Supporting Information

Trifluoromethylarylation of alkenes using anilines

Carlos Corral Suarez [a,b] **and Ignacio Colomer*** [a,b]

[a] Instituto de Química Orgánica General (IQOG), CSIC, Juan de la Cierva 3, 28006 Madrid, Spain.
[b] IMDEA Nanociencia, Faraday 9, 28049 Madrid, Spain.

Table of Contents

1. General experimental details

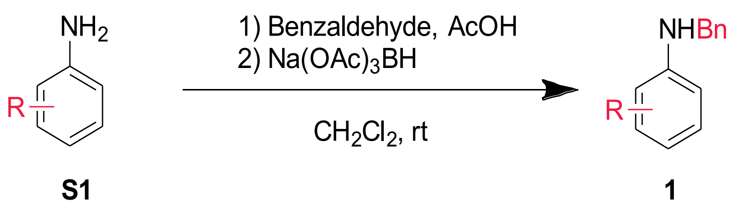
^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker DPX 400 MHz, VARIAN INOVA-300 MHz or VARIAN SYSTEM-500 MHz spectrometers in $CDCl_3$ or $(CD_3)SO$ and referenced to residual solvent peaks. Chemical shifts are quoted in ppm (parts per million) to the nearest 0.01 ppm with signal splitting recorded as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m) and broad singlet (br s). Coupling constants, *J*, are measured in Hz to the nearest 0.1 Hz. ^{1}H and ^{13}C NMR spectra were recorded at room temperature. High resolution mass spectra are given to four decimal places and were registered in a spectrometer GCT Agilent Technologies 6890N using Electronic Impact (EI) techniques at 70 eV, Fast Atom Bombardment and Time-of-Flight (TOF) detector or Agilent 6500 Accurate Mass using electrospray (ESI) and Time-of-Flight (TOF) detector. Melting points (m.p.) were obtained from recrystallized samples using a Lecia VMTG heated-stage microscope and are uncorrected. The solvent systems used for recrystallization are quoted in parentheses. Flash column chromatography was performed using silica gel (60 Å, 0.033-0.070 mm, BDH). TLC analyses were performed on Merck Kiesegel 60 F_{254} 0.25 mm precoated silica plates. Reagents obtained from Sigma-Aldrich, Alfa, Fluorochem, Apollo and TCI were used directly as supplied. All anhydrous reactions were carried out in flame dried glassware and under an inert atmosphere of argon. All reactions were stirred with magnetic followers. 3900 Parr Instrument Company hydrogenator was used when required.

2. Synthesis of starting materials

2.1. Synthesis of *N*-Benzylanilines

N-Benzylanilines were obtained following well established reductive amination procedure.

General procedure for reductive amination



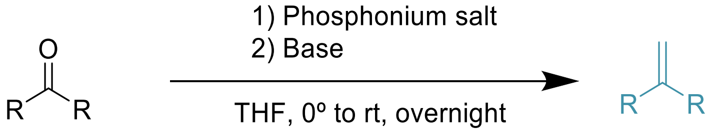
A solution of benzaldehyde (1.0 equiv.), aniline **S1** (1.1 equiv.) and AcOH (0.25 equiv.) in CH_2Cl_2 (0.15 M) was stirred for 30 min. at room temperature and sodium triacetoxyborohydride (1.5 equiv.) was added in one portion. The reaction mixture was monitored until completion by TLC and quenched with saturated NH_4Cl aqueous solution. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by flash column chromatography (EtOAc/Hexane) to afford product **1**.

2.2. Synthesis of alkenes

Alkenes **2a**, **2f**, **2u**, **2y** and **2ac** were commercially available and used directly as provided.

2.2.1. General procedure for Wittig olefination

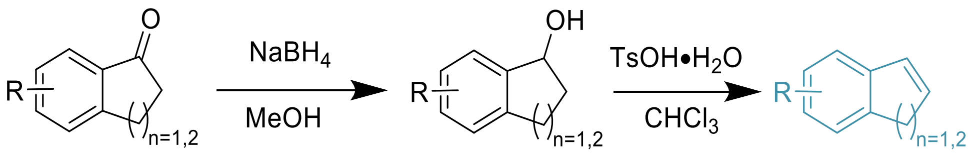
Alkenes **2b-t**, **2x** and **2z-ab** were obtained following well established Wittig olefination procedure using the corresponding aldehyde or ketone.



A suspension of triphenylphosphonium salt (1.3 equiv.) in dry THF (5.0mL/mmol) was placed in a flame-dried round-bottom flask. The solution was cooled to 0 °C and kept under argon. The base (1.5 equiv. of *t*-BuOK or 1.8 equiv. of *n*-BuLi) was added in one portion. After stirring at 0 °C for 30 min the solution turns into an intense bright colour, then the aldehyde or ketone **S2** (1.0 equiv.) was added. The reaction mixture was gradually warmed to room temperature. After stirring overnight, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated and the aqueous phase was extracted twice with Et_2O. The combined organic layers were dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give the corresponding alkene **2** that was purified by chromatography on silica gel using the appropriate mixture of eluents.

2.2.2. General procedure for ketone reduction and dehydration

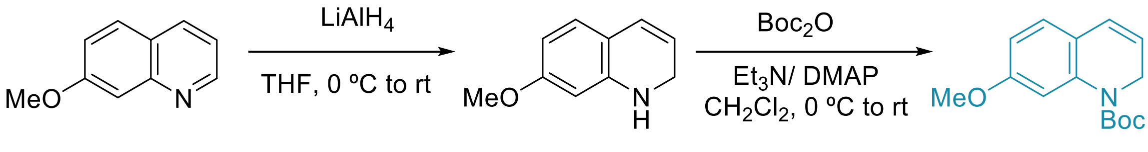
Alkenes **2v** and **2w** were obtained following a two-step procedure consisting on ketone reduction and alcohol dehydration.



Following an adapted procedure,[1,2] $NaBH_4$ (5.0 equiv.) was slowly added over a solution of ketone **S3** (1 equiv.) in MeOH at 0 °C. The resulting solution was then allowed to reach room temperature and stirred for 75 min. until complete conversion (monitored by TLC). The solvent was removed under reduced pressure and the resulting solid was dissolved in Et_2O and successively washed with water and saturated aqueous solution of NH_4Cl. The organic phase was dried over Na_2SO_4, filtered and concentrated under vacuum to afford the desired product **S4**, that was used without further purification. $TsOH{\cdot}H_2O$ (0.1 equiv) was added to a solution of alcohol **S4** in $CHCl_3$ (0.05M) at room temperature under vigorous stirring (important to avoid side reactions). The mixture was stirred and monitored by TLC until completion. The solvent was evaporated, and the crude reaction was purified by chromatography on silica gel (30% Et_2O – hexane) to give alkene **2v** or **2w**.

2.2.3. Quinoline reduction and *N*-Boc protection

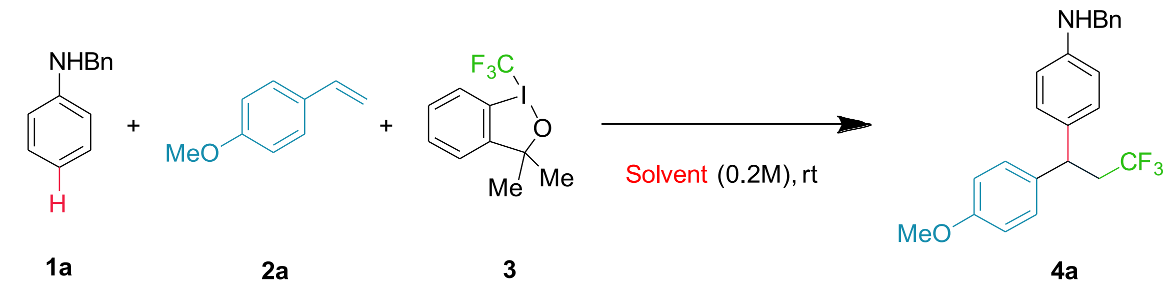
Dihydroquinoline **9** was obtained via quinoline reduction and in-situ N-Boc protection.



Following an adapted procedure[3], suspension of lithium aluminum hydride (2 equiv.) in dry THF (2 mL) was added slowly over an ice-cold solution of quinoline (1.0 equiv.) in dry THF (4 mL). The solution was stirred for 2h at 0 ºC, then lithium aluminum hydride (2 equiv.) in dry THF (2 mL) was again added and the reaction mixture stirred for 2h at 0 ºC. The reaction was then carefully quenched with water and filtered. The filtrate was extracted using ethyl acetate, washed successively with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting crude was immediately protected. The crude was dissolved in dry DCM (0.2 M), and Boc anhydride (1.5 equiv.), triethylamine (3 equiv.) and 4-(Dimethylamino)pyridine (0.10 equiv.) were added to the solution at 0 ºC. The reaction mixture was stirred at room temperature and monitored by TLC until completion. Reaction mixture was diluted with DCM and extracted with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by silica gel chromatography (50% EtOAc – hexane) to give **9**.

3. Optimization details

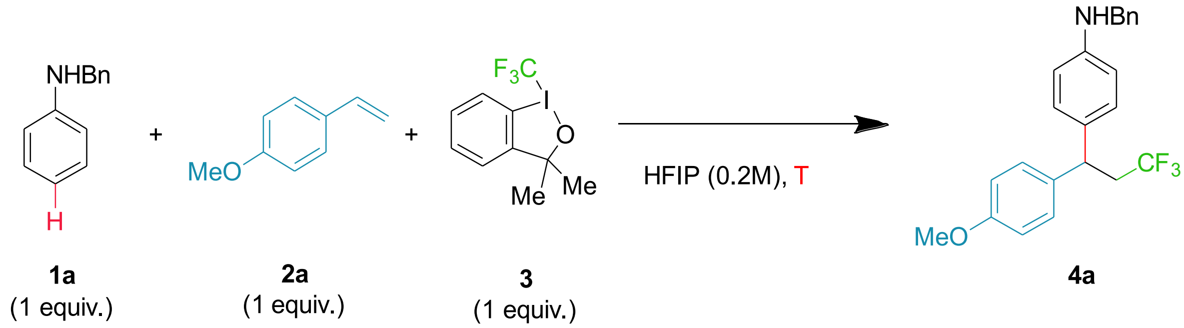
3.1. Table S1. *Effect of the solvent*



Entry	Solvent	Isolated yield, 4a (%)
1	HFIP	58%
2	TFE	11%
3	CH_2Cl_2	nc
4	TFA	nr
5	AcOH	nr[a]
6	Acetonitrile	nc
7	HFIP:CH_2Cl_2 (1:1)	53%

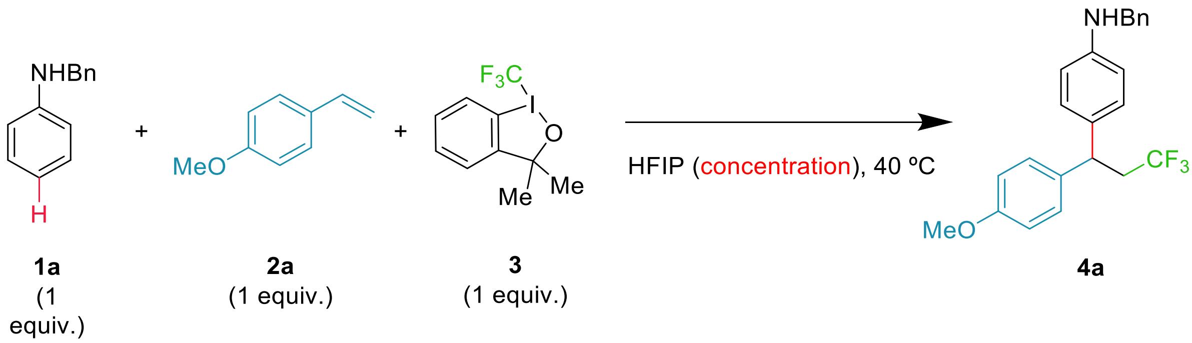
[a] OAc incorporation, instead of aniline, was observed (36% yield). nr: no reaction. nc: no conversion.

3.2. Table S2. *Effect of temperature*



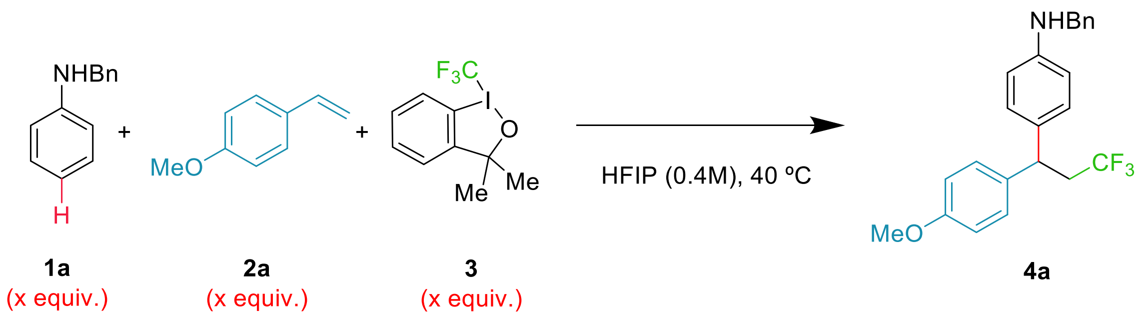
Entry	Temperature (ºC)	Isolated Yield, 4a (%)
1	80	53%
2	40	67%
3	rt	58%

3.3. Table S3. *Effect of the concentration*



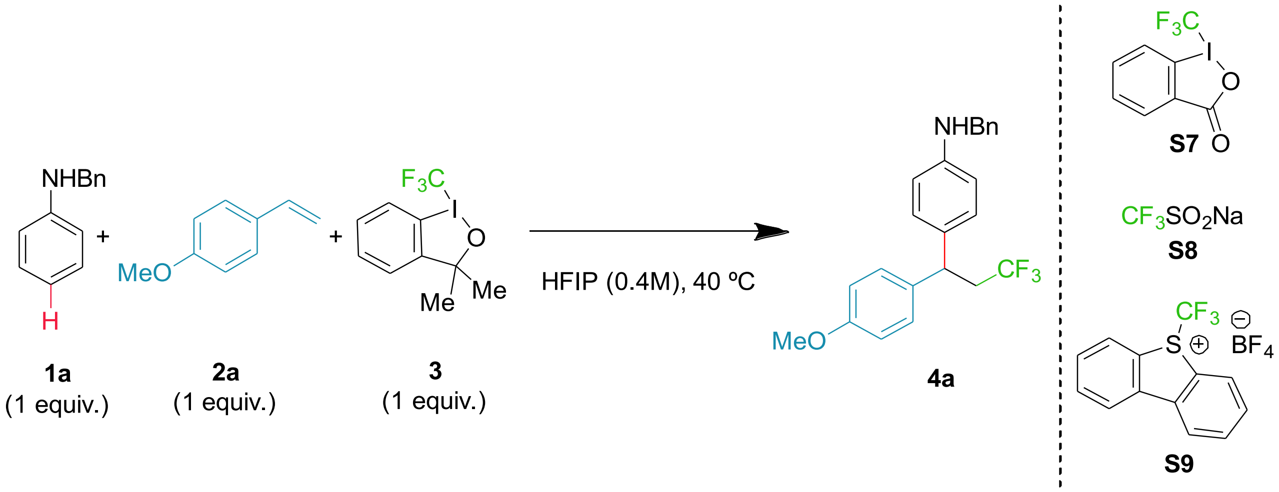
Entry	Concentration (M)	Isolated Yield, 4a (%)
1	0.4M	72%
2	0.2M	67%
3	0.1M	49%

3.4. Table S4. *Effect of stoichiometry in the reaction*



Entry	1a (equiv.)	2a (equiv.)	3 (equiv.)	Isolated Yield, 4a (%)
1	1	1	1	72%
2	2	1	1	65%
3	1	2	1	63%
4	1	1	2	22%

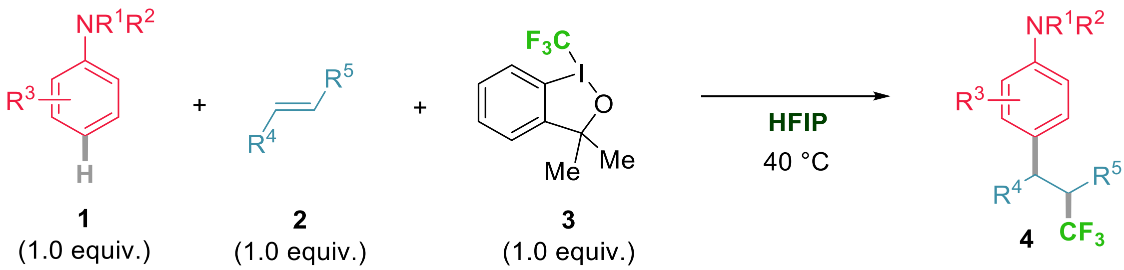
3.5. Table S5. *Effect of additives and trifluoromethyl reagents*



Entry	Deviations from optimized conditions	Isolated Yield, 4a (%)
1	none	72%
2	Addition of 5.0 equiv. of anisole	70%
3	**S7** instead of **3**	34%
4	**S8**, PIDA and rt	nr
5	**S9** instead of **3**	nr
6	Addition of 0.1 equiv. of triflic acid	46%
7	Addition of 0.1 equiv. of $BF_3{\cdot}OEt_2$	37%

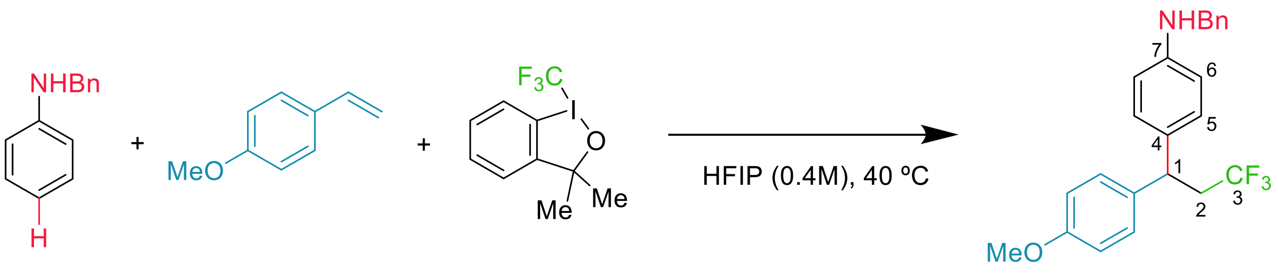
PIDA: (Diacetoxyiodo)benzene. nr: no reaction

4. General procedure for the trifluoromethylarylation of alkenes using anilines in HFIP.



Aniline **1** (1 equiv.) and alkene **2** (1 equiv.) were placed in an oven-dry 10 mL vial and hexafluoroisopropanol (0.4 M) was added, followed by trifluoromethyl reagent **3** (1 equiv.). The vial was sealed, purged with Argon and set in a preheated heating block overnight at 40 ºC, unless other temperature is stated. The reaction mixture was cooled down, the solvent was evaporated under reduced pressure and the crude was purified by chromatography on silica gel using the appropriate mixture of eluents to give the corresponding product, **4**.

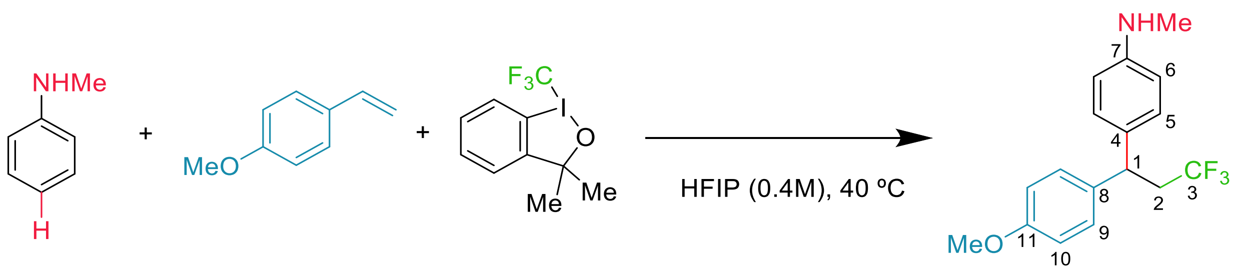
***N*-Benzyl-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4a.**



From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4a** was obtained. Chromatographic purification (gradient elution: 0:100 → 10:90 Et_2O – hexane) gave **4a** (48.2 mg, 72%), as a yellow oil.

Data for **4a**: R_f 0.3 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 7.40 – 7.17 (7H, m, Ar), 7.05 (2H, d, *J* = 8.6 Hz, 5-H), 6.83 (2H, d, *J* = 8.7 Hz, Ar), 6.51 (2H, d, *J* = 8.6 Hz, 6-H), 6.13 (1H, t, *J* = 6.0 Hz, NH), 4.23 (2H, d, *J* = 6.0 Hz, CH_2 Bn), 4.08 (1H, t, *J* = 7.6 Hz, 1-H), 3.69 (3H, s, OMe), 2.99 (2H, m, 2-H_2). **^{13}C NMR (101 MHz, DMSO-d$_6$)** δ 157.6 (1C, C Ar), 147.2 (1C, C Ar), 140.4 (1C, C Ar), 136.3 (1C, C Ar), 131.0 (1C, C Ar), 128.3 (2C, CH Ar), 128.2 (2C, CH Ar), 127.7 (2C, CH Ar), 127.2 (2C, CH Ar), 126.6 (1C, CH Ar), 127.1 (1C, q, *J* = 277.8 Hz, CF_3), 113.8 (2C, CH Ar), 112.3 (2C, CH Ar), 54.9 (1C, OMe), 46.7 (1C, CH_2 Bn), 43.1 (1C, q, *J* = 3.1 Hz, C-1), 38.3 (1C, q, *J* = 25.8 Hz, C-2). **^{19}F NMR (376 MHz, DMSO-d$_6$)** δ –63.6 (3F, CF_3). **HRMS** (EI): calculated for $C_{23}H_{22}F_3NO$ $[M]^+$ requires *m*/*z* 385.1648, found *m*/*z* 385.1635.

***N*-Methyl-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4b.**

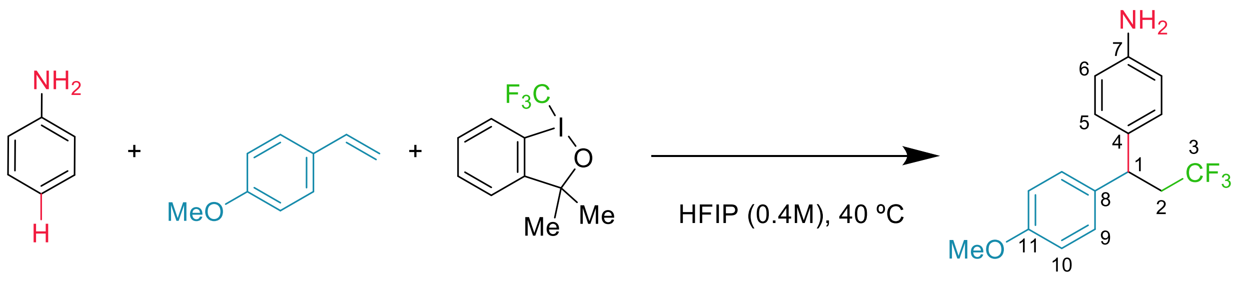


From aniline **1b** (21.4 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4b** was obtained. Chromatographic purification (gradient elution: 0:100 → 30:70 Et_2O – hexane) gave **4b** (28.2 mg, 50%), as a colourless oil.

Data for **4b**: R_f 0.1 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 (2H, d, *J* = 8.7 Hz, 9-H), 7.04 (2H, d, *J* = 8.5 Hz, 5-H), 6.83 (2H, d, *J* = 8.7 Hz, 10-H), 6.55 (2H, d, *J* = 8.6 Hz, 6-H), 4.19 (1H, t, *J* = 7.4 Hz, 1-H), 3.77 (3H, s, OMe), 3.65 (1H, br s, NH), 2.82 (2H, qd, *J* = 10.5 and 7.4 Hz, 2-H_2), 2.80 (3H, s, NMe). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3 (1C, C Ar), 148.1 (1C, C

Ar), 135.9 (1C, C Ar), 132.1 (1C, C Ar), 128.5 (2C, CH Ar), 128.3 (2C, C-5), 126.7 (1C, q, J = 277.8 Hz, CF_3), 114.1 (2C, CH Ar), 112.7 (2C, C-6), 55.4 (1C, OMe), 43.5 (1C, C-1), 40.1 (1C, q, J = 26.9 Hz, C-2), 30.9 (1C, NMe). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.6 (3F, CF_3). **HRMS** (EI): calculated for $C_{17}H_{18}F_3NO$ $[M]^+$ requires m/z 309.1335, found 309.1328.

4-[3,3,3-Trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4c.

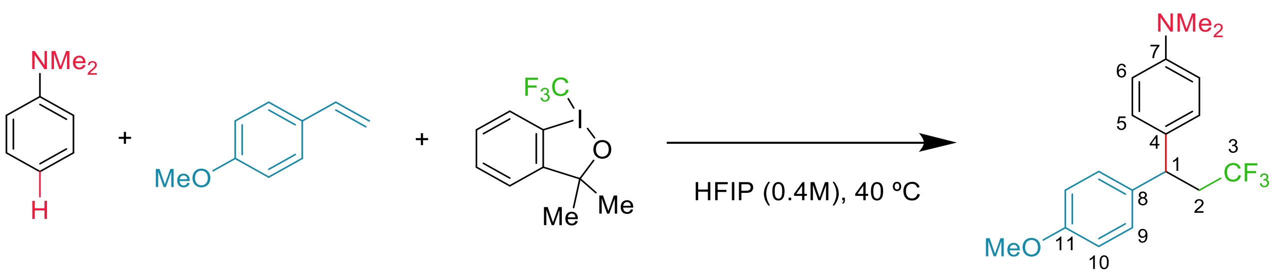


1c 2a 3 4c

From aniline **1c** (18.6 mg, 0.20 mmol), alkene **2a** (26.8 mg, 0.20 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.20 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4c** was obtained. Chromatographic purification (gradient elution: 20:80 → 40:60 Et_2O – hexane) gave **4c** (14.5 mg, 25%), as a brownish oil.

Data for **4c**: R_f 0.10 (60% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.13 (2H, d, J = 8.7 Hz, 9-H), 7.01 (2H, d, J = 8.4 Hz, 5-H), 6.82 (2H, d, J = 8.7 Hz, 10-H), 6.65 (2H, d, J = 8.4 Hz, 6-H), 4.18 (1H, t, J = 7.4 Hz, 1-H), 3.77 (3H, s, OMe), 2.81 (2H, qd, J = 10.5 and 7.5 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3 (1C, C Ar), 144.5 (1C, C Ar), 135.7 (1C, C Ar), 133.8 (1C, C Ar), 128.5 (2C, CH Ar), 128.4 (2C, CH Ar), 126.7 (1C, q, J = 277.6 Hz, CF_3), 115.8 (2C, CH Ar), 114.1 (2C, CH Ar), 55.4 (1C, OMe), 43.6 (1C, C-1), 40.0 (1C, q, J = 27.0 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.6 (3F, CF_3). **HRMS** (ESI): calculated for $C_{16}H_{17}F_3NO$ $[M+H]^+$ requires m/z 296.1257, found 296.1257.

***N,N*-dimethyl-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4d.**

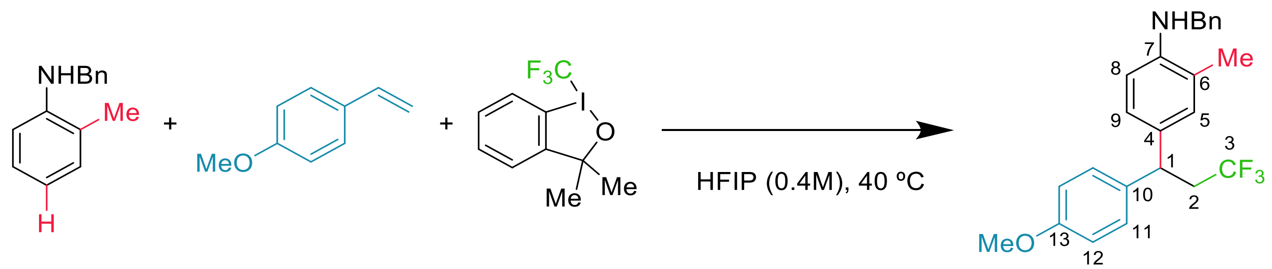


1d 2a 3 4d

From aniline **1d** (24.0 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4d** was obtained. Chromatographic purification (gradient elution: 0:100 → 15:85 Et_2O – hexane) gave **4d** (33.6 mg, 52%), as a colourless oil.

Data for **4d**: ***R**$_f$* 0.15 (20% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.15 (2H, d, *J* = 8.7 Hz, 9-H), 7.09 (2H, d, *J* = 8.8 Hz, 5-H), 6.83 (2H, d, *J* = 8.7 Hz, 10-H), 6.68 (2H, d, *J* = 8.3 Hz, 6-H), 4.20 (1H, t, *J* = 7.4 Hz, 1-H), 3.77 (3H, s, OMe), 2.91 (6H, s, NMe_2), 2.82 (2H, qd, *J* = 10.5 and 7.4 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3 (1C, C Ar), 149.4 (1C, C Ar), 135.9 (1C, C Ar), 131.3 (1C, C Ar), 128.5 (2C, CH Ar), 128.1 (2C, C-5), 126.7 (1C, q, *J* = 277.9 Hz, CF_3), 114.1 (2C, CH Ar), 113.0 (2C, C-6), 55.4 (1C, OMe), 43.4 (1C, q, *J* = 2.7 Hz, C-1), 40.8 (2C, NMe_2), 40.1 (1C, q, *J* = 26.8 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.6 (3F, CF_3). **HRMS** (ESI): calculated for $C_{18}H_{21}F_3NO$ $[M+H]^+$ requires m/z 324.1570, found m/z 324.1572.

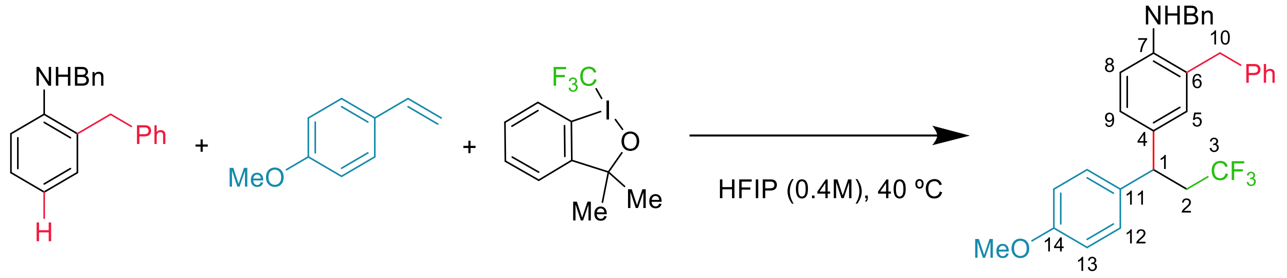
***N*-Benzyl-2-methyl-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4e.**



From aniline **1e** (39.5 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4e** was obtained. Chromatographic purification (gradient elution: 10:90→ 15:85 Et_2O – hexane) gave **4e** (51.4 mg, 64%), as a colourless oil.

Data for **4e**: ***R**$_f$* 0.40 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.29 (5H, m, Ar), 7.18 (2H, d, *J* = 8.7 Hz, 11-H), 6.98 (1H, d, *J* = 8.2 Hz, 9-H), 6.94 (1H, s, 5-H), 6.85 (2H, d, *J* = 8.7 Hz, 12-H), 6.57 (1H, d, *J* = 8.2 Hz, 8-H), 4.35 (2H, s, CH_2 Bn), 4.19 (1H, t, *J* = 7.4 Hz, 1-H), 3.79 (3H, s, OMe), 2.84 (2H, qd, *J* = 10.5 and 7.4 Hz, 2-H_2), 2.15 (3H, s, Me). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2 (1C, C Ar), 144.9 (1C, C Ar), 139.5 (1C, C Ar), 135.9 (1C, C Ar), 131.9 (1C, C Ar), 129.4 (1C, C-9), 128.8 (2C, CH Ar), 128.5 (2C, CH Ar), 127.7 (2C, CH Ar), 127.4 (1C, CH Ar), 126.7 (1C, q, *J* = 277.8 Hz, CF_3), 125.8 (1C, C-5), 122.3 (1C, CH Ar), 114.0 (2C, CH Ar), 110.1 (1C, C-6), 55.3 (1C, OMe), 48.5 (1C, CH_2 Bn), 43.5 (1C, C-1), 40.1 (1C, q, *J* = 26.8 Hz, C-2), 17.8 (1C, Me). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.6 (3F, CF_3). **HRMS** (EI): calculated for $C_{24}H_{24}F_3NO$ $[M]^+$ requires *m/z* 399.1810, found *m/z* 399.1797.

N,2-Dienzyl-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4f.

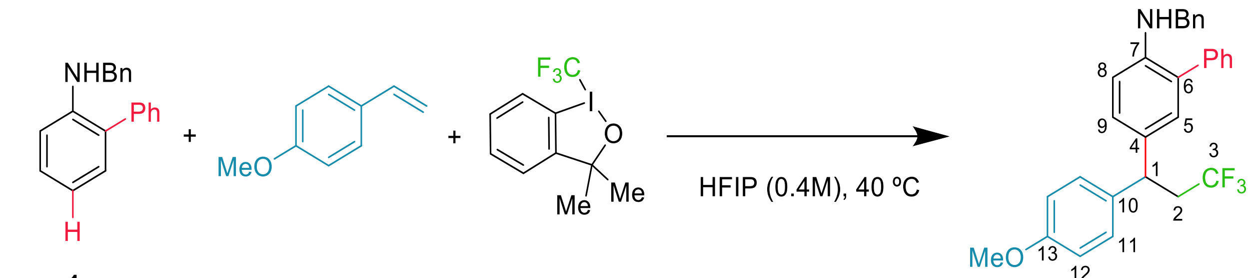


1f **2a** **3** **4f**

From aniline **1f** (52.2 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4f** was obtained. Chromatographic purification (gradient elution: 5:95 → 20:80 Et_2O – hexane) gave **4f** (51.5 mg, 57%), as a colourless oil.

Data for **4f**: R_f 0.50 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.22 (6H, m, Ar), 7.18 (2H, d, *J* = 8.6 Hz, 12-H), 7.16 (2H, d, *J* = 7.9 Hz, Ar), 7.10 (2H, d, *J* = 7.7 Hz, Ar), 7.02 (1H, d, *J* = 8.2 Hz, 9-H), 7.00 (1H, s, 5-H), 6.86 (2H, d, *J* = 8.6 Hz, 13-H), 6.59 (1H, d, *J* = 8.2 Hz, 8-H), 4.23 (2H, s, CH_2 Bn), 4.23 (1H, t, *J* = 8.0 Hz, 1-H), 3.92 (2H, s, 10-H_2), 3.80 (3H, s, OMe), 2.85 (2H, qd, *J* = 10.5 and 8.0 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2 (1C, C Ar), 144.7 (1C, C Ar), 139.2 (2C, C Ar), 135.8 (1C, C Ar), 132.0 (1C, C Ar), 130.0 (1C, C-5), 128.8 (2C, CH Ar), 128.6 (2C, CH Ar), 128.5 (2C, CH Ar), 128.5 (2C, CH Ar), 127.3 (2C, CH Ar), 127.2 (1C, CH Ar), 126.7 (1C, q, *J* = 279.8 Hz, CF_3), 126.7 (1C, CH Ar), 126.6 (1C, C-9), 124.9 (1C, C Ar), 114.0 (2C, CH Ar), 111.2 (1C, C-8), 55.3 (1C, OMe), 48.2 (1C, CH_2 Bn), 43.5 (1C, C-1), 40.1 (1C, q, *J* = 26.8 Hz, C-2), 38.5 (1C, C-10). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.5 (3F, CF_3). **HRMS** (ESI): calculated for $C_{30}H_{29}F_3NO$ $[M+H]^+$ requires *m/z* 476.2196, found *m/z* 476.2191.

N-Benzyl-5-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]-[1,1'-biphenyl]-2-amine, 4g.

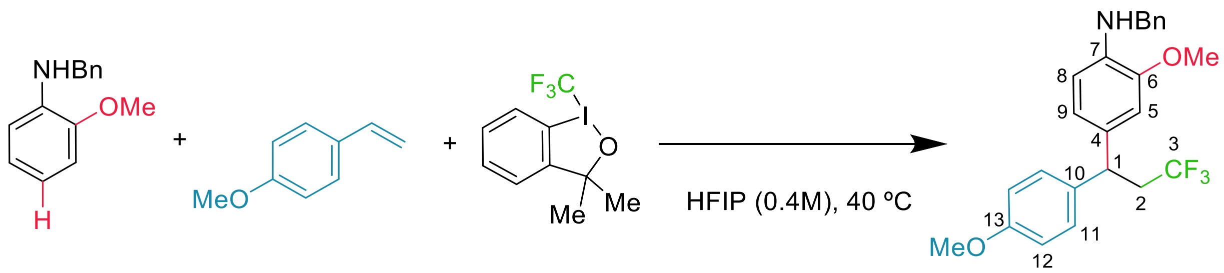


1g **2a** **3** **4g**

From aniline **1g** (43 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4g** was obtained. Chromatographic purification (gradient elution: 10:90 → 15:85 Et_2O – hexane) gave **4g** (43.2 mg 56%), as a colourless oil.

Data for **4g**: ***R**$_f$* 0.50 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (4H, m, Ar), 7.40 – 7.22 (6H, m, Ar), 7.18 (2H, d, *J* = 8.7 Hz, 11-H), 7.04 (1H, dd, *J* = 8.4 and 2.3 Hz, 9-H), 7.00 (1H, d, *J* = 2.2 Hz, 5-H), 6.84 (2H, d, *J* = 8.7 Hz, 12-H), 6.62 (1H, d, *J* = 8.4 Hz, 8-H), 4.30 (2H, s, CH_2 Bn), 4.22 (1H, t, *J* = 7.4 Hz, 1-H), 3.78 (3H, s, OMe), 2.85 (2H, qd, *J* = 10.5 and 7.4 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3 (1C, C Ar), 143.5 (1C, C Ar), 139.3 (1C, C Ar), 135.7 (1C, C Ar), 132.2 (1C, C Ar), 129.4 (2C, CH Ar), 129.3 (1C, C-5), 129.1 (2C, CH Ar), 128.7 (2C, CH Ar), 128.5 (2C, CH Ar), 128.0 (1C, C Ar) 127.5 (1C, C Ar), 127.5 (1C, C-9), 127.2 (4C, CH Ar), 126.6 (1C, q, *J* = 278.8 Hz, CF_3), 114.1 (2C, CH Ar), 111.2 (1C, C-8), 55.3 (1C, OMe), 48.5 (1C, CH_2 Bn), 43.6 (1C, C-1), 40.1 (1C, q, *J* = 26.9 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.6 (3F, CF_3). **HRMS** (ESI): calculated for $C_{29}H_{27}F_3NO$ $[M+H]^+$ requires *m/z* 462.2039, found *m/z* 462.2036.

***N*-Benzyl-2-methoxy-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4h.**

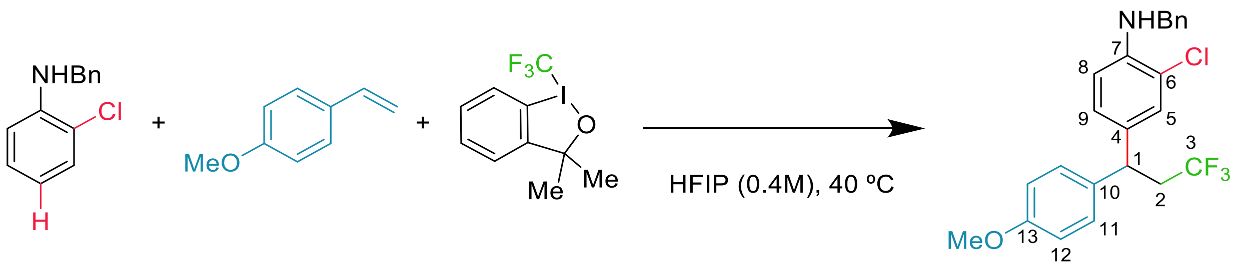


1h **2a** **3** **4h**

From aniline **1h** (42.7 mg, 0.20 mmol), alkene **2a** (26.8 mg, 0.20 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.20 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4h** was obtained. Chromatographic purification (gradient elution: 0:100 → 15:85 Et_2O – hexane) gave **4h** (44.5 mg, 54%), as a colourless oil.

Data for **4h**: ***R**$_f$* 0.5 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.21 (5H, m, Ar), 7.15 (2H, d, *J* = 8.7 Hz, 11-H), 6.83 (2H, d, *J* = 8.7 Hz, 12-H), 6.70 (1H, dd, *J* = 8.1 and 1.9 Hz, 9-H), 6.60 (1H, d, *J* = 1.9 Hz, 5-H), 6.55 (1H, d, *J* = 8.1 Hz, 8-H), 4.30 (2H, s, CH_2 Bn), 4.19 (1H, t, *J* = 7.4 Hz, 1-H), 3.80 (3H, s, OMe), 3.77 (3H, s, OMe), 2.82 (2H, qd, *J* = 10.5 and 7.4 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3 (1C, C Ar), 147.2 (1C, C Ar), 139.3 (1C, C Ar), 136.4 (1C, C Ar), 135.7 (1C, C Ar), 132.3 (1C, C Ar), 128.7 (2C, CH Ar), 128.5 (2C, CH Ar), 127.8 (2C, CH Ar), 127.4 (1C, CH Ar), 126.7 (1C, q, *J* = 278.0 Hz, CF_3), 119.7 (1C, C-9), 114.1 (2C, CH Ar), 110.6 (1C, C-8) 109.3 (1C, C-5), 55.6 (1C, OMe), 55.4 (1C, OMe), 48.5 (1C, CH_2 Bn), 44.0 (1C, C-1), 40.2 (1C, q, *J* = 26.9 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.6 (3F, CF_3). **HRMS** (ESI): calculated for $C_{24}H_{25}F_3NO_2$ $[M+H]^+$ requires m/z 416.1832, found m/z 416.1837.

***N*-Benzyl-2-chloro-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4i.**

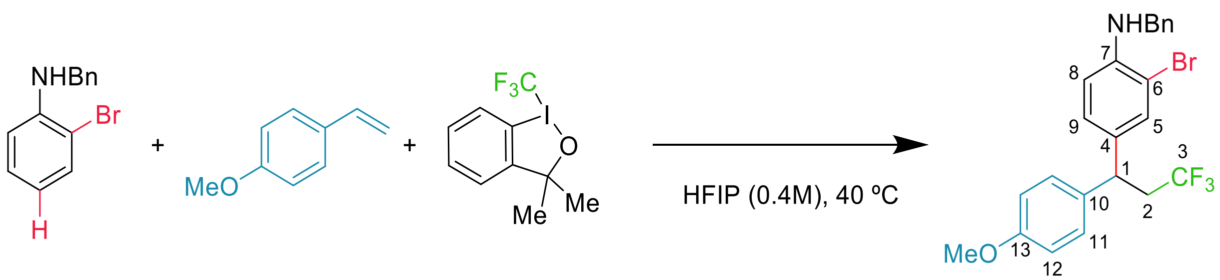


1i **2a** **3** **4i**

From aniline **1i** (42.8 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4i** was obtained. Chromatographic purification (gradient elution: 100% toluene) gave **4i** (41.3 mg, 50%), as a colourless oil.

Data for **4i**: ***R$_f$*** 0.60 (100% toluene). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.41 – 7.24 (5H, m, Ar), 7.14 (1H, s, 5-H), 7.14 (2H, d, *J* = 8.5 Hz, 11-H), 6.96 (1H, dd, *J* = 8.4 and 2.1 Hz, 9-H), 6.85 (2H, d, *J* = 8.7 Hz, 12-H), 6.57 (1H, d, *J* = 8.4 Hz, 8-H), 4.37 (1H, br s, NH), 4.16 (1H, t, *J* = 7.4 Hz, 1-H), 3.78 (2H, s, CH_2 Bn), 2.80 (1H, qd, *J* = 10.4 and 7.5 Hz, 2-H_2). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.4 (1C, C Ar), 142.6 (1C, C Ar), 138.8 (1C, C Ar), 135.1 (1C, C Ar), 132.5 (1C, C Ar), 128.8 (2C, CH Ar), 128.4 (2C, CH Ar), 128.1 (1C, C-5), 127.5 (1C, CH Ar), 127.4 (2C, CH Ar), 126.8 (1C, C-9), 126.5 (1C, q, *J* = 277.7 Hz, CF_3), 119.3 (1C, C Ar), 114.2 (2C, CH Ar), 111.7 (1C, C-8), 55.3 (1C, OMe) 48.1 (1C, CH_2 Bn), 43.3 (1C, C-1), 39.9 (1C, q, *J* = 27.1 Hz, C-2). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –63.6 (3F, CF_3). **HRMS** (EI): calculated for $C_{23}H_{21}ClF_3NO$ $[M]^+$ requires *m/z* 419.1258, found *m/z* 419.1271.

***N*-Benzyl-2-bromo-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4j.**

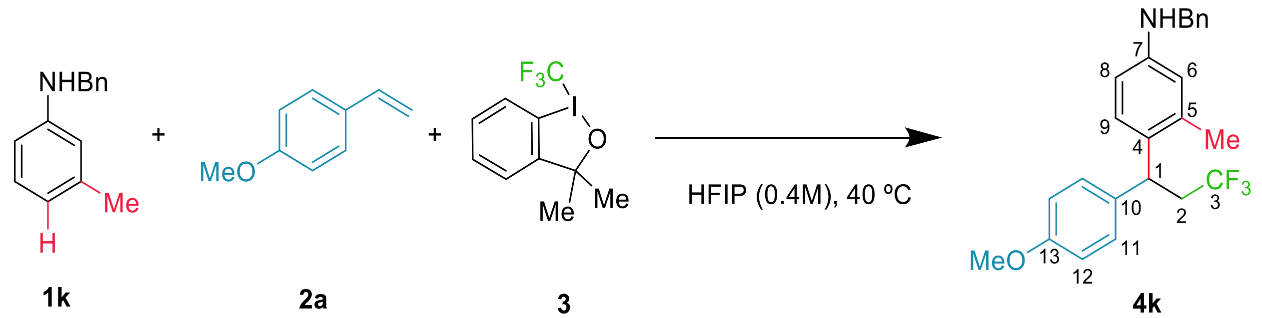


1j **2a** **3** **4j**

From aniline **1j** (52.4 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4j** was obtained. Chromatographic purification (gradient elution: 5:95 → 10:90 Et_2O – hexane) gave **4j** (52.8 mg, 58%), as a colourless oil.

Data for **4j**: ***R$_f$*** 0.30 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.42 – 7.26 (5H, m, Ar), 7.33 (1H, d, *J* = 2.1 Hz, 5-H), 7.15 (2H, d, *J* = 8.7 Hz, 11-H), 7.01 (1H, dd, *J* = 8.4 and 2.1 Hz, 9-H), 6.86 (2H d, J = 8.7 Hz, 12-H), 6.56 (1H, d, J = 8.4 Hz, 8-H), 4.74 (1H, br s, NH), 4.38 (2H, s, CH_2 Bn), 4.17 (1H, t, J = 7.4 Hz, 1-H), 3.79 (3H, s, OMe), 2.80 (2H, qd, J = 10.4 and 7.7 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.5 (1C, C Ar), 143.6 (1C, C Ar), 138.7 (1C, C Ar), 135.1 (1C, C Ar), 133.1 (1C, C Ar), 131.3 (1C, C-5), 128.9 (2C, CH Ar), 128.5 (2C, CH Ar), 127.54 (1C, CH Ar), 127.51 (1C, C-9), 127.4 (2C, CH Ar), 126.5 (1C, q, J = 277.8 Hz, CF_3), 114.2 (2C, C-12), 111.8 (1C, C-8), 109.9 (1C, C Ar), 55.3 (1C, OMe), 48.2 (1C, CH_2 Bn), 43.2 (1C, C-1), 39.9 (1C, q, J = 27.1 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.6 (3F, CF_3). **HRMS** (ESI): calculated for $C_{23}H_{22}BrF_3NO$ $[M+H]^+$ *m*/*z* requires 464.0831, found *m*/*z* 464.0798.

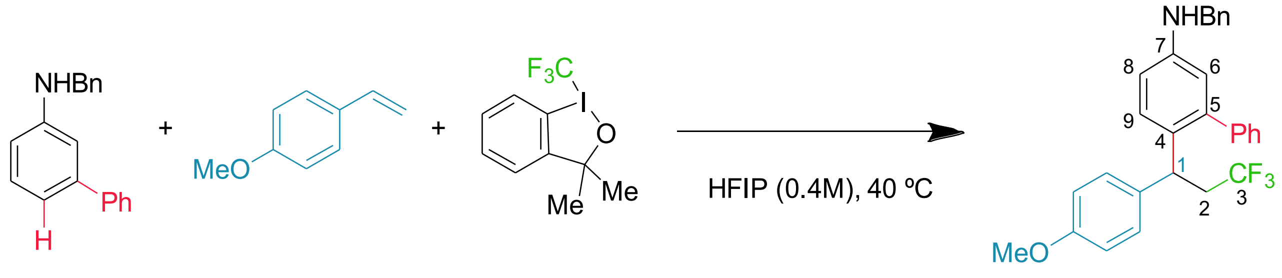
***N*-Benzyl-3-methyl-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4k.**



From aniline **1k** (39.5 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4k** was obtained. Chromatographic purification (gradient elution: 5:95 → 15:95 Et_2O – hexane) gave **4k** (40.3 mg, 50%), as a colourless oil.

Data for **4k**: R_f 0.30 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.25 (5H, m, Ar), 7.13 (2H, d, J = 8.7 Hz, 11-H), 7.05 (1H, d, J = 8.4 Hz, 9-H), 6.81 (2H, d, J = 8.7 Hz, 12-H), 6.53 (1H, dd, J = 8.4 and 2.4 Hz, 8-H), 6.49 (1H, d, J = 2.4 Hz, 6-H), 4.41 (1H, t, J = 7.2 Hz, 1-H), 4.30 (2H, s, CH_2 Bn), 3.77 (3H, s, OMe), 2.79 (2H, m, 2-H_2), 2.24 (3H, s, Me). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2 (1C, C Ar), 146.2 (1C, C Ar), 139.2 (1C, C Ar), 136.9 (1C, C Ar), 135.2 (1C, C Ar), 131.0 (1C, C Ar), 128.9 (2C, CH Ar), 128.8 (2C, CH Ar), 127.9 (2C, CH Ar), 127.5 (1C, CH Ar), 127.3 (1C, C-9), 126.8 (1C, q, J = 277.8 Hz, CF_3), 115.9 (1C, C-6), 114.0 (2C, CH Ar), 111.1 (1C, C-8), 55.3 (1C, OMe), 48.9 (1C, CH_2 Bn), 40.2 (1C, q, J = 26.8 Hz, C-2), 39.2 (1C, C-1), 20.1 (1C, Me). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.7 (1C, CF_3). **HRMS** (ESI): calculated for $C_{24}H_{25}F_3NO$ $[M+H]^+$ *m*/*z* requires 400.1883, found *m*/*z* 400.1878.

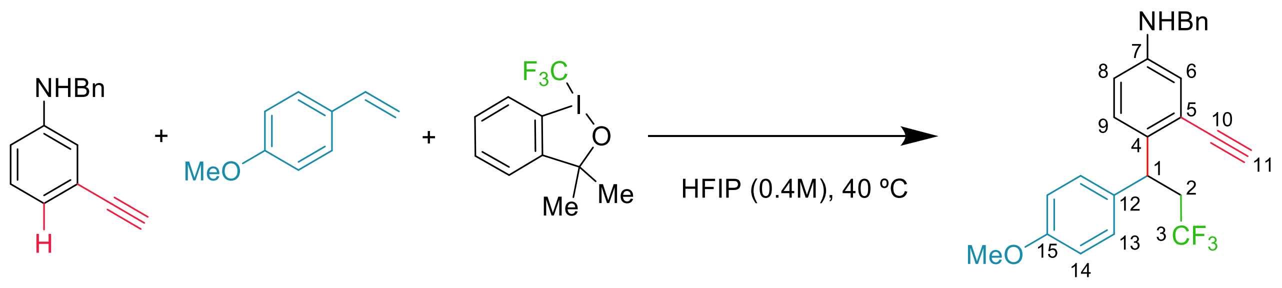
N-Benzyl-6-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]-[1,1'-biphenyl]-3-amine, 4l.



From aniline **1l** (51.4 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4l** was obtained. Chromatographic purification (gradient elution: 0:100 → 20:80 Et_2O – hexane) gave **4l** (55.9 mg, 61%), as a colourless oil.

Data for **4l**: R_f 0.50 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.26 (8H, m, Ar), 7.22 (1H, d, J = 8.5 Hz, 9-H), 7.21 – 7.14 (2H, m, Ar), 6.93 (2H, d, J = 8.7 Hz, Ar), 6.76 (2H, d, J = 8.7 Hz, Ar), 6.69 (1H, dd, J = 8.5 and 2.6 Hz, 8-H), 6.53 (1H, d, J = 2.6 Hz, 6-H), 4.35 (1H, t, J = 7.4 Hz, 1-H), 4.31 (2H, s, CH_2 Bn), 3.77 (3H, s, OMe), 2.88 – 2.63 (2H, m, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.0 (1C, C Ar), 146.0 (1C, C Ar), 143.0 (1C, C Ar), 141.7 (1C, C Ar), 139.1 (1C, C Ar), 135.8 (1C, C Ar), 129.8 (1C, C Ar), 129.3 (2C, CH Ar), 128.7 (2C, CH Ar), 128.5 (2C, CH Ar), 128.1 (2C, CH Ar), 127.8 (2C, CH Ar), 127.7 (1C, CH Ar), 127.5 (1C, CH Ar), 127.1 (1C, CH Ar), 126.3 (1C, q, J = 277.9 Hz, CF_3), 114.9 (1C, C-6), 113.8 (2C, CH Ar), 112.6 (1C, C-8), 55.3 (1C, OMe), 48.7 (1C, CH_2 Bn), 40.3 (1C, q, J = 26.8 Hz, C-2), 39.0 (1C, C-1). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.6 (3F, CF_3). **HRMS** (ESI): calculated for $C_{29}H_{27}F_3NO$ $[M+H]^+$ m/z requires 462.2039, found m/z 462.2037.

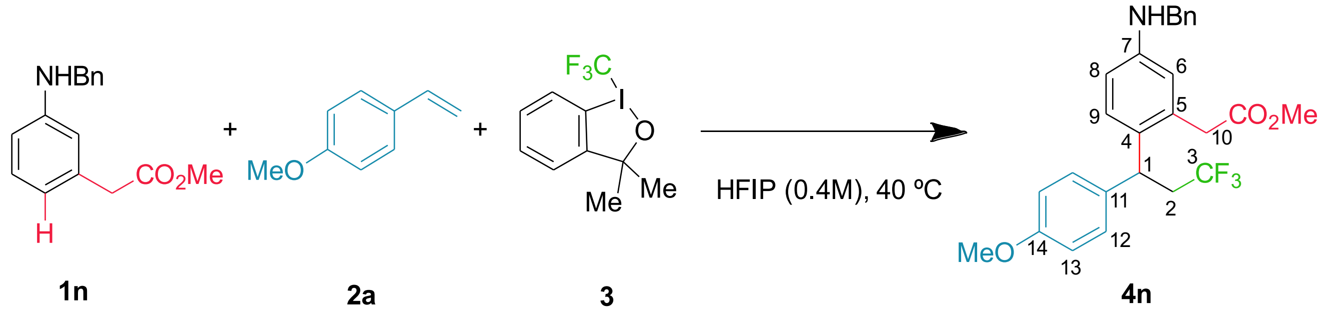
N-Benzyl-3-ethynyl-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4m.



From aniline **1m** (41.5 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4m** was obtained. Chromatographic purification (100% toluene elution) gave **4m** (50.1 mg, 61%), as a colourless oil.

Data for **4m**: ***R**$_f$* 0.20 (100% toluene). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.39 – 7.24 (5H, m, Ar), 7.21 (2H, d, *J* = 8.7 Hz, 13-H), 7.00 (1H, d, *J* = 8.5 Hz, 9-H), 6.83 (2H, d, *J* = 8.7 Hz, 14-H), 6.79 (1H, d, *J* = 2.6 Hz, 6-H), 6.60 (1H, dd, *J* = 8.5 and 2.6 Hz, 8-H), 4.85 (1H, t, *J* = 7.4 Hz, 1-H), 4.28 (2H, s, CH_2 Bn), 3.77 (3H, s, OMe), 3.29 (1H, s, 11-H), 2.83 (2H qd, *J* = 10.4 and 7.5 Hz, 2-H_2). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.3 (1C, C Ar), 146.1 (1C, C Ar), 138.8 (1C, C Ar), 134.9 (1C, C Ar), 134.7 (1C, C Ar), 128.8 (2C, CH Ar), 128.7 (2C, CH Ar), 127.7 (2C, CH Ar), 127.6 (1C, CH Ar), 127.5 (1C, CH Ar), 126.6 (1C, q, *J* = 277.8 Hz, CF_3), 121.9 (1C, C Ar), 117.1 (1C, C-6), 114.6 (1C, C-8), 113.9 (2C, CH Ar), 82.4 (1C, C-10), 81.4 (1C, C-11), 55.3 (1C, OMe), 48.5 (1C, CH_2 Bn), 40.5 (1C, C-1), 39.4 (1C, q, *J* = 27.2 Hz, C-2). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –63.8 (3F, CF_3). **HRMS** (ESI): calculated for $C_{25}H_{23}F_3NO$ $[M+H]^+$ requires *m/z* 410.1726, found *m/z* 410.1723.

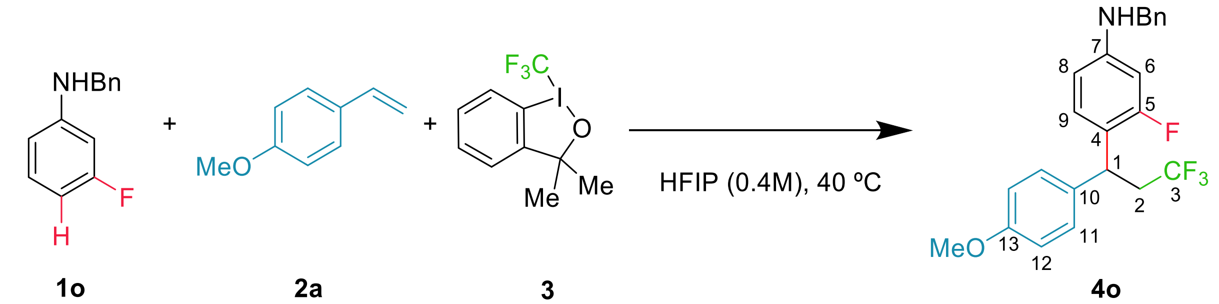
Methyl 2-{5-(benzylamino)-2-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]phenyl}acetate, 4n.



From aniline **1n** (51.0 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4n** was obtained. Chromatographic purification (gradient elution: 0:100 → 20:80 Et_2O – hexane) gave **4n** (49.7 mg, 54%), as an orange oil.

Data for **4n**: ***R**$_f$* 0.1 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.41 – 7.25 (5H, m, Ar), 7.14 (2H, d, *J* = 8.6 Hz, 12-H), 7.10 (1H, d, *J* = 8.4 Hz, 9-H), 6.82 (2H, d, *J* = 8.6 Hz, 13-H), 6.60 (1H, dd, *J* = 8.4, 2.4 Hz, 8-H), 6.53 (1H, d, *J* = 2.3 Hz, 6-H), 4.47 (1H, t, *J* = 7.2 Hz, 1-H), 4.30 (2H, s, CH_2 Bn), 3.77 (3H, s, OMe), 3.64 (1H, d, *J* = 15.5 Hz, 10-H_A), 3.62 (3H, s, CO_2Me), 3.52 (1H, d, *J* = 15.5 Hz, 10-H_B), 2.88 – 2.72 (2H, m, 2-H_2). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 171.9 (1C, C=O), 158.3 (1C, C Ar), 146.6 (1C, C Ar), 139.1 (1C, C Ar), 134.9 (1C, C Ar), 133.1 (1C, C Ar), 130.7 (1C, C Ar), 128.9 (2C, CH Ar), 128.8 (2C, CH Ar), 128.1 (1C, CH Ar), 127.8 (2C, CH Ar), 127.5 (1C, CH Ar), 126.6 (1C, q, *J* = 277.9 Hz, CF_3), 116.0 (1C, CH Ar), 114.0 (2C, CH Ar), 112.4 (1C, CH Ar), 55.3 (1C, OMe), 52.1 (1C, CO_2Me), 48.7 (1C, CH_2 Bn), 40.3 (1C, q, *J* = 26.9 Hz, C-2), 39.02 (1C, C-10), 38.97 (1C, C-1). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –63.7 (3F, CF_3). **HRMS** (ESI): calculated for $C_{26}H_{27}F_3NO_3$ $[M+H]^+$ requires *m/z* 458.1938, found *m/z* 458.1935.

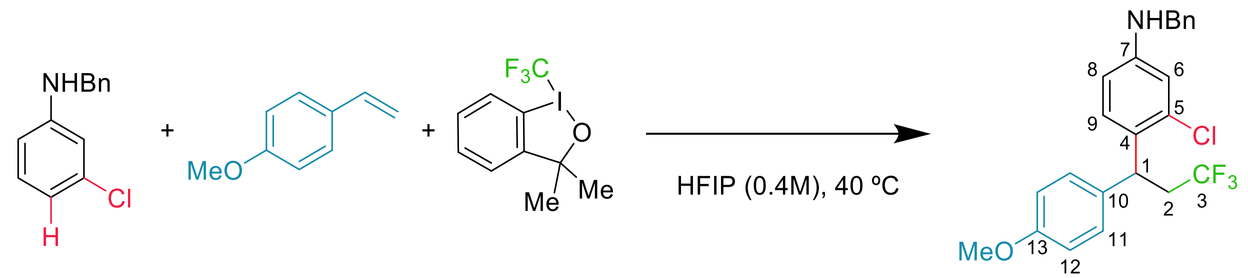
N-Benzyl-3-fluoro-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4o.



From aniline **1o** (40.2 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4o** was obtained. Chromatographic purification (gradient elution: 4:96 Et_2O – toluene) gave **4o** (64.4 mg, 80%), as a colourless oil.

Data for **4o**: R_f 0.50 (4% Et_2O – toluene). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.26 (5H, m, Ar), 7.19 (2H, d, J = 8.7 Hz, 11-H), 6.98 (1H, t, J = 8.5 Hz, 9-H), 6.84 (2H, d, J = 8.7 Hz, 12-H), 6.37 (1H, dd, J = 8.4 and 2.4 Hz, 8-H), 6.30 (1H, dd, J = 12.9 and 2.4 Hz, 6-H), 4.44 (1H, t, J = 7.5 Hz, 1-H), 4.27 (2H, s, CH_2 Bn), 3.78 (3H, s, OMe), 2.96 – 2.73 (2H, m, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.3 (1C, d, J = 243.6 Hz, C-5), 158.3 (1C, C Ar), 148.6 (1C, d, J = 11.1 Hz, C-7), 138.8 (1C, C Ar), 134.6 (1C, C Ar), 129.2 (1C, d, J = 6.4 Hz, C-9), 128.8 (2C, CH Ar), 128.5 (2C, CH Ar), 127.6 (2C, CH Ar), 127.5 (1C, CH Ar), 126.6 (1C, q, J = 277.8 Hz, CF_3), 118.6 (1C, d, J = 14.6 Hz, C-4), 114.0 (2C, CH Ar), 109.0 (1C, C-8), 100.1 (1C, d, J = 26.7 Hz, C-6), 55.3 (1C, OMe), 48.4 (1C, CH_2 Bn), 38.9 (1C, q, J = 27.1 Hz, C-2), 37.6 (1C, C-1). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –64.1 (3F, CF_3), –116.6 (1F, C5-F). **HRMS** (ESI): calculated for $C_{23}H_{22}F_4NO$ $[M+H]^+$ m/z requires 404.1632, found m/z 404.1615.

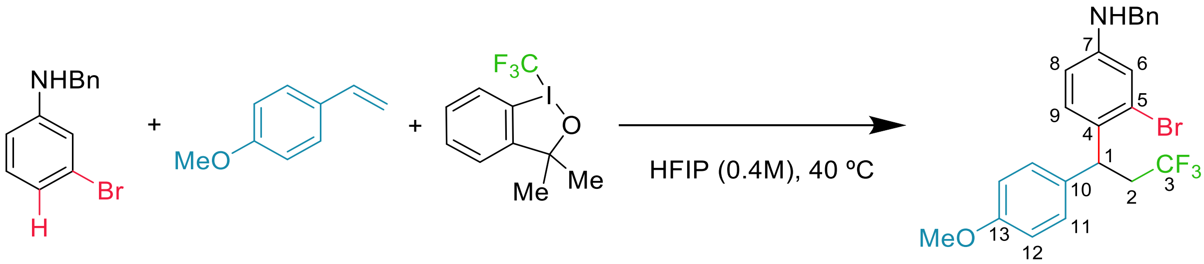
N-Benzyl-3-chloro-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4p.



From aniline **1p** (43.5 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4p** was obtained. Chromatographic purification (gradient elution: 5:95 → 15:85 Et_2O – hexane) gave **4p** (40.8 mg, 50%), as a colourless oil.

Data for **4p**: R_f 0.20 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.26 (5H, m, Ar), 7.20 (2H, d, J = 8.6 Hz, 11-H), 7.03 (1H, d, J = 8.5 Hz, 9-H), 6.85 (2H, d, J = 8.7 Hz, 12-H), 6.66 (1H, d, J = 2.5 Hz, 6-H), 6.51 (1H, dd, J = 8.5 and 2.5 Hz, 8-H), 4.77 (1H, t, J = 7.4 Hz, 1-H), 4.28 (2H, s, CH_2 Bn), 3.78 (3H, s, OMe), 2.81 (2H, qd, J = 10.4 and 7.7 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3 (1C, C Ar), 147.6 (1C, C Ar), 138.7 (1C, C Ar), 134.2 (1C, C Ar), 134.2 (1C, C Ar), 129.1 (1C, C Ar), 128.8 (2C, CH Ar), 128.8 (2C, CH Ar), 128.7 (1C, C-9), 127.6 (2C, CH Ar), 127.5 (1C, CH Ar),126.5 (1C, q, J = 278.0 Hz, CF_3), 114.0 (2C, CH Ar), 113.6 (1C, C-6), 112.0 (1C, C-8), 55.3 (1C, OMe), 48.3 (1C, CH_2 Bn), 39.4 (1C, C-1), 39.2 (1C, q, J = 27.2 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.7 (3F, CF_3). **HRMS** (ESI): calculated for $C_{23}H_{22}ClF_3NO$ $[M+H]^+$ requires *m*/*z* 420.1337, found *m*/*z* 420.1316.

***N*-Benzyl-3-bromo-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4q.**

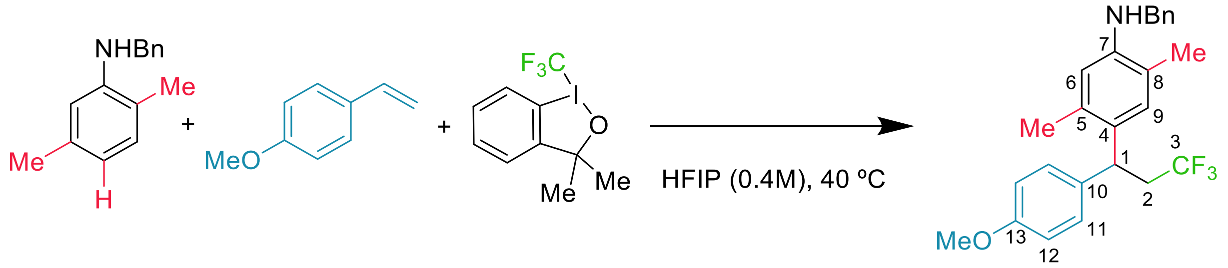


1q **2a** **3** **4q**

From aniline **1q** (52.4 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4q** was obtained. Chromatographic purification (gradient elution: 10:90 → 20:80 Et_2O – hexane) gave **4q** (54.7 mg, 60%), as a colourless oil.

Data for **4q**: R_f 0.40 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.27 (5H, m, Ar), 7.22 (2H, d, J = 8.6 Hz, 12-H), 7.03 (1H, d, J = 8.5 Hz, 9-H), 6.86 (2H, d, J = 8.4 Hz, 11-H), 6.85 (1H, d, J = 3.6 Hz, 6-H), 6.55 (1H, dd, J = 8.6 and 2.5 Hz, 8-H), 4.78 (1H, t, J = 7.3 Hz, 1-H), 4.27 (2H, s, CH_2 Bn), 4.13 (1H, br s, NH), 3.79 (3H, s, OMe), 2.81 (2H, qd, J = 10.2 and 7.9 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3 (1C, C Ar), 147.7 (1C, C Ar), 138.7 (1C, C Ar), 134.2 (1C, C Ar), 130.6 (1C, C Ar), 128.8 (5C, CH Ar), 128.7 (1C, CH Ar), 127.6 (2C, CH Ar), 126.4 (1C, q, J = 280.5 Hz, CF_3), 125.0 (1C, C Ar), 116.8 (1C, C-6), 114.0 (2C, CH Ar), 112.6 (1C, C-8), 55.3 (1C, OMe), 48.3 (1C, CH_2 Bn), 41.8 (1C, C-1), 39.4 (1C, q, J = 27.2 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.6 (3F, CF_3). **HRMS** (EI): calculated for $C_{23}H_{21}BrF_3NO$ $[M]^+$ requires 463.0754 *m*/*z*, found 463.0737 *m*/*z*.

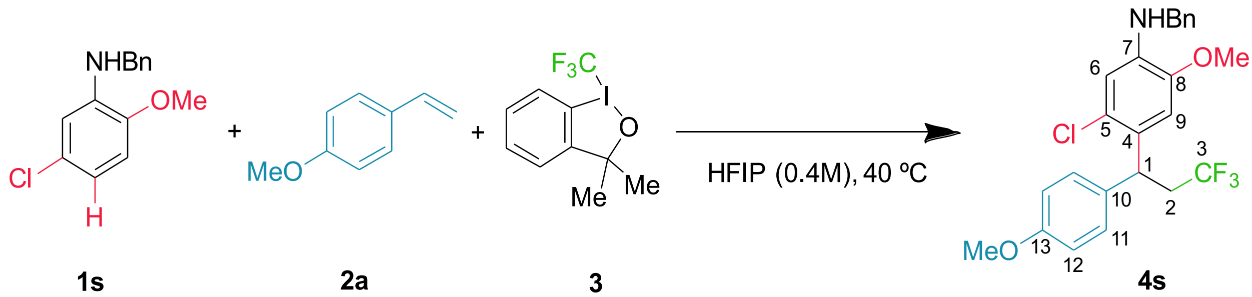
N-Benzyl-2,5-dimethyl-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4r.



From aniline **1r** (42.0 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4r** was obtained. Chromatographic purification (gradient elution: 0:100 → 20:80 Et_2O – hexane) gave **4r** (47.9 mg, 58%), as a white foam.

Data for **4r**: R_f 0.30 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.26 (5H, m, Ar), 7.15 (2H, d, J = 8.6 Hz, 11-H), 6.92 (1H, s, 9-H), 6.82 (2H, d, J = 8.7 Hz, 12-H), 6.47 (1H, s, 6-H), 4.41 (1H, t, J = 7.2 Hz, 1-H), 4.33 (2H, s, CH_2 Bn), 3.78 (3H, s, OMe), 2.93 – 2.71 (2H, m, 2-H_2), 2.25 (3H, s, Me), 2.14 (3H, s, Me). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1 (1C, C Ar), 144.1 (1C, C Ar), 139.2 (1C, C Ar), 135.3 (1C, C Ar), 134.3 (1C, C Ar), 130.0 (1C, C Ar), 128.8 (2C, CH Ar), 128.7 (2C, CH Ar), 128.6 (1C, CH Ar), 128.2 (1C, C-9), 127.9 (1C, CH Ar), 127.5 (1C, CH Ar), 126.8 (1C, q, J = 277.8 Hz, CF_3), 120.1 (1C, C Ar) 113.9 (2C, CH Ar), 112.9 (1C, C-6), 55.3 (1C, OMe), 48.8 (1C, CH_2 Bn), 40.1 (1C, q, J = 26.8 Hz, C-2), 39.1 (1C, C-1), 19.8 (1C, Me), 17.5 (1C, Me).**^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.7 (3F, CF_3). **HRMS** (ESI): calculated for $C_{25}H_{27}F_3NO$ $[M+H]^+$ requires m/z 414.2039, found m/z 414.2048.

N-Benzyl-5-chloro-2-methoxy-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4s.

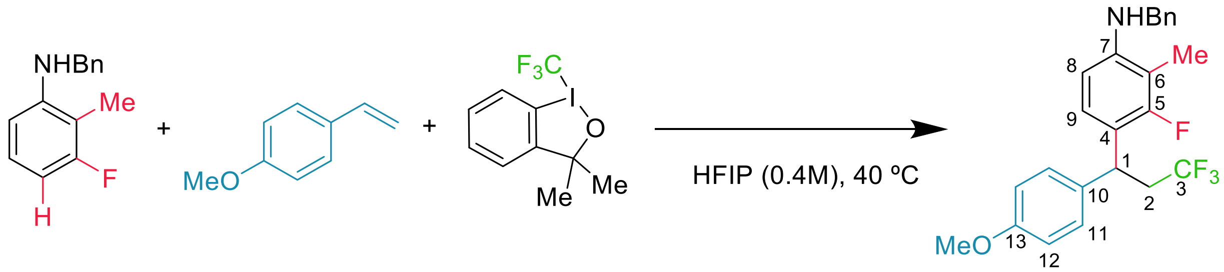


From aniline **1s** (49.1 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4s** was obtained. Chromatographic purification (gradient elution: 5:95 → 10:90 Et_2O – hexane) gave **4s** (52.0 mg, 58%), as a colourless oil.

Data for **4s**: R_f 0.20 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.25 (5H, m, Ar), 7.20 (2H, d, J = 8.6 Hz, 11-H), 6.85 (2H, d, J = 8.7 Hz, 12-H), 6.57 (1H, s, Ar), 6.56 (1H, s, Ar), 4.78 (1H, t, J = 7.4 Hz, 1-H), 4.28 (2H, s, CH_2 Bn), 3.78 (3H, s, OMe), 3.78 (3H, s, OMe), 2.90

– 2.76 (2H, m, 2-H$_2$). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.4 (1C, C Ar), 146.0 (1C, C Ar), 138.6 (1C, C Ar), 137.4 (1C, C Ar), 134.1 (1C, C Ar), 129.9 (1C, C Ar) 128.8 (2C, CH Ar), 128.7 (2C, CH Ar), 127.7 (2C, CH Ar), 127.5 (1C, CH Ar), 126.5 (1C, q, J = 278.2 Hz, CF$_3$), 125.4 (1C, C Ar), 114.0 (2C, CH Ar), 111.1 (1C, CH Ar), 109.0 (1C, CH Ar), 55.7 (1C, OMe), 55.3 (1C, OMe), 48.1 (1C, CH$_2$ Bn), 39.8 (1C, C-1), 39.1 (1C, q, J = 27.3 Hz, C-2). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –63.7 (3F, CF$_3$). **HRMS** (ESI): calculated for $C_{24}H_{24}ClF_3NO_2$ [M+H]$^+$ *m/z* requires 450.1443, found *m/z* 450.1437.

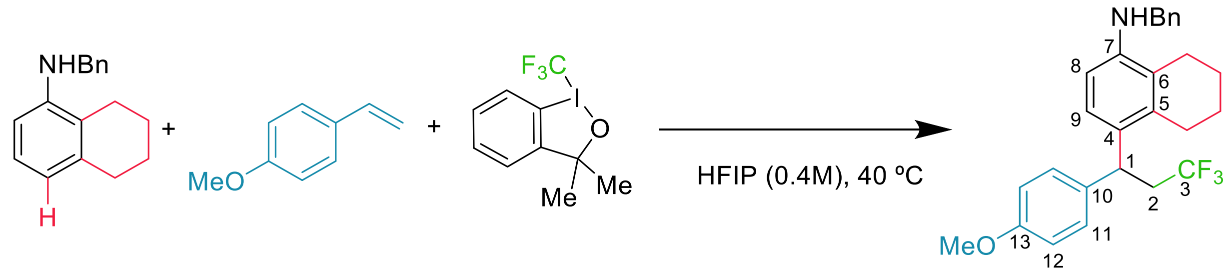
***N*-Benzyl-3-fluoro-2-methyl-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4t.**



From aniline **1t** (43.0 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4t** was obtained. Chromatographic purification (gradient elution: 5:95 → 10:90 Et$_2$O – hexane) gave **4t** (52.7 mg, 64%), as a colourless oil.

Data for **4t**: ***R$_f$*** 0.30 (30% Et$_2$O – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.39 – 7.26 (5H, m, Ar), 7.20 (2H, d, J = 8.6 Hz, 11-H), 6.93 (1H, t, J = 8.4 Hz, 9-H), 6.84 (2H, d, J = 8.7 Hz, 12-H), 6.41 (1H, d, J = 8.4 Hz, 8-H), 4.49 (1H, t, J = 7.4 Hz, 1-H), 4.35 (2H, s, CH$_2$ Bn), 3.78 (3H, s, OMe), 2.98 – 2.74 (2H, m, 2-H$_2$), 2.05 (3H, s, Me). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.8 (1C, d, J = 241.6 Hz, C-5), 158.3 (1C, C Ar), 146.3 (1C, C Ar), 139.0 (1C, C Ar), 134.7 (1C, C Ar), 128.8 (2C, CH Ar), 128.6 (2C, CH Ar), 127.6 (2C, CH Ar), 127.5 (1C, CH Ar), 126.6 (1C, q, J = 277.7 Hz, CF$_3$), 125.9 (1C, d, J = 6.5 Hz, C-9), 119.0 (1C, d, J = 14.3 Hz, C-4), 114.0 (2C, CH Ar), 109.3 (1C, d, J = 18.9 Hz, C-6), 105.9 (1C, C-8), 55.3 (1C, OMe), 48.7 (1C, CH$_2$ Bn), 38.9 (1C, q, J = 27.1 Hz, C-2), 37.8 (1C, quint, J = 2.7 Hz, C-1), 8.6 (1C, d, J = 7.3 Hz, Me). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –64.0 (3F, CF$_3$), –121.3 (1F, C5-F). **HRMS** (ESI): calculated for $C_{24}H_{24}F_4NO$ [M+H]$^+$ *m/z* requires 418.1789, found *m/z* 418.1778.

N-Benzyl-4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]-5,6,7,8-tetrahydronaphthalen-1-amine, 4u.

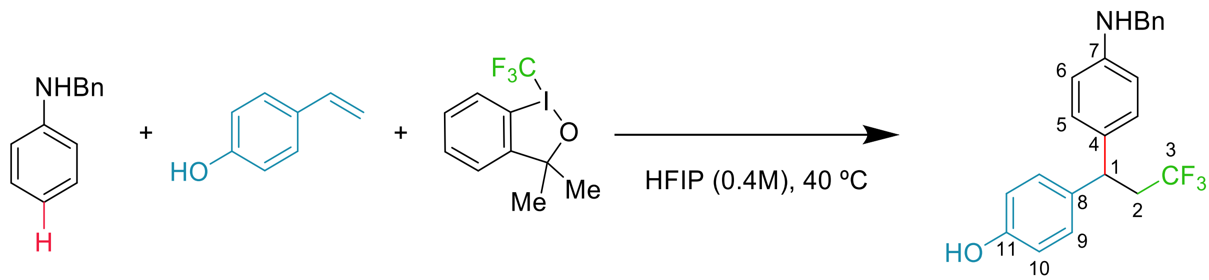


1u **2a** **3** **4u**

From aniline **1u** (47.2 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4u** was obtained. Chromatographic purification (gradient elution: 5:95 → 15:85 Et_2O – hexane) gave **4u** (26.9 mg, 31%), as brownish oil.

Data for **4u**: R_f 0.30 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.27 (m, 5H), 7.15 (2H, d, J = 8.6 Hz, 11-H), 7.04 (1H, d, J = 8.4 Hz, 9-H), 6.81 (2H, d, J = 8.7 Hz, 12-H), 6.56 (1H, d, J = 8.4 Hz, 8-H), 4.46 (1H, t, J = 7.2 Hz, 1-H), 4.36 (2H, s, CH_2 Bn), 3.78 (3H, s, OMe), 2.90 – 2.70 (3H, m, 2-H_2 and CH_2 tetrahydronaphth), 2.57 (1H, dt, J = 16.4 and 6.0 Hz, CH_2 tetrahydronaphth), 2.51 – 2.37 (2H, m, CH_2 tetrahydronaphth), 1.89 – 1.67 (4H, m, 2 x CH_2 tetrahydronaphth). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1 (1C, C Ar), 144.3 (1C, C Ar), 139.5 (1C, C Ar), 135.4 (1C, C Ar), 135.2 (1C, C Ar), 130.3 (1C, C Ar), 129.1 (2C, C-11), 128.8 (2C, CH Ar), 128.20 (1C, q, J = 277.2 Hz, CF_3), 127.8 (2C, CH Ar), 127.4 (1C, CH Ar), 124.3 (1C, C-9), 122.1 (1C, C Ar), 113.9 (2C, C-12), 107.5 (1C, C-8), 55.3 (1C, OMe), 48.7 (1C, CH_2 Bn), 40.58 (1C, q, J = 26.6 Hz, C-2), 38.58 (1C, q, J = 2.6 Hz, C-1), 26.8 (1C, CH_2 tetrahydronaphth), 24.8 (1C, CH_2 tetrahydronaphth), 22.9 (1C, CH_2 tetrahydronaphth), 22.4 (1C, CH_2 tetrahydronaphth). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.6 (3F, CF_3). **HRMS** (ESI): calculated for $C_{27}H_{29}F_3NO$ $[M+H]^+$ m/z requires 440.2196, found m/z 440.2190.

4-{1-[4-(Benzylamino)phenyl]-3,3,3-trifluoropropyl}phenol, 4v.

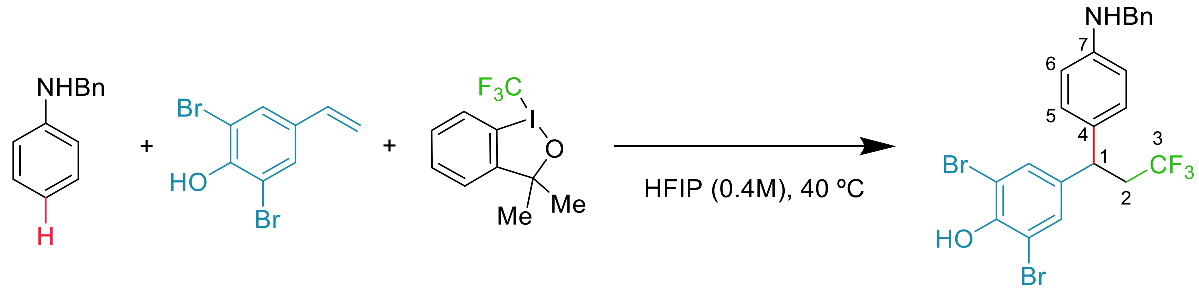


1a **2b** **3** **4v**

From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2b** (24.0 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4v** was obtained. Chromatographic purification (gradient elution: 30:70 → 50:50 Et_2O – hexane) gave **4v** (41.1 mg, 55%), as a colourless oil.

Data for **4v**: ***R**$_f$* 0.20 (50% Et_2O – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.38 – 7.26 (5H, m, Ar), 7.09 (2H, d, *J* = 8.5 Hz, 9-H), 7.03 (2H, d, *J* = 8.5 Hz, 5-H), 6.73 (2H, d, *J* = 8.6 Hz, 10-H), 6.60 (2H d, *J* = 8.5 Hz, 6-H), 4.30 (2H, s, CH_2 Bn), 4.18 (1H, t, *J* = 7.4 Hz, 1-H), 2.80 (2H, qd, *J* = 10.5 and 7.4 Hz, 2-H_2). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 154.2 (1C, C Ar), 146.6 (1C, C Ar), 139.2 (1C, C Ar), 135.9 (1C, C Ar), 132.6 (1C, C Ar), 128.7 (2C, CH Ar), 128.7 (2C, CH Ar), 128.3 (2C, CH Ar), 127.7 (2C, CH Ar), 127.4 (1C, CH Ar), 126.6 (1C, q, *J* = 277.8 Hz, CF_3), 115.5 (2C, CH Ar), 113.4 (2C, CH Ar), 48.7 (1C, CH_2 Bn), 43.5 (1C, C-1), 40.0 (1C, q, *J* = 26.9 Hz, C-2). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –63.5 (3F, CF_3). **HRMS** (ESI): calculated for $C_{22}H_{21}F_3NO$ $[M+H]^+$ *m/z* requires 372.1570, found *m/z* 372.1563.

4-{1-[4-(Benzylamino)phenyl]-3,3,3-trifluoropropyl}-2,6-dibromophenol, 4w.

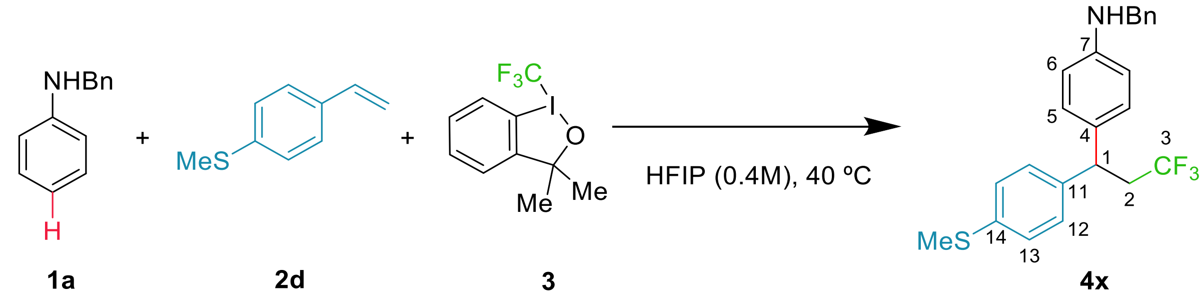


1a **2c** **3** **4w**

From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2c** (55.6 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4w** was obtained. Chromatographic purification (gradient elution: 15:80 → 55:45 Et_2O – hexane) gave **4w** (78.4 mg, 74%), as a colourless oil.

Data for **4w**: ***R**$_f$* 0.20 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.41 – 7.24 (7H, m, Ar), 7.00 (2H, d, *J* = 8.5 Hz, Ar), 6.60 (2H, d, *J* = 8.6 Hz, Ar), 4.31 (2H, s, CH_2 Bn), 4.12 (1H, t, *J* = 7.4 Hz, 1-H), 2.78 (2H, m, 2-H_2).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 148.2 (1C, C Ar), 147.3 (1C, C Ar), 139.3 (1C, C Ar), 138.4 (1C, C Ar), 131.0 (2C, CH Ar), 130.6 (1C, C Ar), 128.8 (2C, CH Ar), 128.2 (2C, CH Ar), 127.6 (2C, CH Ar), 127.5 (1C, CH Ar), 126.3 (1C, q, *J* = 277.8 Hz, CF_3), 113.3 (2C, CH Ar), 110.0 (2C, C Ar), 48.5 (1C, CH_2 Bn), 43.1 (1C, C-1), 39.7 (1C, q, *J* = 27.3 Hz, C-2). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –63.6 (3F, CF_3). **HRMS** (EI): calculated for $C_{22}H_{16}Br_2F_3NO$ $[M]^+$ requires *m/z* 526.9532, found *m/z* 526.9520.

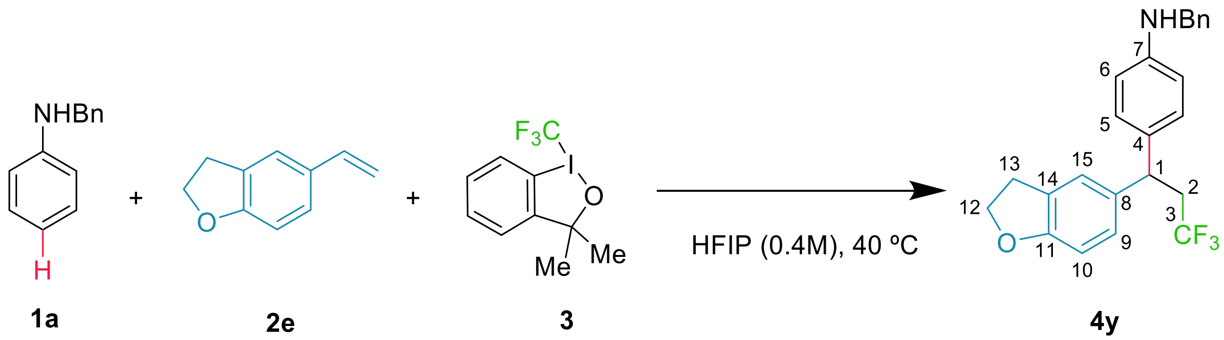
N-Benzyl-4-{3,3,3-trifluoro-1-[4-(methylthio)phenyl]propyl}aniline, 4x.



From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2d** (30.0 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4x** was obtained. Chromatographic purification (gradient elution: 0:100 → 10:90 Et_2O – hexane) gave **4x** (46.2 mg, 60%), as a colourless oil.

Data for **4x**: R_f 0.40 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.27 (5H, m, Ar), 7.21 (2H, d, *J* = 8.5 Hz, 13-H), 7.17 (2H, d, *J* = 8.5 Hz, 12-H), 7.04 (2H, d, *J* = 8.5 Hz, 5-H), 6.59 (2H, d, *J* = 8.5 Hz, 6-H), 4.30 (2H, s, CH_2 Bn), 4.21 (1H, t, *J* = 7.4 Hz, 1-H), 4.01 (1H, s, NH), 2.84 (2H, qd, *J* = 10.5 and 7.5 Hz, 2-H_2), 2.46 (3H, s, SMe). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.0 (1C, C Ar), 140.6 (1C, C Ar), 139.4 (1C, C Ar), 136.5 (1C, C Ar), 131.7 (1C, C Ar), 128.7 (2C, CH Ar), 128.3 (2C, CH Ar), 128.0 (2C, CH Ar), 127.6 (2C, CH Ar), 127.3 (1C, CH Ar), 127.1 (2C, CH Ar), 126.6 (1C, q, *J* = 277.7 Hz, CF_3), 113.1 (2C, CH Ar), 48.5 (1C, CH_2 Bn), 43.8 (1C, C-1), 39.7 (1C, q, *J* = 27.0 Hz, C-2), 16.0 (1C, SMe). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.5 (3F, CF_3). **HRMS** (EI): calculated for $C_{23}H_{22}F_3NS$ $[M]^+$ requires *m/z* 401.1420, found *m/z* 401.1281.

N-Benzyl-4-[1-(2,3-dihydrobenzofuran-5-yl)-3,3,3-trifluoropropyl]aniline, 4y.

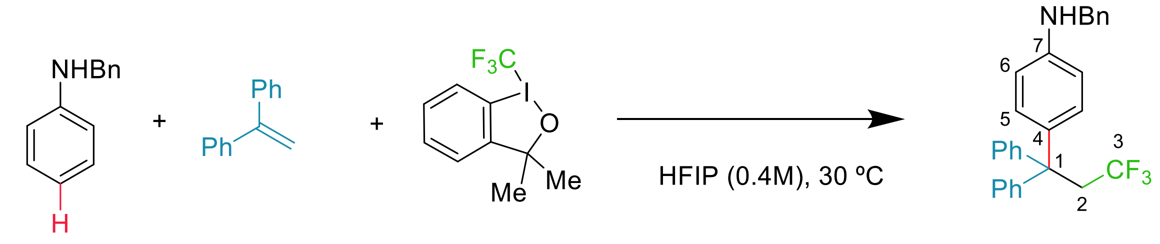


From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2e** (29.2 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4y** was obtained. Chromatographic purification (gradient elution: 10:90→ 20:80 Et_2O – hexane) gave **4y** (56.2 mg, 71%), as a colourless oil.

Data for **4y**: R_f 0.20 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.27 (5H, m, H Ar), 7.06 (2H, d, *J* = 8.3 Hz, 5-H), 7.06 (1H, s, 15-H), 7.00 (1H, d, *J* = 8.2 Hz, 9-H), 6.72 (1H, d, *J* = 8.2 Hz, 10-H), 6.61 (2H, d, *J* = 8.3 Hz, 6-H), 4.54 (2H, t, *J* = 8.7 Hz, 12-H_2), 4.31 (2H, s, CH_2

Bn), 4.19 (1H, t, J = 7.3 Hz, 1-H), 3.15 (2H, t, J = 8.7 Hz, 13-H_2), 2.83 (2H, qd, J = 10.5 and 7.1 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.8 (1C, C Ar), 146.7 (1C, C Ar), 139.3 (1C, C Ar), 135.8 (1C, C Ar), 132.6 (1C, C Ar), 128.7 (2C, CH Ar), 128.2 (2C, CH Ar), 127.6 (2C, CH Ar), 127.4 (1C, C Ar), 127.4 (1C, CH Ar), 127.0 (1C, C-9), 126.7 (1C, q, J = 277.8 Hz, CF_3), 124.1 (1C, C-15), 113.2 (2C, C-6), 109.2 (1C, C-10), 71.3 (1C, C-12), 48.6 (1C, CH_2 Bn), 43.7 (1C, C-1), 40.1 (1C, q, J = 26.8 Hz, C-2), 29.8 (1C, C-13). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –65.5 (3F, CF_3). **HRMS** (ESI): calculated for $C_{24}H_{23}F_3NO$ $[M+H]^+$ requires *m/z* 398.1727, found *m/z* 398.1714.

***N*-Benzyl-4-(3,3,3-trifluoro-1,1-diphenylpropyl)aniline, 4z.**

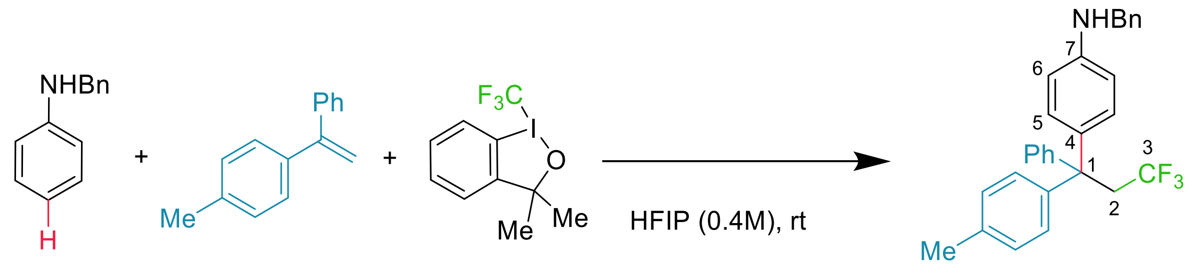


1a **2f** **3** **4z**

From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2f** (36.1 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure at 30 ºC, aniline **4z** was obtained. Chromatographic purification (gradient elution: 0:100 → 10:90 Et_2O – hexane) gave **4z** (54.8 mg, 65%), as a colourless oil.

Data for **4z**: ***R_f*** 0.30 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.18 (15H, m, Ar), 7.10 (2H, d, J = 8.8 Hz, 5-H), 6.58 (2H, d, J = 8.8 Hz, 6-H), 4.32 (2H, s, CH_2 Bn), 4.03 (1H, br s, NH), 3.55 (2H, q, J = 10.6 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.5 (1C, C Ar), 146.0 (2C, C Ar), 139.4 (1C, C Ar), 134.2 (1C, C Ar), 130.0 (2C, CH Ar), 129.0 (4C, CH Ar), 128.7 (2C, CH Ar), 127.9 (4C, CH Ar), 127.7 (2C, CH Ar), 127.4 (1C, CH Ar), 126.3 (2C, CH Ar), 126.2 (1C, q, J = 279.4 Hz, CF_3), 112.2 (2C, CH Ar), 53.5 (1C, C-1), 48.5 (1C, CH_2 Bn), 44.2 (1C, q, J = 26.4 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –55.8 (3F, CF_3). **HRMS** (EI): calculated for $C_{28}H_{24}F_3N$ $[M]^+$ requires *m/z* 431.1856, found *m/z* 431.1868.

***N*-Benzyl-4-[3,3,3-trifluoro-1-phenyl-1-(*p*-tolyl)propyl]aniline, 4aa.**

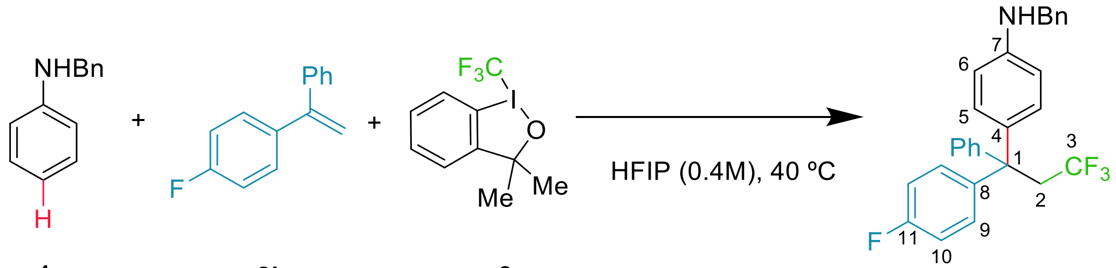


1a **2g** **3** **4aa**

From aniline **1a** (36.1 mg, 0.2 mmol), alkene **2g** (38.9 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP at room temperature, following the general procedure, aniline **4aa** was obtained. Chromatographic purification (gradient elution: 0:100 → 5:95 Et_2O – hexane) gave **4aa** (52.3 mg, 60%), as a colourless oil.

Data for **4aa**: R_f 0.5 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.49 – 7.17 (12H, m, Ar), 7.11 (4H, d, J = 8.7 Hz, Ar), 6.59 (2H, d, J = 8.8 Hz, 6-H), 4.32 (2H, s, CH_2 Bn), 3.53 (2H, q, J = 10.6 Hz, 2-H_2), 2.34 (3H, s, Me). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 146.3 (1C, C Ar), 146.2 (1C, C Ar), 143.1 (1C, C Ar), 139.3 (1C, C Ar), 135.9 (1C, C Ar), 134.6 (1C, C Ar), 130.0 (2C, CH Ar), 129.0 (2C, CH Ar), 128.9 (2C, CH Ar), 128.8 (2C, CH Ar), 128.7 (2C, CH Ar), 127.9 (2C, CH Ar), 127.7 (2C, CH Ar), 127.5 (1C, CH Ar), 126.29 (1C, CH Ar), 126.26 (1C, q, J = 279.3 Hz, CF_3), 112.4 (2C, CH Ar), 53.2 (1C, C-1), 48.7 (1C, CH_2 Bn), 44.3 (1C, q, J = 26.2 Hz, C-2), 21.0 (1C, Me). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –55.8 (3F, CF_3). **HRMS** (ESI): calculated for $C_{28}H_{23}F_4N$ [M]+ requires m/z 449.1767, found m/z 449.1768.

