**Supporting Information**

# Conformational Features of *N*-Trifluoromethyl Amides and Thioamides

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## 1, General

Melting points were determined by using a Yanaco melting point apparatus MP-S3 and are uncorrected. FT-IR spectra were recorded on a Horiba FT-710 or JASCO FT/IR-4X. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a JEOL ECZ400S, Bruker AV-300M, AV-400M or AV-600 and chemical shifts are expressed in parts per million relative to tetramethylsilane (TMS) or the residual solvent peak (7.24 ppm for $CDCl_3$ ($^{1}H$), 77.0 ppm for $CHCl_3$ ($^{13}C$), 5.32 ppm for $CD_2Cl_2$ ($^{1}H$), 5.95 ppm ($^{1}H$) and 73.8 ppm ($^{13}C$) for 1,1,2,2-tetrachloroethane-$d_2$ ($^{1}H$), 3.31 ppm for $CD_3OD$ ($^{1}H$), 2.49 ppm for DMSO-$d_6$ ($^{1}H$), 39.5 ppm for DMSO-$d_6$ ($^{13}C$), 53.8 ppm for $CD_2Cl_2$ ($^{13}C$). $^{19}F$ NMR spectra were recorded using $C_6H_5CF_3$ (–63.7 ppm) as an internal standard. Mass spectra were measured on a JEOL MS700V or HX110. Silica gel (CHROMATOREX PSQ100 (Fuji Silysia Chemical Co., Inc.)) was used for all chromatographic procedures.

## 2, Synthesis

***N*-trifluoromethylacetanilide (2F, AcCF3).** Phenyl isothiocyanate (270 mg, 2.00 mmol), AgF (1.27 g, 10.0 mmol) and triphosgene (237 mg, 0.799 mmol) were placed in a pressure tube (20 mL) and suspended in $CH_3CN$ (10 mL). The suspension was stirred for 18 h at rt, then poured into $Et_2O$ (40 mL) to quench the reaction after confirming the consumption of phenyl isothiocyanate by TLC. The mixture was stirred for 10 min, then filtered through Celite, which was washed with $Et_2O$. The filtrate was evaporated. The residue was re-suspended in $Et_2O$ and filtered through Celite again, and the filtrate was evaporated under reduced pressure. The volatile carbonyl fluoride, obtained as a crude brown oil, was used without further purification. A solution of this oil (241 mg) in toluene (5 mL) was placed in a two-necked flask (10 mL) and MeMgBr (1.0 M in THF, 1.6 mL, 1.6 mmol) was added via a syringe on an ice bath. The mixture was stirred for 1 h at rt, then the reaction was quenched by adding sat. $NH_4Cl$ aq. (15 mL). The resulting mixture was extracted with AcOEt (15 mL x 2), and the combined organic layer was dried over $Na_2SO_4$, filtered, then evaporated under reduced pressure. The crude oil was purified by silica gel column chromatography (eluent $CH_2Cl_2$:hexane = 1:5) to afford **2F** as a colorless oil (142 mg, 35%, 2 steps). $^{1}H$-NMR (400 MHz, $CDCl_3$) δ : 7.48–7.49 (m, 3H), 7.26–7.30 (m, 2H), 2.00 (s, 3H, $CH_3$). $^{13}C\{^{1}H\}$-NMR (150 MHz, $CDCl_3$) δ : 170.2 (*C*=O), 135.9, 129.9, 129.8, 129.3, 120.0 (q, $J$ = 264 Hz, *C*$F_3$), 24.0 (m, *C*$H_3$CO). $^{19}F$-NMR (376 MHz,

$CDCl_3$) δ : –55.3. IR (KBr): 3864, 1729, 1594, 1492, 1448, 1373, 1313, 1270, 1238, 1184 $cm^{-1}$. APCI -HRMS: calcd for $C_9H_9F_3NO$ [M+$H^+$] 204.0631, found 204.0631.

***N*-trifluoromethyl-*N*-(*p*-bromophenyl)acetanilide (6F).** *p*-Bromophenyl isothiocyanate (428 mg, 2.00 mmol), AgF (1.27 g, 10.0 mmol) and triphosgene (237 mg, 0.799 mmol) were placed in a pressure tube (20 mL), and suspended in $CH_3CN$ (10 mL). The suspension was stirred for 21 h at rt, then poured into $Et_2O$ (40 mL) to quench the reaction after confirming the consumption of phenyl isothiocyanate by TLC. The mixture was stirred for 10 min, then filtered though Celite, which was washed with $Et_2O$. The filtrate was evaporated. The residue was re-suspended in $Et_2O$ and filtered through Celite again, and the filtrate was evaporated under reduced pressure. A solution of the obtained crude brown oil (520 mg) in toluene (5 mL) was placed in a two-necked flask (10 mL) and MeMgBr (1.0 M in THF, 2.2 mL, 2.2 mmol) was added via a syringe on an ice bath. The mixture was stirred for 1 h at rt, then the reaction was quenched by adding sat. $NH_4Cl$ aq. (15 mL). The resulting mixture was extracted with AcOEt (15 mL x 2), and the combined organic layer was dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The obtained crude oil was purified by silica gel column chromatography (eluent AcOEt:hexane = 1:10) to afford **6F** as a colorless solid (184 mg, 33%, 2 steps). Recrystallization from hexane afforded colorless plates. mp 51.1–52.5 ºC. $^1$H-NMR (400 MHz, $CDCl_3$) δ : 7.62 (d, *J* = 6.9 Hz, 2H, $Ar_{meta}$), 7.16 (d, *J* = 6.9 Hz, 2H, $Ar_{ortho}$), 2.08 (s, 3H, $CH_3$). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$) δ : 169.7 (C=O), 134.8 ($Ar_{ipso}$), 133.2 ($Ar_{meta}$), 130.9 ($Ar_{ortho}$), 124.1 ($Ar_{C\text{-}Br}$), 119.9 (q, *J* = 264 Hz), 24.0 (q, *J* = 2.9 Hz, *C*$H_3$). $^{19}$F-NMR (282 MHz, $CDCl_3$) δ : –54.8. IR (KBr): 2923, 1909, 1720, 1490, 1428, 1380, 1317, 1274, 1238, 1170 $cm^{-1}$. EI-HRMS: calcd for $C_9H_7{}^{81}BrF_3NO$ [$M^+$] 282.9638, found 282.9648.

***N*-trifluoromethylbenzanilide (7F).** Phenyl isothiocyanate (238 µl, 2.01 mmol), AgF (1.27 g, 10.0 mmol) and triphosgene (237 mg, 0.799 mmol) were placed in a pressure tube (20 mL), and suspended in $CH_3CN$ (10 mL). The suspension was stirred for 18 h at rt, then poured into $Et_2O$ (40 mL) to quench the reaction after confirming the consumption of phenyl isothiocyanate by TLC. The mixture was stirred for 10 min, then filtered through Celite, which was washed with $Et_2O$. The filtrate was evaporated. The residue was re-suspended in $Et_2O$ and filtered through Celite again, and the filtrate was evaporated under reduced pressure. The obtained crude brown oil (193 mg) in toluene (4 mL) was placed in a two-necked flask (10 mL) and PhMgBr (1.0 M in THF, 1.06 mL, 1.12 mmol) was added via a syringe under an ice bath. The mixture was stirred for 20 min at rt, then the reaction was quenched by adding sat. $NH_4Cl$ aq. (15 mL). The resulting mixture was extracted with AcOEt (15 mL x 2), and the combined organic layer was

dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The crude oil was purified by silica gel column chromatography (eluent $CH_2Cl_2$:hexane = 1:2) to afford **7F** as a colorless solid (139 mg, 35%, 2 steps). Recrystallization from hexane afforded colorless plates. mp 50.1 – 51.1 ºC. $^1$H-NMR (400 MHz, $CDCl_3$) δ : 7.47 (d, *J* = 7.2 Hz, 2H, C-$Ph_{ortho}$), 7.29–7.31 (m, 4H), 7.20–7.26 (m, 4H). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$) δ : 170.2 (C=O), 136.4 (C-$Ph_{ipso}$), 133.6 (d, *J* = 1.9 Hz, N-$Ph_{ipso}$), 131.5 (C-$Ph_{para}$), 130.0 (N-$Ph_{ortho}$), 129.4 (N-$Ph_{meta}$), 129.2 (N-$Ph_{para}$), 129.0 (C-$Ph_{ortho}$), 128.0 (C-$Ph_{meta}$), 120.4 (q, *J* = 263 Hz). $^{19}$F-NMR (283 MHz, $CDCl_3$) δ : –58.0. IR (KBr): 1698, 1594, 1535, 1490, 1448, 1319, 1292, 1259, 1193, 1135 $cm^{-1}$. EI-HRMS: calcd for $C_{14}H_{10}F_3NO$ [$M^+$] 265.0709, found 265.0712.

***N*-trifluoromethyl-*N*-pentafluorophenylbenzanilide (8F).** The solution of pentafluorophenyl isothiocyanate (1.27 g, 10.0 mmol) in $CH_3CN$ (10 mL) was added to AgF (1.27 g, 10.0 mmol) and triphosgene (237 mg, 0.80 mmol) in a 50 mL two-neck flask on an ice bath. After 24 h at rt, the reaction did not progress further, as checked by TLC, and $Et_2O$ (50 mL) was added, then the mixture was filtered through Celite. The filtrate was evaporated under reduced pressure, and the residue was suspended in $Et_2O$ (50 mL), and filtered through Celite. After the second filtration, the acid fluoride was obtained as a colorless crude oil (726 mg). The oil was dissolved in toluene (5 mL) in a 100 mL two-necked flask and PhMgBr (1.03 M in THF, 2.0 mL, 2.0 mmol) was added on an ice bath. The mixture was stirred for 10 min at rt, then the reaction was quenched by adding $NH_4Cl$ aq. (50 mL) after confirming the consumption of acid fluoride by TLC. The mixture was extracted with $Et_2O$ (50 mL). The organic layer was washed with brine (50 mL), dried over $Na_2SO_4$, filtered and evaporated under reduced pressure. The obtained crude oil was purified by silica gel column chromatography (eluent $CH_2Cl_2$:hexane = 1:3) to give **8F** as a colorless oil (73 mg, 10%). Recrystallization from hexane in a refrigerator afforded colorless prisms. mp 59.0 – 60.2 ºC. $^1$H-NMR (600 MHz, $CDCl_3$) δ : 7.51 (d, *J* = 7.8 Hz, 2H, $Ph_{ortho}$), 7.49 (t, *J* = 7.8 Hz, 1H, $Ph_{para}$), 7.37 (dd, *J* = 7.8, 7.8 Hz, 2H, $Ph_{meta}$). $^{13}C\{^1H\}$-NMR (150 MHz, $CDCl_3$) δ : 168.4, 144.8 (*J* = 239 Hz, $ArF_{para}$), 142.7 (*J* = 242 Hz, $ArF_{para}$), 137.7 (*J* = 242 Hz, $ArF_{meta}$), 132.7, 132.1, 128.7, 127.4, 119.5 (q, *J* = 267 Hz, *C*$F_3$), 111.7(t, *J* = 15 Hz, $ArF_{ipso}$). $^{19}$F-NMR (376 MHz, $CDCl_3$) δ : –58.3 (s, 3F, $CF_3$), –143.5 (m, 2F, $ArF_{ortho}$), –149.7 (t, *J* = 18.0 Hz, 1F, $ArF_{para}$), –160.9 (m, 2F, $ArF_{meta}$). IR (KBr): 3420, 2924, 1720, 1520, 1282, 1236, 1188, 1145, 1101, 1047, 994, 876, 818, 706 $cm^{-1}$. FAB-HRMS: calcd for $C_{14}H_6F_8NO$ $[M+H]^+$ 356.0316, found 356.0304.

***N*-Trifluoromethylpentafluorobenzoylbenzanilide (9F)** To a solution of phenyl isothiocyanate (135 mg, 1.00 mmol) in $CH_2Cl_2$ (4.0 mL) were added AgF (634 mg, 5.00 mmol) and 2,4,6-collidine (790 μl, 6.00 mmol) on an ice bath. Then, pentafluorobenzoyl chloride (144 μl, 1.00

mmol) was added, and the mixture was stirred for 24 h at rt. After that, the reaction did not progress further, as checked by TLC. $CH_2Cl_2$ (50 mL) was added and the mixture was filtered through Celite. The filtrate was washed with 2 N HCl (50 mL) and brine (50 mL), dried over $Na_2SO_4$ and filtered. The organic layer was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent $CH_2Cl_2$:hexane = 1:10 to 1:5) to give **9F** as a colorless oil (173 mg, 49%). Recrystallization from hexane on an ice bath afforded colorless prisms. mp 30.0 – 30.5 ºC. $^1$H-NMR (600 MHz, $CDCl_3$) δ : 7.43 (t, *J* = 7.2 Hz, 1H, $Ph_{para}$), 7.39 (dd, *J* = 7.2, 7.2 Hz, 2H, $Ph_{meta}$), 7.31 (d, *J* = 7.2 Hz, 2H, $Ph_{ortho}$). $^{13}$C{$^1$H}-NMR (150 MHz, $CDCl_3$) δ : 158.1, 141.3–143.2 (m, 2C, $ArF_{ortho,\ meta}$), 137.1 (*J* = 239 Hz, $ArF_{para}$), 133.8, 130.9, 130.0, 128.8, 117.6 (q, *J* = 266 Hz, *C*$F_3$), 110.9 (t, *J* = 19 Hz, $Ph_{ipso}$). $^{19}$F-NMR (376 MHz, $CDCl_3$) δ : –57.1 (brs, 3F, $CF_3$), –140.5 (d, *J* = 13.5 Hz, 2F, $Ar_{ortho}$), –150.4 (tt, *J* = 20.2, 2.6 Hz, 1F, $Ar_{para}$), –160.4 (m, 2F, $Ar_{meta}$). IR (KBr): 3420, 2925, 1720, 1520, 1282, 1236, 1188, 1145, 1047, 994, 876, 818 cm$^{-1}$. FAB-HRMS: calcd for $C_{14}H_6F_8NO$ $[M+H]^+$ 356.0316, found 356.0337.

***N*-Trifluoromethylthioacetanilide (10F).** *N*-Trifluoromethylacetanilide **2F** (398 mg, 1.96 mmol) was dissolved in *p*-xylene (6 mL) in a 30 mL round flask. Lawesson's reagent (3.17 g, 7.84 mmol) was added, and the mixture was refluxed for 64 h at 150 ºC. Then, EtOH (10 mL) was added. The mixture was heated at 100 ºC for 3 h, then evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent $CH_2Cl_2$:hexane = 1:5) to afford **10F** as a yellow oil (112 mg, 26%). $^1$H-NMR (400 MHz, $CD_2Cl_2$) δ : 7.48–7.51 (m, 3H, $Ar_{meta,\ para}$), 7.24–7.26 (m, 2H, $Ar_{ortho}$), 2.70 (s, 3H, C*H*$_3$CO-). $^{13}$C{$^1$H}-NMR (100 MHz, $CDCl_3$) δ : 207.2 (C=S), 139.5 ($Ar_{ipso}$), 129.9 ($Ar_{meta}$), 129.7 ($Ar_{para}$), 128.5 ($Ar_{ortho}$), 120.0 (q, *J* = 266 Hz, *C*$F_3$), 35.6 (d, *J* = 2.2Hz, *C*$H_3$CS-). $^{19}$F-NMR (376 MHz, $CDCl_3$) δ : –52.4. IR (NaCl): 2924, 2853, 1739, 1465, 1259 cm$^{-1}$. EI-HRMS: calcd for $C_9H_8F_3NS$ $[M^+]$ 219.0324, found 219.0324.

***N*-Methylthioacetanilide (10).** *N*-Methylacetanilide (448 mg, 3.00 mmol) was dissolved in toluene (5 mL) in a 50 mL round flask. Lawesson's reagent (1.22 g, 3.02 mmol) was added, and the mixture was refluxed for 18 h at 120 ºC. EtOH (5 mL) was added, then mixture was refluxed at 100 ºC for a further 3 h and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: AcOEt:hexane = 1:5) to afford **10** as a pale yellow solid (468 mg, 94%). Recrystallization from hexane afforded colorless prisms. mp 55.0 – 56.5 ºC. $^1$H-NMR (400 MHz, $CDCl_3$, 50 ºC) δ : 7.44 (dd, *J* = 7.8, 7.8 Hz, 2H, $Ph_{meta}$), 7.37 (t, *J* = 7.8 Hz, 1H, $Ph_{para}$), 7.16 (d, *J* = 7.8 Hz, 2H, $Ph_{ortho}$), 3.73 (s, 3H, N-C*H*$_3$), 2.38 (s, 3H, C*H*$_3$CO-). $^{13}$C{$^1$H}-NMR (100 MHz, $CDCl_3$) δ : 201.3 (C=S), 145.9 ($Ar_{ipso}$), 130.0 ($Ar_{meta}$), 128.5 ($Ar_{para}$),

125.3 ($Ar_{ortho}$), 45.7 (N-*C*$H_3$), 33.8 (*C*$H_3$CO-). IR (KBr): 2958, 2922, 1590, 1490, 1381, 1316, 1291, 1278, 1194, 1128, 1065, 1023, 967, 803, 779, 706 $cm^{-1}$. EI-HRMS: calcd for $C_9H_{11}NS$ [$M^+$] 165.0607, found 165.0619.

***N*-Trifluoromethylthiobenzanilide (11F).** *N*-Trifluoromethylbenzanilide (376 mg, 1.42 mmol) was dissolved in *p*-xylene (5 mL) in a 50 mL round flask. Lawesson's reagent (2.29 g, 5.66 mmol) was added, and the mixture was refluxed for 67 h at 150 ºC, then purified by silica gel column chromatography (eluent $CH_2Cl_2$:hexane = 1:6) to give **11F** as a black solid (231 mg, 58%). Recrystallization from $CH_2Cl_2$ afforded yellow needles. mp 84.5 – 85.5 ºC. $^1$H-NMR (400 MHz, $CDCl_3$) δ : 7.44 (d, *J* = 8.0 Hz, 2H, C-$Ph_{ortho}$), 7.26–7.36 (m, 6H), 7.20 (dd, *J* = 7.9, 7.1 Hz, 2H, C-$Ph_{meta}$). $^{13}$C{$^1$H}-NMR (150 MHz, $CDCl_3$) δ : 207.9 (C=S), 143.9 ($CPh_{pso}$), 139.3 (N-$Ph_{ipso}$), 130.1 (C-$Ph_{para}$), 129.5 (N-$Ph_{meta}$), 129.4 (N-$Ph_{rtho}$), 129.3 (N-$Ph_{para}$), 127.7 (C-$Ph_{meta}$), 127.5 (C-$Ph_{ortho}$), 120.2 (q, *J* = 266 Hz, *C*$F_3$). $^{19}$F-NMR (376 MHz, $CDCl_3$) δ : –54.6. IR (KBr): 3433, 1591, 1487, 1454, 1442, 1347, 1254, 1184, 1140, 1071, 937, 721, 694 $cm^{-1}$. EI-HRMS: calcd for $C_{14}H_{10}F_3NS$ [$M^+$] 281.0481, found 281.0480.

***N*-Methylthiobenzanilide (11)**. *N*-Methylbenzanilide (680 mg, 3.22 mmol) was dissolved in toluene (8 mL) in a 50 mL round flask. Lawesson's reagent (1.56 g, 3.86 mmol) was added, and the mixture was refluxed for 4 h at 120 ºC. EtOH (8 mL) was added, and refluxing was continued at 100 ºC for another 3 h. Then, the mixture was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (eluent AcOEt:hexane = 1:5) to give **11** as a yellow solid (609 mg, 83%). mp 101.0 – 102.0 ºC. $^1$H-NMR (400 MHz, $CDCl_3$, 50 ºC) δ : 7.18–7.23 (m, 4H), 7.07–7.14 (m, 4H), 7.03 (d, *J* = 7.8 Hz, 2H, N-$Ph_{ortho}$), 3.92 (s, 3H, N-C*H*$_3$). $^{13}$C{$^1$H}-NMR (100 MHz, $CDCl_3$, 50 ºC) δ : 202.7 (C=S), 146.8 (N-$Ar_{ipso}$), 143.7 (C-$Ar_{ipso}$), 129.1 (C-$Ar_{ortho}$), 128.3 (C-$Ar_{para}$), 127.7 (N-$Ar_{meta}$), 127.5 (C-$Ar_{meta}$), 127.2 (N-$Ar_{para}$), 126.3 (N-$Ar_{ortho}$), 46.1 (N-*C*$H_3$). IR (KBr): 3406, 1592, 1492, 1463, 1445, 1380, 1300, 1114, 1067, 761, 695 $cm^{-1}$. EI-HRMS: calcd for $C_{14}H_{13}NS$ [$M^+$] 227.0769, found 227.0764.

***N*-Trifluoromethyl-*N*-benzylacetamide (12F).** Phenyl isothiocyanate (270 mg, 2.00 mmol) and AgF (1.27 g, 10.0 mmol) were placed in a pressure tube (20 mL) and suspended in $CH_3CN$ (10 mL). The suspension was stirred for 18 h at rt, then poured into $Et_2O$ (40 mL) to quench the reaction after confirming the consumption of phenyl isothiocyanate by TLC. The mixture was stirred for 10 min, then filtered through Celite, which was washed with $Et_2O$. The filtrate was evaporated, re-suspended in $Et_2O$ and filtered though Celite again, and the filtrate was evaporated under reduced pressure. The obtained crude brown oil (241 mg) in toluene (5 mL)

was placed in a two-necked flask (10 mL) and MeMgBr (1.0 M in THF, 1.6 mL, 1.6 mmol) was added via a syringe on an ice bath. The mixture was stirred for 1 h at rt, then the reaction was quenched by adding sat. $NH_4Cl$ aq. (15 mL). The resulting mixture was extracted with AcOEt (15 mL x 2), and the combined organic layer was dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The crude oil was purified by silica gel column chromatography (eluent $CH_2Cl_2$:hexane = 1:5) to afford **12F** (142 mg, 35%, 2 steps) as a colorless oil.$^1$H-NMR (600 MHz, $CDCl_3$) δ : 7.33 (t, *J* = 7.8 Hz, 2H, $Ph_{meta}$), 7.27–7.29 (m, 3H), 4.79 (m, 2H, -C$H_2$Ph), 2.36 (q, *J* = 4.5 Hz, 3H, C$H_3$CO). $^{13}$C{$^1$H}-NMR (100 MHz, $CDCl_3$) δ : 169.5 (C=O), 136.5 ($Ph_{ipso}$), 128.6 ($Ph_{meta}$), 127.7 ($Ph_{para}$), 127.4 ($Ph_{ortho}$), 122.0 (q, *J* = 260 Hz, *C*$F_3$), 46.5 (-*C*$H_2$Ph), 23.3 (q, *J* = 4.5 Hz, *C*$H_3$CO). $^{19}$F-NMR (283 MHz, $CDCl_3$) δ : –52.3. IR (KBr): 3839, 3035, 2364, 1712, 1498, 1444, 1373, 1222, 1135, 1068 cm$^{-1}$. EI-HRMS: calcd for $C_{10}H_{10}F_3NO$ [$M^+$] 217.0709, found 217.0710.

***N*-Methyl-*N*-benzylacetamide (12).** NaH (144 mg, 60% oil suspension, 3.60 mmol) was placed in a two-necked flask (50 mL), washed with hexane three times and dried. Then, THF (2 mL) and a THF (8 mL) solution of *N*-benzylacetamide (597 mg, 4.00 mmol) were added on an ice bath, followed by $CH_3I$ (0.75 mL, 12.0 mmol). The mixture was stirred for 3 h at r.t., then the reaction was quenched by adding $H_2O$ (40 mL) after confirming the consumption of *N*-benzylacetamide by TLC. The resulting mixture was extracted with AcOEt (40 mL x 2) after evaporation of THF. The organic layer was dried over $Na_2SO_4$, filtered, then evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent AcOEt:hexane = 1:1) to afford a colorless oil (371 mg, 63%). $^1$H-NMR (400 MHz, tetrachloroethane-$d_2$, 120 ºC) δ : 7.30 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 4.49 (s, 2H). 2.88 (s, 3H).$^{13}$C{$^1$H}-NMR (100 MHz, $CDCl_3$) δ :171.0 (minor), 170.68 (major), 137.3 (major), 136.5 (minor), 128.9 (major), 128.5 (major), 128.0 (major), 127.6 (minor), 127.3 (minor), 126.3 (minor), 54.2 (minor), 50.5 (major), 35.5 (major), 33.7 (minor). IR (KBr): 3031, 2931, 1700, 1641, 1428, 1380, 1317, 1274, 1238, 1170 cm$^{-1}$. EI-HRMS: calcd for $C_{10}H_{13}NO$ [$M^+$] 163.0992, found 163.0997.

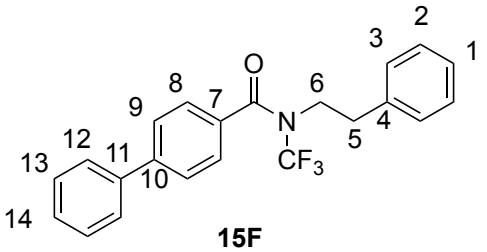
***N*-Trifluoromethyl-*N*-benzylbenzamide (13F, ABCF3).** A $CH_3CN$ (20 mL) solution of benzyl isothiocyanate (596 mg, 4.00 mmol) was added to a 50 mL round flask containing AgF (2.54 g, 20.0 mmol) and triphosgene (474 mg, 1.60 mmol). The mixture was stirred for 20 h at rt, then poured into $Et_2O$ (100 mL) to quench the reaction after confirming the consumption of benzyl isothiocyanate by TLC. The resulting mixture was filtered through Celite, which was washed with $Et_2O$. The filtrate was evaporated and the residue was re-suspended in $Et_2O$ and filtered

through Celite again. The filtrate was evaporated under reduced pressure to give a crude brown oil. A solution of this oil (691 mg) in toluene (5 mL) was placed in a two-necked flask (10 mL) and PhMgBr (1.03 M in THF, 4.4 mL, 4.53 mmol) was added via a syringe on an ice bath. The mixture was stirred for 10 min at rt, then the reaction was quenched by adding sat. $NH_4Cl$ aq. (30 mL). The resulting mixture was extracted with $Et_2O$ (60 mL), and the combined organic layer was dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The obtained crude oil was purified by silica gel column chromatography (eluent $CH_2Cl_2$:hexane = 2:3) to afford **13F** as a colorless oil (472 mg, 42%, 2 steps). $^1$H-NMR (400 MHz, $CDCl_3$) δ : 7.51 (d, *J* = 7.3 Hz, 2H, $COPh_{ortho}$), 7.49 (t, *J* = 7.3 Hz, 1H, $COPh_{para}$), 7.30–7.42 (m, 7H), 4.86 (s, 2H, PhC*H*$_2$).$^{13}$C{$^1$H}-NMR (100 MHz, $CDCl_3$) δ : 170.5 (C=O), 136.2 (-$CH_2Ph_{ipso}$), 135.0 ($COPh_{ipso}$), 131.2 ($COPh_{para}$), 128.7 (-$CH_2Ph_{meta}$), 128.3 ($COPh_{meta}$), 127.8 (-$CH_2Ph_{para}$), 127.3 (-$CH_2Ph_{ortho}$), 127.1 ($COPh_{ortho}$), 121.4 (q, *J* = 264 Hz, *C*$F_3$), 48.5 (-*C*$H_2$Ph). $^{19}$F-NMR (376 MHz, $CDCl_3$) δ : –53.2. IR (KBr): 1690, 1362, 1329, 1212, 1148 cm$^{-1}$. EI-HRMS: calcd for $C_{15}H_{12}F_3NO$ [$M^+$] 279.0865, found 279.0865.

***N*-Methyl-*N*-benzylbenzamide (13).** NaH (100 mg, 60% oil suspension, 2.50 mmol) was placed in two-necked flask (50 mL), washed with hexane three times and dried. To this flask was added a THF (10 mL) solution of *N*-benzylbenzamide (423 mg, 2.00 mmol) in an ice bath, followed by $CH_3I$ (0.19 mL, 3.05 mmol). The mixture was stirred for 19 h at r.t., and reaction was quenched by adding sat. $NH_4Cl$ aq. (30 mL) after the consumption of *N*-benzylbenzamide had been confirmed by TLC. The resulting mixture was extracted with $Et_2O$ (50 mL). The organic layer was dried over $Na_2SO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent AcOEt:hexane = 2:3) to afford the product as a colorless oil (383 mg, 85%). $^1$H-NMR (400 MHz, tetrachloroethane-$d_2$, 100 ºC) δ : 7.44 (d, *J* = 6.8 Hz, 2H, $COPh_{ortho}$), 7.29–7.40 (m, 6H), 7.25 (d, *J* = 7.3 Hz, 2H, -$CH_2Ph_{ortho}$), 4.62 (s, 2H, -C*H*$_2$Ph). 2.93 (s, 3H, *N*-C*H*$_3$).$^{13}$C{$^1$H}-NMR (100 MHz, tetrachloroethane-$d_2$, 100 ºC) δ :171.4 (*C*=O), 137.0 ($COPh_{ipso}$), 136.5 (-$CH_2Ph_{ipso}$), 129.3 ($COPh_{para}$), 128.6 (-$CH_2Ph_{meta}$), 128.2 ($COPh_{meta}$), 127.4 (-$CH_2Ph_{ortho}$), 126.8 ($COPh_{ortho}$), 52.8 (brs, -*C*$H_2$Ph), 35.2 (brs, *N*-*C*$H_3$) (the -$CH_2Ph_{para}$ peak is missing, probably due to overlap). IR (KBr): 3060, 3029, 2923, 1631, 1578, 1497, 1479, 1449, 1400, 1359, 1308, 1264, 1176, 1159, 1070, 1025, 1002, 974, 930, 789, 720 cm$^{-1}$. EI-HRMS: calcd for $C_{15}H_{15}NO$ [$M^+$] 225.1148, found 225.1150.

***N*-Trifluoromethyl-*N*-thiobenzylacetamide (14F).** *N*-Trifluoromethylbenzylacetamide **12F** (282 mg, 1.30 mmol) was dissolved with *p*-xylene (3 mL) in a 30 mL round flask. Lawesson's reagent (2.10 g, 5.19 mmol) was added, and the mixture was refluxed for 43 h at 150 ºC. EtOH

(10 mL) was added, and the resulting mixture was heated at 100 ºC for 3 h, then evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent $CH_2Cl_2$:hexane = 1:6) to afford **14F** as a yellow oil (54 mg, 18%). $^1$H-NMR (400 MHz, $CDCl_3$) δ : 7.33 (dd, *J* = 7.0, 7.0 Hz, 2H, $Ph_{meta}$), 7.26–7.30 (m, 3H), 5.49 (d, *J* = 2.5 Hz, 2H, -C*H*$_2$Ph), 2.93 (q, *J* = 2.0 Hz, 3H, C*H*$_3$CO). $^{13}$C{$^1$H}-NMR (150 MHz, $CDCl_3$) δ : 206.5 (*C*=S), 135.2 ($Ph_{ipso}$), 128.6 ($Ph_{meta}$), 127.7 ($Ph_{para}$), 126.7 ($Ph_{ortho}$), 121.1 (q, *J* = 266 Hz, *C*F$_3$), 53.2 (-*C*H$_2$Ph), 34.0 (q, *J* = 4.4 Hz, *C*H$_3$CO). $^{19}$F-NMR (376 MHz, $CDCl_3$) δ : –51.4 (d, *J* = 2.1 Hz). IR (KBr): 1355, 1355, 1315, 1210, 1150, 1060, 1031, 948 cm$^{-1}$. EI-HRMS: calcd for $C_{10}H_{10}F_3NS$ [M$^+$] 233.0481, found 233.0483.




**15F**

***N*-Phenethyl-*N*-trifluoromethyl-(1,1'-biphenyl)-4-carboxamide (15F).** To a solution of phenethyl isothiocyanate (740 µl, 0.496 mmol) in pyridine (1.0 mL) and $CH_2Cl_2$ (1.0 mL) were added AgF (254 mg, 2.00 mmol) and 4-phenylbenzoyl chloride (151 mg, 0.697 mmol) in an ice bath. After confirming that the reaction did not progress further (18 h), the solution was evaporated to give a black oil, which was purified by silica gel column chromatography (eluent $CH_2Cl_2$:hexane = 1:3 to $CH_2Cl_2$ only to $CH_3OH$: $CH_2Cl_2$=1:200) to give **15F** as a colorless solid (55 mg, 30%). Recrystallization from AcOEt-hexane afforded pale yellow needles. Recrystallization from AcOEt-hexane afforded pale yellow needle. mp 67.0 – 68.0 ºC. $^1$H-NMR (600 MHz, $CDCl_3$) δ : 7.614 (d, *J* = 7.2 Hz, 2H, $H_{12}$), 7.607 (d, *J* = 8.4 Hz, 2H, $H_8$), 7.47 (dd, *J* = 7.2, 7.2 Hz, 2H, $H_{13}$), 7.46 (d, *J* = 8.4 Hz, 2H, $H_9$), 7.40 (t, *J* = 7.2 Hz, 1H, $H_{14}$) , 7.28 (dd, *J* = 7.2, 7.2 Hz, 2H, $H_2$), 7.24 (t, *J* = 7.2 Hz, 1H, $H_1$), 7. 17 (d, *J* = 7.2 Hz, 2H, $H_3$), 3.90 (tq, *J* = 7.8, 1.8 Hz, 2H, -C*H*$_2$CH$_2$Ph), 2.99 (t, *J* = 7.8 Hz, 2H, -CH$_2$C*H*$_2$Ph). $^{13}$C{$^1$H}-NMR (150 MHz, $CDCl_3$) δ : 170.3 (*C*=O), 144.0 ($C_7$), 139.9 ($C_{11}$), 137.5 ($C_4$), 133.8 ($C_{10}$), 129.0 ($C_3$), 128.9 ($C_{13}$), 128.7 ($C_2$), 128.1 ($C_{14}$), 127.7 ($C_9$), 127.2, 126.9, 126.8 ($C_1$), 121.4 (q, *J* = 263 Hz, *C*F$_3$), 46.9 (-*C*H$_2$CH$_2$Ph), 35.3 (-CH$_2$*C*H$_2$Ph). $^{19}$F-NMR (376 MHz, $CDCl_3$) δ : –53.7. IR (KBr): 3889, 3375, 3592, 3542, 3396, 2958, 2854, 2362, 1687, 1606, 1461, 1376, 1261, 1182, 1027, 804, 742, 698, 485 cm$^{-1}$. EI-HRMS: calcd for $C_{22}H_{18}F_3NO$ [M$^+$] 369.1330, found 369.1324.

***N*-Isopropylthioacetanilide (17).** *N*-Isopropylacetanilide (115 mg, 649 µmol) was dissolved in toluene (2 mL) in a 30 mL round flask. Lawesson's reagent (289 mg, 715 µmol) was added, and

the mixture was refluxed for 3 h at 120 ºC. EtOH (4 mL) was added, and the resulting mixture was further refluxed at 100 ºC for 1 h, then evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent AcOEt:hexane = 1:10) to afford **17** as a colorless solid (121 mg, 96%). Recrystallization from $CH_2Cl_2$-hexane afforded colorless prisms. mp 77.5 – 79.0 ºC. $^1$H-NMR (400 MHz, $CDCl_3$) δ : 7.40–7.49 (m, 3H, $Ph_{meta}$ and $Ph_{para}$), 7.05 (d, $J$ = 8.0 Hz, 2H, $Ph_{ortho}$), 6.00 (sept, $J$ = 6.8 Hz, 1H, N-C*H*$(CH_3)_2$), 2.23 (s, 3H, C*H*$_3$CS-), 1.13 (d, $J$ = 6.8 Hz, 6H, N-CH(C*H*$_3$)$_2$). $^{13}$C{$^1$H}-NMR (100 MHz, $CDCl_3$) δ : 200.7 (C=S), 139.9 ($Ar_{ipso}$), 129.4 ($Ar_{meta}$), 128.7 ($Ar_{para}$), 128.1 ($Ar_{ortho}$), 53.3 (N-*C*H$(CH_3)_2$), 34.9 (*C*H$_3$CO-), 20.1 (N-CH(*C*H$_3$)$_2$). IR (KBr): 2925, 2854, 1589, 1492, 1440, 1409, 1360, 1254, 1173, 1128, 1109, 1072, 1038, 972, 956, 875, 807, 766, 711 cm$^{-1}$. EI-HRMS: calcd for $C_{11}H_{15}NS$ [$M^+$] 193.0920, found 193.0925.

**Variable Temperature NMR and line shape analysis.**

Temperature ($T$) was calibrated using 80% ethylene glycol in DMSO-$d_6$ (from +25 to +100 ºC) [1] or $CD_3OD$ (from –90 to +20 ºC). [2] Line shape analysis to determine the kinetic parameter ($k$) was performed by using the DNMR program (installed Bruker TopSpin 4.3.0).

The activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$) were determined by means of Arrhenius plots of ln($k$/$T$) against 1/$T$. The activation enthalpy ($\Delta H^{\ddagger}$) was determined from the slope of the plot using eq 1.

$$\Delta H^{\ddagger} = -R \times \text{Slope} \qquad (1)$$

where $R$ is the gas constant, 1.987 cal/(K· mol).

The activation entropy ($\Delta S^{\ddagger}$) was determined from the intercept using eq 2.

$$\Delta S^{\ddagger} = R \times (\text{intercept} - \ln(h/k_B)) \qquad (2)$$

where $h$ is Planck's constant, $k_B$ is Boltzmann constant, and ln ($h$/$k_B$) =23.7600.

Finally, the rotation barrier at 298 K ($\Delta G^{\ddagger}_{298k}$) was calculated from the calculated values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ according to eq 3 with $T$ = 298 K.

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad (3)$$

## 3, X-ray Crystallography

Crystals for analysis were obtained by slow evaporation of solutions in designated solvents. Variable-temperature single-crystal X-ray diffraction experiments were carried out on a Rigaku RAXIS Rapid II (graphite-monochromated Cu Kα radiation, λ = 1.541Å) or XtaLAB Synergy Custom. Crystals were mounted on MiTeGen dual-thickness MicroMounts using parabar oil : mineral oil = 1:8. Data collection was carried out at low temperature (93 K) using liquid nitrogen as a coolant. The crystal structures were solved by direct methods using SHELXT[6] and refined by SHELXL[7]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were geometrically constrained. The CIF files of all structures are available at www.ccdc.cam.ac.uk. Structure analysis was performed with Mercury ver. 3.9 (CCDC) programs.

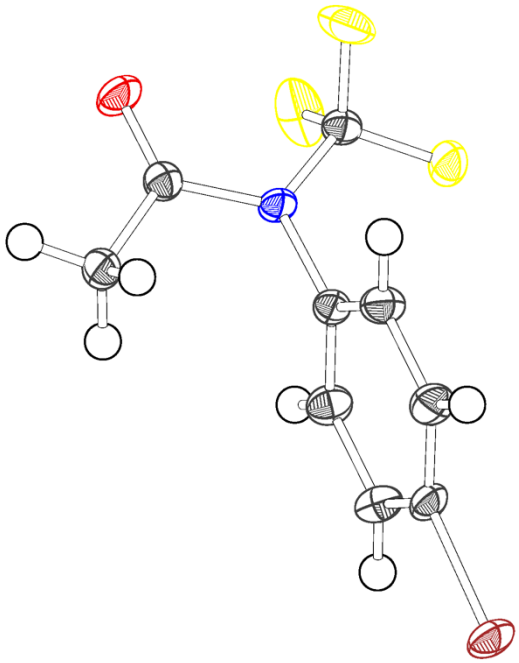


**Figure S1**. Solid-state structure of **6F**. Thermal ellipsoids are shown at the 50% probability level. Color code: C / gray, O / red, N / blue, Br / brown and F / yellow. CCDC Deposit No. 2537702.

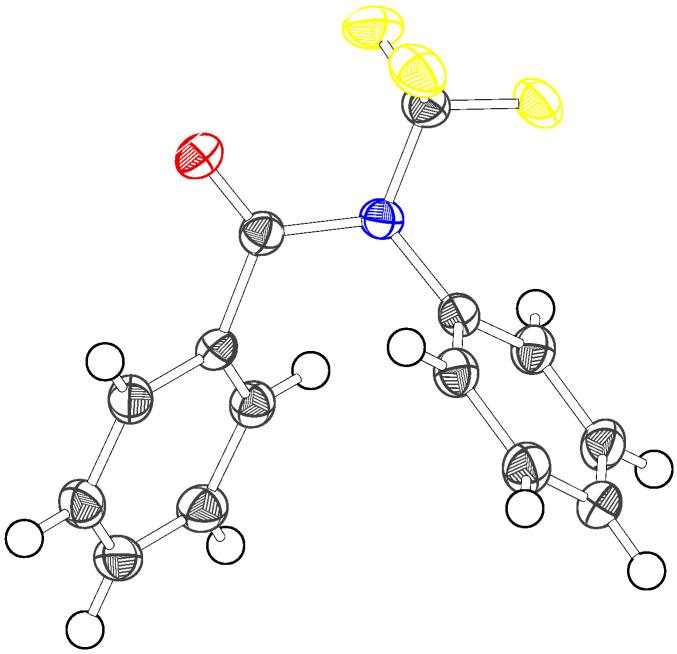


**Figure S2**. Solid-state structure of **7F**. Thermal ellipsoids are shown at the 50% probability level. Color code: C / gray, O / red, N / blue and F / yellow. CCDC Deposit No. 2537703.

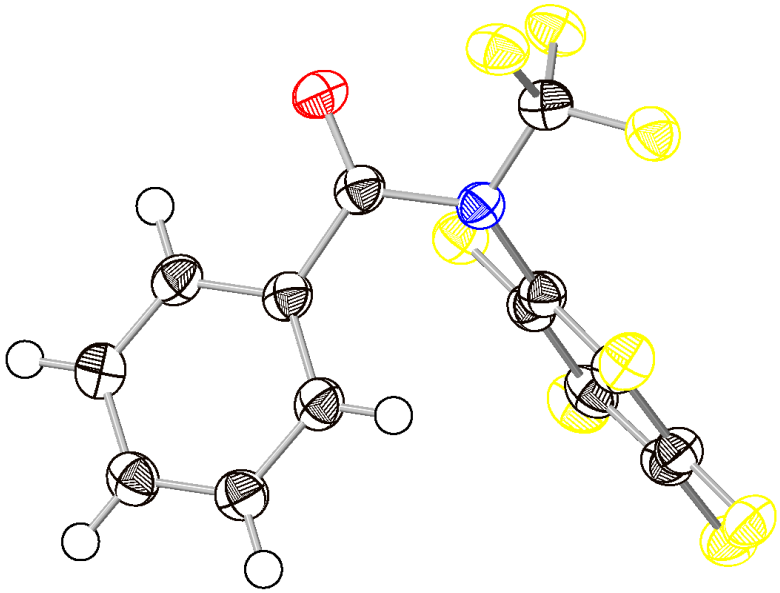


**Figure S3**. Solid-state structure of **8F**. Thermal ellipsoids are shown at the 50% probability level. Color code: C / gray, O / red, N / blue and F / yellow. CCDC Deposit No. 2537704.

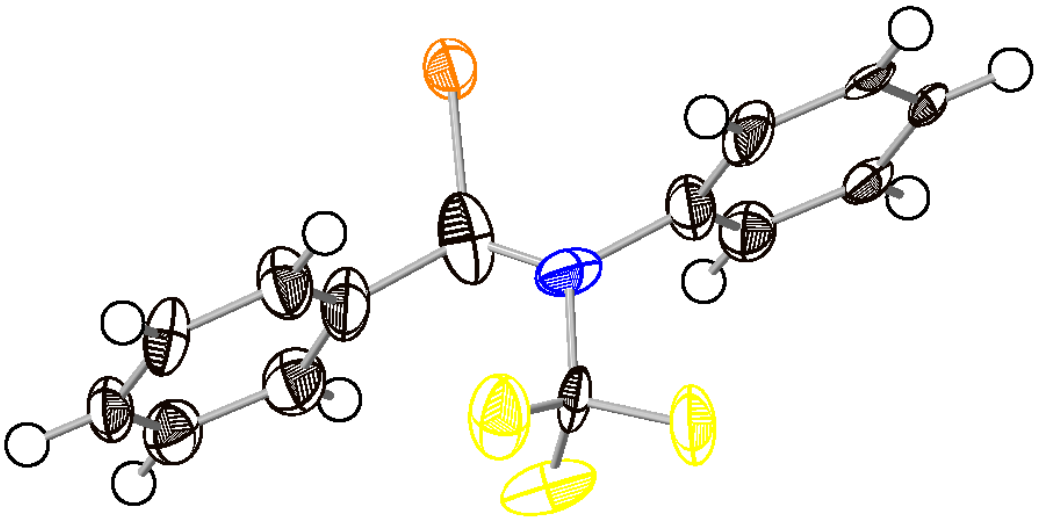


**Figure S4**. Solid-state structure of **11F**. Thermal ellipsoids are shown at the 50% probability level. The minor occupancy component is omitted for clarity. Color code: C / gray, O / red, N / blue, S / orange and F / yellow. CCDC Deposit No. 2537705.

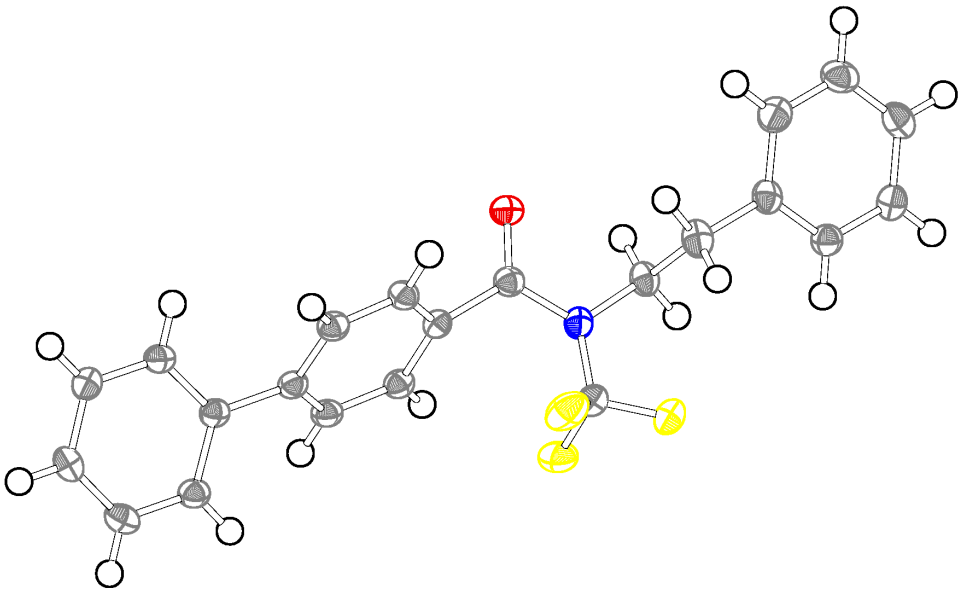


**Figure S5**. Solid-state structure of **15F**. Thermal ellipsoids are shown at the 50% probability level. Color code: C / gray, O / red, N / blue and F / yellow. CCDC Deposit No. 2537706.

