Supporting Information (SI)

HFIP-Catalyzed Direct Dehydroxydifluoroalkylation of Benzylic and Allylic Alcohols with Difluoroenoxysilanes

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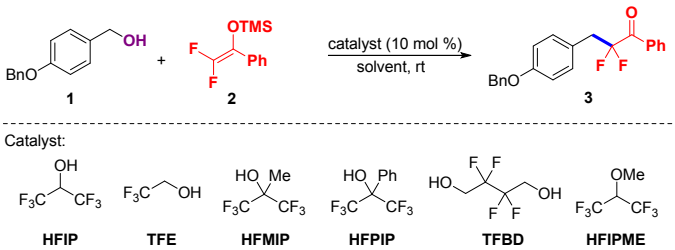
General information

^{1}H, ^{13}C and ^{19}F were recorded on Bruker AV 400 MHz instrument at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), as well as 376 MHz (^{19}F NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external CCl_3F, respectively. $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR), or DMSO-d_6 (2.50 ppm for ^{1}H NMR, 39.5 ppm for ^{13}C NMR) was used as a reference. Data for ^{1}H were reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad singlet), coupling constants (Hz), and integration. Data for ^{13}C NMR were reported as ppm. High-resolution mass spectra analyses were performed on a Waters SYNAPT G2-Si Q-TOF mass spectrometer. Melting points were determined using a X-4 digital micro melting point apparatus. Thin-layer chromatography (TLC) was performed, and visualization of the compounds was accomplished with UV light (254 nm). Flash column chromatography was performed on silica gel (200−300 mesh).

Materials: Unless otherwise indicated, all reactions were carried out in air. All solvents were distilled from appropriate drying agents prior to use. All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography. Difluoroenoxysilanes[1] were prepared according to the reported procedures. Chalcols were prepared according to literature procedures. [2]

Optimization of the reaction conditions



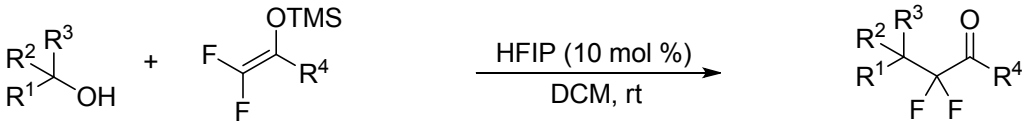
Catalyst:

HFIP	TFE	HFMIP	HFPIP	TFBD	HFIPME

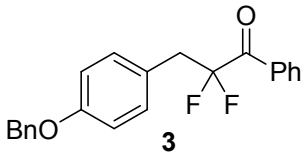
1	**HFIP**	**DCM**	**3 h**	**87**
2	TFE	DCM	6 h	48
3	HFMIP	DCM	12 h	39
4	HFPIP	DCM	12 h	31
5	TFBD	DCM	12 h	6
6	HFIPME	DCM	12 h	trace
7	^{i}PrOH	DCM	12 h	0
8	EtOH	DCM	12 h	0
9	H_2O	DCM	12 h	0
10	HFIP	DCE	6 h	53
11	HFIP	$CHCl_3$	6 h	21
12	HFIP	CCl_4	6 h	17
13	HFIP	$MeNO_2$	6 h	69
14	HFIP	toluene	12 h	trace
15[c]	Tf_2NH	DCM	12 h	10
16[c]	TfOH	DCM	12 h	6
17[c]	PTSA	DCM	12 h	complex
18[c]	$B(C_6F_5)_3$	DCM	12 h	complex
19[d]	–	HFIP	< 1 min	89

[a]General reaction conditions : alcohol **1** (1.0 mmol), difluoroenoxysilane **2** (1.05 mmol), and catalyst (10 mol %) in solvent (3.0 mL) at room temperature unless otherwise noted. [b]Isolated yield. [c]Difluoroenoxysilane was quickly decomposed. [d]HFIP was used as solvent.

General procedure for HFIP-catalyzed direct dehydroxydifluoroalkylation of benzylic and allylic alcohols

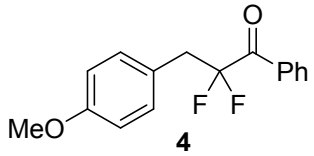


To a mixture of alcohols (0.5 mmol) and difluoroenoxysilanes (0.53 mmol, 1.05 equiv) in DCM (3.0 mL) was added HFIP (0.05 mmol, 5.3 μL) under room temperature. The resulting mixture was stirred at room temperature until the completion of the reaction (monitored by TLC, approximately 2−12 hours). Then the mixture was concentrated under reduced pressure. The residue was purified by column chromatography to afford the desired products, using theindicated eluent.



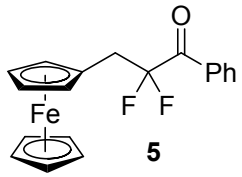
3

3-(4-(benzyloxy)phenyl)-2,2-difluoro-1-phenylpropan-1-one (3): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **3** (white solid, 153.2 mg, 87% yield). M.p.: 69–71 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.36 (m, 6H), 7.35 – 7.30 (m, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 5.04 (s, 2H), 3.46 (t, *J* = 17.7 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –98.89 (t, *J* = 17.7 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.7 (t, *J* = 31.1 Hz), 158.3, 136.9, 134.2, 132.2 (t, *J* = 2.3 Hz), 131.9, 130.1 (t, *J* = 3.3 Hz), 128.6 (d, *J* = 2.1 Hz), 128.0, 127.5, 123.4 (t, *J* = 3.9 Hz), 118.4 (t, *J* = 254.3 Hz), 114.8, 69.9, 39.4 (t, *J* = 23.4 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{18}F_2O_2Na$ 375.1173; Found 375.1166.



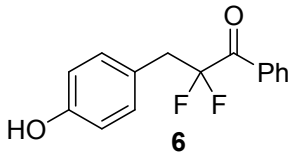
4

2,2-difluoro-3-(4-methoxyphenyl)-1-phenylpropan-1-one (4): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **4** (white solid, 114.6 mg, 83% yield). M.p.: 146–147 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.65 – 7.54 (m, 1H), 7.51 – 7.41 (m, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.88 – 6.81 (m, 2H), 3.79 (s, 3H), 3.47 (t, *J* = 17.7 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –98.93 (t, *J* = 17.7 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.6 (t, *J* = 31.1 Hz), 159.1, 134.2, 132.2 (t, *J* = 2.5 Hz), 131.9, 130.1 (t, *J* = 3.3 Hz), 128.6, 123.1 (t, *J* = 3.9 Hz), 118.3 (t, *J* = 254.2 Hz), 113.8, 55.2, 39.3 (t, *J* = 23.3 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{14}F_2O_2Na$ 299.0860; Found 299.0853.



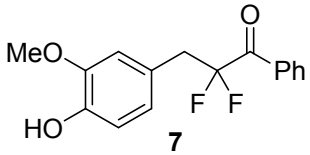
5

3-(ferrocenylmethyl)-2,2-difluoro-1-phenylpropan-1-one (5): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (100/1 to 50/1, v/v) as eluent to give compound **5** (orange yellow solid, 108.2 mg, 61% yield). M.p.: 89–90 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.72 – 7.52 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 4.20 (s, 2H), 4.13 (s, 5H), 4.13 – 4.09 (m, 2H), 3.30 (t, *J* = 17.2 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –98.68 (t, *J* = 16.8 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9 (t, *J* = 30.9 Hz), 134.1, 132.2 (t, *J* = 2.3 Hz), 130.1 (t, *J* = 3.3 Hz), 128.5, 117.7 (t, *J* = 254.5 Hz), 70.3, 68.8, 68.3, 35.4 (t, *J* = 24.0 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{16}F_2FeO_2Na$ 377.0416; Found 377.0412.



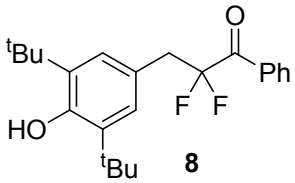
6

2,2-difluoro-3-(4-hydroxyphenyl)-1-phenylpropan-1-one (6): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **6** (pale yellow solid, 82.6 mg, 63% yield). M.p.: 65–66 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 5.37 (s, 1H), 3.45 (t, *J* = 17.6 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –98.92 (t, *J* = 17.2 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.8 (t, *J* = 31.1 Hz), 155.1, 134.2, 132.2 (t, *J* = 2.5 Hz), 132.1, 130.1 (t, *J* = 3.3 Hz), 128.6, 123.2 (t, *J* = 3.8 Hz), 118.4 (t, *J* = 254.4 Hz), 115.3, 39.4 (t, *J* = 23.5 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{12}F_2O_2Na$ 285.0703; Found 285.0708.



7

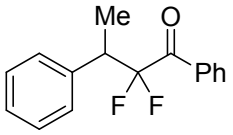
2,2-difluoro-3-(4-hydroxy-3-methoxyphenyl)-1-phenylpropan-1-one (7): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **7** (white solid, 90.6 mg, 62% yield). M.p.: 98–99 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 6.90 – 6.81 (m, 1H), 6.77 (d, *J* = 6.0 Hz, 2H), 5.57 (s, 1H), 3.85 (s, 3H), 3.44 (t, *J* = 17.6 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –98.81 (t, *J* = 17.4 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.7 (t, *J* = 30.9 Hz), 146.3, 145.2, 134.2, 132.3 (t, *J* = 2.3 Hz), 130.0 (t, *J* = 3.3 Hz), 128.6, 123.9, 122.7 (t, *J* = 3.9 Hz), 118.4 (t, *J* = 254.4 Hz), 114.3, 113.2, 55.9, 39.9 (t, *J* = 23.4 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{14}F_2O_3Na$ 315.0809; Found 315.0806.



8

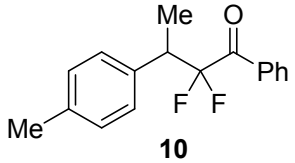
3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,2-difluoro-1-phenylpropan-1-one (8): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **8** (white solid, 132.9 mg, 71% yield). M.p.: 119–120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.02 (s, 2H), 5.15 (s, 1H), 3.43 (t, *J* = 17.4 Hz, 2H), 1.38 (s, 18H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ

–99.03 (t, *J* = 18.5 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.4 (t, *J* = 30.4 Hz), 153.3, 135.9, 133.9, 132.7 (d, *J* = 2.1 Hz), 130.0 (t, *J* = 3.4 Hz), 128.5, 127.4, 121.5 (t, *J* = 4.0 Hz), 118.7 (t, *J* = 254.2 Hz), 40.6 (t, *J* = 23.4 Hz), 34.2, 30.2; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{28}F_2O_2Na$ 397.1955; Found 397.1959.



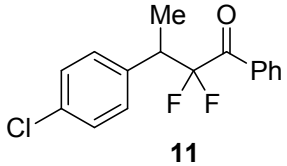
9

2,2-difluoro-1,3-diphenylbutan-1-one (9): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **9** (pale yellow liquid, 107.8 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.24 (m, 5H), 3.83 – 3.63 (m, 1H), 1.51 (d, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –104.77 (dd, *J* = 272.6, 15.6 Hz, 1F), –106.18 (dd, *J* = 272.3, 16.4 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.3 (t, *J* = 30.3 Hz), 137.3 (d, *J* = 3.9 Hz), 133.9, 132.9, 129.9 (t, *J* = 3.4 Hz), 129.1, 128.5, 128.4, 127.7, 119.5 (t, *J* = 257.4 Hz), 43.9 (t, *J* = 22.1 Hz), 14.3 (t, *J* = 4.6 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{14}F_2ONa$ 283.0910; Found 283.0918.



10

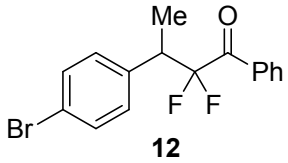
2,2-difluoro-1-phenyl-3-(*p*-tolyl)butan-1-one (10): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **10** (pale yellow liquid, 119.3 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 3.78 – 3.64 (m, 1H), 2.31 (s, 3H), 1.49 (d, *J* = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –104.92 (dd, *J* = 271.8, 15.2 Hz, 1F), –106.28 (dd, *J* = 271.8, 16.5 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.3 (t, *J* = 30.2 Hz), 137.4, 134.2 (d, *J* = 4.4 Hz), 133.9, 132.9, 129.9 (t, *J* = 3.4 Hz), 129.1, 129.0, 128.5, 119.5 (t, *J* = 257.2 Hz), 43.5 (t, *J* = 22.1 Hz), 21.0, 14.3 (t, *J* = 4.6 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{16}F_2ONa$ 297.1067; Found 297.1063.



11

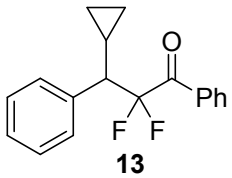
3-(4-chlorophenyl)-2,2-difluoro-1-phenylbutan-1-one (11): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **11** (pale yellow liquid, 117.7 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.24 (dt, *J* = 14.0, 7.6 Hz, 4H), 3.73 (tq, *J* = 14.5, 7.2 Hz, 1H), 1.46 (d, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –104.86 (dd, *J* = 276.7, 15.3 Hz, 1F), –105.76 (dd, *J* = 277.0, 15.8 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.73 (t, *J* = 30.4 Hz), 135.9 (t, *J* = 2.8 Hz), 134.13 (s), 133.56 (s), 132.63 (t, *J* = 2.0 Hz), 130.47

(s), 129.87 (t, J = 3.5 Hz), 128.58 (d, J = 3.7 Hz), 119.20 (t, J = 257.8 Hz), 43.17 (t, J = 22.2 Hz), 14.34 (t, J = 4.7 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{13}ClF_2ONa$ 294.0623; Found 294.0629.



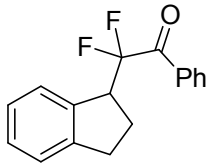
12

3-(4-bromophenyl)-2,2-difluoro-1-phenylbutan-1-one (12): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **12** (yellow liquid, 132.2 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.9 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.51 – 7.34 (m, 4H), 7.19 (d, J = 8.3 Hz, 2H), 3.94 – 3.56 (m, 1H), 1.48 (d, J = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –104.83 (dd, J = 281.1, 18.9 Hz, 1F), –105.62 (dd, J = 277.6, 16.2 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.6 (t, J = 30.4 Hz), 136.4 (t, J = 2.9 Hz), 134.1, 132.6 (t, J = 2.0 Hz), 131.5, 130.8, 129.8 (t, J = 3.5 Hz), 128.6, 121.7, 119.1 (t, J = 257.8 Hz), 43.2 (t, J = 22.2 Hz), 14.3 (t, J = 4.7 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{13}BrF_2ONa$ 338.0118; Found 338.0111.



13

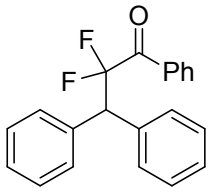
3-cyclopropyl-2,2-difluoro-1,3-diphenylpropan-1-one (13): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **13** (yellow liquid, 124.5 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.7 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.39 – 7.27 (m, 5H), 2.79 (ddd, J = 18.9, 12.6, 10.5 Hz, 1H), 1.49 – 1.33 (m, 1H), 0.76 – 0.57 (m, 1H), 0.51 (ddd, J = 14.0, 9.0, 5.4 Hz, 1H), 0.30 (dq, J = 10.1, 5.1 Hz, 1H), 0.14 –0.01 (m, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –100.46 (dd, J = 266.4, 14.4 Hz, 1F), –106.61 (dd, J = 266.5, 21.5 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ190.9 (t, J = 29.0 Hz), 136.4 (d, J = 2.9 Hz), 133.9, 133.3, 129.8 (t, J = 3.7 Hz), 129.6, 128.6, 128.3, 127.6, 119.6 (t, J = 257.7 Hz), 54.8 (t, J = 21.3 Hz), 10.5 (dd, J = 6.8, 3.7 Hz), 7.1, 3.4; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{16}F_2ONa$ 309.1067; Found 309.1073.



14

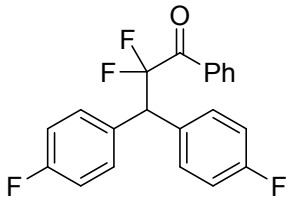
2-(2,3-dihydro-1*H*-inden-1-yl)-2,2-difluoro-1-phenylethanone (14): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **14** (yellow liquid, 97.8 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.5 Hz, 2H), 7.62 (dd, J = 10.6, 4.3 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 7.5 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.17 (td, J = 7.7, 2.1 Hz, 1H), 4.26 – 4.06 (m, 1H), 3.09 (dt, J = 16.1, 8.1 Hz, 1H), 2.98 – 2.84 (m, 1H), 2.36 (ddd, J = 16.6, 13.7, 9.0 Hz, 1H), 2.24 (ddt, J = 13.6, 9.0, 4.7 Hz,

1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –96.68 (dd, *J* = 271.9, 15.1 Hz, 1F), –103.63 (dd, *J* = 271.9, 21.1 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9 (t, *J* = 31.4 Hz), 145.5, 137.9 (dd, *J* = 3.6, 1.3 Hz), 134.2, 132.6 (t, *J* = 2.4 Hz), 130.1 (t, *J* = 3.4 Hz), 128.6, 127.9, 126.3, 126.2 (d, *J* = 2.3 Hz), 124.7, 120.2 (t, *J* = 256.3 Hz), 48.6 (dd, *J* = 23.3, 21.2 Hz), 31.6, 26.0 (dd, *J* = 5.2, 3.2 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{14}F_2ONa$ 295.0910; Found 295.0917.



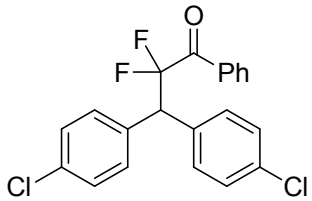
15

2,2-difluoro-1,3,3-triphenylpropan-1-one (15): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **15** (white solid, 154.7 mg, 96% yield). M.p.: 82–83 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 7.83 (m, 2H), 7.67 – 7.52 (m, 1H), 7.48 – 7.37 (m, 6H), 7.34 – 7.22 (m, 6H), 5.03 (t, *J* = 18.1 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –100.00 (d, *J* = 17.8 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9 (t, *J* = 30.1 Hz), 136.3 (t, *J* = 2.1 Hz), 134.0, 132.8 (t, *J* = 2.2 Hz), 129.8 (t, *J* = 3.4 Hz), 129.7, 128.6, 127.5, 118.9 (t, *J* = 259.1 Hz), 54.9 (t, *J* = 21.4 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{16}F_2ONa$ 345.1067; Found 309.1060.



16

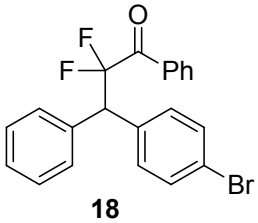
2,2-difluoro-3,3-bis(4-fluorophenyl)-1-phenylpropan-1-one (16): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **16** (white solid, 119.8 mg, 67% yield). M.p.: 46–47 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.35 (dd, *J* = 8.1, 5.5 Hz, 4H), 7.00 (t, *J* = 8.7 Hz, 4H), 5.02 (t, *J* = 17.8 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –100.32 (d, *J* = 19.7 Hz, 2F), –112.65 – –116.65 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.5 (t, *J* = 30.2 Hz), 163.4, 160.9, 134.2, 132.6 (t, *J* = 2.1 Hz), 131.9 (d, *J* = 2.5 Hz), 131.2, 131.2, 130.9, 129.8 (t, *J* = 3.3 Hz), 128.6, 118.6 (t, *J* = 259.4 Hz), 115.7, 115.5, 53.2 (t, *J* = 21.8 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{14}F_4ONa$ 381.0878; Found 381.0872.



17

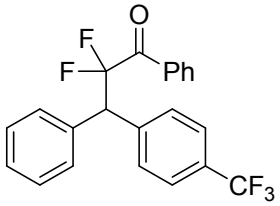
3,3-bis(4-chlorophenyl)-2,2-difluoro-1-phenylpropan-1-one (17): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **17** (white solid, 134.9 mg, 69% yield). M.p.: 92–93 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.66 – 7.59 (m, 1H), 7.46 (dd, *J* = 10.8, 4.9 Hz, 2H), 7.33 –

7.29 (m, 4H), 7.27 (dd, *J* = 5.6, 2.4 Hz, 4H), 4.99 (t, *J* = 17.7 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –99.91 (d, *J* = 18.5 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.2 (t, *J* = 30.3 Hz), 134.5 (t, *J* = 2.1 Hz), 134.3, 133.8, 132.4 (t, *J* = 2.5 Hz), 130.9, 129.9 (t, *J* = 3.3 Hz), 128.9, 128.7, 118.7 (t, *J* = 231.2 Hz), 53.4 (t, *J* = 21.8 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{14}Cl_2F_2ONa$ 413.0287; Found 413.0295.



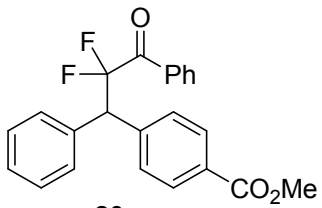
18

3-(4-bromophenyl)-2,2-difluoro-1,3-diphenylpropan-1-one (18): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **18** (white solid, 140.4 mg, 70% yield). M.p.: 80–81 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.33 – 7.26 (m, 5H), 4.99 (t, *J* = 17.9 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –99.40 (dd, *J* = 286.5, 19.5 Hz, 1F), –100.42 (dd, *J* = 286.7, 19.3 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.5 (t, *J* = 30.2 Hz), 135.8 (t, *J* = 2.1 Hz), 135.5 (dd, *J* = 2.7, 1.4 Hz), 134.2, 132.6 (t, *J* = 2.1 Hz), 131.7, 131.3, 129.9 (t, *J* = 3.3 Hz), 129.6, 128.7, 128.6, 127.7, 121.7, 118.7 (t, *J* = 259.5 Hz), 54.2 (t, *J* = 21.6 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{15}BrF_2ONa$ 400.0274; Found 400.0268.



19

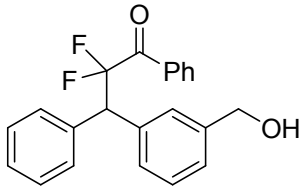
2,2-difluoro-1,3-diphenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (19): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **19** (white solid, 169.8 mg, 87% yield). M.p.: 63–64 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 (q, *J* = 8.6 Hz, 4H), 7.51 – 7.42 (m, 2H), 7.33 (ddd, *J* = 14.4, 10.6, 6.9 Hz, 5H), 5.10 (t, *J* = 17.8 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.65 (s, 3F), –99.59 (qd, *J* = 288.3, 19.8 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.3 (t, *J* = 30.4 Hz), 140.6 (d, *J* = 2.9 Hz), 135.5 (d, *J* = 4.1 Hz), 134.3, 132.5 (t, *J* = 2.2 Hz), 130.0, 129.9 (t, *J* = 3.1 Hz), 129.6, 128.8, 128.7, 127.9, 127.4, 127.3, 127.1 (d, *J* = 1.0 Hz), 125.5 (q, *J* = 3.7 Hz), 118.7 (t, *J* = 260.6 Hz), 54.5 (t, *J* = 21.7 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{15}F_5ONa$ 390.1043; Found 390.1051.



20

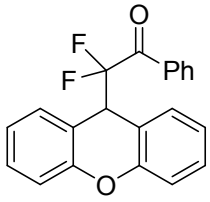
methyl 4-(2,2-difluoro-3-oxo-1,3-diphenylpropyl)benzoate (20): The crude products were

purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **20** (white solid, 119.6 mg, 63% yield). M.p.: 101–102 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 – 7.80 (m, 4H), 7.60 (dd, *J* = 10.7, 4.2 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.33 – 7.25 (m, 3H), 5.10 (t, *J* = 17.4 Hz, 1H), 3.88 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –99.13 (dd, *J* = 286.1, 17.1 Hz, 1F), –100.09 (dd, *J* = 286.2, 17.0 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.4 (t, *J* = 30.3 Hz), 166.7, 141.6 (d, *J* = 2.6 Hz), 135.6 (d, *J* = 2.8 Hz), 134.2, 132.5 (t, *J* = 2.0 Hz), 129.8 (t, *J* = 3.5 Hz), 129.8, 129.7 (d, *J* = 4.6 Hz), 129.3, 128.7, 128.6, 127.8, 118.7 (t, *J* = 259.6 Hz), 54.7 (t, *J* = 21.6 Hz), 52.1; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{18}F_2O_3Na$ 403.1122; Found 403.1128.



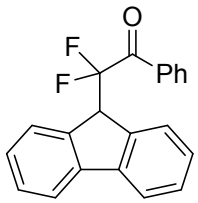
21

2,2-difluoro-3-(3-(hydroxymethyl)phenyl)-1,3-diphenylpropan-1-one (21): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (3/1, v/v) as eluent to give compound **21** (white solid, 149.8 mg, 85% yield). M.p.: 83–84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.39 (m, 6H), 7.36 – 7.23 (m, 5H), 5.07 (t, *J* = 18.1 Hz, 1H), 4.61 (s, 2H), 2.32 (brs, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –99.85 (d, *J* = 16.4 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.8 (t, *J* = 30.2 Hz), 140.1, 136.2 (t, *J* = 1.9 Hz), 135.6 (d, *J* = 2.0 Hz), 134.0, 132.7 (t, *J* = 1.9 Hz), 129.8 (t, *J* = 1.6 Hz), 129.6, 128.5, 127.5, 127.1, 118.8 (t, *J* = 259.1 Hz), 64.7, 54.6 (t, *J* = 21.5 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{18}F_2O_2Na$ 375.1173; Found 375.1180.



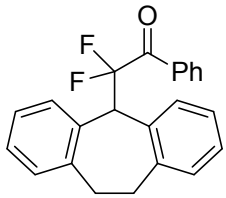
22

2,2-difluoro-1-phenyl-2-(9*H*-xanthen-9-yl)ethanone (22): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (30/1, v/v) as eluent to give compound **22** (pale yellow solid, 129.5 mg, 77% yield). M.p.: 62–63 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.36 – 7.27 (m, 6H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.06 (td, *J* = 7.5, 1.0 Hz, 2H), 4.97 (t, *J* = 14.3 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –103.17 (d, *J* = 13.9 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.0 (t, *J* = 29.6 Hz), 153.5, 133.9, 133.2 (t, *J* = 1.7 Hz), 130.6, 129.8 (t, *J* = 3.7 Hz), 129.5, 128.3, 123.3, 118.1 (t, *J* = 260.5 Hz), 116.8, 116.3 (t, *J* = 3.1 Hz), 44.4 (t, *J* = 23.8 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{14}F_2O_2Na$ 359.0860; Found 359.0852.



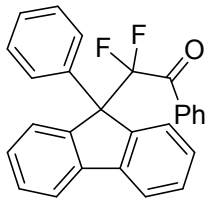
23

2-(9*H*-fluoren-9-yl)-2,2-difluoro-1-phenylethanone (23): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **23** (white solid, 134.5 mg, 84% yield). M.p.: 83–84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.53 (m, 3H), 7.43 (q, *J* = 7.7 Hz, 4H), 7.30 (t, *J* = 7.5 Hz, 2H), 4.98 (t, *J* = 14.7 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –98.15 (d, *J* = 15.5 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.1 (t, *J* = 31.1 Hz), 142.3, 138.9 (t, *J* = 3.7 Hz), 134.1, 132.6 (t, *J* = 2.6 Hz), 130.1 (t, *J* = 3.4 Hz), 128.5 (d, *J* = 4.9 Hz), 127.2, 126.2, 120.0, 119.4 (t, *J* = 258.4 Hz), 51.3 (t, *J* = 23.5 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{14}F_2ONa$ 343.0910; Found 343.0913.



24

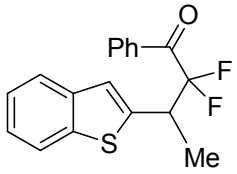
2-(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl)-2,2-difluoro-1-phenylethanone (24): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **24** (white solid, 141.1 mg, 81% yield). M.p.: 142–143 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 6.8 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.17 (t, *J* = 9.9 Hz, 6H), 7.07 (d, *J* = 5.9 Hz, 2H), 5.02 (t, *J* = 18.1 Hz, 1H), 3.76 – 3.54 (m, 2H), 2.91 (dd, *J* = 14.5, 8.2 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –96.05 (d, *J* = 18.7 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.9 (t, *J* = 25.6 Hz), 141.9, 133.8, 133.4, 133.2, 131.8, 130.8, 129.7 (t, *J* = 3.5 Hz), 128.4, 128.3, 125.9, 119.6 (d, *J* = 260.5 Hz), 58.5 (t, *J* = 23.1 Hz), 33.1 (t, *J* = 2.7 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{18}F_2ONa$ 371.1223; Found 371.1216.



25

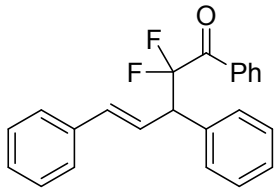
2,2-difluoro-1-phenyl-2-(9-phenyl-9*H*-fluoren-9-yl)ethanone (25): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **25** (white solid, 77.2 mg, 39% yield). M.p.: 136–137 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 4H), 7.45 (t, *J* = 6.9 Hz, 4H), 7.38 – 7.30 (m, 3H), 7.28 – 7.19 (m, 5H), 7.14 (t, *J* = 7.9 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –96.41 (s, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.2 (t, *J* = 30.0 Hz), 144.3 (t, *J* = 3.1 Hz), 141.5, 138.8, 133.9 (t, *J* = 1.8 Hz), 132.9,

129.3 (t, *J* = 3.7 Hz), 128.7, 128.4, 127.7 (dd, *J* = 6.5, 3.0 Hz), 127.4, 127.3, 120.3 (t, *J* = 265.7 Hz), 120.0, 63.8 (t, *J* = 22.0 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{18}F_2ONa$ 419.1223; Found 419.1228.



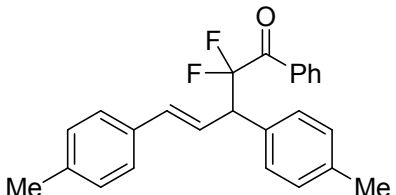
26

3-(benzo[*b*]thiophen-2-yl)-2,2-difluoro-1-phenylbutan-1-one (26): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **26** (white solid, 77.2 mg, 61% yield). M.p.: 84–85 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.78 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.70 (dd, *J* = 6.7, 1.9 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.21 (s, 1H), 4.46 – 3.67 (m, 1H), 1.61 (d, *J* = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –104.25 (dd, *J* = 279.2, 13.9 Hz, 1F), –105.47 (dd, *J* = 279.4, 15.8 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.5 (t, *J* = 30.4 Hz), 140.6 (dd, *J* = 4.7, 1.4 Hz), 139.6, 139.3, 134.2, 132.6 (t, *J* = 2.1 Hz), 129.9 (t, *J* = 3.4 Hz), 128.6, 124.2 (d, *J* = 3.1 Hz), 123.7, 123.4, 122.1, 119.9 (t, *J* = 258.9 Hz), 40.0 (t, *J* = 23.4 Hz), 15.5 (t, *J* = 4.6 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}F_2OSNa$ 339.0631; Found 339.0638.



27

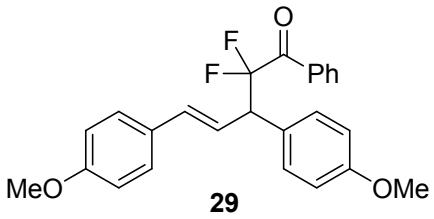
(*E*)-2,2-difluoro-1,3,5-triphenylpent-4-en-1-one (27): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **27** (white solid, 142.8 mg, 82% yield). M.p.: 88–89 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.1 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.45 (t, *J* = 7.1 Hz, 2H), 7.42 – 7.27 (m, 9H), 7.25 – 7.22 (m, 1H), 6.55 (s, 2H), 4.49 (t, *J* = 16.2 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –102.53 (dd, *J* = 275.3, 16.9 Hz, 1F), –103.38 (dd, *J* = 275.3, 16.7 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9 (t, *J* = 29.8 Hz), 136.5, 135.4, 135.3, 134.0, 132.9, 129.8 (d, *J* = 3.4 Hz), 129.6, 128.6 (t, *J* = 7.6 Hz), 127.9, 126.5, 123.6 (t, *J* = 3.9 Hz), 118.7 (t, *J* = 258.9 Hz), 53.3 (t, *J* = 22.0 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{18}F_2ONa$ 371.1223; Found 371.1218.



28

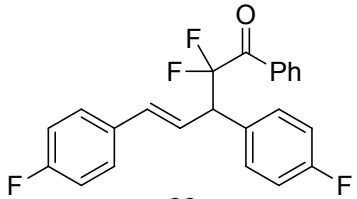
(*E*)-2,2-difluoro-1-phenyl-3,5-di-*p*-tolylpent-4-en-1-one (28): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **28** (white solid, 172.8 mg, 92% yield). M.p.: 96–97 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.19 (m, 4H),

7.12 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.58 – 6.33 (m, 2H), 4.60 – 4.10 (m, 1H), 2.30 (s, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –103.19 (d, *J* = 16.2 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.1 (t, *J* = 29.7 Hz), 137.8, 137.6, 135.0, 134.0, 133.9, 133.0, 132.5, 129.9 (t, *J* = 3.4 Hz), 129.5, 129.4, 129.3, 128.6, 126.5, 122.7 (t, *J* = 4.2 Hz), 118.8 (t, *J* = 258.6 Hz), 53.1 (t, *J* = 22.0 Hz), 21.2 (d, *J* = 10.7 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{22}F_2ONa$ 399.1536; Found 399.1540.



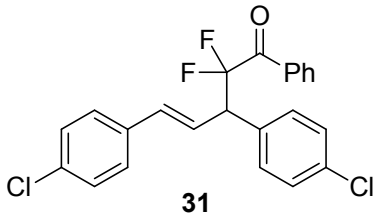
29

(*E*)-2,2-difluoro-3,5-bis(4-methoxyphenyl)-1-phenylpent-4-en-1-one (29): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (30/1, v/v) as eluent to give compound **29** (white solid, 181.7 mg, 89% yield). M.p.: 104–105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.56 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.27 (m, 4H), 6.91 – 6.81 (m, 4H), 6.43 (dt, *J* = 15.8, 11.9 Hz, 2H), 4.50 – 4.31 (m, 1H), 3.79 (s, 3H), 3.79 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –102.78 (dd, *J* = 271.5, 14.8 Hz, 1F), –103.91 (dd, *J* = 269.9, 13.3 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.1 (t, *J* = 29.6 Hz), 159.2 (d, *J* = 24.9 Hz), 134.4, 133.9, 133.0 (d, *J* = 1.6 Hz), 130.6, 129.8 (t, *J* = 3.3 Hz), 129.3, 129.2, 128.5, 127.6, 121.4 (t, *J* = 4.6 Hz), 118.7 (t, *J* = 258.5 Hz), 114.0, 113.8, 55.1 (d, *J* = 5.7 Hz), 52.6 (t, *J* = 22.1 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{22}F_2O_3Na$ 431.1435; Found 431.1429.



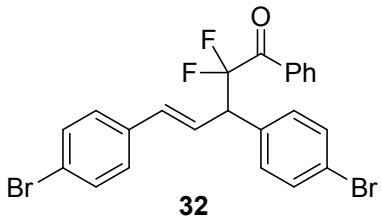
30

(*E*)-2,2-difluoro-3,5-bis(4-fluorophenyl)-1-phenylpent-4-en-1-one (30): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **30** (white solid, 149.8 mg, 78% yield). M.p.: 71–72 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.61 (dd, *J* = 10.7, 4.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.28 (m, 4H), 7.09 – 6.95 (m, 4H), 6.46 (dt, *J* = 15.8, 11.8 Hz, 2H), 4.49 (td, *J* = 16.1, 7.8 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –102.46 (dd, *J* = 277.7, 17.8 Hz, 1F), –103.44 (dd, *J* = 278.3, 17.7 Hz, 1F), –113.67 (dd, *J* = 12.3, 8.1 Hz, 1F), –114.17 (dd, *J* = 12.4, 8.0 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.6 (t, *J* = 29.9 Hz), 163.7 (d, *J* = 15.6 Hz), 161.2 (d, *J* = 15.1 Hz), 134.2 (d, *J* = 2.9 Hz), 132.7 (t, *J* = 1.9 Hz), 132.5 (d, *J* = 3.3 Hz), 131.2, 131.2, 129.8 (t, *J* = 3.4 Hz), 128.7, 128.1, 128.0, 123.1 (d, *J* = 1.8 Hz), 118.5 (t, *J* = 259.4 Hz), 115.7, 115.6, 115.5, 115.4, 52.4 (t, *J* = 22.2 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{16}F_4ONa$ 407.1035; Found 431.1429.



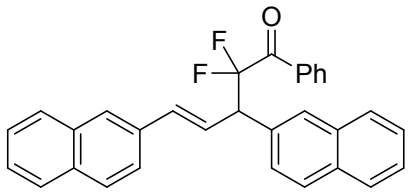
31

(*E*)-3,5-bis(4-chlorophenyl)-2,2-difluoro-1-phenylpent-4-en-1-one (31): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **31** (white solid, 208.8 mg, 82% yield). M.p.: 119–120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.62 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.28 (s, 4H), 6.67 – 6.20 (m, 2H), 4.54 (tdd, *J* = 16.0, 4.5, 2.6 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –102.01 (dd, *J* = 278.9, 16.1 Hz, 1F), –102.84 (dd, *J* = 278.8, 15.6 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.2 (t, *J* = 29.9 Hz), 134.7, 134.3, 134.2, 133.8, 133.7, 133.6, 132.5 (d, *J* = 1.7 Hz), 130.9, 129.8 (t, *J* = 3.3 Hz), 128.8, 128.6, 127.6, 123.7 (t, *J* = 4.1 Hz), 118.3 (t, *J* = 259.4 Hz), 52.4 (t, *J* = 22.1 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{16}Cl_2F_2ONa$ 416.0546; Found 416.0553.



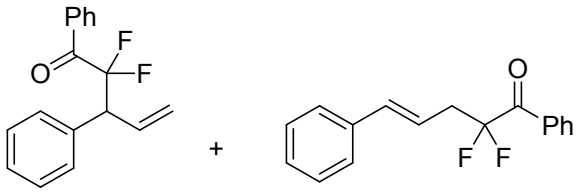
32

(*E*)-3,5-bis(4-bromophenyl)-2,2-difluoro-1-phenylpent-4-en-1-one (32): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **31** (white solid, 217.6 mg, 86% yield). M.p.: 146–147 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.70 – 7.57 (m, 1H), 7.48 (t, *J* = 8.1 Hz, 4H), 7.45 – 7.40 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.18 (m, 2H), 6.61 – 6.30 (m, 2H), 4.50 (td, *J* = 16.1, 6.5 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –102.01 (dd, *J* = 279.7, 16.4 Hz, 1F), –102.81 (dd, *J* = 280.0, 16.2 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.4 (t, *J* = 30.0 Hz), 135.3, 134.5, 134.4, 134.3 (t, *J* = 2.1 Hz), 132.6, 131.9, 131.8, 131.4, 130.0 (t, *J* = 3.3 Hz), 128.8, 128.1, 124.0 (t, *J* = 4.2 Hz), 122.2, 122.0, 118.4 (t, *J* = 259.5 Hz), 52.6 (t, *J* = 22.1 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{16}Br_2F_2ONa$ 528.9413; Found 528.9422.



33

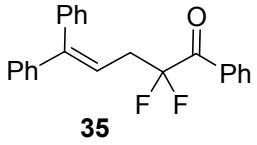
(*E*)-2,2-difluoro-3,5-di(naphthalen-2-yl)-1-phenylpent-4-en-1-one (33): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **33** (white solid, 114.2 mg, 51% yield). M.p.: 123–124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 2H), 7.88 – 7.76 (m, 7H), 7.69 (s, 1H), 7.60 (td, *J* = 6.5, 1.5 Hz, 3H), 7.51 – 7.42 (m, 6H), 6.81 – 6.71 (m, 2H), 4.74 (td, *J* = 16.3, 6.8 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –96.03 (d, *J* = 21.1 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.8 (t, *J* = 29.8 Hz), 135.5, 134.1, 133.9, 133.4, 133.3, 133.1, 132.9 (d, *J* = 3.6 Hz), 129.9 (t, *J* = 3.4 Hz), 128.9, 128.6, 128.4, 128.2, 128.0, 128.0, 127.6 (d, *J* = 1.6 Hz), 127.2, 126.6, 126.3, 126.2 (d, *J* = 2.1 Hz), 126.0, 124.0 (t, *J* = 4.2 Hz), 123.5, 118.8 (t, *J* = 259.2 Hz), 53.4 (t, *J* = 21.9 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{22}F_2ONa$ 471.1536; Found 471.1529.



34 **34'**

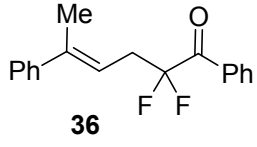
mixture of 2,2-difluoro-1,3-diphenylpent-4-en-1-one (34) and (*E*)-2,2-difluoro-1,5-diphenylpent-4-en-1-one (34') (1.3:1): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give mixture of compounds **34 and 34'** (pale yellow liquid, 113.2 mg, 83% yield, 1.3:1). **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{14}F_2ONa$ 295.0910; Found 295.0903.

^{1}H NMR of 34 (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.53 (dd, *J* = 10.7, 4.2 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.17 (m, 5H), 6.16 (dddd, *J* = 12.8, 8.2, 7.5, 1.6 Hz, 1H), 5.26 (d, *J* = 10.3 Hz, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 4.27 (td, *J* = 16.4, 8.3 Hz, 1H); **^{19}F NMR of 34** (376 MHz, $CDCl_3$) δ –102.77 (dd, *J* = 274.7, 16.9 Hz, 1F), –103.63 (dd, *J* = 274.7, 16.0 Hz, 1F); **^{1}H NMR of 34'** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.27 – 7.23 (m, 2H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.16 (dddd, *J* = 12.8, 8.2, 7.5, 1.6 Hz, 2H), 3.08 (td, *J* = 17.1, 7.3 Hz, 2H); **^{19}F NMR of 34'** (376 MHz, $CDCl_3$) δ –98.84 (t, *J* = 17.1 Hz, 2F); **^{13}C NMR of 34 and 34'** (100 MHz, $CDCl_3$) δ 189.8 (t, *J* = 29.7 Hz), 189.2 (t, *J* = 31.2 Hz), 136.6, 136.2, 135.1 (d, *J* = 2.7 Hz), 134.3, 134.0, 132.9, 132.4 (t, *J* = 4.4 Hz), 132.0 (t, *J* = 2.6 Hz), 130.2 (t, *J* = 3.2 Hz), 129.8 (t, *J* = 3.4 Hz), 129.6, 128.7, 128.6, 128.5, 127.8, 127.7, 126.3, 120.5, 118.8 (t, *J* = 5.3 Hz), 118.7 (t, *J* = 254.2 Hz), 118.6 (t, *J* = 258.7 Hz), 53.9 (t, *J* = 21.8 Hz), 37.8 (t, *J* = 23.6 Hz).



35

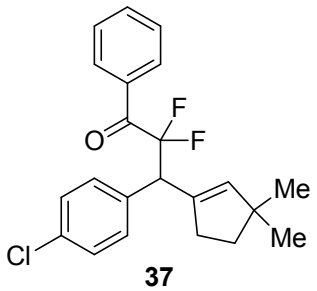
2,2-difluoro-1,5,5-triphenylpent-4-en-1-one (35): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **35** (pale yellow liquid, 137.2 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.25 – 7.15 (m, 5H), 7.13 – 7.04 (m, 2H), 6.14 (t, *J* = 7.4 Hz, 1H), 3.02 (td, *J* = 17.5, 7.4 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –98.89 – –99.41 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.1 (t, *J* = 30.6 Hz), 147.0, 141.7, 139.0, 134.3, 131.8 (t, *J* = 2.2 Hz), 130.1 (t, *J* = 3.2 Hz), 129.6, 128.6, 128.4, 128.2, 127.6, 127.4, 127.3, 118.9 (t, *J* = 254.2 Hz), 117.4 (t, *J* = 5.0 Hz), 35.1 (t, *J* = 23.3 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{18}F_2ONa$ 371.1223; Found 371.1231.



36

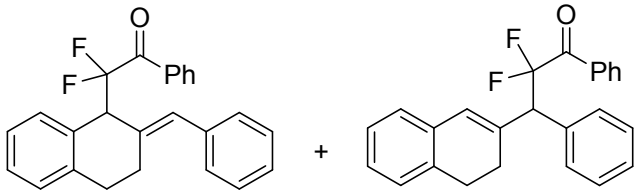
(*E*)-2,2-difluoro-1,5-diphenylhex-4-en-1-one (36): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **36** (pale yellow liquid, 116.6 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.23 (t, *J* = 7.3 Hz, 2H),

7.17 (dd, *J* = 6.1, 3.6 Hz, 1H), 5.71 (td, *J* = 7.4, 1.2 Hz, 1H), 3.07 (td, *J* = 17.3, 7.4 Hz, 2H), 1.98 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –98.84 (t, *J* = 17.1 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.4 (t, *J* = 31.2 Hz), 143.2, 140.7, 134.3, 130.1 (t, *J* = 3.3 Hz), 128.7, 128.2, 127.2, 125.9, 119.2 (t, *J* = 254.3 Hz), 116.5 (t, *J* = 5.3 Hz), 33.9 (t, *J* = 23.4 Hz), 16.3; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{16}F_2ONa$ 309.1067; Found 309.1073.



37

3-(4-chlorophenyl)-3-(3,3-dimethylcyclopent-1-en-1-yl)-2,2-difluoro-1-phenylpropan-1-one (37): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **37** (white solid, 155.2 mg, 83% yield). M.p.: 51–52 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 3.3 Hz, 3H), 5.43 (s, 1H), 4.33 (dd, *J* = 22.6, 12.6 Hz, 1H), 2.25 (t, *J* = 7.1 Hz, 2H), 1.82 – 1.49 (m, 3H), 1.00 (s, 3H), 0.96 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –97.45 (dd, *J* = 278.5, 13.7 Hz, 1F), –105.91 (dd, *J* = 278.7, 24.1 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.0 (dd, *J* = 30.7, 29.0 Hz), 140.4 (d, *J* = 2.0 Hz), 135.1 (d, *J* = 5.3 Hz), 133.9, 133.7, 133.1 (t, *J* = 2.0 Hz), 133.0 (d, *J* = 2.9 Hz), 131.4, 129.7 (t, *J* = 3.3 Hz), 128.6, 128.5, 118.5 (dd, *J* = 262.1, 256.3 Hz), 50.3 (t, *J* = 21.8 Hz), 45.5, 38.6, 34.4, 28.1, 27.9; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{21}ClF_2ONa$ 397.1147; Found 397.1156.

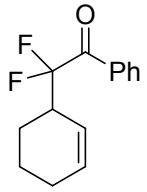


38 **38'**

mixture of (*E*)-2-(2-benzylidene-1,2,3,4-tetrahydronaphthalen-1-yl)-2,2-difluoro-1-phenylethanone (38) and 3-(3,4-dihydronaphthalen-2-yl)-2,2-difluoro-1,3-diphenylpropan-1-one (38') (1:1): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give mixture of compounds **38 and 38'** (pale yellow liquid, 174.1 mg, 93% yield, 1:1). **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{20}F_2ONa$ 397.1380; Found 397.1373.

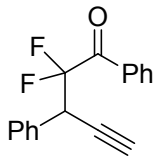
^{1}H NMR of 38 and 38' (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 15.0, 7.8 Hz, 4H), 7.63 (t, *J* = 7.4 Hz, 2H), 7.53 – 7.43 (m, 6H), 7.38 – 7.31 (m, 4H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 2.3 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 3H), 7.16 – 7.11 (m, 2H), 7.11 – 7.05 (m, 3H), 7.01 – 6.96 (m, 1H), 6.56 (s, 1H), 6.38 (s, 1H), 4.58 – 4.28 (m, 2H), 3.24 – 3.02 (m, 1H), 2.92 – 2.76 (m, 3H), 2.73 (t, *J* = 8.1 Hz, 2H), 2.26 (t, *J* = 8.1 Hz, 2H); **^{19}F NMR of 38 and 38'**(376 MHz, $CDCl_3$) δ –97.15 (dd, *J* = 115.7, 15.9 Hz, 1F), –97.87 (dd, *J* = 91.3, 16.0 Hz, 1F), –102.63 (dd, *J* = 179.9, 23.2 Hz, 1F), –103.35 (dd, *J* = 155.2, 23.2 Hz, 1F); **^{13}C NMR of 38 and 38'** (100 MHz, $CDCl_3$) δ 190.8 (t, *J* =

28.6 Hz), 190.0 (t, *J* = 29.8 Hz), 138.6, 136.8, 135.7 (d, *J* = 5.1 Hz), 134.5, 134.5 (d, *J* = 3.1 Hz), 134.0, 133.9, 133.8, 133.6 (d, *J* = 1.8 Hz), 133.2, 133.1, 133.0, 130.7, 130.6 (d, *J* = 3.2 Hz), 130.5 (d, *J* = 2.5 Hz), 130.1, 129.9 – 129.7 (m), 128.9, 128.7, 128.6, 128.4, 128.1, 127.9 (d, *J* = 4.4 Hz), 127.2 (d, *J* = 3.0 Hz), 126.8, 126.4, 126.3, 126.0, 119.6 (dd, *J* = 261.8, 260.1 Hz), 118.9 (dd, *J* = 261.2, 257.3 Hz), 55.6 (t, *J* = 21.3 Hz), 53.0 (t, *J* = 22.0 Hz), 29.2, 28.0, 27.1, 24.1 (d, *J* = 1.6 Hz).



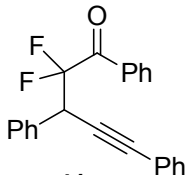
39

2-(cyclohex-2-en-1-yl)-2,2-difluoro-1-phenylethanone (39): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **39** (pale yellow liquid, 75.6 mg, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 5.96 (ddd, *J* = 10.0, 6.5, 3.3 Hz, 1H), 5.68 (dd, *J* = 10.3, 1.8 Hz, 1H), 3.26 – 2.90 (m, 1H), 2.11 – 1.96 (m, 2H), 1.94 – 1.75 (m, 2H), 1.68 – 1.43 (m, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –105.60 (dd, *J* = 275.5, 15.3 Hz, 1F), –107.78 (dd, *J* = 275.5, 16.6 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9 (t, *J* = 30.4 Hz), 134.1, 132.8 (t, *J* = 2.0 Hz), 131.8, 130.1 (t, *J* = 3.6 Hz), 128.7, 121.4 (t, *J* = 5.2 Hz), 119.8 (t, *J* = 255.8 Hz), 40.0 (dd, *J* = 22.7, 20.9 Hz), 24.6, 21.8 (t, *J* = 4.1 Hz), 20.8; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{14}F_2ONa$ 259.0910; Found 259.0916.



40

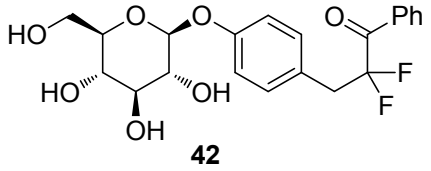
2,2-difluoro-1,3-diphenylpent-4-yn-1-one (40): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **40** (pale yellow liquid, 70.3 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 6.6 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.42 – 7.33 (m, 3H), 4.74 (dd, *J* = 17.7, 11.0 Hz, 1H), 2.41 (d, *J* = 2.1 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –101.17 (dd, *J* = 274.9, 13.6 Hz, 1F), –104.76 (dd, *J* = 275.0, 21.4 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.0 (t, *J* = 29.8 Hz), 134.2, 132.4 (t, *J* = 2.2 Hz), 131.7 (d, *J* = 1.8 Hz), 130.0, 129.9 (d, *J* = 3.5 Hz), 128.5 (d, *J* = 4.2 Hz), 128.4, 116.7 (dd, *J* = 263.4, 260.3 Hz), 78.1 (dd, *J* = 8.8, 2.4 Hz), 74.3, 42.5 (dd, *J* = 27.0, 23.0 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{12}F_2ONa$ 293.0754; Found 293.0759.



41

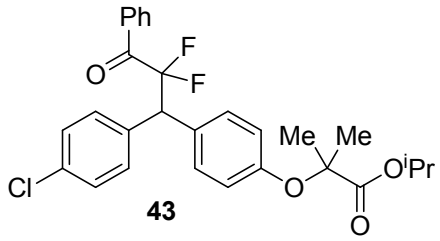
2,2-difluoro-1,3-diphenylpent-4-yn-1-one (41): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **41** (yellow liquid, 150.7 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H),

7.57 (dd, *J* = 14.0, 6.8 Hz, 3H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.31 (m, 5H), 7.30 – 7.19 (m, 3H), 4.89 (dd, *J* = 18.3, 10.4 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –100.50 (dd, *J* = 267.7, 11.7 Hz, 1F), –105.72 (dd, *J* = 267.8, 20.0 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.6 (dd, *J* = 30.2, 28.6 Hz), 134.2, 133.1, 132.9 (t, *J* = 1.7 Hz), 132.4 (d, *J* = 1.9 Hz), 131.7, 130.1, 130.0 (dd, *J* = 3.9, 3.2 Hz), 122.4, 116.9 (dd, *J* = 263.3, 259.9 Hz), 86.2, 83.4 (dd, *J* = 9.4, 2.2 Hz), 43.6 (dd, *J* = 27.4, 23.1 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{16}F_2ONa$ 369.1067; Found 369.1060.



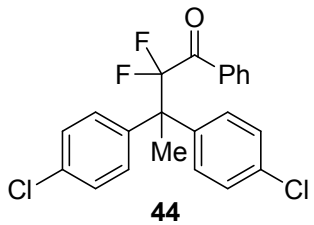
42

2,2-difluoro-1-phenyl-3-(4-(((2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)oxy)phenyl)propan-1-one (42): The crude products were purified by column chromatography with dichloromethane/methanol (10/1 to 5/1, v/v) as eluent to give compound **42** (white solid, 137.9 mg, 65% yield). M.p.: 87–88 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 5.33 (d, *J* = 4.8 Hz, 1H), 5.11 (d, *J* = 4.5 Hz, 1H), 5.04 (d, *J* = 5.2 Hz, 1H), 4.85 (d, *J* = 7.3 Hz, 1H), 4.59 (t, *J* = 5.7 Hz, 1H), 3.75 – 3.66 (m, 1H), 3.51 (ddd, *J* = 24.5, 18.0, 12.3 Hz, 3H), 3.37 – 3.14 (m, 4H); **^{19}F NMR** (376 MHz, DMSO-d_6) δ –98.31 (t, *J* = 20.4 Hz, 2F); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 189.7 (t, *J* = 29.9 Hz), 157.3, 135.2, 132.1, 131.9, 130.0, 129.5, 129.0, 124.5 (t, *J* = 3.1 Hz), 118.8 (t, *J* = 252.8 Hz), 116.4, 100.7, 77.4, 77.0, 73.6, 70.1, 65.4, 63.1, 61.0; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{22}F_2O_7Na$ 447.1231; Found 447.1237.



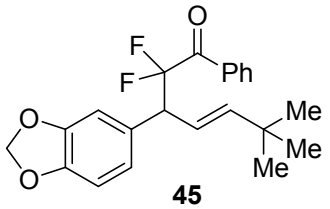
43

isopropyl 2-(4-(1-(4-chlorophenyl)-2,2-difluoro-3-oxo-3-phenylpropyl)phenoxy)-2-methylpropanoate (43): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **43** (colourless liquid, 150.3 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.23 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 5.04 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.93 (t, *J* = 17.8 Hz, 1H), 1.56 (s, 6H), 1.16 (d, *J* = 6.3 Hz, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –99.45 (dd, *J* = 281.1, 17.0 Hz, 1F), –101.50 (dd, *J* = 281.6, 18.8 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.8 (t, *J* = 30.1 Hz), 173.5, 155.1, 135.1 (d, *J* = 3.9 Hz), 134.1, 133.5, 132.8, 130.9, 130.4, 129.7 (t, *J* = 3.3 Hz), 128.8 (d, *J* = 4.6 Hz), 128.7, 128.6, 118.7, 118.6 (t, *J* = 265.5 Hz), 79.1, 68.9, 53.5 (t, *J* = 21.7 Hz), 25.4, 21.5; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{27}ClF_2O_4Na$ 523.1464; Found 523.1456.



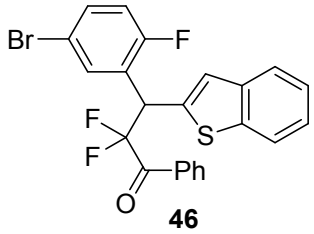
44

3,3-bis(4-chlorophenyl)-2,2-difluoro-1-phenylbutan-1-one (44): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **44** (yellow liquid, 149.7 mg, 74% yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.69 (t, J = 5.9 Hz, 2H), 7.64 (d, J = 7.4 Hz, 1H), 7.45 (t, J = 7.9 Hz, 2H), 7.39 – 7.32 (m, 4H), 7.25 (d, J = 8.6 Hz, 4H), 1.96 (s, 3H); **^{19}F NMR** (376 MHz, DMSO-d_6) δ –97.56 (s, 2F); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 189.4 (t, J = 30.9 Hz), 141.0, 134.6, 133.3 (t, J = 2.1 Hz), 132.4, 130.9, 129.7 (t, J = 3.6 Hz), 129.0, 128.4, 53.4 (t, J = 20.3 Hz), 24.5; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{16}Cl_2F_2ONa$ 427.0444; Found 427.0453.