***N*-Benzyl-4-[3,3,3-trifluoro-1-(4-fluorophenyl)-1-phenylpropyl]aniline, 4ab.**

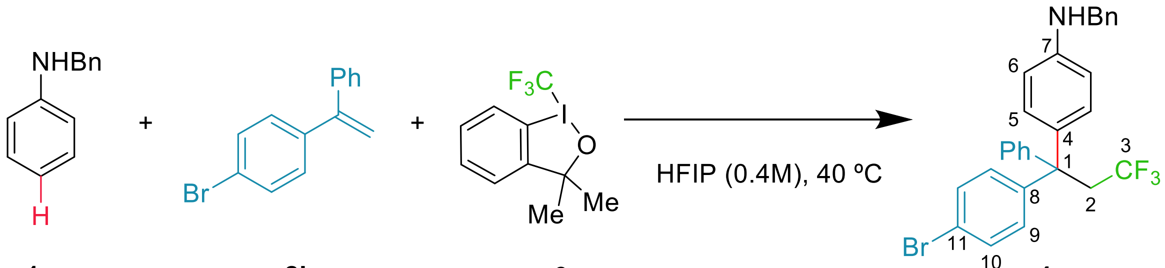


1a **2h** **3** **4ab**

From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2h** (39.6 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4ab** was obtained. Chromatographic purification (gradient elution: 0:100 → 6:94 Et_2O – hexane) gave **4ab** (56.1 mg, 63%), as a colourless oil.

Data for **4ab**: R_f 0.50 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.42 – 7.19 (10H, m, H Ar), 7.33 (2H, dd, J = 31.1 and 4.0 Hz, 9-H), 7.07 (2H, d, J = 8.8 Hz, 5-H), 6.97 (2H, t, J = 8.7 Hz, 10-H), 6.57 (2H, d, J = 8.8 Hz, 6-H), 4.31 (2H, s, CH_2 Bn), 4.03 (1H, br s, NH), 3.51 (2H, q, J = 10.5 Hz, 2-H_2). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 161.3 (1C, d, J = 246.0 Hz, C-11), 146.6 (1C, C Ar), 146.0 (1C, C Ar), 141.5 (1C, d, J = 3.5 Hz, C-8), 139.3 (1C, C Ar), 134.1 (1C, C Ar), 130.8 (2C, d, J = 7.8 Hz, C-9), 129.7 (2C, CH Ar), 128.8 (2C, CH Ar), 128.0 (2C, CH Ar), 127.7 (2C, CH Ar), 127.4 (2C, CH Ar), 126.4 (2C, CH Ar), 123.3 (1C, d, J = 279.4 Hz, CF_3), 114.6 (2C, d, J = 21.0 Hz, C-10), 112.3 (2C, CH Ar), 53.1 (1C, C-1), 48.5 (1C, CH_2 Bn), 44.3 (1C, q, J = 26.4 Hz, C-2). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –55.9 (3F, CF_3), –116.8 (1F, F Ar). **HRMS** (ESI): calculated for $C_{29}H_{27}F_3N$ [M+H]$^+$ requires *m*/*z* 446.2091, found *m*/*z* 446.2092.

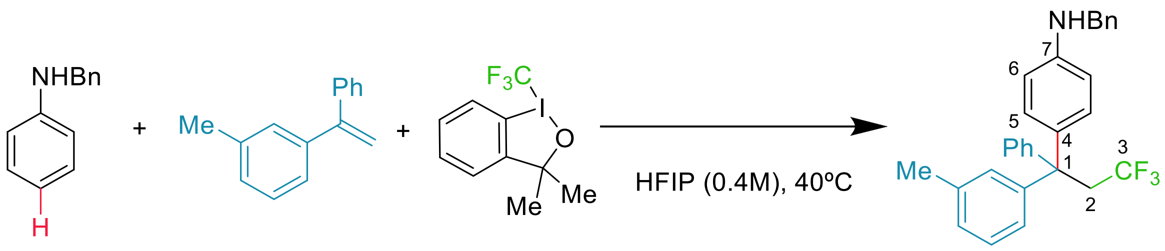
N-Benzyl-4-[1-(4-bromophenyl)-3,3,3-trifluoro-1-phenylpropyl]aniline, 4ac.



From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2i** (51.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4ac** was obtained. Chromatographic purification (gradient elution: 5:95 → 20:80 Et_2O – hexane) gave **4ac** (62.7 mg, 62%), as a colourless oil.

Data for **4ac**: $\boldsymbol{R_f}$ 0.5 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (2H, d, J = 8.8 Hz, 10-H), 7.27 – 7.09 (10H, m, Ar), 7.08 (2H, d, J = 8.8 Hz, 9-H), 6.93 (2H, d, J = 8.8 Hz, 5-H), 6.45 (2H, d, J = 8.8 Hz, 6-H), 4.19 (2H, s, CH_2 Bn), 3.91 (1H, s, NH), 3.37 (2H, q, J = 10.5 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.7 (1C, C Ar), 145.5 (1C, C Ar), 145.0 (1C, C Ar), 139.3 (1C, C Ar), 133.6 (1C, C Ar), 131.0 (2C, CH Ar), 130.9 (2C, CH Ar), 129.8 (2C, CH Ar), 128.8 (2C, CH Ar), 128.8 (2C, CH Ar), 128.1 (2C, CH Ar), 127.7 (2C, CH Ar), 127.4 (1C, CH Ar), 126.5 (1C, CH Ar), 126.0 (1C, q, J = 279.4 Hz, CF_3), 120.4 (1C, C Ar), 112.3 (2C, CH Ar), 53.2 (1C, CH_2 Bn), 48.4 (1C, C-1), 44.1 (1C, q, J = 26.4 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –55.9 (3F, CF_3). **HRMS** (EI): calculated for $C_{28}H_{23}BrF_3N$ $[M]^+$ requires m/z 509.0961, found m/z 509.0952.

N-Benzyl-4-[3,3,3-trifluoro-1-phenyl-1-(m-tolyl)propyl]aniline, 4ad.

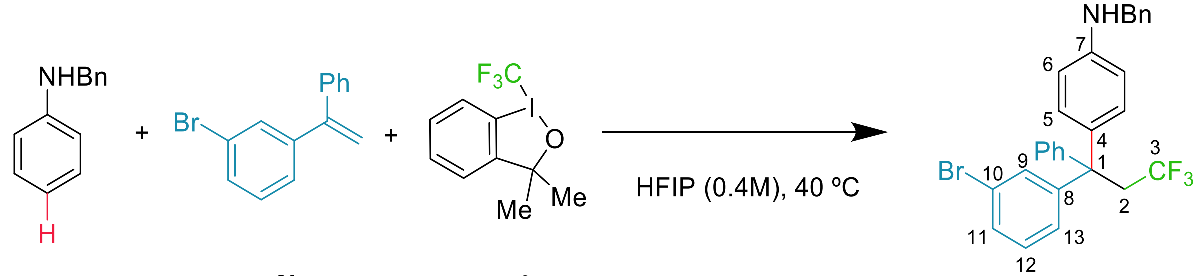


From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2j** (38.9 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4ad** was obtained. Chromatographic purification (gradient elution: 4:96 → 15:85 Et_2O – hexane) gave **4ad** (60.3 mg, 70%), as a colourless oil.

Data for **4ad**: $\boldsymbol{R_f}$ 0.50 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.24 (10H, m, Ar), 7.21 (1H, dt, J = 7.6 and 2.0 Hz, Ar), 7.16 (1H, t, J = 7.6, Hz, Ar), 7.11 (1H, s, J = 2.8 Hz, Ar), 7.08 (2H, d, J = 8.7 Hz, 5-H), 7.01 (1H, d, J = 7.2 Hz, Ar), 6.58 (2H, d, J = 8.7 Hz, 6-H), 4.30 (2H, s, CH_2 Bn), 3.51 (2H, q, J = 10.6 Hz, 2-H_2), 2.30 (3H, s, Me). **^{13}C NMR (101 MHz, $CDCl_3$)** δ

146.17 (1C, C Ar), 146.11 (1C, C Ar), 146.0 (1C, C Ar), 139.2 (1C, C Ar), 137.4 (1C, C Ar), 134.6 (1C, C Ar), 130.1 (2C, CH Ar), 129.5 (1C, CH Ar), 129.1 (2C, CH Ar), 128.7 (2C, CH Ar), 127.9 (4C, CH Ar), 127.8 (1C, CH Ar), 127.5 (1C, CH Ar), 127.1 (1C, CH Ar), 126.3 (1C, CH Ar), 126.2 (1C, q, J = 279.4 Hz, CF_3), 126.1 (1C, CH Ar), 112.5 (2C, CH Ar), 53.5 (1C, C-1), 48.8 (1C, CH_2 Bn), 44.3 (1C, q, J = 26.2 Hz, C-2), 21.8 (1C, Me). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –55.9 (3F, CF_3). **HRMS** (ESI): calculated for $C_{29}H_{27}F_3N$ $[M+H]^+$ requires m/z 446.2091, found m/z 446.2087.

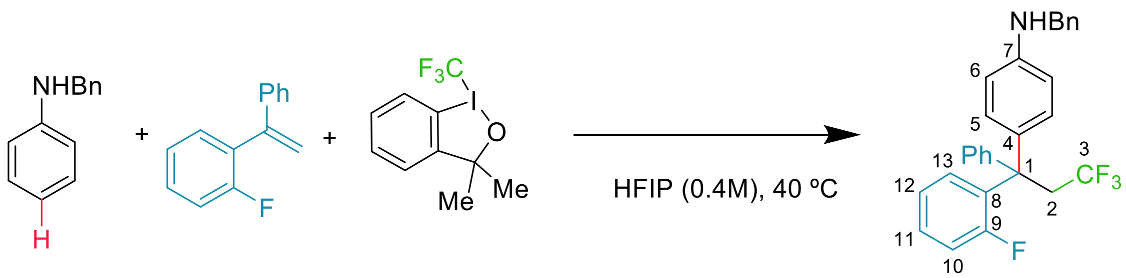
***N*-Benzyl-4-[1-(3-bromophenyl)-3,3,3-trifluoro-1-phenylpropyl]aniline, 4ae.**



From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2k** (51.8 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4ae** was obtained. Chromatographic purification (gradient elution: 5:95 → 15:85 Et_2O – hexane) gave **4ae** (60.4 mg, 60%), as a colourless oil.

Data for **4ae**: ***R**$_f$* 0.50 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (1H, s, 9-H), 7.42 – 7.18 (12H, m, Ar), 7.15 (1H, t, J = 7.9 Hz, 12-H), 7.06 (2H, d, J = 8.6 Hz, 5-H), 6.59 (2H, d, J = 8.7 Hz, 6-H), 4.31 (2H, s, CH_2 Bn), 4.19 (1H, br s, NH), 3.50 (2H, q, J = 10.5 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.5 (1C, C Ar), 146.5 (1C, C Ar), 145.2 (1C, C Ar), 139.2 (1C, C Ar), 133.5 (1C, C Ar), 131.9 (1C, CH Ar), 129.9 (2C, CH Ar), 129.5 (1C, CH Ar), 129.5 (1C, CH Ar), 128.9 (2C, CH Ar), 128.8 (2C, CH Ar), 128.1 (2C, CH Ar), 127.7 (3C, CH Ar), 127.5 (1C, CH Ar), 126.6 (1C, CH Ar), 126.0 (1C, q, J = 279.2 Hz, CF_3), 122.2 (1C, C Ar), 112.5 (2C, CH Ar), 53.4 (1C, C-1), 48.5 (1C, CH_2 Bn), 44.1 (1C, q, J = 26.5 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –55.9 (3F, CF_3). **HRMS** (ESI): calculated for $C_{28}H_{24}BrF_3N$ $[M+H]^+$ requires m/z 510.1039, found m/z 510.1011.

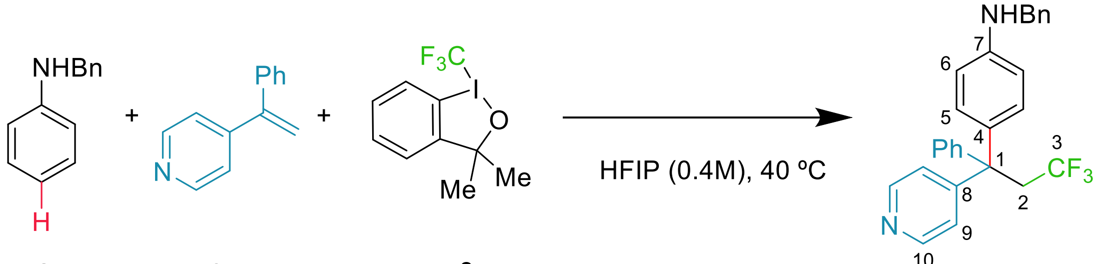
***N*-Benzyl-4-[3,3,3-trifluoro-1-(2-fluorophenyl)-1-phenylpropyl]aniline, 4af.**



From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2l** (39.6 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4af** was obtained. Chromatographic purification (gradient elution: 4:96 → 10:90 Et_2O – hexane) gave **4af** (57.9 mg, 65%), as a colourless oil.

Data for **4af**: R_f 0.45 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.11 (12H, m, Ar), 7.10 – 6.98 (2H, m, Ar), 7.02 (2H, d, J = 8.7 Hz, 5-H), 6.56 (2H, d, J = 8.8 Hz, 6-H), 4.30 (2H, s, CH_2 Bn), 4.00 (1H, s, NH), 3.76 – 3.55 (2H, m, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.6 (1C, d, J = 248.9 Hz, C-9), 146.6 (1C, C Ar), 145.6 (1C, C Ar), 139.4 (1C, C Ar), 133.4 (1C, C Ar), 131.7 (1C, d, J = 3.9 Hz, C-8), 131.4 (1C, d, J = 11.2 Hz, CH Ar), 129.4 (2C, CH Ar), 129.2 (1C, d, J = 8.9 Hz, CH Ar) 128.8 (2C, CH Ar), 128.0 (2C, CH Ar), 127.7 (2C, CH Ar), 127.4 (2C, CH Ar), 126.4 (2C, CH Ar), 126.2 (1C, q, J = 279.6 Hz, CF_3), 123.6 (1C, d, J = 3.2 Hz, CH Ar), 116.3 (1C, d, J = 23.9 Hz, C-10), 112.3 (2C, CH Ar), 52.0 (1C, C-1), 48.5 (1C, CH_2 Bn), 43.6 (1C, q, J = 26.8, 4.6 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –56.7 (3F, d, $^6J_{FF}$ = 2.0 Hz, CF_3), –103.3 (1F, q, $^6J_{FF}$ = 2.1 Hz, F Ar). **HRMS** (EI): calculated for $C_{28}H_{23}F_4N$ $[M]^+$ requires m/z 449.1762, found m/z 449.1766.

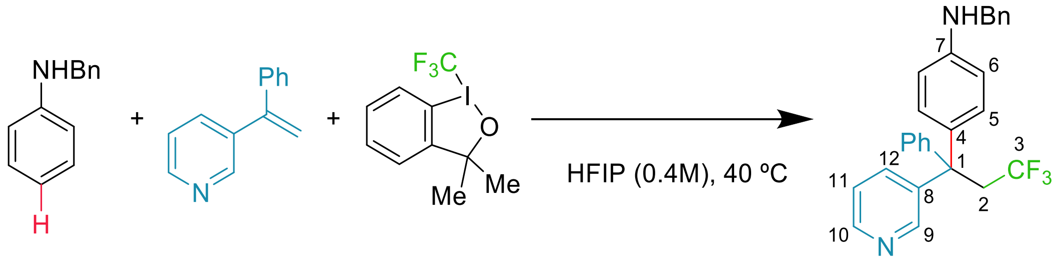
***N*-Benzyl-4-[3,3,3-trifluoro-1-phenyl-1-(pyridin-4-yl)propyl]aniline, 4ag.**



From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2m** (36.2 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4ag** was obtained. Chromatographic purification (gradient elution: 49:50:1 → 69:30:1 Et_2O – hexane – AcOH) gave **4ag** (35.9 mg, 41%), as a colourless oil.

Data for **4ag**: R_f 0.30 (70% Et_2O – hexane with 1% of AcOH). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.52 (2H, s, 10-H), 7.38 – 7.20 (12H, m, Ar), 7.00 (2H, d, J = 8.8 Hz, 5-H), 6.56 (2H, d, J = 8.8 Hz, 6-H), 4.30 (2H, s, CH_2 Bn), 3.49 (2H, q, J = 10.3 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.3 (1C, C Ar), 148.5 (2C, C-10), 147.0 (1C, C Ar), 144.0 (1C, C Ar), 139.1 (1C, C Ar), 132.2 (1C, C Ar), 129.8 (2C, CH Ar), 128.9 (2C, CH Ar), 128.8 (2C, CH Ar), 128.3 (2C, CH Ar), 127.7 (2C, CH Ar), 127.5 (1C, CH Ar), 127.1 (1C, CH Ar), 125.8 (1C q, J = 279.4 Hz, CF_3), 124.3 (2C, C-9), 112.5 (2C, CH Ar), 53.5 (1C, C-1), 48.4 (1C, CH_2 Bn), 43.6 (1C, q, J = 27.0 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –56.1 (3F, CF_3). **HRMS** (ESI): calculated for $C_{27}H_{24}F_3N_2$ $[M+H]^+$ requires m/z 433.1887, found m/z 433.1883.

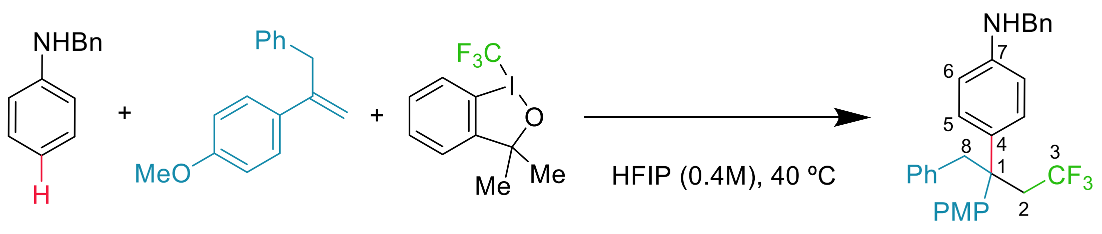
***N*-Benzyl-4[(3,3,3-trifluoro-1-phenyl-1-(pyridin-3-yl)propyl]aniline, 4ah.**



From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2n** (36.2 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4ah** was obtained. Chromatographic purification (gradient elution: 10:90 → 60:40 Et_2O – hexane) gave **4ah** (38.1 mg, 46%), as a colourless oil.

Data for **4ah**: $\boldsymbol{R_f}$ 0.10 (30% Et_2O – hexane). **H NMR (400 MHz, $CDCl_3$)** δ 8.59 (1H, s, 9-H), 8.46 (1H, d, J = 3.3 Hz, 10-H), 7.65 (1H, dt, J = 8.2 and 1.9 Hz, 12-H), 7.39 – 7.15 (11H, m, Ar), 7.02 (2H, d, J = 8.8 Hz, 5-H), 6.56 (2H, d, J = 8.8 Hz, 6-H), 4.30 (2H, s, CH_2 Bn), 4.04 (1H, s, NH), 3.52 (2H, q, J = 10.4 Hz, 2-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.2 (1C, C-9), 147.1 (1C, C Ar), 146.9 (1C, C-10), 145.0 (1C, C Ar), 141.5 (1C, C Ar), 139.2 (1C, C Ar), 137.0 (1C, C-12), 133.12 (1C, C Ar), 129.6 (2C, CH Ar), 128.8 (2C, CH Ar), 128.6 (2C, CH Ar), 128.3 (2C, CH Ar), 127.7 (2C, CH Ar), 127.5 (1C, CH Ar), 126.8 (1C, CH Ar), 125.9 (1C, q, J = 279.1 Hz, CF_3), 122.9 (1C, CH Ar), 112.5 (2C, CH Ar), 52.1 (1C, C-1), 48.4 (1C, CH_2 Bn), 43.9 (1C, q, J = 26.6 Hz, C-2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –56.0 (3F, CF_3). **HRMS** (ESI): calculated for $C_{27}H_{24}F_3N_2$ $[M+H]^+$ requires m/z 433.1887, found m/z 433.1786.

***N*-Benzyl-4-[4,4,4-trifluoro-2-(4-methoxyphenyl)-1-phenylbutan-2-yl]aniline, 4ai.**

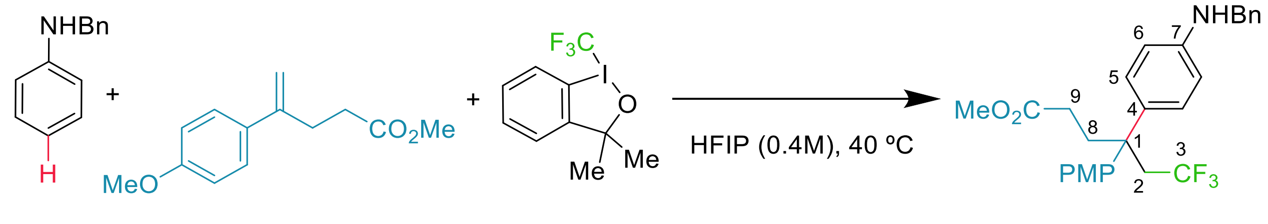


From aniline **1a** (36.6 mg, 0.20 mmol), alkene **2o** (44.9 mg, 0.20 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.20 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4ai** was obtained. Chromatographic purification (gradient elution: 0:100 → 20:80 Et_2O – hexane) gave **4ai** (45.1 mg, 51%), as a yellow oil.

Data for **4ai**: $\boldsymbol{R_f}$ 0.4 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.41 – 7.28 (5H, m, Ar), 7.23 (1H, t, J = 7.0 Hz, NH), 7.15 – 7.01 (5H, m, Ar), 6.84 – 6.76 (4H, m, Ar), 6.58 – 6.47 (4H, m, Ar), 4.25 (2H, s, CH_2 Bn), 3.72 (3H, s, OMe), 3.45 (1H, d, J = 13.3 Hz, 8-H_A), 3.41 (1H, d,

J = 13.2 Hz, 8-H_B), 2.89 – 2.72 (2H, m, 2-H_2). **^{13}C NMR (101 MHz, DMSO-d$_6$)** δ 157.3 (1C, C Ar), 146.4 (1C, C Ar), 140.0 (1C, C Ar), 138.4 (1C, C Ar), 137.0 (1C, C Ar), 133.6 (1C, C Ar), 130.5 (2C, CH Ar), 128.9 (2C, CH Ar), 128.2 (4C, CH Ar), 127.4 (2C, CH Ar), 127.4 (2C, CH Ar), 127.1 (1C, q, J = 279.0 Hz, CF_3), 126.7 (1C, CH Ar), 126.2 (1C, CH Ar), 112.9 (2C, CH Ar), 112.0 (2C, CH Ar), 54.9 (1C, OMe), 46.9 (1C, CH_2 Bn), 46.2 (1C, C-1), 44.4 (1C, C-8), 39.1 (1C, C-2). **^{19}F NMR (376 MHz, DMSO-d$_6$)** δ –55.9 (3F, CF_3). **HRMS** (ESI): calculated for $C_{30}H_{29}F_3NO$ $[M+H]^+$ requires m/z 476.2196 , found m/z 476.2190.

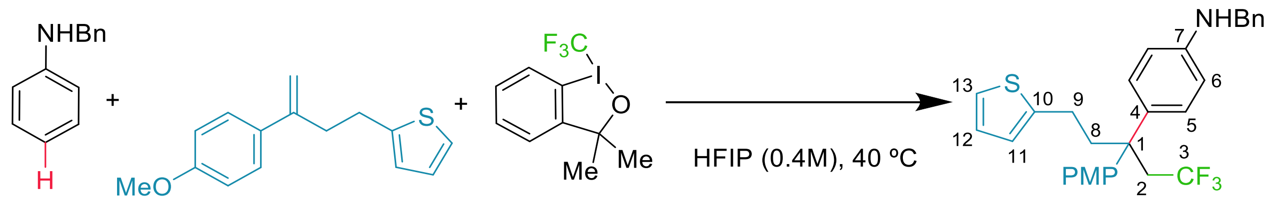
Methyl 4-[4-(benzylamino)phenyl]-6,6,6-trifluoro-4-(4-methoxyphenyl)hexanoate, 4aj.



From aniline **1a** (37.6 mg, 0.205 mmol), alkene **2p** (45.2 mg, 0.205 mmol) and trifluoromethyl reagent **3** (67.7 mg, 0.205 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4aj** was obtained. Chromatographic purification (gradient elution: 0:100 → 20:80 Et_2O – hexane) gave **4aj** (69.0 mg, 71%), as a yellow oil.

Data for **4aj**: $\boldsymbol{R_f}$ 0.15 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.27 (5H, m, Ar), 7.10 (2H, d, J = 8.9 Hz, Ar), 6.95 (2H, d, J = 8.7 Hz, 5-H), 6.81 (2H, d, J = 8.9 Hz, Ar), 6.57 (2H, d, J = 8.7 Hz, 6-H), 4.30 (2H, s, CH_2 Bn), 3.79 (3H, s, OMe), 3.60 (3H, s, CO_2Me), 2.91 (2H, q, J = 10.8 Hz, 2-H_2), 2.63 – 2.54 (2H, m, 9-H_2), 2.12 – 2.03 (2H, m, 8-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.9 (1C, C=O), 158.0 (1C, C Ar), 146.4 (1C, C Ar), 139.2 (1C, C Ar), 138.3 (1C, C Ar), 135.0 (1C, C Ar), 128.8 (2C, CH Ar), 128.7 (2C, CH Ar), 128.3 (2C, CH Ar), 127.8 (2C, CH Ar), 127.5 (1C, CH Ar), 126.7 (1C, q, J = 279.1 Hz, CF_3), 113.5 (2C, CH Ar), 112.8 (2C, C-6), 55.3 (1C, OMe), 51.7 (1C, CO_2Me), 48.7 (1C, CH_2 Bn), 45.3 (1C, C-1), 41.7 (1C, q, J = 25.5 Hz, C-2), 33.2 (1C, C-9), 29.7 (1, C-8). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –58.9 (3F, CF_3). **HRMS** (ESI): calculated for $C_{27}H_{29}F_3NO_3$ $[M+H]^+$ requires m/z 472.2095, found m/z 472.2075.

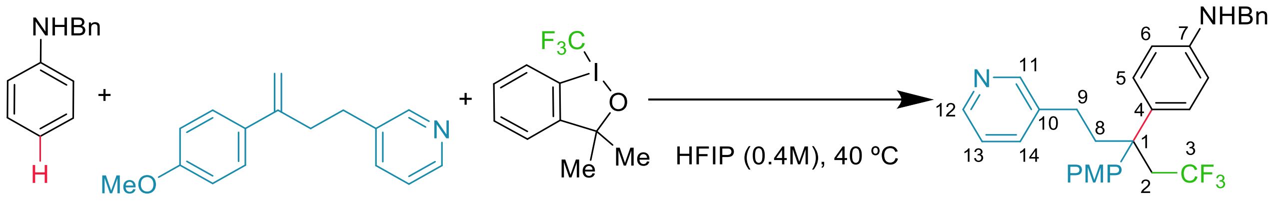
***N*-Benzyl-4-[1,1,1-trifluoro-3-(4-methoxyphenyl)-5-(thiophen-2-yl)pentan-3-yl]aniline, 4ak.**



From aniline **1a** (36.6 mg, 0.20 mmol), alkene **2q** (48.9 mg, 0.20 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.20 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4ak** was obtained. Chromatographic purification (gradient elution: 0:100 → 20:80 Et_2O – hexane) gave **4ak** (60.0 mg, 61%), as a colourless oil.

Data for **4ak**: R_f 0.25 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.27 (5H, m, Ar), 7.13 (2H, d, J = 8.9 Hz, Ar), 7.10 (1H, dd, J = 5.0 and 1.2 Hz, 13-H), 6.99 (2H, d, J = 8.7 Hz, 5-H), 6.90 (1H, dd, J = 5.1 and 3.4 Hz, 12-H), 6.83 (2H, d, J = 8.9 Hz, Ar), 6.73 (1H, dd, J = 3.4 and 1.1 Hz, 11-H), 6.59 (2H, d, J = 8.7 Hz, 6-H), 4.31 (2H, s, CH_2 Bn), 3.80 (3H, s, OMe), 3.00 (2H, qd, J = 10.8 and 2.0 Hz, 2-H_2), 2.65 – 2.58 (2H, m, 9-H_2), 2.57 – 2.51 (2H, m, 8-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.9 (1C, C Ar), 146.4 (1C, C Ar), 145.1 (1C, C Ar), 139.3 (1C, C Ar), 138.9 (1C, C Ar), 135.6 (1C, C Ar), 128.8 (2C, CH Ar), 128.6 (2C, CH Ar), 128.3 (2C, CH Ar), 127.9 (2C, CH Ar), 127.5 (1C, CH Ar), 126.9 (1C, C-12), 126.8 (1C, q, J = 279.0 Hz, CF_3), 124.2 (1C, C-11), 123.1 (1C, C-13), 113.5 (2C, CH Ar), 112.8 (2C, CH Ar), 55.3 (1C, OMe), 48.8 (1C, CH_2 Bn), 45.8 (1C, C-1), 41.5 (1C, q, J = 25.5 Hz, C-2), 40.7 (1C, C-9), 25.2 (1C, C-8). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –58.81 (3F, CF_3). **HRMS** (ESI): calculated for $C_{29}H_{29}F_3NOS$ $[M+H]^+$ requires m/z 496.1917, found m/z 496.1915.

***N*-Benzyl-4-[1,1,1-trifluoro-3-(4-methoxyphenyl)-5-(pyridin-3-yl)pentan-3-yl]aniline, 4al.**



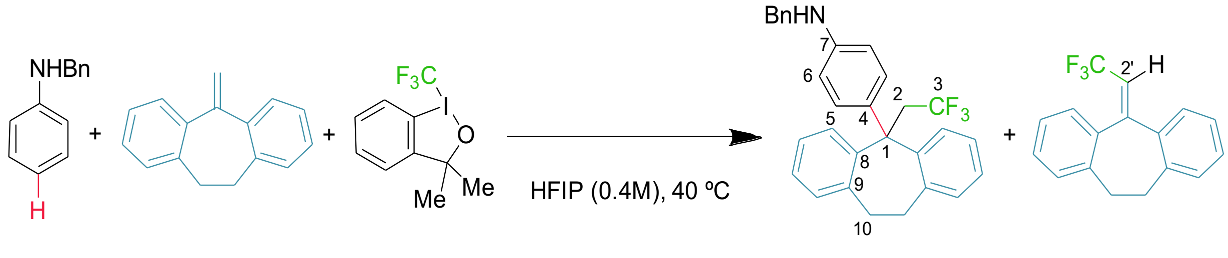
1a **2r** **3** **4al**

From aniline **1a** (36.6 mg, 0.20 mmol), alkene **2r** (47.9 mg, 0.20 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.20 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4al** was obtained. Chromatographic purification (gradient elution: 20:100 → 80:20 Et_2O – hexane) gave **4al** (75.4 mg, 77%), as a colourless oil.

Data for **4al**: R_f 0.1 (70% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.44 (1H, d, J = 3.9 Hz, 12-H), 8.32 (1H, s, 11-H), 7.43 (1H, dt, J = 7.8 and 2.0 Hz, 14-H), 7.40 – 7.27 (5H, m, Ar), 7.21 (1H, dd, J = 7.8 and 4.8 Hz, 13-H), 7.11 (2H, d, J = 8.9 Hz, Ar), 6.96 (2H, d, J = 8.7 Hz, 5-H), 6.82 (2H, d, J = 8.9 Hz, Ar), 6.58 (2H, d, J = 8.7 Hz, 6-H), 4.30 (2H, s, CH_2 Bn), 3.79 (3H, s, OMe), 3.12 – 2.93 (2H, m, 2-H_2), 2.50 (2H, m, 9-H_2), 2.33 (2H, m, 8-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.0 (1C, C Ar), 149.7 (1C, C-12), 147.2 (1C, C-11), 146.6 (1C, C Ar), 139.4 (1C, C Ar), 139.0 (1C, C Ar), 137.9 (1C, C Ar), 136.2 (1C, C-14), 135.5 (1C, C Ar), 128.8 (2C, CH Ar), 128.5 (2C, CH Ar), 128.2 (2C, CH Ar), 128.0 (2C, CH Ar), 127.5 (1C, CH Ar), 126.9 (1C, q, J = 279.5 Hz, CF_3), 123.6

(1C, C-13), 113.6 (2C, CH Ar), 112.7 (2C, CH Ar), 55.3 (1C, OMe), 48.6 (1C, CH_2 Bn), 45.8 (1C, C-1), 41.2 (1C, q, J = 25.6 Hz, C-2), 40.5 (1C, C-9), 28.2 (1C, C-8). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –58.8 (3F, CF_3) **HRMS** (ESI): calculated for $C_{30}H_{230}F_3N_2O$ [M+H]$^+$ requires *m/z* 491.2305, found *m/z* 491.2301.

***N*-Benzyl-4-[5-(2,2,2-trifluoroethyl)-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl]aniline, 4am.**

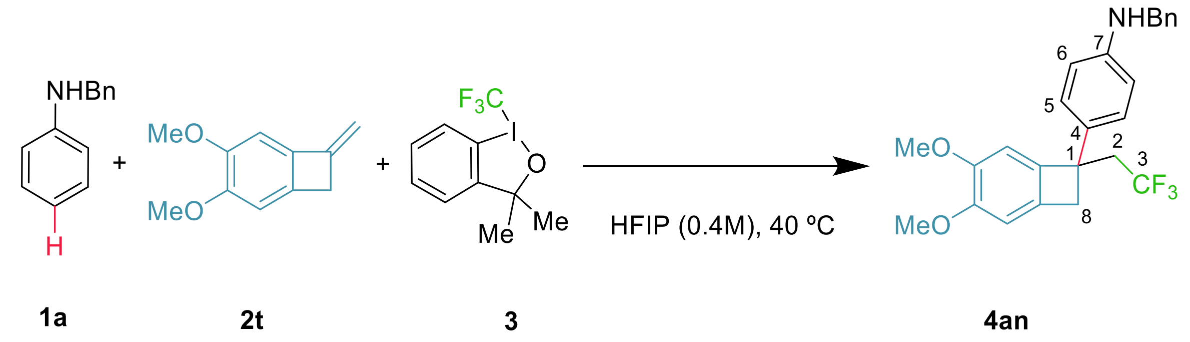


From aniline **1a** (36.6 mg, 0.20 mmol), alkene **2s** (41.3 mg, 0.20 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.20 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4am** was obtained. Chromatographic purification (gradient elution: 5:95 → 10:90 Et_2O – hexane) gave **4am** (38.0 mg, 42%), as a colourless oil and a 2:1 mixture of unreacted alkene **2s** : trifluoromethyl alkene **2s-CF₃** (25.8 mg).

Data for **4am**: ***R*$_f$** 0.5 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.26 (5H, m, Ar), 7.25 – 7.18 (2H, m, Ar), 7.13 – 7.07 (4H, m, Ar), 7.06 – 6.99 (2H, m, Ar), 6.92 (2H, d, J = 8.6 Hz, Ar), 6.57 (2H, d, J = 8.6 Hz, 6-H), 4.29 (2H, s, CH_2 Bn), 3.49 (2H, q, J = 10.2 Hz, 2-H_2), 2.90 (4H, s, 10-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.7 (2C, C Ar), 143.9 (1C, C Ar), 139.7 (2C, C Ar), 138.7 (2C, C Ar), 131.5 (2C, CH Ar), 128.9 (2C, CH Ar), 128.8 (2C, CH Ar), 128.0 (2C, CH Ar), 127.6 (1C, CH Ar), 127.5 (2C, CH Ar), 126.7 (2C, CH Ar), 126.4 (1C, q, J = 280.7 Hz, CF_3), 125.9 (2C, CH Ar), 113.2 (2C, CH Ar), 53.1 (1C, C-1), 49.0 (1C, CH_2 Bn), 46.4 (1C, C-2), 34.1 (2C, C-10). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –56.1 (3F, CF_3). **HRMS** (ESI): calculated for $C_{30}H_{27}F_3N$ [M+H]$^+$ requires *m/z* 458.2091, found *m/z* 458.2094.

Partial data for **2s-CF₃** (from the mixture): ***R*$_f$** 0.5 (5% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 – 6.96 (8H, m, Ar), 6.03 (1H, q, J = 8.1 Hz, 2-H), 3.57 – 3.26 (2H, m, CH_2), 3.10 – 2.75 (2H, m, CH_2). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –56.03 (3F, CF_3).

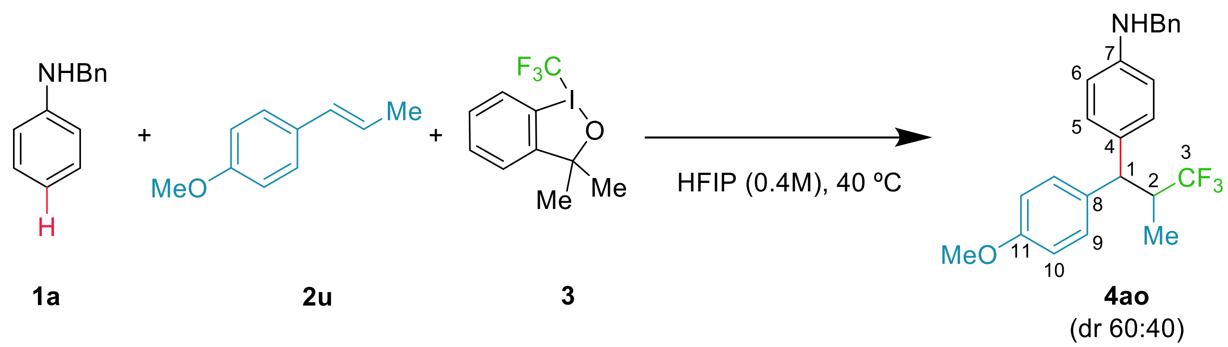
N-Benzyl-4-[5-(2,2,2-trifluoroethyl)-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl]aniline, 4an.



From aniline **1a** (36.6 mg, 0.20 mmol), alkene **2t** (45.2 mg, 0.20 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.20 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4an** was obtained. Chromatographic purification (gradient elution: 0:100 → 50:50 Et_2O – hexane) gave **4an** (16.8 mg, 20%), as a colourless oil.

Data for **4an**: R_f 0.1 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.40 – 7.28 (5H, m, Ar), 7.19 (2H, d, J = 8.6 Hz, 5-H), 6.98 (1H, d, J = 1.2 Hz, Ar), 6.69 (1H, s, Ar), 6.68 (2H, d, J = 8.4 Hz, 6-H) 4.31 (2H, s, CH_2 Bn), 3.92 (3H, s, OMe), 3.84 (3H, s, OMe), 3.38 (1H, d, J = 13.2 Hz, 8-H$_A$), 3.27 (1H, d, J = 13.3 Hz, 8-H$_B$), 3.00 – 2.89 (1H, m, 2-H$_A$), 2.69 (1H, dq, J = 14.9 and 10.8 Hz, 2-H$_B$). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 150.8 (1C, C Ar), 149.8 (1C, C Ar), 139.3 (1C, C Ar), 138.2 (1C, C Ar), 137.0 (1C, C Ar), 133.1 (1C, C Ar), 132.4 (1C, C Ar), 128.8 (2C, CH Ar), 128.2 (1C, CH Ar), 127.7 (4C, CH Ar), 126.5 (1C, q, J = 278.5 Hz, CF_3), 114.0 (2C, C-6) 108.1 (1C, CH Ar), 107.7 (1C, CH Ar), 56.6 (1C, OMe), 56.4 (1C, OMe), 50.5 (1C, C-1), 49.4 (1C, CH_2 Bn), 46.0 (1C, C-8), 44.5 (1C, q, J = 26.3 Hz, C-2). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –61.2 (3F, CF_3). **HRMS** (ESI): calculated for $C_{25}H_{25}F_3NO_2$ $[M+H]^+$ requires m/z 428.1832, found m/z 428.1825.

N-Benzyl-4-(3,3,3-trifluoro-1-(4-methoxyphenyl)-2-methylpropyl)aniline, 4ao.

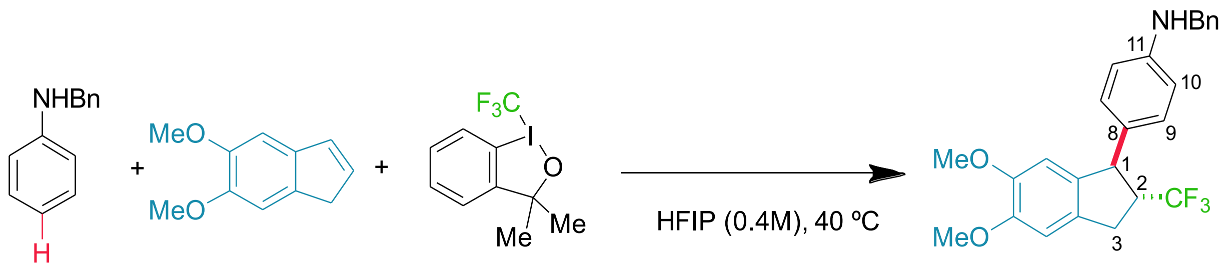


From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2u** (29.6 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4ao** was obtained as a 60:40 diastereomeric ratio. Chromatographic purification (gradient elution: 0:100 → 15:85 Et_2O – hexane) gave **4ao** (55.3 mg, 70%) in a 60:40 diastereomeric ratio, as a colourless oil.

Data for **4ao-major isomer** (from the mixture): $\boldsymbol{R_f}$ 0.30 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.41 – 7.25 (5H, m, Ar), 7.17 (2H, d, J = 8.7 Hz, 9-H), 7.10 (2H, d, J = 8.5 Hz, 5-H), 6.84 (2H, d, J = 8.9 Hz, 10-H), 6.57 (2H, d, J = 8.6 Hz, 6-H), 4.29 (2H s, CH_2 Bn), 3.96 (1H, d, J = 9.5 Hz, 1-H), 3.78 (3H, s, OMe), 3.17 – 2.98 (1H, m, 2-H), 1.07 (3H, d, J = 7.0 Hz, Me). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.2 (1C, C Ar), 146.7 (1C, C Ar), 139.5 (1C, C Ar), 134.9 (1C, C Ar), 132.2 (1C, C Ar), 129.3 (2C, CH Ar), 128.7 (2C, CH Ar), 128.5 (2C, CH Ar), 127.7 (2C, CH Ar), 127.3 (1C, CH Ar), 128.3 (1C, q, J = 281.0 Hz, CF_3), 114.0 (2C, CH Ar), 112.9 (2C, CH Ar), 55.3 (1C, OMe), 50.7 (1C, C-1), 48.6 (1C, CH_2 Bn), 41.9 (1C, q, J = 24.0 Hz, C-2), 13.0 (1C, d, J = 3.1 Hz, Me). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –68.5 (3F, CF_3). **HRMS** (EI): calculated for $C_{24}H_{24}F_3NO$ $[M]^+$ requires m/z 399.1805, found m/z 399.1784.

Partial data for **4ao-minor isomer** (from the mixture): The NMR signals overlapped with those of **4ao-major isomer**, except for: **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.21 (2H, d, J = 8.7 Hz, 9-H), 7.05 (2H, d, J = 8.6 Hz, 5-H), 6.82 (2H, d, J = 8.7 Hz, 10-H), 6.58 (2H, d, J = 8.6 Hz, 6-H), 3.92 (1H, d, J = 9.9 Hz, 1-H), 3.77 (3H, s, OMe), 1.09 (3H, d, J = 6.9 Hz, Me). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.0 (1C, C Ar), 146.9 (1C, C Ar), 135.8 (1C, C Ar), 131.4 (1C, C Ar), 128.7 (2C, CH Ar), 128.6 (1C, CH Ar), 127.6 (2C, CH Ar), 127.4 (1C, CH Ar), 113.8 (2C, CH Ar), 113.1 (2C, CH Ar), 55.2 (1C, OMe), 50.9 (1C, C-1), 48.5 (1C, CH_2 Bn), 42.0 (1C, q, J = 23.9 Hz, C-2), 13.2 (1C, d, J = 3.1 Hz, Me). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –68.4 (3F, CF_3).

***N*-Benzyl-4-[5,6-dimethoxy-2-(trifluoromethyl)-2,3-dihydro-1H-inden-1-yl]aniline, 4ap.**

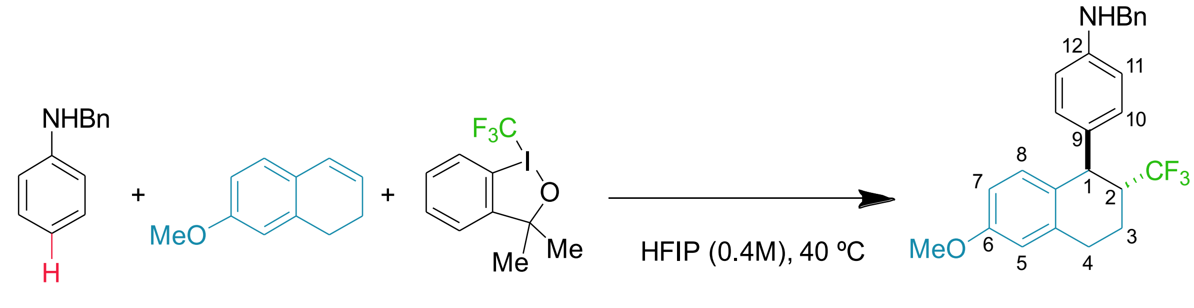


1a **2v** **3** **4ap**

From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2v** (35.2 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP at room temperature, following the general procedure, aniline **4ap** was obtained. Chromatographic purification (gradient elution: 15:85 → 20:80 Et_2O – hexane) gave **4ap** (42.5 mg, 50%), as a colourless oil.

Data for **4ap**: $\boldsymbol{R_f}$ 0.10 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.42 – 7.27 (5H, m, Ar), 6.97 (2H, d, J = 8.5 Hz, 9-H), 6.78 (1H, s, Ar), 6.61 (2H, d, J = 8.5 Hz, 10-H), 6.43 (1H, s, Ar), 4.42 (1H, d, J = 6.9 Hz, 1-H), 4.32 (2H, s, CH_2 Bn), 4.03 (1H, br s, NH), 3.89 (3H, s, OMe), 3.74 (3H, s, OMe), 3.28 – 3.18 (1H, m, 3-H_A), 3.15 – 2.99 (2H, m, 3-H_B and 2-H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 148.9 (2C, C Ar), 147.2 (1C, C Ar), 139.4 (1C, C Ar), 136.5 (1C, C Ar), 132.7 (1C, C Ar), 132.0 (1C, C Ar), 129.1 (2C, C-9), 128.7 (2C, CH Ar), 127.7 (2C, CH Ar), 128.2 (1C, q, J = 278.3 Hz, CF_3), 127.4 (1C, CH Ar), 113.1 (2C, C-10), 108.06 (1C, CH Ar), 107.0 (1C, CH Ar), 56.2 (2C, 2 x OMe), 52.9 (1C, q, J = 25.7 Hz, C-2), 51.3 (1C, C-1), 48.6 (1C, CH_2 Bn), 32.2 (1C, C-3). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –70.3 (3F, CF_3). **HRMS** (EI): calculated for $C_{25}H_{24}F_3NO_2$ $[M]^+$ requires *m/z* 427.1754, found *m/z* 427.1749.

***N*-Benzyl-4-[6-methoxy-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-yl]aniline, 4aq.**

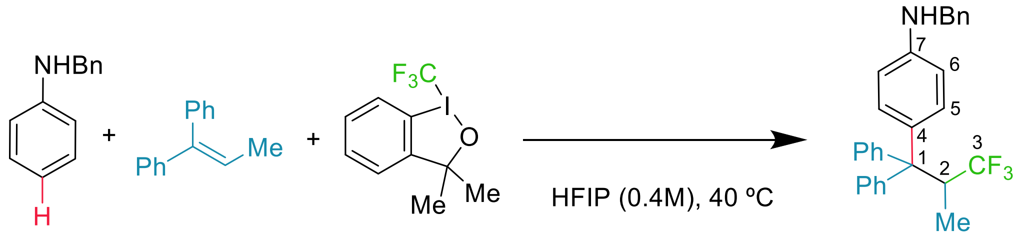


1a **2w** **3** **4aq**

From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2w** (32.0 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4aq** was obtained. Chromatographic purification (gradient elution: 0:100 → 15:85 Et_2O – hexane) gave **4aq** (66.4 mg, 81%) as a colourless oil.

Data for **4aq**: ***R**$_f$* 0.30 (20% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.23 (5H, m, Ar), 6.90 (2H, d, J = 8.5 Hz, 10-H), 6.82 (1H, d, J = 8.2 Hz, 8-H), 6.67 (1H, s, 5-H), 6.66 (1H, d, J = 8.3 Hz, 7-H), 6.59 (2H, d, J = 8.6 Hz, 11-H), 4.31 (2H, s, CH_2 Bn), 4.17 (1H, d, J = 6.8 Hz, 1-H), 3.97 (1H, d, J = 3.6 Hz, NH), 3.79 (3H, s, OMe), 2.91 (2H, t, J = 6.5 Hz, 4-H_2), 2.76 – 2.59 (1H, m, 2-H), 2.18 (1H, dtd, J = 13.5, 6.1 and 3.9 Hz, 3-H_A), 1.90 (1H, ddt, J = 13.7, 8.9 and 7.0 Hz, 3-H_B). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.7 (1C, C Ar), 146.8 (1C, C Ar), 139.5 (1C, C Ar), 137.2 (1C, C Ar), 134.9 (1C, C Ar), 131.6 (1C, C-8), 130.2 (1C, C Ar), 129.6 (2C, C-10), 128.7 (2C, CH Ar), 128.1 (1C, q, J = 281.1 Hz, CF_3), 127.7 (2C, CH Ar), 127.4 (1C, CH Ar), 112.9 (2C, C-11), 112.8 (1C, C-7), 112.7 (1C, C-5), 55.2 (1C, OMe), 48.6 (1C, CH_2 Bn), 46.7 (1C, q, J = 24.4 Hz, C-2), 43.0 (1C, C-1), 27.7 (1C, C-4), 20.9 (1C, C-3). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –69.5 (3F, CF_3). **HRMS** (EI): calculated for $C_{25}H_{24}F_3NO$ $[M]^+$ requires *m/z* 411.1805, found *m/z* 411.1815.

***N*-Benzyl-4-(3,3,3-trifluoro-1,1-diphenylpropyl)aniline, 4ar.**

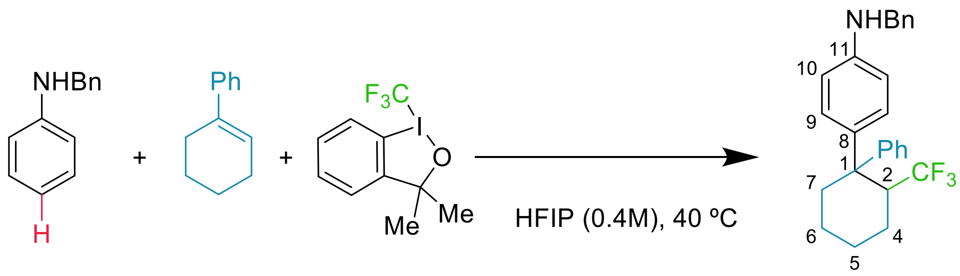


1a **2x** **3** **4ar**

From aniline **1a** (36.0 mg, 0.20 mmol), alkene **2x** (38.2 mg, 0.20 mmol) and trifluoromethyl reagent **3** (64.9 mg, 0.20 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4ar** was obtained. Chromatographic purification (gradient elution: 0:100 → 15:85 Et_2O – hexane) gave **4ar** (61.1 mg, 70%), as a colourless oil.

Data for **4ar**: $\boldsymbol{R_f}$ 0.5 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.27 (10H, m, Ar), 7.23 (3H, m, Ar), 7.17 (4H, m, Ar), 6.58 (2H, d, *J* = 8.6 Hz, H-6), 4.29 (2H, s, CH_2 Bn), 4.28 – 4.10 (1H, m, 2-H), 1.27 (3H, d, *J* = 6.8 Hz, Me). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.7 (1C, C Ar), 139.0 (1C, C Ar), 130.9 (1C, C Ar), 129.9 (1C, C Ar), 129.2 (1C, C Ar), 128.8 (3C, CH Ar), 128.1 (1C, q, *J* = 282.8 Hz, CF_3), 128.0 (3C, CH Ar), 127.7 (3C, CH Ar), 127.62 (3C, CH Ar), 127.56 (3C, CH Ar), 125.9 (2C, CH Ar), 112.5 (2C, CH Ar), 58.2 (1C, C-1), 49.0 (1C, CH_2 Bn), 42.7 (1C, q, *J* = 23.6 Hz, C-2), 11.7 (1C, Me). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –61.6 (3F, CF_3). **HRMS** (ESI): calculated for $C_{29}H_{27}F_3N$ $[M+H]^+$ requires m/z 446.2091, found m/z 446.2084.

***N*-Benzyl-4-[1-phenyl-2-(trifluoromethyl)cyclohexyl]aniline, 4as.**



1a **2y** **3** **4as** (dr 65:35)

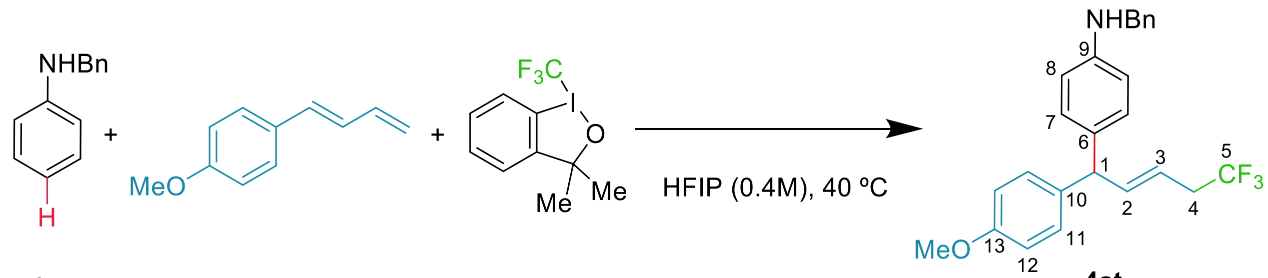
From aniline **1a** (31.6 mg, 0.2 mmol), alkene **2y** (36.7 mg, 0.2 mmol), and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4as** was obtained as a 65:35 diastereomeric ratio. Chromatographic purification (gradient elution: 0:100 → 10:90 Et_2O – hexane) gave **4as** (24 mg, 37%) in a 65:35 diastereomeric ratio, as a colourless oil.

Data for **4as-major isomer** (from the mixture): $\boldsymbol{R_f}$ 0.50 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.09 (10H, m, Ar), 7.09 (2H, d, *J* = 8.7 Hz, 9-H), 6.61 (2H, d, *J* = 8.7 Hz, 10-H), 4.30 (2H, s, CH_2 Bn), 4.08 (1H, s, NH), 3.44 – 3.30 (1H, m, 2-H), 2.74 – 2.59 (1H, m, CH_2 *c*-Hex), 2.48 – 2.36 (1H, m, CH_2 *c*-Hex), 2.14 – 2.00 (2H, m, CH_2 *c*-Hex), 1.77 – 1.65 (1H, m, CH_2 *c*-

Hex), 1.66 – 1.47 (2H, m, CH_2 *c*-Hex), 1.41 – 1.21 (1H, m, CH_2 *c*-Hex). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.5 (1C, C Ar), 145.9 (1C, C Ar), 139.4 (1C, C Ar), 135.3 (1C, C Ar), 128.7 (2C, CH Ar), 128.4 (1C, q, *J* = 283.8 Hz, CF_3), 128.0 (2C, CH Ar), 127.8 (2C, CH Ar), 127.7 (2C, CH Ar), 127.5 (1C, CH Ar), 127.1 (1C, CH Ar), 125.8 (2C, CH Ar), 113.1 (2C, C-10), 48.7 (1C, CH_2 Bn), 46.7 (1C, C-1), 45.9 (1C, q, *J* = 20.9 Hz, C-2), 31.8 (1C, CH_2 *c*-Hex), 23.2 (1C, q, *J* = 3.0 Hz, C-4), 22.0 (1C, CH_2 *c*-Hex), 21.8 (1C, CH_2 *c*-Hex). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –58.0 (3F, CF_3), –58.2 (3F, CF_3). **HRMS** (EI): calculated for $C_{26}H_{26}F_3N$ $[M]^+$ requires *m*/*z* 409.2012, found *m*/*z* 409.2022.

Partial data for **4as-minor isomer** (from the mixture): The NMR signals overlapped with those of **4as-major isomer**, except for: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.03 (2H, d, *J* = 8.7 Hz, 9-H), 6.53 (2H, d, *J* = 8.7 Hz, 10-H), 4.27 (2H, s, CH_2 Bn). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1 (1C, C Ar), 139.5 (1C, C Ar), 135.7 (1C, C Ar), 127.4 (1C, CH Ar), 125.7 (1C, C Ar), 112.4 (2C, C-10), 47.0 (1C, C-2), 32.9 (1C, CH_2 *c*-Hex), 23.3 (1C, q, *J* = 3.2 Hz, C-4), 22.2 (1C, CH_2 *c*-Hex), 22.1 (1C, CH_2 *c*-Hex).

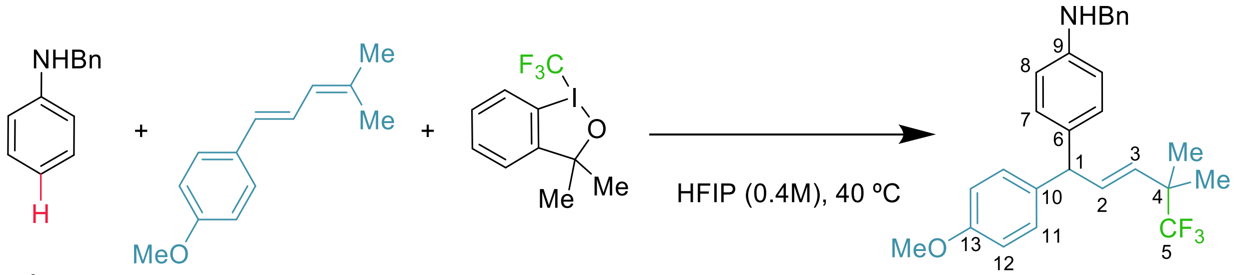
(*E*)-*N*-Benzyl-4-[5,5,5-trifluoro-1-(4-methoxyphenyl)pent-2-en-1-yl]aniline, 4at.



From aniline **1a** (36.6 mg, 0.2 mmol), alkene **2z** (32 mg, 0.2 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4at** was obtained. Chromatographic purification (gradient elution: 0:100 → 15:85 Et_2O – hexane) gave **4at** (44.9 mg, 55%), as a colourless oil.

Data for **4at**: ***Rf*** 0.4 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.26 (5H m, Ar), 7.06 (2H, d, *J* = 8.6 Hz, 11-H), 6.96 (2H, d, *J* = 8.5 Hz, 7-H), 6.83 (2H, d, *J* = 8.7 Hz, 12-H), 6.65 (2H, d, *J* = 8.5 Hz, 8-H), 6.12 (1H, dd, *J* = 15.4 and 7.3 Hz, 2-H), 5.33 (1H, dtd, *J* = 15.4, 7.1 and 1.3 Hz, 3-H), 4.60 (1H, d, *J* = 7.3 Hz, 1-H), 4.30 (2H, s, CH_2 Bn), 3.78 (3H, s, OMe), 2.84 (2H, qd, *J* = 10.6 and 7.2 Hz, 4-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2 (1C, C Ar), 146.1 (1C, C Ar), 141.2 (1C, C-2), 139.0 (1C, C Ar), 135.7 (1C, C Ar), 132.9 (1C, C Ar), 129.5 (2C, CH Ar), 129.4 (2C, CH Ar), 128.8 (2C, CH Ar), 127.9 (2C, CH Ar), 127.5 (1C, CH Ar), 126.0 (1C, q, *J* = 276.7 Hz, CF_3), 118.86 (1C, C-3), 113.9 (2C, CH Ar), 113.6 (2C, CH Ar), 55.4 (1C, OMe), 52.3 (1C, C-1), 49.0 (1C, CH_2 Bn), 37.4 (1C, q, *J* = 29.6 Hz, C-4). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –66.4 (3F, CF_3). **HRMS** (EI): calculated for $C_{25}H_{25}F_3NO$ $[M+H]^+$ requires *m*/*z* 412.1883, found 412.1885.

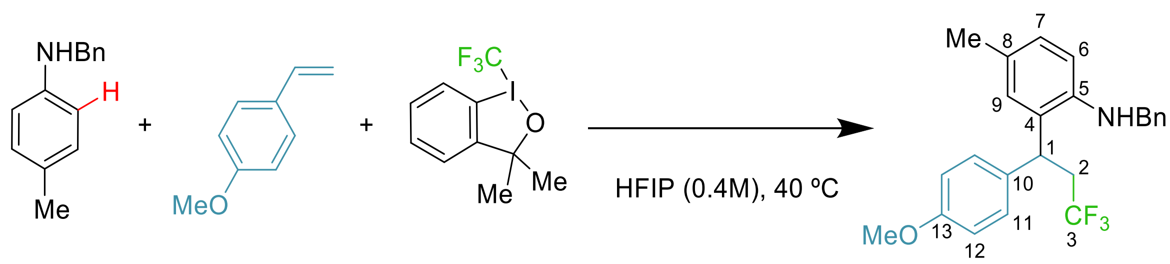
(*E*)-*N*-Benzyl-4-[5,5,5-trifluoro-1-(4-methoxyphenyl)-4,4-dimethylpent-2-en-1-yl]aniline, 4au.



From aniline **1a** (36.7 mg, 0.20 mmol), alkene **2aa** (37.7 mg, 0.20 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.20 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4au** was obtained. Chromatographic purification (gradient elution: 0:100 → 5:95 Et_2O – hexane) gave **4au** (44.5 mg, 52%), as a colourless oil.

Data for **4au**: R_f 0.4 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.28 (5H, m, Ar), 7.07 (2H, d, *J* = 8.7 Hz, 11-H), 6.96 (2H, d, *J* = 8.5 Hz, 7-H), 6.85 (2H, d, *J* = 8.7 Hz, 12-H), 6.62 (2H, d, *J* = 8.5 Hz, 8-H), 6.06 (1H, dd, *J* = 15.7 and 7.5 Hz, 2-H), 5.49 (1H, d, *J* = 15.8 Hz, 3-H), 4.60 (1H, d, *J* = 7.5 Hz, 1-H), 4.32 (2H, s, CH_2 Bn), 3.80 (3H, s, OMe), 1.25 (6H, s, 2 x Me). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1 (1C, C Ar), 146.4 (1C, C Ar), 139.4 (1C, C Ar), 136.1 (1C, C Ar), 135.2 (1C, C-3), 133.0 (1C, C Ar), 131.1 (1C, C-2), 129.5 (2C, CH Ar), 129.4 (2C, CH Ar), 128.8 (2C, CH Ar), 128.6 (1C, q, *J* = 282.0 Hz, CF_3), 127.8 (2C, CH Ar), 127.4 (1C, CH Ar), 113.9 (2C, CH Ar), 113.3 (2C, CH Ar), 55.4 (1C, OMe), 52.2 (1C, C-1), 48.9 (1C, CH_2 Bn), 42.4 (1C, q, *J* = 25.3 Hz, C-4), 21.4 (2C, 2 x Me). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –77.9 (3F, CF_3). **HRMS** (ESI): calculated for $C_{27}H_{29}F_3NO$ $[M+H]^+$ requires *m/z* 440.2196, found *m/z* 440.2185.

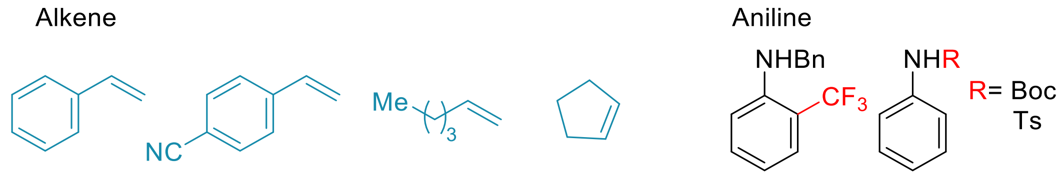
***N*-Benzyl-4-methyl-2-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, S10.**



From aniline **1v** (39.5 mg, 0.20 mmol), alkene **2a** (26.8 mg, 0.20 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.20 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **S10** was obtained. Chromatographic purification (gradient elution: 0:100 → 20:80 Et_2O – hexane) gave **S10** (21.1 mg, 26%), as a colourless oil.

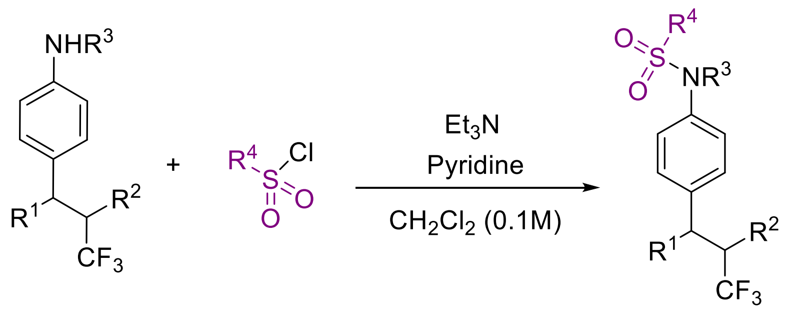
Data for **S10**: ***R**$_f$* 0.50 (20% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.35 (3H, m, H Ar), 7.26 (2H, d, *J* = 8.7 Hz, 11-H), 7.18 (2H, d, *J* = 8.0, H Ar), 7.13 (1H, d, *J* = 2.0 Hz, 9-H), 7.07 (1H, dd, *J* = 8.1 and 1.3 Hz, 7-H), 6.93 (1H, d, *J* = 8.7 Hz, 6-H), 6.68 (2H, d, *J* = 8.1 Hz, 12-H), 4.42 (1H, br s, 1-H), 4.31 (2H, s, CH_2 Bn), 3.90 (3H, s, OMe), 3.13 – 2.89 (2H, m, 2-H_2), 2.42 (3H, s, Me). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.8 (1C, C Ar), 147.3 (1C, C Ar), 142.5 (1C, C Ar), 139.0 (1C, C Ar), 136.1 (1C, C Ar), 133.4 (1C, C Ar), 129.2 (2C, CH Ar), 128.6 (3C, CH Ar) 128.4 (2C, CH Ar), 127.5 (2C, CH Ar), 127.3 (1C, CH Ar), 126.8 (1C, q, *J* = 277.5 Hz, CF_3), 114.4 (2C, CH Ar), 55.4 (1C, OMe), 48.7 (1C, CH_2 Bn), 39.17 (1C, q, *J* = 27.1 Hz, C-2), 38.99 (1C, q, *J* = 2.9 Hz, C-1) 20.9 (1C, Me). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –64.1 (3F, CF_3).

4.1. Unsuccessful or low yielding substrates



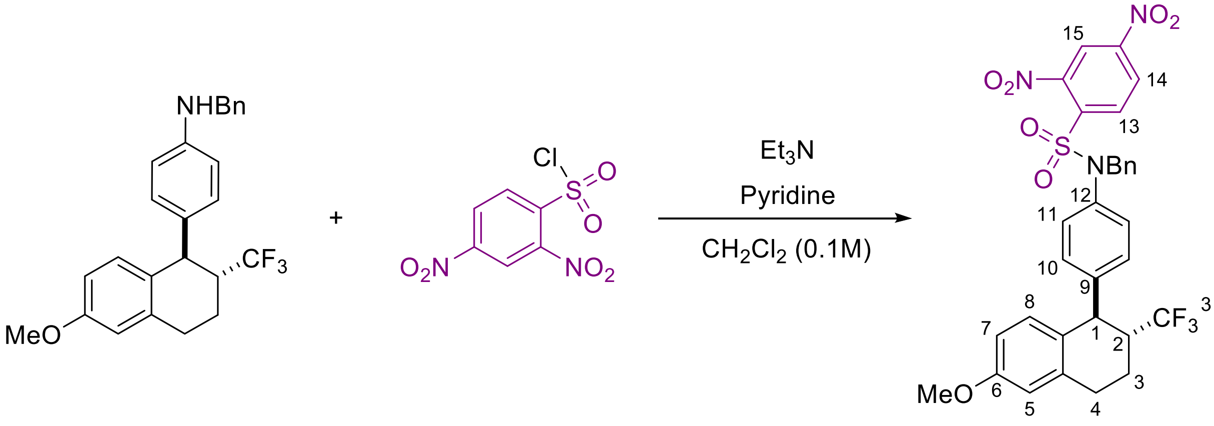
5. Derivatization of trifluoromethyl products

5.1. General procedure for the synthesis of sulfonamides



To an oven-dried vial/flask a solution of aniline in CH_2Cl_2 (0.1 M) was added, followed by triethylamine (2-3 equiv.), pyridine (0-2 equiv.) and sulfonyl chloride (1.2-2.1 equiv.) at 0 ºC. The reaction mixture was let warm up to rt and stirred overnight. The reaction mixture was diluted with CH_2Cl_2, extracted with water and the organic layers dried over Na_2SO_4. The resulting crude was purified by silica gel chromatography using the appropriate mixture of eluents.

***N*-Benzyl-*N*-{4-[(1R,2R)-6-methoxy-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-yl]phenyl}-2,4-dinitrobenzenesulfonamide, 5.**

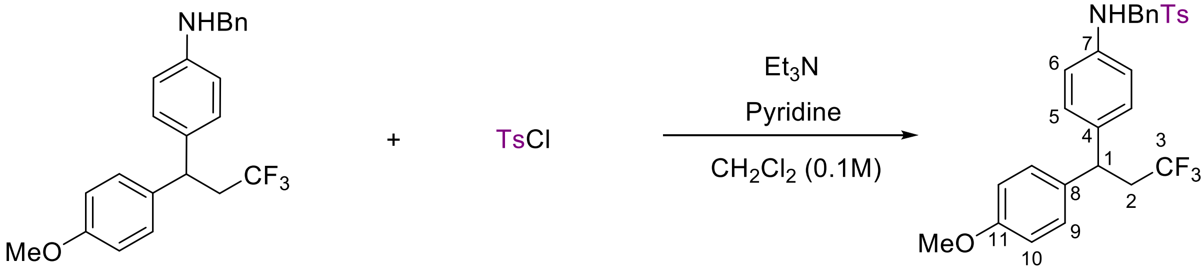


4aq 5

From aniline **4aq** (149.0 mg, 0.362 mmol), triethylamine (101 μL, 0.734 mmol, 2.0 equiv.), pyridine (58.6 μL, 0.734 mmol, 2.0 equiv.) and 2,4-dinitrosulfonyl chloride (145 mg, 0.543 mmol, 1.5 equiv.), in 3.6 mL of dry CH_2Cl_2, following the general procedure, sulfonamide **5** was obtained. Chromatographic purification (gradient elution: 0:100 → 40:70 Et_2O – hexane) gave **5**, as a brown solid. The solid was washed 3 times using a mixture of CH_2Cl_2/pentane to give a white solid (75.1 mg, 32%), that was recrystalized using THF – pentane, to give white crystals for x-ray diffraction.

Data for **5**: R_f 0.2 (40% Et_2O – hexane). **m.p.**: 197 ºC (10% THF – pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (1H, d, *J* = 2.2 Hz, 15-H), 8.22 (1H, dd, *J* = 8.7 and 2.2 Hz, 14-H), 7.66 (1H, d, *J* = 8.7 Hz, 13-H), 7.31 – 7.18 (5H, m, Ar), 6.97 (4H, br s, 10-H and 11-H) 6.63 (1H, d, *J* = 2.7 Hz, 5-H), 6.60 (1H, dd, *J* = 8.5 and 2.7 Hz, 7-H), 6.51 (1H, d, *J* = 8.5 Hz, 8-H), 4.98 (1H, d, *J* = 14.7 Hz, CH_A Bn), 4.92 (1H, d, *J* = 14.8 Hz, CH_B Bn), 4.13 (1H, d, *J* = 8.6 Hz, 1-H), 3.77 (3H, s, OMe), 2.90 (2H, t, *J* = 6.4 Hz, 4-H_2), 2.64 – 2.52 (1H, m, 2-H), 2.23 – 2.11 (1H, m, 3-H_A), 1.91 – 1.77 (1H, m, 3-H_B). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2 (1C, C Ar), 149.8 (1C, C Ar), 148.1 (1C, C Ar), 146.7 (1C, C Ar), 137.8 (1C, C Ar), 137.2 (1C, C Ar), 135.6 (1C, C Ar), 135.5 (1C, C Ar), 134.0 (1C, C-13), 131.2 (1C, C-8), 130.2 (2C, CH Ar), 129.9 (2C, CH Ar), 129.0 (1C, C Ar), 128.9 (2C, CH Ar), 128.7 (2C, CH Ar), 128.2 (1C, CH Ar), 125.4 (1C, C-14), 119.5 (1C, C-15), 113.1 (1C, C-5), 113.0 (1C, C-7), 57.1 (1C, CH_2 Bn), 55.4 (1C, OMe), 47.1 (1C, *J* = 25.0 Hz, C-2), 44.2 (1C, C-1), 28.3 (1C, C-4), 21.8 (1C, C-3). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –69.34 (3F, CF_3). **HMRS** (ESI): calculated for $C_{31}H_{30}F_3N_4O_7S$ $[M+NH_4]^+$ requires *m/z* 659.1782, found *m/z* 659.1783.

N-Benzyl-4-methyl-N-{4-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]phenyl}benzenesulfonamide, S11.

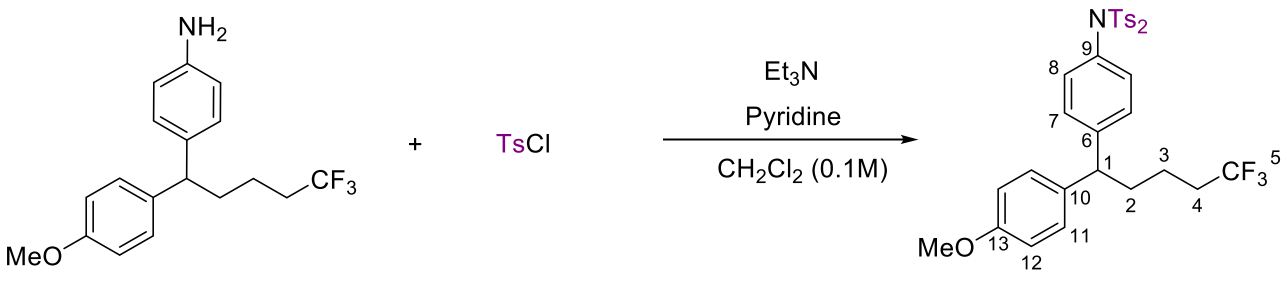


4a **S11**

From aniline **4a** (500.0 mg, 1.297 mmol), triethylamine (542 μL, 3.892 mmol, 3.0 equiv.) and *p*ara-toluenesulfonyl chloride (519. 3 mg, 2.724 mmol, 2.1 equiv.) in 13 mL of dry CH_2Cl_2, following the general procedure, sulfonamide **S11** was obtained. Chromatographic purification (gradient elution: 0:100 → 30:70 Et_2O – hexane) gave **S11**, as a colourless oil.

Data for **S11**: R_f 0.1 (30% EtOAc – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (2H, d, J = 8.3 Hz, Ar), 7.25 (2H, d, J = 8.4 Hz, Ar), 7.22 – 7.15 (5H, m, Ar), 7.07 (2H, d, J = 8.8 Hz, 10-H), 7.05 (2H, d, J = 8.8 Hz, 5-H), 6.91 (2H, d, J = 8.5 Hz, 9-H), 6.82 (2H, d, J = 8.7 Hz, 6-H), 4.68 (2H, s, CH_2 Bn), 4.19 (1H, t, J = 7.4 Hz, 1-H), 3.78 (3H, s, OMe), 2.84 – 2.69 (2H, m, 2-H_2), 2.43 (3H, s, Me). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.6 (1C, C Ar), 143.6 (1C, C Ar), 142.8 (1C, C Ar), 137.8 (1C, C Ar), 136.1 (1C, C Ar), 135.8 (1C, C Ar), 134.3 (1C, C Ar), 129.6 (2C, CH Ar), 129.2 (2C, CH Ar), 128.7 (2C, CH Ar), 128.6 (2C, CH Ar) , 128.5(2C, CH Ar), 128.1 (2C, CH Ar), 127.8 (2C, CH Ar), 127.7 (1C, CH Ar), 126.4 (1C, q, J = 277.8 Hz, CF_3), 114.2 (2C, CH Ar), 55.4 (1C, OMe), 54.8 (1C, CH_2 Bn), 43.9 (1C, C-1), 34.0 (1C, q, J = 27.3 Hz, C-2), 21.7 (1C, Me). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –63.63 (3F, CF_3).

4-Methyl-N-tosyl-N-{4-[5,5,5-trifluoro-1-(4-methoxyphenyl)pentyl]phenyl}benzenesulfonamide, S12.

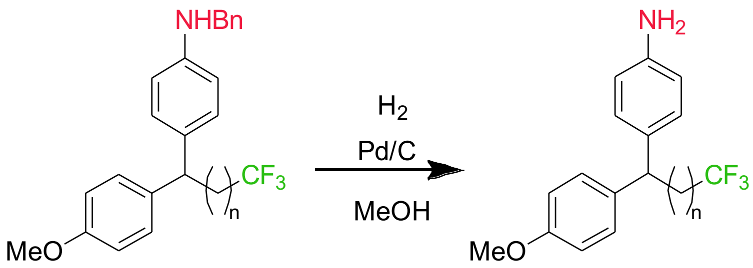


7 **S12**

From aniline **7** (57.0 mg, 0.176 mmol), triethylamine (75 μL, 0.528 mmol, 3.0 equiv.), and *p*ara-toluenesulfonyl chloride (75 mg, 0.388 mmol, 2.2 equiv.) in dry CH_2Cl_2 (0.1M), following the general procedure, sulfonamide **S12** was obtained. Chromatographic purification (gradient elution: 0:100 → 80:20 EtOAc – hexane) gave **S12** (85 mg, 76%), as a colourless oil.

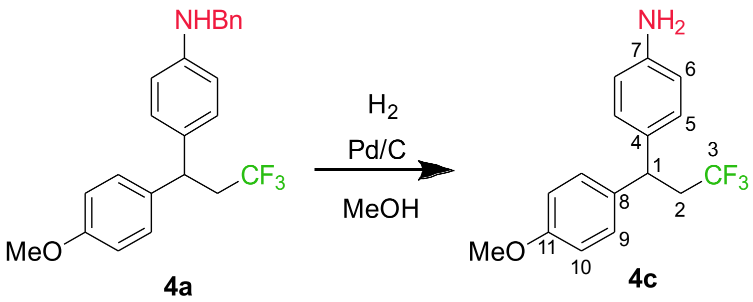
Data for **S12**: ***R**$_f$* 0.35 (50% EtOAc – hexane). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.79 (4H, d, *J* = 8.1 Hz, Ar), 7.31 (4H, d, *J* = 8.1 Hz, Ar), 7.18 (2H, d, *J* = 8.3 Hz, 11-H), 7.13 (2H, d, *J* = 8.6 Hz, 7-H), 6.94 (2H, d, *J* = 8.2 Hz, 12-H), 6.86 (2H, d, *J* = 8.6 Hz, 8-H), 3.86 (1H, t, *J* = 7.6 Hz, 1-H), 3.80 (3H, s, OMe), 2.20 – 1.50 (6H, m, 2-H_2, 3-H_2 and 4-H_2). **HMRS** (ESI): calculated for $C_{32}H_{36}F_3N_2O_5S_2$ $[M+NH_4]^+$ requires *m/z* 649.2013, found *m/z* 649.2016.

5.2. General procedure for hydrogenation



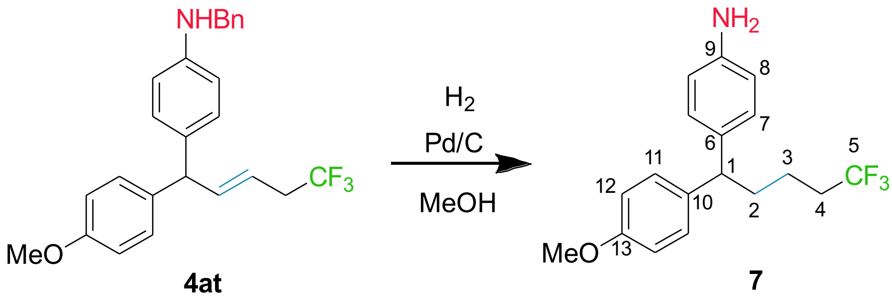
To an oven-dried vial, *N*-Benzyl aniline (1 equiv.) and 10 mol % Pd/C (0.1 equiv.) were added. Then, MeOH was added and the reaction mixture was kept under hydrogen for the specified time. The reaction mixture was diluted with dichloromethane, filtered through a pad of celite and evaporated under reduced pressure. The crude was purified by silica gel chromatography using the appropriate mixture of eluents to give the corresponding free anilines.

4-[3,3,3-Trifluoro-1-(4-methoxyphenyl)propyl]aniline, 4c.



From *N*-Benzyl aniline **4a** (30 mg, 1 equiv., 0.08 mmol) and Pd/C (8.3 mg, 0.1 equiv., 0.008 mmol) in 3.9 mL of MeOH under 4 bar hydrogen pressure, following the general procedure, aniline **4c** was obtained. Chromatographic purification (gradient elution: 0:100 → 50:50 EtOAc – hexane) gave **4c** (16 mg, 70%) as a colourless oil. Spectroscopy data matches with those previously reported.

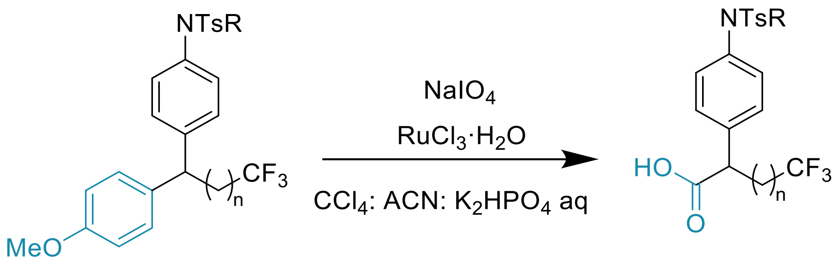
4-[5,5,5-Trifluoro-1-(4-methoxyphenyl)pentyl]aniline, 7.



From *N*-Benzyl aniline **4at** (180 mg, 1 equiv., 0.437 mmol) and Pd/C (48 mg, 0.1 equiv., 0.0437 mmol) in 2.2 mL of MeOH under hydrogen balloon pressure, following the general procedure, aniline **7** was obtained. Chromatographic purification (gradient elution: 0:100 → 30:70 EtOAc – hexane) gave **7** (101 mg, 71%) as a colourless oil.

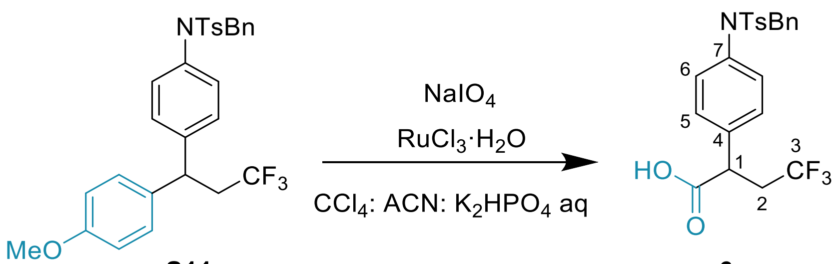
Data for **7**: R_f 0.2 (30% EtOAc – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.13 (2H, d, *J* = 8.7 Hz, 11-H), 7.01 (2H, d, *J* = 8.4 Hz, 7-H), 6.83 (2H, d, *J* = 8.7 Hz, 12-H), 6.65 (2H, d, *J* = 8.4 Hz, 8-H), 3.78 (3H, s, OMe), 3.83 – 3.70 (1H, m, 1-H), 2.16 – 1.97 (4H, m, 2-H$_2$ and 4-H$_2$), 1.62 – 1.44 (2H, m, 3-H$_2$). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 158.0 (1C, C Ar), 144.1 (1C, C Ar), 137.3 (1C, C Ar), 135.4 (1C, C Ar), 128.63 (2C, C-11), 128.58 (2C, C-7), 127.3 (1C, q, *J* = 276.7 Hz, CF$_3$), 115.7 (2C, C-8), 113.98 (2C, C-12), 55.33 (1C, CH$_2$ Bn), 49.48 (1C, C-1), 35.15 (1C, C-2), 33.79 (1C, q, *J* = 28.4 Hz, C-4), 20.68 (1C, q, *J* = 2.9 Hz, C-3). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –66.12 (3F, CF$_3$). **HRMS** (ESI): calculated for $C_{18}H_{21}F_3NO$ [M+H]$^+$ requires *m/z* 324.1570, found *m/z* 324.1558.

5.3. General procedure for Ru-catalyzed oxidation



To a cold (0 °C) solution of *para*-methoxyphenyl (PMP) derivative (1 equiv.) in 40.0 mL/mmol of a 2:2:3 mixture of CCl_4 : MeCN : K_2HPO_4 aq. (0.2M), $NaIO_4$ (20.0 equiv.) was added in one portion. The mixture was stirred at that temperature for 15 min and $RuCl_3{\cdot}H_2O$ (30 mol %) was added in one portion. The mixture was warmed up to room temperature. The reaction was monitored by TLC until completion, diluted with Et_2O, and H_2O and extracted with Et_2O. The water layer was acidified until pH 1 using 1M HCl aq. and extracted with Et_2O. The combined organic layers were dried using Na_2SO_4, filtered and the solvent was evaporated under reduced pressure to give the corresponding carboxylic acid.

2-{4-[(*N*-Benzyl-4-methylphenyl)sulfonamido]phenyl}-4,4,4-trifluorobutanoic acid, 6.

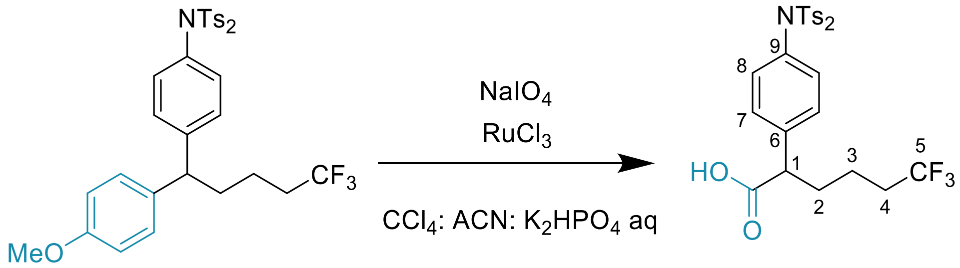


S11 **6**

From aniline **S11** (54 mg, 0.100 mmol), $NaIO_4$ (460 mg, 2.0 mmol) and $RuCl_3{\cdot}H_2O$ (6.8 mg, 0.030 mmol) in 4 mL of the appropriate mixture of solvents, following the general procedure, carboxylic acid **6** was obtained. Chromatographic purification (gradient elution: 30:70 → 70:30 EtOAc – hexane) gave **6** (29.1 mg, 61%) as a white foam.

Data for **6**: R_f 0.3 (70% EtOAc – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (2H, d, J = 8.3 Hz, Ar), 7.35 (2H, d, J = 8.8 Hz, Ar), 7.31 – 7.26 (5H, m, Ar), 7.24 (2H, d, J = 8.5 Hz, 5-H), 7.07 (2H, d, J = 8.5 Hz, 6-H), 4.78 (2H, s, CH_2 Bn), 3.92 (1H, dd, J = 8.6 and 5.4 Hz, 1-H), 3.08 (1H, dqd J = 15.0, 10.3 and 8.5 Hz, 2-H_A), 2.52 (3H, s, Me), 2.60 – 2.42 (1H, m, 2-H_B). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.5 (1C, C=O), 143.8 (1C, C Ar), 139.3 (1C, C Ar), 135.89 (1C, C Ar), 135.87 (1C, C Ar), 135.6 (1C, C Ar), 129.7 (2C, CH Ar), 129.5 (2C, CH Ar), 128.5 (5C, CH Ar), 128.4 (2C, CH Ar), 127.8 (2C, CH Ar), 125.9 (1C, q, J = 276.9 Hz, CF_3), 54.7 (1C, CH_2 Bn), 44.7 (1C, C-1), 37.2 (1C, q, J = 29.0 Hz, C-2), 21.7 (1C, Me). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –65.2 (3F, CF_3). **HRMS** (ESI): calculated for $C_{24}H_{22}F_3NO_4S$ $[M+H]^+$ requires *m/z* 477.1217, found *m/z* 478.1278.

6,6,6-Trifluoro-2-{4-[(4-methyl-*N*-tosylphenyl)sulfonamido]phenyl}hexanoic acid, 8.

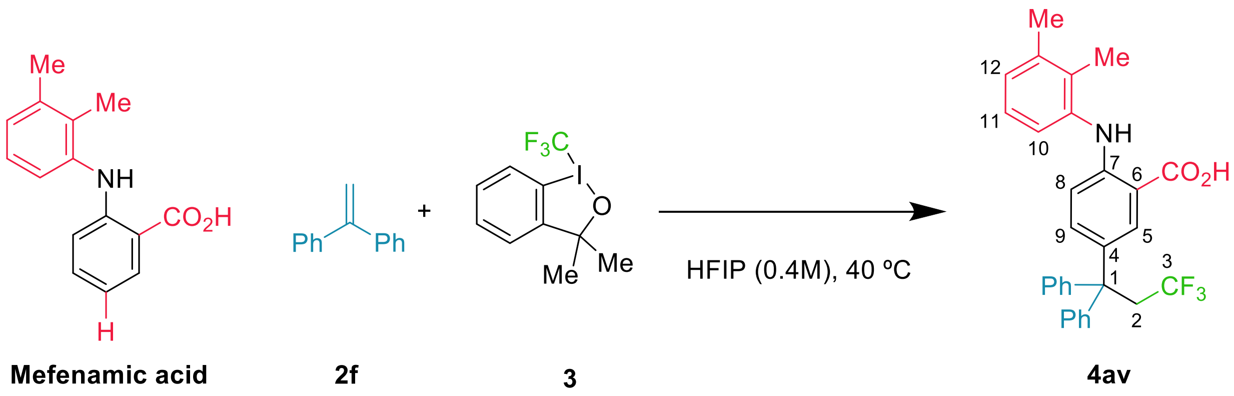


From aniline **S12** (22.7 mg, 0.036 mmol), $NaIO_4$(154 mg, 0.719 mmol) and $RuCl_3{\cdot}H_2O$(2.4 mg, 0.013 mmol) in 1.44 mL of the appropriate mixture of solvents, following the general procedure, carboxylic acid **8** was obtained. Chromatography purification (gradient elution: 50:50 → 100:0 EtOAc – hexane) gave **8** (14.8 mg, 72%) as a colourless oil.

Data for **8**: R_f 0.1 (70% EtOAc – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (4H, d, J = 8.4 Hz, Ar), 7.32 (4H, d, J = 8.2 Hz, Ar), 7.31 (2H, d, J = 8.5 Hz, 7-H), 7.01 (2H, d, J = 8.4 Hz, 8-H), 3.60 (1H, t, J = 7.6 Hz, 1-H), 2.46 (6H, s, 2 x Me), 2.23 – 2.03 (3H, m, 2-H_A and 4-H_2), 1.85 (1H, m, 2-H_B), 1.68 – 1.46 (2H, m, 3-H_2). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.5 (1C, C=O), 145.3 (2C, C Ar), 140.0 (1C, C Ar), 136.7 (2C, C Ar), 134.1 (1C, C Ar), 132.1 (2C, C-7), 129.8 (4C, CH Ar), 128.9 (2C, C-6), 128.7 (4C, CH Ar), 127.0 (1, q, J = 276.3 Hz, CF_3), 50.9 (1C, C-1), 33.6 (1C, q, J = 28.6 Hz, C-4), 32.3 (1C, C-2), 21.9 (2C, 2 x Me), 20.3 (1C, q, J = 3.0 Hz, C-3). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –66.2 (3F, CF_3). **HRMS** (ESI): calculated for $C_{26}H_{30}F_3N_2O_6S_2$ $[M+NH_4]^+$ requires *m/z* 587.1492, found *m/z* 587.1480.

6. Selective derivatization of bioactive molecules

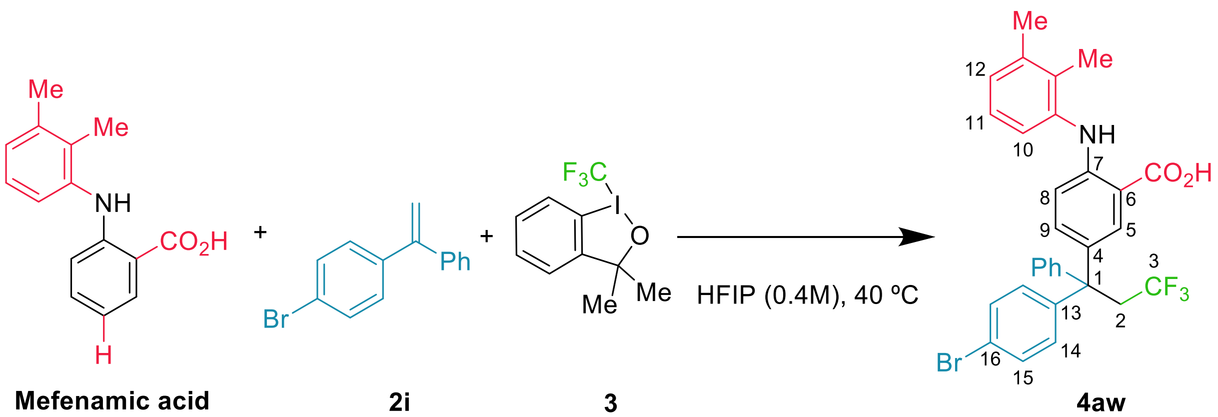
2-[(2,3-Dimethylphenyl)amino]-5-(3,3,3-trifluoro-1,1-diphenylpropyl)benzoic acid, 4av.



From Mefenamic acid (38.3 mg, 0.20 mmol), alkene **2f** (72.2 mg, 0.40 mmol) and trifluoromethyl reagent **3** (132.0 mg, 0.40 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4av** was obtained. Chromatographic purification (gradient elution: 0:100 → 50:50 EtOAc – hexane) gave **4av** (39 mg, 40%), as a brown oil.

Data for **4av**: R_f 0.25 (50% EtOAc – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.08 (1H, s, NH), 8.00 (1H, d, J = 2.6 Hz, 5-H), 7.35 – 7.27 (8H, m, Ar), 7.23 – 7.19 (2H, m, Ar), 7.17 (1H, dd, J = 9.2 and 2.7 Hz, 9-H), 7.13 (1H, dd, J = 7.2 and 1.6 Hz, 12-H), 7.09 (1H, t, J = 7.6 Hz, 11-H), 7.03 (1H, dd, J = 7.4 and 1.7 Hz, 10-H) 6.65 (1H, d, J = 9.0 Hz, 8-H), 3.53 (2H, q, J = 10.5 Hz, 2-H_2), 2.32 (3H, s, Me), 2.18 (3H, s, Me). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.8 (1C, C=O), 149.0 (1C, C-7), 145.4 (2C, C Ar), 138.4 (1C, C Ar), 138.3 (1C, C Ar), 136.7 (1C, C-9), 132.9 (1C, C Ar), 132.8 (1C, C-4), 131.9 (1C, C-5), 128.9 (4C, CH Ar), 128.2 (4C, CH Ar), 127.4 (1C, C-10), 126.6 (2C, CH Ar), 126.12 (1C, C-11), 126.10 (1C, q, J = 279.6 Hz, CF_3), 123.8 (1C, C-12), 113.7 (1C, C-8), 108.6 (1C, C-6), 53.4 (1C, C-1), 44.0 (1C, q, J = 26.6 Hz, C-2), 20.7 (1C, Me), 14.3 (1C, Me). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –56.1 (3F, CF_3). **HRMS** (ESI): calculated for $C_{30}H_{27}F_3NO_2$ $[M+H]^+$ requires m/z 490.1989, found m/z 490.1990.

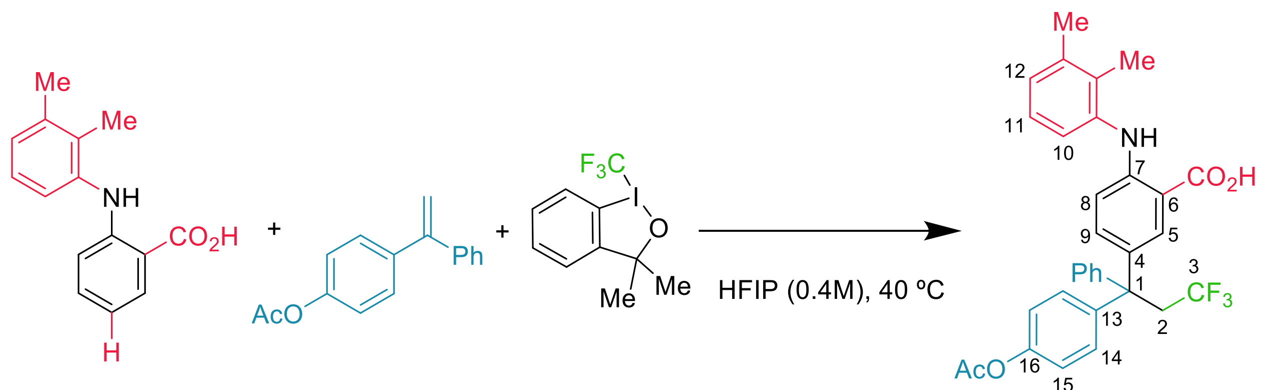
5-[1-(4-Bromophenyl)-3,3,3-trifluoro-1-phenylpropyl]-2-[(2,3-dimethylphenyl)amino]benzoic acid, 4aw.



From Mefenamic acid (48.3 mg, 0.20 mmol), alkene **2i** (104 mg, 0.40 mmol) and trifluoromethyl reagent **3** (132.0 mg, 0.40 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4aw** was obtained. Chromatographic purification (gradient elution: 0:100 → 20:80 EtOAc–hexane) gave **4aw** (49 mg, 43%), as a yellow oil.

