Sodium Borohydride: Repurposing From Reducing Agent to Reductive Cyclization Reagent for *N*-(2-Iodoaryl)Acrylamides

Naveen Sihag,[a] Mini Bharati Ahirwar,[b] Ankit Kumar,[a] Saleem Hafeez,[a] Milind M. Deshmukh*,[c] and M Ramu Yadav*,[a]

[a]Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, 110016, India. Phone number: (+91) 11-2659-1506; *e-mail* address: ramuyadav@chemistry.iitd.ac.in.

[b]Institute for Integrated Cell-Material Sciences, Kyoto University, Kyoto-Daigaku Katsura, Nishikyo-ku, Kyoto 615-8246, Japan

[c]Department of Chemistry, University of Delhi, Delhi, India. *e-mail* address: mdeshmukh@chemistry.du.ac.in

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1. General Information

Experimental: All the inert condition reactions were performed in a nitrogen atmosphere using Glove box and Schlenk line techniques. All glassware was oven-dried overnight at 100 ºC before use. Optimization, scope studies, and control experiments were performed in commercially available 7.0 mL screw cap vials fitted with PTFE/silicone septa purchased from Sigma-Aldrich.

Chromatography: Analytical Thin Layer Chromatography (TLC) was performed on Merck and GLR precoated silica gel 60 F_{254} plates, using UV light as the visualization agent. Chromatographic purification of products was accomplished by column chromatography on Finar silica gel (100-200 mesh). The solvents were removed under reduced pressure using a rotary evaporator to obtain the desired compounds.

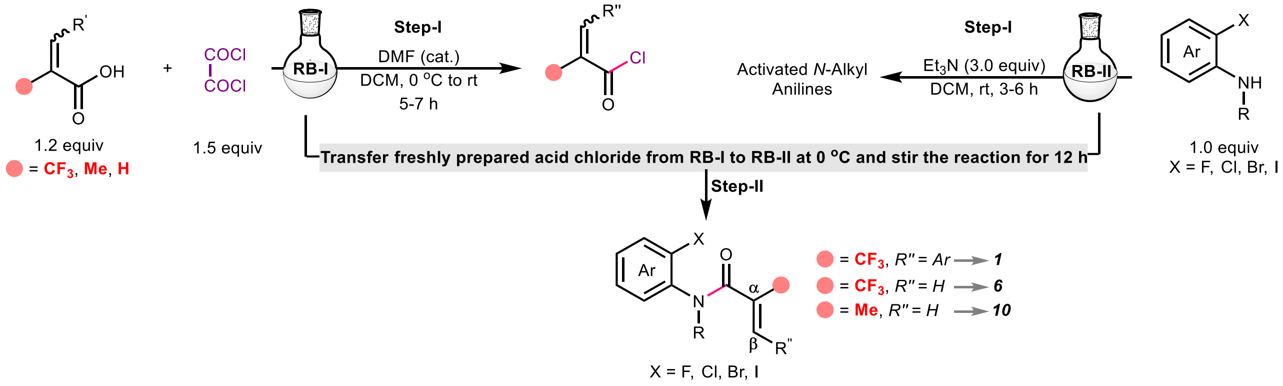
Characterization: All proton nuclear magnetic resonance spectra (^{1}H NMR), proton decoupled carbon nuclear magnetic resonance spectra [^{13}C{^{1}H} NMR], and fluorine nuclear magnetic resonance spectra (^{19}F NMR) were collected on Bruker Ascend 500 MHz and JEOL 400 MHz (the respective frequencies are for ^{1}H (500 MHz and 400 MHz), ^{13}C (126 MHz and 101 MHz), and ^{19}F (471 MHz and 377 MHz). Chemical shifts are reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm), all ^{1}H NMR and ^{13}C NMR spectra referenced to residual solvent signal (^{1}H, $CDCl_3$ = 7.26 ppm) and (^{13}C, $CDCl_3$ = 77.00 ppm). Coupling constants (*J*) are reported in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; dd, doublet of doublets; ddd, doublet of doublet of doublets; dq, doublet of quartet; dp, doublet of pentet; bs, broad singlet; bd, broad doublet; bt, broad triplet; bq, broad quartet; tq, triplet of quartet. High-resolution mass spectra (HRMS) were obtained using Waters Xevo-G2XQTOF instruments with the electrospray ionization (ESI) method. The gas chromatography-mass spectrometry (GC-MS) analysis was performed using an Agilent 5977B GC/MSD spectrometer. Single crystal X-ray diffractions were recorded using a Bruker AXS Smart Apex CCD diffractometer. Trace metal analysis was performed by ICP-MS (Agilent 7900). The melting points of compounds were recorded using the DIGITAL MELTING POINT APP. by UNITECH SALES.

Materials: Unless specified otherwise, used reagents, were obtained from commercial suppliers (BLD Pharma, Spectrochem, GLR, TCI, Sigma-Aldrich, SRL Chemical) and used without further purification. Acrylamide derivatives were synthesized according to the literature. Anhydrous solvents were dried using CaH_2 pre-drying followed by vacuum distillation. Solvents such as tetrahydrofuran (THF) and toluene (PhMe) were dried using conventional drying agents, including sodium wire and benzophenone. Oxalyl chloride was purchased from Spectrochem and distilled under N_2. Triethylamine was distilled and stored over KOH pellets for usage.