**Table S1**. Crystal structure parameters of *N*-$CF_3$ amides.

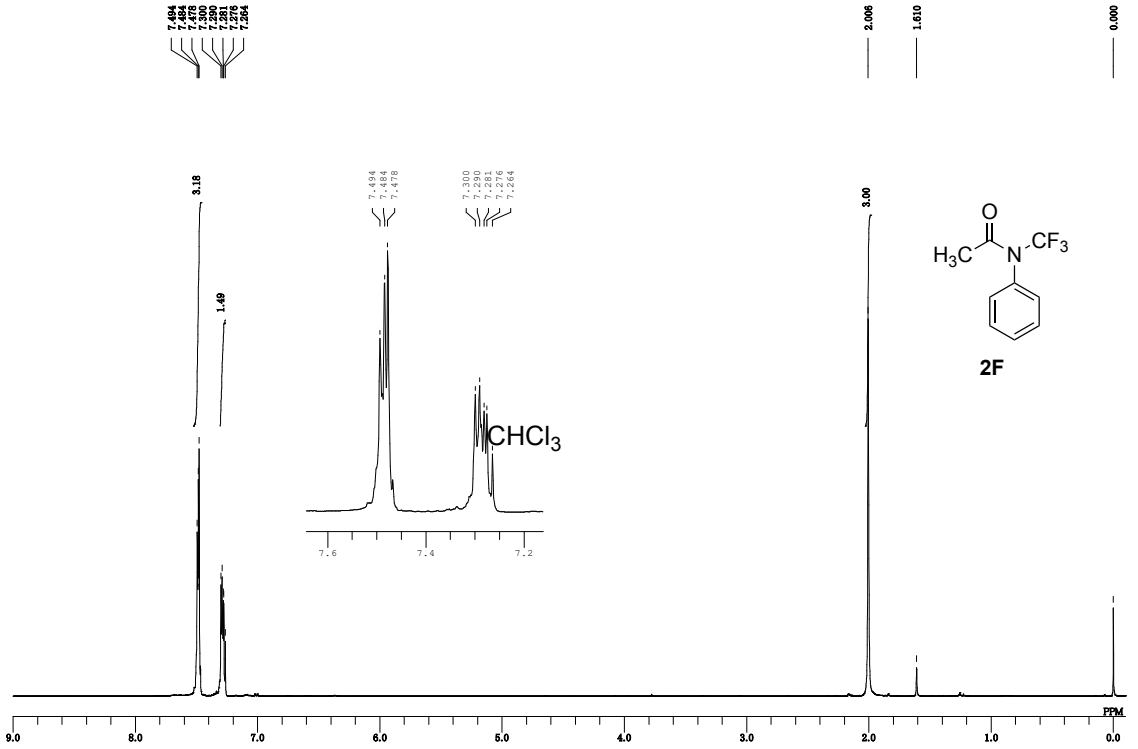
| | | **6F** | **7F** | **8F** | **15F** |
|---|---|---|---|---|---|
| Bond lengths (Å) | (O or S=)C–N | 1.400 | 1.409 | 1.426 | 1.391 |
| | N–Ar (or $CH_2$) | 1.445 | 1.445 | 1.433 | 1.477 |
| | N–$CF_3$ | 1.417 | 1.427 | 1.426 | 1.414 |
| | C=O | 1.207 | 1.207 | 1.199 | 1.216 |
| Dihedral angles (deg) | NAr–Am | 90.0 | 74.3 | 74.7 | – |
| | (O=)C–N–C–F(anti) | −180 | −174 | −170 | −161 |
| Pyramidal parameters (deg) | τ | 0.0 | 18.4 | 24.7 | 10.7 |
| | $\chi_N$ | 0.0 | 25.9 | 29.6 | 9.4 |

[a] Ar; Aryl plane, Am; amide plane (O–C–N), Al; alkenyl plane (mean plane of all atoms attached to alkenyl carbon excluding hydrogen atom). Compound **11F** is excluded from this table due to disorder of its crystal structure.

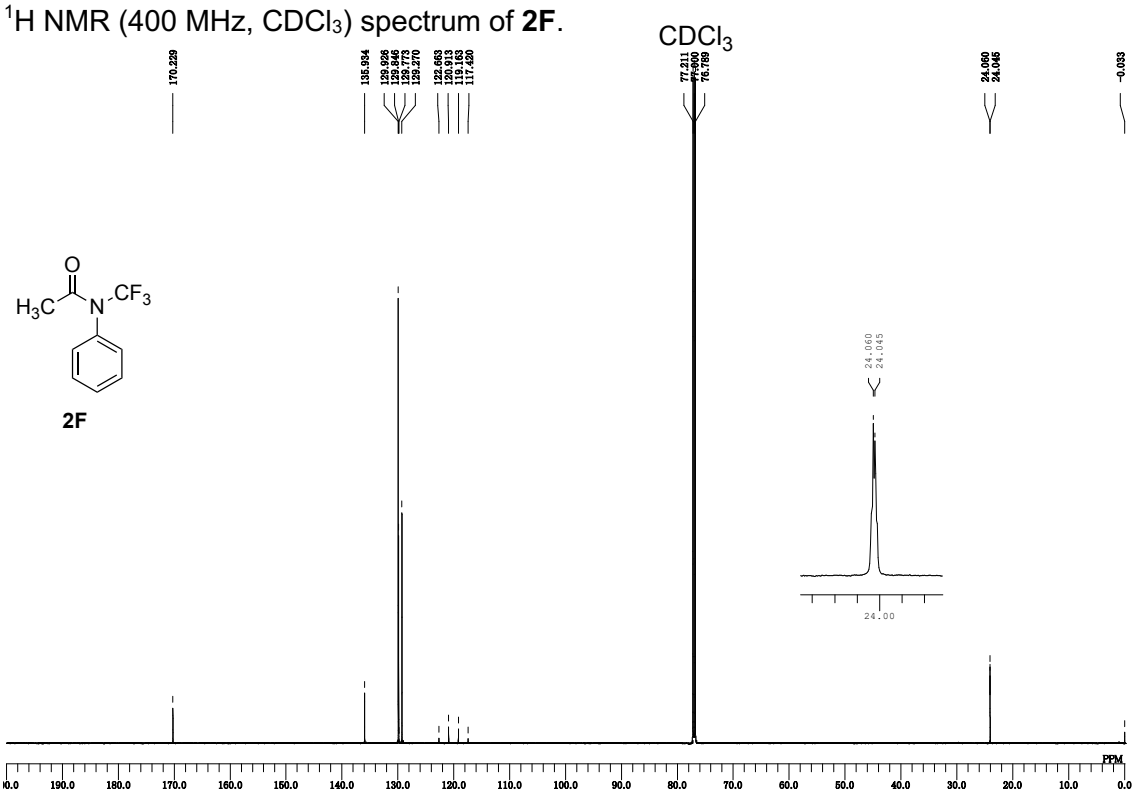
**Table S2**. Crystallographic parameters.

| | **6F** | **7F** | **8F** | **11F** | **15F** |
|---|---|---|---|---|---|
| recrystallization solvent | *n*hex | *n*hex | *n*hex | $CH_2Cl_2$-*n*hex | AcOEt-*n*hex |
| chemical formula | $C_9H_7BrF_3NO$ | $C_{14}H_{10}F_3NO$ | $C_{14}H_5F_8NO$ | $C_{14}H_5F_8NO$ | $C_{22}H_{18}F_3NO$ |
| formula weight | 282.06 | 265.23 | 355.19 | 281.29 | 369.37 |
| crystal system | monoclinic | orthorhombic | orthorhombic | orthorhombic | triclinic |
| space group | $P2_1/m$ | *P*bca | *P*bca | $P2_12_12_1$ | *P1*- |
| a/Å | 7.2582(1) | 8.8738(2) | 13.1072(4) | 5.5662(2) | 6.0692(2) |
| b/Å | 7.1880(1) | 9.876(2) | 13.6722(6) | 7.4317(2) | 9.9307(4) |
| c/Å | 10.0731(2) | 27.5237(7) | 14.4845(5) | 31.1469(8) | 15.4339(6) |
| α/° | 90 | 90 | 90 | 90 | 72.946(4) |
| β/° | 104.213(2) | 90 | 90 | 90 | 82.787(3) |
| γ/° | 90 | 90 | 90 | 90 | 87.031(3) |
| *Z* | 2 | 8 | 8 | 4 | 2 |
| V/Å$^3$ | 509.447(15) | 2439.37(10) | 2595.68(17) | 1288.73(7) | 882.17(6) |
| T/K | 93 | 93 | 93 | 93 | 93 |
| $D_{calc}$/g cm$^{-3}$ | 1.839 | 1.444 | 1.818 | 1.450 | 1.391 |
| μ/mm$^{-1}$ | 5.726(CuKα) | 1.061(CuKα) | 1.764(CuKα) | 2.453(CuKα) | 0.898 (CuKα) |
| reflns collected | 1076 | 2457 | 2534 | 2668 | 3508 |
| unique reflns | 1054 | 2213 | 2161 | 2340 | 2965 |
| $R_1$[I > 2σ(I)] | 0.0253 | 0.0527 | 0.0592 | 0.0959 | 0.0490 |
| w$R_2$ [all] | 0.0719 | 0.1450 | 0.1713 | 0.2545 | 0.1350 |
| GOF | 1.090 | 1.056 | 1.071 | 1.079 | 1.104 |
| CCDC | 2537702 | 2537703 | 2537704 | 2537705 | 2537706 |

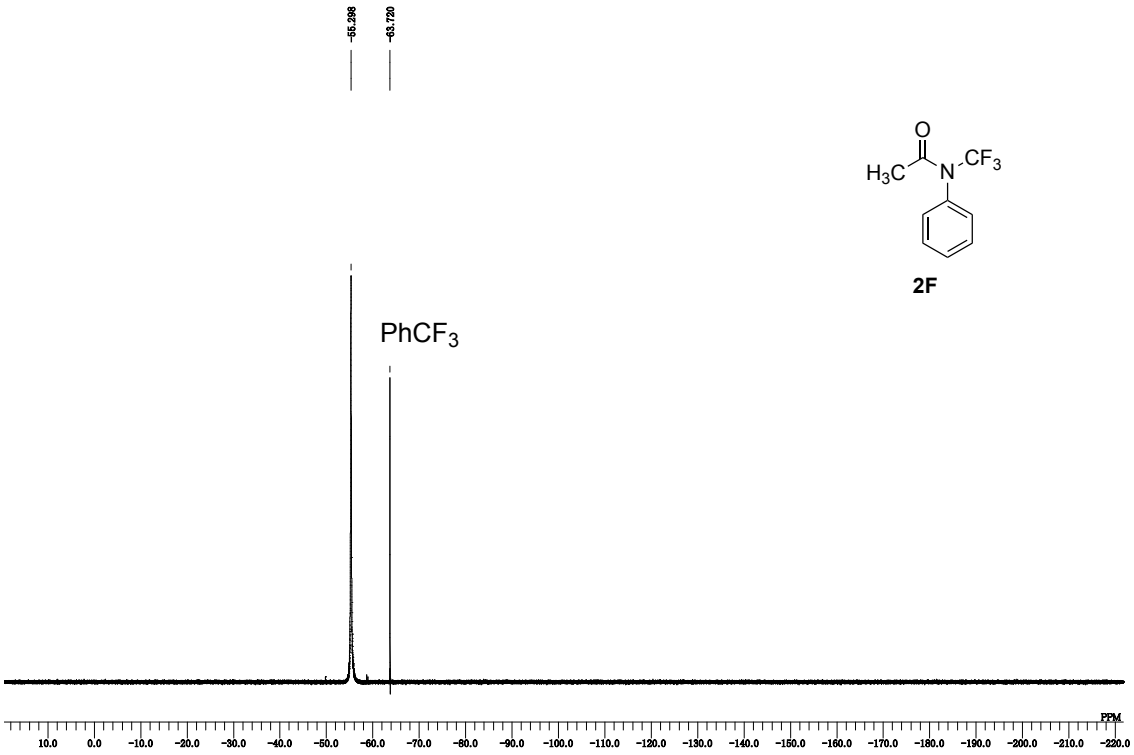
4, NMR Spectra




$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **2F**.




$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) spectrum of **2F**.

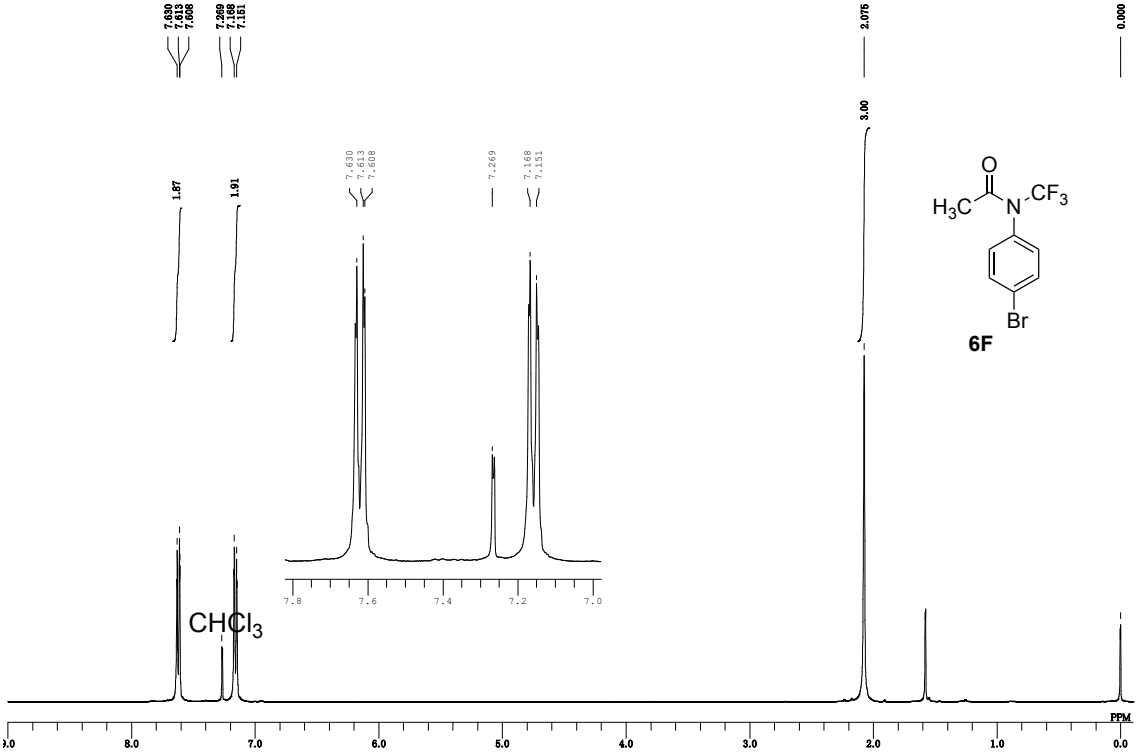






**2F**

$^{19}$F NMR (376 MHz, $CDCl_3$) spectrum of **2F**.

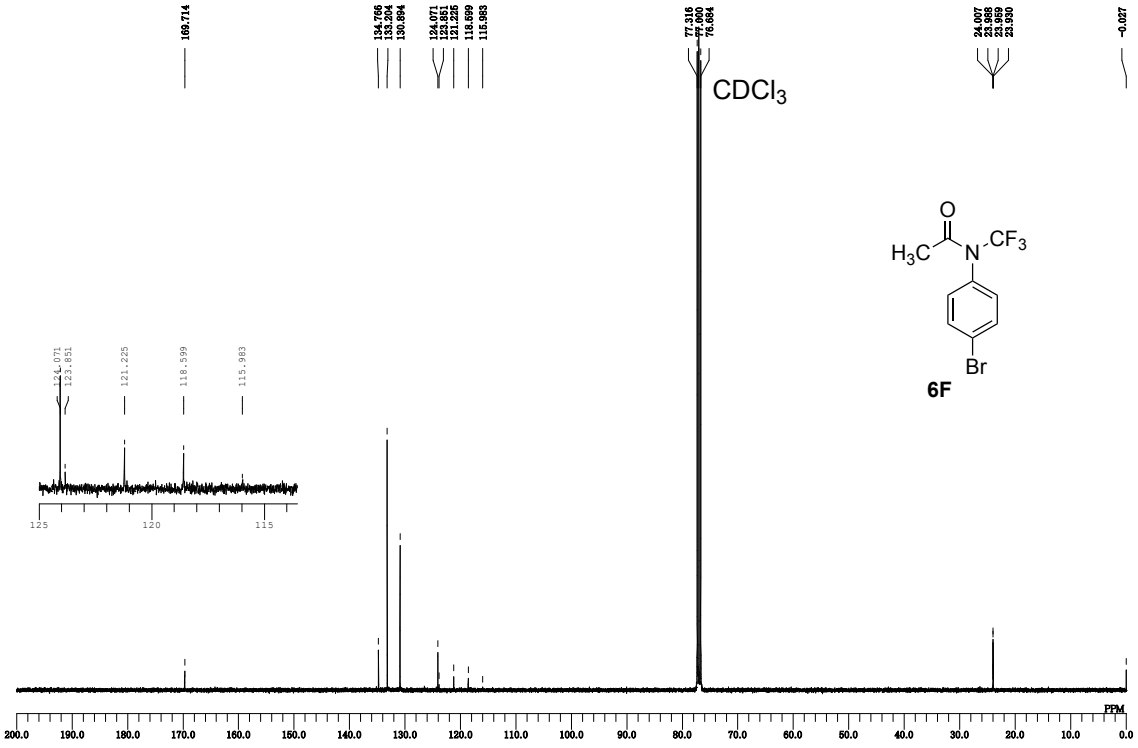




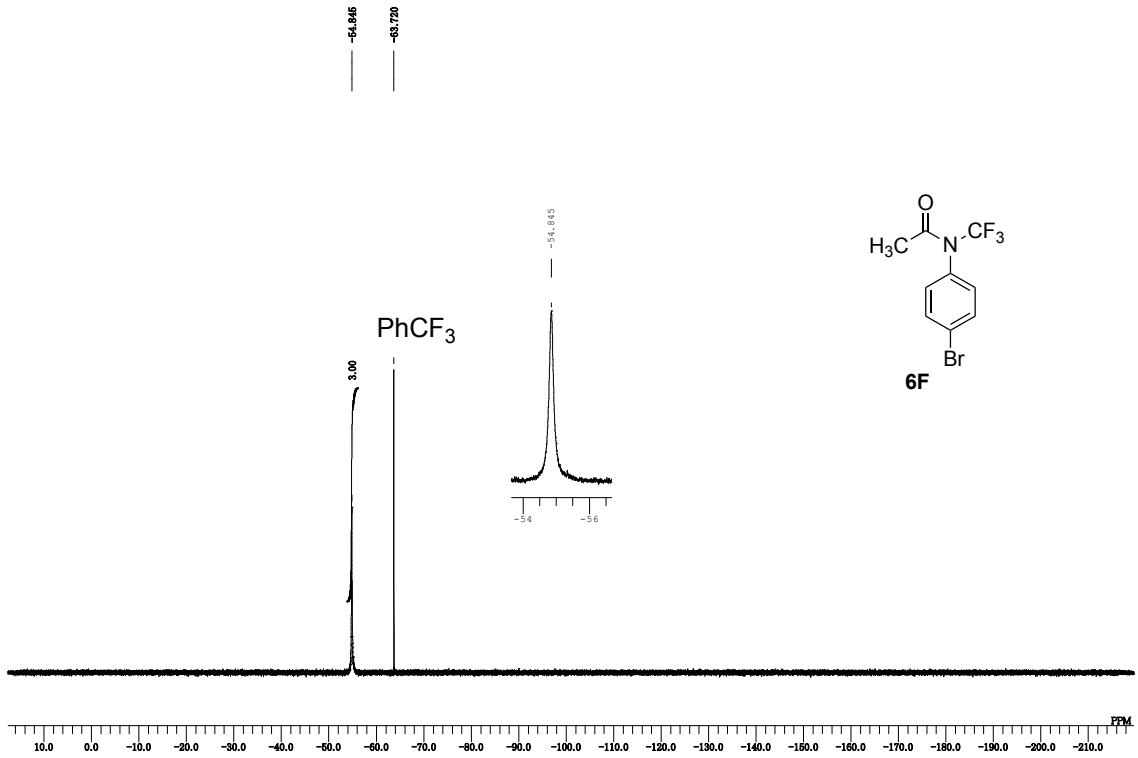


**6F**

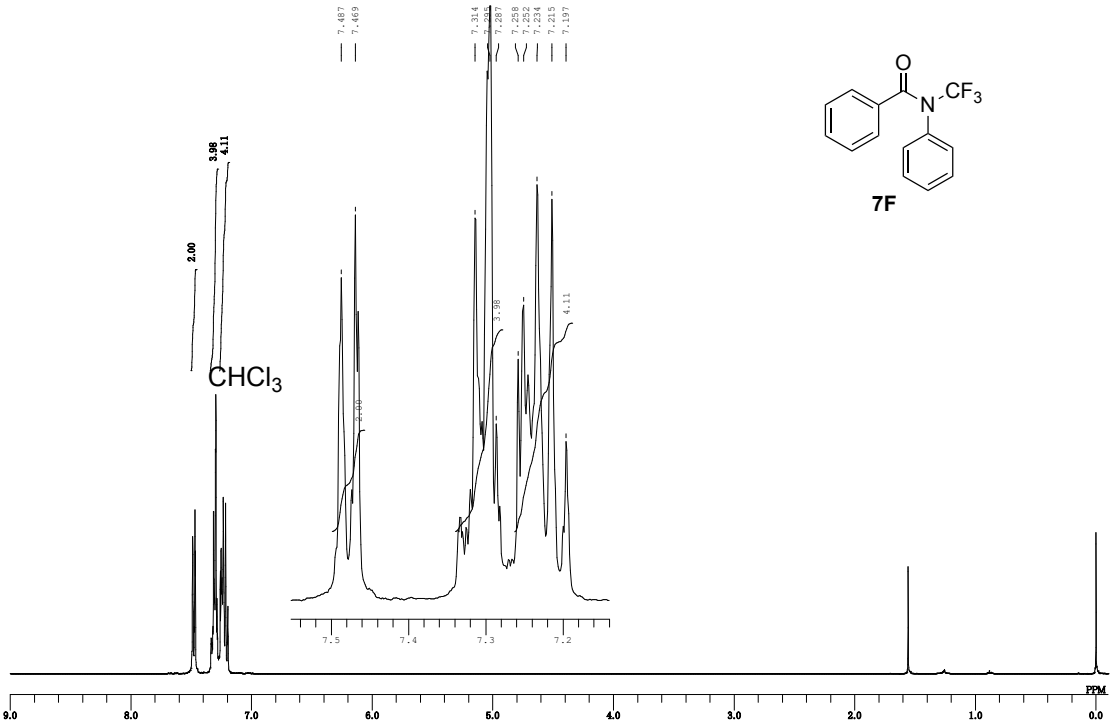
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **6F**.



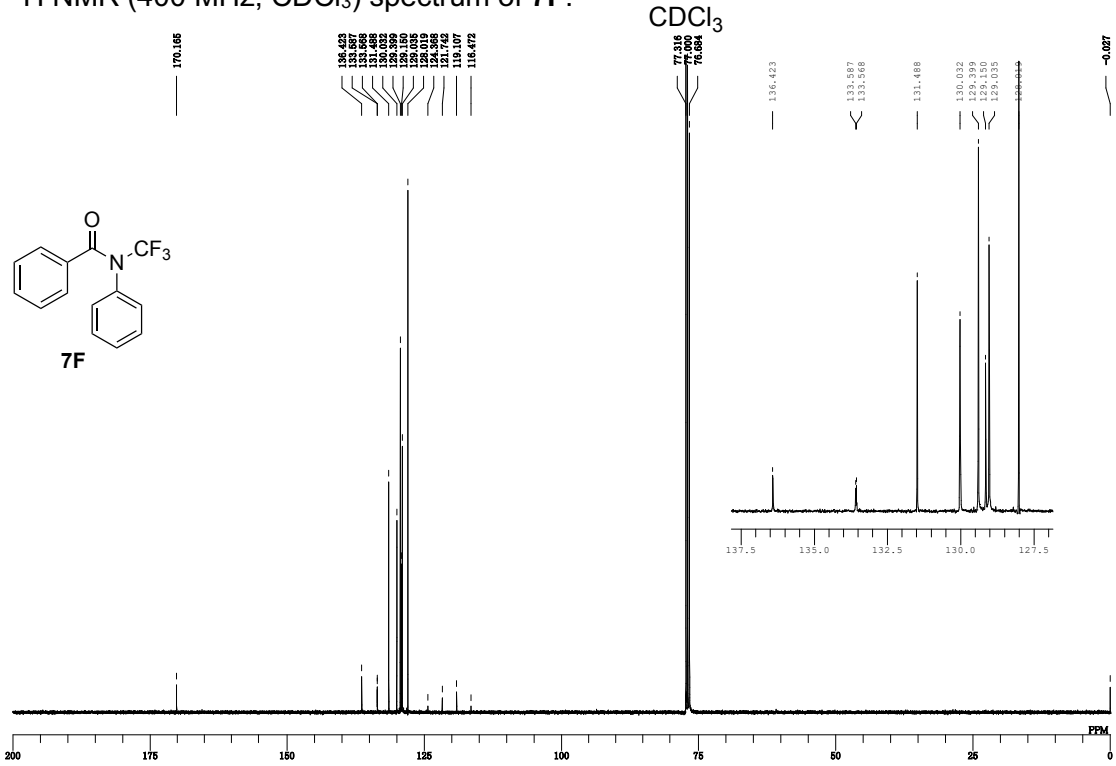

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **6F**.



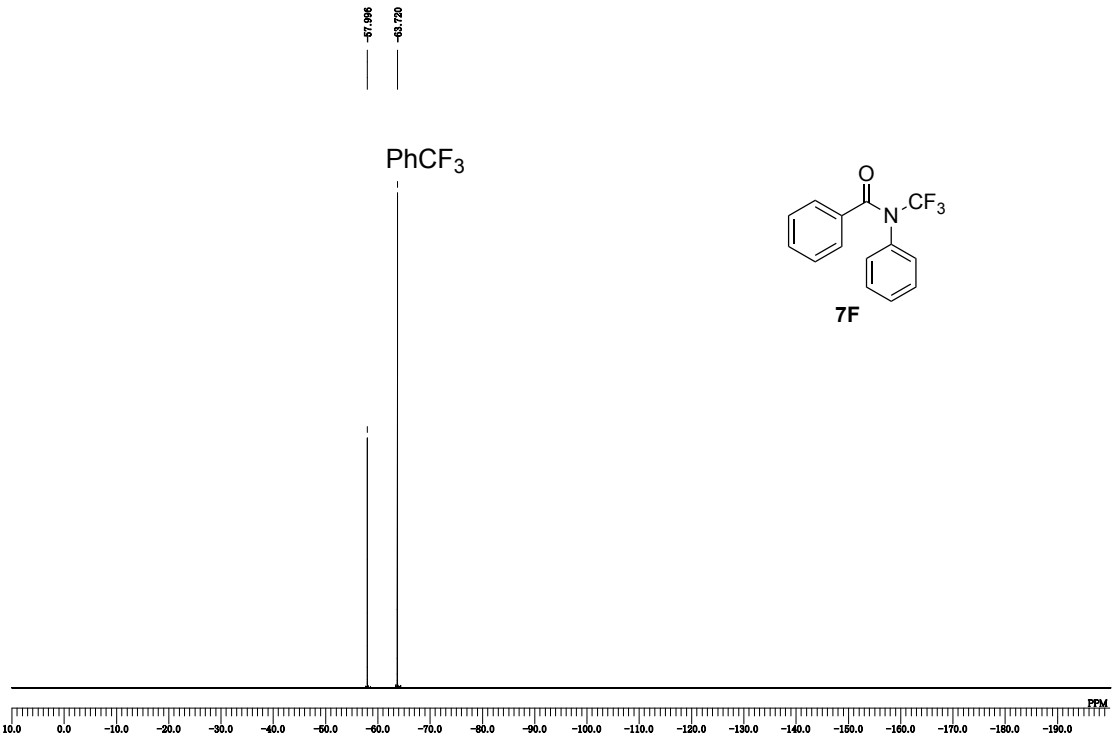

$^{19}F$ NMR (282 MHz, $CDCl_3$) spectrum of **6F**.



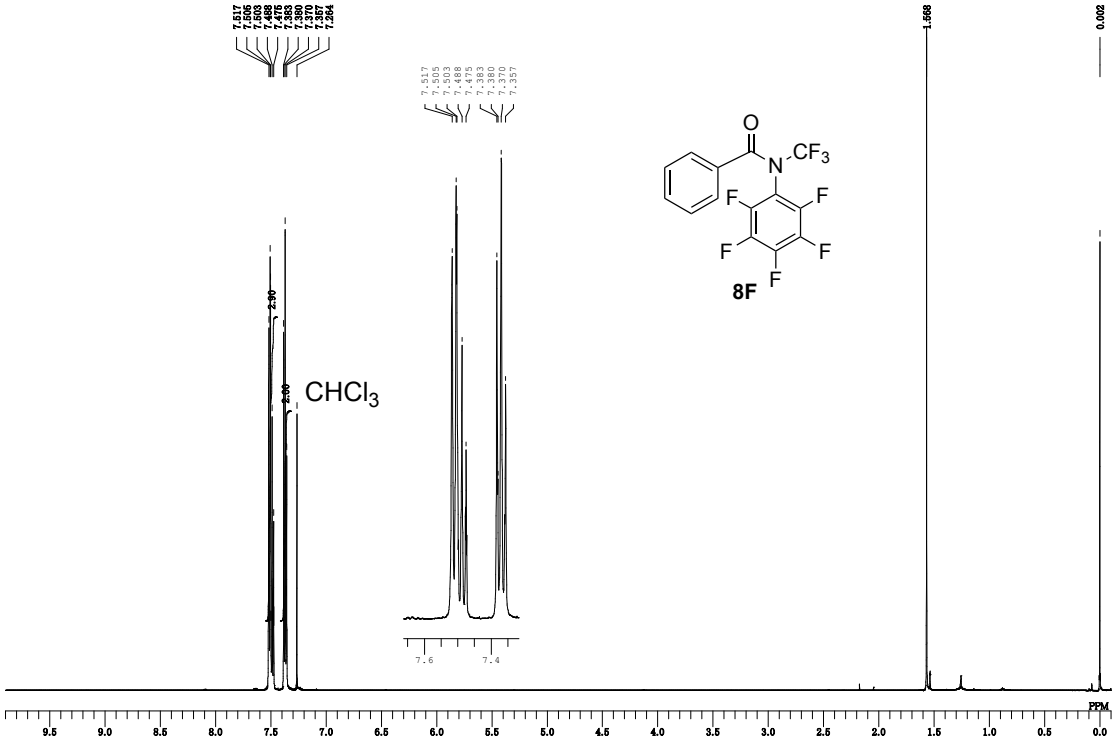

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **7F**.



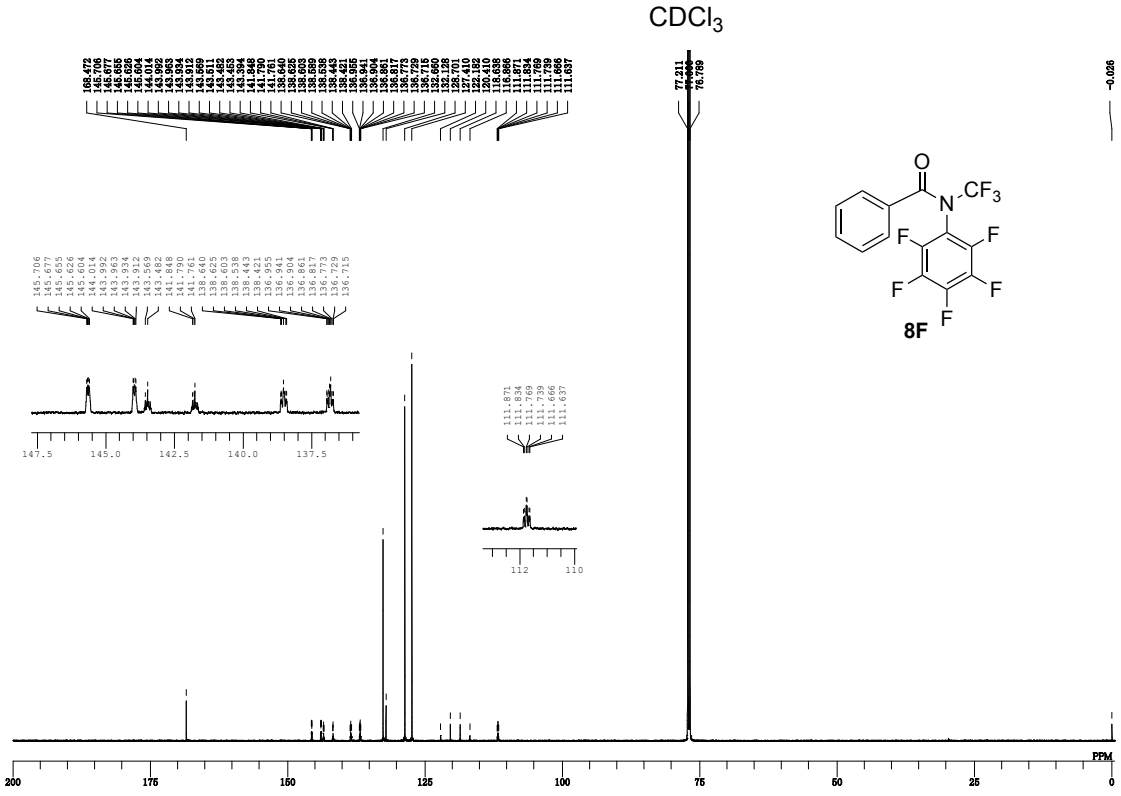

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$) spectrum of **7F**.



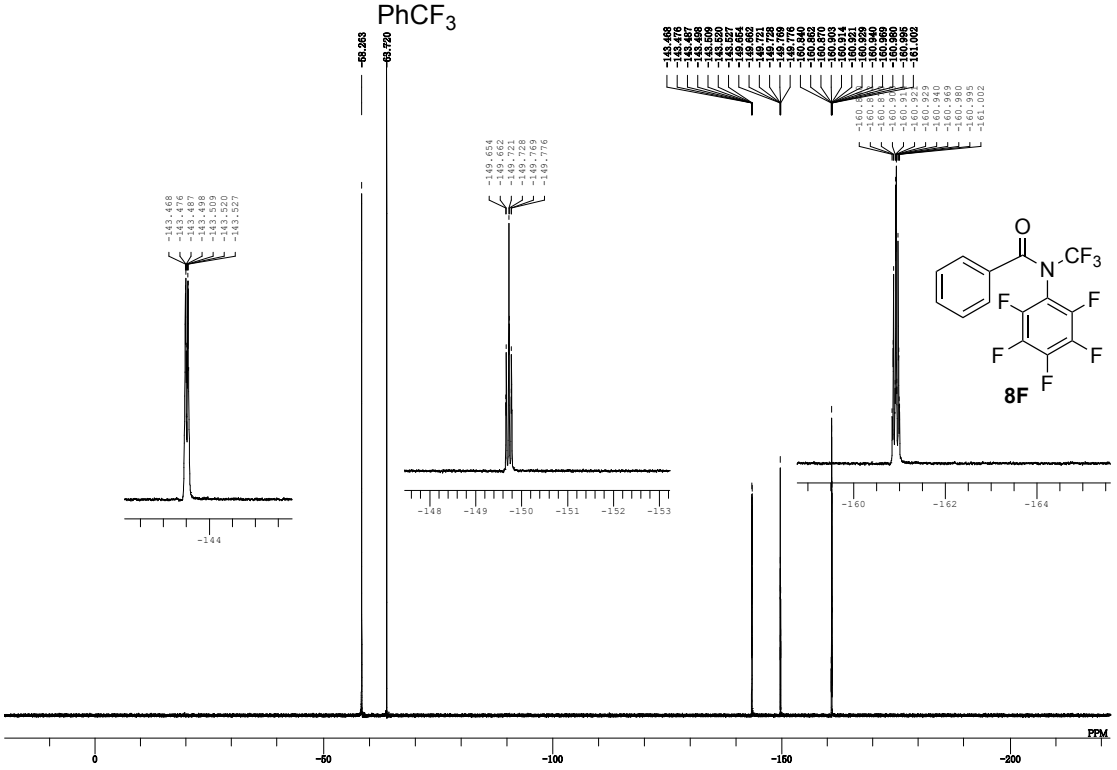

$^{19}$F NMR (283 MHz, $CDCl_3$) spectrum of **7F**.



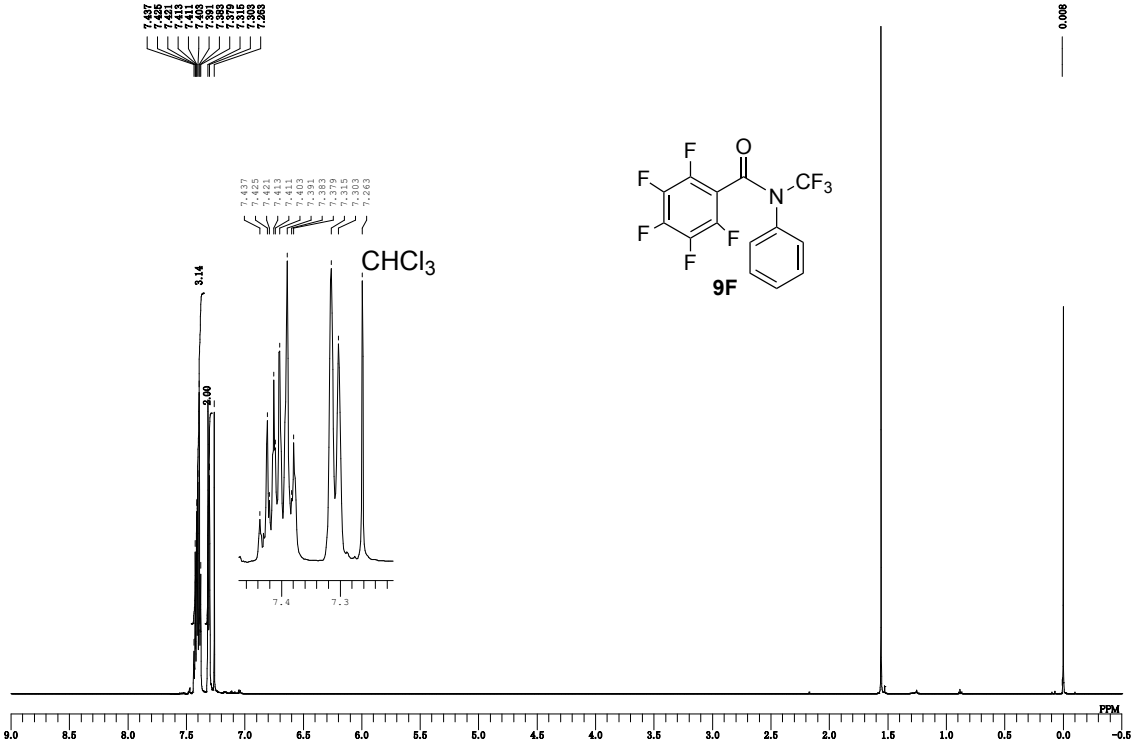

$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **8F**.



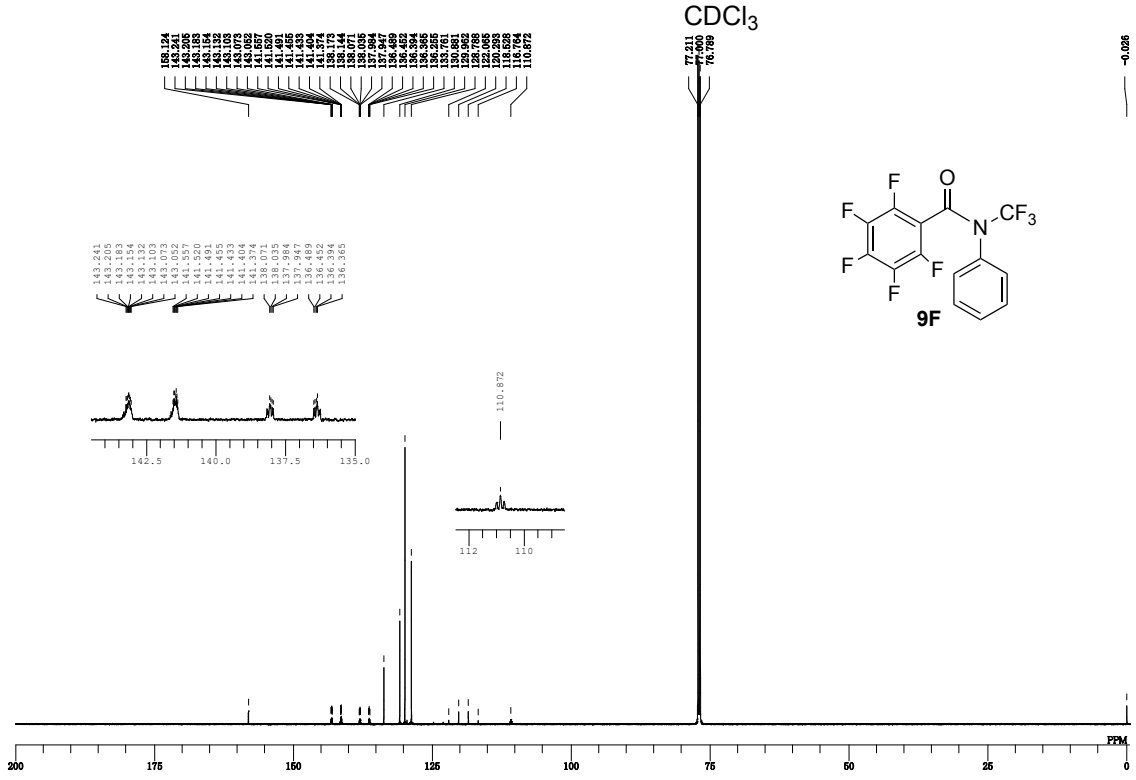

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) spectrum of **8F**.



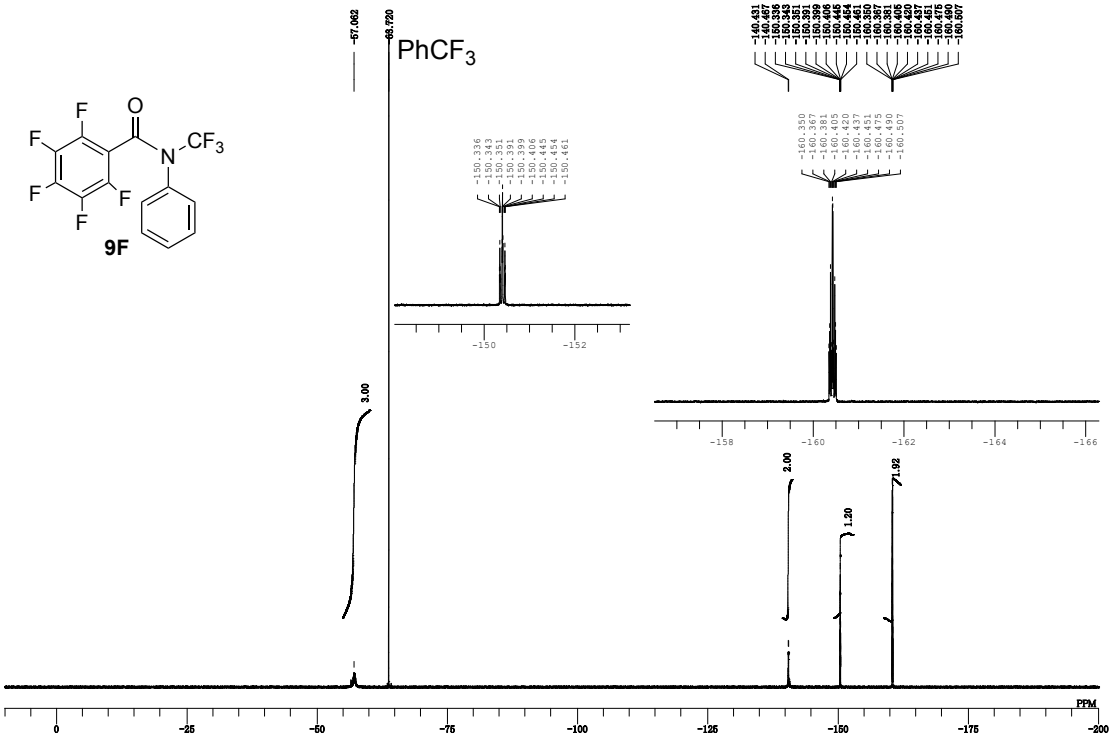

$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **8F**.



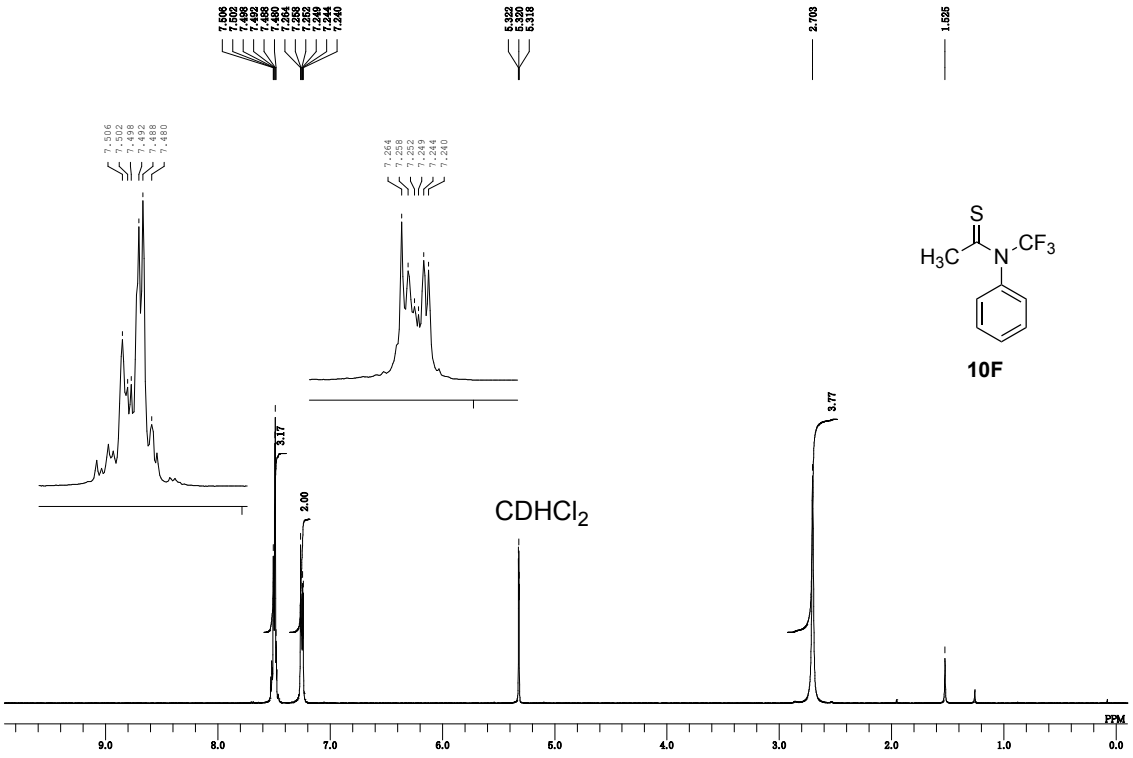

$^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **9F**.



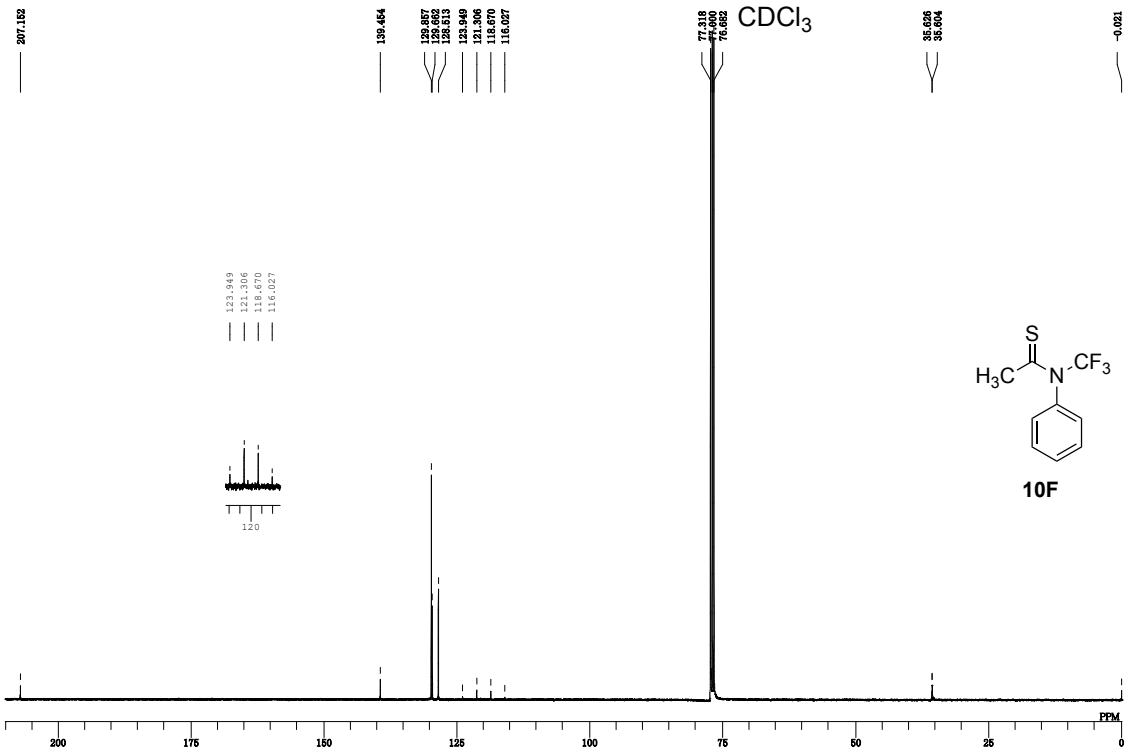

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) spectrum of **9F**.



