Electronic Supplementary Information

Facile synthesis of acyl fluorides through deoxyfluorination of carboxylic acids

Mengjie Cen, Xi Yang, Shanshan Zhang, Liguang Gan, Long Liu*, and Tieqiao Chen*

Key Laboratory of Ministry of Education for Advanced Materials in Tropical Island Resources, Hainan Provincial Key Lab of Fine Chem, Hainan Provincial Fine Chemical Engineering Research Center, Hainan University, Haikou, 570228, China.

E-mail: hainanliulong@hainanu.edu.cn; chentieqiao@hnu.edu.cn

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1. General Information

The reactions were carried out in Schlenk tubes under N₂ atmosphere. For reactions that required heating, a heating mantle was used as the heat source. All solvents and reagents were purchased from Tansoole, Meryer, Heowns, Energy Chemical, Alfa Aesar, and Aladdin. Solvents were purified according to standard operation procedures and reagents were used as received unless otherwise noted. The absorbent materials like KF are stored in the glove box after purchase without any special treatment. Column chromatography was performed using Silica Gel 60 (300-400 mesh). The reactions were monitored by GC and GC-MS; GC-MS results were recorded on a GC-MS QP2010 instrument, and GC analysis was performed on a GC 2014 instrument. The ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a Bruker ADVANCE III spectrometer at 400, 100, and 376 MHz. HRMS were recorded on a LCMS-IT-TOF instrument by the ESI or APCI technique. Infrared spectrum was recorded on a Nicolet 6700 spectrometer.

2. Optimization of Reaction Conditions

Table S1 Reaction Optimization

entry	base		anhydride		F-		solvent	Temp.	yield
1	NaHCO ₃	1 eq.	TFAA	1.5 eq.	KF	2.0 eq.	DME	100 °C	26%
2	KHCO ₃	1 eq.	TFAA	1.5 eq.	KF	2.0 eq.	DME	100 °C	22%
3	K_2CO_3	1 eq.	TFAA	1.5 eq.	KF	2.0 eq.	DME	100 °C	22%
4	Et_3N	1 eq.	TFAA	1.5 eq.	KF	2.0 eq.	DME	100 °C	84%
5	DPIEA	1 eq.	TFAA	1.5 eq.	KF	2.0 eq.	DME	100 °C	23%
6	DBU	1 eq.	TFAA	1.5 eq.	KF	2.0 eq.	DME	100 °C	20%
7	DMAP	1 eq.	TFAA	1.5 eq.	KF	2.0 eq.	DME	100 °C	44%
8	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	DME	100 °C	86%
9	Et_3N	none	TFAA	1.5 eq.	KF	2.0 eq.	DME	100 °C	35%
10	Et_3N	0.5 eq	Ac2O	1.5 eq.	KF	2.0 eq.	DME	100 °C	Trace
11	Et_3N	0.5 eq	Piv2O	1.5 eq.	KF	2.0 eq.	DME	100 °C	42%
12	Et_3N	0.5 eq	Boc2O	1.5 eq.	KF	2.0 eq.	DME	100 °C	4%
13	Et_3N	0.5 eq	TFAA	1.2 eq.	KF	2.0 eq.	DME	100 °C	67%
14	Et_3N	0.5 eq	TFAA	1.5 eq.	LiF	2.0 eq.	DME	100 °C	Trace
15	Et_3N	0.5 eq	TFAA	1.5 eq.	NaF	2.0 eq.	DME	100 °C	40%
16	Et_3N	0.5 eq	TFAA	1.5 eq.	CsF	2.0 eq.	DME	100 °C	57%
17	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	1.5 eq.	DME	100 °C	63%
18	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.5 eq.	DME	100 °C	72%
19	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	THF	100 °C	62%
20	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	dioxane	100 °C	53%
21	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	DMF	100 °C	35%
22	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	Су	100 °C	50%
23	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	toluene	100 °C	30%
24	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	none	100 °C	44%
25	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	DME	RT	30%
26	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	DME	40 °C	32%
27	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	DME	60 °C	43%
28	Et_3N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	DME	80 °C	52%
29	Et ₃ N	0.5 eq	TFAA	1.5 eq.	KF	2.0 eq.	DME	120 °C	75%

3. Characterization Data for the Products

203.0519.

2-Naphthoyl fluoride (2a) ¹. The title compound was prepared according to procedure I and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 76% yield (26.5 mg). $V_{(CO)} = 1705 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 8.64 (s, 1H), 8.01–7.91 (m, 4H), 7.68 (t, J = 7.1 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.7 (d, J = 343.5 Hz), 136.5 (s), 134.1 (d, J = 3.3 Hz), 132.3 (s), 129.7 (s), 129.7 (s), 129.1 (s), 128.0 (s), 127.4 (s), 125.6 (d, J = 4.2 Hz), 122.0 (d, J = 60.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ 18.08. 6-Methoxy-2-naphthoyl fluoride (2b). The title compound was prepared according to procedure I and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 69% yield (28.0 mg). mp 109.7–113.0 °C. $V_{(CO)} = 1796 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 8.58 (s, 1H), 8.00 (dd, J = 8.6, 1.2 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 8.6 Hz, 1H), 7.30–7.25 (m, 1H), 7.22 (d, J = 2.4 Hz, 1H), 4.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.7 (s), 157.9 (d, J = 341.8 Hz), 138.4 (s), 133.8 (d, J = 3.3 Hz), 131.3 (s), 127.8 (s), 127.7 (s), 126.5 (d, J = 4.1 Hz), 120.4 (s), 119.6 (d, J = 60.7 Hz), 105.9 (s), 55.6 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 16.7 (s). HRMS (ESI, negative mode): $C_{12}N_9FO$, for [M - H]-, calculated 203.0514, found

6-Bromo-2-naphthoyl fluoride (2c). The title compound was prepared according to procedure I and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 61% yield (30.9 mg). mp 160.1–162.0 °C. $V_{(CO)} = 1726$ cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.60 (s, 1H), 8.10 (d, J = 1.6 Hz, 1H), 8.03 (dd, J = 8.6, 1.2 Hz, 1H), 7.87 (d, J = 2.7 Hz, 1H), 7.85 (d, J = 2.7 Hz, 1H), 7.69 (dd, J = 8.8, 1.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.3 (d, J = 343.8 Hz), 137.3 (s), 133.8 (d, J = 3.2 Hz), 131.1 (s), 131.0 (s), 130.7 (s), 130.2 (s), 128.2 (s), 126.8 (d, J = 4.1 Hz), 124.4 (s), 122.5 (d, J = 61.2 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ 18.3 (s). HRMS (APCI, negative mode): $C_{11}H_6$ BrFO for [M - H]⁻, calculated 250.9513, found 250.9511.

1-Naphthoyl fluoride (2*d*)². The title compound was prepared according to procedure I and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 60% yield (20.9 mg). $V_{(CO)} = 1811$ cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 9.07 (d, J = 8.7 Hz, 1H), 8.41 (dd, J = 7.4, 1.2 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.80–7.75 (m, 1H), 7.70–7.65 (m, 1H), 7.65–7.60 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.5 (d, J = 344.6 Hz), 136.7 (s), 133.9 (d, J = 4.0 Hz), 133.7 (d, J = 1.7 Hz), 132.2 (d, J = 7.2 Hz), 129.3 (s), 129.0

(s), 127.0 (s), 125.2 (s), 124.5 (s), 120.4 (d, J = 55.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ 30.4.

4-methyl-1-naphthoyl fluoride(2e) ¹. The title compound was prepared according to procedure I and purified by column chromatography on silica gel and eluted with petroleum ether to afford a yellow solid in 89% yield (33.5 mg). $V_{(CO)} = 1793$ cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 9.08 (d, J = 8.6 Hz, 1H), 8.27 (d, J = 7.5 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.74–7.70 (m, 1H), 7.66–7.62 (m, 1H), 7.43 (d, J = 7.5 Hz, 1H), 2.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.5 (d, J = 340.8 Hz), 144.4 (s), 133.6 (d, J = 2.1 Hz), 132.9 (d, J = 4.1 Hz), 132.2 (d, J = 7.4 Hz), 128.7 (s), 126.8 (s), 125.7 (s), 125.6 (s), 124.8 (s), 118.5 (d, J = 55.6 Hz), 20.5 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 28.7 (s).

Anthracene-9-carbonyl fluoride (2f) ³. The title compound was prepared according to procedure I and purified by column chromatography on silica gel and eluted with petroleum ether to afford a yellow solid in 87% yield (39.0 mg). $V_{(CO)} = 1830 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 8.70 (s, 1H), 8.41–8.28 (m, 2H), 8.10 (d, J = 8.5 Hz, 2H), 7.72–7.62 (m, 2H), 7.62–7.52 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 158.5 (d, J = 353.8 Hz), 133.2 (s), 130.8 (s), 130.2 (s), 129.0 (s), 128.6 (s), 125.9 (s), 124.7 (d, J = 3.5 Hz), 120.1 (d, J = 54.8 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ 59.64 (s).

[1,1'-Biphenyl]-4-carbonyl fluoride (2g) ⁴. The title compound was prepared according to procedure II (DMCHA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 84% yield (33.6 mg). $V_{(CO)} = 1709 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 7.5 Hz, 2H), 7.68–7.64 (m, 2H), 7.55–7.50 (m, 2H), 7.49–7.45 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.4 (d, J = 343.2 Hz), 147.1 (s), 138.2 (s), 131.0 (d, J = 3.9 Hz), 128.1 (s), 127.8 (s), 126.6 (s), 126.3 (s), 122.5 (d, J = 61.2 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ 18.1 (s).

[1,1'-Biphenyl]-3-carbonyl fluoride (2h) ³. The title compound was prepared according to procedure II (DMCHA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 67% yield (18.9 mg). $V_{(CO)} = 1815$ cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (dd, $J_I = J_2 = 1.7$ Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.83 (ddd, J = 7.8, 1.8, 1.2 Hz, 1H), 7.54–7.48 (m, 3H), 7.44–7.37 (m, 2H), 7.35–7.31 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.4 (d, J = 344.8 Hz), 142.4 (s), 139.2 (s), 134.9 (s), 130.1 (d, J = 4.2 Hz), 130.0 (s), 129.6 (s), 129.1 (s), 128.3 (s), 127.2 (s), 125.5 (d, J = 60.5 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ 18.7

(s).

[1,1'-Biphenyl]-2-carbonyl fluoride (2i)⁴. The title compound was prepared according to procedure II (DMCHA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a transparent liquid in 75% yield (30.2 mg). $V_{(CO)} = 1802 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 7.9 Hz, 1H), 7.67–7.63 (m, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.45–7.36 (m, 4H), 7.32–7.31 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 157.6 (d, J = 348.1 Hz), 145.5 (d, J = 2.5 Hz), 140.2 (s), 134.0 (s), 132.2 (d, J = 2.8 Hz), 131.8 (d, J = 2.4 Hz), 128.5 (s), 128.3 (s), 128.0 (s), 127.7 (s), 124.2 (d, J = 56.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ 35.1 (s).

4-Cyclohexylbenzoyl fluoride (2j) ⁴. The title compound was prepared according to procedure II (DMCHA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 69% yield (28.4 mg). $V_{(CO)} = 1821 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 7.5 Hz, 2H), 2.66–2.54 (m, 1H), 1.89–1.86 (m, 4H), 1.81–1.71 (m, 1H), 1.47–1.35 (m, 4H), 1.29–1.26 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.6 (d, J = 344.4 Hz), 156.4 (s), 131.7 (d, J = 4.1 Hz), 127.6 (s), 122.4 (d, J = 60.9 Hz), 44.9 (s), 34.0 (s), 26.6 (s), 26.0 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 17.5 (s).

4-Phenoxybenzoyl fluoride(2k) ⁵. The title compound was prepared according to procedure II (DMCHA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 78% yield (33.7mg). $V_{(CO)} = 1695 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 7.94–7.87 (m, 2H), 7.38–7.30 (m, 2H), 7.17 (ddd, J = 9.7, 5.5, 4.2 Hz, 1H), 7.03–6.98 (m, 2H), 6.94 (dd, J = 8.9, 1.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) 164.1 (s) , 158.7 (d, J = 342.4 Hz), 154.7 (s), 133.8 (d, J = 3.9 Hz), 130.3 (s), 125.3 (s), 120.6 (s), 118.5 (d, J = 62.1 Hz), 117.4 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 17.0 (s).

4-(Dimethylamino)benzoyl fluoride (2l) ¹. The title compound was prepared according to procedure II (DMCHA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 49% yield (16.4 mg). $V_{(CO)} = 1786$ cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 9.0 Hz, 2H), 6.59 (d, J = 8.0 Hz, 2H), 3.02 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 158.2 (d, J = 334.9 Hz), 154.6 (s), 133.5 (d, J = 4.3 Hz), 111.0 (d, J = 1.0 Hz), 110.3 (d, J = 61.3 Hz), 40.0 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 12.4 (s).

4-Iodobenzoyl fluoride (2m) ⁶. The title compound was prepared according to procedure II (DMCHA) and purified by column chromatography on silica gel and eluted with petroleum ether to

afford a white solid in 50% yield (25.0 mg). $V_{(CO)} = 1821$ cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.90– δ 7.82 (m, 2H), 7.72–7.63 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 157.1 (d, J = 343.9 Hz), 138.6 (s), 132.5 (d, J = 3.7 Hz), 124.4 (d, J = 62.4 Hz), 104.0 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 18.3 (s).

2-Iodobenzoyl fluoride (2n) ¹. The title compound was prepared according to procedure II (DMCHA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 48% yield (24.0 mg). $V_{(CO)} = 1819 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.0 Hz, 1H), 7.96 (dd, J = 7.9, 1.6 Hz, 1H), 7.44 (ddd, J = 7.9, 7.9, 1.0 Hz, 1H), 7.23 (ddd, J = 7.7, 7.7, 1.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 155.3 (d, J = 345.1 Hz), 142.7 (d, J = 3.7 Hz), 135.2 (s), 133.4 (d, J = 1.8 Hz), 128.4 (s), 128.4 (d, J = 61 Hz), 97.1 (d, J = 5.9 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ 28.7 (s).

4-Nitrobenzoyl fluoride (2o)². The title compound was prepared according to procedure II (BDMA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 71% yield (24.0 mg). $V_{(CO)} = 1830 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, J = 8.0 Hz, 2H), 8.28 (d, J = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 155.5 (d, J = 346.4 Hz), 151.8 (s), 132.6 (d, J = 3.6 Hz), 130.3 (d, J = 63.3 Hz), 124.2 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 21.34 (s).

4-Benzoylbenzoyl fluoride (2p) ⁷. The title compound was prepared according to procedure II (DMCHA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 62% yield (28.3 mg). $V_{(CO)} = 1827$ cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, J = 8.3 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.84–7.77 (m, 2H), 7.69–7.60 (m, 1H), 7.56–7.48 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 195.4 (s), 156.6 (d, J = 345.4 Hz), 143.5 (s), 136.4 (s), 133.4 (s), 131.4 (s), 130.1 (s), 128.6 (s), 127.8 (d, J = 61.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ 19.9 (s).

Benzofuran-2-carbonyl fluoride (2q)⁷. The title compound was prepared according to procedure II (DMCHA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 50% yield (16.4 mg). $V_{(CO)} = 1732$ cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.77–7.75 (m, 2H), 7.63 (d, J = 8.5 Hz, 1H), 7.57 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 7.38 (dd, $J_1 = J_2 = 8.0$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.9 (d, J = 2.3 Hz), 149.4 (d, J = 329.9 Hz), 139.8 (d, J = 89.5 Hz), 129.5 (s), 126.3 (s), 124.6 (s), 123.6 (s), 119.4 (s), 112.7 (s); ¹⁹F NMR (376 MHz, CDCl₃)

 δ 17.4 (s).

Benzo[b]thiophene-2-carbonyl fluoride (2r) ². The title compound was prepared according to procedure II (DMCHA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 64% yield (23.0 mg). $V_{(CO)} = 1670$ cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H), 8.02–7.92 (m, 2H), 7.63–7.57 (m, 1H), 7.50–7.50 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 153.2 (d, J = 335.3 Hz), 143.7 (s), 138.2 (s), 135.2 (d, J = 1.4 Hz), 128.5 (s), 126.5 (s), 126.4 (s), 125.7 (s), 123.0 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 25.1 (s). HRMS (ESI, positive mode): $C_{12}H_{27}FO$ for [M + H]⁺, calculated 303.2119, found 303.2120.

(E)-3-(p-tolyl)acryloyl fluoride(2s) ⁸. The title compound was prepared according to procedure II (BDMA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 50% yield (16.4 mg). $V_{(CO)} = 1694 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 15.9 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.31 (dd, J = 15.9 7.4 Hz, 1H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.3 (d, J = 335.6 Hz), 151.4 (d, J = 6.0 Hz), 142.6 (s), 130.4 (s), 129.9 (s), 128.7 (s), 110.8 (d, J = 69.6 Hz), 21.6 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 25.0 (s).

(E)-3-(4-methoxyphenyl)acryloyl fluoride(2t) ⁸. The title compound was prepared according to procedure II (BDMA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 85% yield (30.0 mg). $V_{(CO)} = 1690 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 15.9 Hz, 1H), 7.56–7.46 (m, 2H), 7.01–6.87 (m, 2H), 6.22 (dd, J = 15.9, 7.3 Hz, 1H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.6 (s), 157.6 (d, J = 334.7 Hz), 151.1 (d, J = 6.3 Hz), 130.6 (s), 125.9 (s), 114.6 (s), 109.1 (d, J = 66.7 Hz), 55.5 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 24.4 (s).

(E)-3-(4-bromophenyl)acryloyl fluoride (2u) 8 . The title compound was prepared according to procedure II (BDMA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 65% yield (29.4 mg). $V_{(CO)} = 1790 \text{ cm}^{-1}$. ^1H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 16.0 Hz, 1H), 7.62–7.52 (m, 2H), 7.45–7.38 (m, 2H), 6.37 (dd, J = 16.0, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl₃) δ 156.8 (d, J = 336.7 Hz), 149.9 (d, J = 6.0 Hz), 132.5 (s), 132.0 (s), 130.0 (s), 126.4 (s), 112.8 (d, J = 67.3 Hz); ^{19}F NMR (376 MHz, CDCl₃) δ 26.0 (s).

(2E,4E,6E,8E)-3,7-dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,4,6,8-tetraenoyl fluoride (2v). 9 The title compound was prepared according to procedure I and purified by column

chromatography on silica gel and eluted with petroleum ether to afford white oil in 72% yield (43.5 mg). $V_{(CO)} = 1848 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 7.09 (dd, J = 15.0, 11.5 Hz, 1H), 6.31–6.24 (m, 2H), 6.11 (s, 1H), 6.08 (d, J = 4.4 Hz, 1H), 5.62 (s, 1H), 2.32 (s, 3H), 1.95 (s, 5H), 1.65 (s, 3H), 1.59–1.51 (m, 2H), 1.44–1.35 (m, 2H), 0.96 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 161.1 (d, J = 17.9 Hz), δ 156.9 (d, J = 331.3 Hz), 142.3 (s), 137.6 (s), 137.0 (s), 134.2 (s), 133.4 (d, J = 3.3 Hz), 130.7 (s), 130.2 (s), 129.0 (s), 111.5 (d, J = 74.3 Hz), 39 .6 (s), 34.3 (s), 33.2 (s), 29.7 (s), 28.9 (s), 21.8 (s), 19.2 (s), 14.6 (s), 13.1 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 42.2 (s).

