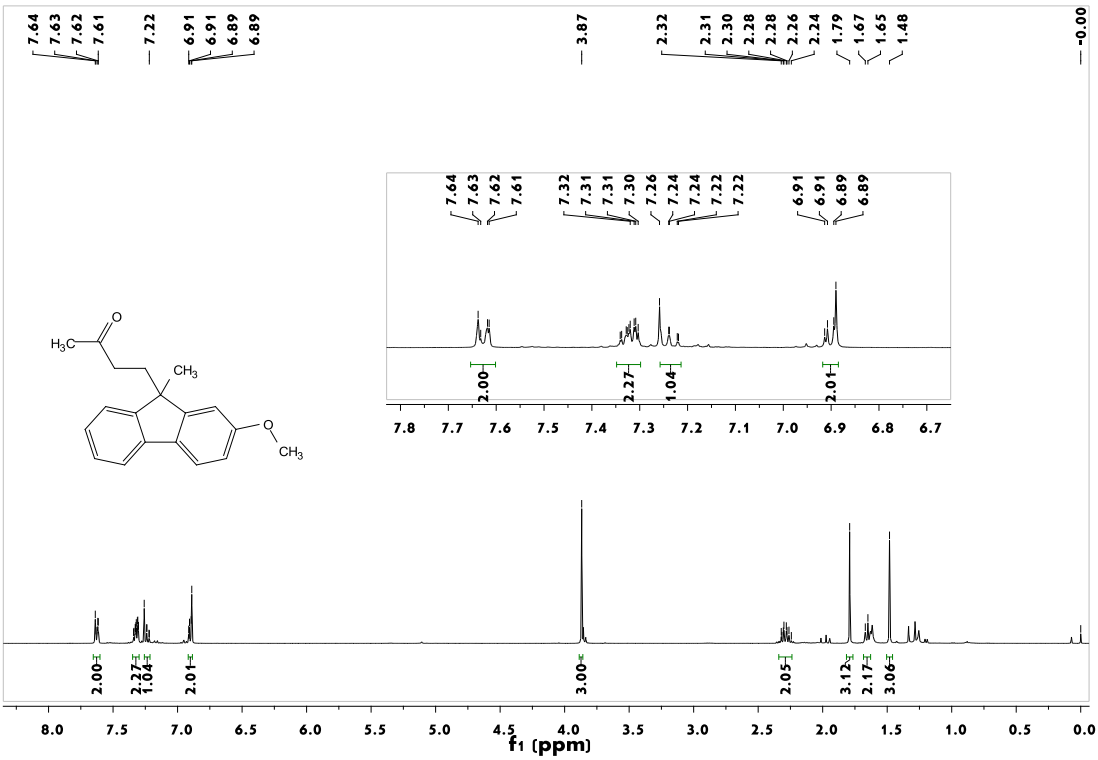
2.58 2.43 2.41 2.39 2.39 2.35 1.87 1.79 1.77 1.76 1.75 1.74 1.73 1.64 0.00
7.60 7.58 7.57 7.55 7.41 7.41 7.39 7.39 7.33 7.25 7.18 7.17 7.16 7.16 7.14 7.14 7.03 7.02 7.00
1.98 1.10 1.01 1.00 1.08 1.10
7.6 7.5 7.4 7.3 7.2 7.1 7.0
N
CH3
CH3
1.98 1.10 1.01 1.00 1.08 1.10 0.93
3.00 2.12 1.06 1.05 3.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


147.89 140.60 140.26 131.05 130.63 129.03 123.56 121.42 119.55 110.81 108.65 94.33 77.55 77.23 76.91 44.75 37.20 27.42 19.03 13.35
140.60 140.26 133.10 130.63 129.03 123.56 123.36 122.65 121.42 119.55