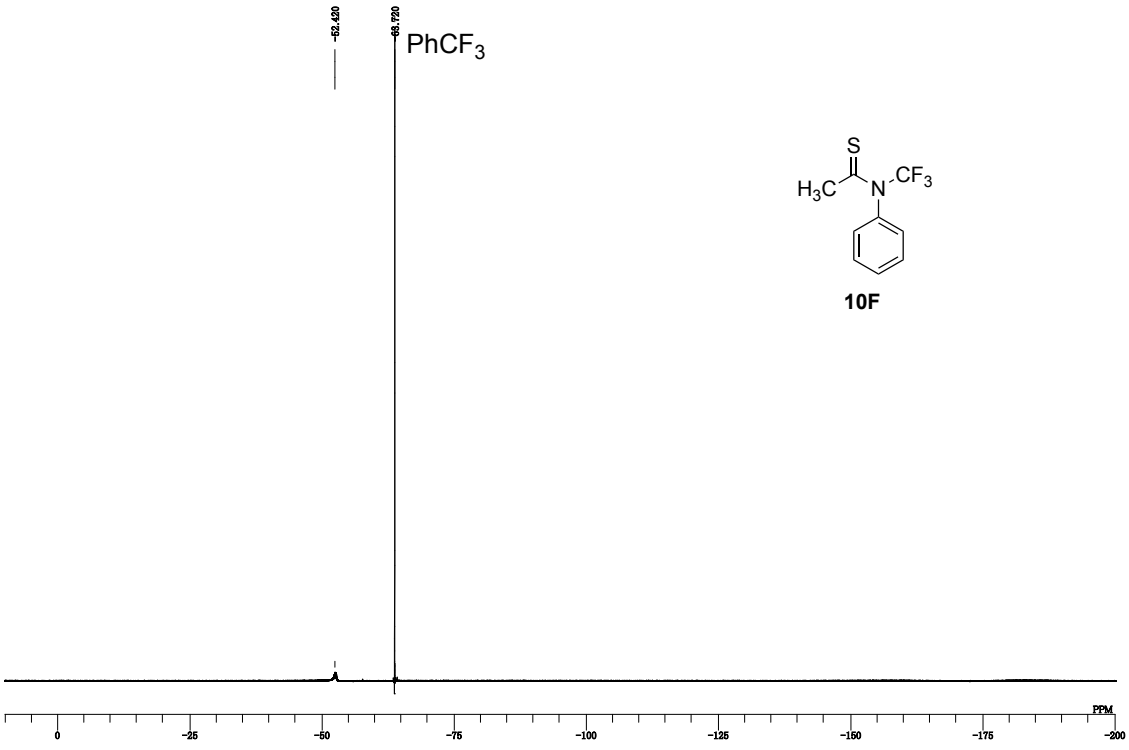

$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **9F**.



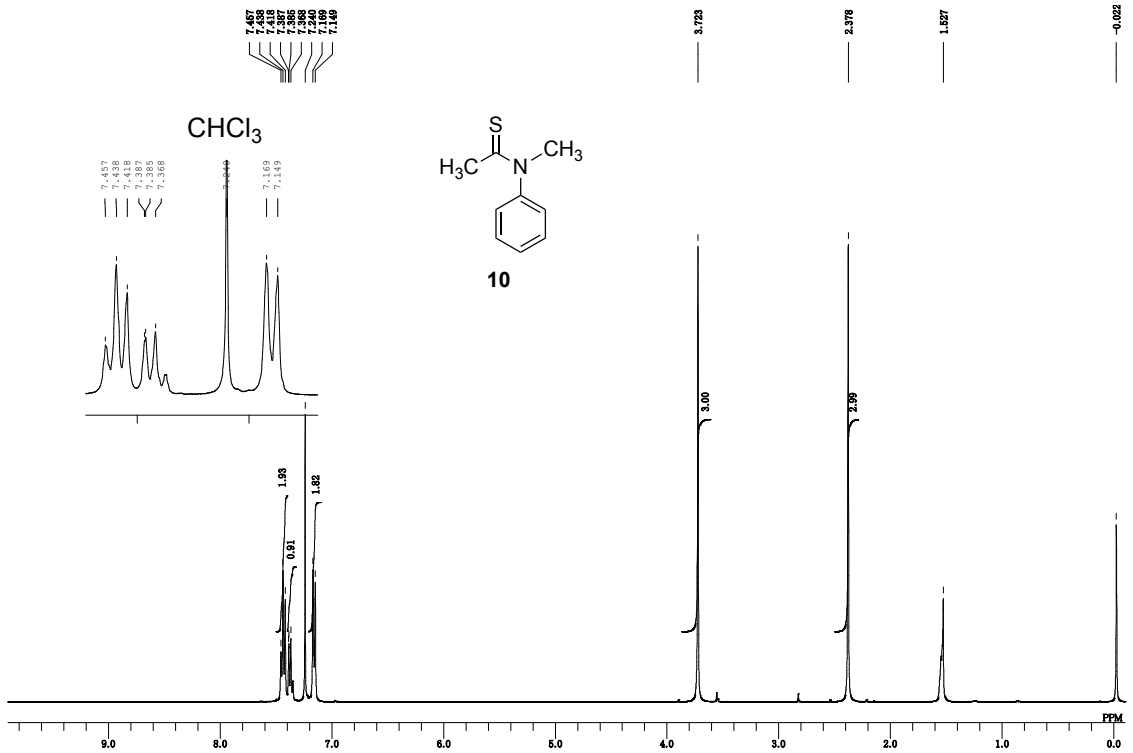

$^{1}H$ NMR (400 MHz, $CD_2Cl_2$) spectrum of **10F**.



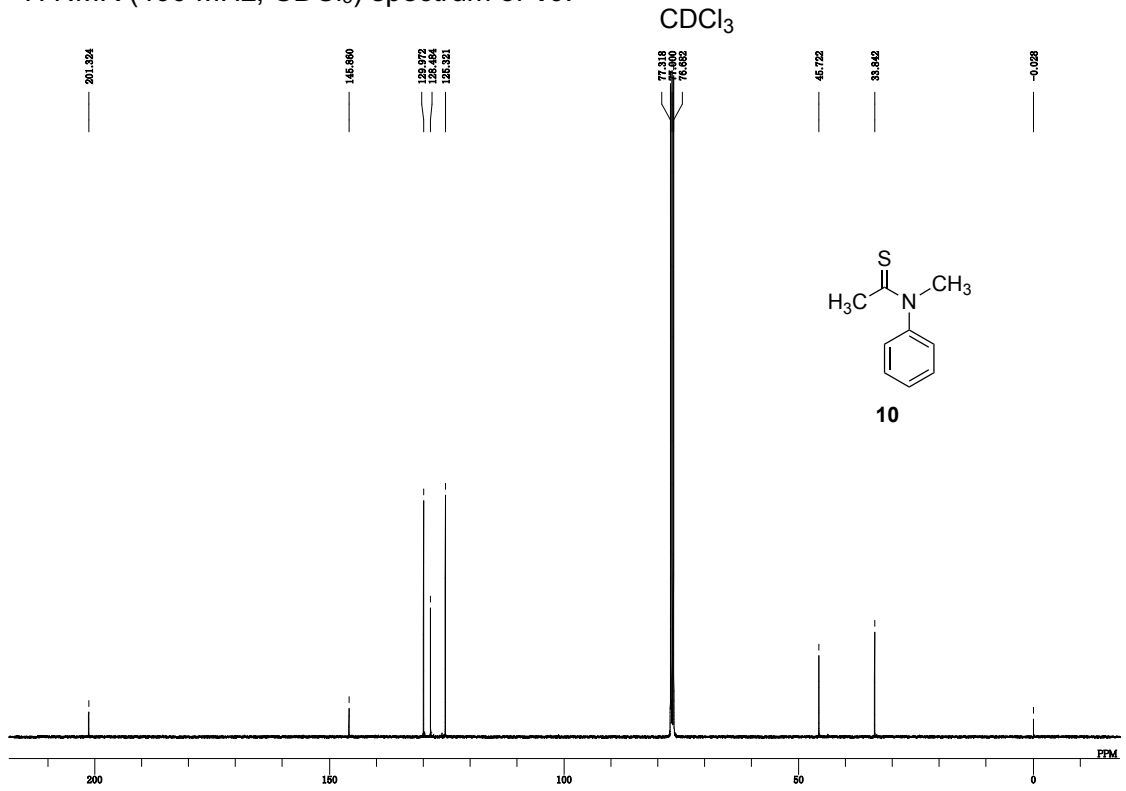

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **10F**.



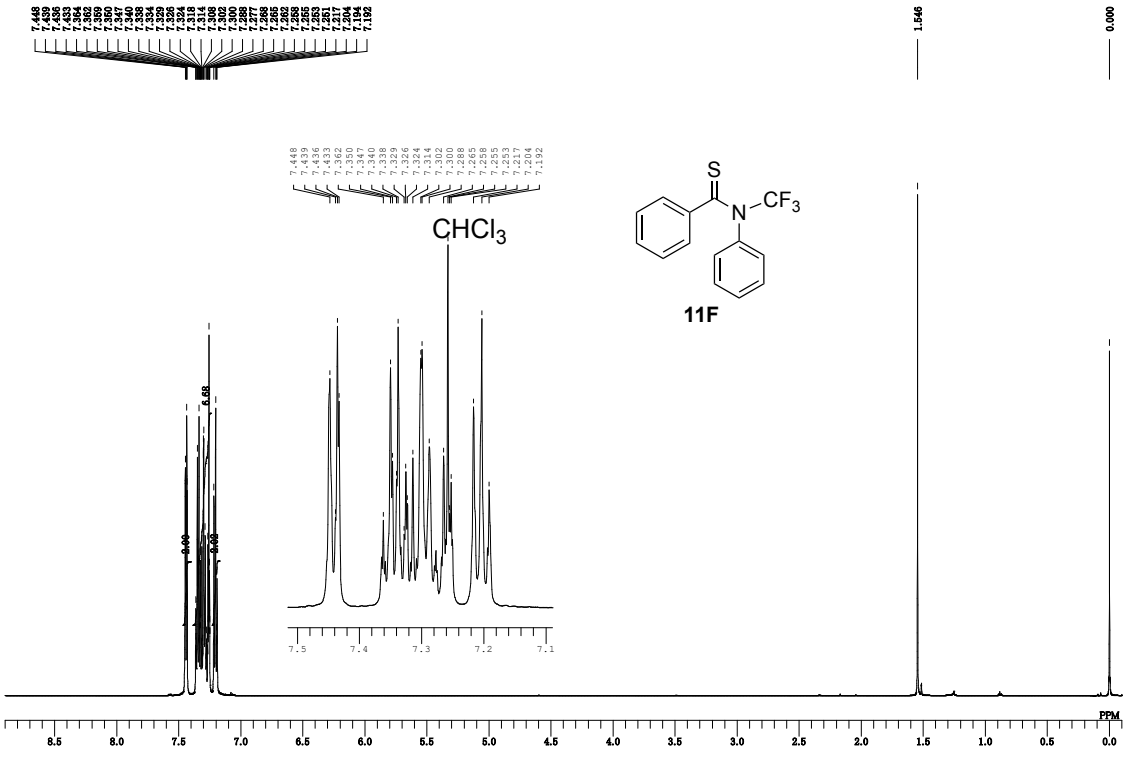

$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **10F**.



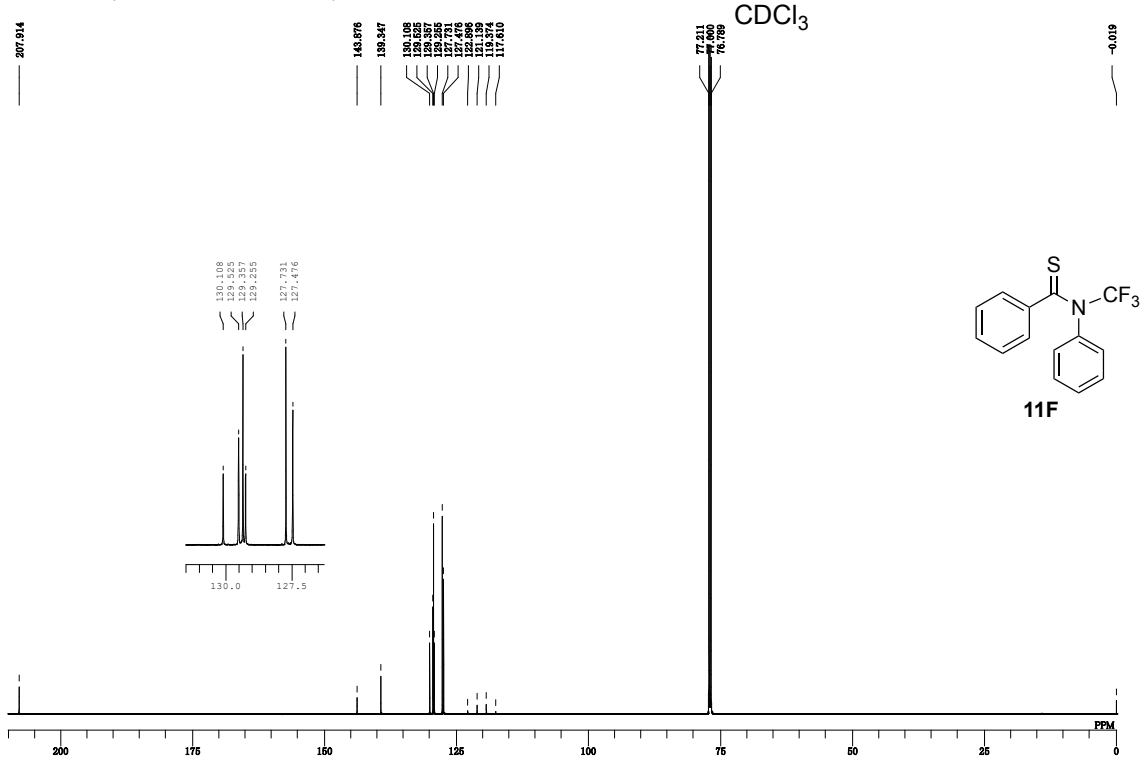

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **10**.



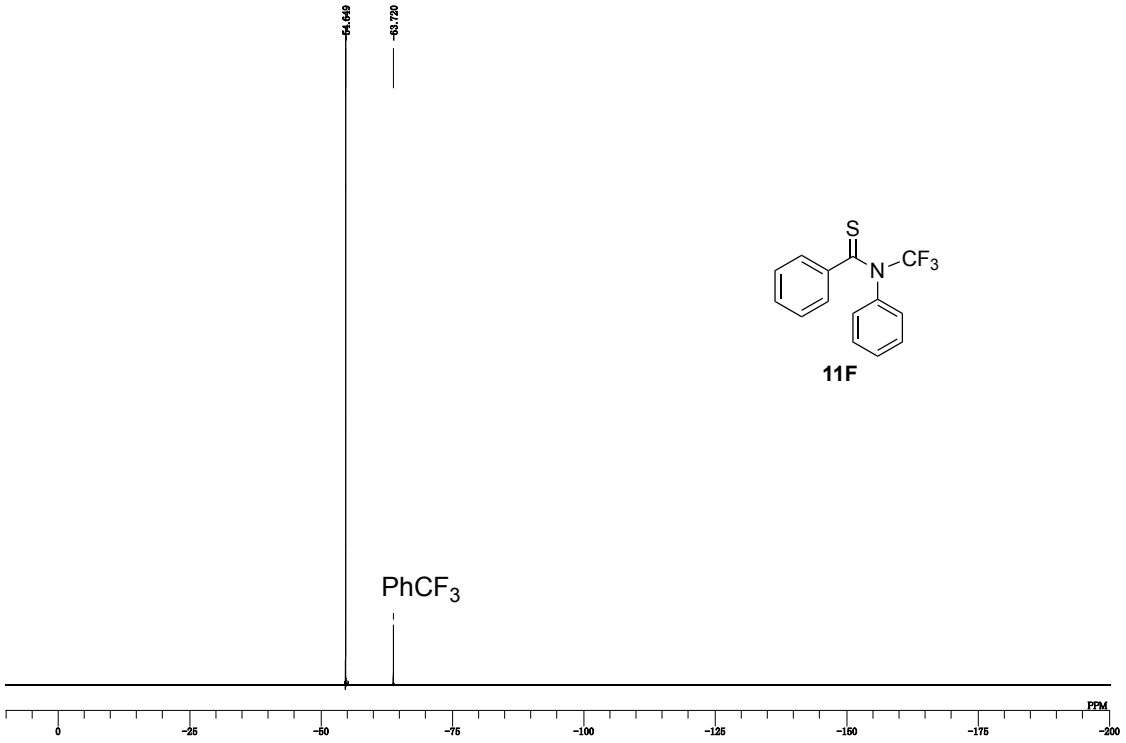

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **10**.



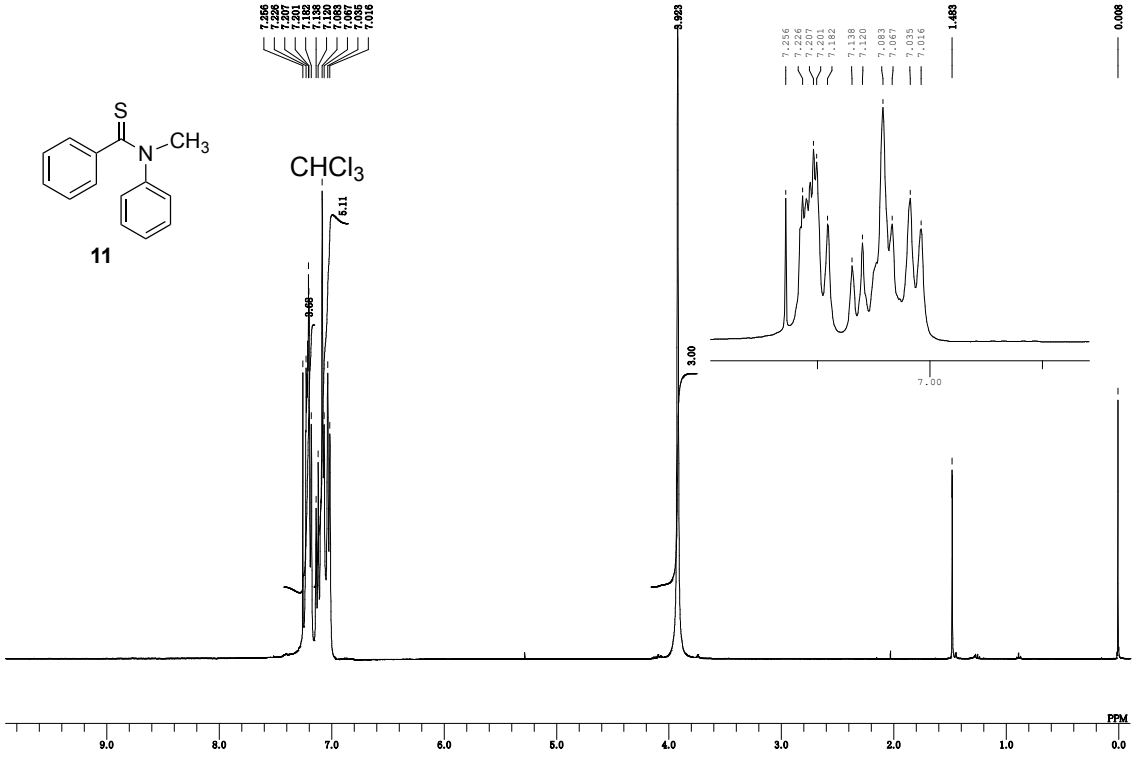

$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **11F**.



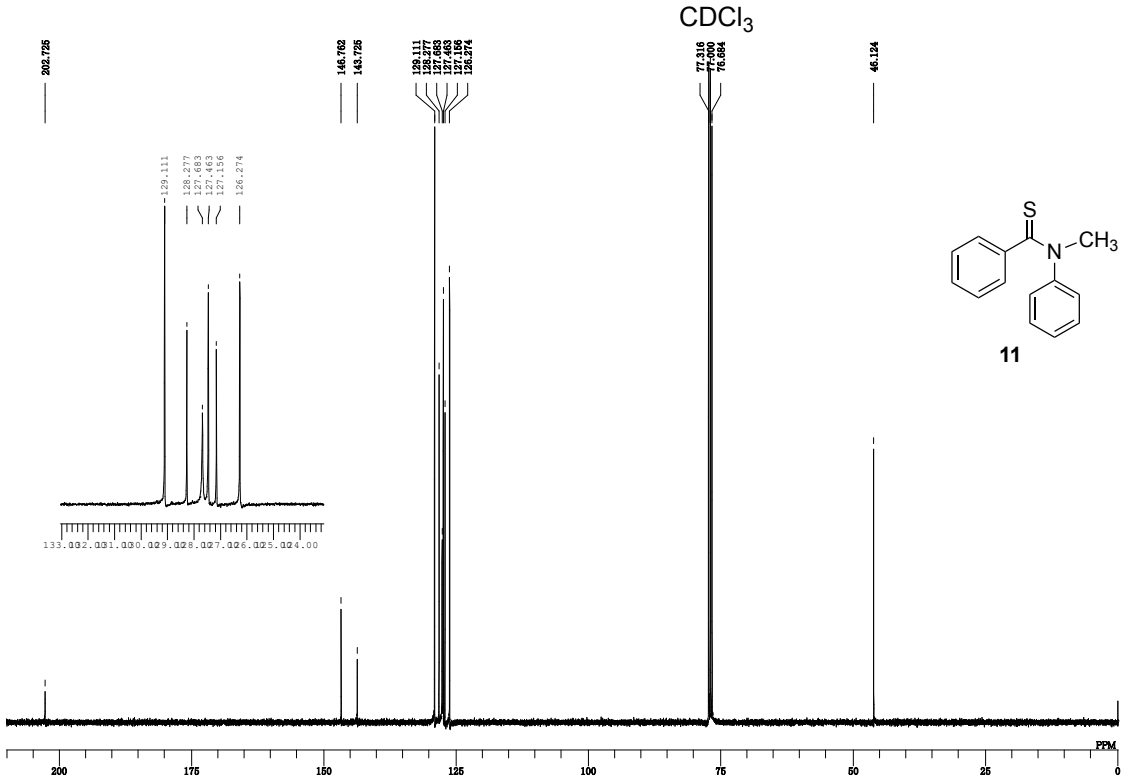

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) spectrum of **11F**.



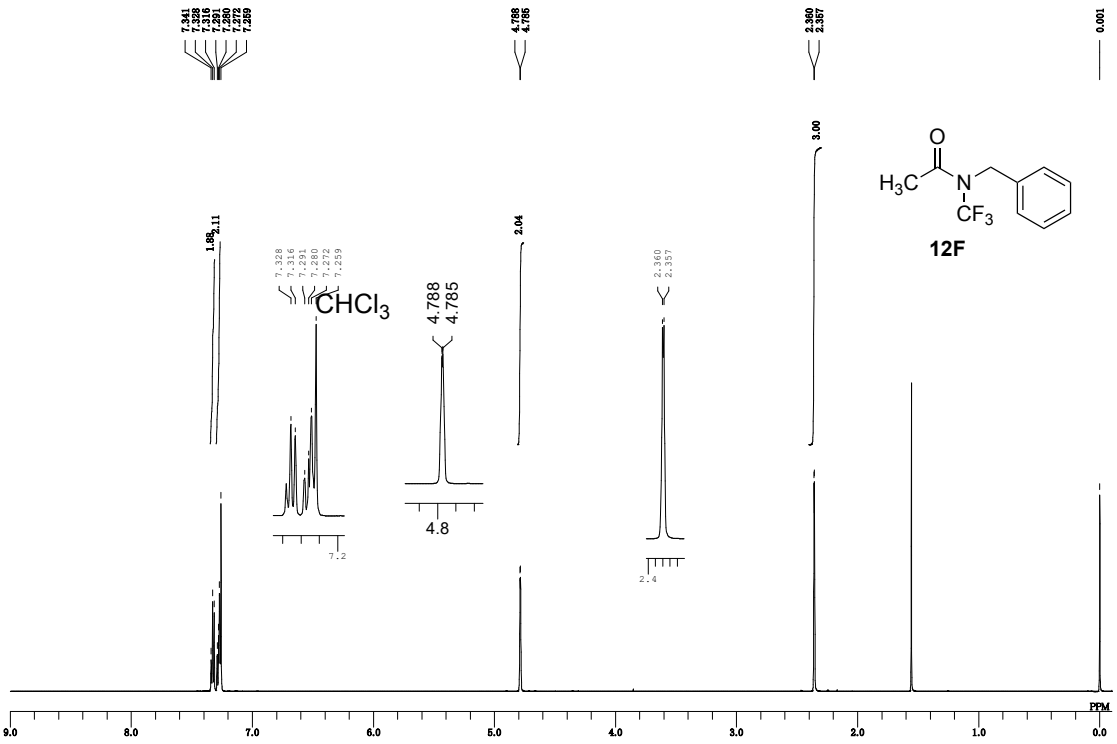

$^{19}$F NMR (376 MHz, $CDCl_3$) spectrum of **11F**.



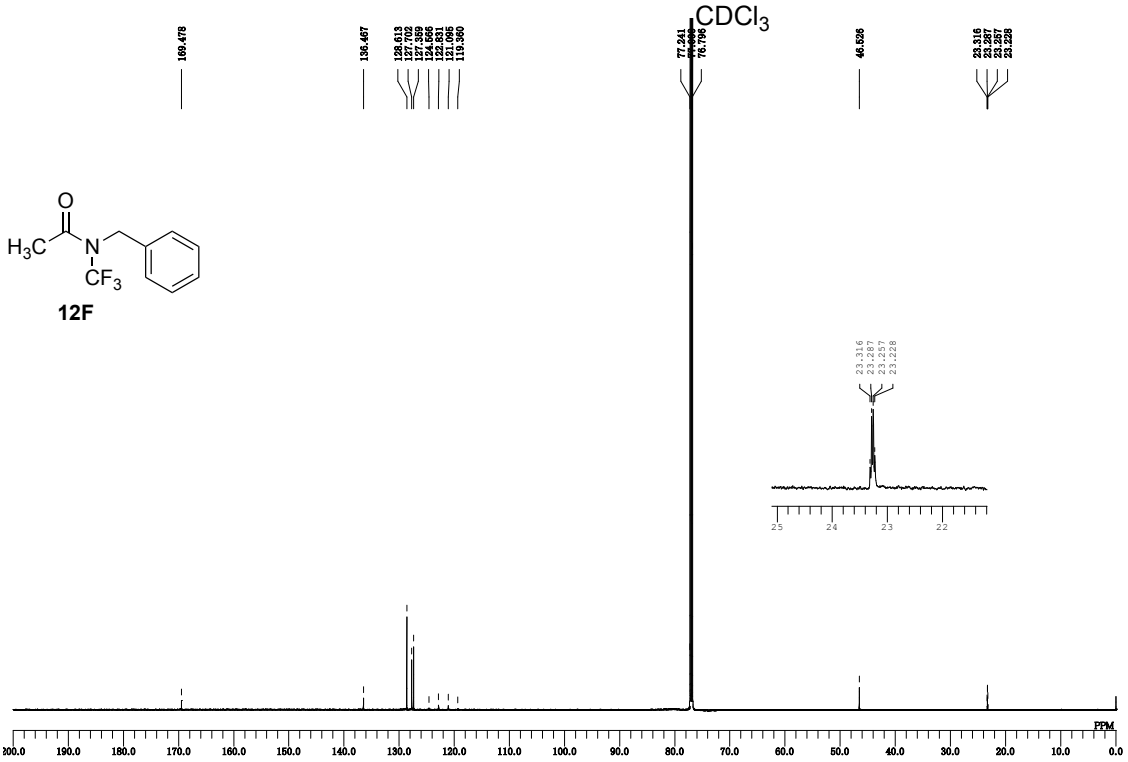

$^{1}$H NMR (400 MHz, $CDCl_3$, 50 ºC) spectrum of **11**.



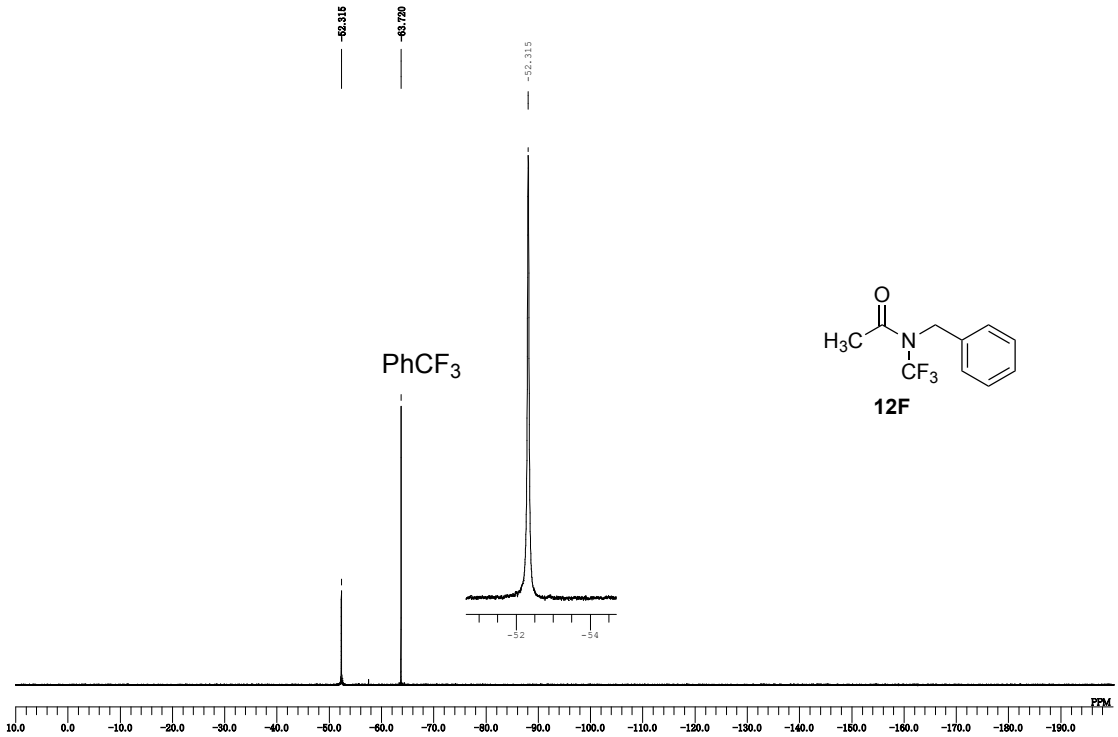

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 50 ºC) spectrum of **11**.



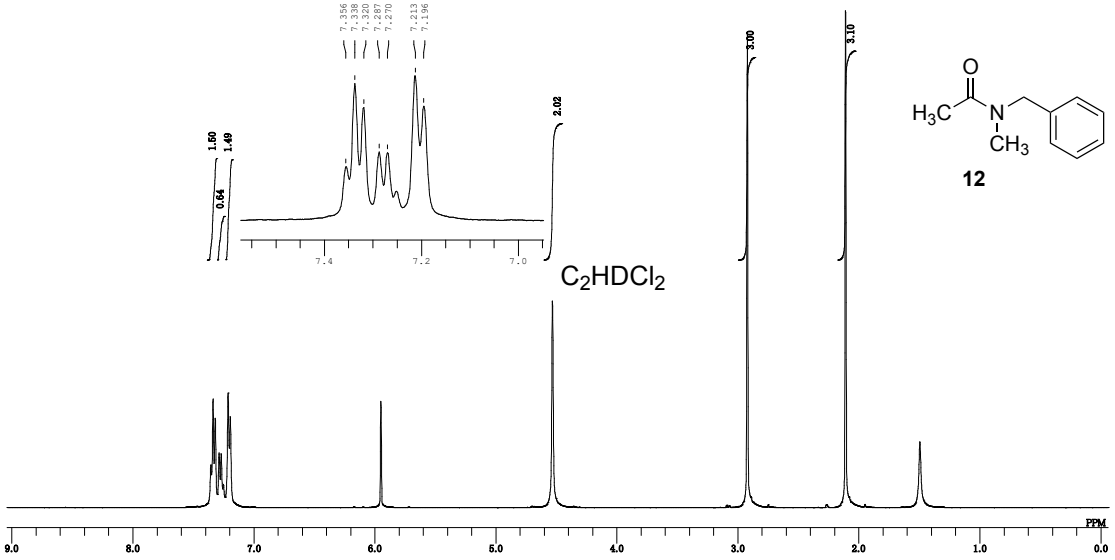

$^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of **12F**.



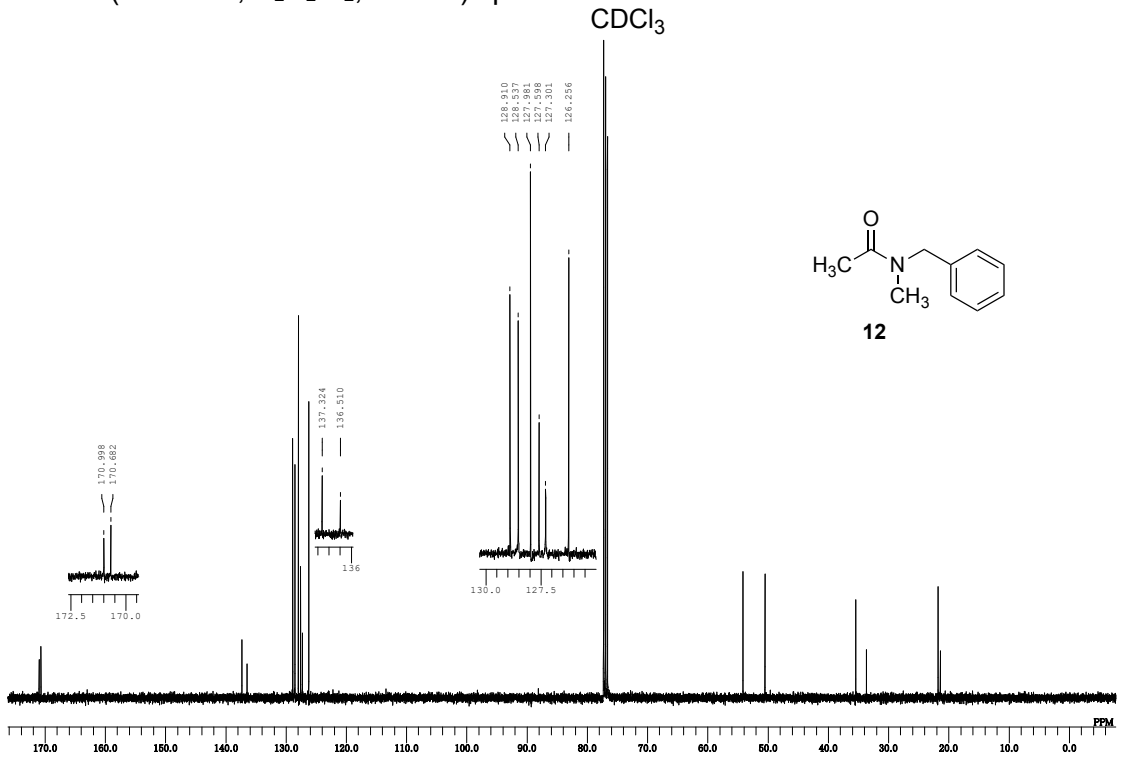

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) spectrum of **12F**.



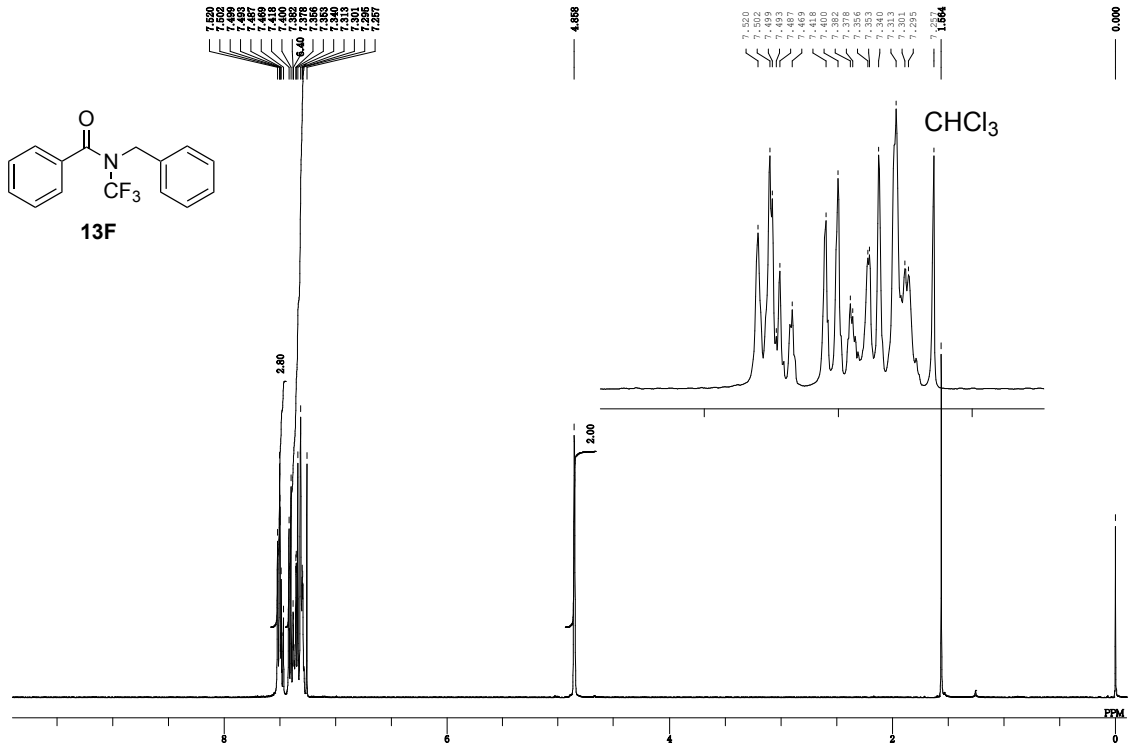

$^{19}F$ NMR (283 MHz, $CDCl_3$) spectrum of **12F**.



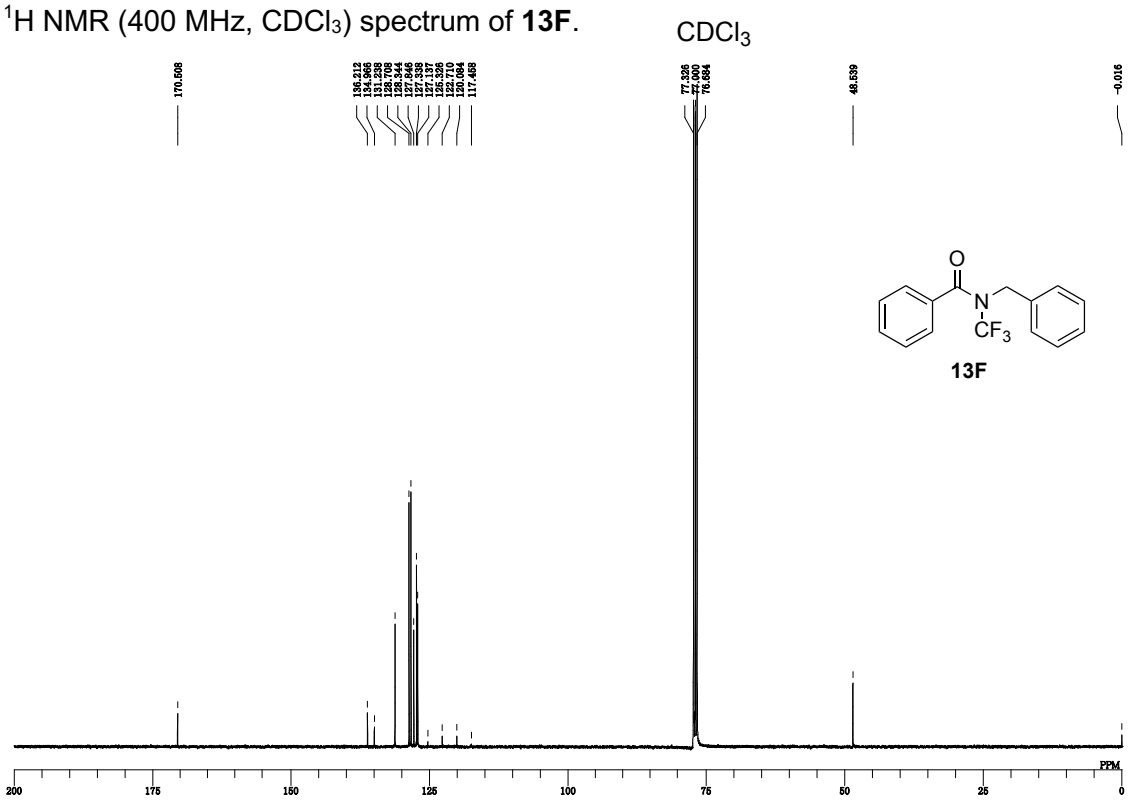

$^{1}$H NMR (400 MHz, $C_2D_2Cl_2$, 120 ºC) spectrum of **12**.



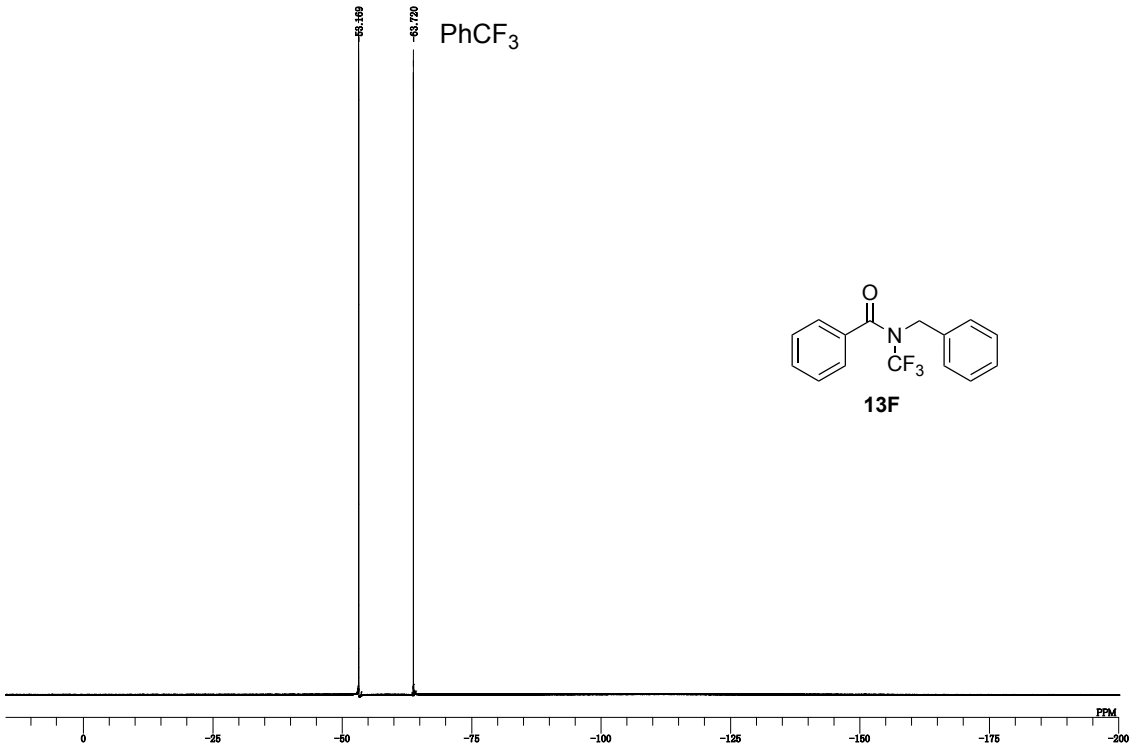

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **12**.



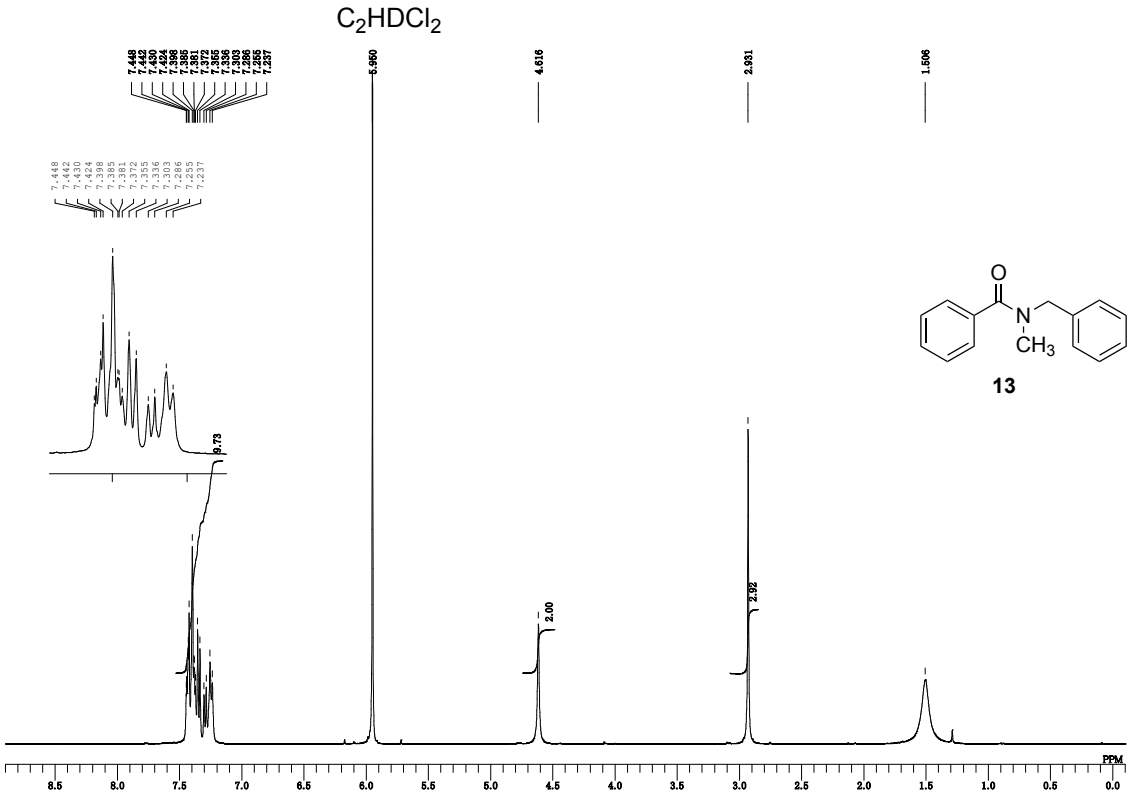

$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **13F**.



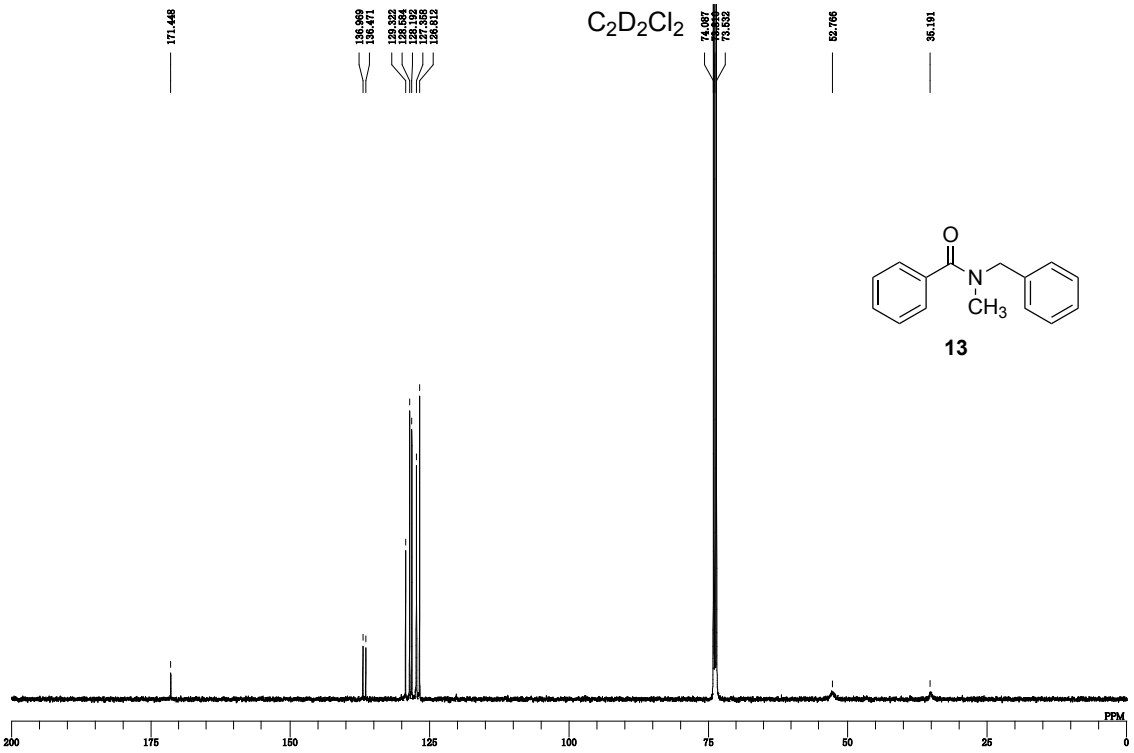

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **13F**.