Data for **4aw**: R_f 0.3 (50% EtOAc – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.09 (1H, s, NH), 7.97 (1H, d, J = 2.6 Hz, 5-H), 7.41 (2H, d, J = 8.7 Hz, 15-H), 7.33 – 7.25 (4H, m, Ar), 7.24 – 7.20 (1H, m, Ar), 7.18 (2H, d, J = 8.7 Hz, 14-H), 7.14 – 7.08 (3H, m, Ar) 7.04 (1H, dd, J = 6.7 and 1.8 Hz, 10-H), 6.64 (1H, d, J = 9.1 Hz, 8-H), 3.49 (2H, q, J = 10.4 Hz, 2-H$_2$), 2.33 (3H, s, Me), 2.18 (3H, s, Me). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.8 (1C, C=O), 149.1 (1C, C-7), 145.0 (1C, C Ar), 144.4 (1C, C-13), 138.5 (1C, C Ar), 138.2 (1C, C Ar), 136.4 (1C, C-9), 133.0 (1C, C Ar), 132.2 (1C, C-4), 131.8 (1C, C-5), 131.3 (2C, C-15), 130.8 (2C, C-14), 128.7 (2C, CH Ar), 128.3 (2, CH Ar), 127.5 (1C, C-10), 126.9 (1C, CH Ar), 126.2 (1C, C-11), 125.9 (1C, q, J = 279.4 Hz, CF$_3$), 123.9 (1C, C-12), 120.8 (1C, C-16), 113.9 (1C, C-8), 108.6 (1C, C-6), 53.1 (1C, C-1), 43.9 (1C, q, J = 26.4 Hz, C-2), 20.7 (1C, Me), 14.3 (1C, Me). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –56.1 (3F, CF$_3$). **HRMS** (ESI): calculated for $C_{30}H_{26}BrF_3NO_2$ $[M+H]^+$ requires m/z 568.1094, found m/z 568.1103.

5-[1-(4-Acetoxyphenyl)-3,3,3-trifluoro-1-phenylpropyl]-2-[(2,3-dimethylphenyl)amino]benzoic acid, 4ax.

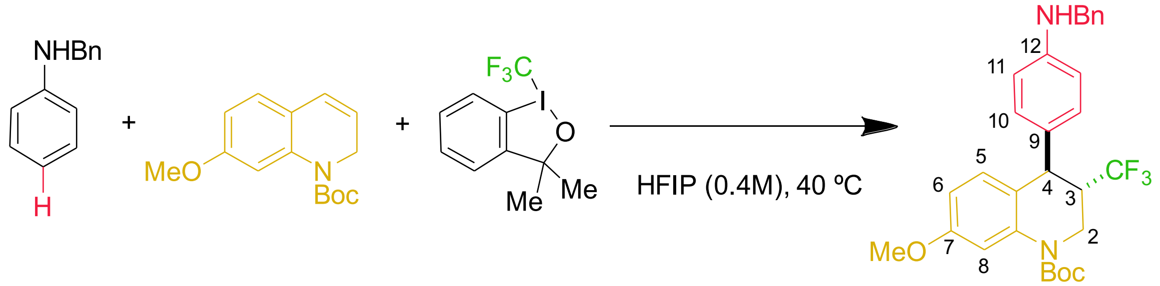


From Mefenamic acid (48.3 mg, 0.20 mmol), alkene **2ab** (95.4 mg, 0.40 mmol) and trifluoromethyl reagent **3** (132.0 mg, 0.40 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **4ax** was obtained. Chromatographic purification (gradient elution: 0:100 → 50:50 EtOAc–hexane) gave **4ax** (37.1 mg, 35%), as a yellow oil.

Data for **4ax**: R_f 0.15 (50% EtOAc – hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.11 (1H, s, NH), 8.00 (1H, d, J = 2.6 Hz, 5-H), 7.34 – 7.29 (6H, m, H Ar), 7.26 – 7.20 (1H, m, Ar), 7.16 – 7.09 (1H, m, Ar), 7.14 (1H, dd, J = 9.0 and 2.7 Hz, 9-H), 7.09 (1H, t, J = 7.5 Hz, 11-H), 7.06 – 7.01 (1H, m, Ar), 7.02 (2H, d, J = 8.8 Hz, 14-H), 6.66 (1H, d, J = 9.1 Hz, 8-H), 3.53 (2H, q, J = 10.4 Hz, 2-H$_2$), 2.34 (3H, s, Me), 2.30 (3H, s, Me OAc), 2.20 (3H, s, Me). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.5 (1C, C=O), 169.4 (1C, C=O Ac), 149.2 (1C, C-16), 149.0 (1C, C-7), 145.2 (1C, C Ar), 142.9 (1C, C Ar), 138.4 (1C, C Ar), 138.3 (1C, C Ar), 136.5 (1C, C-9), 132.9 (1C, C Ar), 132.5 (1C, C-4), 131.7 (1C, C-5), 130.1 (2C, CH Ar), 128.9 (2C, CH Ar), 128.3 (2C, CH Ar), 127.4 (1C, C-10), 126.8 (1C, CH Ar), 126.1 (1C, C-11), 126.0 (1C, q, J = 279.3 Hz, CF_3), 123.8 (1C, C-12), 121.1 (2C, C-14), 113.8 (1C, C-8), 108.5 (1C, C-6), 53.1 (1C, C-1), 44.1 (1C, q, J = 26.4 Hz, C-2), 21.3 (1C, Me OAc), 20.7 (1C, Me), 14.3 (1C, Me). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –56.1 (3F, CF_3). **HRMS** (ESI): calculated for $C_{32}H_{29}F_3NO_4$ $[M+H]^+$ requires *m/z* 548.2044, found *m/z* 548.2041.

7. Sequential trifluoromethylarylation and hydroarylation of quinolines.

***tert*-Butyl 4-[4-(benzylamino)phenyl]-7-methoxy-3-(trifluoromethyl)-3,4-dihydroquinoline-1(2H)-carboxylate, 10.**



1a **9** **3** **10**

From aniline **1a** (34.8 mg, 0.19 mmol), dihydroquinoline **9** (49.7 mg, 0.19 mmol) and trifluoromethyl reagent **3** (62.7 mg, 0.19 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **10** was obtained. Chromatographic purification (gradient elution: 0:100 → 50:50 Et_2O – hexane) gave **10** (38 mg, 40%), as a colourless oil.

Data for **10**: R_f 0.2 (30% Et_2O – hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.27 (5H, m, Ar), 7.22 (1H, d, J = 2.5 Hz, 8-H), 6.87 (2H, d, J = 8.5 Hz, 10-H), 6.83 (1H, dd, J = 8.6 and 0.8 Hz, 6-H), 6.58 (1H, d, J = 8.7 Hz, 5-H), 6.57 (2H, d, J = 8.5 Hz, 11-H), 4.29 (2H, s, CH_2 Bn), 4.17 (1H, d, J = 5.5 Hz, 4-H), 4.03 (1H, dd, J = 13.6 and 4.4 Hz, 2-H_A), 3.85 (1H, dd, J = 13.7 and 7.3 Hz, 2-H_B) 3.79 (3H, s, OMe), 2.85 – 2.70 (1H, m, 3-H), 1.55 (9H, s, 3 x Me Boc). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.9 (1C, C=O Boc), 153.3 (1C, C Ar), 146.8 (1C, C Ar), 139.4 (1C, C Ar), 139.2 (1C, C Ar), 134.5 (1C, C Ar), 131.0 (1C, C-5), 129.2 (2C, CH Ar), 128.8 (2C, CH Ar), 127.8 (2C, CH Ar), 127.5 (1C, CH Ar), 126.94 (1C, q, J = 280.8 Hz, CF_3), 122.9 (1C, C Ar), 113.4 (2C, C-11), 111.7 (1C, C-6), 108.8 (1C, C-8), 81.6 (1C, C *t*-Bu Boc), 55.5 (1C, OMe), 48.7 (1C, CH_2 Bn), 47.3 (1C, q, J = 24.8 Hz, C-3), 41.5 (1C, C-2), 41.4 (1C, C-4), 28.4 (3C, 3 x Me Boc). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –70.1 (3F, CF_3). **HMRS** (ESI): calculated for $C_{29}H_{32}F_3N_2O_3$ $[M+H]^+$ requires *m/z* 513.2360, found *m/z* 513.2358.

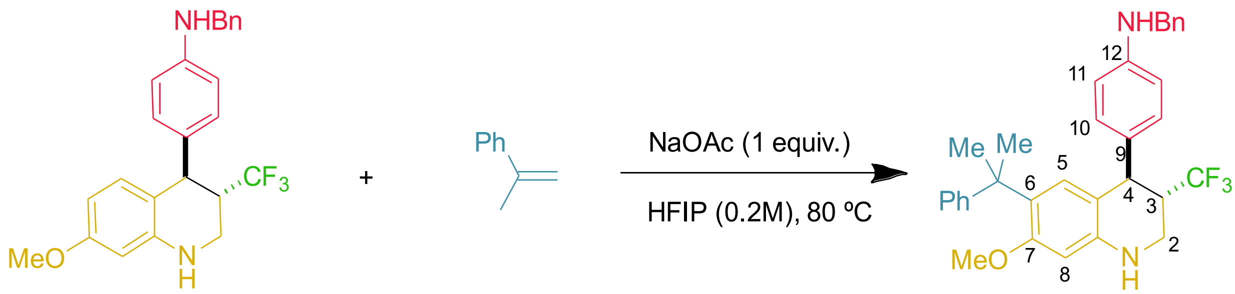
***N*-Benzyl-4-[(3S,4R)-7-methoxy-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinolin-4-yl]aniline, S13.**

10 **S13**

To a stirring solution of aniline **10** (129 mg, 0.25 mmol) in dichloromethane (1 mL), trifluoroacetic acid (252 μm) was added, and the reaction mixture stirred for 30 min and checked by TLC. The reaction mixture was then evaporated under reduced pressure and aniline **S13** was obtained. Chromatographic purification (gradient elution: 20:80 → 50:50 Et_2O – hexane) gave **S13** (100 mg, 96%), as a yellowish foam.

Data for **S13**: ***R**$_f$* 0.15 (40% Et_2O – hexane). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.26 (5H, s, Ar), 7.08 (2H, d, *J* = 8.9 Hz, Ar), 7.03 (2H, d, *J* = 9.1 Hz, Ar) 6.55 (1H, d, *J* = 8.5 Hz, 5-H), 6.22 (1H, dt, *J* = 8.6, 2.3 Hz, 6-H), 6.16 (1H, d, *J* = 2.4 Hz, 8-H), 4.27 (2H, s, CH_2 Bn), 4.22 (1H, d, *J* = 6.6 Hz, 4-H), 3.73 (3H, s, OMe), 3.39 (2H, m, *J* = 10.2 and 5.5 Hz, 2-H_2), 2.86 – 2.62 (1H, m, 3-H).

***N*-Benzyl-4-[(3S,4R)-7-methoxy-6-(2-phenylpropan-2-yl)-3-(trifluoromethyl)-1,2,3,4-tetrahydroquinolin-4-yl]aniline, 11.**



S13 **2ac** **11**

From adapted procedure,[6] aniline **S13** (82.5 mg, 0.20 mmol), alkene **2ac** (47.3 mg, 0.4 mmol), and sodium acetate (16.4 mg, 0.2 mmol), in 1 mL of HFIP, aniline **11** was obtained. Chromatographic purification with deactivated silica (gradient elution: 10:90 → 50:50 Et_2O – hexane) gave **11** (49 mg, 46%; 53% based on recovered starting material), as a white foam. Note: acid-sensitive compound.

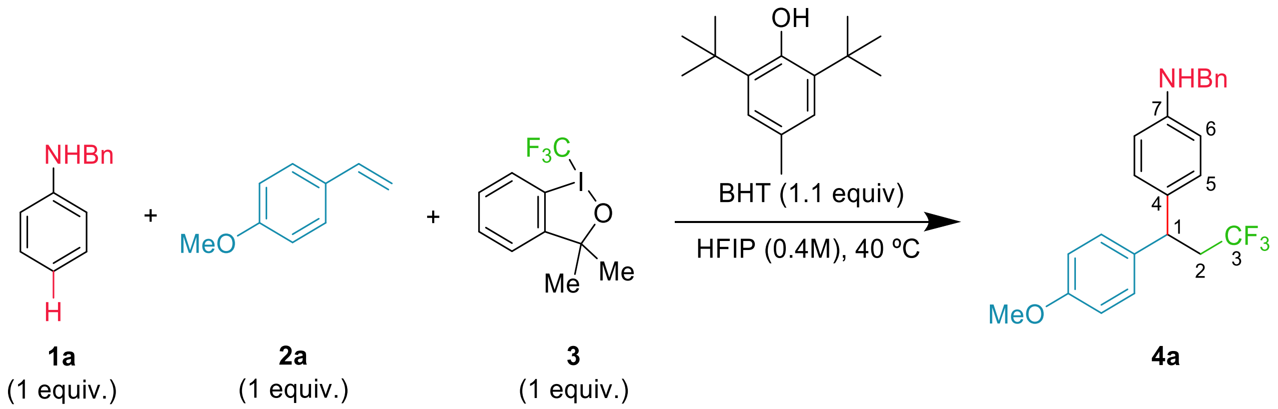
Data for **11**: ***R**$_f$* 0.2 (30% Et_2O – hexane). **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 7.36 (2H d, *J* = 6.9 Hz, Ar Bn), 7.29 (2H t, *J* = 7.6 Hz, Ar Bn), 7.20 (1H t, *J* = 7.1 Hz, Ar Bn), 7.14 (2H t, *J* = 7.6 Hz, Ar Ph), 7.03 (1H, t, *J* = 7.3 Hz, Ar Ph), 7.01 (2H, d, *J* = 8.0 Hz, Ar Ph) 6.84 (2H d, *J* = 8.5 Hz, 10-H), 6.67 (1H, s, 5-H), 6.56 (2H, d, *J* = 8.5 Hz, 11-H), 6.13 (1H t, *J* = 5.9 Hz, NH Bn), 6.11 (1H, s, 8-

H), 5.78 (1H, t, J = 2.8 Hz, NH), 4.24 (2H, d, J = 5.9 Hz, CH_2 Bn), 4.08 (1H, d, J = 5.0 Hz, 4-H), 3.24 – 3.24 (2H, m, 2-H_2), 3.23 (3H, s, OMe), 2.74 (1H, m, 3-H), 1.43 (3H, s, Me), 1.37 (3H, s, Me). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 156.5 (1C, C Ar), 151.7 (1C, C Ar), 147.2 (1C, C Ar), 144.0 (1C, C Ar), 140.3 (1C, C Ar), 132.6(1C, C Ar), 128.8 (2C, C-10), 128.2 (2C, CH Ar), 128.0 (1C, C-5), 127.5 (1C, q, J = 281.1 Hz, CF_3), 127.4 (2C, CH Ar), 127.3 (2C, CH Ar), 126.6 (1C, CH Ar), 125.9 (1C, C Ar), 125.1 (2C, CH Ar), 124.5 (1C, CH Ar), 112.2 (2C, CH Ar), 112.1 (1C, C Ar), 98.6 (1C, C-8), 54.8 (1C, OMe), 46.7 (1C, CH_2 Bn), 43.8 (1C, q, J = 23.8 Hz, C-3), 40.7 (1C, C-Me_2), 40.4 (1C, C-4), 36.9 (1C, C-2), 30.2 (1C, Me), 29.5 (1C, Me). **HRMS** (ESI): calculated for $C_{38}H_{42}F_3N_2O_3$ $[M+H]^+$ requires m/z 631.3143, found m/z 631.3148.

8. Mechanistic studies

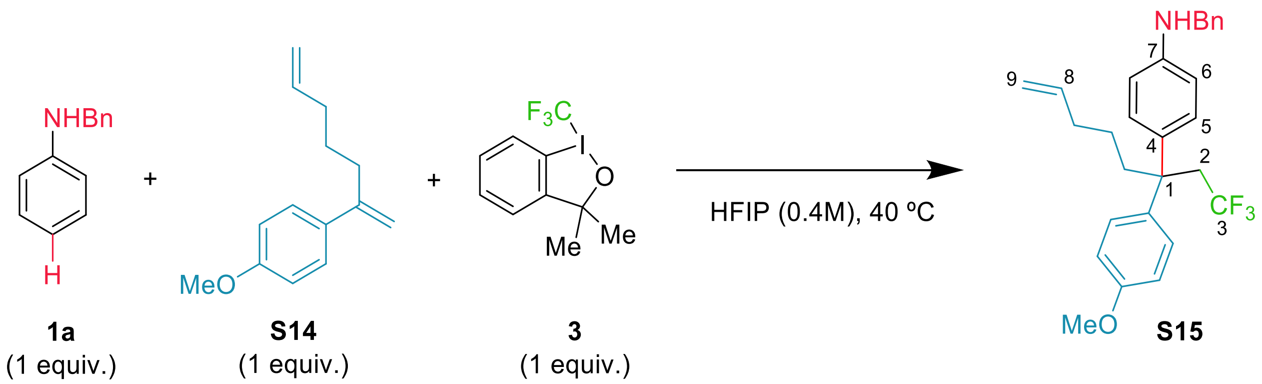
8.1. Control experiments

<u>· Radical trapping</u>



From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol), trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol) and BHT (48.5 mg, 0.22 mmol) in 0.5 mL of HFIP, following the general procedure, aniline **4a** was obtained. Chromatographic purification (gradient elution: 0:100 → 10:90 Et_2O – hexane) gave **4a** (46.3 mg, 62%), as a yellow oil.

<u>· Radical clock experiment</u>

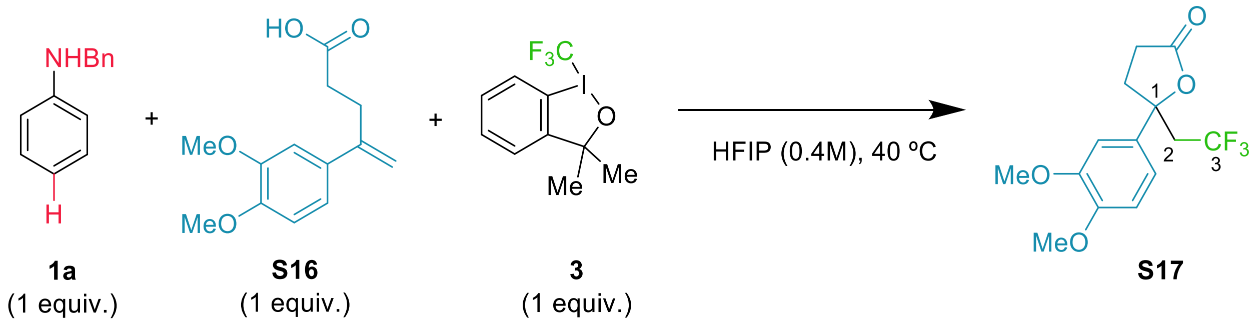


From aniline **1a** (36.7 mg, 0.2 mmol), alkene **S14** (40.5 mg, 0.2 mmol), trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **S15** was obtained. Chromatographic purification (gradient elution: 0:100 → 12:88 Et_2O – hexane) gave **S15** (21.5 mg, 24%), as a yellow oil.

Data for **S15**: R_f 0.2 (20% Et_2O – hexane). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.51 – 7.28 (5H, m, Ar), 7.08 (2H, d, *J* = 8.9 Hz, Ar), 6.94 (2H, d, *J* = 8.7 Hz, Ar), 6.80 (2H, d, *J* = 8.9 Hz, Ar), 6.56 (2H, d, *J* = 8.7 Hz, Ar), 5.71 (1H, ddt, *J* = 16.9, 10.2 and 6.7 Hz, 8-H), 5.06 – 4.86 (2H, m, 9-H_2), 4.30 (2H, s, CH_2), 3.79 (3H, s, OMe), 2.93 (2H, q, *J* = 10.9 Hz, 2-H_2), 2.28 – 2.17 (2H, m, CH_2), 2.10 – 1.94 (4H, m, 2 x CH_2). **HRMS** (ESI): calculated for $C_{28}H_{31}F_3NO$ $[M+H]^+$ requires *m/z* 454.2352, found *m/z* 454.2350.

Note: Compound **S15** is unstable and decomposes during column flash purification.

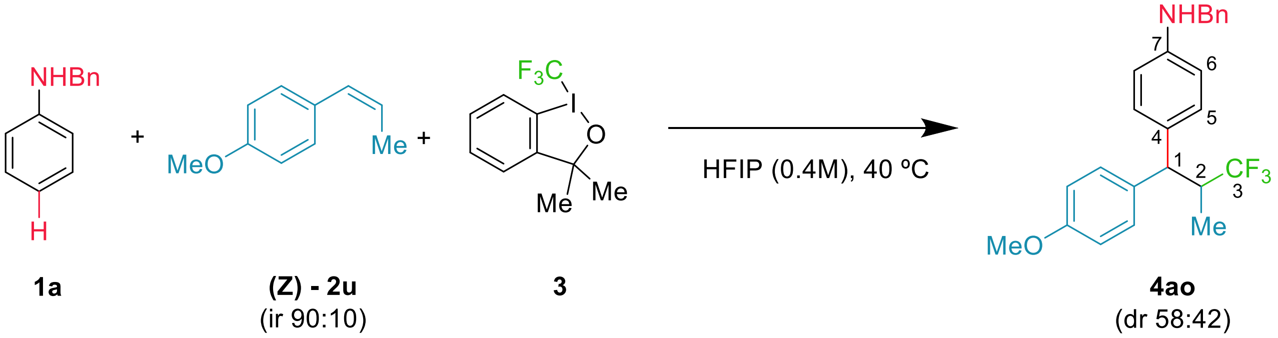
· Intramolecular lactonization



From aniline **1a** (31.9 mg, 0.175 mmol), alkene **S16** (41.1 mg, 0.175 mmol), trifluoromethyl reagent **3** (57.4 mg, 0.175 mmol), in 0.5 mL of HFIP, following the general procedure, aniline **S17** was obtained. Chromatographic purification (gradient elution: 0:100 → 40:90 Et_2O – hexane) gave **S17** (52 mg, 98%), as a colourless oil.

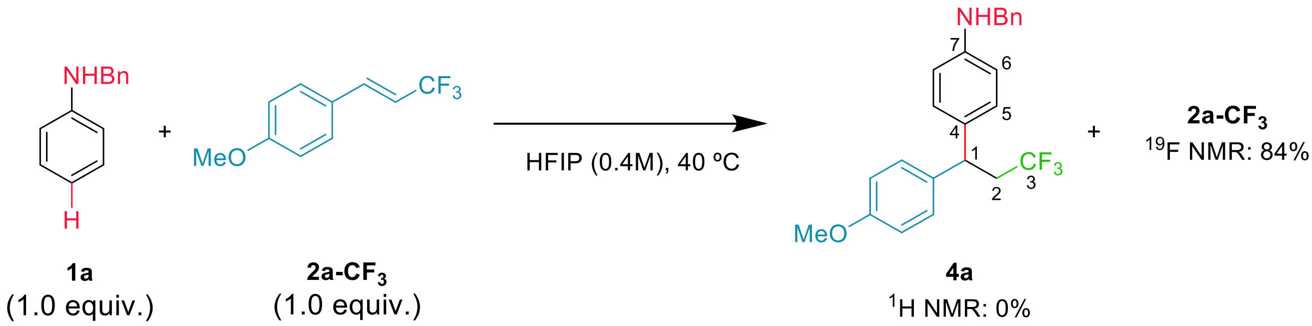
Data for **S17**: R_f 0.1 (40% Et_2O – hexane). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.07 – 6.76 (3H, m, Ar), 3.90 (3H, s, OMe), 3.89 (3H, s, OMe), 2.82 (2H, m, 2-H_2), 2.70 – 2.56 (3H, m, CH_2), 2.56 – 2.39 (1H, m, CH_2).

· Using *E* and *Z* alkene



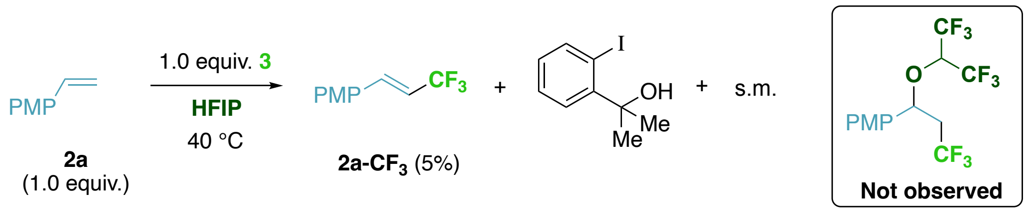
From aniline **1a** (36.7 mg, 0.2 mmol), **(Z)-2u**[4] (dr 90:10) alkene (29.6 mg, 0.2 mmol), trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol) in 0.5 mL of HFIP, following the general procedure, aniline **4ao** was obtained (60%, dr 58:42).

· Michael addition to vinyl-CF_3

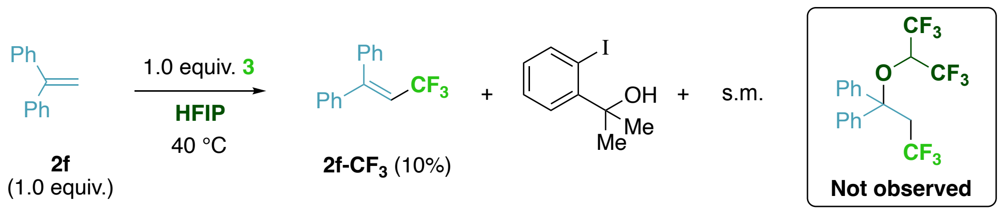


From aniline **1a** (6.3 mg, 0.04 mmol) and alkene **2a-CF$_3$**[5] (6.9 mg, 0.04 mmol) in 85 μmL of HFIP, following the general procedure, starting materials were recovered, without formation of product **4a**.

· Reactivity of styrenes against **3** in HFIP

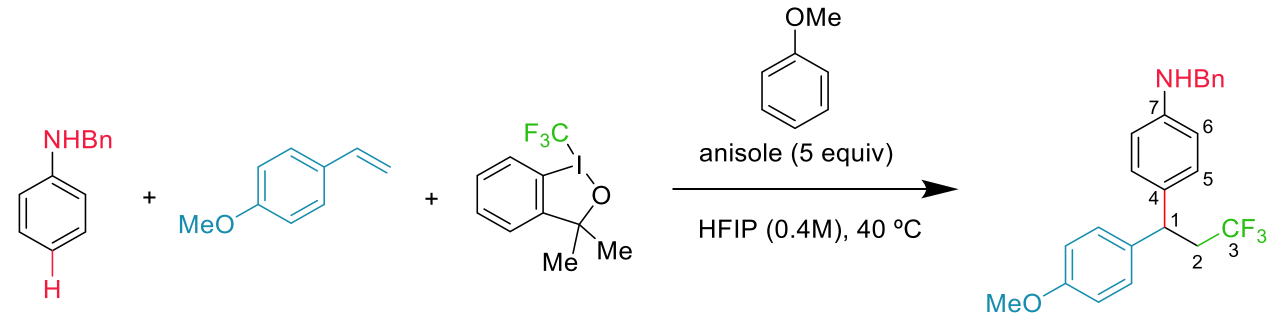


From alkene **2a** (13.4 mg, 0.1 mmol) and trifluoromethyl reagent **3** (33.0 mg, 01 mmol) in 0.25 mL of HFIP, following the general procedure, starting materials were recovered, with 5% of **2a-CF$_3$** formation.



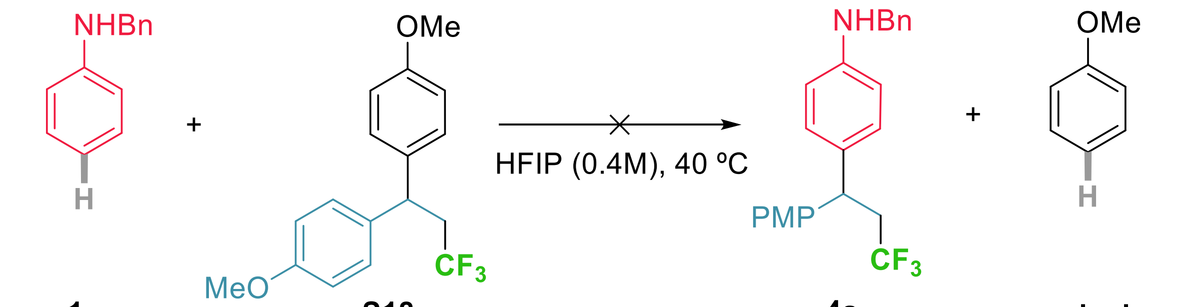
From alkene **2f** (18.0 mg, 0.1 mmol) and trifluoromethyl reagent **3** (33.0 mg, 0.1 mmol) 0.25 mL of HFIP, following the general procedure, starting materials were recovered, with 10% of **2f-CF$_3$** formation.

· Competition experiment



From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol), anisole (109 mg, 1 mmol) and trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol) in 0.5 mL of HFIP, following the general procedure, aniline **4a** was obtained. Chromatographic purification (gradient elution: 0:100 → 20:80 Et_2O – hexane) and (isocratic elution: 4:96 AcOH – Toluene) gave **12** (54.2 mg, 70%), as a colourless oil.

Retroarylation experiment



From aniline **1a** (11.6 mg, 0.064 mmol) and compound **S18**[6] (19.7 mg, 0.064 mmol) in 160 μL of HFIP, following the general procedure, starting materials **1a** and **S18** were recovered, without formation of **4a** or **anisole**.

8.2. Cyclic Voltammetry (CV)

General Information

Voltametric experiments were performed using an IKA Electrasyn 2.0 equipment inside a homemade Faraday's cage, recording the results at a glassy carbon macroelectrode (radius = 3.0 mm) with Bu_4NPF_6 (0.1M) as the supporting electrolyte, using an Ag/Ag^+ (KCl, 3M) reference electrode and a platinum counter electrode at variable scan rates (0.1 – 0.4 V s-1).

The reductive potential of trifluoromethyl reagent **3** was investigated in ACN (Figure S1) and HFIP (Figure S2), bubbling Ar through the solution to degas it. In both cases an irreversible reductive peak is observed, the absolute maximum of which is recorded at –1.75 V for ACN and –0.58 V for HFIP at a scan rate of 0.1 V s^{-1} (Figure S3).

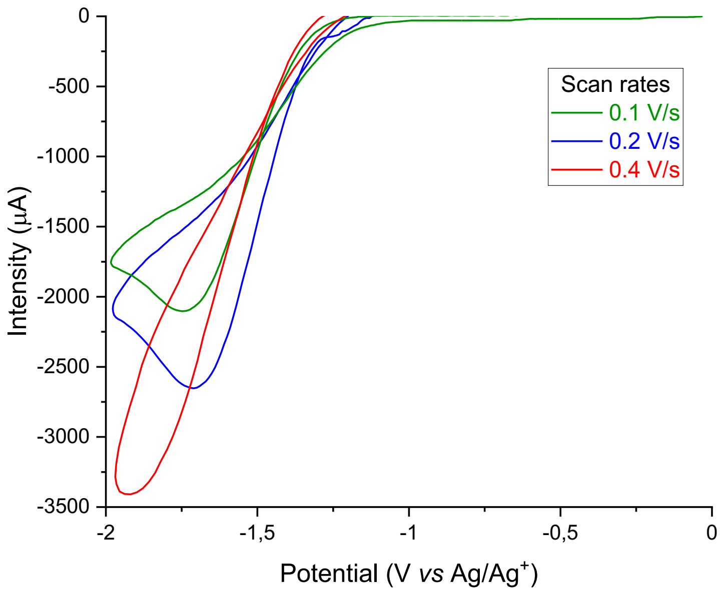


Figure S1. Reduction of trifluoromethyl reagent **3** (30 mM), 0.1 M Bu_4NPF_6 in ACN at different scan rates (mV/s) using glassy C electrode.

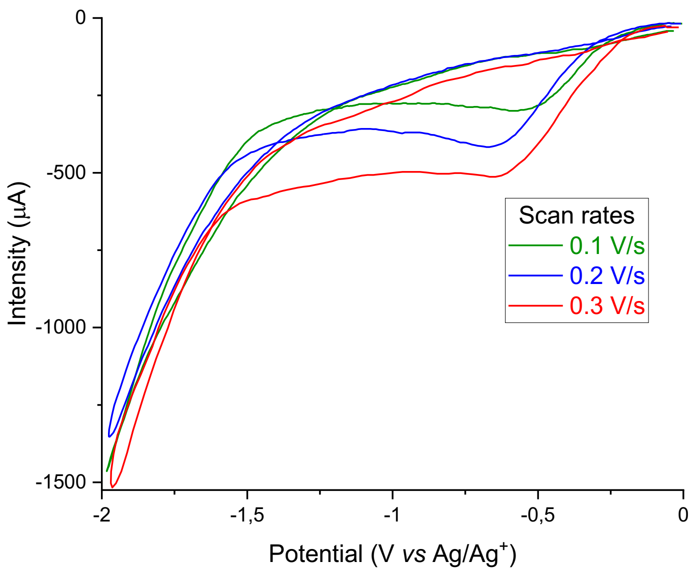


Figure S2. Reduction of trifluoromethyl reagent **3** (30 mM), 0.1 M Bu_4NPF_6 in HFIP at different scan rates (V s^{-1}) using glassy C electrode.

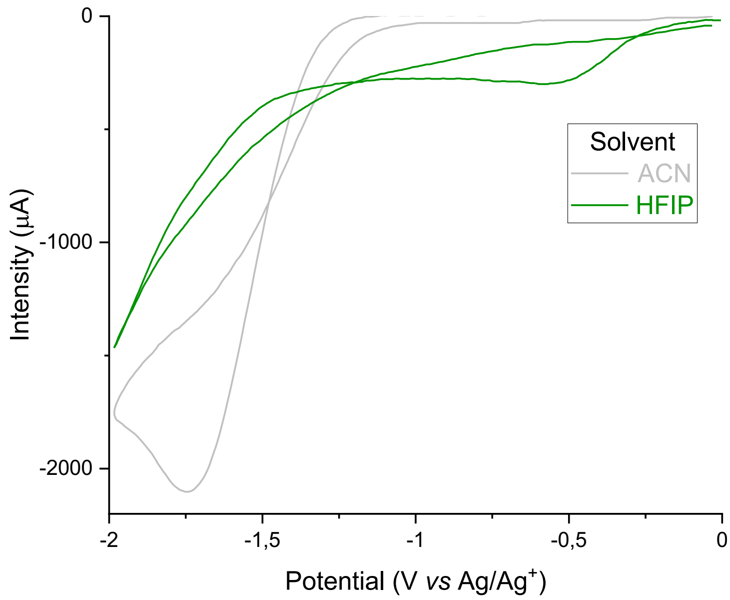


Figure S3. Reduction of **3** (30 mM), 0.1 M Bu_4NPF_6 in HFIP (green) and ACN (grey) at a scan rate of 0.1 V s^{-1}.

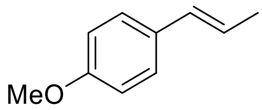
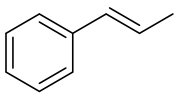
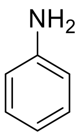
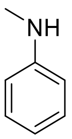
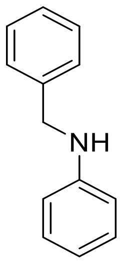
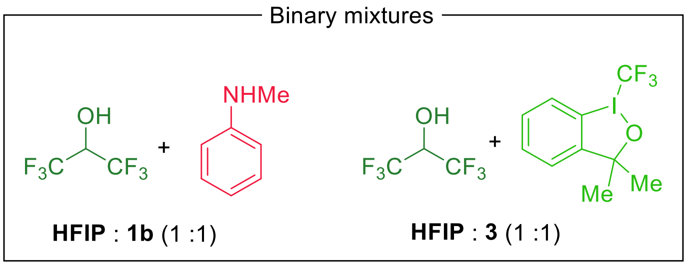
Substrate	HFIP (V)	Acetonitrile (V)
	1.035	1.429; 1.874; 2.275
	1.503	1.934
	1.030	1.120
	0.856	0.965
	0.811	1.032

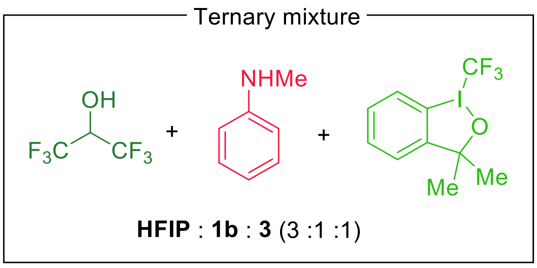
Table S6. Table of oxidation potentials for alkenes and anilines tested in the trifluoromethylarylation of alkenes using anilines in HFIP.

8.3. NMR experiments

8.3.1. ^{1}H NMR study

^{1}H NMR of individual species (HFIP, **1b** and **3**), two binary mixtures (HFIP : **1b** and HFIP : **3**) and one ternary mixture (HFIP : **1b** : **3**) were recorded at a 0.2 mmol scale of aniline **1b** and trifluoromethyl reagent **3**.





<u>Analysis of the binary mixtures</u>

The most significant changes found in ^{1}H NMR, for the HFIP : **1b** binary mixture (Figure S4D) compared to the individual species (Figure S4A and Figure S4B) are the downfield shift (deshieled) of the OH (HFIP), from a frequency of 2.99 ppm to 5.84 ppm ($\Delta\delta$ = 2.85) and the downfield shift (deshieled) of the NH (**1b**), from a frequency of 3.66 ppm to 4.98 ppm ($\Delta\delta$ = 1.32). These data support a H-bonding between the basic amino group of the aniline and the exceptionally good hydrogen bond donor HFIP (Table S7).

The most significant changes found in ^{1}H NMR, for the HFIP : **3** binary mixture (Figure S4E) compared to the individual species (Figure S4A and Figure S4C) is the downfield shift (deshieled) of the OH (HFIP), from a frequency of 2.99 ppm to 6.38 ppm ($\Delta\delta$ = 3.39), supporting a H-bonding between the ether backbone of the trifluoromethyl reagent and the exceptionally good hydrogen bond donor HFIP (Table S7).

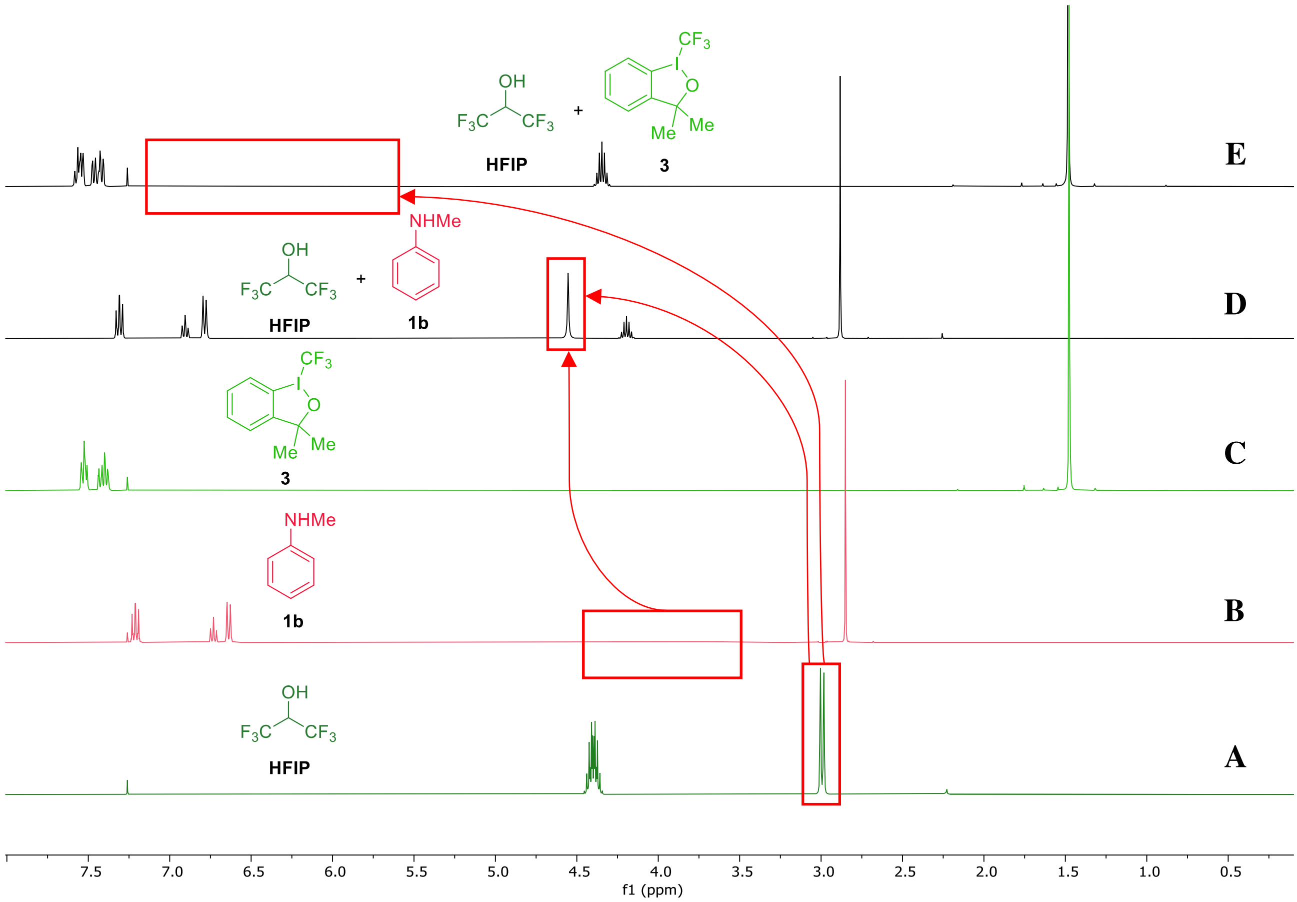


Figure S4. ^{1}H NMR of the individual species (A-C) and the two binary mixtures (D-E).

Signal	Species				
	HFIP	1b	3	Binary mixtures	
				HFIP : **1b** (**Δδ**)	HFIP : **3** (**Δδ**)
OH (**HFIP**)	2.99, d, J = 8.5 Hz	-	-	4.55, br s (+1.56)	6.38, br s (+3.39)
NH (**1b**)	-	3.66, br s	-	4.55, s (+0.89)	-

Table S7. Significant changes for the binary mixtures with respect to individual species.

2) Analysis for the ternary mixture

The most significant changes found in ^{1}H NMR, for the ternary mixture (Figure S5D) compared to the individual species (Figure S5A-C) are the downfield shift (deshieled) of the OH (HFIP), from a frequency of 2.99 ppm to 5.84 ppm ($\Delta\delta$ = 2.85) and the downfield shift (deshieled) of the NH (aniline), from a frequency of 3.66 ppm to 5.84 ppm ($\Delta\delta$ = 2.18). These data support a H-bonding between the exceptionally good hydrogen bond donor HFIP and both the basic amino group of the aniline and the ether backbone of the trifluoromethyl reagent (Table S8).

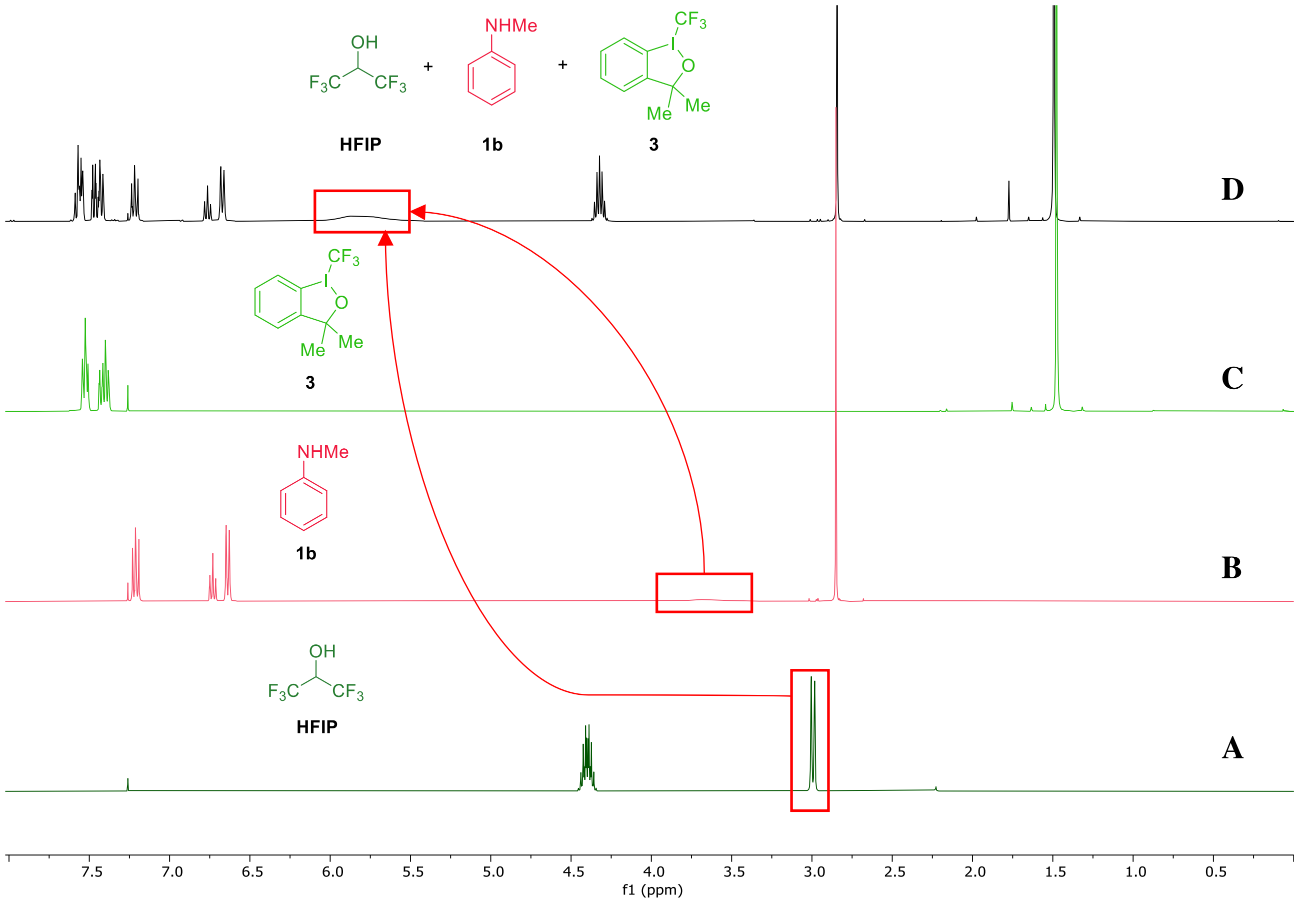


Figure S5. [1]H NMR of the individual species (A-C) and the ternary mixture (D).

Signal	Species			
	HFIP	**1b**	**3**	**HFIP : 1b : 3 (Δδ)**
OH (**HFIP**)	2.99, d, *J* = 8.5 Hz	-	-	5.84, br. s. (+2.85)
NH (**1b**)	-	3.66, br s	-	5.84, br. s. (+2.18)

Table S8. Significant changes for the ternary mixture with respect to individual species.

8.3.2. [19]F NMR study

[19]F NMR of individual species (**3** and HFIP) and four binary mixtures of **3** : HFIP at different ratios (1:1, 1:2, 1:3 and 1:4) were recorded at a 0.2 mmol scale.

The most significant changes found in [19]F NMR for the binary mixtures (Figure S6C-F) compared to the individual species (Figure S6A-B) are the downfield shift (deshieled) of the CF_3 of **3** from a frequency of –40.11 ppm up to –37.66 ppm (Δδ = 2.45) and a downfield shift (deshieled) of the CF_3 (HFIP) from a frequency of –75.79 ppm up to –75.54 ppm (Δδ = 0.25). These data support a more electrophilic CF_3 group within the hypervalent iodine **3** (Table S9).

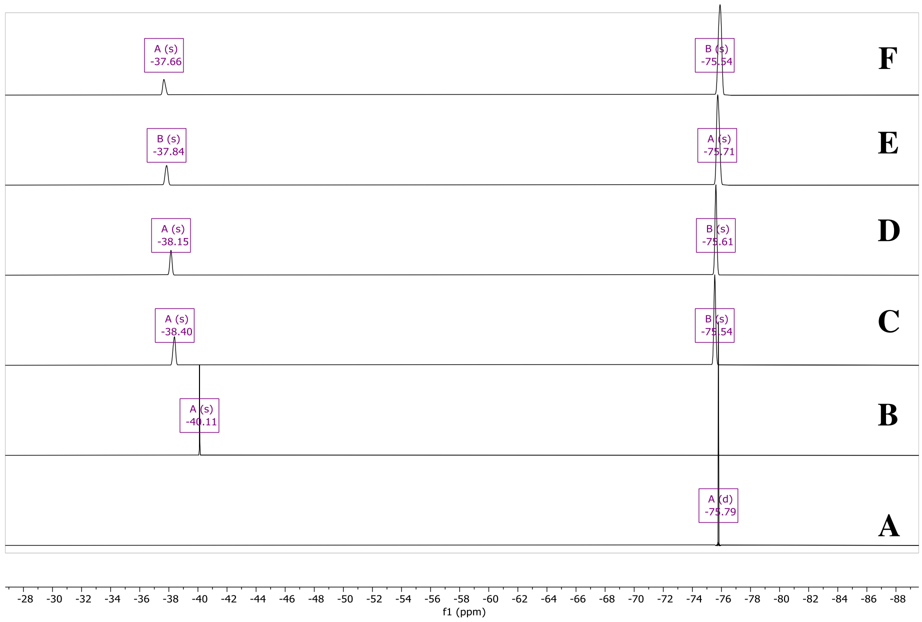


Figure S6. [19]F NMR of HFIP, **3** and binary mixtures of **3**:HFIP.

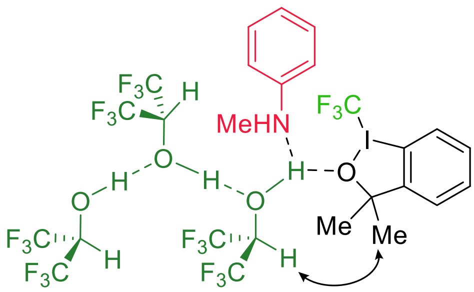
Signal	**Species**					
	3	**HFIP**	**3**:HFIP (1:1) (Δδ)	**3**:HFIP (1:2) (Δδ)	**3**:HFIP (1:3) (Δδ)	**3**:HFIP (1:4) (Δδ)
CF_3 (**3**)	–40.11	-	–38.40 (+1.71)	–38.15 (+1.96)	–37.84 (+2.27)	–37.66 (+2.45)
CF_3 (**HFIP**)	-	–75.79	–75.54 (+0.25)	–75.61 (+0.18)	–75.71 (+0.08)	–75.54 (+0.25)

*Table S9. Significant changes of **3** and HFIP for the binary mixtures with respect to individual species.*

8.3.3. [1]H-[1]H NOESY-2D experiment

NOESY-2D spectra were collected using the standard Bruker pulse programs noesyphsw (90-t_1-90-τ_m-90-Acq) for the ternary mixture HFIP : **1b** : **3** (3:1:1).

The most significant interaction observed in the NOESY-2D, among other, is between CH (HFIP) and Me (**3**), that is highlighted under a red box. This interaction confirms the intermolecular spatial connection between HFIP and **3**. Additionally, there is an interesting cross-peak between interchangeable OH (HFIP) and NH (aniline) signal with NMe (**1b**), highlighted under a green box, that confirms the Hydrogen-bonded ternary species.



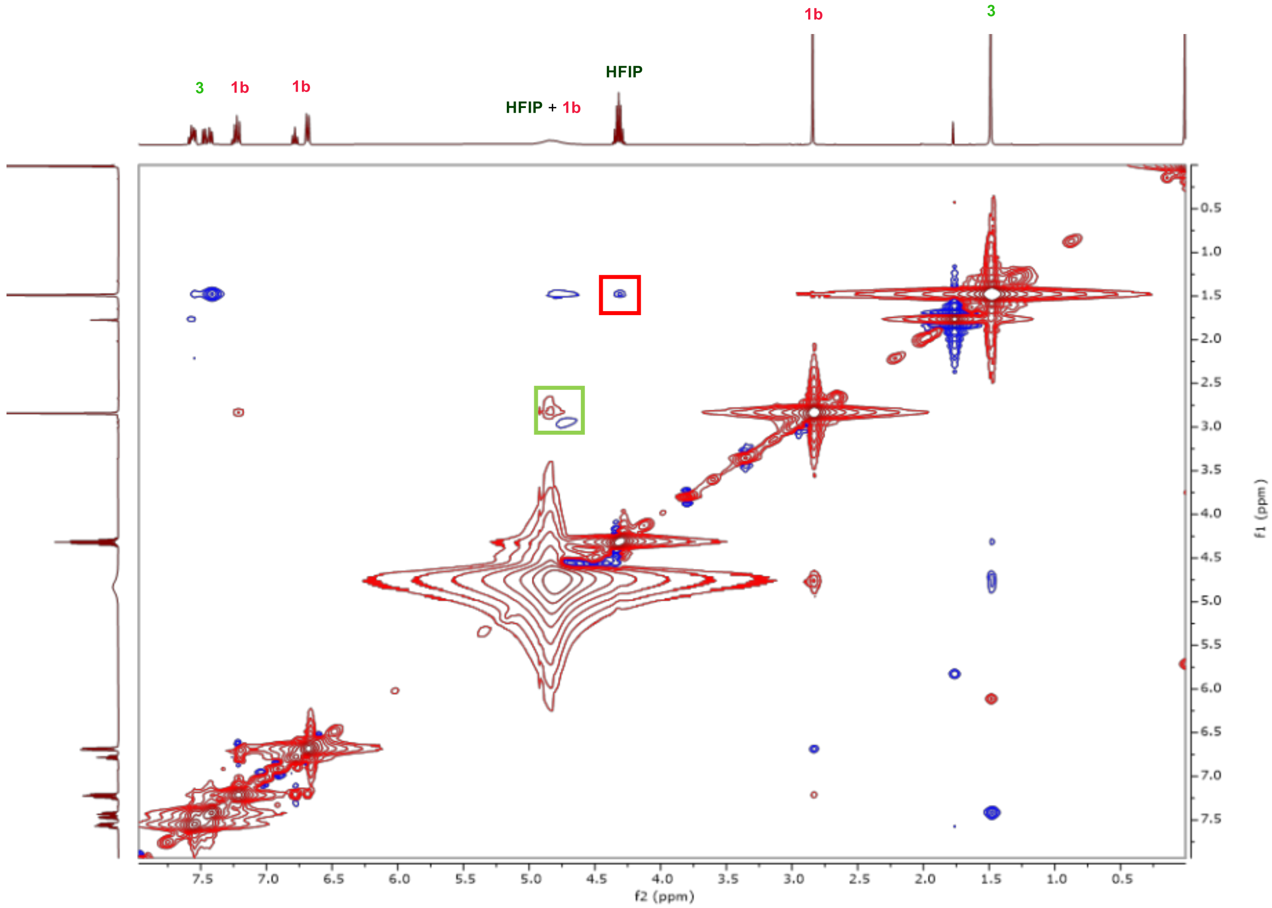


Figure S7. ^{1}H-^{1}H NOESY-2D (400 MHz, $CDCl_3$) of the ternary mixture (HFIP : **1b** : **3**)

8.3.4. ^{1}H-^{19}F HOESY-2D experiments

In order to confirm the proposed intermolecular interaction and taking advantage of the fluorine atoms in both components, HFIP and **3**, a series of ^{1}H-^{19}F Heteronuclear experiments were performed for both the binary (Figures S8-9) and ternary (Figure S10) mixtures.

For the HFIP : **1b** binary mixture the most significant interaction observed are between ^{19}F (HFIP) and NMe and aromatic signals (**1b**), that are highlighted under red boxes (Figure S8). These interactions confirm the intermolecular spatial connection between HFIP and **1b**.

For the HFIP : **3** binary mixture the most significant interaction observed are between ^{19}F (HFIP) and Me (**3**), that is highlighted under a green box (Figure S9). This interaction confirms the intermolecular spatial connection between HFIP and **3**.

For the most interesting ternary mixture the most significant interaction observed are between ^{19}F (HFIP) and NMe and aromatic signals (**1b**), that are highlighted under red boxes. Additionally, there is a strong interaction between ^{19}F (HFIP) and Me (**3**), that is highlighted under a green box (Figure S10). These interactions reinforce the intermolecular spatial connection between the three species within the ternary mixture.

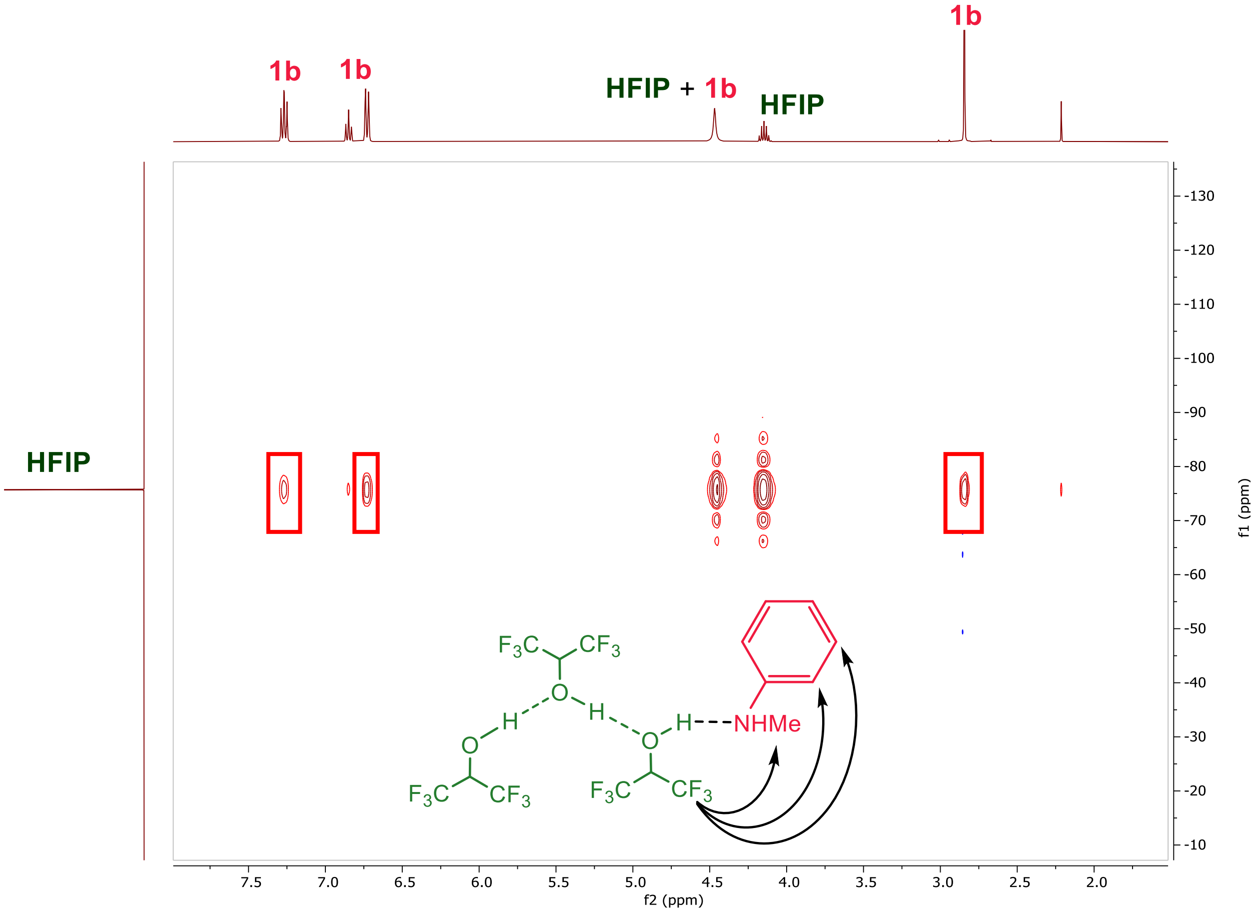


Figure S8. [1]H-[19]F HOESY-2D experiment of the HFIP : **1b** binary mixture.

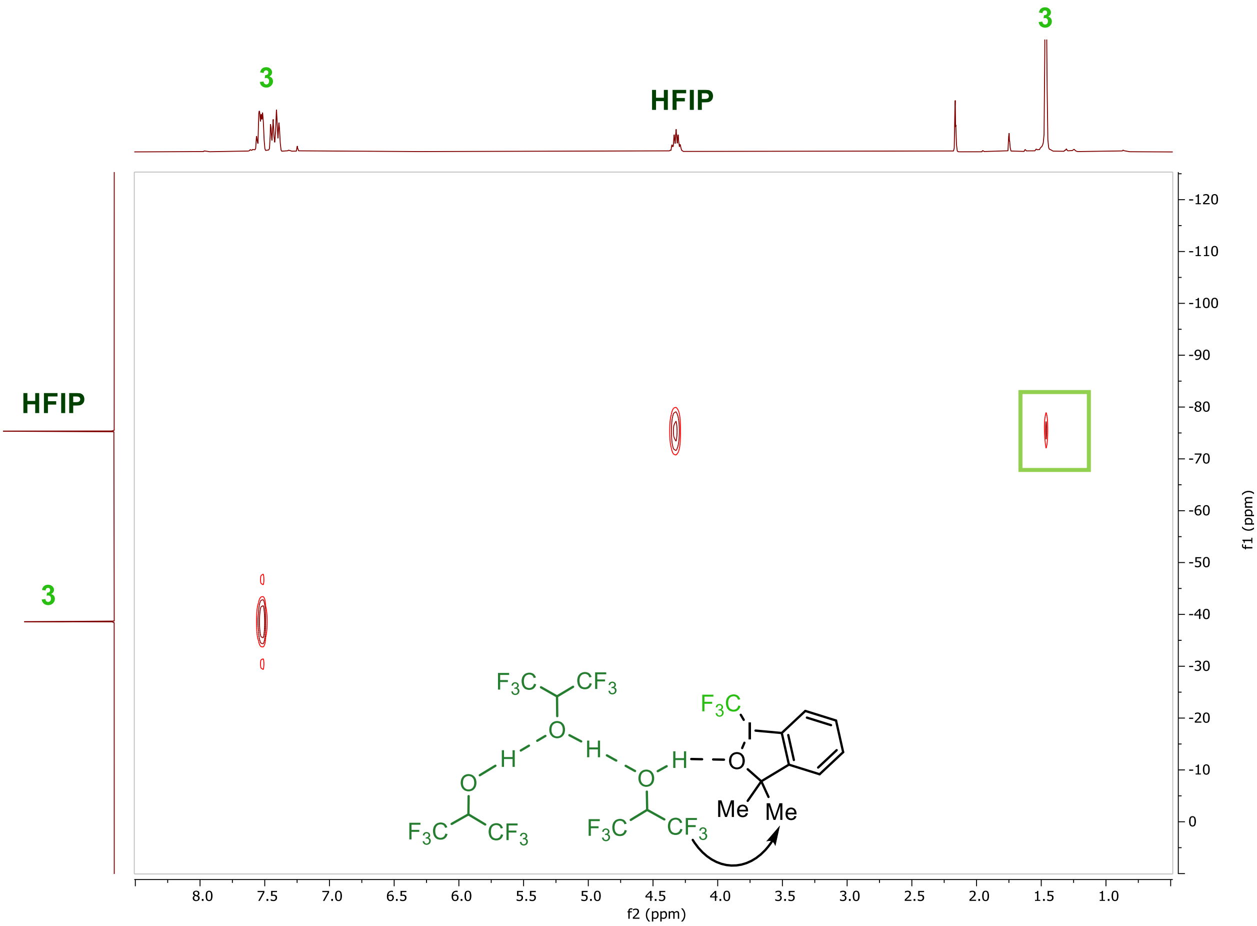


Figure S9. [1]H-[19]F HOESY-2D experiment of the HFIP : **3** binary mixture.

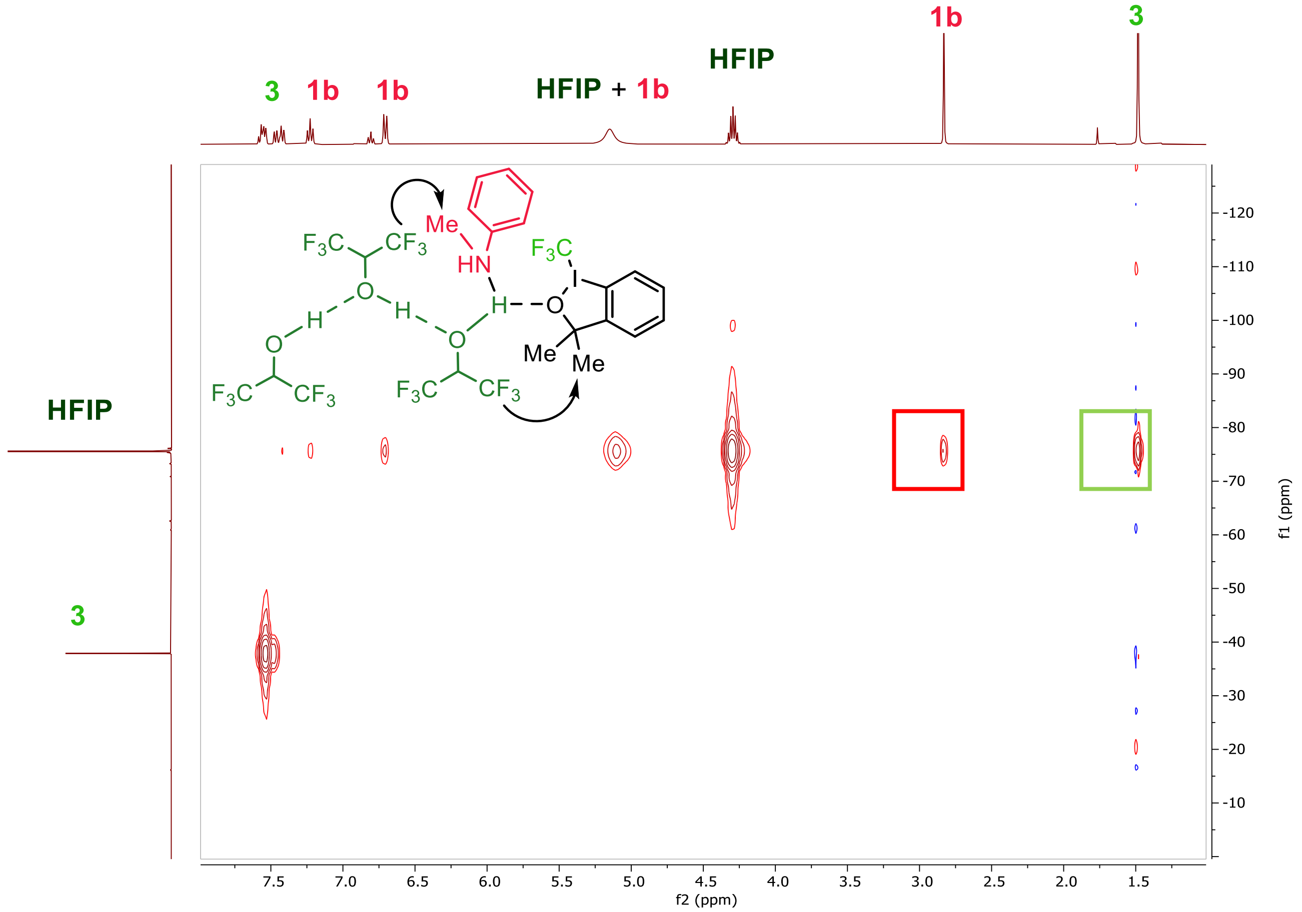


Figure S10. [1]H-[19]F HOESY-2D experiment of the ternary mixture.

8.3.5. Diffusion ordered spectroscopy (DOSY) experiments

DOSY measurements were performed using a Bruker DPX-400 equipped with a BBFO probe head at 298 K with constant temperature control (air flow 400 l h-1) using the 2D sequence for diffusion measurement, double stimulated echo for convection compensation and longitudinal eddy current delay, using bipolar gradient pulses for diffusion and three spoil gradients (Bruker terminology: dstebpgp35) pulse sequence. Diffusion data were collected using 32K data points on well mixed homogeneous samples containing TMS as a suitable internal reference. Experiments were performed in two stages: 1) initially 1D-edited DOSY experiments were used to optimize the diffusion period Δ for each sample (Δ=100 ms) and 2) the 2D dstebpgp35 sequence was then used, based on the optimized Δ from the previous procedure and with δ=4 ms, with gradient amplitudes ranging from 2 to 85% using 16 increments (difflist). Diffusion constants were obtained directly employing the T1/T2 module in TOPSPIN 3.2 using the variable gradient function and plots were generated using the eddosy module.

DOSY experiments were performed as an approach to study the presence of the proposed H-bonded ternary species in solution. Individual species (HFIP, **1b** and **3**), two binary mixtures (HFIP : **1b** and HFIP : **3**) and one ternary mixture (HFIP : **1b** : **3**) were analysed to calculate their diffusion coefficients. The diffusion coefficient for a given species is calculated as the average of the coefficients of all signals belonging to that species.

For the HFIP : **1b** binary mixture (Figure S14 and Table S10, entry 4) there is a moderate reduction in the diffusion coefficients for both HFIP ($\Delta D/D_{TMS} = 0.2$) and **1b** ($\Delta D/D_{TMS} = 0.1$).

For the HFIP : **3** binary mixture (Figure S15 and Table S10, entry 5) there is a strong reduction in the diffusion coefficient for HFIP ($\Delta D/D_{TMS} = 0.52$), while **3** remains at the same value ($\Delta D/D_{TMS} = 0.02$).

For the HFIP : **1b** : **3** ternary mixture (Figure S16 and Table S10, entry 6) there is a strong reduction in the diffusion coefficient for HFIP ($\Delta D/D_{TMS} = 0.38$), a moderate reduction in the diffusion coefficient for **1b** ($\Delta D/D_{TMS} = 0.11$), while **3** remains at the same value ($\Delta D/D_{TMS} = -0.01$). In the ternary mixture, all species diffuse at a similar rate that is very close to the value of the heaviest component **3** ($D/D_{TMS} = 0.54$), where HFIP and **1b** reduces their diffusing rate ($D/D_{TMS} = 0.38$ and 0.11 respectively) to meet that of **3**, as a proof of the proposed supramolecular H-bonded species.

Entry	**Species**		**D (cm²/s)**	**D/D_{TMS}**	**$\Delta D/D_{TMS}$**
1	HFIP		$2.07*10^{-5}$	1.03	-
2	**1b**		$1.72*10^{-5}$	0.96	-
3	**3**		$1.04*10^{-5}$	0.53	-
4	HFIP : **1b** binary mixture	HFIP	$1.55*10^{-5}$	0.83	0.2
		1b	$1.53*10^{-5}$	0.86	0.1
5	HFIP : **3** binary mixture	HFIP	$1.11*10^{-5}$	0.51	0.52
		3	$1.10*10^{-5}$	0.51	0.02
6	HFIP : **1b** : **3** ternary mixture	HFIP	$1.41*10^{-5}$	0.65	0.38
		1b	$1.84*10^{-5}$	0.85	0.11
		3	$1.18*10^{-5}$	0.54	- 0.01

Table S10. Diffusion coefficients: absolute values and relative to TMS.

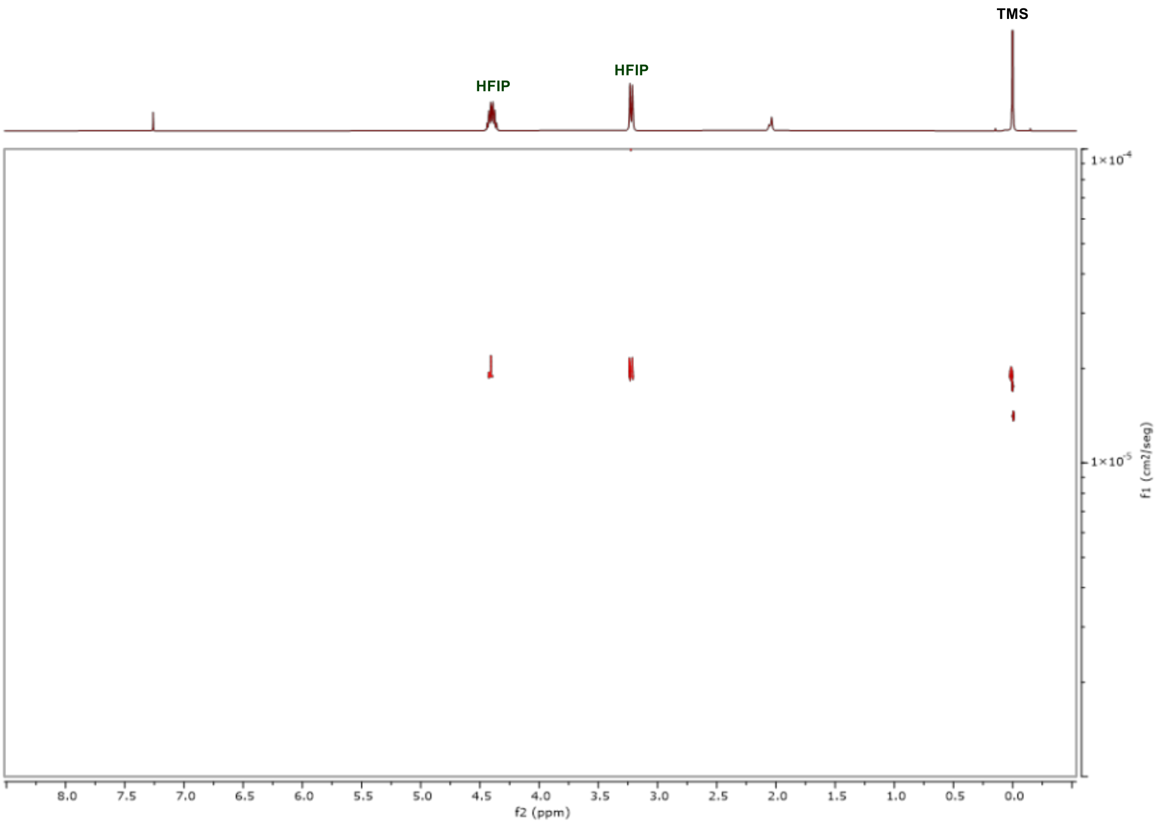


Figure S11. DOSY experiment of HFIP

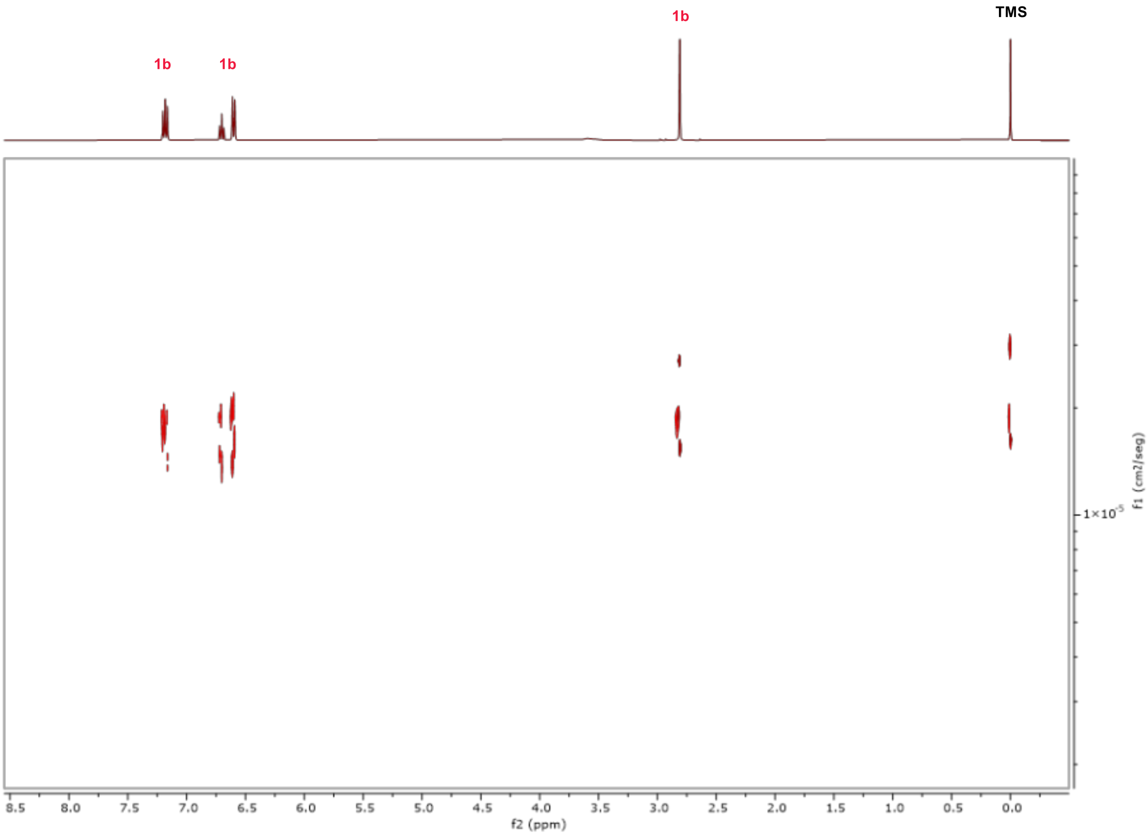


Figure S12. DOSY experiment of **1b**.

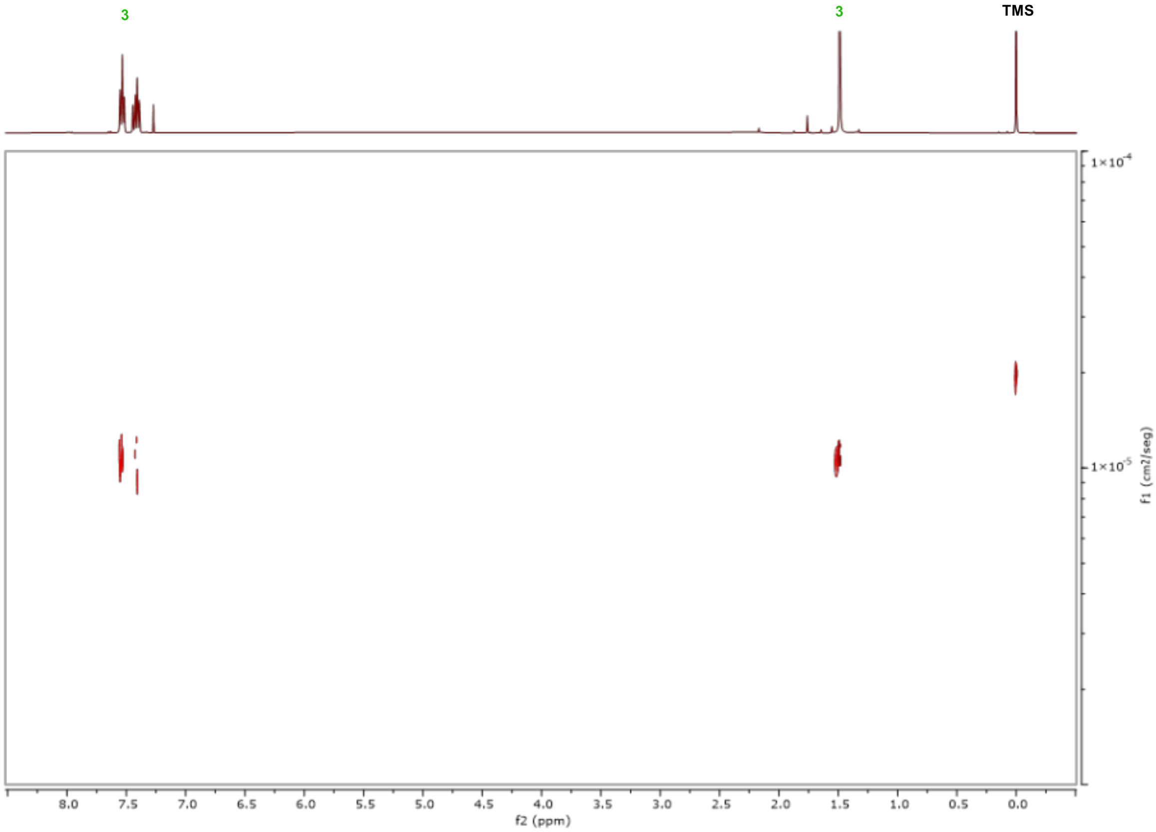


Figure S13. DOSY experiment of **3**.

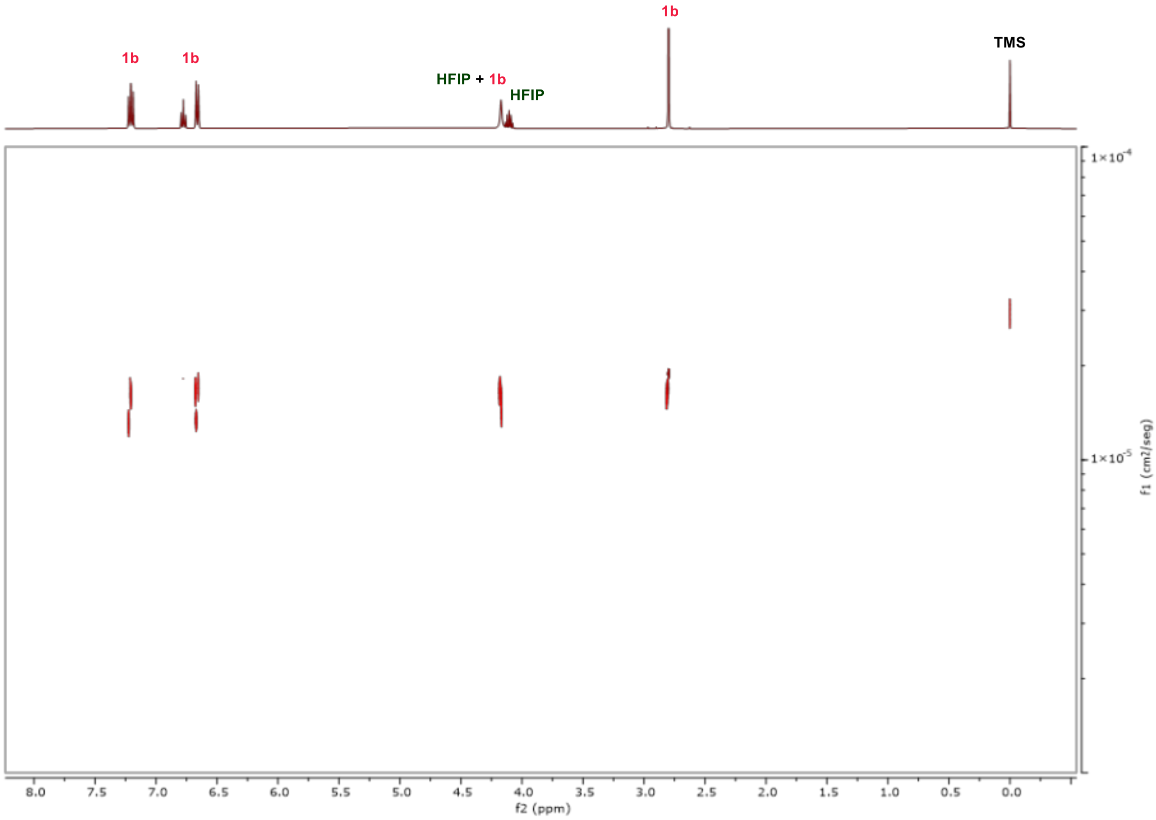


Figure S14. DOSY experiment of the **1b** : HFIP binary mixture.

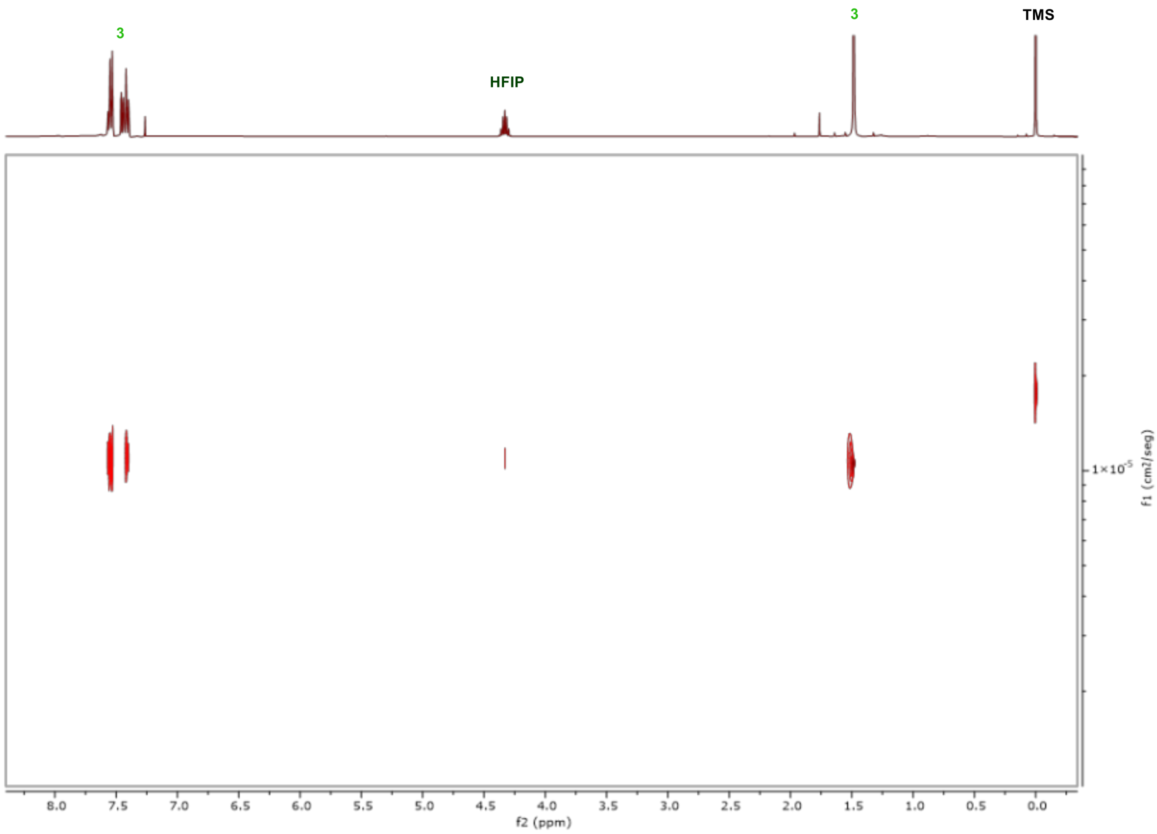


Figure S15. DOSY experiment of the **3** : HFIP binary mixture.

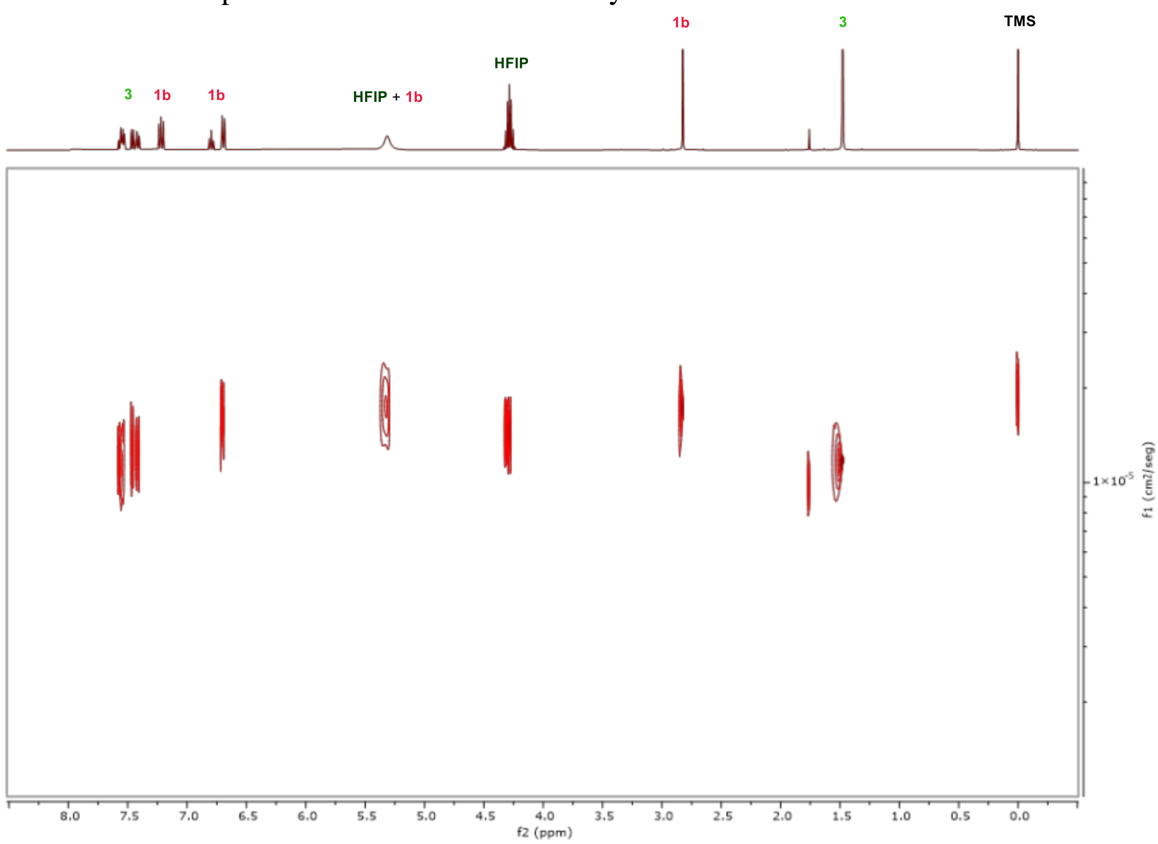
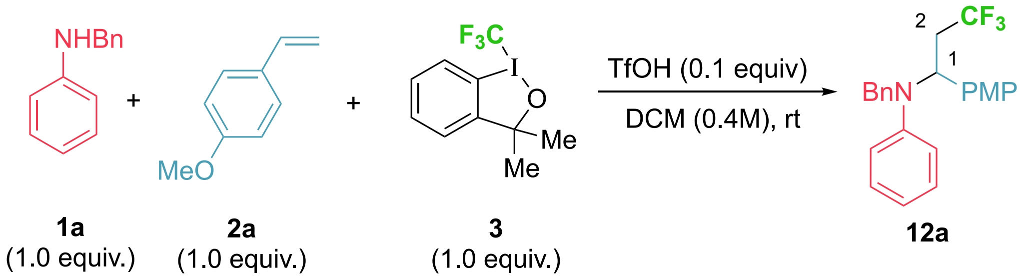


Figure S16. DOSY experiment of the **1b** : **3** : HFIP ternary mixture.

8.4. Kinetic studies

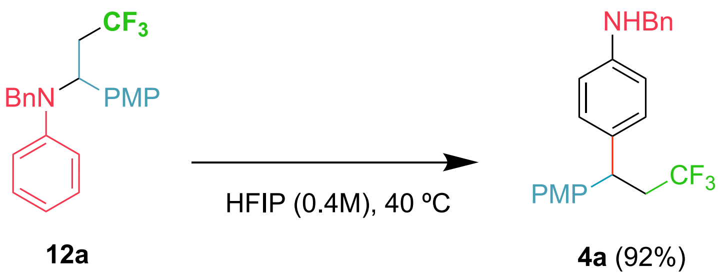
Synthesis of *N*-Benzyl-*N*-[3,3,3-trifluoro-1-(4-methoxyphenyl)propyl]aniline, **12a**



From aniline **1a** (36.7 mg, 0.2 mmol), alkene **2a** (26.8 mg, 0.2 mmol), trifluoromethyl reagent **3** (66.0 mg, 0.2 mmol) and TfOH (1.78 μL, 0.02 mmol) in 0.5 mL of dry DCM, following the general procedure, aniline **12a** was obtained. The crude was quenched with $NaHCO_3$, and extracted with ethyl acetate and brine. The organic phases were dry over Na_2SO_4 and chromatographic purification (gradient elution: 0:100 → 20:80 Et_2O – hexane) and (isocratic elution: 4:96 AcOH – Toluene) gave **12a** (20.5 mg, 27%), as a colourless oil.

Data for **12a**: R_f 0.45 (20% Et_2O – hexane), 0.7 (4% AcOH – toluene). **^{1}H NMR (400 MHz, CD_3OD)** δ 7.25 (2H, d, *J* = 8.7 Hz, Ar), 7.18 – 7.03 (7H, m, Ar), 6.86 (4H, m, Ar), 6.74 (1H, t, *J* = 7.4 and 1.0 Hz, Ar), 5.37 (1H, t, *J* = 6.8 Hz, 1-H), 4.31 (1H, d, *J* = 16.3 Hz, CH_2 Bn), 4.15 (1H, d, *J* = 16.4 Hz, CH_2 Bn), 3.76 (3H, s, OMe), 3.05 – 2.87 (2H, m, 2-H_2). **^{13}C NMR (101 MHz, CD_3OD)** δ 160.7 (1C, C Ar), 149.8 (1C, C Ar), 140.4 (1C, C Ar), 131.9 (1C, C Ar), 130.1 (2C, CH Ar), 129.9 (2C, CH Ar), 129.1 (2C, CH Ar), 128.23 (1C, q, *J* = 276.5 Hz, CF_3), 128.18 (2C, CH Ar), 127.5 (1C, CH Ar), 120.3 (1C, CH Ar), 118.8 (2C, CH Ar), 114.7 (2C, CH Ar), 59.9 (1C, q, *J* = 2.9 Hz, C-1), 55.7 (1C, OMe), 50.5 (1C, CH_2 Bn), 36.3 (1C, q, *J* = 27.1 Hz, C-2). **^{19}F NMR (376 MHz, MeOH-d_4)** δ –64.4 (3F, CF_3).

· Hoffman-Martius rearrangement of product **12a**



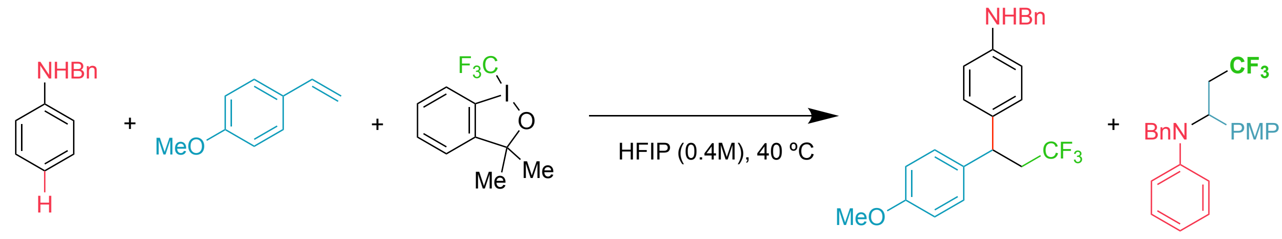
From aniline **12a** (20.5 mg, 0.053 mmol) in 133 μL of HFIP, following the general procedure, aniline **4a** (18.8 mg, 92%) was obtained without further purification.

· Kinetic studies

Kinetic experiments were performed one round and carrying out the reaction following the general protocol. Aliquots at 5, 10, 20, 40, 60, 100, 180 and 300 minutes were taken, diluted with a solution of $CDCl_3$ containing the internal standard and ^{1}H NMR experiments recorded in JEOL JNM-

ECZ400R spectrometer using benzoic acid as internal standard. The integrals were measured over the most clean and isolated signal of each component of the mixture. Concentration of each aliquot was corrected to the concentration in the reaction mixture.

Different anilines were tested: *N*-Benzylaniline **1a**, Aniline **1c** and *N*,*N*-Dimethylaniline **1d**.



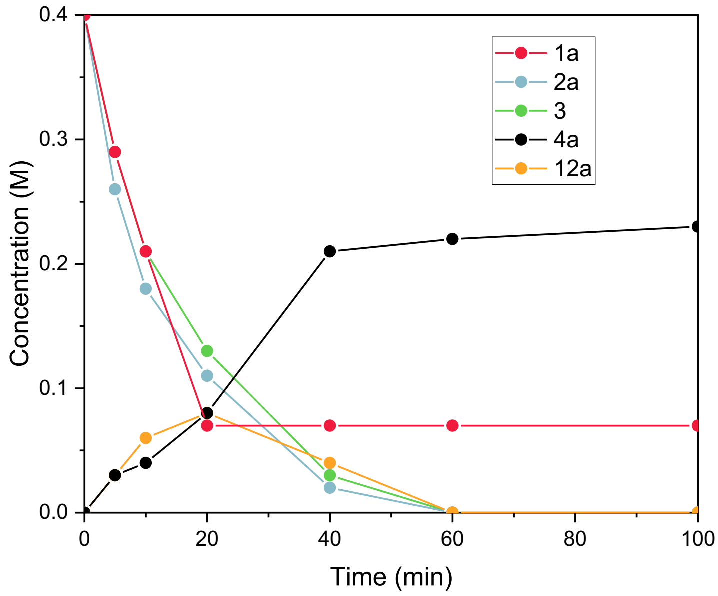
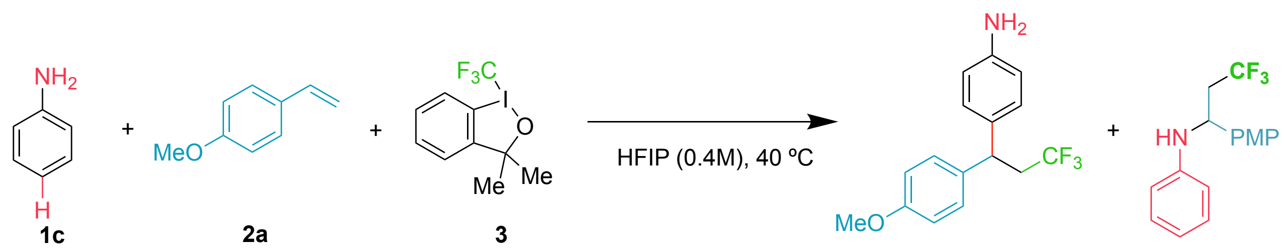


Figure S17. Kinetic experiment for the reaction mixture containing **1a**.



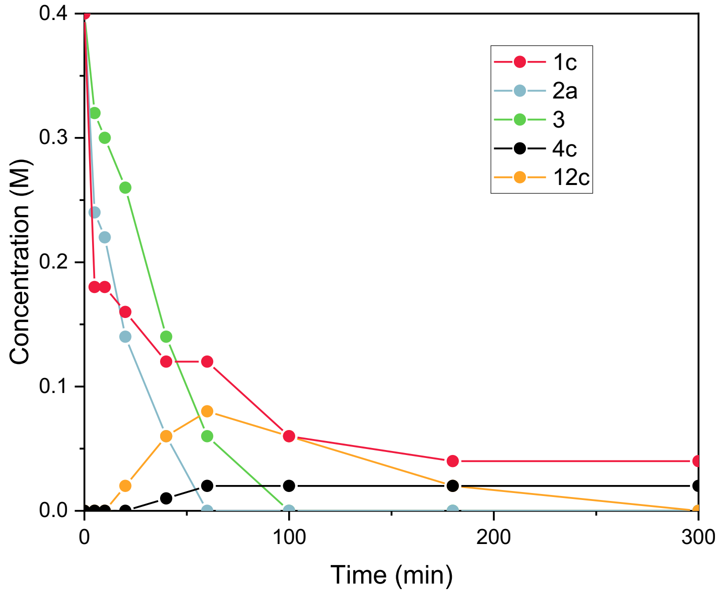
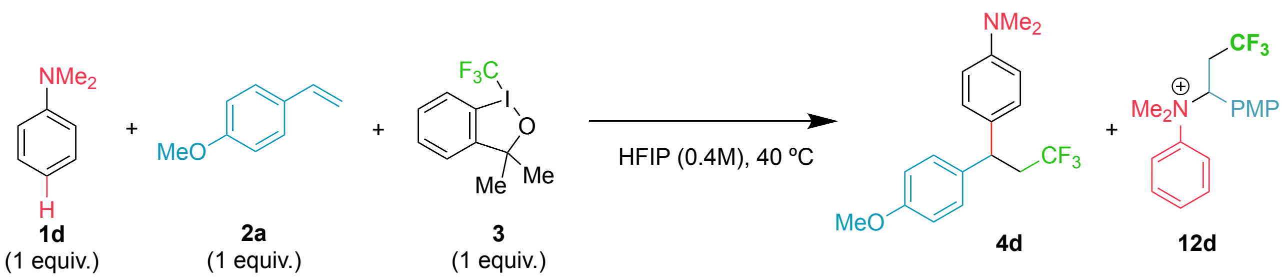


Figure S18. Kinetic experiment for the reaction mixture containing **1c**.



