

Supporting Information for

Intermolecular Hetero-Diels-Alder Reactions of Photogenerated Aza-ortho-Quinone Methides with Aldehydes

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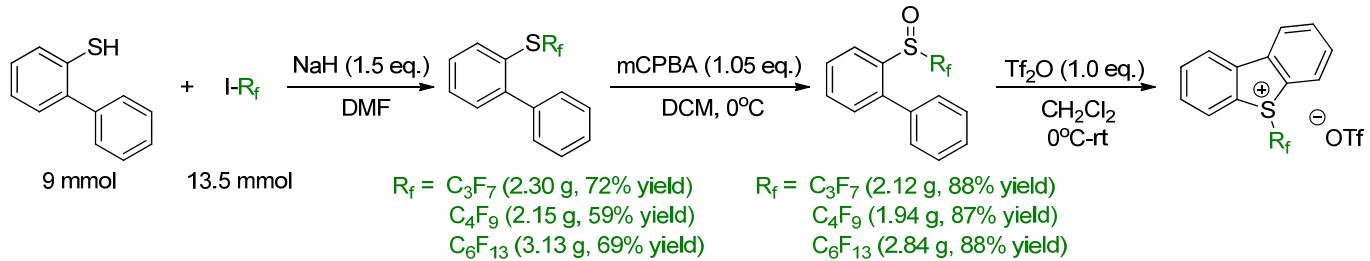
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1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods.¹ Flash column chromatography was performed using 200-300 mesh silica gel. ¹**H NMR** spectra were recorded on 400 spectrophotometers. Chemical shifts (δ (ppm)) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ¹³**C NMR** spectra were recorded on 100 MHz with complete proton decoupling spectrophotometers (CDCl₃: 77.0 ppm, DMSO-d⁶: 39.5 ppm). ¹⁹**F NMR** spectra were recorded on 376 MHz with complete proton decoupling spectrophotometers. The high resolution mass spectra (HRMS) were measured on Bruker micrOTOF-II mass spectrometer by ESI. IR spectra were recorded on an IR spectrophotometer.

2. Preparation of Starting Materials

N-Ts-2-alkenylanilines **1** was prepared according to the known procedure,³ Umemoto reagents are commercially available. Perfluoroalkyl substituted Umemoto reagents were prepared according to the known procedure.⁴



Perfluoropropyl substituted Umemoto reagent (**2b**)

2b 809 mg, white solid, 28% yield; mp 144-146 °C. **1H NMR** (400 MHz, DMSO-d⁶) δ (ppm) 8.68 (d, *J* = 8.1 Hz, 2H), 8.61 (d, *J* = 8.4 Hz, 2H), 8.13 (t, *J* = 7.3 Hz, 2H), 7.93 (t, *J* = 8.3 Hz, 2H). **13C NMR** (101 MHz, DMSO-d⁶) δ (ppm) 142.6, 137.0, 132.6, 131.8, 126.0, 125.5, 40.5. **19F NMR** (376 MHz, DMSO-d⁶) δ (ppm) -77.84 (s, 3F), -79.91 (t, *J* = 11.28 Hz, 2F), -95.56 – -95.64 (m, 2F), -120.26(s, 3F). **IR** (in KBr): 3417, 1637, 1619, 1485, 1448, 1400, 1335, 1259, 1158, 1027, 830, 765, 737, 636 cm⁻¹. **HRMS** (ESI) for: C₁₅H₈F₇S⁺ [M]⁺: calcd: 353.0229, found: 353.0230.

Perfluorobutyl substituted Umemoto reagent (**2c**)

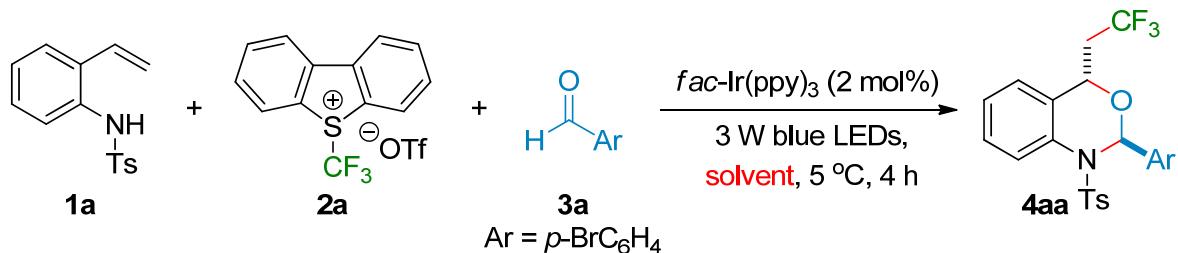
2c 735 mg, white solid, 29% yield; mp 162-164 °C. **1H NMR** (400 MHz, DMSO-d⁶) δ (ppm) 8.68 (d, *J* = 8.1 Hz, 2H), 8.61 (d, *J* = 8.5 Hz, 2H), 8.13 (t, *J* = 7.6 Hz, 2H), 7.93 (t, *J* = 7.8 Hz, 2H). **13C NMR** (101 MHz, DMSO-d⁶) δ (ppm) 142.7, 137.0, 132.6, 131.9, 126.0, 125.6, 40.5. **19F NMR** (376 MHz, DMSO-d⁶) δ (ppm) -77.85 – -77.91 (m, 3F), -80.12 – -80.26 (m, 2F), -94.83 – -94.97 (m, 2F), -116.86 (s, 3F), -125.65 – -125.78(m, 2F). **IR** (in KBr): 3420, 1638, 1401, 1348, 1256, 1219, 1165, 1143, 1028, 771, 724, 700, 636 cm⁻¹. **HRMS** (ESI) for: C₁₆H₈F₉S⁺ [M]⁺: calcd: 403.0198, found: 403.0202.

Perfluorohexyl substituted Umemoto reagent (**2d**)

2d 959 mg, white solid, 27% yield; mp 187-189 °C. **1H NMR** (400 MHz, DMSO-d⁶) δ (ppm) 8.67 (d, *J* = 8.1 Hz, 1H), 8.60 (d, *J* = 7.6 Hz, 1H), 8.13 (t, *J* = 7.6 Hz, 1H), 7.92 (t, *J* = 7.8 Hz, 1H). **13C NMR** (101 MHz, DMSO-d⁶) δ (ppm) 142.7, 137.0, 132.6, 131.9, 126.0, 125.6. **19F NMR** (376 MHz, DMSO-d⁶) δ (ppm) -77.88 – -78.01 (m, 3F), -80.32 – -80.61 (m, 2F), -94.68 – -94.84 (m, 2F), -115.90 (s, 3F), -121.83 (s, 2F), -122.60 (s, 2F), -126.08 (s, 2F). **IR** (in KBr): 3417, 1638, 1619, 1451, 1400, 1360, 1254, 1150, 1028, 881, 771, 736, 636 cm⁻¹. **HRMS** (ESI) for: C₁₈H₈F₁₃S⁺ [M]⁺: calcd: 503.0134, found: 503.0139.

3. Detailed Condition Optimization

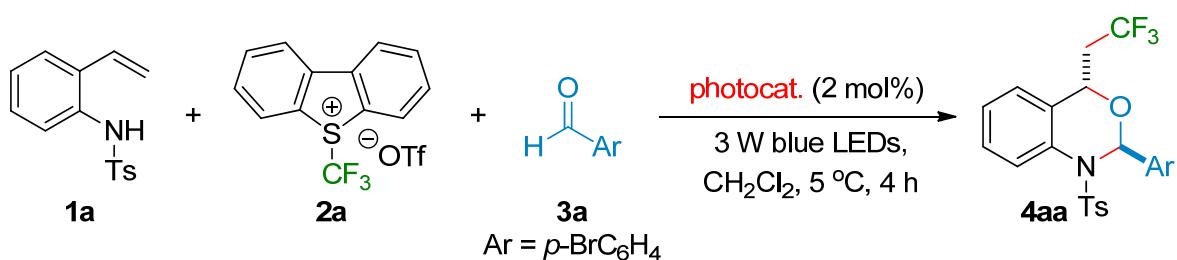
Table S1. Screen of solvent.^[a]



Entry	Solvent	Yield (%) ^[b]	Entry	Solvent	Yield (%) ^[b]
1	THF	trace	6	CH ₃ CN	8
2	CHCl ₃	14	7	MeOH	trace
3	DCM	29	8	DMSO	16
4	Toluene	-	9	1,4-Dioxane	trace
5	DMF	-	10	DCE	13

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol, 1.2 equiv), **3a** (0.15 mmol, 1.5 equiv), *fac*-Ir(ppy)₃ (0.02 mmol, 2.0 mol %), solvent (2.0 mL), 5 °C, 4 h, irradiation with 3 W blue LEDs. [b] Yields determined by ¹H NMR using dimethyl terephthalate as the internal standard.

Table S2. Screen of photocatalysts.^[a]

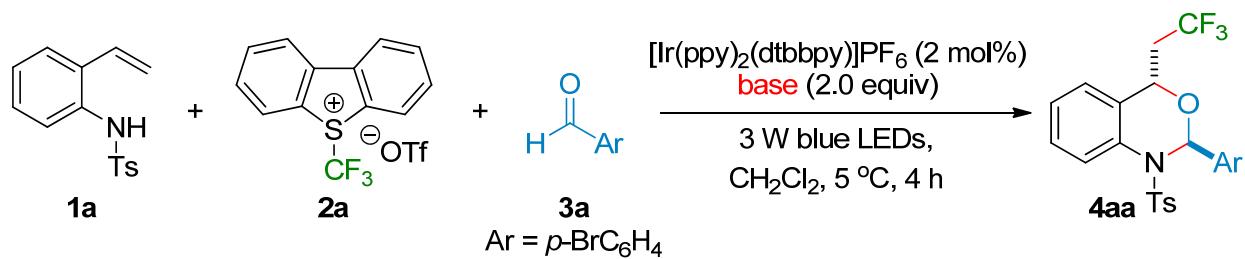


Entry	Photocatalyst	Yield (%) ^[b]
1	<i>fac</i> -Ir(ppy) ₃	31

2	[Ir(ppy)₂(dtbbpy)]PF₆	54
3	Ru(phen) ₃ Cl ₂	23
4	4CZIPN	16
5	[Ir(dFCF ₃ ppy) ₂ phen]PF ₆	15
6	Ir(dFppy) ₃ PF ₆	46

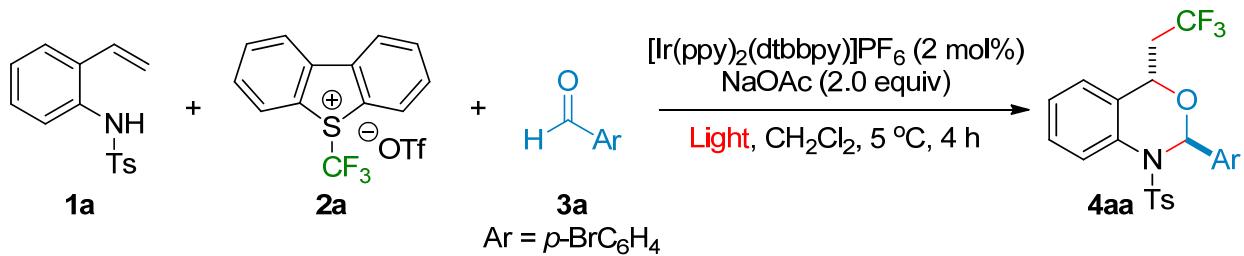
[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol, 1.2 equiv), **3a** (0.15 mmol, 1.5 equiv), photocatalyst (0.02mmol, 2.0 mol %), CH₂Cl₂ (2.0 mL), 5 °C, 4 h, irradiation with 3 W blue LEDs. [b] Yields determined by ¹H NMR using dimethyl terephthalate as the internal standard.

Table S3. Screen of the Bases.^[a]



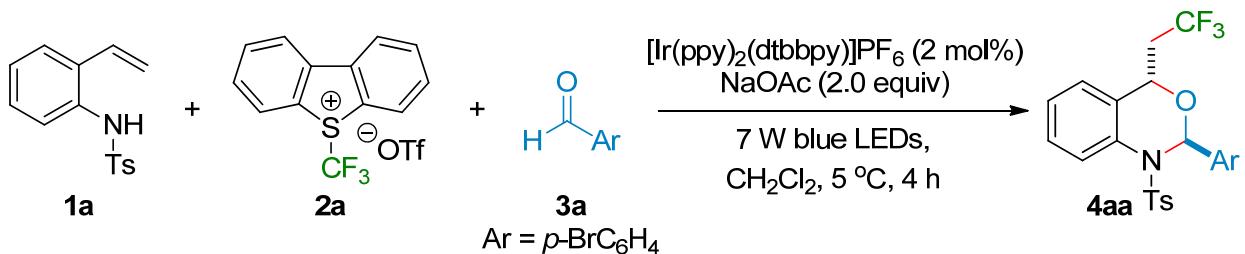
Entry	Base	Yield (%) ^[b]	Entry	Base	Yield (%) ^[b]
1	-	53	6	Na ₂ HPO ₄	25
2	Cs ₂ CO ₃	-	7	DABCO	-
3	K ₂ CO ₃	trace	8	Et ₃ N	-
4	Na ₂ CO ₃	26	9	TMEDA	trace
5	NaOAc	62	10	Pyridine	trace

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol, 1.2 equiv), **3a** (0.15 mmol, 1.5 equiv), Ir(ppy)₂(dtbbpy)PF₆ (0.02mmol, 2.0 mol %), base (0.40 mmol, 2.0 equiv), CH₂Cl₂ (2.0 mL), 5 °C, 4 h, irradiation with 3 W blue LEDs. [b] Yields determined by ¹H NMR using dimethyl terephthalate as the internal standard.

Table S4. Screen of the light sources.^[a]

Entry	Light	Yield (%) ^[b]
1	3 W blue LEDs	57
2	2*3 W blue LEDs	58
3	7 W blue LEDs	70
4	2*3 W 390 nm LEDs	64
5	36 W white LEDs	67

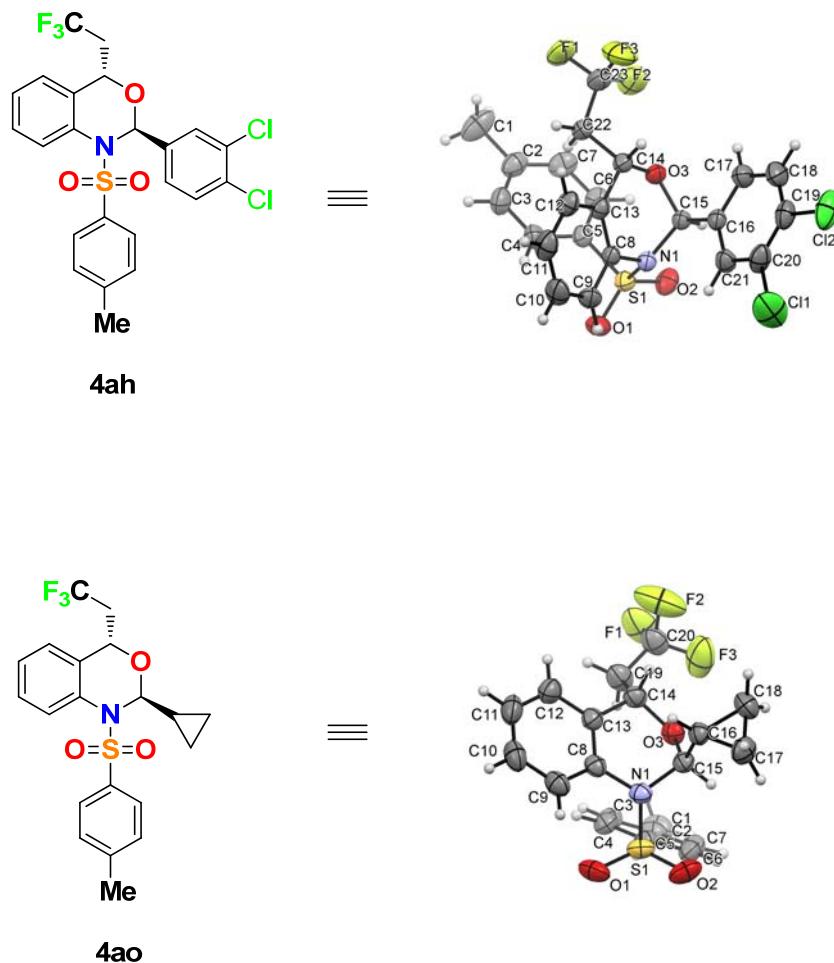
[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol, 1.2 equiv), **3a** (0.15 mmol, 1.5 equiv), $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (0.02 mmol, 2.0 mol %), NaOAc (0.40 mmol, 2.0 equiv), CH_2Cl_2 (2.0 mL), 5 °C, 4 h, irradiation with light. [b] Yields determined by ^1H NMR using dimethyl terephthalate as the internal standard.

Table S5. Control experiments.^[a]

Entry ^[a]	Condition	Yield (%)
1	-	79 ^[b] (76) ^[c]
2	No PC	-
3	No light	-

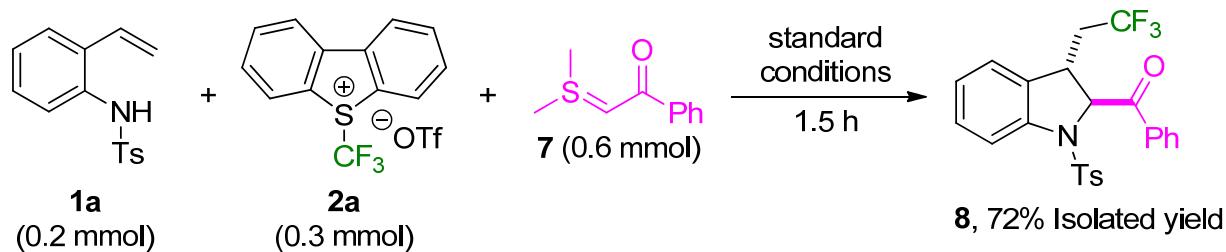
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.30 mmol, 1.5 equiv), **3a** (0.60 mmol, 3.0 equiv), Ir(ppy)₂(dtbbpy)PF₆ (0.04mmol, 2.0 mol %), NaOAc (0.40 mmol, 2.0 equiv), CH₂Cl₂ (2.0 mL), 5 °C, 4 h, irradiation with 7 W blue LEDs. [b] Yields determined by ¹H NMR using dimethyl terephthalate as the internal standard. [c] Isolated yield.

4. X-Ray Structures of Products **4ah** and **4ao**



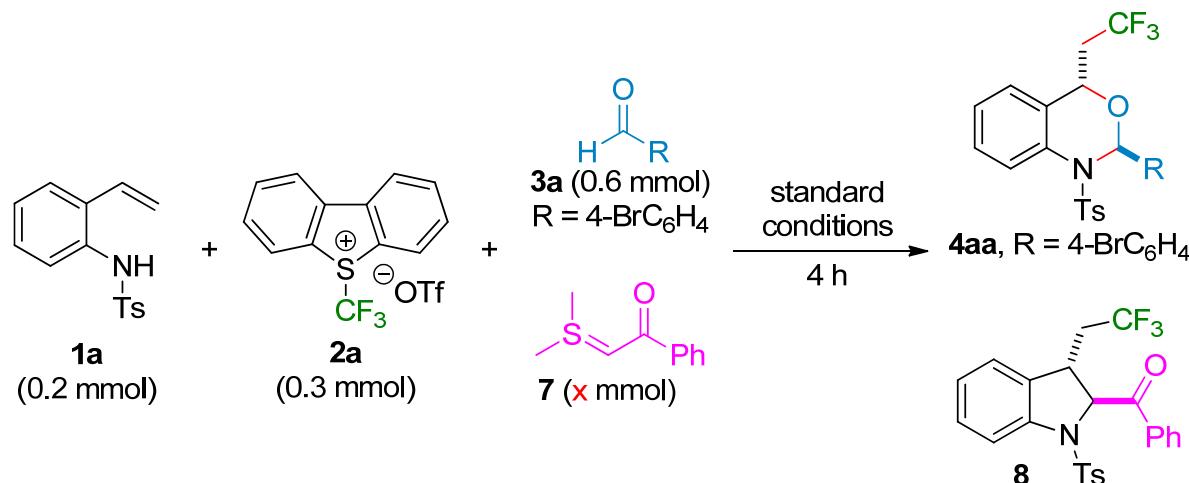
5. Control Experiments

According to our previous work^[5], to further confirm the aza-*o*-QM process, we used the stable sulfur ylide **7** to intercept the *in situ*-formed aza-*o*-QM under standard reaction conditions. (Scheme S1).



Scheme S1. Control experiment of sulfur ylide **7**.

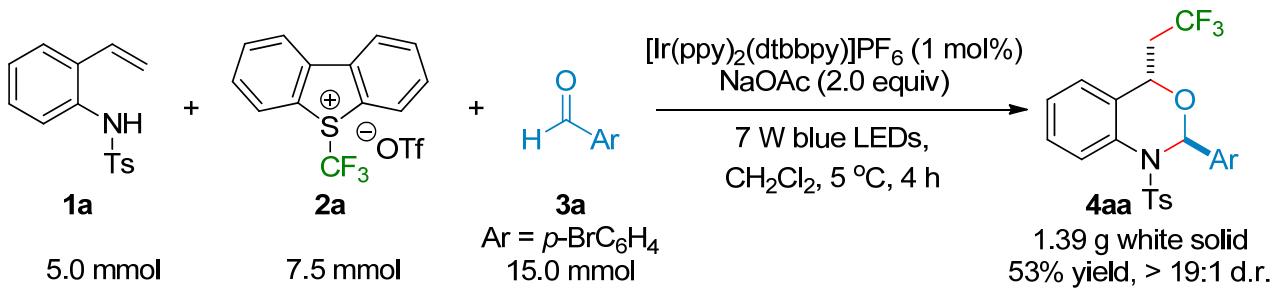
Table S6. Comparison of the reactivities between **3d** and **7**.^[a]



Entry ^[a]	X mmol	Yield of 4aa (%) ^[b]	Yield of 8 (%) ^[b]
1	-	75	-
2	0.1	21	34
3	0.2	trace	40
4	0.4	-	68
5	0.6	-	70

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.30 mmol, 1.5 equiv), **3a** (0.60 mmol, 3.0 equiv), **7** (x mmol), Ir(ppy)₂(dtbbpy)PF₆ (0.04mmol, 2.0 mol %), NaOAc (0.40 mmol, 2.0 equiv), CH₂Cl₂ (2.0 mL), 5 °C, 4 h, irradiation with 7 W blue LEDs. [b] Yields determined by ¹H NMR using dimethyl terephthalate as the internal standard.

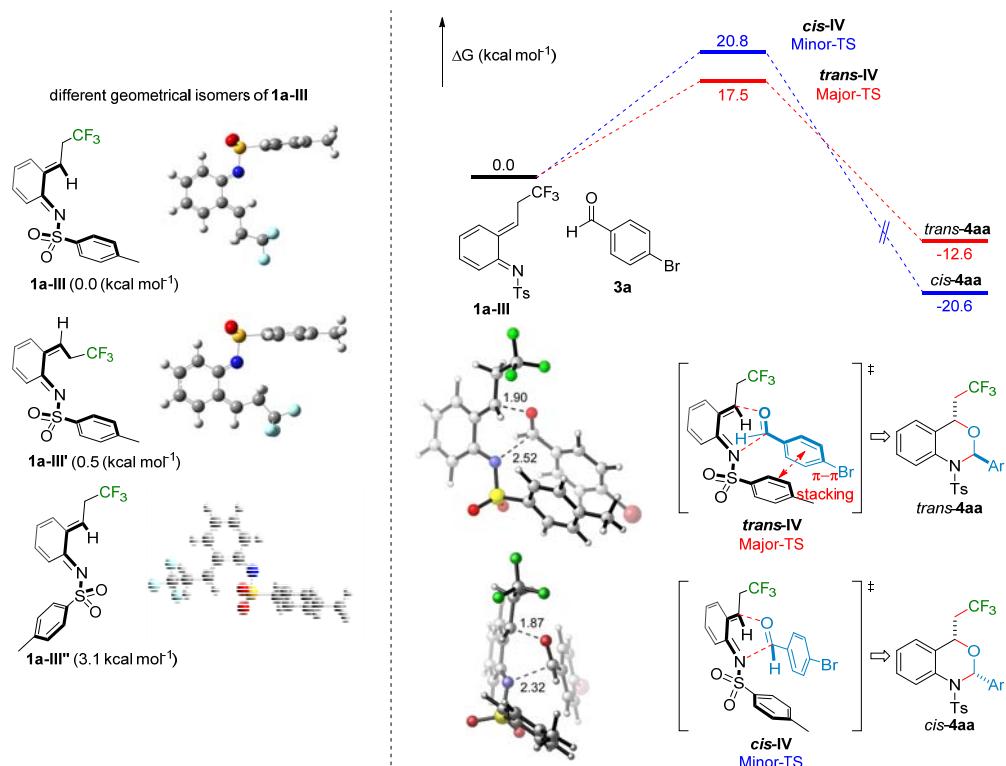
6. Gram-Scale Reaction



1a (1.37 g, 5.0 mmol), **2a** (3.02 g, 1.5 eq.), **3a** (2.78 g, 3.0 eq.), **[Ir(ppy)₂(dtbbpy)]PF₆** (45.67 mg, 1.0 mol%), NaOAc (820 mg, 2.0 eq.) and anhydrous CH₂Cl₂ (30.0 mL) were added to a 50 mL Schlenk flask equipped with a magnetic stir bar. The resulting mixture was degassed by a “freeze-pump-thaw” procedure (3 times). Then the solution was stirred at a distance of ca. 5 cm from a 7 W blue LED at 5 °C. Upon the completion of reaction as monitored by TLC, the solvent was removed by vacuum and the crude reaction mixture was purified by flash chromatography on silica gel (silica: 200–300; eluent: petroleum ether/ethyl acetate (200 : 1–100 : 1) to provide the pure product **4aa** as a white solid in 53 % yield (1.39 g) with d.r. > 19:1.

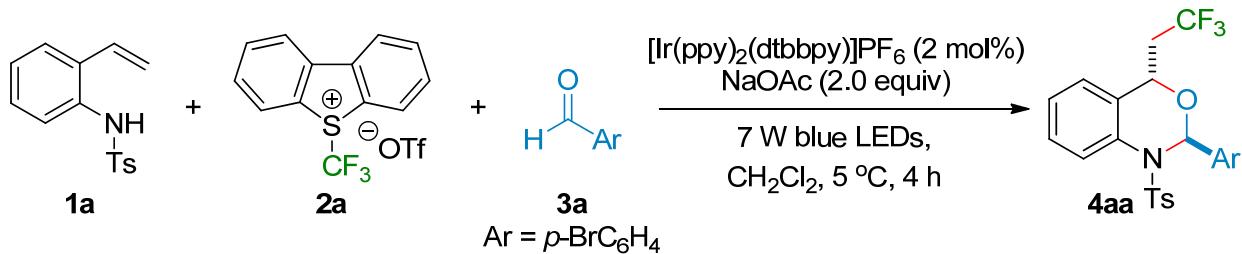
7. DFT Calculation

To better understand the origins of the stereocontrol of the products and if the HDA reaction of in situ-formed aza-o-QMs and aldehydes was concerted or stepwise, we conducted DFT calculations.



8. General Procedure and Spectral Data of Products

8.1 Representative procedure for visible-light induced compound **4aa** synthesis



1a (54.6 mg, 0.2 mmol), **2a** (120.7 mg, 1.5 eq.), **3a** (111.0 mg, 3.0 eq.), $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (3.6 mg, 2.0 mol%), NaOAc (32.8 mg, 2.0 eq.) and anhydrous CH_2Cl_2 (2.0 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stir bar. The resulting mixture was degassed by a “freeze-pump-thaw” procedure (3 times). Then the solution was stirred at a distance of ca. 5 cm from a 7 W blue LED at 5 °C. Upon the completion of reaction as monitored by TLC, the solvent was removed by vacuum and the crude reaction mixture was purified by flash chromatography on silica gel (silica: 200–300; eluent: petroleum ether/ethyl acetate (200 : 1–100 : 1) to provide the pure product **4aa** as a white solid in 76 % yield.

8.2 Spectral data of products

2-(4-bromophenyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (**4aa**)

4aa 79.0 mg, white solid, 75% yield in 4 h; d.r. > 19:1, mp 177–178 °C. **1H NMR** (400 MHz, CDCl_3) δ (ppm) 7.94 (d, $J = 8.2$ Hz, 1H), 7.52 (d, $J = 7.9$ Hz, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.33 (t, $J = 7.8$ Hz, 1H), 7.26 – 7.21 (m, 4H), 7.13 (t, $J = 7.6$ Hz, 1H), 6.91 (s, 1H), 6.65 (d, $J = 7.8$ Hz, 1H), 4.78 (d, $J = 10.1$ Hz, 1H), 2.38 (s, 3H), 2.10 – 1.98 (m, 1H), 1.01 – 0.83 (m, 1H). **13C NMR** (101 MHz, CDCl_3) δ (ppm) 144.4, 135.2, 134.7, 133.0, 132.0, 129.2, 129.1, 128.6, 128.5, 128.3, 127.8, 127.0, 125.3 (q, $J = 278.8$ Hz) 124.7, 122.7, 83.4, 65.2 (q, $J = 3.7$ Hz), 40.4 (q, $J = 28.3$ Hz), 21.4. **19F NMR** (376 MHz, CDCl_3) δ (ppm) -64.05. **IR** (in KBr): 3416, 3129, 1489, 1399, 1255, 1167, 1131, 1059, 1010, 817, 773, 862, 570 cm^{-1} . **HRMS** (ESI) for: $\text{C}_{23}\text{H}_{19}\text{BrF}_3\text{NO}_3\text{S} [\text{M} + \text{H}]^+$: calcd: 526.0294, found: 526.0287.

2-(4-fluorophenyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (**4ab**)

4ab 70.7 mg, white solid, 76% yield in 4 h; d.r. > 19:1, mp 159–160 °C. **1H NMR** (400 MHz, CDCl_3) δ (ppm) 7.95 (d, $J = 8.9$ Hz, 1H), 7.52 (d, $J = 8.3$ Hz, 2H), 7.39 – 7.29 (m, 3H), 7.22 (d, $J = 8.2$ Hz, 2H), 7.13 (t, $J = 7.6$ Hz, 1H), 6.98 – 6.92 (m, 3H), 6.66 (d, $J = 7.7$ Hz, 1H), 4.78 (d, $J = 9.9$ Hz, 1H), 2.39 (s, 3H), 2.11 – 1.98 (m, 1H), 1.02 – 0.85 (m, 1H). **13C NMR** (100 MHz, CDCl_3) δ (ppm) 162.6 (d, $J = 247.6$ Hz), 144.4, 135.2, 133.1, 131.3 (d, $J = 3.1$ Hz), 129.3, 129.2, 128.7 (d, $J = 8.4$ Hz), 128.5, 128.3, 127.8, 126.9, 125.4 (q, $J = 278.8$ Hz), 124.7, 115.8 (d, $J = 21.7$ Hz), 83.4, 65.1 (q, $J = 3.4$ Hz), 40.4 (q, $J = 28.3$ Hz), 21.4. **19F NMR** (376 MHz, CDCl_3) δ (ppm) -64.05, -113.46. **IR** (in KBr): 3416, 3128, 1606, 1510, 1387, 1350, 1254, 1164, 1138, 1085, 770, 688, 589 cm^{-1} . **HRMS** (ESI) for: $\text{C}_{23}\text{H}_{19}\text{F}_4\text{NO}_3\text{S} [\text{M} + \text{H}]^+$: calcd: 466.1095, found: 466.1090.

2-(4-chlorophenyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4ac)

4ac 70.4 mg, white solid, 73% yield in 4 h; d.r. > 19:1, mp 142–144 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 7.95 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 3H), 7.26 – 7.21 (m, 4H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 4.78 (d, *J* = 10.0 Hz, 1H), 2.39 (s, 3H), 2.10 – 1.98 (m, 1H), 1.01 – 0.86 (m, 1H). **13C NMR** (101 MHz, CDCl₃) δ (ppm) 144.4, 135.2, 134.4, 134.1, 133.0, 129.3, 129.1, 129.0, 128.5, 128.3, 128.3, 127.8, 127.0, 125.3 (q, *J* = 278.8 Hz), 124.7, 83.4, 65.2 (q, *J* = 3.4 Hz) 40.4 (q, *J* = 28.3 Hz) 21.4. **19F NMR** (376 MHz, CDCl₃) δ (ppm) -64.06. **IR** (in KBr): 3417, 3127, 1596, 1491, 1400, 1357, 1253, 1165, 1133, 836, 792, 720, 588 cm⁻¹. **HRMS** (ESI) for: C₂₃H₁₉ClF₃NO₃S [M + H]⁺: calcd: 482.0799, found: 482.0795.

(4-methoxyphenyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4ad)

4ad 62.1 mg, white solid, 65% yield in 4 h; d.r. > 19:1, mp 172–174 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 7.95 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.26 (m, 4H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.93 (s, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.79 (d, *J* = 10.0 Hz, 1H), 3.72 (s, 3H), 2.37 (s, 3H), 2.11 – 1.99 (m, 1H), 1.05 – 0.92 (m, 1H). **13C NMR** (100 MHz, CDCl₃) δ (ppm) 159.5, 144.2, 135.4, 133.4, 129.4, 129.2, 128.5, 128.2, 128.1, 127.8, 127.4, 126.7, 125.4 (q, *J* = 278.8 Hz), 124.6, 114.1, 83.7, 64.9 (q, *J* = 3.1 Hz), 55.2, 40.4 (q, *J* = 28.2 Hz), 21.4. **19F NMR** (376 MHz, CDCl₃) δ (ppm) -64.03. **IR** (in KBr): 3420, 2361, 2063, 1637, 1401, 1167, 613 cm⁻¹. **HRMS** (ESI) for: C₂₄H₂₂F₃NO₄S [M + H]⁺: calcd: 478.1294, found: 478.1292.

2-(4-(tert-butyl)phenyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4ae)

4ae 76.5 mg, white solid, 76% yield in 4 h; d.r. > 19:1, mp 157–159 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 7.97 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.26 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 4.83 (d, *J* = 9.9 Hz, 1H), 2.38 (s, 3H), 2.12 – 2.01 (m, 1H), 1.24 (s, 9H), 1.04 – 0.95 (m, 1H). **13C NMR** (101 MHz, CDCl₃) δ (ppm) 151.3, 144.2, 135.5, 133.4, 132.4, 129.4, 129.2, 128.5, 128.1, 127.8, 126.6, 126.5, 125.7, 125.5 (q, *J* = 278.8 Hz), 124.6, 83.9, 65.0 (q, *J* = 3.1 Hz), 40.4 (q, *J* = 28.3 Hz), 34.5, 31.2, 21.4. **19F NMR** (376 MHz, CDCl₃) δ (ppm) -63.98. **IR** (in KBr): 3417, 3120, 2965, 1599, 1400, 1348, 1258, 1170, 1129, 973, 817, 767, 683, 584 cm⁻¹. **HRMS** (ESI) for: C₂₇H₂₈F₃NO₃S [M + H]⁺: calcd: 504.1815, found: 504.1812.

2-(o-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4af)

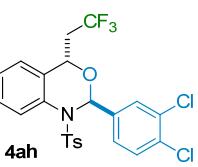
4af 61.8 mg, white solid, 67% yield in 4 h, d.r. > 19:1, mp 173–176 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 8.07 (d, *J* = 8.7 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.10 (m, 3H), 7.04 (d, *J* = 7.8 Hz, 1H), 7.01 (s, 1H), 6.90 (t, *J* = 6.5 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 4.45 (d, *J* = 9.9 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H), 2.18 – 2.06 (m, 1H), 1.20 – 1.06 (m, 1H). **13C NMR** (100 MHz, CDCl₃) δ (ppm) 144.2, 137.7, 135.4, 134.3, 132.9, 131.3, 129.3, 129.1, 128.6, 128.5, 128.4, 127.8, 127.2, 126.5, 125.4, 125.4 (q, *J* = 278.8 Hz), 124.5, 83.4, 64.9 (q, *J* = 3.1 Hz), 40.1 (q, *J* = 28.3 Hz), 21.4, 19.6. **19F NMR** (376 MHz, CDCl₃) δ (ppm) -63.90. **IR** (in KBr): 3417, 3131, 1638, 1400, 1171, 1132, 1089, 688, 587 cm⁻¹. **HRMS** (ESI) for: C₂₄H₂₂F₃NO₃S [M + H]⁺: calcd: 462.1345, found: 462.1346.

2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4ag)

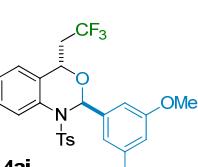
4ag 73.8 mg, white solid, 80% yield in 4 h, d.r. > 19:1, mp 142–145 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 7.96 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.23 – 7.09 (m, 6H), 7.02 (d, *J* = 6.7 Hz, 1H), 6.95 (s, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 4.84 (d, *J* = 10.1 Hz, 1H), 2.38 (s, 3H), 2.26 (s,

3H), 2.11 – 1.99 (m, 1H), 1.05 – 0.91 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.2, 138.4, 135.4, 135.4, 133.3, 129.3, 129.2, 129.1, 128.6, 128.5, 128.1, 127.8, 127.4, 126.7, 125.4 (q, *J* = 278.8 Hz), 124.6, 123.8, 83.9, 65.0 (q, *J* = 3.2 Hz), 40.4 (q, *J* = 28.2 Hz), 21.5, 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -64.03. **IR** (in KBr): 3416, 3129, 1603, 1400, 1259, 1172, 1125, 973, 813, 764, 891, 573 cm⁻¹. **HRMS** (ESI) for: C₂₄H₂₂F₃NO₃S [M + H]⁺: calcd: 462.1345, found: 462.1348.

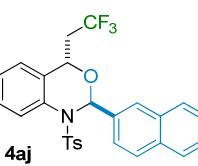
2-(3,4-dichlorophenyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4ah)

4ah  72.3 mg, white solid, 70% yield in 4 h, d.r. > 19:1, mp 149–151 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.95 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.46 (s, 1H), 7.36 – 7.32 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 3H), 7.15 (t, *J* = 7.1 Hz, 1H), 6.90 (s, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 4.80 (d, *J* = 9.9 Hz, 1H), 2.38 (s, 3H), 2.10 – 1.98 (m, 1H), 1.00 – 0.87 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.6, 136.0, 135.0, 133.1, 132.8, 132.7, 130.9, 129.3, 129.0, 128.9, 128.5, 128.5, 127.8, 127.2, 126.2, 125.2 (q, *J* = 278.8 Hz), 124.8, 82.8, 65.3 (q, *J* = 3.1 Hz), 40.5 (q, *J* = 28.3 Hz), 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -64.02. **IR** (in KBr): 3416, 3128, 1597, 1491, 1392, 1359, 1254, 1171, 1121, 1061, 989, 837, 818, 774, 601 cm⁻¹. **HRMS** (ESI) for: C₂₃H₁₈Cl₂F₃NO₃S [M + H]⁺: calcd: 516.0409, found: 516.0411.

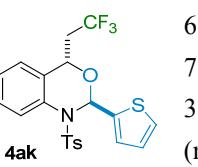
2-(3,5-dimethoxyphenyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4ai)

4ai  67.0 mg, white solid, 66% yield in 4 h, d.r. > 19:1, mp 187–189 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.94 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.92 (s, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 6.54 (s, 2H), 6.30 (s, 1H), 4.91 (d, *J* = 10.0 Hz, 1H), 3.69 (s, 6H), 2.38 (s, 3H), 2.12 – 2.00 (m, 1H), 1.05 – 0.91 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 161.0, 144.3, 138.0, 135.3, 133.3, 129.3, 129.2, 128.5, 128.2, 127.7, 125.4 (q, *J* = 278.8 Hz), 124.7, 104.6, 100.7, 83.8, 65.2 (q, *J* = 3.1 Hz), 55.3, 40.3 (q, *J* = 28.3 Hz), 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -64.01. **IR** (in KBr): 3417, 3120, 2972, 2843, 1610, 1466, 1391, 1331, 1254, 1156, 1030, 941, 819, 768, 691, 575 cm⁻¹. **HRMS** (ESI) for: C₂₅H₂₄F₃NO₃S [M + H]⁺: calcd: 508.1400, found: 508.1392.

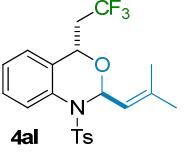
2-(naphthalen-2-yl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4aj)

4aj  79.6 mg, white solid, 80% yield in 4 h, d.r. > 19:1, mp 157–159 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 8.04 (d, *J* = 8.2 Hz, 1H), 7.82 (s, 1H), 7.77 – 7.72 (m, 3H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 9.5 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 3.3 Hz, 1H), 7.22 (s, 1H), 7.14 (s, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 4.87 (d, *J* = 10.0 Hz, 1H), 2.39 (s, 3H), 2.12 – 2.00 (m, 1H), 1.10 – 0.96 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.3, 135.4, 133.4, 133.1, 133.1, 133.0, 129.4, 129.3, 128.7, 128.5, 128.3, 128.2, 127.8, 127.5, 126.8, 126.7, 126.5, 126.3, 125.4 (q, *J* = 278.8 Hz), 124.6, 124.0, 84.7, 65.4 (q, *J* = 3.3 Hz), 40.5 (q, *J* = 28.2 Hz), 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -63.97. **IR** (in KBr): 3449, 2056, 1635, 1399, 1258, 1170, 1131, 1087, 691, 590 cm⁻¹. **HRMS** (ESI) for: C₂₇H₂₂F₃NO₃S [M + H]⁺: calcd: 498.1345, found: 498.1350.

2-(thiophen-2-yl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4ak)

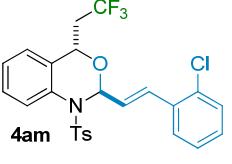
4ak  68.0 mg, white solid, 75% yield in 4 h, d.r. > 19:1, mp 173–177 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.92 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.22 – 7.12 (m, 5H), 6.95 (d, *J* = 3.4 Hz, 1H), 6.86 – 6.84 (m, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.01 (d, *J* = 9.9 Hz, 1H), 2.38 (s, 3H), 2.11 – 1.99 (m, 1H), 1.01 – 0.88 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.4, 139.1, 135.0, 133.1, 129.2, 128.5, 128.2, 128.0, 127.0, 126.9, 126.6, 125.3 (q, *J* = 278.8 Hz), 124.6, 81.8, 65.5 (q, *J* = 3.1 Hz), 40.4 (q, *J* = 28.5 Hz), 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -55.58(minor), -64.12(major). **IR** (in KBr): 3416, 3130, 1596, 1492, 1399, 1351, 1256, 1207, 1166, 1083, 964, 830, 706, 569 cm⁻¹. **HRMS** (ESI) for: C₂₁H₁₈F₃NO₃S₂ [M + H]⁺: calcd: 454.0753, found: 454.0751.

2-(2-methylprop-1-en-1-yl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4al)



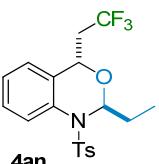
50.0 mg, white solid, 54% yield in 4 h, d.r. > 19:1, mp 118–119 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.82 (d, *J* = 8.1 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 5.1 Hz, 1H), 4.97 (s, 1H), 4.90 (d, *J* = 10.0 Hz, 1H), 2.35 (s, 3H), 2.11 – 1.99 (m, 1H), 1.81 (s, 3H), 1.65 (s, 3H), 0.93 – 0.80 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 143.9, 141.7, 135.6, 133.4, 130.3, 129.0, 128.5, 128.2, 128.0, 125.4 (q, *J* = 276.7 Hz), 124.5, 118.8, 81.3, 65.0 (q, *J* = 4.0 Hz), 40.3 (q, *J* = 28.2 Hz), 25.6, 21.3, 18.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -64.25. **IR** (in KBr): 3416, 3131, 2360, 1638, 1400, 1167, 1131, 675, 573 cm⁻¹. **HRMS** (ESI) for: C₂₁H₂₂F₃NO₃S [M + H]⁺: calcd: 426.1345, found: 426.1346.

2-((E)-2-chlorostyryl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4am)



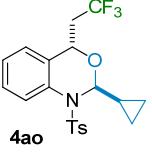
56.9 mg, white solid, 56% yield in 4 h, d.r. > 19:1, mp 167–169 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.90 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.26 (m, 1H), 7.21 (t, *J* = 8.0 Hz, 3H), 7.16 – 7.08 (m, 3H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.55 (s, 1H), 5.96 (dd, *J* = 16.1, 3.4 Hz, 1H), 5.06 (d, *J* = 9.9 Hz, 1H), 2.37 (s, 3H), 2.13 – 2.01 (m, 1H), 0.97 – 0.83 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.3, 135.3, 133.9, 133.5, 133.2, 132.1, 129.7, 129.6, 129.4, 129.2, 128.5, 128.2, 128.0, 127.1, 127.0, 126.8, 126.3, 125.3 (q, *J* = 278.8 Hz), 124.7, 82.9, 65.6 (q, *J* = 3.1 Hz), 40.5 (q, *J* = 28.3 Hz), 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -64.10. **IR** (in KBr): 3417, 3128, 2864, 1542, 1366, 1224, 1125, 1091, 1031, 890, 762, 749, 690, 570 cm⁻¹. **HRMS** (ESI) for: C₂₅H₂₁ClF₃NO₃S [M + H]⁺: calcd: 508.0956, found: 508.0955.

2-ethyl-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4an)



59.9 mg, white solid, 75% yield in 4 h, d.r. = 12:1, mp 122–124 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.82 (d, *J* = 8.2 Hz, 1H, minor), 7.76 (d, *J* = 8.0 Hz, 1H, major), 7.44 – 7.38 (m, 1H, major + minor), 7.34 (d, *J* = 8.0 Hz, 2H, major + minor) 7.25 (t, *J* = 6.6 Hz, 1H, major + minor), 7.14 (d, *J* = 8.0 Hz, 2H, major + minor), 6.91 (d, *J* = 7.7 Hz, 1H, major), 6.85 (d, *J* = 7.8 Hz, 1H, minor), 5.73 (t, *J* = 7.2 Hz, 1H, minor), 5.50 (t, *J* = 6.1 Hz, 1H, major), 4.92 (d, *J* = 10.1 Hz, 1H, minor), 3.67 (d, *J* = 7.5 Hz, 1H, major), 2.57 – 2.45 (m, 1H, major + minor), 2.36 (s, 3H, major + minor), 2.30 – 2.19 (m, 1H, major + minor), 1.78 – 1.71 (m, 2H, major), 1.68 – 1.61 (m, 1H, minor), 0.95 (t, *J* = 7.4 Hz, 3H, major + minor). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) (major + minor) 144.2, 144.9, 135.4, 135.2, 133.9, 133.5, 133.4, 132.6, 129.3, 129.1, 128.6, 128.5, 128.4, 128.3, 128.2, 127.5, 126.8, 125.6 (q, *J* = 278.8 Hz), 124.4, 122.9, 86.9, 85.2, 66.5 (q, *J* = 3.1 Hz), 65.0(q, *J* = 3.1 Hz), 38.4(q, *J* = 28.3 Hz), 29.0, 24.4, 21.5, 21.3, 9.4, 9.2. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -63.86(major), -64.27(minor). **IR** (in KBr): 3416, 3121, 2985, 2883, 1940, 1601, 1458, 1343, 1255, 1163, 998, 883, 822, 769, 585 cm⁻¹. **HRMS** (ESI) for: C₁₉H₂₀F₃NO₃S [M + H]⁺: calcd: 400.1189, found: 400.1189.

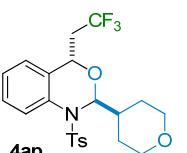
2-cyclopropyl-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4ao)



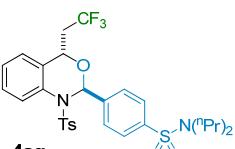
62.5 mg, white solid, 76% yield in 4 h, d.r. > 19:1, mp 150–152 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.86 (d, *J* = 8.2 Hz, 1H, major), 7.81 (d, *J* = 8.1 Hz, 1H, minor), 7.41 (d, *J* = 8.1 Hz, 2H, major + minor), 7.35 (t, *J* = 7.7 Hz, 1H, major + minor), 7.27 – 7.22 (m, 1H, major + minor), 7.15 (d, *J* = 8.0 Hz, 2H, major + minor), 6.94 (d, *J* = 7.7 Hz, 1H, minor), 6.89 (d, *J* = 7.7 Hz, 1H, major), 5.16 (d, *J* = 9.9 Hz, 1H, major), 5.09 (d, *J* = 7.6 Hz, 1H, minor), 5.04 (d, *J* = 8.5 Hz, 1H, major), 3.98 (d, *J* = 9.1 Hz, 1H, minor), 2.35 (s, 3H, major + minor), 2.16 – 2.04 (m, 1H, major + minor), 1.07 – 0.98 (m, 1H, major + minor), 0.95 – 0.87 (m, 1H, major + minor), 0.64 – 0.49 (m, 4H, major + minor). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) (major + minor) δ 144.1, 144.0, 135.4, 135.2, 133.9, 133.4, 132.1, 129.7, 129.3, 129.1, 128.5, 128.3, 128.2, 128.1, 128.0, 127.6, 126.8, 126.7, 125.4 (q, *J* = 278.8 Hz) 124.5, 123.7, 88.2, 87.8, 66.3 (q, *J* = 3.1

Hz), 65.7 (q, J = 3.1 Hz), 40.5 (q, J = 28.2 Hz), 21.5, 21.3, 15.8, 12.5, 4.4, 4.2, 3.5, 3.1. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) - 63.92(minor), -64.17(major). **IR** (in KBr): 3416, 3124, 3009, 2871, 1596, 1493, 1347, 1256, 1165, 1021, 962, 826, 686, 570 cm⁻¹. **HRMS** (ESI) for: C₂₀H₂₀F₃NO₃S [M + H]⁺: calcd: 412.1189, found: 412.1192.

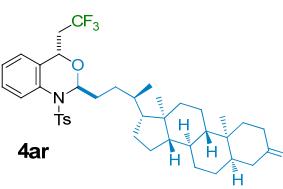
2-(tetrahydro-2H-pyran-4-yl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (4ap)

 61.0 mg, white solid, 67% yield in 4 h, d.r. > 19:1, mp 142-144 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.73 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 7.7 Hz, 1H), 5.33 (d, J = 5.9 Hz, 1H), 3.94 (t, J = 12.0 Hz, 2H), 3.28 (t, J = 11.6 Hz, 3H), 2.61 – 2.49 (m, 1H), 2.37 (s, 3H), 2.27 – 2.19 (m, 1H), 1.83 (s, 1H), 1.70 – 1.60 (m, 2H), 1.59 – 1.36 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.5, 135.3, 135.0, 134.4, 129.5, 129.0, 128.6, 127.2, 127.0, 125.5 (q, J = 278.8 Hz) 122.1, 88.6, 67.5, 67.5, 66.4, 41.1, 36.6 (q, J = 28.5 Hz), 28.3, 27.5, 21.5. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -63.87. **IR** (in KBr): 3416, 3130, 2842, 1602, 1400, 1255, 1169, 1106, 960, 812, 661, 598 cm⁻¹. **HRMS** (ESI) for: C₂₂H₂₄F₃NO₄S [M + H]⁺: calcd: 456.1451, found: 456.1452.

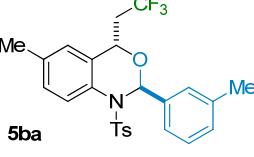
N,N-dipropyl-4-(1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazin-2-yl)-benzenesulfonamide (4aq)

 79.4 mg, white solid, 65% yield in 4 h, d.r. > 19:1, mp 132-135 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.76 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.45 – 7.39 (m, 3H), 7.26 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 7.7 Hz, 1H), 6.74 (s, 1H), 3.74 (d, J = 8.1 Hz, 1H), 3.04 (t, J = 8.0 Hz, 4H), 2.58 – 2.46 (m, 1H), 2.40 (s, 3H), 2.28 – 2.15 (m, 1H), 1.57 – 1.48 (m, 4H), 0.84 (t, J = 7.4 Hz, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.8, 143.0, 140.2, 135.1, 133.8, 133.6, 129.7, 129.2, 128.6, 127.6, 127.4, 127.4, 127.0, 125.5 (q, J = 278.8 Hz), 122.9, 84.2, 67.0 (q, J = 3.1 Hz), 50.0, 37.1 (q, J = 28.5 Hz), 22.0, 21.5, 11.2. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -63.72. **IR** (in KBr): 3416, 3129, 2969, 1600, 1401, 1358, 1249, 1170, 1088, 964, 767, 663, 575 cm⁻¹. **HRMS** (ESI) for: C₂₉H₃₃F₃N₂O₅S₂ [M + H]⁺: calcd: 611.1856, found: 611.1858.

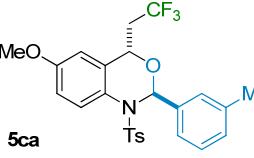
(5R,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((2R)-4-(1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazin-2-yl)butan-2-yl)tetradecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one (4ar)

 99.4 mg, colorless liquid, 71% yield in 4 h, d.r. = 4:1. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.74 (d, J = 8.0 Hz, 1H major), 7.43 – 7.38 (m, 1H, major + minor), 7.34 (d, J = 8.2 Hz, 2H, major + minor), 7.27 – 7.22 (m, 1H, major + minor), 7.15 (t, J = 7.6 Hz, 3H, major + minor), 6.92 (d, J = 7.7 Hz, 1H, major), 6.86 (d, J = 7.7 Hz, 1H, minor), 5.75 (t, J = 6.8 Hz, 1H, minor), 5.54 – 5.47 (m, 1H, major), 4.91 (d, J = 10.0 Hz, 1H, minor), 3.66 (t, J = 10.1 Hz, 1H, major), 2.69 (t, J = 14.2 Hz, 1H, major + minor), 2.56 – 2.45 (m, 1H, major + minor), 2.36 (s, 3H, major + minor), 2.32 – 2.13 (m, 4H, major + minor), 2.08 – 1.94 (m, 4H, major + minor), 1.91 – 1.69 (m, 6H, major + minor), 1.62 – 1.33 (m, 9H, major + minor), 1.26 – 1.07 (m, 6H, major + minor), 1.01 (s, 3H, major + minor), 0.86 (dd, J = 6.4, 3.5 Hz, 3H, major), 0.81 (t, J = 6.9 Hz, 3H, minor), 0.65 (t, J = 3.4 Hz, 3H, major + minor). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) (major + minor) 213.4, 144.1, 143.9, 135.5, 135.3, 133.9 (d, J = 20.7 Hz), 133.5 (d, J = 30.2 Hz), 132.6 (d, J = 3.2 Hz), 129.6, 129.3 (d, J = 2.8 Hz), 129.1, 128.6 – 128.5 (m), 128.3, 128.3 – 128.1 (m), 127.5 (d, J = 5.5 Hz), 126.8 (d, J = 7.8 Hz), 125.6 (q, J = 277.8 Hz), 124.4 (d, J = 1.7 Hz), 122.9 (d, J = 16.2 Hz), 86.3 (d, J = 37.0 Hz), 84.4 (d, J = 15.7 Hz), 66.6 (d, J = 21.4 Hz), 65.0 (d, J = 3.6 Hz), 56.4, 56.0, 55.9, 55.8, 44.4, 42.7, 42.4, 40.7, 40.0, 39.0 – 37.8 (m), 37.2, 37.0, 35.5, 35.1 (d, J = 9.9 Hz), 35.0, 32.4 (d, J = 21.6 Hz), 31.1, 30.9, 28.1 – 28.0 (m), 27.6 (d, J = 15.3 Hz), 26.7, 25.8, 24.2, 22.7, 21.5, 21.3, 21.2, 18.6 (d, J = 4.1 Hz), 12.1. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -63.80 (d, J = 10.2 Hz, major), -64.21 (minor). **IR** (in KBr): 3449, 2056, 1635, 1399, 1170, 1131, 1087, 813, 691, 570 cm⁻¹. **HRMS** (ESI) for: C₄₀H₅₂F₃NO₄S [M + H]⁺: calcd: 700.3642, found: 700.3645.

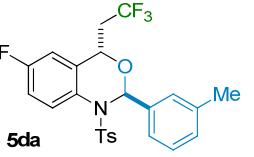
6-methyl-2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5ba)

5ba  62.8 mg, white solid, 66% yield in 4 h, d.r. > 19:1, mp 181–183 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.82 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.12 (m, 5H), 7.10 (d, *J* = 9.9 Hz, 1H), 7.02 (d, *J* = 6.7 Hz, 1H), 6.91 (s, 1H), 6.42 (s, 1H), 4.80 (d, *J* = 10.0 Hz, 1H), 2.38 (s, 3H), 2.26 (s, 3H), 2.21 (s, 3H), 2.10 – 1.98 (m, 1H), 1.00 – 0.86 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.1, 138.4, 136.6, 135.6, 135.4, 130.6, 129.2, 129.1, 129.0, 128.5, 128.5, 127.7, 127.4, 125.5 (q, *J* = 278.8 Hz), 125.0, 123.9, 83.8 65.0 (q, *J* = 3.4 Hz), 40.5 (q, *J* = 28.3 Hz), 21.4, 21.1. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -64.06. **IR** (in KBr): 3417, 3128, 2876, 1598, 1500, 1351, 1253, 1174, 1128, 854, 584 cm⁻¹. **HRMS** (ESI) for: C₂₅H₂₄F₃NO₃S [M + H]⁺: calcd: 476.1502, found: 476.1498.

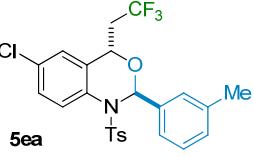
6-methoxy-2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5ca)

5ca  62.9 mg, white solid, 64% yield in 4 h, d.r. > 19:1, mp 144–146 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.85 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.12 (m, 5H), 7.02 (d, *J* = 6.5 Hz, 1H), 6.90 (s, 1H), 6.85 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.11 (s, 1H), 4.79 (d, *J* = 9.8 Hz, 1H), 3.70 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H), 2.05 – 1.94 (m, 1H), 0.99 – 0.85 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 157.9, 144.1, 138.4, 135.5, 135.3, 130.5, 129.4, 129.2, 129.1, 128.6, 128.6, 127.4, 126.0, 125.7 (q, *J* = 278.8 Hz), 123.9, 114.0, 109.5, 83.8, 65.1 (q, *J* = 3.3 Hz), 55.3, 40.4 (q, *J* = 28.2 Hz), 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -64.02. **IR** (in KBr): 3417, 3127, 2875, 1609, 1501, 1351, 1251, 1131, 1031, 810, 585 cm⁻¹. **HRMS** (ESI) for: C₂₅H₂₄F₃NO₄S [M + H]⁺: calcd: 492.1451, found: 492.1455.