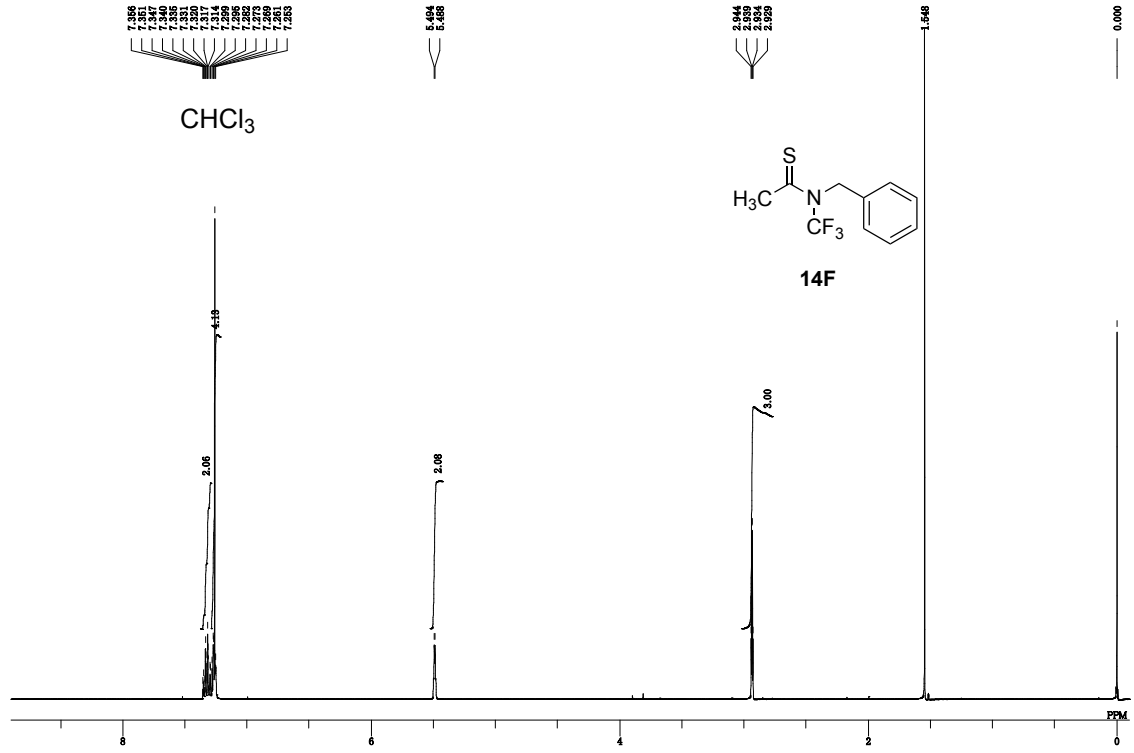

$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **13F**.



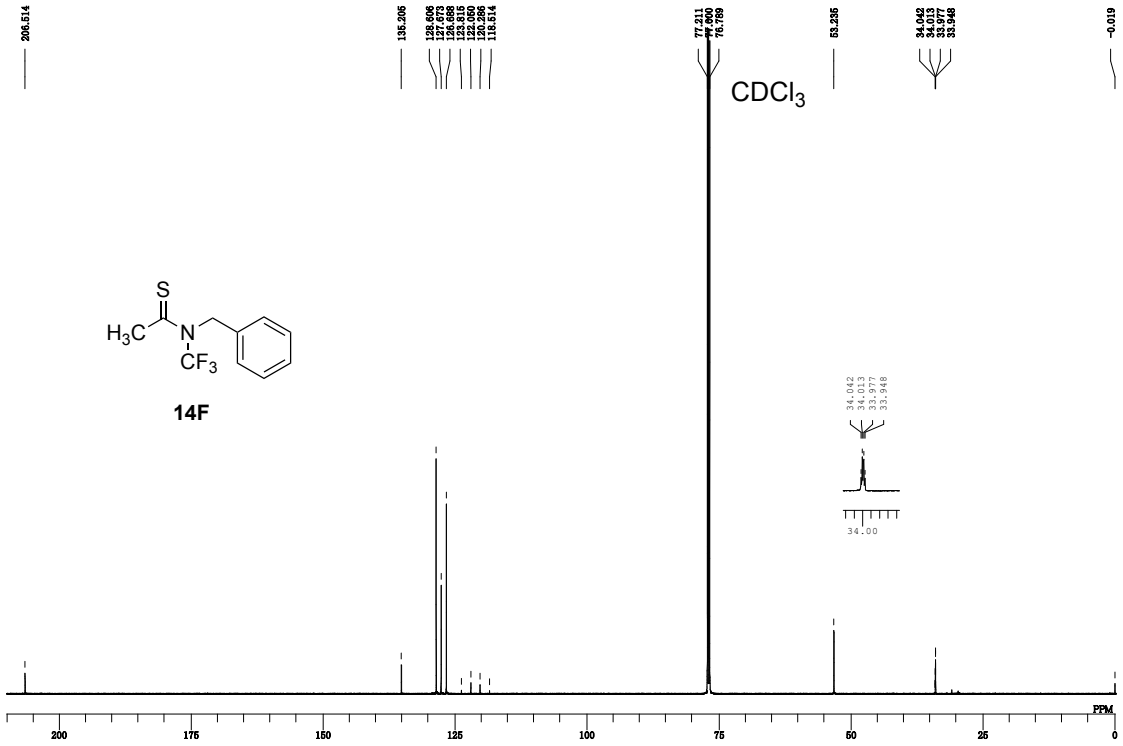

$^{1}H$ NMR (400 MHz, $C_2D_2Cl_2$, 100 ºC) spectrum of **13**.



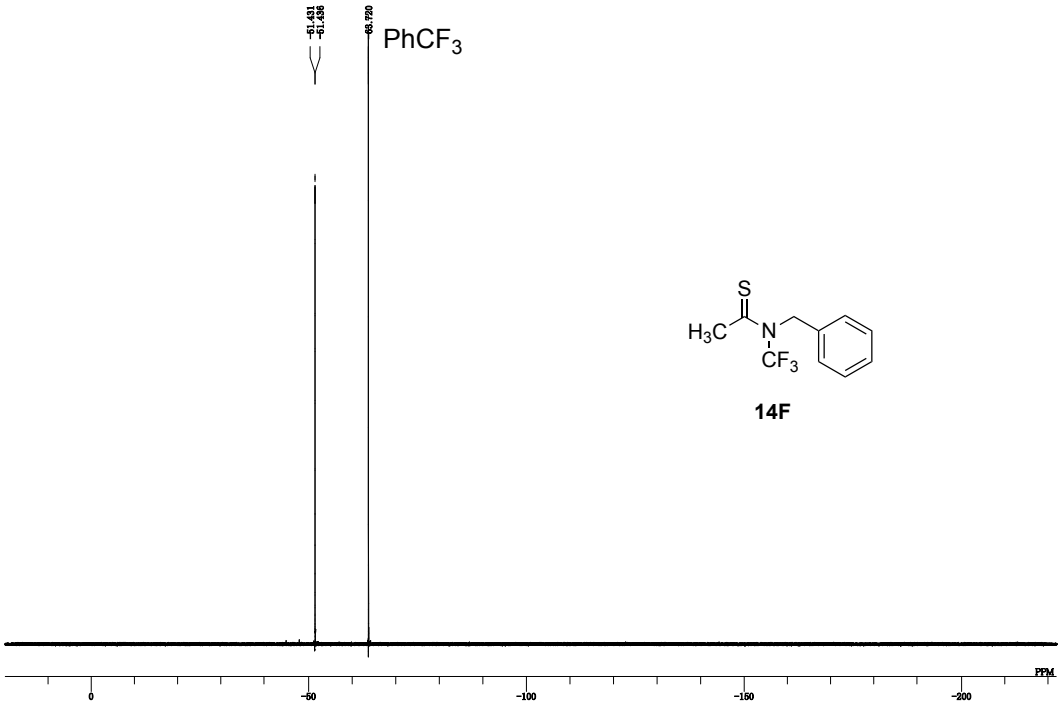

$^{13}C\{^{1}H\}$ NMR (100 MHz, $C_2D_2Cl_2$, 100 ºC) spectrum of **13**.



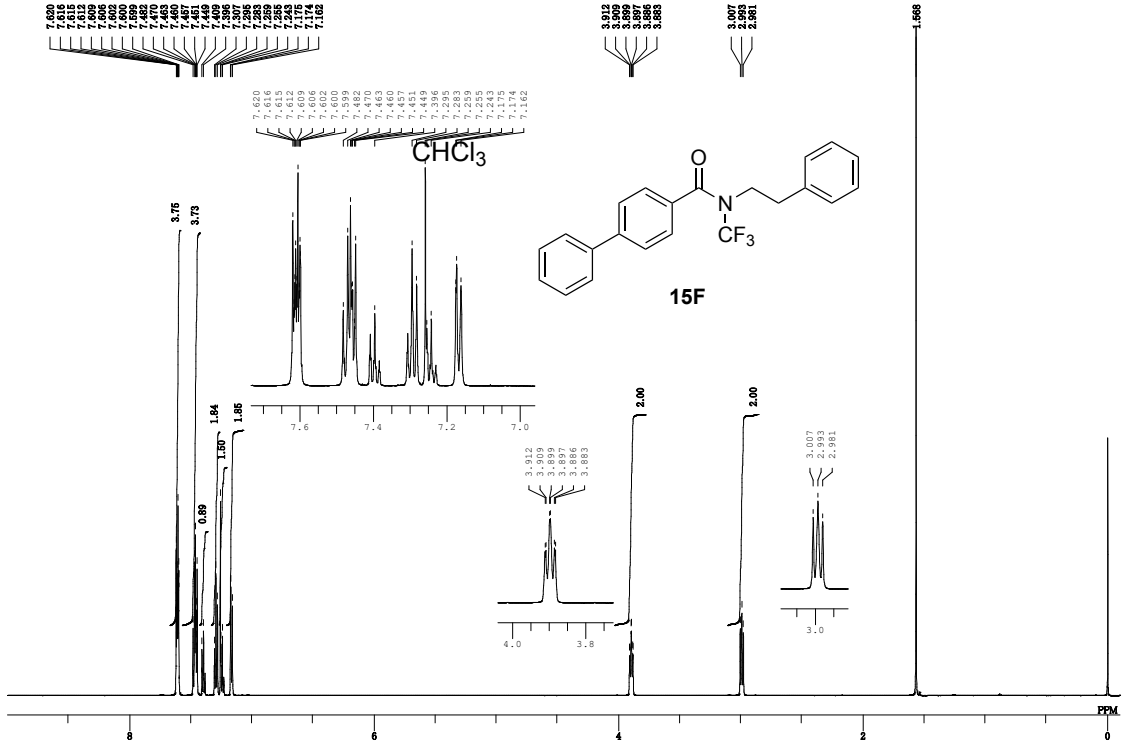

$^{1}H$ NMR (400 MHz, $CDCl_3$) spectrum of **14F**.



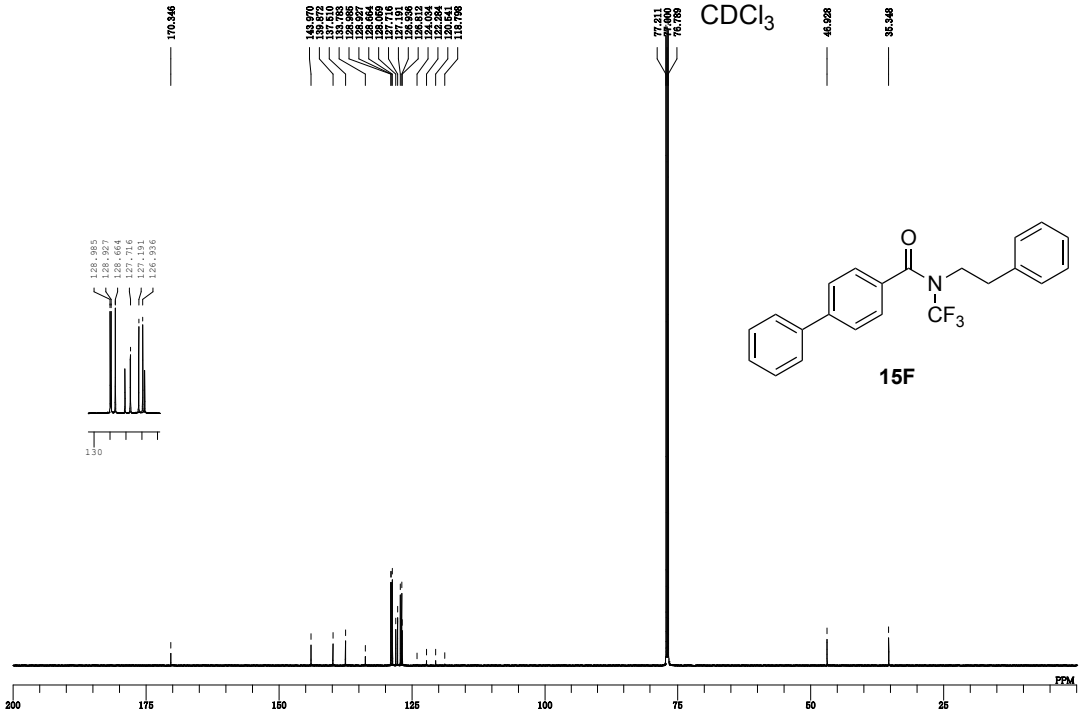

$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) spectrum of **14F**.



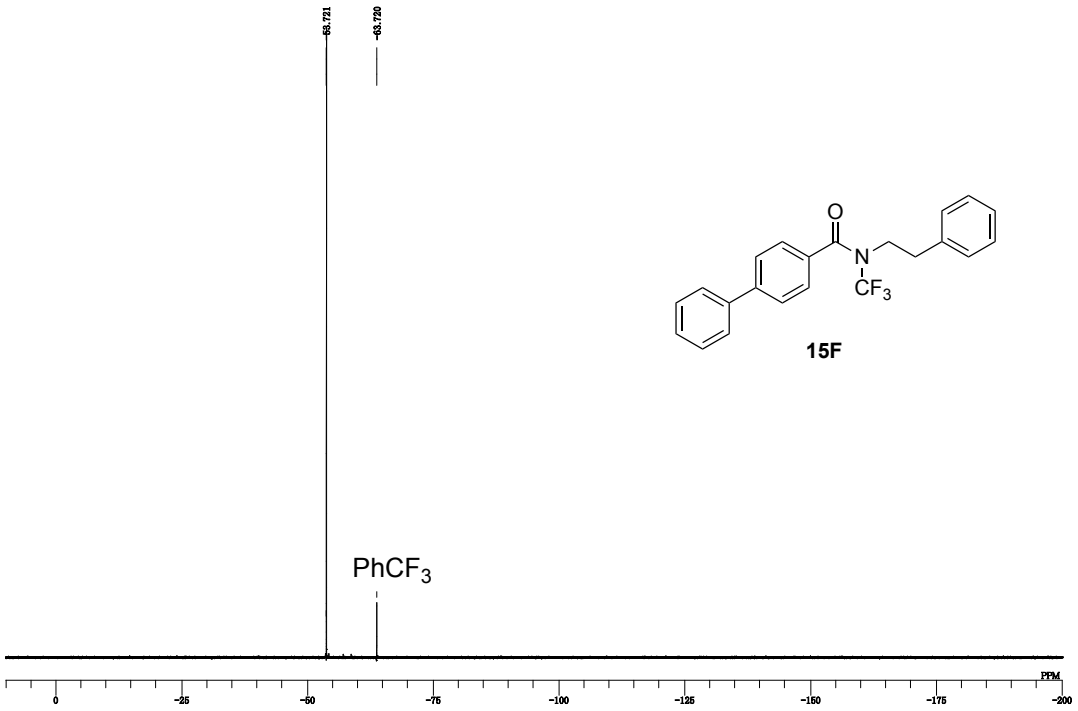

$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **14F**.




$^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **15F**.




$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) spectrum of **15F**.

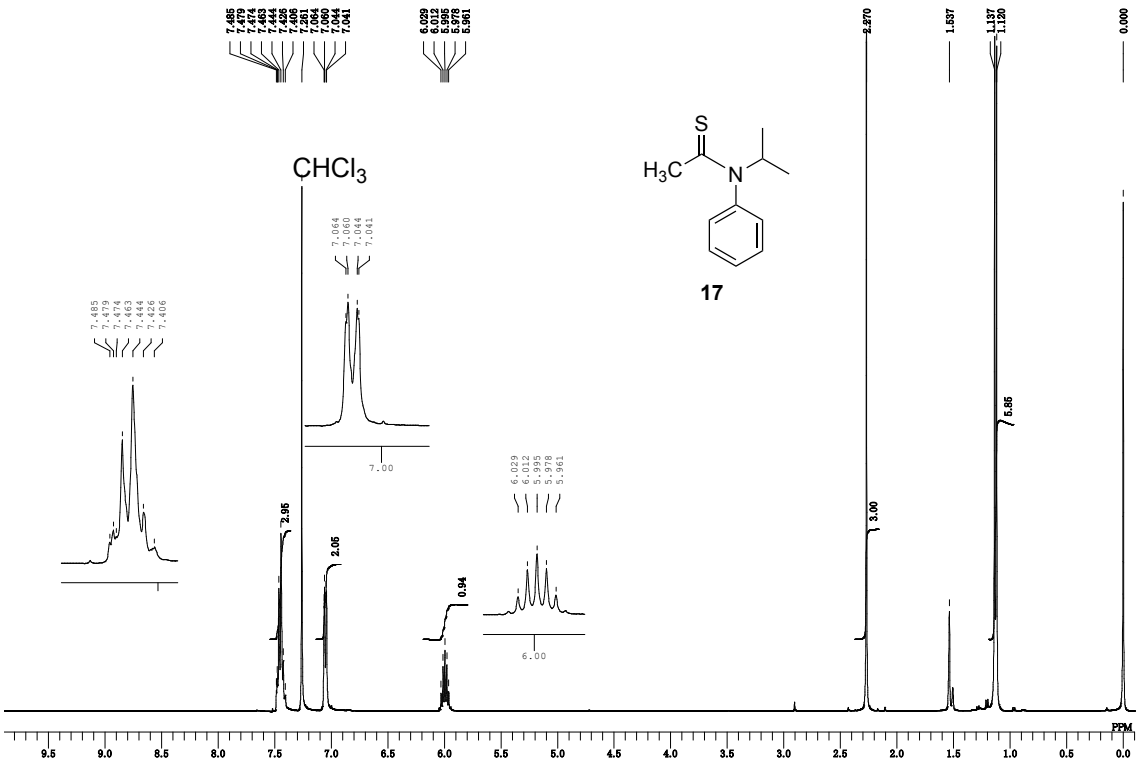




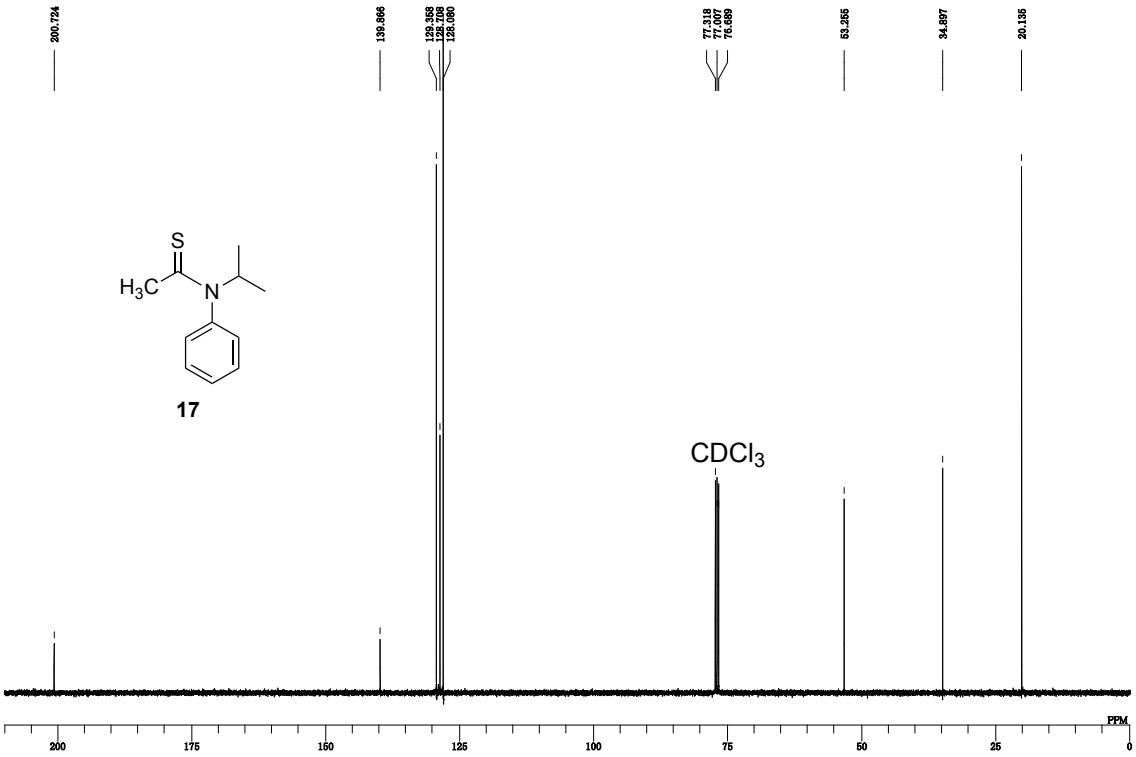


**15F**

$^{19}$F NMR (376 MHz, $CDCl_3$) spectrum of **15F**.




$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **17**.




$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **17**.

5, Figures related to NMR experiment

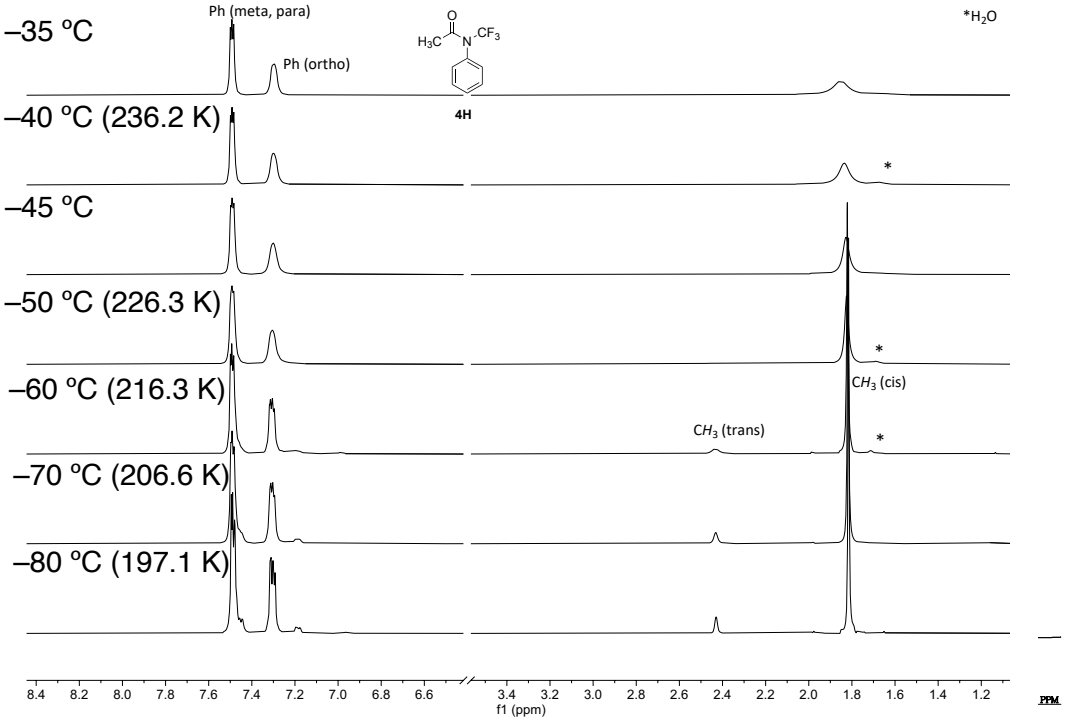



Figure S6. VT-$^{1}$HNMR ($CD_2Cl_2$, 400 MHz) of **2F**.

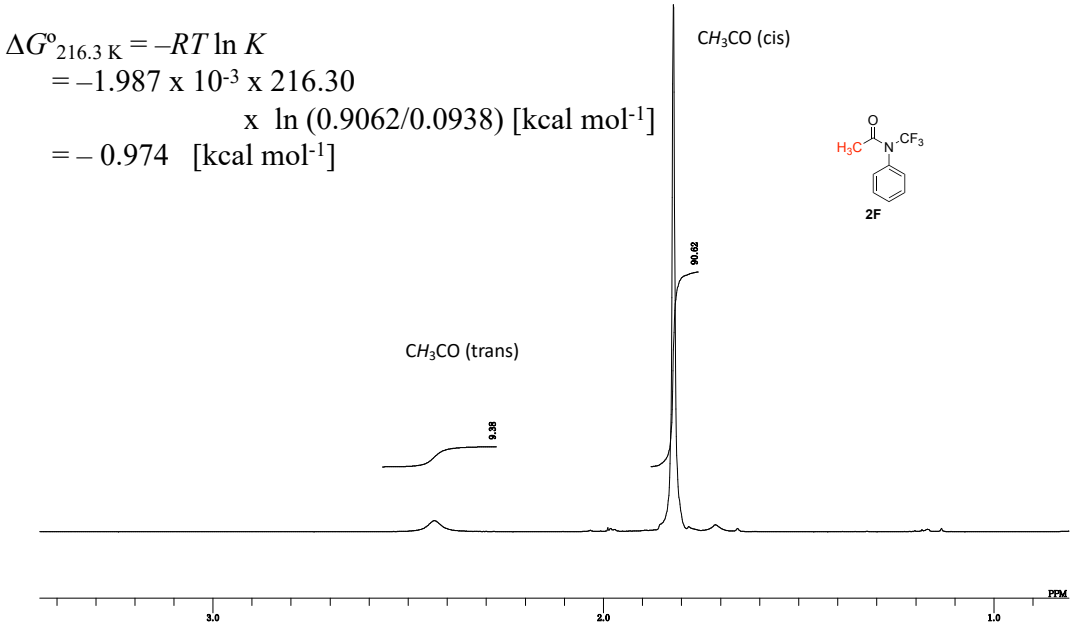



Figure S7. $^{1}$HNMR integration of **2F** ($CD_2Cl_2$, 400 MHz, 216 K).

$\Delta G^{o}_{197.1\ K} = -RT \ln K$

$= -1.987 \times 10^{-3} \times 197.14 \times \ln (0.9662/0.0338)$ [kcal mol$^{-1}$]

$= -1.313$ [kcal mol$^{-1}$]

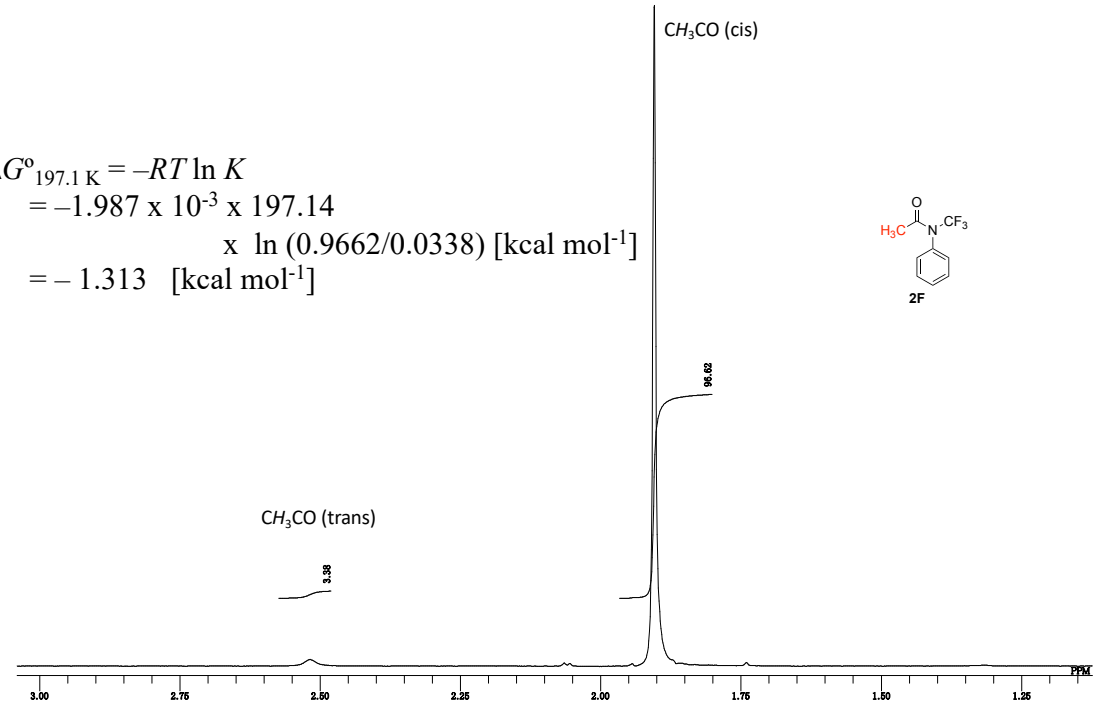



Figure S8. $^{1}$HNMR integration of **2F** ($CD_3OD$, 400 MHz, 197 K).

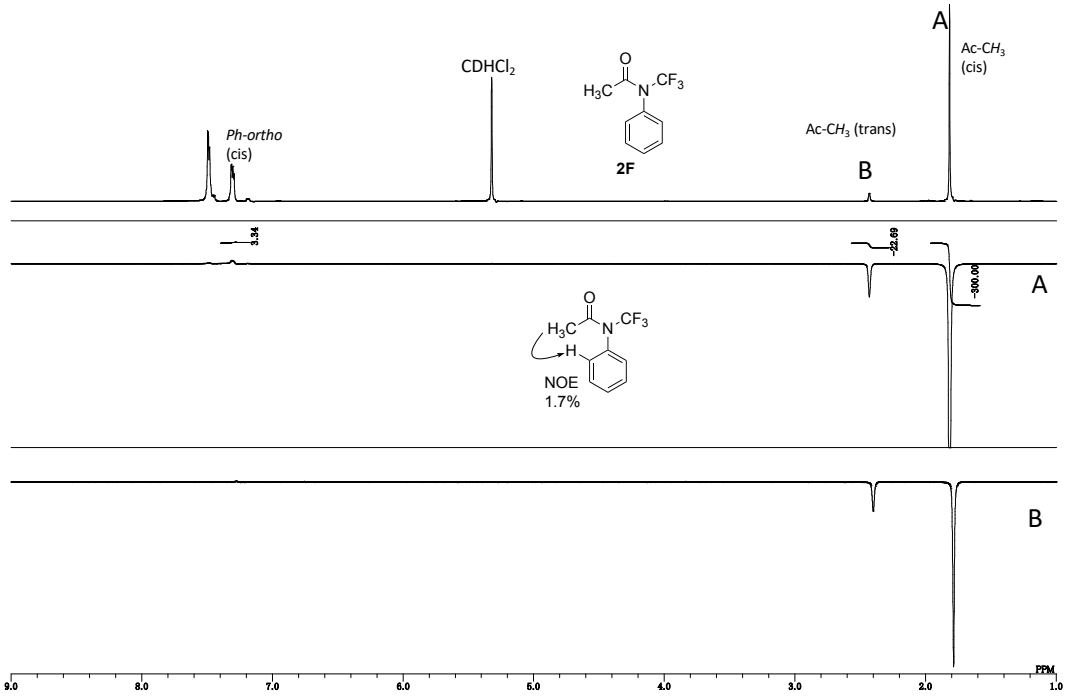



Figure S9. 1D-NOE spectrum of **2F** ($CD_2Cl_2$, 400 MHz, 197 K).

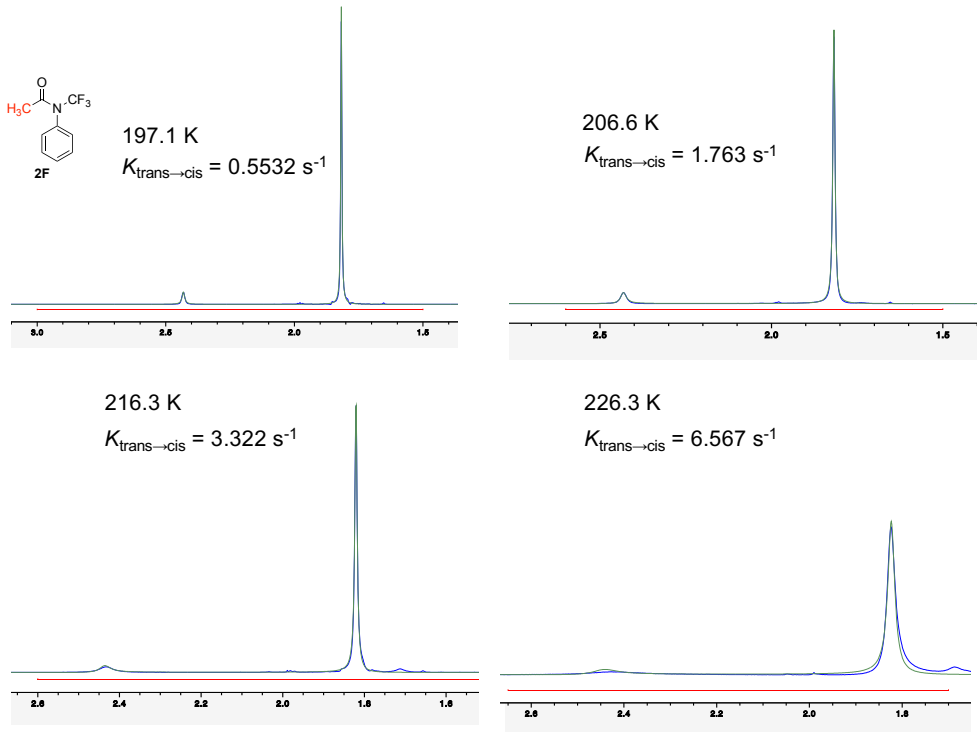



Figure S10. $^{1}$HNMR line-shape analysis ($CD_2Cl_2$, 400 MHz) of **2F**.

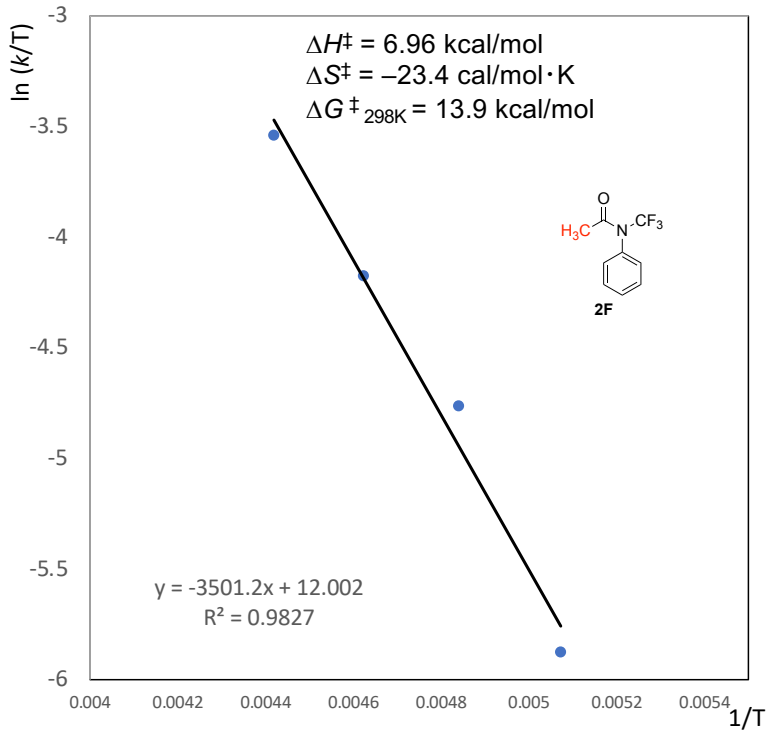



Figure S11. Arrenius plot of line-shape analysis of **2F**.

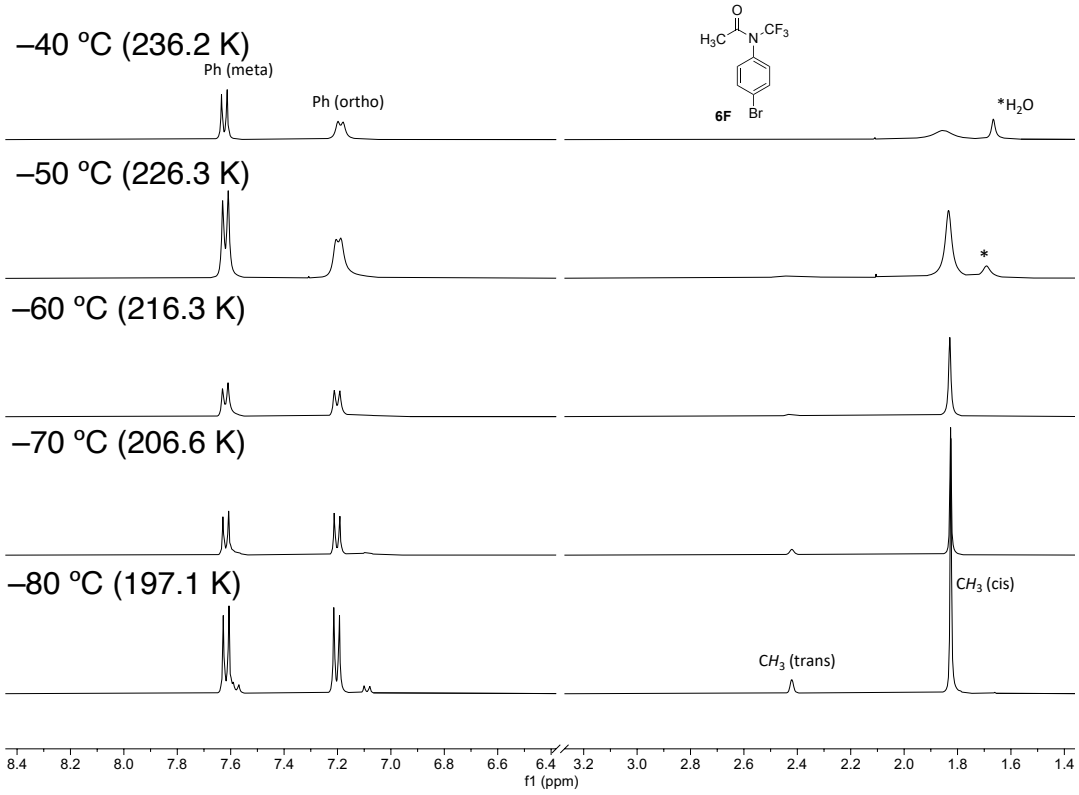



Figure S12. VT-$^1$HNMR ($CD_2Cl_2$, 400 MHz) of **6F**.

$$\Delta G^{o}_{236.2\ K} = -RT \ln K$$
$$= -1.987 \times 10^{-3} \times 216.30 \times \ln (0.8979/0.1021)\ [\text{kcal mol}^{-1}]$$
$$= -0.934\ [\text{kcal mol}^{-1}]$$

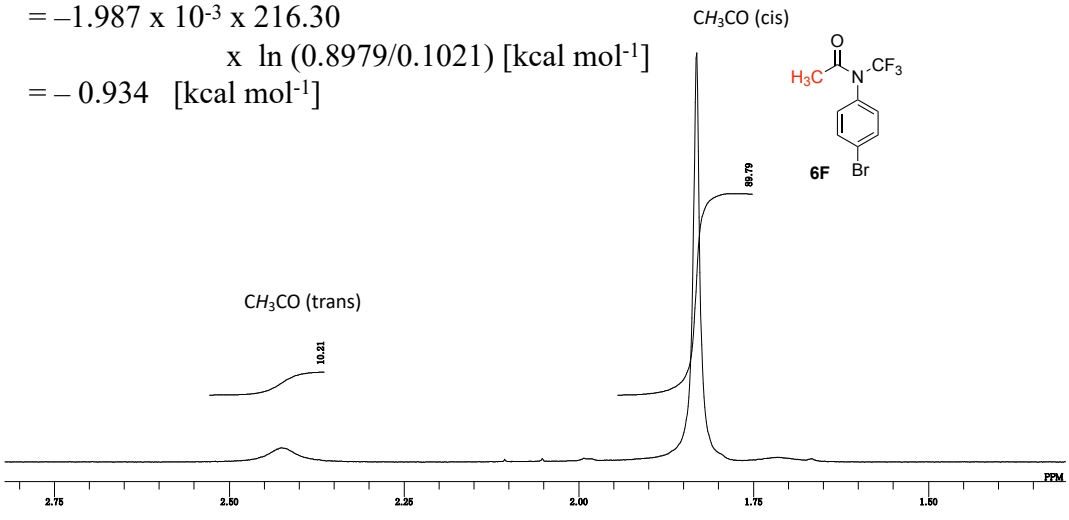



Figure S13. $^1$HNMR integration of **6F** ($CD_2Cl_2$, 400 MHz, 216 K).

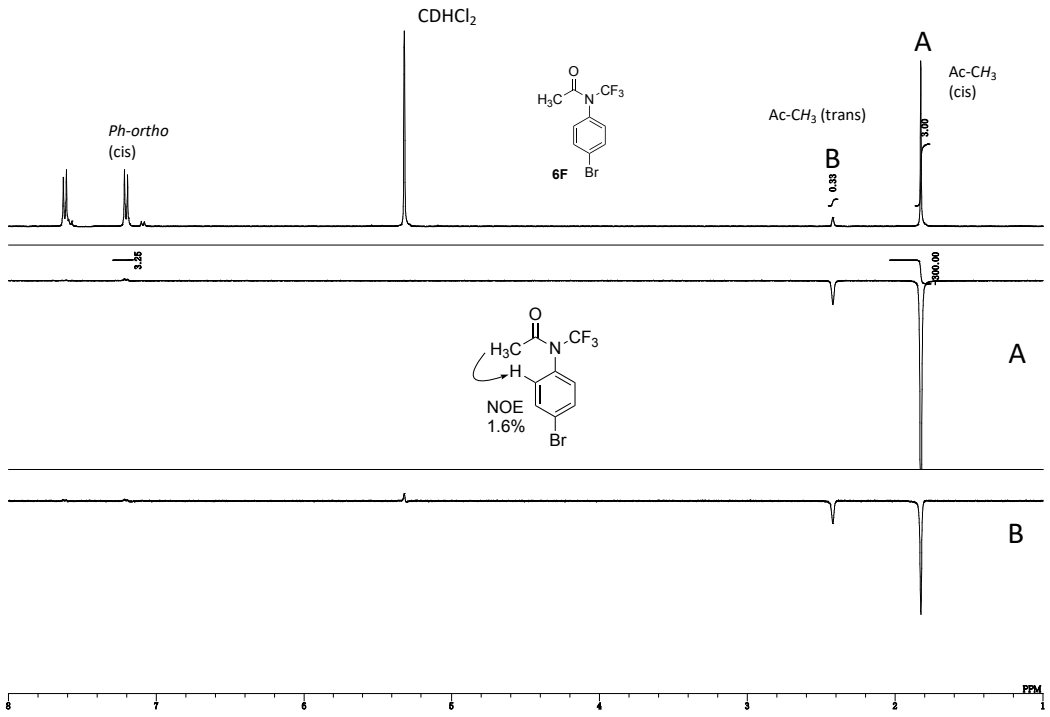



Figure S14. 1D-NOE spectrum of **6F** ($CD_2Cl_2$, 400 MHz, 197 K).

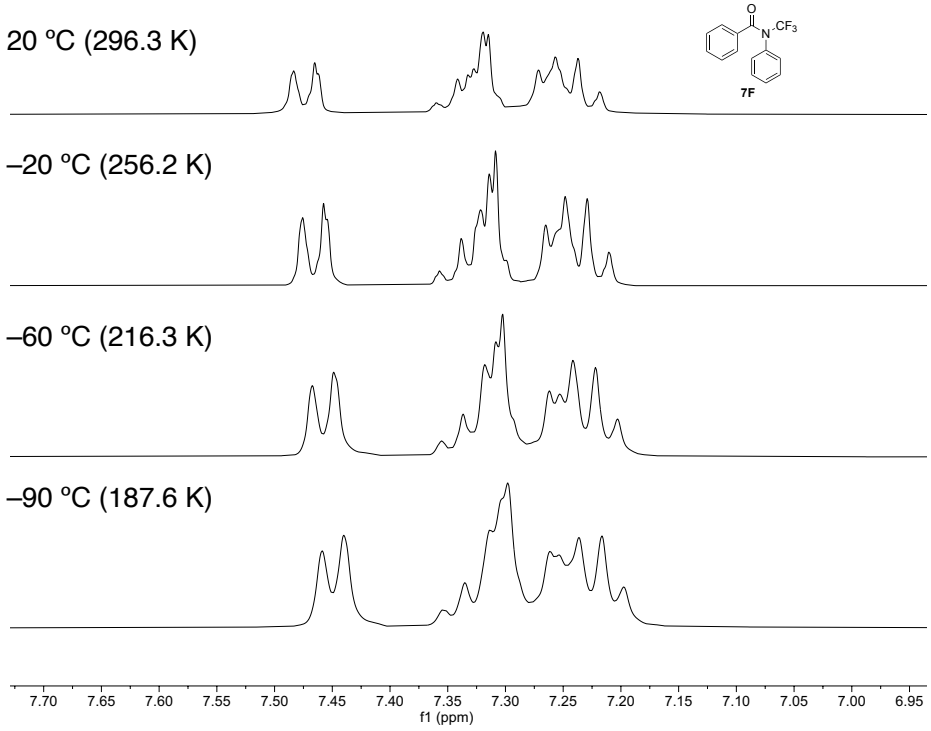



Figure S15. VT-$^1$HNMR ($CD_2Cl_2$, 400 MHz) of **7F**.

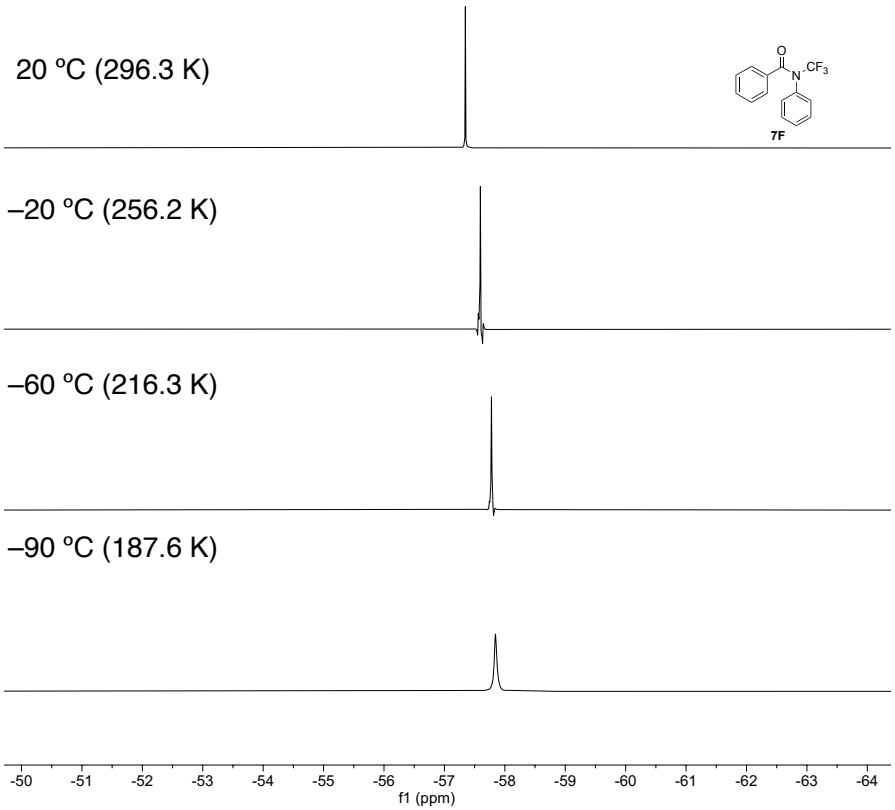



Figure S16. VT-$^{19}$FNMR ($CD_2Cl_2$, 376 MHz) of **7F**.

