Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

O_2-Mediated Transformation of 9-Phenanthrenol: An Approach to the Synthesis of Phenanthrenyl Ketal and 9-Fluorenones

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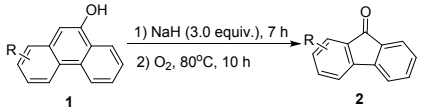
(A) General information

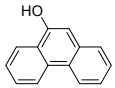
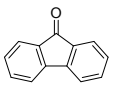
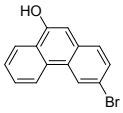
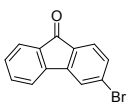
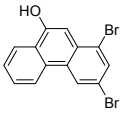
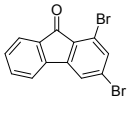
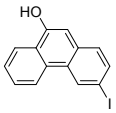
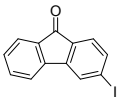
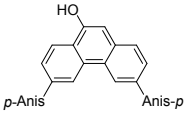
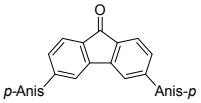
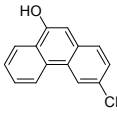
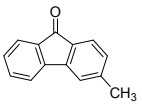
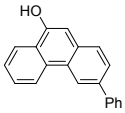
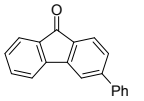
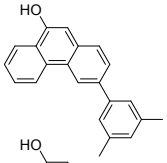
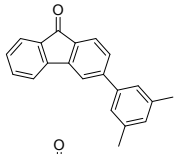
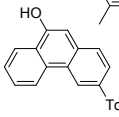
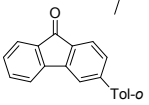
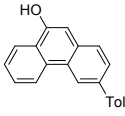
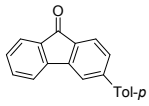
Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere followed by an oxygen atmosphere. All reagents were used without purification as commercially available. All reactions were monitored by thin layer chromatography. Purification of reaction products were carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. The melting point was recorded on a melting point apparatus (MPA100, Stanford Research Systems, Inc.). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 300 MHz spectrometers (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR), 400 MHz spectrometers (400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR) or 500 MHz spectrometers (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Chemical shifts of ^{1}H and ^{13}C signals were given in δ relative to the solvents residual ^{1}H-signal ($CH\text{-}Cl_3$, δ(H) 7.26) or to Me_4Si (δ 0.0). $CDCl_3$ resonance in the ^{13}C spectrum is 77.5 ppm. The following abbreviations are used: s, singlet, d, doublet, t, triplet, q, quartet, quint, quintuplet, m, multiplet, br, broad. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the ESI technique.

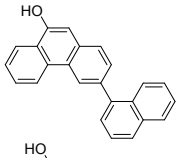
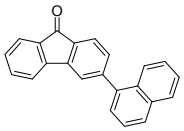
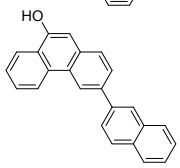
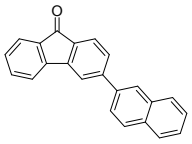
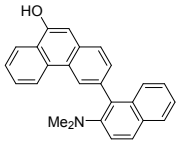
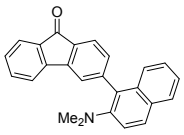
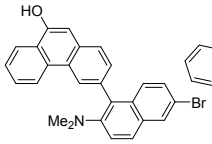
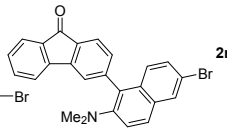
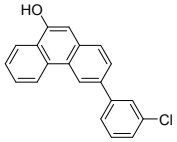
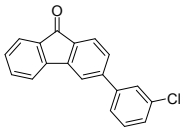
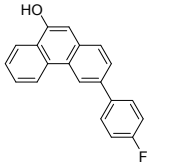
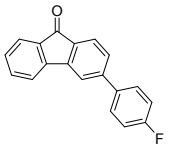
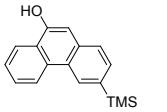
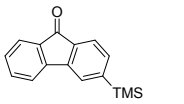
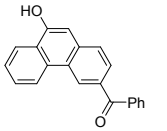
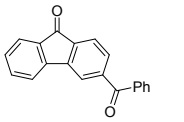
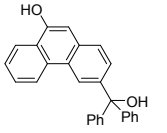
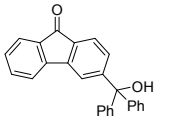
(B) General procedure for the synthesis of compounds 2.

Under a nitrogen atmosphere, compound **1** (0.2 mmol) were dissolved in THF (4 mL) in a Schlenk tube. NaH (0.6 mmol, 14.4 mg) or NaOH (1.4 mmol, 56.0 mg) was then added. After the reaction mixture was stirred at 25 ℃ for 7h, O_2 was charged. The tube was then sealed with screw cap and allowed to heat at 80 ℃ for 10 h. The resultant mixture was neutralized followed by extracting with CH_2Cl_2 (3×5 mL). The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate as an eluent) to afford the products **2**.

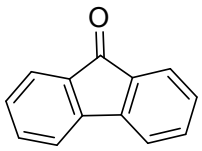


1 2

entry	1	Product 2	Yield(%)[a]
1			**2a**: 90
2[b]			**2b**:91
3[b]			**2c**: 64
4[b]			**2d**: 99
5			**2e**: 62
6			**2f**: 76
7			**2g**: 89
8			**2h**: 60
9			**2i**: 76
10			**2j**: 75

entry	1	Product 2	Yield(%)[a]
11			**2k**: 80
12			**2l**: 81
13			**2m**: 68
14[b]			**2n**: 64
15			**2o**: 77
16			**2p**: 80
17[b]			**2q**: 76
18			**2r**: 84
19			**2s**: 75

(C) ^{1}H and ^{13}C NMR data of products 2.

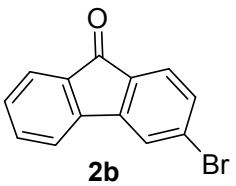


2a

The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2a** (32.4 mg, 90 %). **mp**: 81 ℃, yellow solid; alternatively, under an oxygen atmosphere, compound **3a** (0.1

mmol) were dissolved in THF (2 mL) in a Schlenk tube. NaH (0.6 mmol, 14.4 mg) was then added. The tube was then sealed with screw cap and allowed to heat at 80 ℃ for 10 h. The resultant mixture was neutralized followed by extracting with CH_2Cl_2 (3×5 mL). The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded the product **2a** in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.55 (d, J = 7.2 Hz, 2H), 7.41 - 7.34 (m, 4H) , 7.21 - 7.16 (m, 2H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.2, 144.9, 135.1, 134.7, 129.5, 124.7, 120.7. The data are consistent with that reported in the literature.[1]

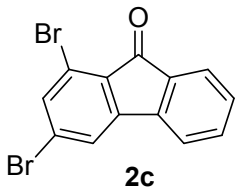
Gram scale synthesis: Under a nitrogen atmosphere, compound **1a** (1g, 5.1 mmol) were dissolved in THF (25 mL) in a Schlenk tube. *t*-BuOK (25.8 mmol, 2.9 g) was then added. After the reaction mixture was stirred at 25 ℃ for 12h, O_2 was charged. The tube was then sealed with screw cap and allowed to heat at 90 ℃ for 36 h. The resultant mixture was neutralized followed by extracting with CH_2Cl_2 (3×20 mL). The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether : ethyl acetate = 10:1) yielded the product **2a** (807.2 mg, 87 %).



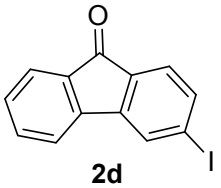
2b

The reaction was performed under general condition using NaOH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2b** (46.9 mg, 91 %). mp: 164 ℃, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.67 (d, J = 8.4 Hz, 2H), 7.52 - 7.49 (m, 3H) , 7.45 - 7.43 (m, 1H) , 7.36 - 7.32 (m, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 193.0, 146.6, 143.5, 135.3, 134.6, 133.2, 132.5, 130.3, 130.1, 125.9, 125.0, 124.3, 121.0. The data are consistent with that reported in the literature. [1]

The reaction was performed under general condition using NaOH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2c** (43.2 mg, 64 %). **mp**: 214 ℃, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71 (d, *J* = 7.2 Hz, 1H) , 7.61 (d, *J* = 8.4 Hz, 2H), 7.56 - 7.52 (m, 2H) , 7.378 (t, *J* = 6.8 Hz, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 190.5, 148.5, 141.6 , 136.6, 135.4, 134.5, 130.9, 130.5, 129.9, 125.3, 123.3, 121.4, 121.1; $C_{13}H_7Br_2O$ ($[M+H]^+$): 338.8838, found: 338.8835.

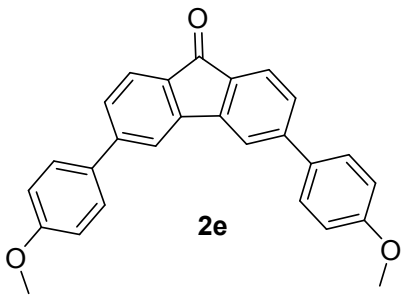


2c



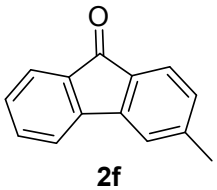
2d

The reaction was performed under general condition using NaOH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2d** (60.6 mg, 99 %). **mp**: 166 ℃, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 - 7.88 (m, 1H) , 7.67 (d, *J* = 7.2 Hz, 2H) , 7.52 - 7.46 (m, 2H) , 7.38 - 7.31 (m, 2H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 193.3, 146.3, 143.5, 138.6, 135.2, 134.4, 133.8, 130.2, 130.1, 125.9, 125.0, 121.0, 102.9 ; $C_{13}H_8IO$ ($[M+H]^+$): 306.9614, found: 306.9612.



2e

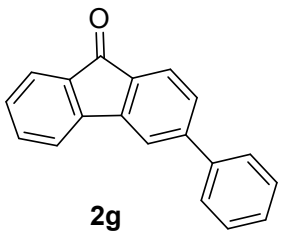
The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2e** (48.6 mg, 62 %). mp: 227 ℃, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (s, 2H) , 7.70 (d, *J* = 6 Hz, 2H) , 7.62 (d, *J* = 7.2 Hz, 4H) , 7.49 - 7.47 (m, 2H) ,7.03 - 7.01 (m, 4H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 193.6, 160.5, 147.8, 145.4, 133.6, 133.1, 128.8, 127.8, 125.1, 119.0, 114.9, 55.9. The data are consistent with that reported in the literature.[2]



2f

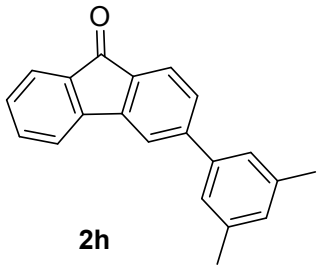
The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2f** (29.4 mg, 76 %). mp: 63 ℃, yellow

solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60 (d, *J* = 7.2 Hz, 1H) , 7.51 (d, *J* = 7.6 Hz, 1H) , 7.44 - 7.43 (m, 2H) , 7.27 - 7.23 (m, 2H) , 7.04 (d, *J* = 7.6 Hz, 1H) , 2.39 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 194.0, 146.2, 145.2, 144.7, 135.1, 134.8, 132.3, 130.0, 129.4, 124.7, 124.5, 121.6, 120.5, 22.6. The data are consistent with that reported in the literature.[3]



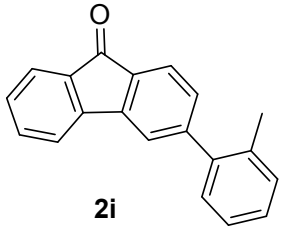
2g

The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2g** (45.6 mg, 89 %). mp: 92 ℃, yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.71 - 7.62 (m, 5H) , 7.56 - 7.39 (m, 6H) , 7.32 - 7.27 (m, 1H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.9, 148.3, 145.6, 144.5, 140.6, 135.1, 135.1, 133.4, 129.7, 129.4, 128.9, 128.4, 127.6, 125.1, 124.7, 120.7, 119.6. The data are consistent with that reported in the literature.[4]



2h

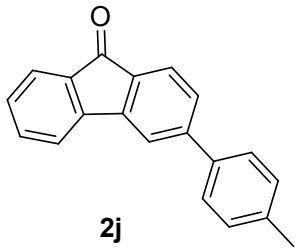
The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2h** (34.1 mg, 60 %). **mp**: 104 ℃, yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.69 - 7.64 (m, 3H) , 7.56 (d, *J* = 6.6 Hz, 1H) , 7.51 - 7.45 (m, 2H) , 7.31 - 7.26 (m, 1H) , 7.24 (s, 2H) , 7.05 (s, 1H) , 2.40 (s, 6H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.0, 148.6, 145.5, 144.7, 140.7, 139.0, 135.2, 135.0, 133.3, 130.6, 129.6, 128.4, 125.6, 125.1, 124.7, 120.7, 119.7, 21.9 ; $C_{21}H_{17}O$ ($[M+H]^+$): 285.1274, found: 285.1276.



2i

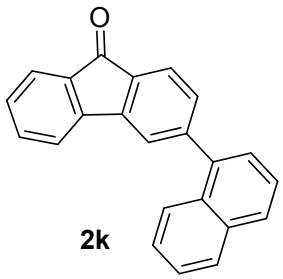
The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2i** (41.0 mg, 76 %). **mp**: 127 ℃, yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.70 - 7.66 (m, 2H) , 7.51 - 7.44 (m, 3H) , 7.31 - 7.24 (m, 6H) , 2.31 (s, 3H) ;

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.0, 149.4, 145.0, 144.7, 141.4, 135.6, 135.1, 133.2, 131.1, 130.4, 129.7, 129.7, 128.5, 126.5, 124.8, 124.6, 121.8, 120.8, 20.9; $C_{20}H_{15}O$ ($[M+H]^+$): 271.1117, found: 271.1113.



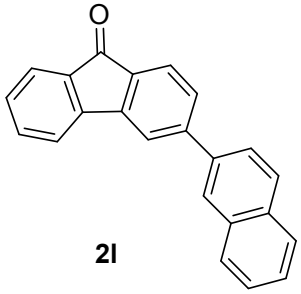
2j

The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2j** (40.5 mg, 75 %). **mp**: 119 ℃, yellow solid; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.70 - 7.64 (m, 3H), 7.56 - 7.45 (m, 5H) , 7.32 - 7.27 (m, 3H) , 2.41 (s, 3H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.9, 148.2, 145.6, 144.6, 138.9, 137.7, 135.2, 135.0, 133.2, 130.1, 129.6, 128.1, 127.5, 125.1, 124.6, 120.7, 119.4, 21.7; $C_{20}H_{15}O$ ($[M+H]^+$): 271.1117, found: 271.1119.



2k

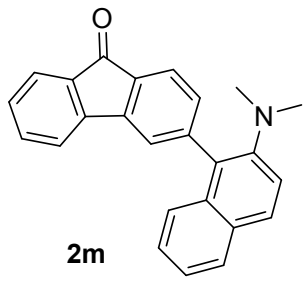
The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2k** (49.0 mg, 80 %). **mp**: 144 ℃, yellow solid; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.95 - 7.89 (m, 3H) , 7.77 (d, *J* = 7.5 Hz, 1H) , 7.70 (d, *J* = 7.5 Hz, 1H) , 7.63 (s, 1H) , 7.57 - 7.44 (m, 6H), 7.42 - 7.39 (m, 1H) , 7.34 - 7.28 (m, 1H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 194.0, 148.1, 145.0, 144.6, 139.6, 135.1, 135.1, 134.2, 133.5, 131.6, 131.3, 129. 7, 129.0, 128.9, 127.1, 126.9, 126.5, 126.0, 125. 8, 124.8, 124.7, 122.6, 120.8; $C_{23}H_{15}O$ ($[M+H]^+$): 307.1117, found: 307.1116.



2l

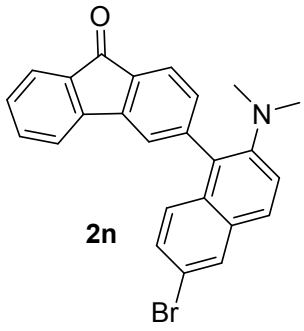
The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2l** (49.6 mg, 81 %). **mp**: 144 ℃, yellow solid; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.04 (s, 1H) , 7.91 - 7.84 (m, 3H) , 7.75 - 7.63 (m, 4H) ,

7.56 - 7.46 (m, 5H) , 7.30 - 7.23 (m, 1H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.9, 148.1, 145.6, 144.5, 137.8, 135.1, 135.0, 133.9, 133.5, 133.3, 129.6, 129.1, 128.8, 128.5, 128.1, 127.0, 127.0, 126.7, 125.5, 125.2, 124.7, 120.7, 119.7; $C_{23}H_{15}O$ ($[M+H]^+$): 307.1117, found: 307.1120.



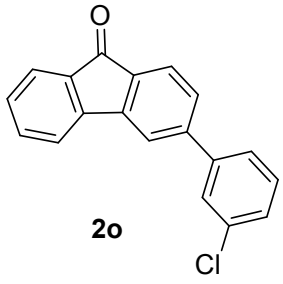
2m

The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2m** (47.5 mg, 68 %). **mp**: 173 ℃, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (d, *J* = 8.8 Hz, 1H) , 7.83 - 7.79 (m, 2H) , 7.71 (d, *J* = 7.2 Hz, 1H) , 7.58 - 7.56 (m, 2H) , 7.50- 7.44 (m, 3H) , 7.37 - 7.29 (m, 4H) , 2.65 (s, 6H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 194.2, 149.5, 147.2, 145.1, 145.0, 135.2, 135.0, 133.5, 133.1, 132.6, 130.3, 129.6, 129.6, 129.5, 128.5, 126.9, 125.2, 124.8, 124.8, 124.4, 124.0, 120.9, 119.9, 44.6; $C_{25}H_{20}NO$ ($[M+H]^+$): 350.1539, found: 350.1544.



2n

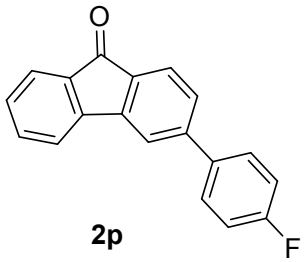
The reaction was performed under general condition using NaOH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2n** (54.7 mg, 64 %). **mp**: 208 ℃, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* = 2 Hz, 1H) , 7.80 (d, *J* = 7.6 Hz, 1H) , 7.75 (d, *J* = 9.2 Hz, 1H) , 7.71 (d, *J* = 7.2 Hz, 1H) , 7.53 (s, 1H) , 7.51 - 7.48 (m, 2H) , 7.46 - 7.45 (m, 1H) , 7.43 (d, *J* = 3.6 Hz, 1H) , 7.38 - 7.36 (m, 1H) , 7.34 - 7.30 (m, 2H) , 2.65 (s, 6H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 194.1, 149.8, 146.6, 145.2, 144.8, 135.1, 135.1, 133.3, 132.5, 131.2, 130.3, 130.1, 129.7, 129.1, 128.7, 127.0, 125.0, 124.9, 124.9, 123.8, 121.0, 121.0, 118.1, 44.4; $C_{25}H_{19}BrNO$ ($[M+H]^+$): 428.0645, found: 428.0646.



2o

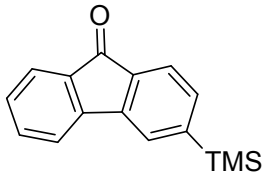
The reaction was performed under general condition using NaH as the base.Flash chromatography (petroleum ether :

ethyl acetate = 10:1) yielded the product **2o** (44.7 mg, 77 %). **mp**: 169 ℃, yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) 7.72 - 7.66 (m, 3H) , 7.62 - 7.44 (m, 5H) , 7.42 - 7.30 (m, 3H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.7, 146.7, 145.7, 144.4, 142.4, 135.4, 135.2, 135.1, 133.9, 130.7, 129.8, 128.9, 128.4, 127.8, 125.8, 125.2, 124.8, 120.8, 119.6; $C_{19}H_{12}ClO$ ($[M+H]^+$): 291.0571, found: 291.0578.



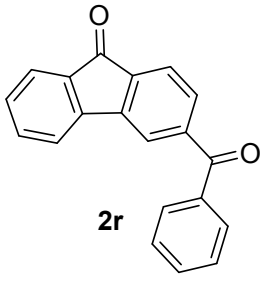
2p

The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2p** (43.8 mg, 80 %). **mp**: 159 ℃, yellow solid ; ^{1}H NMR (300MHz, $CDCl_3$) δ (ppm) 7.70 - 7.57 (m, 5H) , 7.54 - 7.41 (m, 3H) , 7.33 - 7.28 (m, 1H) , 7.20 - 7.13 (m, 2H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 193.8, 163.6 (d, $J_{C\text{-}F}$ = 239.4 Hz), 147.2, 145.7, 144.4, 136.8, 135.1, 133.4, 129.8, 129.4 (d, $J_{C\text{-}F}$ = 8.8 Hz), 128.19, 125.2, 124.8, 120.7, 119.5, 116.4 (d, $J_{C\text{-}F}$ = 21.42 Hz) ; $C_{19}H_{12}FO$ ($[M+H]^+$): 275.0867, found: 275.0863.