142 138 134 130 126 122
N
CH3
CH3
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.98 7.96 7.54 7.47 7.40 7.27 7.24 6.70 6.70
2.48 2.47 2.46 2.45 2.44 2.43 2.42 2.41 2.41 2.39 2.37 1.96 1.94 1.91 1.84 1.81 1.78 1.77 1.68
0.00
8.00 7.98 7.63 7.61 7.56 7.49 7.47 7.44 7.40 7.36 7.28 7.28 7.26 7.26
1.09 1.04 1.01 1.14 2.12 1.14 1.00 2.07 1.06 1.13 3.11
f1 (ppm)


151.40 140.19 139.71 134.69 129.32 124.60 122.28 118.43 115.47 111.24 104.13 94.99 77.55 76.91 45.21 36.80 27.07 13.38
139.49 139.01 133.99 129.93 128.62 125.28 123.32 121.58 118.21 117.73 114.77 110.54
f1 (ppm)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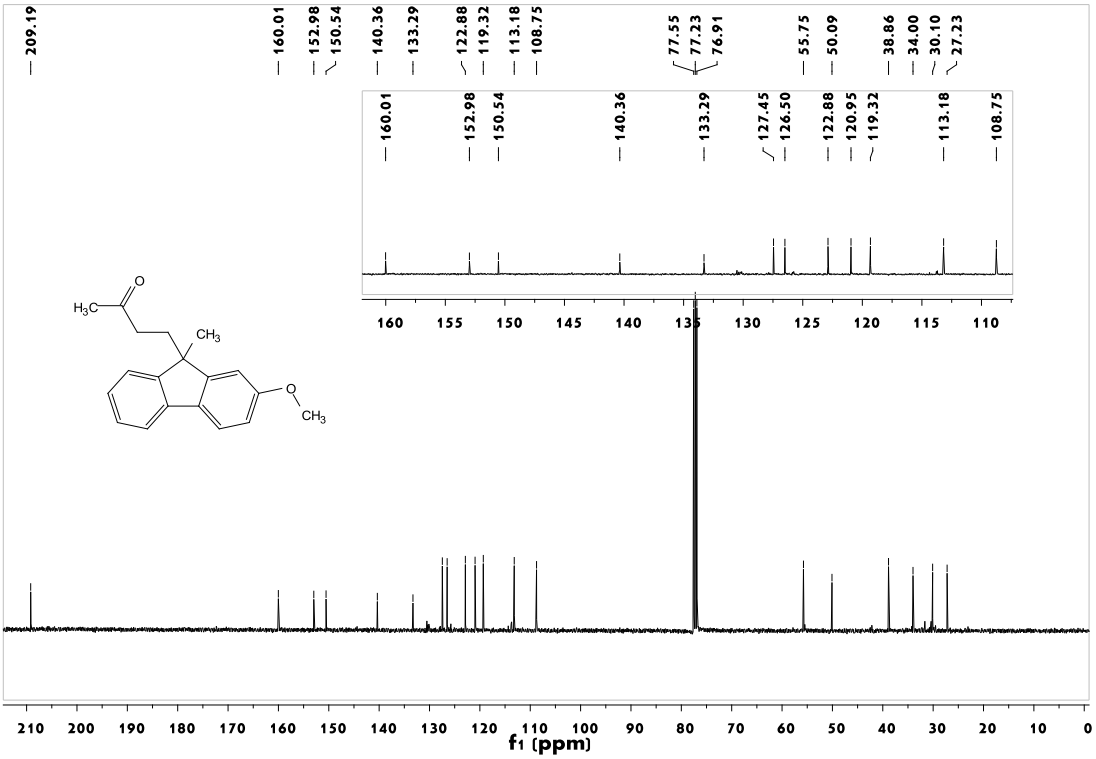
7.63
7.62
7.61
7.22
6.91
6.91
6.89
6.89
3.87
2.32
2.31
2.30
2.28
2.28
2.26
2.24
1.79
1.67
1.65
1.48
-0.00
2.00
2.27
1.04
2.01
3.00
2.05
3.12
2.17
3.06
f1 (ppm)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160.01
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150.54
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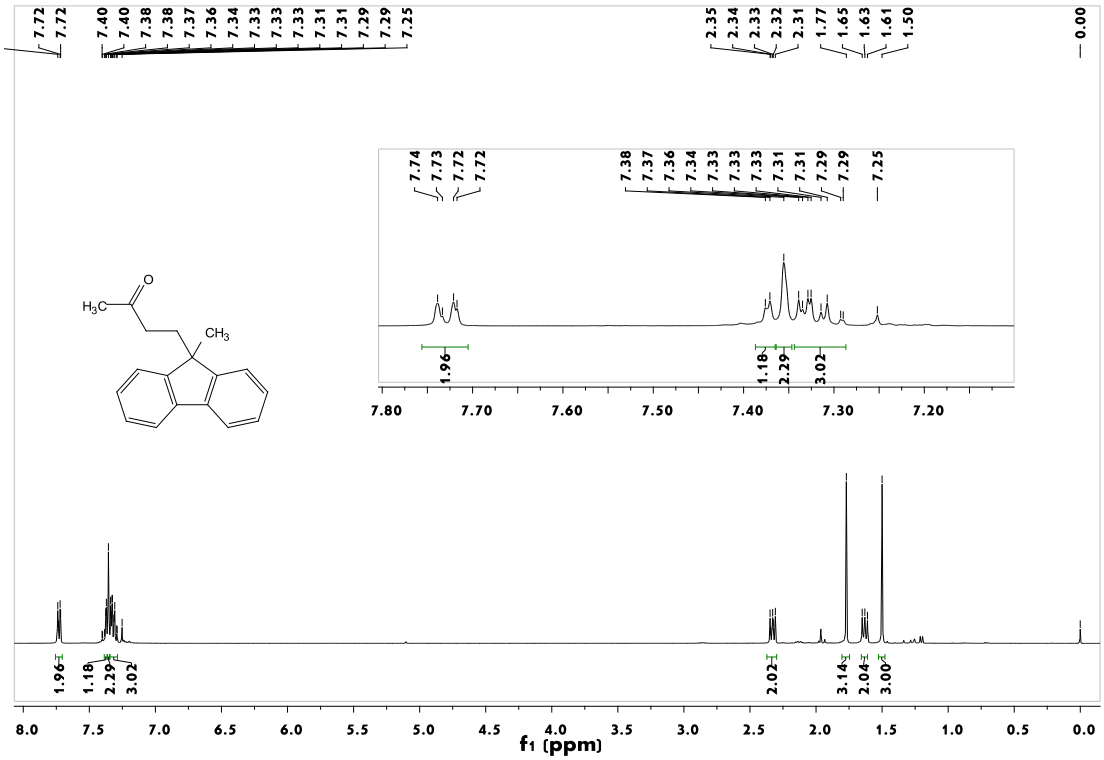
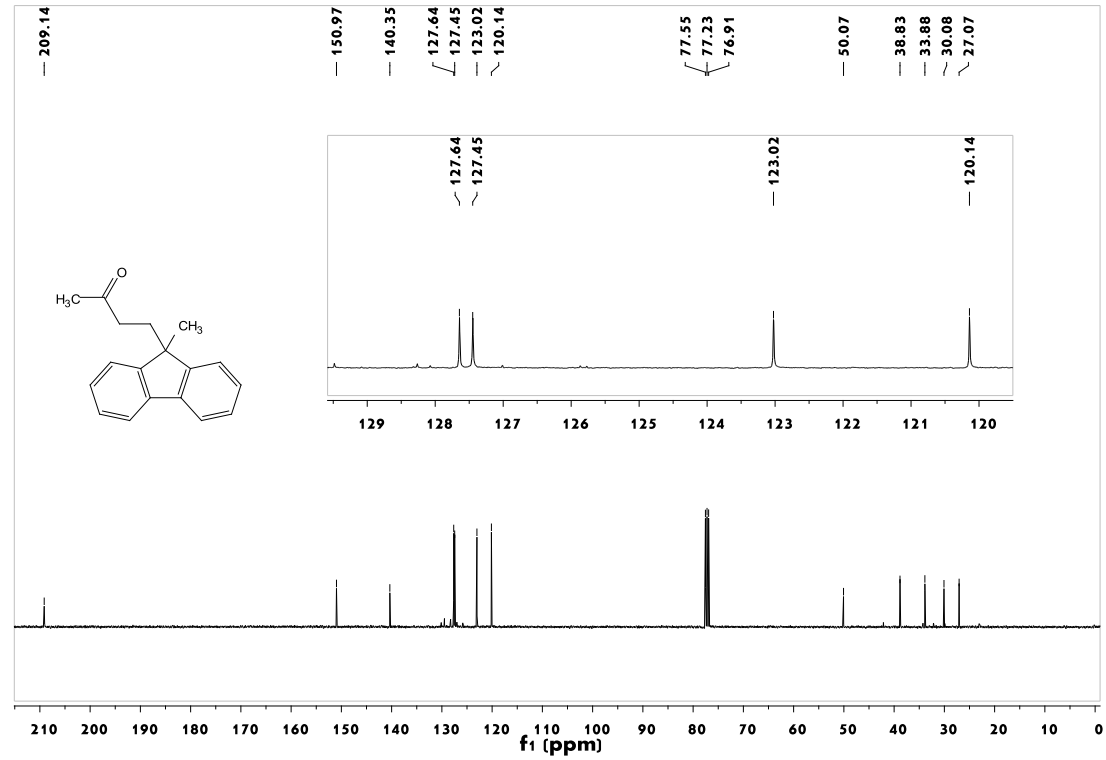
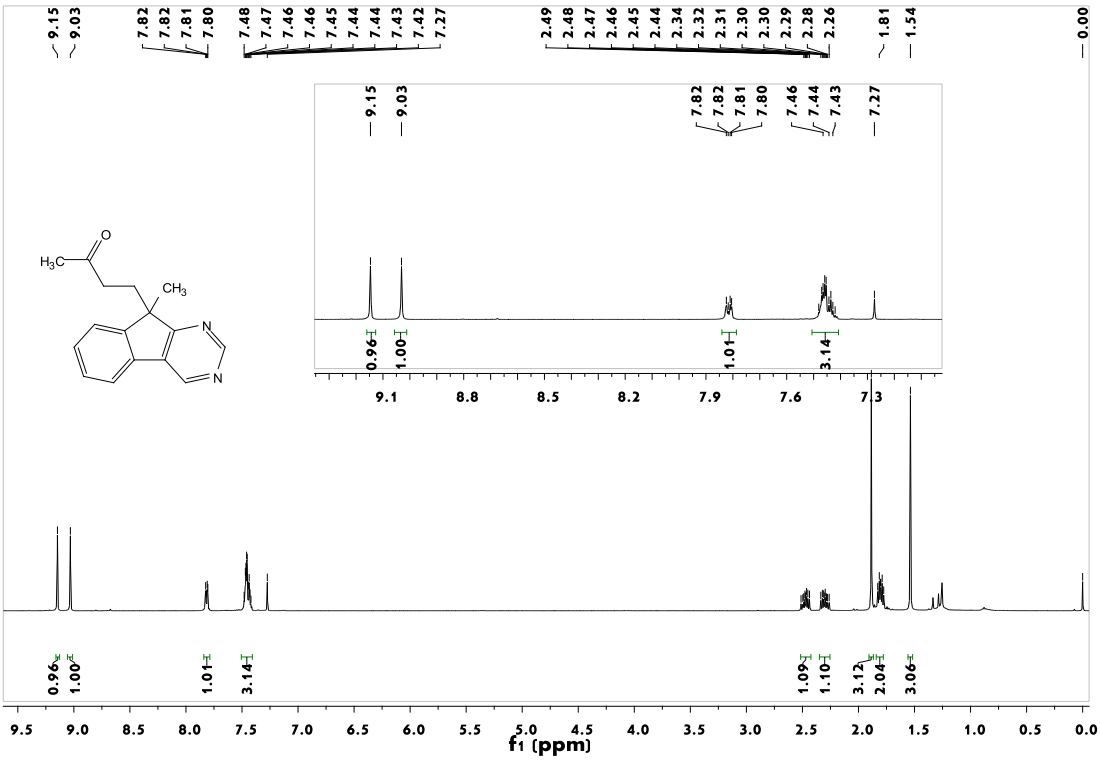
133.29
122.88
119.32
113.18
108.75
77.55
77.23
76.91
55.75
50.09
38.86
34.00