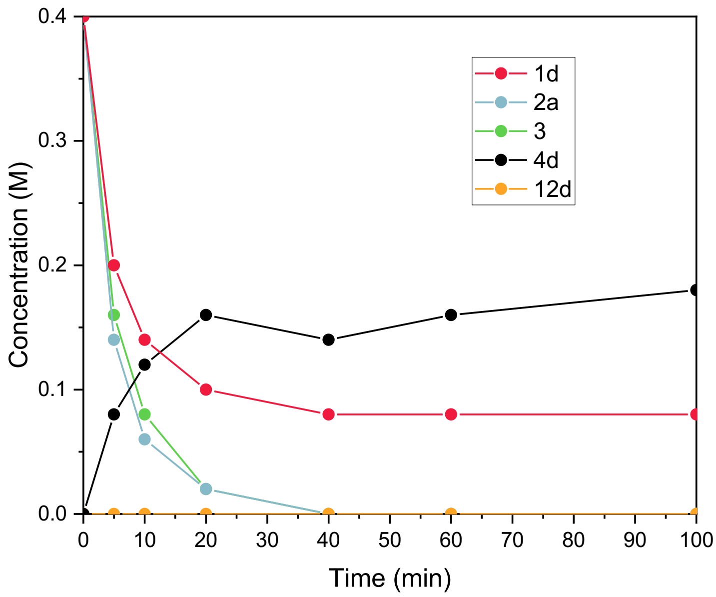


Figure S19. Kinetic experiment for the reaction mixture containing **1d**.

9. References

(1) Yue, J. F., Ran, G. Y., Yang, X. X., Du, W. & Chen, Y. C. Asymmetric Diels–Alder Cycloadditions of Benzofulvene-Based 2,4-Dienals via Trienamine Activation. *Org. Chem. Front.* **5**, 2676–2679 (2018).

(2) Zhang, X., Thimmaiah, M. & Fang, S. Simple and Efficient Synthesis of 4,7-Dimethoxy-1(H)-Indene. *Synth. Commun.* **37**, 1873-1877 (2007).

(3) Jiao, M., Gao, J. & Fang, X. Enantioselective Synthesis of 4-Cyanotetrahydroquinolines via Ni-Catalyzed Hydrocyanation of 1,2-Dihydroquinolines. *Org. Lett.* **22**, 8566-8571 (2020).

(4) Nakayama, K., Maeta, N., Horiguchi, G., Kamiya, H. & Okada, Y. Radical Cation Diels–Alder Reactions by TiO_2 Photocatalysis. *Org. Lett.* **21**, 2246–2250 (2019).

(5) Wang, X.-P., Lin, J.-H., Zhang, C.-P., Xiao, J.-C. & Zheng, X. Copper-Catalyzed Trifluoromethylation of Alkenes with an Electrophilic Trifluoromethylating Reagent. *Beilstein J. Org. Chem.* **9**, 2635–2640 (2013).

(6) Wang, F., Wang, D., Mu, X., Chen, P. & Liu, G. Copper-Catalyzed Intermolecular Trifluoromethylarylation of Alkenes: Mutual Activation of Arylboronic Acid and CF_3^+ Reagent. *J. Am. Chem. Soc.* **136**, 10202–10205 (2014).

10. X-Ray diffraction analysis

Crystal structure report for compound 5

Compound **5** was crystallized using a mixture of THF : Pentane (compound **5**was dissolved in THF, and exposed to pentane vapours) in order to obtain appropriate crystals for X-ray analysis.

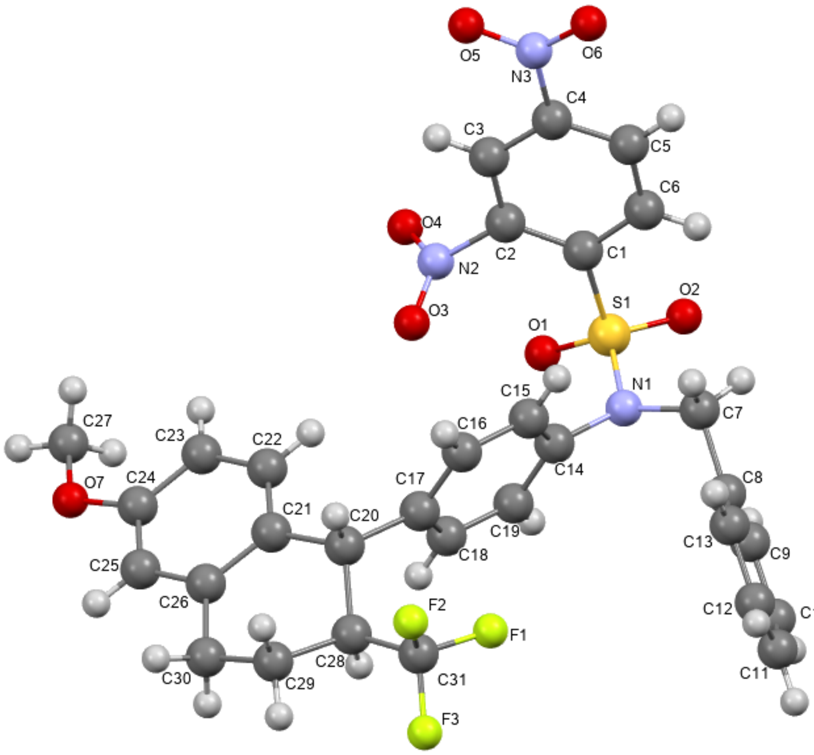


Figure S20. Ball and stick plot of compound **5** with non-hydrogen atoms labelled.

Compound **5** collection details are gathered in the following tables:

Table S11. Sample and crystal data for 5.

Identification code	03673	
Chemical formula	$C_{31}H_{26}F_3N_3O_7S{\cdot}C_4H_8O$	
Formula weight	713.71 g/mol	
Temperature	250(2) K	
Wavelength	0.71073 Å	
Crystal size	0.026 x 0.132 x 0.285 mm	
Crystal habit	clear colourless ribbon	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.9290(19) Å	α = 86.336(14)°
	b = 13.676(4) Å	β = 88.961(14)°
	c = 20.842(6) Å	γ = 85.079(15)°
Volume	1680.2(9) Å^3	
Z	2	
Density (calculated)	1.411 g/cm^3	
Absorption coefficient	0.170 mm^{-1}	
F(000)	744	

Table S12. Data collection and structure refinement for 5.

Theta range for data collection	1.84 to 25.35°
Index ranges	-7<=h<=7, -16<=k<=16, -24<=l<=25
Reflections collected	50261
Independent reflections	6138 [R(int) = 0.0595]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9960 and 0.9530
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2018/2
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6138 / 156 / 492
Goodness-of-fit on F^2	1.049
Δ/σ_{max}	0.001
Final R indices	4077 data; $I>2\sigma(I)$ R1 = 0.0489, wR2 = 0.1248
	all data R1 = 0.0856, wR2 = 0.1489
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0716P)^2+0.6321P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.328 and -0.376 eÅ^{-3}
R.M.S. deviation from mean	0.053 eÅ^{-3}

Table S13. Atomic coordinates and equivalent isotropic atomic displacemente parameters (A2) for 5

U(eq) is defined as one third of the trace of the orthogonalized

	x/a	**y/b**	**z/c**	**U(eq)**
C1	0.6812(4)	0.69387(18)	0.78307(12)	0.0373(6)
C2	0.6965(4)	0.70953(18)	0.71618(12)	0.0357(6)
C3	0.5456(4)	0.77381(19)	0.68213(13)	0.0399(6)
C4	0.3724(4)	0.82130(18)	0.71586(13)	0.0412(6)
C5	0.3492(5)	0.8089(2)	0.78123(14)	0.0468(7)
C6	0.5069(5)	0.74553(19)	0.81473(13)	0.0446(7)
C7	0.5627(5)	0.5148(2)	0.89714(13)	0.0499(7)
C8	0.5603(4)	0.4160(2)	0.93277(12)	0.0417(6)
C9	0.7380(5)	0.3784(2)	0.97172(13)	0.0491(7)
C10	0.7336(6)	0.2885(2)	0.00524(15)	0.0603(9)
C11	0.5535(7)	0.2343(3)	0.00043(17)	0.0715(10)
C12	0.3758(7)	0.2705(3)	0.96267(19)	0.0849(12)
C13	0.3783(6)	0.3611(3)	0.92924(16)	0.0668(9)
C14	0.7235(4)	0.44783(18)	0.79498(11)	0.0350(6)
C15	0.5325(4)	0.45498(19)	0.75776(12)	0.0380(6)

	x/a	y/b	z/c	U(eq)
C16	0.5183(4)	0.39351(19)	0.70810(12)	0.0395(6)
C17	0.6925(4)	0.32407(18)	0.69497(12)	0.0370(6)
C18	0.8835(5)	0.31744(19)	0.73317(13)	0.0439(7)
C19	0.8995(4)	0.37791(19)	0.78311(12)	0.0411(6)
C20	0.6765(5)	0.25892(19)	0.63876(13)	0.0425(6)
C21	0.8654(4)	0.27321(18)	0.58901(12)	0.0377(6)
C22	0.9637(5)	0.36133(19)	0.58105(13)	0.0431(7)
C23	0.1347(5)	0.3771(2)	0.53627(12)	0.0434(7)
C24	0.2086(5)	0.3015(2)	0.49773(12)	0.0445(7)
C25	0.1091(5)	0.2139(2)	0.50430(13)	0.0476(7)
C26	0.9401(5)	0.19789(19)	0.54917(12)	0.0404(6)
C27	0.5093(5)	0.3888(3)	0.45005(15)	0.0604(8)
C28	0.6720(5)	0.1491(2)	0.65904(13)	0.0468(7)
C29	0.6489(5)	0.0918(2)	0.59849(15)	0.0563(8)
C30	0.8512(6)	0.0978(2)	0.55589(14)	0.0537(8)
C31	0.4839(5)	0.1257(2)	0.70474(16)	0.0542(8)
F1	0.4773(4)	0.17316(14)	0.75891(9)	0.0799(6)
F2	0.2793(3)	0.14497(17)	0.67987(11)	0.0865(7)
F3	0.5021(3)	0.03000(13)	0.72425(10)	0.0736(6)
N1	0.7445(4)	0.51288(16)	0.84685(10)	0.0407(5)
N2	0.8774(4)	0.65853(17)	0.67759(10)	0.0425(5)
N3	0.2047(4)	0.88810(18)	0.67887(14)	0.0549(6)
O1	0.0646(3)	0.58918(14)	0.79204(10)	0.0517(5)
O2	0.8914(4)	0.65760(16)	0.88970(10)	0.0634(6)
O3	0.8590(4)	0.57345(14)	0.66738(10)	0.0566(6)
O4	0.0272(3)	0.70723(16)	0.65659(11)	0.0642(6)
O5	0.2416(4)	0.90490(17)	0.62182(12)	0.0720(7)
O6	0.0392(4)	0.92198(17)	0.70802(13)	0.0759(7)
O7	0.3797(4)	0.30662(16)	0.45293(9)	0.0609(6)
S1	0.87011(12)	0.61234(5)	0.83071(3)	0.0437(2)
O8A	0.0962(15)	0.9357(6)	0.8965(5)	0.1069(18)
C32A	0.1215(19)	0.0388(8)	0.8782(8)	0.131(4)
C33A	0.908(2)	0.0860(10)	0.8689(10)	0.179(6)
C34A	0.7384(15)	0.0168(7)	0.9043(8)	0.148(4)
C35A	0.8692(19)	0.9245(8)	0.8997(8)	0.125(4)
O8B	0.124(4)	0.9676(16)	0.8873(13)	0.1069(18)
C32B	0.052(4)	0.0604(15)	0.8529(12)	0.112(5)
C33B	0.843(4)	0.0909(19)	0.8810(16)	0.128(6)
C34B	0.778(4)	0.9904(19)	0.8691(13)	0.130(6)
C35B	0.924(4)	0.934(2)	0.9175(15)	0.127(7)

Table S14. Bond lengths (Å) for 5.

C1-C6	1.383(4)	C1-C2	1.399(4)
C1-S1	1.780(3)	C2-C3	1.373(4)
C2-N2	1.482(3)	C3-C4	1.374(4)
C4-C5	1.368(4)	C4-N3	1.483(4)
C5-C6	1.386(4)	C7-N1	1.489(3)
C7-C8	1.500(4)	C8-C13	1.372(4)
C8-C9	1.385(4)	C9-C10	1.376(4)
C10-C11	1.360(5)	C11-C12	1.366(5)
C12-C13	1.384(5)	C14-C15	1.377(4)
C14-C19	1.383(3)	C14-N1	1.457(3)
C15-C16	1.383(4)	C16-C17	1.378(3)
C17-C18	1.389(4)	C17-C20	1.526(4)
C18-C19	1.380(4)	C20-C21	1.528(4)
C20-C28	1.537(4)	C21-C22	1.382(4)
C21-C26	1.402(3)	C22-C23	1.387(4)
C23-C24	1.386(4)	C24-O7	1.370(3)
C24-C25	1.377(4)	C25-C26	1.380(4)
C26-C30	1.505(4)	C27-O7	1.413(4)
C28-C31	1.495(4)	C28-C29	1.541(4)
C29-C30	1.484(4)	C31-F2	1.327(4)
C31-F1	1.336(4)	C31-F3	1.341(3)
N1-S1	1.620(2)	N2-O3	1.211(3)
N2-O4	1.214(3)	N3-O5	1.216(3)
N3-O6	1.217(3)	O1-S1	1.420(2)
O2-S1	1.424(2)	O8A-C35A	1.368(10)
O8A-C32A	1.457(10)	C32A-C33A	1.380(12)
C33A-C34A	1.581(13)	C34A-C35A	1.431(12)
O8B-C35B	1.427(17)	O8B-C32B	1.451(16)
C32B-C33B	1.406(17)	C32B-C34B	1.97(3)
C33B-C34B	1.494(19)	C34B-C35B	1.473(19)

Table S15. Bond angles (°) for 5.

C6-C1-C2	117.8(2)	C6-C1-S1	117.3(2)
C2-C1-S1	124.86(19)	C3-C2-C1	122.1(2)
C3-C2-N2	115.7(2)	C1-C2-N2	122.2(2)
C2-C3-C4	117.6(2)	C5-C4-C3	122.8(3)
C5-C4-N3	119.5(2)	C3-C4-N3	117.7(3)
C4-C5-C6	118.5(2)	C1-C6-C5	121.2(3)
N1-C7-C8	110.4(2)	C13-C8-C9	117.7(3)
C13-C8-C7	120.9(3)	C9-C8-C7	121.3(3)
C10-C9-C8	121.2(3)	C11-C10-C9	120.3(3)
C10-C11-C12	119.3(3)	C11-C12-C13	120.7(3)
C8-C13-C12	120.7(3)	C15-C14-C19	119.7(2)

C15-C14-N1	121.2(2)	C19-C14-N1	119.1(2)
C14-C15-C16	120.1(2)	C17-C16-C15	121.1(2)
C16-C17-C18	118.0(2)	C16-C17-C20	120.4(2)
C18-C17-C20	121.6(2)	C19-C18-C17	121.4(2)
C18-C19-C14	119.5(2)	C17-C20-C21	111.9(2)
C17-C20-C28	113.9(2)	C21-C20-C28	109.7(2)
C22-C21-C26	118.2(2)	C22-C21-C20	121.0(2)
C26-C21-C20	120.8(2)	C21-C22-C23	122.7(2)
C24-C23-C22	118.5(2)	O7-C24-C25	116.2(2)
O7-C24-C23	124.3(3)	C25-C24-C23	119.5(2)
C24-C25-C26	122.1(2)	C25-C26-C21	119.1(2)
C25-C26-C30	118.5(2)	C21-C26-C30	122.3(2)
C31-C28-C20	114.4(2)	C31-C28-C29	108.2(2)
C20-C28-C29	108.9(2)	C30-C29-C28	111.1(2)
C29-C30-C26	114.4(2)	F2-C31-F1	105.1(3)
F2-C31-F3	106.6(3)	F1-C31-F3	104.9(2)
F2-C31-C28	113.7(3)	F1-C31-C28	115.0(3)
F3-C31-C28	110.8(2)	C14-N1-C7	116.9(2)
C14-N1-S1	117.77(16)	C7-N1-S1	117.99(18)
O3-N2-O4	125.5(2)	O3-N2-C2	117.6(2)
O4-N2-C2	116.8(2)	O5-N3-O6	124.8(3)
O5-N3-C4	117.9(3)	O6-N3-C4	117.3(3)
C24-O7-C27	118.9(2)	O1-S1-O2	120.19(13)
O1-S1-N1	108.56(12)	O2-S1-N1	107.31(13)
O1-S1-C1	107.15(12)	O2-S1-C1	105.99(12)
N1-S1-C1	106.94(12)	C35A-O8A-C32A	107.2(8)
C33A-C32A-O8A	108.1(9)	C32A-C33A-C34A	105.8(10)
C35A-C34A-C33A	98.9(10)	O8A-C35A-C34A	111.6(9)
C35B-O8B-C32B	105.4(17)	C33B-C32B-O8B	105.1(18)
C33B-C32B-C34B	49.2(11)	O8B-C32B-C34B	73.4(13)
C32B-C33B-C34B	85.4(18)	C35B-C34B-C33B	98.(2)
C35B-C34B-C32B	82.1(14)	C33B-C34B-C32B	45.4(10)
O8B-C35B-C34B	92.0(19)		

Table S16. Torsion angles (°) for 5.

C6-C1-C2-C3	0.1(4)	S1-C1-C2-C3	-179.78(19)
C6-C1-C2-N2	179.6(2)	S1-C1-C2-N2	-0.3(4)
C1-C2-C3-C4	-1.7(4)	N2-C2-C3-C4	178.8(2)
C2-C3-C4-C5	1.8(4)	C2-C3-C4-N3	-177.9(2)
C3-C4-C5-C6	-0.2(4)	N3-C4-C5-C6	179.5(2)
C2-C1-C6-C5	1.5(4)	S1-C1-C6-C5	-178.6(2)
C4-C5-C6-C1	-1.5(4)	N1-C7-C8-C13	-115.1(3)

N1-C7-C8-C9	66.8(3)	C13-C8-C9-C10	0.7(4)
C7-C8-C9-C10	178.8(3)	C8-C9-C10-C11	0.3(5)
C9-C10-C11-C12	-0.9(5)	C10-C11-C12-C13	0.3(6)
C9-C8-C13-C12	-1.2(5)	C7-C8-C13-C12	-179.4(3)
C11-C12-C13-C8	0.7(6)	C19-C14-C15-C16	-1.0(4)
N1-C14-C15-C16	178.9(2)	C14-C15-C16-C17	0.3(4)
C15-C16-C17-C18	0.1(4)	C15-C16-C17-C20	-178.2(2)
C16-C17-C18-C19	0.3(4)	C20-C17-C18-C19	178.6(2)
C17-C18-C19-C14	-1.0(4)	C15-C14-C19-C18	1.4(4)
N1-C14-C19-C18	-178.5(2)	C16-C17-C20-C21	119.0(3)
C18-C17-C20-C21	-59.2(3)	C16-C17-C20-C28	-115.8(3)
C18-C17-C20-C28	66.0(3)	C17-C20-C21-C22	-27.5(3)
C28-C20-C21-C22	-154.9(2)	C17-C20-C21-C26	154.0(2)
C28-C20-C21-C26	26.5(3)	C26-C21-C22-C23	-1.2(4)
C20-C21-C22-C23	-179.8(2)	C21-C22-C23-C24	0.5(4)
C22-C23-C24-O7	-178.2(3)	C22-C23-C24-C25	0.8(4)
O7-C24-C25-C26	177.8(3)	C23-C24-C25-C26	-1.3(4)
C24-C25-C26-C21	0.6(4)	C24-C25-C26-C30	-176.2(3)
C22-C21-C26-C25	0.6(4)	C20-C21-C26-C25	179.2(2)
C22-C21-C26-C30	177.3(3)	C20-C21-C26-C30	-4.1(4)
C17-C20-C28-C31	57.3(3)	C21-C20-C28-C31	-176.4(2)
C17-C20-C28-C29	178.4(2)	C21-C20-C28-C29	-55.3(3)
C31-C28-C29-C30	-170.3(3)	C20-C28-C29-C30	64.9(3)
C28-C29-C30-C26	-41.4(4)	C25-C26-C30-C29	-171.8(3)
C21-C26-C30-C29	11.5(4)	C20-C28-C31-F2	65.0(3)
C29-C28-C31-F2	-56.5(3)	C20-C28-C31-F1	-56.2(4)
C29-C28-C31-F1	-177.7(3)	C20-C28-C31-F3	-174.9(2)
C29-C28-C31-F3	63.6(3)	C15-C14-N1-C7	55.8(3)
C19-C14-N1-C7	-124.3(3)	C15-C14-N1-S1	-93.7(3)
C19-C14-N1-S1	86.1(3)	C8-C7-N1-C14	63.6(3)
C8-C7-N1-S1	-146.9(2)	C3-C2-N2-O3	-103.6(3)
C1-C2-N2-O3	76.8(3)	C3-C2-N2-O4	73.3(3)
C1-C2-N2-O4	-106.2(3)	C5-C4-N3-O5	173.1(3)
C3-C4-N3-O5	-7.2(4)	C5-C4-N3-O6	-7.1(4)
C3-C4-N3-O6	172.6(3)	C25-C24-O7-C27	-171.3(3)
C23-C24-O7-C27	7.8(4)	C14-N1-S1-O1	-42.5(2)
C7-N1-S1-O1	168.20(19)	C14-N1-S1-O2	-173.86(18)
C7-N1-S1-O2	36.9(2)	C14-N1-S1-C1	72.8(2)
C7-N1-S1-C1	-76.5(2)	C6-C1-S1-O1	-164.3(2)
C2-C1-S1-O1	15.6(3)	C6-C1-S1-O2	-34.8(3)
C2-C1-S1-O2	145.1(2)	C6-C1-S1-N1	79.5(2)
C2-C1-S1-N1	-100.7(2)	C35A-O8A-C32A-C33A	-2.0(17)
O8A-C32A-C33A-C34A	19.(2)	C32A-C33A-C34A-C35A	-27.(2)

C32A-O8A-C35A-C34A	-18.0(18)	C33A-C34A-C35A-O8A	27.(2)
C35B-O8B-C32B-C33B	19.(3)	C35B-O8B-C32B-C34B	-20.(2)
O8B-C32B-C33B-C34B	-51.(3)	C32B-C33B-C34B-C35B	70.(3)
C32B-O8B-C35B-C34B	25.(3)	C33B-C34B-C35B-O8B	-61.(3)
C32B-C34B-C35B-O8B	-18.(2)		

Table S17. Anisotropic atomic displacement parameters (Å^2) for 5.

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

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0386(15)	0.0345(14)	0.0395(15)	-0.0105(11)	-0.0002(11)	-0.0008(11)
C2	0.0320(14)	0.0331(13)	0.0430(15)	-0.0119(11)	0.0050(11)	-0.0037(11)
C3	0.0439(16)	0.0352(14)	0.0411(15)	-0.0053(11)	0.0021(12)	-0.0053(12)
C4	0.0390(15)	0.0310(14)	0.0531(17)	-0.0045(12)	-0.0011(12)	0.0008(11)
C5	0.0427(16)	0.0398(15)	0.0565(18)	-0.0100(13)	0.0096(13)	0.0069(12)
C6	0.0520(17)	0.0404(15)	0.0404(15)	-0.0089(12)	0.0079(13)	0.0056(13)
C7	0.0508(17)	0.0596(19)	0.0361(15)	-0.0093(13)	0.0068(13)	0.0162(14)
C8	0.0398(15)	0.0557(17)	0.0294(13)	-0.0119(12)	0.0028(11)	0.0031(13)
C9	0.0427(16)	0.0581(19)	0.0468(16)	-0.0099(14)	-0.0054(13)	0.0005(14)
C10	0.064(2)	0.064(2)	0.0495(18)	-0.0021(16)	-0.0065(15)	0.0111(17)
C11	0.096(3)	0.061(2)	0.058(2)	-0.0044(17)	0.015(2)	-0.013(2)
C12	0.082(3)	0.103(3)	0.078(3)	-0.015(2)	0.008(2)	-0.046(3)
C13	0.052(2)	0.099(3)	0.0515(19)	-0.0074(19)	-0.0087(15)	-0.0148(19)
C14	0.0376(14)	0.0347(14)	0.0316(13)	-0.0048(11)	0.0036(11)	0.0038(11)
C15	0.0322(14)	0.0380(14)	0.0427(15)	-0.0063(12)	0.0077(11)	0.0055(11)
C16	0.0315(14)	0.0434(15)	0.0433(15)	-0.0049(12)	0.0008(11)	-0.0006(11)
C17	0.0373(14)	0.0355(14)	0.0385(14)	-0.0055(11)	0.0062(11)	-0.0036(11)
C18	0.0401(15)	0.0394(15)	0.0508(16)	-0.0135(13)	0.0044(13)	0.0118(12)
C19	0.0360(15)	0.0434(15)	0.0428(15)	-0.0077(12)	-0.0040(12)	0.0079(12)
C20	0.0432(16)	0.0393(15)	0.0452(16)	-0.0103(12)	0.0004(12)	-0.0001(12)
C21	0.0414(15)	0.0342(14)	0.0369(14)	-0.0044(11)	-0.0005(11)	0.0012(11)
C22	0.0483(16)	0.0374(15)	0.0441(15)	-0.0114(12)	0.0058(13)	-0.0020(12)
C23	0.0526(17)	0.0388(15)	0.0400(15)	-0.0054(12)	-0.0004(13)	-0.0074(13)
C24	0.0500(17)	0.0514(17)	0.0318(14)	-0.0052(12)	0.0045(12)	-0.0018(13)
C25	0.0635(19)	0.0415(16)	0.0381(15)	-0.0118(12)	0.0074(14)	-0.0013(14)
C26	0.0499(16)	0.0350(14)	0.0360(14)	-0.0068(11)	0.0007(12)	0.0007(12)
C27	0.057(2)	0.074(2)	0.0534(18)	-0.0097(16)	0.0079(15)	-0.0187(17)
C28	0.0482(17)	0.0431(16)	0.0491(16)	-0.0067(13)	0.0055(13)	-0.0024(13)
C29	0.063(2)	0.0464(17)	0.0621(19)	-0.0166(14)	0.0097(16)	-0.0127(15)
C30	0.072(2)	0.0380(16)	0.0516(17)	-0.0102(13)	0.0080(15)	-0.0032(14)
C31	0.057(2)	0.0404(17)	0.065(2)	-0.0070(15)	0.0085(16)	-0.0049(14)
F1	0.1122(17)	0.0664(12)	0.0648(12)	-0.0167(10)	0.0405(11)	-0.0282(12)
F2	0.0449(11)	0.1063(17)	0.1051(16)	-0.0054(13)	0.0110(11)	0.0083(11)
F3	0.0848(14)	0.0456(11)	0.0901(14)	-0.0012(9)	0.0140(11)	-0.0102(9)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	0.0473(13)	0.0420(13)	0.0316(11)	-0.0091(9)	0.0033(10)	0.0071(10)
N2	0.0397(13)	0.0440(14)	0.0443(13)	-0.0114(11)	0.0075(10)	-0.0018(11)
N3	0.0530(16)	0.0398(14)	0.0705(19)	-0.0035(13)	-0.0109(14)	0.0058(12)
O1	0.0332(10)	0.0539(12)	0.0682(13)	-0.0139(10)	-0.0045(9)	0.0034(9)
O2	0.0784(15)	0.0605(13)	0.0528(12)	-0.0243(10)	-0.0255(11)	0.0062(11)
O3	0.0648(14)	0.0404(12)	0.0654(13)	-0.0193(10)	0.0169(11)	-0.0013(10)
O4	0.0468(12)	0.0678(14)	0.0809(15)	-0.0157(12)	0.0265(11)	-0.0190(11)
O5	0.0846(17)	0.0603(15)	0.0666(16)	0.0117(12)	-0.0116(13)	0.0096(12)
O6	0.0579(14)	0.0648(15)	0.0999(18)	-0.0078(13)	-0.0025(13)	0.0261(12)
O7	0.0706(14)	0.0654(14)	0.0495(12)	-0.0183(10)	0.0231(11)	-0.0172(11)
S1	0.0421(4)	0.0446(4)	0.0447(4)	-0.0147(3)	-0.0089(3)	0.0063(3)
O8A	0.097(3)	0.073(5)	0.144(4)	0.013(4)	0.032(3)	0.011(3)
C32A	0.109(6)	0.078(6)	0.206(11)	0.011(6)	0.014(6)	-0.018(4)
C33A	0.124(7)	0.096(6)	0.303(16)	0.053(8)	0.029(8)	0.021(5)
C34A	0.096(5)	0.103(6)	0.243(12)	-0.018(7)	0.035(6)	0.011(4)
C35A	0.101(5)	0.079(4)	0.194(11)	-0.008(5)	0.030(6)	-0.013(4)
O8B	0.097(3)	0.073(5)	0.144(4)	0.013(4)	0.032(3)	0.011(3)
C32B	0.094(9)	0.092(8)	0.138(12)	0.027(7)	0.049(8)	0.021(6)
C33B	0.100(9)	0.112(9)	0.160(14)	0.022(8)	0.050(9)	0.030(6)
C34B	0.096(7)	0.123(10)	0.162(13)	0.025(9)	0.025(7)	0.016(7)
C35B	0.101(8)	0.117(11)	0.154(14)	0.044(11)	0.032(7)	0.002(7)

Table S18. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Ǻ^2) for 5.

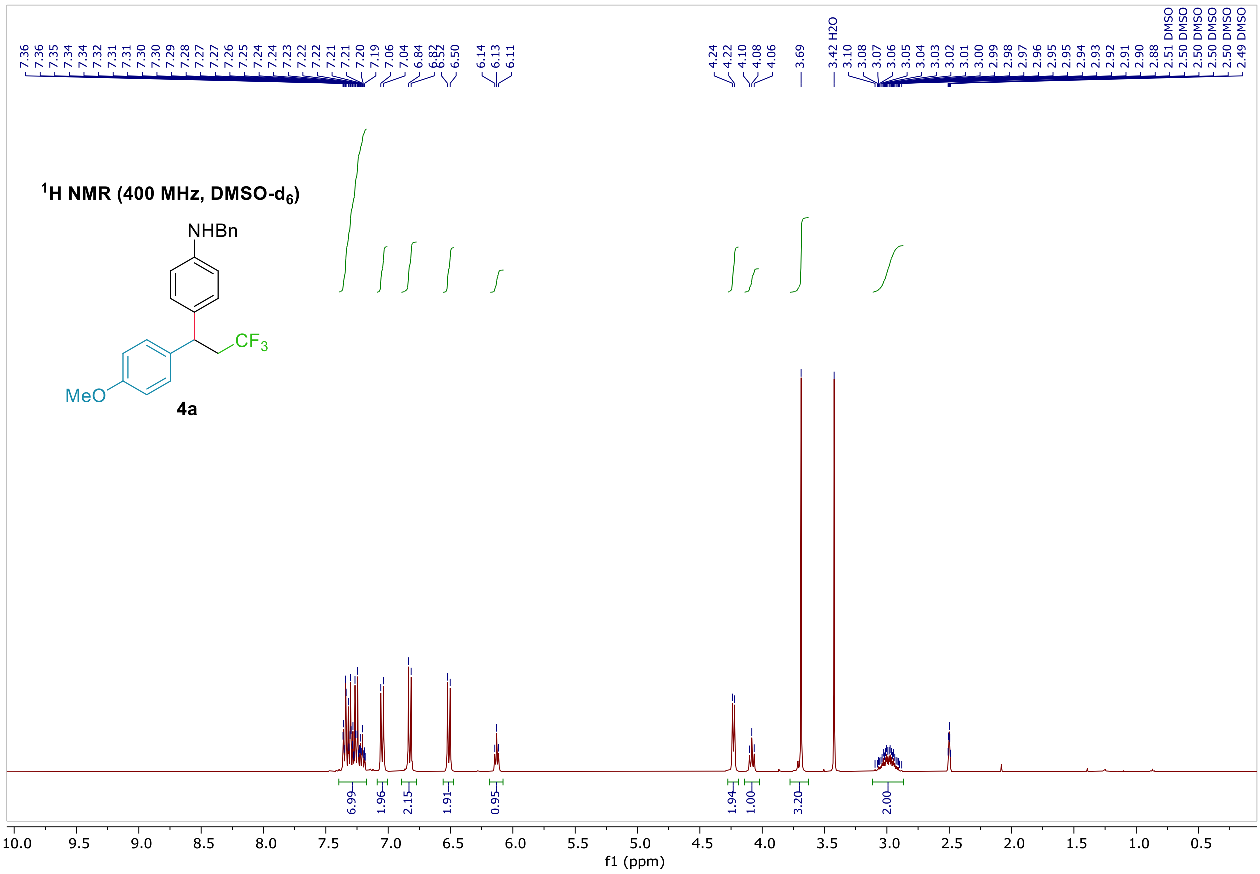
	x/a	y/b	z/c	U(eq)
H3	0.5603	0.7849	0.6373	0.048000
H5	0.2291	0.8427	0.8029	0.056000
H6	0.4952	0.7375	0.8598	0.054000
H7A	0.4156	0.5327	0.8770	0.060000
H7B	0.5885	0.5646	0.9274	0.060000
H9	0.8640	0.4149	0.9753	0.059000
H10	0.8556	0.2645	1.0316	0.072000
H11	0.5514	0.1725	1.0229	0.086000
H12	0.2506	0.2334	0.9594	0.102000
H13	0.2539	0.3853	0.9038	0.080000
H15	0.4117	0.5017	0.7661	0.046000
H16	0.3875	0.3992	0.6829	0.047000
H18	1.0044	0.2707	0.7248	0.053000
H19	1.0290	0.3716	0.8089	0.049000
H20	0.5316	0.2799	0.6171	0.051000
H22	0.9125	0.4126	0.6070	0.052000
H23	1.1991	0.4377	0.5321	0.052000

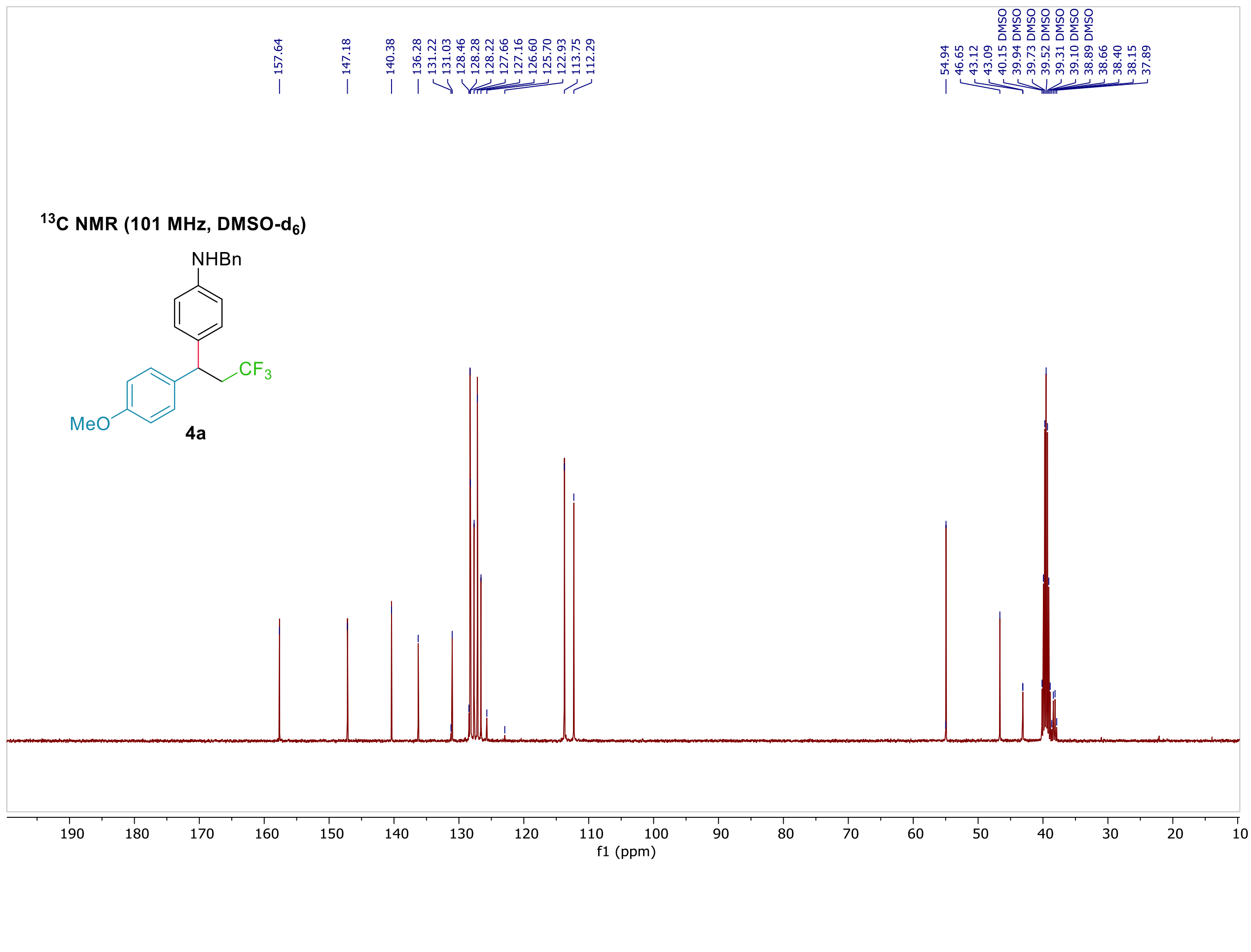
	x/a	y/b	z/c	U(eq)
H25	1.1579	0.1635	0.4774	0.057000
H27A	1.6291	0.3802	0.4181	0.091000
H27B	1.5752	0.3948	0.4917	0.091000
H27C	1.4126	0.4479	0.4384	0.091000
H28	0.8176	0.1259	0.6796	0.056000
H29A	0.6300	0.0228	0.6113	0.068000
H29B	0.5138	0.1190	0.5749	0.068000
H30A	0.8131	0.0788	0.5131	0.064000
H30B	0.9718	0.0502	0.5728	0.064000
H32A	0.1987	1.0688	0.9123	0.158000
H32B	0.2122	1.0446	0.8386	0.158000
H33A	-0.1250	1.0954	0.8229	0.215000
H33B	-0.1030	1.1504	0.8873	0.215000
H34A	-0.2901	1.0327	0.9490	0.178000
H34B	-0.4056	1.0188	0.8817	0.178000
H35A	-0.1631	0.8809	0.9373	0.150000
H35B	-0.1752	0.8936	0.8612	0.150000
H32C	0.1622	1.1088	0.8579	0.134000
H32D	0.0356	1.0515	0.8070	0.134000
H33C	-0.2445	1.1443	0.8563	0.154000
H33D	-0.1501	1.1042	0.9265	0.154000
H34C	-0.3829	0.9835	0.8779	0.156000
H34D	-0.1830	0.9721	0.8253	0.156000
H35C	-0.1013	0.9566	0.9610	0.153000
H35D	-0.0833	0.8631	0.9173	0.153000

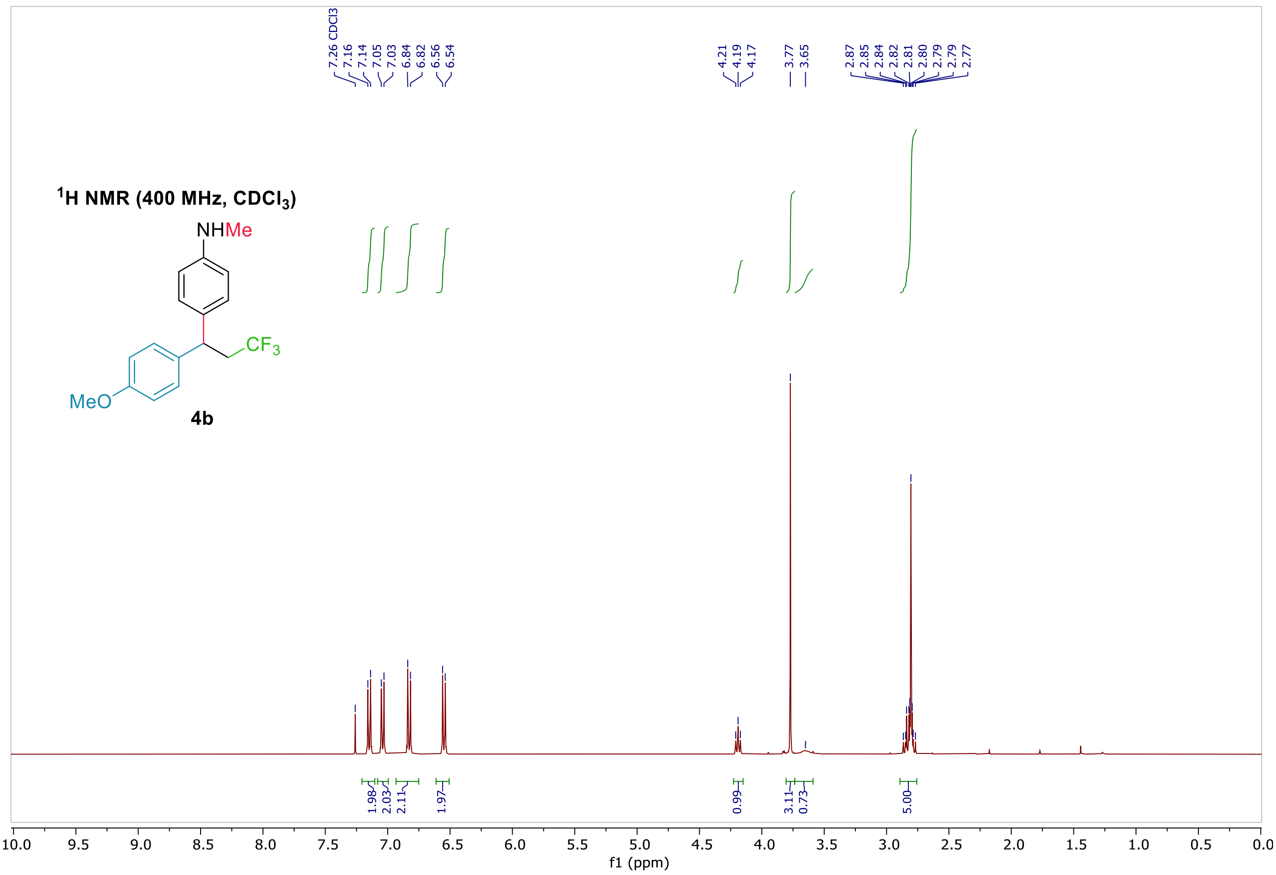
Table S19. Hydrogen bond distances (Å) and angles (°) for 5.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
C3-H3···O7#2	0.94	2.33	3.098(3)	138.4
C5-H5···O8A^a	0.94	2.48	3.314(11)	148.5
C5-H5···O8B^b	0.94	2.56	3.37(3)	145.0
C7-H7B···O2	0.98	2.38	2.870(4)	110.1
C15-H15···O1#1	0.94	2.36	3.286(3)	167.7

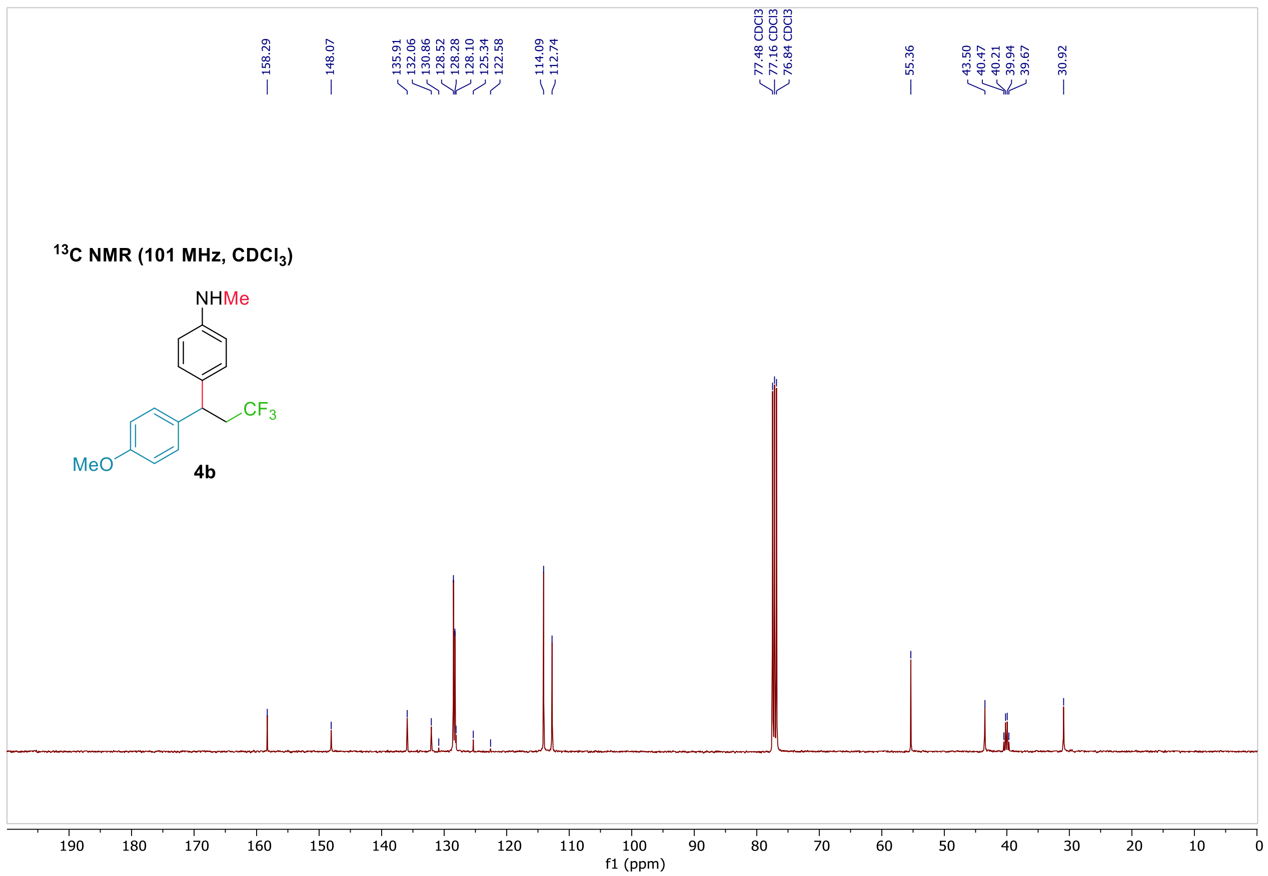
11. NMR spectra



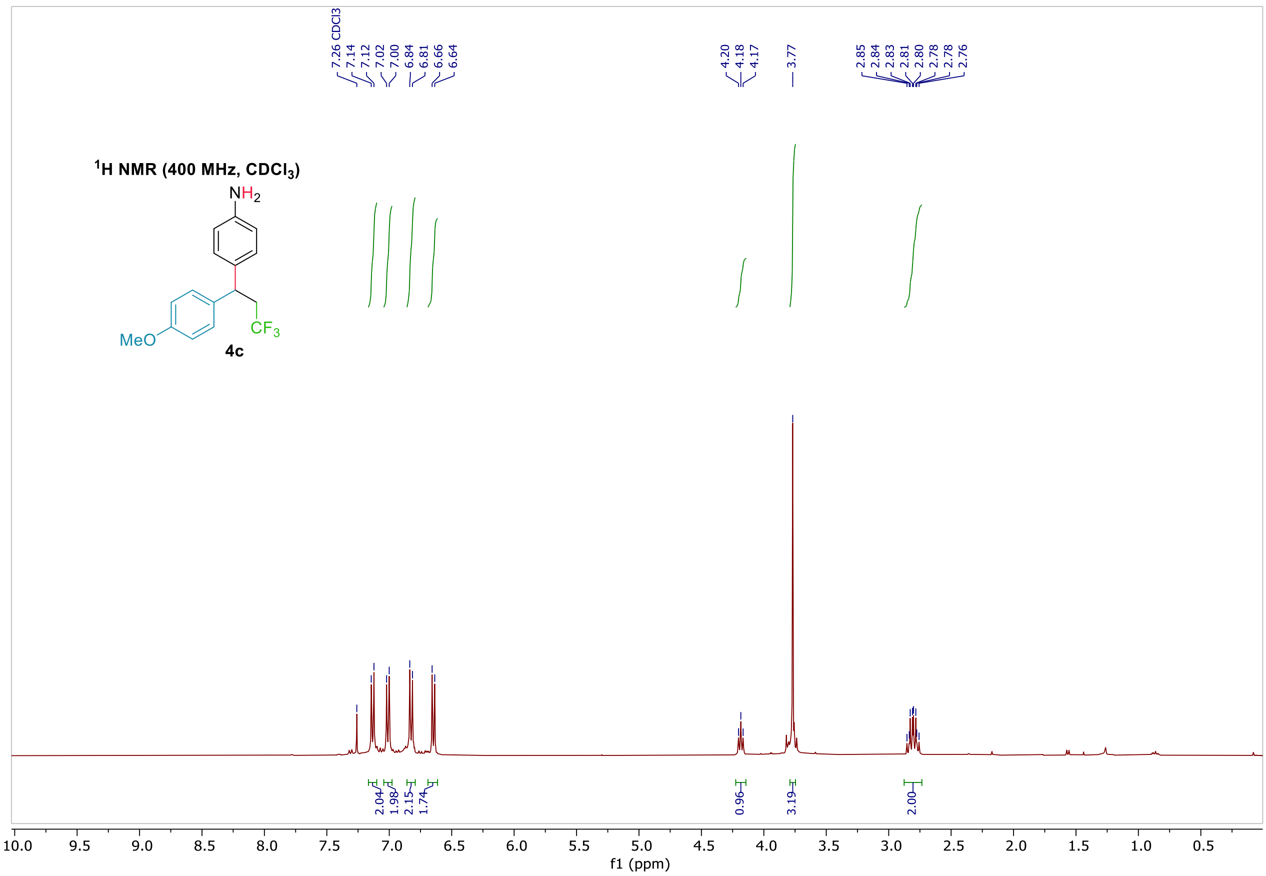




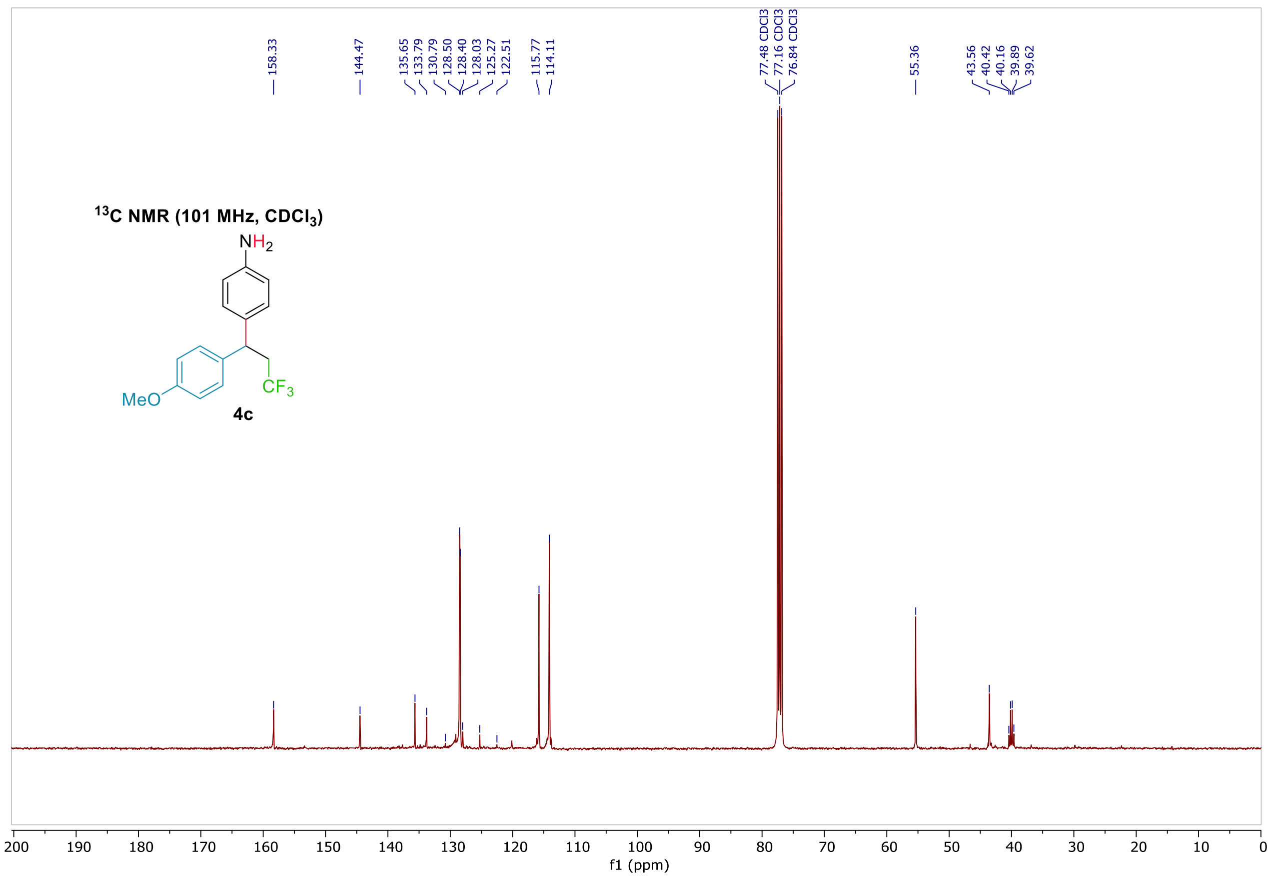
7.26 CDCl3
7.16
7.14
7.05
7.03
6.84
6.82
6.56
6.54
4.21
4.19
4.17
3.77
3.65
2.87
2.85
2.84
2.82
2.81
2.80
2.79
2.79
2.77
1H NMR (400 MHz, CDCl3)
NHMe
CF3
MeO
4b
1.98
2.03
2.11
1.97
0.99
3.11
0.73
5.00
f1 (ppm)



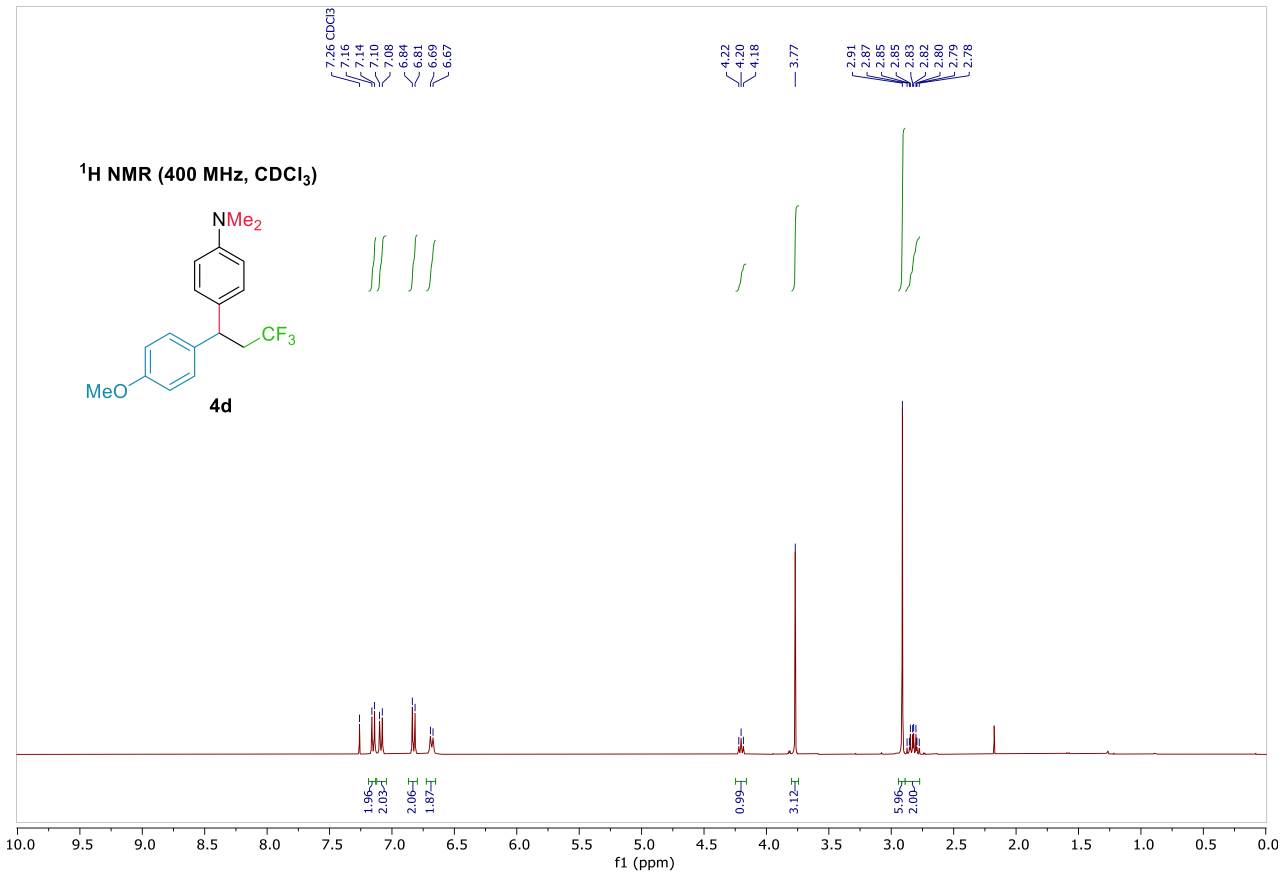
158.29
148.07
135.91
132.06
130.86
128.52
128.28
128.10
125.34
122.58
114.09
112.74
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.36
43.50
40.47
40.21
39.94
39.67
30.92
13C NMR (101 MHz, CDCl3)
NHMe
CF3
MeO
4b
f1 (ppm)



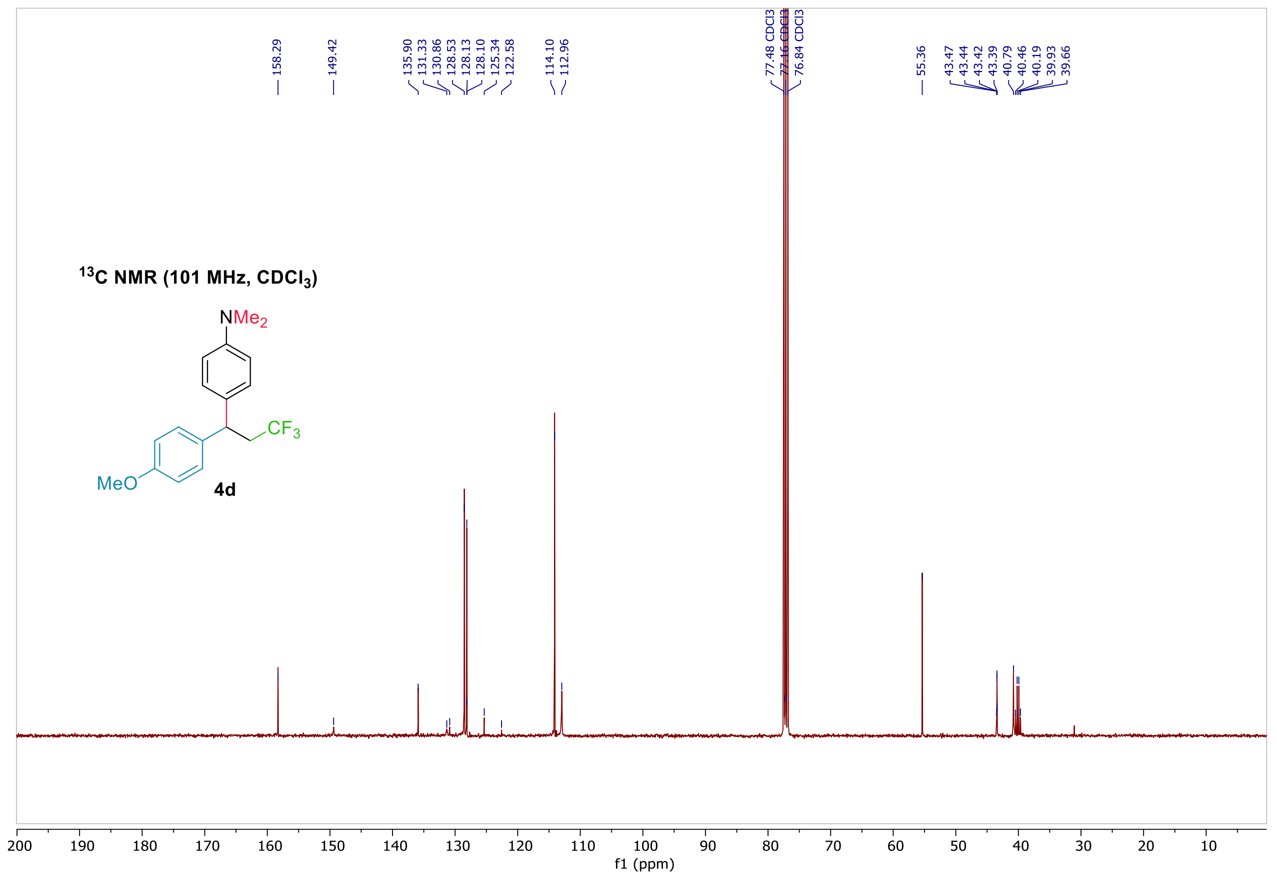
7.26 CDCl3
7.14
7.12
7.02
7.00
6.84
6.81
6.66
6.64
4.20
4.18
4.17
3.77
2.85
2.84
2.83
2.81
2.80
2.78
2.76
1H NMR (400 MHz, CDCl3)
NH2
CF3
MeO
4c
2.04
1.98
2.15
1.74
0.96
3.19
2.00
f1 (ppm)



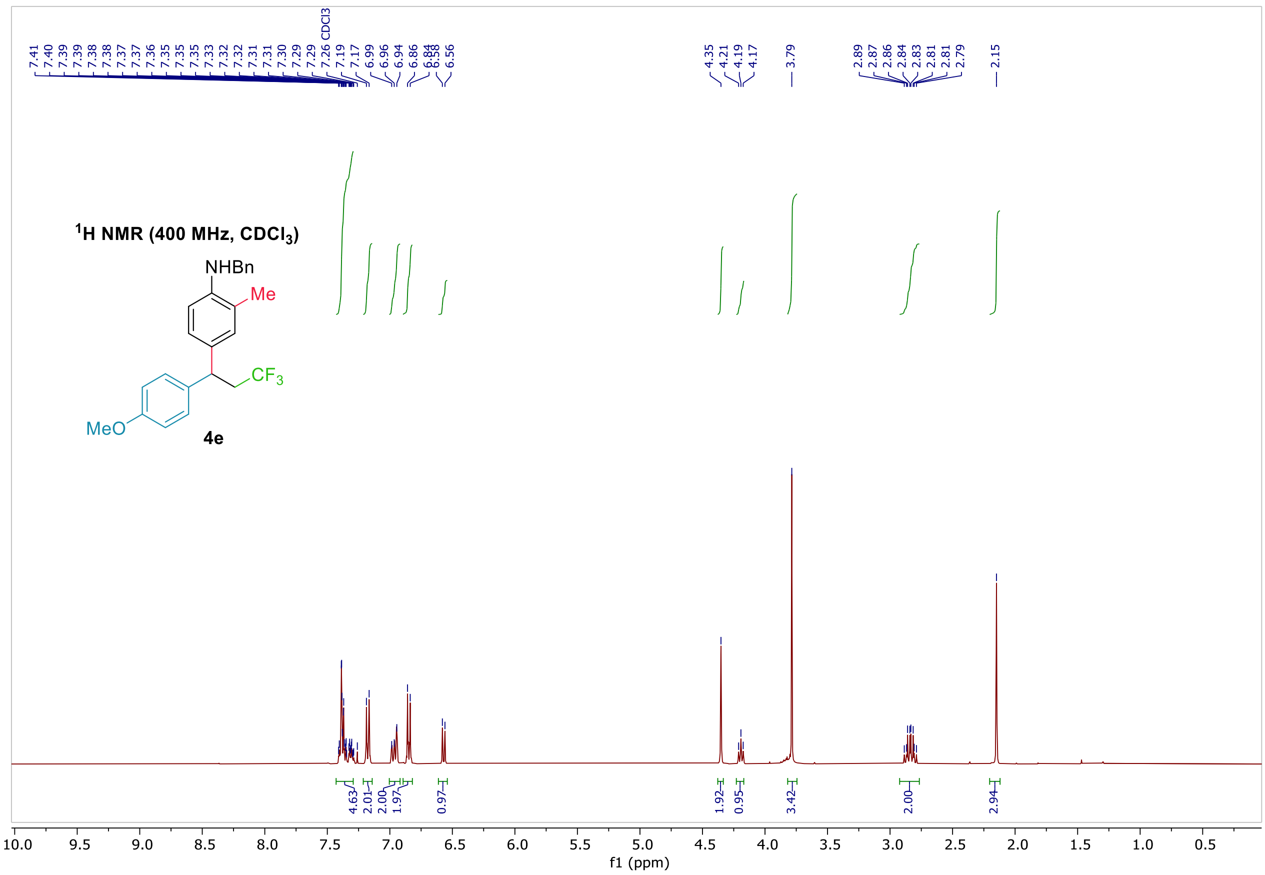
158.33
144.47
135.65
133.79
130.79
128.50
128.40
128.03
125.27
122.51
115.77
114.11
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.36
43.56
40.42
40.16
39.89
39.62
13C NMR (101 MHz, CDCl3)
NH2
CF3
MeO
4c
f1 (ppm)

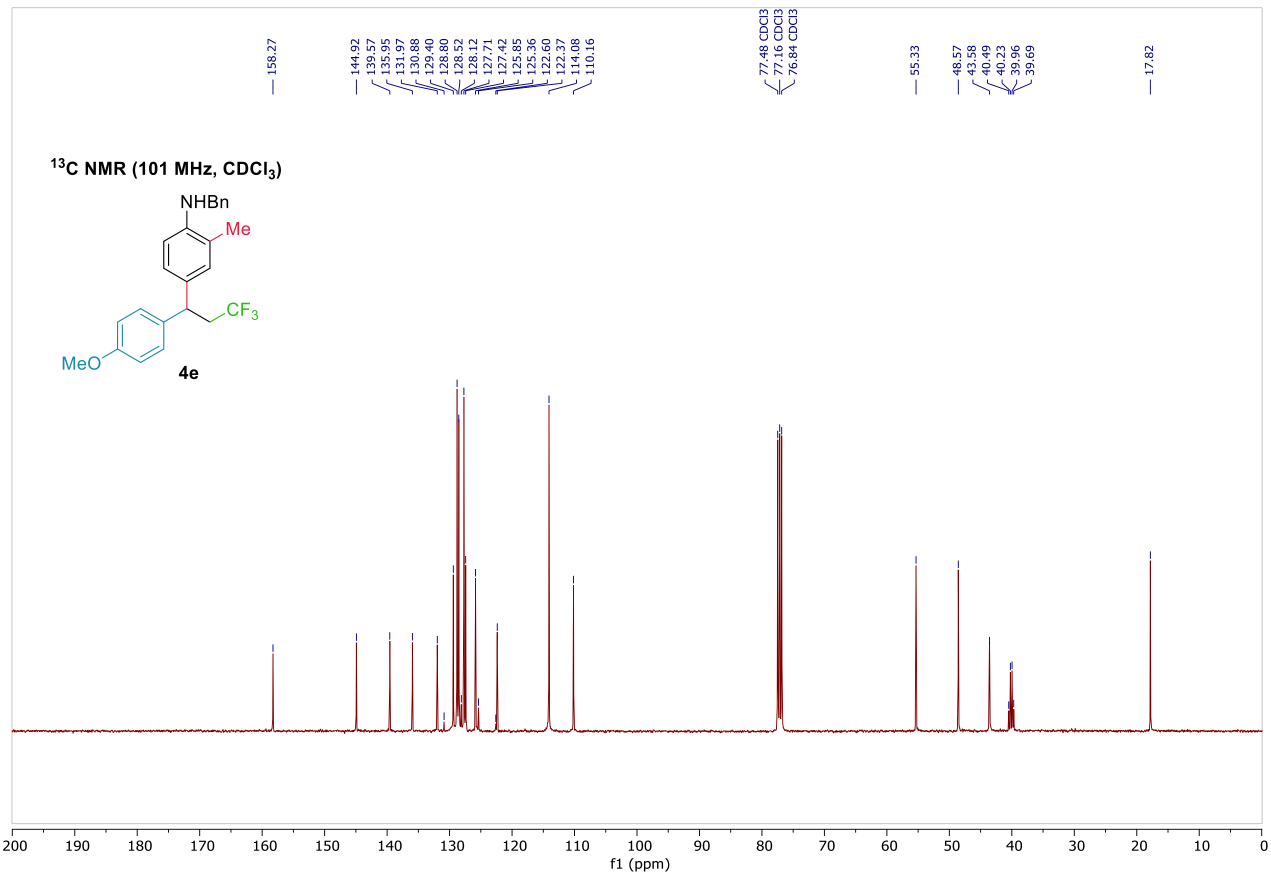


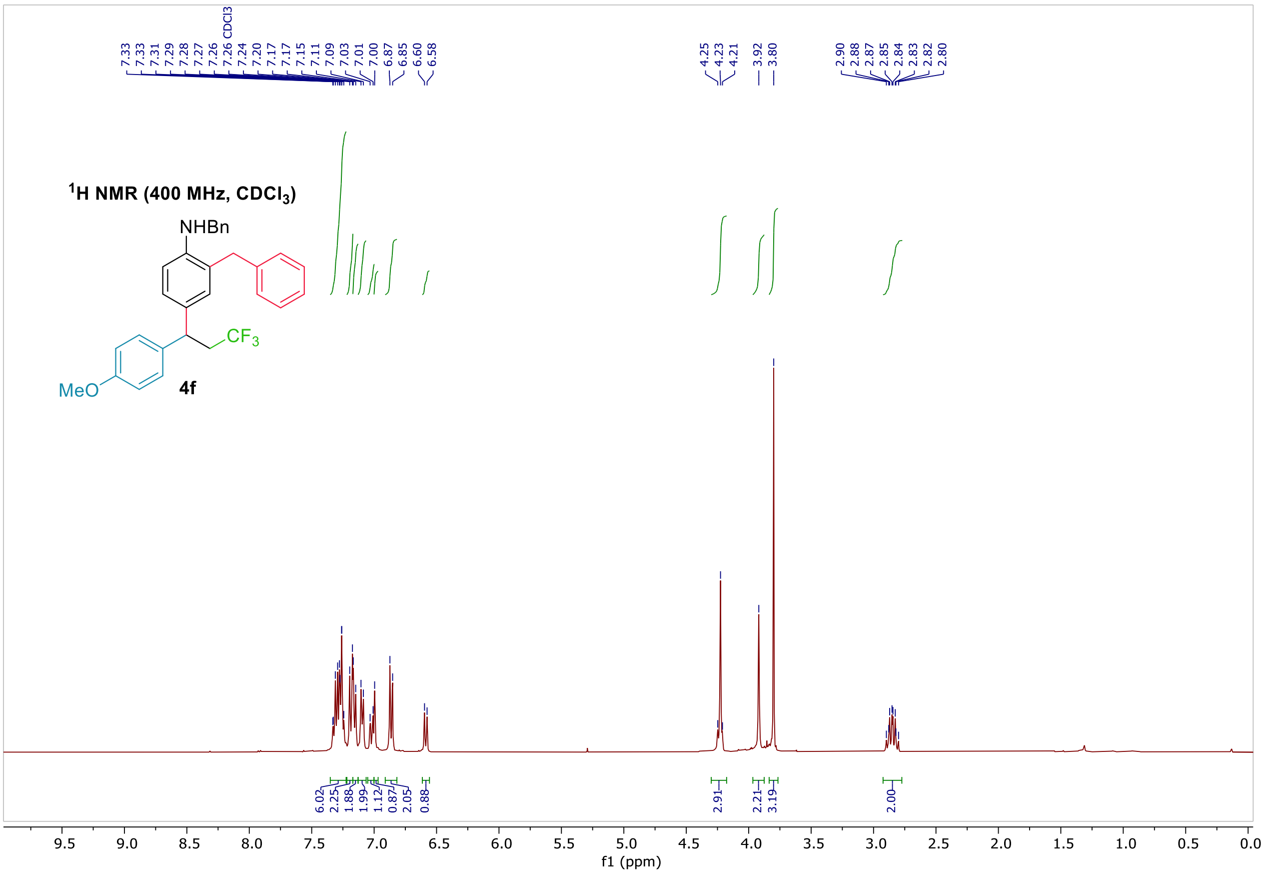
1H NMR (400 MHz, CDCl3)
NMe2
CF3
MeO
4d



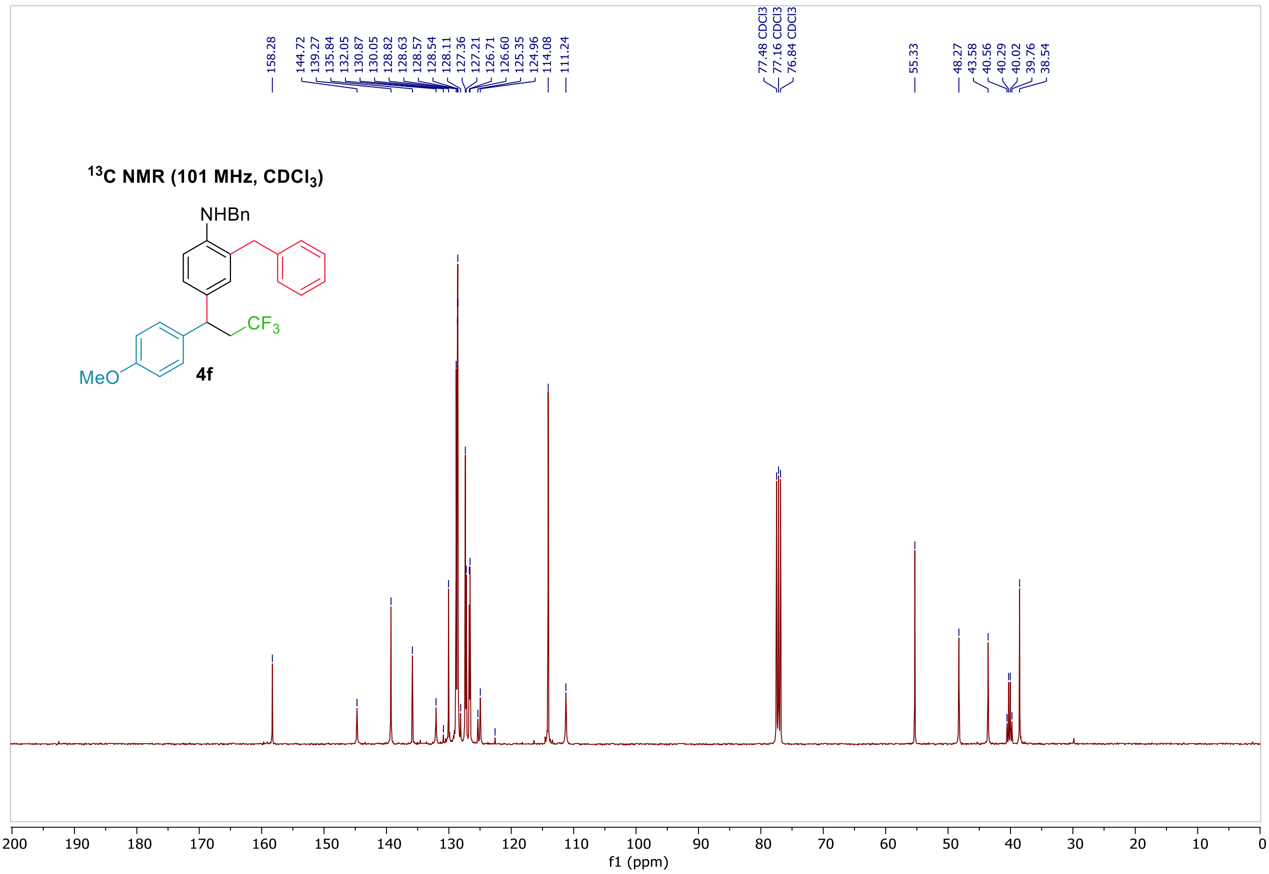
13C NMR (101 MHz, CDCl3)
NMe2
CF3
MeO
4d


1H NMR (400 MHz, CDCl3)
NHBn
Me
CF3
MeO
4e
f1 (ppm)

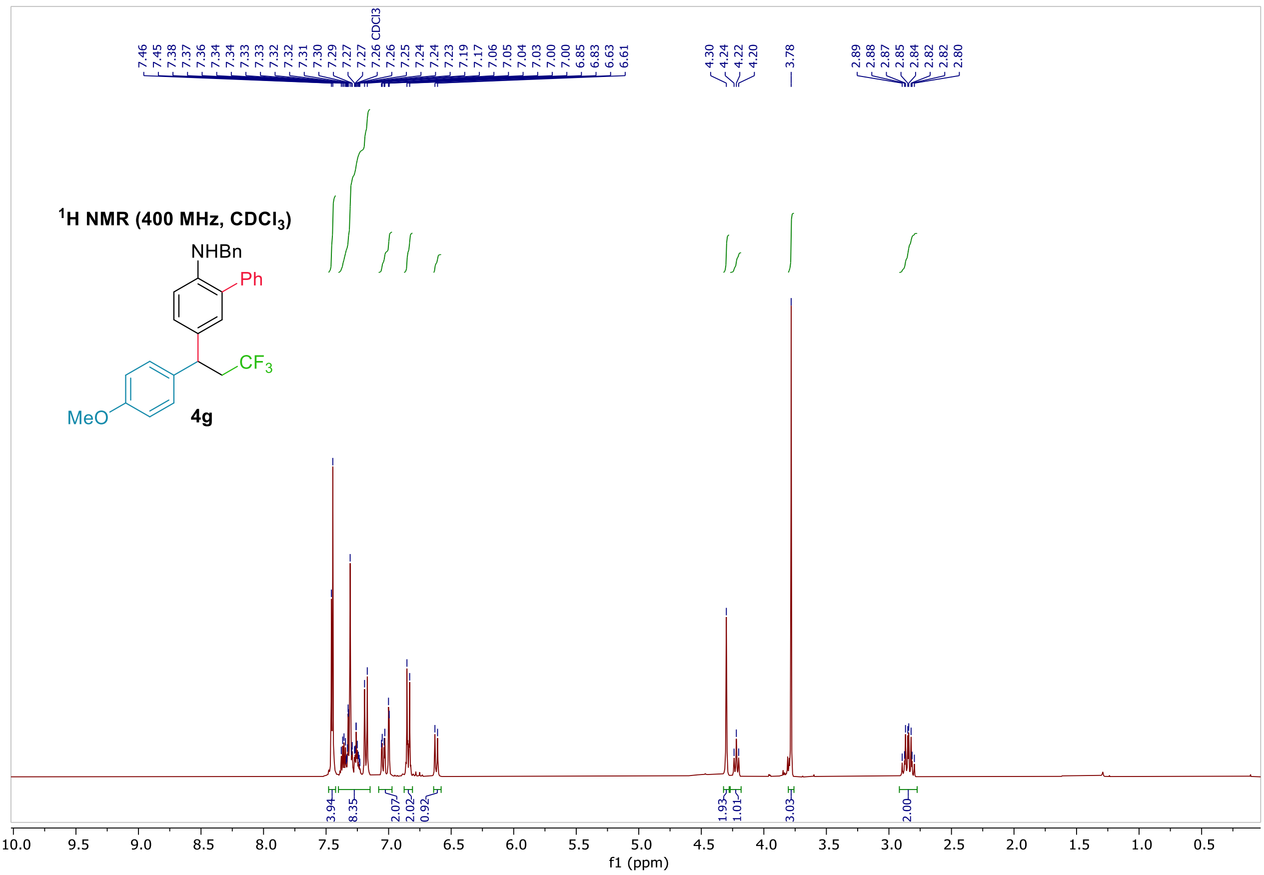

13C NMR (101 MHz, CDCl3)
NHBn
Me
CF3
MeO
4e
f1 (ppm)



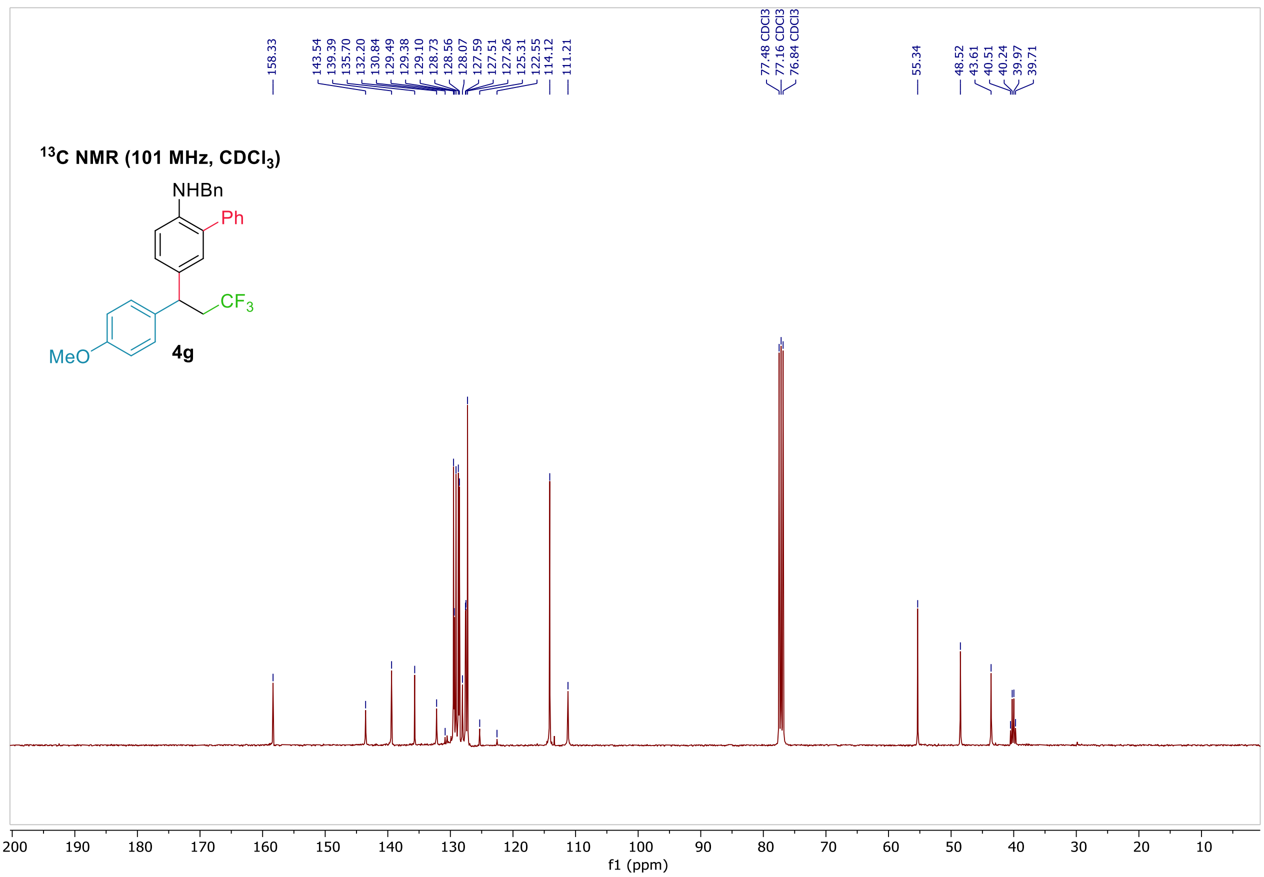
1H NMR (400 MHz, CDCl3)
NHBn
CF3
MeO
4f
f1 (ppm)



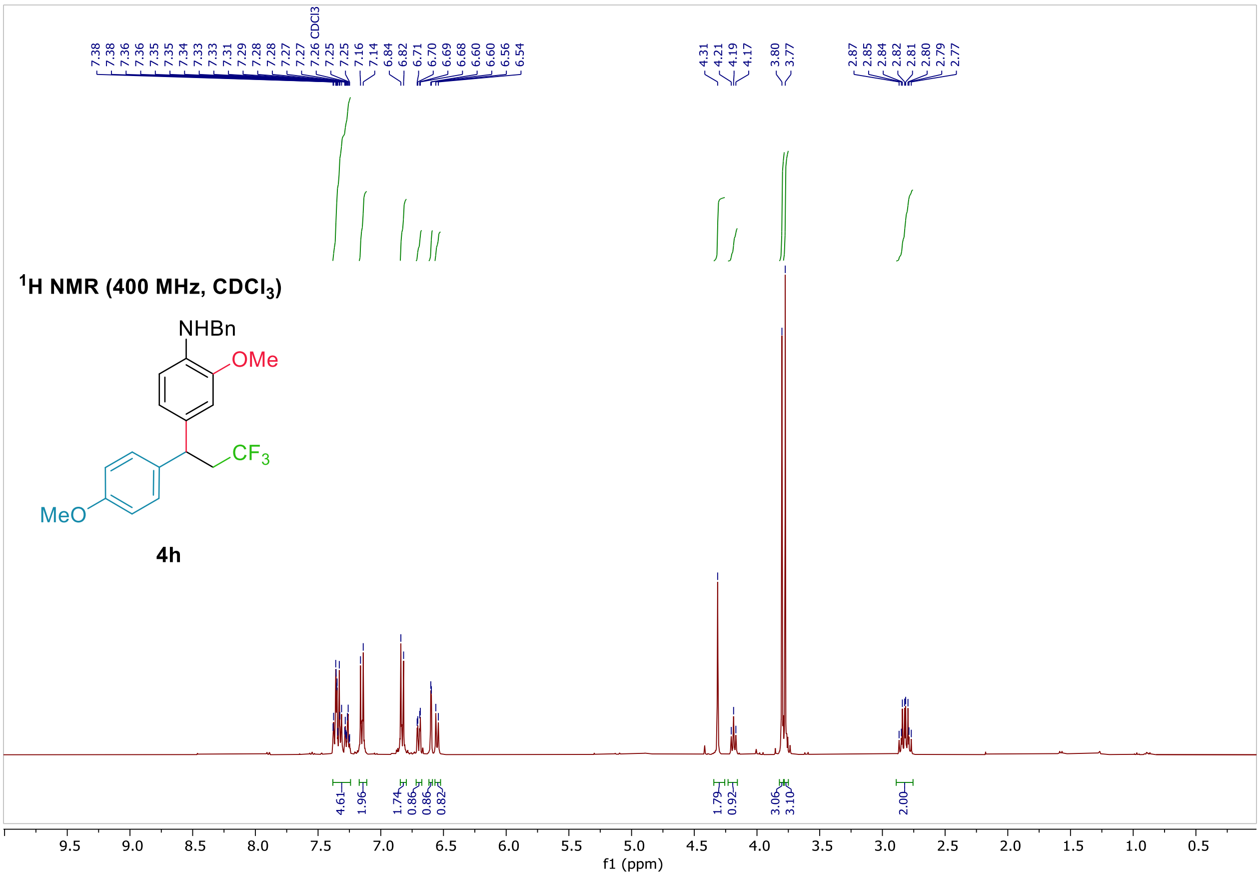
13C NMR (101 MHz, CDCl3)
NHBn
CF3
MeO
4f
f1 (ppm)



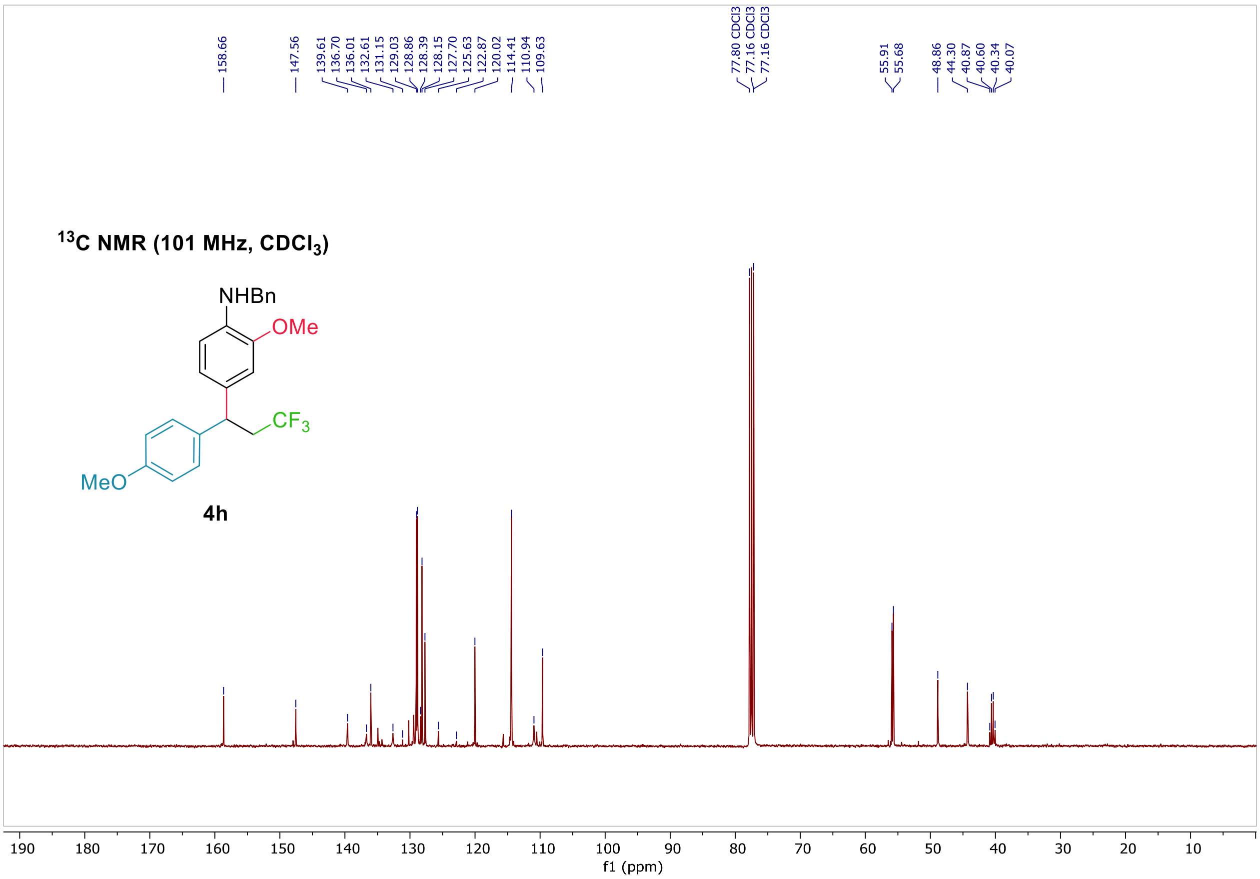
^{1}H NMR (400 MHz, CDCl$_3$)
NHBn
Ph
CF$_3$
MeO
4g
f1 (ppm)



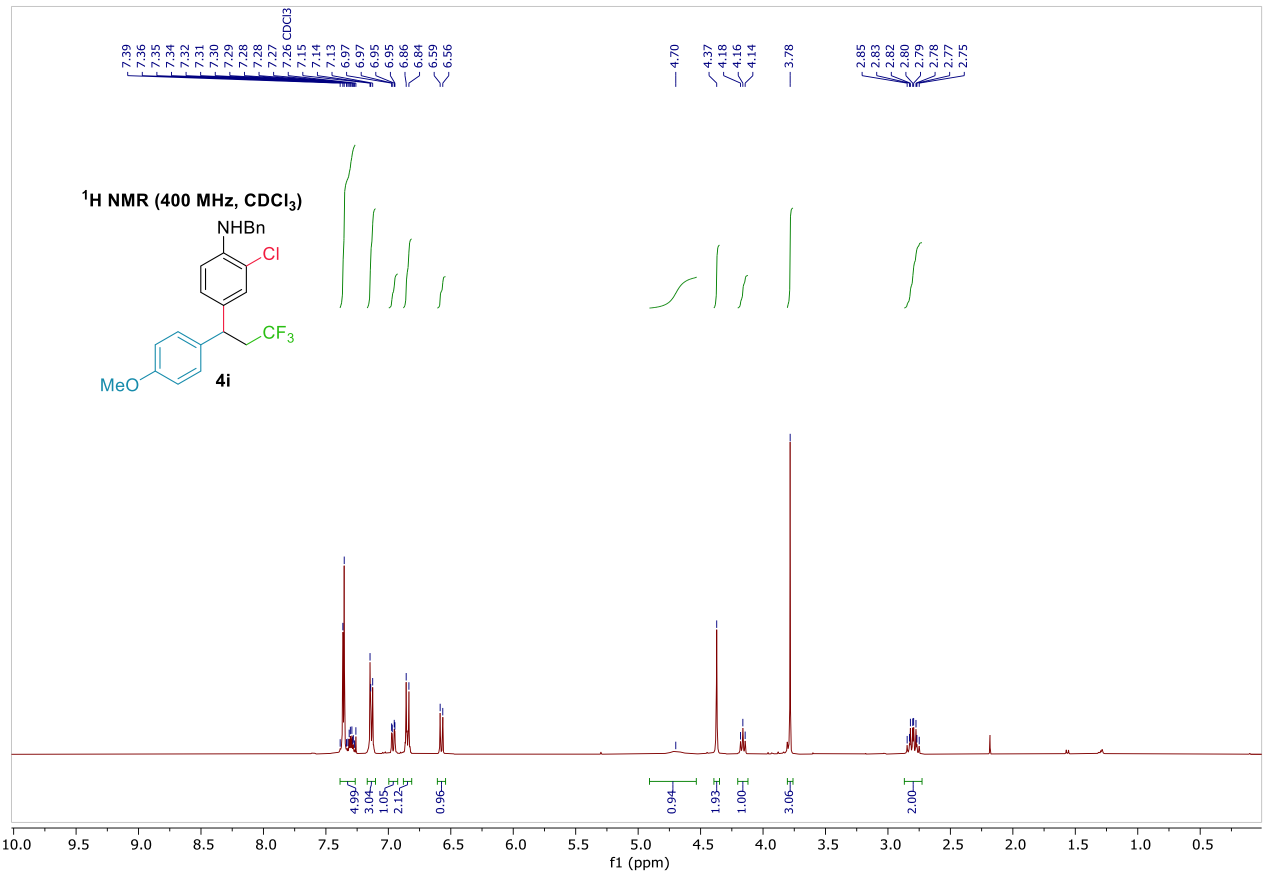
^{13}C NMR (101 MHz, CDCl$_3$)
NHBn
Ph
CF$_3$
MeO
4g
f1 (ppm)


1H NMR (400 MHz, CDCl3)
NHBn
OMe
CF3
MeO
f1 (ppm)

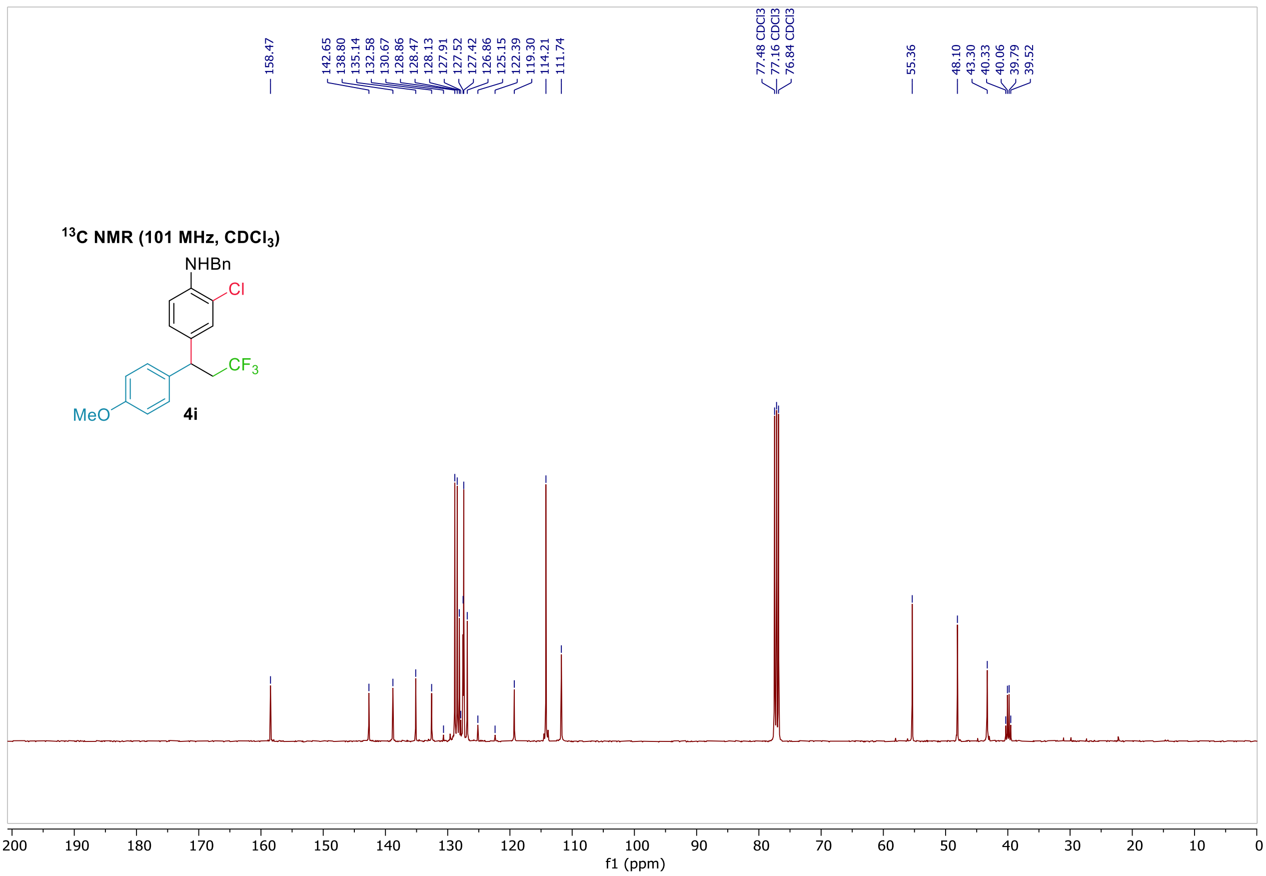
4h


13C NMR (101 MHz, CDCl3)
NHBn
OMe
CF3
MeO
f1 (ppm)

