Supporting Information for

Facile generation and reaction of densely trifluoromethylated alkyl radicals by dual photoredox and acid catalysis

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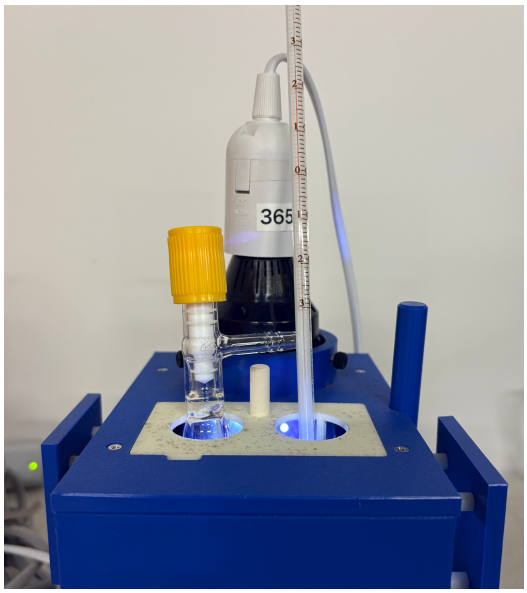
Materials and Methods

All the chemicals for synthesis of the substrates and catalysts were commercially available (Aldrich or Tokyo Chemical Industry Co., Ltd. (TCI), FUJIFILM Wako Pure Co., Lt, Kanto Chemical Co., Inc.) unless otherwise noted. All the reactions were carried out by standard Schlenk techniques unless otherwise noted. Anhydrous organic solvents and deuterated solvents were purchased from Kanto Chemical Co., Inc. Thin-layer chromatography was performed on TLC plates with 60 F_{254} (Merck).

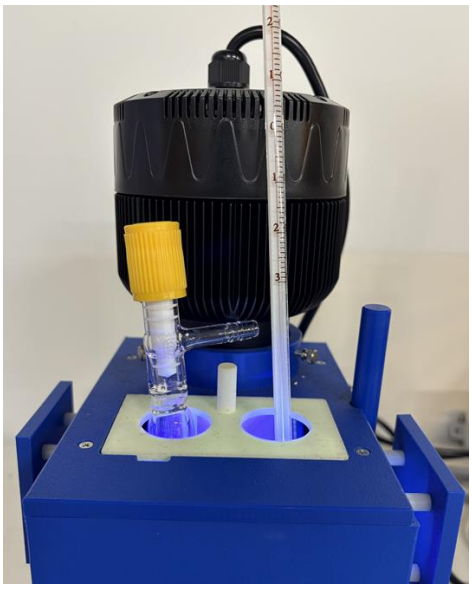
The following apparatuses were used for experiments and measurements.

Photoreactor: EvoluChem PhotoRedOx Box (365 nm: 9 or 25 mW/cm^2). Automated column chromatography: Biotage Isolera Prime (Biotage SNAP Ultra cartrideges, silica particle size 25 μm or Biotage Sfär Duo HC cartridges, silica particle size 20 μm). Recycling preparative HPLC (GPC): Japan Analytical Industry Co., Ltd. (JAI) LC-9201 (columns: JAIGEL-1HR and JAIGEL-2HR, eluent: $CHCl_3$ or columns: JAIGEL-2HR plus and JAIGEL-2.5HR plus, eluent: THF). NMR spectra: JEOL JNM-ECX400 or JEOL GSX-400 spectrometer (400 MHz for ^{1}H, 376 MHz for ^{19}F, 101 MHz for ^{13}C) and Magritek Spinsolve 60 Ultra (62 MHz for ^{1}H, 58 MHz for ^{19}F). The chemical shifts were referenced to an external tetramethylsilane signal (0.0 ppm) by using the solvent resonance for ^{1}H and ^{13}C NMR and referenced to an external CF_3COOH (−76.5 ppm) or an internal $C_6H_5CF_3$ (–63.7 ppm) or C_6F_6 (–164.9 ppm) signals for ^{19}F NMR. The coupling constants were quoted in Hz (*J*). The splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). The splitting patterns that could not be interpreted or easily visualized were designated as apparent patterns or broad (br). High-resolution mass spectra (HRMS) (ESI/APCI/APPI Mass spectra): Thermo Fisher Exactive or Orbitrap Exploris 120 at Center for Analytical Instrumentation, Chiba University. DFT calculations: Gaussian 16, Revision C.02 program package. UV-vis: JASCO V-770. Fluorescence: HITACHI F-7100. CV & DPV: Hokutodenkou HZ-7000. GC-MS(EI): Agilent 8890GC/5977MSD (Column: HP-5ms, 30 m (length) x 0.25 mm (ID) x 0.25 μm (thickness)). Single-crystal X-ray measurements: Rigaku XtaLAB PRO at the Instrumental Analysis Center, Yokohama National University. The crystallographic data was deposited at Cambridge Crystallographic Data Centre: CCDC 2519485 (**5aa**).

Apparatus for Photoreaction



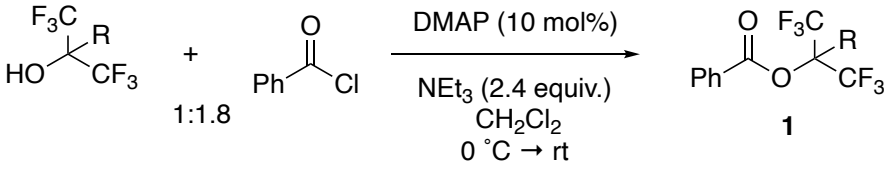
365 nm LED (9 mW/cm^2)



365 nm LED (25 mW/cm^2)

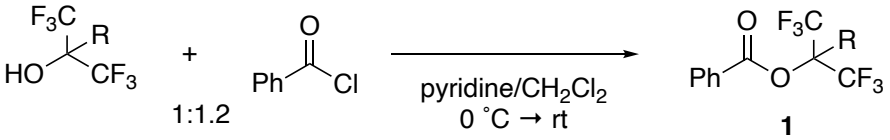
Preparation of Perfluorinated Alkyl Benzoate 1

General procedures A



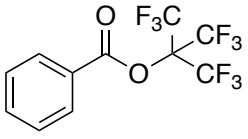
To an anhydrous CH_2Cl_2 solution of $HOC(CF_3)_2R$ (1.0 equiv.) in the presence of DMAP (10 mol%) and NEt_3 (2.4 equiv.) was slowly added benzoyl chloride (1.8 equiv.) over 5 min at 0 ºC under N_2 atmosphere. The reaction mixture was stirred at room temperature for several days. Then, the reaction was quenched by addition of water at 0 ˚C. The mixture was extracted with Et_2O, washed with brine and dried over $MgSO_4$. After filtration, the solvent was carefully removed under reduced pressure because some products were volatile. The desired product was obtained after purification by automated column chromatography with silica gel cartridges (Biotage SNAP Ultra, particle size 25 μm) on a Biotage Isolera Prime.

General procedures B



To an anhydrous pyridine and CH_2Cl_2 solution of $HOC(CF_3)_2R$ (1.0 equiv.) was slowly added benzoyl chloride (1.2 equiv.) at 0 ºC over 5 min under N_2 atmosphere. The mixture was stirred at room temperature. To the resulting mixture was added 1N HCl aq. and diehtyl ether at 0 ˚C. The organic phase was washed with 1N HCl aq., saturated $NaHCO_3$ aq., and brine. Then, the organic layer was dried over $MgSO_4$, filtered and removed under reduced pressure. The desired product was obtained after purification by automated column chromatography with silica gel cartridges (Biotage SNAP Ultra, particle size 25 μm) on a Biotage Isolera Prime.

1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl benzoate (**1a**)



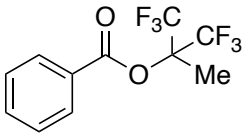
1a

According to the general procedures A, the use of nonafluoro-*tert*-butyl alcohol (1.67 g, 7.08 mmol), DMAP (0.0776 g, 0.635 mmol), NEt_3 (1.87 g, 18.4 mmol), CH_2Cl_2 (15 mL), and benzoyl chloride (1.96 g, 13.9 mmol) for 6 days afforded **1a** as a colorless liquid (1.65 g, 4.86 mmol, 69% yield). Column eluent: hexane/EtOAc = 80:20.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.06 (apparent m, 2H; Ar-*H*(*o*)), 7.69 (apparent m, 1H; Ar-*H*(*p*)), 7.53

(apparent m, 2H; Ar-*H*(*m*)). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –69.1 (s, 9F; C(CF_3)$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 160.0, 135.1, 130.8, 129.1, 127.2, 120.0 (q, $^1J_{CF}$ = 292 Hz), 80.5 (m). **HRMS** (APCI) calcd m/z for $[C_{11}H_5F_9O_2+H]^+$ 341.0219, found 341.0214 $[M+H]^+$.

1,1,1,3,3,3-Hexafluoro-2-methylpropan-2-yl benzoate (**1b**)

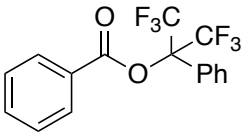


1b

According to the general procedures B, the use of 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (1.15 g, 6.32 mmol), anhydrous pyridine (2.0 mL), anhydrous CH_2Cl_2 (10 mL), and benzoyl chloride (1.43 g, 10.2 mmol) for 3 days afforded **1b** as a colorless liquid (0.77 g, 2.69 mmol, 43% yield). Column eluent: hexane/EtOAc = 95:5.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.03 (apparent m, 2H; Ar-*H*(*o*)), 7.63 (apparent m, 1H; Ar-*H*(*p*)), 7.49 (apparent m, 2H; Ar-*H*(*m*)), 2.12 (m, 3H; CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –75.9 (s, 6F; CMe(CF_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 162.8, 134.5, 130.3, 129.0, 128.9, 122.3 (q, $^1J_{CF}$ = 289 Hz), 81.0 (m), 14.2. **HRMS** (APCI) calcd m/z for $[C_{11}H_8F_6O_2+H]^+$ 287.0501, found 287.0502 $[M+H]^+$.

1,1,1,3,3,3-Hexafluoro-2-phenylpropan-2-yl benzoate (**1c**)

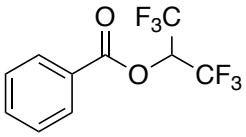


1c

According to the general procedures A, the use of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (1.11 g, 4.53 mmol), DMAP (0.0500 g, 0.409 mmol), NEt_3 (0.834 g, 8.24 mmol), CH_2Cl_2 (10 mL), and benzoyl chloride (1.93 g, 13.7 mmol) for 4 days afforded **1c** as a colorless oil (0.935 g, 2.70 mmol, 60% yield). Column eluent: hexane/EtOAc = 95:5.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.15 (apparent m., 2H; Ar-*H(o)*), 7.69 (apparent m, 1H; Ar-*H*(*p*)), 7.56–7.44 (7H; Ar–*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –70.1 (s, 6F; CPh(CF_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 162.0, 134.6, 130.5, 130.4, 129.0, 128.7, 128.3, 127.3,126.8, 122.1 (q, $^1J_{CF}$ = 291 Hz), 83.8 (m). **HRMS** (APCI) calcd m/z for $[C_{16}H_{10}F_6O_2+H]^+$ 349.0658, found 349.0656 $[M+H]^+$.

1,1,1,3,3,3-Hexafluoropropan-2-yl benzoate (**1d**)



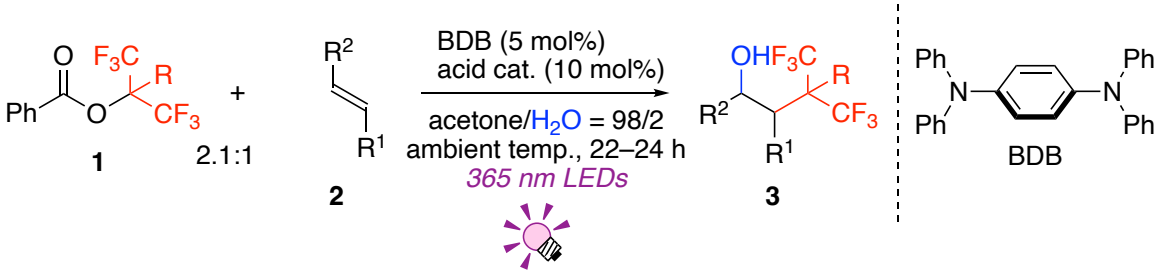
1d

According to the general procedures B, the use of 1,1,1,3,3,3-hexafluoropropan-2-ol (3.21 g, 19.1 mmol), anhydrous pyridine (2.4 mL), anhydrous CH_2Cl_2 (12 mL), and benzoyl chloride (3.18 g, 22.6 mmol) afforded **1d** as a white powder (2.55 g, 9.38 mmol, 49% yield). Column eluent: hexane/EtOAc = 92:8.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.14-8.12 (2H; Ar-*H*), 7.71-7.66 (1H; Ar-*H*), 7.55-7.51 (2H; Ar-*H*), 6.03 (m, 1H; C*H*$(CF_3)_2$). **^{19}F NMR** (376 MHz, CD_3CN): δ –73.1 (d, $^3J_{HF}$ = 8 Hz). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 163.44, 134.9, 130.7, 129.0, 127.0, 120.8 (q, $^1J_{CF}$ = 283 Hz), 67.1 (m). **HRMS** (APCI) calcd m/z for $[C_{10}H_6F_6O_2+H]^+$ 273.0345, found 273.0347 $[M+H]^+$.

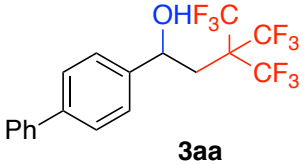
Procedures for Synthesis and Characterization of Product 3 (Table 2)

General procedures



A 10 mL Schlenk tube was charged with 1,4-bis(diphenylamino)benzene (BDB) (5 mol%), acid catalyst (10 mol%), benzoate **1** (0.25–0.50 mmol), alkene **2** (0.12–0.26 mmol), anhydrous acetone (2.5–5 mL), and H_2O (0.05–0.10 mL). The tube was degassed by three freeze-pump-thaw cycles and refilled with Ar. The tube was placed at a distance of –1 cm away from LED lamps (λ = 365 nm: 9 or 25 mW/cm^2) and irradiated for 22–24 h with stirring at room temperature (under wind blowing). After the reaction, the reaction mixture was concentrated under reduced pressure. Before purification, NMR yields were determined by addition of $C_6H_5CF_3$ as an internal standard and $CDCl_3$ to the residue. Then, after concentration of a $CDCl_3$ solution, the residue was purified by flash column chromatography with automated column chromatography with silica gel cartridges (Biotage SNAP Ultra, silica particle size 25 μm or Biotage Sfär Duo HC, silica particle size 20 μm) on a Biotage Isolera One. Further purification by GPC was performed as required.

1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3aa**)

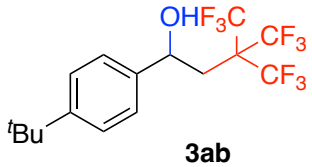


3aa

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), TsOH•H_2O (0.0025 g, 13.1 μmol), benzoate **1a** (0.0857 g, 0.252 mmol), 4-vinylbiphenyl (**2a**) (0.0225 g, 0.125 mmol), anhydrous acetone (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 28 ˚C afforded **3aa** as a pale yellow powder (0.0383 g, 0.0920 mmol, 74% yield (85% NMR yield)). Column eluent: hexane/EtOAc = 90:10.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.63-7.35 (9H; Ar-*H*), 5.25 (d, $^3J_{HH}$ = 8 Hz, 1H; *H*COH), 2.66 (dd, $^3J_{HH}$ = 8 Hz, $^2J_{HH}$ = 16 Hz, 1H; H*H*C), 2.48 (d, $^2J_{HH}$ = 16 Hz, 1H; *H*HC), 2.09 (br. d, 1H; O*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –65.6 (s, 9F; C(C*F*$_3$)$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 143.2, 141.6, 140.6, 129.0, 127.9, 127.7, 127.3, 125.9, 122.1 (q, $^1J_{CF}$ = 289 Hz), 68.7, 58.5 (m), 37.4. **HRMS** (APPI) calcd m/z for $[C_{18}H_{13}F_9O+Cl]^-$ 451.0517, found 451.0526 for $[M+Cl]^-$.

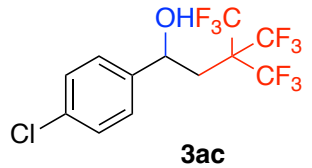
1-(4-*tert*-Butylphenyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ab**)



3ab

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), TsOH•H_2O (0.0023 g, 12.1 μmol), benzoate **1a** (0.0861 g, 0.253 mmol), 4-*tert*-butylstyrene (**2b**) (0.0221 g, 0.138 mmol), anhydrous acetone (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 23 ˚C afforded **3ab** as a brown oil (0.0360 g, 0.0908 mmol, 66% yield (91% NMR yield)). Column eluent: hexane/EtOAc = 90:10. **^{1}H NMR** (400 MHz, $CDCl_3$, rt): δ 7.42 (apparent m, 2H; Ar-*H*), 7.31 (apparent m, 2H; Ar-*H*), 5.17 (d, $^3J_{HH}$ = 8 Hz, 1H; HO*H*C), 2.63 (dd, $^3J_{HH}$ = 8 Hz, $^2J_{HH}$ = 16 Hz, 1H; *H*HC), 2.44 (d, $^2J_{HH}$ = 16 Hz, 1H; H*H*C), 2.02 (br. s, 1H; O*H*), 1.34 (br. s, 9H; C(C*H*$_3$)$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –65.6 (s, 9F; C(C*F*$_3$)$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 151.7, 141.4, 126.1, 125.2, 122.2 (q, $^1J_{CF}$ = 291 Hz), 68.7, 58.6 (m), 37.4, 34.8, 31.4. **HRMS** (APCI) calcd m/z for $[C_{16}H_{17}F_9O+Cl]^-$ 431.0830, found 431.0826 for $[M+Cl]^-$.

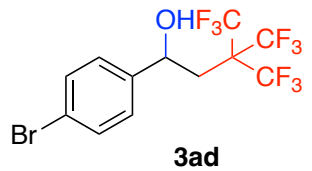
1-(4-Chlorophenyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ac**)



3ac

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), TsOH•H_2O (0.0025 g, 13.1 μmol), benzoate **1a** (0.0867 g, 0.255 mmol), 4-chlorostyrene (**2c**) (0.0207 g, 0.149 mmol), anhydrous acetone (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 22 ˚C afforded **3ac** as a yellow oil (0.0273 g, 0.0729 mmol, 49% yield (85% NMR yield)). Column eluent: hexane/EtOAc = 90:10. **^{1}H NMR** (400 MHz, $CDCl_3$, rt): δ 7.37 (apparent m, 2H; Ar-*H*), 7.32 (apparent m, 2H; Ar-*H*), 5.18 (d, $^3J_{HH}$ = 8 Hz, 1H; HO*H*C), 2.59 (dd, $^3J_{HH}$ = 8 Hz, $^2J_{HH}$ = 16 Hz, 1H; *H*HC), 2.38 (d, $^2J_{HH}$ = 16 Hz, 1H; H*H*C), 2.03 (br. s, 1H; O*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –65.7 (s, 9F; C(C*F*$_3$)$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 142.7, 134.4, 129.3, 126.9, 122.1 (q, $^1J_{CF}$ = 290 Hz), 68.3, 58.5 (m), 37.5. **HRMS** (APCI) calcd m/z for $[C_{12}H_8ClF_9O+Cl]^-$ 408.9814, found 408.9814 for $[M+Cl]^-$.

1-(4-Bromophenyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ad**)

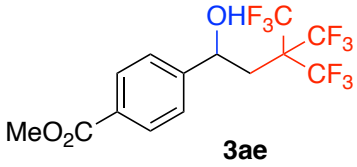


3ad

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), TsOH•H_2O (0.0023 g, 12.1 μmol), benzoate **1a** (0.0848 g, 0.249 mmol), 4-bromostyrene (**2d**) (0.0297 g, 0.162 mmol), anhydrous

acetone (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 24 ˚C afforded **3ac** as a yellow oil (0.0250 g, 0.0597 mmol, 37% yield (61% NMR yield)). Column eluent: hexane/EtOAc = 90:10. **^{1}H NMR** (400 MHz, $CDCl_3$, rt): δ 7.52 (apparent m, 2H; Ar-*H*), 7.25 (apparent m, 2H; Ar-*H*), 5.16 (d, $^3J_{HH}$ = 8 Hz, 1H; HO*H*C), 2.58 (dd, $^3J_{HH}$ = 8 Hz, $^2J_{HH}$ = 16 Hz, 1H; *H*HC), 2.37 (d, $^2J_{HH}$ = 16 Hz, 1H; H*H*C), 2.16 (br. d, 1H; O*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –65.6 (s, 9F; C(C*F*$_3$)$_3$). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 143.2, 132.3, 127.2, 122.4, 122.0, 68.3, 58.5, 37.4. **HRMS** (APCI) calcd m/z for $[C_{12}H_8BrF_9O+Cl]^-$ 452.9309, found 452.9306 for $[M+Cl]^-$.

1-(4-Methoxycarbonyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ae**)

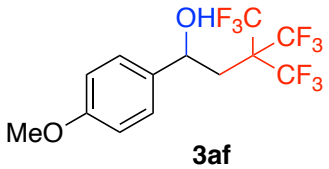


3ae

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), TsOH•H_2O (0.0023 g, 12.1 μmol), benzoate **1a** (0.0859 g, 0.253 mmol), 4-methoxycarbonylstyrene (**2e**) (0.0203 g, 0.125 mmol), anhydrous acetone (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 26 ˚C afforded **3ae** as a white solid (0.0130 g, 0.0326 mmol, 26% yield (58% NMR yield)). Column eluent: hexane/EtOAc = 90:10.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.05 (d, $^3J_{HH}$ = 8 Hz, 2H; Ar-*H*), 7.44 (d, $^3J_{HH}$ = 12 Hz, 2H; Ar-*H*), 5.25 (d, $^3J_{HH}$ = 8 Hz, 1H; HO*H*C), 3.92 (s, 3H; C*H*$_3$O), 2.61 (dd, $^3J_{HH}$ = 8 Hz, $^2J_{HH}$ = 16 Hz, 1H; *H*HC), 2.39 (d, $^2J_{HH}$ = 16 Hz, 1H; H*H*C), 2.28 (br. s, 1H; O*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –68.9 (s, 9F; C(C*F*$_3$)$_3$). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 166.8, 149.0, 130.5, 130.3, 125.5, 122.0, 68.5, 58.5, 52.4, 37.3. **HRMS** (APCI) calcd m/z for $[C_{14}H_{11}F_9O_3+H]^+$ 399.0637, found 399.0631 $[M+H]^+$.

1-(4-Methoxyphenyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3af**)



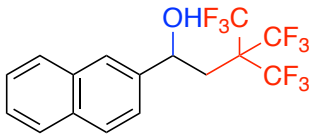
3af

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), TsOH•H_2O (0.0026 g, 13.7 μmol), benzoate **1a** (0.0862 g, 0.253 mmol), 4-methoxystyrene (**2f**) (0.0169 g, 0.126 mmol), anhydrous acetone (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 27 ˚C afforded **3af** as a reddish oil (0.0091 g, 0.0246 mmol, 20% yield (57% NMR yield)). Column eluent: hexane/EtOAc = 85:15, then preparative GPC eluent: $CHCl_3$.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.29 (apparent m, 2H; Ar-*H*), 6.91 (apparent m, 2H; Ar-*H*), 5.14 (d, $^3J_{HH}$ = 8 Hz, 1H; HO*H*C), 3.81 (s, 3H; C*H*$_3$O), 2.51 (dd, $^3J_{HH}$ = 8 Hz, $^2J_{HH}$ = 16 Hz, 1H; *H*HC), 2.41 (d, $^2J_{HH}$ = 16 Hz, 1H; H*H*C), 2.01 (br. s, 1H; O*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –65.6 (s, 9F; C(C*F*$_3$)$_3$). **^{13}C{^{1}H, ^{19}F}**

NMR (101 MHz, $CDCl_3$): δ 159.7, 136.5, 126.7, 122.1, 114.4, 68.5, 58.5, 55.5, 37.5. **HRMS** (APCI) calcd m/z for $[C_{13}H_{11}F_9O_2\text{-}OH]^+$ 353.0577, found 353.0577 for $[M\text{-}OH]^+$.

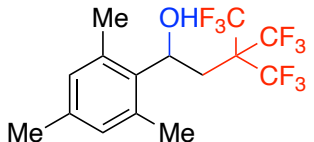
1-(2-Naphthyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ag**)



3ag

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), TsOH•H_2O (0.0025 g, 13.1 μmol), benzoate **1a** (0.0880 g, 0.259 mmol), 2-vinylnaphthalene (**2g**) (0.0193 g, 0.125 mmol), anhydrous acetone (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 26 ˚C afforded **3ag** as a white soild (0.0224 g, 0.0574 mmol, 46% yield (78% NMR yield)). Column eluent: hexane/EtOAc = 90:10. **^{1}H NMR** (400 MHz, $CDCl_3$, rt): δ 7.90–7.83 (4H; Ar-*H*), 7.53–7.46 (3H; Ar-*H*), 5.36 (d, $^3J_{HH}$ = 8 Hz, 1H; HO*H*C), 2.71 (dd, $^3J_{HH}$ = 8 Hz, $^2J_{HH}$ = 16 Hz, 1H; *H*HC), 2.52 (d, $^2J_{HH}$ = 16 Hz, 1H; H*H*C), 2.22 (apparent d, 1H; O*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –65.6 (s, 9F; C(C*F*$_3$)$_3$). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 141.5, 133.4, 133.3, 129.3, 128.2, 127.9, 126.8, 126.6, 124.2, 123.1, 122.1, 69.0, 58.6, 37.4. **HRMS** (APCI) calcd m/z for $[C_{16}H_{11}F_9O+Cl]^-$ 425.0360, found 425.0359 for $[M+Cl]^-$.

1-Mesityl-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ah**)

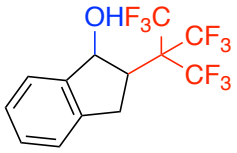


3ah

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), TsOH•H_2O (0.0025 g, 13.1 μmol), benzoate **1a** (0.0861 g, 0.253 mmol), mesitylstyrene (**2h**) (0.0196 g, 0.134 mmol), anhydrous acetone (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 22 ˚C afforded **3ah** as a reddish oil (0.0112 g, 0.0293 mmol, 22% yield (40% NMR yield)). Column eluent: CH_2Cl_2/MeOH = 90:10, then preparative GPC eluent: $CHCl_3$.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 6.86 (s, 2H; Ar-*H*), 5.62 (d, $^3J_{HH}$ = 12 Hz, 1H; HO*H*C), 2.95 (dd, $^3J_{HH}$ = 8 Hz, $^2J_{HH}$ = 16 Hz, 1H; *H*HC), 2.42, 2.38 (7H; C*H*$_3$ and H*H*C), 2.26 (s, 3H; C*H*$_3$), 1.87 (d, $^2J_{HH}$ = 4 Hz, 1H; O*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –68.9 (s, 9F; C(C*F*$_3$)$_3$). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 138.2, 137.8, 136.5, 129.0, 122.2, 65.5, 58.7, 34.4, 20.9, 20.6. **HRMS** (APCI) calcd m/z for $[C_{15}H_{15}F_9O+Cl]^-$ 417.0673, found 417.0666 $[M+Cl]^-$.

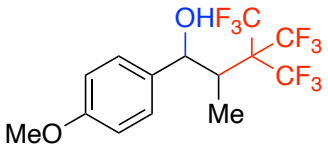
2-(1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl)-2,3-dihydro-1*H*-inden-1-ol (**3ai**)



3ai

According to the general procedures, the use of BDB (0.0052 g, 12.6 μmol), TsOH•H_2O (0.0048 g, 25.2 μmol), benzoate **1a** (0.1692 g, 0.497 mmol), indene (**2i**) (0.0300 g, 0.258 mmol), anhydrous acetone (4.9 mL), and water (0.1 mL) under irradiation (25 mW/cm^2, 22 h) around 28 ˚C afforded **3ai** as a yellow oil (0.0380 g, 0.108 mmol, 42% yield (55% NMR yield)). Column eluent: hexane/EtOAc = 80:20.
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.42–7.21 (4H; Ar-*H*), 5.64 (apparent t, $^3J_{HH}$ = 8 Hz, 1H; HO*H*C), 3.41 (apparent dd, $^3J_{HH}$ = 12 Hz, 16 Hz, 1H; C*H*), 3.29 (apparent dd, $^3J_{HH}$ = 8 Hz, 20 Hz, 1H; C*H*), 3.07 (m, 1H; C*H*), 2.33 (d, $^3J_{HH}$ = 8 Hz, 1H; O*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –66.4 (s, 9F; CF_3). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 141.7, 138.7, 129.3, 127.8, 124.8, 124.3, 122.4, 76.9, 61.5, 48.8, 33.5. **HRMS** (APCI) calcd m/z for $[C_{13}H_9F_9O+Cl]^-$ 387.0204, found 387.0197 $[M+Cl]^-$.

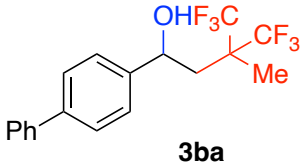
4,4,4-Trifluoro-1-(4-methoxyphenyl)-2-methyl-3,3-bis(trifluoromethyl)butan-1-ol (**3aj**)



3aj

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), TsOH•H_2O (0.0025 g, 13.1 μmol), benzoate **1a** (0.0850 g, 0.250 mmol), anethole (**2j**) (0.0203 g, 0.137 mmol), anhydrous acetone (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 23 ˚C afforded **3aj** as a yellow oil (0.0056 g, 0.0146 mmol, 11% yield (27% NMR yield)). Column eluent: hexane/EtOAc = 80:20.
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.29 (apparent m, 2H; Ar-*H*), 6.91 (apparent m, 2H; Ar-*H*), 5.54 (br. d, 1H; HO*H*C), 3.82 (s, 3H; OCH_3), 2.56 (q, $^3J_{HH}$ = 8 Hz, 1H; *H*CMeC$(CF_3)_3$), 1.84 (br. d, $^3J_{HH}$ = 8 Hz, 1H; O*H*), 1.23 (d, $^3J_{HH}$ = 8 Hz, 3H; CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –62.9 (s, 9F; C(C$F_3)_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 159.2, 135.5, 126.6, 122.6 (q, $^1J_{CF}$ = 291 Hz), 114.0, 69.7, 61.7 (m), 55.5, 42.6, 7.85. **HRMS** (APCI) calcd m/z for $[C_{14}H_{13}F_9O_2\text{-}OH]^+$ 367.0732, found 367.0732 for $[M\text{-}OH]^+$.

1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluoro-3-methyl-3-(trifluoromethyl)butan-1-ol (**3ba**)

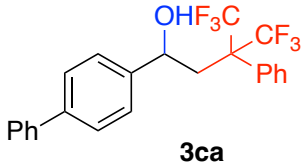


3ba

According to the general procedures, the use of BDB (0.0025 g, 6.06 μmol), $Zn(OTf)_2$ (0.0068 g, 18.7 μmol), benzoate **1b** (0.0674 g, 0.236 mmol), 4-vinylbiphenyl (**2a**) (0.0226 g, 0.125 mmol) , anhydrous

acetone (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 24 h) around 24 ˚C afforded **3ba** as a yellow oil (0.0287 g, 0.0792 mmol, 63% yield (99% NMR yield)). Column eluent: hexane/EtOAc = 91:9. **^{1}H NMR** (400 MHz, $CDCl_3$, rt): δ 7.62-7.35 (9H; Ar-*H*), 5.09 (m, 1H; *H*COH), 2.24–2.21 (2H; H*H*C, *H*HC), 1.98 (br., 1H; O*H*), 1.60 (s, 3H; CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –70.8 (q, $^4J_{FF}$ = 8 Hz, 3F; CF_3), –73.2 (q, $^4J_{FF}$ = 8 Hz, 3F; CF_3). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 143.7, 141.4, 140.7, 129.0, 127.8, 127.6, 127.3, 126.0, 125.995 (q, $^1J_{CF}$ = 332 Hz), 125.5 (q, $^1J_{CF}$ = 286 Hz), 70.4, 50.2 (m), 39.12, 14.2. **HRMS** (APPI) calcd m/z for $[C_{18}H_{16}F_9O+Cl]^-$ 397.0799, found 397.0809 for $[M+Cl]^-$.

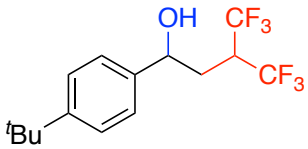
1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluoro-3-phenyl-3-(trifluoromethyl)butan-1-ol (**3ca**)



3ca

According to the general procedures, the use of BDB (0.0025 g, 6.06 μmol), $Zn(OTf)_2$ (0.0081 g, 22.3 μmol), benzoate **1c** (0.0966 g, 0.277 mmol), 4-vinylbiphenyl (**2a**) (0.0227 g, 0.126 mmol), anhydrous acetone (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 24 h) around 22 ˚C afforded **3ca** as a yellow oil (0.0236 g, 0.0556 mmol, 44% yield (54% NMR yield)). Column eluent: hexane/EtOAc = 85:15. **^{1}H NMR** (400 MHz, $CDCl_3$, rt): δ 7.66-7.37 (14H; Ar-*H*), 4.93 (d, $^3J_{HH}$ = 8 Hz, 1H; *H*COH), 3.03 (dd, $^3J_{HH}$ = 8 Hz, 16 Hz, 1H; H*H*C), 2.79 (dd, $^3J_{HH}$ = 4 Hz, 16 Hz, 1H; *H*HC), 1.77 (br., 1H; O*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –65.5 (q, $^4J_{FF}$ = 11 Hz, 3F; CF_3), –66.3 (q, $^4J_{FF}$ = 11 Hz, 3F; CF_3). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 143.5, 141.3, 140.8, 129.4, 129.3, 129.2, 129.0, 128.7, 127.7, 127.6, 127.3, 126.3, 124.8(2C), 70.1, 58.3 (m), 38.6. **HRMS** (APCI) calcd m/z for $[C_{23}H_{18}F_6O+Cl]^-$ 459.0956, found 459.0954 for $[M+Cl]^-$.

4,4,4-Trifluoro-1-(4-*tert*-butylphenyl)-3-(trifluoromethyl)butan-1-ol (**3db**)



3db

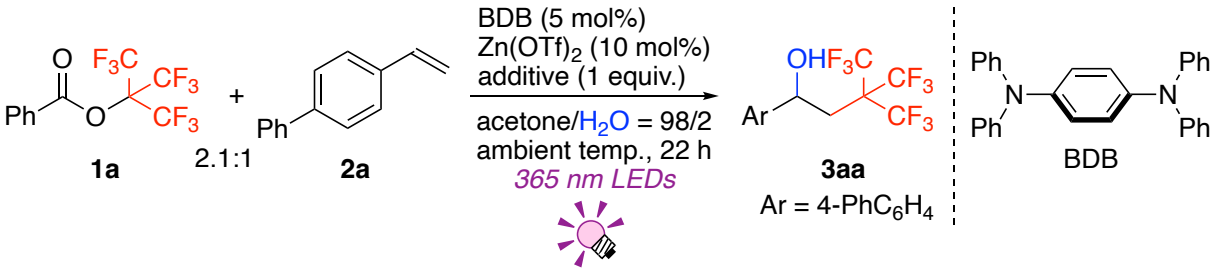
According to the general procedures, the use of BDB (0.0051 g, 12.4 μmol), $Zn(OTf)_2$ (0.0096 g, 26.4 μmol), benzoate **1d** (0.1360 g, 0.500 mmol), 4-*tert*-butylstyrene (**2b**) (0.0390 g, 0.243 mmol), anhydrous acetone (4.9 mL), and water (0.10 mL) under irradiation (25 mW/cm^2, 22 h) around 29 ˚C afforded **3db** as a colorless oil (0.0195 g, 0.0594 mmol, 24% yield (92% NMR yield)). Column eluent: hexane/EtOAc = 90:10.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (d, $^3J_{HH}$ = 12 Hz, 2H; Ar-*H*), 7.30 (d, $^3J_{HH}$ = 8 Hz, 2H; Ar-*H*), 4.85 (apparent br. d, $^3J_{HH}$ = 12 Hz, 1H; C*H*(OH)), 3.38 (m, 1H; C*H*$(CF_3)_2$), 2.23-2.08 (2H; CH_2), 1.93 (apparent d, $^3J_{HH}$ = 4 Hz, 1H; *OH*), 1.32 (s, 9H; C(CH_3)$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –70.0 (apparent m, 3F; *CF*$_3$), –70.8 (apparent m, 3F; *CF*$_3$). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 151.8, 140.0, 126.0, 125.6,

124.3, 124.1, 70.7, 44.9, 34.8, 33.0, 31.4. **HRMS** (APCI) calcd m/z for $[C_{15}H_{18}F_6O+Cl]^-$ requires 363.0956 found 363.0947 for $[M+Cl]^-$.

Evaluation of Radical Nonafluoro-*tert*-butylation with Respect to Functionalities Using FGE Kit[1]

General procedures



A 10 mL Schlenk tube was charged with 1,4-bis(diphenylamino)benzene (BDB) (0.0026–0.0029 g, 6.30–7.03 μmol, 5 mol%), $Zn(OTf)_2$ (0.0045–0.0051 g, 12.4–14.0 μmol, 10 mol%), benzoate **1a** (0.0859–0.1621 g, 0.253–0.477 mmol), alkene **2a** (0.0225–0.0245 g, 0.125–0.136 mmol), additive (0.125–0.166 mmol), anhydrous acetone (2.5 mL), and H_2O (0.05 mL). The tube was degassed by three freeze-pump-thaw cycles and refilled with Ar. The tube was placed at a distance of –1 cm away from LED lamps (λ = 365 nm, 9 mW/cm^2) and irradiated for 22 h with stirring at room temperature (under wind blowing). After the reaction, the reaction mixture was concentrated under reduced pressure. The NMR yield of **3aa** was determined by ^{19}F NMR spectroscopy with $C_6H_5CF_3$ as an internal standard. The experiment was carried out twice for each additive, and the yield as an average value was shown in Figure S1. The additives (FGE kit) were listed in Figure S2.

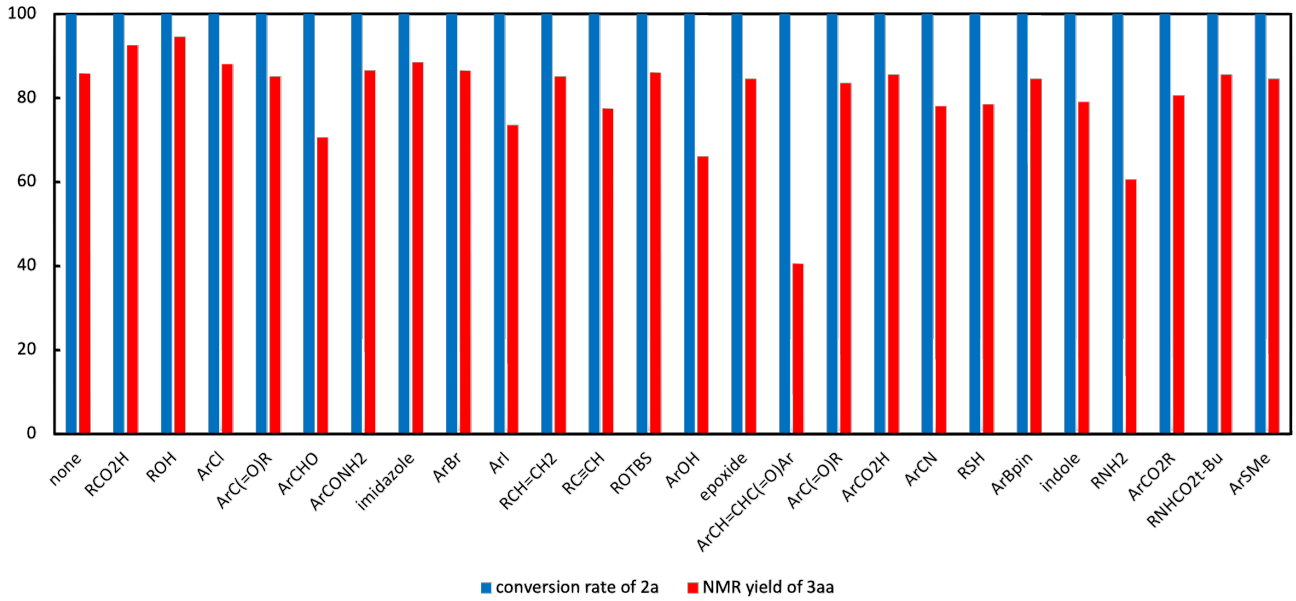


Figure S1. Evaluation of the Present RPCO Reaction Using FGE Kit.