45

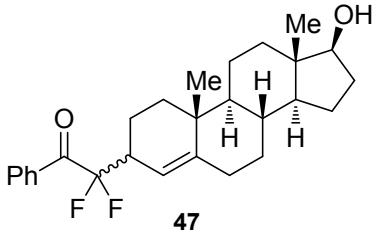
(*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)-2,2-difluoro-6,6-dimethyl-1-phenylhept-4-en-1-one (45): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **45** (yellow liquid, 182.4 mg, 98% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 6.85 (s, 1H), 6.75 (s, 2H), 5.94 (d, J = 1.2 Hz, 2H), 5.70 – 5.42 (m, 2H), 4.31 – 3.80 (m, 1H), 0.93 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –102.41 (dd, J = 264.8, 12.7 Hz, 1F), –106.41 (dd, J = 264.8, 18.8 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.3 (t, J = 29.1 Hz), 147.8, 147.7, 147.1, 133.9, 133.3, 129.8 (t, J = 3.6 Hz), 129.4 (d, J = 3.3 Hz), 128.6, 123.0, 118.8 (t, J = 258.4 Hz), 118.5 (dd, J = 5.8, 2.3 Hz), 109.7, 108.2, 101.1, 53.0 (t, J = 21.9 Hz), 333, 29.1; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{22}F_2O_3Na$ 395.1435; Found 395.1442.



46

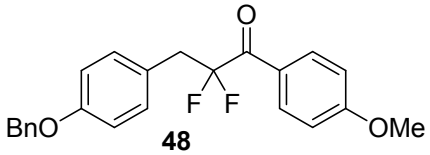
3-(benzo[*b*]thiophen-2-yl)-3-(5-bromo-2-fluorophenyl)-2,2-difluoro-1-phenylpropan-1-one (46): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (40/1, v/v) as eluent to give compound **46** (pale yellow liquid, 206.8 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.5 Hz, 2H), 7.79 – 7.70 (m, 3H), 7.64 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.42 (ddd, J = 8.7, 4.6, 2.5 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.01 (t, J = 9.1 Hz, 1H), 5.79 (dd, J = 21.0, 12.5 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –97.64 (dd, J = 290.1, 6.4 Hz, 1F), –102.13 (dd, J = 290.4, 23.8 Hz, 1F), –118.35 (d, J = 3.3 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.0 (t, J = 30.0 Hz), 160.9, 158.4, 139.8, 139.3, 137.0 (d, J = 5.8 Hz), 134.5,

133.2 (d, J = 2.2 Hz), 132.9, 132.8, 131.9 (t, J = 2.4 Hz), 130.0 (t, J = 3.2 Hz), 128.8, 125.0 (d, J = 2.7 Hz), 124.9 (d, J = 1.9 Hz), 124.7, 124.5, 123.7, 122.0, 117.8 (t, J = 261.5 Hz), 117.5, 117.3, 116.9 (d, J = 3.5 Hz), 42.0 (td, J = 23.3, 4.0 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{14}BrF_3ONa$ 496.9799; Found 496.9791.



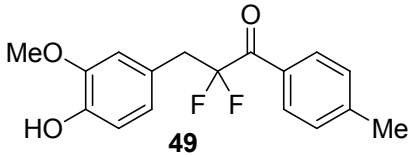
47

3-(benzo[*b*]thiophen-2-yl)-3-(5-bromo-2-fluorophenyl)-2,2-difluoro-1-phenylpropan-1-one (47): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (10/1, v/v) as eluent to give compound **47** (pale yellow liquid, 152.1 mg, 71% yield, dr = 100:1 determined by ^{19}F NMR). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.7 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 5.25 (d, J = 3.5 Hz, 1H), 3.62 (t, J = 8.5 Hz, 1H), 3.13 – 2.78 (m, 1H), 2.32 – 2.17 (m, 1H), 2.13 – 1.99 (m, 2H), 1.86 – 1.76 (m, 2H), 1.70 (ddd, J = 17.7, 9.8, 7.6 Hz, 2H), 1.64 – 1.39 (m, 9H), 1.01 (s, 3H), 0.96 – 0.77 (m, 4H), 0.75 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –103.81 (dd, J = 270.5, 17.5 Hz, 1F), –104.93 (dd, J = 269.8, 16.5 Hz, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.4 (t, J = 30.3 Hz), 150.9, 134.1, 132.9 (d, J = 1.8 Hz), 130.2 (t, J = 3.5 Hz), 128.6, 120.2 (t, J = 256.3 Hz), 112.8 (t, J = 4.8 Hz), 81.8, 53.2, 50.6, 43.0, 38.7 (t, J = 21.7 Hz), 36.9, 36.6, 35.9, 33.8, 32.7, 32.6, 30.5, 23.3, 21.1, 19.6, 18.1 (t, J = 3.2 Hz), 11.1; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{34}F_2O_2Na$ 451.2425; Found 451.2434.



48

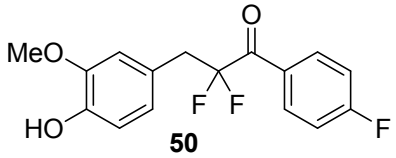
3-(4-(benzyloxy)phenyl)-2,2-difluoro-1-(4-methoxyphenyl)propan-1-one (48): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **48** (white solid, 153.2 mg, 86% yield). M.p.: 76–77 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.8 Hz, 2H), 7.41 (dt, J = 15.4, 7.2 Hz, 4H), 7.33 (dd, J = 8.3, 5.6 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.3 Hz, 4H), 5.05 (s, 2H), 3.88 (s, 3H), 3.45 (t, J = 17.8 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –98.52 (t, J = 17.4 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.0 (t, J = 30.6 Hz), 164.3, 158.3, 136.9, 132.7 (t, J = 3.4 Hz), 131.9, 128.6, 127.9, 127.4, 125.1 (t, J = 2.3 Hz), 123.7 (t, J = 3.6 Hz), 118.6 (t, J = 254.4 Hz), 114.7, 113.9, 70.0, 55.5, 39.5 (t, J = 23.5 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}F_2O_3Na$ 405.1278; Found 405.1271.



49

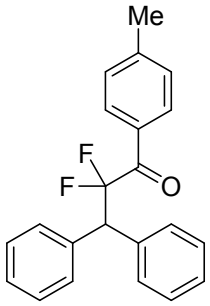
2,2-difluoro-3-(4-hydroxy-3-methoxyphenyl)-1-(*p*-tolyl)propan-1-one (49): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **49** (white solid, 113.3 mg, 74% yield). M.p.: 102–103 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 6.84 (d, J = 8.2 Hz, 1H), 6.77 (d, J = 7.5 Hz, 2H), 5.62 (s, 1H), 3.83 (s, 3H), 3.42 (t, J = 17.6 Hz, 2H), 2.40 (s, 3H); **^{19}F NMR** (376

MHz, $CDCl_3$) δ –98.80 (t, *J* = 17.7 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.3 (t, *J* = 30.6 Hz), 146.3, 145.4, 145.1, 130.2 (t, *J* = 3.2 Hz), 129.7 (d, *J* = 2.3 Hz), 129.3, 123.8, 122.9 (t, *J* = 3.8 Hz), 118.4 (t, *J* = 254.3 Hz), 114.2, 113.2, 55.8, 40.0 (t, *J* = 23.5 Hz), 21.7; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{16}F_2O_3Na$ 329.0965; Found 329.0960.



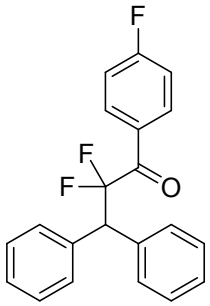
50

2,2-difluoro-1-(4-fluorophenyl)-3-(4-hydroxy-3-methoxyphenyl)propan-1-one (50): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **50** (white solid, 110.1 mg, 71% yield). M.p.: 106–107 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.78 (d, *J* = 7.1 Hz, 2H), 5.65 (s, 1H), 3.85 (s, 3H), 3.44 (t, *J* = 17.7 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –98.51 (t, *J* = 17.2 Hz, 2F), –101.87 – –102.72 (m, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.2 (t, *J* = 31.4 Hz), 167.6, 165.0, 146.3, 145.2, 133.0 (dt, *J* = 9.4, 3.5 Hz), 128.6 (d, *J* = 2.8 Hz), 123.8, 122.6 (t, *J* = 3.8 Hz), 120.9, 118.4, 116.0, 115.8, 114.3, 113.2, 55.9, 39.7 (t, *J* = 23.4 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{13}F_3O_3Na$ 333.0714; Found 333.0718.



51

2,2-difluoro-3,3-diphenyl-1-(*p*-tolyl)propan-1-one (51): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **51** (white solid, 153.1 mg, 91% yield). M.p.: 108–109 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 4H), 7.32 – 7.15 (m, 8H), 5.02 (t, *J* = 18.0 Hz, 1H), 2.37 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –99.84 (d, *J* = 17.6 Hz, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.3 (t, *J* = 29.9 Hz), 145.1, 136.4, 130.2 (t, *J* = 1.7 Hz), 13.0 (t, *J* = 3.3 Hz), 129.7, 129.3, 128.5, 127.4, 119.0 (t, *J* = 259.2 Hz), 55.0 (t, *J* = 21.5 Hz), 21.7; **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{18}F_2ONa$ 359.1223; Found 359.1229.

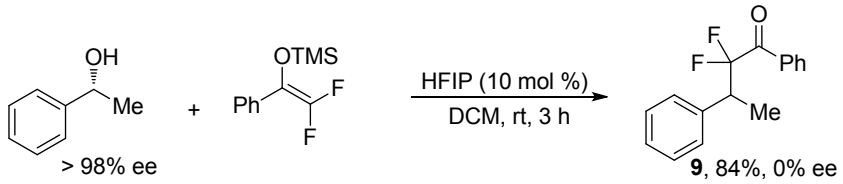


52

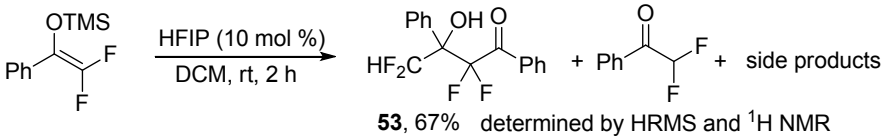
2,2-difluoro-1-(4-fluorophenyl)-3,3-diphenylpropan-1-one (52): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (20/1, v/v) as eluent to give compound **52** (white solid, 141.2 mg, 83% yield). M.p.: 113–114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 4H), 7.32 – 7.20 (m, 6H), 7.13 – 7.03 (m, 2H), 5.00 (t, *J* = 18.2 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –99.72 (d, *J* = 17.6 Hz, 2F), –101.25 – –103.91 (m, 1F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.3 (t, *J* = 30.5 Hz), 167.4, 164.9, 136.2 (t, *J* = 1.7 Hz), 132.8 (dt, *J* = 9.6, 3.5 Hz), 129.6, 129.1 (d, *J* = 2.3 Hz), 128.6, 127.5, 119.0 (t, *J* = 259.1 Hz), 116.0, 115.7, 54.8 (t, *J* = 21.4 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{15}F_3ONa$ 340.1075; Found 340.1077.

Mechanistic experiments

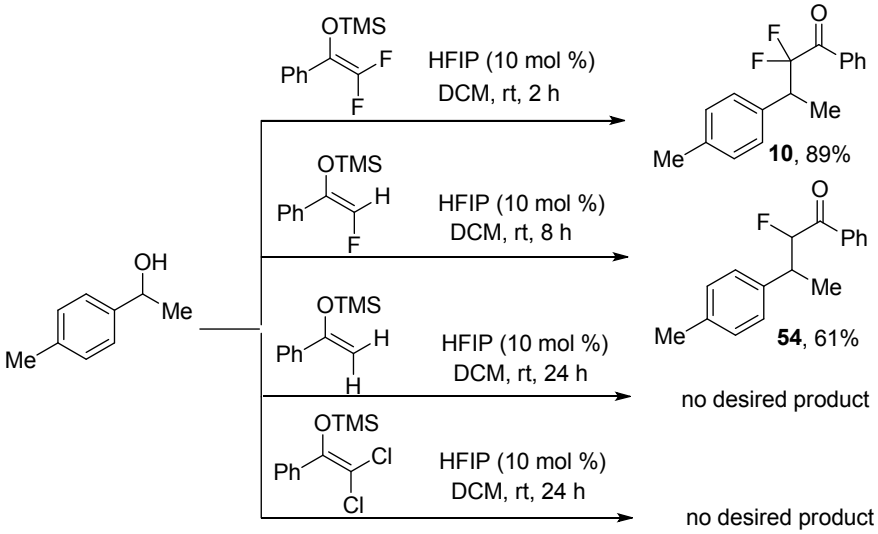
a) HFIP-catalyzed direct alkylation of α,α-difluoroenoxysilane with (*R*)-1-phenylethanol



b) Control experiment



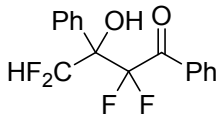
c) Exploration the fluorine effect of HFIP-catalyzed direct alkylation reaction



a) (*R*)-1-phenylethanol (> 98% ee) was treated with difluoroenoxysilane under standard condition, which afforded the desired product **9** in racemic form.

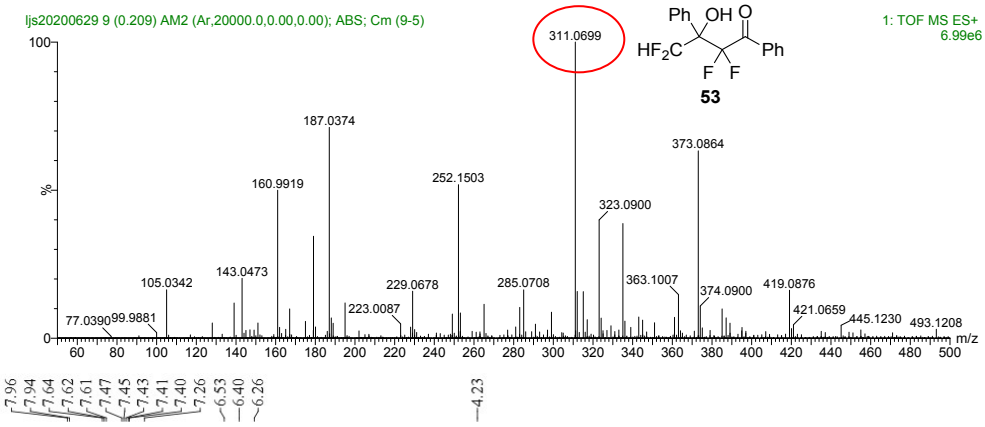
b) To a solution of difluoroenoxysilane (0.3 mmol) in DCM (1.0 mL) was added HFIP (0.03 mmol, 3.0 μL) under room temperature. The resulting mixture was stirred at room temperature until the completion of the reaction (monitored by TLC, approximately 2 hours). Then the mixture was concentrated under reduced pressure. The residue was purified by column chromatography. The self-aldol product **48** was detected by GC-MS analysis in the process of reaction.

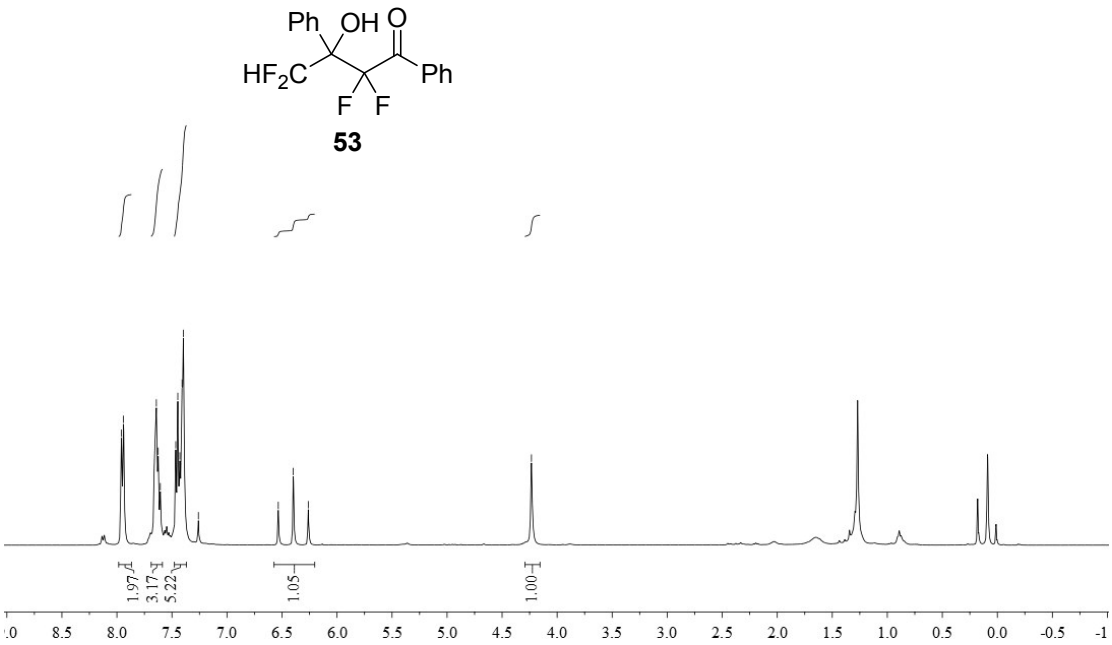
c) The monofluoroenoxysilane, non-fluorinated silyl enol ether and dichloroenoxysilane were reacted under standard condition.

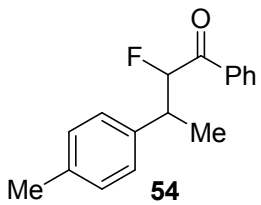


53

2,2-difluoro-1,3-diphenylpent-4-yn-1-one (53): The crude products were purified by column chromatography with petroleum ether/ethyl acetate (10/1, v/v) as eluent to give compound **53** (yellow liquid, 31.4 mg, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.73 – 7.58 (m, 3H), 7.49 – 7.36 (m, 5H), 6.40 (t, J = 54.6 Hz, 1H), 4.23 (s, 1H); **HRMS** (ESI) m/z: [M – H^+] Calcd for $C_{16}H_{11}F_4O_2$ 311.0695; Found 311.0699.







54

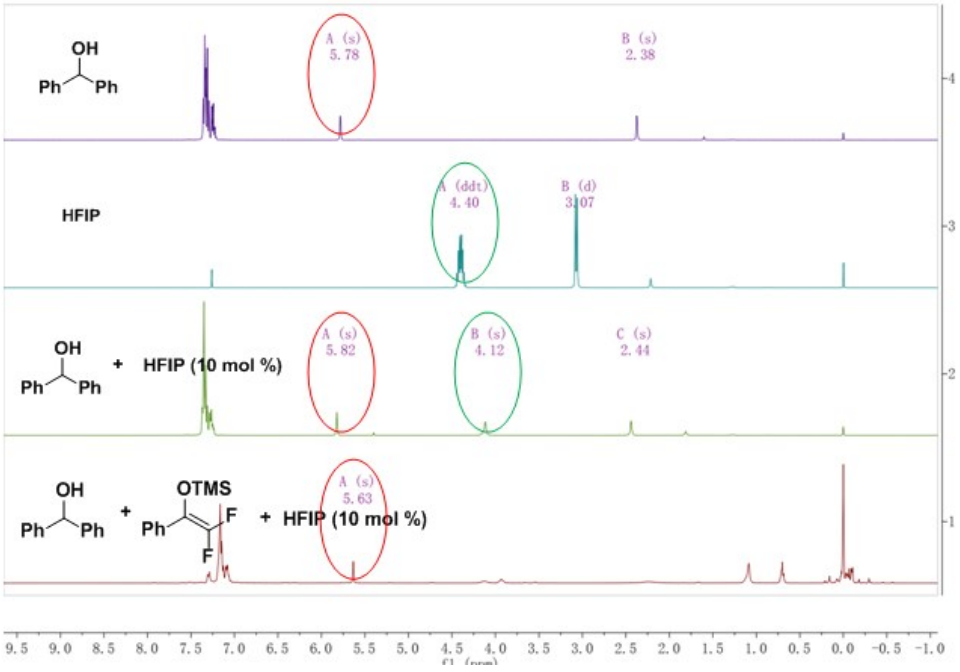
2-fluoro-1-phenyl-3-(*p*-tolyl)butan-1-one (54): The crude products were purified by column

chromatography with petroleum ether/ethyl acetate (50/1, v/v) as eluent to give compound **54** (pale yellow liquid, 78.2 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.15 – 7.05 (m, 4H), 5.55 (dd, *J* = 49.0, 5.6 Hz, 1H), 3.64 – 3.27 (m, 1H), 2.31 (s, 3H), 1.43 (d, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –191.76 (dd, *J* = 49.6, 24.8 Hz), –197.41 (dd, *J* = 49.8, 26.7 Hz); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.7 (d, *J* = 20.5 Hz), 137.1 (d, *J* = 1.4 Hz), 136.8, 135.1 (d, *J* = 1.5 Hz), 133.4, 129.3, 129.1, 128.9 (d, *J* = 4.2 Hz), 128.6, 128.5, 128.0 (d, *J* = 0.5 Hz), 127.6 (d, *J* = 1.0 Hz), 98.4, 96.5, 42.3 (d, *J* = 20.0 Hz), 21.0, 17.6 (d, *J* = 5.4 Hz); **HRMS** (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{17}FONa$ 279.1161; Found 279.1168.

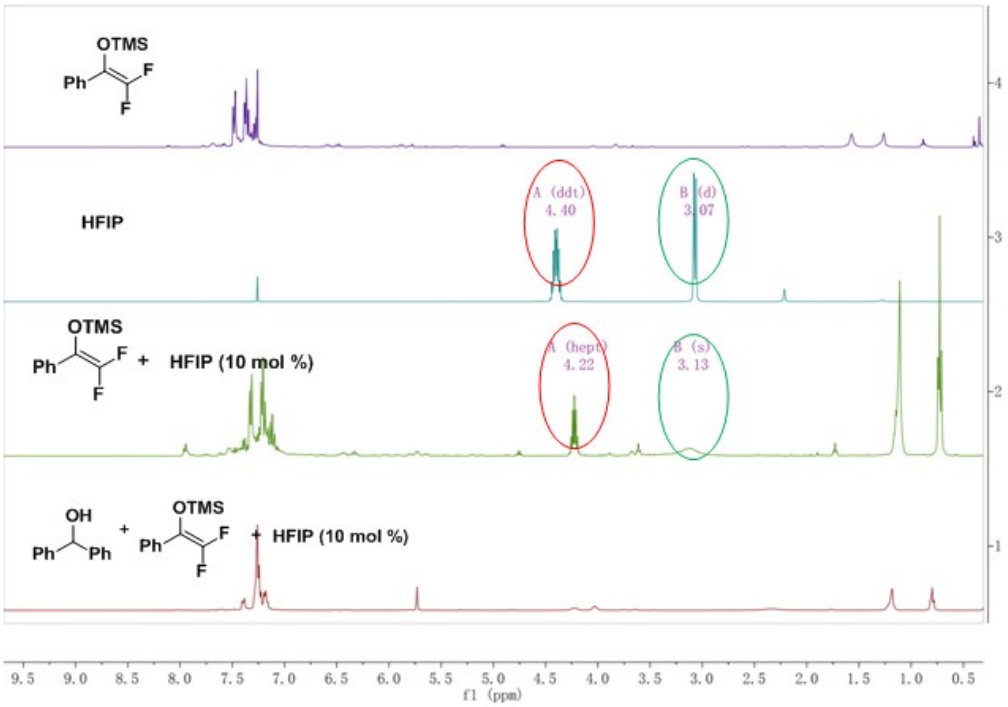
^{1}H-NMR studies: We speculate that hydrogen-bond interactions between several reaction components may play crucial roles in achieving high reactivity. We have performed NMR studies to explore the potential interactions between HFIP and substrate **benzhydrol** or substrate **difluoroenoxysilane**.

Initial result showed that the ^{1}H-NMR signal of the CH group of HFIP changed from δ 4.40 to δ 4.12 when mixing with benzhydrol (HFIP: benzhydrol = 1:10, Figure S1). ^{1}H-NMR signal of the hydroxyl group of HFIP changed greatly.

Initial result showed that the ^{1}H-NMR signal of the CH group of HFIP changed from δ 4.40 to δ 4.22 when mixing with difluoroenoxysilane (HFIP: difluoroenoxysilane = 1:10, Figure S2). ^{1}H-NMR signal of the hydroxyl group of HFIP changed from δ 3.07 to δ 3.13 when mixing with difluoroenoxysilane.

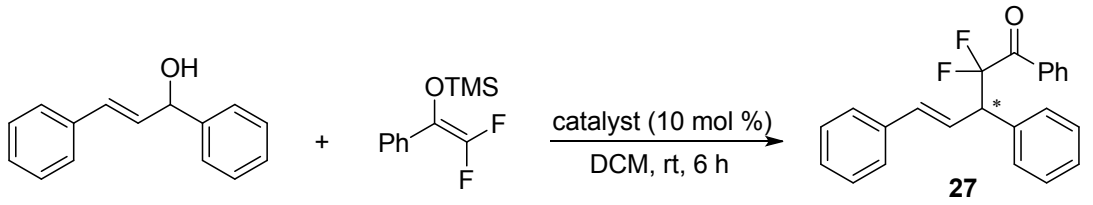


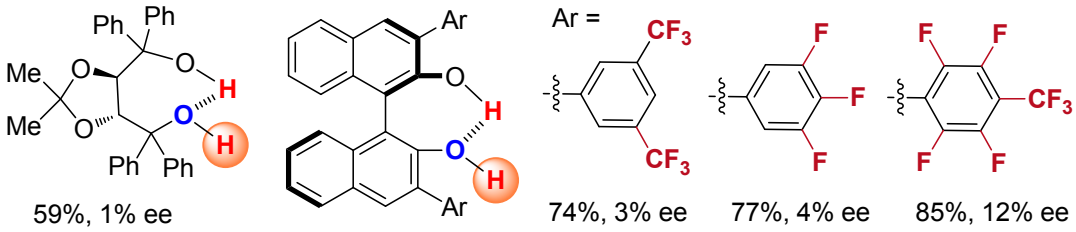
^{1}H NMR of benzhydrol and HFIP in $CDCl_3$ (400 MHz NMR)



^{1}H NMR of difluoroenoxysilane and HFIP in $CDCl_3$ (400 MHz NMR)

Preliminary investigation of catalytic asymmetric variant





Single H-bond network catalysts developed by Rawal and Schaus respectively[3]

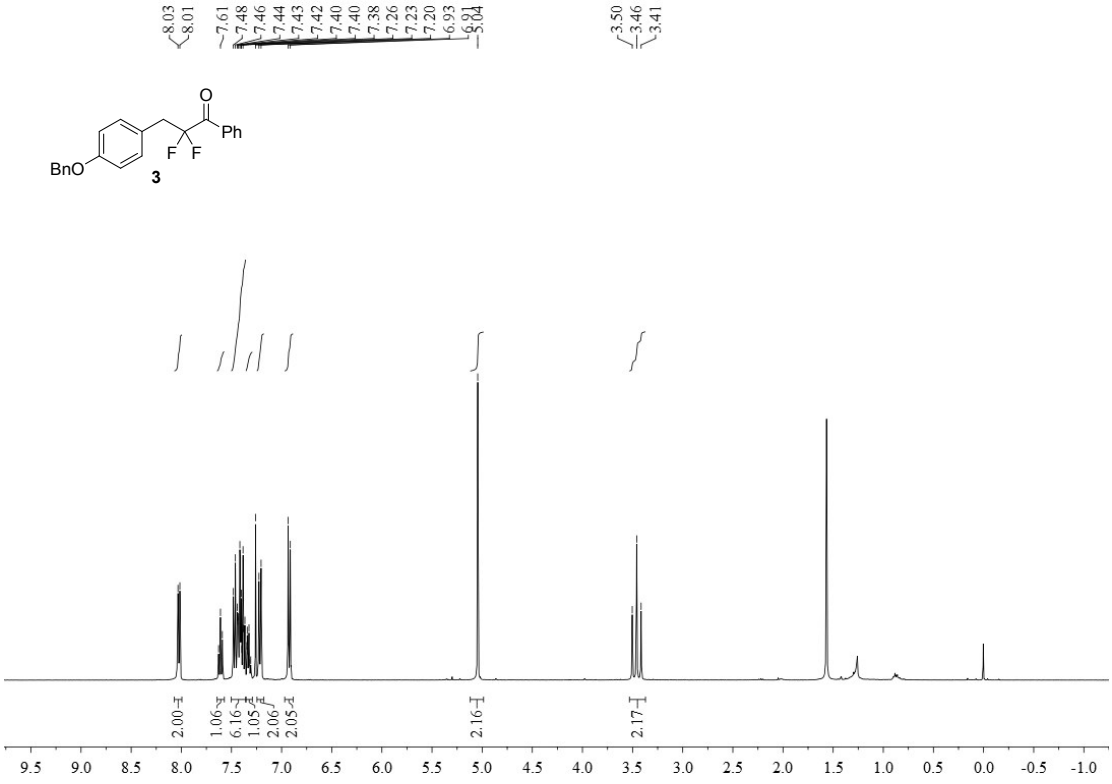
Reference

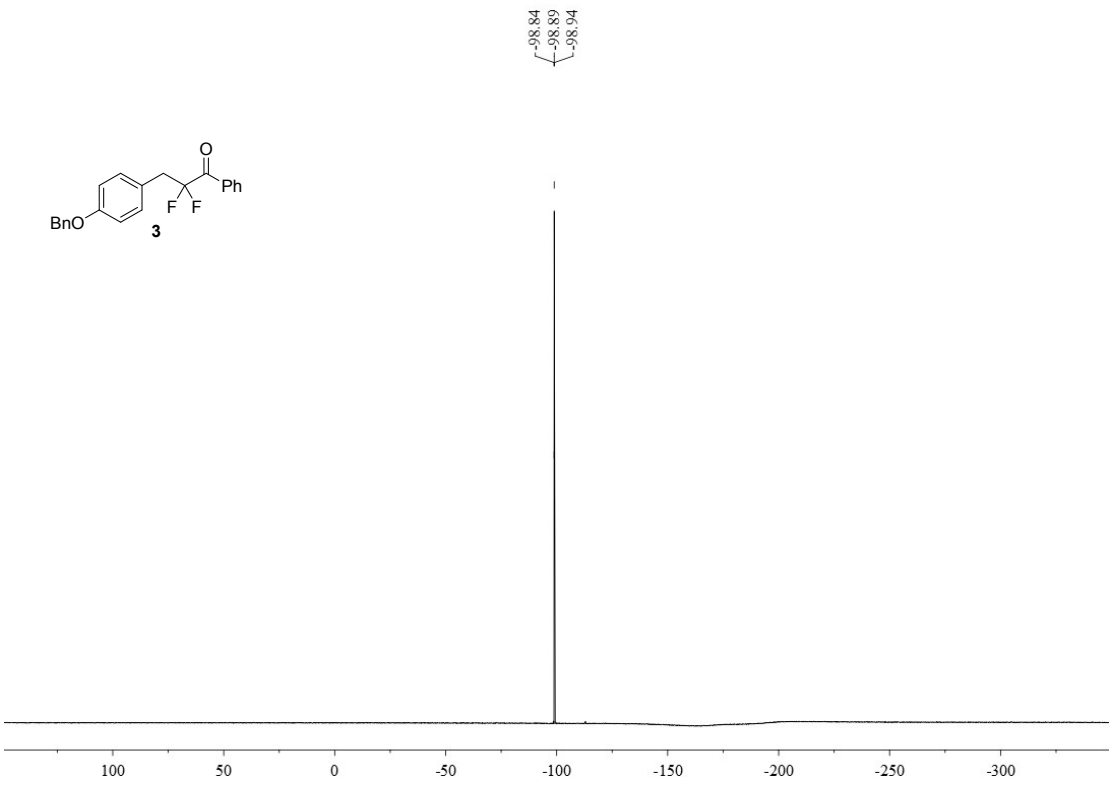
1. H. Amii, T. Kobayashi, Y. Hatamoto and K. Uneyama, *Chem. Commun.*, 1999, 1323.

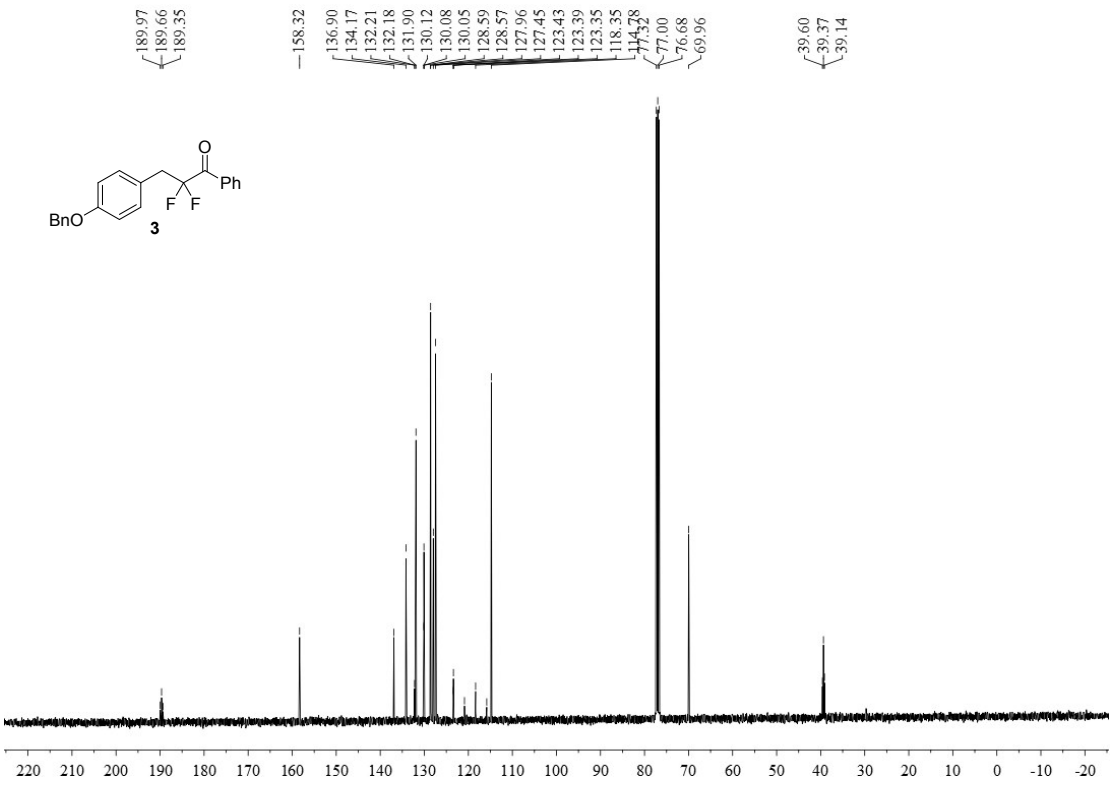
2. A. S. Henderson, J. F. Bower and M. C. Galan, *Org. Biomol. Chem.,* 2014, **12**, 9180.

3. (a) Huang, Y.; Unni, A.; Thadani, A. N.; Rawal, V. H. *Nature* **2003**, *424*, 146. (b) McDougal, N. T.; Schaus, S. E. *J. Am. Chem. Soc.* **2003**, *125*, 12094−12095.