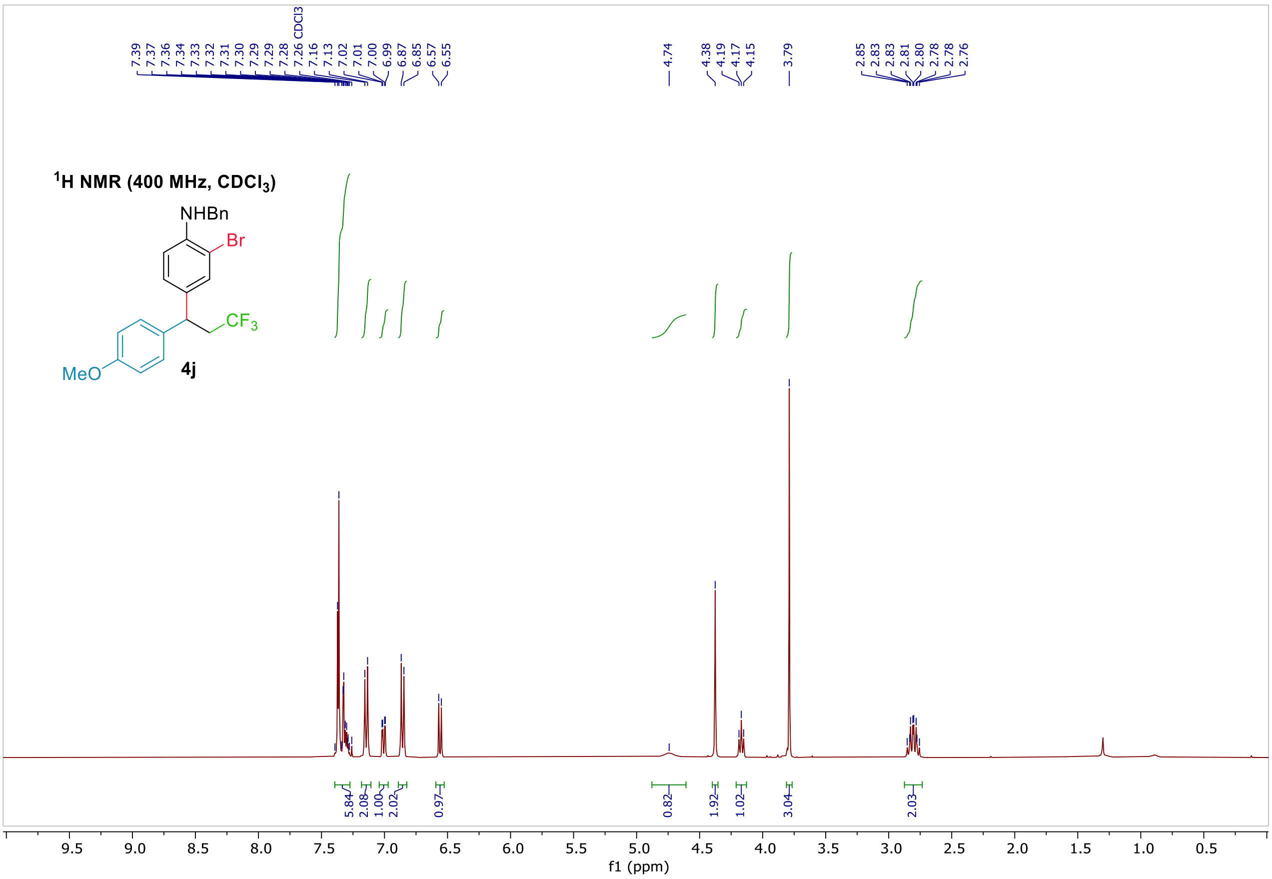
4h



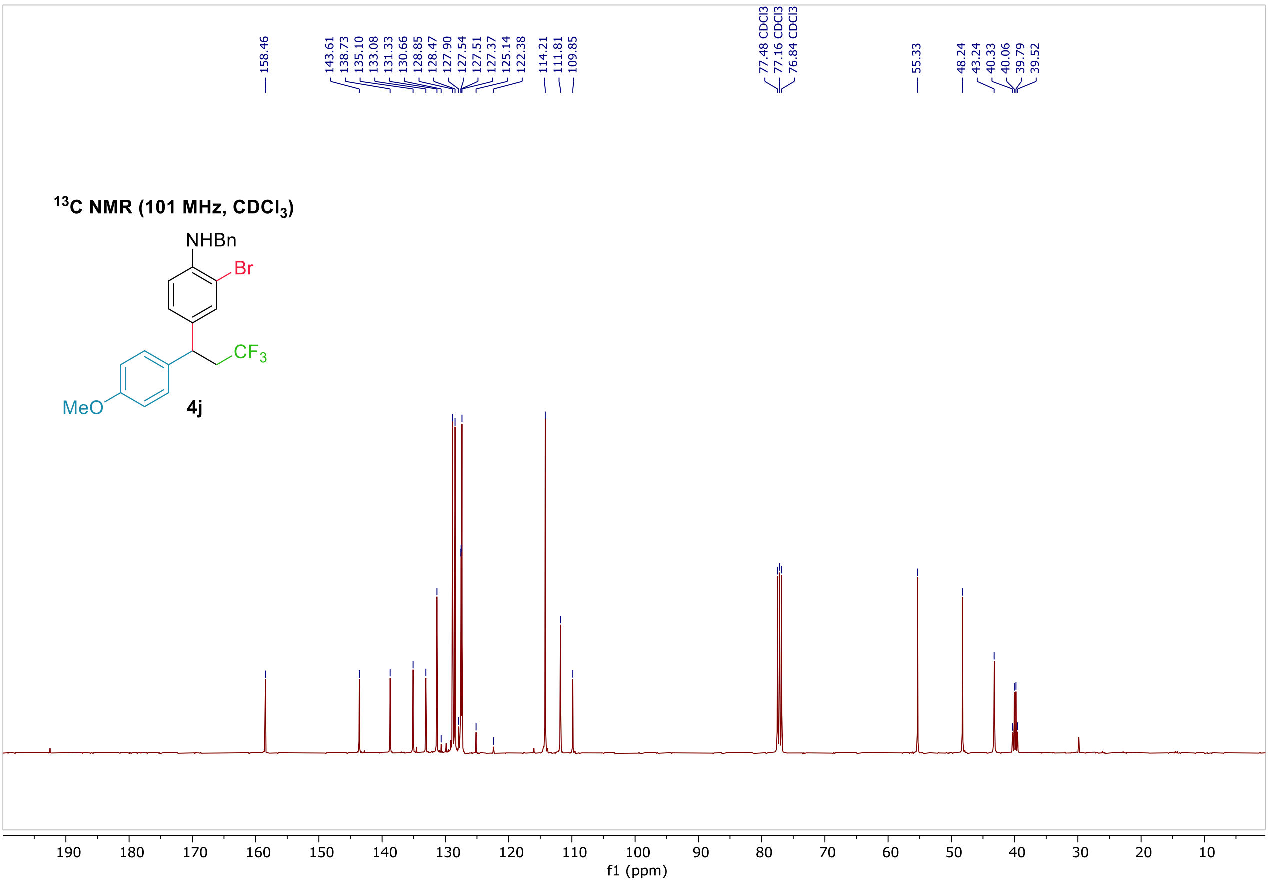
7.39 7.36 7.35 7.34 7.32 7.31 7.30 7.29 7.28 7.28 7.27 7.26 CDCl3 7.15 7.14 7.13 6.97 6.97 6.95 6.95 6.86 6.84 6.59 6.56
4.70 4.37 4.18 4.16 4.14 3.78
2.85 2.83 2.82 2.80 2.79 2.78 2.77 2.75
1H NMR (400 MHz, CDCl3)
NHBn
Cl
CF3
MeO
4i
4.99 3.04 1.05 2.12 0.96 0.94 1.93 1.00 3.06 2.00
f1 (ppm)



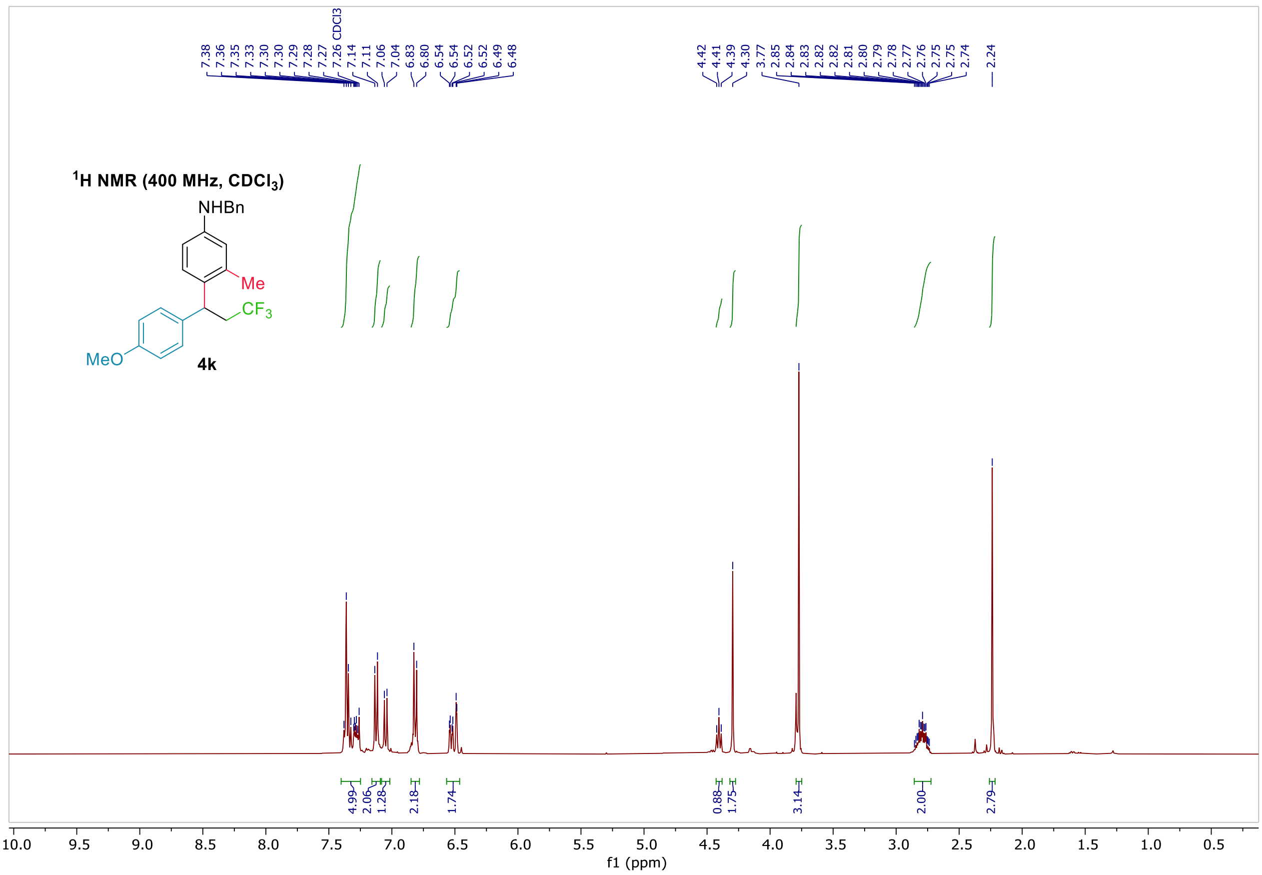
158.47
142.65 138.80 135.14 132.58 130.67 128.86 128.47 128.13 127.91 127.52 127.42 126.86 125.15 122.39 119.30 114.21 111.74
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
55.36
48.10 43.30 40.33 40.06 39.79 39.52
13C NMR (101 MHz, CDCl3)
NHBn
Cl
CF3
MeO
4i
f1 (ppm)



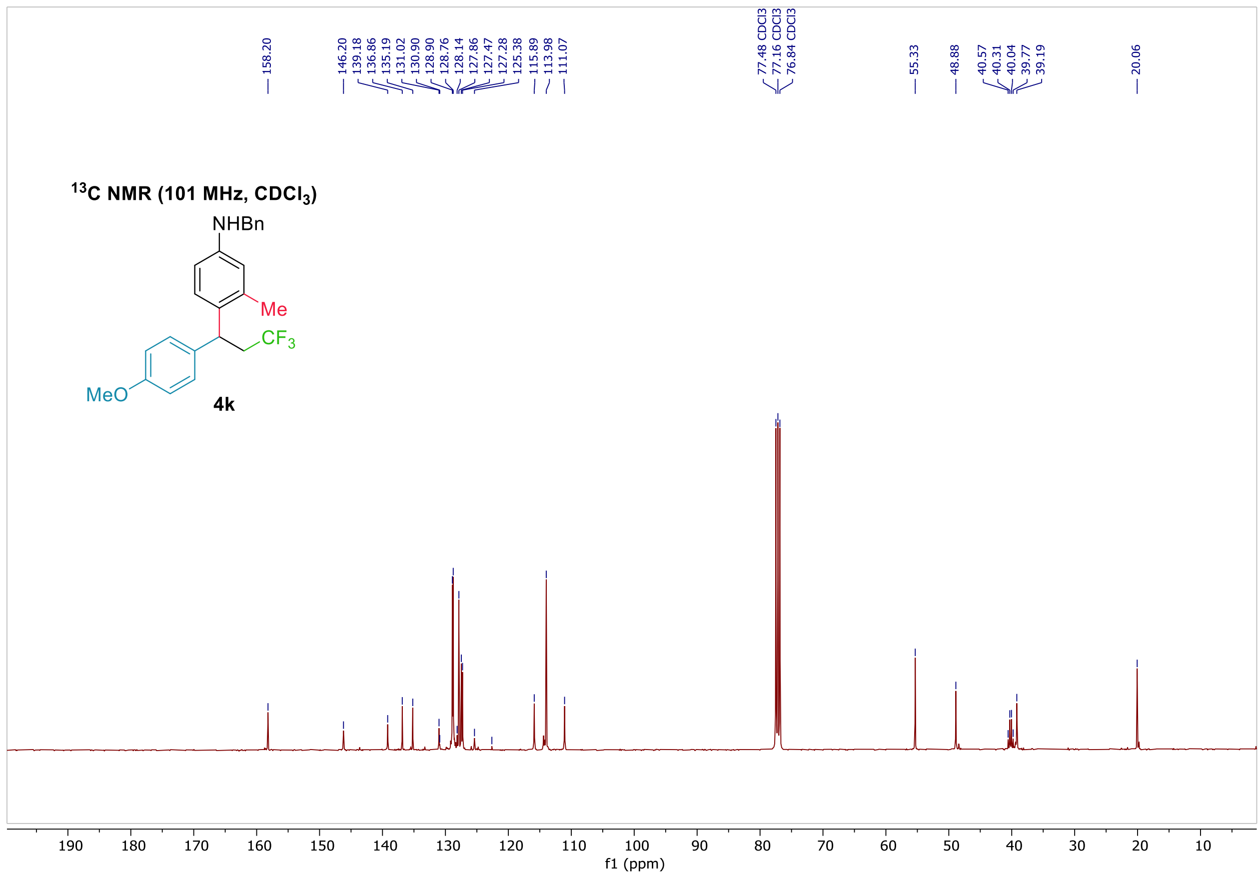
1H NMR (400 MHz, CDCl3)
NHBn
Br
CF3
MeO
4j
f1 (ppm)



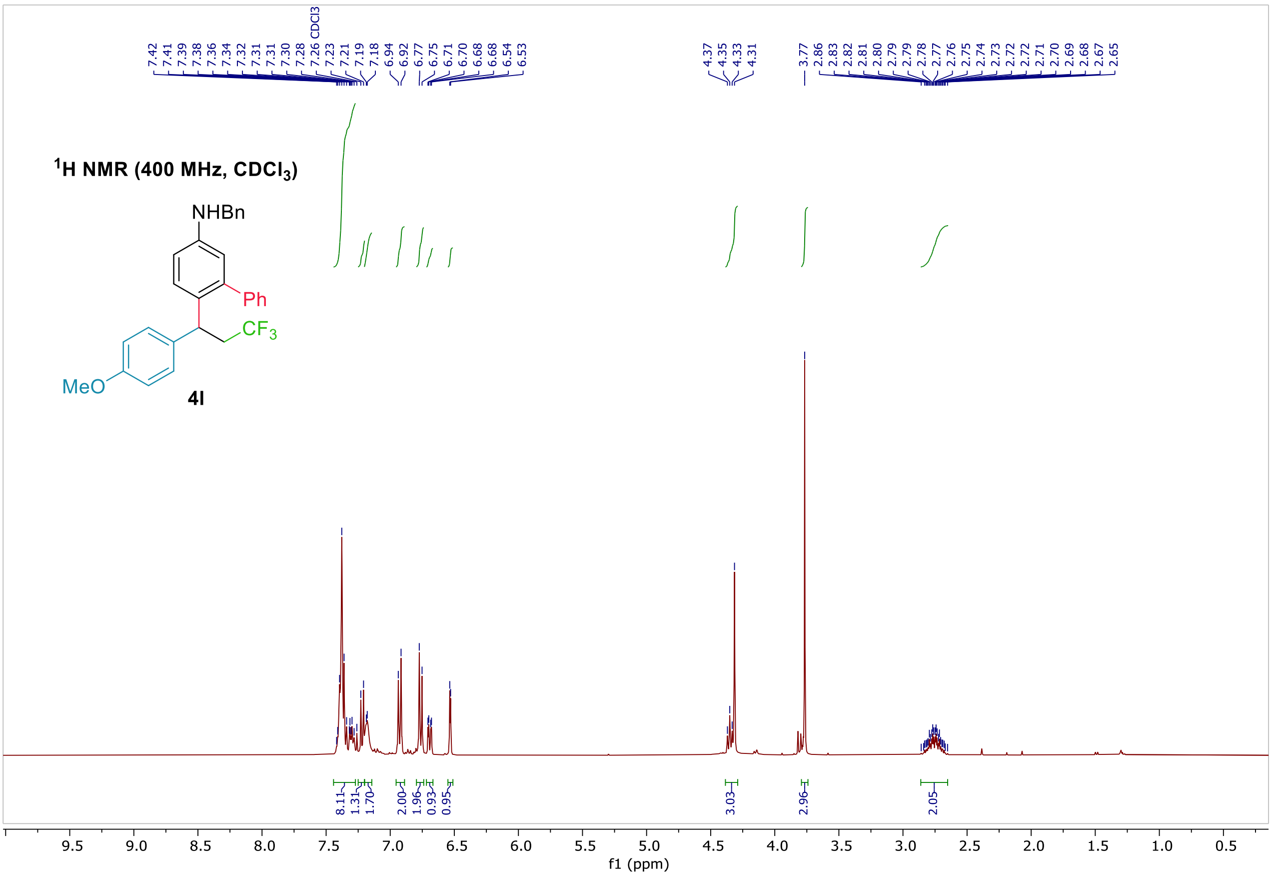
13C NMR (101 MHz, CDCl3)
NHBn
Br
CF3
MeO
4j
f1 (ppm)



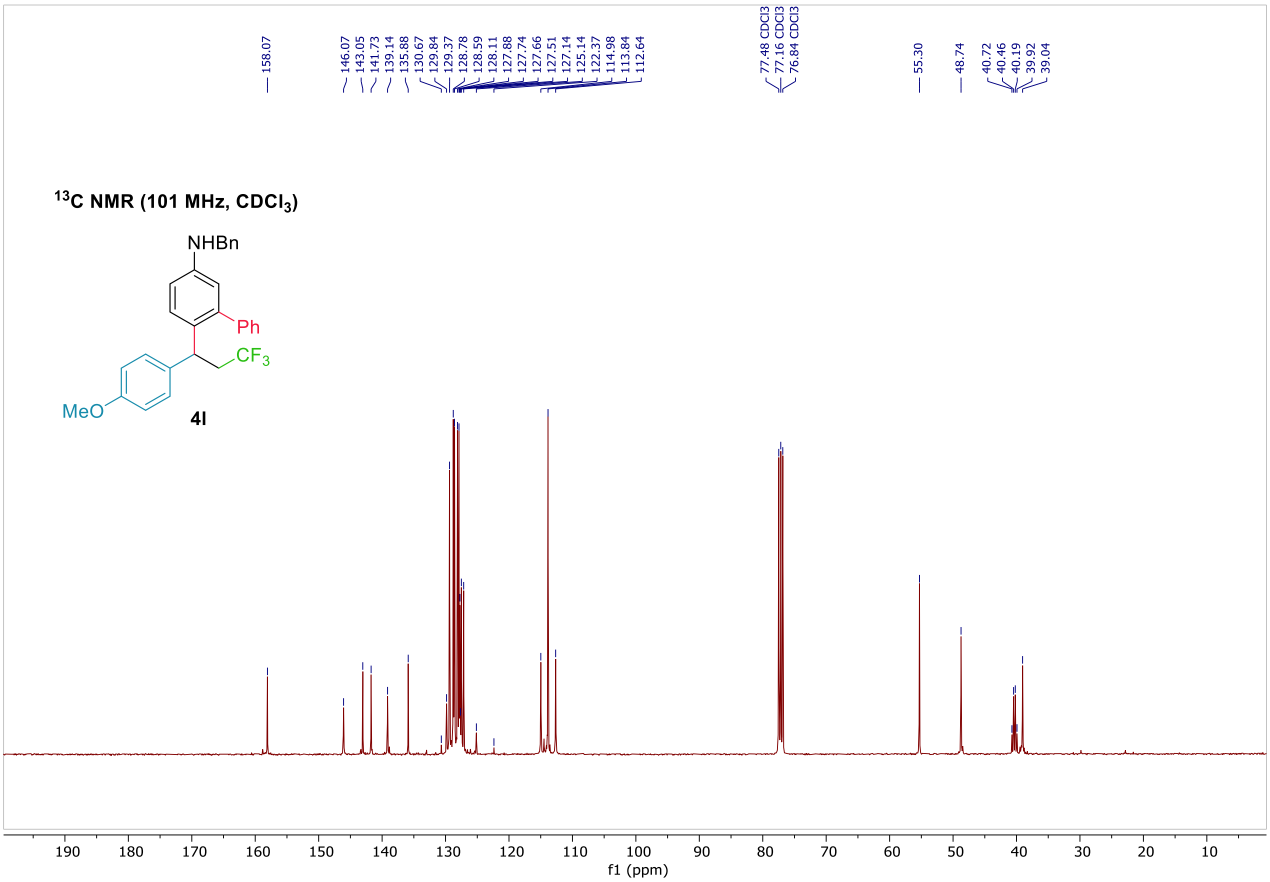
^{1}H NMR (400 MHz, CDCl$_3$)
NHBn
Me
CF$_3$
MeO
4k
f1 (ppm)



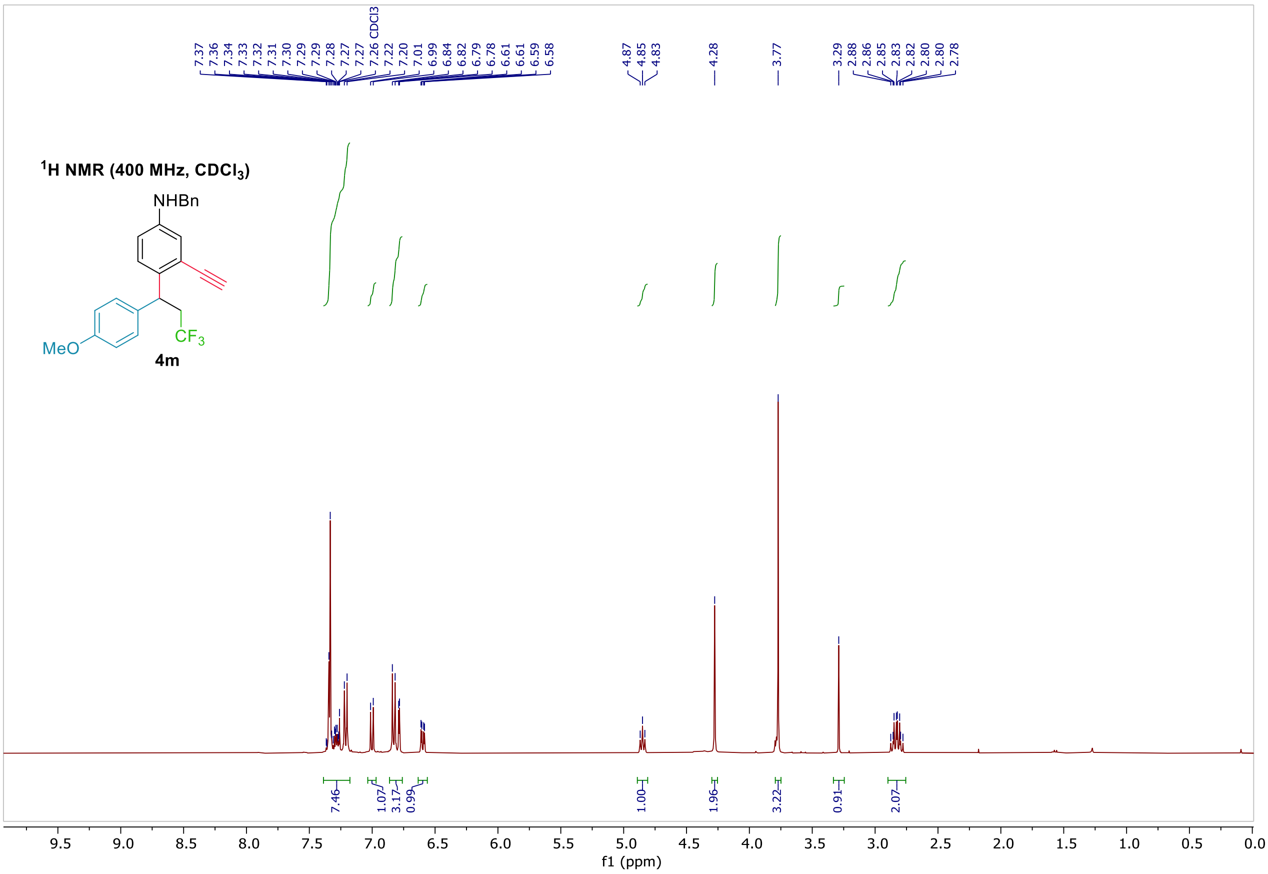
^{13}C NMR (101 MHz, CDCl$_3$)
NHBn
Me
CF$_3$
MeO
4k
f1 (ppm)



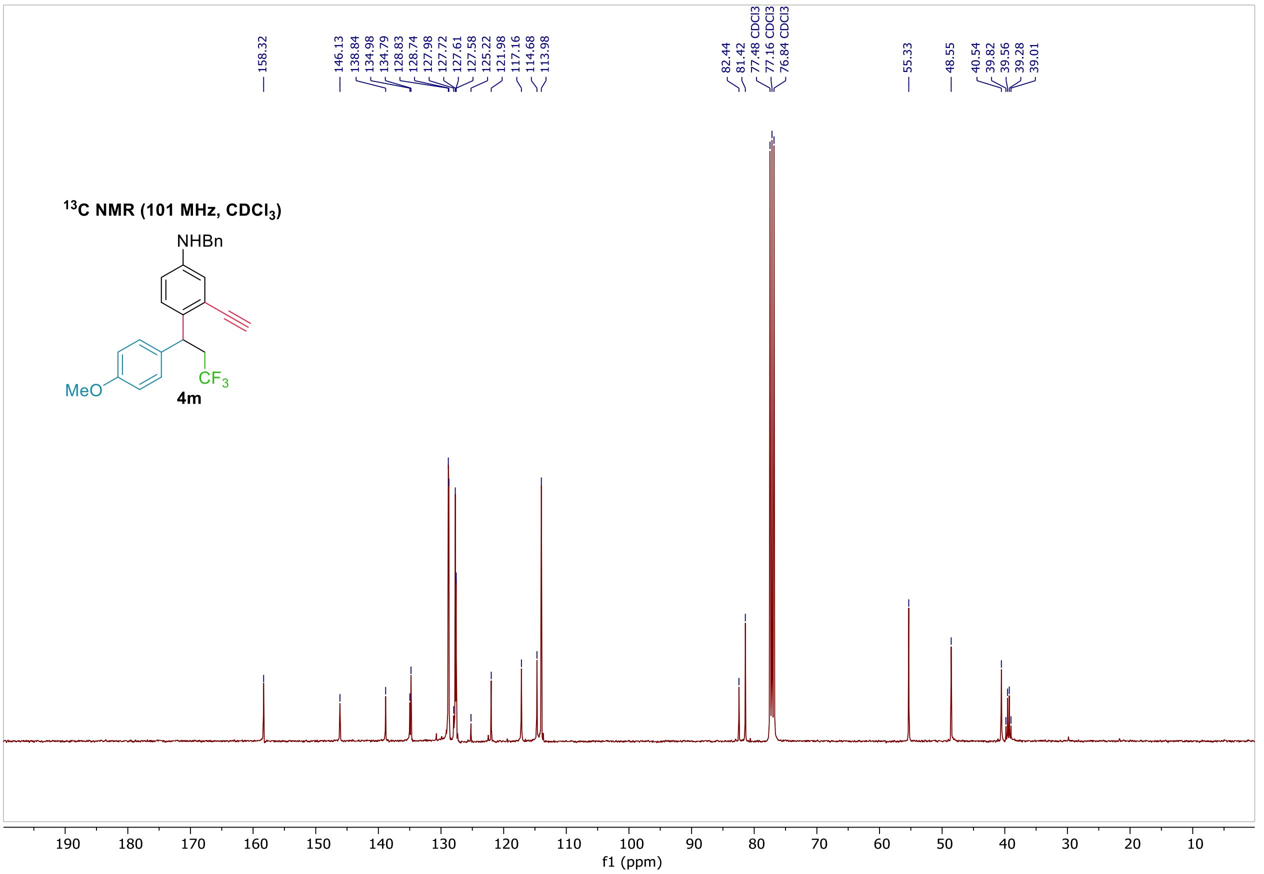
^{1}H NMR (400 MHz, CDCl$_3$)
NHBn
Ph
CF$_3$
MeO
4l
f1 (ppm)



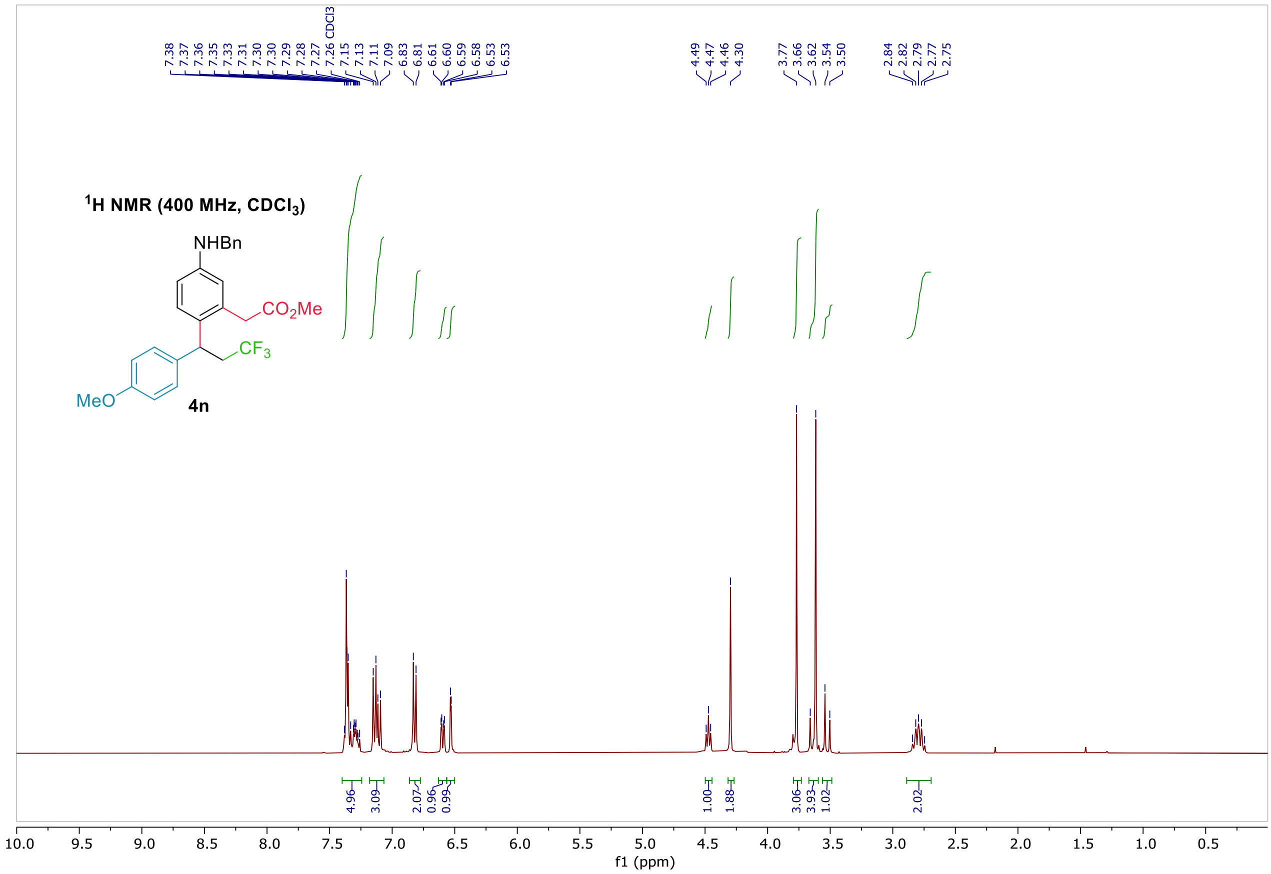
^{13}C NMR (101 MHz, CDCl$_3$)
NHBn
Ph
CF$_3$
MeO
4l
f1 (ppm)

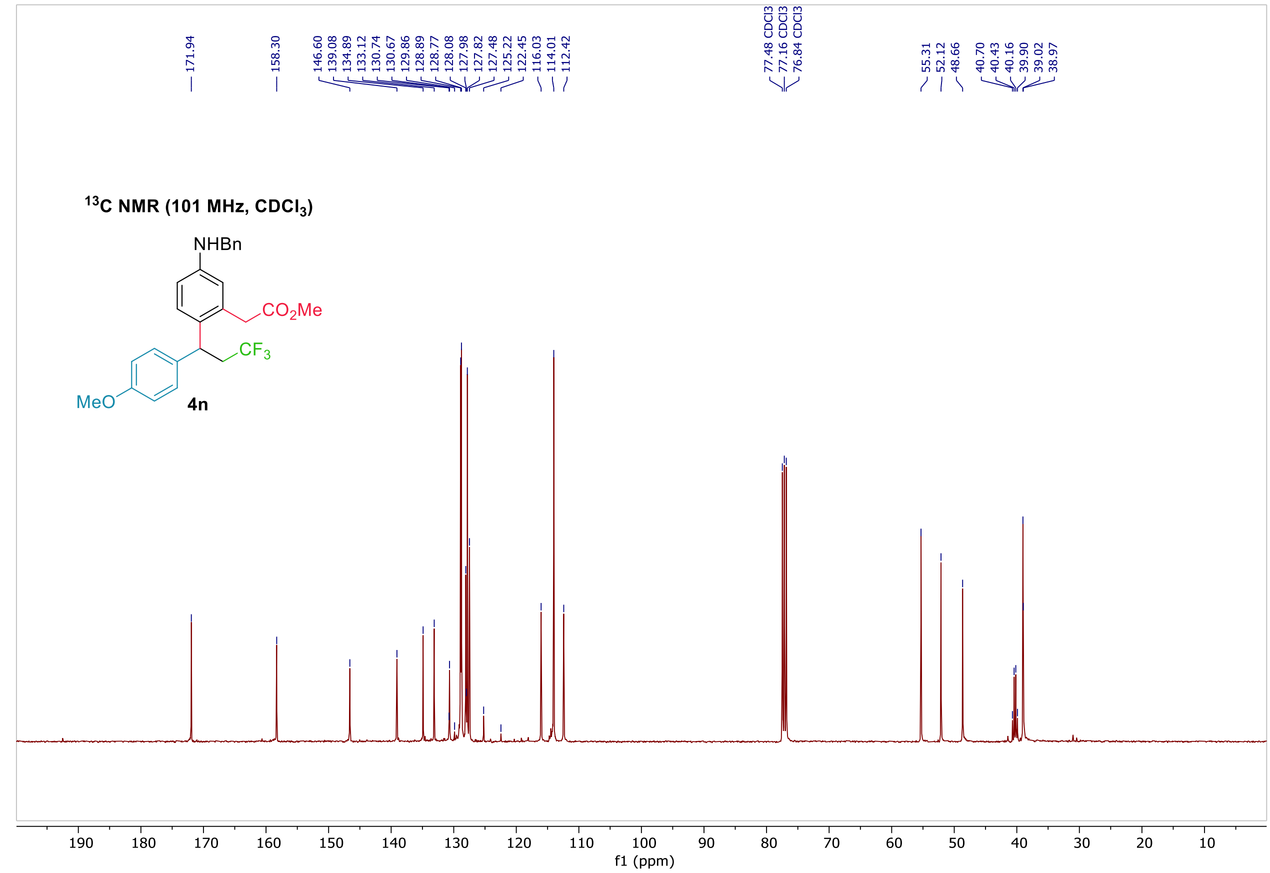


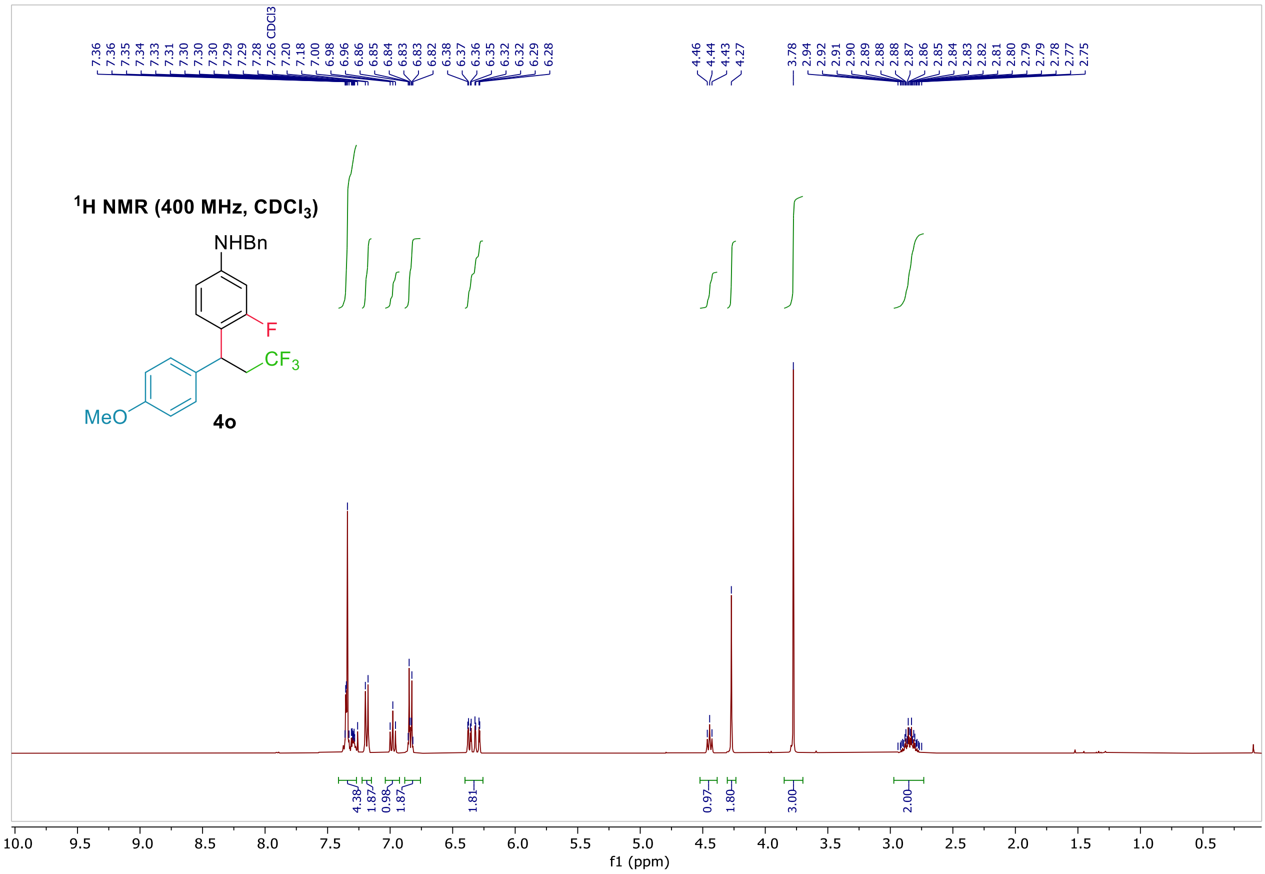
1H NMR (400 MHz, CDCl3)
NHBn
MeO
CF3
4m
7.37 7.36 7.34 7.33 7.32 7.31 7.30 7.29 7.29 7.28 7.27 7.27 7.26 CDCl3 7.22 7.20 7.01 6.99 6.84 6.82 6.79 6.78 6.61 6.61 6.59 6.58
4.87 4.85 4.83
4.28
3.77
3.29 2.88 2.86 2.85 2.83 2.82 2.80 2.80 2.78
7.46 1.07 3.17 0.99 1.00 1.96 3.22 0.91 2.07
f1 (ppm)

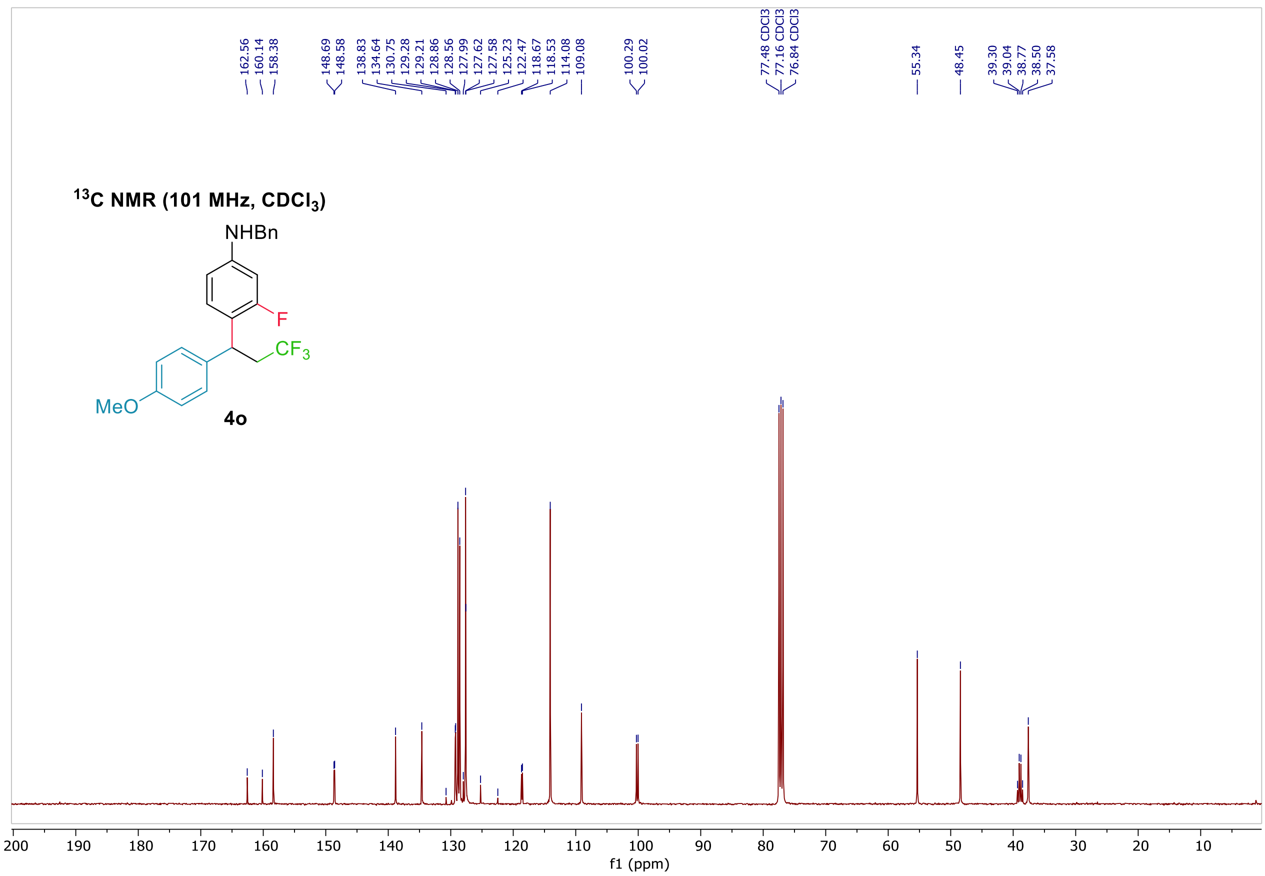


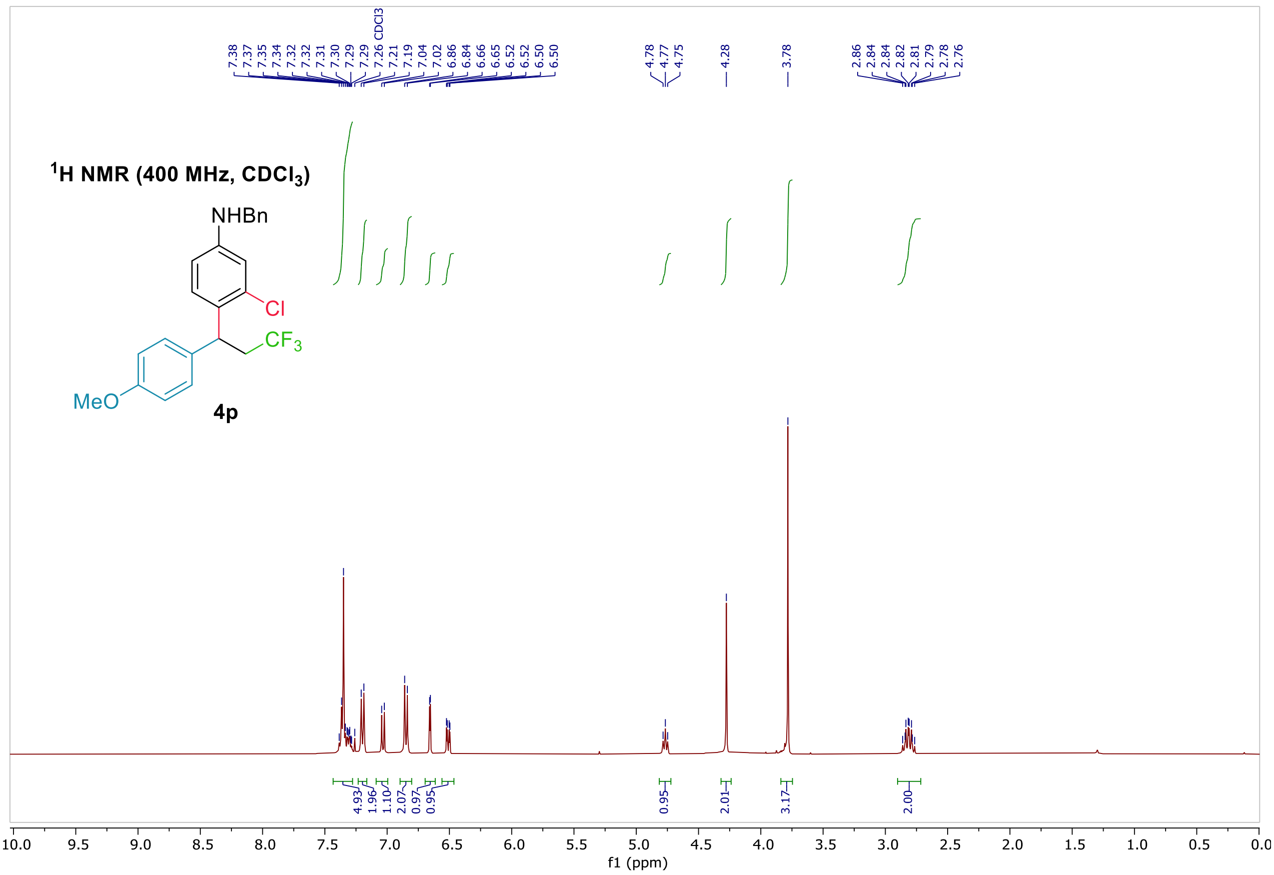
13C NMR (101 MHz, CDCl3)
NHBn
MeO
CF3
4m
158.32
146.13 138.84 134.98 134.79 128.83 128.74 127.98 127.72 127.61 127.58 125.22 121.98 117.16 114.68 113.98
82.44 81.42 77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
55.33
48.55
40.54 39.82 39.56 39.28 39.01
f1 (ppm)


1H NMR (400 MHz, CDCl3)
NHBn
CO2Me
CF3
MeO
4n
f1 (ppm)

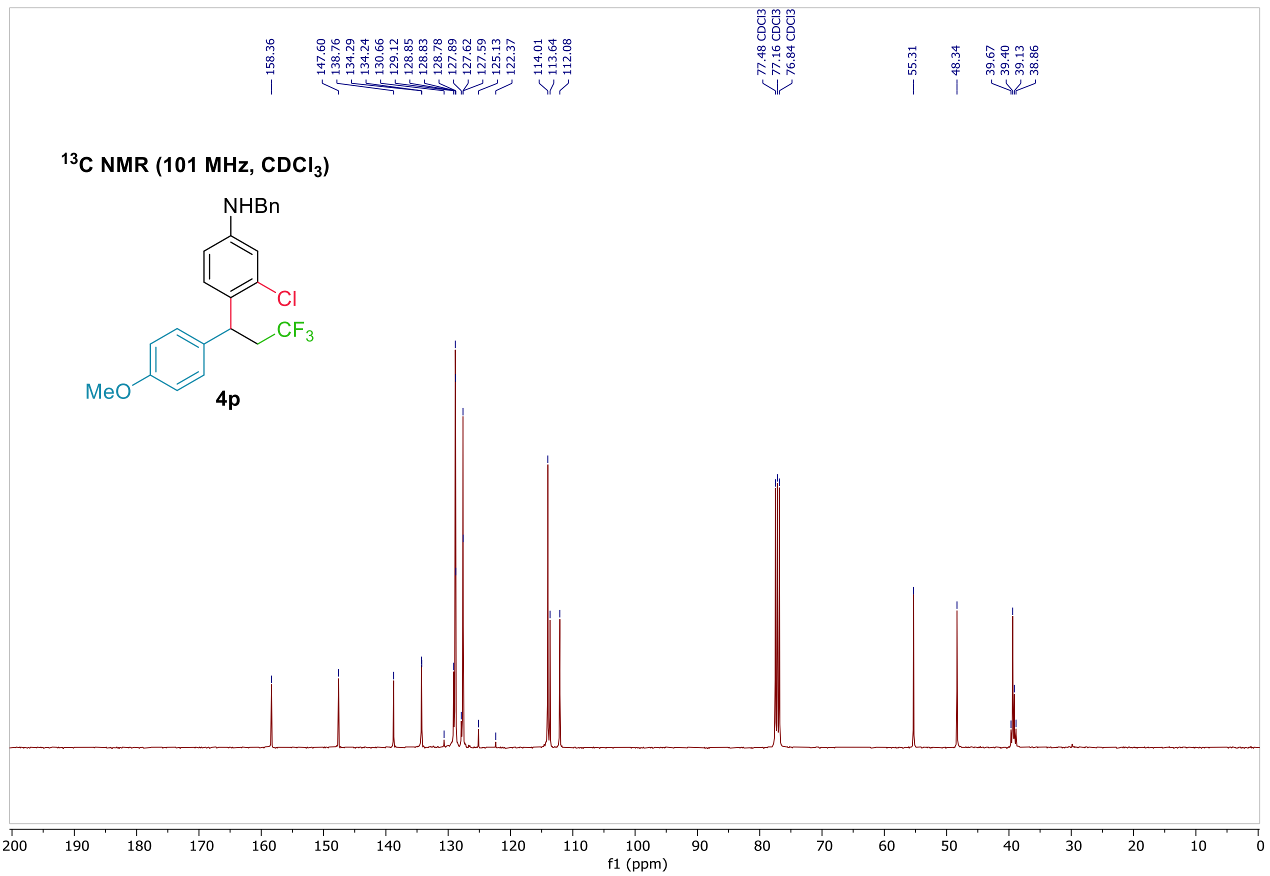

13C NMR (101 MHz, CDCl3)
NHBn
CO2Me
CF3
MeO
4n
f1 (ppm)


1H NMR (400 MHz, CDCl3)
NHBn
F
CF3
MeO
4o
f1 (ppm)

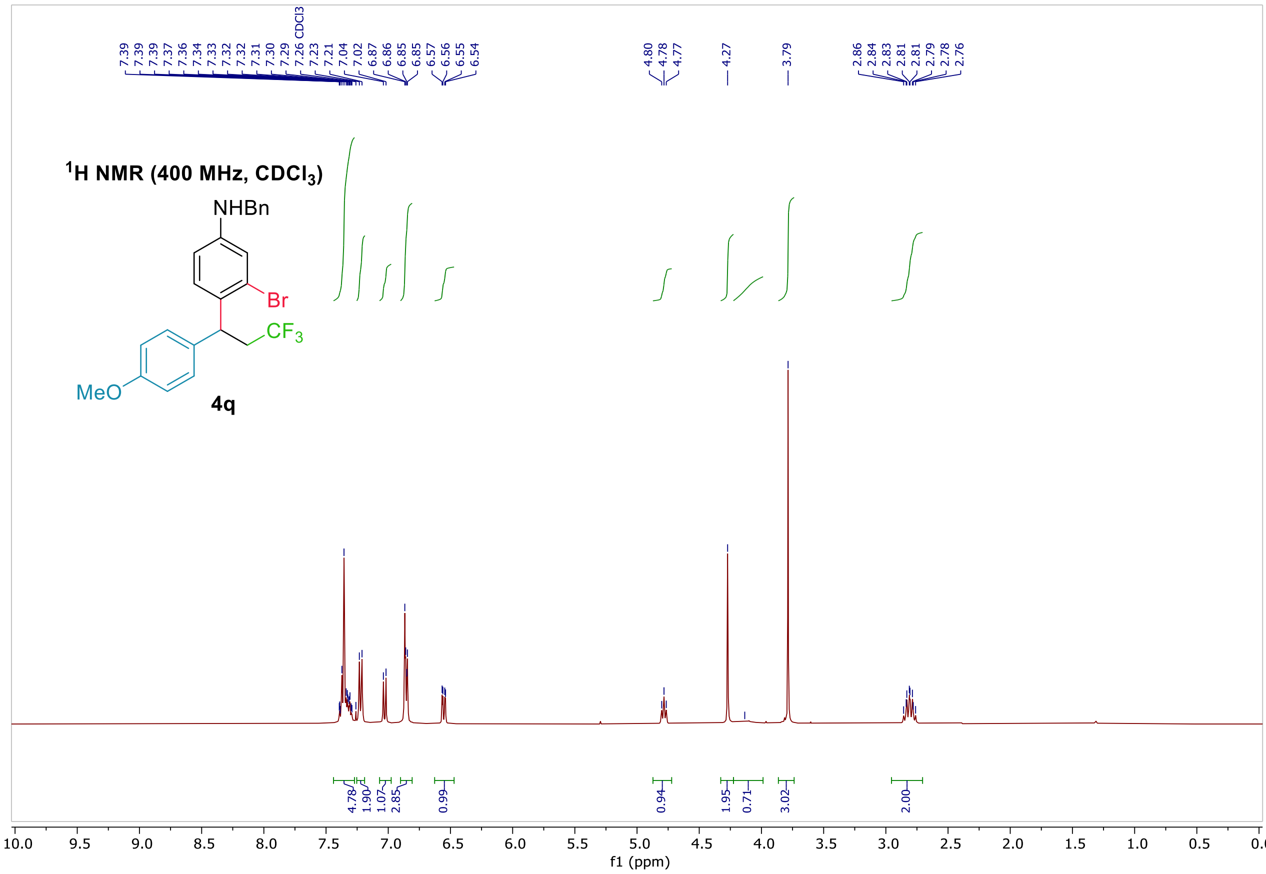

13C NMR (101 MHz, CDCl3)
NHBn
F
CF3
MeO
4o
f1 (ppm)



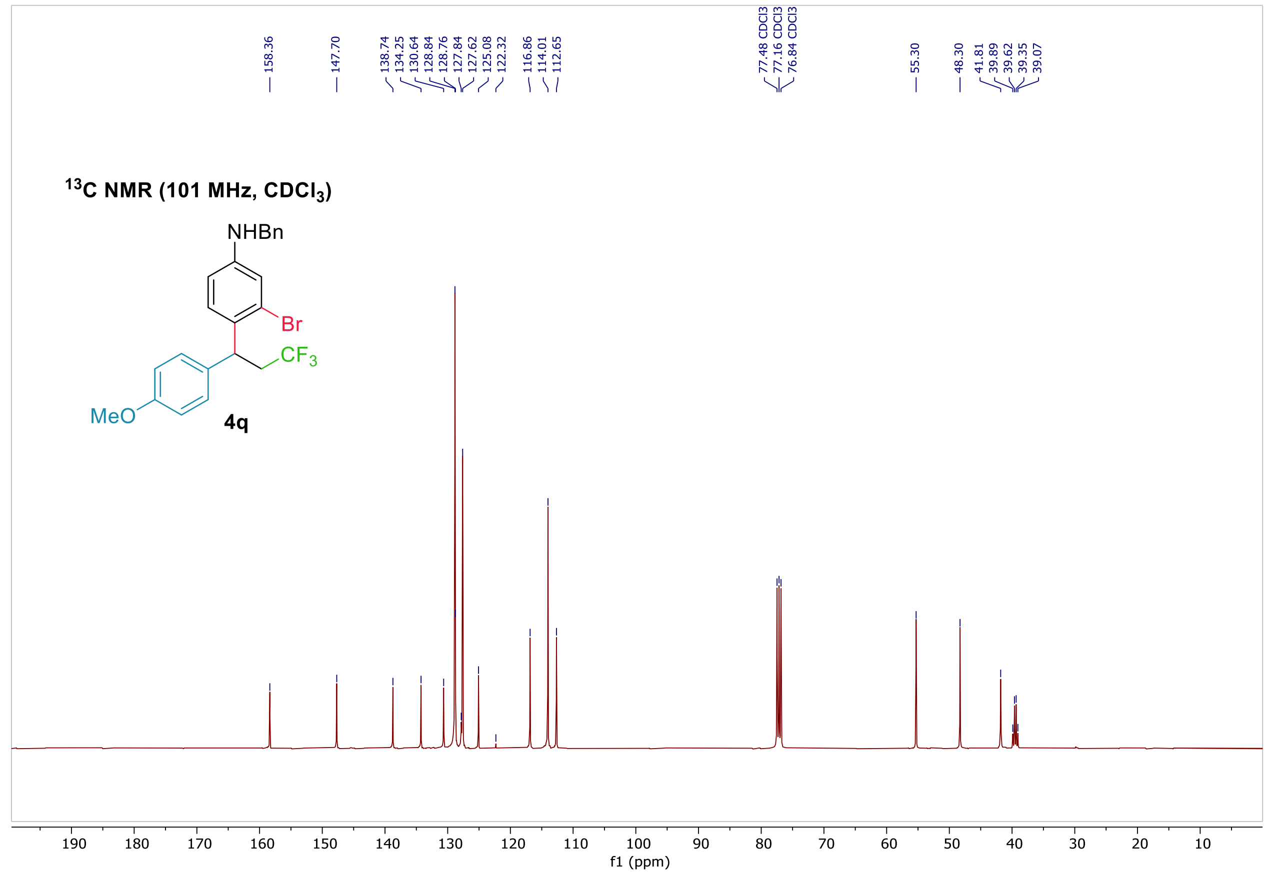
1H NMR (400 MHz, CDCl3)
NHBn
Cl
CF3
MeO
4p
7.38
7.37
7.35
7.34
7.32
7.32
7.31
7.30
7.29
7.29
7.26 CDCl3
7.21
7.19
7.04
7.02
6.86
6.84
6.66
6.65
6.52
6.52
6.50
6.50
4.78
4.77
4.75
4.28
3.78
2.86
2.84
2.84
2.82
2.81
2.79
2.78
2.76
4.93
1.96
1.10
2.07
0.97
0.95
0.95
2.01
3.17
2.00
f1 (ppm)



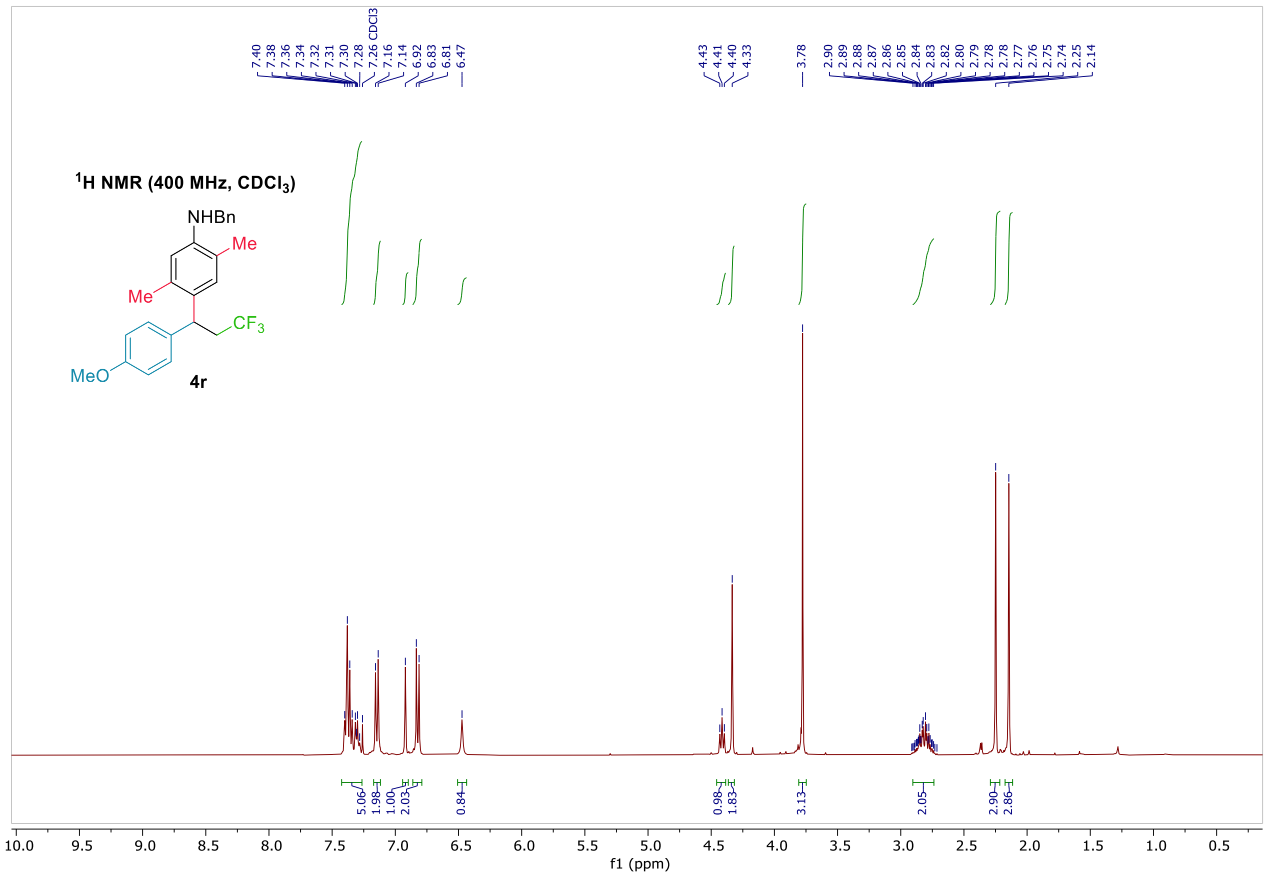
13C NMR (101 MHz, CDCl3)
NHBn
Cl
CF3
MeO
4p
158.36
147.60
138.76
134.29
134.24
130.66
129.12
128.85
128.83
128.78
127.89
127.62
127.59
125.13
122.37
114.01
113.64
112.08
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.31
48.34
39.67
39.40
39.13
38.86
f1 (ppm)



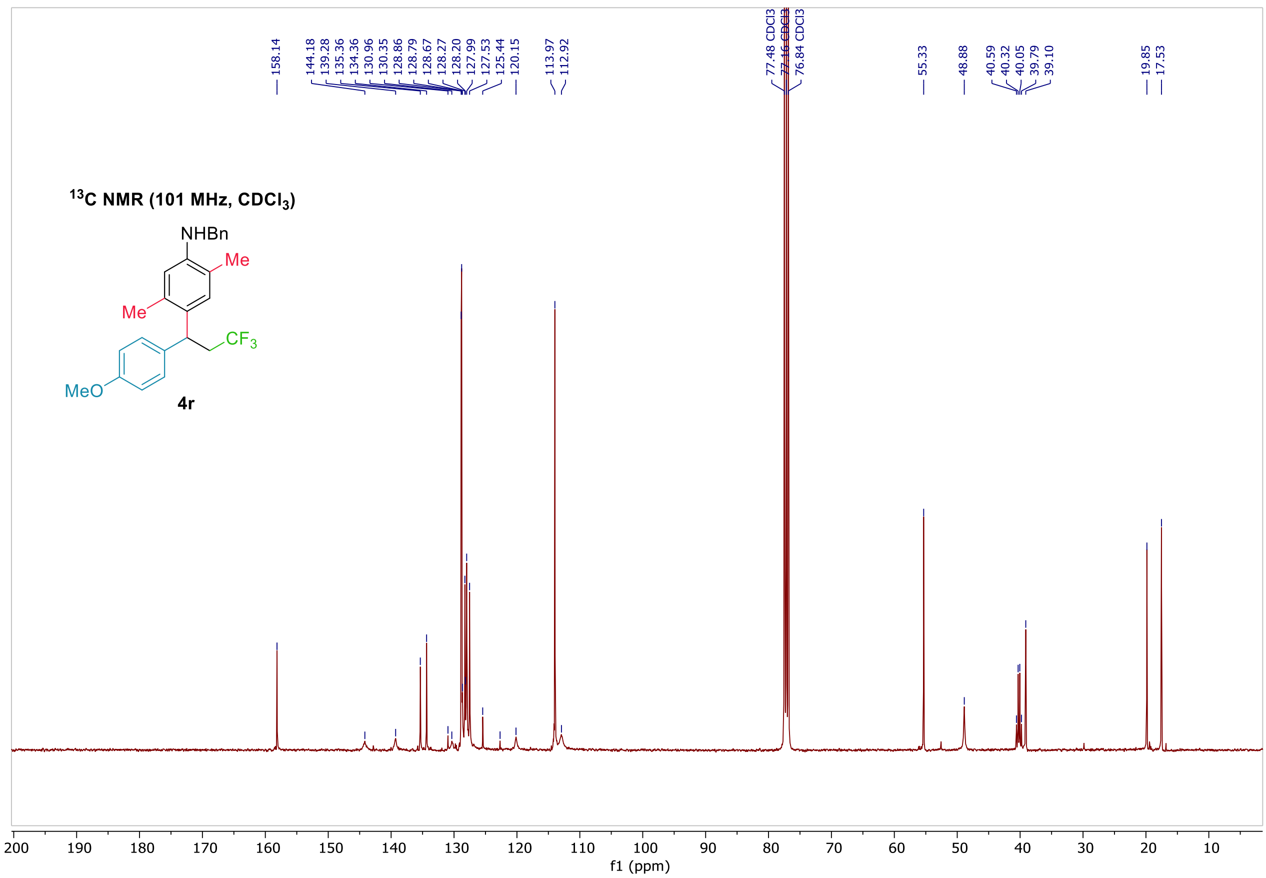
^{1}H NMR (400 MHz, CDCl$_3$)
NHBn
Br
CF$_3$
MeO
4q
f1 (ppm)



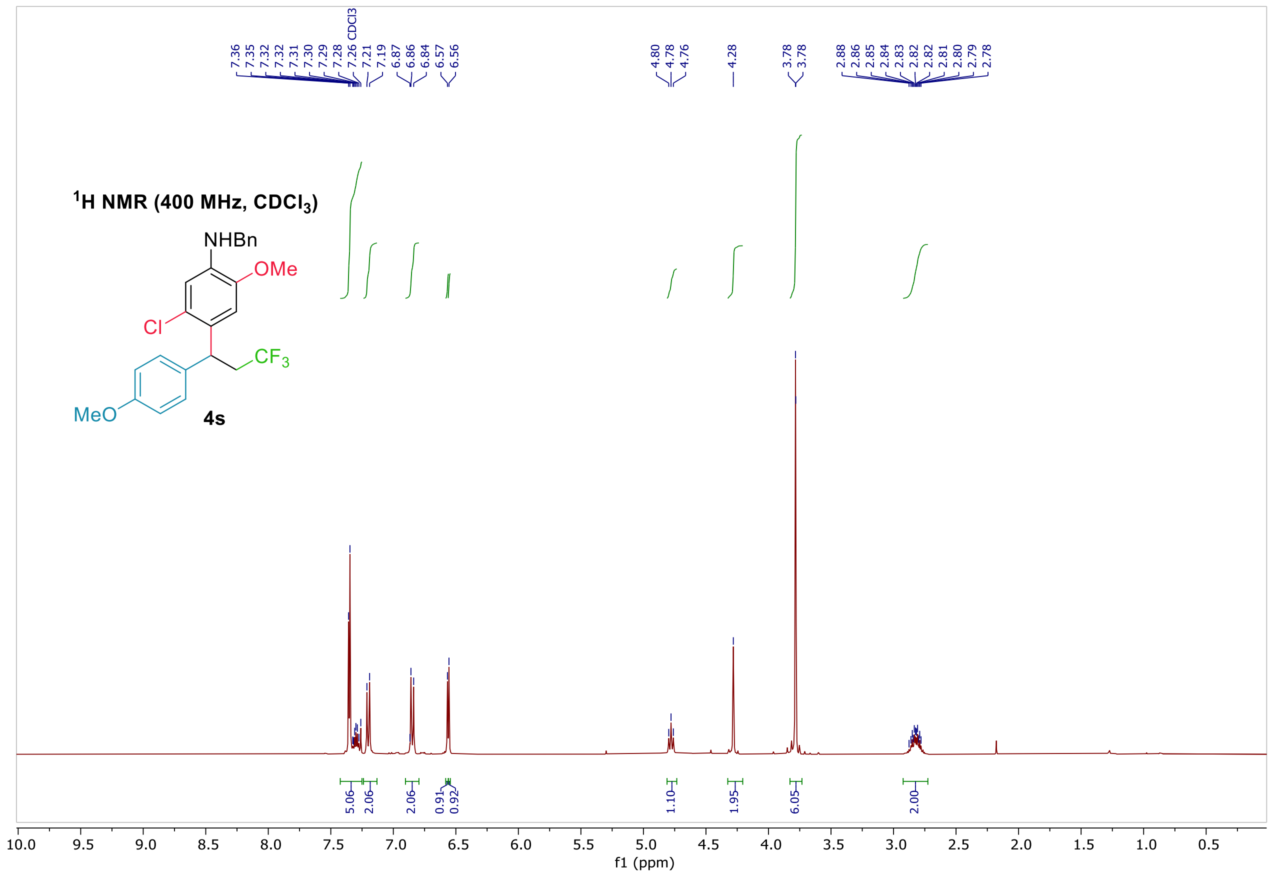
^{13}C NMR (101 MHz, CDCl$_3$)
NHBn
Br
CF$_3$
MeO
4q
f1 (ppm)



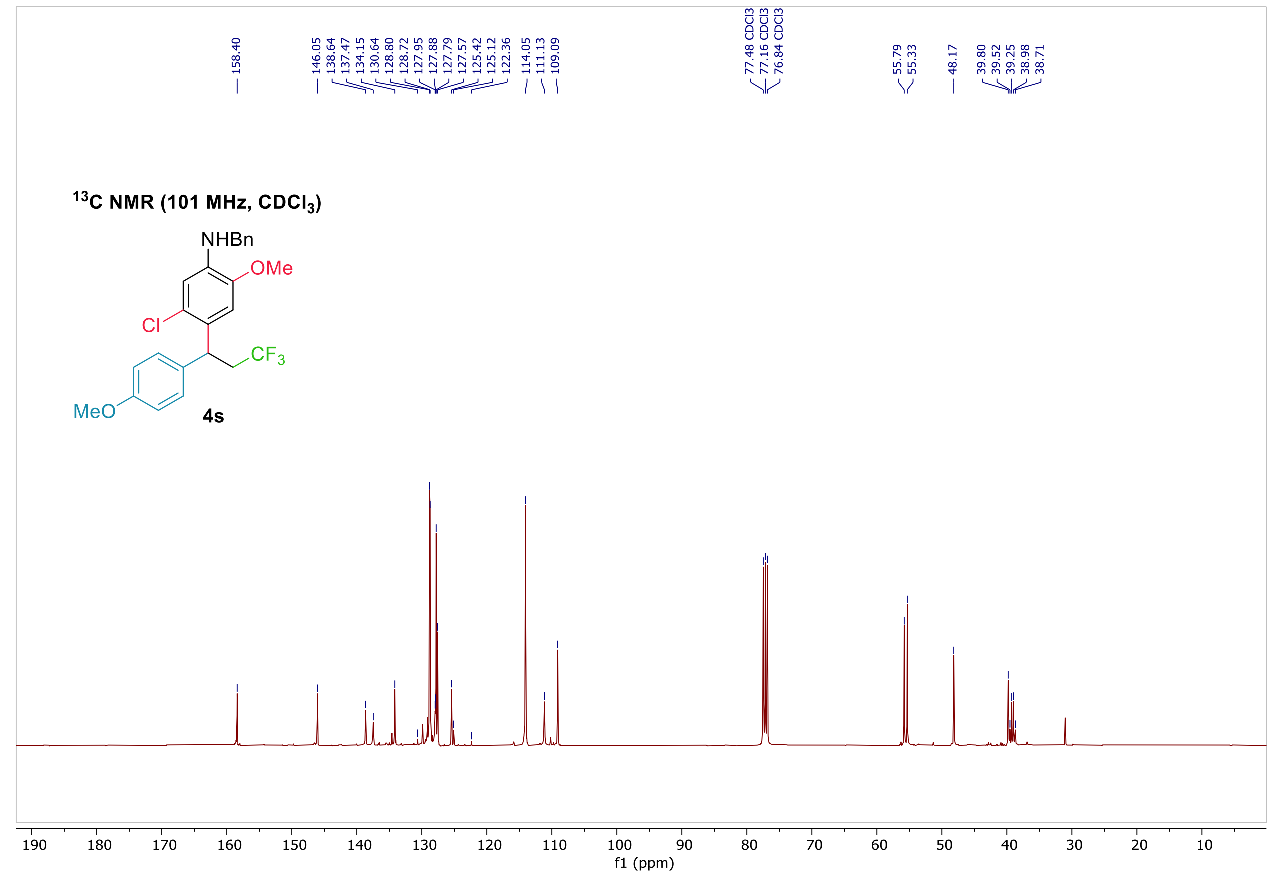
1H NMR (400 MHz, CDCl3)
NHBn
Me
Me
CF3
MeO
4r
f1 (ppm)



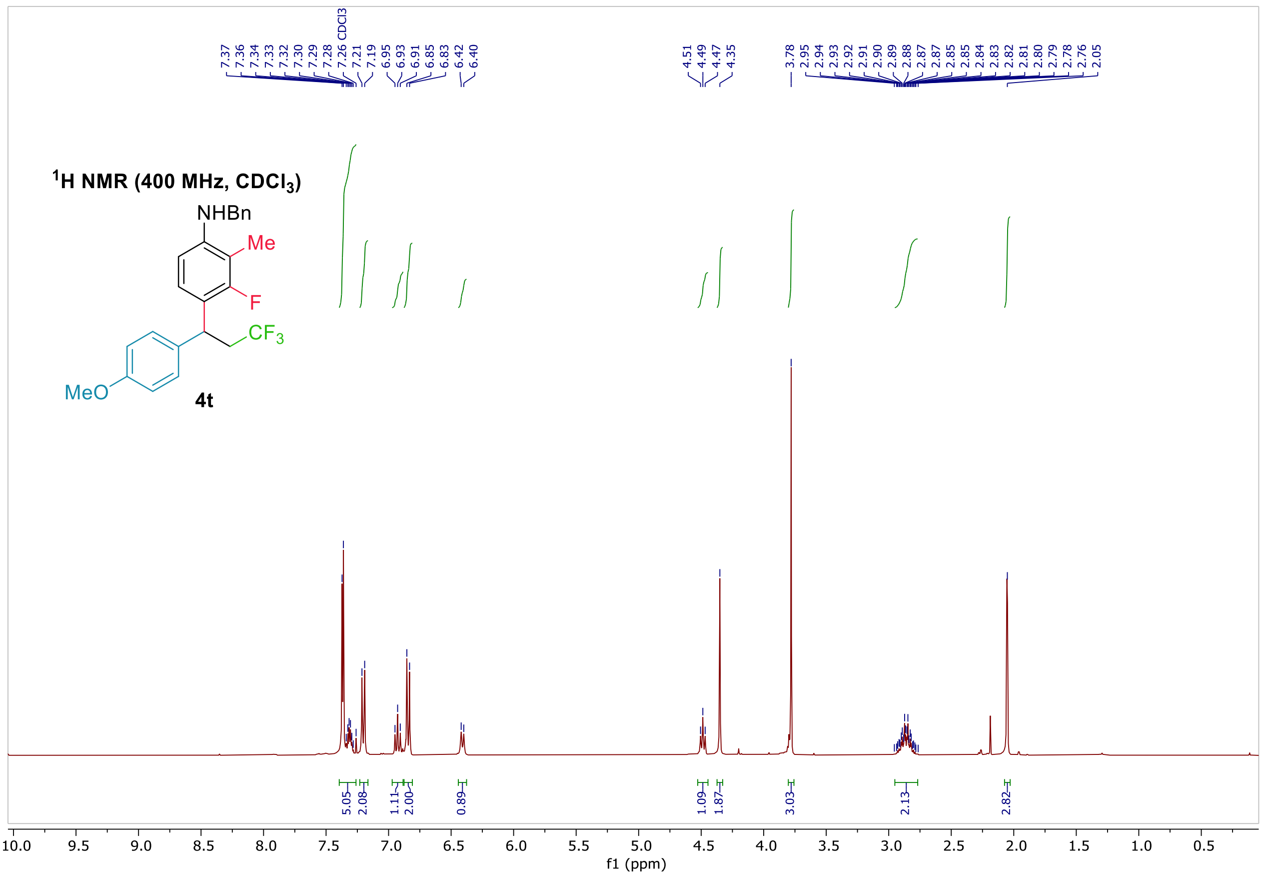
13C NMR (101 MHz, CDCl3)
NHBn
Me
Me
CF3
MeO
4r
f1 (ppm)



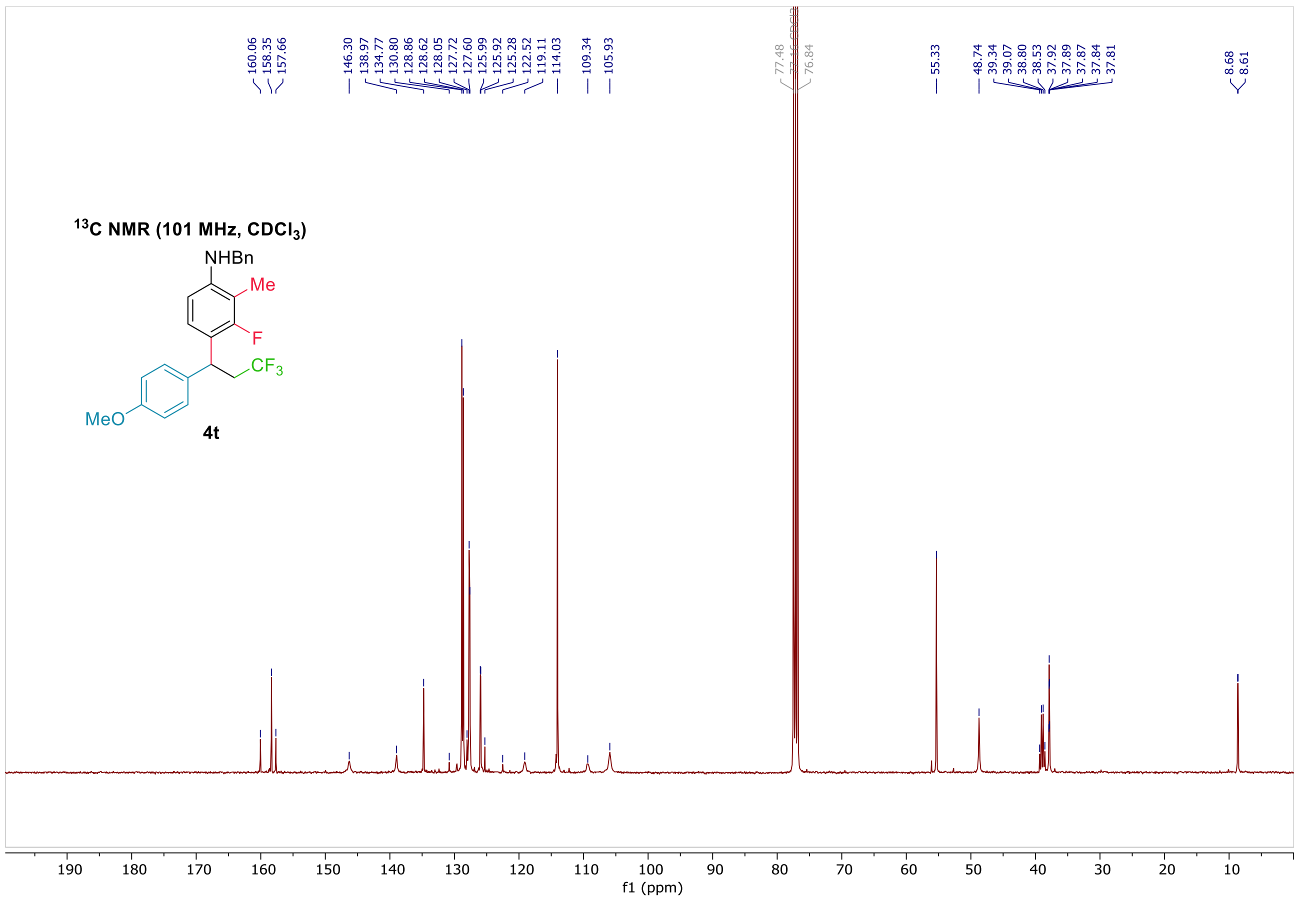
1H NMR (400 MHz, CDCl3)
NHBn
OMe
Cl
CF3
MeO
4s
7.36
7.35
7.32
7.32
7.31
7.30
7.29
7.28
7.26 CDCl3
7.21
7.19
6.87
6.86
6.84
6.57
6.56
4.80
4.78
4.76
4.28
3.78
3.78
2.88
2.86
2.85
2.84
2.83
2.82
2.82
2.81
2.80
2.79
2.78
5.06
2.06
2.06
0.91
0.92
1.10
1.95
6.05
2.00
f1 (ppm)



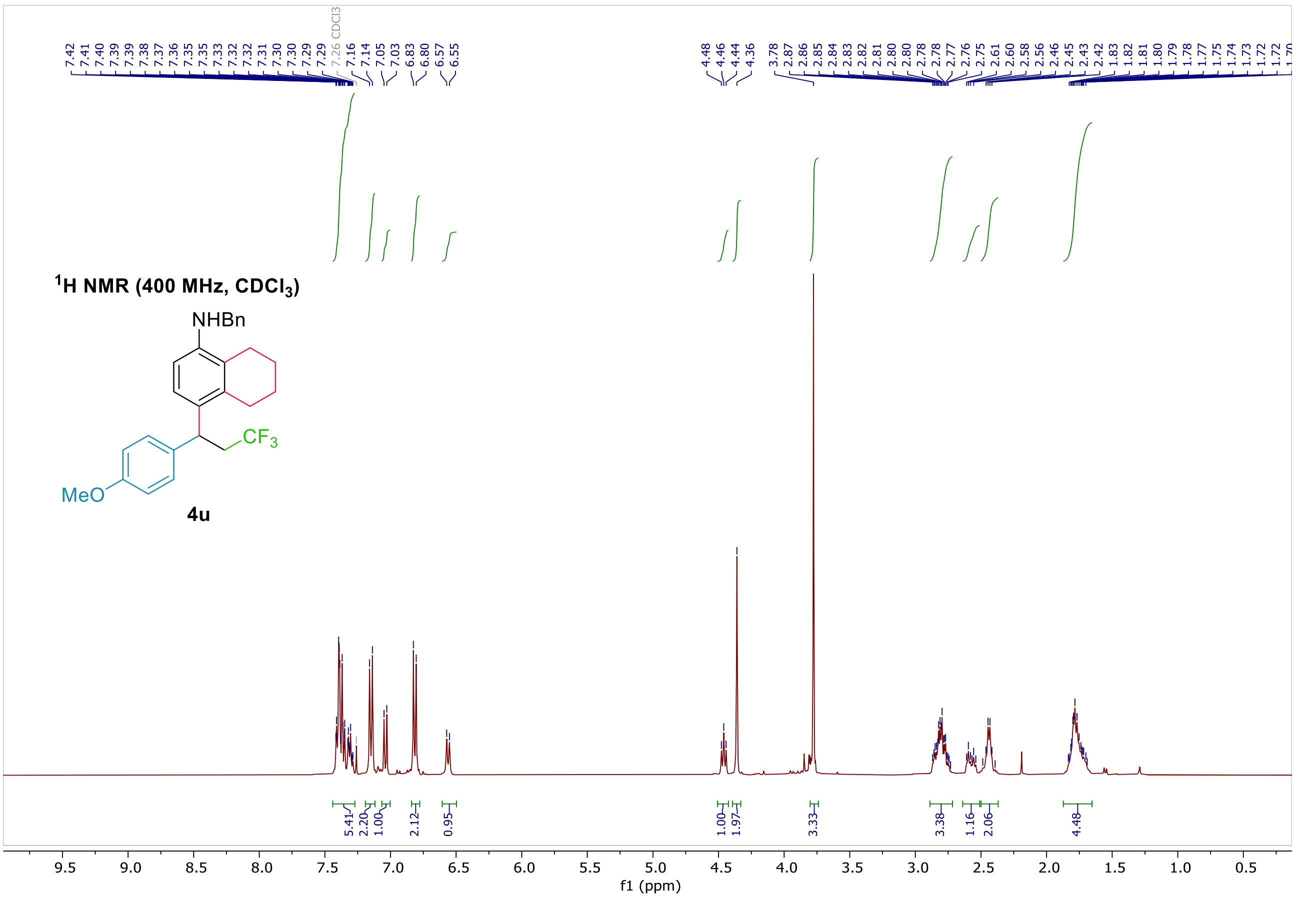
13C NMR (101 MHz, CDCl3)
NHBn
OMe
Cl
CF3
MeO
4s
158.40
146.05
138.64
137.47
134.15
130.64
128.80
128.72
127.95
127.88
127.79
127.57
125.42
125.12
122.36
114.05
111.13
109.09
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.79
55.33
48.17
39.80
39.52
39.25
38.98
38.71
f1 (ppm)

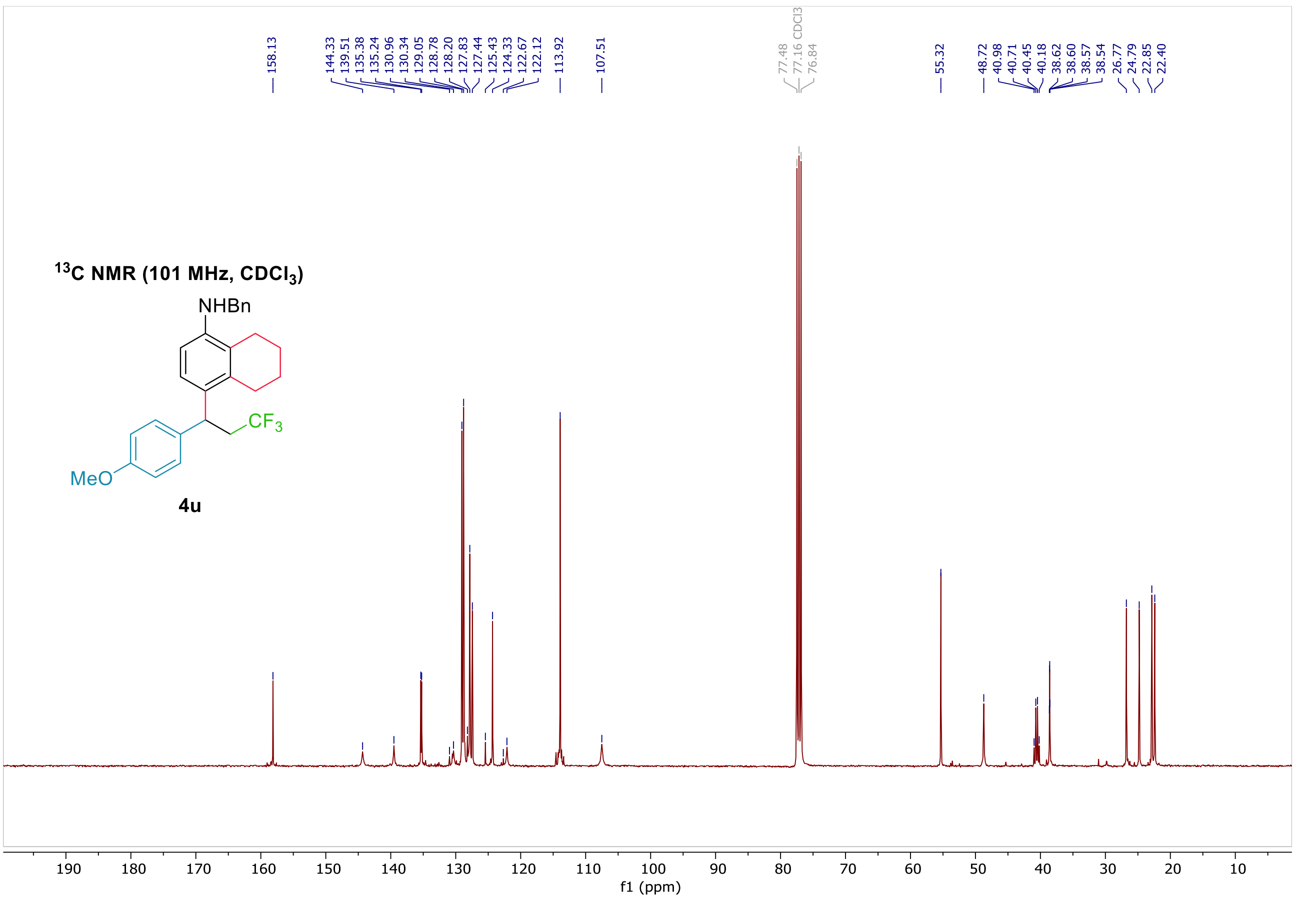


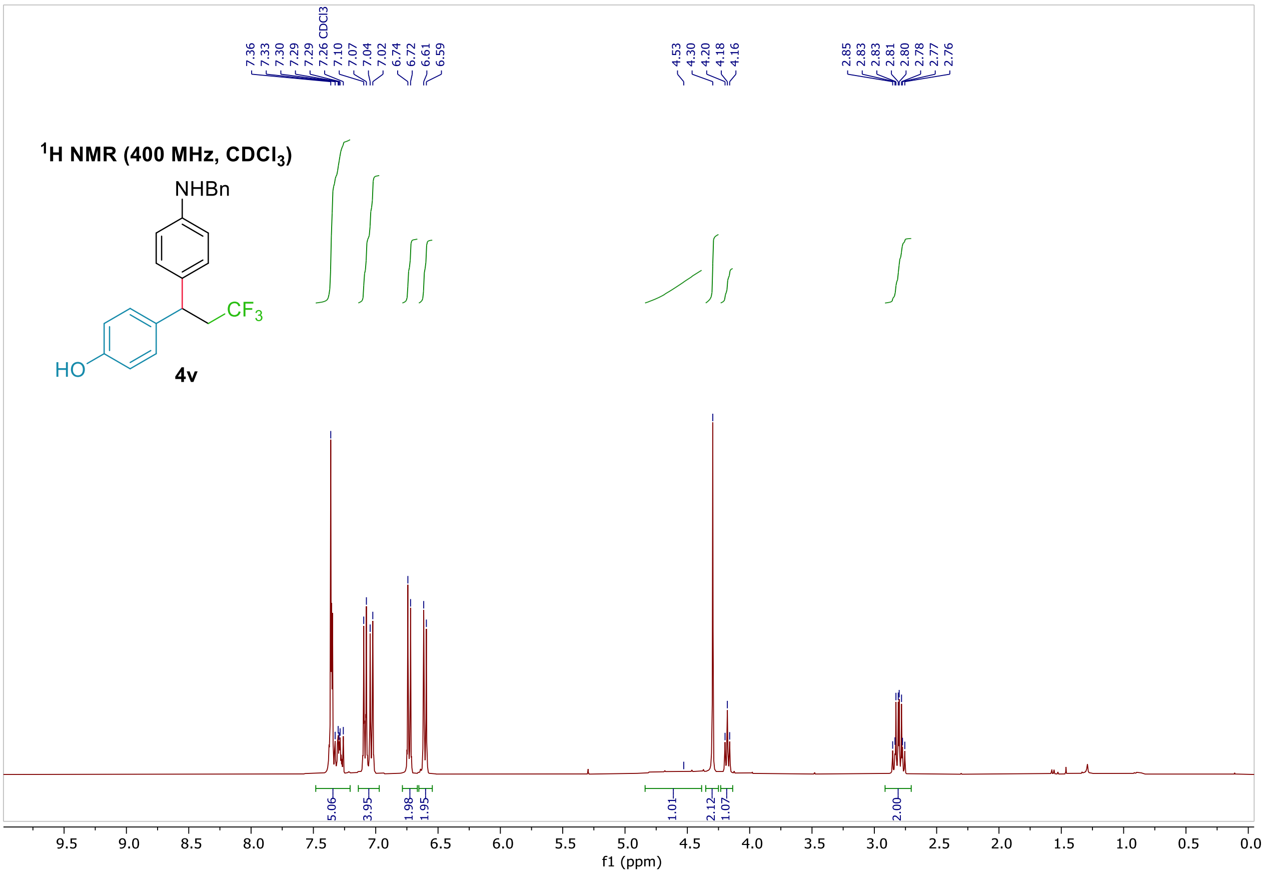
1H NMR (400 MHz, CDCl3)
NHBn
Me
F
CF3
MeO
4t
f1 (ppm)

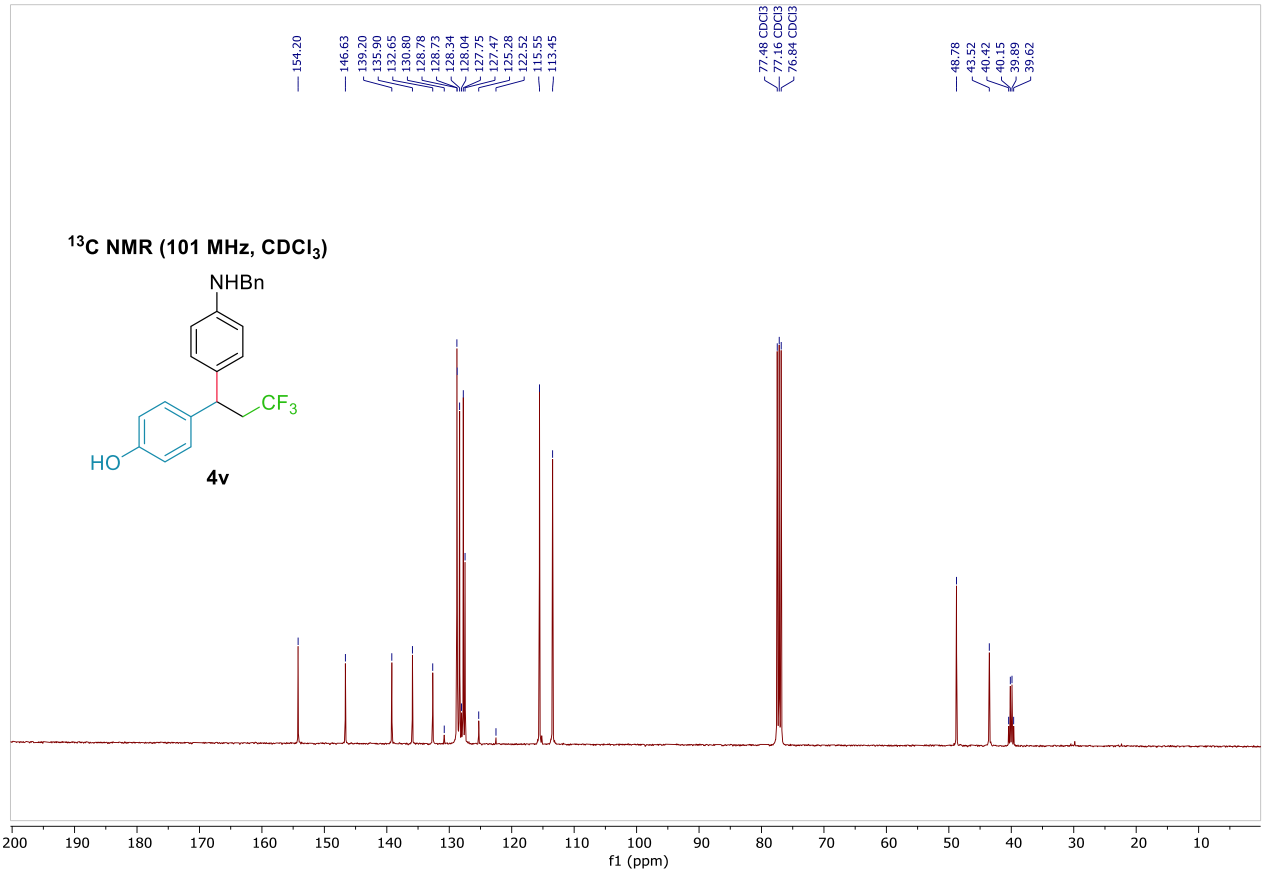


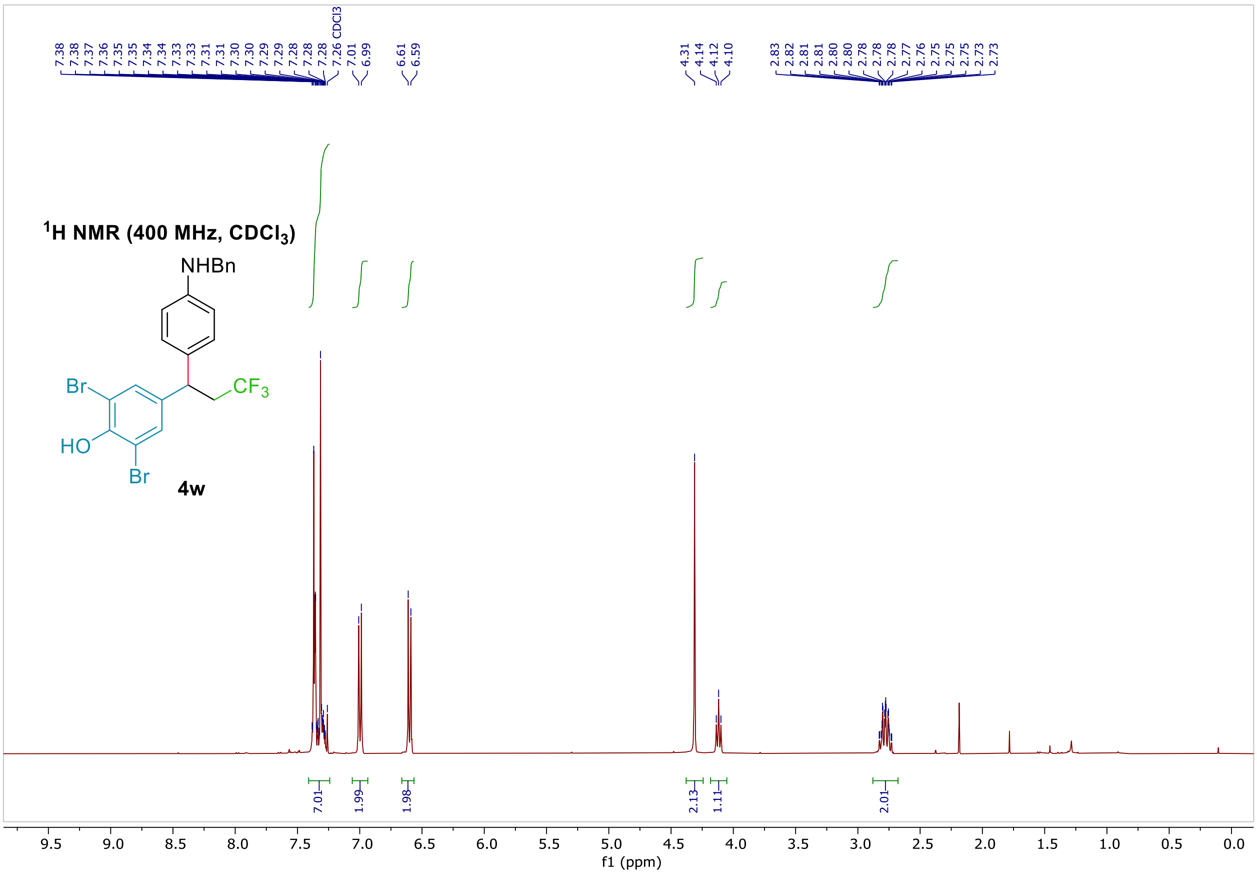
13C NMR (101 MHz, CDCl3)
NHBn
Me
F
CF3
MeO
4t
f1 (ppm)