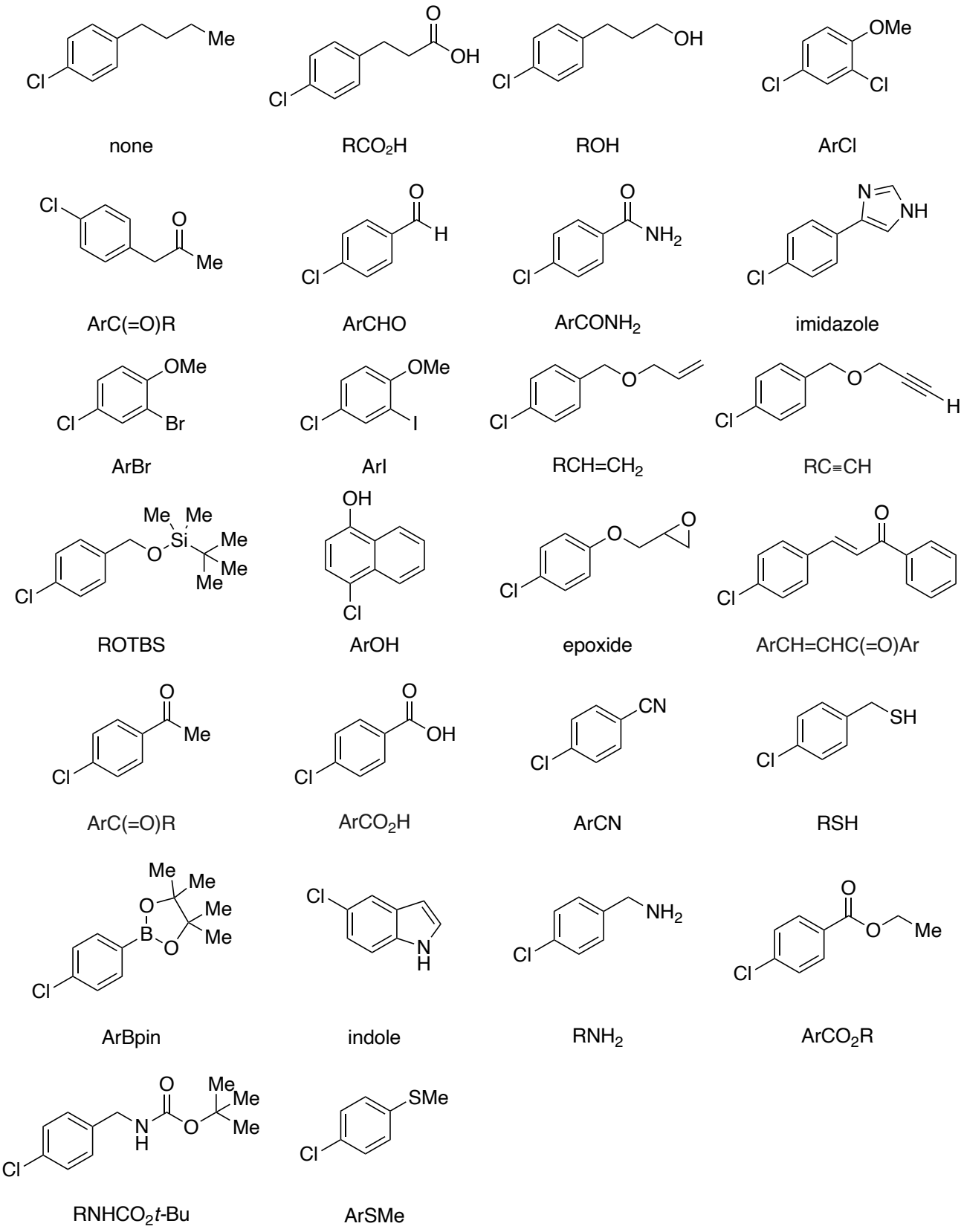
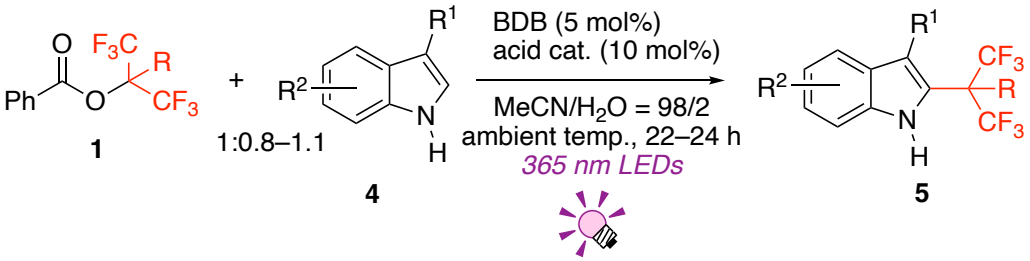


Figure S2. List of Additives.

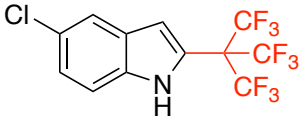
Procedures for Synthesis and Characterization of Product 5 (Table 3)

General procedures



A 10 mL Schlenk tube was charged with 1,4-bis(diphenylamino)benzene (BDB) (5 mol%), acid catalyst (10 mol%), benzoate **1** (0.120–0.315 mmol), indole **4** (0.125–0.270 mmol), anhydrous MeCN (2.5–5 mL), and H_2O (0.05–0.10 mL). The tube was degassed by three freeze-pump-thaw cycles and refilled with Ar. The tube was placed at a distance of –1 cm away from LED lamps (λ = 365 nm, 9 or 25 mW/cm^2) and irradiated for 22–24 h with stirring at room temperature (under wind blowing). After the reaction, the reaction mixture was concentrated under reduced pressure. Before purification, NMR yields were determined by addition of $C_6H_5CF_3$ as an internal standard and $CDCl_3$ to the residue. Then, after concentration of a $CDCl_3$ solution, the residue was purified by flash column chromatography with silica gel or automated column chromatography with silica gel cartridges (Biotage SNAP Ultra, silica particle size 25 μm or Biotage Sfär Duo HC, silica particle size 20 μm) on a Biotage Isolera One. Further purification by GPC was performed as required.

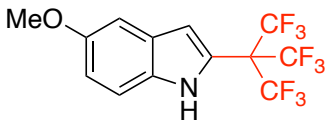
5-Chloro-2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-1*H*-indole (**5aa**)



5aa

According to the general procedures, the use of BDB (0.0025 g, 6.06 μmol), TsOH•H_2O (0.0024 g, 12.6 μmol), benzoate **1a** (0.0411 g, 0.121 mmol), 5-chloro-1*H*-indole (**4a**) (0.0208 g, 0.137 mmol), anhydrous MeCN (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 24 h) around 25 ˚C afforded **5aa** as a white soild (0.0324 g, 0.0877 mmol, 73% yield (95% NMR yield)). Column eluent: hexane/EtOAc = 90:10. Recrystalization from MeOH afforded colorless crystals that are suitable for X-ray analysis.
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.42 (br. s, 1H; N–*H*), 7.65 (d, 1H; Ar-*H*), 7.37 (br. d, 1H; Ar-*H*), 7.28 (dd, 1H; Ar-*H*), 6.94 (br. m, 1H; Ar-*H*). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –64.0 (s, 9F; C*F*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 135.0, 127.6, 127.0, 125.4, 121.4 (q, $^1J_{CF}$ = 293 Hz), 121.1, 119.9, 112.6, 108.4, 60.6 (m). **HRMS** (APCI) calcd m/z for $[C_{12}H_5ClF_9N–H]^-$ 367.9894, found 367.9884 for $[M–H]^-$.

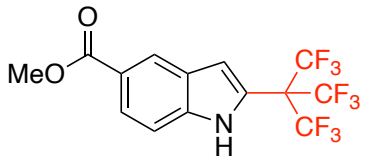
5-Methoxy-2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-1*H*-indole (**5ab**)



5ab

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), TsOH•H_2O (0.0024 g, 12.6 μmol), benzoate **1a** (0.0489 g, 0.144 mmol), 5-methoxy-1*H*-indole (**4b**) (0.0184 g, 0.125 mmol), anhydrous MeCN (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 25 ˚C afforded **5ab** as a yellow soild (0.0279 g, 0.0764 mmol, 61% yield (78% NMR yield)). Column eluent: hexane/EtOAc = 90:10. **^{1}H NMR** (400 MHz, $CDCl_3$, rt): δ 8.34 (br. s, 1H; N–*H*), 7.34 (d, $^3J_{HH}$ = 12 Hz, 1H; Ar-*H*), 7.10 (br. s, 1H; Ar-*H*), 6.86 (dd, $^3J_{HH}$ = 12 Hz, $^4J_{HH}$ = 4 Hz, 1H; Ar-*H*), 6.92 (br. s, 1H; Ar-*H*), 3.86 (s, 3H; C*H*$_3$O). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –67.4 (s, 9F; C*F*$_3$). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 155.1, 131.8, 127.1, 121.5, 118.7, 115.9, 112.4, 108.4, 102.3, 60.6, 55.9. **HRMS** (APCI) calcd m/z for $[C_{13}H_8F_9NO+H]^+$ 366.0530, found 366.0535 $[M+H]^+$.

5-Methoxycarbonyl-2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-1*H*-indole (**5ac**)

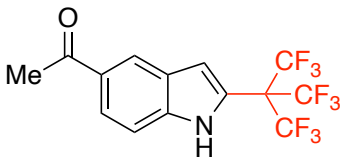


5ac

According to the general procedures, the use of BDB (0.0050 g, 12.1 μmol), TsOH•H_2O (0.0046 g, 24.2 μmol), benzoate **1a** (0.0888 g, 0.261 mmol), 5-methoxycarbonyl-1*H*-indole (**4c**) (0.0473 g, 0.270 mmol), anhydrous MeCN (5.0 mL), and water (0.10 mL) under irradiation (25 mW/cm^2, 24 h) around 28 ˚C afforded **5ac** as a white soild (0.0661 g, 0.169 mmol, 65% yield (84% NMR yield)). Column eluent: hexane/EtOAc = 88:12.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.71 (br. s, 1H; N–*H*), 8.45 (apparent t, 1H; Ar-*H*), 8.03 (dd, $^3J_{HH}$ = 10 Hz, $^4J_{HH}$ = 4 Hz,1H; Ar-*H*), 7.47 (d, $^3J_{HH}$ = 8 Hz, 1H; Ar-*H*), 7.09 (br. s, 1H; Ar-*H*), 3.95 (s, 3H; C*H*$_3$O). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –67.3 (s, 9F; C*F*$_3$). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 167.7, 139.1, 126.2, 125.9, 124.8, 123.5, 121.4, 120.0, 111.3, 110.0, 60.6, 52.2. **HRMS** (APCI) calcd m/z for $[C_{14}H_{18}F_9NO_2+H]^+$ 394.0484, found 394.0478 $[M+H]^+$.

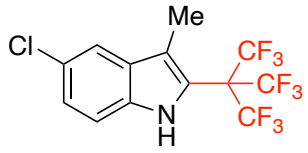
5-Acetyl-2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-1*H*-indole (**5ad**)



5ad

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), TsOH•H_2O (0.0024 g, 12.6 μmol), benzoate **1a** (0.0440 g, 0.129 mmol), 5-acetyl-1*H*-indole (**4d**) (0.0199 g, 0.125 mmol), anhydrous MeCN (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 25 ˚C afforded **5ad** as a white soild (0.0125 g, 0.0331 mmol, 27% yield (53% NMR yield)). Column eluent: hexane/EtOAc = 80:20. **^{1}H NMR** (400 MHz, $CDCl_3$, rt): δ 8.77 (br. s, 1H; N–*H*), 8.35 (apparent t, $^4J_{HH}$ = 4 Hz, 1H; Ar-*H*), 8.01 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 4 Hz,1H; Ar-*H*), 7.50 (d, $^3J_{HH}$ = 8 Hz, 1H; Ar-*H*), 7.12 (br. s, 1H; Ar-*H*), 2.68 (s, 3H; C*H*$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –67.3 (s, 9F; C*F*$_3$). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 198.0, 139.1, 131.3, 126.1, 124.8, 124.0, 121.4, 120.2, 111.6, 110.3, 60.6, 26.8. **HRMS** (APCI) calcd m/z for $[C_{14}H_8F_9NO+H]^+$ 378.0535, found 378.0530 $[M+H]^+$.

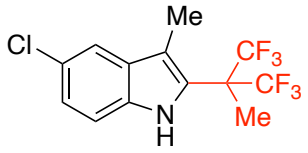
5-Chloro-2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-3-methyl-1*H*-indole (**5ae**)



5ae

According to the general procedures, the use of BDB (0.0025 g, 6.06 μmol), TsOH•H_2O (0.0023 g, 12.1 μmol), benzoate **1a** (0.0407 g, 0.120 mmol), 5-chloro-3-methyl-1*H*-indole (**4e**) (0.0228 g, 0.137 mmol), anhydrous MeCN (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 24 h) afforded **5ae** as a white soild (0.0249 g, 0.0649 mmol, 54% yield (>99% NMR yield)). Column eluent: hexane/EtOAc = 90:10. **^{1}H NMR** (400 MHz, $CDCl_3$, rt): δ 8.38 (br. s, 1H; N–*H*), 7.64 (apparent d, 1H; Ar-*H*), 7.33–7.27 (2H; Ar-*H*), 2.40 (apparent. m, 3H; C*H*$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –62.4 (apparent s, 9F; C*F*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 133.7, 130.0, 126.4, 125.4, 121.7 (q, $^1J_{CF}$ = 292 Hz), 119.6, 116.5, 115.6, 112.4, 61.6 (m), 10.3. **HRMS** (APCI) calcd m/z for $[C_{13}H_7ClF_9N–H]^-$ 382.0051, found 382.0043 for $[M–H]^-$.

5-Chloro-2-(1,1,1,3,3,3-hexafluoro-2-methyl-propan-2-yl)-3-methyl-1*H*-indole (**5be**)



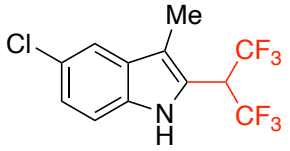
5be

According to the general procedures, the use of BDB (0.0052 g, 12.6 μmol), $Zn(OTf)_2$ (0.0091 g, 25.0 μmol), benzoate **1a** (0.0901 g, 0.315 mmol), 5-chloro-3-methyl-1*H*-indole (**4e**) (0.0414 g, 0.250 mmol), anhydrous MeCN (4.9 mL), and water (0.1 mL) under irradiation (25 mW/cm^2, 22 h) around 28 ˚C afforded **5be** as a white powder (0.0168 g, 0.0510 mmol, 20% yield (50% NMR yield)). Column eluent: hexane/EtOAc = 90:10, then preparative GPC eluent: $CHCl_3$.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.30 (br. s, 1H; N–*H*), 7.58 (apparent d, $^4J_{HH}$ = 4 Hz, 1H; Ar-*H*), 7.28 (d, $^3J_{HH}$ = 8 Hz, 1H; Ar-*H*), 7.22 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 4 Hz, 1H; Ar-*H*), 2.44 (s, 3H; C*H*$_3$), 2.06 (s, 3H; C*H*$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –73.1 (s, 9F; C*F*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 133.6, 130.0,

125.8, 124.7, 124.3, 122.7, 118.8, 113.9, 112.1, 52.8, 15.1, 10.7. **HRMS** (APCI) calcd m/z for $[C_{13}H_{10}ClF_6N+H]^+$ 330.0479, found 330.0476 $[M+H]^+$.

5-Chloro-2-(1,1,1,3,3,3-hexafluoropropan-2-yl)-3-methyl-1*H*-indole (**5de**)

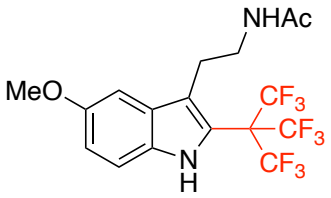


5de

According to the general procedures, the use of BDB (0.0026 g, 6.30 μmol), $Zn(OTf)_2$ (0.0045 g, 12.4 μmol), benzoate **1e** (0.0408 g, 0.150 mmol), 5-chloro-3-methyl-1*H*-indole (**4e**) (0.0207 g, 0.125 mmol), anhydrous MeCN (2.5 mL), and water (0.05 mL) under irradiation (9 mW/cm^2, 22 h) around 26 ˚C afforded **5de** as a colorless oil (0.0230 g, 0.0729 mmol, 58% yield (98% NMR yield)). Column eluent: hexane/EtOAc = 90:10.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.18 (br. s, 1H; N–*H*), 7.57 (apparent d, 1H; Ar-*H*), 7.31 (d, $^3J_{HH}$ = 8 Hz, 1H; Ar-*H*), 7.24 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 4 Hz 1H; Ar-*H*), 4.48 (m, $^3J_{HF}$ = 8 Hz, 1H; C*H*$(CF_3)_2$), 2.30 (s, 3H; C*H*$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –65.2 (d, $^3J_{HF}$ = 8 Hz, 6F; CH(C*F*$_3)_2$). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 134.7, 128.8, 126.0, 124.4, 122.7, 119.4, 119.1, 115.0, 112.4, 46.3, 8.6. **HRMS** (APCI) calcd m/z for $[C_{12}H_8ClF_9N+H]^+$ 316.0322, found 316.0319 for $[M+H]^+$.

N-(2-(2-(1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl)-5-methoxy-1*H*-indol-3-yl)ethyl)acetamide (**5af**)

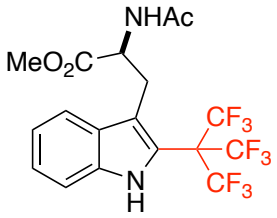


5af

According to the general procedures, the use of BDB (0.0050 g, 12.1 μmol), TsOH•H_2O (0.0046 g, 24.2 μmol), benzoate **1a** (0.0822 g, 0.242 mmol), melatonin (**4f**) (0.0622 g, 0.268 mmol), anhydrous MeCN (5.0 mL), and water (0.10 mL) under irradiation (25 mW/cm^2, 24 h) around 29 ˚C afforded **5af** as a pale yellow solid (0.0416 g, 0.0924 mmol, 38% yield (60% NMR yield)). Column eluent: hexane/EtOAc = 50:50.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.45 (br. s, 1H; N–*H*), 7.45 (d, $^4J_{HH}$ = 4 Hz, 1H; Ar-*H*), 7.30 (d, $^3J_{HH}$ = 8 Hz, 1H; Ar-*H*), 6.99 (apparent dd, $^3J_{HH}$ = 8 Hz, 1H; Ar-*H*), 5.80 (br. s, 1H; N*H*Ac), 3.91 (s, 3H; C*H*$_3$O), 3.49–3.44 (2H; C*H*$_2$), 3.14–3.12 (2H; C*H*$_2$), 2.00 (s, 3H; C*H*$_3$CO). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –65.8 (s, 9F; C*F*$_3$). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 170.5, 155.0, 130.6, 128.9, 121.7, 117.3, 116.6, 114.1, 112.3, 101.0, 61.6, 56.0, 39.8, 25.7, 23.5. **HRMS** (APCI) calcd m/z for $[C_{17}H_{15}F_9N_2O_2+H]^+$ 451.1063, found 451.1054 for $[M+H]^+$.

Methyl (*S*)-2-acetamido-3-(2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-1*H*-indol-3-yl)propanoate (**5ag**)



5ag

According to the general procedures, the use of BDB (0.0050 g, 12.1 μmol), TsOH•H_2O (0.0046 g, 24.2 μmol), benzoate **1a** (0.0850 g, 0.250 mmol), methyl acetyl-*L*-tryptophanate (**4g**) (0.0699 g, 0.269 mmol), anhydrous MeCN (5.0 mL), and water (0.10 mL) under irradiation (25 mW/cm^2, 24 h) around 29 ˚C afforded **5ag** as a pale orange solid (0.0543 g, 0.114 mmol, 45% yield (95% NMR yield)). Column eluent: hexane/EtOAc = 50:50.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.66 (br. s, 1H; N–*H*), 7.88 (d, $^3J_{HH}$ = 8 Hz, 1H; Ar-*H*), 7.40 (d, $^3J_{HH}$ = 8 Hz, 1H; Ar-*H*), 7.32 (apparent t, $^3J_{HH}$ = 8 Hz, 1H; Ar-*H*), 7.20 (apparent t, $^3J_{HH}$ = 8 Hz, 1H; Ar-*H*), 6.17 (br. s, 1H; N*H*Ac), 4.98 (apparent q, $^3J_{HH}$ = 8 Hz, 1H; C*H*NHAc), 3.53 (s, 3H; CH_3O), 3.38 (apparent d, $^3J_{HH}$ = 8 Hz, 2H; CH_2), 1.87 (s, 3H; CH_3CO). **^{19}F NMR** (376 MHz, $CDCl_3$): δ –65.5 (s, 9F; CF_3). **^{13}C{^{1}H, ^{19}F} NMR** (101 MHz, $CDCl_3$): δ 172.8, 169.8, 135.5, 128.2, 125.2, 121.6, 121.0, 120.3, 115.4, 114.6, 111.5, 61.4, 52.8, 52.5, 28.6, 23.0. **HRMS** (APCI) calcd m/z for $[C_{18}H_{15}F_9N_2O_3+H]^+$ 479.1012, found 479.1003 for $[M+H]^+$.

Cyclic Voltammogram for Benzoate

Cyclic voltammetry was performed using Hokutodenkou HZ-7000 analyzer under N_2 at room temperature. The measurement was performed in acetonitrile ([compound] = 0.034 M, [$(NBu_4)PF_6$] = 0.10 M) with platinum disk (working electrode), wire electrode (counter electrode), and a $Ag/AgNO_3$ reference electrode. The scan rate was 100 mV/s. Ferrocene (Fc) was used as a reference.

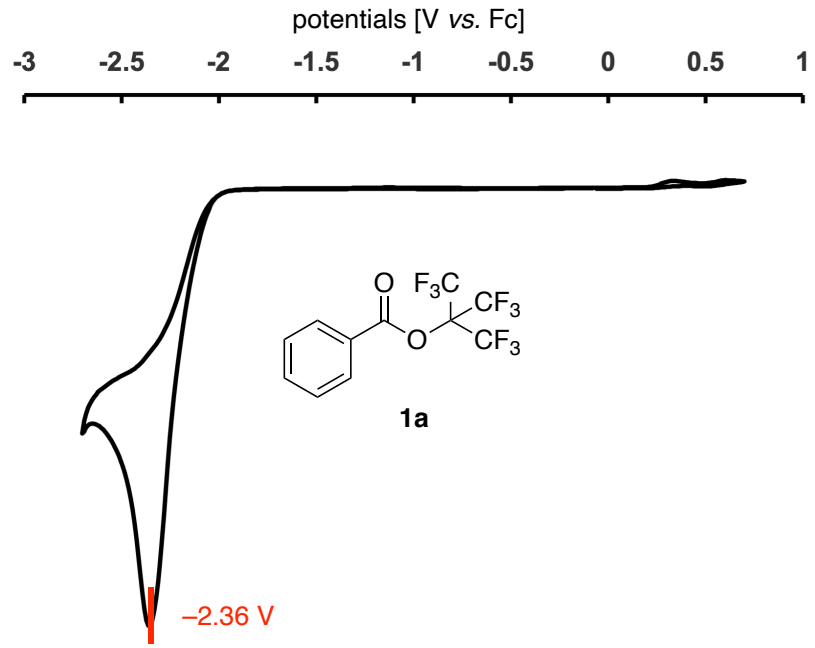


Figure S3. Cyclic Voltammogram for **1a.**

UV-Vis Spectra for Catalyst and Substrates

UV-Vis spectra of acetonitrile solutions of BDB, 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl benzoate (**1a**), 4-*tert*-butylstyrene (**2b**), and 5-chloro-1*H*-indole (**4a**) at room temperature were shown in Figure S4.

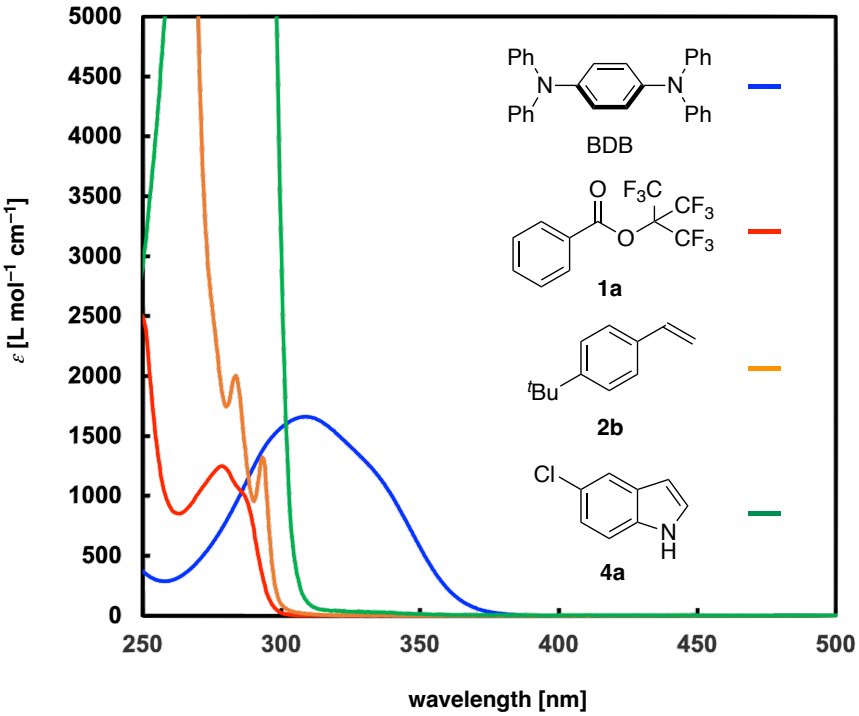


Figure S4. UV-Vis spectra for BDB, **1a**, **2b**, and **4a** in MeCN.

UV-Vis spectra for a mixture of **1a** and **4a** in MeCN were shown in Figure S5. These results suggested that EDA complex is not formed clearly.

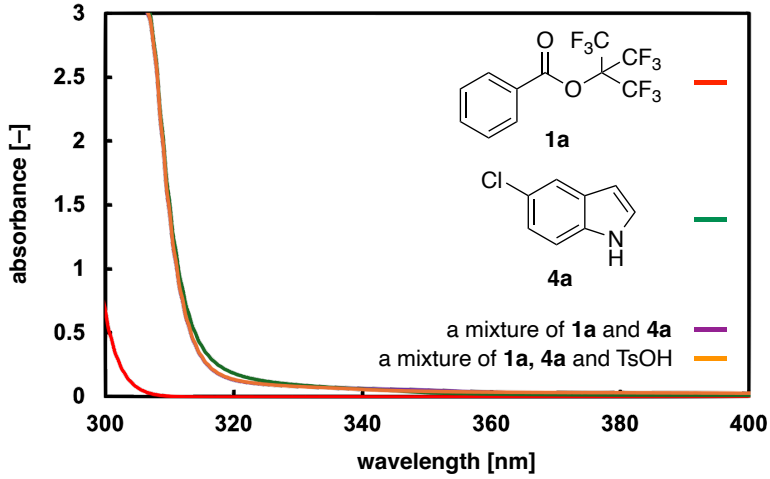


Figure S5. UV-Vis spectra for reaction mixture. Conditions: [**1a**] = 0.048 M, [**4a**] = 0.058 M, [TsOH•H_2O] =

Emission Quenching Experiments

Quenching experiments of BDB were performed in an acetonitrile solution at room temperature. Acetonitrile solutions of 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl benzoate (**1a**), 4-*tert*-butylstyrene (**2b**) or 5-chloro-1*H*-indole (**4a**) were added to the solutions of BDB (1.5×10^{-4} M). The solutions were degassed by N_2 bubbling (2 min) before the measurements (excitation wavelength = 322 or 350 nm). Intensities observed at 410 nm were plotted against concentration of each quencher. When **4a** was used as a quencher, increase of emission intesity was observed because **4a** is emissive. Thus, the quenching experiment using **4a** was not shown below.

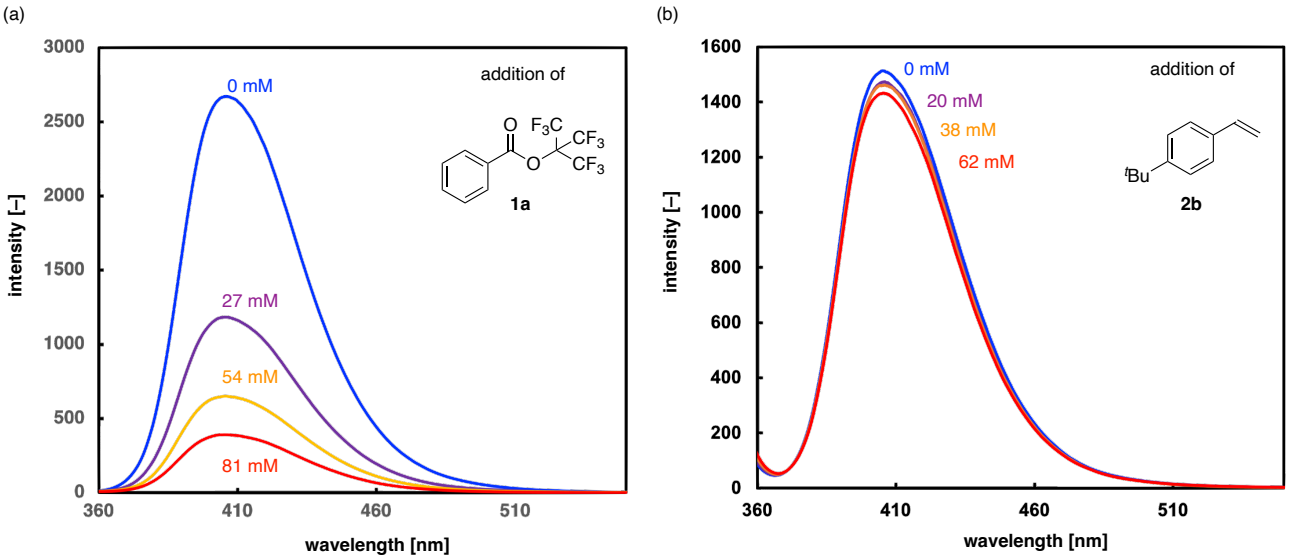


Figure S6. Emission Quenching Experiments. (a) **1a** was used as a quencher. The solution was excited at 322 nm. (b) **2b** was used as a quencher. The solution was excited at 350 nm.

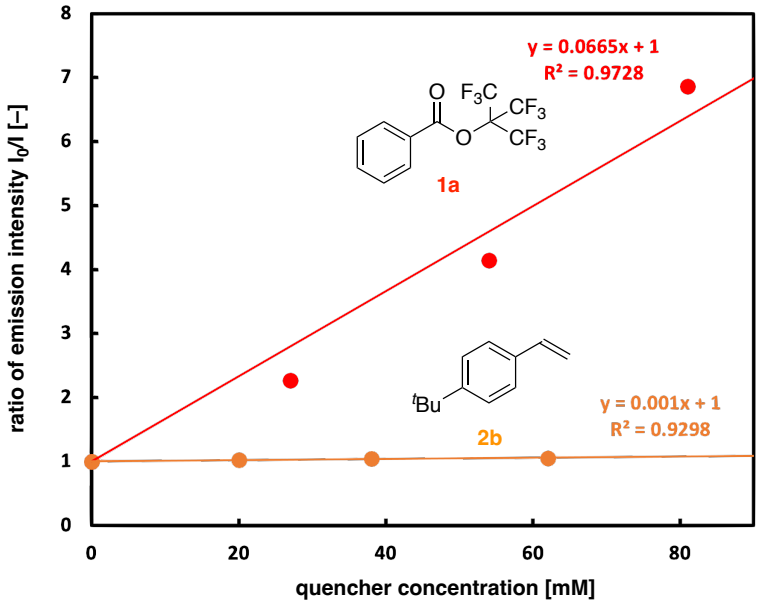


Figure S7. Stern-Volmer plots.

Determination of Quantum Yield[2]

-measurement of photon flux

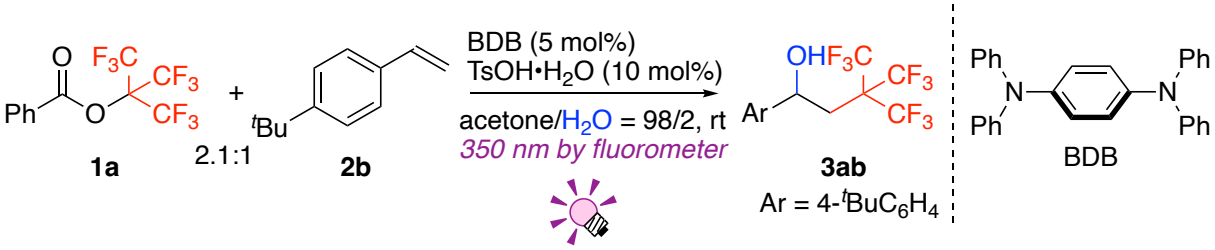
The light intensity of F-7100 (λ= 350 nm, slit width = 2.5 nm) was measured using Ophir StarLite power meter (photodiode sensor: PD300-UV SENSOR). Photon flux was calculated according to the equation below.

$$photon\ flux = \frac{power\ of\ light\ (\mathrm{W}) \times wavelength\ of\ irradiation\ light\ (\mathrm{m})}{Plank\ constant\ (\mathrm{J \cdot s}) \times speed\ of\ light\ (\mathrm{m/s}) \times Avogadro\ constant\ (1/mol)}$$

$$= \frac{121 \times 10^{-6} \times 350 \times 10^{-9}}{6{,}626 \times 10^{-34} \times 2.998 \times 10^{8} \times 6.02 \times 10^{23}} = 3.54 \times 10^{-10}$$

Calculated photon flux (N_{ph}/N_A: N_{ph} = the number of photons (s^{-1}), N_A = Avogadro constant (mol^{-1})): 3.54×10^{-10} einstein·s^{-1}

-measurement of quantum yield



A cuvette equipped with a sphere moiety for freeze was charged with a 5 mL solution of a mixture of BDB (0.0066 g, 16.0 μmol), TsOH•H_2O (0.0069 g, 36.3 μmol), **2b** (0.0497 g, 0.310 mmol), **1a** (0.1709 g, 0.502 mmol), hexadecane (0.0155 g) as an internal standard, acetone (6.2 mL), and H_2O (0.12 mL) under Ar. The solution was degassed by three freeze-pump-thaw cycles, and the mixture was irradiated by F-7100 (λ = 350 nm, slit width = 2.5 nm). A portion of the reaction mixture was diluted with acetone, and monitored by GC-MS. The yield was determined by MS spectrum. The quantum yields (Φ) were calculated by the following formula.

$$\Phi = \frac{mol\ of\ \boldsymbol{3ab} \times N_A}{N_{ph} \times reaction\ time\ (s)}$$

yield of **3ab** (16 h): 7.4 x 10^{-3}% yield (1.81 x 10^{-8} mol), Φ = 0.128%
yield of **3ab** (21.5 h): 1.1 x 10^{-2}% yield (2.81 x 10^{-8} mol), Φ = 0.133%
yield of **3ab** (26.5 h): 1.4 x 10^{-2}% yield (3.47 x 10^{-8} mol), Φ = 0.126%
average Φ = 0.129%

Transition State Analysis for Generation of Radicals

Quantum chemical calculations were performed by using Gaussian 16, Revision C.02 program package.[3] The geometry optimizations were carried out at the (U)B3LYP/6-31G(d) level of theory. SMD (acetone) was used as a solvent effect. The molecular geometries for the transition states were first estimated by Reaction plus software package,[4] based on the nudged elastic band (NEB) method [5], and were subsequently re-optimized using Gaussian 16, Revision C.02 program package. It was confirmed that the transition state had only one imaginary frequency. Gibbs free energies were calculated as a sum of the single-point electronic energy and thermal correction to the Gibbs free energy.

(1) Transition state analysis for generation of $\cdot C(CF_3)_3$ from [**1a**]$^{\cdot -}$

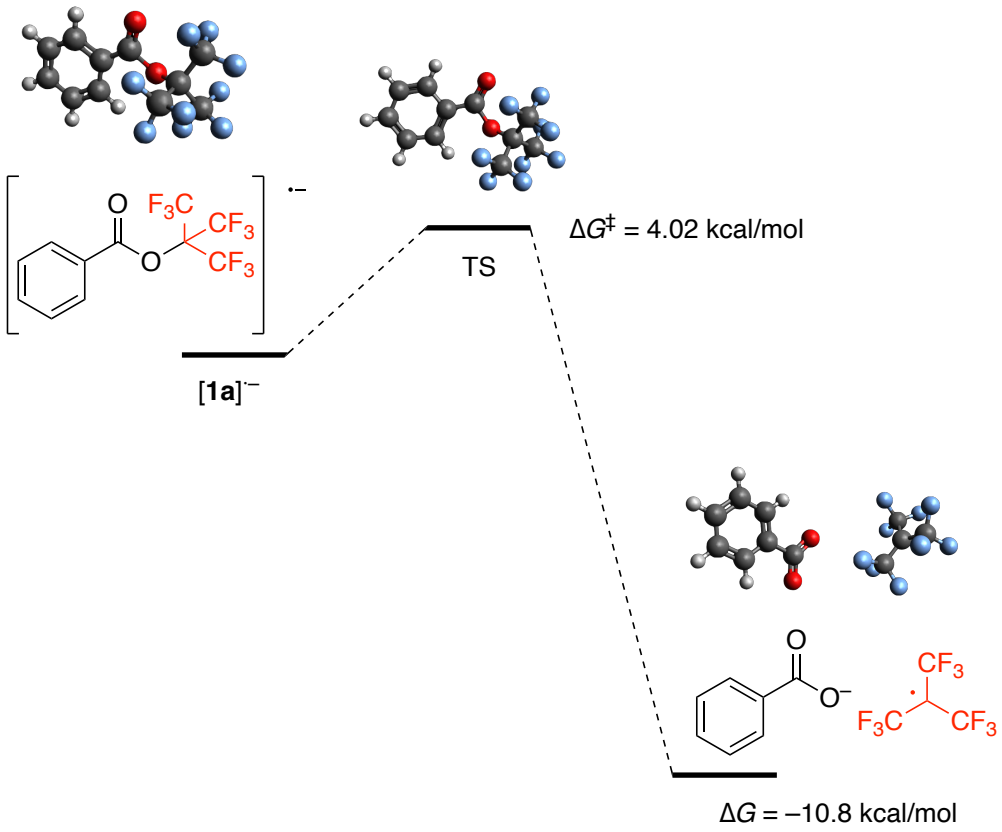


Table S1. Cartesian coordinates and electronic energies after geometry optimization of [**1a**]$^{\cdot -}$.

1	C	0	-4.507058	1.177137	-0.431348
2	C	0	-3.197859	0.762277	-0.710499
3	C	0	-2.684779	-0.407289	-0.127579
4	C	0	-3.470347	-1.114710	0.795577
5	C	0	-4.779613	-0.700855	1.075363
6	C	0	-5.301141	0.441387	0.455984
7	H	0	-4.899857	2.058286	-0.896327
8	H	0	-2.585842	1.339834	-1.372746

9	H	0	-3.067242	-1.976029	1.287957
10	H	0	-5.381208	-1.257879	1.764331
11	H	0	-6.304760	0.752768	0.662386
12	C	0	-1.214127	-0.798512	-0.348357
13	C	0	1.146807	0.043713	0.143883
14	C	0	1.935892	-1.251796	-0.220458
15	C	0	1.138739	1.005121	-1.063669
16	C	0	1.866334	0.691693	1.342842
17	O	0	-0.228883	-0.226093	0.542332
18	O	0	-0.953477	-1.584589	-1.279559
19	F	0	0.510071	0.429490	-2.108717
20	F	0	0.493762	2.142648	-0.729349
21	F	0	2.408098	1.298662	-1.417408
22	F	0	1.435920	-1.929705	-1.258020
23	F	0	3.202935	-0.906810	-0.537948
24	F	0	1.950260	-2.071760	0.852012
25	F	0	3.142150	0.976782	1.007080
26	F	0	1.230732	1.830394	1.690263
27	F	0	1.859483	-0.160869	2.388953

Sum of electronic and zero-point Energies= -1471.128301 hartree
Sum of electronic and thermal Energies= -1471.109032 hartree
Sum of electronic and thermal Enthalpies= -1471.108088 hartree
Sum of electronic and thermal Free Energies= -1471.178010 hartree

Table S2. Cartesian coordinates and electronic energies of [**1a**]$^{\cdot-}$ at the transition state.

1	C	0	-3.926009	-1.538700	-0.179224
2	C	0	-2.656945	-1.007759	-0.339208
3	C	0	-2.439722	0.414117	-0.319346
4	C	0	-3.607866	1.239189	-0.136292
5	C	0	-4.864687	0.684363	0.021423
6	C	0	-5.056351	-0.714271	0.006167
7	H	0	-4.049333	-2.621038	-0.199281
8	H	0	-1.811980	-1.670939	-0.484600
9	H	0	-3.476432	2.317545	-0.123485
10	H	0	-5.721436	1.343288	0.158938
11	H	0	-6.046590	-1.143949	0.131141
12	C	0	-1.186085	1.056067	-0.471240

13	C	0	1.086054	-0.045211	-0.093816
14	C	0	1.530321	1.171882	0.793862
15	C	0	0.949026	-1.312545	0.818043
16	C	0	2.170667	-0.296095	-1.191033
17	O	0	-0.102785	0.088127	-0.800604
18	O	0	-0.906216	2.263734	-0.477850
19	F	0	0.042058	-1.090964	1.786095
20	F	0	0.522869	-2.365474	0.097745
21	F	0	2.104108	-1.676616	1.407489
22	F	0	0.607379	1.480067	1.714889
23	F	0	2.663508	0.857024	1.467412
24	F	0	1.803533	2.261005	0.067791
25	F	0	1.851855	-1.370738	-1.931753
26	F	0	2.253897	0.755338	-2.020161
27	F	0	3.393833	-0.510312	-0.668517

Sum of electronic and zero-point Energies= -1471.124527 hartree
Sum of electronic and thermal Energies= -1471.106248 hartree
Sum of electronic and thermal Enthalpies= -1471.105304 hartree
Sum of electronic and thermal Free Energies= -1471.171596 hartree

Table S3. Cartesian coordinates and electronic energies after geometry optimization of the pair state of anion and $\cdot C(CF_3)_3$.