2q

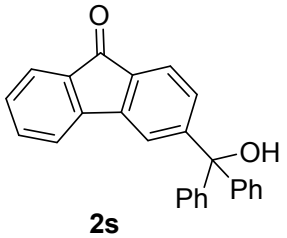
The reaction was performed under general condition using NaOH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2q** (38.3 mg, 76 %). **mp**: 68 ℃, yellow solid ; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.64 - 7.59 (m, 3H) , 7.53 (d, J = 7.2 Hz, 1H) , 7.45 - 7.44 (m, 2H) , 7.27 - 7.23 (t, 1H) , 0.32 (s, 9H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 195.4, 150.8, 146.1, 144.5, 135.9, 135.7, 135.5, 135.5, 130.2, 126.0, 125.6, 124.5, 121.7, 0 ; $C_{16}H_{17}OSi$ ($[M+H]^+$): 253.1043, found: 253.1042.



2r

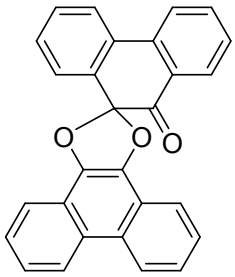
The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2r** (47.7 mg, 84 %). **mp**: 136 ℃, yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95

(s, 1H) , 7.85 (d, J = 7.6 Hz, 2H) , 7.76 - 7.51 (m, 8H) , 7.37 - 7.34 (t, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 196.4, 193.5, 145.0, 144.2, 143.7, 137.4, 137.2, 135.7, 134.7, 133.6, 131.7, 130.5, 130.2, 129.0, 125.1, 124.3, 121.7, 121.4 ; $C_{20}H_{13}O_2$ ($[M+H]^+$): 285.0910, found: 285.0914.



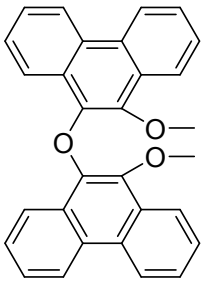
2s

The reaction was performed under general condition using NaH as the base. Flash chromatography (petroleum ether : ethyl acetate = 10:1) yielded the product **2t** (54.3 mg, 75 %). **mp**: 204 ℃ , yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.62 - 7.54 (m, 3H) , 7.40 - 7.25 (m, 13H) , 7.15 (d, J = 7.2 Hz, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 194.1, 154.5, 146.5, 144.8, 144.7, 135.1, 135.0, 133.5, 129.6, 129.3, 128.7, 128.3, 128.2, 124.7, 124.2, 121.0, 120.4, 82 ; $C_{26}H_{19}O_2$ ($[M+H]^+$): 363.1380, found: 363.1374.



3a

The reaction was performed under general condition using NaH (1.0 eq) as the base. Flash chromatography (petroleum ether : ethyl acetate = 5:1) yielded the product **3a** (33.6 mg, 84 %). **mp**: 250 ℃, red solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.67 (d, J = 8 Hz, 2H) , 8.06 - 7.90 (m, 6H) , 7.73 - 7.69 (m, 1H) , 7.61 - 7.55 (m, 5H) , 7.44 (t, J = 7.2 Hz, 1H) , 7.39 - 7.35 (m, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 189.0, 138.0, 137.2, 136.0, 133.6, 132.8, 132.1, 130.0, 129.5, 129.4, 128.9, 128.5, 128.02, 127.4, 125.4, 124.9, 124.1, 123.8, 121.5, 120.9, 108.6 ; $C_{28}H_{17}O_3$ ($[M+H]^+$): 401.1172, found:401.1172.



3a-2-Me

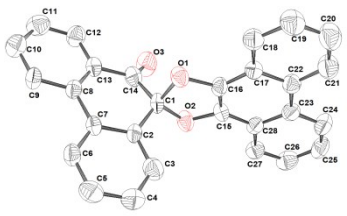
Under an oxygen atmosphere, Compound **3a** (0.1 mmol) were dissolved in THF (2 mL) in a Schlenk tube. NaOH (1.4 mmol, 56.0 mg) was then added. The tube was then sealed with screw cap and allowed to heat at 80 ℃ for 0.5 h. Then methyl iodide (0.5 mmol, 0.03 mL) was added through syringe. After 12 hours, the resultant

mixture was neutralized followed by extracting with CH_2Cl_2 (3×5 mL). The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate as an eluent) to afford the products. Flash chromatography (petroleum ether : ethyl acetate = 20:1) yielded the product **3a-2-Me** (28.0 mg, 65 %). **mp**: 167 ℃, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.73 - 8.68 (m, 4H) , 8.52 - 8.50 (m, 2H) , 8.02 - 8.00 (m, 2H) , 7.68 - 7.56 (m, 8H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 143.1, 141.5, 129.4, 129.2, 129.1, 128.7, 127.4, 126.6, 126.1, 123.3, 123.3, 123.2, 122.8, 62.4; $C_{30}H_{23}O_3$ ($[M+H]^+$): 431.1642, found: 431.1637.

(D) Mechanistic Investigation.

Process about the detection of CO_2 and CO: Because CO_2 may be absorbed by the base, in the gram scale synthesis of **2a** (with KOBu-t as the base), we neutralized the reaction solution with H_2SO_4. The reaction mixture was heated and all the gas (including part of THF vapor) were introduced to saturated solution of $Ca(OH)_2$ via syringe needle. $CaCO_3$ precipitates appeared clearly, proving the formation of CO_2. Using aqueous $NaPdCl_2$, no Pd black was fomed from reduction of Pd(II) with CO.

(E) Crystallographic data of 3a.



(CCDC Deposition Number 1971464)

Table 1. Crystal data and structure refinement for **3a**.

Identification code	**3a**
Empirical formula	C28 H16 O3
Formula weight	400.41
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.6460(10) A alpha = 98.358(2) deg.
	b = 9.6188(11) A beta = 108.221(2) deg.
	c = 12.4676(14) A gamma = 99.589(2) deg.
Volume	949.28(19) A^3
Z, Calculated density	2, 1.401 Mg/m^3
Absorption coefficient	0.090 mm^-1
F(000)	416
Crystal size	0.4 x 0.2 x 0.1 mm
Theta range for data collection	1.759 to 27.997 deg.
Limiting indices	-9<=h<=11, -12<=k<=12, -15<=l<=16
Reflections collected / unique	6958 / 4561 [R(int) = 0.0784]
Completeness to theta = 25.242	99.9 %
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	4561 / 0 / 281
Goodness-of-fit on F^2	0.843
Final R indices [I>2sigma(I)]	R1 = 0.0610, wR2 = 0.1415
R indices (all data)	R1 = 0.1648, wR2 = 0.2225
Extinction coefficient	0.014(4)
Largest diff. peak and hole	0.251 and -0.251 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	2968(4)	2910(4)	832(3)	39(1)
C(2)	4655(4)	3317(4)	724(3)	38(1)
C(3)	5781(5)	4540(4)	1432(3)	55(1)
C(4)	7406(5)	4858(4)	1432(3)	58(1)
C(5)	7873(5)	3939(5)	701(3)	55(1)
C(6)	6752(5)	2751(4)	-25(3)	44(1)
C(7)	5106(4)	2407(4)	-48(3)	37(1)
C(8)	3865(4)	1136(4)	-868(3)	37(1)
C(9)	4295(5)	150(4)	-1587(3)	43(1)
C(10)	3114(5)	-1009(4)	-2368(3)	57(1)
C(11)	1458(5)	-1215(5)	-2447(4)	61(1)

C(12)	994(5)	-251(4)	-1750(3)	52(1)
C(13)	2173(4)	913(4)	-961(3)	39(1)
C(14)	1627(5)	1921(4)	-223(3)	45(1)
C(15)	2483(4)	4190(4)	2314(3)	38(1)
C(16)	2909(4)	3008(4)	2655(3)	38(1)
C(17)	3036(4)	2726(4)	3740(3)	39(1)
C(18)	3476(5)	1479(4)	4103(3)	48(1)
C(19)	3577(5)	1295(5)	5198(3)	62(1)
C(20)	3200(6)	2296(5)	5917(4)	67(1)
C(21)	2780(5)	3516(4)	5583(3)	58(1)
C(22)	2698(4)	3798(4)	4510(3)	42(1)
C(23)	2246(4)	5088(4)	4146(3)	43(1)
C(24)	1850(5)	6150(4)	4817(3)	56(1)
C(25)	1420(5)	7339(4)	4435(3)	59(1)
C(26)	1379(5)	7555(4)	3367(4)	58(1)
C(27)	1731(4)	6534(4)	2649(3)	47(1)
C(28)	2144(4)	5286(4)	3012(3)	38(1)
O(1)	3131(3)	2101(2)	1769(2)	46(1)
O(2)	2408(3)	4161(3)	1187(2)	47(1)
O(3)	164(3)	1942(3)	-414(2)	67(1)

Table 3. Bond lengths [A] and angles [deg] for **3a**.

C(1)-O(2)	1.432(4)
C(1)-O(1)	1.479(4)
C(1)-C(2)	1.500(5)
C(1)-C(14)	1.515(5)
C(2)-C(3)	1.375(5)
C(2)-C(7)	1.396(4)
C(3)-C(4)	1.388(5)
C(4)-C(5)	1.375(5)
C(5)-C(6)	1.359(5)
C(6)-C(7)	1.396(5)
C(7)-C(8)	1.484(5)
C(8)-C(9)	1.386(4)
C(8)-C(13)	1.408(5)
C(9)-C(10)	1.385(5)
C(10)-C(11)	1.382(5)
C(11)-C(12)	1.372(5)
C(12)-C(13)	1.390(5)

C(13)-C(14)	1.474(5)
C(14)-O(3)	1.216(4)
C(15)-C(16)	1.338(4)
C(15)-O(2)	1.382(4)
C(15)-C(28)	1.397(4)
C(16)-O(1)	1.387(4)
C(16)-C(17)	1.393(4)
C(17)-C(18)	1.410(4)
C(17)-C(22)	1.435(4)
C(18)-C(19)	1.380(5)
C(19)-C(20)	1.369(5)
C(20)-C(21)	1.368(5)
C(21)-C(22)	1.386(5)
C(22)-C(23)	1.454(5)
C(23)-C(24)	1.382(5)
C(23)-C(28)	1.431(4)
C(24)-C(25)	1.365(5)
C(25)-C(26)	1.368(5)
C(26)-C(27)	1.369(5)

C(27)-C(28)	1.404(4)
O(2)-C(1)-O(1)	105.8(2)
O(2)-C(1)-C(2)	111.3(3)
O(1)-C(1)-C(2)	108.0(3)
O(2)-C(1)-C(14)	110.5(3)
O(1)-C(1)-C(14)	105.4(3)
C(2)-C(1)-C(14)	115.3(3)
C(3)-C(2)-C(7)	120.5(3)
C(3)-C(2)-C(1)	119.7(3)
C(7)-C(2)-C(1)	119.7(3)
C(2)-C(3)-C(4)	120.7(4)
C(5)-C(4)-C(3)	119.0(4)
C(6)-C(5)-C(4)	120.5(4)
C(5)-C(6)-C(7)	121.8(3)
C(2)-C(7)-C(6)	117.4(3)
C(2)-C(7)-C(8)	120.7(3)
C(6)-C(7)-C(8)	121.8(3)
C(9)-C(8)-C(13)	117.3(3)
C(9)-C(8)-C(7)	122.3(3)

C(13)-C(8)-C(7)	120.3(3)
C(10)-C(9)-C(8)	121.6(3)
C(11)-C(10)-C(9)	120.4(4)
C(12)-C(11)-C(10)	119.3(4)
C(11)-C(12)-C(13)	120.7(4)
C(12)-C(13)-C(8)	120.7(3)
C(12)-C(13)-C(14)	119.1(3)
C(8)-C(13)-C(14)	120.2(3)
O(3)-C(14)-C(13)	122.5(4)
O(3)-C(14)-C(1)	120.2(3)
C(13)-C(14)-C(1)	117.2(3)
C(16)-C(15)-O(2)	110.9(3)
C(16)-C(15)-C(28)	123.8(3)
O(2)-C(15)-C(28)	125.3(3)
C(15)-C(16)-O(1)	110.7(3)
C(15)-C(16)-C(17)	123.6(3)
O(1)-C(16)-C(17)	125.6(3)
C(16)-C(17)-C(18)	123.9(3)
C(16)-C(17)-C(22)	116.1(3)

C(18)-C(17)-C(22)	120.0(3)
C(19)-C(18)-C(17)	119.8(4)
C(20)-C(19)-C(18)	120.2(4)
C(21)-C(20)-C(19)	120.9(4)
C(20)-C(21)-C(22)	122.4(4)
C(21)-C(22)-C(17)	116.8(3)
C(21)-C(22)-C(23)	122.8(3)
C(17)-C(22)-C(23)	120.4(3)
C(24)-C(23)-C(28)	116.3(3)
C(24)-C(23)-C(22)	124.2(3)
C(28)-C(23)-C(22)	119.5(3)
C(25)-C(24)-C(23)	122.1(4)
C(24)-C(25)-C(26)	121.7(4)
C(25)-C(26)-C(27)	119.2(3)
C(26)-C(27)-C(28)	120.2(3)
C(15)-C(28)-C(27)	123.1(3)
C(15)-C(28)-C(23)	116.5(3)
C(27)-C(28)-C(23)	120.4(3)
C(16)-O(1)-C(1)	105.2(2)

C(15)-O(2)-C(1)	106.7(2)

Symmetry transformations used to generate equivalent atoms:

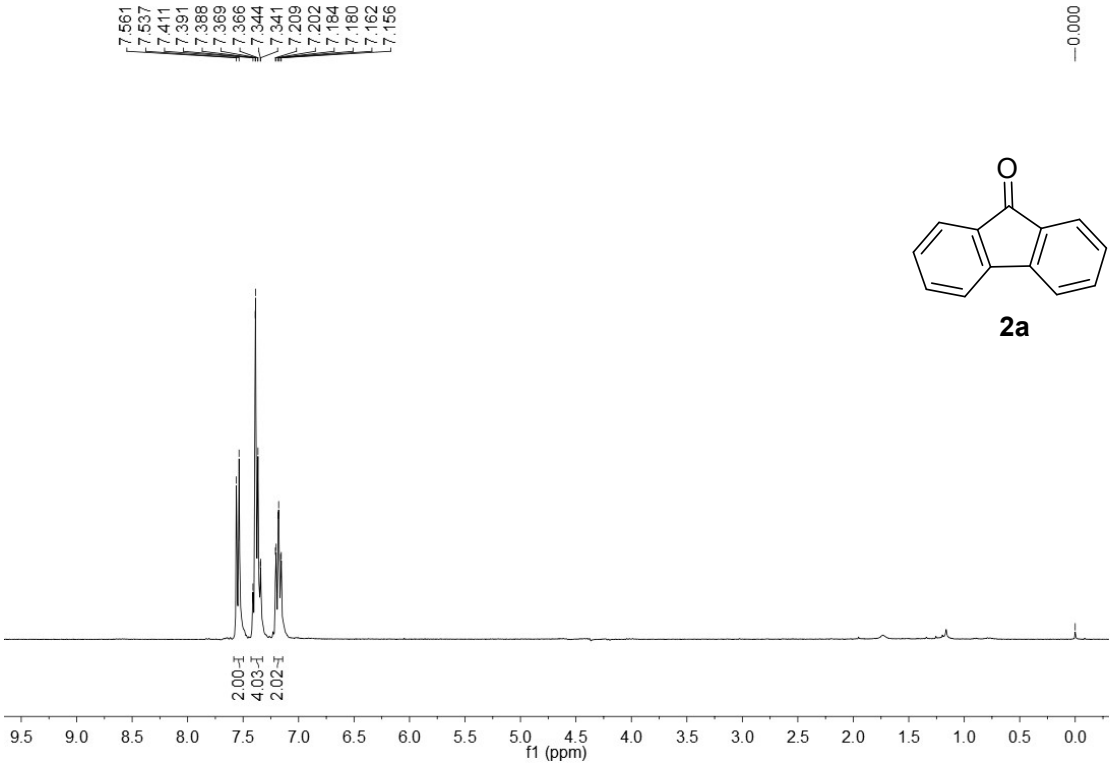
Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **3a**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

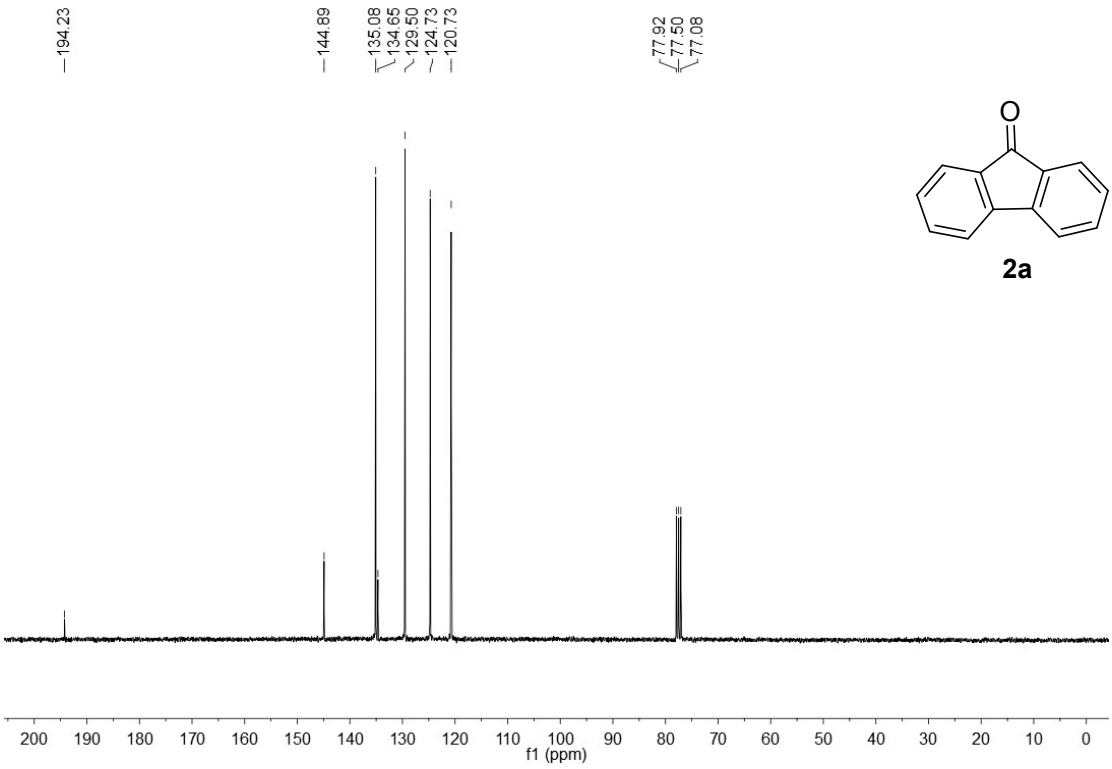
	U11	U22	U33	U23	U13	U12
C(1)	46(2)	47(2)	26(2)	4(2)	16(2)	16(2)
C(2)	43(2)	41(2)	28(2)	2(2)	14(2)	8(2)
C(3)	55(3)	59(3)	60(3)	14(2)	30(2)	17(2)
C(4)	52(3)	53(3)	63(3)	9(2)	20(2)	3(2)
C(5)	38(2)	64(3)	62(3)	16(2)	17(2)	7(2)
C(6)	44(2)	56(3)	32(2)	3(2)	16(2)	11(2)
C(7)	40(2)	44(2)	29(2)	8(2)	15(2)	12(2)
C(8)	46(2)	37(2)	31(2)	7(2)	15(2)	14(2)
C(9)	43(2)	50(2)	35(2)	-2(2)	15(2)	13(2)
C(10)	58(3)	54(3)	58(3)	5(2)	20(2)	18(2)

C(11)	52(3)	53(3)	70(3)	8(2)	15(2)	8(2)
C(12)	48(2)	56(3)	45(2)	2(2)	12(2)	11(2)
C(13)	42(2)	46(2)	32(2)	9(2)	15(2)	15(2)
C(14)	44(2)	54(3)	44(2)	14(2)	20(2)	18(2)
C(15)	41(2)	47(2)	33(2)	11(2)	18(2)	13(2)
C(16)	39(2)	41(2)	38(2)	2(2)	19(2)	12(2)
C(17)	40(2)	38(2)	38(2)	6(2)	15(2)	7(2)
C(18)	54(2)	45(2)	47(2)	13(2)	19(2)	15(2)
C(19)	73(3)	63(3)	56(3)	25(2)	21(2)	27(2)
C(20)	85(3)	74(3)	48(2)	21(2)	23(2)	27(3)
C(21)	70(3)	61(3)	47(2)	13(2)	22(2)	20(2)
C(22)	41(2)	45(2)	38(2)	7(2)	13(2)	8(2)
C(23)	42(2)	39(2)	46(2)	4(2)	17(2)	7(2)
C(24)	67(3)	50(3)	46(2)	-3(2)	19(2)	15(2)
C(25)	72(3)	46(3)	57(3)	-8(2)	26(2)	18(2)
C(26)	60(3)	41(2)	77(3)	9(2)	24(2)	19(2)
C(27)	46(2)	43(2)	51(2)	9(2)	16(2)	13(2)
C(28)	36(2)	36(2)	40(2)	2(2)	12(2)	7(2)
O(1)	57(2)	46(2)	49(2)	17(1)	29(1)	23(1)

O(2)	62(2)	49(2)	47(2)	18(1)	30(1)	28(1)
O(3)	43(2)	84(2)	74(2)	0(2)	23(2)	22(2)

(F) ^{1}H and ^{13}C NMR spectra of products 2.