30.10
27.23
127.45
126.50
120.95
f1 (ppm)


7.72 7.72 7.40 7.40 7.38 7.38 7.37 7.36 7.34 7.33 7.33 7.33 7.31 7.31 7.29 7.29 7.25
2.35 2.34 2.33 2.32 2.31 1.77 1.65 1.63 1.61 1.50
0.00
7.74 7.73 7.72 7.72 7.38 7.37 7.36 7.34 7.33 7.33 7.33 7.31 7.31 7.29 7.29 7.25
1.96 1.18 2.29 3.02
7.80 7.70 7.60 7.50 7.40 7.30 7.20
H3C O CH3
1.96 1.18 2.29 3.02 2.02 3.14 2.04 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


209.14 150.97 140.35 127.64 127.45 123.02 120.14 77.55 77.23 76.91 50.07 38.83 33.88 30.08 27.07
127.64 127.45 123.02 120.14
129 128 127 126 125 124 123 122 121 120
H3C O CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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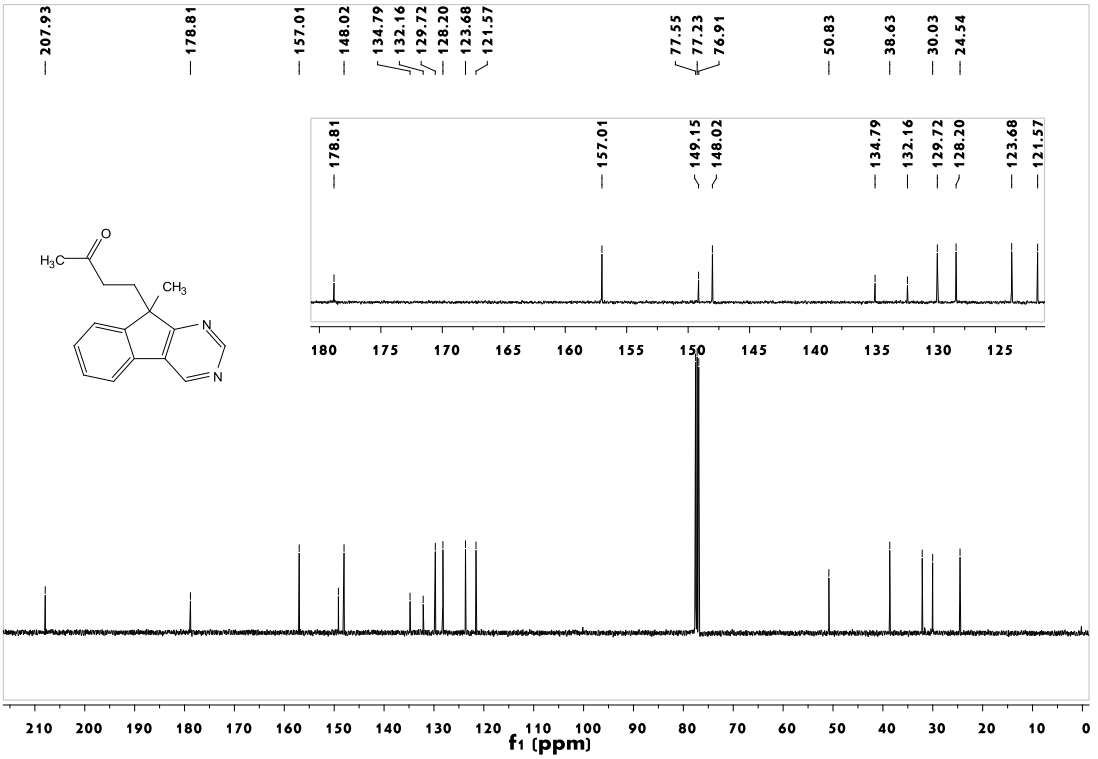
9.03
7.82
7.82
7.81
7.80
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.27
2.49
2.48
2.47
2.46
2.45
2.44
2.34
2.32
2.31
2.30
2.30
2.29
2.28
2.26
1.81
1.54
0.00
0.96
1.00
1.01
3.14
1.09
1.10
3.12
2.04
3.06
f1 (ppm)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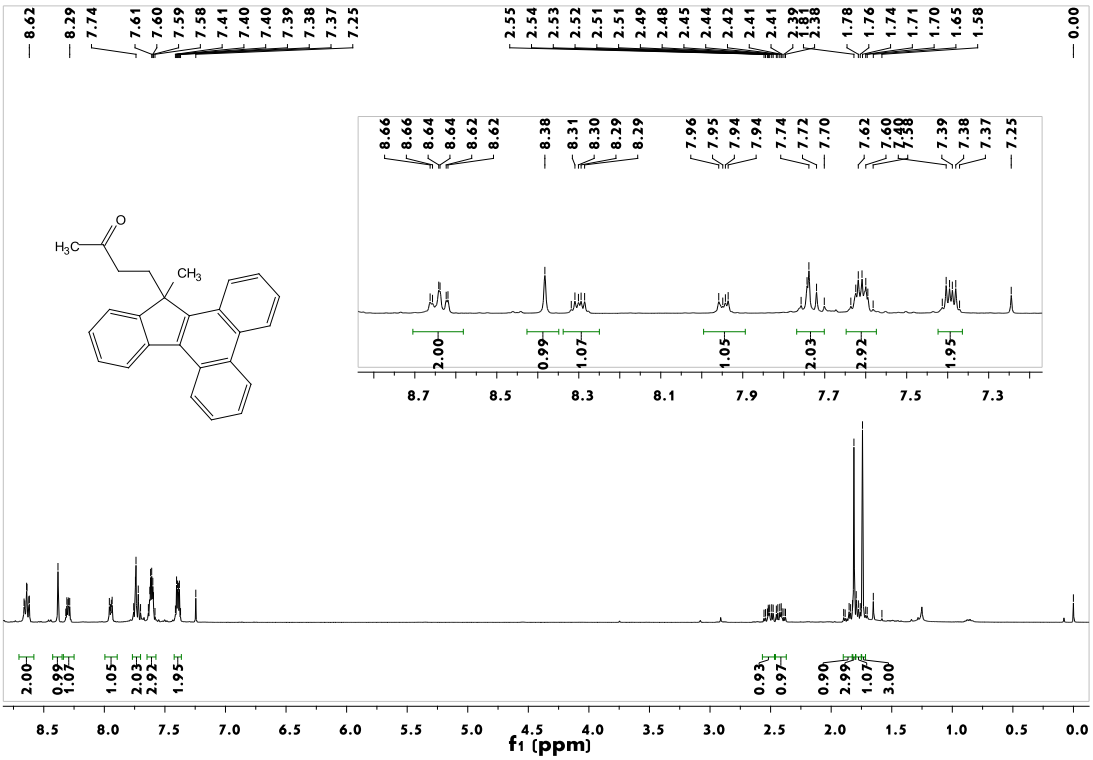
178.81
157.01
148.02
134.79
132.16
129.72
128.20
123.68
121.57
77.55
77.23
76.91
50.83
38.63
30.03
24.54
149.15