Benzo[d][1,3]dioxole-5-carbonyl fluoride (2w) ². The title compound was prepared according to procedure I and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 78% yield (26.2 mg). $V_{(CO)} = 1730 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (dd, J = 8.2, 1.7 Hz, 1H), 7.42 (d, J = 1.7 Hz, 1H), 6.91 (dd, J = 8.2, 0.9 Hz, 1H), 6.11 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 156.9 (d, J = 338.1 Hz), 153.7 (s), 148.3 (s), δ 128.3 (d, J = 4.1 Hz), 118.4 (d, J = 62.4 Hz), 110.7 (d, J = 4.1 Hz), 108.6 (s), 102.4 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ 16.4 (s).

2-(Naphthalen-2-yl)acetyl fluoride (2x)². The title compound was prepared according to procedure II (BDMA) and purified by column chromatography on silica gel and eluted with petroleum ether to afford a white solid in 32% yield (12.0 mg). $V_{(CO)} = 1719 \text{ cm}^{-1}$. ¹H NMR (400 MHz, CDCl₃) δ 7.74–7.70 (m, 3H), 7.65 (s, 1H), 7.42–7.35 (m, 2H), 7.32 (dd, J = 8.4, 1.4 Hz, 1H), 3.73 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 161.3 (d, J = 377.9 Hz), 133.1 (d, J = 58.4 Hz), 128.8 (s), 128.5 (s), 128.1 (d, J = 2.4 Hz), 127.8 (s), 126.8 (s), 126.6 (s), 126.4 (s), 39.2 (d, J = 54.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ 45.2 (s).

morpholino(naphthalen-2-yl)methanone (3). ¹H NMR (400 MHz, CDCl₃) δ 7.83–7.76 (m, 4H), 7.49–7.45 (m, 2H), 7.41 (dd, J = 9.6, 1.6 Hz, 1H), 3.57 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 169.4 (s), 132.7 (s), 131.6 (s), 132.5 (s), 127.4 (s), 127.3 (s), 126.8 (s), 126.2 (s), 126.0 (s), 125.8 (s), 123.2 (s), 76.5 (s), 76.1 (s), 75.8 (s).

S-(pyridin-4-yl) naphthalene-2-carbothioate (4). ¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, J = 6.0 Hz, 2H), 8.51 (s, 1H), 7.91 (dd, J = 8.8, 2.4 Hz, 2H), 7.83 (m, 2H), 7.60–7.48 (m, 2H), 7.44 (dd, J = 4.4, 2.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 187.5 (s), 145.0 (s), 138.9 (s), 136.1 (s), 133.4 (s), 132.4 (s), 129.7 (s), 129.4 (s), 129.1 (s), 128.9 (s), 128.6 (s), 127.9 (s), 127.3 (s), 123.1 (s). naphthalen-2-yl(perfluorophenyl)methanone (5). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1H), 7.91

(dd, J = 8.8, 2.0 Hz, 1H), 7.87–7.78 (m, 3H), 7.56 (m, 1H), 7.51–7.44 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 184.1 (s), 144. 2–143.9 (m), 143.9–142.6 (m), 141.7–141.5 (m), 140.3–140.0 (m), 138.1–137.8 (m), 135.4 (s), 132.4 (s), 131.9 (s), 131.3 (s), 128.8 (s), 128.7 (s), 128.2 (s), 126.9 (s), 126.3 (s), 122.7 (s), 113.3–112.9 (m).

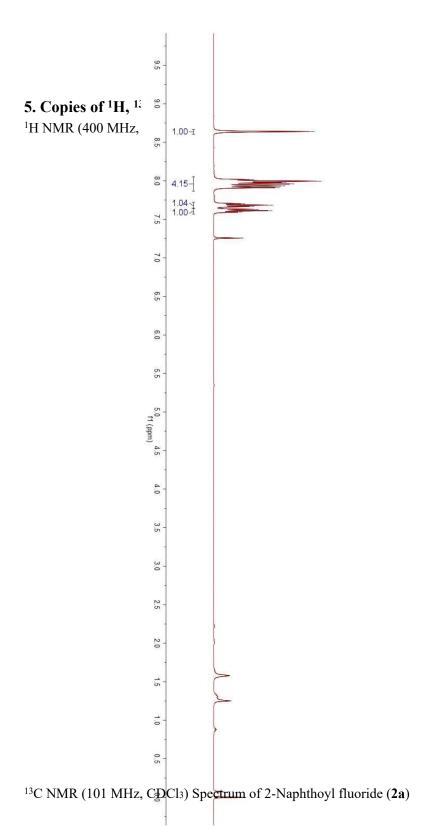
2-(naphthalen-2-yl)benzo[d]oxazole (6). ¹H NMR (400 MHz, CDCl₃) δ 8.70 (s, 1H), 8.23 (dd, J = 8.6, 1.6 Hz, 1H), 7.89 (dd, J = 8.8, 5.3 Hz, 2H), 7.84–7.77 (m, 1H), 7.73 (dd, J = 6.2, 3.0 Hz, 1H), 7.58–7.43 (m, 3H), 7.34–7.24 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 163.2 (s), 150.9 (s), 142.2 (s), 134.8 (s), 133.0 (s), 128.9 (s), 128.8 (s), 128.2 (s), 127.9 (s), 127.9 (s), 126.9 (s), 125.2 (s), 124.7 (s), 124.4 (s), 123.9 (s), 120.04 (s), 110.64 (s).

triisopropyl(naphthalen-2-ylethynyl)silane (7). ¹H NMR (400 MHz, CDCl₃) δ 7.9 (s, 1H), 7.70–7.65 (m, 3H), 7.43 (dd, J = 8.4, 1.2 Hz, 1H), 7.40–7.37 (m, 2H), 1.08 (s, 18H), 1.00 (s, 3H); ¹³CNMR (100 MHz, CDCl₃) δ 132.9 (s), 132.8 (s), 131.9 (s), 128.9 (s), 127.9 (s), 127.8 (s), 126.7 (s), 126.5 (s), 120.9 (s), 107.5 (s), 90.9 (s), 18.6 (s), 11.4 (s).

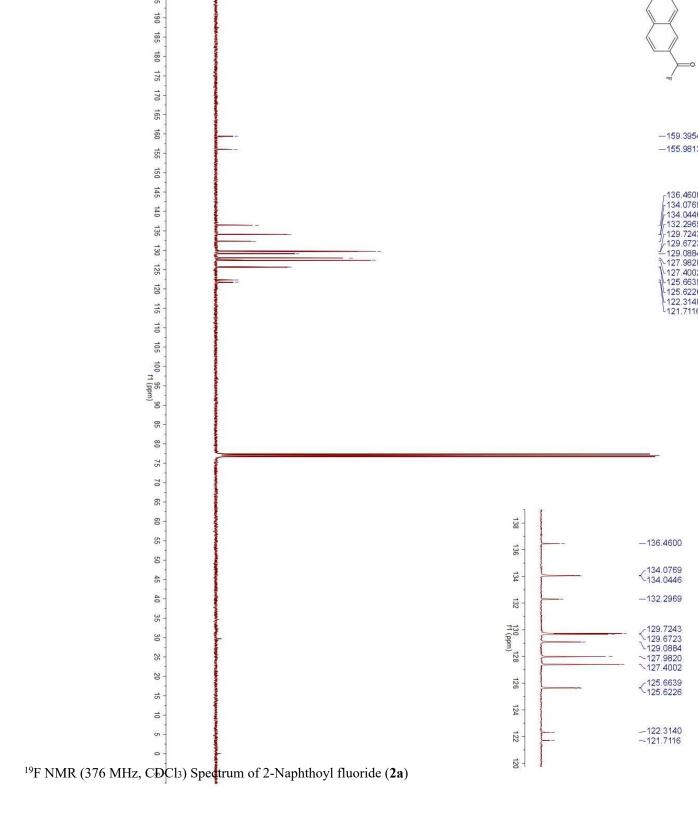
cyano(phenyl)methyl-2-naphthoate (8). ¹H NMR (400 MHz, CDCl₃) δ 8.54 (s, 1H), 7.95 (dd, J = 8.4, 1.6 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.79 (dd, J = 8.8, 4.4 Hz, 2H), 7.60–7.55 (m, 2H), 7.55–7.50 (m, 1H), 7.49–7.44 (m, 1H), 7.40 (m, 3H), 6.66 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 164.9 (s), 135.9 (s), 132.4 (s), 132.1 (s), 131.9 (s), 130.5 (s), 129.5 (s), 129.4 (s), 128.9 (s), 128.6 (s), 127.9 (s), 127.9 (s), 127.1 (s), 125.3 (s), 125.1 (s), 116.3 (s), 63.5 (s).

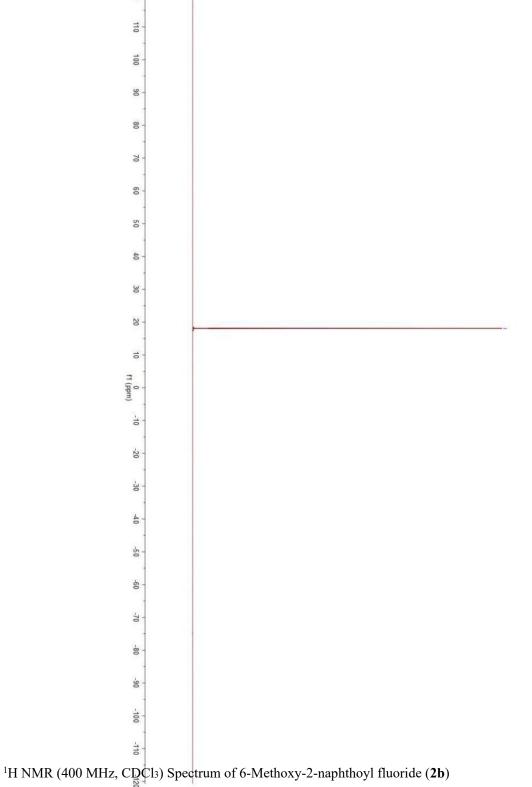
4 References

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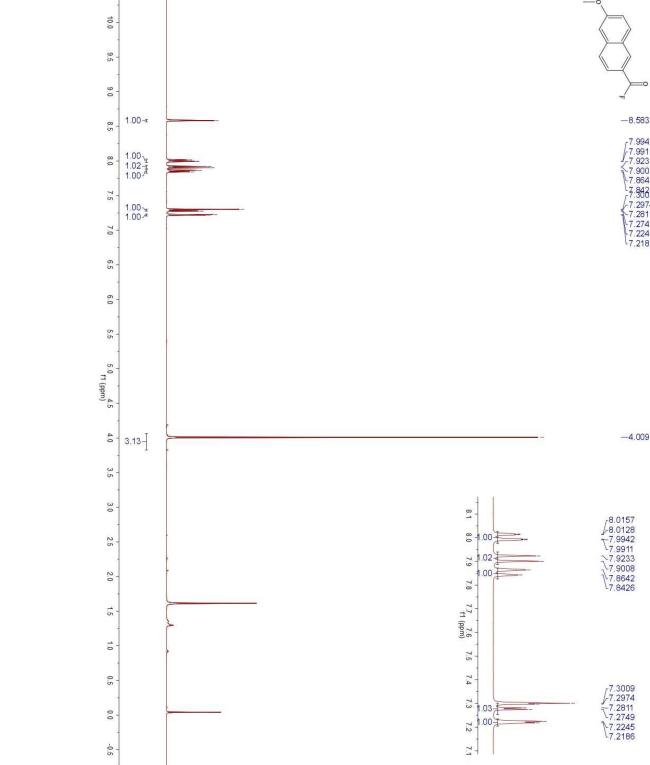


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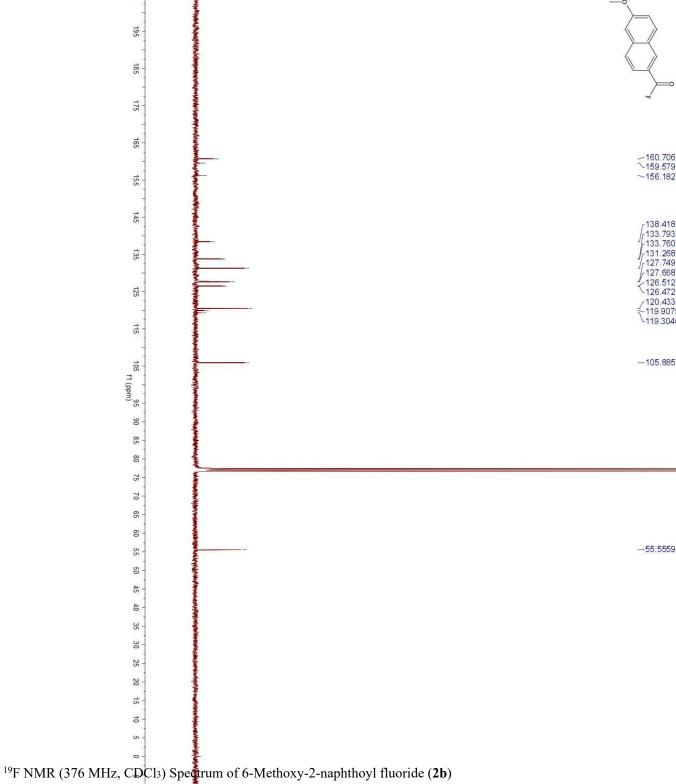


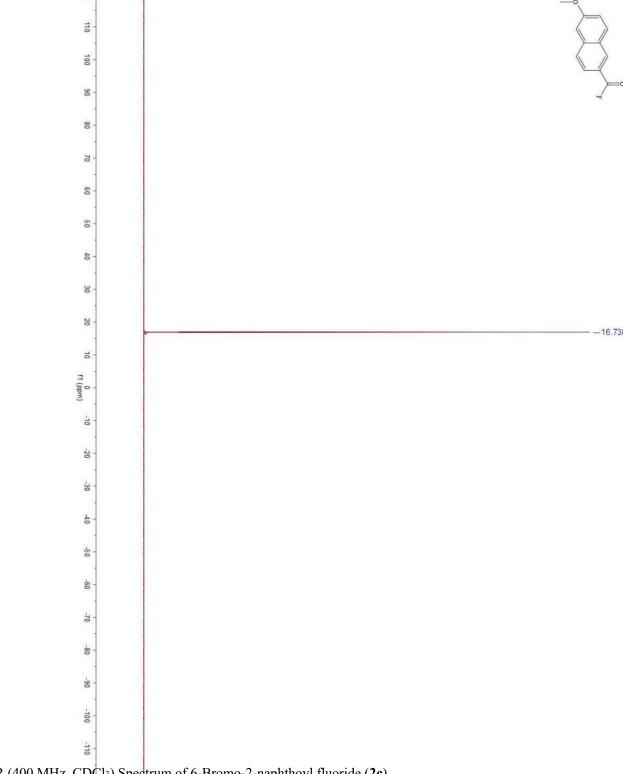


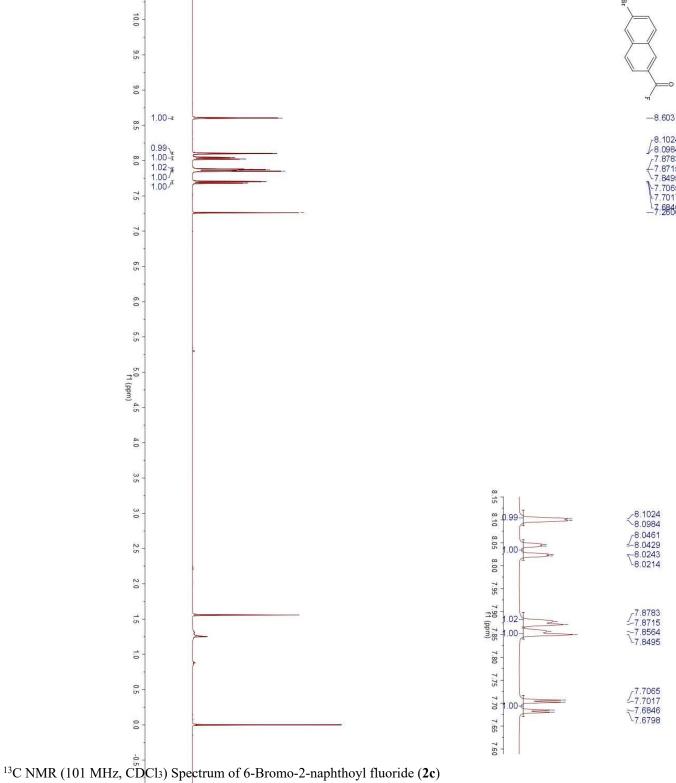
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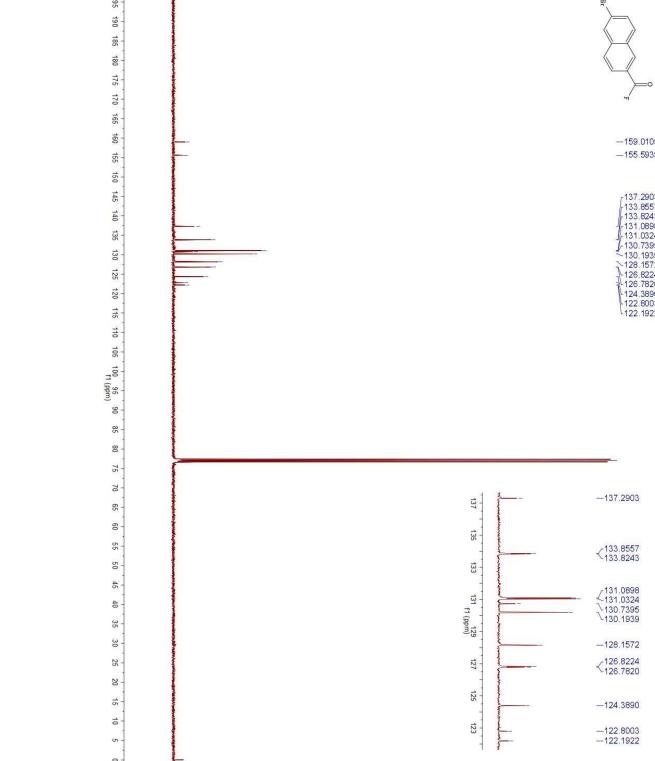


¹³C NMR (101 MHz, CDCl₃) Spectrum of 6-Methoxy-2-naphthoyl fluoride (2b)