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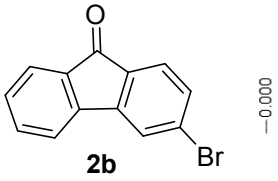
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Br
2b

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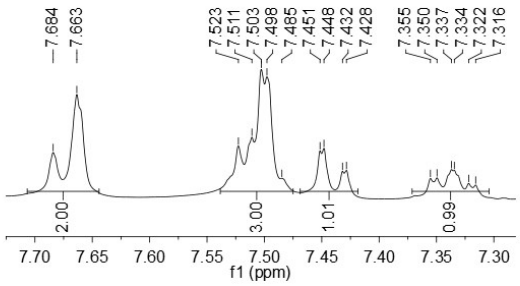
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7.350
7.337
7.334
7.322
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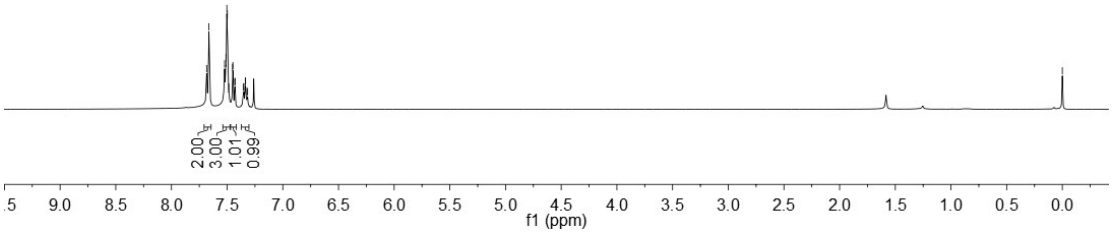
f1 (ppm)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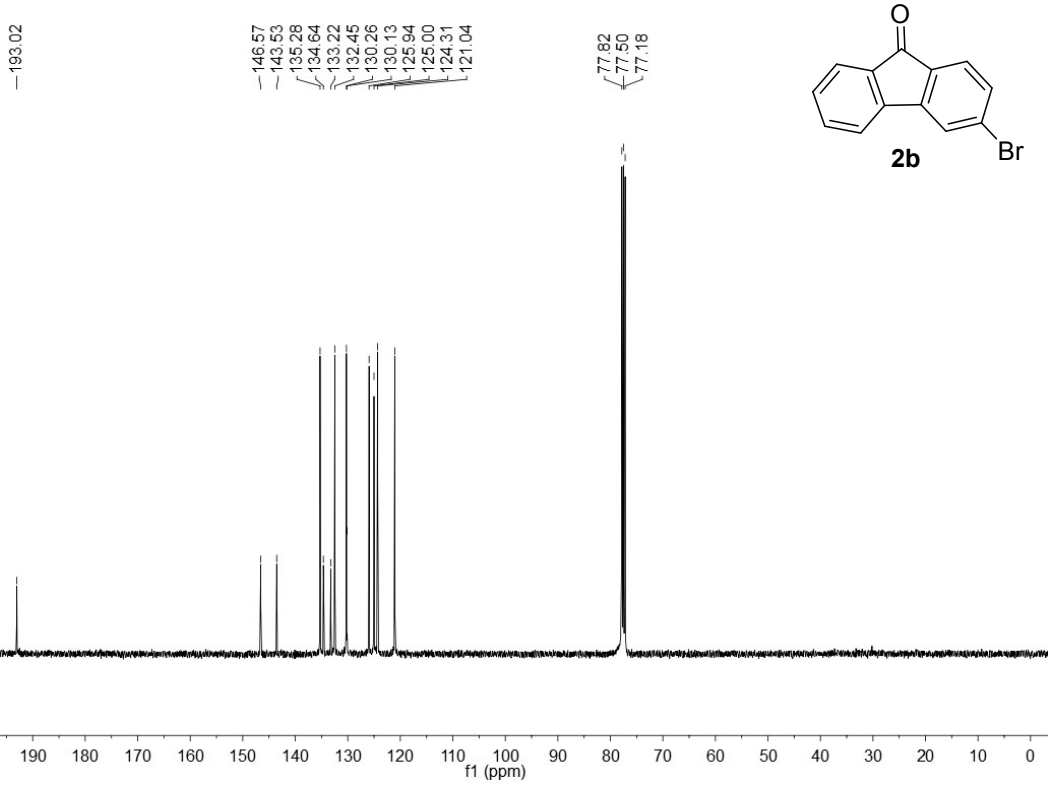
f1 (ppm)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125.94
125.00
124.31
121.04
77.82
77.50
77.18
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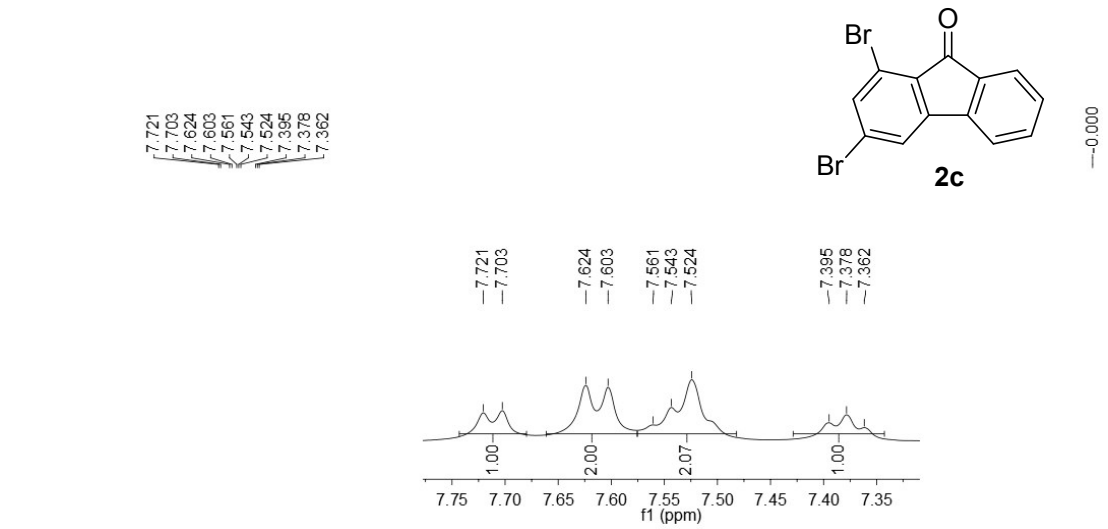
f1 (ppm)

O
Br
2b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Br
O
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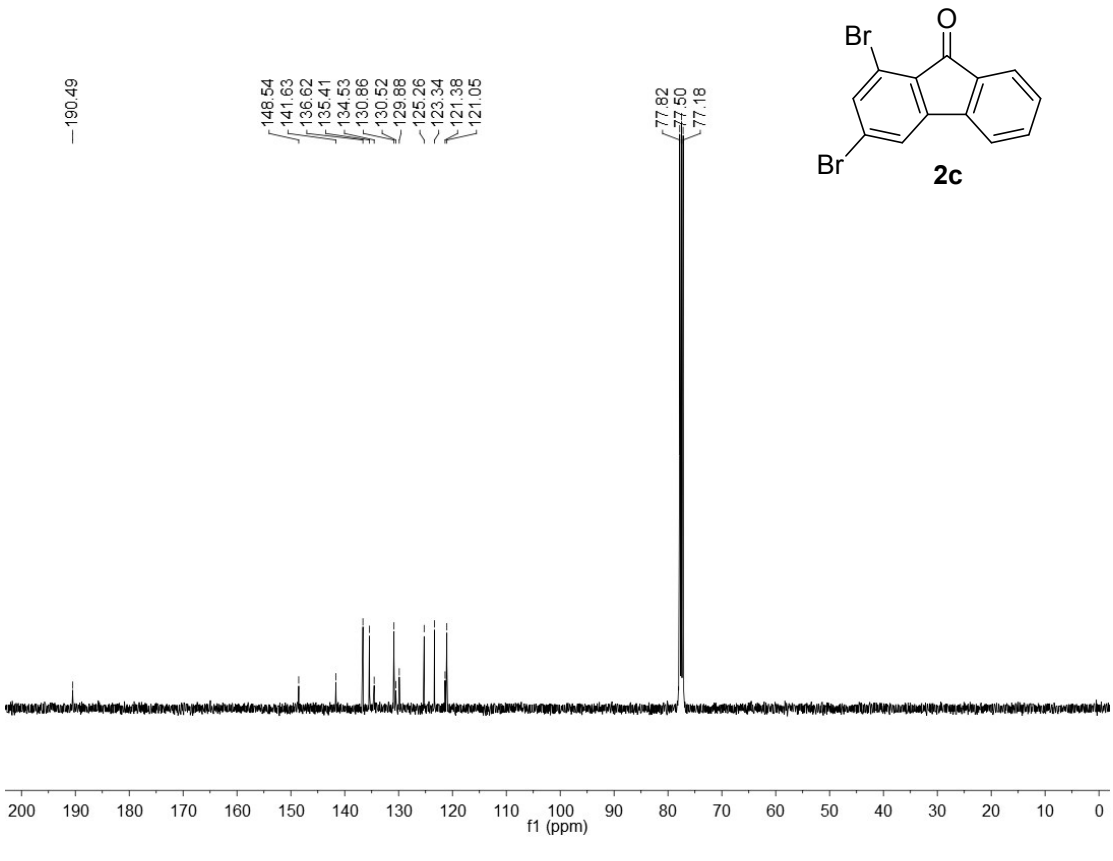
f1 (ppm)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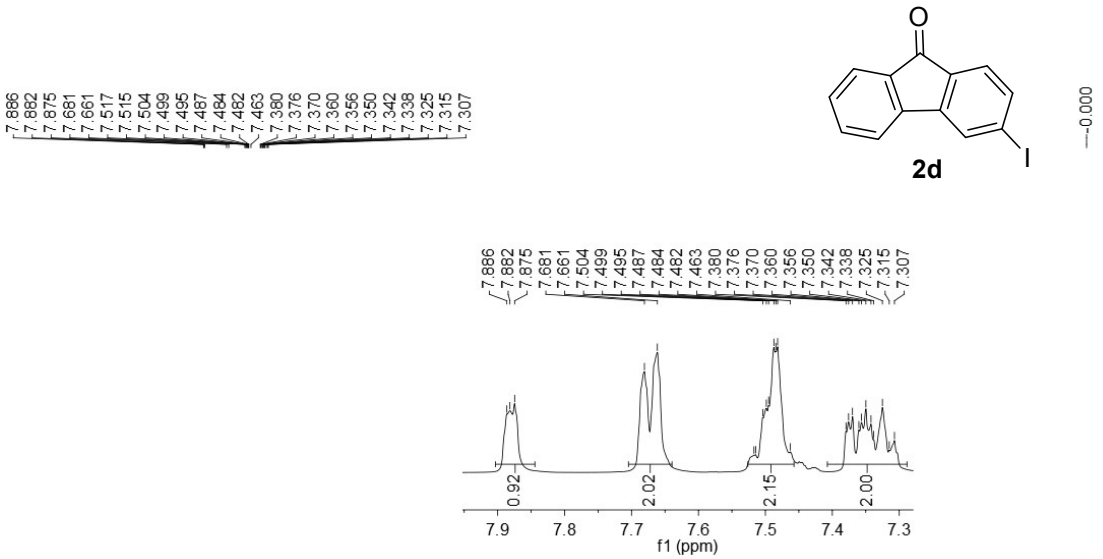
121.05
77.82
77.50
77.18
Br
Br
O
2c
f1 (ppm)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7.370
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7.342
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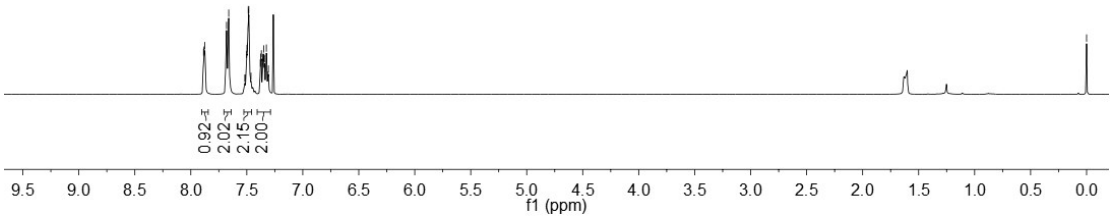
f1 (ppm)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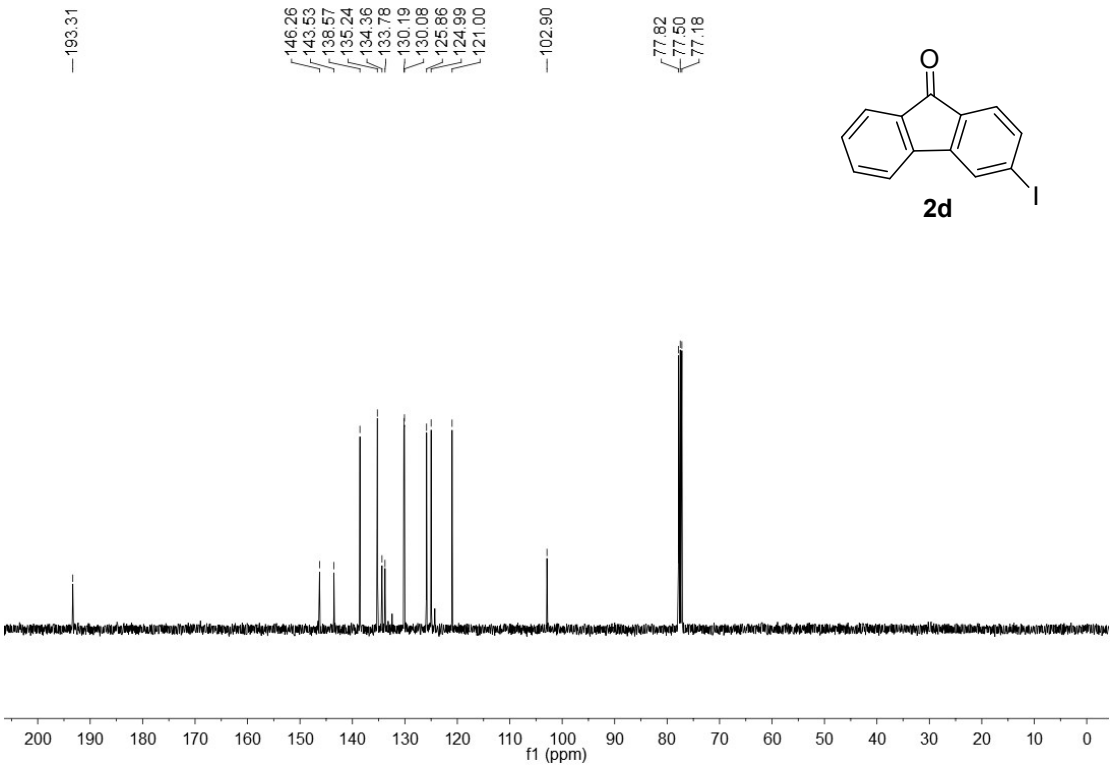
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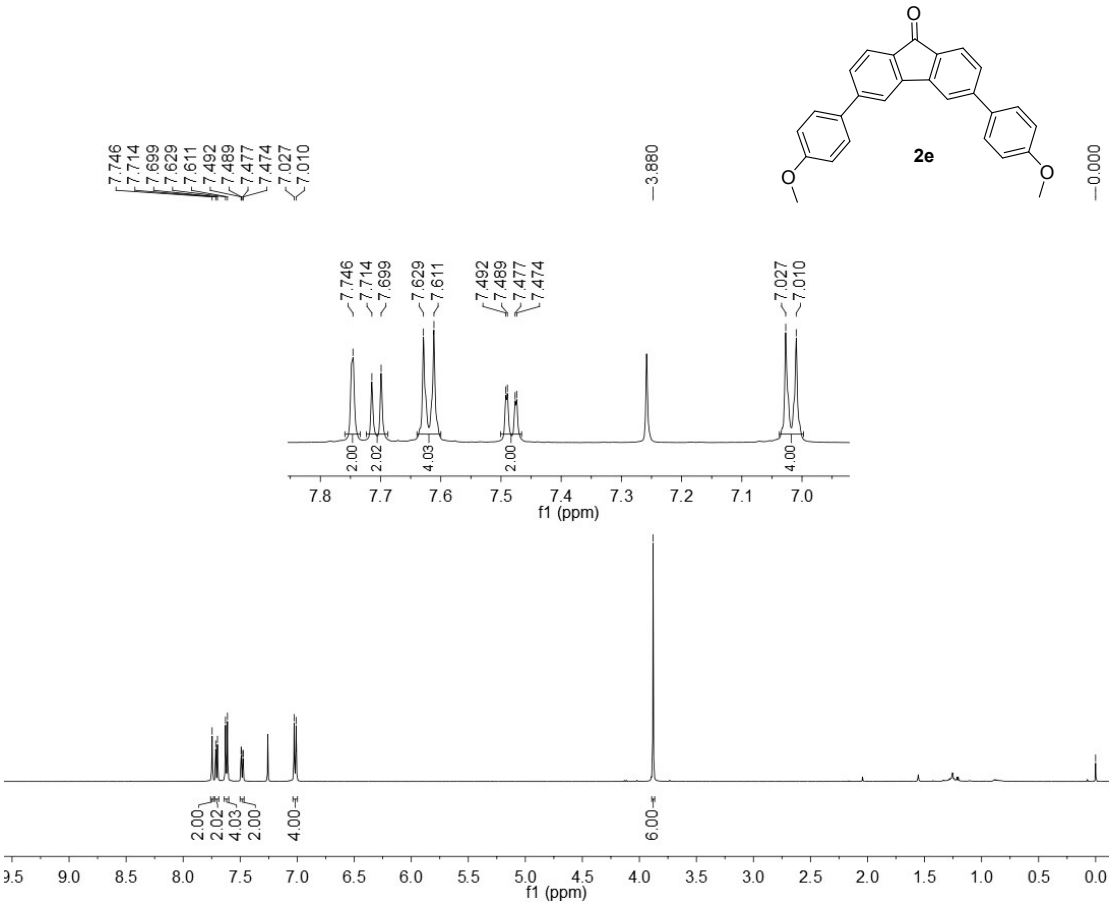
77.18
O
I
2d
f1 (ppm)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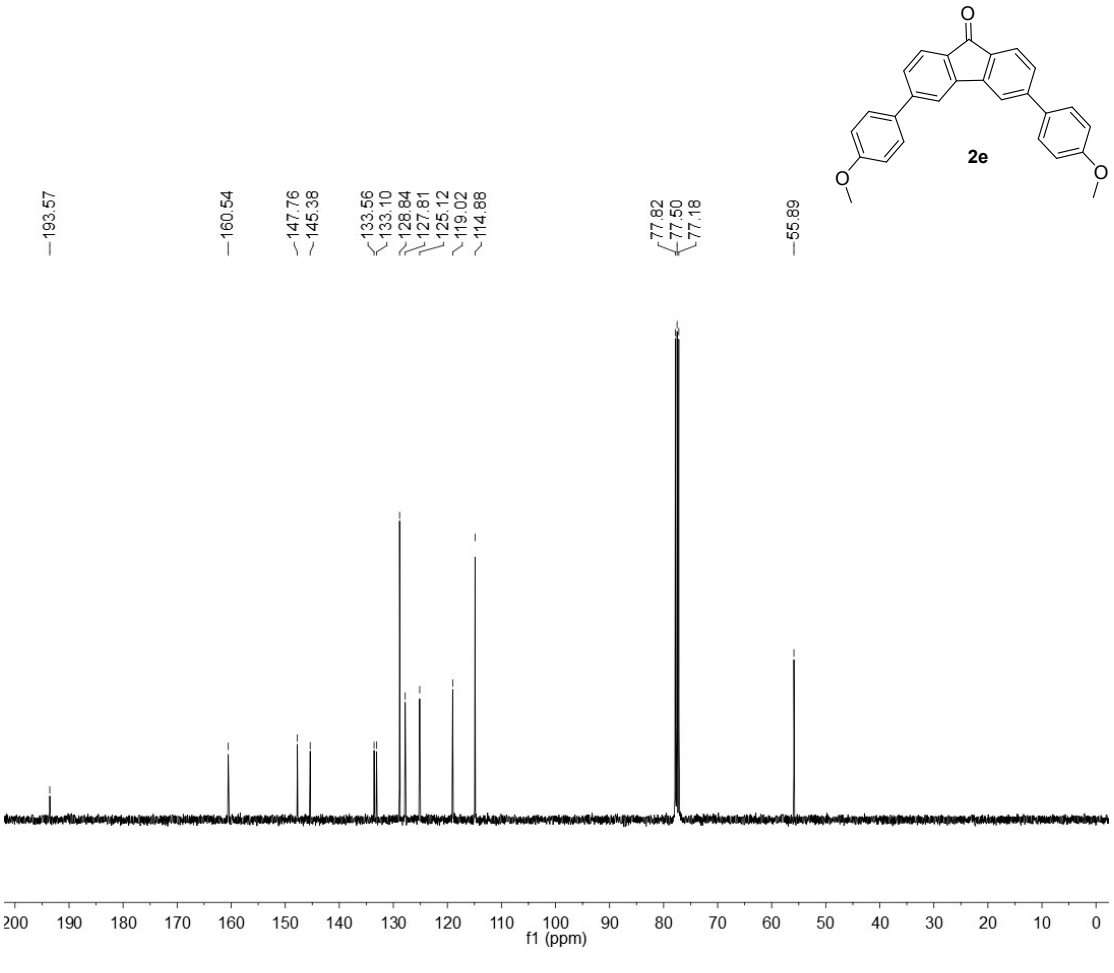
f1 (ppm)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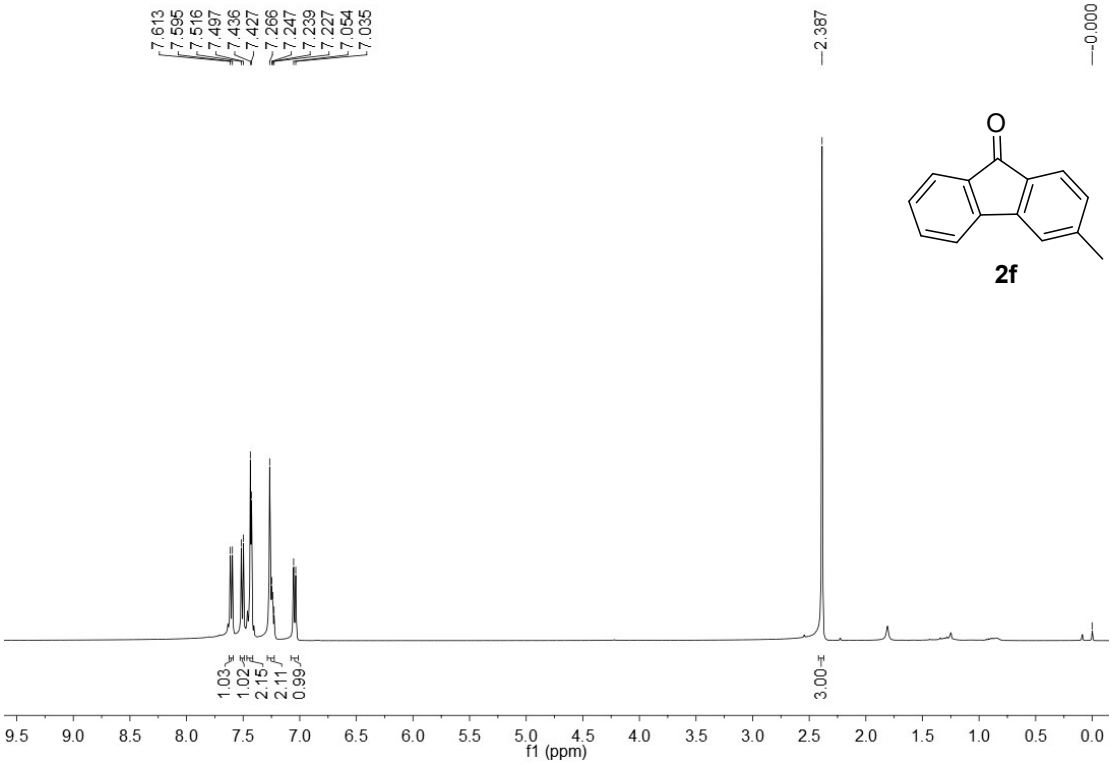
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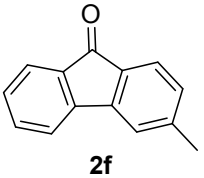
0.99
3.00
f1 (ppm)