NMR spectra of the related compounds



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BnO
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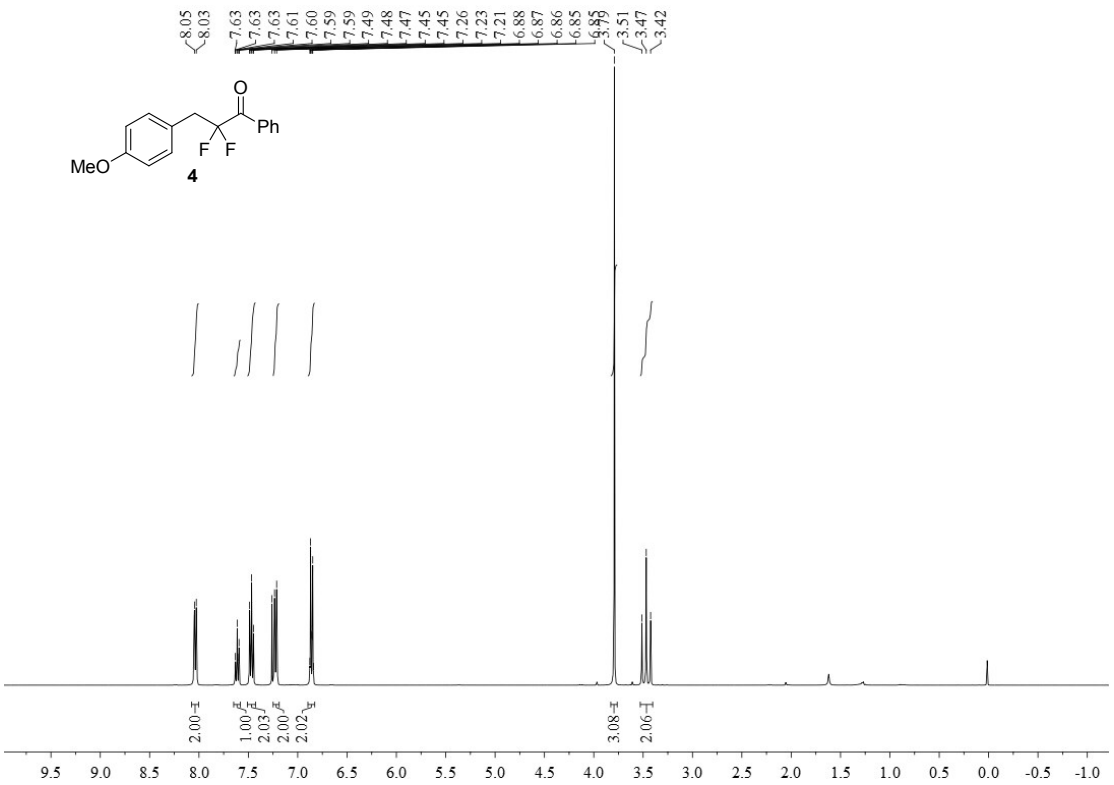
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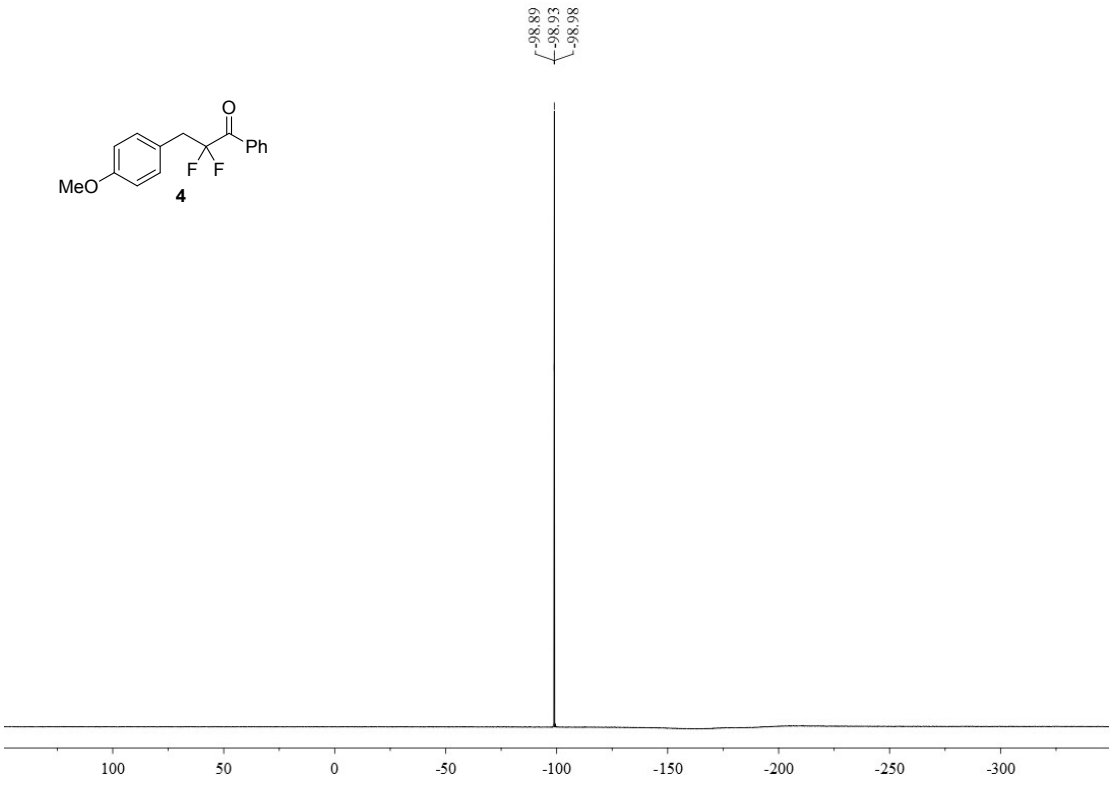
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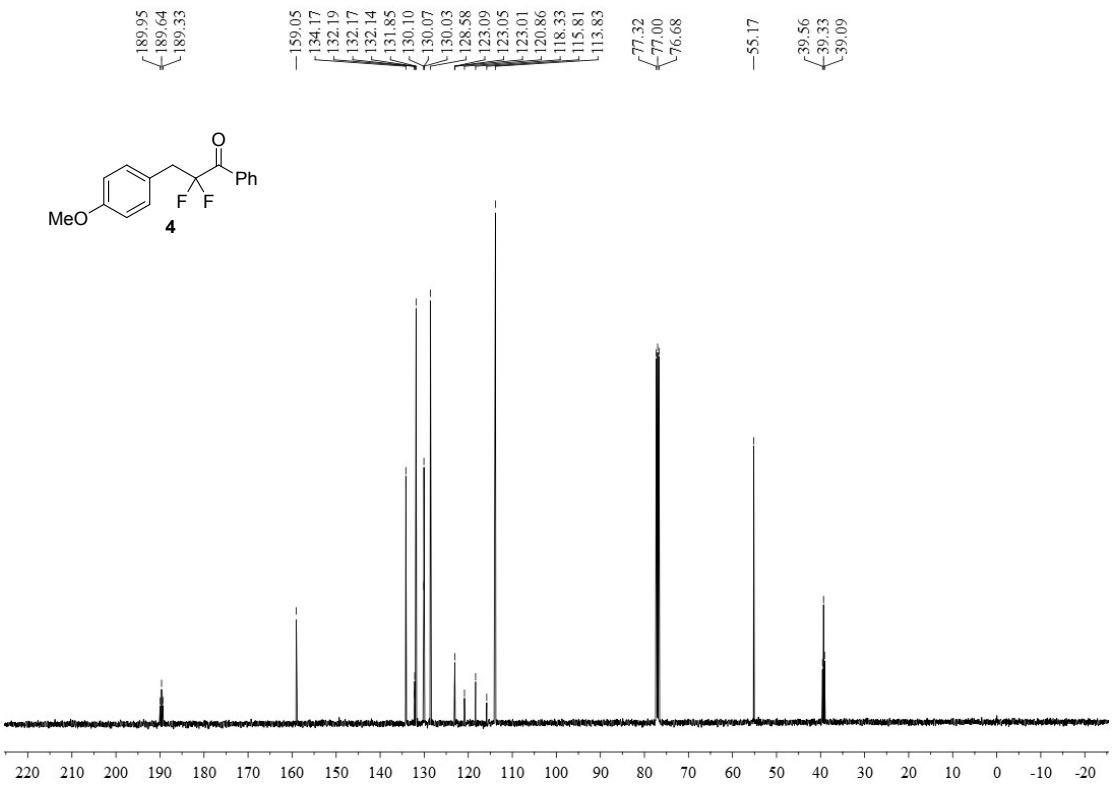
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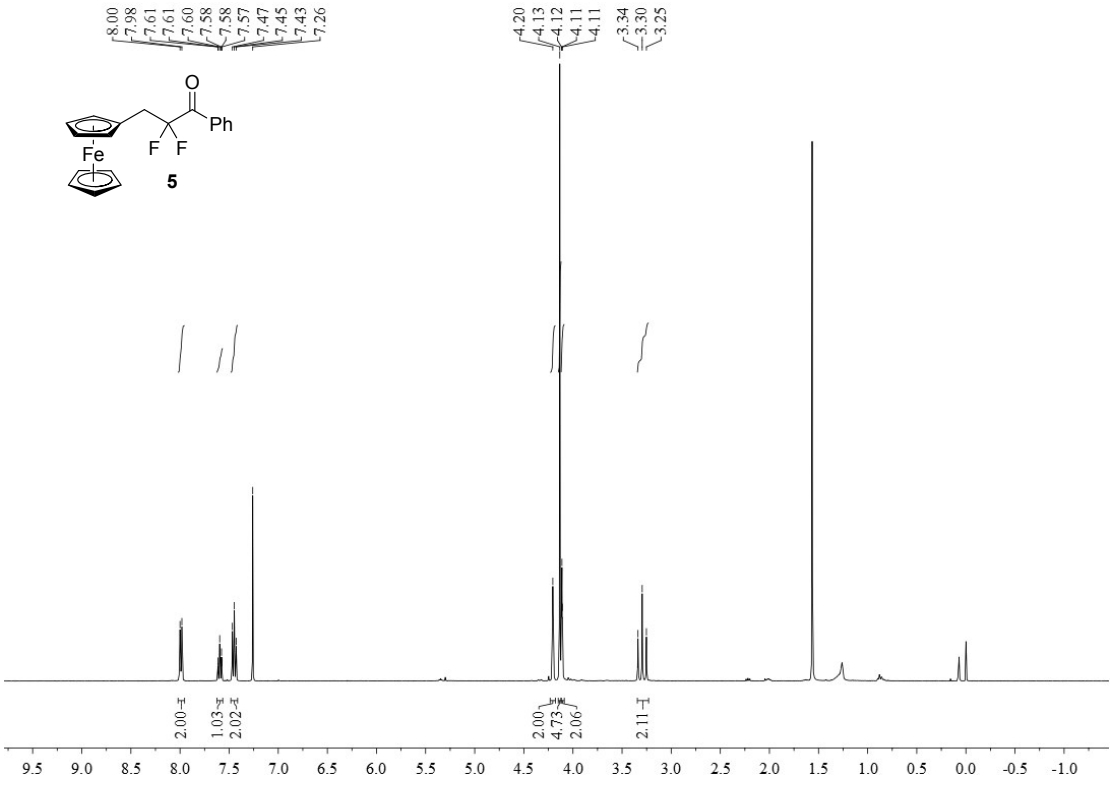
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Fe
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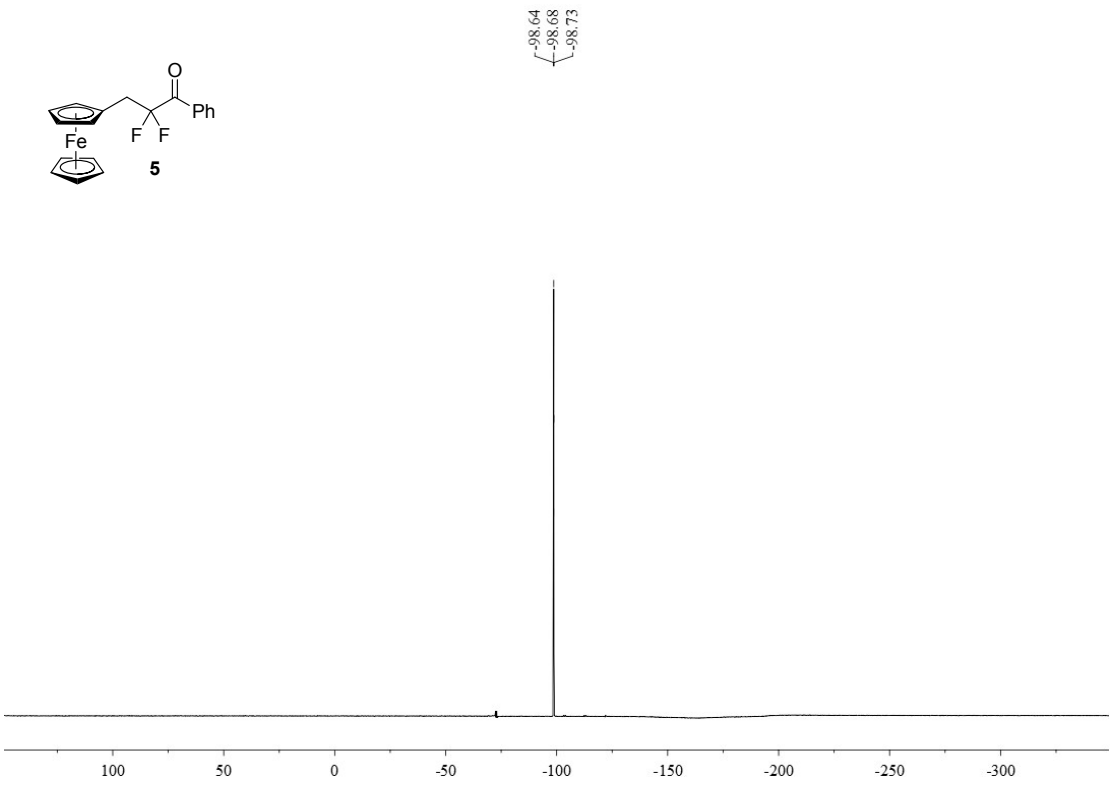
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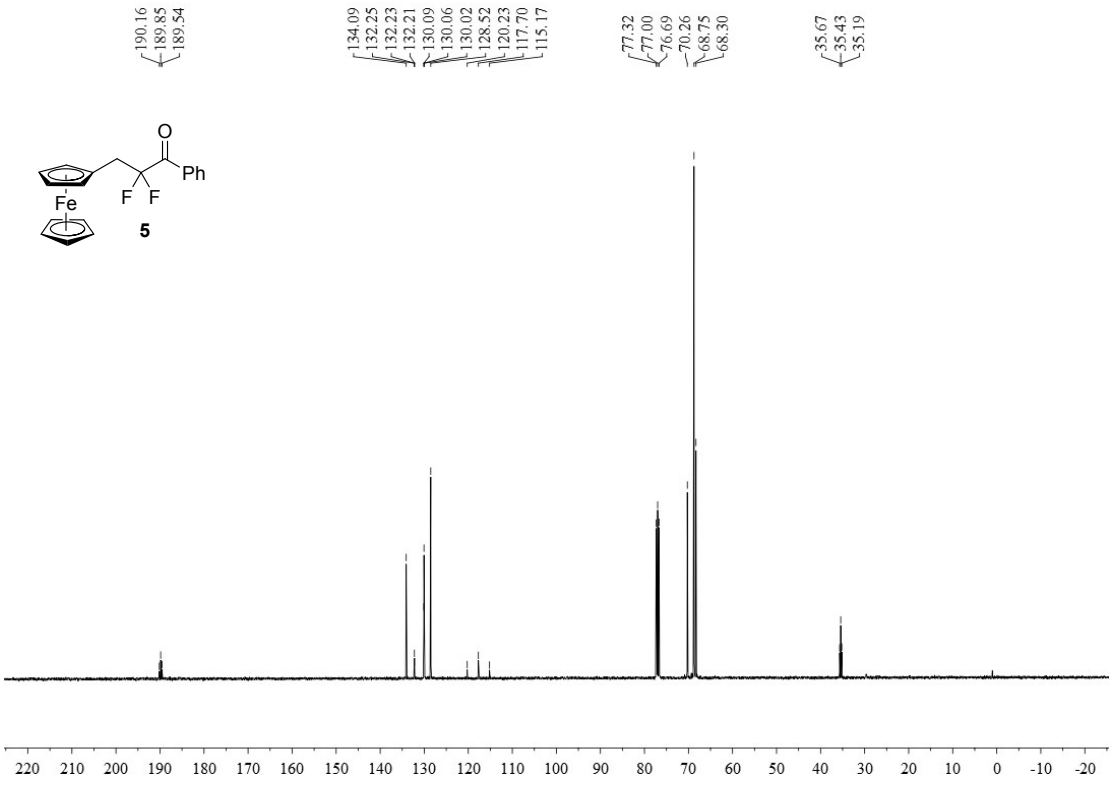
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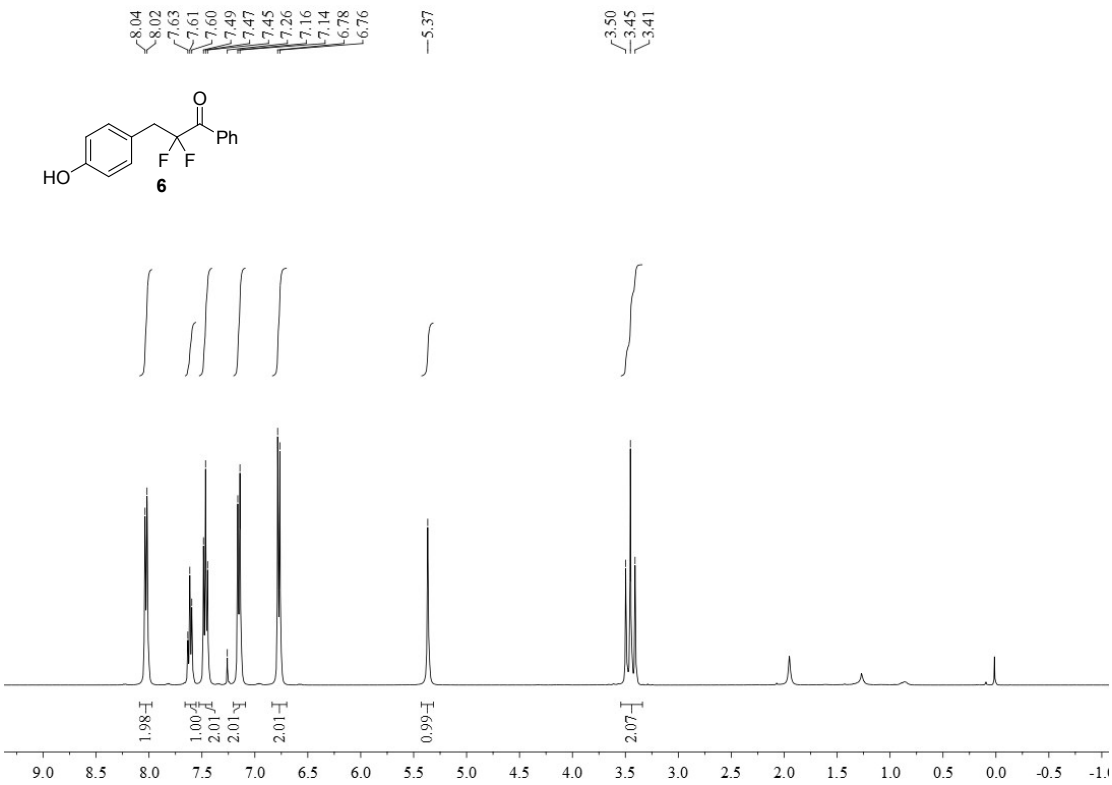
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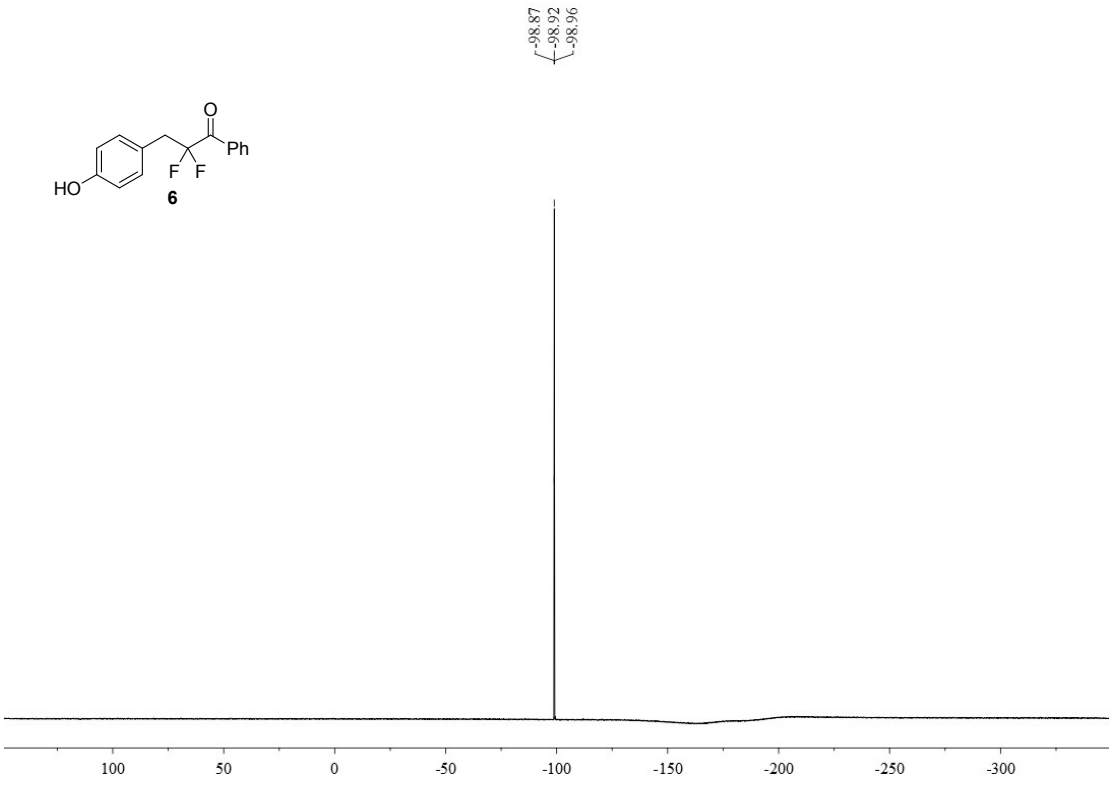
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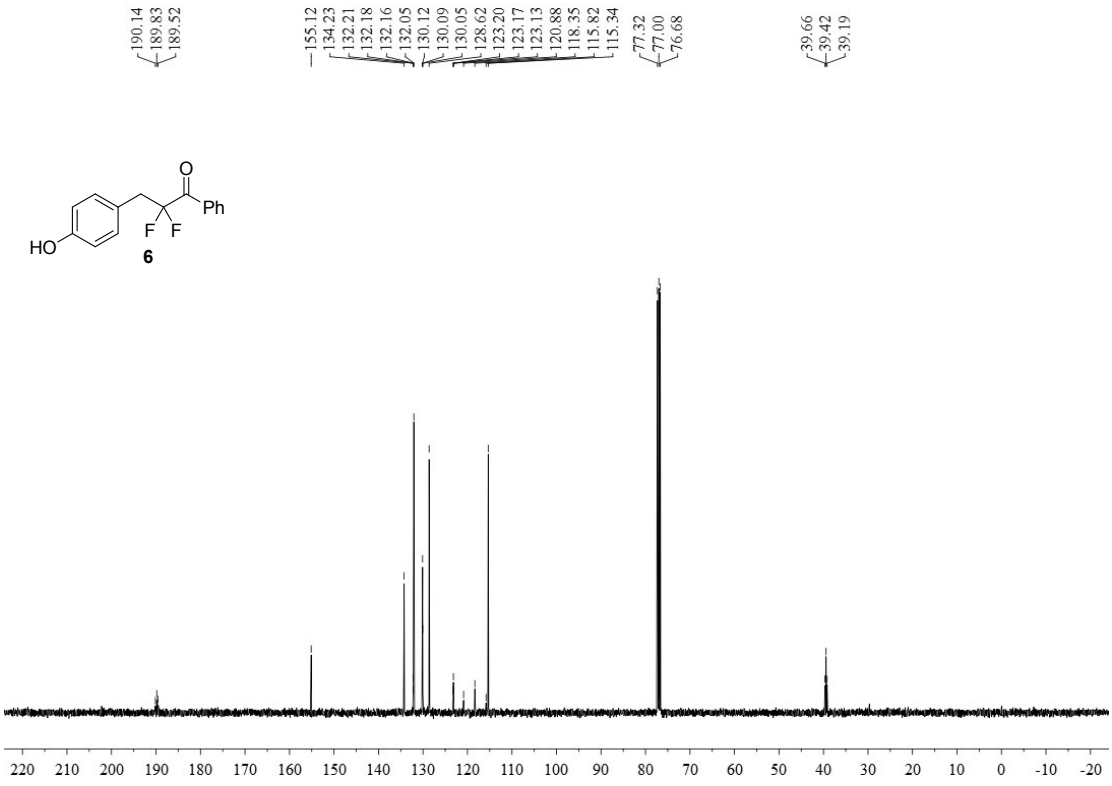
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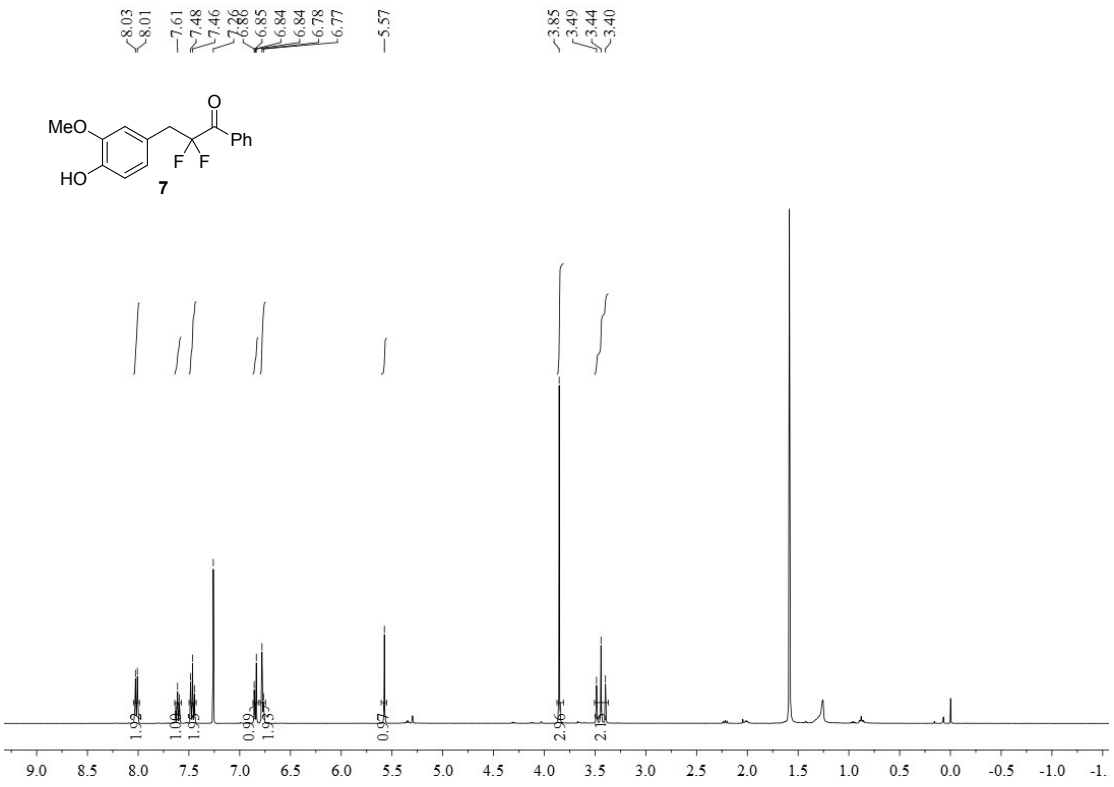
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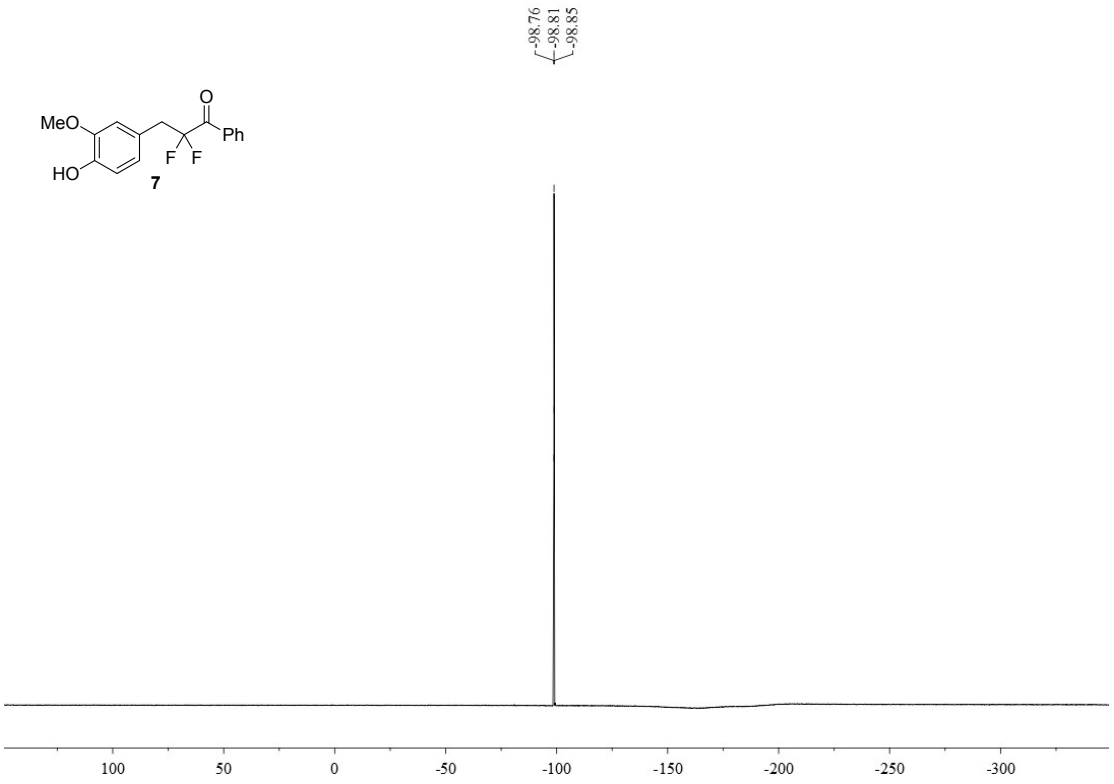
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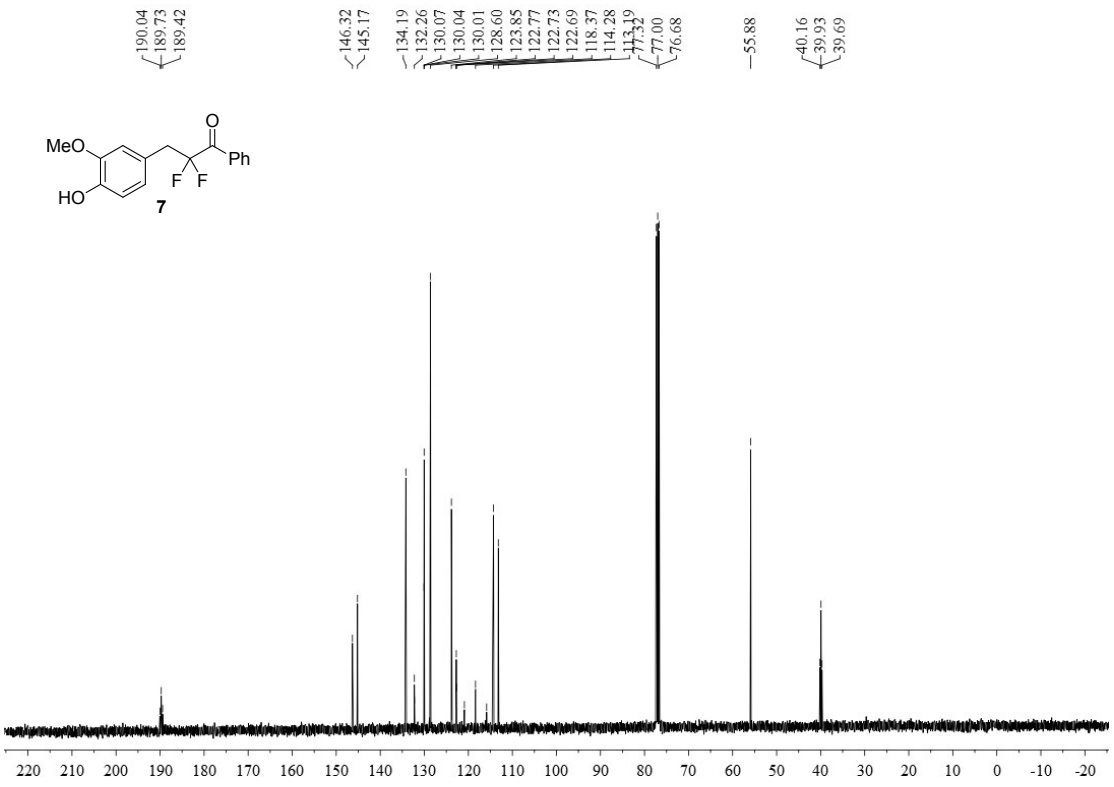
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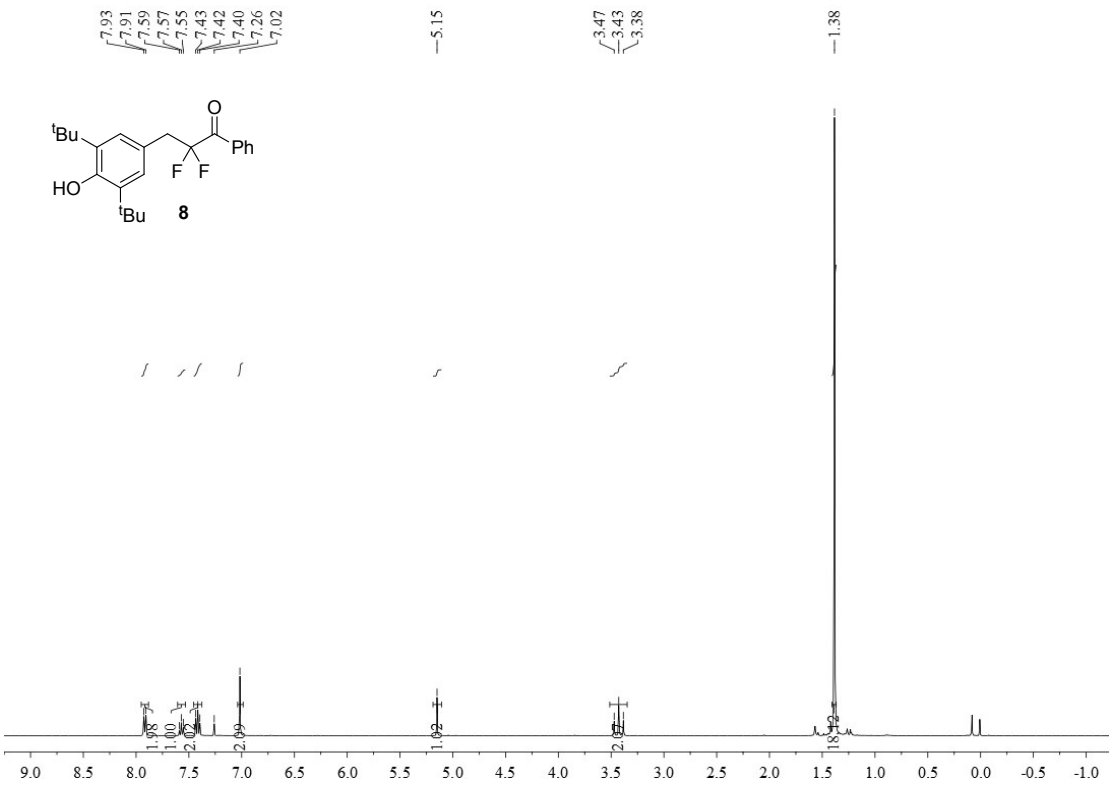
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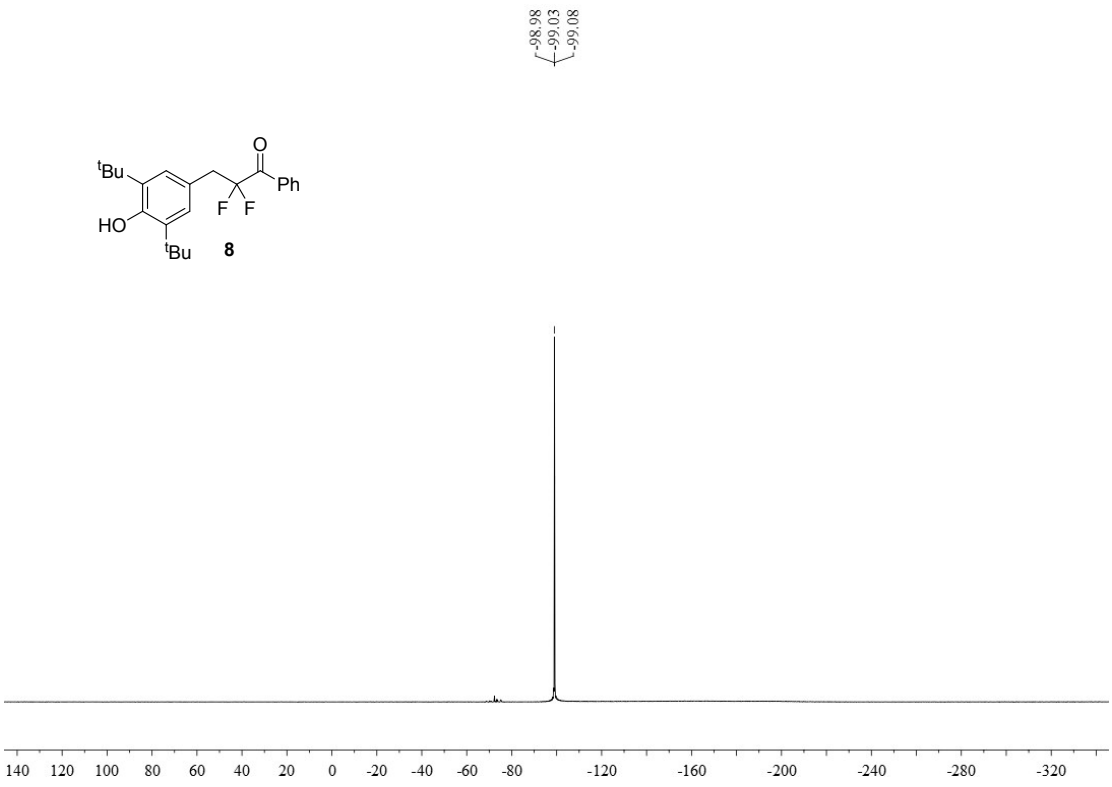
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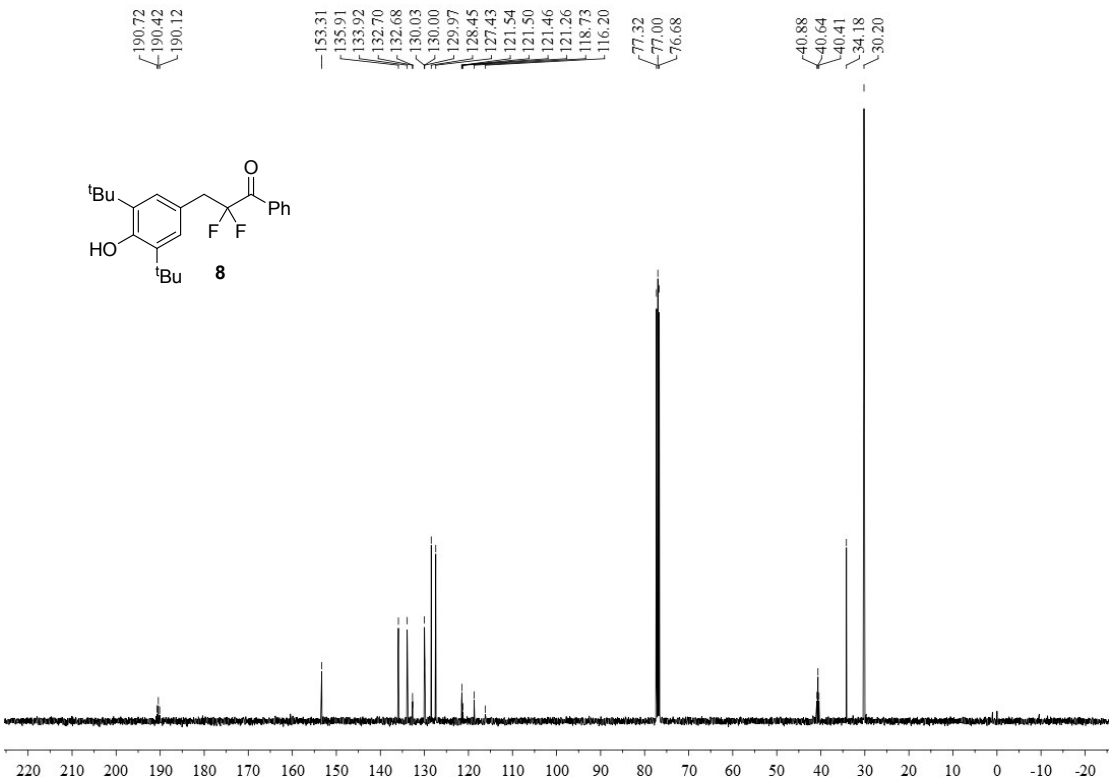
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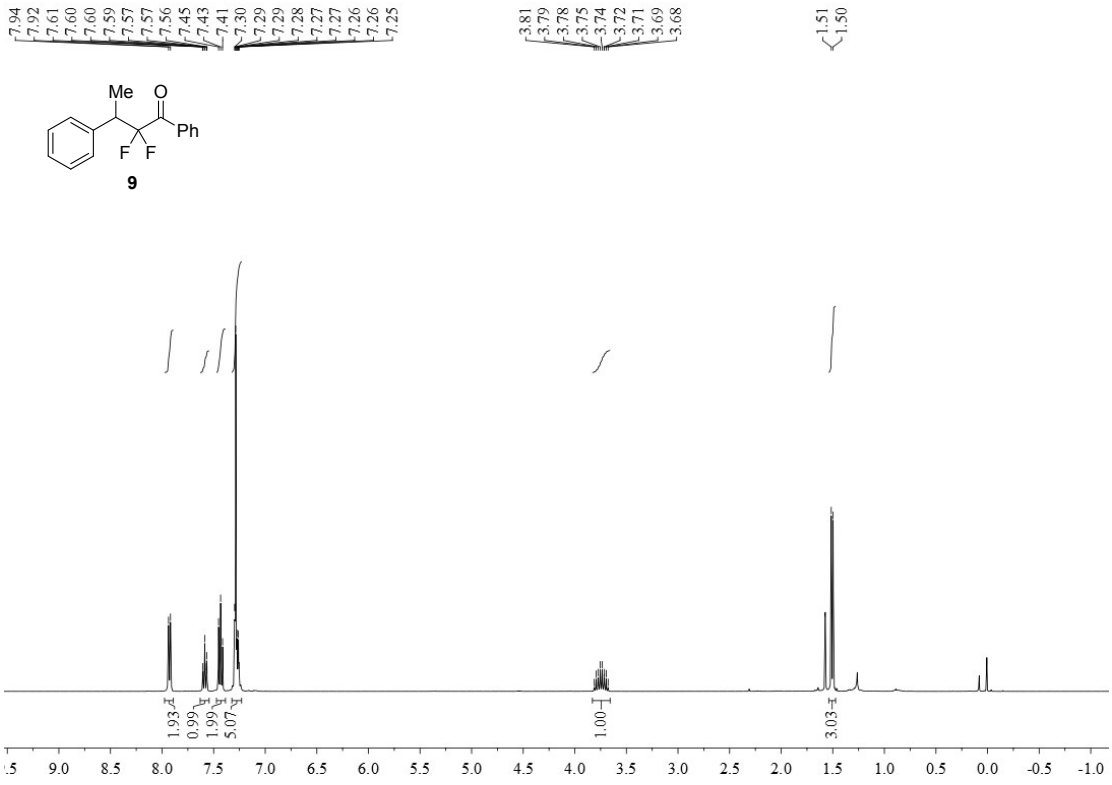
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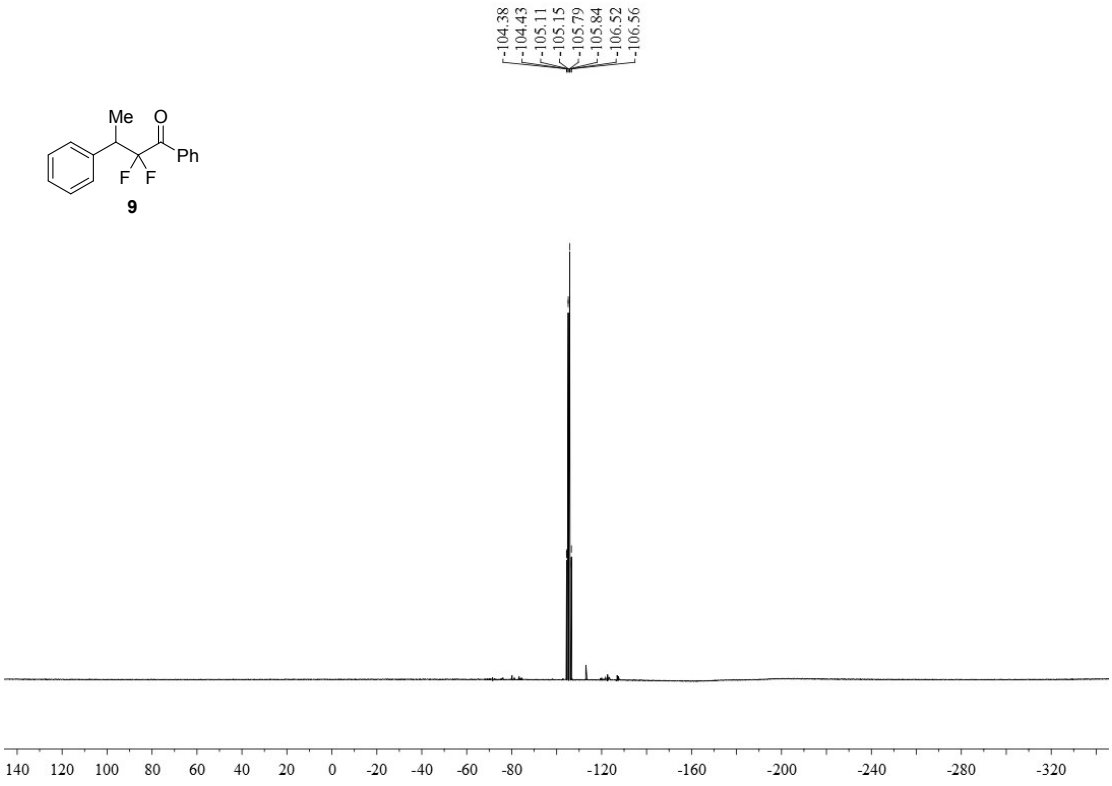
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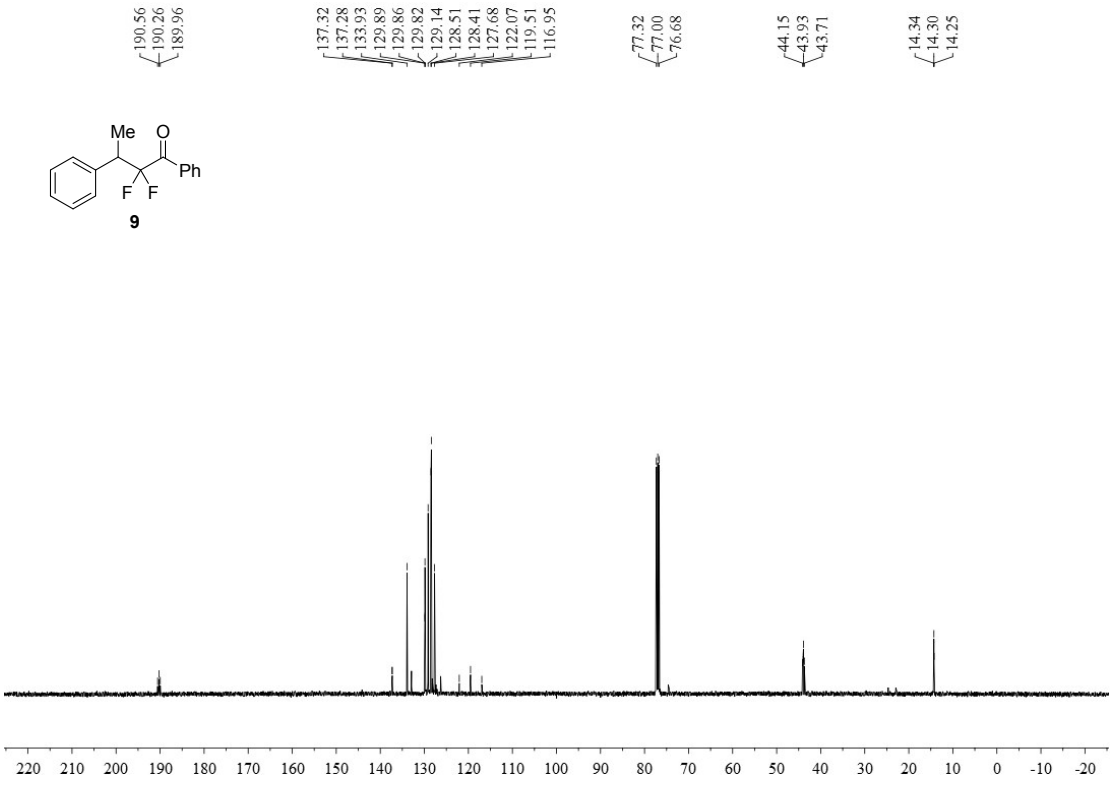
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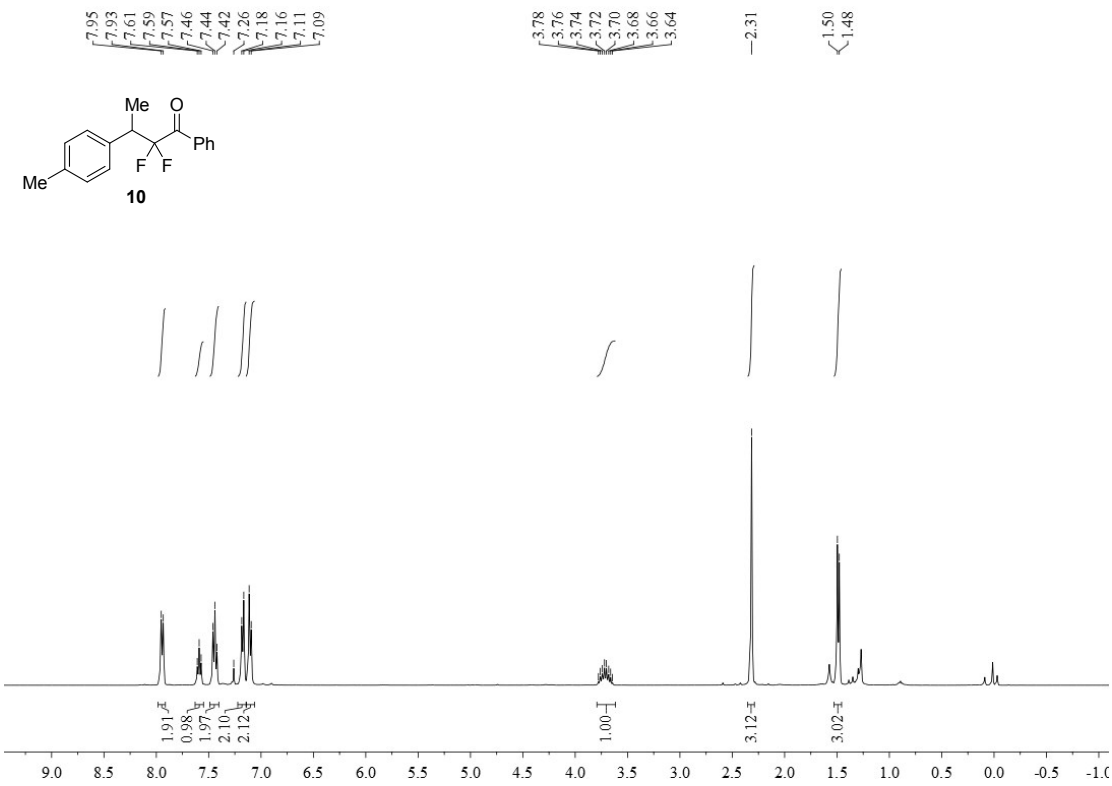
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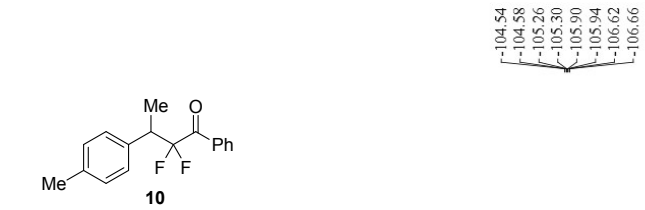
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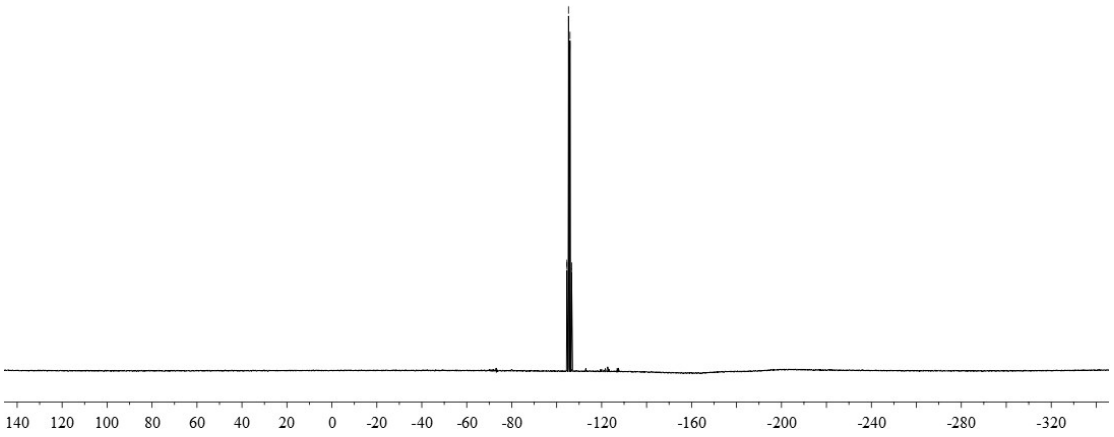
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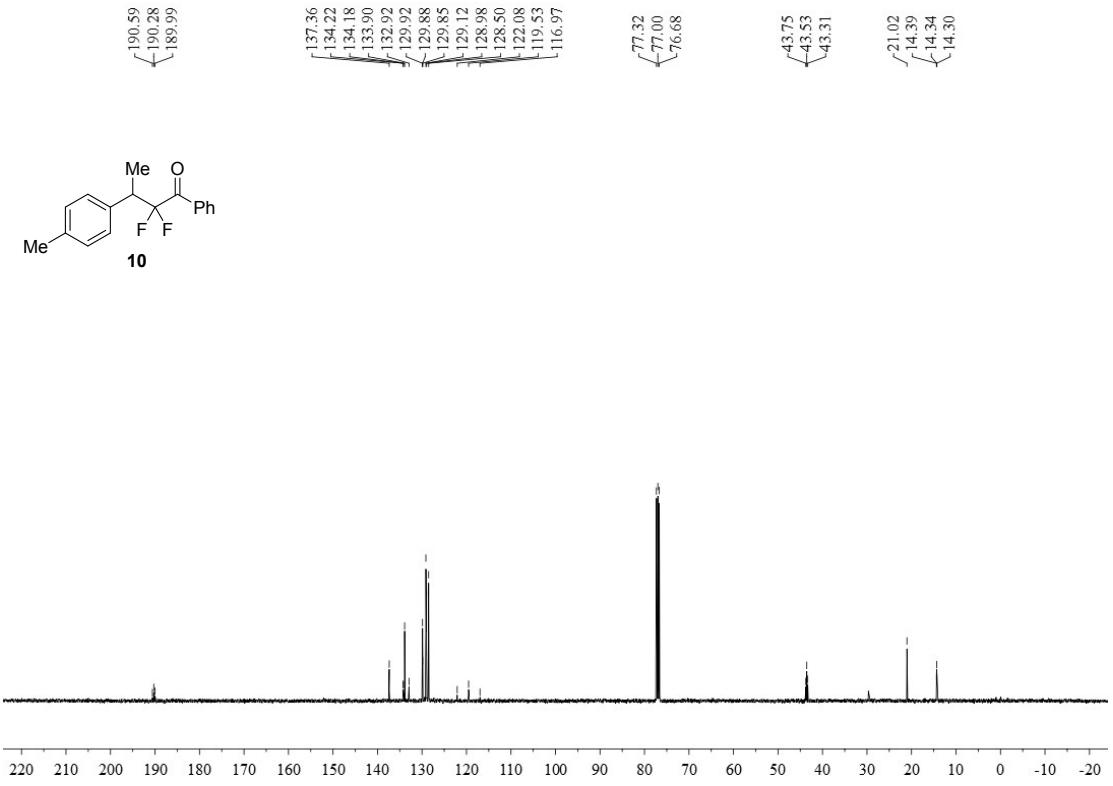
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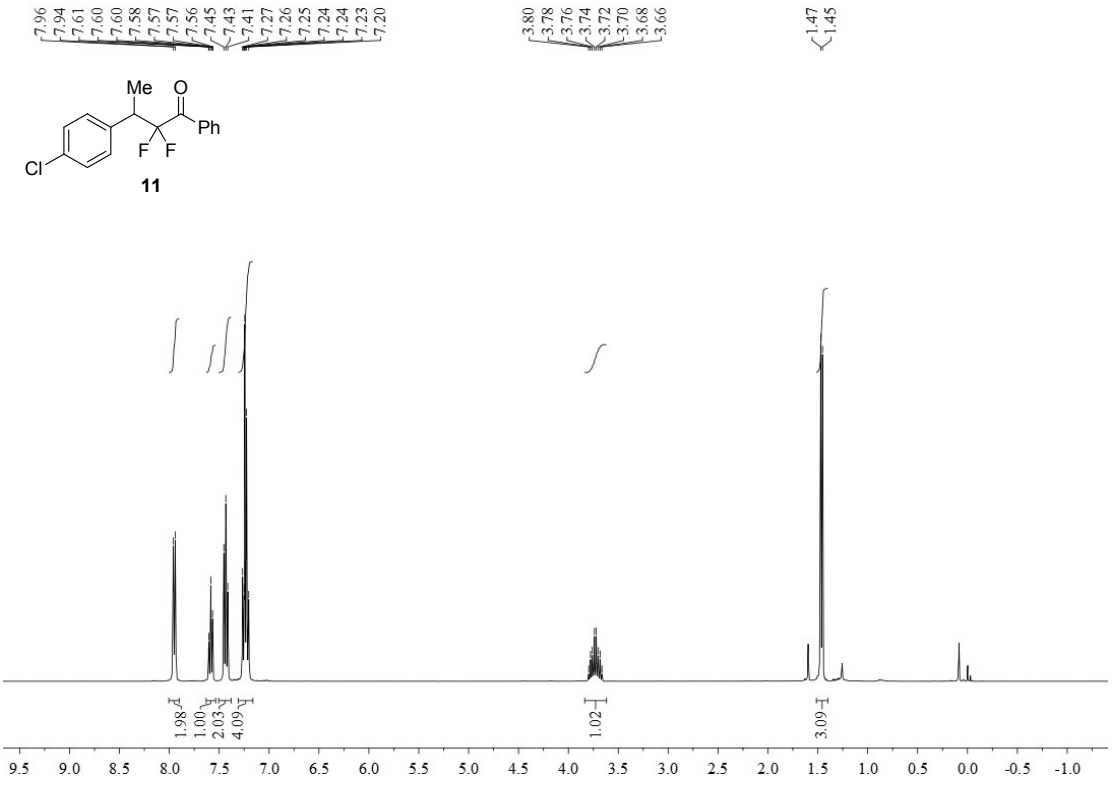
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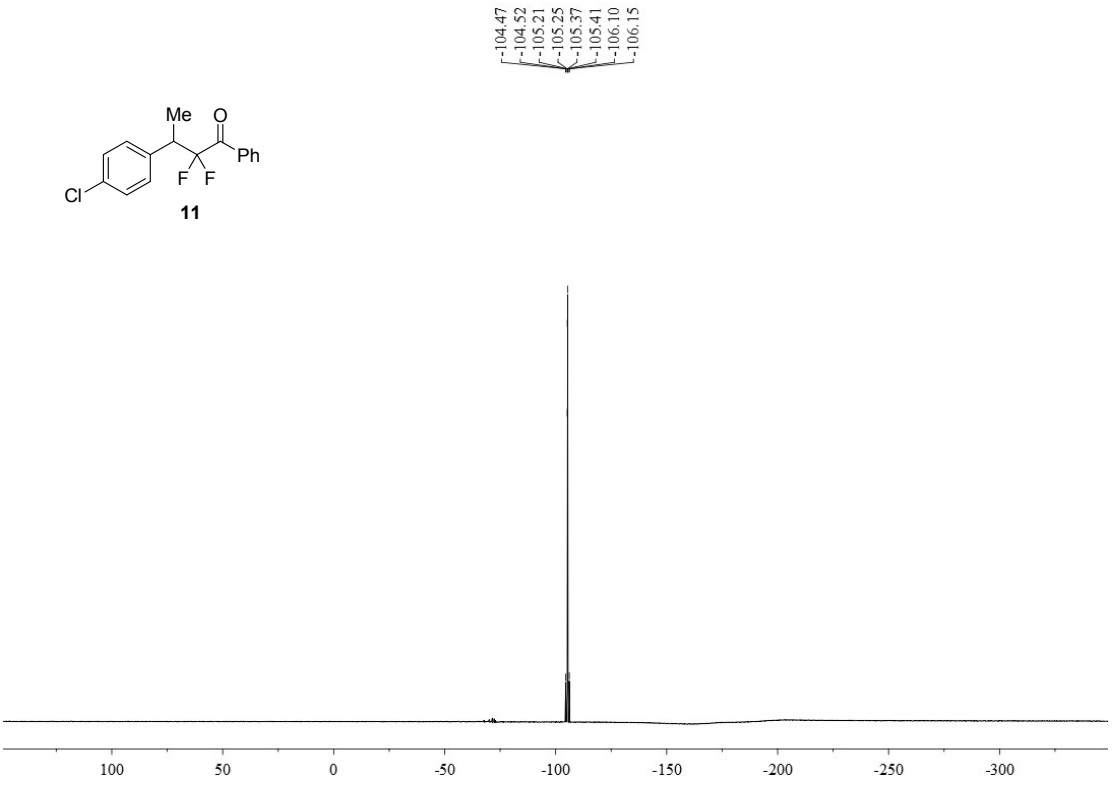
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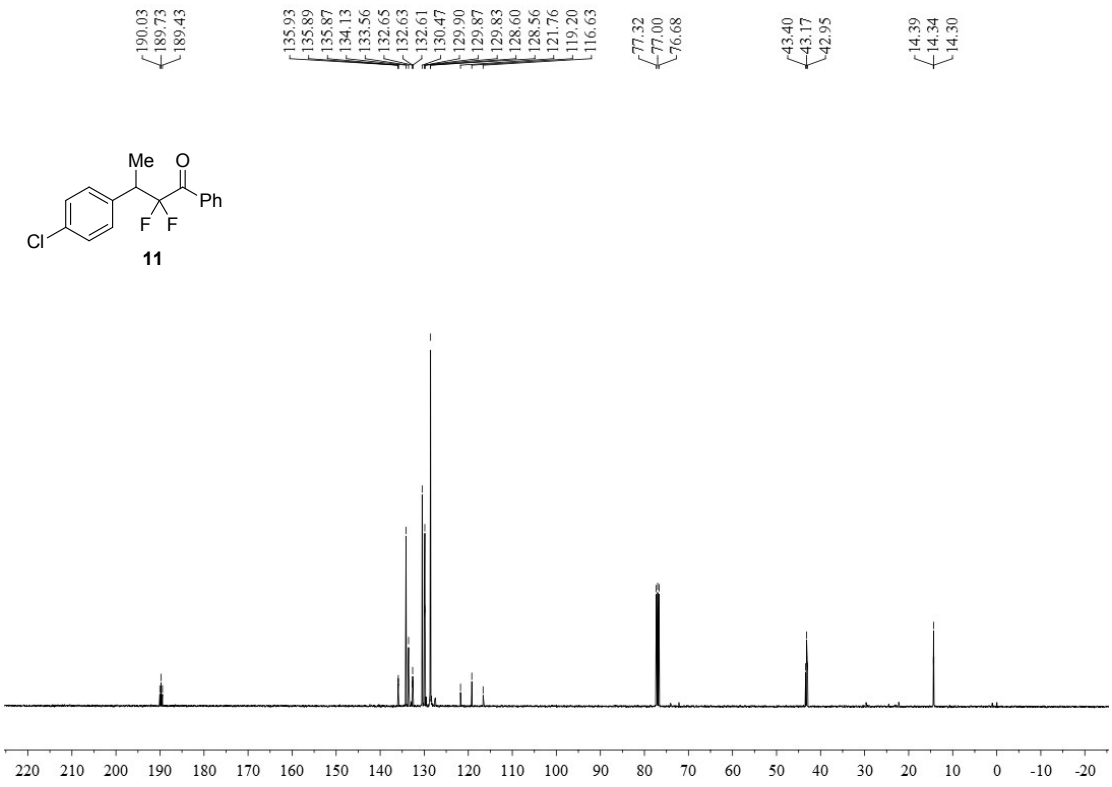
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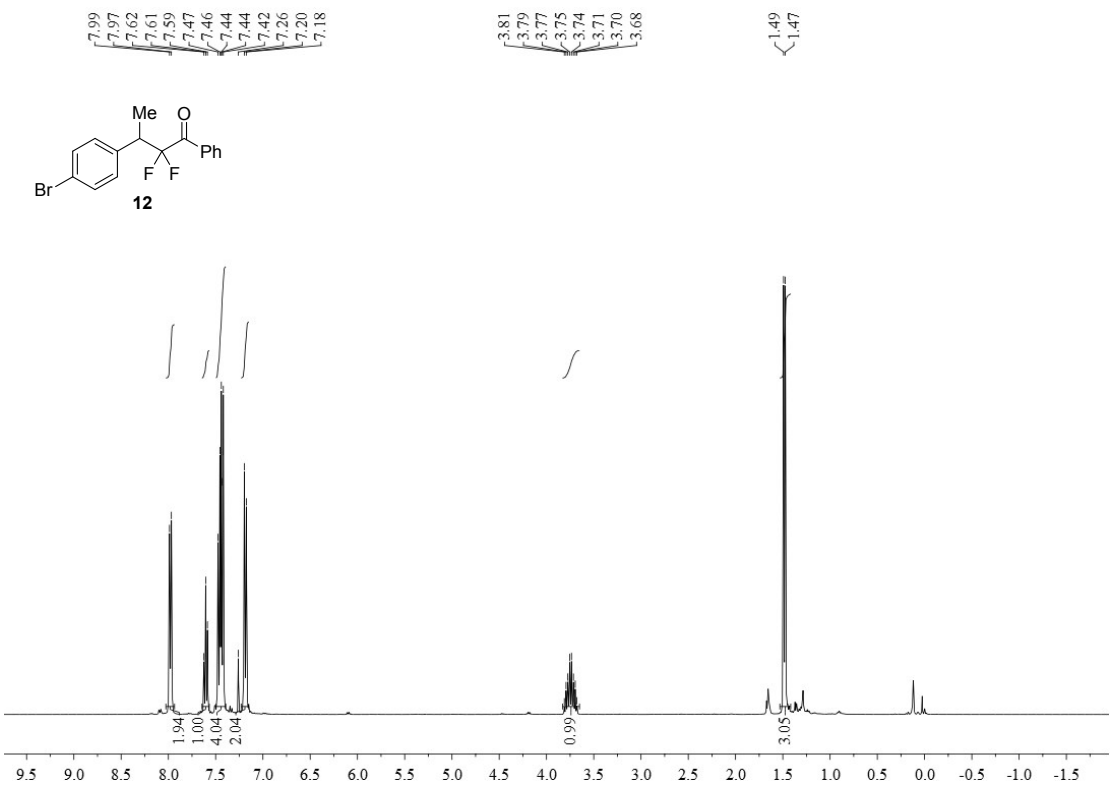
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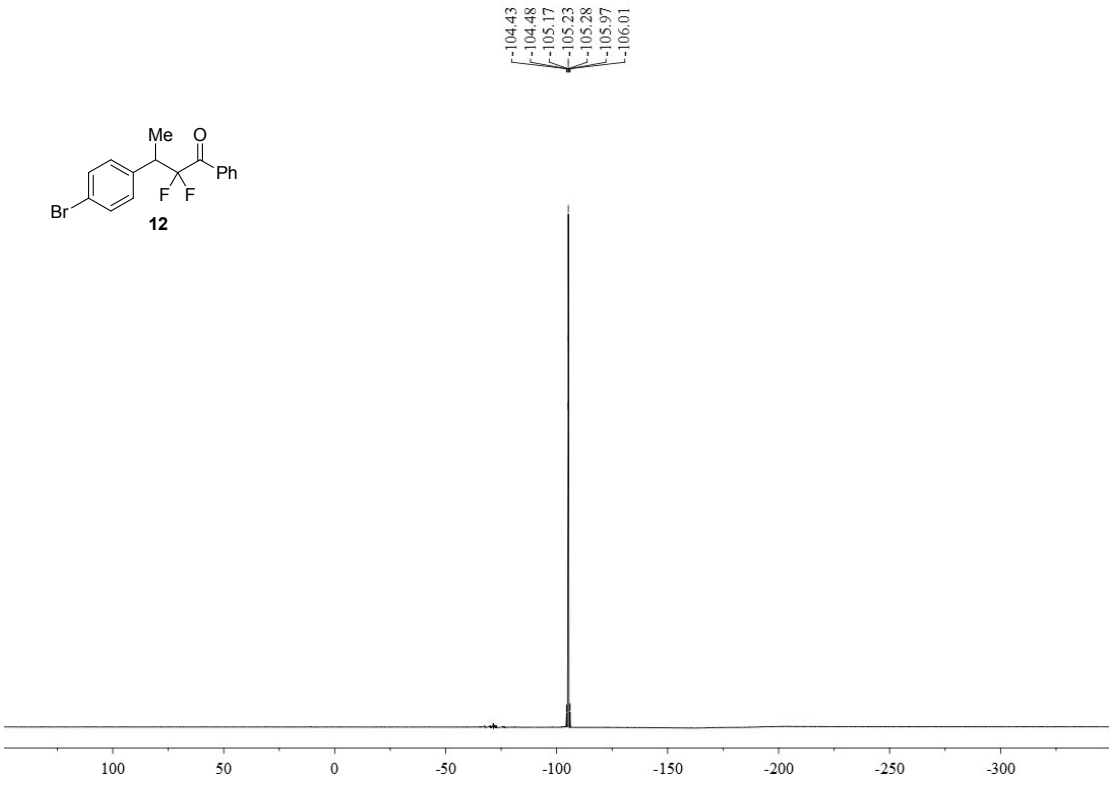
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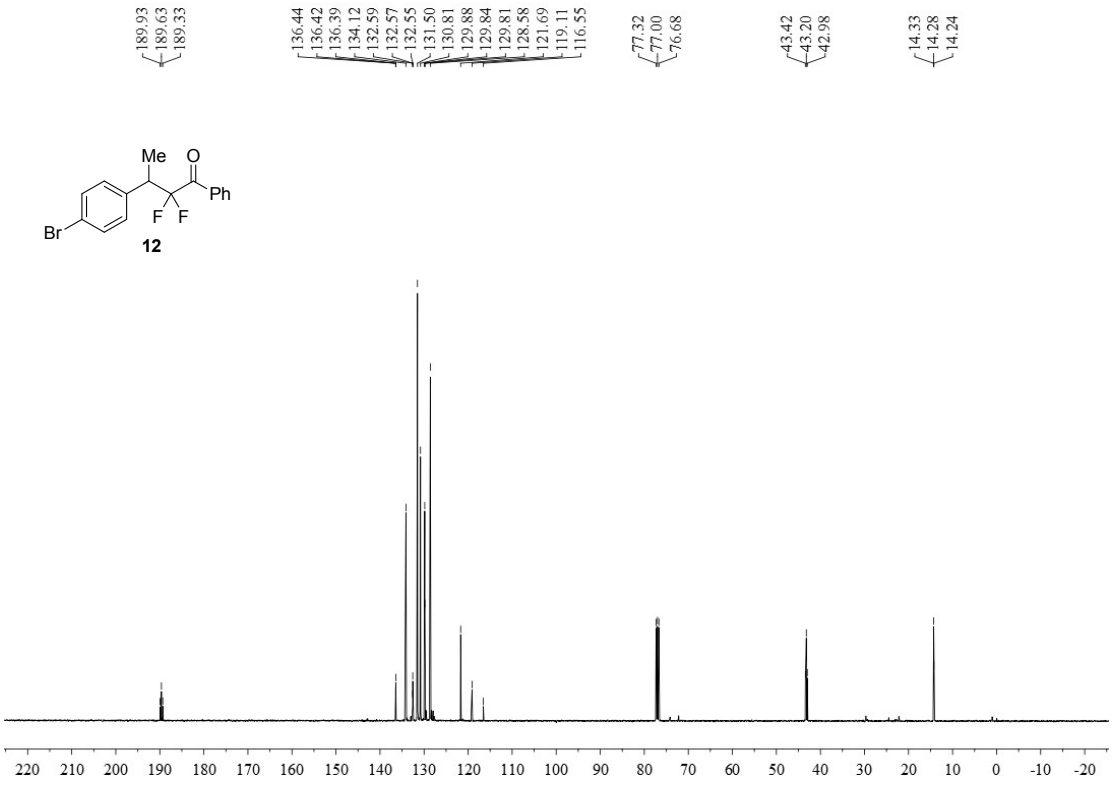
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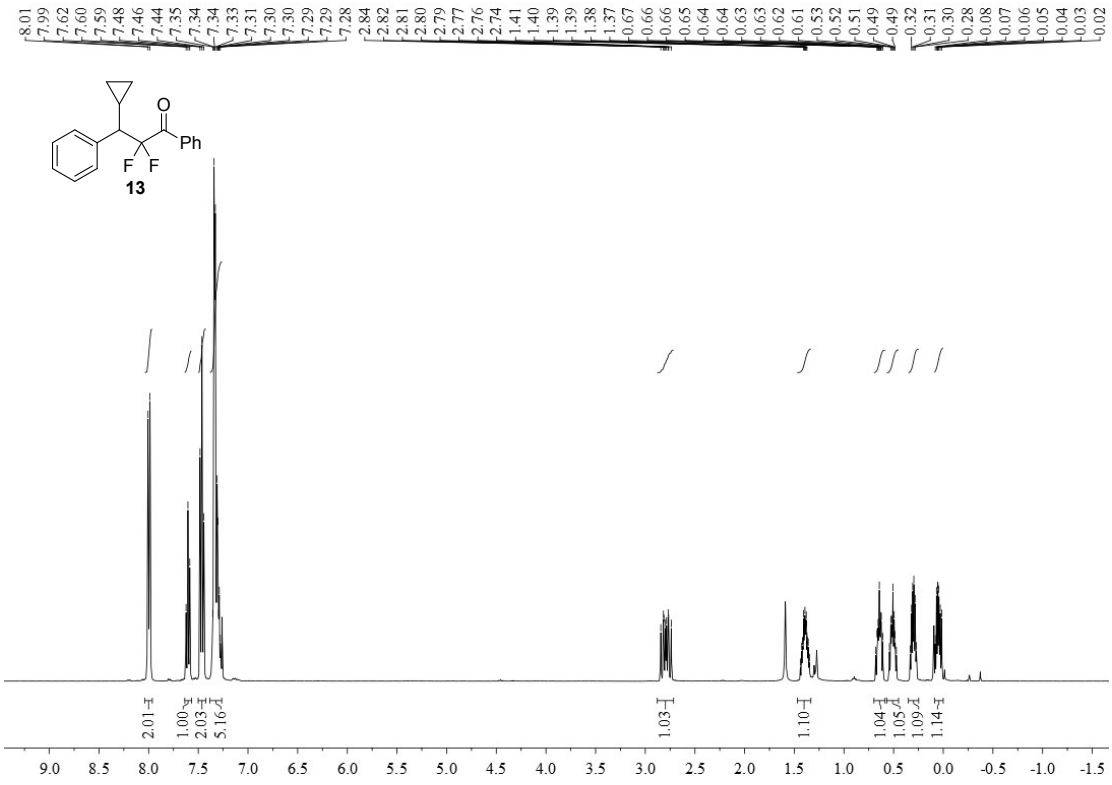
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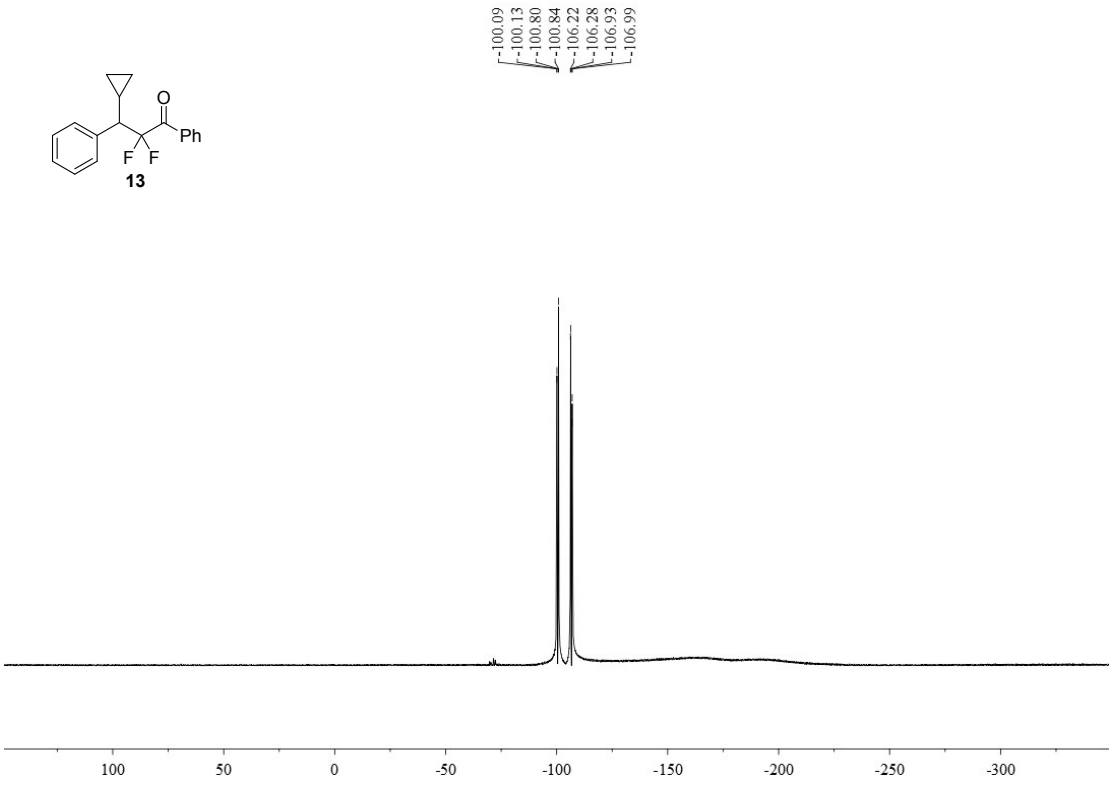
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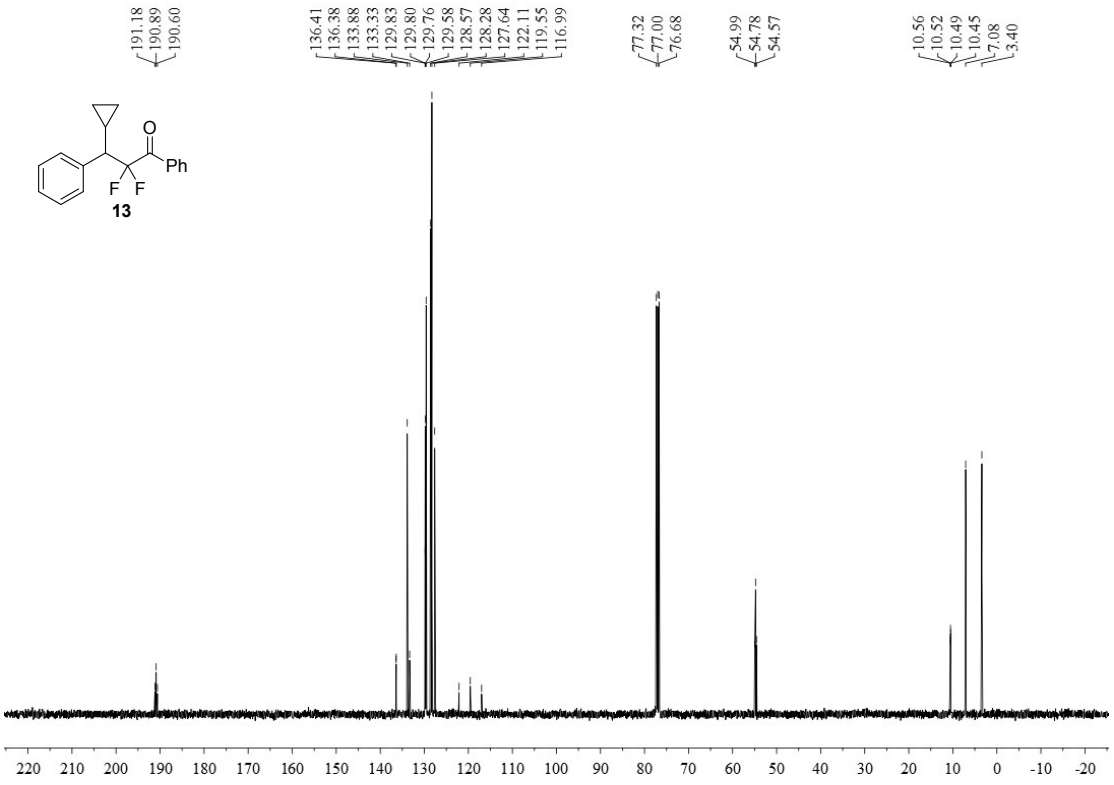
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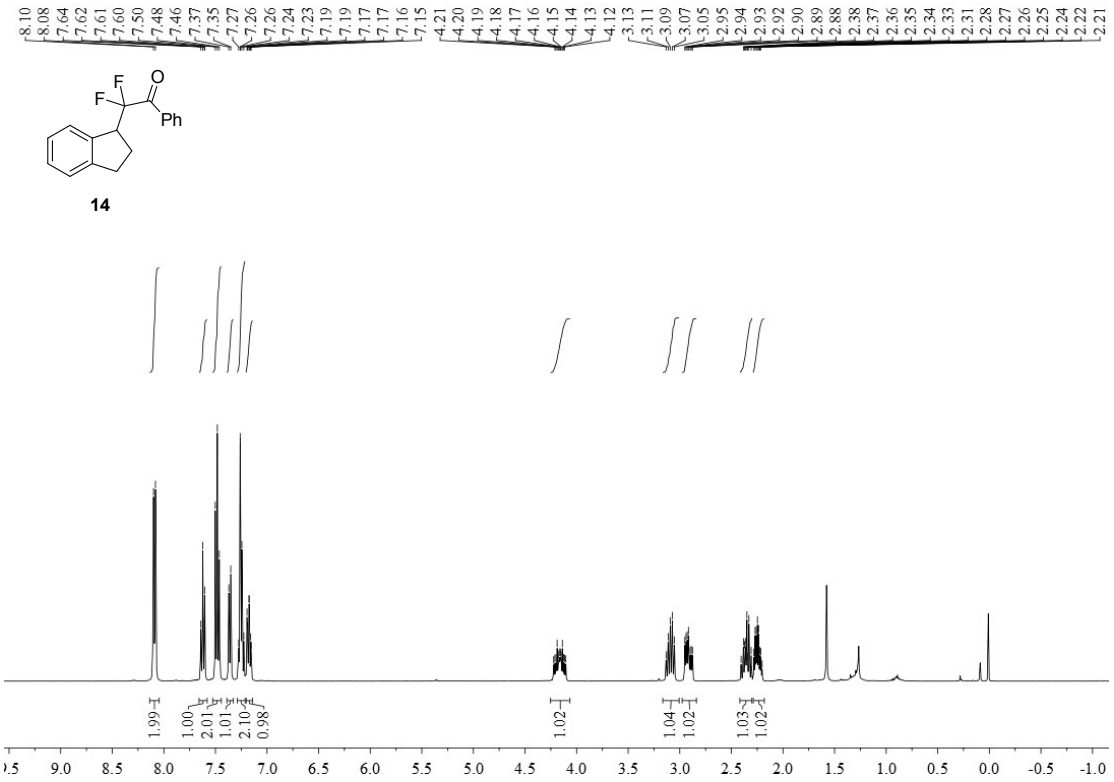
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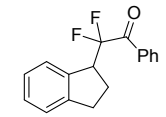
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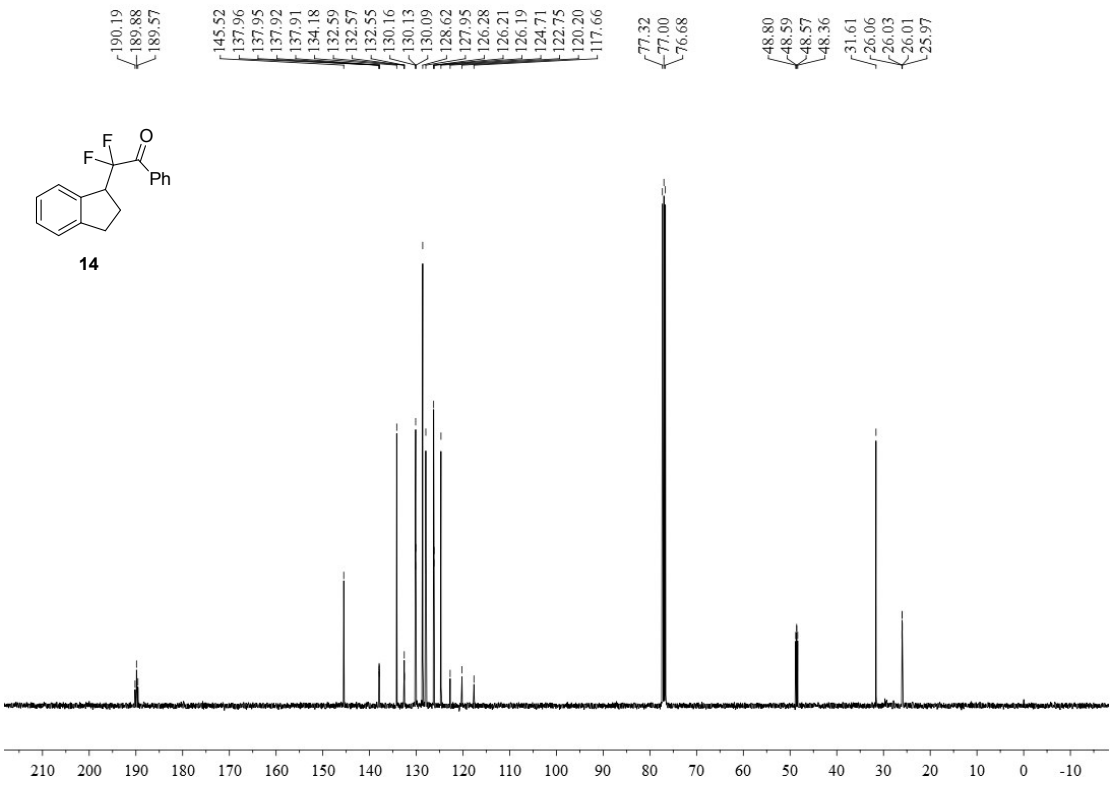
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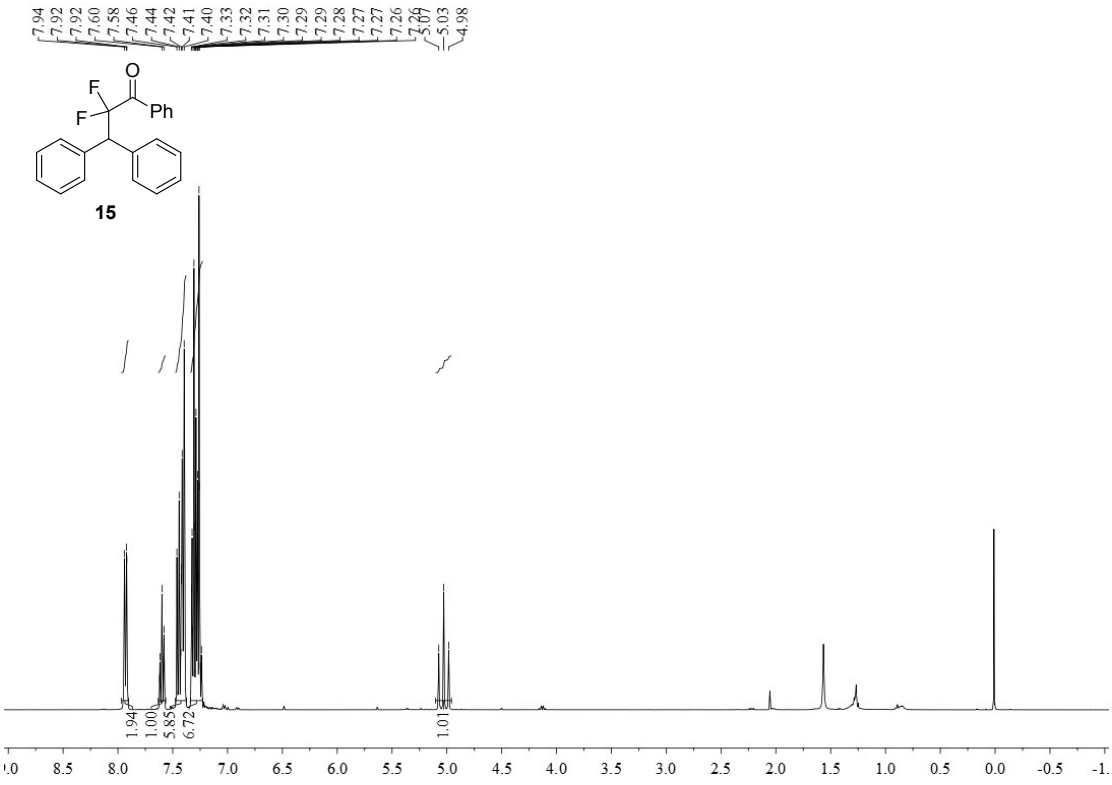
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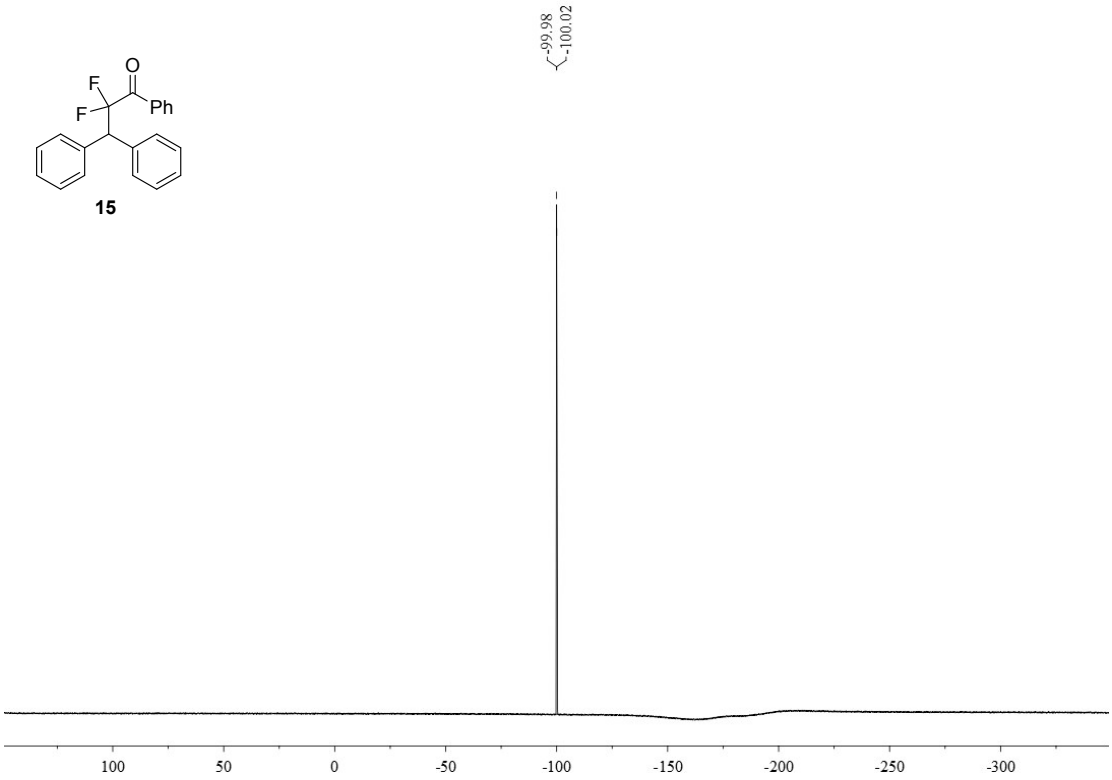