2. Synthesis of Substrates

2.1 General Procedure for the Synthesis of *o*-Halo Trifluoromethyl/methyl Acrylamides and *o*-Halo *β*-Phenyl Trifluoromethyl Acrylamides.

General Procedure I (GP I):



Scheme S1. Synthesis of *o*-halo *α*- & *β*-substituted acrylamides.

Step 1. Round Bottom Flask I (RB–I): A two−necked round bottom flask equipped with a magnetic stir bar was charged with acrylic acid[1a] (1.2 equiv), and dry DCM (0.2 M) was added under a nitrogen atmosphere. The flask was then cooled to 0 °C using an ice bath, and freshly distilled oxalyl chloride (1.5 equiv with respect to acrylic acid) was added dropwise to the solution. Afterward, 2-4 drops of dry DMF were added, and the in situ-generated gases were removed by keeping an empty balloon. The solution was slowly allowed to attain room temperature and stirred for 5 to 7 hours with a nitrogen (N_2) balloon until the solution turned yellow-orange. The acyl chloride was used directly for the next step without further purification.

Round Bottom Flask II (RB–II): In a separate two-necked round-bottom flask equipped with a magnetic stir bar, *o*-halo aniline derivatives (1.0 equiv), triethylamine (3.0 equiv), and dry DCM (0.2 M) were added and stirred for 3-6 h at room temperature to activate anilines.

Step 2. Then, freshly prepared acryloyl chloride **RB–I** was added dropwise to **RB–II** for 10 to 15 minutes at 0 °C under a nitrogen atmosphere. The resultant mixture was allowed to warm up to room temperature and stirred overnight with a nitrogen (N_2) balloon until the aniline derivative was completely consumed (monitored by TLC). The reaction mixture was washed with water and extracted with DCM (3.0 times). The organic layer was sequentially washed with 1.0 N HCl solution, 1.0 N NaOH solution, and brine. The final organic solution was dried over anhydrous Na_2SO_4, filtered, and concentrated using a rotary evaporator. The residue was purified by SiO_2 column chromatography (100−200 mesh) using a mixture of hexane, DCM, and ethyl acetate to afford the desired acrylamides.

Acrylamides **1a**, **1c**, **1d, 1e, 1o**, **1p**, and **1u** were prepared according to the previous reports.[1b, 1c,1d] All known substrate characterization data were consistent with the reported literature.

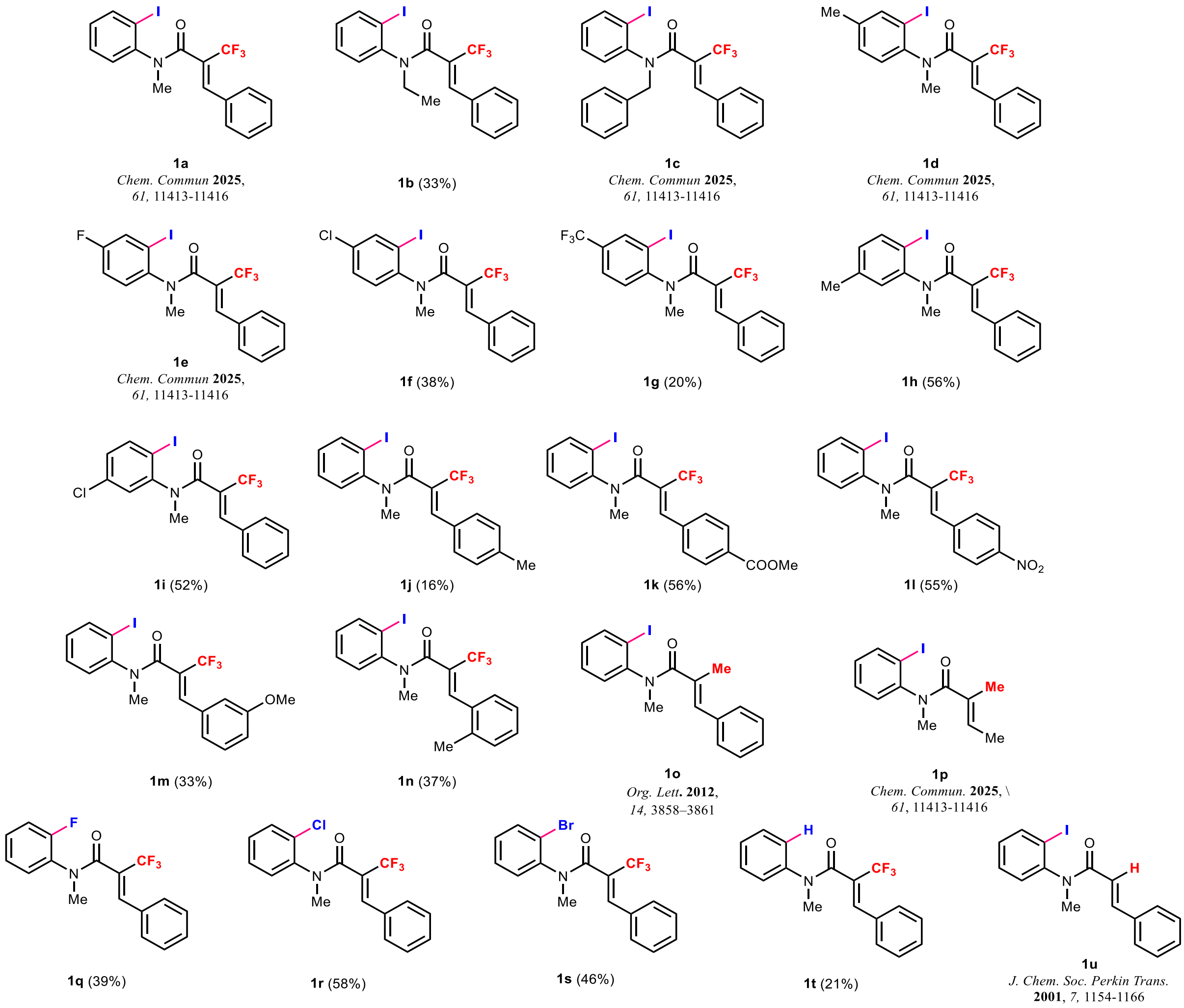
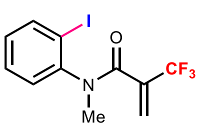
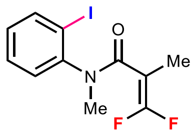