1H NMR (400 MHz, CDCl3)
NHBn
CF3
MeO
4u
f1 (ppm)

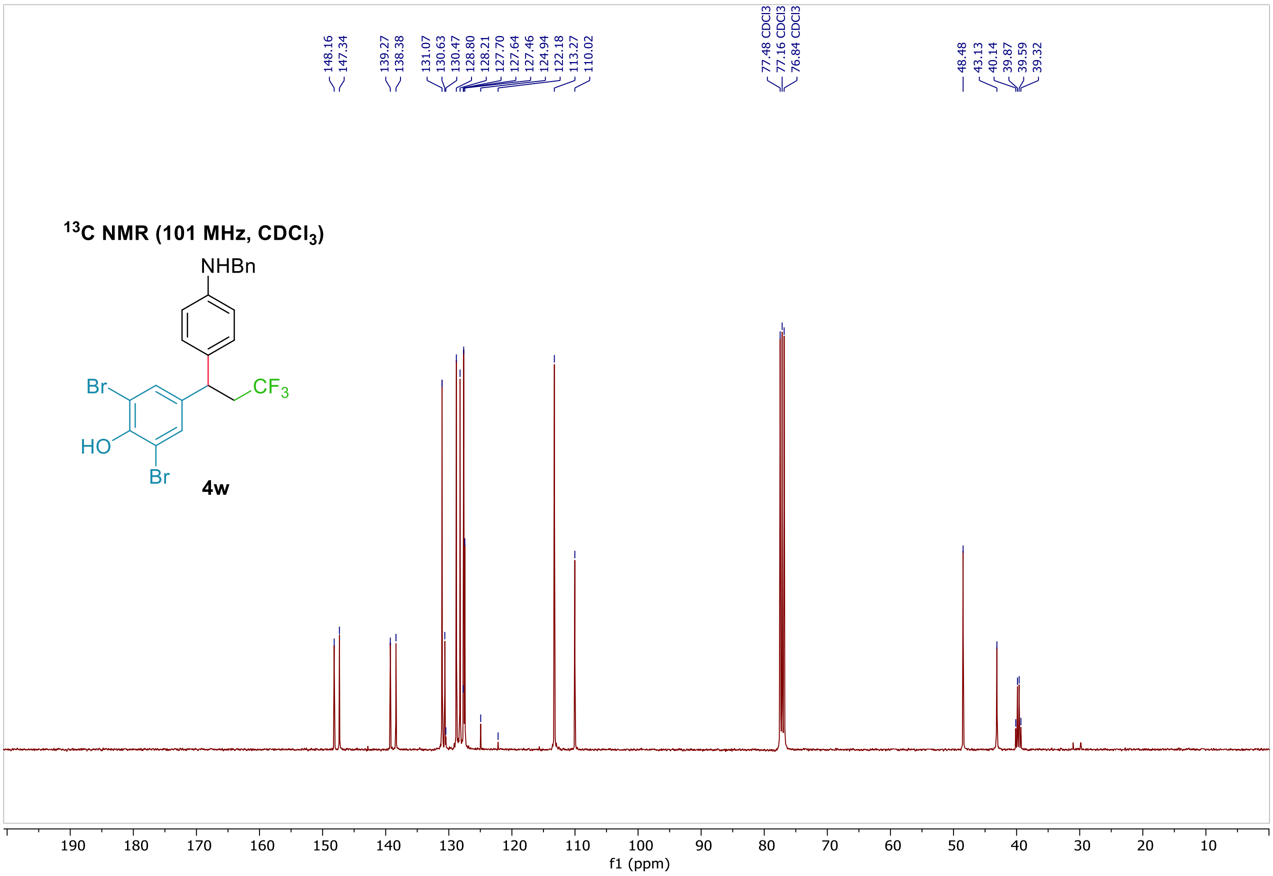

13C NMR (101 MHz, CDCl3)
NHBn
CF3
MeO
4u
f1 (ppm)


1H NMR (400 MHz, CDCl3)
NHBn
CF3
HO
4v
7.36
7.33
7.30
7.29
7.29
7.26 CDCl3
7.10
7.07
7.04
7.02
6.74
6.72
6.61
6.59
4.53
4.30
4.20
4.18
4.16
2.85
2.83
2.83
2.81
2.80
2.78
2.77
2.76
5.06
3.95
1.98
1.95
1.01
2.12
1.07
2.00
f1 (ppm)

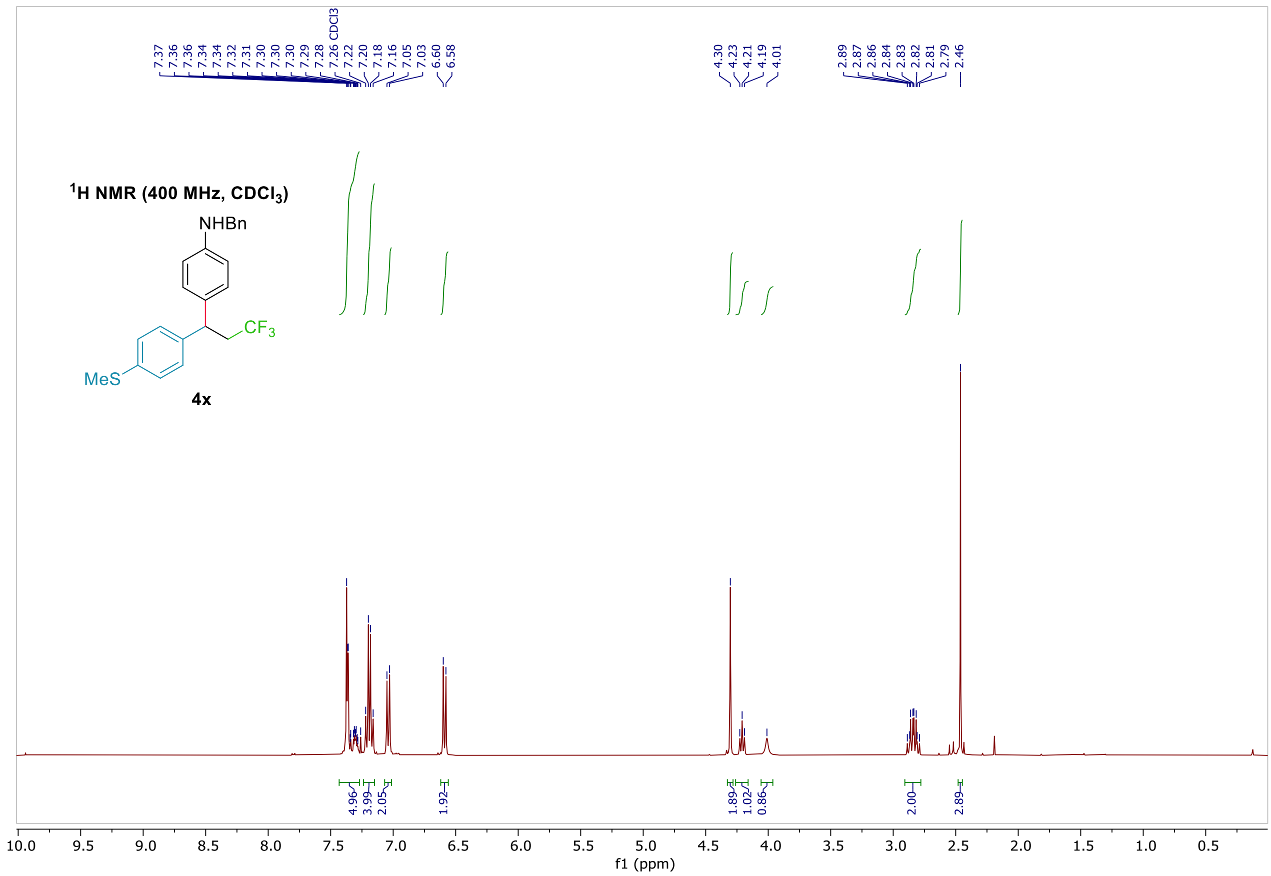

13C NMR (101 MHz, CDCl3)
NHBn
CF3
HO
4v
154.20
146.63
139.20
135.90
132.65
130.80
128.78
128.73
128.34
128.04
127.75
127.47
125.28
122.52
115.55
113.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
48.78
43.52
40.42
40.15
39.89
39.62
f1 (ppm)



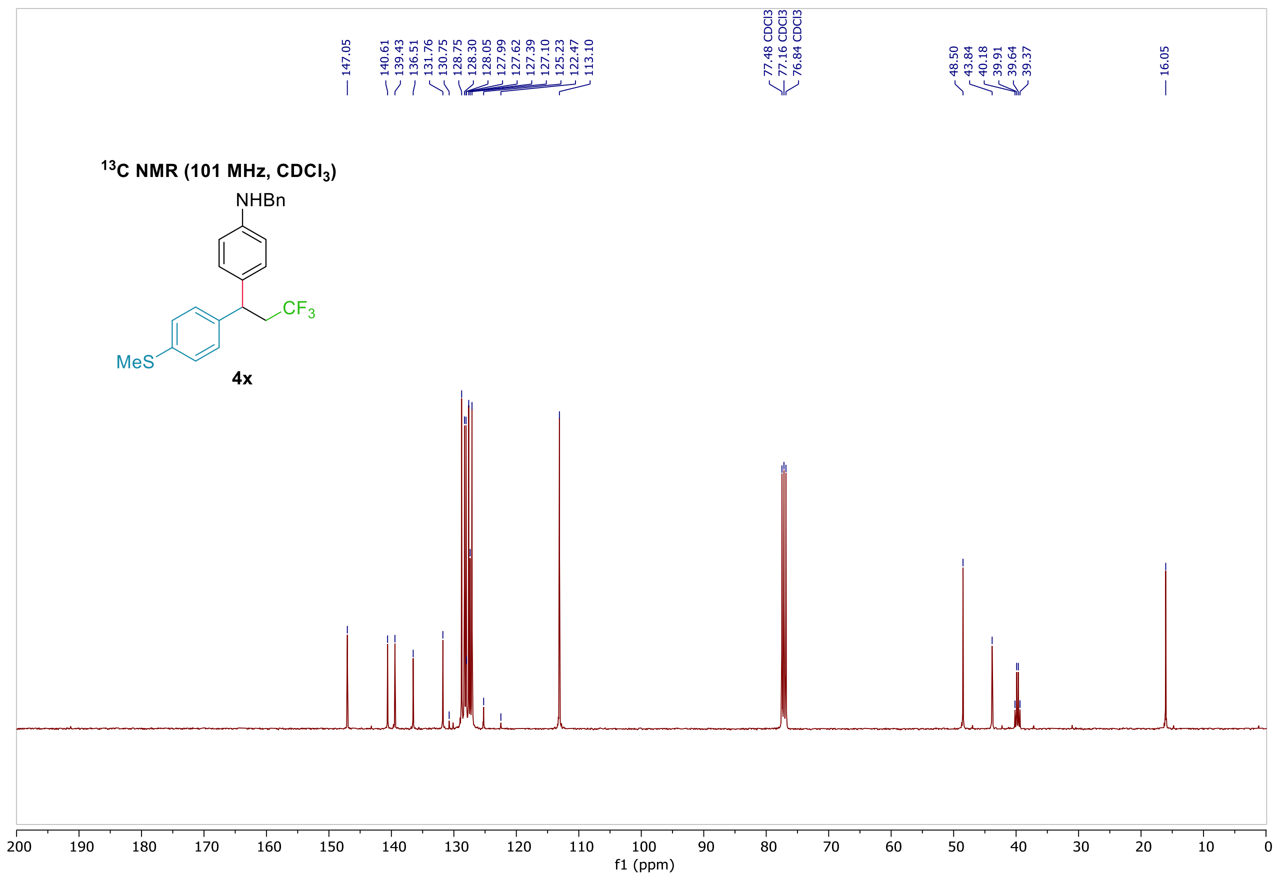
¹H NMR (400 MHz, CDCl3)
NHBn
Br
CF3
HO
Br
4w
f1 (ppm)



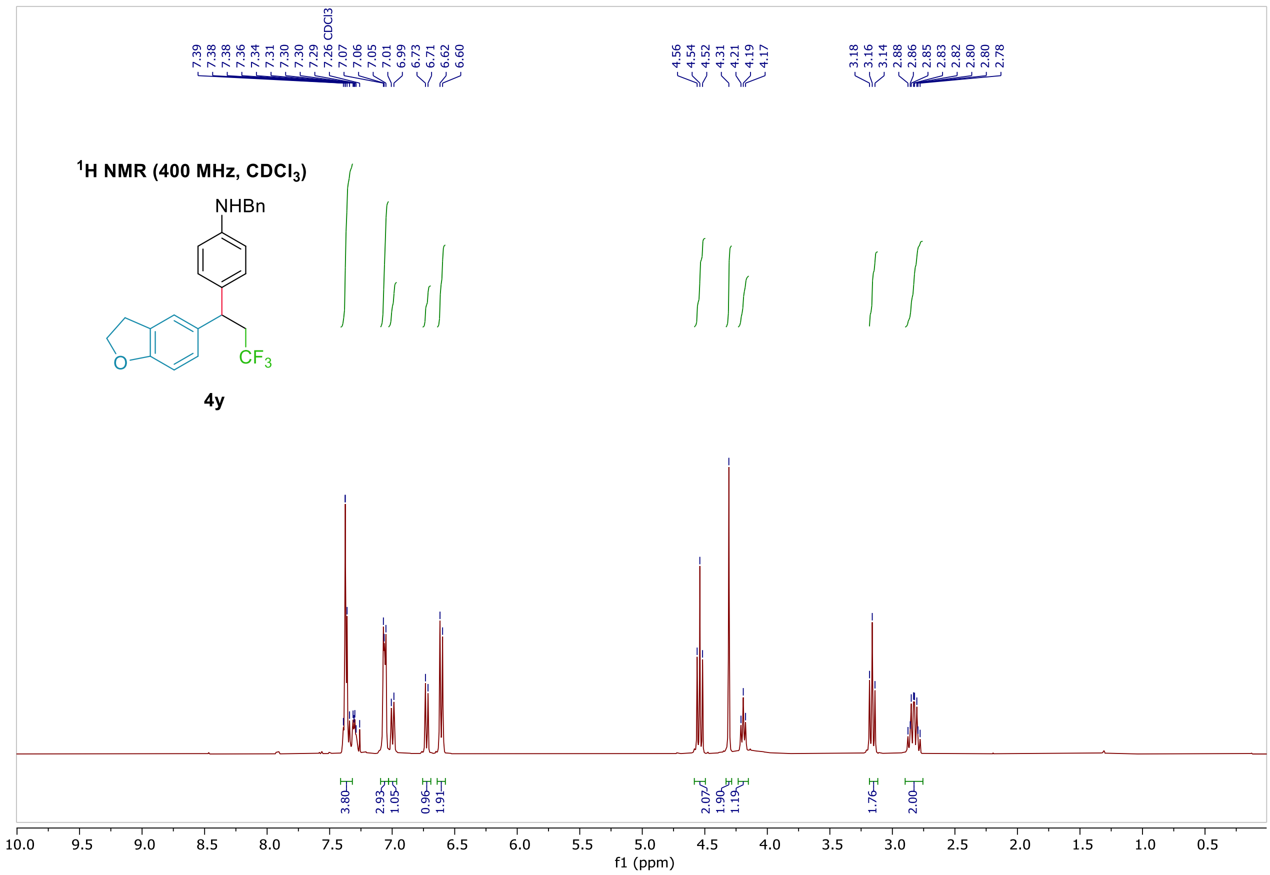
¹³C NMR (101 MHz, CDCl3)
NHBn
Br
CF3
HO
Br
4w
f1 (ppm)



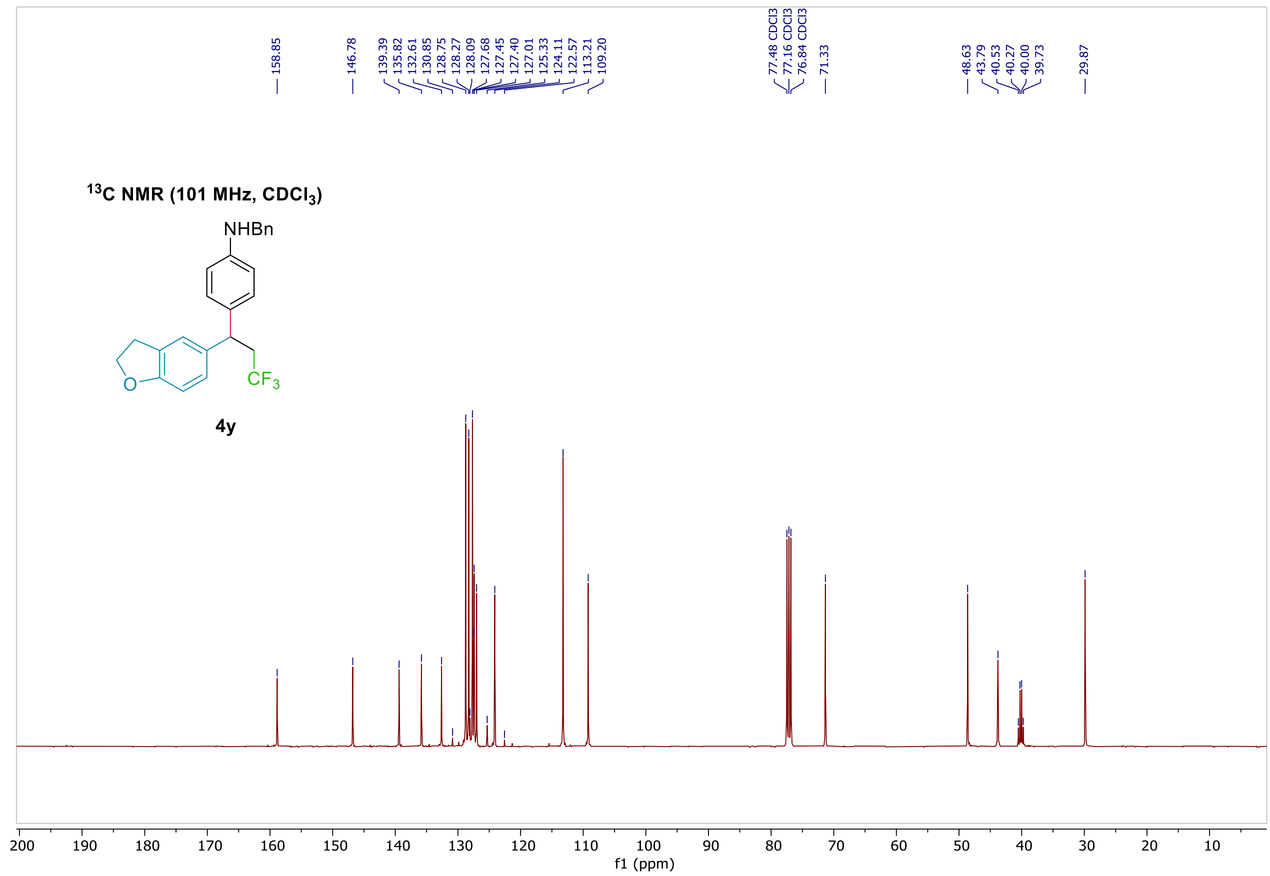
^{1}H NMR (400 MHz, $CDCl_3$)
NHBn
CF_3
MeS
4x
7.37 7.36 7.36 7.34 7.34 7.32 7.31 7.30 7.30 7.29 7.28 7.26 CDCl3 7.22 7.20 7.18 7.16 7.05 7.03 6.60 6.58
4.30 4.23 4.21 4.19 4.01
2.89 2.87 2.86 2.84 2.83 2.82 2.81 2.79 2.46
4.96 3.99 2.05 1.92 1.89 1.02 0.86 2.00 2.89
f1 (ppm)



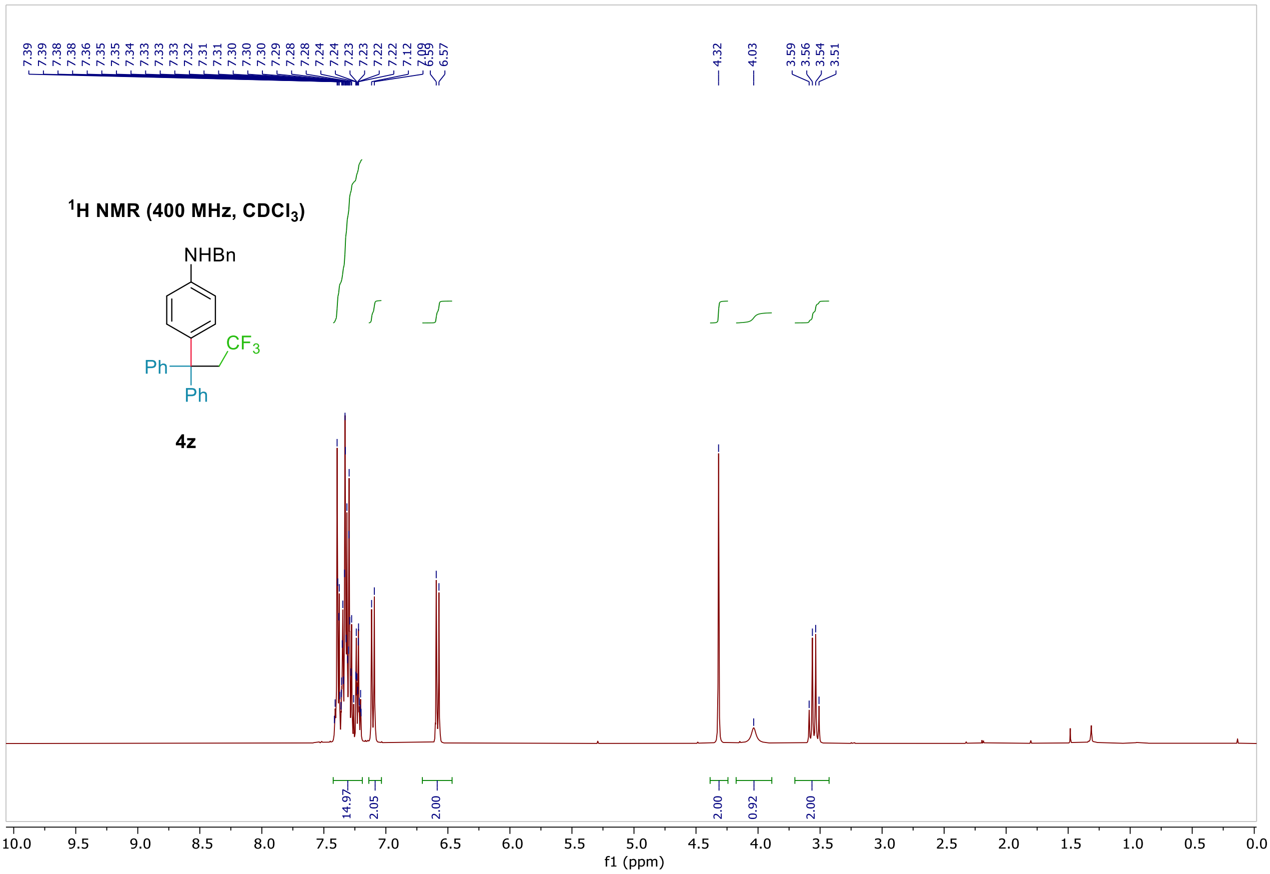
^{13}C NMR (101 MHz, $CDCl_3$)
NHBn
CF_3
MeS
4x
147.05 140.61 139.43 136.51 131.76 130.75 128.75 128.30 128.05 127.99 127.62 127.39 127.10 125.23 122.47 113.10
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
48.50 43.84 40.18 39.91 39.64 39.37
16.05
f1 (ppm)



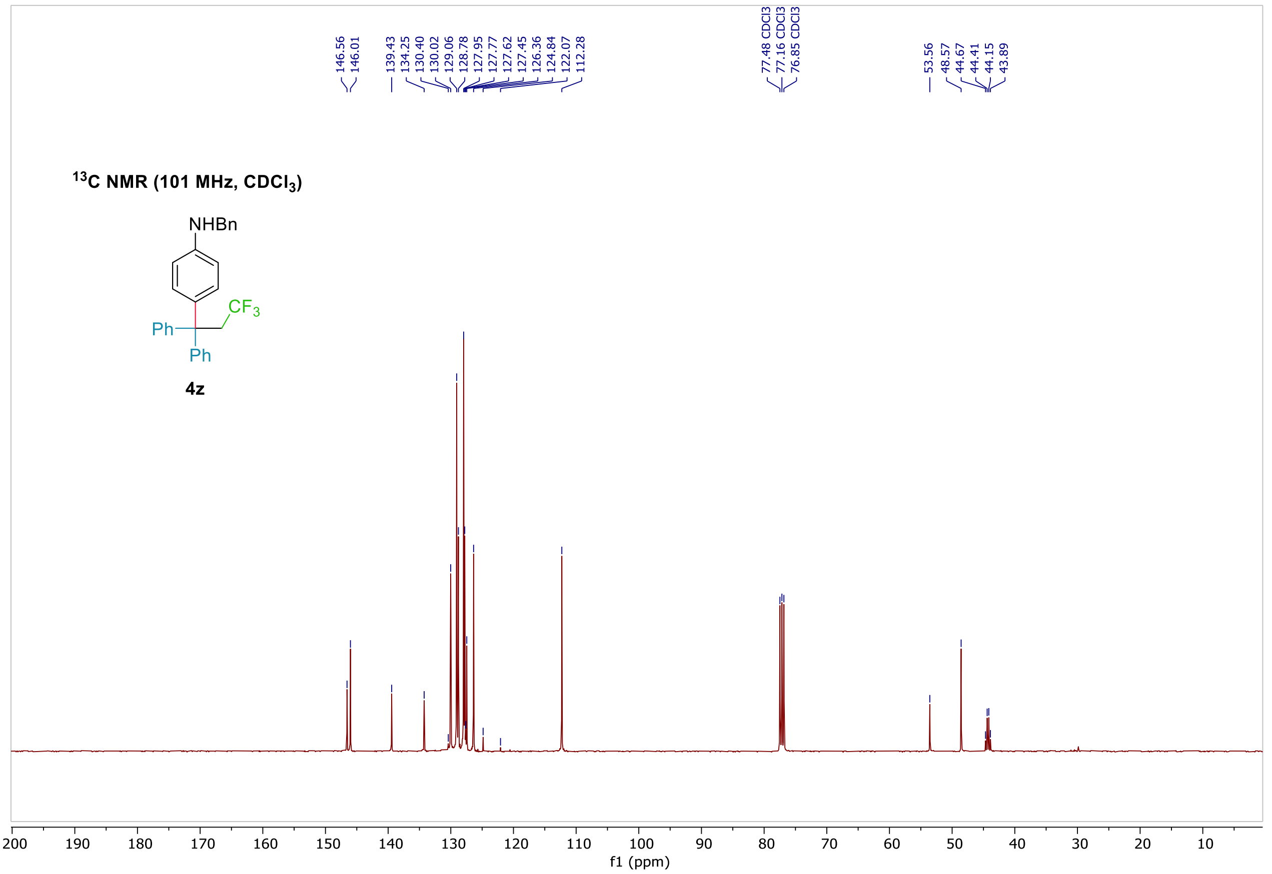
7.39
7.38
7.38
7.36
7.34
7.31
7.30
7.30
7.29
7.26 CDCl3
7.07
7.06
7.05
7.01
6.99
6.73
6.71
6.62
6.60
4.56
4.54
4.52
4.31
4.21
4.19
4.17
3.18
3.16
3.14
2.88
2.86
2.85
2.83
2.82
2.80
2.80
2.78
^{1}H NMR (400 MHz, CDCl$_3$)
NHBn
CF$_3$
O
4y
3.80
2.93
1.05
0.96
1.91
2.07
1.90
1.19
1.76
2.00
f1 (ppm)



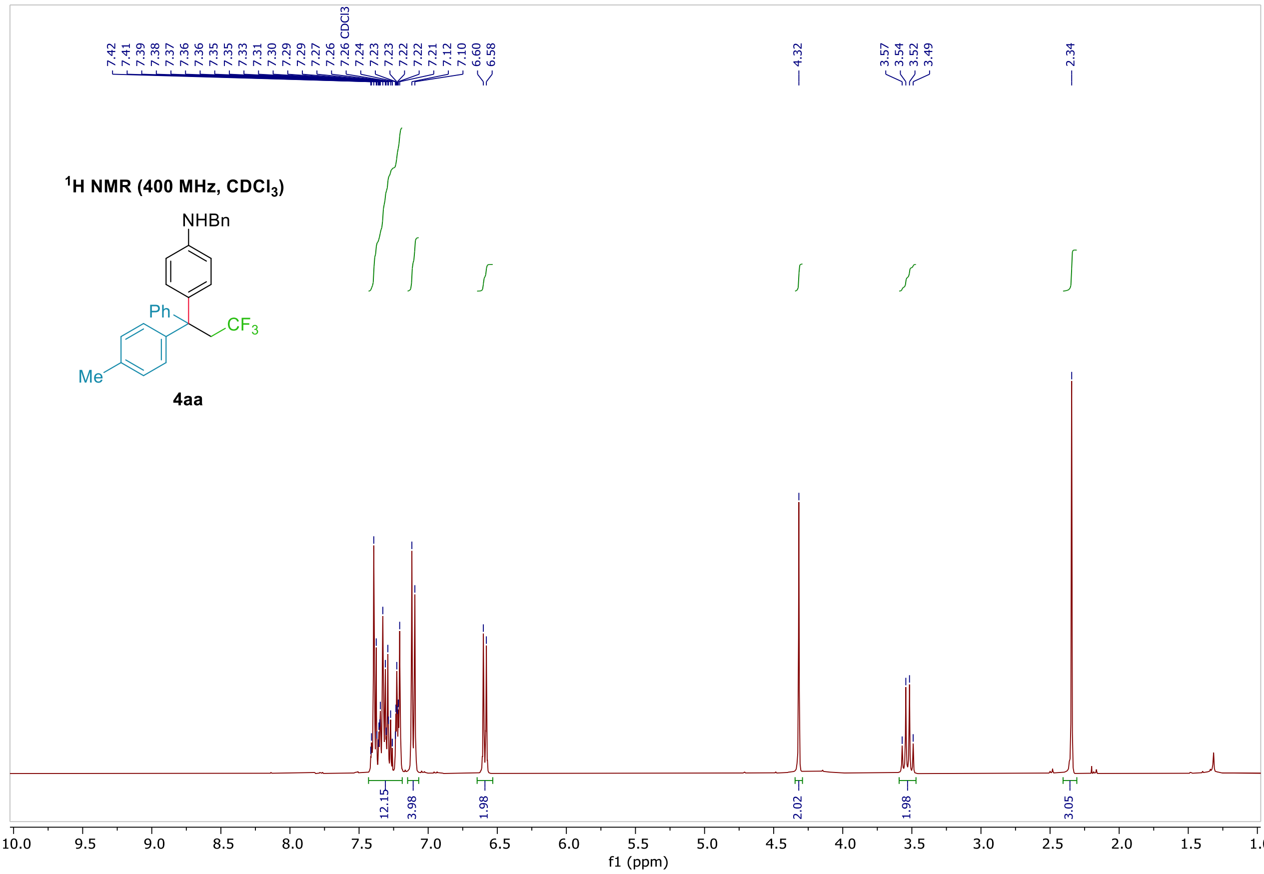
158.85
146.78
139.39
135.82
132.61
130.85
128.75
128.27
128.09
127.68
127.45
127.40
127.01
125.33
124.11
122.57
113.21
109.20
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.33
48.63
43.79
40.53
40.27
40.00
39.73
29.87
^{13}C NMR (101 MHz, CDCl$_3$)
NHBn
CF$_3$
O
4y
f1 (ppm)



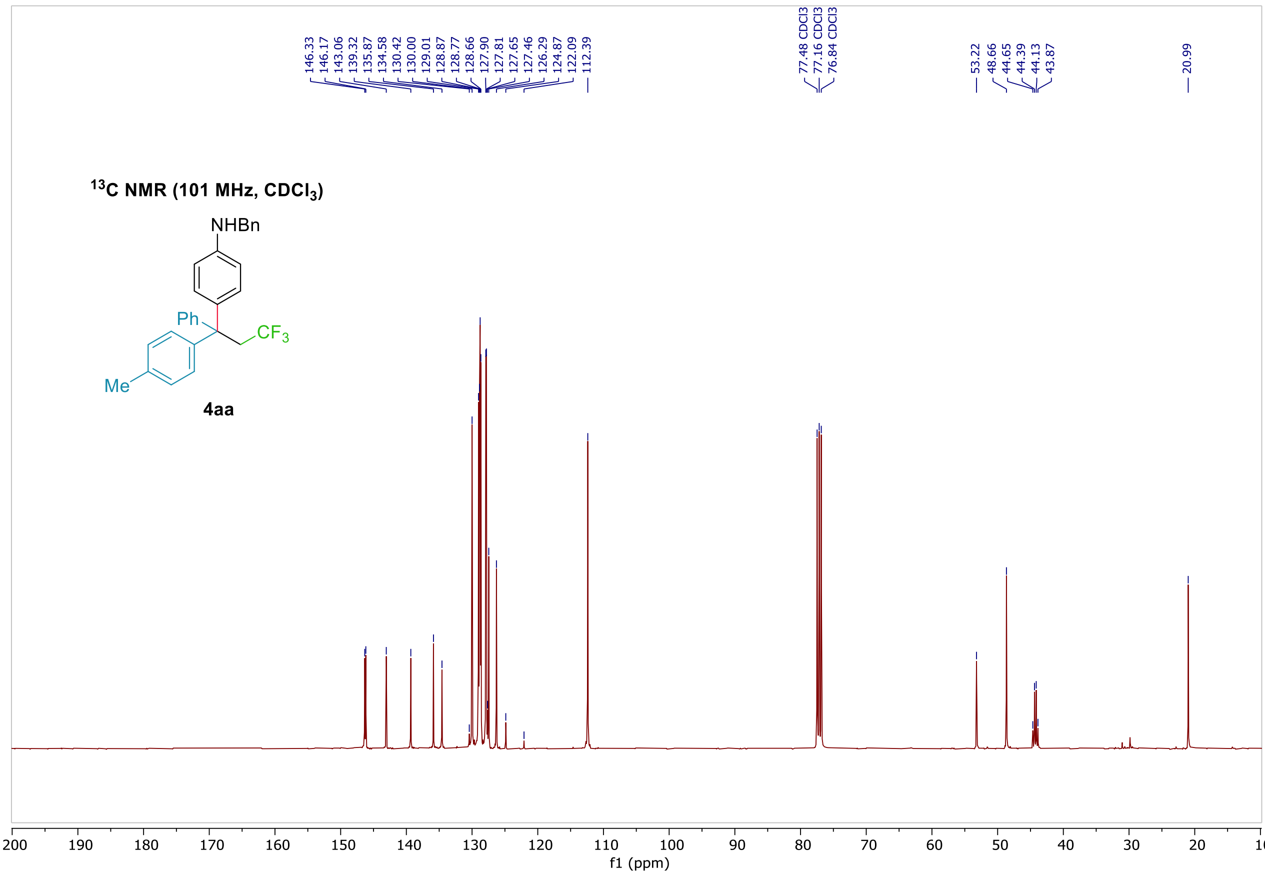
7.39
7.39
7.38
7.38
7.36
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.28
7.28
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.22
7.12
7.10
6.59
6.57
4.32
4.03
3.59
3.56
3.54
3.51
1H NMR (400 MHz, CDCl3)
NHBn
CF3
Ph
Ph
4z
14.97
2.05
2.00
2.00
0.92
2.00
f1 (ppm)



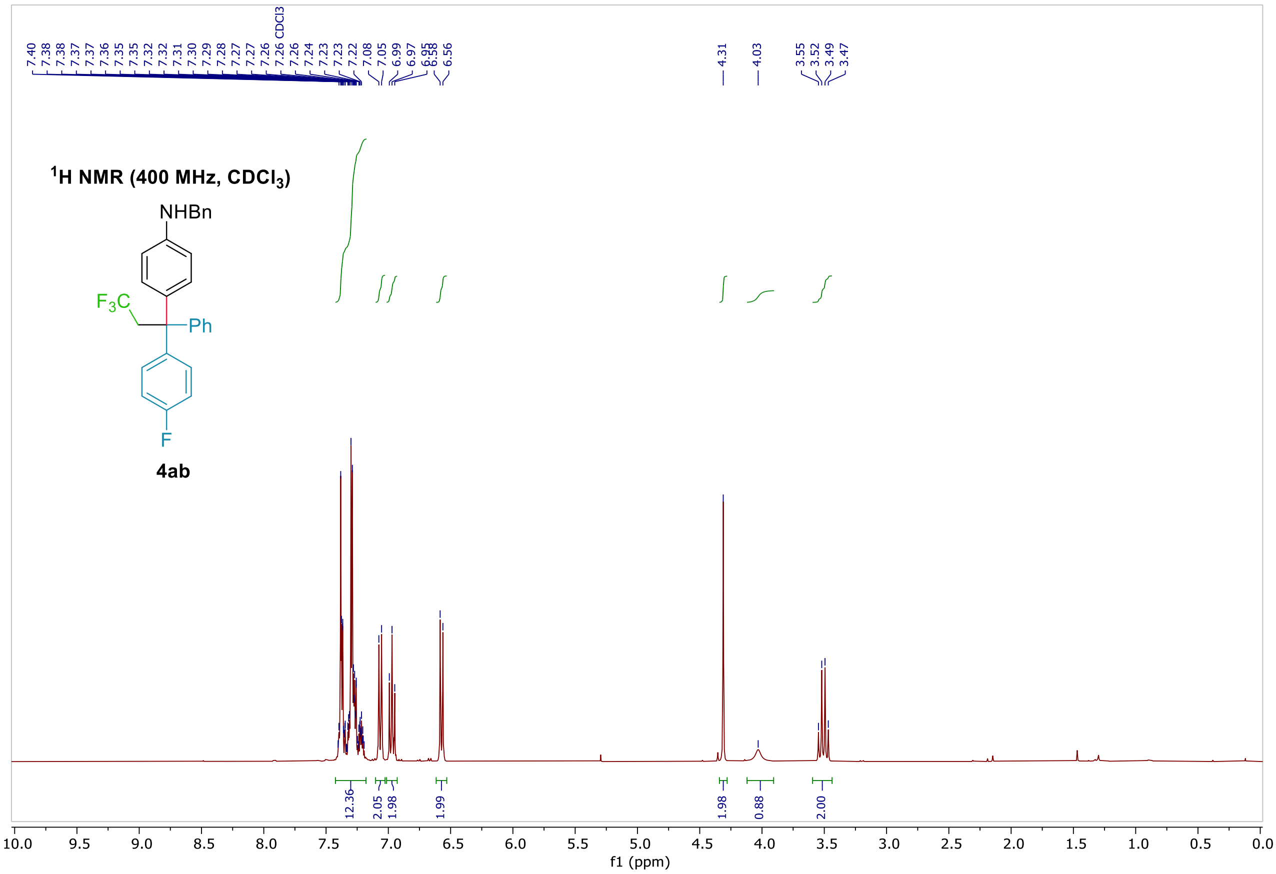
146.56
146.01
139.43
134.25
130.40
130.02
129.06
128.78
127.95
127.77
127.62
127.45
126.36
124.84
122.07
112.28
77.48 CDCl3
77.16 CDCl3
76.85 CDCl3
53.56
48.57
44.67
44.41
44.15
43.89
13C NMR (101 MHz, CDCl3)
NHBn
CF3
Ph
Ph
4z
f1 (ppm)



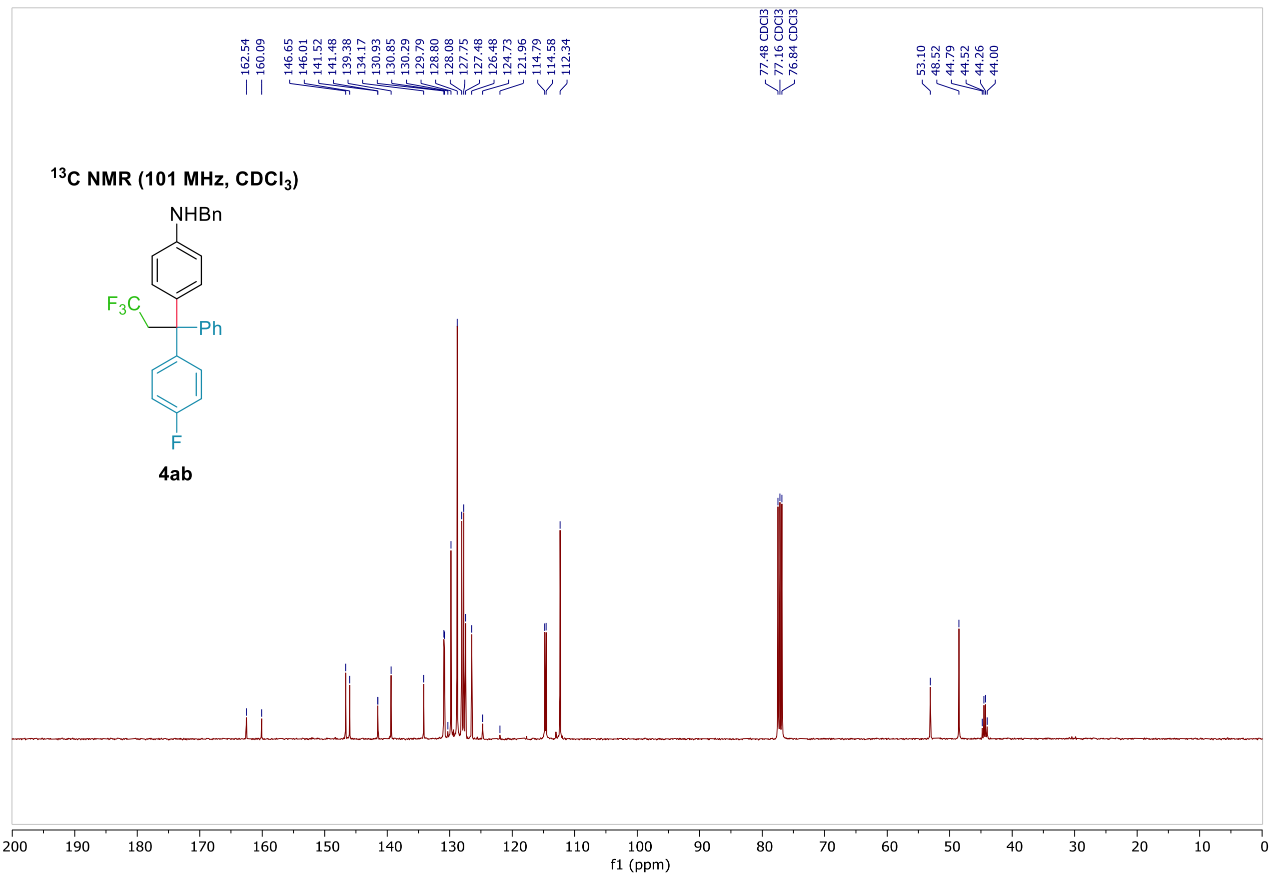
^{1}H NMR (400 MHz, $CDCl_3$)
4aa
f1 (ppm)



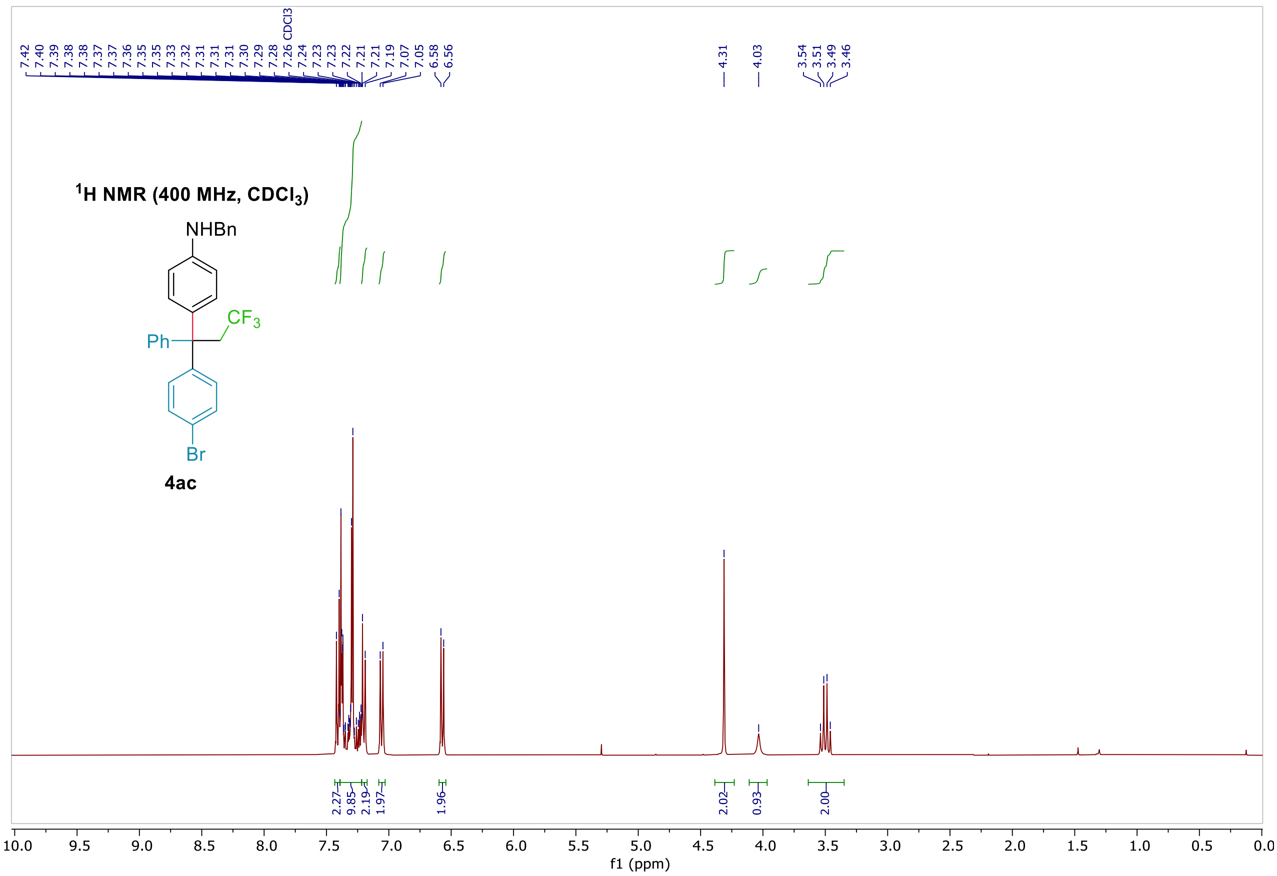
^{13}C NMR (101 MHz, $CDCl_3$)
4aa
f1 (ppm)

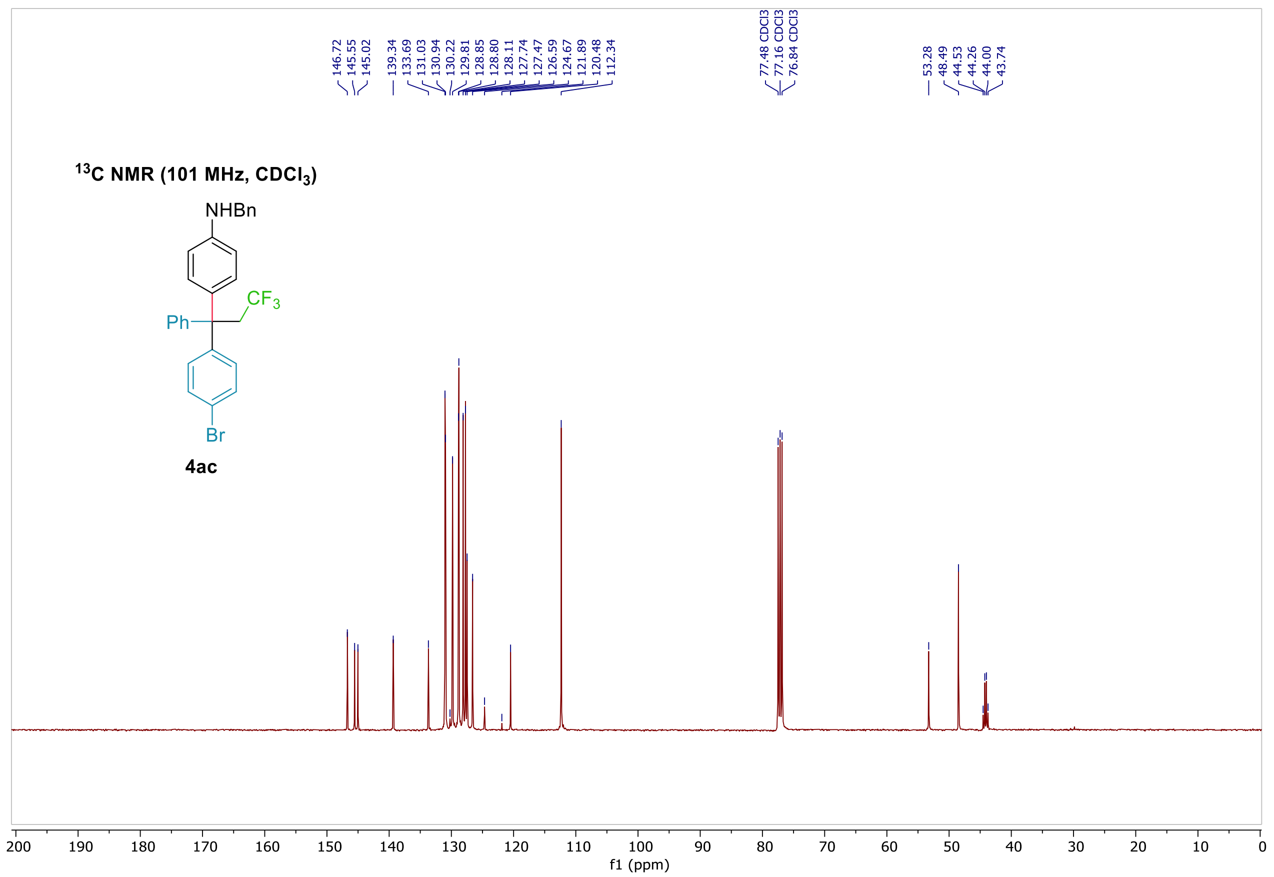


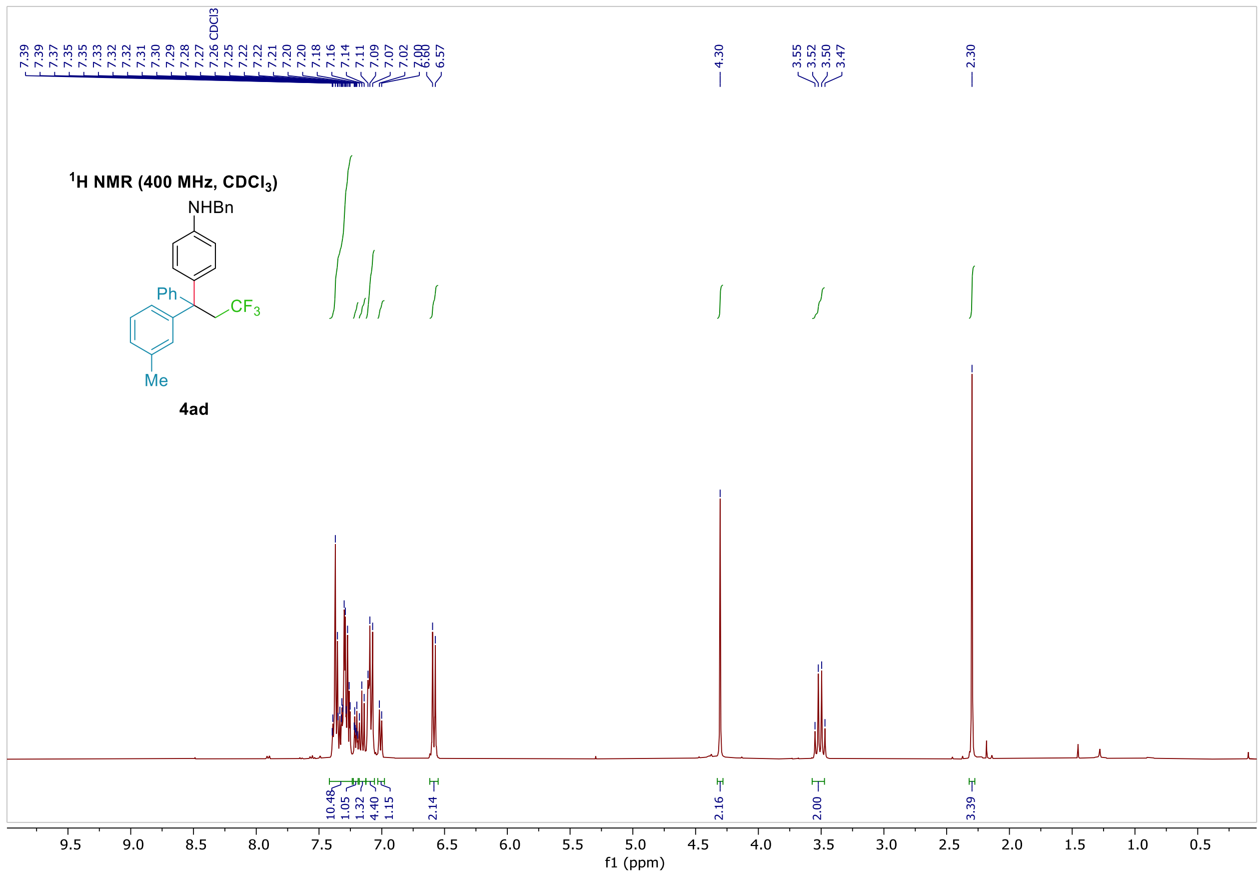
^{1}H NMR (400 MHz, CDCl$_3$)
NHBn
F$_3$C
Ph
F
4ab
f1 (ppm)



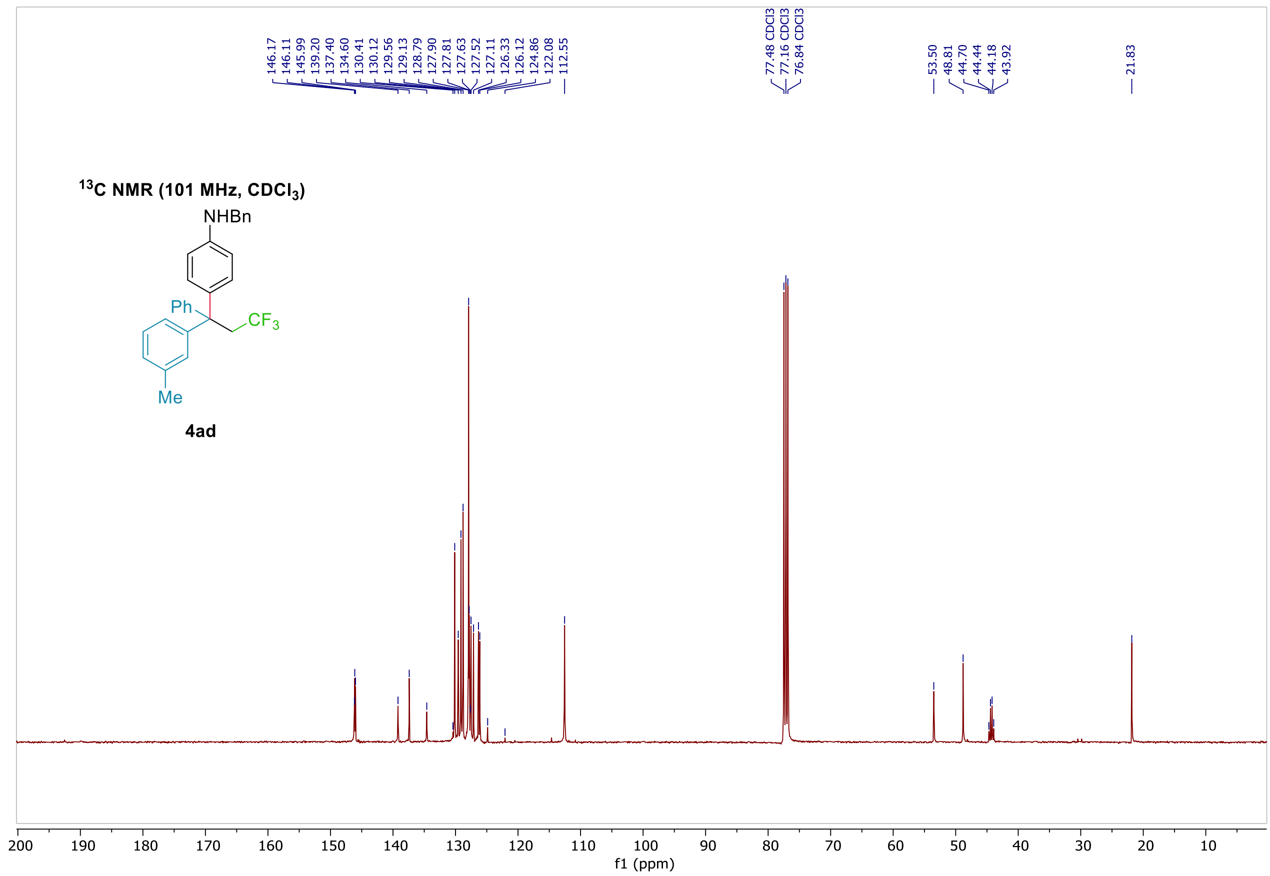
^{13}C NMR (101 MHz, CDCl$_3$)
NHBn
F$_3$C
Ph
F
4ab
f1 (ppm)


1H NMR (400 MHz, CDCl3)
NHBn
CF3
Ph
Br
4ac
7.42 7.40 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.33 7.32 7.31 7.31 7.31 7.30 7.29 7.28 7.26 CDCl3 7.24 7.23 7.23 7.22 7.21 7.21 7.19 7.07 7.05 6.58 6.56
4.31
4.03
3.54 3.51 3.49 3.46
2.27 9.85 2.19 1.97 1.96 2.02 0.93 2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

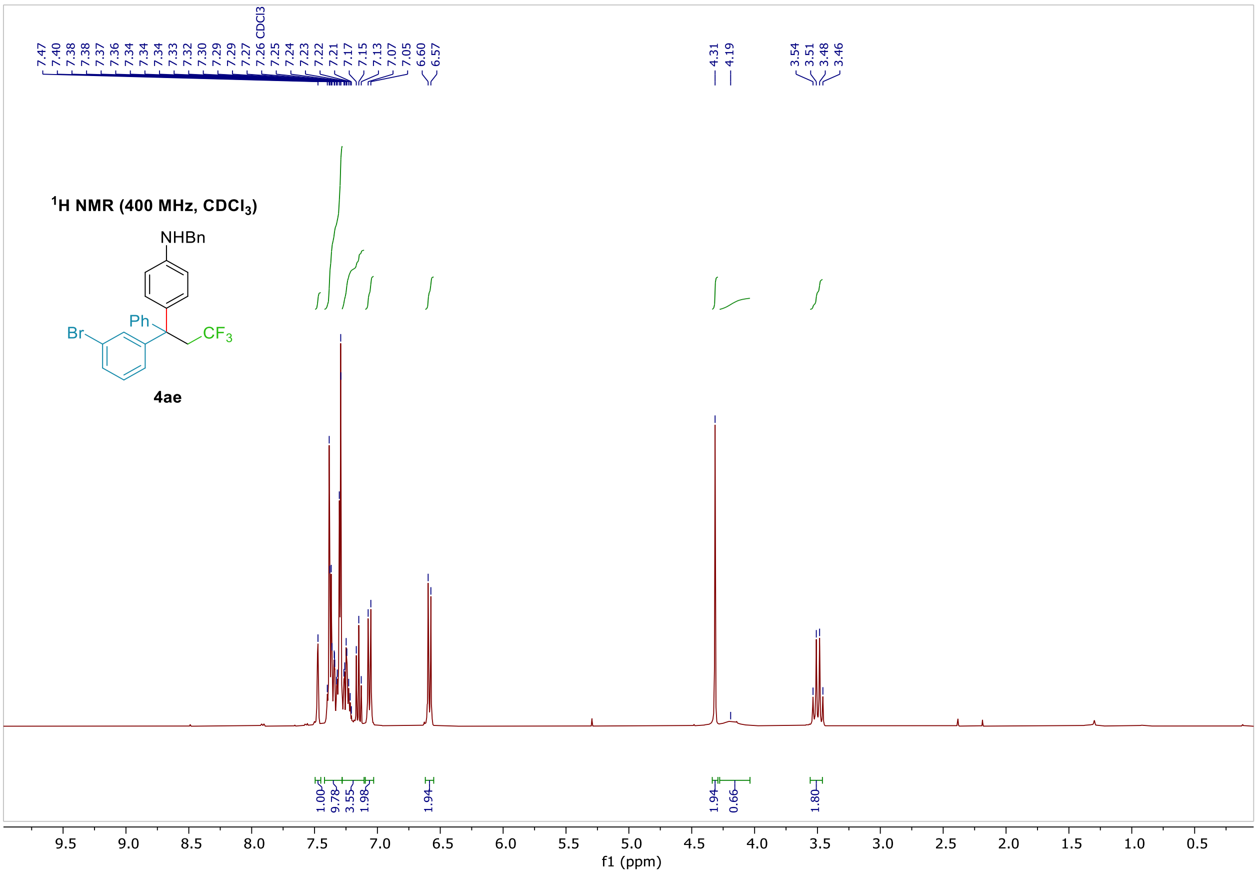

13C NMR (101 MHz, CDCl3)
NHBn
CF3
Ph
Br
4ac
146.72 145.55 145.02
139.34 133.69 131.03 130.94 130.22 129.81 128.85 128.80 128.11 127.74 127.47 126.59 124.67 121.89 120.48 112.34
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
53.28 48.49 44.53 44.26 44.00 43.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



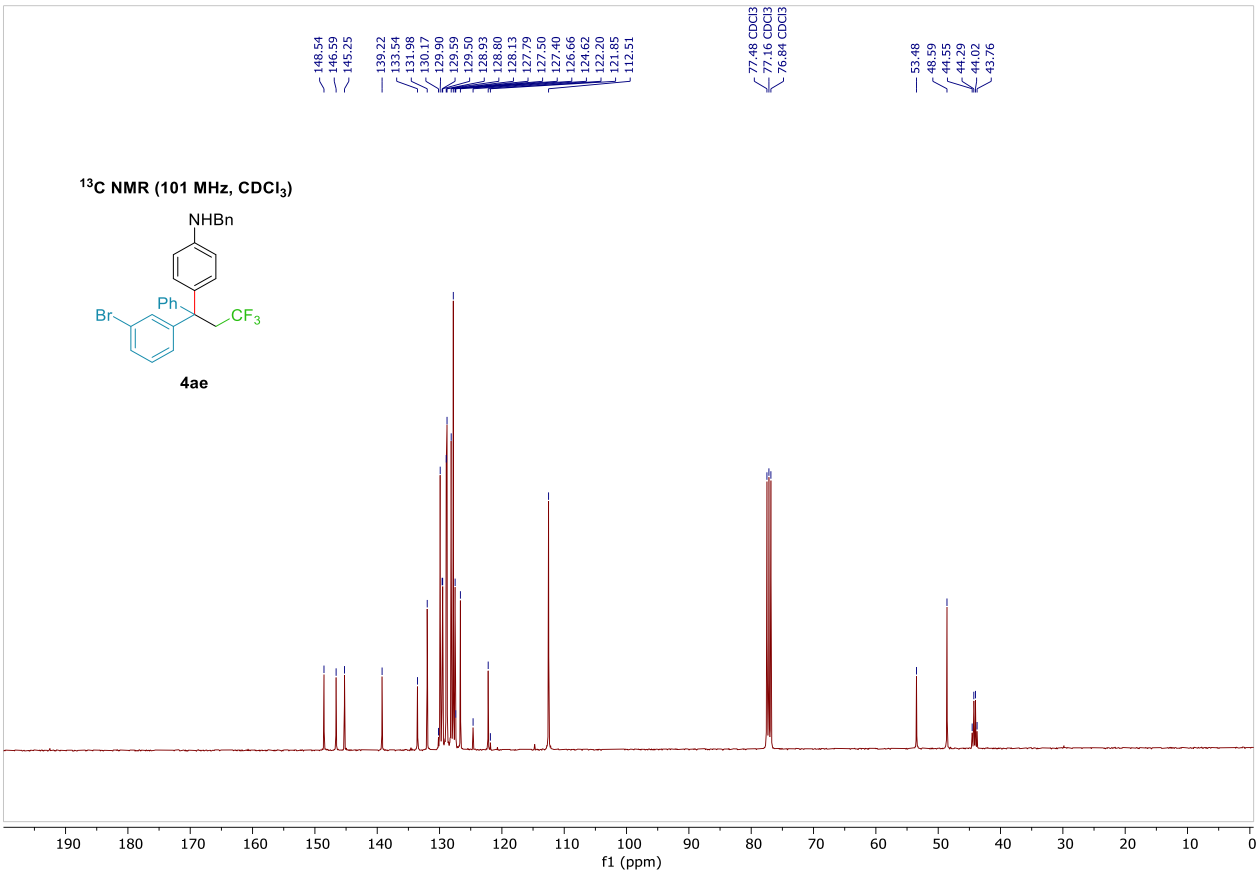
^{1}H NMR (400 MHz, CDCl$_3$)
NHBn
Ph
CF$_3$
Me
4ad
f1 (ppm)



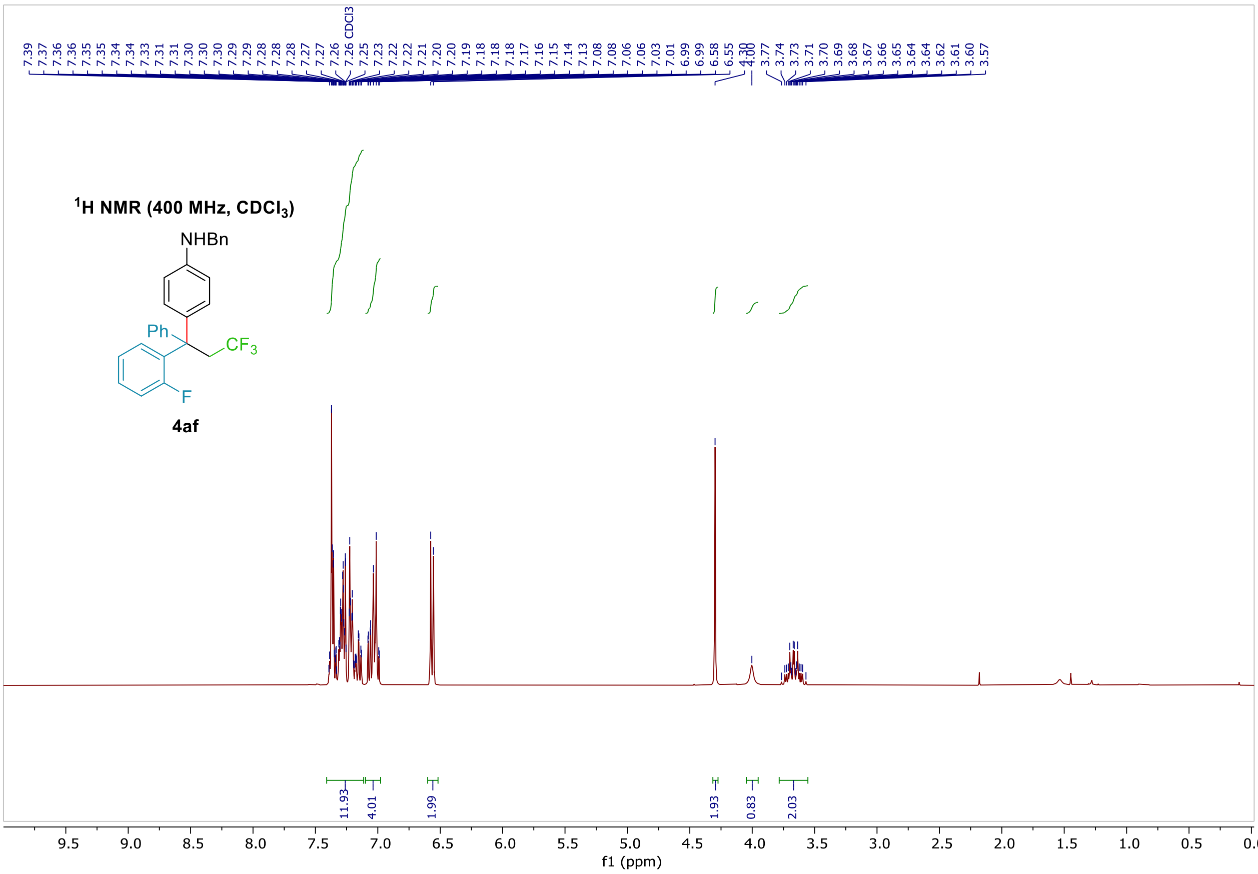
^{13}C NMR (101 MHz, CDCl$_3$)
NHBn
Ph
CF$_3$
Me
4ad
f1 (ppm)



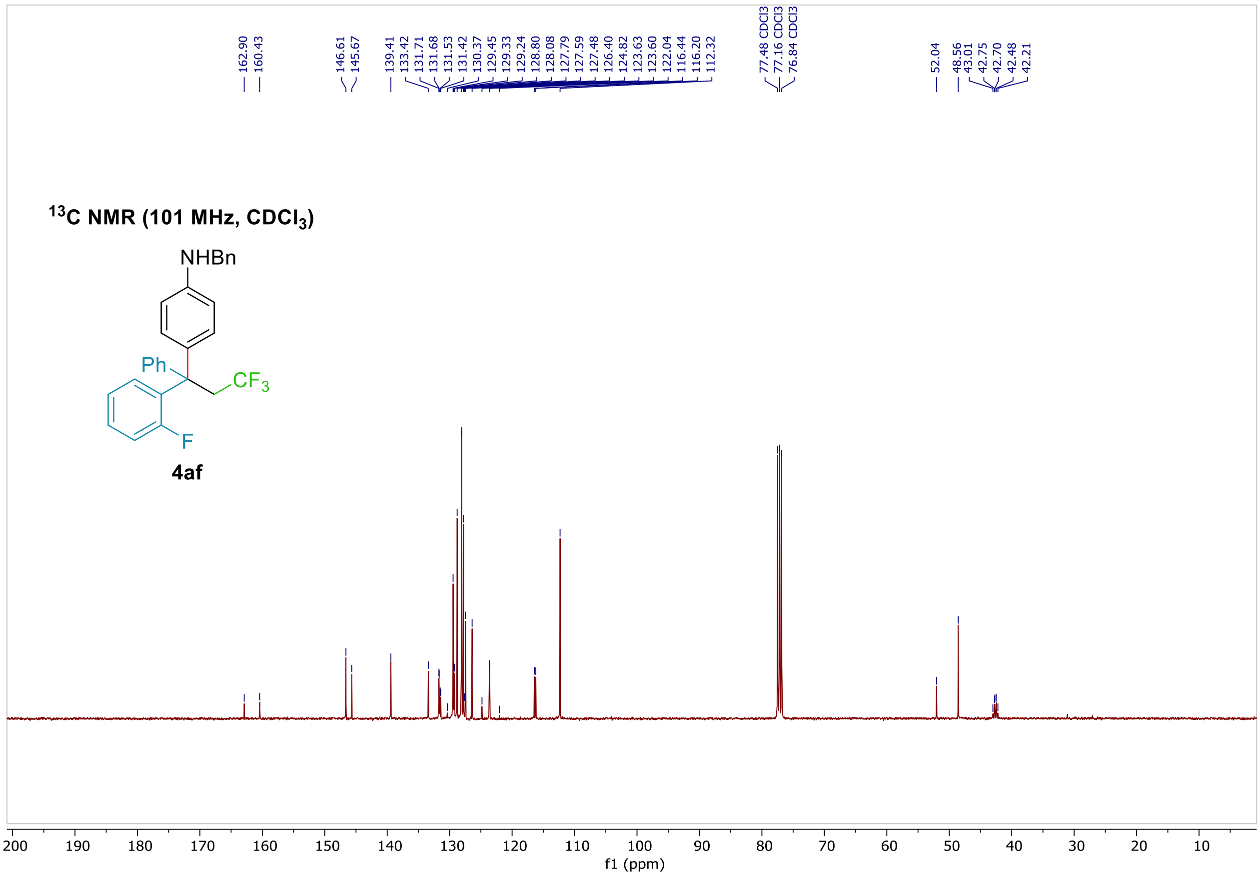
7.47
7.40
7.38
7.38
7.37
7.36
7.34
7.34
7.34
7.33
7.32
7.30
7.29
7.29
7.27
7.26 CDCl3
7.25
7.24
7.23
7.22
7.21
7.17
7.15
7.13
7.07
7.05
6.60
6.57
4.31
4.19
3.54
3.51
3.48
3.46
1H NMR (400 MHz, CDCl3)
NHBn
Br
Ph
CF3
4ae
1.00
9.78
3.55
1.98
1.94
1.94
0.66
1.80
f1 (ppm)



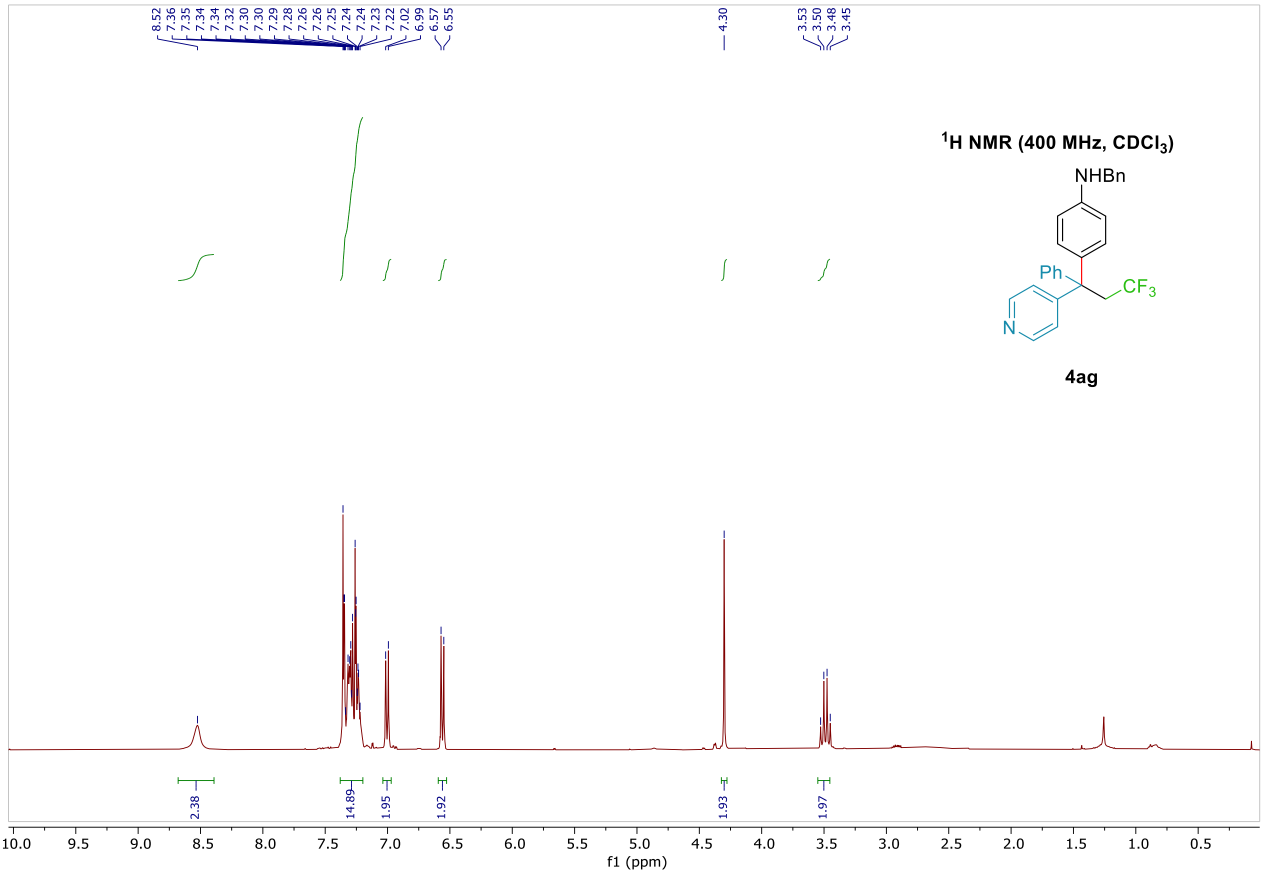
148.54
146.59
145.25
139.22
133.54
131.98
130.17
129.90
129.59
129.50
128.93
128.80
128.13
127.79
127.50
127.40
126.66
124.62
122.20
121.85
112.51
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
53.48
48.59
44.55
44.29
44.02
43.76
13C NMR (101 MHz, CDCl3)
NHBn
Br
Ph
CF3
4ae
f1 (ppm)



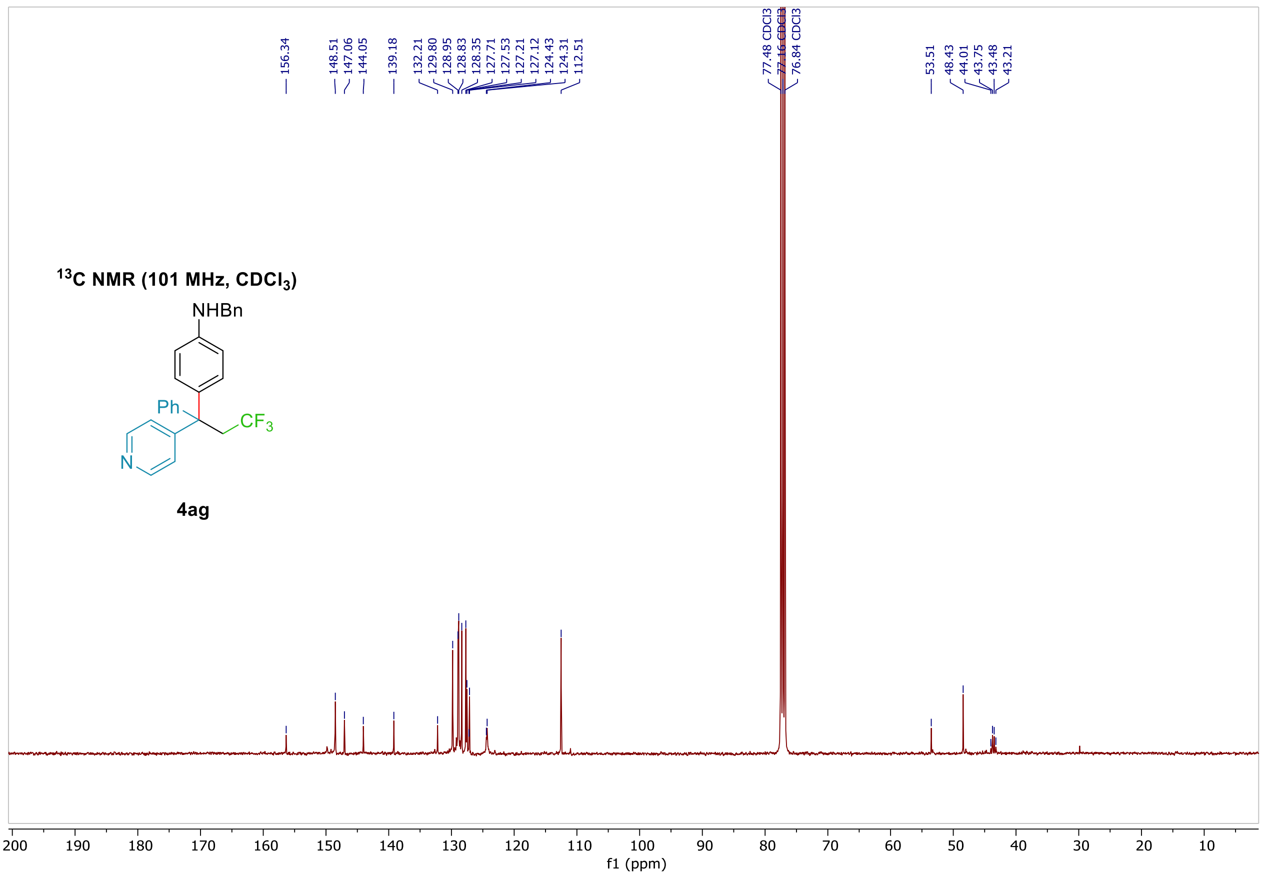
1H NMR (400 MHz, CDCl3)
NHBn
Ph
CF3
F
4af
f1 (ppm)



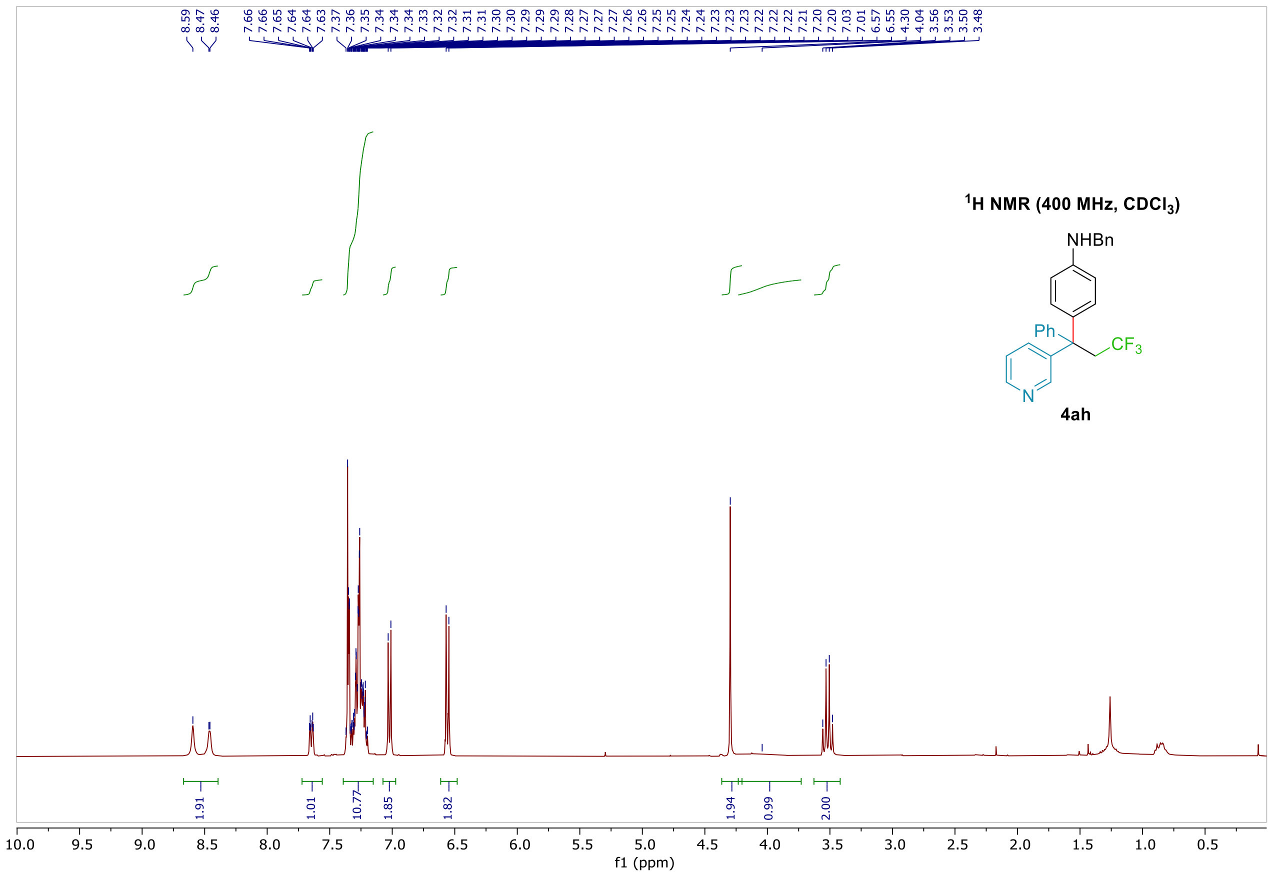
13C NMR (101 MHz, CDCl3)
NHBn
Ph
CF3
F
4af
f1 (ppm)

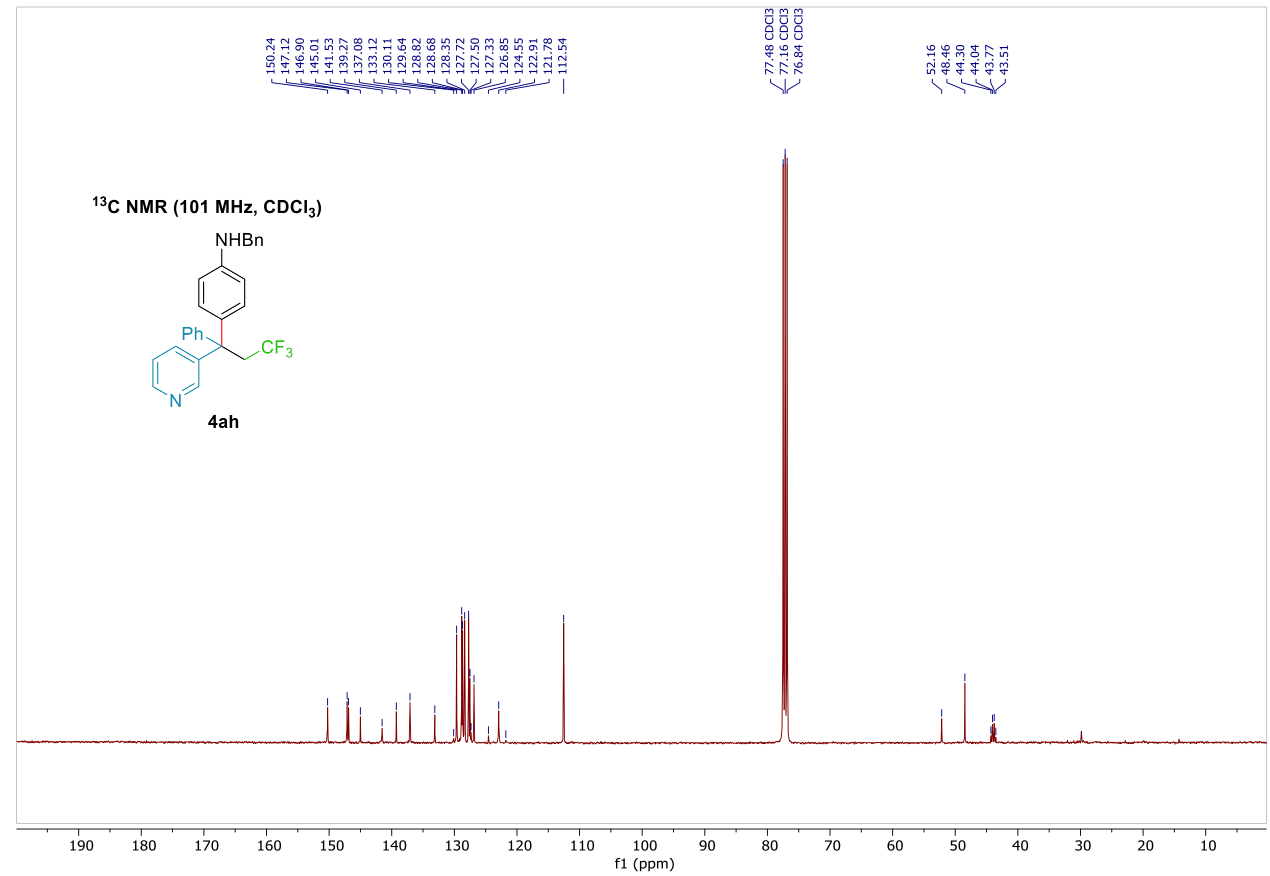


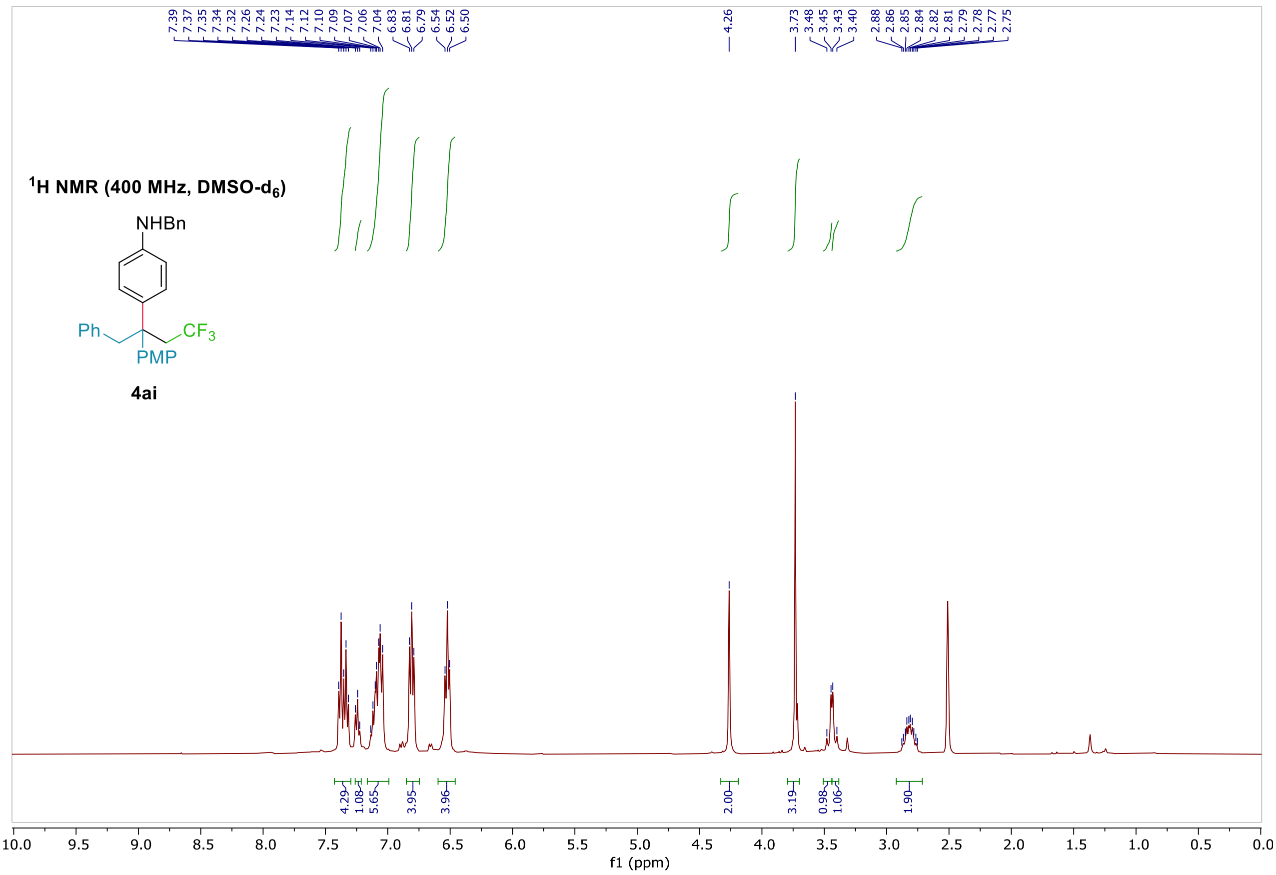
8.52
7.36
7.35
7.34
7.34
7.32
7.30
7.29
7.28
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.02
6.99
6.57
6.55
4.30
3.53
3.50
3.48
3.45
1H NMR (400 MHz, CDCl3)
NHBn
Ph
CF3
N
4ag
2.38
14.89
1.95
1.92
1.93
1.97
f1 (ppm)



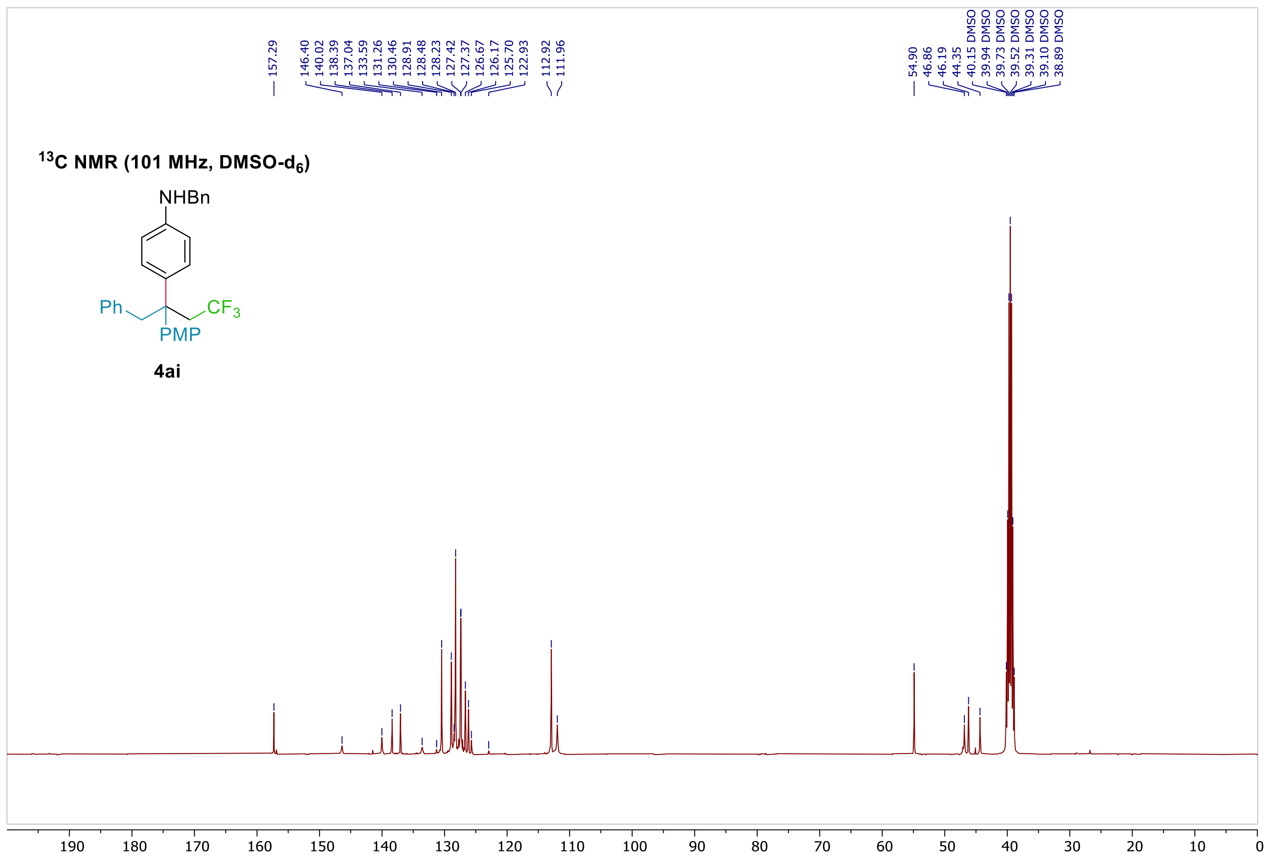
156.34
148.51
147.06
144.05
139.18
132.21
129.80
128.95
128.83
128.35
127.71
127.53
127.21
127.12
124.43
124.31
112.51
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
53.51
48.43
44.01
43.75
43.48
43.21
13C NMR (101 MHz, CDCl3)
NHBn
Ph
CF3
N
4ag
f1 (ppm)