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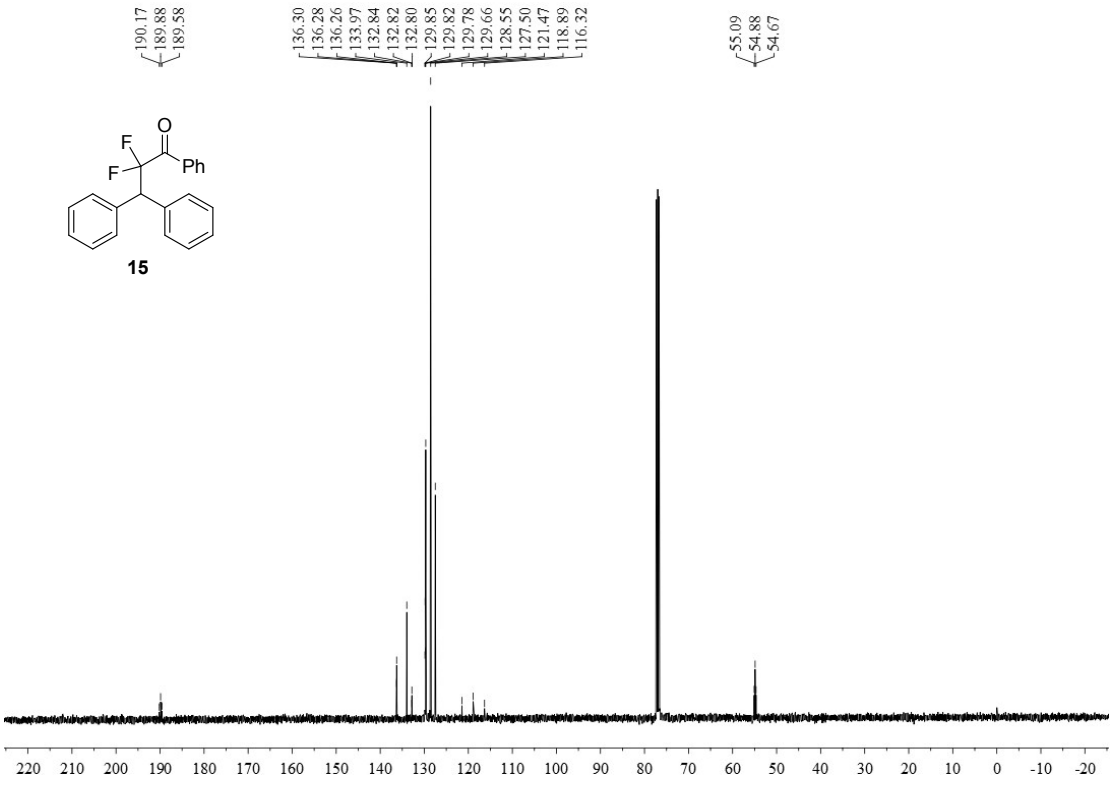
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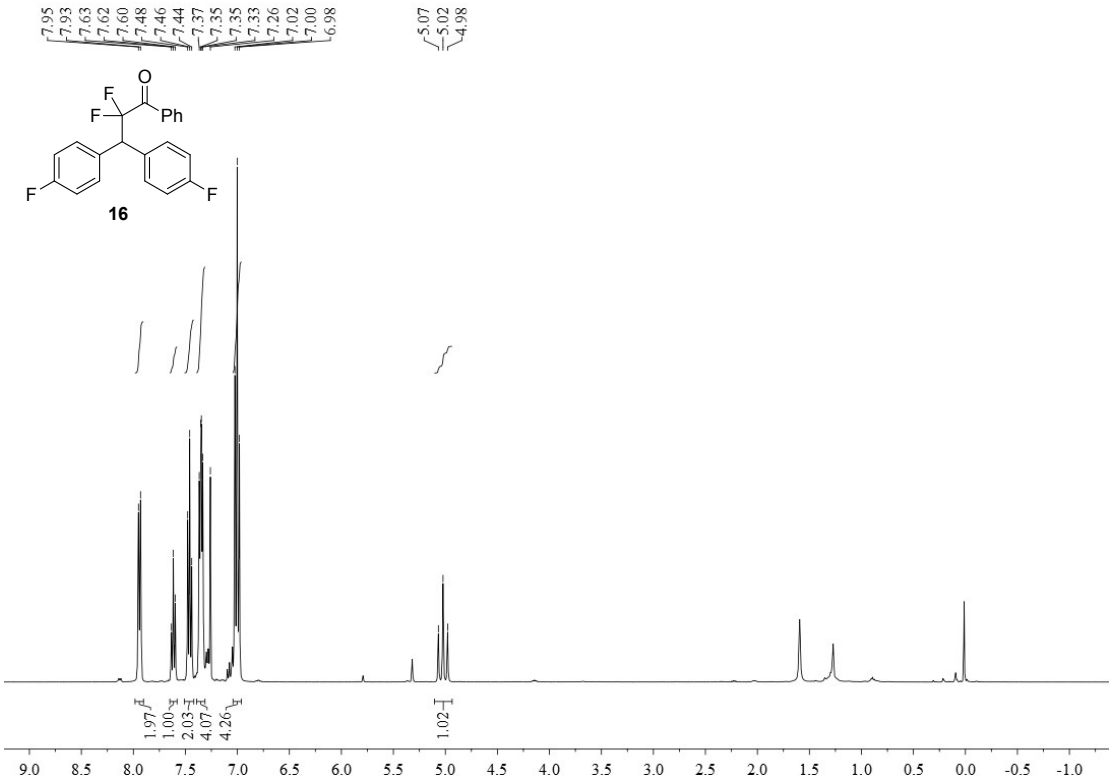
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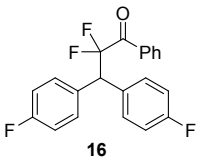
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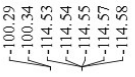
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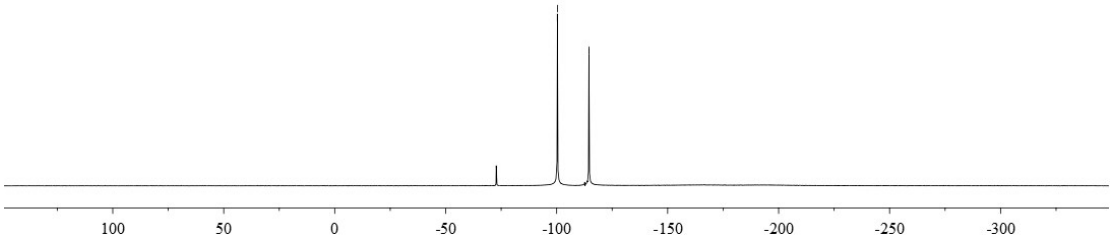
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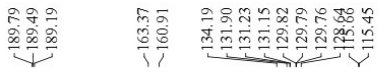
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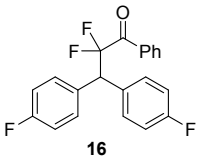
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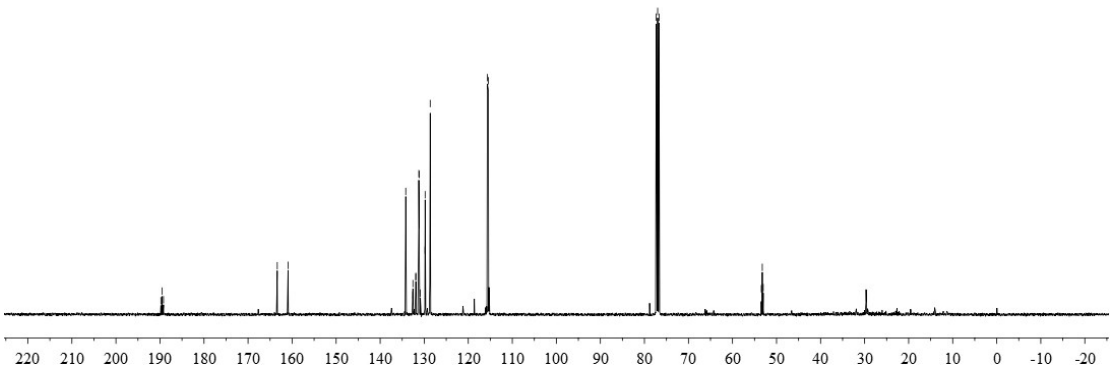
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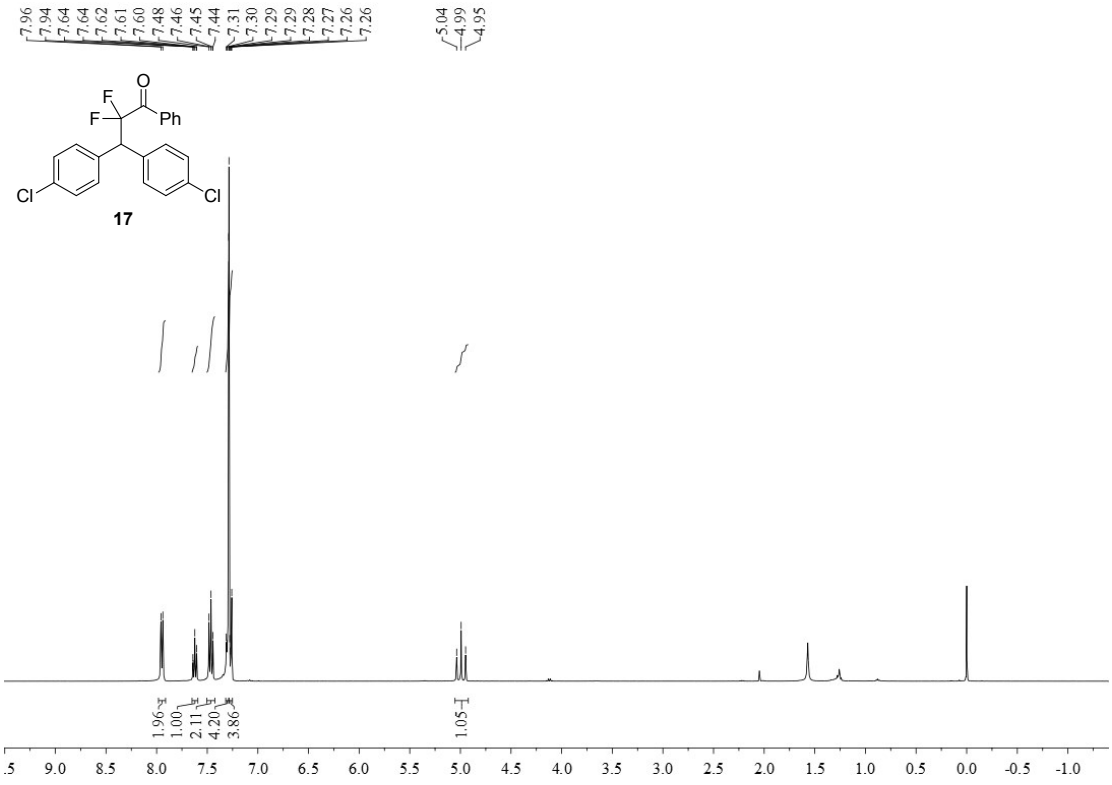
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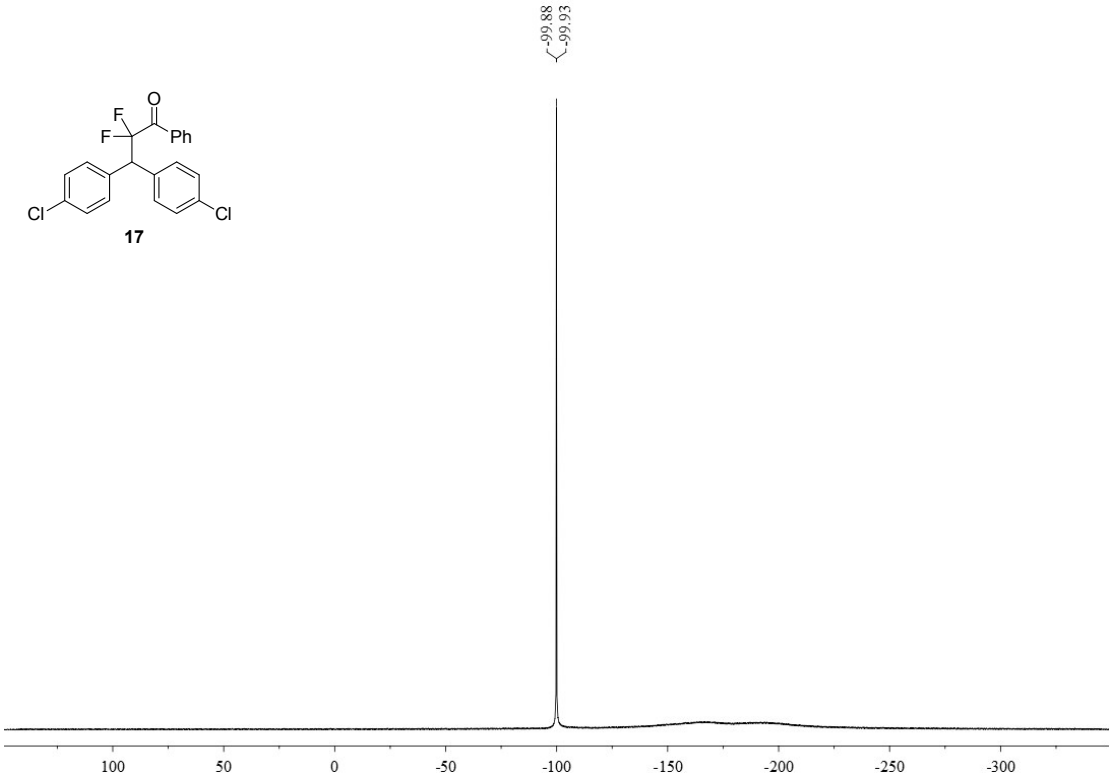
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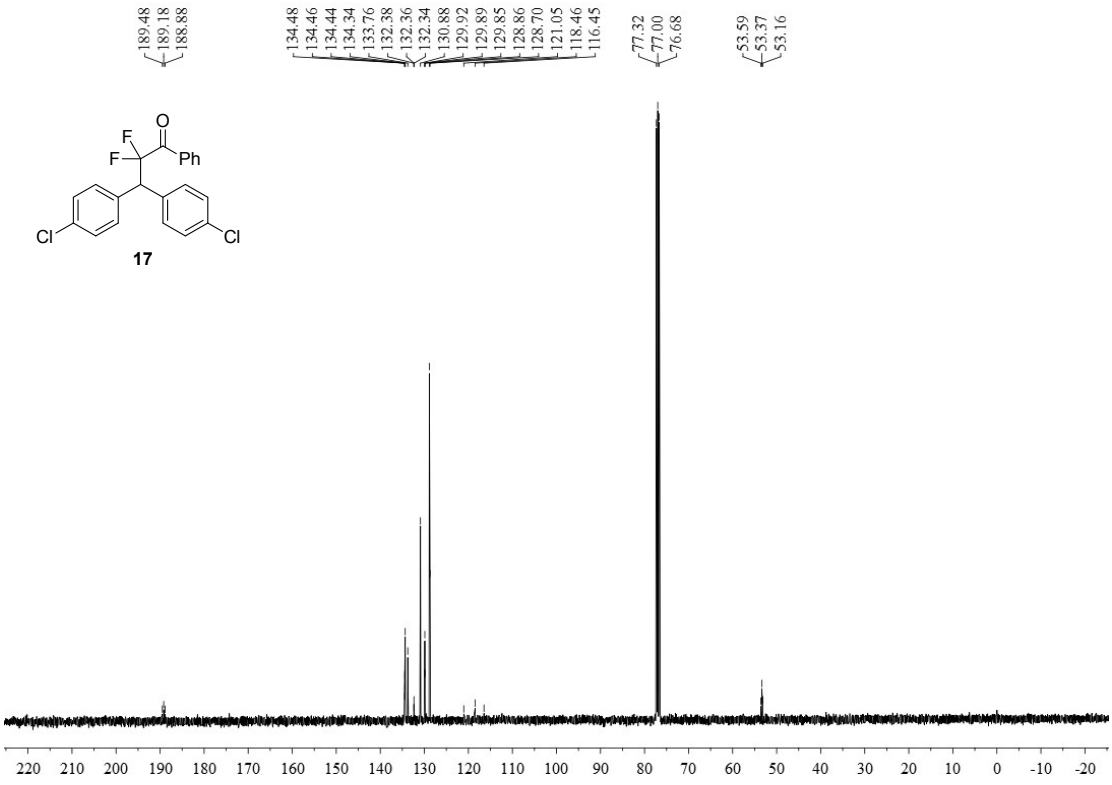
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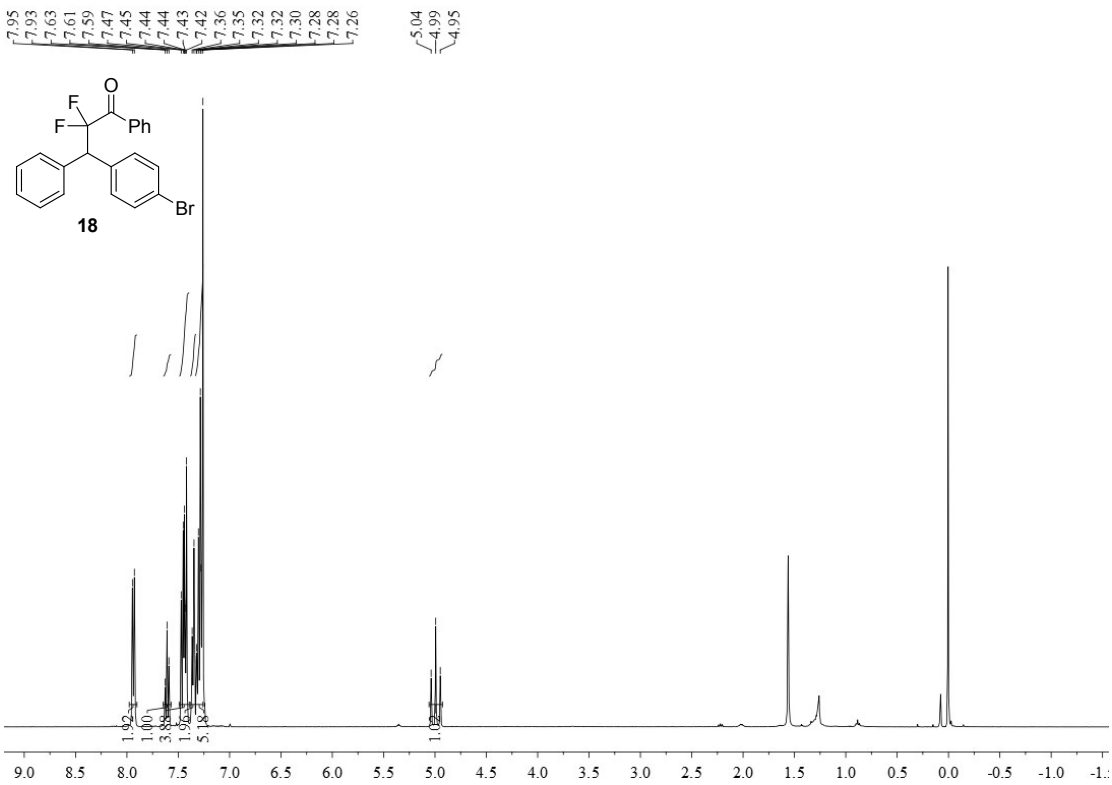
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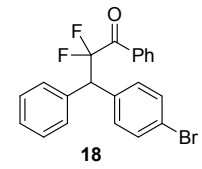
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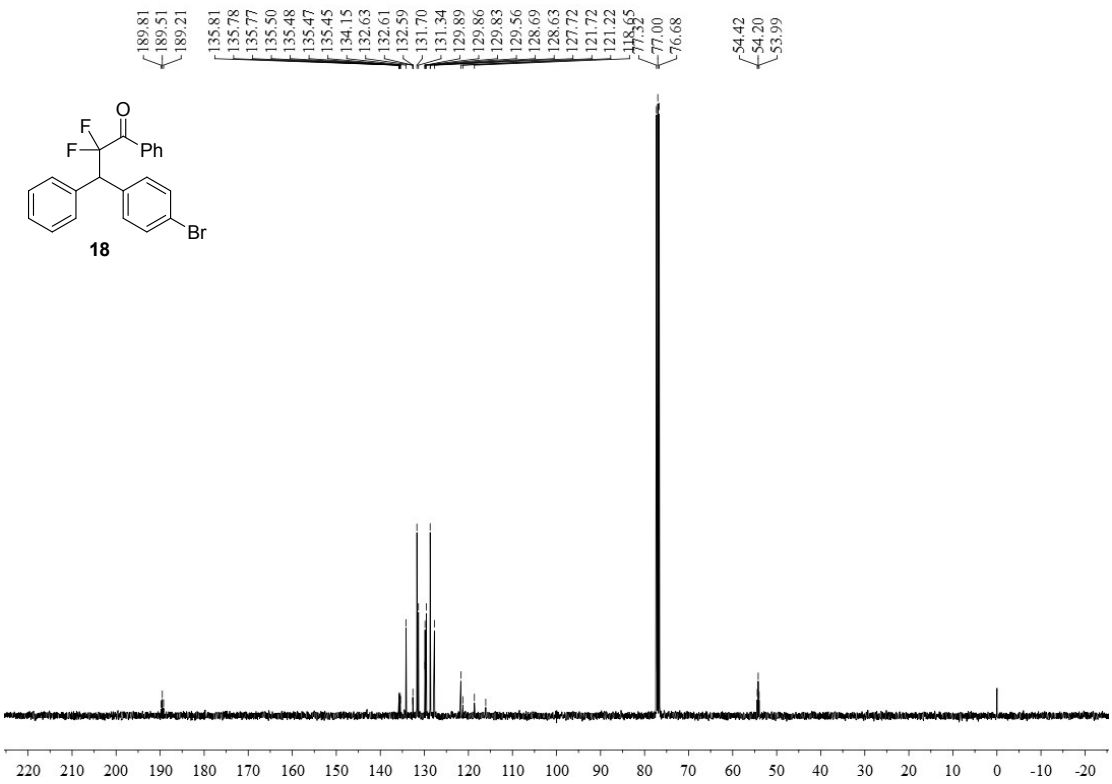
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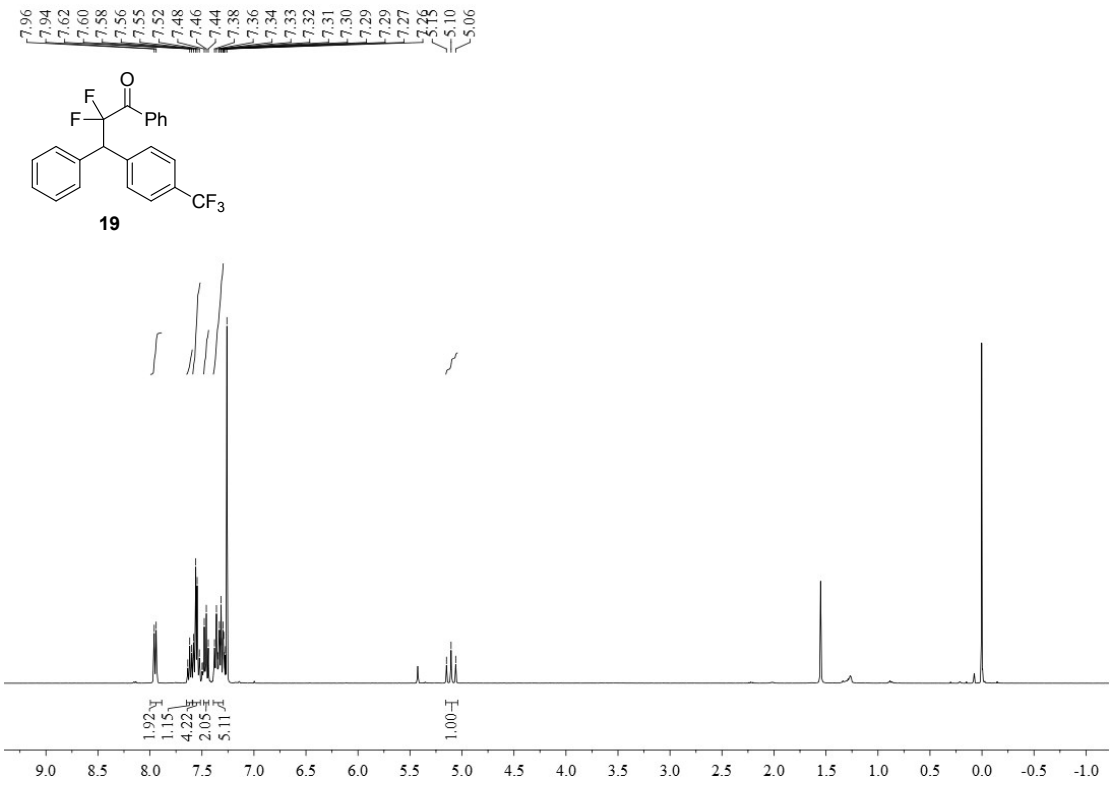
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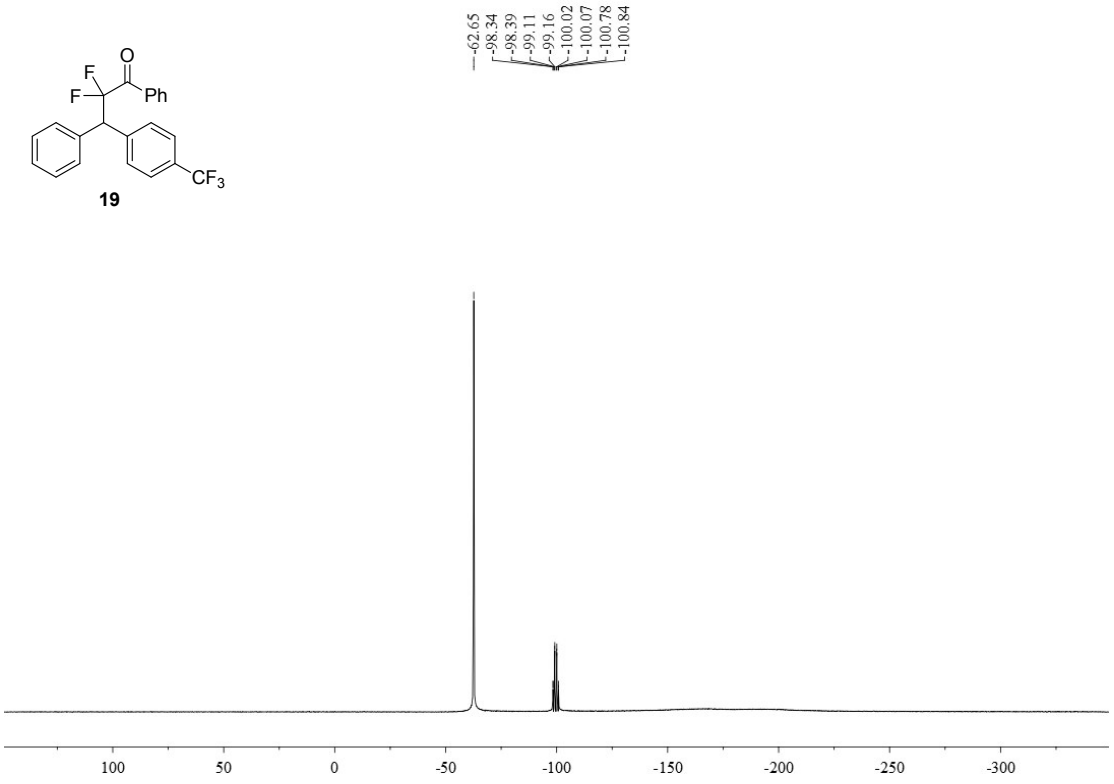
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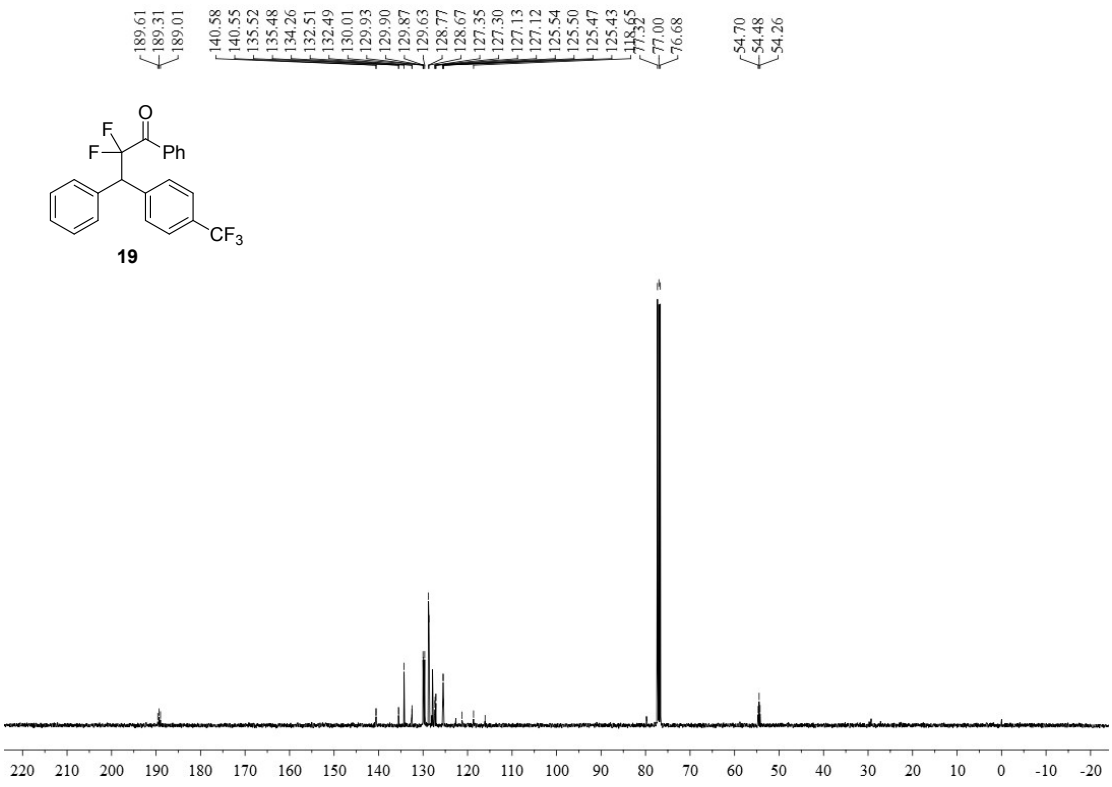
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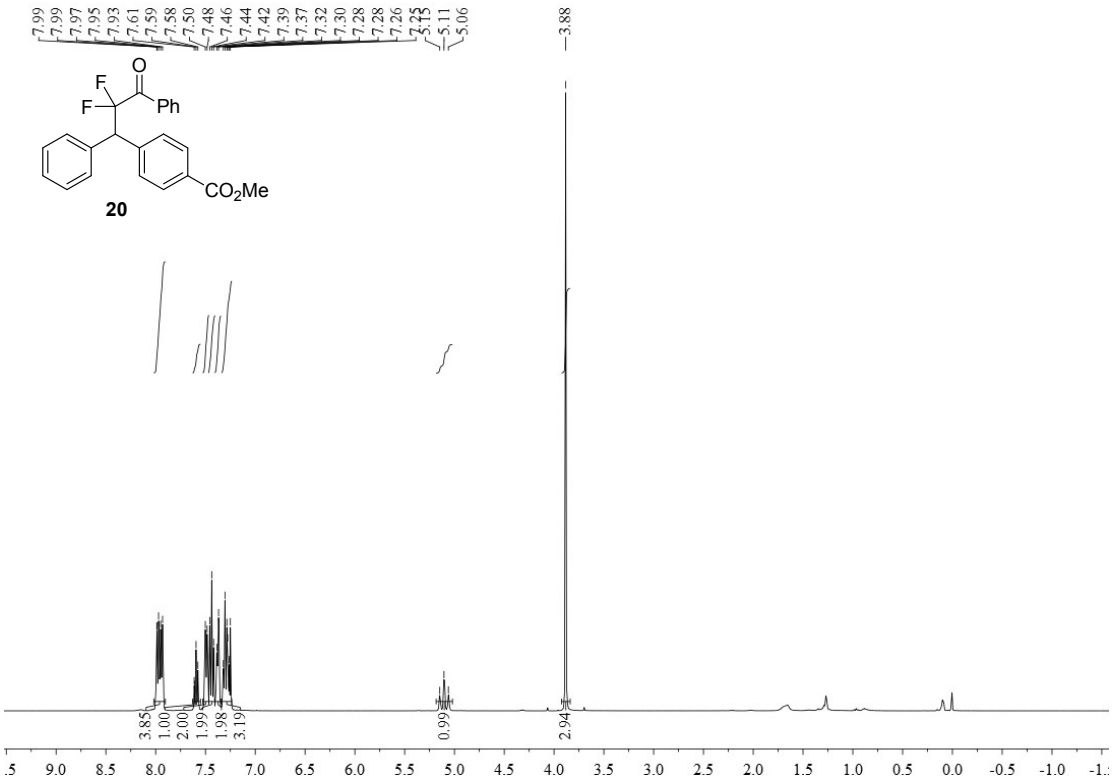
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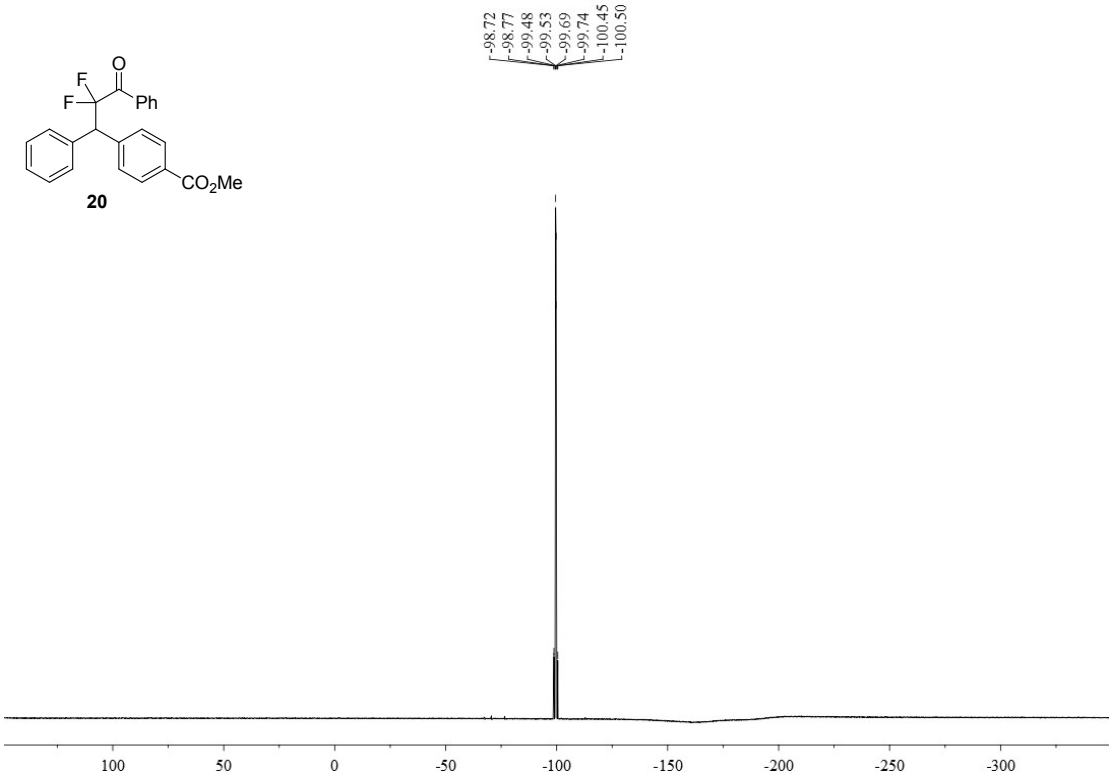
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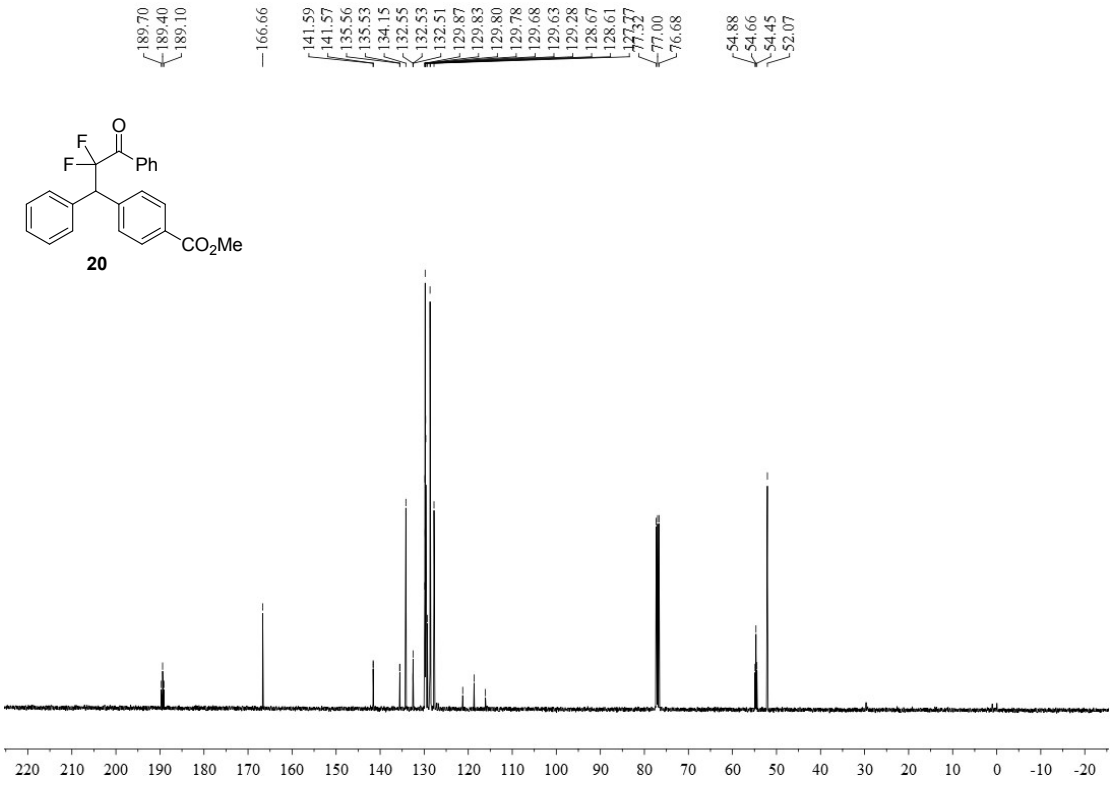
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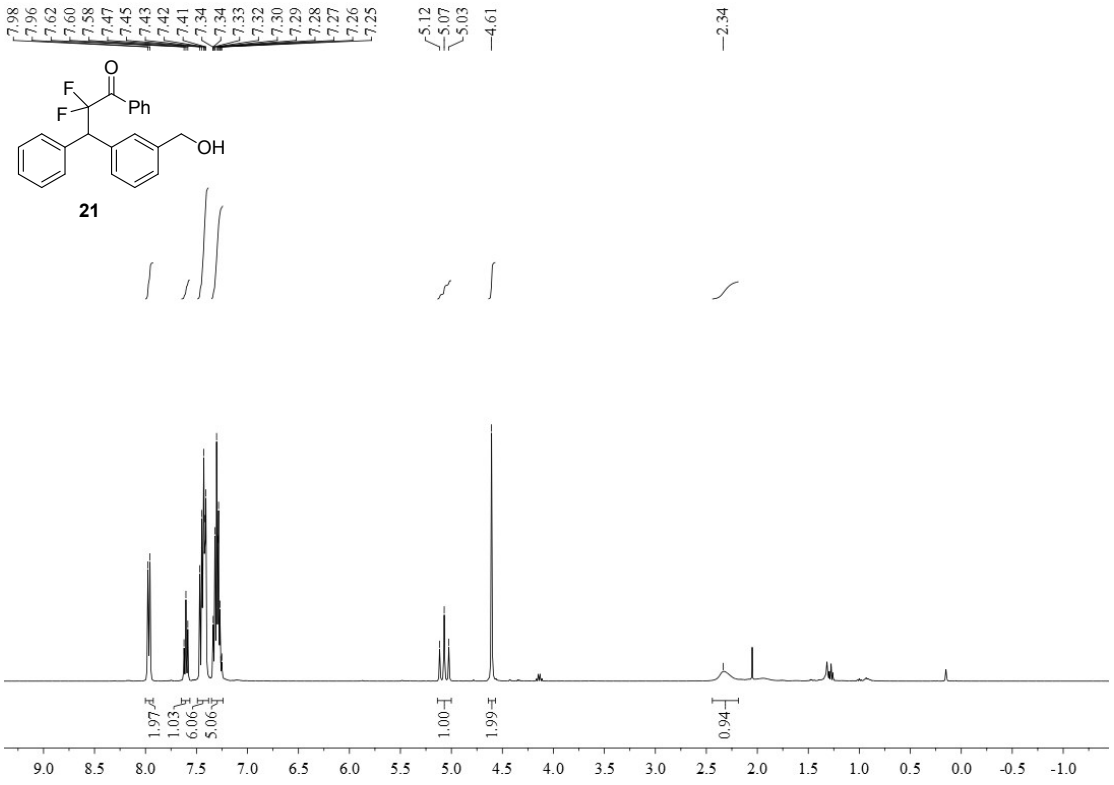
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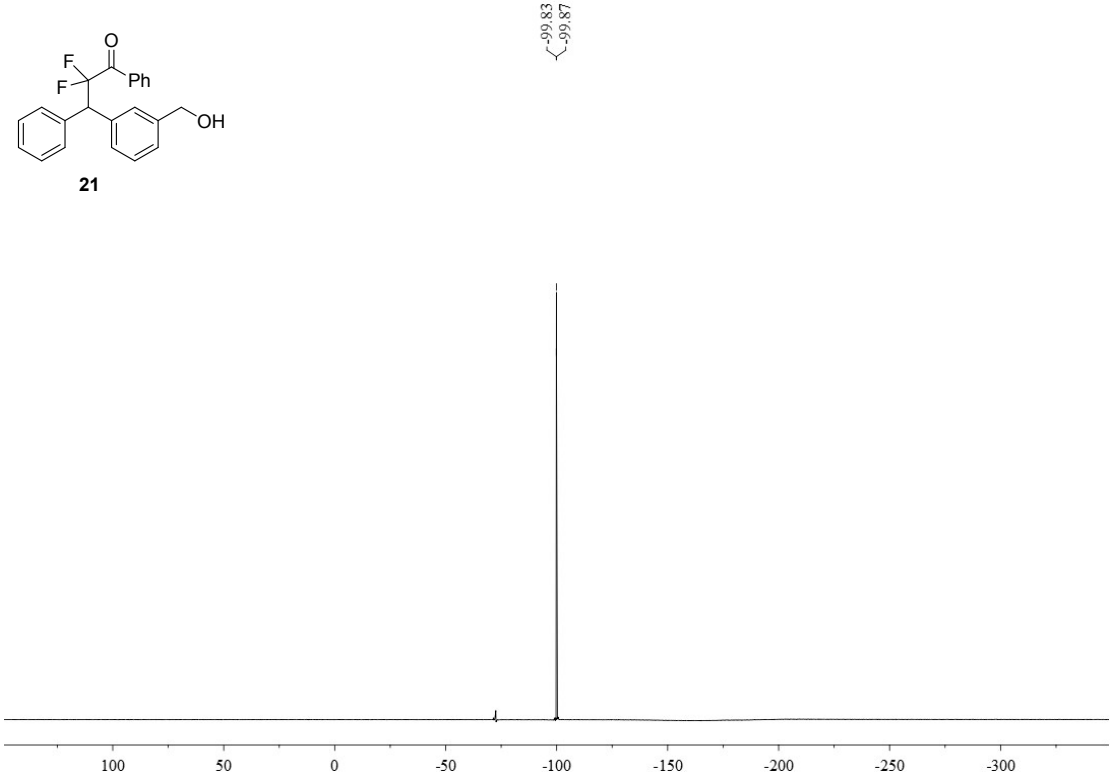
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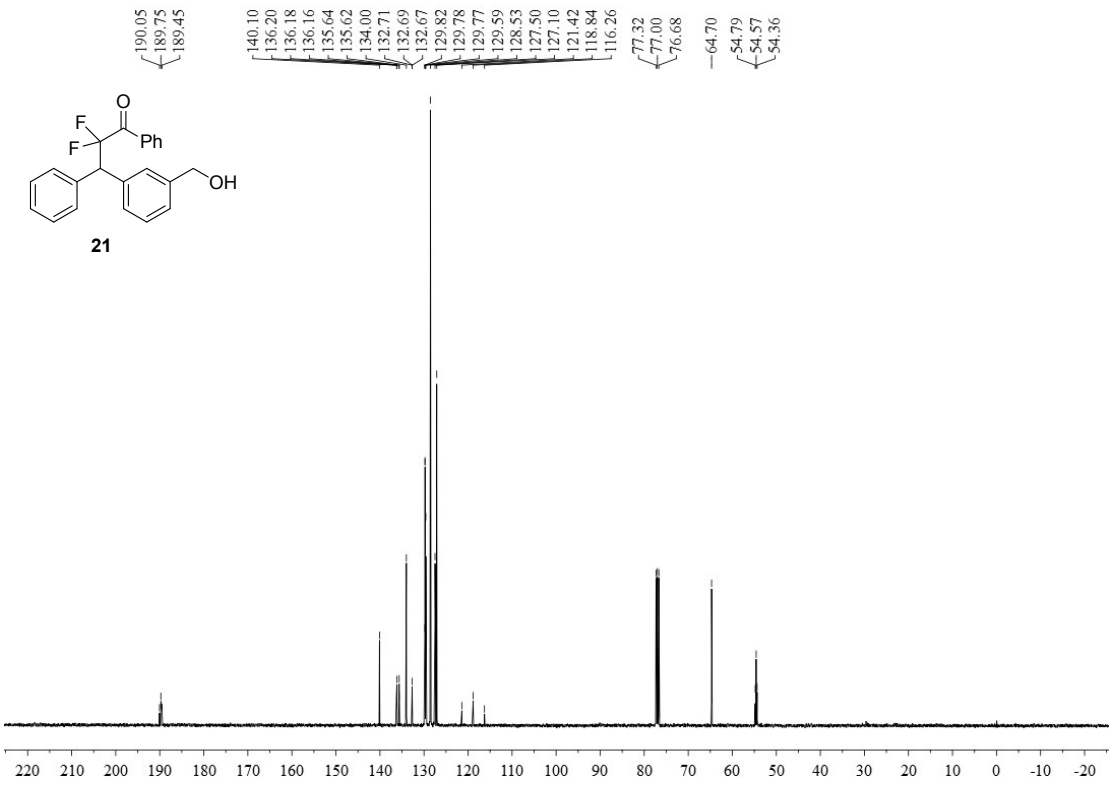
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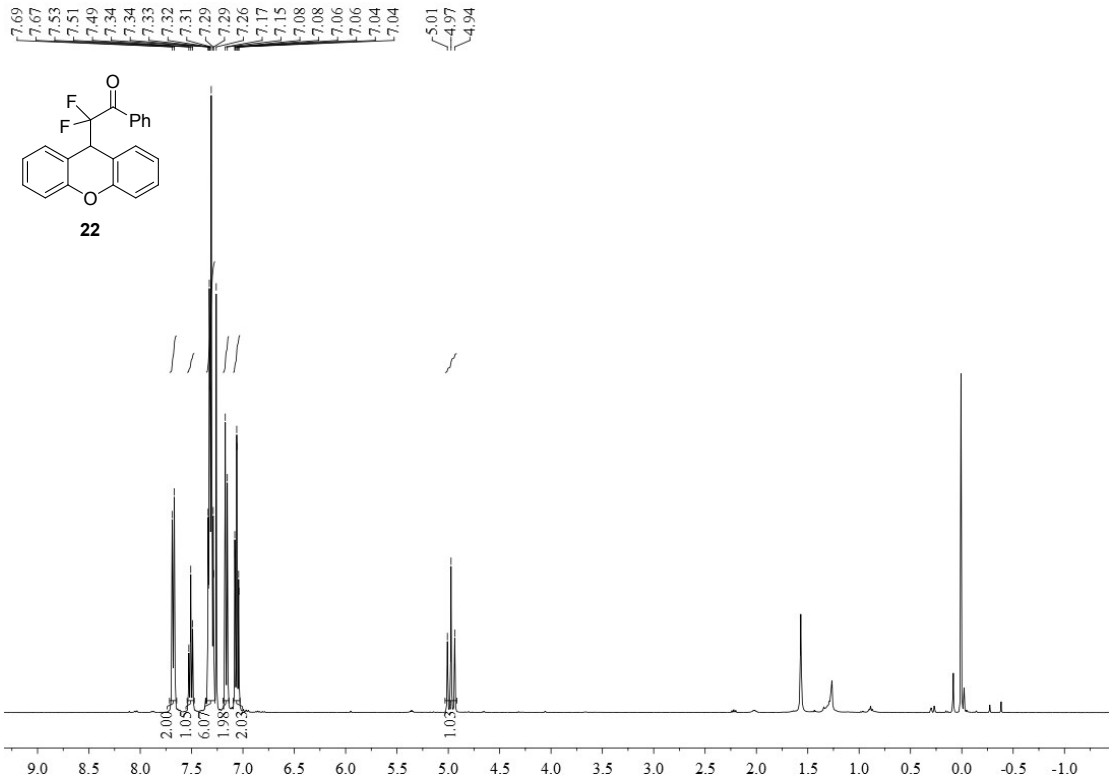
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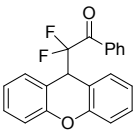
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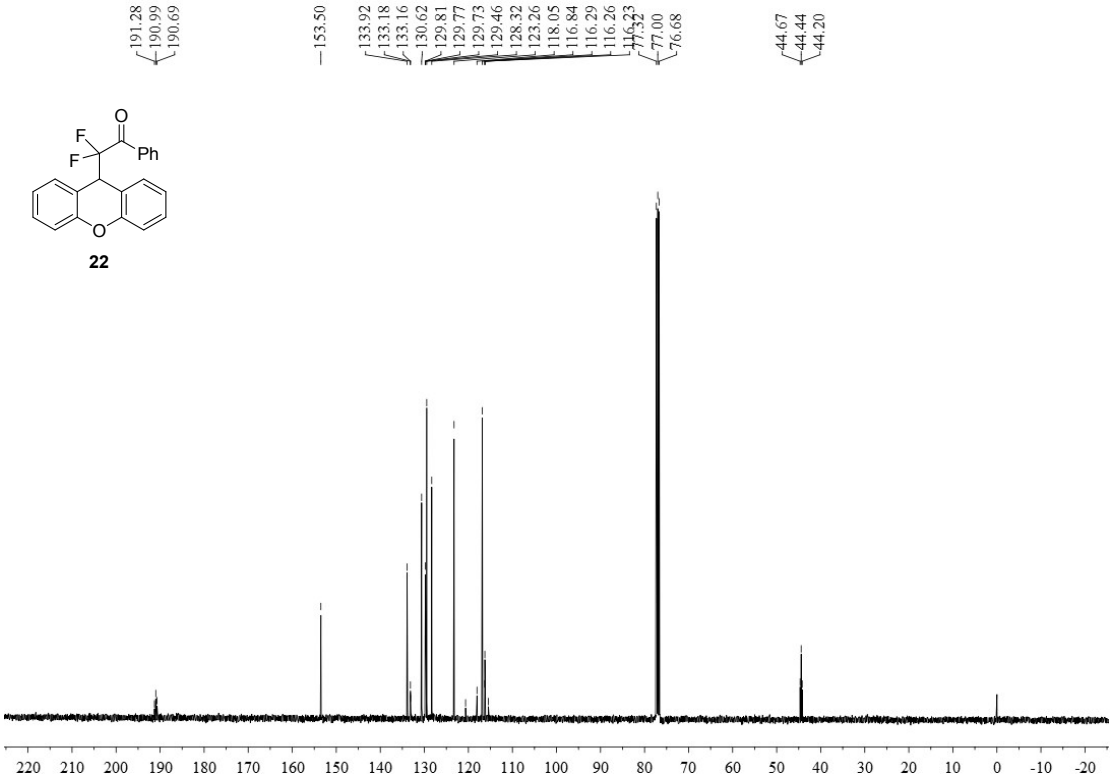
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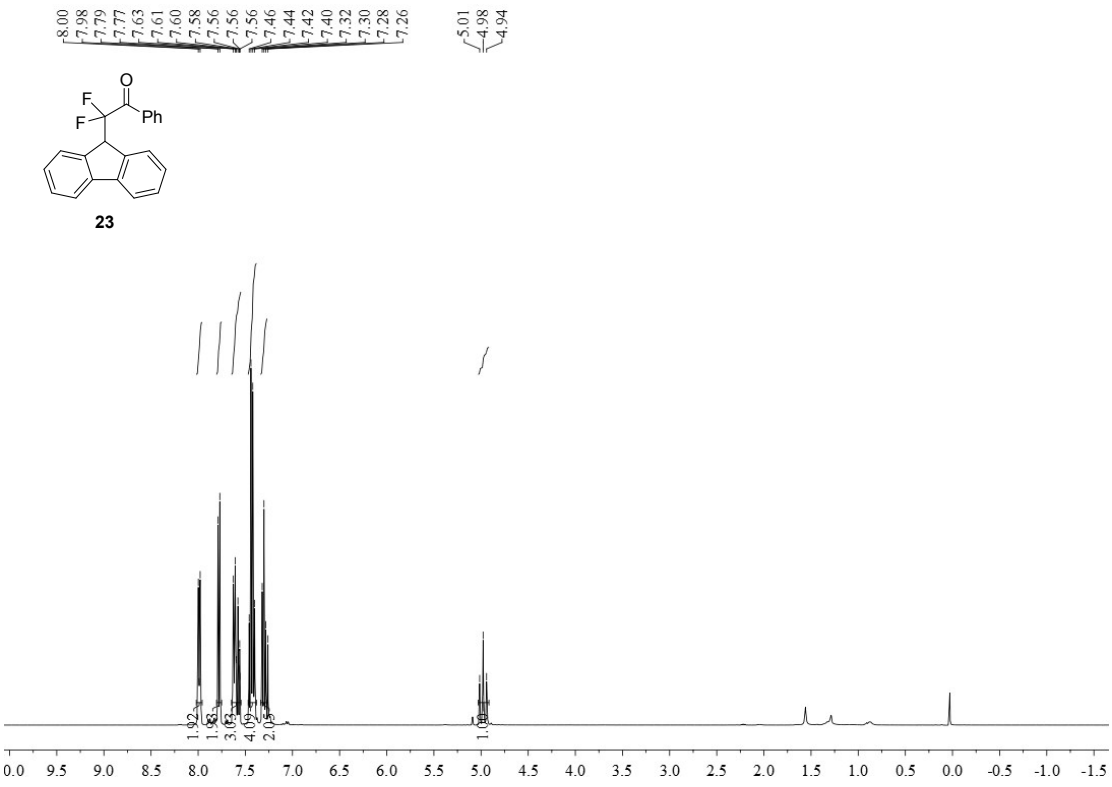
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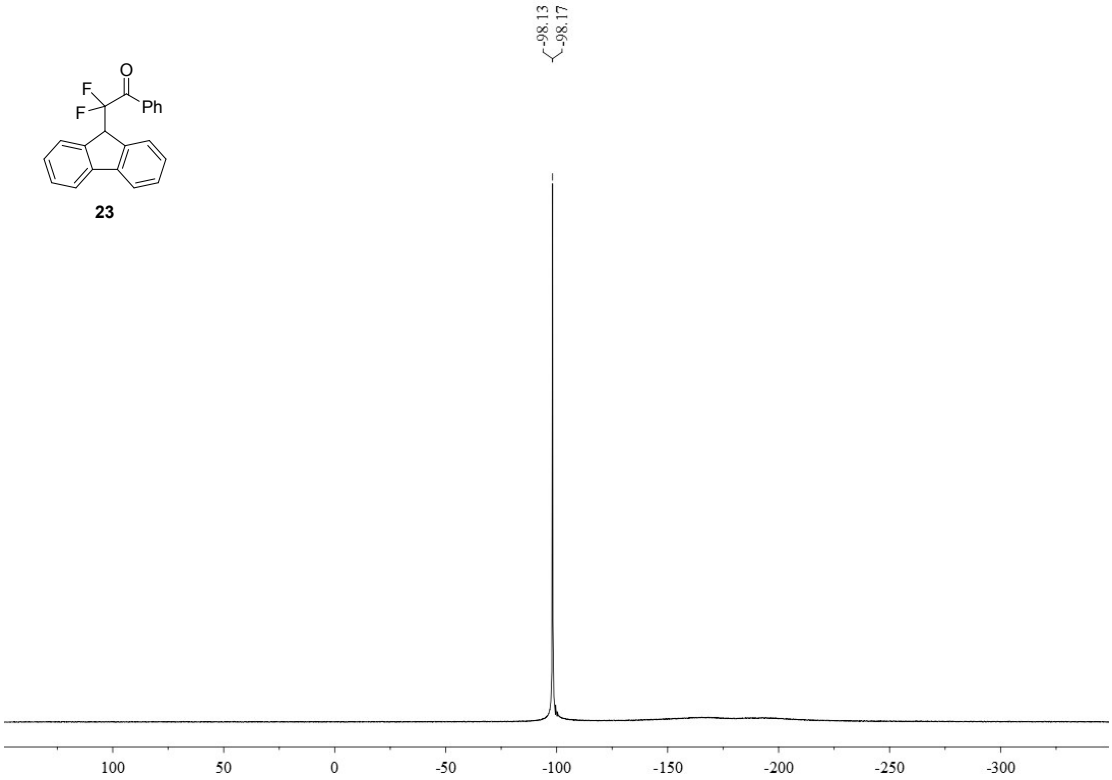
23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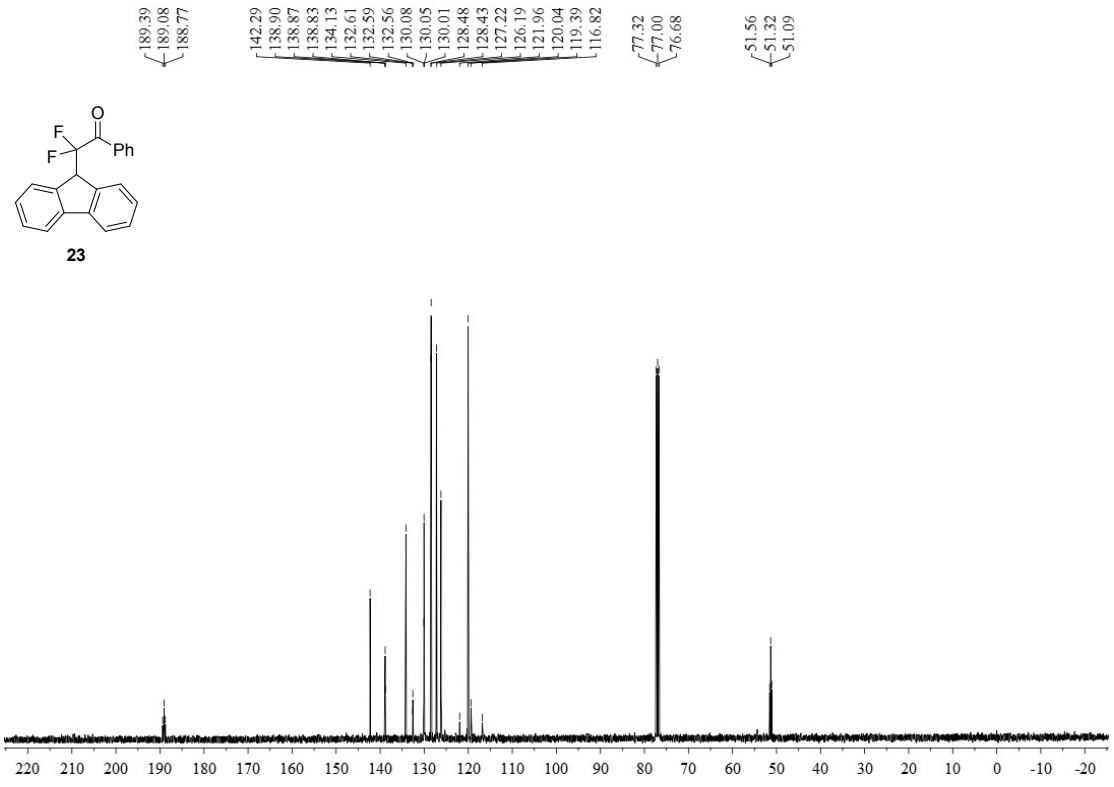
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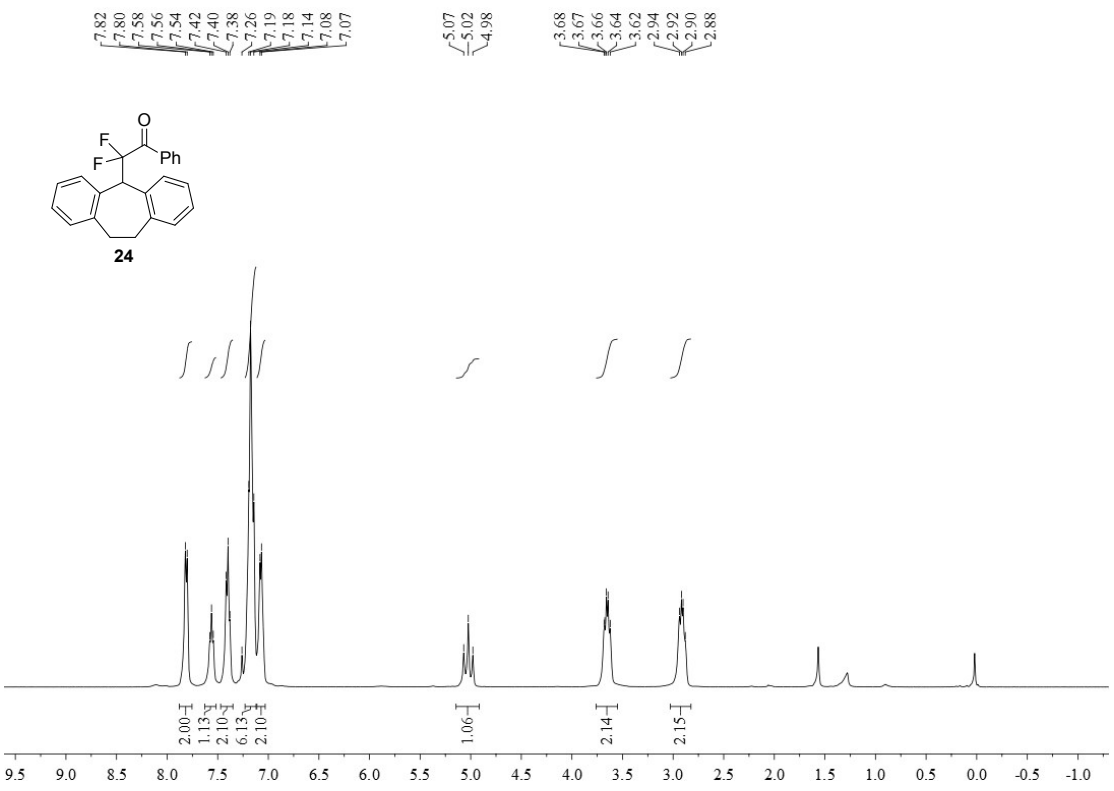
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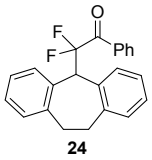
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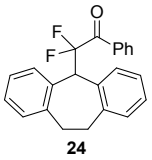
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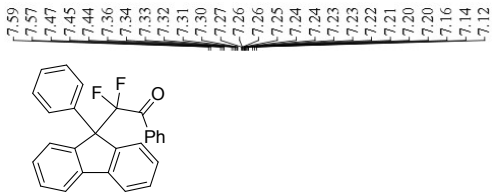
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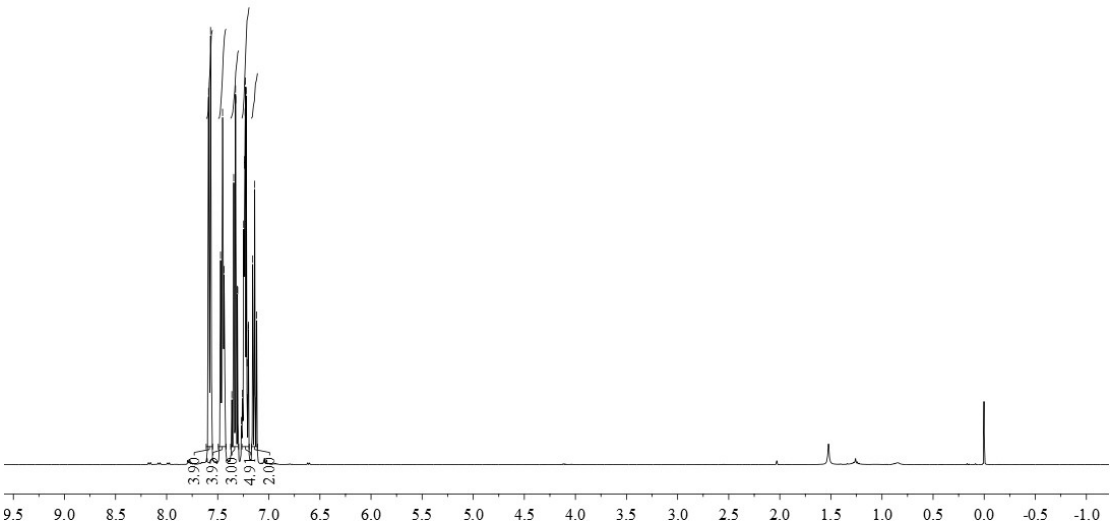
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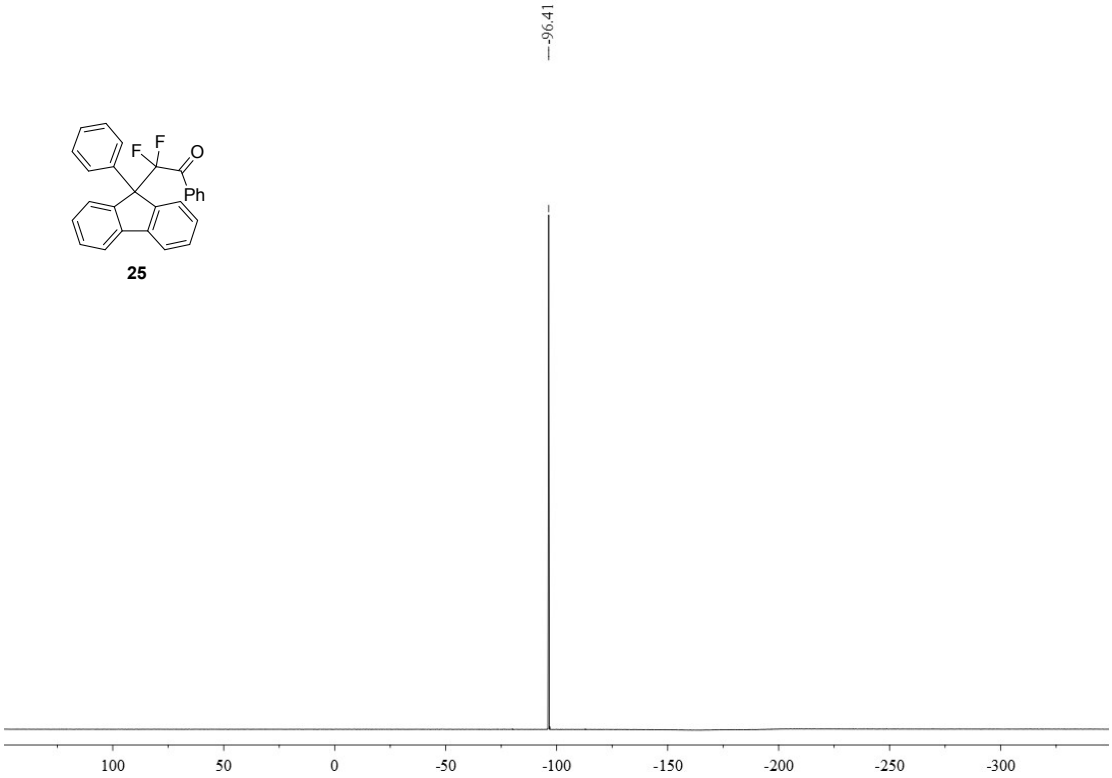
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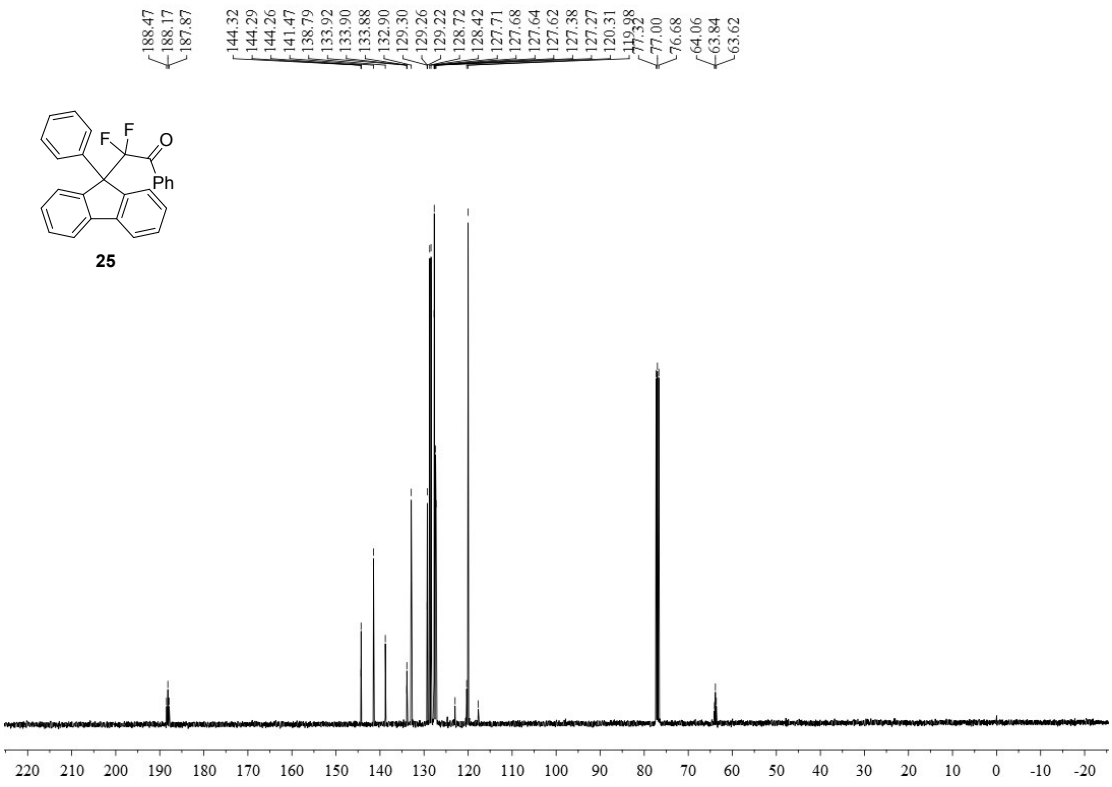
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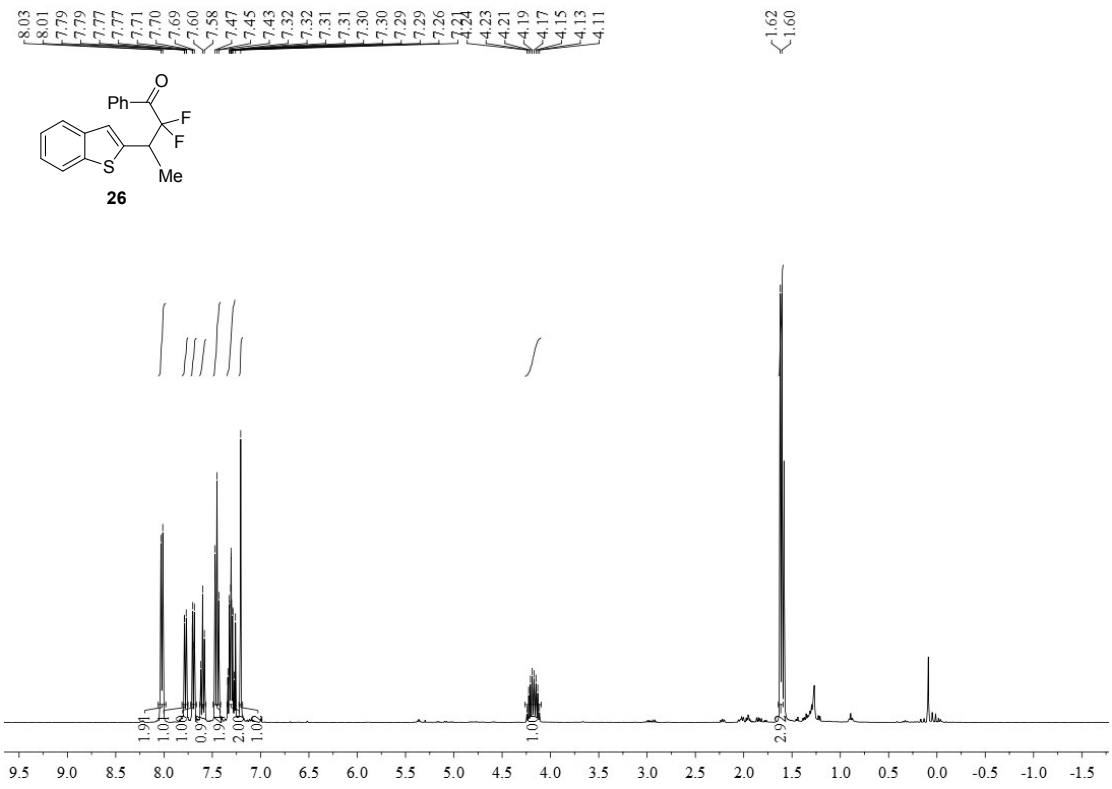
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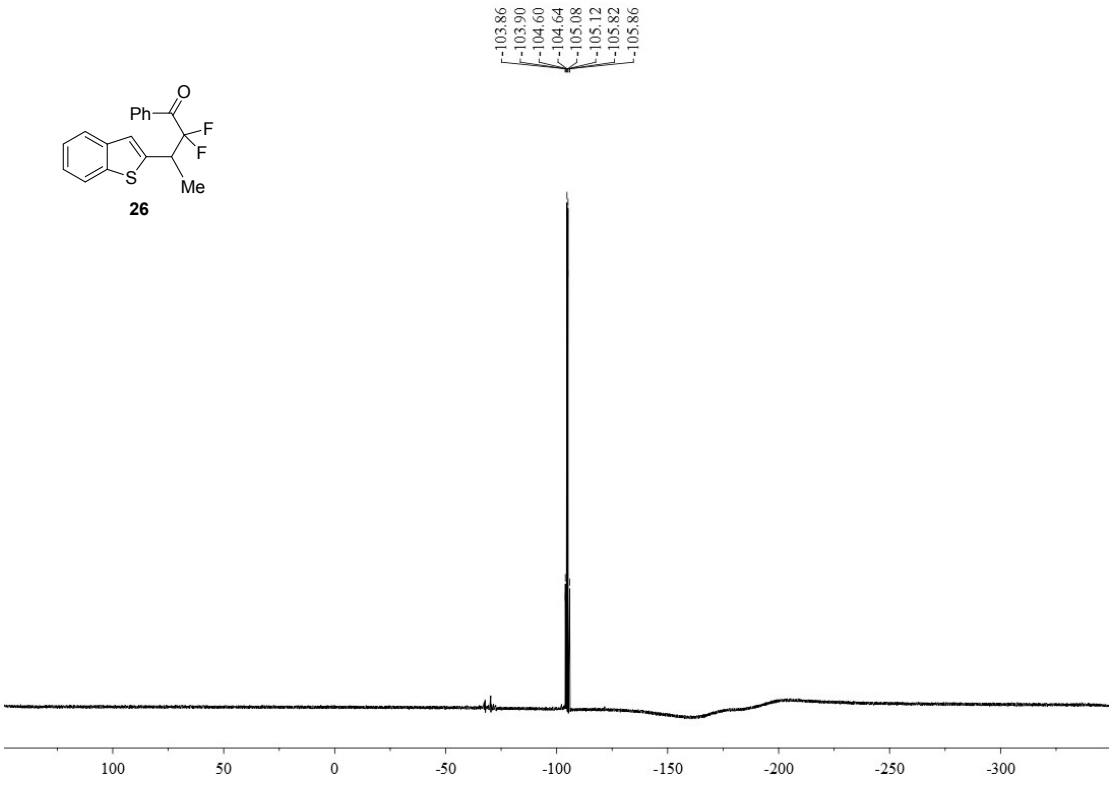