Figure S1. *N*−(2−Haloaryl)−*N*−substituted *β*-phenyl trifluoromethyl/methyl acrylamides.

Acrylamides **6**, **7**, **8,** and **10a-10k** were prepared according to the previous reports.[1b,2] All known substrate characterization data were consistent with the reported literature.



6
Chem. Commun. **2025**, *61*, 11413-11416



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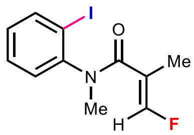

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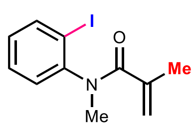

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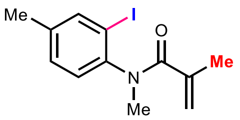
Org. Chem. Front. **2023**, *10*, 1289-1295



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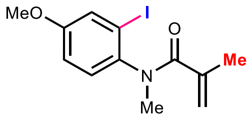

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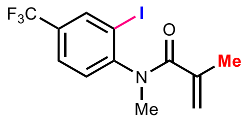

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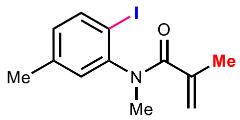

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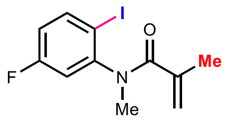

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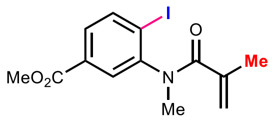

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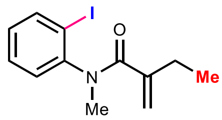

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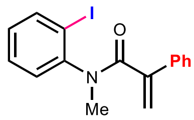

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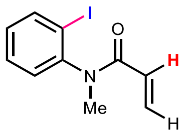
Chem. Commun. **2015**, *51*, 14862-14865



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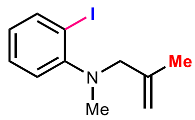
Org. Lett. **2013**, *15*, 550–553

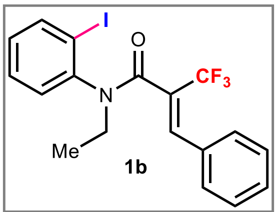


10k
J. Org. Chem. **2023**, *88*, 5097-5107

Figure S2. *N*−(2−iodoaryl)−*N*−methyl acrylamides.

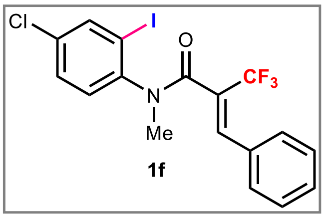
Characterization data of starting materials:

***(Z)-N*-Ethyl-*N*-(2-iodophenyl)-3-phenyl-2-(trifluoromethyl)acrylamide (1b):**



According to **GP-I**, amide coupling of 3-phenyl-2-(trifluoromethyl) acrylic acid[1a] (1.30 g, 6.0 mmol, used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with *N*-ethyl-2-iodoaniline (1.24 g, 5.0 mmol) afforded the desired amide **1b** (737.1 mg) in 33% yield as a white solid; R_f = 0.50 (3% EtOAc, 30% DCM in hexane); Melting point: 87–89 ºC. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.39 (td, *J* = 7.7, 1.4 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.13 – 7.02 (m, 4H), 4.39 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.31 (dq, *J* = 14.1, 7.1 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)** δ 164.8 (bq, *J* = 2.4 Hz), 143.7, 140.5, 139.4 (bq, *J* = 4.5 Hz), 132.4, 131.3, 129.9, 129.5, 129.3, 128.7 (bs; supposed to be quartet but not split clearly), 128.2, 126.4 (q, *J* = 32.0 Hz), 121.7 (q, *J* = 275.7 Hz), 99.4, 43.8, 12.0; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -56.7; **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{18}H_{16}F_3INO$: 446.0223, found 446.0210.