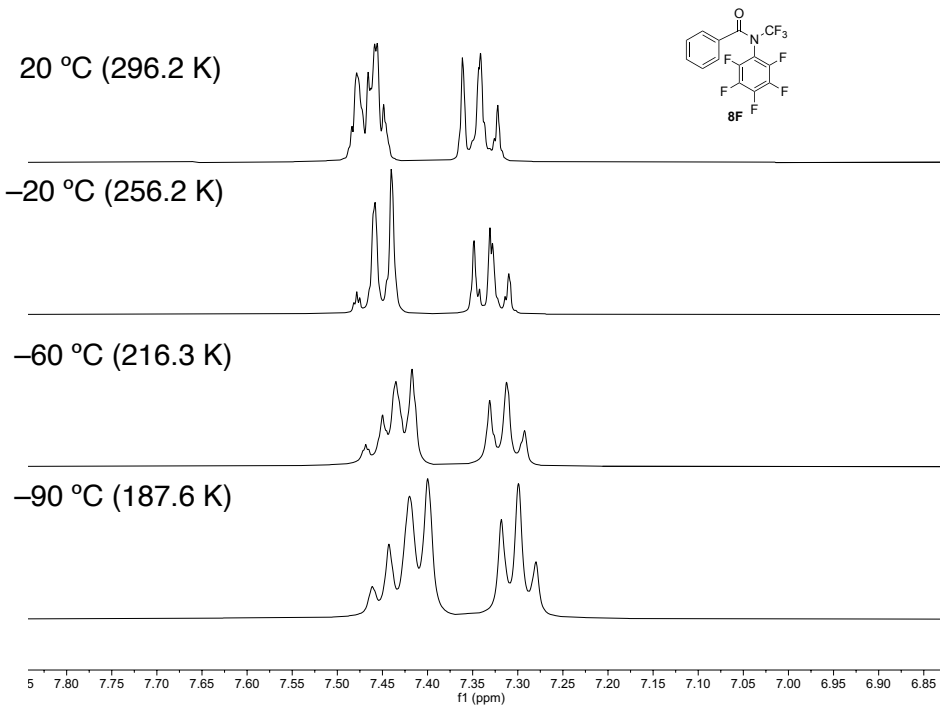



Figure S17. VT-$^{1}$HNMR ($CD_2Cl_2$, 400 MHz) of **8F**.

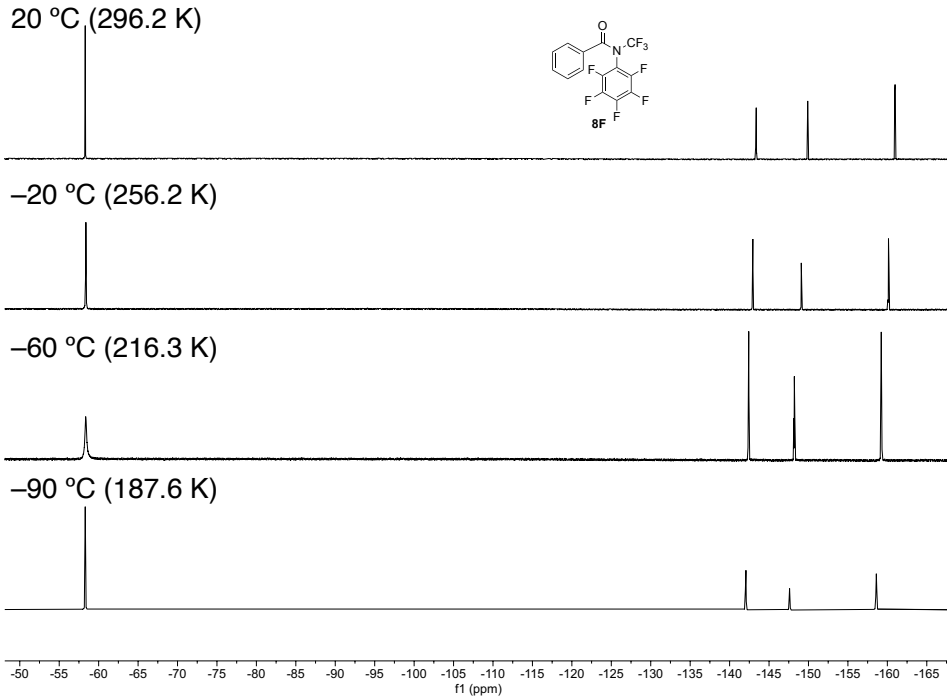



Figure S18. VT-$^{19}$FNMR ($CD_2Cl_2$, 376 MHz) of **8F**.

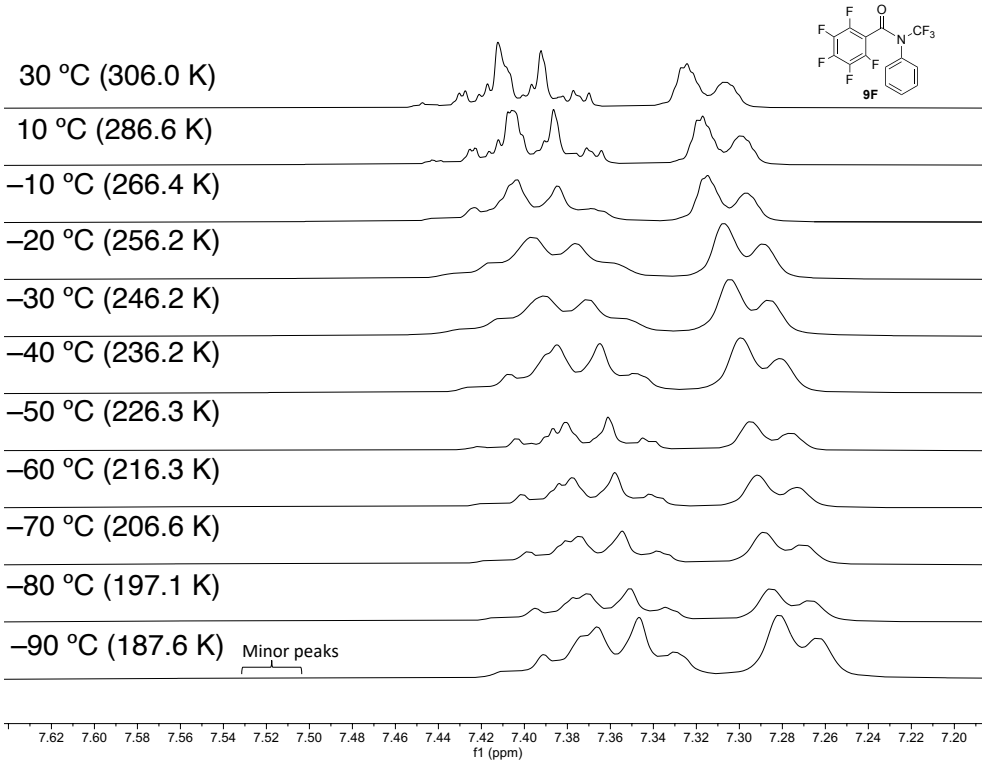



Figure S19. VT-$^{1}$HNMR ($CD_2Cl_2$, 400 MHz) of **9F**.

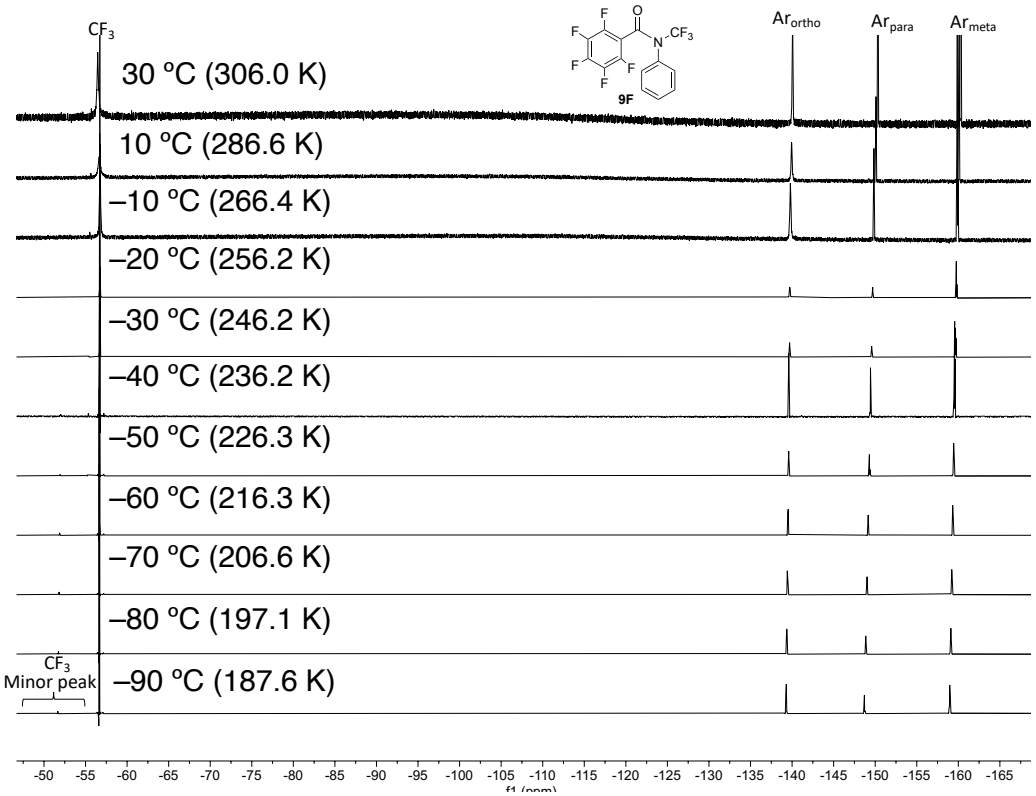



Figure S20. VT-$^{19}$FNMR ($CD_2Cl_2$, 376 MHz) of **9F**.

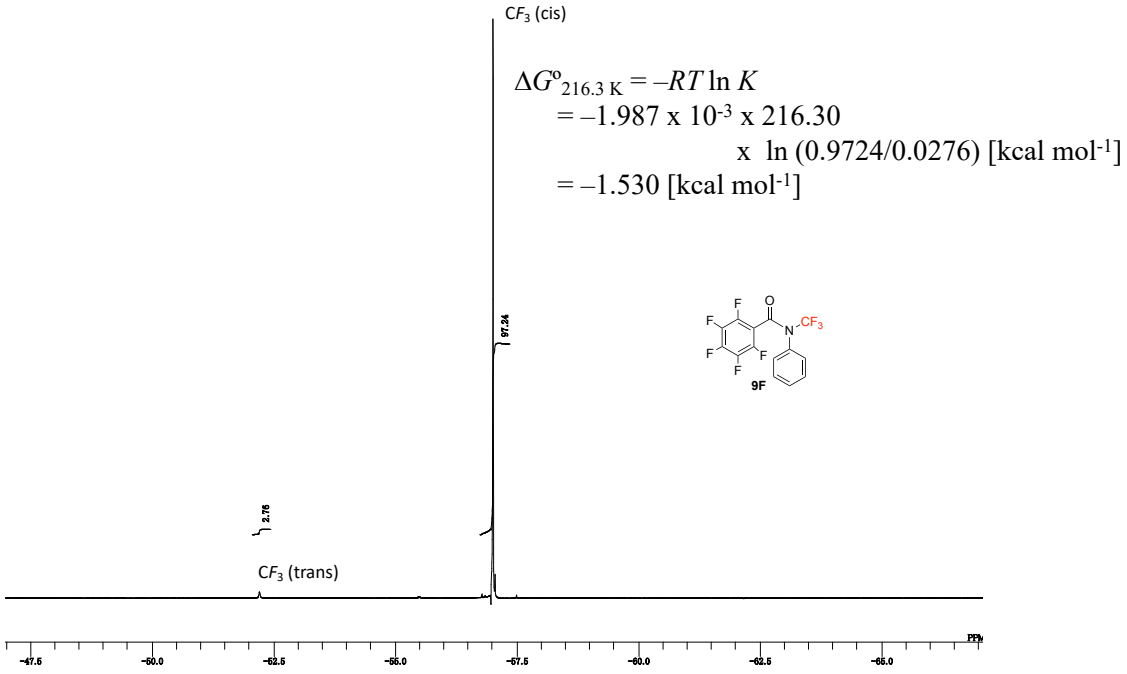



Figure S21. $^{19}$FNMR integration of **9F** ($CD_2Cl_2$, 376 MHz, 216 K).

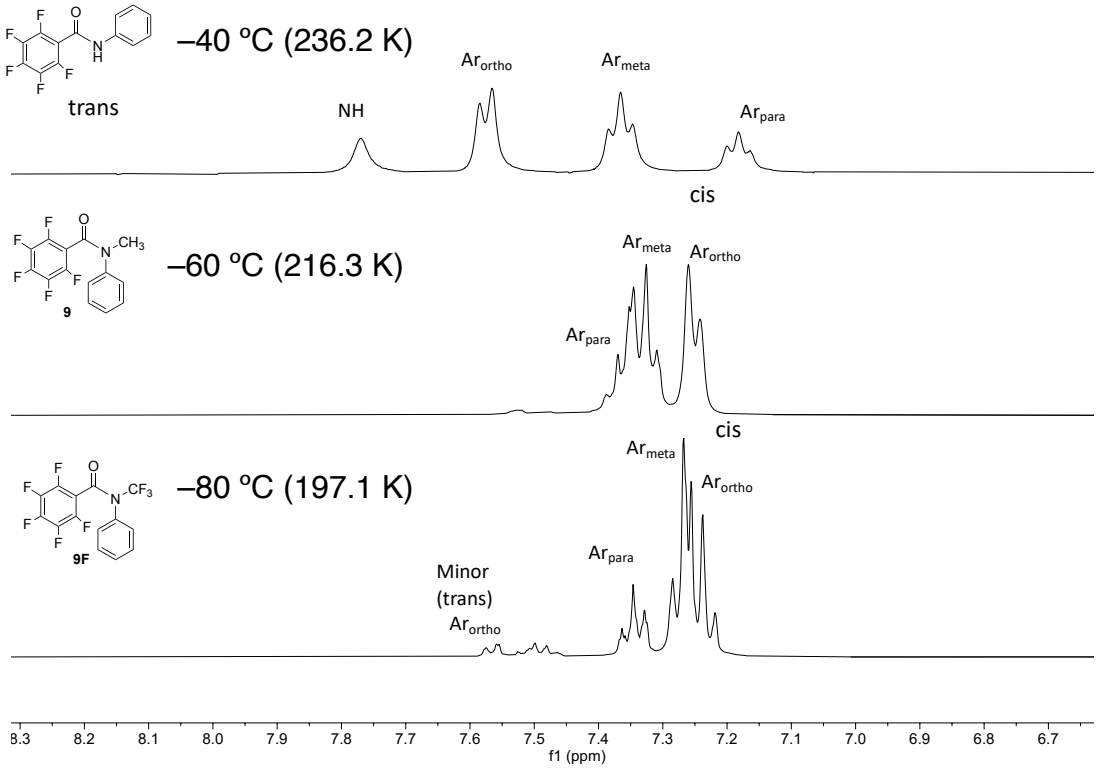



Figure S22. Comparison of aromatic region of $^{1}$HNMR ($CD_2Cl_2$) of **9F**.

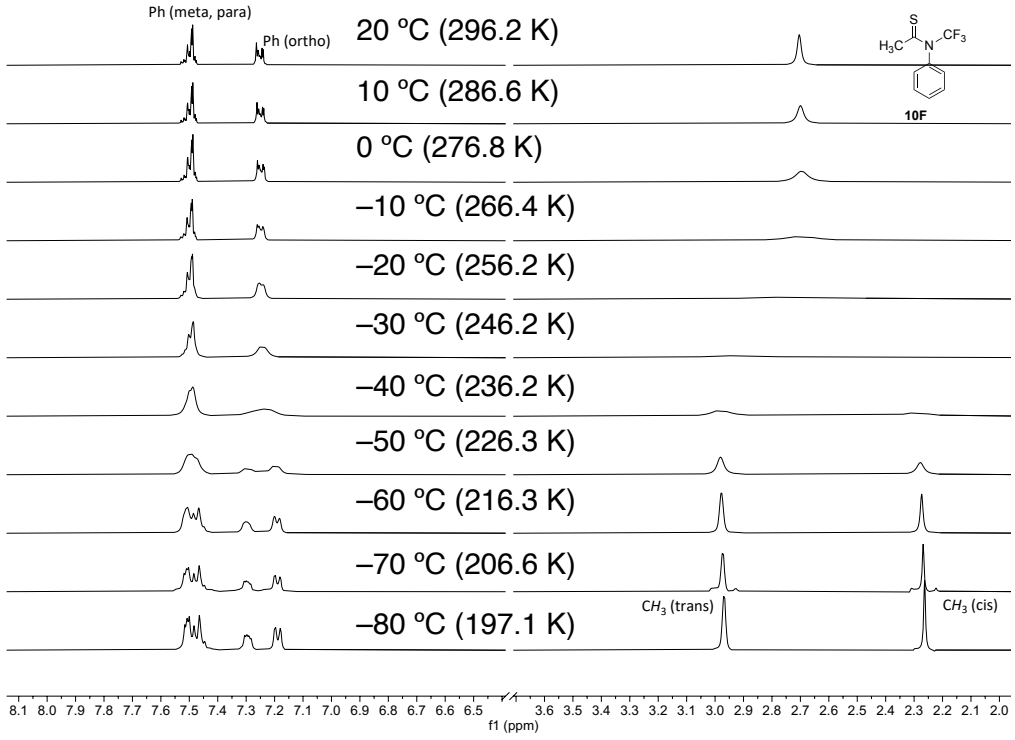



Figure S23. VT-$^{1}$HNMR ($CD_2Cl_2$, 400 MHz) of **10F**.

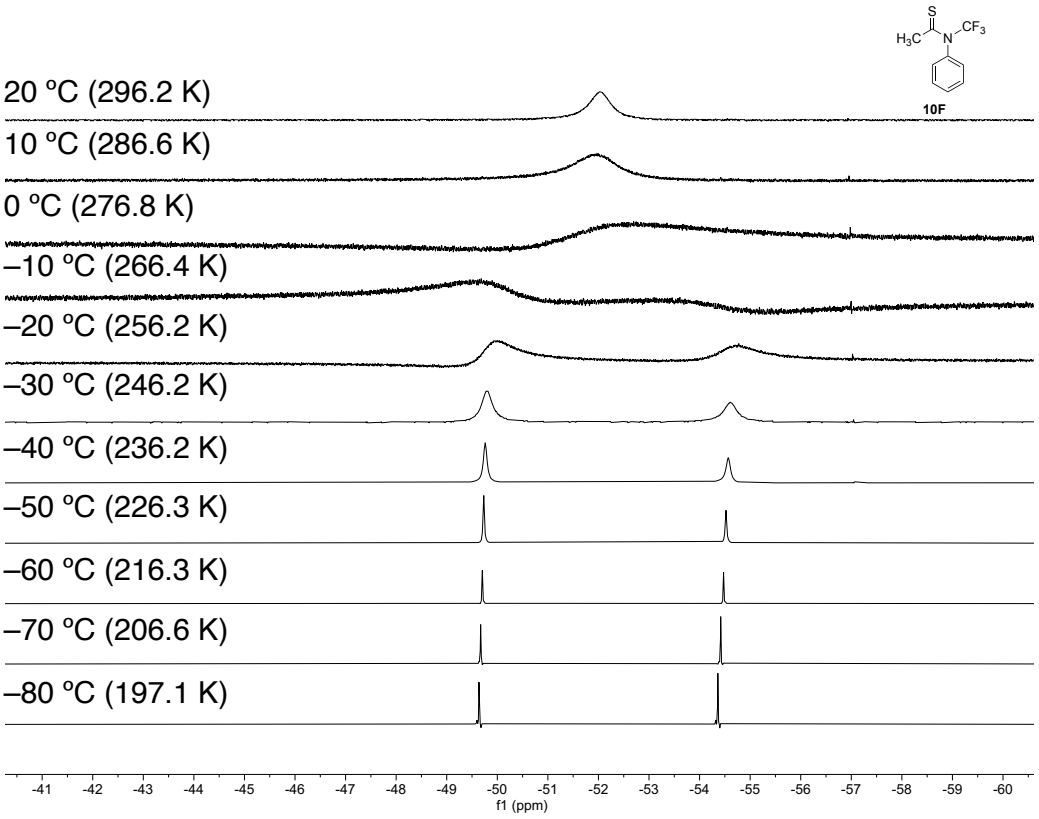



Figure S24. VT-$^{19}$FNMR ($CD_2Cl_2$, 376 MHz) of **10F**.

$$\Delta G^{o}_{236.2\,K} = -RT \ln K$$
$$= -1.987 \times 10^{-3} \times 216.30 \times \ln (0.4351/0.5649)\ [\text{kcal mol}^{-1}]$$
$$= 0.112\ [\text{kcal mol}^{-1}]$$

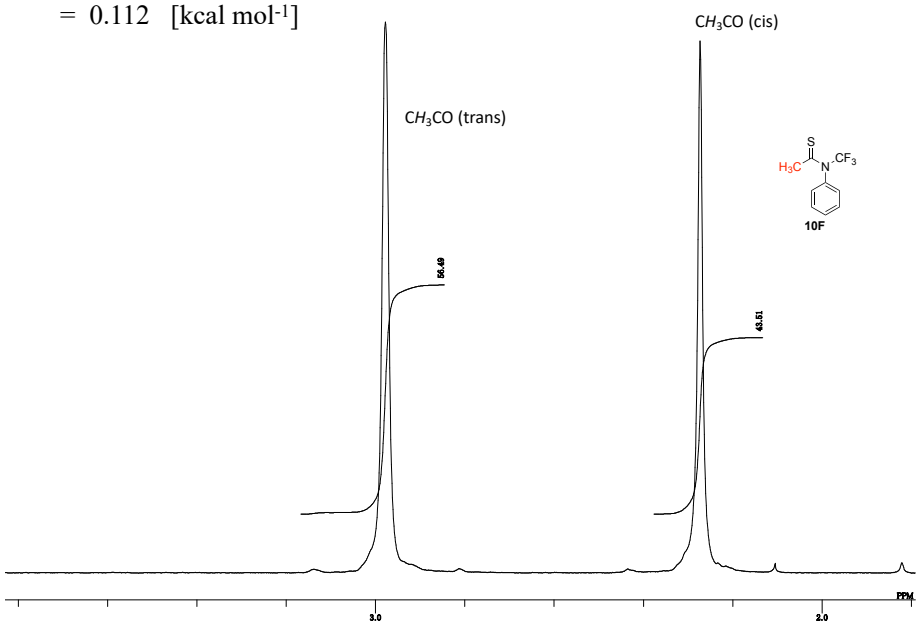



Figure S25. $^1$HNMR integration of **10F** ($CD_2Cl_2$, 400 MHz, 216 K).

$$\Delta G^{o}_{216.3\ K} = -RT \ln K$$
$$= -1.987 \times 10^{-3} \times 216.30 \times \ln (0.6394/0.3606)\ [\text{kcal mol}^{-1}]$$
$$= -0.246\ [\text{kcal mol}^{-1}]$$

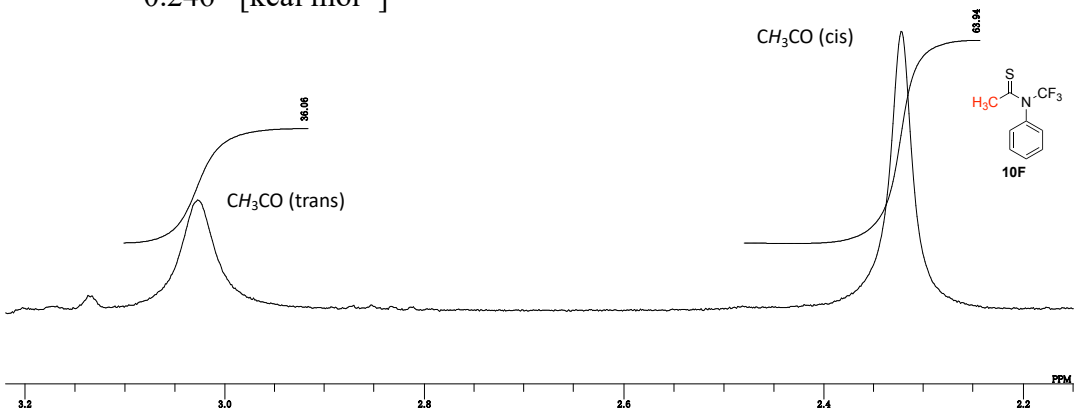



Figure S26. $^{1}$HNMR integration of **10F** ($CD_3OD$, 400 MHz, 216 K).

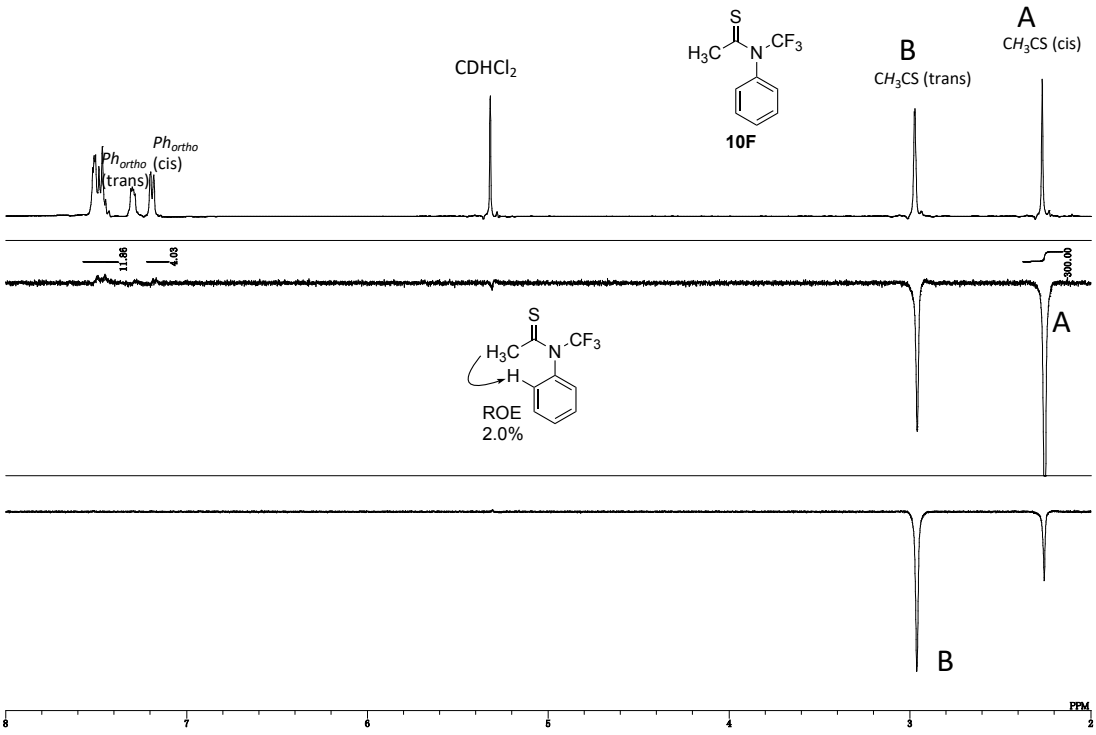



Figure S27. 1D-ROE spectrum of **10F** ($CD_2Cl_2$, 400 MHz, 207 K).

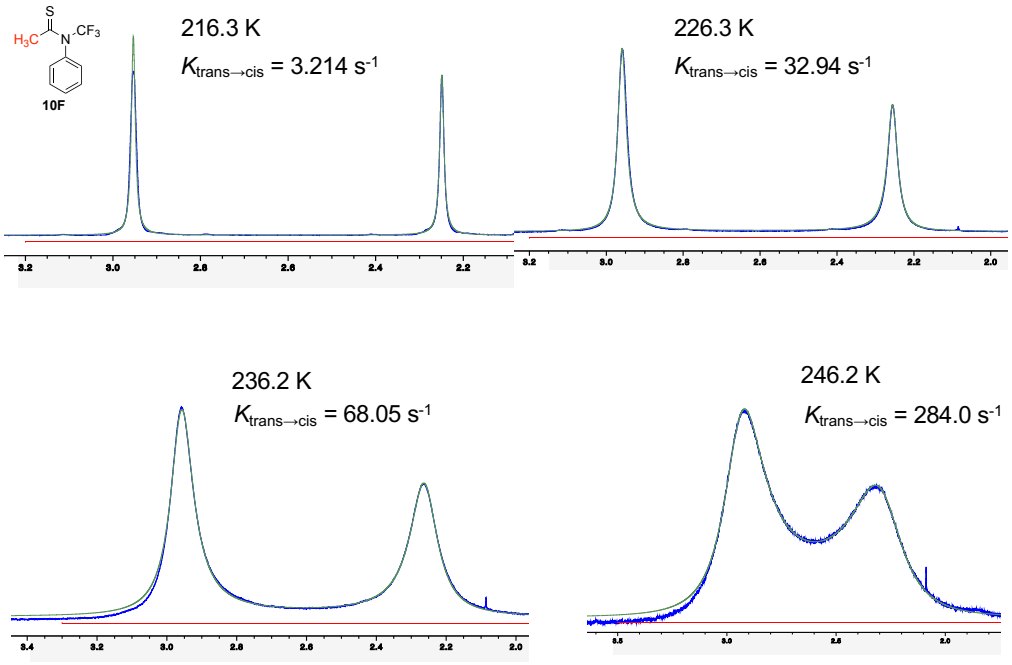



Figure S28. $^{1}$HNMR line-shape analysis ($CD_2Cl_2$, 400 MHz) of **10F**.

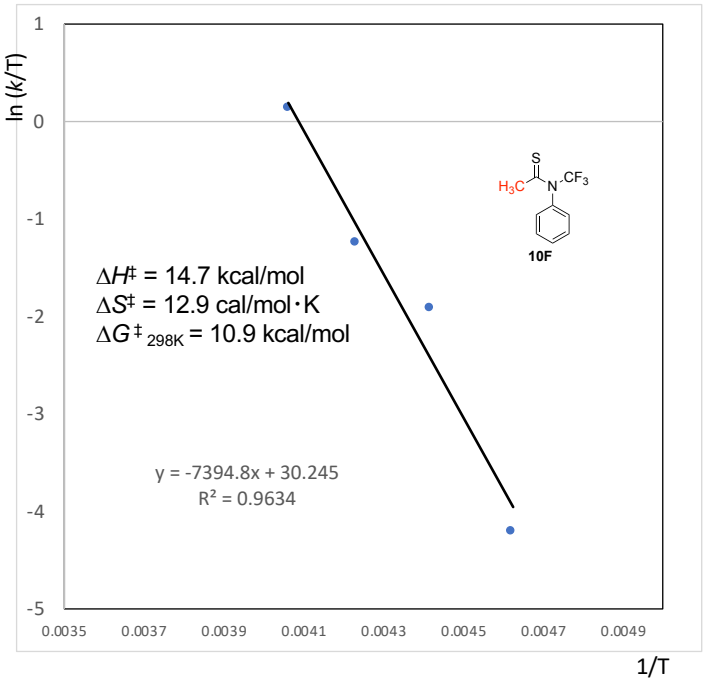



Figure S29. Arrenius plot of line-shape analysis of **10**.

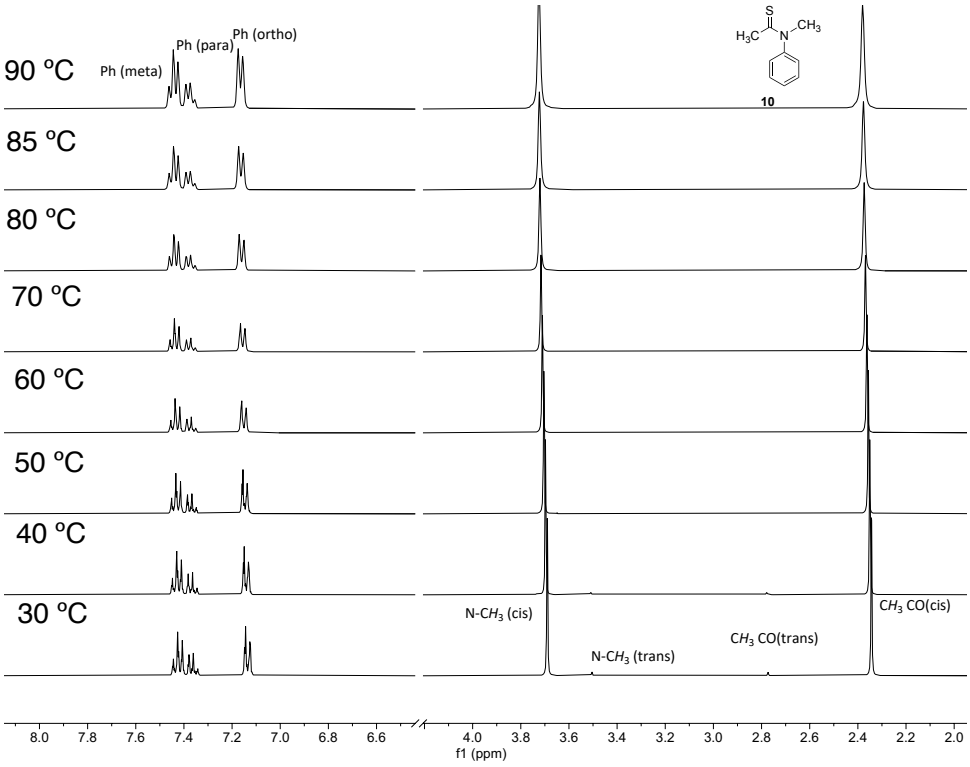
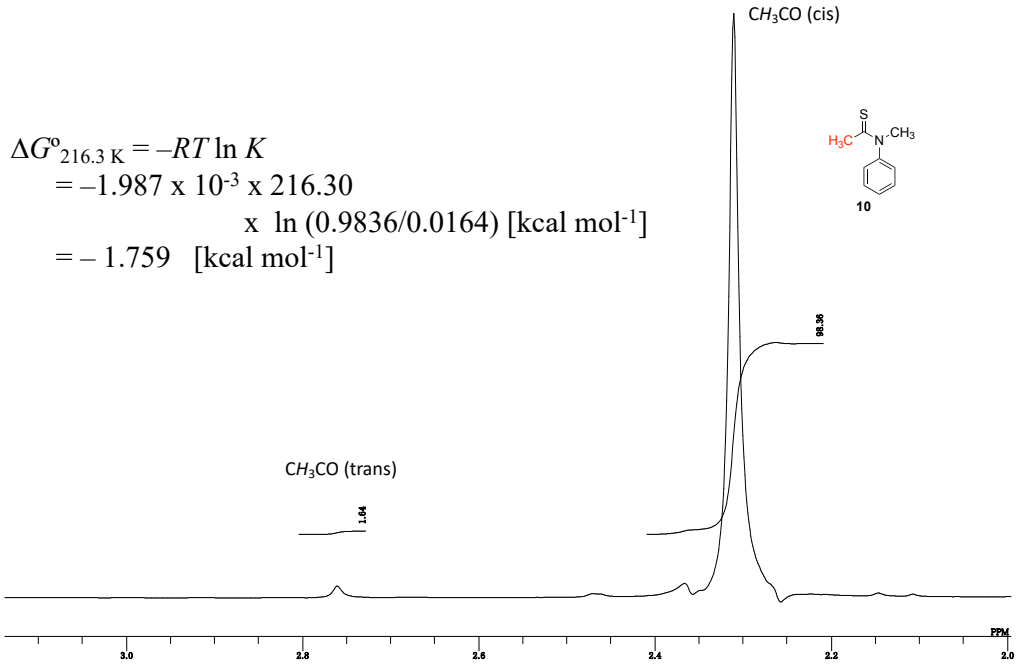



Figure S30. VT-$^{1}$HNMR (Tetrachloroethane-$d_2$, 400 MHz) of **10**.




$$\Delta G^{o}_{216.3\ K} = -RT \ln K$$
$$= -1.987 \times 10^{-3} \times 216.30 \times \ln (0.9836/0.0164)\ [\text{kcal mol}^{-1}]$$
$$= -1.759\ [\text{kcal mol}^{-1}]$$

Figure S31. $^{1}$HNMR integration of **10** ($CD_2Cl_2$, 400 MHz, 216 K).

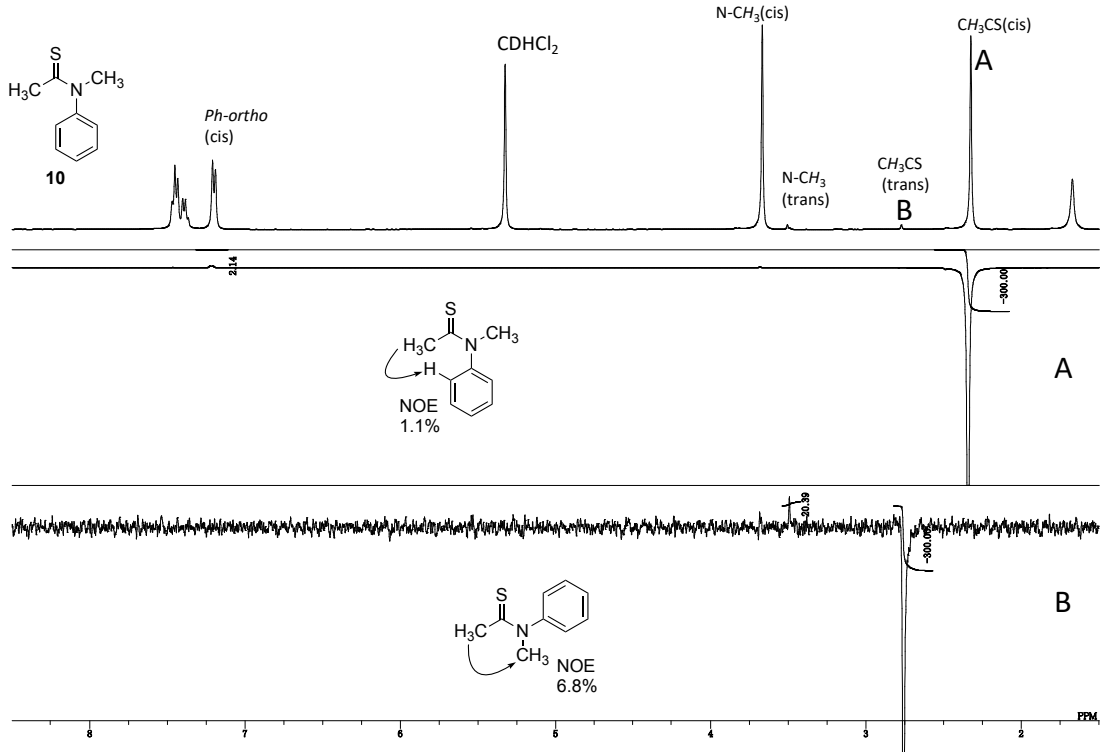



Figure S32. 1D-NOE spectrum of **10** ($CD_2Cl_2$, 400 MHz, 236 K).

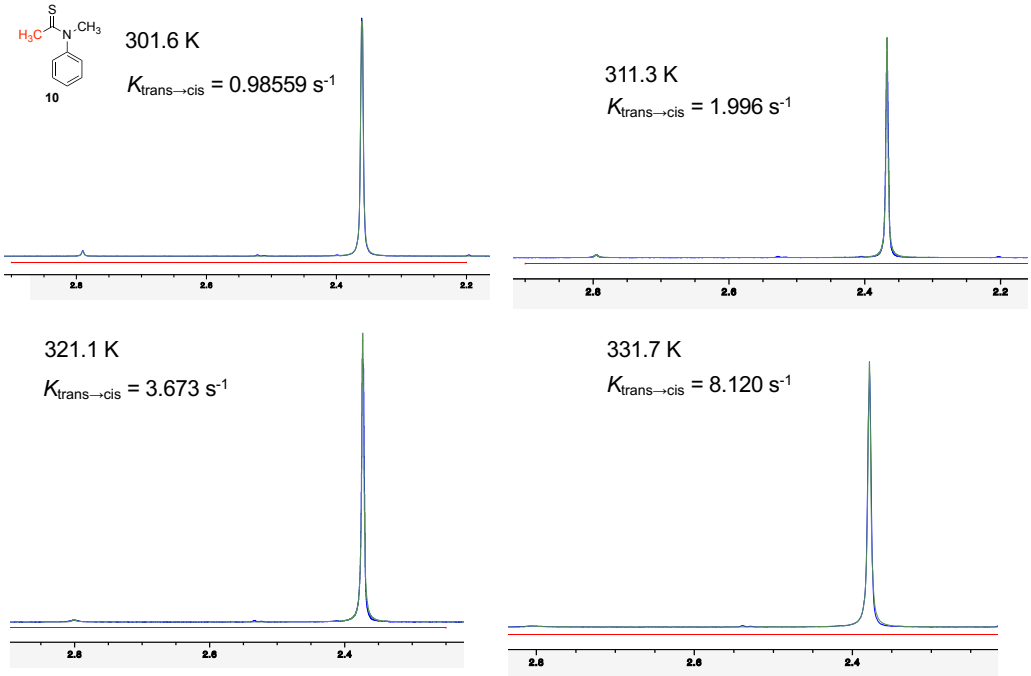



Figure S33. $^1$HNMR line-shape analysis (Tetrachloroethane-$d_2$, 400 MHz) of **10**.

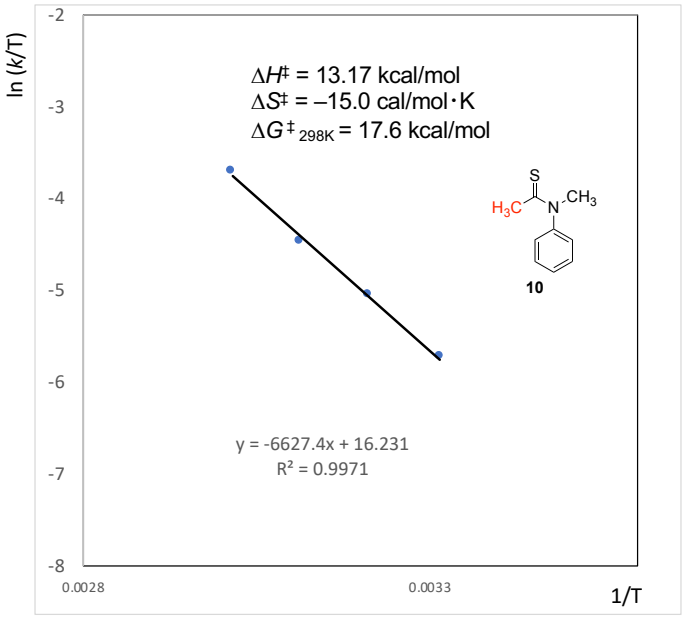



Figure S34. Arrenius plot of line-shape analysis of **10**.

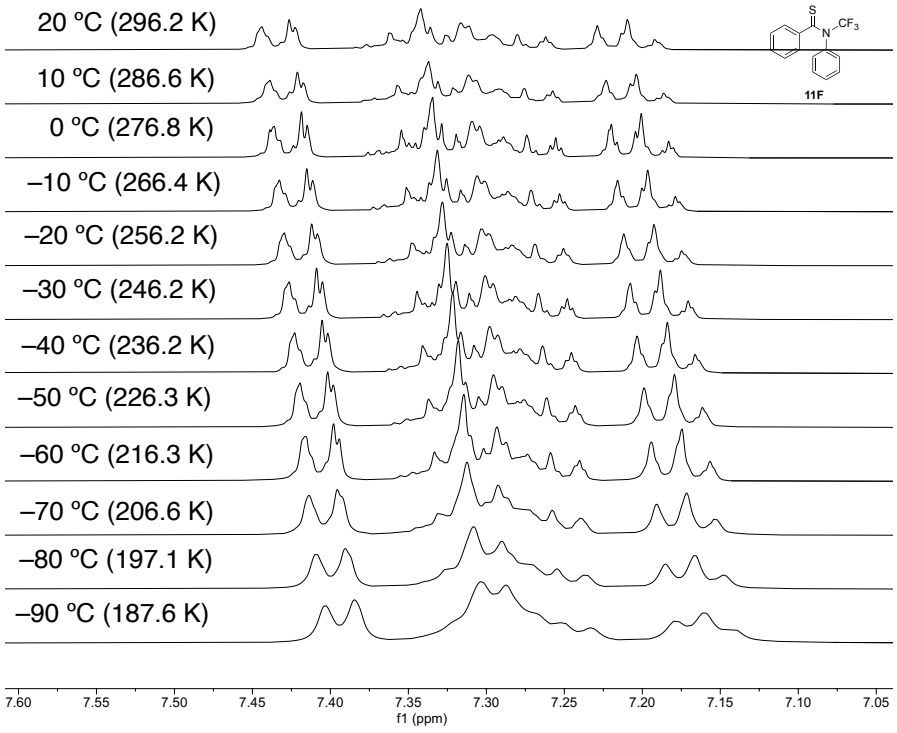



Figure S35. VT-$^{1}$HNMR ($CD_2Cl_2$, 400 MHz) of **11F**.

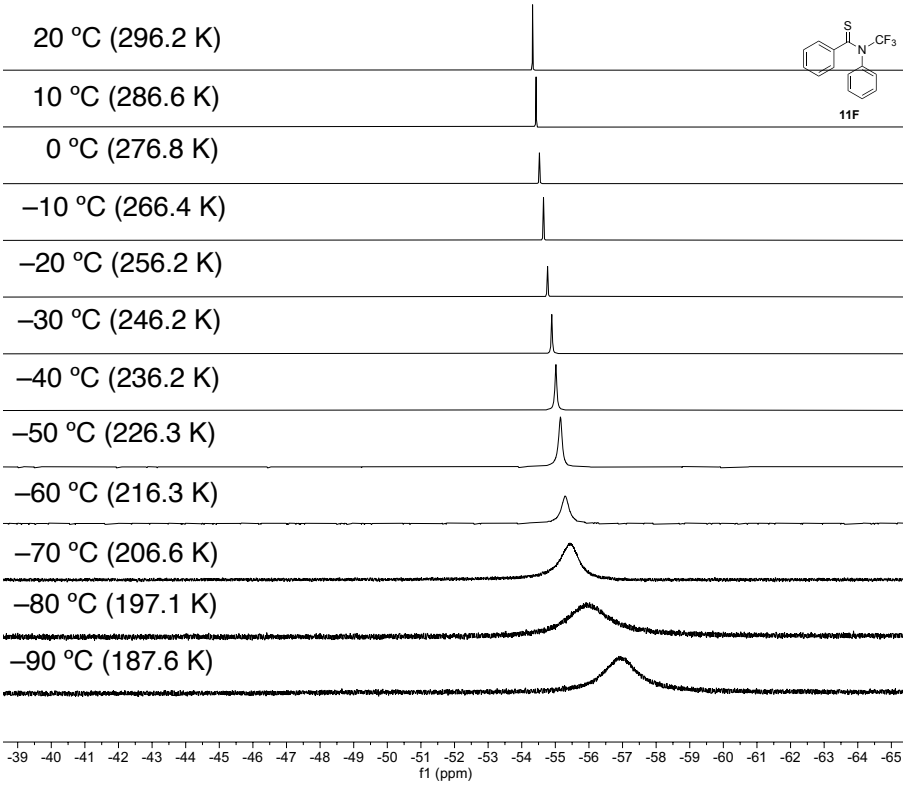



Figure S36. VT-$^{19}$FNMR ($CD_2Cl_2$, 376 MHz) of **11F**.

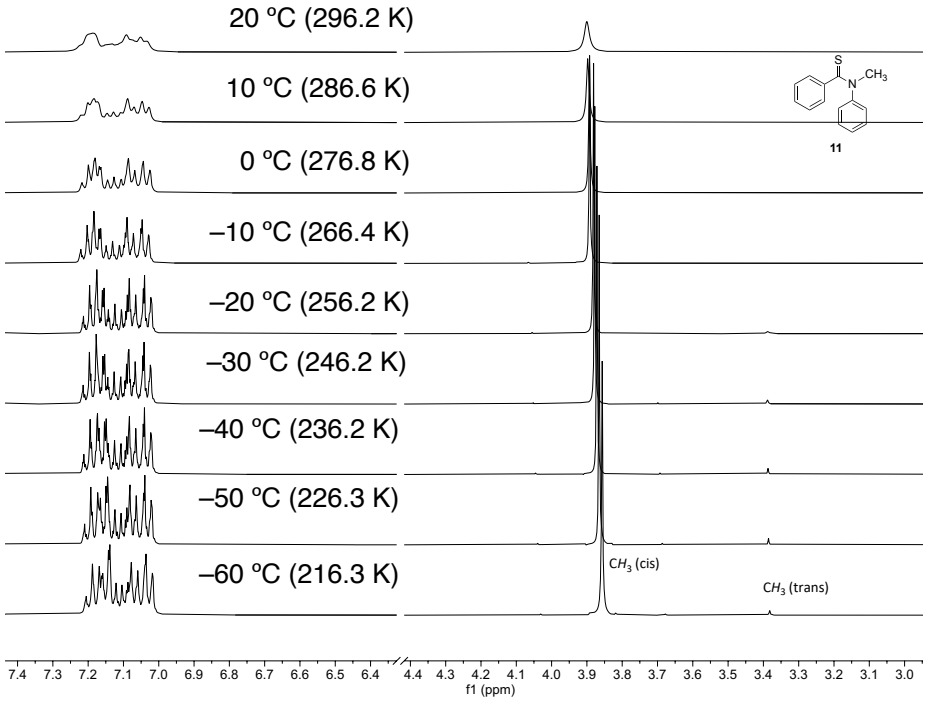



Figure S37. VT-$^{1}$HNMR ($CD_2Cl_2$, 400 MHz) of **11**.