1	C	0	0.000000	0.000000	0.000000
2	C	0	-0.000000	1.540000	0.000000
3	C	0	-1.333679	-0.770000	0.000000
4	C	0	1.333679	-0.770000	0.000000
5	F	0	1.102270	1.990000	-0.636396
6	F	0	-0.000000	1.990000	1.272792
7	F	0	-1.102270	1.990000	-0.636396
8	F	0	1.172255	-1.949594	-0.636396
9	F	0	2.274526	-0.040406	-0.636396
10	F	0	1.723391	-0.995000	1.272792
11	F	0	-1.723391	-0.995000	1.272792
12	F	0	-2.274526	-0.040406	-0.636396
13	F	0	-1.172255	-1.949594	-0.636396

Sum of electronic and zero-point Energies= -1050.883819 hartree

Sum of electronic and thermal Energies= -1050.872937 hartree
Sum of electronic and thermal Enthalpies= -1050.871993 hartree
Sum of electronic and thermal Free Energies= -1050.923025 hartree

1	C	0	-1.815496	1.214951	-0.000001
2	C	0	-0.417364	1.202884	-0.000001
3	C	0	0.278771	-0.010742	0.000000
4	C	0	-0.434120	-1.214702	0.000001
5	C	0	-1.832320	-1.205921	0.000001
6	C	0	-2.525796	0.009259	-0.000000
7	H	0	-2.350743	2.159796	-0.000001
8	H	0	0.149789	2.126511	-0.000001
9	H	0	0.113846	-2.150212	-0.000001
10	H	0	-2.380623	-2.143218	0.000001
11	H	0	-3.611621	0.016374	0.000003
12	C	0	1.790167	-0.024119	0.000000
13	O	0	2.373309	-1.127280	-0.000002
14	O	0	2.353730	1.147416	0.000002

Sum of electronic and zero-point Energies= -420.240413 hartree
Sum of electronic and thermal Energies= -420.233531 hartree
Sum of electronic and thermal Enthalpies= -420.232586 hartree
Sum of electronic and thermal Free Energies= -420.272233 hartree

(2) Transition state analysis for generation of ·C(CF$_3$)$_3$ from H[**1a**]·

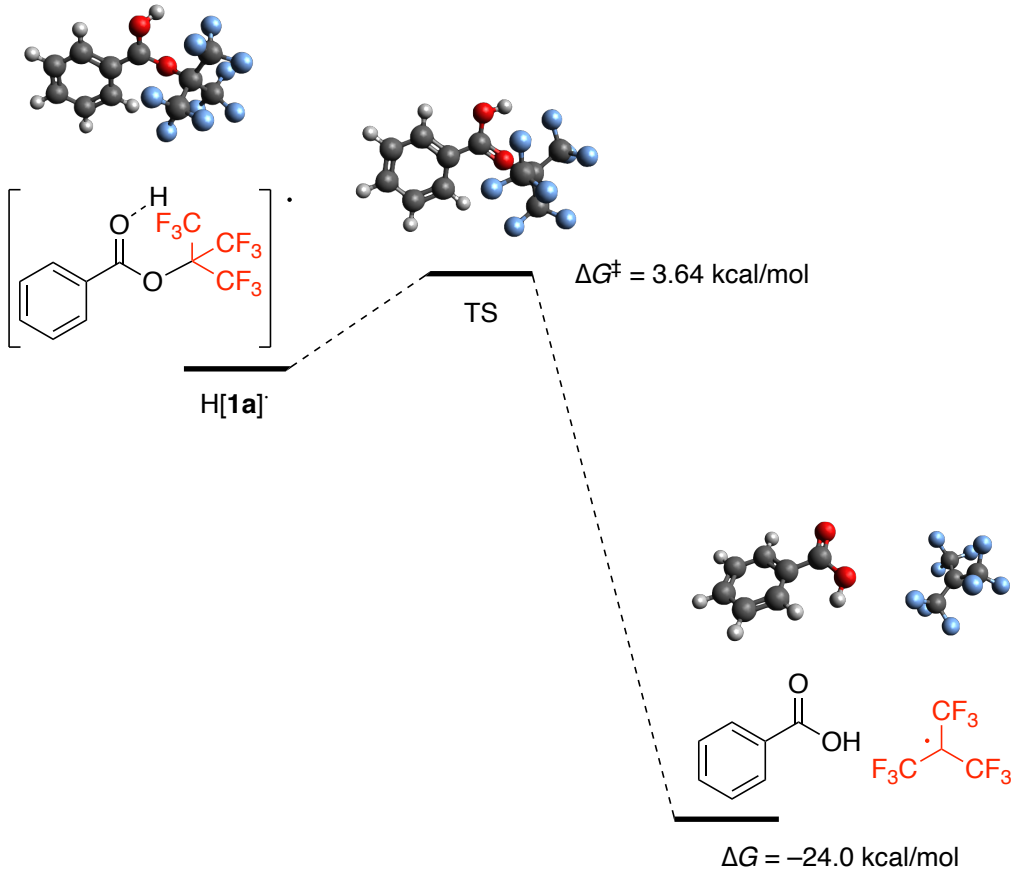


Table S4. Cartesian coordinates and electronic energies after geometry optimization of H[**1a**]·.

1	C	0	-3.878632	1.554072	0.201325
2	C	0	-2.607282	1.027407	0.377238
3	C	0	-2.402014	-0.382975	0.349301
4	C	0	-3.534137	-1.225010	0.142237
5	C	0	-4.795249	-0.674974	-0.033590
6	C	0	-4.983201	0.715096	-0.007783
7	H	0	-4.015092	2.632236	0.228315
8	H	0	-1.763446	1.687168	0.544268
9	H	0	-3.398415	-2.301132	0.124347
10	H	0	-5.645471	-1.333841	-0.191384
11	H	0	-5.974467	1.137365	-0.145590
12	C	0	-1.122570	-0.946745	0.528928
13	C	0	1.095081	0.060093	0.076926
14	C	0	1.997030	-1.220411	0.014460
15	C	0	0.741339	0.538759	-1.362982
16	C	0	1.849793	1.190890	0.850736
17	O	0	-0.053372	-0.146789	0.886777

18	O	0	-0.897613	-2.275394	0.430992
19	F	0	-0.105707	-0.310220	-1.960737
20	F	0	0.162218	1.748004	-1.331945
21	F	0	1.853250	0.620022	-2.113187
22	F	0	1.590143	-2.066447	-0.942285
23	F	0	3.274887	-0.898658	-0.236719
24	F	0	1.949449	-1.868428	1.191167
25	F	0	2.864810	1.686858	0.128758
26	F	0	1.016884	2.195487	1.146458
27	F	0	2.342039	0.704864	2.000580
28	H	0	-0.287944	-2.564879	1.138306

Sum of electronic and zero-point Energies= -1471.580686 hartree
Sum of electronic and thermal Energies= -1471.561168 hartree
Sum of electronic and thermal Enthalpies= -1471.560224 hartree
Sum of electronic and thermal Free Energies= -1471.629746 hartree

Table S5. Cartesian coordinates and electronic energies of H[**1a**]· at the transition state.

1	C	0	-3.833011	-1.565842	-0.199805
2	C	0	-2.582100	-1.008209	-0.433472
3	C	0	-2.409155	0.396210	-0.397362
4	C	0	-3.532384	1.214970	-0.125063
5	C	0	-4.778073	0.641934	0.104111
6	C	0	-4.938113	-0.748405	0.069488
7	H	0	-3.950124	-2.645866	-0.227841
8	H	0	-1.732641	-1.648774	-0.639649
9	H	0	-3.415821	2.292908	-0.098786
10	H	0	-5.630905	1.282510	0.312469
11	H	0	-5.913949	-1.190932	0.249052
12	C	0	-1.129928	0.987884	-0.675249
13	C	0	1.192790	-0.072408	-0.033758
14	C	0	0.830582	0.100121	1.443839
15	C	0	1.488566	-1.531616	-0.404186
16	C	0	2.298427	0.884991	-0.493274
17	O	0	-0.076480	0.286766	-1.043692
18	O	0	-0.998791	2.320631	-0.512639
19	F	0	0.565733	-2.361373	0.114380
20	F	0	1.502803	-1.709835	-1.730015

21	F	0	2.692455	-1.909154	0.077579
22	F	0	-0.326495	-0.512707	1.735686
23	F	0	1.786574	-0.421240	2.238824
24	F	0	0.696148	1.400014	1.757003
25	F	0	3.384685	0.787525	0.296438
26	F	0	2.670866	0.626856	-1.752657
27	F	0	1.886888	2.172460	-0.448625
28	H	0	-0.136926	2.600287	-0.873737

Sum of electronic and zero-point Energies= -1471.574235 hartree
Sum of electronic and thermal Energies= -1471.554865 hartree
Sum of electronic and thermal Enthalpies= -1471.553921 hartree
Sum of electronic and thermal Free Energies= -1471.623947 hartree

Table S6. Cartesian coordinates and electronic energies after geometry optimization of the pair state of benzoic acid and $\cdot C(CF_3)_3$.

1	C	0	0.000000	0.000000	0.000000
2	C	0	-0.000000	1.540000	0.000000
3	C	0	-1.333679	-0.770000	0.000000
4	C	0	1.333679	-0.770000	0.000000
5	F	0	1.102270	1.990000	-0.636396
6	F	0	-0.000000	1.990000	1.272792
7	F	0	-1.102270	1.990000	-0.636396
8	F	0	1.172255	-1.949594	-0.636396
9	F	0	2.274526	-0.040406	-0.636396
10	F	0	1.723391	-0.995000	1.272792
11	F	0	-1.723391	-0.995000	1.272792
12	F	0	-2.274526	-0.040406	-0.636396
13	F	0	-1.172255	-1.949594	-0.636396

Sum of electronic and zero-point Energies= -1050.883819 hartree
Sum of electronic and thermal Energies= -1050.872937 hartree
Sum of electronic and thermal Enthalpies= -1050.871993 hartree
Sum of electronic and thermal Free Energies= -1050.923025 hartree

1	C	0	-2.563090	0.026966	0.009930
2	C	0	-1.884827	-1.190084	0.129569
3	C	0	-0.492680	-1.215953	0.113103

4	C	0	0.236081	-0.022655	-0.006204
5	C	0	-0.449760	1.195608	-0.131279
6	C	0	-1.844718	1.217082	-0.125703
7	H	0	-3.649524	0.046846	0.017537
8	H	0	-2.441529	-2.117269	0.232919
9	H	0	0.045870	-2.154116	0.198284
10	H	0	0.085540	2.132650	-0.266246
11	H	0	-2.368377	2.162620	-0.233264
12	C	0	1.728095	-0.119804	-0.028622
13	H	0	1.847368	1.715494	0.561951
14	O	0	2.329027	-1.143686	-0.284941
15	O	0	2.434229	1.002037	0.250448

Sum of electronic and zero-point Energies= -420.712618 hartree
Sum of electronic and thermal Energies= -420.705401 hartree
Sum of electronic and thermal Enthalpies= -420.704457 hartree
Sum of electronic and thermal Free Energies= -420.744926 hartree

Crystallographic Data of 5aa

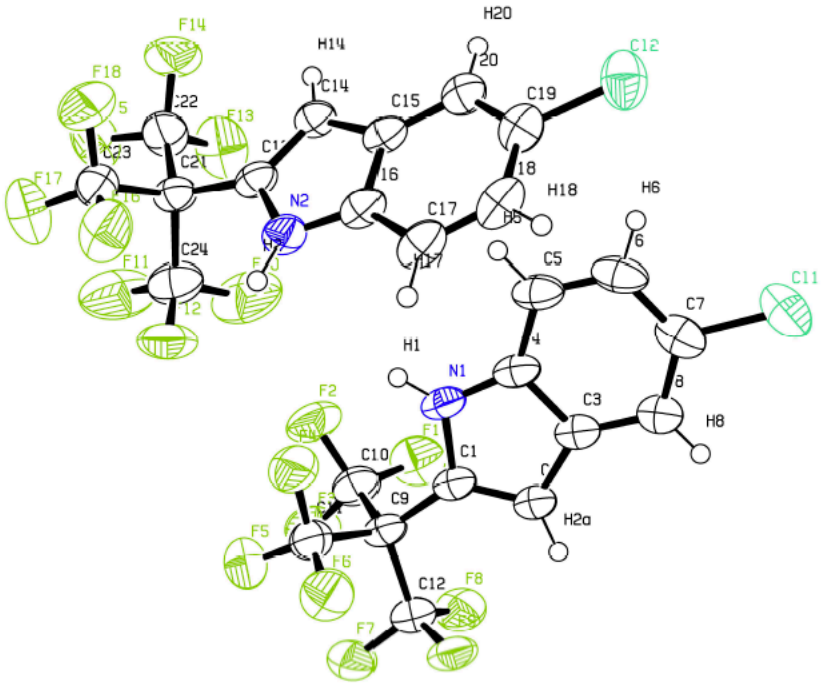


Figure S8. An ORTEP Drawing of **5aa**.

Table S7. Crystal Data and Structure Refinement for **5aa**.

Empirical formula	$C_{12}H_5ClF_9N$
Formula weight	369.62
Temperature/K	223
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.5848(3)
b/Å	7.2834(2)
c/Å	32.0201(8)
α/°	90
β/°	96.310(2)
γ/°	90
Volume/Å^3	2685.38(12)
Z	8
ρ_{calc}g/cm^3	1.828
μ/mm^{-1}	3.568
F(000)	1456.0
Crystal size/mm^3	0.185 × 0.145 × 0.018
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.7 to 146.518
Index ranges	-10 ≤ h ≤ 14, -8 ≤ k ≤ 8, -32 ≤ l ≤ 39
Reflections collected	14724
Independent reflections	5223 [R_{int} = 0.0446, R_{sigma} = 0.0502]
Data/restraints/parameters	5223/0/415
Goodness-of-fit on F^2	1.110
Final R indexes [I>=2σ (I)]	R_1 = 0.0751, wR_2 = 0.2268
Final R indexes [all data]	R_1 = 0.0832, wR_2 = 0.2333
Largest diff. peak/hole / e Å^{-3}	0.77/-0.69

Table S8. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5aa.** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Cl2	6183.3(12)	5297.4(17)	1765.9(4)	64.0(4)
Cl1	3149.4(14)	10303.7(18)	1732.2(4)	71.0(4)
F9	1127(2)	9803(4)	4008.1(9)	65.0(8)
F7	1847(2)	10483(5)	4632.9(9)	67.7(8)
F8	1979(3)	12380(4)	4133.7(10)	69.9(8)
F2	5204(2)	10126(5)	4366.2(10)	75.3(9)
F5	3502(3)	7957(5)	4768.2(9)	74.0(8)
F3	4043(3)	11584(5)	4722.0(9)	78.1(9)
F4	4151(3)	6858(4)	4222.7(10)	75.2(9)
F1	4301(3)	12488(4)	4101.0(10)	75.5(9)
F6	2339(3)	6869(4)	4265.1(10)	74.2(8)
F12	6286(2)	4688(5)	4435.4(10)	75.6(9)
F14	10015(2)	5287(6)	3969.6(10)	83.7(11)
F16	7427(3)	1735(4)	4238.3(11)	79.8(9)
F13	9049(3)	7652(5)	4116.5(10)	83.1(10)
F15	9744(3)	5830(6)	4603.1(9)	89.6(12)
F17	8561(3)	2804(5)	4739.0(9)	85.1(10)
F18	9208(3)	2074(5)	4164.6(11)	86.2(10)
N1	4248(3)	8938(5)	3522.2(11)	44.6(8)
N2	6543(3)	3984(5)	3569.6(11)	46.0(8)
F10	6800(3)	7265(5)	4209.7(15)	106.5(13)
F11	7627(3)	6160(7)	4792.4(12)	113.2(16)
C2	2532(3)	10303(5)	3343.8(13)	40.8(8)
C14	8078(3)	5397(5)	3346.2(12)	39.3(8)
C15	7254(3)	5025(5)	2989.6(13)	40.3(8)
C4	4139(3)	9101(5)	3097.1(14)	42.8(9)
C8	2753(4)	10348(5)	2546.5(13)	44.6(9)
C1	3257(3)	9645(5)	3674.2(13)	40.2(8)
C3	3066(3)	9976(5)	2968.3(13)	40.1(8)

C13	7624(3)	4733(5)	3693.9(13)	41.7(8)
C16	6309(3)	4131(5)	3145.8(13)	42.9(9)
C20	7234(3)	5382(5)	2562.5(13)	43.9(9)
C9	3189(3)	9758(5)	4140.6(13)	41.5(9)
C12	2012(3)	10633(6)	4231.4(14)	49.2(10)
C19	6267(4)	4849(5)	2301.8(14)	46.9(9)
C21	8099(3)	4797(6)	4153.0(13)	43.5(9)
C7	3508(4)	9847(6)	2265.1(14)	51.9(10)
C18	5324(4)	3934(6)	2455.4(15)	52.3(10)
C5	4894(4)	8608(6)	2804.0(15)	52.2(10)
C17	5333(3)	3592(6)	2873.2(15)	50.6(10)
C6	4570(4)	8966(6)	2390.6(16)	55.5(11)
C23	8335(4)	2834(6)	4331.7(14)	51.9(10)
C11	3295(4)	7847(7)	4357.1(15)	53.5(10)
C10	4186(4)	11010(7)	4340.2(15)	54.4(11)
C22	9249(4)	5904(8)	4215.9(15)	59.5(12)
C24	7207(4)	5752(7)	4408.4(18)	64.1(13)

Table S9. Bond Lengths (Å) for **5aa**.

Cl2 – C19	1.739(5)	C2 – C1	1.364(6)
Cl1 – C7	1.743(5)	C2 – C3	1.431(5)
F9 – C12	1.329(5)	C14 – C15	1.431(6)
F7 – C12	1.325(5)	C14 – C13	1.371(6)
F8 – C12	1.310(5)	C15 – C16	1.412(5)
F2 – C10	1.338(5)	C15 – C20	1.390(6)
F5 – C11	1.314(5)	C4 – C3	1.418(5)
F3 – C10	1.320(5)	C4 – C5	1.398(5)
F4 – C11	1.335(5)	C8 – C3	1.386(6)
F1 – C10	1.336(6)	C8 – C7	1.372(6)
F6 – C11	1.322(5)	C1 – C9	1.507(6)
F12 – C24	1.329(6)	C13 – C21	1.513(6)
F14 – C22	1.329(6)	C16 – C17	1.406(5)

F16 – C23	1.330(5)	C20 – C19	1.377(6)
F13 – C22	1.327(6)	C9 – C12	1.561(5)
F15 – C22	1.309(5)	C9 – C11	1.554(6)
F17 – C23	1.302(5)	C9 – C10	1.553(5)
F18 – C23	1.317(5)	C19 – C18	1.414(6)
N1 – C4	1.358(5)	C21 – C23	1.553(6)
N1 – C1	1.394(5)	C21 – C22	1.551(6)
N2 – C13	1.384(5)	C21 – C24	1.551(6)
N2 – C16	1.358(5)	C7 – C6	1.406(7)
F10 – C24	1.332(7)	C18 – C17	1.359(6)
F11 – C24	1.306(6)	C5 – C6	1.361(7)

Table S10. Bond Angles (°) for **5aa**.

C4 – N1 – C1	109.1(3)	C13 – C21 – C24	109.5(3)
C16 – N2 – C13	109.3(3)	C22 – C21 – C23	108.5(3)
C1 – C2 – C3	107.9(3)	C24 – C21 – C23	108.6(4)
C13 – C14 – C15	107.4(3)	C24 – C21 – C22	108.1(4)
C16 – C15 – C14	106.3(3)	C8 – C7 – Cl1	119.4(4)
C20 – C15 – C14	133.4(4)	C8 – C7 – C6	122.3(4)
C20 – C15 – C16	120.3(4)	C6 – C7 – Cl1	118.3(3)
N1 – C4 – C3	108.2(3)	C17 – C18 – C19	120.4(4)
N1 – C4 – C5	130.8(4)	C6 – C5 – C4	118.6(4)
C5 – C4 – C3	120.9(4)	C18 – C17 – C16	118.6(4)
C7 – C8 – C3	118.1(4)	C5 – C6 – C7	120.3(4)
N1 – C1 – C9	120.1(3)	F16 – C23 – C21	111.6(3)
C2 – C1 – N1	108.7(3)	F17 – C23 – F16	106.4(4)
C2 – C1 – C9	130.9(3)	F17 – C23 – F18	108.8(4)
C4 – C3 – C2	106.0(4)	F17 – C23 – C21	113.1(4)
C8 – C3 – C2	134.1(4)	F18 – C23 – F16	106.2(4)
C8 – C3 – C4	119.9(4)	F18 – C23 – C21	110.5(4)
N2 – C13 – C21	120.8(3)	F5 – C11 – F4	107.2(4)
C14 – C13 – N2	108.7(3)	F5 – C11 – F6	108.2(4)
C14 – C13 – C21	130.3(3)	F5 – C11 – C9	112.9(4)
N2 – C16 – C15	108.2(3)	F4 – C11 – C9	111.4(3)

N2 – C16 – C17	131.0(4)	F6 – C11 – F4	105.7(4)
C17 – C16 – C15	120.7(4)	F6 – C11 – C9	111.1(3)
C19 – C20 – C15	117.9(4)	F2 – C10 – C9	110.7(4)
C1 – C9 – C12	110.4(3)	F3 – C10 – F2	107.1(4)
C1 – C9 – C11	112.5(3)	F3 – C10 – F1	107.8(4)
C1 – C9 – C10	108.8(3)	F3 – C10 – C9	113.8(4)
C11 – C9 – C12	108.1(3)	F1 – C10 – F2	106.3(4)
C10 – C9 – C12	108.0(3)	F1 – C10 – C9	110.7(4)
C10 – C9 – C11	108.9(3)	F14 – C22 – C21	111.5(4)
F9 – C12 – C9	110.6(3)	F13 – C22 – F14	107.0(4)
F7 – C12 – F9	107.4(3)	F13 – C22 – C21	110.1(4)
F7 – C12 – C9	111.7(4)	F15 – C22 – F14	107.2(4)
F8 – C12 – F9	108.2(4)	F15 – C22 – F13	108.3(4)
F8 – C12 – F7	108.0(4)	F15 – C22 – C21	112.5(4)
F8 – C12 – C9	110.8(3)	F12 – C24 – F10	105.6(4)
C20 – C19 – Cl2	119.9(3)	F12 – C24 – C21	111.0(4)
C20 – C19 – C18	122.0(4)	F10 – C24 – C21	109.9(4)
C18 – C19 – Cl2	118.1(3)	F11 – C24 – F12	106.8(5)
C13 – C21 – C23	111.1(3)	F11 – C24 – F10	109.7(5)
C13 – C21 – C22	111.0(3)	F11 – C24 – C21	113.4(4)

Table S11. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **5aa**.

The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl2	83.4(8)	53.4(7)	52.5(6)	-3.1(5)	-4.8(5)	1.9(6)
Cl1	108.3(11)	54.1(7)	55.0(7)	4.8(5)	28.5(6)	9.7(6)
F9	28.2(11)	100(2)	67.7(16)	-3.8(14)	9.0(10)	-0.8(12)
F7	56.3(15)	93(2)	56.5(15)	-3.6(14)	18.9(12)	7.9(14)
F8	68.2(17)	60.0(18)	85.0(19)	-0.7(14)	24.8(14)	22.7(14)
F2	32.5(12)	100(2)	92(2)	-12.2(17)	-1.1(12)	-5.3(13)
F5	74.5(19)	85(2)	62.0(17)	17.5(15)	3.9(13)	1.7(16)
F3	61.5(17)	102(3)	69.9(18)	-29.1(17)	3.8(13)	-16.6(16)
F4	68.7(18)	65.1(19)	95(2)	22.5(16)	21.9(15)	24.0(15)
F1	70.1(18)	58.8(18)	97(2)	-4.3(15)	8.2(15)	-24.9(14)

F6	63.8(17)	60.1(18)	98(2)	13.6(15)	4.1(15)	-18.5(14)
F12	44.3(14)	106(3)	81(2)	-8.0(17)	26.0(13)	-4.5(14)
F14	31.6(12)	142(3)	79(2)	4.5(19)	9.9(12)	-16.2(15)
F16	72.7(19)	53.0(17)	110(2)	22.4(16)	-5.5(16)	-13.5(14)
F13	90(2)	70(2)	85(2)	5.9(16)	-7.7(16)	-39.1(17)
F15	67.0(18)	139(3)	58.6(17)	16.3(19)	-12.4(14)	-41(2)
F17	113(3)	83(2)	55.8(17)	17.2(15)	-2.4(16)	-13(2)
F18	76(2)	82(2)	104(2)	7.9(18)	23.4(17)	36.1(17)
N1	29.3(14)	41.1(18)	65(2)	1.9(15)	11.3(13)	5.2(13)
N2	30.8(15)	45.0(19)	62(2)	9.5(15)	4.4(13)	-11.3(13)
F10	90(3)	65(2)	169(4)	-5(2)	36(2)	28.5(19)
F11	80(2)	163(4)	98(3)	-74(3)	15.4(19)	5(2)
C2	32.3(17)	38(2)	54(2)	-1.0(16)	9.9(15)	-0.8(14)
C14	31.6(16)	33.2(19)	53(2)	2.4(15)	5.7(14)	-4.7(14)
C15	31.5(17)	32.4(19)	57(2)	0.6(15)	4.5(15)	2.5(14)
C4	33.2(17)	30.0(18)	68(3)	-0.4(17)	15.9(16)	-0.3(14)
C8	48(2)	30.4(18)	58(2)	-1.2(16)	15.2(17)	0.1(15)
C1	30.8(17)	32.3(18)	59(2)	-0.1(16)	9.9(15)	-0.3(14)
C3	36.7(18)	25.0(17)	60(2)	-2.0(15)	13.5(16)	-1.4(14)
C13	27.8(16)	38(2)	59(2)	3.4(16)	3.9(15)	-2.2(14)
C16	31.6(17)	30.3(18)	66(3)	5.6(17)	2.5(16)	-4.6(14)
C20	42(2)	33.3(19)	57(2)	-0.5(16)	6.1(16)	2.0(15)
C9	27.3(16)	39(2)	59(2)	-0.4(17)	7.0(15)	-1.3(14)
C12	38(2)	50(2)	61(3)	-4.9(19)	10.4(17)	2.8(17)
C19	53(2)	27.2(19)	59(2)	-2.6(16)	-0.8(18)	2.0(16)
C21	33.6(18)	44(2)	54(2)	0.8(17)	8.7(16)	-1.9(15)
C7	70(3)	31(2)	59(3)	-1.4(17)	25(2)	-5.9(18)
C18	45(2)	34(2)	74(3)	-2.9(19)	-11.8(19)	-0.5(17)
C5	45(2)	38(2)	77(3)	0(2)	25(2)	6.4(17)
C17	35.7(19)	36(2)	77(3)	3.1(19)	-4.4(18)	-7.8(16)
C6	62(3)	34(2)	77(3)	-4(2)	39(2)	2.2(19)
C23	48(2)	52(3)	56(2)	5.5(19)	5.4(18)	2.7(19)
C11	44(2)	55(3)	63(3)	9(2)	8.7(18)	1.9(19)
C10	38(2)	55(3)	70(3)	-5(2)	2.4(18)	-8.7(19)

C22	46(2)	73(3)	58(3)	5(2)	1.3(19)	-19(2)
C24	56(3)	52(3)	87(4)	-11(2)	18(2)	5(2)

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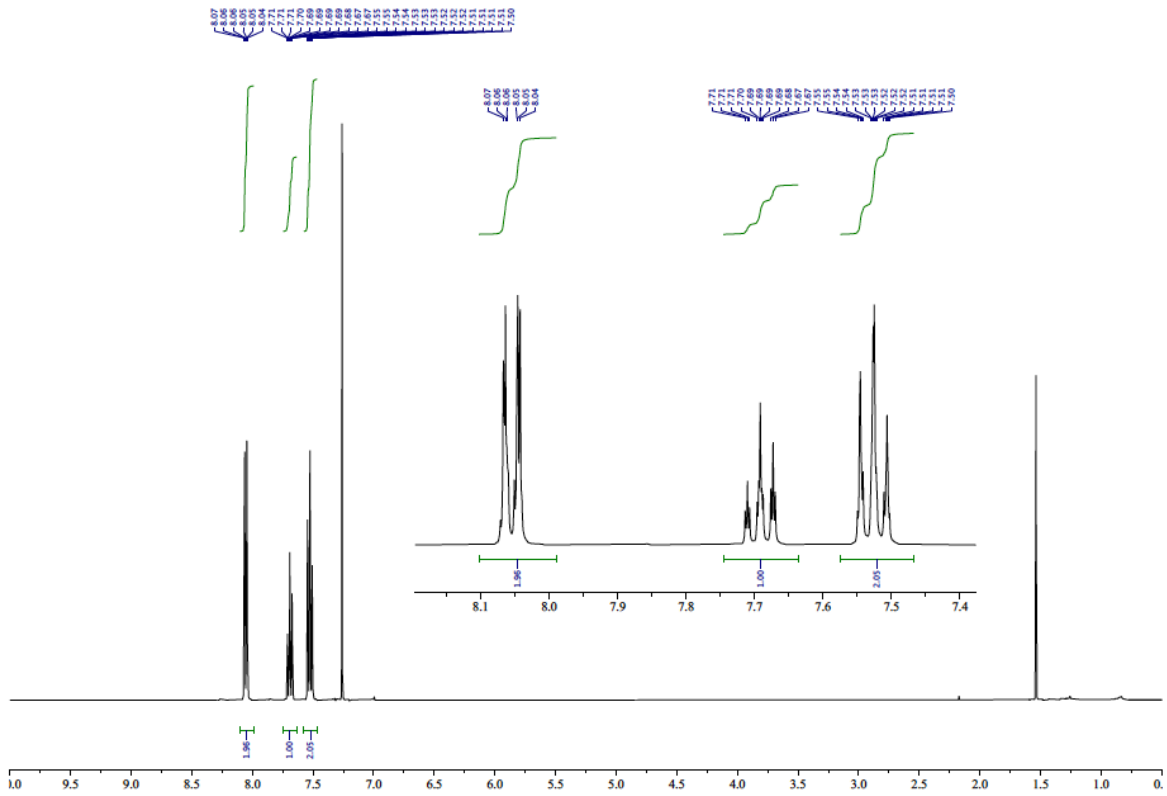
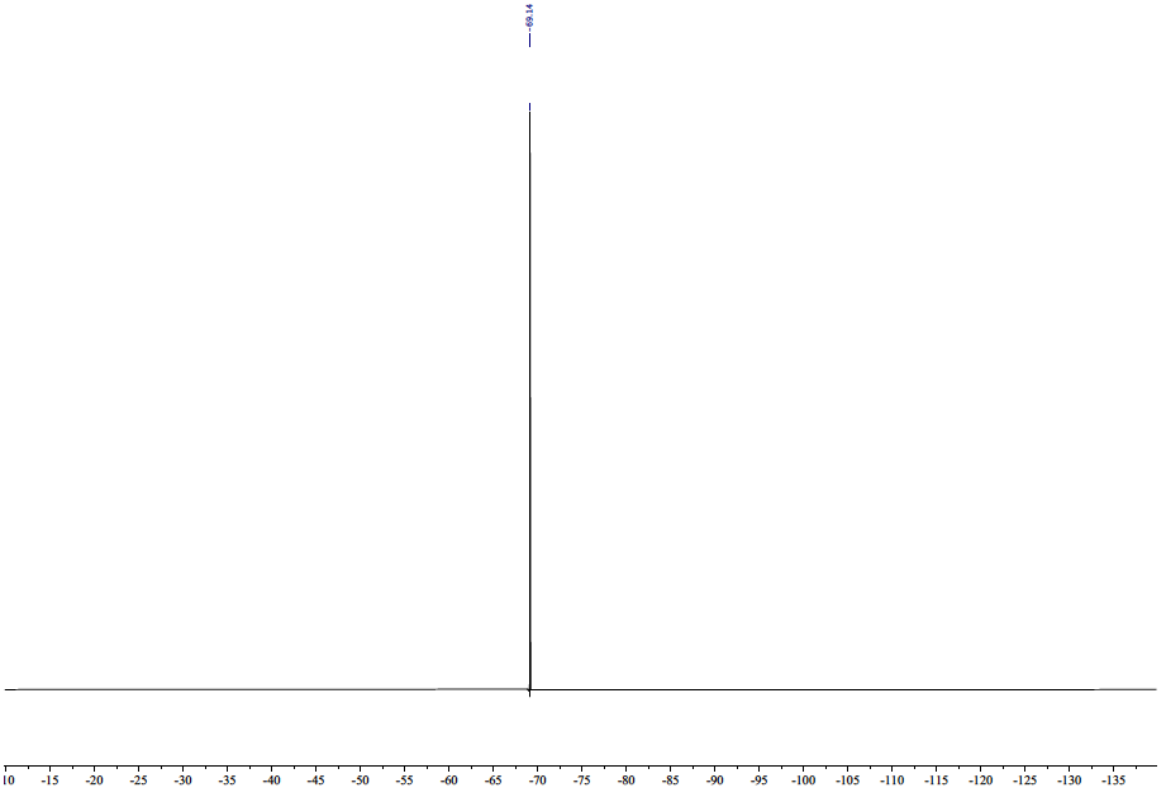
NMR spectra

1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl benzoate (**1a**)

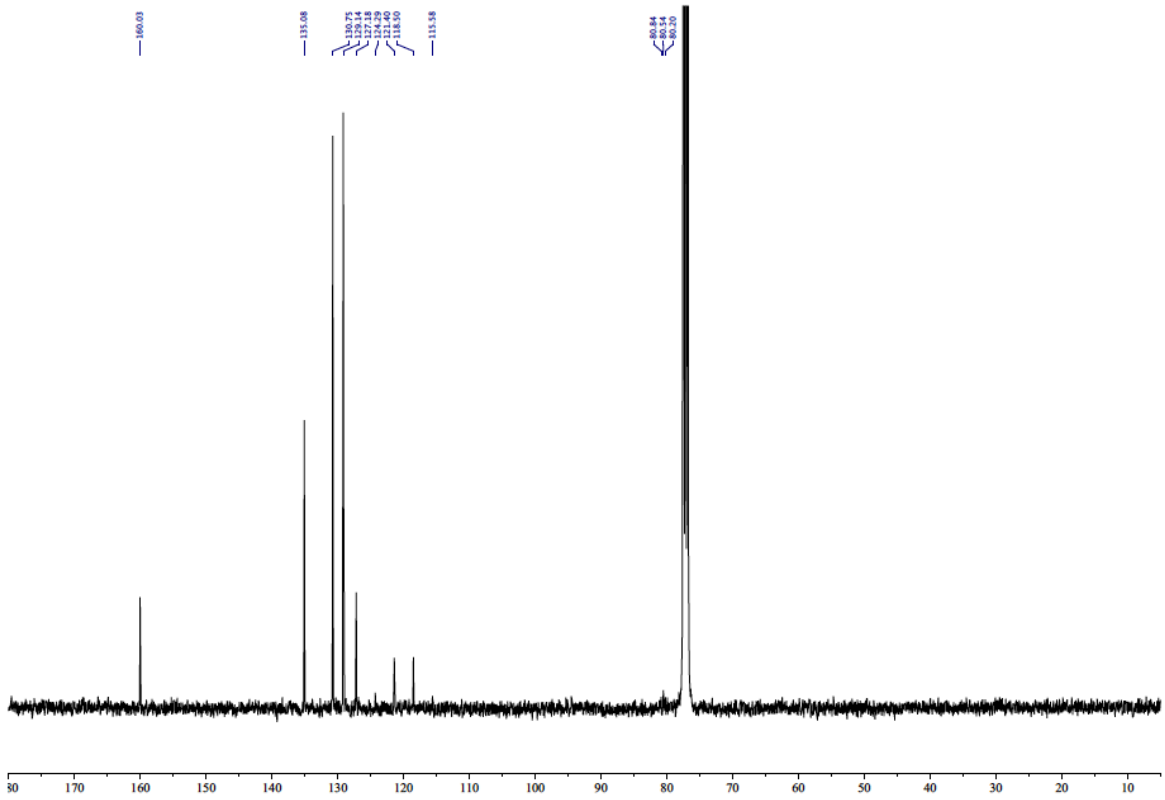
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

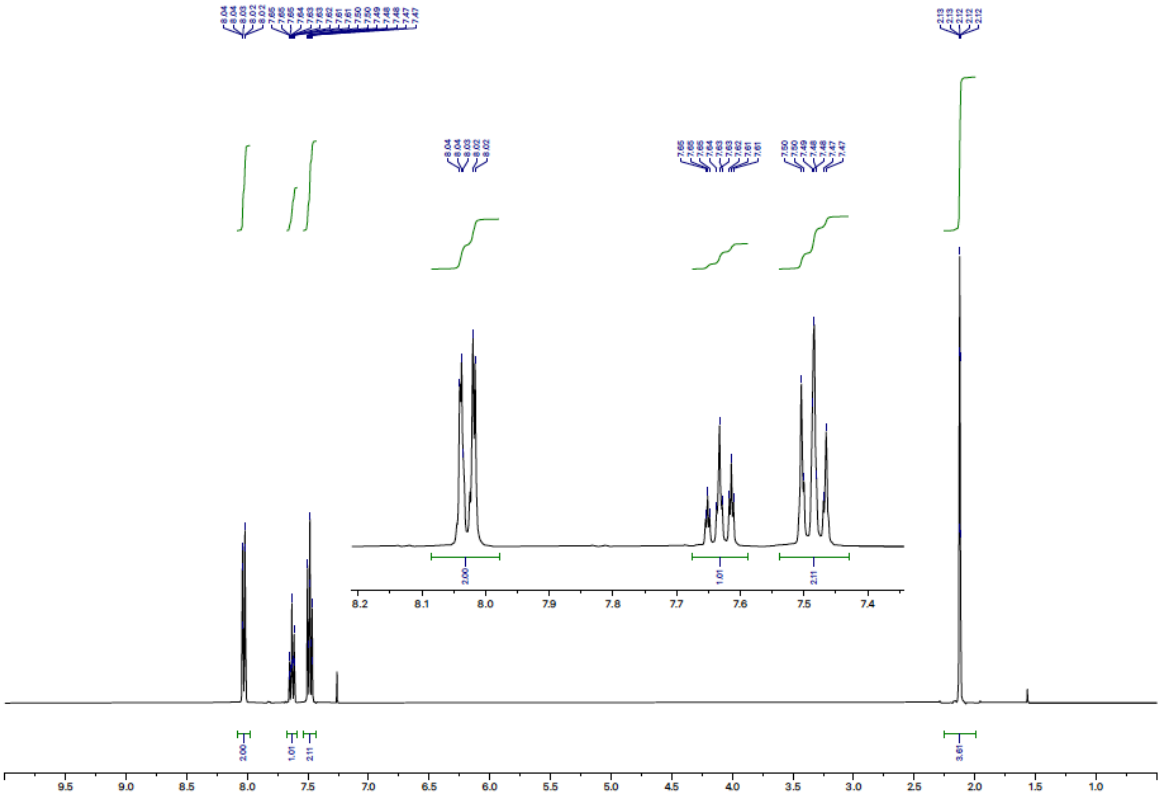


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



1,1,1,3,3,3-Hexafluoro-2-methylpropan-2-yl benzoate (**1b**)

^{1}H NMR (400 MHz, $CDCl_3$, rt)



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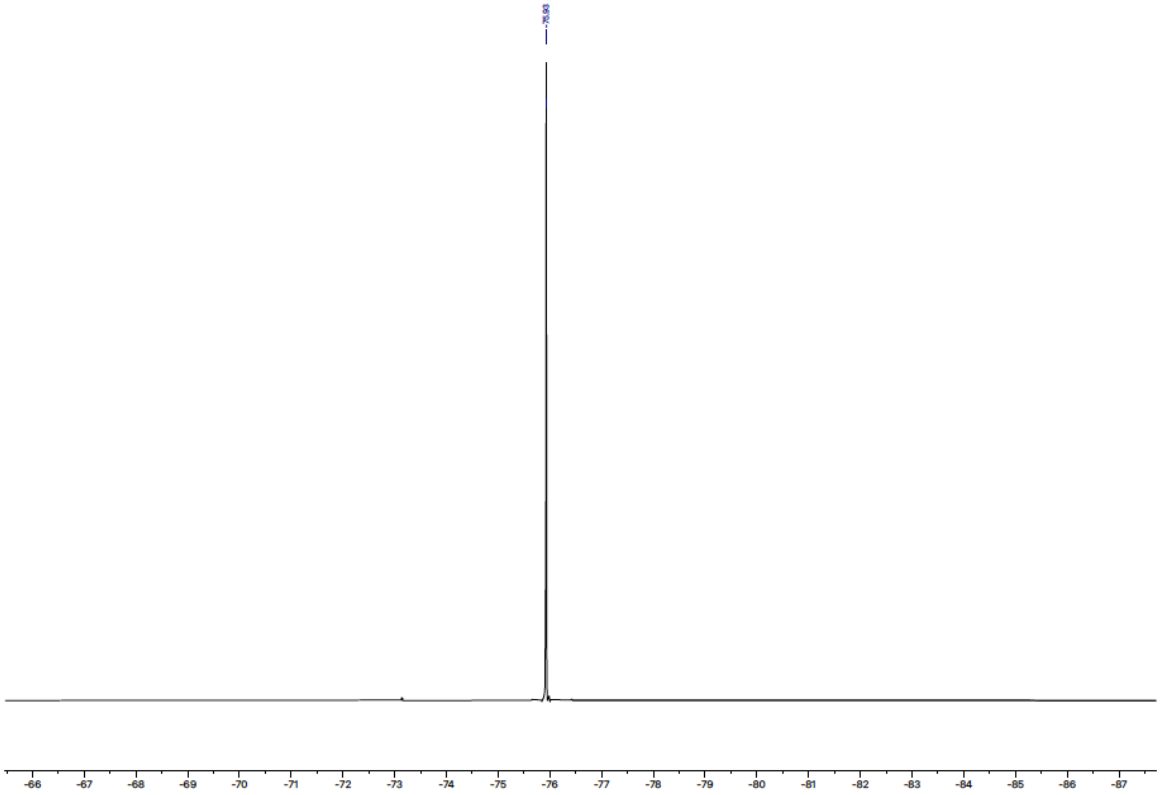
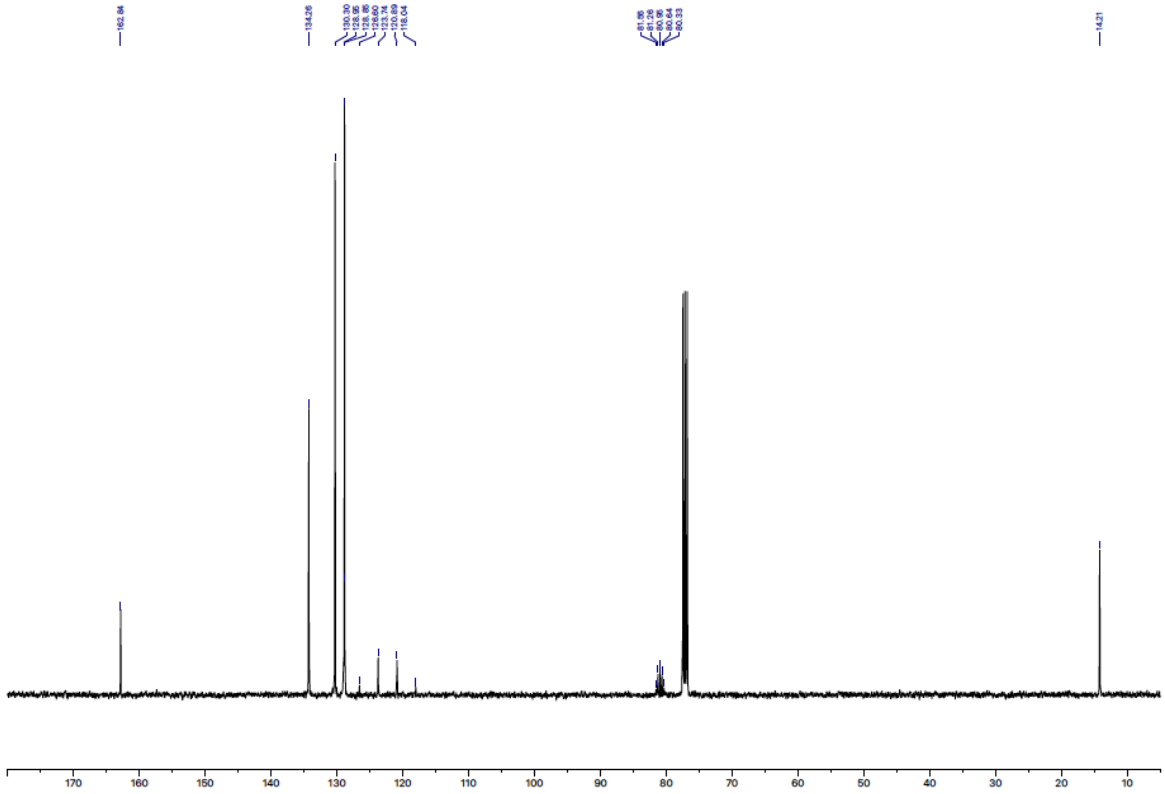