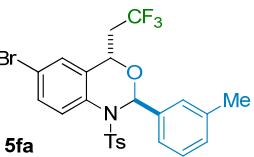
6-fluoro-2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5da)

5da  69.0 mg, white solid, 72% yield in 4 h, d.r. > 19:1, mp 161–163 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.95 (dd, *J* = 9.1, 5.2 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.13 (m, 3H), 7.05 – 7.00 (m, 2H), 6.94 (s, 1H), 6.37 (dd, *J* = 8.6, 2.7 Hz, 1H), 4.80 (d, *J* = 9.9 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 3H), 2.05 – 1.93 (m, 1H), 1.05 – 0.91 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 161.8, 159.4, 144.4, 138.6, 135.2, 135.1, 131.3 (d, *J* = 7.1 Hz), 130.0 (d, *J* = 8.3 Hz), 129.4, 129.3, 128.7, 128.5, 127.4, 125.2 (q, *J* = 274.7 Hz), 123.8, 115.7 (d, *J* = 22.5 Hz), 111.4 (d, *J* = 23.7 Hz), 83.9, 64.9, 40.2 (q, *J* = 28.6 Hz), 21.6, 21.5. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -64.05, -113.03. **IR** (in KBr): 3416, 3131, 2361, 1638, 1400, 1170, 1126, 1051, 807, 585 cm⁻¹. **HRMS** (ESI) for: C₂₄H₂₁F₄NO₃S [M + H]⁺: calcd: 480.1251, found: 480.1254.

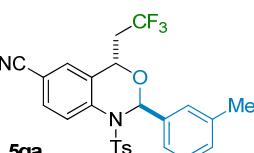
6-chloro-2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5ea)

5ea  73.4 mg, white solid, 74% yield in 4 h, d.r. > 19:1, mp 170–173 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.92 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.24 (m, 3H), 7.19 – 7.13 (m, 3H), 7.05 (d, *J* = 6.6 Hz, 1H), 6.93 (s, 1H), 6.65 (d, *J* = 2.2 Hz, 1H), 4.80 (d, *J* = 9.9 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 3H), 2.09 – 1.97 (m, 1H), 1.07 – 0.93 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.5, 138.6, 135.1, 134.9, 132.3, 132.0, 130.9, 129.4, 129.4, 129.2, 128.7, 128.5, 128.5, 127.3, 125.2 (q, *J* = 278.8 Hz), 124.7, 123.8, 83.9, 64.8 (q, *J* = 3.4 Hz), 40.2 (q, *J* = 28.6 Hz), 21.5, 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -64.00. **IR** (in KBr): 3416, 3128, 2362, 1598, 1460, 1400, 1200, 1088, 875, 741, 584 cm⁻¹. **HRMS** (ESI) for: C₂₄H₂₁ClF₃NO₃S [M + H]⁺: calcd: 496.0956, found: 496.0954.

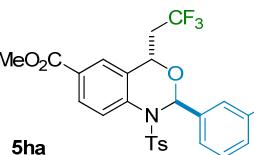
6-bromo-2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5fa)

5fa  78.9 mg, white solid, 73% yield in 4 h, d.r. > 19:1, mp 173–175 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.85 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.42 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.25 (d, *J* = 6.9 Hz, 2H), 7.18 – 7.13 (m, 3H), 7.05 (d, *J* = 6.6 Hz, 1H), 6.93 (s, 1H), 6.80 (d, *J* = 1.8 Hz, 1H), 4.81 (d, *J* = 9.9 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 3H), 2.10 – 1.98 (m, 1H), 1.09 – 0.95 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.5, 138.6, 135.1, 135.0, 132.6, 131.4, 131.2, 129.4, 128.7, 128.4, 127.7, 127.3, 125.2 (q, *J* = 278.8 Hz), 123.8, 120.2, 83.9, 64.7 (q, *J* = 3.4 Hz), 40.2 (q, *J* = 28.5 Hz), 21.5, 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -63.98. **IR** (in KBr): 3415, 3113, 2860, 2362, 1616, 1480, 1352, 1134, 1053, 836, 689, 582 cm⁻¹. **HRMS** (ESI) for: C₂₄H₂₁BrF₃NO₃S [M + H]⁺: calcd: 540.0450, found: 540.0449.

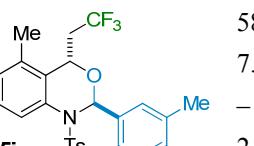
2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine-6-carbonitrile (5ga)

5ga  75.9 mg, white solid, 78% yield in 4 h, d.r. > 19:1, mp 215–216 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 8.14 (d, *J* = 8.6 Hz, 1H), 7.59 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.25 (m, 2H), 7.19 – 7.11 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.01 (s, 1H), 6.98 (s, 1H), 4.87 (d, *J* = 9.6 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 3H), 2.18 – 2.05 (m, 1H), 1.25 – 1.11 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 145.0, 138.9, 137.9, 135.0, 134.6, 131.6, 130.3, 129.7, 129.6, 128.9, 128.3, 128.0, 127.2, 125.1 (q, *J* = 278.8 Hz), 123.7, 117.7, 110.2, 84.0, 64.7 (q, *J* = 3.3 Hz), 40.1 (q, *J* = 28.7 Hz), 21.5, 21.5. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -63.79. **IR** (in KBr): 3420, 3093, 2877, 2235, 1609, 1492, 1290, 1220, 1128, 786, 587 cm⁻¹. **HRMS** (ESI) for: C₂₅H₂₁F₃N₂O₃S [M + H]⁺: calcd: 487.1298, found: 487.1297.

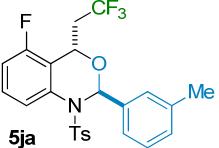
methyl-2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine-6-carboxylate (5ha)

5ha  81.0 mg, white solid, 78% yield in 4 h, d.r. > 19:1, mp 134–136 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 8.08 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.37 (s, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 4.9 Hz, 3H), 7.03 (s, 1H), 6.98 (s, 1H), 4.89 (d, *J* = 10.0 Hz, 1H), 3.85 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H), 2.20 – 2.11 (m, 1H), 1.16 – 1.02 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 165.9, 144.6, 138.6, 137.7, 135.3, 135.0, 129.4, 129.2, 129.1, 128.7, 128.3, 128.1, 127.4, 127.3, 126.3, 125.3 (q, *J* = 278.8 Hz), 123.8, 84.0, 65.1 (q, *J* = 3.3 Hz), 52.3, 40.2 (q, *J* = 28.5 Hz), 21.5, 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -63.87. **IR** (in KBr): 3420, 3105, 2863, 1724, 1355, 1268, 1137, 1044, 812, 581 cm⁻¹. **HRMS** (ESI) for: C₂₆H₂₄F₃NO₅S [M + H]⁺: calcd: 520.1400, found: 520.1403.

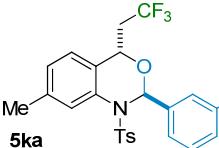
5-methyl-2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5ia)

5ia  58.0 mg, white solid, 61% yield in 4 h, d.r. > 19:1, mp 176–179 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.78 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.14 – 7.08 (m, 3H), 6.98 (d, *J* = 6.9 Hz, 1H), 6.91 (s, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 5.00 (d, *J* = 12 Hz, 1H), 2.38 (s, 3H), 2.24 (s, 3H), 1.92 (s, 3H), 1.89 – 1.83 (m, 1H), 0.45 – 0.31 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.4, 138.3, 136.3, 136.00, 133.7, 133.6, 129.5, 129.5, 128.9, 128.4, 128.3, 127.9, 127.0, 126.0 (q, *J* = 278.8 Hz), 124.3, 123.4, 83.4, 65.0 (q, *J* = 3.2 Hz), 39.0 (q, *J* = 27.7 Hz), 21.5, 21.4, 18.5. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -64.59. **IR** (in KBr): 3450, 3123, 2971, 1603, 1468, 1306, 1132, 815, 678, 572 cm⁻¹. **HRMS** (ESI) for: C₂₅H₂₄F₃NO₃S [M + H]⁺: calcd: 476.1502, found: 476.1494.

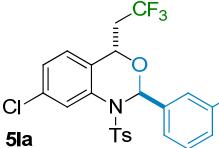
5-fluoro-2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5ja)


5ja 71.0 mg, white solid, 74% yield in 4 h, d.r. > 19:1, mp 135–137 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.80 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.27 – 7.24 (m, 2H), 7.15 (d, *J* = 5.2 Hz, 3H), 7.04 (s, 1H), 6.95 (s, 1H), 6.80 (t, *J* = 8.9 Hz, 1H), 4.96 (d, *J* = 10.1 Hz, 1H), 2.39 (s, 3H), 2.36 – 2.30 (m, 1H), 2.26 (s, 3H), 0.81 – 0.67 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 159.2, 156.7, 144.6, 138.6, 135.2 (d, *J* = 22.4 Hz), 135.2 (d, *J* = 5.5 Hz), 129.5, 129.3, 129.1 (d, *J* = 9.8 Hz), 128.7, 128.4, 127.2, 125.4 (q, *J* = 278.8 Hz), 123.7, 123.6 (d, *J* = 3.3 Hz), 117.6 (d, *J* = 15.6 Hz), 113.6 (d, *J* = 21.2 Hz), 83.9, 62.3 (q, *J* = 3.6 Hz), 38.4 – 37.5 (m), 21.5, 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -63.82, -115.05. **IR** (in KBr): 3419, 3127, 1619, 1473, 1360, 1124, 1076, 1028, 808, 680, 604 cm⁻¹. **HRMS** (ESI) for: C₂₄H₂₁F₄NO₃S [M + H]⁺: calcd: 480.1251, found: 480.1255.

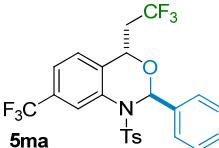
7-methyl-2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5ka)


5ka 59.9 mg, white solid, 63% yield in 4 h, d.r. > 19:1, mp 202–205 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 7.76 (s, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.12 (m, 5H), 7.01 (d, *J* = 6.8 Hz, 1H), 6.91 (d, *J* = 10.8 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 4.81 (d, *J* = 10.0 Hz, 1H), 2.38 (s, 6H), 2.26 (s, 3H), 2.08 – 1.96 (m, 1H), 1.01 – 0.85 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.1, 138.4, 138.1, 135.6, 135.5, 133.1, 129.2, 129.1, 128.6, 128.5, 128.0, 127.8, 127.4, 126.3, 125.5 (q, *J* = 278.8 Hz), 124.4, 123.8, 83.9, 65.0 (q, *J* = 3.4 Hz), 40.4 (q, *J* = 28.1 Hz), 21.5, 21.4, 21.3. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -63.99. **IR** (in KBr): 3417, 3131, 2361, 1618, 1400, 1292, 1217, 1167, 927, 770, 657, 581 cm⁻¹. **HRMS** (ESI) for: C₂₅H₂₄F₃NO₃S [M + H]⁺: calcd: 476.1502, found: 476.1500.

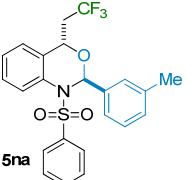
7-chloro-2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5la)


5la 71.4 mg, white solid, 72% yield in 4 h, d.r. > 19:1, mp 209–211 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 8.01 (d, *J* = 2.1 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 9.3 Hz, 2H), 7.19 – 7.13 (m, 3H), 7.08 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.05 (d, *J* = 7.0 Hz, 1H), 6.93 (s, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 4.82 (d, *J* = 9.1 Hz, 1H), 2.40 (s, 3H), 2.28 (s, 3H), 2.08 – 1.96 (m, 1H), 1.09 – 0.95 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.5, 138.7, 135.2, 135.0, 134.6, 133.7, 129.4, 128.8, 128.5, 127.7, 127.4, 127.3, 127.0, 125.8, 125.2 (q, *J* = 278.8 Hz), 123.9, 83.9, 64.9 (q, *J* = 3.3 Hz), 40.3 (q, *J* = 28.4 Hz), 21.5, 21.7. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -63.95. **IR** (in KBr): 3419, 3115, 1600, 1489, 1252, 1207, 1128, 977, 813, 694, 580 cm⁻¹. **HRMS** (ESI) for: C₂₄H₂₁ClF₃NO₃S [M + H]⁺: calcd: 496.0956, found: 496.0951.

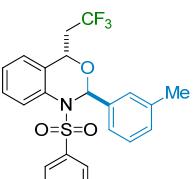
2-(m-tolyl)-1-tosyl-4-(2,2,2-trifluoroethyl)-7-(trifluoromethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5ma)


5ma 63.5 mg, white solid, 60% yield in 4 h, d.r. > 19:1, mp 171–173 °C. **¹H NMR** (400 MHz, CDCl₃) δ (ppm) 8.28 (s, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.13 (m, 3H), 7.05 (d, *J* = 6.9 Hz, 1H), 6.98 (s, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.89 (d, *J* = 10.0 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H), 2.14 – 2.03 (m, 1H), 1.18 – 1.04 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ (ppm) 144.7, 138.8, 135.1, 134.8, 134.2, 132.9, 130.7 (d, *J* = 33.3 Hz), 129.5, 129.4, 128.8, 128.4, 127.3, 125.4, 125.2 (q, *J* = 278.8 Hz), 124.5 (q, *J* = 3.9 Hz), 123.8, 123.4 (q, *J* = 273.7 Hz), 123.1 (q, *J* = 3.5 Hz), 84.0, 65.0 (q, *J* = 3.4 Hz), 40.2 (q, *J* = 28.7 Hz), 21.5, 21.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ (ppm) -62.70, -63.96. **IR** (in KBr): 3417, 3140, 2879, 1597, 1399, 1330, 1130, 913, 757, 669, 579 cm⁻¹. **HRMS** (ESI) for: C₂₅H₂₁F₆NO₃S [M + H]⁺: calcd: 530.1219, found: 530.1211.

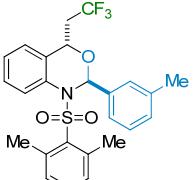
1-(phenylsulfonyl)-2-(m-tolyl)-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5na)


5na 59.1 mg, white solid, 66% yield in 4 h, d.r. > 19:1, mp 158–160 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 7.98 (d, *J* = 9.2 Hz, 1H), 7.64 (d, *J* = 9.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.19 – 7.08 (m, 4H), 7.02 (d, *J* = 7.0 Hz, 1H), 6.97 (s, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.84 (d, *J* = 9.8 Hz, 1H), 2.25 (s, 3H), 2.12 – 2.00 (m, 1H), 1.05 – 0.91 (m, 1H). **13C NMR** (100 MHz, CDCl₃) δ (ppm) 138.5, 138.3, 135.3, 133.2, 133.1, 129.3, 129.2, 128.6, 128.4, 128.2, 127.7, 127.4, 126.8, 125.2 (q, *J* = 278.8 Hz), 124.6, 123.8, 83.9, 65.0 (q, *J* = 3.4 Hz), 40.3 (q, *J* = 28.2 Hz), 21.5. **19F NMR** (376 MHz, CDCl₃) δ (ppm) -63.88. **IR** (in KBr): 3416, 3125, 2885, 1606, 1492, 1388, 1257, 1086, 973, 726, 595 cm⁻¹. **HRMS** (ESI) for: C₂₃H₂₀F₃NO₃S [M + H]⁺: calcd: 448.1189, found: 448.1187.

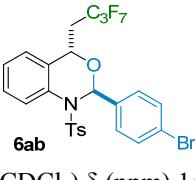
1-((4-fluorophenyl)sulfonyl)-2-(m-tolyl)-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5oa)


5oa 79.1 mg, white solid, 85% yield in 4 h, d.r. > 19:1, mp 155–157 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 7.98 (d, *J* = 9.1 Hz, 1H), 7.69 – 7.66 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.19 – 7.07 (m, 6H), 7.03 (d, *J* = 6.4 Hz, 1H), 6.97 (s, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 4.87 (d, *J* = 9.6 Hz, 1H), 2.26 (s, 3H), 2.23 – 2.14 (m, 1H), 1.24 – 1.10 (m, 1H). **13C NMR** (100 MHz, CDCl₃) δ (ppm) 166.7, 164.2, 138.6, 135.1, 134.4, 133.1, 131.2 (d, *J* = 9.4 Hz), 129.3, 129.1, 128.7, 128.3, 127.5 (d, *J* = 17.2 Hz), 126.9, 125.4 (q, *J* = 278.8 Hz), 124.7, 123.9, 115.9 (d, *J* = 22.6 Hz), 84.1, 65.1 (q, *J* = 3.3 Hz), 40.3 (q, *J* = 28.4 Hz), 21.5. **19F NMR** (376 MHz, CDCl₃) δ (ppm) -63.75, -104.08. **IR** (in KBr): 3417, 3109, 2884, 1593, 1387, 1259, 1205, 1124, 837, 764, 664, 573 cm⁻¹. **HRMS** (ESI) for: C₂₃H₁₉F₄NO₃S [M + H]⁺: calcd: 466.1095, found: 466.1090.

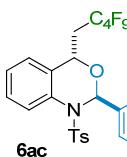
1-(mesylsulfonyl)-2-(m-tolyl)-4-(2,2,2-trifluoroethyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (5pa)


5pa 72.5 mg, white solid, 74% yield in 4 h, d.r. > 19:1, mp 189–191 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 7.63 (d, *J* = 7.6 Hz, 1H), 7.23 – 7.08 (m, 5H), 7.00 (d, *J* = 7.0 Hz, 1H), 6.93 (s, 2H), 6.87 (s, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 4.98 (d, *J* = 9.9 Hz, 1H), 2.46 (s, 6H), 2.28 (s, 3H), 2.25 (s, 3H), 2.23 – 2.14 (m, 1H), 1.52 – 1.44 (m, 1H). **13C NMR** (100 MHz, CDCl₃) δ (ppm) 143.1, 140.9, 138.4, 135.8, 133.5, 133.3, 132.4, 130.3, 129.0, 128.5, 128.1, 127.8, 127.4, 126.8, 125.6 (q, *J* = 278.8 Hz), 125.0, 123.8, 82.8, 65.8 (q, *J* = 3.4 Hz), 41.0 (q, *J* = 28.0 Hz), 23.6, 21.5, 20.8. **19F NMR** (376 MHz, CDCl₃) δ (ppm) -64.10. **IR** (in KBr): 3416, 3130, 2426, 1604, 1400, 1254, 1123, 767, 687, 587 cm⁻¹. **HRMS** (ESI) for: C₂₆H₂₆F₃NO₃S [M + H]⁺: calcd: 490.1658, found: 490.1659.

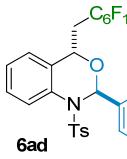
2-(4-bromophenyl)-4-(2,2,3,3,4,4,4-heptafluorobutyl)-1-tosyl-2,4-dihydro-1H-benzo[d][1,3]oxazine (6ab)


6ab 102.7 mg, white solid, 82% yield in 4 h, d.r. > 19:1, mp 110–112 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 7.95 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.14 (t, *J* = 8.1 Hz, 1H), 6.91 (s, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 4.89 (d, *J* = 9.6 Hz, 1H), 2.35 (s, 3H), 2.05 – 1.92 (m, 1H), 1.04 – 0.88 (m, 1H). **13C NMR** (100 MHz, CDCl₃) δ (ppm) 144.5, 135.2, 134.6, 133.2, 132.0, 129.4, 129.2, 128.6, 128.5, 128.4, 128.0, 127.1, 124.8, 122.7, 83.5, 64.4 (t, *J* = 5.05 Hz), 38.0 – 37.3 (m), 21.3. **19F NMR** (376 MHz, CDCl₃) δ (ppm) -80.41 (t, *J* = 11.3 Hz, 3F), -127.88 (d, *J* = 11.5 Hz, 2F), -128.06 (d, *J* = 8.3 Hz, 2F). **IR** (in KBr): 3449, 3141, 2363, 1634, 1400, 1225, 1170, 1114, 574 cm⁻¹. **HRMS** (ESI) for: C₂₅H₁₉BrF₇NO₃S [M + H]⁺: calcd: 626.0230, found: 626.0226.

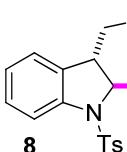
2-(4-bromophenyl)-1-tosyl-4-(2,2,3,3,4,4,5,5,6,6,6-undecafluorohexyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (6ac)

 101.5 mg, white solid, 75% yield in 4 h, d.r. > 19:1, mp 150-152 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 7.95 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.90 (s, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 4.89 (d, *J* = 9.5 Hz, 1H), 2.34 (s, 3H), 2.05 – 1.91 (m, 1H), 1.05 – 0.89 (m, 1H). **13C NMR** (100 MHz, CDCl₃) δ (ppm) 144.4, 135.3, 134.6, 133.2, 132.0, 129.5, 129.2, 128.6, 128.5, 128.4, 128.0, 127.1, 124.8, 122.7, 83.5, 64.5 (d, *J* = 4.5 Hz), 37.8 (t, *J* = 21.0 Hz), 21.2. **19F NMR** (376 MHz, CDCl₃) δ (ppm) -80.98 – -81.05 (m, 3F), -111.33 – -115.12 (m, 2F), -124.55 – -124.75 (m, 2F), -125.89 – -126.04 (m, 2F). **IR** (in KBr): 3447, 3140, 2361, 1634, 1400, 1222, 1165, 1131, 873, 709, 576 cm⁻¹. **HRMS** (ESI) for: C₂₆H₁₉BrF₉NO₃S [M + H]⁺: calcd: 676.0198, found: 676.0199.

2-(4-bromophenyl)-1-tosyl-4-(2,2,3,3,4,4,5,5,6,6,6-undecafluorohexyl)-2,4-dihydro-1H-benzo[d][1,3]oxazine (6ad)

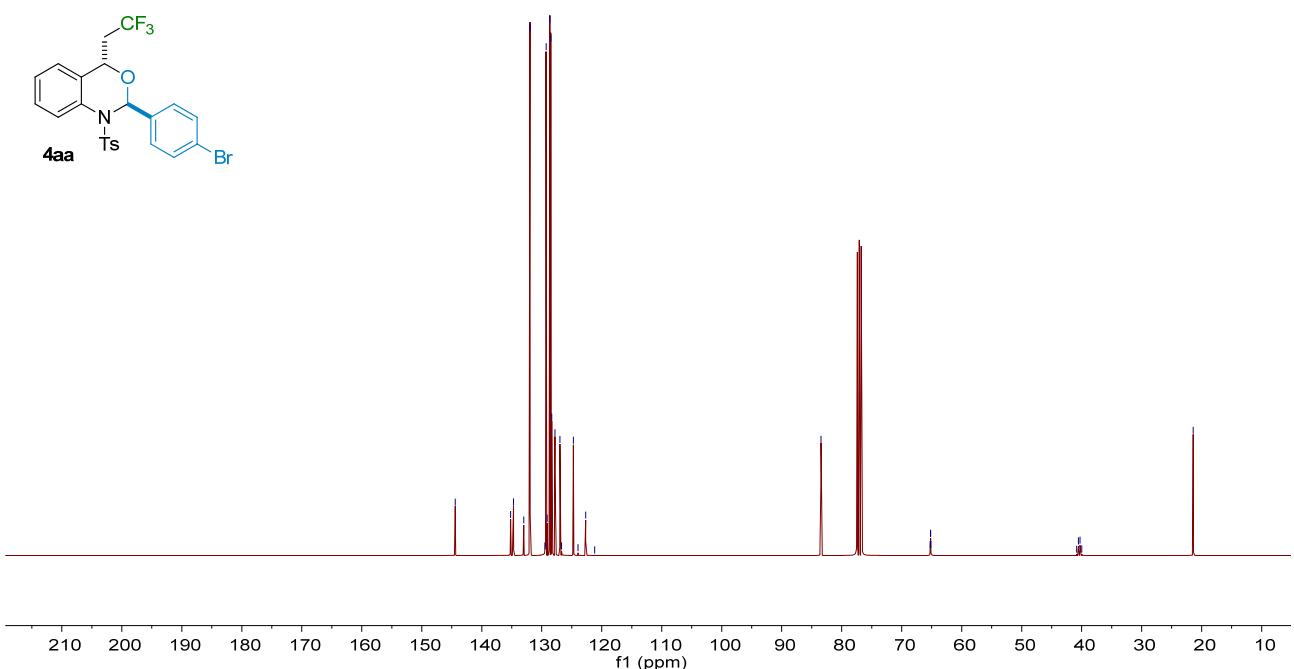
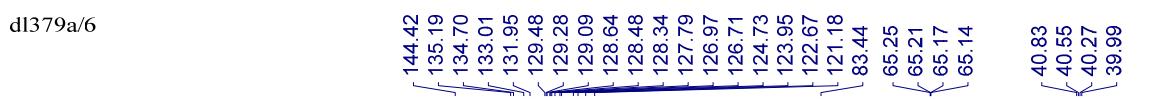
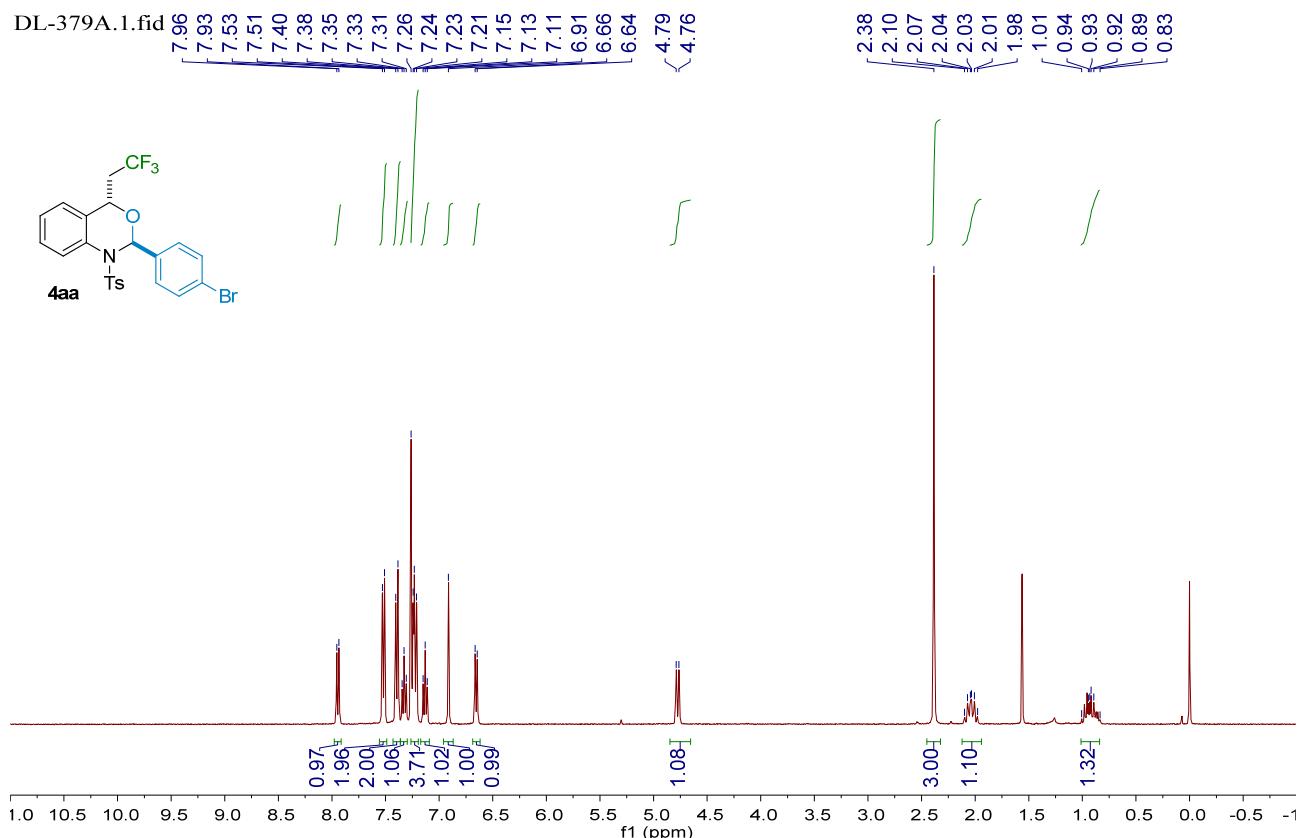
 118.0 mg, white solid, 76% yield in 4 h, d.r. > 19:1, mp 142-144 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 7.95 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.91 (s, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 4.90 (d, *J* = 9.4 Hz, 1H), 2.34 (s, 3H), 2.06 – 1.92 (m, 1H), 1.05 – 0.90 (m, 1H). **13C NMR** (100 MHz, CDCl₃) δ (ppm) 144.4, 135.3, 134.6, 133.2, 132.0, 129.5, 129.3, 128.6, 128.5, 128.4, 128.0, 127.1, 124.8, 122.7, 83.5, 64.5 (d, *J* = 4.5 Hz), 37.9 (t, *J* = 20.9 Hz), 21.1. **19F NMR** (376 MHz, CDCl₃) δ (ppm) -80.72 – -80.79 (m, 3F), -111.13 – -114.89 (m, 2F), -121.88 (s, 2F), -122.86 (s, 2F), -123.63 – -123.82 (m, 2F), -126.10 – -126.21 (m, 2F). **IR** (in KBr): 3417, 3133, 2361, 1636, 1400, 1235, 1165, 815, 690, 575 cm⁻¹. **HRMS** (ESI) for: C₂₈H₁₉BrF₁₃NO₃S [M + H]⁺: calcd: 776.0134, found: 776.0139.

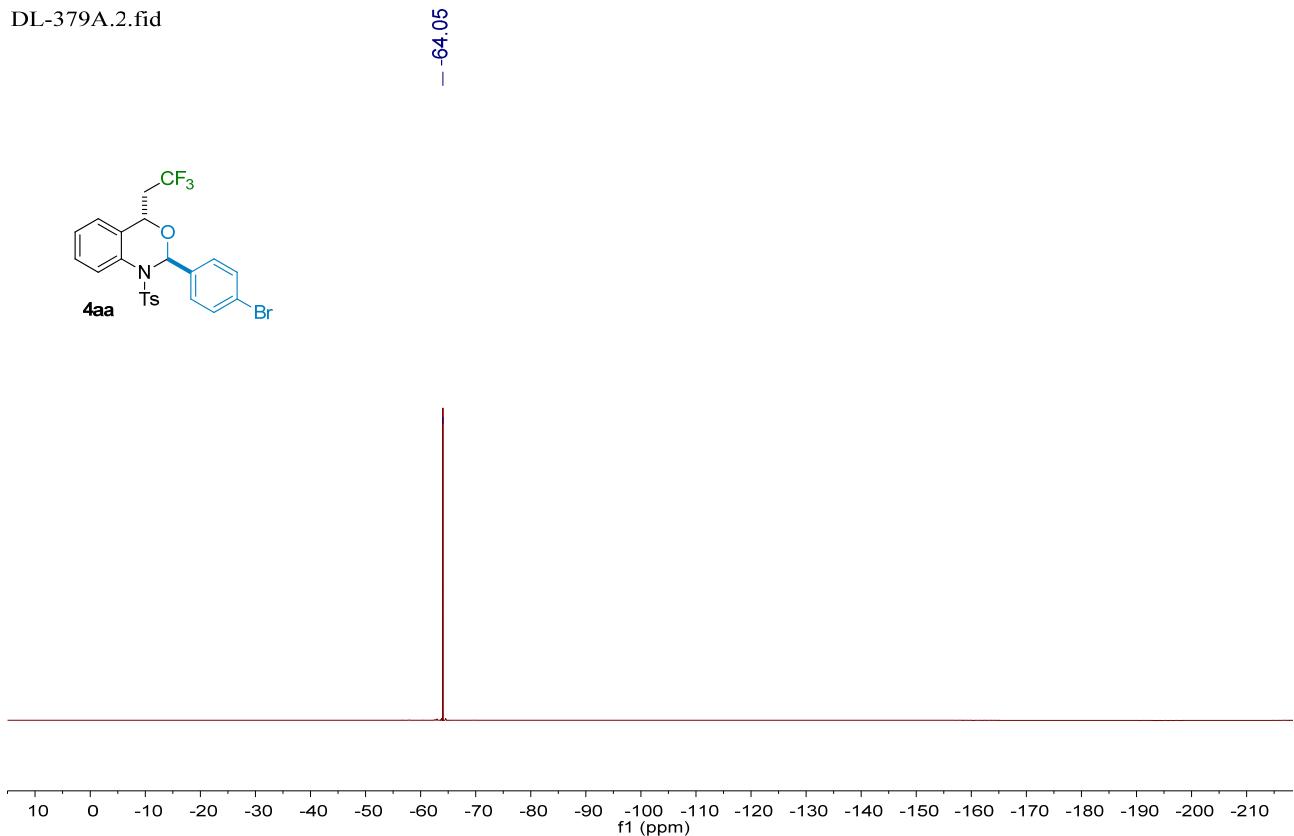
phenyl(1-tosyl-3-(2,2,2-trifluoroethyl)indolin-2-yl)methanone (8)

 66.2 mg, white solid, 72% yield in 4 h, d.r. > 19:1, mp 88-90 °C. **1H NMR** (400 MHz, CDCl₃) δ (ppm) 7.94 (d, *J* = 7.7 Hz, 2H), 7.69 – 7.58 (m, 4H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.30 (dd, *J* = 8.5, 4.7 Hz, 1H), 7.24 (d, *J* = 2.9 Hz, 1H), 7.06 (d, *J* = 3.8 Hz, 2H), 5.52 (d, *J* = 2.4 Hz, 1H), 3.48 – 3.45 (m, 1H), 2.39 (s, 3H), 2.08 – 1.95 (m, 1H), 1.61 – 1.52 (m, 1H). **13C NMR** (100 MHz, CDCl₃) δ (ppm) 194.6, 144.7, 141.1, 134.6, 134.0, 133.7, 131.6, 129.7, 129.1, 128.7, 128.6, 127.0, 125.3 (q, *J* = 276.2 Hz), 124.7, 124.7, 115.8, 68.2, 39.4 (q, *J* = 2.7 Hz), 39.0 (q, *J* = 27.6 Hz), 21.2. **19F NMR** (376 MHz, CDCl₃) δ (ppm) -64.9. **IR** (in KBr): 3356, 1705, 1599, 1385, 1359, 1137, 1005, 959, 584 cm⁻¹. **HRMS** (ESI) for: C₂₄H₂₀NO₃F₃S [M + Na]⁺: calcd: 482.1008, found: 482.1005.

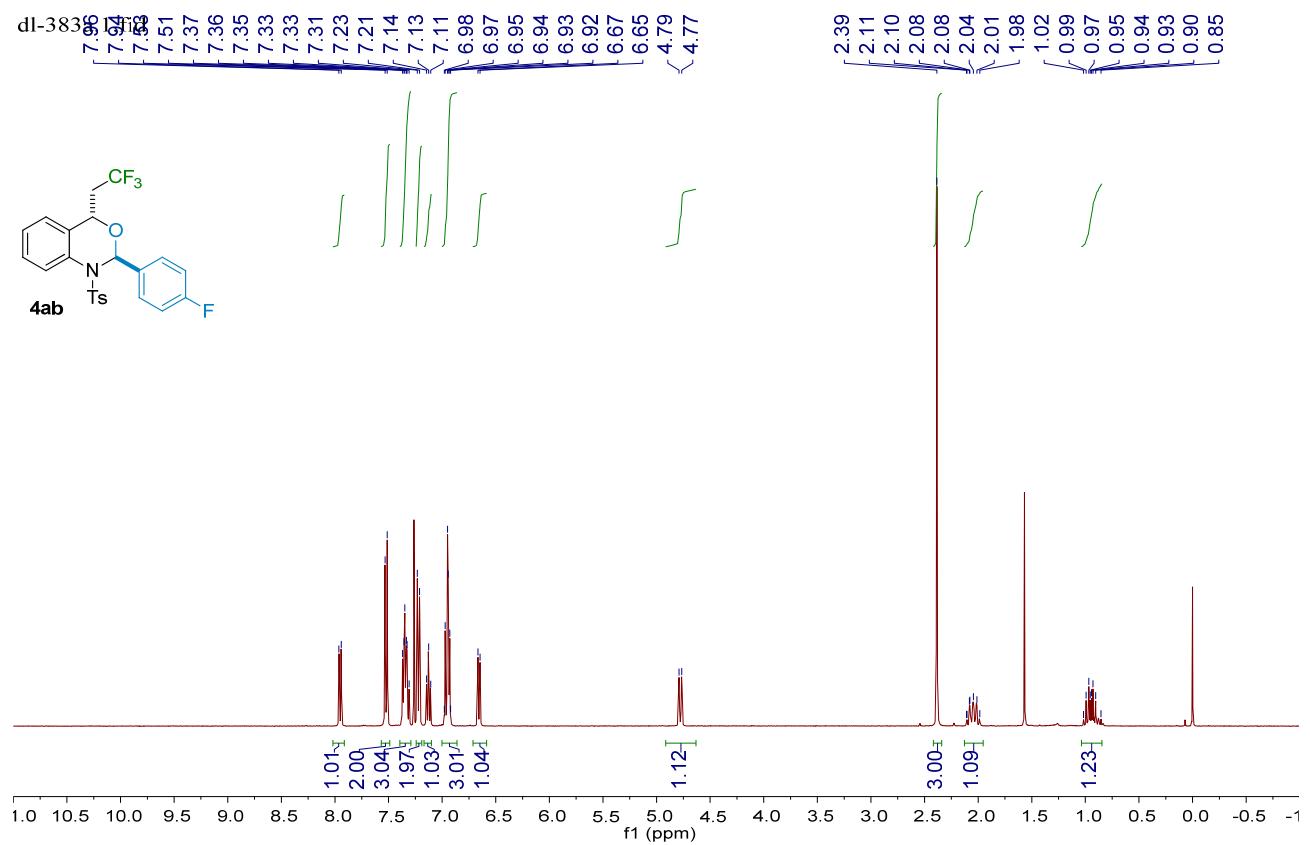
9. Copies of ^1H NMR, ^{13}C NMR and ^{19}F NMR Spectra

^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3) and ^{19}F NMR (376 MHz, CDCl_3) spectra of 4aa

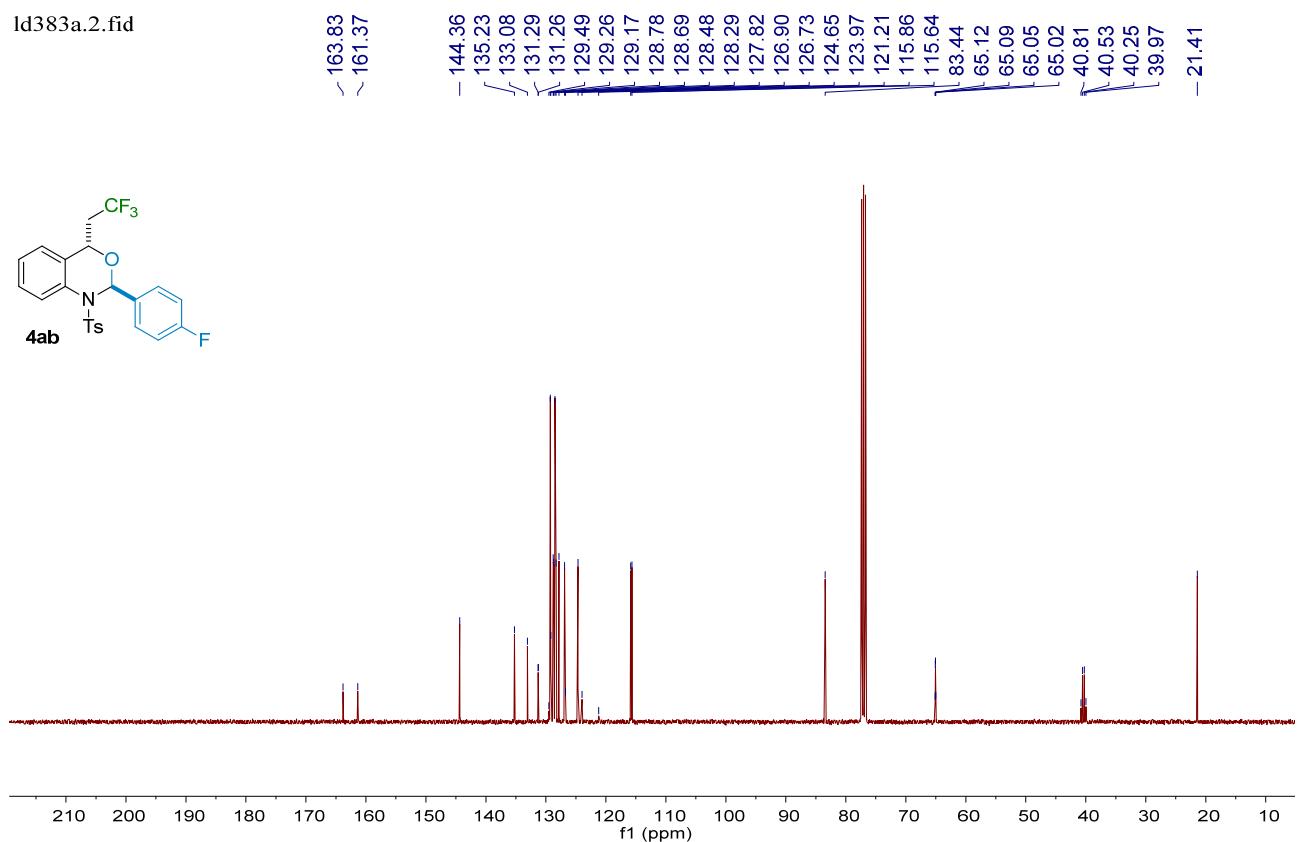




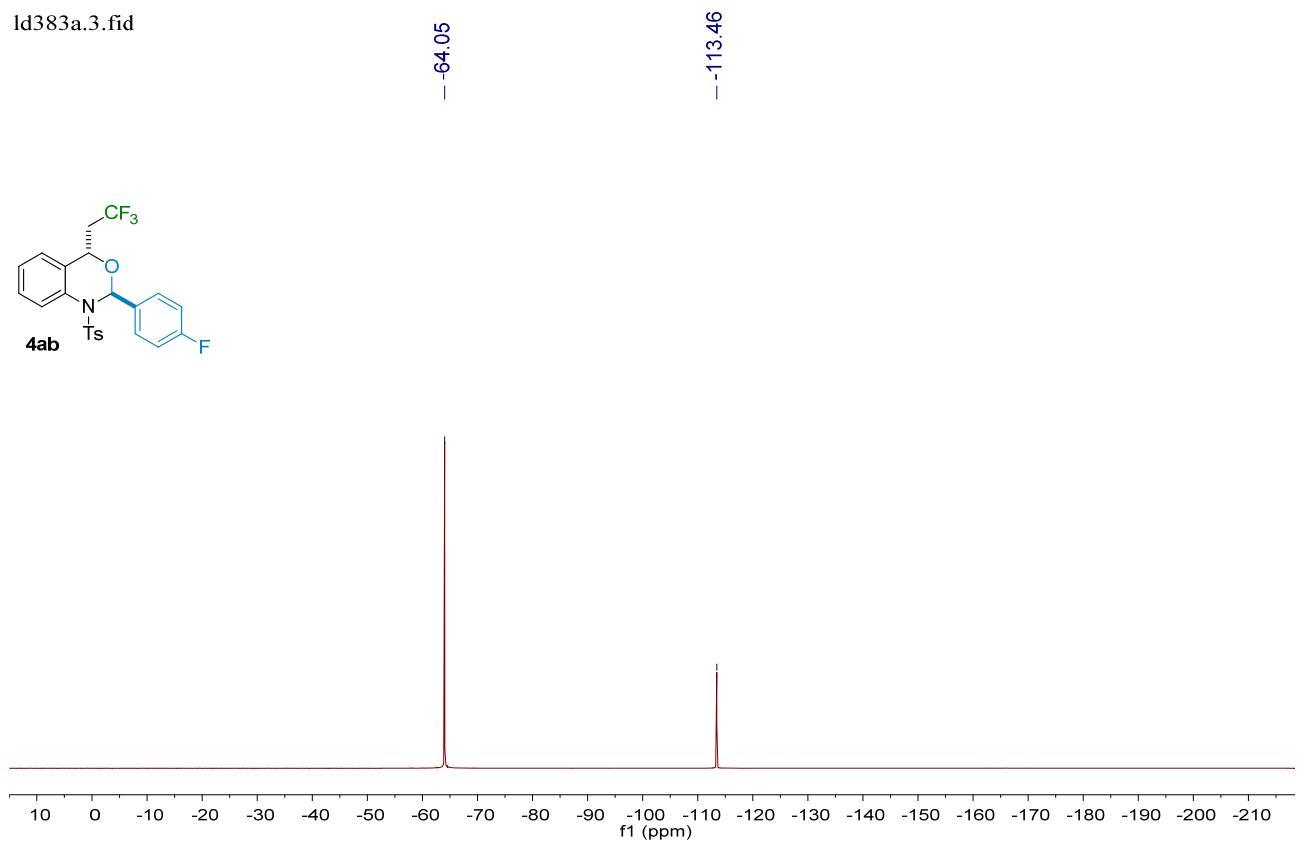
¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of **4ab**



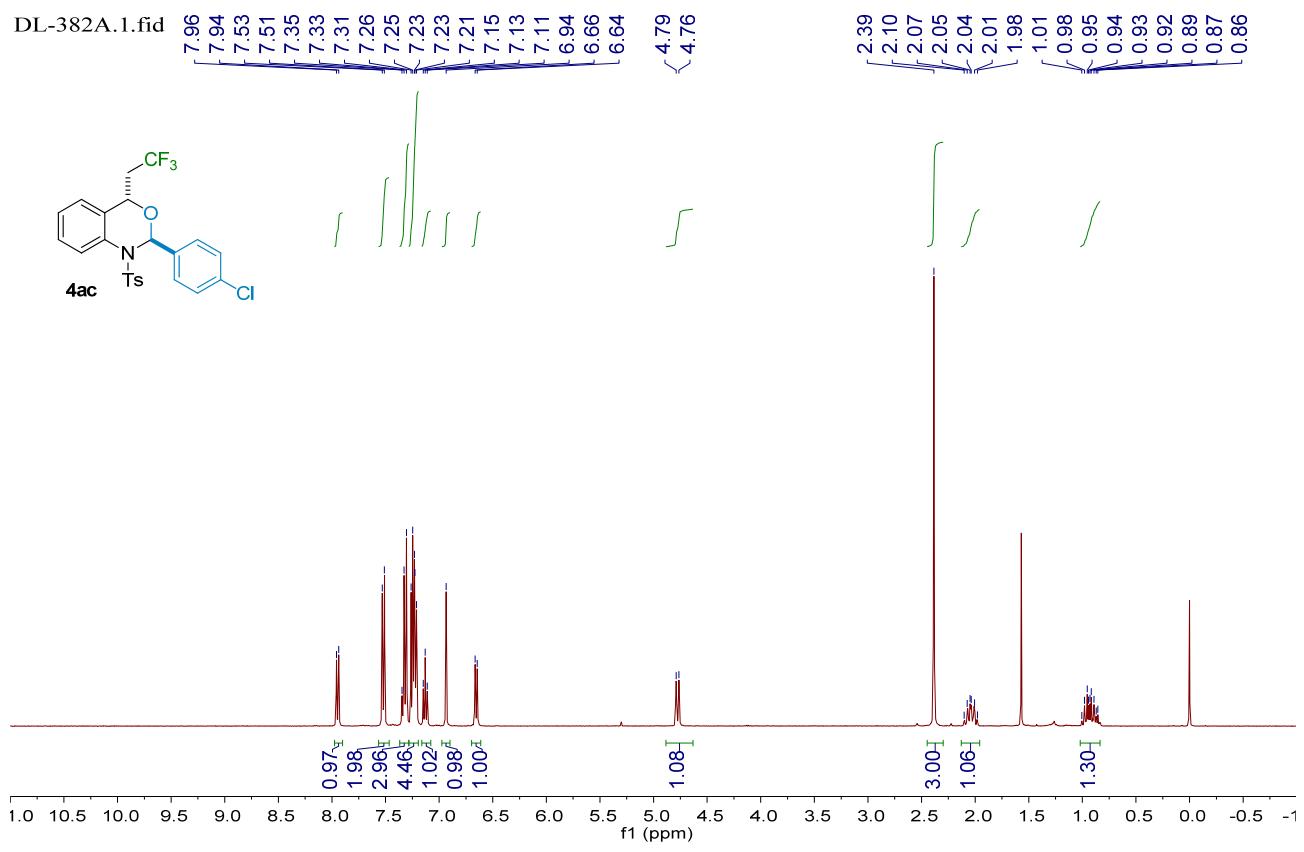
ld383a.2.fid



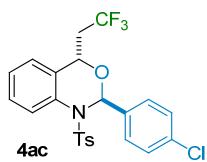
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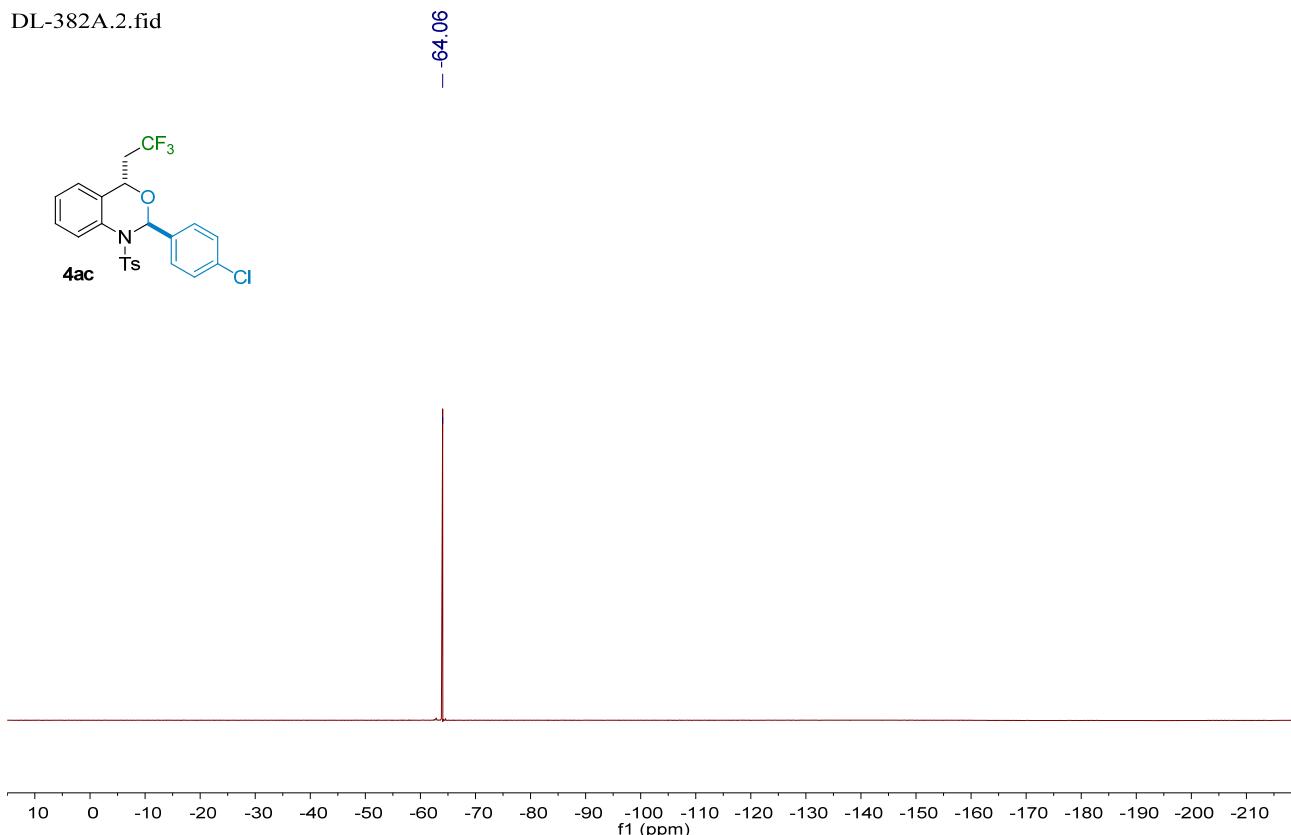


¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of 4ac

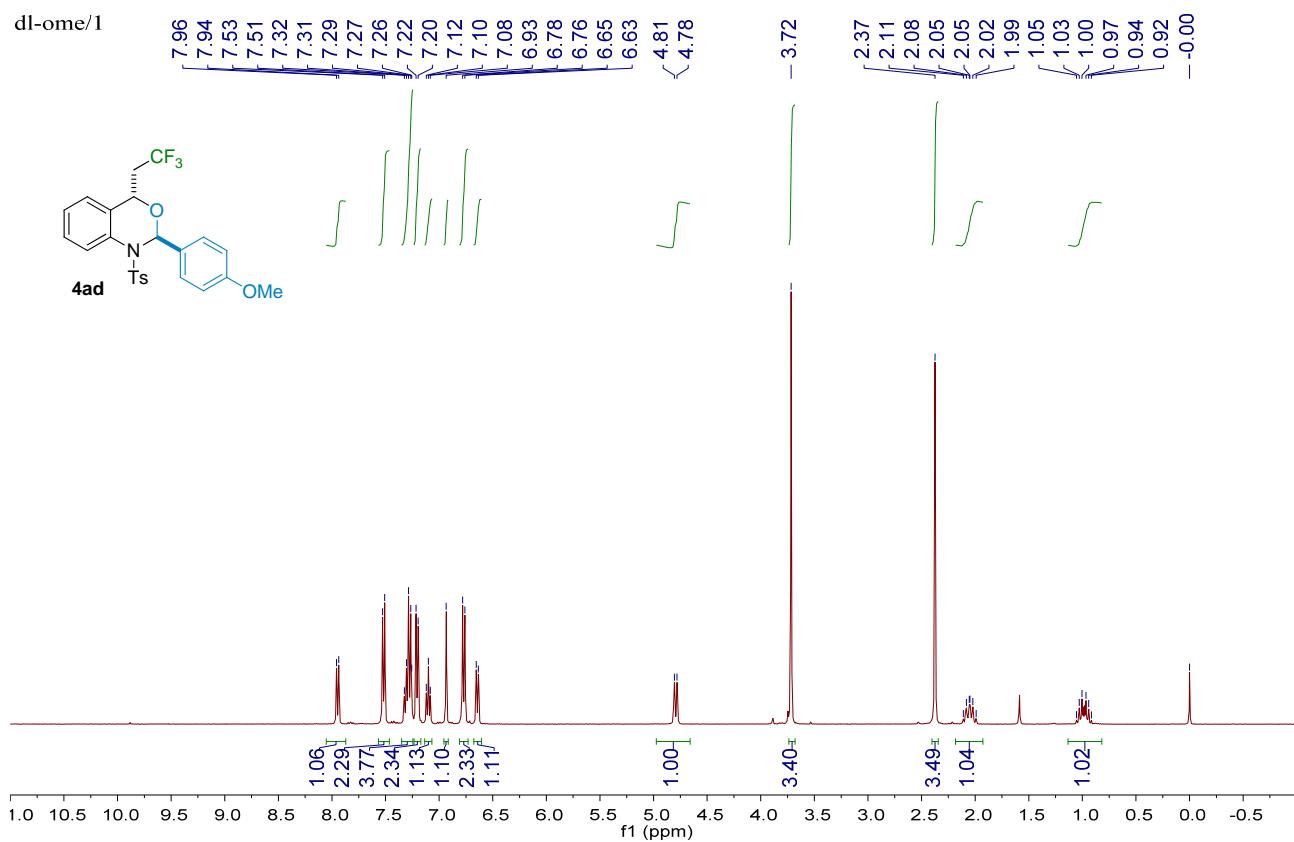


DL-382A.3.fid

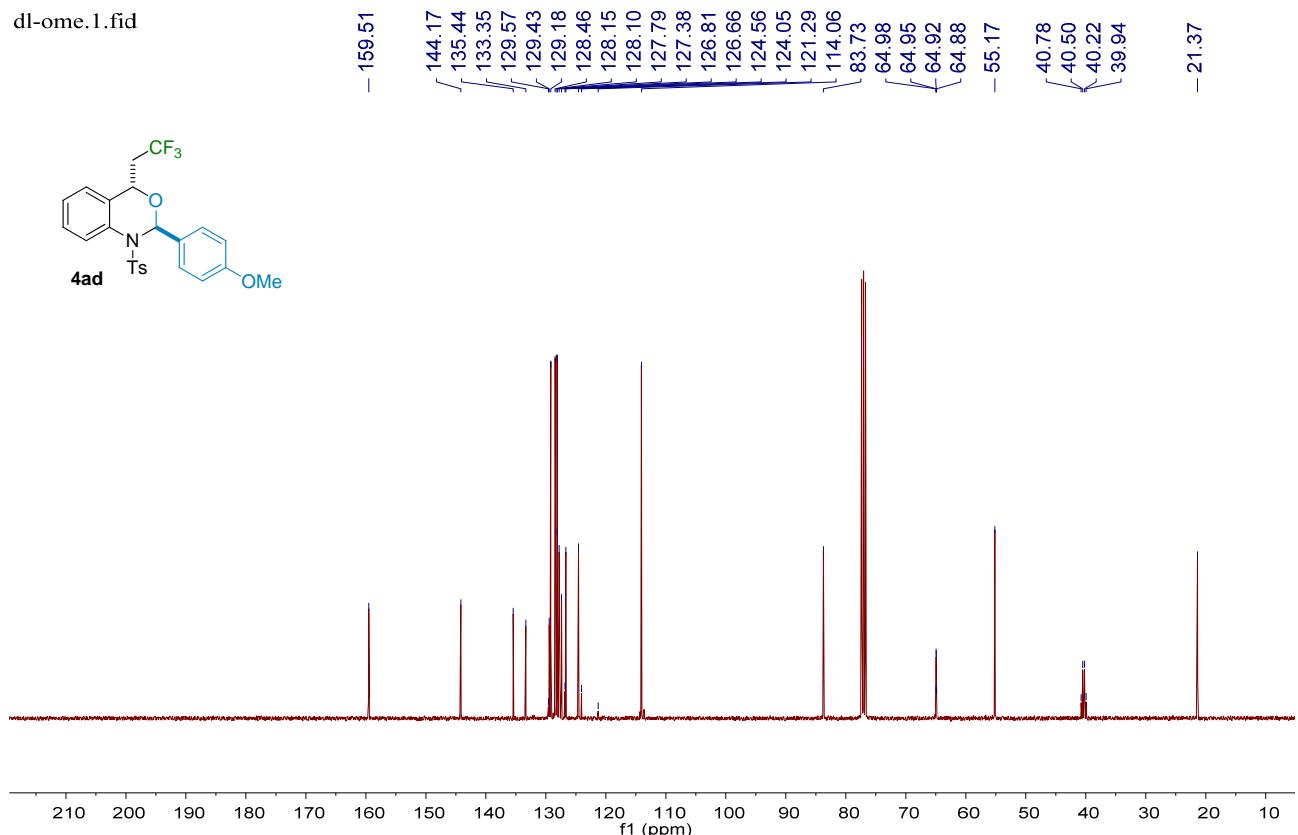




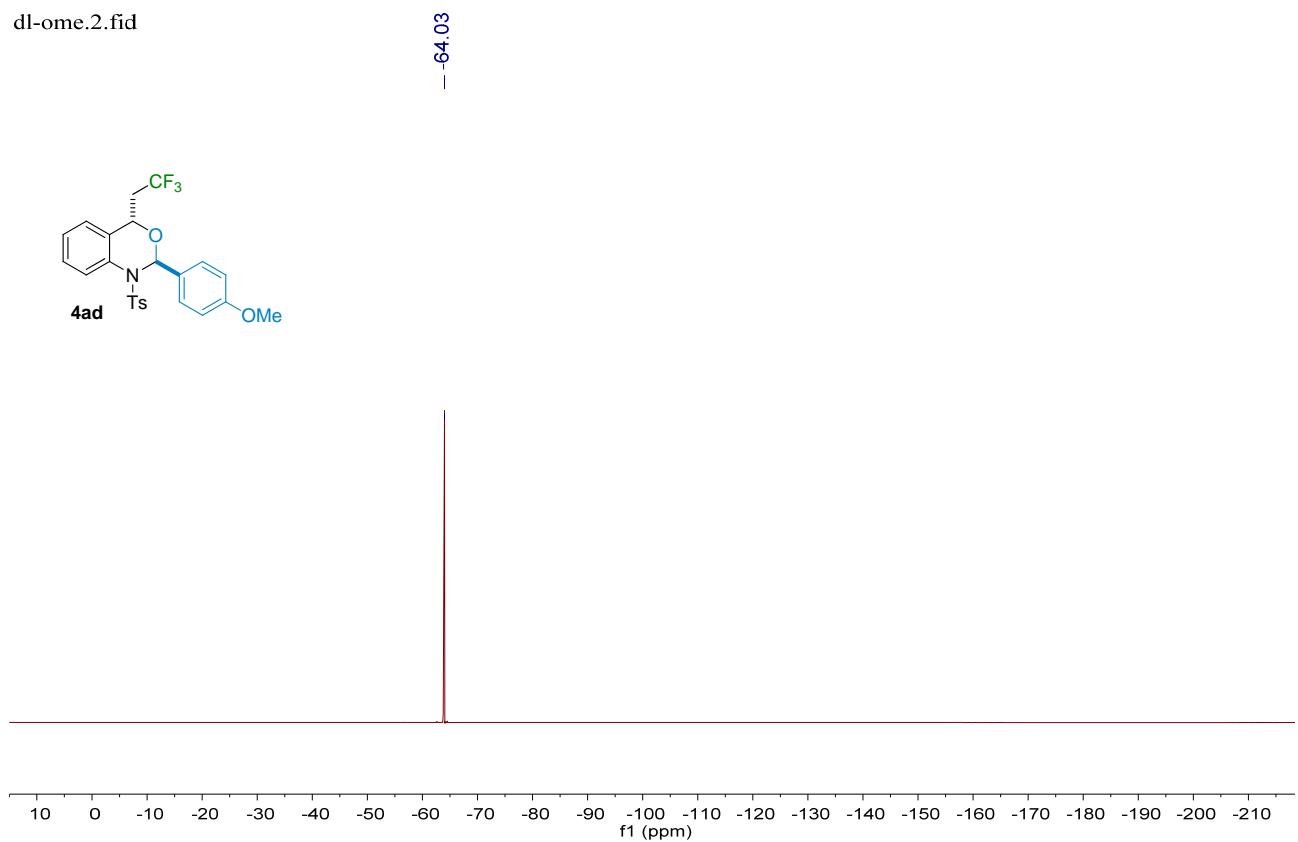
¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of **4ad**