2f



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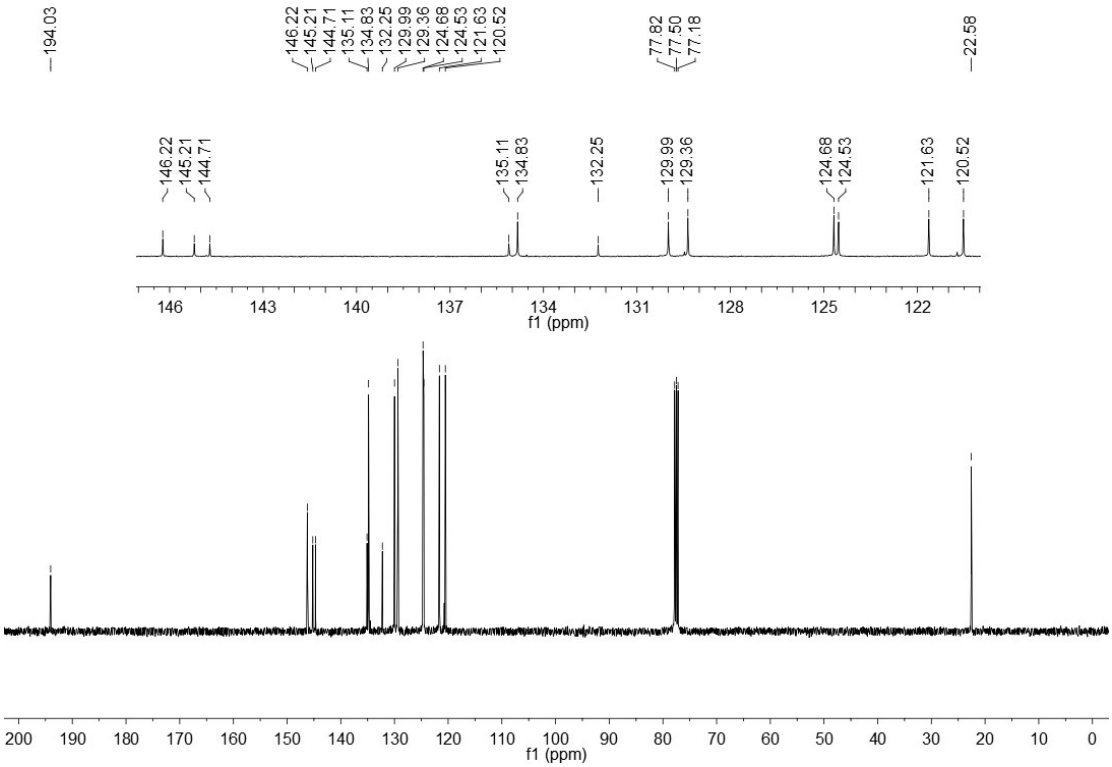
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77.18
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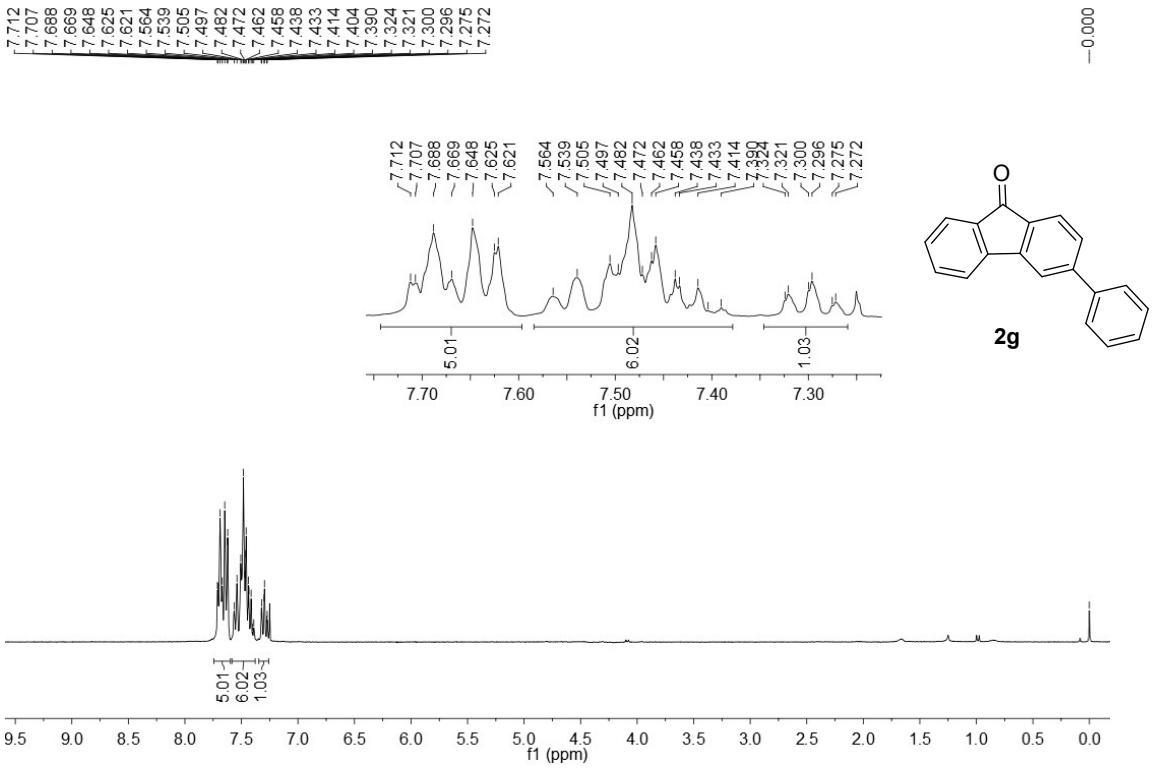
f1 (ppm)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1.03
7.70
7.60
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7.30
f1 (ppm)
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2g
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8.5
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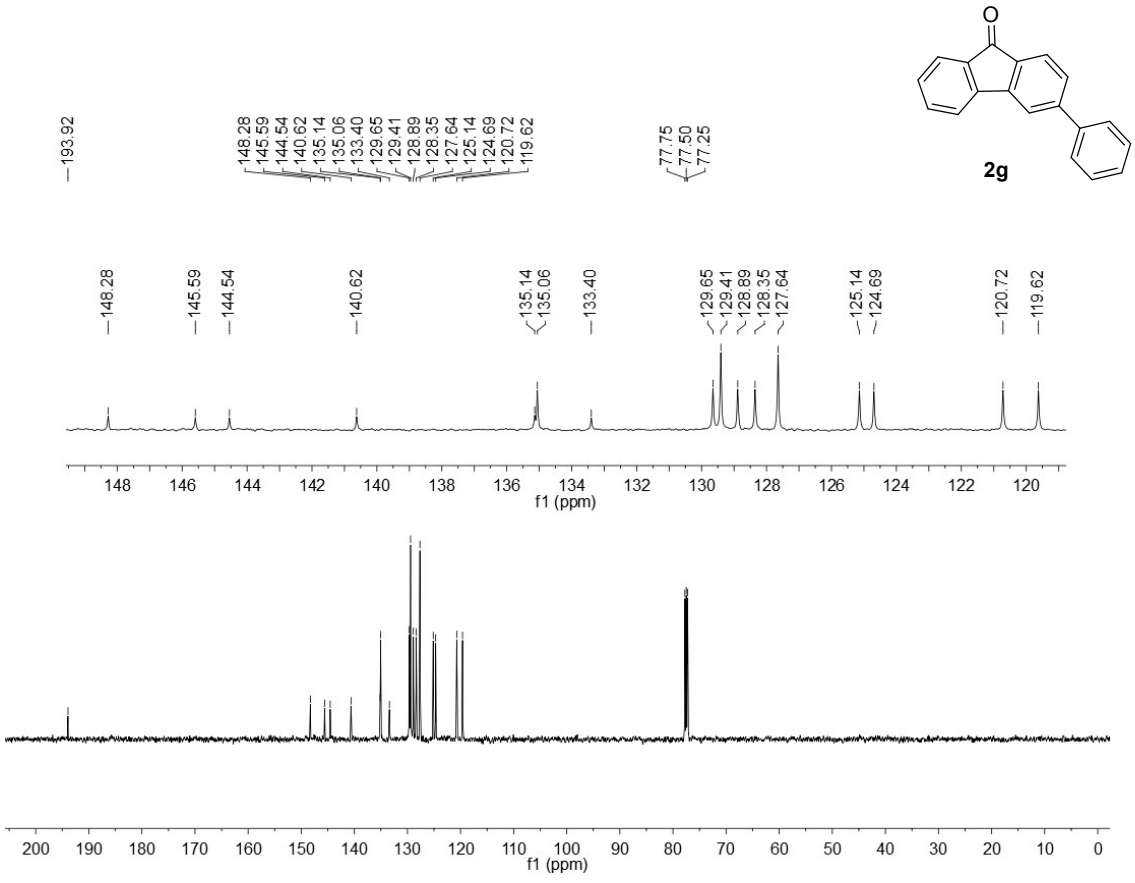
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119.62
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77.50
77.25
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
f1 (ppm)
O
2g
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140
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70
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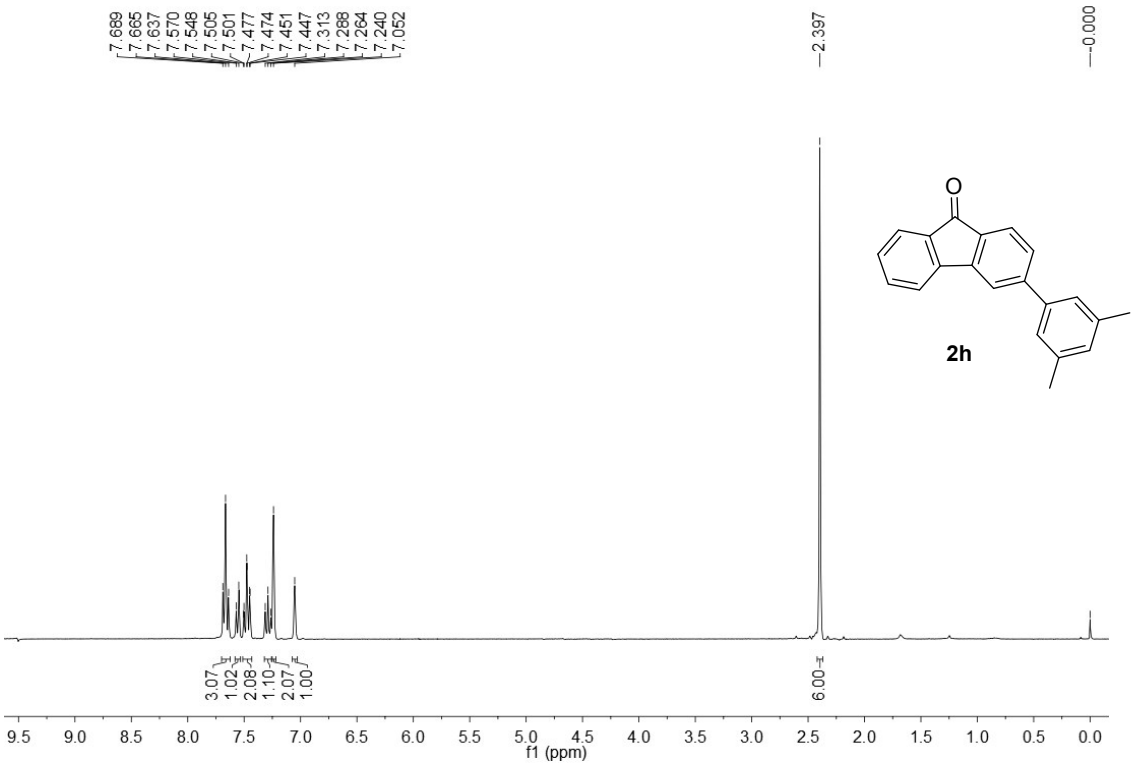
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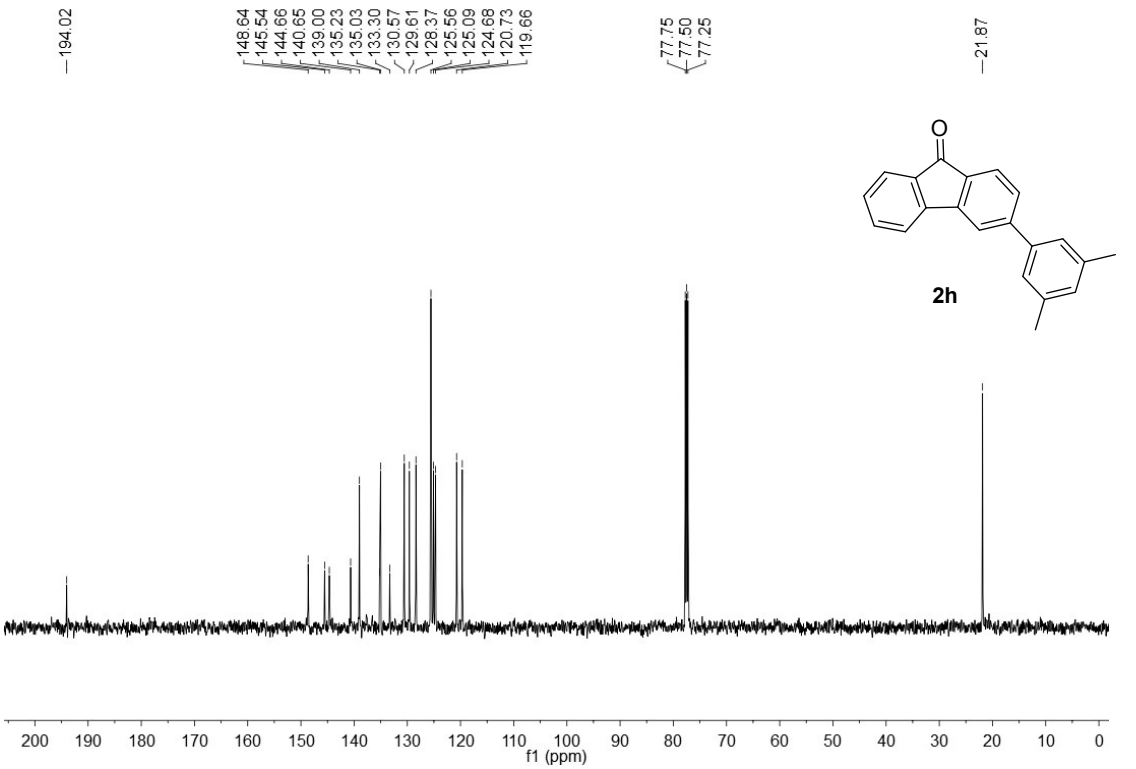
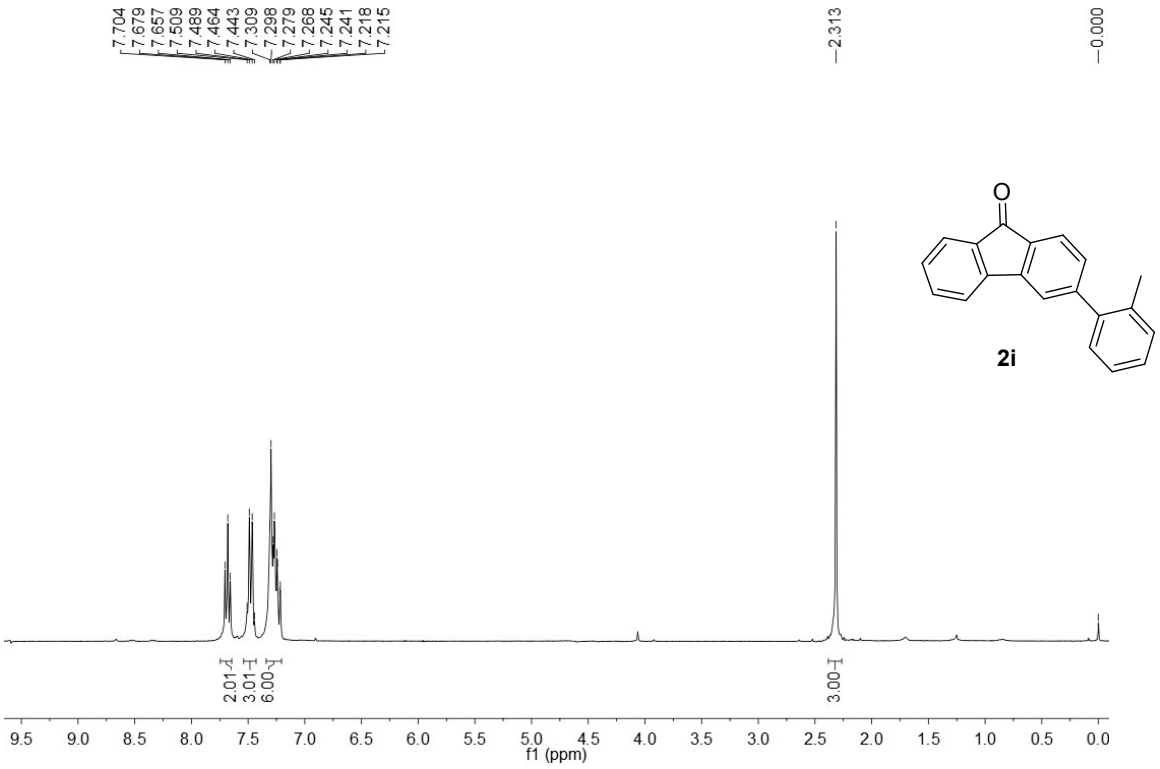
7.264
7.240
7.052
2.397
0.000
O
2h
3.07
1.02
2.08
1.10
2.07
1.00
6.00
f1 (ppm)