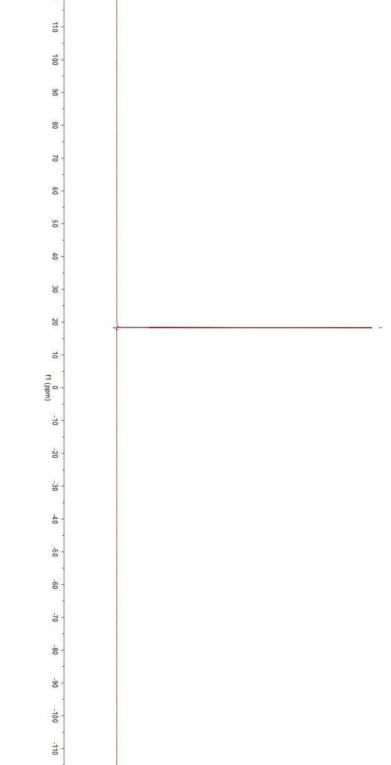




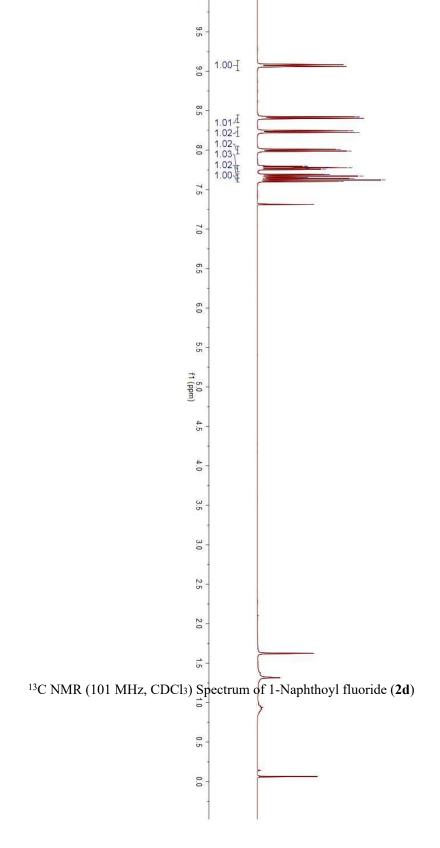


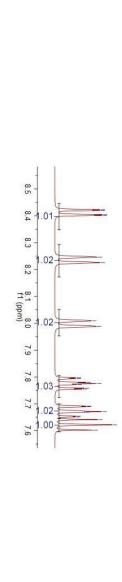


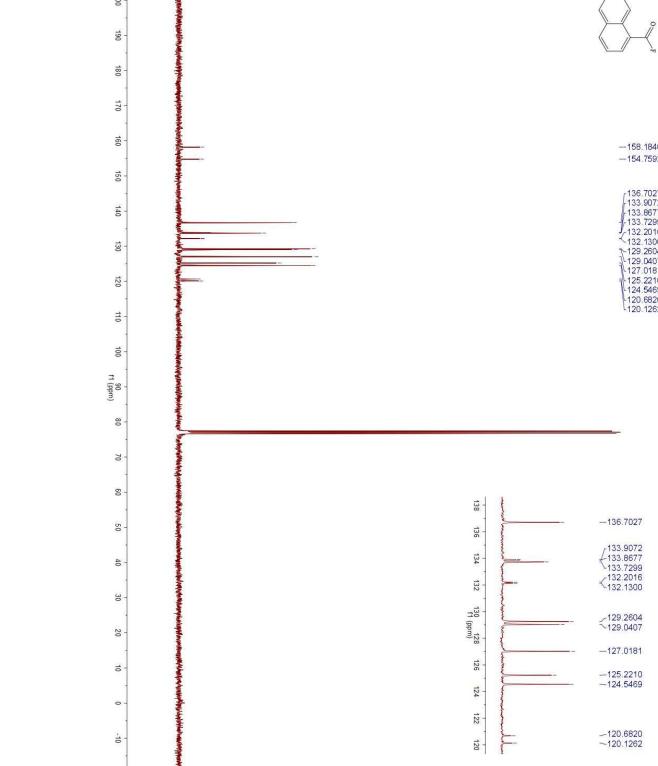
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of 6-Bromo-2-naphthoyl fluoride (2c)



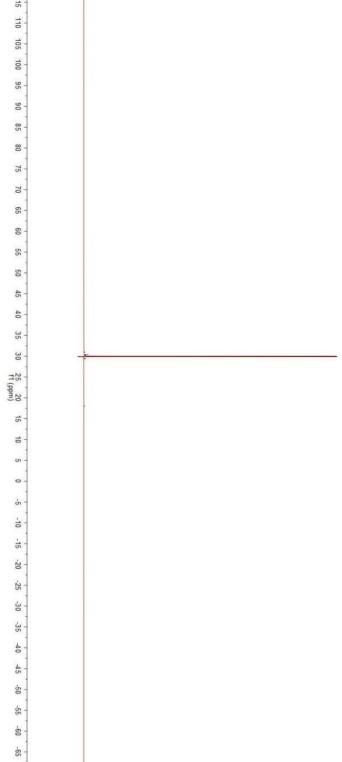
¹H NMR (400 MHz, CDCl₃) Spectrum of 1-Naphthoyl fluoride (**2d**)





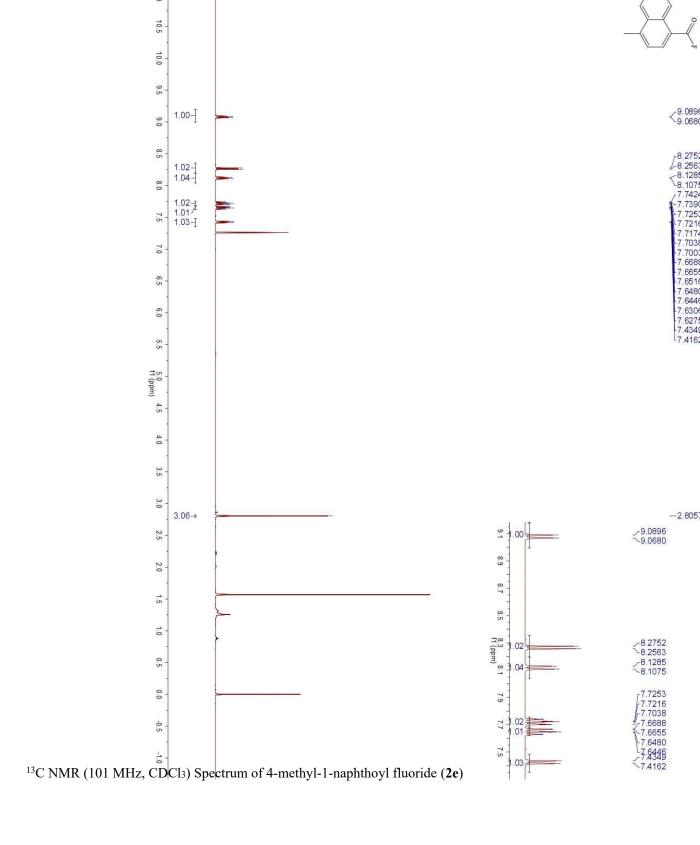


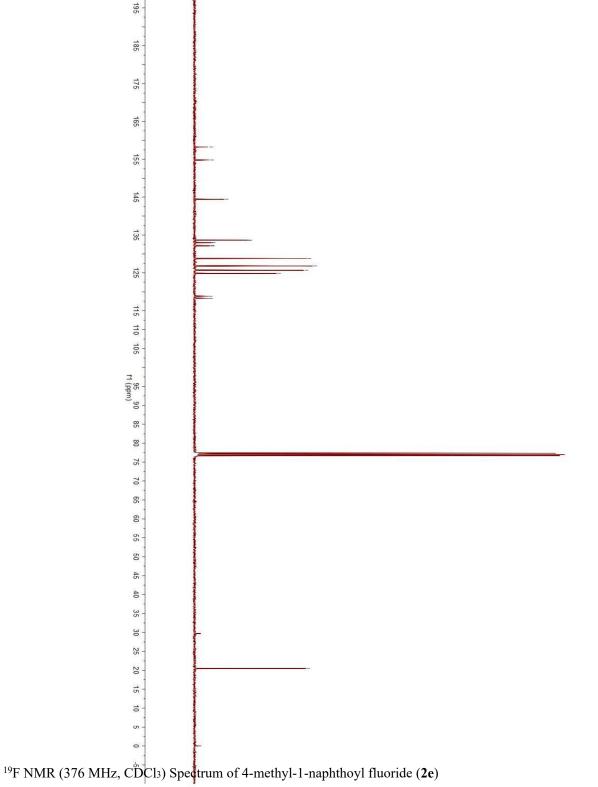
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of 1-Naphthoyl fluoride (2d)



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¹H NMR (400 MHz, CDCl₃) Spectrum of 4-methyl-1-naphthoyl fluoride (2e)





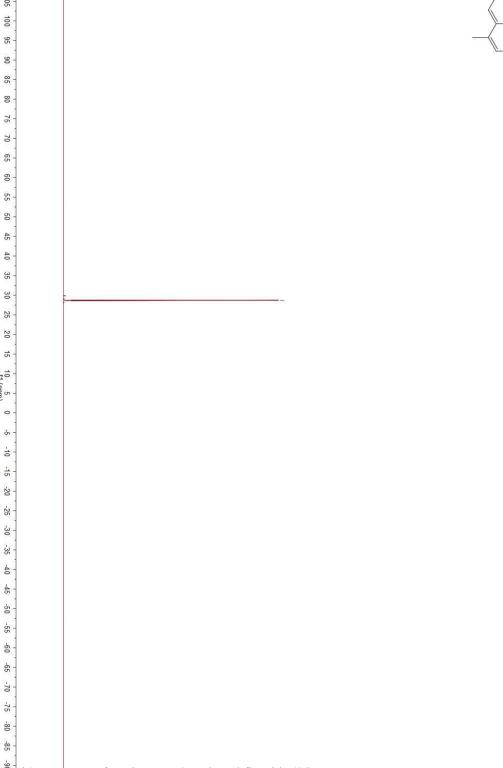
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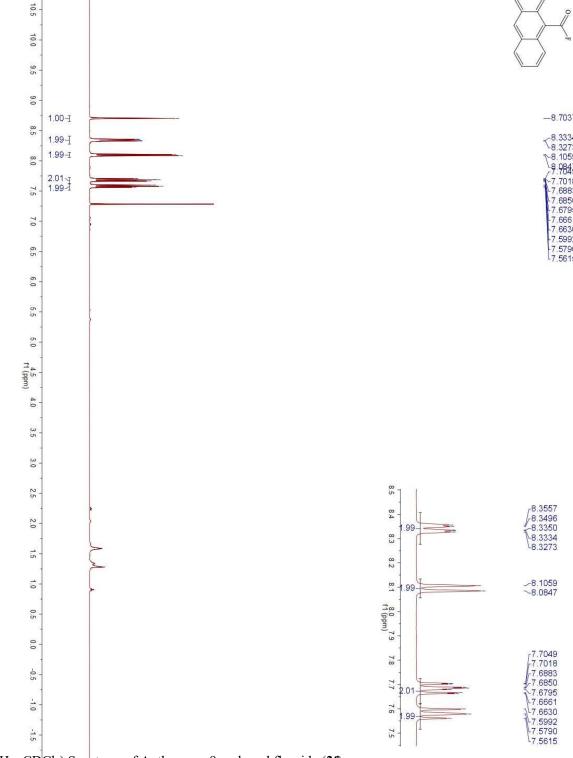
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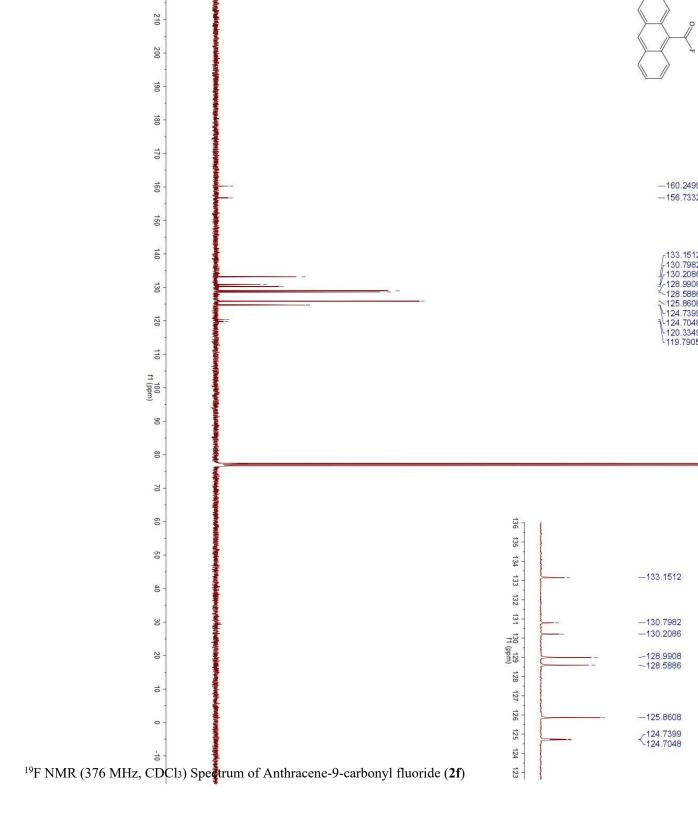


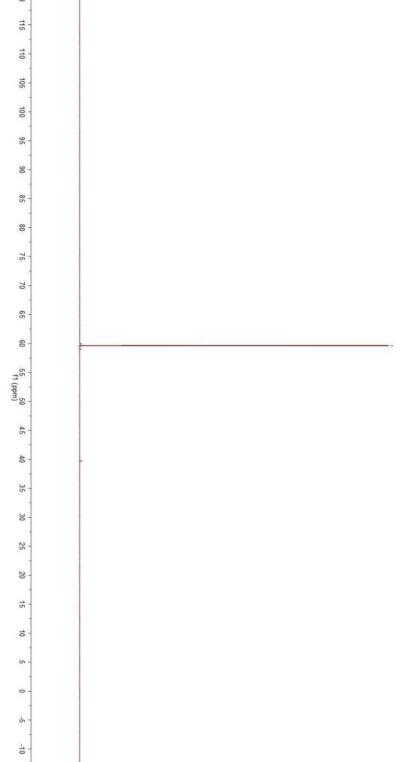
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¹H NMR (400 MHz, CDCl₃) Spectrum of Anthracene-9-carbonyl fluoride (2f)

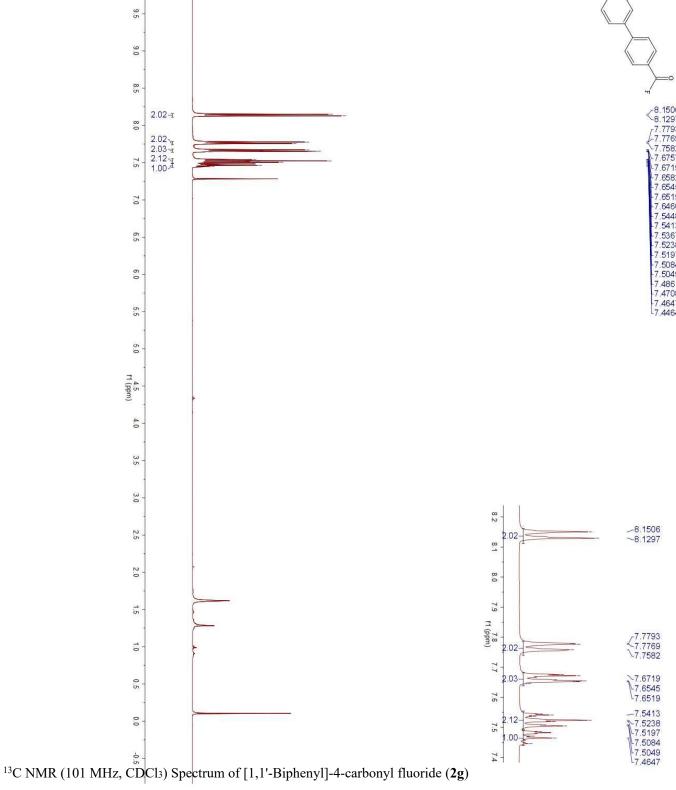


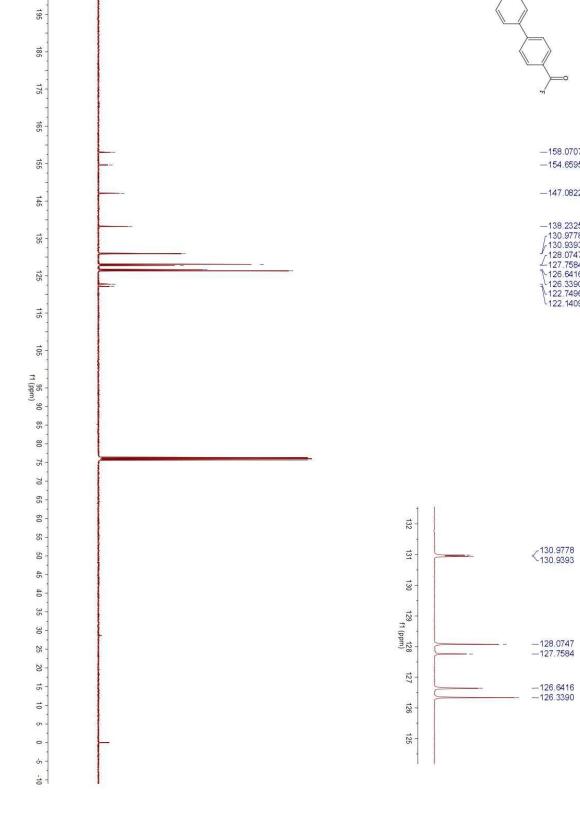
¹³C NMR (101 MHz, CDCl₃) Spectrum of Anthracene-9-carbonyl fluoride (2f)