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



1,1,1,3,3,3-Hexafluoro-2-phenylpropan-2-yl benzoate (**1c**)

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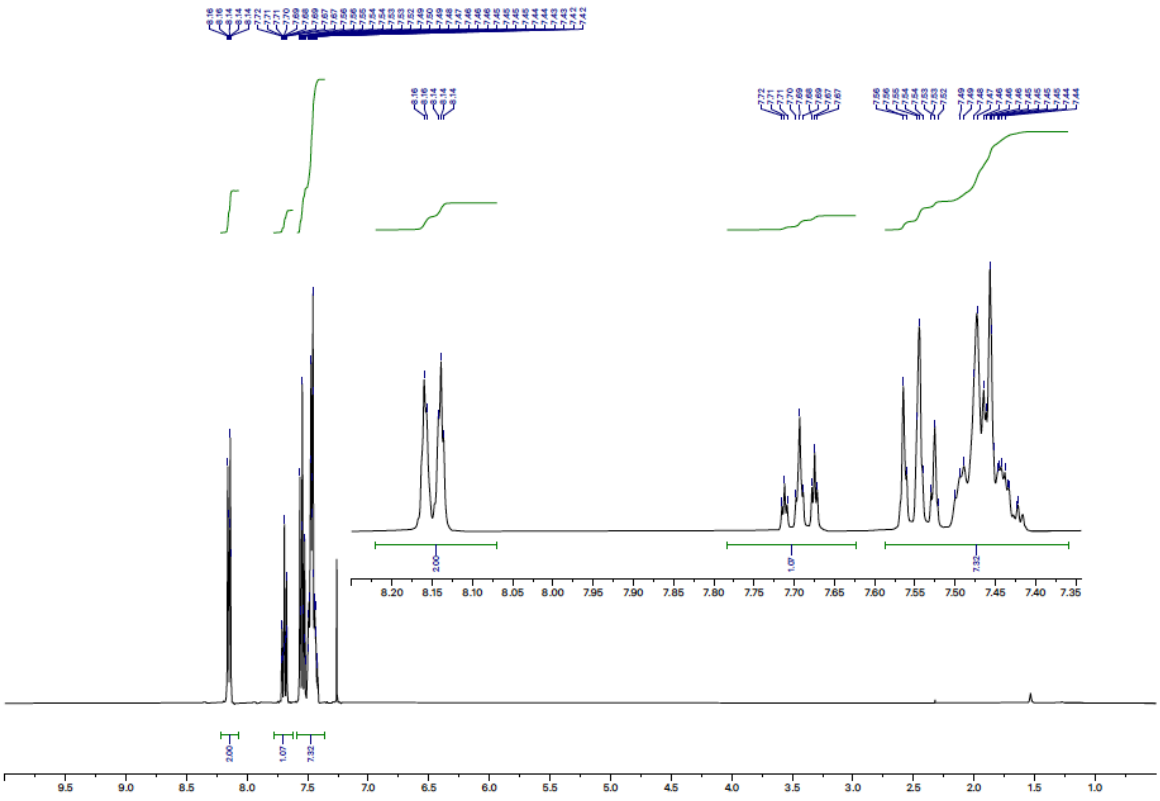
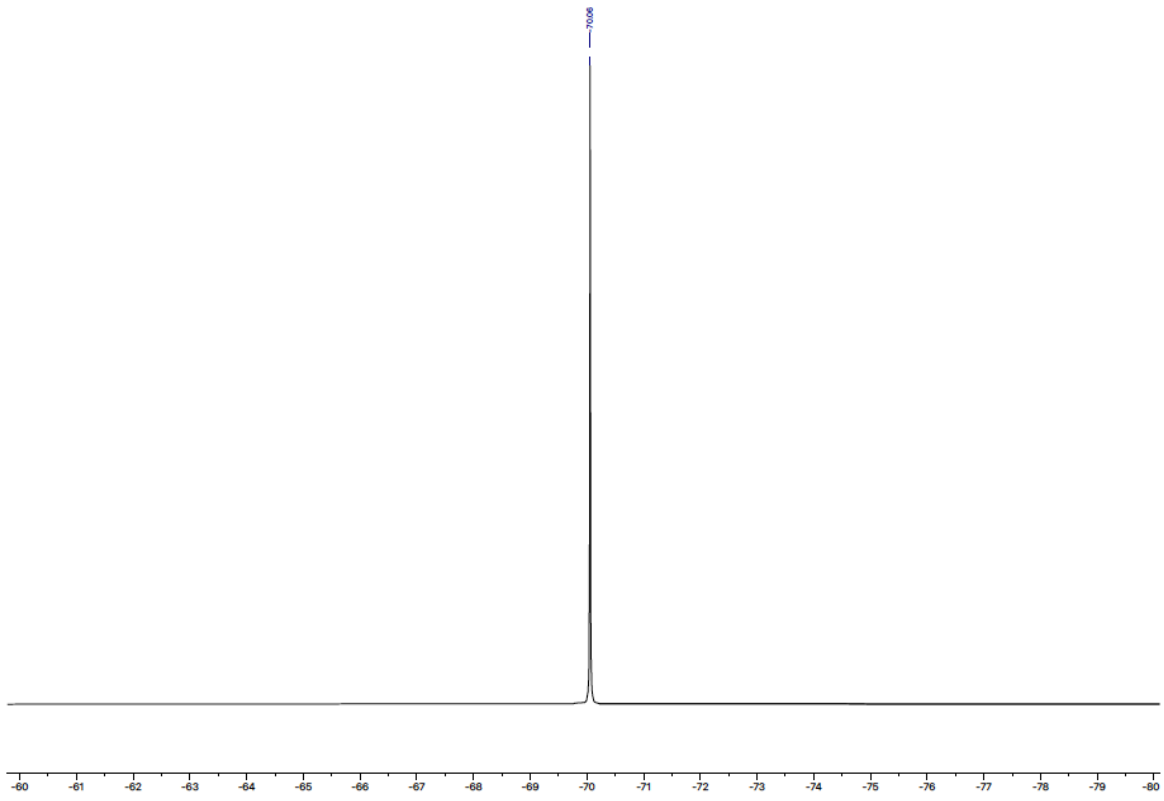
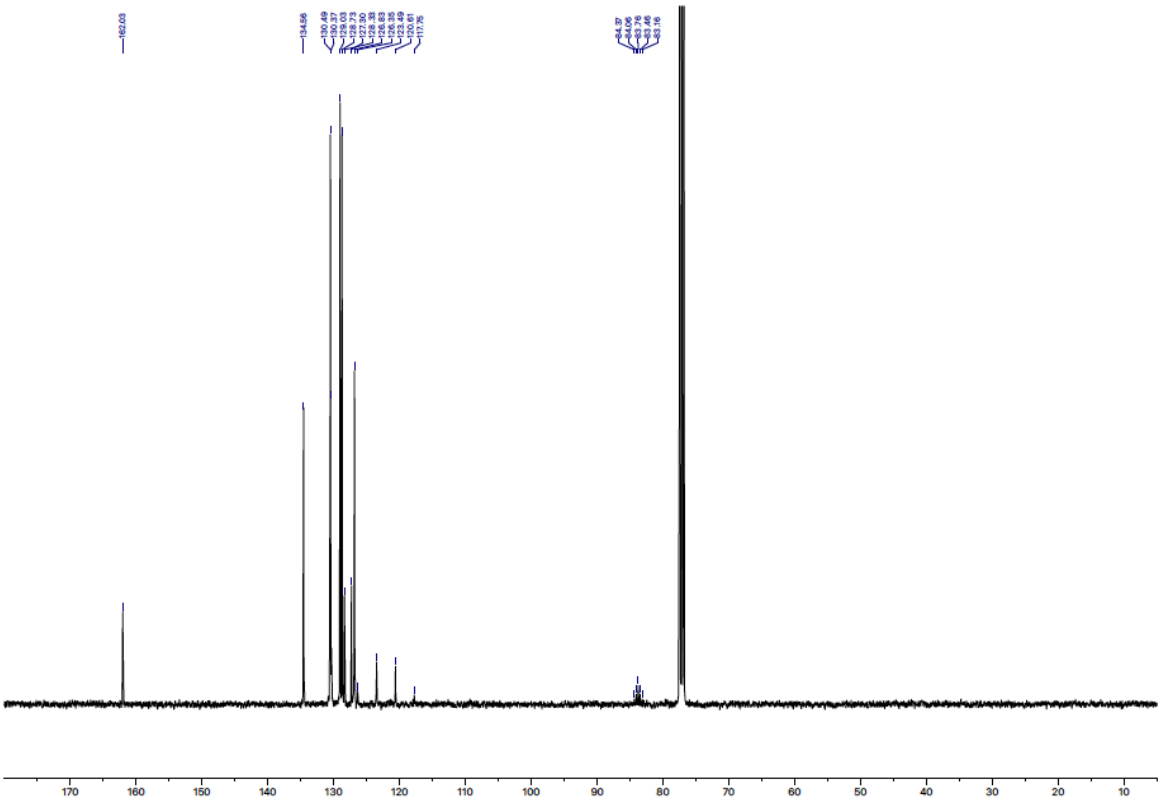


^{19}F NMR (376 MHz, $CDCl_3$, rt)

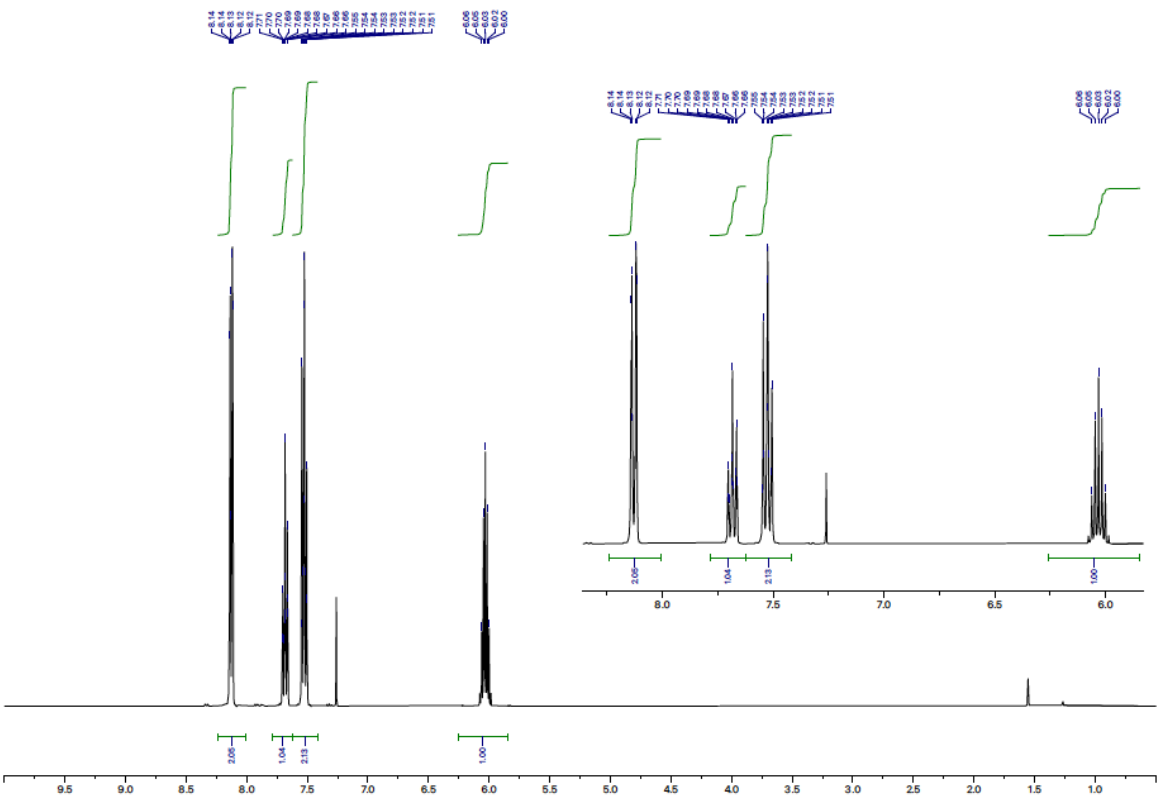


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)

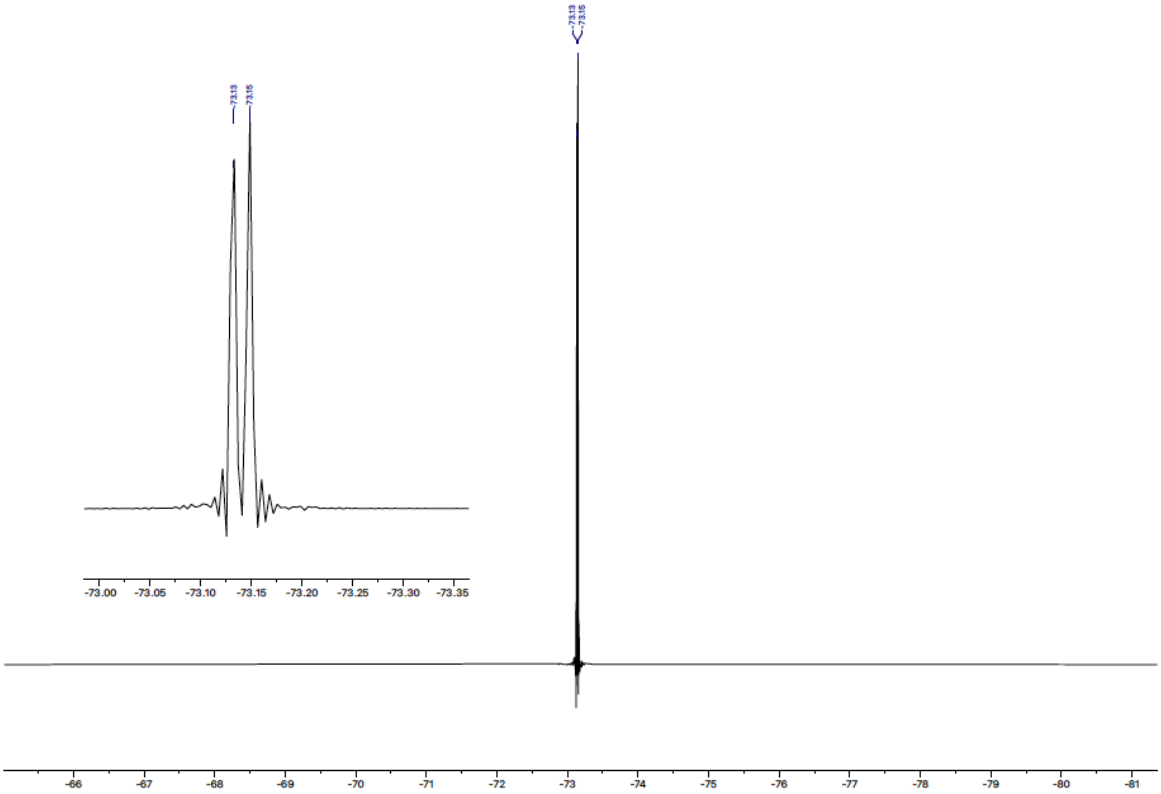


1,1,1,3,3,3-Hexafluoropropan-2-yl benzoate (**1d**)

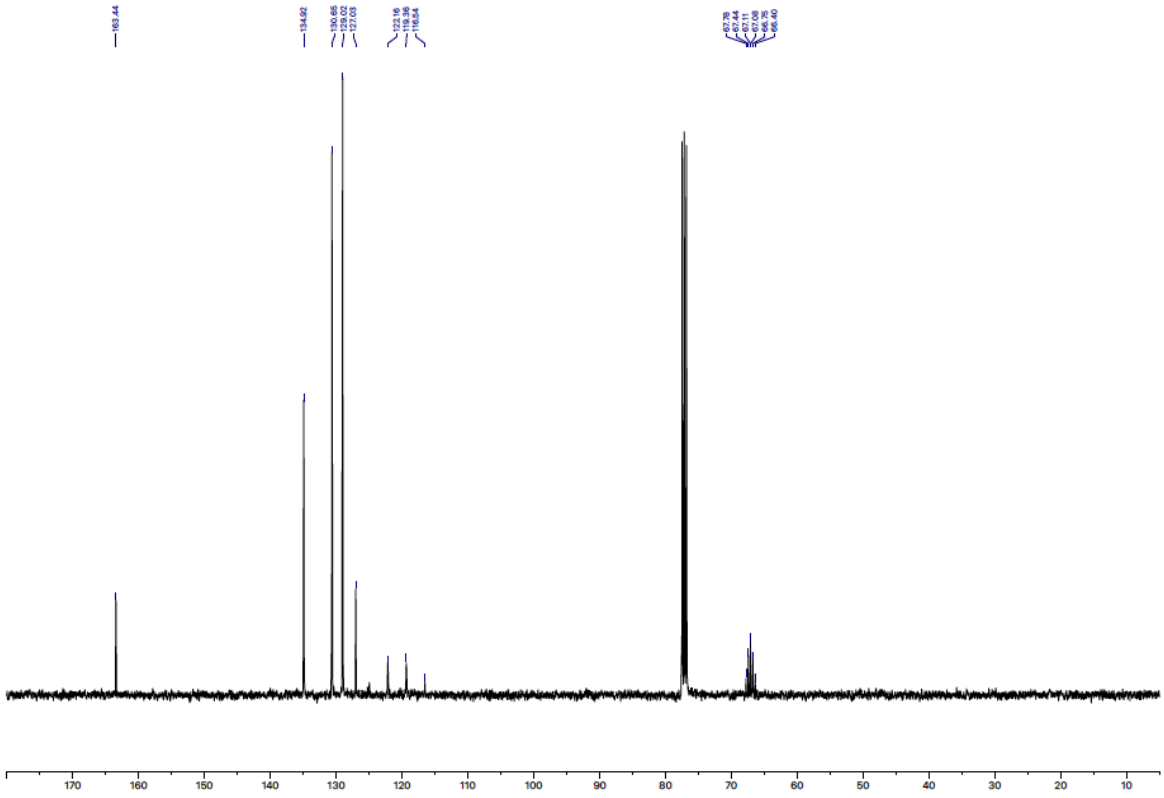
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

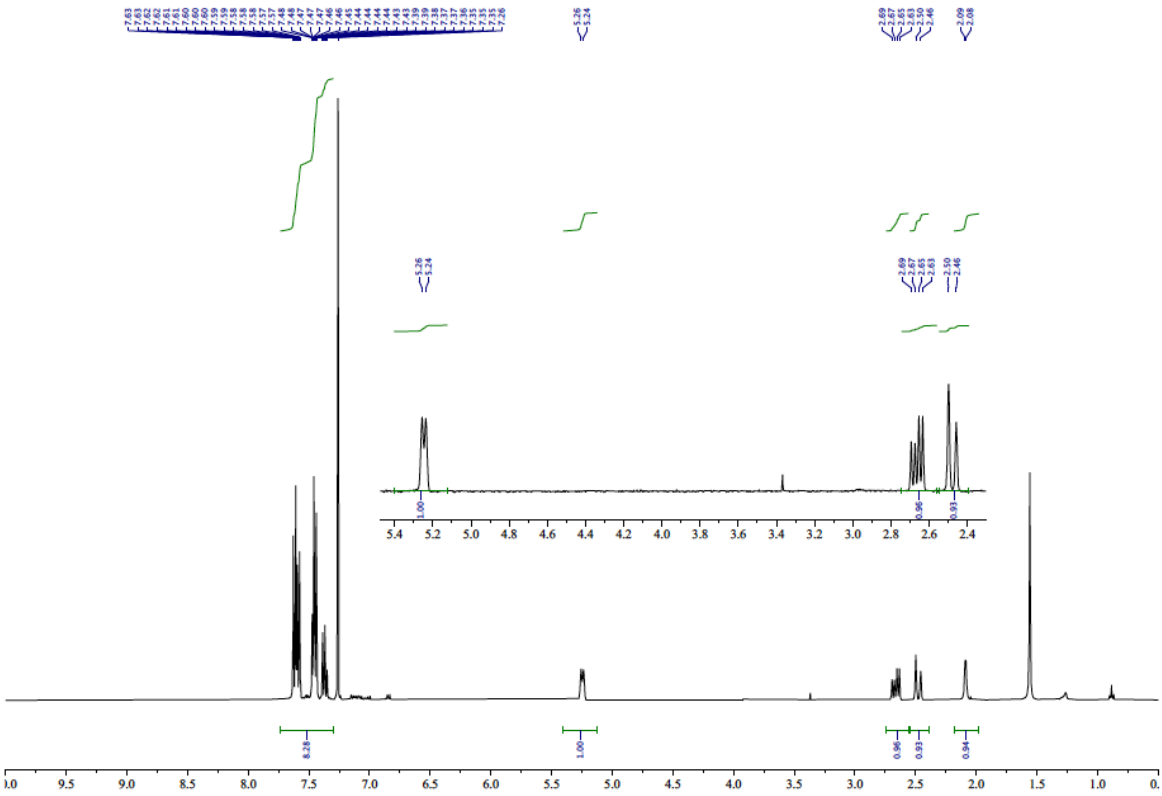


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)

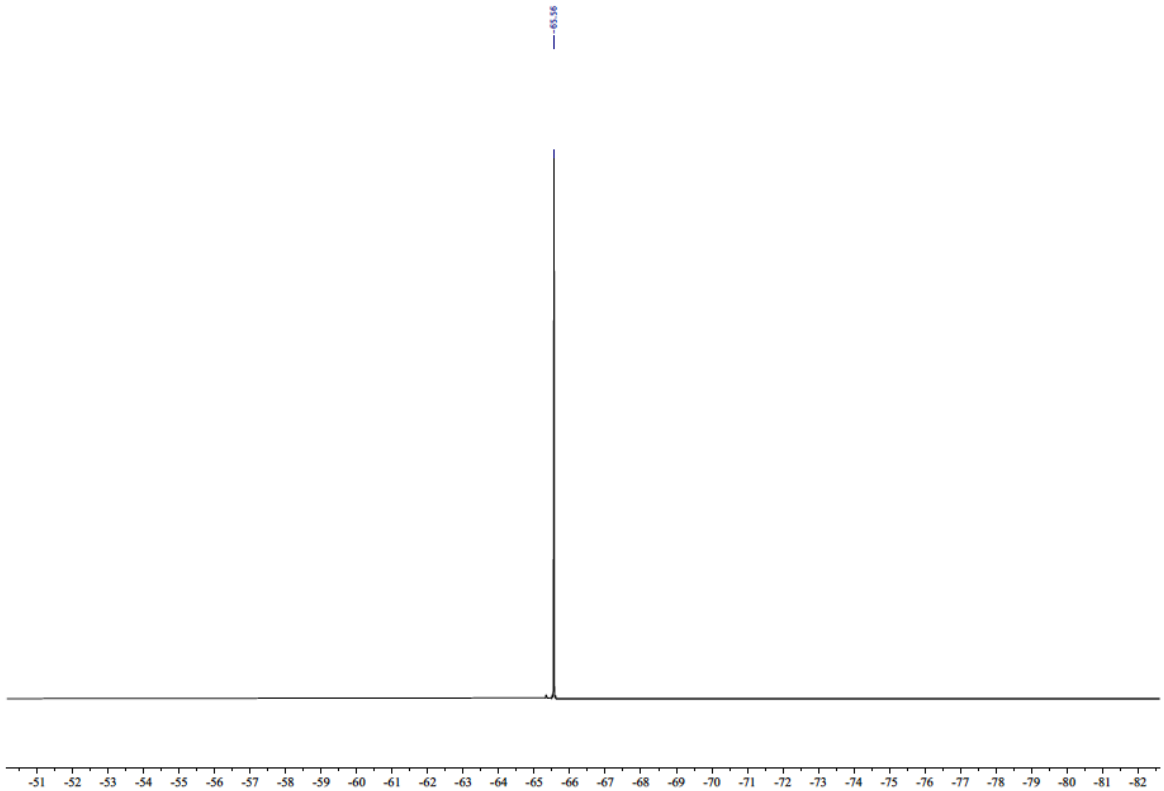


1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3aa**)

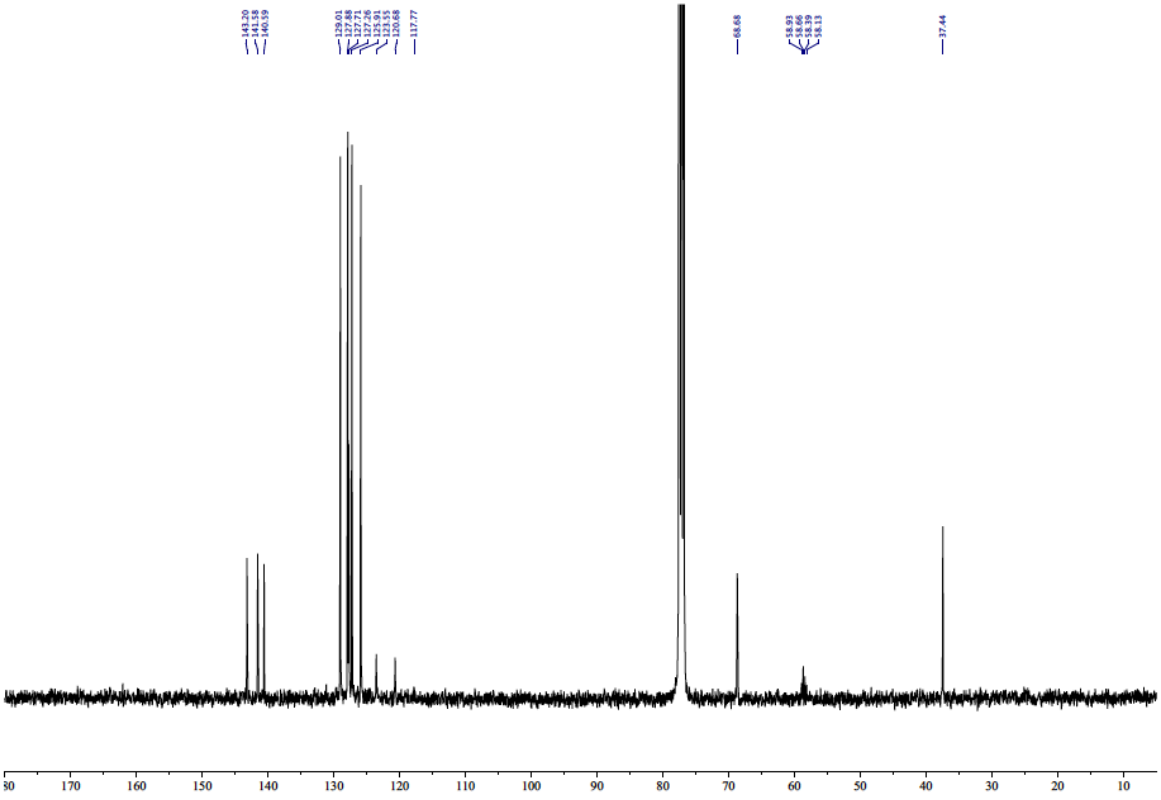
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

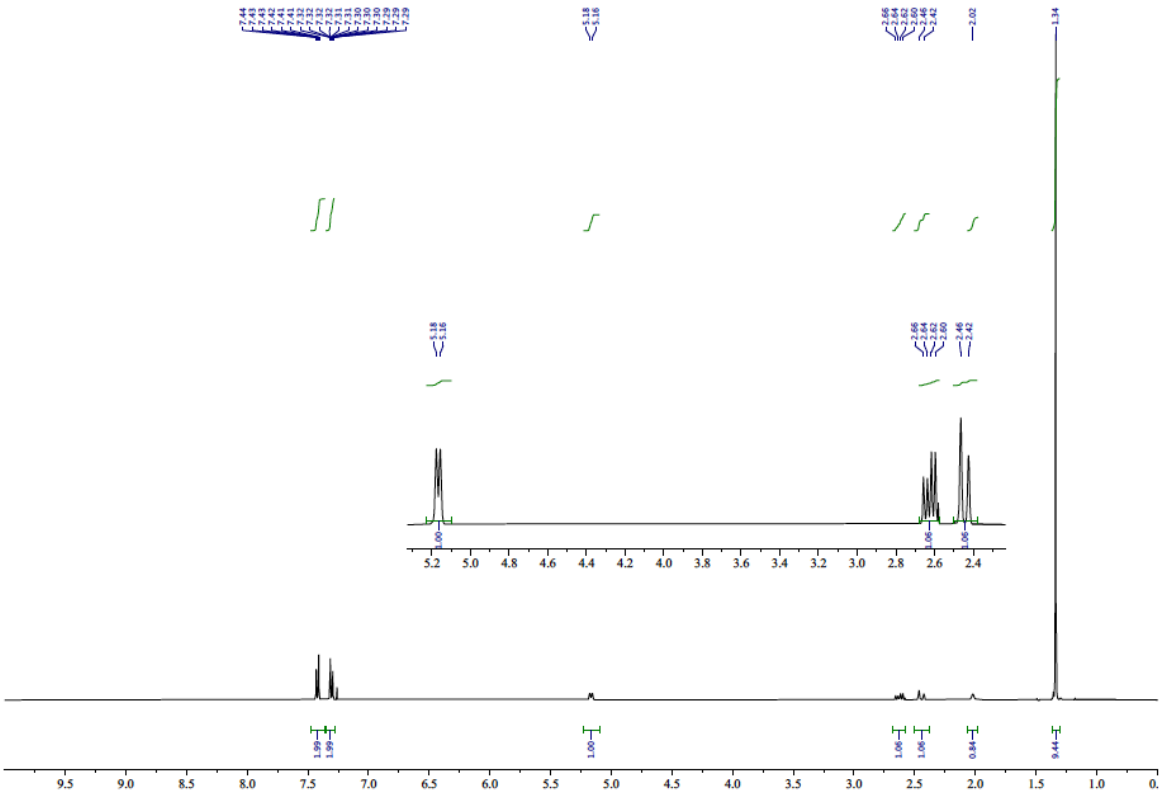


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)



1-(4-*tert*-Butylphenyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ab**)

^{1}H NMR (400 MHz, $CDCl_3$, rt)



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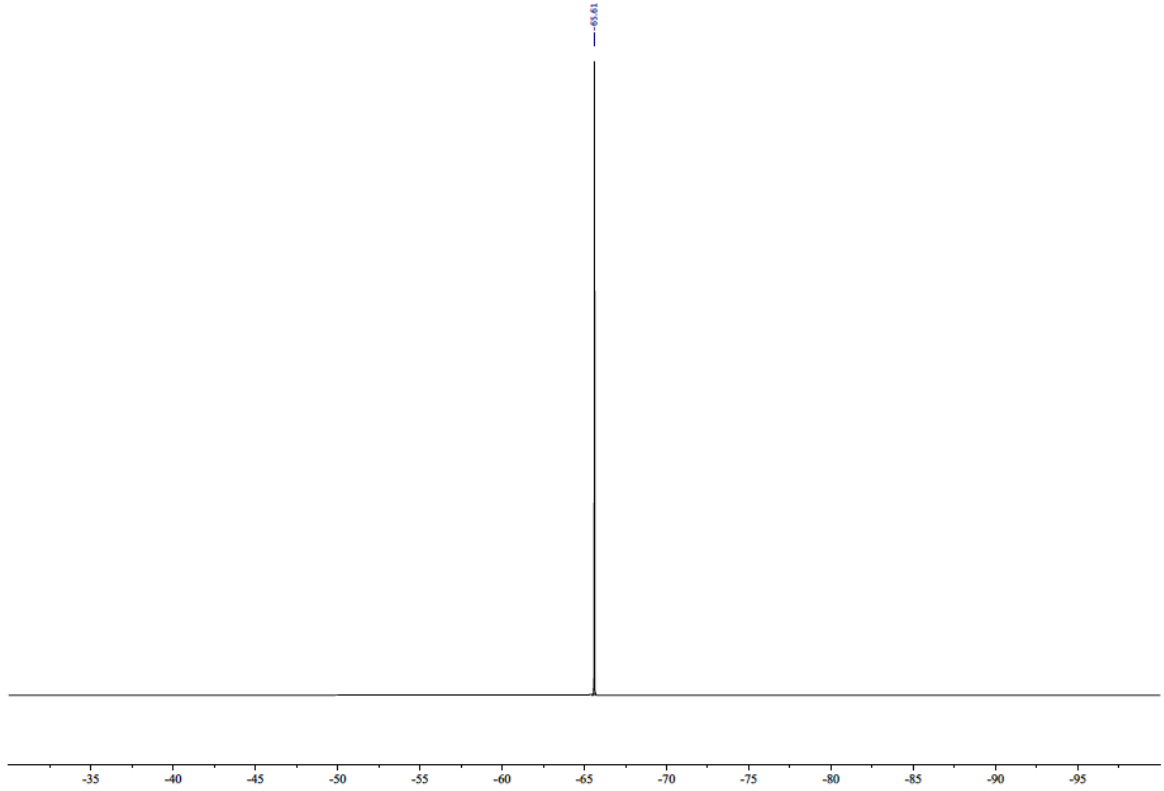
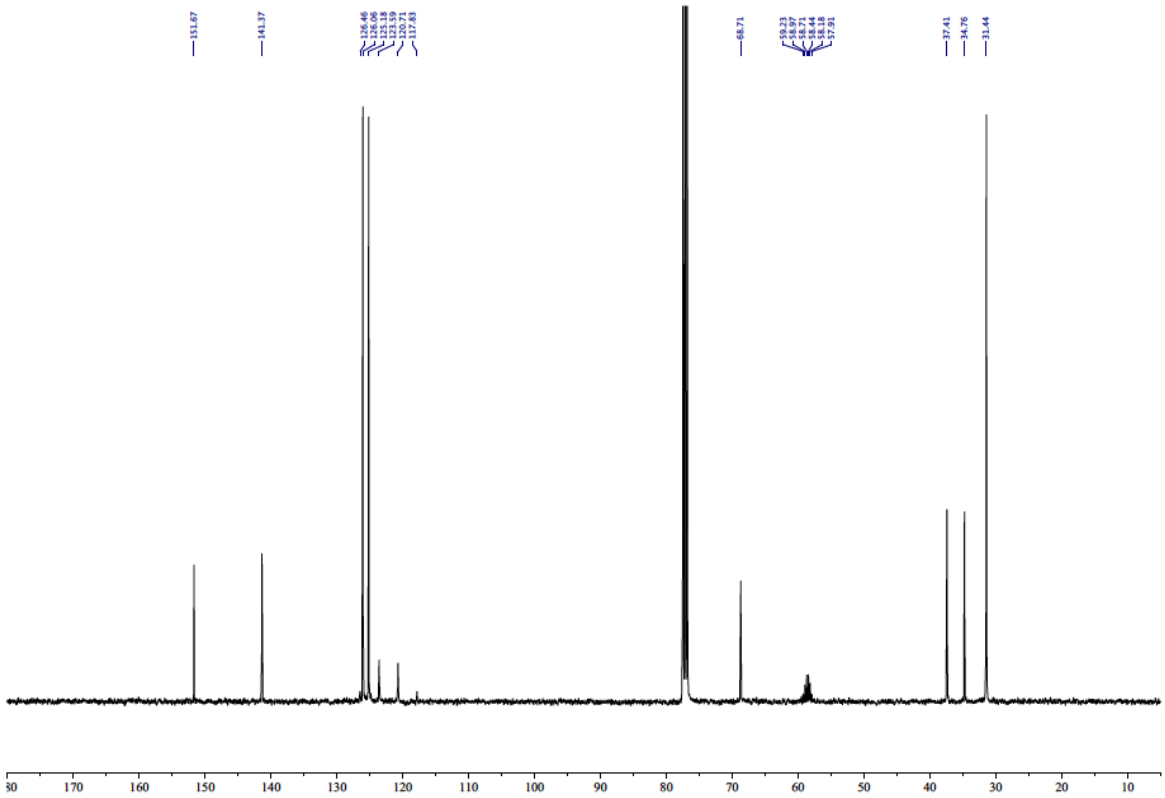
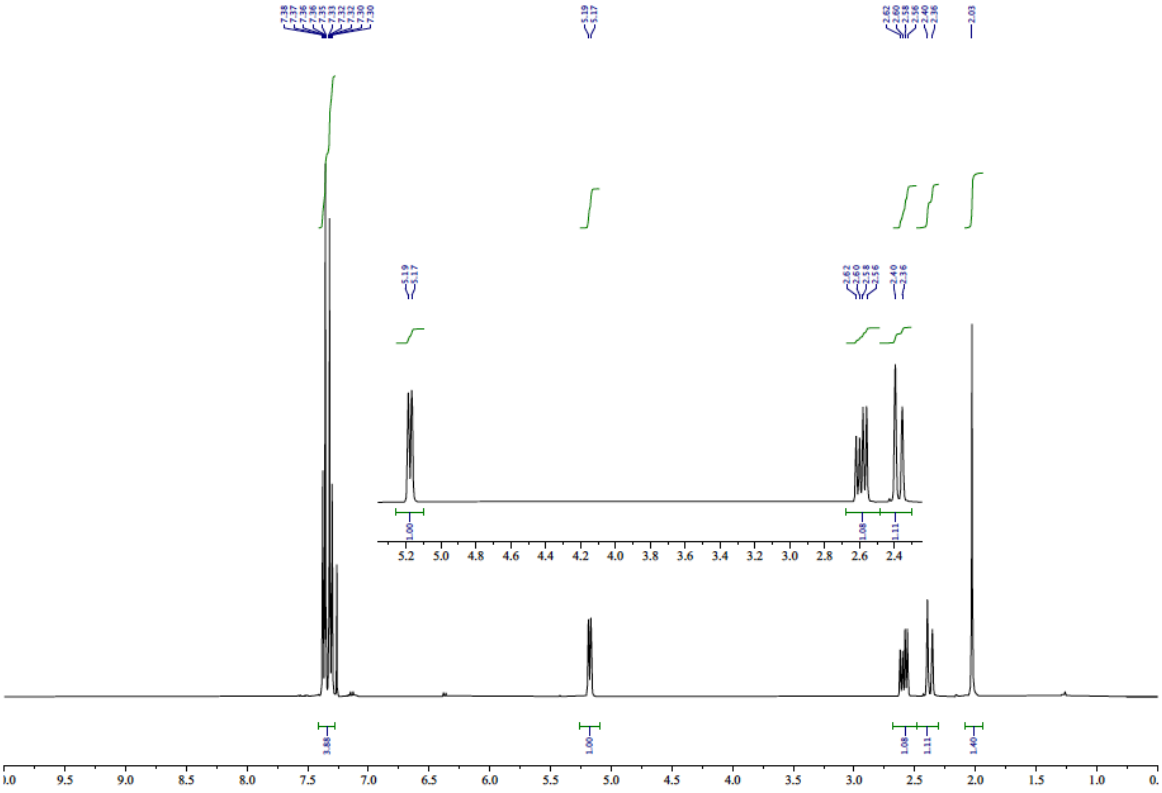


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)

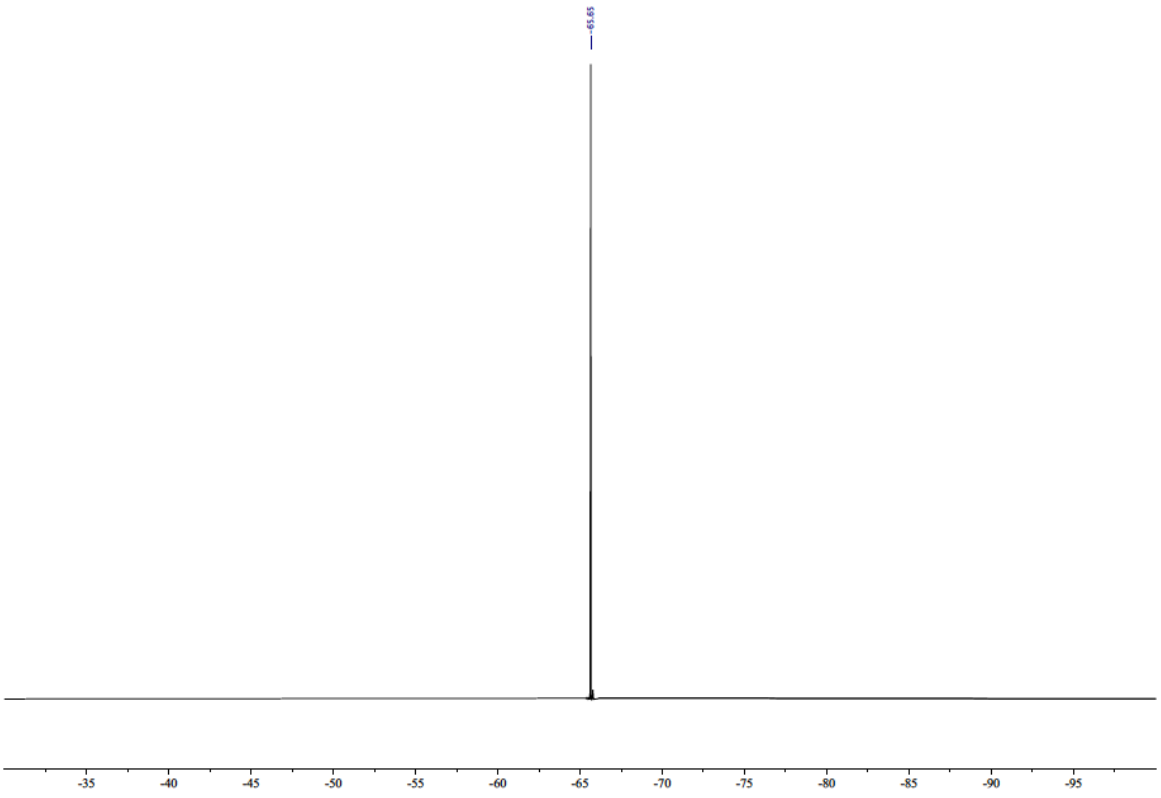


1-(4-Chlorophenyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ac**)

