Enantioselective Copper-Catalyzed Defluorosilylation of Trifluoro-methylated Alkenes with Silylboronates

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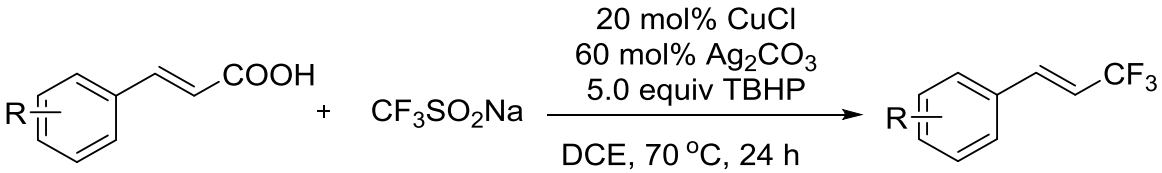
1. General Information

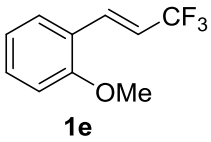
All new compounds were fully characterized. All reactions and manipulations involving air-sensitive compounds were performed using standard Schlenk techniques or in a glovebox. Anhydrous CH_3CN and anhydrous MeOH were purchased from J&K Chemical and were used as received. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AVANCE III 400 MHz or 500 MHz spectrometer. Chemical shifts (δ values) were reported in ppm with $CDCl_3$ (^{1}H, ^{13}C NMR). Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI). IR spectra were recorded on a FT-IR spectrometer. Optical rotations were measured on an automatic polarimeter with $[\alpha]D^{25}$ values reported in degrees; concentration (*c*) is in g/100 mL. Chiral HPLC analyses were performed on UltiMate 3000 liquid chromatography. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The preparation of the **1a-1d, 1j, 1k, 1n-1q** were described according to the literatures[1].

2. General Procedure for Synthesis of Starting Materials



According to the literatures[1a,2], to a reaction flask equipped with a reflux condenser was added α,β-unsaturated carboxylic acid (5.0 mol, 1.0 equiv), CF_3SO_2Na (2.34 g, 15.0 mol, 3.0 equiv), CuCl (0.01g, 1.0 mol, 0.2 equiv), Ag_2CO_3 (0.83 g, 3 mol, 0.6 equiv), and DCE (50 mL). Then aqueous TBHP (70 wt. % in H_2O) (3.2 mL, 25 mmol, 5 equiv) was added at 0 °C with stirring. The reaction was heated at 70 °C and stirring for 24 h. The resulting mixture was filtered through a pad of celite and was washed with CH_2Cl_2 (20 mL). After concentrated in vacuum, the residue was purified by column chromatography to afford the corresponding product.

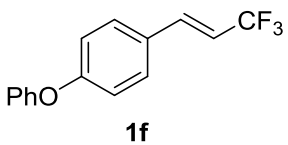
(*E*)-1-methoxy-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1e)



1e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.30 (m, 3H), 7.09 – 6.77 (m, 2H), 6.35 (dq, *J* = 16.3, 6.7 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.9, 133.1 (q, *J* = 7.1 Hz), 131.1, 128.7, 124.0 (q, *J* = 268.8 Hz), 122.3, 120.7, 116.4 (q, *J* = 33.3 Hz), 111.1, 55.4. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -63.2. **ATR-FTIR (cm^{-1})**: 1661, 1600, 1492, 1439, 1314, 1108, 978, 846. **EI-MS (m/z, relative intensity)**: 202 (M^+, 95), 119 (100), 107 (58), 91 (78), 63 (15). **HRMS m/z (ESI):** calcd for $C_{10}H_{10}F_3O$ $(M + H)^+$ 203.0678, found 203.0679.

(*E*)-1-phenoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1f)

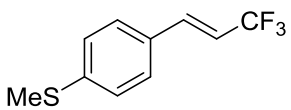


1f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.32 (m, 4H), 7.21 – 6.93 (m, 6H), 6.20 – 5.98 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.1, 156.2, 136.8 (q, *J* = 6.8 Hz), 129.9, 129.1, 128.1, 124.1, 123.7 (q, *J* = 268.7 Hz), 119.6, 118.5, 114.6 (q, *J* = 33.8 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -63.0. **ATR-FTIR (cm^{-1})**: 1506, 1272, 1104, 976, 819, 778, 694. **EI-MS (m/z, relative intensity)**: 222 (33), 201 (21), 153 (100), 152 (55), 101 (8), 76 (14).

(*E*)-methyl(4-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)sulfane (1g)

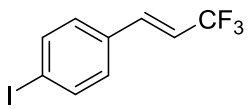
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (*d*, J = 8.4 Hz, 2H), 7.24 (*d*, J = 8.4 Hz, 2H), 7.09 (dd, *J* = 16.1, 2.1 Hz, 1H), 6.15 (dq, *J* = 16.1, 6.6 Hz, 1H), 2.50 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.4, 137.0 (q, *J* = 6.8 Hz), 129.9, 127.9, 126.1, 123.7 (q, *J* = 269.7 Hz), 114.9 (q, *J* = 33.8 Hz), 15.2. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -63.1. **ATR-FTIR (cm^{-1})**: 1656, 1494, 1343, 1316, 1270, 1094, 974, 804, 501. **EI-MS (m/z, relative intensity)**: 218 (M^+, 100), 203 (25), 183 (18), 151 (15), 134 (19).



1g

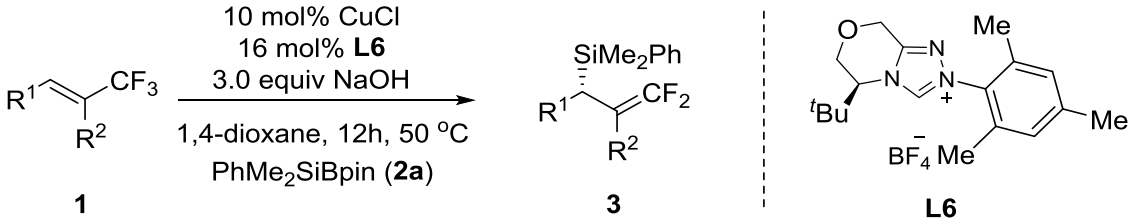
(*E*)-1-iodo-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (1l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.07 (dd, *J* = 16.1, 2.1 Hz, 1H), 6.21 (dq, *J* = 16.1, 6.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.2, 136.7 (q, *J* = 6.7 Hz). 132.9, 129.1, 123.4 (q, *J* = 269.7 Hz), 116.7 (q, *J* = 34.0 Hz), 96.1. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -63.5. **ATR-FTIR (cm^{-1})**: 1655, 1507, 1487, 1398, 1314, 1113, 1006, 972, 803. **EI-MS (m/z, relative intensity)**: 297 (M^+, 95), 151 (100), 102 (20), 75 (18).



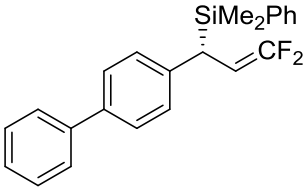
1l

3. Experimental Procedures and Characterization of Products



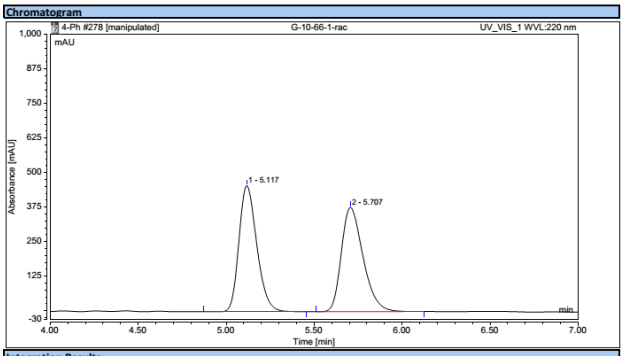
To a 25 mL Schlenk tube was added trifluoramethyl alkenes **1** (0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-dioxane (2 mL) under Ar. The reaction mixture was stirred at 50 ^oC for 12 hours. The solution was then cooled to rt and the solvent was removed under vacuum directly. The crude products were purified by column chromatography on silica gel to afford the pure products.

(*R*)-(1-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)dimethyl(phenyl)silane (3aa)



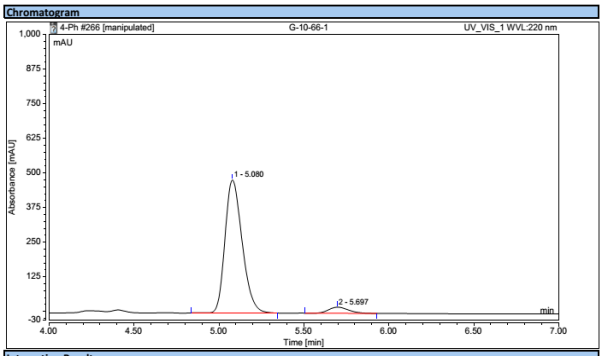
3aa

Following the general procedure, the reaction of **1a** (49.6 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3aa** (65.7 mg, 89%, 90% ee) as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 – 7.55 (m, 2H), 7.51 – 7.31 (m, 10H), 6.97 (d, *J* = 8.2 Hz, 2H), 4.61 (ddd, *J* = 22.7, 11.8, 3.8 Hz, 1H), 3.24 (dd, *J* = 11.8, 1.9 Hz, 1H), 0.35 (s, 3H), 0.35 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3 (t, *J* = 286.5 Hz), 140.8, 140.1 (dd, *J* = 2.5, 1.8 Hz), 137.9, 135.7, 134.2, 129.5, 128.7, 127.7, 127.5, 127.0, 126.8, 78.1 (dd, *J* = 22.2, 21.6 Hz), 31.0 (d, *J* = 1.7 Hz), -4.7, -4.9. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.7 (d, *J* = 47.4 Hz), -89.9 (d, *J* = 46.8 Hz). **ATR-FTIR (cm^{-1})**: 2734, 1489, 1257, 1177, 1114, 928, 810, 766, 698. **EI-MS (m/z, relative intensity)**: 364 (M^+, 1), 210 (33), 135 (100), 107 (8). HPLC analysis (OD-H, 0.5 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 88% ee: t_1 (major) = 5.1 min, t_2 (minor) = 5.7 min. $[\alpha]_D^{22}$ = –53.069 (c = 3.280, $CHCl_3$).



Integration Results

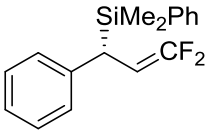
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.117	53.842	456.751	50.02	54.78	n.a.
2		5.707	53.806	377.001	49.98	45.22	n.a.
Total:			107.648	833.751	100.00	100.00	



Integration Results

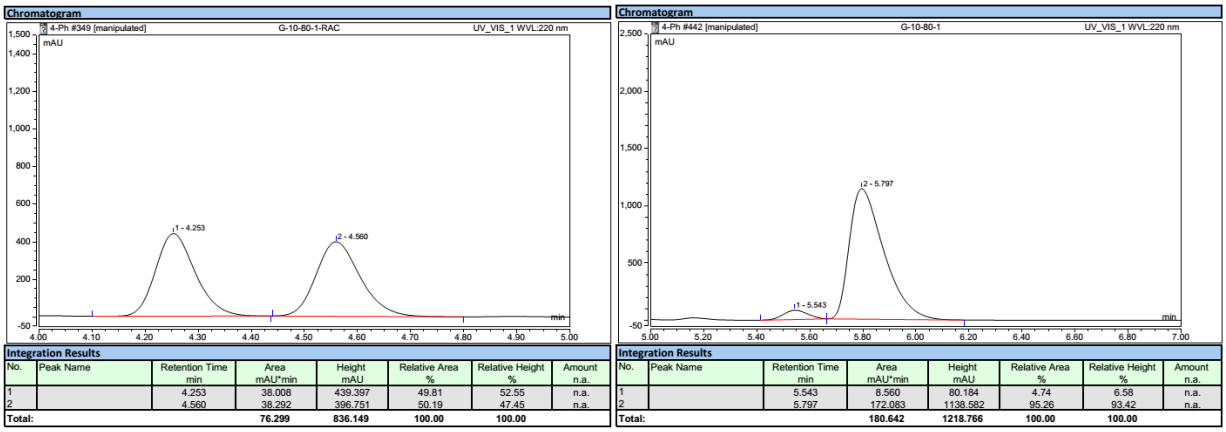
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.080	56.222	480.861	94.99	95.63	n.a.
2		5.697	2.964	21.972	5.01	4.37	n.a.
Total:			59.186	502.833	100.00	100.00	

(*R*)-(3,3-difluoro-1-phenylallyl)dimethyl(phenyl)silane (3ba)

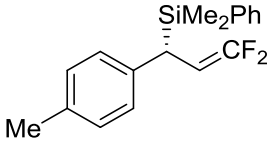


3ba

Following the general procedure, the reaction of **1b** (34.4 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3ba** (40.1 mg, 69%, 91% ee) as a colorless liquid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.32 (m, 5H), 7.25 – 7.17 (m, 2H), 7.16 – 7.06 (m, 1H), 6.96 – 6.78 (m, 2H), 4.56 (ddd, *J* = 22.2, 11.8, 4.4 Hz, 1H), 3.17 (dd, *J* = 11.8, 1.9 Hz, 1H), 0.30 (s, 3H), 0.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.2 (t, *J* = 286.4 Hz), 140.9 (dd, *J* = 2.4, 1.8 Hz), 135.8, 134.2, 129.4, 128.2, 127.6, 127.1, 125.1, 78.2 (dd, *J* = 22.2, 21.6 Hz), 31.2 (d, *J* = 1.7 Hz), -4.7, -5.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.9 (d, *J* = 47.6 Hz), -90.1 (d, *J* = 47.8 Hz). **ATR-FTIR (cm^{-1})**: 2921, 2442, 1737, 1684, 1264, 1177, 1114, 812. **EI-MS (m/z, relative intensity)**: 288 (M^+, 1), 211 (3), 192 (7), 135 (100), 133 (20), 107 (10). HPLC analysis (OD-H, 0.1 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 91% ee: t_1 (major) = 5.8 min, t_2 (minor) = 5.5 min. $[\alpha]_D^{22}$ = –24.435 (c = 1.255, $CHCl_3$).

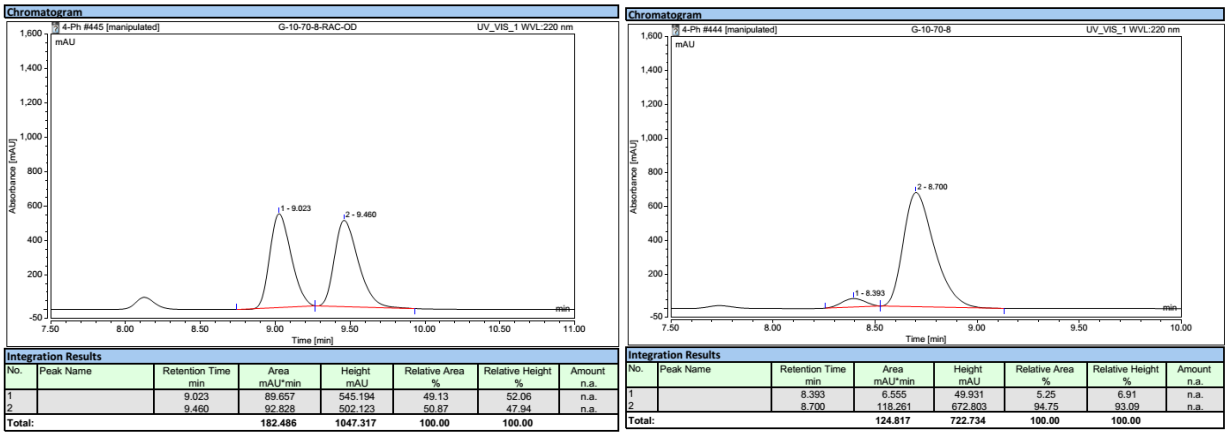


(*R*)-(3,3-difluoro-1-(p-tolyl)allyl)dimethyl(phenyl)silane (3ca)

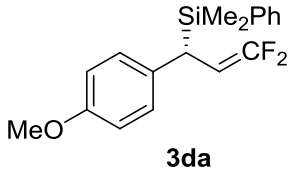


3ca

Following the general procedure, the reaction of **1c** (37.2 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3ca** (38.6 mg, 64%, 90% ee) as a colorless liquid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.29 (m, 5H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 2H), 4.60 – 4.45 (m, 1H), 3.13 (d, *J* = 11.9 Hz, 1H), 2.30 (s, 3H), 0.29 (s, 3H), 0.28 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.2 (t, *J* = 286.2 Hz), 137.7 (t, *J* = 2. 0 Hz), 136.0, 134.2, 133.8, 129.4, 128.9, 127.6, 127.0, 78.4 (t, *J* = 21.8 Hz), 30.6 (d, *J* = 1.6 Hz), 20.9, -4.6, -5.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -90.1 (d, *J* = 47.8 Hz), -90.4 (d, *J* = 48.2 Hz). **ATR-FTIR (cm^{-1})**: 1736, 1512, 1261, 1219, 1116, 917, 770. **EI-MS (m/z, relative intensity)**: 302 (M^+, 1), 225 (6), 191 (7), 148 (16), 135 (100), 133 (20), 107 (9). HPLC analysis (OD-H, 0.1 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 90% ee: t_1 (major) = 8.7 min, t_2 (minor) = 8.4 min. $[\alpha]_D^{22}$ = –26.572 (c = 1.415, $CHCl_3$).

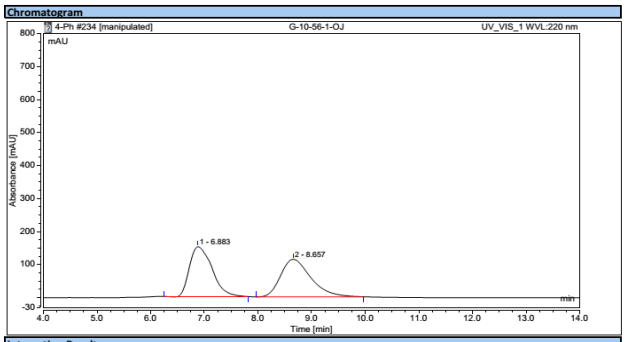


(*R*)-(3,3-difluoro-1-(4-methoxyphenyl)allyl)dimethyl(phenyl)silane (3da)



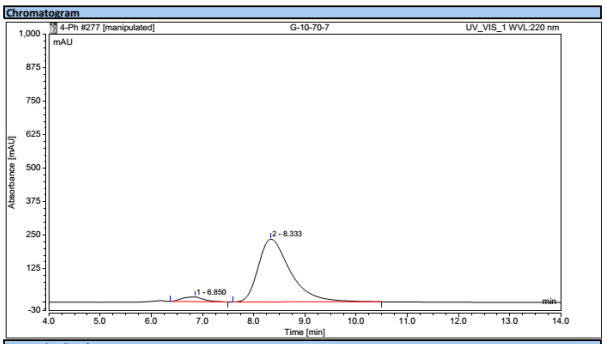
3da

Following the general procedure, the reaction of **1d** (40.4 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3da** (47.7 mg, 75%, 90% ee) as a colorless liquid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.28 (m, 5H), 6.92 – 6.60 (m, 4H), 4.51 (ddd, *J* = 22.0, 11.8, 4.7 Hz, 1H), 3.78 (s, 3H), 3.11 (dd, *J* = 11.8, 1.9 Hz, 1H), 0.29 (s, 3H), 0.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.2, 155.2 (t, *J* = 286.3 Hz), 136.0, 134.2, 132.9 (t, *J* = 2.0 Hz), 129.4, 128.0, 127.6, 113.7, 78.5 (t, *J* = 21.7 Hz), 55.2, 30.0 (d, *J* = 1.6 Hz), -4.7, -4.9. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -90.1 (d, *J* = 47.8 Hz), -90.3 (d, *J* = 47.4 Hz). **ATR-FTIR (cm^{-1})**: 2957, 1734, 1653, 1558, 1507, 1247, 917, 734. **EI-MS (m/z, relative intensity)**: 318 (M^+, 4), 303 (16), 225 (14), 164 (11), 149 (22), 135 (100), 107 (9). HPLC analysis (OJ-H, 0.5 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 90% ee: t_1 (major) = 8.3 min, t_2 (minor) = 6.9 min. $[\alpha]_D^{22}$ = –38.301 (c = 2.080, $CHCl_3$).



Integration Results

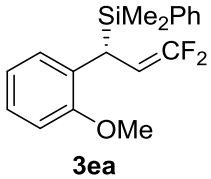
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.883	73.759	151.114	49.76	57.01	n.a.
2		8.657	74.469	113.952	50.24	42.99	n.a.
Total:			148.229	265.066	100.00	100.00	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.850	8.365	17.278	4.69	6.86	n.a.
2		8.333	169.881	234.539	95.31	93.14	n.a.
Total:			178.245	251.818	100.00	100.00	

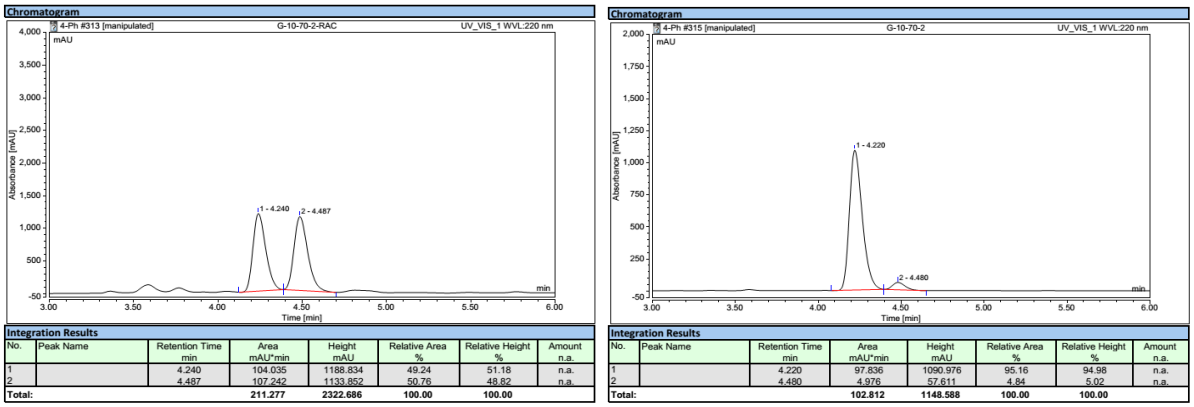
(*R*)-(3,3-difluoro-1-(2-methoxyphenyl)allyl)dimethyl(phenyl)silane (3ea)



3ea

Following the general procedure, the reaction of **1e** (40.4 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3ea** (40.9 mg, 64%, 90% ee) as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.27 (m, 5H), 7.15 – 7.04 (m, 1H), 6.92 – 6.79 (m, 2H), 6.76 (d, *J* = 8.1 Hz, 1H), 4.62 (ddd, *J* = 20.8, 11.9, 6.0 Hz, 1H), 3.70 (dd, *J* = 11.9, 1.8 Hz, 1H), 3.62 (s, 3H),

0.28 (s, 3H), 0.27 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.8, 155.2 (t, *J* = 286.1 Hz), 136.8, 134.0, 129.6 (t, *J* = 2.0 Hz), 129.1, 127.39, 127.35, 125.9, 120.3, 110.0, 78.0 (dd, *J* = 22.1, 21.2 Hz), 54.7, 23.6 (d, *J* = 1.8 Hz), -4.5, -4.9. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -90.3 (d, *J* = 49.0 Hz), -90.5 (d, *J* = 49.0 Hz). **ATR-FTIR (cm^{-1})**: 2390, 1734, 1684, 1653, 1559, 1540, 1243. **EI-MS (m/z, relative intensity)**: 318 (M^+, 3), 303 (2), 288 (2), 207 (1), 149 (42), 135 (100), 107 (10). HPLC analysis (OD-H, 0.5 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 90% ee: t_1 (major) = 4.2 min, t_2 (minor) = 4.5 min. $[\alpha]_D^{22}$ = –38.394 (c = 1.805, $CHCl_3$).



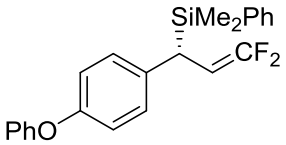
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.240	104.035	1188.834	49.24	51.18	n.a.
2		4.487	107.242	1133.852	50.76	48.82	n.a.
Total:			211.277	2322.686	100.00	100.00	

Integration Results

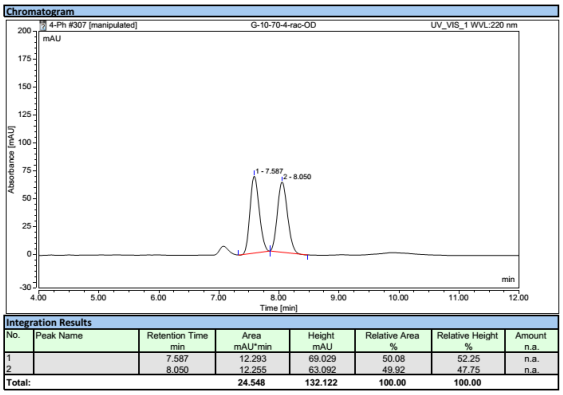
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.220	97.836	1090.976	95.16	94.98	n.a.
2		4.480	4.976	57.611	4.84	5.02	n.a.
Total:			102.812	1148.588	100.00	100.00	

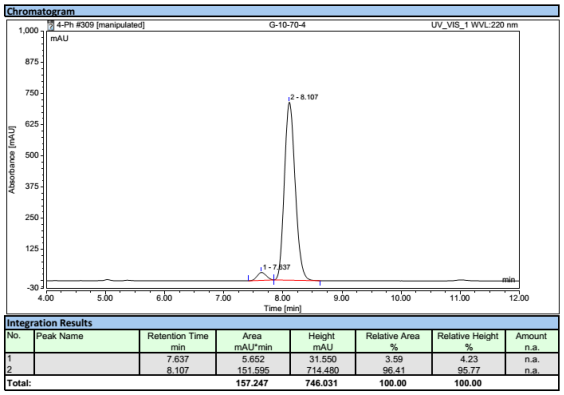
(*R*)-(3,3-difluoro-1-(4-phenoxyphenyl)allyl)dimethyl(phenyl)silane (3fa)



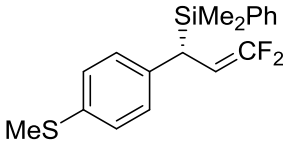
3fa

Following the general procedure, the reaction of **1f** (52.8 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 °C for 12 h after column chromatography on silica afford **3fa** (68.2 mg, 89%, 93% ee) as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.31 (m, 7H), 7.16 – 7.06 (m, 1H), 7.04 – 6.96 (m, 2H), 6.95 – 6.76 (m, 4H), 4.54 (ddd, *J* = 22.5, 11.8, 4.0 Hz, 1H), 3.18 (dd, *J* = 11.8, 1.9 Hz, 1H), 0.33 (s, 3H), 0.33 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.7, 155.3 (t, *J* = 286.5 Hz), 154.4, 136.0 (t, *J* = 2.0 Hz), 135.7, 134.2, 129.6, 129.5, 128.2, 127.6, 122.8, 119.1, 118.3, 78.2 (t, *J* = 21.9 Hz), 30.5 (d, *J* = 1.6 Hz), -4.8, -4.9. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.7 (d, *J* = 47.6 Hz), -90.0 (d, *J* = 46.8 Hz). **ATR-FTIR (cm^{-1})**: 2927, 1734, 1708, 1684, 1635, 1521, 1507, 1457, 1239, 777. **EI-MS (m/z, relative intensity)**: 380 (M^+, 4), 226 (4), 136 (11), 135 (100), 133 (33), 107 (9). HPLC analysis (OD-H, 0.5 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 93% ee: t_1 (major) = 8.1 min, t_2 (minor) = 7.6 min. $[\alpha]_D^{22}$ = –36.010 (c = 2.105, $CHCl_3$).



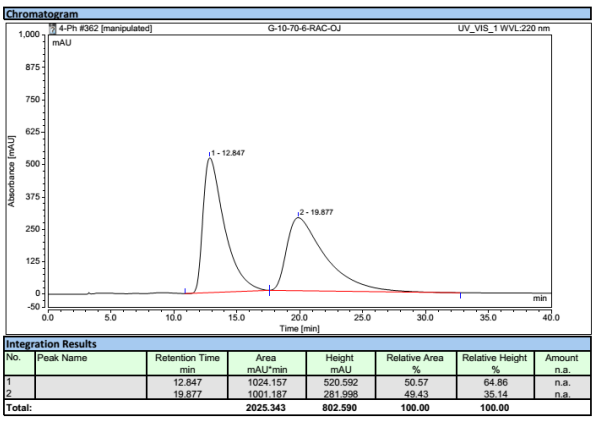


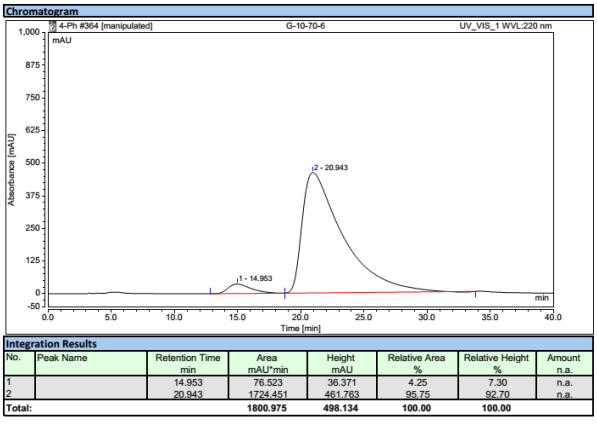
(*R*)-(3,3-difluoro-1-(4-(methylthio)phenyl)allyl)dimethyl(phenyl)silane (3ga)



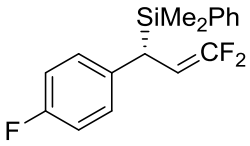
3ga

Following the general procedure, the reaction of **1g** (53.6 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3ga** (57.9 mg, 87%, 92% ee) as a white solid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.29 (m, 5H), 7.18 – 7.05 (m, 2H), 6.85 – 6.73 (m, 2H), 4.51 (ddd, *J* = 22.2, 11.7, 4.3 Hz, 1H), 3.13 (dd, *J* = 11.7, 1.8 Hz, 1H), 2.46 (s, 3H), 0.30 (s, 3H), 0.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.2 (t, *J* = 286.6 Hz), 138.1 (t, *J* = 2.5 Hz), 135.6, 134.4, 134.2, 129.5, 127.6, 127.6, 127.0, 78.0 (t, *J* = 22.2 Hz), 30.7 (d, *J* = 1.7 Hz), 16.3, -4.7, -5.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.7 (d, *J* = 46.7 Hz), -89.9 (d, *J* = 46.7 Hz). **ATR-FTIR (cm^{-1})**: 1736, 1492, 1255, 1178, 917, 810, 775. **EI-MS (m/z, relative intensity)**: 334 (M^+, 3), 135 (100), 133 (28), 107 (8). HPLC analysis (OJ-H, 0.2 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 92% ee: t_1 (major) = 20.9 min, t_2 (minor) = 15.0 min. $[\alpha]_D^{22}$ = –54.487 (c = 1.560, $CHCl_3$).



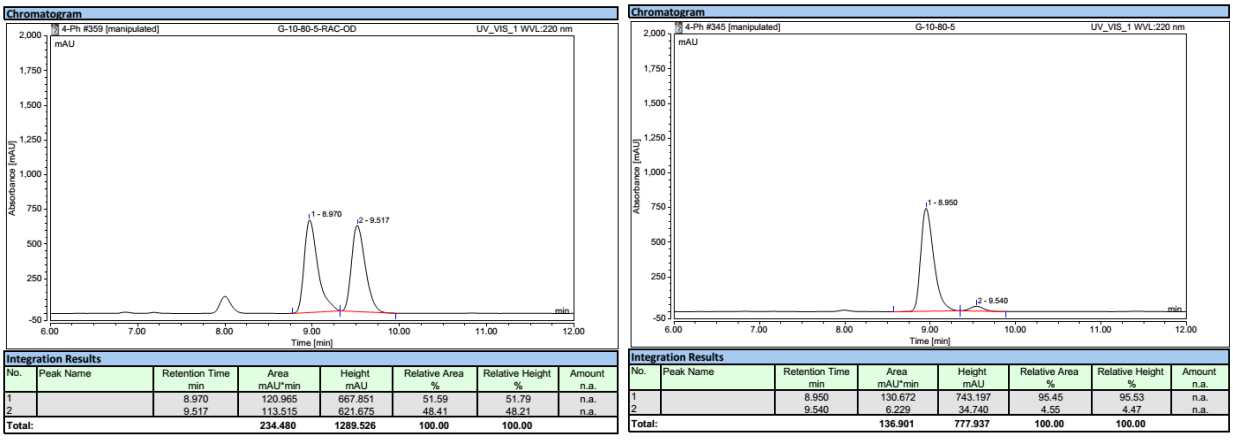


(*R*)-(3,3-difluoro-1-(4-fluorophenyl)allyl)dimethyl(phenyl)silane (3ha)

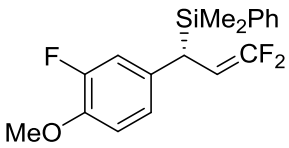


3ha

Following the general procedure, the reaction of **1h** (38.0 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3ha** (50.7 mg, 83%, 91% ee) as a colorless liquid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.32 (m, 5H), 6.95 – 6.85 (m, 2H), 6.85 – 6.69 (m, 2H), 4.51 (ddd, *J* = 22.2, 11.7, 4.1 Hz, 1H), 3.16 (dd, *J* = 11.7, 1.8 Hz, 1H), 0.31 (s, 3H), 0.30 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.7 (d, *J* = 243.1 Hz), 155.3 (t, *J* = 286.8 Hz), 136.5 (dd, *J* = 4.6, 2.9 Hz), 135.5, 134.2, 129.5, 128.3 (d, *J* = 7.7 Hz), 127.7, 115.0 (d, *J* = 21.2 Hz), 78.2 (t, *J* = 22.0 Hz), 30.4 (d, *J* = 1.5 Hz), -4.9, -5.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.6 (d, *J* = 46.6 Hz), -89.8 (d, *J* = 46.6 Hz), -118.42. **ATR-FTIR (cm^{-1})**: 1737, 1508, 1428, 1260, 917, 811, 783, 701. **EI-MS (m/z, relative intensity)**: 306 (M^+, 1), 210 (4), 152 (21), 135 (100), 107 (11). HPLC analysis (OD-H, 0.1 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 91% ee: t_1 (major) = 9.0 min, t_2 (minor) = 9.5 min. $[\alpha]_D^{22}$ = –22.433 (c = 2.0, $CHCl_3$).



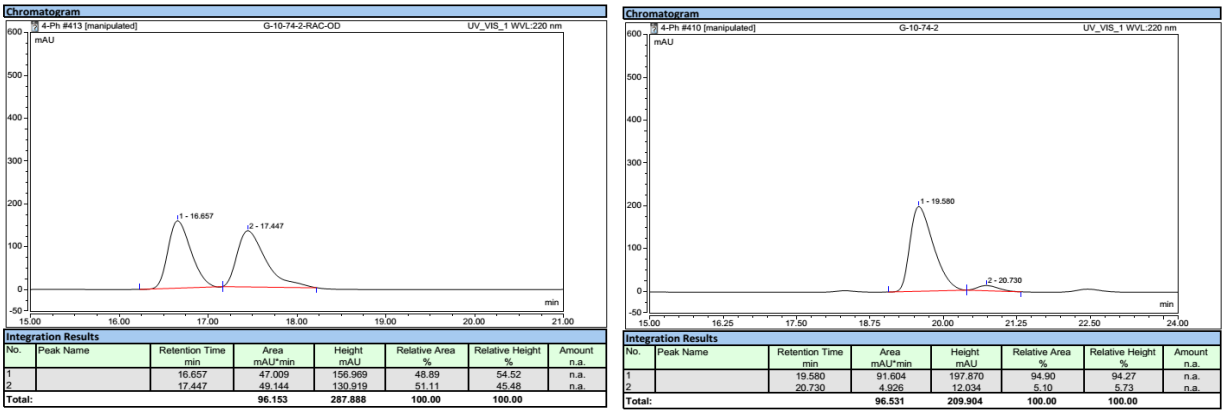
(*R*)-(3,3-difluoro-1-(3-fluoro-4-methoxyphenyl)allyl)dimethyl(phenyl)silane (3ia)



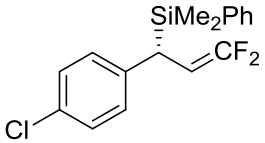
3ia

Following the general procedure, the reaction of **1i** (44.0 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3ia** (42.6 mg, 63%, 90% ee) as a colorless liquid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.29 (m, 5H), 6.85 – 6.70 (m, 1H), 6.64 – 6.45 (m, 2H), 4.44 (ddd, *J* = 22.3, 11.7, 4.0 Hz, 1H), 3.85 (s, 3H), 3.08 (dd, *J* =

11.7, 1.8 Hz, 1H), 0.29 (s, 3H), 0.28 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3 (t, *J* = 286.9 Hz), 152.1 (d, *J* = 245.4 Hz), 145.0 (d, *J* = 10.8 Hz), 135.5, 134.1, 129.6, 127.7, 122.5 (d, *J* = 3.4 Hz), 114.9, 114.8, 113.3 (d, *J* = 2.2 Hz), 78.0 (t, *J* = 21.7 Hz), 56.3, 30.2, -4.8, -5.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.5 (d, *J* = 46.7 Hz), -89.8 (d, *J* = 46.7 Hz), -135.3. **ATR-FTIR (cm^{-1})**: 1737, 1515, 1258, 1182, 1117, 917, 814. **EI-MS (m/z, relative intensity)**: 321 (8), 167 (10), 151 (9), 135 (100), 133 (20), 107 (9). HPLC analysis (OD-H, 0.1 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 90% ee: t_1 (major) = 19.6 min, t_2 (minor) = 20.7 min. $[\alpha]_D^{22}$ = –29.925 (c = 1.780, $CHCl_3$).

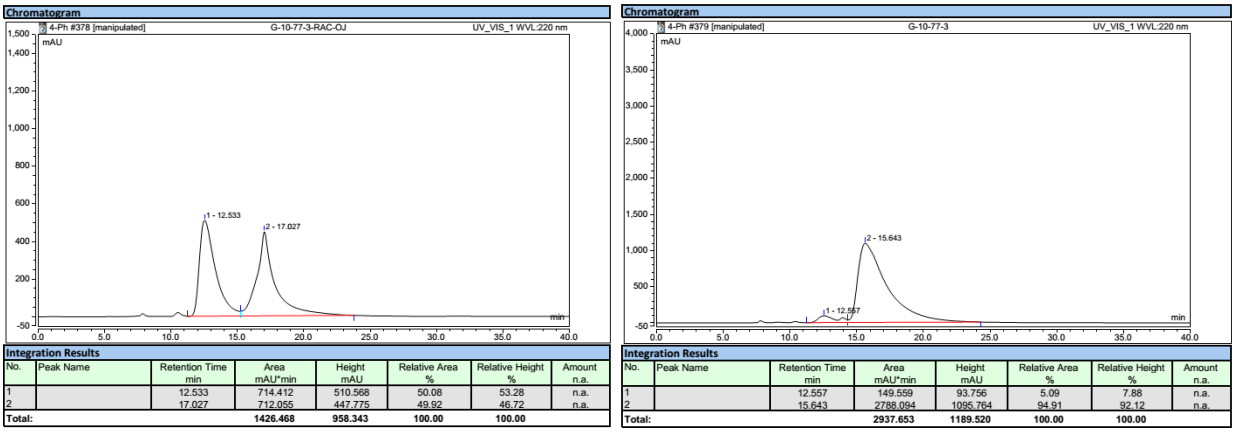


(*R*)-(1-(4-chlorophenyl)-3,3-difluoroallyl)dimethyl(phenyl)silane (3ja)

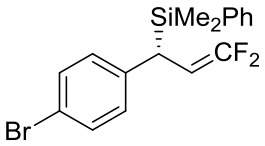


3ja

Following the general procedure, the reaction of **1j** (41.2 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 °C for 12 h after column chromatography on silica afford **3ja** (49.6 mg, 77%, 90% ee) as a colorless liquid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.27 (m, 5H), 7.21 – 7.09 (m, 2H), 6.85 – 6.70 (m, 2H), 4.49 (ddd, *J* = 22.3, 11.7, 4.0 Hz, 1H), 3.14 (dd, *J* = 11.7, 1.8 Hz, 1H), 0.30 (s, 3H), 0.28 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3 (t, *J* = 287.0 Hz), 139.5 (dd, *J* = 2.5, 1.9 Hz), 135.3, 134.2, 130.7, 129.6, 128.3, 128.2, 127.7, 77.8 (dd, *J* = 22.6, 21.5 Hz), 30.8 (d, *J* = 1.8 Hz), -4.9, -5.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.3 (d, *J* = 46.2 Hz), -89.5 (d, *J* = 45.7 Hz). **ATR-FTIR (cm^{-1})**: 1736, 1491, 1255, 918, 836. **EI-MS (m/z, relative intensity)**: 322 (M^+, 1), 210 (3), 191 (4), 136 (12), 135 (100), 133 (10), 107 (9). HPLC analysis (OJ-H, 0.1 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 90% ee: t_1 (major) = 15.6 min, t_2 (minor) = 12.6 min. $[\alpha]_D^{22}$ = –43.672 (c = 1.035, $CHCl_3$).

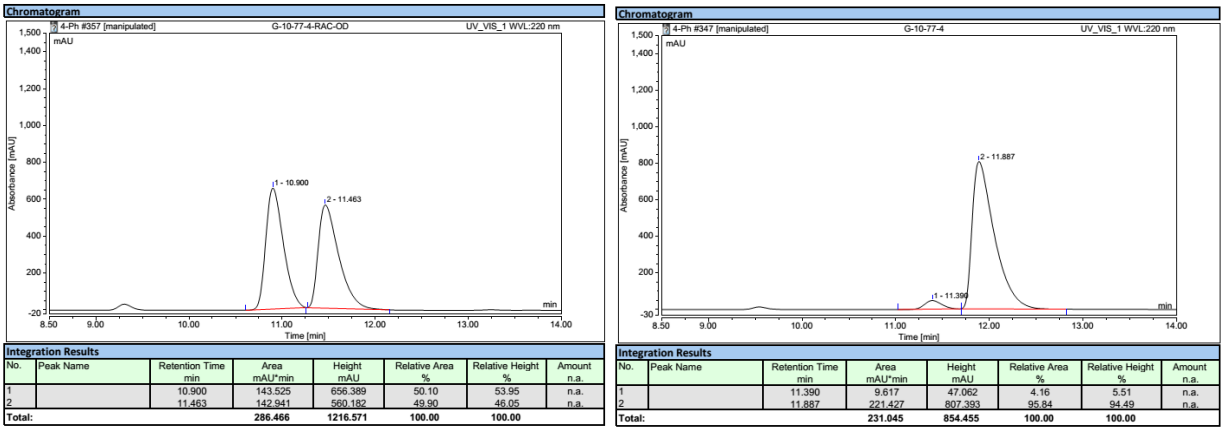


(*R*)-(1-(4-bromophenyl)-3,3-difluoroallyl)dimethyl(phenyl)silane (3ka)

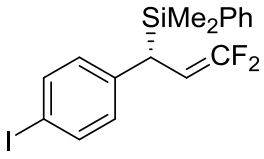


3ka

Following the general procedure, the reaction of **1k** (50.2 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3ka** (65.3 mg, 89%, 92% ee) as a colorless liquid: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.29 (m, 7H), 6.79 – 6.64 (m, 2H), 4.50 (ddd, *J* = 22.3, 11.7, 3.9 Hz, 1H), 3.13 (dd, *J* = 11.7, 1.8 Hz, 1H), 0.31 (s, 3H), 0.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3 (t, *J* = 287.0 Hz), 140.1 (dd, *J* = 2.5, 1.8 Hz), 135.2, 134.2, 131.2, 129.6, 128.8, 127.7, 118.6, 77.7 (dd, *J* = 22.7, 21.4 Hz), 30.8 (d, *J* = 1.9 Hz), -4.9, -5.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.3 (d, *J* = 45.9 Hz), -89.5 (d, *J* = 45.9 Hz). **ATR-FTIR (cm^{-1})**: 1737, 1488, 1259, 1178, 918, 808, 701. **EI-MS (m/z, relative intensity)**: 368 (M^++1, 1), 367 (M^+, 0.5), 366 (M^+-1, 1), 135 (100), 107 (11). HPLC analysis (OD-H, 0.1 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 90% ee: t_1 (major) = 11.9 min, t_2 (minor) = 11.4 min. $[\alpha]_D^{22}$ = – 24.636 (c = 0.985, $CHCl_3$).

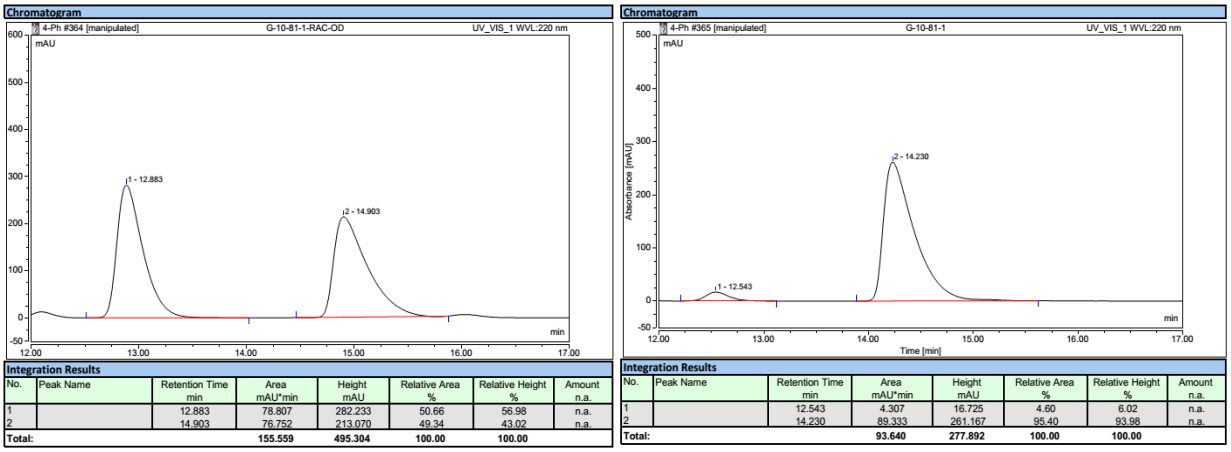


(*R*)-(3,3-difluoro-1-(4-iodophenyl)allyl)dimethyl(phenyl)silane (3la)

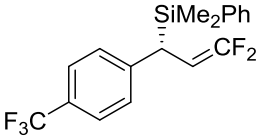


3la

Following the general procedure, the reaction of **1l** (59.4 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3la** (40.1 mg, 48%, 91% ee) as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 – 7.46 (m, 2H), 7.40 – 7.31 (m, 5H), 6.68 – 6.50 (m, 2H), 4.48 (ddd, *J* = 22.4, 11.7, 3.9 Hz, 1H), 3.11 (dd, *J* = 11.7, 1.9 Hz, 1H), 0.29 (s, 3H), 0.28 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3 (t, *J* = 287.1 Hz), 140.8, 137.1, 134.2, 129.6, 129.1, 127.7, 89.7, 77.7 (t, *J* = 22.2 Hz), 30.9, -4.9, -5.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.2 (d, *J* = 45.8 Hz), -89.5 (d, *J* = 46.0 Hz). **ATR-FTIR (cm^{-1})**: 1734, 1700, 1684, 1654, 1488, 1260, 1178, 918, 808. **EI-MS (m/z, relative intensity)**: 287 (8), 151 (44), 135 (100), 133 (33), 105 (28), 73 (25). HPLC analysis (OD-H, 0.1 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 91% ee: t_1 (major) = 14.2 min, t_2 (minor) = 12.5 min. $[\alpha]_D^{22}$ = –21.220 (c = 0.90, $CHCl_3$).



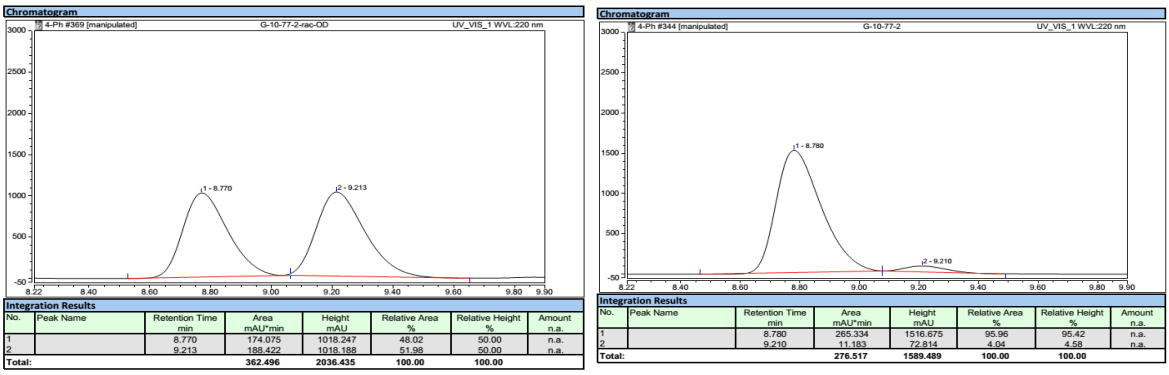
(*R*)-(3,3-difluoro-1-(4-(trifluoromethyl)phenyl)allyl)dimethyl(phenyl)silane (3ma)



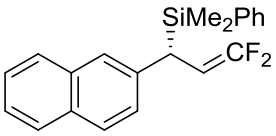
3ma

Following the general procedure, the reaction of **1m** (48.0 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3ma** (44.1 mg, 62%, 92% ee) as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.29 (m, 7H), 6.94 (d, *J* = 8.2 Hz, 2H), 4.55 (ddd, *J* = 22.5, 11.6, 3.5 Hz, 1H), 3.24 (dd, *J* = 11.6, 1.6 Hz, 1H), 0.31 (s, 3H), 0.30 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.5 (t, *J* = 287.3 Hz), 145.4, 135.0, 134.1, 129.7, 127.8, 127.2,

125.1 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.7 Hz), 77.5 (dd, *J* = 23.2, 21.3 Hz), 31.6 (d, *J* = 1.9 Hz), -4.9, -5.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.2, -88.9 (d, *J* = 45.6 Hz), -89.2 (d, *J* = 45.4 Hz). **ATR-FTIR (cm^{-1})**: 1734, 1701, 1683, 1487, 1261, 1177, 818. **EI-MS (m/z, relative intensity)**: 202 (75), 151 (14), 135 (100), 107 (12). HPLC analysis (OD-H, 0.1 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 92% ee: t_1 (major) = 9.2 min, t_2 (minor) = 8.8 min. $[\alpha]_D^{22}$ = –26.367 (c = 1.445, $CHCl_3$).

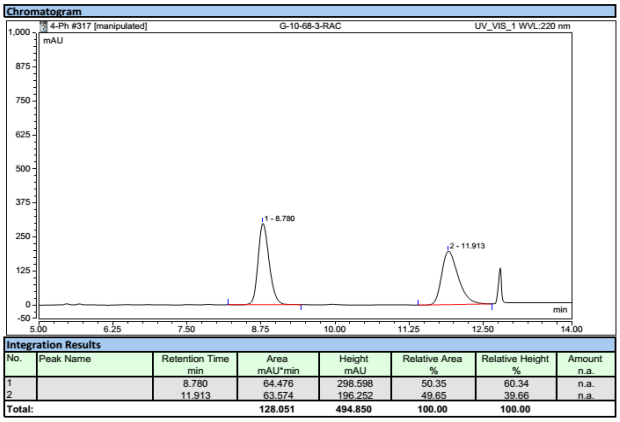


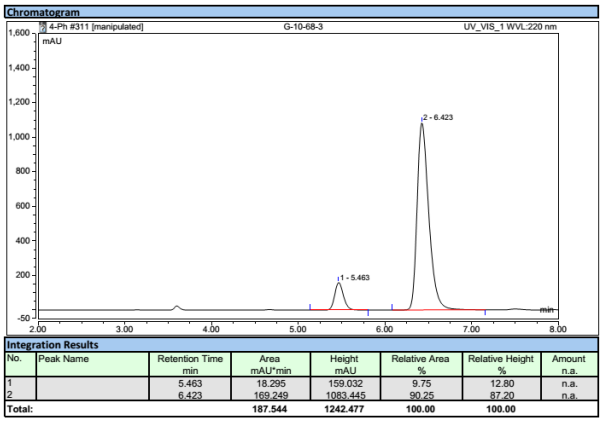
(*R*)-(3,3-difluoro-1-(naphthalen-2-yl)allyl)dimethyl(phenyl)silane (3na)



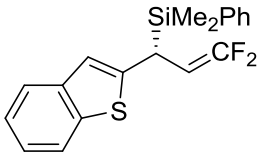
3na

Following the general procedure, the reaction of **1n** (44.4 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3na** (55.4 mg, 82%, 80% ee) as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 – 7.75 (m, 1H), 7.72 – 7.62 (m, 2H), 7.48 – 7.28 (m, 8H), 7.02 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.67 (ddd, *J* = 22.3, 11.7, 4.2 Hz, 1H), 3.35 (dd, *J* = 11.7, 1.9 Hz, 1H), 0.33 (s, 3H), 0.31 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.4 (t, *J* = 286.7 Hz), 138.6 (dd, *J* = 2.3, 1.8 Hz), 135.7, 134.3, 133.5, 131.5, 129.5, 127.7, 127.6, 127.5, 127.3, 126.5, 126.0, 125.0, 124.8, 78.2 (t, *J* = 21.7 Hz), 31.4 (d, *J* = 1.7 Hz), -4.6, -4.9. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.6 (d, *J* = 46.7 Hz), -89.8 (d, *J* = 46.7 Hz). **ATR-FTIR (cm^{-1})**: 1735, 1701, 1685, 1508, 1310, 1121, 954, 815. **EI-MS (m/z, relative intensity)**: 338 (M^+, 1), 242 (6), 184 (22), 135 (100), 107 (6). HPLC analysis (OD-H, 0.5 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 80% ee: t_1 (major) = 6.4 min, t_2 (minor) = 5.5 min. $[\alpha]_D^{22}$ = –43.733 (c = 1.125, $CHCl_3$).



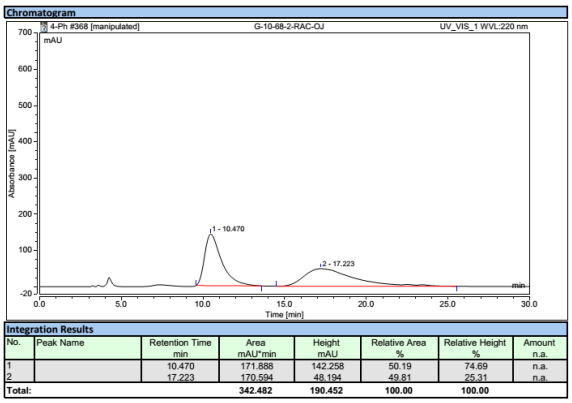


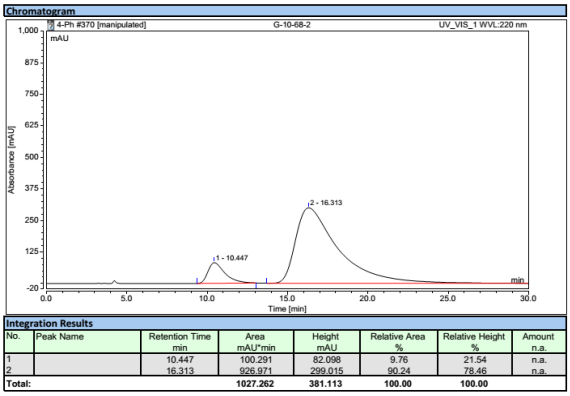
(*R*)-(1-(benzo[b]thiophen-2-yl)-3,3-difluoroallyl)dimethyl(phenyl)silane (3oa)



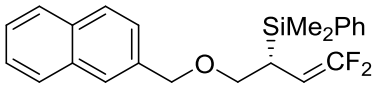
3oa

Following the general procedure, the reaction of **1o** (45.6 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 50 ^oC for 12 h after column chromatography on silica afford **3oa** (44.8 mg, 67%, 80% ee) as a yellow oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.40 – 7.35 (m, 2H), 7.33 – 7.24 (m, 2H), 6.73 (s, 1H), 4.54 (ddd, *J* = 21.8, 11.6, 4.1 Hz, 1H), 3.54 (dd, *J* = 11.6, 1.6 Hz, 1H), 0.43 (s, 3H), 0.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.5 (t, *J* = 287.4 Hz), 145.4 (t, *J* = 20.2 Hz), 140.1, 138.4, 135.4, 134.2, 129.7, 127.8, 124.1, 123.2, 122.4, 121.9, 119.1, 78.5 (dd, *J* = 23.4, 21.6 Hz), 27.4 (d, *J* = 2.2 Hz), -4.6, -4.7. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.2 (d, *J* = 45.0 Hz), -89.4 (d, *J* = 45.0 Hz). **ATR-FTIR (cm^{-1})**: 1736, 1508, 1288, 1120, 948, 809. **EI-MS (m/z, relative intensity)**: 344 (M^+, 6), 190 (19), 135 (100), 107 (8). HPLC analysis (OJ-H, 0.5 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 80% ee: t_1 (major) = 16.3 min, t_2 (minor) = 10.4 min. $[\alpha]_D^{22}$ = –41.123 (c = 0.475, $CHCl_3$).



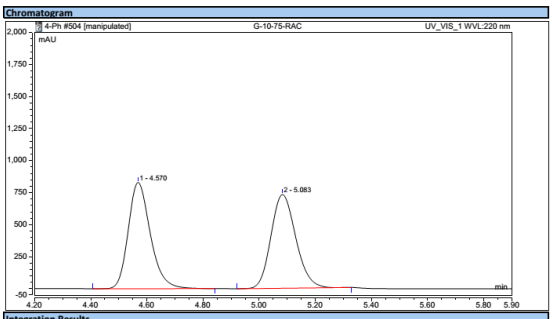


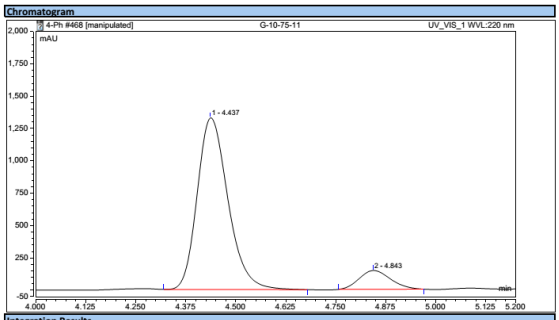
(*R*)-(4,4-difluoro-1-(naphthalen-2-yloxy)but-3-en-2-yl)dimethyl(phenyl)silane (3pa)



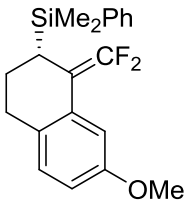
3pa

Following the general procedure, the reaction of **1p** (53.2 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L7** (13.9 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 0 ^oC for 12 h after column chromatography on silica afford **3pa** (63.3 mg, 86%, 80% ee) as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 – 7.65 (m, 3H), 7.60 (s, 1H), 7.41 – 7.32 (m, 4H), 7.32 – 7.17 (m, 4H), 4.46 (dd, *J* = 27.9, 12.2 Hz, 2H), 4.10 (ddd, *J* = 25.4, 11.3, 2.8 Hz, 1H), 3.48 – 3.35 (m, 2H), 2.36 – 1.91 (m, 1H), 0.23 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.9 (t, *J* = 285.4 Hz), 136.6, 135.8, 133.8, 133.2, 132.9, 129.3, 128.0, 127.84, 127.77, 127.7, 126.2, 126.0, 125.8, 125.6, 77.7 (t, *J* = 21.8 Hz), 72.7, 70.8, 24.4, -3.9, -4.6. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -89.1 (d, *J* = 50.2 Hz), -91.2 (d, *J* = 50.3 Hz). **ATR-FTIR (cm^{-1})**:1735, 1701, 1685, 1508, 1310, 1121, 954, 815. **EI-MS (m/z, relative intensity)**: 292 (4), 214 (30), 199 (28), 141 (100) 135 (68), 115 (19). HPLC analysis (AD-H, 1.0 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 80% ee: t_1 (major) = 16.3 min, t_2 (minor) = 10.4 min. $[\alpha]_D^{22}$ = +2.442 (c = 1.720, $CHCl_3$).





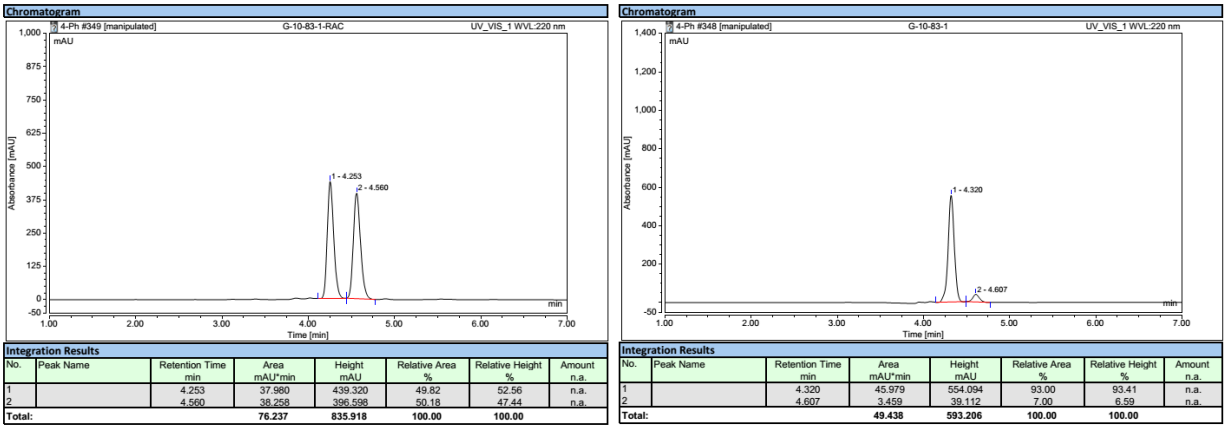
(*S*)-(1-(difluoromethylene)-7-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)dimethyl(phenyl)silane (3qa)



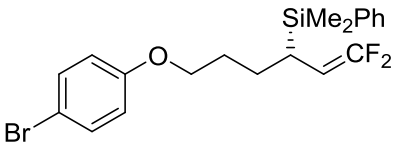
3qa

Following the general procedure, the reaction of **1q** (45.6 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 0 ^oC for 12 h after column chromatography on silica afford **3qa** (39.2 mg, 57%, 86% ee) as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.42 (m, 2H), 7.39 – 7.28 (m, 3H), 7.02 (t, *J* = 2.5 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.72 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.81 (s, 3H), 2.75 – 2.49 (m, 2H),

2.45 – 2.30 (m, 1H), 2.10 – 1.87 (m, 1H), 1.84 – 1.63 (m, 1H), 0.25 (d, *J* = 1.2 Hz, 3H), 0.15 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.6, 152.4 (dd, *J* = 294.1, 283.8 Hz), 137.5, 133.7, 130.9 (t, *J* = 4.6 Hz), 130.6 (d, *J* = 5.4 Hz), 129.1, 129.0, 127.6, 112.9, 112.4 (dd, *J* = 11.3, 0.7 Hz), 90.3 (dd, *J* = 24.1, 9.0 Hz), 55.3, 28.4, 24.1, 21.9, -3.5 (d, *J* = 1.8 Hz), -4.42. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.5 (d, *J* = 46.1 Hz), -91.2 (d, *J* = 46.1 Hz). **ATR-FTIR (cm^{-1})**:1700, 1653, 1496, 1247, 1111, 813, 777. **EI-MS (m/z, relative intensity)**: 344 (M^+, 2), 329 (5), 247 (11), 233 (19), 175 (12), 135 (100), 107 (11). HPLC analysis (OD-H, 2.0 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 86% ee: t_1 (major) = 4.3 min, t_2 (minor) = 4.6 min. $[\alpha]_D^{22}$ = +92.715 (c = 1.725, $CHCl_3$).



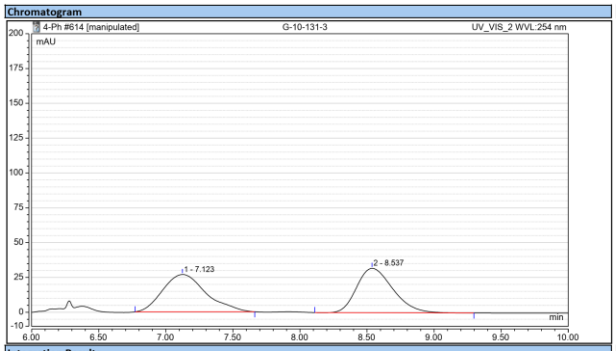
(*R*)-(6-(4-bromophenoxy)-1,1-difluorohex-1-en-3-yl)dimethyl(phenyl)silane (3ra)



3ra

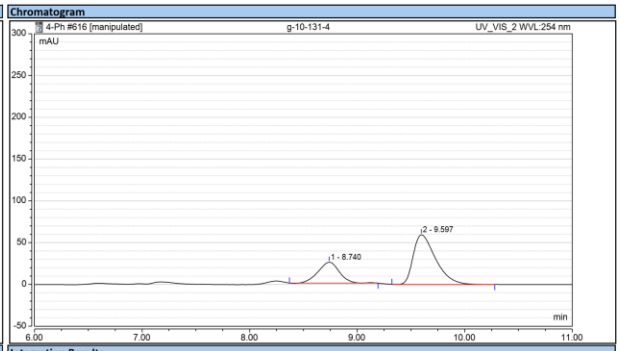
Following the general procedure, the reaction of **1r** (61.6 mg, 0.20 mmol, 1.0 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) at 0 ^oC for 12 h after column chromatography on silica afford **3ra** (80.6 mg, 95%, 42% ee) as a colorless oil: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 – 7.48 (m, 2H), 7.44 – 7.33 (m, 5H), 6.80 – 6.70 (m, 2H), 4.03 – 3.91 (m, 1H), 3.93 – 3.82 (m, 2H), 1.91 – 1.54 (m, 4H), 1.39 – 1.27 (m, 1H), 0.34 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.07, 156.11 (t, J = 285.5 Hz), 136.61 , 133.89 , 132.15 , 129.26 , 127.80 , 116.23 , 112.62 , 78.92 (t, J = 21.1 Hz), 67.46 , 28.75 , 25.70 , 21.93 , -4.55 , -5.38. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -88.9 (d, *J* = 51.1 Hz), -92.1 (d, *J* = 51.7 Hz). **ATR-FTIR (cm^{-1})**: 1728, 1499, 1285, 1120, 949, 819, 723, 711. **EI-MS (m/z, relative intensity)**: 308 (30), 306 (30), 293 (10), 291 (10), 191 (15), 135 (100), 107 (12). HPLC

analysis (OD-H, 0.5 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 42% ee: t_1 (major) = 9.6 min, t_2 (minor) = 8.7 min.



Integration Results

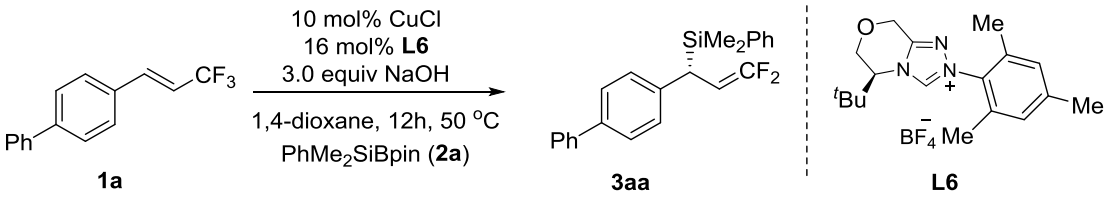
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.123	10.017	26.809	50.11	45.68	n.a.
2		8.537	9.973	31.873	49.89	54.32	n.a.
Total:			**19.990**	**58.682**	**100.00**	**100.00**	



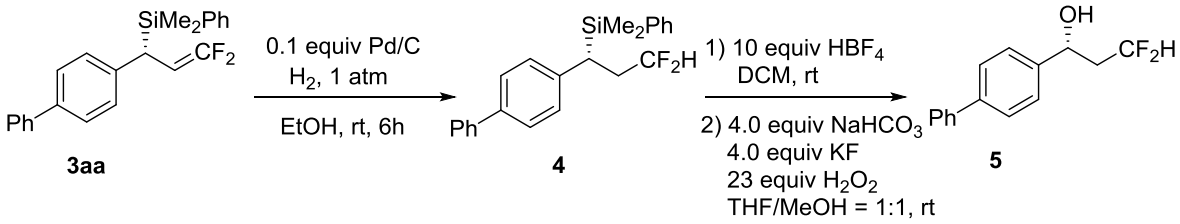
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.740	5.732	24.957	28.69	29.63	n.a.
2		9.597	14.250	59.279	71.31	70.37	n.a.
Total:			**19.982**	**84.236**	**100.00**	**100.00**	

4. Gram-sale Synthesis and Downstream Transformation

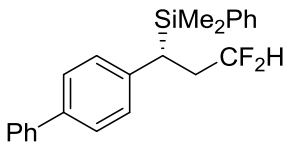


To a 200 mL Schlenk tube was added trifluoramethyl alkenes **1a** (1.24g, 5 mmol, 1.0 equiv), CuCl (49.5 mg, 0.5 mmol, 10 mol%), **L6** (309.8 mg, 0.8 mmol, 16 mol%), NaOH (600 mg, 15 mmol, 3.0 equiv), $PhMe_2SiBpin$ **2a** (3.93 g, 15 mmol, 3.0 equiv) and 1,4-Dioxane (50 mL) under Ar. The reaction mixture was stirred at 50 ^oC for 12 hours. The solution was then cooled to rt and the solvent was removed under vaccum directly. The crude products were purified by column chromatography on silica gel to afford the pure products **3aa** as a viscous liquid (91%, 1.66 g, 90% ee). HPLC analysis (OD-H, 0.5% IPA/hexanes, 1.0 mL/min, 254 nm) indicated 90% ee: t_1 (major) = 5.1 min, t_2 (minor) = 5.7 min.



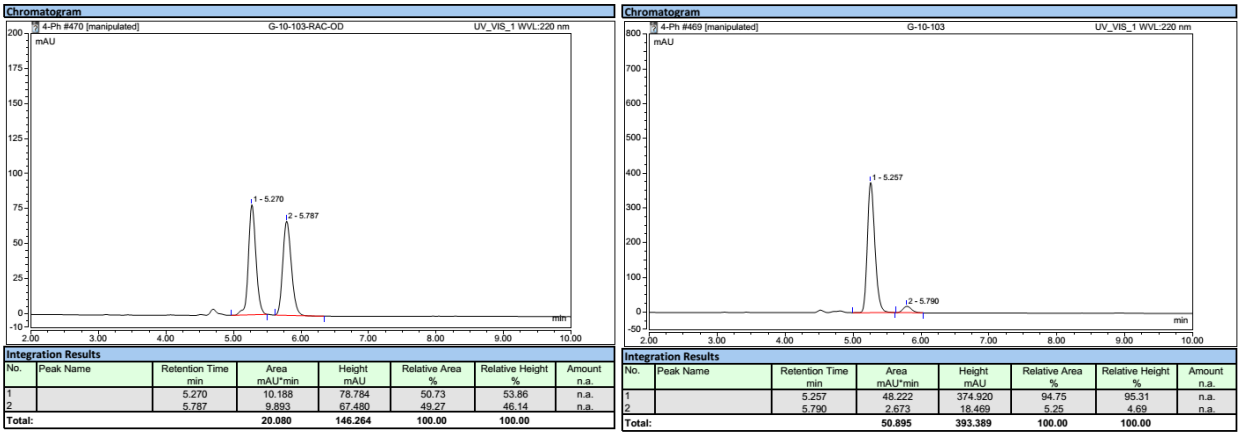
To the *gem*-difluoroallylsilanes **3aa** (90% ee, 72.8 mg, 0.2 mmol, 1.0 euqiv) in ethanol (5 mL), was added palladium on activated carbon (5%, 0.1 equiv, 42.4 mg). The reaction solution was purged with hydrogen balloon for 15 minutes and then went 6 hours under hydrogen balloon. Then, the reaction was filtered over a short path of Celite, concentrated in vacuum, and the crude mixture was purified by flash column chromatography to afford the final product **4** (70.3 mg, 96%, 90% ee) as a colorless liquid.

(*R*)-(1-([1,1'-biphenyl]-4-yl)-3,3-difluoropropyl)dimethyl(phenyl)silane (4)



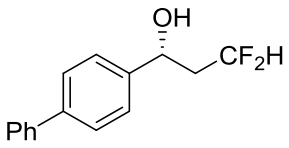
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.50 – 7.28 (m, 10H), 7.07 – 6.91 (m, 2H), 5.74 – 5.38 (m, 1H), 2.59 – 2.46 (m, 1H), 2.38 – 2.11 (m, 2H), 0.30 (s, 3H), 0.26 (s, 3H). **^{13}C NMR (101 MHz,**

$CDCl_3$) δ 140.7, 139.8, 138.1, 136.0, 134.1, 129.5, 128.7, 128.0, 127.8, 127.04, 126.99, 126.8, 116.9 (t, *J* = 240.0 Hz), 34.2 (dd, *J* = 22.4, 20.7 Hz), 30.0 (d, *J* = 7.1 Hz), -4.2, -5.5. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -115.0 (d, *J* = 278.4 Hz), -119.0 (d, *J* = 278.4 Hz). **ATR-FTIR (cm^{-1})**:1734, 1701, 1654, 1508, 772, 668. **EI-MS (m/z, relative intensity)**: 366 (M^+, 2), 310 (10), 207 (33), 136 (35), 135 (100), 128 (30), 91 (30), 73 (29). HPLC analysis (OD-H, 1.0 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 86% ee: t_1 (major) = 5.3 min, t_2 (minor) = –5.8 min. $[\alpha]_D^{22}$ = –5.942 (c = 0.46, $CHCl_3$).



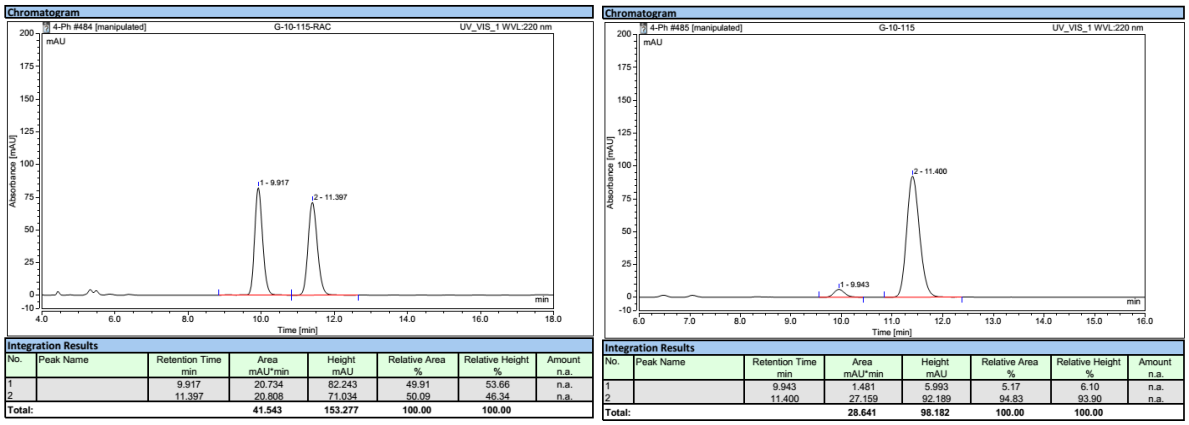
To a solution of **4** (90% ee, 73.2 mg, 0.2 mmol, 1.0 equiv) in CH_2Cl_2 (3 mL) was added $HBF_4{\cdot}OEt_2$ (2 mmol, 10 equiv) at rt. The mixture was allowed to stir at rt for 12 h. A saturated aqueous solution of sodium bicarbonate (5 mL) was added to quench the reaction. Layers were separated and the organic layer was washed with a saturated aqueous solution of sodium bicarbonate. The aqueous layer was extracted by diethyl ether (3 × 3 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated in vacuum. The yellow oil was dissolved in THF/MeOH (1/1) (3 mL). $NaHCO_3$ (67.2 mg, 0.8 mmol, 4.0 equiv), KF (46.5 mg, 0.8 mmol, 4.0 equiv) and H_2O_2 (521 mg, 4.6 mmol, 23 equiv) were added sequentially at rt. The resulting mixture was allowed to stir at rt for 12 h. The reaction was quenched by passing the mixture through a short plug of silica gel and eluting with CH_2Cl_2. The filtrate was concentrated in vacuo and the crude product was purified by silica gel chromatography (hexanes:EtOAc=5:1) to afford the desired diol **5** as a white solid (39.2 mg, 79% yield over two steps, ee = 90%).

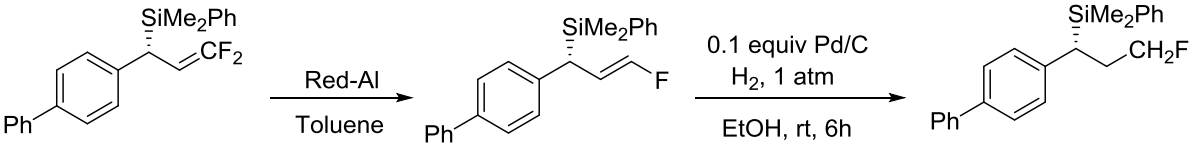
(*R*)-1-([1,1'-biphenyl]-4-yl)-3,3-difluoropropan-1-ol (5)[4]



5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.40 (m, 4H), 7.38 – 7.27 (m, 4H), 7.27 – 7.19 (m, 1H), 5.90 (tdd, *J* = 56.8, 6.3, 3.4 Hz, 1H), 4.85 (dd, *J* = 9.6, 3.7 Hz, 1H), 2.38 – 1.97 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.9, 141.2, 140.5, 128.8, 127.50, 127.47, 127.1, 126.1, 116.0 (t, *J* = 238.5 Hz), 69.2 (t, *J* = 4.4 Hz), 43.1 (t, *J* = 20.8 Hz). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -116.8 (d, *J* = 286.7 Hz), -117.7 (d, *J* = 286.7 Hz). **ATR-FTIR (cm^{-1})**:1734, 1701, 1653, 1420, 767, 458. **HRMS m/z (ESI):** calcd for $C_{15}H_{15}F_2O$ $(M + H)^+$ 249.1085, found 249.1088. HPLC analysis (OD-H, 10 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 90% ee: t_1 (major) = 11.4 min, t_2 (minor) = 9.9 min. $[\alpha]_D^{22}$ = +34.054 (c = 0.37, $CHCl_3$).

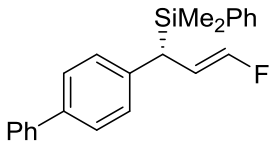




3aa **6** **7**

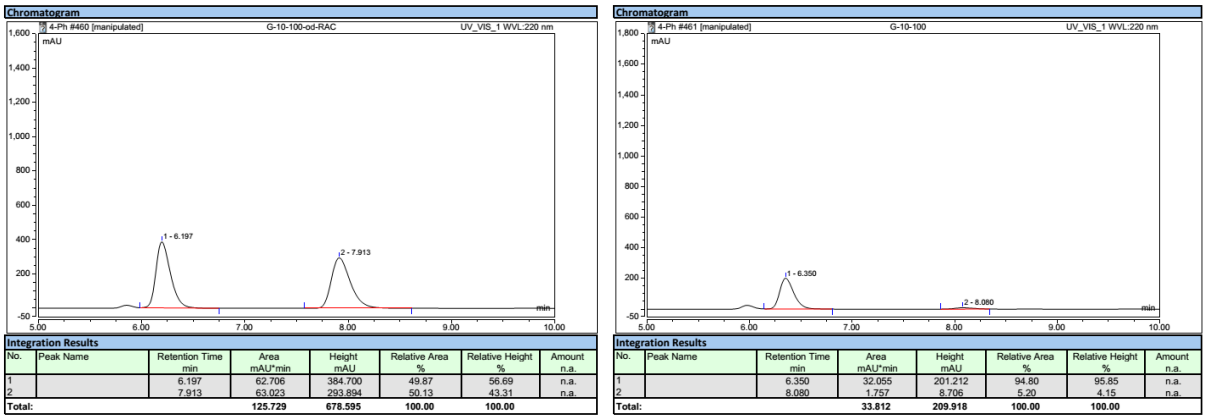
The 25 mL Schlenk tube was added **3aa** (90% ee, 72.8 mg, 1.0 equiv) and toluene (2 mL) under argon. The Red-Al (160 ul, 3.5 M in toluene, 0.56 mol, 2.8 equiv) was added at 0 ^{o}C and the reaction was stirred for 2 h at 0 ^{o}C. Then the Red-Al (160 ul, 3.5 M in toluene, 0.56 mol, 2.8 equiv) was added and the mixture was stirred at 80 ^{o}C for another 4 h. The solution was cooled to room temperature and the crude product was purified by flash column chromatography on silica gel (PE) to afford the corresponding product **6** as colorless liquid (49.1 mg, 71%, ee = 90%), *E*/*Z* = 10:1 (determined by ^{19}F NMR).

(*R*,*E*)-(1-([1,1'-biphenyl]-4-yl)-3-fluoroallyl)dimethyl(phenyl)silane (6)



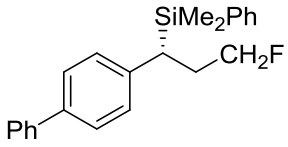
6

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.50 – 7.28 (m, 10H), 7.04 – 6.90 (m, 2H), 6.48 (dd, *J* = 85.8, 10.9 Hz, 1H), 5.85 – 5.60 (m, 1H), 2.99 (d, *J* = 11.0 Hz, 1H), 0.32 (s, 3H), 0.29 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.0 (d, *J* = 255.2 Hz), 140.9, 140.6 (d, *J* = 2.5 Hz), 137.9, 136.1, 134.3, 129.4, 128.7, 127.72, 127.68, 127.0, 126.91, 126.85, 111.1 (d, *J* = 10.9 Hz), 33.7 (d, *J* = 6.2 Hz), -4.4, -4.9. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -130.2. **ATR-FTIR (cm^{-1})**:1735, 1700, 1655, 1558, 1419, 1221, 1114, 773. **HRMS m/z (ESI):** calcd for $C_{23}H_{24}FSi$ $(M + H)^+$ 347.1626, found 347.1629. HPLC analysis (OD-H, 0.5 % IPA/hexanes, 1.0 mL/min, 254 nm) indicated 90% ee: t_1 (major) = 6.4 min, t_2 (minor) = 8.1 min. $[\alpha]_D^{22}$ = –40.678 (c = 0.295, $CHCl_3$).



To the **6** (90% ee, 69.2 mg, 0.2 mmol, 1.0 euqiv) in ethanol (5 mL), was added palladium on activated carbon (5%, 0.1 equiv, 42.4 mg). The reaction solution was purged with hydrogen balloon for 15 minutes and then went 6 hours under hydrogen balloon. Then, the reaction was filtered over a short path of Celite, concentrated in vacuo, and the crude mixture was purified by flash column chromatography to afford the final product **7** (64.7 mg, 93%, 89% ee) as a colorless oil.