f1 (ppm)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8.29
7.74
7.61
7.60
7.59
7.58
7.41
7.40
7.40
7.39
7.38
7.37
7.25
2.55
2.54
2.53
2.52
2.51
2.51
2.49
2.48
2.45
2.44
2.42
2.41
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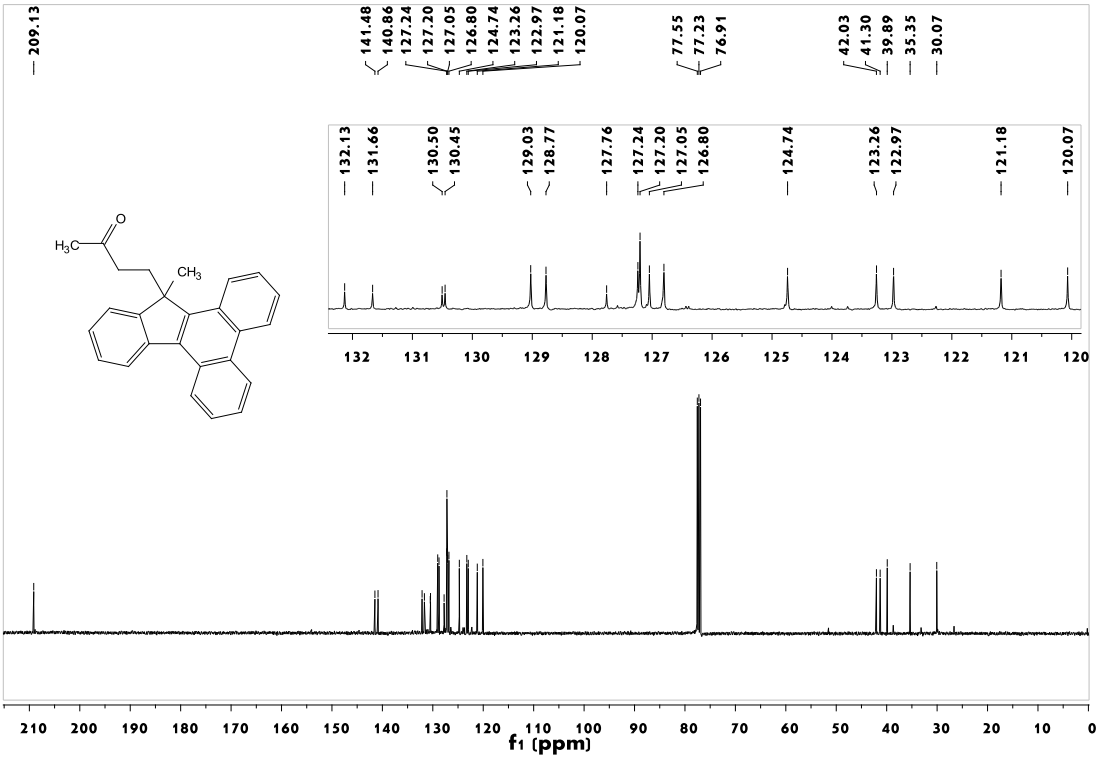
2.39
2.38
1.78
1.76
1.74
1.71
1.70
1.65
1.58
0.00
H3C
O
CH3
2.00
0.99
1.07
1.05
2.03
2.92
1.95
0.93
0.97
0.90
2.99
1.07
3.00
f1 (ppm)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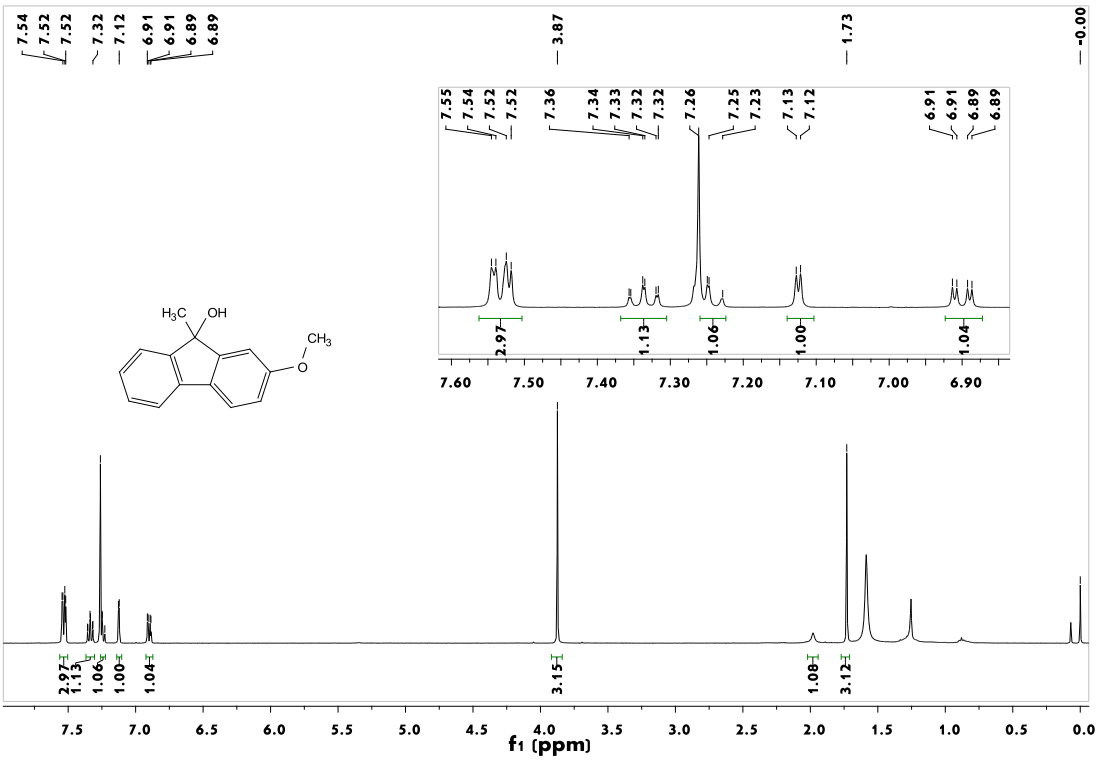
127.20
127.05
126.80
124.74
123.26
122.97
121.18
120.07
77.55
77.23
76.91
42.03
41.30
39.89
35.35
30.07
H3C
O
CH3