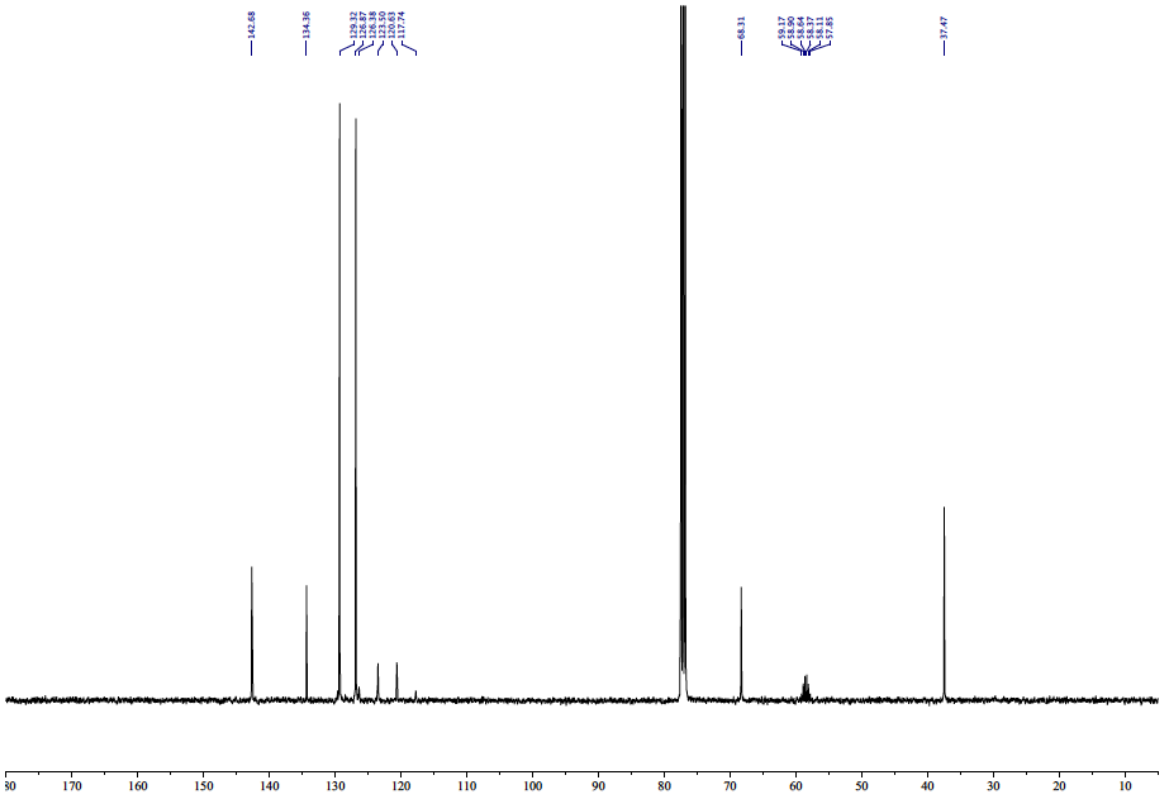
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

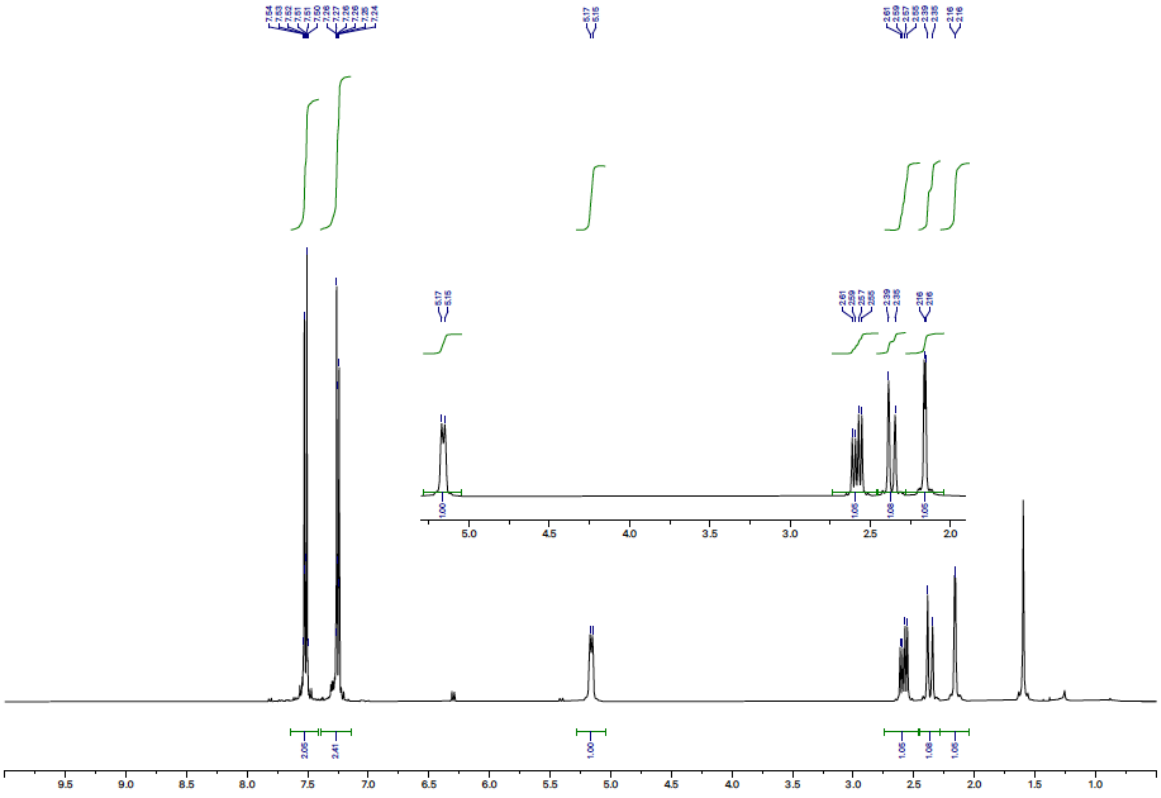


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)

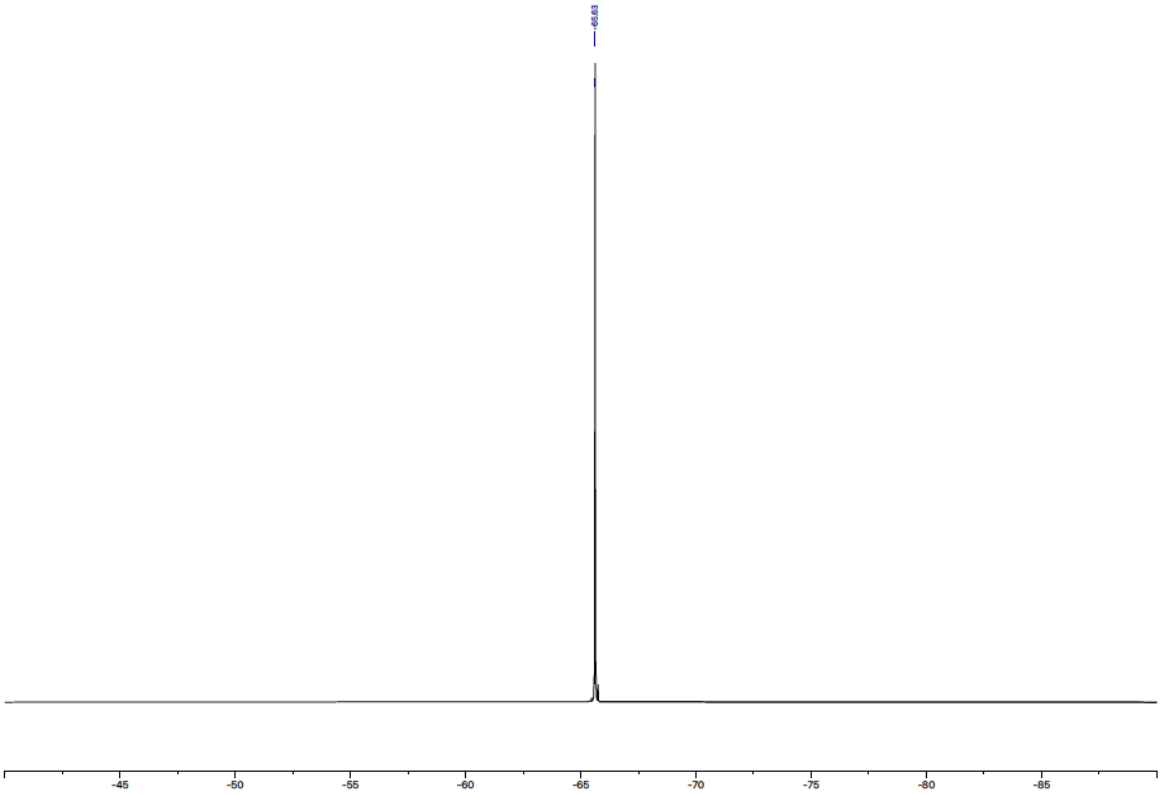


1-(4-Bromophenyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ad**)

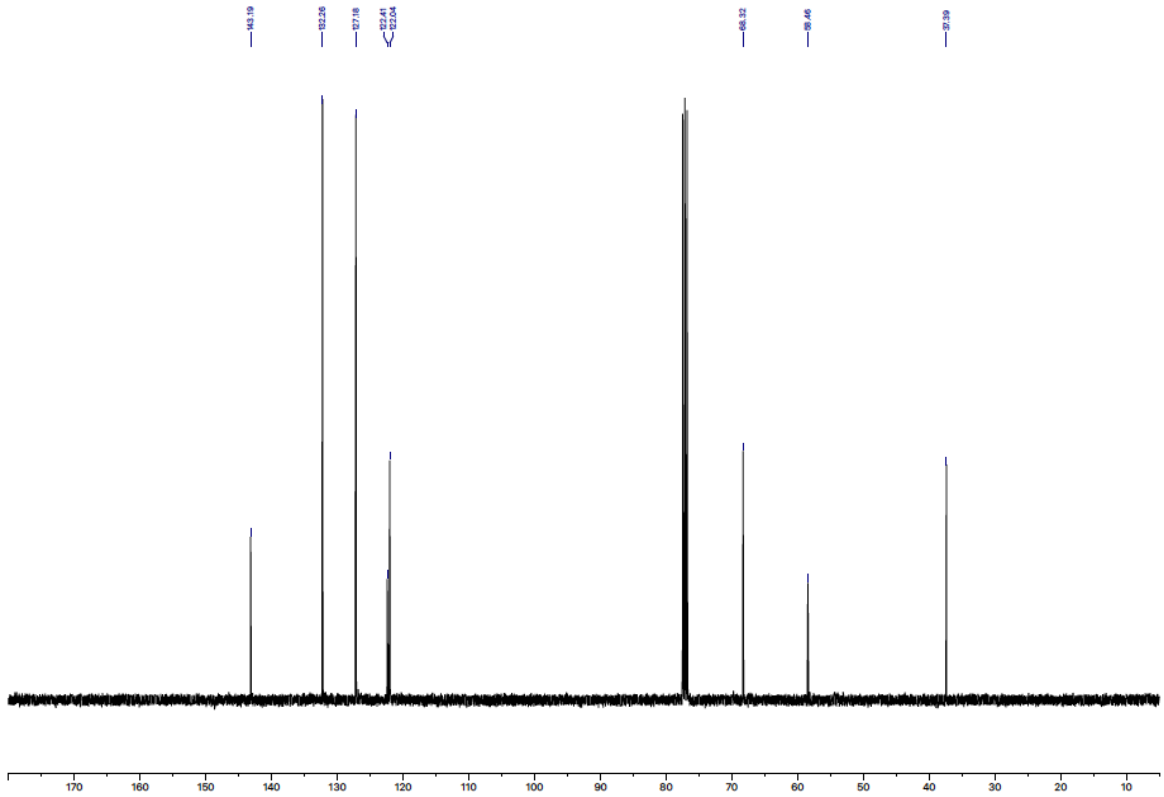
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

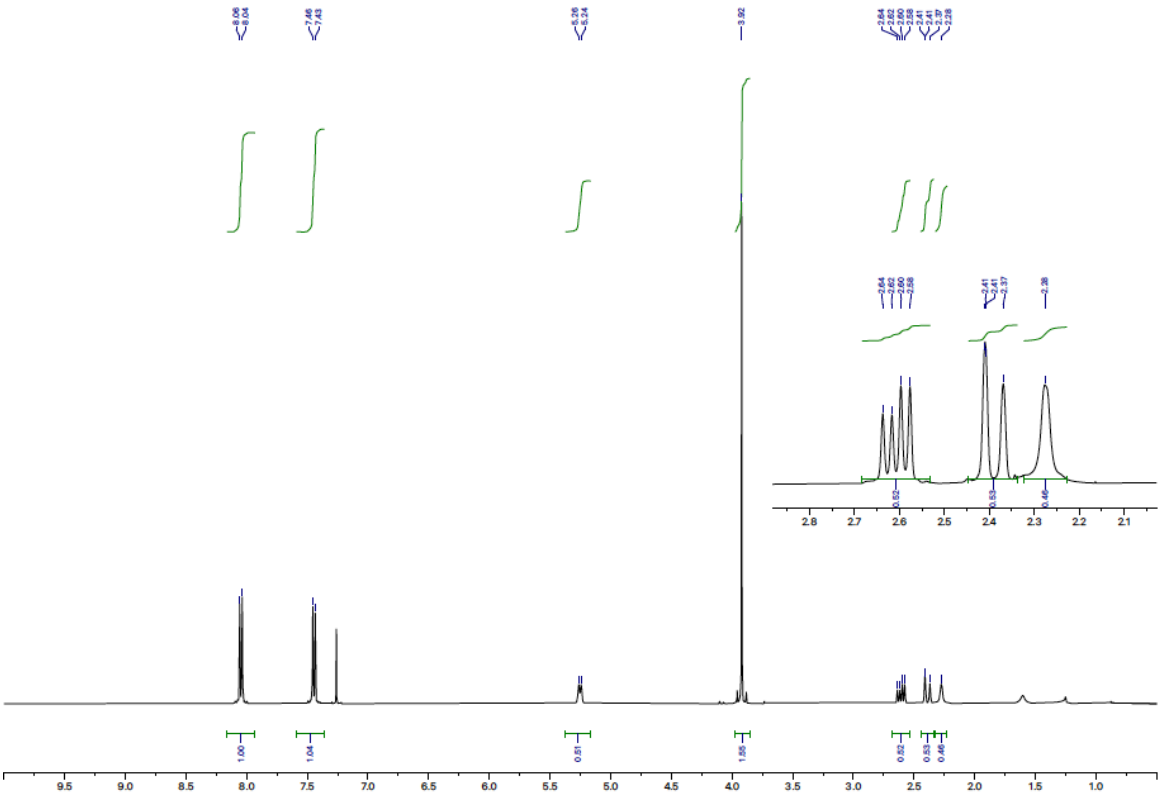


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

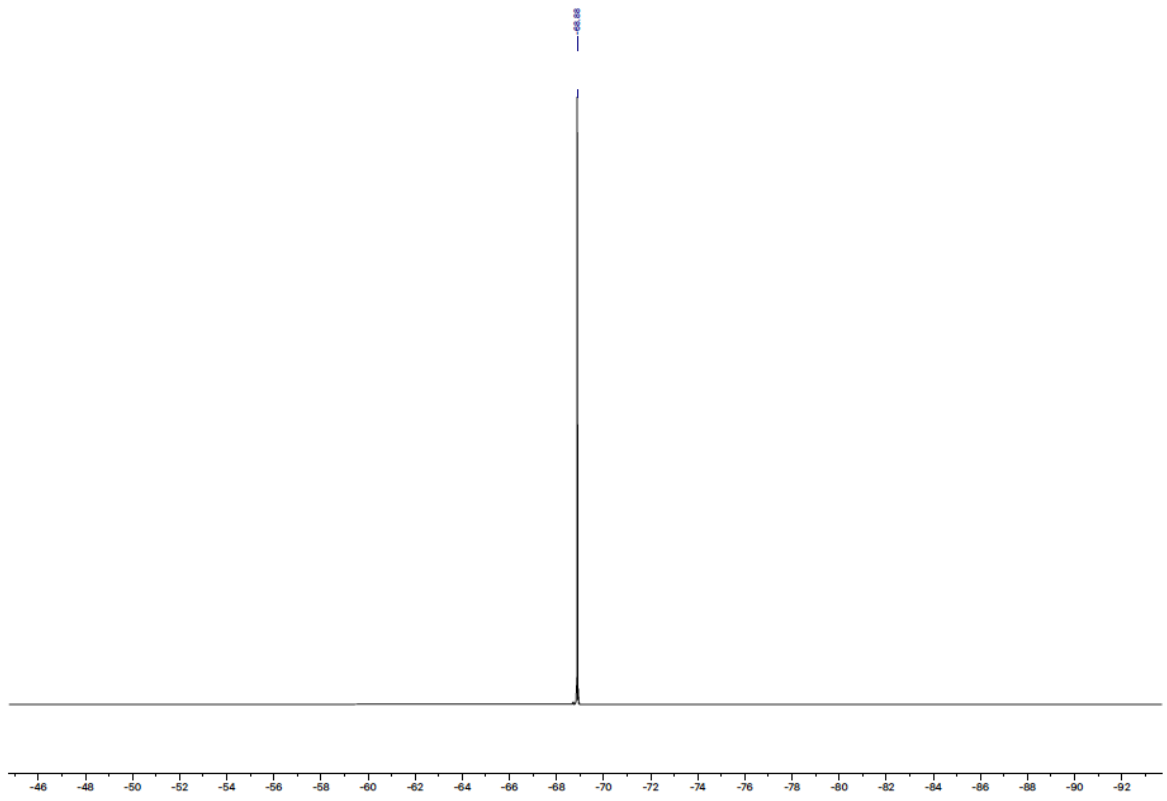


1-(4-Methoxycarbonyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ae**)

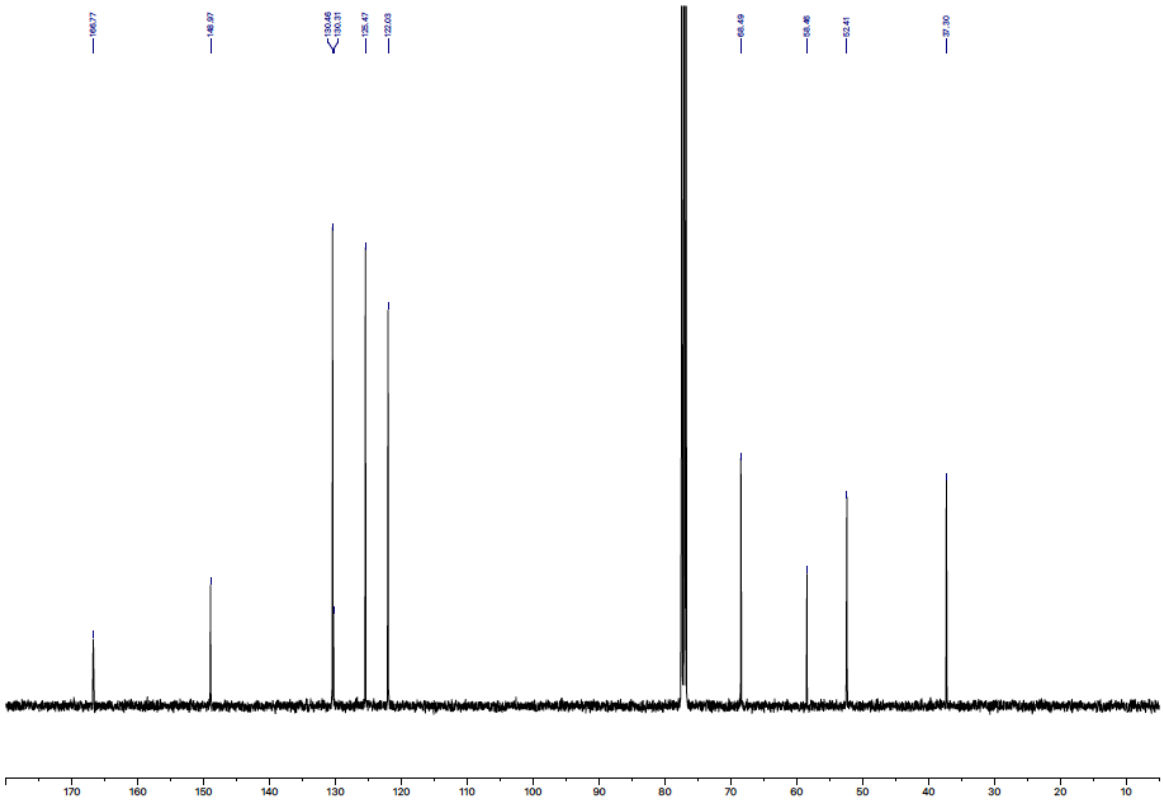
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

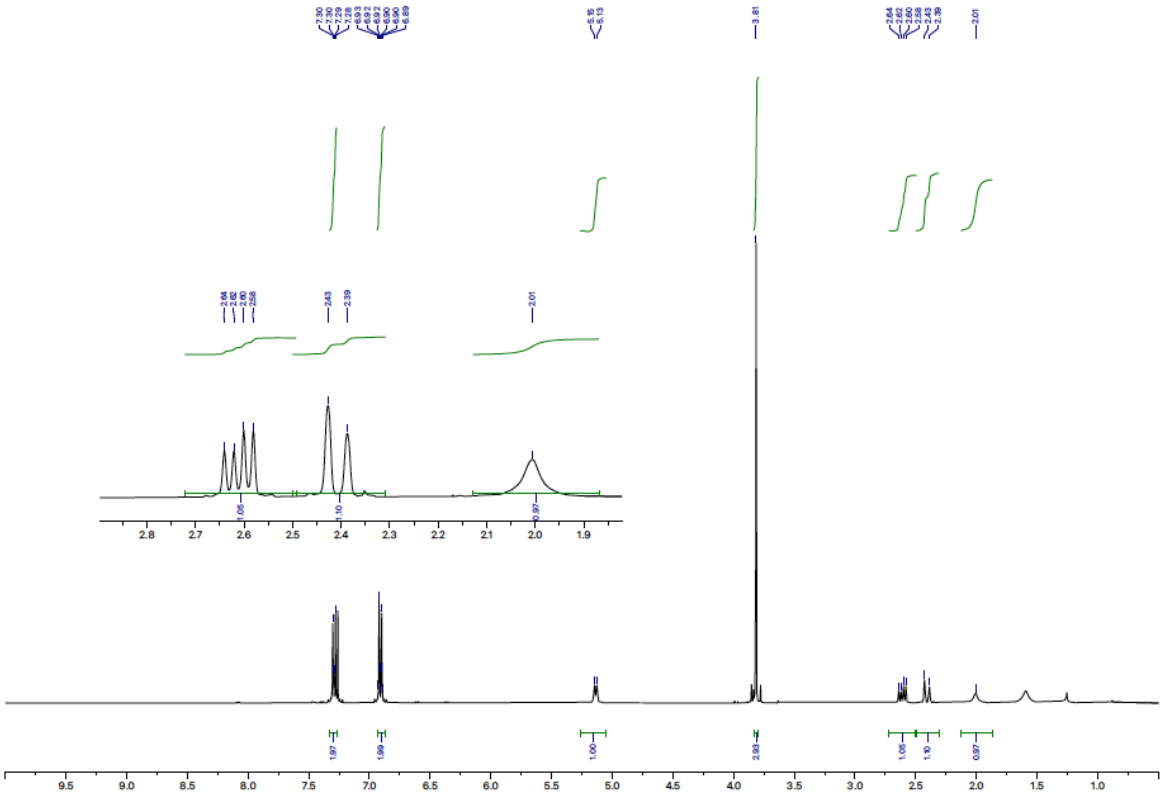


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

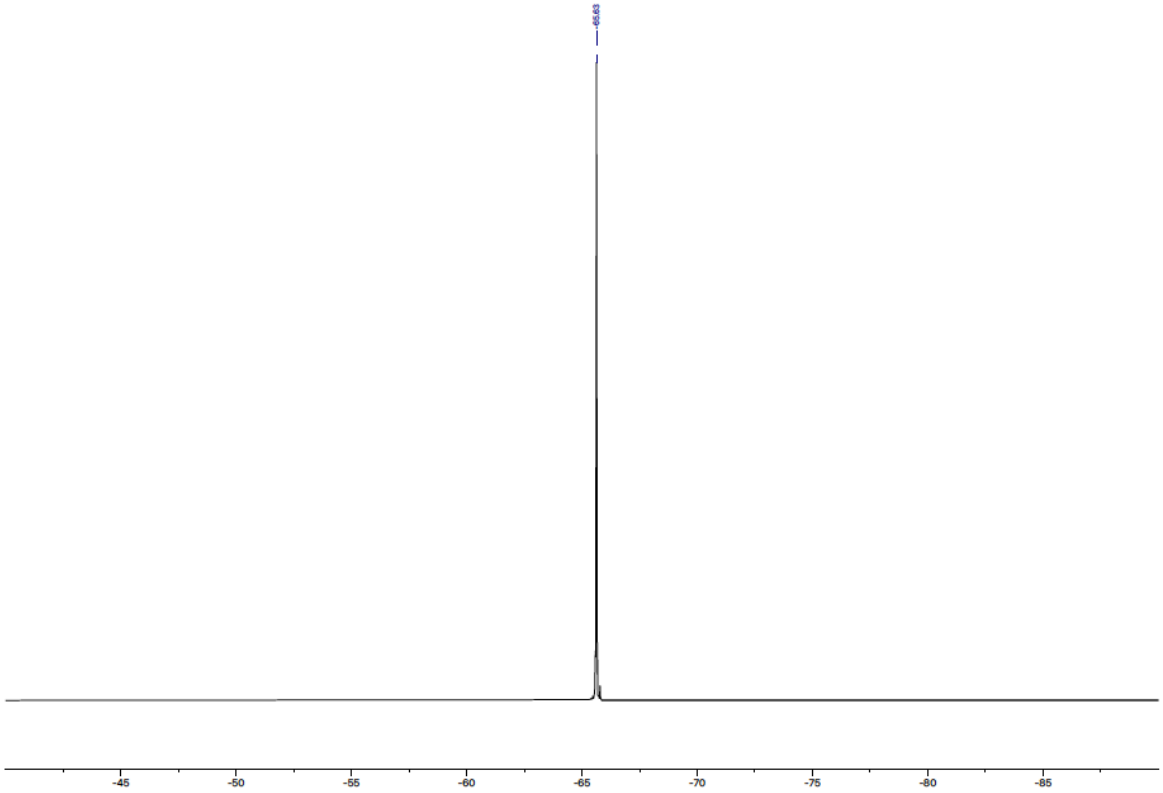


1-(4-Methoxyphenyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3af**)

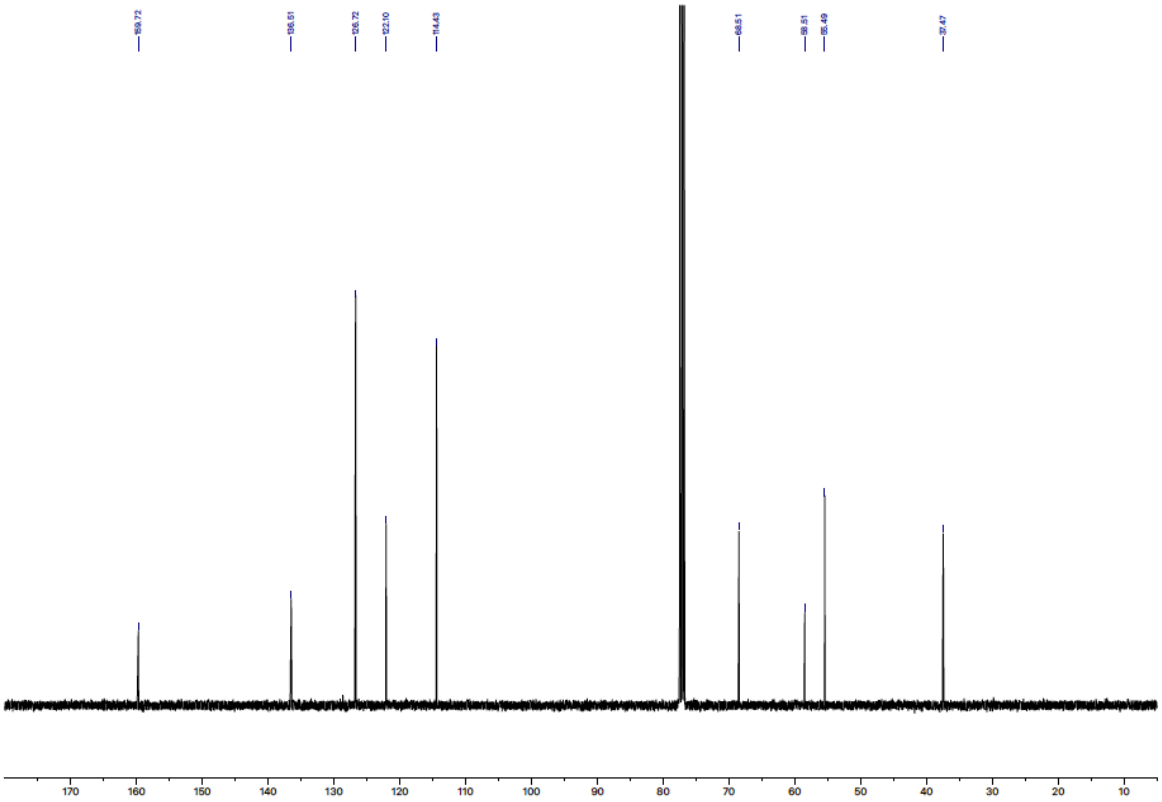
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

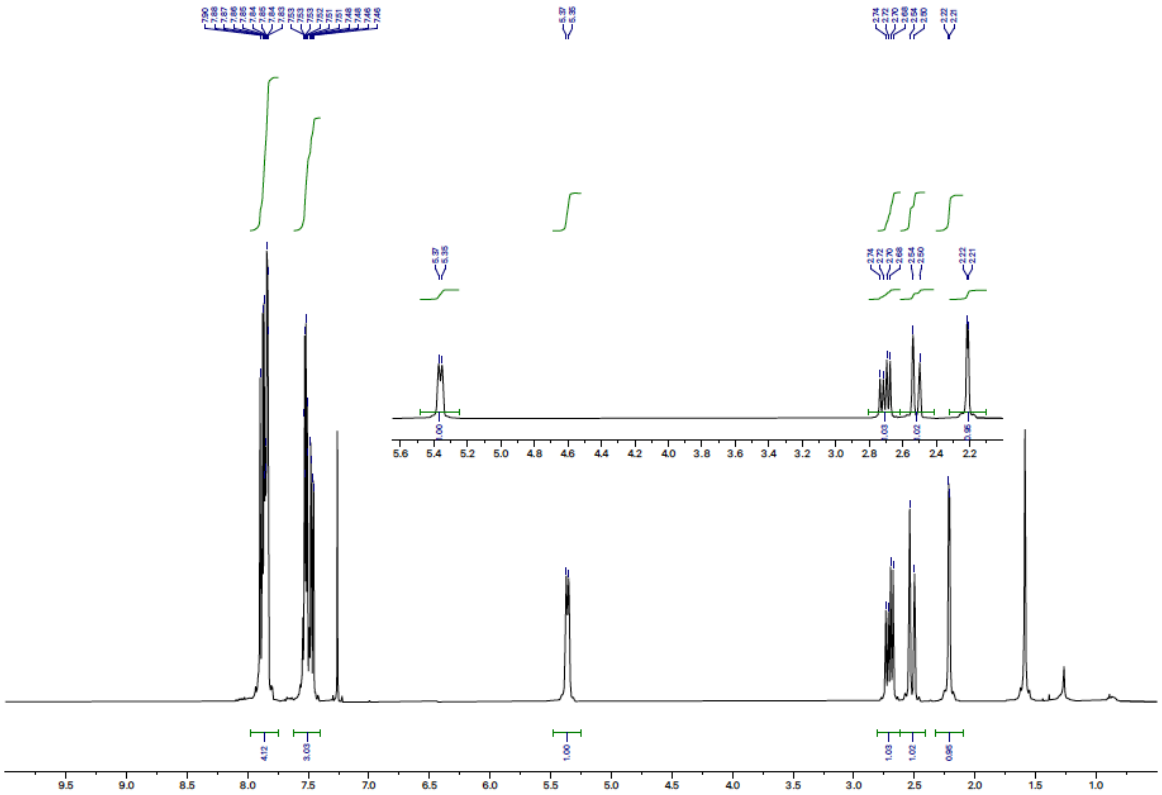


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

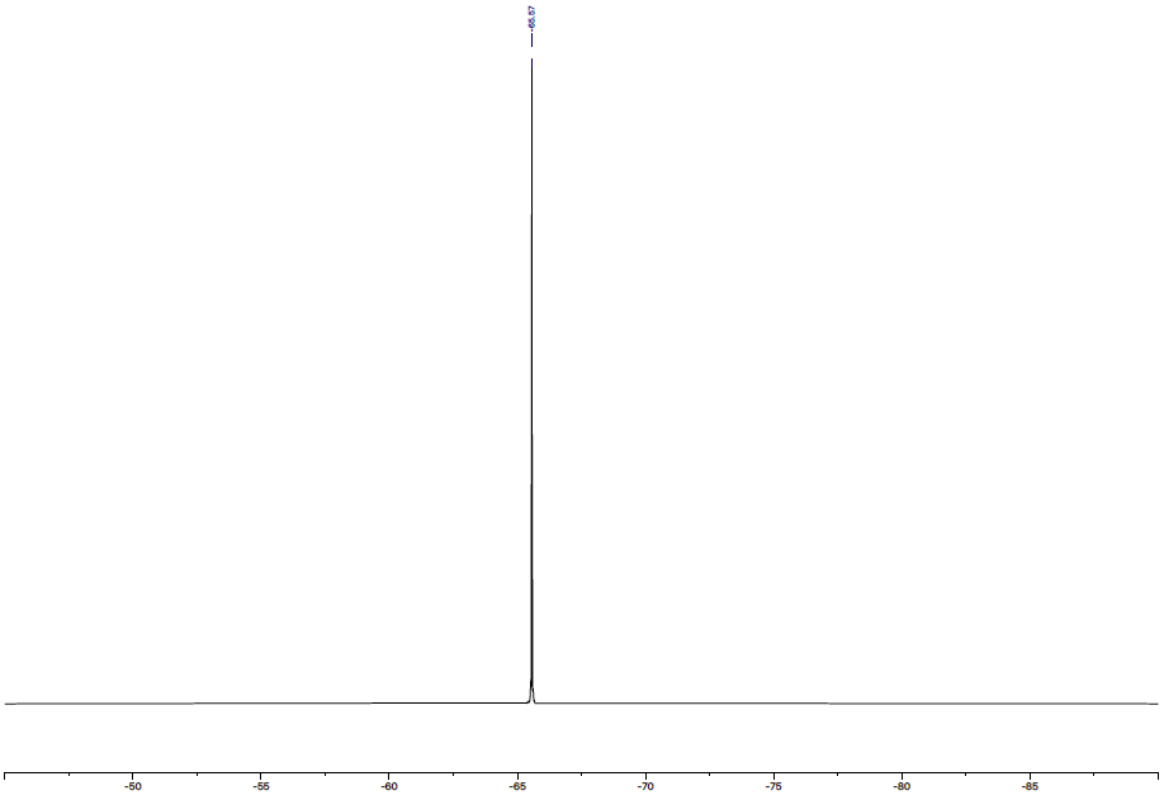


1-(2-Naphthyl)-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ag**)

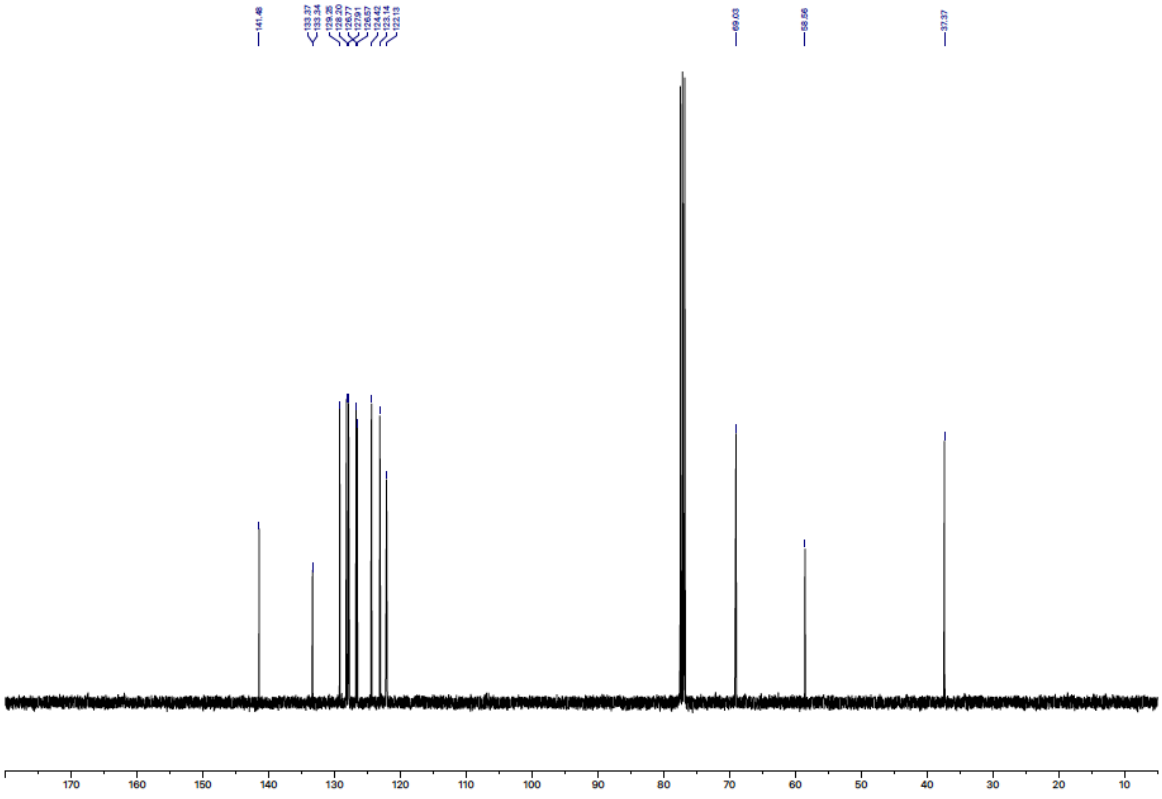
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

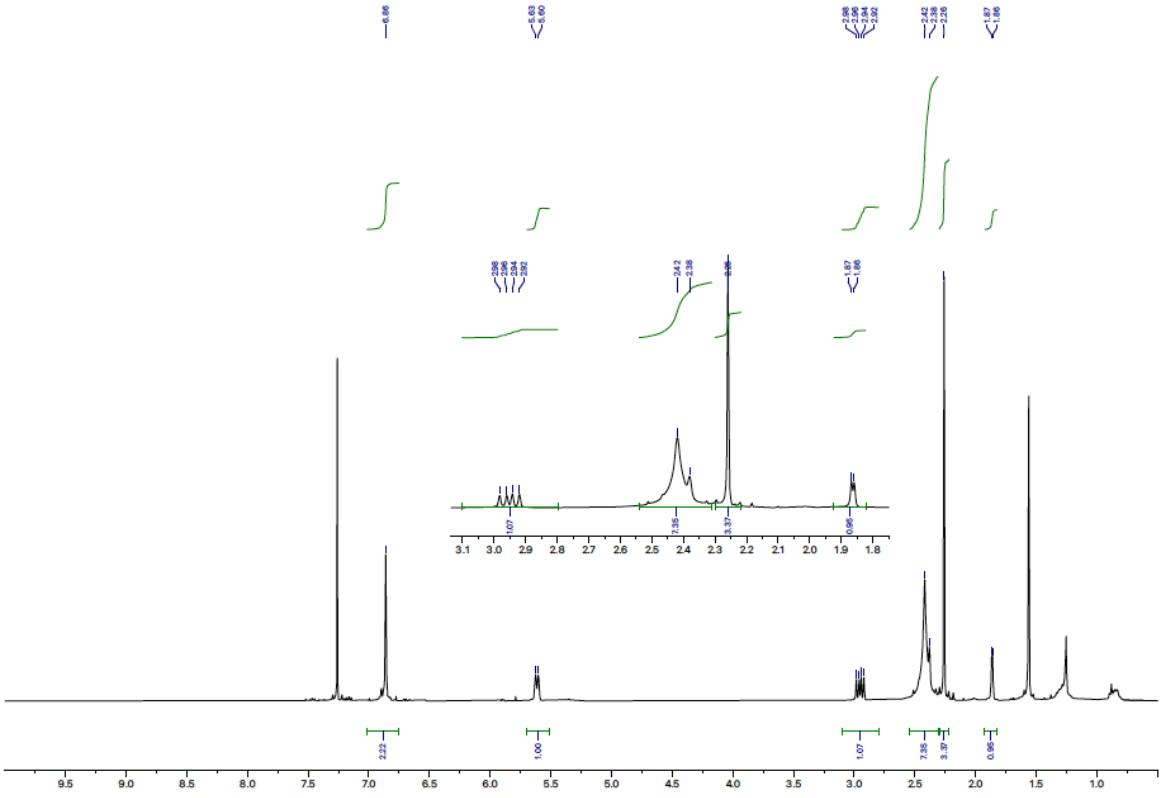


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

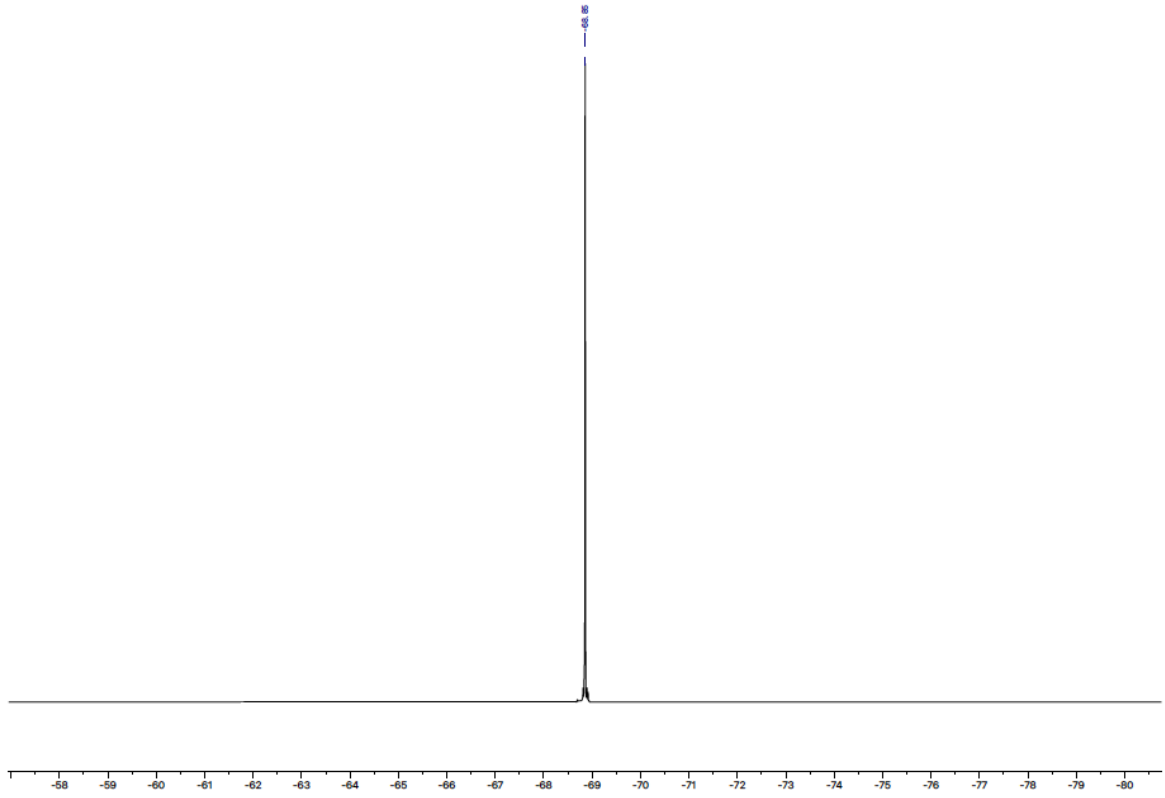


1-Mesityl-4,4,4-trifluoro-3,3-bis(trifluoromethyl)butan-1-ol (**3ah**)