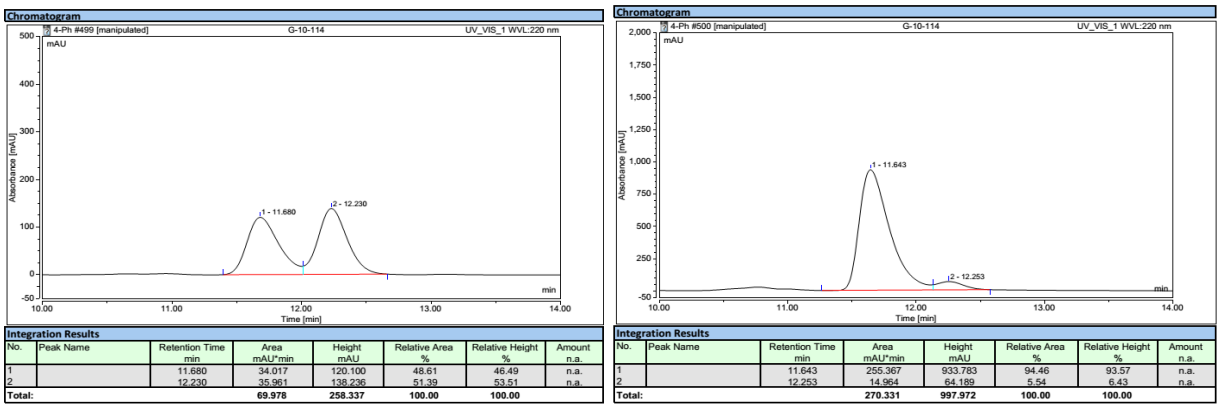
(*R*)-(1-([1,1'-biphenyl]-4-yl)-3-fluoropropyl)dimethyl(phenyl)silane (7)



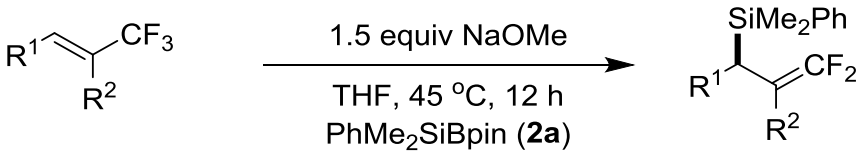
7

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.57 (m, 2H), 7.54 – 7.29 (m, 10H), 7.14 – 6.96 (m, 2H), 4.73 – 3.93 (m, 2H), 2.49 (dd, *J* = 12.5, 3.3 Hz, 1H), 2.38 – 1.84 (m, 2H), 0.32 (s, 3H), 0.28 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.0, 140.7, 137.7, 136.9, 134.2, 129.3, 128.8, 128.3, 127.8, 127.0, 126.9, 126.8, 83.0 (d, *J* = 165.7 Hz), 31.3 (d, *J* = 4.5 Hz), 30.2 (d, *J* = 19.9 Hz),

-3.9, -5.3. **ATR-FTIR (cm^{-1})**:1734, 1700, 1655, 1254, 1177, 1114, 918, 810, 766. **EI-MS (m/z, relative intensity)**: 348 (M^+, 1), 194 (100), 179 (25), 135 (95), 107 (12). HPLC analysis (OD-H, 1.0 % IPA/hexanes, 0.5 mL/min, 254 nm) indicated 89% ee: t_1 (major) = 11.6 min, t_2 (minor) = 12.3 min.



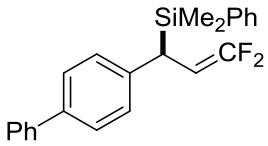
5. Mechanistic investigations



1 *rac*-**3**

To a 25 mL Schlenk tube was purged with argon for three times, and then added fluoroalkenes **1** (0.20 mmol), $PhMe_2SiBpin$ (3.0 equiv), NaOMe (3.0 equiv) and THF (1 mL). The formed mixture was stirred at 45 ℃ under Ar for 12 h monitored by TLC. The solution was then cooled to rt and the solvent was removed under vaccum directly. The crude products were purified by column chromatography on silica gel to afford the pure products.

(1-([1,1'-Biphenyl]-4-yl)-3,3-difluoroallyl)dimethyl(phenyl)silane (*rac*-3aa)



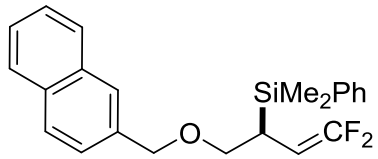
rac-**3aa**

Following the above procedure, the reaction of **1a** (49.6 mg, 0.2 mmol), $PhMe_2SiBpin$ (3.0 equiv, 0.6 mmol, 157.2 mg), NaOMe (3.0 equiv, 0.6 mmol, 32.4 mg) in THF (1 mL) at 60 °C under Ar for 12 h. The crude product was purified by column chromatography on silica gel to afford *rac*-**3aa** (23.3 mg, 32%) as a colorless liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 – 7.55 (m, 2H), 7.52 – 7.28 (m, 10H), 6.98 – 6.92 (m, 2H), 4.59 (ddd, *J* = 22.7,

11.8, 3.8 Hz, 1H), 3.22 (dd, *J* = 11.8, 1.9 Hz, 1H), 0.33 (s, 3H), 0.33 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.3 (t, *J* = 286.5 Hz), 140.8, 140.1, 137.9, 135.8, 134.2, 129.5, 128.7, 127.7, 127.5, 127.0, 126.8, 78.1 (t, *J* = 21.9 Hz), 31.0, -4.7, -4.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -89.7 (d, *J* = 47.1 Hz), -90.0 (d, *J* = 47.1 Hz). **ATR-FTIR (cm^{-1})**: 3068, 3027, 2584, 1745, 1603, 1494, 1427, 1250, 1213, 1113, 641, 545. **HRMS m/z (ESI)**: calcd for $C_{23}H_{23}F_2Si$ $(M + H)^+$ 365.1532, found 365.1528.

(4,4-Difluoro-1-(naphthalen-2-ylmethoxy)but-3-en-2-yl)dimethyl(phenyl)silane (*rac*-3pa)

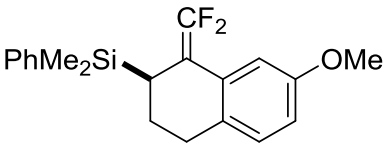
Following the above procedure, the reaction of **1p** (53.2 mg, 0.2 mmol), $PhMe_2SiBpin$ (3.0 equiv, 0.6 mmol, 157.2 mg), NaOMe (3.0 equiv, 0.6 mmol, 32.4 mg) in THF (1 mL) at 45 °C under Ar for 12 h. The crude product was purified by column chromatography on silica gel to afford ***rac*-3pa** (55.8 mg, 73%) as a colorless liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 – 7.77 (m, 3H), 7.71 (s, 1H), 7.53 – 7.43 (m, 4H), 7.43 – 7.27 (m, 4H), 4.57 (dd, *J* = 28.0, 12.2 Hz, 2H), 4.19 (ddd, *J* = 25.3, 11.3, 2.8 Hz, 1H), 3.59 – 3.46 (m, 2H), 2.38 – 2.01 (m, 1H), 0.33 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.9 (t, *J* = 285.4 Hz), 136.6, 135.8, 133.8, 133.2, 132.9, 129.3, 128.1, 127.9, 127.8, 127.7, 126.2, 126.0, 125.8, 125.6, 77.7 (t, *J* = 21.8 Hz), 72.7, 70.8, 24.4, -3.9, -4.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -89.12 (d, *J* = 50.3 Hz), -91.26 (d, *J* = 50.3 Hz). **ATR-FTIR (cm^{-1})**: 3446, 2854, 2596, 1737, 1645, 1507, 1338, 1249, 1097, 913, 743, 697. **HRMS m/z (ESI)**: calcd for $C_{23}H_{24}F_2NaOSi$ $(M + Na)^+$ 405.1457, found 405.1467.



***rac*-3pa**

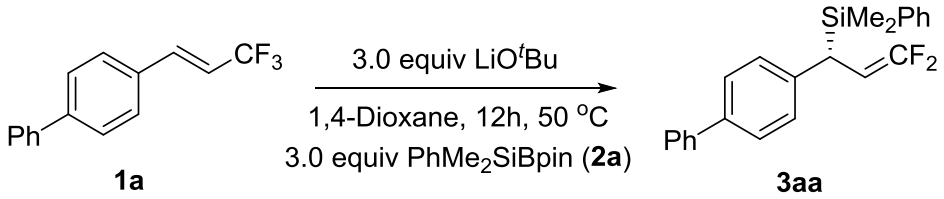
(1-(Difluoromethylene)-1,2,3,4-tetrahydronaphthalen-2-yl)dimethyl(phenyl)silane (*rac*-3qa)

Following the above procedure, the reaction of **1q** (45.6 mg, 0.2 mmol), $PhMe_2SiBpin$ (3.0 equiv, 0.6 mmol, 157.2 mg), NaOMe (3.0 equiv, 0.6 mmol, 32.4 mg) in THF (1 mL) at 45 °C under Ar for 12 h. The crude product was purified by column chromatography on silica gel to afford ***rac*-3qa** (67.4 mg, 98%) as a colorless liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 – 7.42 (m, 2H), 7.42 – 7.29 (m, 3H), 7.05 (t, *J* = 2.5 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.85 – 6.55 (m, 1H), 3.83 (s, 3H), 2.76 – 2.49 (m, 2H), 2.48 – 2.30 (m, 1H), 2.17 – 1.91 (m, 1H), 1.85 – 1.60 (m, 1H), 0.28 (d, *J* = 1.2 Hz, 3H),



***rac*-3qa**

0.18 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.6, 152.4 (dd, *J* = 294.1, 283.9 Hz), 137.4, 133.7, 130.9 (t, *J* = 4.6 Hz), 130.6 (d, *J* = 5.4 Hz), 129.1, 128.9, 127.6, 112.9, 112.38 (d, *J* = 10.9 Hz), 90.3 (dd, *J* = 24.1, 8.9 Hz), 55.3, 28.4, 24.1, 21.9, -3.52 (d, *J* = 1.7 Hz), -4.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -88.5 (d, *J* = 45.9 Hz), -91.2 (d, *J* = 46.0 Hz). **ATR-FTIR (cm^{-1})**:3069, 2954, 2836, 1708, 1496, 1427, 1246, 1111, 873. **HRMS m/z (ESI)**: calcd for $C_{20}H_{23}F_2OSi$ $(M + H)^+$ 345.1481, found 345.1487.



1a **3aa**

To a 25 mL Schlenk tube was purged with argon for three times, and then added (trifluoromethyl)alkenes **1a** (49.6 mg, 0.2 mmol, 1.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv), LiO^{t}Bu (48 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (1 mL). The formed mixture was stirred at 50 ℃ under Ar for 12 h monitored by TLC. The solution was then cooled to rt and the solvent was removed under vacuum directly. The conversion rate of **1a** (> 99%) and yield of **3aa** (18%) was determined by ^{19}F NMR and use octafluoronaphthalene as the internal standard (Figure S1).

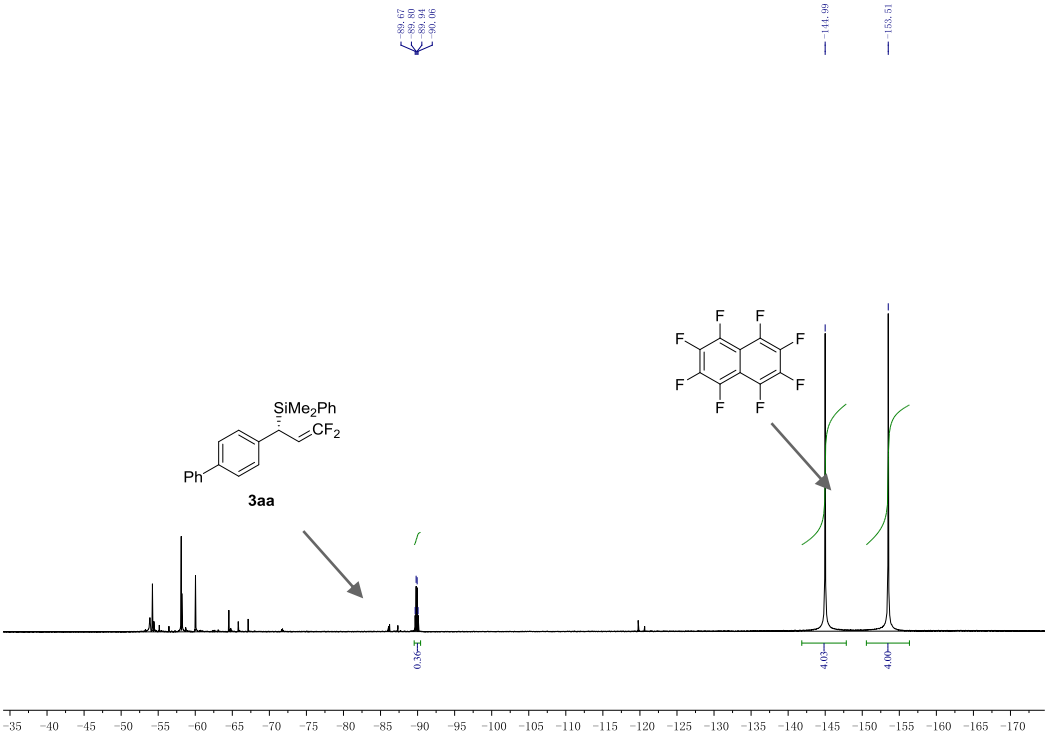
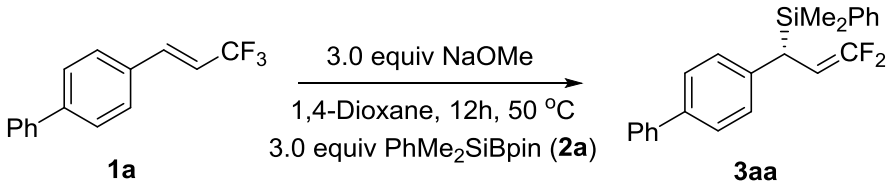


Figure S1



To a 25 mL Schlenk tube was purged with argon for three times, and then added (trifluoromethyl)alkenes **1a** (49.6 mg, 0.2 mmol, 1.0 equiv), $PhMe_2SiBpin$ **2a** (157.2 mg, 0.6 mmol, 3.0 equiv), NaOMe (32.4 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (1 mL). The formed mixture was stirred at 50 ℃ under Ar for 12 h monitored by TLC. The solution was then cooled to rt and the solvent was removed under vacuum directly. The conversion rate of **1a** (> 99%) and yield of **3aa** (26%) was determined by ^{19}F NMR and use octafluoronaphthalene as the internal standard (Figure S2).

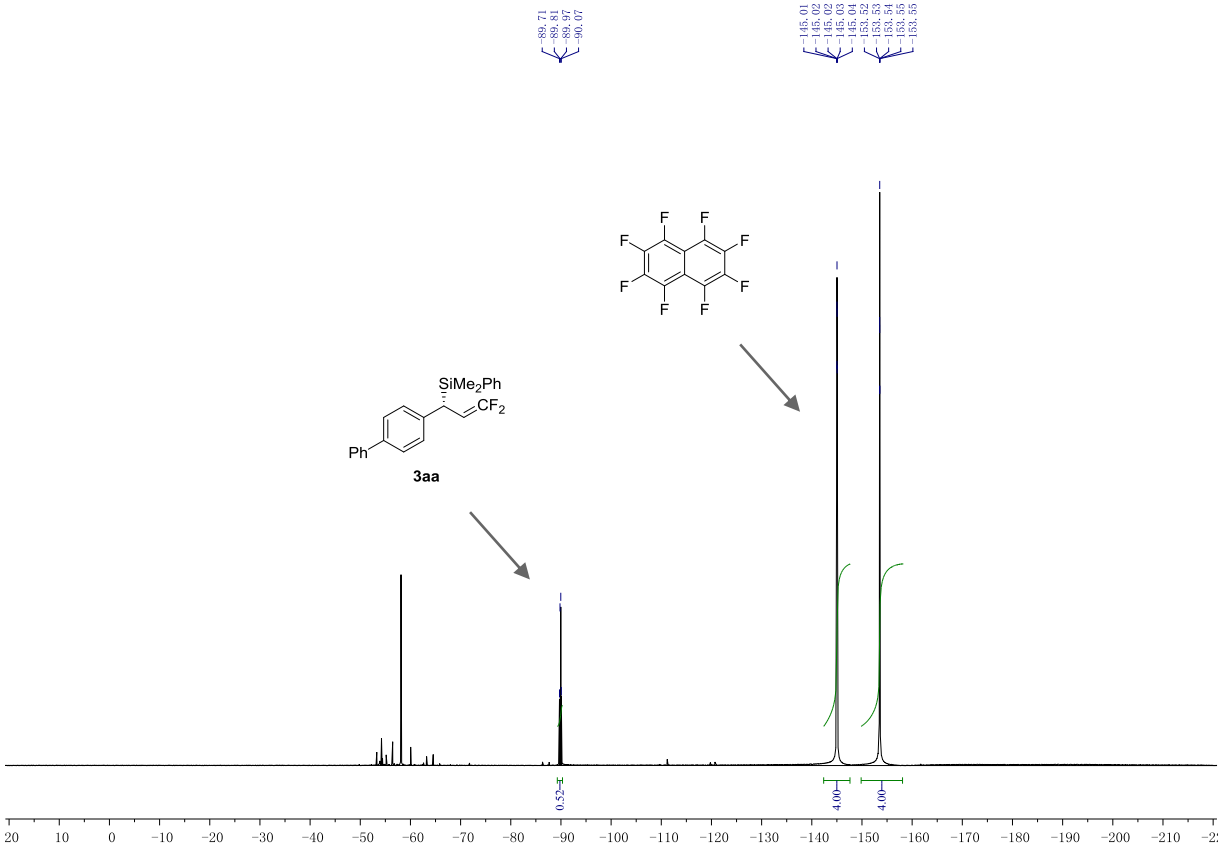
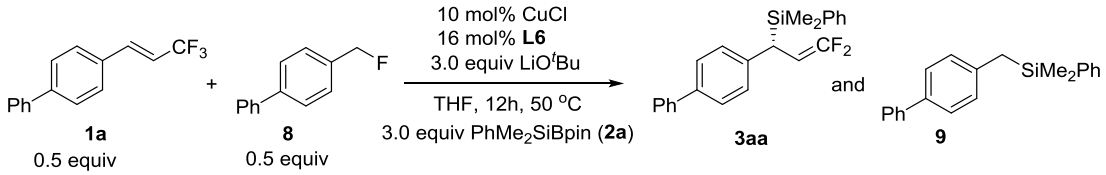
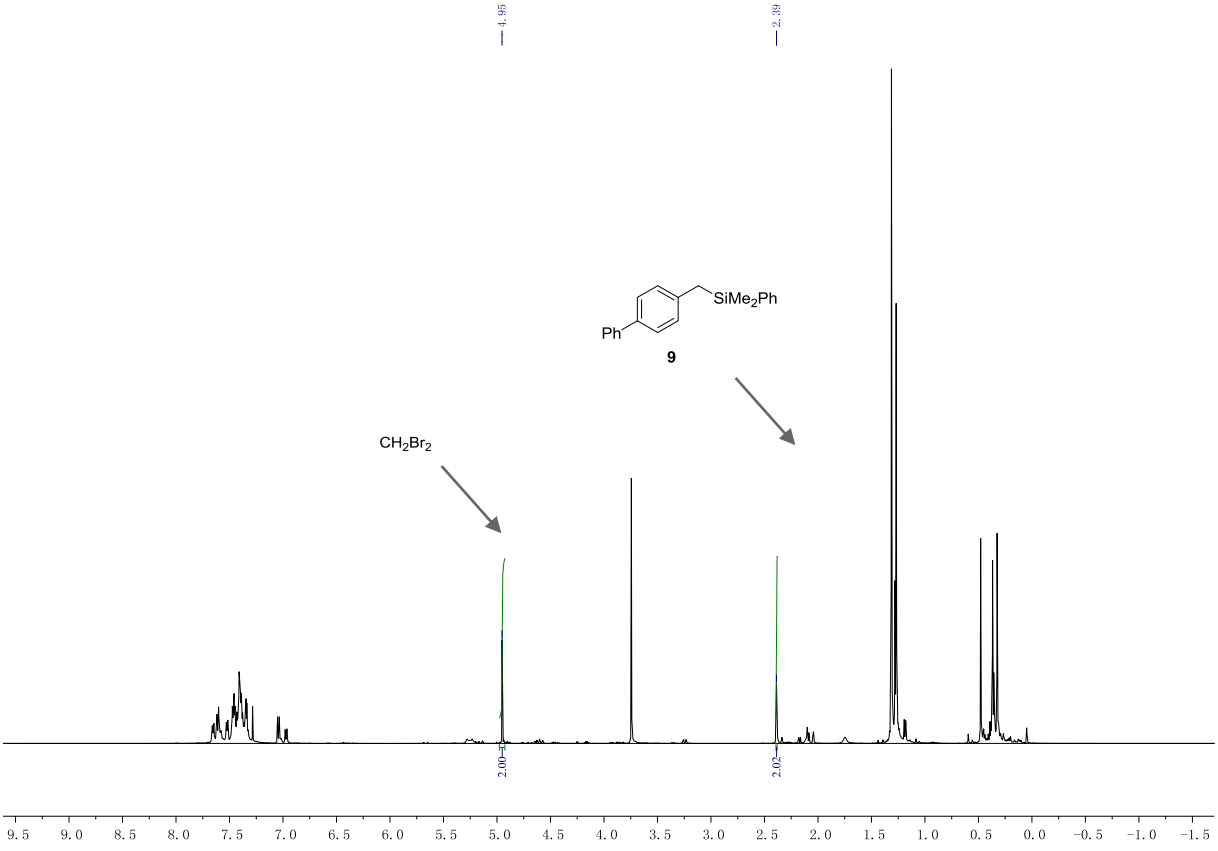


Figure S2



To a 25 mL Schlenk tube was added trifluoramethyl alkenes **1a** (24.8 mg, 0.1 mmol, 0.5 equiv), **12** (16 mg, 0.1 mmol, 0.5 equiv)[3], CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), LiO^{t}Bu (48 mg, 0.6 mmol, 3.0 equiv), PhMe2SiBpin **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) under Ar. The reaction mixture was stirred at 50 ^{o}C for 12 hours. The solution was then cooled to rt and the solvent was removed under vacuum directly. The conversion rate of **1a** (> 99%) and **8** (>99%), and the yield of **3aa** (47%) and **9**[5] (> 99%) was determined by ^{19}F NMR and ^{1}H NMR. We use octafluoronaphthalene (0.1 mmol) and CH_2Br_2 (0.1 mmol) as the internal standard. HPLC analysis indicated 90% ee of **3aa** (Figure S3).



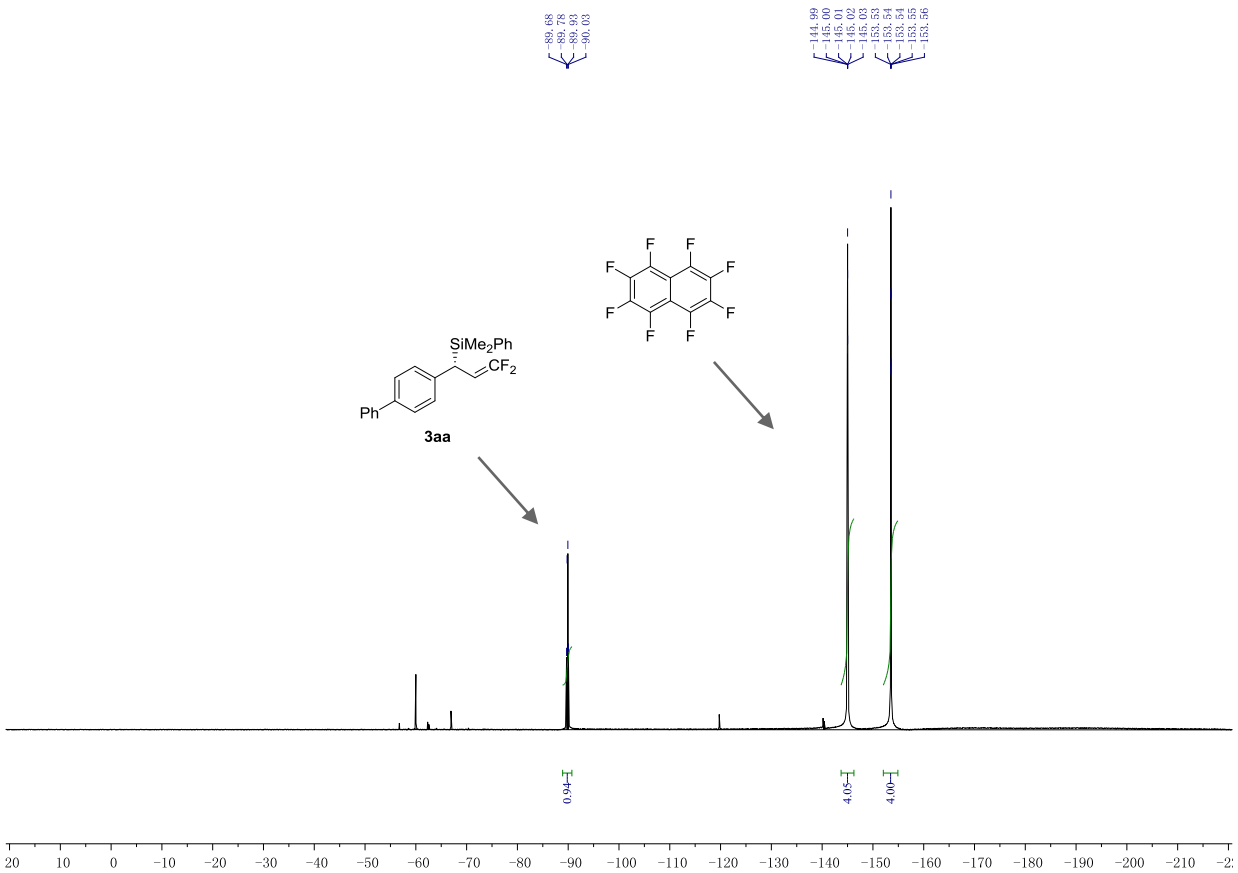
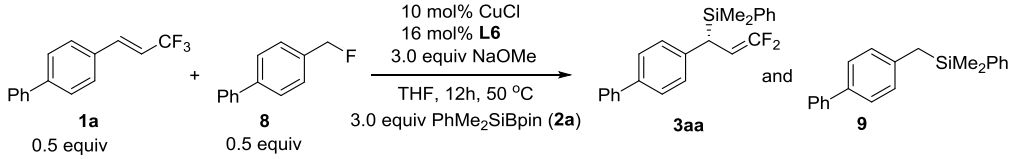


Figure S3



To a 25 mL Schlenk tube was added trifluoramethyl alkenes **1a** (24.8 mg, 0.1 mmol, 0.5 equiv), **8**(16 mg, 0.1 mmol, 0.5 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOMe (32.4 mg, 0.6 mmol, 3.0 equiv), PhMe2SiBpin **2a** (157.2 mg, 0.6 mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) under Ar. The reaction mixture was stirred at 50 ^{o}C for 12 hours. The solution was then cooled to rt and the solvent was removed under vacuum directly. The conversion rate of **1a** (> 99%) and **12** (94%), and the yield of **3aa** (64%) and **9** (73%) was determined by ^{19}F NMR and ^{1}H NMR. We use octafluoronaphthalene (0.1 mmol) and CH_2Br_2 (0.1 mmol) as the internal standard. HPLC analysis indicated 90% ee of **3aa** (Figure S4).

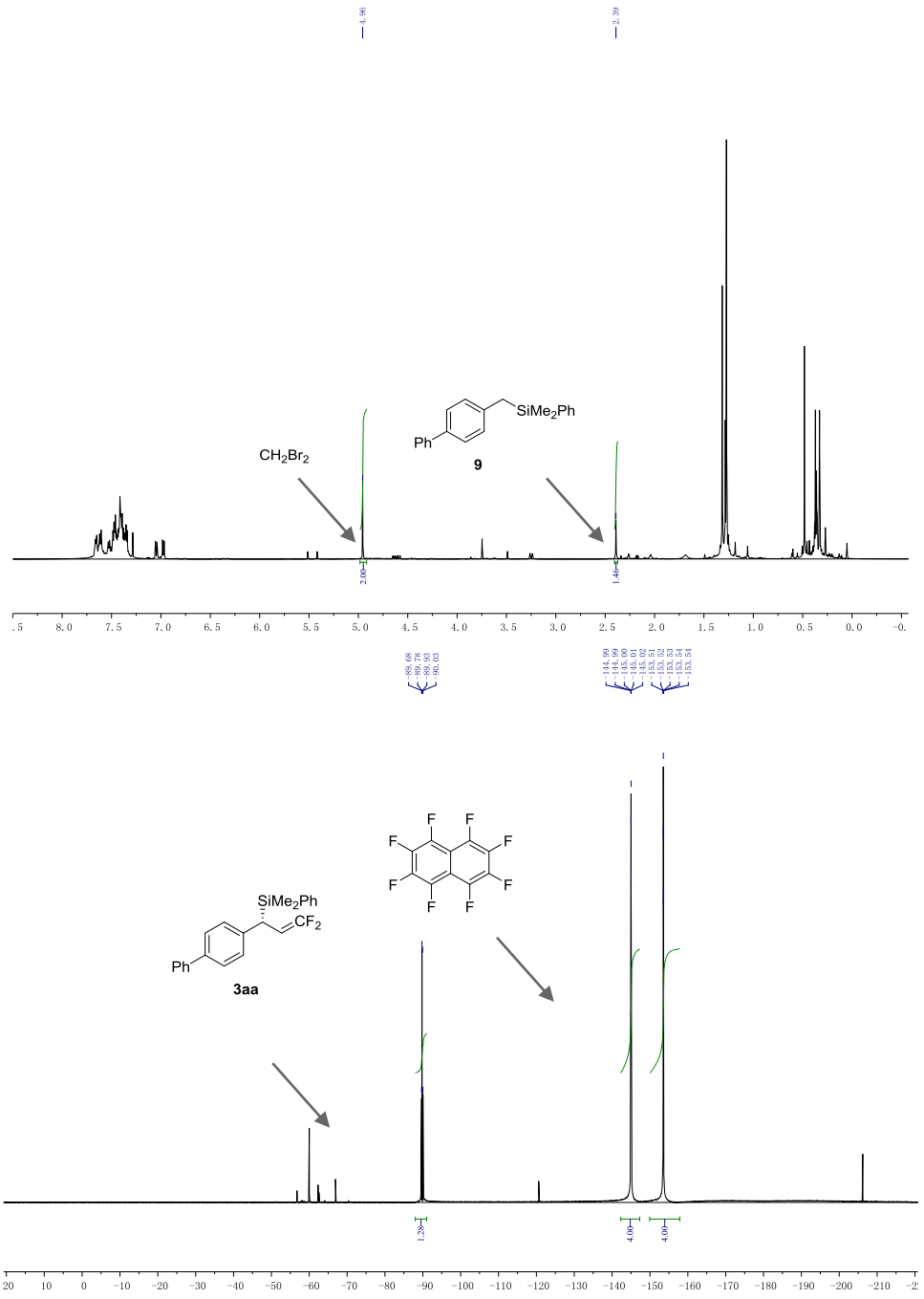
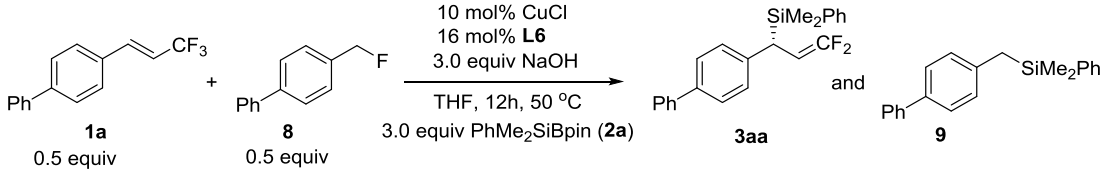


Figure S4



To a 25 mL Schlenk tube was added trifluoramethyl alkenes **1a** (24.8 mg, 0.1 mmol, 0.5 equiv), **8** (16 mg, 0.1 mmol, 0.5 equiv), CuCl (2.0 mg, 0.02 mmol, 10 mol%), **L6** (12.4 mg, 0.032 mmol, 16 mol%), NaOH (24 mg, 0.6 mmol, 3.0 equiv), PhMe2SiBpin **2a** (157.2 mg, 0.6

mmol, 3.0 equiv) and 1,4-Dioxane (2 mL) under Ar. The reaction mixture was stirred at 50 ^{o}C for 12 hours. The solution was then cooled to rt and the solvent was removed under vacuum directly. The conversion rate of **1a** (79%) and **8** (11%), and the yield of **3aa** (75%) and **9** (0%) was determined by ^{19}F NMR and ^{1}H NMR. We use octafluoronaphthalene (0.1 mmol) and CH_2Br_2 (0.1 mmol) as the internal standard. HPLC analysis indicated 90% ee of **3aa** (Figure S5).

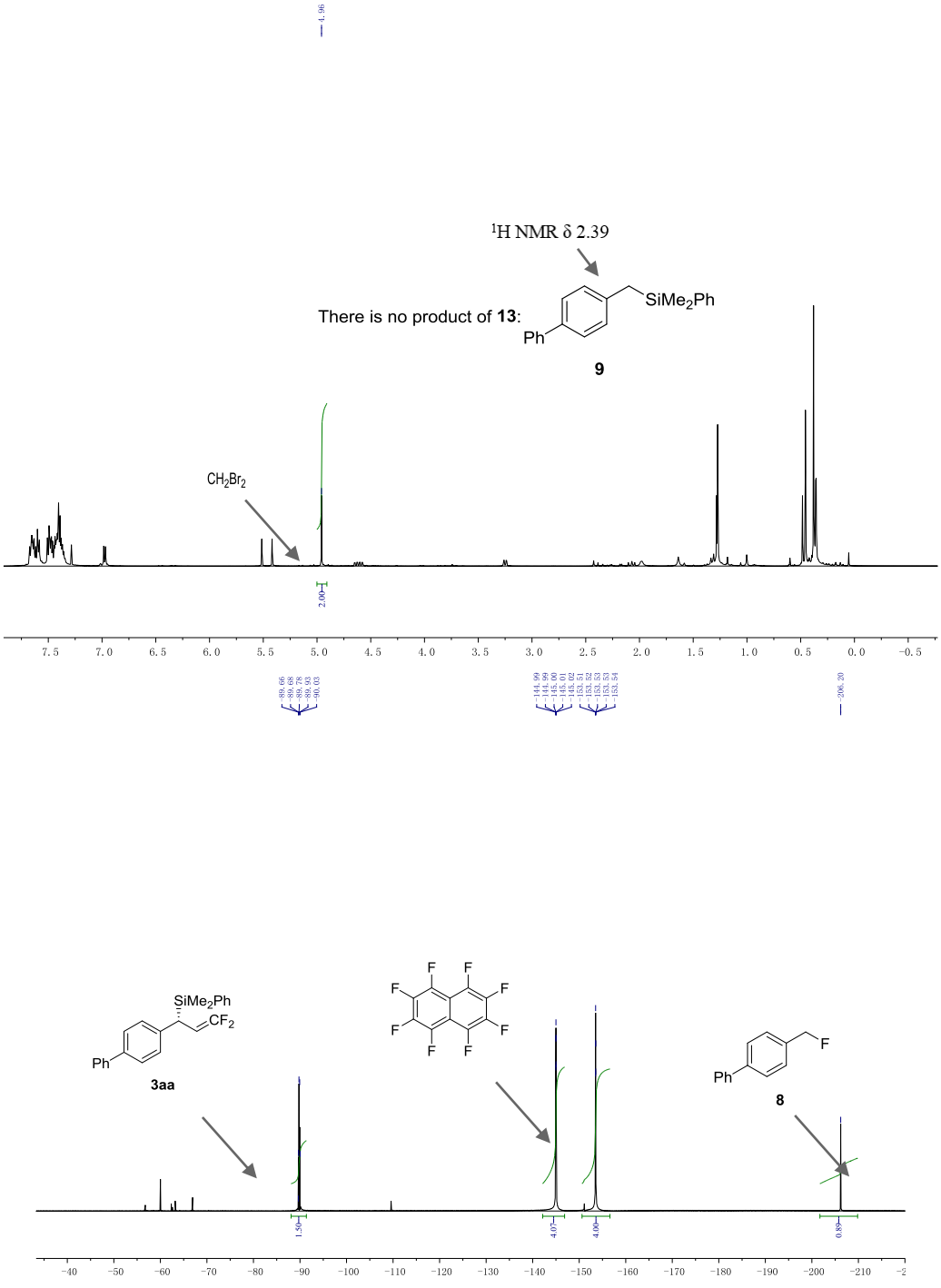


Figure S5

6. Crystallographic Data

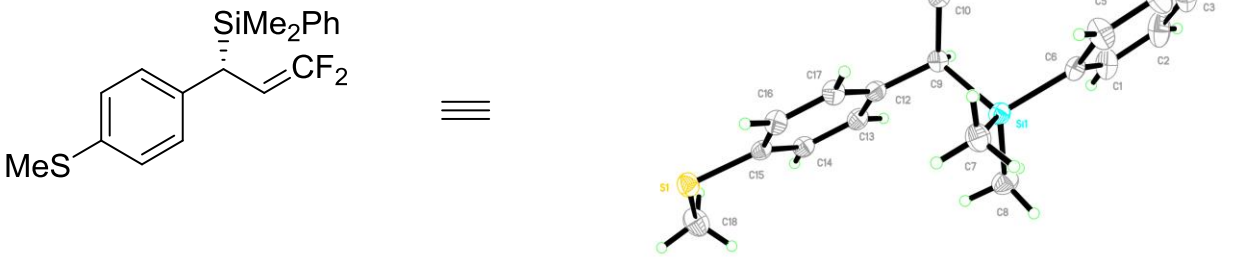


Table 1. Crystal data and structure refinement for 1_b.

Identification code	1_b	
Empirical formula	C18 H20 F2 S Si	
Formula weight	334.49	
Temperature	193(2) K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 14.4514(9) Å	α= 90 °.
	b = 8.0034(5) Å	β= 90.633(2) °.
	c = 15.2488(10) Å	γ = 90 °.
Volume	1763.57(19) $Å^3$	
Z	4	
Density (calculated)	1.260 Mg/m^3	
Absorption coefficient	1.569 mm^{-1}	
F(000)	704	
Crystal size	0.190 x 0.180 x 0.110 mm^3	
Theta range for data collection	2.521 to 52.993 °.	
Index ranges	-17<=h<=17, -9<=k<=6, -17<=l<=18	
Reflections collected	8375	
Independent reflections	4420 [R(int) = 0.0691]	

Completeness to theta = 52.993 °	95.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4420 / 1 / 403
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.1099
R indices (all data)	R1 = 0.0411, wR2 = 0.1108
Absolute structure parameter	0.034(18)
Extinction coefficient	n/a
Largest diff. peak and hole	0.334 and -0.176 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1_b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7169(2)	4317(5)	5321(2)	51(1)
C(2)	6634(3)	4096(6)	4569(2)	63(1)
C(3)	5798(3)	4858(6)	4478(2)	61(1)
C(4)	5486(2)	5862(6)	5139(2)	66(1)
C(5)	6022(2)	6081(6)	5899(2)	56(1)
C(6)	6875(2)	5319(4)	6005(2)	37(1)
C(7)	7225(2)	7425(5)	7635(2)	50(1)
C(8)	8838(2)	5521(6)	6791(2)	54(1)
C(9)	7343(2)	3569(5)	7733(2)	39(1)
C(10)	6322(2)	3284(5)	7795(2)	47(1)
C(11)	5879(2)	2228(7)	7298(2)	63(1)
C(12)	7844(2)	3651(4)	8614(2)	37(1)
C(13)	8677(2)	2804(4)	8733(2)	39(1)
C(14)	9162(2)	2861(4)	9523(2)	38(1)
C(15)	8822(2)	3795(4)	10219(2)	34(1)
C(16)	7990(2)	4645(4)	10105(2)	41(1)
C(17)	7513(2)	4565(4)	9319(2)	40(1)
C(18)	10489(2)	3071(6)	11093(2)	62(1)
C(19)	3749(2)	7395(5)	7991(2)	49(1)
C(20)	2975(2)	6826(4)	7662(2)	38(1)
C(21)	2894(2)	5208(4)	7174(2)	34(1)

C(22)	2329(2)	5320(4)	6333(2)	34(1)
C(23)	2607(2)	4425(4)	5592(2)	40(1)
C(24)	2092(2)	4464(4)	4823(2)	42(1)
C(25)	1283(2)	5384(4)	4759(2)	39(1)
C(26)	989(2)	6272(4)	5488(2)	39(1)
C(27)	1512(2)	6224(4)	6260(2)	38(1)
C(28)	-407(2)	6247(7)	3972(3)	73(1)
C(29)	3887(2)	2797(5)	9160(2)	40(1)
C(30)	4397(2)	3018(5)	9929(2)	46(1)
C(31)	4103(2)	4125(5)	10558(2)	44(1)
C(32)	3303(2)	4999(5)	10416(2)	50(1)
C(33)	2791(2)	4779(5)	9650(2)	45(1)
C(34)	3076(2)	3690(4)	9006(2)	33(1)
C(35)	2591(2)	1489(4)	7390(2)	40(1)
C(36)	1167(2)	3938(5)	8141(2)	47(1)
F(1)	6241(2)	1255(4)	6700(2)	80(1)
F(2)	4966(1)	2018(5)	7292(1)	98(1)
F(3)	4571(1)	6690(4)	7901(2)	88(1)
F(4)	3841(1)	8739(3)	8484(1)	68(1)
S(1)	9371(1)	3954(1)	11261(1)	45(1)
S(2)	695(1)	5377(1)	3735(1)	57(1)
Si(1)	7575(1)	5512(1)	7039(1)	36(1)
Si(2)	2416(1)	3540(1)	7936(1)	31(1)

Table 3. Bond lengths [Å] and angles [°] for 1_b.

C(1)-C(6)	1.386(4)	C(5)-H(5)	0.9500	C(9)-C(10)	1.497(4)
C(1)-C(2)	1.387(5)	C(6)-Si(1)	1.871(3)	C(9)-C(12)	1.520(4)
C(1)-H(1)	0.9500	C(7)-Si(1)	1.853(4)	C(9)-Si(1)	1.912(3)
C(2)-C(3)	1.359(5)	C(7)-H(7A)	0.9800	C(9)-H(9)	1.0000
C(2)-H(2)	0.9500	C(7)-H(7B)	0.9800	C(10)-C(11)	1.300(5)
C(3)-C(4)	1.368(6)	C(7)-H(7C)	0.9800	C(10)-H(10)	0.9500
C(3)-H(3)	0.9500	C(8)-Si(1)	1.868(3)	C(11)-F(1)	1.311(5)
C(4)-C(5)	1.397(4)	C(8)-H(8A)	0.9800	C(11)-F(2)	1.329(3)
C(4)-H(4)	0.9500	C(8)-H(8B)	0.9800	C(12)-C(17)	1.389(4)
C(5)-C(6)	1.384(4)	C(8)-H(8C)	0.9800	C(12)-C(13)	1.393(4)

C(13)-C(14)	1.388(4)	C(29)-C(34)	1.390(4)	C(5)-C(6)-C(1)	116.6(3)
C(13)-H(13)	0.9500	C(29)-C(30)	1.390(4)	C(5)-C(6)-Si(1)	122.3(2)
C(14)-C(15)	1.392(4)	C(29)-H(29)	0.9500	C(1)-C(6)-Si(1)	121.0(2)
C(14)-H(14)	0.9500	C(30)-C(31)	1.376(5)	Si(1)-C(7)-H(7A)	109.5
C(15)-C(16)	1.391(4)	C(30)-H(30)	0.9500	Si(1)-C(7)-H(7B)	109.5
C(15)-S(1)	1.772(3)	C(31)-C(32)	1.368(5)	H(7A)-C(7)-H(7B)	109.5
C(16)-C(17)	1.378(4)	C(31)-H(31)	0.9500	Si(1)-C(7)-H(7C)	109.5
C(16)-H(16)	0.9500	C(32)-C(33)	1.386(4)	H(7A)-C(7)-H(7C)	109.5
C(17)-H(17)	0.9500	C(32)-H(32)	0.9500	H(7B)-C(7)-H(7C)	109.5
C(18)-S(1)	1.785(3)	C(33)-C(34)	1.380(4)	Si(1)-C(8)-H(8A)	109.5
C(18)-H(18A)	0.9800	C(33)-H(33)	0.9500	Si(1)-C(8)-H(8B)	109.5
C(18)-H(18B)	0.9800	C(34)-Si(2)	1.886(3)	H(8A)-C(8)-H(8B)	109.5
C(18)-H(18C)	0.9800	C(35)-Si(2)	1.860(3)	Si(1)-C(8)-H(8C)	109.5
C(19)-C(20)	1.303(4)	C(35)-H(35A)	0.9800	H(8A)-C(8)-H(8C)	109.5
C(19)-F(4)	1.319(4)	C(35)-H(35B)	0.9800	H(8B)-C(8)-H(8C)	109.5
C(19)-F(3)	1.323(4)	C(35)-H(35C)	0.9800	C(10)-C(9)-C(12)	114.2(2)
C(20)-C(21)	1.499(4)	C(36)-Si(2)	1.863(3)	C(10)-C(9)-Si(1)	109.7(2)
C(20)-H(20)	0.9500	C(36)-H(36A)	0.9800	C(12)-C(9)-Si(1)	111.7(2)
C(21)-C(22)	1.515(3)	C(36)-H(36B)	0.9800	C(10)-C(9)-H(9)	106.9
C(21)-Si(2)	1.905(3)	C(36)-H(36C)	0.9800	C(12)-C(9)-H(9)	106.9
C(21)-H(21)	1.0000			Si(1)-C(9)-H(9)	106.9
C(22)-C(27)	1.389(4)	C(6)-C(1)-C(2)	121.5(3)	C(11)-C(10)-C(9)	122.8(3)
C(22)-C(23)	1.399(4)	C(6)-C(1)-H(1)	119.2	C(11)-C(10)-H(10)	118.6
C(23)-C(24)	1.383(4)	C(2)-C(1)-H(1)	119.2	C(9)-C(10)-H(10)	118.6
C(23)-H(23)	0.9500	C(3)-C(2)-C(1)	120.9(3)	C(10)-C(11)-F(1)	126.4(3)
C(24)-C(25)	1.385(4)	C(3)-C(2)-H(2)	119.6	C(10)-C(11)-F(2)	124.6(4)
C(24)-H(24)	0.9500	C(1)-C(2)-H(2)	119.6	F(1)-C(11)-F(2)	108.9(3)
C(25)-C(26)	1.390(4)	C(2)-C(3)-C(4)	119.2(3)	C(17)-C(12)-C(13)	117.4(2)
C(25)-S(2)	1.768(3)	C(2)-C(3)-H(3)	120.4	C(17)-C(12)-C(9)	122.8(2)
C(26)-C(27)	1.392(4)	C(4)-C(3)-H(3)	120.4	C(13)-C(12)-C(9)	119.8(3)
C(26)-H(26)	0.9500	C(3)-C(4)-C(5)	120.1(3)	C(14)-C(13)-C(12)	121.7(3)
C(27)-H(27)	0.9500	C(3)-C(4)-H(4)	120.0	C(14)-C(13)-H(13)	119.2
C(28)-S(2)	1.779(4)	C(5)-C(4)-H(4)	120.0	C(12)-C(13)-H(13)	119.2
C(28)-H(28A)	0.9800	C(6)-C(5)-C(4)	121.7(3)	C(13)-C(14)-C(15)	120.0(2)
C(28)-H(28B)	0.9800	C(6)-C(5)-H(5)	119.1	C(13)-C(14)-H(14)	120.0
C(28)-H(28C)	0.9800	C(4)-C(5)-H(5)	119.1	C(15)-C(14)-H(14)	120.0

C(16)-C(15)-C(14)	118.6(2)	C(23)-C(22)-C(21)	119.7(2)	C(32)-C(31)-H(31)	120.5
C(16)-C(15)-S(1)	117.1(2)	C(24)-C(23)-C(22)	121.1(3)	C(30)-C(31)-H(31)	120.5
C(14)-C(15)-S(1)	124.3(2)	C(24)-C(23)-H(23)	119.4	C(31)-C(32)-C(33)	120.8(3)
C(17)-C(16)-C(15)	120.7(3)	C(22)-C(23)-H(23)	119.4	C(31)-C(32)-H(32)	119.6
C(17)-C(16)-H(16)	119.7	C(23)-C(24)-C(25)	121.2(3)	C(33)-C(32)-H(32)	119.6
C(15)-C(16)-H(16)	119.7	C(23)-C(24)-H(24)	119.4	C(34)-C(33)-C(32)	121.3(3)
C(16)-C(17)-C(12)	121.6(3)	C(25)-C(24)-H(24)	119.4	C(34)-C(33)-H(33)	119.4
C(16)-C(17)-H(17)	119.2	C(24)-C(25)-C(26)	118.7(2)	C(32)-C(33)-H(33)	119.4
C(12)-C(17)-H(17)	119.2	C(24)-C(25)-S(2)	117.2(2)	C(33)-C(34)-C(29)	117.6(2)
S(1)-C(18)-H(18A)	109.5	C(26)-C(25)-S(2)	124.0(2)	C(33)-C(34)-Si(2)	120.3(2)
S(1)-C(18)-H(18B)	109.5	C(25)-C(26)-C(27)	119.6(3)	C(29)-C(34)-Si(2)	122.1(2)
H(18A)-C(18)-H(18B)	109.5	C(25)-C(26)-H(26)	120.2	Si(2)-C(35)-H(35A)	109.5
S(1)-C(18)-H(18C)	109.5	C(27)-C(26)-H(26)	120.2	Si(2)-C(35)-H(35B)	109.5
H(18A)-C(18)-H(18C)	109.5	C(22)-C(27)-C(26)	122.4(3)	H(35A)-C(35)-H(35B)	109.5
H(18B)-C(18)-H(18C)	109.5	C(22)-C(27)-H(27)	118.8	Si(2)-C(35)-H(35C)	109.5
C(20)-C(19)-F(4)	125.8(3)	C(26)-C(27)-H(27)	118.8	H(35A)-C(35)-H(35C)	109.5
C(20)-C(19)-F(3)	125.4(3)	S(2)-C(28)-H(28A)	109.5	H(35B)-C(35)-H(35C)	109.5
F(4)-C(19)-F(3)	108.8(2)	S(2)-C(28)-H(28B)	109.5	Si(2)-C(36)-H(36A)	109.5
C(19)-C(20)-C(21)	123.7(3)	H(28A)-C(28)-H(28B)	109.5	Si(2)-C(36)-H(36B)	109.5
C(19)-C(20)-H(20)	118.2	S(2)-C(28)-H(28C)	109.5	H(36A)-C(36)-H(36B)	109.5
C(21)-C(20)-H(20)	118.2	H(28A)-C(28)-H(28C)	109.5	Si(2)-C(36)-H(36C)	109.5
C(20)-C(21)-C(22)	114.1(2)	H(28B)-C(28)-H(28C)	109.5	H(36A)-C(36)-H(36C)	109.5
C(20)-C(21)-Si(2)	109.20(18)	C(34)-C(29)-C(30)	121.0(3)	H(36B)-C(36)-H(36C)	109.5
C(22)-C(21)-Si(2)	111.22(19)	C(34)-C(29)-H(29)	119.5	C(15)-S(1)-C(18)	103.87(14)
C(20)-C(21)-H(21)	107.4	C(30)-C(29)-H(29)	119.5	C(25)-S(2)-C(28)	103.99(15)
C(22)-C(21)-H(21)	107.4	C(31)-C(30)-C(29)	120.4(3)	C(7)-Si(1)-C(8)	111.60(18)
Si(2)-C(21)-H(21)	107.4	C(31)-C(30)-H(30)	119.8	C(7)-Si(1)-C(6)	109.47(14)
C(27)-C(22)-C(23)	116.9(2)	C(29)-C(30)-H(30)	119.8	C(8)-Si(1)-C(6)	110.46(14)
C(27)-C(22)-C(21)	123.3(2)	C(32)-C(31)-C(30)	119.0(3)	C(7)-Si(1)-C(9)	110.53(14)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1_b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	69(2)	43(2)	41(2)	-1(2)	3(1)	17(2)
C(2)	103(3)	48(2)	39(2)	-6(2)	-1(2)	20(2)
C(3)	91(2)	51(2)	41(2)	3(2)	-14(2)	2(2)
C(4)	63(2)	71(3)	64(2)	-8(2)	-19(2)	19(2)
C(5)	52(2)	67(3)	49(2)	-13(2)	-3(1)	18(2)
C(6)	44(1)	33(2)	34(1)	3(1)	6(1)	4(1)
C(7)	55(2)	50(2)	44(2)	-6(2)	0(1)	3(2)
C(8)	40(1)	58(2)	63(2)	8(2)	11(1)	2(2)
C(9)	40(1)	41(2)	37(1)	0(1)	0(1)	-1(1)
C(10)	41(1)	62(2)	37(1)	1(2)	3(1)	-8(2)
C(11)	55(2)	95(3)	38(2)	3(2)	-1(1)	-25(2)
C(12)	35(1)	36(2)	39(1)	5(1)	2(1)	-1(1)
C(13)	38(1)	38(2)	41(1)	2(1)	7(1)	3(1)
C(14)	34(1)	38(2)	43(1)	3(1)	4(1)	4(1)
C(15)	36(1)	28(2)	39(1)	6(1)	3(1)	-1(1)
C(16)	41(1)	41(2)	41(1)	0(1)	4(1)	7(1)
C(17)	37(1)	42(2)	42(1)	1(2)	2(1)	10(1)
C(18)	49(2)	71(3)	65(2)	1(2)	-16(1)	14(2)
C(19)	48(2)	40(2)	59(2)	2(2)	-12(1)	-11(2)
C(20)	45(1)	27(2)	43(2)	3(1)	-7(1)	3(1)
C(21)	33(1)	30(2)	39(1)	1(1)	-3(1)	-1(1)
C(22)	36(1)	32(2)	34(1)	6(1)	0(1)	-4(1)
C(23)	42(1)	37(2)	41(1)	1(1)	-1(1)	5(1)
C(24)	54(2)	39(2)	33(1)	-2(1)	-1(1)	4(1)
C(25)	47(1)	32(2)	36(1)	5(1)	-3(1)	-4(1)
C(26)	39(1)	37(2)	41(1)	7(1)	0(1)	3(1)
C(27)	41(1)	37(2)	37(1)	-3(1)	1(1)	2(1)
C(28)	61(2)	89(3)	70(2)	15(3)	-21(2)	9(2)
C(29)	42(1)	38(2)	40(1)	-7(1)	-1(1)	5(1)
C(30)	44(1)	49(2)	46(2)	-1(2)	-8(1)	7(1)
C(31)	49(2)	49(2)	33(1)	-3(2)	-6(1)	-2(2)
C(32)	68(2)	46(2)	37(2)	-13(2)	0(1)	9(2)
C(33)	50(2)	43(2)	40(1)	-4(2)	-1(1)	16(2)

C(34)	36(1)	29(2)	34(1)	2(1)	2(1)	0(1)
C(35)	45(1)	34(2)	42(2)	-5(1)	-6(1)	-2(1)
C(36)	36(1)	51(2)	54(2)	4(2)	1(1)	2(2)
F(1)	76(1)	90(2)	75(1)	-23(2)	-2(1)	-19(1)
F(2)	58(1)	173(3)	63(1)	-19(2)	4(1)	-51(2)
F(3)	48(1)	92(2)	124(2)	-45(2)	-11(1)	-1(1)
F(4)	77(1)	45(1)	80(1)	-12(1)	-31(1)	-6(1)
S(1)	46(1)	47(1)	42(1)	3(1)	-6(1)	2(1)
S(2)	70(1)	60(1)	41(1)	2(1)	-17(1)	9(1)
Si(1)	34(1)	38(1)	36(1)	1(1)	4(1)	3(1)
Si(2)	30(1)	28(1)	36(1)	1(1)	-2(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for 1_b.

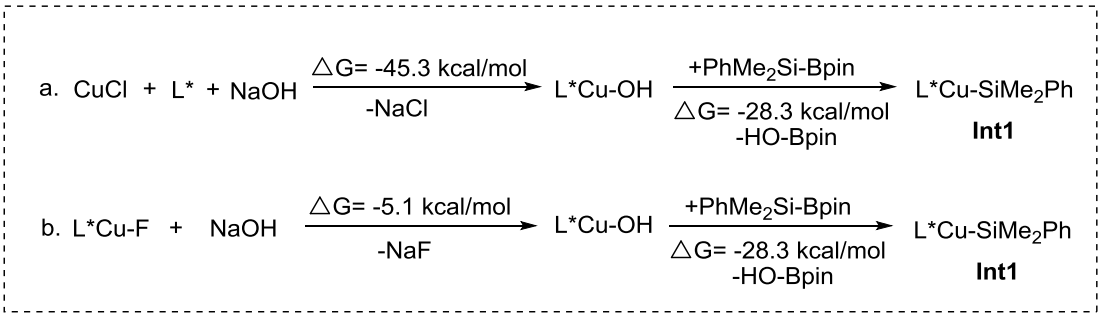
	x	y	z	U(eq)
H(1)	7750	3768	5368	61
H(2)	6854	3402	4111	76
H(3)	5434	4697	3963	73
H(4)	4906	6411	5080	79
H(5)	5793	6771	6355	68
H(7A)	7327	8404	7262	74
H(7B)	7596	7531	8174	74
H(7C)	6568	7352	7782	74
H(8A)	8986	4555	6424	80
H(8B)	9195	5461	7340	80
H(8C)	8994	6551	6479	80
H(9)	7606	2595	7409	47
H(10)	5984	3902	8216	56
H(13)	8920	2170	8262	47
H(14)	9727	2263	9589	46
H(16)	7748	5287	10573	49
H(17)	6943	5149	9257	49
H(18A)	10431	1863	11003	93
H(18B)	10882	3285	11609	93
H(18C)	10769	3580	10575	93

H(20)	2431	7474	7737	46
H(21)	3534	4858	7011	41
H(23)	3158	3780	5619	48
H(24)	2297	3848	4329	51
H(26)	434	6908	5460	47
H(27)	1302	6832	6754	46
H(28A)	-714	5559	4414	110
H(28B)	-786	6275	3436	110
H(28C)	-328	7385	4198	110
H(29)	4096	2024	8732	48
H(30)	4951	2401	10021	55
H(31)	4452	4279	11084	52
H(32)	3095	5767	10846	60
H(33)	2233	5389	9568	54
H(35A)	2254	620	7708	61
H(35B)	3252	1218	7388	61
H(35C)	2357	1546	6784	61
H(36A)	817	3836	7589	70
H(36B)	1090	5067	8378	70
H(36C)	936	3120	8564	70

7. Computational details

All DFT calculations were carried out with Gaussian 16 package[6]. Geometry optimizations and vibrational frequencies of all the stationary points were performed by using the M06-2X[7] and M06-L[8] functional. The def2-SVP basis set was employed for the Cu atom, and the 6-31G(d,p) basis set was used for all the other atoms. To get more reliable energies, single point energies were computed at the M06-2X/cc-pVTZ level for all the species (the def2-TZVP basis set for the Cu atom). The solvent effect was treated with the polarizable continuum model (PCM)[9] with 1,4-dioxane as the solvent. The 3D structures were generated with CYL view package.[10]

Activation free energy barriers here are defined as the free energy difference between the transition state and the lowest-energy stationary point before it in the reaction pathways.



Scheme S1. Gibbs free energy for the generation of silyl-Cu intermediate (**Int1**).

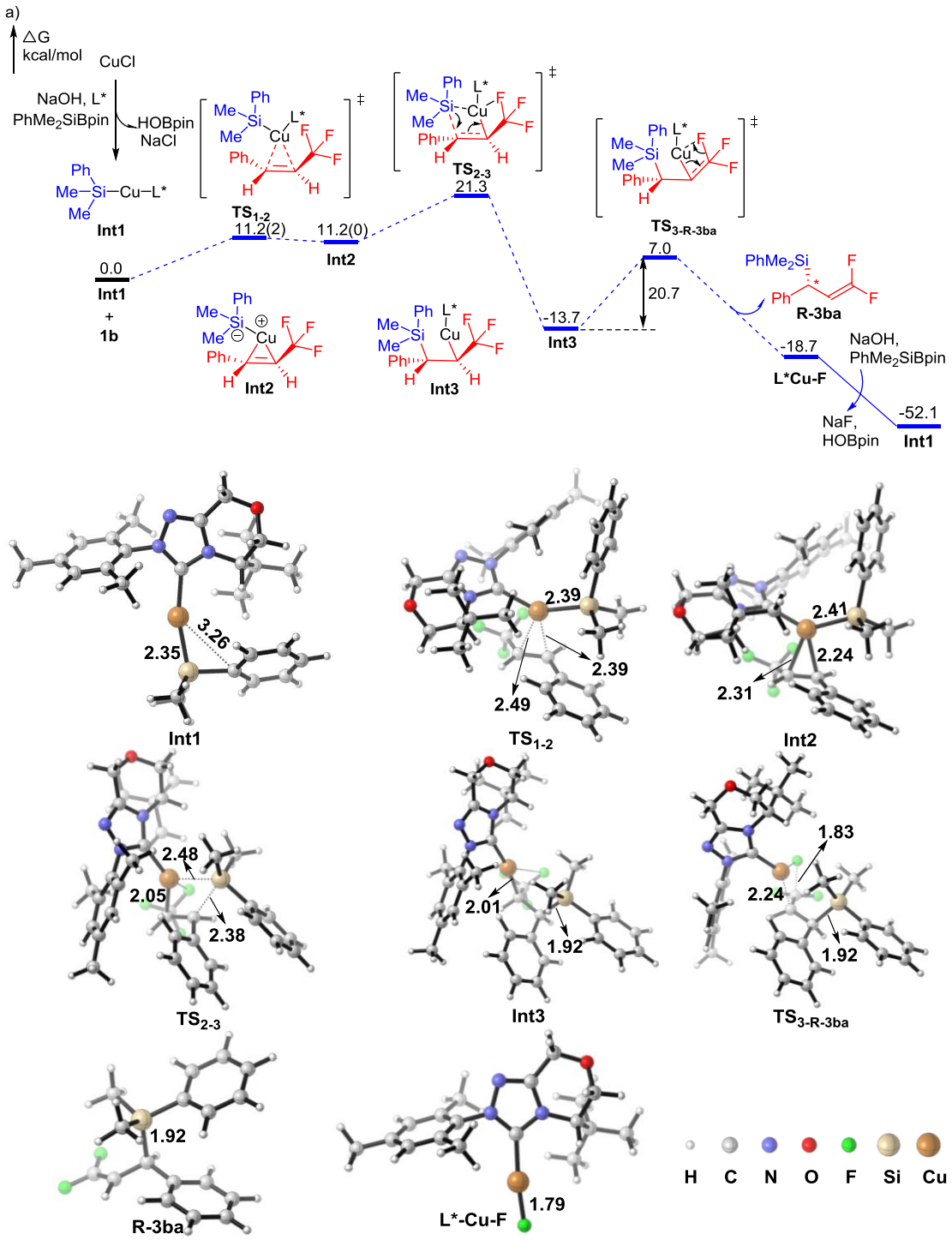


Figure S6. a) The computed free-energy surfaces for the model reaction of trifluormethyl alkene **1b** and silyl-copper intermediate **Int1** (in kcal/mol). b) 3D structures of the species involved in the reaction.

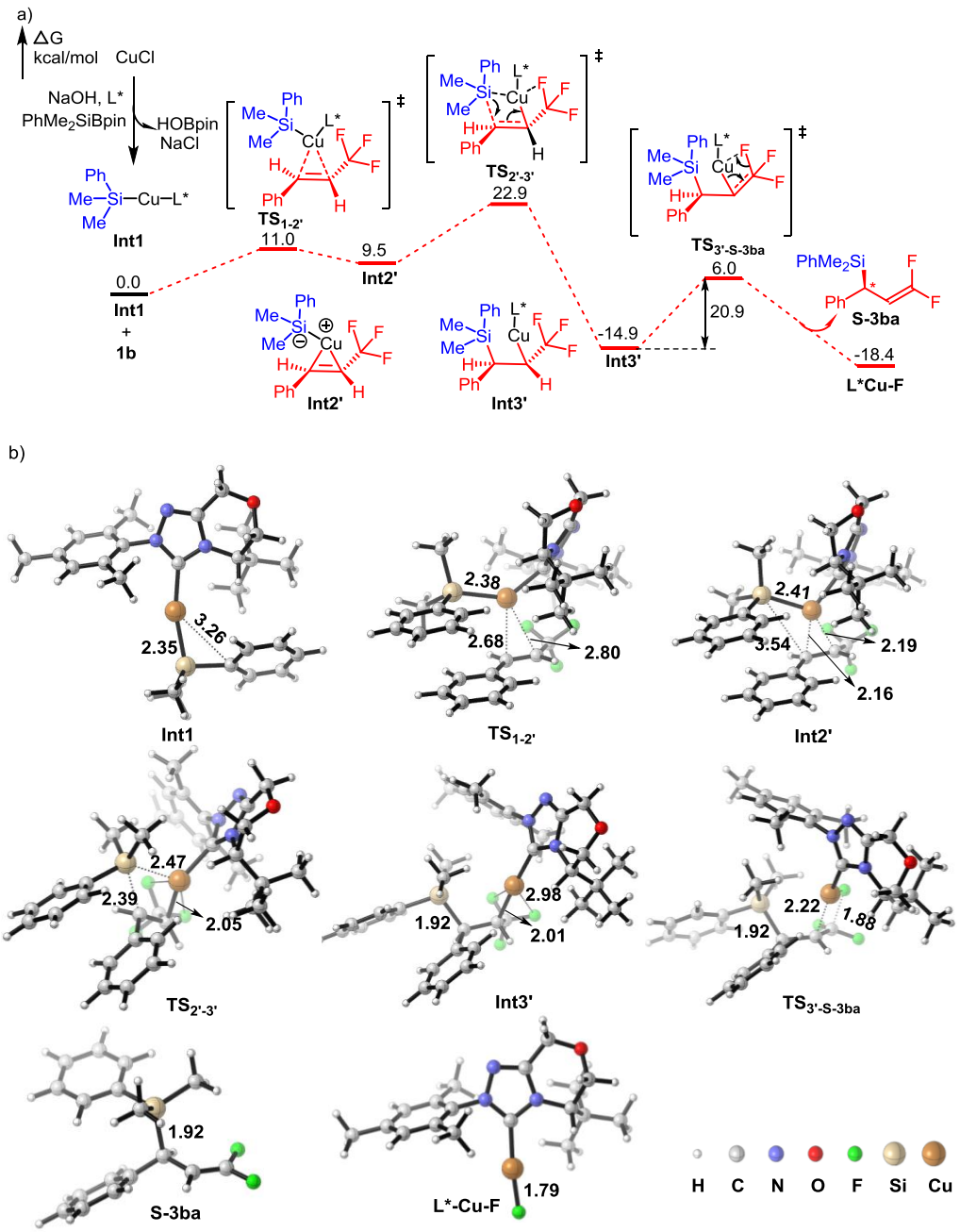


Figure S7. a) Computed free-energy surfaces for the model reaction of trifluormethyl alkene **1b** and silyl-copper intermediate **Int1** (in kcal/mol). b) 3D structures of the species involved in the reaction.

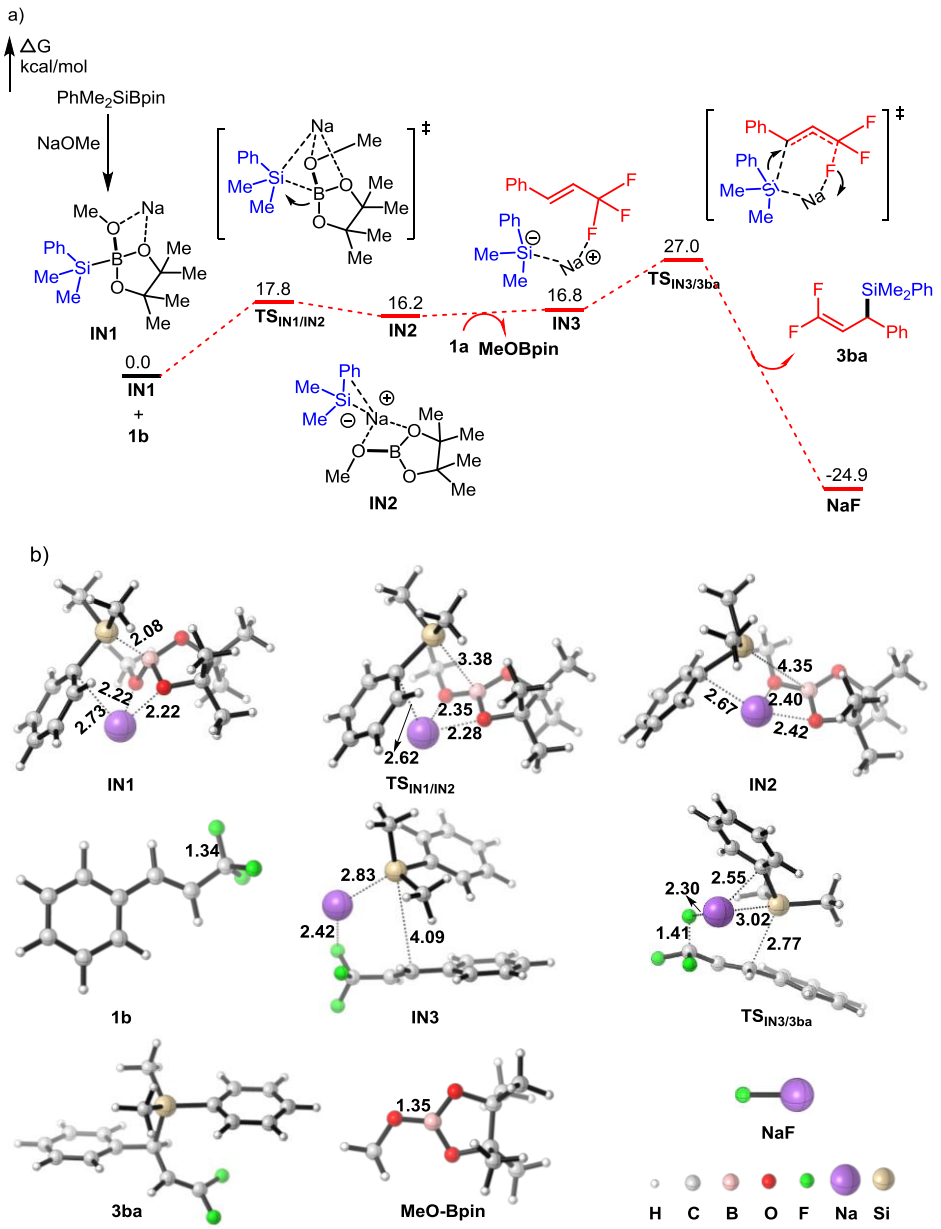


Figure S8 a) Computed free-energy surfaces for the model reaction between trifluormethyl alkene **1b** and silyborane/alkoxy base complex **IN1**. b) 3D structures of the species involved in this defluorosilylation reaction (with NaOMe as the base).

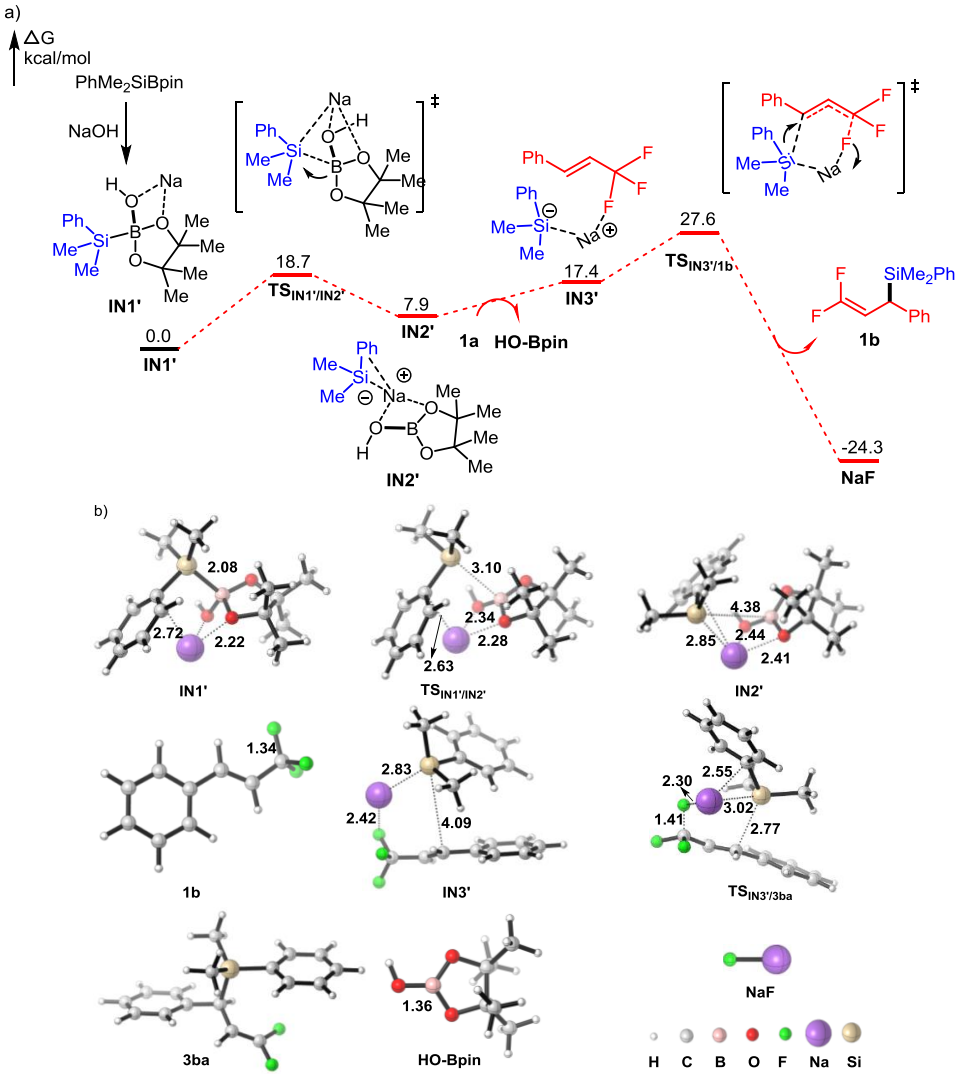


Figure S9 a) Computed free-energy surfaces for the model reaction between trifluormethyl alkene **1b** and silyborane/alkoxy base complex **IN1′** b) 3D structures of the species involved in this defluorosilylation reaction (with NaOH as the base).

We have previously reported that alkoxy base could mediate defluorosilylation reaction of fluoroalkenes, proceeding through the S_N2' or S_N^V substitution of the transient silyl anion complex towards fluoroalkenes. Therefore, the background reaction involving NaOH-mediated defluorosilylation reaction with silylboronate was also investigated by theoretical calculations (Figure S9). Starting from NaOH-silylboronate complex, the heterolytic cleavage of B–Si bond (*via* $\mathbf{TS_{IN1'/N2'}}$) in **IN1′** generates silyl sodium complex **IN2′**, in which HOBpin is closely bounded to sodium cation. This step is endergonic by 7.9 kcal/mol with a barrier of 18.7 kcal/mol. Then, the release of HO-Bpin accompanied by the association of trifluormethyl alkene (**1b)** with $PhMe_2Si^-Na^+$ forms intermediate **IN3**. The subsequent nucleophilic addition of

PhMe$_2$Si anion to C=C bond alone with the elimination of F anion *via* **TS$_{IN3/3ba}$** produces the defluorosilylation product **3ba**. This step is exergonic by 24.3 kcal/mol over a rate-limiting barrier of 27.6 kcal/mol, which is much higher than the Cu-catalyzed enantioselective defluorosilylation pathway (via **TS$_{2\text{-}3}$**, $\Delta G^{\neq}$ =21.6 kcal/mol). Thus, this potential background reaction would be completely suppressed under standard reaction conditions.

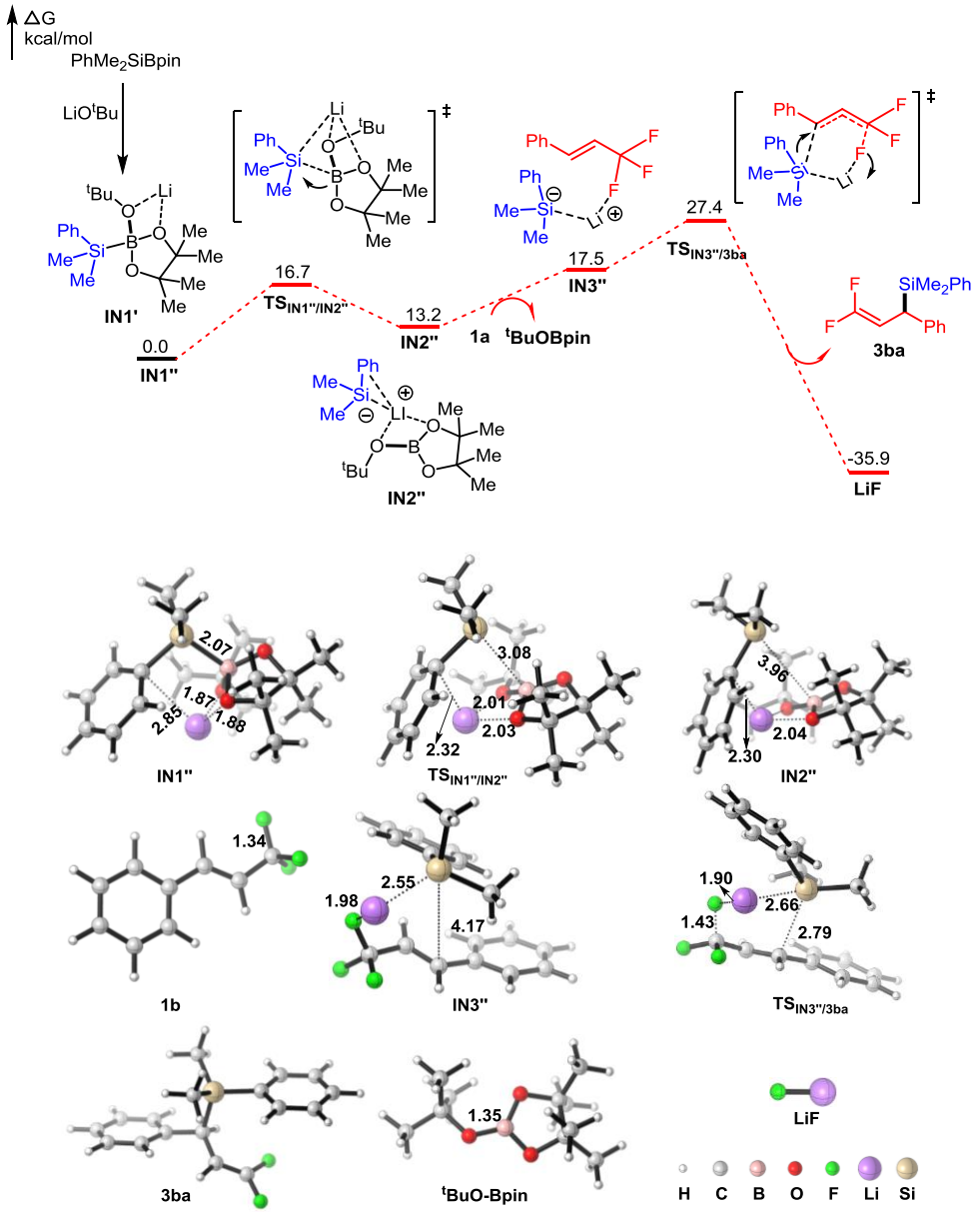


Figure S10. a) Computed free-energy surfaces for the model reaction between trifluormethyl alkene **1b** and silyborane/alkoxy base complex **IN1''**. b) 3D structures of the species involved in this defluorosilylation reaction (with LiO^{t}Bu as the base).

As shown below (Figure 11-12), to ensure the reliability of the DFT calculation results, we have recalculated Gibbs free energy profile of the model reaction between 1-(trifluoromethyl)alkene and silyl-copper intermediate **Int1** with M06-L functional, which is much suitable for the transitional metal system. Although the calculated energies of the reaction intermediates for two DFT methods were different, the calculated stereoselectivity trends for the reaction were identical (R-selectivity). The energy barrier difference between these two competing pathways with M06-L functional is $\Delta\Delta G^{\neq}$ = 6.6 kcal/mol [28.3 kcal/mol (R) *vs* 34.9 (S), See **Figure S1**], which could account for the experimental results observed in product-selectivity.

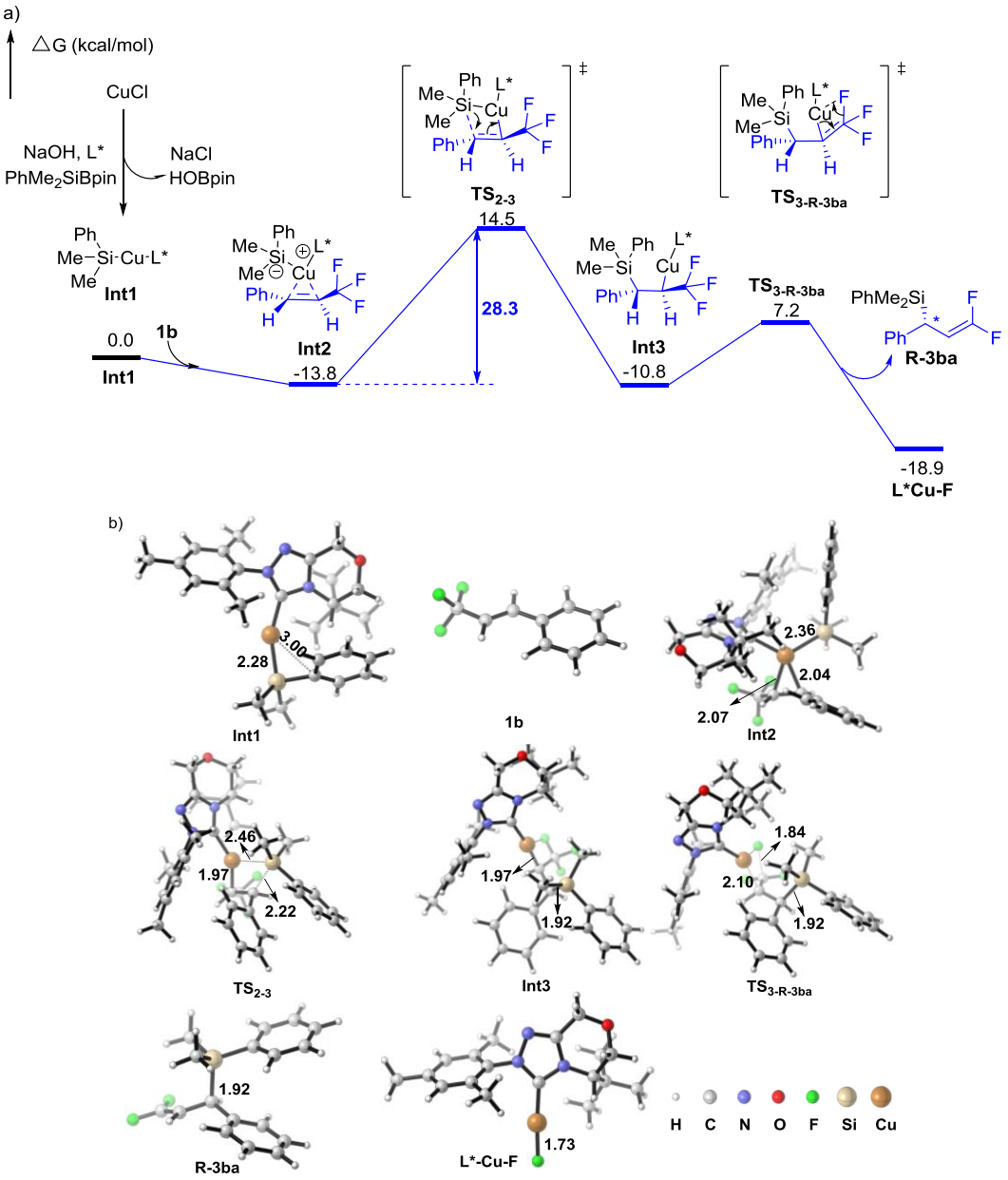


Figure S11. a) Computed free-energy surfaces for the model reaction between1-(trifluoromethyl) -alkene (**1b**) and silyl-copper intermediate **Int1 with M06-L functional**. b) 3D structures of the species involved in the reaction.