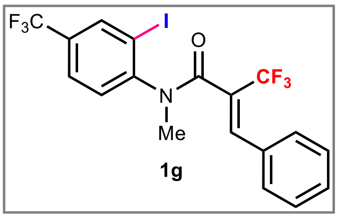
(*Z*)-*N*-(4-Chloro-2-iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl) acrylamide (1f):



According to **GP-I**, amide coupling of 3-phenyl-2-(trifluoromethyl) acrylic acid[1a] (1.04 g, 4.8 mmol, used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with 4-chloro-*N*-methyl-2-iodoaniline (1.07 g, 4.0 mmol) afforded the desired amide **1f** (698.5 mg) in 38% yield as a white solid; $R_f = 0.43$ (3% EtOAc, 30% DCM in hexane); Melting point: 75–77 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, $J = 2.3$ Hz, 1H), 7.38 (dd, $J = 8.4$, 2.3 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.19 – 7.11 (m, 4H), 3.32 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 165.3 (bq, $J = 1.9$ Hz), 144.5, 140.3 (bq, $J = 3.7$ Hz), 139.7, 134.8, 132.1, 130.3, 130.1, 129.7, 128.9 (bq, $J = 1.9$ Hz; quartet not split clearly), 128.4, 126.1 (q, $J = 32.8$ Hz), 121.5 (q, $J = 275.0$ Hz), 98.8, 36.8; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -56.5; **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{17}H_{13}ClF_3INO$: 465.9677, found 465.9684.

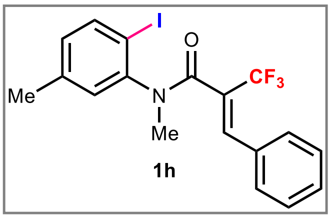
(*Z*)-*N*-(4-Trifluoromethyl-2-iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)-acrylamide (1g):



According to **GP-I**, amide coupling of 3-phenyl-2-(trifluoromethyl) acrylic acid[1a] (1.30 g, 6.0 mmol, used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with 4-trifluoromethyl-*N*-methyl-2-iodoaniline (1.51 g, 5.0 mmol) afforded the desired amide **1g** (510.2 mg) in 20% yield as a white solid; $R_f = 0.43$ (3% EtOAc, 30% DCM in hexane); Melting point: 73–75 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.41 – 7.27 (m, 4H), 7.15 (s, 1H), 7.13 – 7.03 (m, 2H), 3.36 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 165.1 (q, $J = 1.4$ Hz; quartet not split clearly), 149.1, 140.7 (q, $J = 3.1$ Hz), 137.5 (bq, $J = 3.2$ Hz), 131.9, 131.88 (q, $J = 33.5$), 130.1, 129.8, 128.8, 128.4, 127.0 (q, $J = 3.4$ Hz), 125.9 (q, $J = 32.6$ Hz), 122.3 (q, $J = 273.0$ Hz), 121.5 (q, $J = 274.8$ Hz), 98.5, 36.7; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -56.6, -62.6; **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{18}H_{13}F_6INO$: 499.9941, found 499.9945.

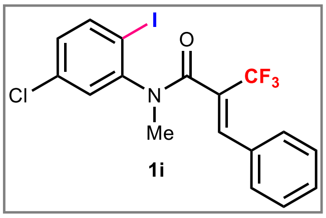
(*Z*)-*N*-(5-Methyl-2-iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl) acrylamide (1h):



According to **GP-I**, amide coupling of 3-phenyl-2-(trifluoromethyl) acrylic acid[1a] (1.30 g, 6.0 mmol, used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with 5-methyl-*N*-methyl-2-iodoaniline (1.14 g, 5.0 mmol) afforded the desired amide **1h** (1.25 g) in 56% yield as a white solid; R_f = 0.43 (3% EtOAc, 30% DCM in hexane); Melting point: 101−103 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.23 (m, 3H), 7.17 – 7.03 (m, 4H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.33 (s, 3H), 2.28 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 165.5 (bq, *J* = 2.3 Hz), 145.6, 140.6, 140.0, 139.8 (q, *J* = 3.8 Hz), 132.4, 130.9, 130.5, 129.4, 128.8 (bq, *J* = 2.3 Hz), 128.3, 126.2 (q, *J* = 32.5 Hz), 121.6 (q, *J* = 274.7 Hz), 94.0, 36.7, 20.7; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -56.7; **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{18}H_{16}F_3INO$; 446.0223, found 446.0216.

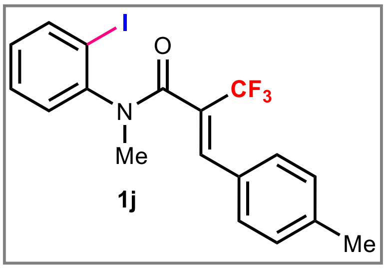
(*Z*)-*N*-(5-Chloro-2-iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl) acrylamide (1i):



According to **GP-I**, amide coupling of 3-phenyl-2-(trifluoromethyl)acrylic acid[1a] (1.04 g, 4.8 mmol used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound, with 5-Chloro-2-iodo-*N*-methylaniline (1.07 g, 4.0 mmol), afforded the desired amide **1i** (968.0 mg) in 52% yield as a white solid; R_f = 0.40 (3% EtOAc, 30% DCM in hexane); Melting point: 105−107 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 1H), 7.35 – 7.24 (m, 4H), 7.20 – 7.10 (m, 3H), 7.08 (dd, *J* = 8.3, 1.7 Hz, 1H), 3.33 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 165.2 (bq, *J* = 1.8 Hz; quartet not split clearly), 146.7, 141.0, 140.3 (bq, *J* = 3.6 Hz), 135.7, 132.1, 130.22, 130.15, 129.7, 128.9 (bq, *J* = 1.4 Hz; quartet not split clearly), 128.4, 126.1 (q, *J* = 32.9 Hz), 121.5 (q, *J* = 275.0 Hz), 95.8, 36.7; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -56.6; **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{17}H_{13}ClF_3INO$; 465.9677, found 465.9691.