8.59 8.47 8.46 7.66 7.66 7.65 7.64 7.64 7.63 7.37 7.36 7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.27 7.27 7.27 7.26 7.25 7.25 7.24 7.24 7.23 7.23 7.23 7.22 7.22 7.22 7.21 7.20 7.20 7.03 7.01 6.57 6.55 4.30 4.04 3.56 3.53 3.50 3.48
1H NMR (400 MHz, CDCl3)
NHBn
Ph
CF3
N
4ah
1.91
1.01
10.77
1.85
1.82
1.94
0.99
2.00
f1 (ppm)

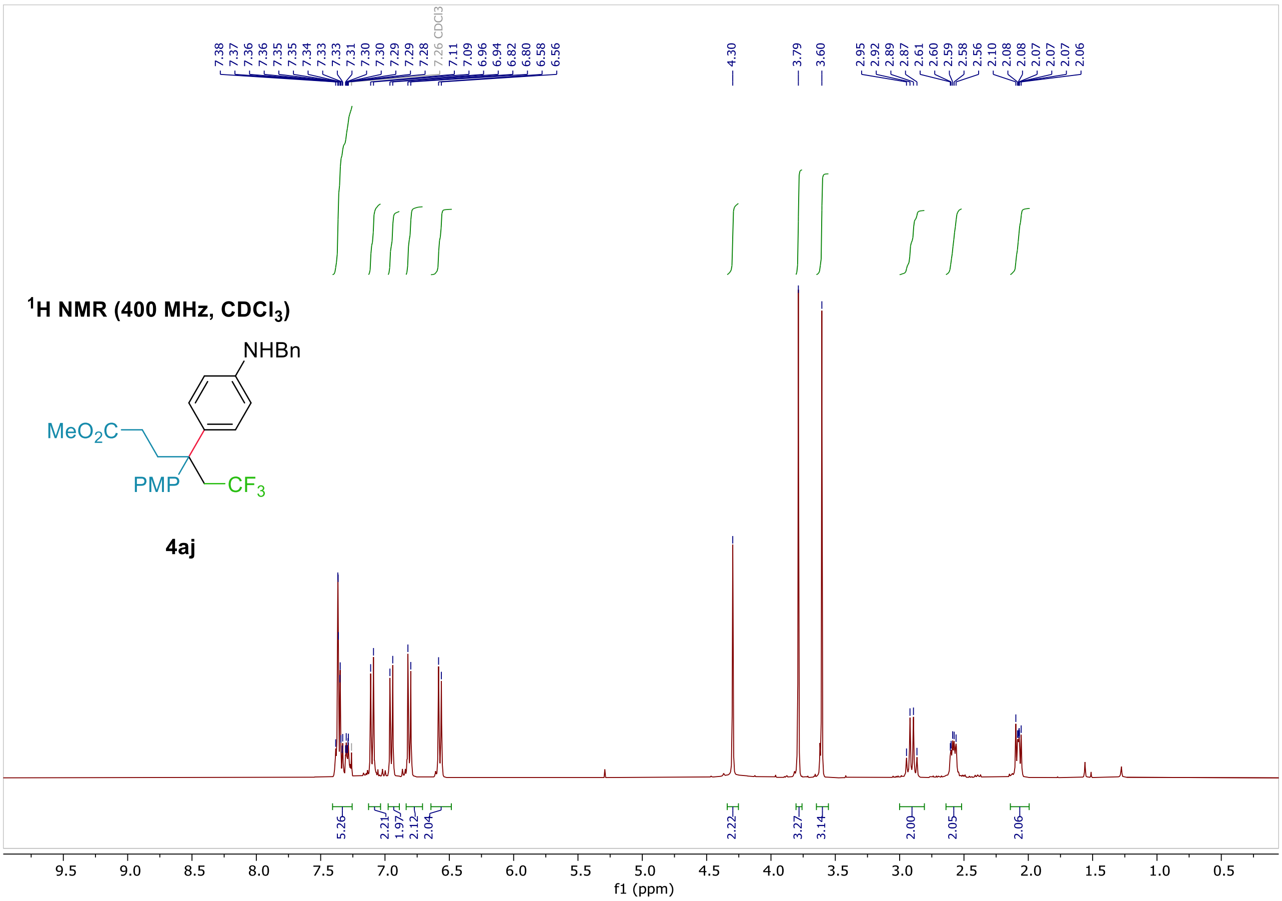

150.24 147.12 146.90 145.01 141.53 139.27 137.08 133.12 130.11 129.64 128.82 128.68 128.35 127.72 127.50 127.33 126.85 124.55 122.91 121.78 112.54
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
52.16 48.46 44.30 44.04 43.77 43.51
13C NMR (101 MHz, CDCl3)
NHBn
Ph
CF3
N
4ah
f1 (ppm)



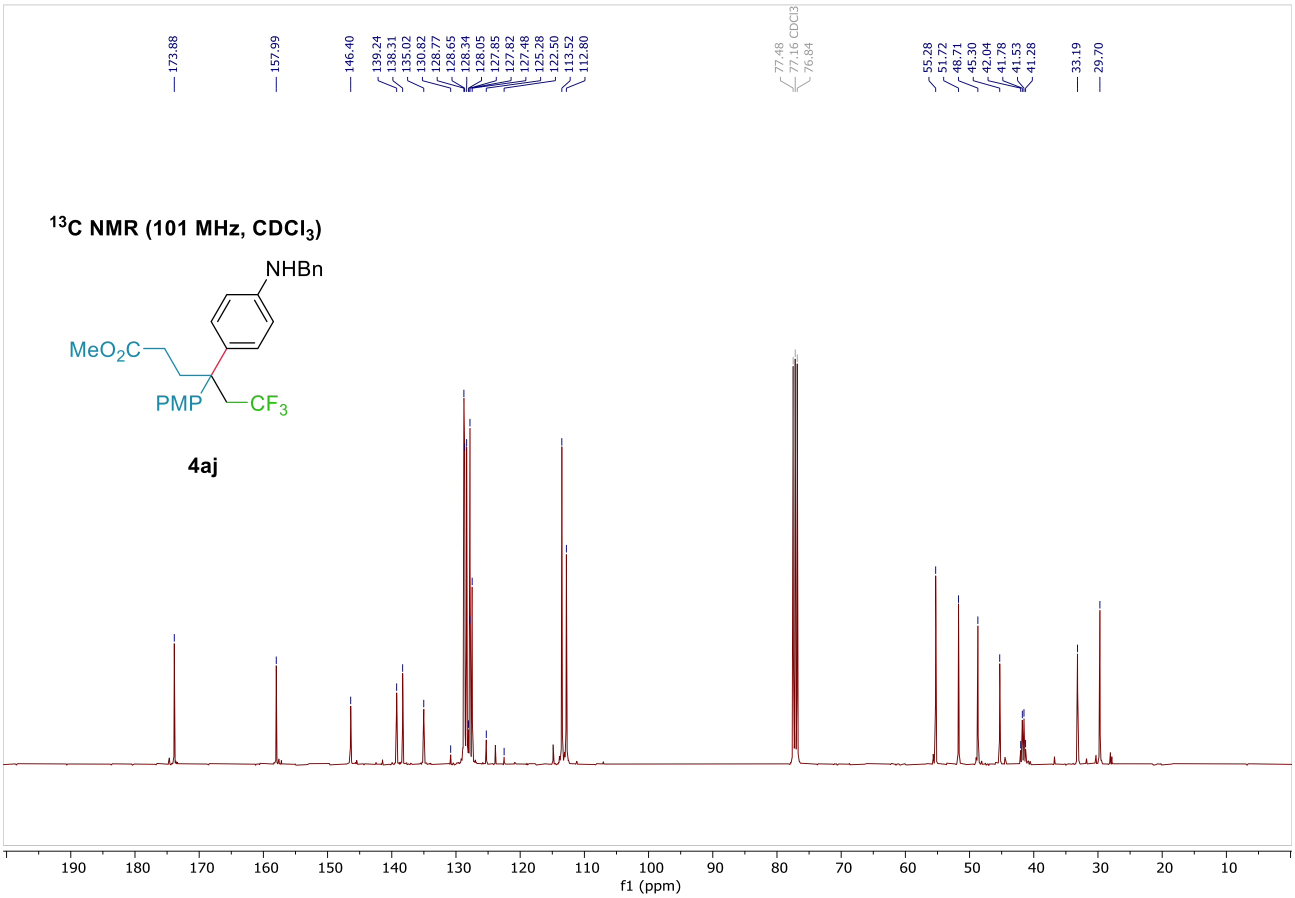
7.39 7.37 7.35 7.34 7.32 7.26 7.24 7.23 7.14 7.12 7.10 7.09 7.07 7.06 7.04 6.83 6.81 6.79 6.54 6.52 6.50
4.26
3.73 3.48 3.45 3.43 3.40
2.88 2.86 2.85 2.84 2.82 2.81 2.79 2.78 2.77 2.75
1H NMR (400 MHz, DMSO-d6)
NHBn
Ph
CF3
PMP
4ai
4.29 1.08 5.65 3.95 3.96 2.00 3.19 0.98 1.06 1.90
f1 (ppm)



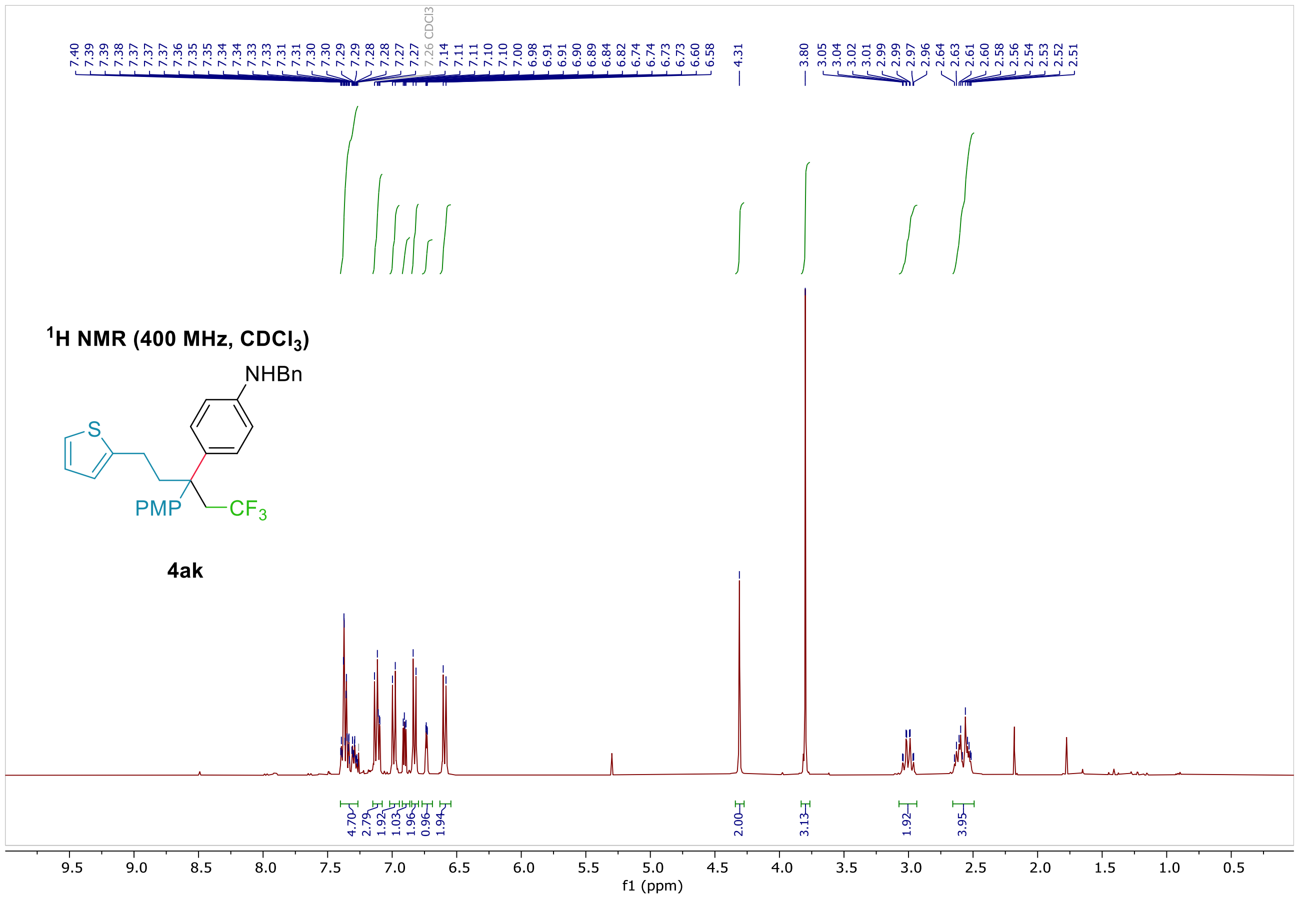
157.29
146.40 140.02 138.39 137.04 133.59 131.26 130.46 128.91 128.48 128.23 127.42 127.37 126.67 126.17 125.70 122.93
112.92 111.96
54.90 46.86 46.19 44.35 40.15 DMSO 39.94 DMSO 39.73 DMSO 39.52 DMSO 39.31 DMSO 39.10 DMSO 38.89 DMSO
13C NMR (101 MHz, DMSO-d6)
NHBn
Ph
CF3
PMP
4ai
f1 (ppm)

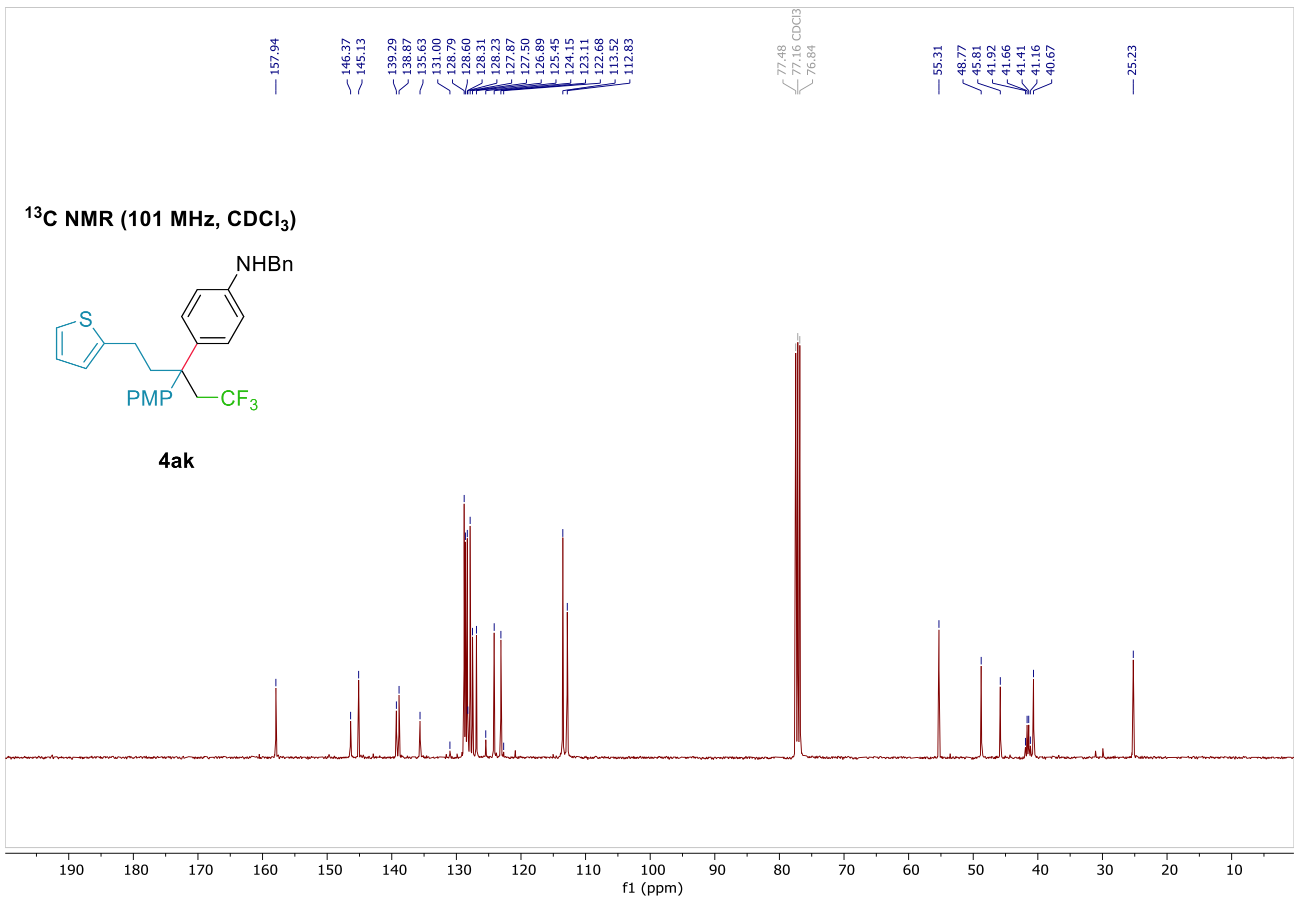


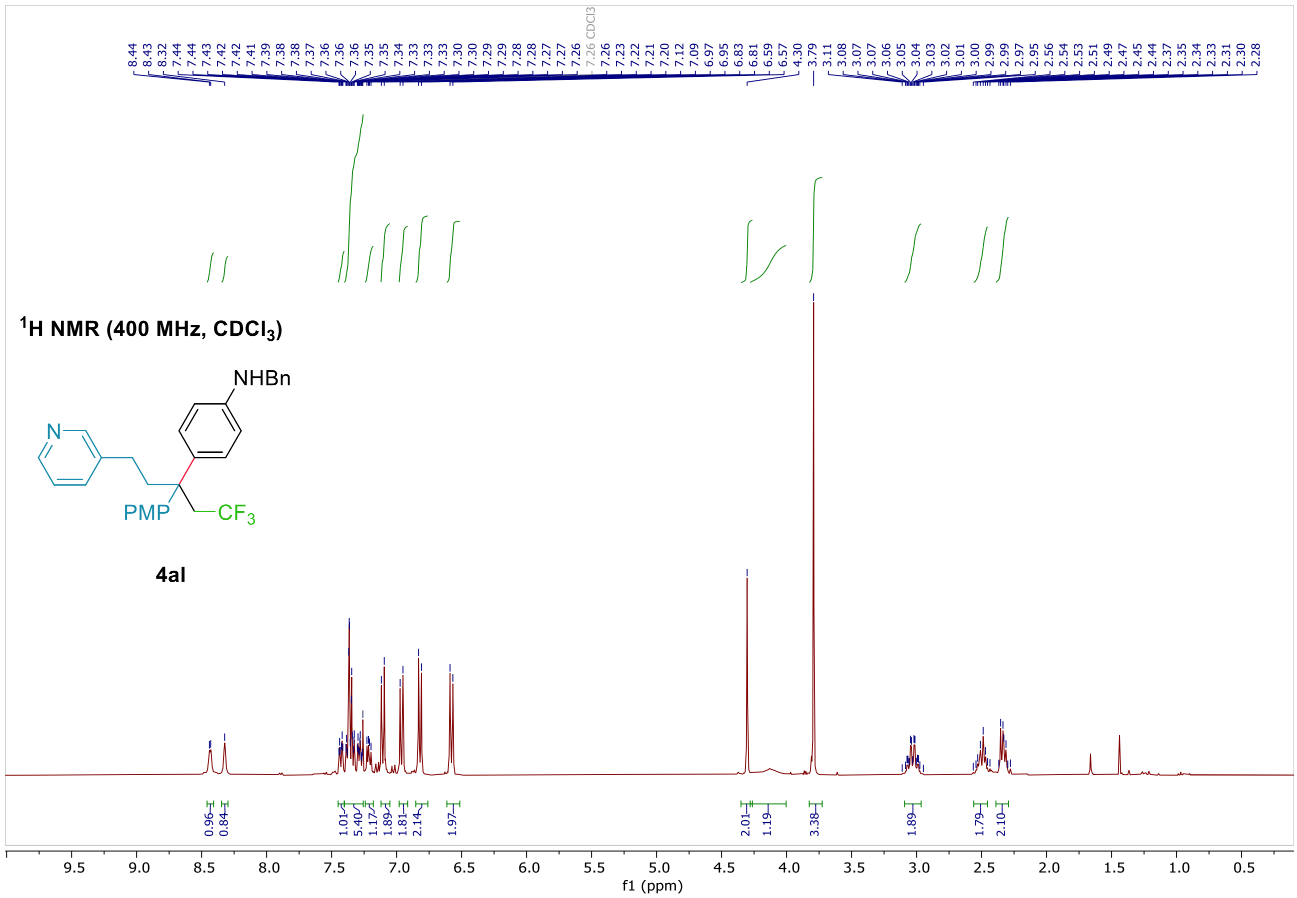
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.31
7.30
7.30
7.29
7.29
7.28
7.26 CDCl3
7.11
7.09
6.96
6.94
6.82
6.80
6.58
6.56
4.30
3.79
3.60
2.95
2.92
2.89
2.87
2.61
2.60
2.59
2.58
2.56
2.10
2.08
2.08
2.07
2.07
2.06
1H NMR (400 MHz, CDCl3)
NHBn
MeO2C
PMP
CF3
4aj
5.26
2.21
1.97
2.12
2.04
2.22
3.27
3.14
2.00
2.05
2.06
f1 (ppm)

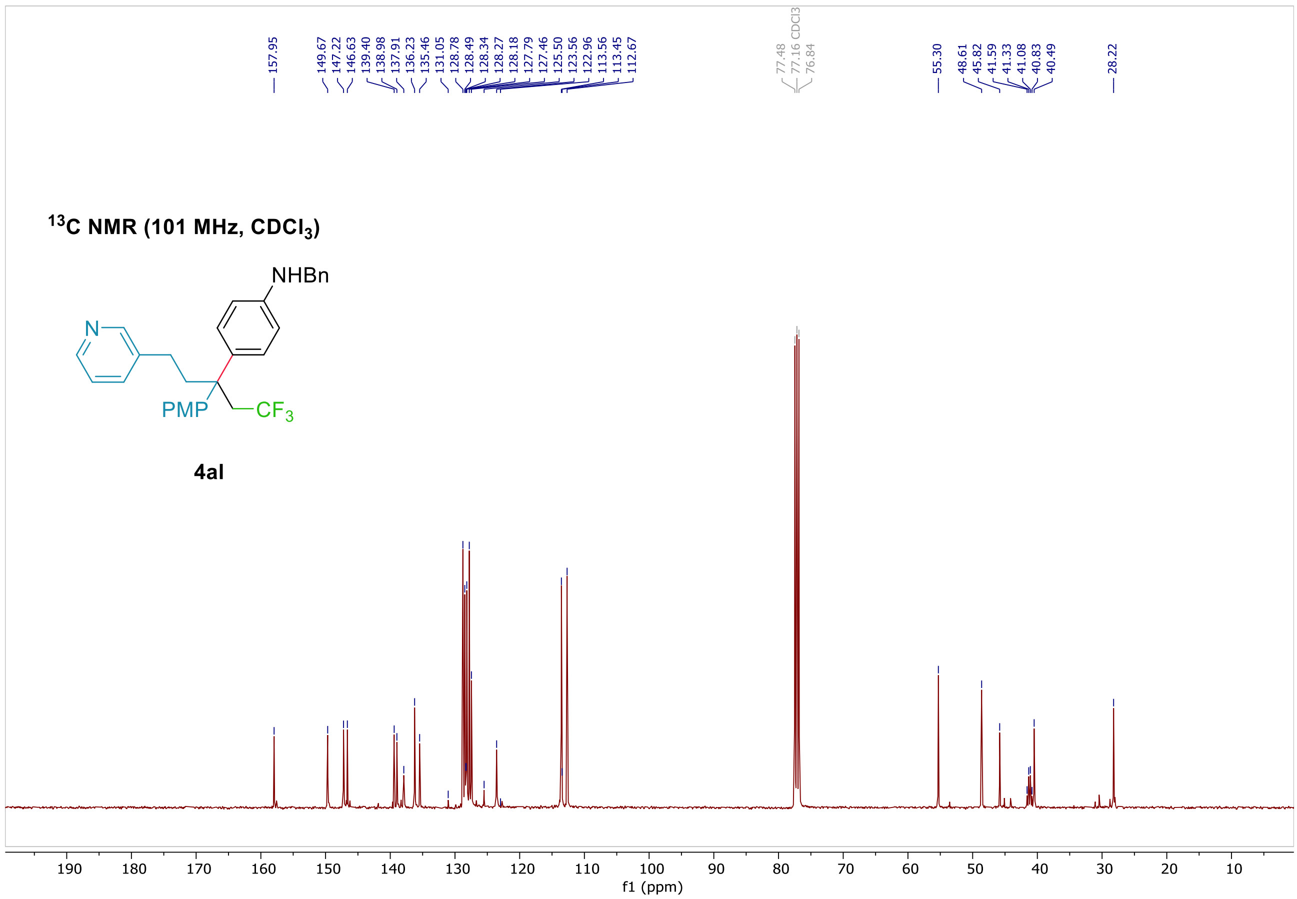


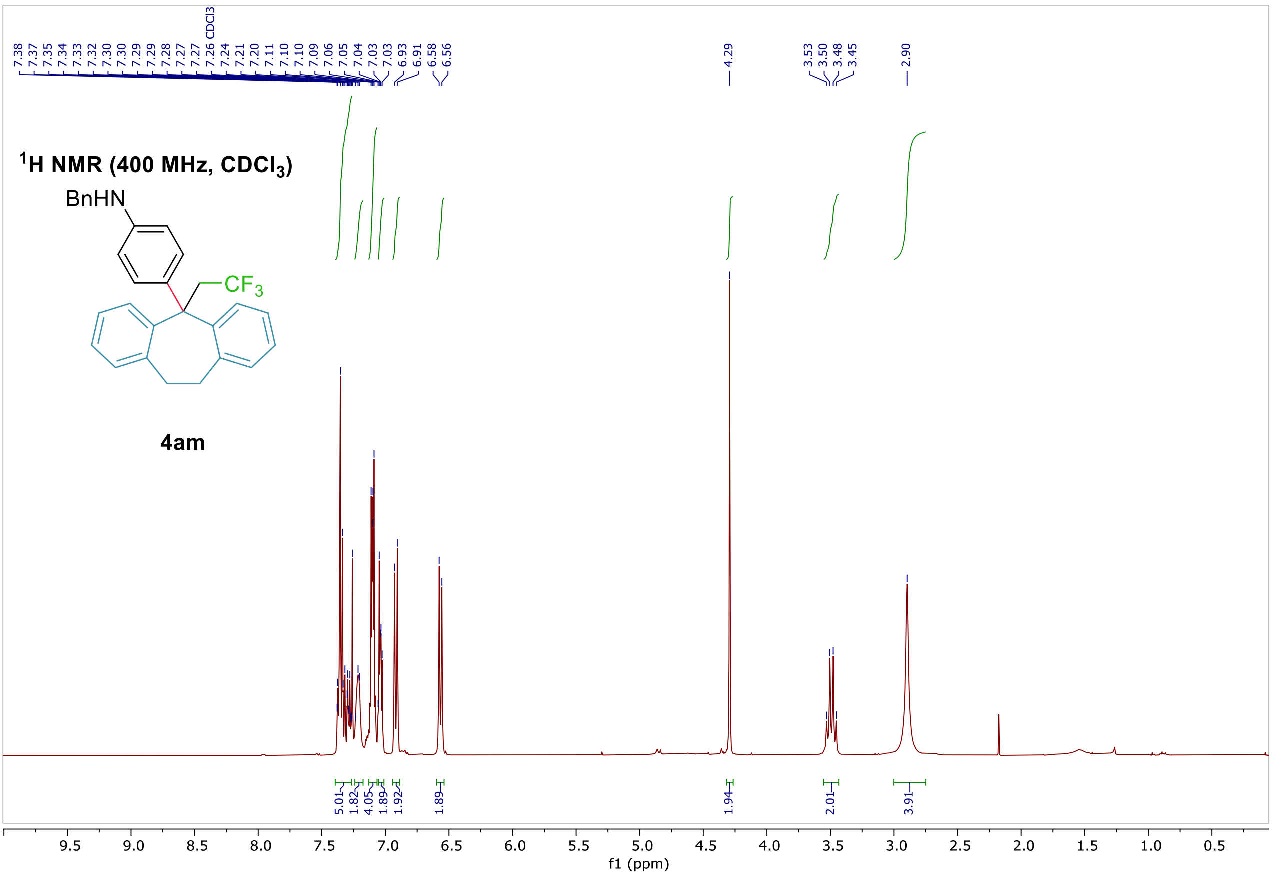
173.88
157.99
146.40
139.24
138.31
135.02
130.82
128.77
128.65
128.34
128.05
127.85
127.82
127.48
125.28
122.50
113.52
112.80
77.48
77.16 CDCl3
76.84
55.28
51.72
48.71
45.30
42.04
41.78
41.53
41.28
33.19
29.70
13C NMR (101 MHz, CDCl3)
NHBn
MeO2C
PMP
CF3
4aj
f1 (ppm)


^{1}H NMR (400 MHz, CDCl$_3$)
NHBn
S
PMP
CF$_3$
4ak
f1 (ppm)

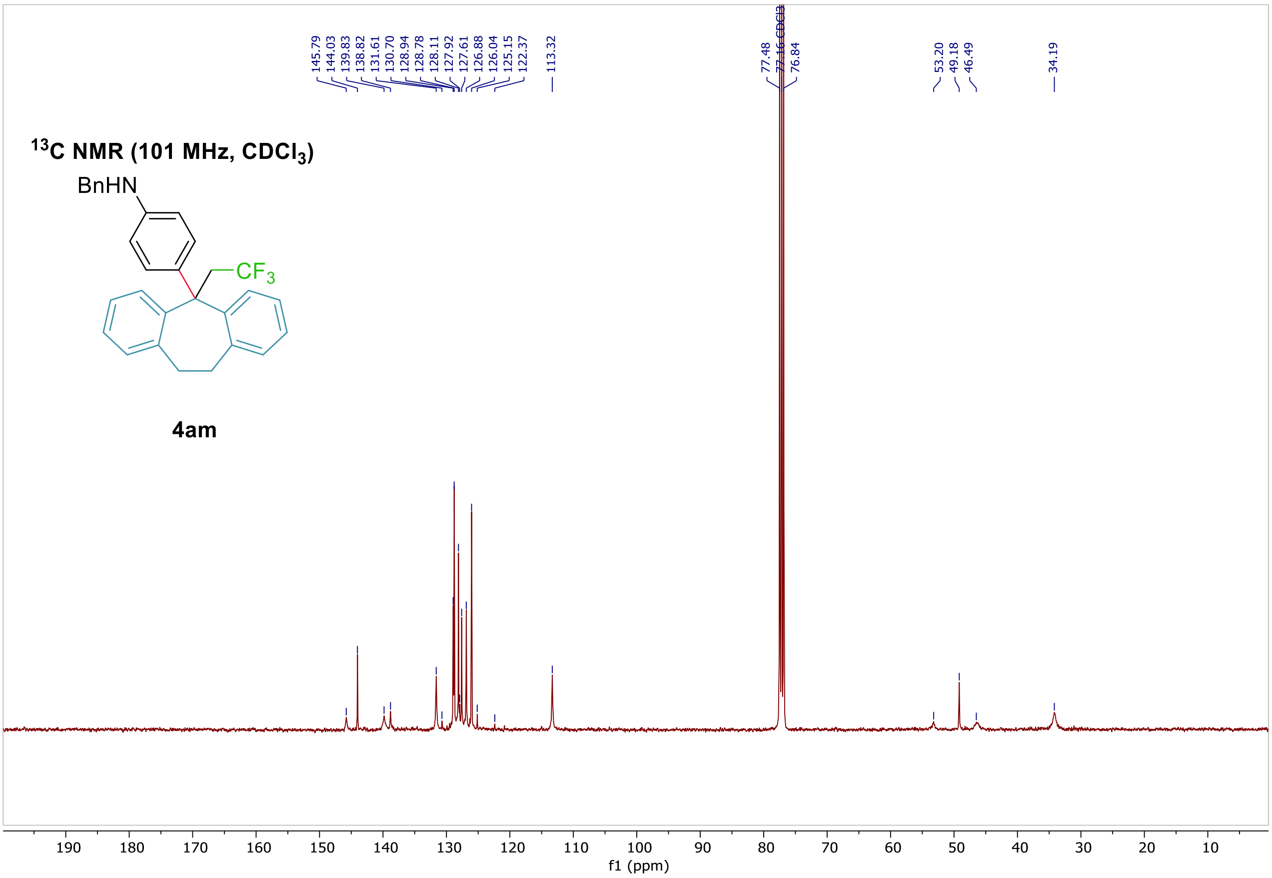

^{13}C NMR (101 MHz, CDCl$_3$)
NHBn
S
PMP
CF$_3$
4ak
f1 (ppm)


1H NMR (400 MHz, CDCl3)
NHBn
N
PMP
CF3
4al
f1 (ppm)

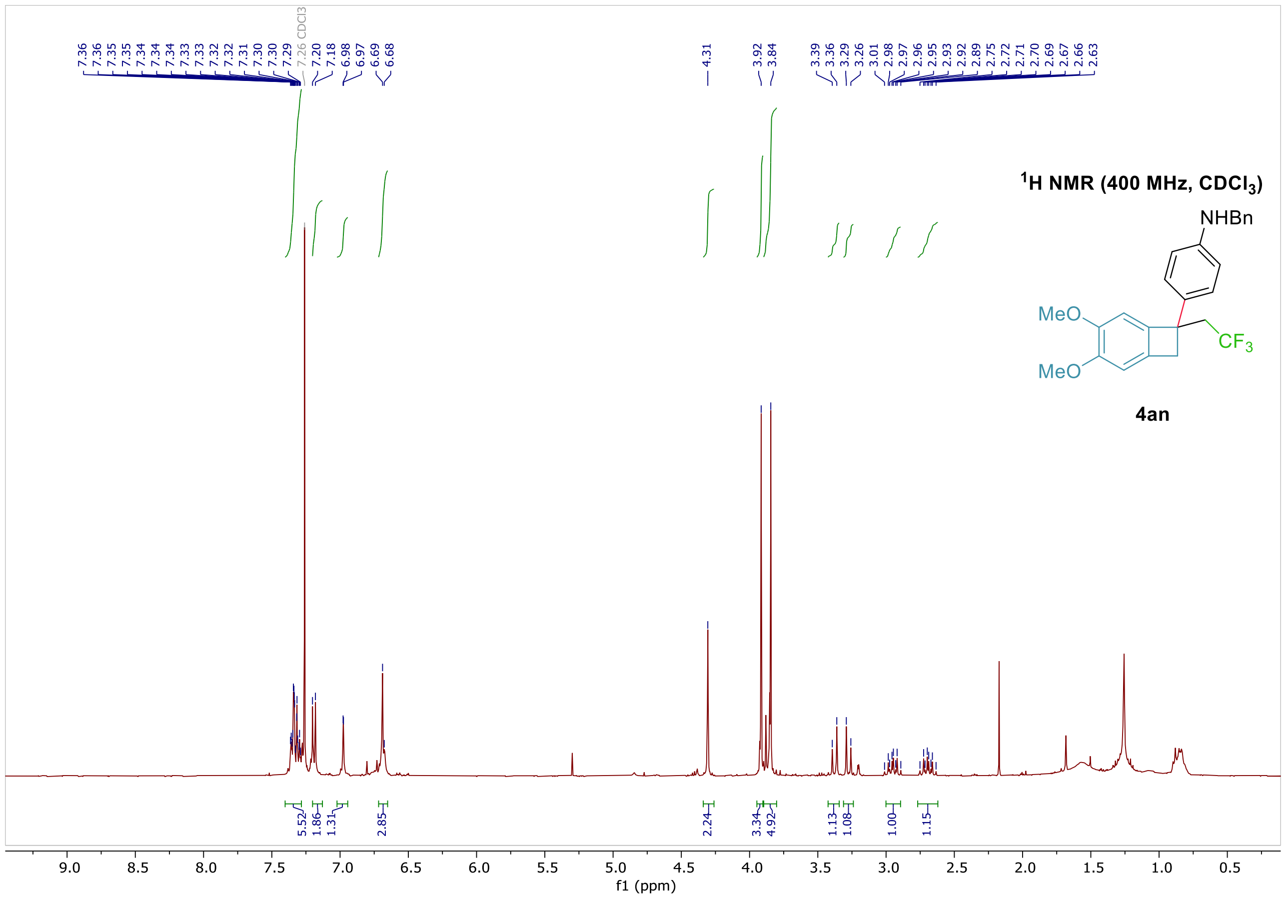

13C NMR (101 MHz, CDCl3)
NHBn
N
PMP
CF3
4al
f1 (ppm)



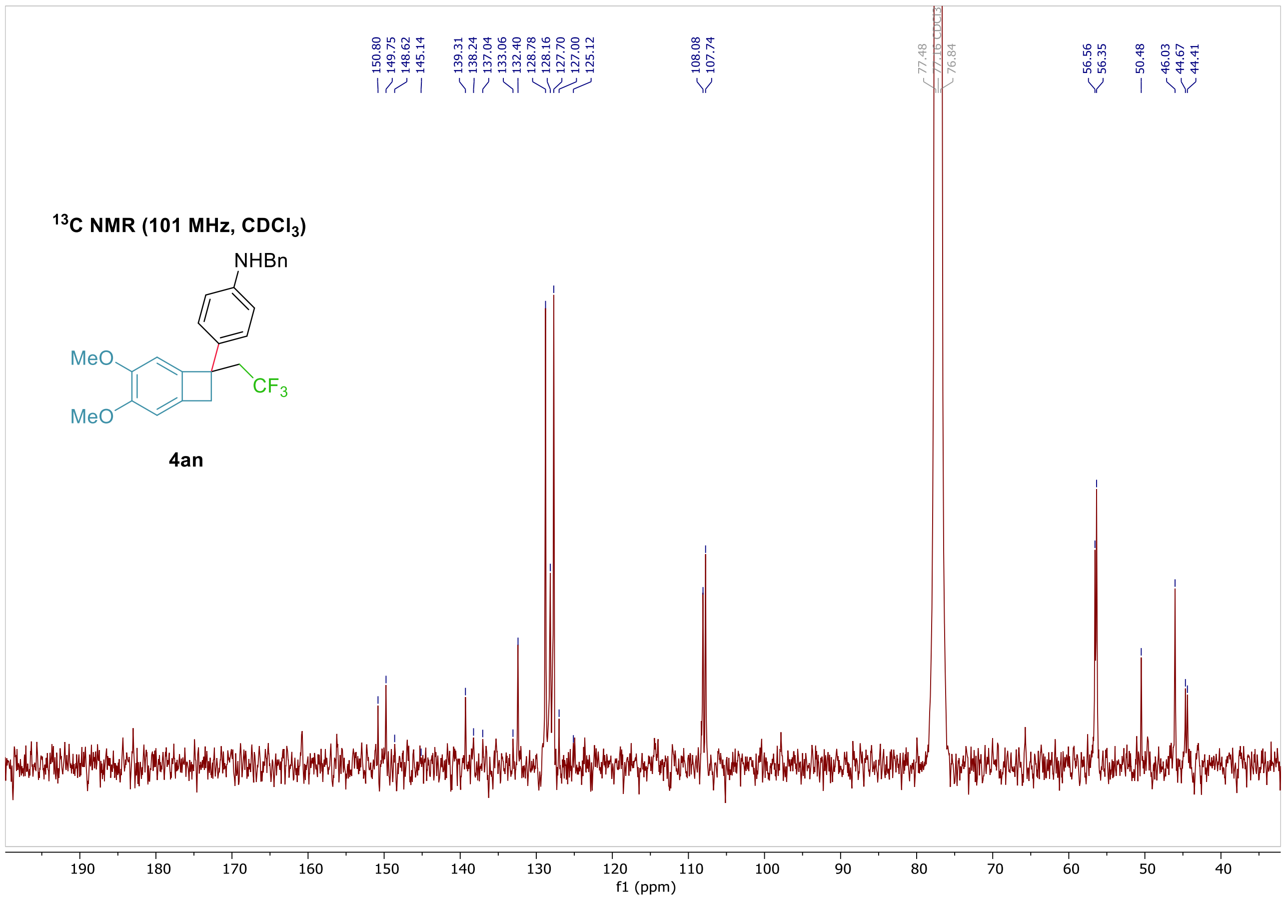
7.38 7.37 7.35 7.34 7.33 7.32 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 CDCl3 7.24 7.21 7.20 7.11 7.10 7.10 7.09 7.06 7.05 7.04 7.03 7.03 6.93 6.91 6.58 6.56
4.29
3.53 3.50 3.48 3.45
2.90
1H NMR (400 MHz, CDCl3)
BnHN
CF3
4am
5.01 1.82 4.05 1.89 1.92 1.89 1.94 2.01 3.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



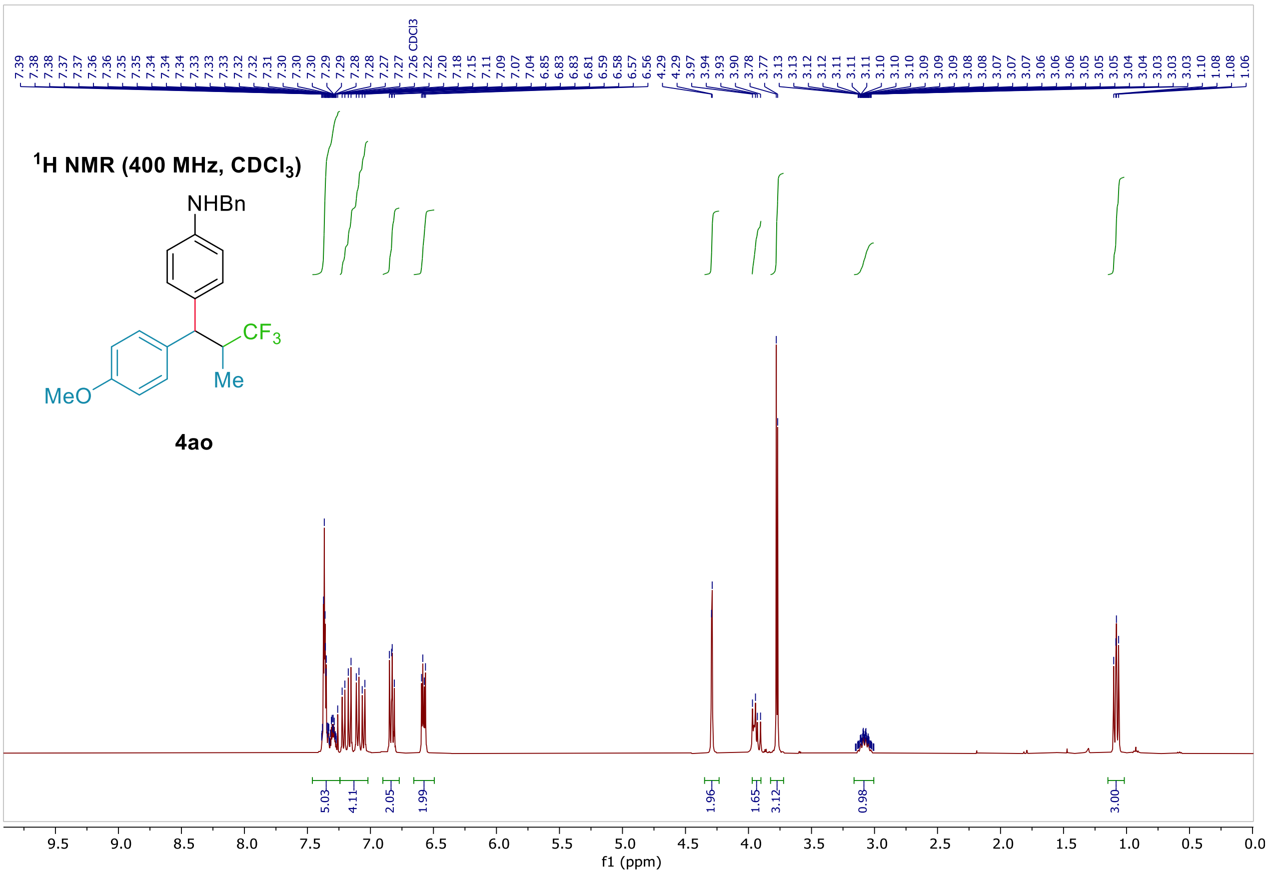
145.79 144.03 139.83 138.82 131.61 130.70 128.94 128.78 128.11 127.92 127.61 126.88 126.04 125.15 122.37
113.32
77.48 77.16 CDCl3 76.84
53.20 49.18 46.49
34.19
13C NMR (101 MHz, CDCl3)
BnHN
CF3
4am
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



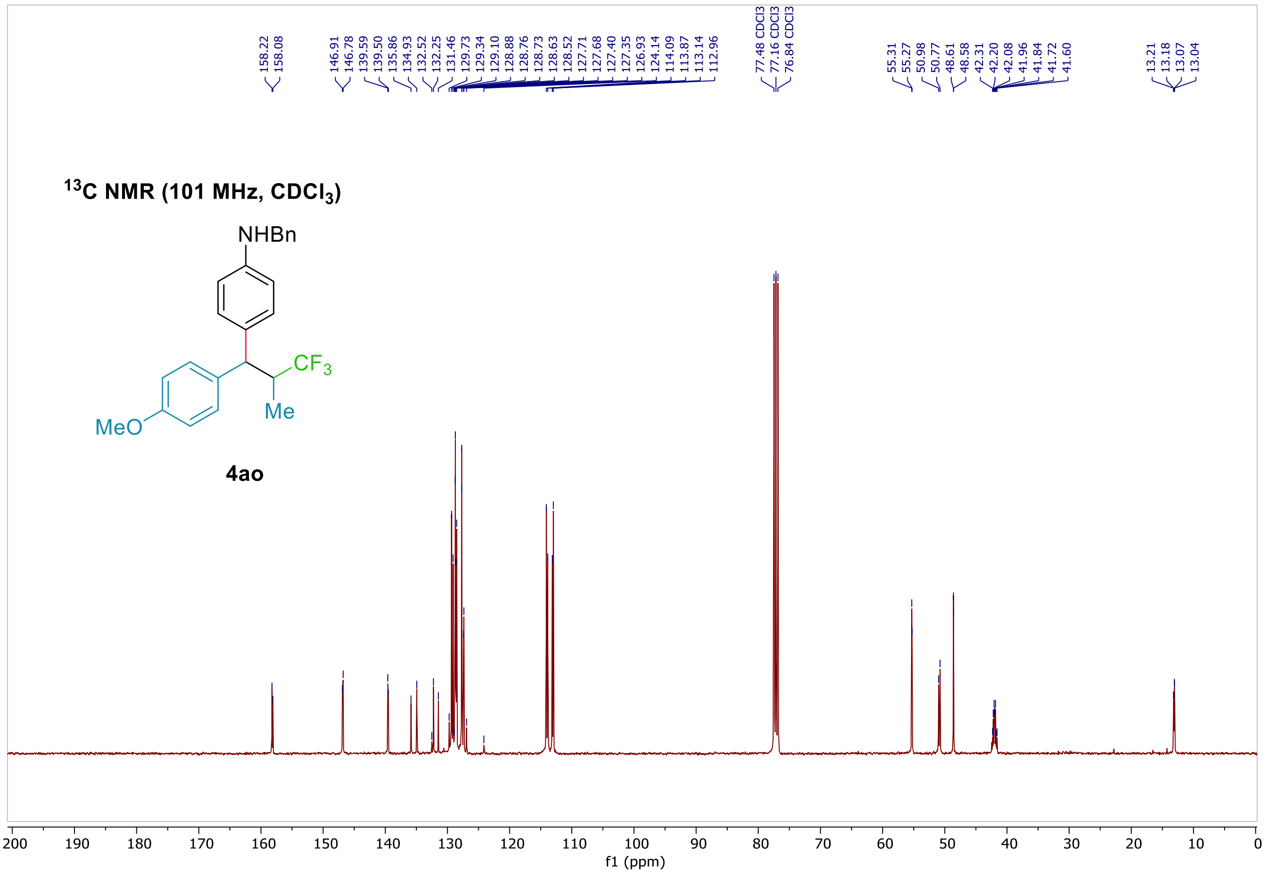
1H NMR (400 MHz, CDCl3)
NHBn
MeO
MeO
CF3
4an
f1 (ppm)



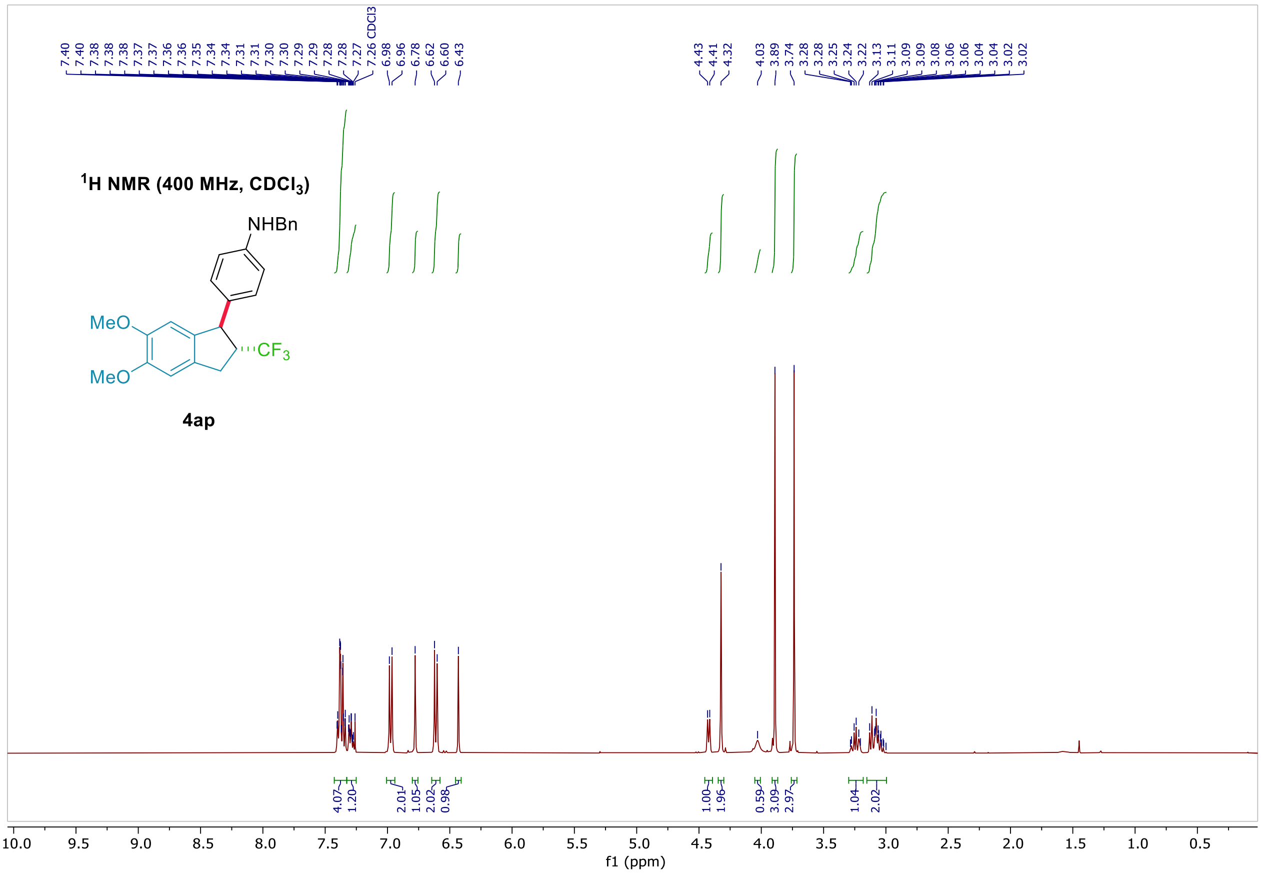
13C NMR (101 MHz, CDCl3)
NHBn
MeO
MeO
CF3
4an
f1 (ppm)



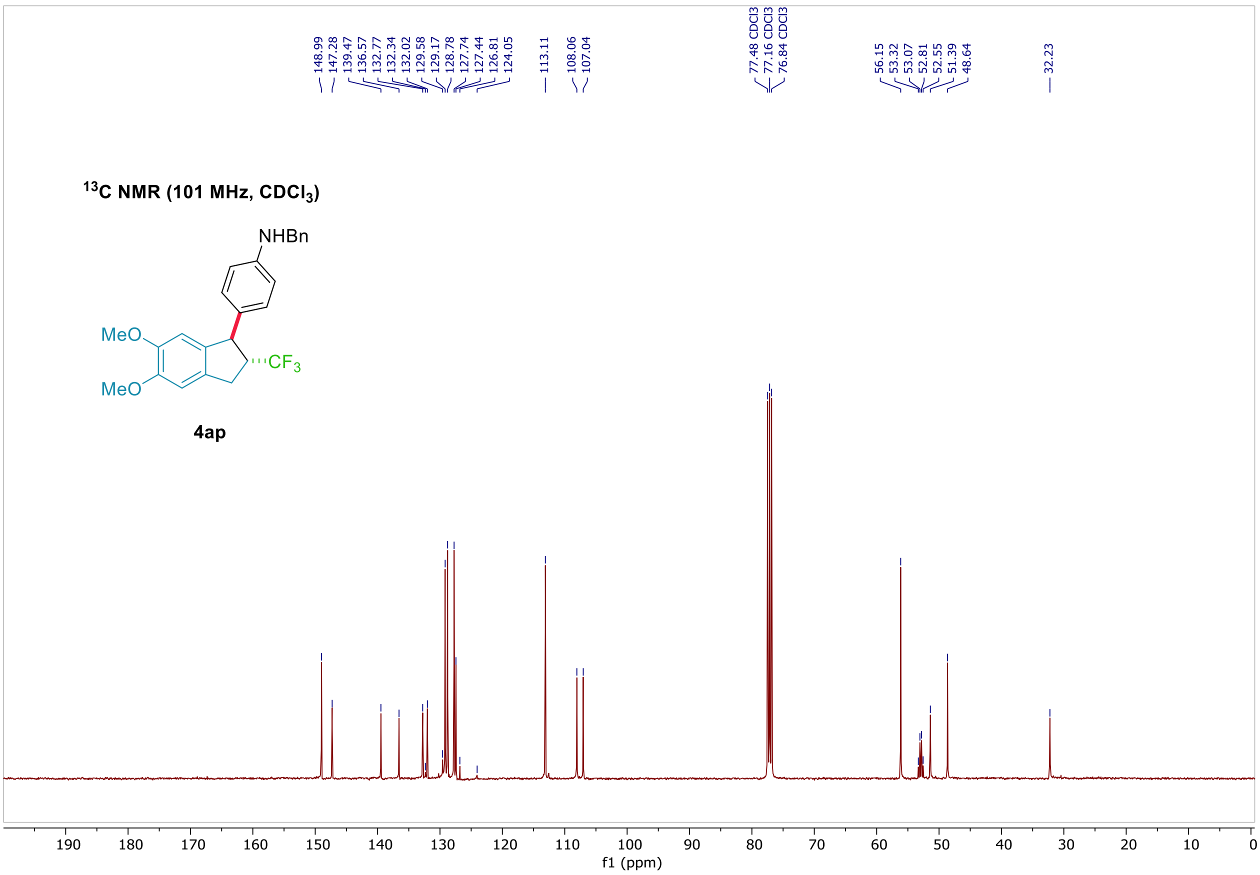
1H NMR (400 MHz, CDCl3)
NHBn
CF3
MeO
Me
4ao
f1 (ppm)



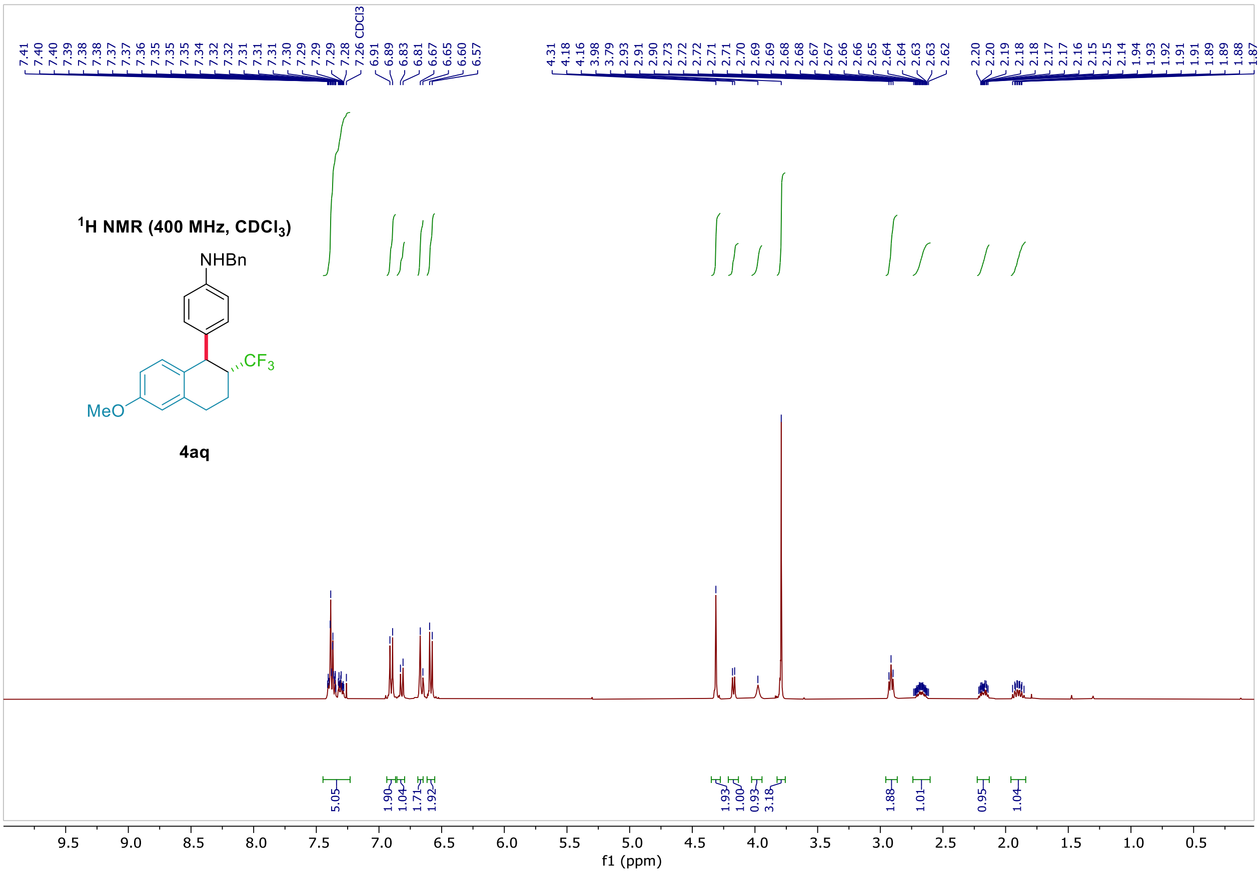
13C NMR (101 MHz, CDCl3)
NHBn
CF3
MeO
Me
4ao
f1 (ppm)

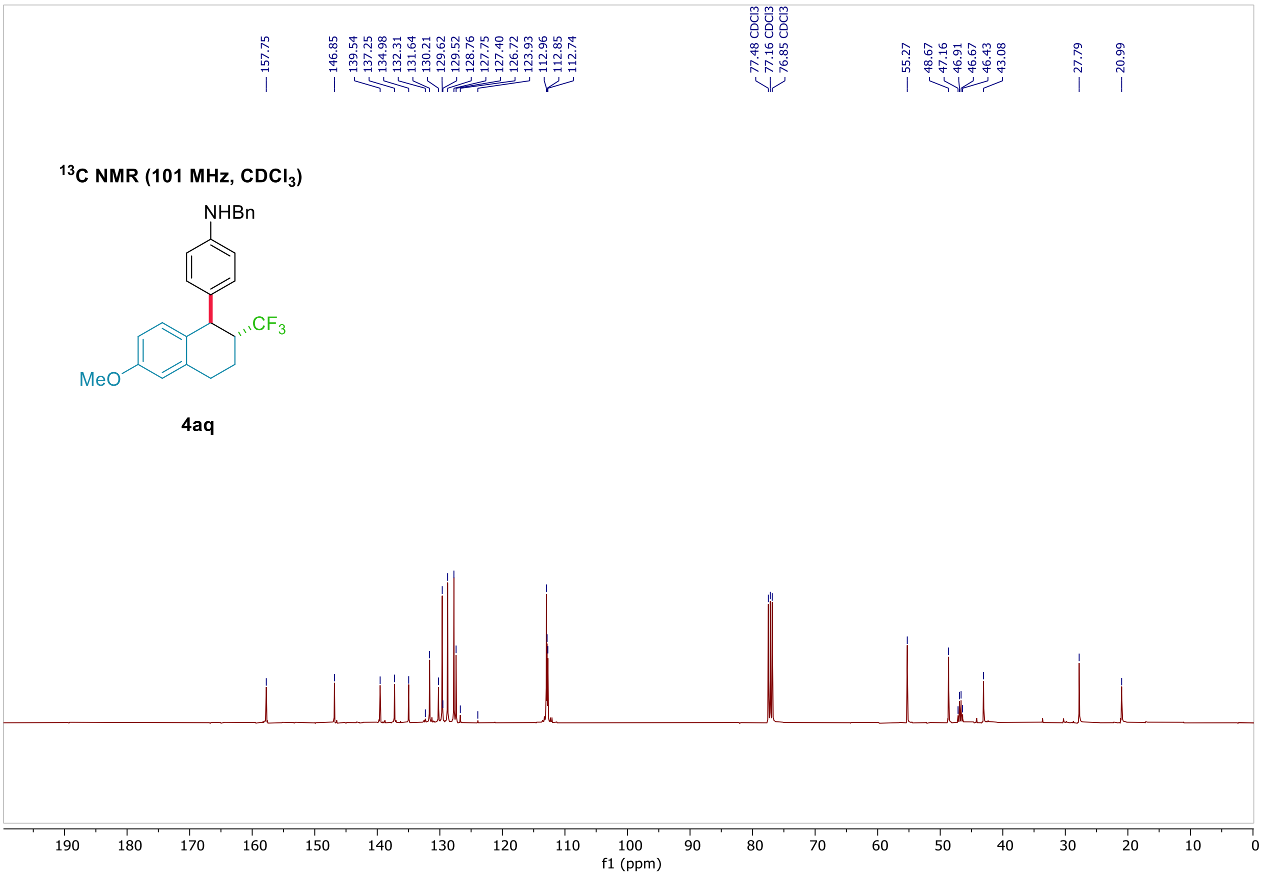


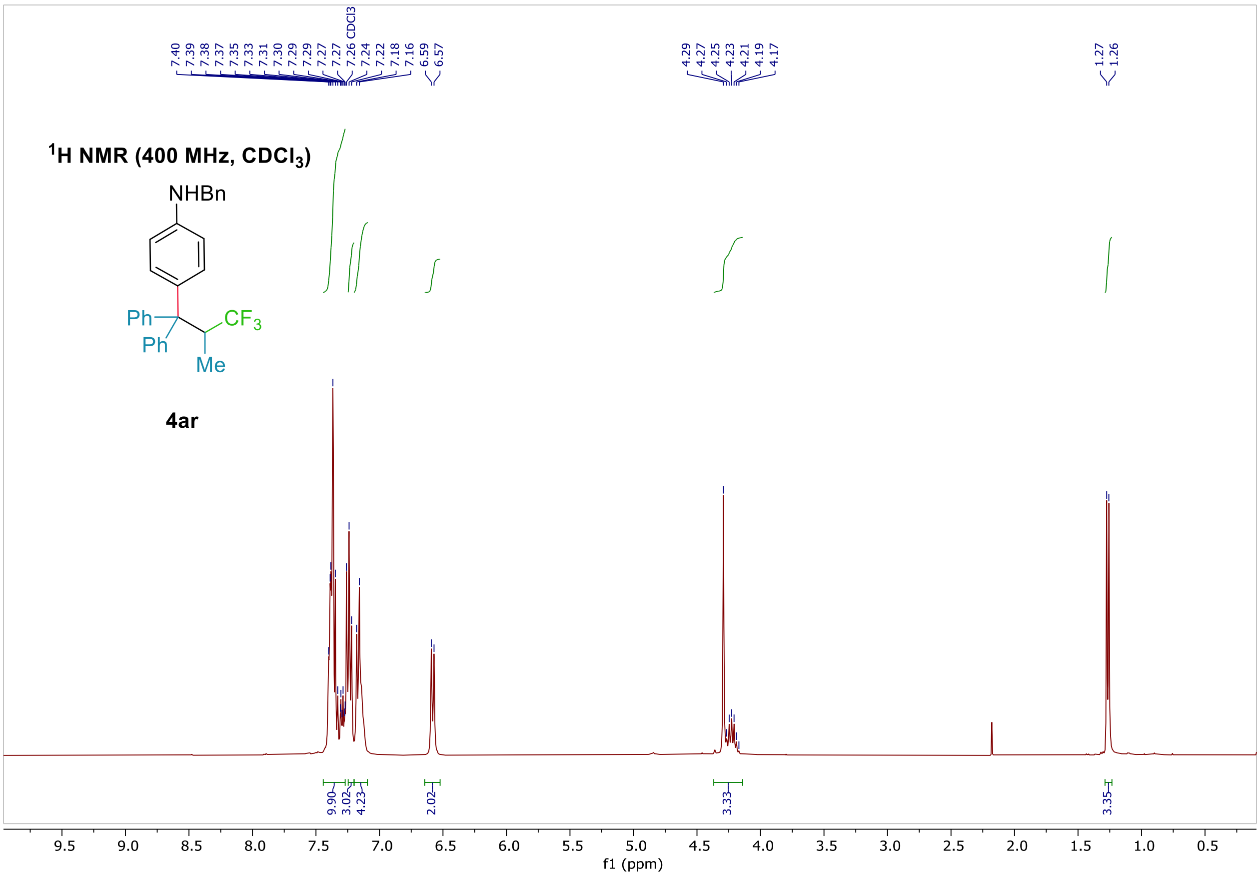
1H NMR (400 MHz, CDCl3)
NHBn
MeO
MeO
CF3
4ap
f1 (ppm)



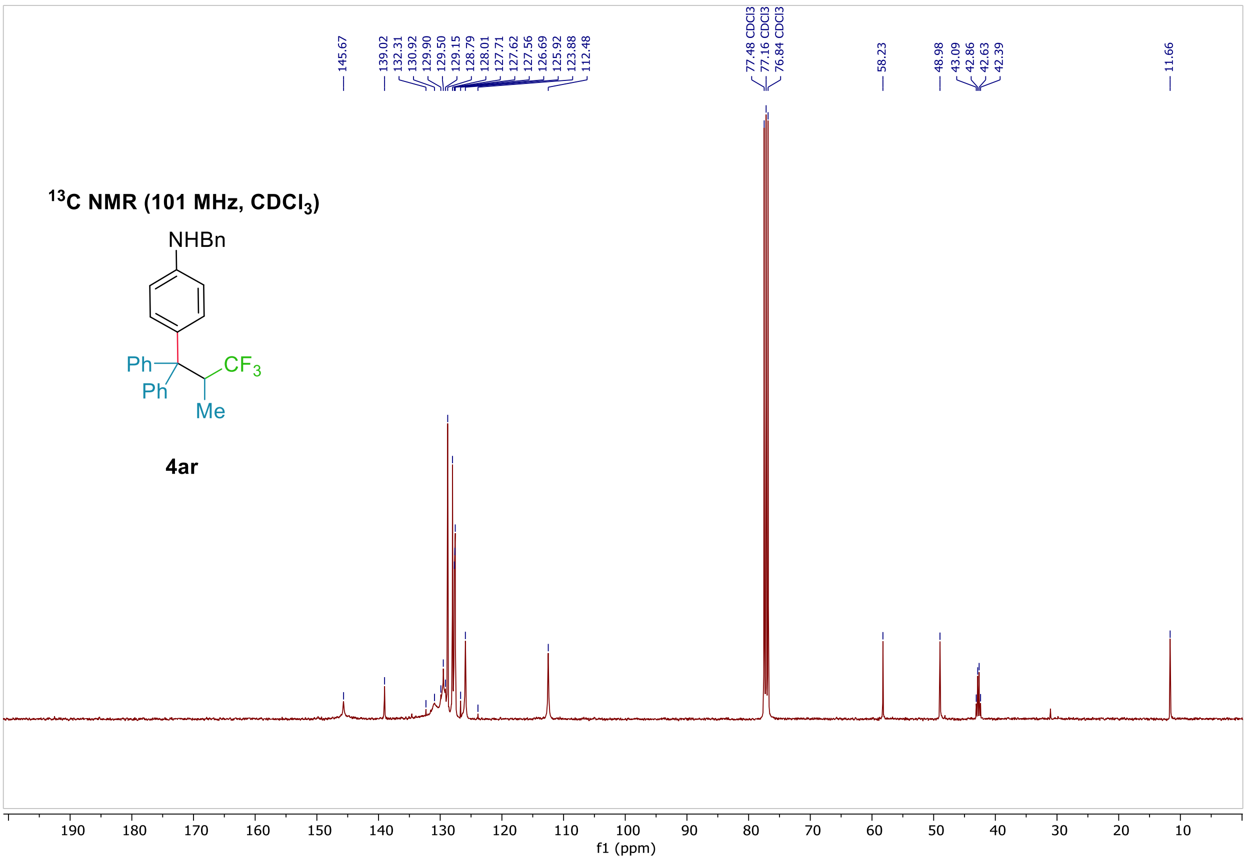
13C NMR (101 MHz, CDCl3)
NHBn
MeO
MeO
CF3
4ap
f1 (ppm)


1H NMR (400 MHz, CDCl3)
NHBn
CF3
MeO
4aq
f1 (ppm)

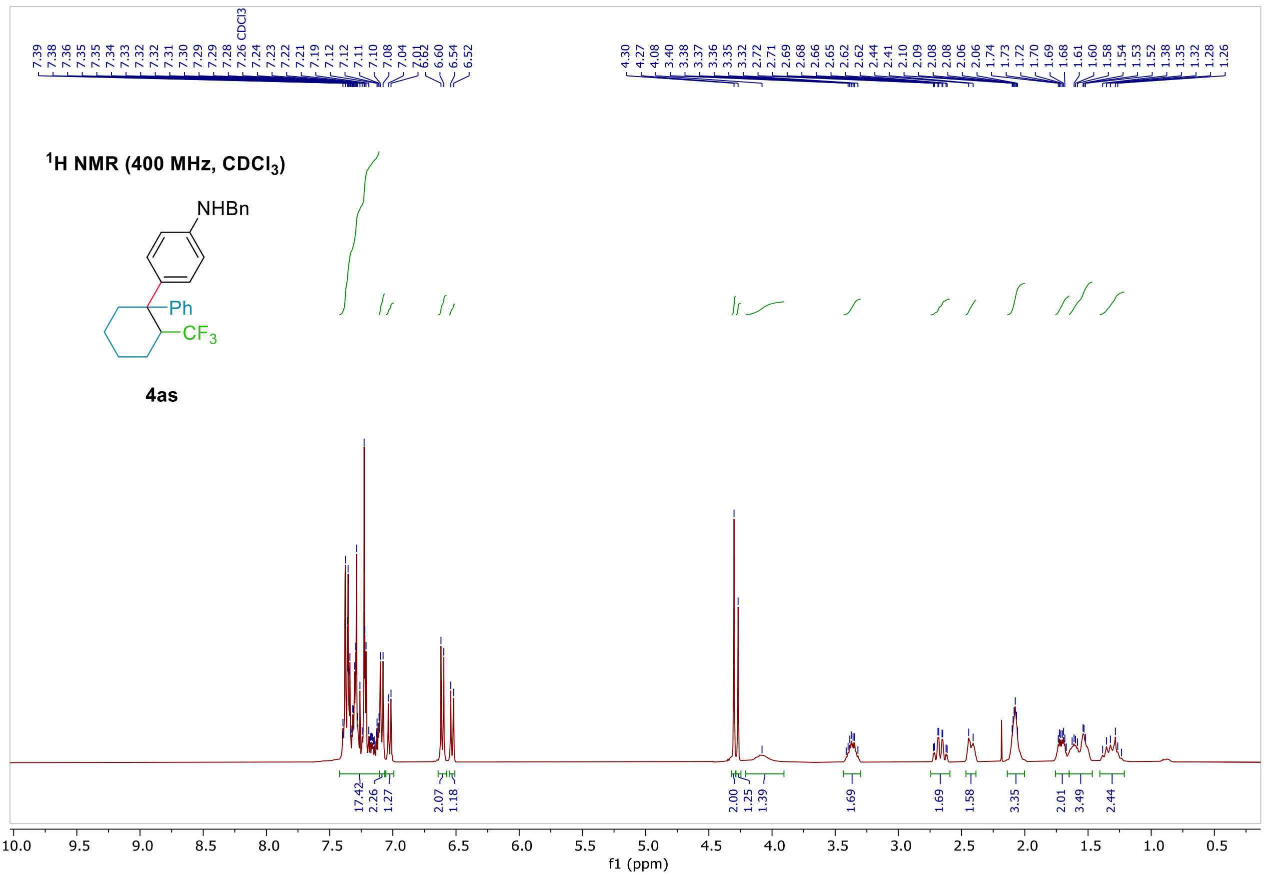

13C NMR (101 MHz, CDCl3)
NHBn
CF3
MeO
4aq
f1 (ppm)

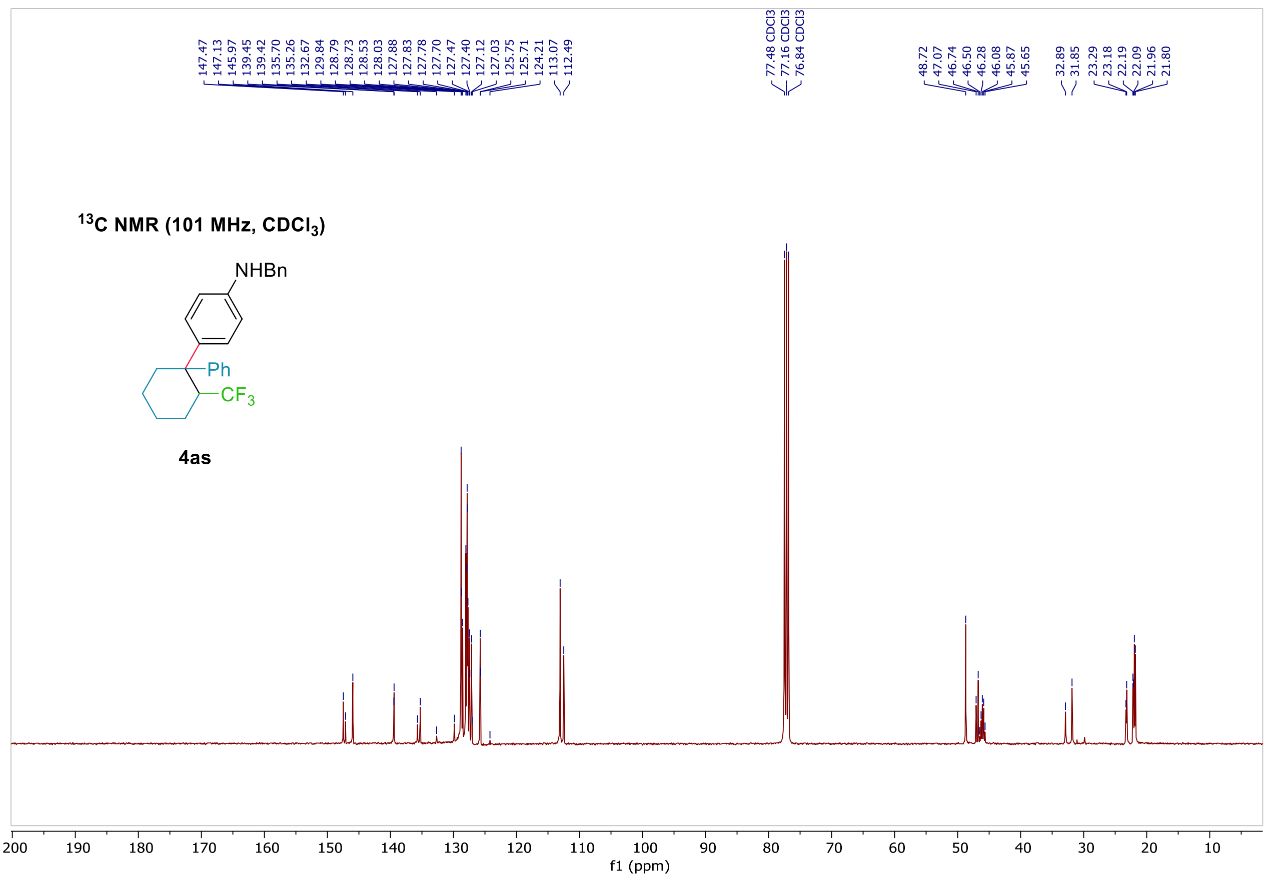


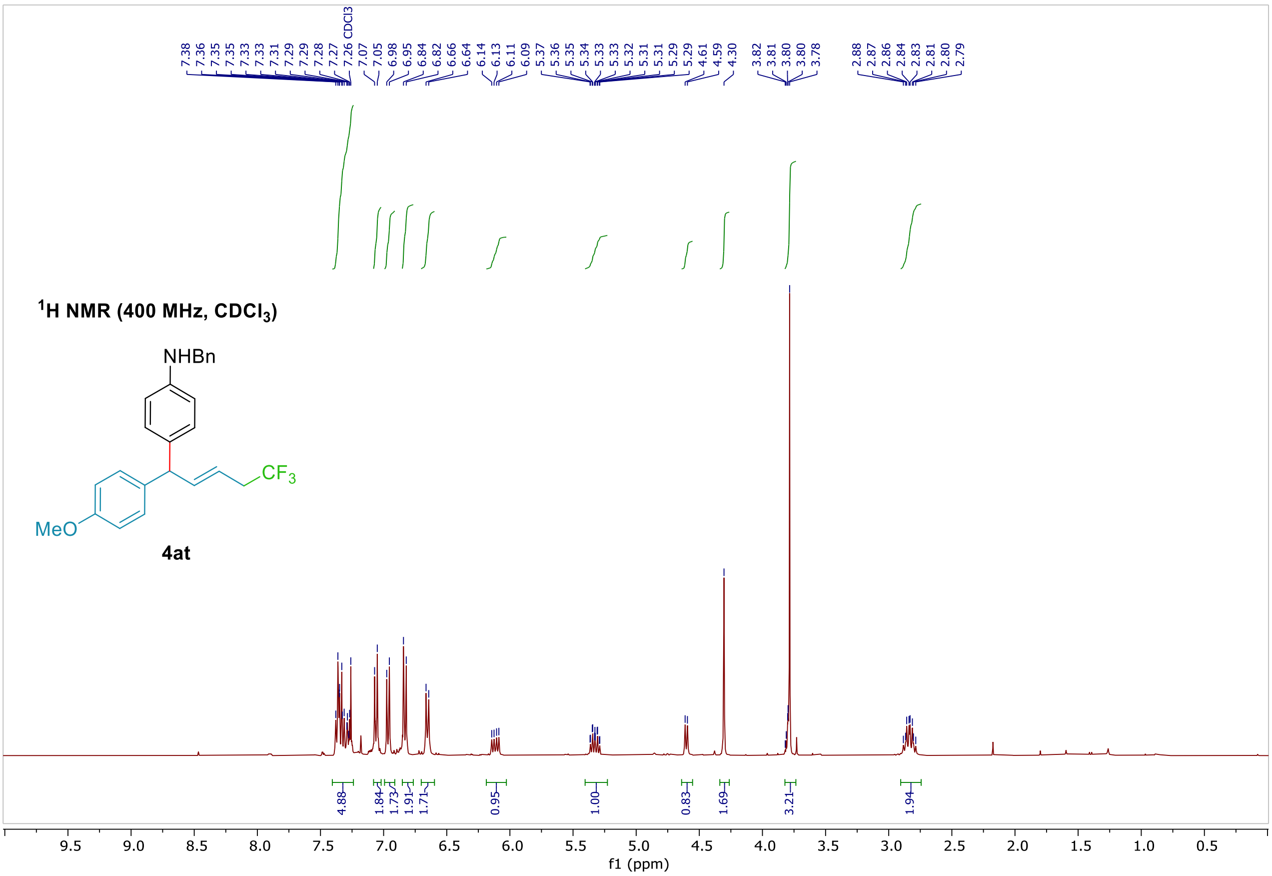
7.40 7.39 7.38 7.37 7.35 7.33 7.31 7.30 7.29 7.29 7.27 7.27 7.26 CDCl3 7.24 7.22 7.18 7.16 6.59 6.57
4.29 4.27 4.25 4.23 4.21 4.19 4.17
1.27 1.26
1H NMR (400 MHz, CDCl3)
NHBn
Ph
Ph
CF3
Me
4ar
9.90 3.02 4.23
2.02
3.33
3.35
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



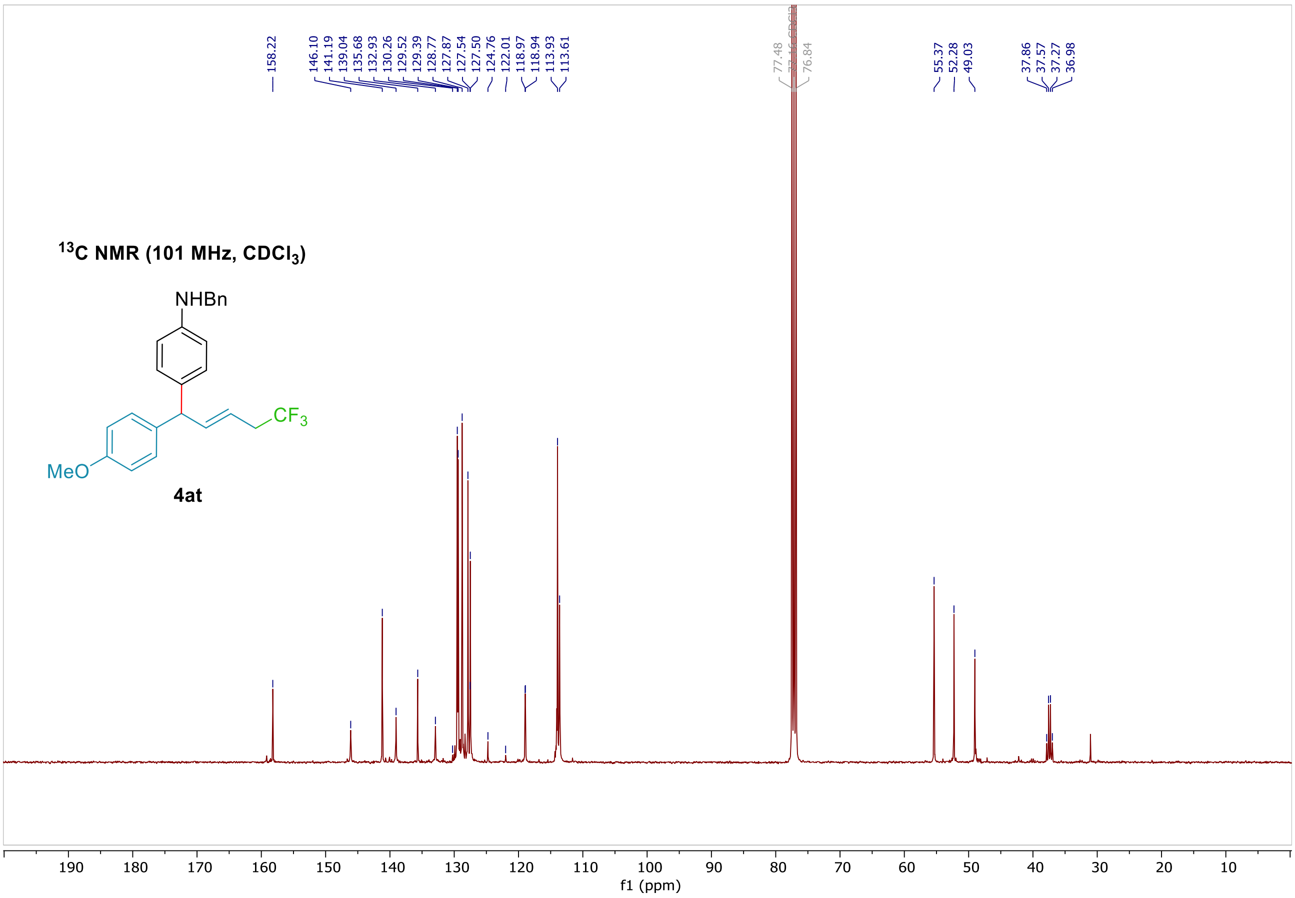
145.67
139.02 132.31 130.92 129.90 129.50 129.15 128.79 128.01 127.71 127.62 127.56 126.69 125.92 123.88 112.48
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
58.23
48.98 43.09 42.86 42.63 42.39
11.66
13C NMR (101 MHz, CDCl3)
NHBn
Ph
Ph
CF3
Me
4ar
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.39 7.38 7.36 7.35 7.35 7.34 7.33 7.32 7.32 7.31 7.30 7.29 7.29 7.28 7.26 CDCl3 7.24 7.23 7.22 7.21 7.19 7.12 7.12 7.11 7.10 7.08 7.04 7.01 6.62 6.60 6.54 6.52
4.30 4.27 4.08 3.40 3.38 3.37 3.36 3.35 3.32 2.72 2.71 2.69 2.68 2.66 2.65 2.62 2.62 2.44 2.41 2.10 2.09 2.08 2.08 2.06 2.06 1.74 1.73 1.72 1.70 1.69 1.68 1.61 1.60 1.58 1.54 1.53 1.52 1.38 1.35 1.32 1.28 1.26
1H NMR (400 MHz, CDCl3)
NHBn
Ph
CF3
4as
17.42 2.26 1.27 2.07 1.18 2.00 1.25 1.39 1.69 1.69 1.58 3.35 2.01 3.49 2.44
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

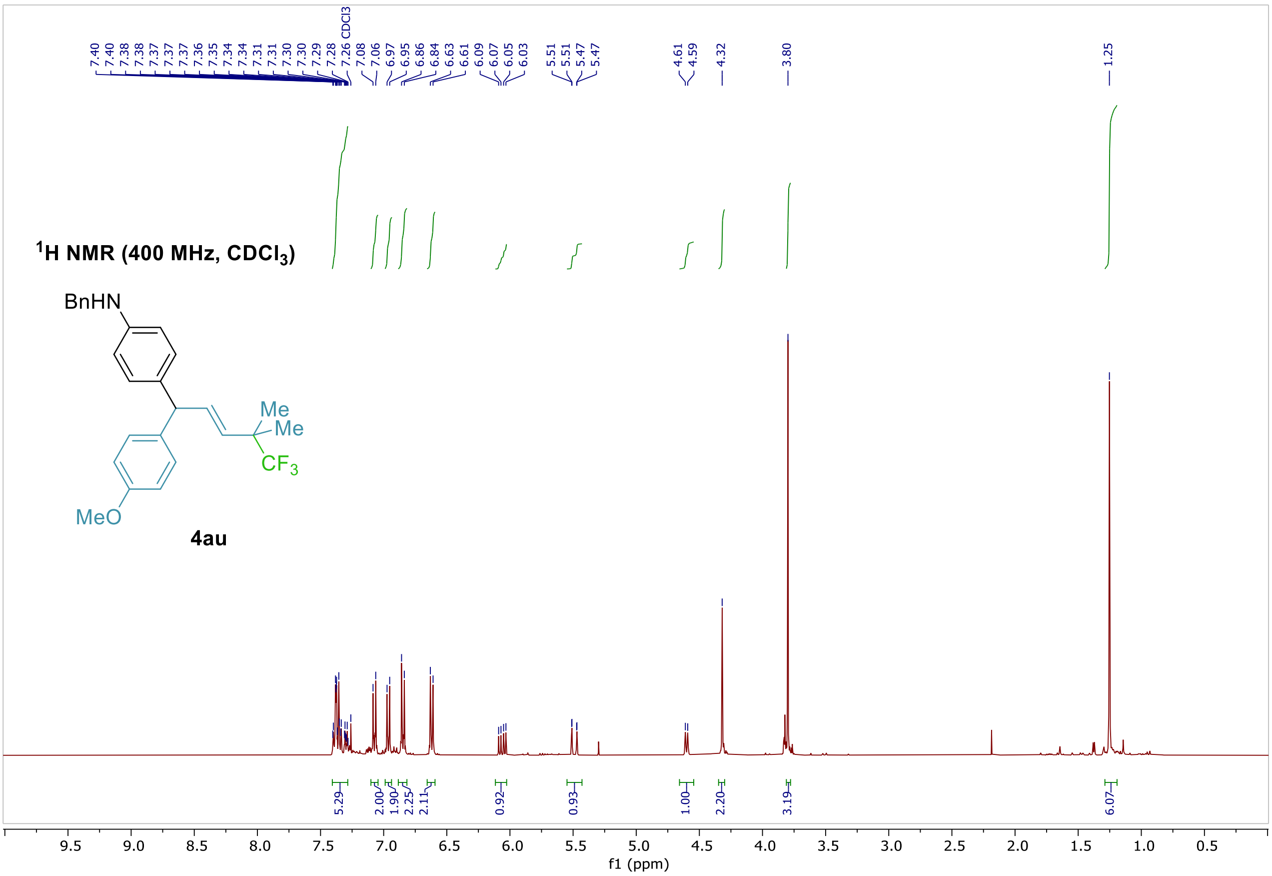

147.47 147.13 145.97 139.45 139.42 135.70 135.26 132.67 129.84 128.79 128.73 128.53 128.03 127.88 127.83 127.78 127.70 127.47 127.40 127.12 127.03 125.75 125.71 124.21 113.07 112.49
77.48 CDCl3 77.16 CDCl3 76.84 CDCl3
48.72 47.07 46.74 46.50 46.28 46.08 45.87 45.65 32.89 31.85 23.29 23.18 22.19 22.09 21.96 21.80
13C NMR (101 MHz, CDCl3)
NHBn
Ph
CF3
4as
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



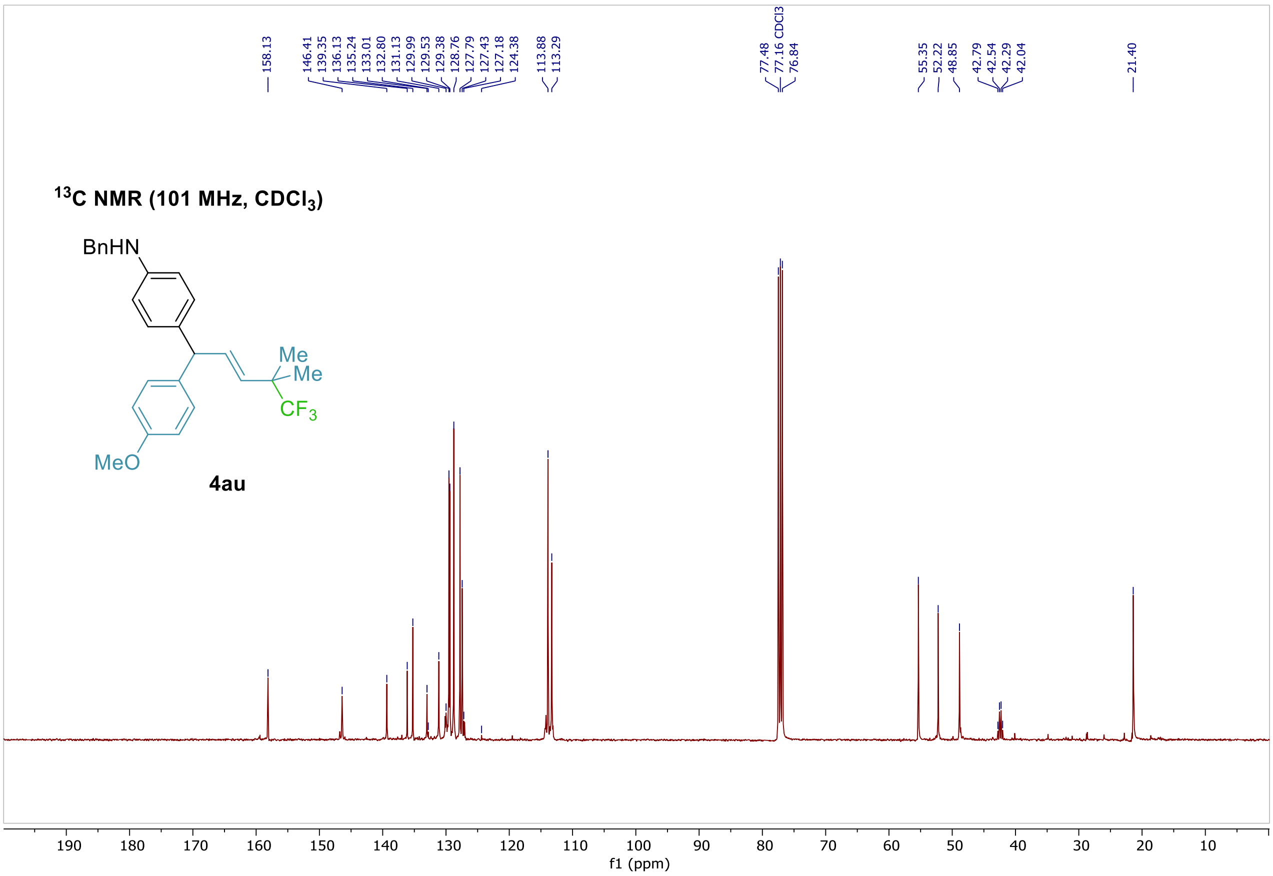
^{1}H NMR (400 MHz, CDCl$_3$)
NHBn
CF$_3$
MeO
4at
f1 (ppm)



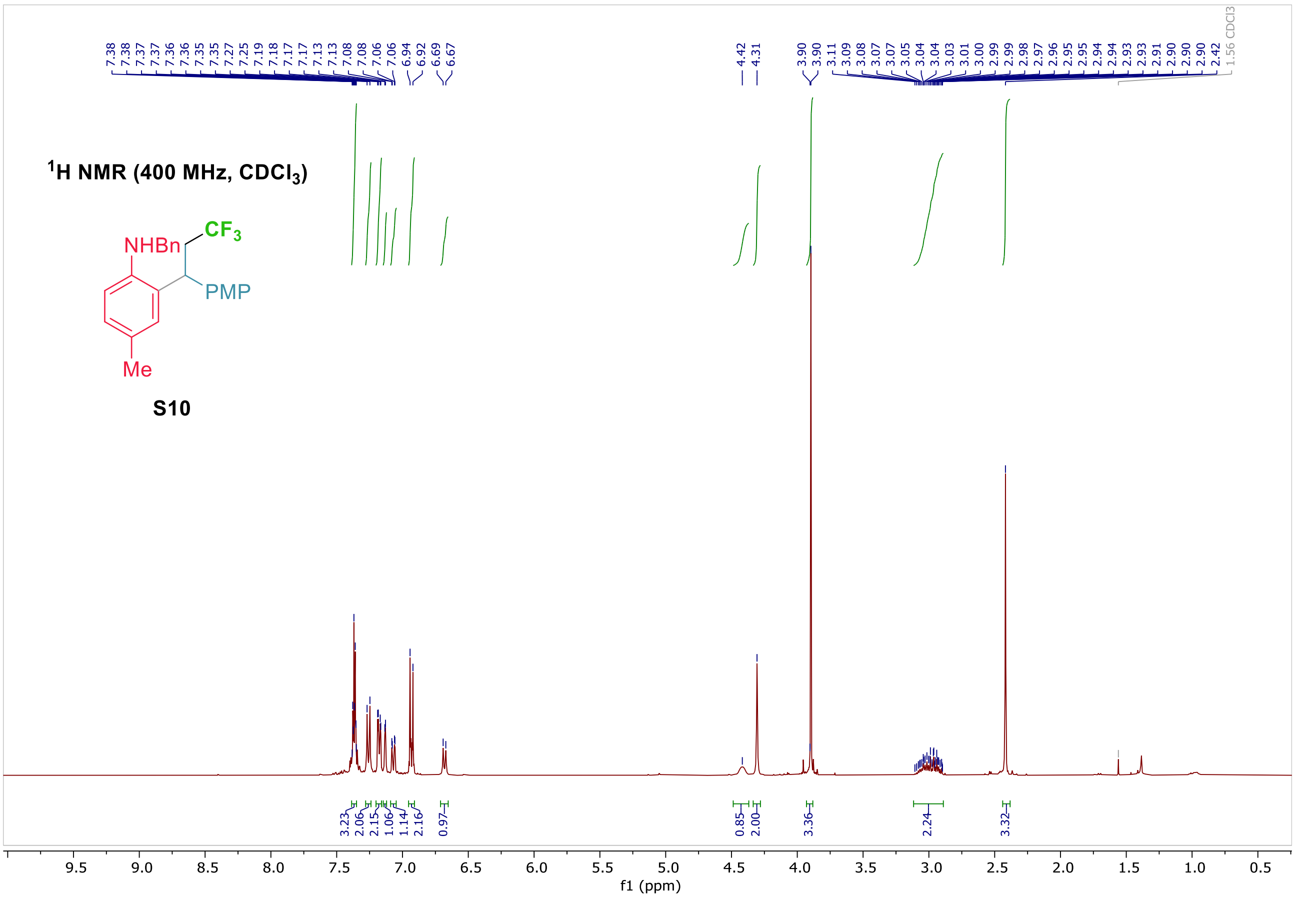
^{13}C NMR (101 MHz, CDCl$_3$)
NHBn
CF$_3$
MeO
4at
f1 (ppm)