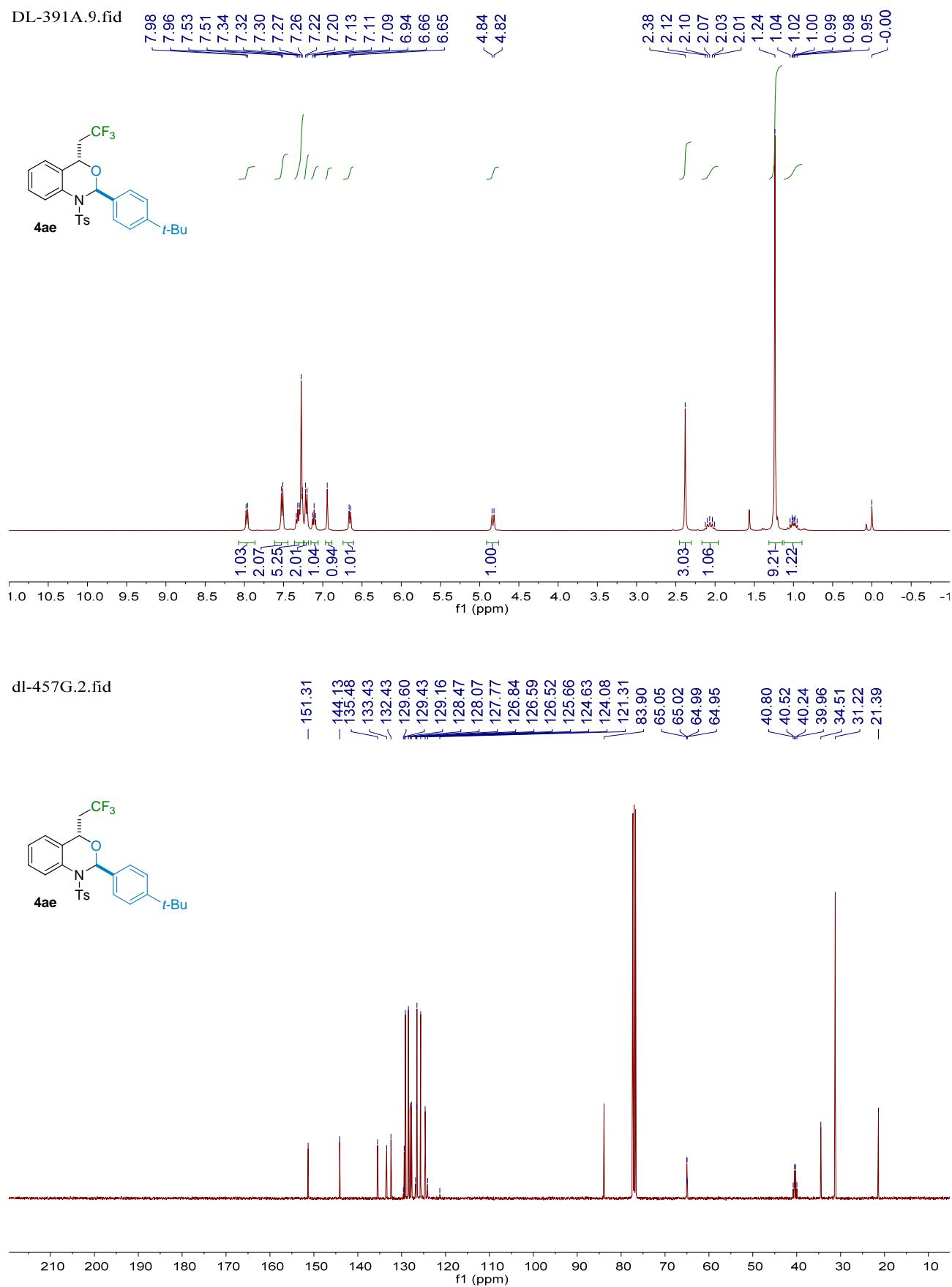
dl-ome.1.fid

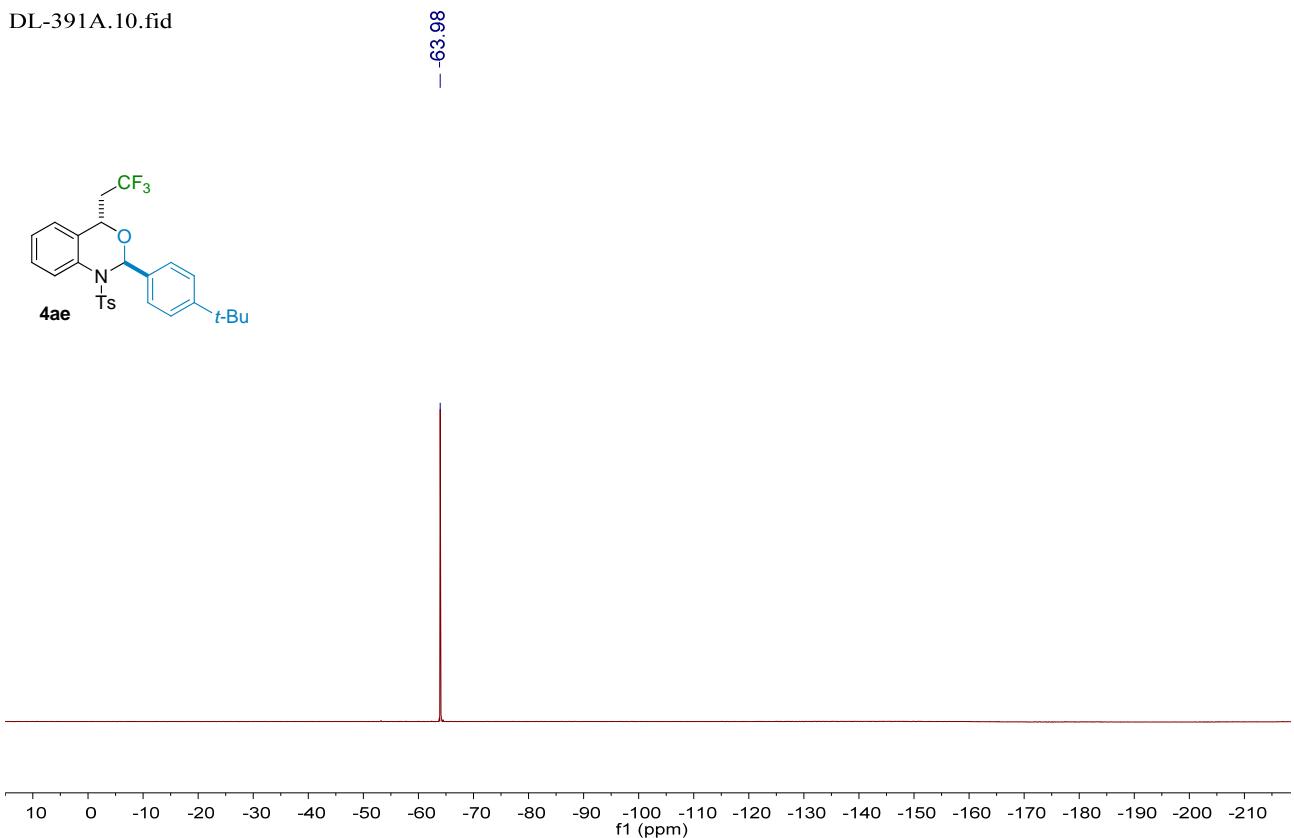


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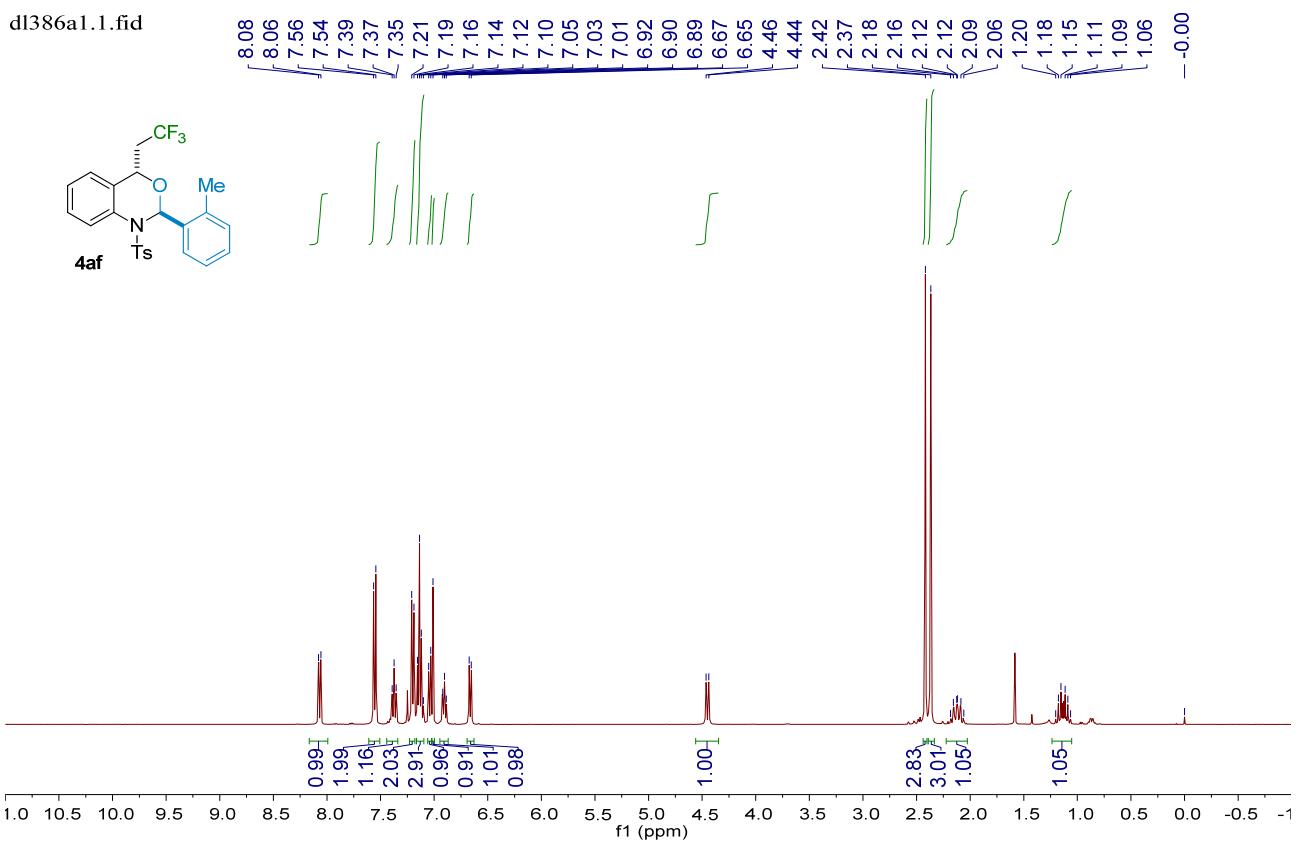


¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of 4ae

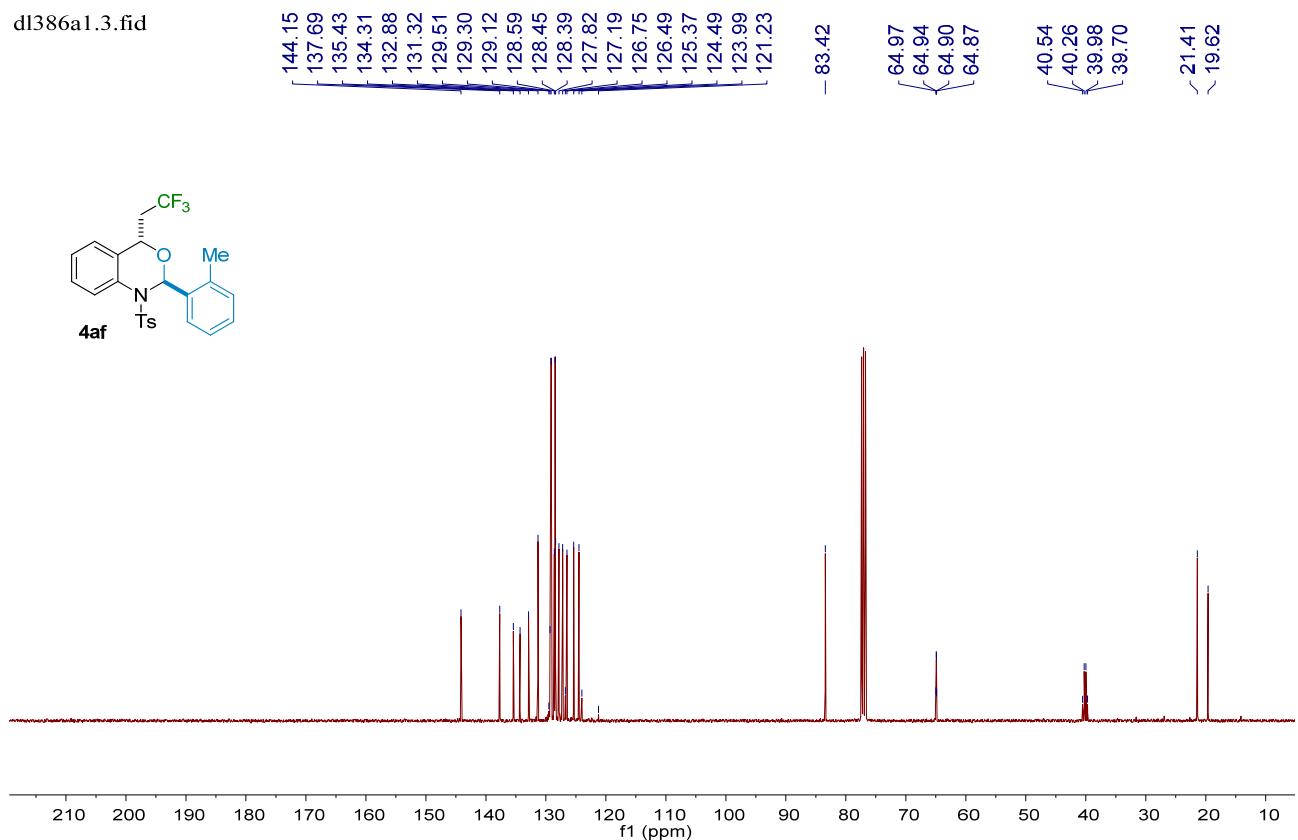




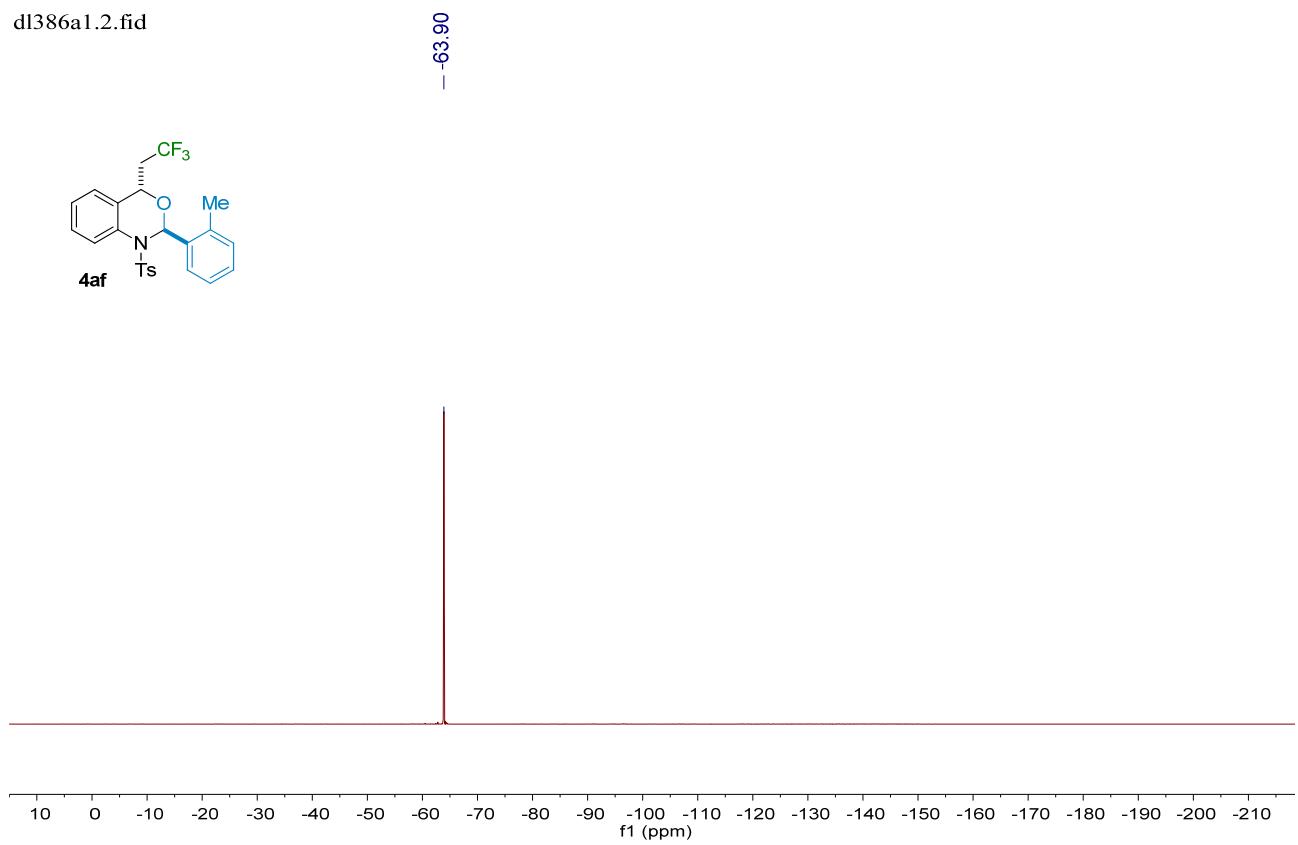
¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of **4af**



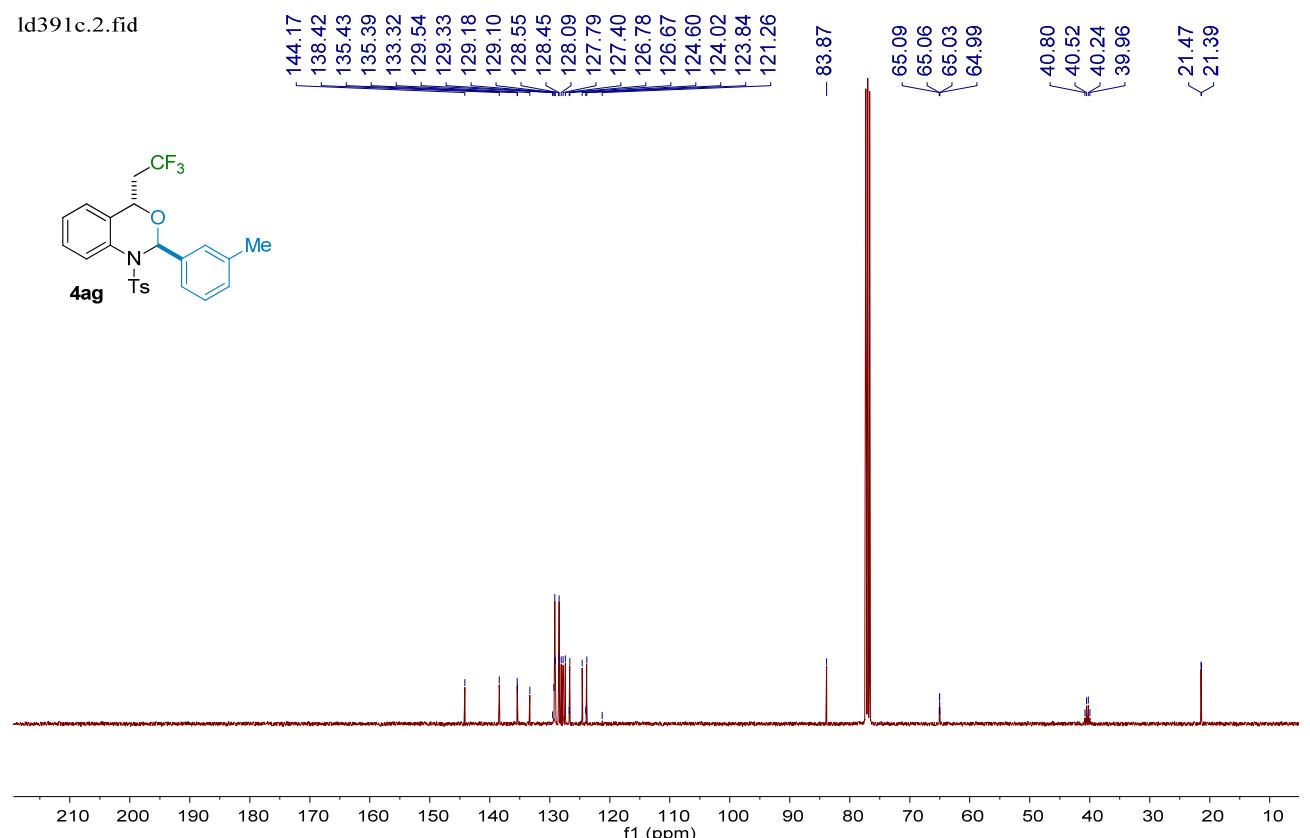
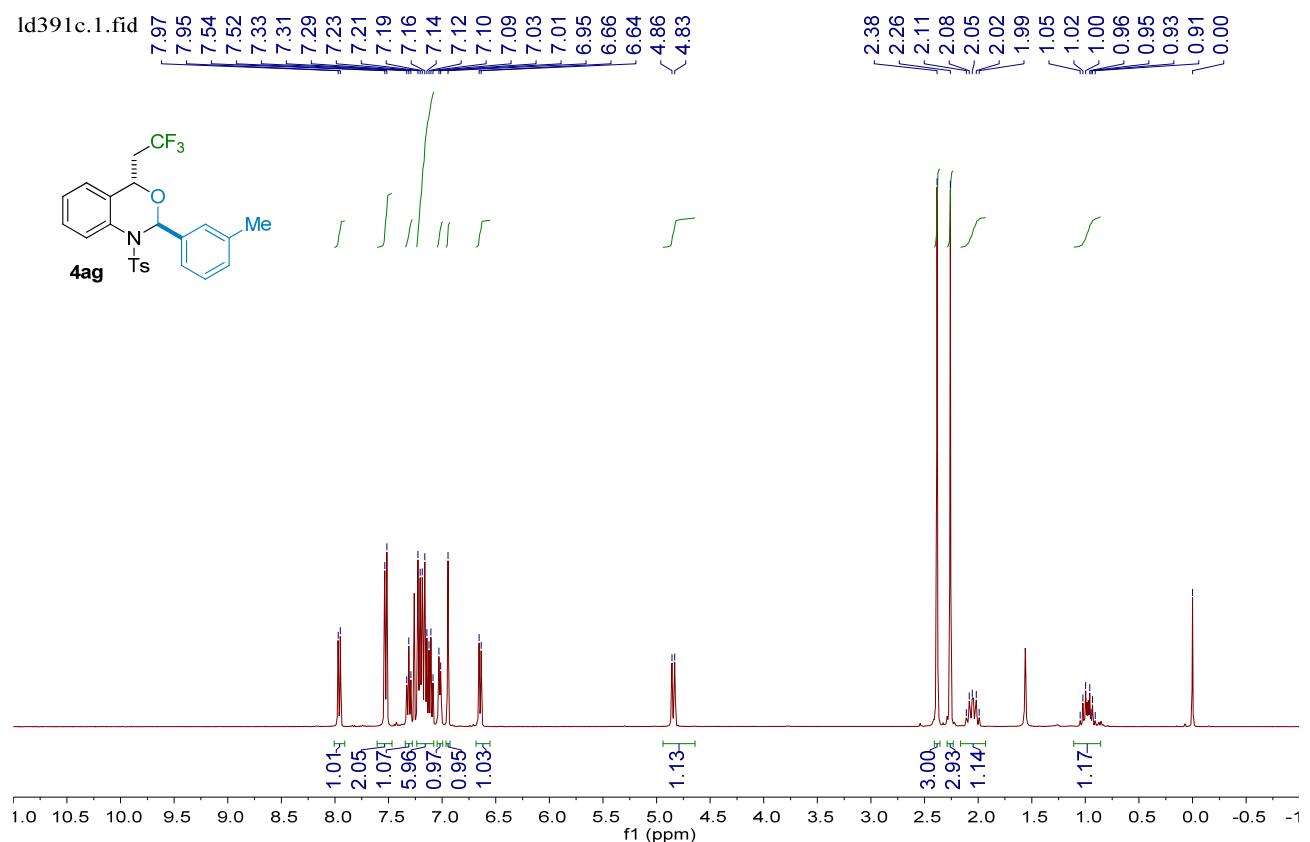
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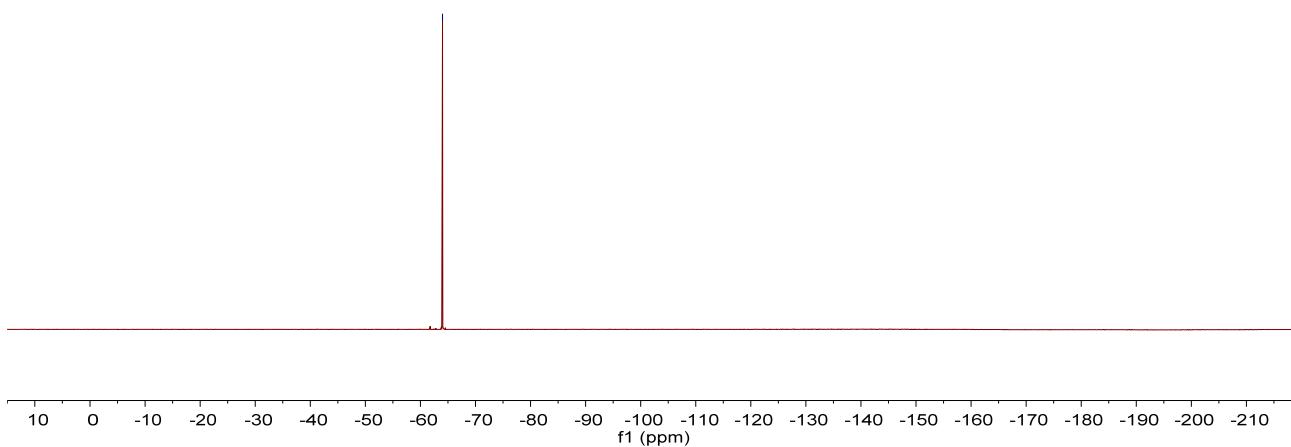
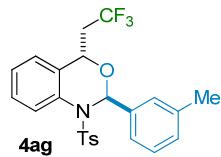


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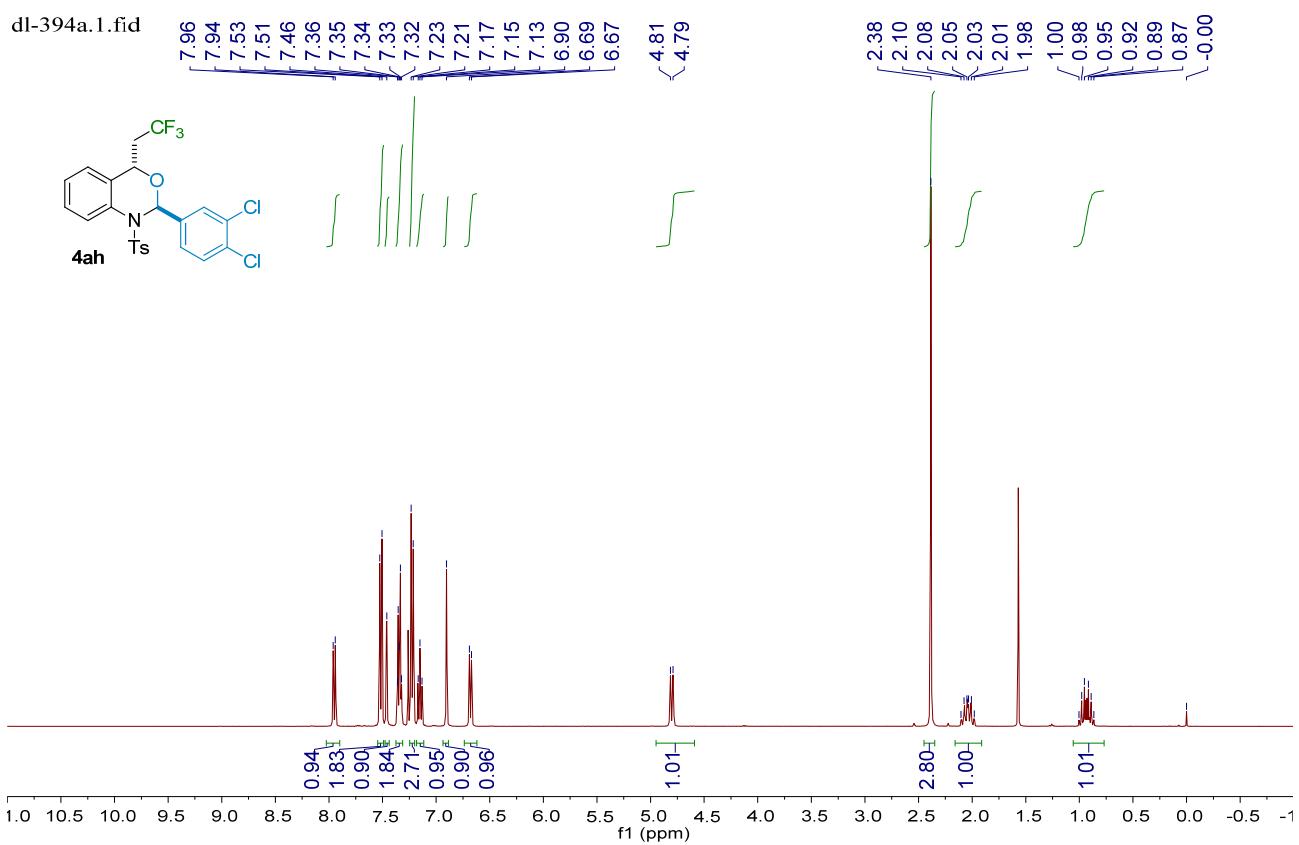


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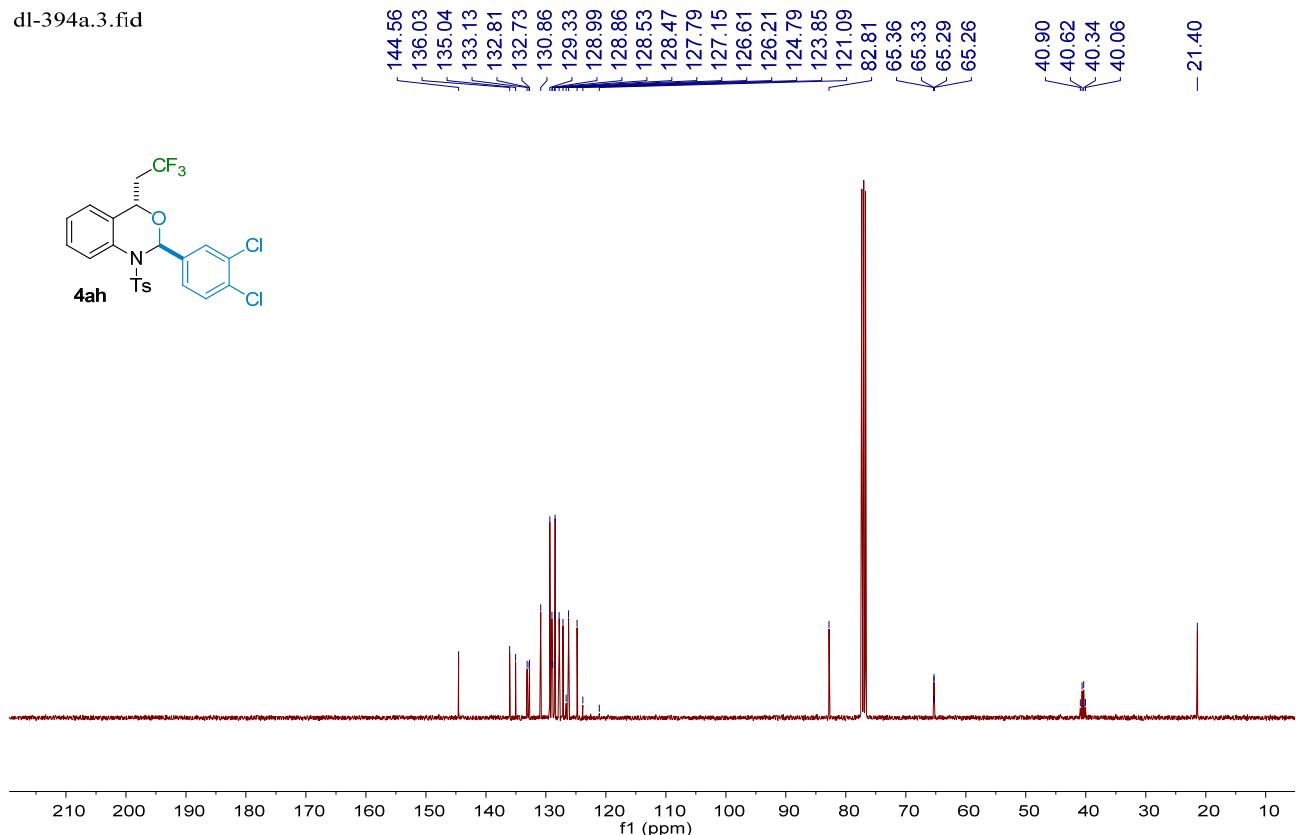
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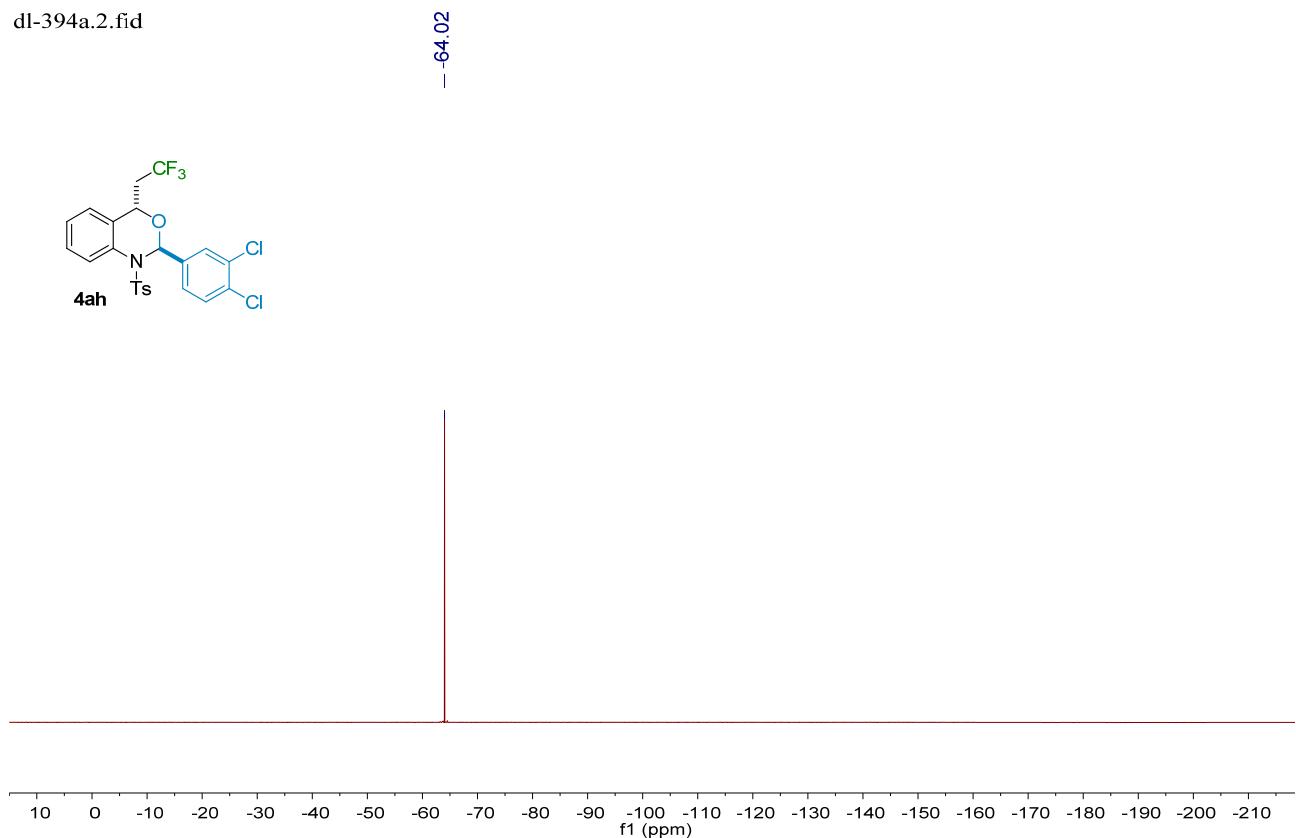
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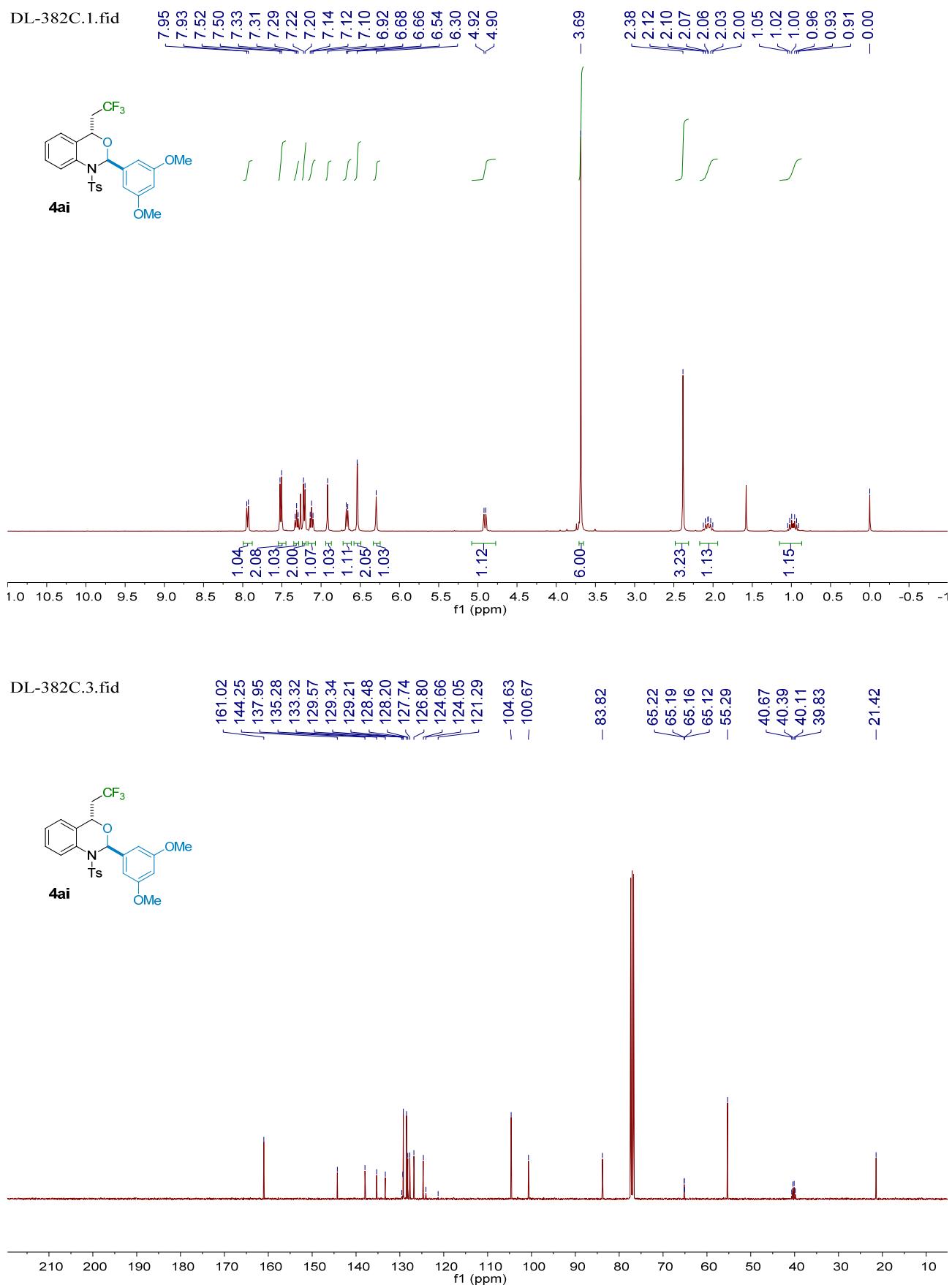
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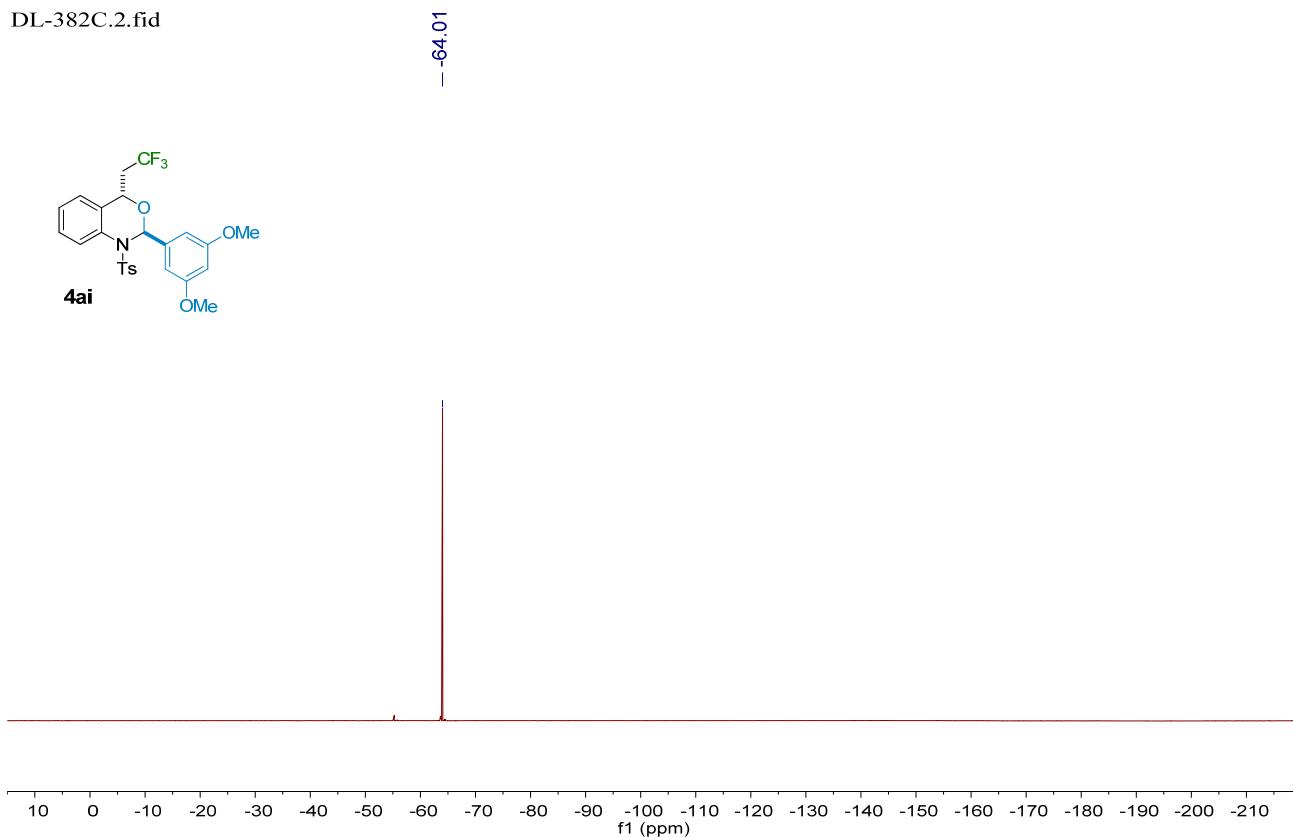
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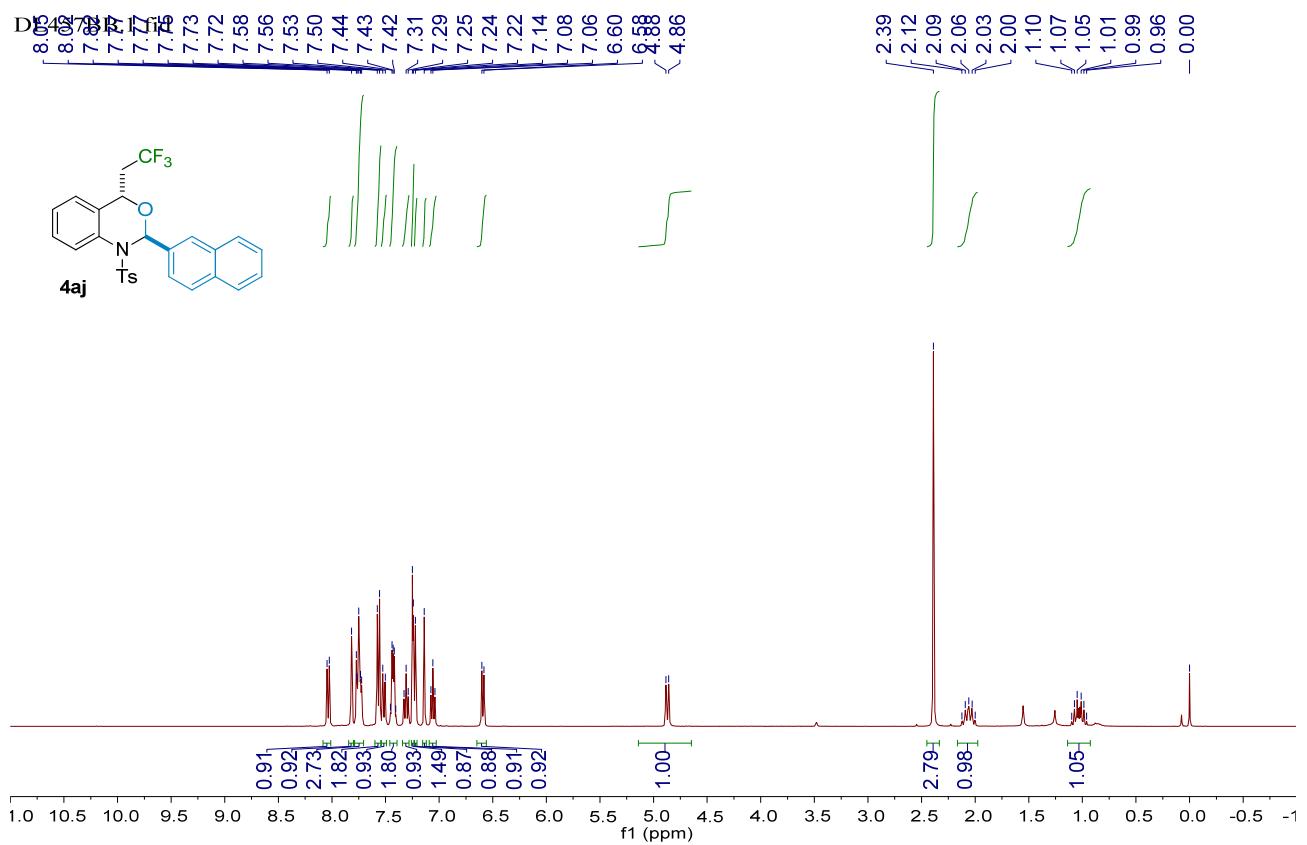
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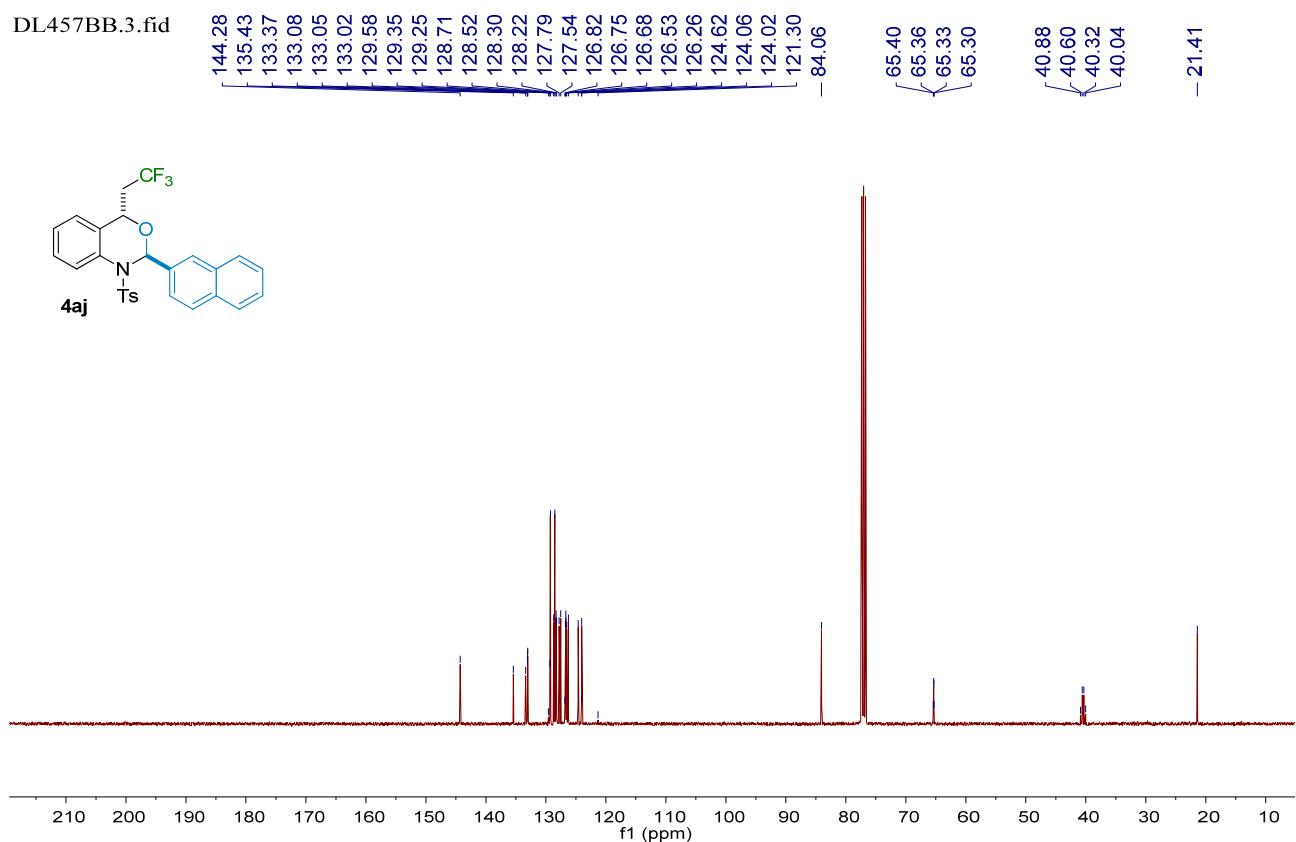
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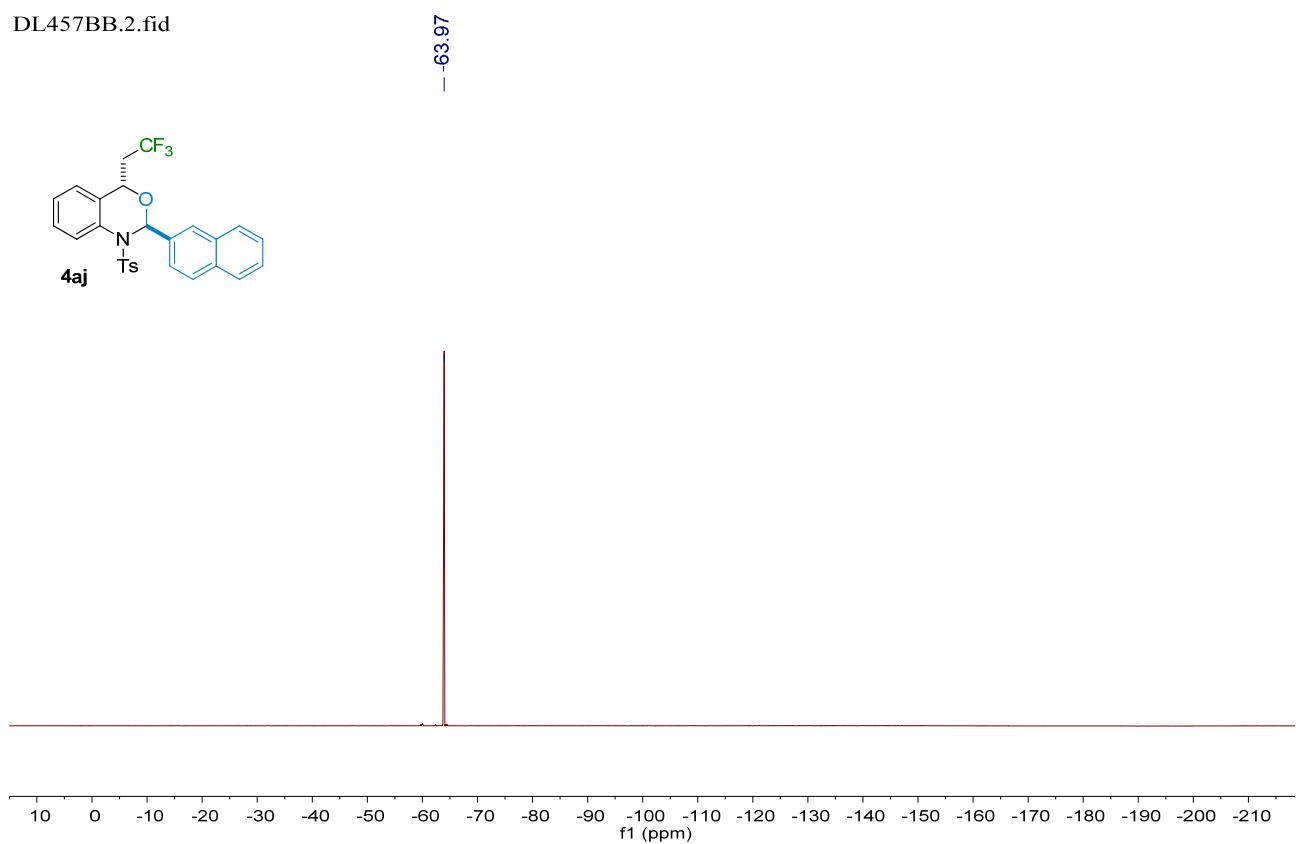
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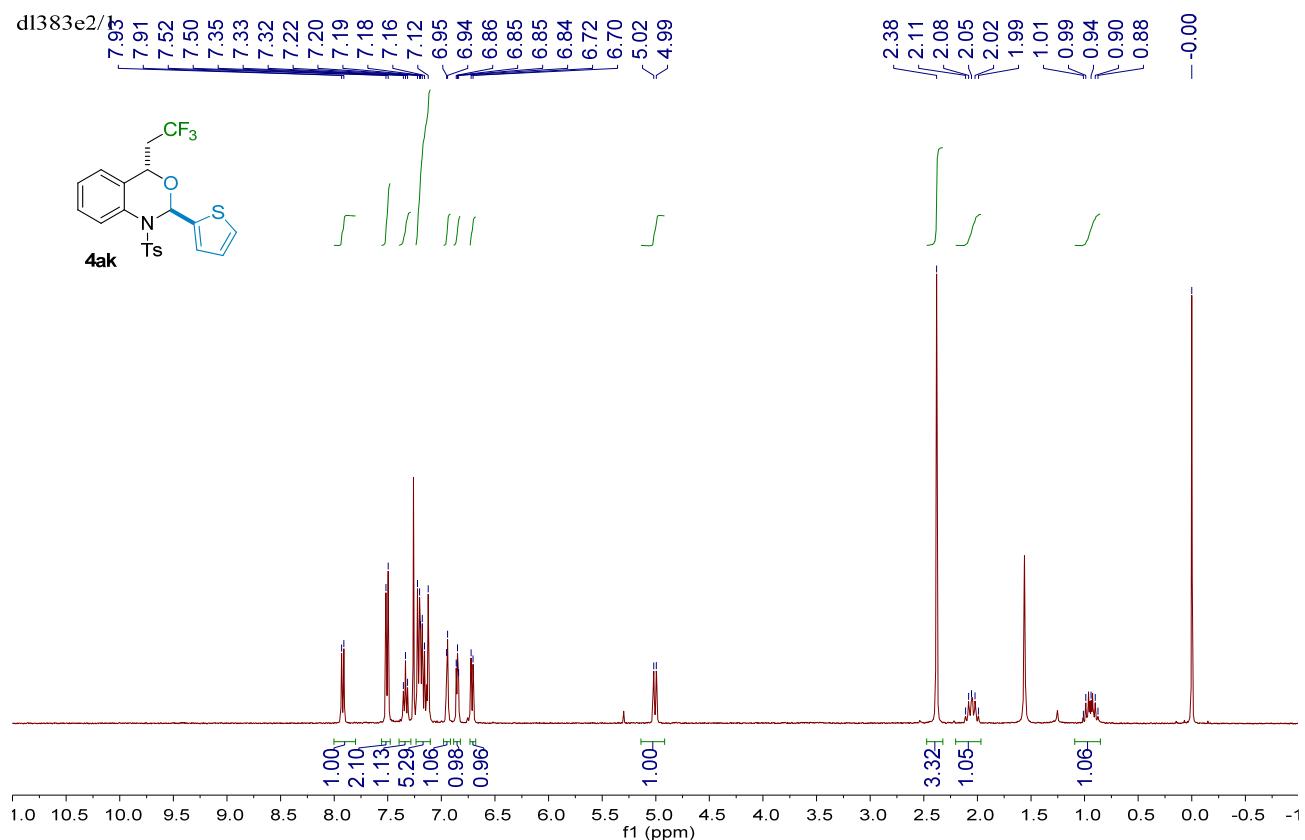
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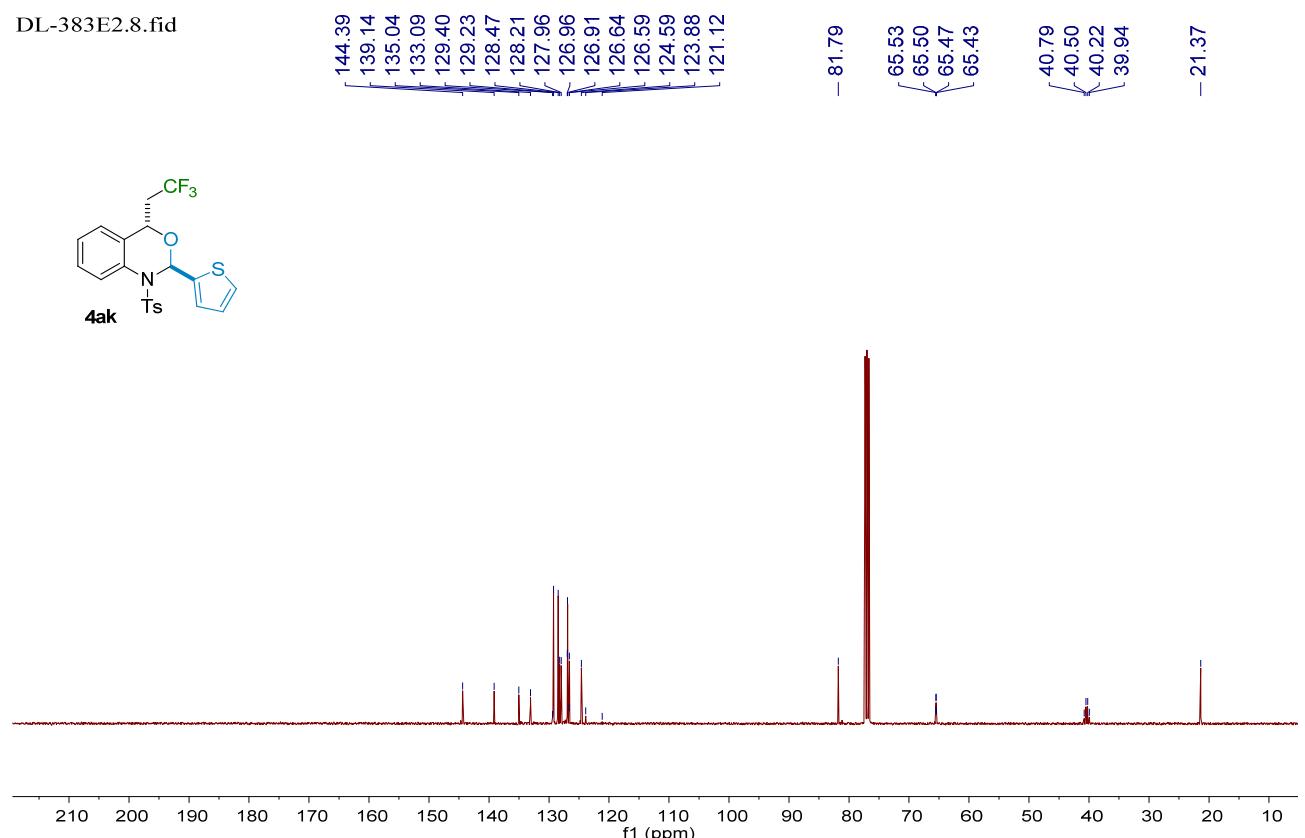
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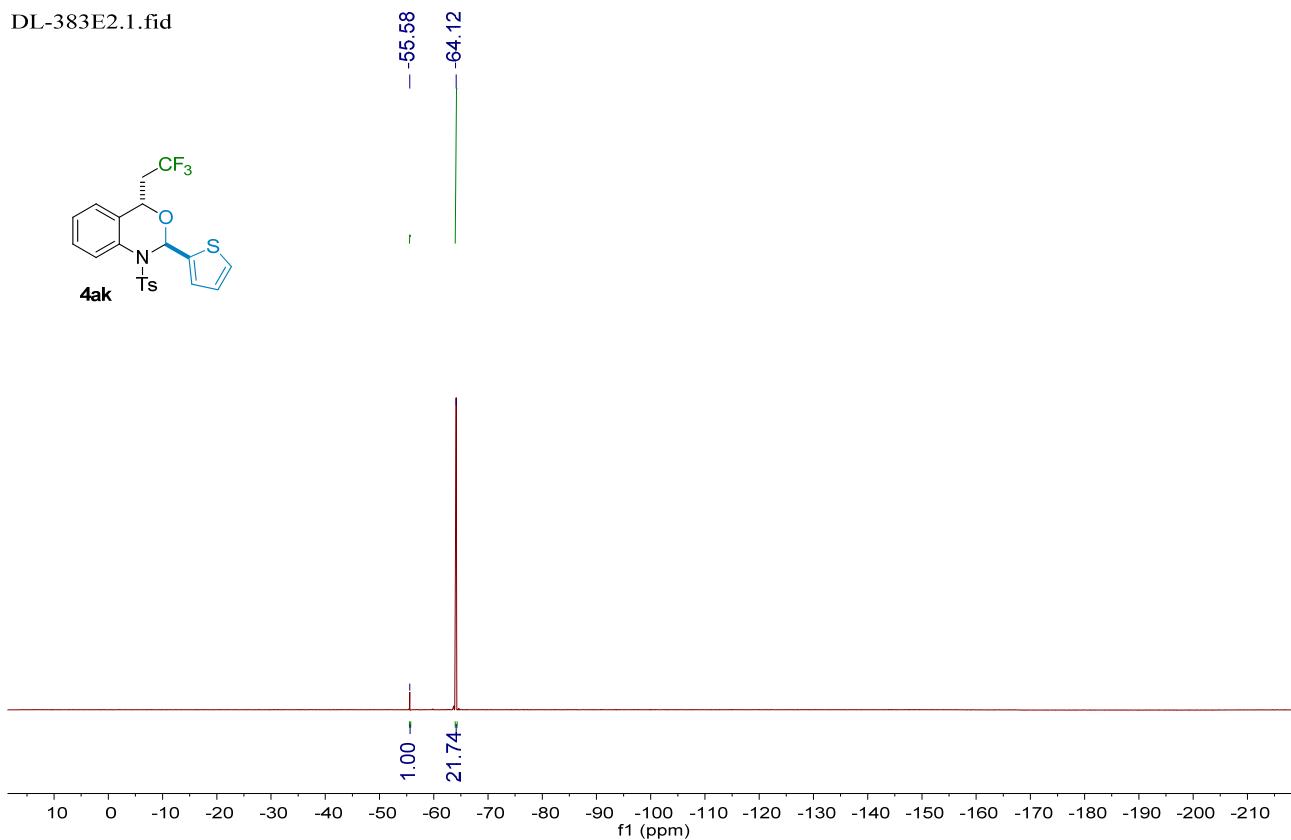
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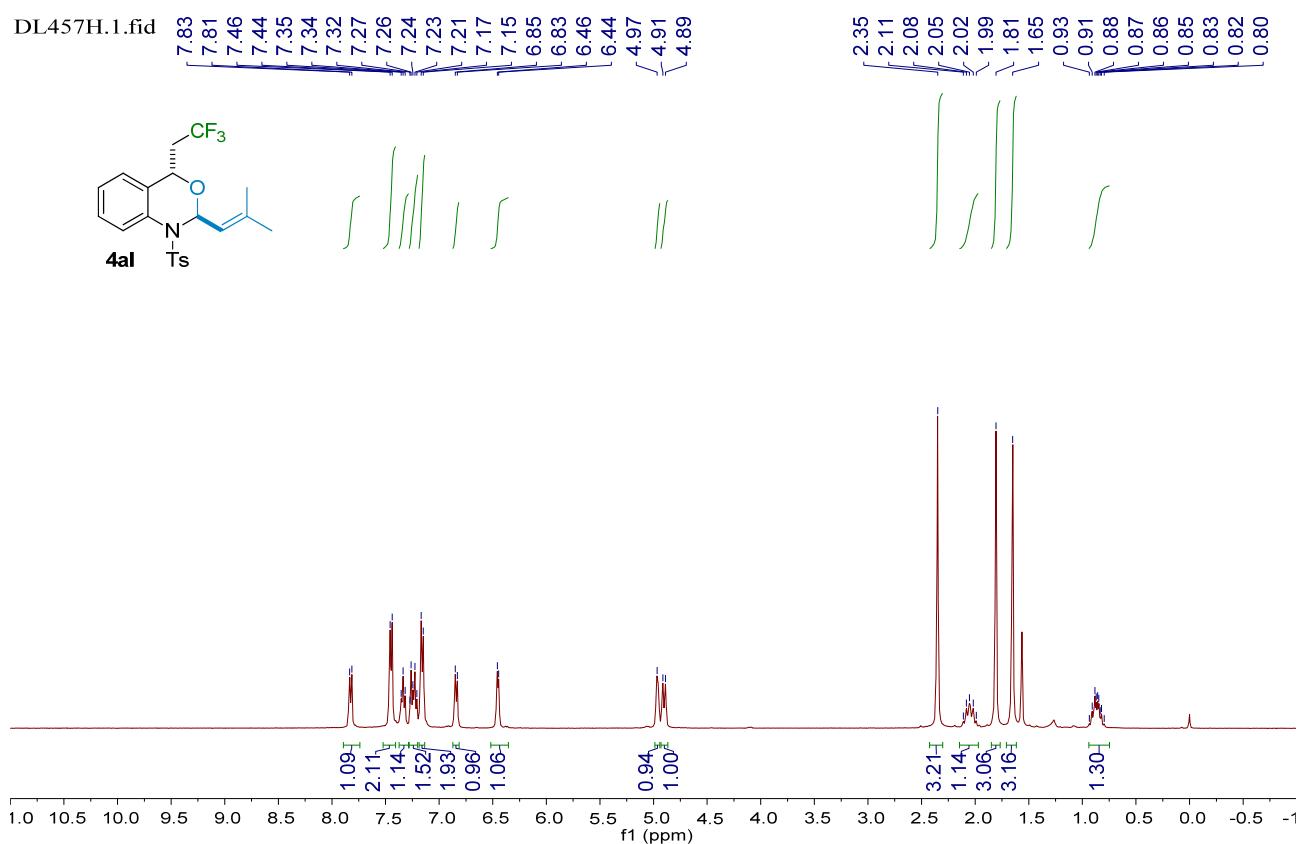