194.02
148.64
145.54
144.66
140.65
139.00
135.23
135.03
133.30
130.57
129.61
128.37
125.56
125.09
124.68
120.73
119.66
77.75
77.50
77.25
21.87
O
2h
f1 (ppm)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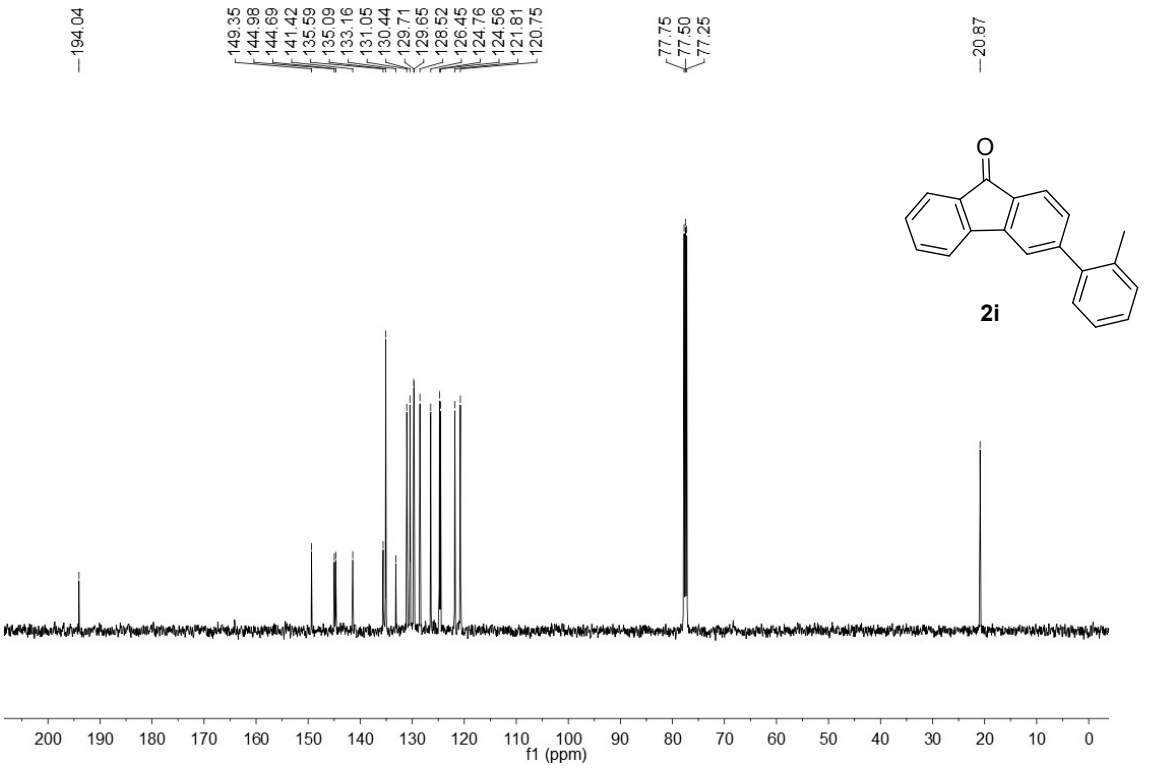
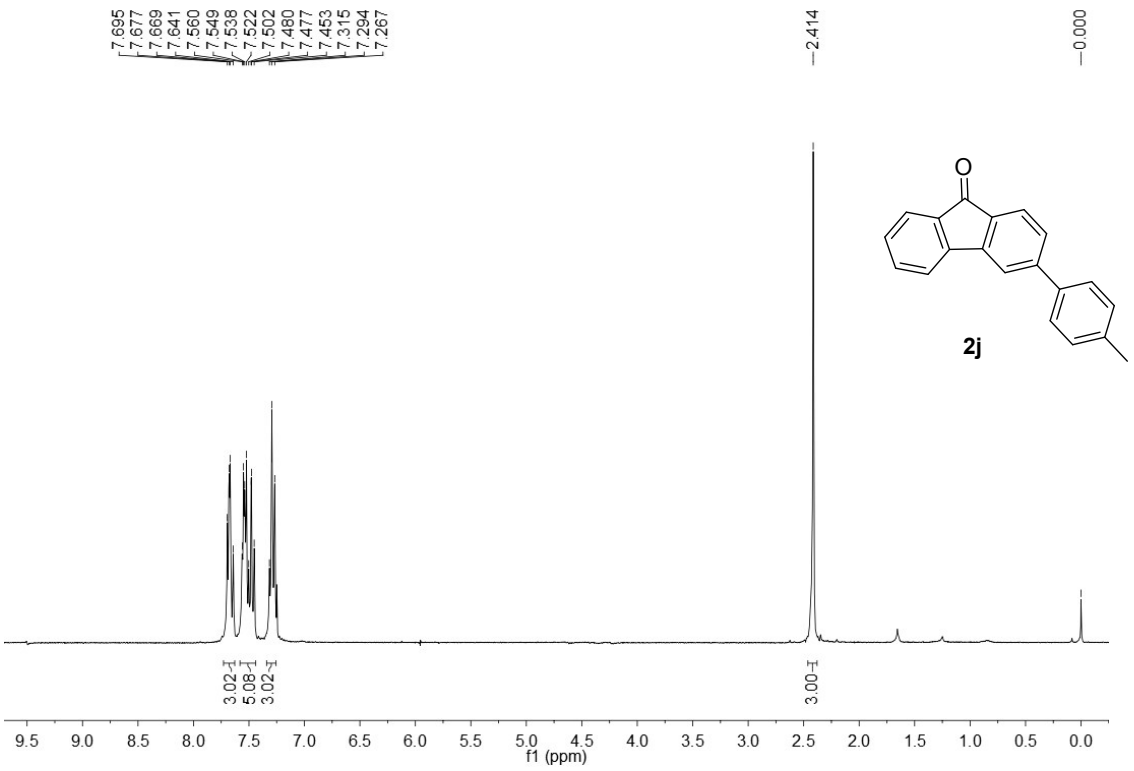
7.679
7.657
7.509
7.489
7.464
7.443
7.309
7.298
7.279
7.268
7.245
7.241
7.218
7.215
2.313
0.000
O
2i
2.01
3.01
6.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


194.04
149.35
144.98
144.69
141.42
135.59
135.09
133.16
131.05
130.44
129.71
129.65
128.52
126.45
124.76
124.56
121.81
120.75
77.75
77.50
77.25
20.87
O
2i
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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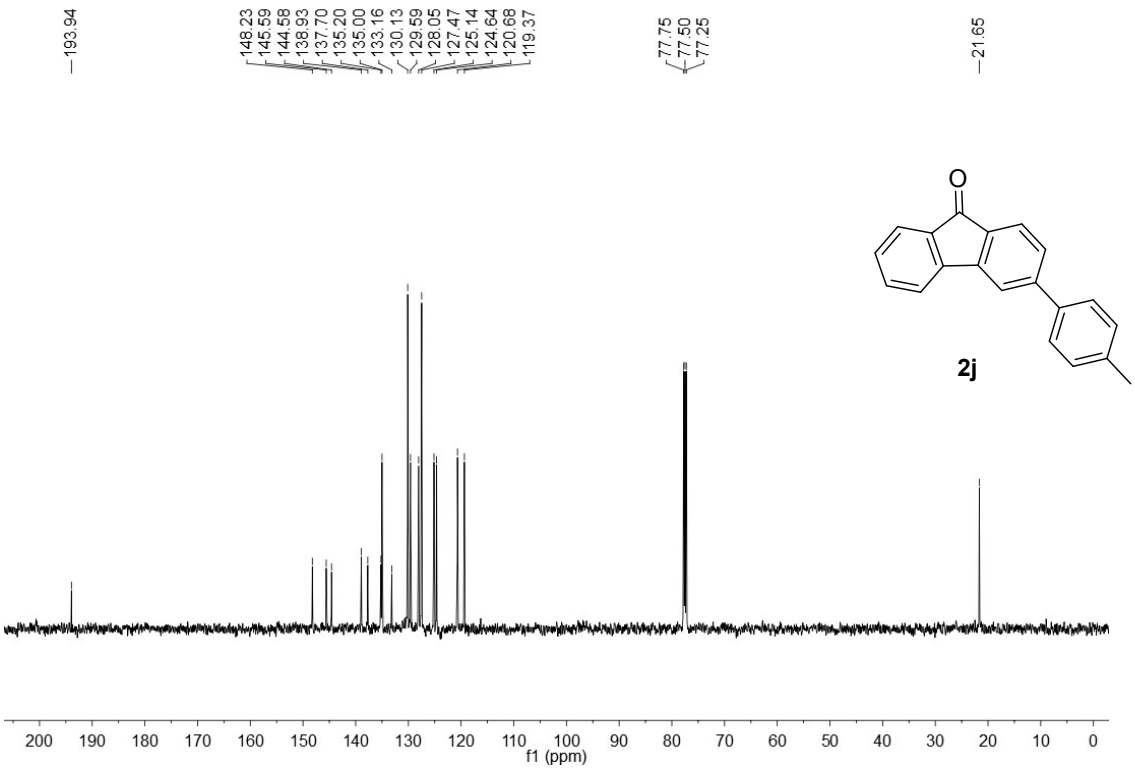
7.560
7.549
7.538
7.522
7.502
7.480
7.477
7.453
7.315
7.294
7.267
2.414
0.000
O
2j
3.02
5.08
3.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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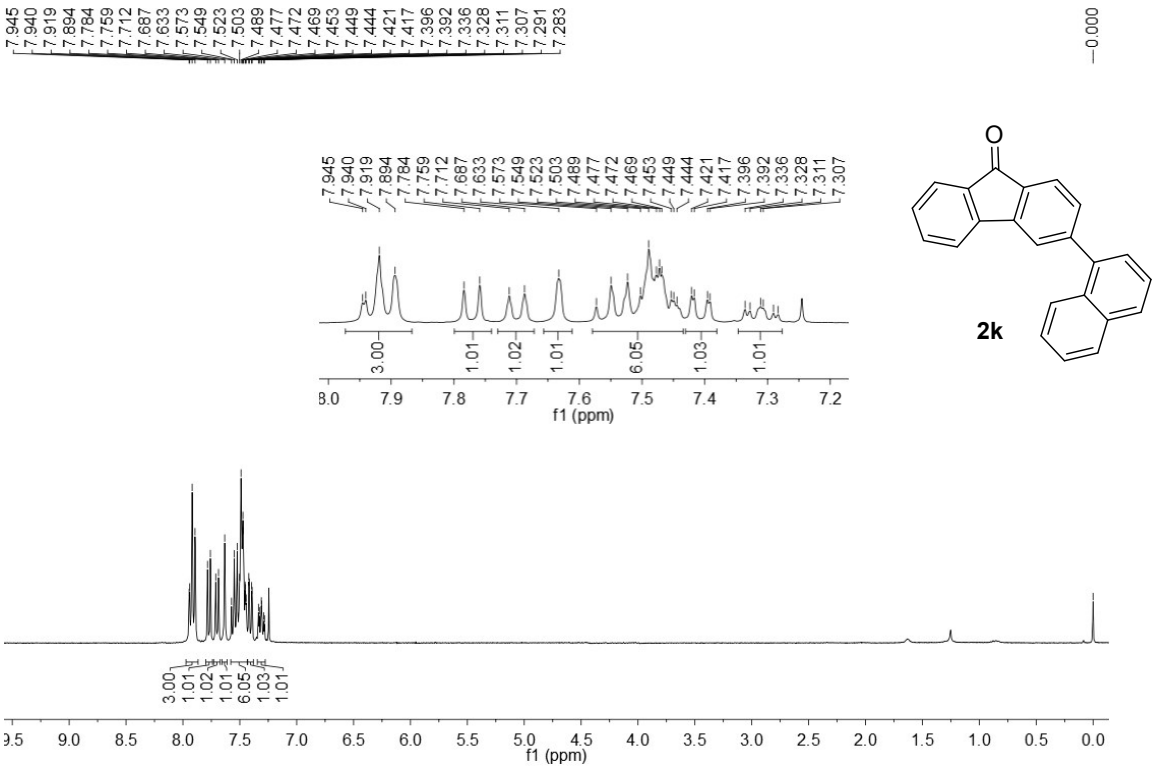
144.58
138.93
137.70
135.20
135.00
133.16
130.13
129.59
128.05
127.47
125.14
124.64
120.68
119.37
77.75
77.50
77.25
21.65
O
2j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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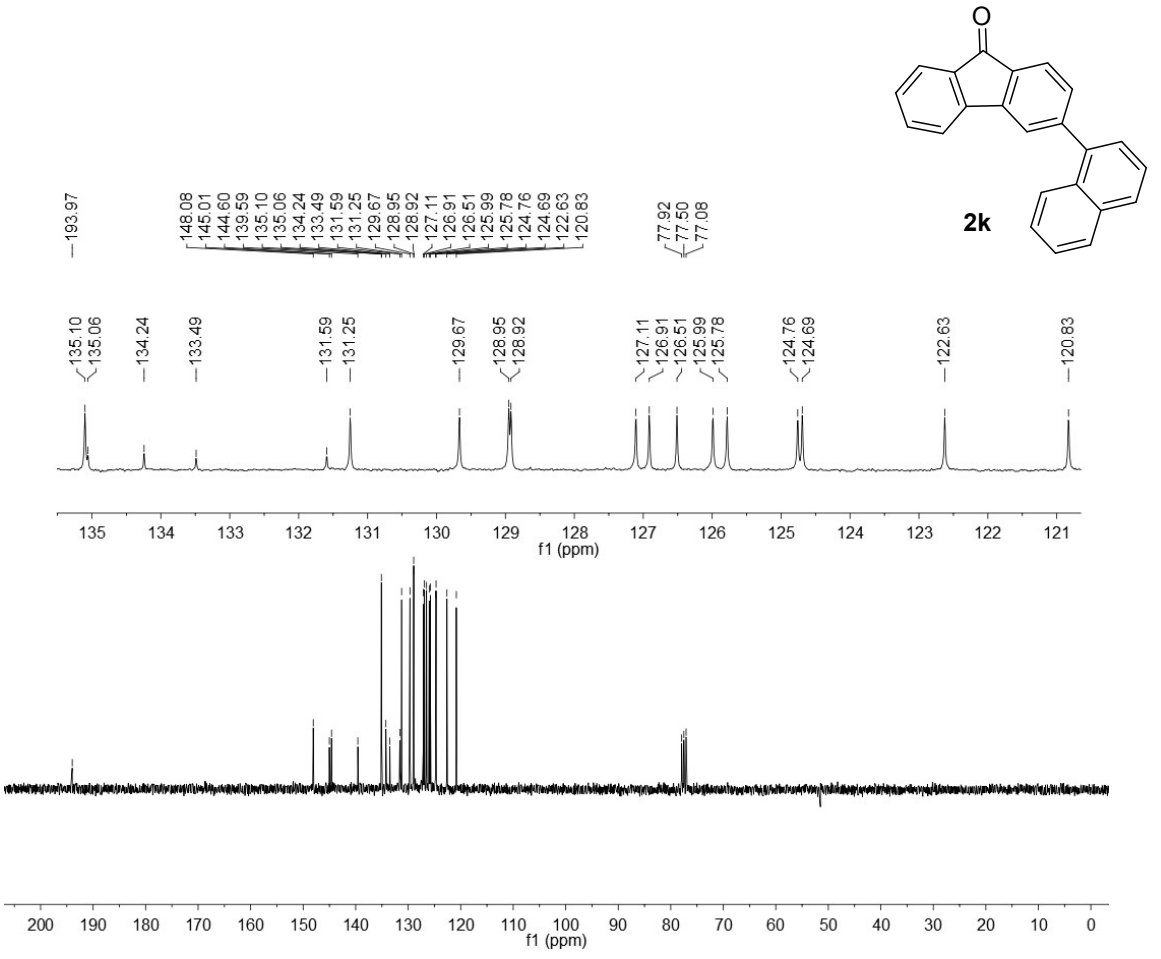
7.940
7.919
7.894
7.784
7.759
7.712
7.687
7.633
7.573
7.549
7.523
7.503
7.489
7.477
7.472
7.469
7.453
7.449
7.444
7.421
7.417
7.396
7.392
7.336
7.328
7.311
7.307
7.291
7.283
0.000
3.00
1.01
1.02
1.01
6.05
1.03
1.01
f1 (ppm)
O
2k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148.08
145.01
144.60
139.59
135.10
135.06
134.24
133.49
131.59
131.25
129.67
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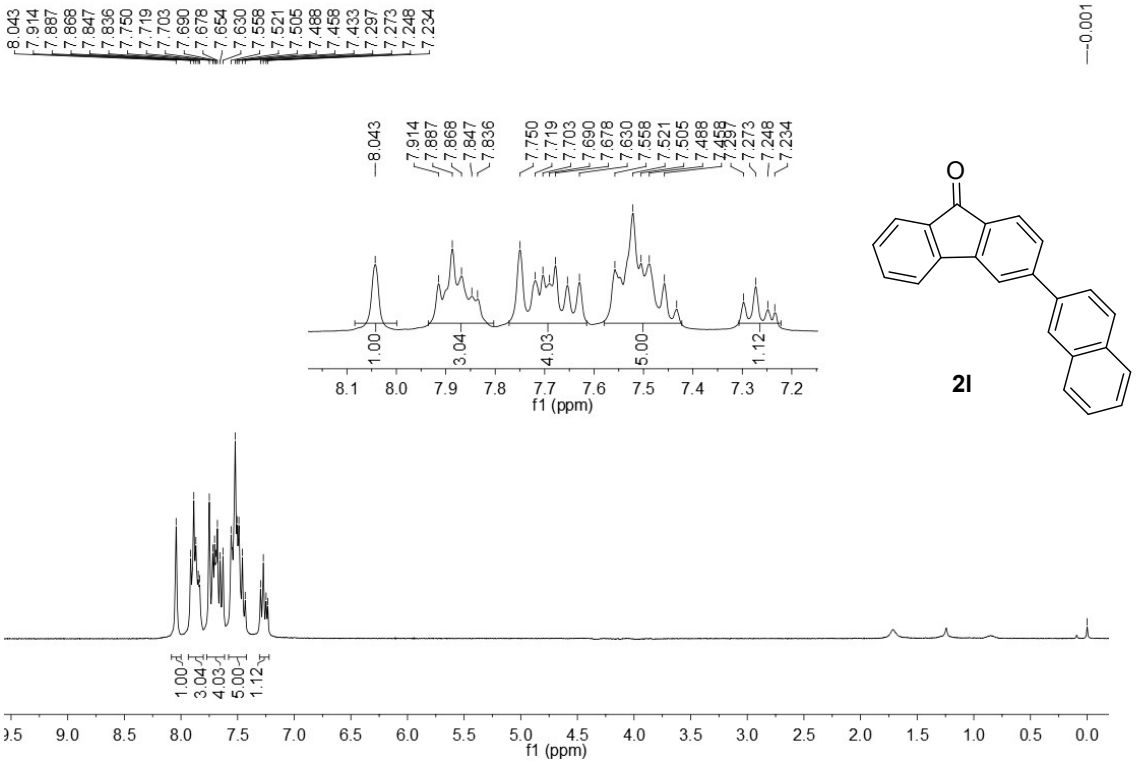
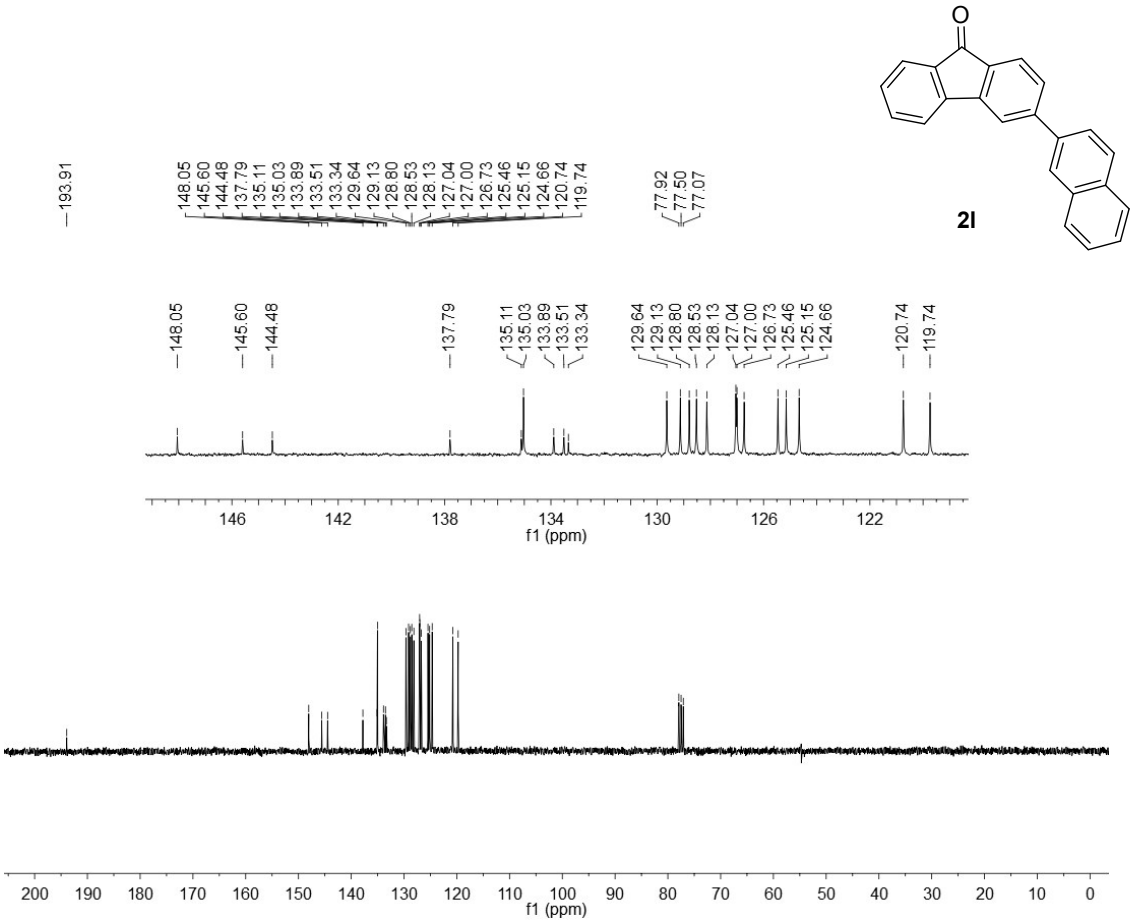
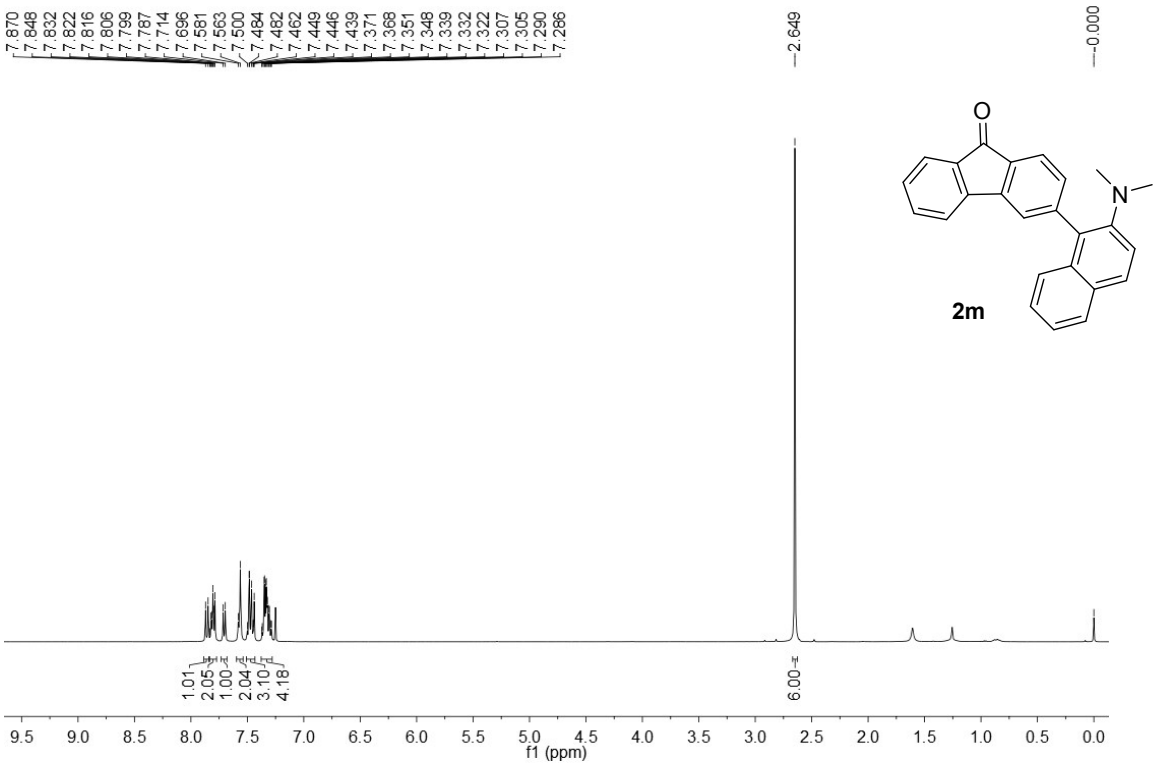
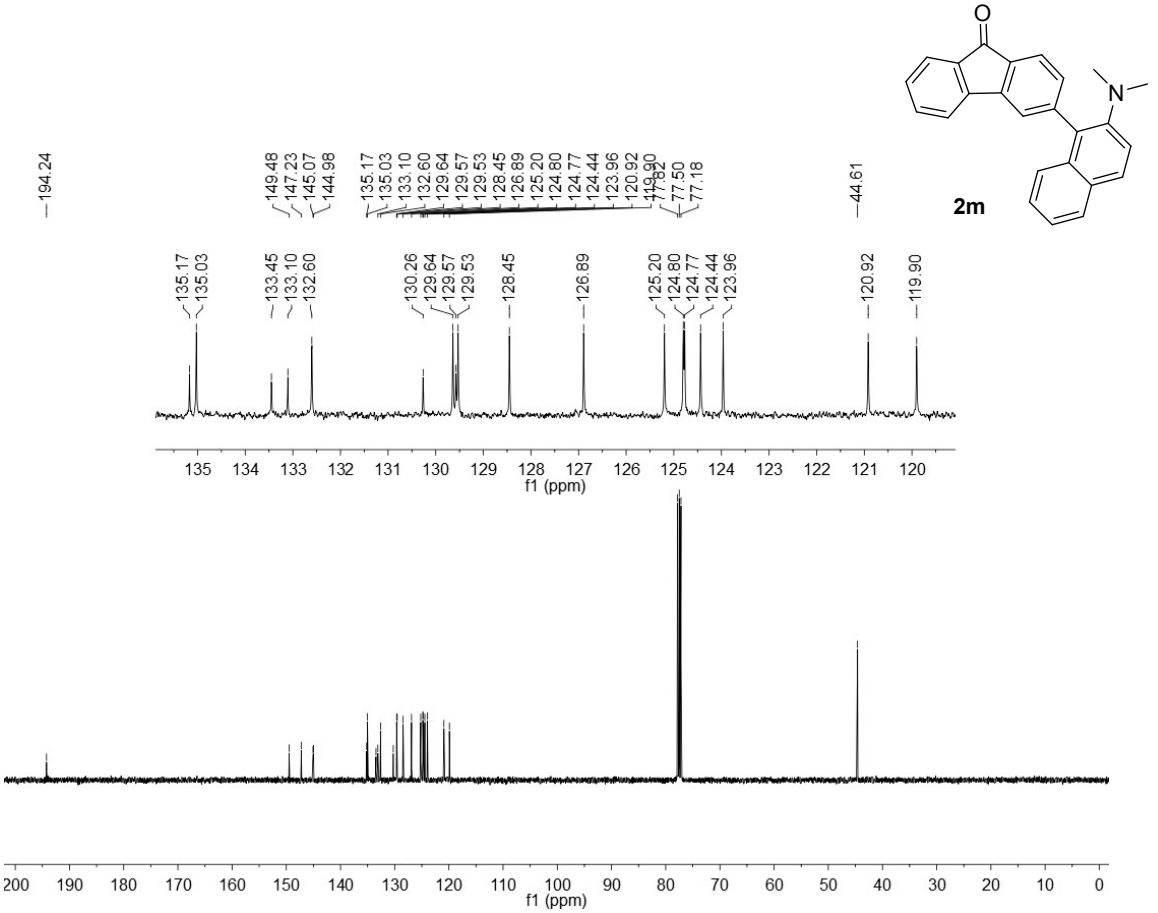
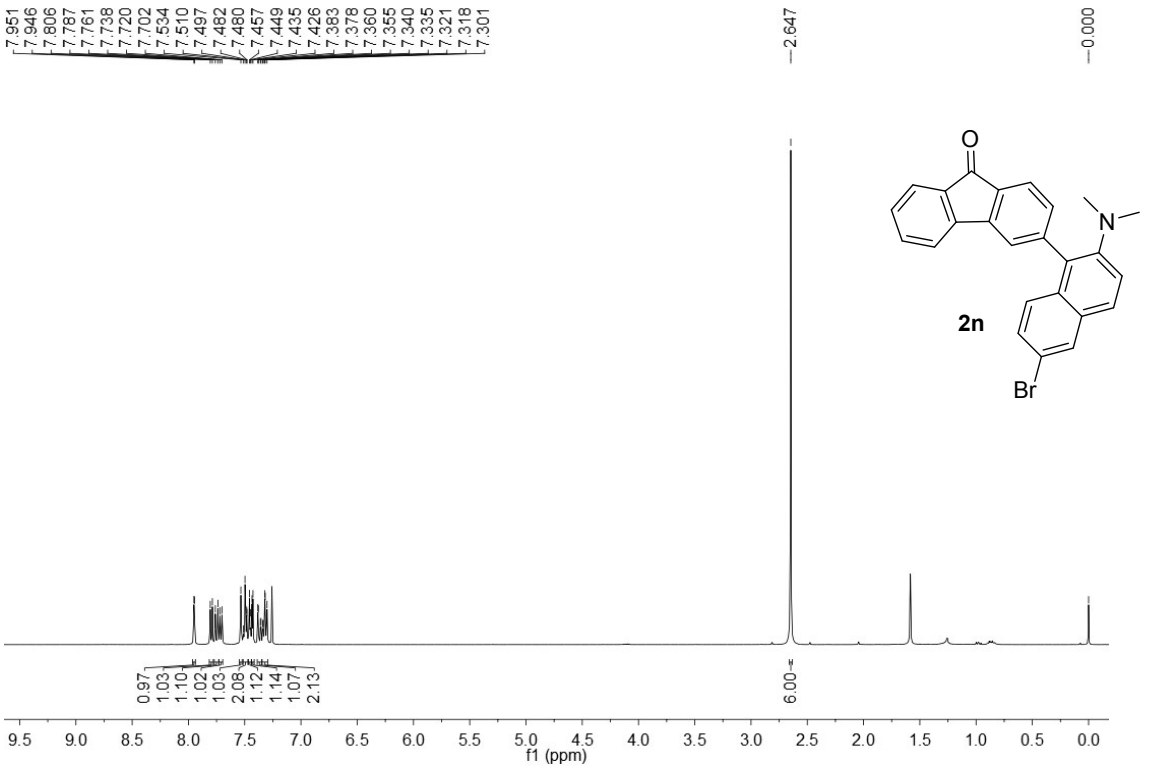
128.92
127.11
126.91
126.51
125.99
125.78
124.76
124.69
122.63
120.83
77.92
77.50
77.08
f1 (ppm)
O
2k