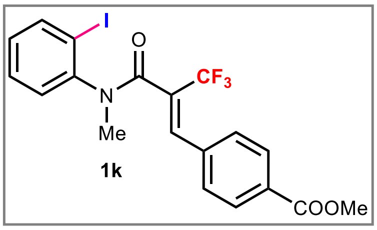
(*Z*)-*N*-(2-Iodophenyl)-*N*-methyl-3-(*p*-tolyl)-2-(trifluoromethyl)acrylamide (1j):



According to **GP-I**, amide coupling of 3-(4-methyl)-2-(trifluoromethyl)acrylic acid[1a] (828.7 mg, 3.6 mmol, used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with 2-iodo-*N*-methylaniline (699.0 mg, 3.0 mmol) afforded the desired amide **1j** (213.2 mg) in 16% yield as a colorless semi-solid; R_f = 0.40 (3% EtOAc, 30% DCM in hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.38 (td, *J* = 7.8, 1.1 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.14 – 6.97 (m, 6H), 3.34 (s, 3H), 2.30 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 165.6 (q, *J* = 6.1 Hz), 145.8, 140.3, 140.1 (q, *J* = 4.4 Hz), 139.9, 129.9, 129.8, 129.7, 129.3, 128.98 (q, *J* = 3.0 Hz; one ^{13}C value merged with this quartet), 125.0 (bq, *J* = 32.6 Hz), 121.7 (q, *J* = 274.7 Hz), 98.3, 36.7, 21.2; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -56.7; **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{18}H_{16}F_3INO$; 446.0223, found 446.0222.

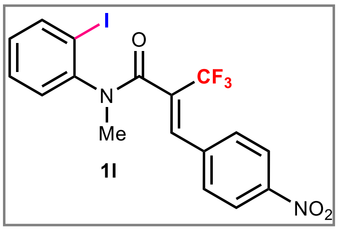
Methyl-(*Z*)-4-(3,3,3-trifluoro-2-((2-iodophenyl)(methyl)carbamoyl)prop-1-en-1-yl)benzoate (1k):



According to **GP-I**, amide coupling of 3-(4-(methoxycarbonyl)phenyl)-2-(trifluoromethyl)acrylic acid[1a] (987.1 mg, 3.6 mmol used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with 2-Iodo-*N*-methylaniline (699.0 mg, 3.0 mmol) afforded the desired amide **1k** (827.0 mg) in 56% yield as a white solid; R_f = 0.25 (3% EtOAc, 30% DCM in hexane); Melting point: 100−102 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.18 (s, 1H), 7.13 – 7.06 (m, 3H), 3.89 (s, 3H), 3.36 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 166.3, 164.8 (bq, *J* = 2.2 Hz), 145.5, 140.4, 138.7 (q, *J* = 3.7 Hz), 136.8, 130.6, 130.1, 130.0, 129.8, 129.4, 128.4 (bq, *J* = 2.2 Hz), 128.0 (q, *J* = 32.4 Hz), 121.3 (q, *J* = 275.1 Hz), 98.4, 52.2, 36.7; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -56.5; **HRMS (ESI−TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{19}H_{15}F_3INO_3Na$: 511.9941, found 511.9954.

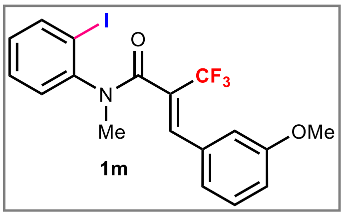
(*Z*)-*N*-(2-Iodophenyl)-*N*-methyl-3-(4-nitrophenyl)-2-(trifluoromethyl)acrylamide (1l):



According to **GP-I**, amide coupling of 2-(Trifluoromethyl)-3-(4-(nitro)phenyl)acrylic acid[1a] (877.5 mg, 3.36 mmol used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with 2-Iodo-*N*-methylaniline (652.5 mg, 2.8 mmol) afforded the desired amide **1l** (728.0 mg) in 55% yield as a white solid; R_f = 0.27 (3% EtOAc, 30% DCM in hexane); Melting point: 73–75 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 – 8.10 (m, 2H), 8.0 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.44 (td, *J* = 7.7, 1.4 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.21 – 7.09 (m, 3H), 3.36 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 164.2 (q, *J* = 2.0 Hz), 147.9, 145.3, 140.5, 138.8, 137.1 (q, *J* = 3.9 Hz), 130.3, 130.1, 129.8 (bq, *J* = 0.8 Hz), 129.6 (q, *J* = 32.6 Hz), 129.2 (q, *J* = 2.3 Hz), 123.5, 121.0 (q, *J* = 275.3 Hz), 98.5, 36.7; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -56.4; **HRMS (ESI−TOF)** ***m/z***: $[M+H]^+$ calcd. for $C_{17}H_{13}F_3IN_2O_3$; 476.9917, found 476.9916.