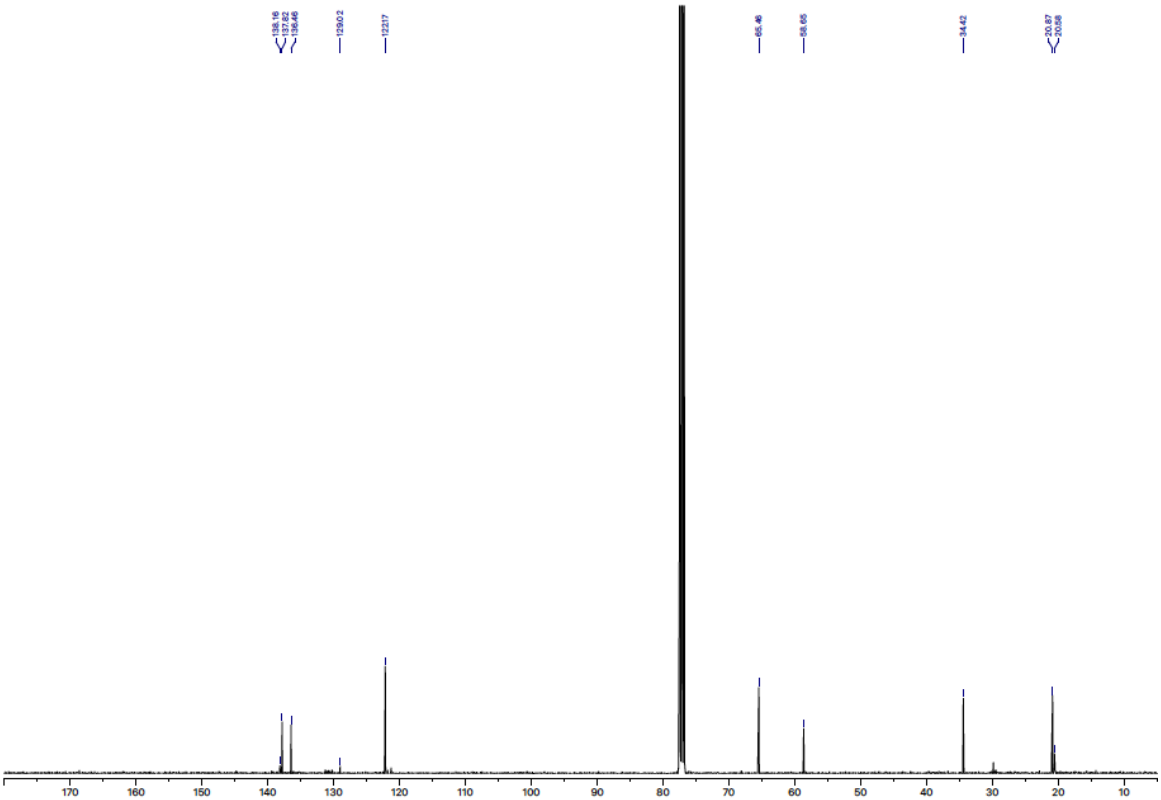
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

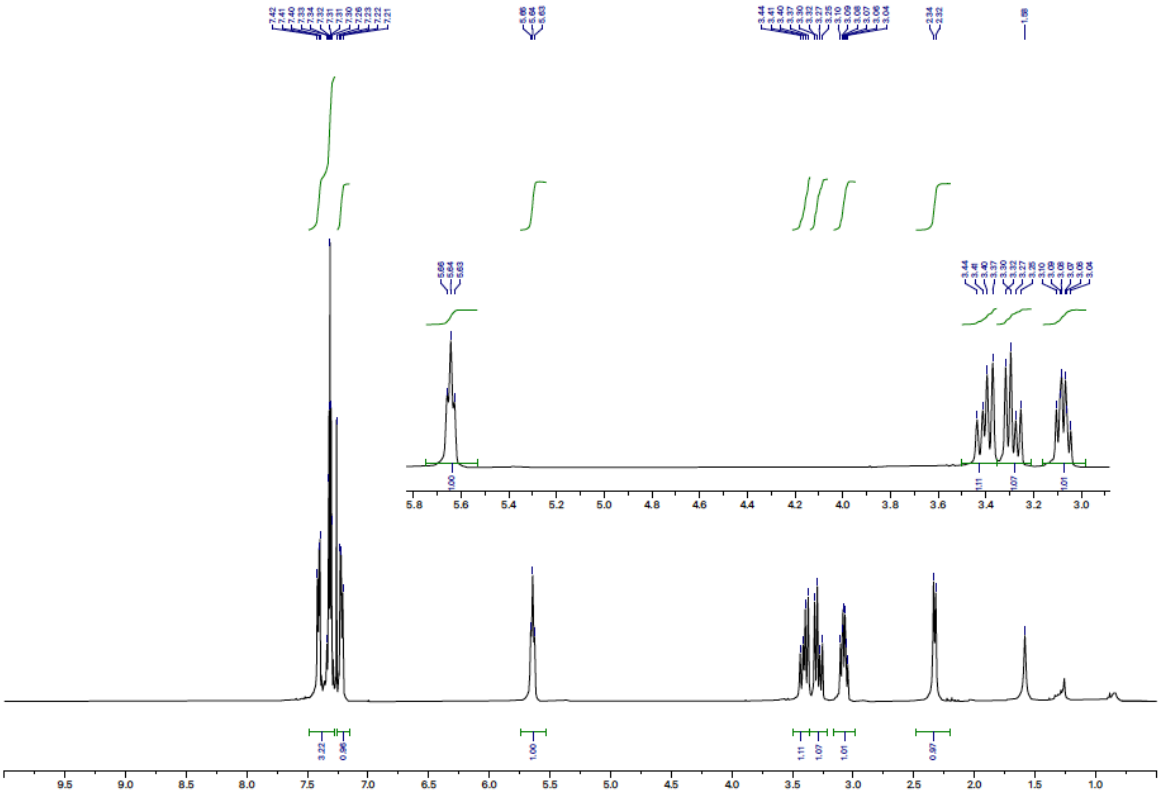


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

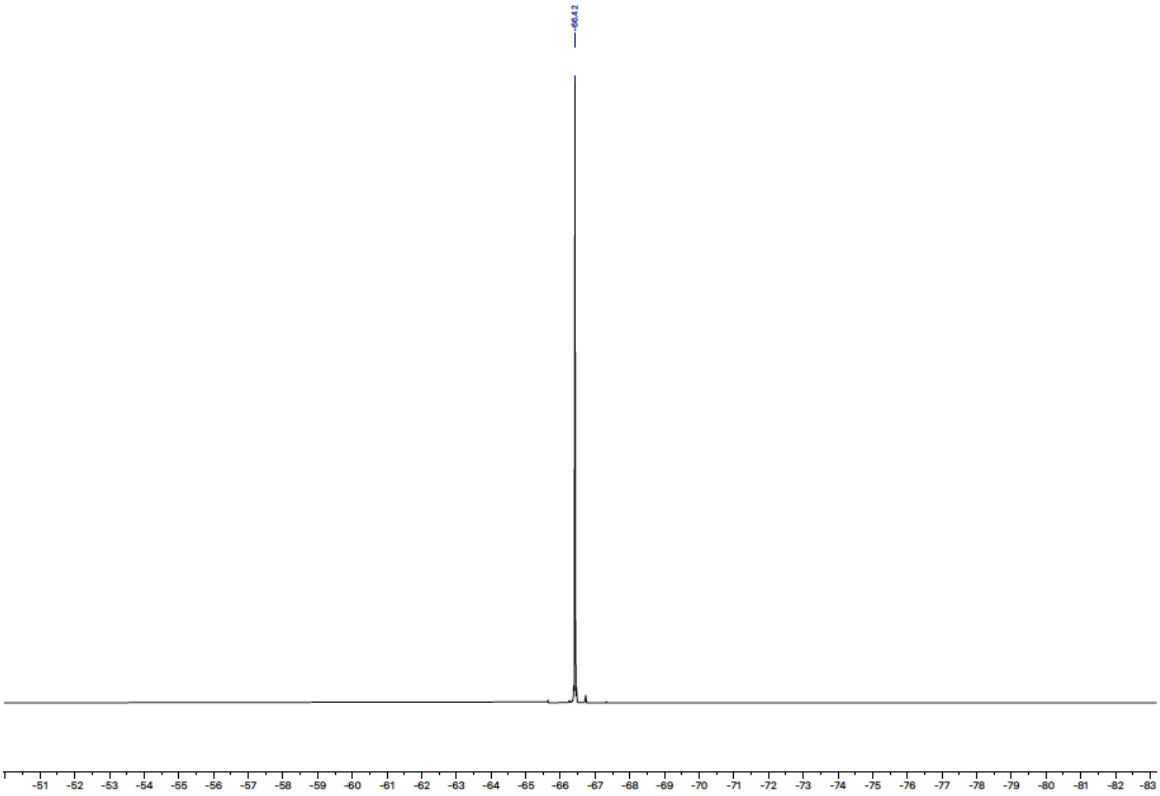


2-(1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl)-2,3-dihydro-1*H*-inden-1-ol (**3ai**)

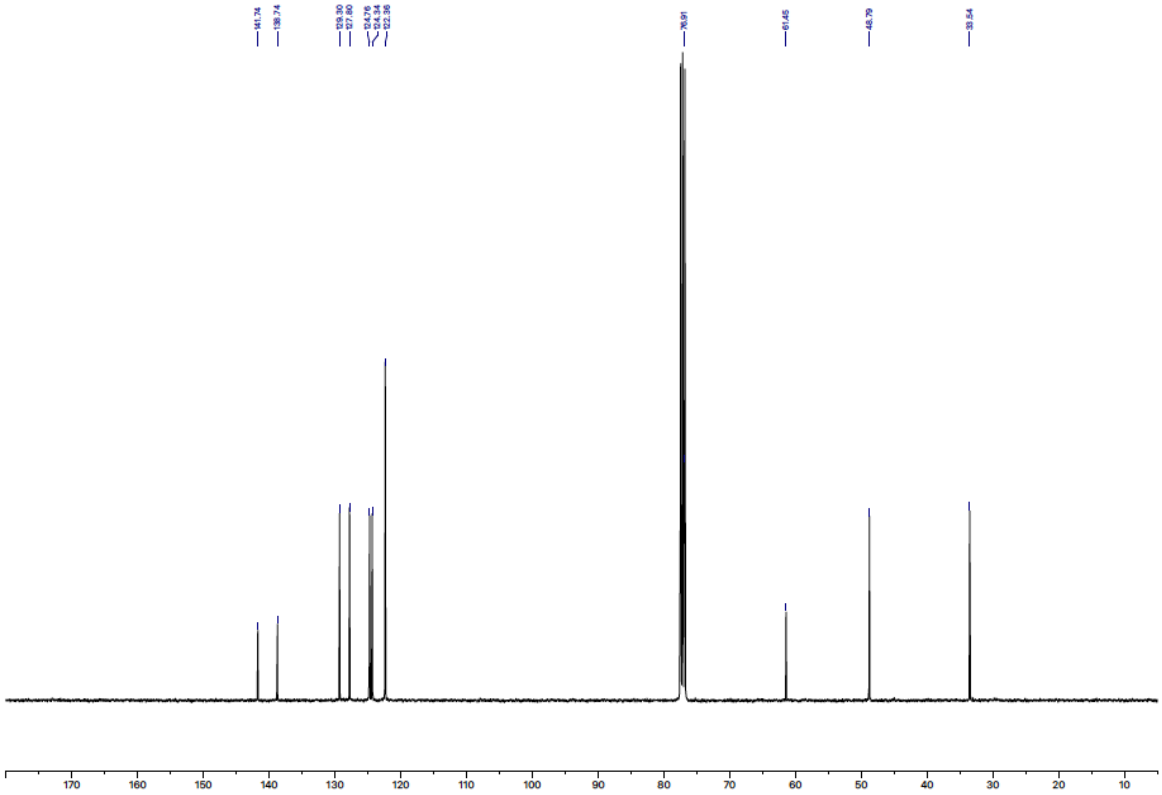
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

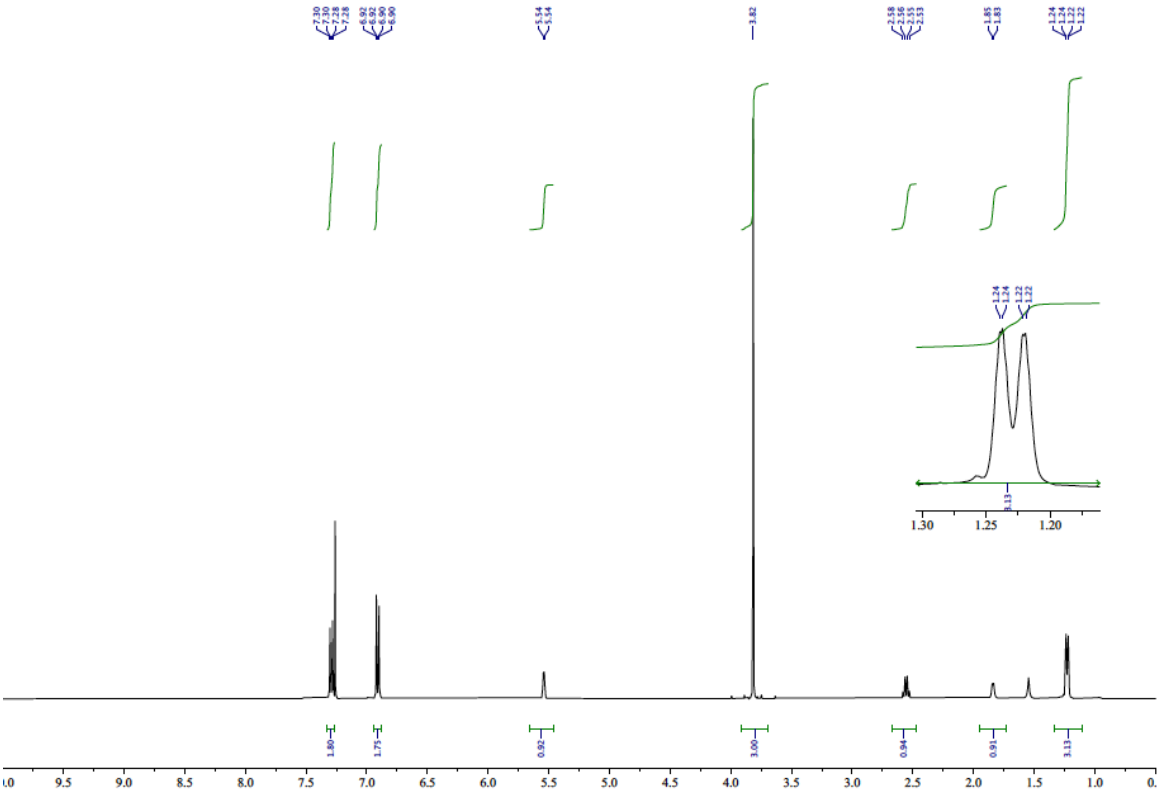


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

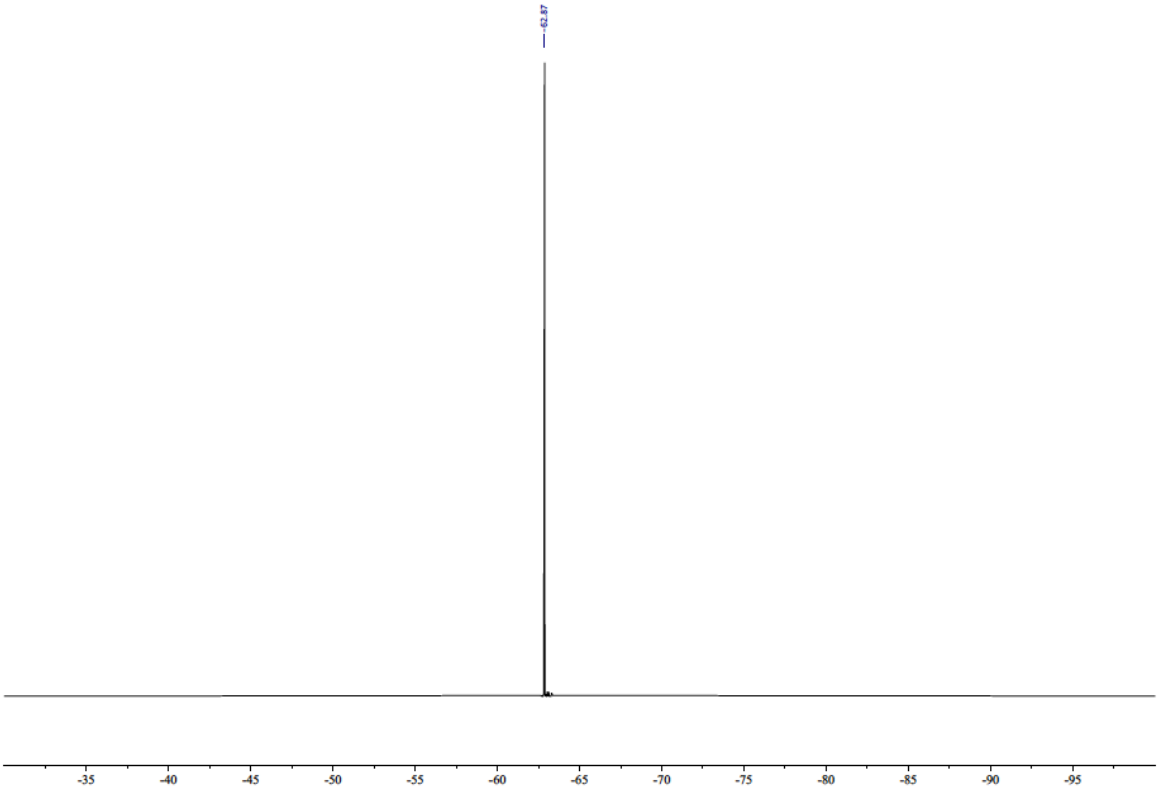


4,4,4-Trifluoro-1-(4-methoxyphenyl)-2-methyl-3,3-bis(trifluoromethyl)butan-1-ol (**3aj**)

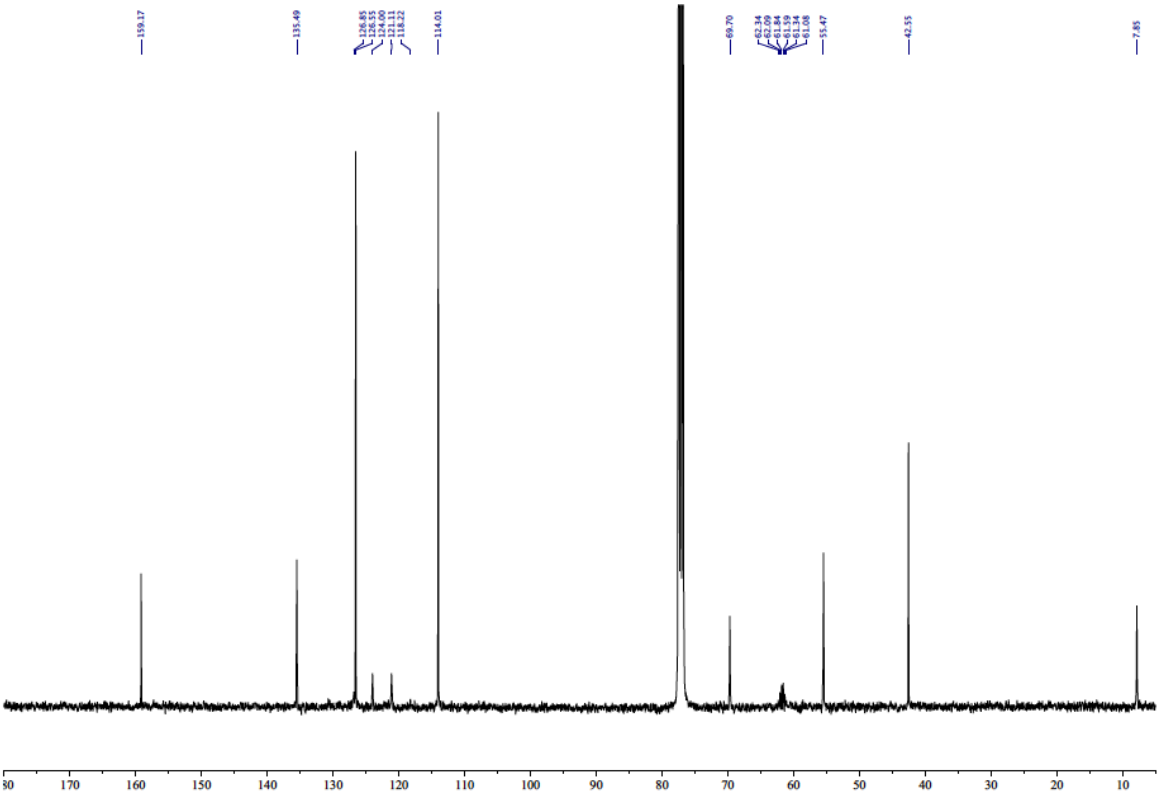
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

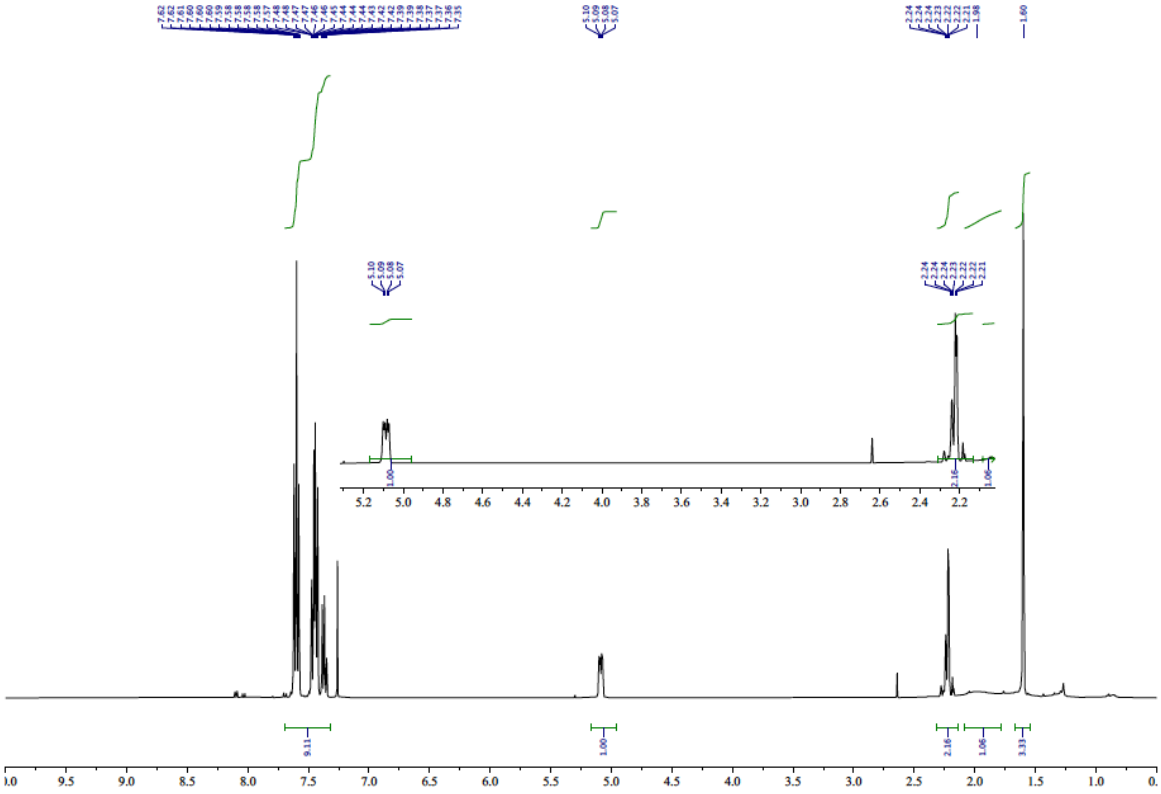


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)

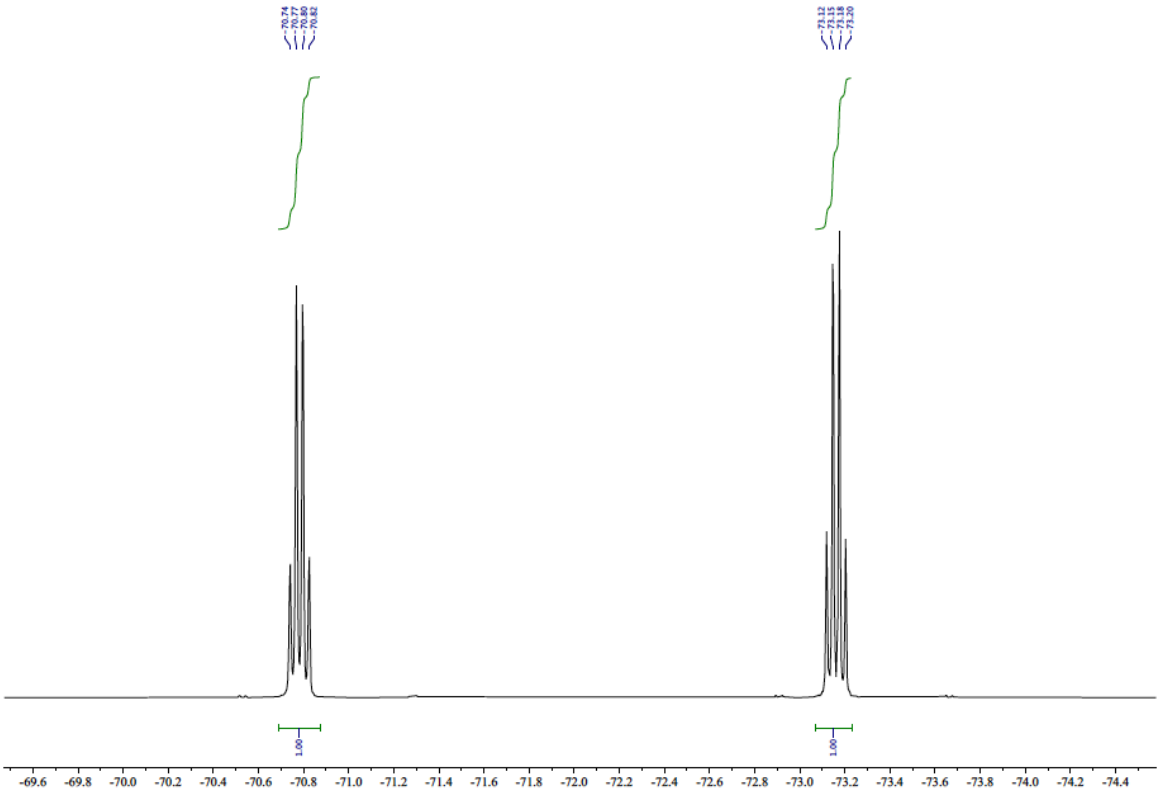


1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluoro-3-methyl-3-(trifluoromethyl)butan-1-ol (**3ba**)

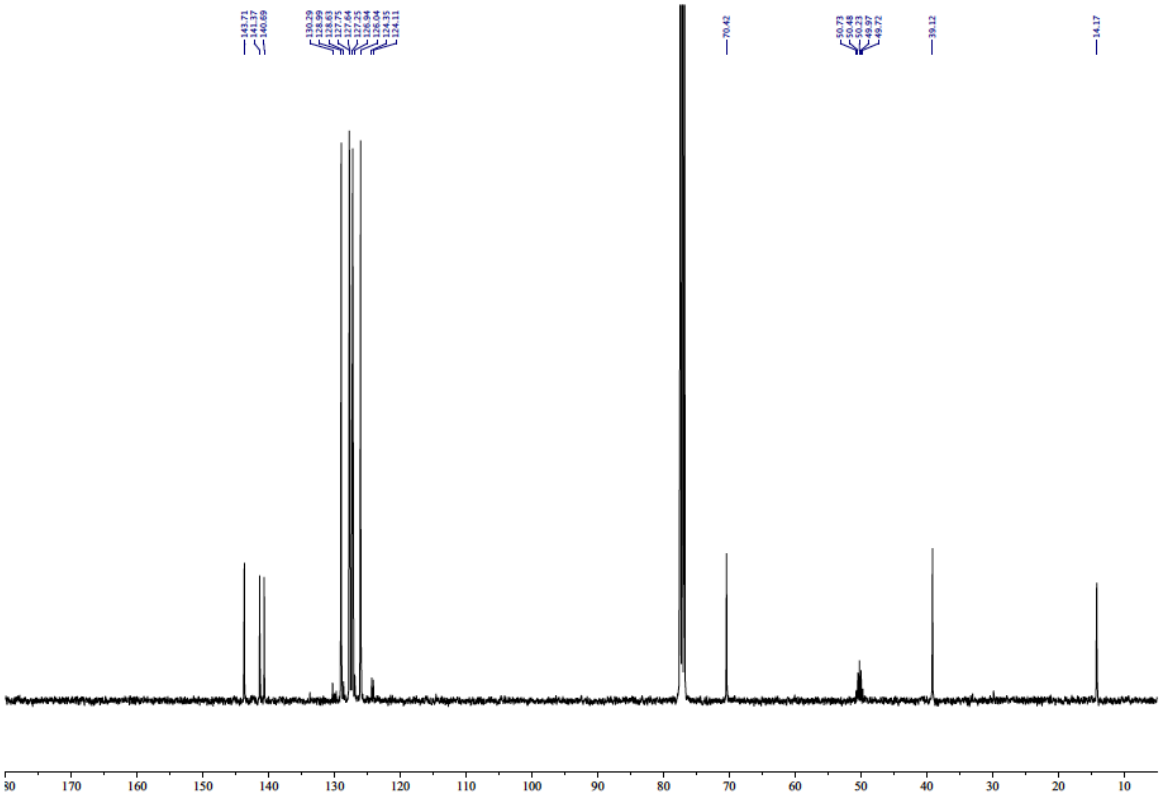
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

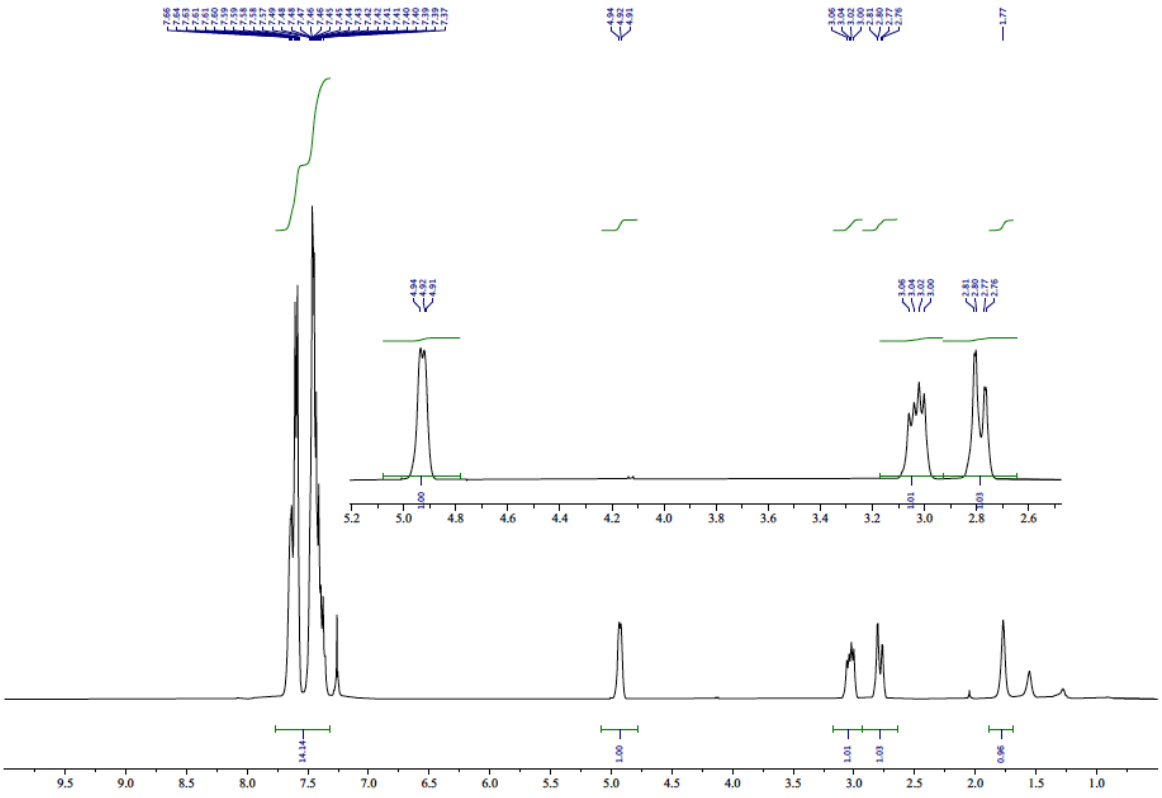


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)

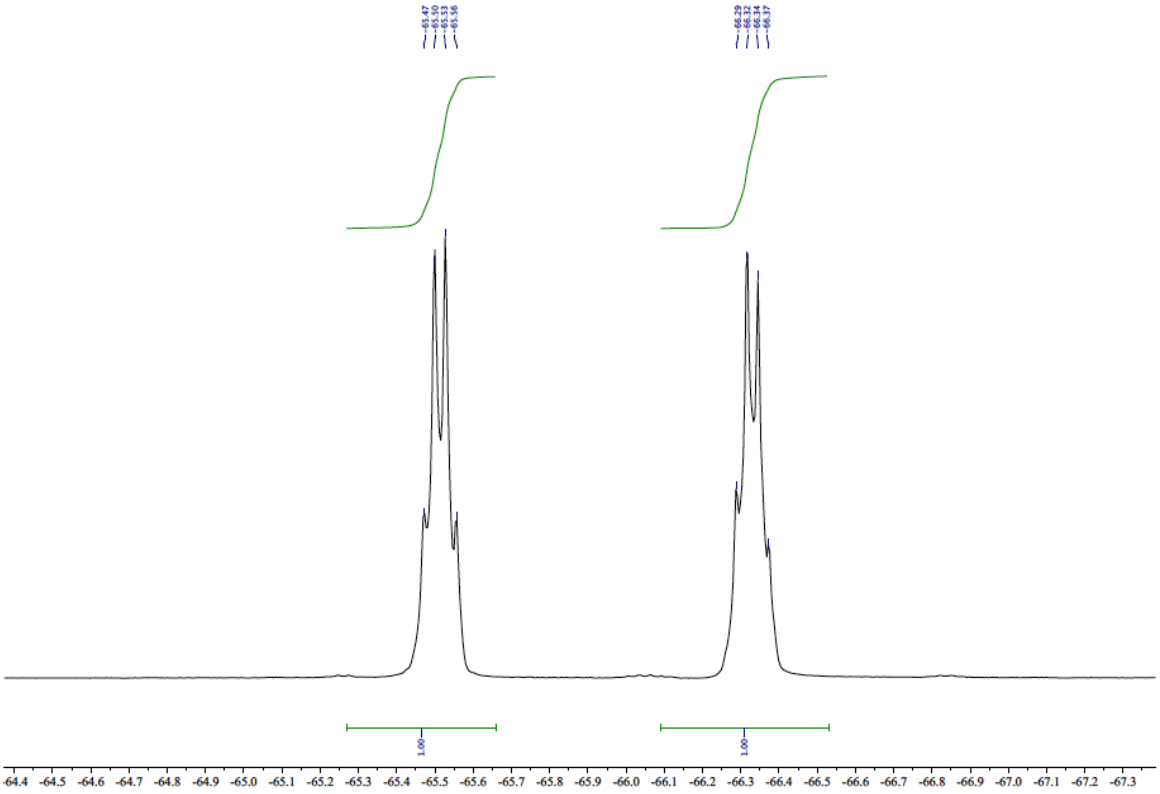


1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluoro-3-phenyl-3-(trifluoromethyl)butan-1-ol (**3ca**)

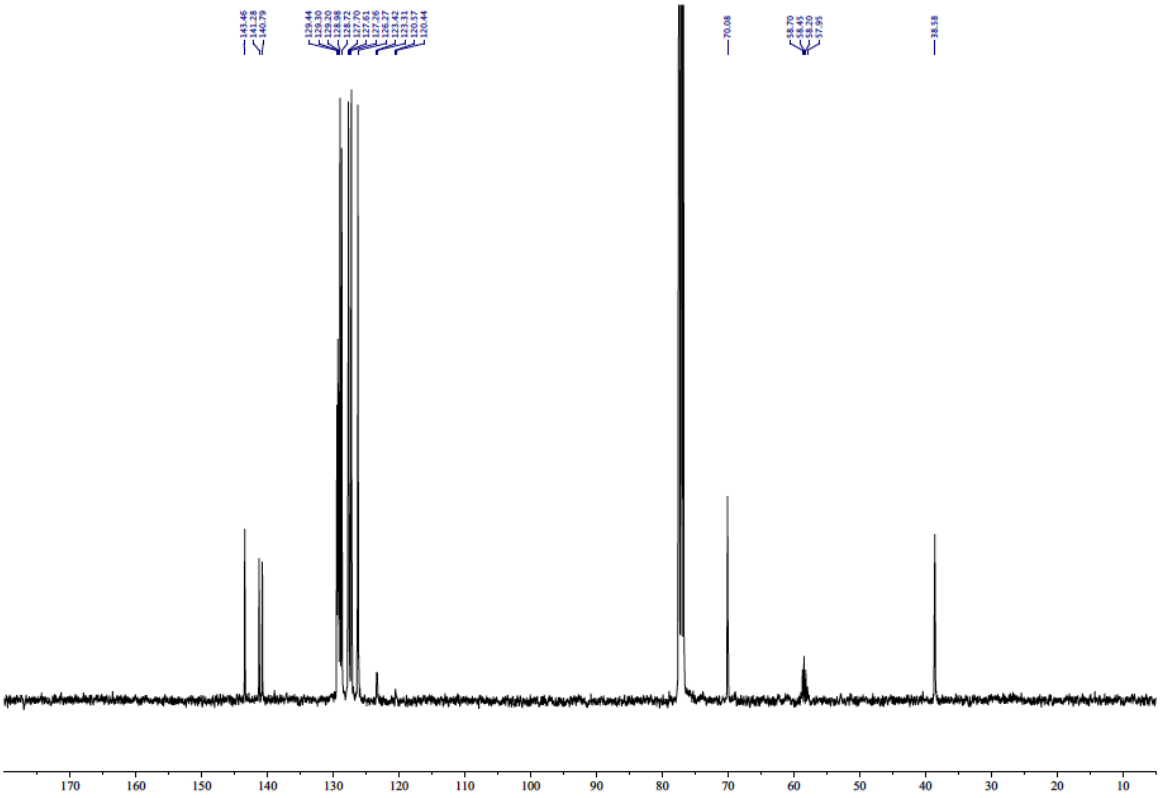
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

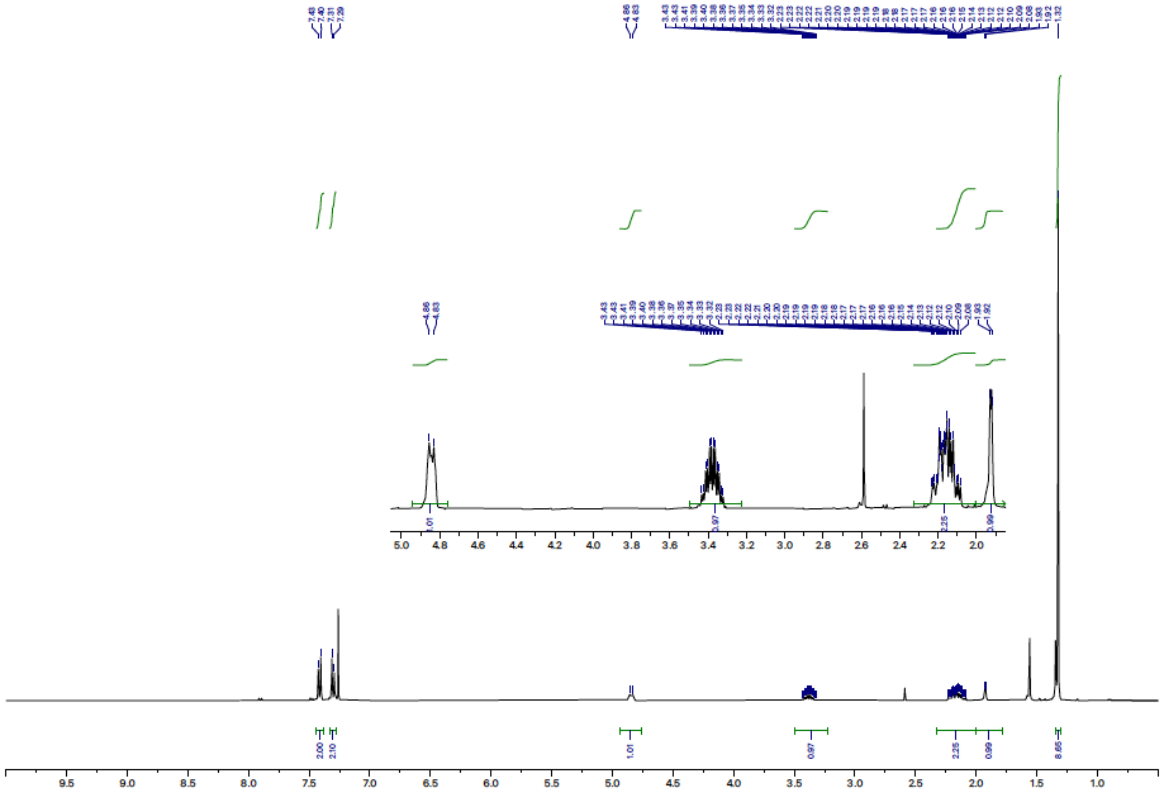


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)