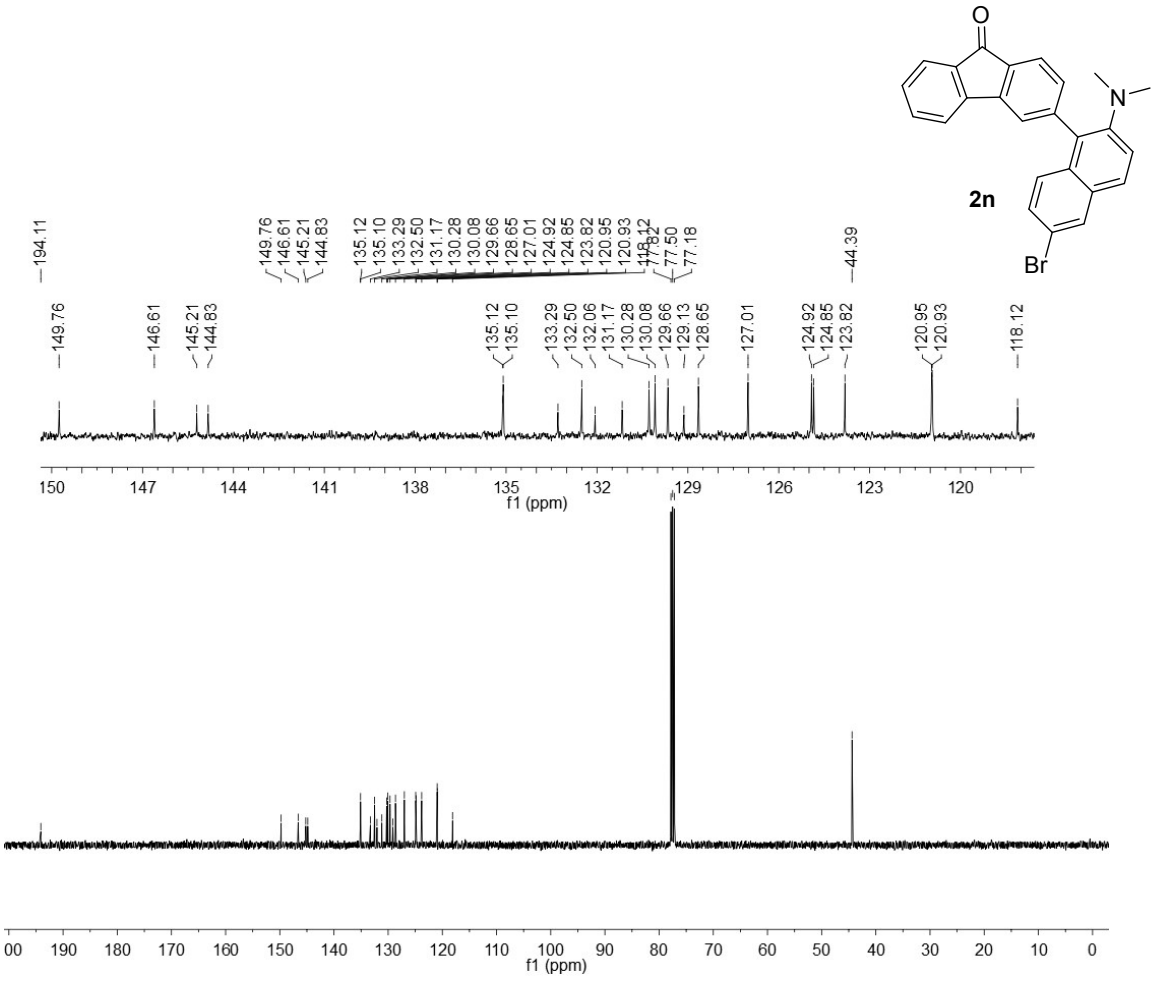

8.043
7.914
7.887
7.868
7.847
7.836
7.750
7.719
7.703
7.690
7.678
7.654
7.630
7.558
7.521
7.505
7.488
7.458
7.433
7.297
7.273
7.248
7.234
0.001
1.00
3.04
4.03
5.00
1.12
f1 (ppm)
O
2l


193.91
148.05
145.60
144.48
137.79
135.11
135.03
133.89
133.51
133.34
129.64
129.13
128.80
128.53
128.13
127.04
127.00
126.73
125.46
125.15
124.66
120.74
119.74
77.92
77.50
77.07
f1 (ppm)
O
2l


7.870
7.848
7.832
7.822
7.816
7.806
7.799
7.787
7.714
7.696
7.581
7.563
7.500
7.484
7.482
7.462
7.449
7.446
7.439
7.371
7.368
7.351
7.348
7.339
7.332
7.322
7.307
7.305
7.290
7.286
2.649
0.000
1.01
2.05
1.00
2.04
3.10
4.18
6.00
f1 (ppm)
2m

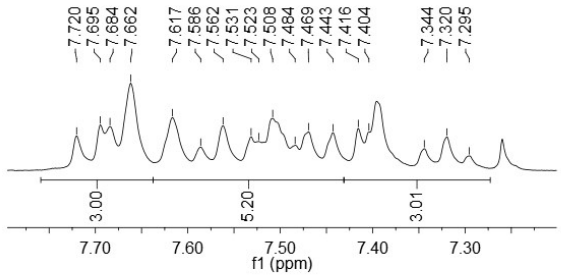

194.24
149.48
147.23
145.07
144.98
135.17
135.03
133.10
132.60
129.64
129.57
129.53
128.45
126.89
125.20
124.80
124.77
124.44
123.96
120.92
119.90
77.82
77.50
77.18
44.61
f1 (ppm)
2m

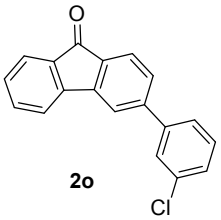

7.951
7.946
7.806
7.787
7.761
7.738
7.720
7.702
7.534
7.510
7.497
7.482
7.480
7.457
7.449
7.435
7.426
7.383
7.378
7.360
7.355
7.340
7.335
7.321
7.318
7.301
2.647
0.000
0.97
1.03
1.10
1.02
1.03
2.08
1.12
1.14
1.07
2.13
6.00
f1 (ppm)
O
N
Br
2n


194.11
149.76
146.61
145.21
144.83
135.12
135.10
133.29
132.50
131.17
130.28
130.08
129.66
128.65
127.01
124.92
124.85
123.82
120.95
120.93
118.12
77.82
77.50
77.18
44.39
f1 (ppm)
O
N
Br
2n

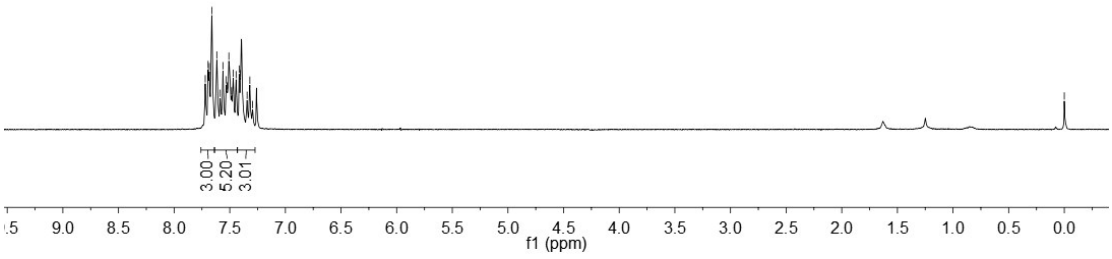

7.720
7.695
7.684
7.662
7.617
7.586
7.562
7.531
7.523
7.508
7.484
7.469
7.443
7.416
7.404
7.344
7.320
7.295

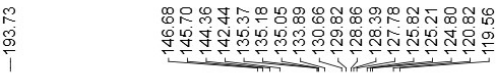

0.000


7.720
7.695
7.684
7.662
7.617
7.586
7.562
7.531
7.523
7.508
7.484
7.469
7.443
7.416
7.404
7.344
7.320
7.295
3.00
5.20
3.01
7.70
7.60
7.50
7.40
7.30
f1 (ppm)


O
Cl

2o


3.00
5.20
3.01
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)