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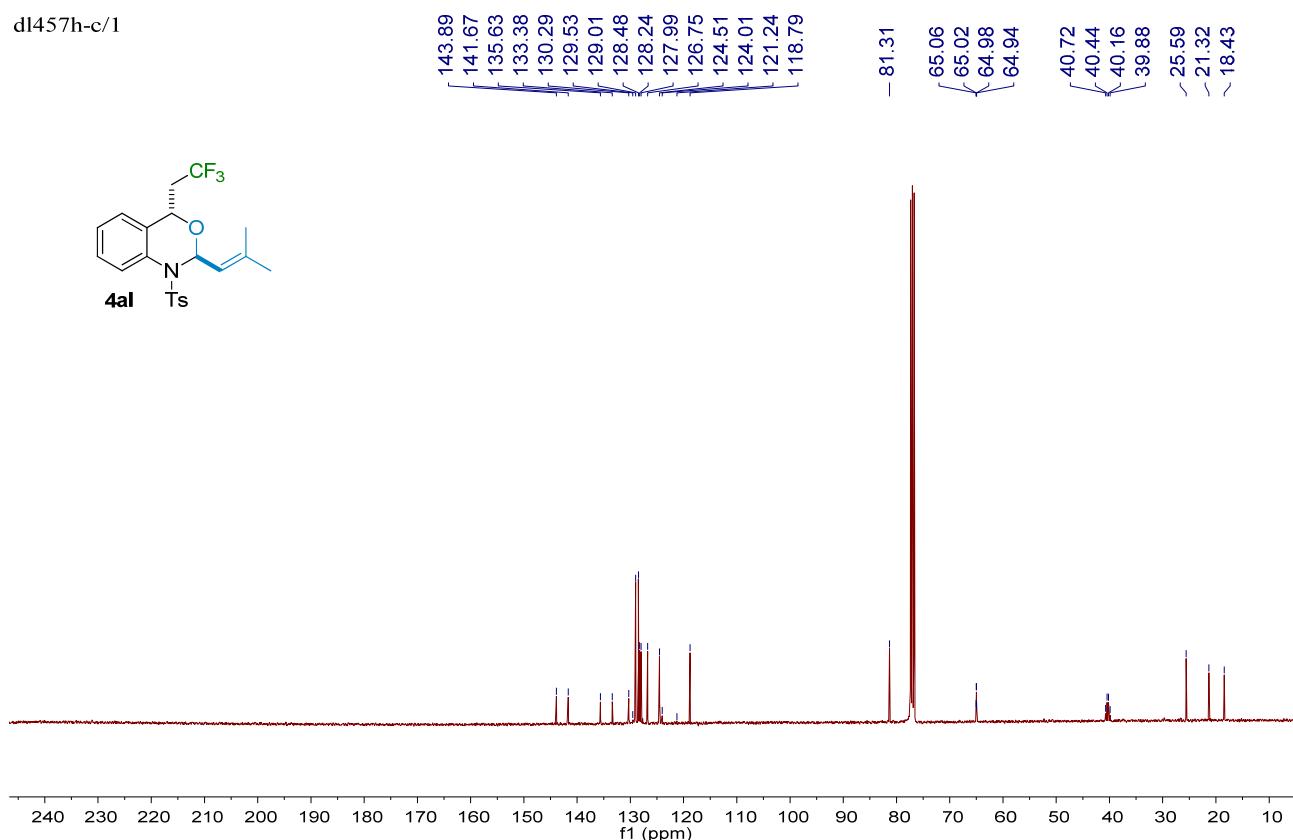


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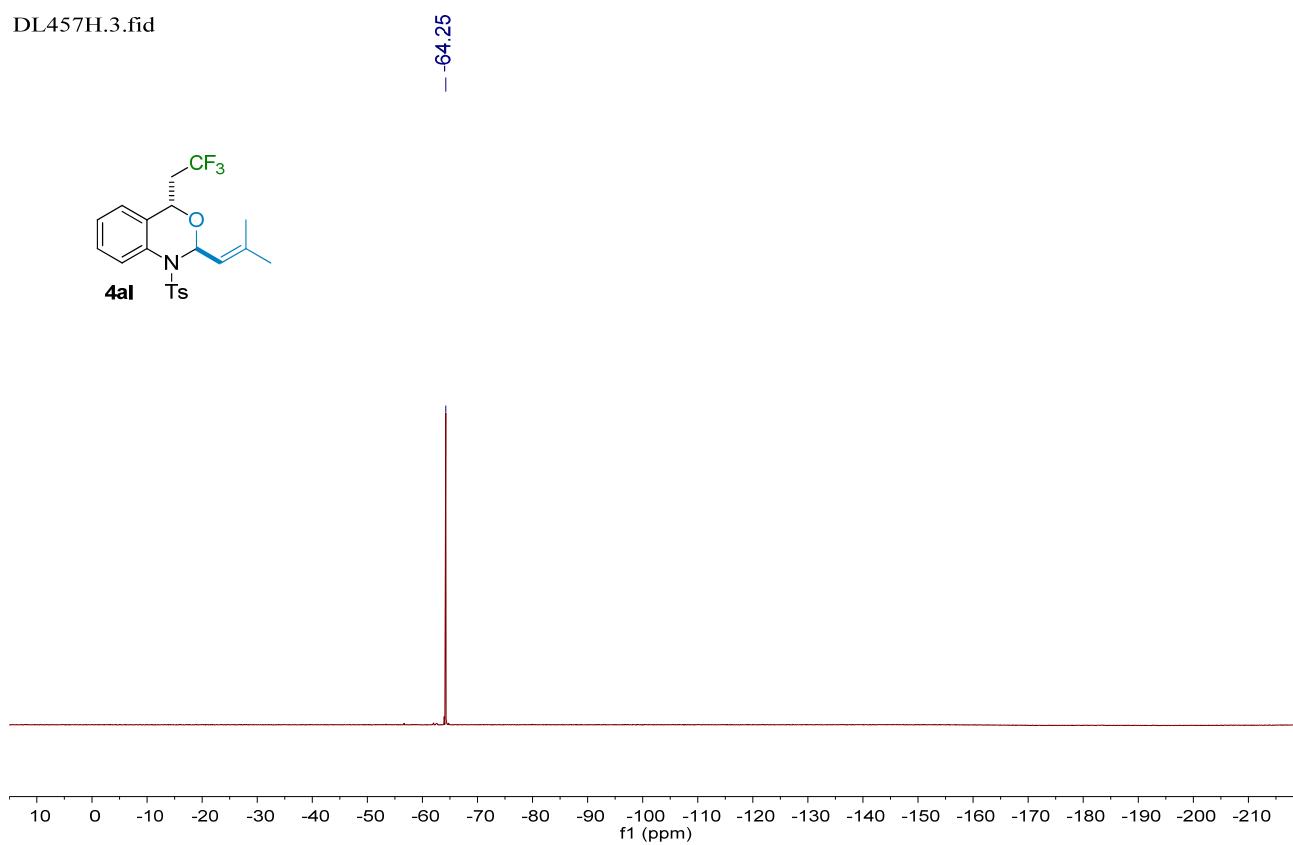
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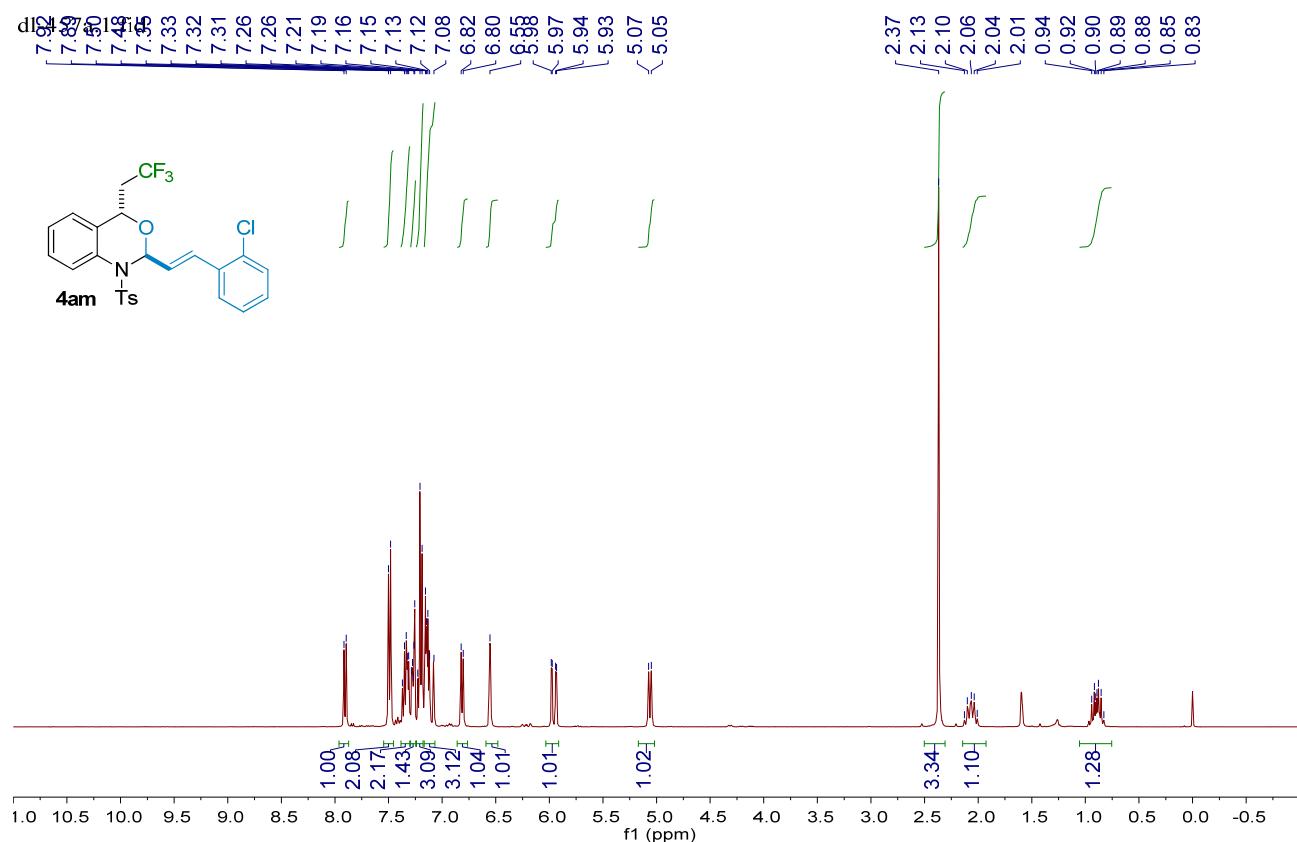
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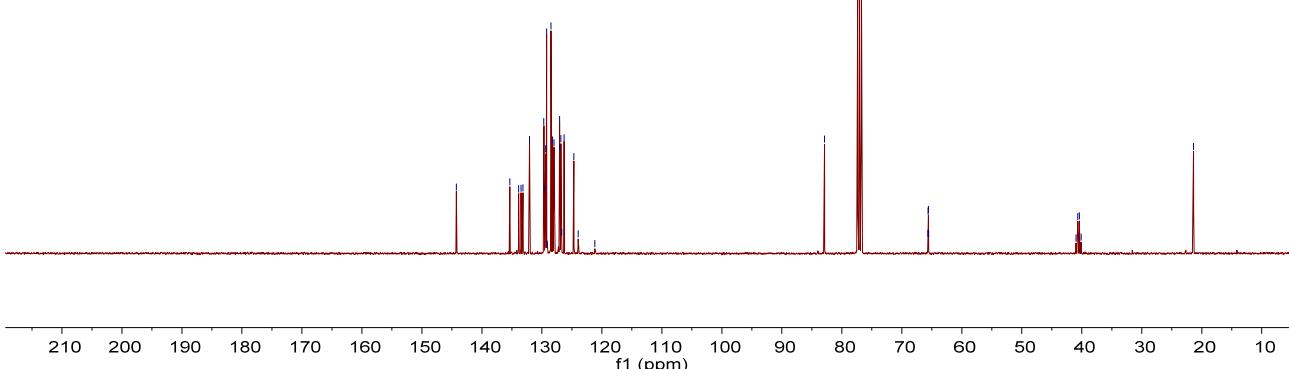
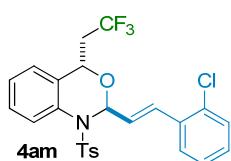
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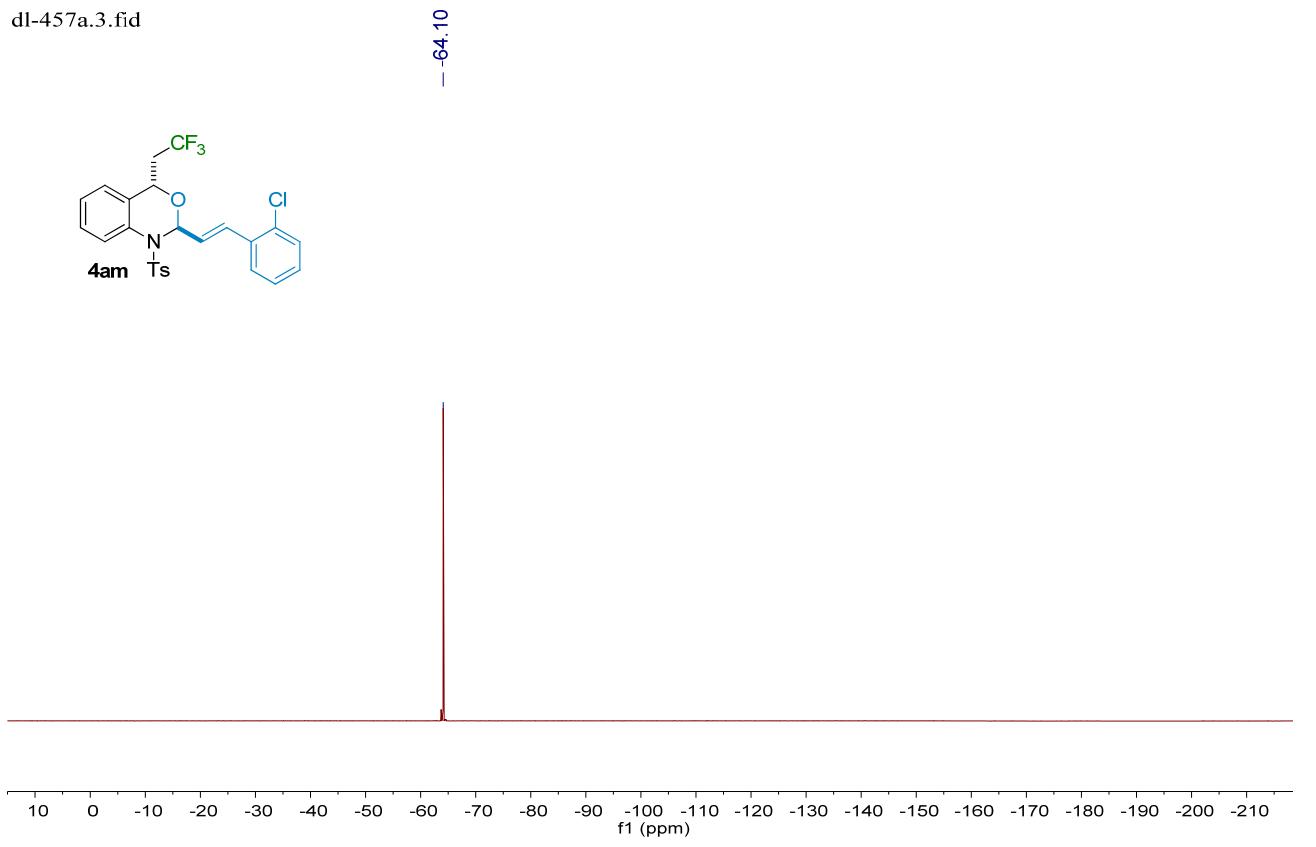
¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of 4am



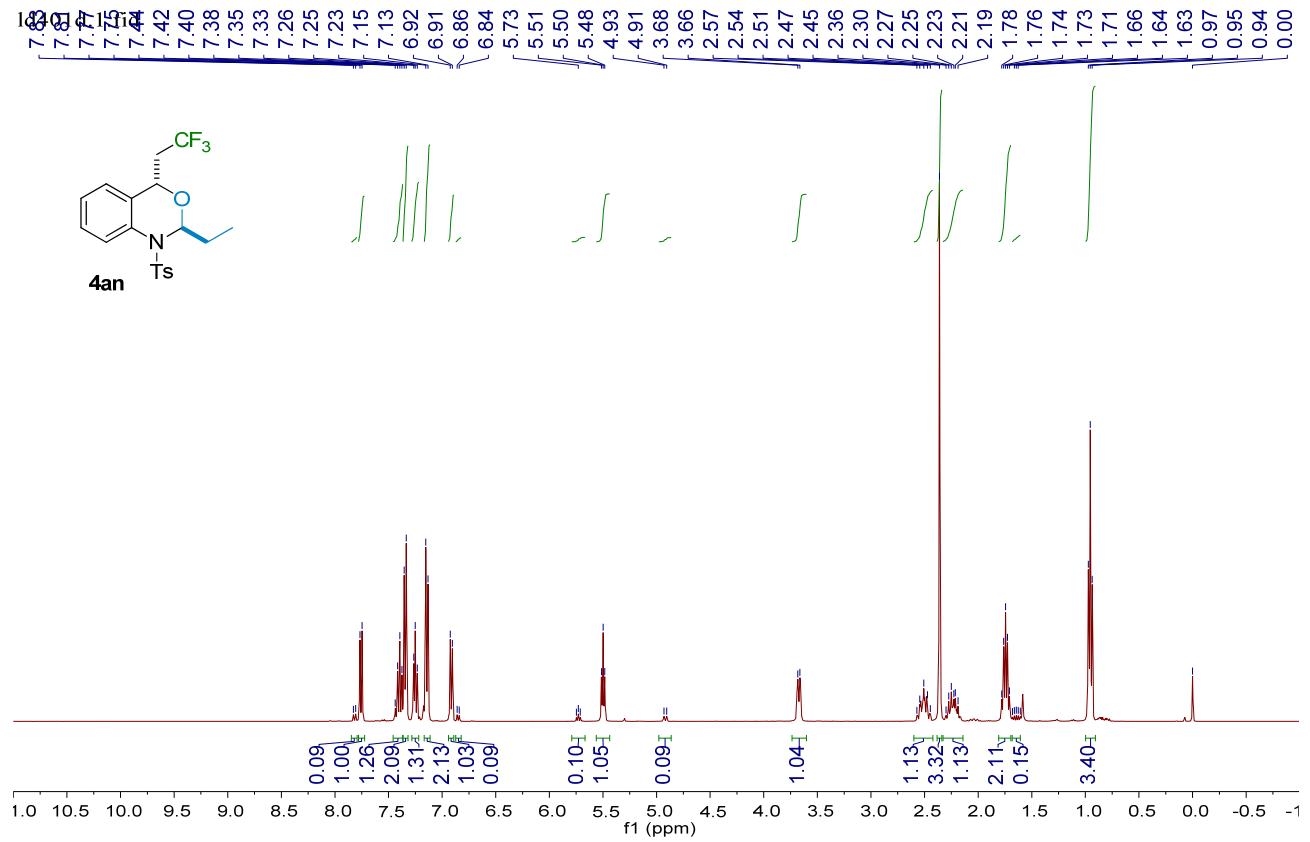
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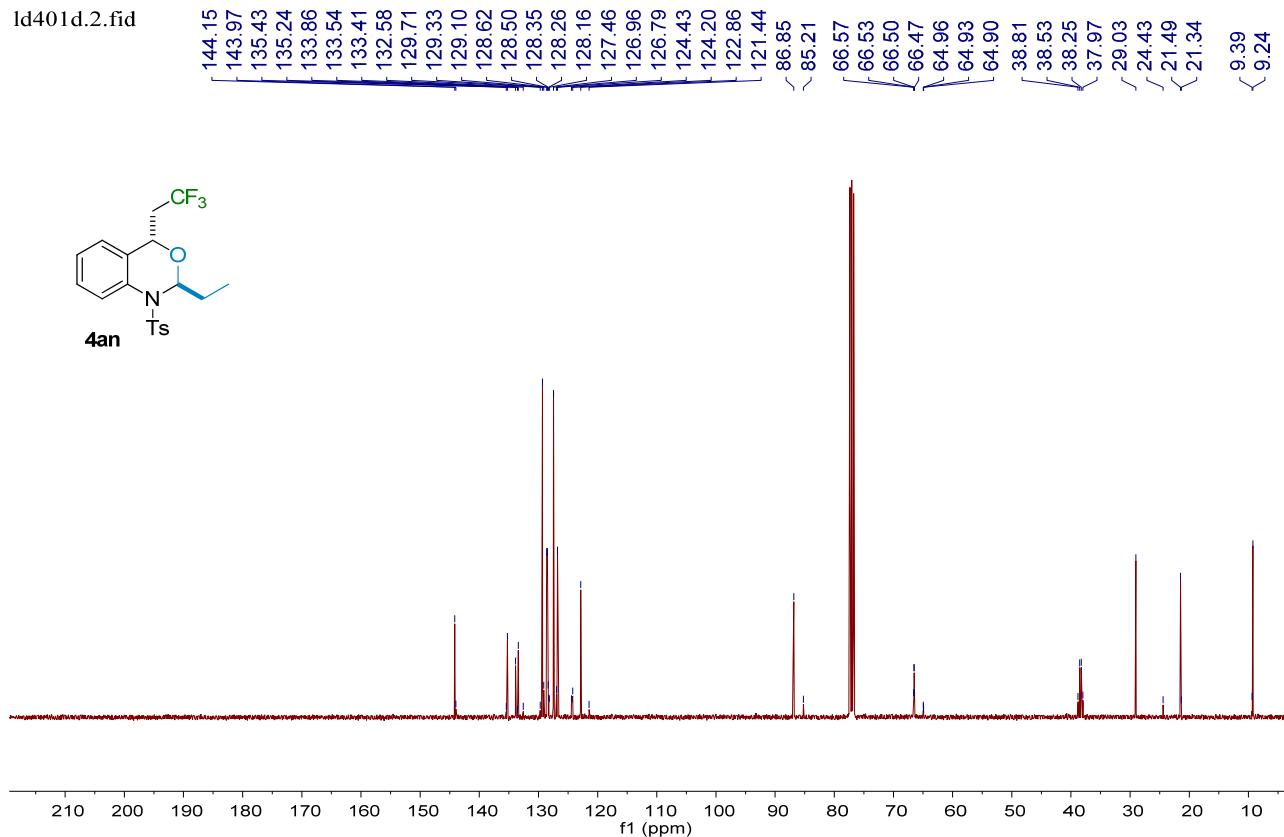
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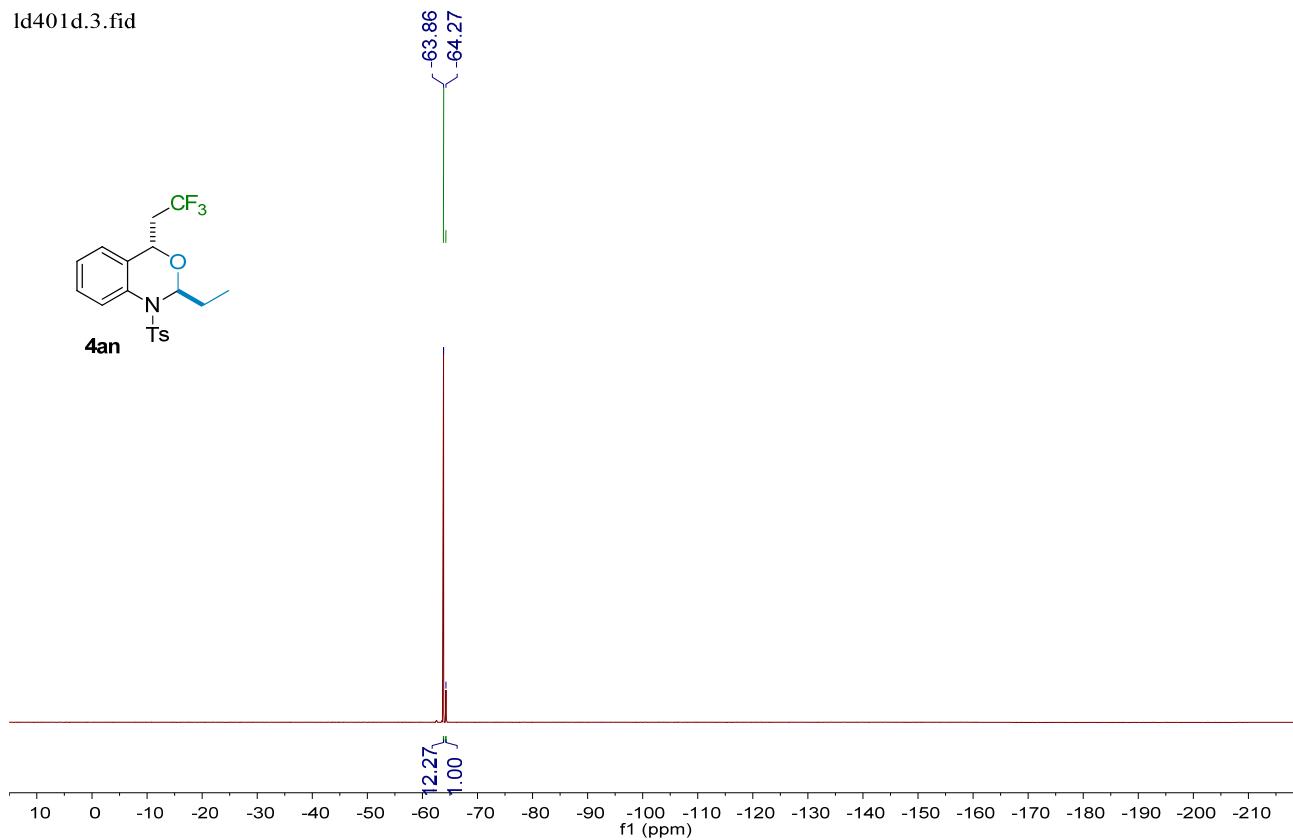
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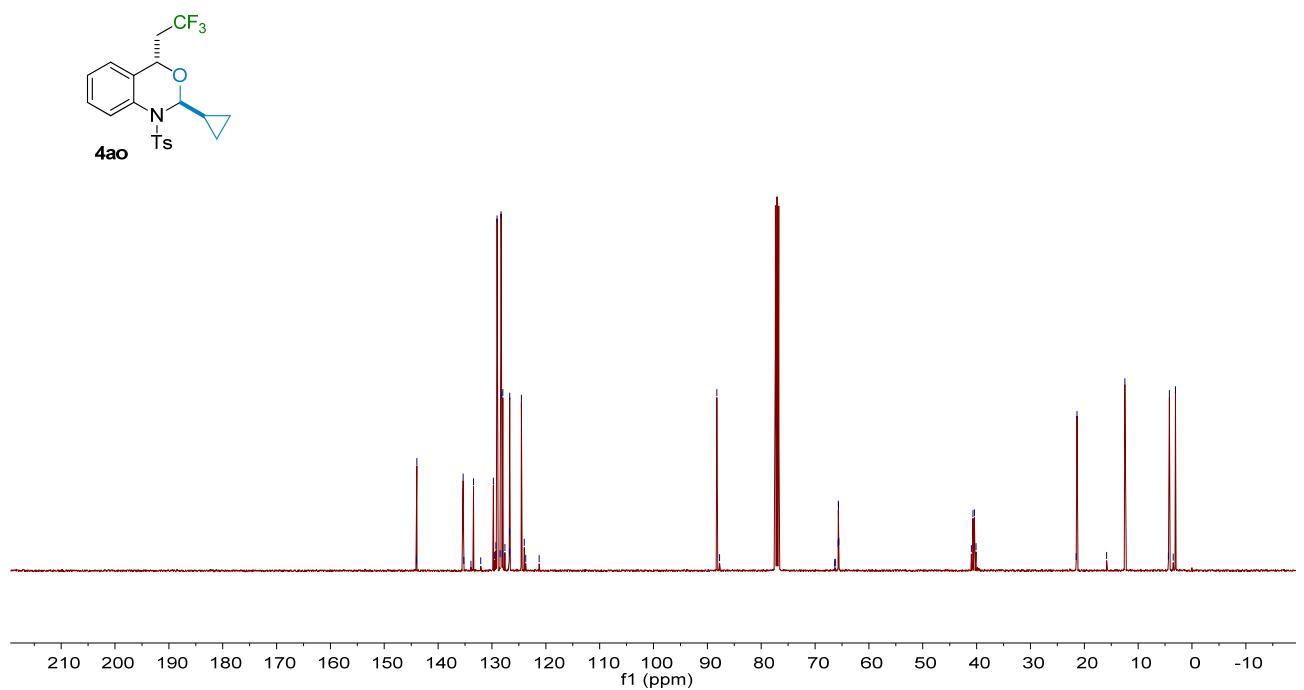
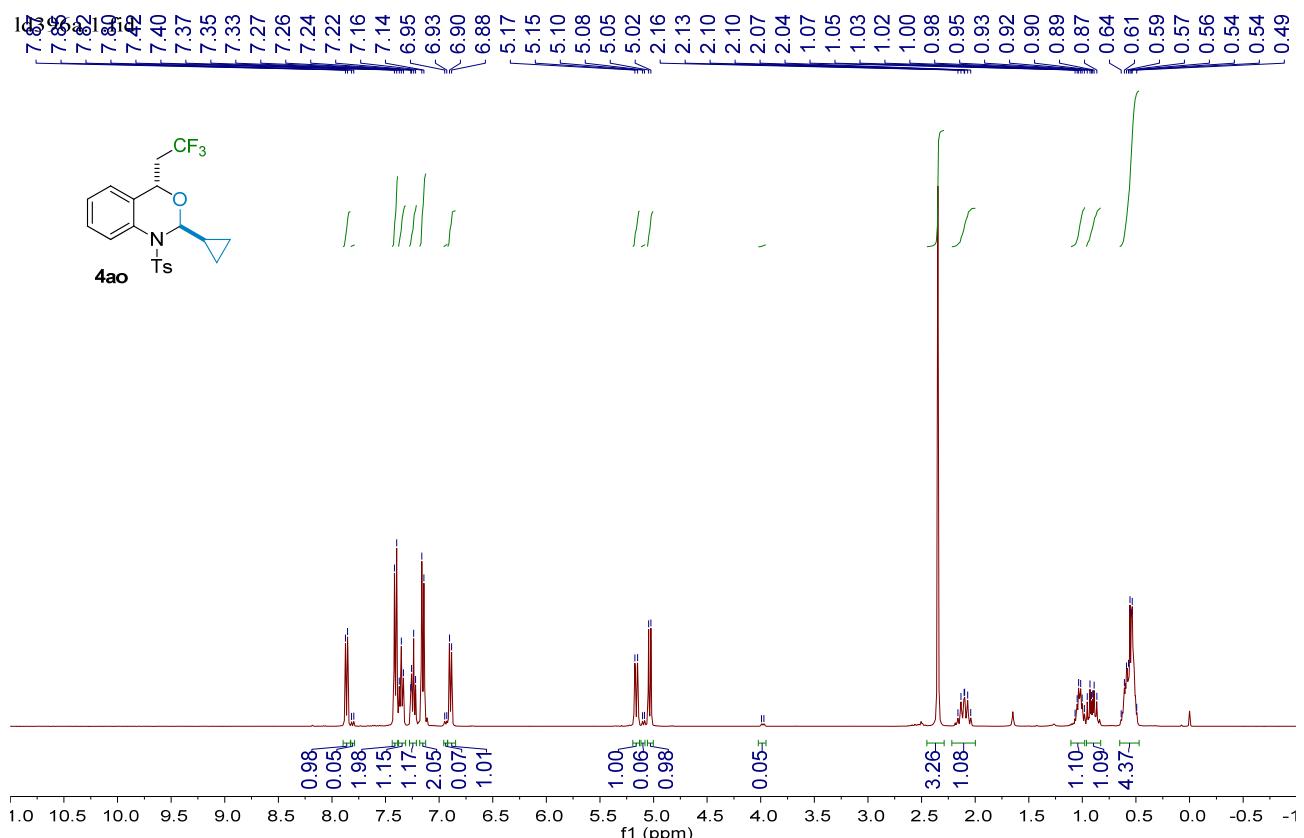
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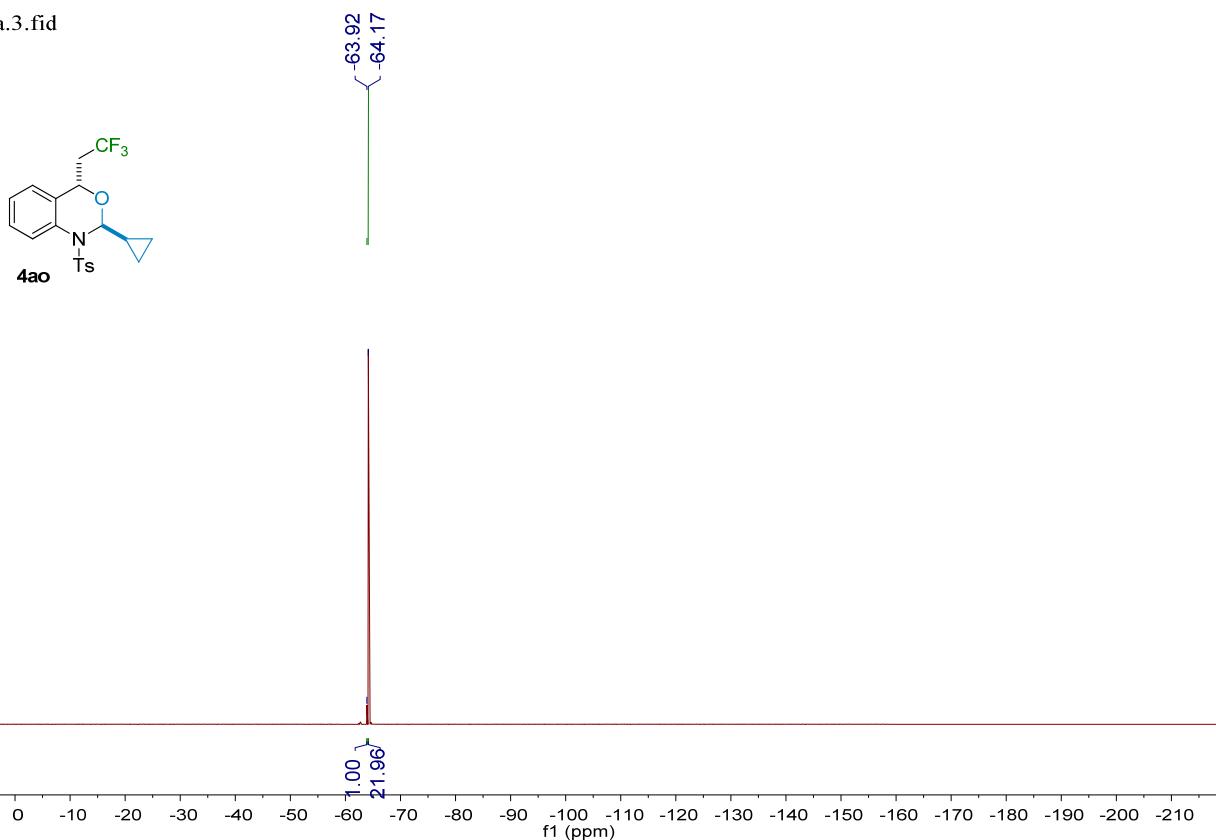
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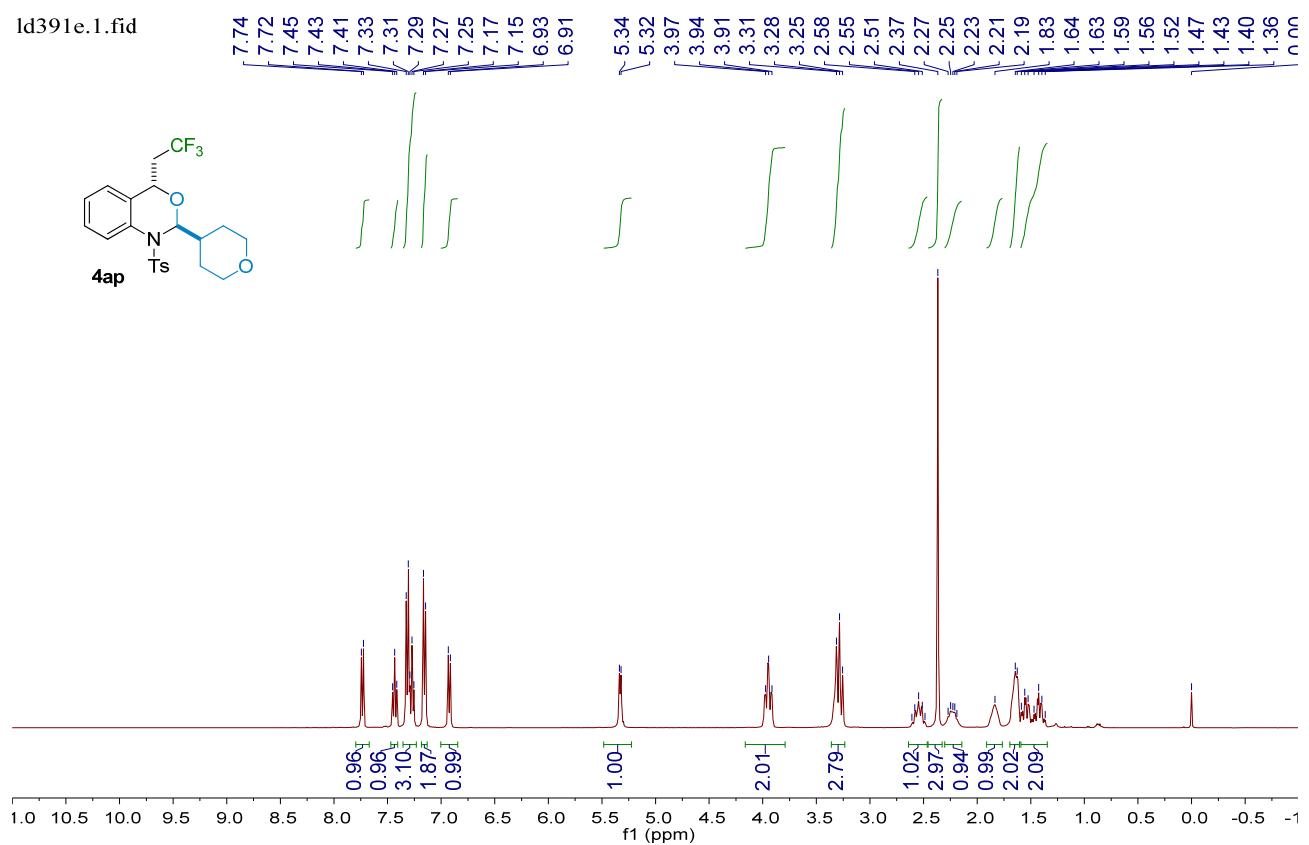


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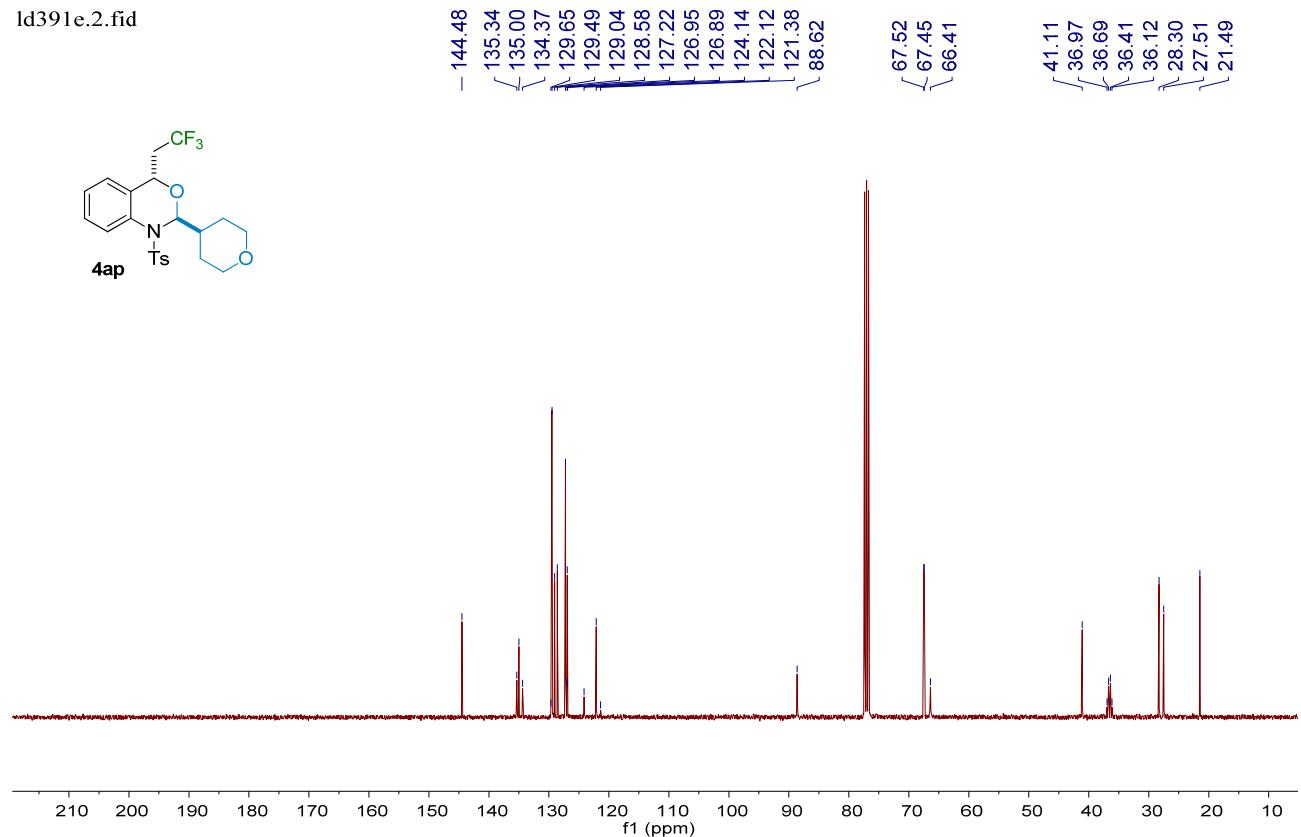