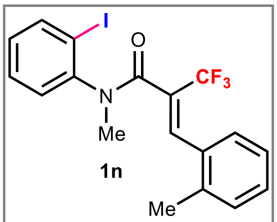
***(Z)*-*N*-(2-Iodophenyl)-3-(3-methoxyphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (1m):**



According to **GP-I**, amide coupling of 3-(3-methoxyphenyl)-2-(trifluoromethyl) acrylic acid[1a] (1.48 g, 6.0 mmol, used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with *N*-methyl-2-iodoaniline (1.17 g, 5.0 mmol) afforded the desired amide **1m** (922.4 mg) in 40% yield as a white solid; R_f = 0.35 (3% EtOAc, 30% DCM in hexane); Melting point: 51–53 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.38 (td, *J* = 7.1, 1.0 Hz, 1H), 7.23 (bd, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.12 (bs, 1H), 7.04 (td, *J* = 7.8, 1.5 Hz, 1H), 6.81 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 6.60 (bs, 1H), 3.70 (s, 3H), 3.32 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 165.1 (q, *J* = 2.4 Hz), 159.1, 145.5, 140.2, 139.8 (q, *J* = 3.8 Hz), 133.3, 129.84, 129.83, 129.6, 129.2, 126.2 (q, *J* = 32.4 Hz), 121.4 (q, *J* = 274.8 Hz), 121.0 (q, *J* = 2.2 Hz), 114.8, 113.9 (q, *J* = 2.5 Hz), 98.3, 54.9, 36.5; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -56.5; **HRMS (ESI−TOF)** ***m/z***: $[M+H]^+$ calcd. for $C_{18}H_{16}F_3INO_2$: 462.0172, found 462.0166.

***(Z)*-*N*-(2-Iodophenyl)-*N*-methyl-3-(o-tolyl)-2-(trifluoromethyl)acrylamide (1n):**

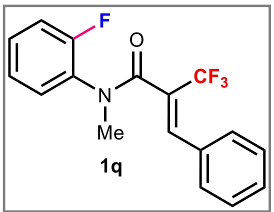


1n

According to **GP-I**, amide coupling of 3-(*o*-tolyl)-2-(trifluoromethyl)acrylic acid[1a] (829.0 mg, 3.6 mmol used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with 2-iodo-*N*-methylaniline (699.0 mg, 3.0 mmol) afforded the desired amide **1n** (445.0 mg) in 33% yield as a white solid; R_f = 0.42 (3% EtOAc, 30% DCM in hexane); Melting point: 70–72 ºC.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.97 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43 (td, *J* = 7.7, 1.3 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.01 (m, 5H), 3.36 (s, 3H), 1.64 (s, 3H); **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)** δ 165.1 (bq, *J* = 1.8 Hz; quartet not split clearly), 146.2, 140.7, 139.8 (q, *J* = 3.5 Hz), 135.4, 132.3, 130.1, 129.8, 129.5, 129.4, 129.0, 127.9 (bq, *J* = 2.7 Hz), 127.5 (q, *J* = 31.0 Hz; one of the quartet peak merged with other previous peak), 125.6, 121.6 (q, *J* = 275.3 Hz), 98.6, 37.0, 19.3; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -56.6; **HRMS (ESI−TOF) *m/z***: [M+Na]$^+$ calcd. for $C_{18}H_{15}F_3INNaO$: 468.0043, found 468.0050.

***(Z)*-*N*-(2-Fluorophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide (1q):**

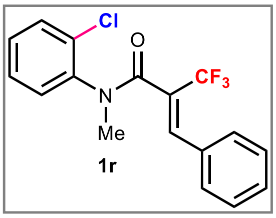


1q

According to **GP-I**, amide coupling of 3-phenyl-2-(trifluoromethyl) acrylic acid[1a] (778.2 mg, 3.6 mmol, used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with *N*-methyl-2-fluoroaniline (375.4 mg, 3.0 mmol) afforded the desired amide **1q** (381.2 mg) in 39% yield as a white solid; R_f = 0.33 (3% EtOAc, 30% DCM in hexane); Melting point: 74–76 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.31 (m, 1H), 7.30 – 7.23 (m, 4H), 7.19 (t, *J* = 8.1 Hz, 2H), 7.09 – 6.89 (m, 3H), 3.39 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 165.6 (q, *J* = 2.5 Hz), 157.5 (d, *J* = 249.8 Hz), 140.6 (bs), 132.2, 131.2 (d, *J* = 12.7 Hz), 130.0 (d, *J* = 7.7 Hz), 129.4, 128.6 (q, *J* = 1.4 Hz; quartet not split clearly), 128.2, 126.4 (q, *J* = 32.5 Hz), 125.1 (d, *J* = 3.9 Hz), 121.4 (q, *J* = 274.7 Hz), 116.7 (d, *J* = 20.0 Hz), 36.6 (one aromatic carbon peak merged with other peak at 128.2); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -56.9, -121.0; **HRMS (ESI−TOF) *m/z***: [M+H]$^+$ calcd. for $C_{17}H_{14}F_4NO$: 324.1006, found 324.1012.