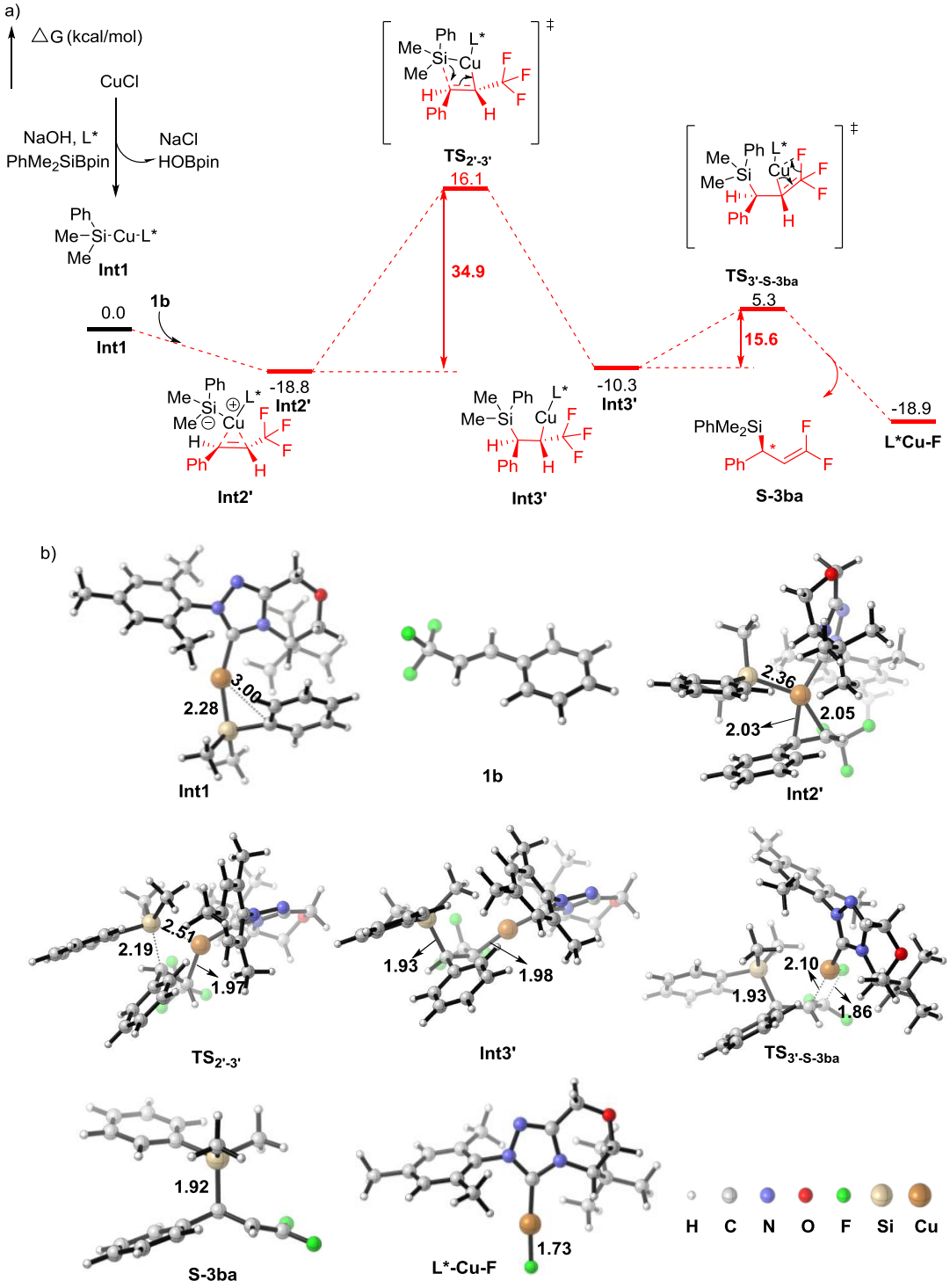


Figure S12. a) Computed free-energy surfaces for the model reaction between1-(trifluoromethyl) -alkene (**1b**) and silyl-copper intermediate **Int1 with M06-L functional**. b) 3D structures of the species involved in the reaction.

Cartesian Coordinates and Energies of the Optimized Structures

CuCl

M06-2X/6-31G(d,p) Electronic E: -2100.453746 a.u.
M06-2X/6-31G(d,p) Gibbs free E: -2100.476337 a.u.
M06-2X/cc-pVTZ Electronic E: -2100.728514 a.u.

Cu	-2.5277471521	-0.3008844872	-2.2183114057
Cl	-4.2872938479	-1.2121765128	-3.0880765943

NHC (L*)

M06-2X/6-31G(d,p) Electronic E: -940.035685 a.u.
M06-2X/6-31G(d,p) Gibbs free E: -939.677166 a.u.
M06-2X/cc-pVTZ Electronic E: -940.345469 a.u.

C	0.5943171703	2.0332275283	-1.5657926840
C	-1.6860960363	2.9881118199	-1.7970728589
C	-0.8779989467	4.0846986613	-2.4949660724
C	1.2402600936	3.3668511320	-1.8107609912
C	-1.0971409685	0.5400182832	-1.4429358276
H	-2.4817202503	2.6686782647	-2.4800502153
H	-0.6011743289	3.7403557052	-3.5032659035
H	1.9970126202	3.5680314560	-1.0504926567
N	1.1913177965	0.9053764831	-1.3363606575
N	0.1345834316	0.0181954030	-1.2652367006
N	-0.7665844320	1.8582336706	-1.6423692334
H	-1.4596972151	5.0003087191	-2.5945843779
H	1.7312523265	3.3501805386	-2.7951617715
O	0.2882393313	4.4091661072	-1.7572615865
C	0.4165305889	-1.3615254308	-1.0111611854
C	0.9885502320	-2.1282980922	-2.0287483561
C	0.1232120234	-1.8894425664	0.2488698102
C	1.2646835316	-3.4678521396	-1.7586822447
C	0.4113362707	-3.2349701522	0.4724145033
C	0.9793394077	-4.0378224837	-0.5176878754
H	1.7099266662	-4.0809595956	-2.5387557515
H	0.1925063035	-3.6646866360	1.4471959637
C	-0.4765169552	-1.0234767187	1.3243435851
H	0.1481787337	-0.1425026577	1.5044570437
H	-1.4644551413	-0.6622708228	1.0246482463
H	-0.5712333741	-1.5784735567	2.2593500955
C	1.2869601380	-1.5154529746	-3.3705950604
H	0.4015442124	-1.0089366738	-3.7671715435
H	2.0782161357	-0.7650282739	-3.2880932776
H	1.6013210183	-2.2795240816	-4.0836895417
C	1.2524415303	-5.4975359974	-0.2591452394

H	1.5098149154	-5.6719571086	0.7882780153
H	0.3693889012	-6.1035020671	-0.4868656363
H	2.0731302394	-5.8629194543	-0.8806631750
C	-2.3428101027	3.3821656645	-0.4377546159
C	-1.3298533839	3.3509989040	0.7142016264
H	-0.9594004848	2.3350144776	0.8860280150
H	-0.4790458720	4.0079123822	0.5164876080
H	-1.8185294230	3.6863654642	1.6344404833
C	-2.9454873464	4.7883176441	-0.5437611091
H	-3.5873444293	4.8846379184	-1.4273346945
H	-3.5627203470	4.9883543249	0.3369869372
H	-2.1697724575	5.5587110605	-0.5897205264
C	-3.4699527236	2.3835839846	-0.1402166541
H	-4.2700751051	2.4684521994	-0.8840790384
H	-3.0982659048	1.3558723047	-0.1605022993
H	-3.9004570294	2.5877335526	0.8453405285

NHC-CuCl

M06-2X/6-31G(d,p) Electronic E: -3040.582591 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -3040.227100 a.u.

M06-2X/cc-pVTZ Electronic E: -3041.158963 a.u.

C	0.7017770746	2.0873343514	-1.0841069783
C	-1.4773532124	3.0520693826	-1.8283774492
C	-0.5331102034	4.1873804916	-2.2373796697
C	1.3536403792	3.4404599514	-1.0514181473
C	-0.8793116081	0.5937488165	-1.5519566382
H	-2.0598716828	2.7555285635	-2.7088823760
H	-0.0080902139	3.9035457982	-3.1616301746
H	1.8563522823	3.5972391022	-0.0954425944
N	1.2606820795	0.9385640007	-0.8458673505
N	0.2685728904	0.0398961330	-1.1372172714
N	-0.5927645118	1.9223472054	-1.5059842506
H	-1.0861727219	5.1061892428	-2.4263222998
H	2.1059126540	3.4813027148	-1.8523876083
O	0.4020286335	4.4684707617	-1.2104007849
C	0.5005604029	-1.3648110041	-0.9584456971
C	0.5400487956	-2.1994615365	-2.0780436713
C	0.6698124924	-1.8387901321	0.3471756667
C	0.7598025781	-3.5595793295	-1.8550940871
C	0.8911519635	-3.2027952760	0.5141771973
C	0.9352863091	-4.0776777897	-0.5734560373
H	0.7967009580	-4.2289107697	-2.7108649948
H	1.0247463783	-3.5934682253	1.5199293816
C	0.6026173908	-0.9056308462	1.5270557631

H	1.4745324317	-0.2468250056	1.5583909441
H	-0.2853298717	-0.2670666566	1.4699985032
H	0.5594596440	-1.4715673763	2.4588145006
C	0.3453379481	-1.6757841610	-3.4770546265
H	-0.7202205301	-1.5626609594	-3.7087307821
H	0.8188512705	-0.7000819867	-3.6122751603
H	0.7700303666	-2.3715882143	-4.2026558866
C	1.1384119440	-5.5552741625	-0.3605286115
H	1.7907093329	-5.7454693646	0.4948934189
H	0.1817710245	-6.0495894442	-0.1637304825
H	1.5787408635	-6.0250127033	-1.2426074943
C	-2.4740055541	3.3698223087	-0.6753749353
C	-1.7692968562	3.5487929230	0.6754171245
H	-1.2163052134	2.6454617767	0.9576646270
H	-1.0763287769	4.3917043357	0.6642231654
H	-2.5210889745	3.7254977910	1.4507025837
C	-3.2323618378	4.6556186758	-1.0345706614
H	-3.6557594815	4.6033991445	-2.0439677616
H	-4.0597957609	4.7982865710	-0.3345561452
H	-2.5919209155	5.5394506434	-0.9691059797
C	-3.4926555925	2.2268665306	-0.5490984818
H	-3.9826555105	2.0053347508	-1.5045244215
H	-3.0292739839	1.3068243212	-0.1813883175
H	-4.2689355964	2.5091402702	0.1681637295
Cu	-2.5213880668	-0.2975905402	-2.2151684208
Cl	-4.2936533310	-1.2154699845	-3.0912199959

NHC-CuOH

M06-2X/6-31G(d,p) Electronic E: -2656.139457 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2655.772721 a.u.

M06-2X/cc-pVTZ Electronic E: -2656.719454 a.u.

C	0.7037450156	2.1035787573	-1.0493541908
C	-1.4573684971	3.1020655600	-1.8015267128
C	-0.4980324338	4.2370894892	-2.1736005359
C	1.3661411320	3.4501391044	-0.9790391525
C	-0.8889228849	0.6352419681	-1.5645528669
H	-2.0276376610	2.8261119987	-2.6964606321
H	0.0383781668	3.9671593445	-3.0955322911
H	1.8577504057	3.5826819278	-0.0136053353
N	1.2514797774	0.9458640049	-0.8327128536
N	0.2539994281	0.0618695968	-1.1537685684
N	-0.5888166544	1.9593945879	-1.4863772590
H	-1.0400565415	5.1646445923	-2.3520491445
H	2.1289892000	3.5029356359	-1.7692671726

O	0.4247226441	4.4894529457	-1.1276968494
C	0.4703471737	-1.3483350942	-0.9958895625
C	0.4547904173	-2.1876702292	-2.1131302447
C	0.6738268226	-1.8285048433	0.3064916069
C	0.6615795087	-3.5528544020	-1.8891546770
C	0.8794494234	-3.1931803912	0.4704893496
C	0.8761852950	-4.0718891294	-0.6168731789
H	0.6566581863	-4.2236392474	-2.7447725221
H	1.0372295311	-3.5840987126	1.4729329176
C	0.6500363181	-0.8990349312	1.4915255991
H	1.5360585474	-0.2593328185	1.5103020957
H	-0.2242835425	-0.2405831456	1.4541983833
H	0.6113129208	-1.4697734587	2.4207127471
C	0.2125667112	-1.6979145334	-3.5183554649
H	-0.8531350981	-1.7627491784	-3.7739414172
H	0.5239865198	-0.6593529823	-3.6494217824
H	0.7686547448	-2.3165806023	-4.2262882669
C	1.0852852486	-5.5483763417	-0.4011080482
H	1.9758647333	-5.7336449912	0.2055927943
H	0.2329817430	-5.9872079952	0.1266395568
H	1.2012047469	-6.0750764588	-1.3502611819
C	-2.4703038864	3.4055189734	-0.6594779525
C	-1.7879529795	3.5402548600	0.7077232391
H	-1.2587123702	2.6198110451	0.9793570617
H	-1.0779653513	4.3689163272	0.7276112374
H	-2.5503435267	3.7157192281	1.4730127984
C	-3.2052941638	4.7102522745	-0.9975955009
H	-3.6085962027	4.6909213087	-2.0164305736
H	-4.0451450342	4.8443249454	-0.3105835051
H	-2.5555604154	5.5838839837	-0.8954584686
C	-3.5044053991	2.2723942126	-0.5845115344
H	-3.9858089245	2.0981288689	-1.5533611163
H	-3.0549655756	1.3307087262	-0.2593263984
H	-4.2819535546	2.5374010697	0.1382769899
Cu	-2.3994388072	-0.3416258072	-2.3607948865
O	-3.5602014255	-1.3637370939	-3.3722373762
H	-3.5667945419	-2.2442385598	-2.9804529630

1b

M06-2X/6-31G(d,p) Electronic E: -646.451363 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -646.348894 a.u.

M06-2X/cc-pVTZ Electronic E: -646.701908 a.u.

C	-6.8693045360	0.8231330080	0.0390386417
C	-6.1691507894	-0.0616094750	0.7487193993

H	-6.4017993984	-1.1204747845	0.7941977594
C	-4.9791659181	0.3362345680	1.5533409018
F	-3.8730641177	-0.3115610599	1.1467611402
F	-5.1414281724	0.0312983927	2.8530356465
F	-4.7176225934	1.6492900897	1.4835899978
H	-6.5439273030	1.8610823946	0.0580252239
C	-8.0529335817	0.5451185083	-0.7875368272
C	-8.6349327536	-0.7266579050	-0.8790625654
C	-8.6216212296	1.5976645305	-1.5135569327
C	-9.7504214371	-0.9352205317	-1.6786575688
H	-8.2178911173	-1.5584183115	-0.3202157133
C	-9.7390392348	1.3895774119	-2.3158379013
H	-8.1789493653	2.5876209370	-1.4463631561
C	-10.3058495226	0.1216132084	-2.4006726592
H	-10.1910052044	-1.9249037832	-1.7393373781
H	-10.1657410083	2.2169819095	-2.8729713932
H	-11.1777827170	-0.0453111078	-3.0244876155

$PhMe_2Si$-Bpin

M06-2X/6-31G(d,p) Electronic E: -1011.936714 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1011.635869 a.u.

M06-2X/cc-pVTZ Electronic E: -1012.214280 a.u.

Si	0.1316798839	-0.6247158175	-0.6110339337
C	-1.6905952960	-1.1130381641	-0.5660428118
H	-1.8722289220	-1.9899926029	-1.1943833504
H	-1.9949539660	-1.3578598261	0.4556069085
H	-2.3277611915	-0.2985910893	-0.9233836732
C	0.6450064834	-0.2009629006	-2.3736275443
H	1.7104859436	0.0398995535	-2.4242711196
H	0.4482434388	-1.0324054436	-3.0576383237
H	0.0869549340	0.6665169116	-2.7374517022
C	1.1724431994	-2.0739645744	0.0170388020
C	1.2972033105	-2.3008201806	1.3970161485
C	1.8274874937	-2.9561219633	-0.8529113816
C	2.0368356611	-3.3736158168	1.8884415442
H	0.8118725885	-1.6221736206	2.0970103965
C	2.5715857663	-4.0300267538	-0.3680220793
H	1.7611949608	-2.8033925092	-1.9278367052
C	2.6755875763	-4.2410064584	1.0046073043
H	2.1193981978	-3.5315149738	2.9595622485
H	3.0715770964	-4.7007331493	-1.0602355056
H	3.2555610605	-5.0763389859	1.3846673124
C	1.6556596560	2.5426083588	1.7209870945
C	0.4059155524	2.1509725741	2.5683904784

B	0.5103358836	0.8802062117	0.6815712231
O	1.3628013547	1.9275751516	0.4409735247
O	0.0092276622	0.8953972188	1.9616894745
C	1.8504941802	4.0361673075	1.5214333501
H	1.9859602237	4.5349310377	2.4863471578
H	2.7441225503	4.2107508707	0.9174288738
H	0.9974548411	4.4842894838	1.0099642787
C	2.9426513948	1.8952900908	2.2286270292
H	3.7270539695	2.0405945144	1.4824026181
H	3.2695015325	2.3413781762	3.1717689941
H	2.8053161332	0.8194241693	2.3750647876
C	0.6816637475	1.9185322832	4.0446240286
H	1.0730630813	2.8296435723	4.5079611318
H	-0.2476774277	1.6484910174	4.5520519800
H	1.4007800732	1.1113238197	4.1920074832
C	-0.7627638355	3.1168649918	2.3874748644
H	-1.6577285020	2.6734116584	2.8298985716
H	-0.5675531297	4.0742170127	2.8782446206
H	-0.9569661609	3.2990378443	1.3267209008

Int1

M06-2X/6-31G(d,p) Electronic E: -3181.168210 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -3180.660324 a.u.

M06-2X/cc-pVTZ Electronic E: -3181.834794 a.u.

C	0.4017827399	1.8909296381	-1.3158302767
C	-1.8565930478	2.6687194082	-2.0189097554
C	-0.9969992939	3.7732187316	-2.6376673894
C	0.9843084790	3.2677018356	-1.4752288730
C	-1.1205401878	0.2777705634	-1.5263446434
H	-2.5093435974	2.2553249484	-2.7985252168
H	-0.5124326243	3.3877707378	-3.5474891958
H	1.5150986110	3.5628000625	-0.5680802996
N	1.0338815491	0.8056313841	-0.9807607538
N	0.0759689277	-0.1666117723	-1.1154283713
N	-0.9001858463	1.6155687256	-1.6456049838
H	-1.6045761777	4.6345105821	-2.9112493746
H	1.7036175933	3.2425974537	-2.3065343277
O	-0.0190546062	4.2292291843	-1.7172875992
C	0.3978364210	-1.5301586269	-0.8093781099
C	0.4688164105	-2.4620825238	-1.8467399834
C	0.6166902661	-1.8692060270	0.5302959199
C	0.7726675909	-3.7810506981	-1.5046595103
C	0.9219091299	-3.1961206339	0.8184511942
C	1.0054718114	-4.1641706780	-0.1853455167

H	0.8312857241	-4.5252384348	-2.2948873605
H	1.0899612710	-3.4839431951	1.8534644950
C	0.5048928284	-0.8328141754	1.6164996246
H	1.3093344898	-0.0961916188	1.5411660690
H	-0.4422883589	-0.2886482347	1.5380550711
H	0.5520797164	-1.3022249857	2.6002583466
C	0.2167278391	-2.0750528390	-3.2801168571
H	-0.8573367970	-1.9649442221	-3.4736265241
H	0.6930340641	-1.1220392208	-3.5258351268
H	0.6029877963	-2.8415940226	-3.9539943772
C	1.3619827882	-5.5878961104	0.1559484036
H	0.8690045311	-5.9064935148	1.0776924541
H	1.0711001538	-6.2716442503	-0.6440437491
H	2.4412126911	-5.6902559039	0.3080665819
C	-2.7541464130	3.0918745634	-0.8166017423
C	-1.9474701838	3.3085062751	0.4703411728
H	-1.4503748884	2.3855891630	0.7898233595
H	-1.1949932819	4.0909214267	0.3510790510
H	-2.6296218837	3.6048430003	1.2731552407
C	-3.4903648254	4.3862751399	-1.1866198195
H	-3.9981275429	4.2887539981	-2.1532526954
H	-4.2544085605	4.5966083080	-0.4328886892
H	-2.8126106691	5.2444714632	-1.2205560763
C	-3.8028763384	1.9987621176	-0.5721982491
H	-4.4147876685	1.8294160894	-1.4652961880
H	-3.3413427579	1.0490183474	-0.2822540853
H	-4.4672812944	2.3045623866	0.2422305482
Cu	-2.7756259391	-0.7134298710	-2.1603420468
Si	-4.7762306987	-1.2991777617	-3.2487275026
C	-6.1687997393	-2.2599875426	-2.3653188820
H	-7.1076662755	-2.2191573188	-2.9302673654
H	-5.8880537169	-3.3129118620	-2.2605668639
H	-6.3595781192	-1.8736546445	-1.3592165302
C	-4.7077531337	-2.0648597550	-5.0006178471
H	-5.7041776644	-2.1141233519	-5.4533745217
H	-4.0639989561	-1.4806125659	-5.6660638438
H	-4.3016958592	-3.0809219524	-4.9630055579
C	-5.4873915875	0.4618852865	-3.5271062482
C	-4.7584482091	1.3930412085	-4.2885160436
C	-6.6372284258	0.9380846100	-2.8811183057
C	-5.1453241954	2.7263116942	-4.3948260774
H	-3.8533792268	1.0653868153	-4.8022278628
C	-7.0314257405	2.2743597087	-2.9709672553
H	-7.2354262505	0.2549016341	-2.2820540891

C	-6.2851933540	3.1755105941	-3.7251293878
H	-4.5601111903	3.4185944441	-4.9952740500
H	-7.9231737956	2.6123960718	-2.4504831556
H	-6.5871419904	4.2162225033	-3.7947413146

Int2

M06-2X/6-311G(d,p) Electronic E: -3827.639400 a.u.

M06-2X/6-311G(d,p) Gibbs free E: -3827.001216 a.u.

M06-2X/cc-pVTZ Electronic E: -3828.546673 a.u.

C	-3.4747641405	0.9305608158	-0.8794316868
C	-2.8050458997	-1.4431829490	-1.2435449832
C	-3.9776766185	-1.3467294773	-2.2248435632
C	-4.8526727486	0.6871336259	-1.4248524062
C	-1.3350423277	0.4666558308	-0.4532797024
H	-1.9231962696	-1.7914629525	-1.7957804352
H	-3.6429227986	-0.8014420756	-3.1206700962
H	-5.6112840457	1.0465651092	-0.7271673891
N	-2.9715562306	2.0627159098	-0.4916787896
N	-1.6609957307	1.7491618184	-0.2309083914
N	-2.5266094689	-0.0601739038	-0.8492732392
H	-4.3209304753	-2.3349020875	-2.5290897171
H	-4.9534863254	1.2438488510	-2.3676792113
O	-5.0842753107	-0.6889652629	-1.6343229255
C	-0.7799678654	2.7511456960	0.2958546793
C	-0.3930007227	3.8185132496	-0.5145517017
C	-0.3695104661	2.6207540418	1.6296275187
C	0.4945872125	4.7489346862	0.0313153924
C	0.5140898941	3.5745618296	2.1252893577
C	0.9665865775	4.6359864006	1.3367895766
H	0.8211906571	5.5827897163	-0.5854841562
H	0.8520444258	3.4840103679	3.1545693404
C	-0.8993000872	1.5142336029	2.5009171152
H	-1.9949376596	1.5017491146	2.4830886393
H	-0.5424109096	0.5420010089	2.1516890682
H	-0.5587168322	1.6377830042	3.5311097681
C	-0.9412265386	4.0054492046	-1.9041649781
H	-1.1568344269	3.0533609203	-2.3876954009
H	-1.8752813771	4.5747953931	-1.8660940711
H	-0.2308076914	4.5585114828	-2.5222357760
C	1.9452049598	5.6335538131	1.9010819181
H	2.9168260181	5.1627894158	2.0807663740
H	2.0975456489	6.4718054784	1.2181856925
H	1.5934355495	6.0298499824	2.8577169054
C	-2.9995922142	-2.3866776320	-0.0224719559

C	-4.1043605909	-1.8989773980	0.9233413427
H	-3.8874162876	-0.8915416883	1.2961560413
H	-5.0808677853	-1.8858549986	0.4367536360
H	-4.1540985055	-2.5646405388	1.7905492703
C	-3.3455618343	-3.7875267523	-0.5459245364
H	-2.6212438466	-4.1246386873	-1.2973238519
H	-3.3228185320	-4.5029445939	0.2805775814
H	-4.3459547277	-3.8273461228	-0.9852609959
C	-1.6862580057	-2.4765007129	0.7694245895
H	-0.8428691450	-2.7802753953	0.1354900518
H	-1.4243281467	-1.5255703374	1.2417806343
H	-1.7891365121	-3.2239424018	1.5624963006
Cu	0.5387069706	-0.4140741945	-0.4686854907
Si	2.1859656107	-0.9811748769	1.1918839143
C	2.3567645318	-2.8689934226	1.4848756112
H	2.9886547618	-3.0755377867	2.3565192979
H	2.8098633133	-3.3532099142	0.6135622750
H	1.3864614575	-3.3500632684	1.6523211427
C	3.9747911186	-0.3948964244	0.8345819401
H	4.6528059956	-0.6458503647	1.6581085955
H	4.0253714584	0.6866753572	0.6721903822
H	4.3594129296	-0.8785474007	-0.0697090015
C	1.8587908914	-0.3141922151	2.9568568738
C	2.3711397331	0.9170180120	3.3932309356
C	1.0564411241	-1.0236120280	3.8661186042
C	2.1040917714	1.4146017800	4.6686439663
H	2.9962407070	1.5043459010	2.7228484884
C	0.7741012135	-0.5333548434	5.1389905432
H	0.6395521554	-1.9854562571	3.5704227739
C	1.2994967965	0.6921484269	5.5473293266
H	2.5266457173	2.3672927676	4.9786034140
H	0.1498344179	-1.1085972898	5.8172231766
H	1.0888610617	1.0760465261	6.5409314063
C	1.7945109340	-1.0670494071	-2.2137706701
C	0.5883510123	-0.7279722469	-2.7589762736
C	0.3033198249	0.6461148400	-3.2500233303
F	0.8749819663	1.5913063107	-2.4818384399
F	-1.0263703530	0.8927013417	-3.2770157474
F	0.7412771594	0.8536347920	-4.5046461550
C	2.2393300525	-2.4638712827	-2.0365055710
C	1.3299719553	-3.5185713992	-1.8853214735
C	3.6074387267	-2.7506349648	-2.0379090777
C	1.7783121243	-4.8230976262	-1.7312735006
H	0.2622675750	-3.3132109900	-1.8670184202

C	4.0582678124	-4.0592475022	-1.8871534266
H	4.3212312046	-1.9416723764	-2.1641314610
C	3.1461643634	-5.0985011927	-1.7294775837
H	1.0613398272	-5.6271664624	-1.6009855089
H	5.1236706508	-4.2642055273	-1.8887957869
H	3.4962252495	-6.1172645578	-1.6013853086
H	2.5627495094	-0.3023087256	-2.1104384027
H	-0.1140438948	-1.4814799093	-3.0991906713

Int3

M06-2X/6-31G(d,p) Electronic E: -3827.674987 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -3827.037353 a.u.

M06-2X/cc-pVTZ Electronic E: -3828.585790 a.u.

C	-3.9826078143	1.0484074717	-1.2563327728
C	-3.6123634153	-1.4096192723	-0.9367042605
C	-4.7244748443	-1.4472444261	-1.9917208663
C	-5.3334922963	0.8217996562	-1.8708197181
C	-1.9764496062	0.4774382613	-0.4898956728
H	-2.7588788588	-1.9863718863	-1.3129642042
H	-4.2909105430	-1.2317059259	-2.9797376812
H	-6.0790292220	1.4666579413	-1.4026628662
N	-3.3681448063	2.1826952807	-1.0899632530
N	-2.1417696635	1.8010424712	-0.6143228245
N	-3.1797194076	-0.0047249505	-0.8921543990
H	-5.1930980922	-2.4296968837	-2.0304608329
H	-5.2759357695	1.0730658494	-2.9401059767
O	-5.7486812098	-0.5134073989	-1.6953525926
C	-1.1384868679	2.7593464315	-0.2481039692
C	-0.4814485181	3.4576843160	-1.2641507975
C	-0.8141119392	2.9062016284	1.1066504641
C	0.5342410400	4.3367960376	-0.8903327235
C	0.2158794481	3.7893915398	1.4257494370
C	0.8989402990	4.5107153685	0.4456480491
H	1.0601311473	4.8902630381	-1.6645501255
H	0.4906625669	3.9173303358	2.4700648477
C	-1.5224450404	2.1386250550	2.1945837885
H	-2.5654583376	1.9368821964	1.9365460971
H	-1.0304681023	1.1754131364	2.3813302146
H	-1.5009897331	2.7054733756	3.1273202540
C	-0.8486563003	3.2440027532	-2.7080994864
H	-0.7857125106	2.1825442178	-2.9704271687
H	-1.8739631797	3.5683271146	-2.9051918316
H	-0.1740270013	3.7989395251	-3.3615124094
C	2.0157926225	5.4438735276	0.8353558494

H	2.8409164871	4.8850206779	1.2877566675
H	2.4052768413	5.9813002539	-0.0321290722
H	1.6733050686	6.1794445902	1.5684653960
C	-3.9827340275	-1.9676853123	0.4684032472
C	-5.0927669773	-1.1533084051	1.1442328518
H	-4.8059378789	-0.0999589035	1.2448496021
H	-6.0315101402	-1.2022065215	0.5901540455
H	-5.2605793879	-1.5437706890	2.1526280771
C	-4.4406778159	-3.4235214784	0.2959643490
H	-3.7032626266	-4.0110839028	-0.2623886855
H	-4.5577285378	-3.8866234815	1.2792937707
H	-5.4045946902	-3.4964773940	-0.2145708504
C	-2.7467749122	-1.9599333440	1.3809781029
H	-1.8850193333	-2.4620050075	0.9245252347
H	-2.4429804980	-0.9450554636	1.6521163030
H	-2.9795214691	-2.4864920420	2.3112670901
Cu	-0.2905470872	-0.2480454988	0.2946135978
Si	2.3007031222	-1.8209181499	-1.2455075155
C	0.9947212415	-3.1791849163	-1.1821503363
H	0.8417522063	-3.5771455405	-2.1905247928
H	0.0436358541	-2.7728558276	-0.8210123347
H	1.2673225233	-4.0007740769	-0.5168723086
C	1.6828133951	-0.4987584649	-2.4447315729
H	1.3629485914	-0.9663161909	-3.3814298564
H	2.4503840497	0.2461163613	-2.6700569448
H	0.8243696709	0.0405646206	-2.0250985217
C	3.8915487373	-2.5687409296	-1.9381529200
C	4.7771717119	-1.8219137704	-2.7298603910
C	4.2490652942	-3.8913942516	-1.6368847585
C	5.9674067807	-2.3702169137	-3.2016527100
H	4.5404588525	-0.7892084939	-2.9752801056
C	5.4378034624	-4.4481416561	-2.1036368657
H	3.5877213038	-4.5026135640	-1.0263762948
C	6.2995457472	-3.6865992892	-2.8891703441
H	6.6361201448	-1.7710858012	-3.8123355734
H	5.6908839382	-5.4746674449	-1.8562903425
H	7.2262980353	-4.1169638376	-3.2561862159
C	2.6830651685	-1.0223694603	0.4537508364
C	1.4125845209	-0.6900066459	1.2729624210
H	1.6313303145	0.1873422363	1.9004597763
C	1.1037131850	-1.7592154263	2.2486559355
F	0.8008115595	-2.9543050291	1.6765792279
F	0.0357680932	-1.4408641494	3.0303998688
F	2.1033224851	-2.0514638538	3.1279937272

H	3.3307270241	-1.7226746873	1.0035880050
C	3.5197075910	0.1961667390	0.1381154311
C	2.9417068527	1.4464536592	-0.1309088619
C	4.9122059374	0.0829532610	0.0280090312
C	3.7290354410	2.5298483398	-0.5129243794
H	1.8623518458	1.5703891146	-0.0571930097
C	5.7009099401	1.1682799467	-0.3420519687
H	5.3779817372	-0.8786922014	0.2290188216
C	5.1118648269	2.3991673544	-0.6197512954
H	3.2521852481	3.4801121936	-0.7355921405
H	6.7777817961	1.0492150007	-0.4146150019
H	5.7225066712	3.2469287119	-0.9140057656

TS_{1-2}

M06-2X/6-31G(d,p) Electronic E: -3827.639293 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -3827.000602 a.u.

M06-2X/cc-pVTZ Electronic E: -3828.547155 a.u.

C	-3.6996662581	0.2298316149	0.9405085907
C	-3.0210977663	-2.1398079693	0.5685062659
C	-4.1778423106	-2.0372447148	-0.4308173197
C	-5.0695141162	-0.0118731669	0.3742786011
C	-1.5644066775	-0.2336846598	1.3889931320
H	-2.1303759149	-2.4846765813	0.0284259229
H	-3.8292110531	-1.4834387183	-1.3161370203
H	-5.8385920819	0.3383895644	1.0651565821
N	-3.2036861156	1.3598238484	1.3439593622
N	-1.8961878622	1.0461195308	1.6191446153
N	-2.7500192977	-0.7592702632	0.9753298312
H	-4.5144691862	-3.0232487652	-0.7492981771
H	-5.1591772756	0.5540771949	-0.5641608290
O	-5.2949075850	-1.3864317334	0.1475518060
C	-1.0173463565	2.0466662092	2.1521132112
C	-0.6517686356	3.1289121045	1.3505332696
C	-0.5795915749	1.8986638546	3.4754211609
C	0.2358270231	4.0598495663	1.8943520440
C	0.3045990715	2.8538461677	3.9687214038
C	0.7317657187	3.9320743526	3.1898045392
H	0.5445445370	4.9052307327	1.2841497716
H	0.6634231254	2.7495478478	4.9896042712
C	-1.0732692628	0.7725395490	4.3433375497
H	-2.1676556133	0.7213075246	4.3257001493
H	-0.6824060310	-0.1865761759	3.9935339528
H	-0.7367112957	0.9058277367	5.3738221213
C	-1.2194613759	3.3236075738	-0.0302343801

H	-1.3720598561	2.3738706281	-0.5427857192
H	-2.1911018184	3.8239051481	0.0276565529
H	-0.5514181416	3.9432435420	-0.6319345811
C	1.7083758878	4.9320454211	3.7533889623
H	2.6796673630	4.4625875489	3.9377349181
H	1.8617350974	5.7683880240	3.0683881612
H	1.3533893761	5.3313628384	4.7076797947
C	-3.2344827046	-3.0903632864	1.7810306902
C	-4.3504205569	-2.6053470095	2.7151742437
H	-4.1352706210	-1.6013292792	3.0980477885
H	-5.3202271786	-2.5857573293	2.2155578502
H	-4.4139752791	-3.2768792343	3.5769349632
C	-3.5784126040	-4.4867456628	1.2445723280
H	-2.8459281226	-4.8220887241	0.5003580582
H	-3.5687908047	-5.2072818612	2.0668761407
H	-4.5732583318	-4.5200374415	0.7922254640
C	-1.9321129291	-3.1888246387	2.5899432813
H	-1.0807388877	-3.4907928632	1.9661353694
H	-1.6738829806	-2.2411045639	3.0707774007
H	-2.0483421197	-3.9399193271	3.3776284311
Cu	0.3166606377	-1.0927293562	1.4732210154
Si	2.0236431787	-1.7102377390	3.0377270942
C	2.1834227068	-3.6004529289	3.3215710864
H	2.8374365135	-3.8218335227	4.1731450943
H	2.6063842629	-4.0821937247	2.4334719493
H	1.2124266103	-4.0720044985	3.5107892232
C	3.8145654860	-1.1464667697	2.6505072942
H	4.5067667893	-1.4204923290	3.4546901101
H	3.8797387243	-0.0636369540	2.5023341624
H	4.1715376030	-1.6226301910	1.7307911296
C	1.7303001379	-1.0353010865	4.8067630600
C	2.2348121286	0.2074291162	5.2195668710
C	0.9444596402	-1.7381806760	5.7352315088
C	1.9763866751	0.7217515474	6.4899989890
H	2.8456768699	0.7914776401	4.5332122040
C	0.6708023517	-1.2314620659	7.0037477522
H	0.5325490615	-2.7075643446	5.4578683424
C	1.1880782680	0.0050684764	7.3881609996
H	2.3925798414	1.6832822765	6.7808899467
H	0.0590867780	-1.8023409068	7.6970099803
H	0.9838191307	0.4020631038	8.3779546805
C	1.5676441016	-1.7758493447	-0.4487968073
C	0.3753391113	-1.4347391760	-0.9926440518
C	0.0670778051	-0.0399247116	-1.4122845617

F	0.6279452679	0.8740248948	-0.6016616387
F	-1.2658139428	0.1861305937	-1.4203297497
F	0.4958410525	0.2316374375	-2.6566573972
C	2.0041773136	-3.1704583566	-0.2479049369
C	1.0877346579	-4.2146757240	-0.0717640736
C	3.3705103365	-3.4654404671	-0.2537044592
C	1.5277622294	-5.5204272140	0.0956949188
H	0.0225177447	-3.9984183434	-0.0433139102
C	3.8127411765	-4.7754632598	-0.0911880445
H	4.0886634774	-2.6627429601	-0.3942980562
C	2.8936017397	-5.8054405504	0.0865196521
H	0.8066405752	-6.3172172502	0.2457764551
H	4.8763929263	-4.9888562319	-0.0981412132
H	3.2373764669	-6.8250665627	0.2245139965
H	2.3214894773	-1.0056163898	-0.2927619692
H	-0.3388575301	-2.1796176052	-1.3275411728

TS_{2-3}

M06-2X/6-31G(d,p) Electronic E: -3827.621632 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -3826.982867 a.u.

M06-2X/cc-pVTZ Electronic E: -3828.531076 a.u.

C	-3.7585091485	1.4394484421	0.0592972871
C	-1.6721084307	2.6402507983	0.7158490298
C	-2.6781980291	3.3365324742	1.6379678562
C	-4.6280730025	2.5400770233	0.5971019858
C	-1.8708135353	0.3075774324	-0.2828929282
H	-0.8586943955	2.2432370824	1.3354663132
H	-2.9119313306	2.6714732133	2.4833361970
H	-5.3602717556	2.8466509042	-0.1520230812
N	-4.1495064741	0.3139592477	-0.4585129414
N	-2.9731599199	-0.3563903553	-0.6656446345
N	-2.3905965115	1.4791486883	0.1749150444
H	-2.2671910617	4.2636063662	2.0351082811
H	-5.1671688974	2.1568691310	1.4758085419
O	-3.8636796634	3.6739557135	0.9395357964
C	-2.9625828118	-1.6772354266	-1.2214305651
C	-3.3569704282	-2.7400826336	-0.4039987442
C	-2.5181653015	-1.8505049123	-2.5365830343
C	-3.2718425103	-4.0264569705	-0.9340580908
C	-2.4316457181	-3.1588348689	-3.0114738969
C	-2.7914328509	-4.2543202613	-2.2251741718
H	-3.5715546514	-4.8706125875	-0.3172718234
H	-2.0753148666	-3.3247356865	-4.0252771747
C	-2.1435887445	-0.6796993234	-3.4062817578

H	-2.8178302626	0.1659365305	-3.2428293449
H	-1.1228135285	-0.3483455993	-3.1851333211
H	-2.1923717146	-0.9623841790	-4.4595122873
C	-3.8377205729	-2.4919911917	1.0005869728
H	-3.1233995238	-1.8714795269	1.5522353083
H	-4.7940892668	-1.9613441983	0.9983635279
H	-3.9625874435	-3.4340307595	1.5367730064
C	-2.6265435589	-5.6552272388	-2.7522962791
H	-3.2195085526	-6.3697316131	-2.1769499266
H	-2.9248593291	-5.7220462940	-3.8013668593
H	-1.5758832356	-5.9584091426	-2.6861681370
C	-1.0383609452	3.5188404743	-0.4005932663
C	-2.0596023346	3.9445080018	-1.4624695490
H	-2.5165038817	3.0719912413	-1.9434494406
H	-2.8523029992	4.5653254313	-1.0414608193
H	-1.5465387088	4.5140661246	-2.2434460690
C	-0.4259515502	4.7629285120	0.2583256032
H	0.2282577937	4.4909725163	1.0951633810
H	0.1802367256	5.3021610145	-0.4743670333
H	-1.1910096655	5.4539564234	0.6229749993
C	0.0865211969	2.7301178759	-1.0838274993
H	0.8052192153	2.3358491936	-0.3569507920
H	-0.2922398250	1.8912686527	-1.6750165260
H	0.6356662088	3.3831274103	-1.7689021496
Cu	-0.0444192378	-0.4734629319	-0.5037865087
Si	1.2140692963	-0.9990970933	1.5642057221
C	1.9667481064	0.7272716994	1.8200150142
H	2.5714392436	0.7610880469	2.7321184805
H	1.1859801702	1.4900294647	1.9056984242
H	2.6032398061	1.0039055491	0.9733583784
C	-0.3042117808	-1.2404976768	2.6881478398
H	-0.0174944832	-1.3144778339	3.7429039431
H	-0.8379648837	-2.1579052261	2.4173161887
H	-1.0026102350	-0.4056245226	2.5669694201
C	2.4962655041	-2.2359095033	2.1867377634
C	2.1119879084	-3.4634296203	2.7452120541
C	3.8686127385	-1.9921659396	2.0324365724
C	3.0551314943	-4.4157558911	3.1193804754
H	1.0554762879	-3.6927688211	2.8667921967
C	4.8204209987	-2.9408633771	2.4027905312
H	4.2056629603	-1.0456410508	1.6122506763
C	4.4134523986	-4.1579351971	2.9433919760
H	2.7318799049	-5.3633068755	3.5398840888
H	5.8774778966	-2.7302188530	2.2705036821

H	5.1514140837	-4.9009993352	3.2298356329
C	1.6986471439	-1.6809347809	-0.6629442681
C	1.2385859372	-1.1372656562	-1.9632174561
H	0.8741435697	-1.8551204214	-2.6918853887
C	2.0543015904	-0.0682125664	-2.5341054390
F	2.3925445252	0.8666152412	-1.5961585386
F	1.4384458966	0.5976560397	-3.5397406167
F	3.2550356481	-0.4506411509	-3.0628881010
H	2.7123712567	-1.3716937791	-0.3854785867
C	1.5067815019	-3.1620362647	-0.5291474115
C	0.2284339989	-3.7205839498	-0.4365964991
C	2.6132705032	-4.0162318033	-0.5197154039
C	0.0604349578	-5.0978089421	-0.3168414785
H	-0.6461150388	-3.0695980494	-0.4397207852
C	2.4473713614	-5.3924345292	-0.3989503929
H	3.6119002845	-3.5922262191	-0.5781467906
C	1.1703541735	-5.9395570822	-0.2937908784
H	-0.9421282898	-5.5076727904	-0.2304985338
H	3.3203504983	-6.0374141303	-0.3748866609
H	1.0413801014	-7.0122303270	-0.1897403102

$TS_{3\text{-}R\text{-}3ba}$

M06-2X/6-31G(d,p) Electronic E: -3827.642181 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -3827.004783 a.u.

M06-2X/cc-pVTZ Electronic E: -3828.552587 a.u.

C	-3.4672639901	0.4953598769	-1.0712106467
C	-2.7387836084	-1.8900948754	-1.1470931345
C	-3.7184311924	-1.8761577672	-2.3245464273
C	-4.7107881560	0.1973766227	-1.8600987833
C	-1.4722383546	0.0861945387	-0.1728136936
H	-1.7792198865	-2.2798073692	-1.5080540639
H	-3.2371172551	-1.3897670880	-3.1864490894
H	-5.5855096295	0.6184468795	-1.3615363380
N	-3.0749313631	1.6520900549	-0.6250257111
N	-1.8531027968	1.3695031571	-0.0758062000
N	-2.5287170754	-0.4748883730	-0.8152771141
H	-3.9976301641	-2.8877237547	-2.6147037583
H	-4.6162234385	0.6626609993	-2.8521801198
O	-4.9127050150	-1.1935843356	-1.9838987792
C	-1.0404878204	2.3779101163	0.5425258832
C	-0.3489793686	3.2667588326	-0.2868653447
C	-0.8934853733	2.3641779307	1.9325795012
C	0.5257812765	4.1659003181	0.3162141532
C	-0.0081961645	3.2897400156	2.4891464125

C	0.7120294248	4.1863796801	1.7013386842
H	1.0858972791	4.8561606068	-0.3097358399
H	0.1312943960	3.2935639417	3.5669879017
C	-1.6218762387	1.3729802260	2.8038968828
H	-2.6284898430	1.1756211450	2.4254032557
H	-1.0789293498	0.4210883903	2.8581855351
H	-1.7050270135	1.7620990614	3.8206284115
C	-0.5283380214	3.2166060174	-1.7805928613
H	-0.2908362144	2.2178840568	-2.1670114087
H	-1.5628459060	3.4330960112	-2.0609233678
H	0.1251345199	3.9408634632	-2.2699809007
C	1.7040225186	5.1338037487	2.3243510032
H	2.7082686200	4.6982644729	2.3073238973
H	1.7448299850	6.0796440819	1.7792229008
H	1.4505014480	5.3441437577	3.3654900111
C	-3.1699295180	-2.7225080070	0.0993798763
C	-4.2397064327	-2.0034313604	0.9315525108
H	-3.8534841781	-1.0672249403	1.3487355639
H	-5.1329475278	-1.7868798908	0.3412581077
H	-4.5271204778	-2.6405729516	1.7733606129
C	-3.7195876133	-4.0739942117	-0.3776110656
H	-3.0274173708	-4.5690277585	-1.0687673652
H	-3.8573744392	-4.7344881415	0.4825816243
H	-4.6897010604	-3.9658712027	-0.8713346949
C	-1.9461316563	-2.9841614676	0.9902754610
H	-1.1450008224	-3.4834727110	0.4321190386
H	-1.5375222562	-2.0724479317	1.4343835334
H	-2.2322545353	-3.6426107251	1.8162468841
Cu	0.2380783927	-0.4215523060	0.7520351514
Si	3.1446346341	-1.9364568836	0.0216666633
C	2.8136283336	-3.1578086930	1.4067764961
H	2.7051957490	-4.1634609281	0.9877434817
H	1.8901652110	-2.8793595884	1.9239620152
H	3.6165165659	-3.1764971261	2.1482902637
C	1.6963414760	-2.0230434774	-1.1955098847
H	1.8656349257	-2.8556763733	-1.8864417998
H	1.5748172098	-1.1113540217	-1.7883660053
H	0.7515206810	-2.2297590463	-0.6758643549
C	4.7156871643	-2.4250338001	-0.8990039627
C	4.9078374381	-2.0663738731	-2.2423731057
C	5.7480434644	-3.1219435090	-0.2562583335
C	6.0828900776	-2.3868702666	-2.9160560807
H	4.1320548586	-1.5116295919	-2.7677877587
C	6.9285607363	-3.4462143276	-0.9227957612

H	5.6307365708	-3.4218571405	0.7827935634
C	7.0967041298	-3.0783227025	-2.2550621524
H	6.2103522439	-2.0959581530	-3.9543353023
H	7.7142995099	-3.9870605957	-0.4041844105
H	8.0144714044	-3.3299369101	-2.7777276789
C	3.3737754751	-0.1342724181	0.6613346153
C	2.1961777250	0.3999741429	1.4643244110
H	1.9119254793	1.4430787556	1.3346470823
C	1.9047034990	-0.0958822021	2.7132664661
F	0.4926298261	-1.2605997450	2.6357935308
F	1.3220913261	0.6763608665	3.6188842958
F	2.6970325671	-0.9775076832	3.3027180266
H	4.2822188319	-0.1618611999	1.2835591513
C	3.6764976933	0.7366528869	-0.5363066653
C	2.6643584755	1.3694533328	-1.2712484470
C	4.9981258896	0.8966605514	-0.9729463904
C	2.9635579480	2.1213068815	-2.4054894429
H	1.6302460788	1.2765332033	-0.9456506870
C	5.2996284654	1.6494803477	-2.1027088208
H	5.7981097488	0.4102889230	-0.4202419605
C	4.2819701649	2.2651784637	-2.8284108338
H	2.1597829908	2.5982943034	-2.9590050797
H	6.3336895668	1.7543631753	-2.4164221936
H	4.5148831305	2.8544655879	-3.7094750405

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M06-2X/6-31G(d,p) Electronic E: -1147.461559 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1147.206358 a.u.

M06-2X/cc-pVTZ Electronic E: -1147.800961 a.u.

Si	2.2313573796	-1.9353522905	-1.1909295063
C	1.2011597374	-3.4518190200	-0.7777984070
H	1.0237421441	-4.0550834148	-1.6732116012
H	0.2280756436	-3.1541601132	-0.3766254813
H	1.6897954507	-4.0825014622	-0.0296204105
C	1.2841649000	-0.7907040479	-2.3424624051
H	0.9599135108	-1.3419281977	-3.2300048369
H	1.9003528925	0.0490196453	-2.6757338334
H	0.3927569376	-0.3889149144	-1.8500938108
C	3.8541619553	-2.4507949461	-1.9906495757
C	4.7162554257	-1.4947127003	-2.5535630538
C	4.2491090960	-3.7951145275	-2.0369022189
C	5.9239582717	-1.8676305304	-3.1354287016
H	4.4489764141	-0.4395103799	-2.5257374242
C	5.4567707556	-4.1755681625	-2.6195917986

H	3.6045238077	-4.5624346421	-1.6143476084
C	6.2957105281	-3.2106363813	-3.1695965684
H	6.5761969721	-1.1112554586	-3.5609018465
H	5.7410983057	-5.2229717350	-2.6449777115
H	7.2370655112	-3.5031996541	-3.6244457087
C	2.6145118335	-1.0078446266	0.4509345341
C	1.3296287903	-0.5509363436	1.0829073828
H	0.9200485931	0.4279843017	0.8645018236
C	0.6256036977	-1.3105205242	1.9030869700
F	0.9716682864	-2.5359716966	2.2731699936
F	-0.5160244903	-0.9705863511	2.4774453177
H	3.0824042947	-1.7562526522	1.1020289050
C	3.6078828858	0.0979422911	0.1893803500
C	3.2230035665	1.3112526933	-0.3936214092
C	4.9681474801	-0.1127346597	0.4378147293
C	4.1689860668	2.2790322003	-0.7222784469
H	2.1743702337	1.5018750982	-0.6072066797
C	5.9158932529	0.8515236587	0.1093084632
H	5.2858343024	-1.0535590310	0.8795303142
C	5.5207849709	2.0523515780	-0.4750033077
H	3.8472021345	3.2118959663	-1.1746260749
H	6.9658265187	0.6621301006	0.3092410817
H	6.2579959528	2.8056019300	-0.7327054378

NHC-CuF （L*CuF）

M06-2X/6-31G(d,p) Electronic E: -2680.169462 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2679.812665 a.u.

M06-2X/cc-pVTZ Electronic E: -2680.767258 a.u.

C	0.4384403210	1.8873216480	-1.2945846443
C	-1.8157319615	2.6912127776	-2.0042210434
C	-0.9419095330	3.8019850829	-2.5962054764
C	1.0350476237	3.2587333604	-1.4382471759
C	-1.1006463343	0.2952001253	-1.5302580924
H	-2.4399018151	2.2767135196	-2.8049732446
H	-0.4606024697	3.4304584711	-3.5132791562
H	1.5689441869	3.5395122811	-0.5284798718
N	1.0590620415	0.7888669943	-0.9829653907
N	0.0913121669	-0.1708030728	-1.1319184064
N	-0.8688944447	1.6340569812	-1.6201775724
H	-1.5391238426	4.6757744879	-2.8528278272
H	1.7531286609	3.2363914182	-2.2706790526
O	0.0390581682	4.2301764377	-1.6670305336
C	0.3956223551	-1.5406330316	-0.8345199814
C	0.4863247882	-2.4598580445	-1.8810688717

C	0.5783535978	-1.8953883696	0.5058258796
C	0.7744437435	-3.7840180796	-1.5479473302
C	0.8689289638	-3.2275646648	0.7857856296
C	0.9724616730	-4.1836389130	-0.2273689541
H	0.8460649639	-4.5198002809	-2.3448573157
H	1.0086327031	-3.5289273498	1.8211206687
C	0.4465643072	-0.8689943883	1.5992668566
H	1.2629890693	-0.1427673715	1.5561810341
H	-0.4906905026	-0.3111444060	1.4983990153
H	0.4579563774	-1.3486499595	2.5790904746
C	0.2673596351	-2.0481502640	-3.3126489676
H	-0.7955763064	-1.8693355474	-3.5082478700
H	0.8031078691	-1.1236677945	-3.5458594623
H	0.6111603451	-2.8302691286	-3.9912651184
C	1.3123004042	-5.6135683975	0.1047124950
H	0.8113965286	-5.9341288976	1.0213771893
H	1.0182950698	-6.2878373529	-0.7021616898
H	2.3897446231	-5.7283327962	0.2608867277
C	-2.7520634136	3.1082748278	-0.8323795921
C	-1.9730740126	3.5026057131	0.4292543343
H	-1.3391976732	2.6788268631	0.7776443050
H	-1.3436734592	4.3784281823	0.2636666624
H	-2.6824334138	3.7284611647	1.2314063240
C	-3.6074167322	4.2942175065	-1.3010272574
H	-4.0978098617	4.0811583709	-2.2575137411
H	-4.3899899270	4.4927824487	-0.5639199257
H	-3.0178405844	5.2090249131	-1.4061585141
C	-3.6913865167	1.9447218810	-0.4804945255
H	-4.2300230414	1.5618941009	-1.3549854983
H	-3.1498045116	1.1092517427	-0.0275645173
H	-4.4315619534	2.2874149229	0.2488502654
Cu	-2.7661154444	-0.6274996147	-2.0021504341
F	-4.3473748911	-1.3082527779	-2.5028175172

Int2'

M06-2X/6-31G(d,p) Electronic E: -3827.639736 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -3827.002315 a.u.

M06-2X/cc-pVTZ Electronic E: -3828.548578 a.u.

C	-0.3203753230	2.4506833385	-1.1105215730
C	-2.5944045091	3.0880046155	-1.9154644656
C	-1.7307537987	3.9193631170	-2.8686759233
C	0.3023772449	3.6742095559	-1.7195854392
C	-1.9231977180	0.9475798681	-0.7094206885
H	-3.2595297353	2.4546228241	-2.5172013264

H	-1.3167192163	3.2577568541	-3.6443337326
H	0.9163979339	4.1969368302	-0.9838580833
N	0.2943301642	1.4768496574	-0.5120562389
N	-0.7103271955	0.5706470973	-0.2743877906
N	-1.6582987586	2.1783685671	-1.2412234157
H	-2.3216690495	4.6931287841	-3.3573725628
H	0.9486840459	3.3556526648	-2.5502981973
O	-0.6830262095	4.5740299355	-2.1728842931
C	-0.3868085470	-0.6568357692	0.3932661195
C	-0.2911308924	-1.8299280963	-0.3566111196
C	-0.1628778146	-0.6184474072	1.7708601644
C	0.0194136464	-3.0058185341	0.3248348537
C	0.1449827645	-1.8176955017	2.4080586842
C	0.2329483039	-3.0192737580	1.7030749302
H	0.0981394470	-3.9330073036	-0.2375296933
H	0.3150920403	-1.8140252086	3.4819383919
C	-0.2701196814	0.6769213804	2.5282744948
H	0.5224232961	1.3701071050	2.2319536875
H	-1.2287635993	1.1625687103	2.3209533289
H	-0.1975531453	0.5015820932	3.6028835663
C	-0.5258646147	-1.8224802202	-1.8424591086
H	-1.5839437156	-1.6441257492	-2.0674282680
H	0.0466816817	-1.0268839191	-2.3290862887
H	-0.2387245713	-2.7784752165	-2.2839937524
C	0.5284489930	-4.3099990903	2.4224991222
H	-0.3977735956	-4.7721636677	2.7788857986
H	1.0231608476	-5.0264675477	1.7628906104
H	1.1687682046	-4.1412196065	3.2913833488
C	-3.4755183903	3.8932375807	-0.9195709166
C	-2.6430121698	4.7141798277	0.0725381481
H	-1.9554896031	4.0731290470	0.6363916457
H	-2.0587287115	5.4867496730	-0.4293959313
H	-3.3115269765	5.1943665242	0.7941353909
C	-4.3885612071	4.8256823600	-1.7288816236
H	-4.9172389500	4.2820194544	-2.5207555358
H	-5.1395029260	5.2676106737	-1.0680513503
H	-3.8326042950	5.6482800645	-2.1863845251
C	-4.3581969031	2.9186907561	-0.1269980709
H	-4.9352332016	2.2621253980	-0.7936991801
H	-3.7620960199	2.2926423416	0.5423325615
H	-5.0720763927	3.4821497769	0.4828499978
Cu	-3.6763639907	-0.0727974600	-1.0876591239
Si	-3.9016090082	-0.4428700862	-3.4628226421
C	-3.8468349105	-2.2645564633	-4.0533872669

H	-3.8355834650	-2.3415890270	-5.1470218408
H	-2.9445660684	-2.7635483332	-3.6842161912
H	-4.7067815554	-2.8355982215	-3.6858744587
C	-2.4902125312	0.3987832066	-4.4650058810
H	-2.4579763939	0.0364979489	-5.4987853784
H	-2.6455770124	1.4831595729	-4.5098995404
H	-1.5077929292	0.2208859399	-4.0114205114
C	-5.4786035172	0.2829327817	-4.2702765037
C	-5.9940313001	1.5086291222	-3.8216566767
C	-6.1751025719	-0.3535413098	-5.3077206903
C	-7.1275340077	2.0864898697	-4.3848510828
H	-5.5105599340	2.0124243037	-2.9842010938
C	-7.3175066069	0.2089581786	-5.8770915764
H	-5.8224604872	-1.3123406626	-5.6817080273
C	-7.7966447411	1.4336369429	-5.4186596684
H	-7.5027896125	3.0328481251	-4.0042278716
H	-7.8351918856	-0.3095186996	-6.6796145441
H	-8.6874631644	1.8726272333	-5.8581143953
C	-5.4499311231	-1.0503236185	-0.3347587892
C	-4.7772910177	-0.5354100781	0.7485894108
H	-5.0868983082	0.3779253110	1.2448284584
C	-3.8465376598	-1.3762232639	1.5466525091
F	-3.1242556486	-2.2108331039	0.7733769900
F	-2.9860197000	-0.6207366802	2.2512235929
F	-4.4847824773	-2.1524052953	2.4451210221
H	-5.2163289778	-2.0677961508	-0.6461611005
C	-6.6759941097	-0.4756762423	-0.9263942116
C	-7.2851503129	0.6812128776	-0.4237695075
C	-7.2734960093	-1.1282054189	-2.0113889007
C	-8.4515075227	1.1728867960	-0.9992212573
H	-6.8592737317	1.1975107971	0.4314171519
C	-8.4415742599	-0.6410161591	-2.5830525140
H	-6.7981734367	-2.0162698497	-2.4208860305
C	-9.0344472581	0.5137828418	-2.0793090853
H	-8.9106439958	2.0703953241	-0.5969153891
H	-8.8755184923	-1.1500209012	-3.4371441760
H	-9.9409530114	0.9026480312	-2.5316955786

Int3'

M06-2X/6-31G(d,p) Electronic E: -3827.673923 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -3827.038169 a.u.

M06-2X/cc-pVTZ Electronic E: -3828.585865 a.u.

C	-0.0576867634	3.0082334805	-1.1495762352
C	-2.1538755016	4.3291704803	-0.8439246048

C	-1.3376297209	5.3246618980	-1.6755029961
C	0.7393784539	4.2412988676	-1.4667231414
C	-1.8921019288	1.7993444651	-0.7965042981
H	-3.1157849909	4.1680330699	-1.3457611974
H	-1.3490913029	5.0072830795	-2.7290234849
H	1.6425911343	4.2778110094	-0.8552300090
N	0.3630176864	1.7784139037	-1.1402651948
N	-0.7820363690	1.0594088238	-0.9173785731
N	-1.4116795532	3.0638123857	-0.9339534728
H	-1.7620147583	6.3257639295	-1.6149577472
H	1.0354041642	4.1996069448	-2.5250301955
O	-0.0039038224	5.4106623770	-1.2050374371
C	-0.7286353786	-0.3690344372	-0.7962594224
C	-0.4799143768	-1.1225507180	-1.9483545706
C	-0.9288932424	-0.9475506235	0.4606692631
C	-0.4318523799	-2.5071047584	-1.8141486414
C	-0.8695829104	-2.3396809161	0.5407771034
C	-0.6296372403	-3.1314544807	-0.5805461648
H	-0.2479799021	-3.1147710049	-2.6968707391
H	-1.0287108169	-2.8142579208	1.5058189556
C	-1.2333562344	-0.1252246716	1.6860706689
H	-0.7167055935	0.8381337869	1.6696752070
H	-2.3096247903	0.0698652742	1.7660038701
H	-0.9301955783	-0.6645124775	2.5854776619
C	-0.2823262096	-0.4515808554	-3.2813961441
H	-1.1045431214	0.2391254724	-3.4956345682
H	0.6439569696	0.1295308529	-3.2946494952
H	-0.2405499094	-1.1931481193	-4.0806506131
C	-0.6428375529	-4.6335697053	-0.4769280461
H	-1.6529783837	-5.0129859866	-0.6653645004
H	0.0256617241	-5.0894671686	-1.2107158704
H	-0.3442598742	-4.9661415569	0.5195615007
C	-2.4431843082	4.7421261148	0.6296318126
C	-1.1753114459	4.7643160447	1.4928801248
H	-0.6927713146	3.7805974819	1.5146881751
H	-0.4517103841	5.4986161395	1.1352794293
H	-1.4480653993	5.0152305015	2.5224627024
C	-3.0833529579	6.1377627793	0.6198354571
H	-3.9291798996	6.1865033497	-0.0754089590
H	-3.4606082327	6.3732110555	1.6184808998
H	-2.3640936560	6.9157571981	0.3499440758
C	-3.4424268423	3.7568591917	1.2547671813
H	-4.3433489388	3.6432448563	0.6396918982
H	-3.0061393980	2.7646283370	1.4036051958

H	-3.7514594105	4.1260003314	2.2371575729
Cu	-3.7276689976	1.0952627593	-0.4314151195
Si	-5.3068850017	-1.4962217479	-2.1055161317
C	-3.9963293979	-2.5229784892	-1.2352810756
H	-3.4468807680	-3.1066693488	-1.9817562835
H	-3.2828955970	-1.8727012909	-0.7198658292
H	-4.4148370336	-3.2058187937	-0.4918180532
C	-4.4229988782	-0.4061120184	-3.3680062681
H	-3.8634003539	-1.0331604051	-4.0704511770
H	-5.1142105594	0.2243768612	-3.9339757135
H	-3.7022937567	0.2520248265	-2.8670985489
C	-6.4729644244	-2.6696907904	-3.0170599989
C	-6.8902891892	-2.4398872014	-4.3352213641
C	-7.0061024239	-3.7837222535	-2.3510798482
C	-7.8014277949	-3.2850467922	-4.9653684431
H	-6.5063708250	-1.5793848546	-4.8784597831
C	-7.9198192728	-4.6325507672	-2.9712046968
H	-6.7068398893	-3.9925945307	-1.3253582759
C	-8.3187553100	-4.3832895198	-4.2828161812
H	-8.1108876326	-3.0851439736	-5.9868376013
H	-8.3201303366	-5.4870666856	-2.4339767364
H	-9.0307398919	-5.0423397252	-4.7701847512
C	-6.3789755707	-0.4220353500	-0.9348879907
C	-5.5608248130	0.4195993694	0.0751002624
H	-6.1538223976	1.3109638774	0.3298369875
C	-5.4186194236	-0.2816872758	1.3726517504
F	-4.7105734672	-1.4376101671	1.3048233637
F	-4.7769807547	0.4891917581	2.2955558021
F	-6.5901912463	-0.6364066399	1.9714901261
H	-7.0557126257	-1.1124675935	-0.4063495514
C	-7.2436065491	0.4248962067	-1.8409627361
C	-6.8600818381	1.7132550057	-2.2380117889
C	-8.4399980956	-0.0871505763	-2.3628306074
C	-7.6388838560	2.4578195008	-3.1206475464
H	-5.9354135137	2.1325728254	-1.8492395468
C	-9.2207273004	0.6545830675	-3.2433461937
H	-8.7548630405	-1.0869441260	-2.0737959795
C	-8.8240203877	1.9333945883	-3.6288075574
H	-7.3186256987	3.4547149316	-3.4096077292
H	-10.1441466651	0.2315948862	-3.6271541992
H	-9.4335081598	2.5150003709	-4.3130444190

$TS_{1'-2'}$

M06-2X/6-31G(d,p) Electronic E: -3827.635964 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -3826.999067 a.u.

M06-2X/cc-pVTZ Electronic E: -3828.545769 a.u.

C	-0.3249557226	2.5901017815	-0.7973438756
C	-2.5540298468	3.1325329771	-1.7879024668
C	-1.6671865808	4.0786669414	-2.6040089089
C	0.2684841371	3.8835672059	-1.2759903281
C	-1.8523481010	0.9636757516	-0.6656302471
H	-3.1161777455	2.4938038158	-2.4834003069
H	-1.1467736433	3.5025915579	-3.3836163690
H	0.7729117510	4.4017204250	-0.4582470835
N	0.2947164157	1.6135367625	-0.2081701168
N	-0.6633543515	0.6312717023	-0.1366364001
N	-1.6220802652	2.2462589789	-1.0775906708
H	-2.2636041851	4.8509730190	-3.0888653734
H	1.0113704292	3.6541723132	-2.0536487115
O	-0.7278413504	4.7451769450	-1.7770041751
C	-0.3234407057	-0.6215859564	0.4706048238
C	-0.2486964342	-1.7692023758	-0.3192055357
C	-0.0761017325	-0.6362181258	1.8490445028
C	0.0632979894	-2.9715376691	0.3206884179
C	0.2299087743	-1.8579831761	2.4381850237
C	0.2977997400	-3.0371938973	1.6908664525
H	0.1265208372	-3.8782623133	-0.2760040002
H	0.4161696062	-1.8930989509	3.5090727708
C	-0.1439563760	0.6278976083	2.6634162006
H	0.7261051628	1.2619129240	2.4713188571
H	-1.0346678455	1.2093697045	2.4090236731
H	-0.1758394292	0.3930824896	3.7288049389
C	-0.5070925803	-1.7459400947	-1.8021678130
H	-1.5791264242	-1.8453701446	-2.0141096850
H	-0.1749215730	-0.8108270461	-2.2602113172
H	0.0088163805	-2.5761828644	-2.2889629059
C	0.6078565524	-4.3482088964	2.3660216504
H	-0.2388595575	-4.6788829959	2.9755638108
H	0.8204357729	-5.1302870807	1.6344238486
H	1.4715853252	-4.2543708833	3.0296898549
C	-3.5767070045	3.8184909454	-0.8396239432
C	-2.9016389283	4.7229839215	0.1987806376
H	-2.1610851124	4.1670770581	0.7855290002
H	-2.3999465341	5.5739221233	-0.2642585328
H	-3.6584920247	5.0993262827	0.8942865770
C	-4.5459051671	4.6442760276	-1.6981411737
H	-4.9812305622	4.0407061899	-2.5029861589
H	-5.3652883506	5.0124079715	-1.0742155546

H	-4.0608092904	5.5164115266	-2.1446178589
C	-4.3826284380	2.7450102205	-0.0958392895
H	-4.8551776930	2.0349523603	-0.7889213305
H	-3.7554529395	2.1774040061	0.5968417833
H	-5.1787241485	3.2263166448	0.4828076180
Cu	-3.4406404676	-0.1031452133	-1.4400465372
Si	-4.0859393762	-0.7693892123	-3.6364065316
C	-4.3872350921	-2.6296221386	-3.9997983939
H	-4.5839849692	-2.8194735901	-5.0616563438
H	-3.4877099291	-3.1968179803	-3.7334343096
H	-5.2171107753	-3.0550205737	-3.4261809088
C	-2.7191587154	-0.3497385653	-4.9220396027
H	-3.0218383825	-0.6262414640	-5.9390288239
H	-2.4876093786	0.7213037472	-4.9228183469
H	-1.7920785845	-0.8869270019	-4.6893345466
C	-5.6186267306	0.1450007705	-4.3440985775
C	-6.0171065202	1.3737934835	-3.7989863229
C	-6.3773561850	-0.3443125394	-5.4178813274
C	-7.0991789478	2.0928833860	-4.2997401228
H	-5.4767164626	1.7638167358	-2.9362680969
C	-7.4711356982	0.3572330762	-5.9238534571
H	-6.1111344451	-1.2967757317	-5.8725026586
C	-7.8341921391	1.5821466082	-5.3674483811
H	-7.3832223639	3.0382966673	-3.8442526829
H	-8.0404942826	-0.0499905796	-6.7551205497
H	-8.6858614374	2.1305327197	-5.7593053325
C	-5.6350439805	-1.0026028939	-0.1982272978
C	-5.0052215479	-0.4558661030	0.8534265877
H	-5.3345954713	0.4585970278	1.3349144025
C	-3.8486581199	-1.1196133382	1.5175877457
F	-3.1691476697	-1.9228606057	0.6777473426
F	-2.9846616169	-0.2066979484	1.9986526819
F	-4.2174536252	-1.8780021572	2.5637885185
H	-5.2642367089	-1.9484185900	-0.5913585666
C	-6.8359248880	-0.4690047895	-0.8591724625
C	-7.4575701729	0.7220015759	-0.4580168860
C	-7.3822048281	-1.1849577311	-1.9292272445
C	-8.5915936209	1.1788037218	-1.1156985294
H	-7.0575902389	1.2951245284	0.3731167561
C	-8.5169380799	-0.7279287464	-2.5894478465
H	-6.8957413853	-2.0994700381	-2.2568019899
C	-9.1236637502	0.4558608905	-2.1839576381
H	-9.0622014134	2.1034412851	-0.7972022586
H	-8.9097214440	-1.2828808350	-3.4345338196

H	-10.0011827854	0.8237144319	-2.7057719501

$TS_{2'-3'}$

M06-2X/6-31G(d,p) Electronic E: -3827.617139 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -3826.978362 a.u.

M06-2X/cc-pVTZ Electronic E: -3828.527818 a.u.

C	-3.3589178155	2.0116017293	1.0110473631
C	-1.3076538231	3.1996189430	0.2057348859
C	-1.7525257723	4.1805975122	1.2975444284
C	-3.9053238313	3.2613287524	1.6382625780
C	-1.7854706947	0.7133148951	0.1208078463
H	-0.2697530453	2.8999206386	0.4022352299
H	-1.4486160291	3.7877396070	2.2797311778
H	-4.9373251357	3.4327540062	1.3271909041
N	-3.8589780352	0.8136216813	1.0694986701
N	-2.8772811049	0.0378040560	0.5072874207
N	-2.1205157710	1.9980356567	0.4217298542
H	-1.2892481322	5.1573412713	1.1576023616
H	-3.8878636416	3.1285700721	2.7299292743
O	-3.1536348278	4.3917933506	1.2614917710
C	-3.0368566146	-1.3813132953	0.3837319394
C	-3.0793195411	-2.1507301854	1.5501237796
C	-3.1054594092	-1.9382665952	-0.8978582258
C	-3.1652261651	-3.5339212344	1.4045973450
C	-3.1837299748	-3.3266711480	-0.9873905612
C	-3.2053338340	-4.1374040283	0.1468543386
H	-3.1885834068	-4.1546691363	2.2968585277
H	-3.2178640411	-3.7840261459	-1.9729228122
C	-3.0898284505	-1.0847172241	-2.1383574575
H	-3.7156932719	-0.1954085627	-2.0152045039
H	-2.0704023437	-0.7568882143	-2.3673631551
H	-3.4594587463	-1.6561723478	-2.9915041830
C	-3.0220335052	-1.5086695775	2.9116685559
H	-2.2322075721	-0.7511399156	2.9590346878
H	-3.9646060682	-1.0074711351	3.1484914216
H	-2.8220203913	-2.2592573958	3.6784001618
C	-3.2403258926	-5.6374009376	0.0114618256
H	-2.2361929164	-6.0249381663	-0.1878322787
H	-3.6067859933	-6.1109116982	0.9247714043
H	-3.8813825082	-5.9440655511	-0.8185734074
C	-1.3841362775	3.7376796384	-1.2523566526
C	-2.7609812867	4.3235856226	-1.5904683488
H	-3.5586995213	3.5936012261	-1.4126231729
H	-2.9845577670	5.2166838916	-1.0047683080

H	-2.7843966089	4.5879150587	-2.6521280675
C	-0.3079752599	4.8219515248	-1.4058968588
H	0.6885677035	4.4252699814	-1.1802630876
H	-0.2965825669	5.1827573683	-2.4380371520
H	-0.4904693866	5.6859067875	-0.7609054800
C	-1.0811031436	2.6163978304	-2.2556785896
H	-0.1239674466	2.1221701764	-2.0562960217
H	-1.8597835436	1.8488738829	-2.2596515973
H	-1.0276315567	3.0432182530	-3.2616641854
Cu	-0.0631939092	-0.0692251852	-0.4909436725
Si	1.4188981171	-0.3736092044	1.4643389880
C	0.6373655890	-1.9702060434	2.1139483747
H	0.8448189650	-2.1011091344	3.1811701064
H	-0.4467592159	-1.9653474250	1.9653831146
H	1.0190247398	-2.8427406072	1.5761367106
C	0.8052919495	1.0965944640	2.5168442671
H	1.1593389774	1.0056851798	3.5497233527
H	1.1703879164	2.0522833475	2.1247853271
H	-0.2896165902	1.1343214134	2.5247537102
C	3.2775790986	-0.4627169423	1.7885531296
C	4.0452141840	0.7049667322	1.9153229576
C	3.9568434462	-1.6891959229	1.8024281987
C	5.4305201023	0.6544962246	2.0308201086
H	3.5555780433	1.6761998586	1.8963595493
C	5.3446584070	-1.7500321449	1.9218642422
H	3.3970274096	-2.6185265386	1.7159019093
C	6.0849632640	-0.5763549350	2.0300607220
H	6.0020158198	1.5741918195	2.1133709141
H	5.8467692817	-2.7129259578	1.9287630763
H	7.1664005253	-0.6193406690	2.1160974194
C	1.8643360297	-0.8447176634	-0.8384861796
C	0.9334601123	-1.0988271810	-1.9628409841
H	1.1739244256	-0.6449157079	-2.9180636170
C	0.4425560302	-2.4766592767	-2.0473283472
F	-0.0250846378	-2.9156362377	-0.8428894258
F	-0.5608716535	-2.6403850767	-2.9394115694
F	1.3743166587	-3.4132125892	-2.4003640209
H	2.2648778746	-1.7575047393	-0.3820541343
C	2.9507623522	0.1425320634	-1.1408777089
C	2.7079800273	1.5177153281	-1.1726647313
C	4.2469196462	-0.3102922017	-1.4029790903
C	3.7281592507	2.4221448667	-1.4549043528
H	1.7106075337	1.8833325092	-0.9298487100
C	5.2731500806	0.5898671822	-1.6706102358

H	4.4518028911	-1.3766603228	-1.3705873116
C	5.0181317803	1.9596556785	-1.7001056057
H	3.5183033225	3.4875936442	-1.4694669413
H	6.2780119746	0.2199792419	-1.8493747585
H	5.8202141481	2.6608882337	-1.9064724270

$TS_{3'\text{-}S\text{-}3ba}$

M06-2X/6-31G(d,p) Electronic E: -3827.642250 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -3827.005224 a.u.

M06-2X/cc-pVTZ Electronic E: -3828.553627 a.u.

C	-0.3723414895	3.1310850397	-1.2969223871
C	-2.4306948305	4.2982714345	-0.5128893761
C	-1.7699664553	5.4303664696	-1.3059404999
C	0.3439951469	4.4316691874	-1.5284125169
C	-2.1066276727	1.8003555898	-0.8686866486
H	-3.4535467356	4.1684268792	-0.8880402082
H	-1.9138697806	5.2467058657	-2.3813615087
H	1.3188704942	4.4206253199	-1.0377626340
N	0.0756732362	1.9336764903	-1.5278818831
N	-1.0058387808	1.1367561771	-1.2534565017
N	-1.6825763275	3.0924245134	-0.8912847139
H	-2.2140323778	6.3937821267	-1.0612145420
H	0.4988525094	4.5554394351	-2.6101334723
O	-0.3879363834	5.5189206673	-1.0056962971
C	-0.9003120694	-0.2892161145	-1.3674136996
C	-0.7766607344	-0.8438959197	-2.6450625167
C	-0.9425936570	-1.0629592255	-0.2036181876
C	-0.7031552296	-2.2308448563	-2.7429769198
C	-0.8824182548	-2.4492386411	-0.3587975726
C	-0.7701378674	-3.0484007814	-1.6125582167
H	-0.6112939805	-2.6842951957	-3.7270113187
H	-0.9201652302	-3.0744582074	0.5301138090
C	-1.0406502733	-0.4465544018	1.1674728943
H	-0.4673519005	0.4835193197	1.2235668721
H	-2.0807575996	-0.2230838631	1.4357787879
H	-0.6420031464	-1.1379309490	1.9128244030
C	-0.7674233322	0.0309039536	-3.8695974702
H	-1.6476688990	0.6833062990	-3.8815080950
H	0.1167855231	0.6734283347	-3.8915404934
H	-0.7814948291	-0.5782052375	-4.7748263273
C	-0.7531917505	-4.5491798400	-1.7462408438
H	-1.7744046003	-4.9391376373	-1.8134347508
H	-0.2193775811	-4.8616226916	-2.6464954031
H	-0.2782099561	-5.0179271477	-0.8814343694

C	-2.4981897511	4.4915270842	1.0337052805
C	-1.1357794951	4.2764492037	1.7054805127
H	-0.7780698019	3.2519706058	1.5565643673
H	-0.3838711014	4.9726482874	1.3280661563
H	-1.2405981652	4.4298610056	2.7838174937
C	-2.9890913742	5.9170699496	1.3239102080
H	-3.9076421950	6.1471480640	0.7715639157
H	-3.2099858634	6.0158912613	2.3898984684
H	-2.2325982351	6.6658495002	1.0722456299
C	-3.5049025808	3.5006819985	1.6380228863
H	-4.4804928508	3.5619539437	1.1402735934
H	-3.1655700228	2.4614731949	1.6022443194
H	-3.6624792579	3.7409068679	2.6941327608
Cu	-3.8530619573	1.0582224393	-0.2326714428
Si	-5.4734830112	-1.6468772403	-1.5622533008
C	-4.5929897067	-2.3957739486	-0.0818300534
H	-3.8061077155	-3.0651522620	-0.4461163167
H	-4.1413724639	-1.6303783829	0.5579450350
H	-5.2811598621	-2.9787411853	0.5370741119
C	-4.2089365564	-1.0617014389	-2.8274952828
H	-3.4846932589	-1.8560647501	-3.0349391723
H	-4.6845086190	-0.7526358462	-3.7626948341
H	-3.6441418412	-0.2005941713	-2.4474863830
C	-6.5941060577	-2.9483711477	-2.3432909528
C	-6.5660383514	-3.2484191639	-3.7114525650
C	-7.5421701580	-3.6125504312	-1.5493233418
C	-7.4466324889	-4.1745205573	-4.2679678561
H	-5.8491749251	-2.7480011808	-4.3578878080
C	-8.4285624959	-4.5358993435	-2.0970572763
H	-7.5943250503	-3.4035596526	-0.4817351180
C	-8.3807123190	-4.8184846272	-3.4610809493
H	-7.4060173913	-4.3909927591	-5.3311793641
H	-9.1545766174	-5.0356375912	-1.4630211973
H	-9.0696190956	-5.5382008757	-3.8924052113
C	-6.6312972158	-0.1751717009	-1.1030896931
C	-6.0637437104	0.8358684965	-0.1152521368
H	-6.2943974018	1.8871601889	-0.2736533963
C	-5.9231949431	0.5119846030	1.2118412169
F	-6.2800673501	-0.6742827196	1.6647401977
F	-4.1154285831	0.2238395079	1.6485772564
F	-6.0458332918	1.4333254992	2.1489472299
H	-7.5389722078	-0.6344979386	-0.6831565922
C	-7.0163974095	0.4653286774	-2.4167151267
C	-6.2741860971	1.5147166350	-2.9741187120

C	-8.0991983165	-0.0346882738	-3.1518877250
C	-6.6061891524	2.0482514024	-4.2165505638
H	-5.4148244124	1.9050121485	-2.4334585141
C	-8.4316434315	0.4963195931	-4.3942093984
H	-8.6815963747	-0.8558460680	-2.7411536105
C	-7.6877613729	1.5435882387	-4.9332609262
H	-6.0154374503	2.8622404758	-4.6262623264
H	-9.2780227659	0.0915427059	-4.9404420680
H	-7.9489840603	1.9617542853	-5.8999648167

S-3ba

M06-2X/6-31G(d,p) Electronic E: -1147.461579 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1147.205919 a.u.

M06-2X/cc-pVTZ Electronic E: -1147.800941 a.u.

Si	-5.3089444468	-1.5498409274	-1.9815592173
C	-4.3099151852	-2.6350163475	-0.8168427296
H	-3.7427153720	-3.3836330837	-1.3781642704
H	-3.5963355980	-2.0307365274	-0.2492237282
H	-4.9492748857	-3.1551110260	-0.0978979334
C	-4.1667117780	-0.5248705388	-3.0665751312
H	-3.4597652256	-1.1792998544	-3.5848693350
H	-4.7222369016	0.0361176633	-3.8232000854
H	-3.5906381423	0.1865267233	-2.4660499064
C	-6.4335793856	-2.6114707653	-3.0520882885
C	-7.1370649539	-2.0531156383	-4.1323746054
C	-6.6098835022	-3.9779141381	-2.7929047107
C	-7.9835174650	-2.8285498631	-4.9188405669
H	-7.0344968414	-0.9925356131	-4.3564785645
C	-7.4552309986	-4.7605656634	-3.5774298000
H	-6.0779758774	-4.4440975608	-1.9666955835
C	-8.1431545900	-4.1853253082	-4.6420288236
H	-8.5199432790	-2.3751742690	-5.7466246073
H	-7.5751804260	-5.8171145352	-3.3586544850
H	-8.8021986075	-4.7919298160	-5.2554726769
C	-6.3994761721	-0.3730039248	-0.9193340536
C	-5.5195440770	0.4997937874	-0.0686171182
H	-5.1953880337	1.4723843363	-0.4189294563
C	-5.0789936191	0.1277977400	1.1200054095
F	-5.3696482084	-1.0298787923	1.6978992856
F	-4.2943466235	0.8420467734	1.9091992794
H	-6.9815645180	-1.0335160855	-0.2651523432
C	-7.3499306026	0.3849453804	-1.8139002914
C	-6.9277591510	1.4813259543	-2.5754523954
C	-8.6656640996	-0.0620611536	-1.9735193625

C	-7.7926203068	2.1067732666	-3.4700033684
H	-5.9082523340	1.8465240542	-2.4811099298
C	-9.5318271190	0.5597676827	-2.8675415485
H	-9.0066980696	-0.9190914742	-1.3987858734
C	-9.0984596721	1.6469412180	-3.6223260672
H	-7.4428325021	2.9548372172	-4.0503705918
H	-10.5472976891	0.1917373707	-2.9750927675
H	-9.7719787507	2.1332937381	-4.3202727680

NaOH

M06-2X/6-31G(d,p) Electronic E: -238.064597 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -238.076852 a.u.

M06-2X/cc-pVTZ Electronic E: -238.133051 a.u.

Na	1.0323471015	0.5230435709	2.4821626689
O	-0.9720272612	0.6590819436	2.4905791487
H	-1.4978127903	1.4624859955	2.5195962724

IN1′ (NaOH)

M06-2X/6-31G(d,p) Electronic E: -1250.090147 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1249.775641 a.u.

M06-2X/cc-pVTZ Electronic E: -1250.417933 a.u.