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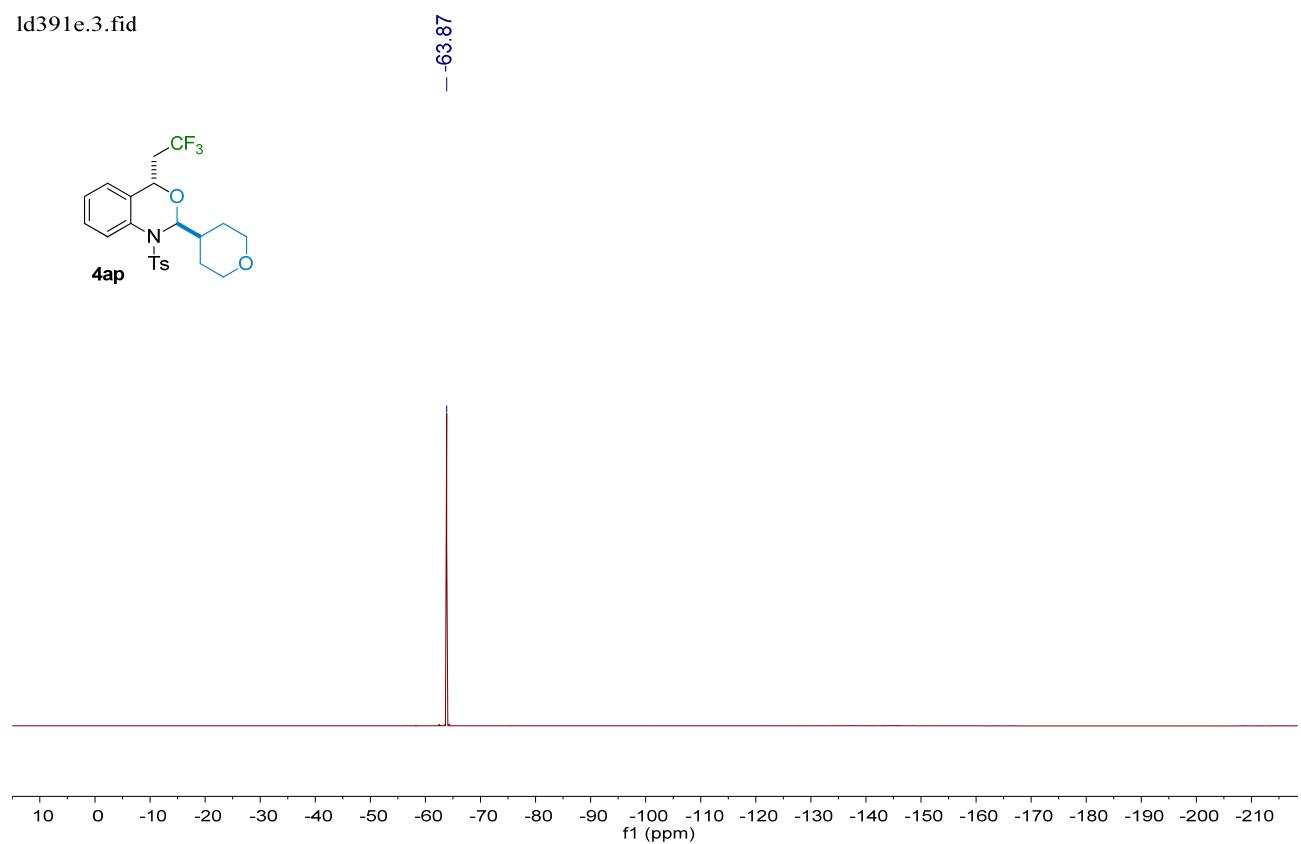
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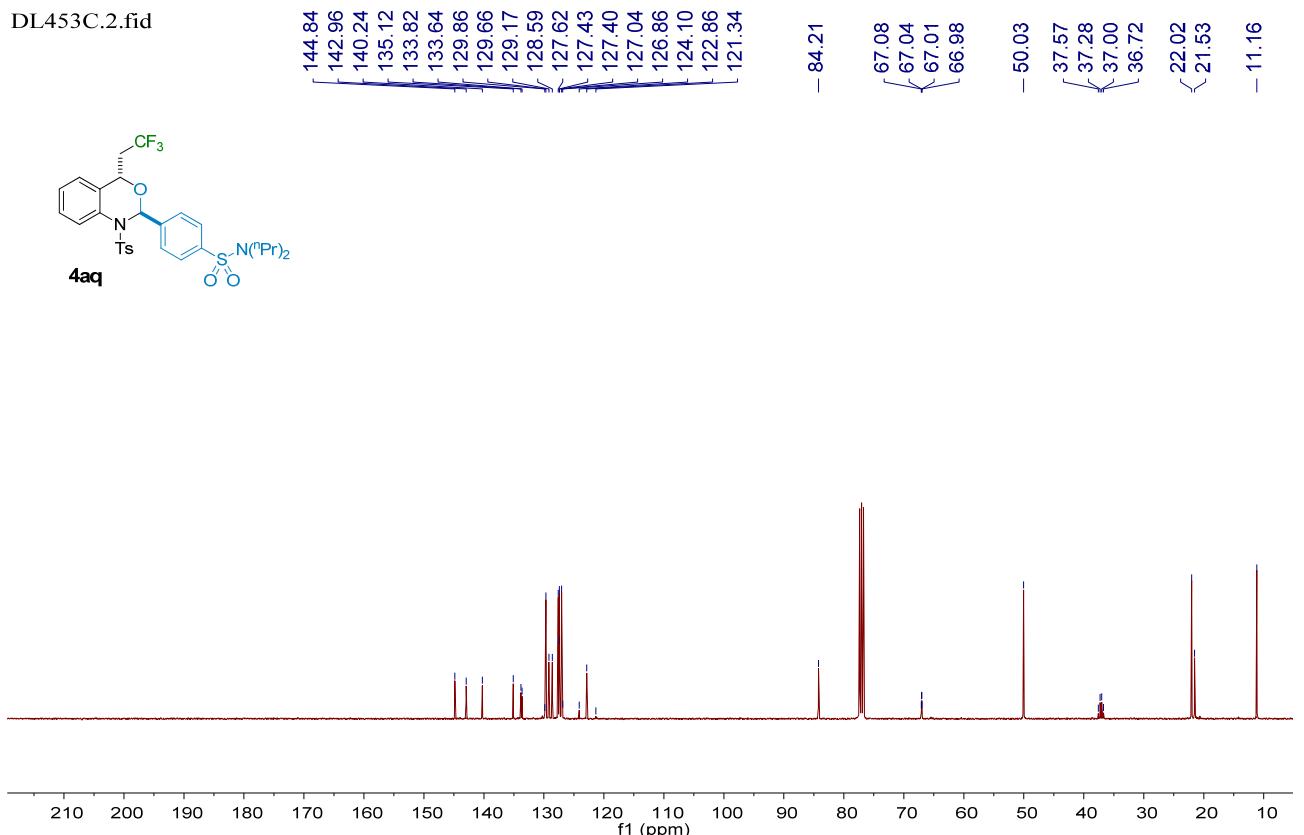
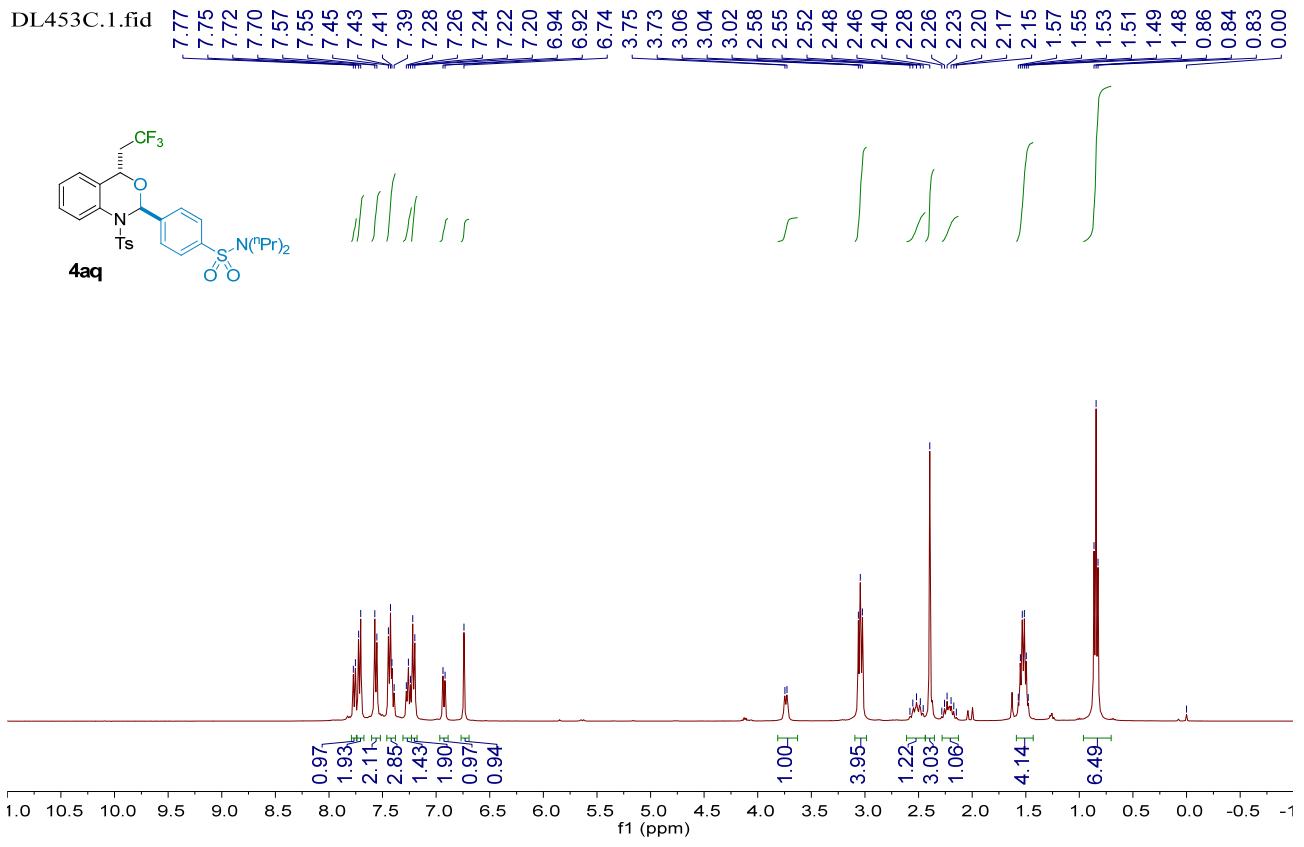
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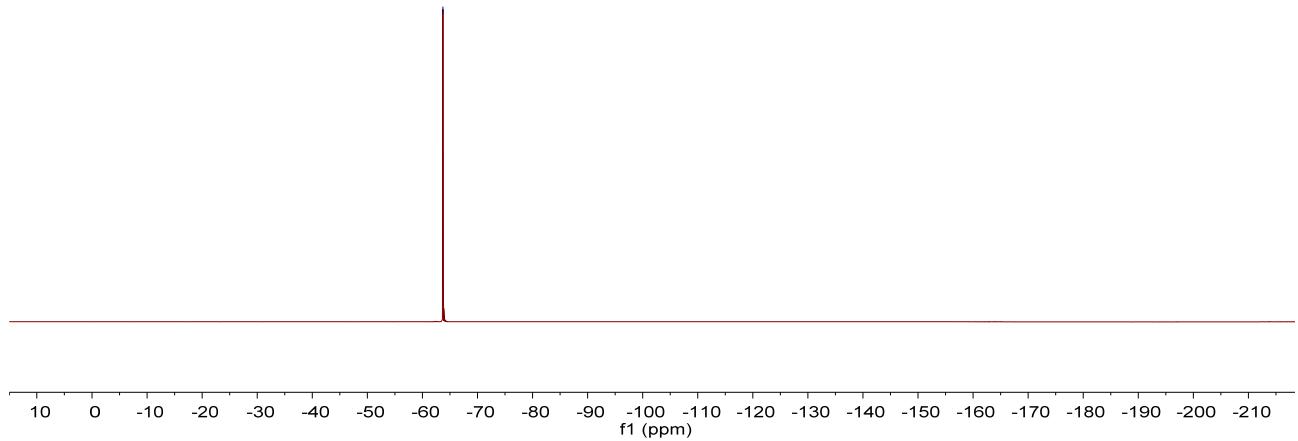
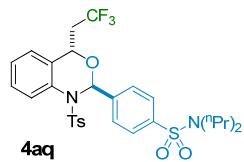
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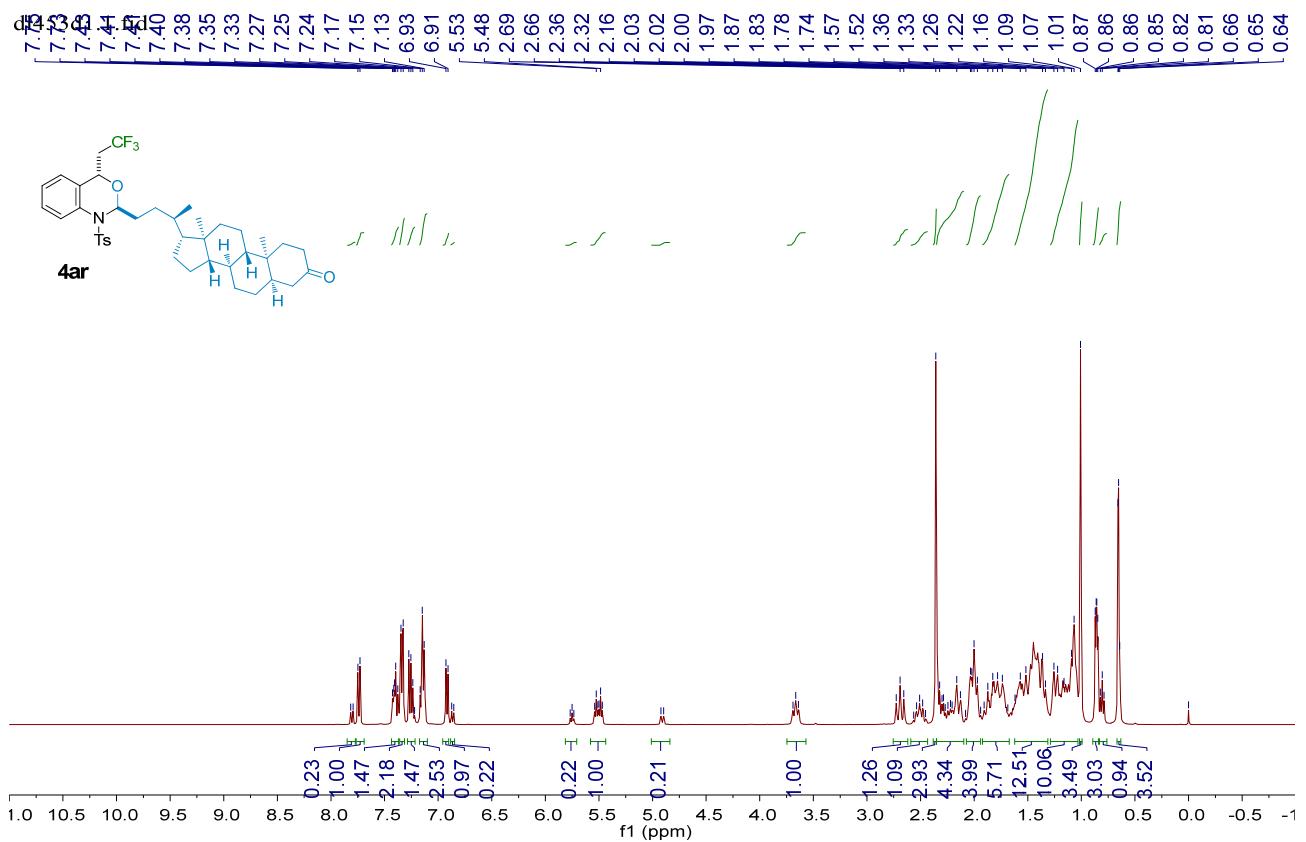
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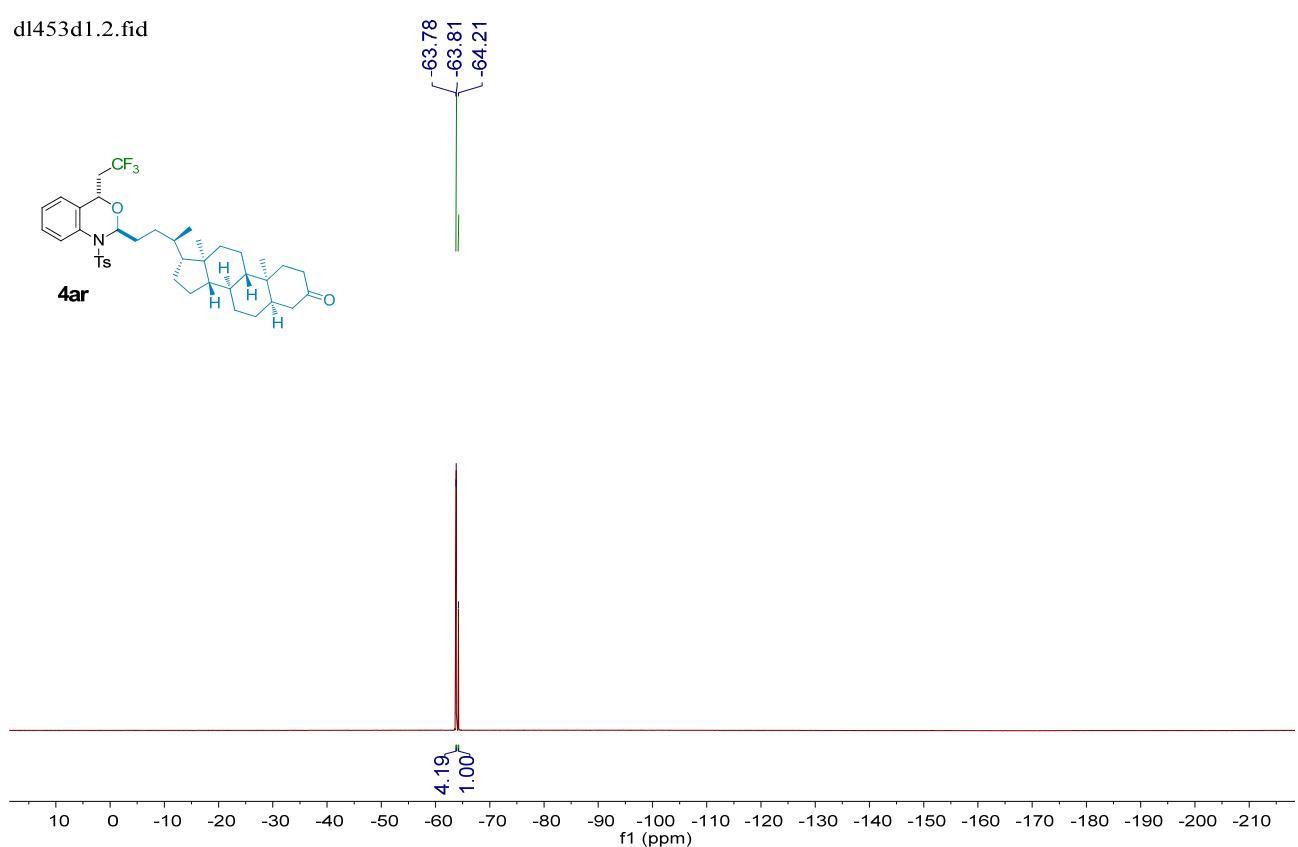
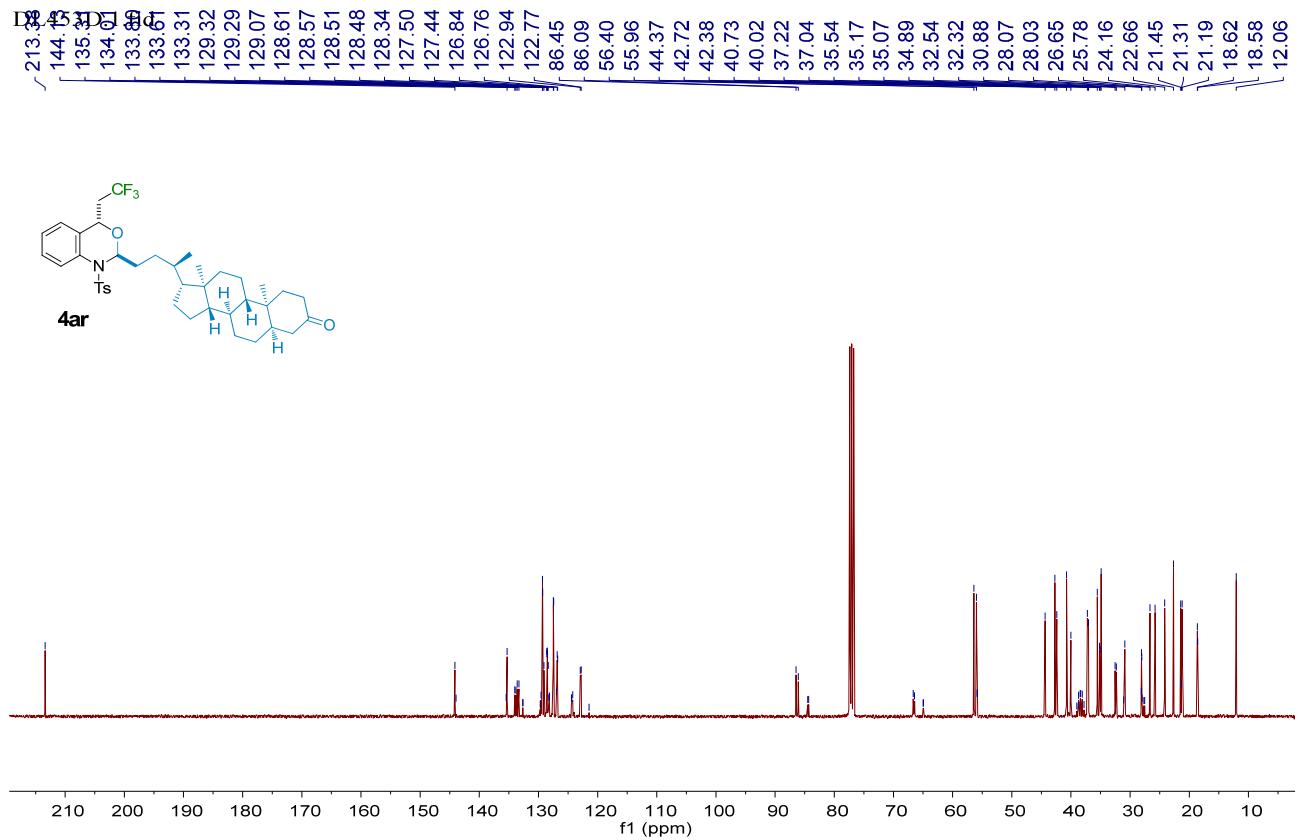


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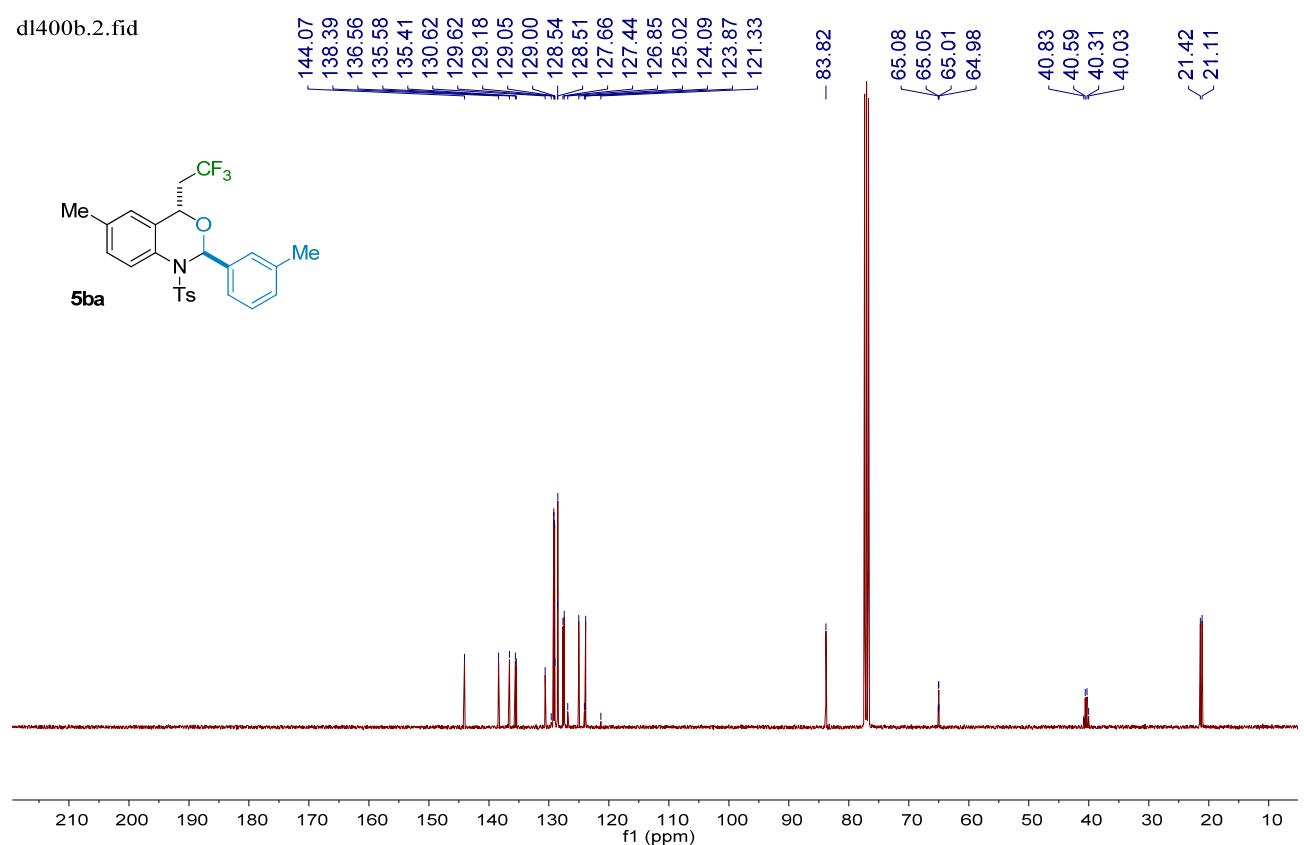
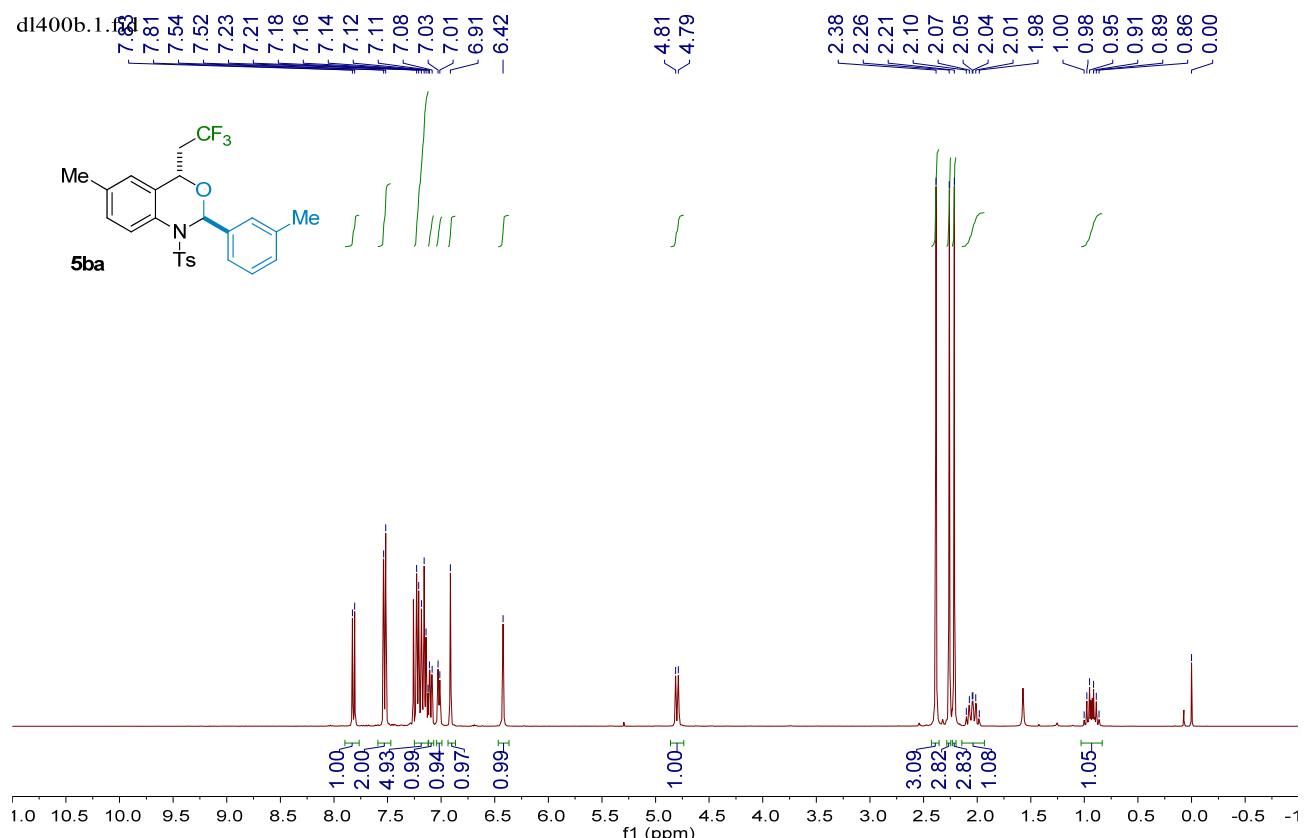


^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3) and ^{19}F NMR (376 MHz, CDCl_3) spectra of **4ar**

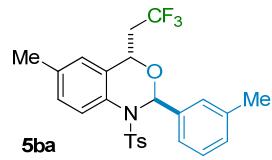




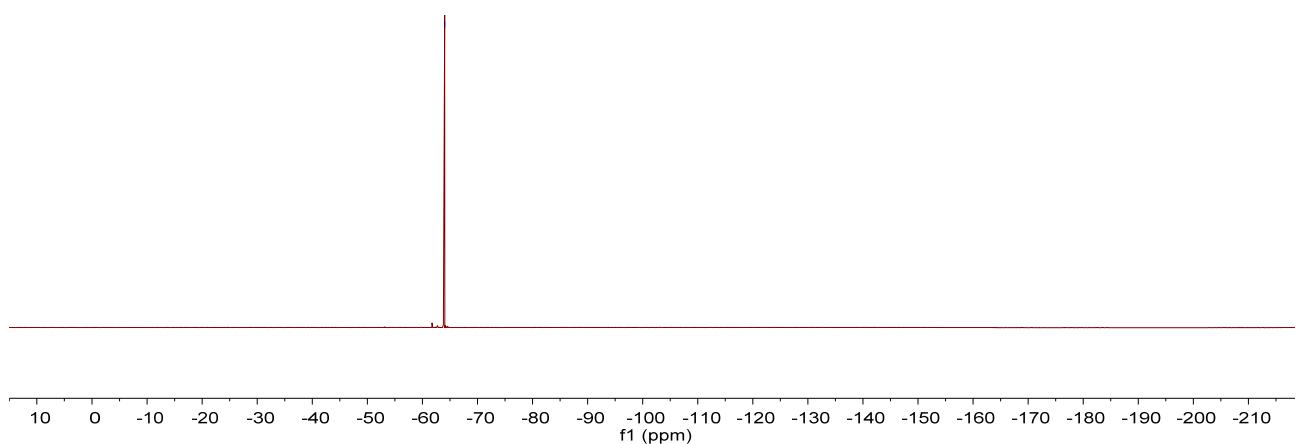
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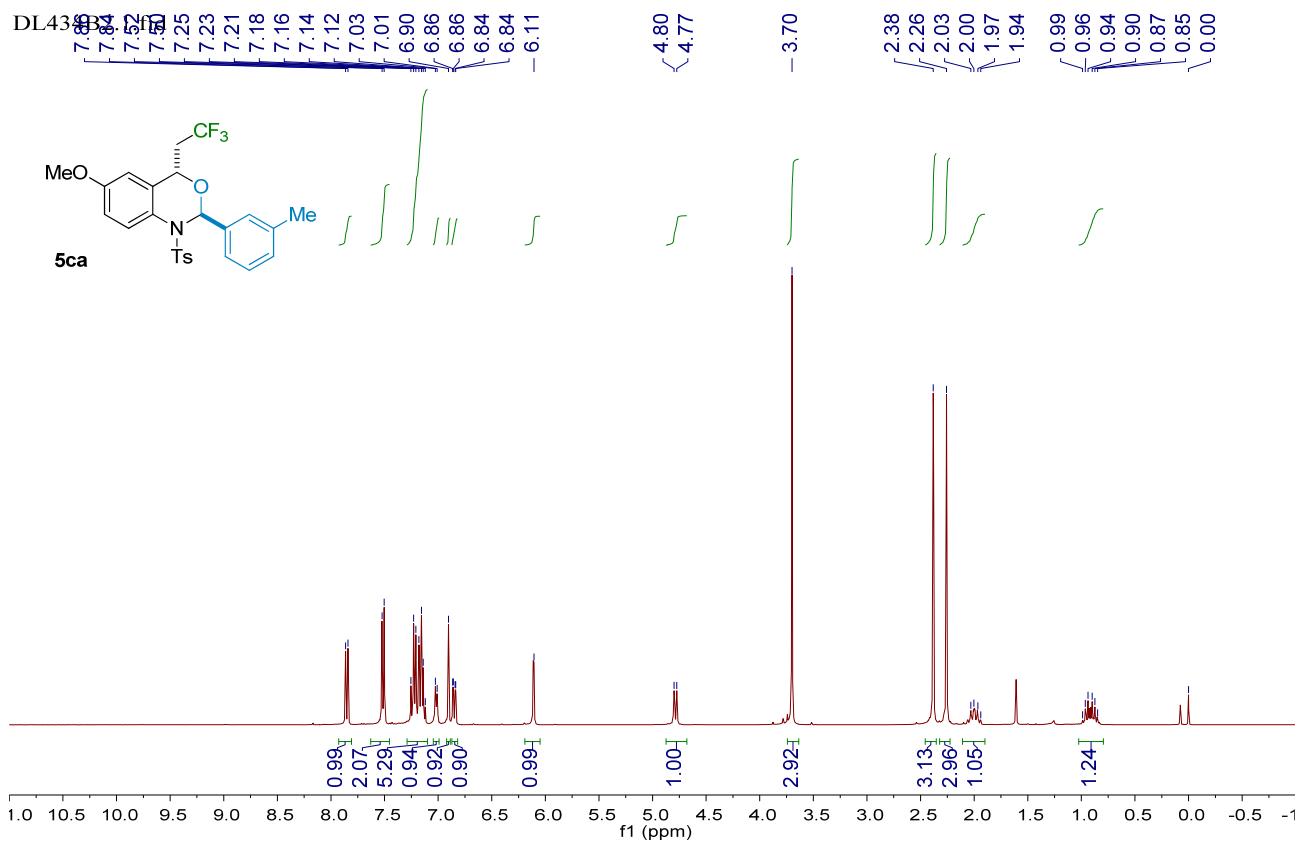
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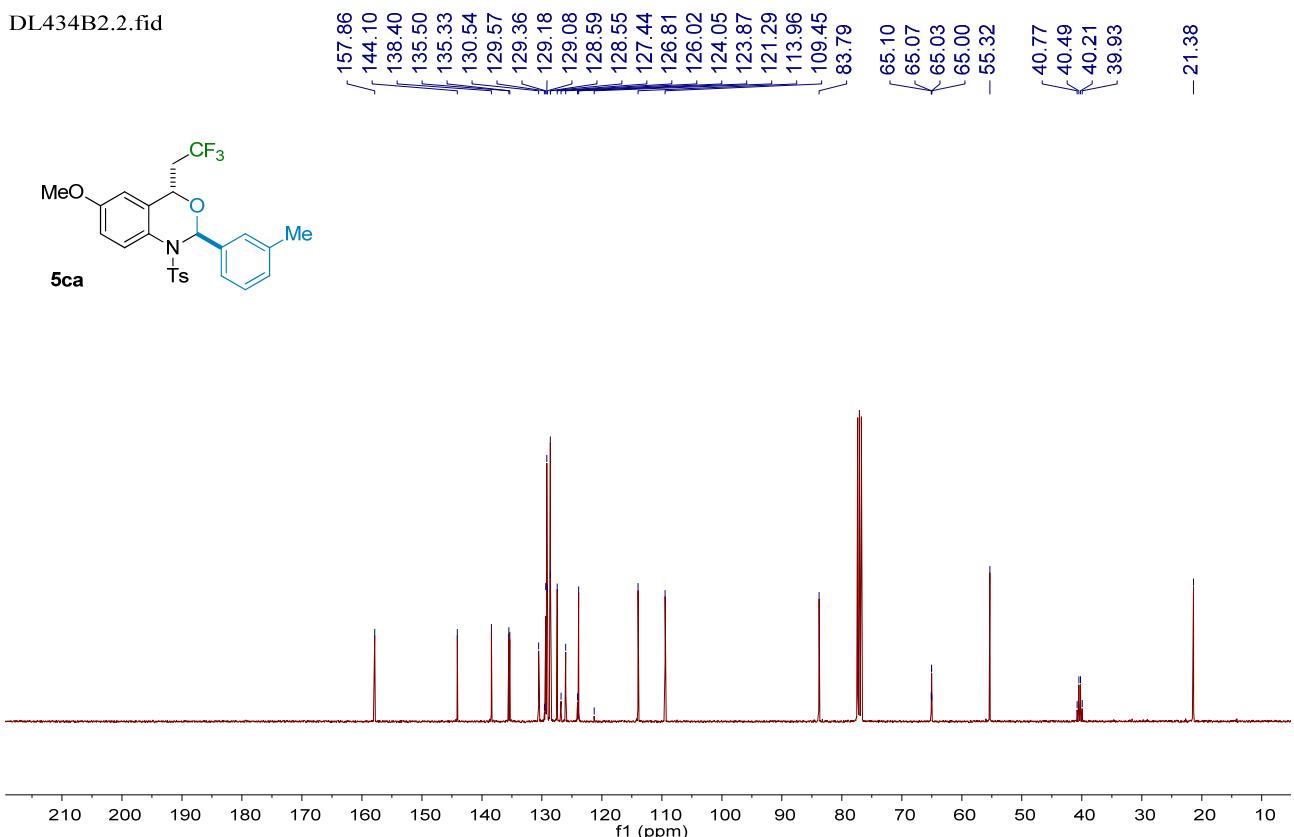
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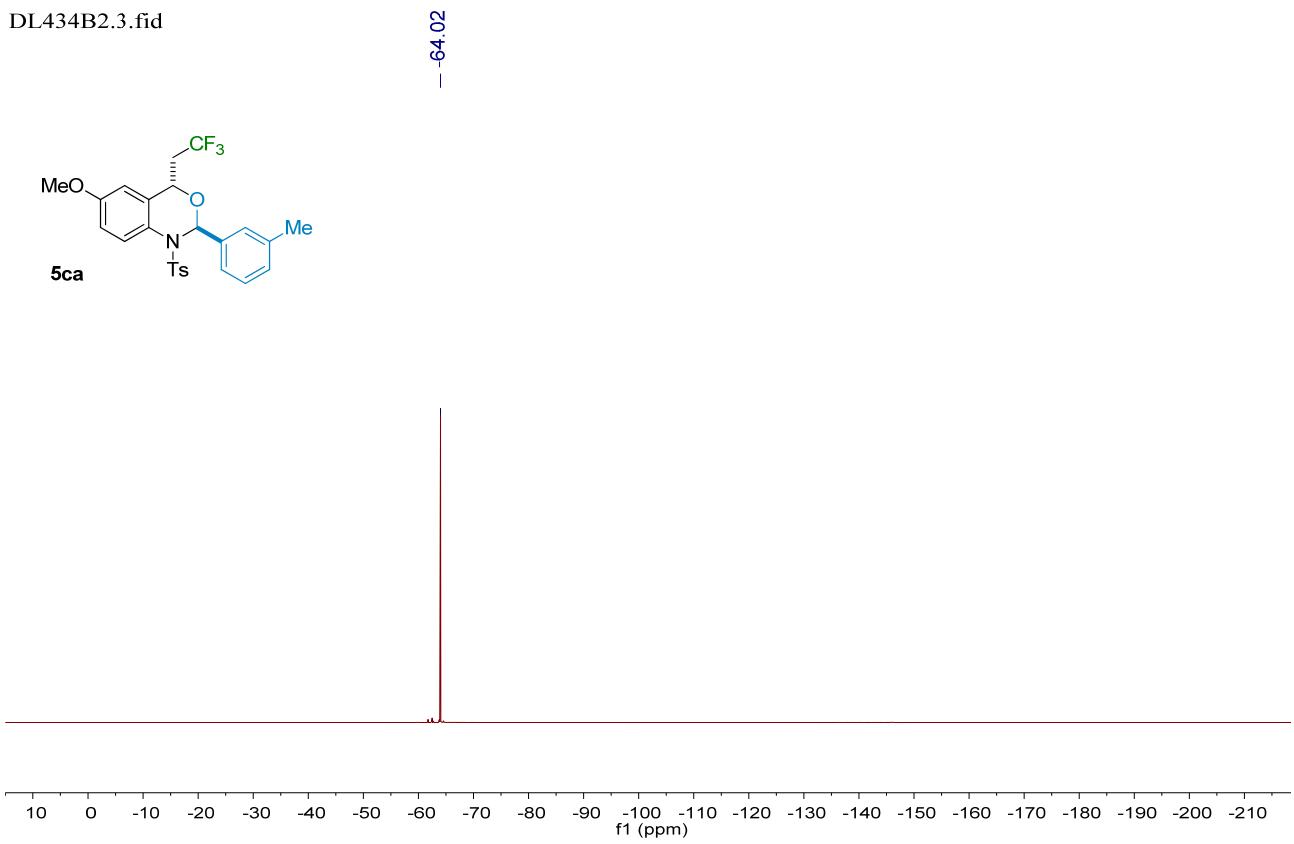
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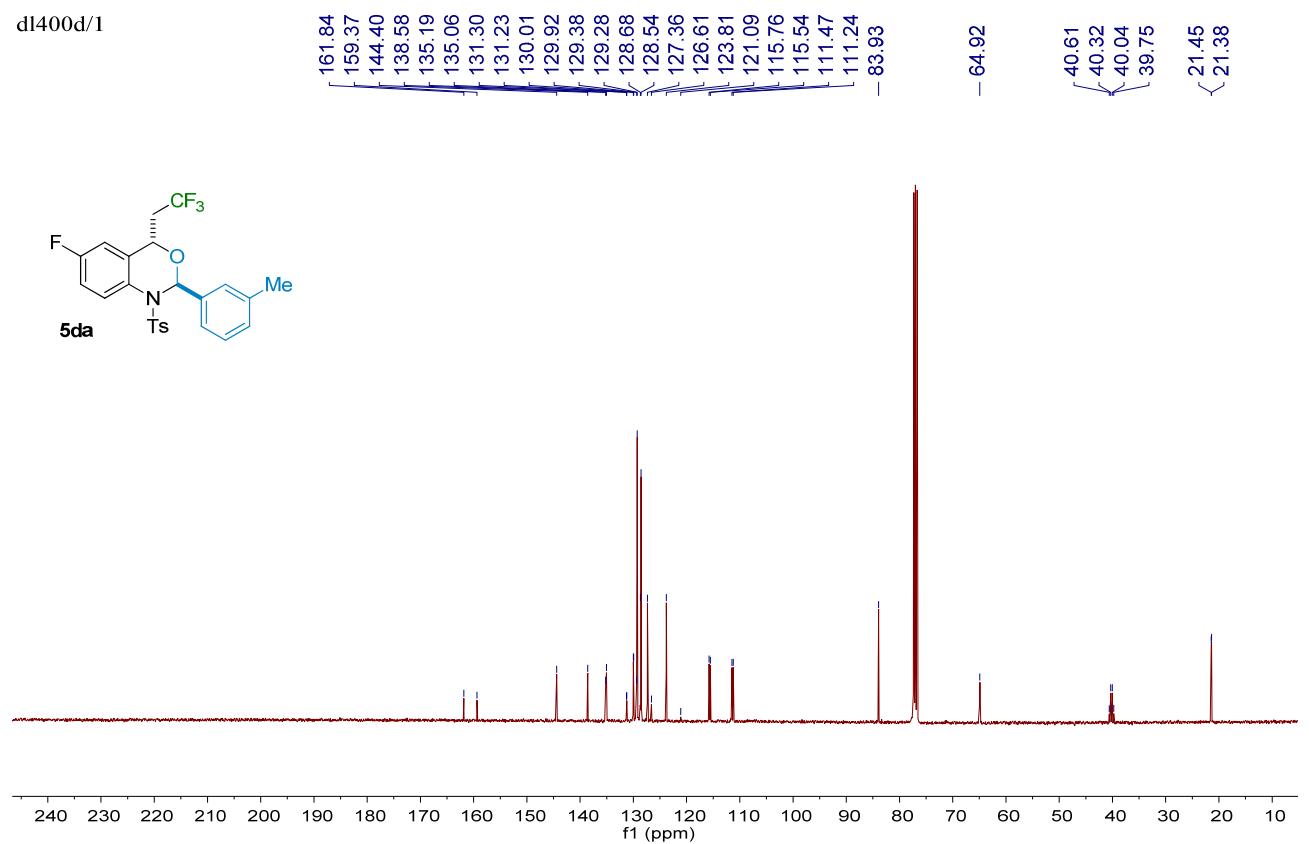
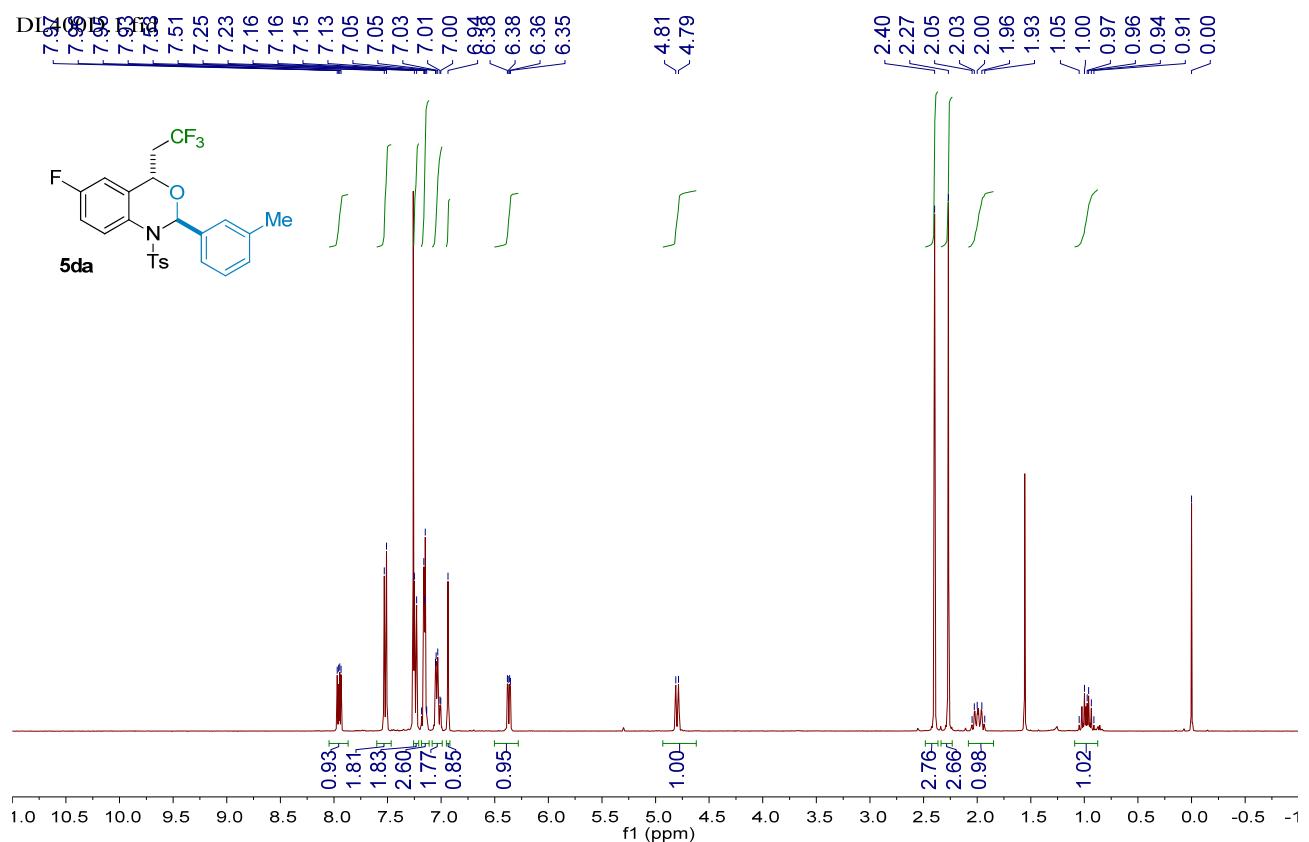
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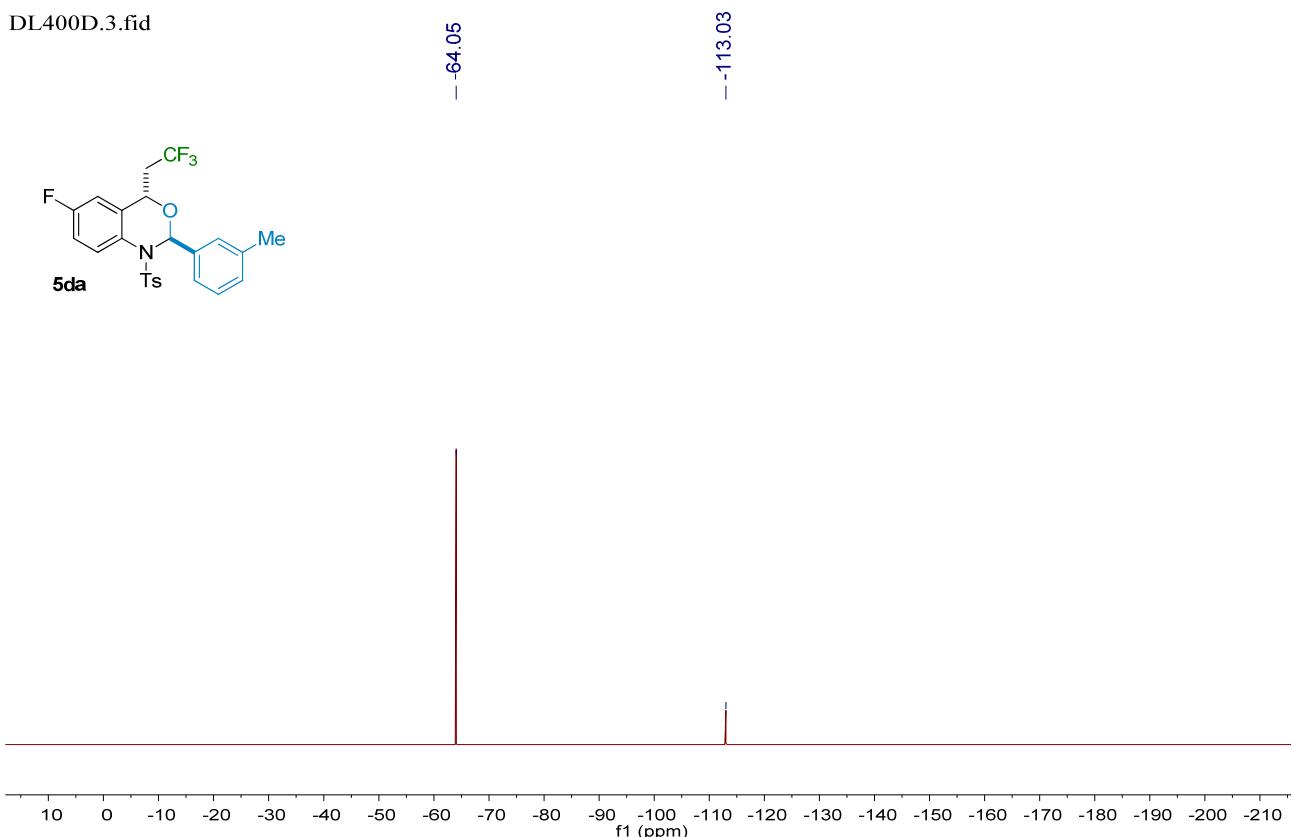


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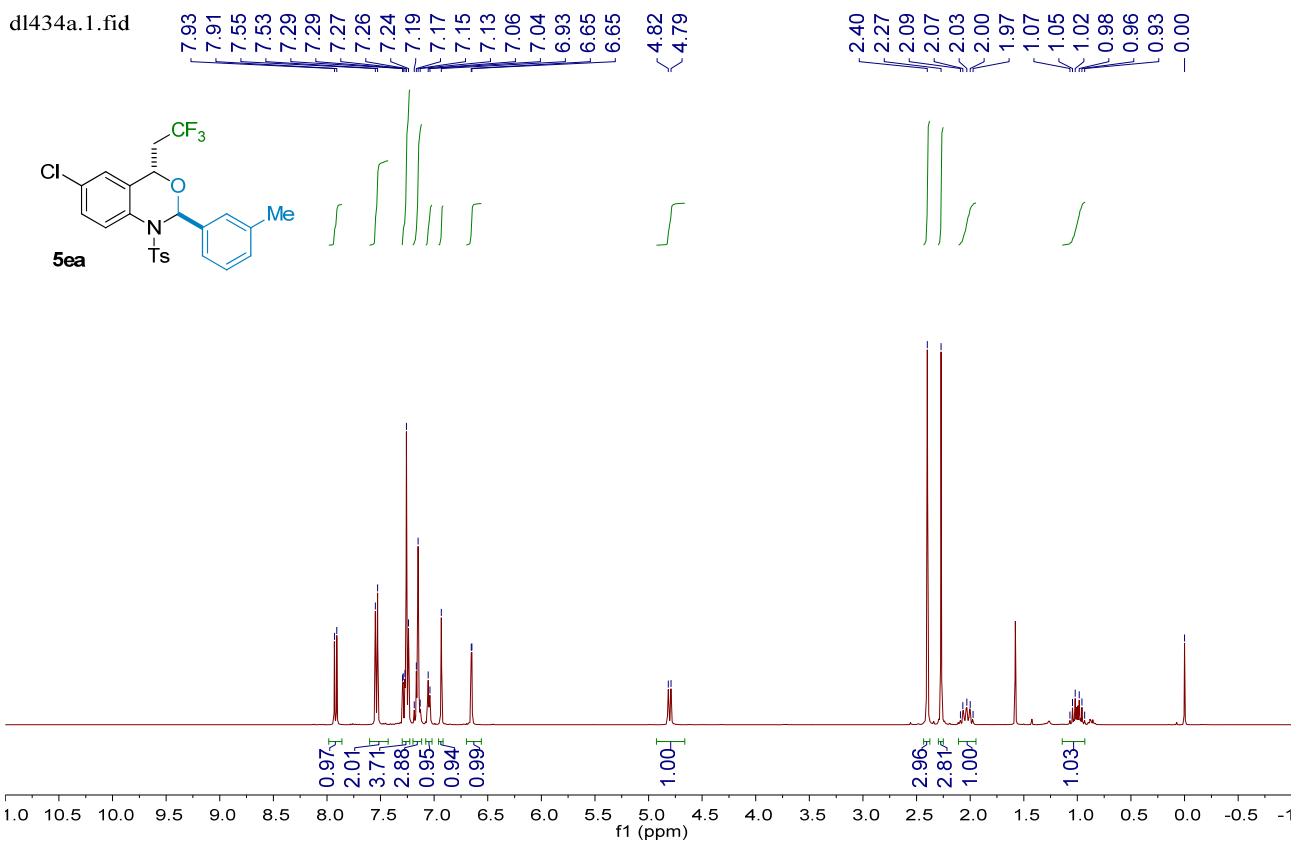


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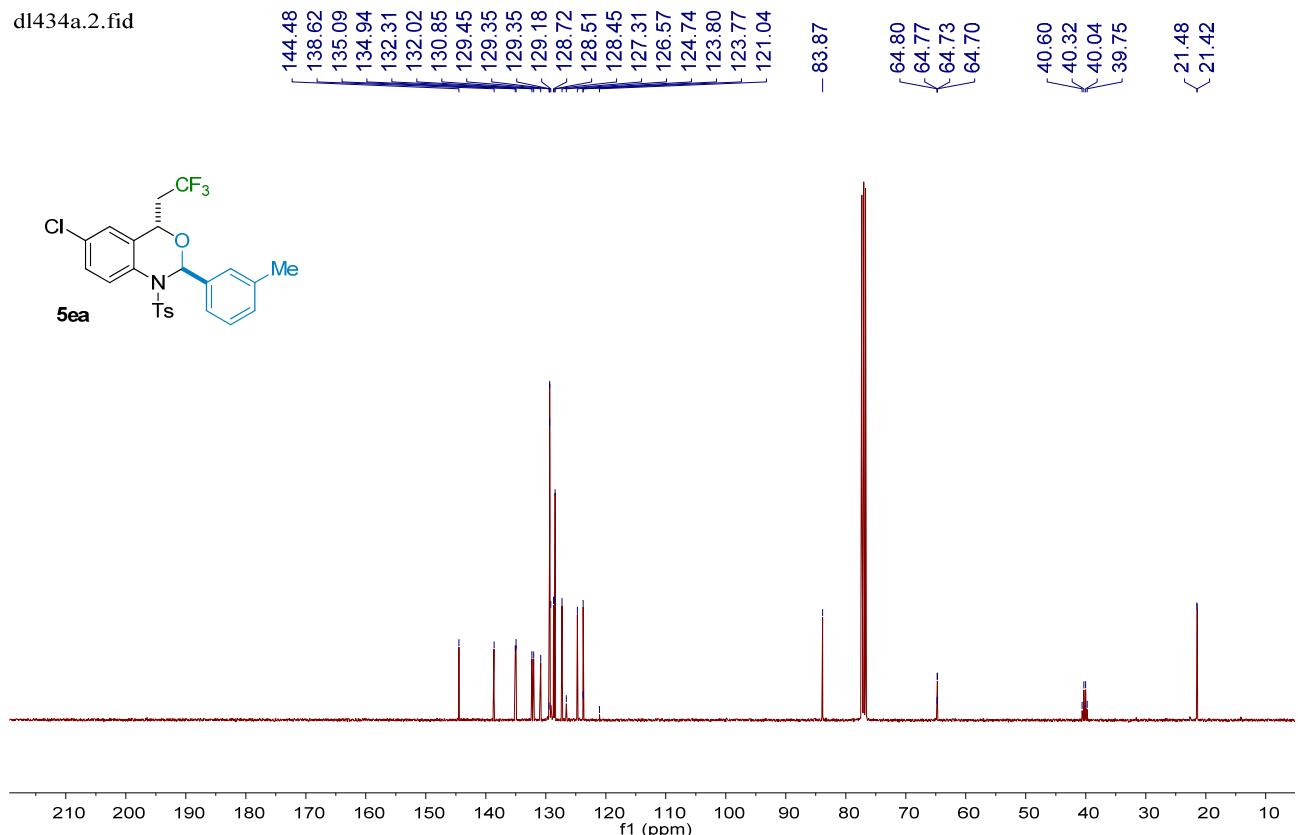