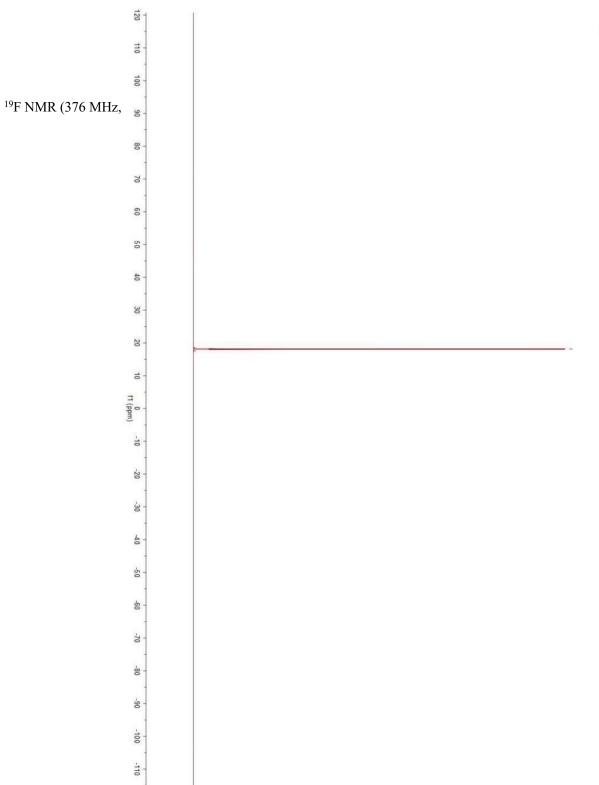


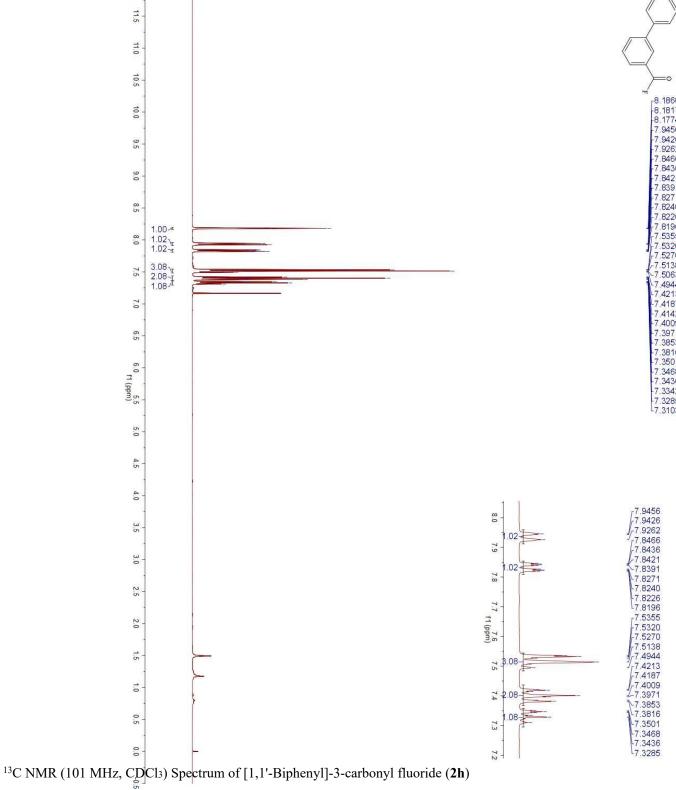


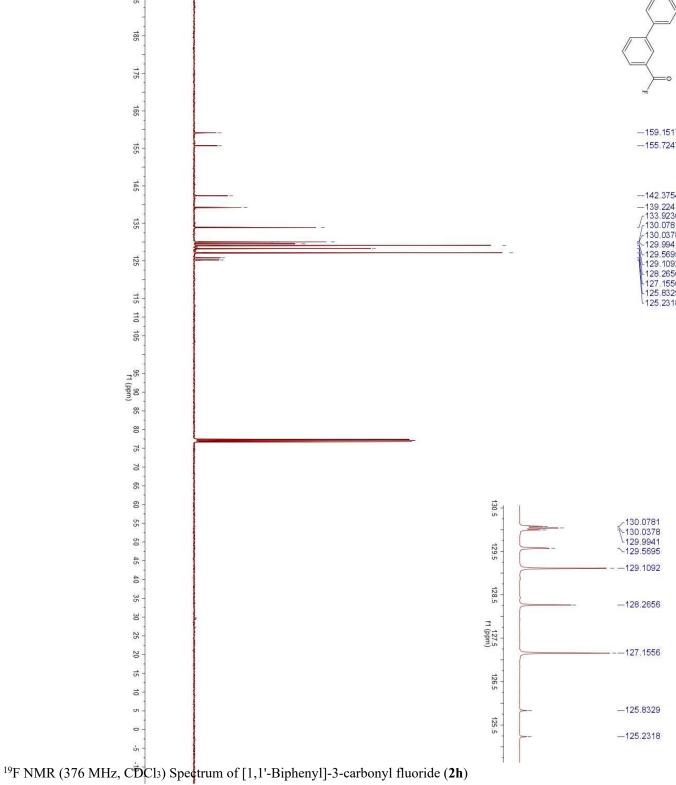
¹H NMR (400 MHz, CDCl₃) Spectrum of [1,1'-Biphenyl]-4-carbonyl fluoride (2g)

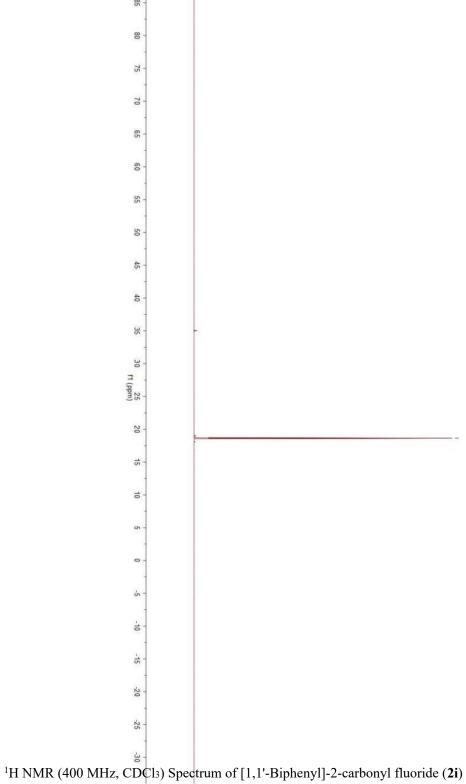


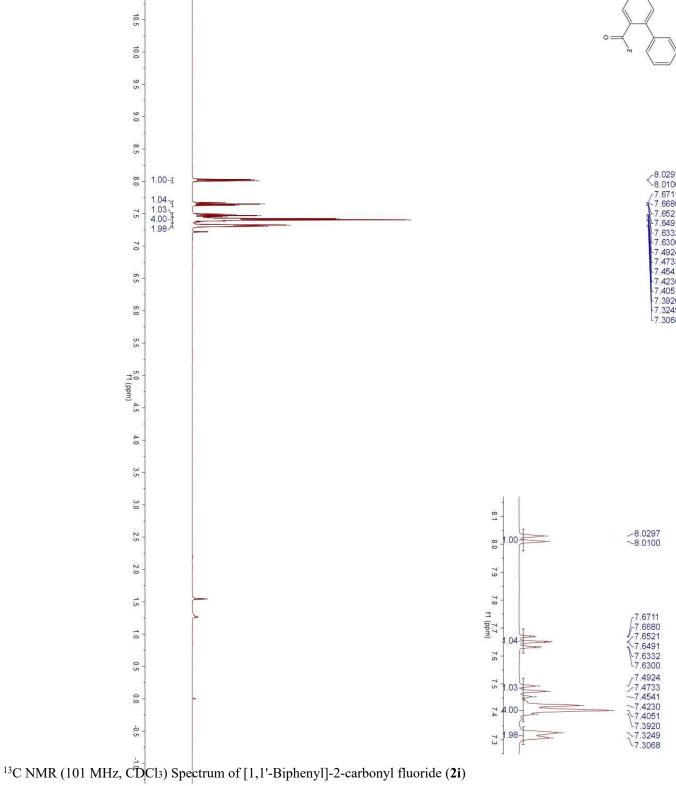


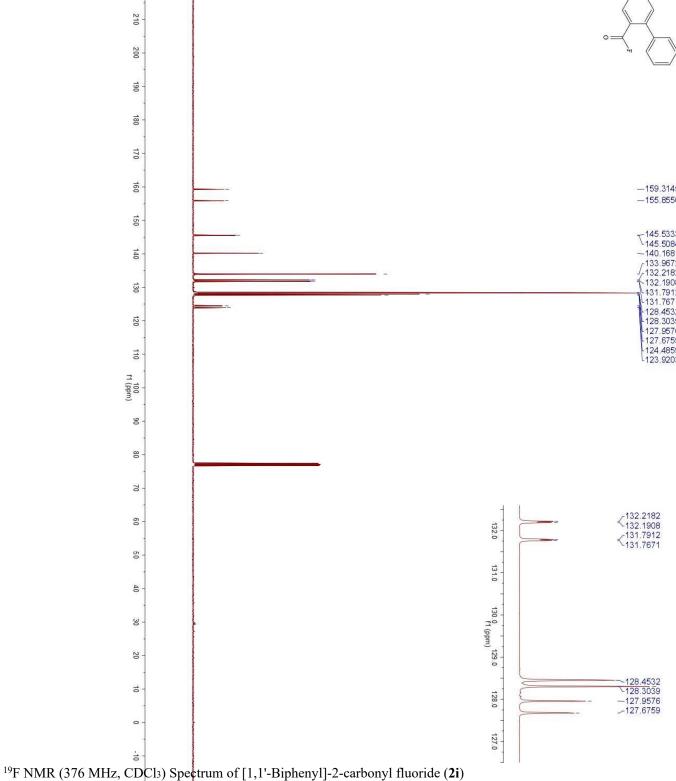


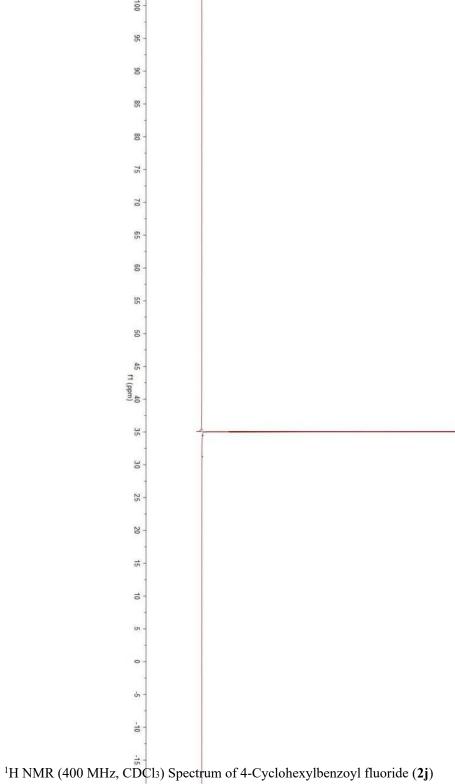


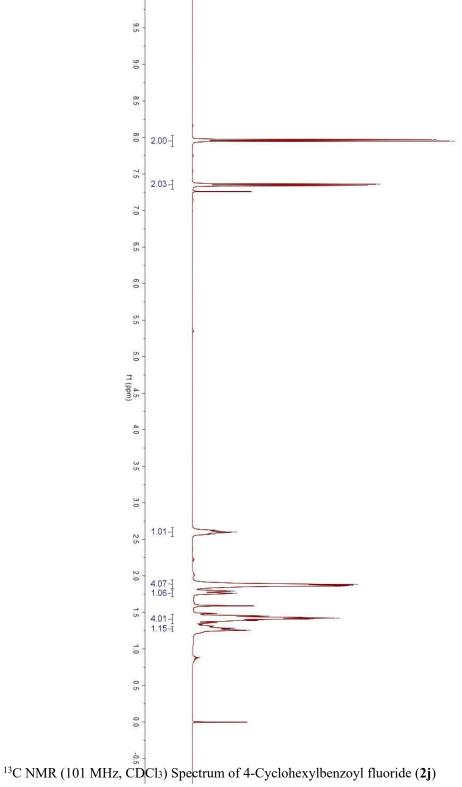






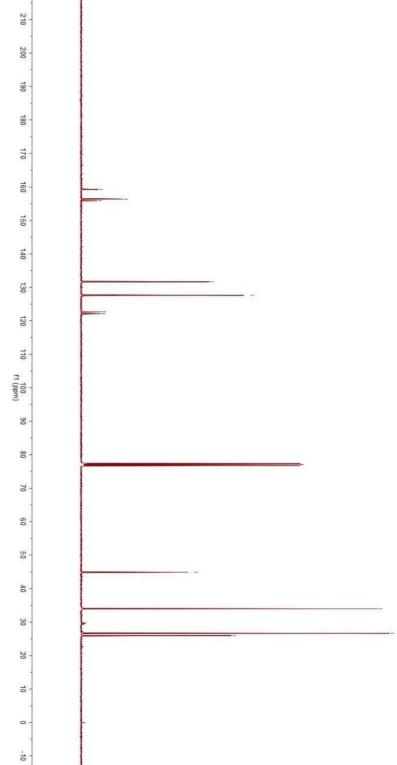






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1.884 1.875 1.867 1.486 1.432 1.423 1.423 1.285 1.282 1.274 1.255



_159.257 _156.365 _155.851

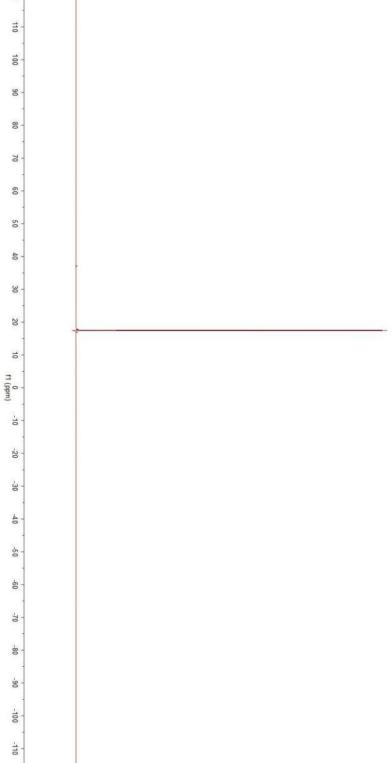
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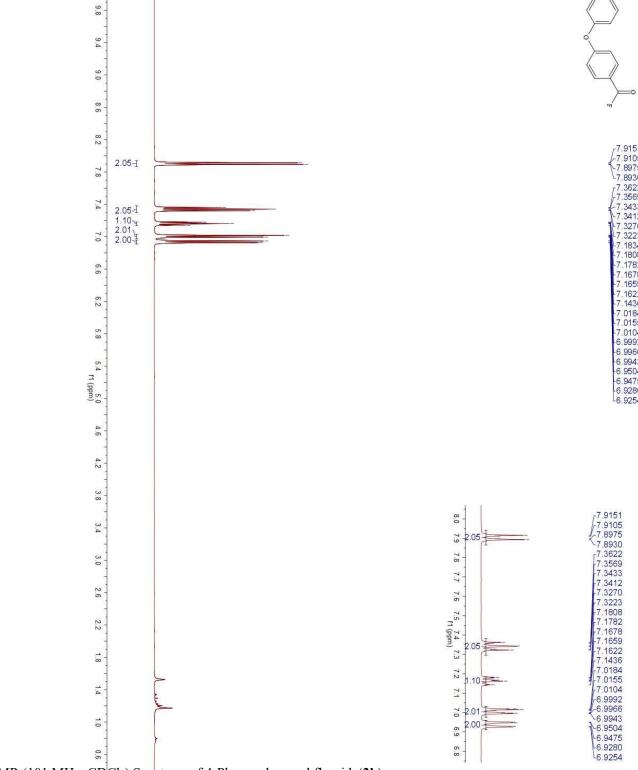
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26.6330 25.9551

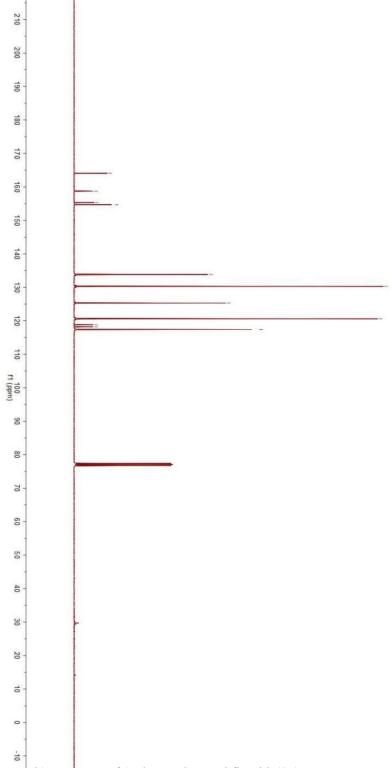
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of 4-Cyclohexylbenzoyl fluoride (2j)



¹H NMR (400 MHz, CDCl₃) Spectrum of 4-Phenoxybenzoyl fluoride(**2k**)



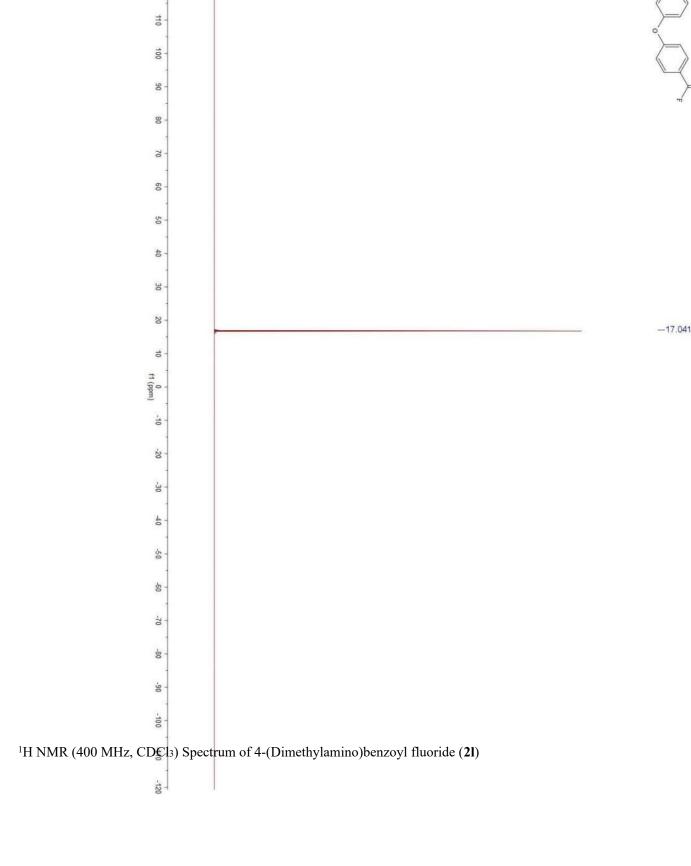
¹³C NMR (101 MHz, CDCl₃) Spectrum of 4-Phenoxybenzoyl fluoride(**2k**)