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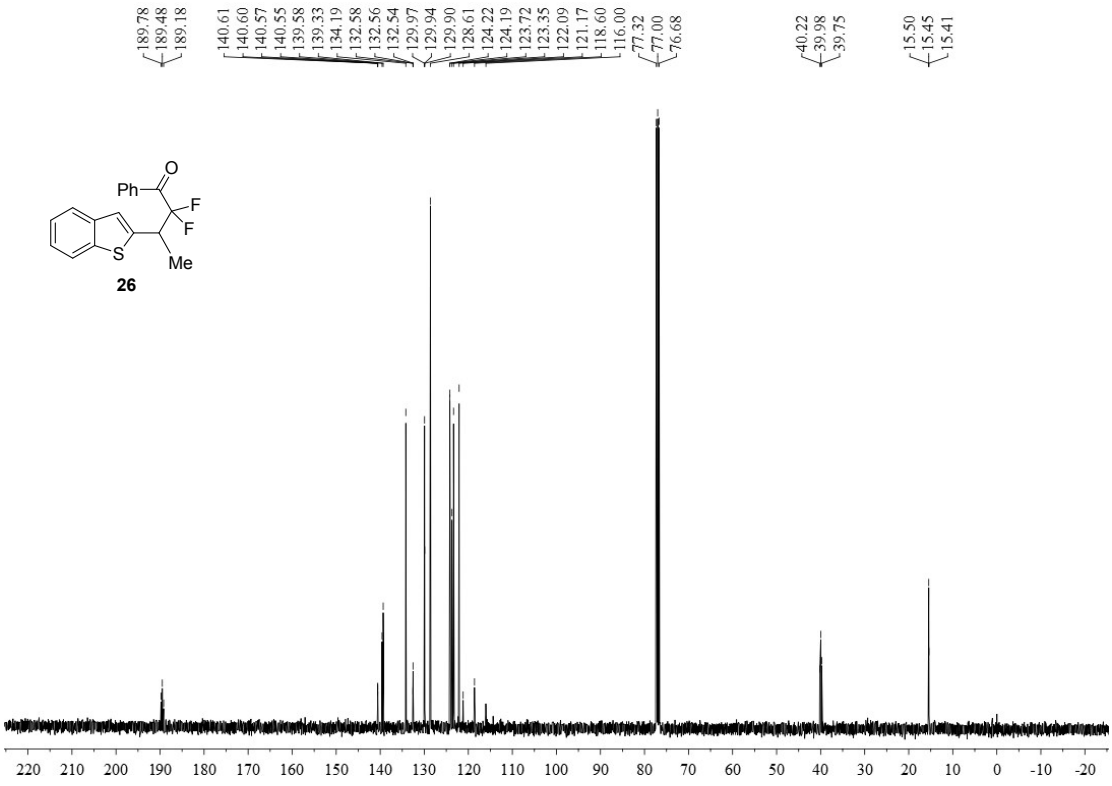
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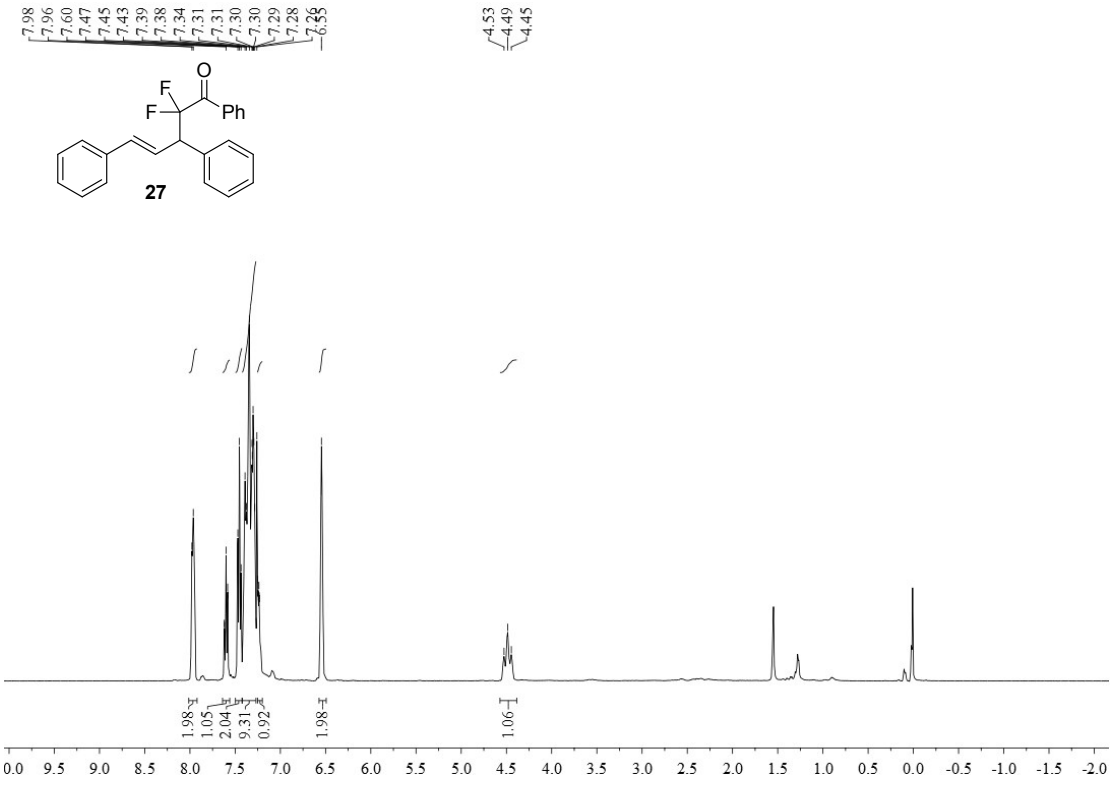
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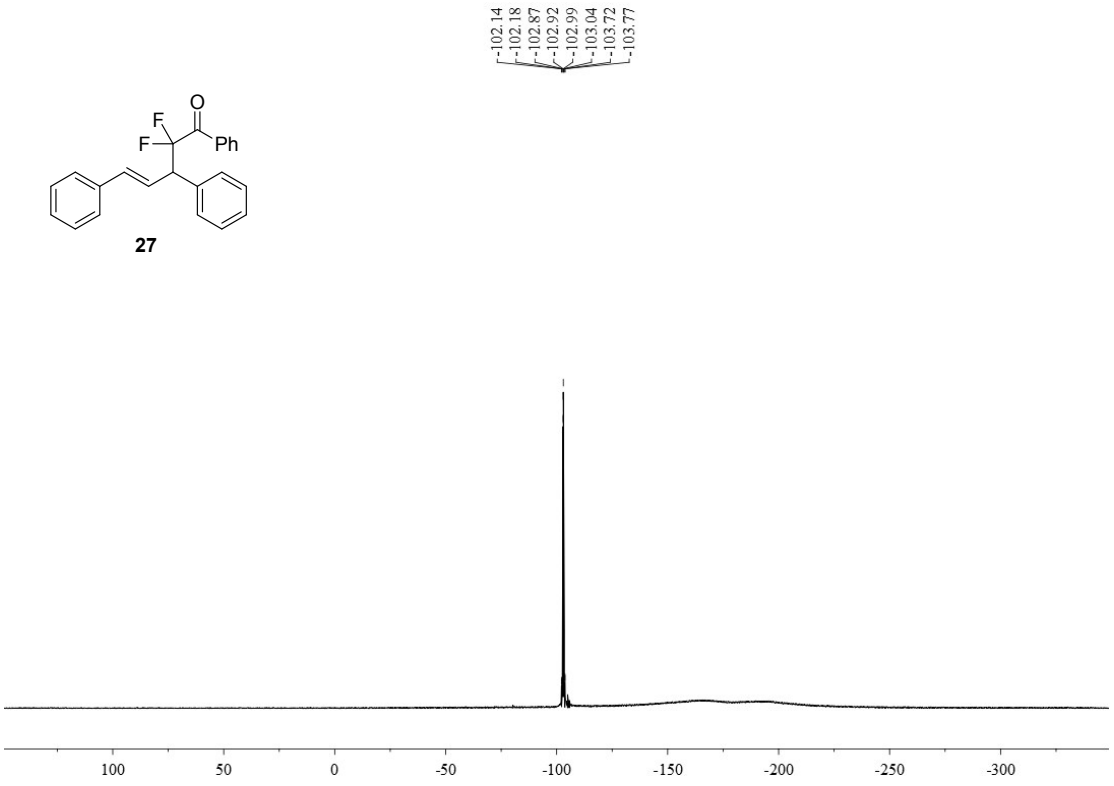
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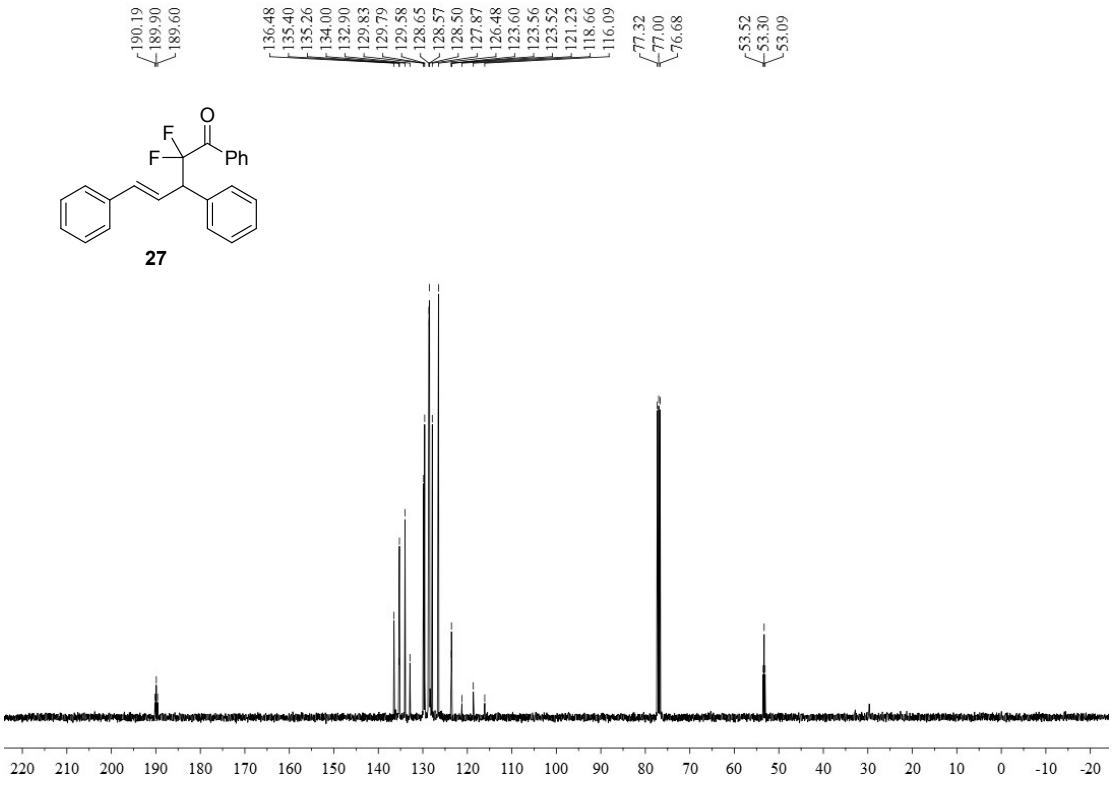
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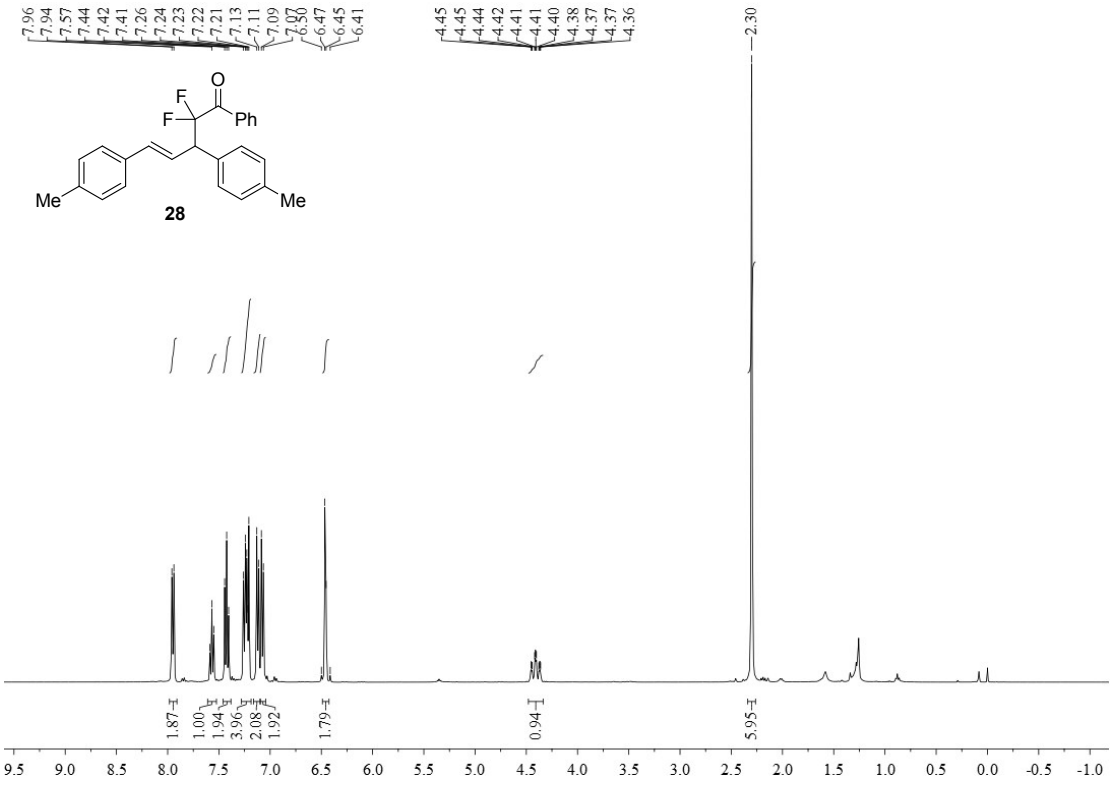
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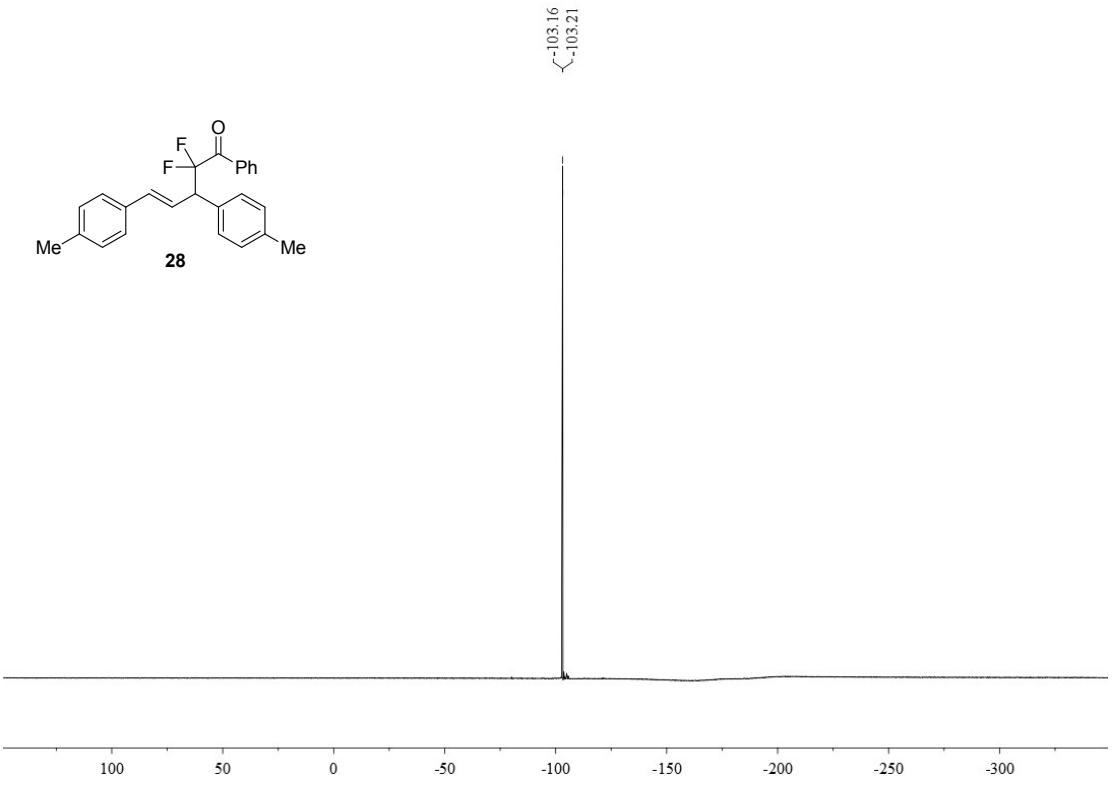
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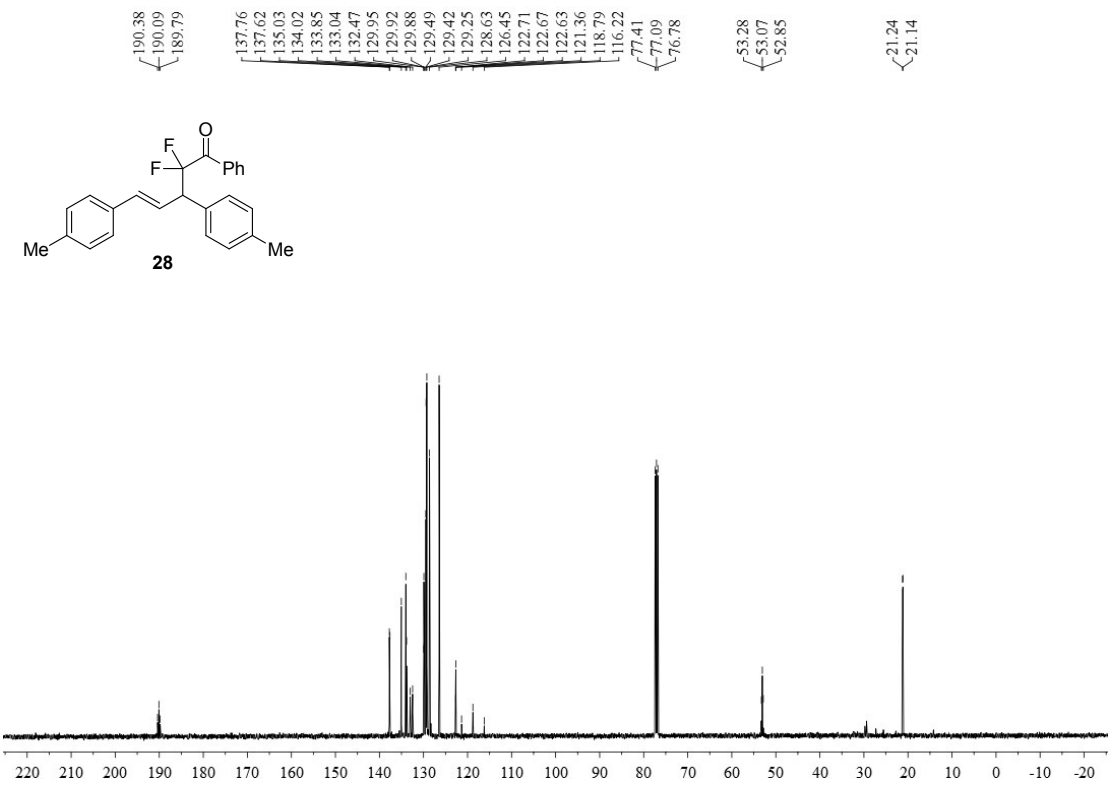
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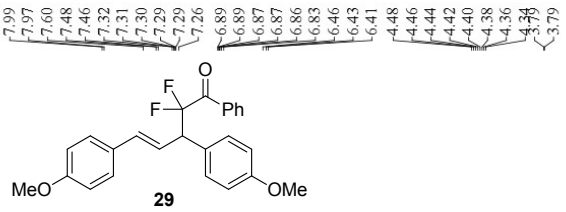
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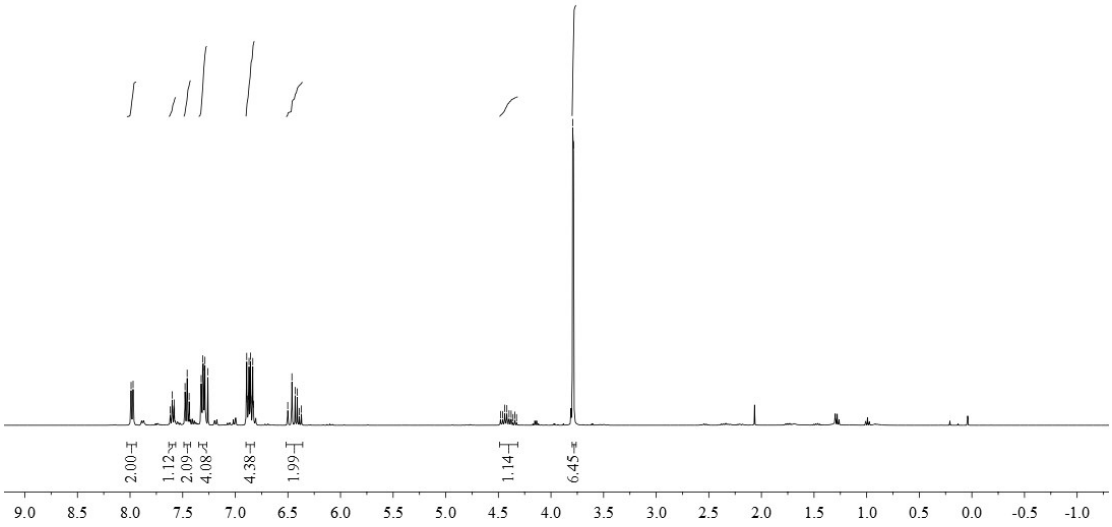
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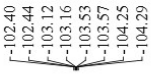
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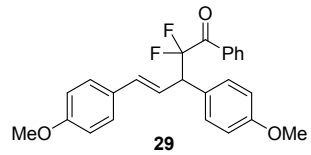
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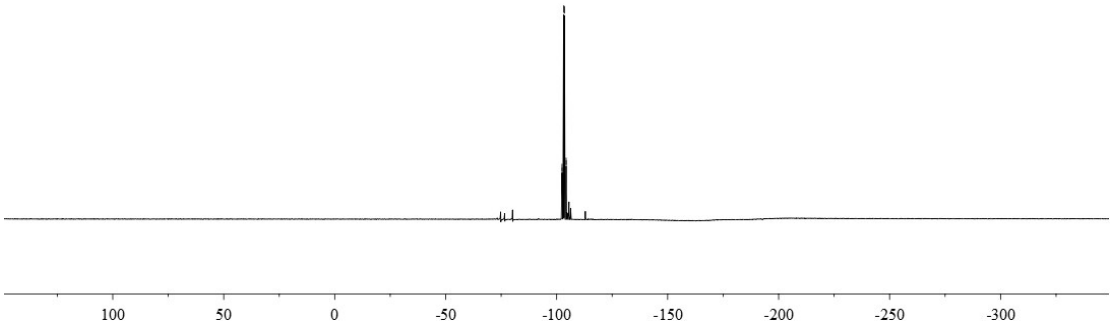
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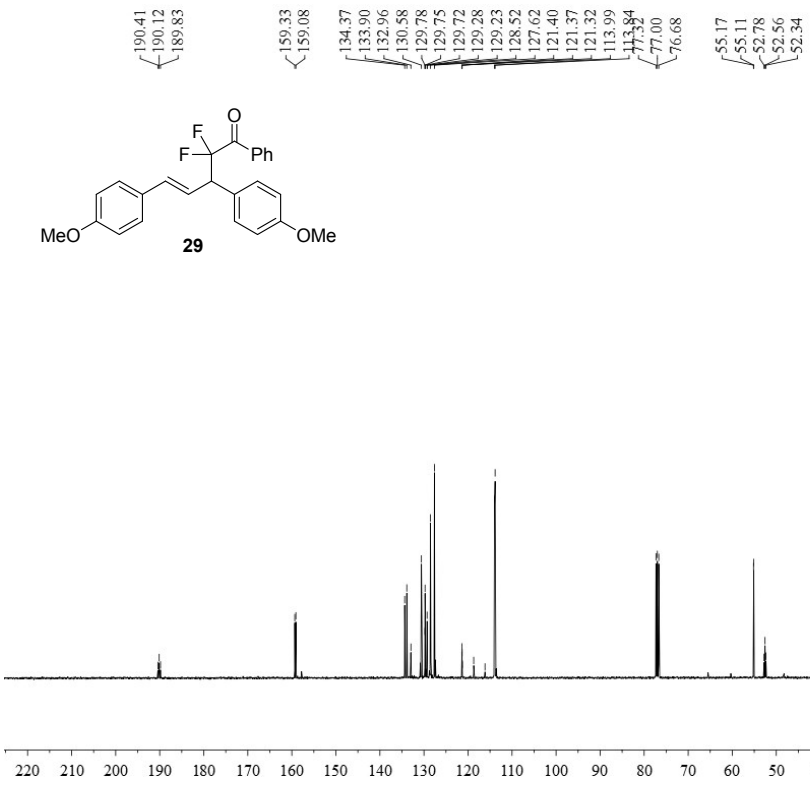
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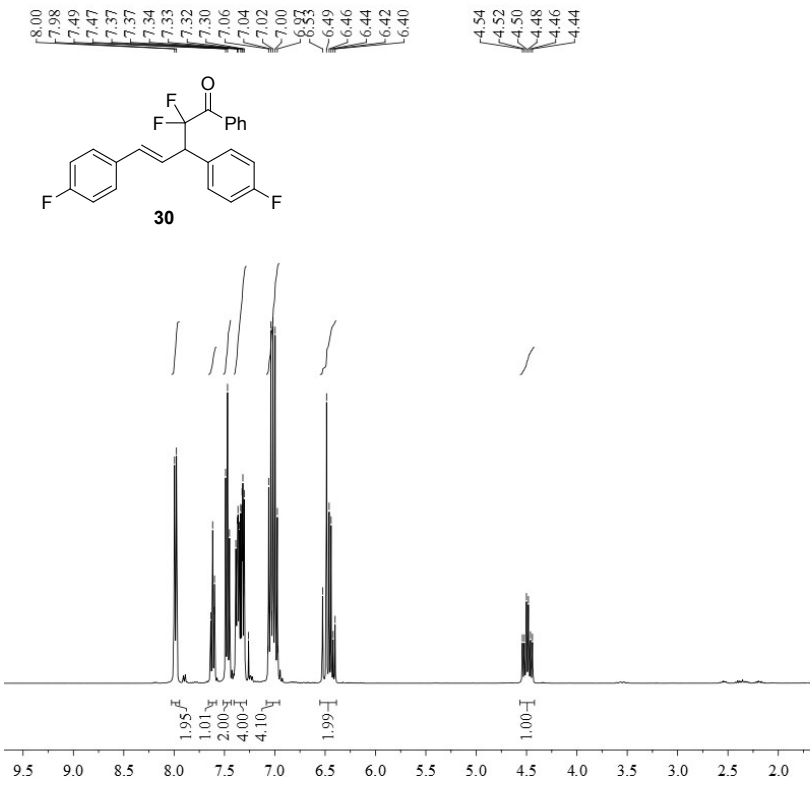
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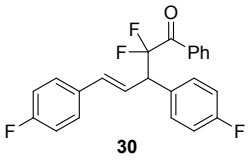
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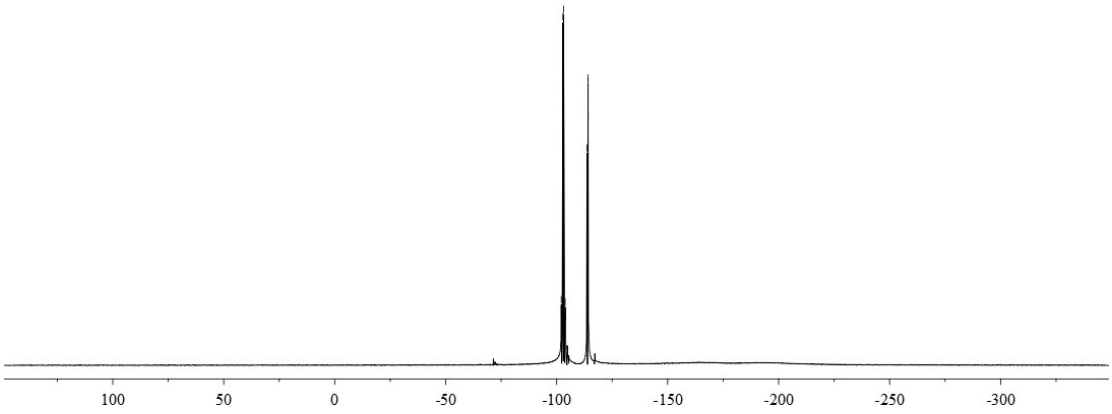
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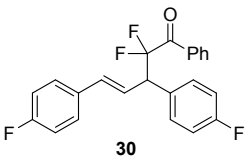
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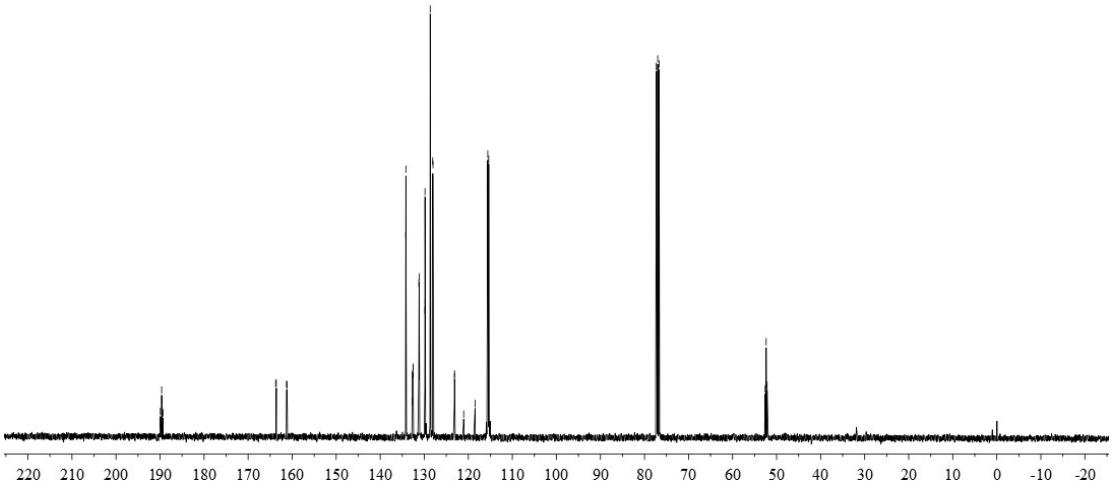
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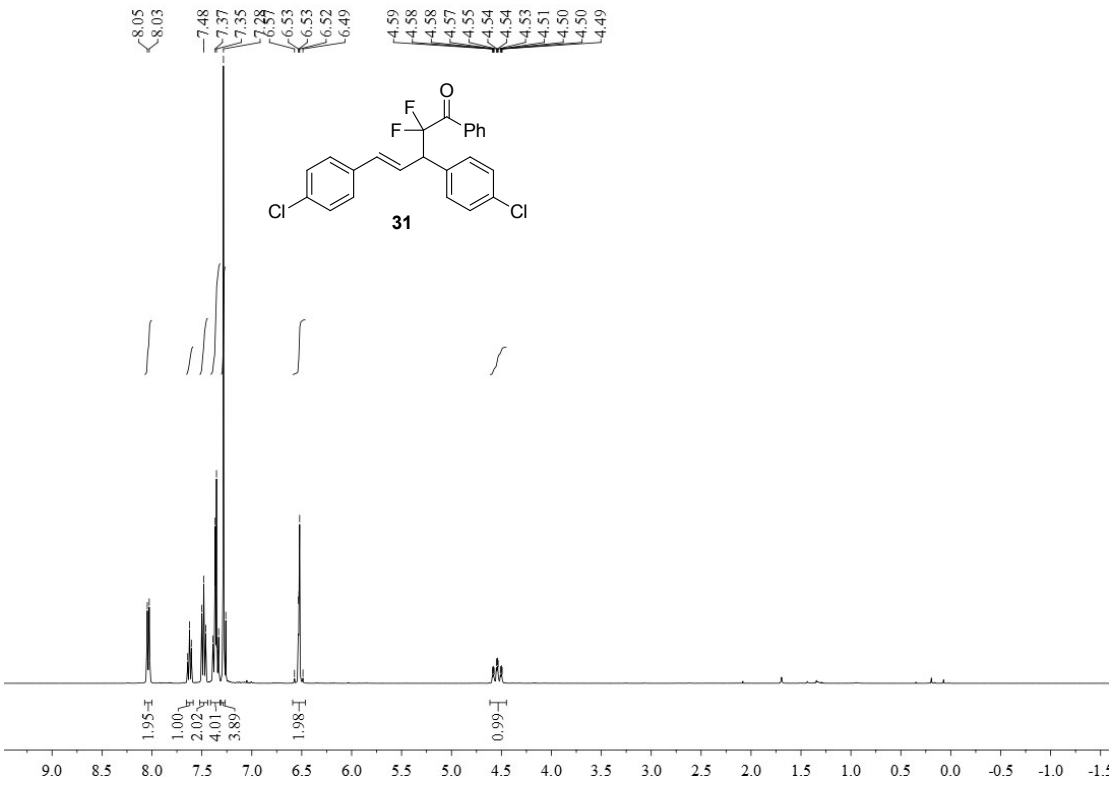
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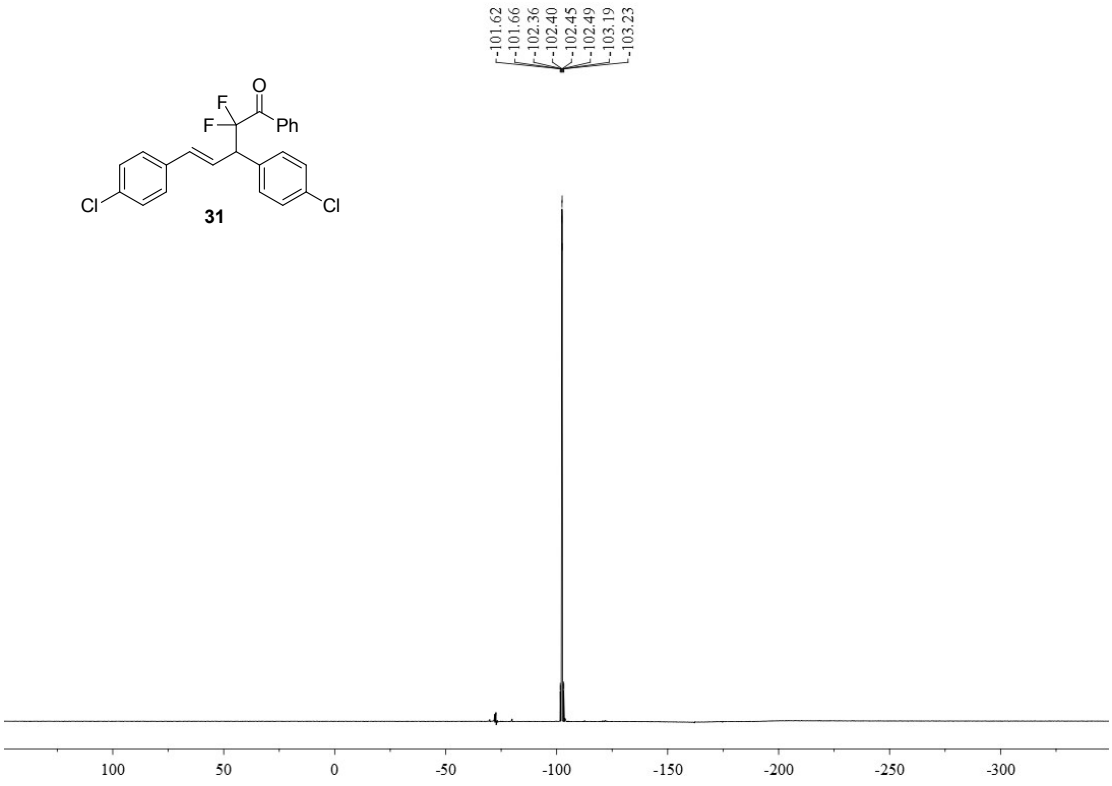
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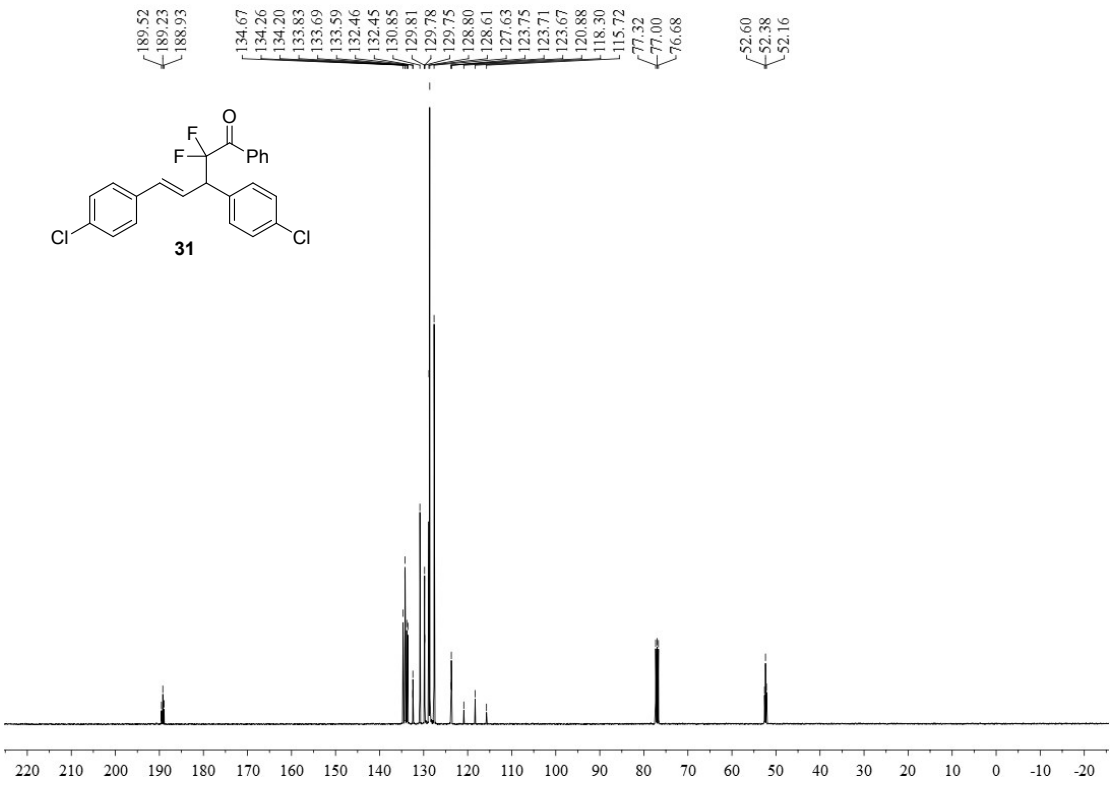
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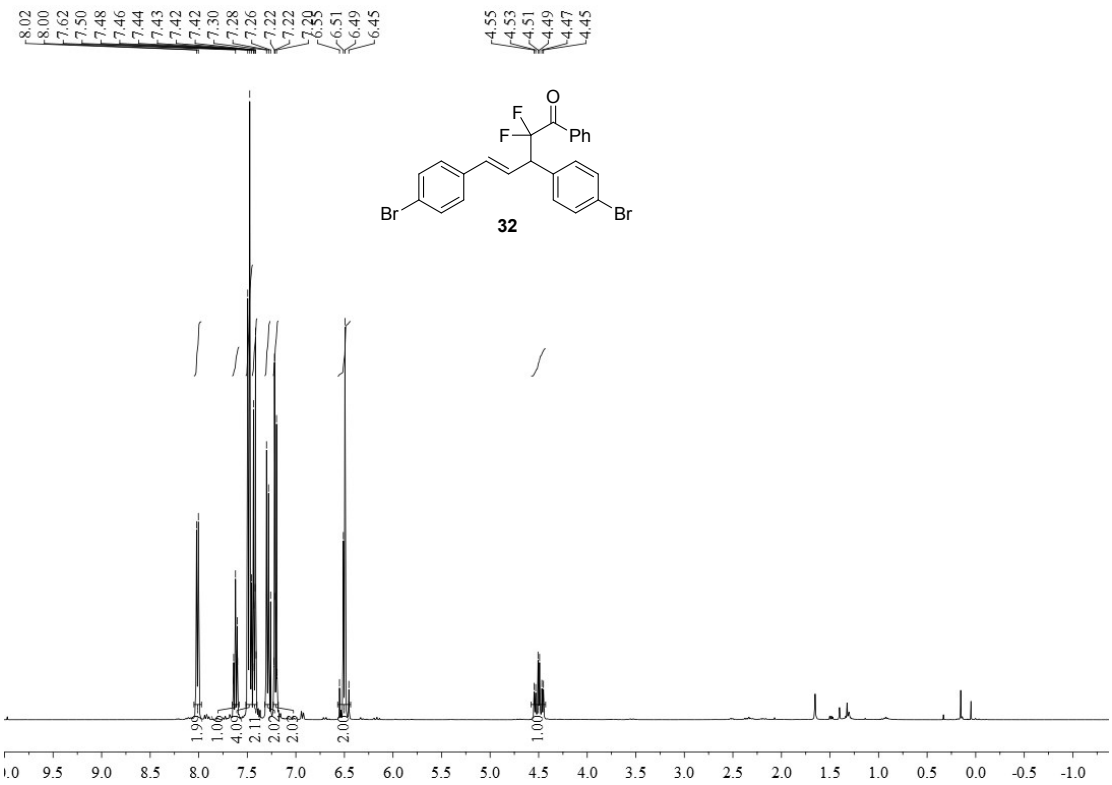
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4.09
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2.02
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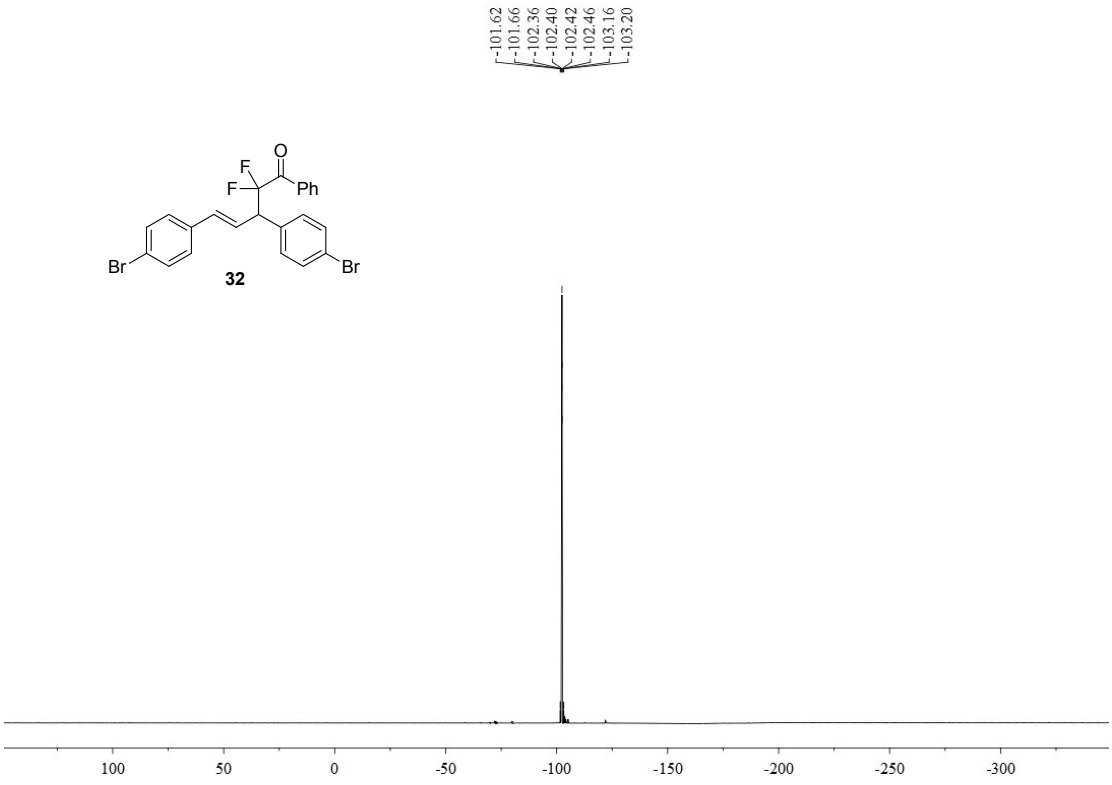
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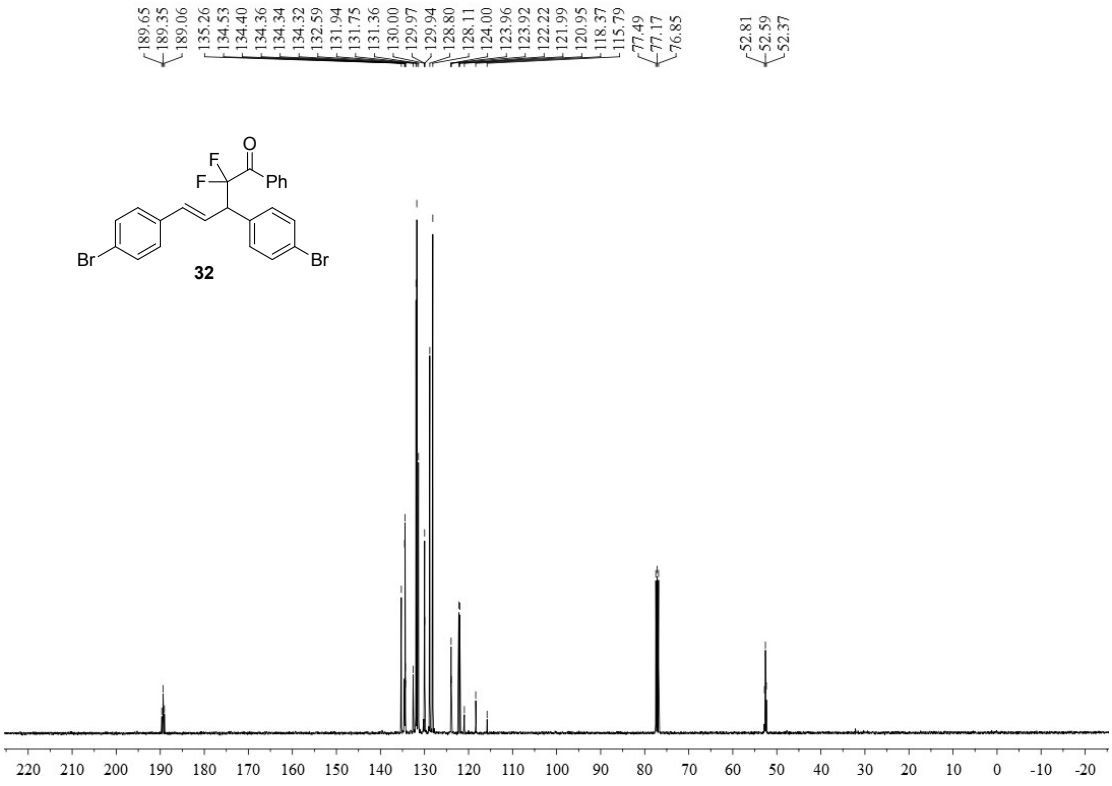
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121.99
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77.17
76.85
52.81
52.59
52.37
F
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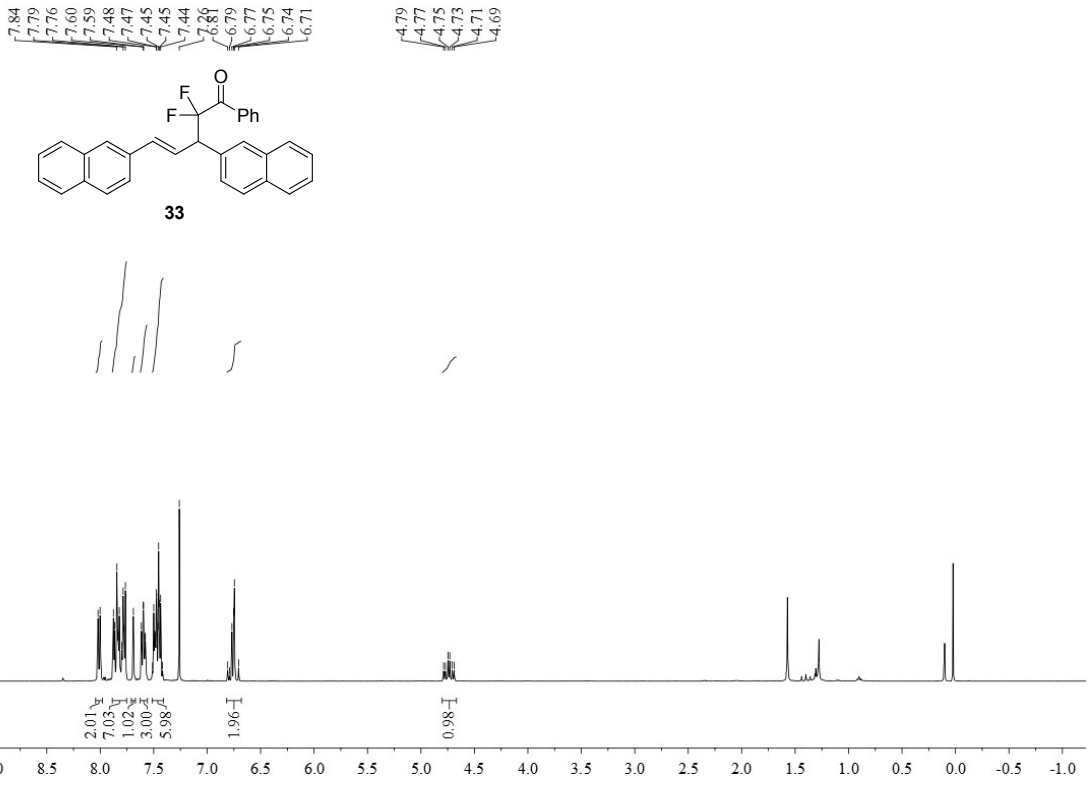
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4.71
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F
O
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2.01
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1.02
3.00
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1.96
0.98
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8.0
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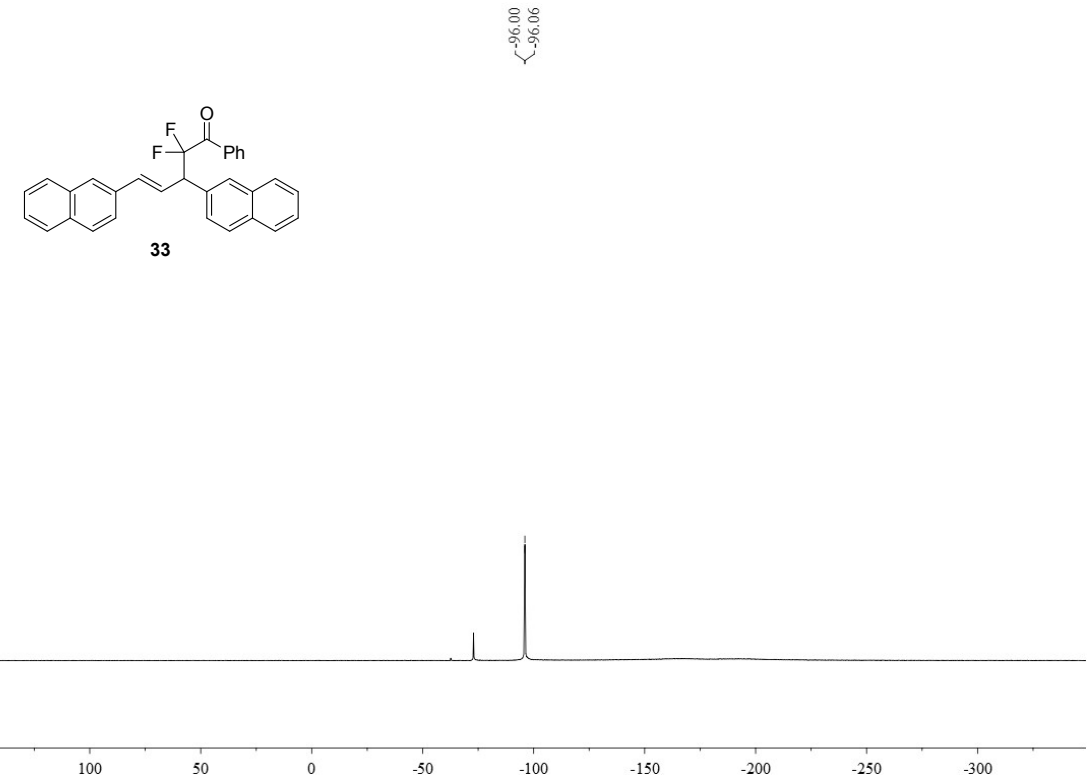
-1.0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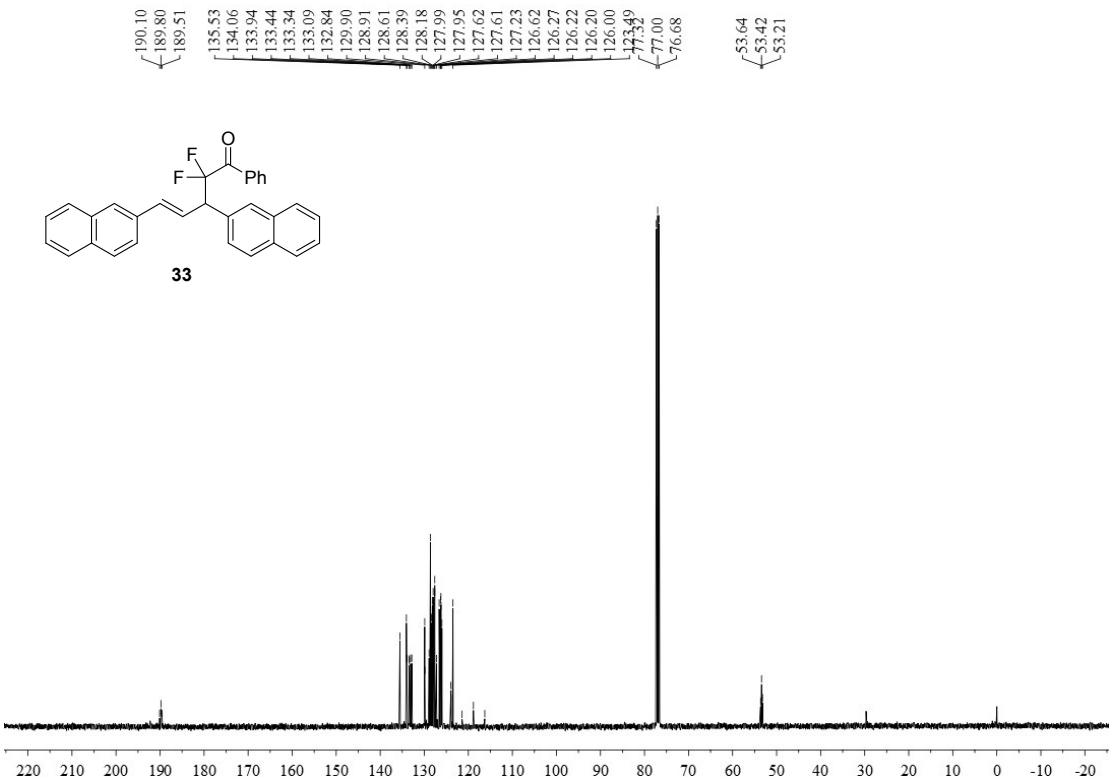
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126.00
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77.00
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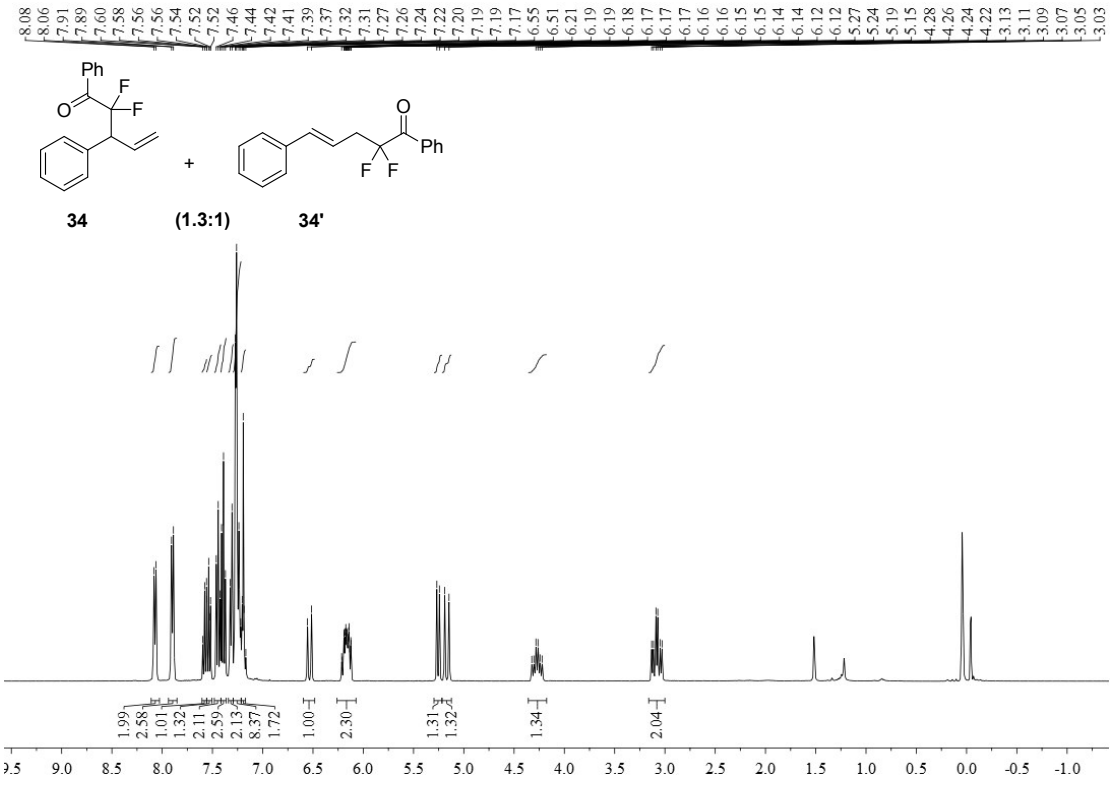
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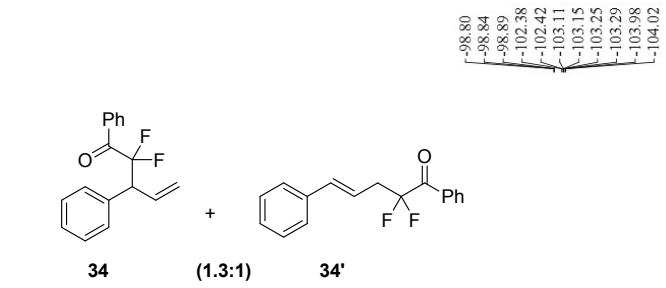
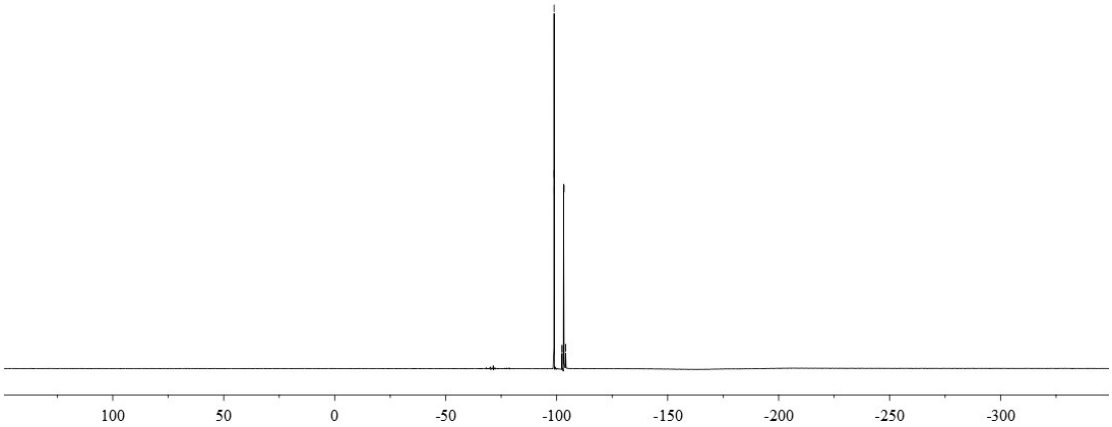
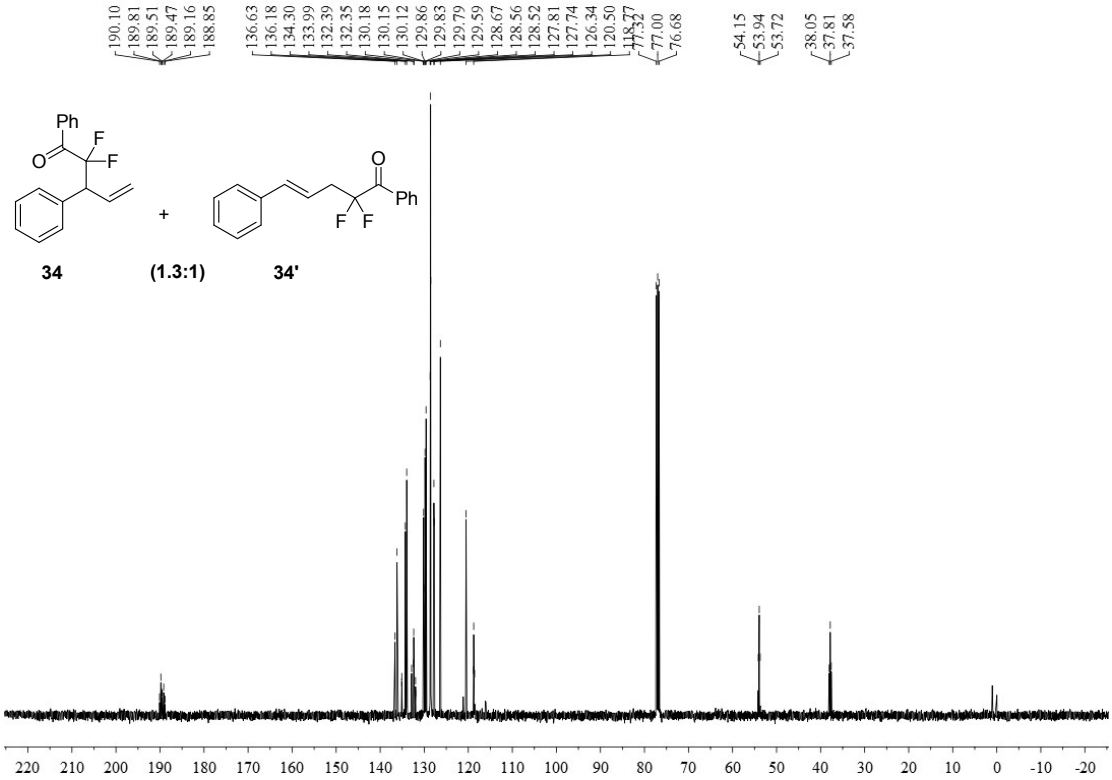
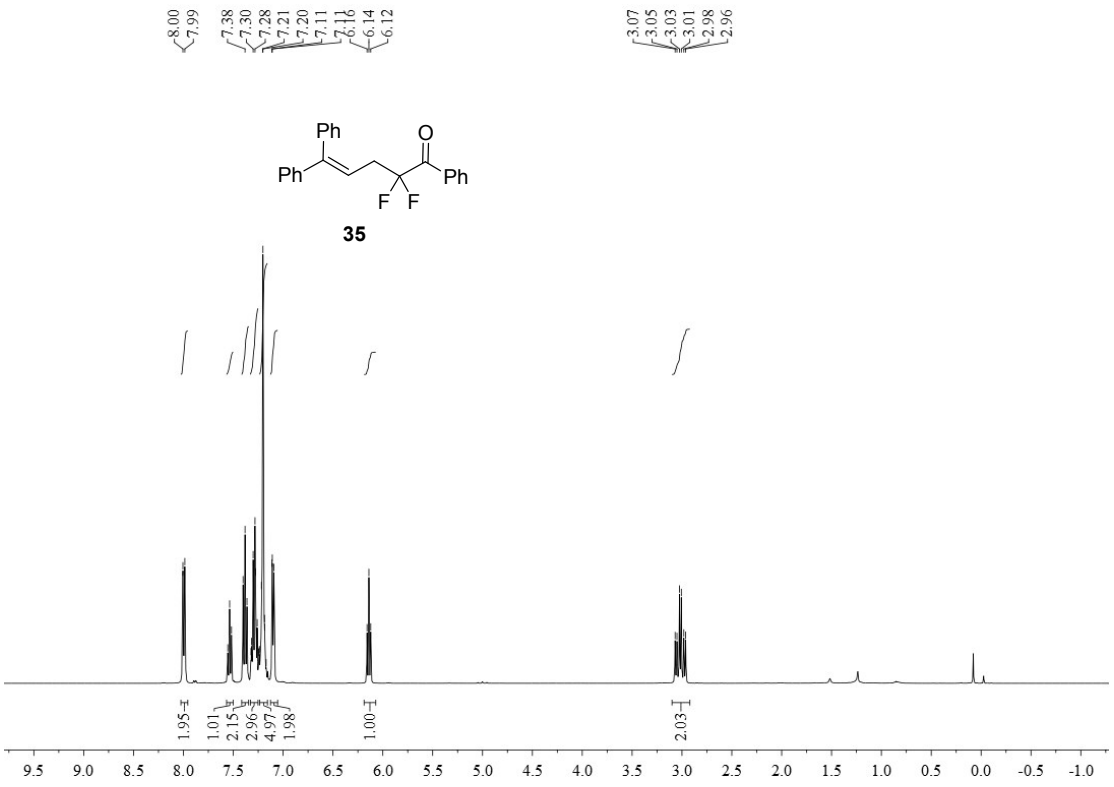