Si	1.5811240376	-1.5606723349	0.0042600413
C	3.4643497375	-1.3662611547	-0.1175940980
H	3.8683322688	-1.9105082146	-0.9770357552
H	3.7622675342	-0.3174367243	-0.2085295855
H	3.9393229793	-1.7602848132	0.7869111573
C	1.2104598283	-3.4204851131	-0.1416587979
H	0.1399049179	-3.6410488070	-0.0708945782
H	1.5758441403	-3.8368766602	-1.0860093145
H	1.7021301318	-3.9580932315	0.6752095665
C	0.8386601053	-0.7463058798	-1.5637456643
C	1.2882107520	0.5121808050	-2.0058295119
C	-0.3317514779	-1.2459222452	-2.1628853418
C	0.6002585477	1.2420555150	-2.9773699417
H	2.1844241151	0.9422826489	-1.5641386097
C	-1.0314574877	-0.5245017207	-3.1327982708
H	-0.7145317979	-2.2170882762	-1.8562329081
C	-0.5710481441	0.7290488430	-3.5380274056
H	0.9762480223	2.2095185016	-3.2973273462
H	-1.9316287918	-0.9407678167	-3.5756789612
H	-1.1096088274	1.2927551278	-4.2932818261
C	0.9851585392	0.5249022141	3.5148712492
C	1.3433846430	1.5225530423	2.3674228029
B	0.5577716495	-0.5296813084	1.4895611584

O	1.0167222345	-0.7299169126	2.8493847313
O	0.6827838308	0.9470302243	1.2453203064
C	1.9918456551	0.5025922416	4.6584936843
H	2.0911276649	1.4930305054	5.1161130588
H	1.6543491388	-0.1964661657	5.4287301812
H	2.9718666843	0.1735631904	4.3084634279
C	-0.4219854314	0.7729885931	4.0709898973
H	-0.6961134006	-0.0758483963	4.7029991359
H	-0.4688533658	1.6854485404	4.6745264459
H	-1.1476999673	0.8360810096	3.2568342022
C	0.8345798987	2.9422178969	2.5797368337
H	1.2472598305	3.3718792114	3.4985268639
H	1.1434249566	3.5764684070	1.7424932029
H	-0.2556025148	2.9620710931	2.6470142533
C	2.8467134677	1.5406336882	2.0821390642
H	3.0188989669	2.0482849347	1.1276740422
H	3.4050420435	2.0678112636	2.8617600255
H	3.2259962919	0.5179796638	2.0053196408
Na	-0.9466805930	0.8514312046	-0.2645734631
O	-0.9083545083	-0.7778248973	1.2523137367
H	-1.1001298160	-1.7195874335	1.2844061701

$TS_{IN1'-IN2'}$ (NaOH)

M06-2X/6-31G(d,p) Electronic E: -1250.058090 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1249.744576 a.u.

M06-2X/cc-pVTZ Electronic E: -1250.387074 a.u.

B	-1.1135669293	-0.0081784684	1.0042215936
O	-1.1548248039	-1.0362005016	0.0577100718
O	-2.2480042446	0.7602149722	0.9950254071
C	-2.2739040710	-0.7533307660	-0.8157837087
C	-3.1923985406	0.1109993257	0.1171674776
C	-2.8873249623	-2.0689676304	-1.2664670545
H	-3.8022923828	-1.8850323545	-1.8376912675
H	-2.1843790947	-2.5971100400	-1.9167228533
H	-3.1267768839	-2.7118272256	-0.4177041383
C	-1.7423398749	0.0282375383	-2.0125407072
H	-0.9532281246	-0.5578804813	-2.4932394312
H	-2.5336367876	0.2111165164	-2.7447033251
H	-1.3129992861	0.9804531710	-1.6909213140
C	-4.0001441573	1.1729442094	-0.6100076219
H	-4.6640399227	0.7114781323	-1.3479650320
H	-4.6147446952	1.7180203661	0.1104272289
H	-3.3469642273	1.8863639353	-1.1137365528
C	-4.1021941237	-0.7425856550	0.9993839127

H	-4.5630694178	-0.0986603966	1.7516746337
H	-4.8939732998	-1.2213055550	0.4167325182
H	-3.5286072715	-1.5171894698	1.5170814407
Si	1.1173632908	1.8019061514	-0.1815060976
C	2.2926732607	3.0511519280	0.7160721986
H	2.4810070509	2.7742575491	1.7596241384
H	3.2628863463	3.1583769613	0.2157351890
H	1.8192109969	4.0390849586	0.7404565388
C	1.1474266512	2.4968406956	-1.9862383301
H	2.1672795557	2.6659897548	-2.3518338314
H	0.6413410893	1.8376412686	-2.7007127537
H	0.6188675895	3.4563171193	-2.0187463707
C	2.2898991246	0.2753583705	-0.3616508985
C	2.1931315292	-0.6134777970	-1.4567253407
C	3.1175946104	-0.1554161326	0.7007835739
C	2.8305037437	-1.8559523224	-1.4745065266
H	1.5871537813	-0.3265439849	-2.3141248952
C	3.7619772026	-1.3945247686	0.6968495214
H	3.2458369231	0.4941106165	1.5651305233
C	3.6084767509	-2.2659121867	-0.3868160481
H	2.7256183904	-2.5064624788	-2.3388241968
H	4.3886501414	-1.6820543536	1.5369174768
H	4.1076566059	-3.2293035118	-0.3960961247
O	-0.2240704300	-0.2174966105	2.0510920367
Na	0.9319953184	-1.7247922726	0.6822152862
H	0.1040585785	0.6279524234	2.3827576535

IN2′ (NaOH)

M06-2X/6-31G(d,p) Electronic E: -1250.073203 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1249.760761 a.u.

M06-2X/cc-pVTZ Electronic E: -1250.403234 a.u.

B	0.5637392217	-1.6281450258	-0.3211134840
O	1.5406320078	-1.7387046492	0.6555621766
O	0.9931640075	-1.0211159163	-1.4622874701
C	2.6327704055	-0.8835880477	0.2222645200
C	2.4293880728	-0.8712929744	-1.3319091095
C	3.9472988051	-1.4835513745	0.6877858795
H	4.7876610621	-0.9088296572	0.2870902926
H	4.0011062643	-1.4463704374	1.7787697096
H	4.0476477931	-2.5224272491	0.3701975899
C	2.3989249430	0.4833065341	0.8564275452
H	2.3620618980	0.3766254917	1.9442230793
H	3.1975868641	1.1845389679	0.6013046729
H	1.4415400728	0.8993491953	0.5274899979

C	2.8436913327	0.4218412015	-2.0122688279
H	3.9064692450	0.6201152985	-1.8431547259
H	2.6785463174	0.3356438076	-3.0888378324
H	2.2611979643	1.2665851561	-1.6410109156
C	3.0669441183	-2.0751110387	-2.0193818856
H	2.7156031373	-2.1164771501	-3.0526695583
H	4.1571944989	-1.9984422783	-2.0239230923
H	2.7831998498	-3.0068269292	-1.5211235504
Si	-1.3406622360	0.8364871782	2.7626516146
C	-0.4386769730	2.5338706619	2.6370364920
H	0.5015631641	2.4788667501	2.0779661494
H	-1.0697809894	3.2964231731	2.1639884923
H	-0.1872983144	2.8865836337	3.6434623270
C	-2.9210277304	1.3031660189	3.7598896193
H	-3.4214372015	2.1845989085	3.3420718684
H	-3.6465970463	0.4834331802	3.7851482829
H	-2.6577561118	1.5261600247	4.7994795379
C	-2.0364680819	0.5978088614	0.9783700864
C	-3.1310454936	-0.2570124546	0.7418768799
C	-1.3805062728	1.0938795204	-0.1628167180
C	-3.5287133400	-0.6201227429	-0.5425506427
H	-3.6768534749	-0.6665601537	1.5914216087
C	-1.7529401351	0.7246928381	-1.4559674491
H	-0.5504028740	1.7882310428	-0.0399731142
C	-2.8250316947	-0.1450373924	-1.6551595973
H	-4.3807235465	-1.2799802529	-0.6827145004
H	-1.2001057829	1.1074370274	-2.3090509702
H	-3.1201043440	-0.4358388106	-2.6583515678
O	-0.6710734562	-2.1149228069	-0.0271012707
Na	-0.1940783795	-1.7422008832	2.3336284473
H	-1.3859941263	-1.7630971572	-0.5825617969

HO-Bpin

M06-2X/6-31G(d,p) Electronic E: -486.966866 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -486.802422 a.u.

M06-2X/cc-pVTZ Electronic E: -487.148831 a.u.

C	2.8997113818	0.8086842707	-0.2134912759
C	2.8761408876	-0.7307602303	0.0682017317
B	0.7771466941	0.0545282597	-0.2015184364
O	1.5260716528	1.1837654099	0.0186505958
O	1.5341951631	-1.0899798491	-0.3290930075
C	3.8686819875	-1.5434997454	-0.7459144313
H	4.8921727485	-1.2196117926	-0.5331513153
H	3.7825539458	-2.6000681783	-0.4801375384

H	3.6815486856	-1.4420325393	-1.8159028782
C	3.2145077058	1.1320723298	-1.6727032473
H	3.0060072093	2.1894298853	-1.8508878661
H	4.2641385750	0.9372046428	-1.9082938173
H	2.5886184624	0.5395009556	-2.3465188147
C	3.7959809164	1.6111253063	0.7150616601
H	4.8341693141	1.2755225910	0.6289603499
H	3.7539178445	2.6679038621	0.4402574178
H	3.4779994185	1.5144161151	1.7541414765
C	3.0070338245	-1.0568942224	1.5542919984
H	2.7697969414	-2.1125039149	1.7059840953
H	4.0220605311	-0.8716731578	1.9155037568
H	2.3101358689	-0.4571203252	2.1470318983
O	-0.5770794570	0.0894788286	-0.2830756758
H	-0.9473627819	-0.7924354017	-0.3920040064

IN3

M06-2X/6-31G(d,p) Electronic E: -1409.543239 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1409.292541 a.u.

M06-2X/cc-pVTZ Electronic E: -1409.941495 a.u.

Si	0.1523995154	-1.3263046922	0.9186046735
C	-0.6084025763	0.1463233791	1.8957581038
H	-0.6114259339	1.0736827070	1.3129707965
H	-1.6447823128	-0.0594387786	2.1919254006
H	-0.0294911065	0.3348638652	2.8066988425
C	-0.1678193622	-2.8011828776	2.1176819639
H	-1.2139139112	-2.8321444125	2.4446852111
H	0.0622877713	-3.7618210548	1.6446058869
H	0.4632975106	-2.7196777830	3.0096944858
C	-1.1638382498	-1.6549009332	-0.4453837803
C	-1.1502604898	-2.8684753139	-1.1562520850
C	-2.1610878110	-0.7325484192	-0.7985661001
C	-2.0787514224	-3.1561035924	-2.1517282340
H	-0.3915964917	-3.6144647900	-0.9175552507
C	-3.0939849787	-1.0059542053	-1.8002583573
H	-2.2199450142	0.2251830393	-0.2829141365
C	-3.0593015476	-2.2194936624	-2.4803173642
H	-2.0420520409	-4.1095795929	-2.6719466038
H	-3.8513391986	-0.2654260981	-2.0444122842
H	-3.7870688877	-2.4363975487	-3.2566424189
Na	2.7407496606	-1.0485780726	-0.1993204434
C	0.8132104701	2.0849557444	-1.2406713566
C	1.7113958053	1.7912108102	-2.1846599332
H	1.4883178875	1.7768443488	-3.2462656819

C	3.1101191843	1.4338732173	-1.8446450871
F	3.3922722366	0.1408817500	-2.2025832036
F	4.0195697655	2.1887608037	-2.4578623915
F	3.3636701782	1.4826650278	-0.5185479677
H	1.1377492162	2.1042572511	-0.2015127422
C	-0.6009849810	2.4002421116	-1.4750218397
C	-1.2612204359	2.0286610884	-2.6524316287
C	-1.3182237695	3.0668082390	-0.4742174649
C	-2.6047673697	2.3315296796	-2.8282812050
H	-0.7337911462	1.4642443270	-3.4149797539
C	-2.6648499611	3.3667949636	-0.6489237361
H	-0.8135495796	3.3477458407	0.4460839933
C	-3.3100896753	2.9994766995	-1.8274543222
H	-3.1102852905	2.0257558341	-3.7383575264
H	-3.2102973025	3.8808913000	0.1351892047
H	-4.3630413549	3.2240368099	-1.9629876735

$TS_{IN3\text{-}3ba}$

M06-2X/6-31G(d,p) Electronic E: -1409.529791 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1409.276207 a.u.

M06-2X/cc-pVTZ Electronic E: -1409.928141 a.u.

Si	-2.0201226027	3.6549720852	2.2479083121
C	-2.8338903853	4.2460114857	0.6237052052
H	-2.0760286967	4.4688880260	-0.1370019199
H	-3.5265710475	3.5033383369	0.2134299740
H	-3.3970123300	5.1672369879	0.8036764030
C	-3.4302859774	3.5735237967	3.5378704442
H	-4.3111522516	3.0463379671	3.1562108181
H	-3.1099232750	3.0809246124	4.4614612907
H	-3.7313896963	4.5932075951	3.8034901830
C	-1.5704902787	1.8269254370	1.8493873014
C	-1.3022520458	0.8909076187	2.8746484992
C	-1.2540375231	1.4158731669	0.5353847614
C	-0.7552551057	-0.3617063622	2.6117782312
H	-1.5268492079	1.1595253990	3.9062716081
C	-0.6918499999	0.1653693083	0.2650754419
H	-1.4528044281	2.0914590071	-0.2936906563
C	-0.4345453370	-0.7293254050	1.3015901917
H	-0.5793259369	-1.0576960928	3.4274139029
H	-0.4646459332	-0.1130398552	-0.7603552404
H	-0.0033808352	-1.7033072919	1.0942618344
Na	0.8275469811	2.6977746552	1.9305624279
C	-0.4317645040	5.9244501315	2.2044435859
C	0.0177479860	6.0802866497	0.9171042005

H	-0.5537545460	6.5616007132	0.1340455013
C	1.0776722847	5.2075566396	0.4494352268
F	0.6174763001	3.9511952221	0.0103148635
F	1.7962885734	5.6636119732	-0.5761019004
F	1.9557406232	4.8366661694	1.4374085530
H	0.2530928008	5.5130354301	2.9345782501
C	-1.5455572056	6.6955276777	2.7928755880
C	-1.7106355381	6.7070291869	4.1853685991
C	-2.4347210207	7.4449608159	2.0128603627
C	-2.7300977746	7.4372629408	4.7805170744
H	-1.0355018709	6.1144979038	4.7982953865
C	-3.4617705478	8.1722990867	2.6076563526
H	-2.3313602436	7.4544801579	0.9324942443
C	-3.6151566244	8.1726697850	3.9913491628
H	-2.8396549386	7.4302604702	5.8603145562
H	-4.1441519978	8.7426573312	1.9854336495
H	-4.4172076932	8.7396663565	4.4523517992

3ba

M06-2X/6-31G(d,p) Electronic E: -1147.460687 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1147.206141 a.u.

M06-2X/cc-pVTZ Electronic E: -1147.800556 a.u.

Si	-1.9196439190	4.2822549794	2.2802208118
C	-2.5350219967	4.5591710772	0.5264598721
H	-1.7072528951	4.6941359635	-0.1768461695
H	-3.1259588869	3.7024932575	0.1895776606
H	-3.1680563862	5.4497806611	0.4773873600
C	-3.3447877752	4.2869540596	3.5035321940
H	-4.0188714893	3.4443831838	3.3246813582
H	-2.9900359788	4.2239808904	4.5371378476
H	-3.9179723942	5.2138962699	3.4080577484
C	-0.9548467689	2.6727792443	2.3850544381
C	-0.8709689264	1.9594916382	3.5891993459
C	-0.2293615514	2.1894188254	1.2860102362
C	-0.0875741488	0.8134411497	3.6977726370
H	-1.4246403091	2.3028201636	4.4605946652
C	0.5587535026	1.0457437562	1.3872494960
H	-0.2743281377	2.7156596293	0.3349449146
C	0.6312435398	0.3568577831	2.5956317830
H	-0.0367702464	0.2771126002	4.6402740141
H	1.1148880163	0.6911918445	0.5249835257
H	1.2451859940	-0.5346068355	2.6776553143
C	-0.6986913348	5.6897018187	2.7550203046
C	0.4626297927	5.6840371643	1.8014345850

H	0.4413063217	6.2733459046	0.8927796166
C	1.5346328653	4.9337892642	1.9885209551
F	2.5687166074	4.8602985258	1.1666118704
F	1.7323574480	4.1519710026	3.0371143188
H	-0.3343095217	5.4253605125	3.7555017990
C	-1.4435177316	6.9998225875	2.8389399295
C	-1.9018067295	7.4643926015	4.0770606328
C	-1.7624235649	7.7441335170	1.6969211126
C	-2.6468669801	8.6356780383	4.1744188913
H	-1.6653923819	6.8986585228	4.9749016284
C	-2.5036255965	8.9189782279	1.7919108725
H	-1.4337799904	7.4028515776	0.7187571336
C	-2.9494737163	9.3709298619	3.0310653819
H	-2.9861482546	8.9772424897	5.1473595994
H	-2.7340809476	9.4815405045	0.8926024591
H	-3.5262857680	10.2868681468	3.1049964162

NaF

M06-2X/6-31G(d,p) Electronic E: -262.106416 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -262.126395 a.u.

M06-2X/cc-pVTZ Electronic E: -262.191235 a.u.

Na	0.0383210000	-0.9039852086	0.0000000000
F	0.0383210000	1.0179732086	0.0000000000

NaOMe

M06-2X/6-31G(d,p) Electronic E: -277.349984 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -277.337356 a.u.

M06-2X/cc-pVTZ Electronic E: -277.424135 a.u.

Na	1.0165811489	-0.1560269707	2.4599155082
O	-0.5138763607	1.0849331331	2.5032675925
C	-1.5147297364	2.0060202156	2.5375863690
H	-1.5076514060	2.7174956082	1.6803565107
H	-2.5380596370	1.5666609519	2.5255479344
H	-1.5028878587	2.6579175220	3.4408064852

IN1 (NaOMe)

M06-2X/6-31G(d,p) Electronic E: -1289.369764 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1289.028472 a.u.

M06-2X/cc-pVTZ Electronic E: -1289.707614 a.u.

B	0.6816786225	0.5074275858	-0.3482208198
O	0.8117852088	-0.8722943794	0.2336071613
O	2.0128658330	1.0726674393	-0.3032614933
C	2.1633601975	-1.0458133483	0.6560453737
C	2.9361595987	-0.0051429526	-0.2183351538

C	2.5815391067	-2.4930809906	0.4300154201
H	3.6439418954	-2.6326473090	0.6560213384
H	2.0073662421	-3.1523080590	1.0889553561
H	2.4059515952	-2.7961732743	-0.6049434655
C	2.2448519801	-0.7052594784	2.1448792783
H	1.5102386245	-1.3092595336	2.6863111502
H	3.2369744309	-0.9118173601	2.5576501771
H	2.0079479684	0.3504596101	2.3008857993
C	4.2267390186	0.5025778302	0.4136060104
H	4.9198065789	-0.3223432242	0.6119037135
H	4.7160569667	1.2017955776	-0.2701278795
H	4.0243241428	1.0280858316	1.3483861278
C	3.2325675202	-0.5362093587	-1.6263813343
H	3.5828311472	0.2985617242	-2.2400796255
H	4.0091019160	-1.3080052014	-1.6174037496
H	2.3246109477	-0.9359070330	-2.0839864560
Si	-0.7971313444	1.4980008756	0.7321445226
C	-1.3657910460	3.2464905814	0.2455784369
H	-1.7949131059	3.2885153046	-0.7600568196
H	-2.1186728704	3.6220404440	0.9462966158
H	-0.5153726000	3.9352873062	0.2635276321
C	-0.5485712029	1.5439702117	2.6134958860
H	-1.4506142953	1.8963233042	3.1246836280
H	-0.2849446641	0.5627230233	3.0181930975
H	0.2689225161	2.2276661342	2.8657448307
C	-2.2856246343	0.3321997130	0.4154241888
C	-2.5498724136	-0.7725202152	1.2447472661
C	-3.0014527349	0.4019005454	-0.7948197435
C	-3.4647819782	-1.7645988852	0.8821003815
H	-2.0185306710	-0.8687949505	2.1888586768
C	-3.9227043064	-0.5784979279	-1.1658813085
H	-2.8204704588	1.2334059251	-1.4734751157
C	-4.1510545078	-1.6730499930	-0.3291307951
H	-3.6466066932	-2.6046304558	1.5462655873
H	-4.4620812724	-0.4912246724	-2.1045949842
H	-4.8666510995	-2.4386207225	-0.6122764378
C	0.1813565454	1.3305781706	-2.6116567803
H	-0.1983606813	1.0159630818	-3.5889732880
H	-0.4476202770	2.1577111669	-2.2483306684
H	1.1998921714	1.7184466118	-2.7346642052
O	0.1646600948	0.2367423327	-1.7337777989
Na	-0.9133470123	-1.5671830061	-0.9931207340

$TS_{IN1-IN2}$ (NaOMe)

M06-2X/6-31G(d,p) Electronic E: -1289.337463 a.u.
M06-2X/6-31G(d,p) Gibbs free E: -1288.997466 a.u.
M06-2X/cc-pVTZ   Electronic E: -1289.678005 a.u.

B	-1.0804749595	-0.0847369728	0.9771320210
O	-1.1736913167	-1.0437961062	-0.0360823785
O	-2.1989156222	0.6984585212	1.0808990451
C	-2.3282485838	-0.6873992249	-0.8337310314
C	-3.1888931391	0.1310386377	0.1948130800
C	-2.9882871350	-1.9641573555	-1.3296784228
H	-3.9263295944	-1.7311154243	-1.8426328627
H	-2.3280681518	-2.4631712092	-2.0444111629
H	-3.1983178338	-2.6530557417	-0.5097447770
C	-1.8434921279	0.1531810727	-2.0100404071
H	-1.0846906816	-0.4147528820	-2.5576820965
H	-2.6664345318	0.3821203670	-2.6928940506
H	-1.3831293572	1.0799722598	-1.6598107227
C	-3.9954765281	1.2589987802	-0.4265425141
H	-4.6979150114	0.8645872317	-1.1676481058
H	-4.5683440603	1.7680351255	0.3523366386
H	-3.3425440566	1.9888028017	-0.9064491737
C	-4.0864633885	-0.7592497807	1.0527396720
H	-4.5045110011	-0.1560125279	1.8617994628
H	-4.9101341212	-1.1816107411	0.4708422091
H	-3.5134450044	-1.5784928149	1.4972924769
Si	1.1258887831	1.7868426413	-0.3367794094
C	2.2477404099	3.1252757233	0.5050793823
H	2.4664875629	2.8863324467	1.5525537749
H	3.2046900043	3.2637114054	-0.0126109243
H	1.7286252737	4.0903199421	0.5099792261
C	1.2076506780	2.3582204756	-2.1860280586
H	2.2353066902	2.4730153919	-2.5524181250
H	0.6848499878	1.6713612284	-2.8620277796
H	0.7099599611	3.3297333669	-2.2872495252
C	2.3498553548	0.2931160366	-0.3738346815
C	2.4329787979	-0.5895730725	-1.4756335145
C	3.0360490737	-0.1217686444	0.7922670911
C	3.1095423964	-1.8109498506	-1.4105838325
H	1.9422759382	-0.3142789042	-2.4074541609
C	3.7187389671	-1.3361620098	0.8707613194
H	3.0155842728	0.5216679191	1.6707169509
C	3.7463651387	-2.2026608721	-0.2287074323
H	3.1469035890	-2.4571533678	-2.2837696004
H	4.2326882481	-1.6117082358	1.7879488079
H	4.2769729894	-3.1476193358	-0.1737658518

C	0.0801775030	0.6174110171	2.9641690603
H	0.7136557687	0.1620628116	3.7263971010
H	0.5779238383	1.4902931016	2.5283993276
H	-0.8679572664	0.9288649970	3.4102171451
O	-0.1463000232	-0.3536353346	1.9505063834
Na	0.9433602687	-1.7713158932	0.4306464260

IN2 (NaOMe)

M06-2X/6-31G(d,p) Electronic E: -1289.340528 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1289.003043 a.u.

M06-2X/cc-pVTZ Electronic E: -1289.682107 a.u.

B	1.4916832515	-0.2293690885	-1.2141236699
O	1.6082315431	-1.3459555359	-0.4066499488
O	2.6510218873	0.4626912366	-1.3870126686
C	2.9248403050	-1.2536755257	0.2082275549
C	3.7028397408	-0.3638861215	-0.8235568323
C	3.4850335817	-2.6545381987	0.3807950010
H	4.5134290500	-2.6059029065	0.7512687031
H	2.8867584641	-3.2005804834	1.1144837069
H	3.4741987030	-3.2097986485	-0.5580994678
C	2.7425565223	-0.5718960978	1.5596582864
H	2.0626227435	-1.1701431411	2.1724515747
H	3.6953991423	-0.4870479824	2.0883336922
H	2.3010017440	0.4227013148	1.4473710195
C	4.7540052155	0.5410941877	-0.2054748500
H	5.5100282189	-0.0549537218	0.3146799379
H	5.2507365076	1.1130984495	-0.9925727692
H	4.3068130753	1.2414346976	0.5010052561
C	4.2932230118	-1.1708132772	-1.9763816566
H	4.6378568205	-0.4790006700	-2.7481050039
H	5.1417994763	-1.7743658297	-1.6447585291
H	3.5432060655	-1.8338416668	-2.4178116088
Si	-1.4117026909	1.5009297430	1.5301234707
C	-1.7801685687	3.2452760507	0.7877776625
H	-1.7604688887	3.2475252718	-0.3077476630
H	-2.7634068972	3.6160548143	1.1016912503
H	-1.0260180721	3.9670130383	1.1194911078
C	-1.9805525153	1.7448930209	3.3566794837
H	-3.0096181469	2.1194380301	3.4239547295
H	-1.9150825938	0.8223562995	3.9433117981
H	-1.3266629460	2.4744442222	3.8473726320
C	-2.8902430294	0.4716944906	0.7960756137
C	-3.6249239333	-0.4551601745	1.5632661551
C	-3.1641464611	0.4778898368	-0.5883659185

C	-4.5636837075	-1.3151807913	0.9934924148
H	-3.4630542815	-0.4976351407	2.6391474684
C	-4.1012123784	-0.3755902299	-1.1697056934
H	-2.6289396756	1.1791344873	-1.2290539524
C	-4.8053039121	-1.2836170447	-0.3794889452
H	-5.1164057754	-2.0067553683	1.6239769149
H	-4.2887289325	-0.3275606899	-2.2392262450
H	-5.5372086617	-1.9495636971	-0.8255112778
C	0.0640193715	1.3295908844	-2.3587210446
H	-0.7625880364	1.2197051592	-3.0606837043
H	-0.1904810396	2.0727240170	-1.5979114972
H	0.9650394109	1.6394814100	-2.8922394043
O	0.2679537550	0.0654855006	-1.7246657919
Na	-0.6933354631	-0.9336621311	0.2350627085

MeOBpin

M06-2X/6-31G(d,p) Electronic E: -526.244824 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -526.055921 a.u.

M06-2X/cc-pVTZ Electronic E: -526.437079 a.u.

B	0.8947288195	-1.0577349571	-2.5604517426
O	1.1932130451	-0.8097196280	-1.2422133482
O	1.7872310498	-1.9094130284	-3.1750572537
C	2.5140717677	-1.3460494839	-1.0209637140
C	2.6123712748	-2.4543027279	-2.1218633526
C	2.6079014319	-1.8587003258	0.4065803177
H	3.5674692058	-2.3586738717	0.5714075971
H	2.5357372716	-1.0186187596	1.1017042717
H	1.8014113012	-2.5585071727	0.6301883144
C	3.5062479196	-0.2068889931	-1.2466898449
H	3.2459788996	0.6214043775	-0.5838264144
H	4.5313261231	-0.5196671843	-1.0308171220
H	3.4595173231	0.1510406944	-2.2794584208
C	4.0120853424	-2.6933330802	-2.6625097842
H	4.6827411152	-3.0114196833	-1.8582561652
H	3.9838285957	-3.4836823699	-3.4167432290
H	4.4177182062	-1.7920918376	-3.1244576568
C	1.9726871497	-3.7712004014	-1.6875658215
H	1.8804183334	-4.4223787076	-2.5599690428
H	2.5791090851	-4.2805549549	-0.9340028949
H	0.9735220009	-3.6009077386	-1.2759401451
C	-0.4421362031	-0.8448579771	-4.5252279402
H	-1.5029028333	-0.6737007275	-4.7136508193
H	0.1448491235	-0.2095953573	-5.1950990560
H	-0.1987502106	-1.8906891115	-4.7302170477

O	-0.1812861379	-0.5099489926	-3.1708526850

LiO^{t}Bu

M06-2X/6-31G(d,p) Electronic E: -240.538263 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -240.442018 a.u.

M06-2X/cc-pVTZ Electronic E: -240.628386 a.u.

O	-0.5703957221	1.1300240094	2.5046339377
C	-1.5805584905	2.0613903267	2.5386225623
Li	0.7460755243	0.1416589201	2.4843141035
C	-1.4742892230	2.9048369769	3.8207604742
H	-2.2635465685	3.6617982018	3.8920400934
H	-1.5399474578	2.2493705082	4.6953910288
H	-0.5033076511	3.4108530369	3.8458680662
C	-1.4780504588	2.9922753735	1.3181553206
H	-1.5488333620	2.4001499661	0.3997543144
H	-2.2660857914	3.7536777772	1.3037029420
H	-0.5060439616	3.4969462598	1.3244642544
C	-2.9466548720	1.3547968010	2.5162150111
H	-3.0287670091	0.7471529771	1.6090726956
H	-3.0275075348	0.6880679126	3.3810044340
H	-3.7840128415	2.0612917429	2.5403160617

IN1'' (LiO^{t}Bu)

M06-2X/6-31G(d,p) Electronic E: -1252.538062 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1252.111200 a.u.

M06-2X/cc-pVTZ Electronic E: -1252.893042 a.u.

B	-0.7422302728	0.6661584046	0.4761210573
O	-0.8967943374	-0.6535554454	-0.2659239874
O	-2.0769931101	1.2035501615	0.5400915792
C	-2.2684608190	-0.8010251201	-0.6416234218
C	-3.0047974354	0.1390243848	0.3674287160
C	-2.6640692886	-2.2687111697	-0.5454514066
H	-3.7330404626	-2.3956538158	-0.7457489346
H	-2.1109093772	-2.8510575991	-1.2889548375
H	-2.4495799748	-2.6748023665	0.4458184927
C	-2.4169637165	-0.3177768998	-2.0840176821
H	-1.7050579609	-0.8590898220	-2.7147268073
H	-3.4258390326	-0.4960508672	-2.4677015665
H	-2.1959203602	0.7500167017	-2.1504275043
C	-4.3118804294	0.7171833280	-0.1620968751
H	-5.0150806717	-0.0790080369	-0.4291363210
H	-4.7746627707	1.3353693839	0.6120411670
H	-4.1364325866	1.3445253171	-1.0374728702
C	-3.2645352438	-0.5476222632	1.7135851410

H	-3.5677837195	0.2154656998	2.4370163433
H	-4.0650507856	-1.2909312662	1.6405571402
H	-2.3579497838	-1.0277824532	2.0882351082
Si	0.6864136568	1.7222357485	-0.5914080380
C	1.3371075260	3.4101038362	-0.0062670551
H	1.7179135254	3.4211858919	1.0187141007
H	2.1378044194	3.7605299161	-0.6667819660
H	0.5250327243	4.1436185366	-0.0561308357
C	0.2444311692	1.9909506650	-2.4190445432
H	1.0655890193	2.4907368609	-2.9428323125
H	0.0435113155	1.0448223230	-2.9293784031
H	-0.6487685243	2.6170823402	-2.5157670826
C	2.1789892748	0.5158034362	-0.6025135907
C	2.0564286406	-0.7580312529	-1.1941765274
C	3.3964662694	0.7995253614	0.0360934578
C	3.0814405674	-1.7051372021	-1.1246804989
H	1.1410391926	-1.0079915923	-1.7282913478
C	4.4272299473	-0.1366245280	0.1076105490
H	3.5471919255	1.7776289010	0.4881669997
C	4.2700233799	-1.3975156978	-0.4642621440
H	2.9590074917	-2.6735660385	-1.6020052762
H	5.3563163604	0.1184788517	0.6088112180
H	5.0714474525	-2.1275631717	-0.4103916307
C	0.0906460020	0.8862695929	2.9683157867
O	-0.1768570225	0.1333042144	1.7874869505
Li	0.4993869964	-1.3051960386	0.8103540645
C	-0.6401993097	2.2298816559	2.9625738238
H	-1.7162856516	2.0790805375	2.8613713311
H	-0.4325998617	2.7627909344	3.8955525726
H	-0.3118888306	2.8542817409	2.1270141542
C	-0.4023947526	0.0432337205	4.1458845136
H	-0.1776229522	0.5331111946	5.0982014526
H	-1.4830492030	-0.1063657538	4.0767873145
H	0.0861910557	-0.9371891142	4.1408248637
C	1.5998246295	1.1006107573	3.0874012017
H	2.1224842889	0.1369940900	3.0916231038
H	1.9713342095	1.6821160787	2.2412901726
H	1.8500223272	1.6311991680	4.0113218502

$TS_{IN1''-IN2''}$ (LiO^tBu)

M06-2X/6-31G(d,p) Electronic E: -1252.505579 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1252.082324 a.u.

M06-2X/cc-pVTZ Electronic E: -1252.862778 a.u.

B	-0.8666401114	0.2694740016	0.8978627721

O	-0.8960946445	-0.7441395201	-0.0720012252
O	-2.0386826385	0.9789318737	0.9630198046
C	-2.0891310886	-0.5342707161	-0.8637242456
C	-2.9942696907	0.2762455287	0.1346770786
C	-2.6478146879	-1.8929555917	-1.2567552630
H	-3.6103495673	-1.7756292880	-1.7639669470
H	-1.9574546279	-2.3825181413	-1.9490498298
H	-2.7842445575	-2.5387520268	-0.3877667400
C	-1.7131948326	0.2606310548	-2.1089354337
H	-0.9344002282	-0.2847022943	-2.6499816760
H	-2.5771114685	0.3756886642	-2.7696535166
H	-1.3178766521	1.2432752198	-1.8430140943
C	-3.9032209171	1.2946329811	-0.5323058435
H	-4.5880394917	0.7993439277	-1.2277945639
H	-4.4977459221	1.8045788939	0.2295590320
H	-3.3232391189	2.0424712865	-1.0743332239
C	-3.7968158231	-0.6279582784	1.0691940781
H	-4.2586661281	-0.0094242838	1.8427160303
H	-4.5862590927	-1.1627243419	0.5342553018
H	-3.1459011066	-1.3589443857	1.5592438700
Si	1.2224190894	1.9367387579	-0.6442214442
C	2.4952248559	3.2330386718	0.0257937510
H	2.7369552192	3.0930139878	1.0855047260
H	3.4382007080	3.2219273465	-0.5335044343
H	2.0687356565	4.2385516371	-0.0623364159
C	1.2894045730	2.3179585837	-2.5418472010
H	2.3148564211	2.3587647125	-2.9275677332
H	0.7361054089	1.5838561437	-3.1383991162
H	0.8234365566	3.2907643488	-2.7368471480
C	2.2566387472	0.3141813309	-0.5538760295
C	2.0446705431	-0.7579175599	-1.4548864488
C	3.0083220430	-0.0073196990	0.6019380682
C	2.4754783936	-2.0597897995	-1.1905586629
H	1.4841466446	-0.5714735076	-2.3682820587
C	3.4423375307	-1.3034674467	0.8838713862
H	3.2176670328	0.7806450285	1.3226314120
C	3.1563111092	-2.3506976203	-0.0013742236
H	2.2678051278	-2.8545788237	-1.9013278970
H	3.9903136145	-1.5051332707	1.8002054309
H	3.4784184897	-3.3629984650	0.2173972722
C	0.0730707065	0.6185446553	3.1949600305
O	0.0580807947	-0.0042073066	1.8891491067
Li	0.9603201623	-1.2396438523	0.5836180674
C	1.2782639320	0.0230407288	3.9113908332

H	2.1973550243	0.2546929332	3.3671656266
H	1.3573139529	0.4336283387	4.9212038898
H	1.1776300581	-1.0644560410	3.9865487457
C	-1.2183315066	0.2536579415	3.9244088392
H	-2.0832608523	0.6743726398	3.4074485605
H	-1.3282977447	-0.8340902554	3.9750528421
H	-1.1931724028	0.6466786993	4.9446039542
C	0.2166404689	2.1274646308	3.0392217319
H	0.2406955792	2.5984530717	4.0264057286
H	1.1385688751	2.3682699908	2.5045324878
H	-0.6213404162	2.5368589049	2.4696219580

IN2'' (LiO^{t}Bu)

M06-2X/6-31G(d,p) Electronic E: -1252.508368 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1252.086833 a.u.

M06-2X/cc-pVTZ Electronic E: -1252.866672 a.u.

B	-1.1080138563	0.0127200882	1.1648859747
O	-1.1630199936	-0.8457697251	0.0769102203
O	-2.0914329821	0.9472012352	1.1894236470
C	-2.1710046798	-0.3074058870	-0.8265633391
C	-3.0367349147	0.5719098276	0.1502541889
C	-2.9202489772	-1.4699840255	-1.4555826833
H	-3.7453761698	-1.0969985507	-2.0697423014
H	-2.2411547296	-2.0295947600	-2.1038833146
H	-3.3204118947	-2.1500815261	-0.7021628958
C	-1.4485430912	0.5072406819	-1.8902047864
H	-0.7542981921	-0.1503863704	-2.4211158178
H	-2.1569408233	0.9169534609	-2.6151556385
H	-0.8656056323	1.3174801674	-1.4402494155
C	-3.5892676669	1.8395314792	-0.4760484792
H	-4.2438187956	1.5933652288	-1.3176366072
H	-4.1756905046	2.3857042336	0.2664813382
H	-2.7842699105	2.4863137276	-0.8267877779
C	-4.1426155623	-0.2188047586	0.8442307787
H	-4.5768157451	0.4031455953	1.6303818281
H	-4.9336249590	-0.4982471333	0.1439026098
H	-3.7462922677	-1.1284286805	1.3059710718
Si	1.8954876323	1.7743926703	-0.7212599555
C	3.5452662024	2.6139717476	-0.1385147145
H	3.7051832330	2.5016068639	0.9402656159
H	4.4335840118	2.2287848915	-0.6534290984
H	3.4901661932	3.6915762214	-0.3294684694
C	2.0417445742	1.9581083313	-2.6478237686
H	2.9610053491	1.5217021932	-3.0582682963

H	1.1911994749	1.5061071916	-3.1725696806
H	2.0346760465	3.0223168521	-2.9098555165
C	2.3942437715	-0.0788932165	-0.5372242121
C	1.9795110488	-1.0757435877	-1.4569523533
C	2.9795187596	-0.5686896253	0.6582552131
C	2.0695377897	-2.4422450479	-1.1791356865
H	1.5502469430	-0.7647413605	-2.4065583745
C	3.0789973834	-1.9296648153	0.9489857446
H	3.3333825208	0.1500338495	1.3952706537
C	2.6003426614	-2.8835787592	0.0395369657
H	1.7153036172	-3.1673877320	-1.9063343367
H	3.5132199443	-2.2530242854	1.8910629438
H	2.6590572492	-3.9423037504	0.2665327864
C	0.0781222801	0.3901096294	3.3288336582
O	-0.1200492995	-0.2852415749	2.0537424550
Li	0.7710070362	-1.3162753558	0.5267999658
C	1.2309548709	-0.3484901231	3.9933349543
H	2.1320961264	-0.2755917577	3.3794727577
H	1.4398030828	0.0891887819	4.9725889493
H	0.9804257244	-1.4048617513	4.1292236709
C	0.4293626600	1.8470807059	3.0624453643
H	1.3168541188	1.9152221808	2.4271548240
H	-0.3908461561	2.3536902316	2.5469250448
H	0.6205885365	2.3585864180	4.0101680661
C	-1.2001493061	0.2523574512	4.1506468114
H	-2.0324280257	0.7663098425	3.6643962000
H	-1.4566999077	-0.8035865436	4.2782270113
H	-1.0508177989	0.6932469243	5.1396522056

^{t}Bu-OBpin

M06-2X/6-31G(d,p) Electronic E: -644.146566 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -643.875972 a.u.

M06-2X/cc-pVTZ Electronic E: -644.373198 a.u.

B	0.9059093595	-1.1751823418	-2.5940503908
O	1.1111711624	-1.0306632269	-1.2399370803
O	1.9596669418	-1.8046658098	-3.2307332011
C	2.4857441843	-1.3830671654	-0.9916282199
C	2.8036179673	-2.3383993492	-2.1879065921
C	2.5926524325	-2.0273546461	0.3807109785
H	3.6087773353	-2.3960438319	0.5526120733
H	2.3622128658	-1.2870690625	1.1508005258
H	1.8925420588	-2.8577369444	0.4837902569
C	3.3006104171	-0.0919577244	-1.0419825879
H	2.8848874611	0.6135662352	-0.3189837301

H	4.3503338404	-0.2703982856	-0.7938011755
H	3.2476095834	0.3622844640	-2.0358721507
C	4.2480224197	-2.3148576518	-2.6584118808
H	4.9176812757	-2.6215985023	-1.8489683928
H	4.3745845335	-3.0128424240	-3.4898128700
H	4.5379059555	-1.3195063267	-2.9982084167
C	2.3451695413	-3.7727430493	-1.9322207176
H	2.3980063340	-4.3316775612	-2.8698326370
H	2.9791621010	-4.2701256844	-1.1934312502
H	1.3107523878	-3.7922755212	-1.5760541323
C	-0.5635035491	-0.9470329497	-4.5597785299
O	-0.2288308975	-0.7281649652	-3.1762566466
C	-0.6425102958	-2.4473216088	-4.8365885846
H	0.3346740437	-2.9162155231	-4.7009648312
H	-1.3593013036	-2.9141074776	-4.1547270743
H	-0.9763484623	-2.6234290100	-5.8630057218
C	0.4724842963	-0.2677599466	-5.4531307571
H	0.1780889860	-0.3556031580	-6.5028053291
H	0.5409988697	0.7944307677	-5.2011643334
H	1.4546253589	-0.7275629863	-5.3250023136
C	-1.9314803652	-0.2974401595	-4.7369866024
H	-1.8747834256	0.7682698630	-4.5005463417
H	-2.2784243603	-0.4117492879	-5.7673712038
H	-2.6585061334	-0.7629050981	-4.0664451291

IN3''

M06-2X/6-31G(d,p) Electronic E: -1254.811877 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1254.555531 a.u.

M06-2X/cc-pVTZ Electronic E: -1255.191544 a.u.

Si	0.2084857266	-1.2655582780	1.2150617833
C	-0.7162472082	0.2504205536	1.9479200946
H	-0.6286985830	1.1258330139	1.2935114484
H	-1.7855214984	0.0518965464	2.0938272400
H	-0.2952440982	0.5250494253	2.9209641855
C	-0.4029961561	-2.7134080708	2.3253914514
H	-1.4947343797	-2.7110886774	2.4232390091
H	-0.1069490466	-3.6837536156	1.9124771697
H	0.0260437632	-2.6424473455	3.3308429596
C	-0.7332771527	-1.5839306915	-0.4384894482
C	-0.2816011842	-2.5878421652	-1.3133872280
C	-1.8168134196	-0.8101901209	-0.8820504346
C	-0.8649286388	-2.8122226124	-2.5570829644
H	0.5620297225	-3.2112515575	-1.0126601326
C	-2.4136322838	-1.0238437484	-2.1264956920

H	-2.2017503650	-0.0093329564	-0.2528810668
C	-1.9368058046	-2.0213429044	-2.9732763310
H	-0.4862828457	-3.5989586409	-3.2039705390
H	-3.2501516498	-0.4021818908	-2.4356447798
H	-2.3971644127	-2.1868277818	-3.9427612298
C	0.5018655313	1.9405065155	-1.4361331698
C	0.9063379834	0.8450046236	-2.0840251669
H	0.2502983424	0.2050599570	-2.6690740473
C	2.3265423556	0.4186598630	-2.0430843019
F	2.4462608393	-0.9047445780	-1.6706386677
F	2.9439331018	0.5055066339	-3.2203349702
F	3.0697682966	1.0899762567	-1.1427070873
H	1.2226953890	2.4770836511	-0.8220718370
C	-0.8589442310	2.4896265078	-1.4572241967
C	-1.7701520622	2.1802946656	-2.4748441483
C	-1.2582373485	3.3501753656	-0.4279291928
C	-3.0589008102	2.6971935585	-2.4442176082
H	-1.4661489817	1.5358870255	-3.2937927033
C	-2.5511979587	3.8616400776	-0.3931400267
H	-0.5517254618	3.6042522696	0.3576695024
C	-3.4546913625	3.5335199511	-1.4005188124
H	-3.7564607134	2.4514209797	-3.2384737638
H	-2.8514943593	4.5170051564	0.4174182230
H	-4.4626540436	3.9346396259	-1.3787945105
Li	2.5780250084	-1.1145305879	0.2965799903

$TS_{IN3'\text{-}3ba}$

M06-2X/6-31G(d,p) Electronic E: -1254.795876 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1254.540101 a.u.

M06-2X/cc-pVTZ Electronic E: -1255.175149 a.u.

Si	-2.0178605923	3.6286652381	2.3258831545
C	-2.9780958052	4.2597524983	0.8018088726
H	-2.2920709473	4.6289786139	0.0286135155
H	-3.6107967683	3.4844964357	0.3572617910
H	-3.6214148471	5.0964128190	1.0908641439
C	-3.2806027502	3.4709279779	3.7482996930
H	-4.1835564936	2.9344583146	3.4392945564
H	-2.8562417091	2.9573624554	4.6164380376
H	-3.5758314628	4.4733544820	4.0771800189
C	-1.5445595387	1.8304171719	1.8352187340
C	-1.2115533196	0.8639592126	2.8145518942
C	-1.2855424136	1.4701916975	0.4937116172
C	-0.6810668840	-0.3767633783	2.4798913661
H	-1.3811593572	1.0966238112	3.8646957076

C	-0.7359399077	0.2295697143	0.1524442211
H	-1.5340979159	2.1702048989	-0.3012806529
C	-0.4326796606	-0.6997246148	1.1418742364
H	-0.4598616166	-1.0986509974	3.2608242183
H	-0.5572602161	-0.0103784961	-0.8917280725
H	-0.0123072673	-1.6650176417	0.8797552956
C	-0.4144030232	5.9193170526	2.2540600382
C	0.1137172163	6.0391151502	0.9917695621
H	-0.3830337505	6.5390534078	0.1705405287
C	1.1543525384	5.1137550466	0.6105667406
F	0.6282014173	3.8607209907	0.1416035239
F	1.9672036082	5.4887445786	-0.3687876411
F	1.9136176738	4.6707007130	1.6564020609
H	0.2134043806	5.5036967890	3.0311527376
C	-1.5494691026	6.7188222515	2.7536710705
C	-1.7874332419	6.7774265123	4.1341066103
C	-2.3883006217	7.4470737257	1.9009023583
C	-2.8282742913	7.5391808942	4.6489302131
H	-1.1504276270	6.2023149765	4.8018439274
C	-3.4340633607	8.2070583478	2.4151557610
H	-2.2341388457	7.4084373391	0.8272032277
C	-3.6583286600	8.2578022398	3.7888728642
H	-2.9947235769	7.5713786400	5.7208626527
H	-4.0769791714	8.7617948804	1.7392470195
H	-4.4749342123	8.8509904828	4.1871005131
Li	0.4589291239	2.8446907683	1.7430158827

LiF

M06-2X/6-31G(d,p) Electronic E: -107.397062 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -107.414327 a.u.

M06-2X/cc-pVTZ Electronic E: -107.456937 a.u.

F	0.0383210000	0.9064806194	0.0000000000
Li	0.0383210000	-0.6805346194	0.0000000000

M06-L

CuCl

M06-L/6-31G(d,p) Electronic E: -2100.447535 a.u.

M06-L/6-31G(d,p) Gibbs free E: -2100.470034 a.u.

M06-L/cc-pVTZ Electronic E: -2100.726151 a.u.

Cu	-2.5519209505	-0.3134040133	-2.2302604849
Cl	-4.2631200495	-1.1996569867	-3.0761275151

NHC

M06-L/6-31G(d,p) Electronic E: -940.326974 a.u.

M06-L/6-31G(d,p) Gibbs free E: -939.974223 a.u.

M06-L/cc-pVTZ Electronic E: -940.579556 a.u.

C	0.5885295310	2.0333026823	-1.6283334189
C	-1.6973037947	2.9990341560	-1.7770729586
C	-0.9132543967	4.0906746766	-2.4964478572
C	1.2226811409	3.3557543575	-1.9017053906
C	-1.1140758774	0.5468866159	-1.4292728437
H	-2.5152590981	2.6822978507	-2.4374574616
H	-0.6808604184	3.7561535820	-3.5211269525
H	2.0197177850	3.5620275147	-1.1831521578
N	1.1990734287	0.9026331610	-1.4120170502
N	0.1225314171	0.0163866055	-1.2954954057
N	-0.7784277115	1.8641592376	-1.6521916702
H	-1.4921222991	5.0120884865	-2.5693880158
H	1.6777903036	3.3385917801	-2.9068136601
O	0.2868256093	4.4143092833	-1.8066785584
C	0.4073094129	-1.3583177089	-1.0298392294
C	1.0341393934	-2.1239712661	-2.0200850227
C	0.0612285667	-1.8928054893	0.2174379667
C	1.3073288801	-3.4618932372	-1.7350912978
C	0.3507656107	-3.2373341167	0.4519901085
C	0.9703847787	-4.0382975117	-0.5090640216
H	1.7929841707	-4.0705558894	-2.4964600010
H	0.0914869997	-3.6670771998	1.4184391226
C	-0.5876806638	-1.0470307004	1.2683829886
H	0.0000559389	-0.1447544826	1.4716220537
H	-1.5770793409	-0.7037048219	0.9489828482
H	-0.6973583311	-1.5997511424	2.2040664706
C	1.3916723574	-1.5248128460	-3.3441592564
H	0.5402995737	-0.9922698174	-3.7813333053
H	2.1965250854	-0.7898664961	-3.2456587786
H	1.7142138317	-2.2940979404	-4.0492408270
C	1.2432311164	-5.4872230184	-0.2402604061
H	1.4176880249	-5.6750801746	0.8226278232
H	0.3947186408	-6.1135706287	-0.5390867918
H	2.1141194197	-5.8449998636	-0.7960089603
C	-2.3221531807	3.3881046362	-0.4013462060
C	-1.2824841311	3.3790601828	0.7213710476
H	-0.8740522333	2.3751877628	0.8805322225
H	-0.4530108461	4.0601349811	0.5141374985
H	-1.7528084803	3.6916410434	1.6593783568
C	-2.9487222239	4.7799242315	-0.5002874854
H	-3.6202979392	4.8631264589	-1.3632491072

H	-3.5435721847	4.9834340804	0.3954664369
H	-2.1926217024	5.5679202804	-0.5769457014
C	-3.4212923658	2.3753552372	-0.0711005922
H	-4.2402615543	2.4320249162	-0.7975058632
H	-3.0338926345	1.3520001065	-0.0893052995
H	-3.8389746092	2.5776154444	0.9208486098

NHC-CuCl

M06-L/6-31G(d,p) Electronic E: -3040.880998 a.u.

M06-L/6-31G(d,p) Gibbs free E: -3040.531590 a.u.

M06-L/cc-pVTZ Electronic E: -3041.406324 a.u.

C	0.7003671867	2.0904350377	-1.0757670130
C	-1.4749793786	3.0564176357	-1.8301721194
C	-0.5345381637	4.1885922694	-2.2319872526
C	1.3421331754	3.4373976670	-1.0347112024
C	-0.8840121844	0.5919398966	-1.5644213927
H	-2.0534192175	2.7540067406	-2.7143107887
H	-0.0068808828	3.9126714425	-3.1589279804
H	1.8412505797	3.6013881289	-0.0763989419
N	1.2701246264	0.9394049059	-0.8362180900
N	0.2703841484	0.0338334881	-1.1415342398
N	-0.5917418334	1.9283079150	-1.5055159004
H	-1.0844592190	5.1105517406	-2.4212511056
H	2.1130081128	3.4829073668	-1.8216495124
O	0.3991591519	4.4768570406	-1.1996197478
C	0.5020317257	-1.3670530831	-0.9578306743
C	0.5225027996	-2.2107179627	-2.0754061168
C	0.6938581505	-1.8398921130	0.3474807528
C	0.7473113065	-3.5697935204	-1.8500442788
C	0.9190716974	-3.2048865135	0.5139740330
C	0.9468463076	-4.0861064000	-0.5695412346
H	0.7704041227	-4.2417559994	-2.7059152414
H	1.0678409994	-3.5905424353	1.5210528513
C	0.6407198907	-0.9148635049	1.5231698832
H	1.5051528673	-0.2445632981	1.5496032038
H	-0.2480259669	-0.2742893376	1.4866558537
H	0.6155911528	-1.4756943041	2.4595529872
C	0.3017725664	-1.6943683347	-3.4627366450
H	-0.7610154235	-1.4807829036	-3.6418295399
H	0.8428347973	-0.7604270881	-3.6433428225
H	0.6205195447	-2.4273218801	-4.2065377383
C	1.1559642113	-5.5541556899	-0.3572820164
H	1.8208542991	-5.7501989272	0.4880911606
H	0.2079770258	-6.0593972322	-0.1408306208

H	1.5790812342	-6.0342889704	-1.2431282817
C	-2.4868625871	3.3690817036	-0.6879637784
C	-1.8051551736	3.5177542480	0.6736555306
H	-1.2691455636	2.6044317803	0.9572025701
H	-1.0981945699	4.3495652365	0.6930032146
H	-2.5633921329	3.6951209013	1.4428594577
C	-3.2213084966	4.6655967941	-1.0393747059
H	-3.6381081904	4.6347430352	-2.0526343272
H	-4.0550876107	4.8179964597	-0.3483403963
H	-2.5720507916	5.5428381577	-0.9611783840
C	-3.5168883722	2.2394426686	-0.5989223310
H	-3.9986207443	2.0413836249	-1.5640035501
H	-3.0712789993	1.3004979894	-0.2541199457
H	-4.3011480221	2.5078590159	0.1159568478
Cu	-2.4556440050	-0.2318924346	-2.1962354815
Cl	-4.2049211513	-1.1328589580	-3.0358019486

Si-B

M06-L/6-31G(d,p) Electronic E: -1012.185831 a.u.

M06-L/6-31G(d,p) Gibbs free E: -1011.888595 a.u.

M06-L/cc-pVTZ Electronic E: -1012.414073 a.u.

Si	0.0712242449	-0.6256417233	-0.6082402000
C	-1.7313709890	-1.1562080076	-0.4675630036
H	-1.9341423681	-2.0522002763	-1.0618957818
H	-1.9852153936	-1.3819630722	0.5727282160
H	-2.4104380266	-0.3684944986	-0.8076646548
C	0.5115669566	-0.2353646181	-2.3936030613
H	1.5576784970	0.0707865303	-2.4869644747
H	0.3565347266	-1.1000675180	-3.0470354943
H	-0.1043090498	0.5801900652	-2.7831238609
C	1.1703058913	-2.0350992973	0.0106606094
C	1.2335418199	-2.3239282051	1.3847651295
C	1.9453399040	-2.8229847036	-0.8529873273
C	2.0237255011	-3.3605230497	1.8734116773
H	0.6579010957	-1.7179471234	2.0856326651
C	2.7409882795	-3.8608800988	-0.3712934903
H	1.9308332662	-2.6228453717	-1.9234540937
C	2.7800918447	-4.1329692980	0.9938233831
H	2.0542892615	-3.5646474840	2.9407745695
H	3.3323046288	-4.4570639944	-1.0617573101
H	3.4005767111	-4.9411349364	1.3717856804
C	1.6784634236	2.4841590423	1.7271541448
C	0.3829107107	2.1762679574	2.5355457183
B	0.4634211741	0.8903623596	0.6514830812

O	1.3882923875	1.8819020967	0.4291430228
O	-0.0853665914	0.9421679051	1.9124816627
C	1.9695729195	3.9566392549	1.5271489489
H	2.1169456808	4.4551852148	2.4911057180
H	2.8844360395	4.0813094097	0.9423637619
H	1.1587754044	4.4614851353	0.9988481358
C	2.9023757687	1.7601519304	2.2695842745
H	3.7222783933	1.8510546604	1.5532788913
H	3.2312489366	2.1830477243	3.2235238219
H	2.6990028022	0.6944406826	2.4153200216
C	0.6007543057	1.9160253195	4.0117638985
H	1.0378112960	2.7936936592	4.4995387163
H	-0.3540755193	1.7028584884	4.4992111670
H	1.2627903702	1.0638223151	4.1774563826
C	-0.7104580933	3.2132951332	2.3274284049
H	-1.6485506840	2.8389470855	2.7441959133
H	-0.4675502123	4.1574129390	2.8241953502
H	-0.8676133144	3.4150063676	1.2639727859

Int1

M06-L/6-31G(d,p) Electronic E: -3181.583375 a.u.

M06-L/6-31G(d,p) Gibbs free E: -3181.078916 a.u.

M06-L/cc-pVTZ Electronic E: -3182.180893 a.u.

C	-0.0824819186	1.9738037486	-1.3329907074
C	-2.5015170035	2.5082718729	-1.6358163417
C	-1.8765780094	3.7017833785	-2.3455594469
C	0.3101671587	3.3986608075	-1.5481390679
C	-1.4547646241	0.2065614894	-1.3018066625
H	-3.1987601947	2.0222357346	-2.3325319481
H	-1.5158865671	3.3835196705	-3.3374295617
H	0.9628426222	3.7470098193	-0.7433269899
N	0.7185656304	0.9577882753	-1.1486491695
N	-0.1561550717	-0.1171239001	-1.1293257806
N	-1.3885194803	1.5694216351	-1.4261343444
H	-2.6062598108	4.4974626743	-2.4981799465
H	0.8811294108	3.4657947778	-2.4891702714
O	-0.8104455261	4.2584655435	-1.5824409768
C	0.3634401894	-1.4379497381	-0.9515405544
C	0.2393581736	-2.3669672463	-1.9921901167
C	0.9781517575	-1.7532841427	0.2687775596
C	0.7569095279	-3.6466157163	-1.7772288647
C	1.4809117638	-3.0425886835	0.4271248766
C	1.3828195663	-4.0029293734	-0.5834878540
H	0.6698025418	-4.3830786472	-2.5740808604

H	1.9539805537	-3.3061197386	1.3716729857
C	1.0736593914	-0.7458322583	1.3717845455
H	1.7839829410	0.0501766453	1.1291260183
H	0.1099387516	-0.2561988208	1.5505979949
H	1.3942065685	-1.2171003193	2.3031439548
C	-0.4328951855	-2.0277697406	-3.2856806255
H	-1.5288663543	-2.0252315425	-3.1746017846
H	-0.1583328628	-1.0302202716	-3.6433514372
H	-0.1790226594	-2.7556388163	-4.0593815777
C	1.9522221533	-5.3751796841	-0.3901844506
H	1.7054111329	-5.7782477841	0.5963747279
H	1.5835147173	-6.0751735875	-1.1436206795
H	3.0456030216	-5.3650166561	-0.4608937061
C	-3.2735335747	2.8076594038	-0.3160782927
C	-2.3369262443	3.1062438746	0.8560662490
H	-1.6851214948	2.2536996527	1.0792398275
H	-1.7077425832	3.9787836616	0.6650761270
H	-2.9277021455	3.3031359798	1.7565079743
C	-4.1980444497	4.0037133876	-0.5539969380
H	-4.8048021191	3.8634820869	-1.4567722199
H	-4.8826975323	4.1181972291	0.2917026583
H	-3.6412256886	4.9407822386	-0.6525005367
C	-4.1415169600	1.5959490357	0.0331848475
H	-4.8251550958	1.3499522383	-0.7894593417
H	-3.5409118826	0.7040847994	0.2454204950
H	-4.7432001249	1.8072595812	0.9236072746
Cu	-3.0648359244	-0.8075485359	-1.7108068583
Si	-4.9777102306	-1.2242267615	-2.8797508333
C	-6.7051023665	-1.2395738492	-2.0860115275
H	-7.4944809779	-1.0538531616	-2.8246413417
H	-6.9120967365	-2.2094963231	-1.6228039831
H	-6.8034107092	-0.4851143191	-1.2980310575
C	-5.0303640910	-2.5147409703	-4.2793990185
H	-5.9042028508	-2.3806109537	-4.9271949507
H	-4.1376805043	-2.4550334837	-4.9113560902
H	-5.0688202416	-3.5324139221	-3.8775314413
C	-4.8358431166	0.4711115394	-3.7622831772
C	-3.7349421559	0.7226254622	-4.6065924497
C	-5.6742716912	1.5653208233	-3.4867309611
C	-3.4864271952	1.9802826767	-5.1473444643
H	-3.0452412955	-0.0936843916	-4.8319563712
C	-5.4282935725	2.8355623760	-4.0124417217
H	-6.5403775595	1.4251323192	-2.8395896073
C	-4.3313643016	3.0505668399	-4.8436414274

H	-2.6301138532	2.1333583539	-5.8012251305
H	-6.0989433315	3.6594104597	-3.7757287995
H	-4.1369567043	4.0381422473	-5.2544508488

1b

M06-L/6-31G(d,p) Electronic E: -646.623292 a.u.

M06-L/6-31G(d,p) Gibbs free E: -646.521715 a.u.

M06-L/cc-pVTZ Electronic E: -646.818392 a.u.

C	-6.8769483666	0.8284984917	0.0336717898
C	-6.1701529712	-0.0508265515	0.7546077864
H	-6.4106772336	-1.1091050220	0.7998069802
C	-4.9816041282	0.3314477301	1.5530418976
F	-3.8664445020	-0.3025635183	1.1186430174
F	-5.1267636038	-0.0137578879	2.8541190991
F	-4.7226887241	1.6537392141	1.5193021186
H	-6.5505336223	1.8676134953	0.0457304756
C	-8.0497163859	0.5498727346	-0.7849639619
C	-8.6358111131	-0.7235284053	-0.8742324289
C	-8.6218366733	1.5993126902	-1.5196756636
C	-9.7500375407	-0.9348442579	-1.6731642120
H	-8.2172601052	-1.5529225559	-0.3102743659
C	-9.7371375231	1.3874775203	-2.3219069307
H	-8.1770343582	2.5898773328	-1.4554991754
C	-10.3048000435	0.1188166108	-2.4013138089
H	-10.1917257468	-1.9254627080	-1.7297436837
H	-10.1635052280	2.2128122495	-2.8843880245
H	-11.1769521304	-0.0509991625	-3.0257529093

Int2

M06-L/6-31G(d,p) Electronic E: -3828.239008 a.u.

M06-L/6-31G(d,p) Gibbs free E: -3827.606417 a.u.

M06-L/cc-pVTZ Electronic E: -3829.047912 a.u.

C	-3.5128062007	0.2685845365	0.9512171164
C	-2.9464507926	-2.1506609484	0.7069897084
C	-4.1214583361	-2.0673775698	-0.2621983974
C	-4.8899177335	0.0540667509	0.4190213403
C	-1.3801942016	-0.2667367488	1.3593788202
H	-2.0766325207	-2.5546751357	0.1702080342
H	-3.7734238385	-1.6109005412	-1.2041206444
H	-5.6420762051	0.4892627024	1.0818578954
N	-2.9604031457	1.4059184622	1.2771757471
N	-1.6459776084	1.0439070787	1.5305292889
N	-2.6099065088	-0.7608037598	1.0186840662
H	-4.5209032258	-3.0566290010	-0.4904961043

H	-4.9681013718	0.5673763632	-0.5536256707
O	-5.1975283882	-1.3186422535	0.2860725615
C	-0.7638173551	2.0016653894	2.1278427079
C	-0.1827388682	3.0071103238	1.3509573947
C	-0.5741773896	1.9088407483	3.5158733248
C	0.6913240807	3.8874080167	1.9961540404
C	0.2919586154	2.8223839941	4.1100385984
C	0.9553859198	3.8000822060	3.3624648463
H	1.1769109966	4.6641125559	1.4076458640
H	0.4583156666	2.7608077295	5.1842018551
C	-1.3042172242	0.8824042402	4.3239169277
H	-2.3813107793	0.9068918331	4.1203318383
H	-0.9507191455	-0.1288298592	4.0920798412
H	-1.1462970458	1.0396442488	5.3927523205
C	-0.5170794537	3.1928267204	-0.0959996217
H	-0.8636387987	2.2749609680	-0.5688786288
H	-1.3146003087	3.9361904388	-0.2069781949
H	0.3478235451	3.5583139826	-0.6553083991
C	1.9530328415	4.7048846413	4.0170116972
H	2.1534103728	5.5952018498	3.4159928173
H	1.6204096554	5.0277922801	5.0076991409
H	2.9091975094	4.1858455000	4.1581681789
C	-3.1462989876	-3.0232845298	1.9775500733
C	-4.3124469501	-2.5441582287	2.8433915041
H	-4.1869750297	-1.4954094759	3.1380117192
H	-5.2740738880	-2.6384740124	2.3355974361
H	-4.3501152307	-3.1347994564	3.7643502180
C	-3.3916674613	-4.4637164363	1.5211738292
H	-2.5878097589	-4.8206004535	0.8653213585
H	-3.4260544201	-5.1297485285	2.3881013823
H	-4.3403814240	-4.5791583022	0.9884436334
C	-1.8718577883	-2.9957795129	2.8263610815
H	-0.9767979663	-3.2639230937	2.2482957571
H	-1.6880985642	-2.0138224110	3.2727223223
H	-1.9593407344	-3.7145212455	3.6480561494
Cu	0.3522694534	-1.2014969856	1.1104751023
Si	2.0622573226	-1.0141615049	2.7044642418
C	3.4348061863	-2.3312542108	2.6733612027
H	4.1681660508	-2.1448974462	3.4664671465
H	3.9729425235	-2.3240445038	1.7195704082
H	3.0440660690	-3.3455824872	2.8113393616
C	2.9470391403	0.6368238742	2.3686585329
H	3.8066962087	0.7917791469	3.0334793659
H	2.2720383873	1.4916116170	2.4862911261

H	3.3215366958	0.6650789414	1.3387192866
C	1.5373390869	-0.9835330004	4.5310201515
C	1.8055822060	0.1013387886	5.3796065175
C	0.8394135032	-2.0698222699	5.0876585413
C	1.3856482338	0.1126092321	6.7096193605
H	2.3484883605	0.9626843585	4.9905037582
C	0.4146460829	-2.0701589269	6.4131832862
H	0.6182156124	-2.9354439518	4.4607509320
C	0.6824747109	-0.9714901501	7.2298894575
H	1.6068065225	0.9705418553	7.3418571509
H	-0.1267700187	-2.9252702688	6.8121291458
H	0.3493783178	-0.9636418748	8.2645546852
C	1.4620796349	-2.1122996382	-0.3432139226
C	0.2369817688	-1.6731651023	-0.9046457714
C	0.1533677520	-0.3859259596	-1.6162256506
F	0.9202366139	0.5669179107	-1.0205469030
F	-1.1247851048	0.0902643288	-1.6530907628
F	0.5551804468	-0.4324232671	-2.9122140953
C	1.7087235097	-3.5381377316	-0.0837932667
C	0.6632045383	-4.4168379826	0.2403397009
C	3.0038571852	-4.0644809286	-0.1726039158
C	0.9025714592	-5.7615907127	0.4868022877
H	-0.3523756632	-4.0288404049	0.3129932145
C	3.2469101655	-5.4129870603	0.0669788194
H	3.8264490926	-3.4024256399	-0.4332354439
C	2.2000704794	-6.2673370125	0.4037332544
H	0.0760046944	-6.4169739544	0.7492008906
H	4.2604245995	-5.7969475803	-0.0071327145
H	2.3912607017	-7.3181711964	0.5996277351
H	2.3507165021	-1.4964764332	-0.4855118320
H	-0.4999325855	-2.4032889243	-1.2292401605

TS2-3

M06-L/6-31G(d,p) Electronic E: -3828.217651 a.u.

M06-L/6-31G(d,p) Gibbs free E: -3827.584473 a.u.

M06-L/cc-pVTZ Electronic E: -3829.003375 a.u.

C	-0.4668526836	2.3527215593	-1.4618533163
C	-2.6400149057	3.4325806758	-2.0067157917
C	-1.7258183633	4.1963556816	-2.9585031954
C	0.3015668025	3.5080279812	-2.0139609796
C	-2.2678687597	1.0864836333	-1.0510156312
H	-3.4656686810	3.0133397031	-2.5978311334
H	-1.4870837887	3.5576359517	-3.8248321340
H	1.0530773999	3.8497373718	-1.2979911996

N	0.0326464113	1.2578724107	-0.9573422821
N	-1.0953660080	0.5002266467	-0.7043673558
N	-1.8383594714	2.2979114891	-1.5326973439
H	-2.2100540017	5.0989662784	-3.3312546365
H	0.8341870035	3.1749702187	-2.9204007682
O	-0.5331435736	4.6102005470	-2.3073876870
C	-0.9818121159	-0.7994942936	-0.1215440091
C	-0.4796875681	-1.8451541193	-0.9058892683
C	-1.3961633873	-0.9800521073	1.2070993164
C	-0.4448216811	-3.1188348703	-0.3370806559
C	-1.3554360598	-2.2765756813	1.7189367934
C	-0.8973149015	-3.3578021786	0.9622594022
H	-0.0678622778	-3.9489712439	-0.9327916150
H	-1.6864092665	-2.4435505727	2.7424949421
C	-1.8524831040	0.1706088462	2.0486176000
H	-1.1753109608	1.0261227106	1.9551785201
H	-2.8509683827	0.5122371136	1.7431044732
H	-1.9006767612	-0.1150460114	3.1014789222
C	0.0033620586	-1.6012971175	-2.3011296856
H	-0.6925531391	-0.9718966528	-2.8658307215
H	0.9644711041	-1.0766179325	-2.3013387091
H	0.1308419109	-2.5409444959	-2.8429735664
C	-0.9217732482	-4.7448193071	1.5258622365
H	-0.2926759873	-5.4283255582	0.9498797991
H	-0.5863502533	-4.7664951472	2.5665850625
H	-1.9413919634	-5.1484973974	1.5126556590
C	-3.2572844430	4.2509339279	-0.8307642095
C	-2.2458675619	4.5076175385	0.2883092884
H	-1.9047574853	3.5710130483	0.7436842802
H	-1.3724661504	5.0608254491	-0.0649874372
H	-2.7215665195	5.0935399961	1.0808444359
C	-3.7696496710	5.5862664231	-1.3749634388
H	-4.4185799101	5.4470169482	-2.2479283340
H	-4.3614007113	6.0942774064	-0.6081162479
H	-2.9529548246	6.2582518126	-1.6565288387
C	-4.4420441643	3.4723053599	-0.2574819779
H	-5.1980491597	3.2637441591	-1.0226788278
H	-4.1390010254	2.5144220794	0.1807185455
H	-4.9286502941	4.0462625963	0.5379238270
Cu	-3.9505262267	0.2400096488	-0.7382660702
Si	-5.0902533727	-0.5001971733	-2.7845289315
C	-5.8631152077	1.1941432975	-3.1113679115
H	-6.5897769368	1.4506340144	-2.3345347840
H	-6.3814326218	1.2092152901	-4.0761254585

H	-5.1134202050	1.9912226372	-3.1243476824
C	-3.4964456791	-0.7597781979	-3.7794426203
H	-3.7093424489	-0.9490525842	-4.8384208938
H	-2.9337755020	-1.6192627669	-3.3980661476
H	-2.8441568546	0.1163147347	-3.7015622575
C	-6.3004514497	-1.7746310860	-3.4707555548
C	-5.8580293885	-2.9737230268	-4.0493356721
C	-7.6867783488	-1.5835198624	-3.3587355888
C	-6.7552336050	-3.9428092457	-4.4891533471
H	-4.7893401594	-3.1652762385	-4.1388731252
C	-8.5925692433	-2.5471489056	-3.7962486403
H	-8.0695724311	-0.6623748869	-2.9177468040
C	-8.1266870073	-3.7327345436	-4.3601981858
H	-6.3852860198	-4.8667719067	-4.9265756517
H	-9.6612267316	-2.3739636291	-3.6973929826
H	-8.8296149797	-4.4888972840	-4.6996253429
C	-5.5841430022	-1.0945967935	-0.7004284925
C	-5.2137036517	-0.4326192578	0.6128119024
H	-4.8364919349	-1.1217392500	1.3676864371
C	-6.2255055921	0.4702519591	1.1533836341
F	-6.6837259606	1.3619356778	0.2150519116
F	-5.7798279881	1.2061778760	2.2059515380
F	-7.3713764329	-0.1391434821	1.6151822019
H	-6.6295002742	-0.8836445890	-0.9697309607
C	-5.3087088953	-2.5645812424	-0.7191742024
C	-4.0003464436	-3.0486985217	-0.8175212230
C	-6.3574769489	-3.4861237418	-0.6307864196
C	-3.7452334956	-4.4173109911	-0.8472672160
H	-3.1761566898	-2.3356584820	-0.8886408876
C	-6.1055628575	-4.8538531906	-0.6619636181
H	-7.3797659606	-3.1194478244	-0.5620712885
C	-4.7987301278	-5.3259522195	-0.7752512619
H	-2.7198029277	-4.7691118273	-0.9386195869
H	-6.9351134015	-5.5541955848	-0.6103205202
H	-4.6036784711	-6.3942606766	-0.8099834015

Int3

M06-L/6-31G(d,p) Electronic E: -3828.254738 a.u.

M06-L/6-31G(d,p) Gibbs free E: -3827.624252 a.u.

M06-L/cc-pVTZ Electronic E: -3829.040937 a.u.

C	-3.8046544173	0.9788940623	-1.3432770954
C	-3.3446262757	-1.4576995951	-0.9756476906
C	-4.3612936083	-1.5520412522	-2.1111130702
C	-5.0855136817	0.6832681018	-2.0483131051

C	-1.8307006799	0.5052727523	-0.4160702756
H	-2.4319493490	-1.9890718202	-1.2817874396
H	-3.8625719423	-1.3238934019	-3.0667695976
H	-5.9018865169	1.2879194862	-1.6459422202
N	-3.2585799258	2.1519258077	-1.1535741751
N	-2.0463667209	1.8262109336	-0.5754130476
N	-2.9878923863	-0.0338622148	-0.9016872866
H	-4.7799569672	-2.5561362418	-2.1835182255
H	-4.9710254160	0.9471826000	-3.1130761374
O	-5.4583470540	-0.6715347697	-1.9069437051
C	-1.1115760748	2.8286932513	-0.1644861384
C	-0.4600429182	3.5837792046	-1.1466908019
C	-0.8345598678	2.9673522636	1.2046934354
C	0.5011569917	4.5013614900	-0.7223612729
C	0.1425585767	3.8923403724	1.5710114379
C	0.8233028808	4.6637057073	0.6263866964
H	1.0265485393	5.0919152666	-1.4712052057
H	0.3781137700	4.0108393234	2.6271044167
C	-1.5357173921	2.1534819344	2.2505387239
H	-2.5766954237	1.9450825000	1.9838850441
H	-1.0444360536	1.1803027682	2.3971091800
H	-1.5246741294	2.6705577554	3.2126915736
C	-0.7648440980	3.3919781786	-2.5990734528
H	-0.7106795044	2.3345716206	-2.8815450460
H	-1.7766625335	3.7278479249	-2.8459284601
H	-0.0594524473	3.9448244202	-3.2223737188
C	1.8894348802	5.6241599896	1.0562771790
H	2.7345103214	5.0949079768	1.5102992380
H	2.2755636877	6.2027530139	0.2134681178
H	1.5189575811	6.3286489327	1.8074180373
C	-3.7867556993	-2.0439429566	0.3969915377
C	-4.9741336592	-1.2898839888	0.9978088022
H	-4.7457197271	-0.2260189505	1.1351037046
H	-5.8705135525	-1.3660648107	0.3794785149
H	-5.2031043729	-1.6989351322	1.9869794725
C	-4.1575646591	-3.5140473396	0.1811641546
H	-3.3522640004	-4.0627795220	-0.3214381589
H	-4.3288554229	-3.9984292855	1.1465150240
H	-5.0732052946	-3.6340169090	-0.4053367567
C	-2.6216358647	-1.9888983626	1.3885473658
H	-1.7120291707	-2.4610358283	0.9967466380
H	-2.3625678272	-0.9642023727	1.6735191984
H	-2.8921940391	-2.5185400525	2.3076488201
Cu	-0.2402955463	-0.1788105994	0.4034170519

Si	2.1406795280	-1.7392297362	-1.2740838533
C	0.6912998855	-2.9398183345	-1.2061950441
H	0.3965450539	-3.2091347889	-2.2261385125
H	-0.1704951430	-2.4671666299	-0.7172277517
H	0.9132298796	-3.8577295414	-0.6581462752
C	1.6596188257	-0.3385873715	-2.4350721945
H	1.2066176563	-0.7178716907	-3.3568013975
H	2.5116114326	0.2950121732	-2.7002812522
H	0.9235894312	0.3119326632	-1.9430631509
C	3.6478597232	-2.6521608985	-1.9375174854
C	4.3925678060	-2.2070369105	-3.0394437961
C	4.1036480337	-3.8014059441	-1.2698469418
C	5.5397632436	-2.8773818317	-3.4596048787
H	4.0761371150	-1.3133181053	-3.5756287113
C	5.2485507583	-4.4772862490	-1.6814452252
H	3.5556819780	-4.1722514514	-0.4025869644
C	5.9700928567	-4.0145012272	-2.7804777746
H	6.1005922437	-2.5104438258	-4.3155640011
H	5.5807872727	-5.3629502330	-1.1459004953
H	6.8659302405	-4.5375425281	-3.1045727741
C	2.6343227543	-0.9841733338	0.4250042245
C	1.4250700826	-0.6631484260	1.3293182292
H	1.6830769136	0.2042103108	1.9580846333
C	1.1687350086	-1.7498027704	2.2981001807
F	0.8942680239	-2.9548498472	1.7138690514
F	0.1080147161	-1.4754349674	3.1146980231
F	2.2069328765	-2.0200821444	3.1528274451
H	3.3080513214	-1.7069324688	0.9139041129
C	3.4597524576	0.2251527481	0.0762676860
C	2.8946504541	1.5046356656	-0.0420084548
C	4.8194961051	0.0803445177	-0.2383437807
C	3.6590829126	2.5881357290	-0.4678452991
H	1.8355724932	1.6461067754	0.1783791625
C	5.5842732767	1.1627707137	-0.6602627032
H	5.2756736078	-0.9051341561	-0.1546575758
C	5.0066359127	2.4252761405	-0.7801997219
H	3.1914039551	3.5657743483	-0.5623667629
H	6.6363592134	1.0193270305	-0.8933006177
H	5.6011390846	3.2729573634	-1.1099806336

TS3-R-1b

M06-L/6-31G(d,p) Electronic E: -3828.229632 a.u.

M06-L/6-31G(d,p) Gibbs free E: -3827.598137 a.u.

M06-L/cc-pVTZ Electronic E: -3829.013184 a.u.

C	-3.3703291547	0.5531726627	-0.8488286705
C	-2.3838407074	-1.7372474779	-1.0935119640
C	-3.3445099774	-1.7293501312	-2.2800305913
C	-4.5428325060	0.1967605571	-1.6987641642
C	-1.3744296803	0.2641042483	0.1190459785
H	-1.3737390554	-1.9391161042	-1.4764753209
H	-2.9028777052	-1.1456494221	-3.1039933036
H	-5.4774795959	0.4947865542	-1.2174124845
N	-3.1033267791	1.7231149224	-0.3321811047
N	-1.8737030278	1.5124720975	0.2613772088
N	-2.3676852705	-0.3534537413	-0.5966298557
H	-3.5235530154	-2.7408466607	-2.6460269088
H	-4.4715439673	0.7454014810	-2.6531350101
O	-4.6129049920	-1.1948015069	-1.9278209510
C	-1.1573984692	2.5682986763	0.9079125269
C	-0.6043911287	3.5792430357	0.1088564480
C	-0.9500508858	2.4998037998	2.2912702865
C	0.1762181405	4.5462314007	0.7368661866
C	-0.1570011974	3.4948108866	2.8691919998
C	0.4113861276	4.5211788577	2.1152741210
H	0.6267218018	5.3306421553	0.1310854003
H	0.0264973906	3.4551429559	3.9415887857
C	-1.5211077365	1.3968312232	3.1300693831
H	-2.4915550326	1.0580051024	2.7545188177
H	-0.8585889391	0.5206854410	3.1519861444
H	-1.6515607587	1.7302367236	4.1625530822
C	-0.8177796802	3.5894721183	-1.3725697123
H	-0.5837352962	2.6130642234	-1.8145347960
H	-1.8603654890	3.8018504681	-1.6288298151
H	-0.1874157524	4.3405503423	-1.8535154317
C	1.2409021087	5.5856550411	2.7658702908
H	0.6524008982	6.4929502525	2.9435230632
H	1.6309519996	5.2590784536	3.7328392021
H	2.0874873740	5.8764550930	2.1377494210
C	-2.6704642783	-2.7834316282	0.0192997642
C	-4.0040175510	-2.5346092059	0.7239696471
H	-4.0417643133	-1.5306128256	1.1628451930
H	-4.8558989469	-2.6403340309	0.0488235182
H	-4.1244937040	-3.2494568991	1.5442681279
C	-2.6726714981	-4.1710520850	-0.6288364325
H	-1.7560476555	-4.3472692391	-1.2050895763
H	-2.7234171166	-4.9413072861	0.1458970855
H	-3.5290573944	-4.3258547011	-1.2918634221
C	-1.5449354672	-2.7451686392	1.0560073662

H	-0.5549148166	-2.7961906280	0.5833287564
H	-1.5632007800	-1.8422087486	1.6716969380
H	-1.6299352370	-3.6013580452	1.7331090039
Cu	0.2914872391	-0.1764797215	0.9384543692
Si	2.9112878223	-2.0432674840	-0.2991920802
C	2.3497096857	-3.2358539113	1.0318118571
H	1.9664911607	-4.1513664140	0.5688216813
H	1.5599763231	-2.7999518507	1.6520161853
H	3.1664746839	-3.5175654532	1.7022736504
C	1.5569636130	-1.8585354020	-1.5913651165
H	1.1121489951	-2.8270107744	-1.8455818406
H	1.9186047720	-1.3884852963	-2.5110830572
H	0.7582927924	-1.2095441148	-1.2035086793
C	4.4869474997	-2.6858808706	-1.1042120136
C	4.6895632947	-2.6642337159	-2.4922368249
C	5.5526776475	-3.1284585704	-0.3032389650
C	5.8983368677	-3.0627824755	-3.0579199737
H	3.8914592917	-2.3167434250	-3.1466192378
C	6.7657589870	-3.5263132375	-0.8586653357
H	5.4361343079	-3.1569370540	0.7803984145
C	6.9406209559	-3.4935572506	-2.2407607857
H	6.0289523081	-3.0341181965	-4.1366668255
H	7.5750110102	-3.8618860613	-0.2152358994
H	7.8861223377	-3.8025024259	-2.6785150053
C	3.3289931862	-0.2921837440	0.3939561892
C	2.2932958708	0.2904239414	1.3485892095
H	2.2061405859	1.3795931889	1.3357261238
C	2.1910321277	-0.1945579190	2.6525490922
F	0.6206677348	-1.1411791660	2.7885779366
F	1.8980190170	0.6300270187	3.6460462968
F	2.9586493750	-1.1820307359	3.0863786526
H	4.3034734759	-0.3999121608	0.8997003344
C	3.5400548874	0.5918356569	-0.8079246425
C	2.4987803543	1.3505894793	-1.3630164389
C	4.7878771806	0.6276973266	-1.4466765322
C	2.6991649092	2.1116898391	-2.5113579292
H	1.5169940973	1.3251605233	-0.8887109451
C	4.9883179468	1.3850373718	-2.5959124244
H	5.6088827912	0.0436010425	-1.0336005043
C	3.9440171339	2.1334996150	-3.1354467106
H	1.8757057346	2.6921772074	-2.9210852919
H	5.9672156587	1.3940574690	-3.0682739355
H	4.1006590557	2.7306699833	-4.0294702291

NHC-CuF

M06-L/6-31G(d,p) Electronic E: -2680.488117 a.u.

M06-L/6-31G(d,p) Gibbs free E: -2680.134375 a.u.

M06-L/cc-pVTZ Electronic E: -2681.022489 a.u.