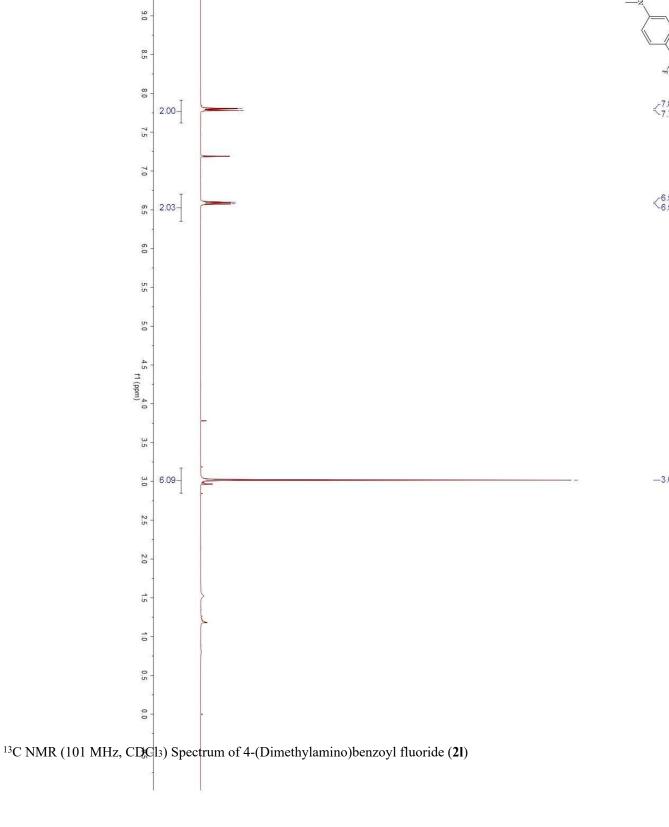


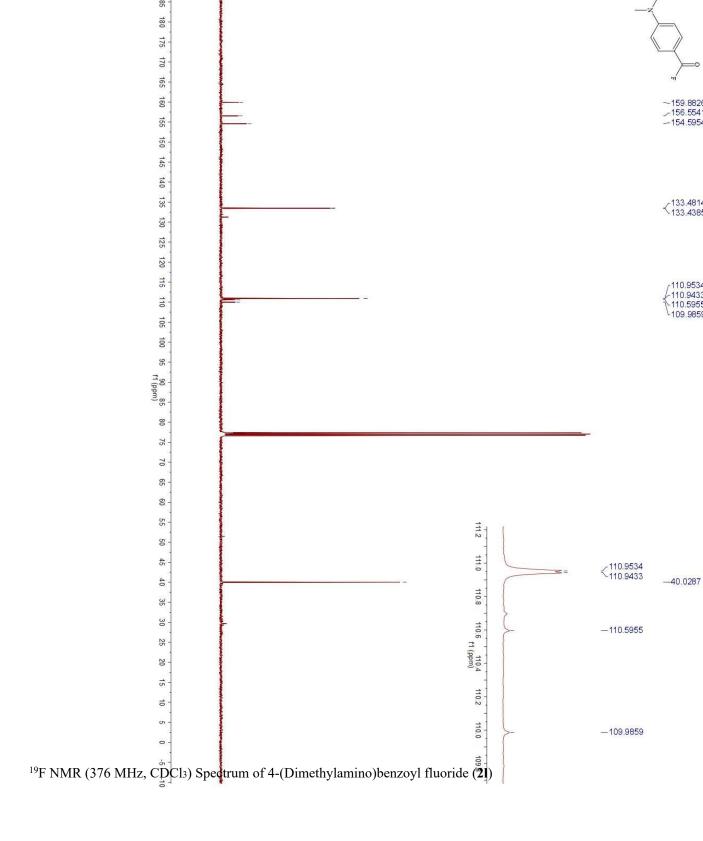
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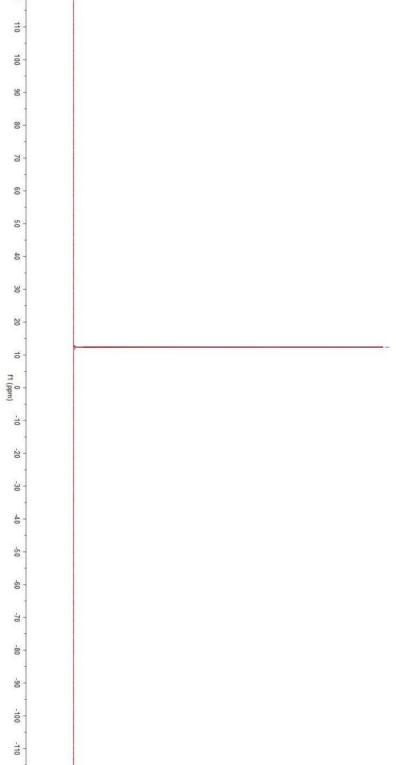
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¹⁹F NMR (376 MHz, CDCl₃) Spectrum of 4-Phenoxybenzoyl fluoride(2k)



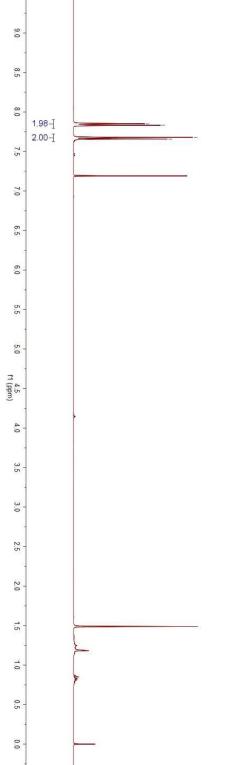






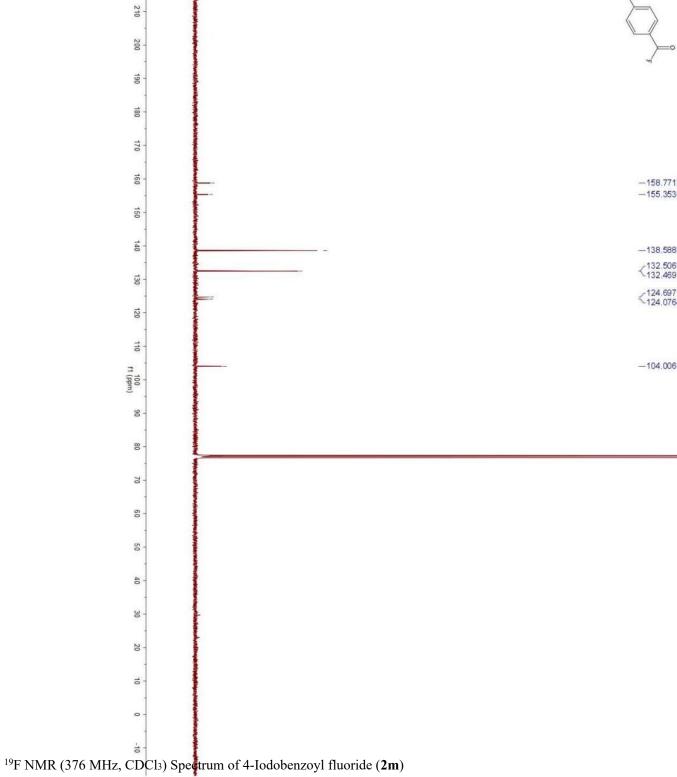
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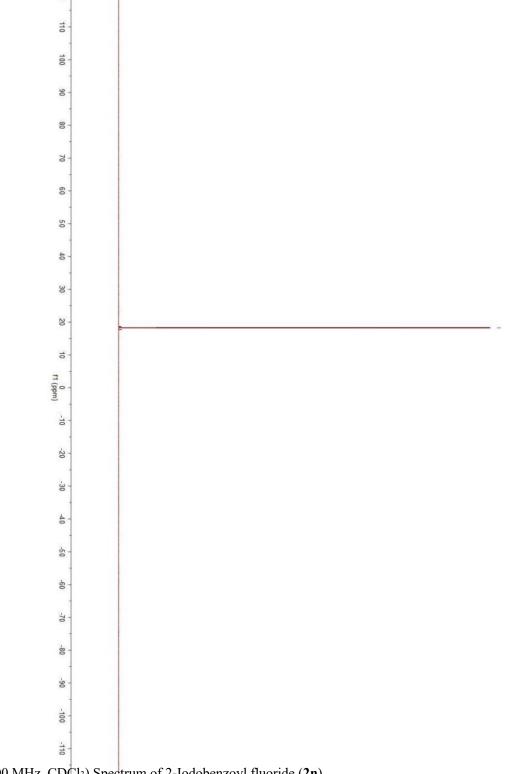
¹H NMR (400 MHz, CDCl₃) Spectrum of 4-Iodobenzoyl fluoride (**2m**)

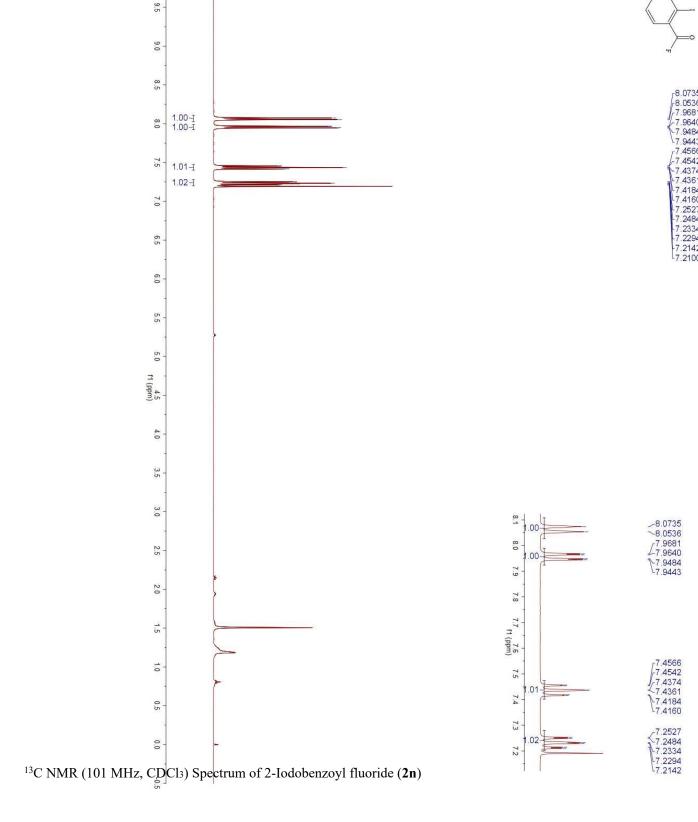


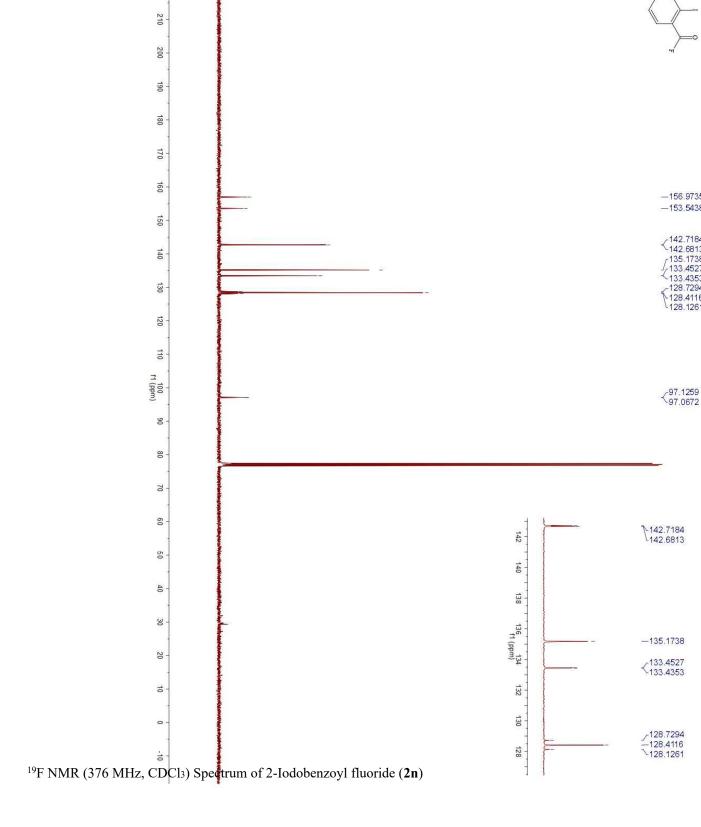
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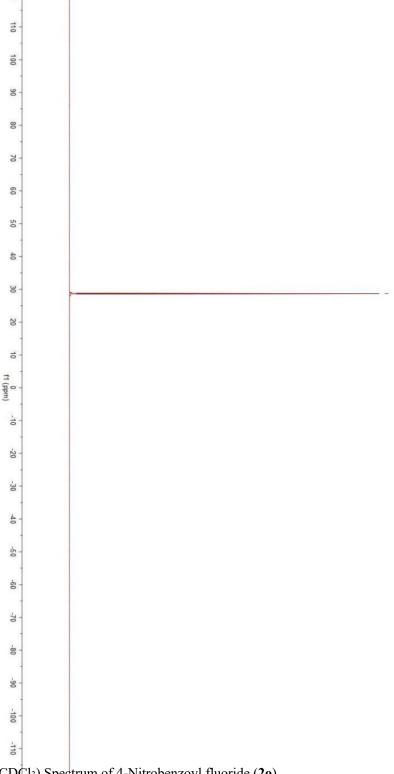
¹³C NMR (101 MHz, CDCl₃) Spectrum of 4-Iodobenzoyl fluoride (**2m**)





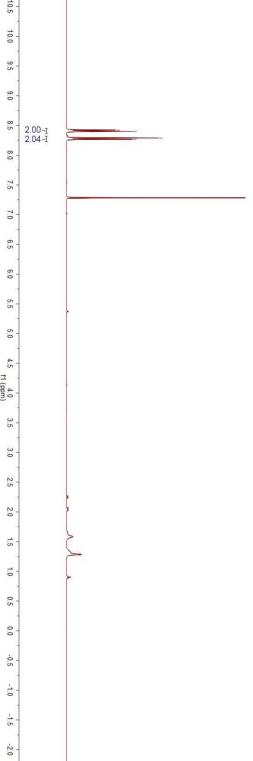




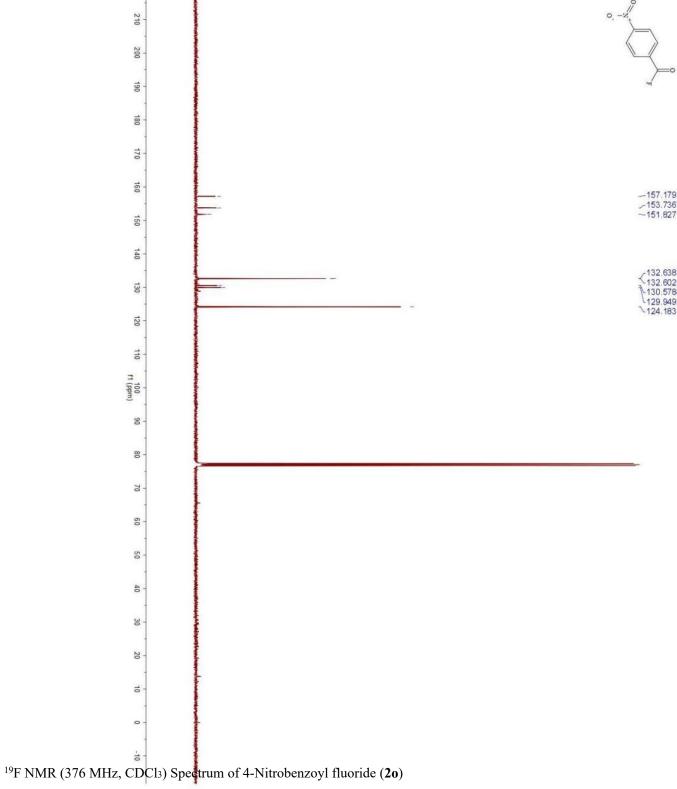


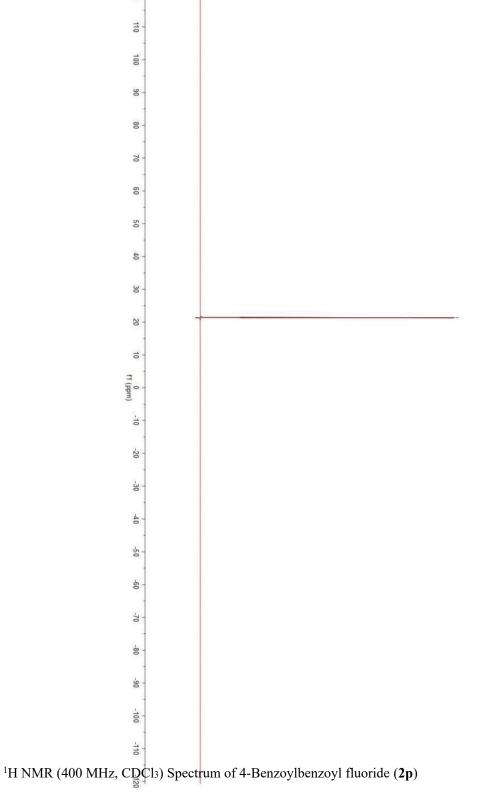
-28,686

¹H NMR (400 MHz, CDCl₃) Spectrum of 4-Nitrobenzoyl fluoride (**20**)

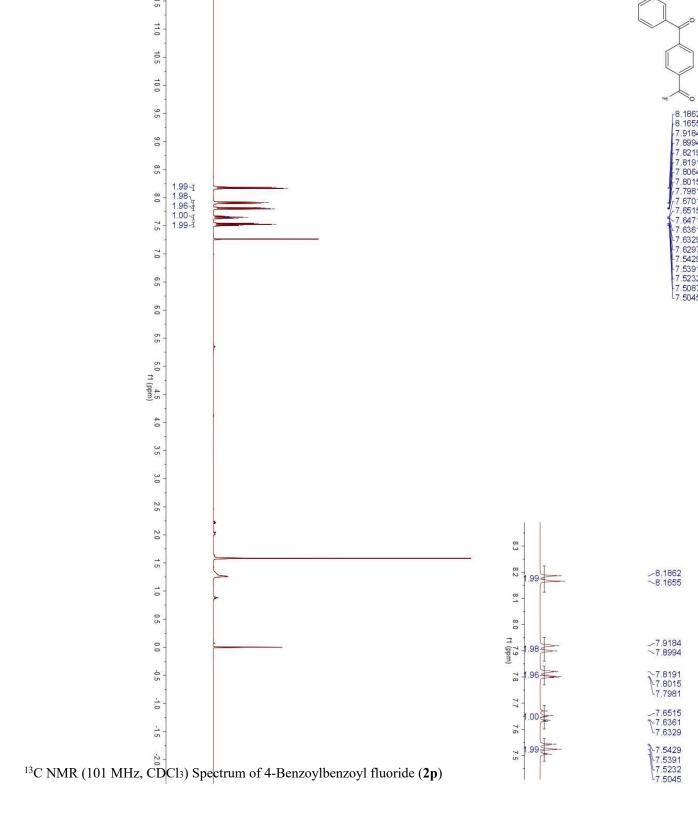


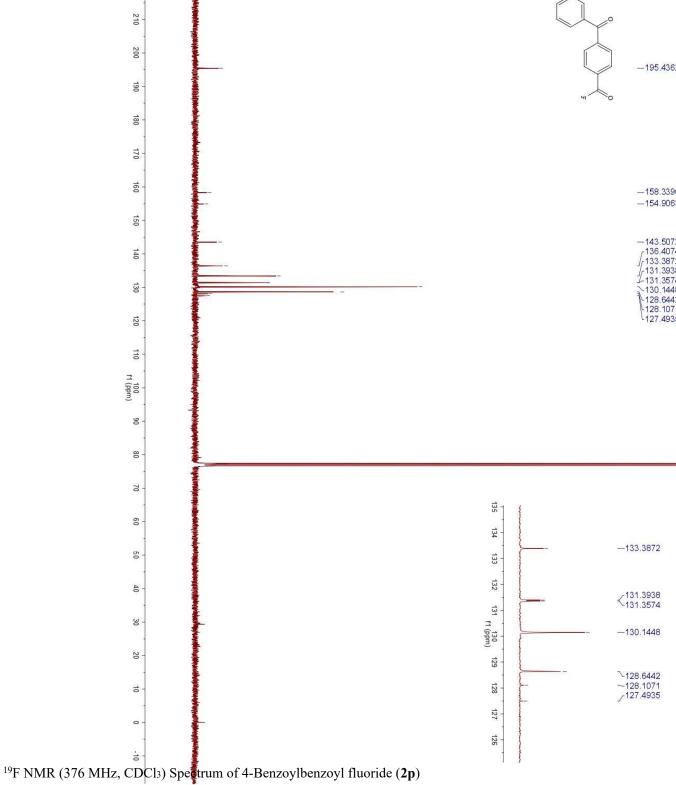
¹³C NMR (101 MHz, CDCl₃) Spectrum of 4-Nitrobenzoyl fluoride (20)