34 **(1.3:1)** **34'**





34 **(1.3:1)** **34'**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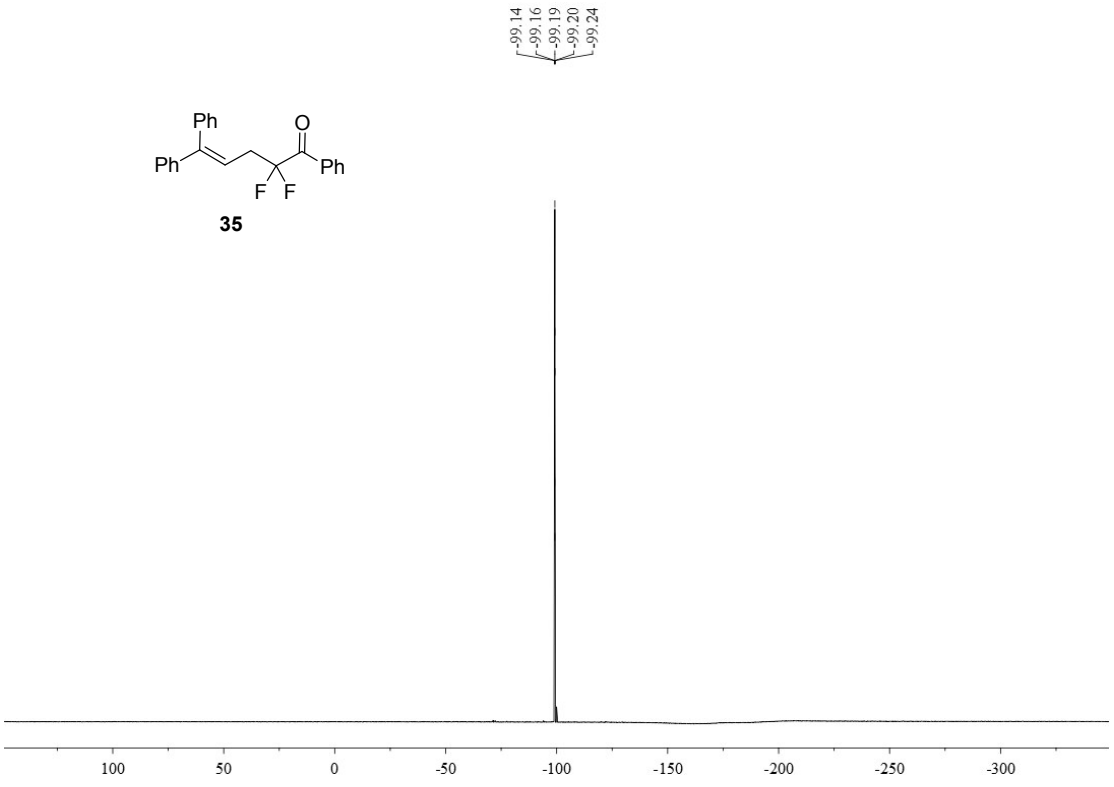
7.11
6.16
6.14
6.12
3.07
3.05
3.03
3.01
2.98
2.96
Ph
O
Ph
Ph
F F
35
1.95
1.01
2.15
2.96
4.97
1.98
1.00
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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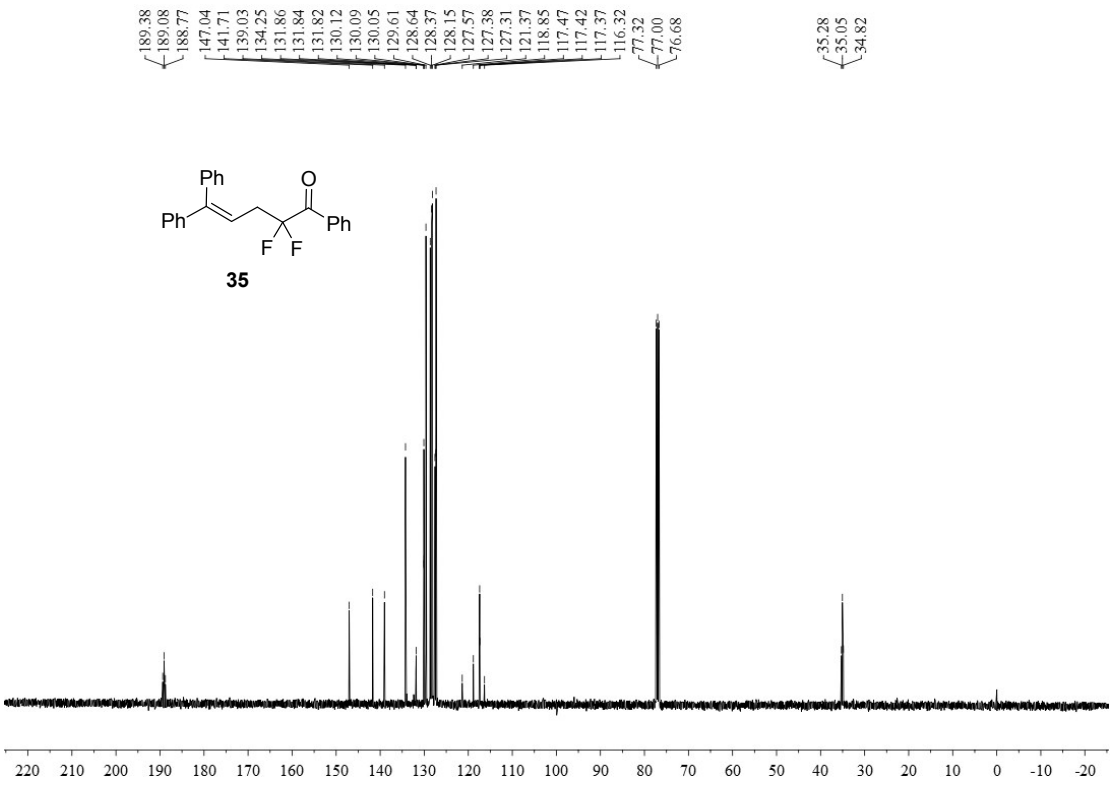
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118.85
117.47
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116.32
77.32
77.00
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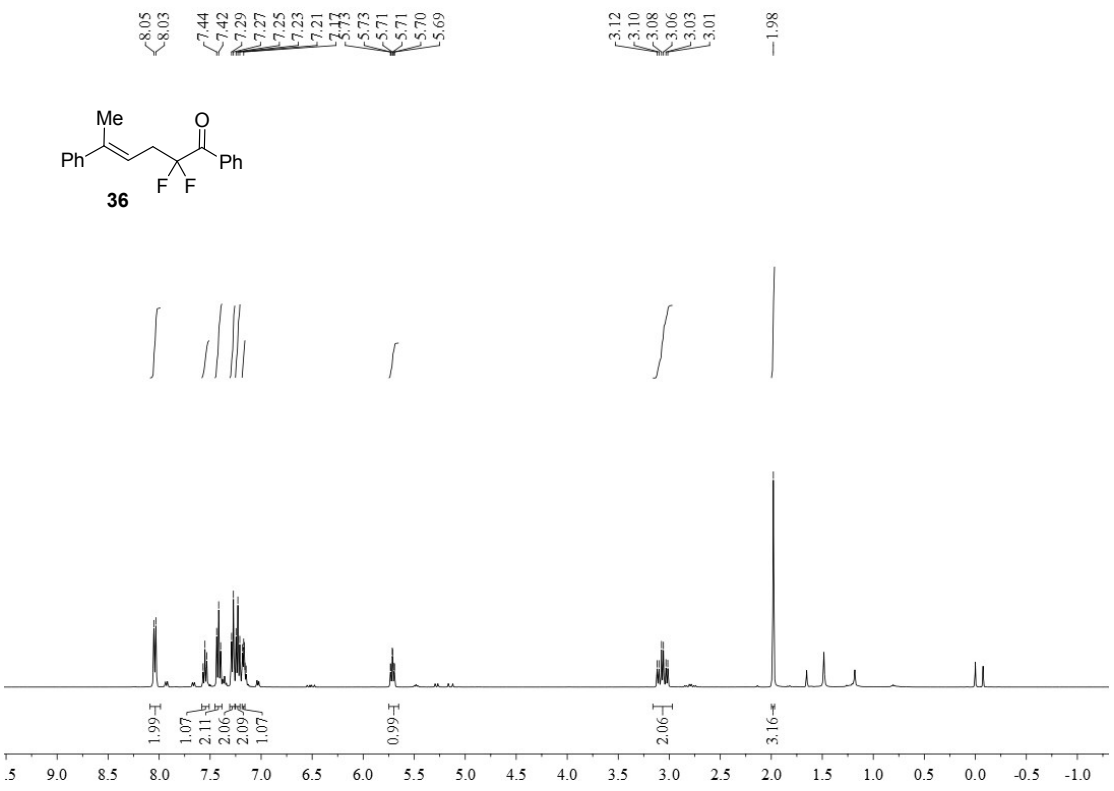
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20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3.01
1.98
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36
1.99
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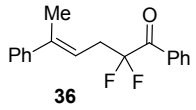
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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36