C	0.4400678233	1.8973184600	-1.2786857534
C	-1.8069854647	2.7047245473	-2.0043954630
C	-0.9364106893	3.8202600747	-2.5746925741
C	1.0269528727	3.2647105737	-1.4004017851
C	-1.1010374374	0.2979102644	-1.5611168001
H	-2.4231982486	2.2885108702	-2.8140105756
H	-0.4492048708	3.4659060284	-3.4972405457
H	1.5533859453	3.5467328668	-0.4849235616
N	1.0712346073	0.7954150934	-0.9716235699
N	0.0977724231	-0.1732780702	-1.1491352515
N	-0.8623777559	1.6483058124	-1.6235086670
H	-1.5307894102	4.6991289708	-2.8255407486
H	1.7669869949	3.2557511032	-2.2176471708
O	0.0392813673	4.2486238752	-1.6334013934
C	0.3978960855	-1.5380571704	-0.8424555129
C	0.4499869241	-2.4776865107	-1.8783231505
C	0.6157569230	-1.8817274399	0.4985010406
C	0.7392439199	-3.7992919117	-1.5342951638
C	0.9070720253	-3.2135411152	0.7860786474
C	0.9770402369	-4.1859018579	-0.2150455529
H	0.7798355972	-4.5462808006	-2.3249625732
H	1.0713199009	-3.5007606604	1.8233315862
C	0.5129137331	-0.8556490992	1.5835455806
H	1.3307121134	-0.1303231950	1.5314084559
H	-0.4171560331	-0.2807772322	1.5006880092
H	0.5350789286	-1.3248036431	2.5691400011
C	0.1867155774	-2.0906198826	-3.2992537125
H	-0.8698700842	-1.8276774468	-3.4444941205
H	0.7677619187	-1.2107607741	-3.5942371125
H	0.4293244255	-2.9083555150	-3.9806142854
C	1.3156286726	-5.6060166232	0.1213776822
H	0.8474271415	-5.9212843762	1.0579951413
H	0.9978336643	-6.2941847918	-0.6655994669
H	2.3962821149	-5.7362325546	0.2487746625
C	-2.7643751565	3.1018776278	-0.8419079715
C	-2.0111090247	3.4630604643	0.4400906474
H	-1.3805878833	2.6336818134	0.7821191551
H	-1.3776999845	4.3432419705	0.3146387917
H	-2.7304180342	3.6688585983	1.2392278243
C	-3.6027441067	4.2978735849	-1.3008544487

H	-4.0855051734	4.1082659690	-2.2664478534
H	-4.3949673131	4.4964513561	-0.5734357839
H	-3.0082311753	5.2123031842	-1.3877652860
C	-3.7108882141	1.9374624988	-0.5358171069
H	-4.2325680428	1.5738099052	-1.4292274566
H	-3.1832792785	1.0836373495	-0.0985669087
H	-4.4671811738	2.2593431778	0.1875665062
Cu	-2.6770609167	-0.5668743238	-2.0431046313
F	-4.2060084649	-1.2728450460	-2.5690897734

NHC-CuOH

M06-L/6-31G(d,p) Electronic E: -2656.456048 a.u.

M06-L/6-31G(d,p) Gibbs free E: -2656.093525 a.u.

M06-L/cc-pVTZ Electronic E: -2656.979849 a.u.

C	0.6995195373	2.0848568826	-1.0784663689
C	-1.4703376282	3.0649801831	-1.8221389288
C	-0.5257962162	4.1945451053	-2.2203719603
C	1.3465362103	3.4293004681	-1.0256478429
C	-0.8943924615	0.5936911194	-1.5839426674
H	-2.0539364999	2.7704570489	-2.7058665772
H	0.0012933212	3.9188397346	-3.1478592195
H	1.8432387774	3.5852750355	-0.0645825968
N	1.2685205306	0.9314679797	-0.8525129633
N	0.2648297839	0.0301830360	-1.1675571273
N	-0.5935895161	1.9314059629	-1.5075739713
H	-1.0707400250	5.1201349929	-2.4069132273
H	2.1203470587	3.4779304668	-1.8096637549
O	0.4093563005	4.4753092952	-1.1867303435
C	0.4929118362	-1.3702321097	-0.9893852311
C	0.5386889660	-2.2071570922	-2.1103178801
C	0.6564282371	-1.8539025534	0.3168112065
C	0.7610850940	-3.5685083685	-1.8895215422
C	0.8817234957	-3.2185275211	0.4799155631
C	0.9375155736	-4.0926101086	-0.6096279475
H	0.8031109714	-4.2352676865	-2.7490297227
H	1.0073237926	-3.6107509044	1.4878401461
C	0.5684192712	-0.9349781497	1.4950983275
H	1.4140684012	-0.2414563078	1.5303716039
H	-0.3368480304	-0.3182383500	1.4496465509
H	0.5486747956	-1.4984653010	2.4301146613
C	0.3414576507	-1.6781125850	-3.4957317319
H	-0.7109991702	-1.4082363795	-3.6663461293
H	0.9238386573	-0.7679646920	-3.6705339881
H	0.6274780229	-2.4207221448	-4.2435146543

C	1.1662941812	-5.5583488657	-0.3992449042
H	2.0386578024	-5.7424922835	0.2353680102
H	0.3114239957	-6.0268539695	0.1003122345
H	1.3216247883	-6.0824303450	-1.3451444278
C	-2.4766018139	3.3783602360	-0.6745149236
C	-1.7917439081	3.4856926296	0.6895304487
H	-1.2793806237	2.5540519016	0.9562736410
H	-1.0637075513	4.2989376407	0.7227733655
H	-2.5453053474	3.6694456540	1.4620119303
C	-3.1838023867	4.6969711155	-0.9979170234
H	-3.5993928603	4.6966833690	-2.0122636658
H	-4.0158088327	4.8510798230	-0.3048641945
H	-2.5167358471	5.5589473787	-0.9001058643
C	-3.5295176177	2.2687935189	-0.6084901903
H	-4.0242548165	2.1123226907	-1.5741740556
H	-3.1004985652	1.3091341574	-0.3027038924
H	-4.3001968527	2.5322787593	0.1232040408
Cu	-2.4485222053	-0.2247430854	-2.2215339605
O	-3.9510697717	-0.9382711432	-2.9186593173
H	-3.7696595054	-1.8657402385	-3.0959229340

R-1b

M06-L/6-31G(d,p) Electronic E: -1147.734006 a.u.

M06-L/6-31G(d,p) Gibbs free E: -1147.481513 a.u.

M06-L/cc-pVTZ Electronic E: -1148.007072 a.u.

Si	2.2211095839	-1.9423860876	-1.2243756100
C	1.1845342253	-3.4482973065	-0.8102407179
H	0.9818034310	-4.0496668191	-1.7014502610
H	0.2202643040	-3.1519774415	-0.3867852239
H	1.6750733442	-4.0951418503	-0.0764452806
C	1.2911558849	-0.7722326675	-2.3563849139
H	1.0032167477	-1.2716695881	-3.2858280908
H	1.8956260993	0.0993843473	-2.6257400417
H	0.3758789663	-0.4060538833	-1.8799250510
C	3.8410883311	-2.4618172989	-2.0179228023
C	4.6590109738	-1.5204665361	-2.6661958915
C	4.3003408828	-3.7866701400	-1.9570253341
C	5.8805935740	-1.8836536147	-3.2246562621
H	4.3422460015	-0.4791521767	-2.7239236491
C	5.5208244075	-4.1590123551	-2.5163084628
H	3.6922555752	-4.5456554541	-1.4667026745
C	6.3136226205	-3.2062716426	-3.1510451812
H	6.4961475898	-1.1350864666	-3.7166072141
H	5.8526734128	-5.1923217923	-2.4579738360

H	7.2664946071	-3.4931913466	-3.5877285335
C	2.6045063140	-1.0172701397	0.4250768588
C	1.3202319575	-0.5715108906	1.0495500499
H	0.8725584907	0.3734305571	0.7628120143
C	0.6372308630	-1.2883308125	1.9314271904
F	1.0101262975	-2.4768058322	2.3948199187
F	-0.5154284475	-0.9310955222	2.4800296272
H	3.0697043372	-1.7748492986	1.0692947176
C	3.6022154040	0.0826896445	0.1800310016
C	3.2231378529	1.3305448813	-0.3319104634
C	4.9672394089	-0.1566525286	0.3808655457
C	4.1744841514	2.3022136423	-0.6311738589
H	2.1712023218	1.5474981405	-0.5062833368
C	5.9203587526	0.8110964952	0.0811769229
H	5.2812714305	-1.1251375982	0.7661395594
C	5.5284957480	2.0471653561	-0.4276750392
H	3.8542653487	3.2629498197	-1.0254587685
H	6.9729875590	0.5978547263	0.2465195510
H	6.2703666473	2.8054604798	-0.6606914587

Int2'

M06-L/6-31G(d,p) Electronic E: -3828.243411 a.u.

M06-L/6-31G(d,p) Gibbs free E: -3827.612584 a.u.

M06-L/cc-pVTZ Electronic E: -3829.054100 a.u.

C	-0.4404453561	2.3359624286	-1.3788096729
C	-2.7721030435	3.0238991091	-1.9558120380
C	-1.9977012047	3.8868945535	-2.9497527001
C	0.1354136889	3.5378841243	-2.0479987517
C	-2.0315041115	0.8586467362	-0.8294173179
H	-3.4933180702	2.4071027725	-2.5169170523
H	-1.6882361837	3.2717182295	-3.8099257405
H	0.8728698040	4.0269287679	-1.4070499693
N	0.2189913418	1.3559514152	-0.8263082680
N	-0.7863222343	0.4599014230	-0.4918671305
N	-1.7901728204	2.0909686921	-1.3876226433
H	-2.6191786363	4.6989546510	-3.3283261475
H	0.6546875493	3.2130496219	-2.9654574992
O	-0.8599699781	4.4920658824	-2.3498459372
C	-0.4237741559	-0.6965009015	0.2735398351
C	-0.3371465841	-1.9429074563	-0.3519916621
C	-0.1458140615	-0.5144579442	1.6326021323
C	0.0417102543	-3.0332968158	0.4302523672
C	0.2262990744	-1.6352103242	2.3723709874
C	0.3240449872	-2.9011945906	1.7909544030

H	0.1125495084	-4.0134878988	-0.0381009914
H	0.4370143275	-1.5160289040	3.4338053262
C	-0.2741001752	0.8356266001	2.2645461184
H	0.4832928431	1.5307003652	1.8871882437
H	-1.2507238491	1.2816029038	2.0417943324
H	-0.1708345992	0.7734830266	3.3496991572
C	-0.6662363390	-2.0988561277	-1.8010919444
H	-1.7123247670	-1.8264087678	-1.9955857595
H	-0.0532554876	-1.4431794120	-2.4291102626
H	-0.5186948832	-3.1281145660	-2.1346893342
C	0.6908655695	-4.0962520799	2.6167983013
H	-0.1986659740	-4.5511267657	3.0670659579
H	1.1756595329	-4.8699480524	2.0157795866
H	1.3625199204	-3.8305952405	3.4374450402
C	-3.5676803537	3.8032117640	-0.8698153381
C	-2.6599924613	4.6372302132	0.0355548516
H	-1.8989659756	4.0145930732	0.5216212074
H	-2.1465131803	5.4310485331	-0.5099630689
H	-3.2572316716	5.0971377087	0.8296932797
C	-4.5748838577	4.7109112167	-1.5823685620
H	-5.1799194159	4.1506983244	-2.3056123858
H	-5.2580725255	5.1540105814	-0.8519590664
H	-4.0919053710	5.5374840007	-2.1115549284
C	-4.3457151597	2.8168362354	0.0030221324
H	-4.9558613581	2.1304769602	-0.6016075530
H	-3.6870915932	2.2104010921	0.6314817407
H	-5.0275649161	3.3619533747	0.6648984053
Cu	-3.7365896847	-0.1212348455	-1.0176447751
Si	-3.8604534168	-0.4354595485	-3.3550265663
C	-4.0052116093	-2.2531965516	-3.9066799564
H	-4.0350704016	-2.3442231976	-4.9994161424
H	-3.1453864363	-2.8382746089	-3.5623459247
H	-4.9035732934	-2.7400888538	-3.5134131954
C	-2.3135472659	0.1982113784	-4.2829206183
H	-2.3468134625	-0.0721886880	-5.3453377477
H	-2.2387403305	1.2904931840	-4.2357776630
H	-1.3844635138	-0.2066838213	-3.8654287952
C	-5.2922027996	0.4914287523	-4.2095376003
C	-5.9451295350	1.5659107422	-3.5878861520
C	-5.7257373746	0.1503309361	-5.5009357836
C	-6.9649931580	2.2775337885	-4.2145967631
H	-5.6730399764	1.8255521248	-2.5632801937
C	-6.7491283591	0.8483684402	-6.1387536045
H	-5.2540793328	-0.6817913815	-6.0237986939

C	-7.3712503781	1.9182755348	-5.4973356788
H	-7.4567407946	3.0961237260	-3.6926725270
H	-7.0638424259	0.5583078950	-7.1386576790
H	-8.1719013161	2.4623314119	-5.9917941378
C	-5.4131602617	-1.0925442728	-0.4080965336
C	-4.7290766344	-0.5919005161	0.7230631957
H	-5.1047848020	0.2782345817	1.2554432251
C	-3.9296450358	-1.4967825713	1.5709672291
F	-3.1965780537	-2.3738958082	0.8361914432
F	-3.0741367646	-0.8159222328	2.3688483581
F	-4.6815223354	-2.2623792149	2.4098657668
H	-5.2122348943	-2.1262601354	-0.6948988595
C	-6.6651504756	-0.5370492620	-0.9409997373
C	-7.2893934196	0.5933684852	-0.3900399739
C	-7.2841611241	-1.1594177213	-2.0366171001
C	-8.4707471812	1.0905412778	-0.9290808010
H	-6.8552849714	1.0833798418	0.4779580103
C	-8.4666106050	-0.6671409666	-2.5716233633
H	-6.8128192129	-2.0357758276	-2.4776365861
C	-9.0647800917	0.4658578447	-2.0236804428
H	-8.9349862825	1.9671050135	-0.4847241322
H	-8.9156804446	-1.1614786395	-3.4287300977
H	-9.9851155918	0.8585561730	-2.4463500832

TS2-3’

M06-L/6-31G(d,p) Electronic E: -3828.214621 a.u.

M06-L/6-31G(d,p) Gibbs free E: -3827.581849 a.u.

M06-L/cc-pVTZ Electronic E: -3829.000248 a.u.

C	-4.7384852254	1.5484652533	-0.8230395169
C	-4.4088703946	-0.8651184246	-1.3986496438
C	-5.5296453581	-0.5073611981	-2.3700432494
C	-6.1203192883	1.5514314805	-1.3854227193
C	-2.6928998381	0.7324171958	-0.4141848112
H	-3.5402422970	-1.2380429967	-1.9652278801
H	-5.1170460521	0.0450081926	-3.2289280947
H	-6.8400886168	1.9432911065	-0.6613381856
N	-4.0632813007	2.5891445031	-0.4134487032
N	-2.8110682845	2.0554184267	-0.1575826685
N	-3.9704777920	0.4142081683	-0.8204717226
H	-6.0159992403	-1.4071040354	-2.7508842183
H	-6.1358014394	2.2224256076	-2.2600932118
O	-6.5496088042	0.2543037816	-1.7344547476
C	-1.7546414411	2.9254498273	0.2524588895
C	-0.7844759733	3.2911101172	-0.6904148275

C	-1.7331848130	3.3816531708	1.5732810821
C	0.2633239570	4.1002137382	-0.2521526967
C	-0.6672503538	4.1955569184	1.9594796067
C	0.3453479373	4.5534173011	1.0681350359
H	1.0292976729	4.3947667397	-0.9679329804
H	-0.6206418862	4.5455237928	2.9891286365
C	-2.8079980024	2.9875245978	2.5364310523
H	-3.7625013186	3.4593558065	2.2811854580
H	-2.9856140632	1.9057752732	2.5186305279
H	-2.5483553998	3.2736780840	3.5575433242
C	-0.8819101406	2.8463167918	-2.1177295344
H	-0.8314142900	1.7531569858	-2.2139939712
H	-1.8345892406	3.1536690510	-2.5626489354
H	-0.0710196422	3.2684116689	-2.7152591094
C	1.4975905097	5.4052498545	1.5055961829
H	1.5504227389	6.3348810916	0.9296320060
H	1.4256432089	5.6712151382	2.5625355208
H	2.4519587508	4.8893700502	1.3548249122
C	-4.7616717741	-1.9413417519	-0.3384335355
C	-6.0310256090	-1.6143889458	0.4477621879
H	-5.9668932156	-0.6310153698	0.9275679006
H	-6.9244929577	-1.6194709183	-0.1801065057
H	-6.1677594868	-2.3569845125	1.2409796862
C	-4.9270006518	-3.2737467068	-1.0754688113
H	-4.0234118661	-3.5299238326	-1.6390461496
H	-5.1097004824	-4.0771958656	-0.3556371689
H	-5.7741679795	-3.2663791321	-1.7685838105
C	-3.5968722225	-2.0788234185	0.6379129106
H	-2.6544294563	-2.2517706697	0.1068337466
H	-3.4759996936	-1.1880395090	1.2641164775
H	-3.7606589477	-2.9332309607	1.3030845183
Cu	-1.1595481566	-0.3839591981	-0.6998039587
Si	0.4485835430	-1.0161574667	1.1245166775
C	-0.5270952584	-2.4424438744	1.8850007931
H	0.0310300879	-2.8579775037	2.7307301156
H	-1.4999834859	-2.1129603962	2.2575512254
H	-0.7044190074	-3.2529773982	1.1719378068
C	0.1480043233	0.5841802168	2.0897791669
H	0.6229669937	0.5324789403	3.0776410785
H	0.5461768084	1.4664425081	1.5769256888
H	-0.9245394430	0.7502291264	2.2280473437
C	2.2682814707	-1.4358570079	1.4152110799
C	3.2236324393	-0.4512884289	1.7070707637
C	2.7194828927	-2.7597454894	1.2972674692

C	4.5705525226	-0.7688386731	1.8606904681
H	2.9120610551	0.5890978790	1.7950953664
C	4.0648154805	-3.0875951970	1.4477333511
H	2.0046359936	-3.5547844264	1.0810958802
C	4.9951425363	-2.0892102975	1.7267643372
H	5.2918774359	0.0147683454	2.0789991497
H	4.3875597451	-4.1210052356	1.3490010353
H	6.0464760784	-2.3393033994	1.8420519945
C	0.6776993558	-1.3685654219	-1.0330329890
C	-0.3369241944	-1.4145039191	-2.1667369065
H	-0.0040916574	-0.9021290260	-3.0675926250
C	-0.8380815788	-2.7517267733	-2.4713100094
F	-1.2634510025	-3.4241560718	-1.3499438558
F	-1.8899982786	-2.7560436424	-3.3389772161
F	0.0800115056	-3.6056522708	-3.0370453583
H	0.9946441090	-2.3841699451	-0.7492677699
C	1.8603834658	-0.5181290053	-1.3846097951
C	1.8358008983	0.8647196609	-1.1909562085
C	3.0064962327	-1.0965827311	-1.9391265701
C	2.9316902669	1.6560923549	-1.5254477037
H	0.9497029038	1.3143742152	-0.7406075258
C	4.1064614581	-0.3110053285	-2.2678666080
H	3.0312090249	-2.1731519291	-2.0982176813
C	4.0747993588	1.0681560700	-2.0603137224
H	2.8958736690	2.7295468320	-1.3519340864
H	4.9962701384	-0.7774368722	-2.6821774311
H	4.9376943331	1.6781053134	-2.3123470237

Int3'

M06-L/6-31G(d,p) Electronic E: -3828.257050 a.u.

M06-L/6-31G(d,p) Gibbs free E: -3827.622974 a.u.

M06-L/cc-pVTZ Electronic E: -3829.043668 a.u.

C	-5.0520044853	1.6526385226	-2.0936875110
C	-5.0065607861	-0.8177013647	-2.5024400264
C	-5.9916868572	-0.4045236827	-3.5928206215
C	-6.3494258940	1.7989265207	-2.8155522586
C	-3.1706520097	0.6093762798	-1.4858898006
H	-4.1791219595	-1.3867438333	-2.9518110894
H	-5.4380382159	0.0028687431	-4.4535610058
H	-7.0735404475	2.3573136747	-2.2168982407
N	-4.3136035960	2.6067841170	-1.5875354168
N	-3.1655950789	1.9297832090	-1.2152524524
N	-4.4163354267	0.4402023646	-2.0282703217
H	-6.5755096514	-1.2573450947	-3.9418079800

H	-6.1685943090	2.3760096786	-3.7378860978
O	-6.9328330627	0.5481349764	-3.1128292101
C	-2.0964290880	2.5995674554	-0.5425751804
C	-1.2142995052	3.3909803392	-1.2875950756
C	-1.9478707213	2.3864610651	0.8317758037
C	-0.1358378934	3.9568509012	-0.6123844929
C	-0.8283275311	2.9452135209	1.4527026178
C	0.0932649955	3.7188041228	0.7462641378
H	0.5673008427	4.5722305786	-1.1716557912
H	-0.6708387669	2.7615188110	2.5145482425
C	-2.9408795179	1.5660737576	1.5950972808
H	-3.9691655327	1.8823527509	1.3880953874
H	-2.8725171497	0.5071371889	1.3191283215
H	-2.7668884957	1.6384101583	2.6706148757
C	-1.4005374929	3.5674478546	-2.7613660182
H	-1.3176300765	2.6058522389	-3.2825898489
H	-2.3892255428	3.9708177864	-2.9995886905
H	-0.6449233070	4.2375902668	-3.1764139093
C	1.3175109582	4.2689020399	1.4103186473
H	1.3317566723	5.3635926072	1.3925258886
H	1.3912731207	3.9490110636	2.4527065839
H	2.2226121149	3.9333712710	0.8909309389
C	-5.5894732909	-1.6844646231	-1.3487977124
C	-6.7523305413	-1.0027303903	-0.6266923150
H	-6.4615928608	-0.0185629553	-0.2387591173
H	-7.6240605917	-0.8661185293	-1.2690722787
H	-7.0512303792	-1.6116564681	0.2327411534
C	-6.0515932851	-3.0123113606	-1.9549459664
H	-5.2334528999	-3.5139090669	-2.4844324609
H	-6.3881575605	-3.6849584753	-1.1608440537
H	-6.8891287570	-2.8907739555	-2.6484808485
C	-4.4941109565	-1.9899530438	-0.3253590036
H	-3.6056262681	-2.4267047439	-0.7921448025
H	-4.1840949057	-1.0947912459	0.2240846968
H	-4.8701256929	-2.7092064090	0.4094627021
Cu	-1.7543590351	-0.6816282911	-1.4559290377
Si	0.9528757214	-1.9197440937	0.8230504374
C	0.9886505009	-3.6653316025	1.5169932312
H	1.1082567648	-3.6562471060	2.6047793267
H	0.0797791970	-4.2185842255	1.2756586683
H	1.8303799921	-4.2289355177	1.1006419818
C	-0.5412511860	-0.9290278503	1.3804681523
H	-0.5081212700	-0.6747148768	2.4454161848
H	-0.5882632361	0.0143799738	0.8197992146

H	-1.4705004778	-1.4744940056	1.1829709314
C	2.4989659478	-1.0325932992	1.4406880201
C	2.5291197347	0.3641000440	1.5883211448
C	3.6878358222	-1.7327181367	1.6954303335
C	3.6937227393	1.0304344772	1.9593418867
H	1.6276458332	0.9462635603	1.3901653759
C	4.8583153630	-1.0747636945	2.0666051066
H	3.7044387306	-2.8177408757	1.5955113996
C	4.8636512711	0.3115283939	2.1966024530
H	3.6925637184	2.1129041184	2.0639624931
H	5.7661825306	-1.6427542920	2.2541422380
H	5.7747096470	0.8301951064	2.4834706995
C	1.0049299778	-1.9358563744	-1.1029850508
C	-0.3625106897	-2.0447397337	-1.8132607757
H	-0.1682717343	-2.0008886690	-2.8961739890
C	-1.0014223748	-3.3616162011	-1.6112951879
F	-1.4995096705	-3.5418128757	-0.3401610804
F	-2.0702821735	-3.5466679756	-2.4439414170
F	-0.2009794704	-4.4554510517	-1.8070847199
H	1.6171354440	-2.8213024547	-1.3488926916
C	1.7987001513	-0.7384017564	-1.5578396343
C	1.2489175885	0.5465456620	-1.6632679079
C	3.1703657088	-0.8762859741	-1.8151579920
C	2.0383154120	1.6396653989	-2.0146017989
H	0.1844317581	0.6963327684	-1.4609334084
C	3.9641476548	0.2131720697	-2.1534168102
H	3.6190719269	-1.8650453336	-1.7294807295
C	3.3997846980	1.4826715756	-2.2585074969
H	1.5817282163	2.6231055734	-2.0937340735
H	5.0255733388	0.0694907366	-2.3388812870
H	4.0123725751	2.3378693063	-2.5307392006

TS3'-1b

M06-L/6-31G(d,p) Electronic E: -3828.230844 a.u.

M06-L/6-31G(d,p) Gibbs free E: -3827.600015 a.u.

M06-L/cc-pVTZ Electronic E: -3829.015708 a.u.

C	-0.6104814301	3.0546174186	-1.4504619375
C	-2.6456827577	4.1499420753	-0.5148153496
C	-2.1538403500	5.2609362298	-1.4370473041
C	-0.0146717810	4.3705663666	-1.8278952321
C	-2.2171095208	1.6526780841	-0.7642860715
H	-3.6931078811	3.9232553179	-0.7665352628
H	-2.4071512729	5.0064529612	-2.4790804558
H	1.0061117509	4.4597771742	-1.4476609835

N	-0.1083467740	1.8703593285	-1.6741233419
N	-1.1151740245	1.0246475012	-1.2363062269
N	-1.8625842774	2.9709361589	-0.8968843339
H	-2.6265182716	6.2141239355	-1.2000003308
H	0.0350037364	4.4316161463	-2.9276537587
O	-0.7524042463	5.4573273286	-1.3033445035
C	-0.9207309084	-0.3911968129	-1.2709631444
C	-0.7735986707	-1.0194335288	-2.5148581915
C	-0.8806156075	-1.0983348100	-0.0602973941
C	-0.6126021070	-2.4043551313	-2.5260605446
C	-0.7147273999	-2.4823694091	-0.1314419143
C	-0.5903952380	-3.1541334168	-1.3480864286
H	-0.5108093302	-2.9104096644	-3.4848455580
H	-0.6848587126	-3.0499088438	0.7972094195
C	-1.0090785942	-0.4201246246	1.2684083662
H	-0.5129674607	0.5557398896	1.2778588007
H	-2.0599030272	-0.2522876878	1.5389861246
H	-0.5628890849	-1.0352812421	2.0535984511
C	-0.8077208248	-0.2387345472	-3.7913311680
H	0.1091437081	0.3419813992	-3.9318647790
H	-0.9256045558	-0.9038460179	-4.6499406725
H	-1.6366725846	0.4771577284	-3.8008793632
C	-0.4697572645	-4.6467746034	-1.3880338765
H	0.1065317374	-5.0290524540	-0.5411485296
H	-1.4570207129	-5.1211886919	-1.3385815925
H	0.0068334406	-4.9914929031	-2.3091634300
C	-2.5785390592	4.4402350585	1.0164508683
C	-1.1473037558	4.3948446708	1.5555690342
H	-0.6927098650	3.4089583218	1.4073717061
H	-0.5065781018	5.1441323081	1.0857503181
H	-1.1582369043	4.5829977317	2.6337787736
C	-3.1780879817	5.8249551603	1.2741674657
H	-4.1655142683	5.9340486081	0.8102909051
H	-3.3044124127	5.9796719729	2.3494841537
H	-2.5342567718	6.6284871476	0.9037807981
C	-3.4176813011	3.4028529448	1.7673933593
H	-4.4468154073	3.3618675718	1.3889329502
H	-3.0008664766	2.3921131092	1.7097036994
H	-3.4713286911	3.6644608568	2.8292399023
Cu	-3.8555267061	0.9814765953	-0.0743914234
Si	-5.3907598950	-1.5957229834	-1.7003382663
C	-4.4503871560	-2.3928042531	-0.2874457654
H	-3.6296985094	-2.9943659347	-0.6931122417
H	-4.0245184066	-1.6541146208	0.4009745522

H	-5.0905083839	-3.0513699645	0.3070224057
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H	-3.4416569955	-1.7071673972	-3.2452371153
H	-4.6874252093	-0.6130662322	-3.8951309298
H	-3.6412137212	-0.0845056054	-2.5757774447
C	-6.5544083834	-2.8509357350	-2.4838150974
C	-6.5897184876	-3.0965624933	-3.8640157361
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S-1b

M06-L/6-31G(d,p) Electronic E: -1147.734026 a.u.

M06-L/6-31G(d,p) Gibbs free E: -1147.481406 a.u.

M06-L/cc-pVTZ Electronic E: -1148.007025 a.u.

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F	-4.3489360451	0.8261921614	1.9487663464
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C	-7.8227846606	2.1713679564	-3.3836656456
H	-5.9462799323	1.9375639970	-2.3721152766
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H	-8.9360269962	-1.0239115956	-1.5198077511
C	-9.1047379363	1.6668268134	-3.5886090635
H	-7.5004894223	3.0684083483	-3.9056307124
H	-10.4989725301	0.1124284914	-3.0576598591
H	-9.7881722457	2.1663888461	-4.2690702029

8. References

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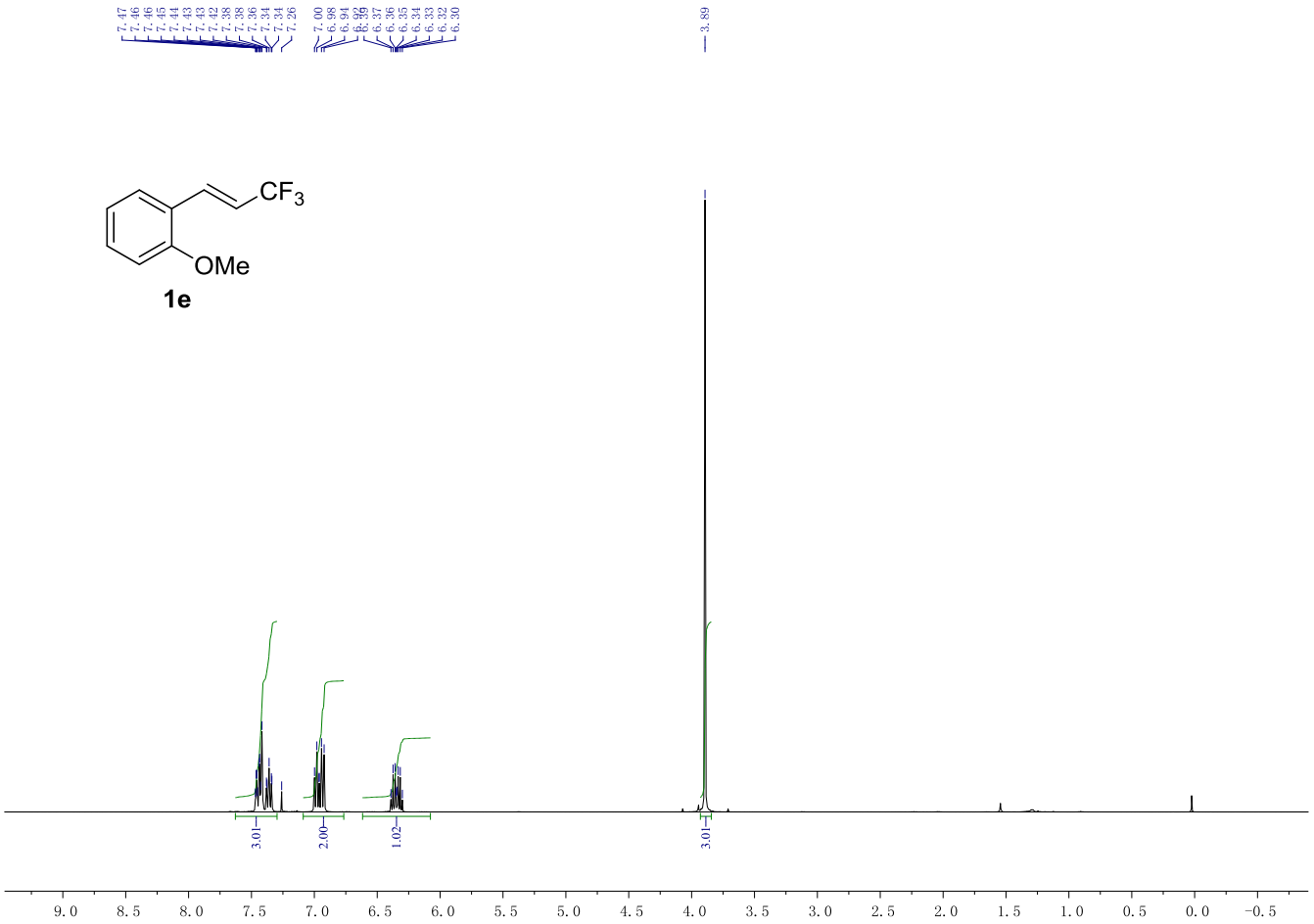
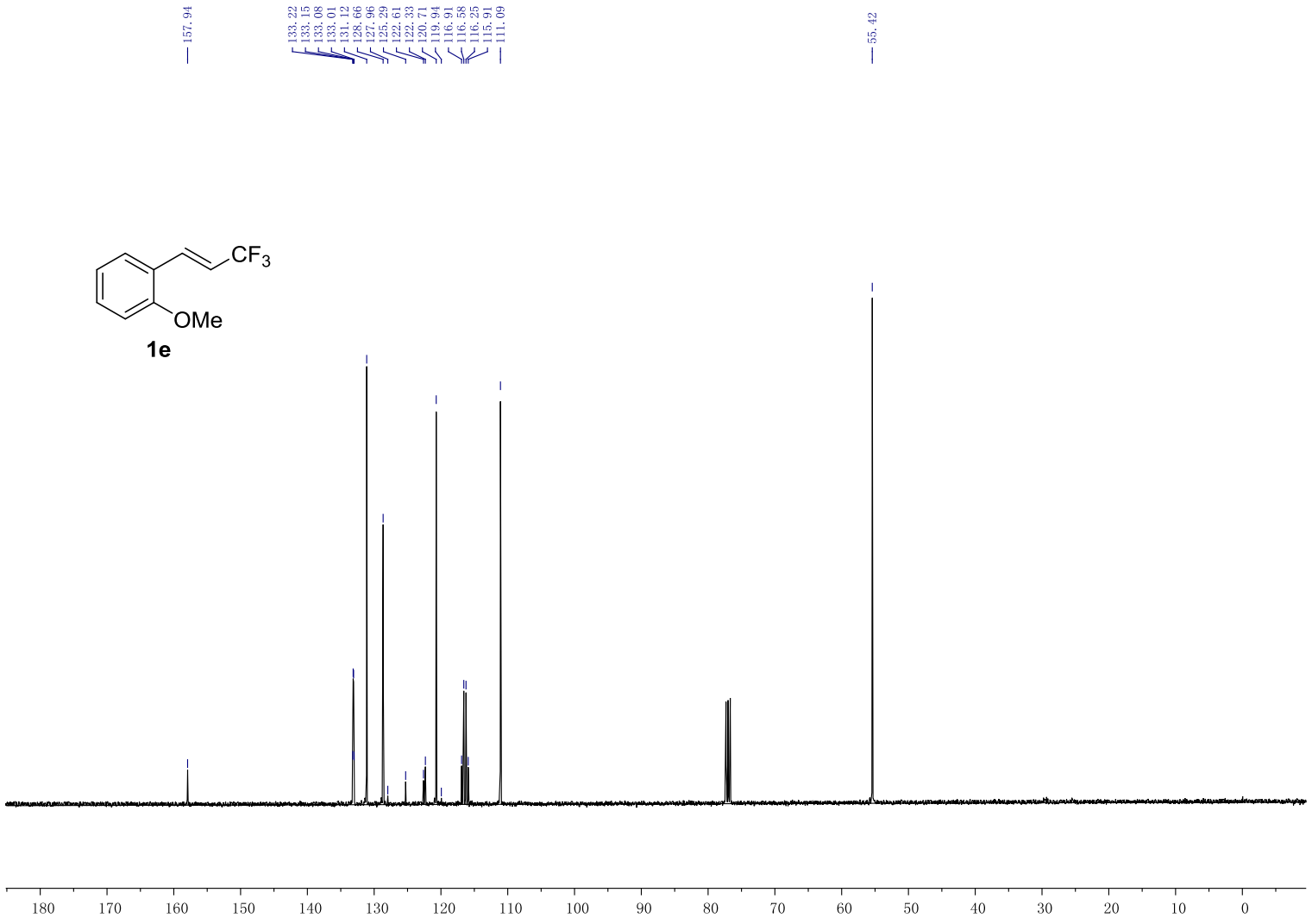
9. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

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116.58
116.25
115.91
111.09
55.42
CF3
OMe
1e
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20
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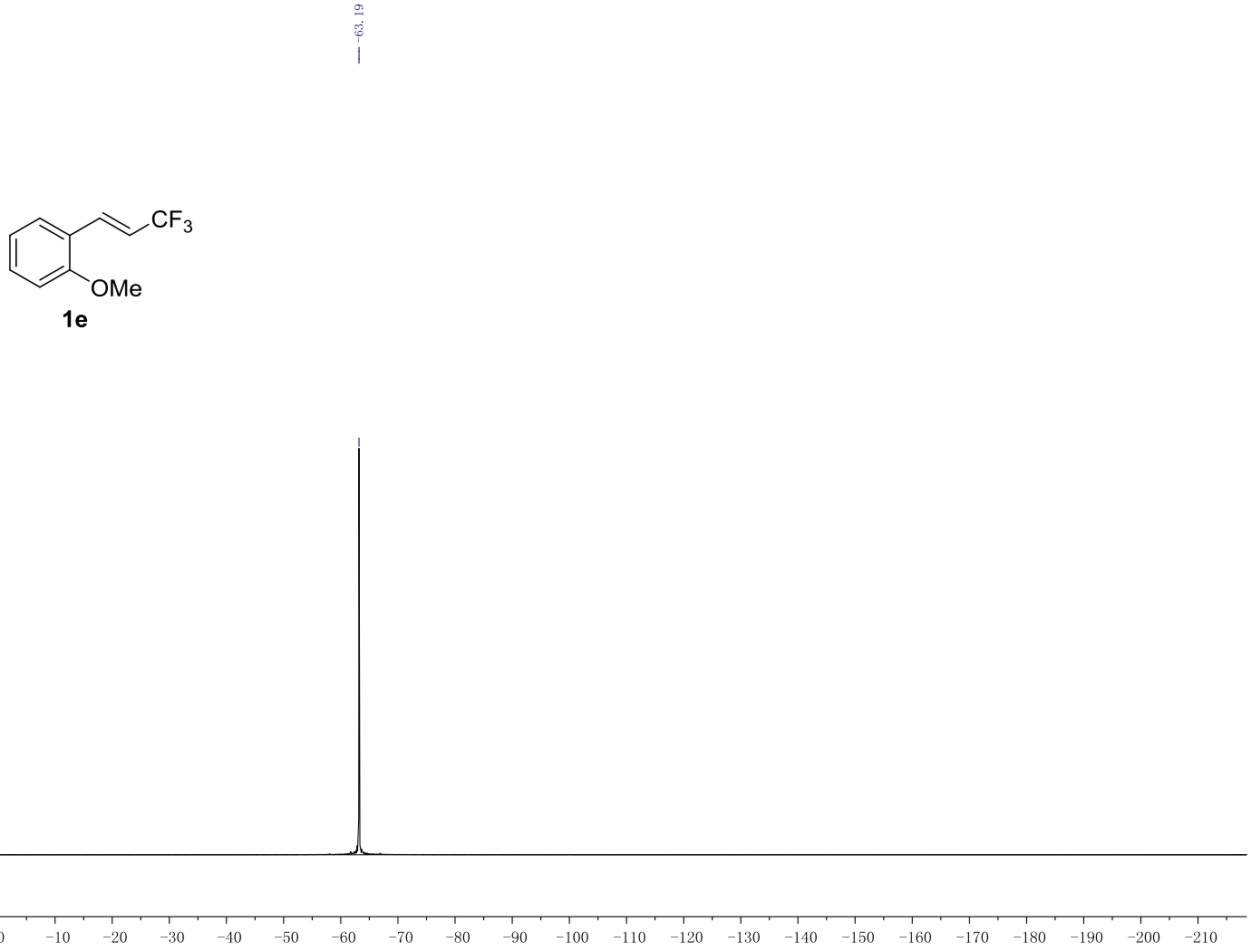
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−140
−150
−160
−170
−180
−190
−200
−210

1e


7.47
7.46
7.43
7.41
7.40
7.39
7.38
7.38
7.37
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7.19
7.17
7.16
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7.05
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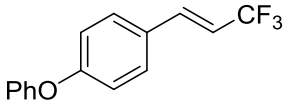
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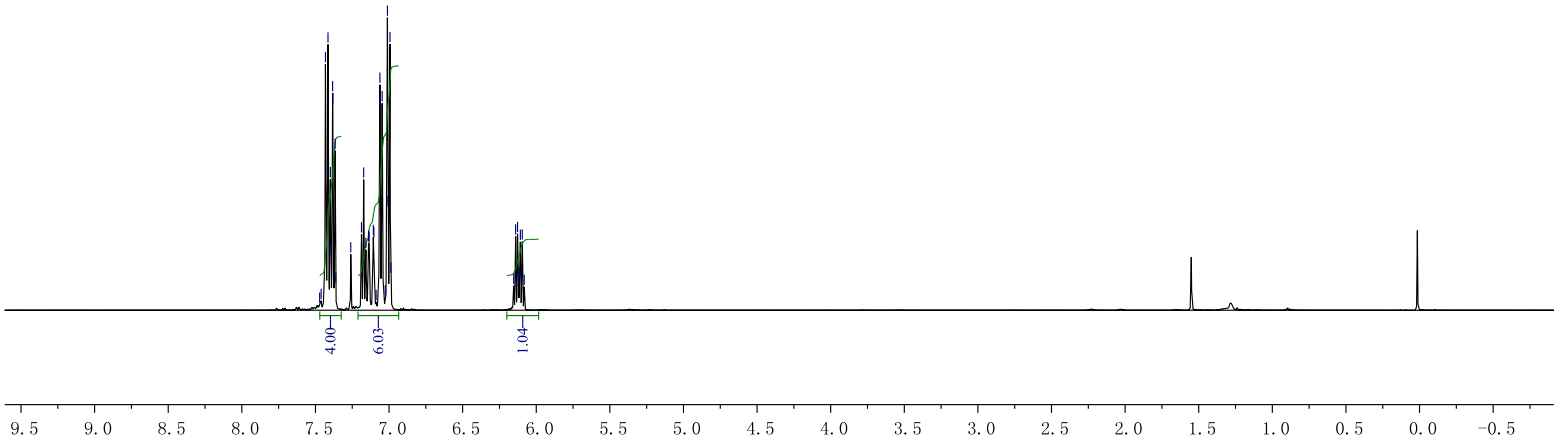
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5.0
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3.5
3.0
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2.0
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1.0
0.5
0.0
-0.5

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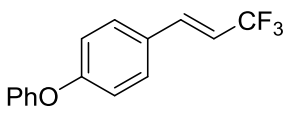

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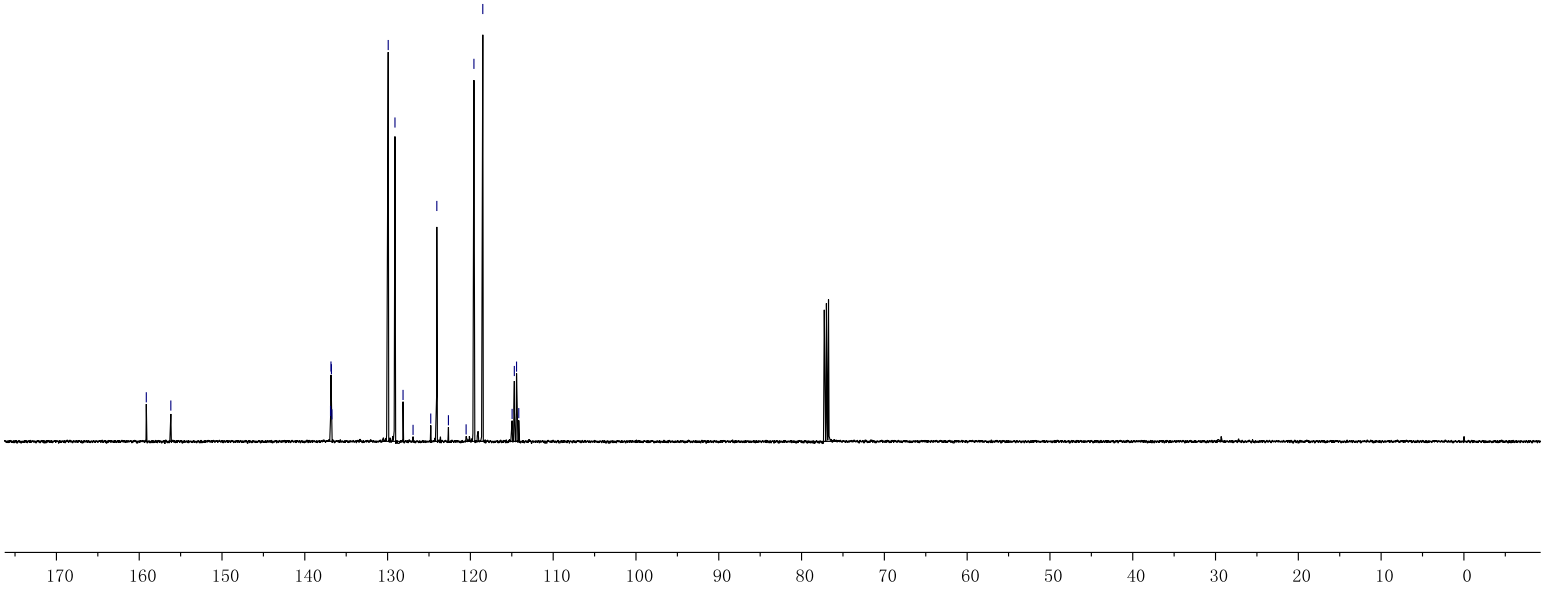

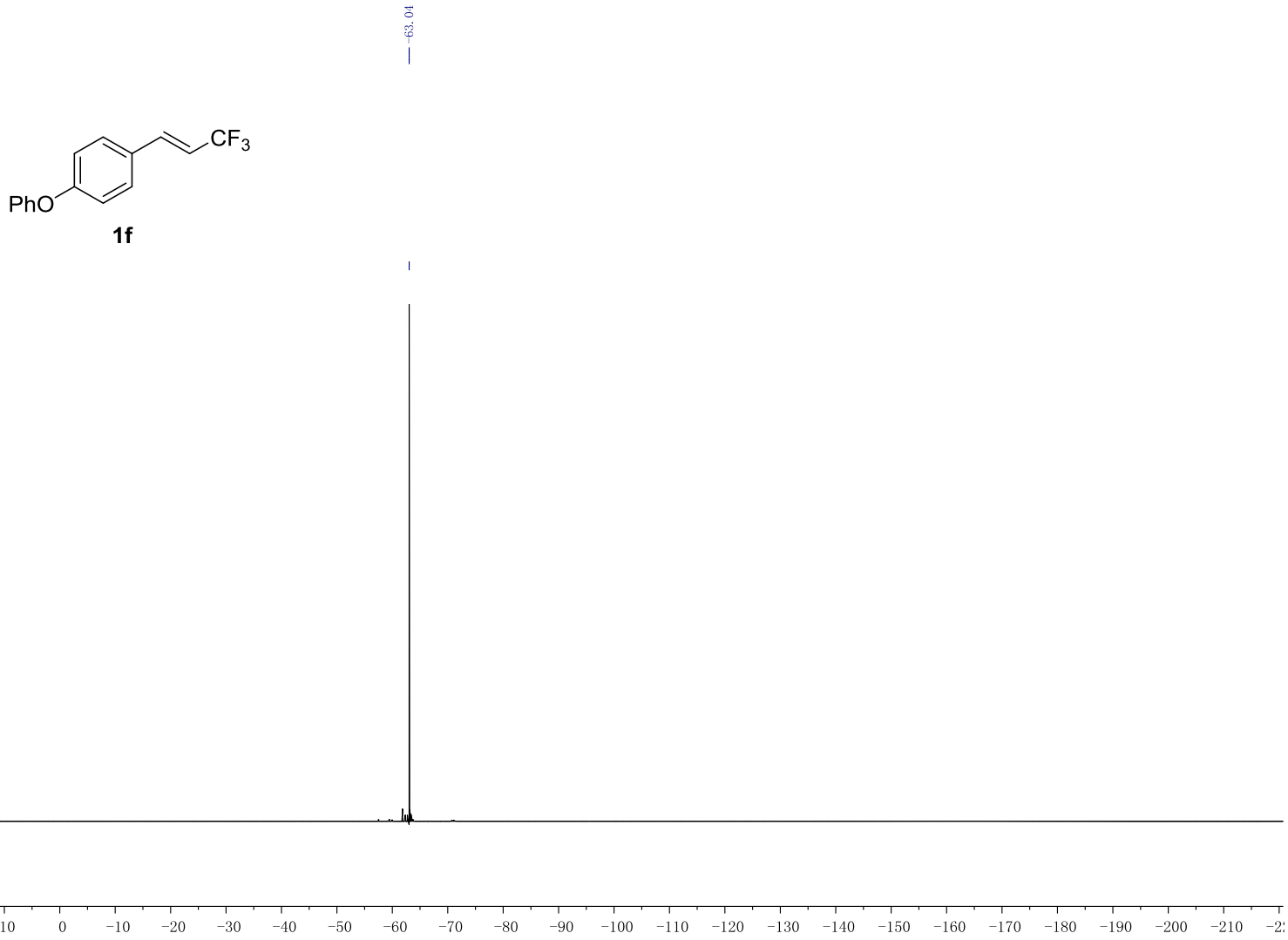
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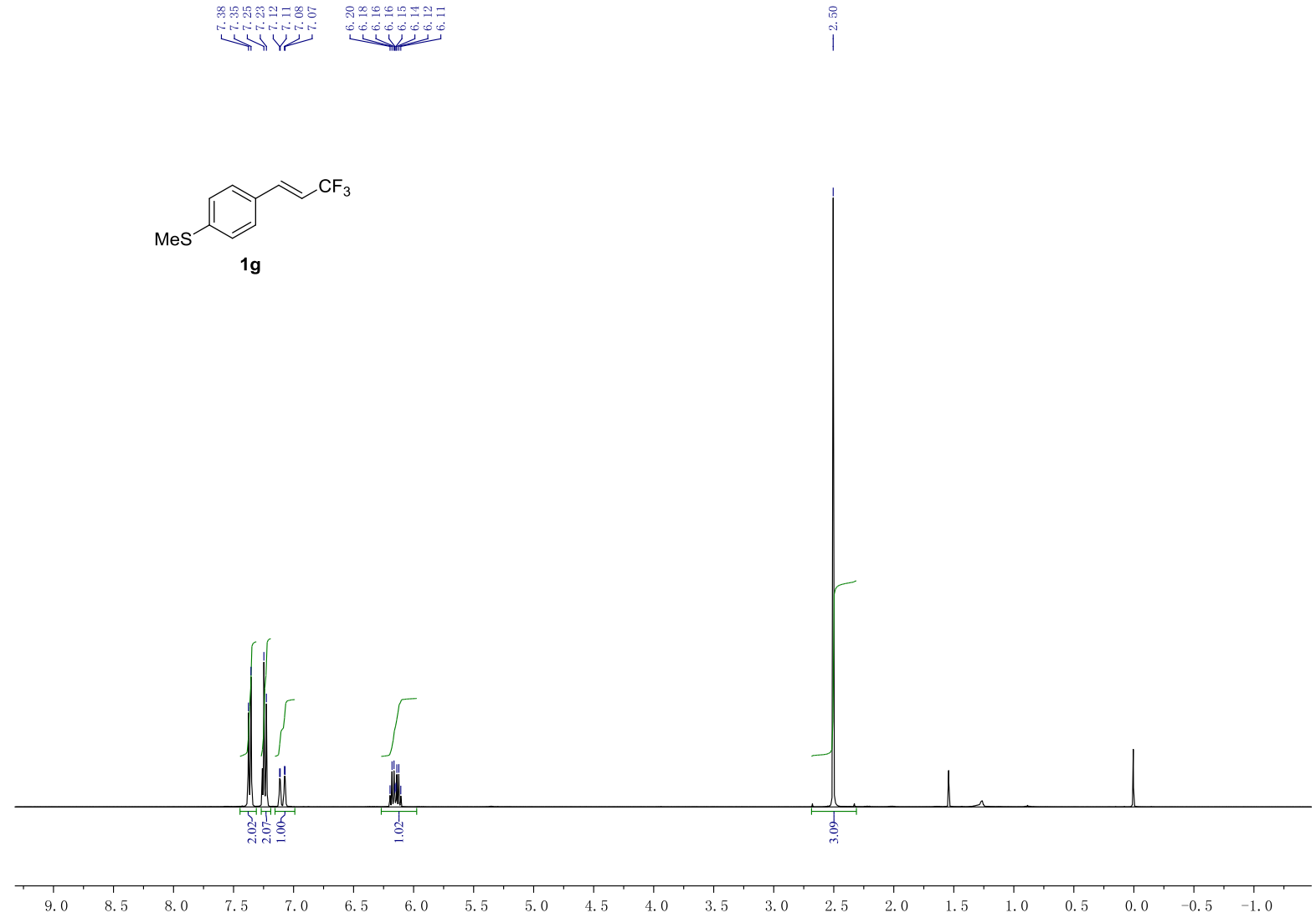
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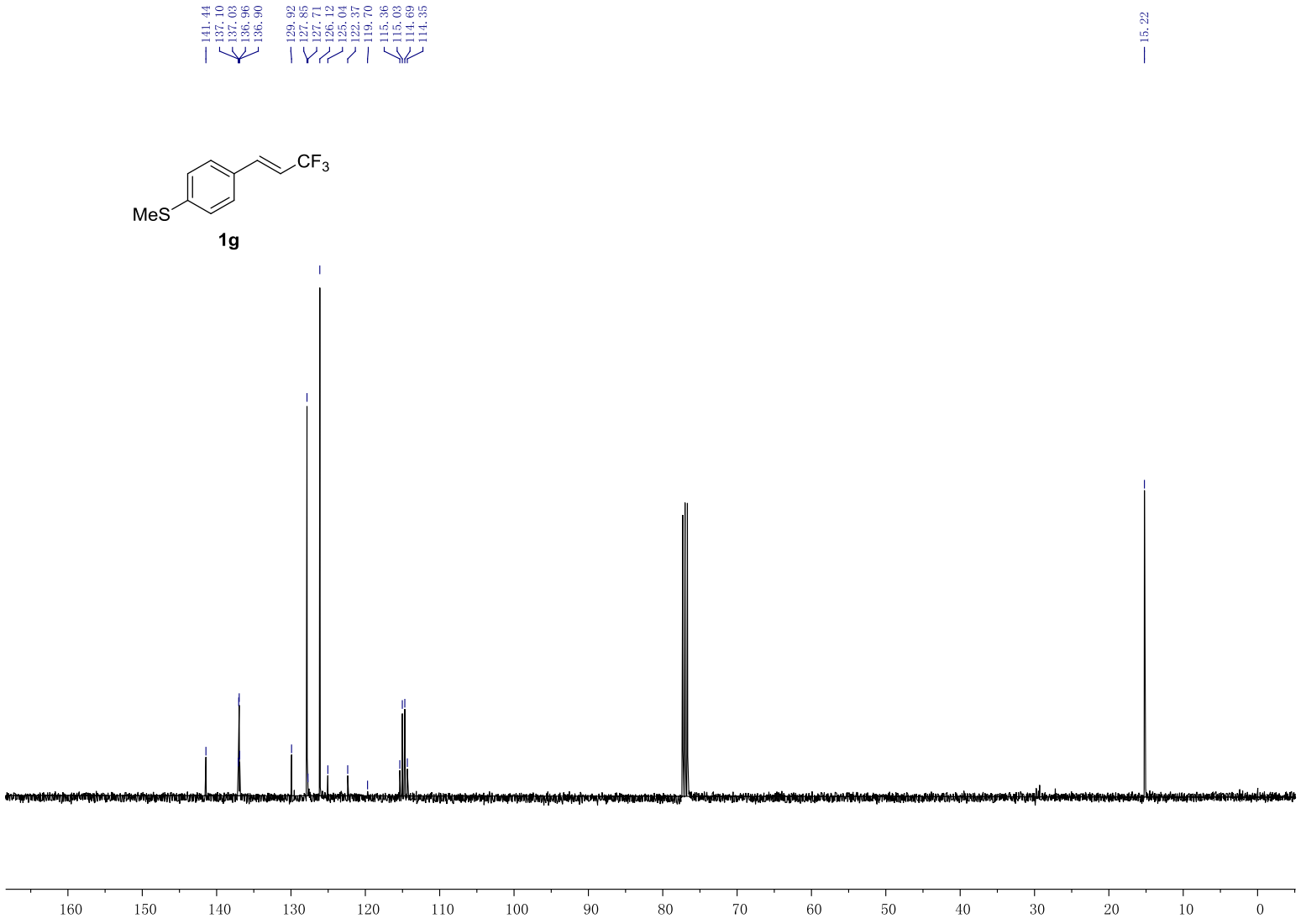
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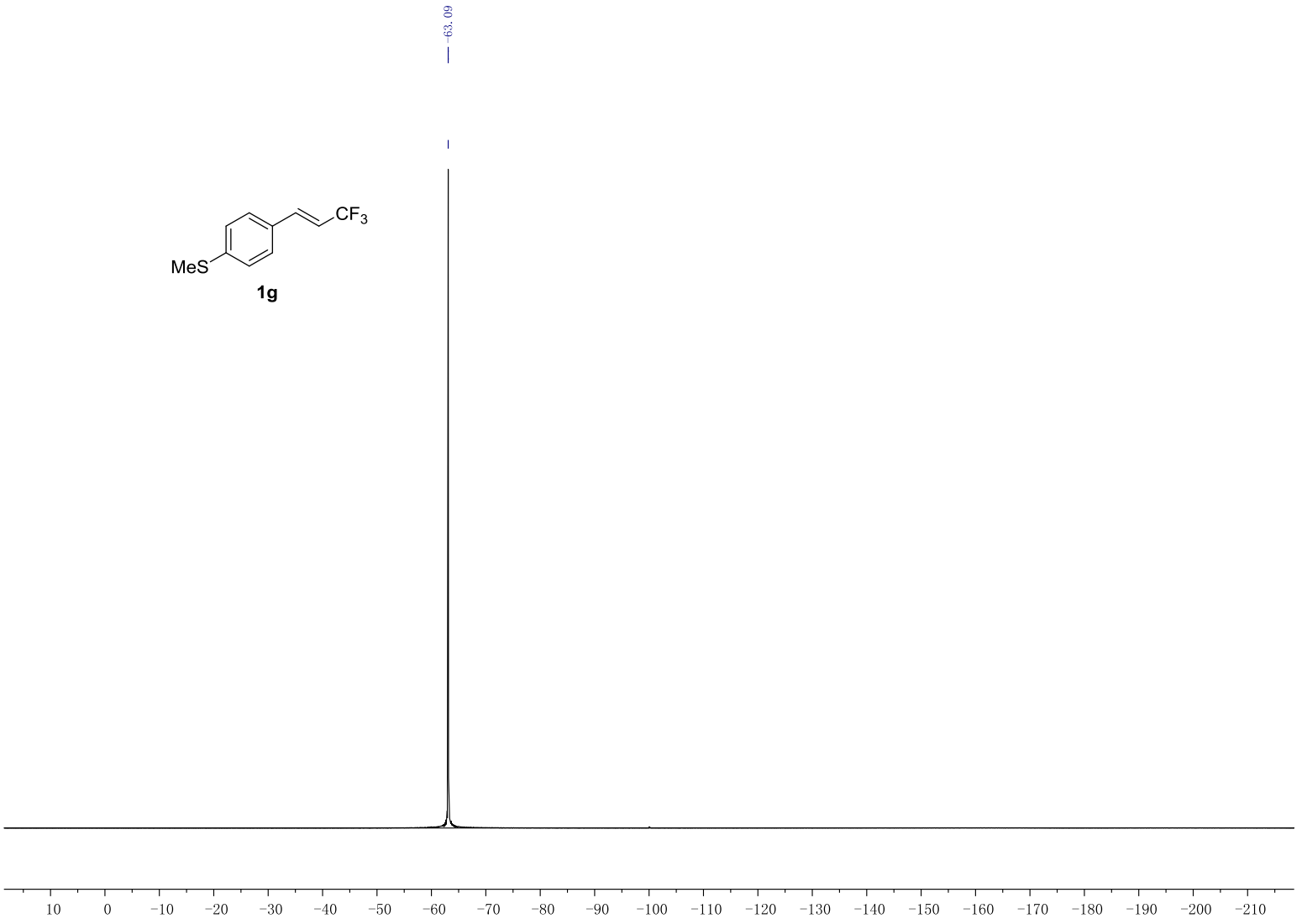
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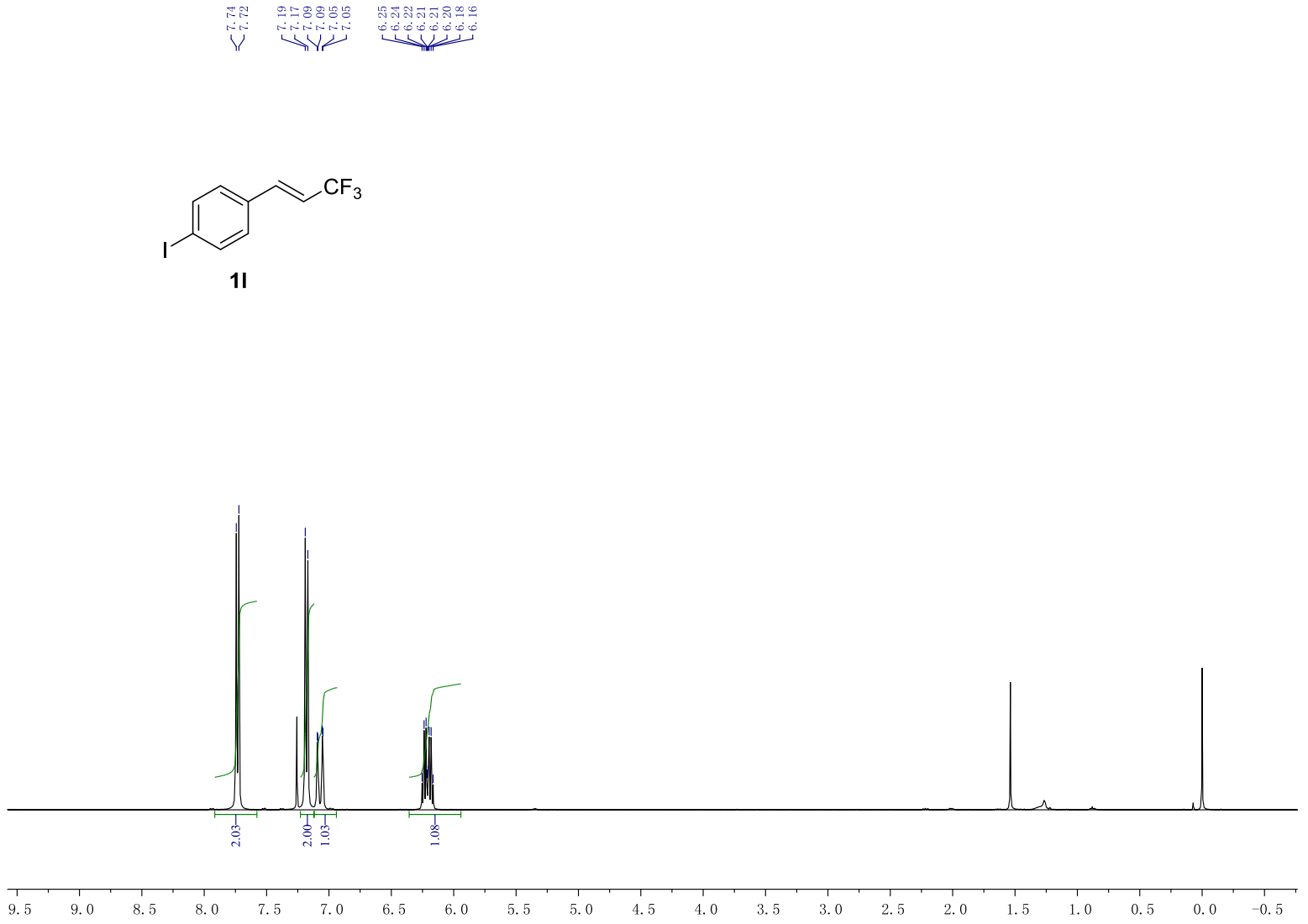
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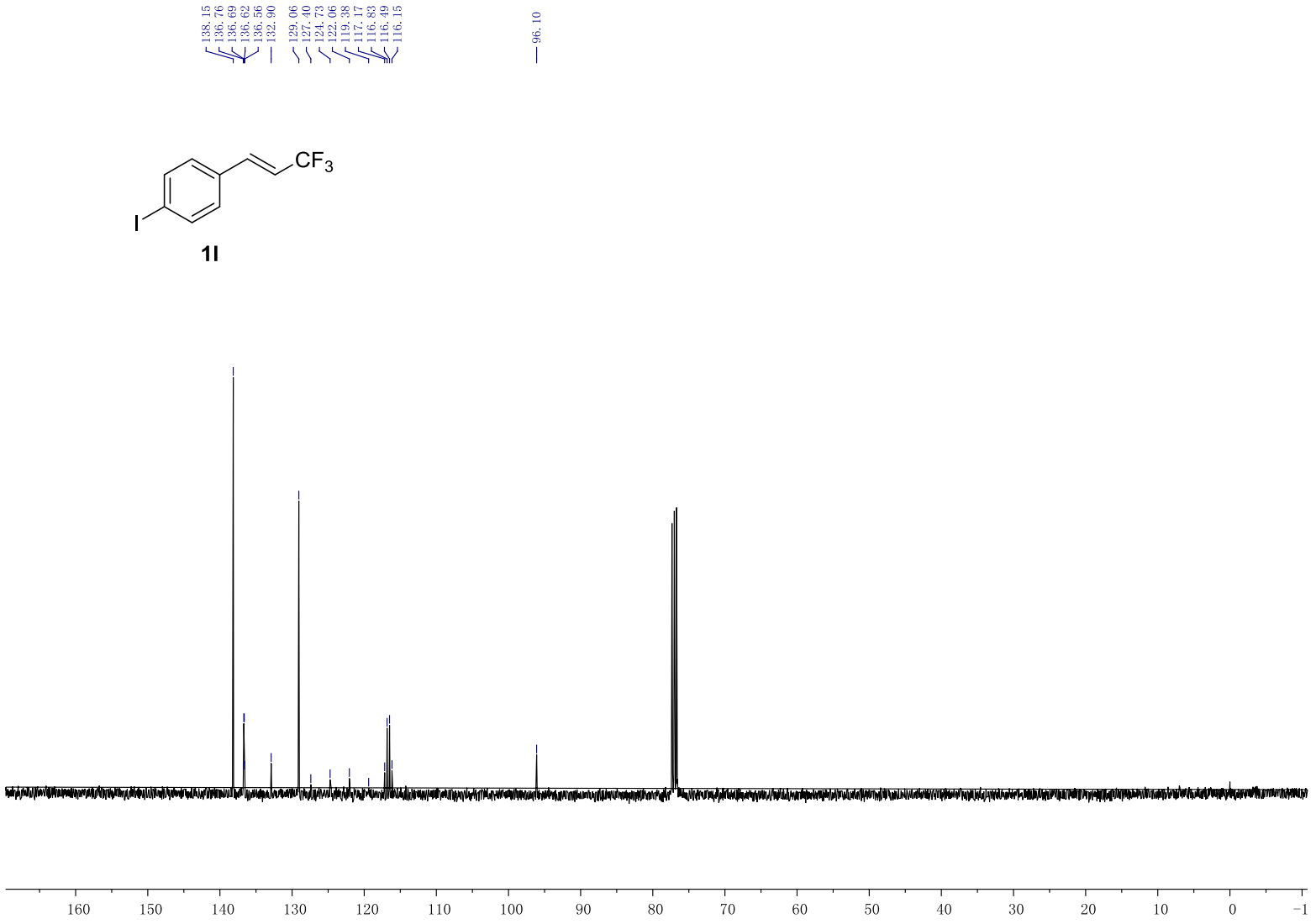
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CF3
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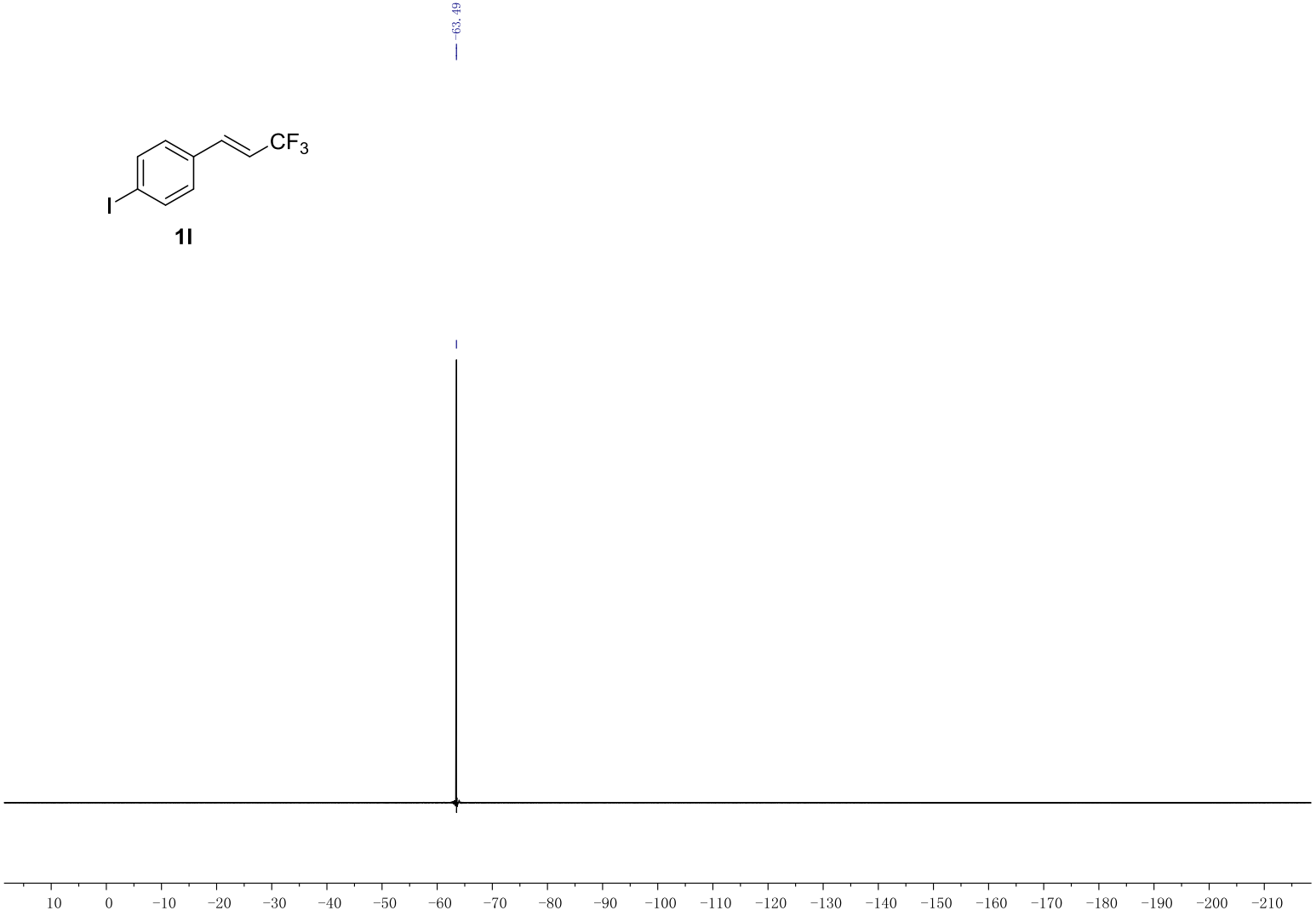
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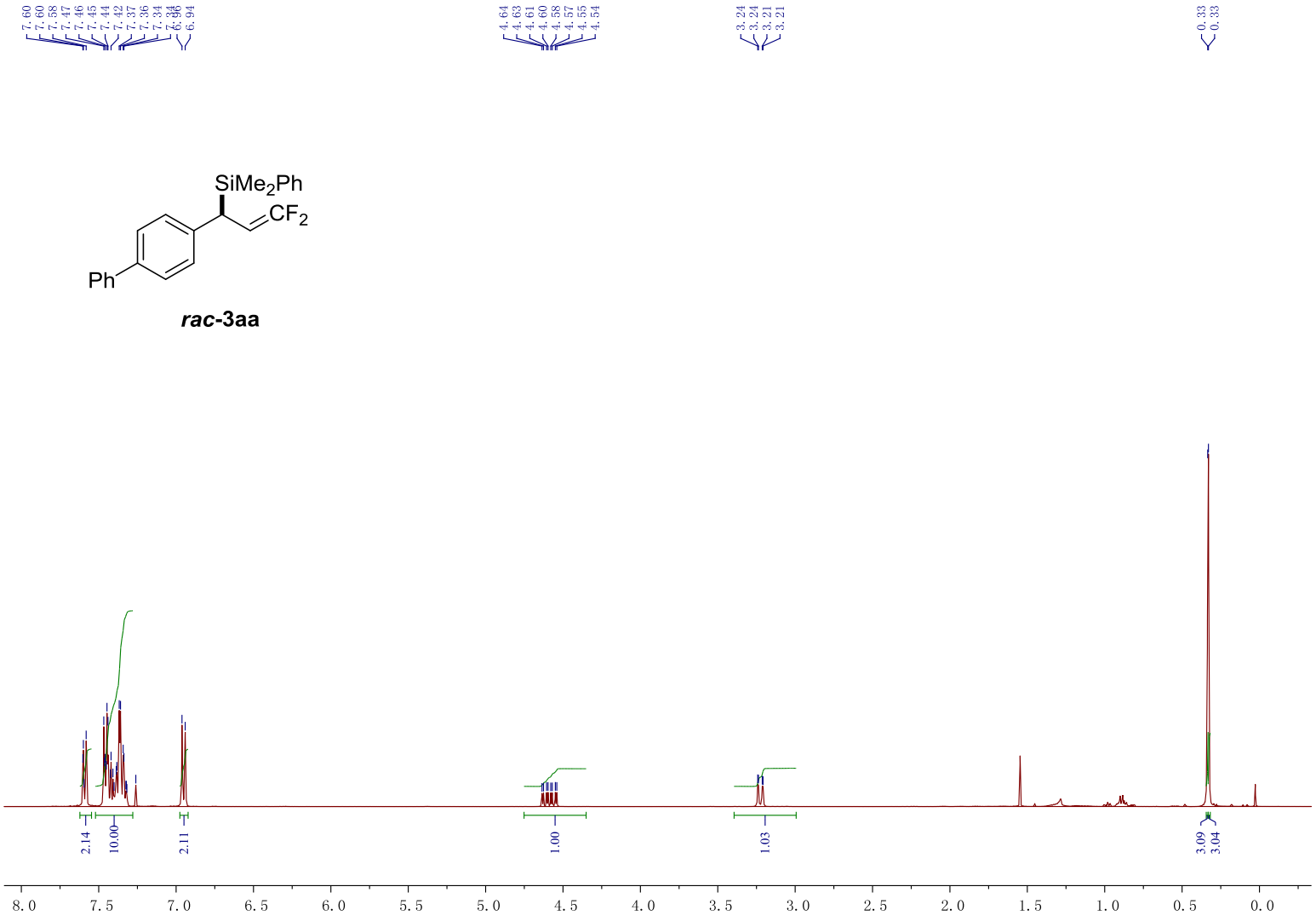
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***rac*-3aa**

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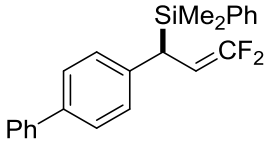

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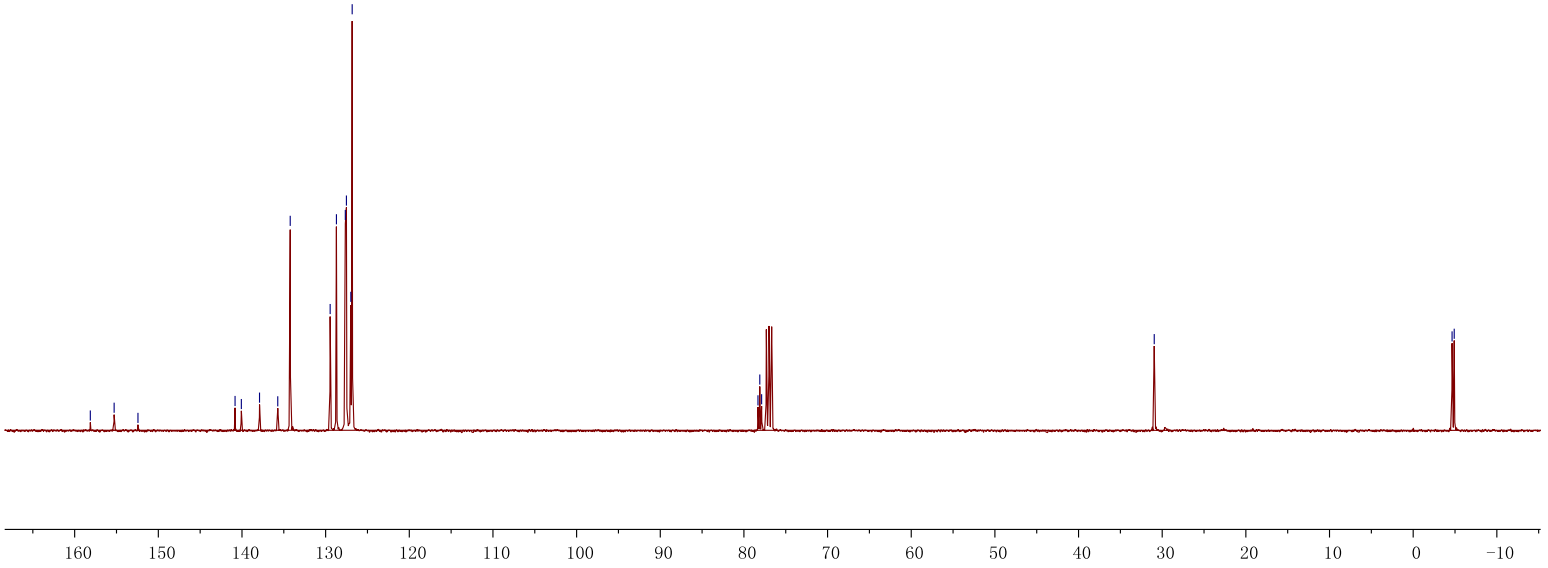

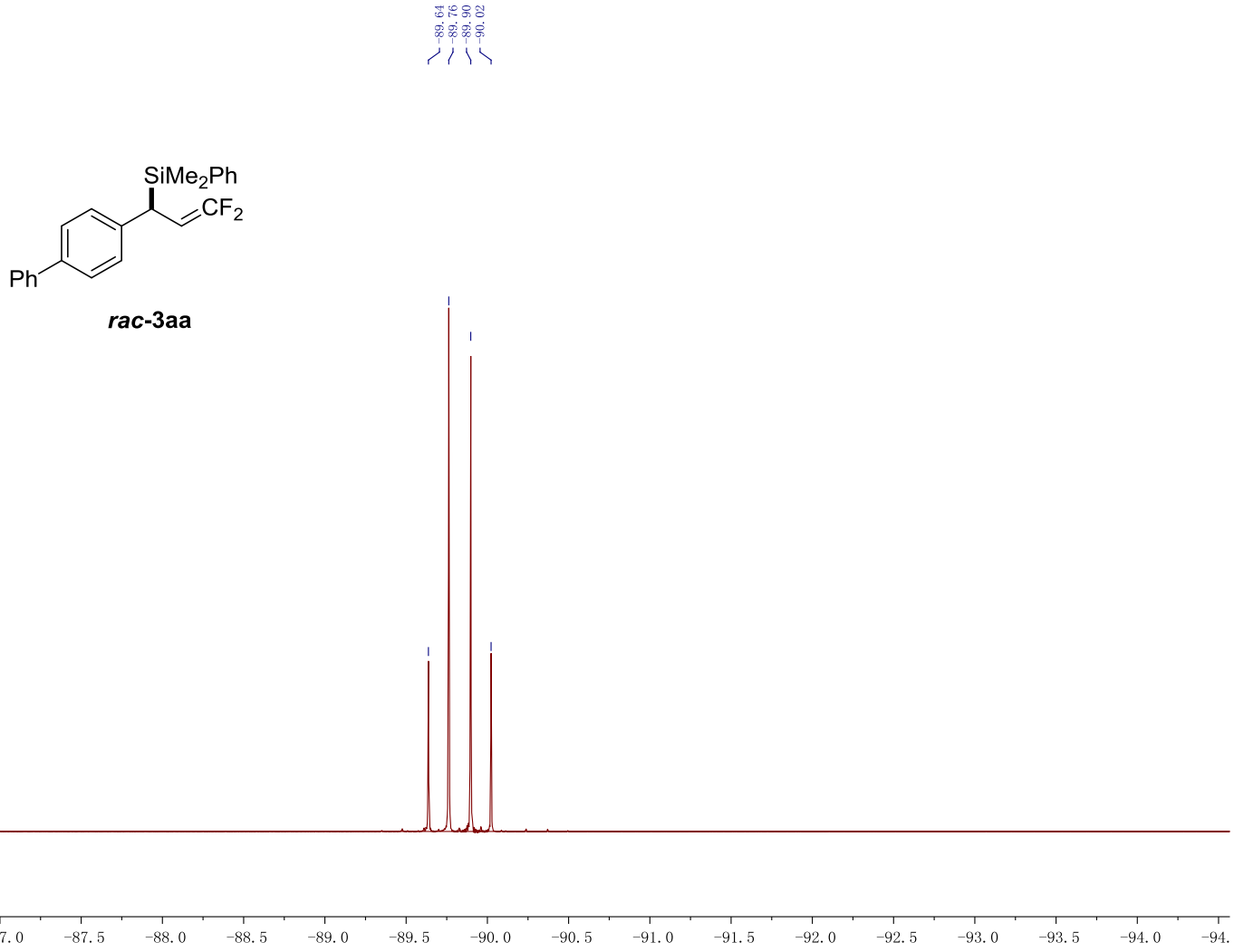
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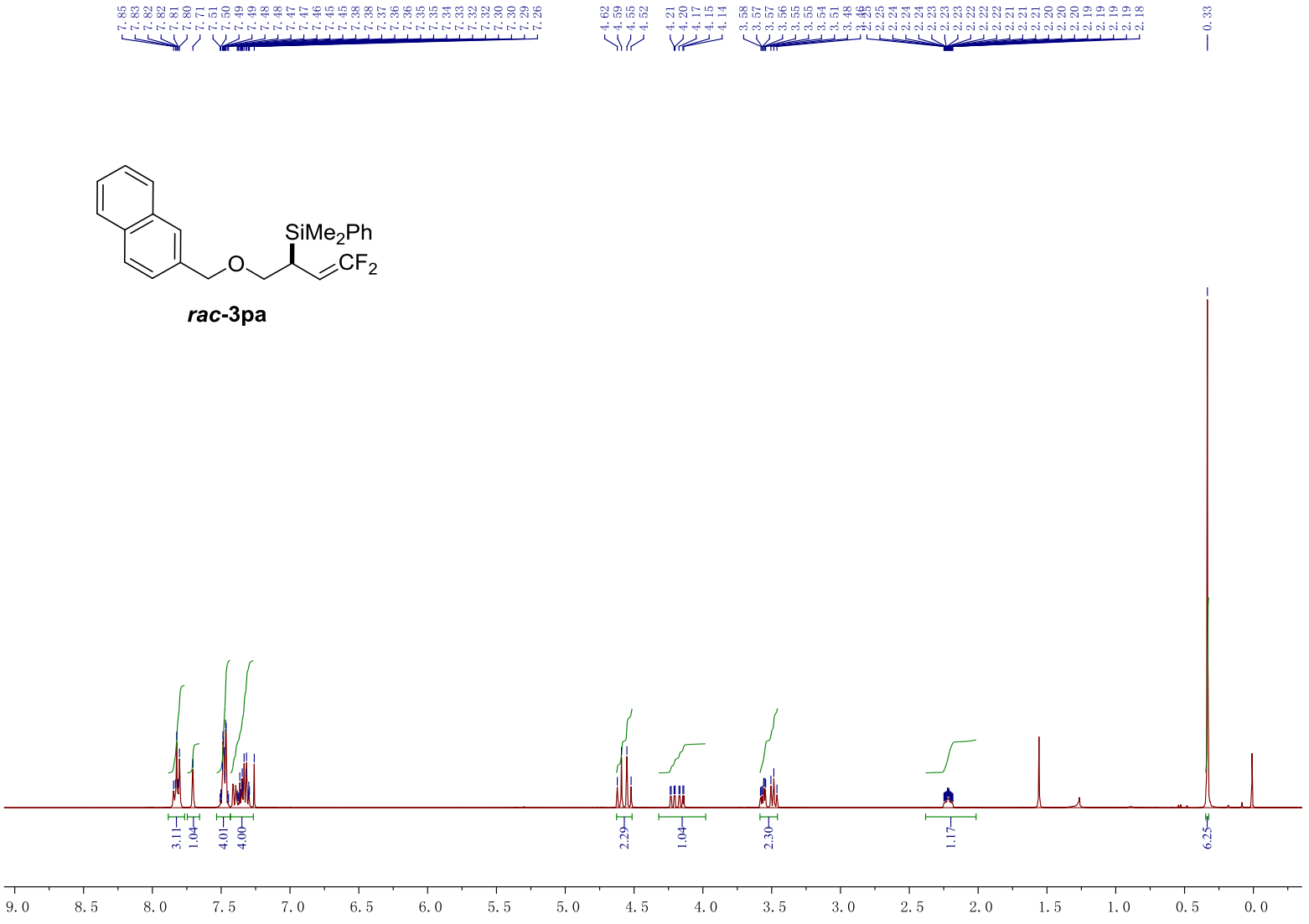
-94.