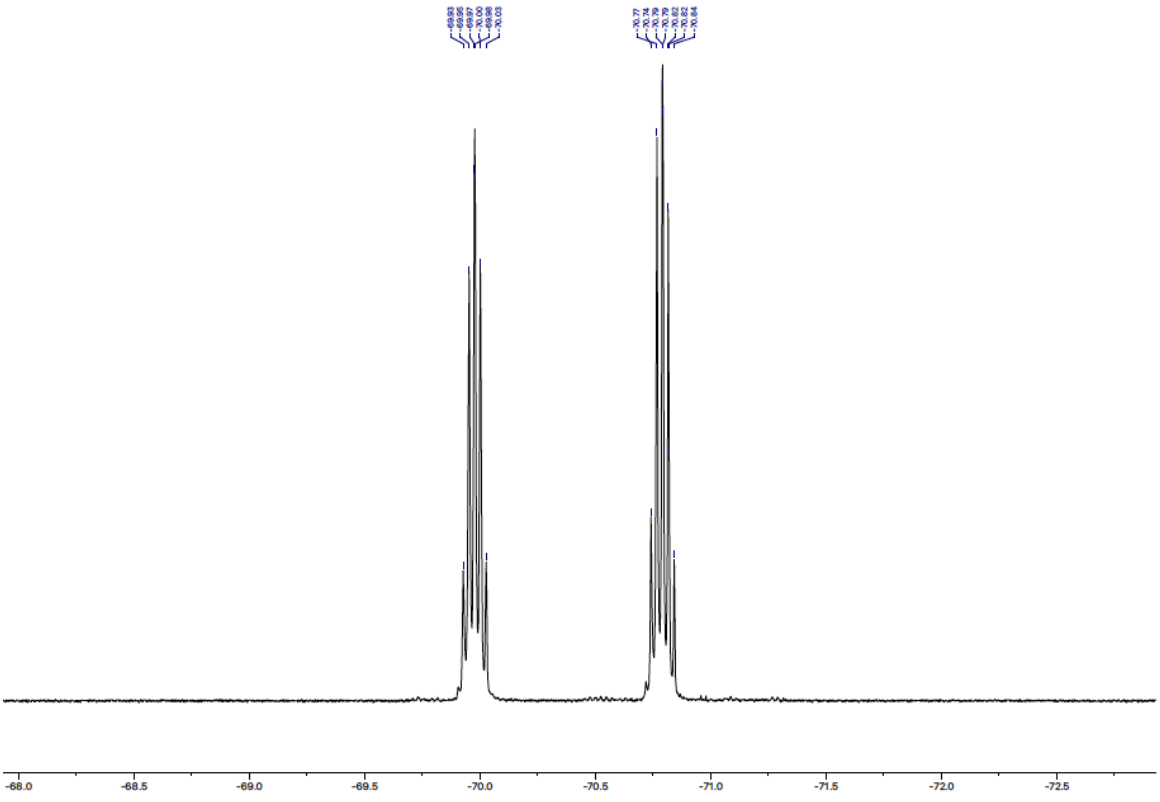


4,4,4-Trifluoro-1-(4-*tert*-butylphenyl)-3-(trifluoromethyl)butan-1-ol (**3db**)

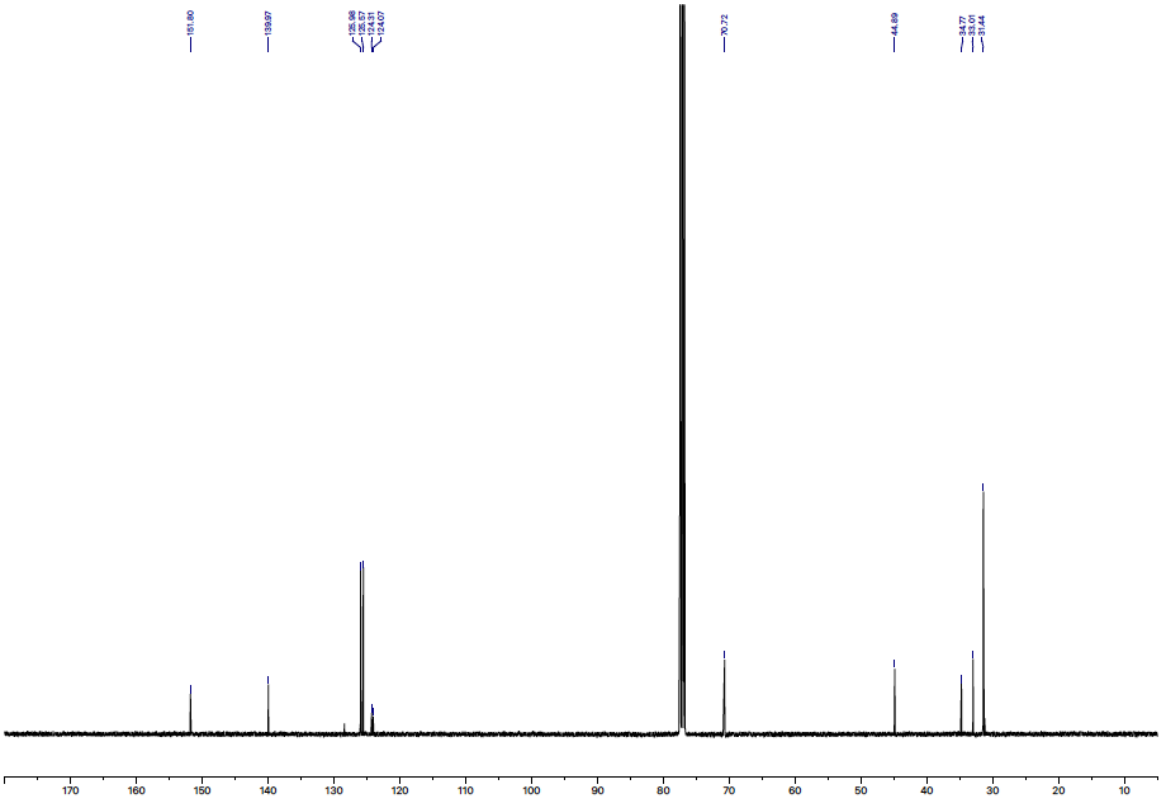
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

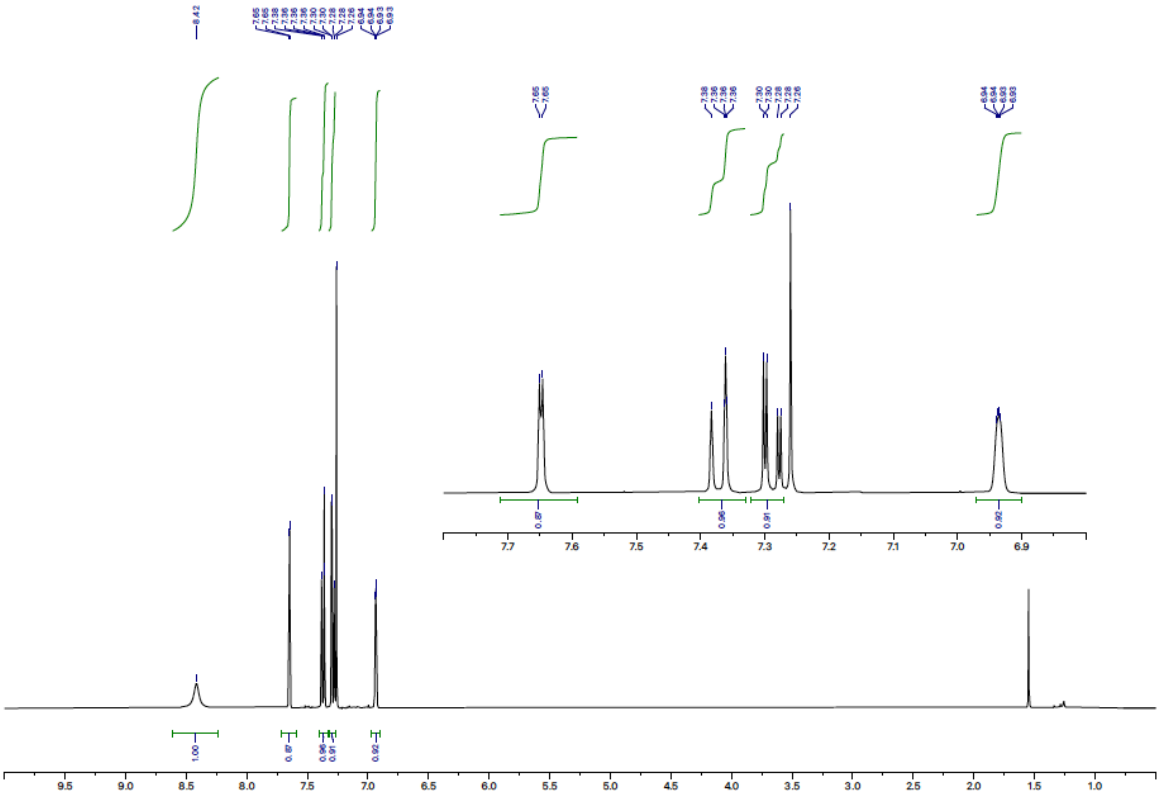


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

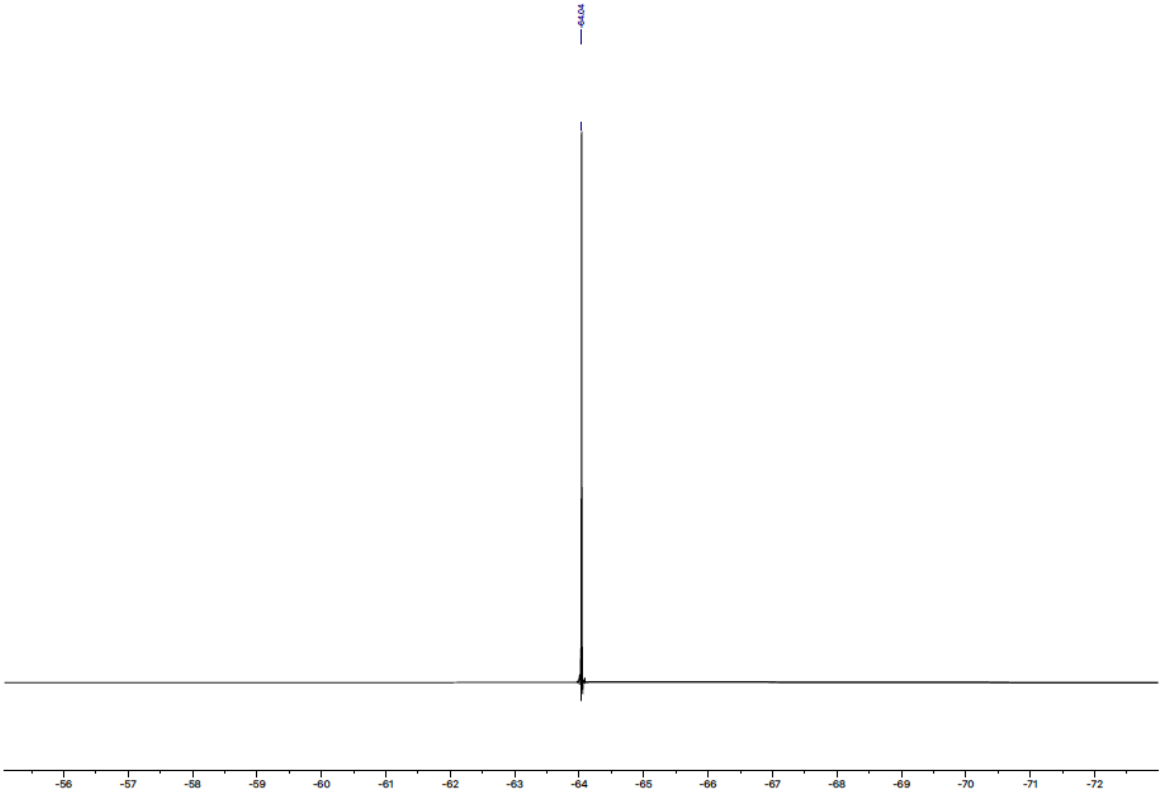


5-Chloro-2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-1*H*-indole (**5aa**)

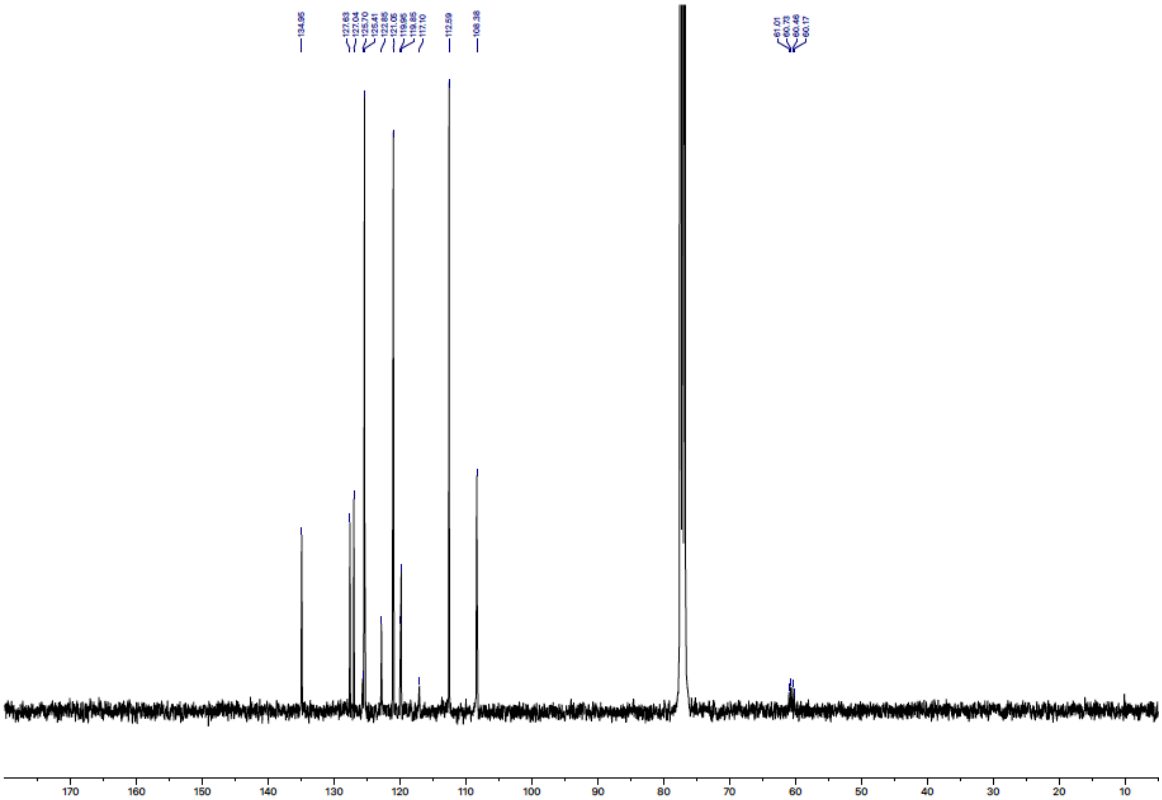
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

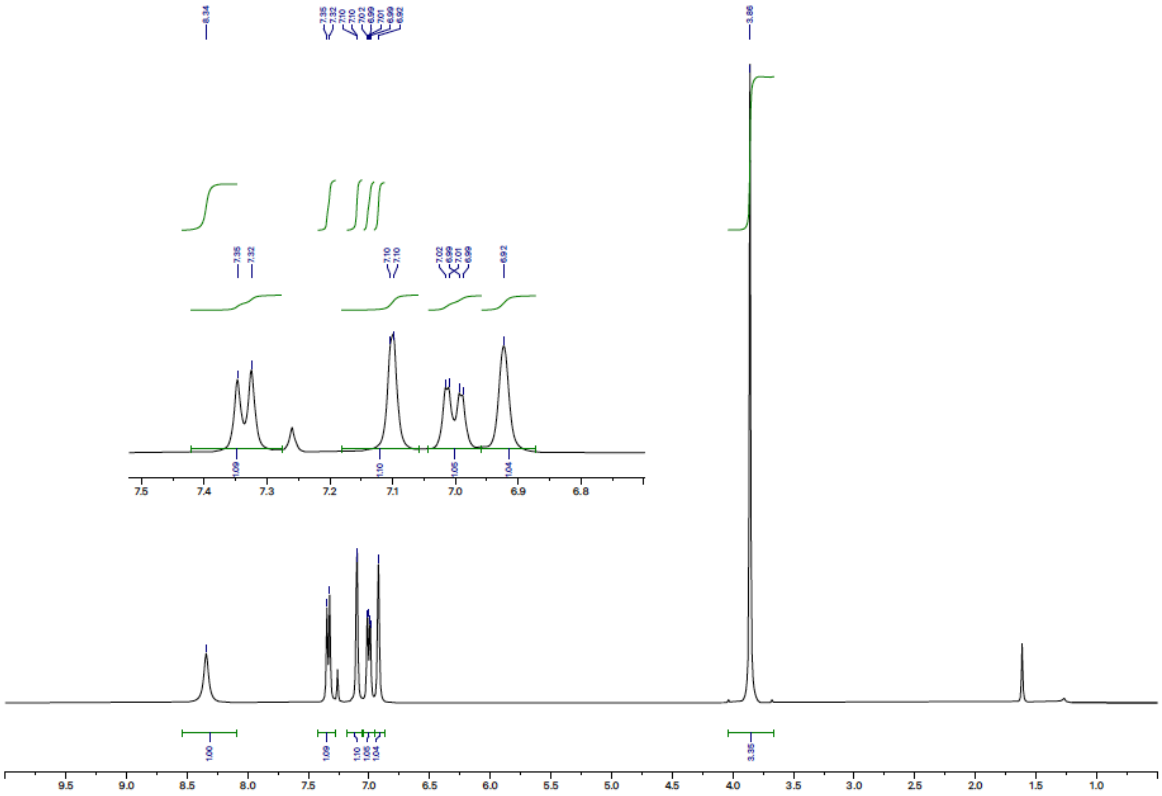


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)

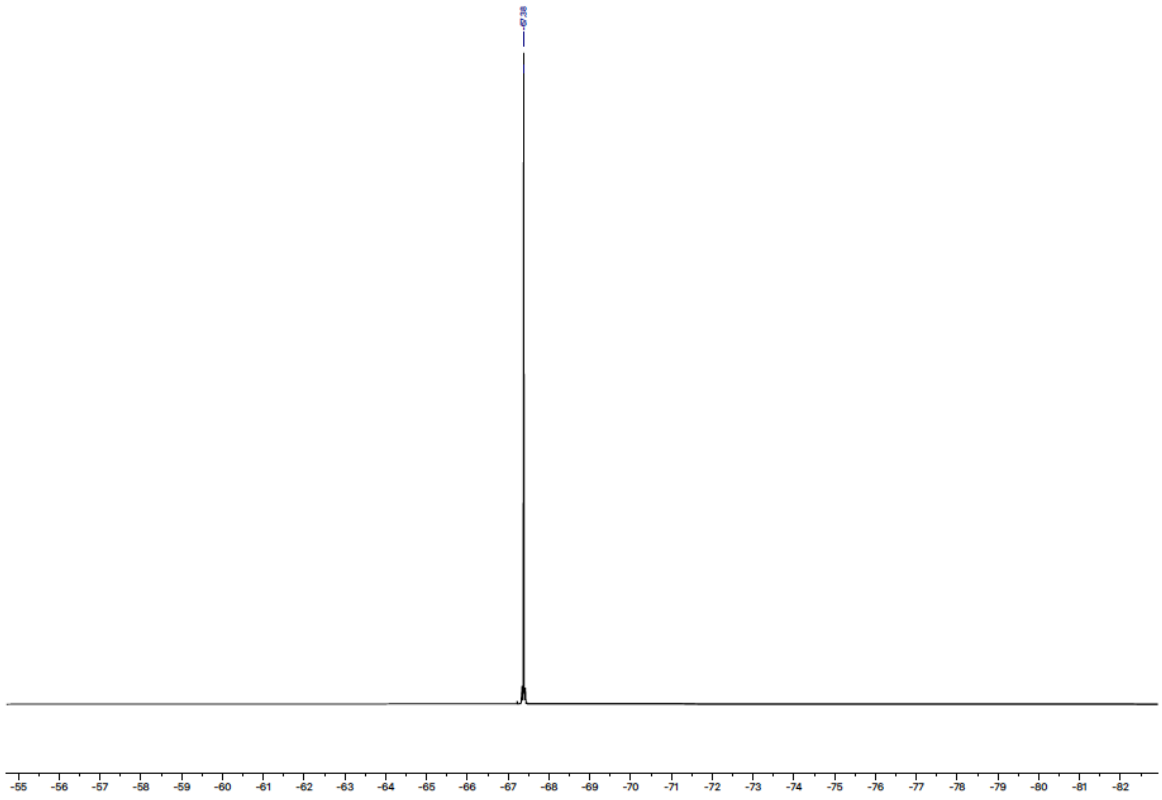


5-Methoxy-2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-1*H*-indole (**5ab**)

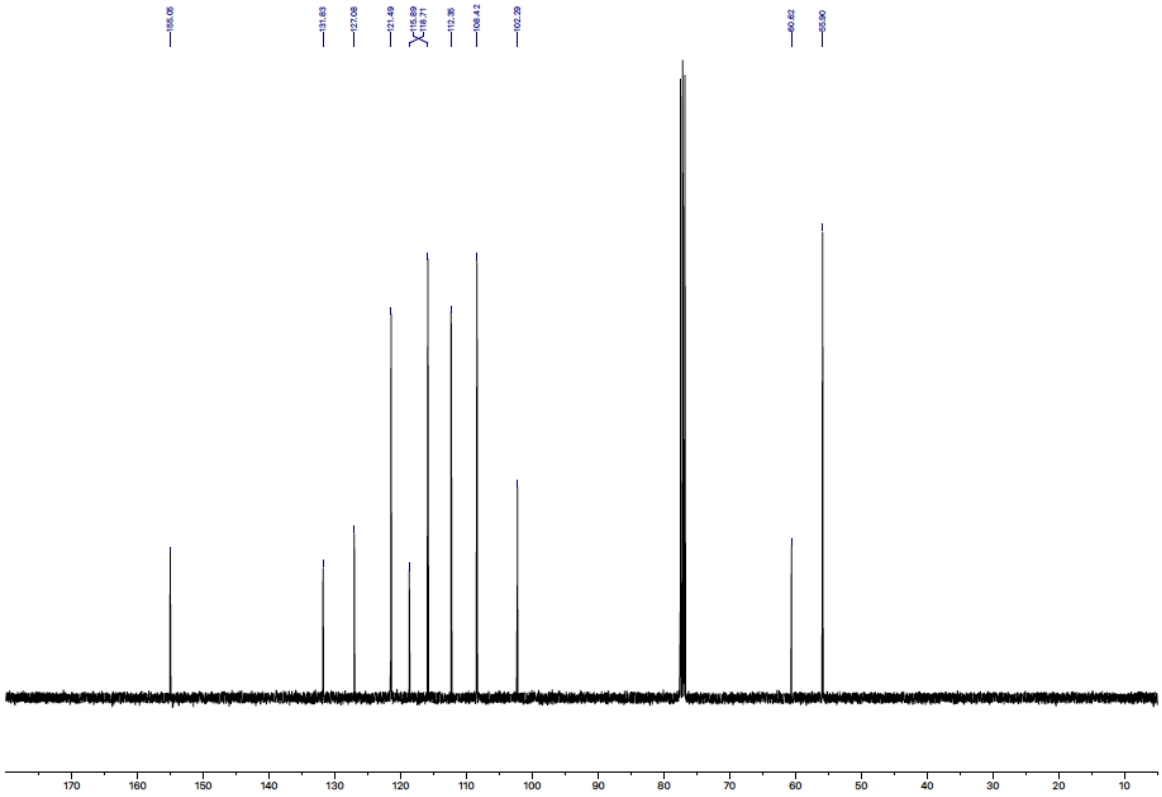
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

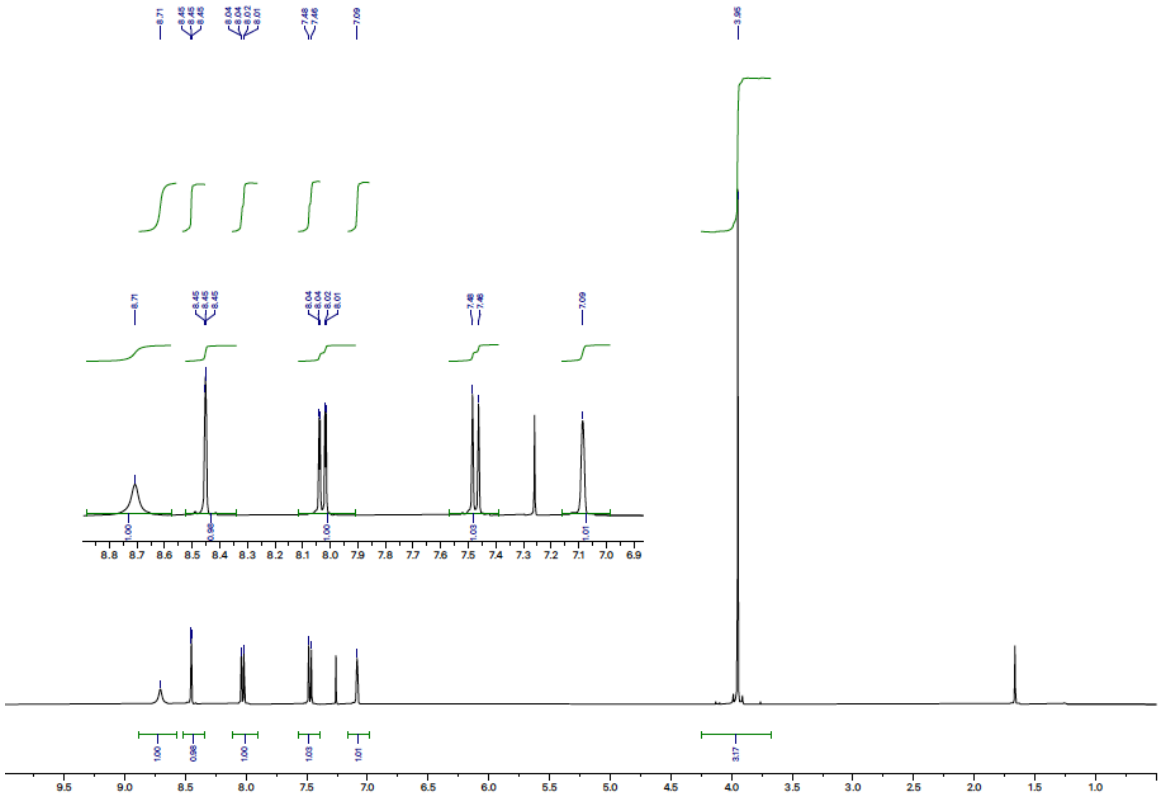


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

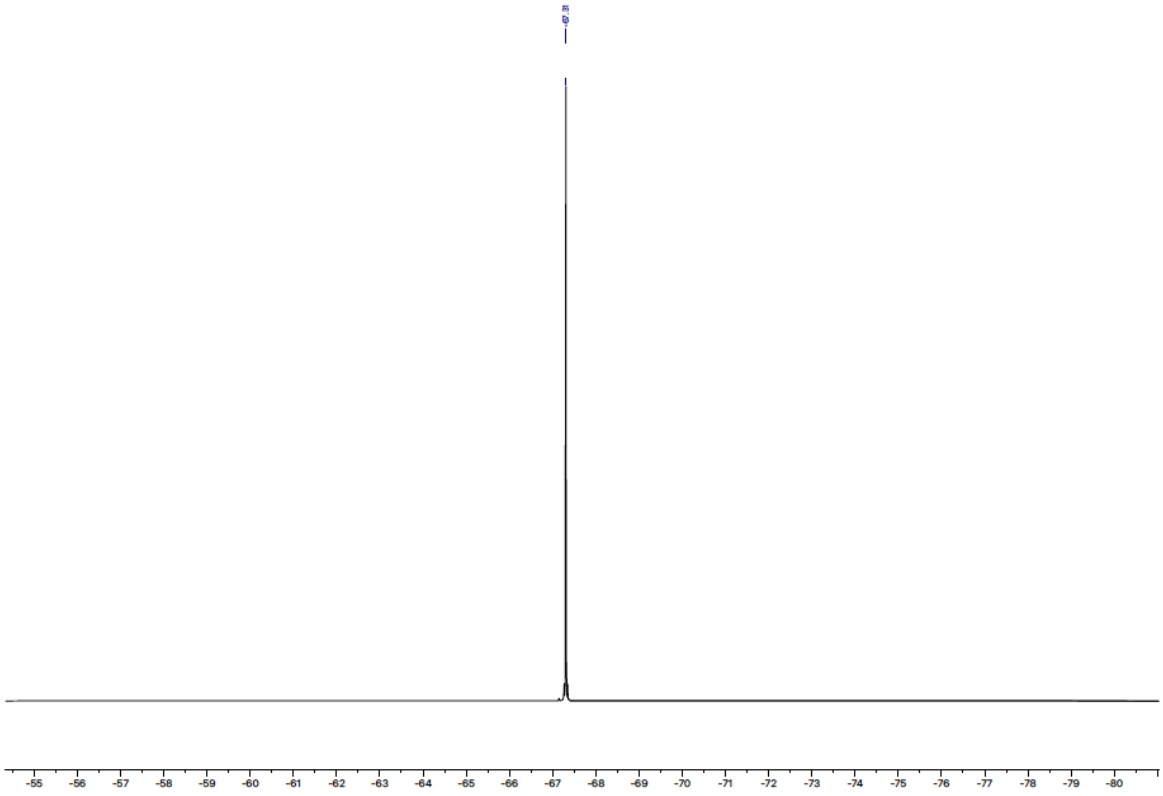


5-Methoxycarbonyl-2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-1*H*-indole (**5ac**)

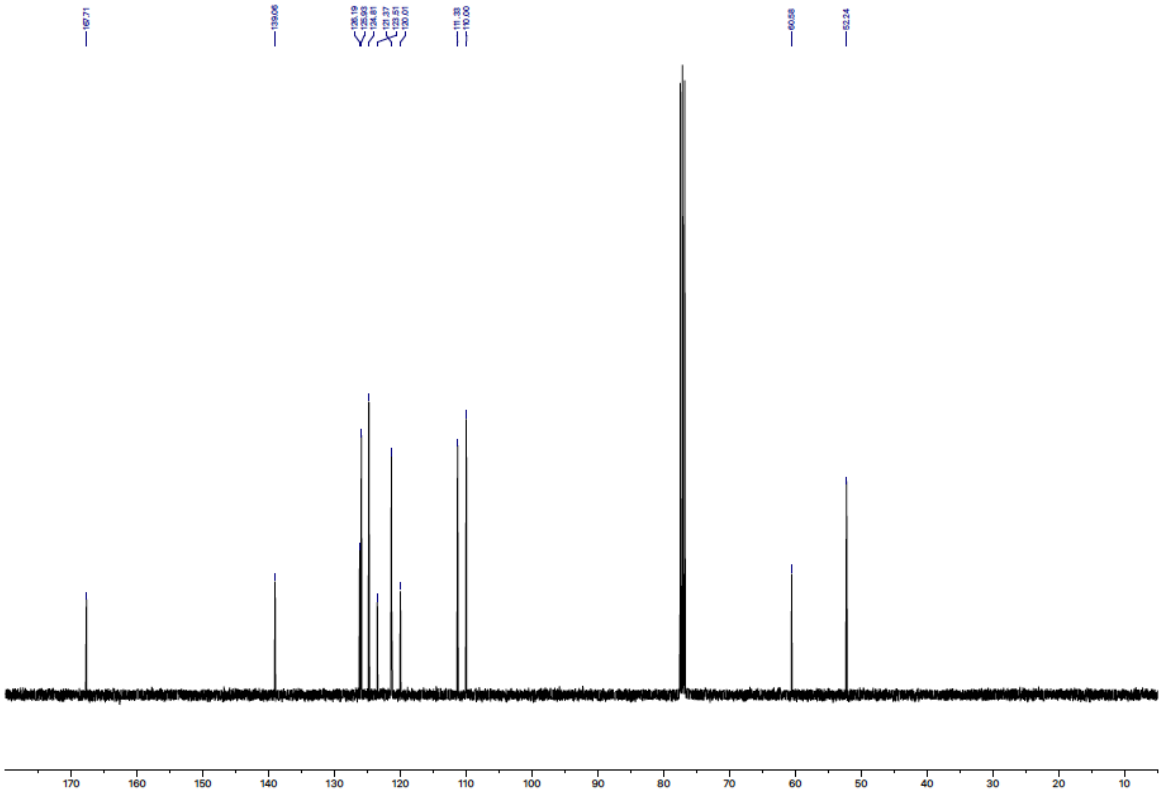
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

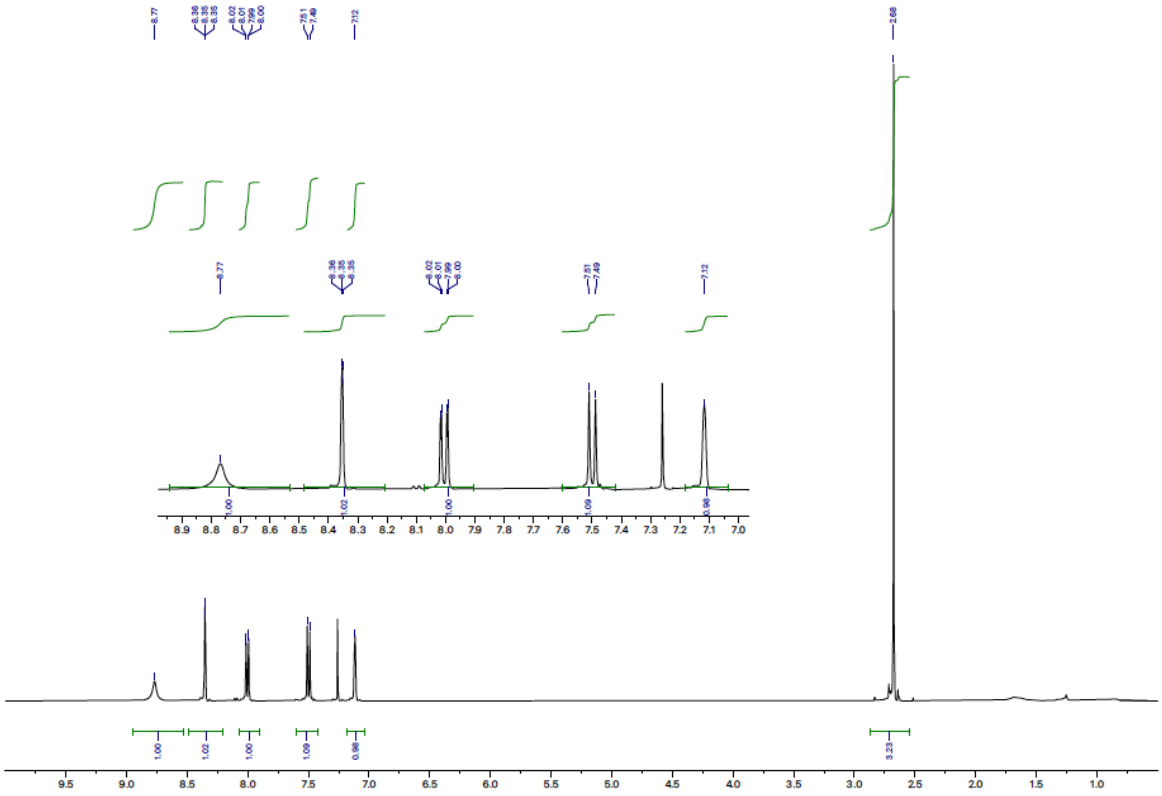


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

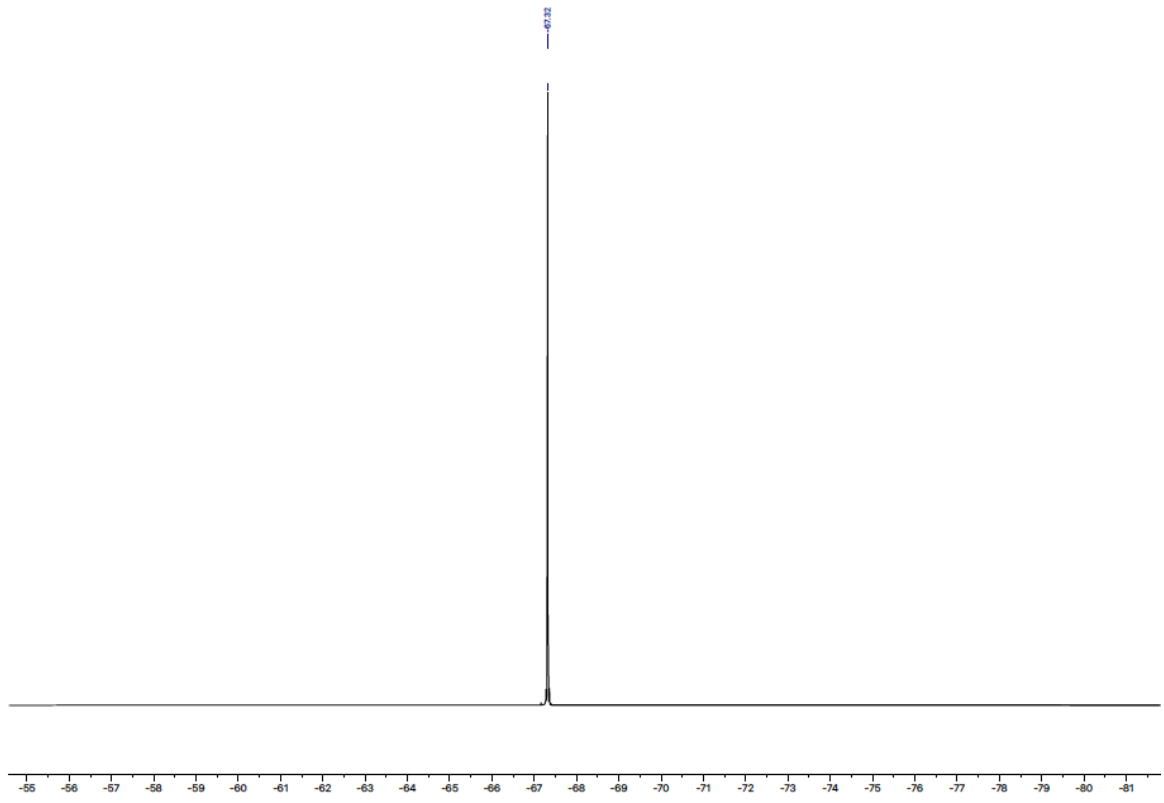


5-Acetyl-2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-1*H*-indole (**5ad**)

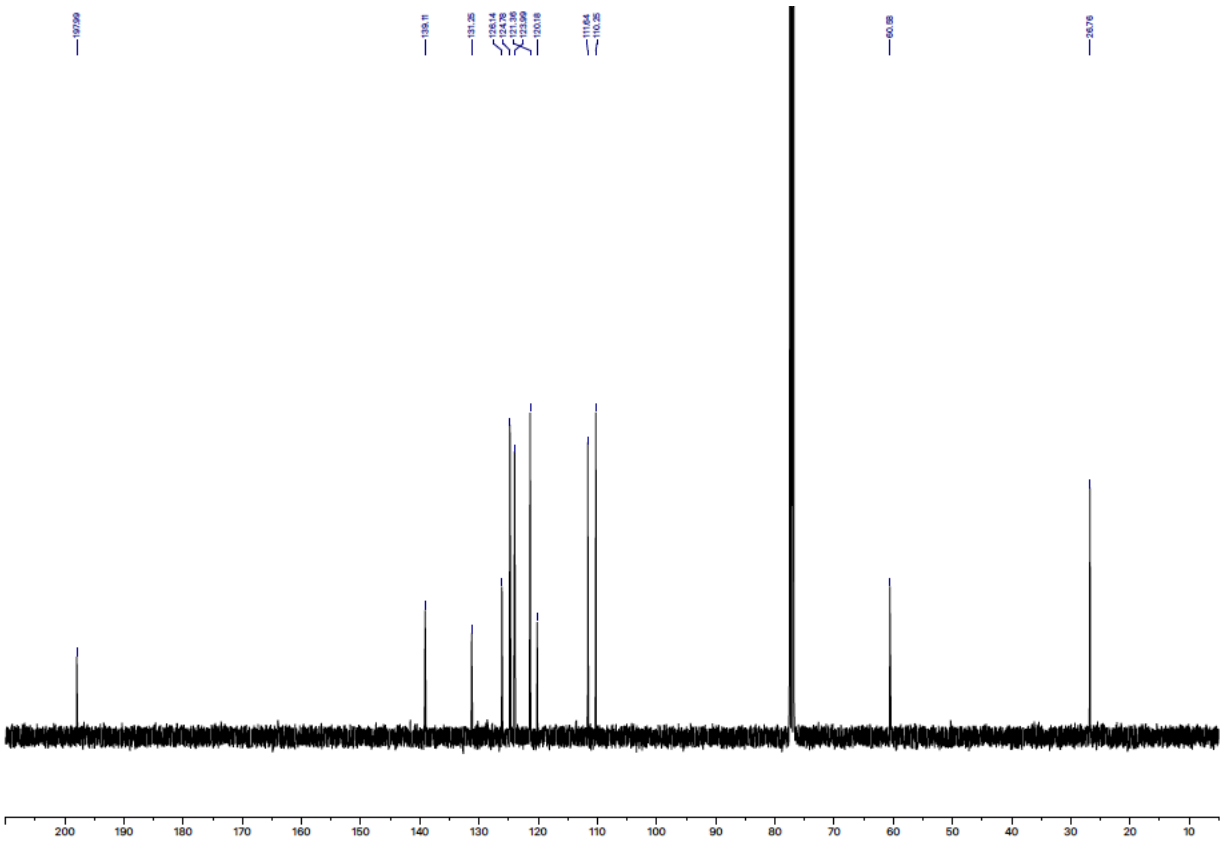
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