193.73
146.68
145.70
144.36
142.44
135.37
135.18
135.05
133.89
130.66
129.82
128.86
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127.78
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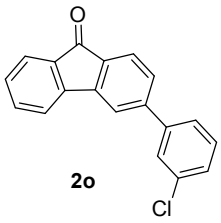
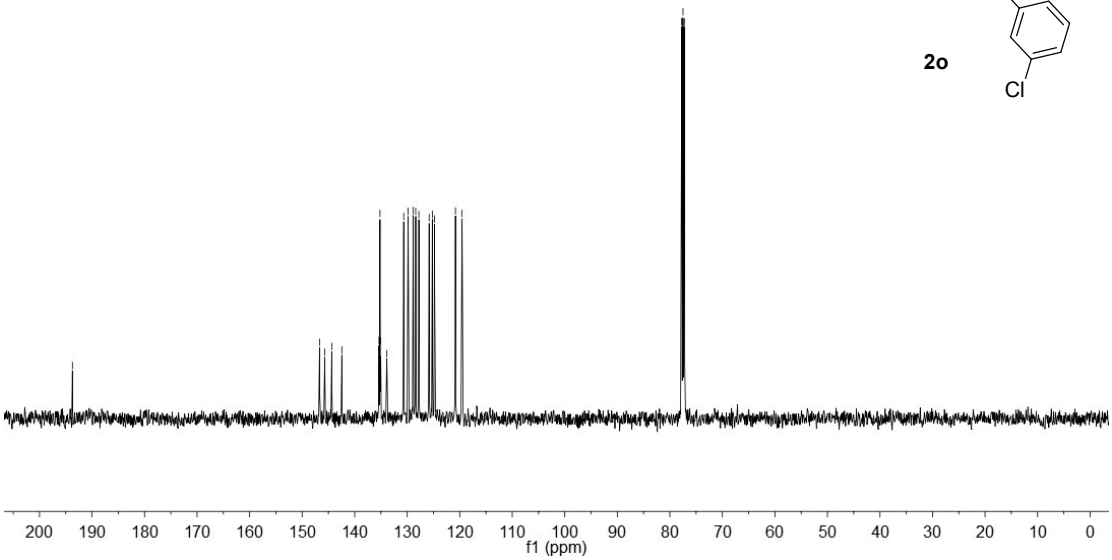
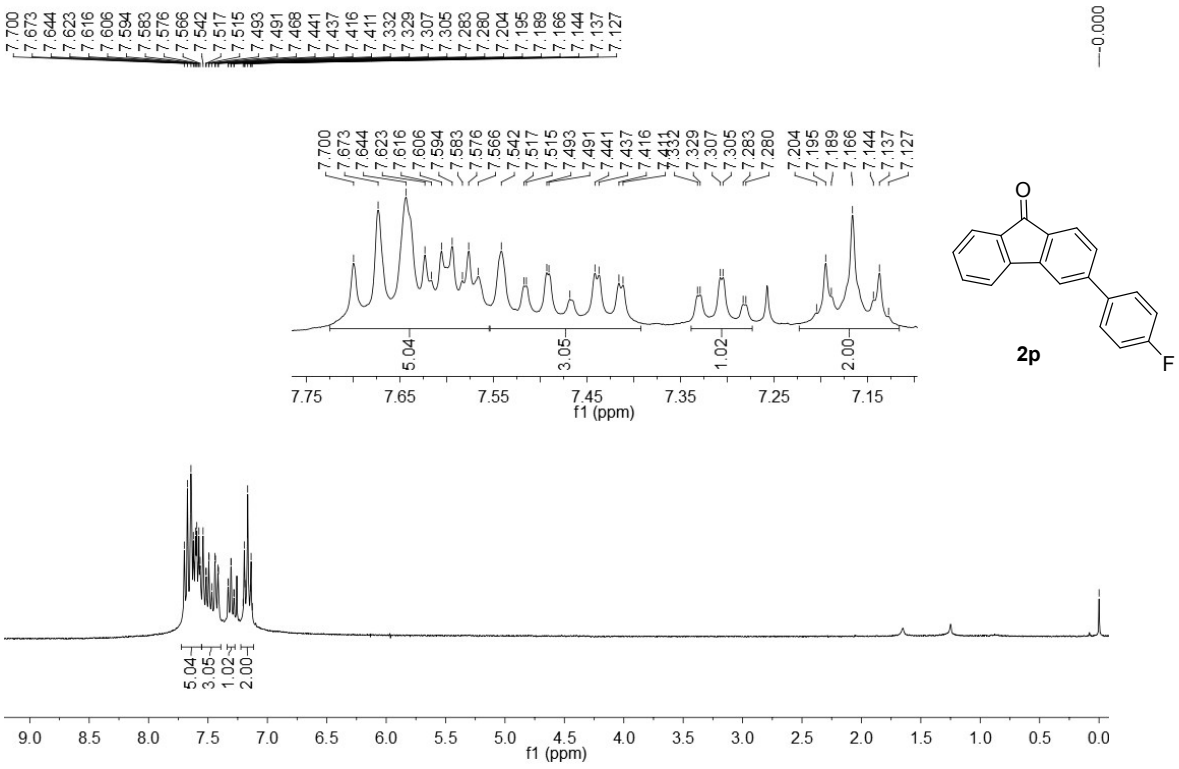
124.80
120.82
119.56
77.75
77.50
77.25


O
Cl

2o


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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7.673
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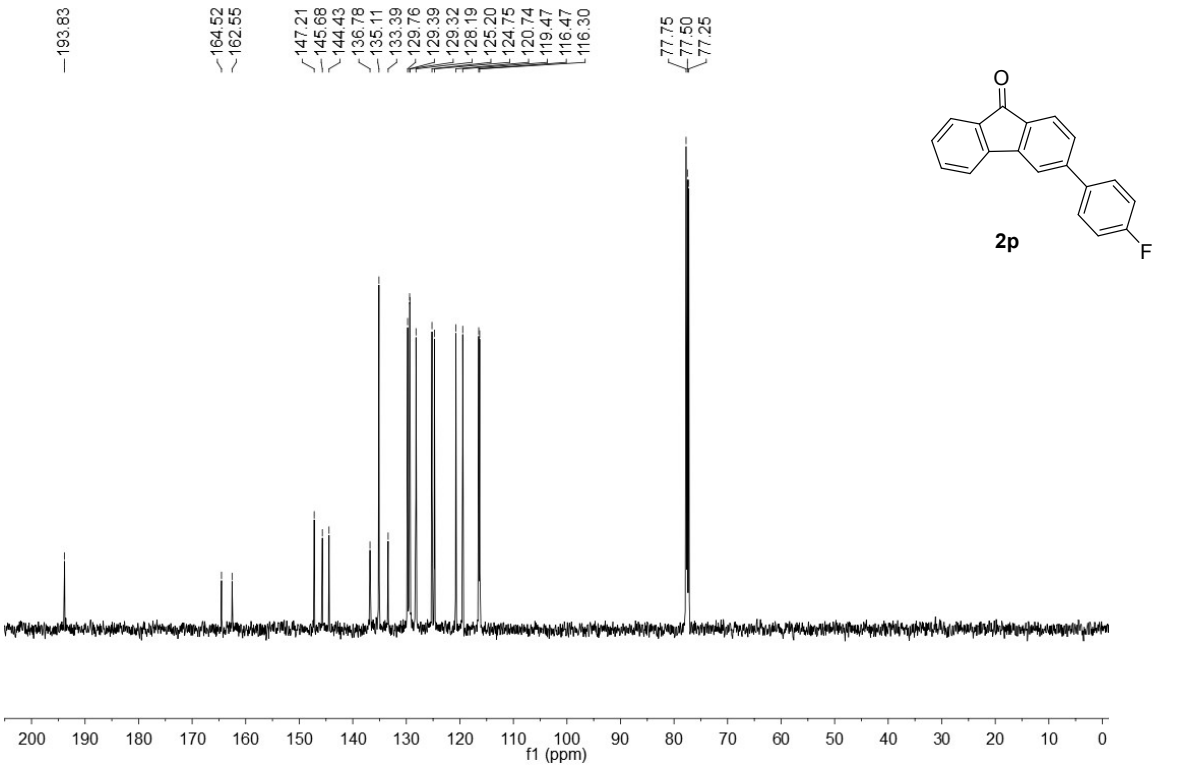
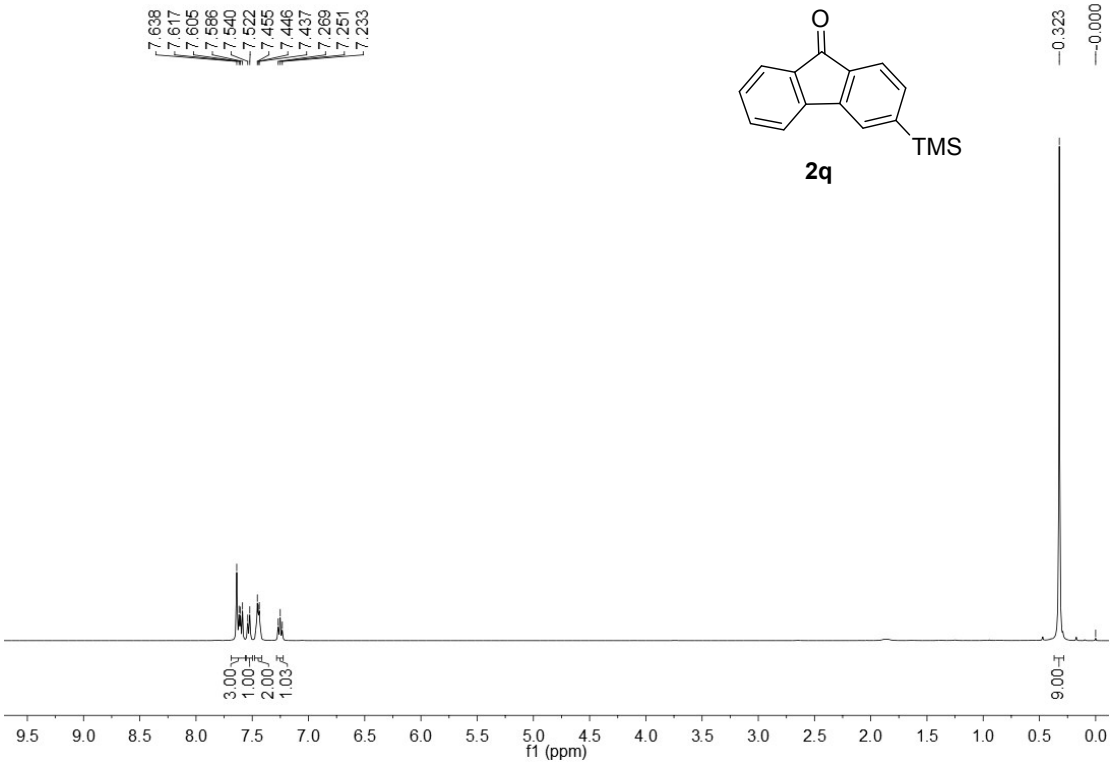
7.623
7.616
7.606
7.594
7.583
7.576
7.566
7.542
7.517
7.515
7.493
7.491
7.468
7.441
7.437
7.416
7.411
7.332
7.329
7.307
7.305
7.283
7.280
7.204
7.195
7.189
7.166
7.144
7.137
7.127
0.000
5.04
3.05
1.02
2.00
f1 (ppm)
O
F
2p


193.83
164.52
162.55
147.21
145.68
144.43
136.78
135.11
133.39
129.76
129.39
129.32
128.19
125.20
124.75
120.74
119.47
116.47
116.30
77.75
77.50
77.25
f1 (ppm)
O
F
2p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7.617
7.605
7.586
7.540
7.522
7.455
7.446
7.437
7.269
7.251
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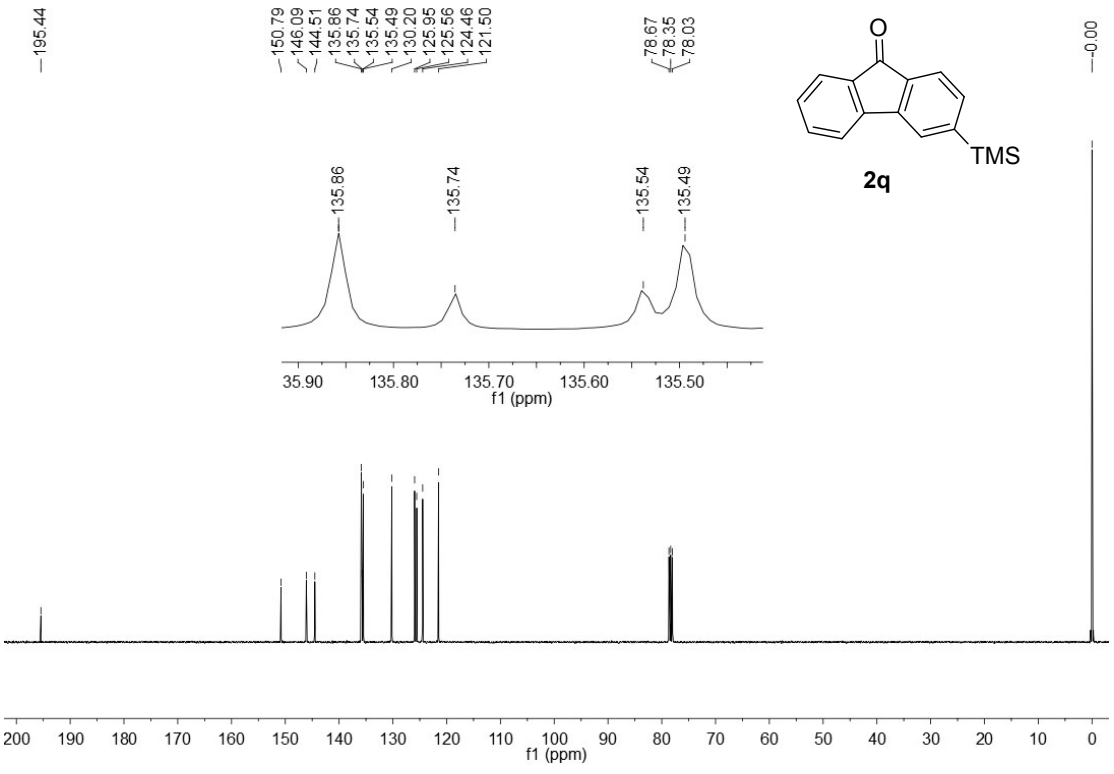
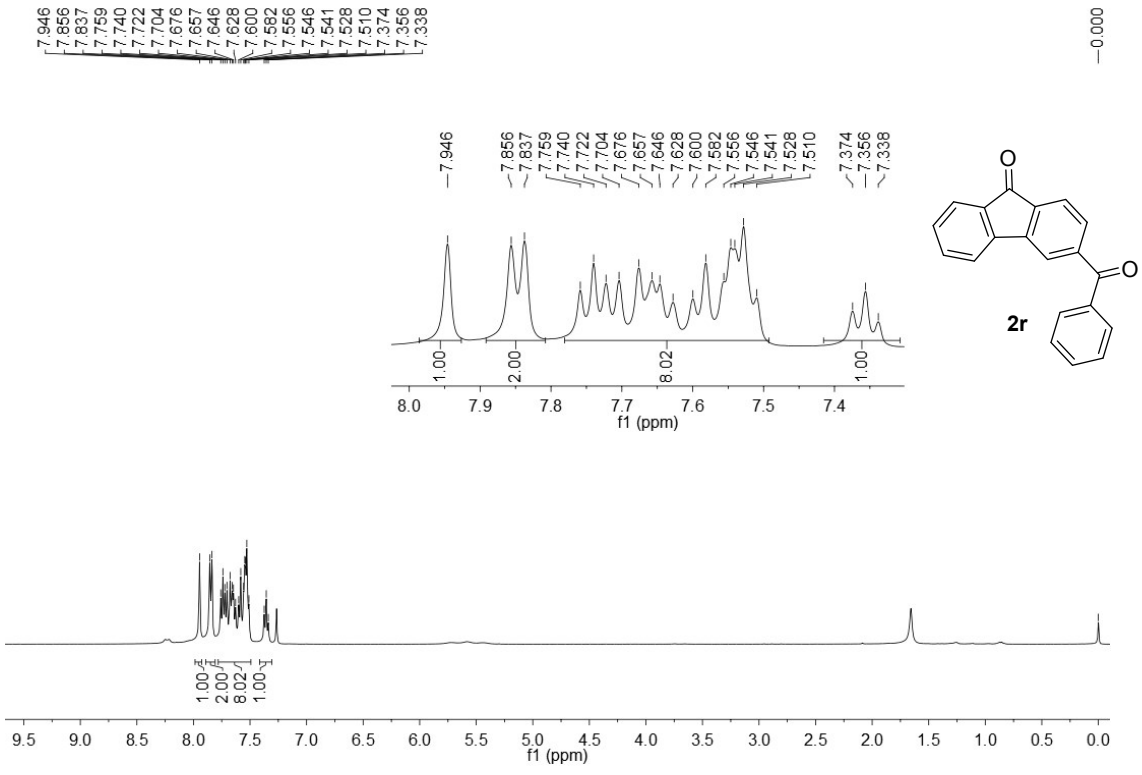
0.323
0.000
O
TMS
2q
3.00
1.00
2.00
1.03
9.00
f1 (ppm)


195.44
150.79
146.09
144.51
135.86
135.74
135.54
135.49
130.20
125.95
125.56
124.46
121.50
78.67
78.35
78.03
0.00
O
TMS
2q
135.86
135.74
135.54
135.49
35.90
135.80
135.70
135.60
135.50
f1 (ppm)
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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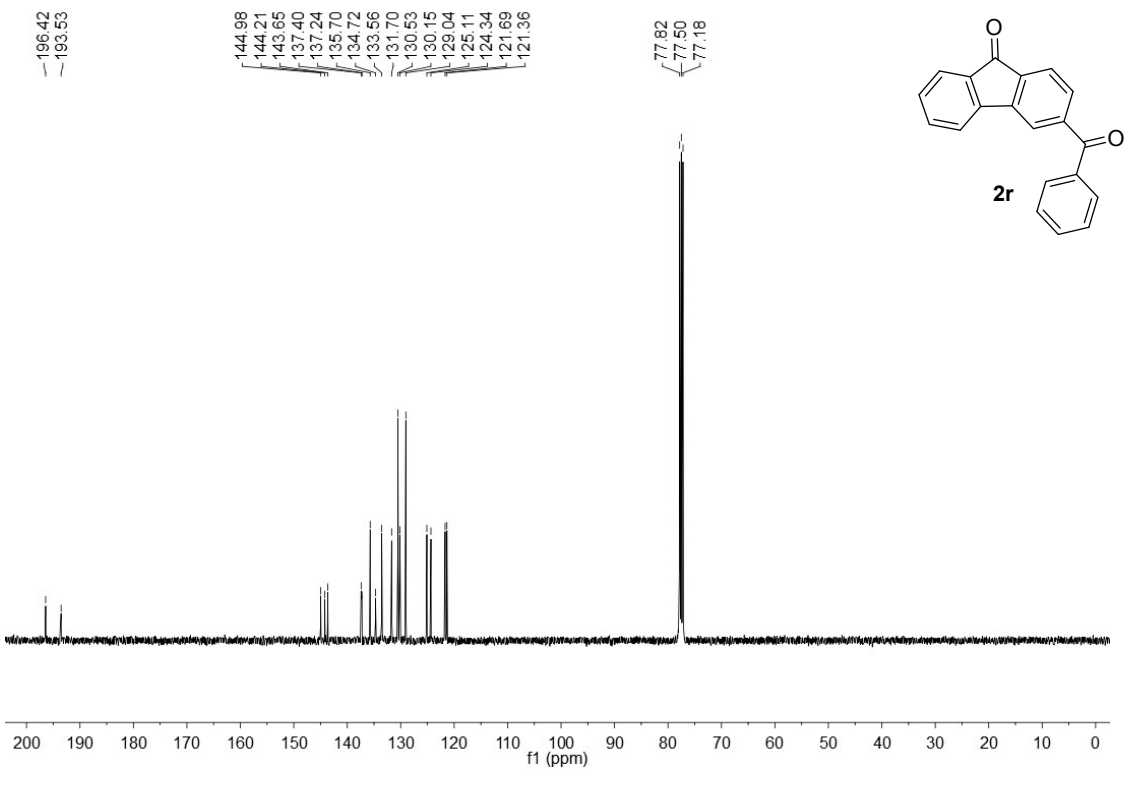
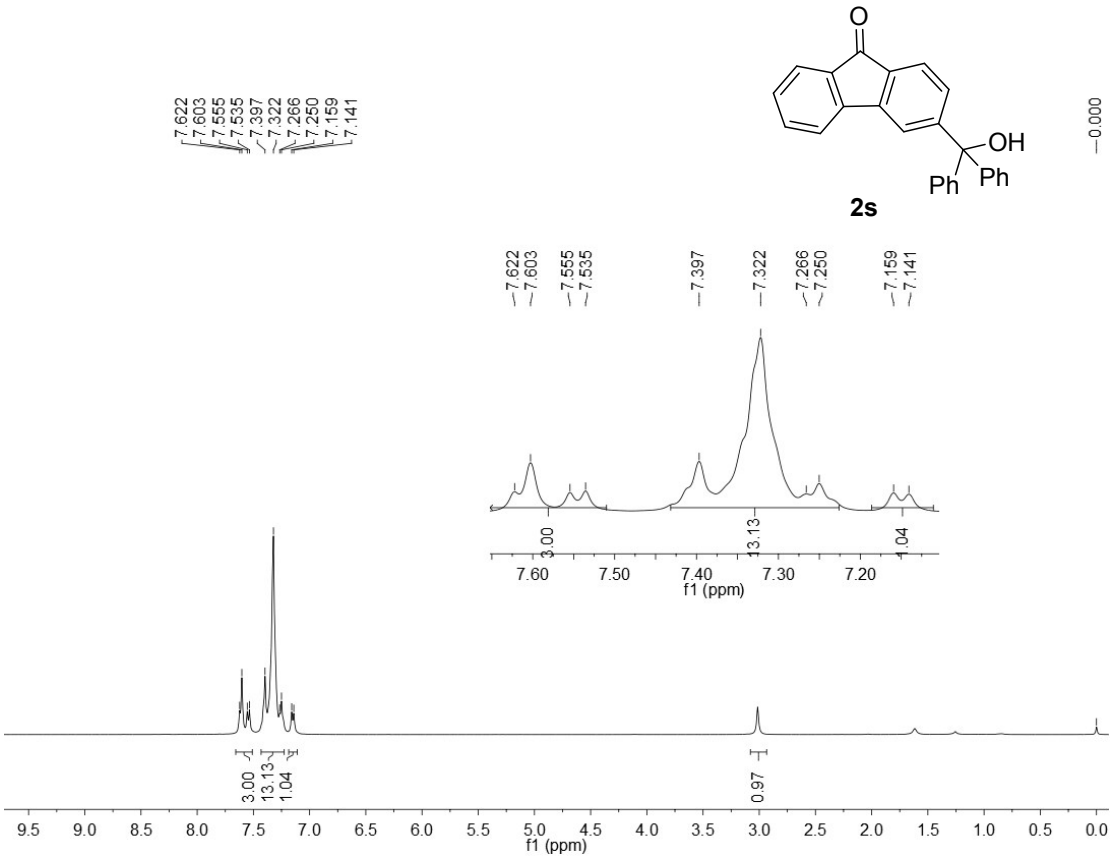
7.722
7.704
7.676
7.657
7.646
7.628
7.600
7.582
7.556
7.546
7.541
7.528
7.510
7.374
7.356
7.338
0.000
1.00
2.00
8.02
1.00
f1 (ppm)
2r