***rac*-3aa**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4.62 4.59 4.55 4.52
4.21 4.20 4.17 4.15 4.14
3.58 3.57 3.57 3.56 3.55 3.55 3.54 3.51 3.48
2.25 2.24 2.24 2.24 2.23 2.23 2.22 2.22 2.22 2.21 2.21 2.20 2.20 2.19 2.19 2.19 2.19 2.18
0.33
SiMe2Ph
CF2
O
rac-3pa
3.11 1.04 4.01 4.00 2.29 1.04 2.30 1.17 6.25
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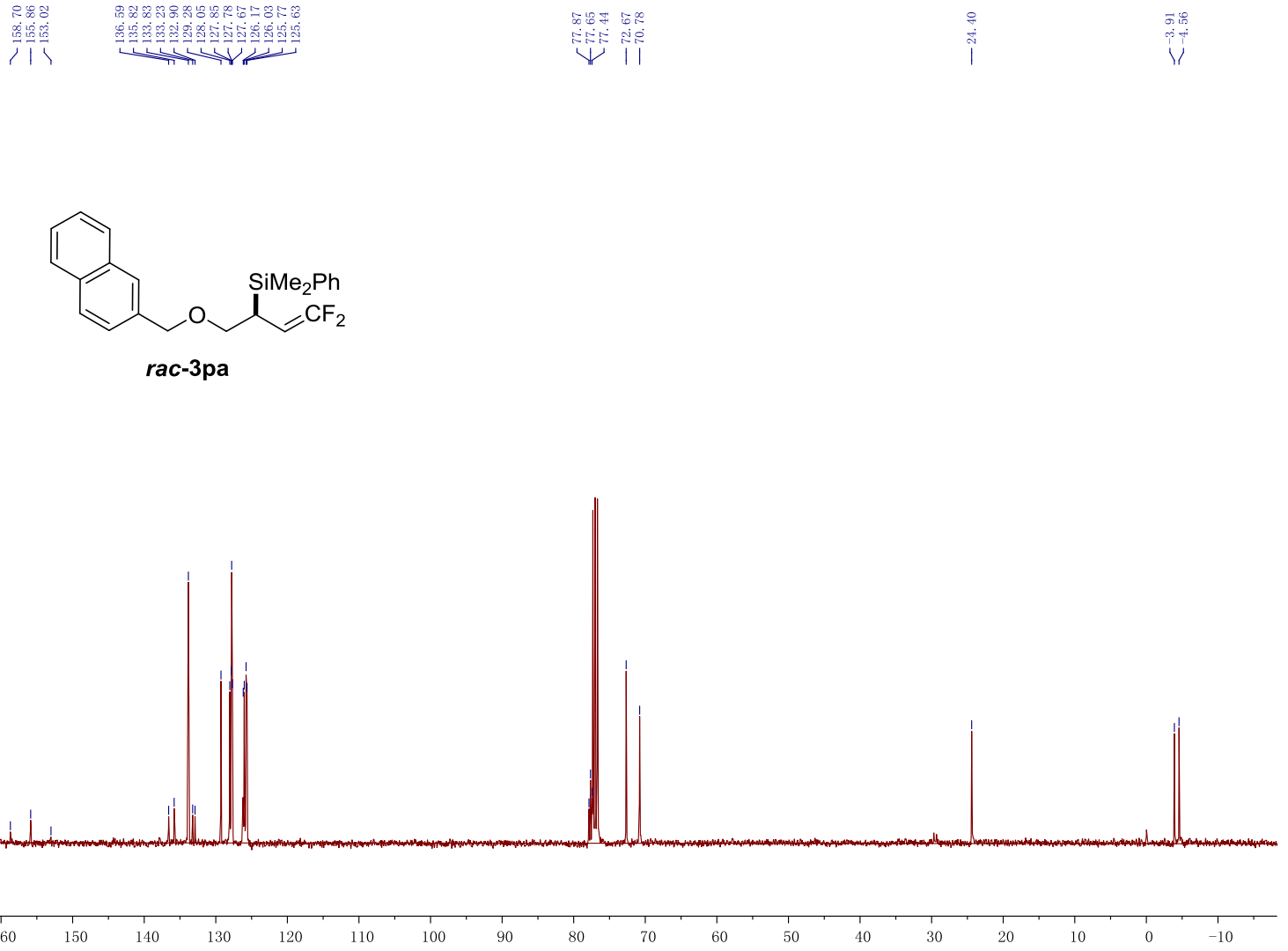
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77.44
72.67
70.78
24.40
-3.91
-4.56
SiMe2Ph
O
CF2
170
160
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130
120
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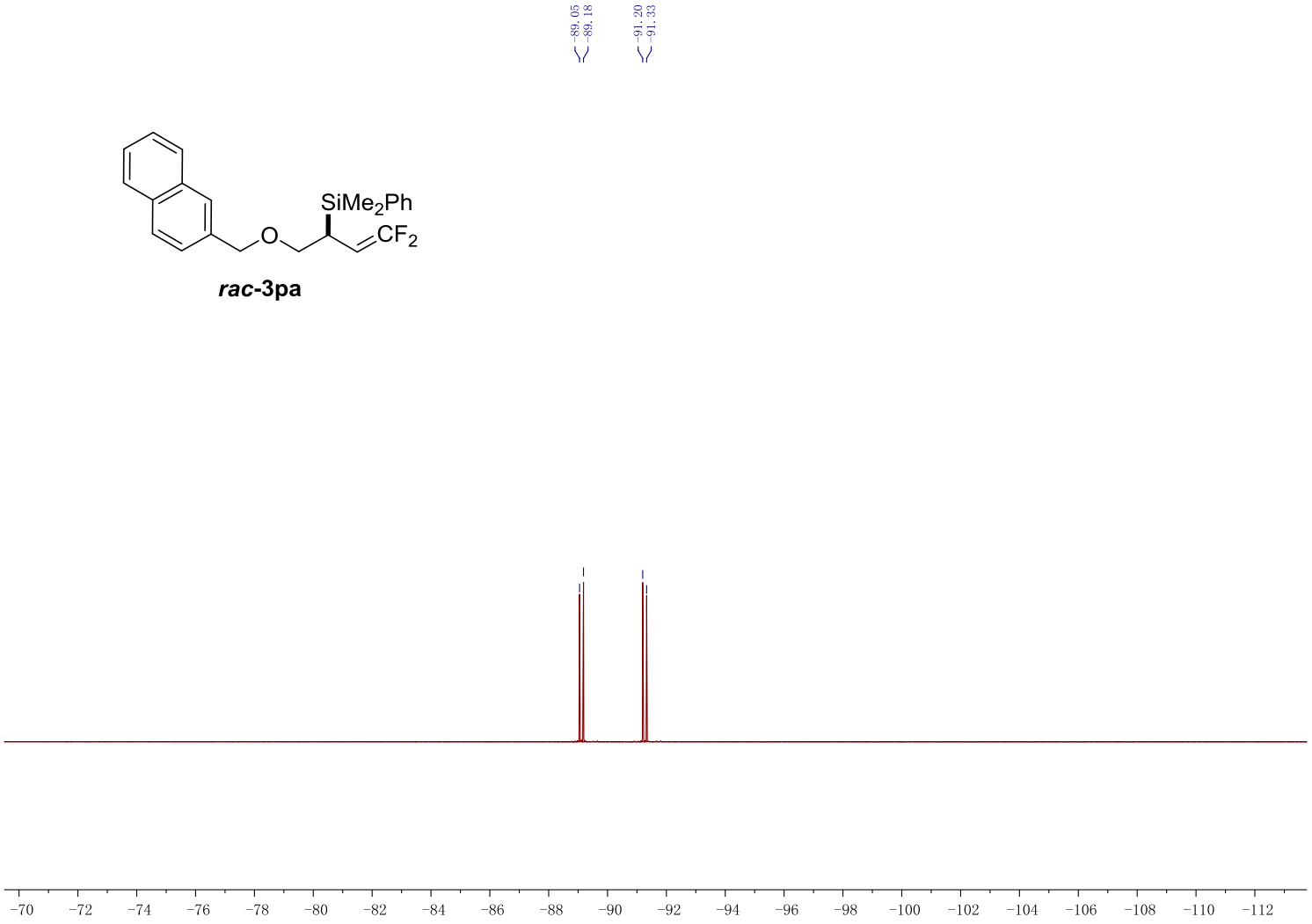
***rac*-3pa**

SiMe2Ph
O
CF2

***rac*-3pa**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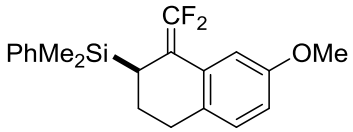
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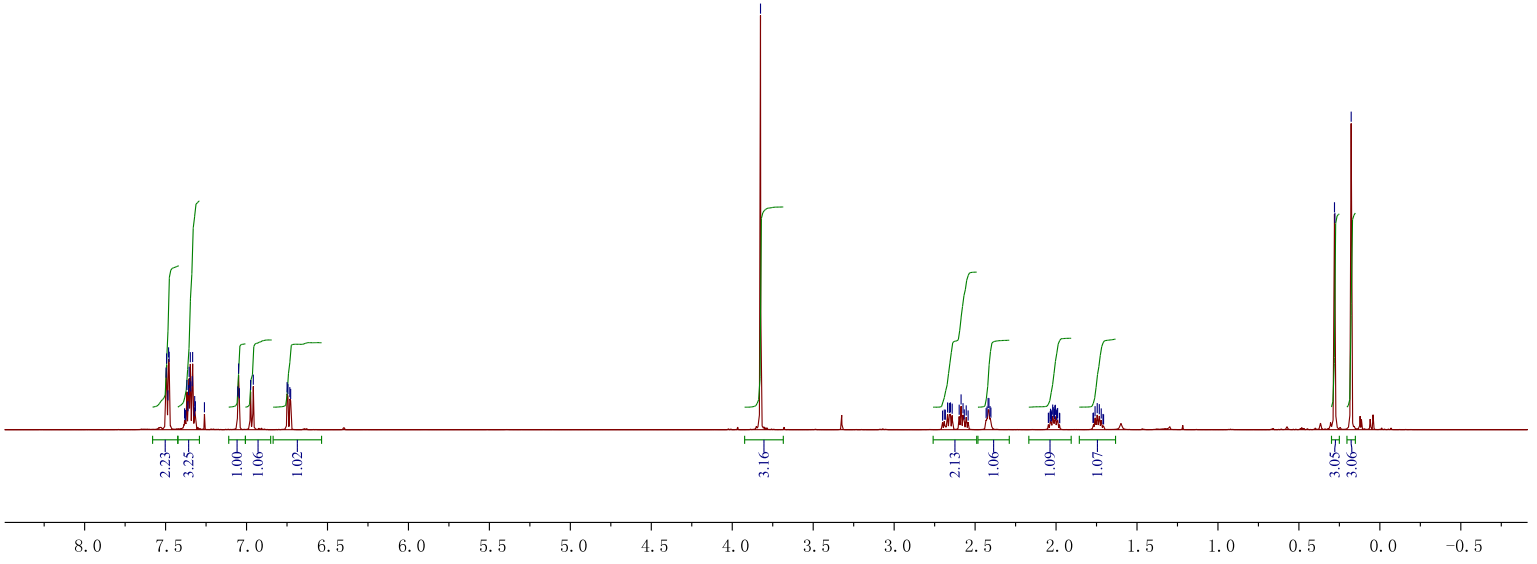
rac-**3qa**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7.0
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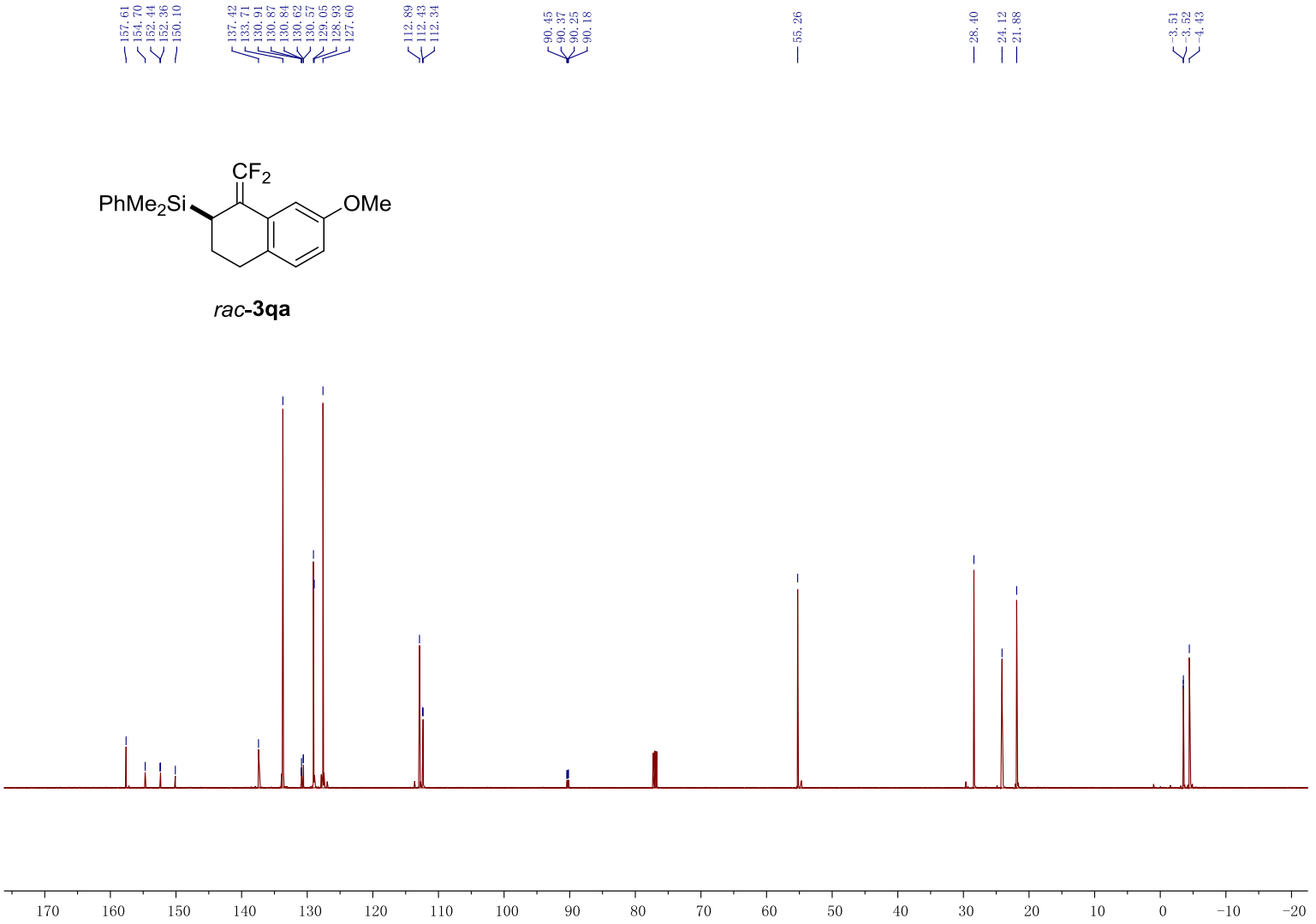
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24.12
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CF2
PhMe2Si
OMe
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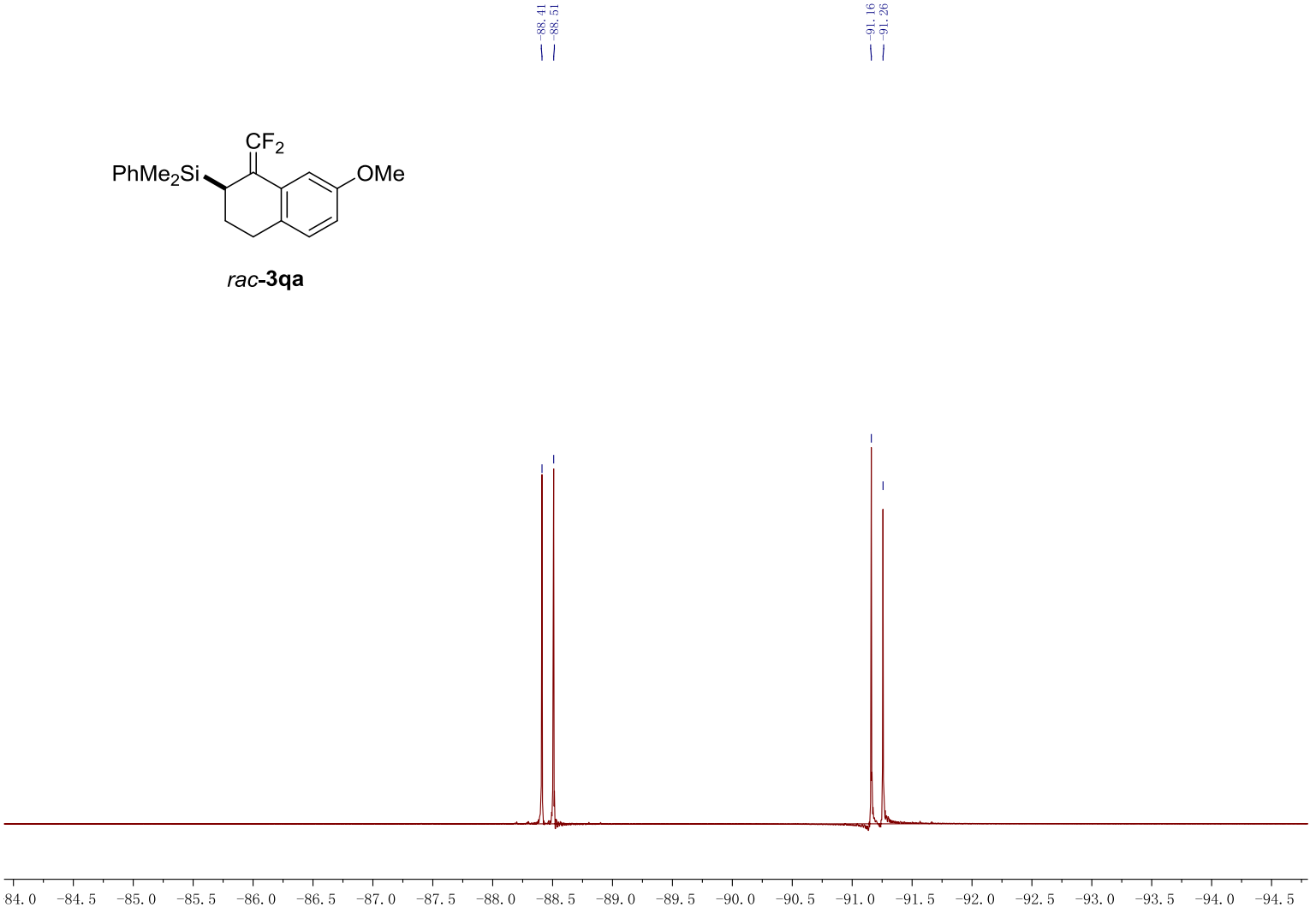
rac-**3qa**

CF2
PhMe2Si
OMe

rac-**3qa**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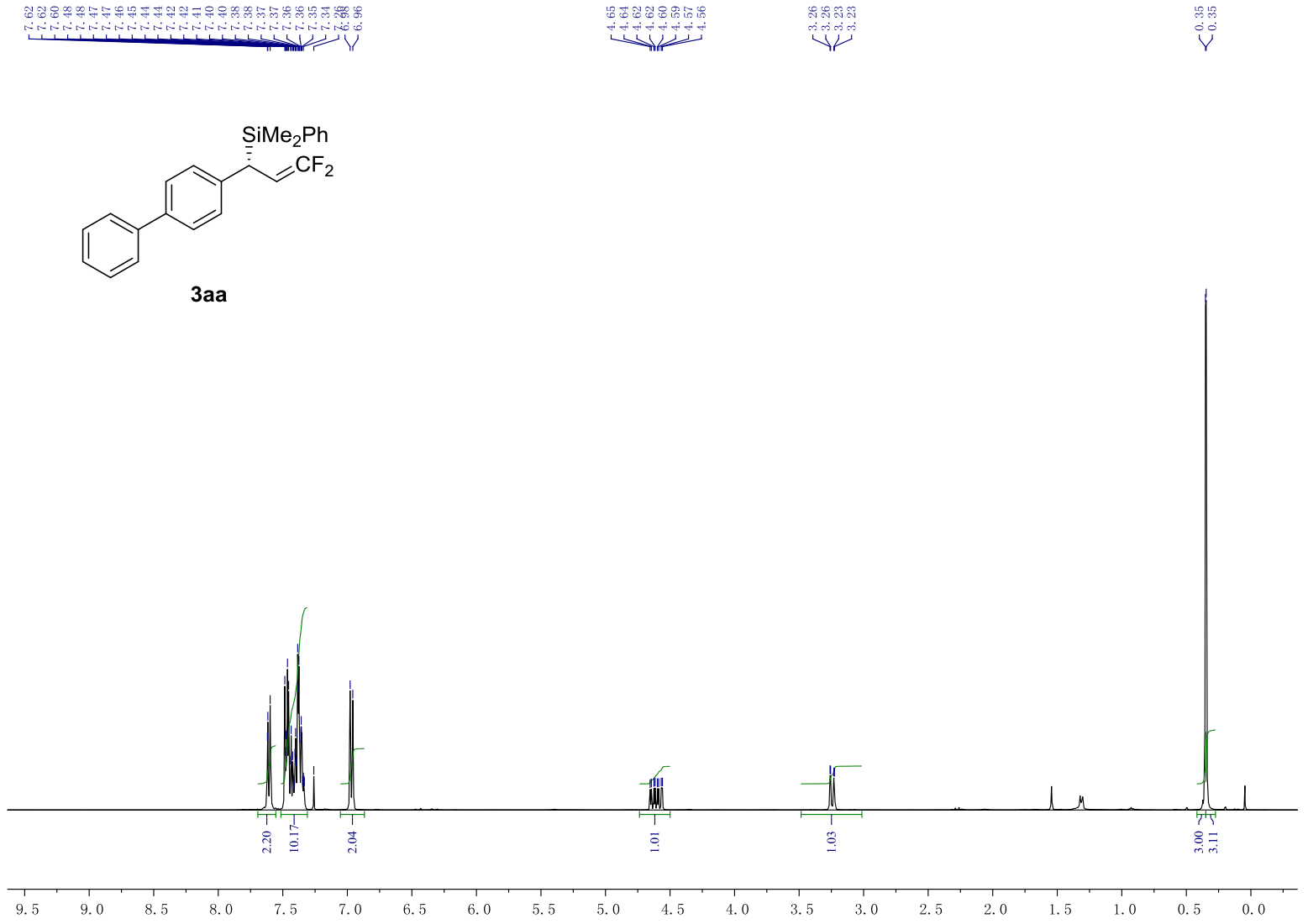
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7.34
7.26
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6.96
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4.64
4.62
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4.60
4.59
4.57
4.56
3.26
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3.23
3.23
0.35
0.35
SiMe2Ph
CF2
3aa
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1.01
1.03
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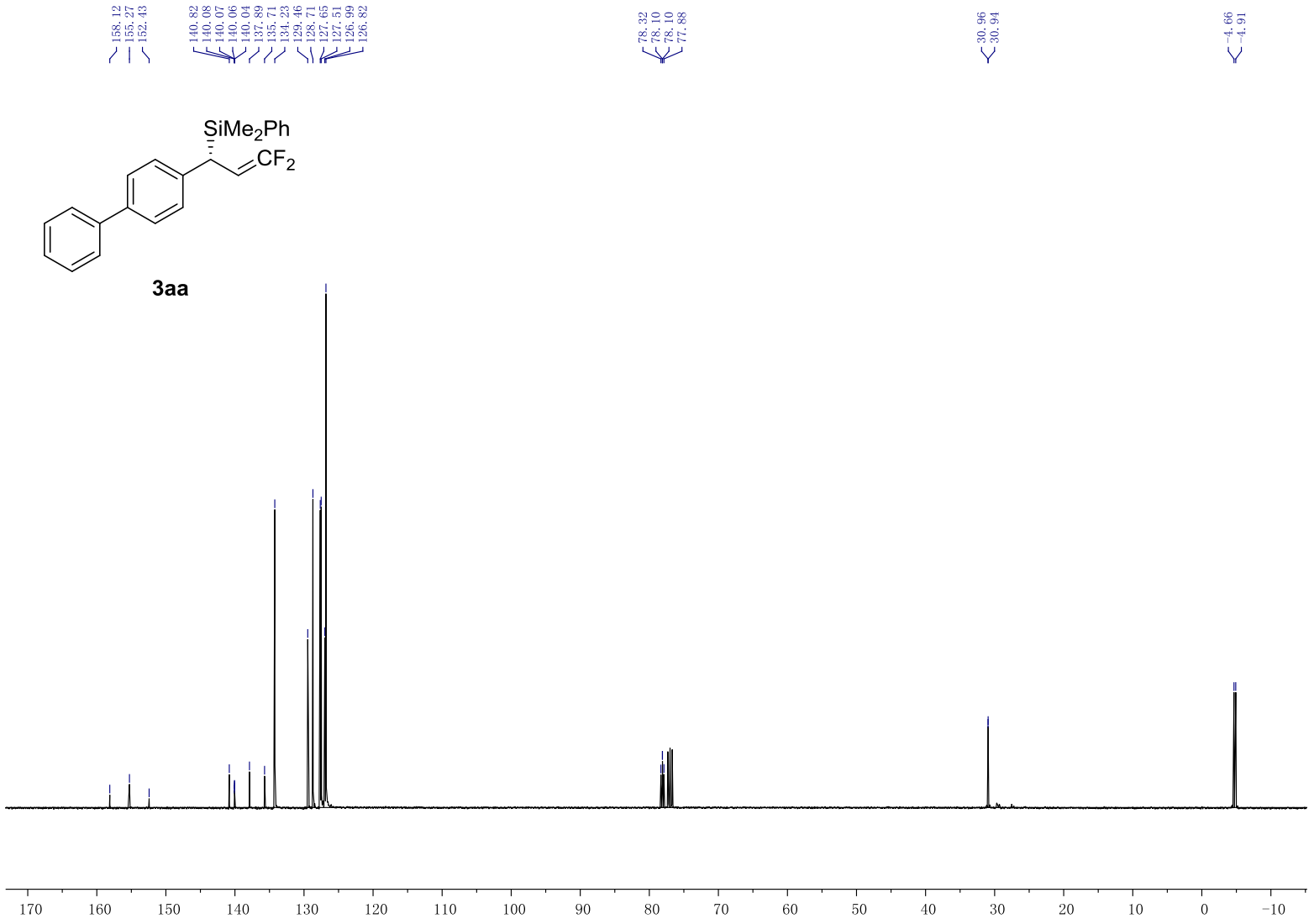
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30.94
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SiMe2Ph
CF2
3aa
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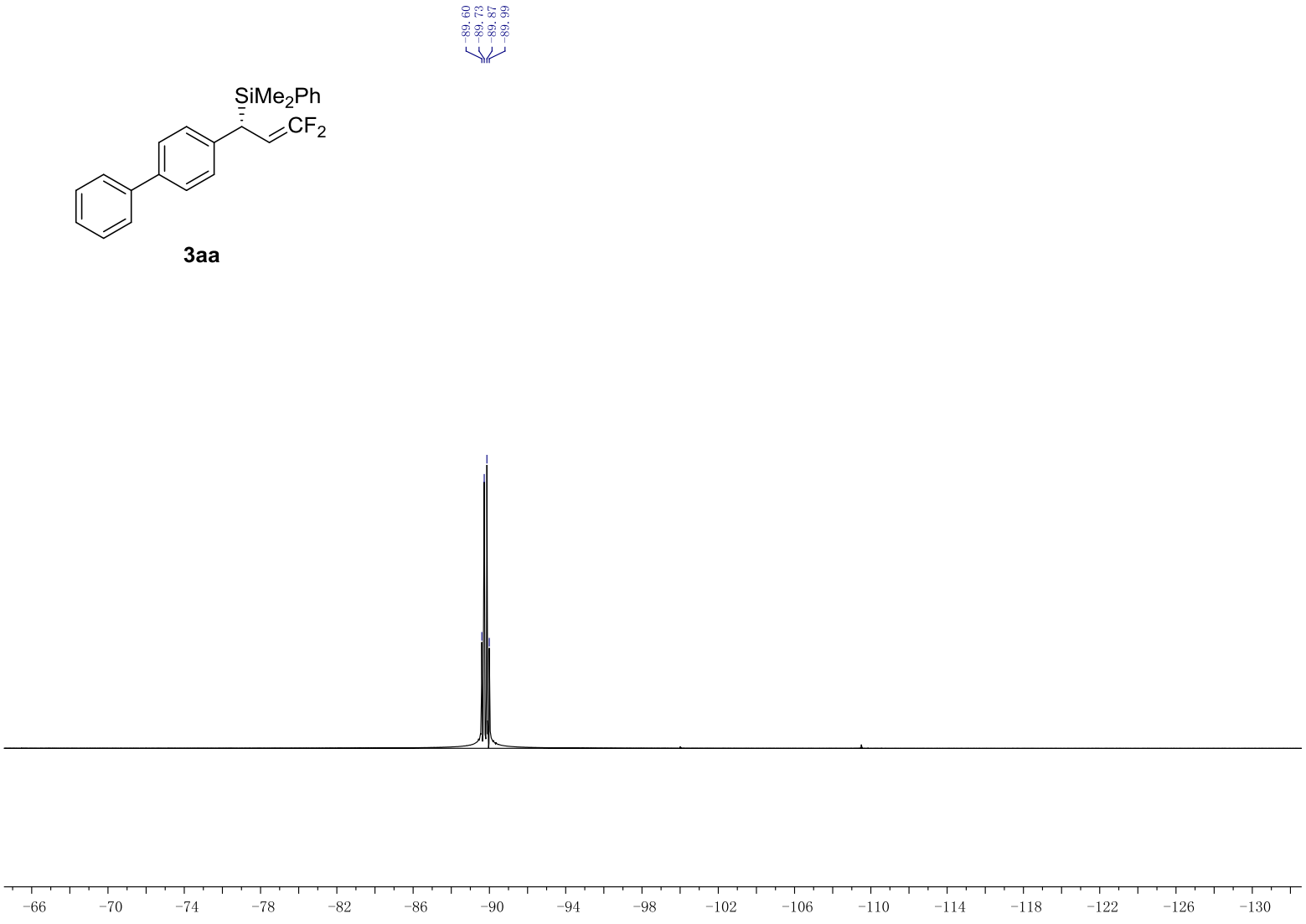
SiMe2Ph
CF2

3aa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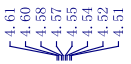
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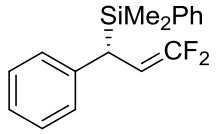
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CF2

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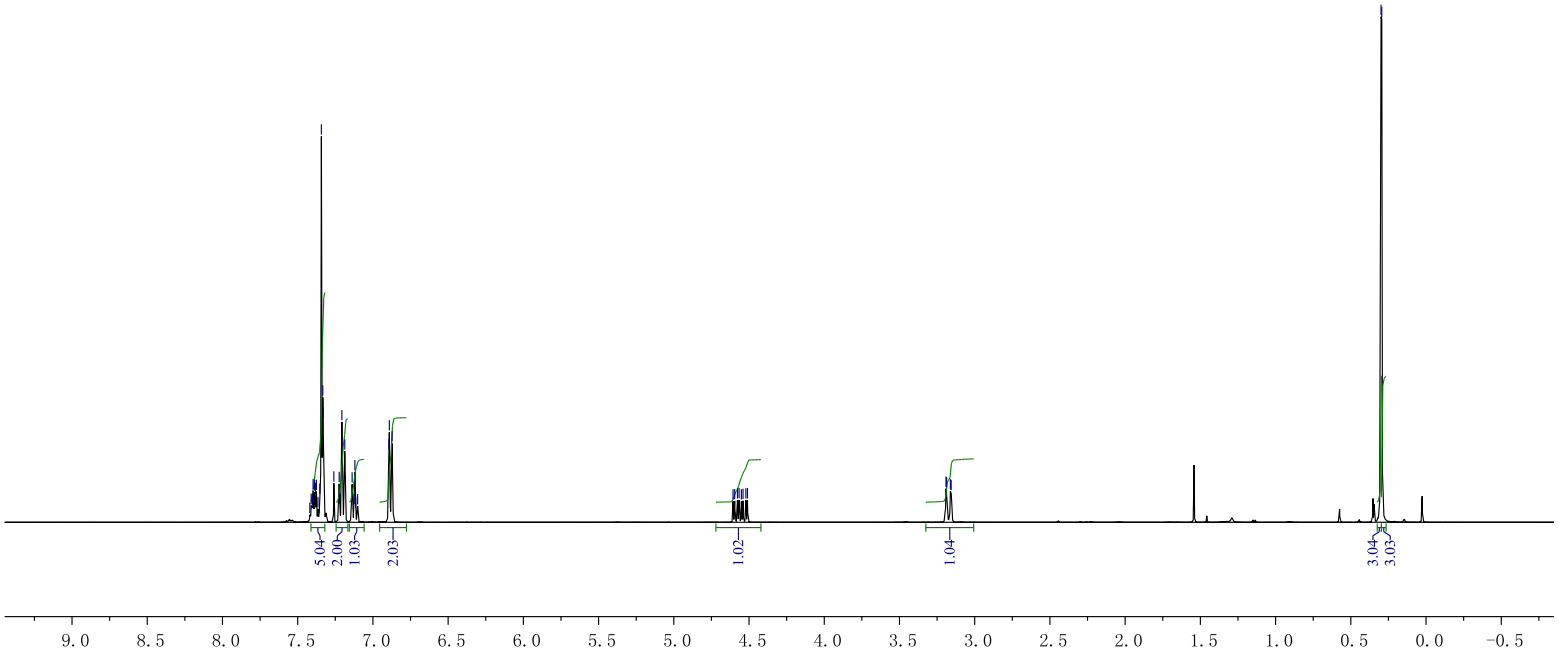
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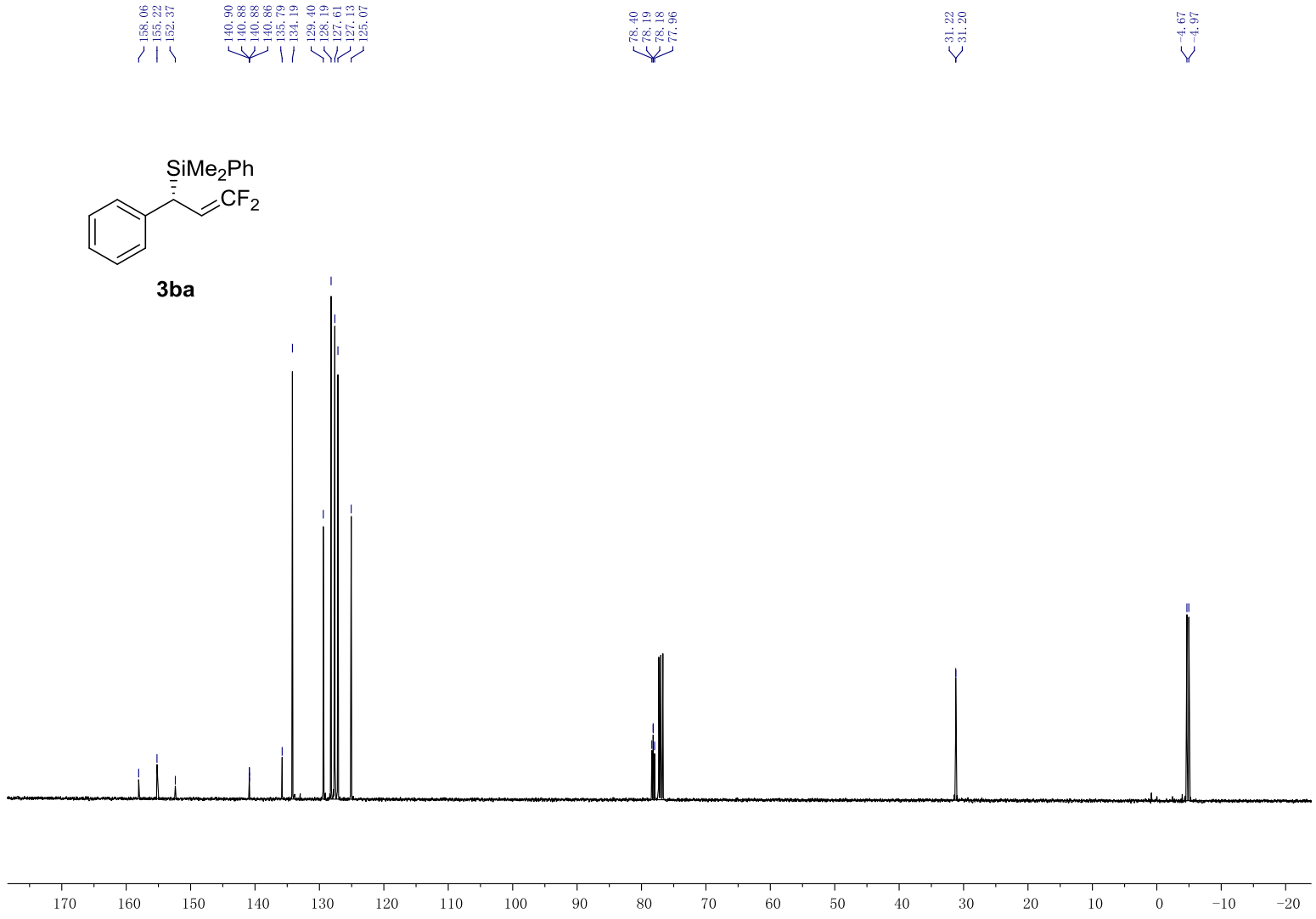
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31.20
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SiMe2Ph
CF2
3ba
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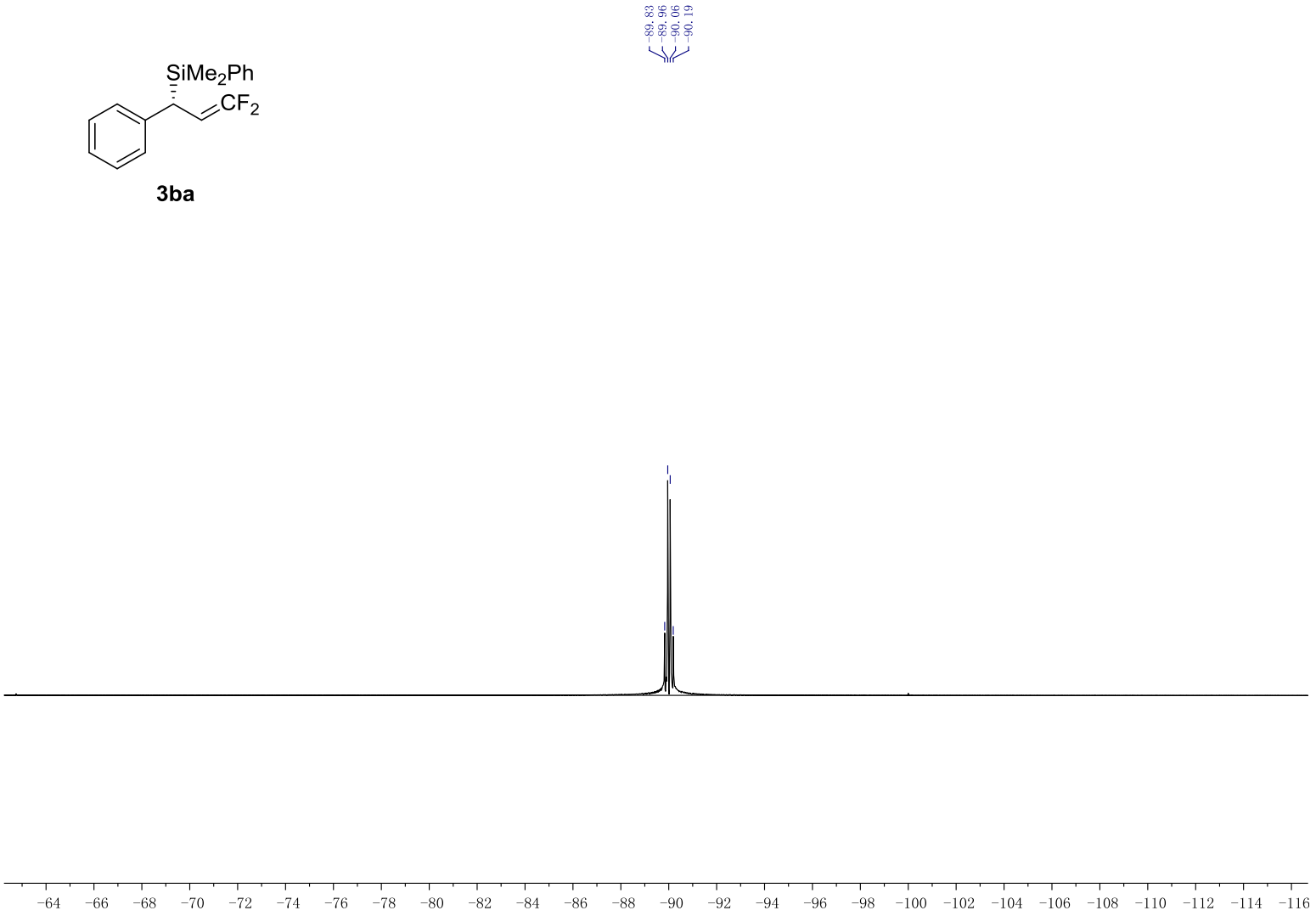
SiMe2Ph
CF2

3ba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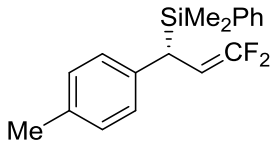
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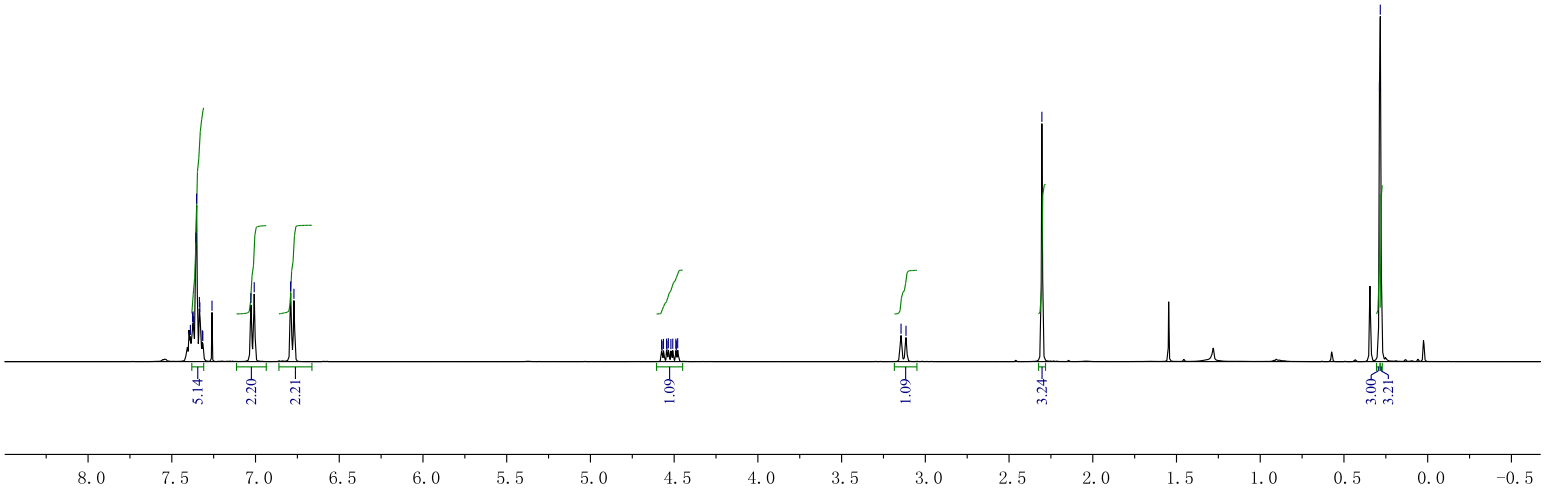
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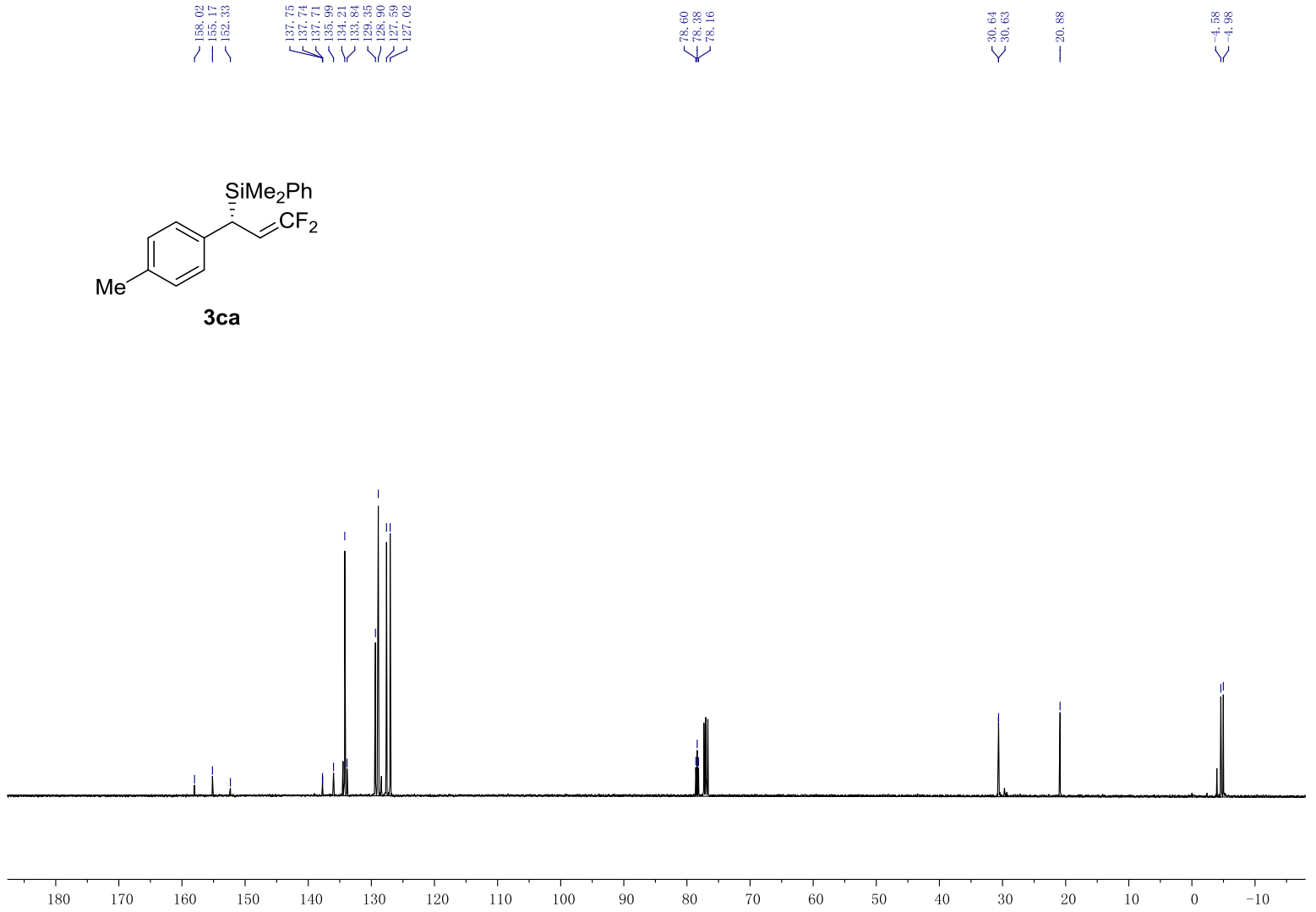
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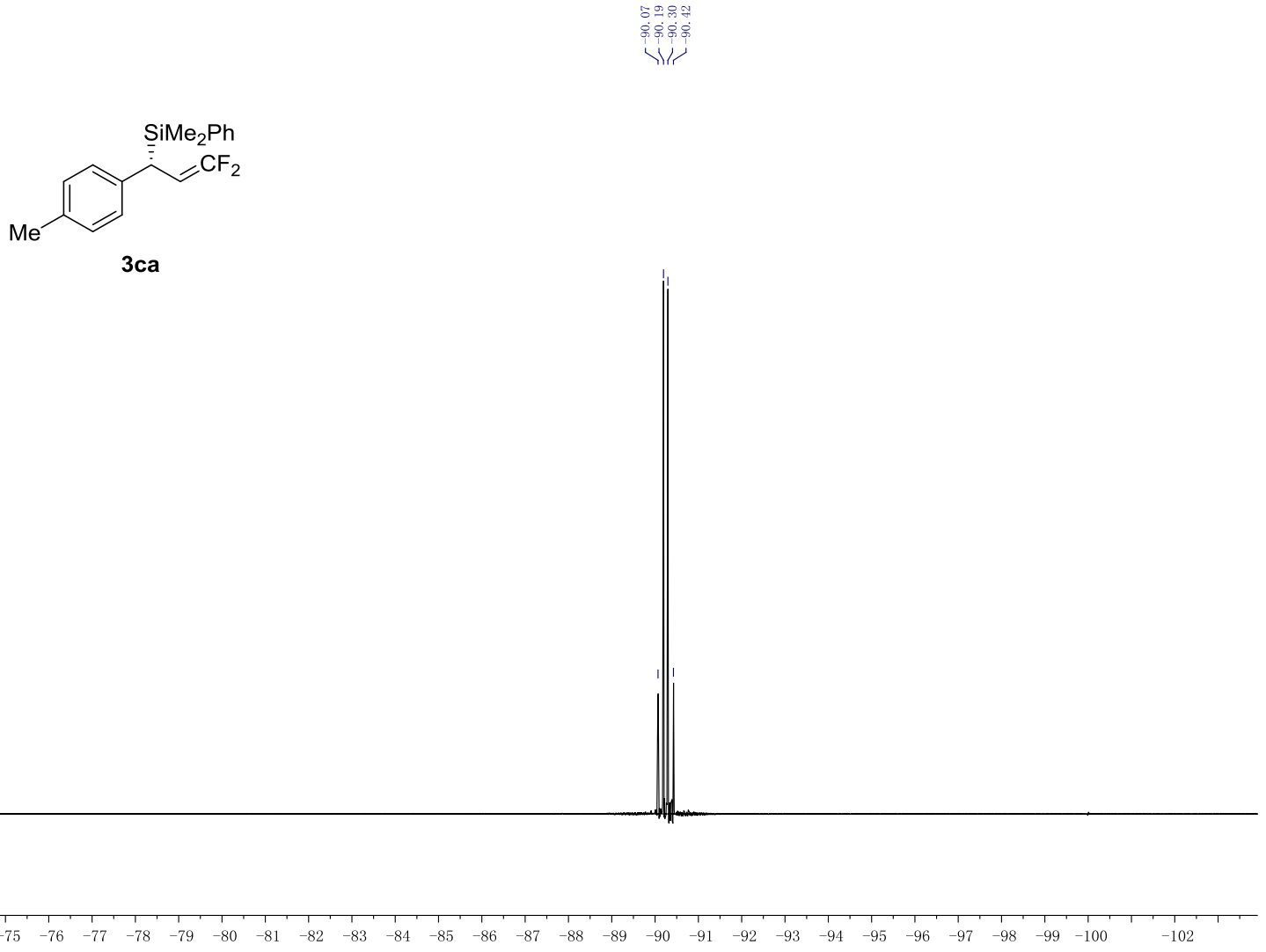
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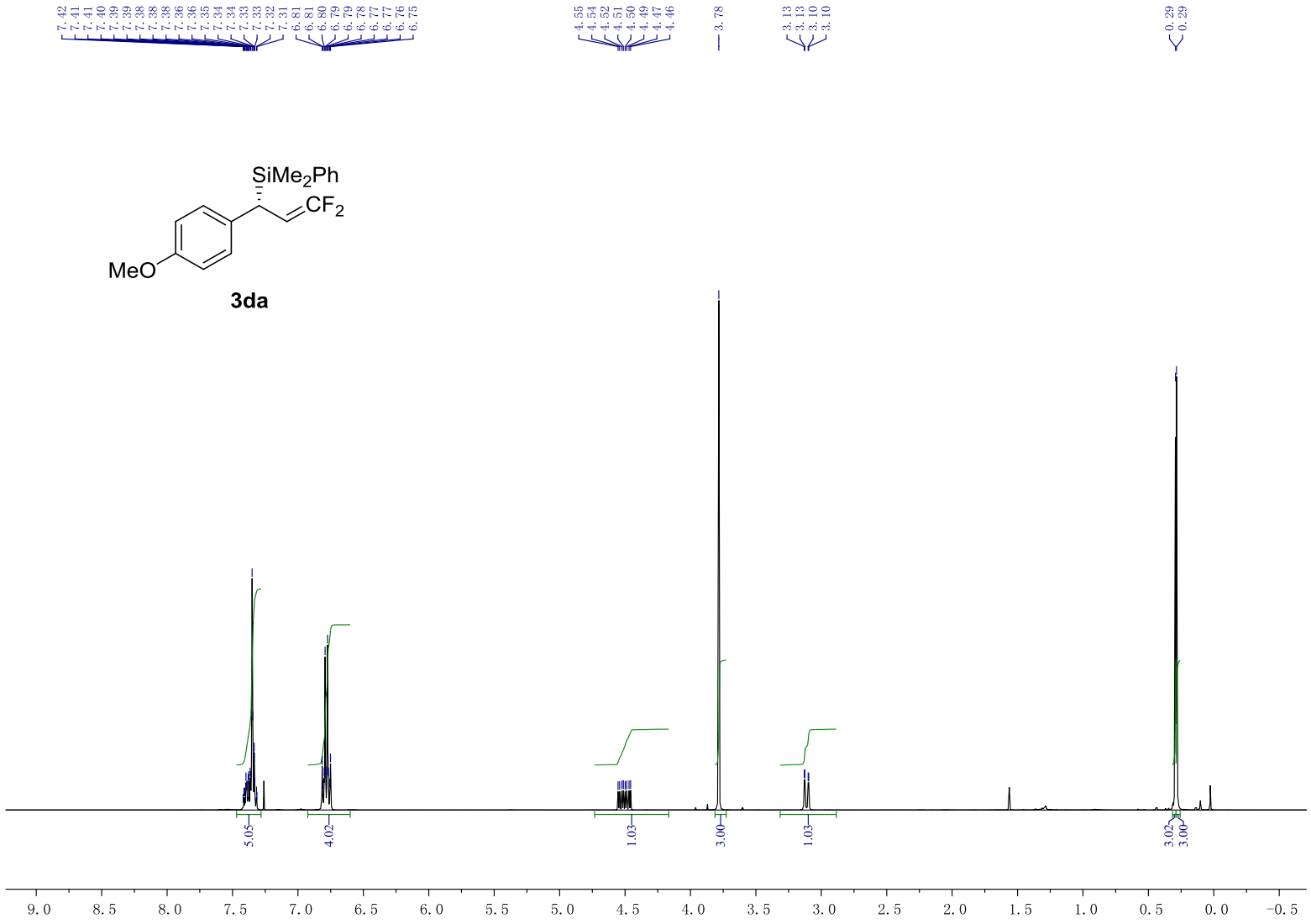
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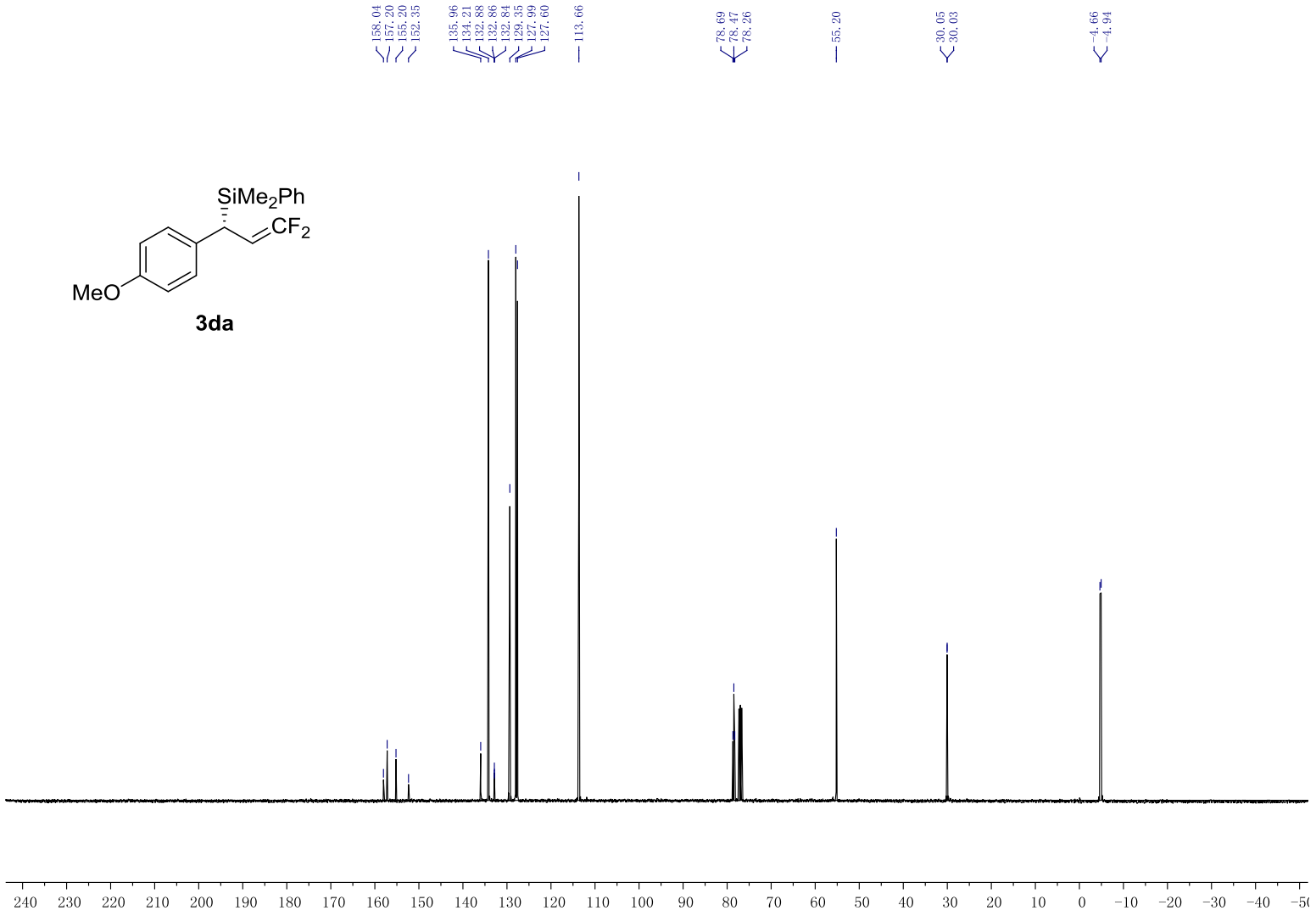
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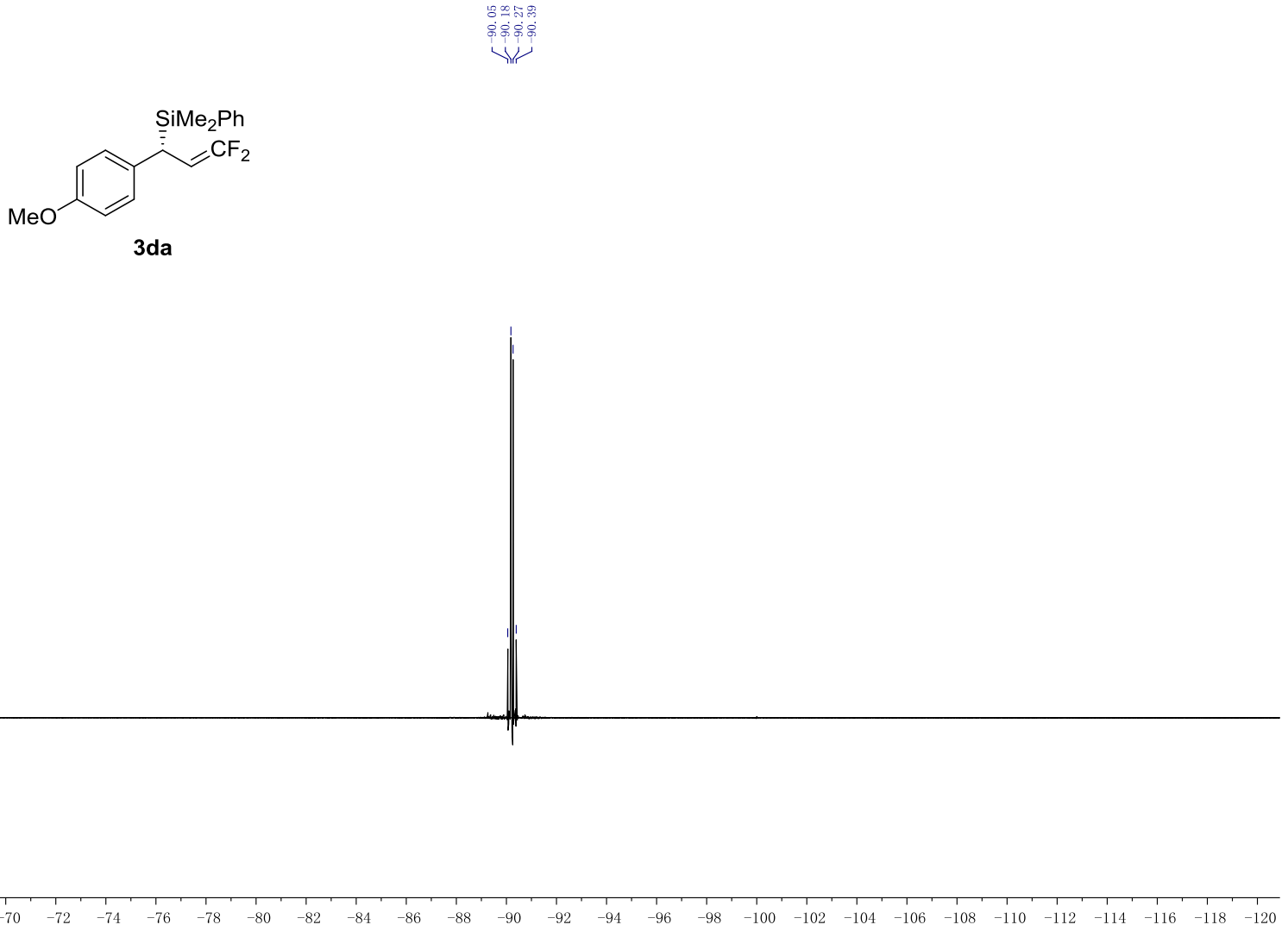
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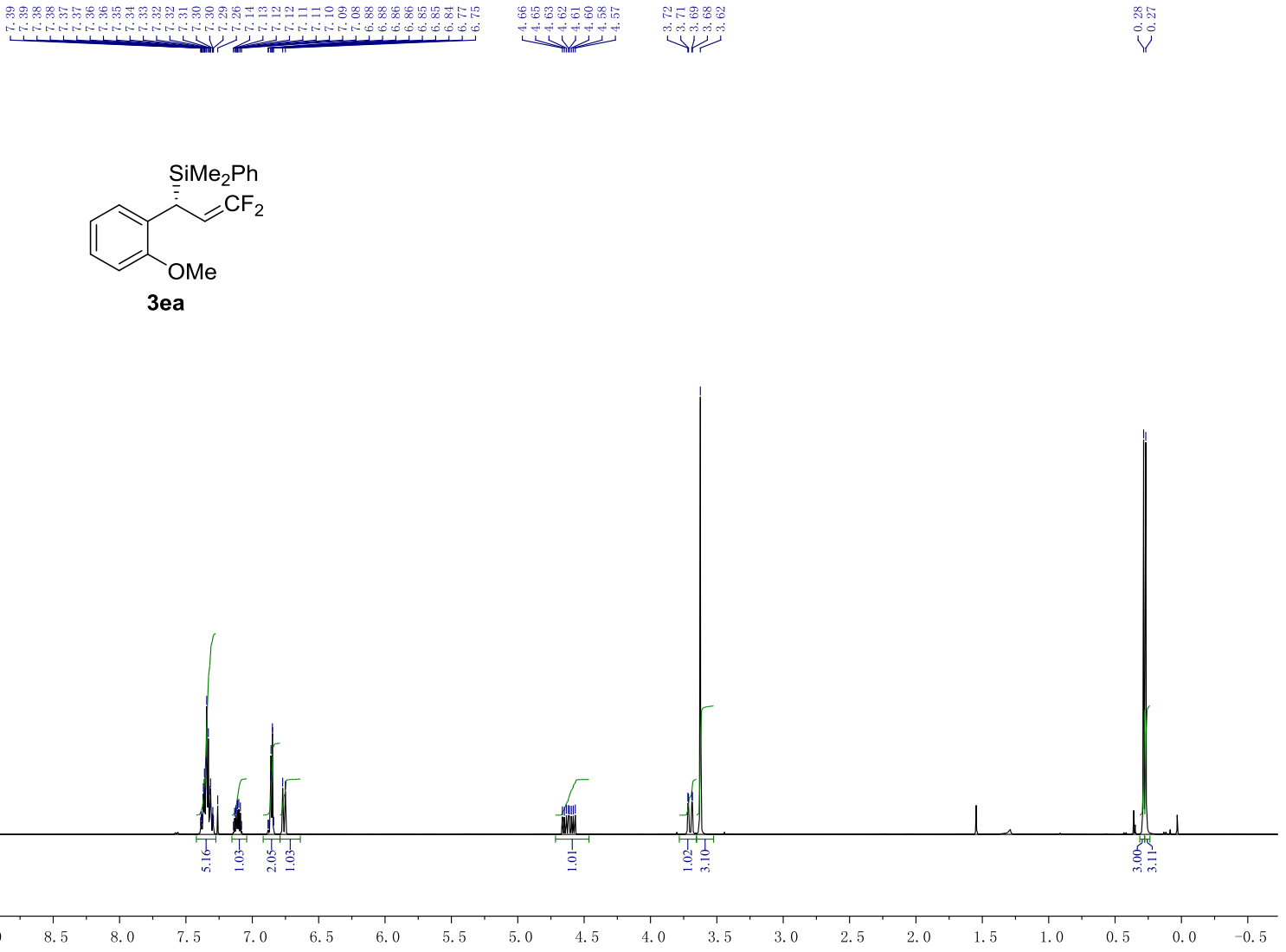
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OMe
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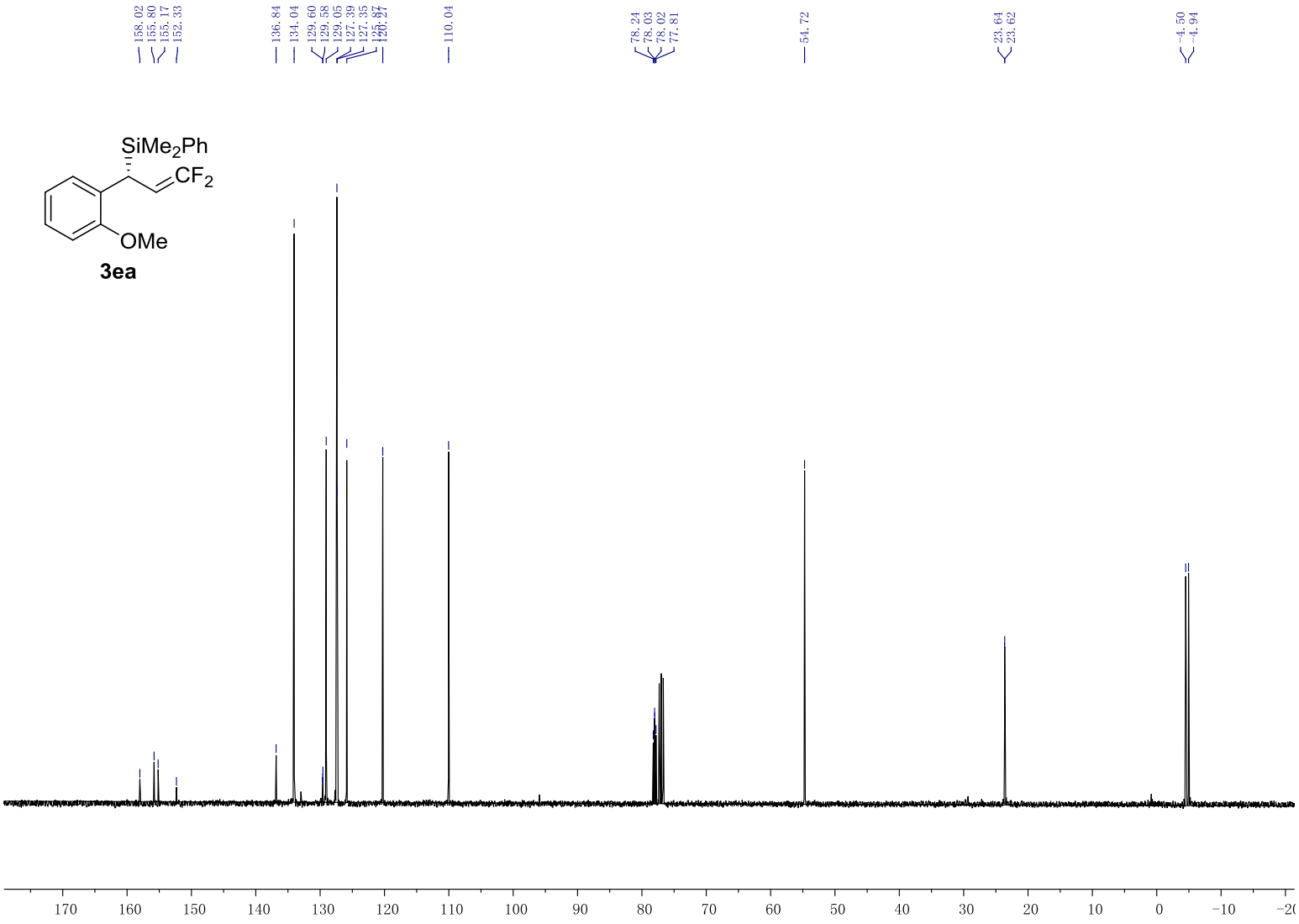
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127.35
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78.03
78.02
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23.64
23.62
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SiMe2Ph
CF2
OMe
3ea
170
160
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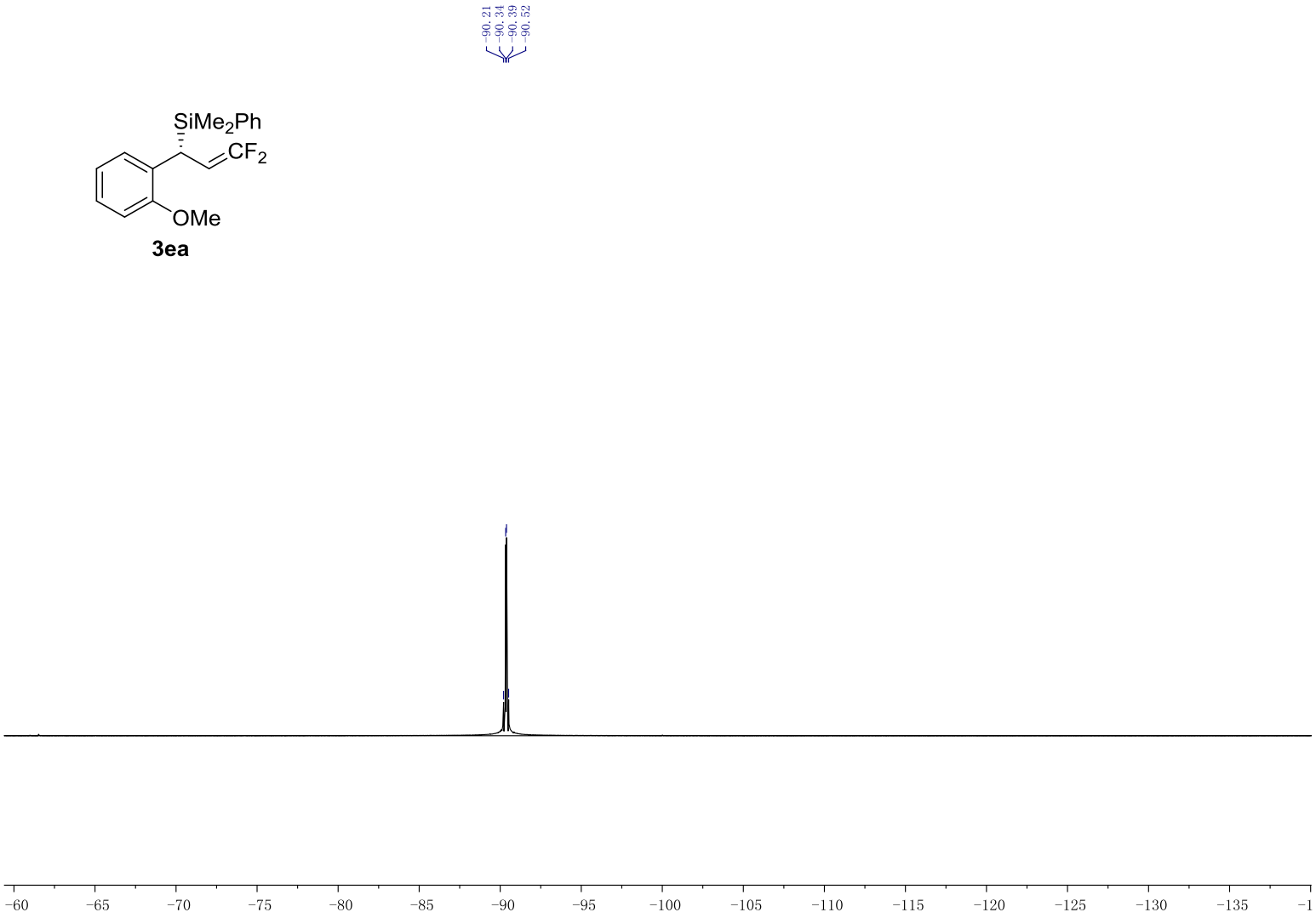
SiMe2Ph
CF2
OMe

3ea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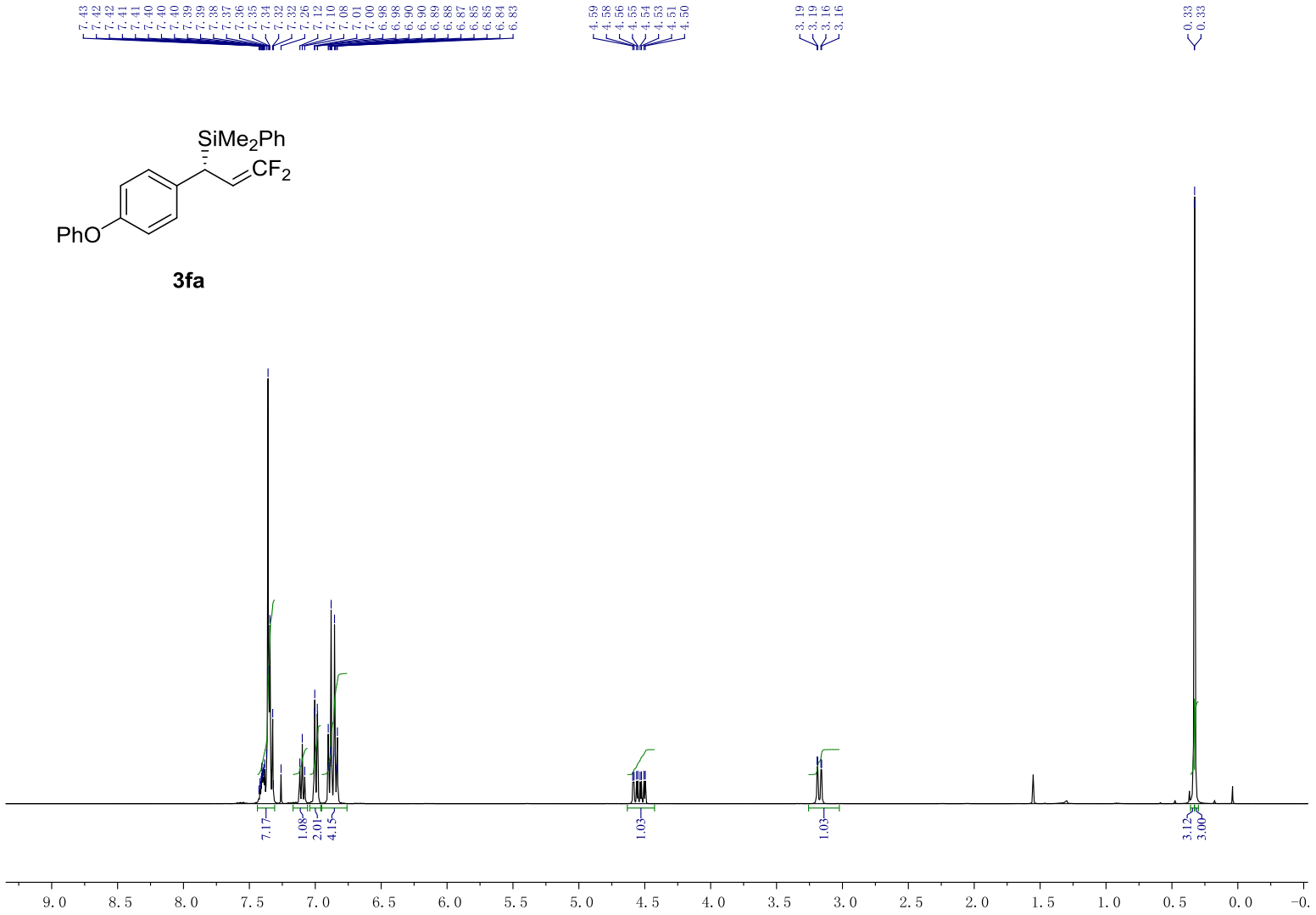
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CF2
PhO
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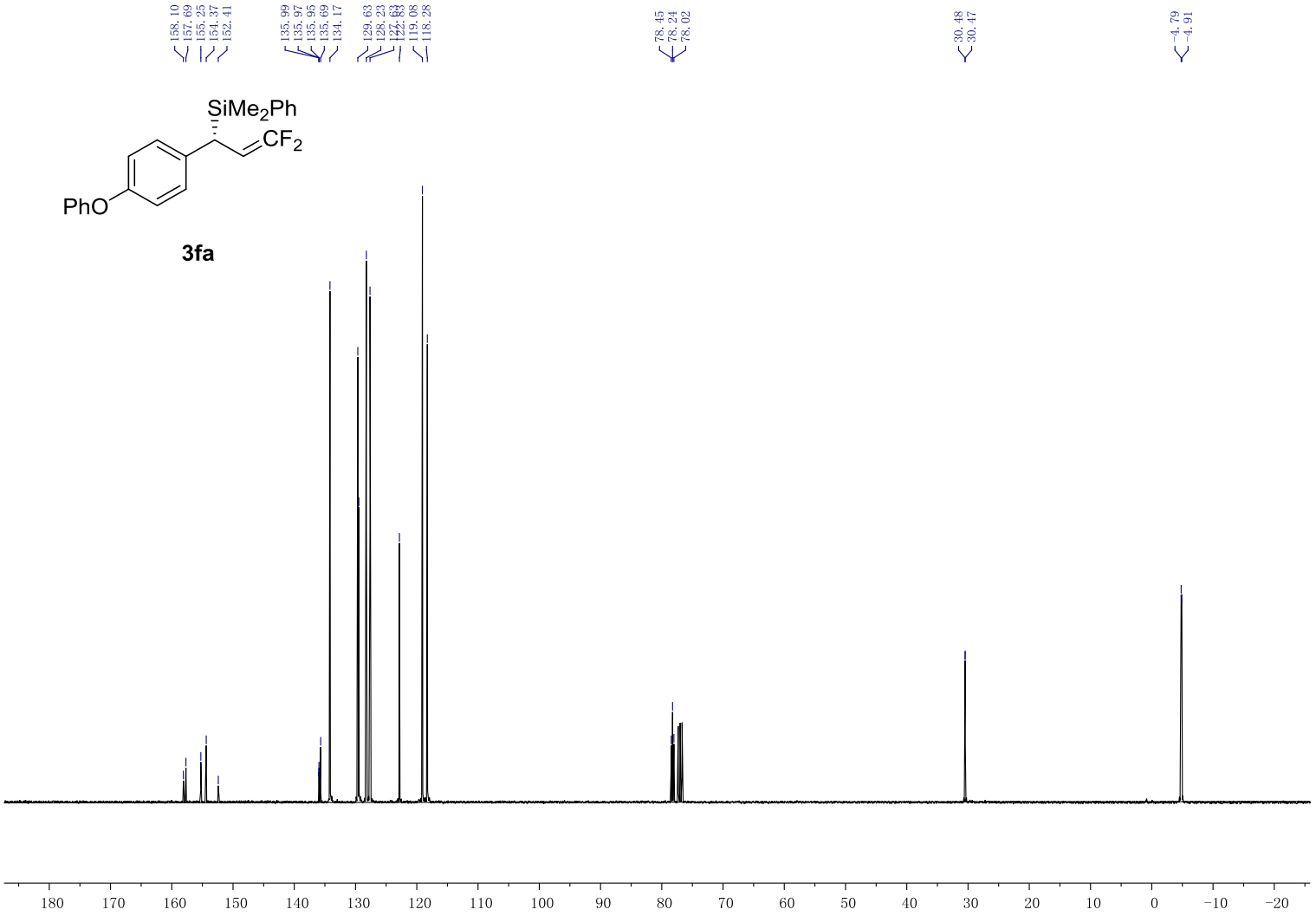
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CF2
PhO
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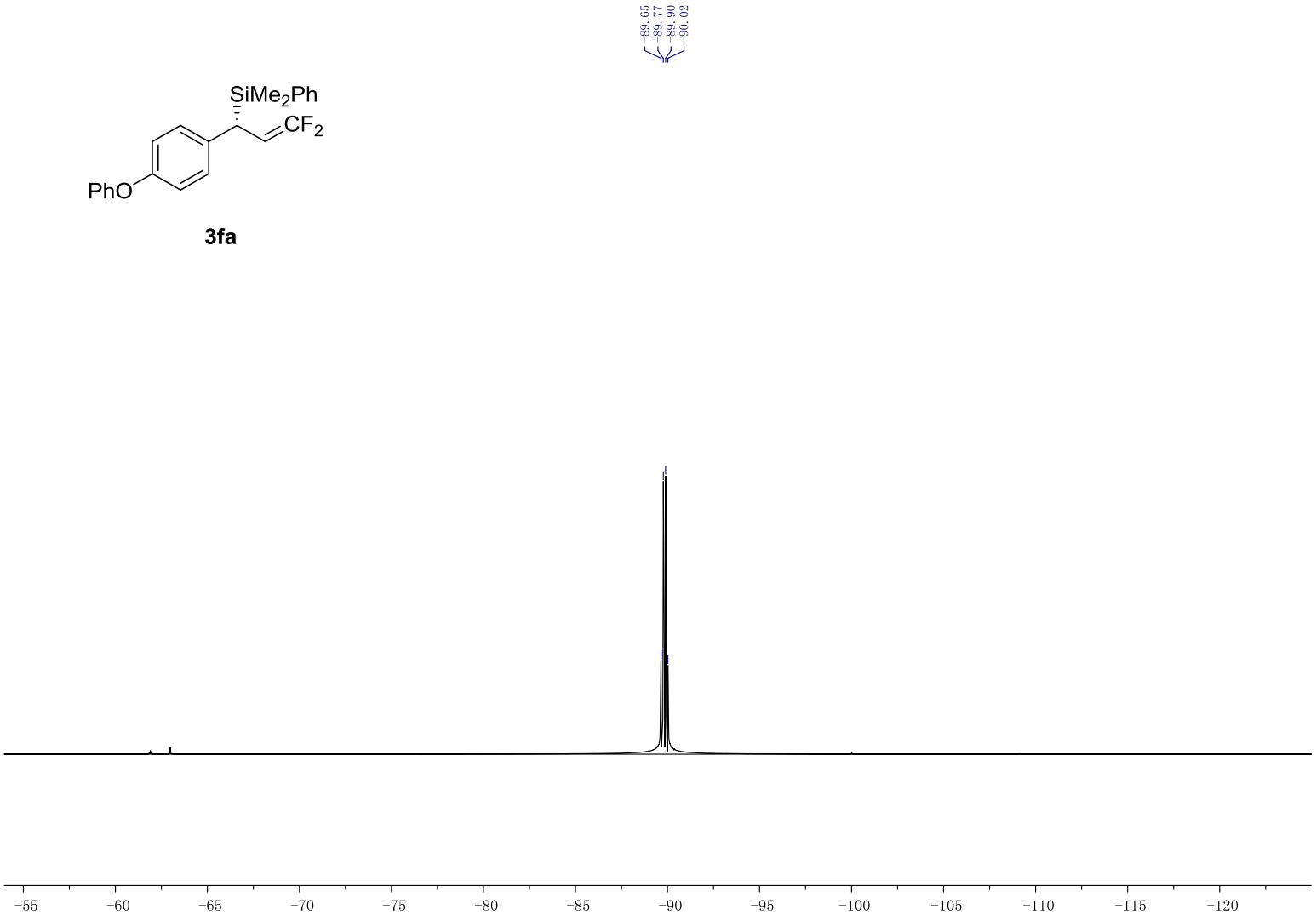
PhO