f1 (ppm)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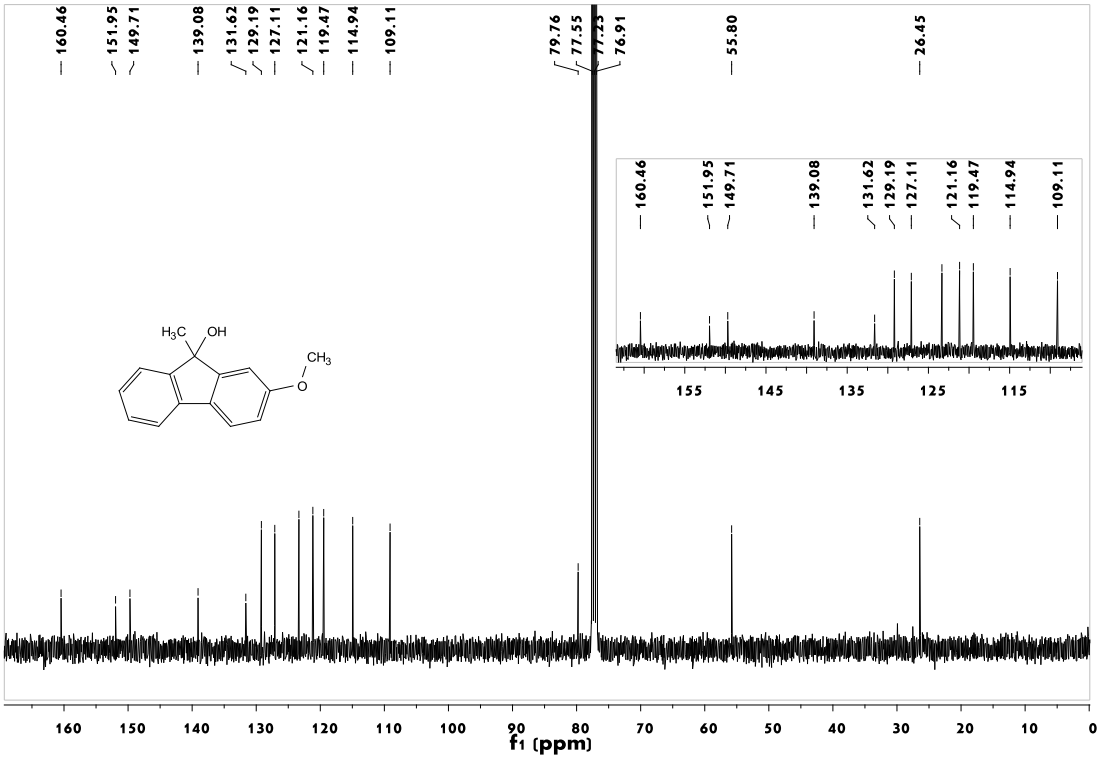
7.52
7.32
7.12
6.91
6.91
6.89
6.89
3.87
1.73
-0.00
H3C
OH
CH3
O
2.97
1.13
1.06
1.00
1.04
3.15
1.08
3.12
f1 (ppm)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121.16
119.47
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109.11
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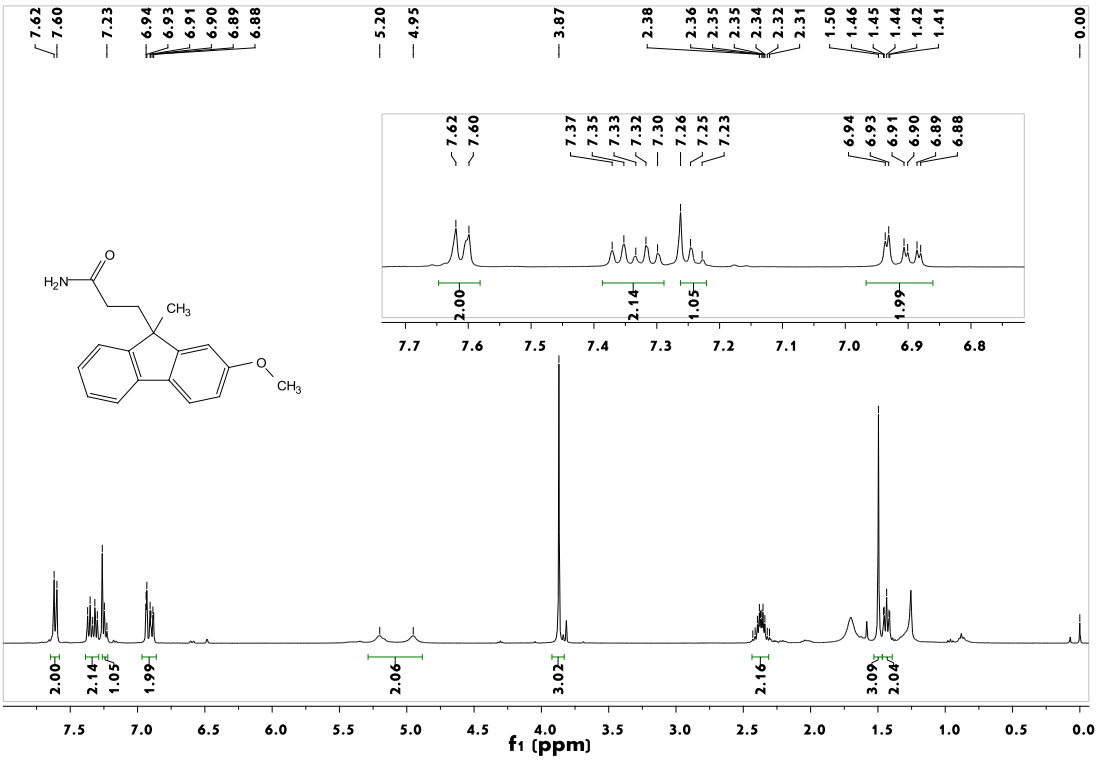
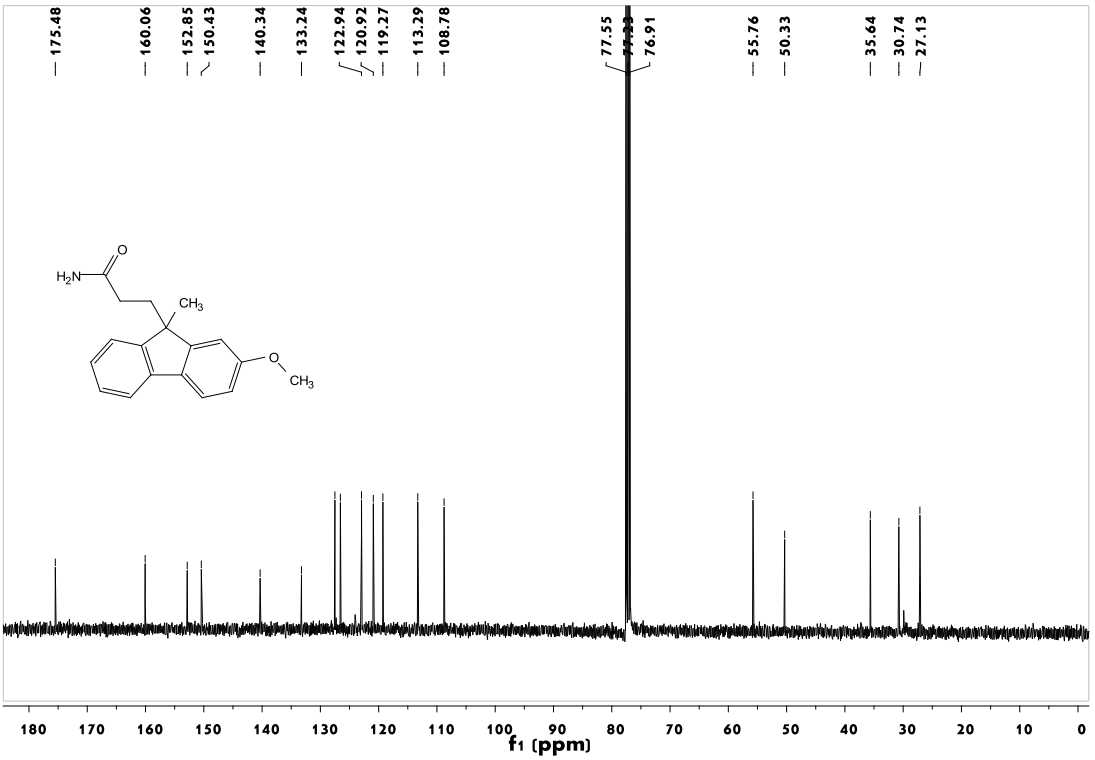
77.55
77.23
76.91
55.80
26.45
H3C
OH
CH3
O
f1 (ppm)


7.62
7.60
7.23
6.94
6.93
6.91
6.90
6.89
6.88
5.20
4.95
3.87
2.38
2.36
2.35
2.35
2.34
2.32
2.31
1.50
1.46
1.45
1.44
1.42
1.41
0.00
7.62
7.60
7.37
7.35
7.33
7.32
7.30
7.26
7.25
7.23
6.94
6.93
6.91
6.90
6.89
6.88
2.00
2.14
1.05
1.99
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
H2N
O
CH3
O
CH3
2.00
2.14
1.05
1.99
2.06
3.02
2.16
3.09
2.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


175.48
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150.43
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133.24
122.94
120.92
119.27
113.29
108.78
77.55
77.23
76.91
55.76
50.33
35.64
30.74
27.13
H2N
O
CH3
O
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)