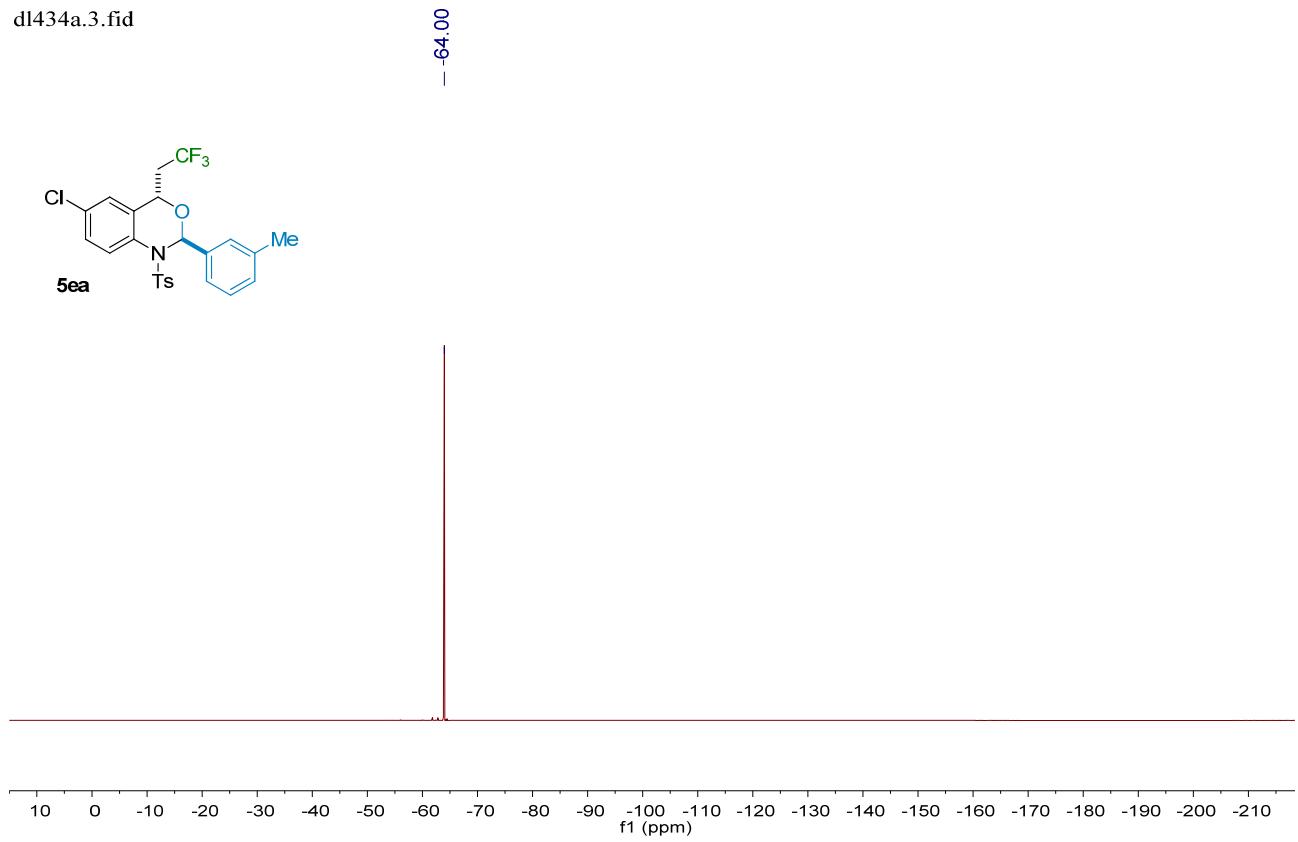
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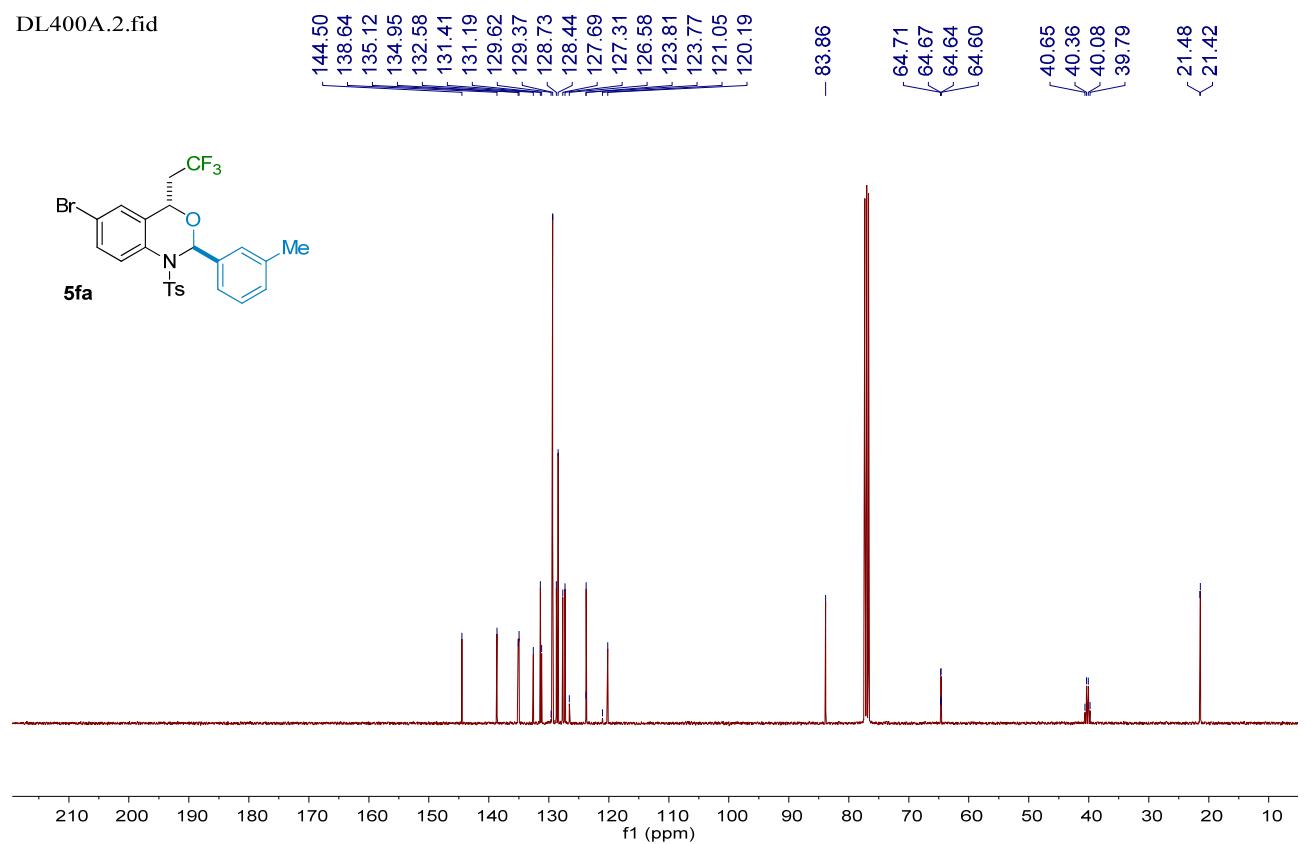
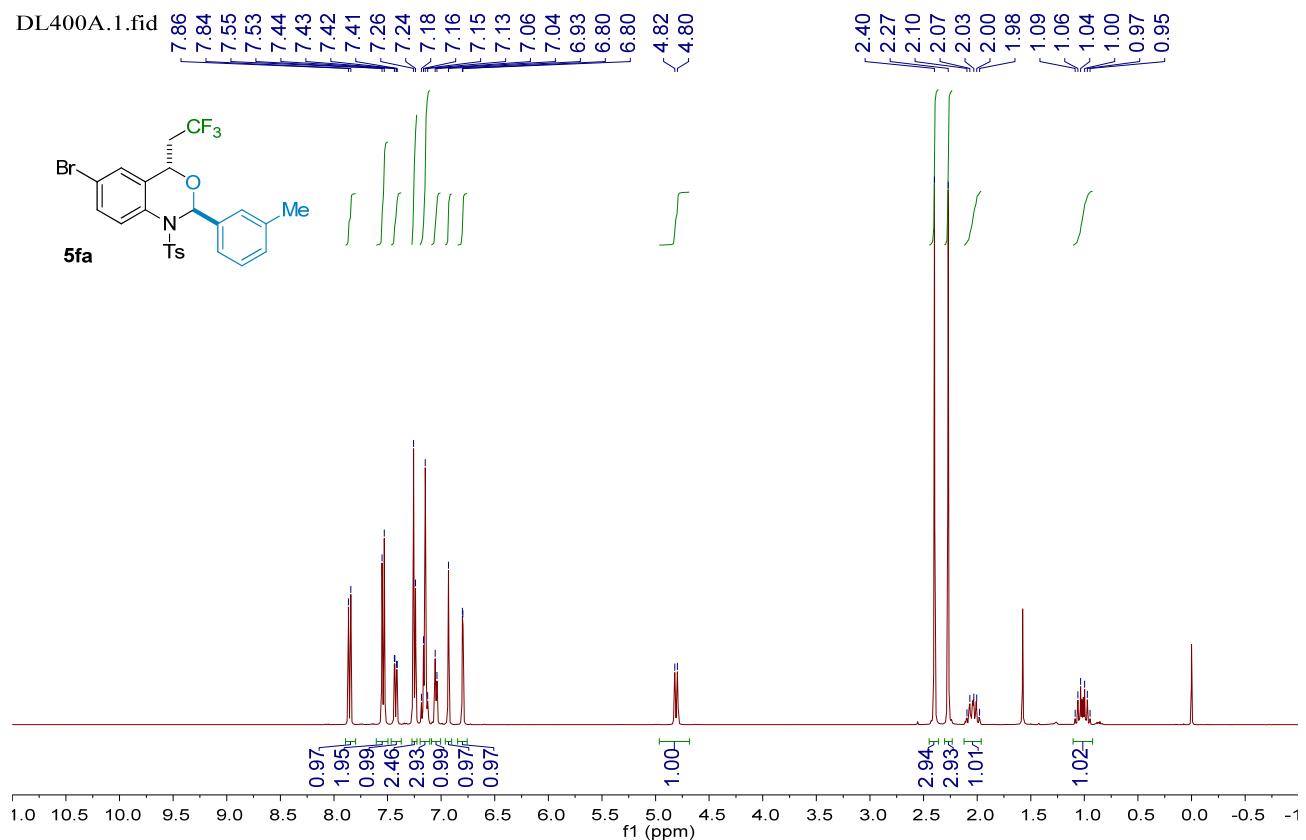
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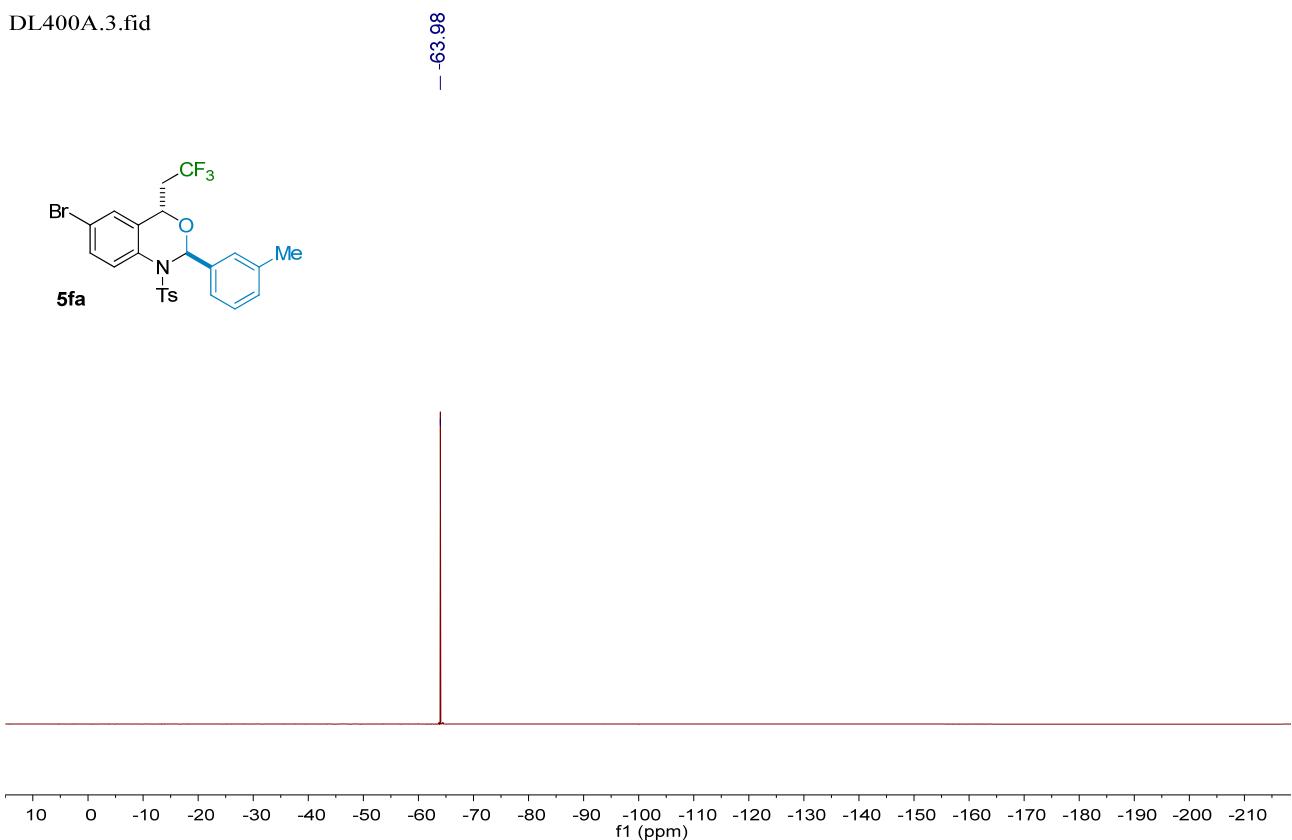
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¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of 5fa

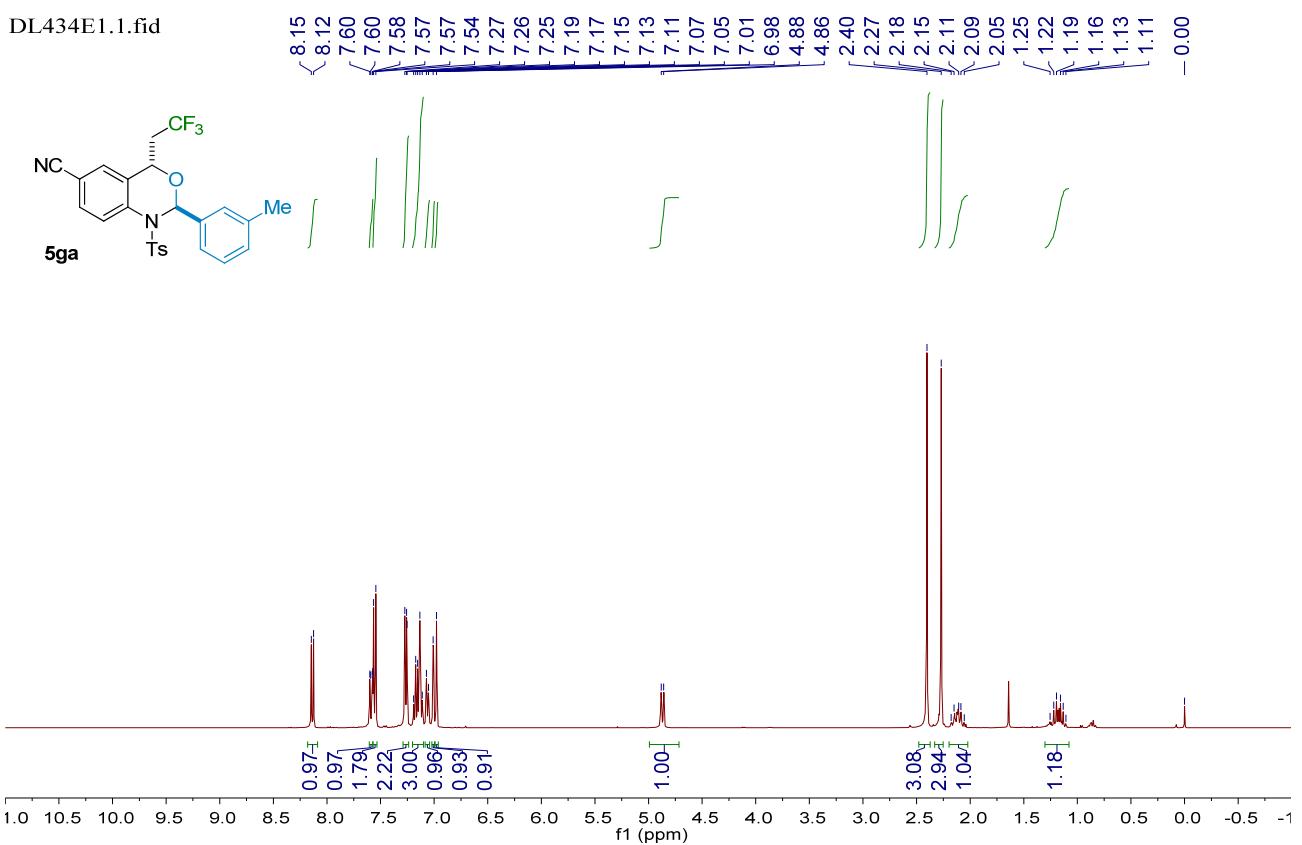


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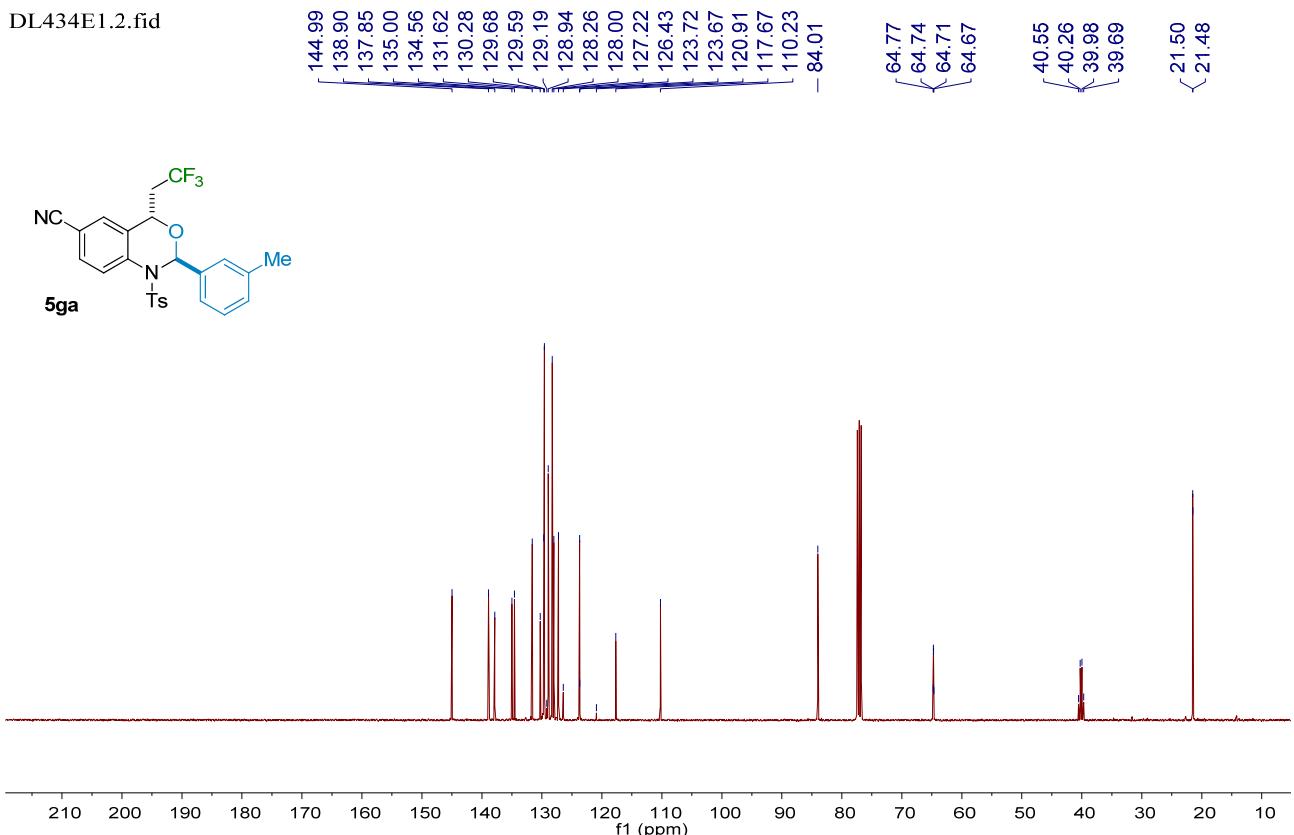


^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3) and ^{19}F NMR (376 MHz, CDCl_3) spectra of **5ga**

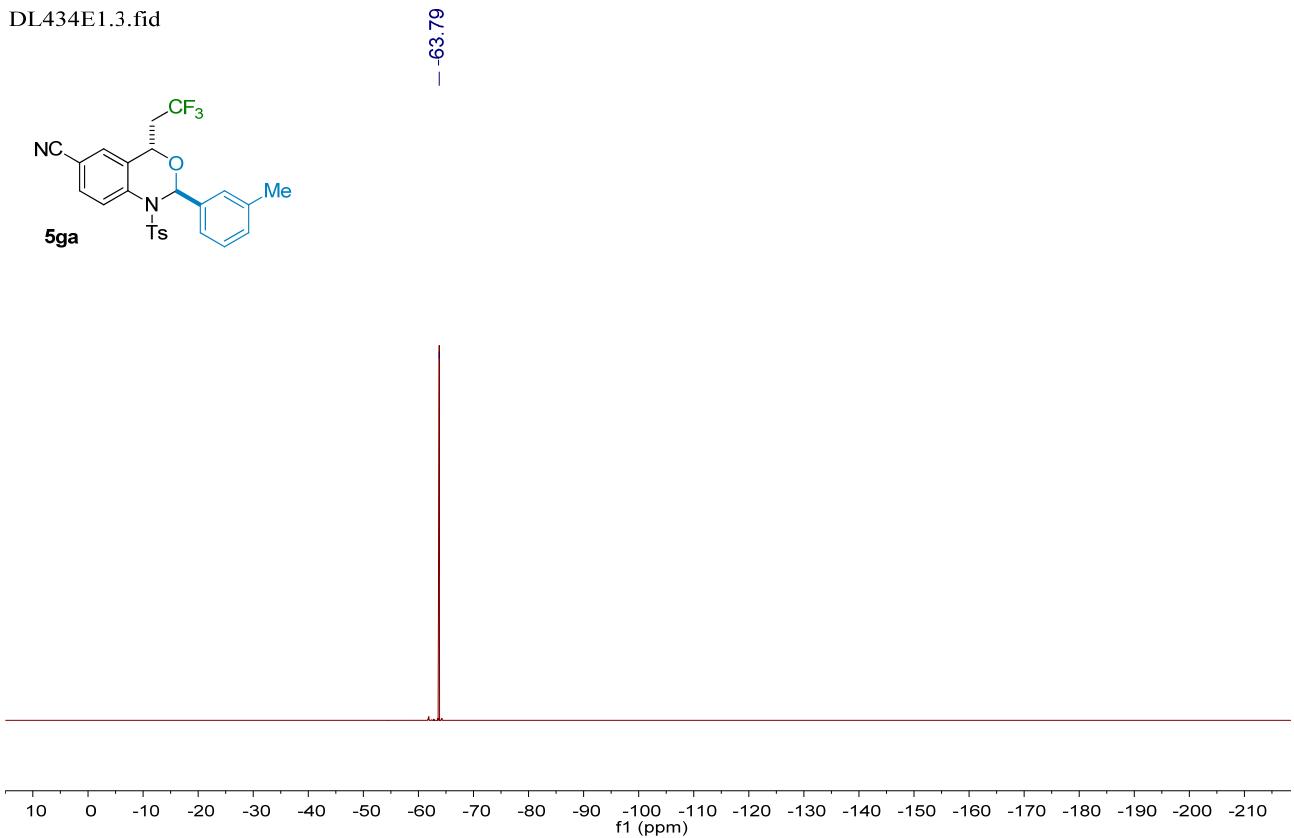
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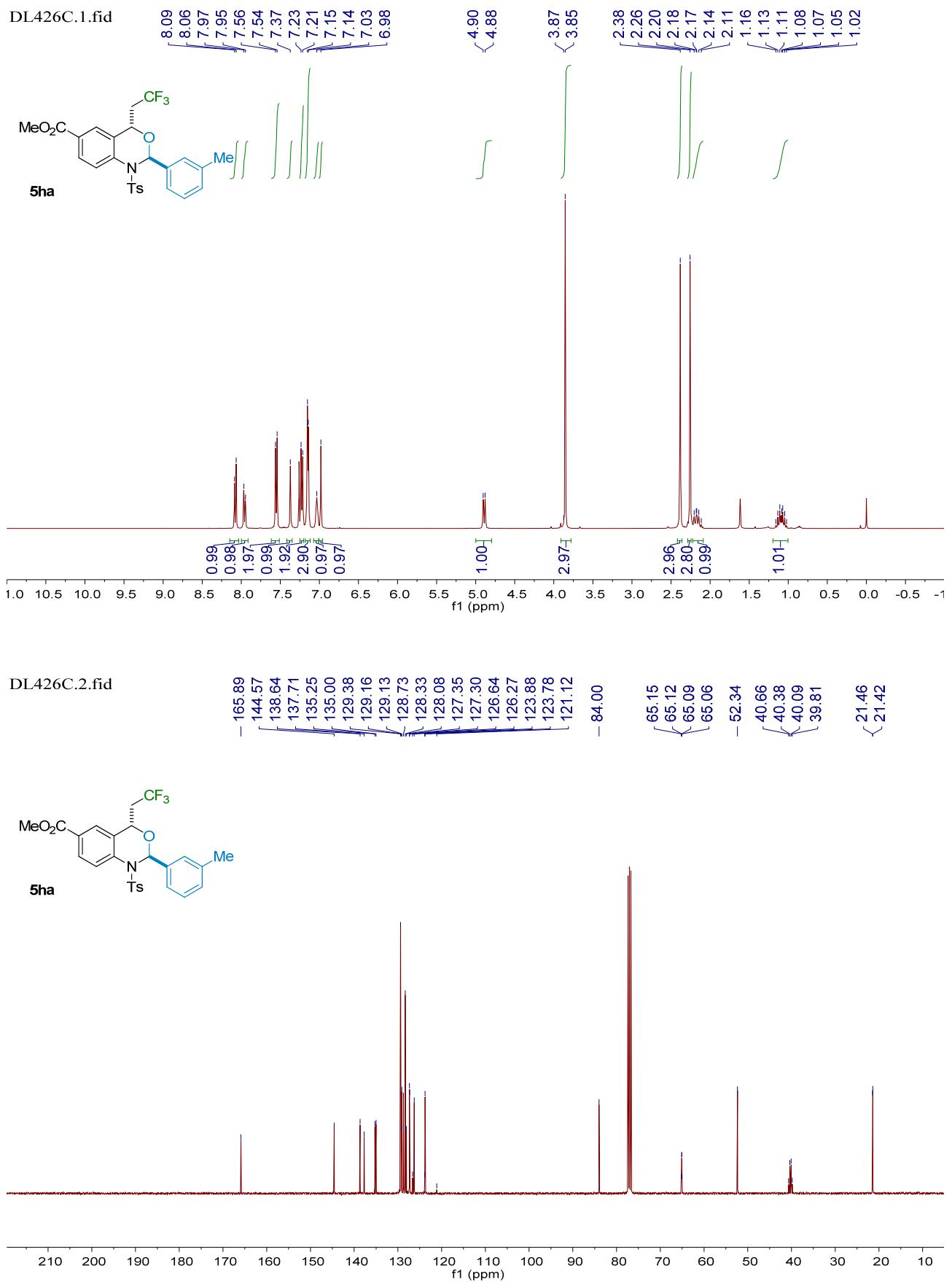
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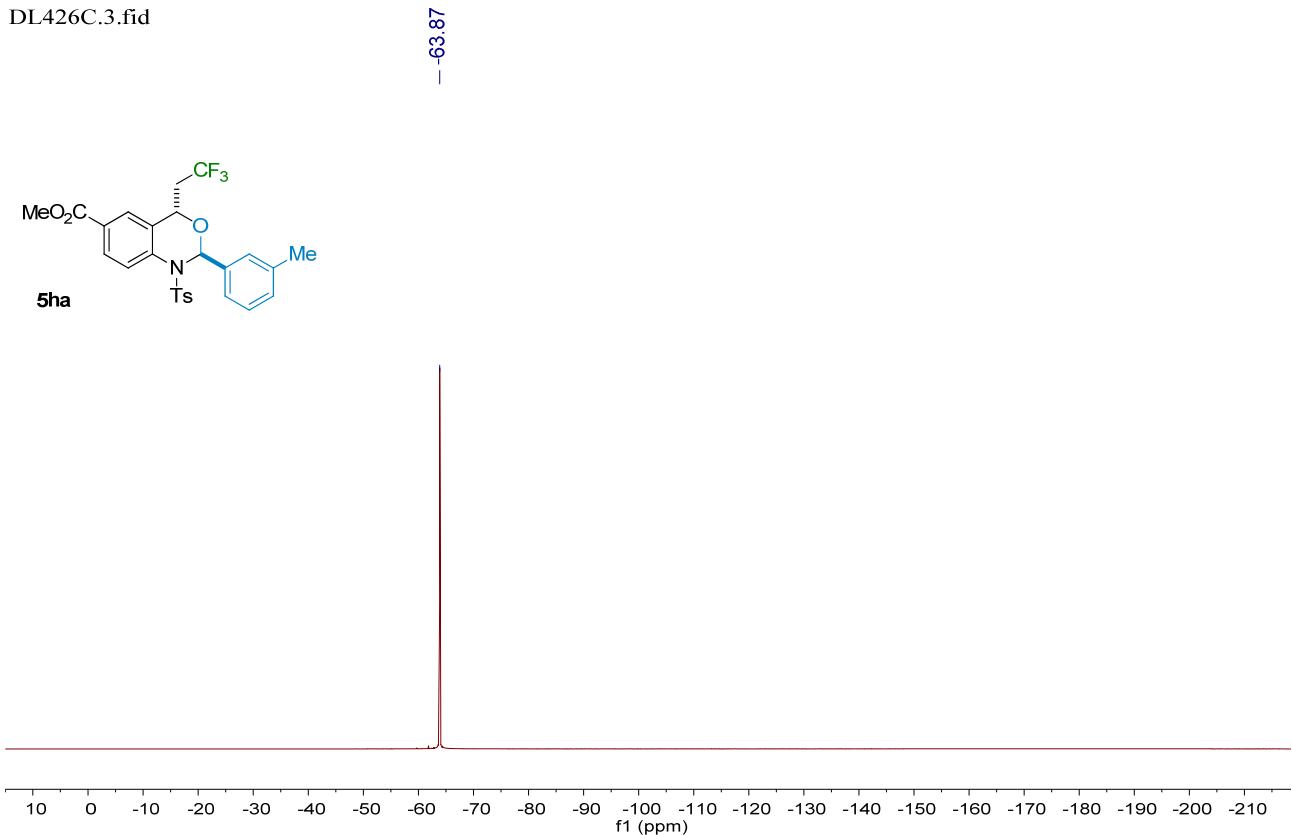
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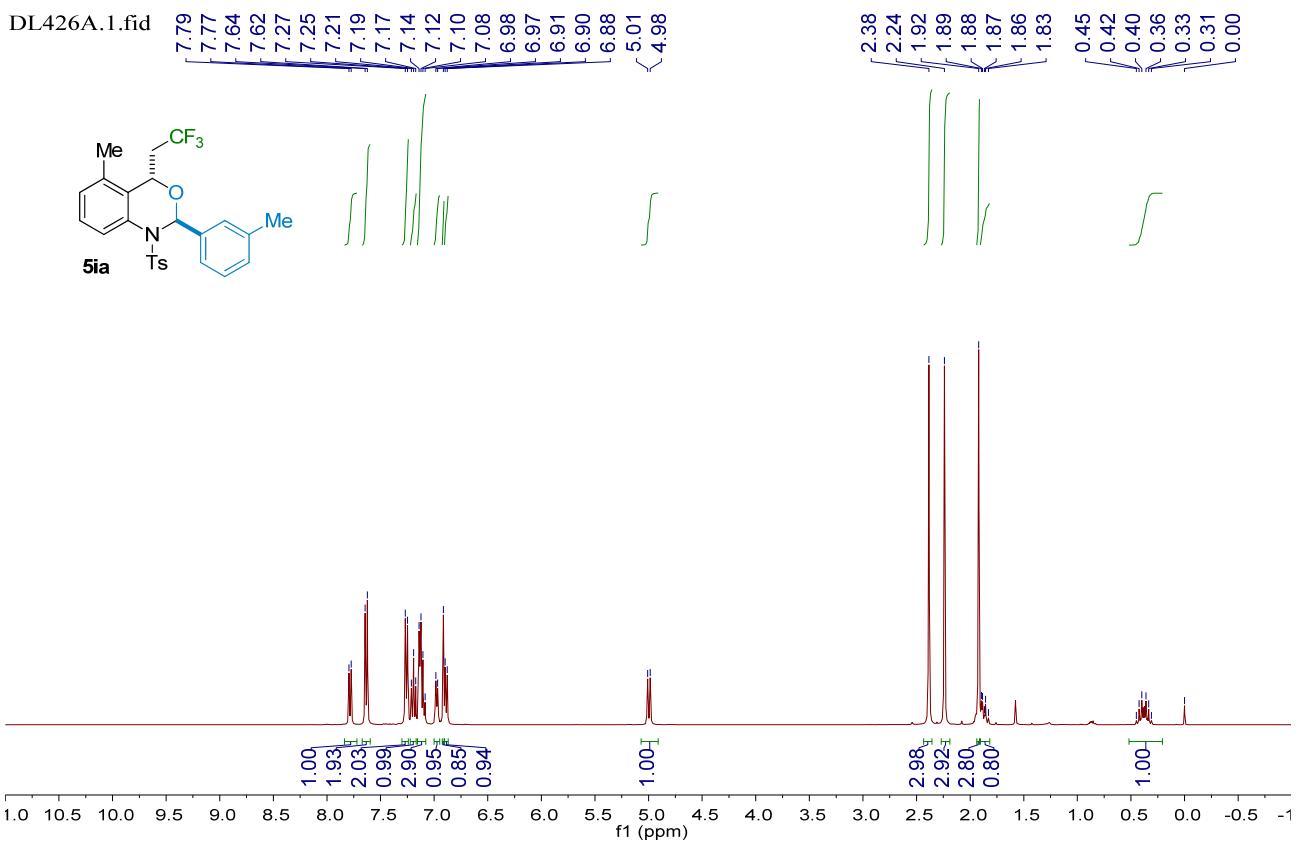
¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of 5ha



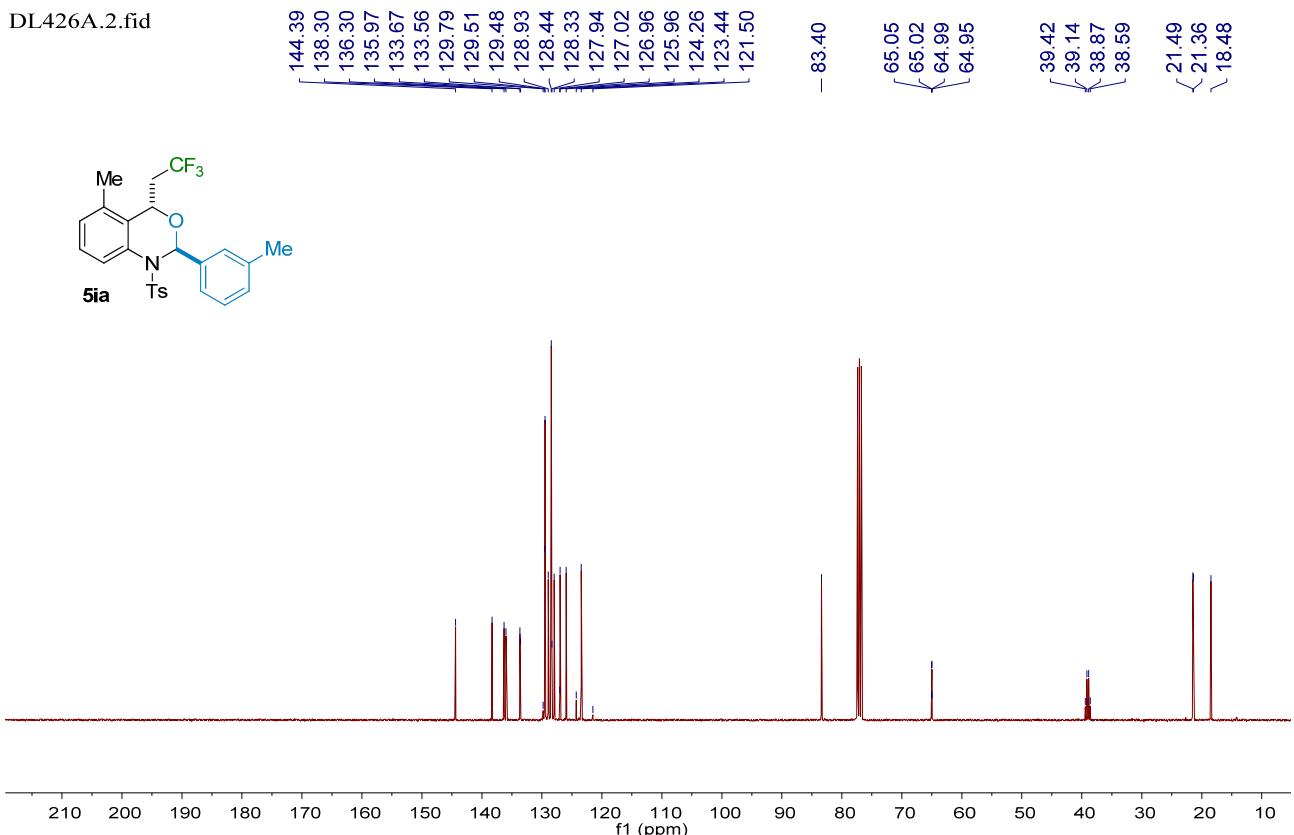
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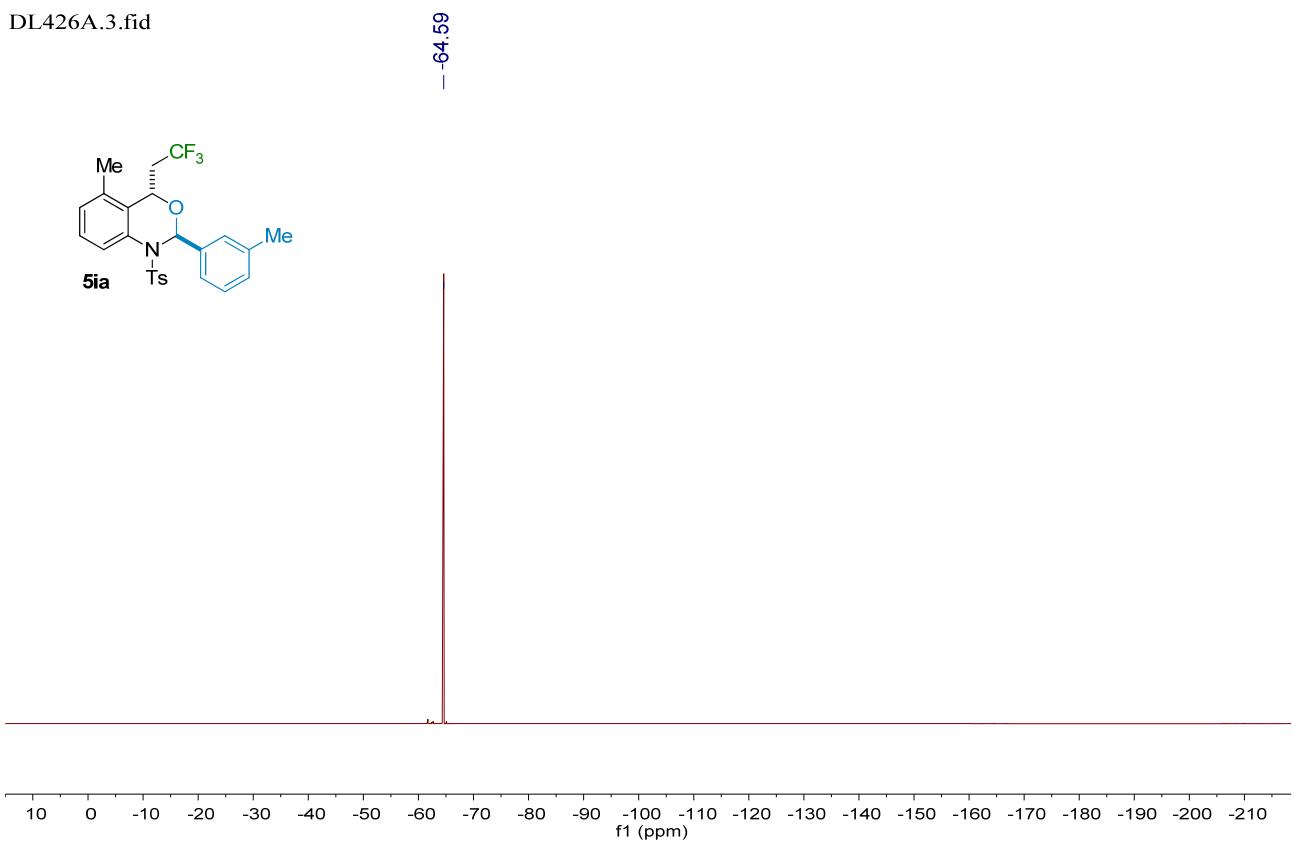
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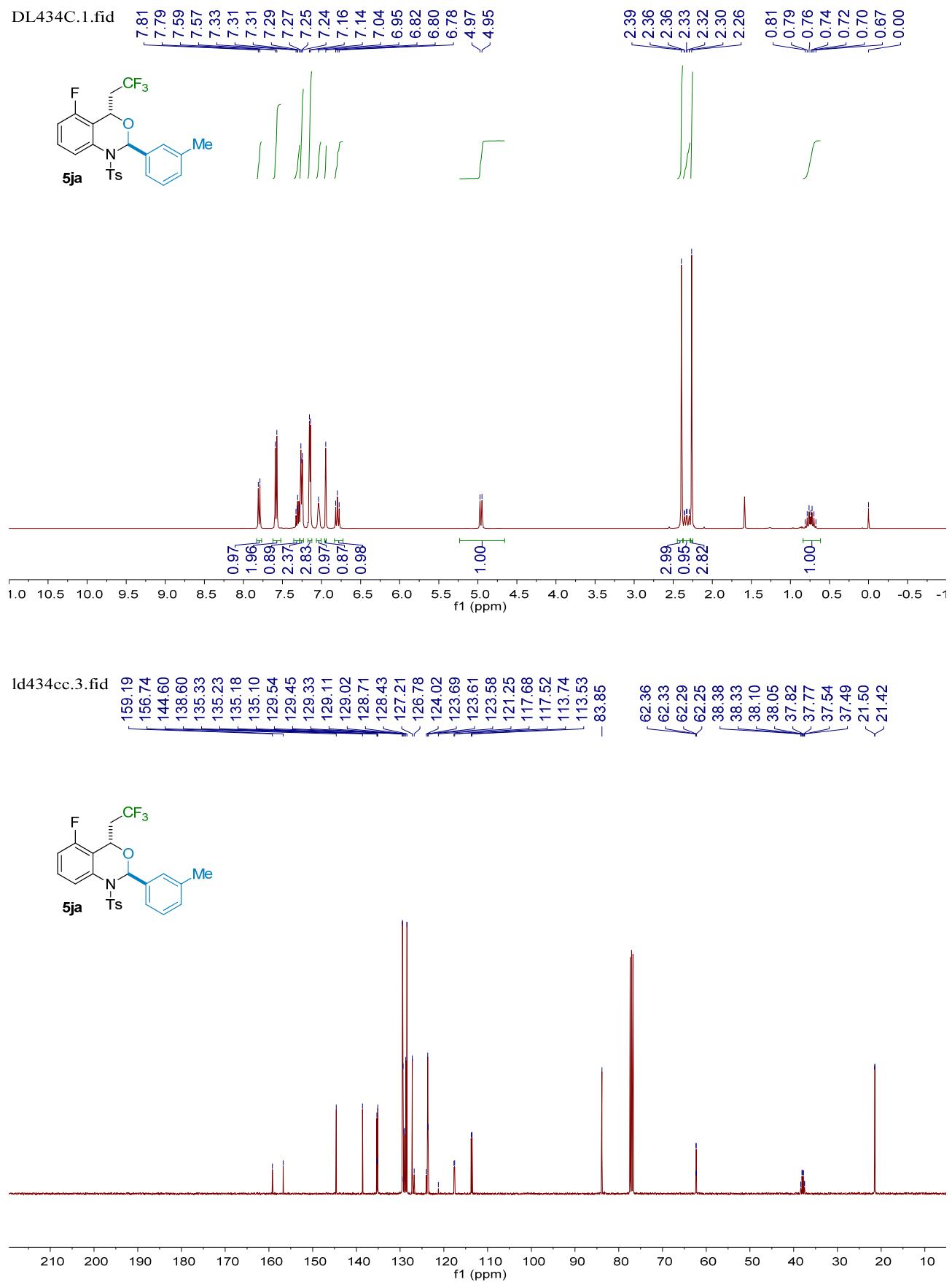
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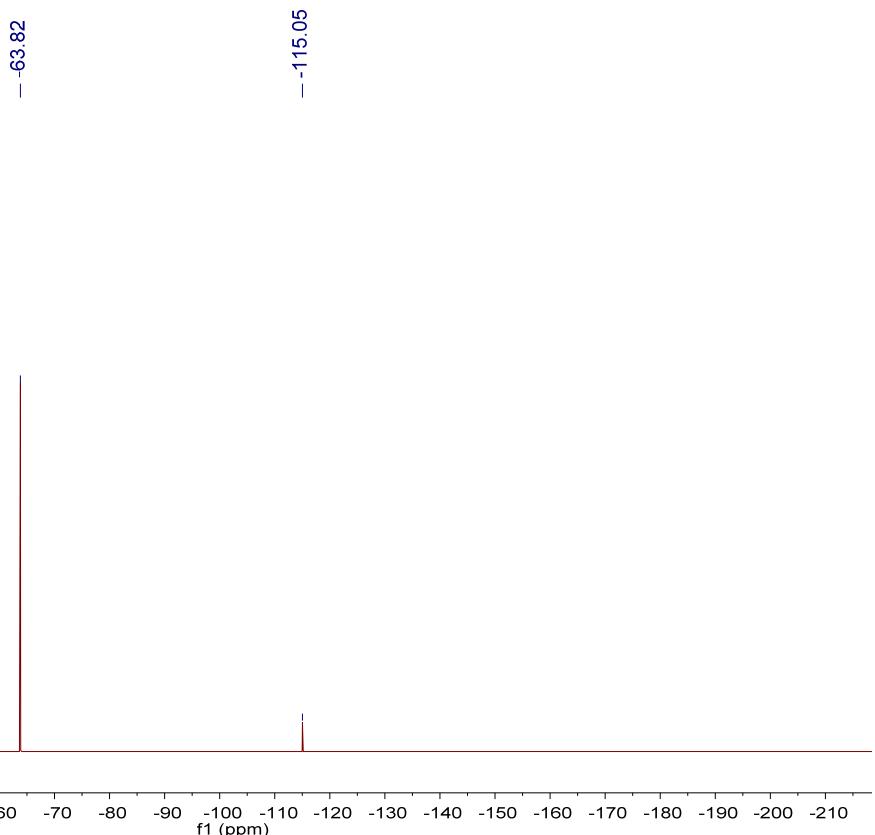
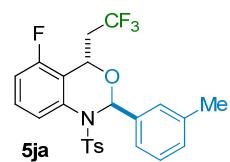
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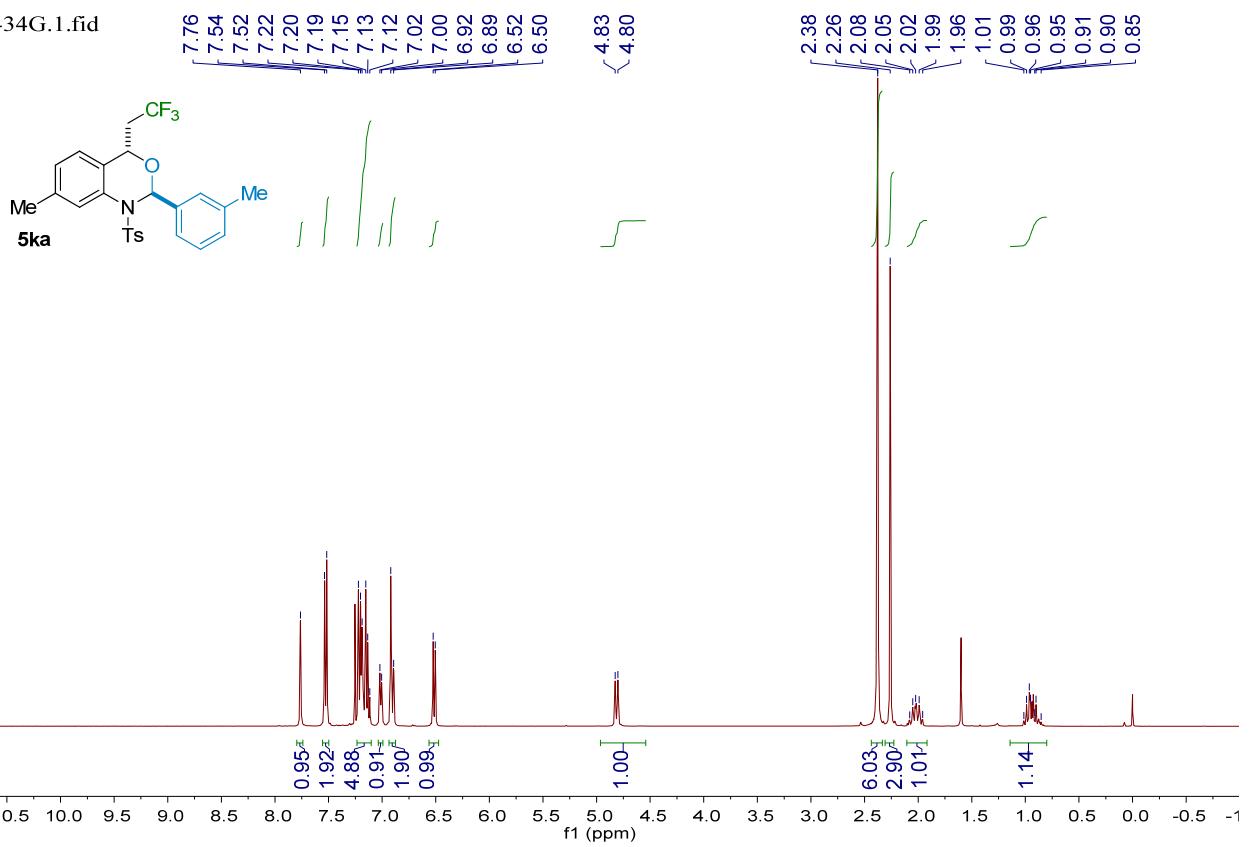


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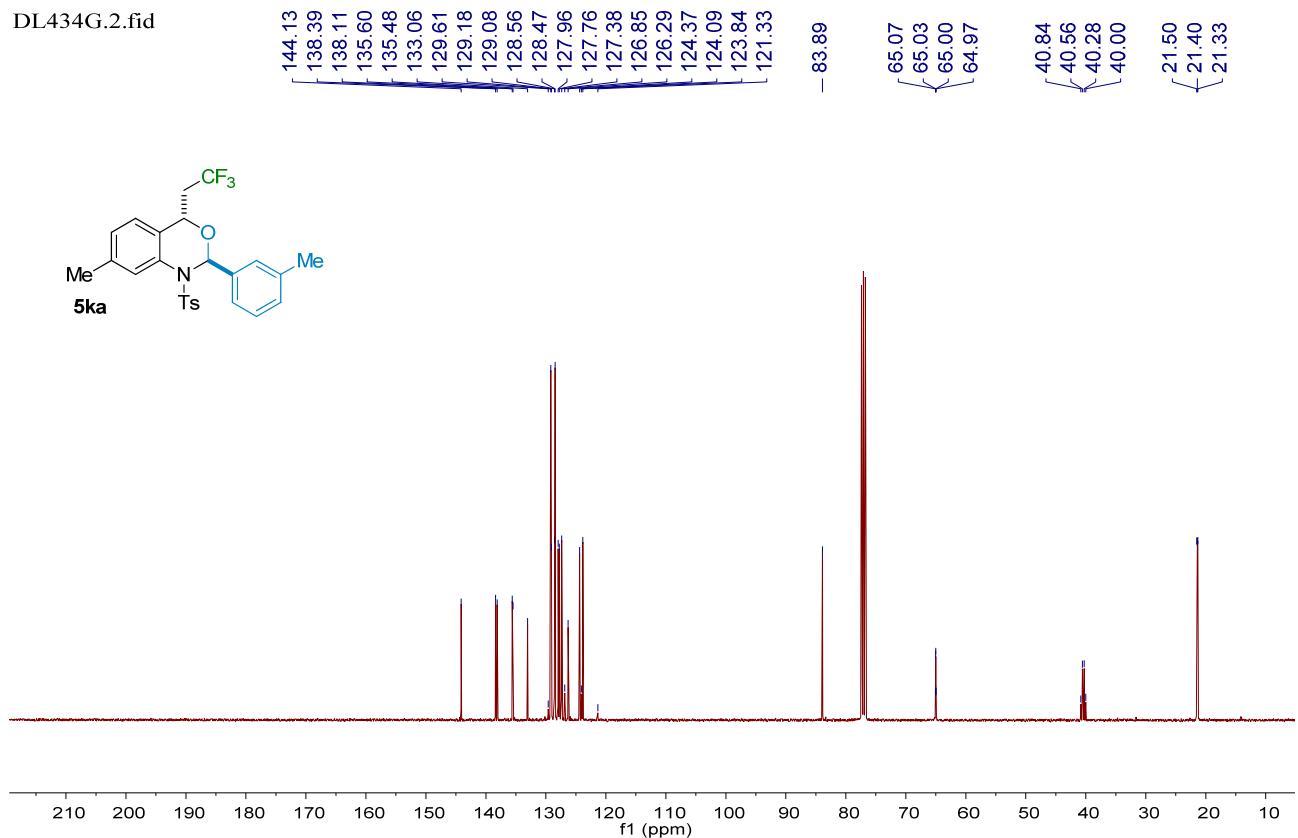