3fa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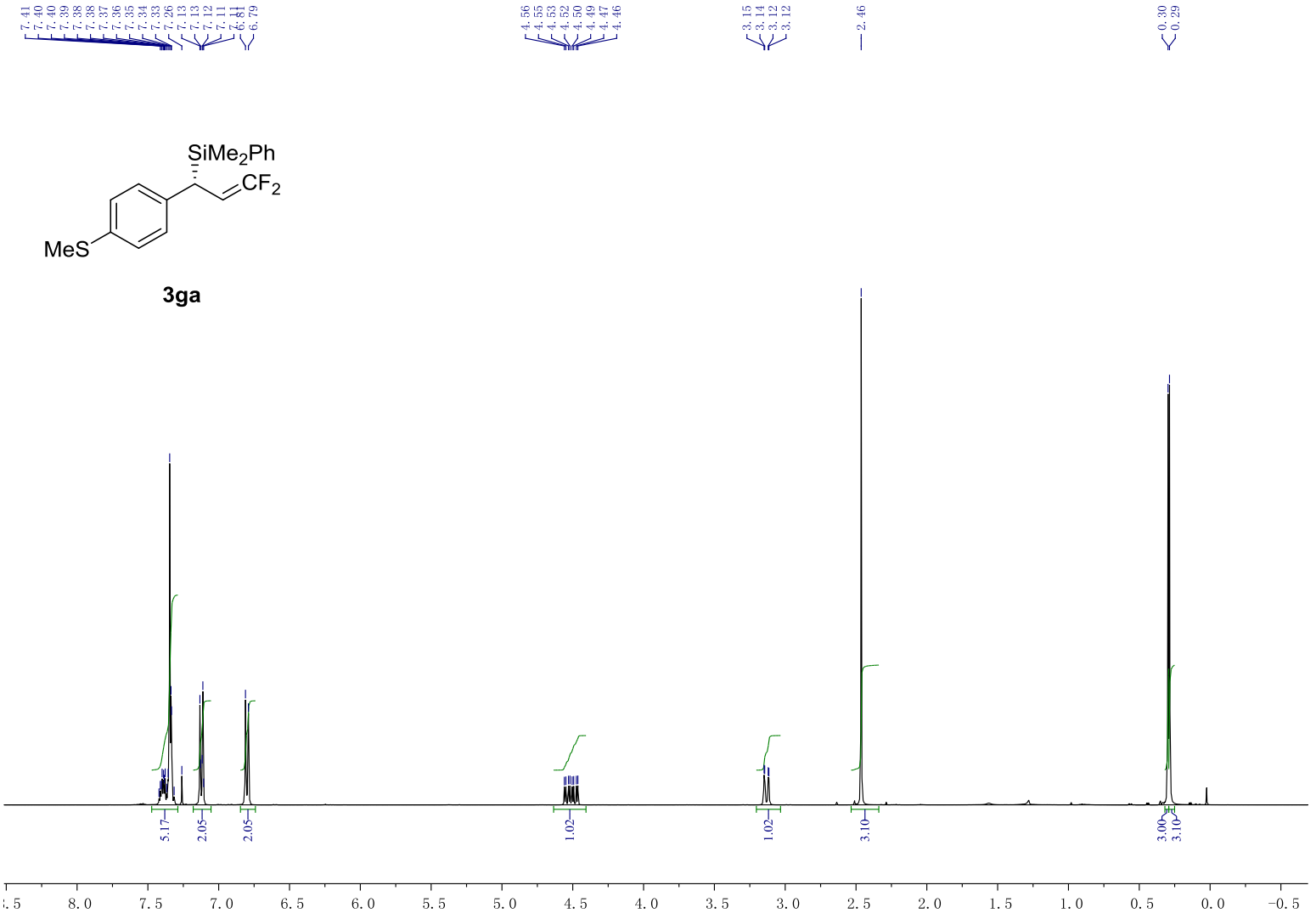
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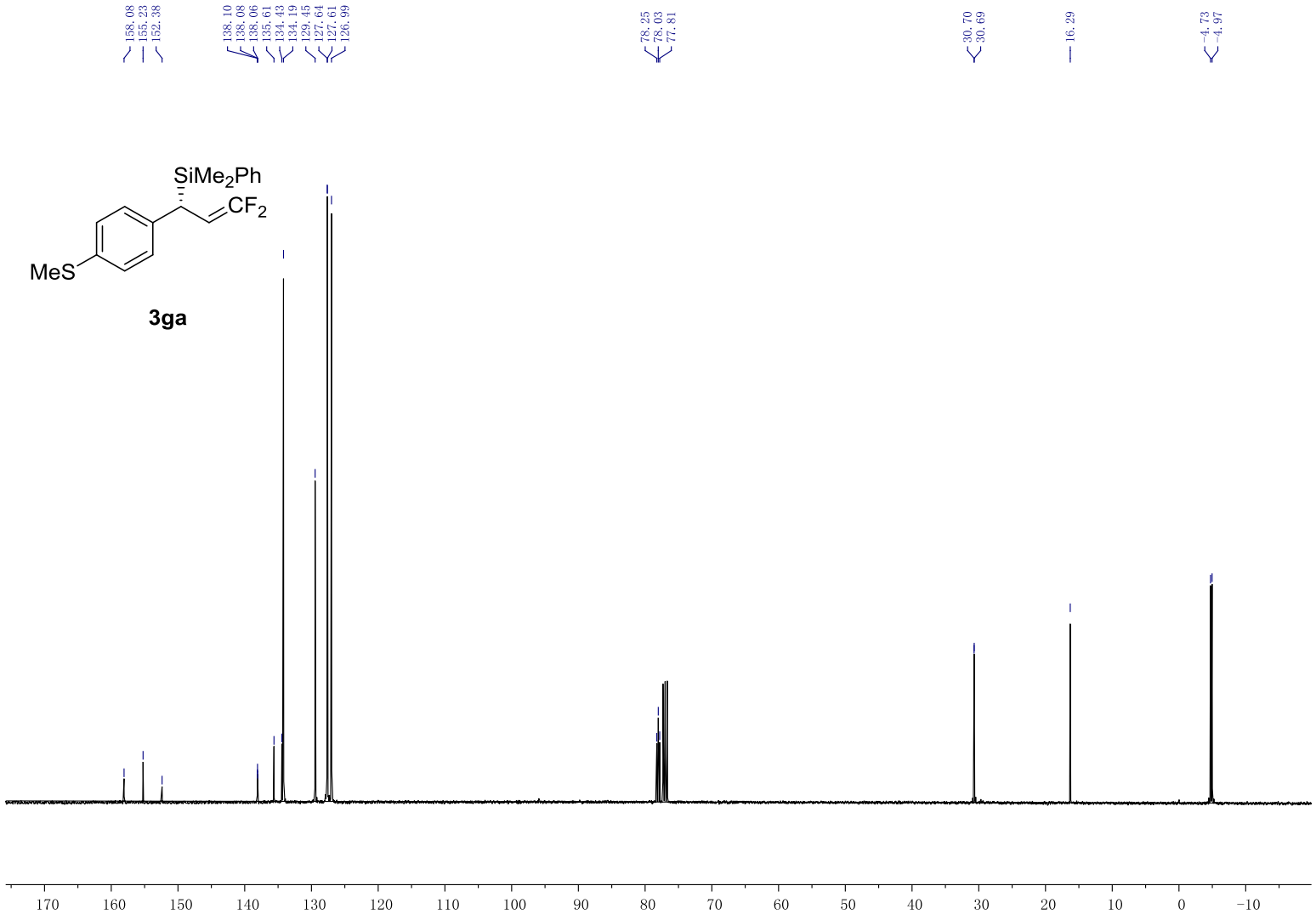
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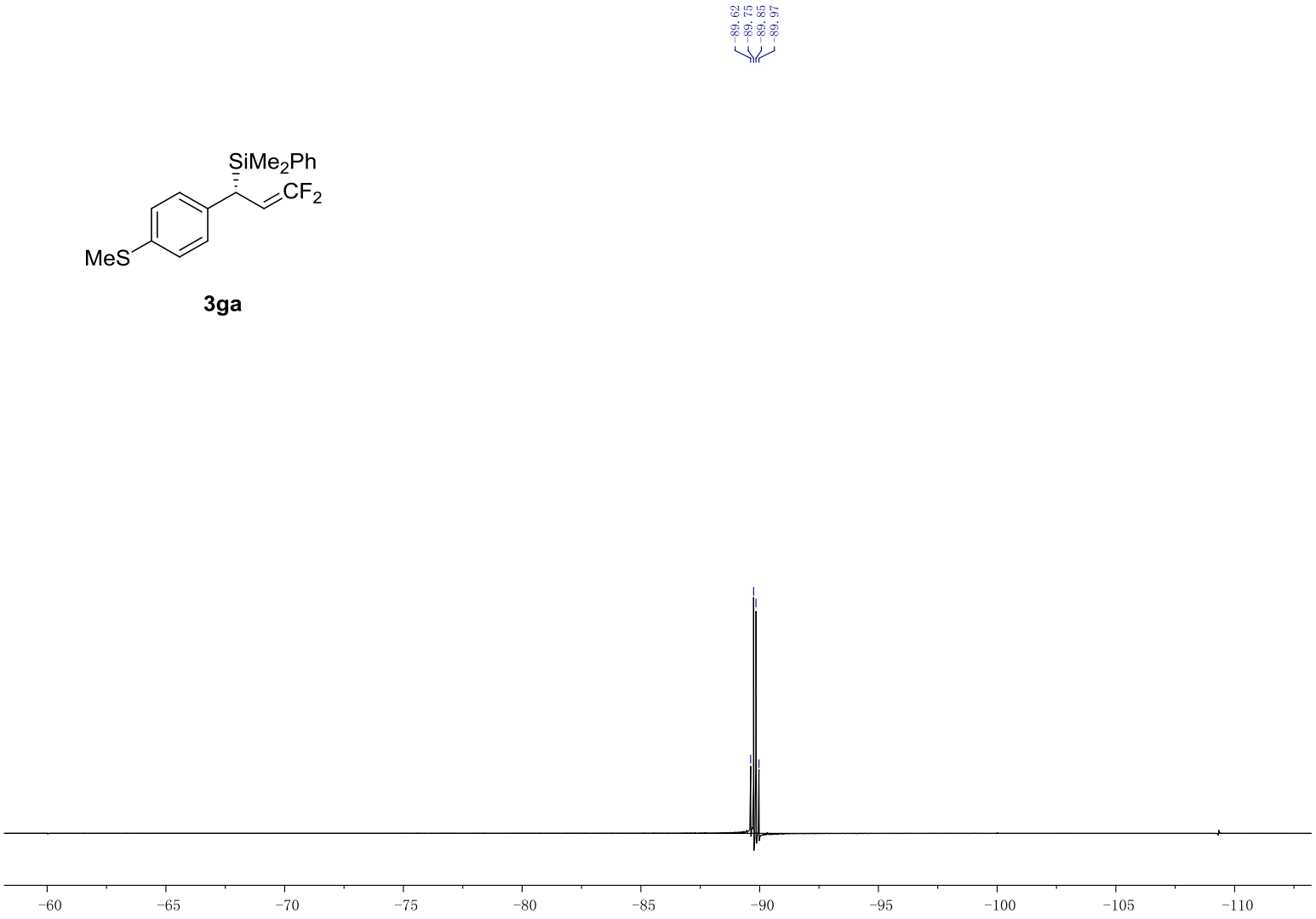
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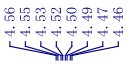
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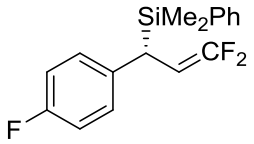
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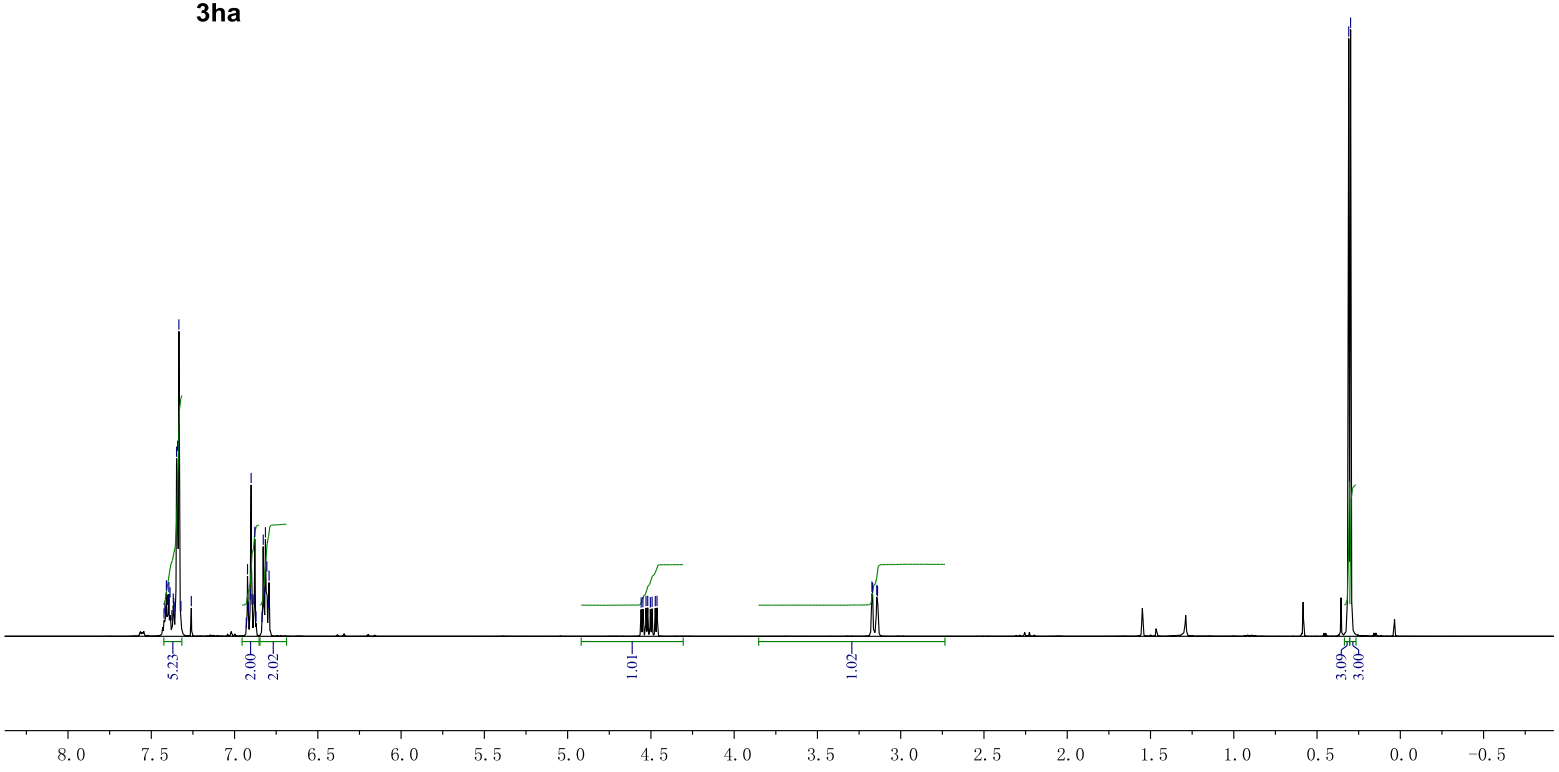
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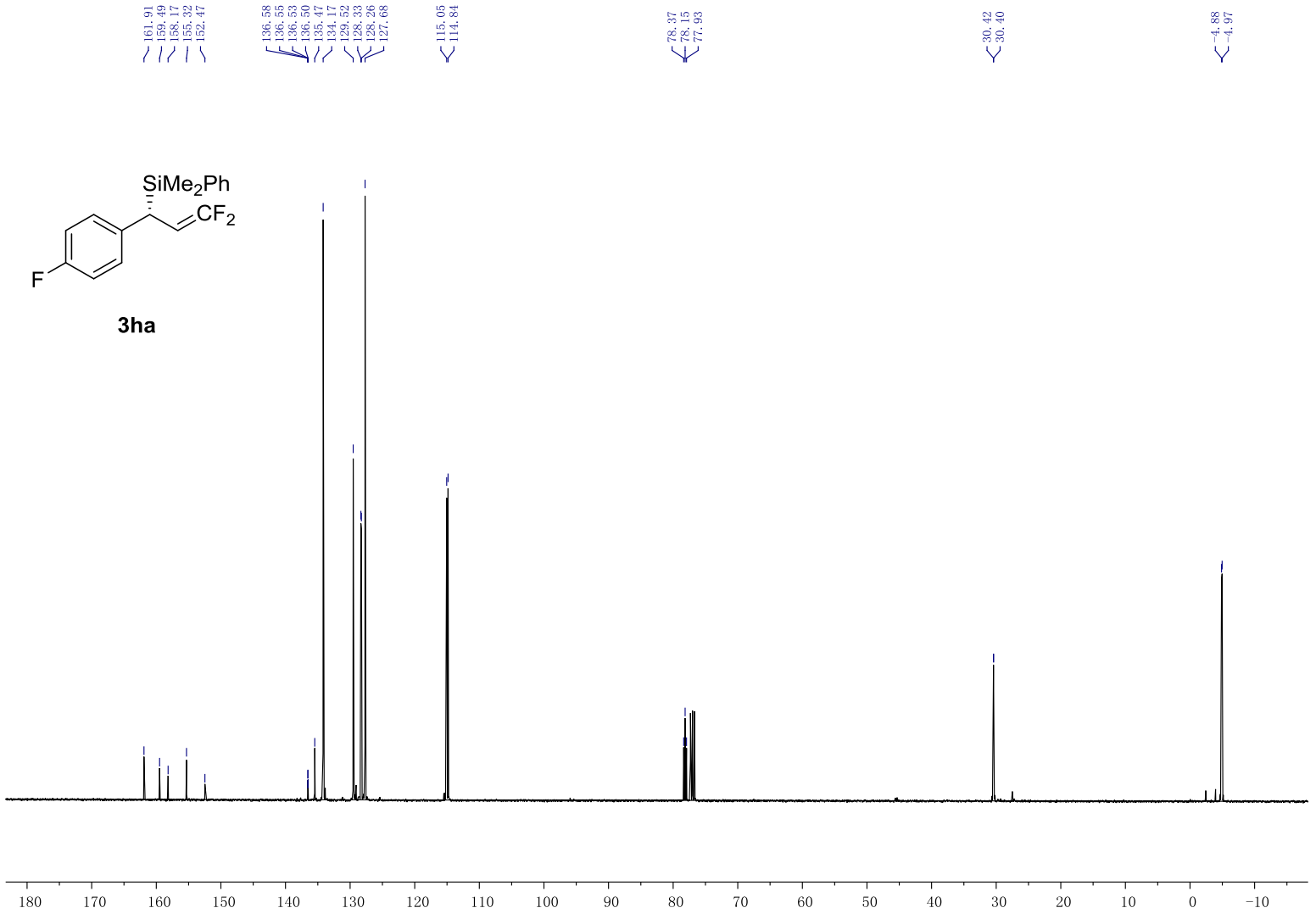
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CF2
F
3ha
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F

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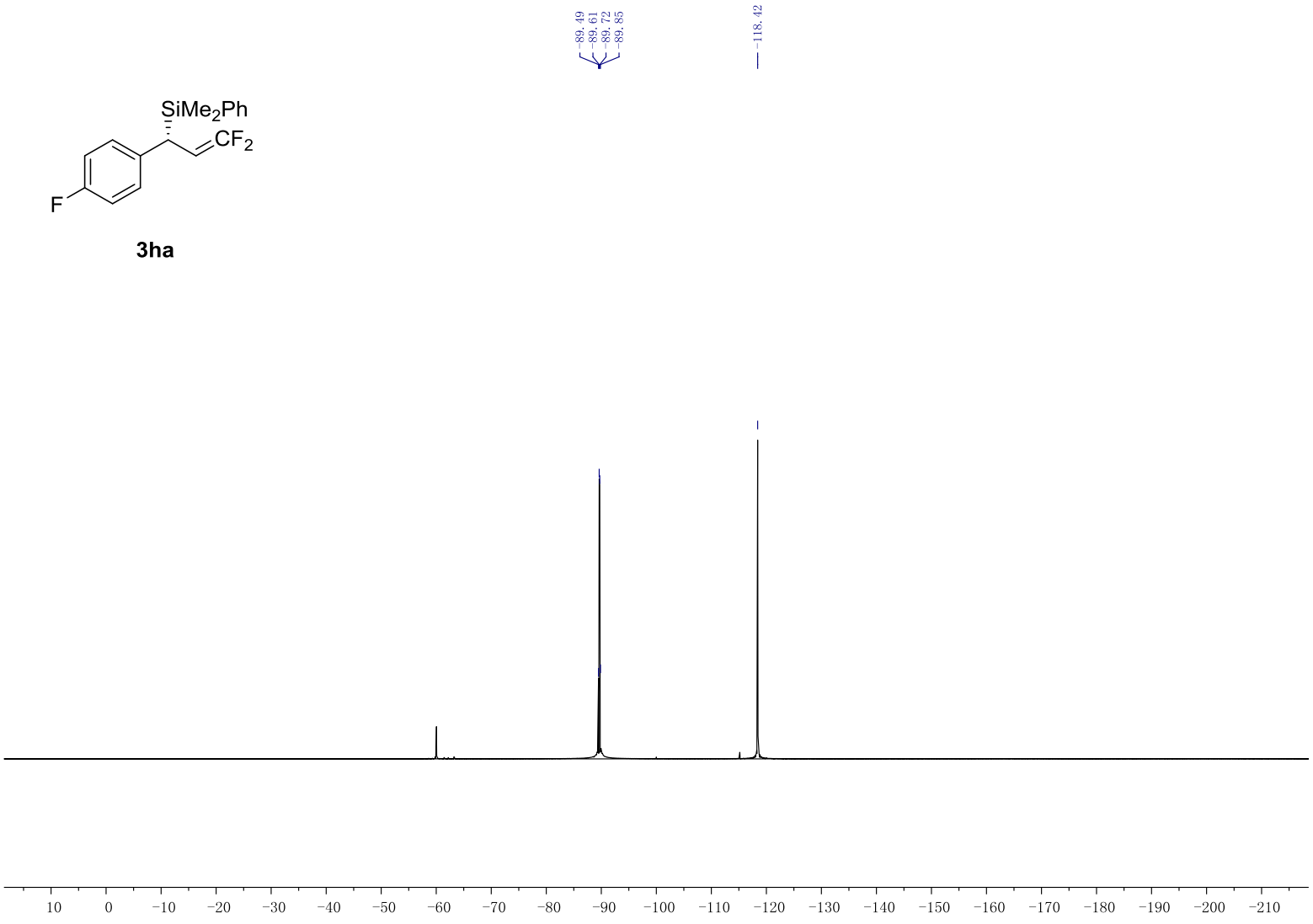
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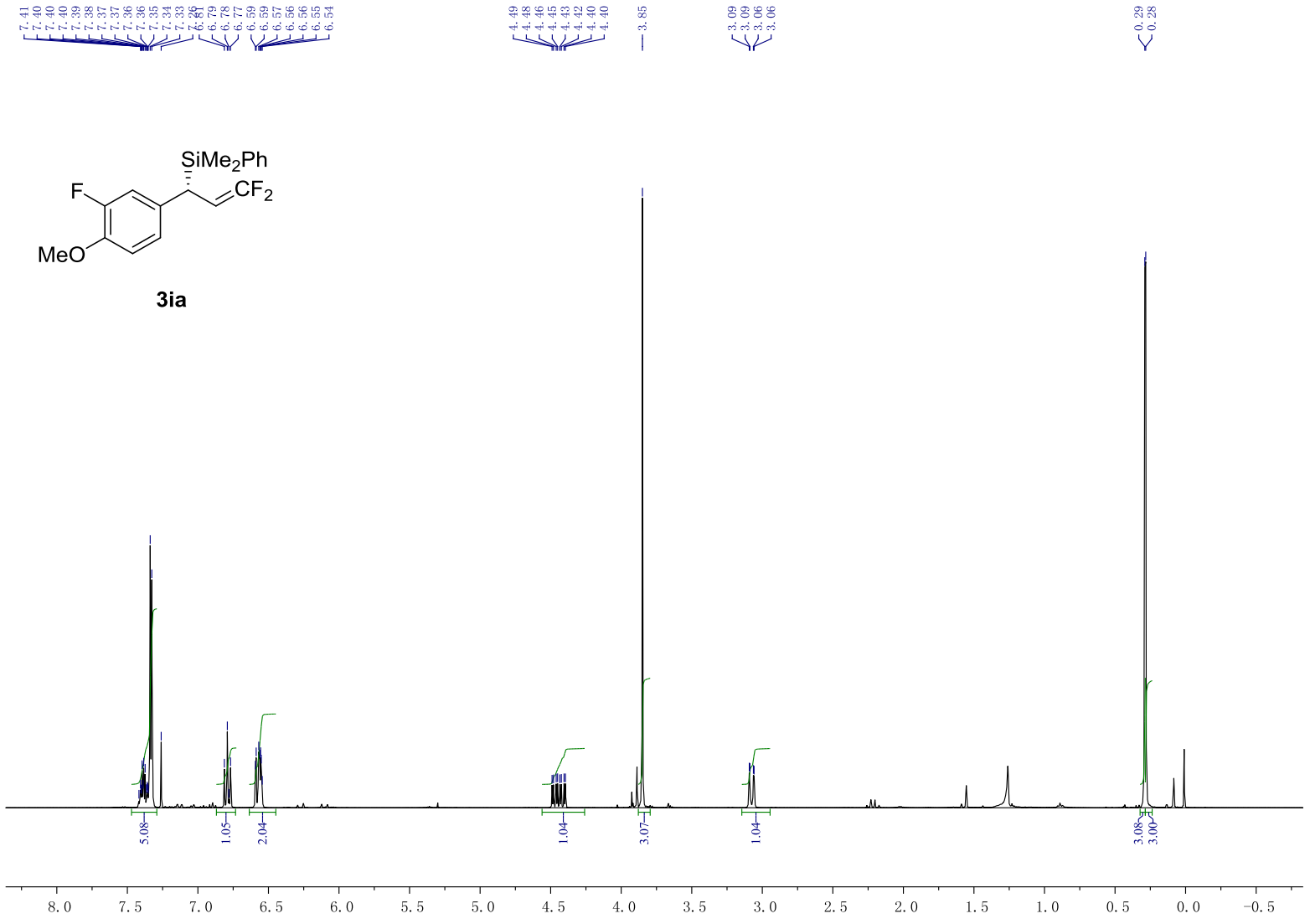
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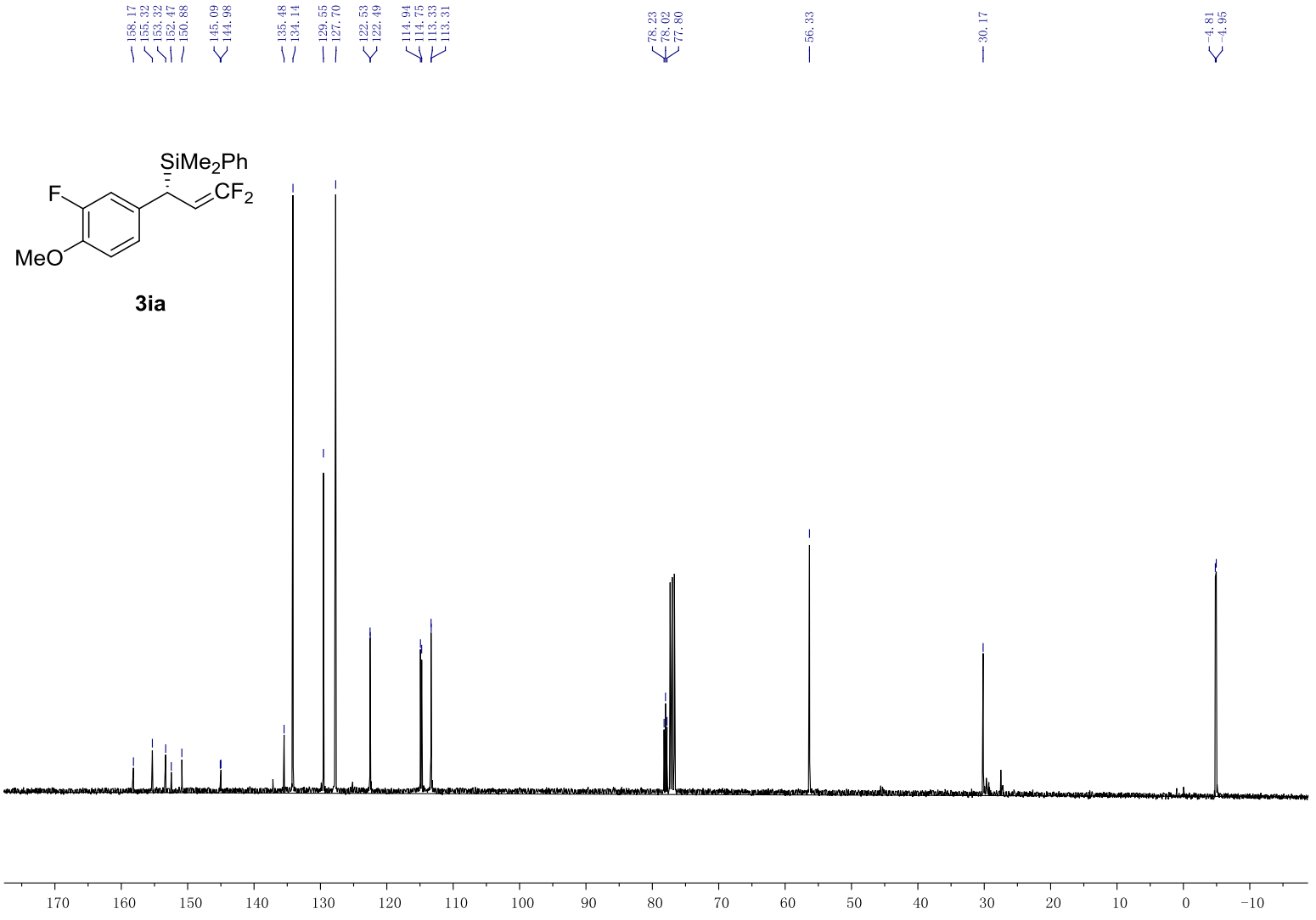
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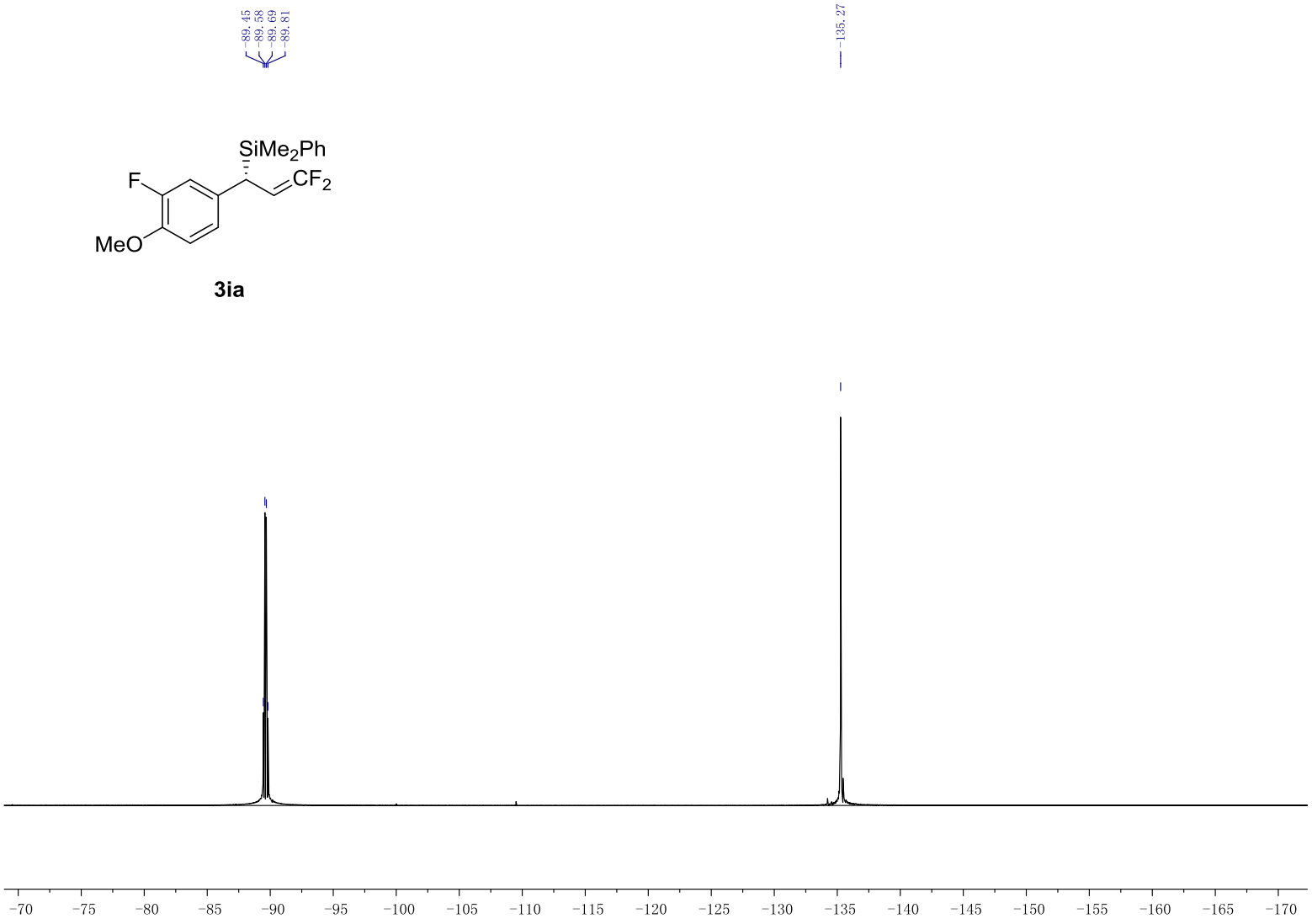
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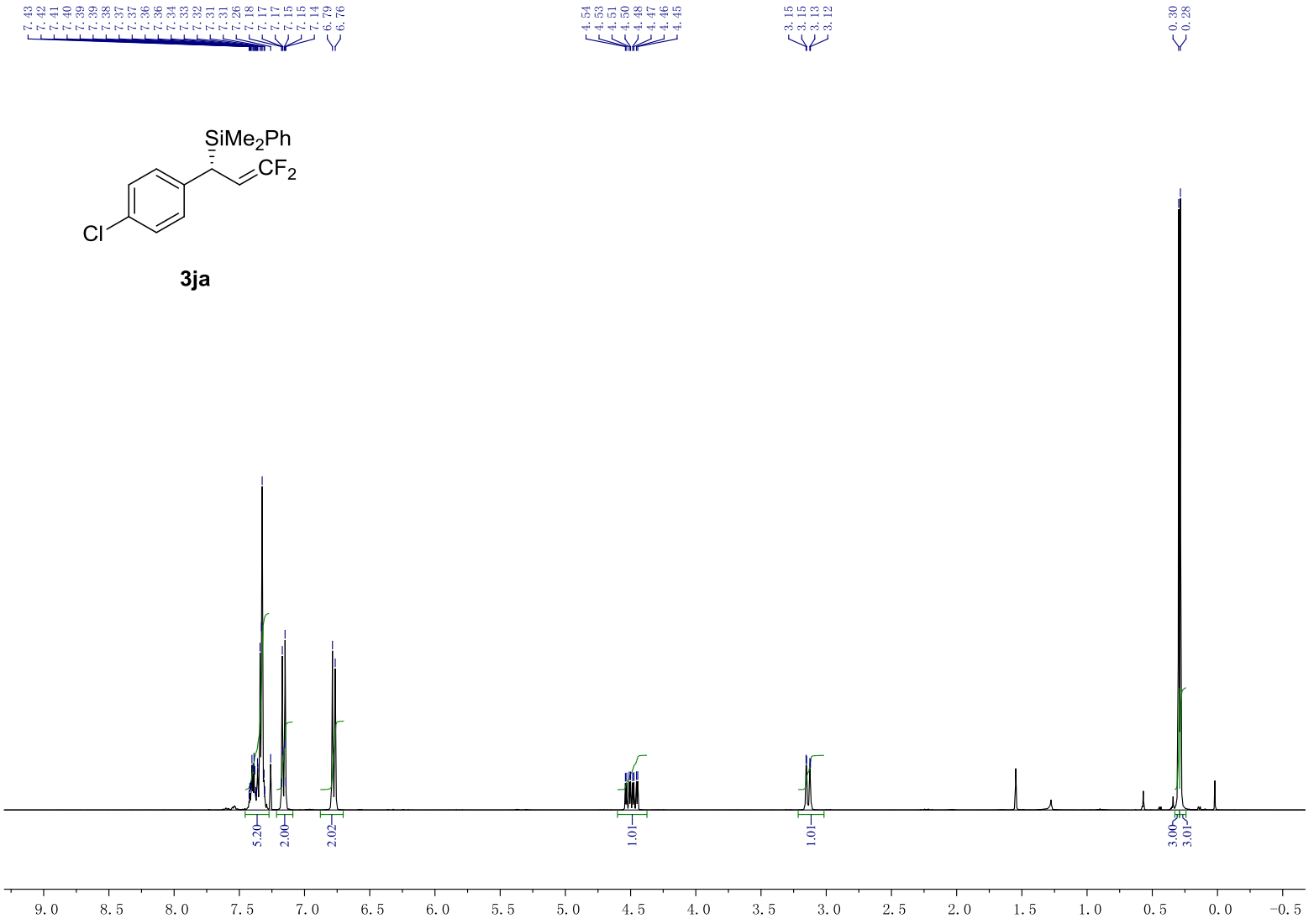
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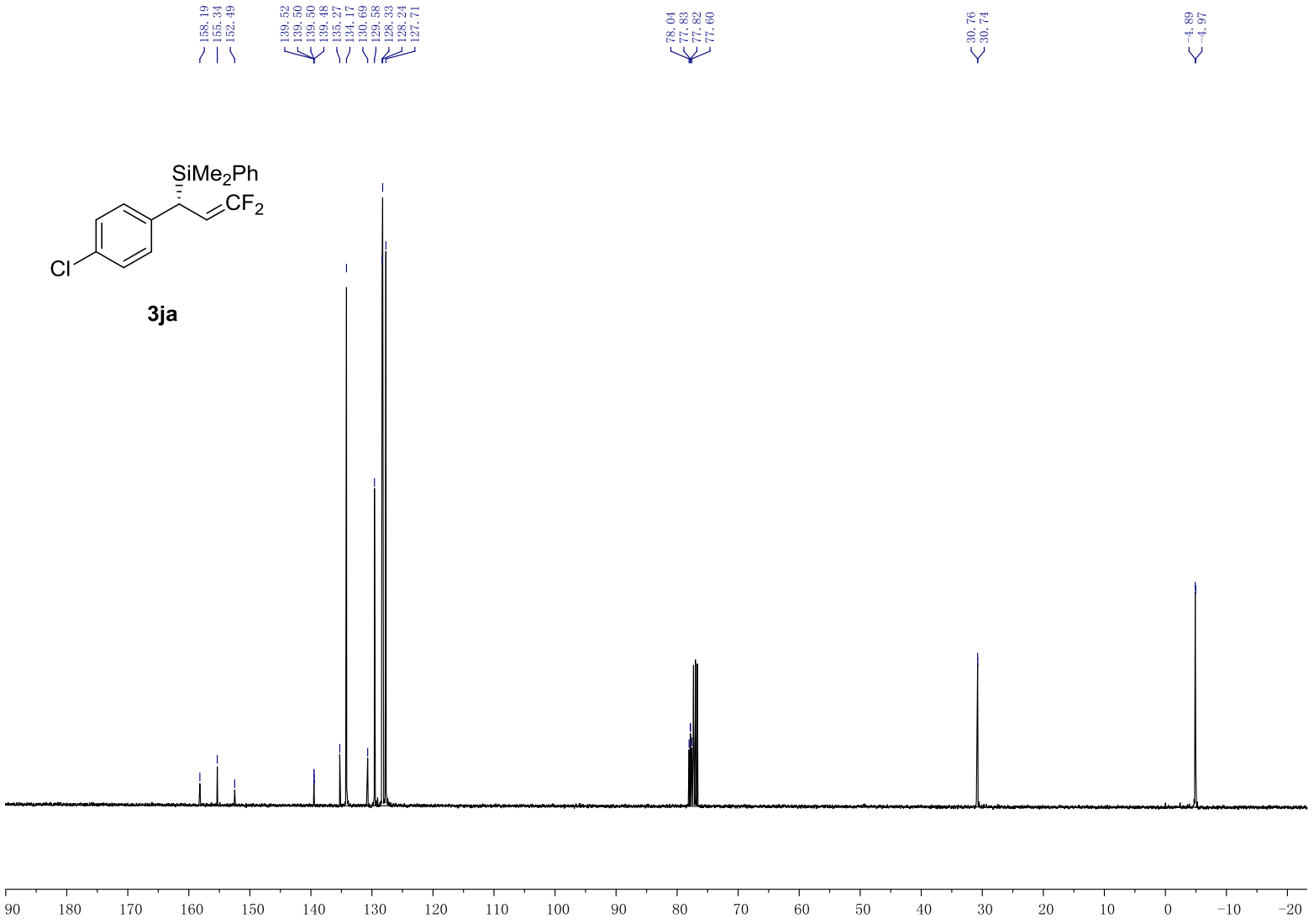
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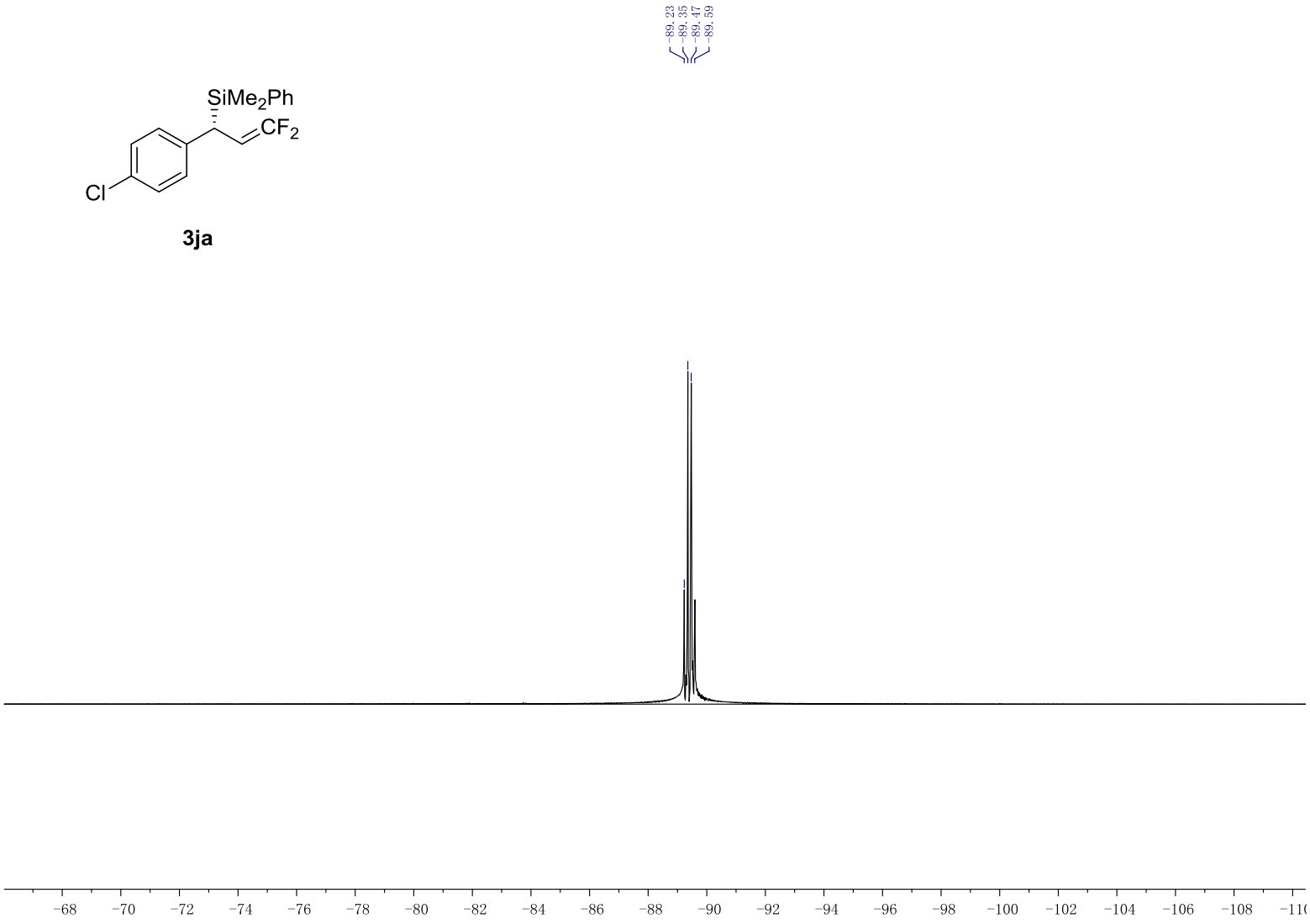
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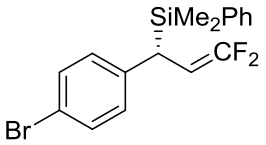
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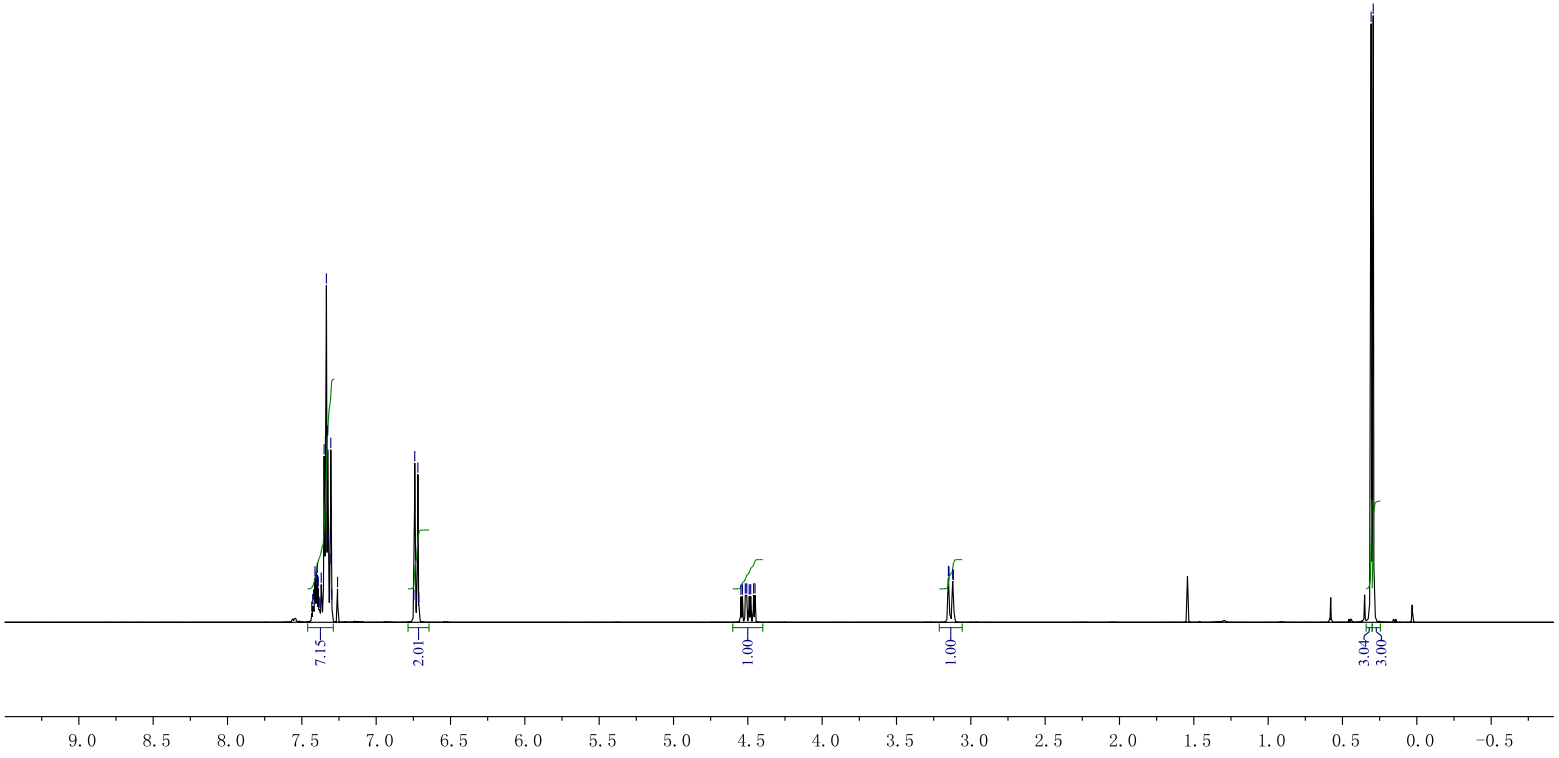
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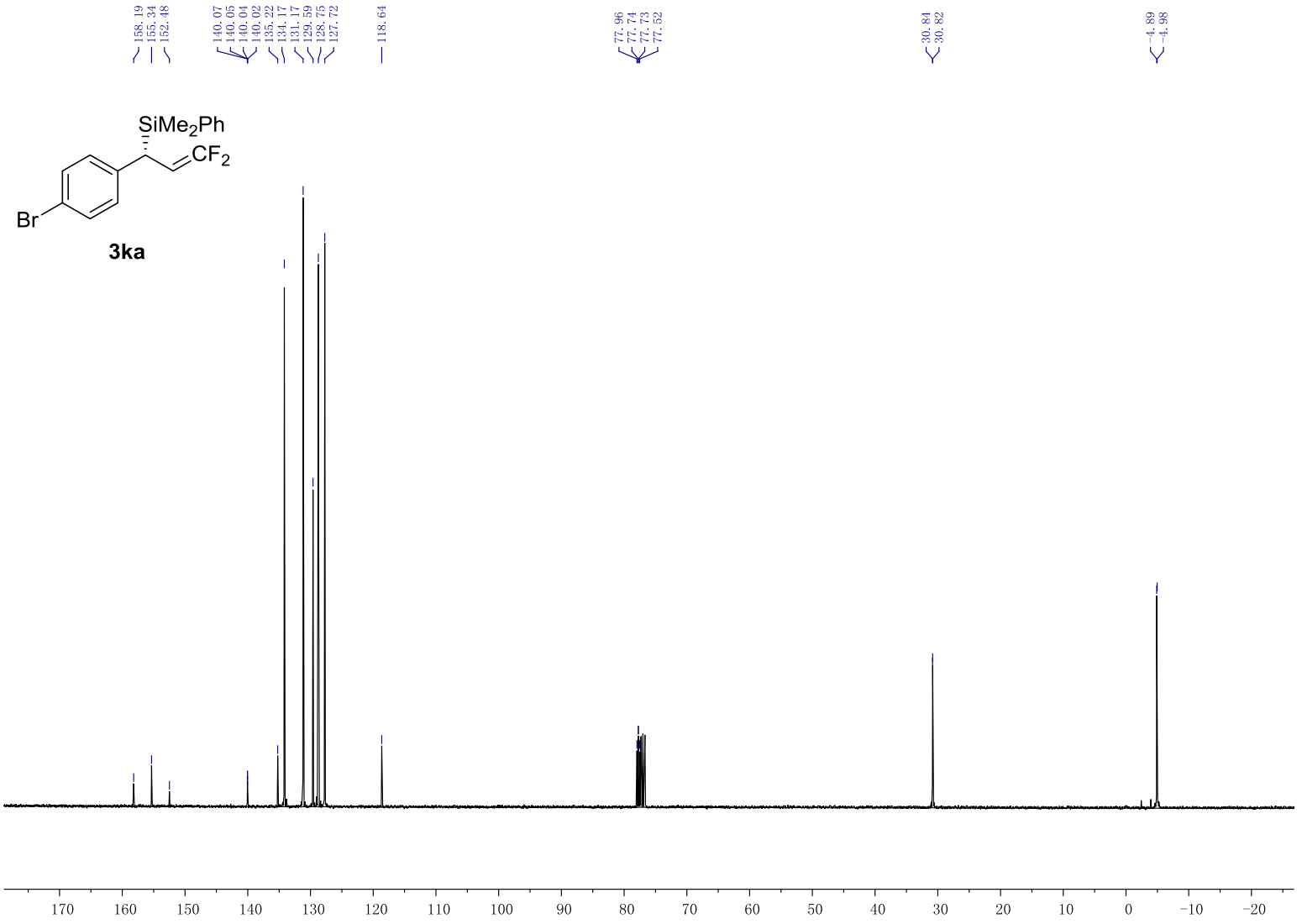
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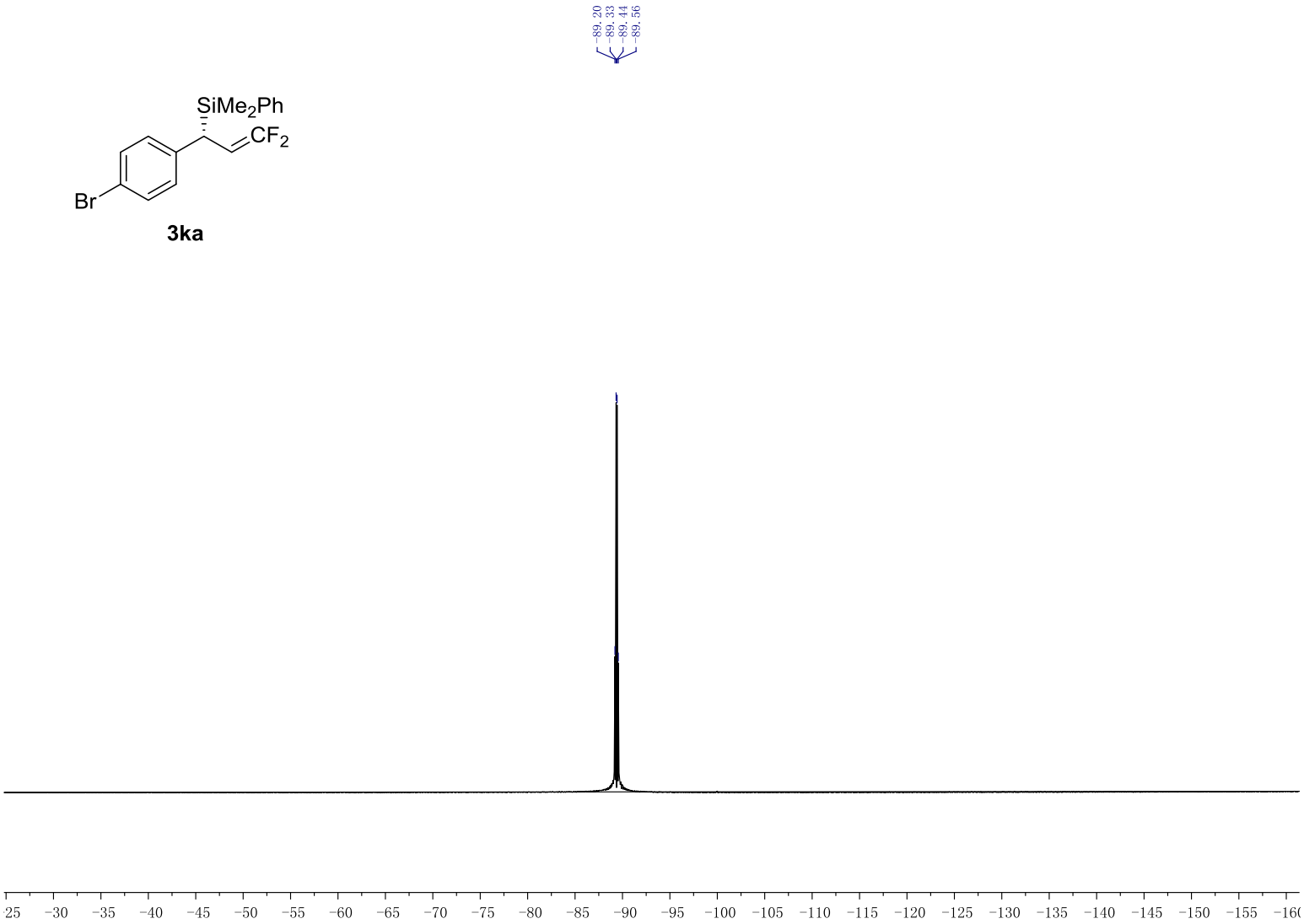
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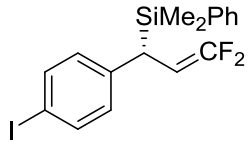
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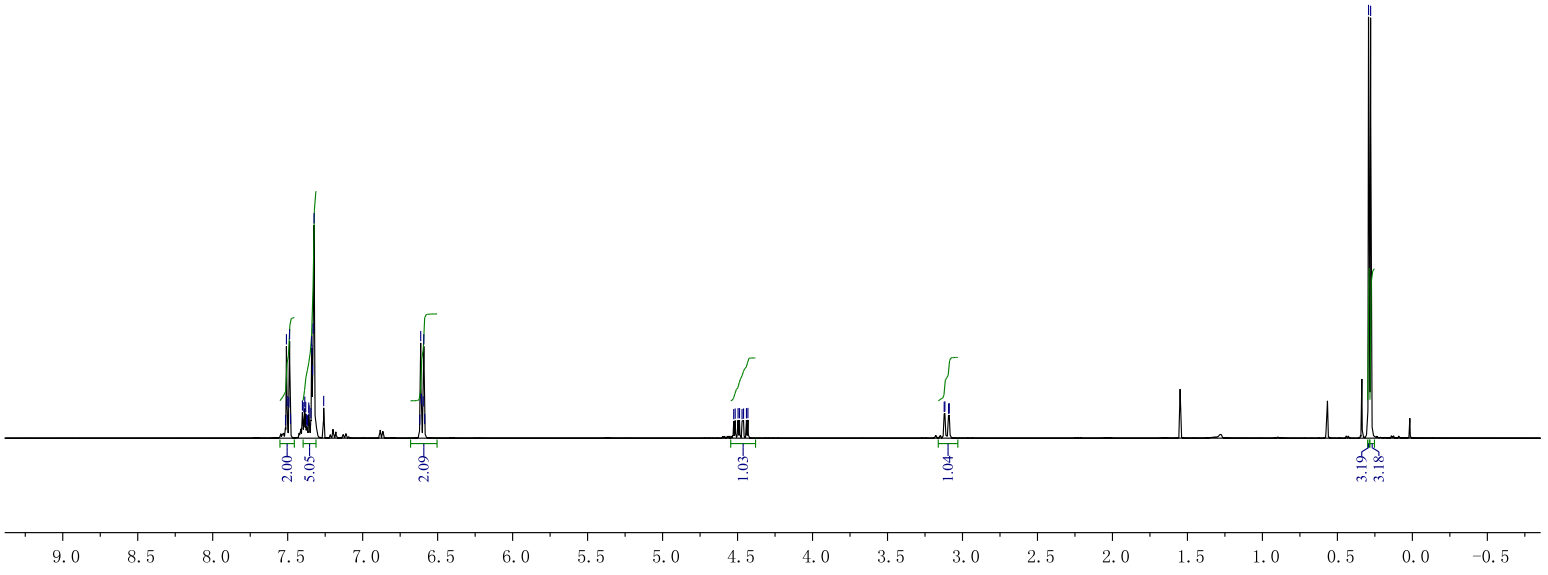
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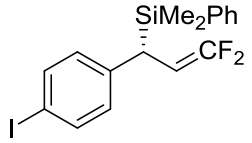

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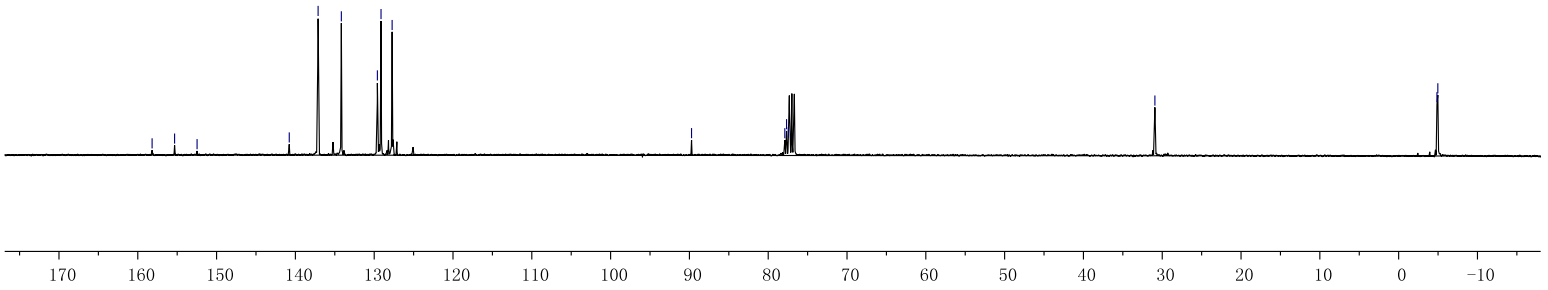

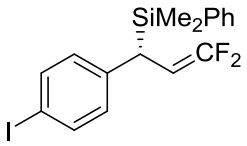
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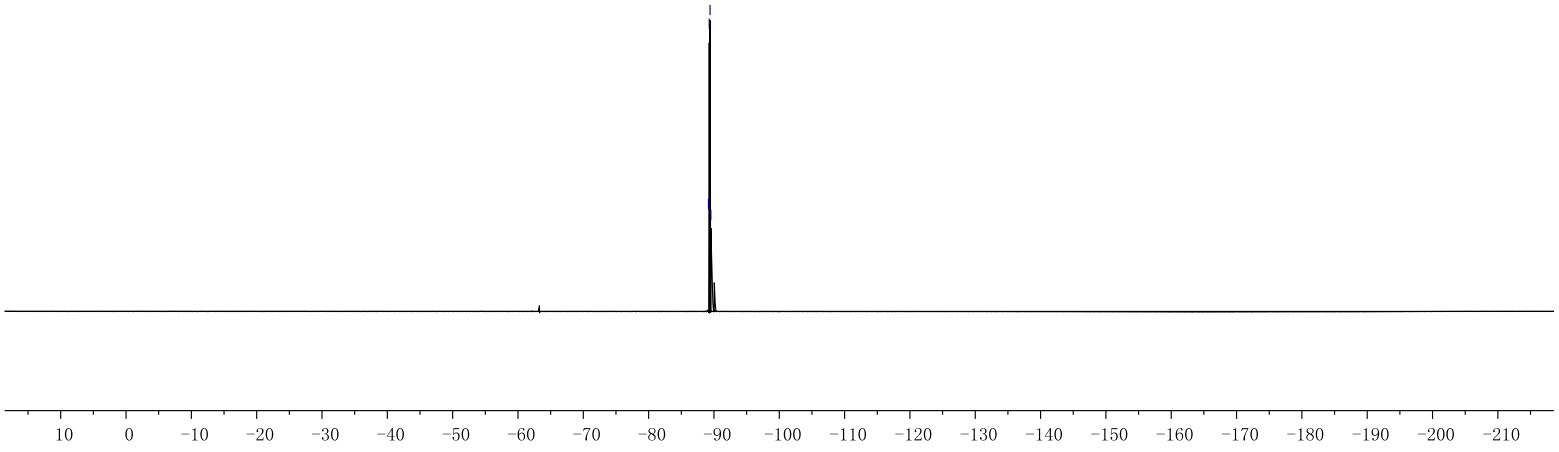
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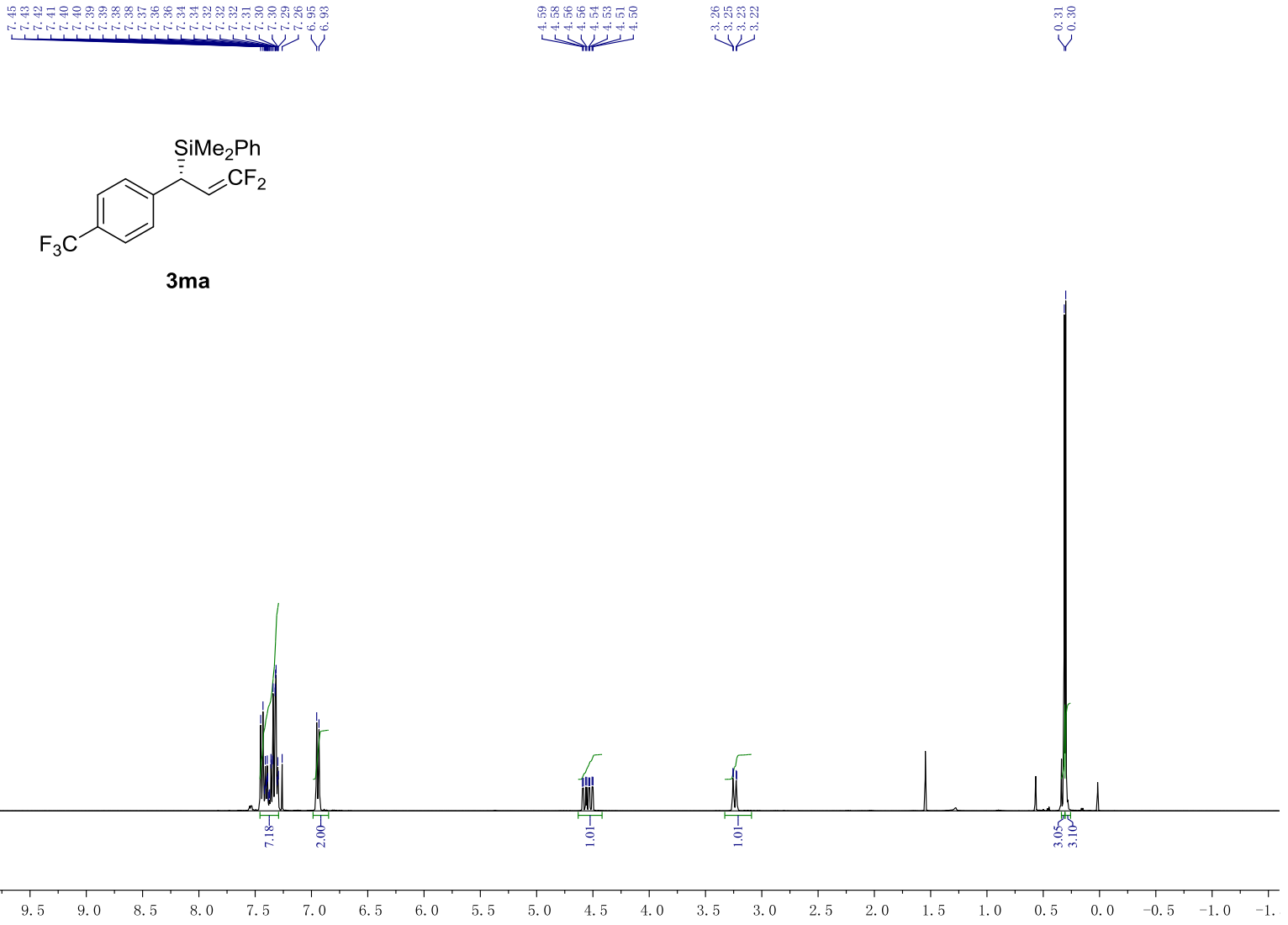
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4.53
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0.30
SiMe2Ph
CF2
F3C
3ma
7.18
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1.01
1.01
3.05
3.10
9.5
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8.0
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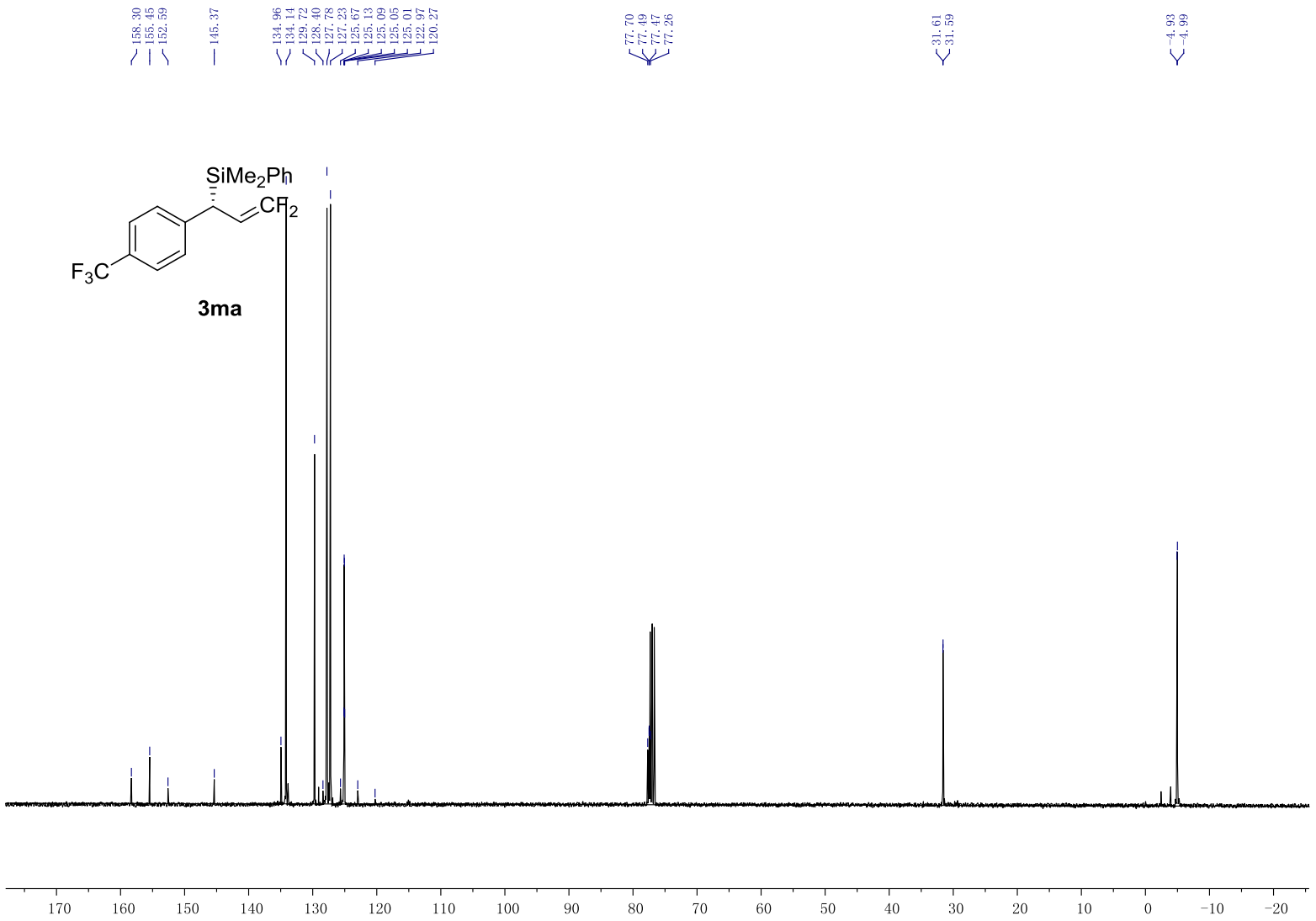
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125.09
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125.01
122.97
120.27
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77.47
77.26
31.61
31.59
-4.93
-4.99
SiMe2Ph
CF2
F3C
3ma
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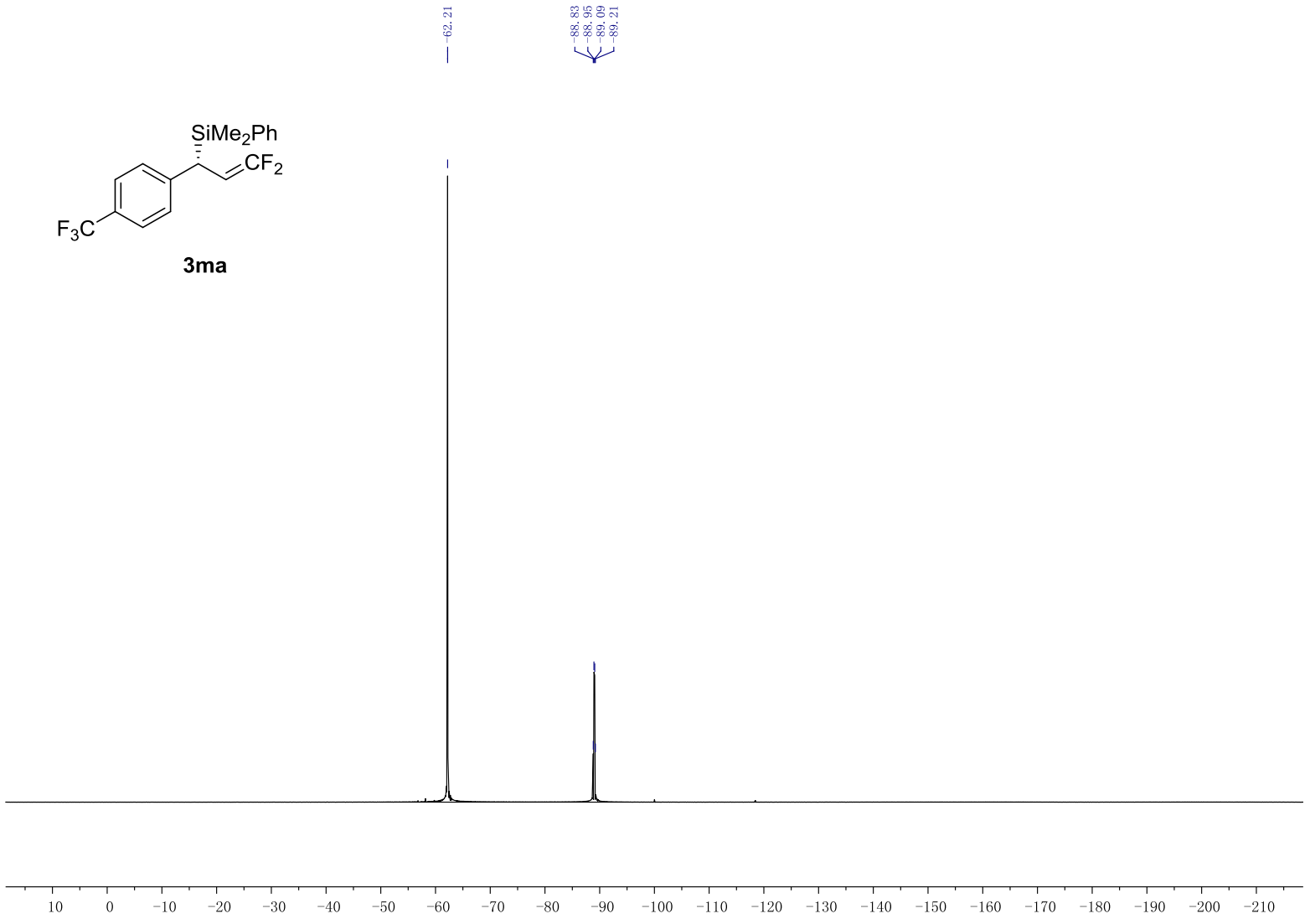
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-150
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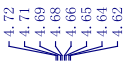
7.00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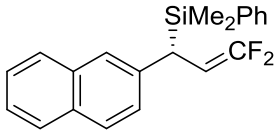
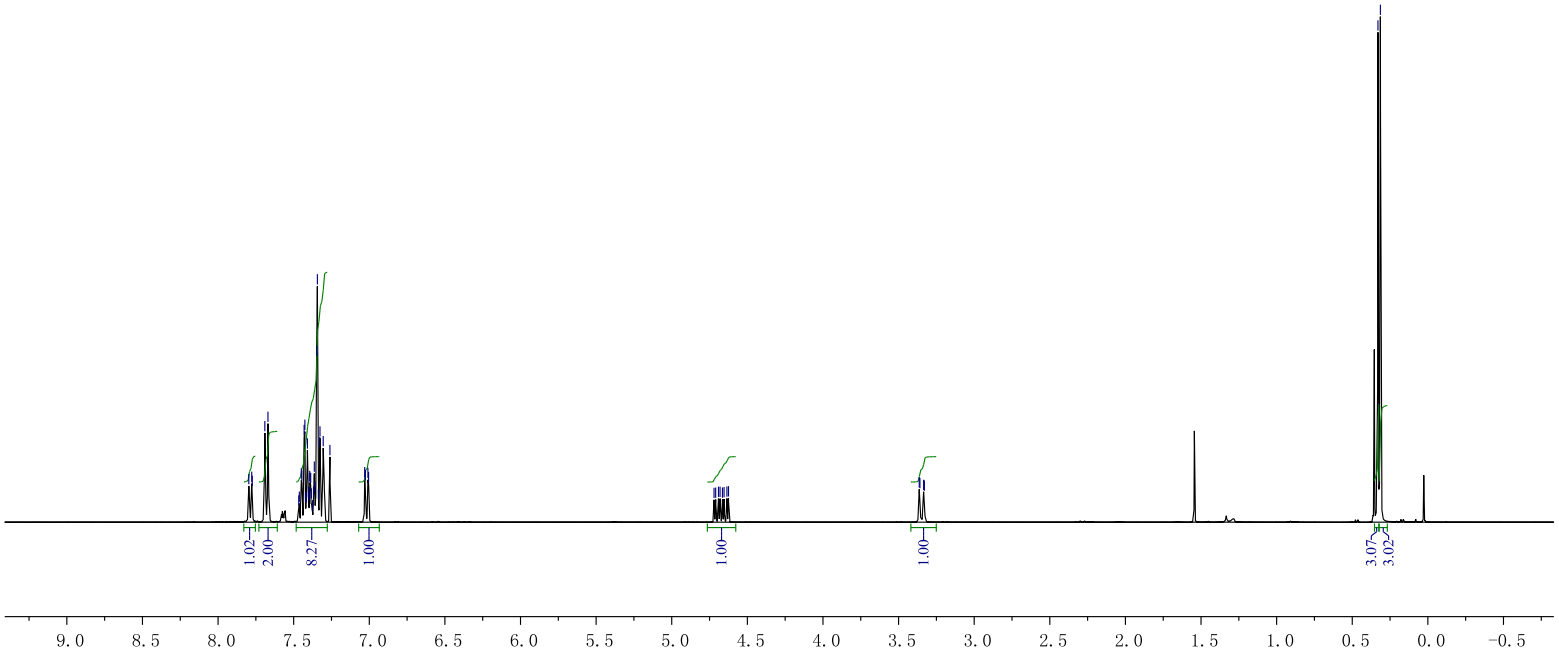
0.31