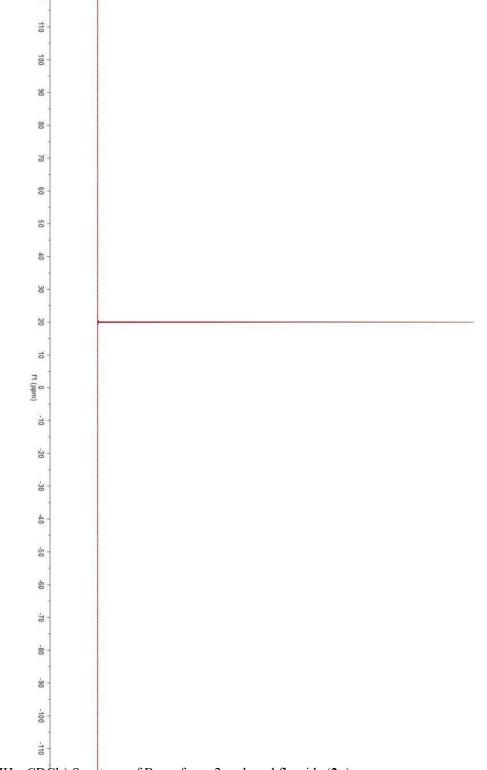




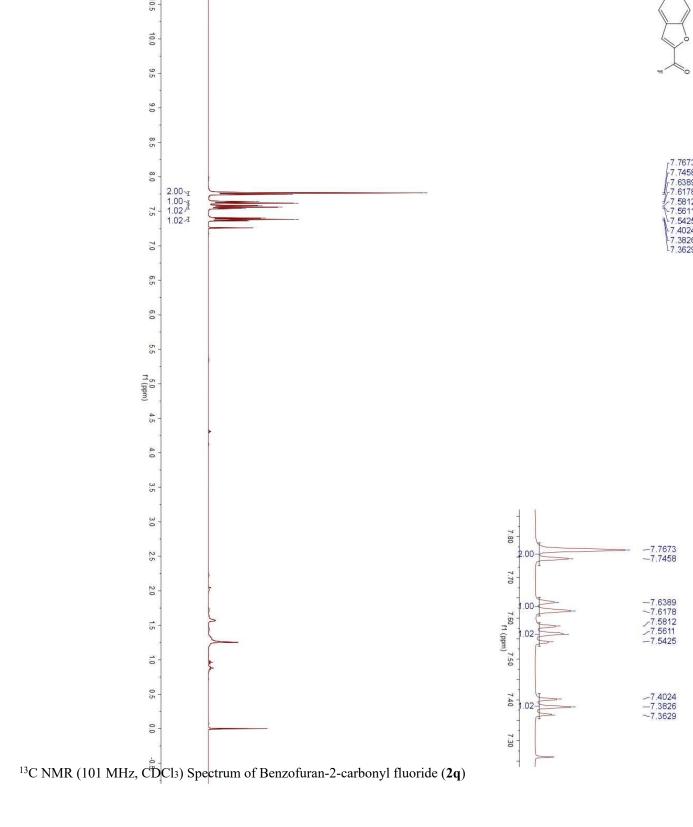
S56

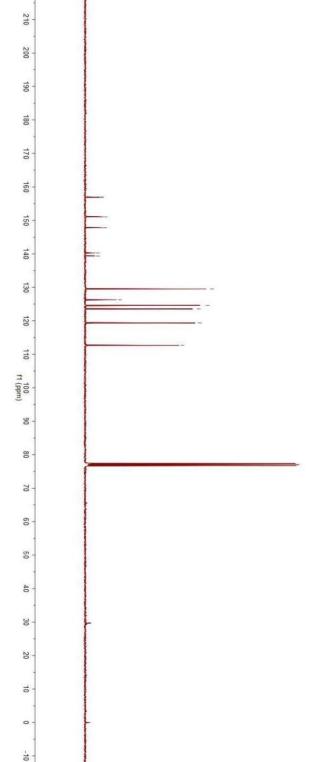






¹H NMR (400 MHz, CDCl₃) Spectrum of Benzofuran-2-carbonyl fluoride (**2q**)



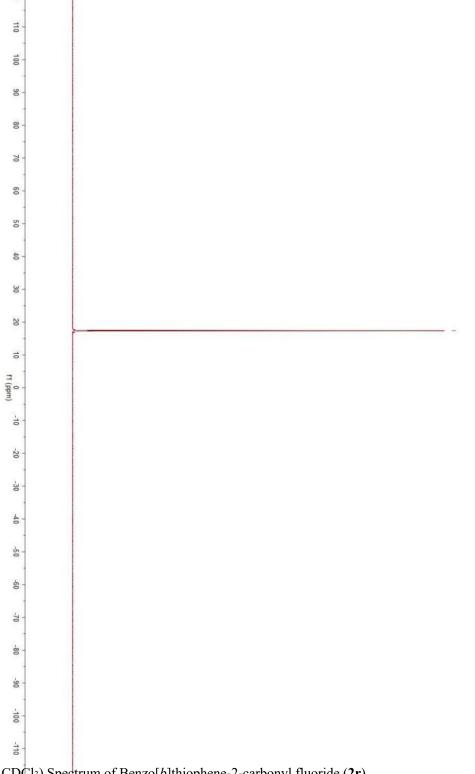


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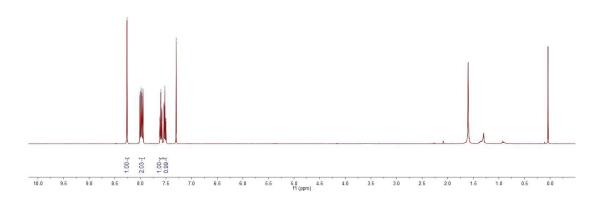
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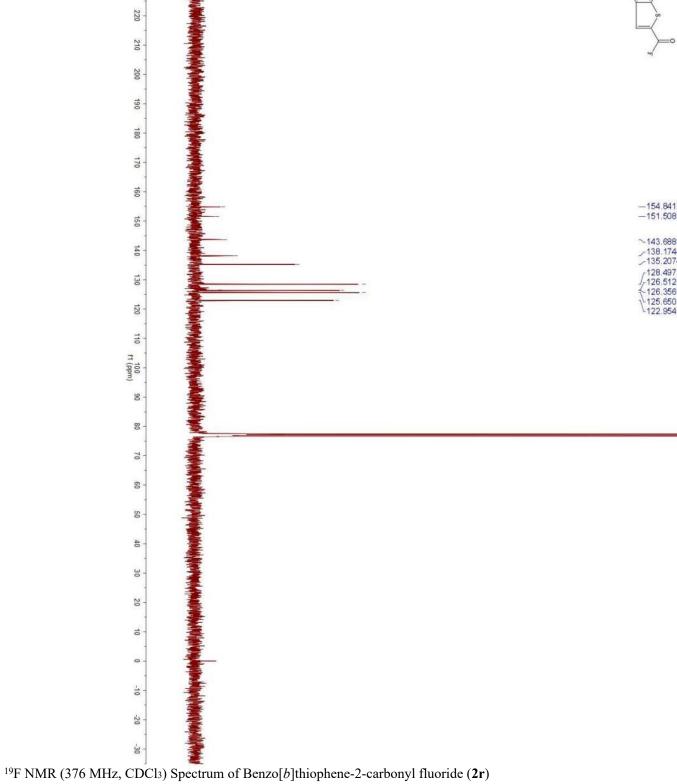
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of Benzofuran-2-carbonyl fluoride (2q)



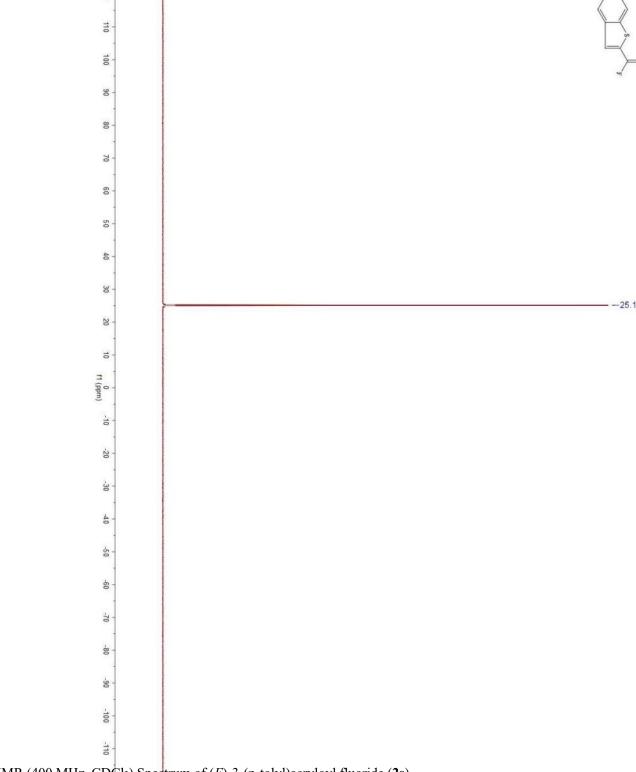




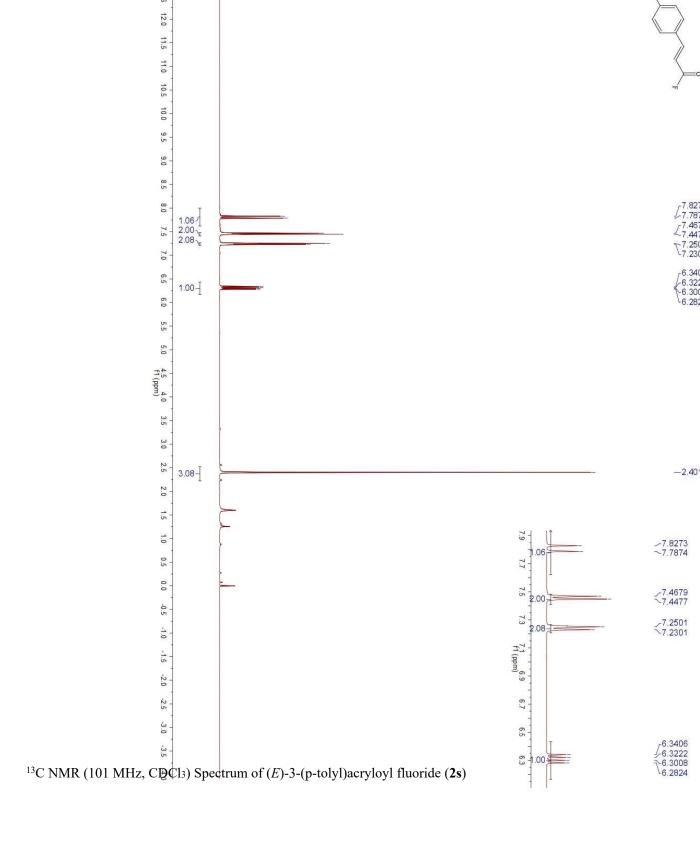
 $^{13}\mathrm{C}$ NMR (101 MHz, CDCl₃) Spectrum of Benzo[b]thiophene-2-carbonyl fluoride (2r)

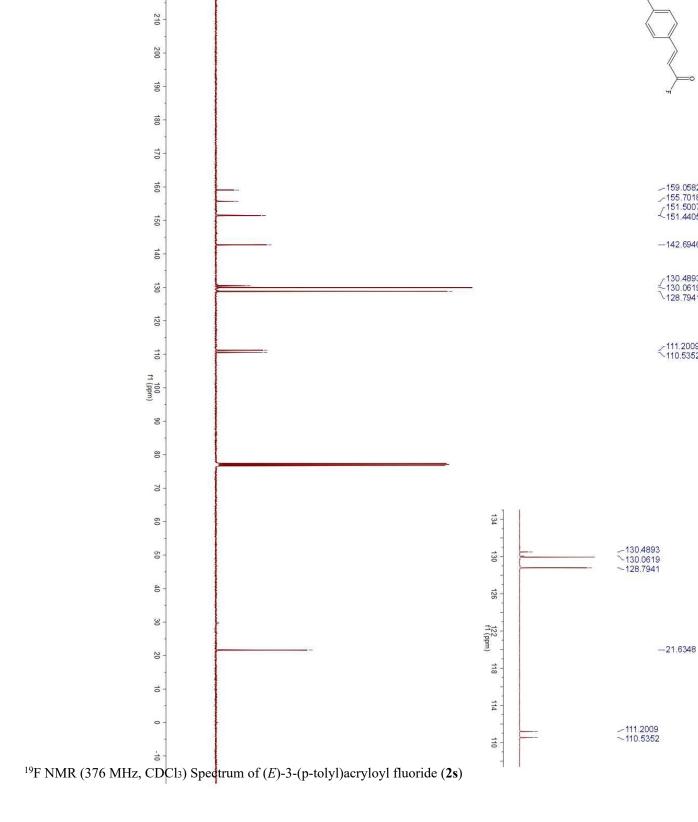


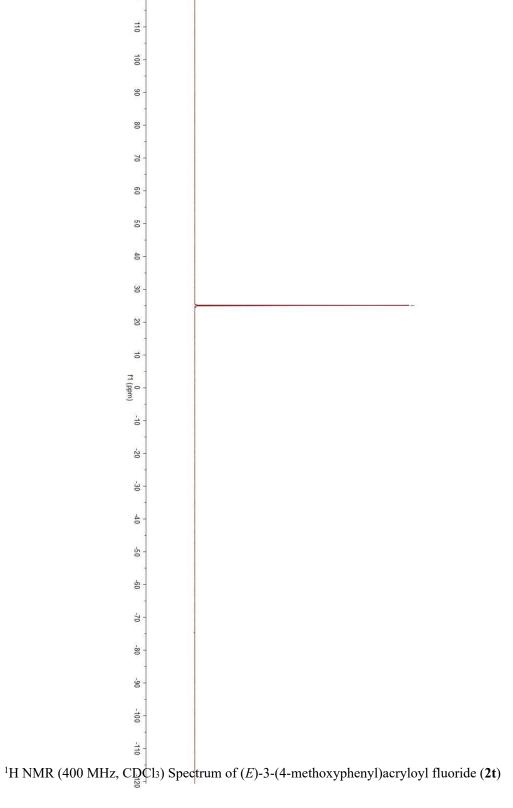
230



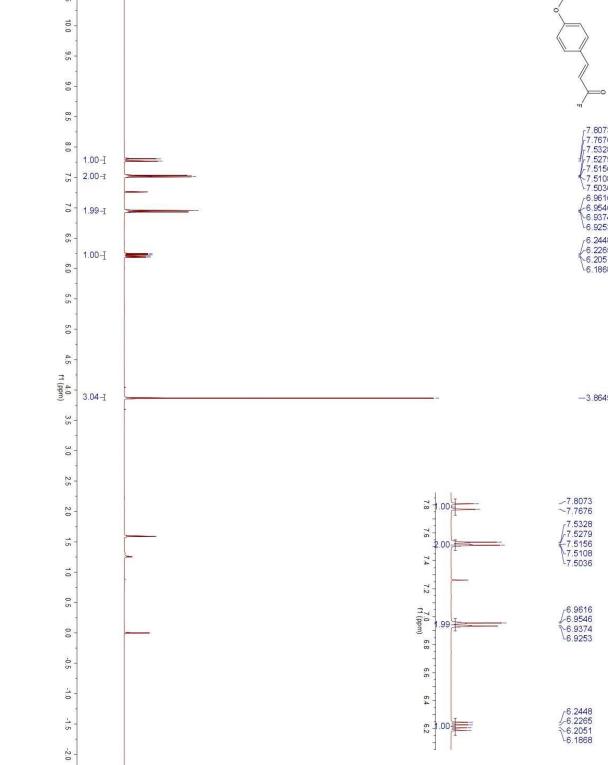
¹H NMR (400 MHz, CDCl₃) Spectrum of (*E*)-3-(p-tolyl)acryloyl fluoride (2s)



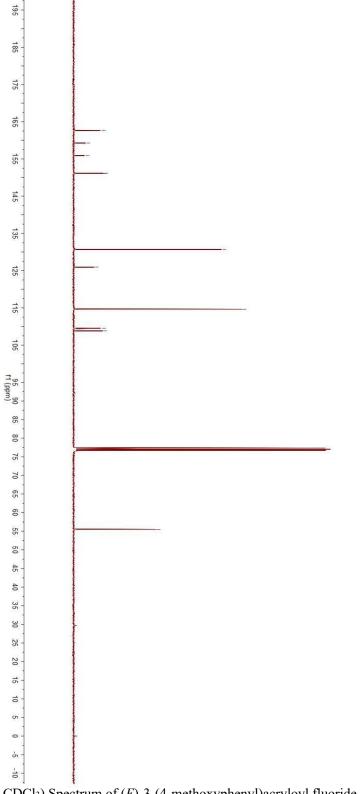




-25.082



¹³C NMR (101 MHz, CDCl₃) Spectrum of (*E*)-3-(4-methoxyphenyl)acryloyl fluoride (**2t**)



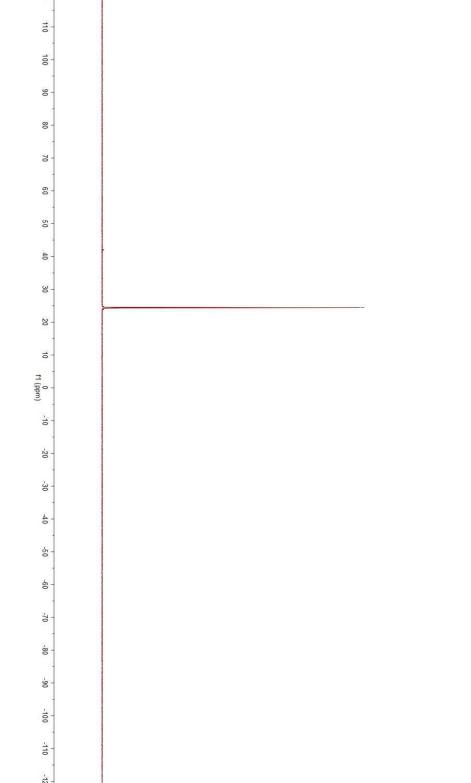
~162.672 -159.275 ~155.928 £151.146 £151.083