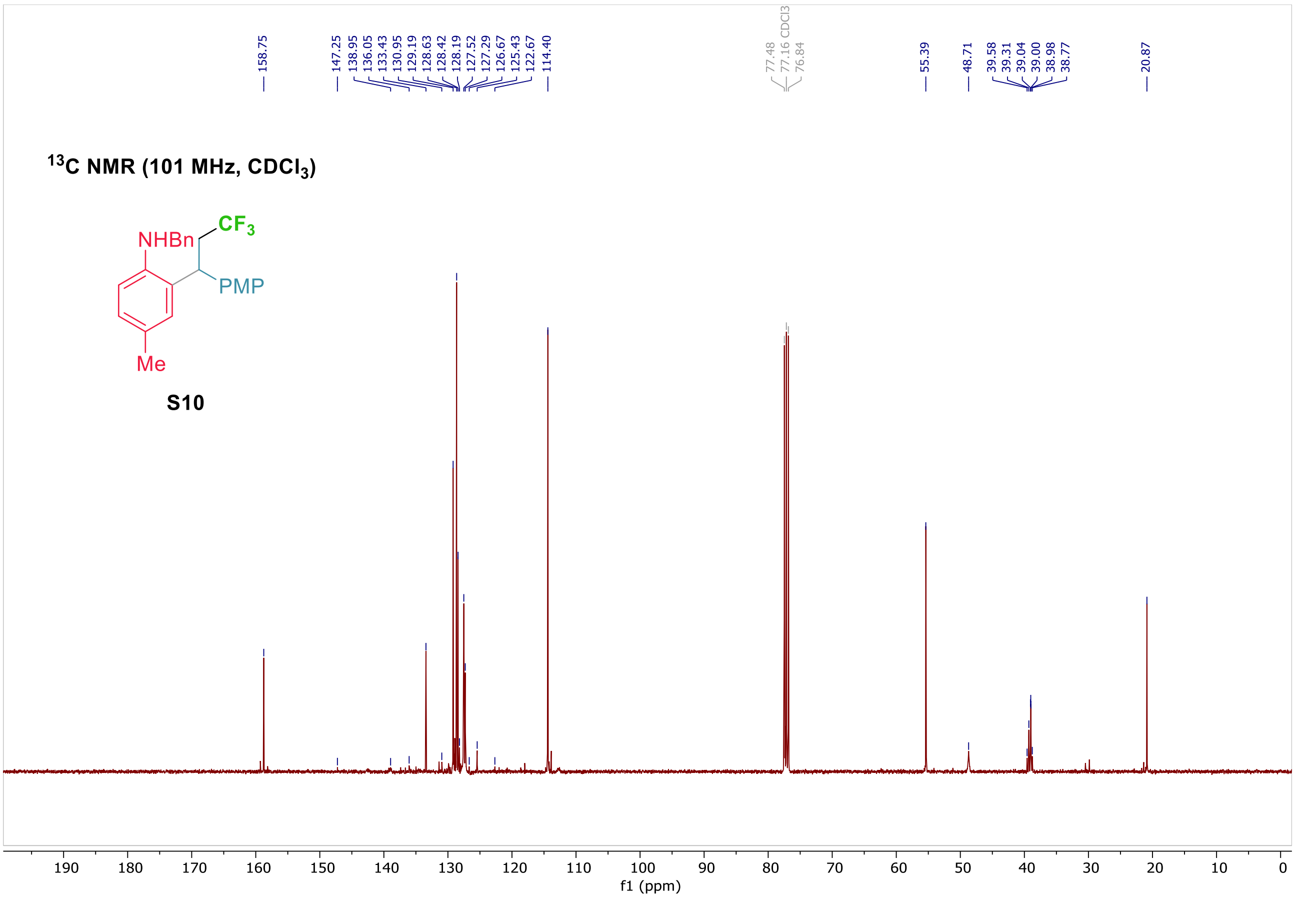
7.40
7.40
7.38
7.38
7.37
7.37
7.37
7.36
7.35
7.34
7.34
7.31
7.31
7.30
7.30
7.29
7.28
7.26 CDCl3
7.08
7.06
6.97
6.95
6.86
6.84
6.63
6.61
6.09
6.07
6.05
6.03
5.51
5.51
5.47
5.47
4.61
4.59
4.32
3.80
1.25
¹H NMR (400 MHz, CDCl3)
BnHN
Me
Me
CF3
MeO
4au
5.29
2.00
1.90
2.25
2.11
0.92
0.93
1.00
2.20
3.19
6.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



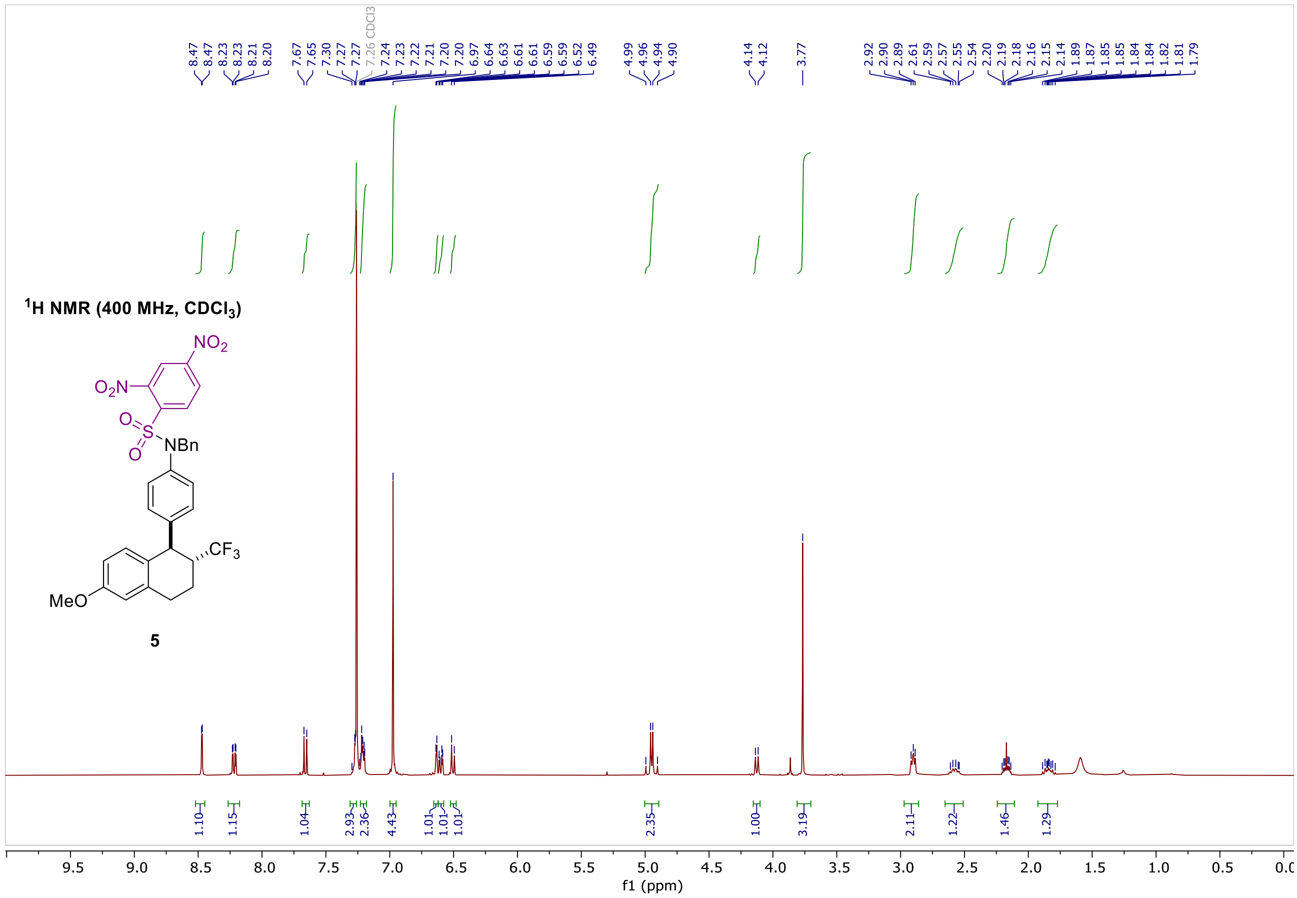
158.13
146.41
139.35
136.13
135.24
133.01
132.80
131.13
129.99
129.53
129.38
128.76
127.79
127.43
127.18
124.38
113.88
113.29
77.48
77.16 CDCl3
76.84
55.35
52.22
48.85
42.79
42.54
42.29
42.04
21.40
¹³C NMR (101 MHz, CDCl3)
BnHN
Me
Me
CF3
MeO
4au
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



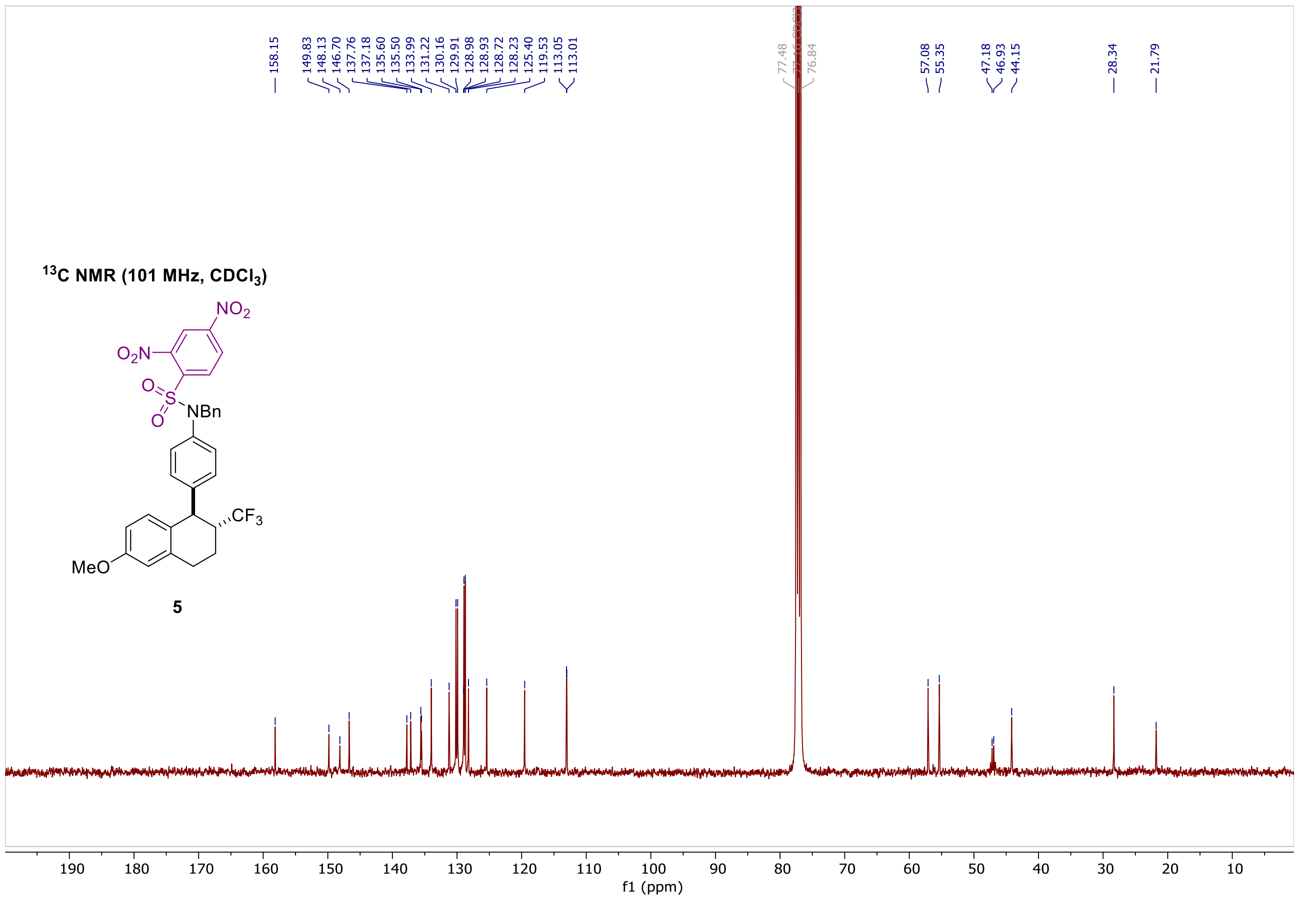
1H NMR (400 MHz, CDCl3)
NHBn
CF3
PMP
Me
S10
f1 (ppm)



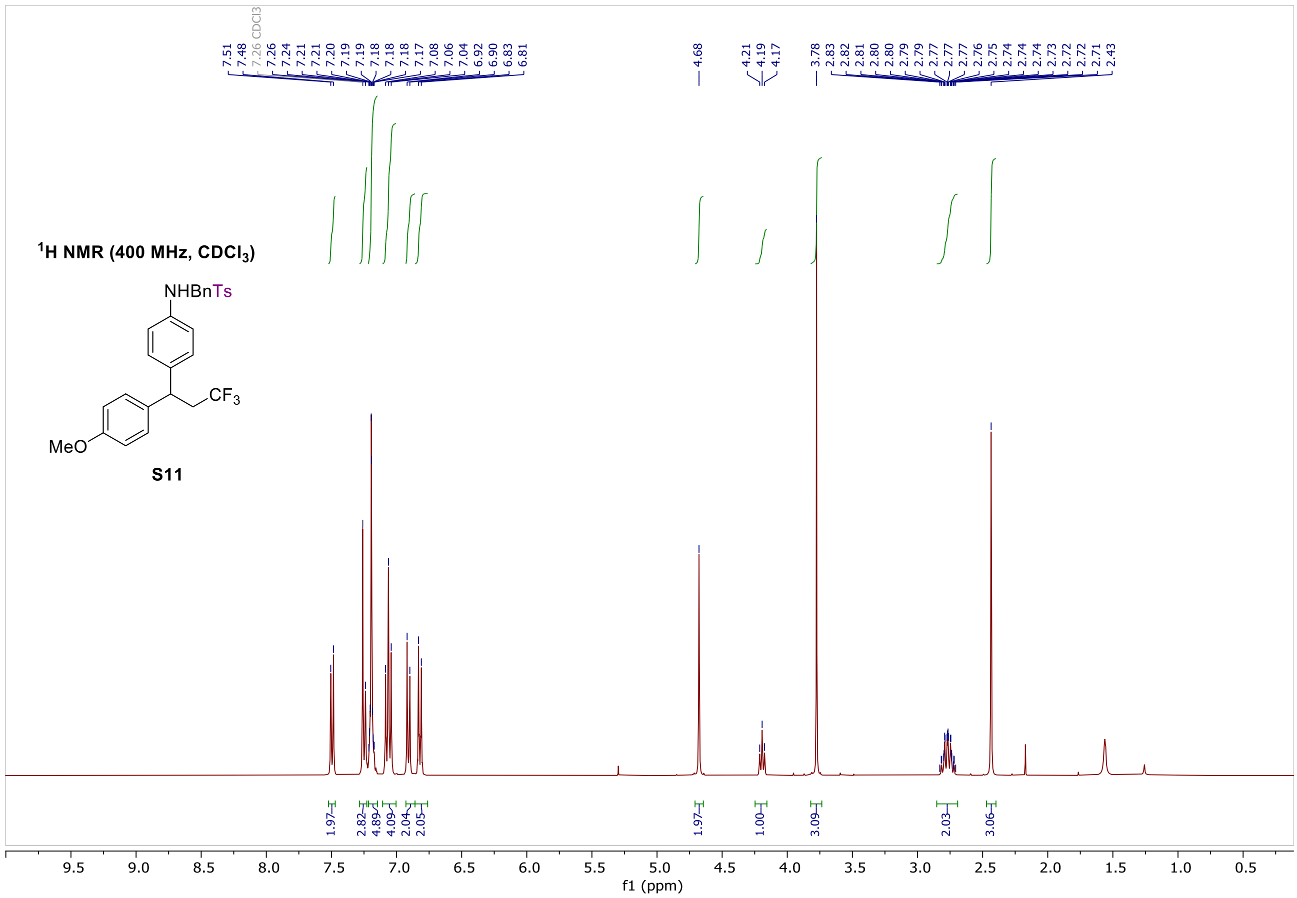
13C NMR (101 MHz, CDCl3)
NHBn
CF3
PMP
Me
S10
f1 (ppm)



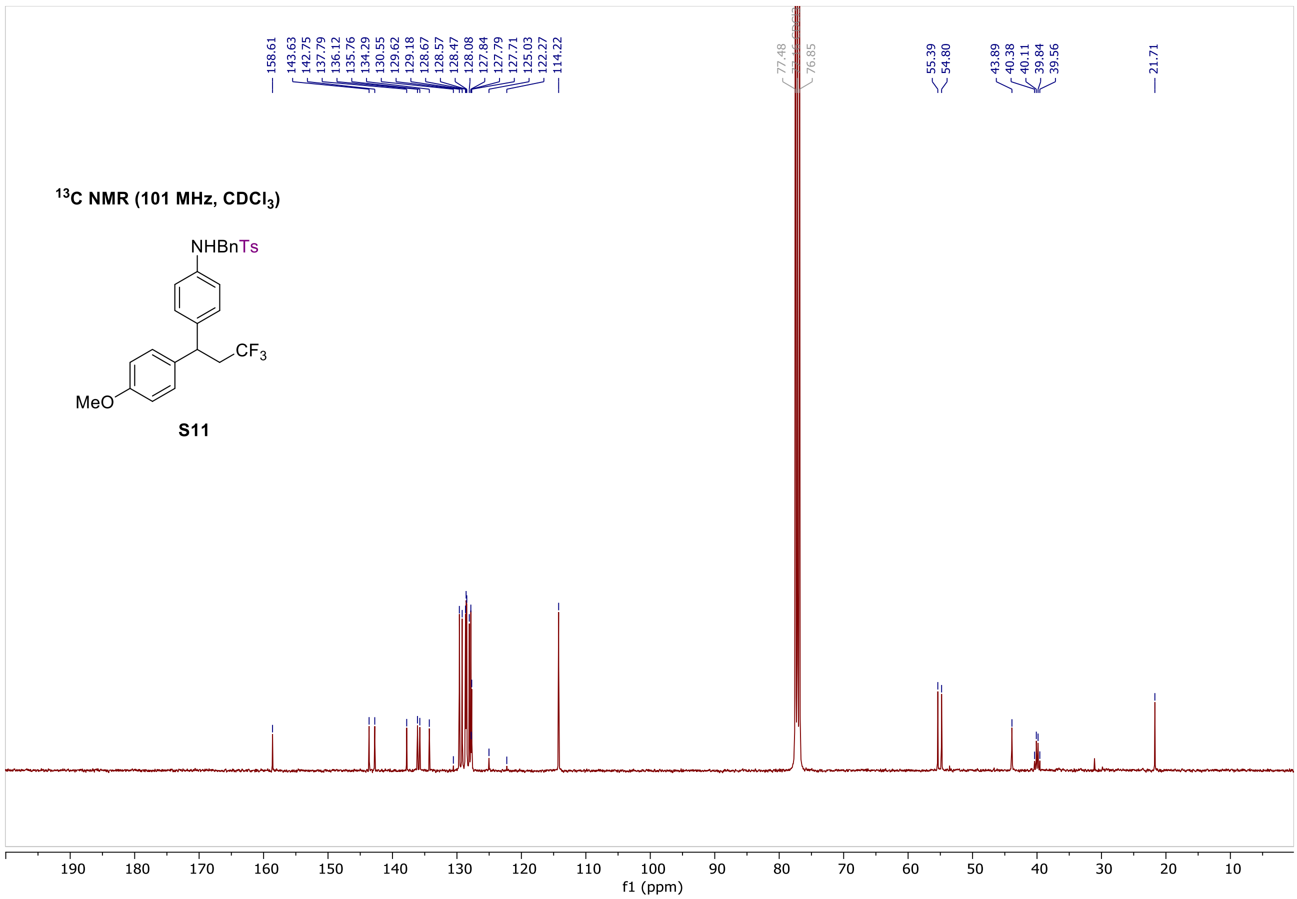
1H NMR (400 MHz, CDCl3)
5
f1 (ppm)



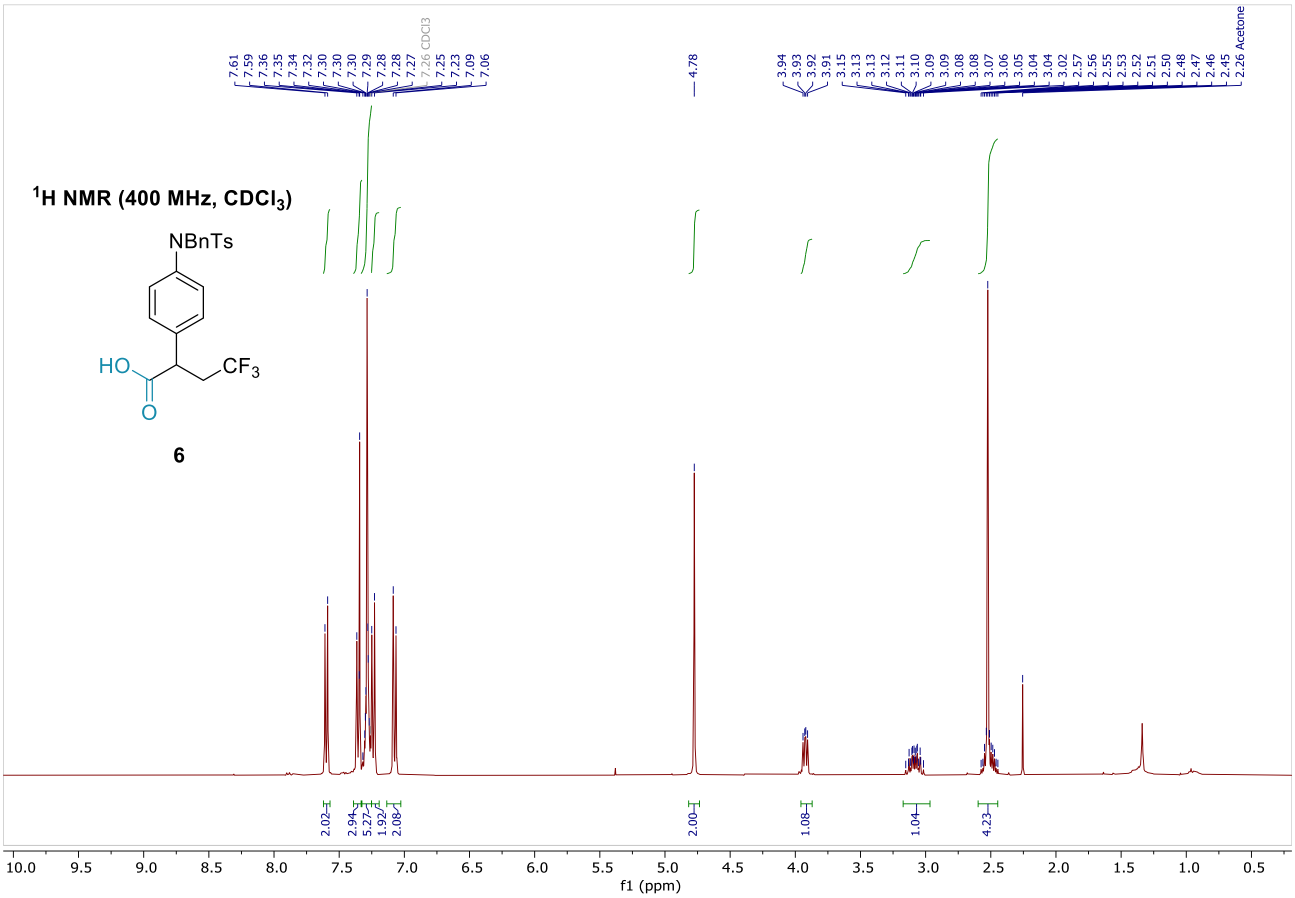
13C NMR (101 MHz, CDCl3)
5
f1 (ppm)



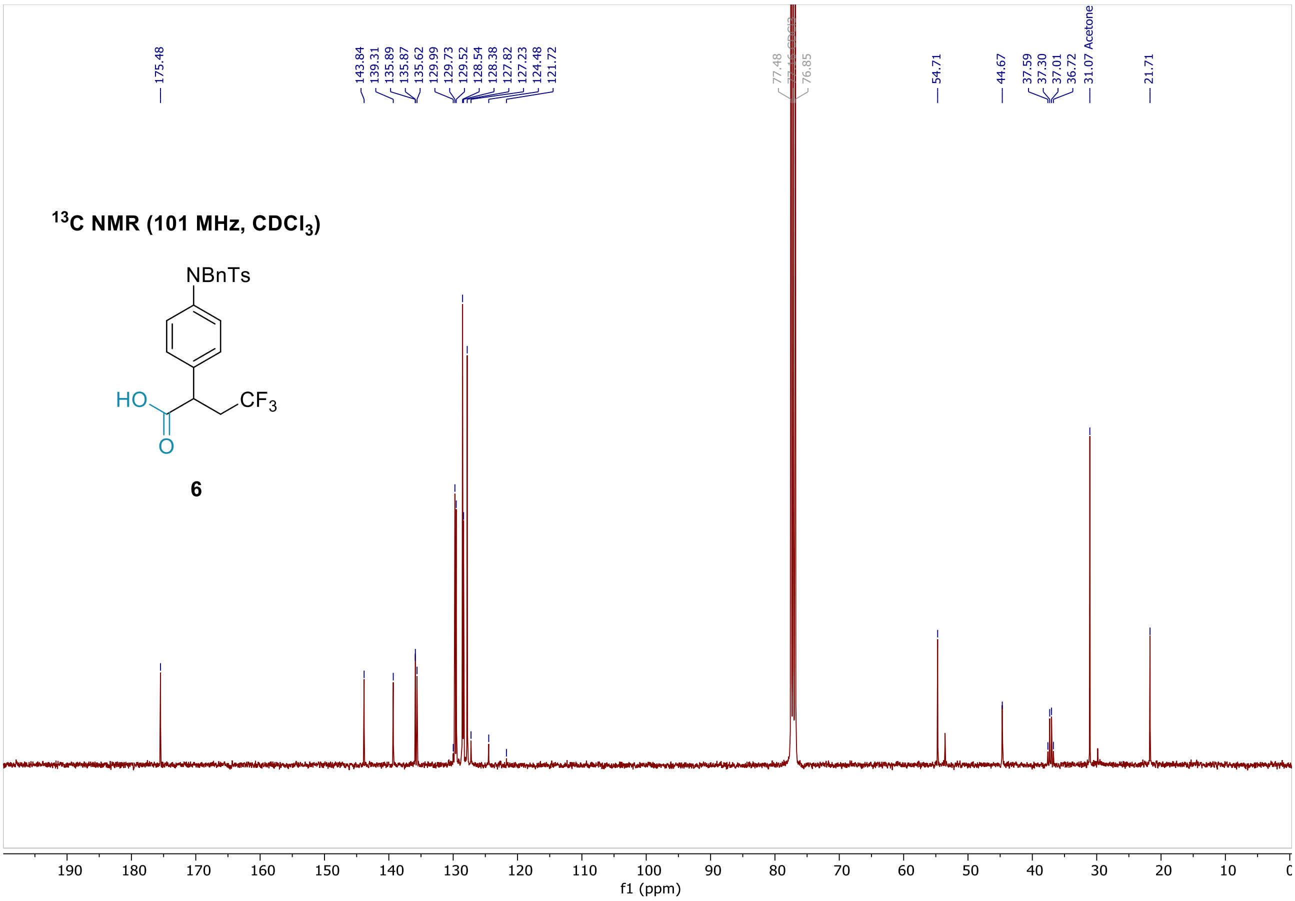
1H NMR (400 MHz, CDCl3)
NHBnTs
CF3
MeO
S11
f1 (ppm)



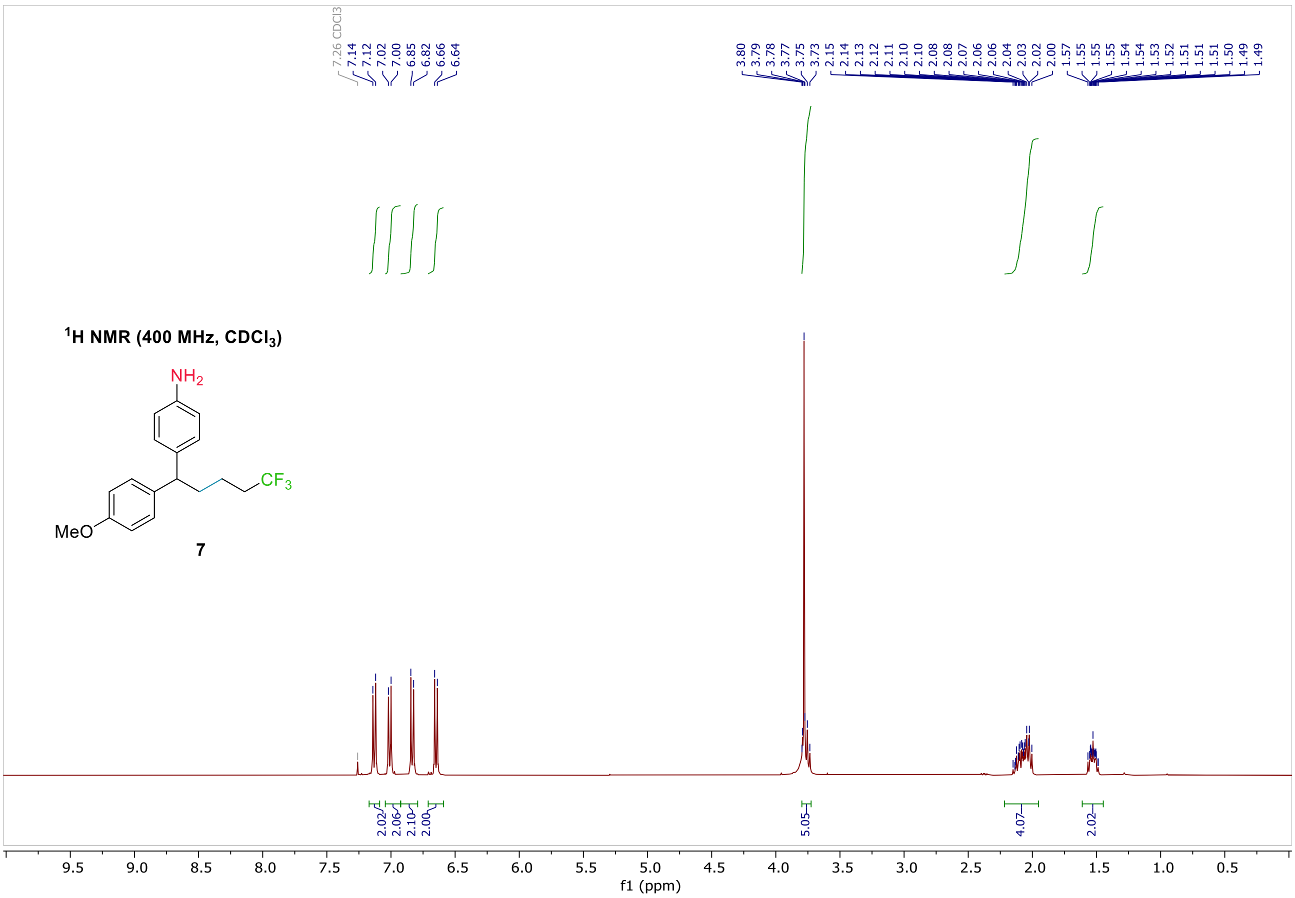
13C NMR (101 MHz, CDCl3)
NHBnTs
CF3
MeO
S11
f1 (ppm)



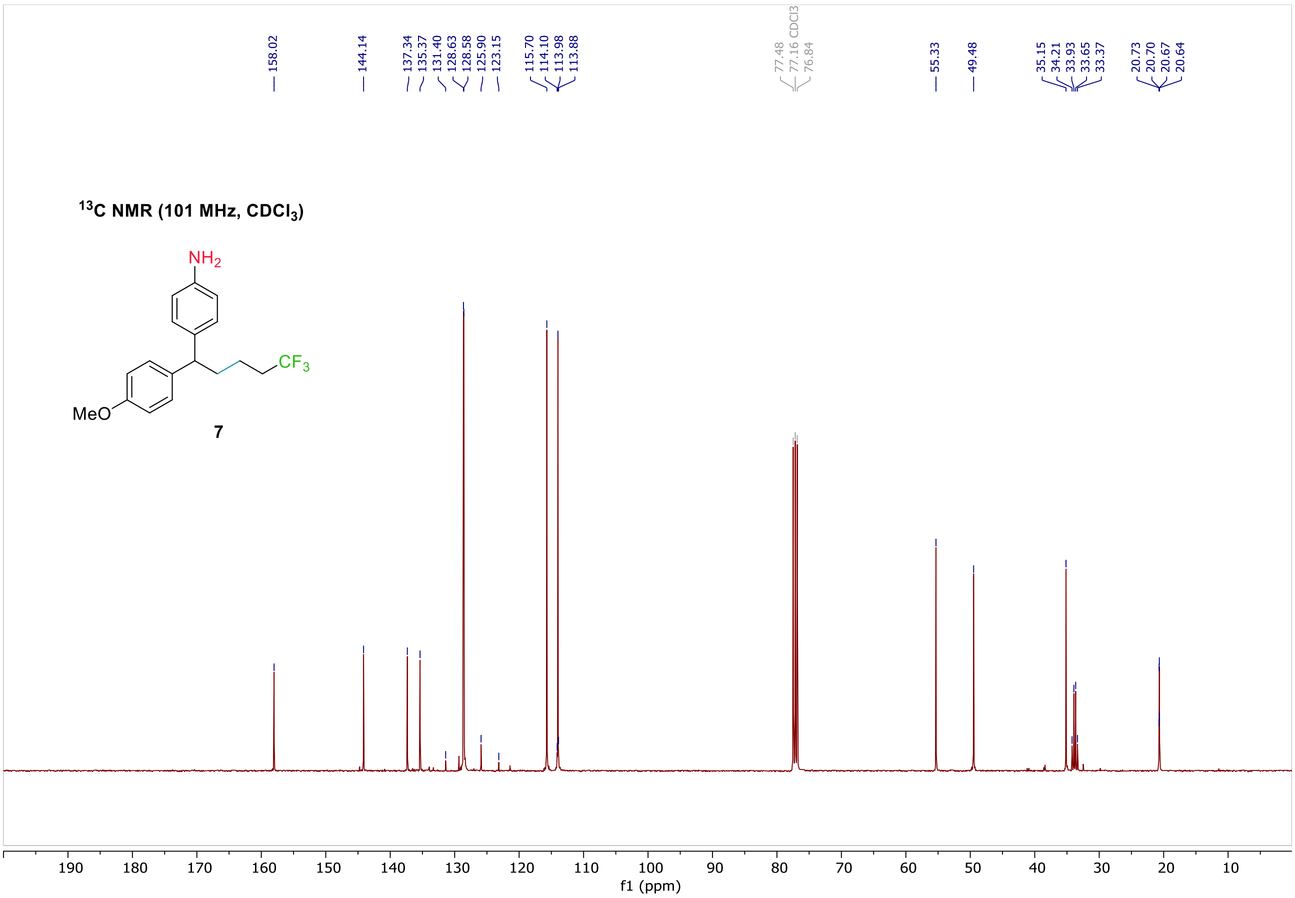
1H NMR (400 MHz, CDCl3)
NBnTs
HO
CF3
O
6
f1 (ppm)



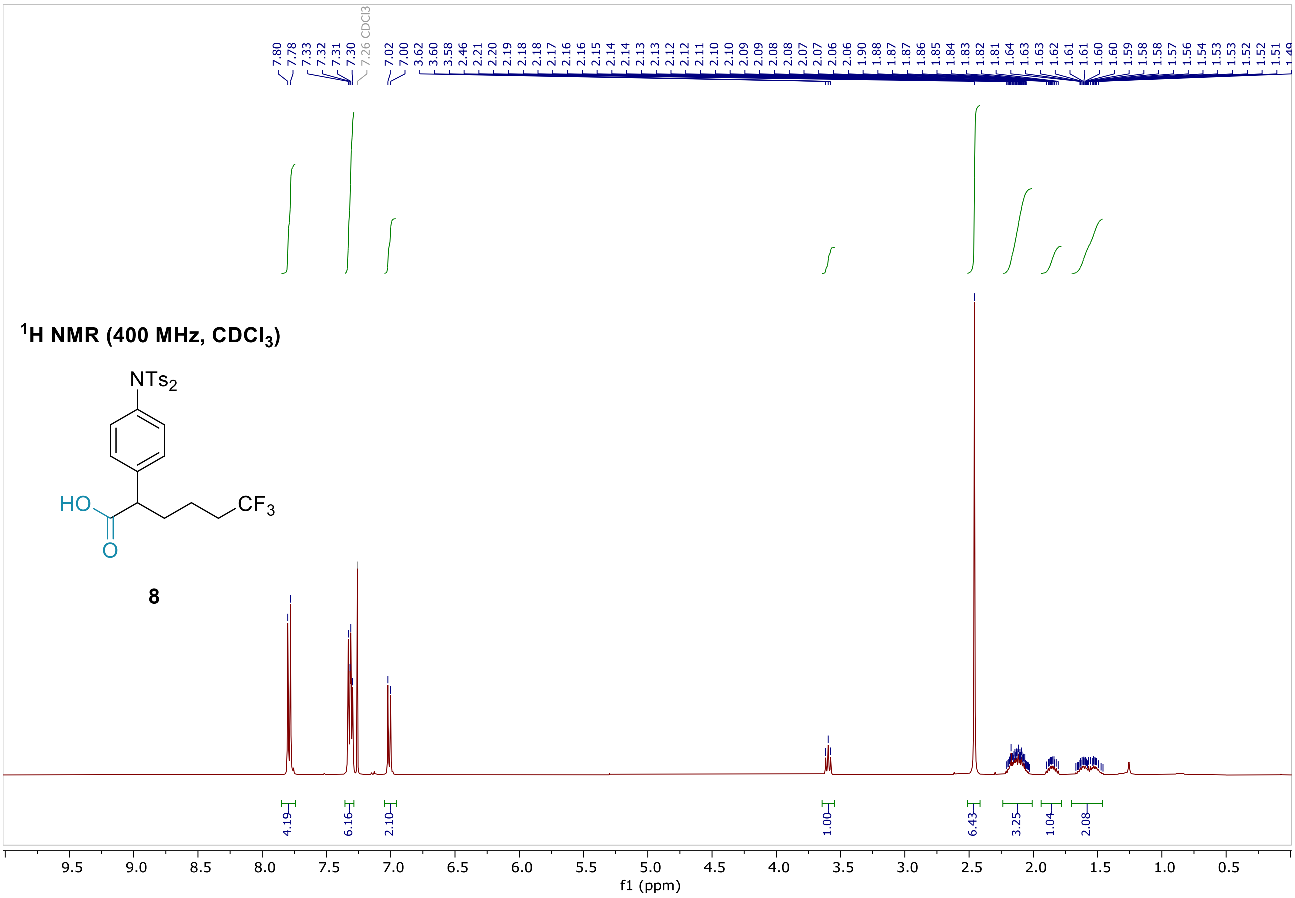
13C NMR (101 MHz, CDCl3)
NBnTs
HO
CF3
O
6
f1 (ppm)



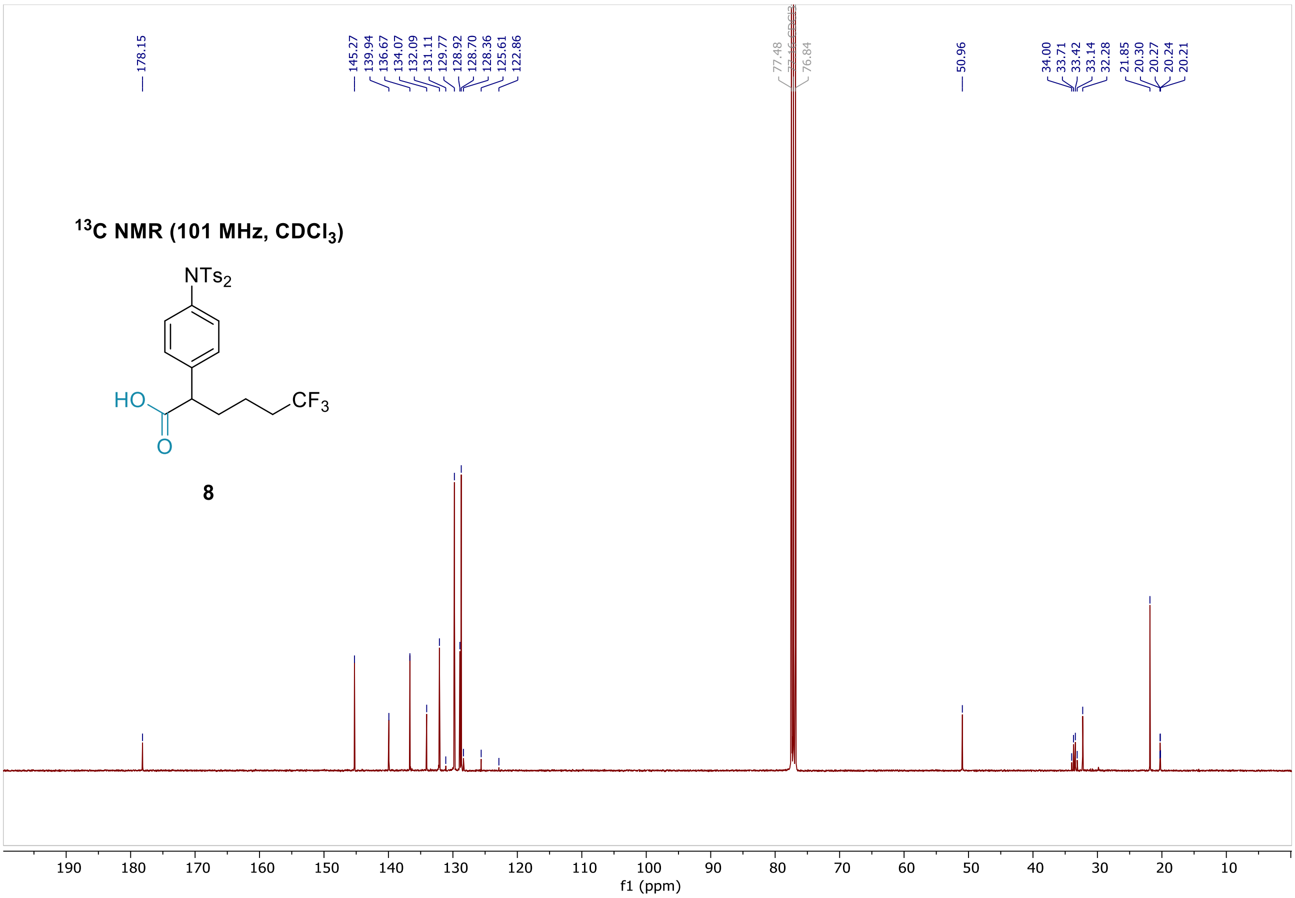
1H NMR (400 MHz, CDCl3)
NH2
CF3
MeO
7
7.26 CDCl3
7.14
7.12
7.02
7.00
6.85
6.82
6.66
6.64
3.80
3.79
3.78
3.77
3.75
3.73
2.15
2.14
2.13
2.12
2.11
2.10
2.10
2.08
2.08
2.07
2.06
2.06
2.04
2.03
2.02
2.00
1.57
1.55
1.55
1.55
1.54
1.54
1.53
1.52
1.51
1.51
1.51
1.50
1.49
1.49
2.02
2.06
2.10
2.00
5.05
4.07
2.02
f1 (ppm)



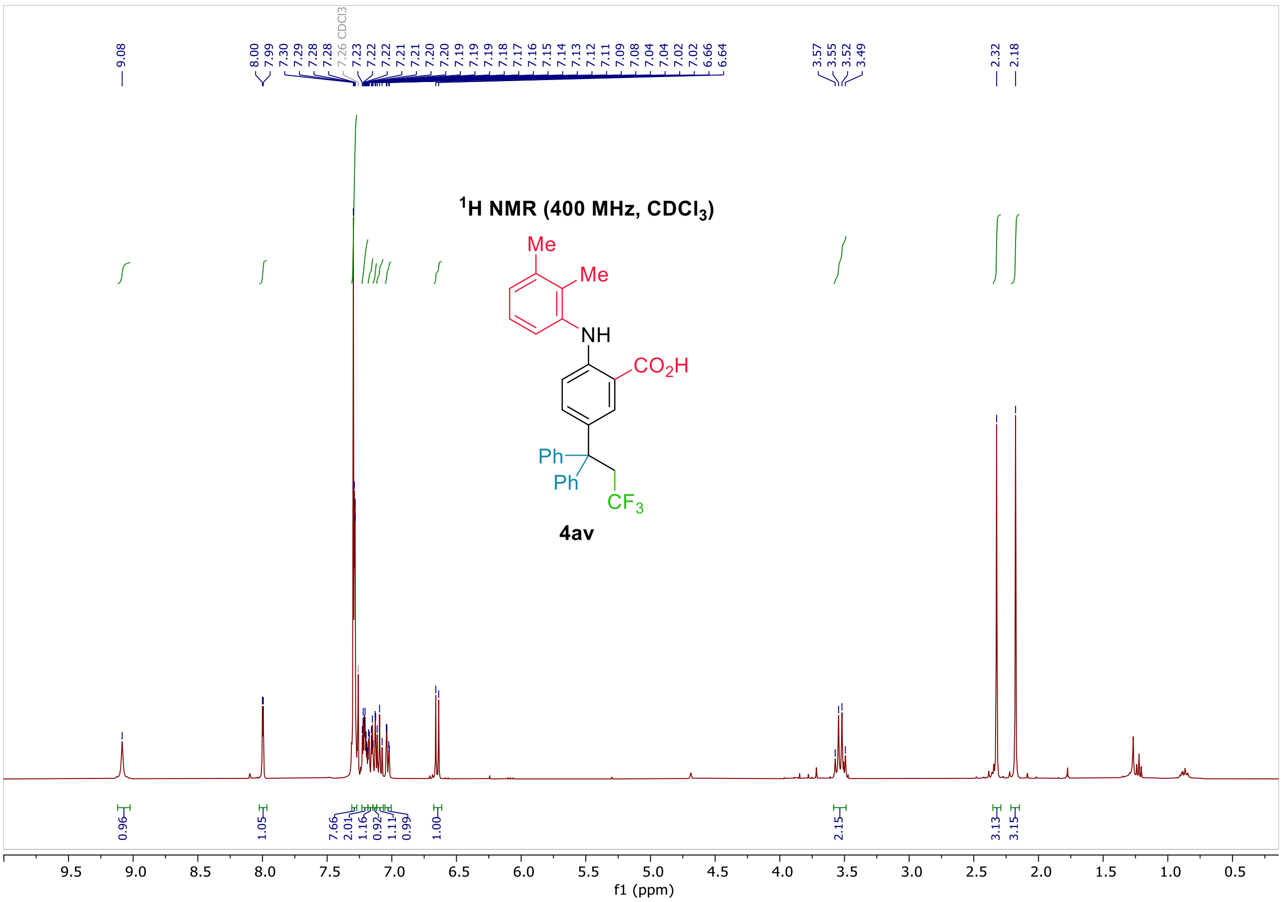
13C NMR (101 MHz, CDCl3)
NH2
CF3
MeO
7
158.02
144.14
137.34
135.37
131.40
128.63
128.58
125.90
123.15
115.70
114.10
113.98
113.88
77.48
77.16 CDCl3
76.84
55.33
49.48
35.15
34.21
33.93
33.65
33.37
20.73
20.70
20.67
20.64
f1 (ppm)

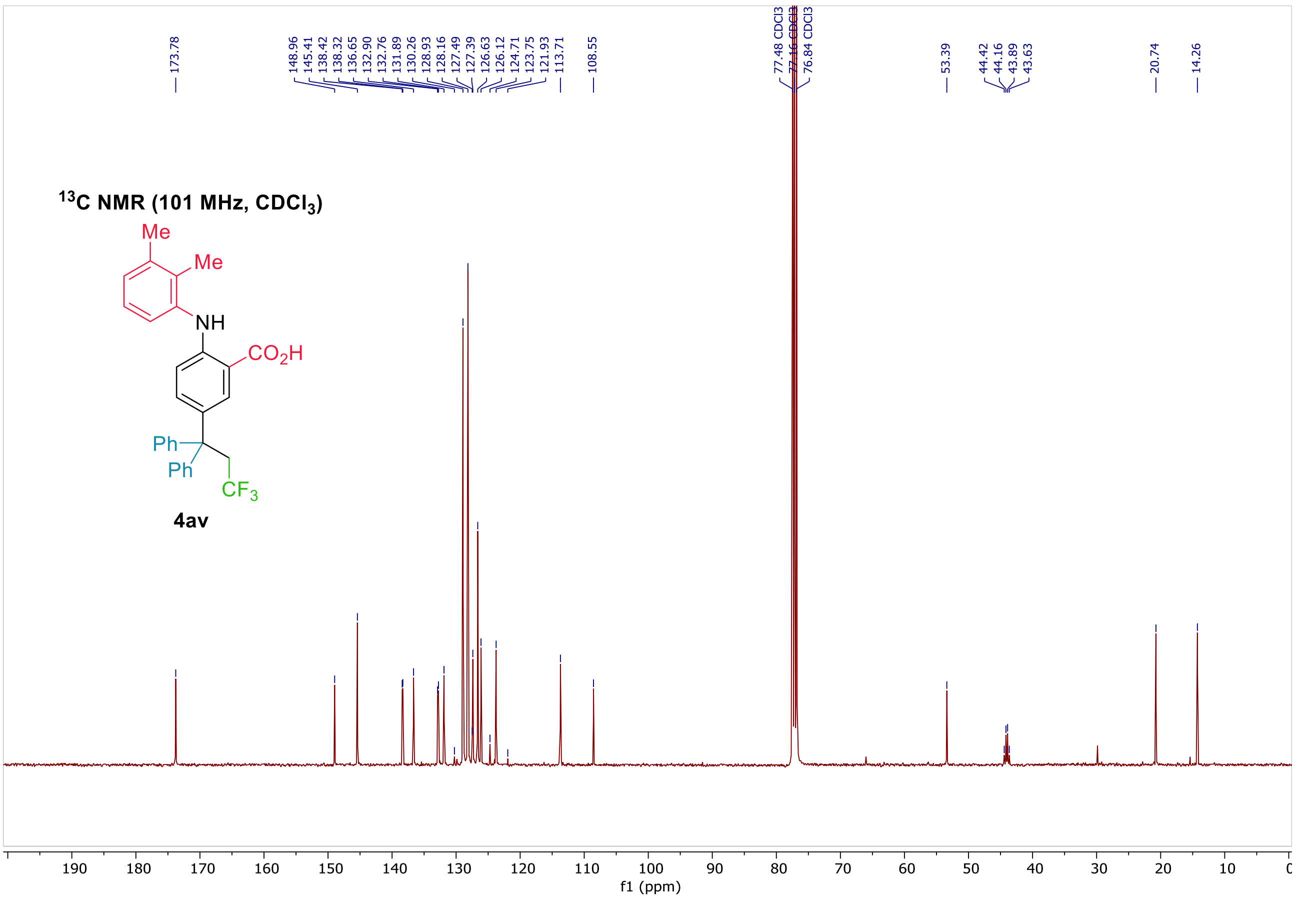


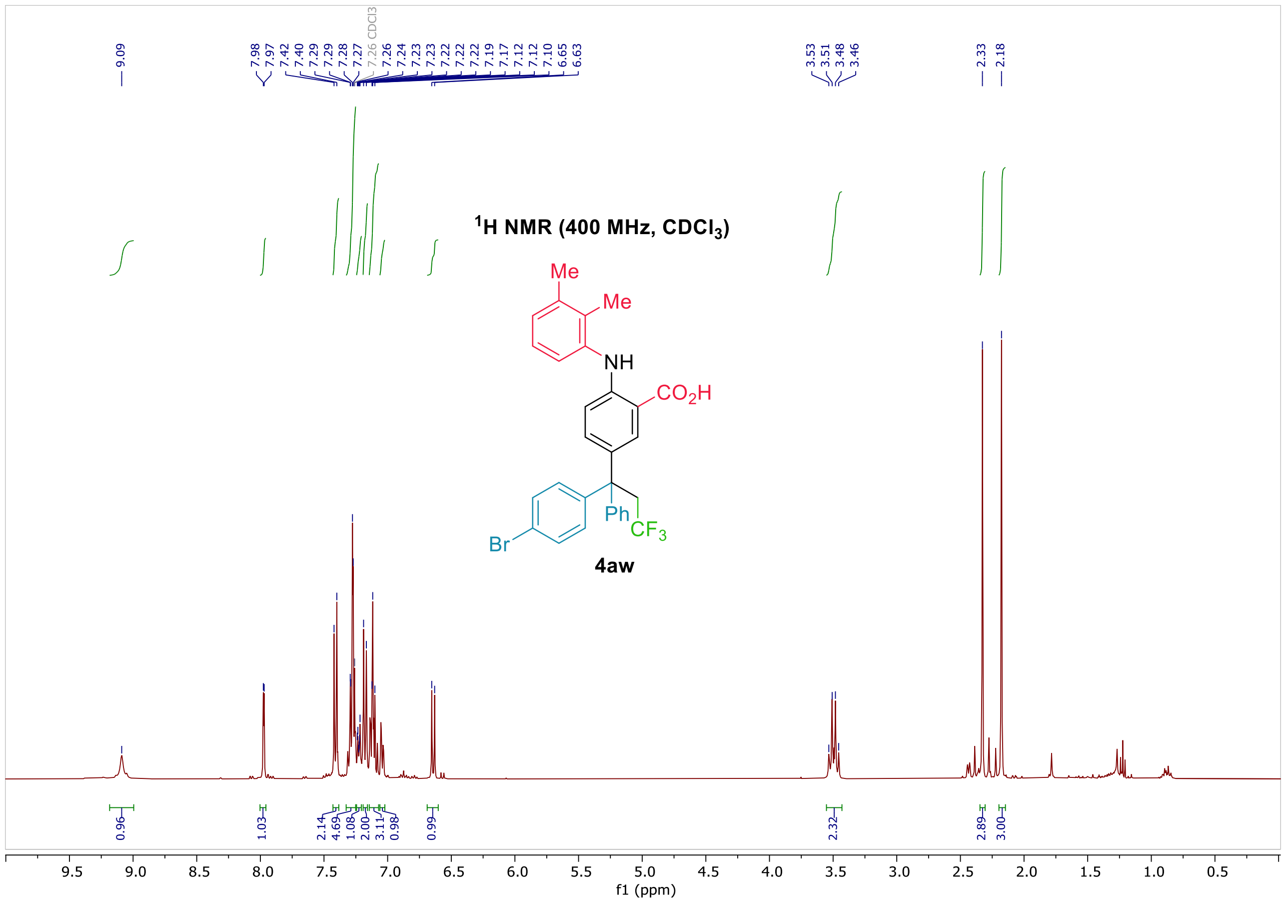
^{1}H NMR (400 MHz, CDCl$_3$)
NTs$_2$
HO
CF$_3$
O
8
4.19
6.16
2.10
1.00
6.43
3.25
1.04
2.08
f1 (ppm)

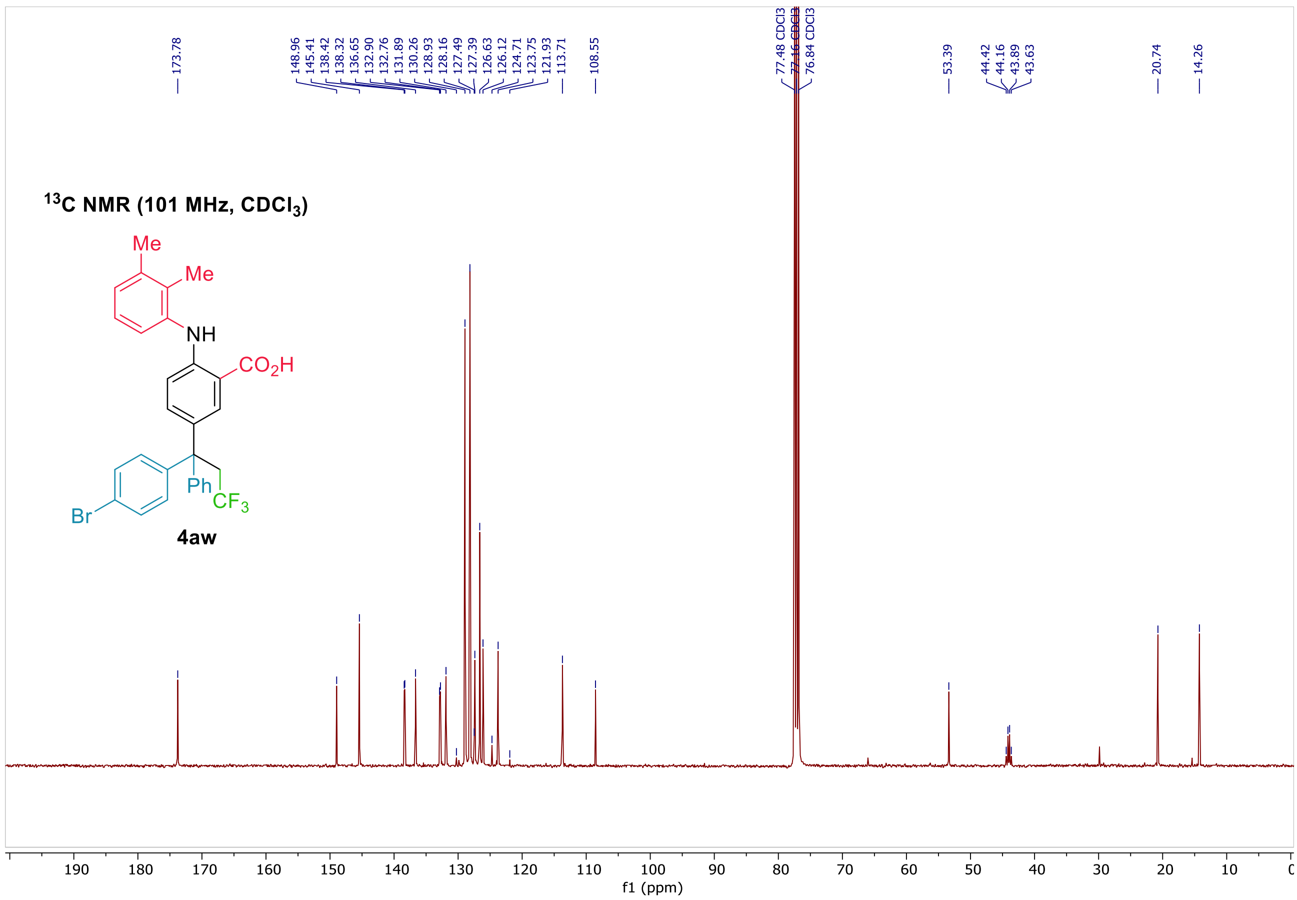


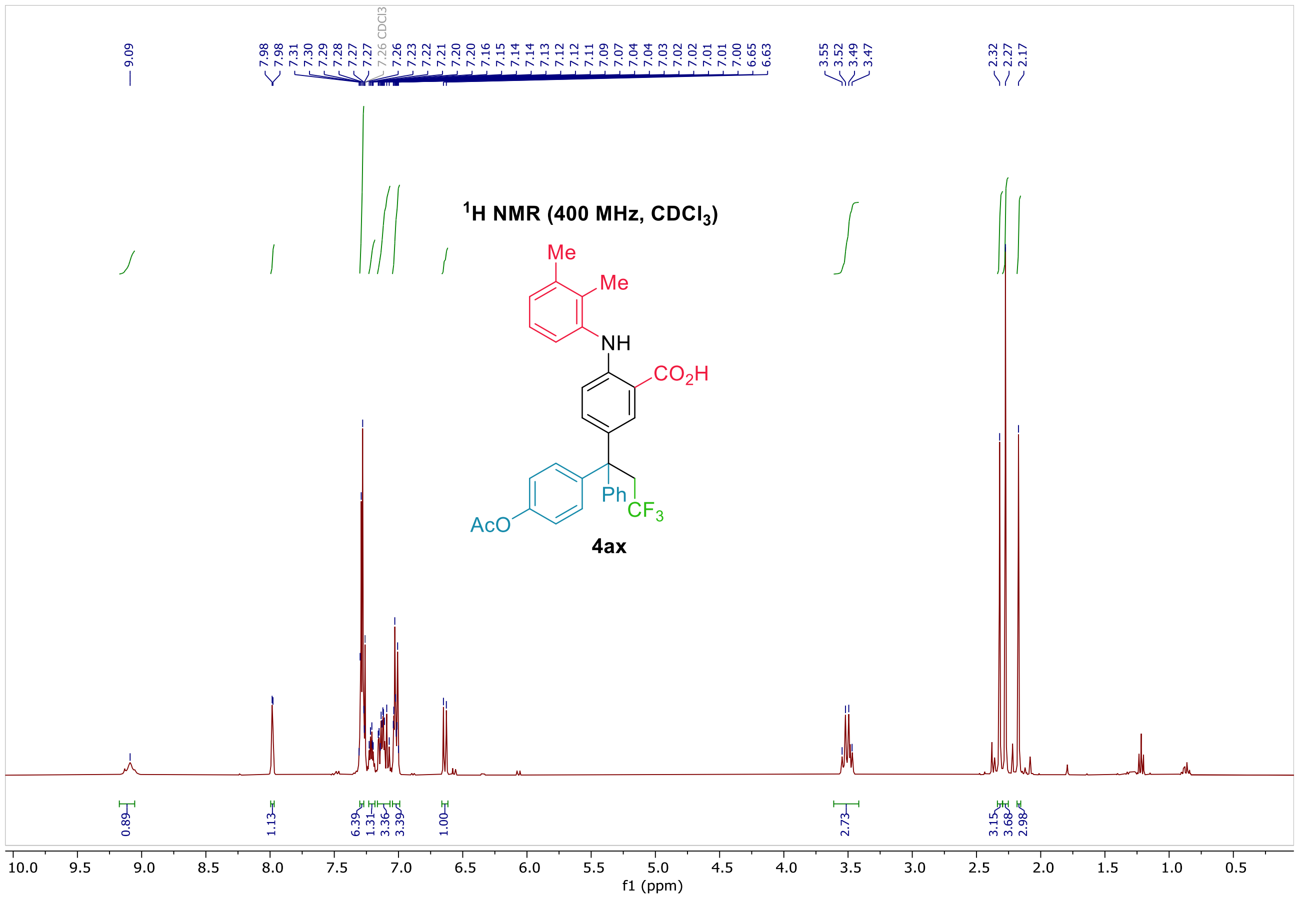
178.15
145.27
139.94
136.67
134.07
132.09
131.11
129.77
128.92
128.70
128.36
125.61
122.86
77.48
76.84
50.96
34.00
33.71
33.42
33.14
32.28
21.85
20.30
20.27
20.24
20.21
^{13}C NMR (101 MHz, CDCl$_3$)
NTs$_2$
HO
CF$_3$
O
8
f1 (ppm)


1H NMR (400 MHz, CDCl3)
Me
Me
NH
CO2H
Ph
Ph
CF3
4av
f1 (ppm)

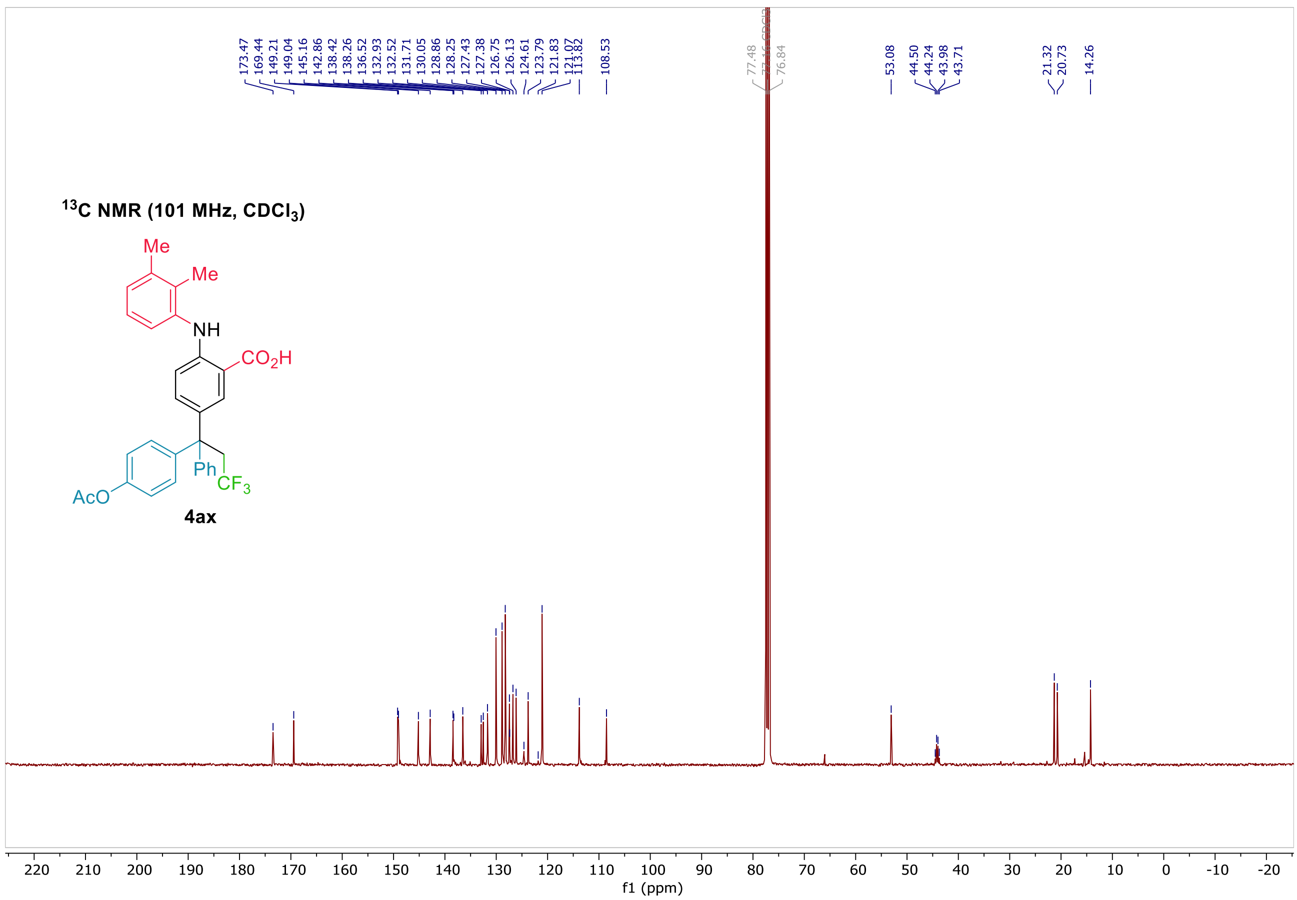

13C NMR (101 MHz, CDCl3)
Me
Me
NH
CO2H
Ph
Ph
CF3
4av
f1 (ppm)


1H NMR (400 MHz, CDCl3)
Me
Me
NH
CO2H
Br
Ph
CF3
4aw
f1 (ppm)

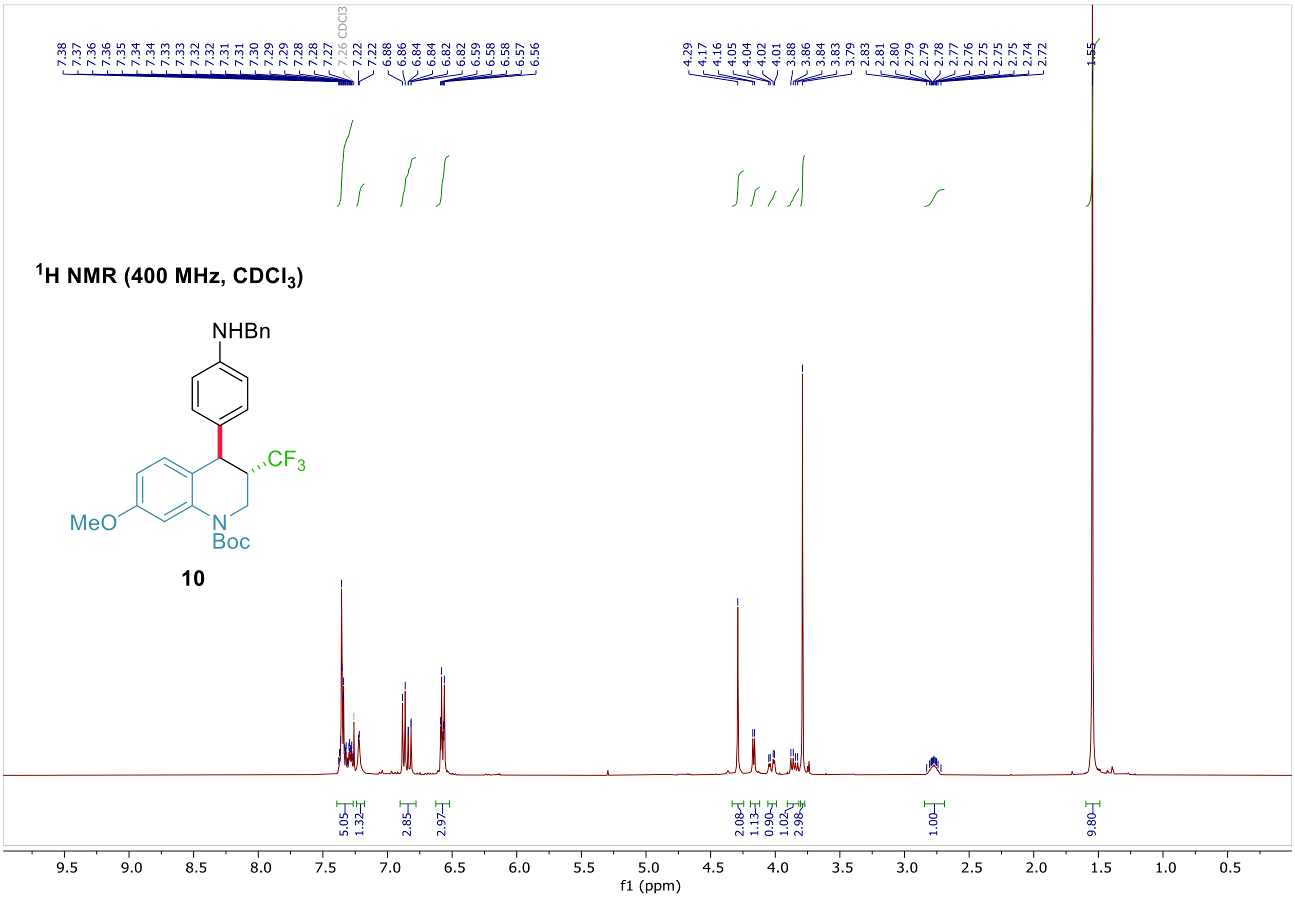

13C NMR (101 MHz, CDCl3)
Me
Me
NH
CO2H
Br
Ph
CF3
4aw
f1 (ppm)



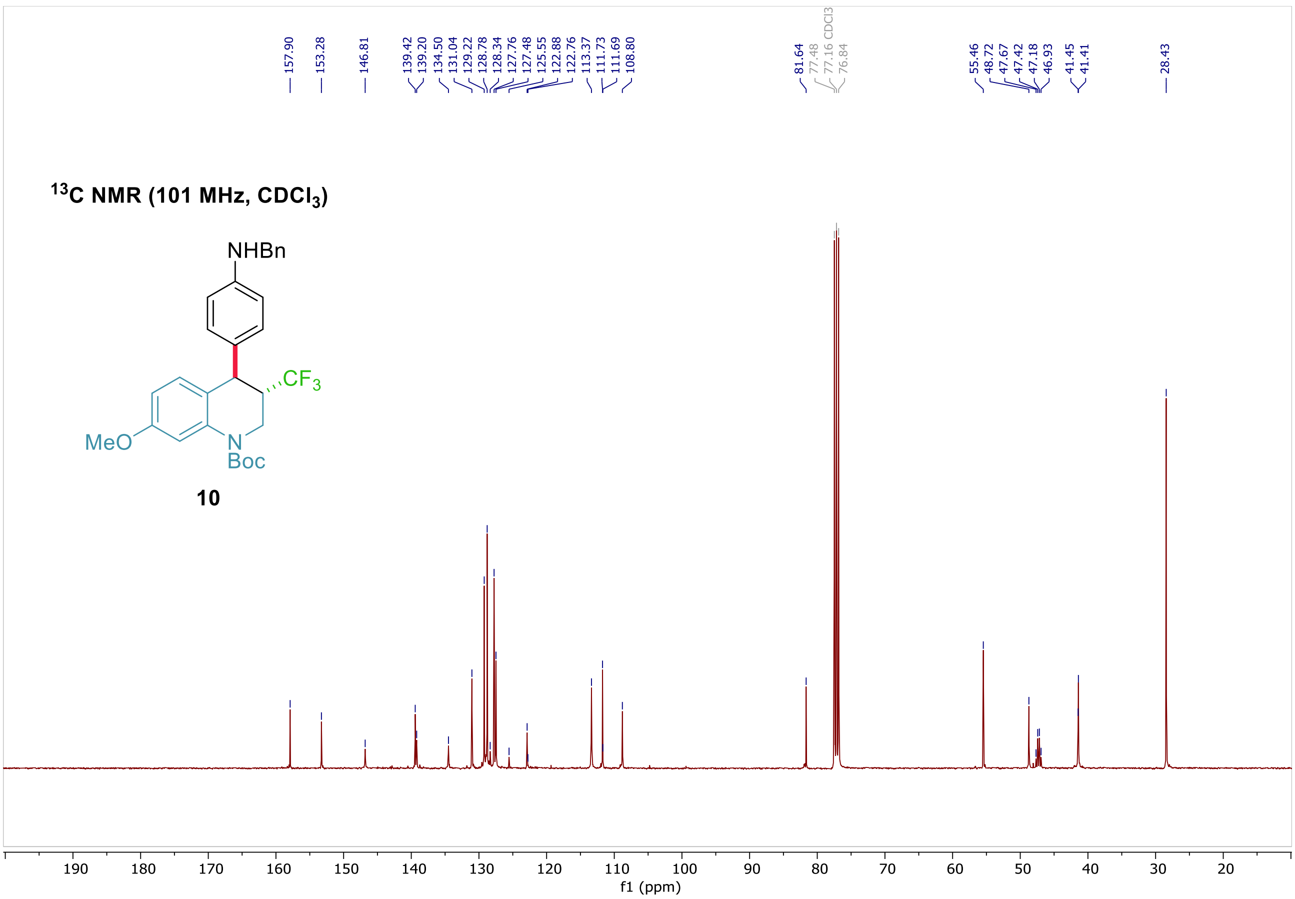
1H NMR (400 MHz, CDCl3)
Me
Me
NH
CO2H
Ph
CF3
AcO
4ax
f1 (ppm)



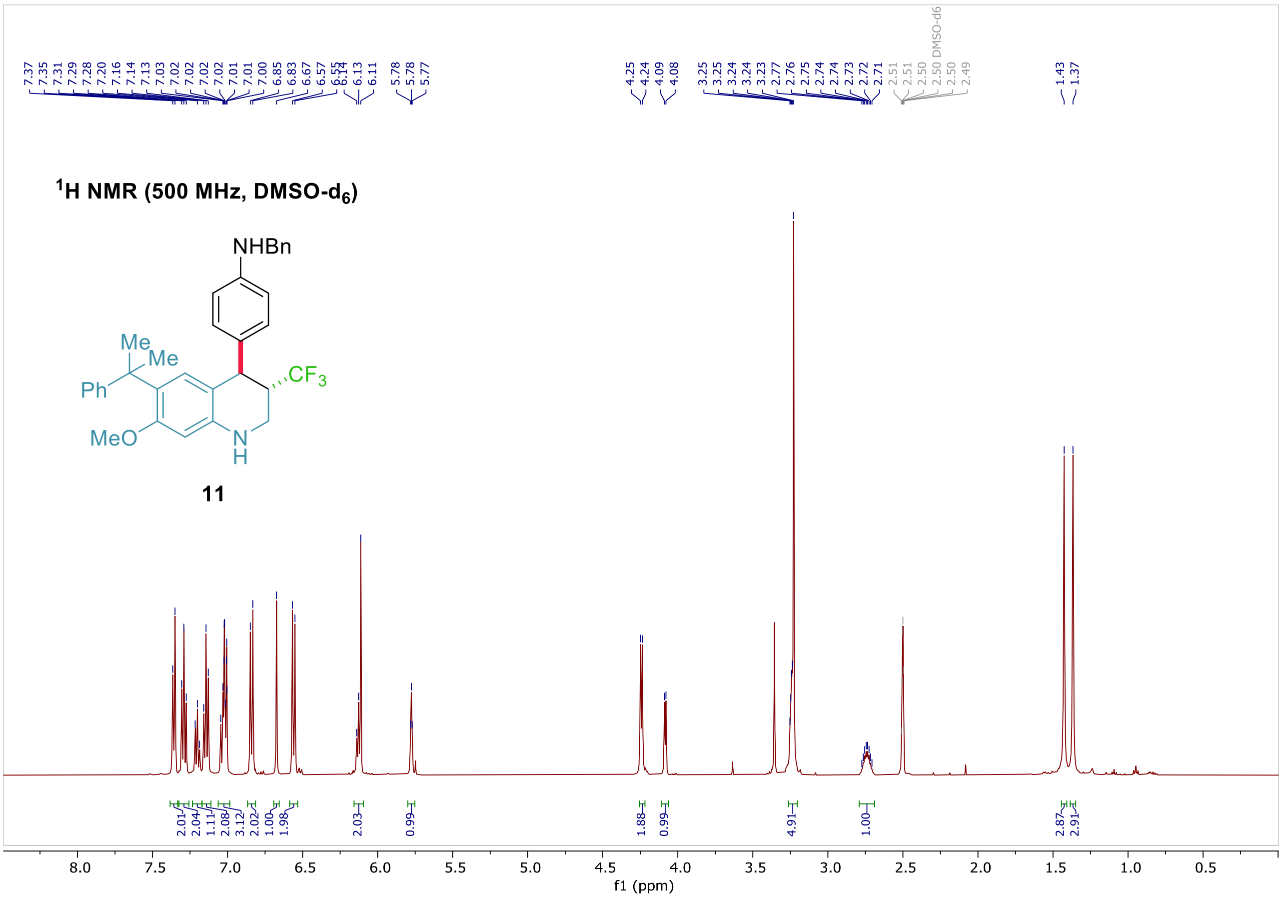
13C NMR (101 MHz, CDCl3)
Me
Me
NH
CO2H
Ph
CF3
AcO
4ax
f1 (ppm)

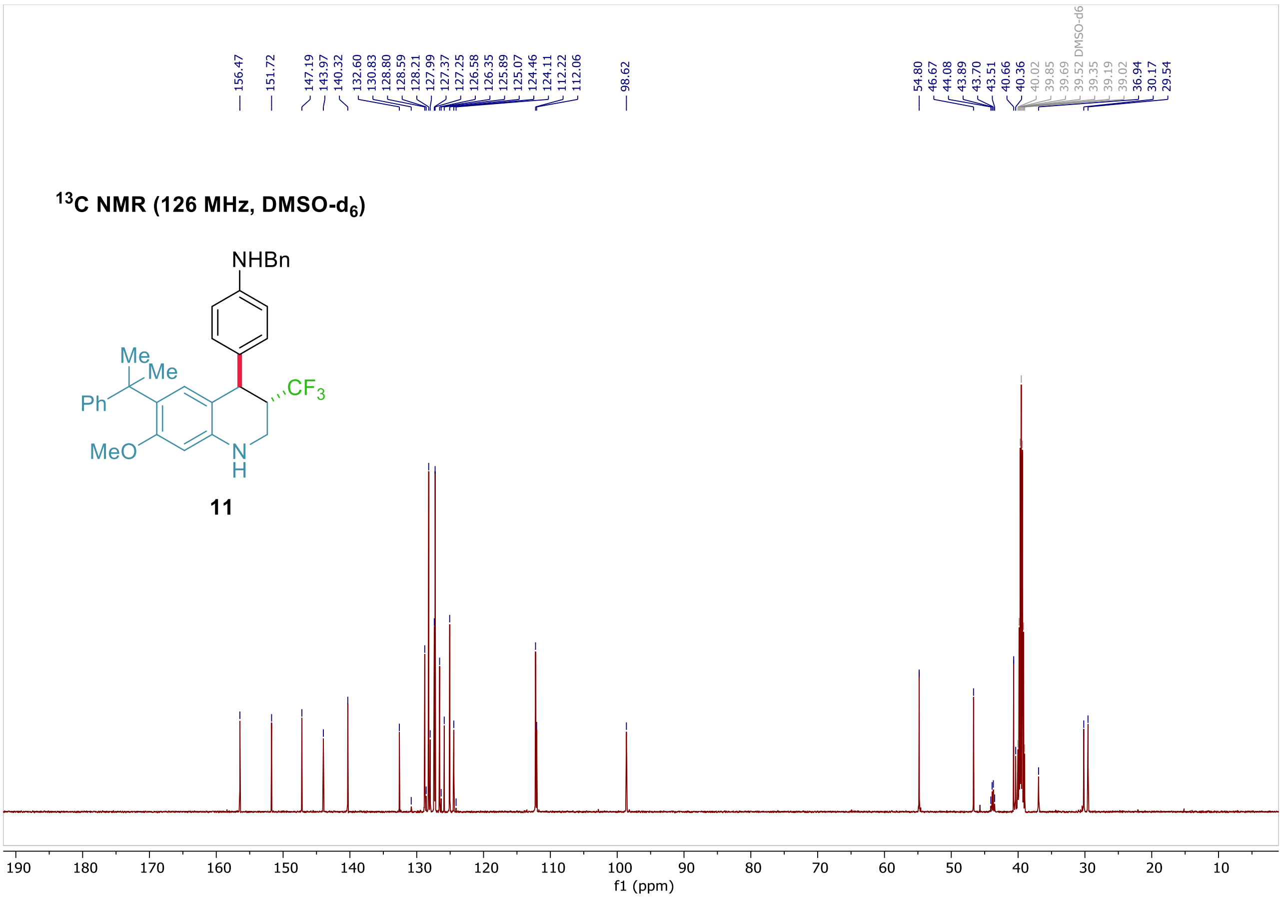


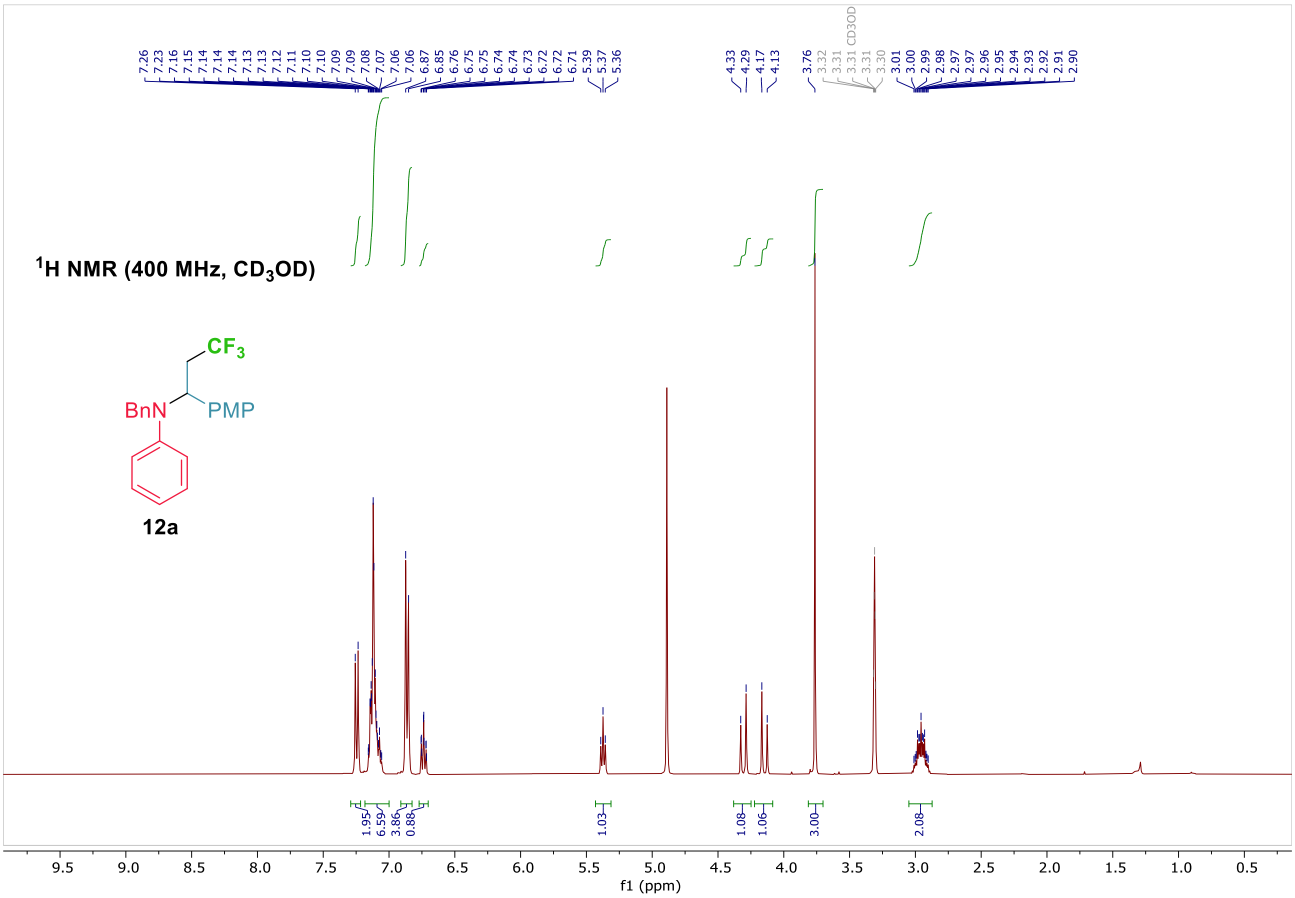
7.38
7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.26 CDCl3
7.22
7.22
6.88
6.86
6.84
6.84
6.82
6.82
6.59
6.58
6.58
6.57
6.56
4.29
4.17
4.16
4.05
4.04
4.02
4.01
3.88
3.86
3.84
3.83
3.79
2.83
2.81
2.80
2.79
2.79
2.78
2.77
2.76
2.75
2.75
2.75
2.74
2.72
1.55
1H NMR (400 MHz, CDCl3)
NHBn
CF3
MeO
N
Boc
10
5.05
1.32
2.85
2.97
2.08
1.13
0.90
1.02
2.98
1.00
9.80
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



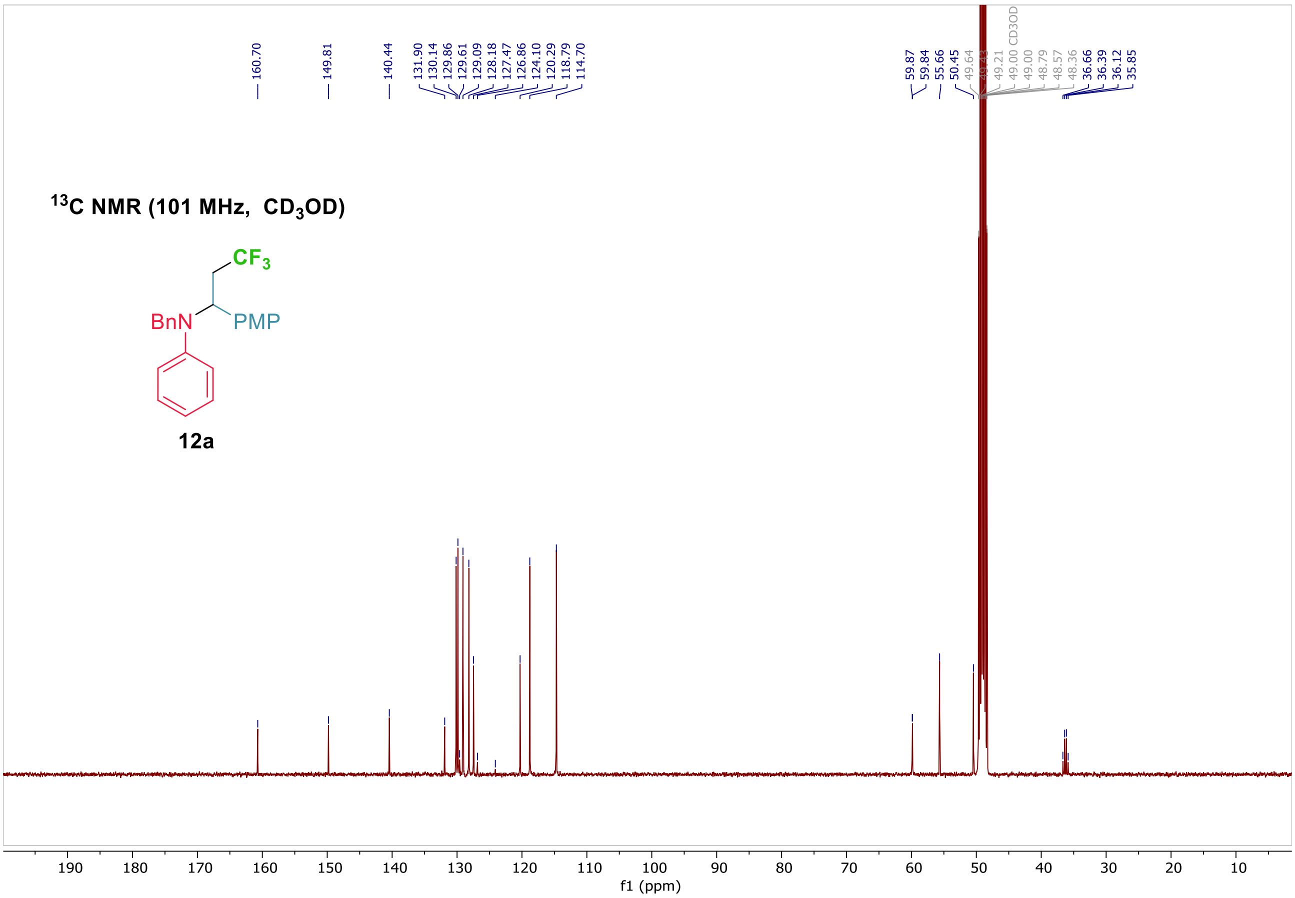
157.90
153.28
146.81
139.42
139.20
134.50
131.04
129.22
128.78
128.34
127.76
127.48
125.55
122.88
122.76
113.37
111.73
111.69
108.80
81.64
77.48
77.16 CDCl3
76.84
55.46
48.72
47.67
47.42
47.18
46.93
41.45
41.41
28.43
13C NMR (101 MHz, CDCl3)
NHBn
CF3
MeO
N
Boc
10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



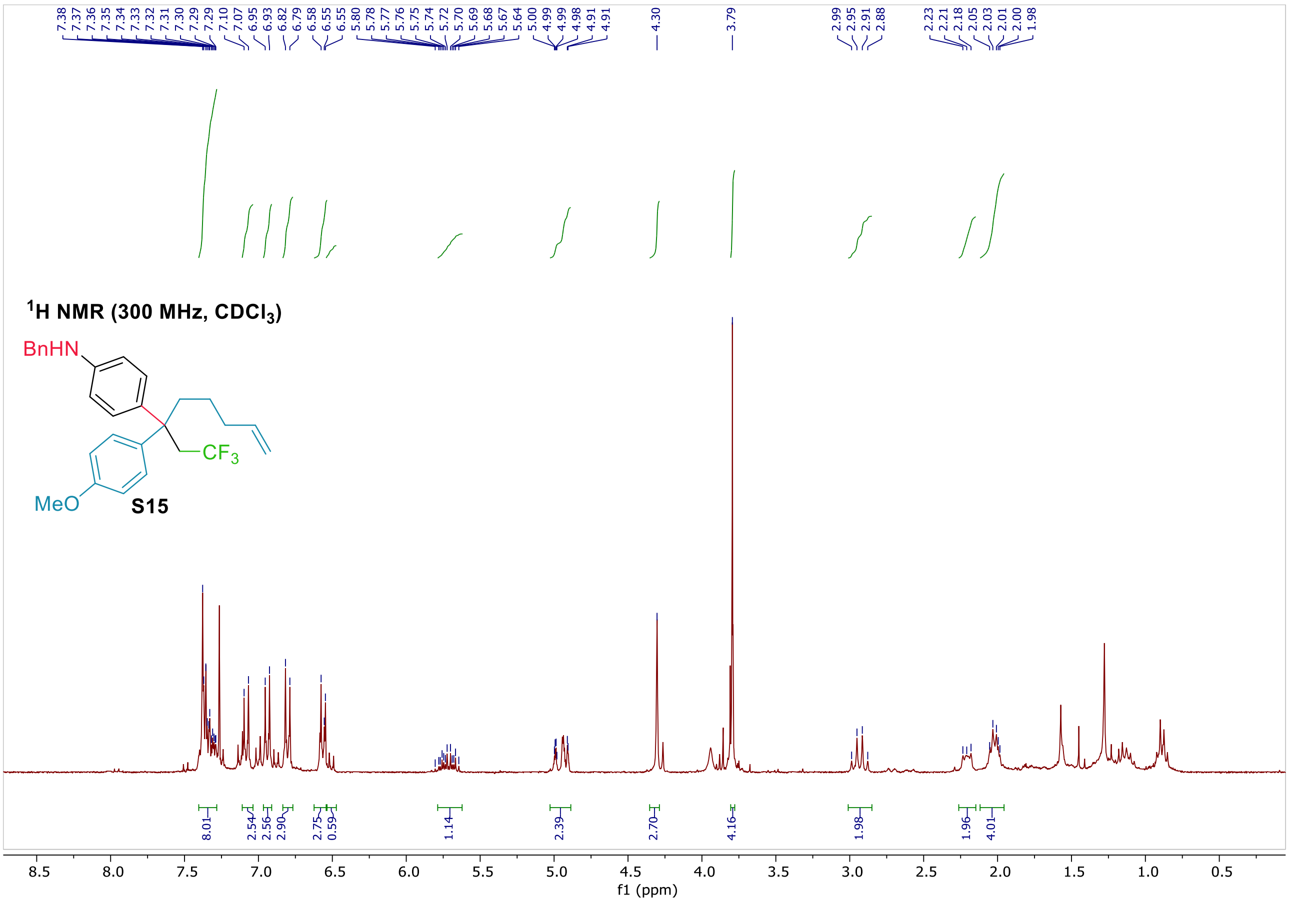




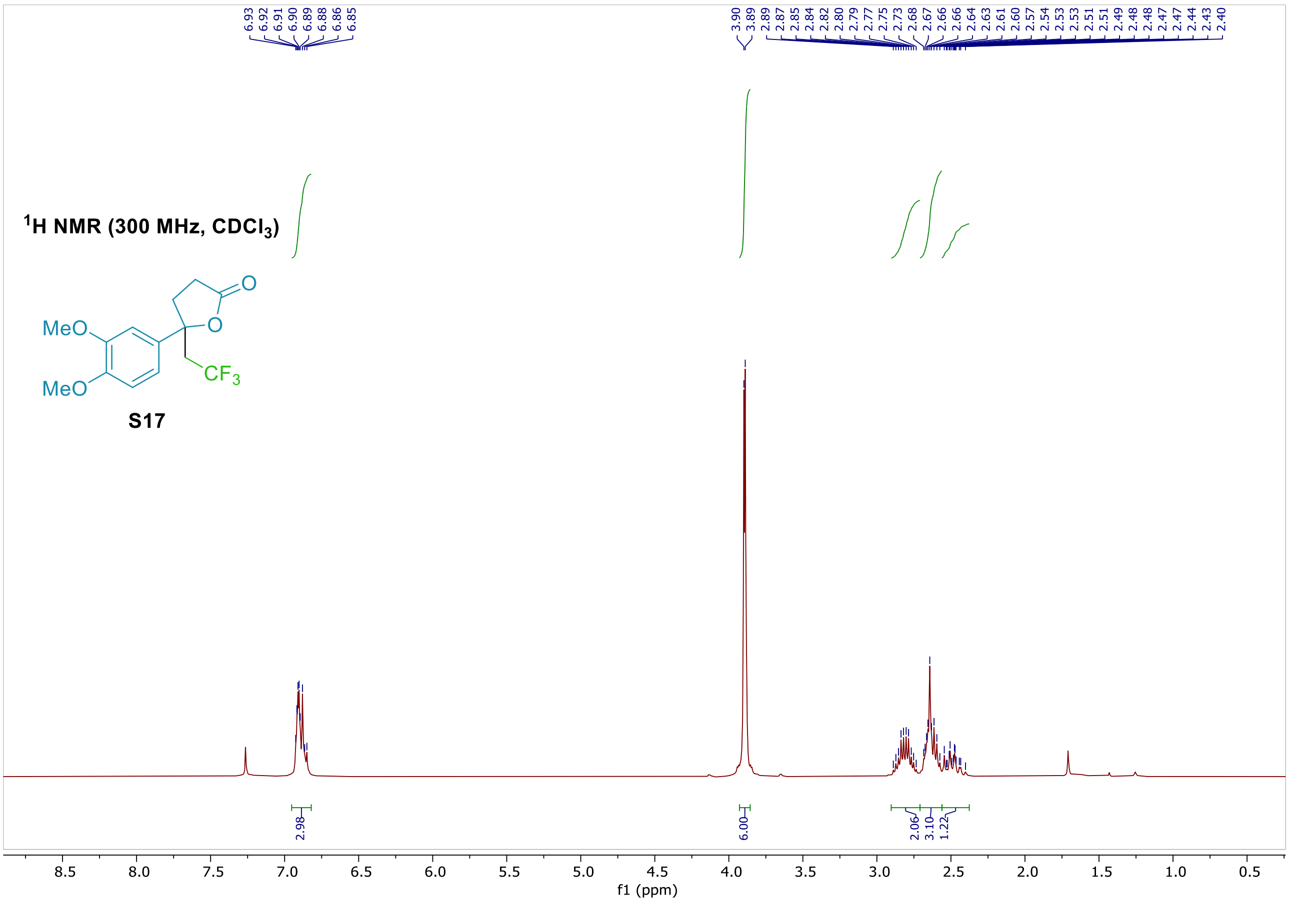
1H NMR (400 MHz, CD3OD)
CF3
BnN
PMP
12a
7.26 7.23 7.16 7.15 7.14 7.14 7.13 7.13 7.12 7.11 7.10 7.10 7.09 7.09 7.08 7.07 7.06 6.87 6.85 6.76 6.75 6.75 6.74 6.74 6.73 6.72 6.72 6.71 5.39 5.37 5.36
4.33 4.29 4.17 4.13 3.76 3.32 3.31 3.31 3.31 3.30 CD3OD
3.01 3.00 2.99 2.98 2.97 2.97 2.96 2.95 2.94 2.93 2.92 2.91 2.90
1.95 6.59 3.86 0.88 1.03 1.08 1.06 3.00 2.08
f1 (ppm)



13C NMR (101 MHz, CD3OD)
CF3
BnN
PMP
12a
160.70 149.81 140.44 131.90 130.14 129.86 129.61 129.09 128.18 127.47 126.86 124.10 120.29 118.79 114.70
59.87 59.84 55.66 50.45 49.64 49.21 49.00 49.00 48.79 48.57 48.36 CD3OD 36.66 36.39 36.12 35.85
f1 (ppm)



1H NMR (300 MHz, CDCl3)
BnHN
CF3
MeO
S15
7.38 7.37 7.36 7.35 7.34 7.33 7.32 7.31 7.30 7.29 7.29 7.10 7.07 6.95 6.93 6.82 6.79 6.58 6.55 6.55 5.80 5.78 5.77 5.76 5.75 5.74 5.72 5.70 5.69 5.68 5.67 5.64 5.00 4.99 4.99 4.98 4.91 4.91 4.30 3.79 2.99 2.95 2.91 2.88 2.23 2.21 2.18 2.05 2.03 2.01 2.00 1.98
8.01 2.54 2.56 2.90 2.75 0.59 1.14 2.39 2.70 4.16 1.98 1.96 4.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



1H NMR (300 MHz, CDCl3)
MeO
MeO
O
O
CF3
S17
6.93 6.92 6.91 6.90 6.89 6.88 6.86 6.85
3.90 3.89 2.89 2.87 2.85 2.84 2.82 2.80 2.79 2.77 2.75 2.73 2.68 2.67 2.66 2.66 2.64 2.63 2.61 2.60 2.57 2.54 2.53 2.53 2.51 2.49 2.48 2.48 2.47 2.44 2.43 2.40
2.98 6.00 2.06 3.10 1.22
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)