196.42
193.53
144.98
144.21
143.65
137.40
137.24
135.70
134.72
133.56
131.70
130.53
130.15
129.04
125.11
124.34
121.69
121.36
77.82
77.50
77.18
f1 (ppm)
2r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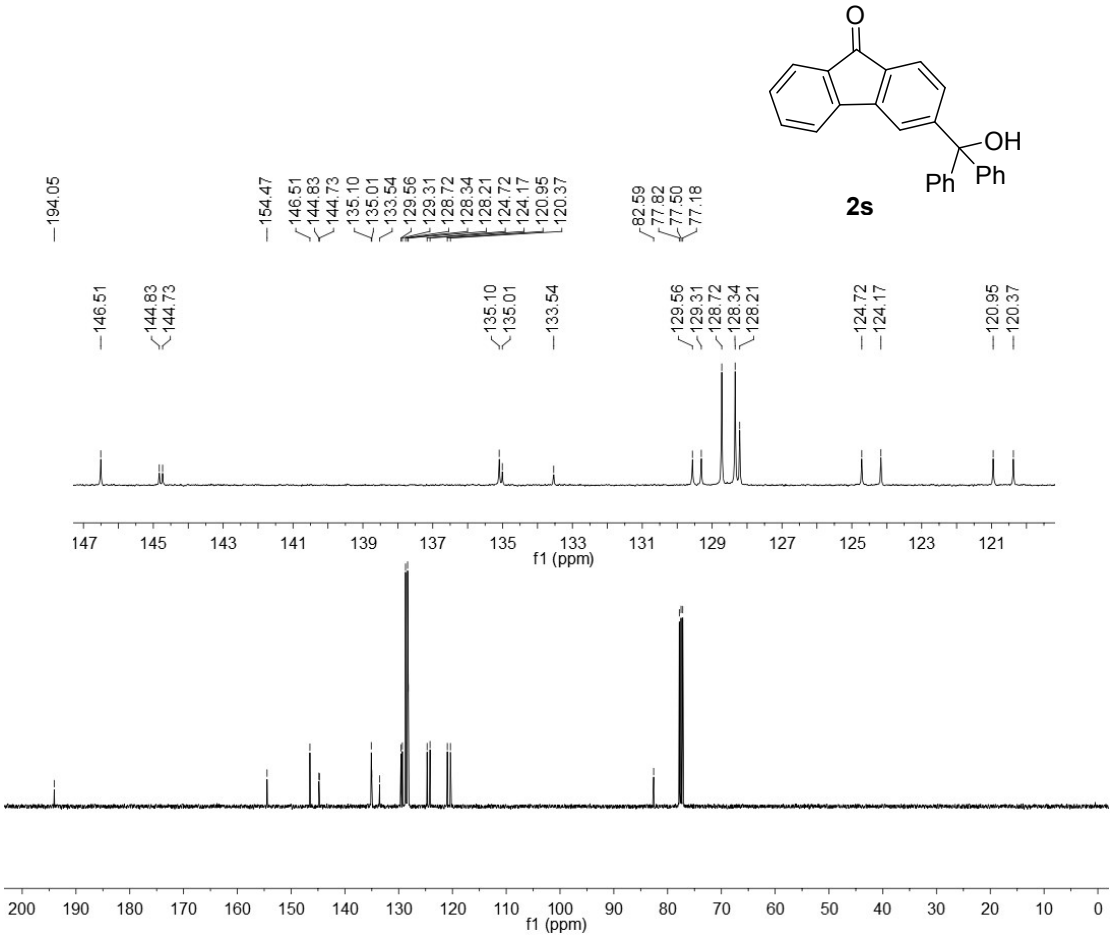
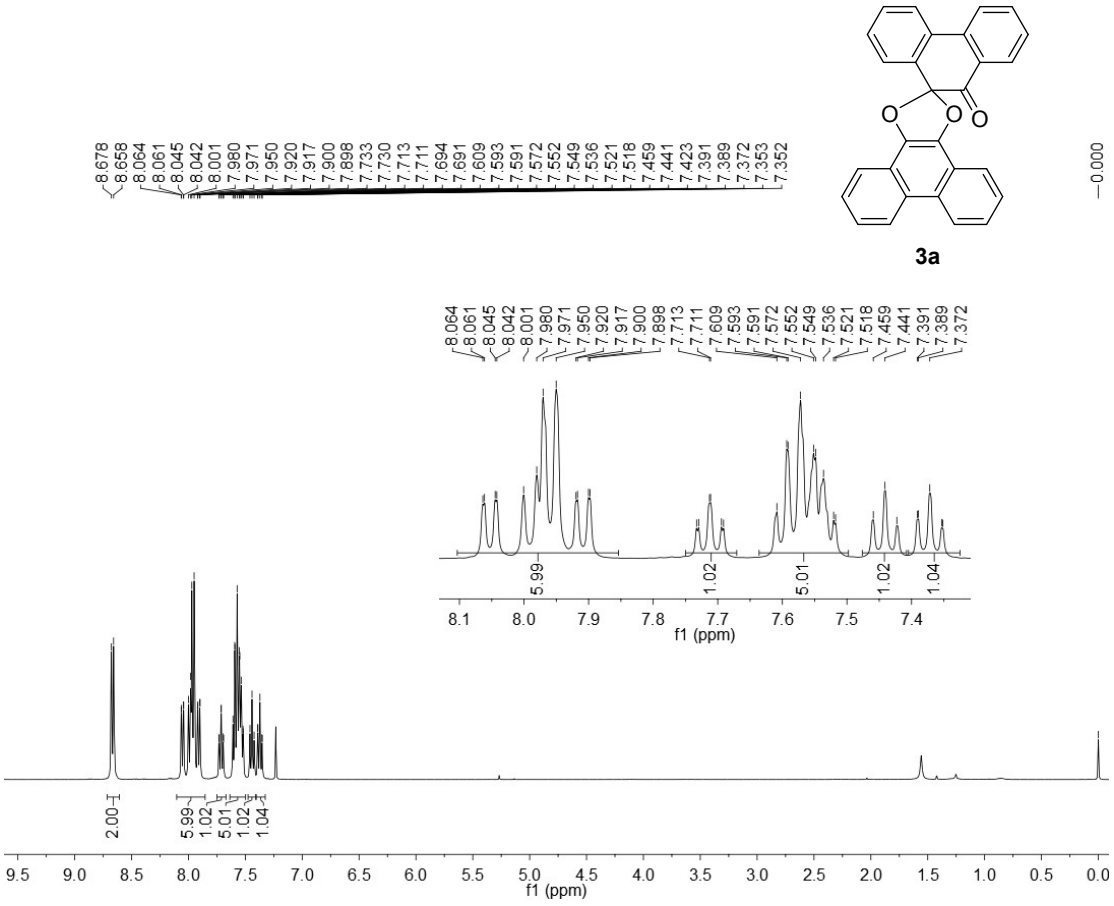
7.603
7.555
7.535
7.397
7.322
7.266
7.250
7.159
7.141
0.000
O
OH
Ph
Ph
2s
3.00
13.13
1.04
0.97
f1 (ppm)


194.05
154.47
146.51
144.83
144.73
135.10
135.01
133.54
129.56
129.31
128.72
128.34
128.21
124.72
124.17
120.95
120.37
82.59
77.82
77.50
77.18
O
OH
Ph
Ph
2s
f1 (ppm)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8.061
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8.042
8.001
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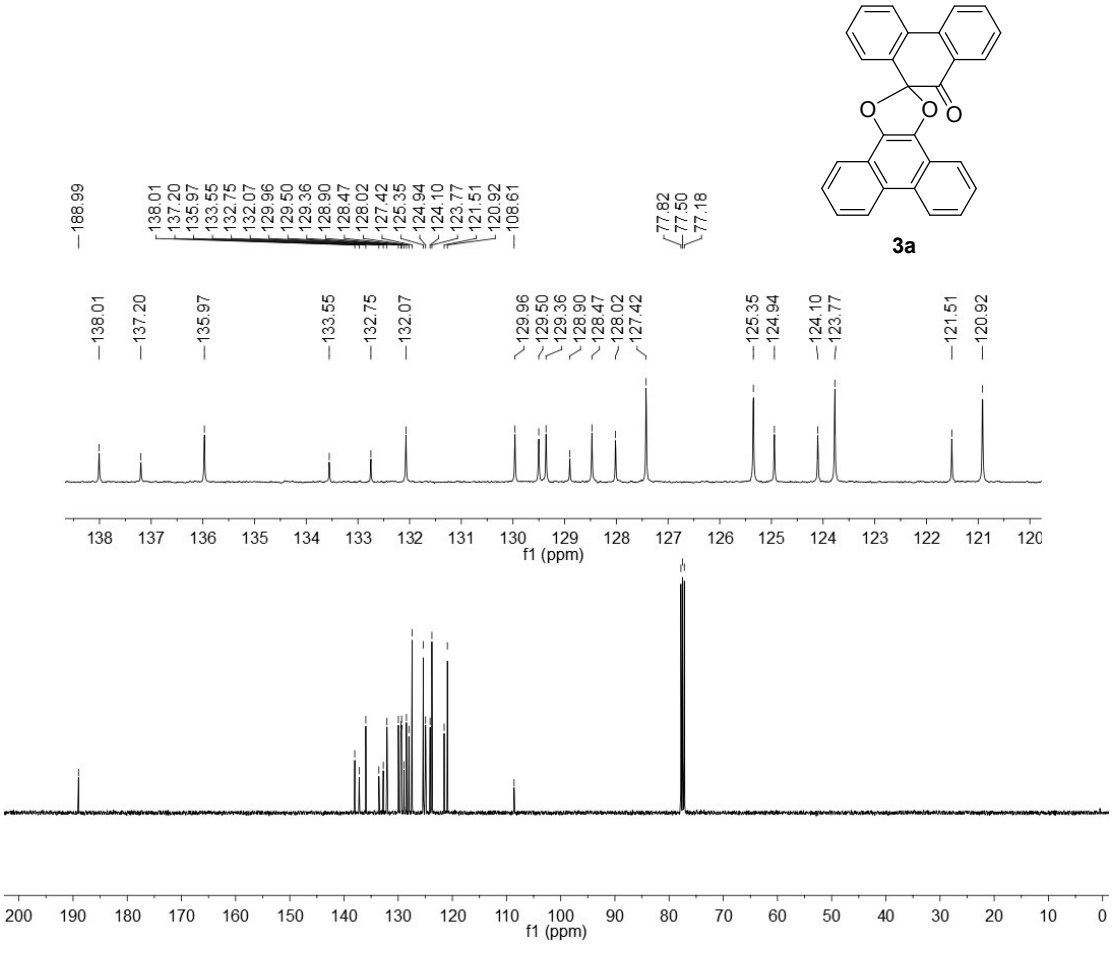
7.971
7.950
7.920
7.917
7.900
7.898
7.733
7.730
7.713
7.711
7.694
7.691
7.609
7.593
7.591
7.572
7.552
7.549
7.536
7.521
7.518
7.459
7.441
7.423
7.391
7.389
7.372
7.353
7.352
0.000
3a
5.99
1.02
5.01
1.02
1.04
f1 (ppm)
2.00
f1 (ppm)


188.99
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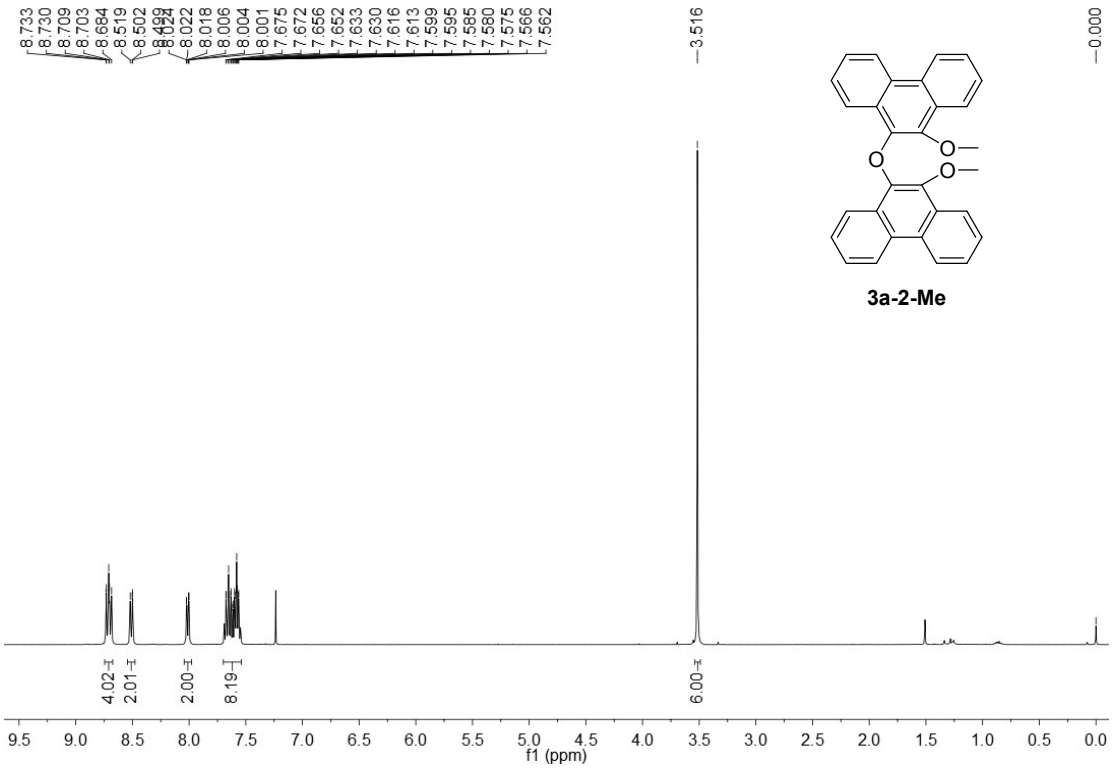
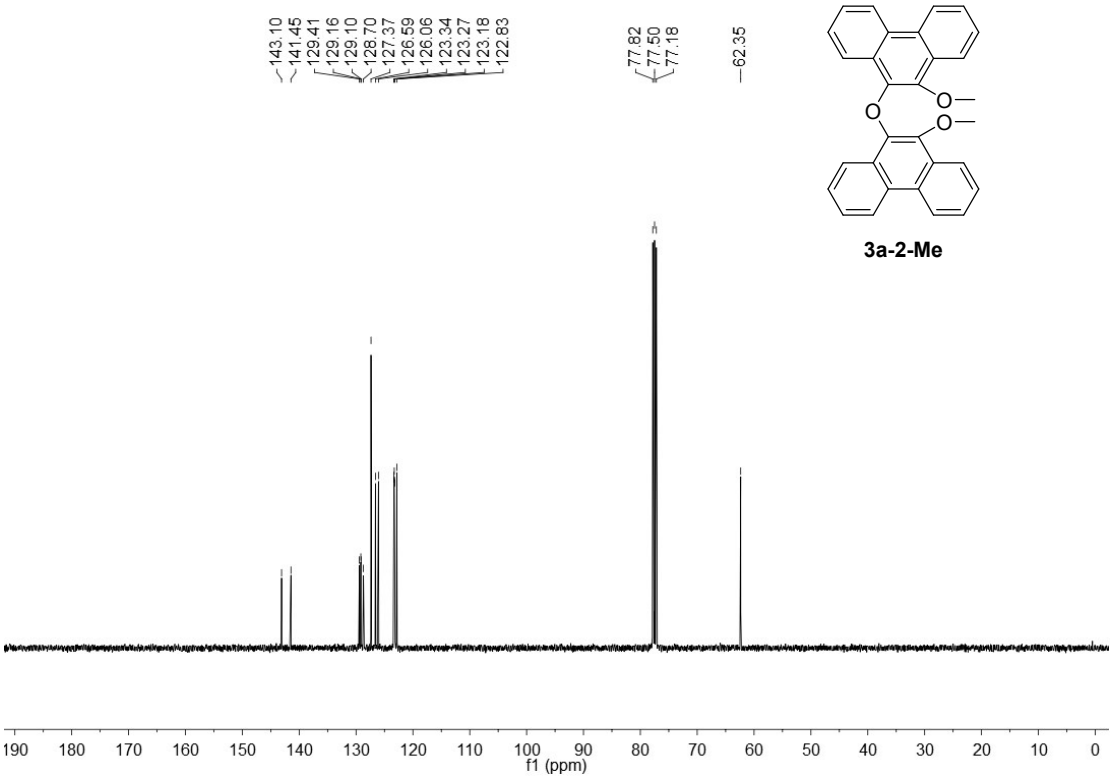
137.20
135.97
133.55
132.75
132.07
129.96
129.50
129.36
128.90
128.47
128.02
127.42
125.35
124.94
124.10
123.77
121.51
120.92
108.61
77.82
77.50
77.18
3a
f1 (ppm)
f1 (ppm)


8.733
8.730
8.709
8.703
8.684
8.519
8.502
8.022
8.018
8.006
8.004
8.001
7.675
7.672
7.656
7.652
7.633
7.630
7.616
7.613
7.599
7.595
7.585
7.580
7.575
7.566
7.562
3.516
0.000
4.02
2.01
2.00
8.19
6.00
f1 (ppm)

3a-2-Me


143.10
141.45
129.41
129.16
129.10
128.70
127.37
126.59
126.06
123.34
123.27
123.18
122.83
77.82
77.50
77.18
62.35
f1 (ppm)

3a-2-Me

Referece:

[1] V. H. Bindu, S. P. Parvathaneni, V. J. Rao, *Catal. Lett.* **2017**, *147*, 1434-1440.

[2] K. Nakazono, C. Yamashita, T. Ogawa, H. Iguchi, T. Takata, *Polym. J.* **2015**, *47*, 355-361.

[3] H. Li, R. Y. Zhu, W. J. Shi, K. H. He, Z. J. Shi, *Org. Lett.* **2012**, *14*, 4850-4853.

[4] L. Sicard, C. Quinton, J. D. Peltier, D. Tondelier, B. Geffroy, U. Biapo, R. Metivier, O. Jeannin, J. Rault-Berthelot, C. Poriel, *Chem. Eur. J.* **2017**, *23*, 7719-7727.