-130.693 -125.941

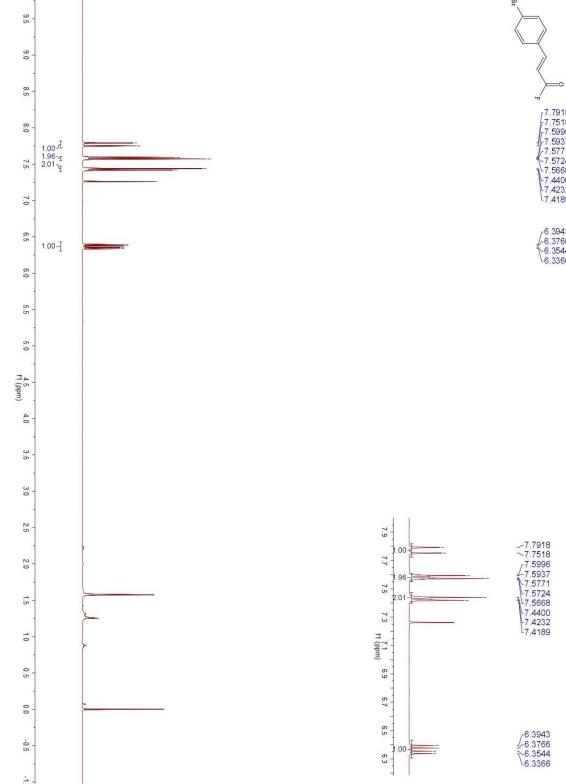
-114.6533 ∠109.499 ∠108.832

-55.5130

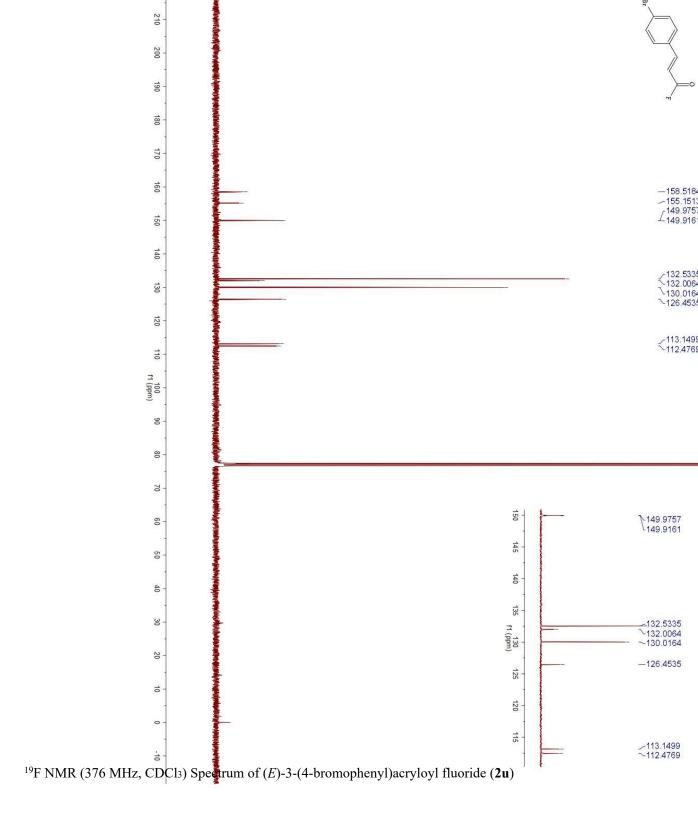
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of (*E*)-3-(4-methoxyphenyl)acryloyl fluoride (**2t**)

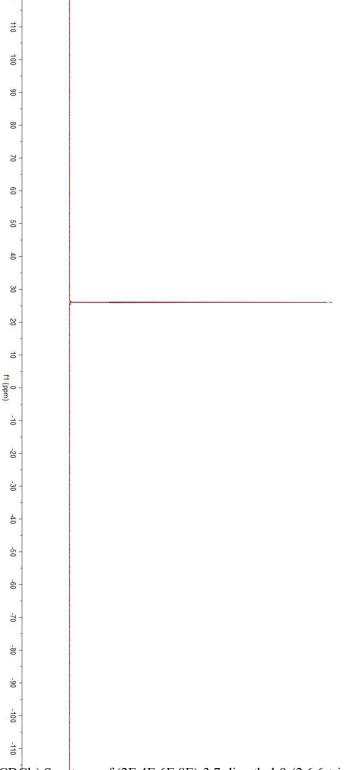


¹H NMR (400 MHz, CDCl₃) Spectrum of (E)-3-(4-bromophenyl)acryloyl fluoride (2u)



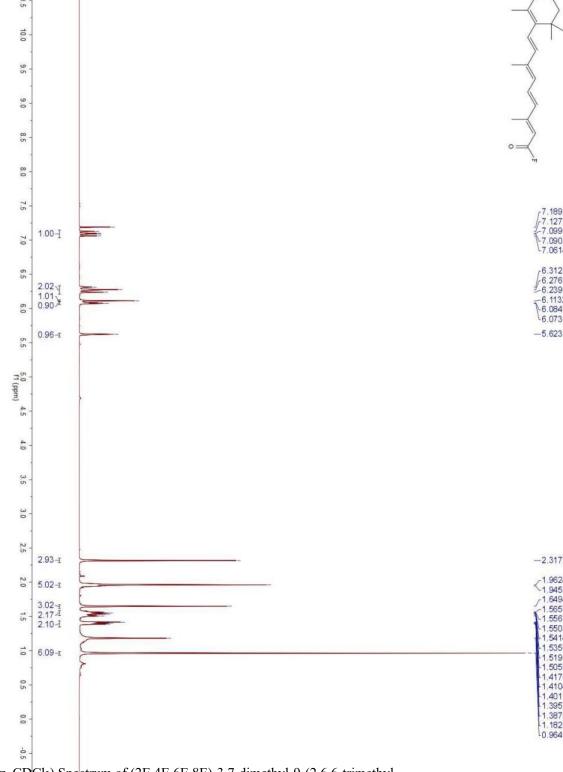
13C NMR (101 MHz, CDCl₃) Spectrum of (E)-3-(4-bromophenyl)acryloyl fluoride (**2u**)



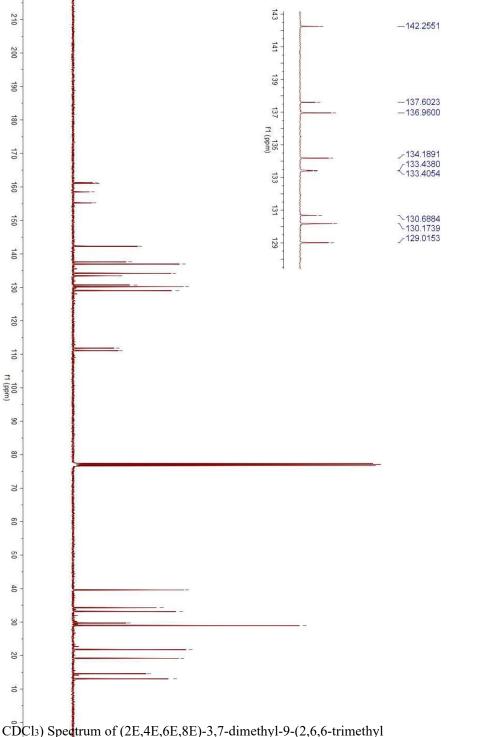


-26.026

¹H NMR (400 MHz, CDCl₃) Spectrum of (2E,4E,6E,8E)-3,7-dimethyl-9-(2,6,6-trimethyl cyclohex-1-en-1-yl)nona-2,4,6,8-tetraenoyl fluoride (**2v**)



¹³C NMR (101 MHz, CDCl₃) Spectrum of (2E,4E,6E,8E)-3,7-dimethyl-9-(2,6,6-trimethyl cyclohex-1-en-1-yl)nona-2,4,6,8-tetraenoyl fluoride (**2v**)



161.223 161.045 158.501 155.219

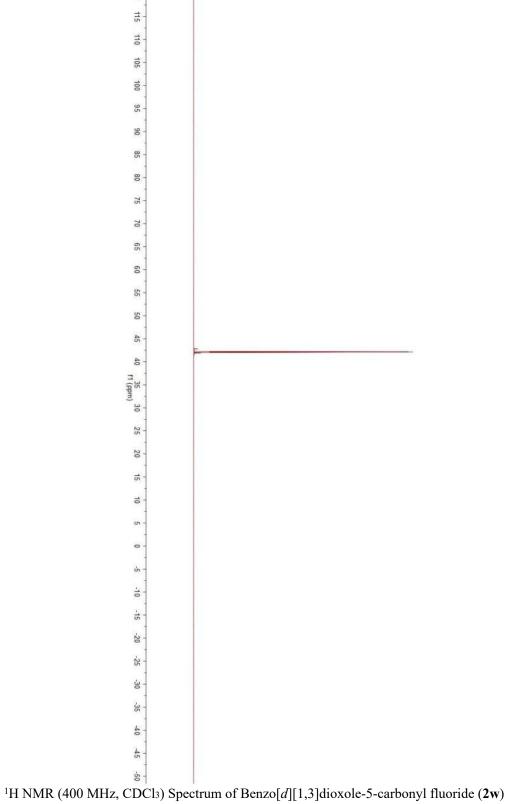
142.255 137.602: 136.960: 134.189 133.438: 130.688: 130.173: 129.015:

<111.8387 111.0998

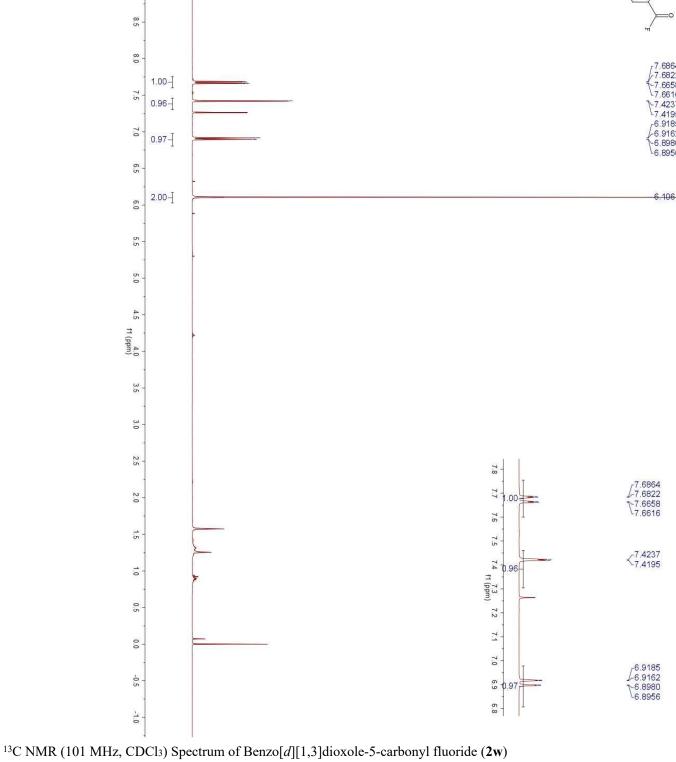
-39.6047 -34.2833 -33.1711 -29.7236 -28.9744

-21.7788 -19.1888 -14.5883 -13.0539

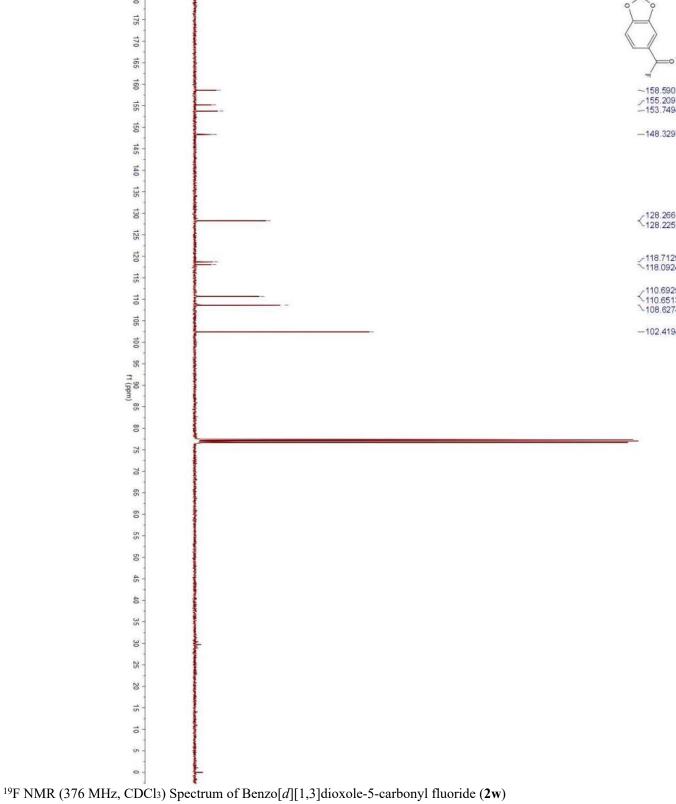
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of (2E,4E,6E,8E)-3,7-dimethyl-9-(2,6,6-trimethyl cyclohex-1-en-1-yl)nong-2,4,6,8-tetraenoyl fluoride (**2v**)

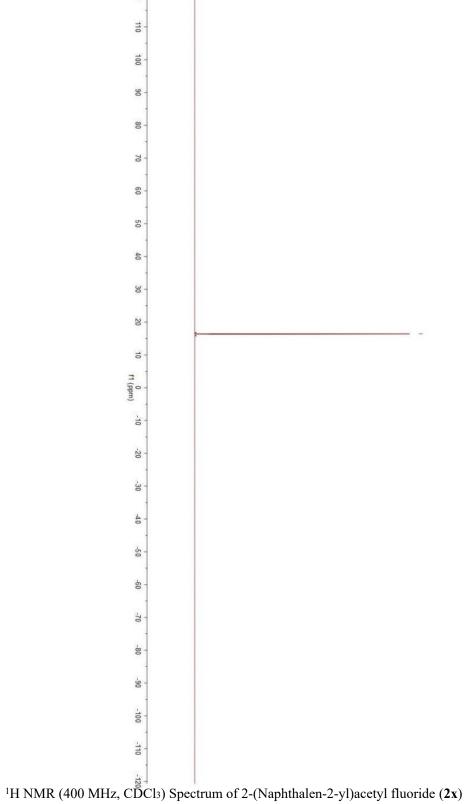


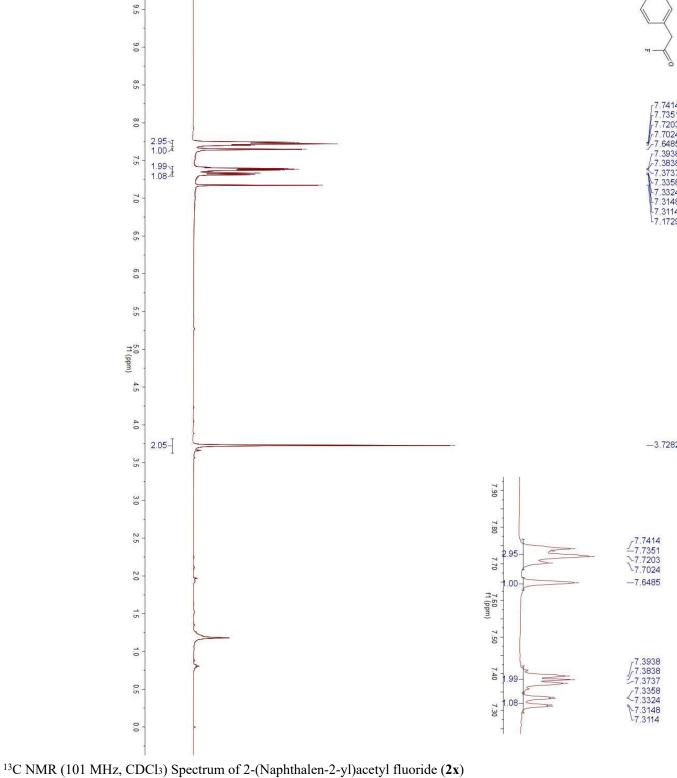
-42.149

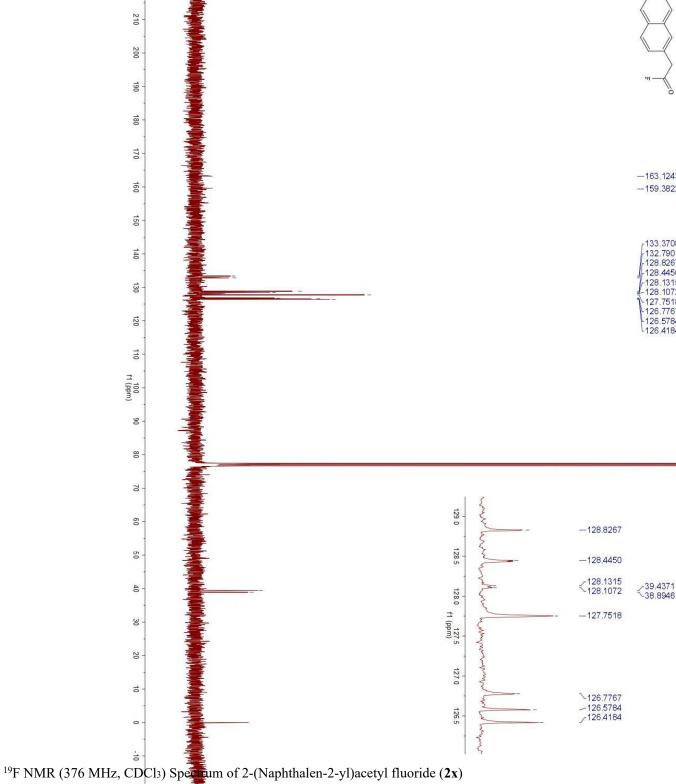


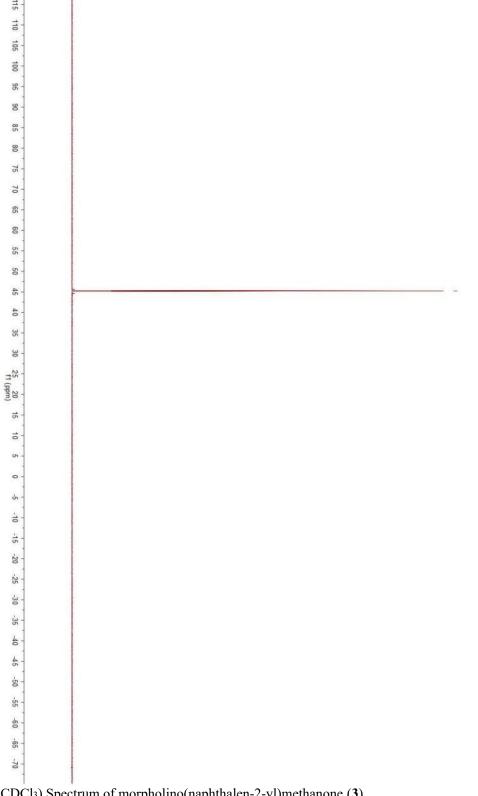
9.0





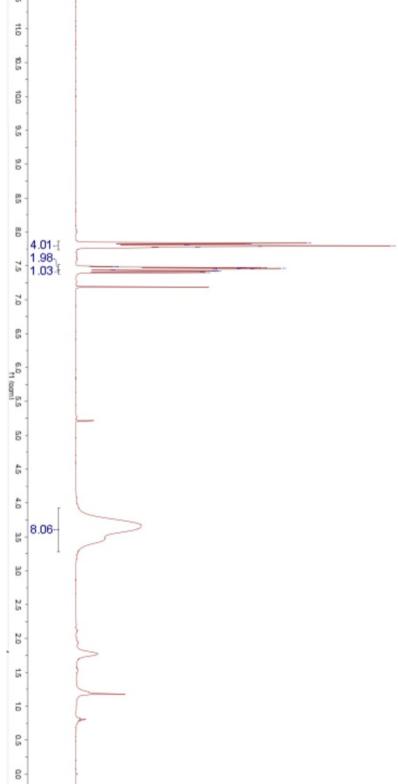




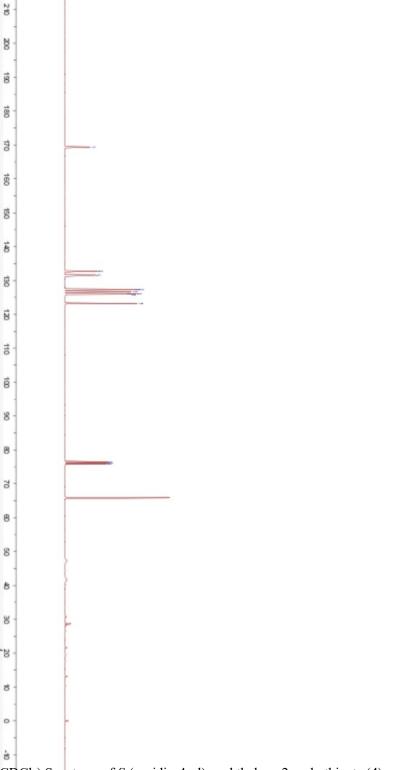


-45.228

¹H NMR (400 MHz, CDCl₃) Spectrum of morpholino(naphthalen-2-yl)methanone (3)