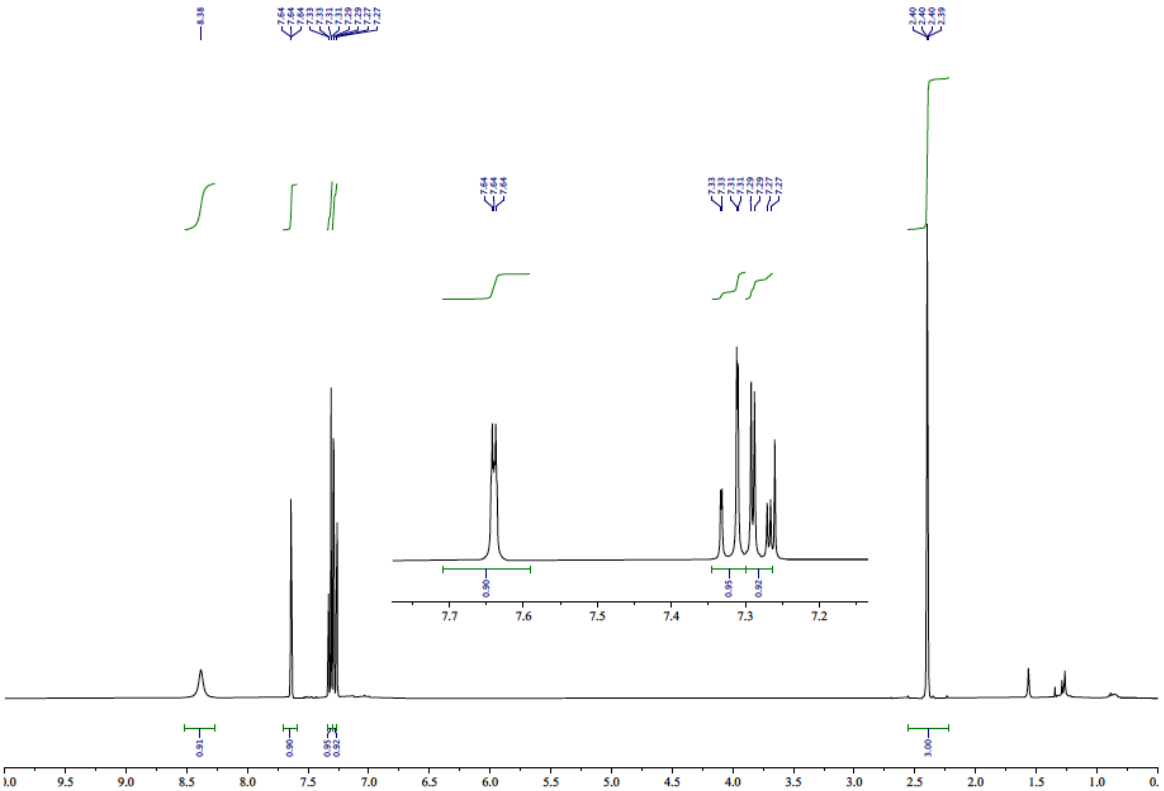


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

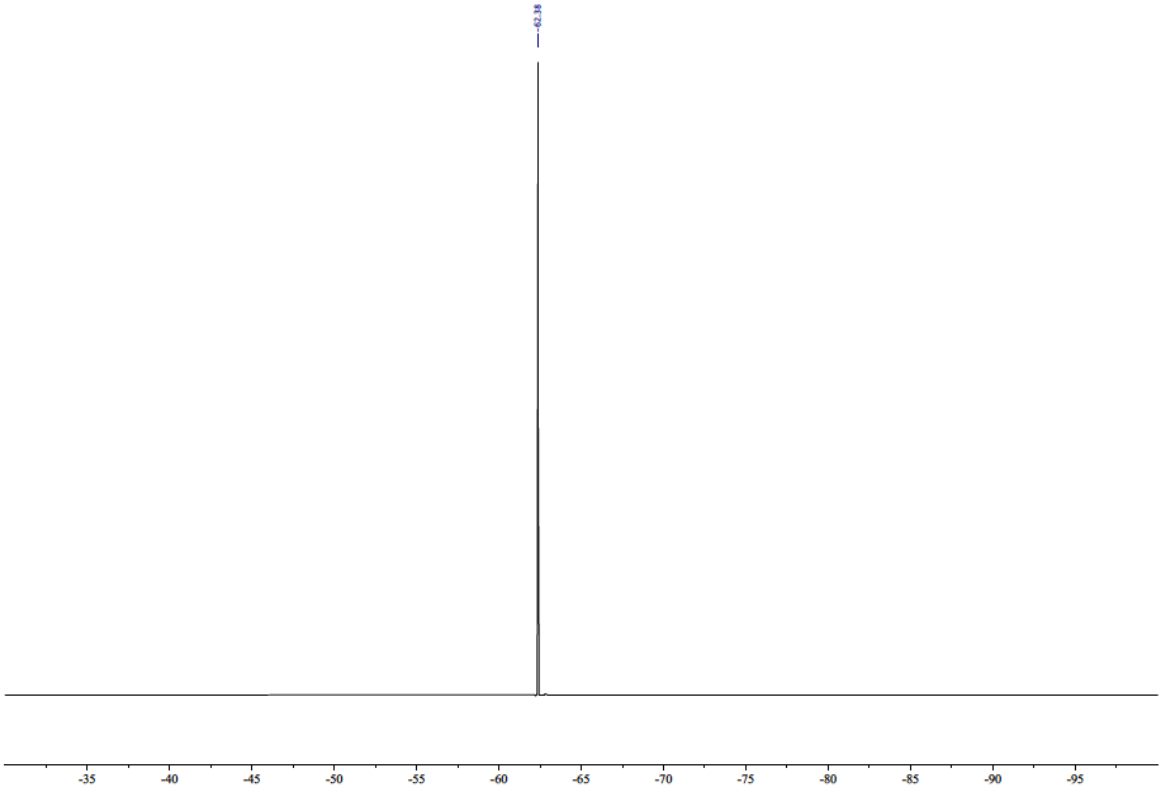


5-Chloro-2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-3-methyl-1*H*-indole (**5ae**)

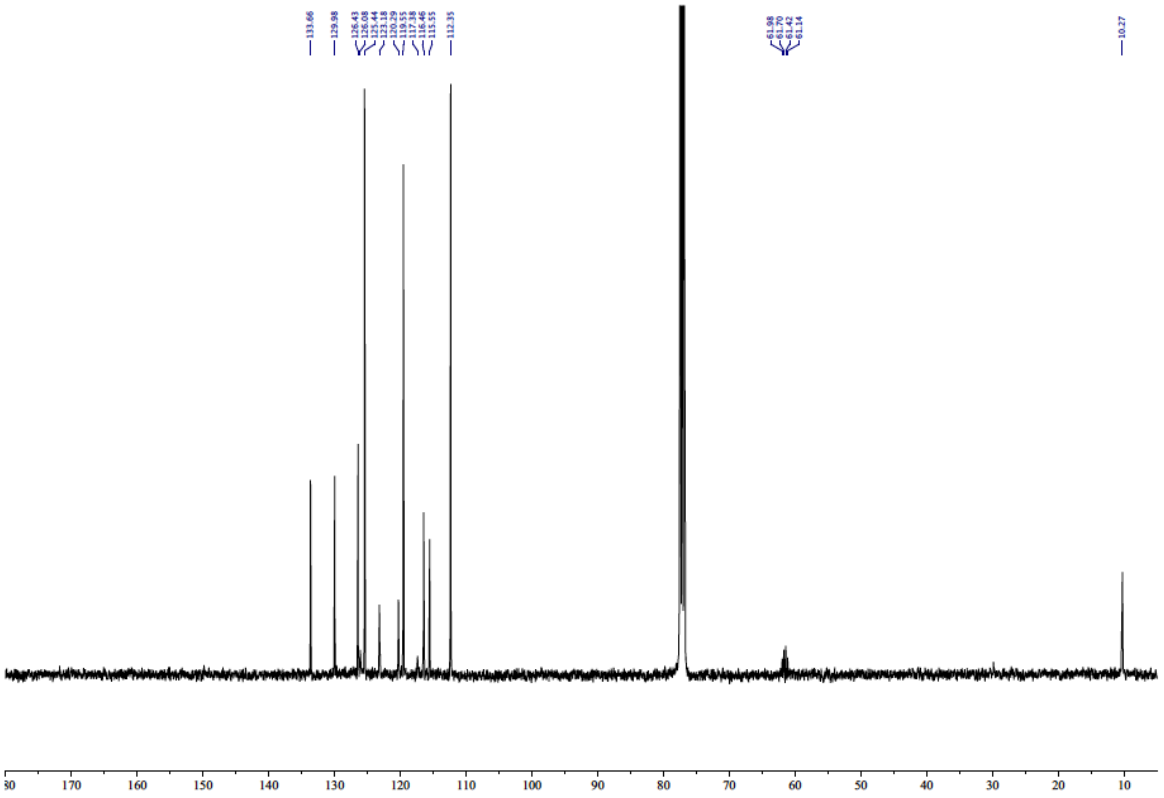
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

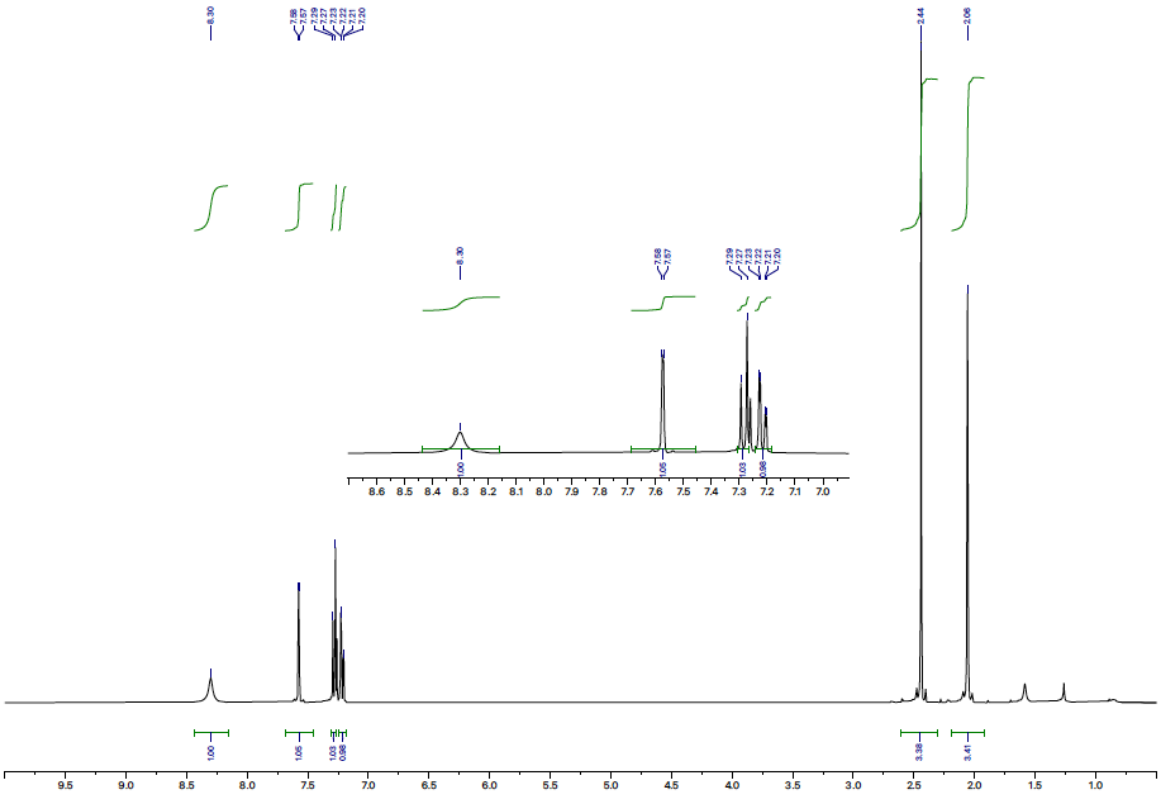


^{13}C {^{1}H} (101 MHz, $CDCl_3$, rt)

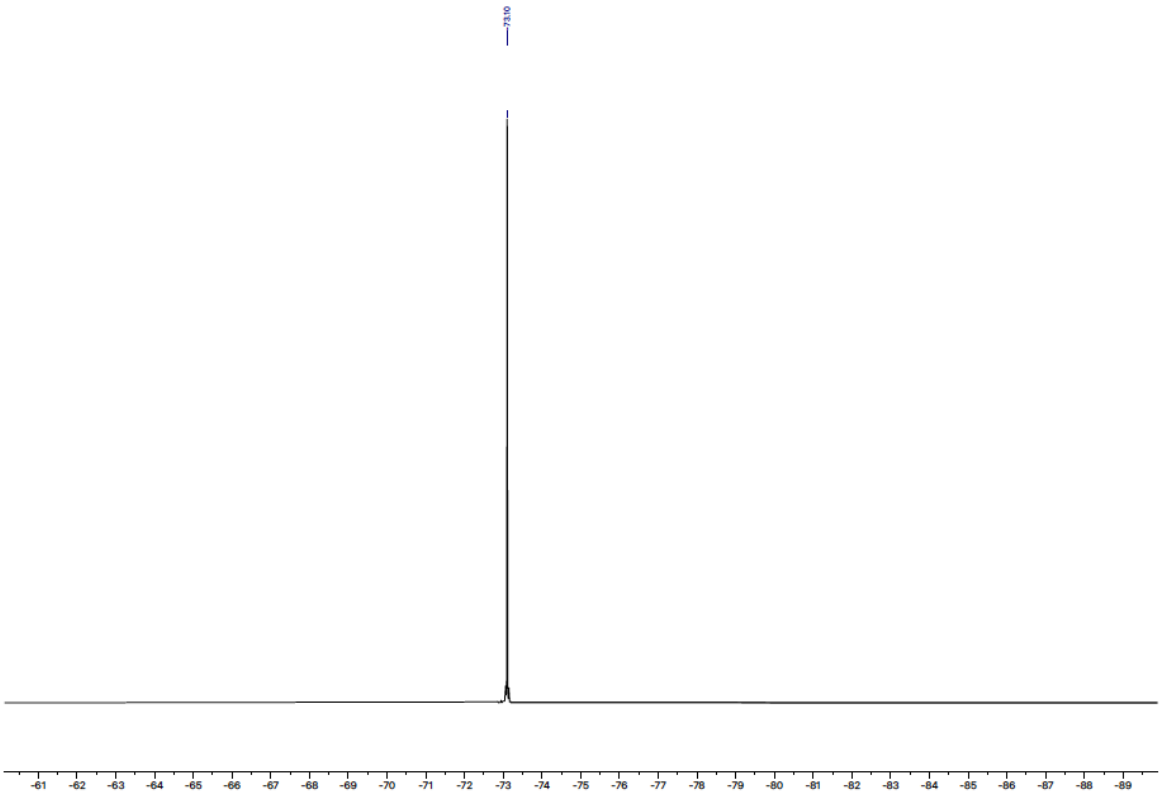


5-Chloro-2-(1,1,1,3,3,3-hexafluoro-2-methyl-propan-2-yl)-3-methyl-1*H*-indole (**5be**)

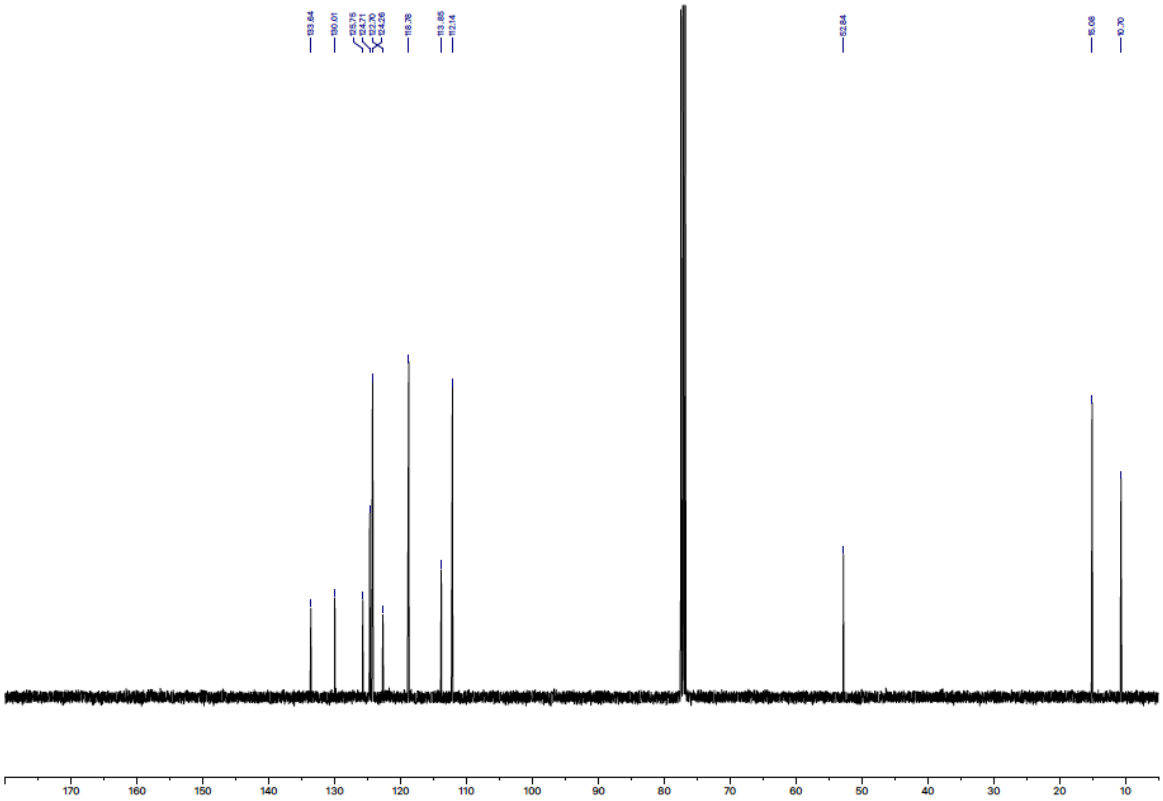
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

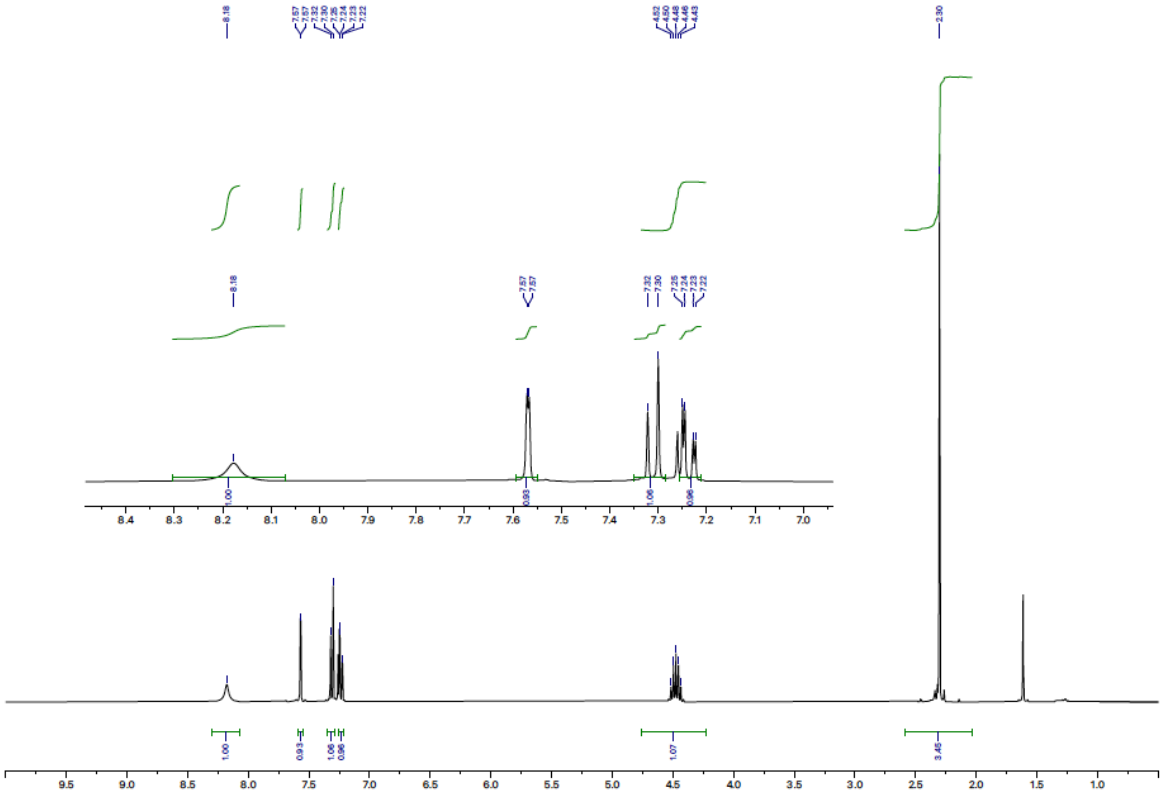


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

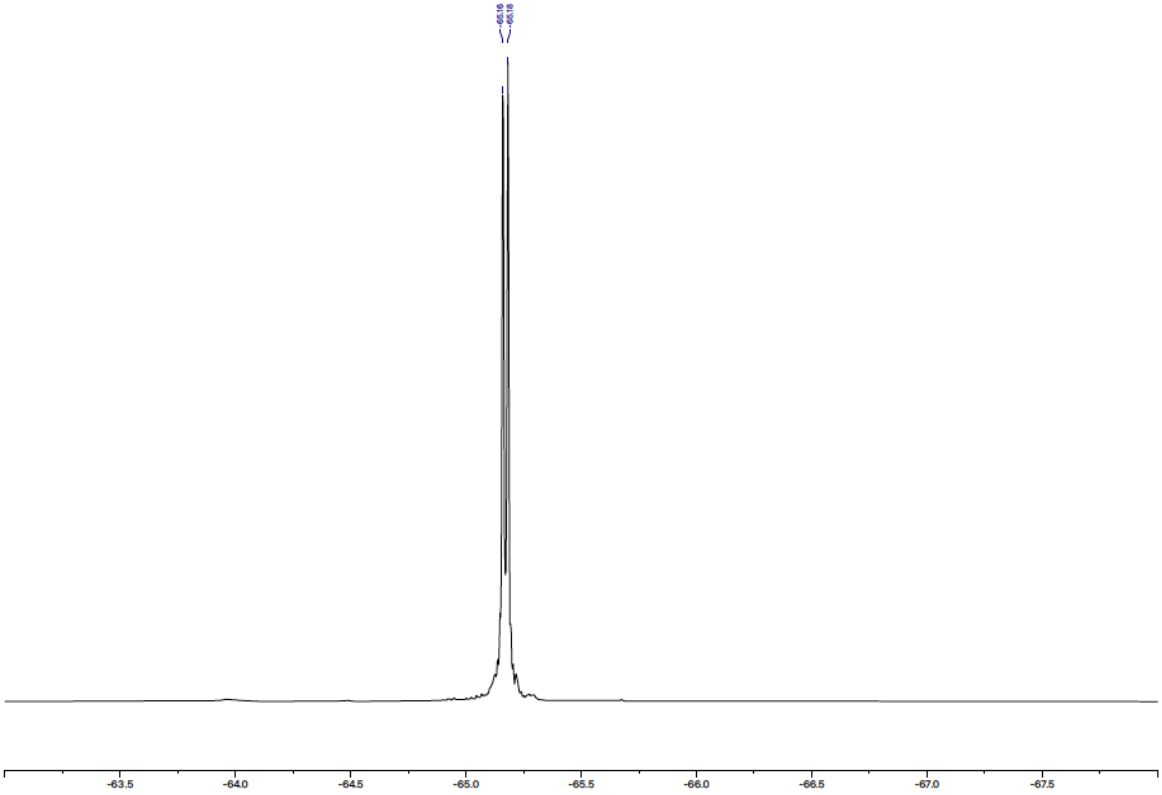


5-Chloro-2-(1,1,1,3,3,3-hexafluoropropan-2-yl)-3-methyl-1*H*-indole (**5de**)

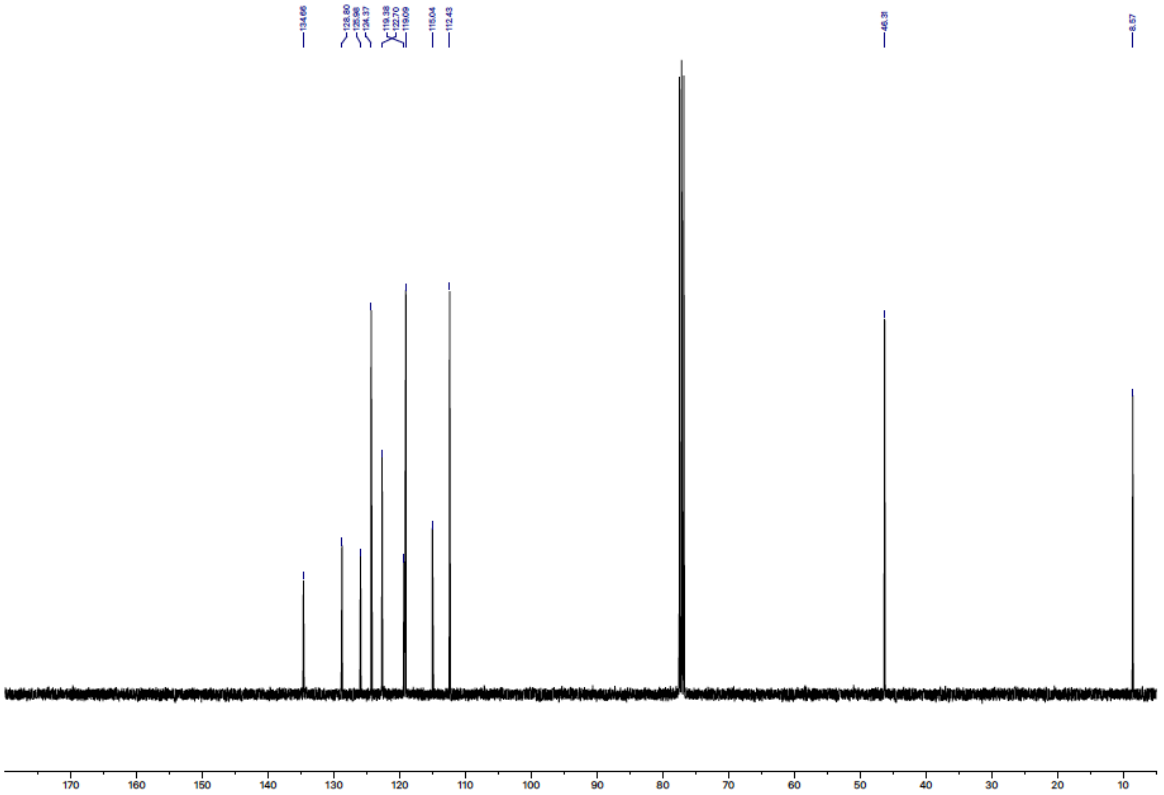
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

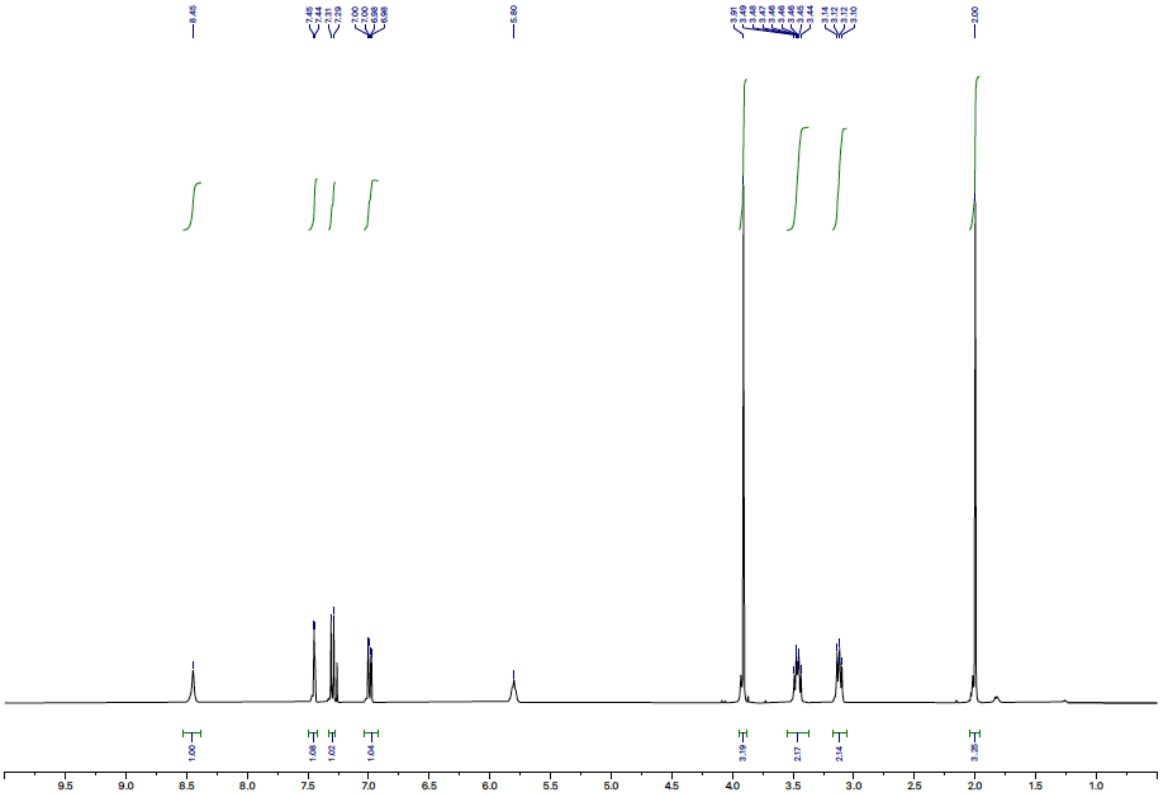


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

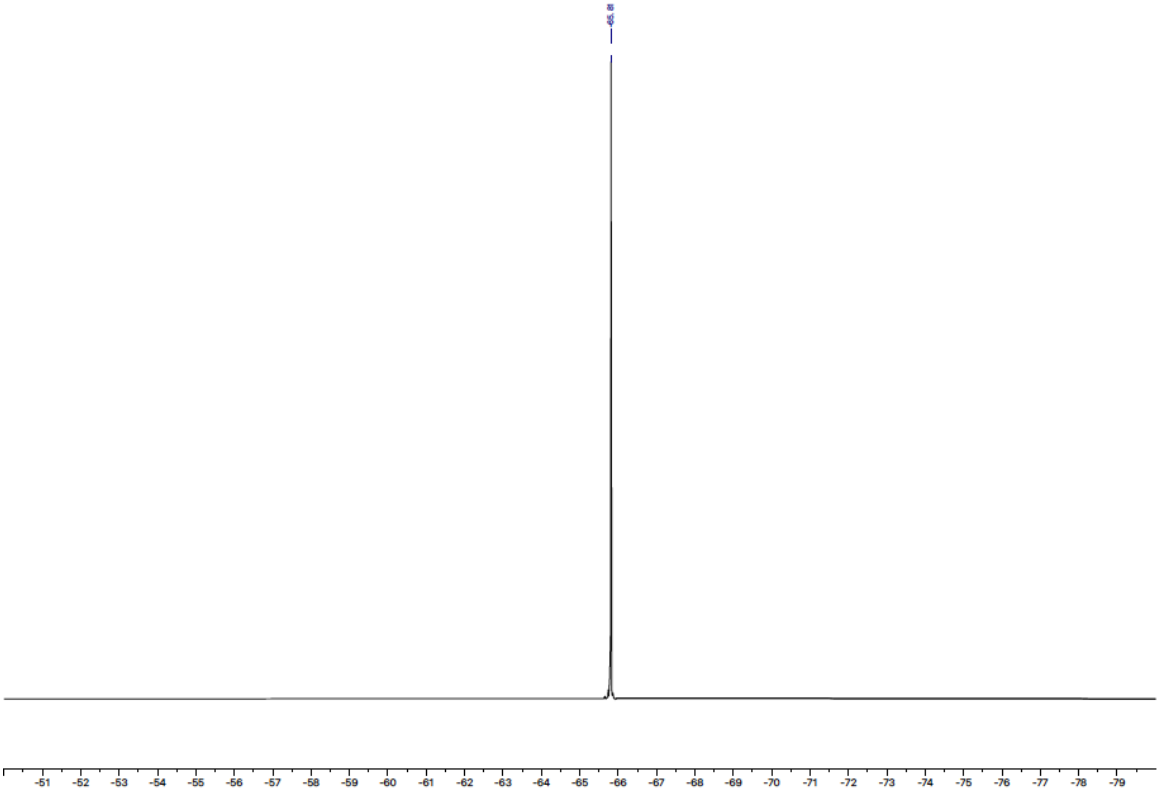


N-(2-(2-(1,1,1,3,3,3-Hexafluoro-2-(trifluoromethyl)propan-2-yl)-5-methoxy-1*H*-indol-3-yl)ethyl)acetamide (**5af**)

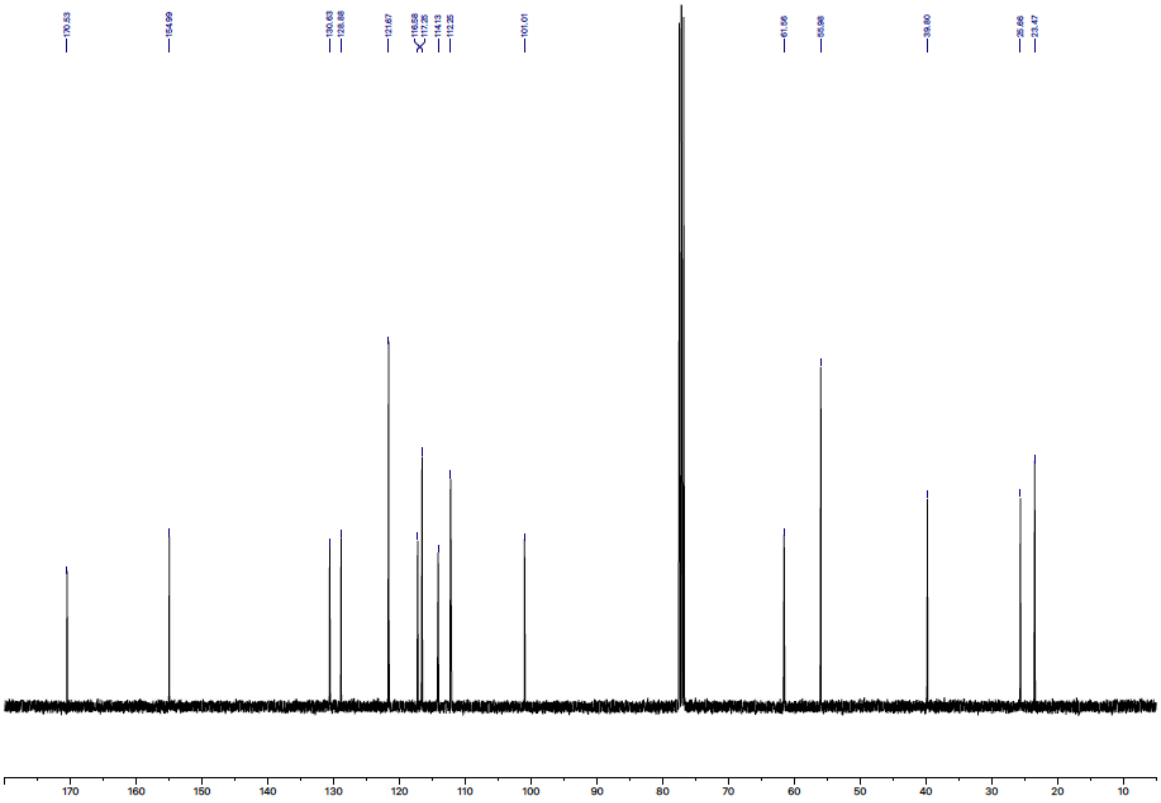
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)

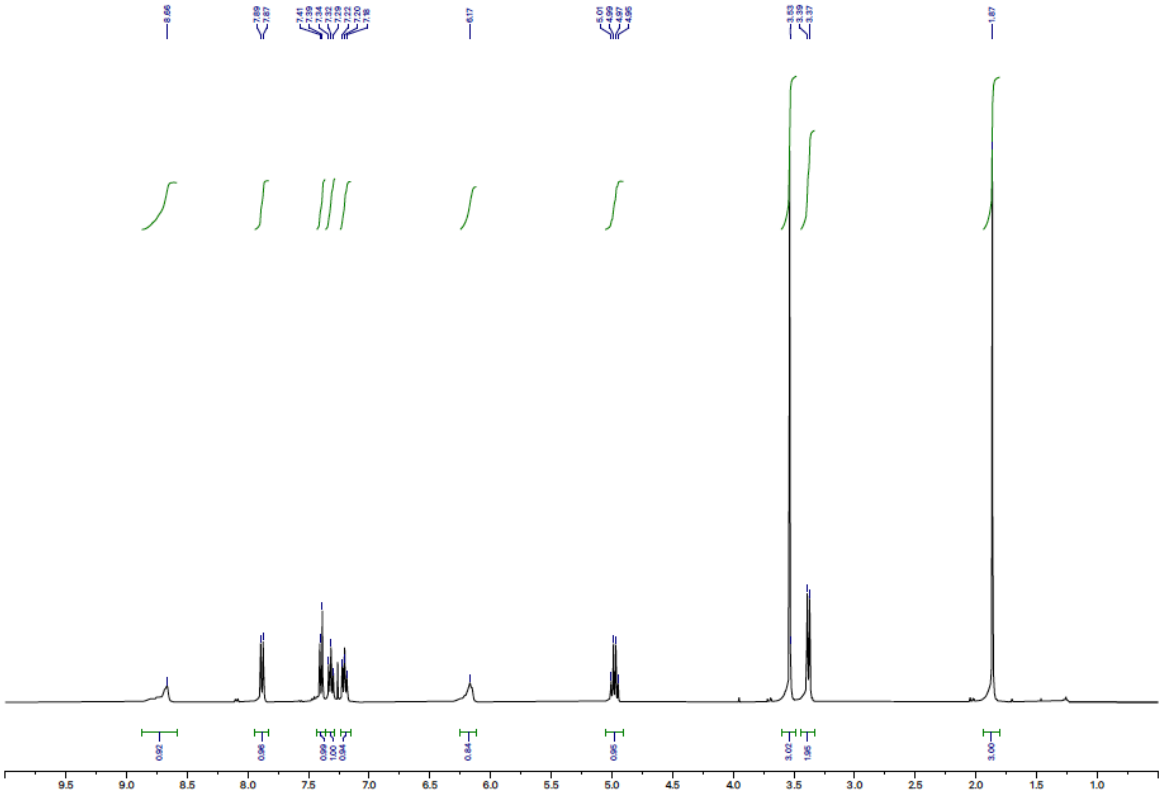


^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)

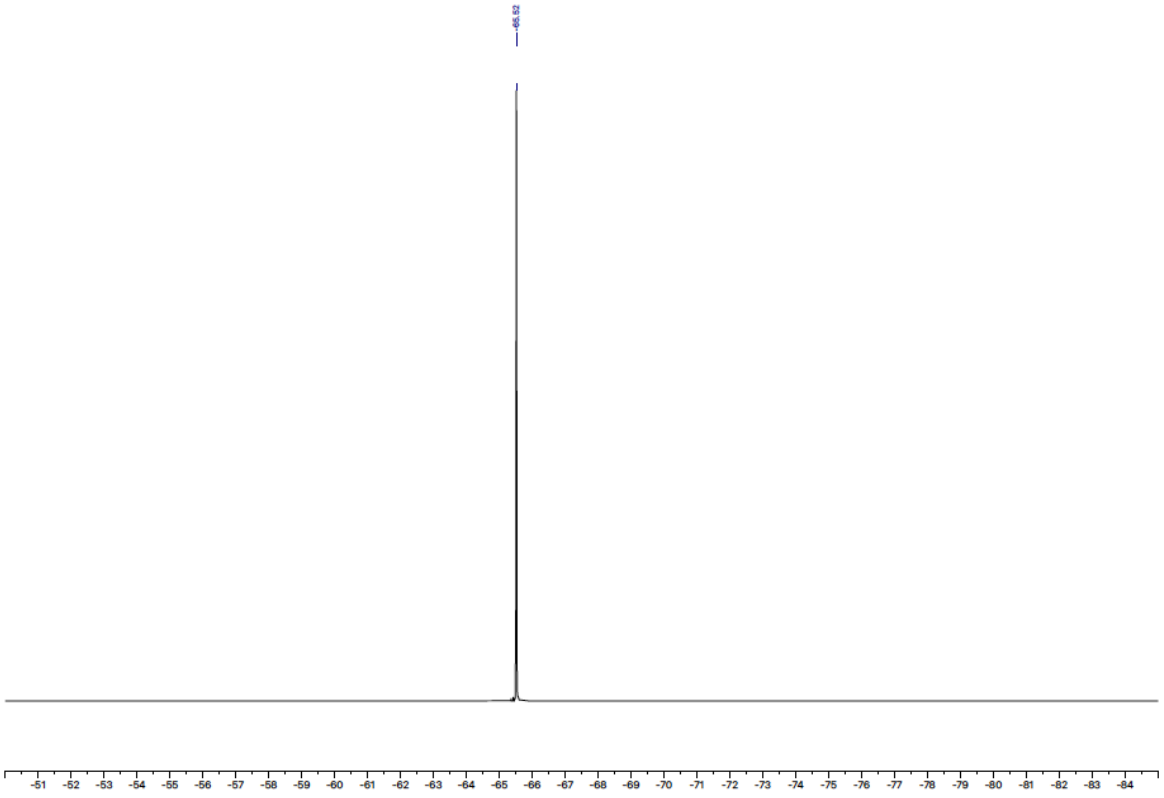


Methyl (*S*)-2-acetamido-3-(2-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-1*H*-indol-3-yl)propanoate (**5ag**)

^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)



^{13}C {^{1}H, ^{19}F} (101 MHz, $CDCl_3$, rt)