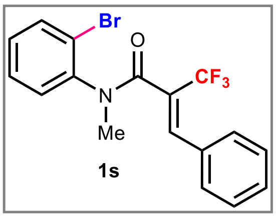
***(Z)*-*N*-(2-Chlorophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide (1r):**



According to **GP-I**, amide coupling of 3-phenyl-2-(trifluoromethyl) acrylic acid[1a] (778.2 mg, 3.6 mmol, used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with *N*-methyl-2-chloroaniline (424.7 mg, 3.0 mmol) afforded the desired amide **1r** (595.5 mg) in 58% yield as a white solid; R_f = 0.40 (3% EtOAc, 30% DCM in hexane); Melting point: 99–101 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.55 – 7.50 (m, 1H), 7.36 – 7.23 (m, 6H), 7.07 – 6.98 (m, 3H), 3.36 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** *δ* 165.3 (q, *J* = 2.4 Hz), 140.8, 139.8 (q, *J* = 3.8 Hz), 132.1, 131.9, 130.6, 130.0, 129.7, 129.3, 128.5 (q, *J* = 2.4 Hz), 128.2, 128.1, 126.1 (q, *J* = 32.4 Hz), 121.4 (q, *J* = 274.8 Hz), 36.0; **^{19}F NMR (377 MHz, CDCl$_3$)** *δ* -56.8; **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{17}H_{14}ClF_3NO$: 340.0711, found 340.0706.

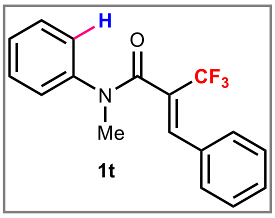
***(Z)-N*-(2-Bromophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide (1s):**



According to **GP-I**, amide coupling of 3-phenyl-2-(trifluoromethyl) acrylic acid[1a] (1.3 g, 6.0 mmol, used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with *N*-methyl-2-bromoaniline (930.1 g, 5.0 mmol) afforded the desired amide **1s** (1038.3 mg) in 54% yield as a white solid; R_f = 0.40 (3% EtOAc, 30% DCM in hexane); Melting point: 105–107 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.32 (td, *J* = 7.0, 1.2 Hz, 1H), 7.26 – 7.16 (m, 5H), 7.10 – 7.00 (m, 3H), 3.32 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** *δ* 165.1 (q, *J* = 2.4 Hz), 142.2, 139.8 (q, *J* = 3.8 Hz), 133.8, 132.0, 130.0, 129.8, 129.2, 128.9, 128.5 (q, *J* = 2.4 Hz), 128.1, 125.9 (q, *J* = 32.4 Hz), 122.1, 121.4 (q, *J* = 274.8 Hz), 36.0; **^{19}F NMR (377 MHz, CDCl$_3$)** *δ* -56.7; **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{17}H_{14}BrF_3NO$: 384.0205, found 384.0201.

(*Z*)-*N*-Methyl-*N*,3-diphenyl-2-(trifluoromethyl)acrylamide (1t):

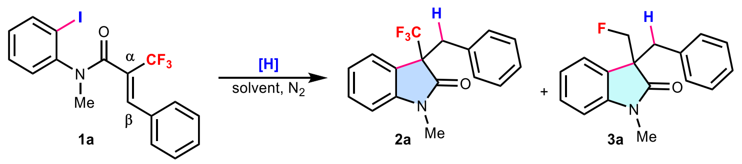


According to **GP-I**, amide coupling of 3-phenyl-2-(trifluoromethyl) acrylic acid[1a] (518.8 mg, 2.4 mmol, used ~30:70 to ~40:60 ratio of *Z*/*E* isomer compound) with *N*-methylaniline (214.3 mg, 2.0 mmol) afforded the desired amide **1t** (126.6 mg) in 21% yield as a white solid; R_f = 0.27 (3% EtOAc, 30% DCM in hexane); Melting point: 70–72 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.39 (m, 2H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.29 – 7.21 (m, 5H), 7.00 (bs, 2H), 6.78 (s, 1H), 3.46 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** *δ* 165.4 (q, *J* = 2.3 Hz), 143.7, 141.7 – 141.3 (m), 132.4, 129.6, 129.3, 128.5 (q, *J* = 2.3 Hz; quartet not split clearly), 128.2, 127.7, 126.9, 126.6 (q, *J* = 32.4 Hz; a quartet peak merged with previous one), 121.6 (q, *J* = 274.8 Hz), 37.5; **^{19}F NMR (377 MHz, CDCl$_3$)** *δ* -57.0; **HRMS (ESI−TOF)** ***m/z***: [M+H]$^+$ calcd. for $C_{17}H_{15}F_3NO$: 306.1100, found 306.1105.