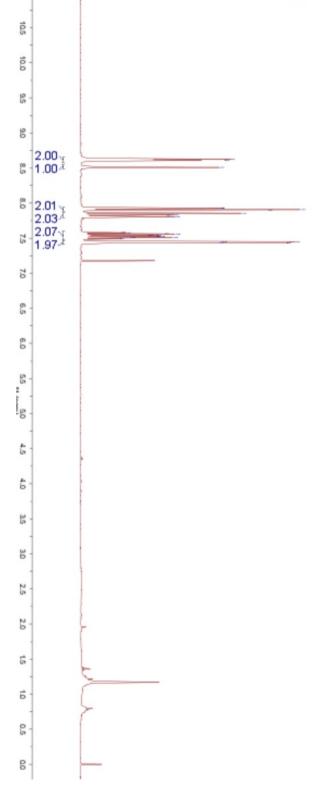
¹³C NMR (101 MHz, CDCl₃) Spectrum of morpholino(naphthalen-2-yl)methanone (3)



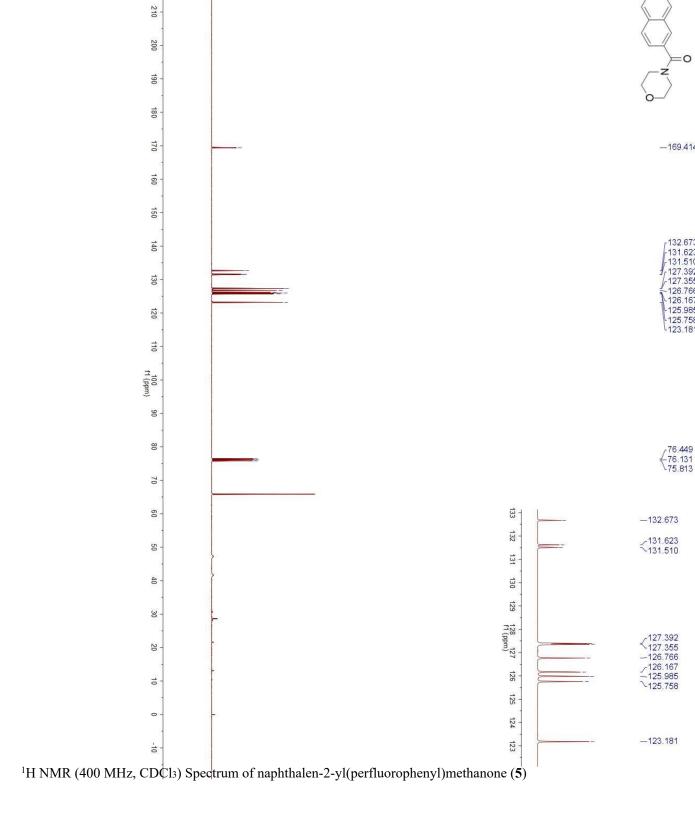
132.67 131.62 -131.51 127.39 -127.35 -126.76 126.16 125.98 125.75

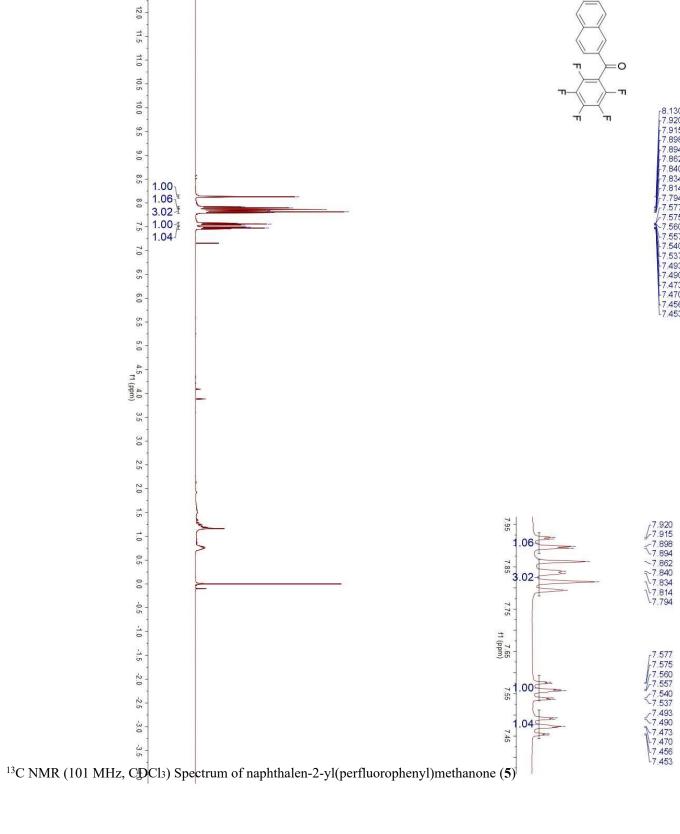
76.449 76.131 75.813

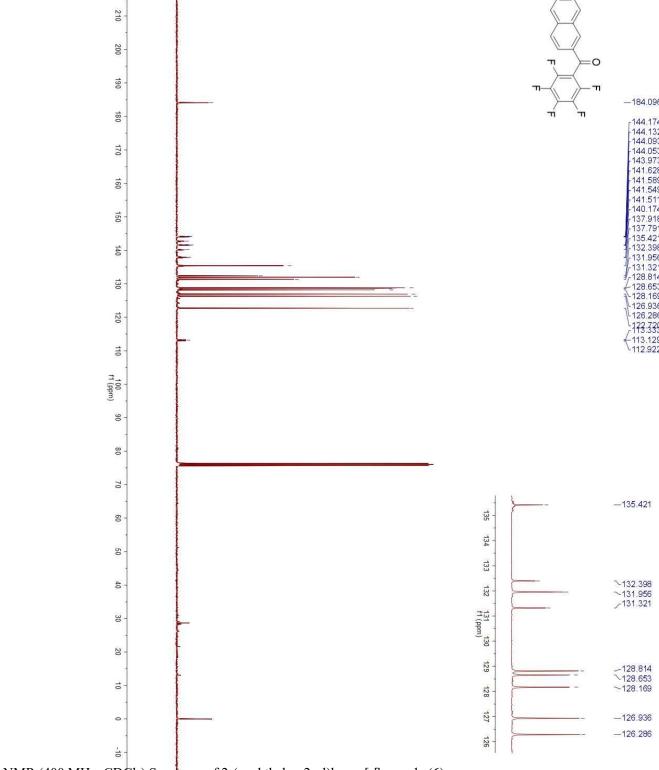
¹H NMR (400 MHz, CDCl₃) Spectrum of S-(pyridin-4-yl) naphthalene-2-carbothioate (4)



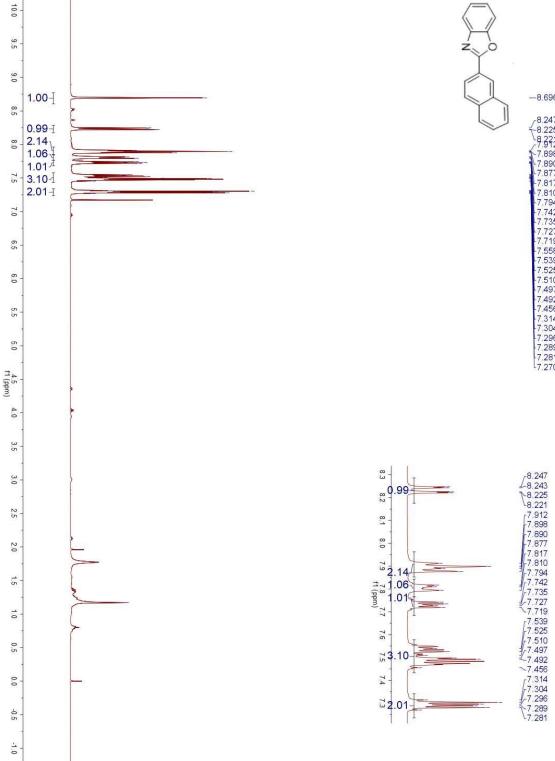
 13 C NMR (101 MHz, CDCl₃) Spectrum of S-(pyridin-4-yl) naphthalene-2-carbothioate (4)



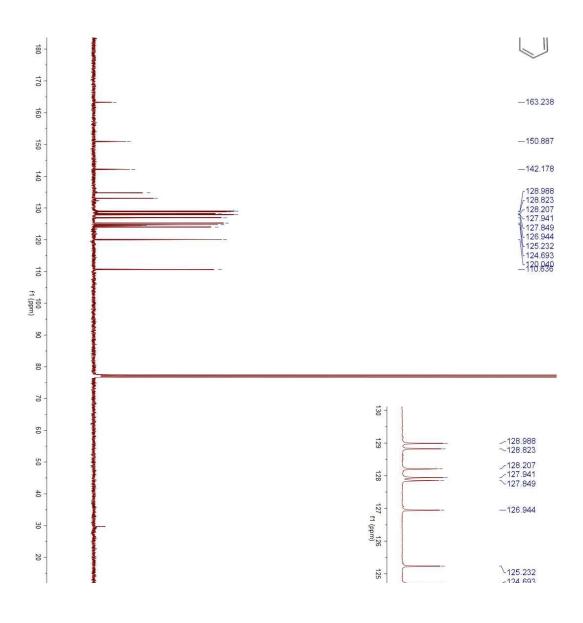




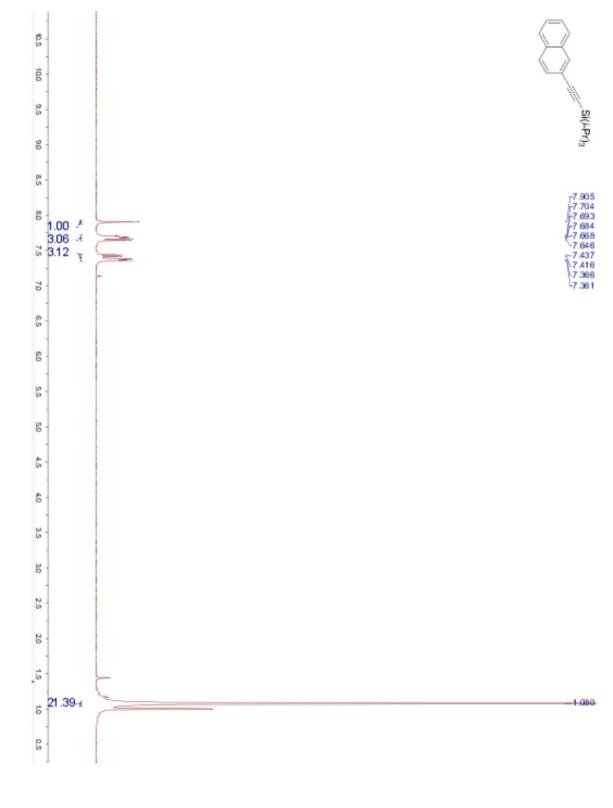
¹H NMR (400 MHz, CDCl₃) Spectrum of 2-(naphthalen-2-yl)benzo[d]oxazole (6)



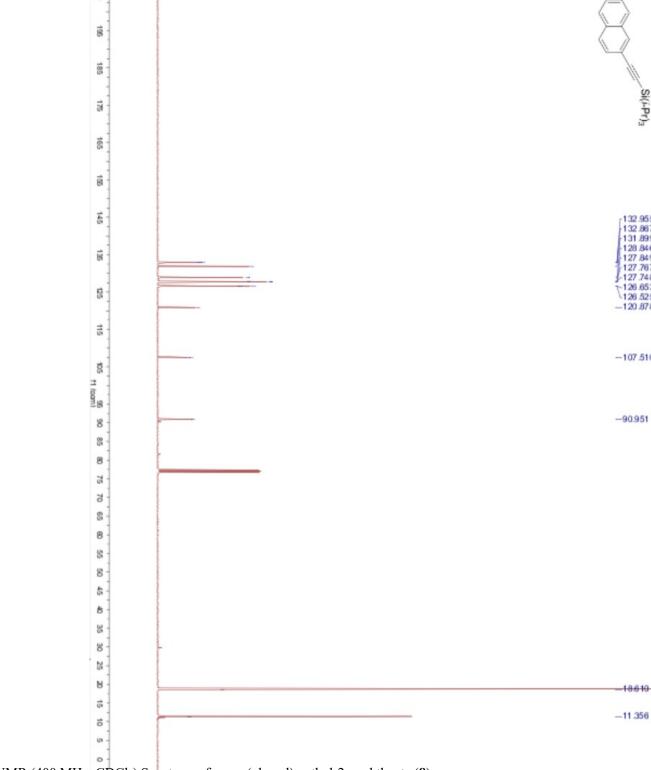
¹³C NMR (101 MHz, CDCl₃) Spectrum of 2-(naphthalen-2-yl)benzo[d]oxazole (6)



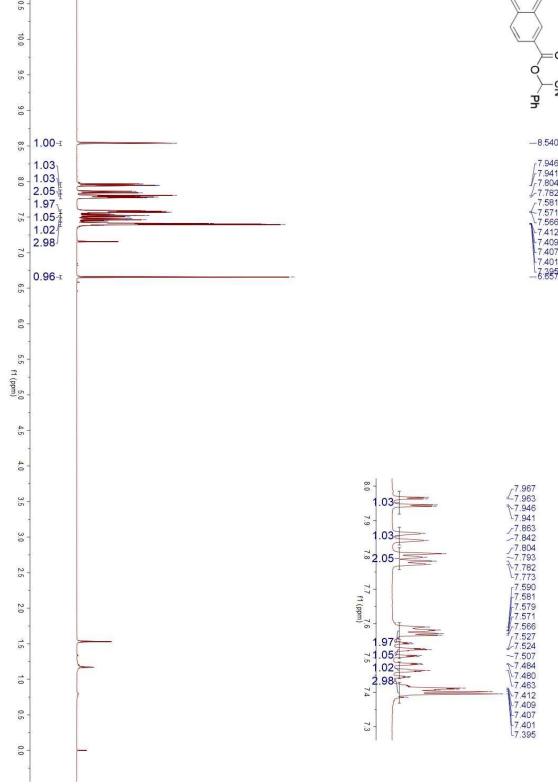
¹H NMR (400 MHz, CDCl₃) Spectrum of triisopropyl(naphthalen-2-ylethynyl)silane (7)



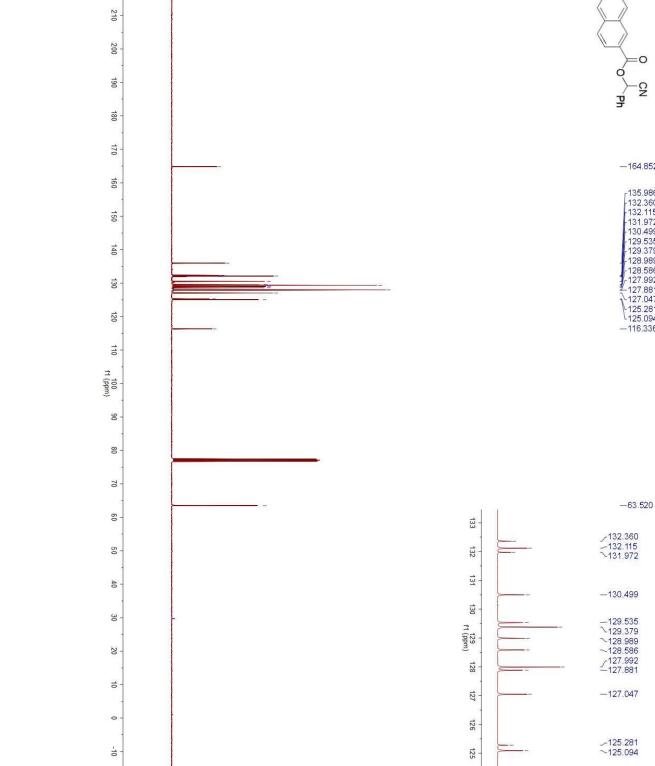
¹³C NMR (101 MHz, CDCl₃) Spectrum of triisopropyl(naphthalen-2-ylethynyl)silane (7)



¹H NMR (400 MHz, CDCl₃) Spectrum of cyano(phenyl)methyl-2-naphthoate (8)



¹³C NMR (101 MHz, CDCl₃) Spectrum of cyano(phenyl)methyl-2-naphthoate (8)



6. Copies of Infrared spectrum of the Products