SiMe2Ph
CF2

3na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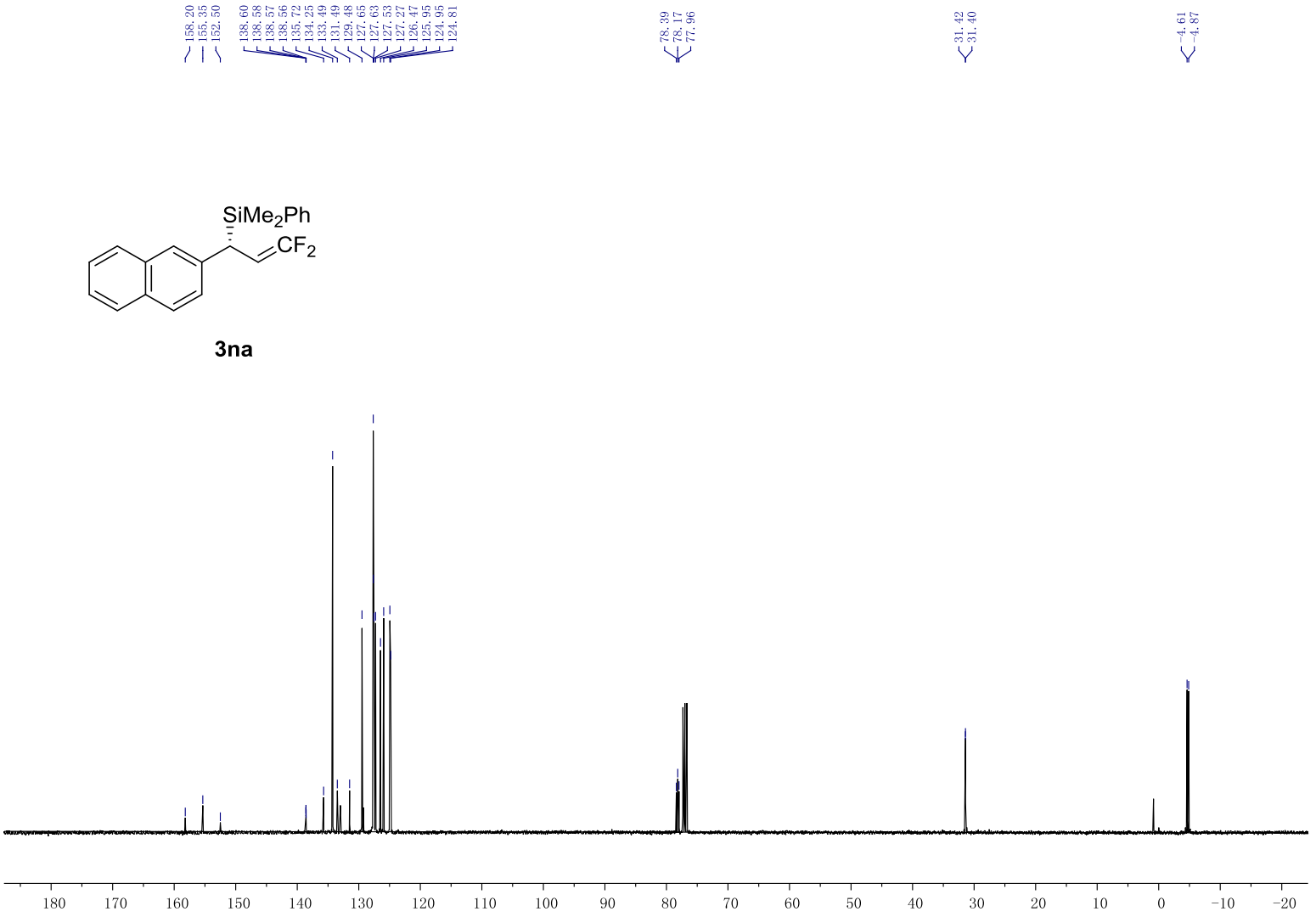
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124.95
124.81
78.39
78.17
77.96
31.42
31.40
-4.61
-4.87
SiMe2Ph
CF2
3na
180
170
160
150
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130
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-10
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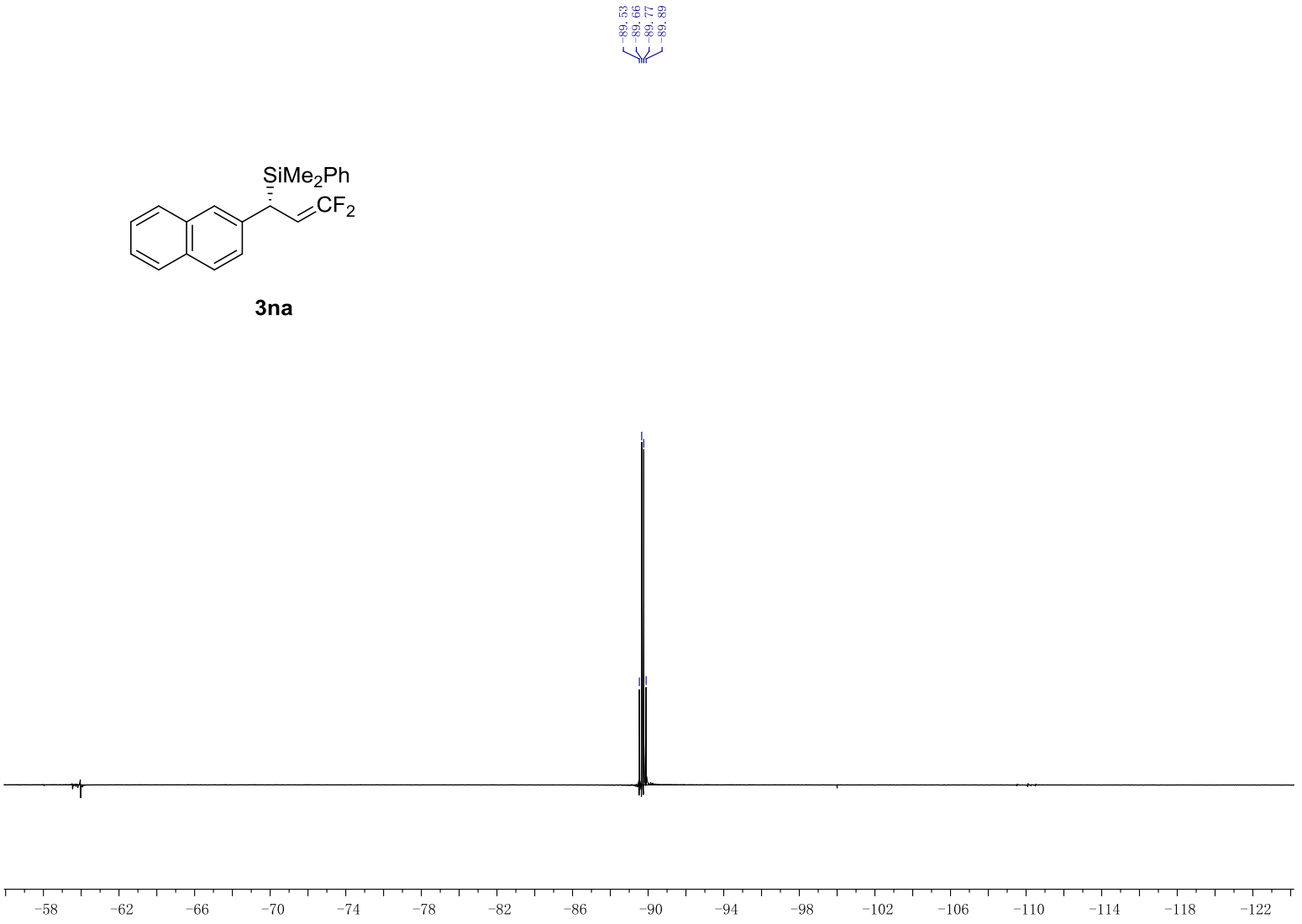
SiMe2Ph
CF2

3na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-98
-102
-106
-110
-114
-118
-122


7.74
7.73
7.62
7.60
7.48
7.48
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7.27
7.25
6.73


4.57
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3.53


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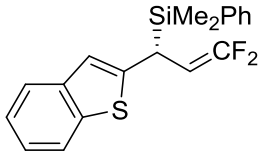
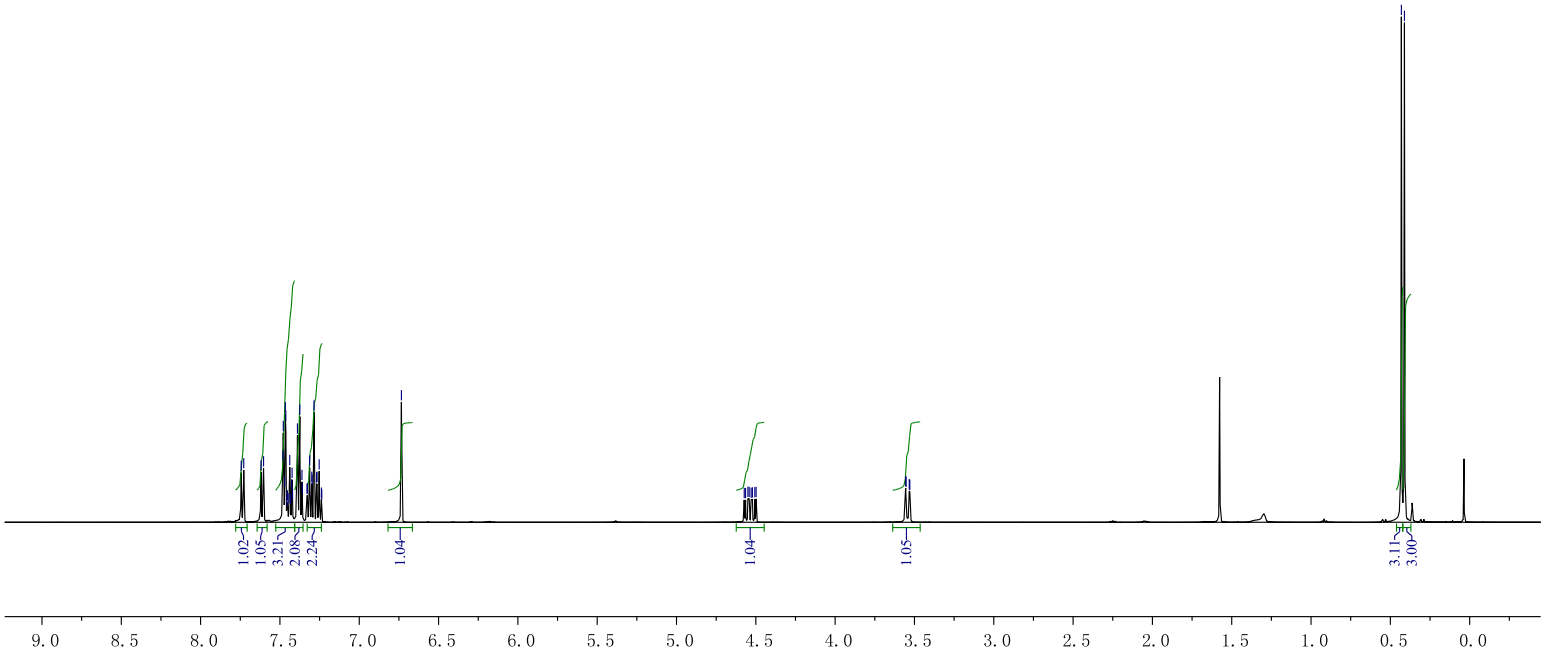

SiMe2Ph
CF2
S

3oa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1.04
1.05
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3.00
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8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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2.0
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1.0
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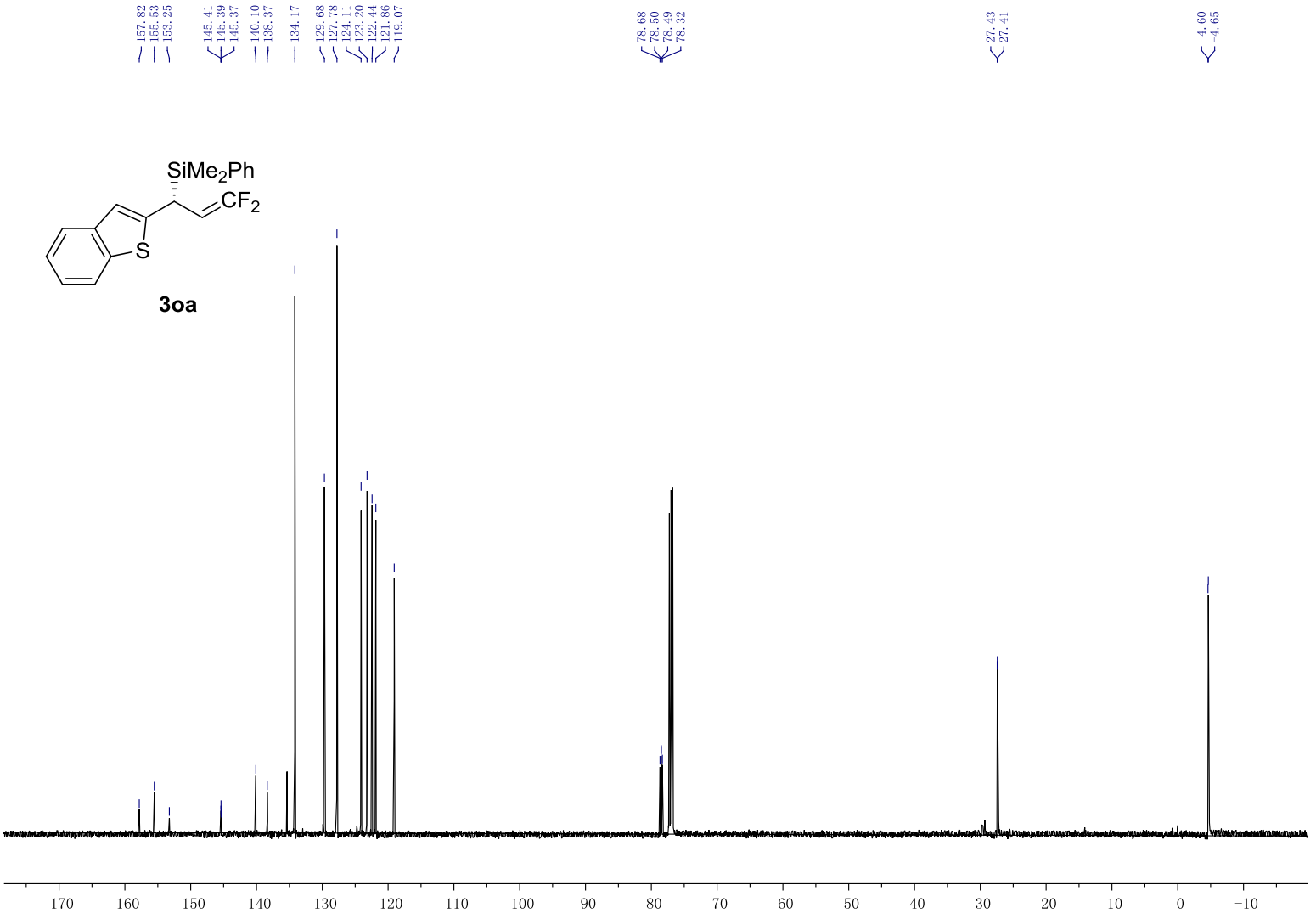
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119.07
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27.43
27.41
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-4.65
SiMe2Ph
CF2
S
3oa
170
160
150
140
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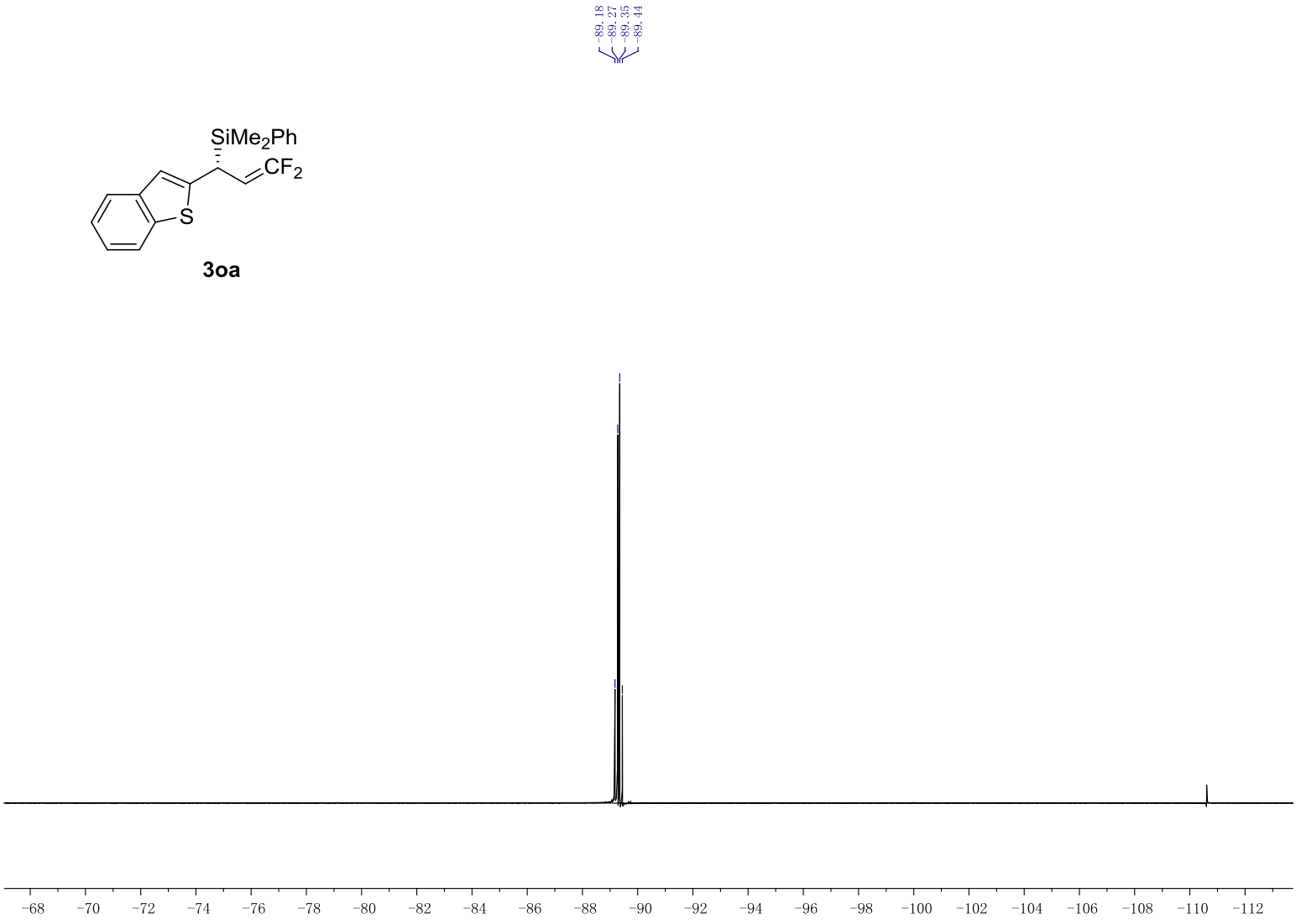
SiMe2Ph
CF2
S

3oa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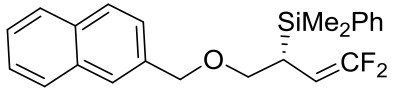
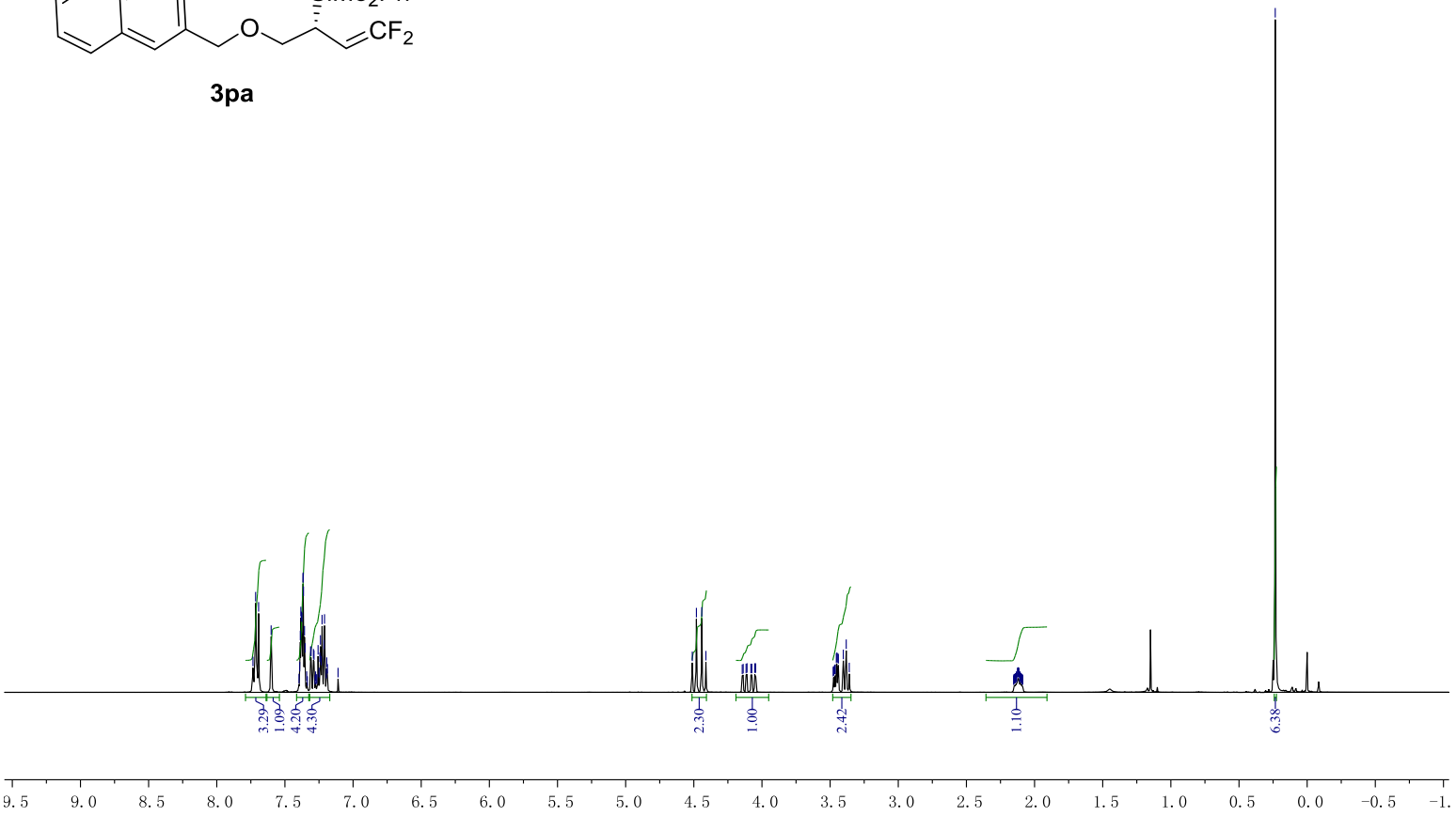

SiMe2Ph
O
CF2

3pa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1.10
6.38
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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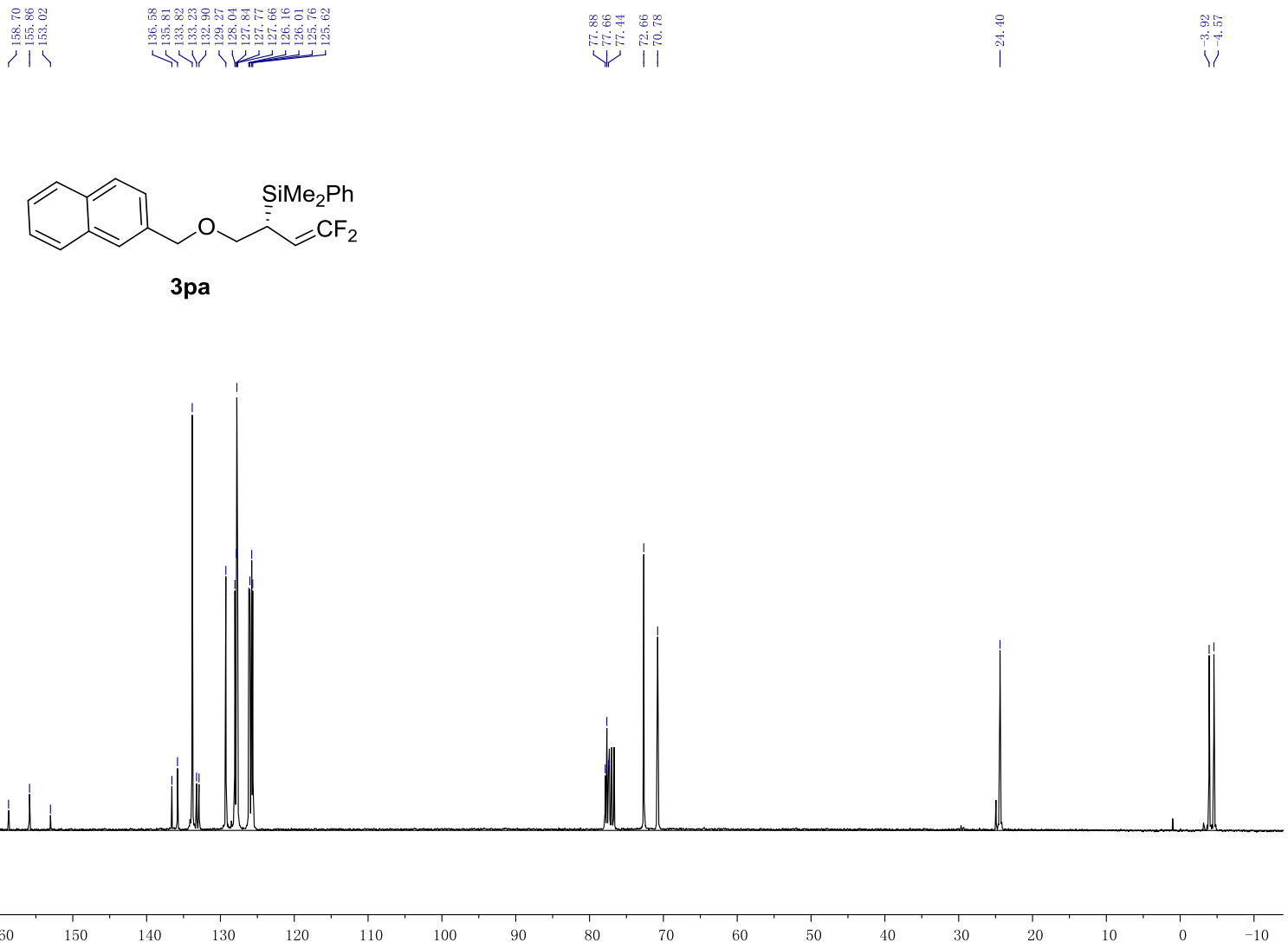
−1.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125.62
77.88
77.66
77.44
72.66
70.78
24.40
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-4.57
SiMe2Ph
O
CF2
160
150
140
130
120
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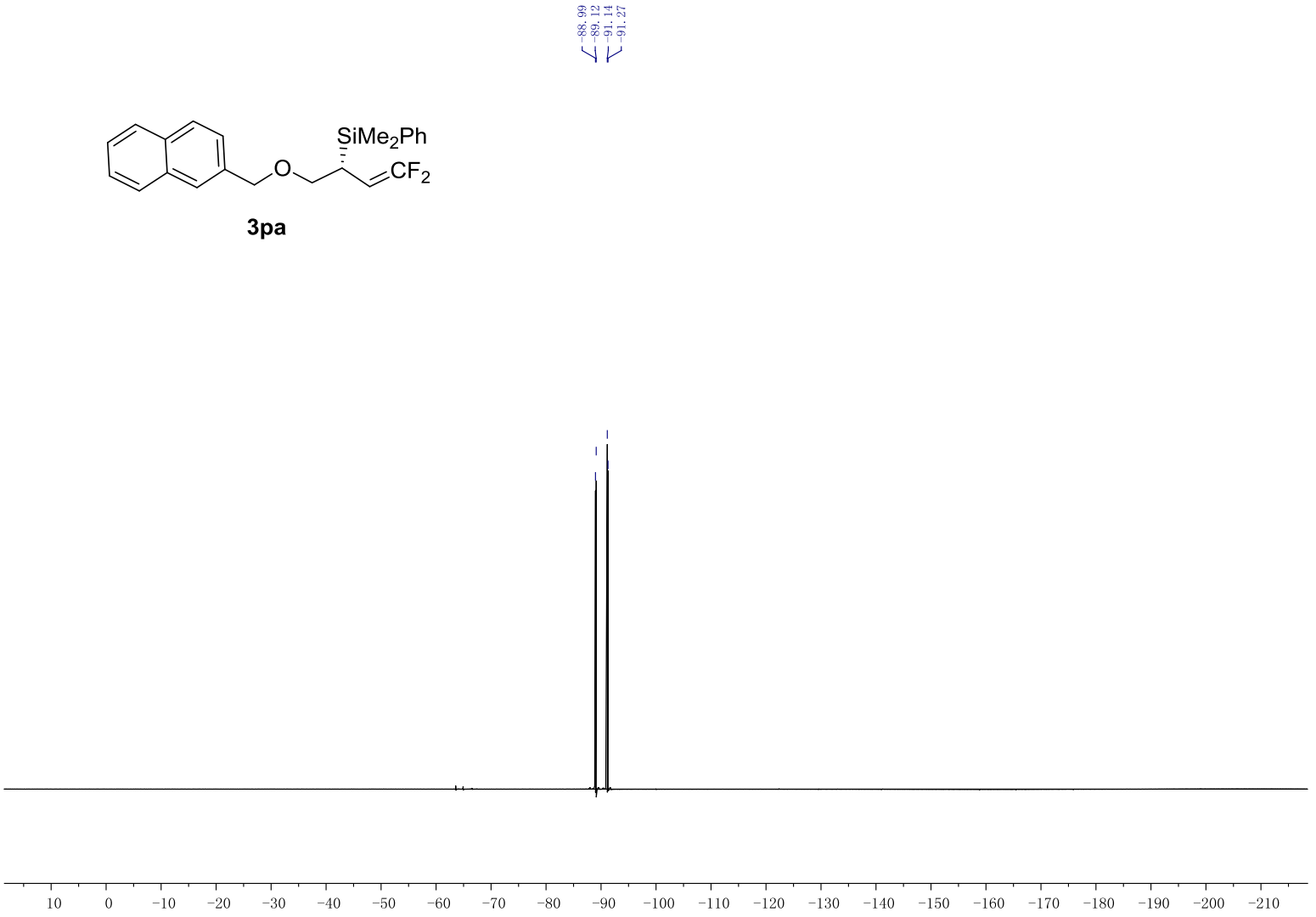
3pa

SiMe2Ph
O
CF2

3pa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-140
-150
-160
-170
-180
-190
-200
-210


7.48
7.47
7.46
7.46
7.45
7.35
7.34
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7.33
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7.32
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7.29
7.26
7.02
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6.94
6.72
6.71
6.70


3.81
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2.40
2.39
2.38
2.03
2.02
2.02
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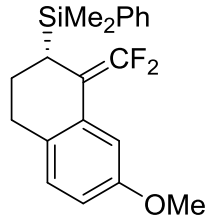
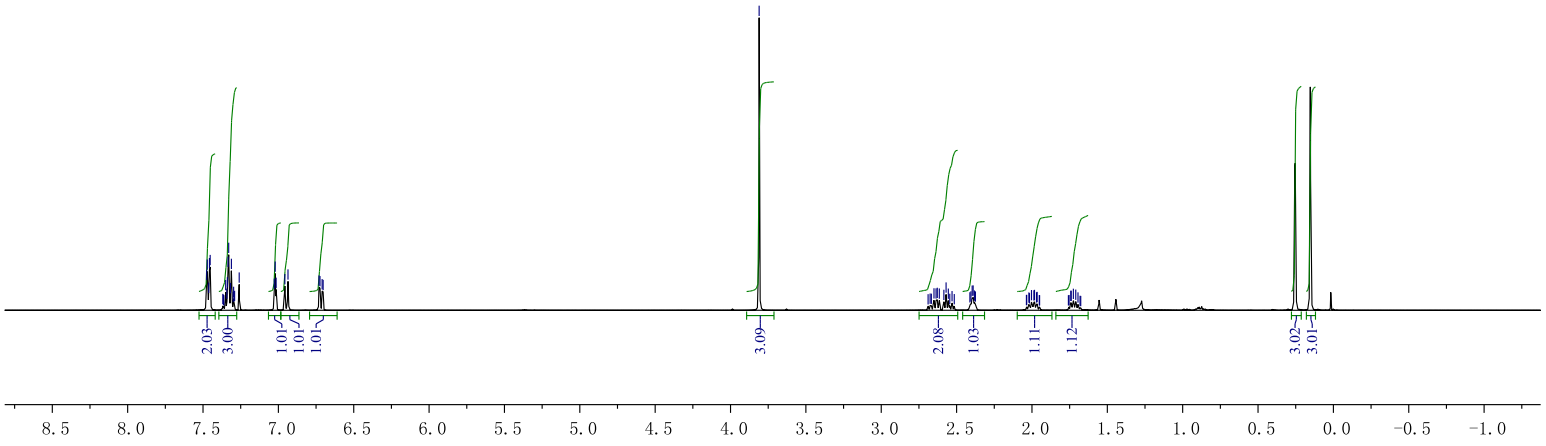
1.68
1.68


SiMe2Ph
CF2
OMe

3qa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3.01
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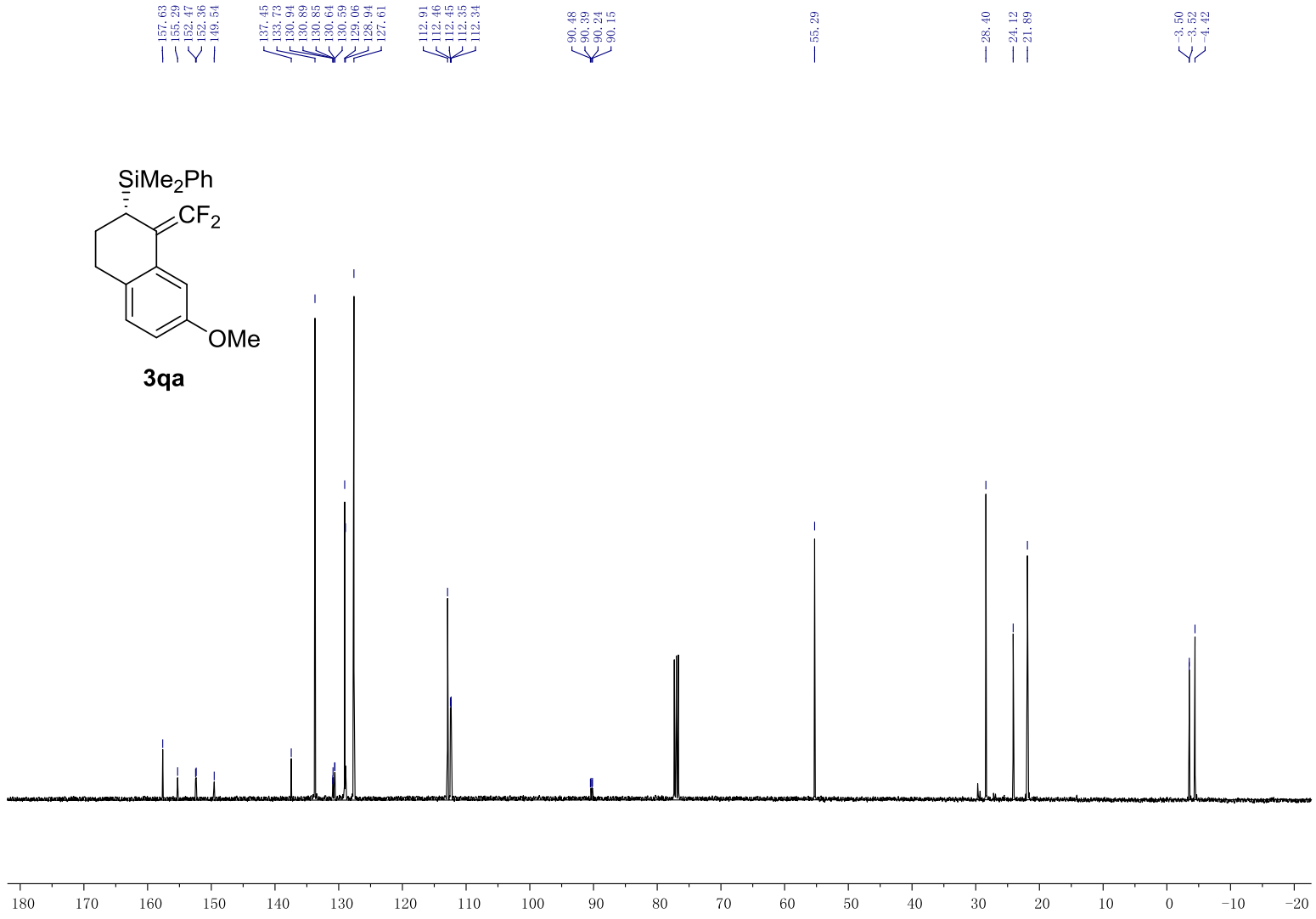
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55.29
28.40
24.12
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SiMe2Ph
CF2
OMe
3qa
180
170
160
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120
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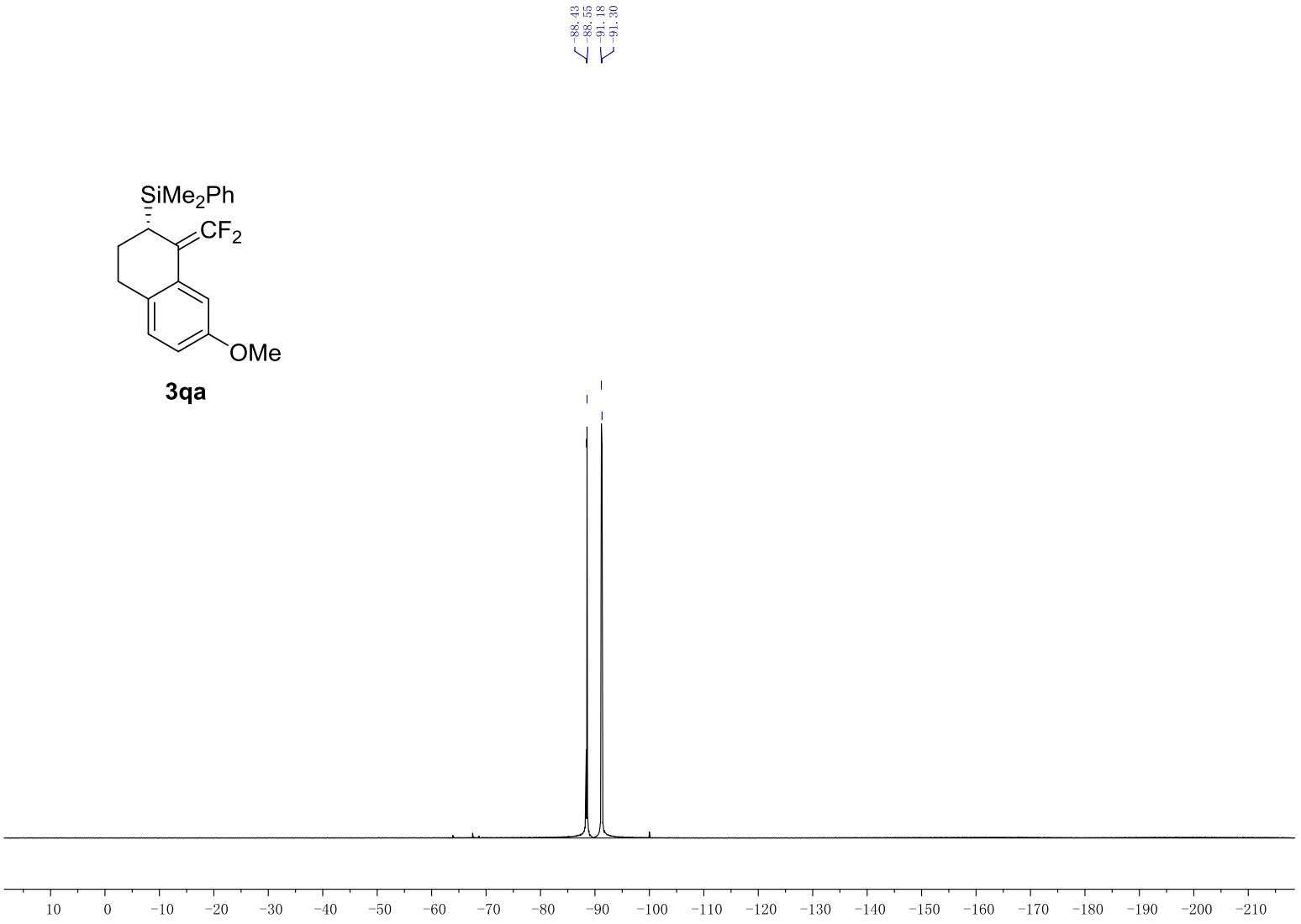
-20

SiMe2Ph
CF2
OMe

3qa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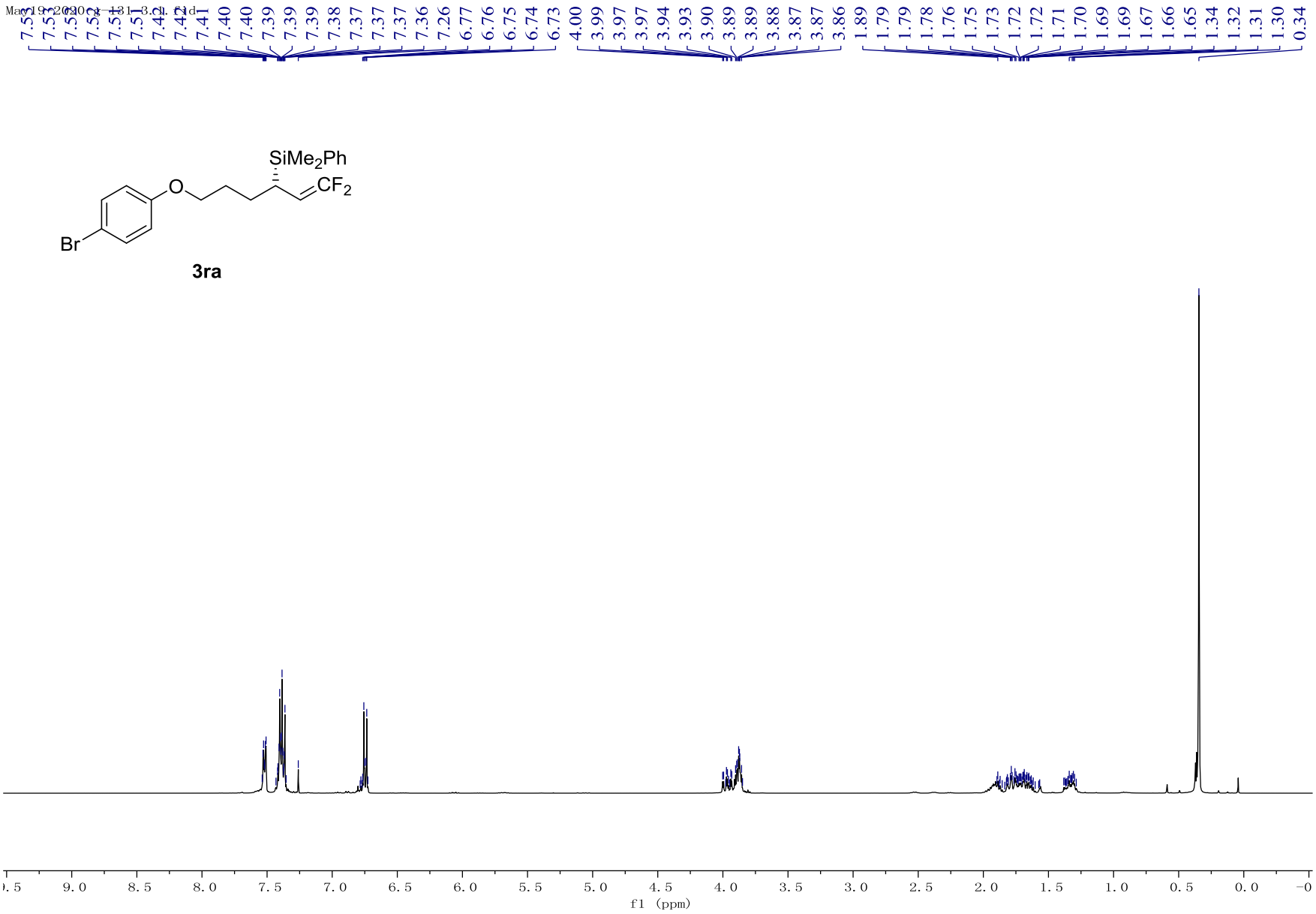
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4.00 3.99 3.97 3.97 3.94 3.93 3.90 3.89 3.89 3.88 3.87 3.87 3.86
1.89 1.79 1.79 1.78 1.76 1.75 1.73 1.72 1.72 1.71 1.70 1.69 1.69 1.67 1.66 1.65 1.34 1.32 1.31 1.30 0.34
SiMe2Ph
CF2
O
Br
3ra
f1 (ppm)

May19-2020-g-15-1-2-ff

158.95
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156.11
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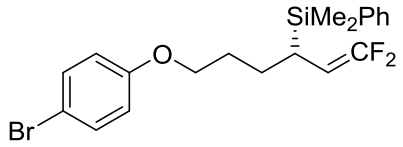

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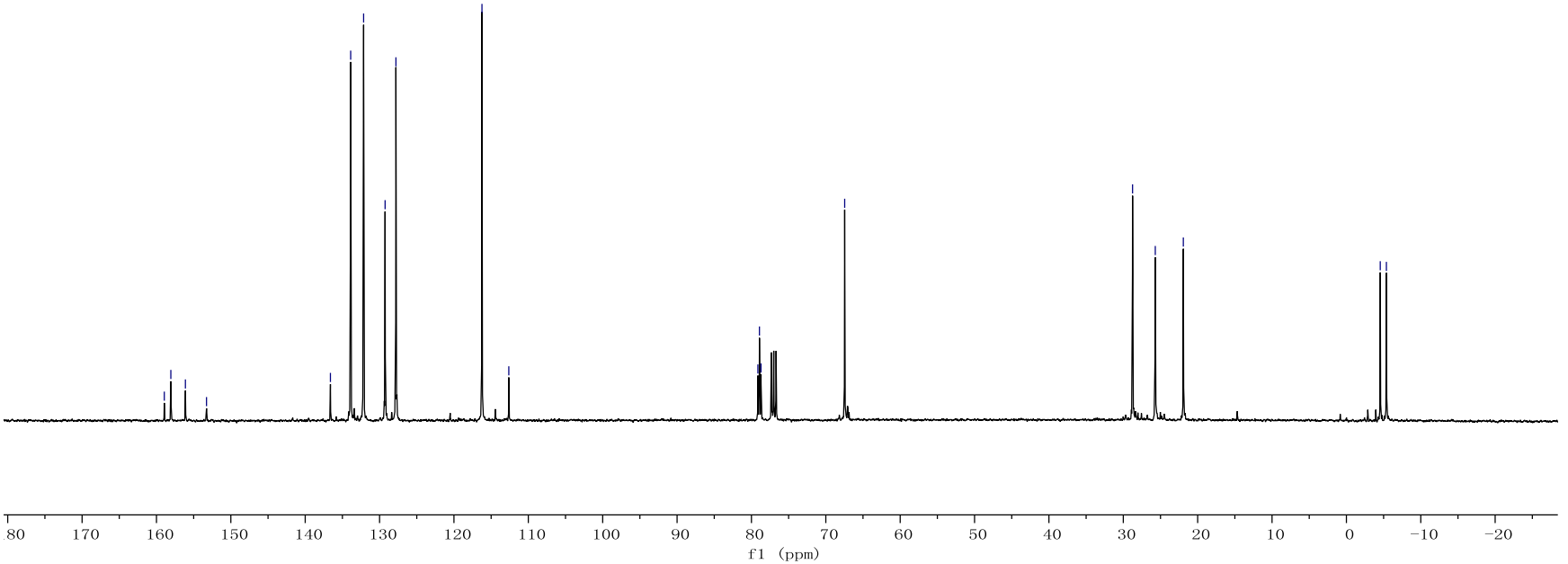

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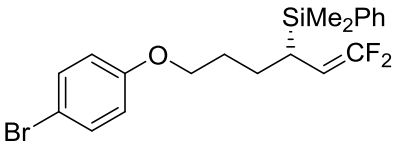

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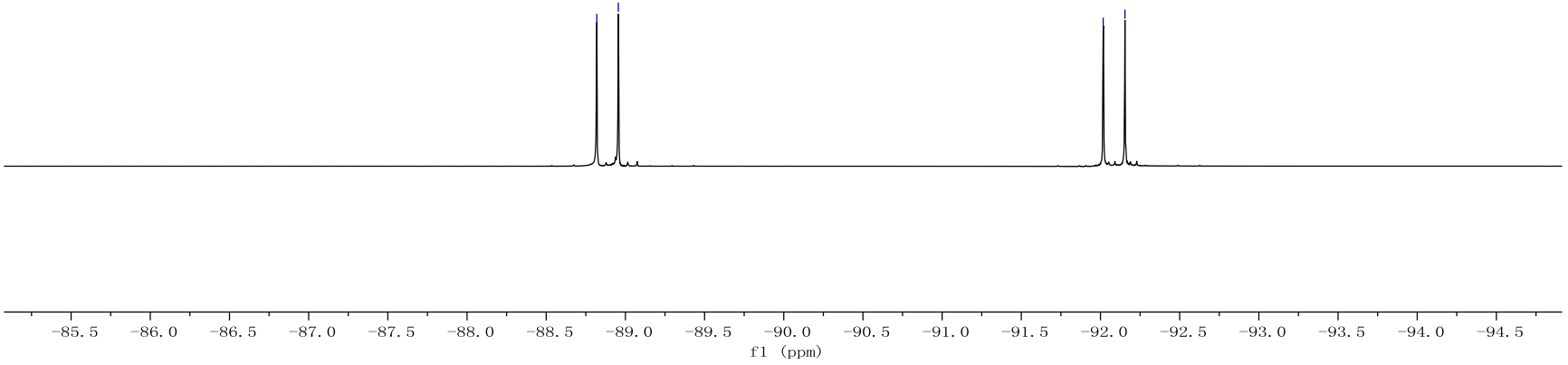


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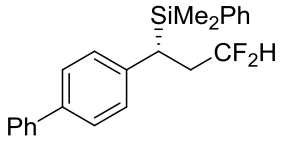
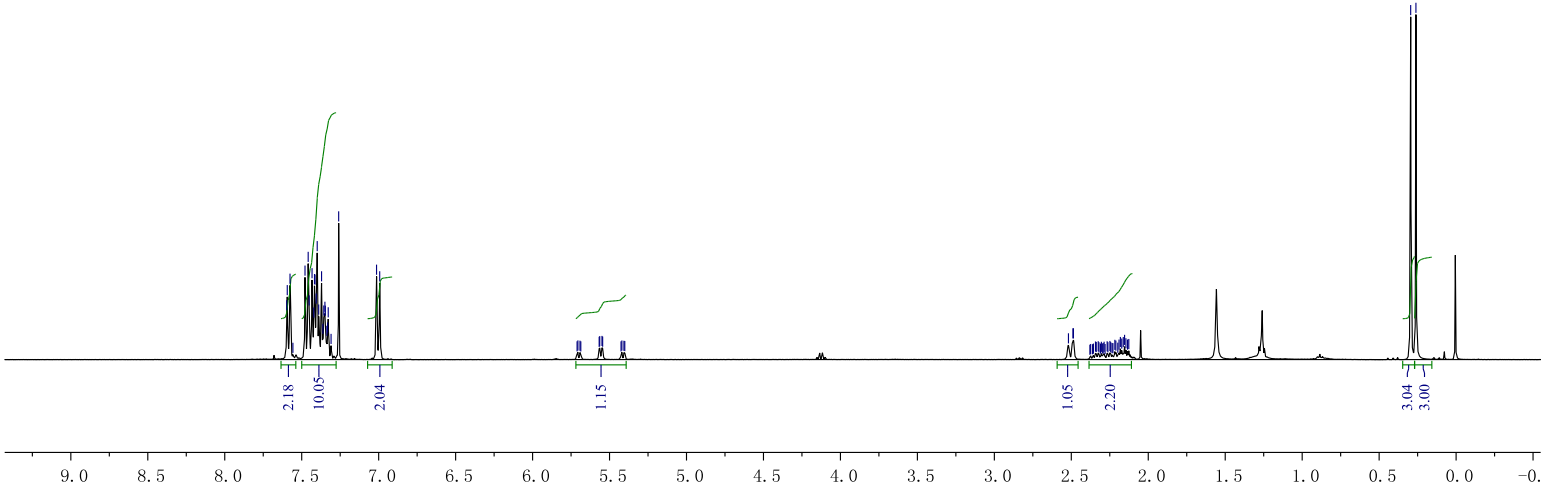

SiMe2Ph
CF2H
Ph

4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3.04
3.00
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8.5
8.0
7.5
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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.


140.73
139.75
138.06
136.02
134.13
128.74
128.02
127.84
127.04
126.99
116.86
114.47
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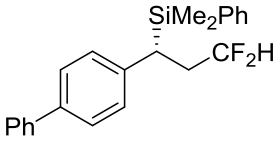
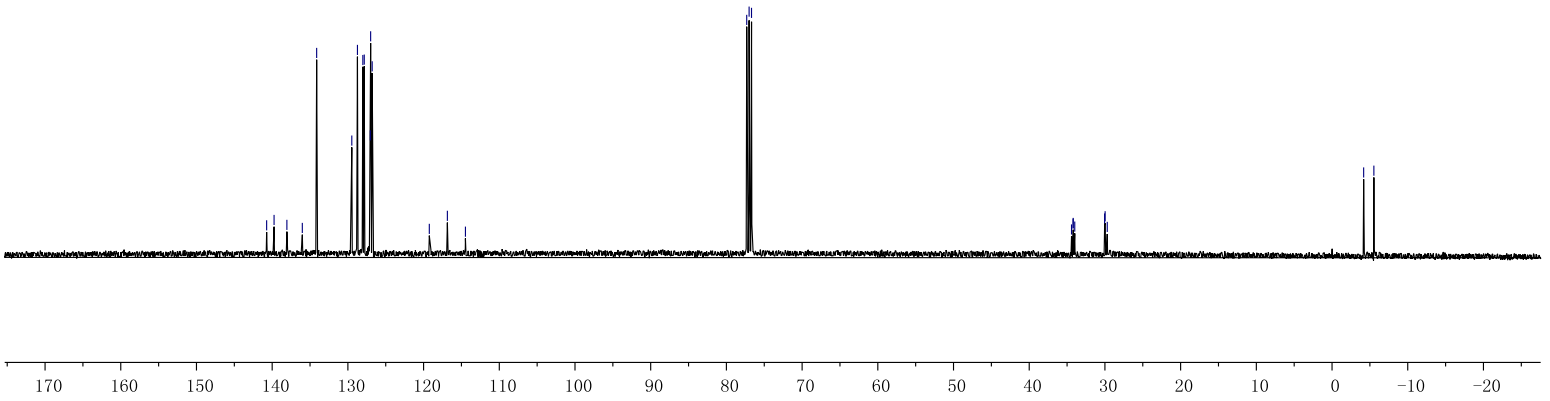

SiMe2Ph
CF2H
Ph

4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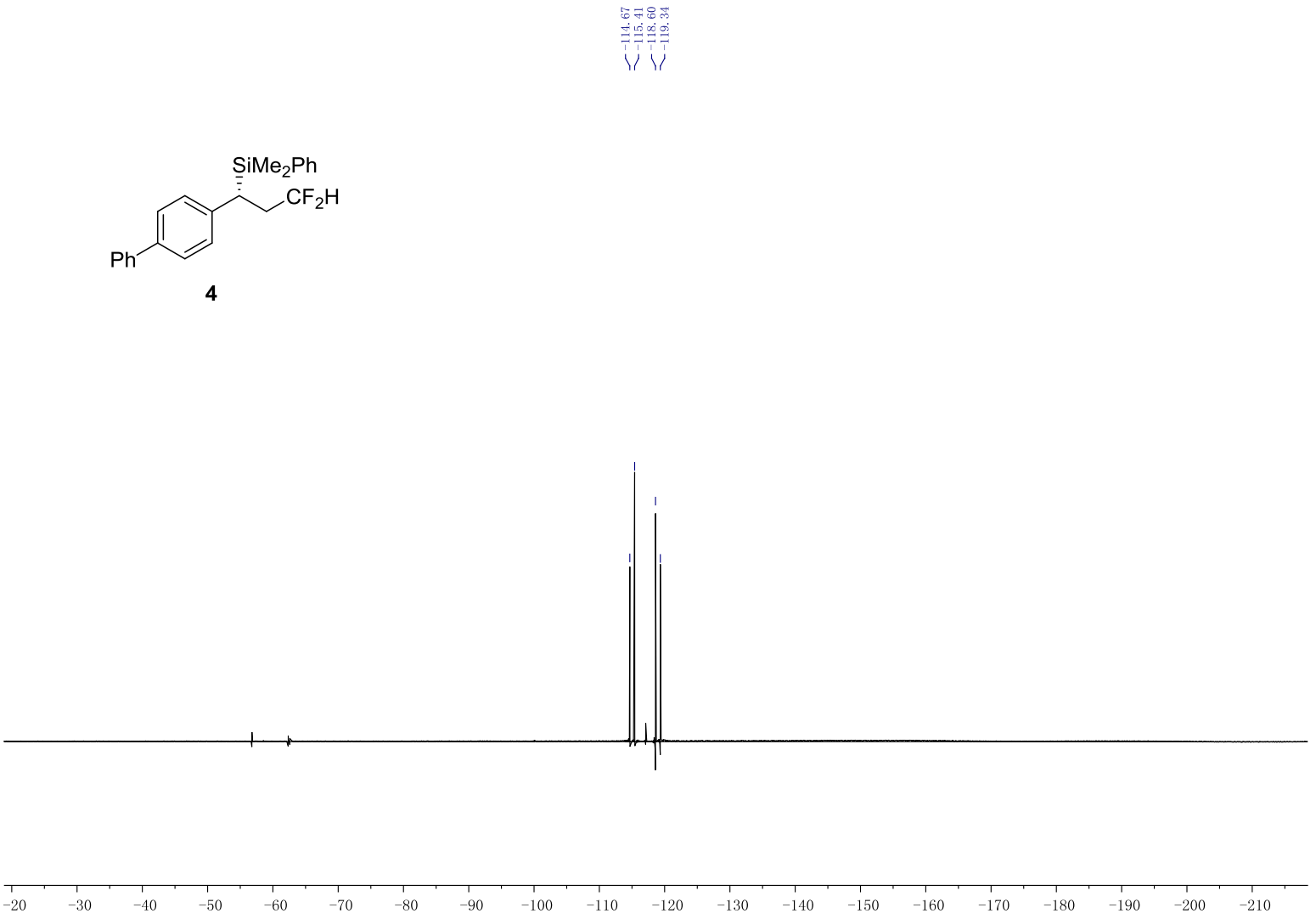
-20

SiMe2Ph
CF2H
Ph

4


-114.67
-115.41
-118.60
-119.34
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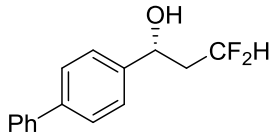
6.05 6.04 6.04 6.03 5.91 5.90 5.89 5.89 5.77 5.76 5.75 5.74
4.87 4.86 4.84 4.83
2.32 2.31 2.30 2.29 2.28 2.28 2.26 2.26 2.25 2.25 2.24 2.23 2.23 2.22 2.20 2.19 2.19 2.17 2.16 2.14 2.13 2.12 2.11 2.10 2.09 2.09 2.08 2.07 2.06 2.05 2.04 2.03 2.02 2.02 2.01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CF2H
Ph

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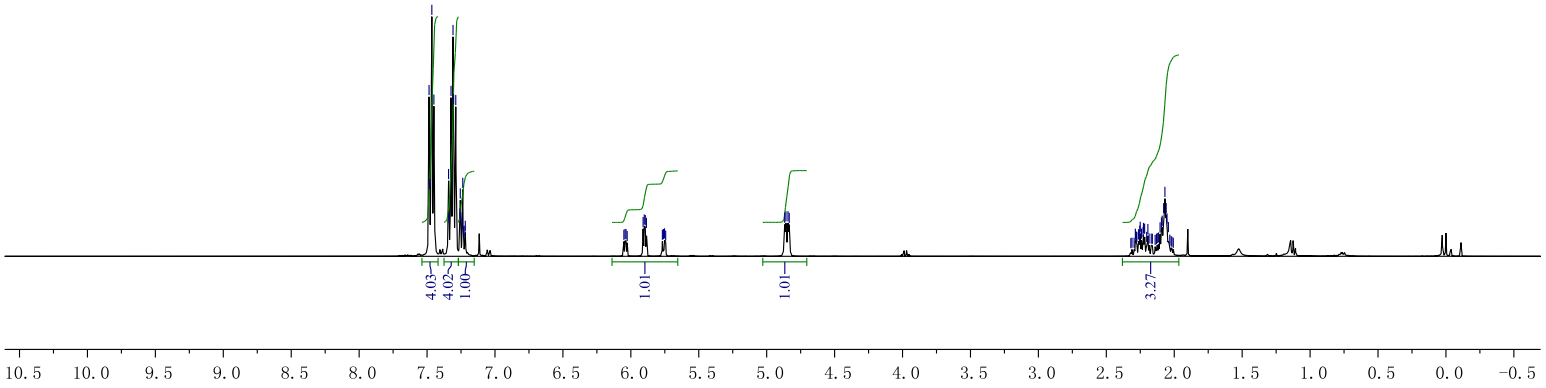
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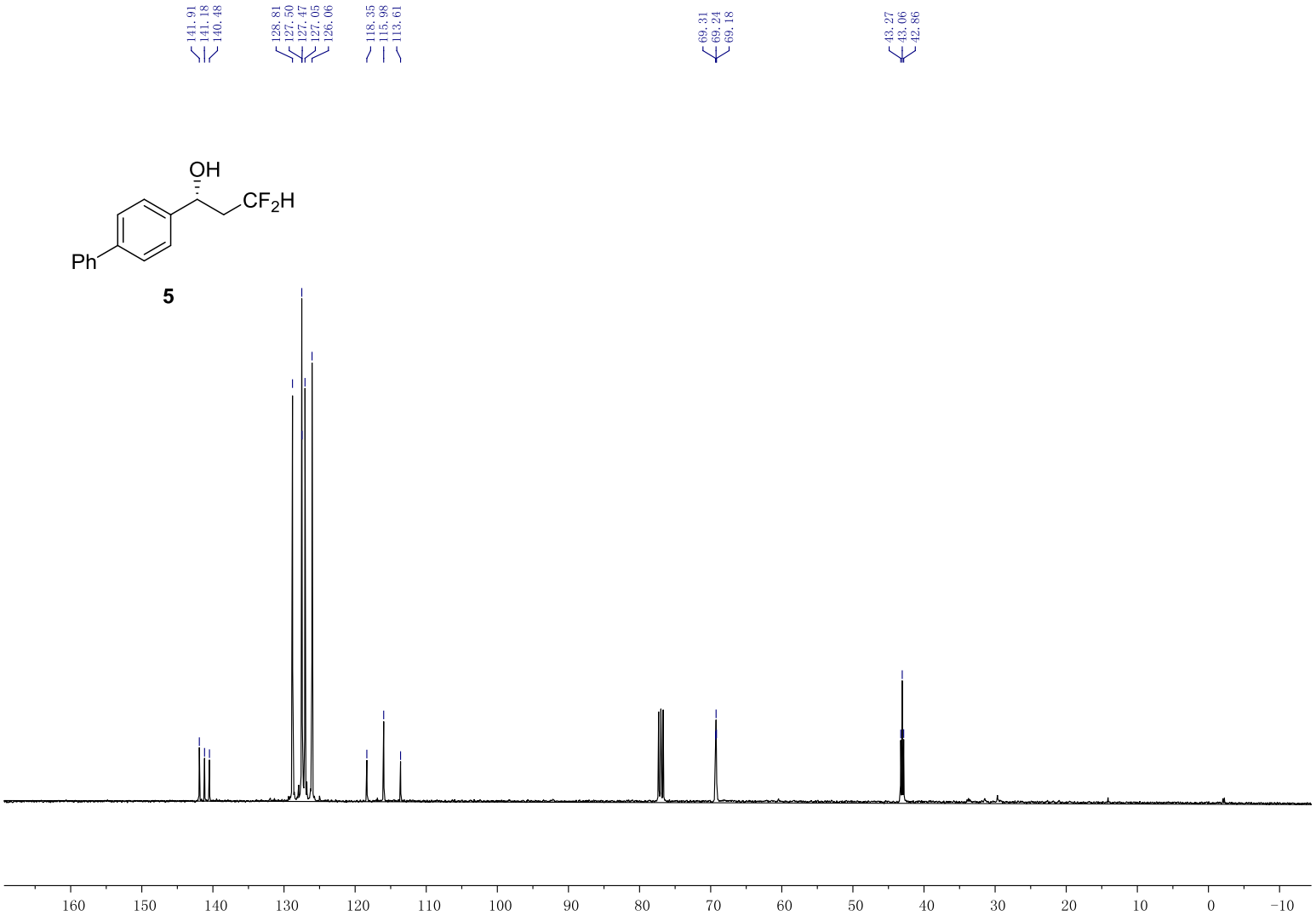
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126.06
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69.18
43.27
43.06
42.86
OH
CF2H
Ph
5
160
150
140
130
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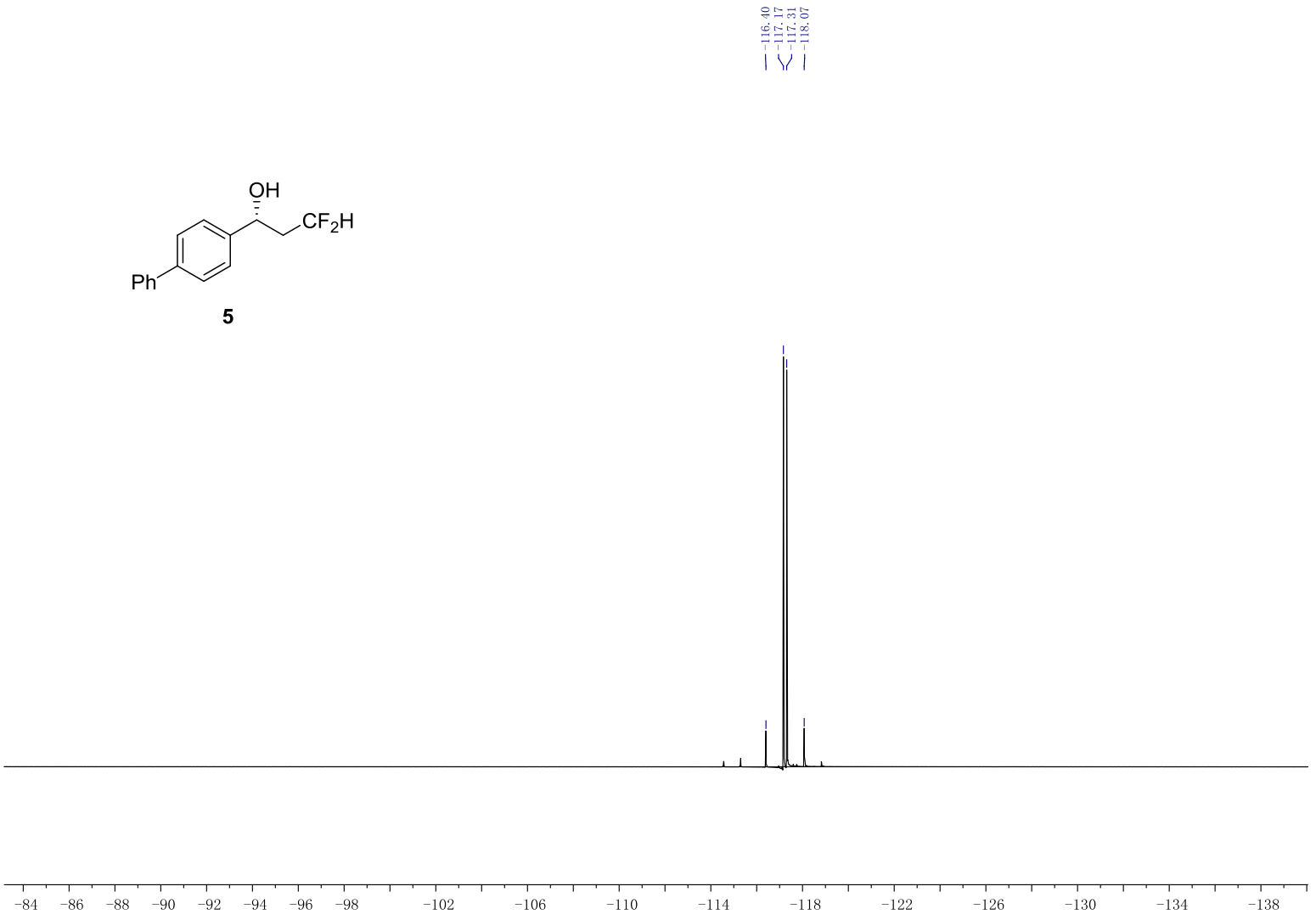
100
90
80
70
60
50
40
30
20
10
0
−10

OH
CF2H
Ph

5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7.59
7.59
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7.41
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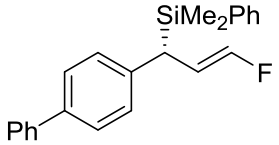
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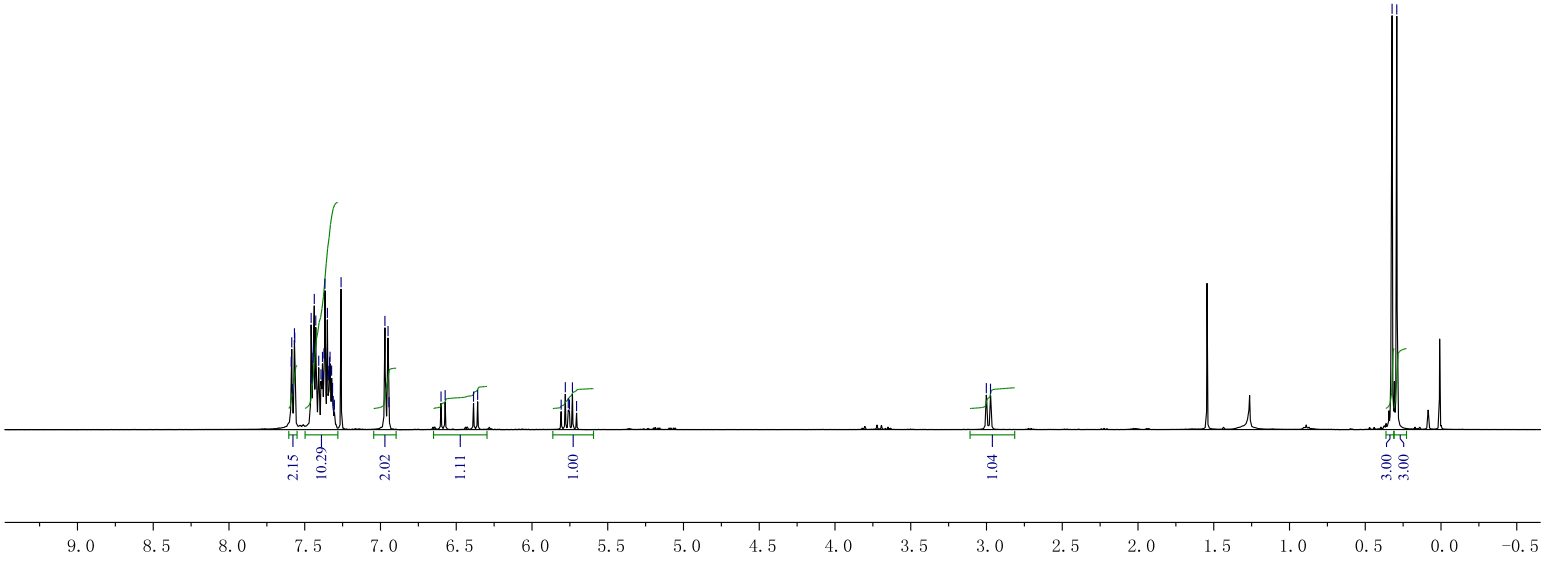
F
Ph

6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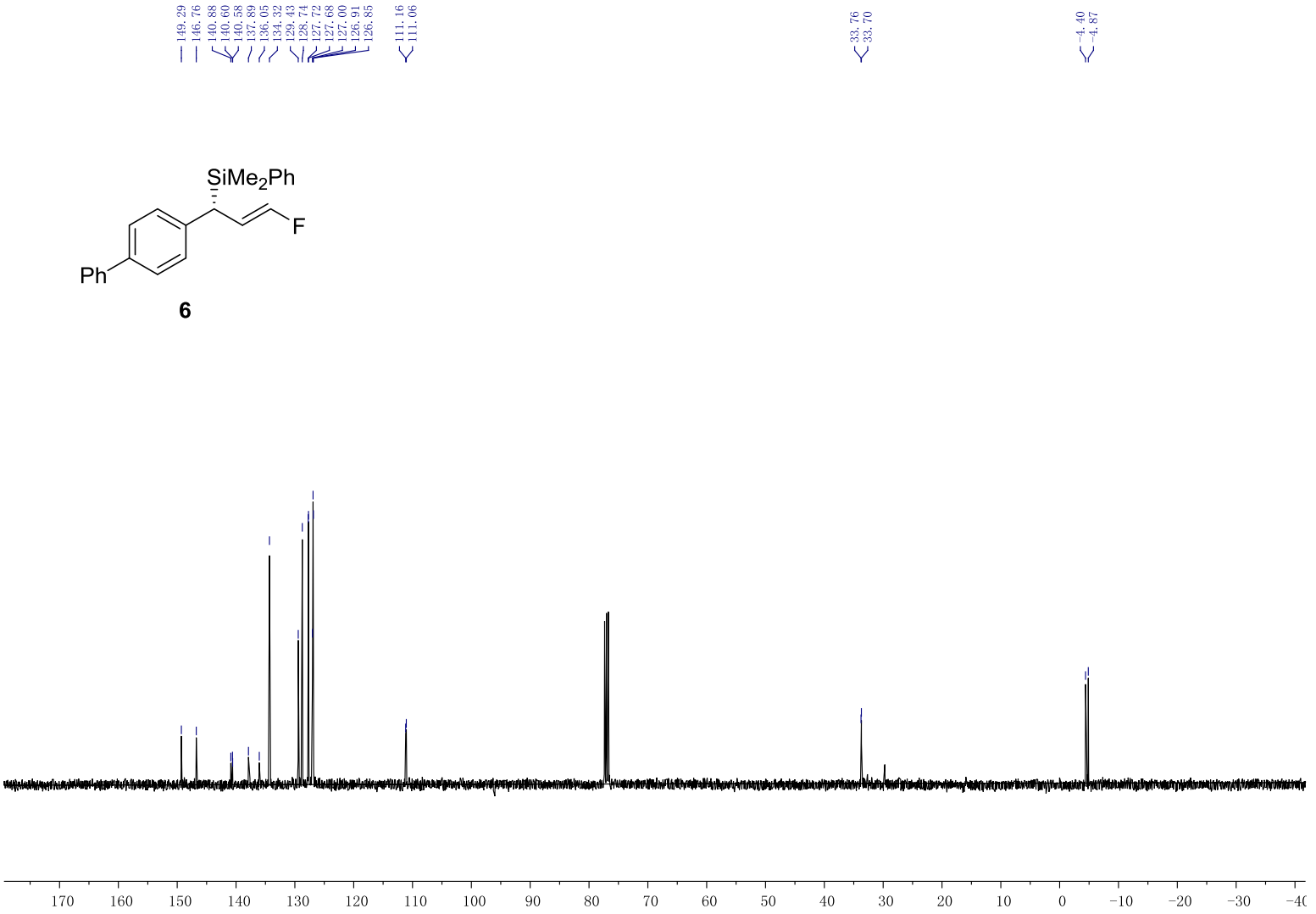
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126.85
111.16
111.06
33.76
33.70
-4.40
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SiMe2Ph
F
Ph
6
170
160
150
140
130
120
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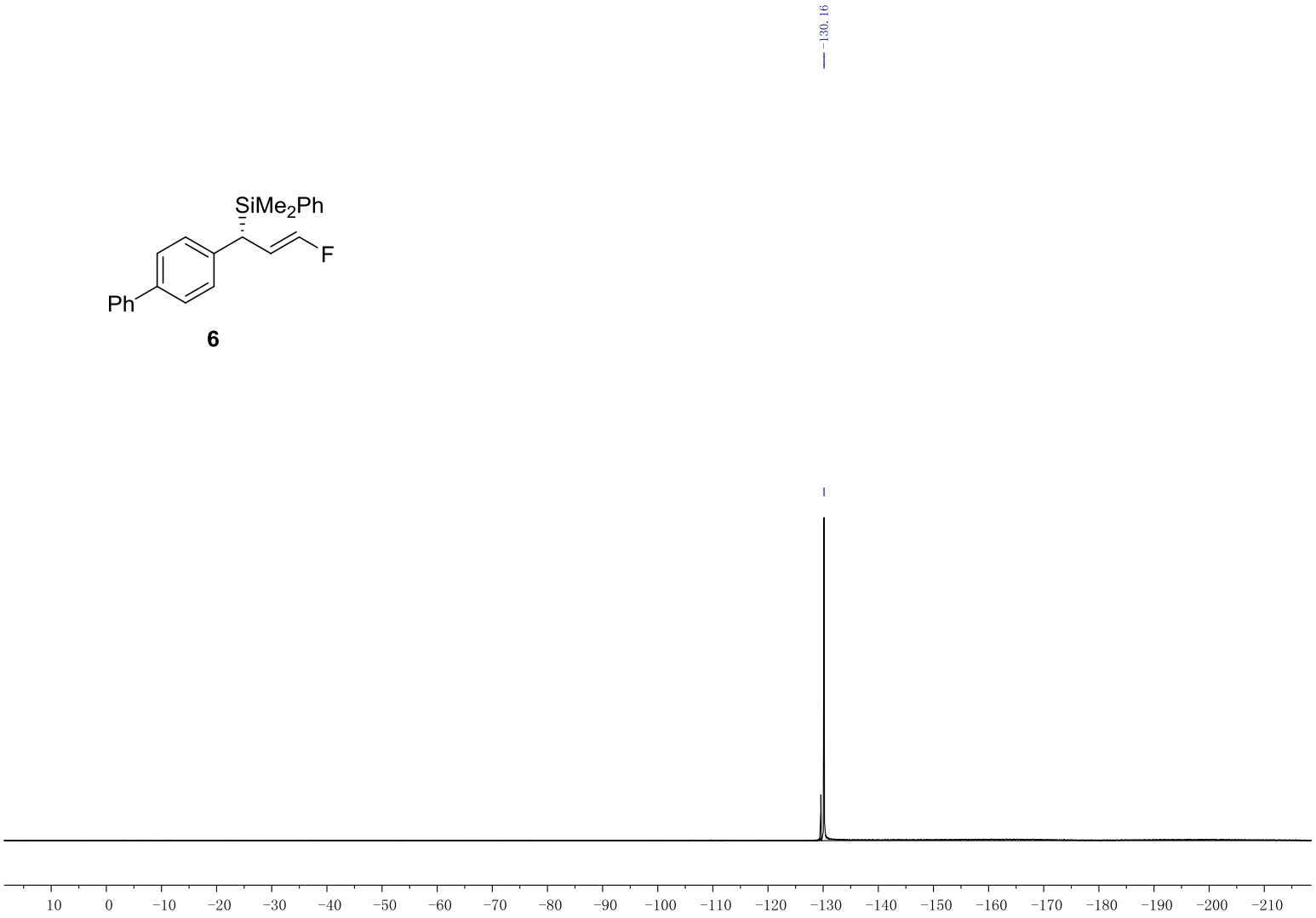
SiMe2Ph
F
Ph

6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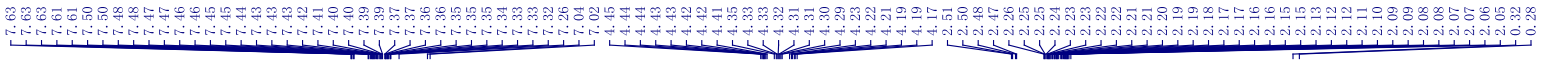
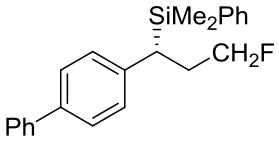
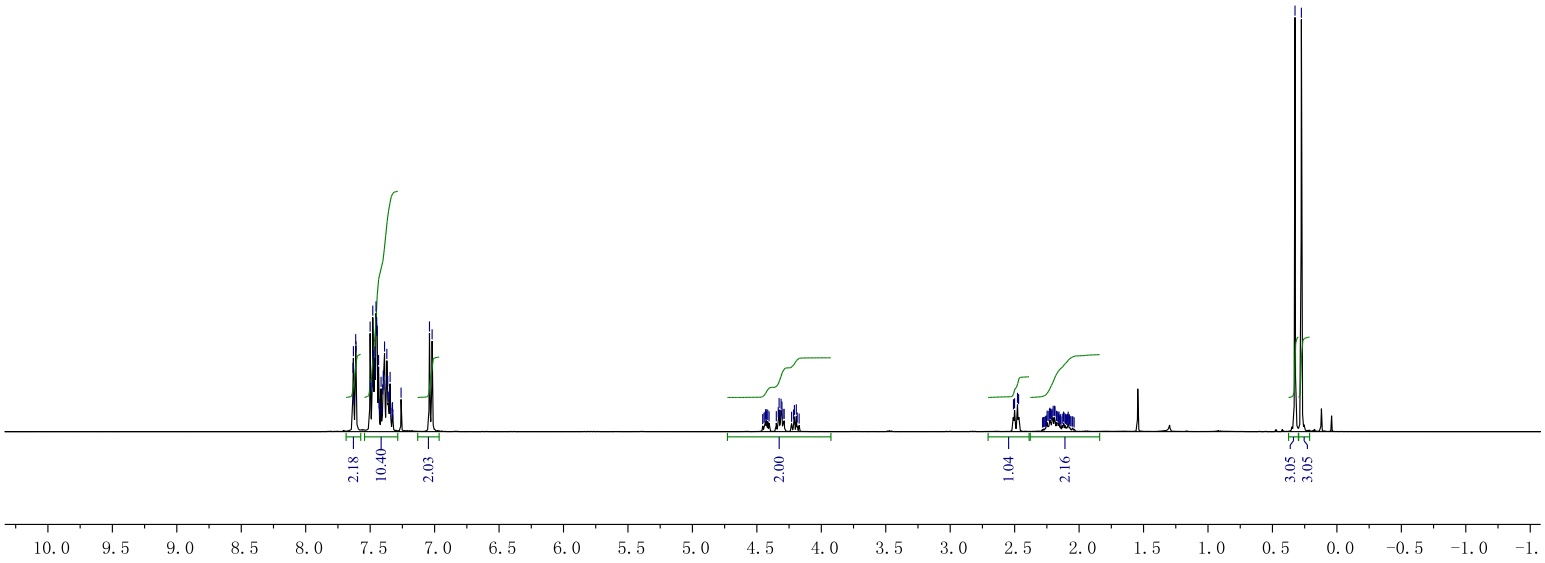



SiMe2Ph
CH2F
Ph

7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3.05
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9.0
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5.0
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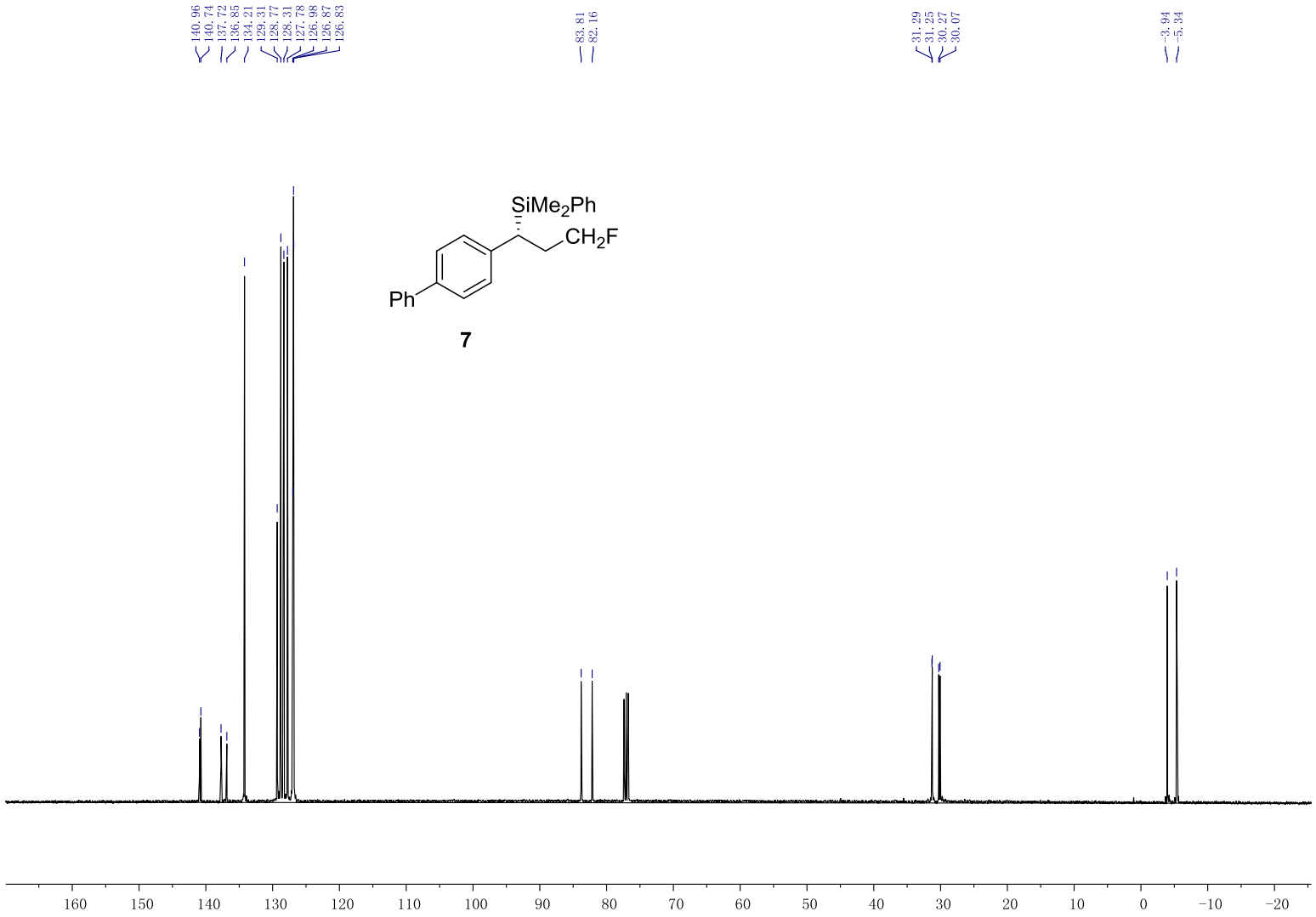
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126.83
83.81
82.16
31.29
31.25
30.27
30.07
-3.94
-5.34
SiMe2Ph
CH2F
Ph
7
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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-20