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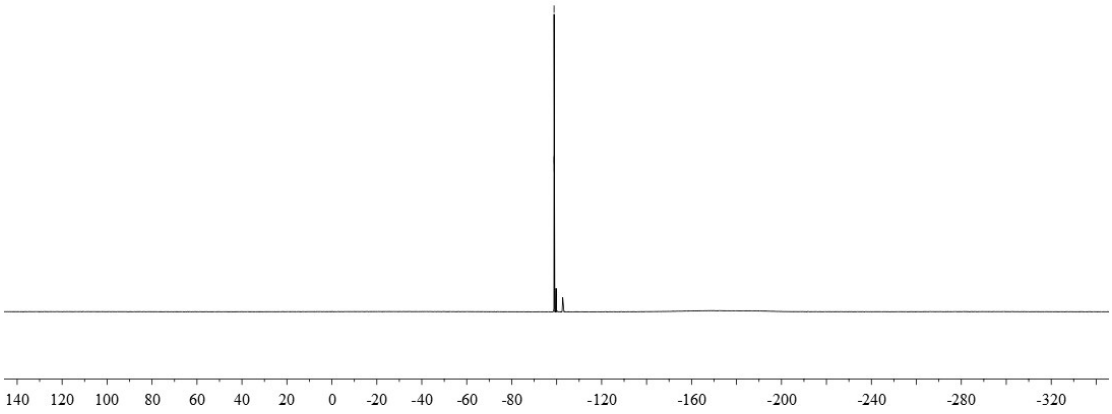
98.89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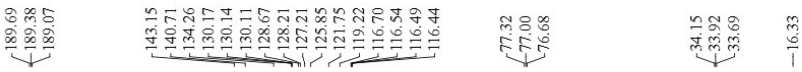
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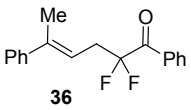
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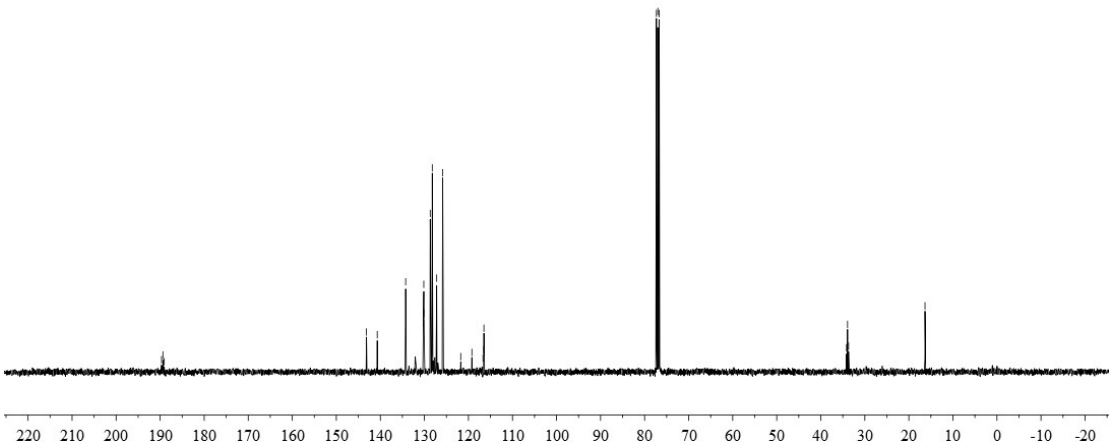
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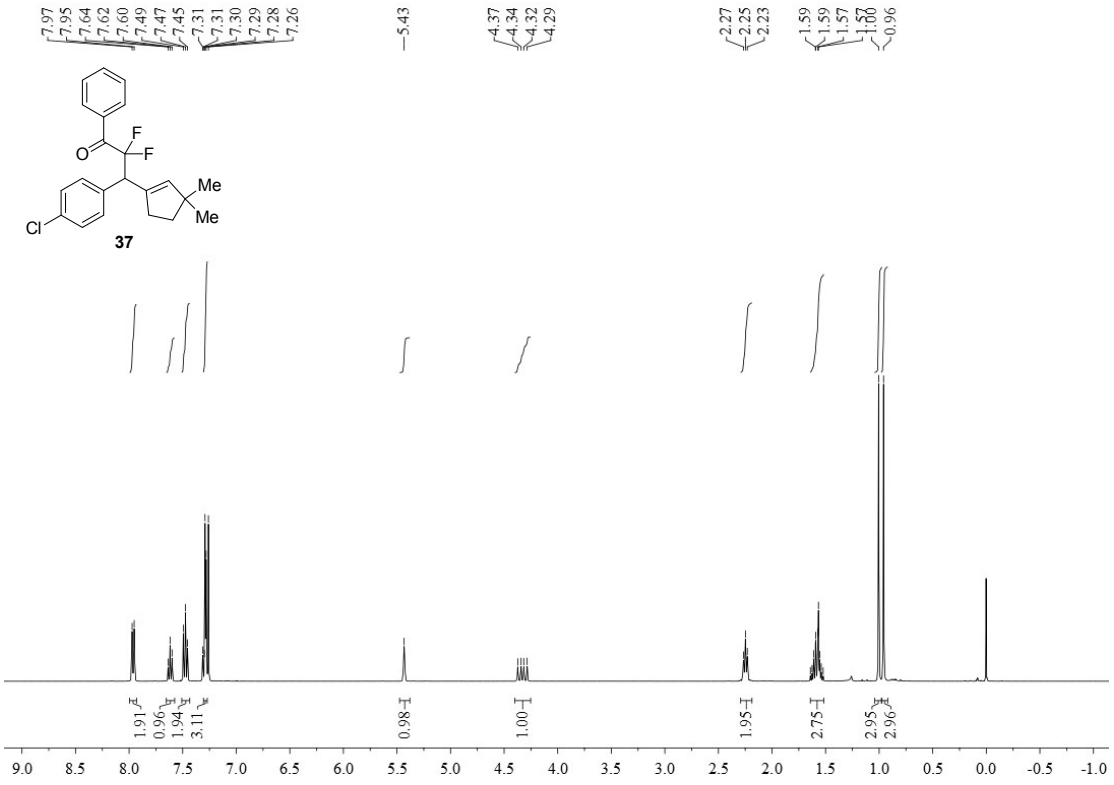
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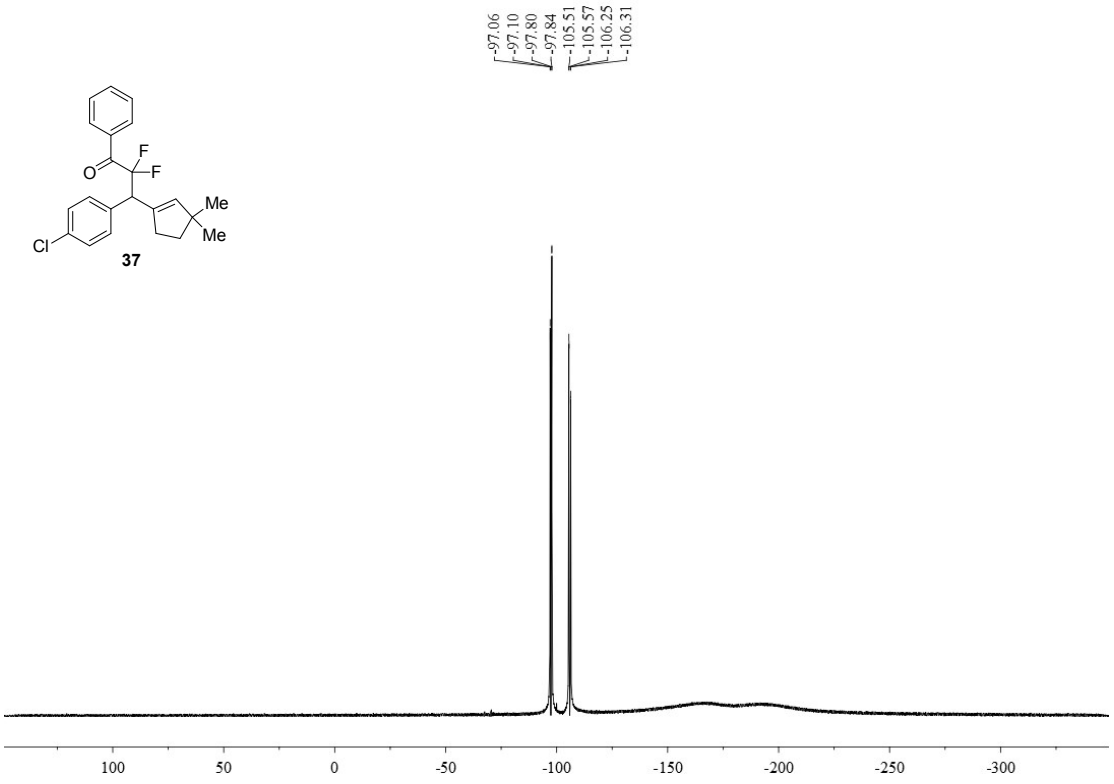
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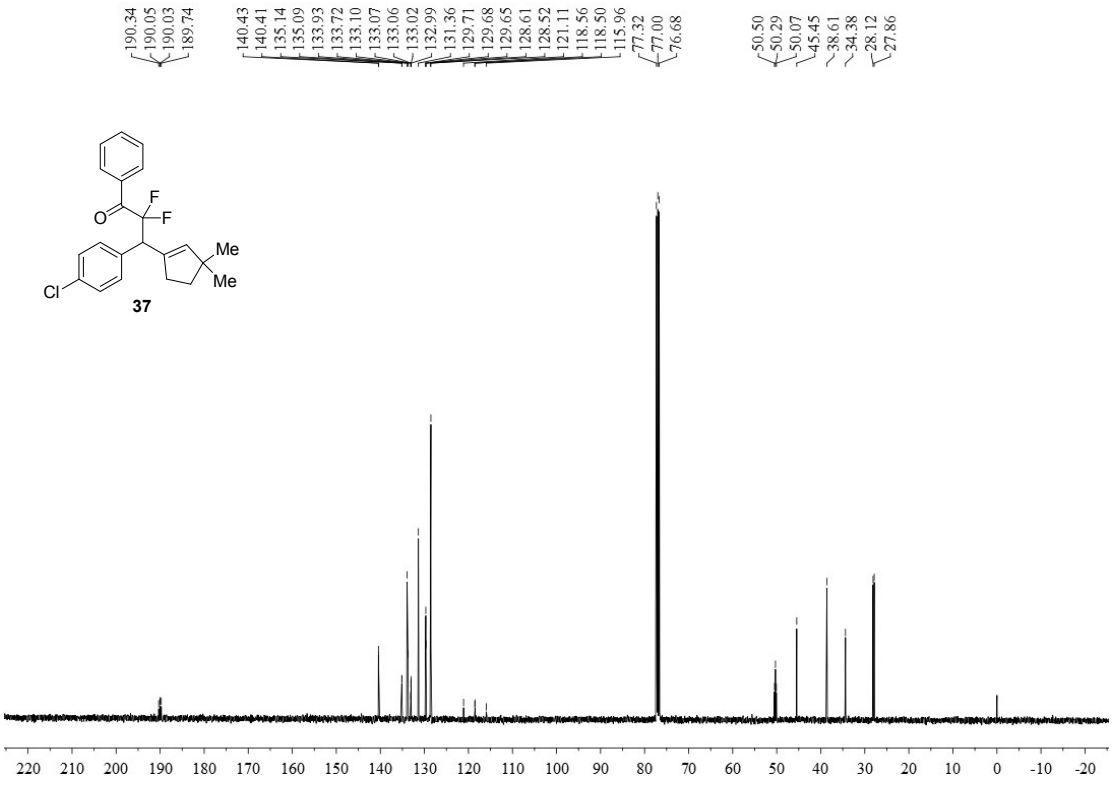
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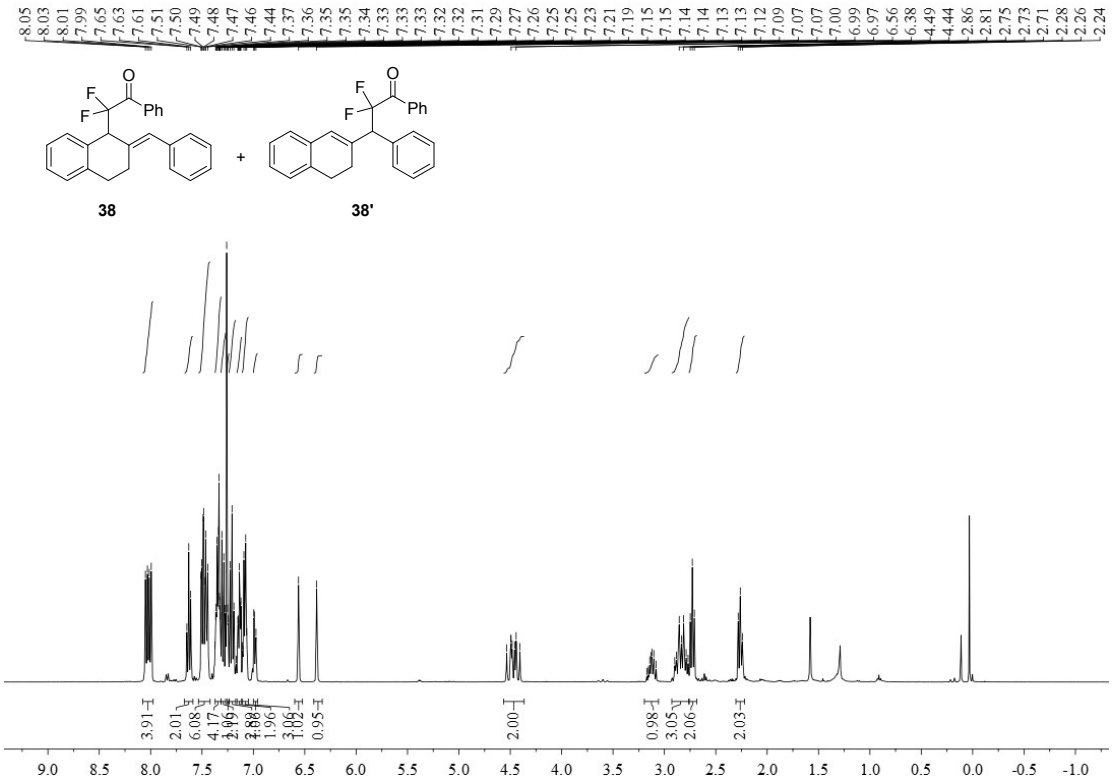
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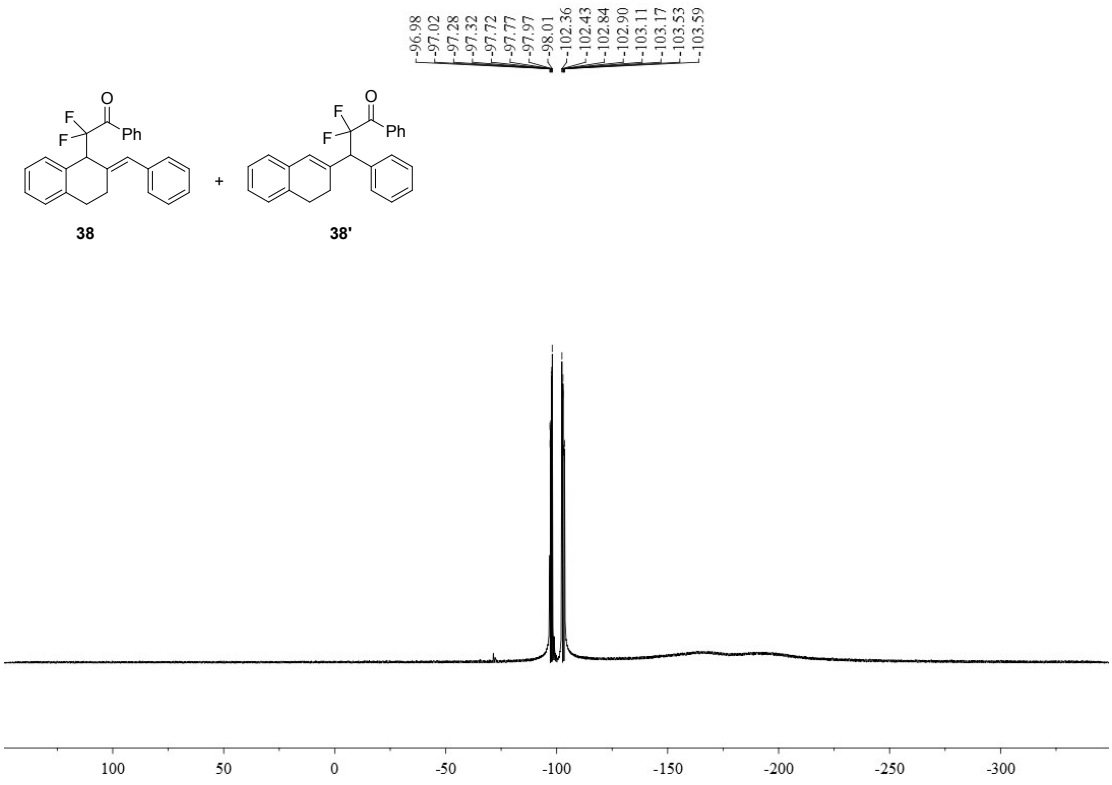
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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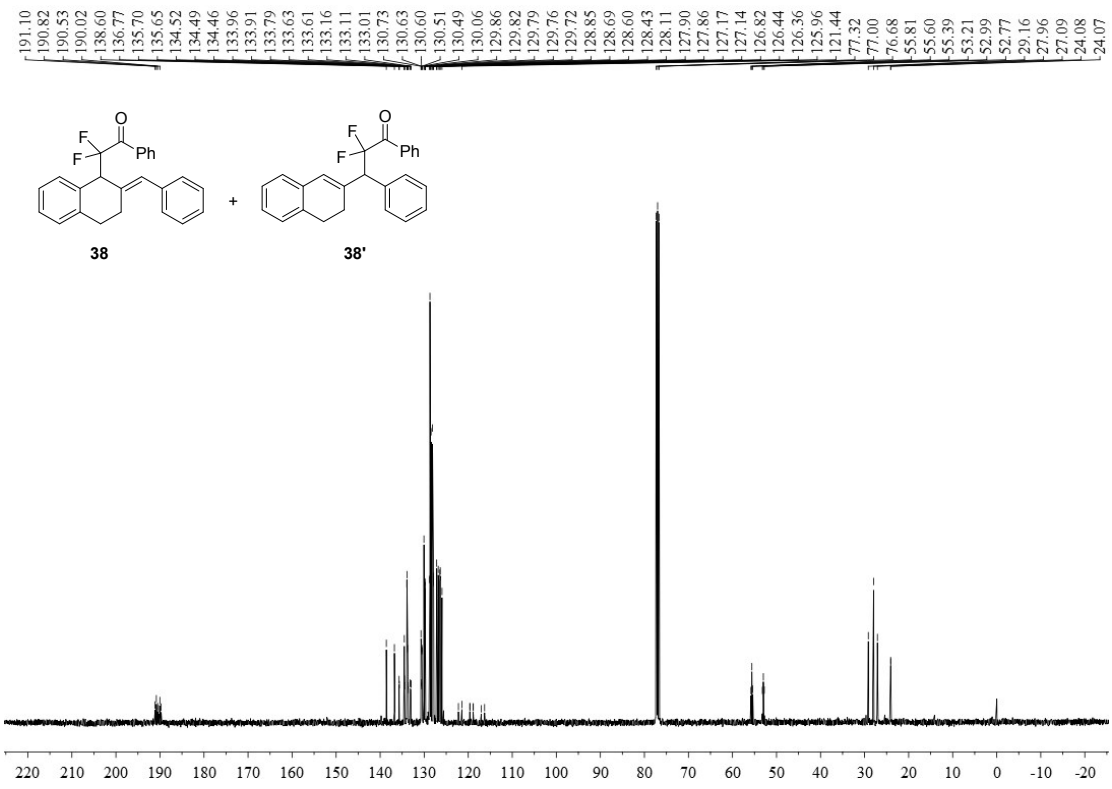
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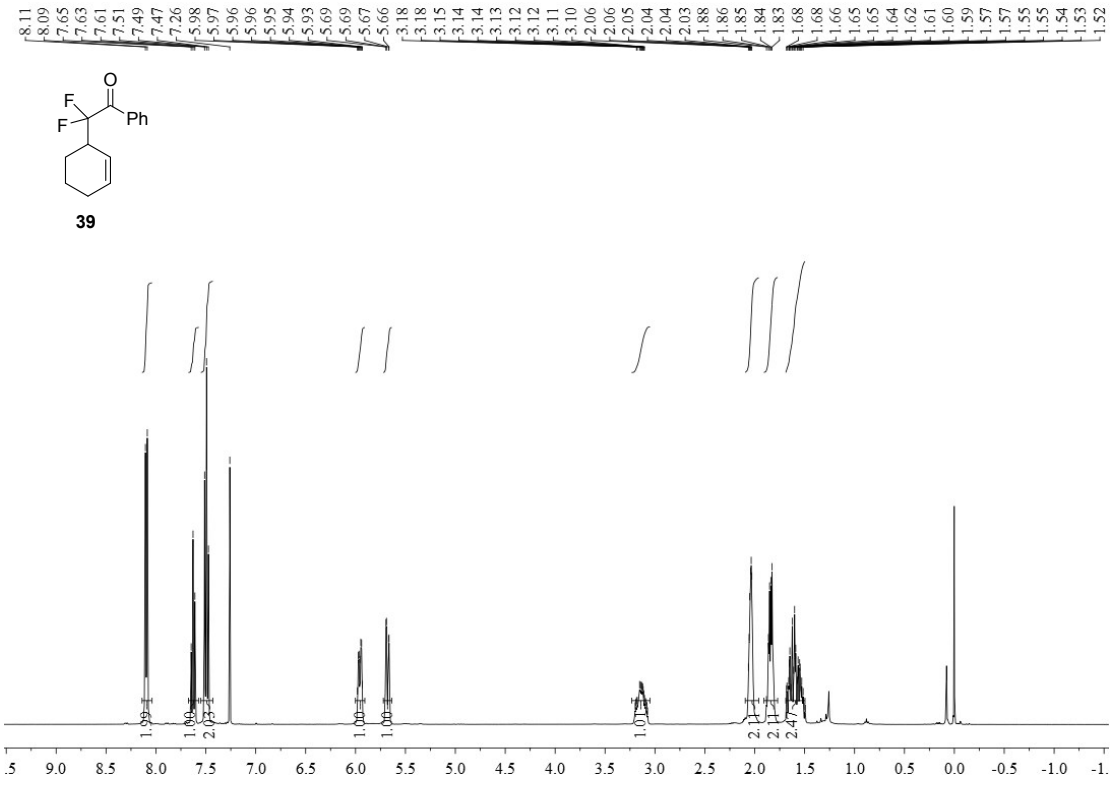
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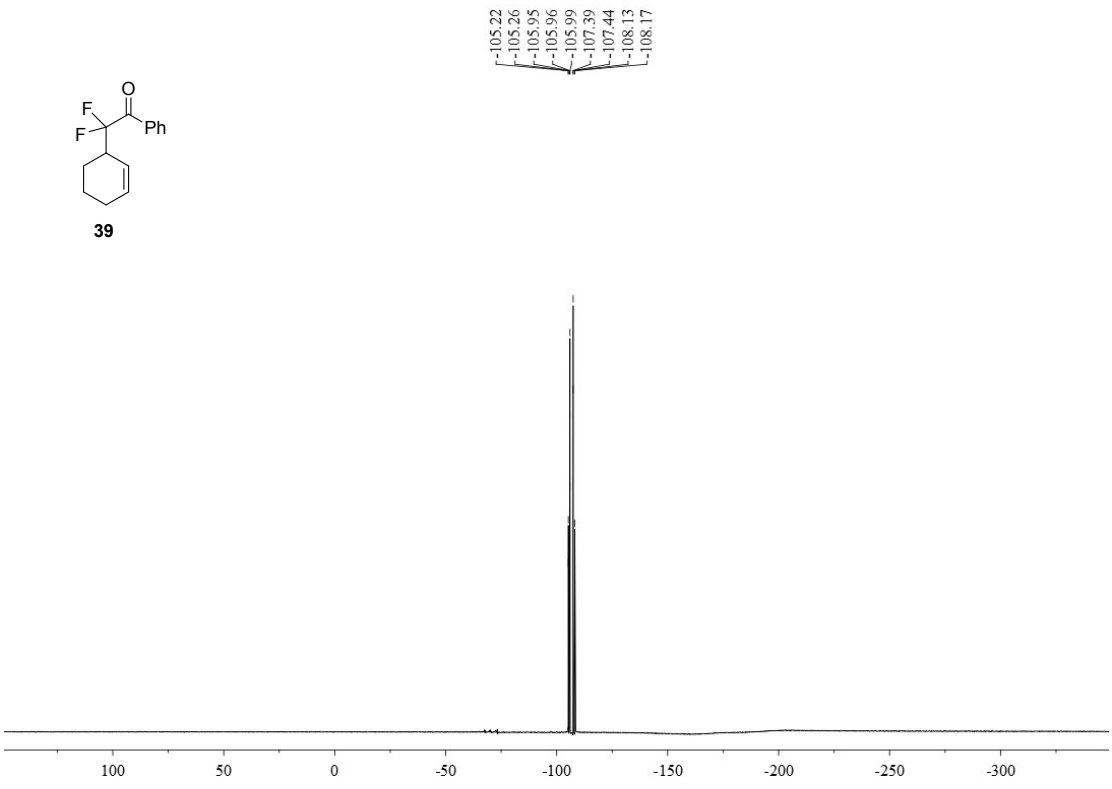
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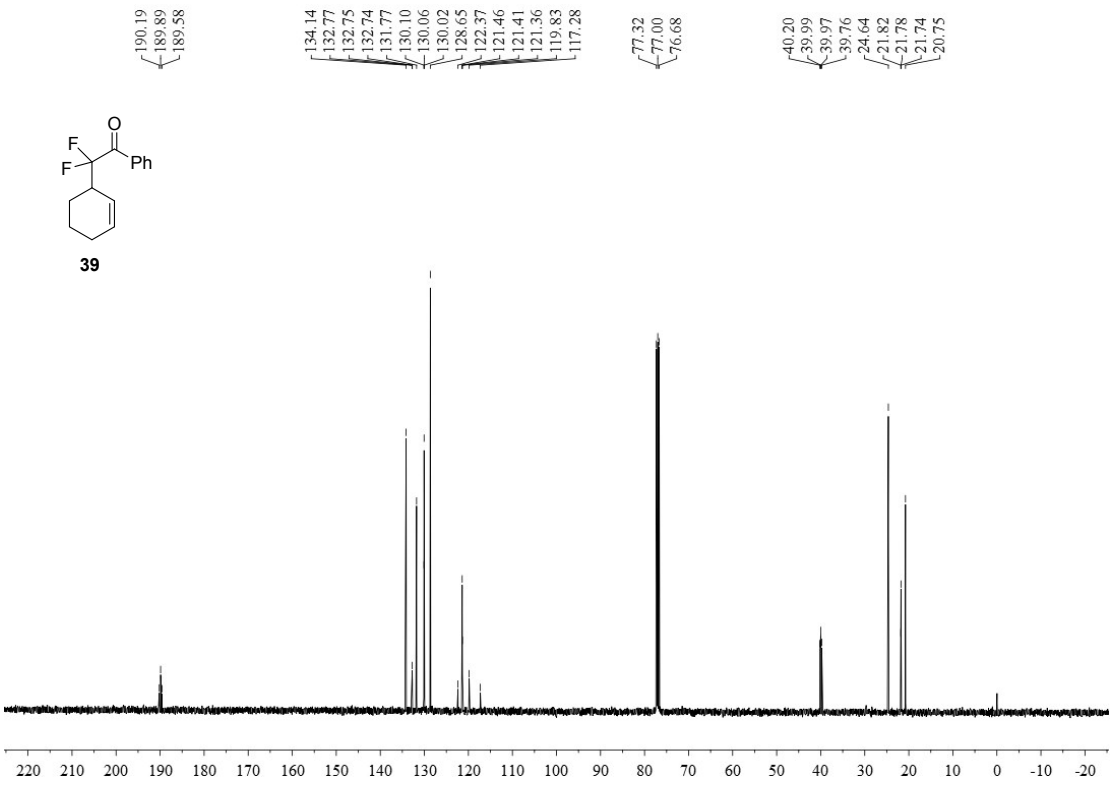
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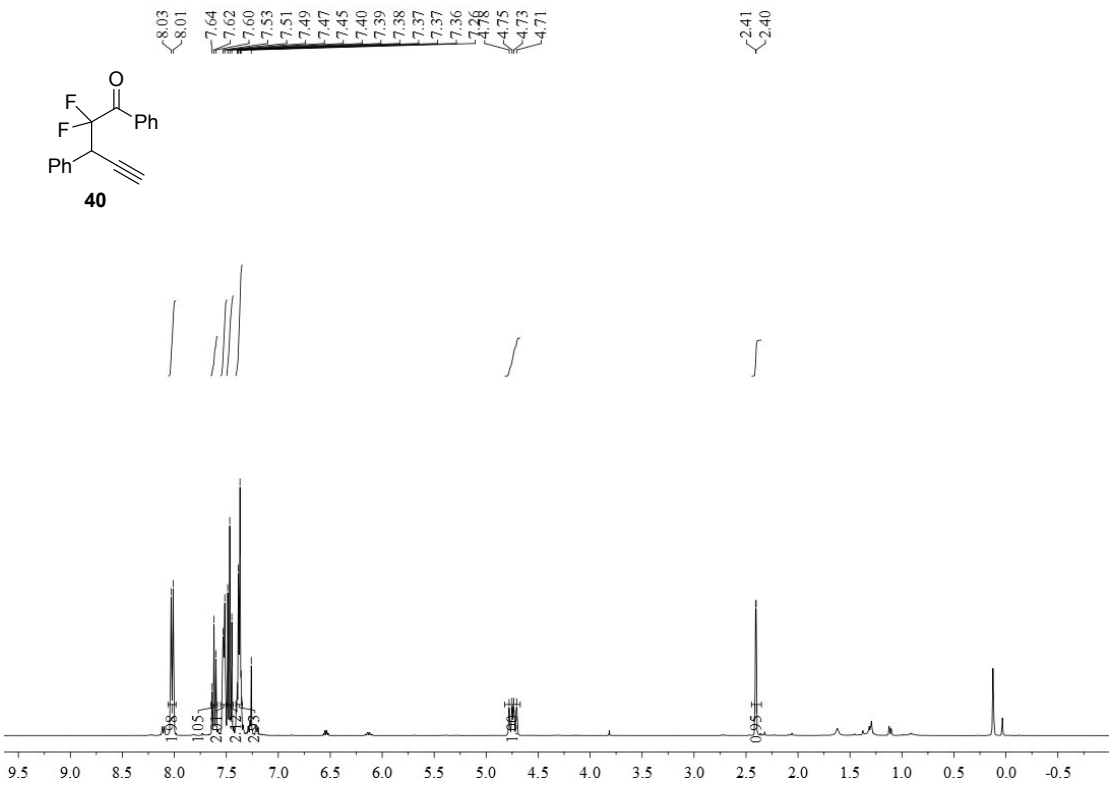
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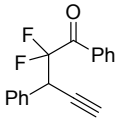
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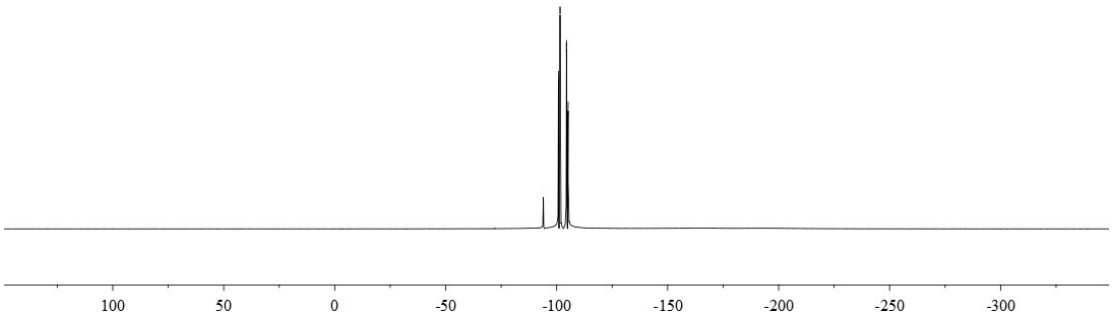
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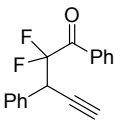
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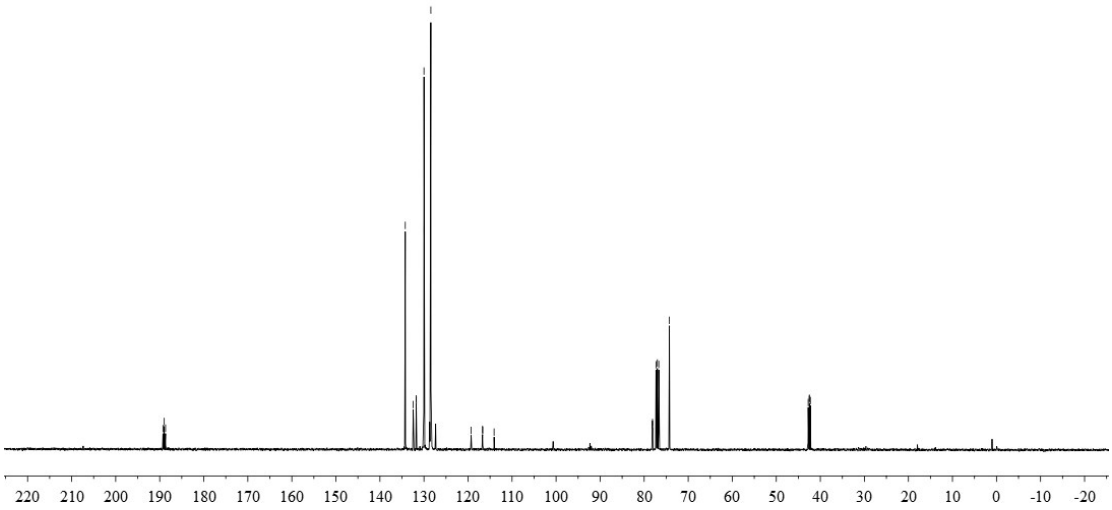
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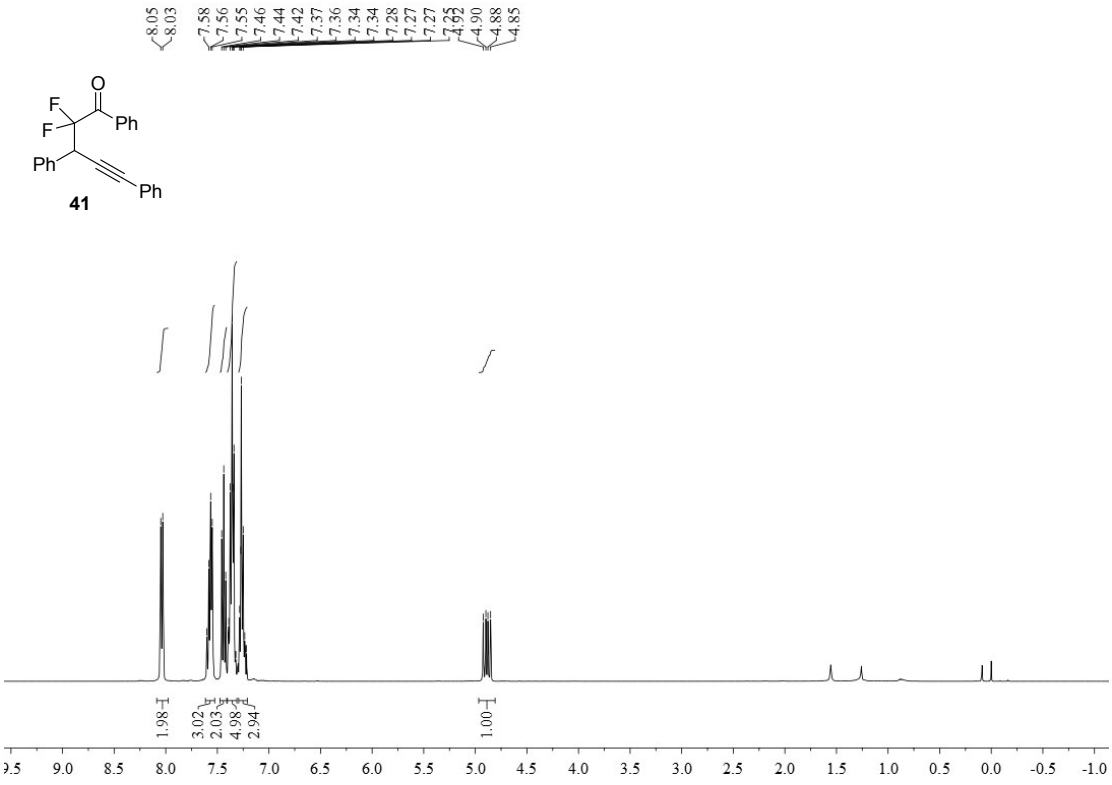
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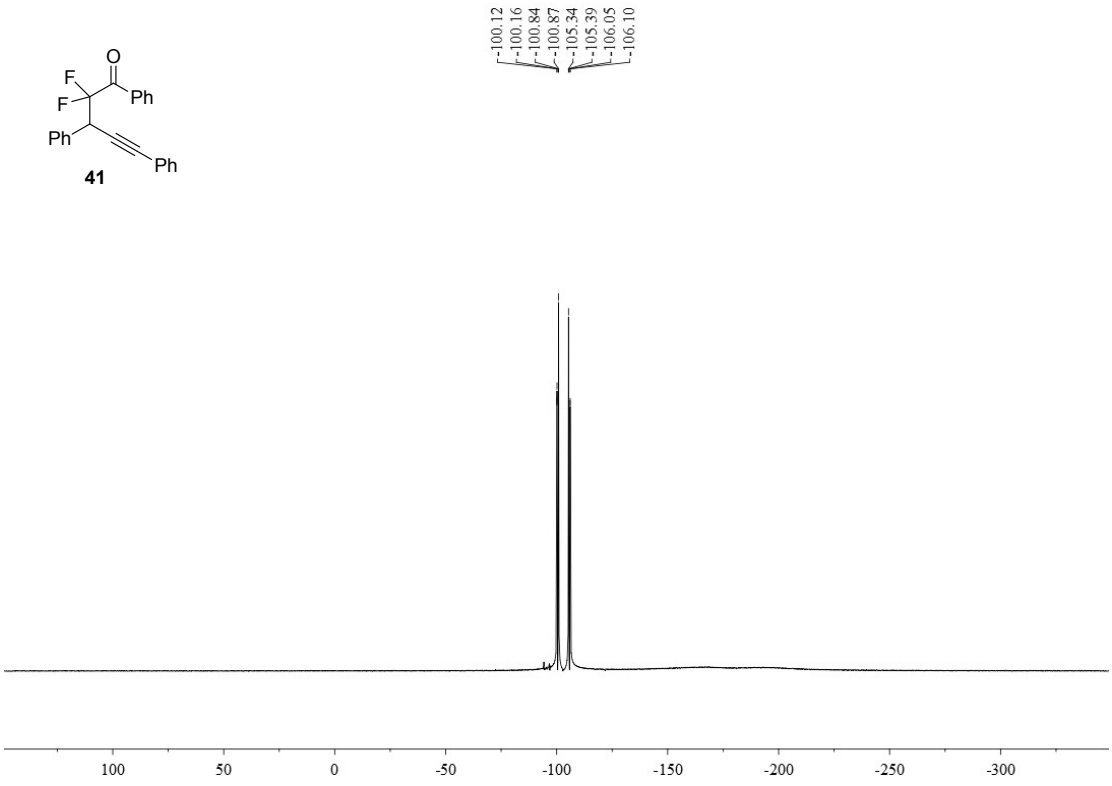
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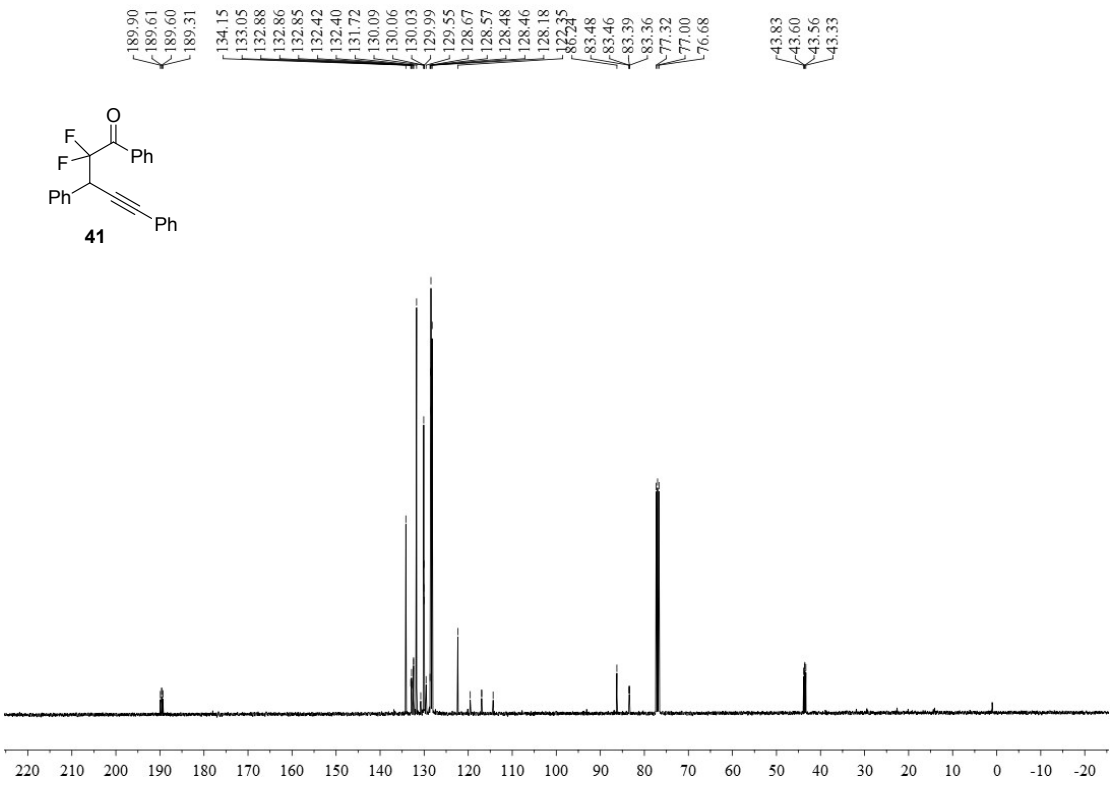
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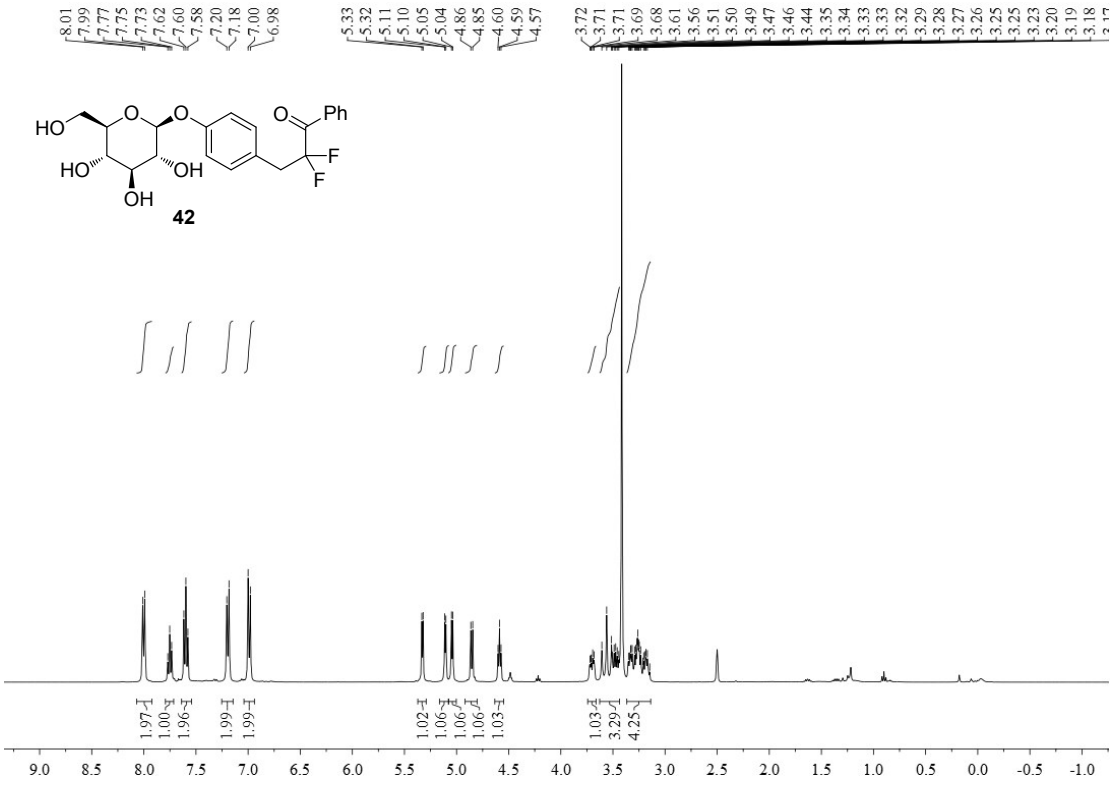
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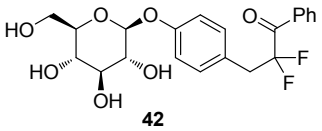
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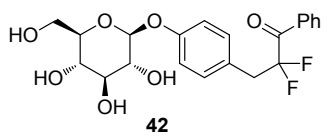
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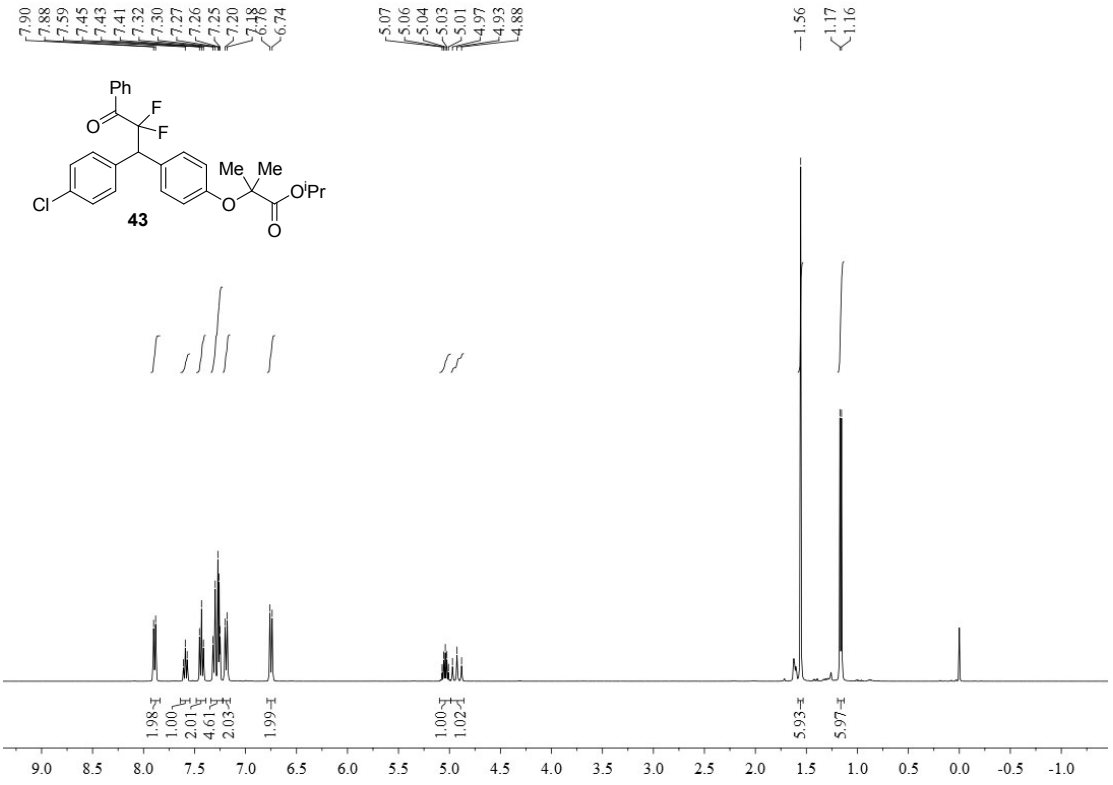
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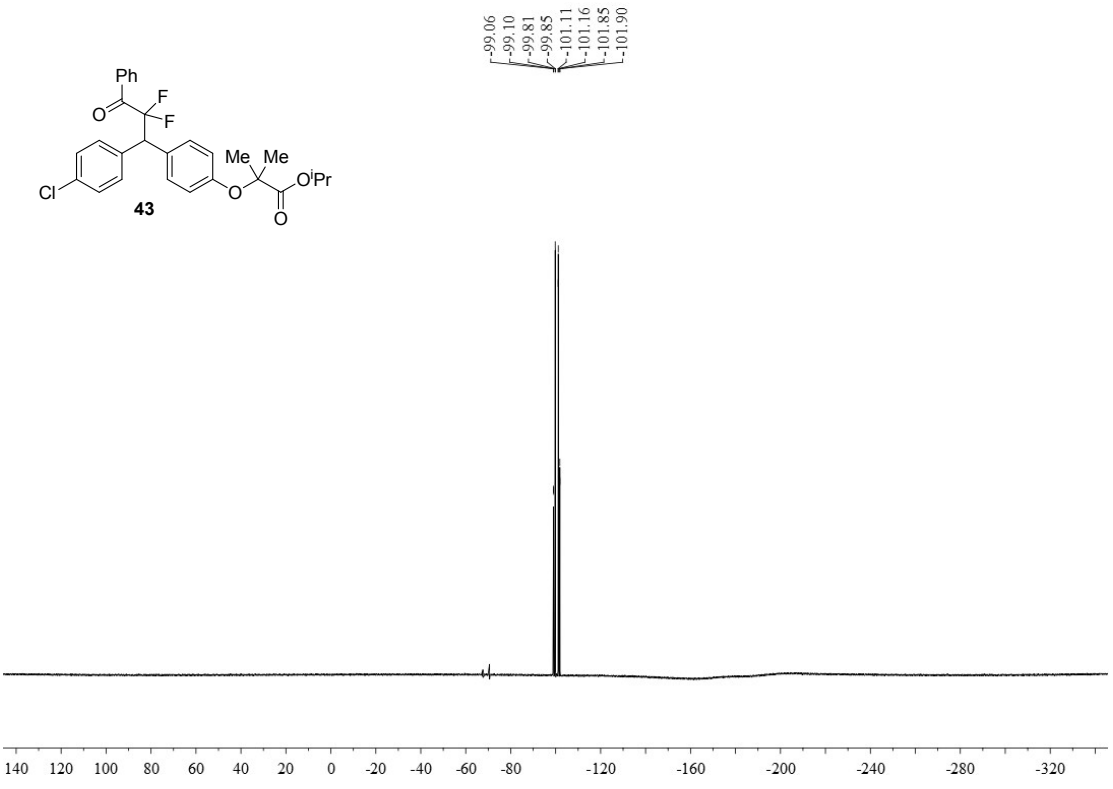
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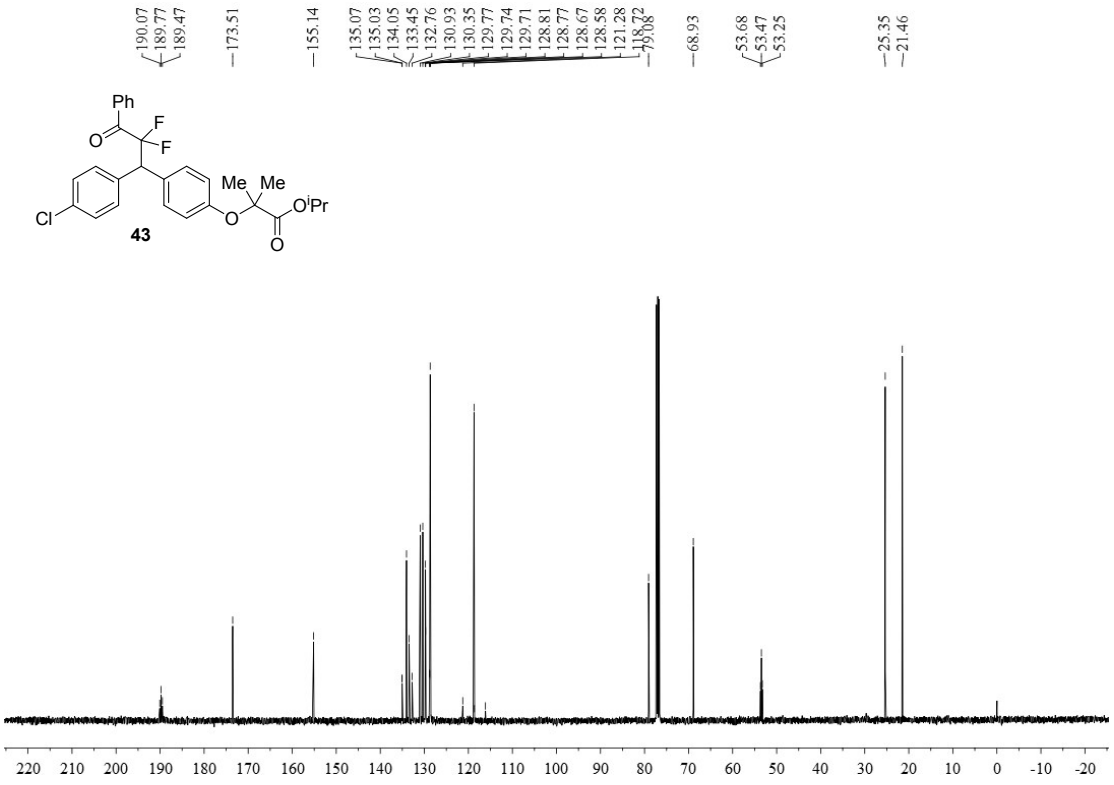
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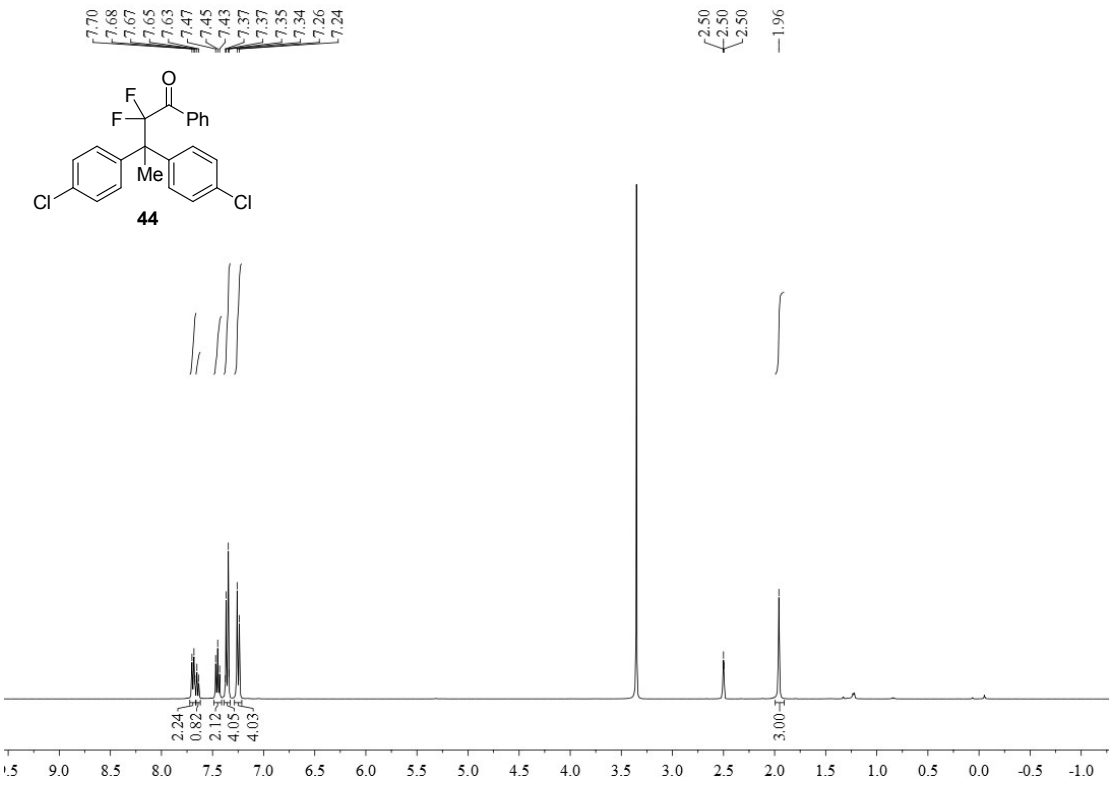
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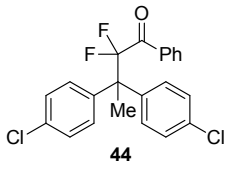
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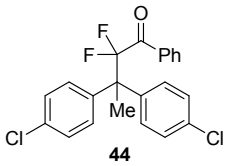
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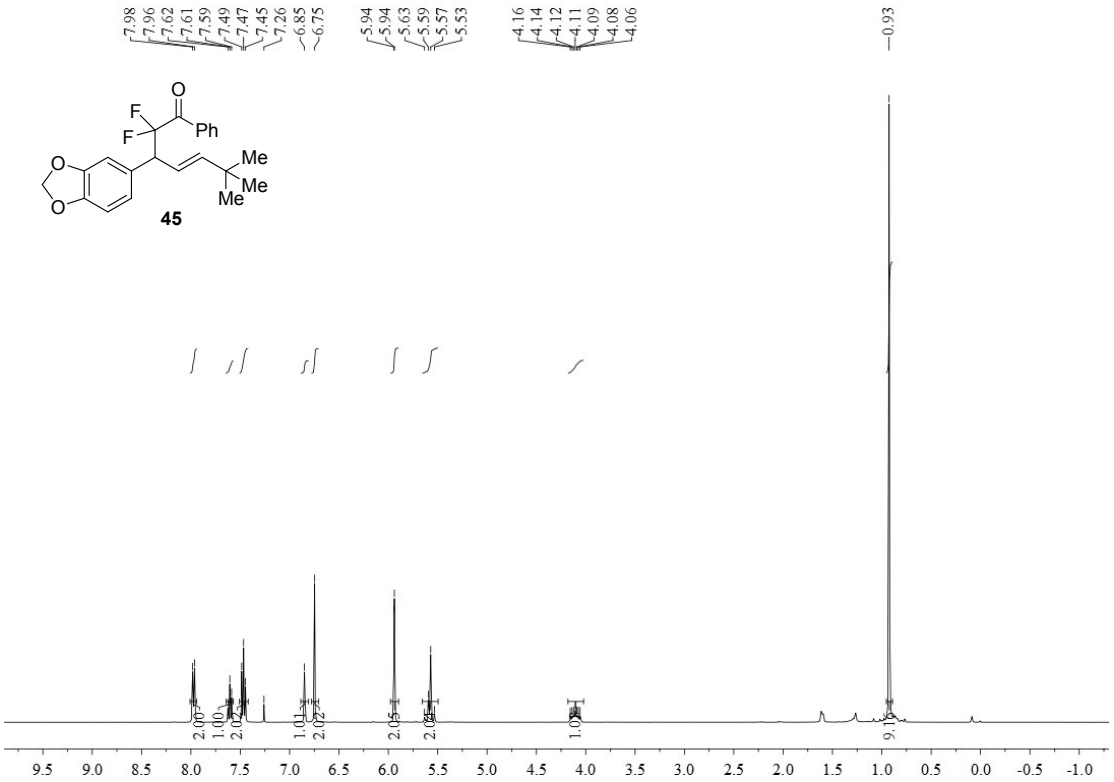
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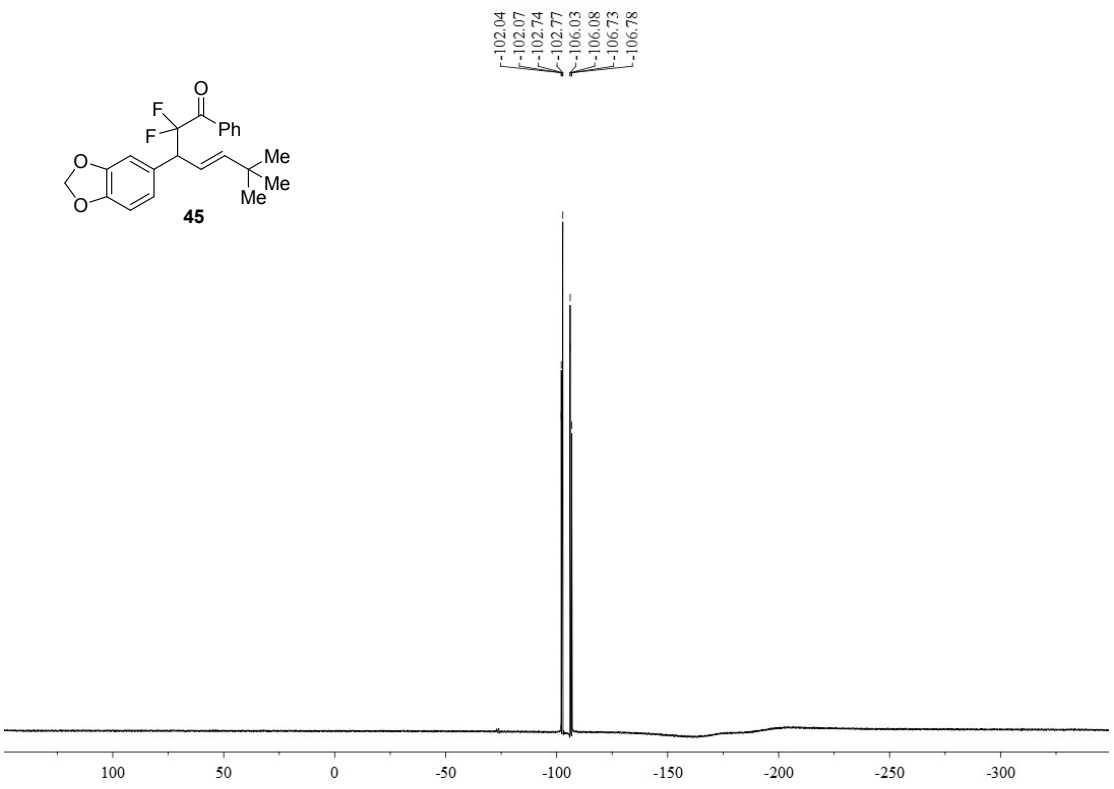
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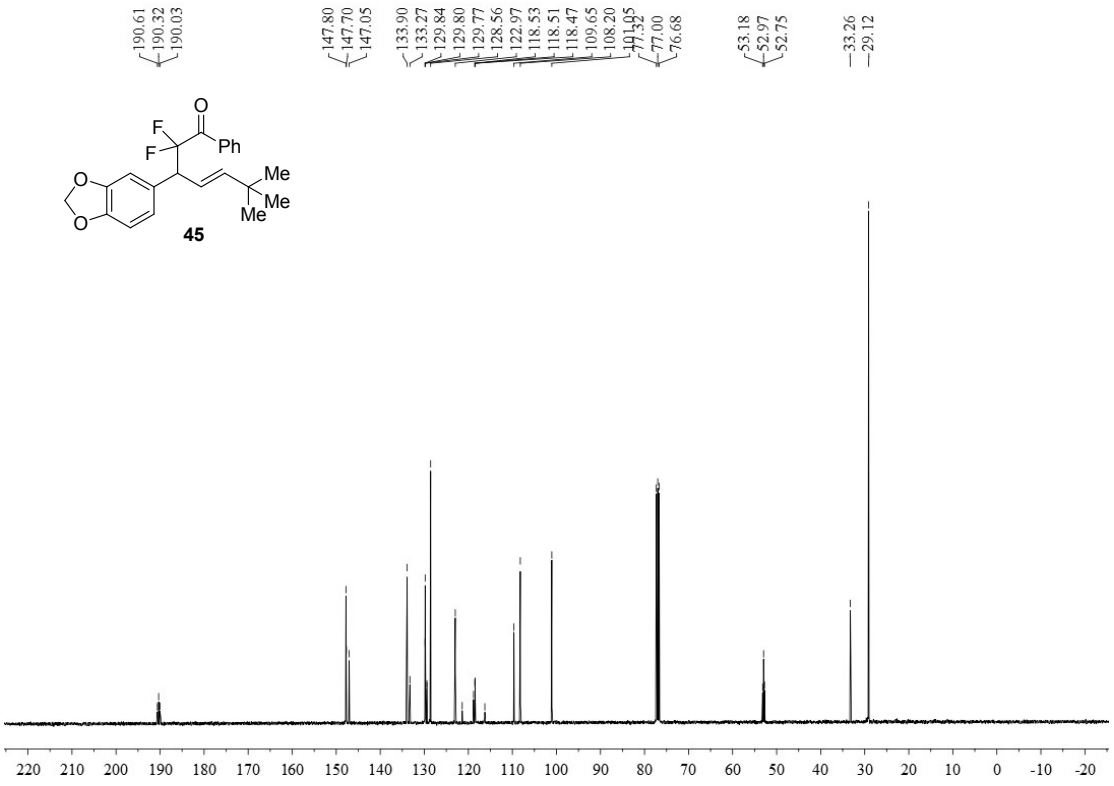
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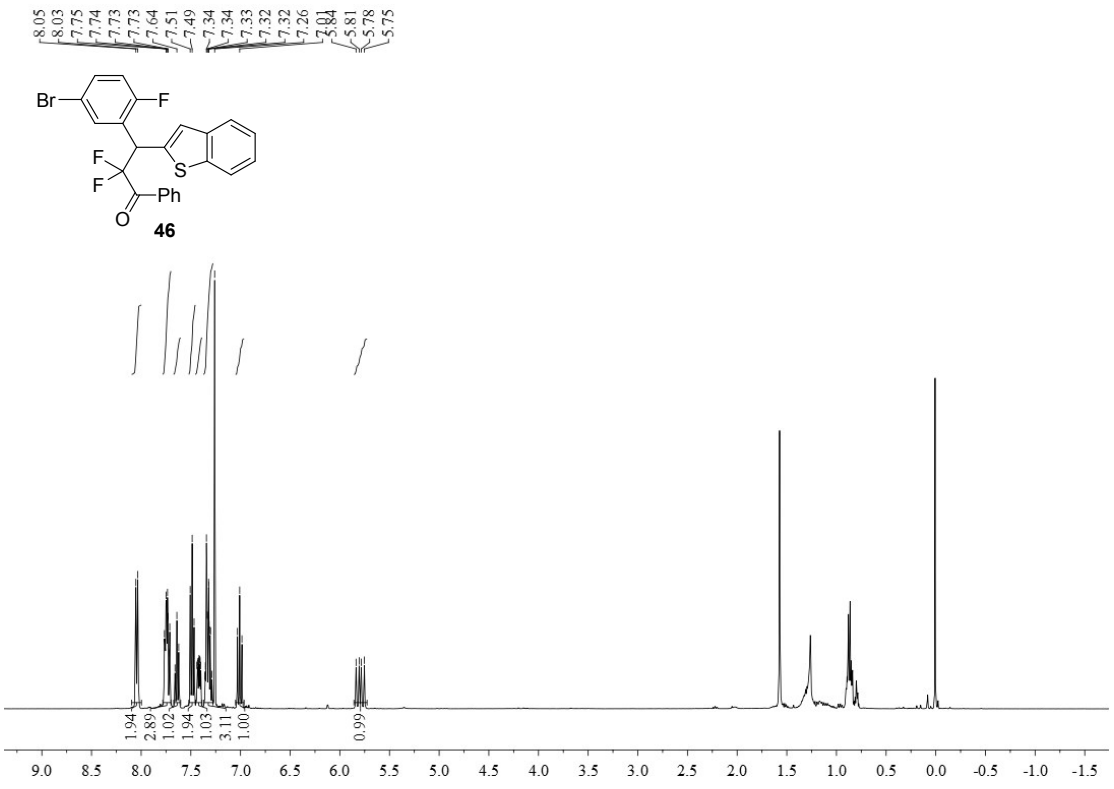
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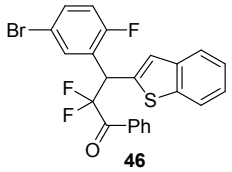
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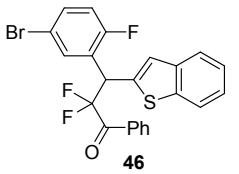
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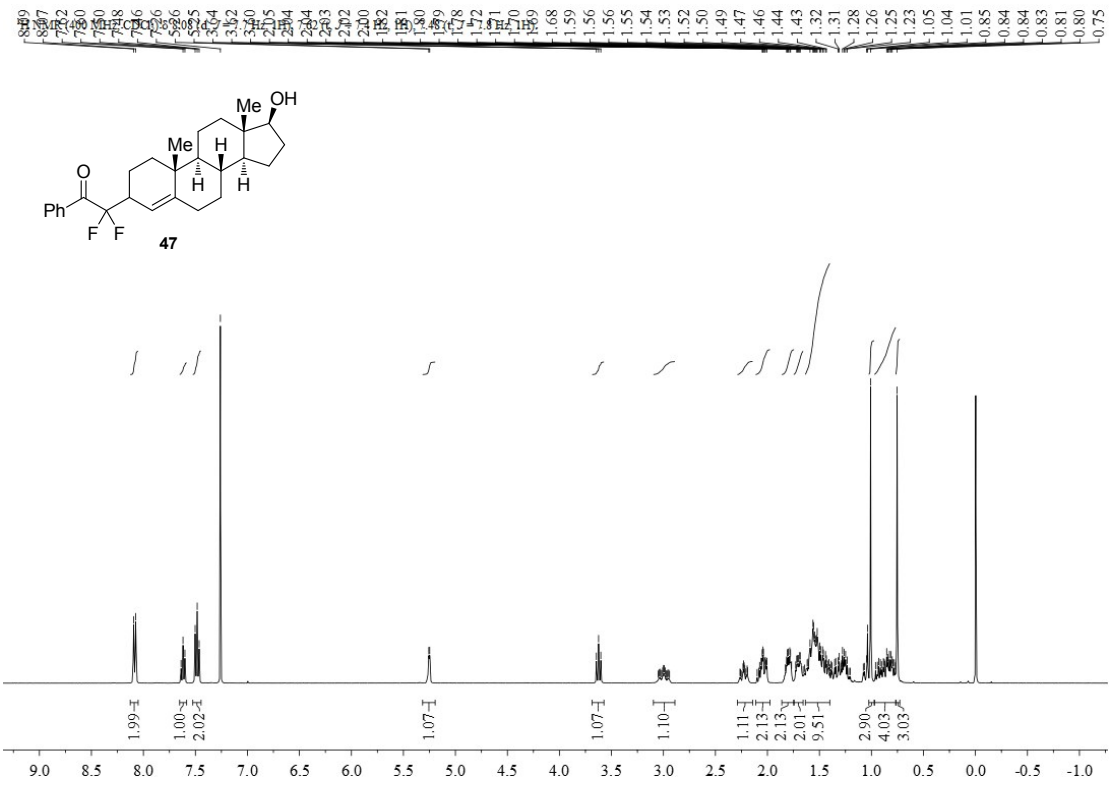
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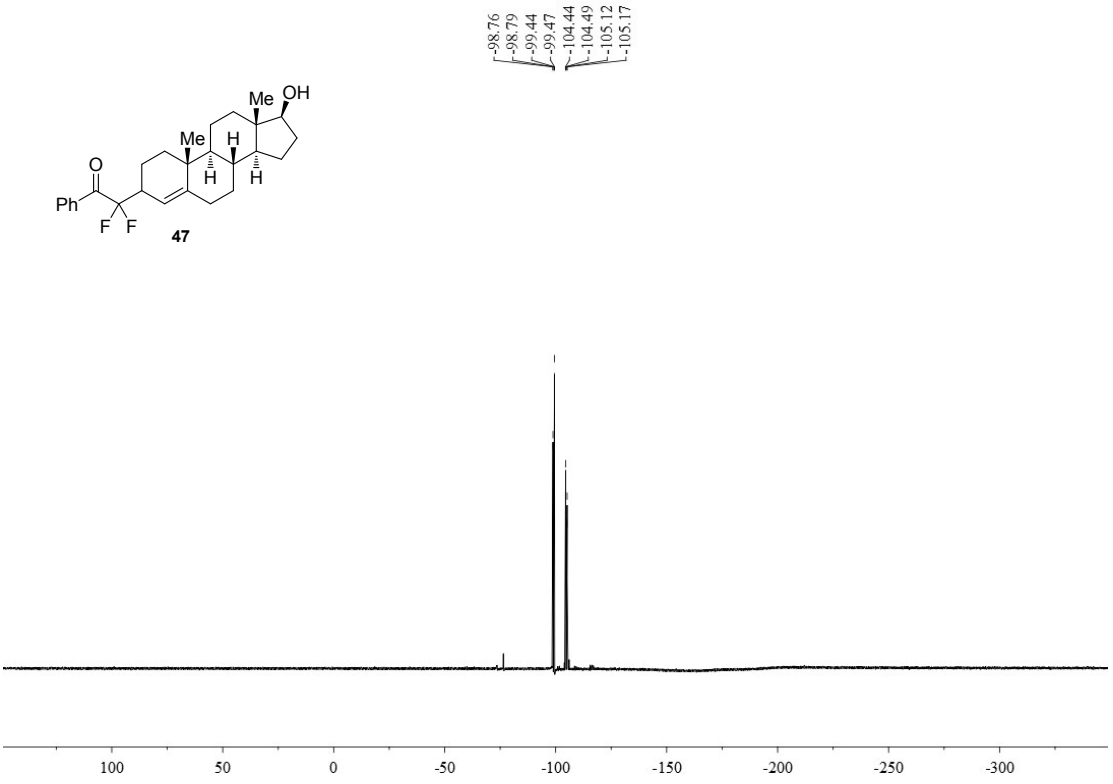
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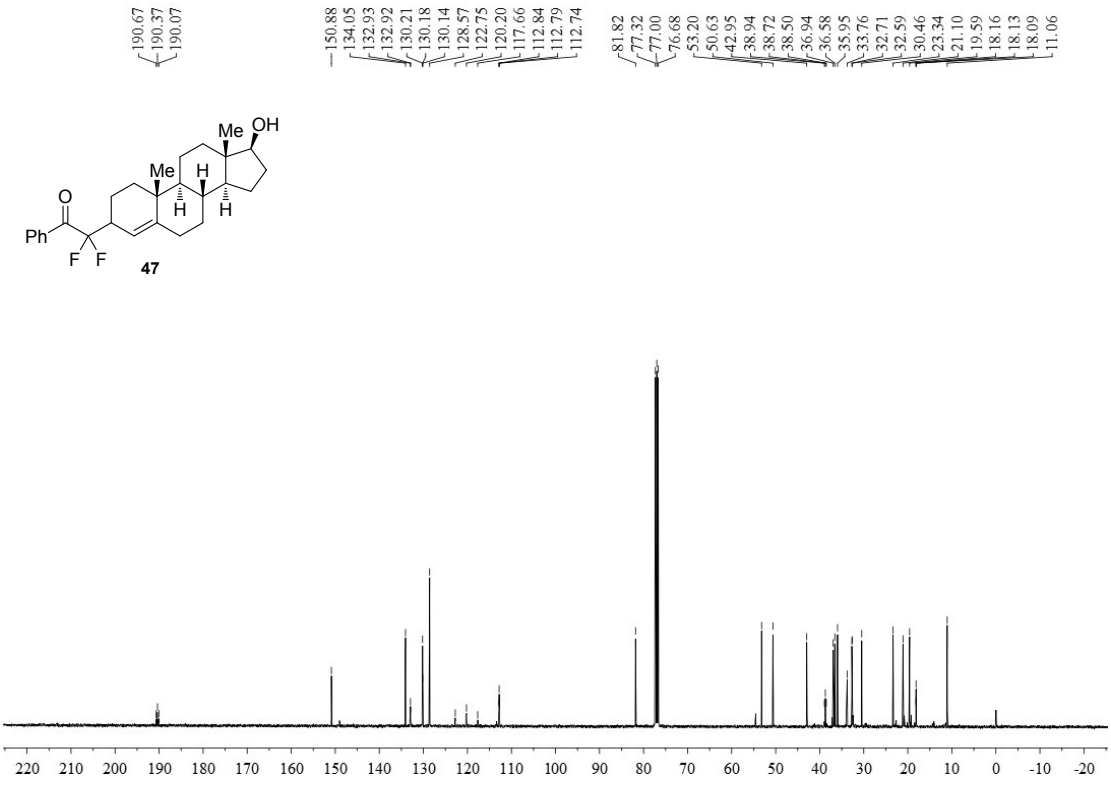
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112.79
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77.00
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32.59
30.46
23.34
21.10
19.59
18.16
18.13
18.09
11.06
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H
H
O
Ph
F F
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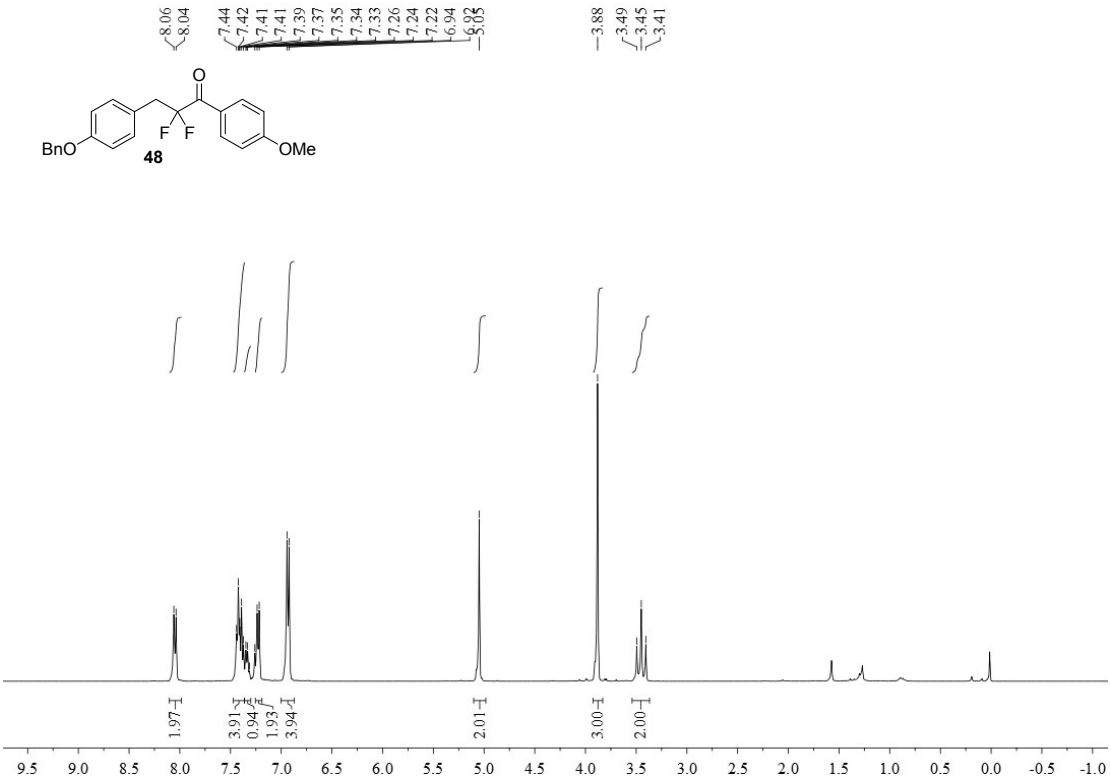
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6.92
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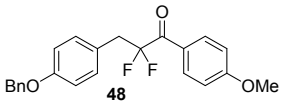
3.49
3.45
3.41
O
F F
BnO
OMe
48
1.97
3.91
0.94
1.93
3.94
2.01
3.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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BnO
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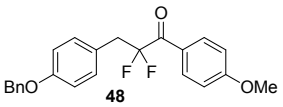
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BnO
OMe