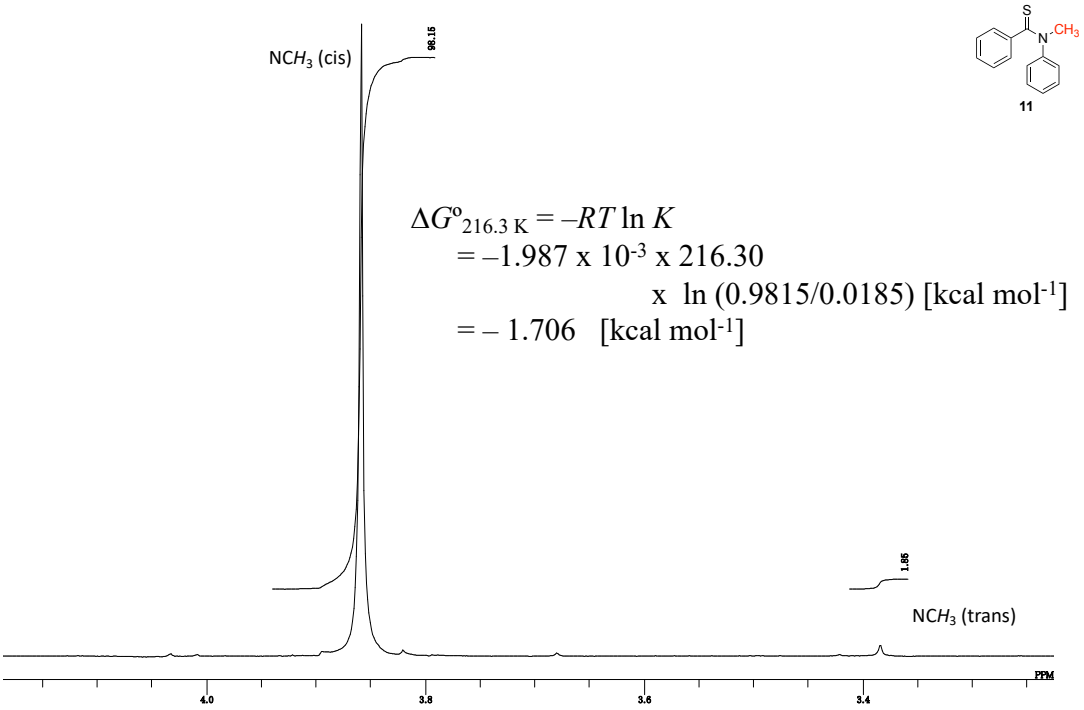



Figure S38. $^{1}$HNMR integration of **11** ($CD_2Cl_2$, 400 MHz, 216 K).

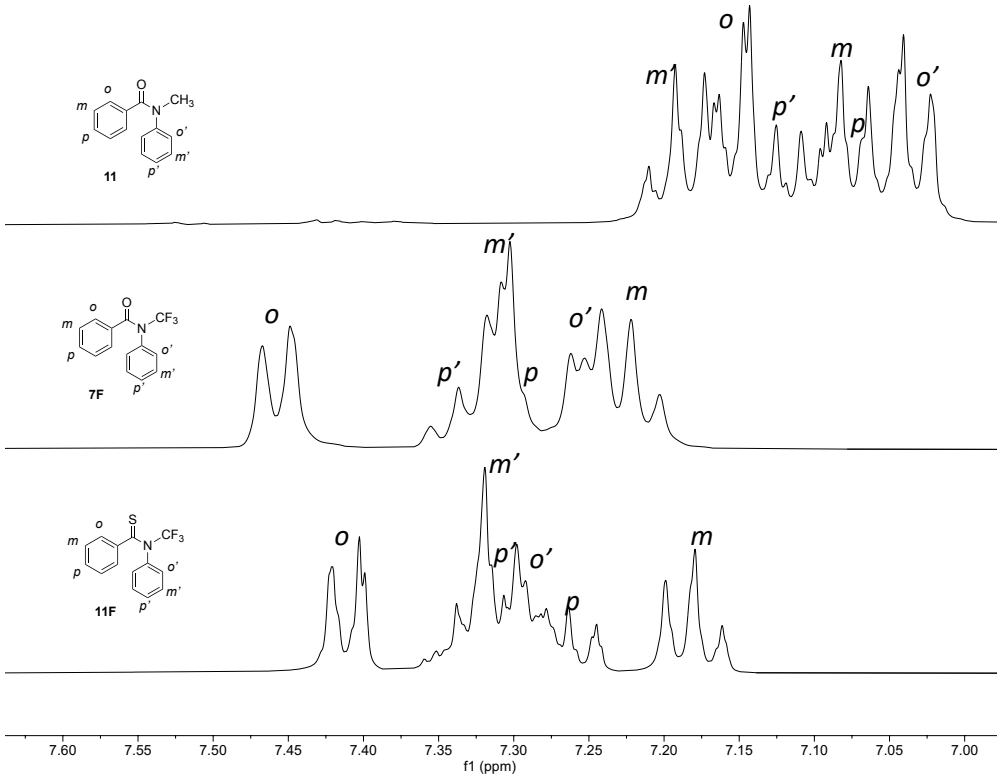



Figure S39. Comparison of $^{1}$HNMR spectrum ($CD_2Cl_2$, 400 MHz, 216 K).

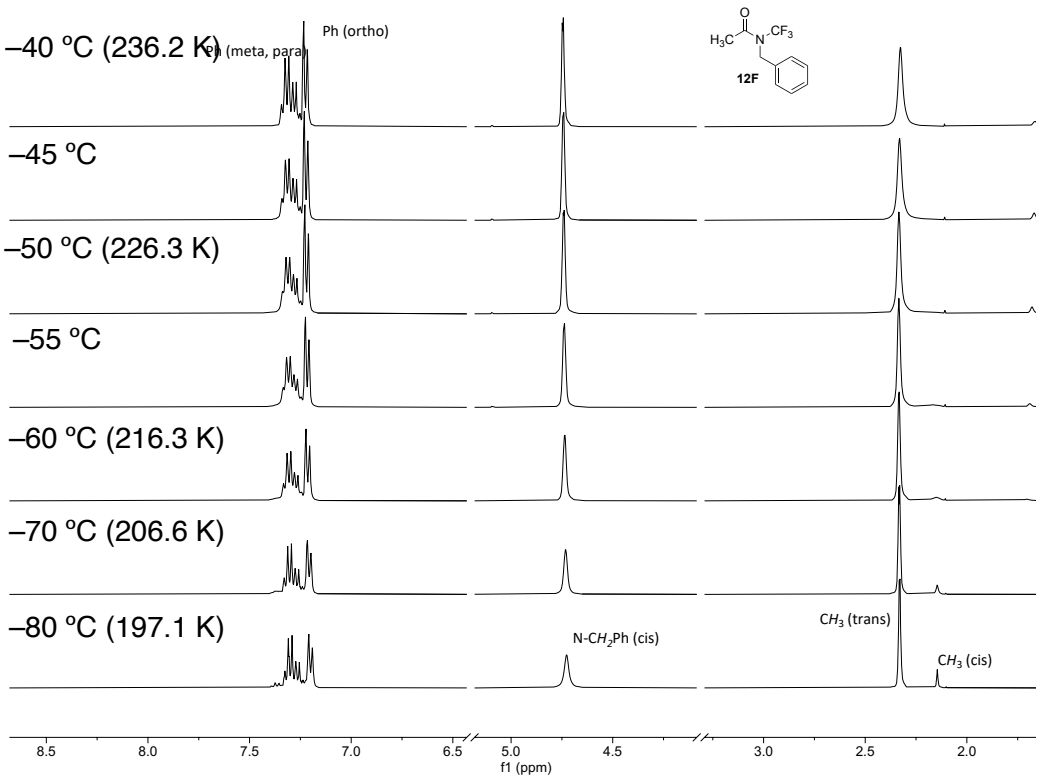



Figure S40. VT-$^{1}$HNMR ($CD_2Cl_2$, 400 MHz) of **12F**.

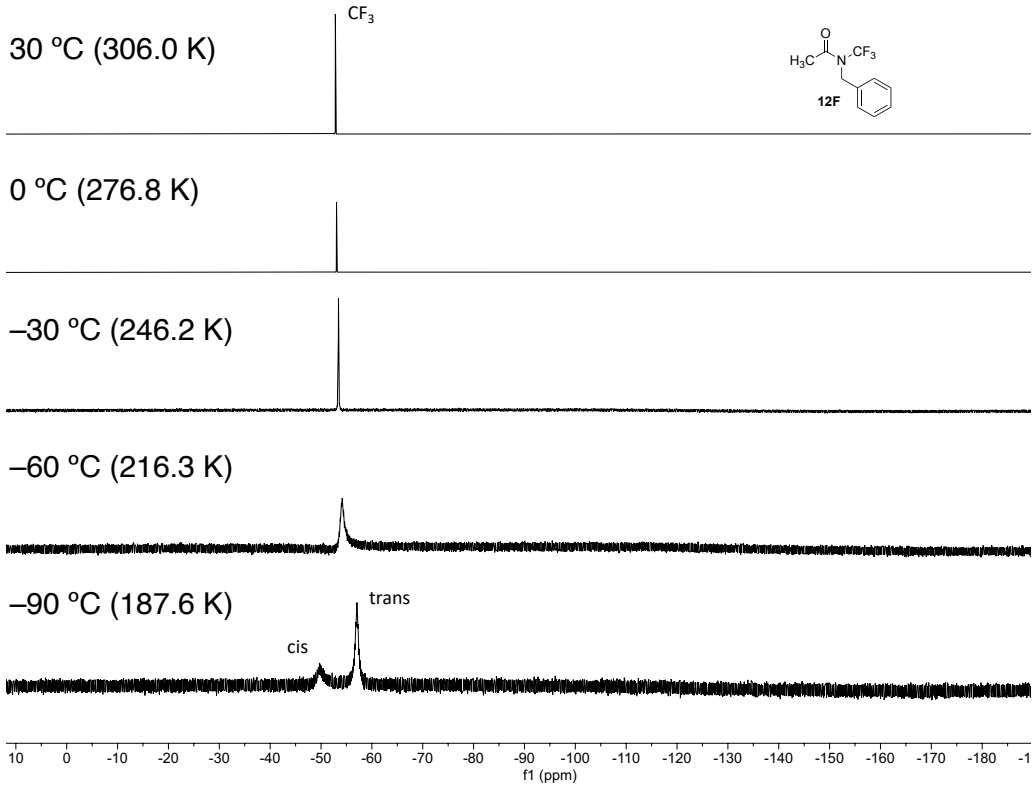



Figure S41. VT-$^{19}$FNMR ($CD_2Cl_2$, 376 MHz) of **12F**.

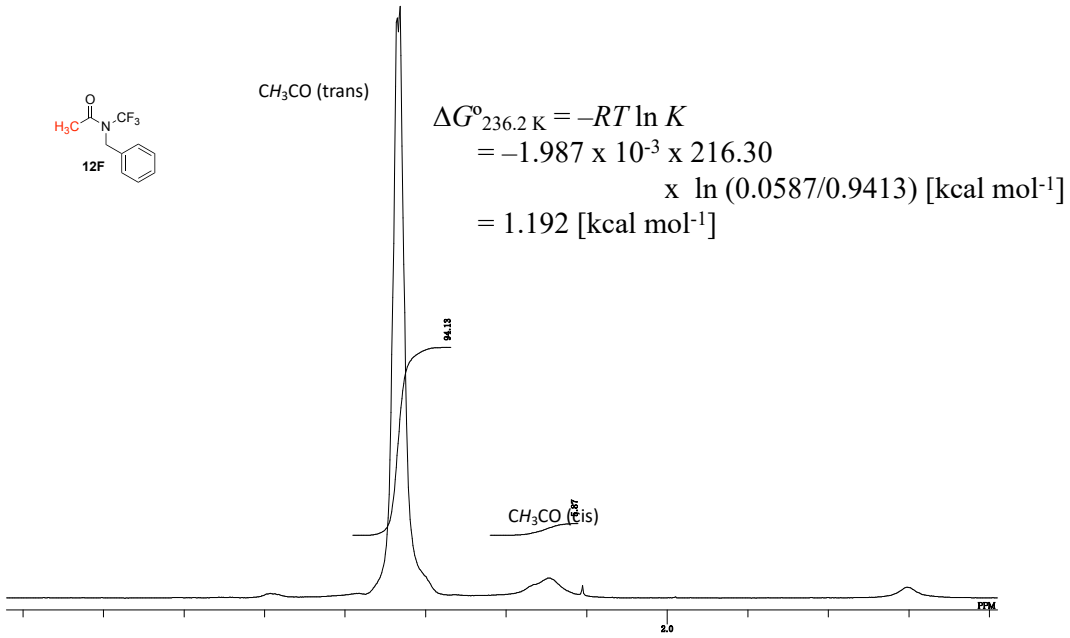



Figure S42. $^{1}$HNMR integration of **12F** ($CD_2Cl_2$, 400 MHz, 216 K).

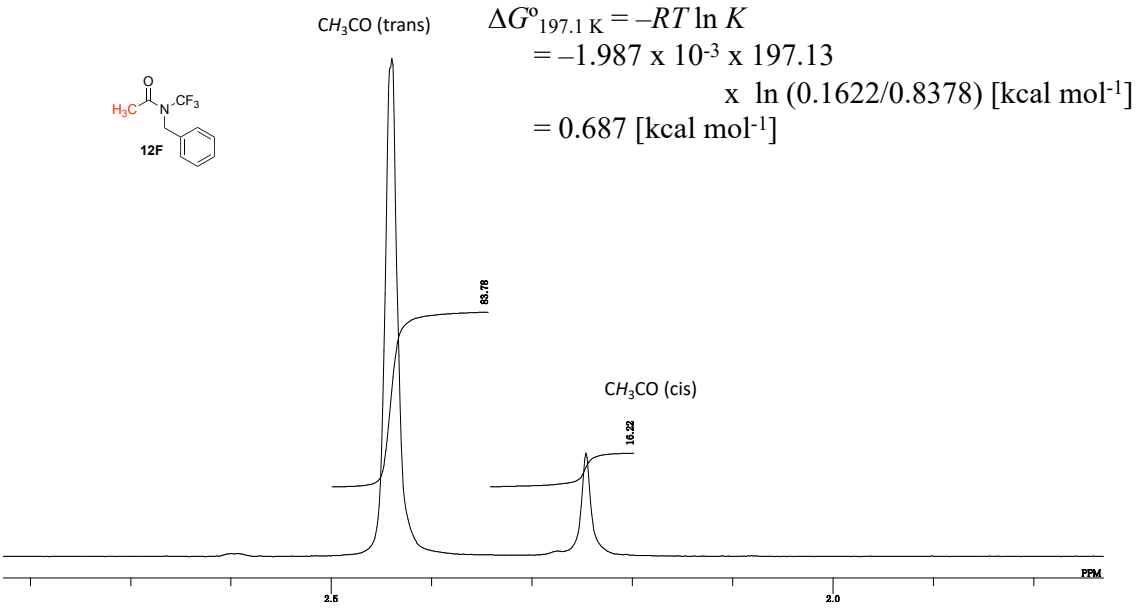



Figure S43. $^{1}$HNMR integration of **12F** ($CD_3OD$, 400 MHz, 197 K).

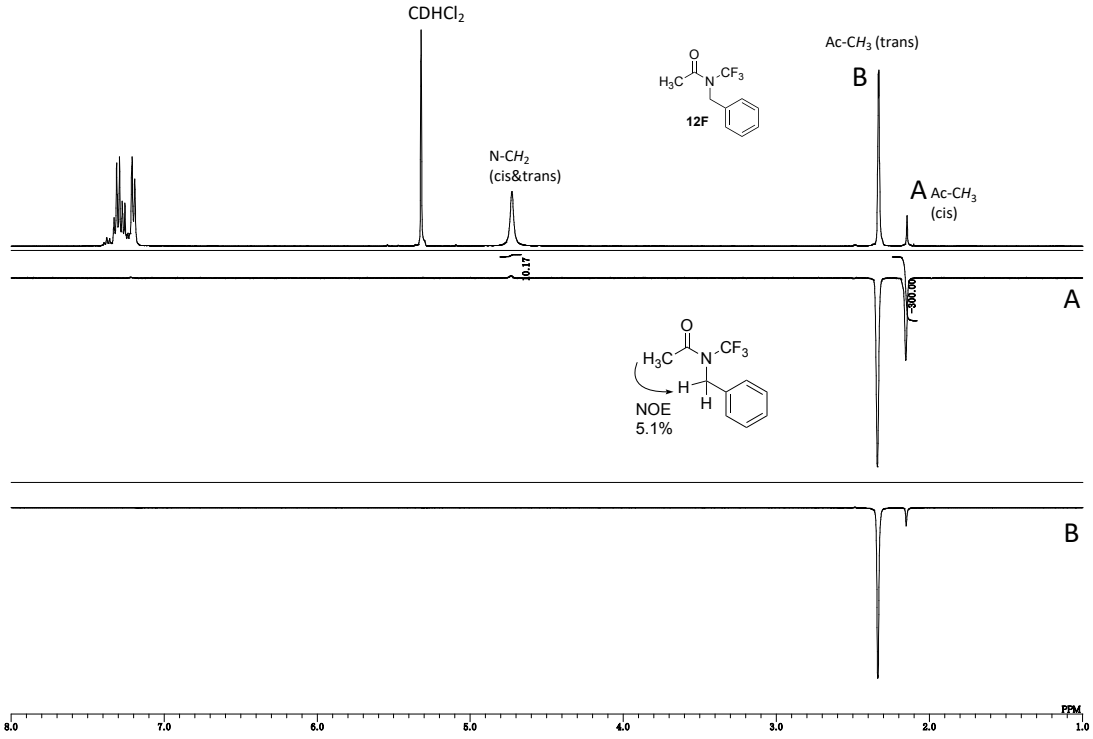



Figure S44. 1D-NOE spectrum of **12F** ($CD_2Cl_2$, 400 MHz, 197 K).

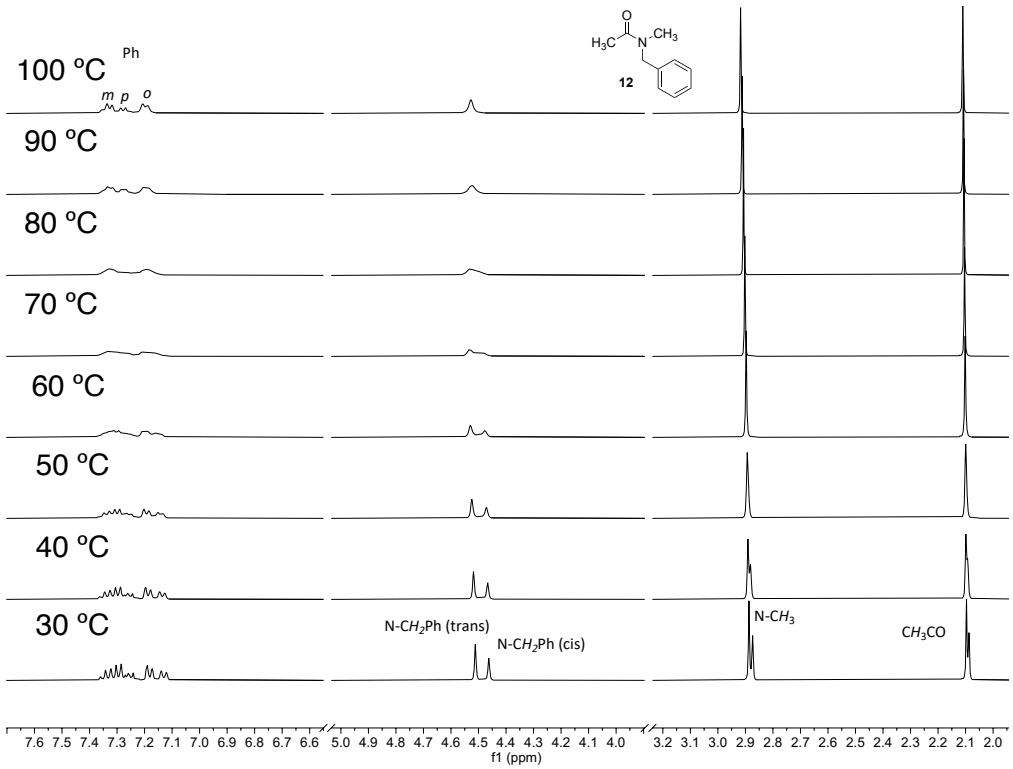



Figure S45. VT-$^1$HNMR (Tetrachlroethane-$d_2$, 400 MHz) of **12**.

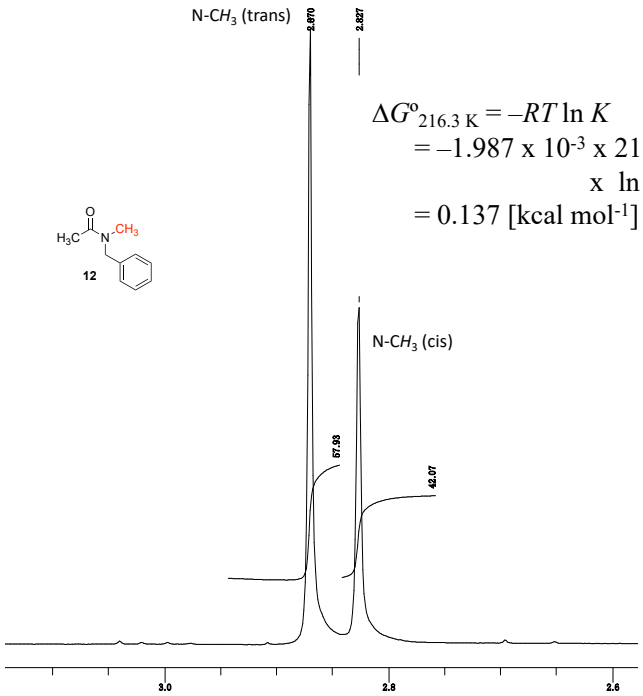



Figure S46. $^{1}$HNMR integration of **12** ($CD_2Cl_2$, 400 MHz, 216 K).

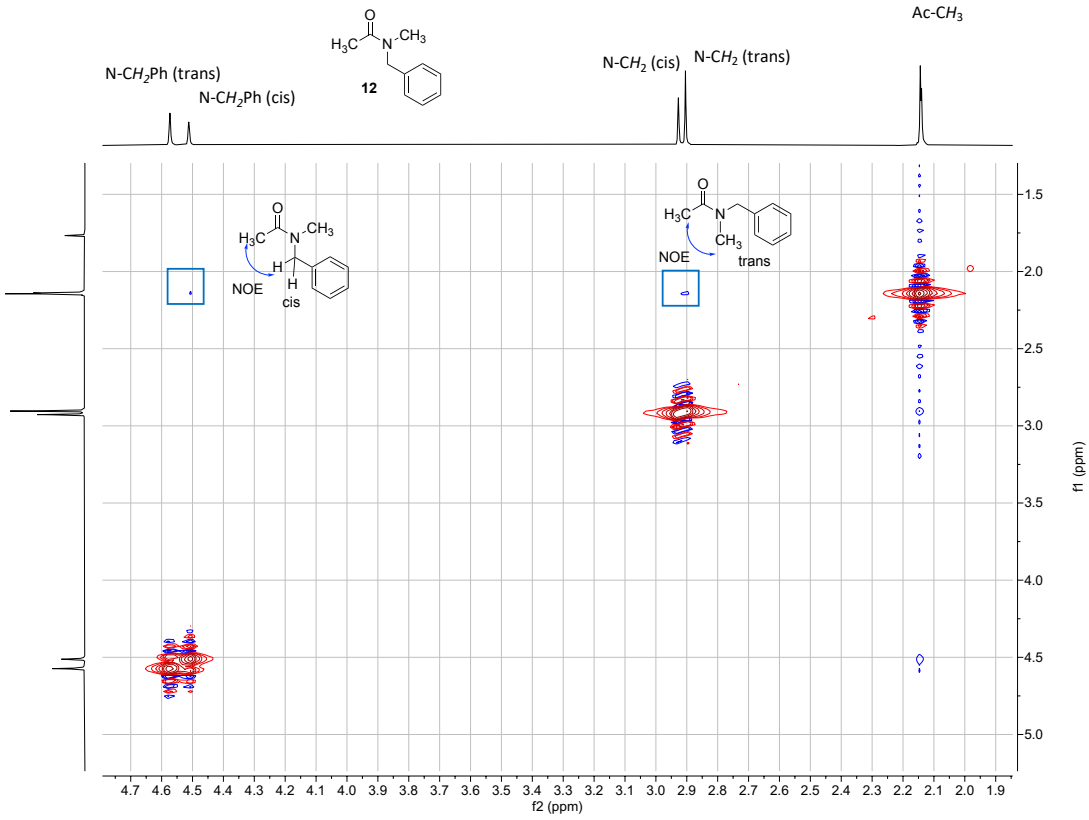



Figure S47. NOESY spectrum of **12** ($CDCl_3$, 400 MHz, rt).

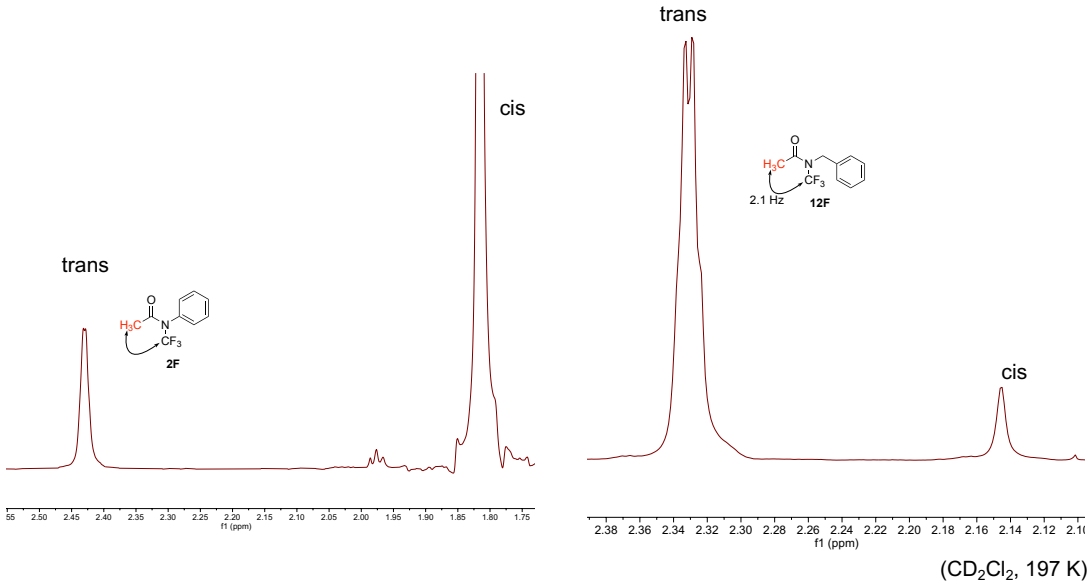



Figure S48. Through space F-H coupling of **2F** and **12F** in $^{1}$H NMR ($CD_2Cl_2$, 400 MHz, 197 K).

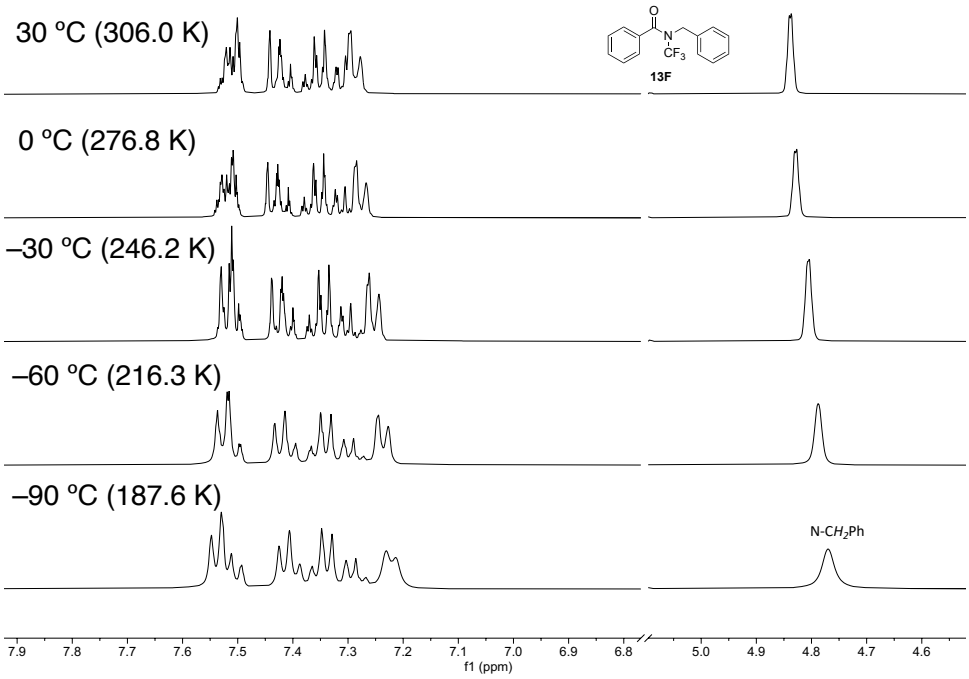



Figure S49. VT-$^{1}$HNMR ($CD_2Cl_2$, 400 MHz) of **13F**.

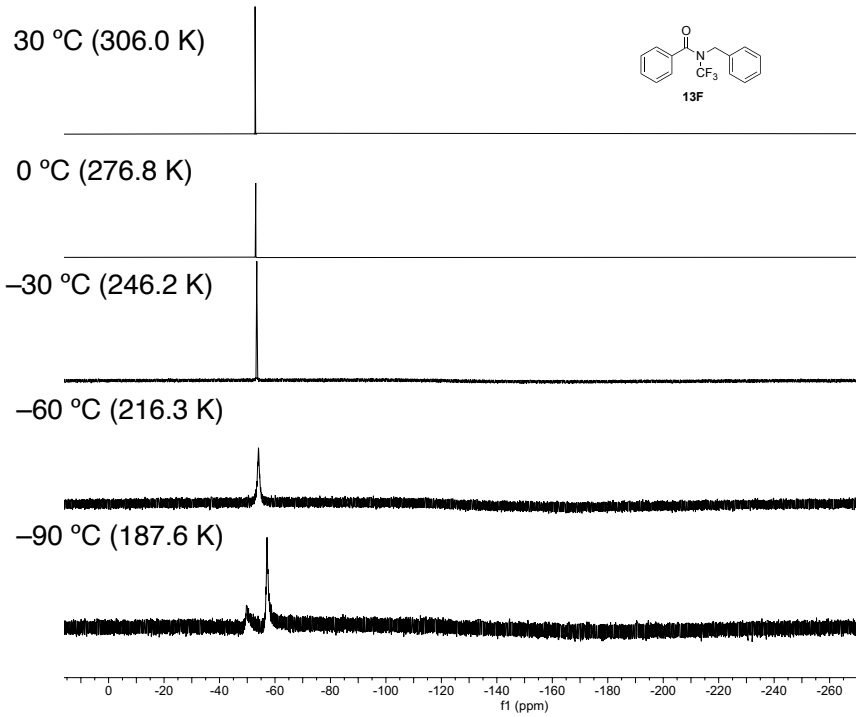



Figure S50. VT-$^{19}$FNMR ($CD_2Cl_2$, 376 MHz) of **13F**.

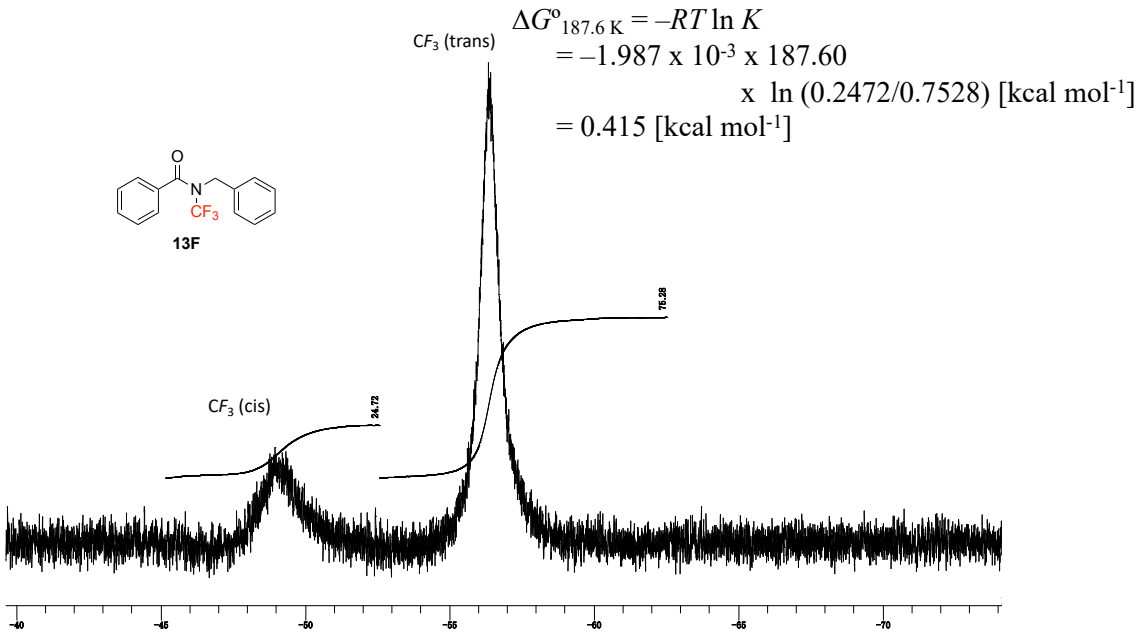



Figure S51. $^{19}$FNMR integration of **13F** ($CD_2Cl_2$, 400 MHz, 188 K).

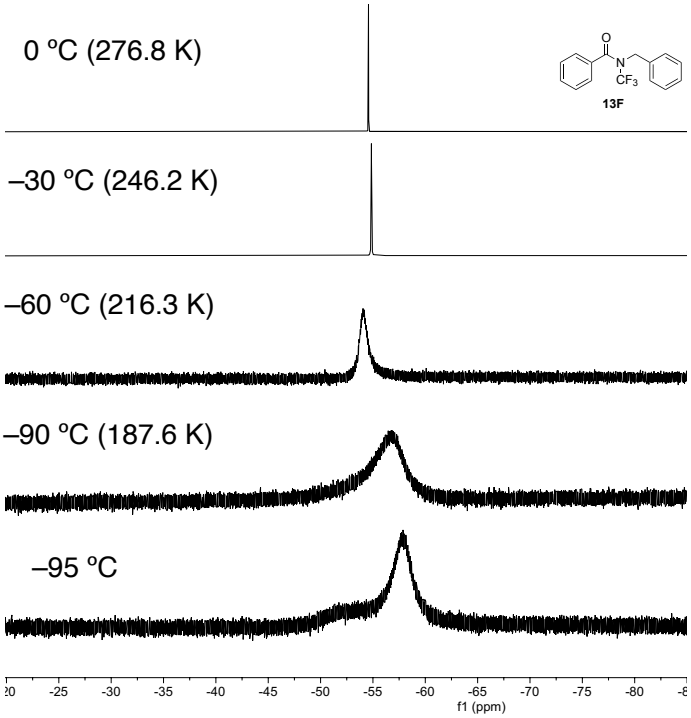



Figure S52. VT-$^{19}$FNMR ($CD_3OD$, 376 MHz) of **13F**.

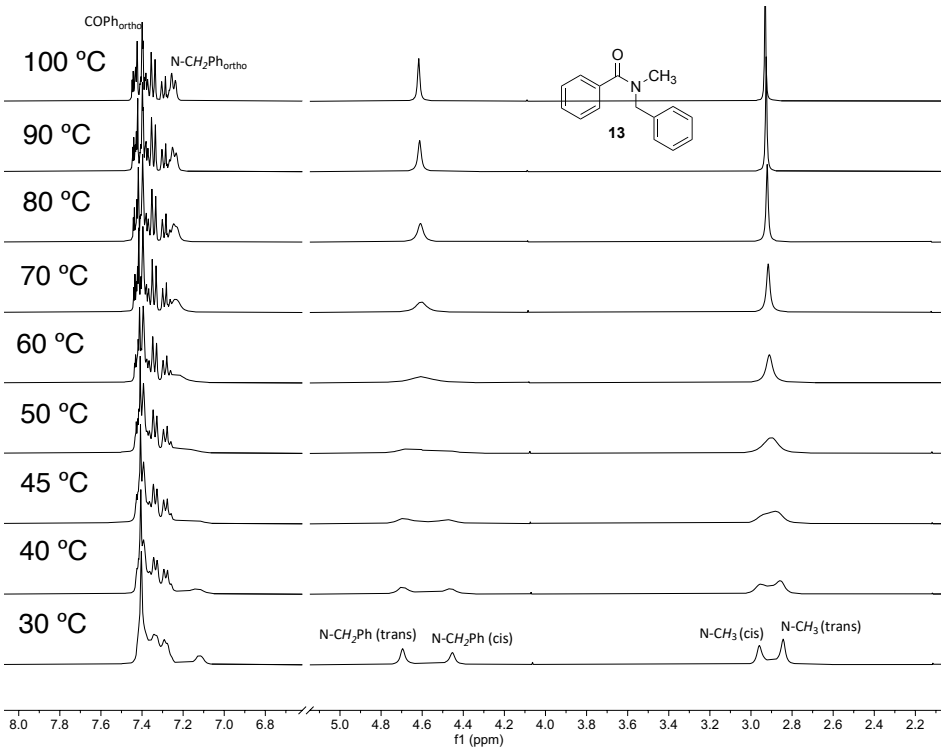



Figure S53. VT-$^1$HNMR (Tetrachlroethane-$d_2$, 400 MHz) of **13**.

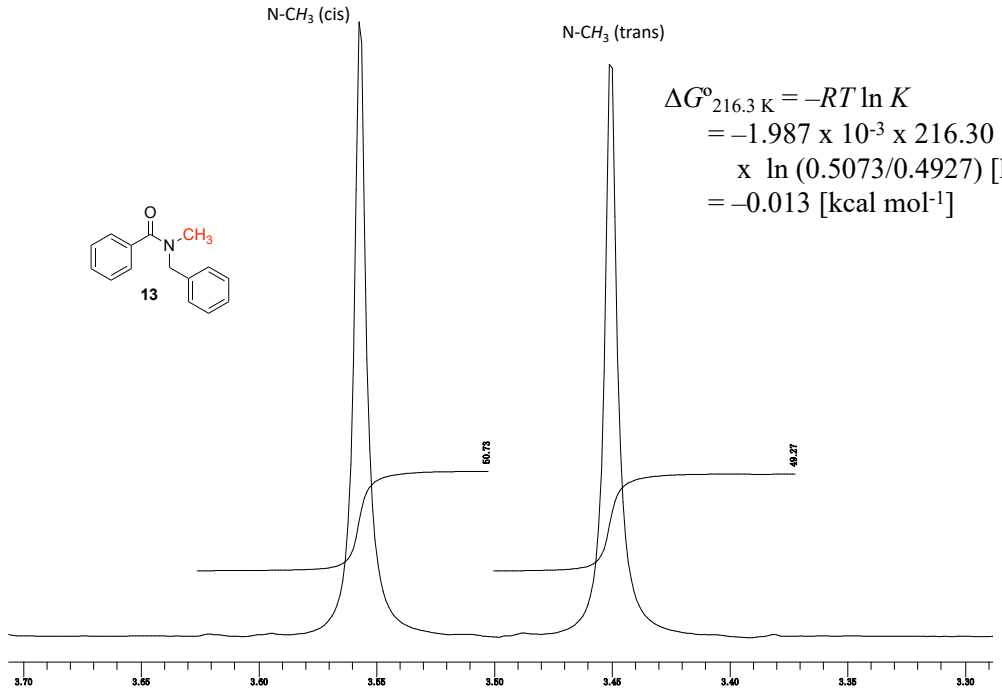



Figure S54. $^{1}$HNMR integration of **13** ($CD_2Cl_2$, 400 MHz, 216 K).

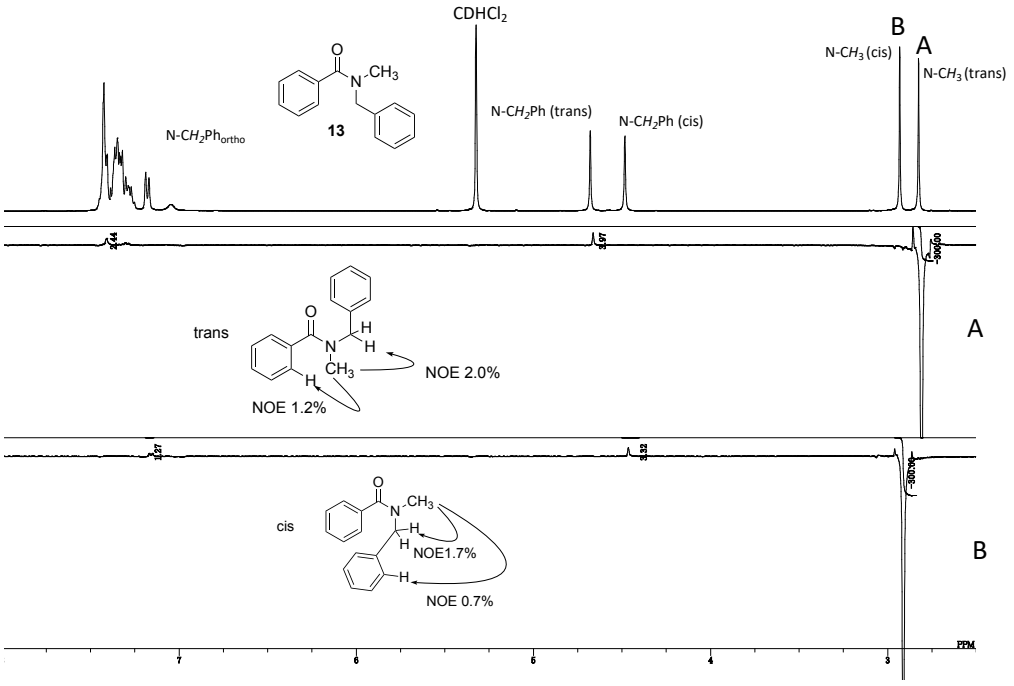



Figure S55. 1D-NOE spectrum of **13** ($CD_2Cl_2$, 400 MHz, 216 K).

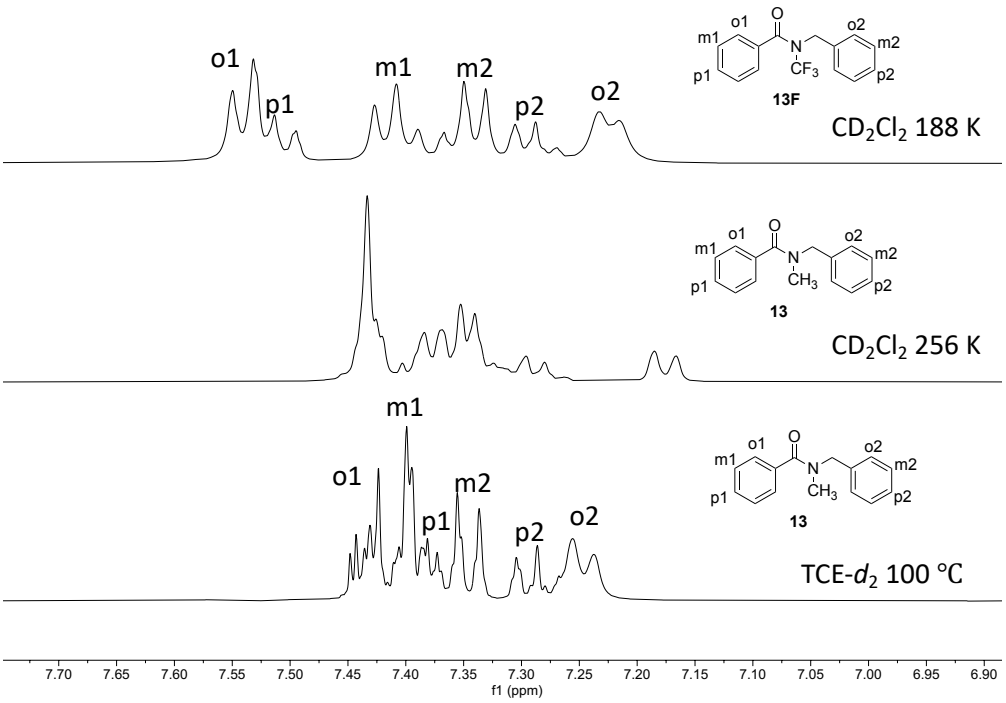



Figure S56. Comparison of $^{1}$HNMR spectrum (400 MHz)

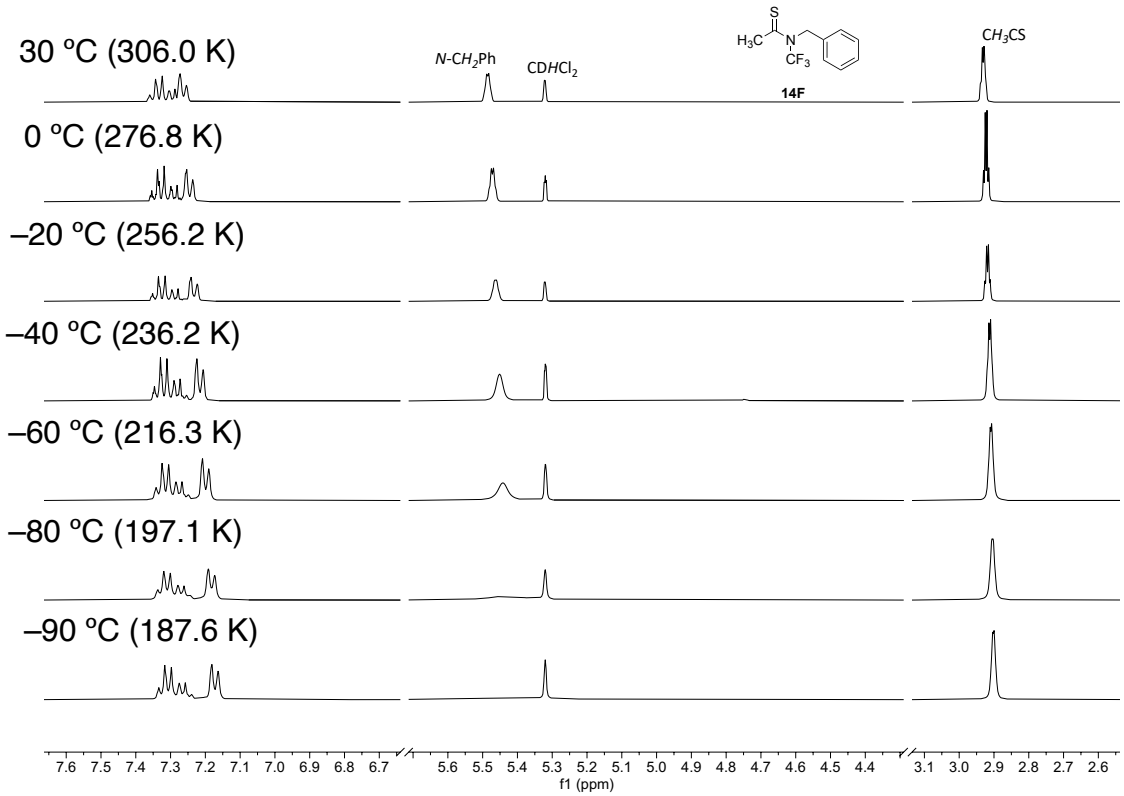



Figure S57. VT-$^{1}$HNMR ($CD_2Cl_2$, 400 MHz) of **14F**.

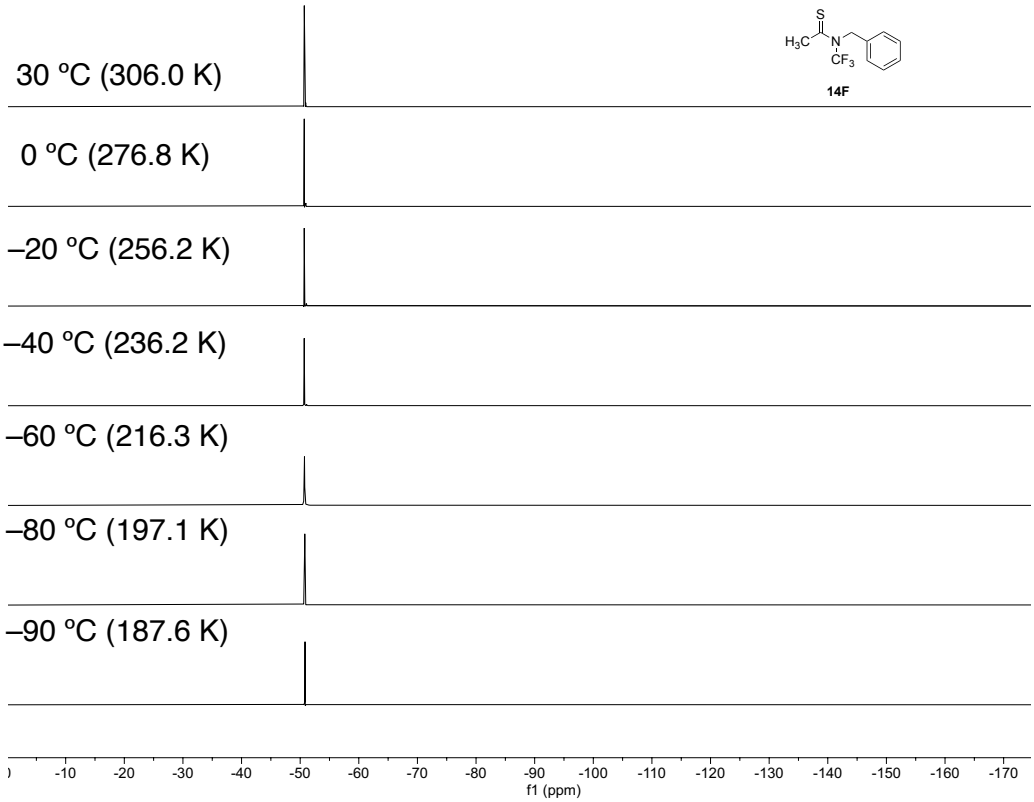



Figure S58. VT-$^{19}$FNMR ($CD_2Cl_2$, 376 MHz) of **14F**.