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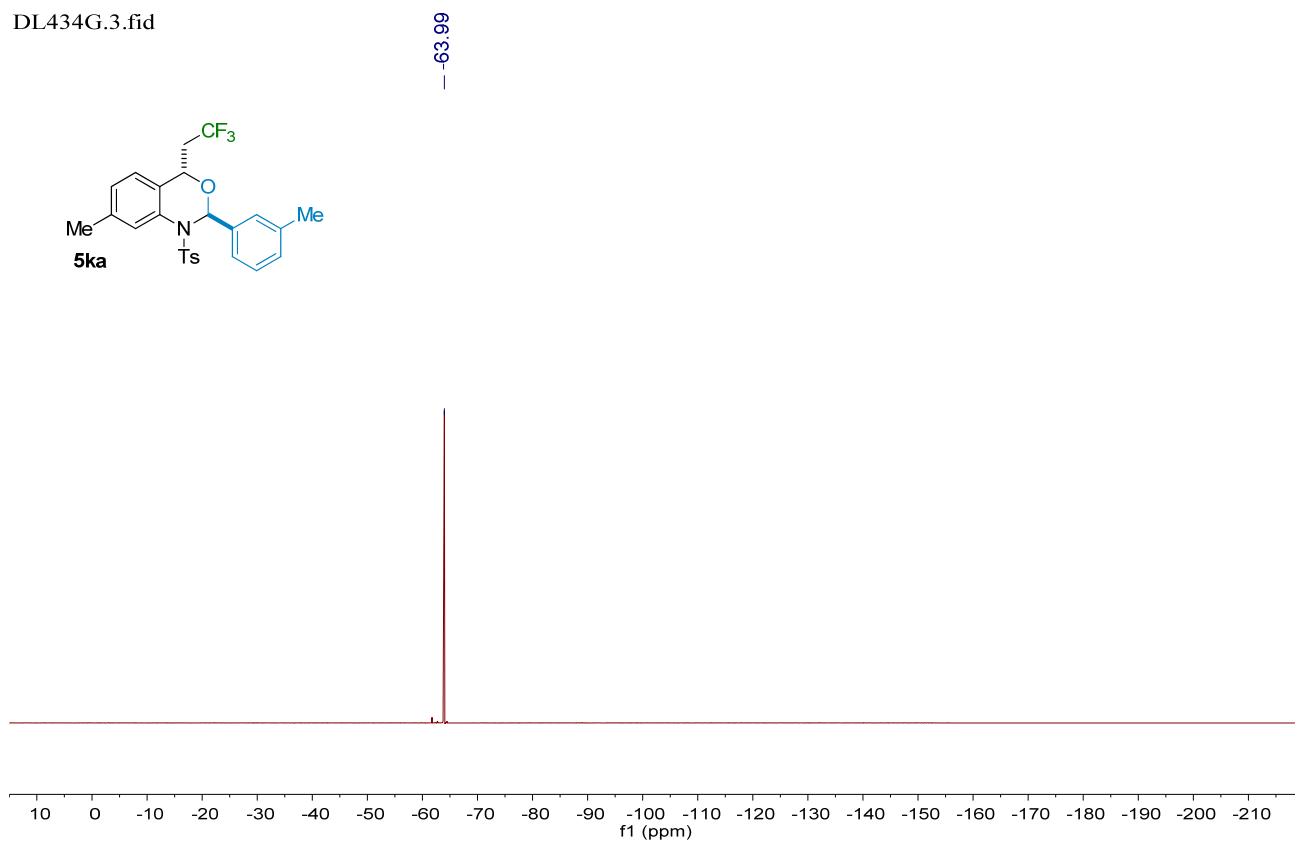
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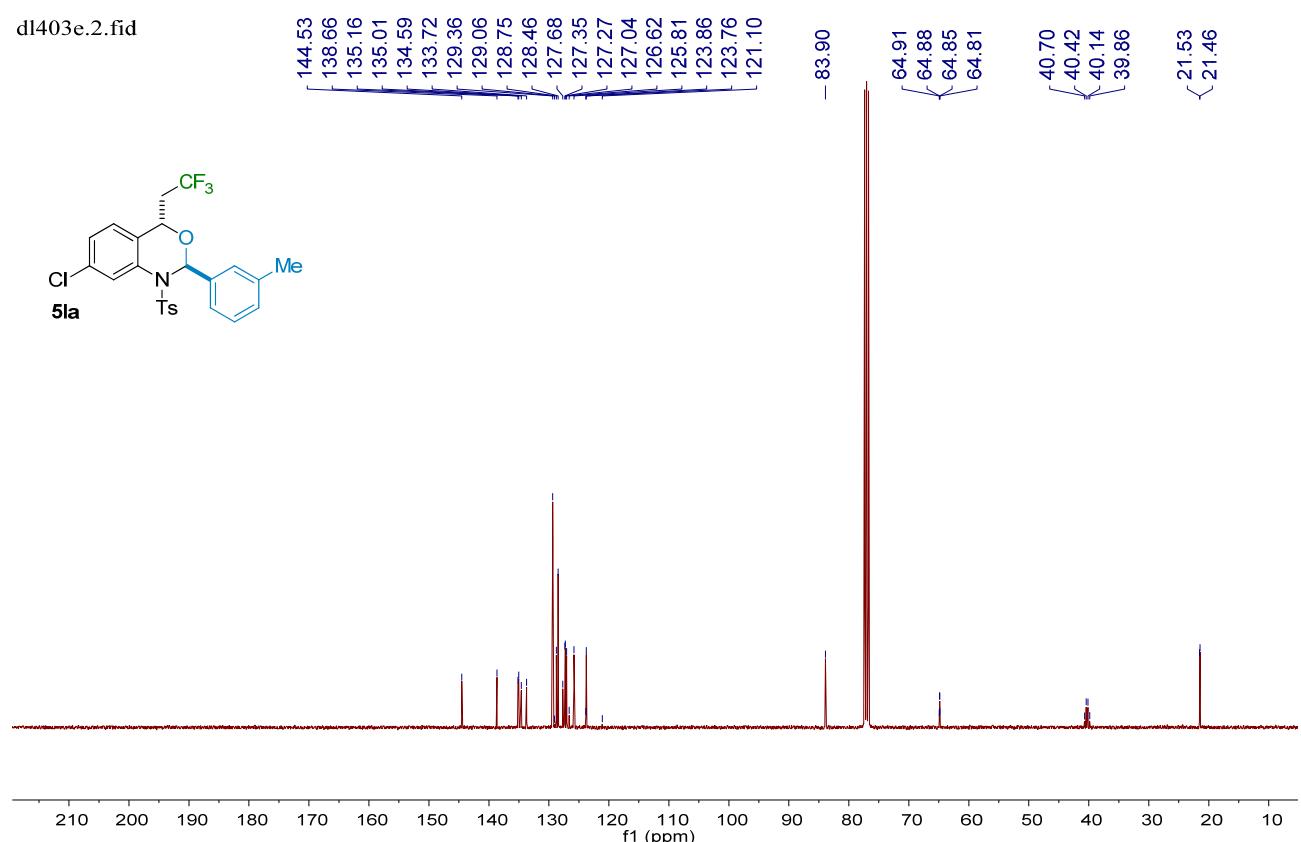
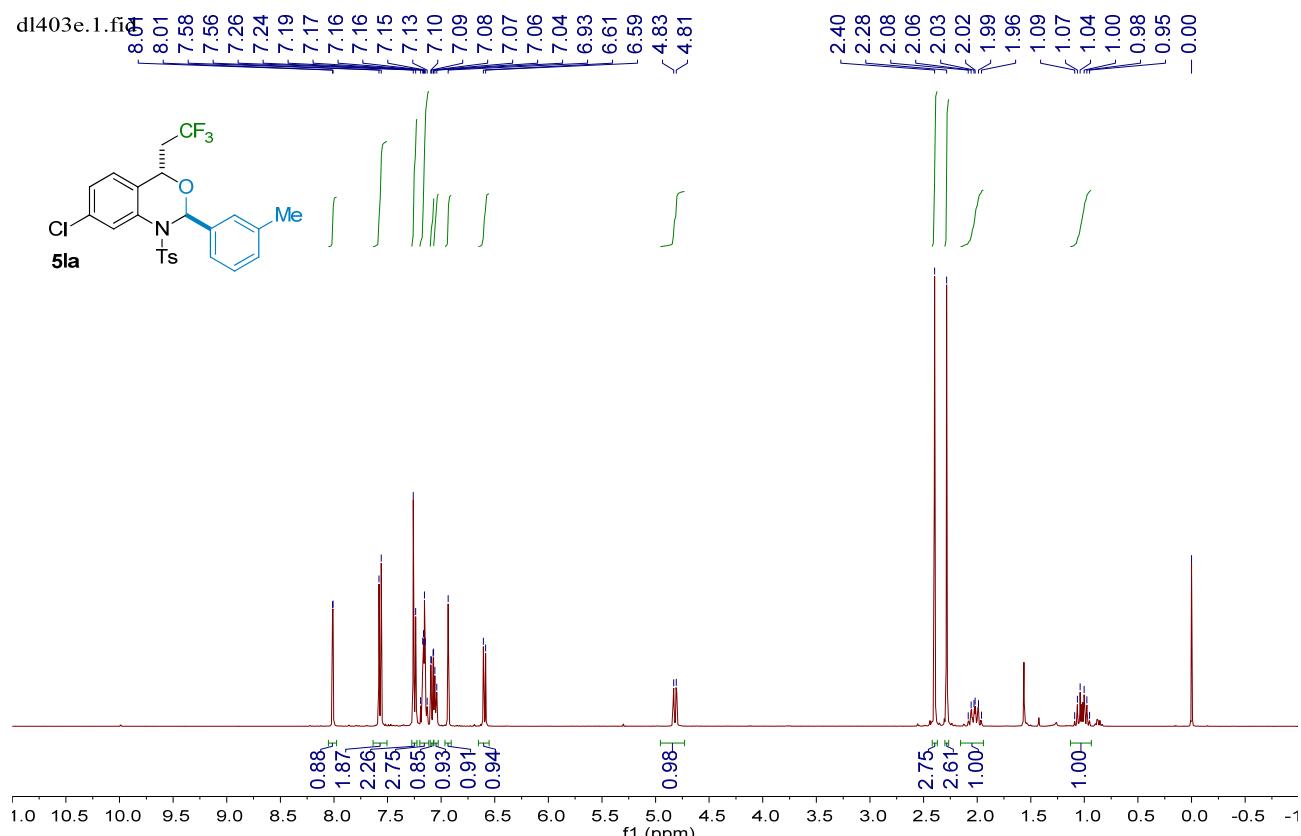
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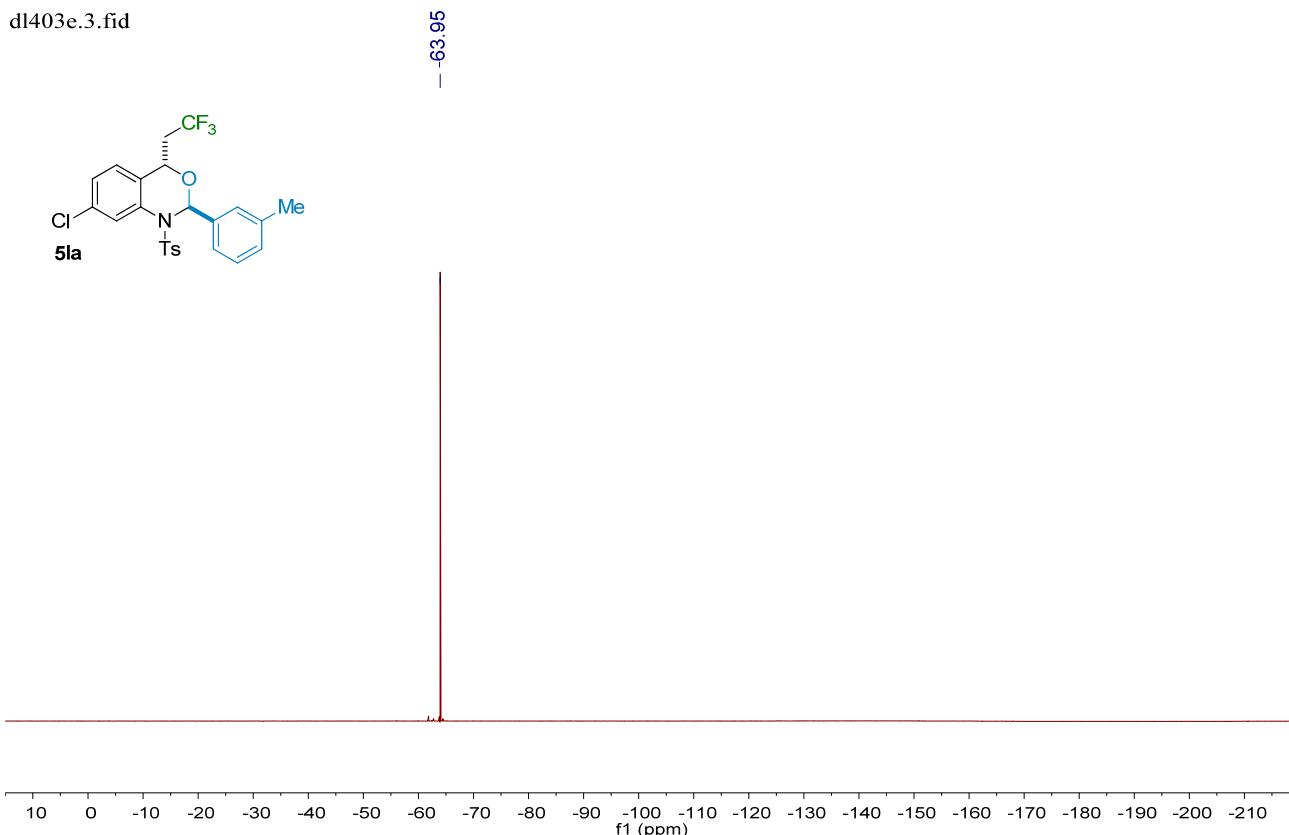
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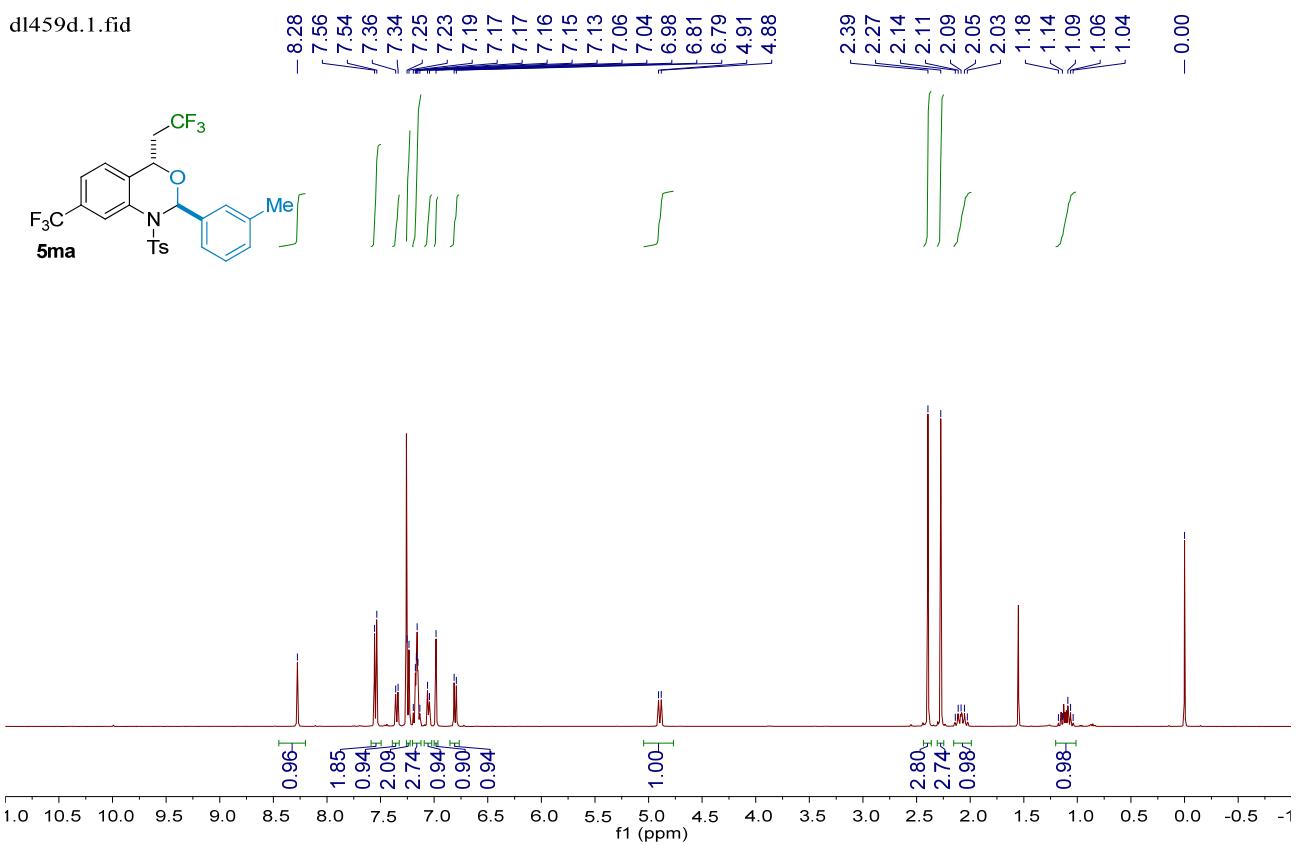
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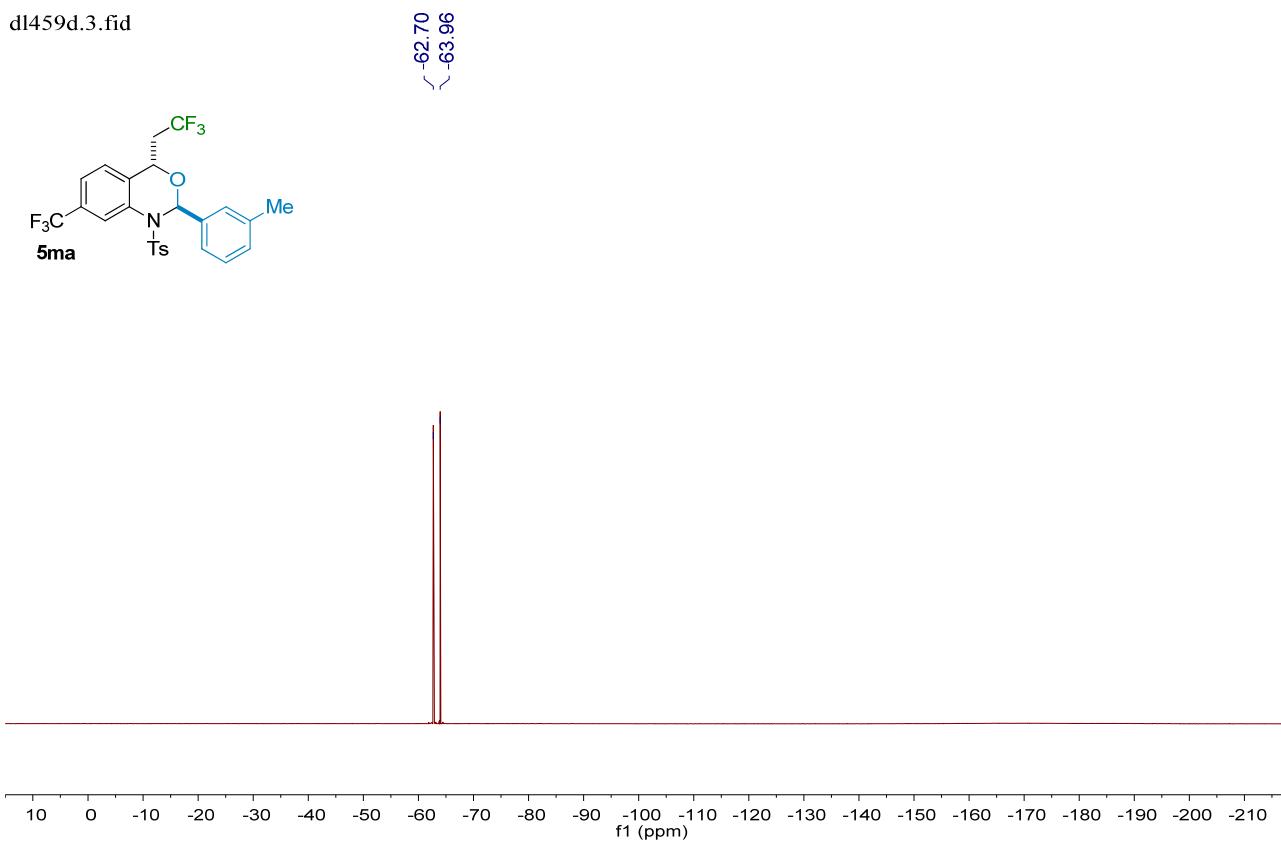
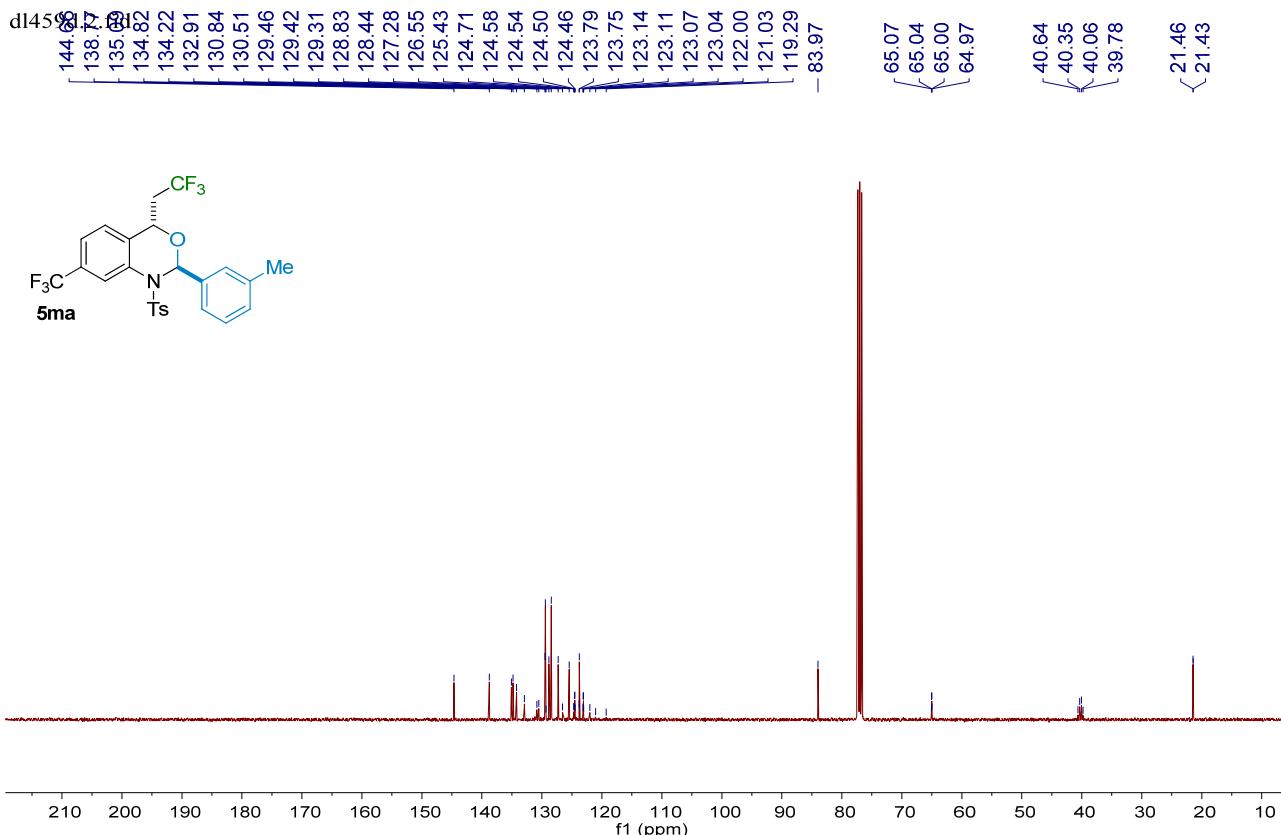


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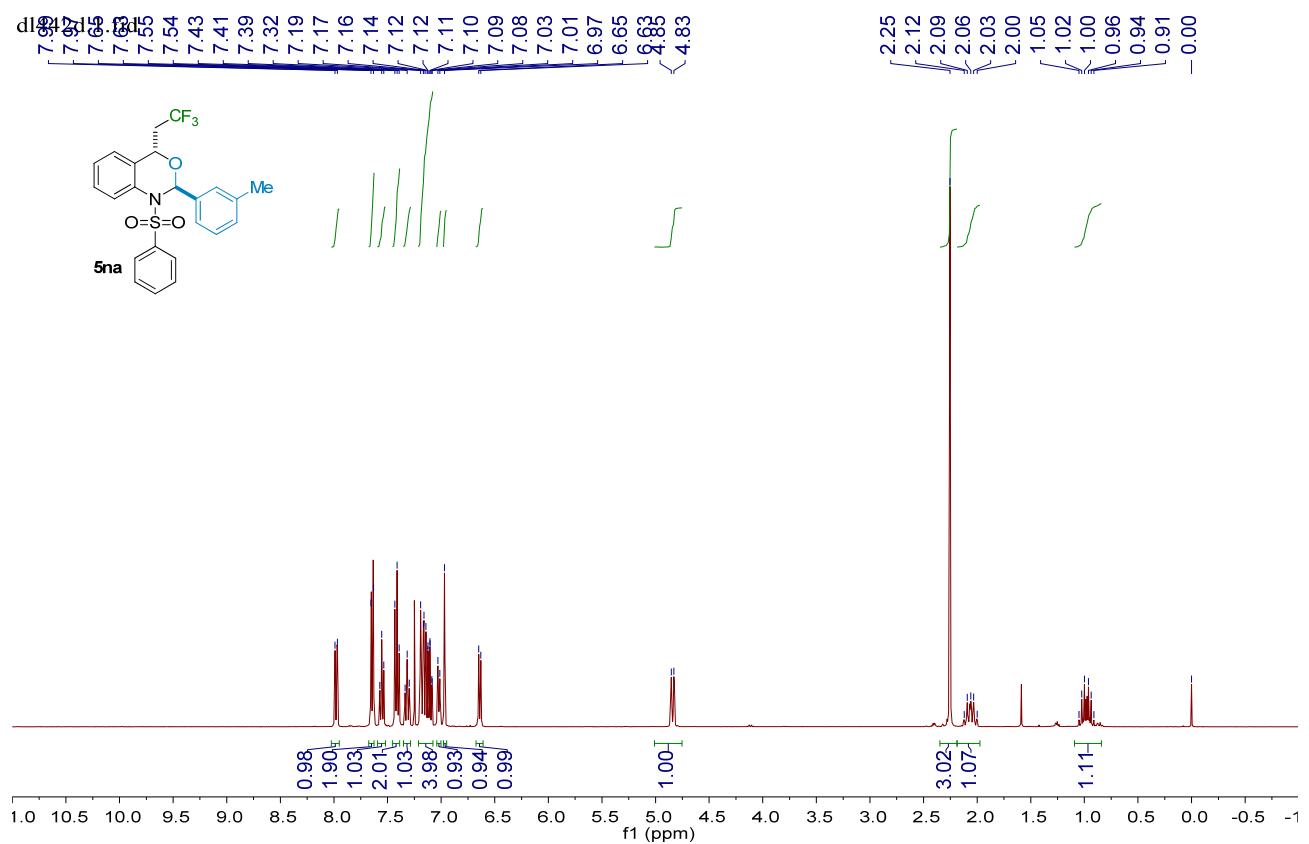


¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of **5ma**

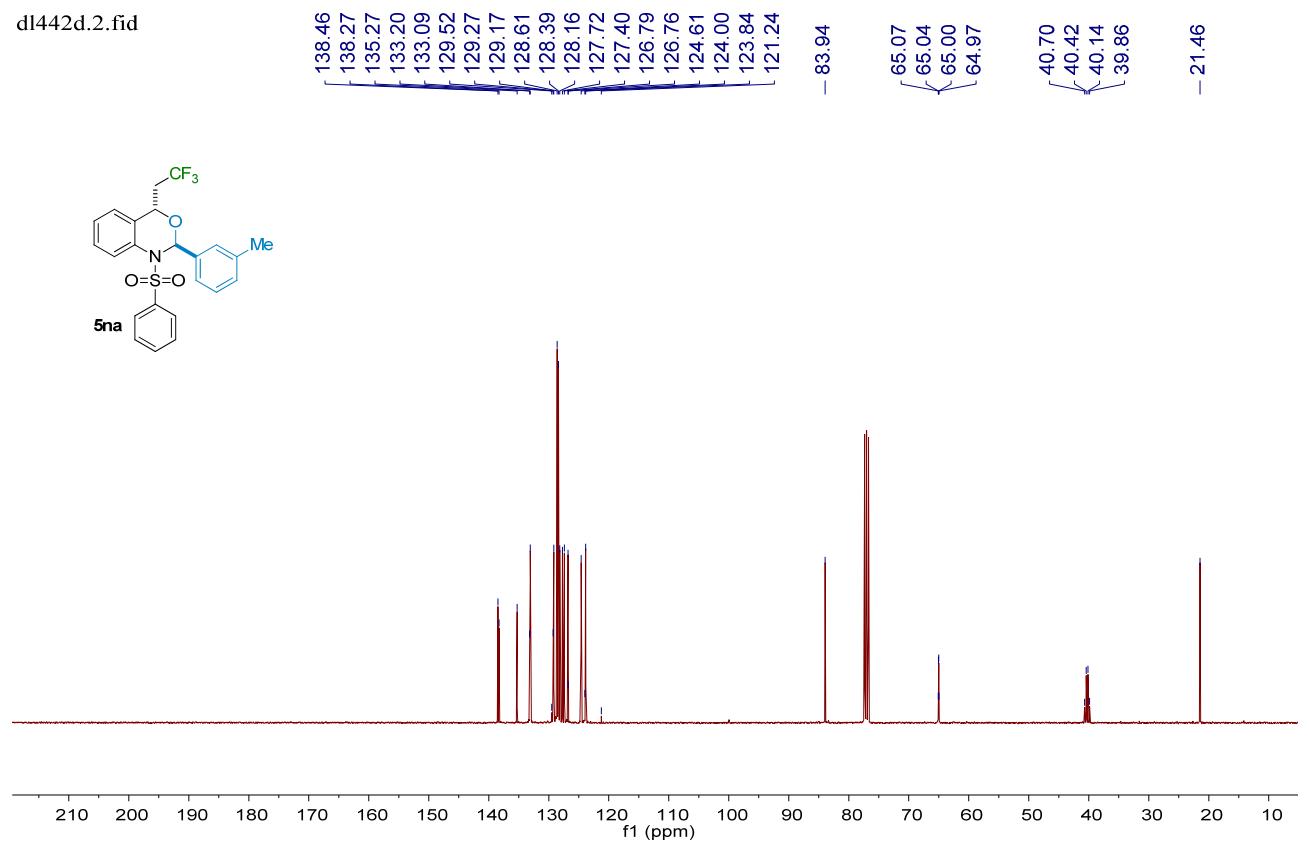


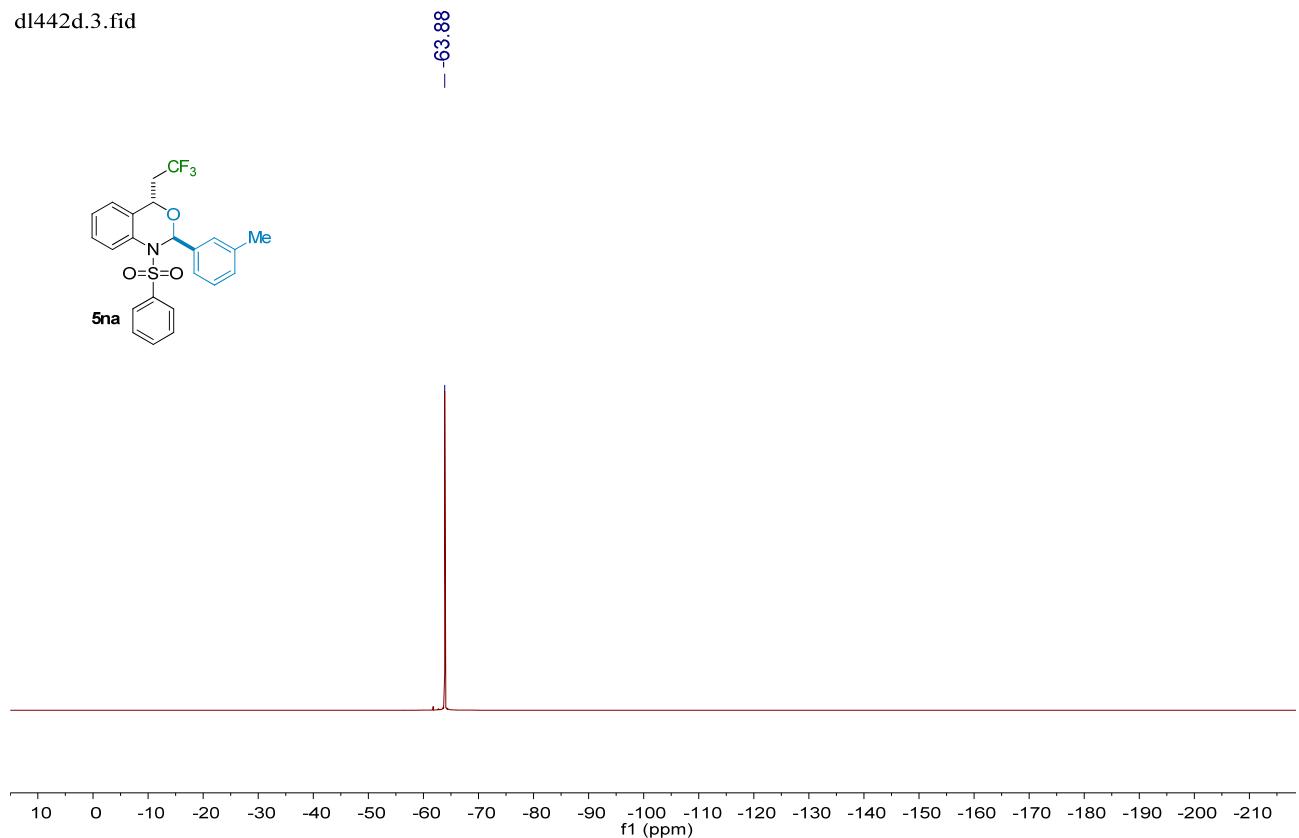


¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of 5na

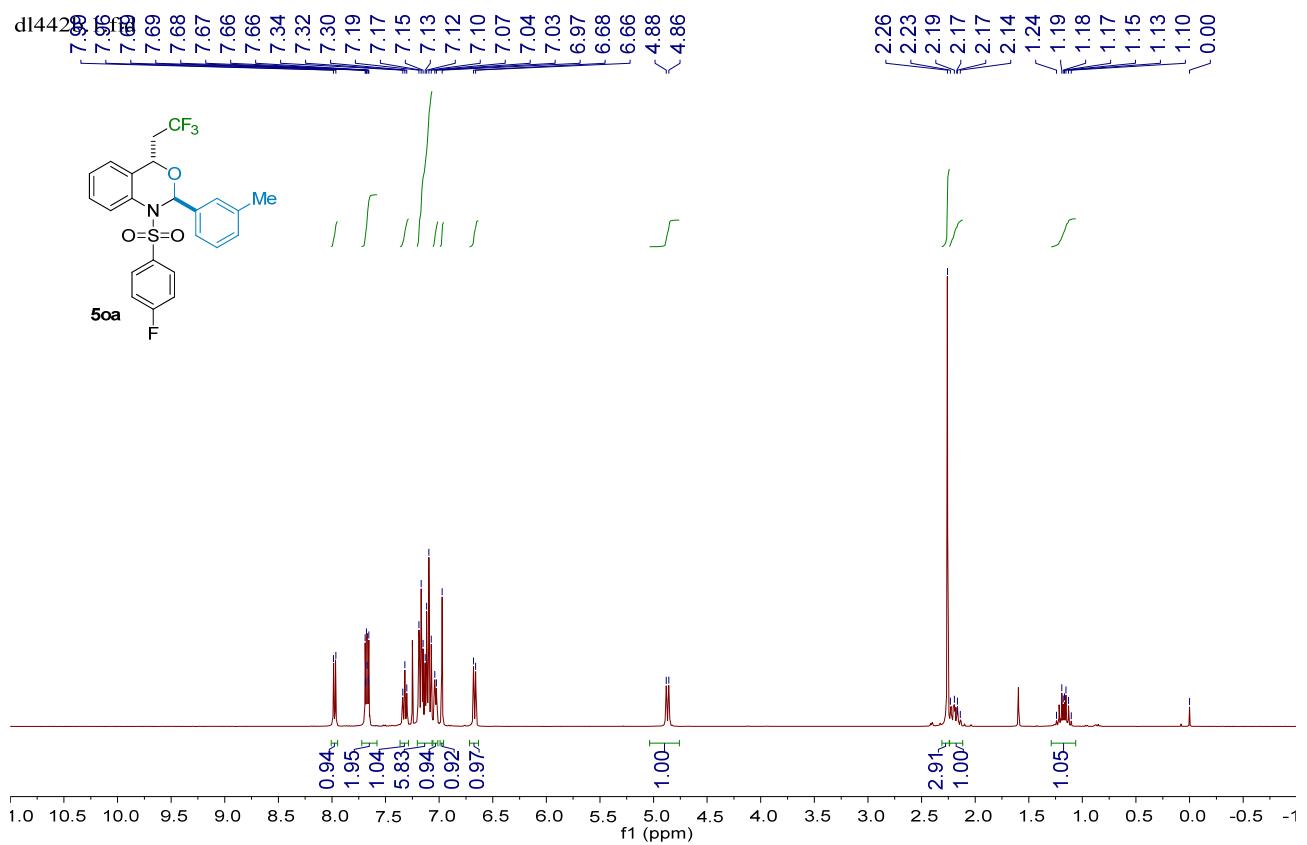


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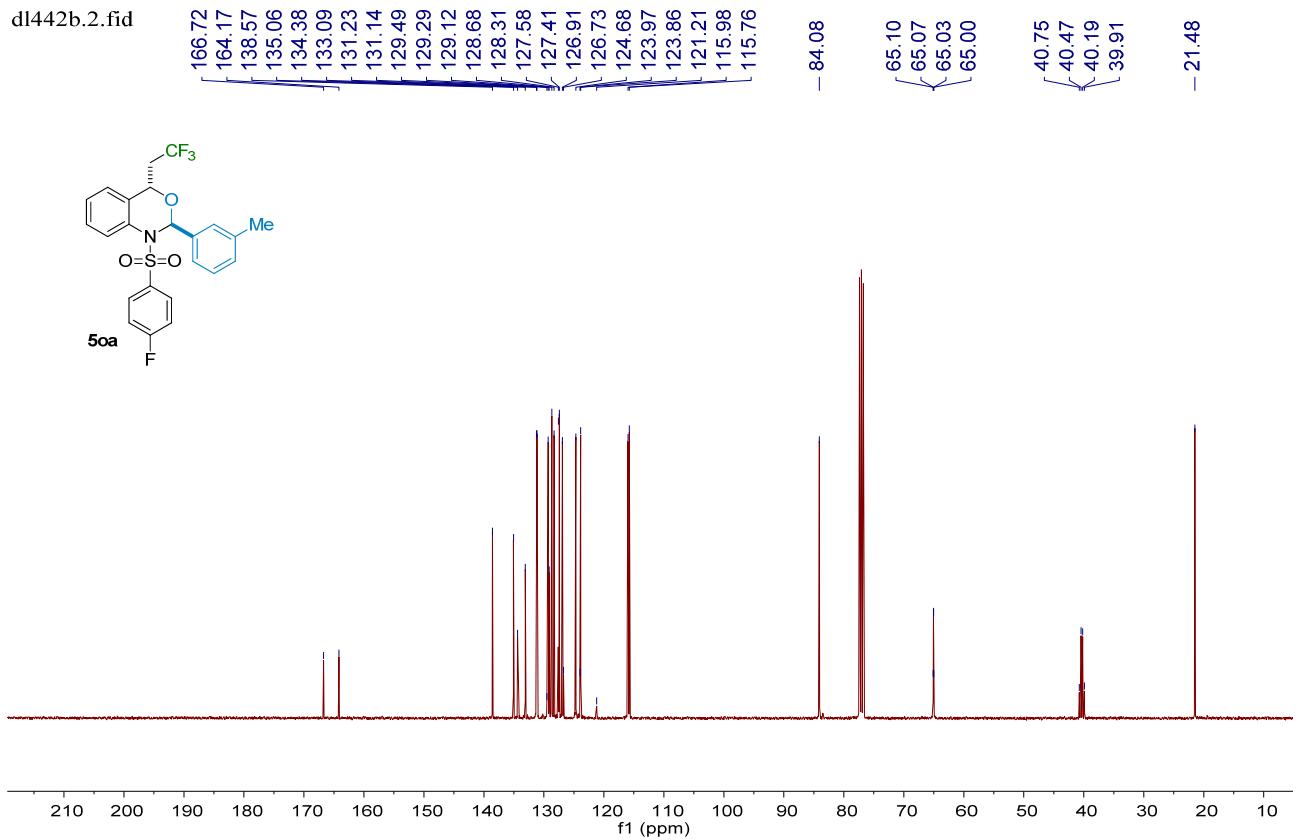




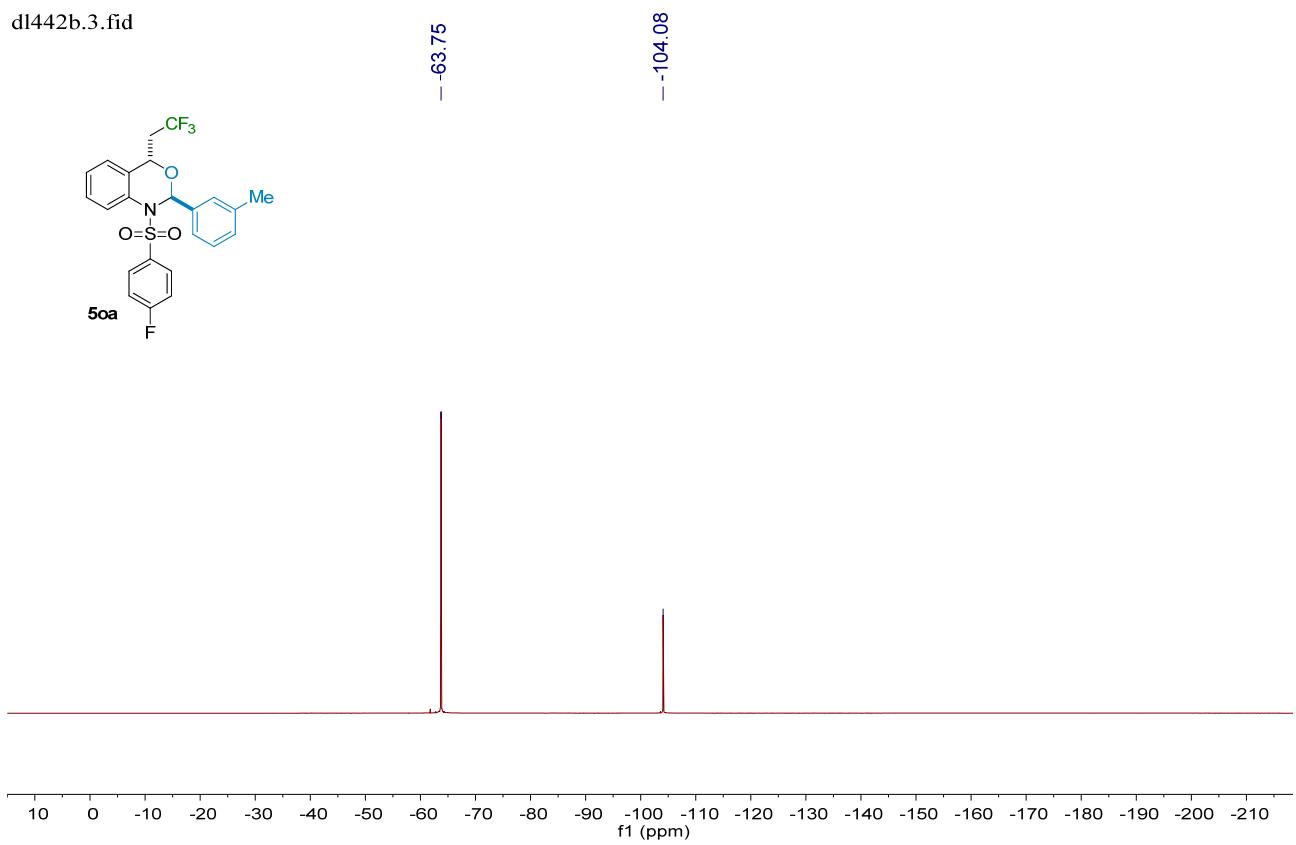
^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3) and ^{19}F NMR (376 MHz, CDCl_3) spectra of **5oa**



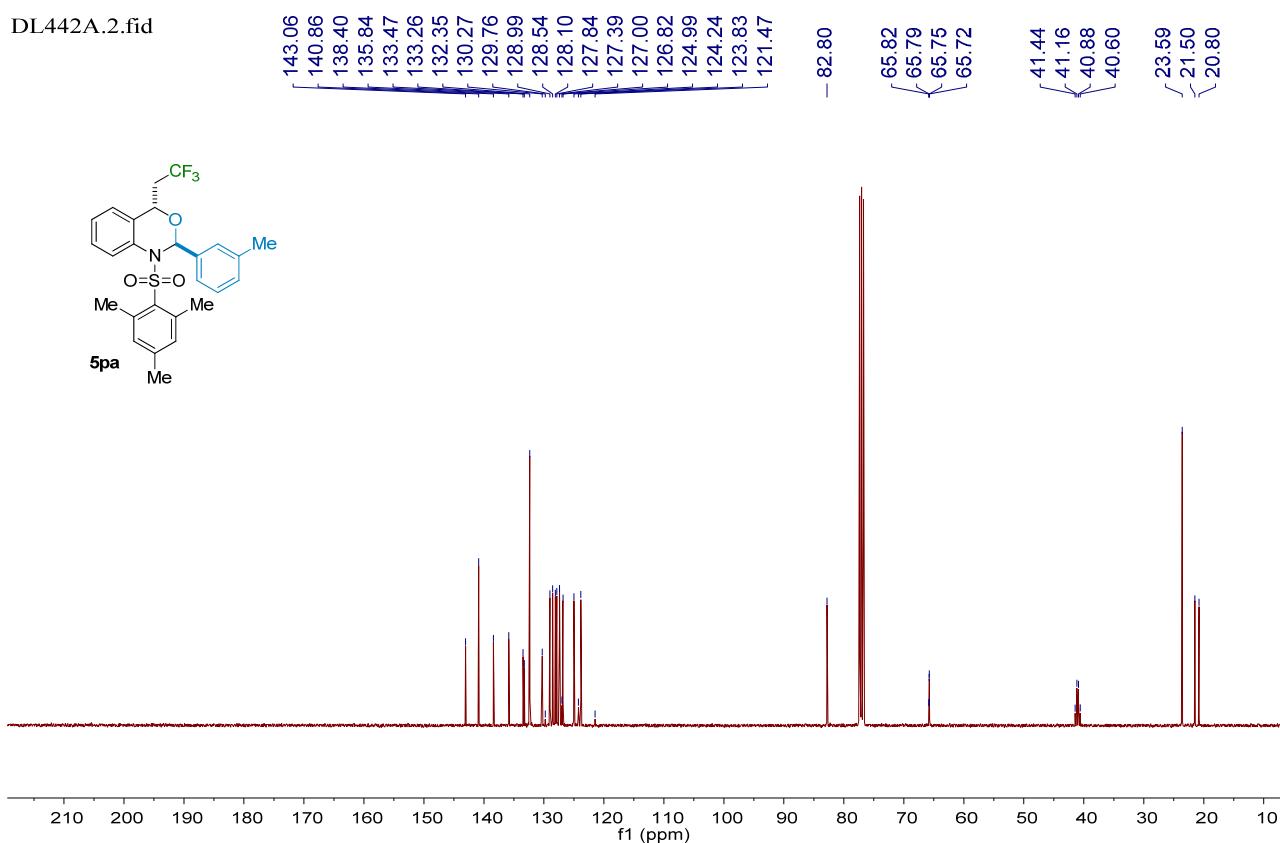
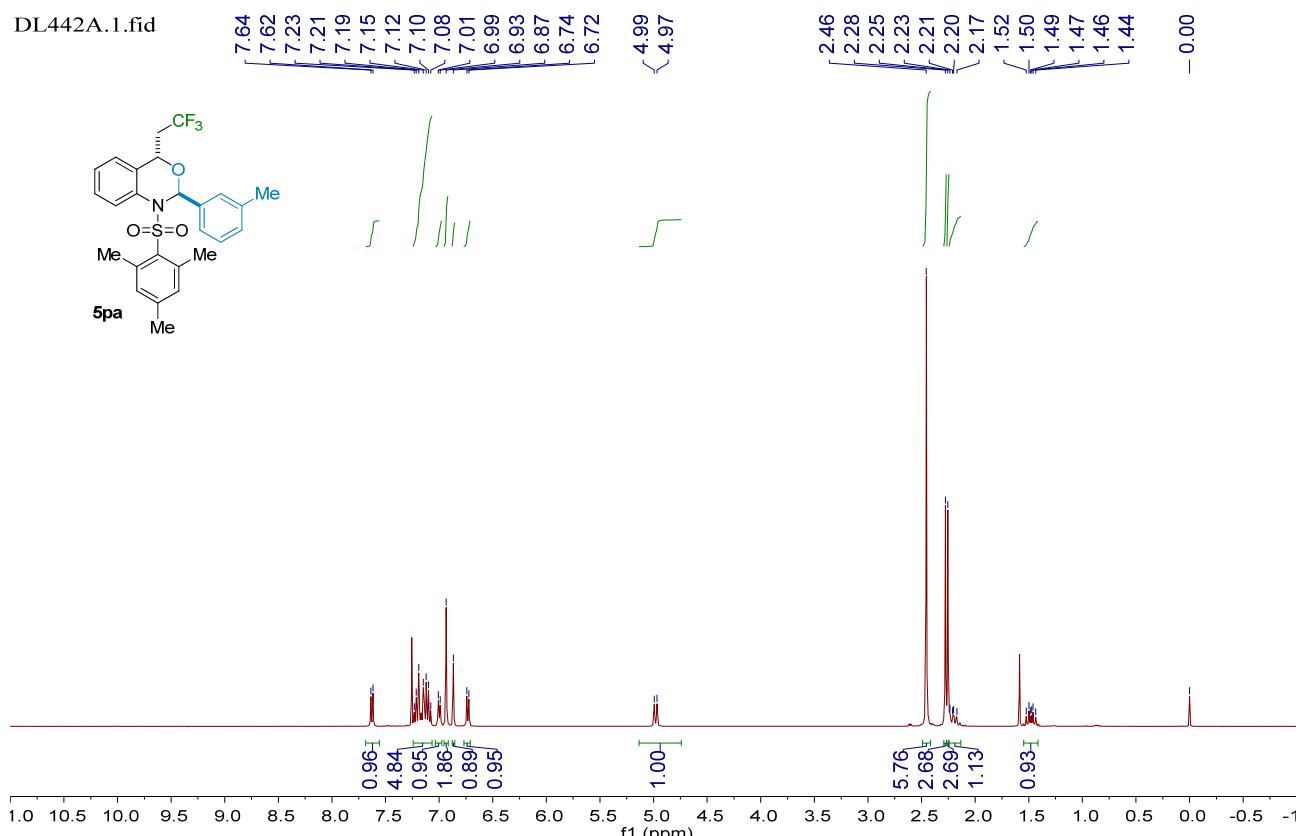
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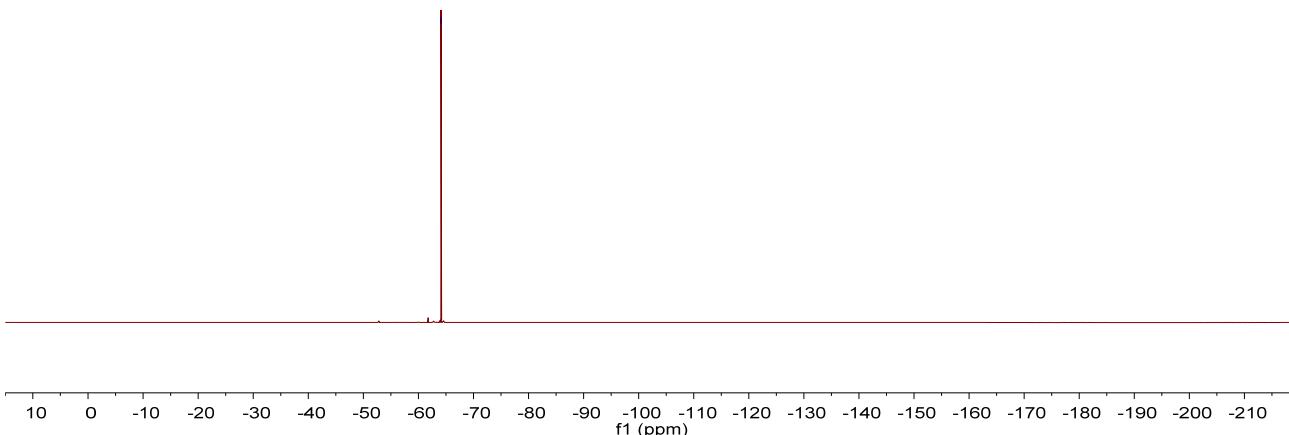
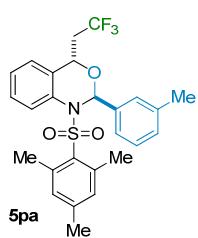
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¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of 5pa

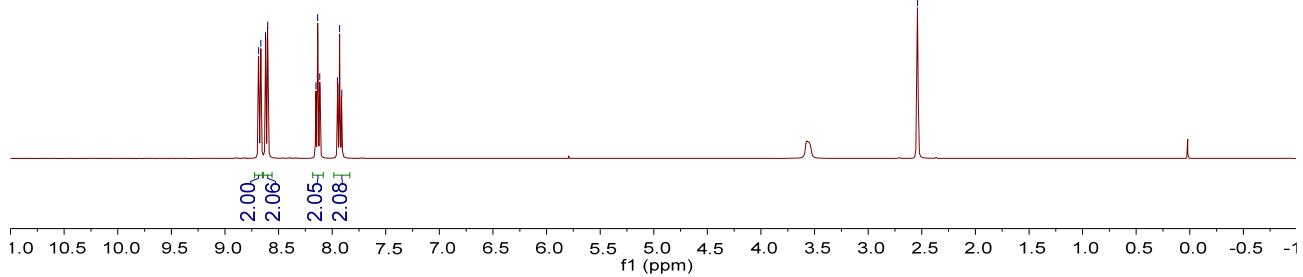
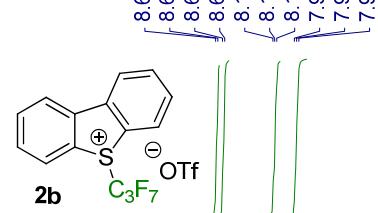


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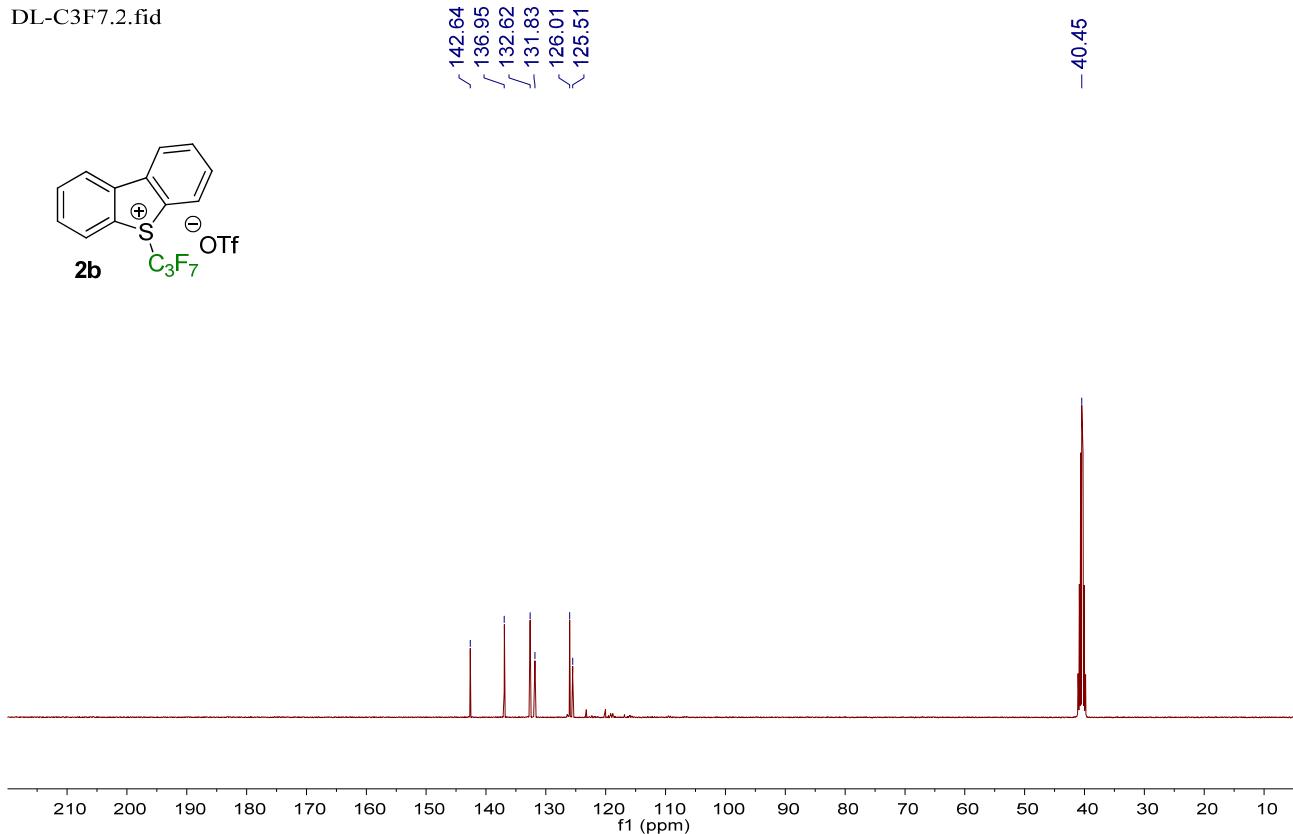


^1H NMR (400 MHz, DMSO- d^6), ^{13}C NMR (100 MHz, DMSO- d^6) and ^{19}F NMR (376 MHz, DMSO- d^6) spectra of **2b**