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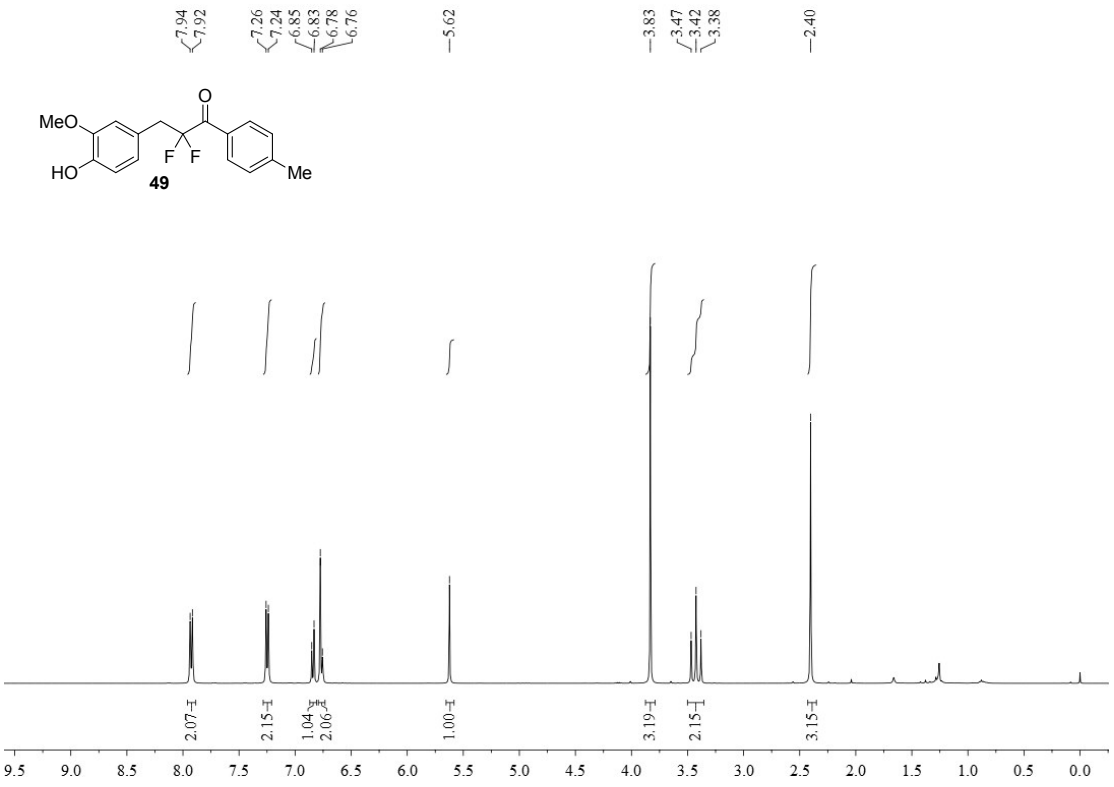
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MeO
HO
F F
O
Me
49
2.07
2.15
1.04
2.06
1.00
3.19
2.15
3.15
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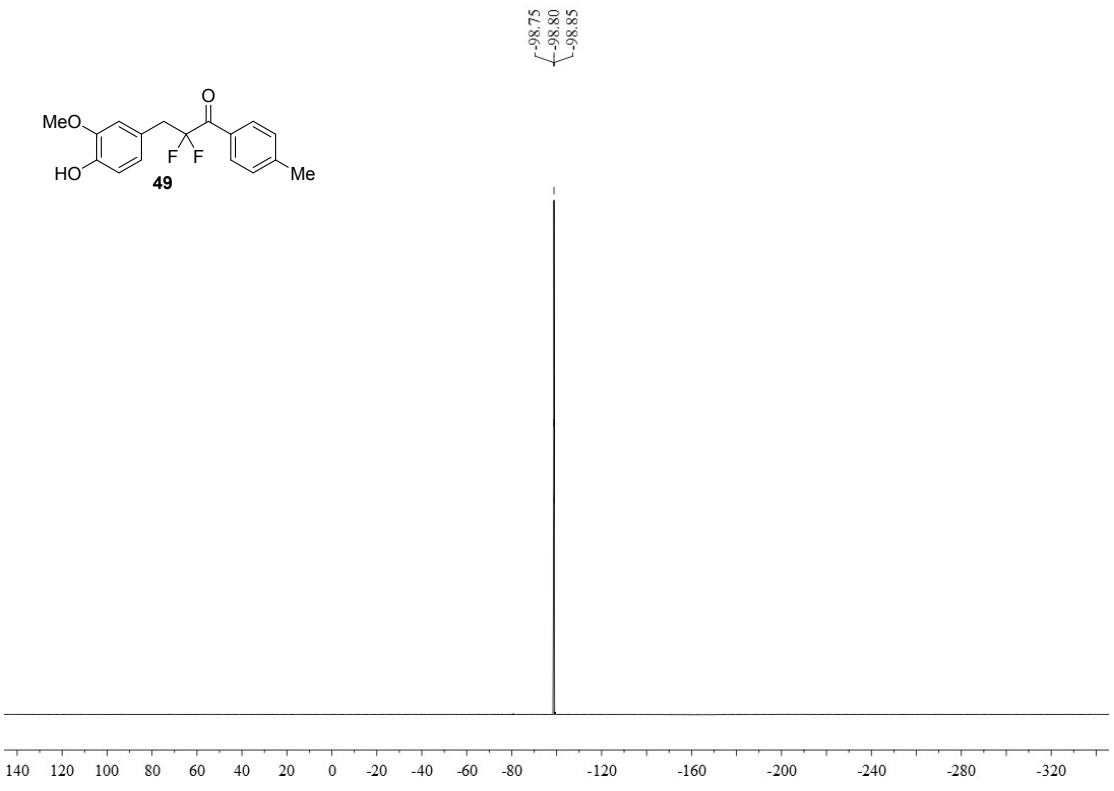
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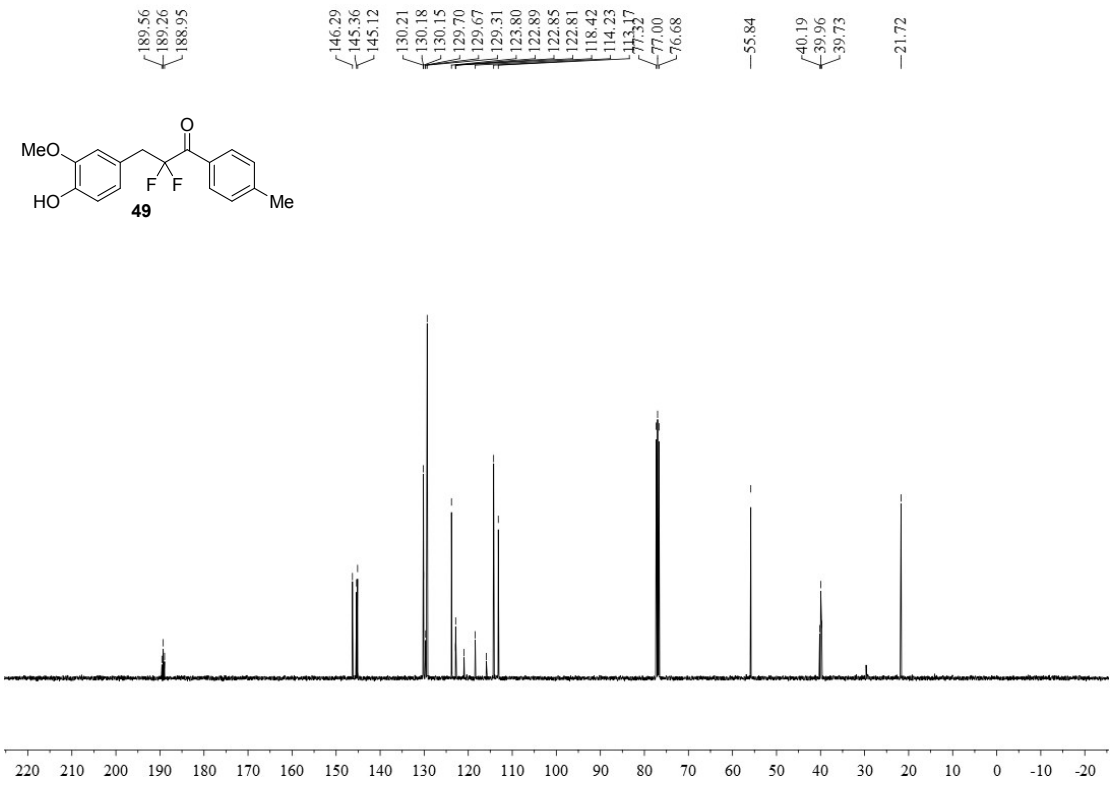
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39.96
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HO
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O
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49
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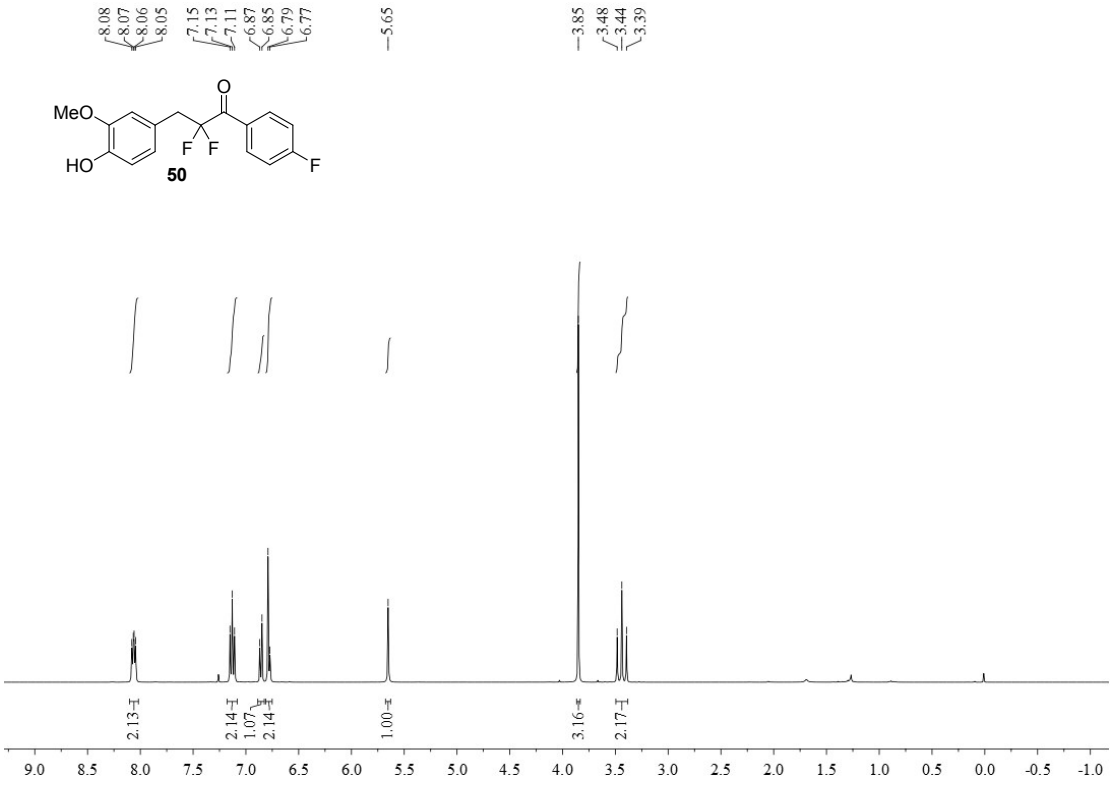
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F F
O
F
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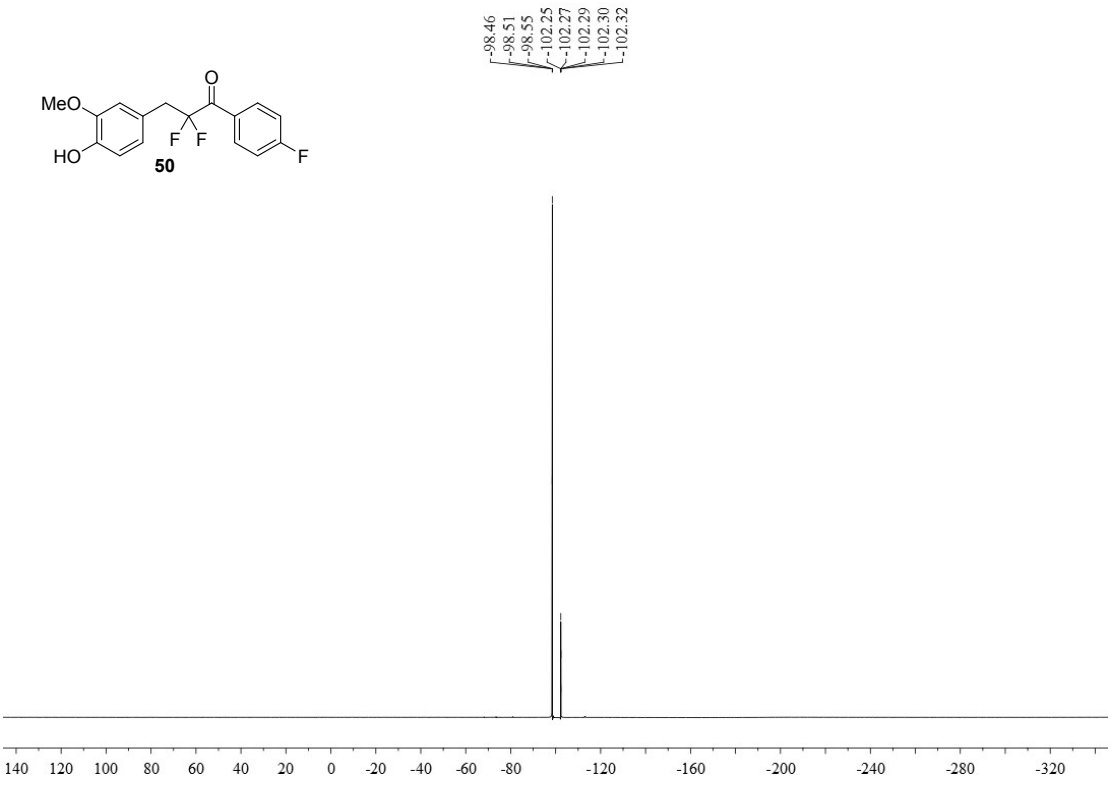
2.14
1.07
2.14
1.00
3.16
2.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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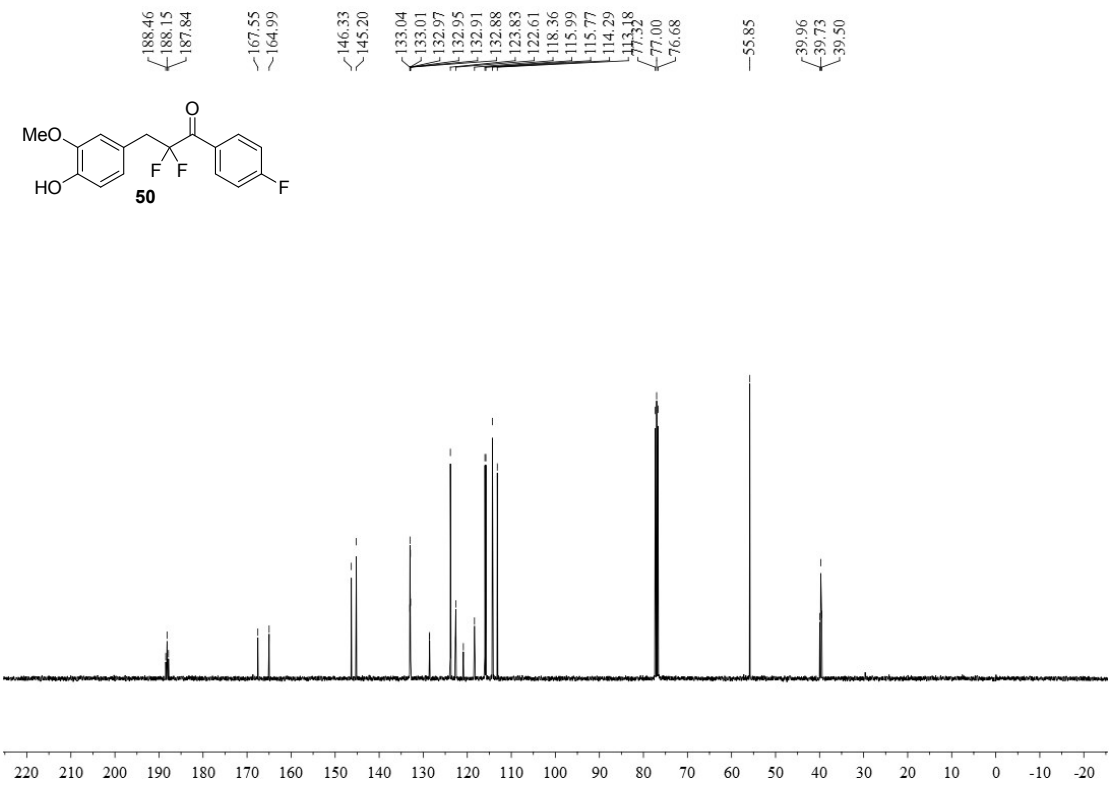
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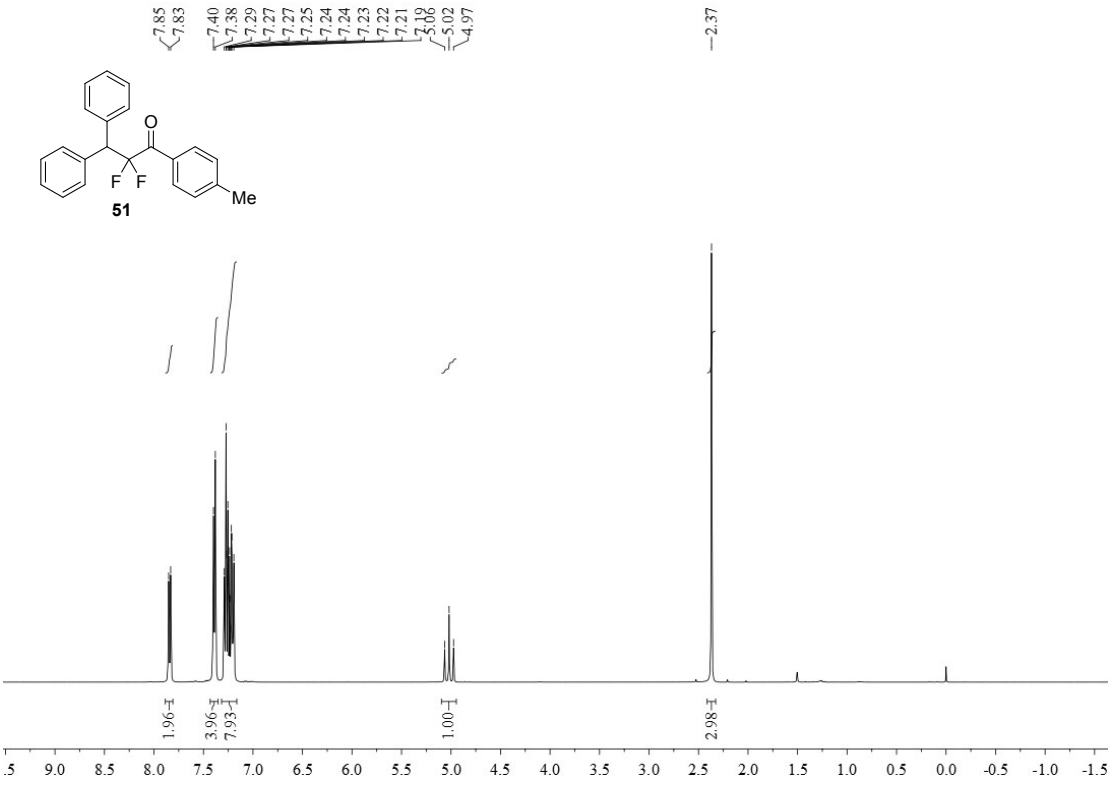
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O
F F
Me
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2.98
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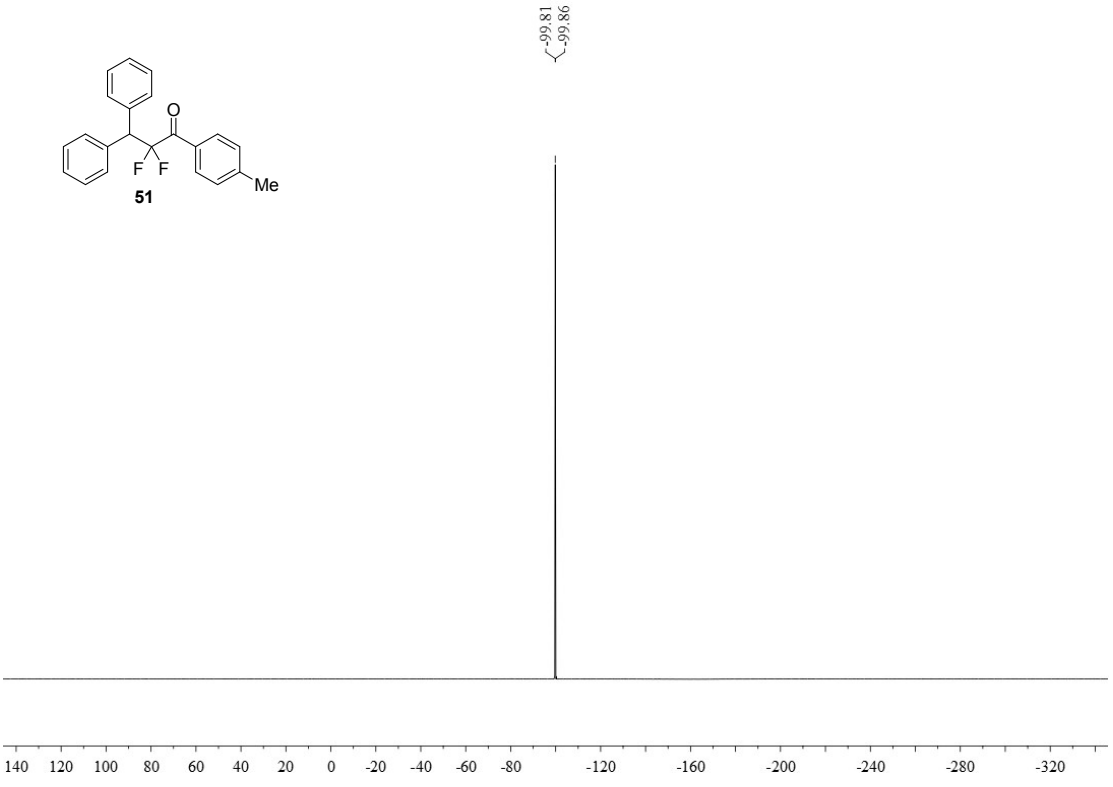
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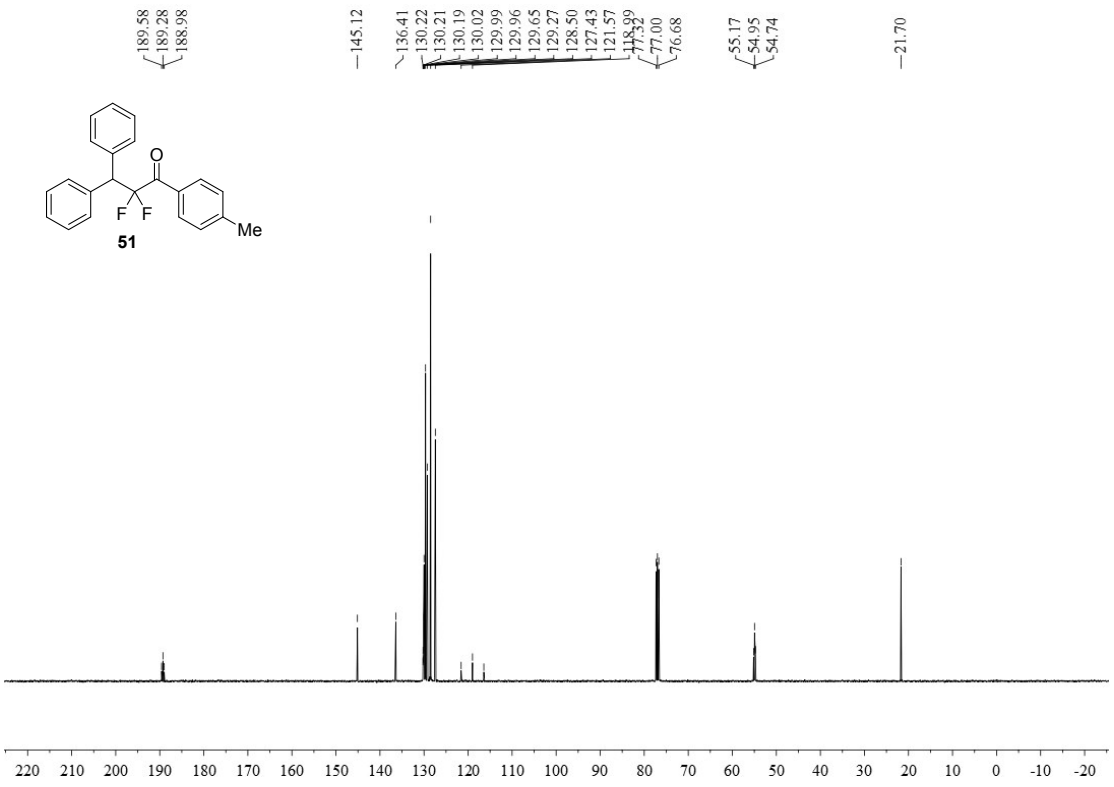
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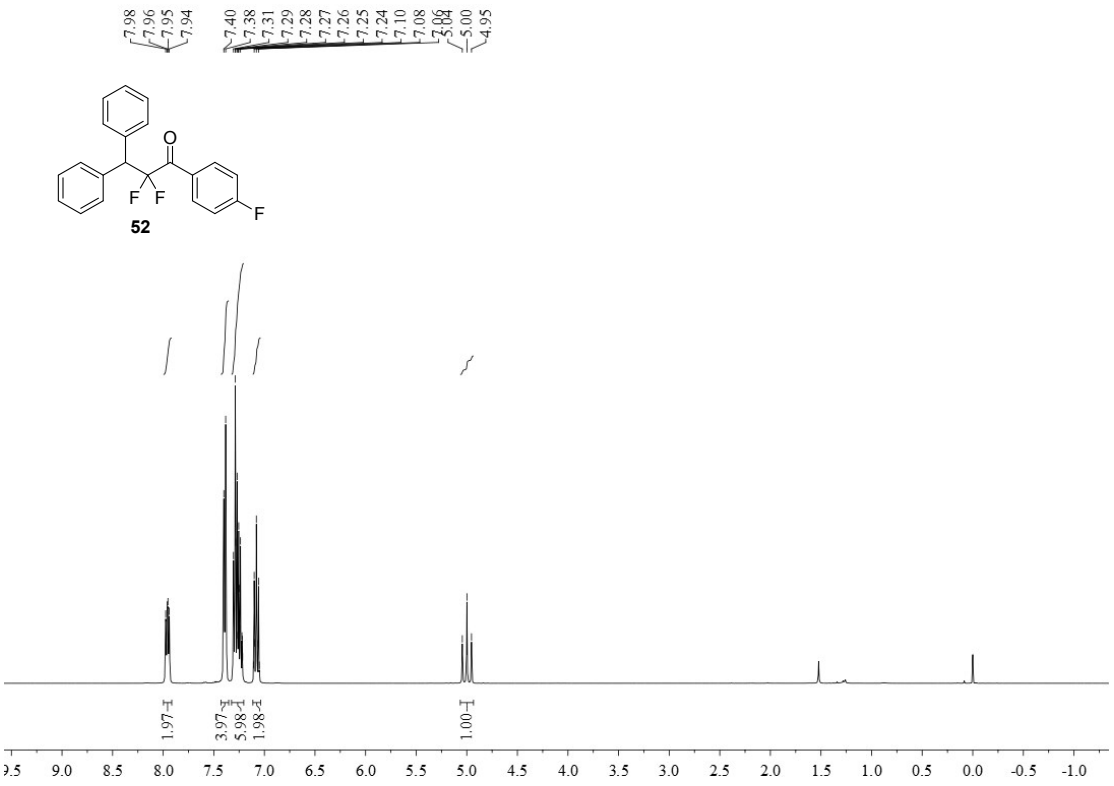
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F
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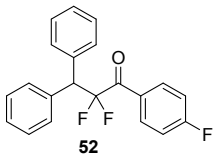
1.98
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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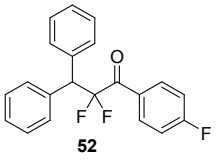
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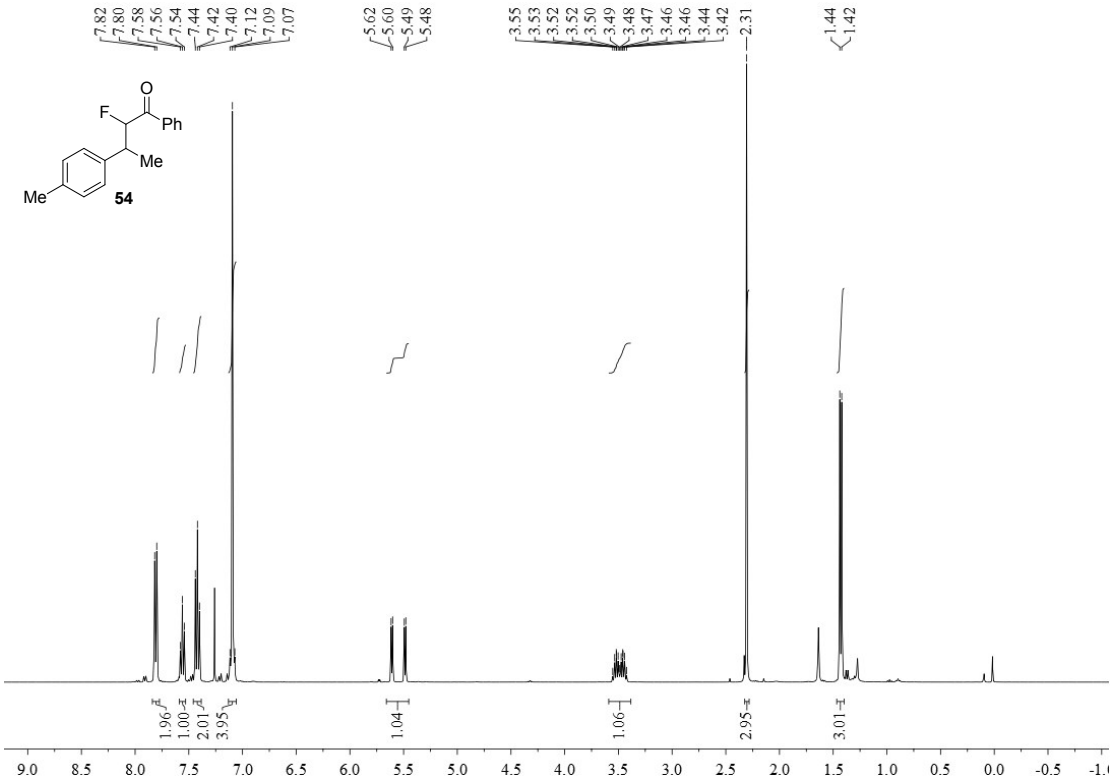
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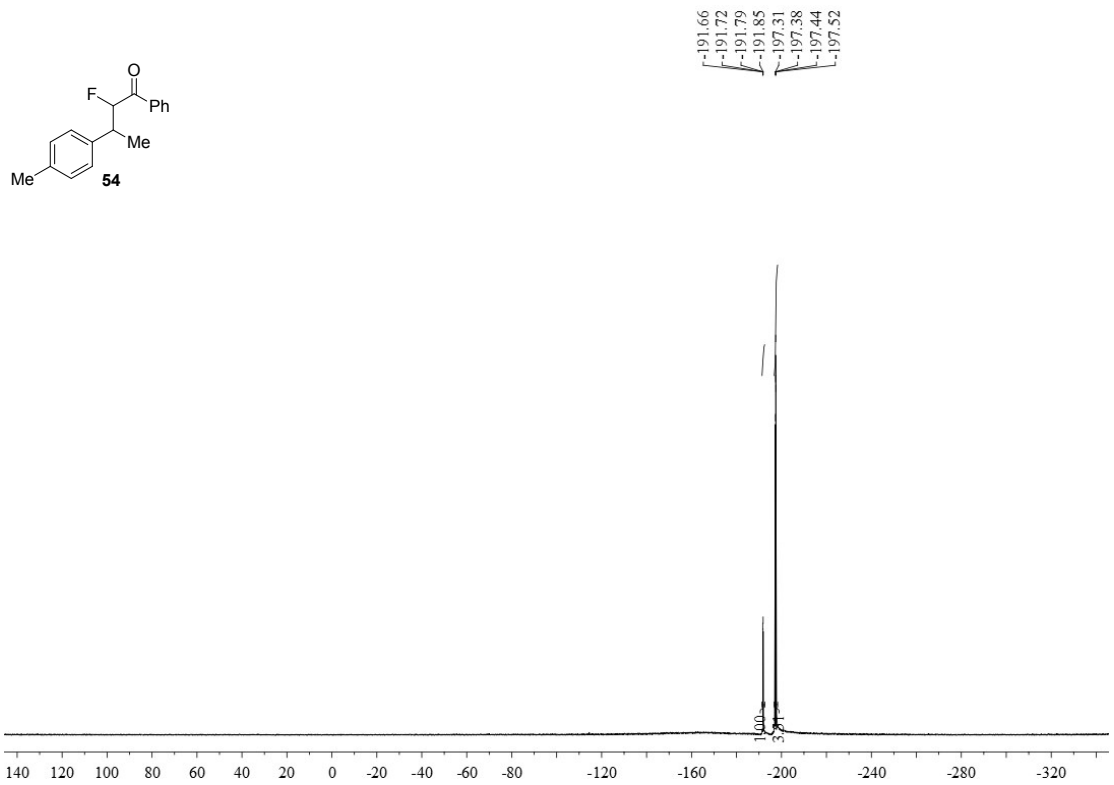
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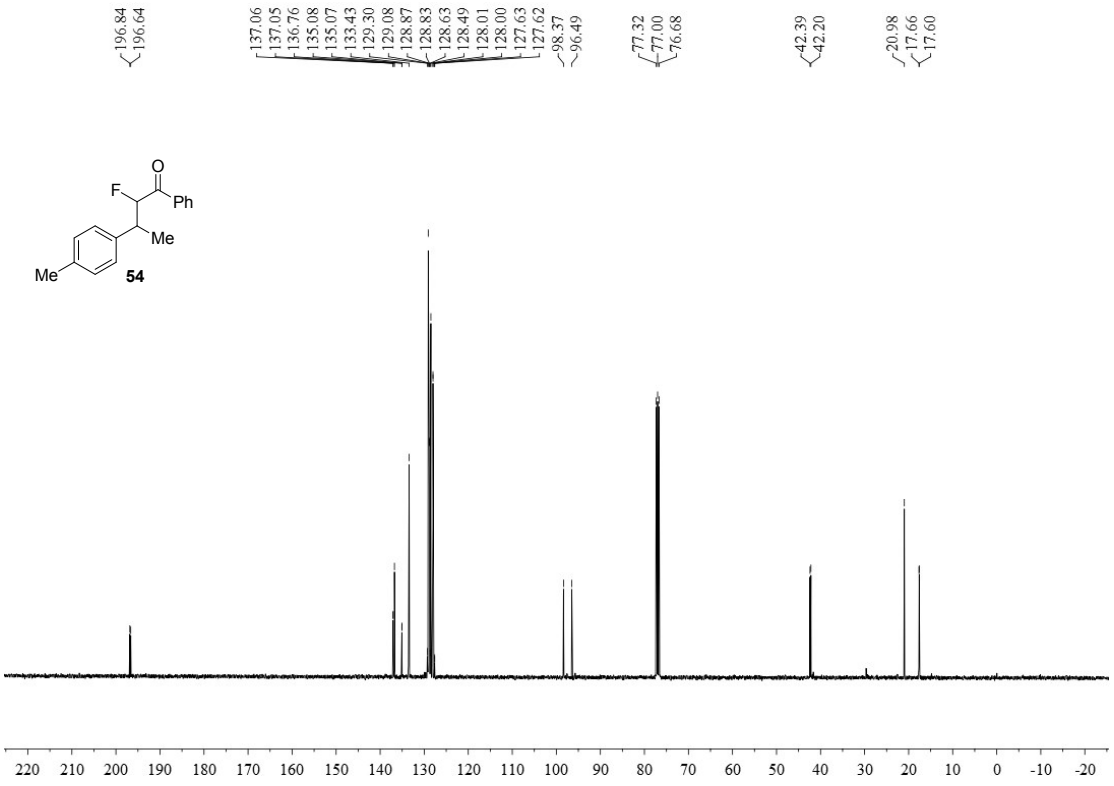
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