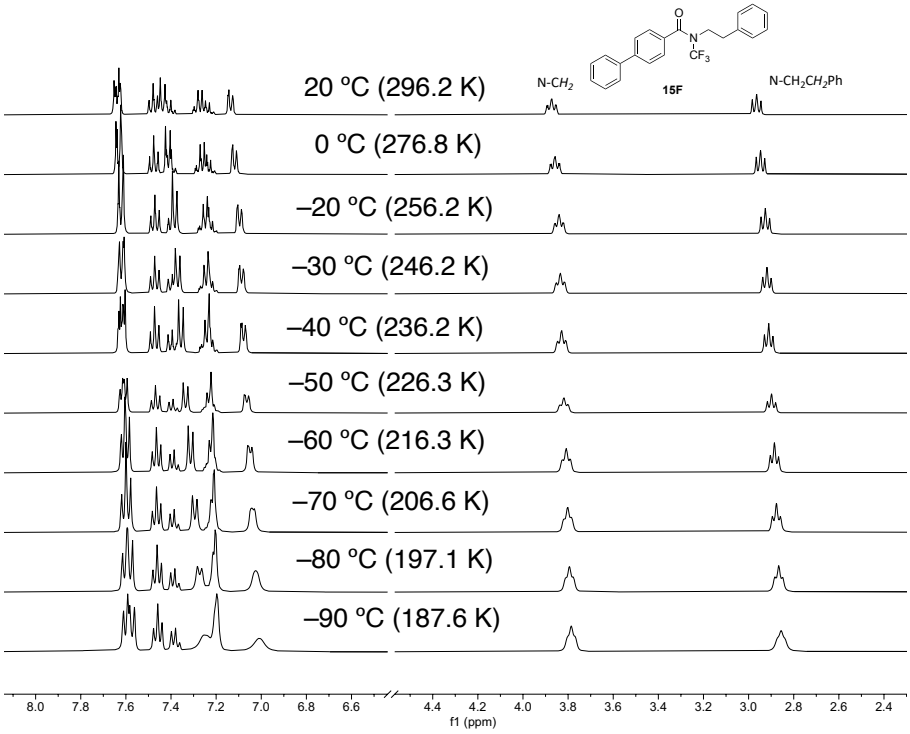



Figure S59. VT-$^{1}$HNMR ($CD_2Cl_2$, 400 MHz) of **15F**.

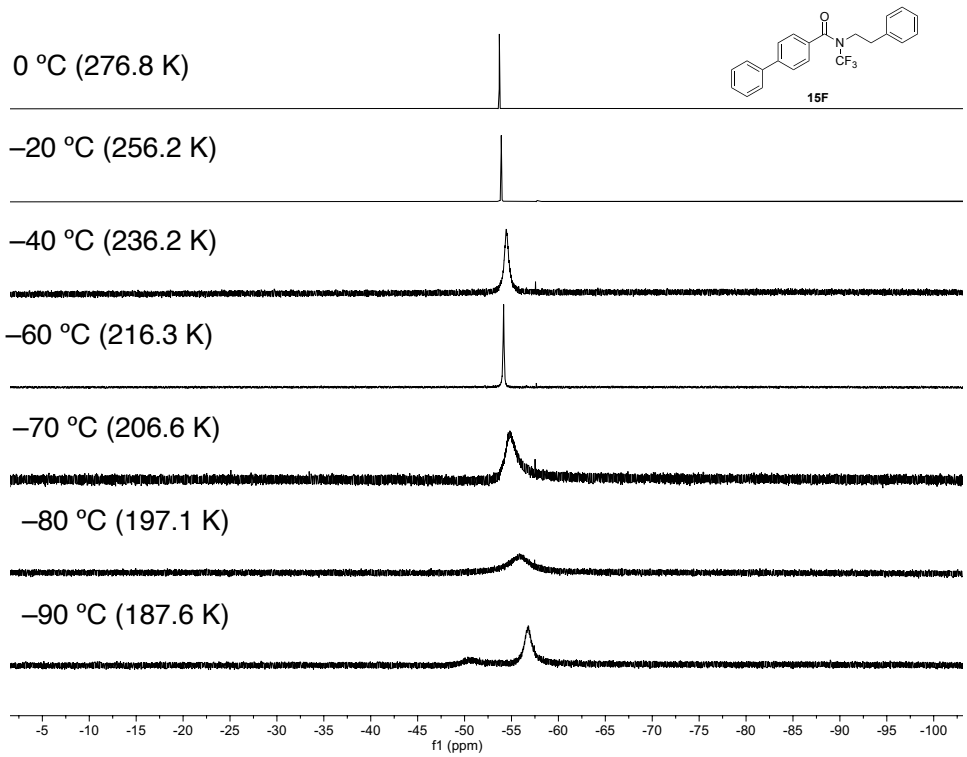



Figure S60. VT-$^{19}$FNMR ($CD_2Cl_2$, 376 MHz) of **15F**.

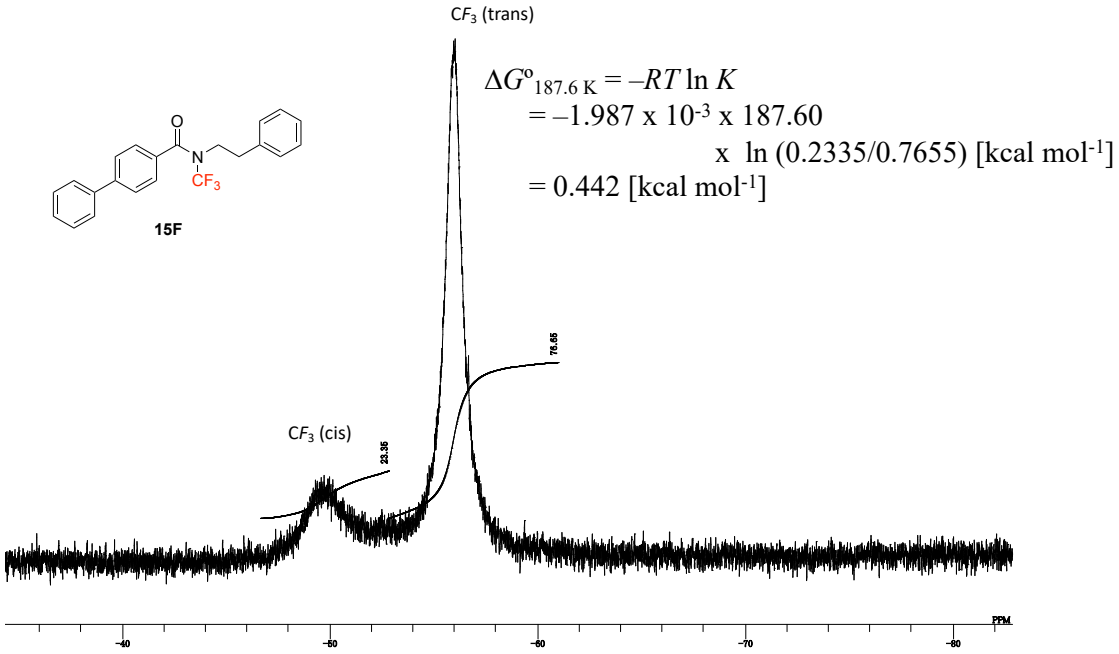



Figure S61. $^{19}$FNMR integration of **15F** ($CD_2Cl_2$, 400 MHz, 188 K).

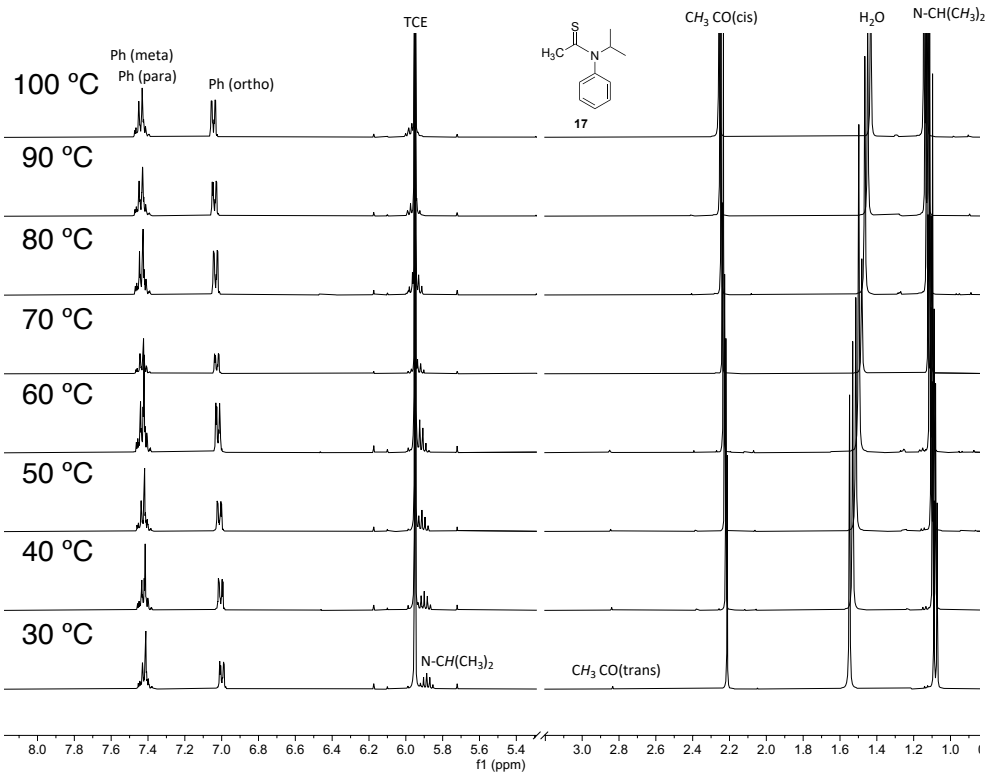



Figure S62. VT-$^{1}$HNMR (Tetrachlroethane-$d_2$, 400 MHz) of **17**.

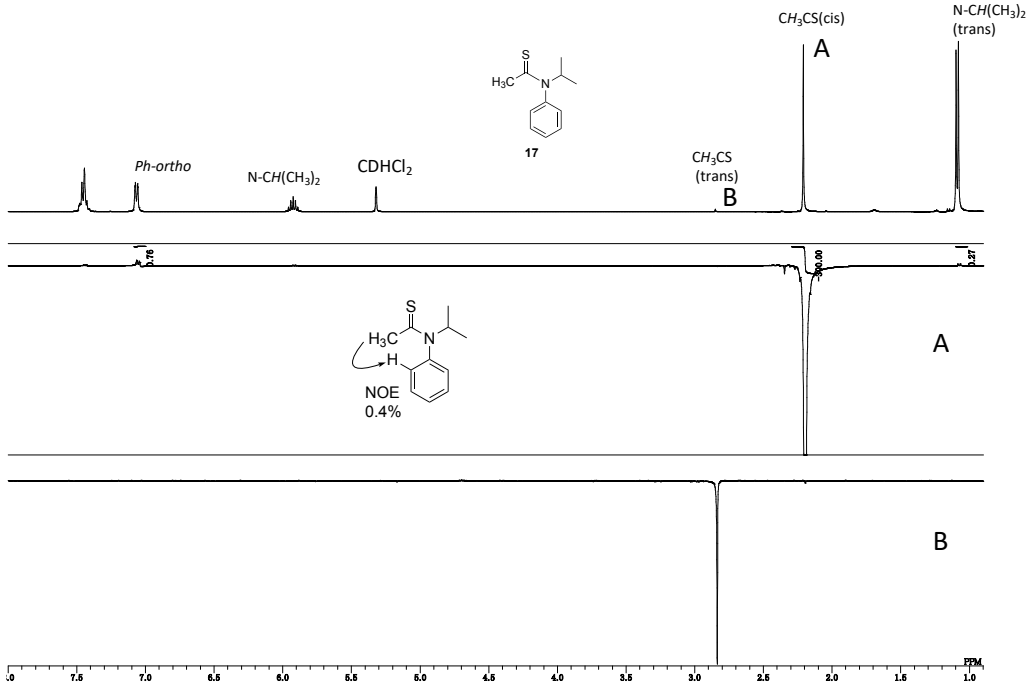



Figure S63. 1D-NOE spectrum of **17** ($CD_2Cl_2$, 400 MHz, 277 K).

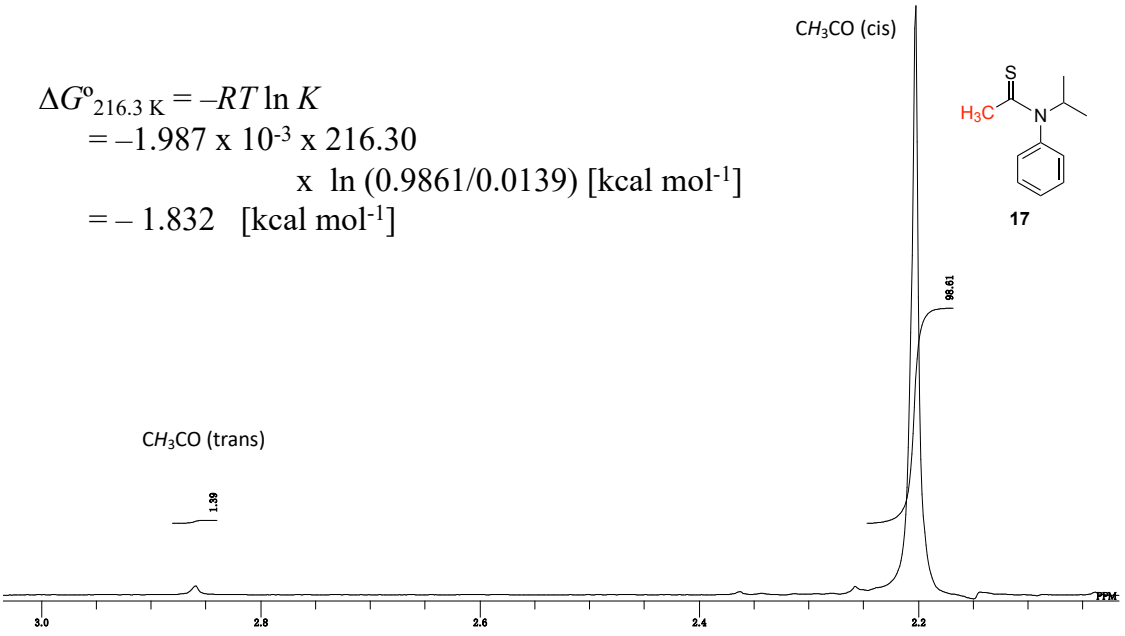



Figure S64. $^{1}$HNMR integration of **17** ($CD_2Cl_2$, 400 MHz, 216 K).

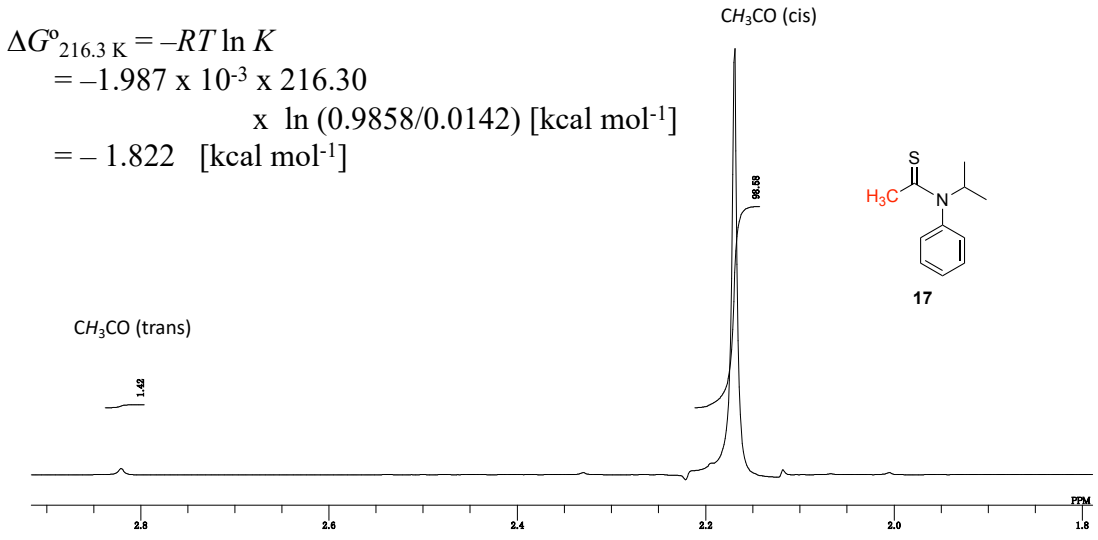



Figure S65. $^{1}$HNMR integration of **17** ($CD_3OD$, 400 MHz, 216 K).

## 6, DFT calculations

All calculations were performed using the Gaussian16 suite (Rev C. 01).[3] Relaxed scans of the dihedral angle, (O=)C–N–C–F, were conducted with 5-degree intervals ranging from 0º dihedral angle to 180º (for **7**, from 0º to 360º with 5-degree intervals) at the M06-2X_6311(d,p) level with SMD ($CH_2Cl_2$) solvation at 213 K. If a large change in energy occurred due to the rotation of the N–Ph bond, another scan was performed in the reverse direction from the structure after rotation of the N–Ph bond, and the lower energy structure was adopted. NBO 7.0 program was used for NBO calculation.[4]

**2** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

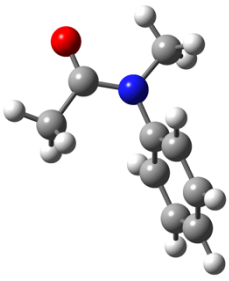
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –479.508221

Sum of electronic and thermal energies = –479.318326

Sum of electronic and thermal enthalpies = –479.317651

Sum of electronic and thermal free energies = –479.348213



| | | | |
|---|---|---|---|
| O | 3.185336 | -0.172568 | 0.111467 |
| N | 1.040182 | 0.497293 | 0.178396 |
| C | 1.500558 | 1.874791 | 0.354968 |
| C | 2.003495 | -0.463970 | 0.020107 |
| C | -0.358377 | 0.250379 | 0.064828 |
| C | -2.467423 | 0.695126 | -1.018384 |
| H | -3.035936 | 1.212156 | -1.782644 |
| C | -3.103473 | -0.190964 | -0.152936 |
| C | -1.098286 | 0.913471 | -0.914919 |
| H | -0.594104 | 1.592567 | -1.593831 |
| C | 1.563956 | -1.877782 | -0.286894 |
| H | 2.418606 | -2.395047 | -0.718781 |
| H | 1.274822 | -2.392326 | 0.631938 |
| C | -2.365322 | -0.847180 | 0.827543 |
| H | -2.855626 | -1.528354 | 1.513264 |
| C | -0.998422 | -0.618915 | 0.946875 |
| H | -0.423053 | -1.105077 | 1.726035 |
| H | 0.719702 | -1.912314 | -0.975549 |
| H | -4.169575 | -0.364569 | -0.238875 |
| H | 1.969045 | 2.255277 | -0.556361 |
| H | 0.647842 | 2.498945 | 0.613561 |
| H | 2.234974 | 1.913929 | 1.159580 |

**2** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

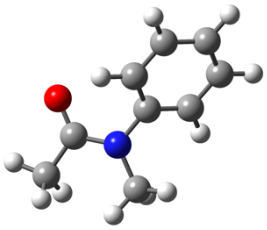
**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –479.506557

Sum of electronic and thermal energies = –479.316525

Sum of electronic and thermal enthalpies = –479.315850



Sum of electronic and thermal free energies = –479.345365

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O | 1.558665 | -1.654288 | -0.591782 | H | 3.935798 | -0.983490 | -0.579090 |
| N | 1.000161 | 0.398591 | 0.220514 | H | 3.557710 | 0.752861 | -0.698996 |
| C | 1.434072 | 1.753798 | 0.563922 | C | -2.339953 | -1.229871 | 0.442180 |
| C | 1.903696 | -0.555381 | -0.197765 | H | -2.769147 | -2.163760 | 0.786746 |
| C | -0.399700 | 0.163107 | 0.103293 | C | -0.967883 | -1.036171 | 0.541085 |
| C | -2.597881 | 0.959342 | -0.511982 | H | -0.333863 | -1.809059 | 0.951848 |
| H | -3.224123 | 1.742154 | -0.924168 | H | 3.686346 | -0.012695 | 0.888043 |
| C | -3.162615 | -0.236260 | -0.082942 | H | -4.232376 | -0.393058 | -0.154096 |
| C | -1.223785 | 1.159387 | -0.423694 | H | 1.628720 | 2.363584 | -0.323115 |
| H | -0.790752 | 2.089962 | -0.771505 | H | 2.335149 | 1.716060 | 1.172766 |
| C | 3.364020 | -0.167096 | -0.144312 | H | 0.653124 | 2.229386 | 1.154643 |

**2F** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

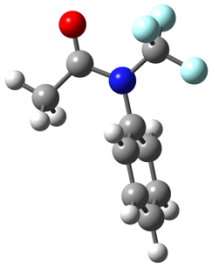
Number of imaginary frequencies: 0 (3 at 6311+(d, p))

SCF Done: E(RM062X) = –777.252648

Sum of electronic and thermal energies = –777.085579

Sum of electronic and thermal enthalpies = –777.084905

Sum of electronic and thermal free energies = –777.118713



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| F | 0.715111 | -2.056552 | -0.108064 | C | -2.794088 | -0.136324 | 1.260487 |
| F | 2.160963 | -1.042281 | 1.117749 | H | -3.293965 | -0.172897 | 2.220923 |
| O | 2.496670 | 1.510993 | 0.005213 | C | -3.531738 | -0.225503 | 0.083110 |
| N | 0.653208 | 0.196966 | -0.092907 | C | -1.411034 | -0.000818 | 1.206506 |
| C | 1.469595 | -0.960538 | -0.026479 | H | -0.817200 | 0.069353 | 2.111104 |
| C | 1.292847 | 1.443649 | -0.055035 | C | 0.387670 | 2.642279 | -0.102639 |
| C | -0.779739 | 0.046643 | -0.031606 | H | 1.012598 | 3.531967 | -0.120705 |
| | | | | H | -0.247626 | 2.612257 | -0.989717 |
| | | | | F | 2.357830 | -1.014656 | -1.021675 |
| | | | | C | -2.889433 | -0.183539 | -1.151361 |
| | | | | H | -3.463676 | -0.256880 | -2.067077 |
| | | | | C | -1.506542 | -0.048899 | -1.212405 |
| | | | | H | -0.985304 | -0.015496 | -2.162274 |
| | | | | H | -0.263423 | 2.664598 | 0.773607 |
| | | | | H | -4.609342 | -0.330430 | 0.127838 |

**2F** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

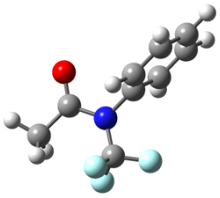
Number of imaginary frequencies: 0 (3 at 6311+(d, p))

SCF Done: E(RM062X) = –777.0

Sum of electronic and thermal energies = –777.083326

Sum of electronic and thermal enthalpies = –777.082652

Sum of electronic and thermal free energies = –777.116761



| | | | |
|---|---|---|---|
| F | -0.578631 | -1.757343 | -1.120180 |
| F | -2.387021 | -0.600228 | -1.251723 |
| O | -0.489537 | 2.279907 | 0.875442 |
| N | -0.608467 | 0.250525 | -0.101021 |
| C | -1.348436 | -0.894508 | -0.462825 |
| C | -1.200321 | 1.392845 | 0.474380 |
| C | 0.829627 | 0.126822 | -0.036493 |
| C | 2.979911 | 0.451636 | -1.045368 |
| H | 3.586060 | 0.792882 | -1.876153 |
| C | 3.583603 | -0.101681 | 0.080720 |
| C | 1.595153 | 0.566797 | -1.107874 |
| H | 1.104122 | 0.993048 | -1.974953 |
| C | -2.702793 | 1.459145 | 0.536287 |
| H | -2.961528 | 2.293624 | 1.183637 |
| H | -3.104369 | 1.638319 | -0.462609 |
| F | -1.855140 | -1.553330 | 0.597949 |
| C | 2.805086 | -0.539542 | 1.148717 |
| H | 3.274698 | -0.969334 | 2.025506 |
| C | 1.420005 | -0.424002 | 1.094349 |
| H | 0.796607 | -0.754688 | 1.917678 |
| H | -3.143131 | 0.540783 | 0.924822 |
| H | 4.662654 | -0.191474 | 0.126264 |

**7** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

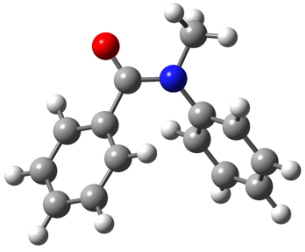
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –671.20098

Sum of electronic and thermal energies = –670.975278

Sum of electronic and thermal enthalpies = –670.974604

Sum of electronic and thermal free energies = –671.009248



| | | | |
|---|---|---|---|
| C | 10.077075 | 3.723246 | 6.820428 |
| C | 10.257643 | 4.804688 | 5.964143 |
| C | 9.328996 | 5.840182 | 5.936104 |
| C | 8.215467 | 5.792168 | 6.771660 |
| C | 8.038679 | 4.722961 | 7.641150 |
| C | 8.975150 | 3.689716 | 7.673064 |
| N | 8.775878 | 2.591600 | 8.564154 |
| C | 9.771204 | 2.063049 | 9.344626 |
| C | 10.930284 | 2.942393 | 9.722610 |
| C | 10.779392 | 4.294718 | 10.033247 |
| C | 11.877868 | 5.037052 | 10.451378 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 13.131206 | 4.438011 | 10.548432 | H | 7.185486 | 4.688681 | 8.309812 |
| C | 13.281797 | 3.087268 | 10.247199 | H | 9.805648 | 4.764912 | 9.959947 |
| C | 12.180671 | 2.338225 | 9.849331 | H | 11.755189 | 6.084201 | 10.701771 |
| O | 9.702826 | 0.921528 | 9.770199 | H | 13.987627 | 5.021982 | 10.865227 |
| C | 7.608349 | 1.739809 | 8.330474 | H | 14.254270 | 2.616164 | 10.329332 |
| H | 10.790497 | 2.906942 | 6.835322 | H | 12.278852 | 1.280861 | 9.633162 |
| H | 11.121740 | 4.829957 | 5.310596 | H | 7.300241 | 1.281378 | 9.268226 |
| H | 9.469355 | 6.678867 | 5.264565 | H | 6.798083 | 2.351092 | 7.938602 |
| H | 7.487598 | 6.594883 | 6.754593 | H | 7.842427 | 0.948365 | 7.612146 |

**7** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

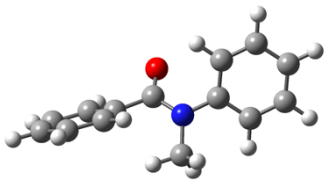
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –671.215367

Sum of electronic and thermal energies = –670.970114

Sum of electronic and thermal enthalpies = –670.969440

Sum of electronic and thermal free energies = –671.004131



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.644226 | 1.239746 | 0.19028 | C | 1.890869 | -0.230486 | 0.09290 |
| C | -4.016061 | 1.115761 | 0.37931 | C | 2.372992 | 0.996674 | 0.54883 |
| C | -4.632169 | -0.124533 | 0.24975 | C | 3.741937 | 1.240743 | 0.57115 |
| C | -3.864756 | -1.237875 | -0.07927 | C | 4.631563 | 0.268106 | 0.12351 |
| C | -2.493164 | -1.122831 | -0.27738 | C | 4.152290 | -0.959320 | -0.32650 |
| C | -1.874492 | 0.120812 | -0.13433 | C | 2.785983 | -1.214765 | -0.32508 |
| N | -0.474145 | 0.297230 | -0.35587 | O | 0.106158 | -1.637499 | 0.70207 |
| C | 0.431307 | -0.591496 | 0.16750 | C | -0.084925 | 1.446160 | -1.18099 |
| | | | | H | -2.167539 | 2.206719 | 0.30114 |
| | | | | H | -4.600529 | 1.992277 | 0.63390 |
| | | | | H | -5.700698 | -0.222503 | 0.40063 |
| | | | | H | -4.335980 | -2.207518 | -0.19193 |
| | | | | H | -1.903299 | -1.989716 | -0.53643 |
| | | | | H | 1.681955 | 1.753944 | 0.90192 |
| | | | | H | 4.113469 | 2.190017 | 0.93880 |
| | | | | H | 5.697568 | 0.463719 | 0.13251 |
| | | | | H | 4.843276 | -1.720746 | -0.66876 |
| | | | | H | 2.403918 | -2.176596 | -0.64710 |
| | | | | H | -0.843341 | 1.583937 | -1.95158 |
| | | | | H | -0.000728 | 2.367504 | -0.60035 |
| | | | | H | 0.865891 | 1.246181 | -1.66865 |

## **7F** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

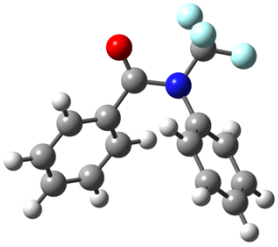
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –968.962476

Sum of electronic and thermal energies = –968.740228

Sum of electronic and thermal enthalpies = –968.739553

Sum of electronic and thermal free energies = –968.777139



| | | | |
|---|---|---|---|
| F | -3.038370 | -0.535487 | -0.796449 |
| F | -2.530403 | -1.504242 | 1.050321 |
| F | -2.058738 | -2.448020 | -0.830476 |
| O | 0.135759 | -2.462852 | 0.684531 |
| N | -0.848015 | -0.616897 | -0.249387 |
| C | 1.611477 | -0.760978 | -0.042815 |
| C | 0.267896 | -1.377075 | 0.186386 |
| C | 2.644217 | -1.159965 | 0.803979 |
| H | 2.424334 | -1.863340 | 1.597937 |
| C | -0.878592 | 0.800395 | 0.020629 |
| C | -1.262997 | 1.686727 | -0.980155 |
| H | -1.548029 | 1.298444 | -1.950209 |
| C | 1.871651 | 0.110664 | -1.099655 |
| H | 1.074818 | 0.399393 | -1.773293 |
| C | -0.518999 | 1.267612 | 1.279634 |
| H | -0.238407 | 0.559914 | 2.051932 |
| C | -0.518917 | 2.634599 | 1.531021 |
| H | -0.229937 | 3.000343 | 2.508451 |
| C | 3.926728 | -0.663743 | 0.615524 |
| H | 4.726269 | -0.965375 | 1.280929 |
| C | -2.109096 | -1.285567 | -0.198399 |
| C | -1.276471 | 3.049778 | -0.718077 |
| H | -1.577526 | 3.742269 | -1.494452 |
| C | -0.897813 | 3.525602 | 0.534053 |
| H | -0.901493 | 4.590421 | 0.732067 |
| C | 3.159537 | 0.591075 | -1.295938 |
| H | 3.364193 | 1.260200 | -2.122554 |
| C | 4.184240 | 0.212906 | -0.433962 |
| H | 5.186240 | 0.596382 | -0.585261 |

## **7F** (trans)

**M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –968.957946

Sum of electronic and thermal energies = –968.735781

Sum of electronic and thermal enthalpies = –968.735106

Sum of electronic and thermal free energies = –968.773294

| | | | |
|---|---|---|---|
| F | 1.201743 | 1.833825 | -1.439286 |
| F | 0.138997 | 2.317554 | 0.356144 |
| F | -0.920073 | 1.501224 | -1.336299 |
| O | -0.119702 | -2.083949 | -0.307768 |
| N | 0.461383 | 0.105645 | -0.185806 |
| C | -1.924490 | -0.616628 | 0.072224 |

| | | | |
|---|---|---|---|
| C | -0.488608 | -0.946831 | -0.180006 |
| C | -2.880155 | -1.461052 | -0.490363 |
| H | -2.549834 | -2.273198 | -1.126041 |
| C | 1.842511 | -0.210935 | 0.089060 |
| C | 2.571257 | -1.002174 | -0.790437 |
| H | 2.089360 | -1.396328 | -1.674973 |
| C | -2.316302 | 0.409720 | 0.929920 |
| H | -1.574266 | 1.050189 | 1.390415 |
| C | 2.424973 | 0.300555 | 1.241641 |
| H | 1.832421 | 0.910979 | 1.912309 |
| C | 3.760087 | 0.022913 | 1.513920 |
| H | 4.220261 | 0.422606 | 2.409073 |
| C | -4.226725 | -1.256251 | -0.226044 |
| H | -4.969943 | -1.903463 | -0.675173 |
| C | 0.212854 | 1.419213 | -0.646850 |
| C | 3.899661 | -1.286728 | -0.504255 |
| H | 4.472014 | -1.909184 | -1.180898 |
| C | 4.495494 | -0.772530 | 0.643713 |
| H | 5.533540 | -0.994293 | 0.859745 |
| C | -3.663877 | 0.598938 | 1.207869 |
| H | -3.967855 | 1.390189 | 1.881928 |
| C | -4.618989 | -0.226211 | 0.623756 |
| H | -5.669916 | -0.070837 | 0.836488 |

## **7F** (cis)

**M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

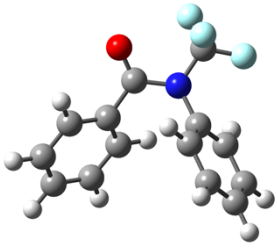
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –968.947647

Sum of electronic and thermal energies = –968.725143

Sum of electronic and thermal enthalpies = –968.724469

Sum of electronic and thermal free energies = –968.761707



| | | | |
|---|---|---|---|
| F | -3.038370 | -0.535487 | -0.796449 |
| F | -2.530403 | -1.504242 | 1.050321 |
| F | -2.058738 | -2.448020 | -0.830476 |
| O | 0.135759 | -2.462852 | 0.684531 |
| N | -0.848015 | -0.616897 | -0.249387 |
| C | 1.611477 | -0.760978 | -0.042815 |
| C | 0.267896 | -1.377075 | 0.186386 |
| C | 2.644217 | -1.159965 | 0.803979 |
| H | 2.424334 | -1.863340 | 1.597937 |
| C | -0.878592 | 0.800395 | 0.020629 |
| C | -1.262997 | 1.686727 | -0.980155 |
| H | -1.548029 | 1.298444 | -1.950209 |
| C | 1.871651 | 0.110664 | -1.099655 |
| H | 1.074818 | 0.399393 | -1.773293 |
| C | -0.518999 | 1.267612 | 1.279634 |
| H | -0.238407 | 0.559914 | 2.051932 |
| C | -0.518917 | 2.634599 | 1.531021 |
| H | -0.229937 | 3.000343 | 2.508451 |
| C | 3.926728 | -0.663743 | 0.615524 |
| H | 4.726269 | -0.965375 | 1.280929 |
| C | -2.109096 | -1.285567 | -0.198399 |
| C | -1.276471 | 3.049778 | -0.718077 |
| H | -1.577526 | 3.742269 | -1.494452 |
| C | -0.897813 | 3.525602 | 0.534053 |
| H | -0.901493 | 4.590421 | 0.732067 |
| C | 3.159537 | 0.591075 | -1.295938 |
| H | 3.364193 | 1.260200 | -2.122554 |

| | | | |
|---|---|---|---|
| C | 4.184240 | 0.212906 | -0.433962 |
| H | 5.186240 | 0.596382 | -0.585261 |

## **9F** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

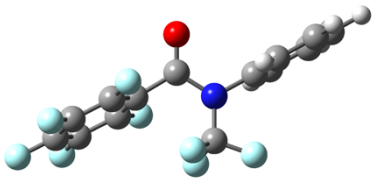
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –1465.118535

Sum of electronic and thermal energies = –1464.934881

Sum of electronic and thermal enthalpies = –1464.934207

Sum of electronic and thermal free energies = –1464.976676



| | | | |
|---|---|---|---|
| F | -0.757915 | 0.724329 | -1.838585 |
| F | 1.090819 | 1.712588 | -1.348592 |
| F | -0.638426 | 1.976418 | -0.098213 |
| O | -0.066306 | -1.910809 | 1.081077 |
| N | 0.473174 | -0.031026 | -0.065368 |
| C | -1.889868 | -0.578420 | 0.385435 |
| C | -0.423837 | -0.920733 | 0.503106 |
| C | -2.682096 | -1.183082 | -0.574767 |
| C | 1.887290 | -0.252527 | 0.140599 |
| C | 2.612607 | -0.961954 | -0.806719 |
| H | 2.114524 | -1.338932 | -1.692539 |
| C | -2.487303 | 0.267153 | 1.304014 |
| C | 2.480427 | 0.243377 | 1.293497 |
| H | 1.879486 | 0.787647 | 2.013186 |
| C | 3.838263 | 0.024979 | 1.499145 |
| H | 4.314385 | 0.406003 | 2.394455 |
| C | -4.043597 | -0.947721 | -0.629570 |
| C | 0.045136 | 1.087329 | -0.831279 |
| C | 3.970365 | -1.172961 | -0.593983 |
| H | 4.549393 | -1.723382 | -1.325598 |
| C | 4.580793 | -0.680579 | 0.556396 |
| H | 5.638747 | -0.848936 | 0.719507 |
| C | -3.847607 | 0.514732 | 1.268828 |
| C | -4.623677 | -0.099140 | 0.299579 |
| F | -1.743904 | 0.864671 | 2.232665 |
| F | -4.411826 | 1.329645 | 2.152621 |
| F | -5.927856 | 0.131015 | 0.256863 |
| F | -4.794643 | -1.523761 | -1.560935 |
| F | -2.127003 | -1.985082 | -1.479688 |

## **9F** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

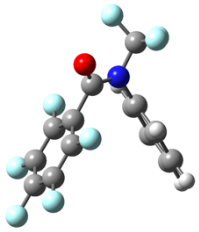
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –1465.122481

Sum of electronic and thermal energies = –1464.938117

Sum of electronic and thermal enthalpies = –1464.937443

Sum of electronic and thermal free energies = –1464.980960



| | | | |
|---|---|---|---|
| F | -3.146921 | -0.434067 | -0.417882 |
| F | -2.462941 | -1.832969 | 1.062089 |
| F | -2.265953 | -2.298210 | -1.028707 |
| O | 0.130687 | -2.675078 | 0.166471 |
| N | -0.915254 | -0.674046 | -0.180191 |
| C | 1.519645 | -0.784066 | -0.160277 |
| C | 0.198549 | -1.491537 | -0.031743 |
| C | 2.459225 | -0.897249 | 0.853518 |
| C | -0.842121 | 0.744737 | 0.084896 |
| C | -1.133669 | 1.648796 | -0.929645 |
| H | -1.422263 | 1.282131 | -1.907229 |
| C | 1.865579 | -0.076539 | -1.301950 |
| C | -0.463711 | 1.174751 | 1.352692 |
| H | -0.249691 | 0.443961 | 2.125902 |
| C | -0.359352 | 2.538409 | 1.602385 |
| H | -0.058702 | 2.883265 | 2.584238 |
| C | 3.705594 | -0.307605 | 0.744937 |
| C | -2.189732 | -1.313519 | -0.139673 |
| C | -1.039146 | 3.010363 | -0.666427 |
| H | -1.264535 | 3.724325 | -1.449220 |
| C | -0.648433 | 3.453824 | 0.594511 |
| H | -0.570147 | 4.516328 | 0.792219 |
| C | 3.109863 | 0.512610 | -1.432273 |
| C | 4.030031 | 0.394015 | -0.404165 |
| F | 2.158154 | -1.544011 | 1.975719 |
| F | 4.587968 | -0.404549 | 1.732657 |
| F | 5.224189 | 0.955607 | -0.519506 |
| F | 3.429350 | 1.180713 | -2.534558 |
| F | 1.001160 | 0.040640 | -2.307232 |

## **9** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

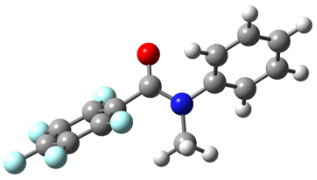
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –1167.379809

Sum of electronic and thermal energies = –1167.172800

Sum of electronic and thermal enthalpies = –1167.172126

Sum of electronic and thermal free energies = –1167.212971



| | | | |
|---|---|---|---|
| C | -2.386293 | -0.566954 | 1.017774 |
| C | -3.749100 | -0.832765 | 1.079284 |
| C | -4.603216 | -0.343982 | 0.093936 |
| C | -4.090223 | 0.407161 | -0.959067 |
| C | -2.725755 | 0.669086 | -1.031025 |
| C | -1.879277 | 0.182629 | -0.039980 |
| N | -0.476669 | 0.481658 | -0.091864 |
| C | 0.392921 | -0.551576 | -0.225364 |
| C | 1.863823 | -0.225091 | -0.093110 |
| C | 2.397300 | 0.277148 | 1.083332 |

| | | | |
|---|---|---|---|
| C | 3.757983 | 0.468297 | 1.242180 |
| C | 4.613380 | 0.142690 | 0.203246 |
| C | 4.106375 | -0.366039 | -0.980462 |
| C | 2.741905 | -0.555840 | -1.113929 |
| O | 0.063840 | -1.702122 | -0.432666 |
| C | -0.100336 | 1.887574 | 0.055432 |
| H | -1.710733 | -0.937506 | 1.780074 |
| H | -4.144580 | -1.418367 | 1.900833 |
| H | -5.665890 | -0.549344 | 0.146587 |
| H | -4.750207 | 0.785598 | -1.730713 |
| H | -2.314494 | 1.244038 | -1.853266 |
| H | -0.743686 | 2.494802 | -0.580874 |
| H | -0.218358 | 2.210749 | 1.092039 |
| H | 0.928070 | 2.041684 | -0.263346 |
| F | 1.589912 | 0.594933 | 2.097029 |
| F | 4.247782 | 0.952397 | 2.379212 |
| F | 5.920391 | 0.321020 | 0.340995 |
| F | 4.932656 | -0.669283 | -1.976671 |
| F | 2.283535 | -1.041336 | -2.264632 |

## **9** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

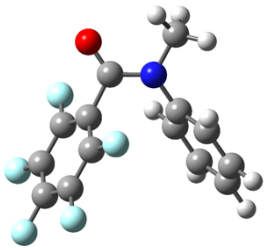
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –1167.384358

Sum of electronic and thermal energies = –1167.177383

Sum of electronic and thermal enthalpies = –1167.176708

Sum of electronic and thermal free energies = –1167.217539



| | | | |
|---|---|---|---|
| C | -1.155767 | -0.310854 | 1.301940 |
| C | -1.782998 | -1.525902 | 1.555797 |
| C | -2.655805 | -2.069785 | 0.618276 |
| C | -2.897989 | -1.399387 | -0.578211 |
| C | -2.262027 | -0.192538 | -0.845199 |
| C | -1.388240 | 0.346940 | 0.095806 |
| N | -0.738118 | 1.592595 | -0.175246 |
| C | 0.610624 | 1.727255 | -0.157208 |
| C | 1.400948 | 0.438813 | -0.219335 |
| C | 1.330498 | -0.403756 | -1.316912 |
| C | 2.106505 | -1.546313 | -1.401035 |
| C | 2.974837 | -1.856412 | -0.368311 |
| C | 3.059682 | -1.030636 | 0.740343 |
| C | 2.280768 | 0.110911 | 0.798991 |
| O | 1.188092 | 2.795462 | -0.134538 |
| C | -1.547702 | 2.810258 | -0.213855 |
| H | -0.483397 | 0.131456 | 2.029759 |
| H | -1.596422 | -2.040834 | 2.490764 |
| H | -3.148644 | -3.013540 | 0.819782 |
| H | -3.575495 | -1.821860 | -1.310738 |
| H | -2.425715 | 0.329630 | -1.781136 |
| H | -1.050743 | 3.550190 | -0.838120 |
| H | -2.522868 | 2.570610 | -0.633723 |
| H | -1.677197 | 3.218535 | 0.792226 |
| F | 2.352842 | 0.872797 | 1.889720 |
| F | 3.881846 | -1.343379 | 1.737219 |
| F | 3.724202 | -2.948886 | -0.438903 |
| F | 2.029453 | -2.341660 | -2.463585 |
| F | 0.501721 | -0.125907 | -2.323428 |

## **10** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

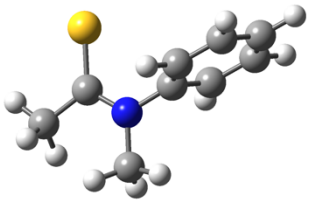
**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

Number of imaginary frequencies: (1 at 6311+(d, p))

SCF Done: E(RM062X) = –802.457631

Sum of electronic and thermal energies = –802.270528

Sum of electronic and thermal enthalpies = –802.269854



Sum of electronic and thermal free energies = –802.299383

| | | | |
|---|---|---|---|
| N | 1.01899 | 0.34801 | 0.175996 |
| C | 1.42926 | 1.46334 | 1.04052 |
| C | 1.8903 | -0.37267 | -0.53608 |
| C | -0.40016 | 0.13741 | 0.06366 |
| C | -2.50615 | 0.71648 | -0.9298 |
| H | -3.07948 | 1.29249 | -1.64654 |
| C | -3.14548 | -0.19035 | -0.08946 |
| C | -1.12719 | 0.88494 | -0.85453 |
| H | -0.61152 | 1.58113 | -1.50662 |
| C | 3.33905 | 0.00355 | -0.3741 |
| H | 3.94666 | -0.56423 | -1.07164 |
| H | 3.48525 | 1.07271 | -0.54866 |
| C | -2.40685 | -0.92874 | 0.83173 |
| H | -2.90343 | -1.63504 | 1.48654 |
| C | -1.02858 | -0.76417 | 0.91358 |
| H | -0.43589 | -1.33432 | 1.61996 |
| H | 3.6699 | -0.21548 | 0.64531 |
| H | -4.21934 | -0.32175 | -0.1515 |
| H | 1.66801 | 2.34794 | 0.44428 |
| H | 2.29395 | 1.18566 | 1.64127 |
| H | 0.60191 | 1.69691 | 1.70647 |

## **10** (cis)

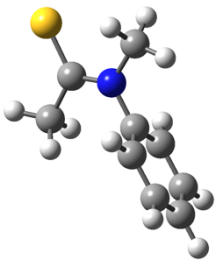
**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –802.460566

Sum of electronic and thermal energies = –802.272787



Sum of electronic and thermal enthalpies = –802.272113

Sum of electronic and thermal free energies = –802.303354

| | | | |
|---|---|---|---|
| N | 1.08135 | 0.5073 | 0.14659 |
| C | 1.47117 | 1.85958 | 0.55056 |
| C | 1.99458 | -0.44102 | -0.0836 |
| C | -0.33124 | 0.24309 | 0.05648 |

| | | | |
|---|---|---|---|
| C | -2.41508 | 0.4849 | -1.11262 |
| H | -2.97671 | 0.8505 | -1.96407 |
| C | -3.05961 | -0.22134 | -0.10019 |
| C | -1.04658 | 0.72039 | -1.03736 |
| H | -0.52722 | 1.26441 | -1.81849 |
| C | 1.48327 | -1.78985 | -0.52148 |
| H | 2.30748 | -2.37843 | -0.91395 |
| H | 1.05161 | -2.31829 | 0.33301 |
| C | -2.33643 | -0.68925 | 0.99298 |
| H | -2.83726 | -1.23392 | 1.78452 |
| C | -0.96763 | -0.45439 | 1.07726 |
| H | -0.38989 | -0.80644 | 1.92465 |
| H | 0.70365 | -1.6924 | -1.27985 |
| H | -4.12566 | -0.40506 | -0.16261 |
| H | 2.15266 | 2.2877 | -0.18591 |
| H | 0.57246 | 2.46721 | 0.6243 |
| H | 1.97811 | 1.83027 | 1.51723 |
| S | 3.64063 | -0.16755 | 0.1078 |

## **10F** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

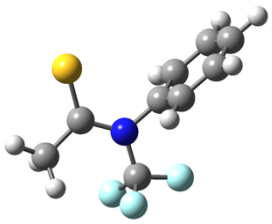
Number of imaginary frequencies: 0 (1 at 6311+(d, p))