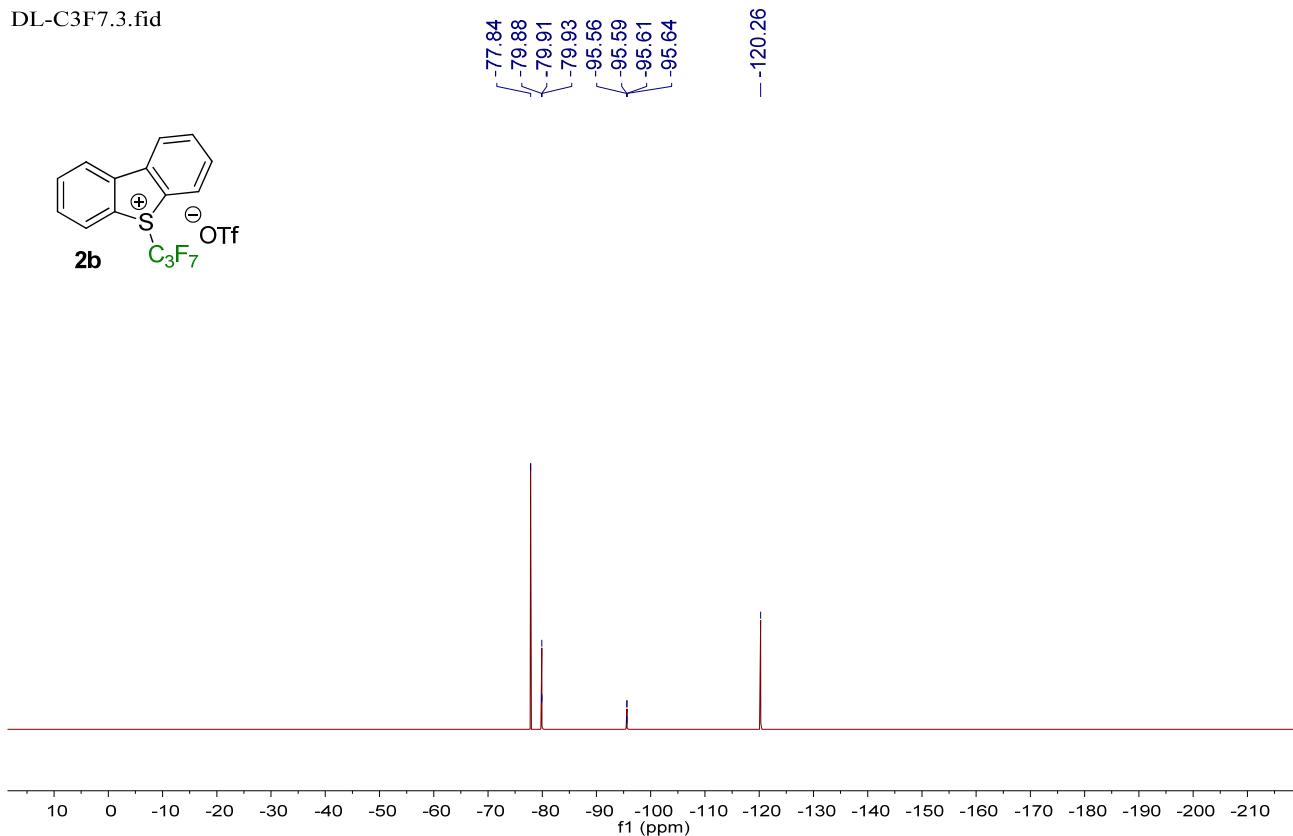
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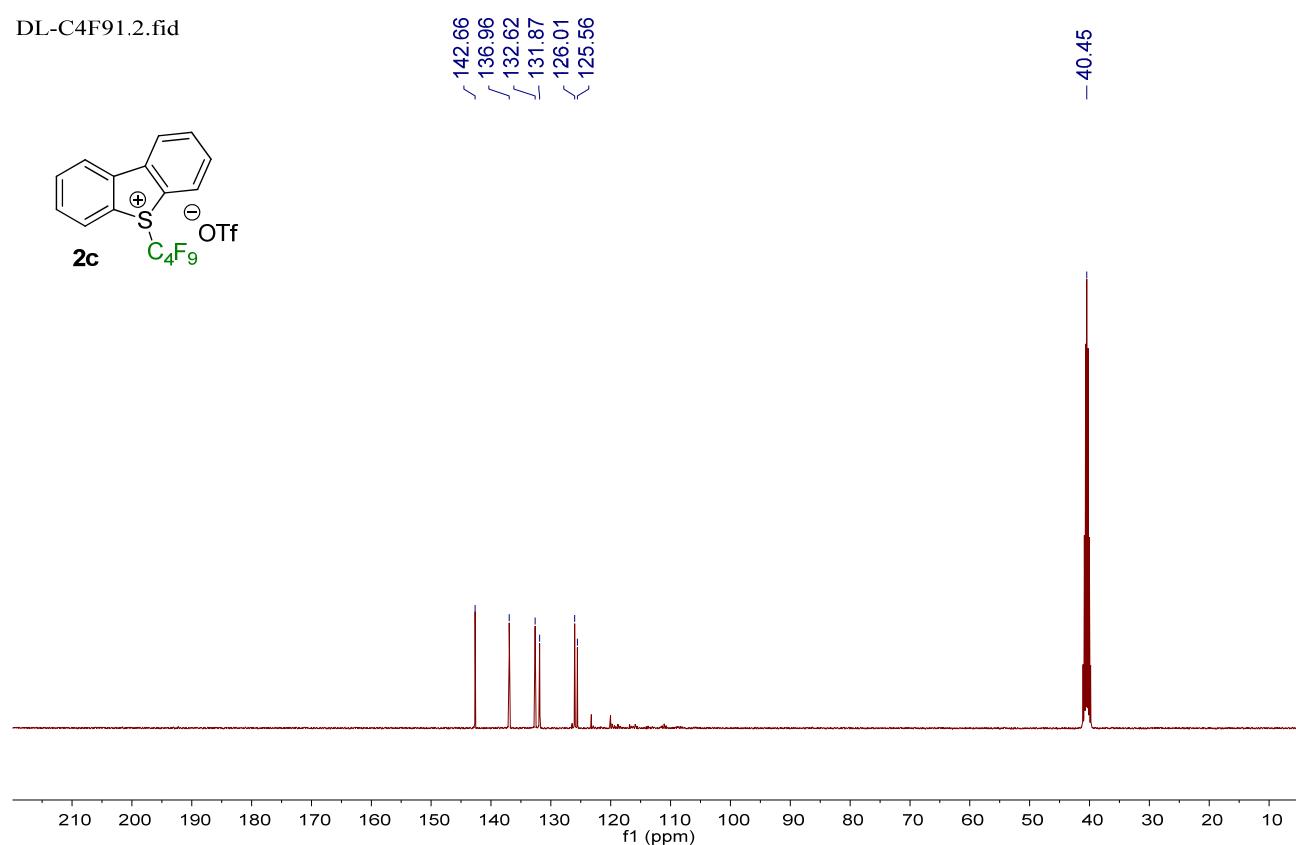
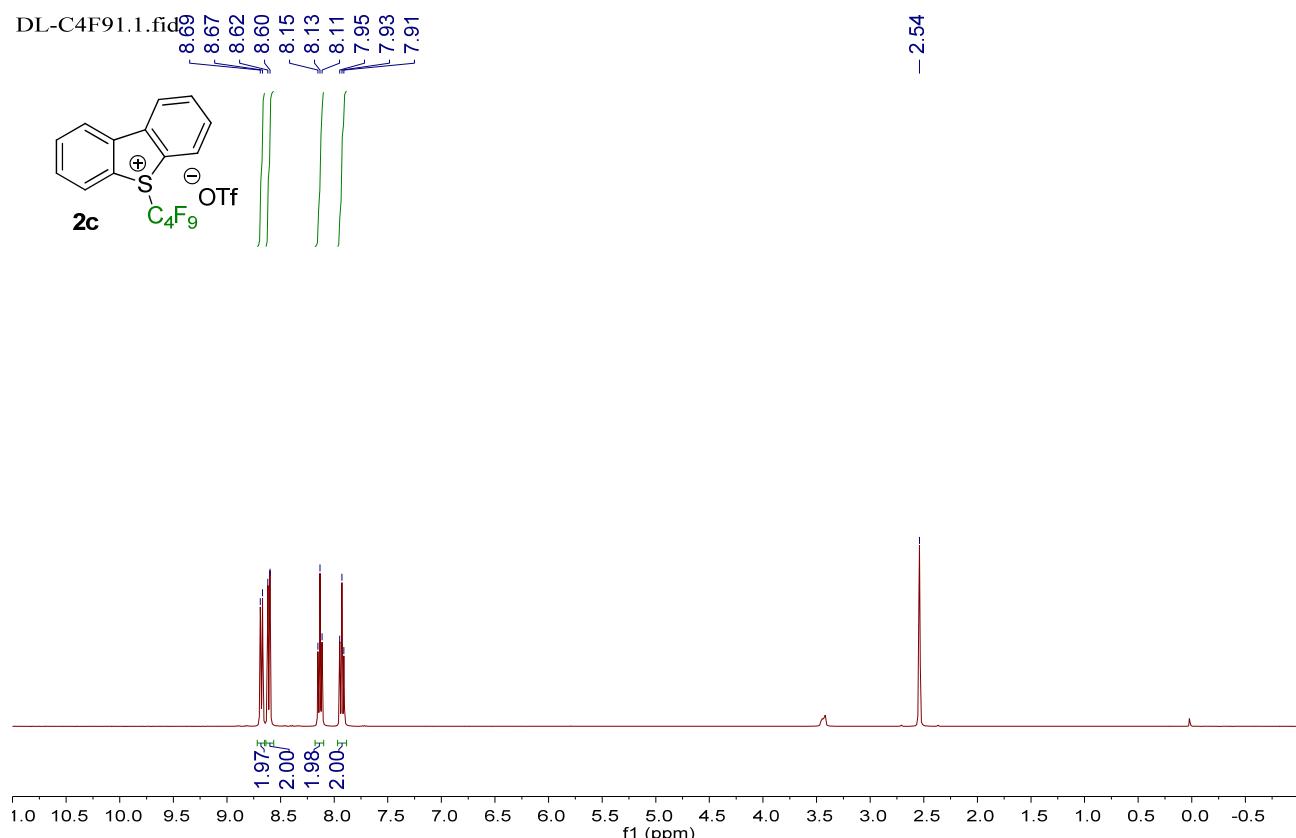
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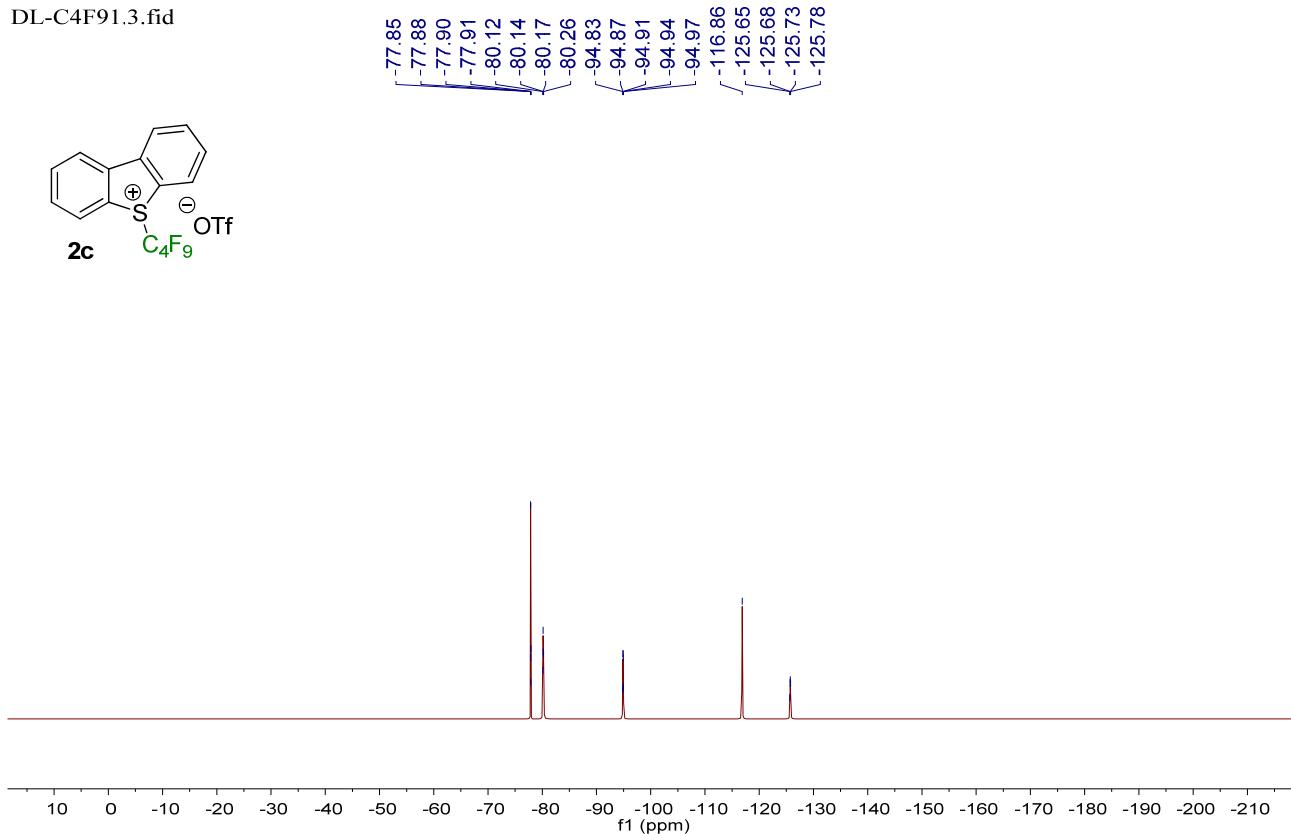
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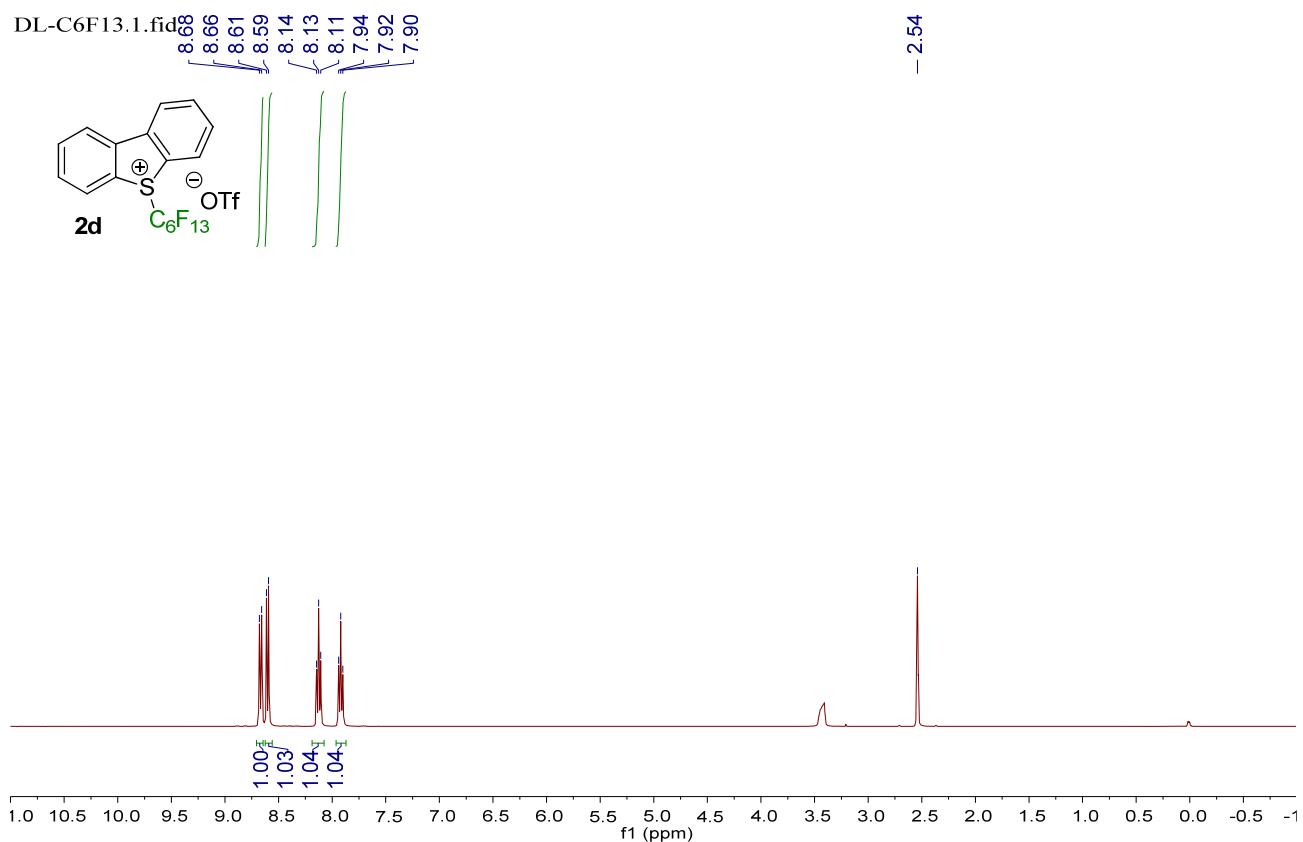
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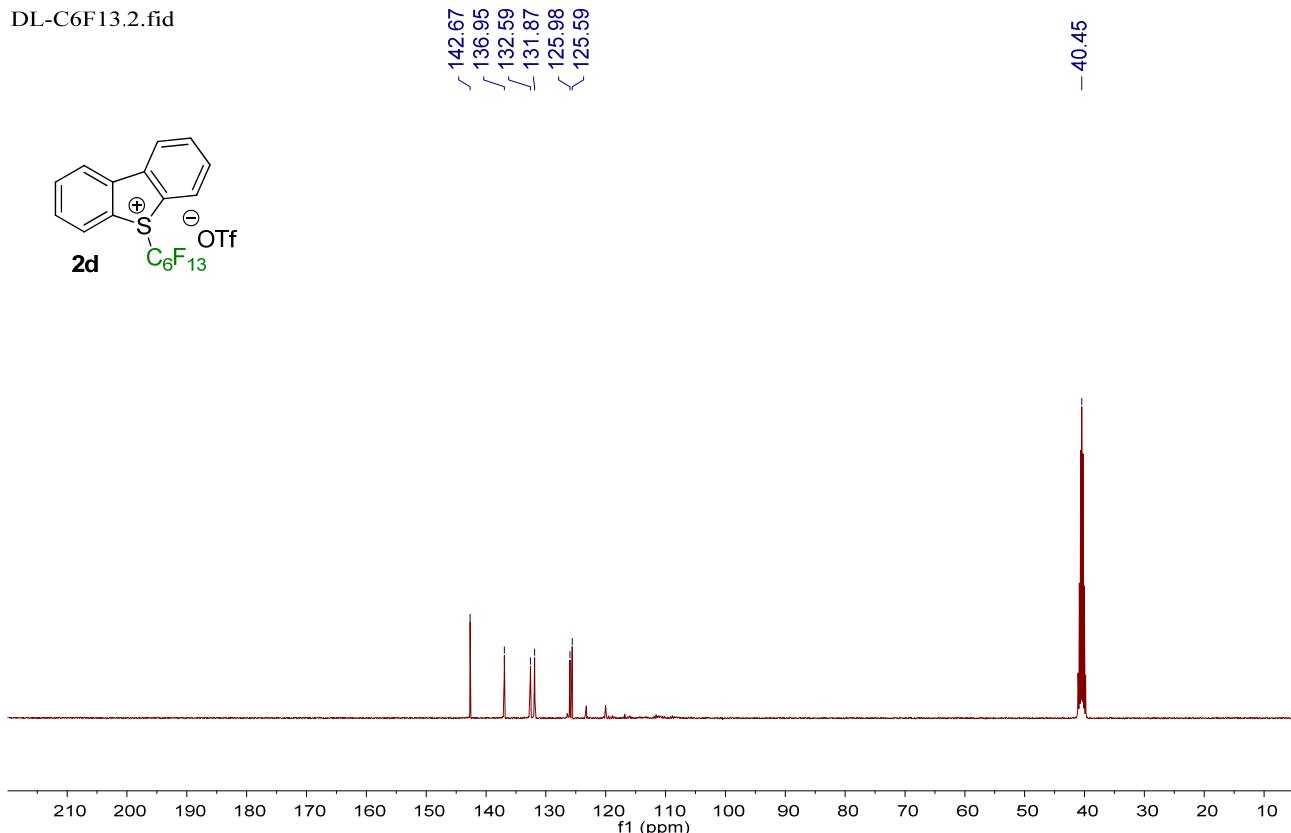
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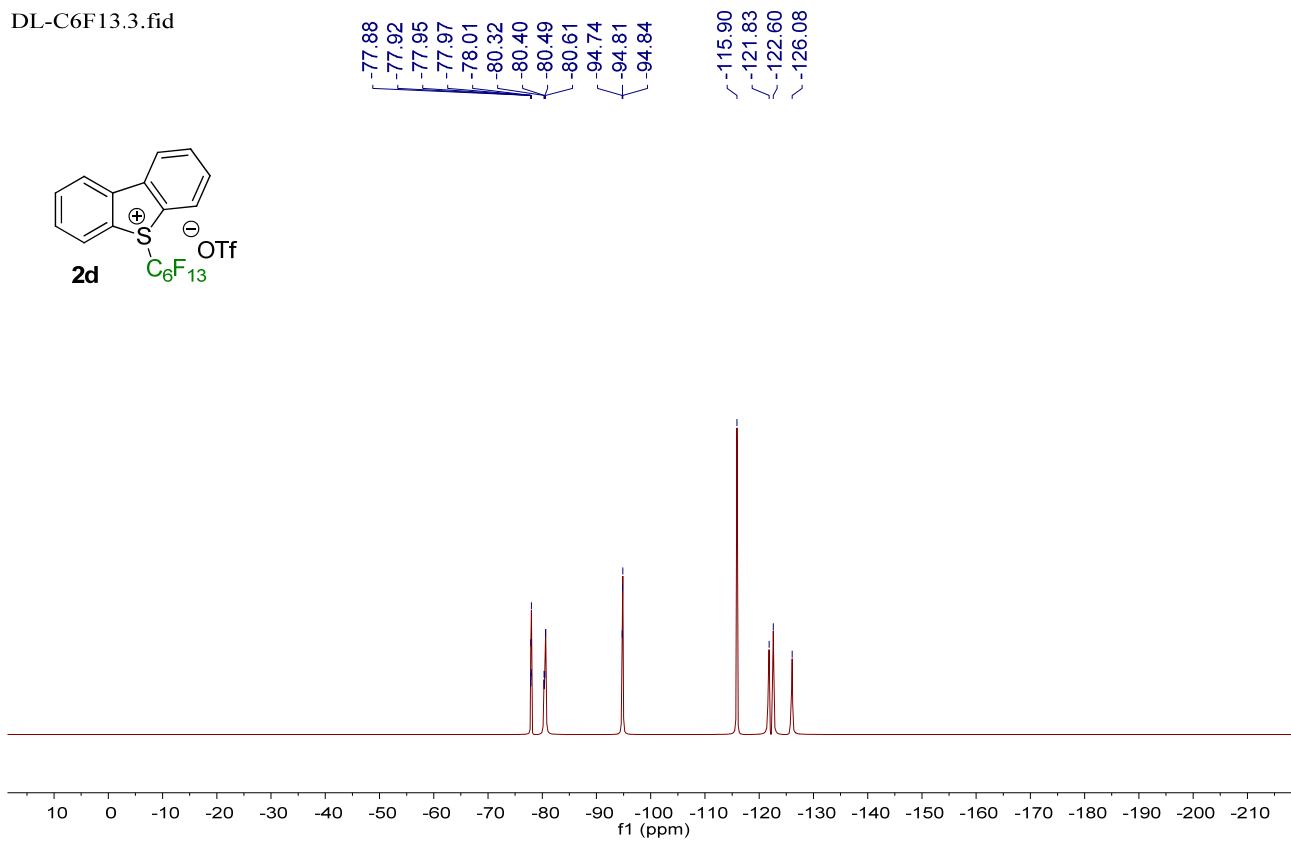
^1H NMR (400 MHz, DMSO-d⁶), ^{13}C NMR (100 MHz, DMSO-d⁶) and ^{19}F NMR (376 MHz, DMSO-d⁶) spectra of **2d**



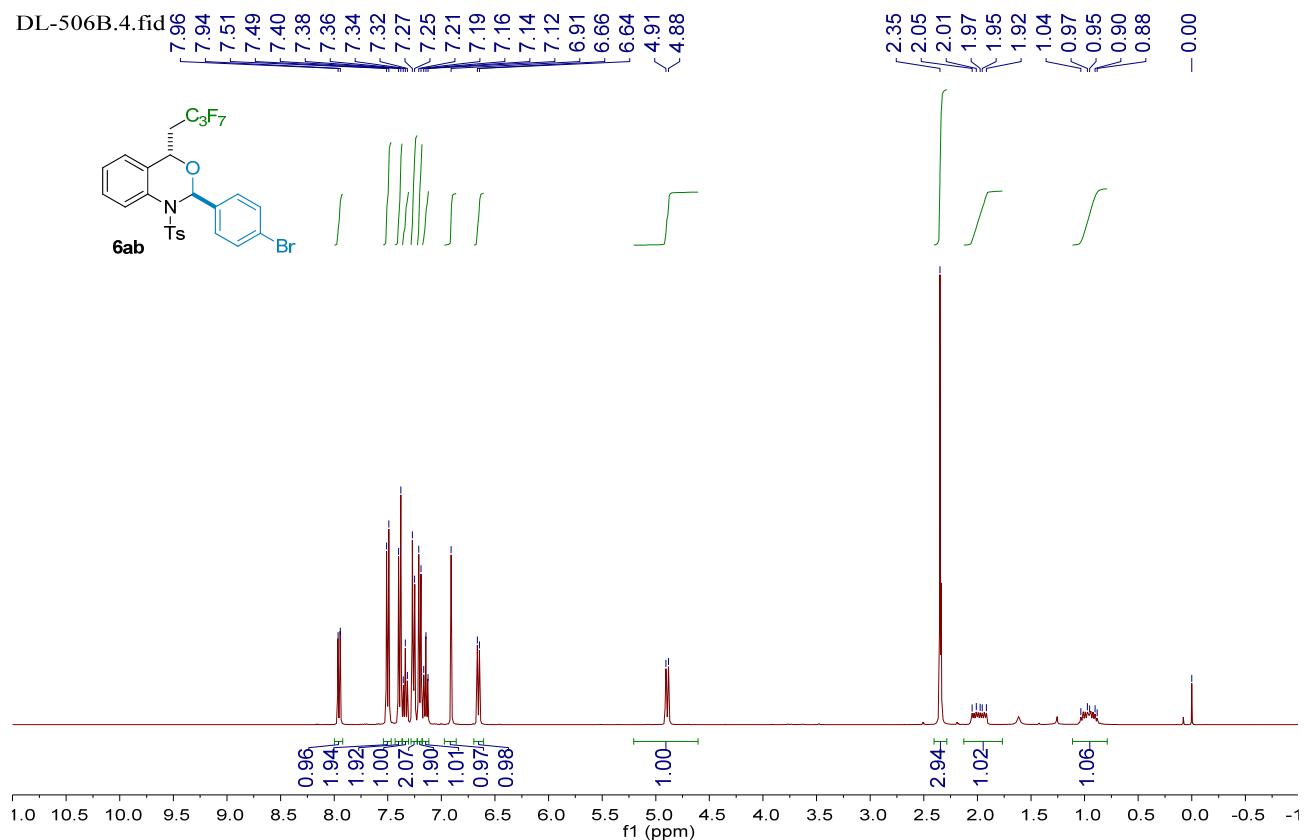
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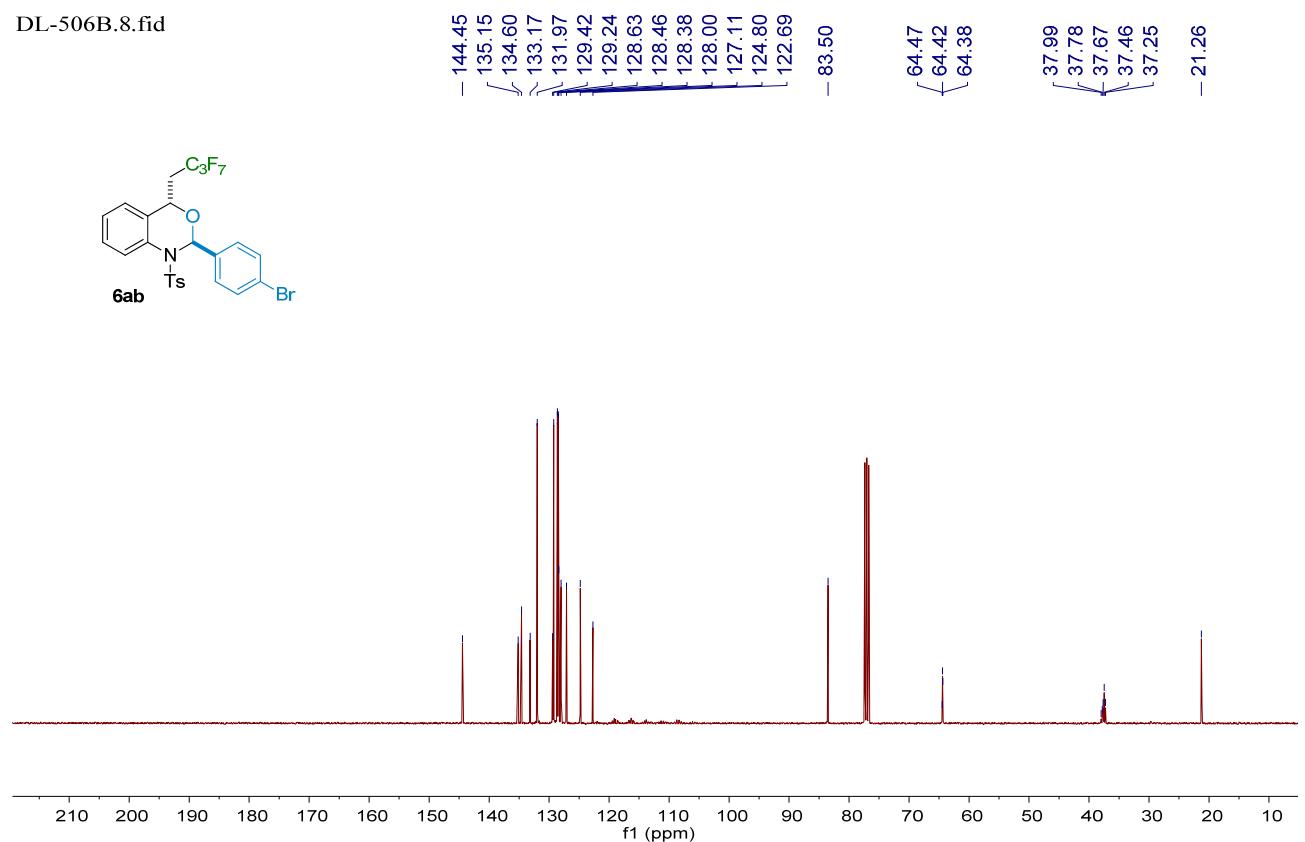
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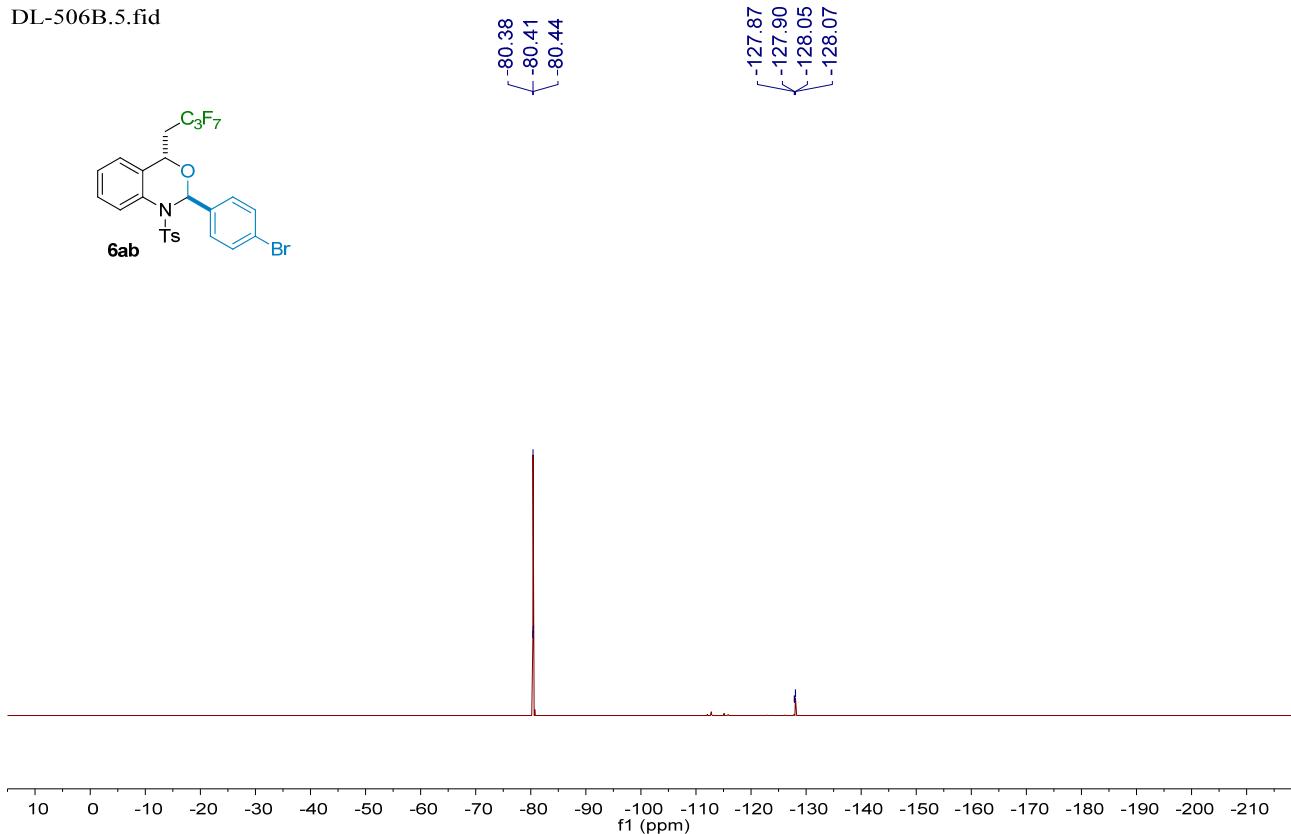


¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of 6ab

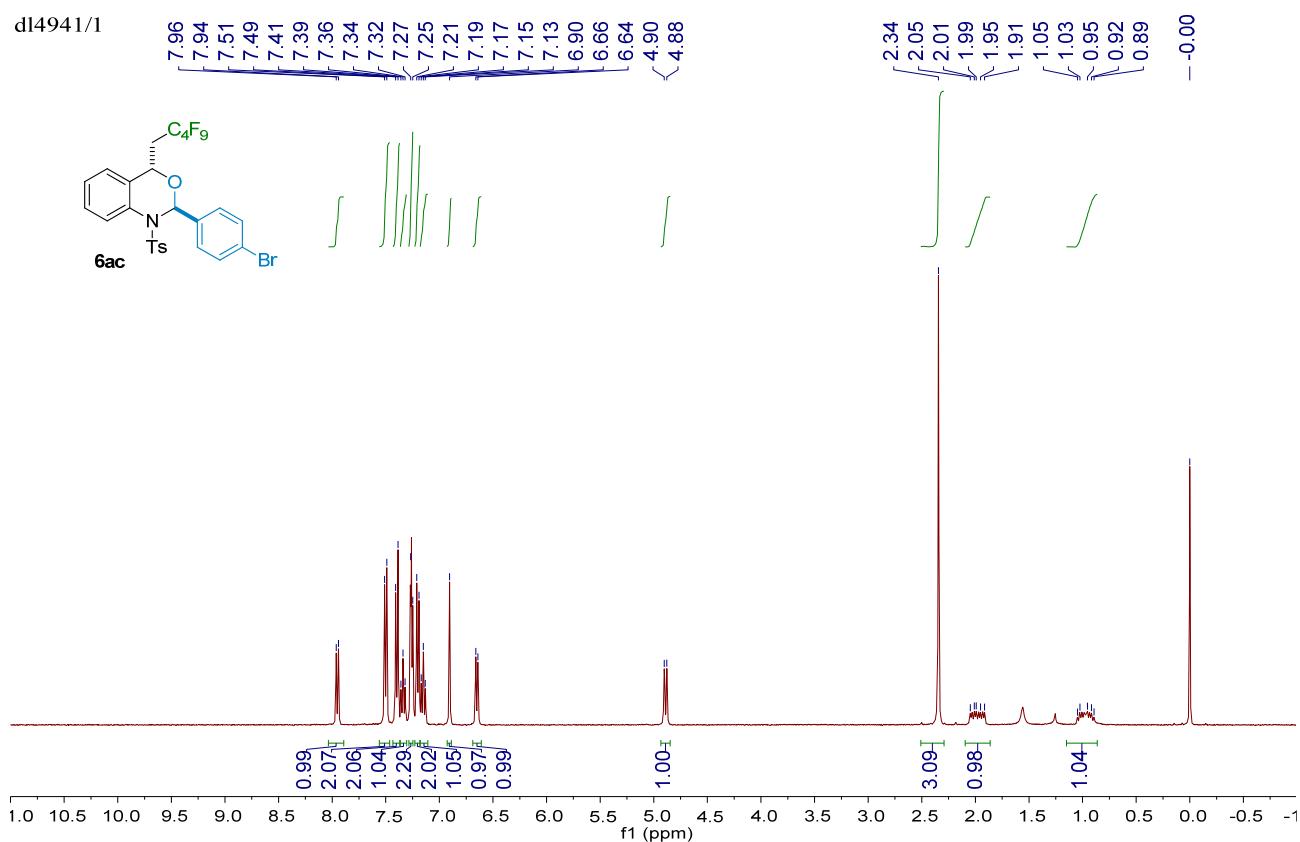


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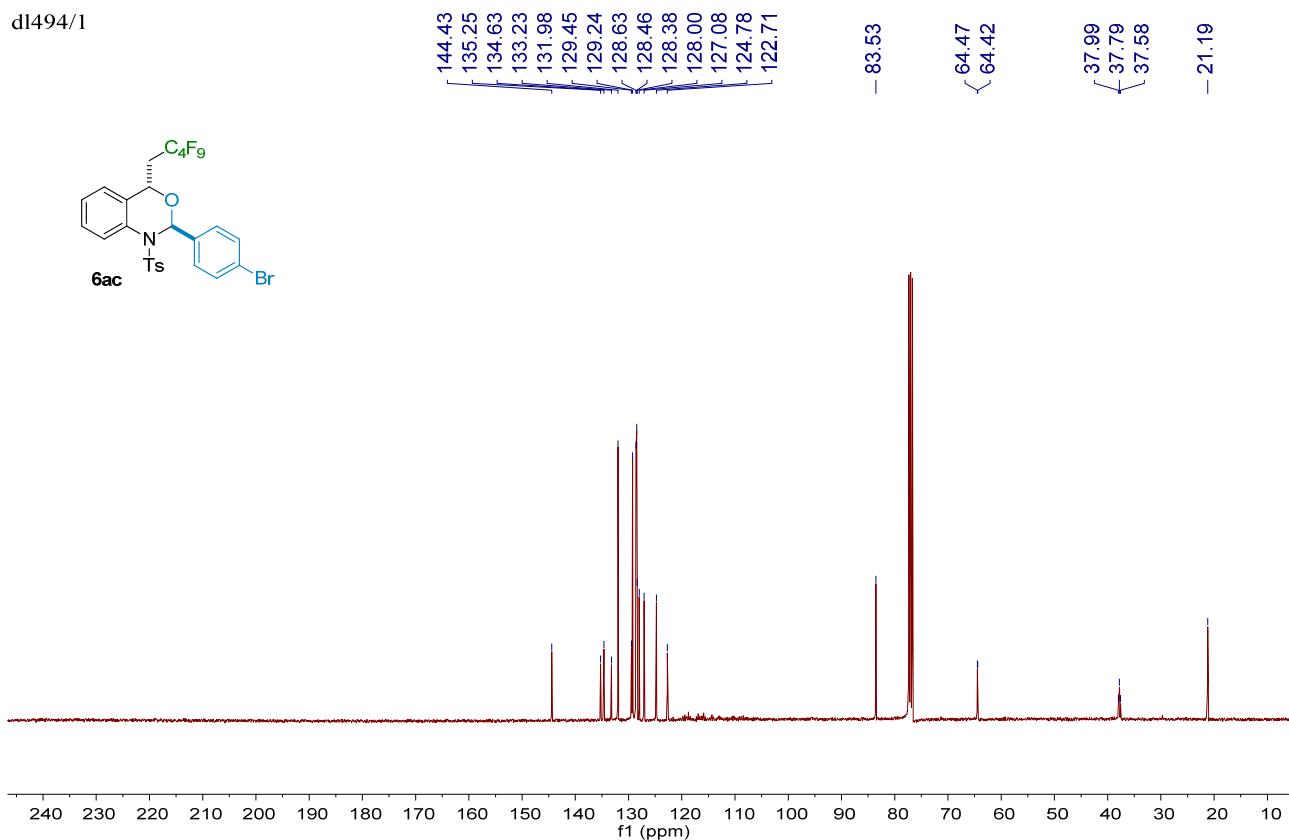




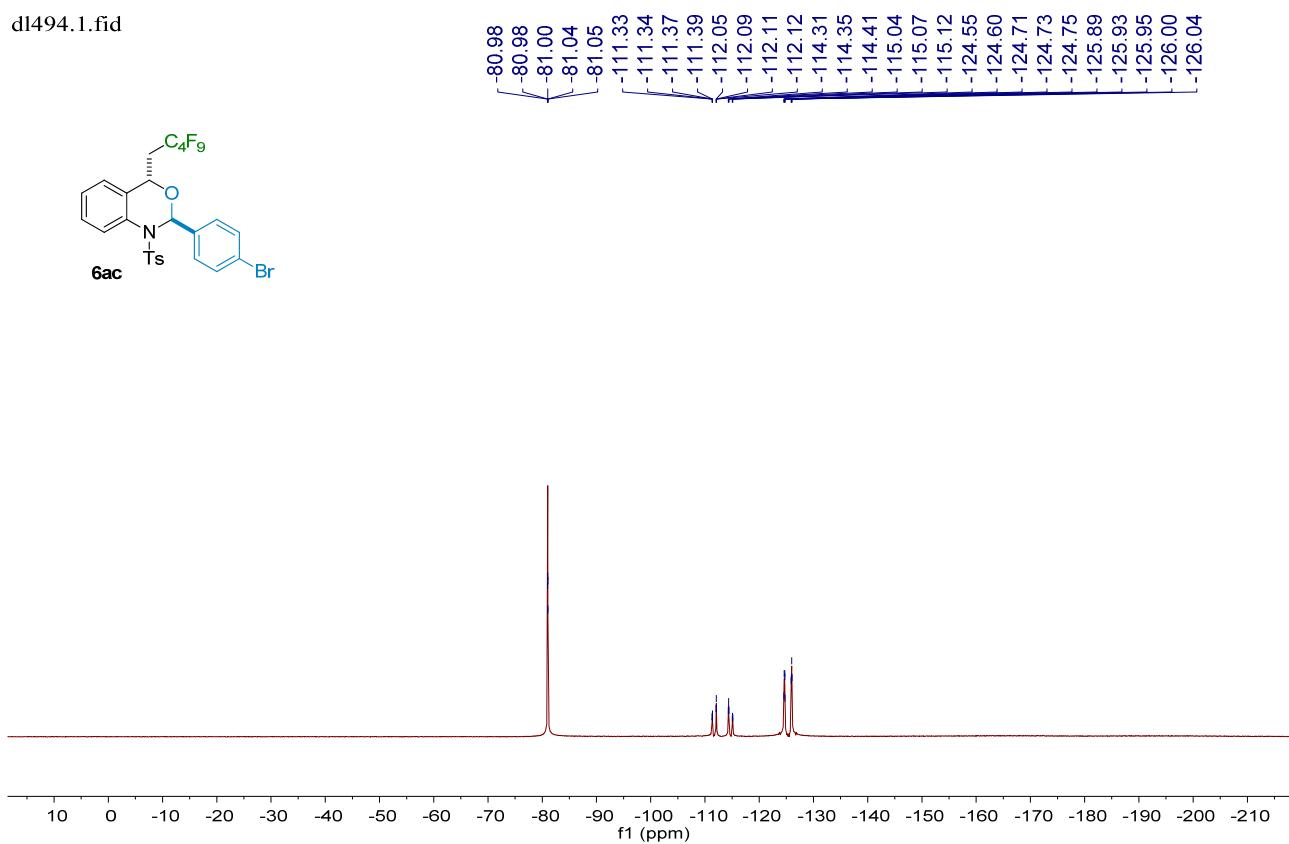
¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of 6ac



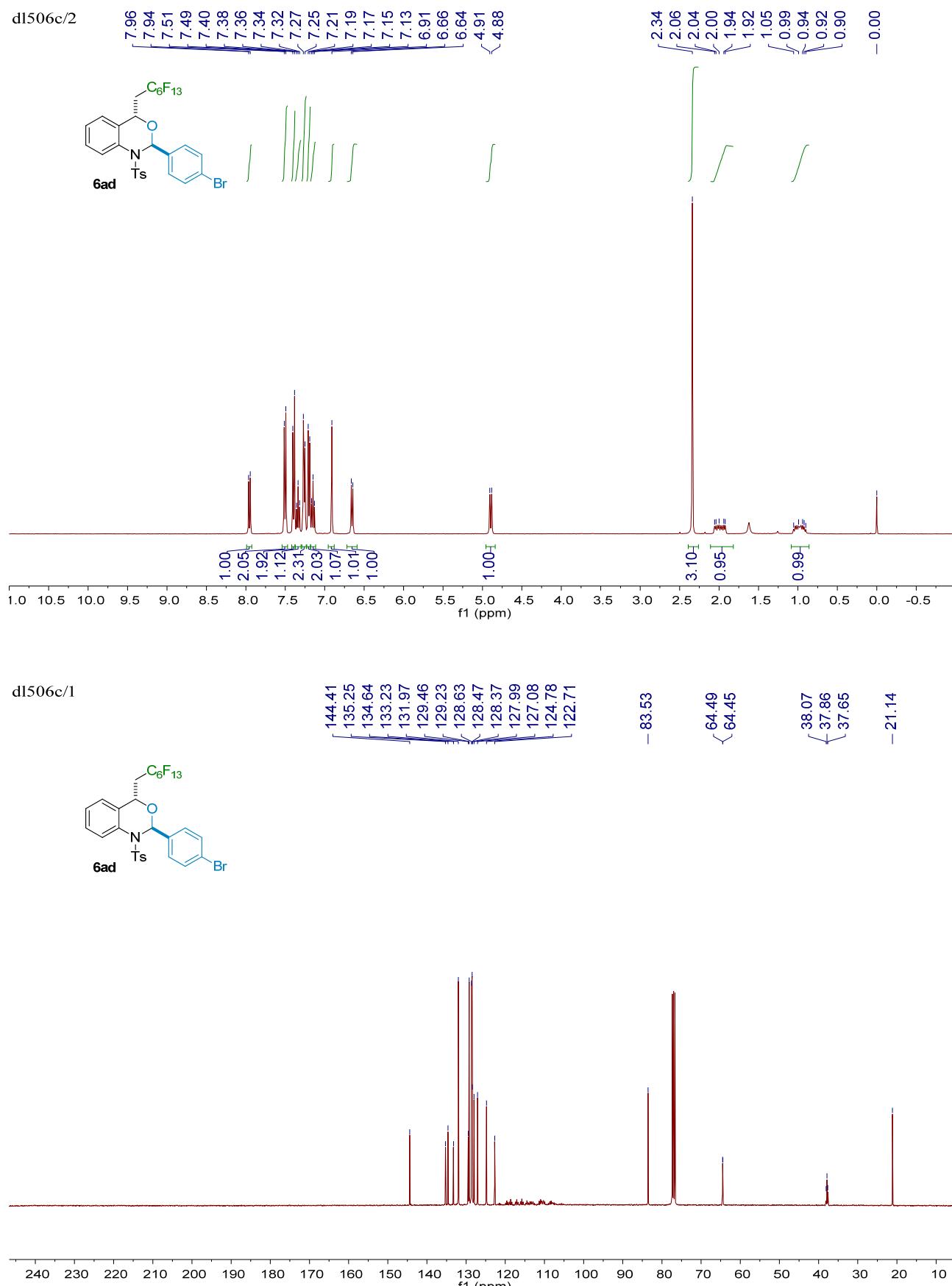
dl494/1

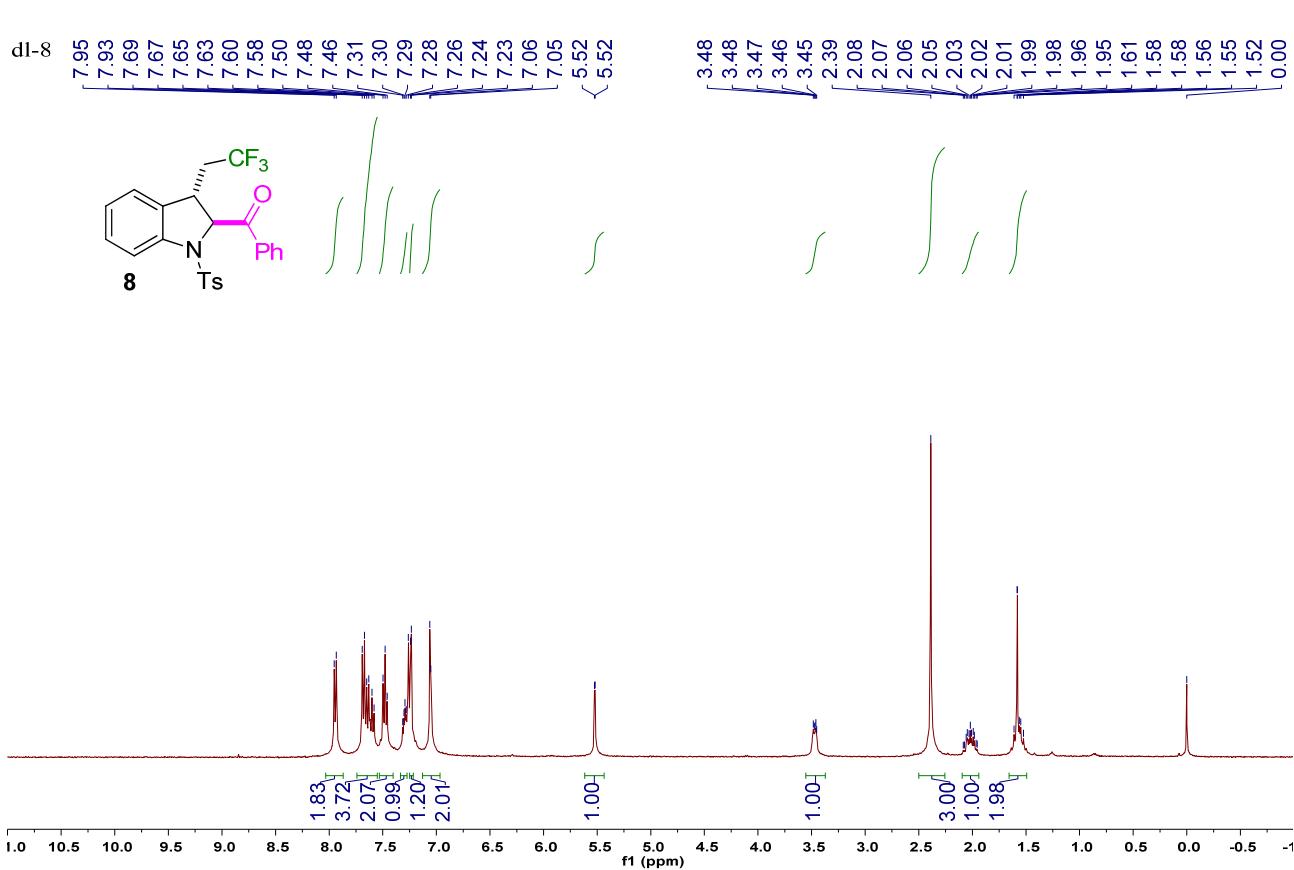
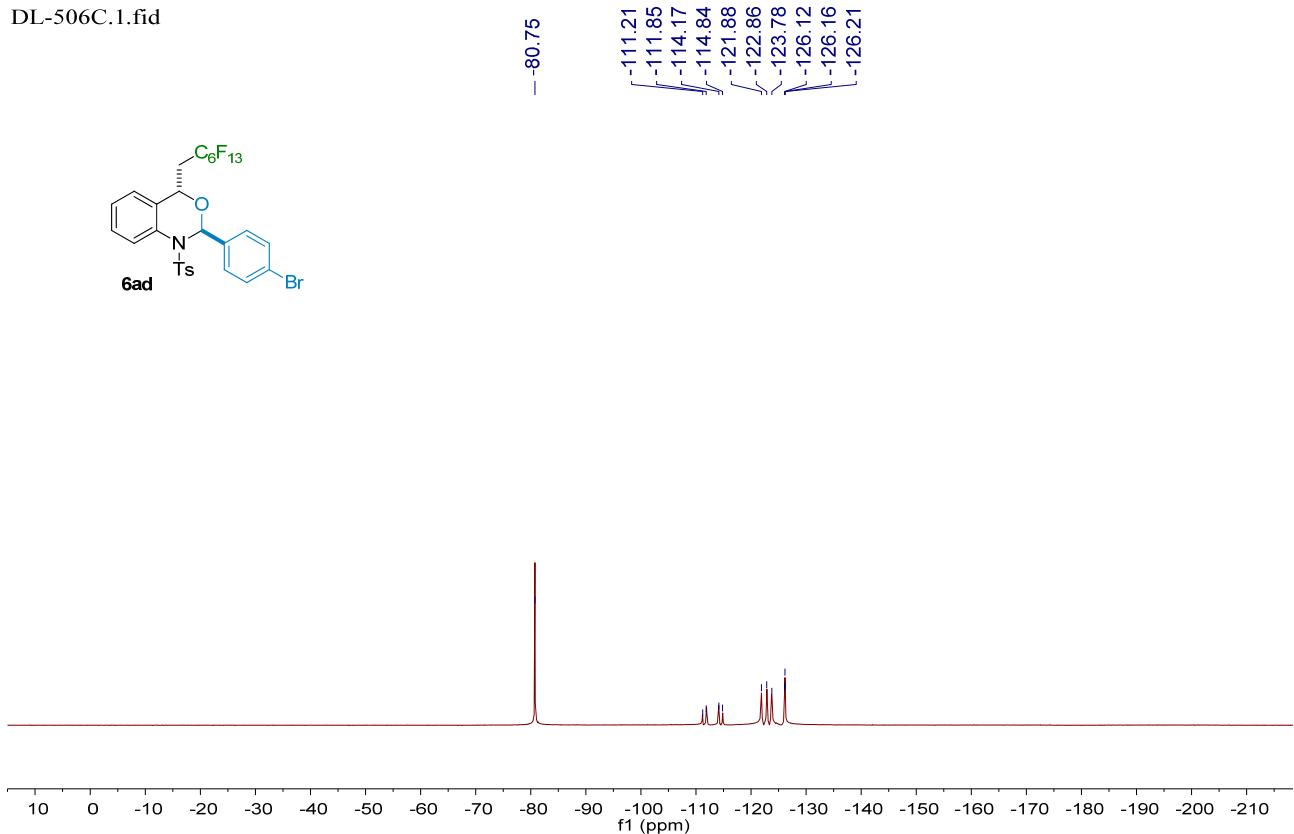


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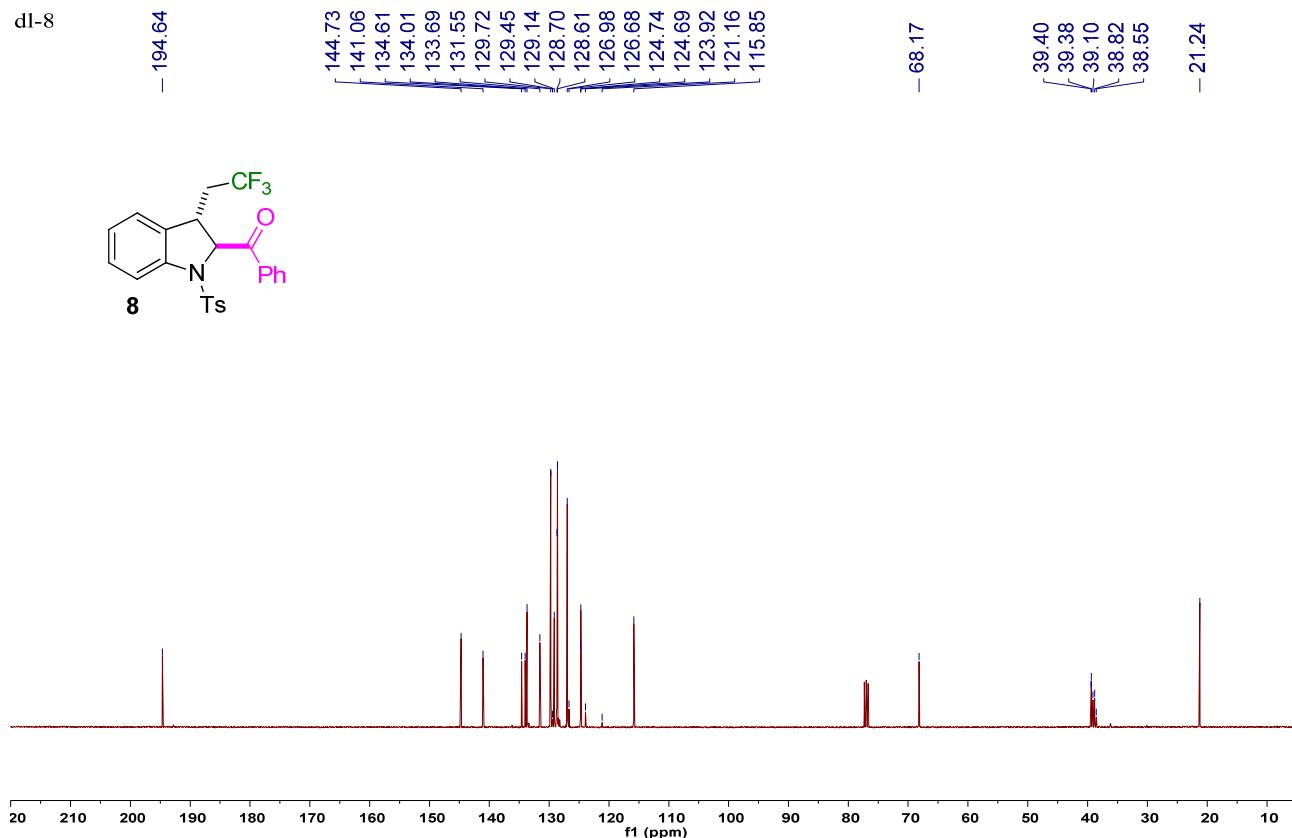


¹H NMR (400 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and ¹⁹F NMR (376 MHz, CDCl₃) spectra of 6ad

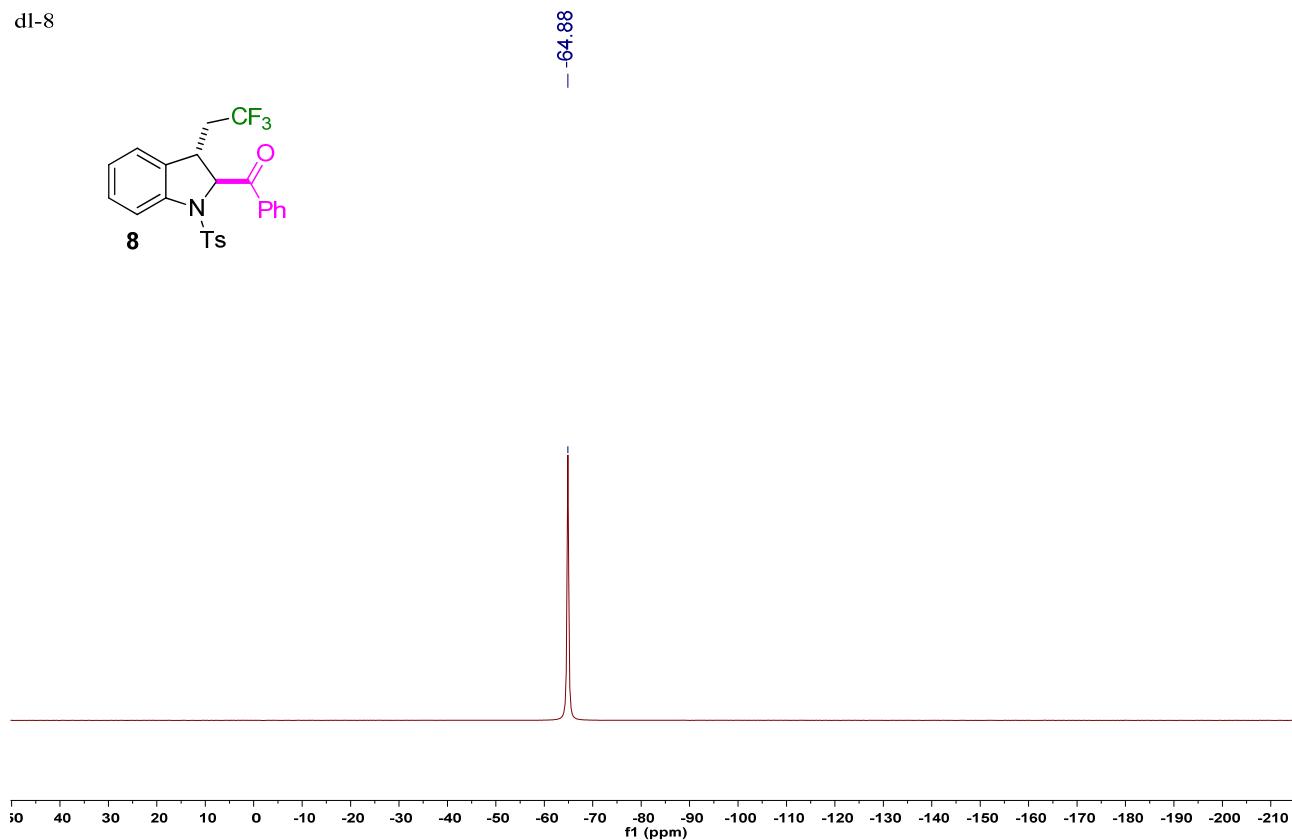




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