SCF Done: E(RM062X) = –1100.195354

Sum of electronic and thermal energies = –1100.030954

Sum of electronic and thermal enthalpies = –1100.030280

Sum of electronic and thermal free energies = –1100.062482



| | | | |
|---|---|---|---|
| F | -0.53098 | -1.71684 | -1.06937 |
| F | -2.31225 | -0.54524 | -1.30354 |
| N | -0.59804 | 0.28742 | -0.02623 |
| C | -1.33459 | -0.8604 | -0.45408 |
| C | -1.21314 | 1.40012 | 0.497 |
| C | 0.8436 | 0.14797 | 0.00263 |
| C | 2.96736 | 0.41775 | -1.06414 |
| H | 3.55966 | 0.73934 | -1.91231 |
| C | 3.58666 | -0.13858 | 0.05208 |
| C | 1.58485 | 0.56094 | -1.09459 |
| H | 1.08026 | 0.99366 | -1.95068 |
| C | -2.71875 | 1.42379 | 0.51505 |
| H | -3.04604 | 2.23281 | 1.16038 |
| H | -3.08954 | 1.60838 | -0.49618 |
| F | -1.89969 | -1.51178 | 0.57278 |
| C | 2.8269 | -0.55631 | 1.14118 |
| H | 3.30933 | -0.99163 | 2.00799 |
| C | 1.4437 | -0.41482 | 1.12031 |
| H | 0.83222 | -0.72599 | 1.9599 |
| H | -3.14644 | 0.48483 | 0.86884 |
| H | 4.66447 | -0.24866 | 0.07226 |
| S | -0.33821 | 2.68348 | 1.05694 |

## **10F** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

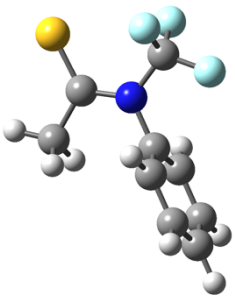
Number of imaginary frequencies: 0 (1 at 6311+(d, p))

SCF Done: E(RM062X) = –1100.195792

Sum of electronic and thermal energies = –1100.031525

Sum of electronic and thermal enthalpies = –1100.030851

Sum of electronic and thermal free energies = –1100.063627



| | | | |
|---|---|---|---|
| F | 0.63774 | -2.04837 | 0.01468 |
| F | 2.23603 | -1.08683 | 1.07002 |
| N | 0.68853 | 0.20829 | -0.03178 |
| C | 1.45886 | -1.00131 | -0.00803 |
| C | 1.28984 | 1.44164 | -0.07076 |
| C | -0.75446 | 0.06509 | 0.00057 |
| C | -2.78595 | -0.13239 | 1.25366 |
| H | -3.30292 | -0.18285 | 2.20425 |
| C | -3.50233 | -0.20126 | 0.06191 |
| C | -1.40178 | 0.00027 | 1.22761 |
| H | -0.82229 | 0.05584 | 2.14228 |
| C | 0.33266 | 2.60067 | -0.09919 |
| H | 0.89369 | 3.52943 | -0.12611 |
| H | -0.31514 | 2.53694 | -0.97726 |
| F | 2.232 | -1.13067 | -1.08391 |
| C | -2.83876 | -0.14285 | -1.16056 |
| H | -3.39673 | -0.20112 | -2.08725 |
| C | -1.45475 | -0.0115 | -1.19601 |
| H | -0.91589 | 0.03481 | -2.13566 |
| H | -0.31083 | 2.58553 | 0.78423 |
| H | -4.58074 | -0.30379 | 0.08593 |
| S | 2.92477 | 1.67837 | -0.08608 |

## **11** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

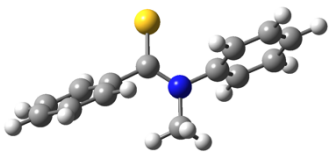
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –994.169250

Sum of electronic and thermal energies = –993.926549

Sum of electronic and thermal enthalpies = –993.925875

Sum of electronic and thermal free energies = –993.962122



| | | | |
|---|---|---|---|
| C | -2.415557 | -0.334457 | 1.152754 |
| C | -3.789348 | -0.539395 | 1.222240 |
| C | -4.595628 | -0.244659 | 0.126144 |
| C | -4.029636 | 0.259271 | -1.041831 |
| C | -2.656773 | 0.467580 | -1.118365 |
| C | -1.861960 | 0.162022 | -0.020608 |
| N | -0.445027 | 0.409698 | -0.076943 |
| C | 0.411804 | -0.578425 | -0.355253 |
| C | 1.864497 | -0.278525 | -0.181177 |
| C | 2.340365 | 0.099720 | 1.076305 |
| C | 3.699538 | 0.317469 | 1.268443 |
| C | 4.585118 | 0.182841 | 0.202713 |
| C | 4.109696 | -0.184923 | -1.053081 |
| C | 2.754571 | -0.429700 | -1.243801 |
| C | -0.063346 | 1.808710 | 0.162655 |
| H | -1.769834 | -0.565617 | 1.992712 |
| H | -4.229084 | -0.930143 | 2.132187 |
| H | -5.665487 | -0.407403 | 0.182274 |
| H | -4.656010 | 0.487834 | -1.895948 |
| H | -2.197292 | 0.852827 | -2.021906 |
| H | 1.646986 | 0.206602 | 1.904074 |
| H | 4.066275 | 0.593925 | 2.250009 |
| H | 5.643778 | 0.360530 | 0.351526 |
| H | 4.796520 | -0.291158 | -1.884537 |
| H | 2.381024 | -0.736480 | -2.213707 |
| H | -0.777056 | 2.446388 | -0.359152 |
| H | -0.100521 | 2.036613 | 1.230527 |
| H | 0.933935 | 2.002451 | -0.221750 |
| S | -0.054345 | -2.117745 | -0.830204 |

## **11** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

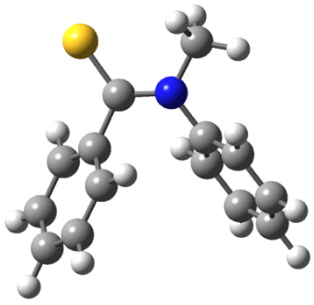
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –994.173112

Sum of electronic and thermal energies = –993.930406

Sum of electronic and thermal enthalpies = –993.929731

Sum of electronic and thermal free energies = –993.964941



| | | | |
|---|---|---|---|
| C | -1.158589 | -0.384403 | 1.270994 |
| C | -1.806244 | -1.599631 | 1.464709 |
| C | -2.680919 | -2.089269 | 0.499522 |
| C | -2.911907 | -1.358481 | -0.663181 |
| C | -2.262574 | -0.146926 | -0.868048 |
| C | -1.379885 | 0.329312 | 0.097206 |
| N | -0.714015 | 1.587162 | -0.113794 |
| C | 0.620548 | 1.712307 | -0.066213 |
| C | 1.427605 | 0.457182 | -0.142523 |
| C | 1.243146 | -0.420077 | -1.213779 |
| C | 2.020937 | -1.567041 | -1.314914 |
| C | 2.970928 | -1.855398 | -0.338942 |
| C | 3.155476 | -0.981428 | 0.728892 |
| C | 2.397180 | 0.180014 | 0.820466 |

| | | | |
|---|---|---|---|
| C | -1.564655 | 2.776664 | -0.198947 |
| H | -0.479799 | 0.010405 | 2.018301 |
| H | -1.630169 | -2.159678 | 2.375390 |
| H | -3.184508 | -3.036147 | 0.653838 |
| H | -3.592788 | -1.735371 | -1.417112 |
| H | -2.422715 | 0.423596 | -1.776369 |
| H | 0.500400 | -0.197316 | -1.971731 |
| H | 1.882837 | -2.237185 | -2.155259 |
| H | 3.569271 | -2.755950 | -0.412863 |
| H | 3.895729 | -1.200259 | 1.489466 |
| H | 2.545844 | 0.871425 | 1.641763 |
| H | -1.253321 | 3.394676 | -1.041140 |
| H | -2.594905 | 2.456004 | -0.329503 |
| H | -1.476418 | 3.364464 | 0.717679 |
| S | 1.397190 | 3.193989 | 0.003690 |

## **11F** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –1291.905356

Sum of electronic and thermal energies = –1291.685411

Sum of electronic and thermal enthalpies = –1291.684737

Sum of electronic and thermal free energies = –1291.722993

| | | | |
|---|---|---|---|
| F | 1.07056 | 1.52845 | -1.6409 |
| F | -0.12859 | 2.11443 | 0.03321 |
| F | -1.00934 | 1.00839 | -1.59262 |
| N | 0.44075 | -0.1063 | -0.21292 |
| C | -1.89986 | -0.67811 | 0.25102 |
| C | -0.46804 | -1.07506 | 0.15028 |
| C | -2.87579 | -1.38076 | -0.45682 |
| H | -2.57969 | -2.18469 | -1.12016 |
| C | 1.85347 | -0.28346 | 0.05342 |
| C | 2.6833 | -0.808597 | -0.92801 |
| H | 2.26872 | -1.08582 | -1.89012 |
| C | -2.26877 | 0.35287 | 1.11771 |
| H | -1.51328 | 0.88135 | 1.68719 |
| C | 2.33947 | 0.08404 | 1.3002 |
| H | 1.66101 | 0.48738 | 2.0437 |
| C | 3.69295 | -0.086104 | 1.57294 |
| H | 4.08522 | 0.19532 | 2.54271 |
| C | -4.21278 | -1.03459 | -0.31688 |
| H | -4.96764 | -1.57022 | -0.88017 |
| C | 0.08135 | 1.12559 | -0.84642 |
| C | 4.033702 | -0.97485 | -0.646696 |
| H | 4.69284 | -1.38678 | -1.40126 |
| C | 4.53683 | -0.61567 | 0.60175 |
| H | 5.59048 | -0.7489 | 0.81697 |
| C | -3.61217 | 0.67568 | 1.27272 |
| H | -3.89772 | 1.46338 | 1.95968 |
| C | -4.58359 | -0.00908 | 0.54998 |
| H | -5.62911 | 0.25168 | 0.66491 |
| S | -0.00356 | -2.60755 | 0.54062 |

## **11F** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

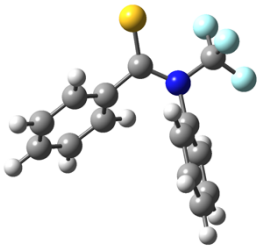
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –1291.907148

Sum of electronic and thermal energies = –1291.687203

Sum of electronic and thermal enthalpies = –1291.686528

Sum of electronic and thermal free energies = –1291.724507



| | | | |
|---|---|---|---|
| F | -2.98793 | -0.38143 | -0.85048 |
| F | -2.68177 | -1.56578 | 0.90896 |
| F | -2.15006 | -2.34532 | -1.03154 |
| N | -0.85244 | -0.6742 | -0.17962 |
| C | 1.55114 | -0.79386 | -0.05011 |
| C | 0.23814 | -1.45434 | 0.17912 |
| C | 2.56804 | -0.88847 | 0.90111 |
| H | 2.38019 | -1.40606 | 1.83432 |
| C | -0.81933 | 0.75112 | 0.09819 |
| C | -1.02928 | 1.6683 | -0.9247 |
| H | -1.22035 | 1.31707 | -1.93155 |
| C | 1.78664 | -0.12715 | -1.25649 |
| H | 1.00195 | -0.07147 | -2.00216 |
| C | -0.57141 | 1.16566 | 1.40118 |
| H | -0.41878 | 0.42632 | 2.18035 |
| C | -0.51714 | 2.52696 | 1.68168 |
| H | -0.31843 | 2.85865 | 2.69358 |
| C | 3.80408 | -0.30463 | 0.65507 |
| H | 4.58501 | -0.3653 | 1.40367 |
| C | -2.15641 | -1.25238 | -0.27967 |
| C | -0.98311 | 3.02577 | -0.63318 |
| H | -1.14339 | 3.74887 | -1.4237 |
| C | -0.72306 | 3.45522 | 0.66638 |
| H | -0.68141 | 4.51534 | 0.88649 |
| C | 3.0328 | 0.431004 | -1.50833 |
| H | 3.2173 | 0.92905 | -2.45274 |
| C | 4.04014 | 0.35095 | -0.55026 |
| H | 5.00846 | 0.79744 | -0.74388 |
| S | 0.14641 | -2.98752 | 0.76553 |

## **12** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

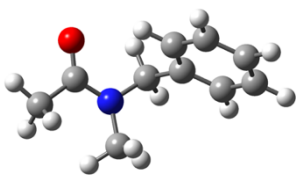
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –518.814716

Sum of electronic and thermal energies = –518.594768

Sum of electronic and thermal enthalpies = –518.594094

Sum of electronic and thermal free energies = –518.627178



| | | | |
|---|---|---|---|
| C | -2.328383 | -0.422014 | 0.149172 |
| O | -2.268021 | -1.336206 | 0.961384 |
| N | -1.483142 | 0.646415 | 0.194237 |

| | | | |
|---|---|---|---|
| C | -0.398544 | 0.655756 | 1.171332 |
| H | -0.307721 | 1.667499 | 1.573956 |
| H | -0.681446 | -0.018574 | 1.978239 |
| C | -3.365257 | -0.425350 | -0.952641 |
| H | -4.030561 | 0.436599 | -0.869053 |
| H | -2.891527 | -0.391997 | -1.936214 |
| H | -3.946042 | -1.340043 | -0.860451 |
| C | 0.919913 | 0.225175 | 0.563812 |
| C | 1.991393 | 1.109978 | 0.467283 |
| C | 1.064047 | -1.073485 | 0.066093 |
| C | 3.193917 | 0.707075 | -0.111411 |
| H | 1.884140 | 2.120871 | 0.848362 |
| C | 2.261017 | -1.476752 | -0.512854 |
| H | 0.230603 | -1.764779 | 0.144128 |
| C | 3.330298 | -0.586150 | -0.602691 |
| H | 4.020536 | 1.405120 | -0.180141 |
| H | 2.363925 | -2.487352 | -0.891575 |
| H | 4.263976 | -0.901672 | -1.053858 |
| C | -1.394629 | 1.637857 | -0.868130 |
| H | -0.964617 | 2.550827 | -0.453220 |
| H | -0.755769 | 1.298630 | -1.690626 |
| H | -2.380417 | 1.879467 | -1.260109 |

## **12** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

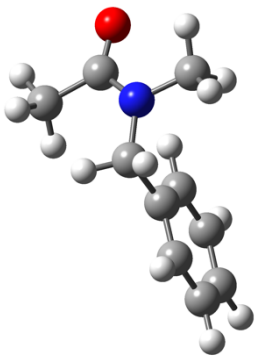
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –518.815186

Sum of electronic and thermal energies = –518.595398

Sum of electronic and thermal enthalpies = –518.594723

Sum of electronic and thermal free energies = –518.627266



| | | | |
|---|---|---|---|
| C | -2.348711 | -0.413497 | 0.184657 |
| O | -3.166573 | -0.836844 | -0.619457 |
| N | -1.570715 | 0.670511 | -0.102029 |
| C | -0.435388 | 1.076592 | 0.705468 |
| H | -0.349027 | 2.164668 | 0.648939 |
| H | -0.627456 | 0.835982 | 1.751782 |
| C | -2.171577 | -1.062974 | 1.540429 |
| H | -1.145541 | -1.410470 | 1.682404 |
| H | -2.408651 | -0.364106 | 2.345337 |
| H | -2.849793 | -1.911658 | 1.590497 |
| C | 0.883286 | 0.451836 | 0.279487 |
| C | 2.081469 | 1.058357 | 0.661287 |
| C | 0.930345 | -0.730322 | -0.457739 |
| C | 3.303991 | 0.489527 | 0.323251 |
| H | 2.052974 | 1.984459 | 1.227461 |
| C | 2.154686 | -1.300438 | -0.800087 |
| H | 0.009388 | -1.208749 | -0.775476 |
| C | 3.343893 | -0.694395 | -0.409681 |
| H | 4.225864 | 0.972903 | 0.626171 |
| H | 2.176598 | -2.218553 | -1.376040 |
| H | 4.295766 | -1.137623 | -0.678152 |
| C | -1.662760 | 1.236277 | -1.440648 |
| H | -1.251231 | 2.245512 | -1.424104 |
| H | -1.107140 | 0.639007 | -2.171808 |

| | | | |
|---|---|---|---|
| H | -2.705802 | 1.274204 | -1.748774 |

**12F** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

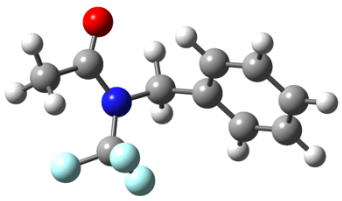
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –816.559841

Sum of electronic and thermal energies = –816.362276

Sum of electronic and thermal enthalpies = –816.361601

Sum of electronic and thermal free energies = –816.396977



| | | | |
|---|---|---|---|
| C | -1.872522 | 1.256397 | -0.233949 |
| O | -1.570727 | 2.299853 | -0.766312 |
| N | -1.163147 | 0.088674 | -0.544217 |
| C | 0.014745 | 0.178914 | -1.429959 |
| H | -0.009015 | -0.654359 | -2.130346 |
| H | -0.117446 | 1.102299 | -1.989152 |
| C | -3.020836 | 1.162269 | 0.737447 |
| H | -3.859519 | 0.646978 | 0.266267 |
| H | -2.754446 | 0.624485 | 1.647191 |
| H | -3.314310 | 2.179291 | 0.985185 |
| C | 1.318459 | 0.200983 | -0.663817 |
| C | 2.255589 | -0.816281 | -0.827446 |
| C | 1.591263 | 1.245347 | 0.223347 |
| C | 3.456201 | -0.789979 | -0.121410 |
| H | 2.042090 | -1.633934 | -1.508235 |
| C | 2.785840 | 1.270088 | 0.932256 |
| H | 0.864995 | 2.041842 | 0.350920 |
| C | 3.722118 | 0.251920 | 0.759923 |
| H | 4.178949 | -1.586328 | -0.256840 |
| H | 2.990162 | 2.085246 | 1.616819 |
| H | 4.654187 | 0.272178 | 1.312693 |
| C | -1.333031 | -1.100471 | 0.193118 |
| F | -0.927856 | -0.991896 | 1.472661 |
| F | -2.609031 | -1.501830 | 0.237288 |
| F | -0.626974 | -2.089871 | -0.351233 |
| C | 2.706414 | -0.432361 | 1.466668 |
| H | 0.612783 | 0.037840 | 1.463969 |
| C | 3.852940 | -0.614703 | 0.702895 |
| H | 4.678825 | -0.605263 | -1.284569 |
| H | 2.744134 | -0.556504 | 2.542767 |
| H | 4.789020 | -0.880776 | 1.179767 |
| C | -1.662563 | -0.923547 | -0.279850 |
| F | -1.005465 | -1.832679 | -1.003944 |
| F | -1.660322 | -1.360672 | 0.985957 |
| F | -2.933981 | -0.936924 | -0.691735 |

**12F** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

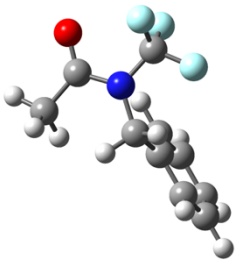
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –816.560061

Sum of electronic and thermal energies = –816.362614

Sum of electronic and thermal enthalpies = –816.361939

Sum of electronic and thermal free energies = –816.396874



| | | | |
|---|---|---|---|
| C | -1.595397 | 1.391004 | 0.331634 |
| O | -2.584943 | 1.211315 | 1.002731 |
| N | -1.054533 | 0.348096 | -0.424525 |
| C | 0.157455 | 0.470577 | -1.237839 |
| H | 0.032285 | -0.123806 | -2.142235 |
| H | 0.227233 | 1.506790 | -1.565347 |
| C | -0.886087 | 2.715786 | 0.253969 |
| H | 0.180232 | 2.611581 | 0.463613 |
| H | -1.000855 | 3.149731 | -0.742075 |
| H | -1.344383 | 3.375613 | 0.986687 |
| C | 1.434229 | 0.065727 | -0.526869 |
| C | 2.588497 | -0.122809 | -1.290003 |
| C | 1.500795 | -0.092823 | 0.855212 |
| C | 3.790777 | -0.458945 | -0.680530 |
| H | 2.540544 | -0.007442 | -2.368503 |
| C | 2.706414 | -0.432361 | 1.466668 |
| H | 0.612783 | 0.037840 | 1.463969 |
| C | 3.852940 | -0.614703 | 0.702895 |
| H | 4.678825 | -0.605263 | -1.284569 |
| H | 2.744134 | -0.556504 | 2.542767 |
| H | 4.789020 | -0.880776 | 1.179767 |
| C | -1.662563 | -0.923547 | -0.279850 |
| F | -1.005465 | -1.832679 | -1.003944 |
| F | -1.660322 | -1.360672 | 0.985957 |
| F | -2.933981 | -0.936924 | -0.691735 |

## **13** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

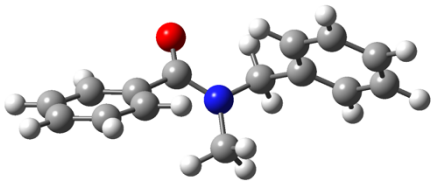
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –710.525381

Sum of electronic and thermal energies = –710.250284

Sum of electronic and thermal enthalpies = –710.249610

Sum of electronic and thermal free energies = –710.286280



| | | | |
|---|---|---|---|
| C | -2.457498 | -0.486304 | 0.188041 |
| O | -2.561124 | -1.371380 | 1.027044 |
| N | -1.473591 | 0.453111 | 0.224387 |
| C | -0.391974 | 0.315029 | 1.193371 |
| H | -0.379209 | 1.191429 | 1.848380 |
| H | -0.607577 | -0.563843 | 1.799410 |
| C | 0.948366 | 0.168239 | 0.504568 |

| | | | |
|---|---|---|---|
| C | 2.004255 | 1.029149 | 0.792012 |
| C | 1.134781 | -0.844353 | -0.440157 |
| C | 3.234433 | 0.878507 | 0.153777 |
| H | 1.863196 | 1.822830 | 1.518912 |
| C | 2.358756 | -0.995107 | -1.080025 |
| H | 0.313315 | -1.517472 | -0.668403 |
| C | 3.413535 | -0.132619 | -0.783162 |
| H | 4.048939 | 1.555064 | 0.386192 |
| H | 2.493576 | -1.786046 | -1.809050 |
| H | 4.368337 | -0.249716 | -1.282547 |
| C | -1.436610 | 1.669410 | -0.577118 |
| H | -1.164018 | 2.502780 | 0.075515 |
| H | -0.694552 | 1.603690 | -1.378251 |
| H | -2.412278 | 1.879003 | -1.007322 |
| C | -3.430848 | -0.446291 | -0.959154 |
| C | -3.002841 | -0.326009 | -2.281589 |
| C | -4.780436 | -0.665485 | -0.685499 |
| C | -3.923006 | -0.409089 | -3.321381 |
| H | -1.949853 | -0.183202 | -2.499474 |
| C | -5.702186 | -0.723614 | -1.724198 |
| H | -5.097354 | -0.790917 | 0.343314 |
| C | -5.273931 | -0.597047 | -3.043377 |
| H | -3.584692 | -0.327807 | -4.347704 |
| H | -6.752505 | -0.877729 | -1.506162 |
| H | -5.991196 | -0.652692 | -3.854098 |

**13** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

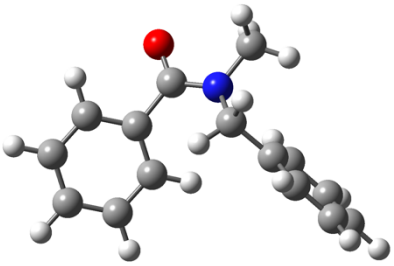
**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –710.526149

Sum of electronic and thermal energies = –710.251358

Sum of electronic and thermal enthalpies = –710.250684



Sum of electronic and thermal free energies = –710.287278

| | | | |
|---|---|---|---|
| C | -2.425753 | -0.616527 | 0.241969 |
| O | -3.424376 | -0.889460 | -0.408879 |
| N | -1.438205 | 0.173931 | -0.265973 |
| C | -0.473710 | 0.914380 | 0.533364 |
| H | -0.633381 | 1.984135 | 0.355707 |
| H | -0.669141 | 0.744442 | 1.591992 |
| C | 0.973666 | 0.580591 | 0.222548 |
| C | 1.977799 | 1.405122 | 0.735057 |
| C | 1.333650 | -0.527325 | -0.541632 |
| C | 3.317037 | 1.121243 | 0.497090 |
| H | 1.704295 | 2.274860 | 1.324923 |
| C | 2.676462 | -0.810913 | -0.785091 |
| H | 0.560150 | -1.169718 | -0.949746 |
| C | 3.670988 | 0.010000 | -0.265792 |
| H | 4.085874 | 1.768740 | 0.903087 |
| H | 2.942229 | -1.675313 | -1.382930 |
| H | 4.714980 | -0.210558 | -0.455575 |
| C | -1.612243 | 0.646911 | -1.634239 |
| H | -0.651403 | 1.002522 | -2.006576 |
| H | -1.964490 | -0.167287 | -2.264818 |
| H | -2.339426 | 1.464333 | -1.679011 |
| C | -2.255903 | -1.193778 | 1.620826 |
| C | -1.046663 | -1.726251 | 2.069978 |

| | | | |
|---|---|---|---|
| C | -3.391967 | -1.286347 | 2.425395 |
| C | -0.973822 | -2.331504 | 3.320279 |
| H | -0.164891 | -1.684975 | 1.439880 |
| C | -3.312804 | -1.872974 | 3.682594 |
| H | -4.332838 | -0.897169 | 2.054377 |
| C | -2.103193 | -2.397361 | 4.131164 |
| H | -0.034920 | -2.753051 | 3.659474 |
| H | -4.195409 | -1.928263 | 4.309017 |
| H | -2.042620 | -2.862927 | 5.108066 |
| C | 3.413535 | -0.132619 | -0.783162 |
| H | 4.048939 | 1.555064 | 0.386192 |
| H | 2.493576 | -1.786046 | -1.809050 |
| H | 4.368337 | -0.249716 | -1.282547 |
| C | -1.436610 | 1.669410 | -0.577118 |
| H | -1.164018 | 2.502780 | 0.075515 |
| H | -0.694552 | 1.603690 | -1.378251 |
| H | -2.412278 | 1.879003 | -1.007322 |
| C | -3.430848 | -0.446291 | -0.959154 |
| C | -3.002841 | -0.326009 | -2.281589 |
| C | -4.780436 | -0.665485 | -0.685499 |
| C | -3.923006 | -0.409089 | -3.321381 |
| H | -1.949853 | -0.183202 | -2.499474 |
| C | -5.702186 | -0.723614 | -1.724198 |
| H | -5.097354 | -0.790917 | 0.343314 |
| C | -5.273931 | -0.597047 | -3.043377 |
| H | -3.584692 | -0.327807 | -4.347704 |
| H | -6.752505 | -0.877729 | -1.506162 |
| H | -5.991196 | -0.652692 | -3.854098 |

## **13F** (trans)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

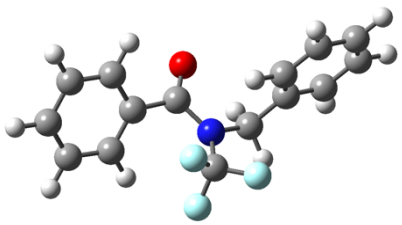
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –1008.268174

Sum of electronic and thermal energies = –1008.015731

Sum of electronic and thermal enthalpies = –10008.015057

Sum of electronic and thermal free energies = –1008.054369



| | | | |
|---|---|---|---|
| C | -0.698916 | -0.589072 | 0.747092 |
| O | -0.185036 | -1.532664 | 1.301835 |
| N | 0.059162 | 0.565826 | 0.525096 |
| C | 1.354944 | 0.665231 | 1.206895 |
| H | 1.575666 | 1.722945 | 1.360736 |
| H | 1.227518 | 0.210550 | 2.188732 |
| C | 2.504752 | -0.006826 | 0.482571 |
| C | 3.771070 | 0.052718 | 1.066895 |
| C | 2.347276 | -0.677822 | -0.726508 |
| C | 4.862638 | -0.548959 | 0.452558 |
| H | 3.899879 | 0.574399 | 2.010438 |
| C | 3.440871 | -1.281620 | -1.343324 |
| H | 1.371483 | -0.734307 | -1.197334 |
| C | 4.700063 | -1.219698 | -0.757484 |
| H | 5.840219 | -0.494407 | 0.917688 |
| H | 3.304351 | -1.801458 | -2.284658 |
| H | 5.549602 | -1.689997 | -1.238704 |
| C | -0.247749 | 1.568992 | -0.418449 |

| | | | |
|---|---|---|---|
| F | -0.989300 | 1.114607 | -1.426872 |
| F | -0.903111 | 2.617395 | 0.113611 |
| F | 0.876301 | 2.069008 | -0.941125 |
| C | -2.138511 | -0.617611 | 0.345919 |
| C | -3.006197 | 0.435163 | 0.635363 |
| C | -2.623974 | -1.790394 | -0.231999 |
| C | -4.357223 | 0.316288 | 0.329564 |
| H | -2.637376 | 1.332775 | 1.116585 |
| C | -3.970457 | -1.894840 | -0.555733 |
| H | -1.941360 | -2.609076 | -0.427300 |
| C | -4.837526 | -0.841815 | -0.274413 |
| H | -5.034342 | 1.128342 | 0.565807 |
| H | -4.345041 | -2.799040 | -1.020433 |
| H | -5.889752 | -0.927166 | -0.519592 |

## **13F** (cis)

**M062X _6311+(d, p), SMD($CH_2Cl_2$), 213 K**

**//M062X _6311(d, p), SMD($CH_2Cl_2$), 213 K**

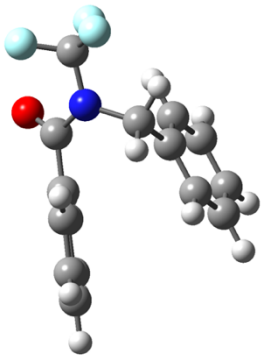
Number of imaginary frequencies: 0

SCF Done: E(RM062X) = –1008.269462

Sum of electronic and thermal energies = –1008.017087

Sum of electronic and thermal enthalpies = –1008.016421

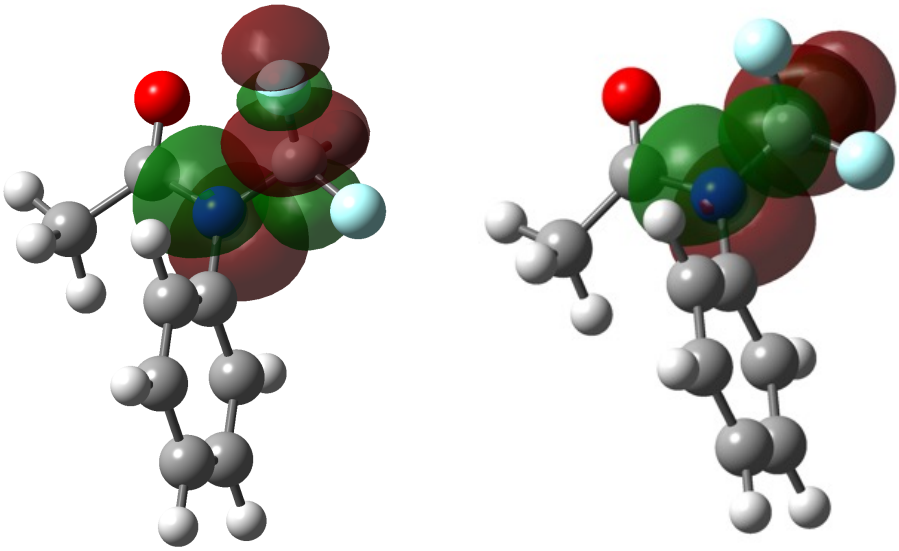
Sum of electronic and thermal free energies = –1008.055039



| | | | |
|---|---|---|---|
| C | -1.352939 | 1.264563 | 0.217590 |
| O | -2.128012 | 1.183480 | 1.139362 |
| N | -1.205717 | 0.230609 | -0.723632 |
| C | 0.128007 | -0.083518 | -1.299219 |
| H | 0.089662 | -1.116612 | -1.643417 |
| H | 0.308161 | 0.542300 | -2.172643 |
| C | 1.249830 | 0.072808 | -0.296967 |
| C | 2.381597 | 0.813962 | -0.628164 |
| C | 1.157735 | -0.509134 | 0.968014 |
| C | 3.411816 | 0.975676 | 0.293736 |
| H | 2.446041 | 1.283140 | -1.604736 |
| C | 2.183840 | -0.343266 | 1.891743 |
| H | 0.275560 | -1.081976 | 1.236399 |
| C | 3.312590 | 0.401051 | 1.557071 |
| H | 4.284895 | 1.560881 | 0.028957 |
| H | 2.101737 | -0.794796 | 2.873643 |
| H | 4.109383 | 0.534077 | 2.279577 |
| C | -2.161768 | -0.808599 | -0.675064 |
| F | -2.075600 | -1.568407 | -1.772838 |
| F | -2.008366 | -1.639595 | 0.372553 |
| F | -3.402790 | -0.333821 | -0.621013 |
| C | -0.498296 | 2.466334 | -0.010625 |
| C | -0.318311 | 2.997687 | -1.286776 |
| C | 0.092213 | 3.071953 | 1.097697 |
| C | 0.470166 | 4.130559 | -1.454034 |
| H | -0.803655 | 2.535488 | -2.139379 |
| C | 0.899069 | 4.188683 | 0.922520 |
| H | -0.067586 | 2.648761 | 2.082861 |
| C | 1.089716 | 4.716091 | -0.353026 |
| H | 0.602945 | 4.554513 | -2.442311 |
| H | 1.378242 | 4.648673 | 1.778470 |
| H | 1.716752 | 5.589761 | -0.488008 |

| | **2**[a] | **2F** | **7** | **7F** | **9** | **9F** | **10** | **10F** | **11** | **11F** | **12** | **12F** | **13** | **13F** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| cis / trans (NMR) | 96/4 [a] | 91/9 | 98/2 [b] | n.d. | 90/10 [c] | 97/3 | 98/2 | 43/56 | 98/2 | n.d. | 42/58 | 6/94 | 50/50 | 25/75 |
| $\Delta G^{o}_{213k}$(kcal/mol) | –1.4 [a] | –0.97 | –1.8 [b] | n.d. | –1.1 [c] | –1.5 | –1.8 | +0.1 | –1.7 | n.d. | +0.1 | +1.2 | –0.0 | +0.4 |
| $\Delta G^{o}_{calc}$(kcal/mol) | –1.8 | –1.2 | –3.2 | –2.4 | –2.9 | –2.7 | –2.5 | –0.7 | –1.8 | –1.0 | –0.1 | +0.1 | –0.6 | –0.4 |
| (C=)O(S) NPA charge (cis/trans) | –0.691/ –0.678 | –0.633/ –0.621 | –0.668/ –0.647 | –0.602/ –0.601 | –0.642/ –0.643 | –0.576/ –0.576 | –0.296/ –0.294 | –0.145/ –0.134 | –0.241/ –0.251 | –0.063/ –0.090 | –0.699/ –0.707 | –0.637/ –0.638 | –0.682/ –0.693 | –0.604/ –0.613 |
| C–N Wiberg bond index (cis/trans) | 1.15/ 1.13 | 1.04/ 1.02 | 1.15/ 1.12 | 1.02/ 1.02 | 1.20/ 1.20 | 1.07/ 1.07 | 1.29/ 1.28 | 1.13/ 1.13 | 1.27/ 1.29 | 1.08/ 1.12 | 1.18/1.19 | 1.06/ 1.06 | 1.18/1.20 | 1.03/1.05 |
| Total steric exchange energy (kcal/mol) (cis/trans) | 664.1/ 666.1 | 858.0/ 859.1 | 1092. 3/110 1.4 | 1200.4/ 1194.8 | 1234. 4/123 3.3 | 1319.8/ 1339.5 | 709.4/7 09.3 | 846.4/843 .9 | 1158.0/ 1146.2 | 1272.0/ 1265.3 | 734.9/736 .2 | 840.4/8 43.4 | 1177.8/11 70.7 | 1265.2/12 64.0 |
| Lp (O or S, $F_{CF3}$ in parenthesis) steric exchange energies ( cis/trans , kcal/mol) | 35.1/3 1.9 | 27.8/2 9.0 (55.8/ 56.4) | 34.0/3 2.6 | 31.7/31 .3 (51.1/5 4.1) | 31.6/3 1.4 | 28.3/29. 9 (55.8/5 5.2) | 42.8/42. 4 | 44.0/42.9 (53.2/53. 9) | 44.8/44. 2 | 46.2/42. 8 (52.7/5 4.7) | 31.7/32.7 | 30.3/31. 4 (52.3/5 4.4) | 34.2/34.9 | 30.6/33.0 (51.2/56. 0) |

**Table S3.** Thermodynamic parameters obtained by NMR ($CD_2Cl_2$) and DFT calculations (M062X/6-311+G(d,p) with SMD ($CH_2Cl_2$)//M062X/6-311G(d,p) with SMD ($CH_2Cl_2$)). [a] Ref. 5. [b] Ref. 6. [c] Ref. 7.



***n*(N)→σ*(C–F)**
18.00 kcal/mol

14.05 kcal/mol

Figure S66. NBO Analysis of **2F** (M062X/6-311+G(d,p) with SMD ($CH_2Cl_2$)//M062X/6-311G(d,p) with SMD ($CH_2Cl_2$)).

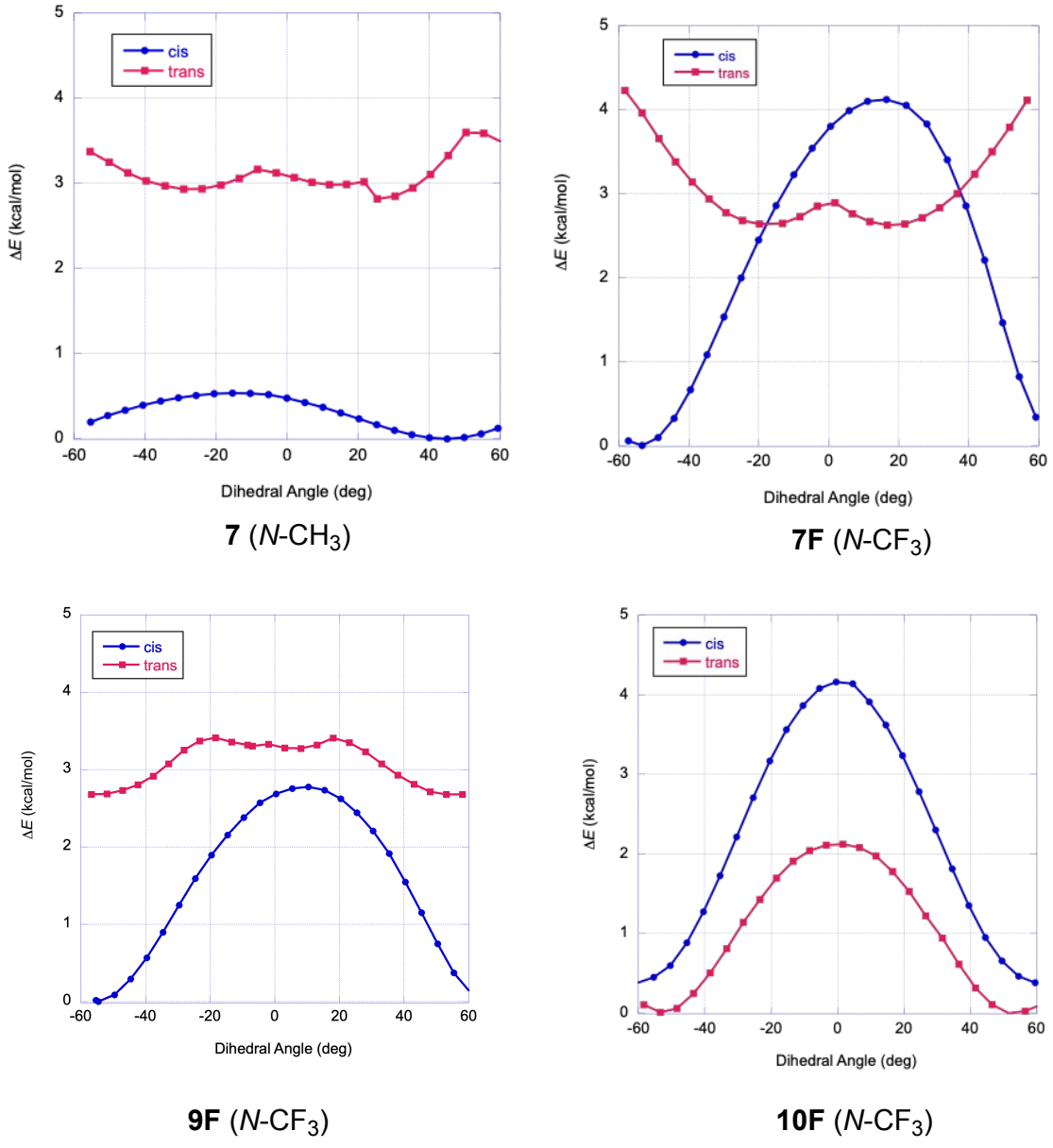
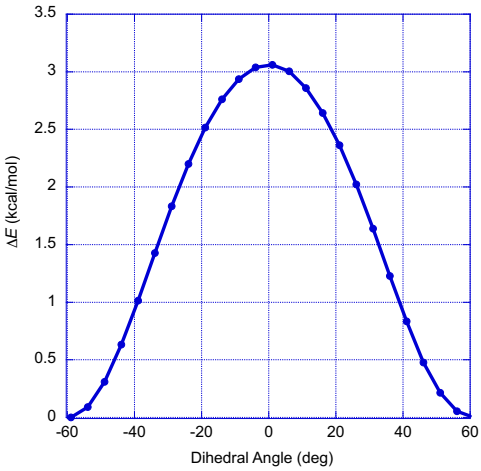
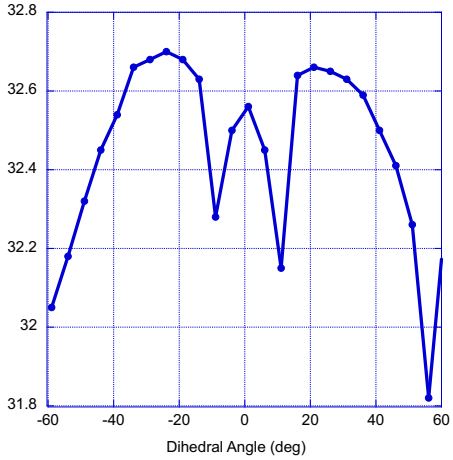



Figure S67. Scanning profiles of dihedral angles of **7**, **7F**, **9F** and **10F** (M06-2X/6-311G(d, p), SMD ($CH_2Cl_2$) level).

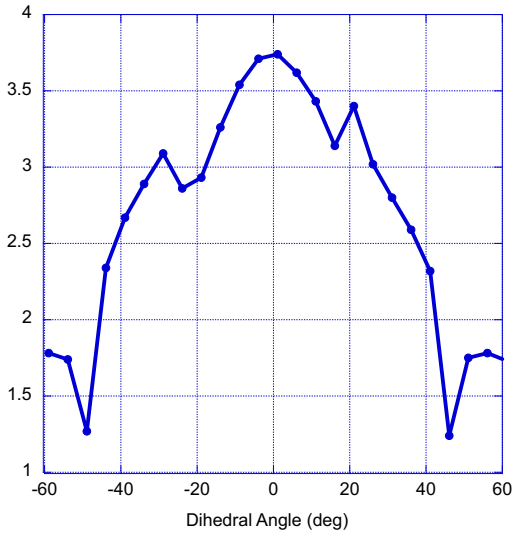
(a) Total Energy (*E*)




(b) *n*(N) → σ*(C–F) Interaction energy (kcal/mol)




(c) Pairwise steric exchange energy between the lone pairs of fluorine and oxygen atoms (kcal/mol)




(d) Wiberg bond index of amide C–N bond

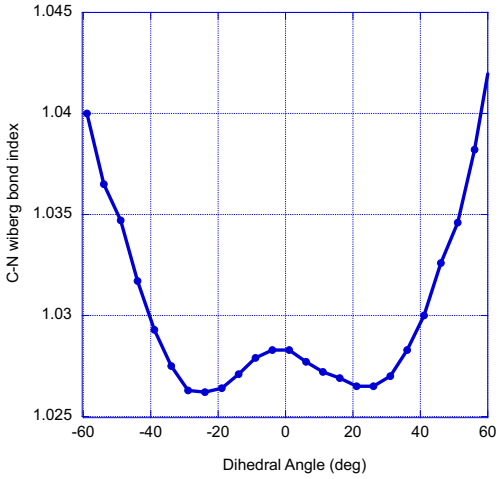
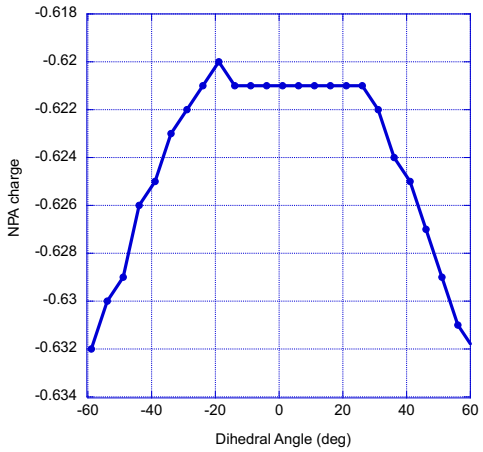
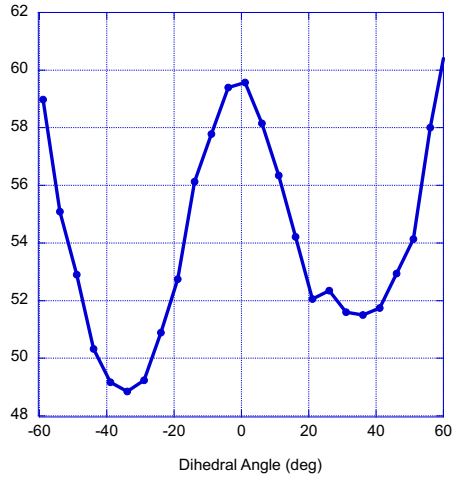



Figure S68. Scanning profiles of dihedral angles of cis conformer of **2F** with some parameters (M062X/6-311+G(d,p) with SMD ($CH_2Cl_2$)//M062X/6-311G(d,p) with SMD ($CH_2Cl_2$)).

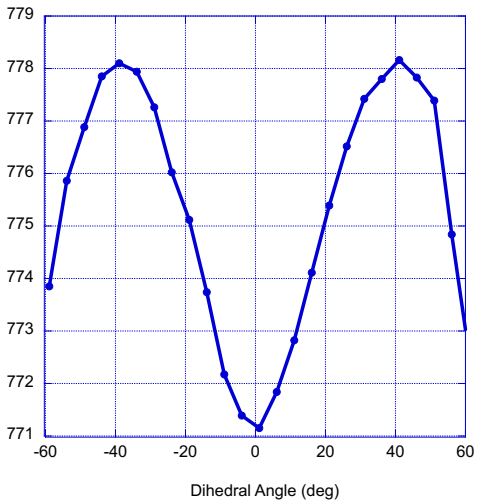
(e) NPA amide oxygen negative charge (a.u.)



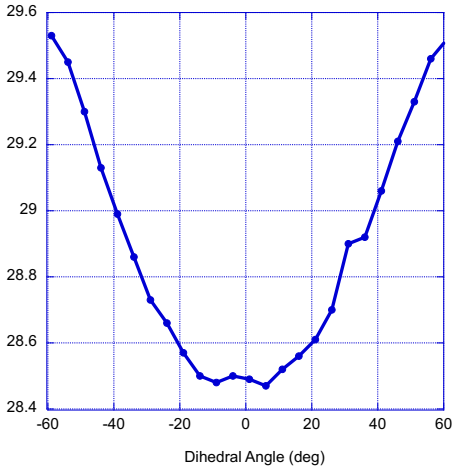

(f) *n*(N) → π*(C=O) interaction energy (kcal/mol)




(g) Total steric exchange energy (kcal/mol)




(h) O lone pair steric exchange energy (kcal/mol)




(i) F lone pair steric exchange energy (kcal/mol)

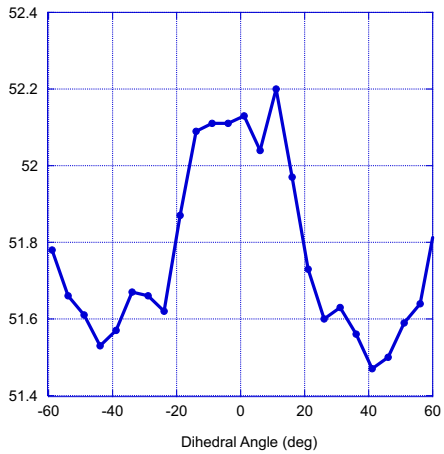



Figure S68 (continued).

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