3. Experimental Procedures

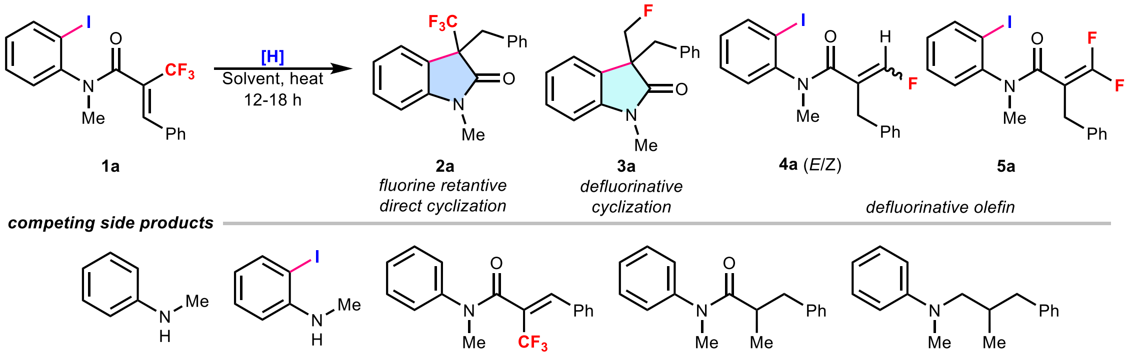
3.1 General Procedure for Optimization Studies (GP-II):



Scheme S2. Reductive Cyclization of *N*-(2-iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide.

General Procedure II (GP II): An oven-dried reaction vial (7.0 mL) equipped with a magnetic stir bar was charged with *N*-(2-iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide (**1a**, 43.1 mg, 0.1 mmol) and [H] (3 equiv). Then, the reaction vial was introduced into the glove box, and solvent (0.1 M) was added. The reaction vial was capped, taken outside, and stirred at a given temperature (using a heating block) for 12-18 hours. After the reaction time was completed, the vial was cooled to room temperature, quenched with water, and extracted with DCM (3 times). The mixture was then concentrated under vacuum. The crude mixture was then purified by column chromatography on silica gel (Hexane/Ethyl Acetate/Dichloromethane) to afford the desired product **2a**, along with **3a** & **4a**.

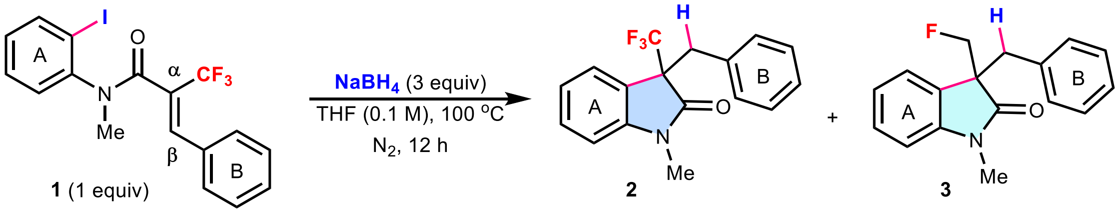
Table S1. Optimization studies of the reductive Heck reaction of tri-substituted acrylamides.[a]



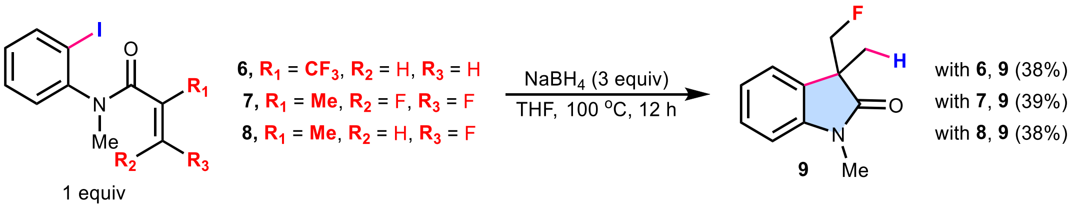
Entry	[Hydride]	Solvent	2a (%)	3a (%)	4a (%)
1	$NaBH_4$	THF	45	20	trace
2	$NaBH_4$	DMSO	-	19	44
3	$NaBH_4$	DMA	-	30	-
4	$NaBH_4$	DMF	-	55	22
5	$NaBH_4$	NMP	-	60	-
6	$NaBH_4$	1,4-Dioxane	22	20	-
7	$NaBH_4$	DCM, MeOH, Toluene	-	-	-
8	NaH	THF	-	-	-
9	$LiAlH_4$	THF	-	-	-
10	$LiBH_4$, $NaBH_3CN$ $(^nBu)_4N(BH_4)$, KBH_4	THF	-	-	-
11[b]	**$NaBH_4$**	**THF**	**70**	**10**	-
12[c]	$NaBH_4$	THF	**30%**	**<5**	-
13[d]	$NaBH_4$	THF	**41%**	**<5**	-
14[e]	$NaBH_4$	THF	**58%**	**<5**	-

[a]**Reaction conditions: 1a** (0.1 mmol), [**H**] (3 equiv), solvent (0.1 M) at 70 °C for 18 h. [b]at 100 °C for 12 h, isolated yield. **5a** is observed <5% in few cases. [c]0.5 equiv $NaBH_4$. [d]1.0 equiv $NaBH_4$. [e]2.0 equiv $NaBH_4$.

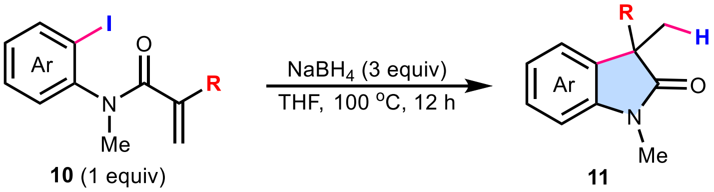
3.2 General Procedure for Scope studies (GP-III):



Scheme S3. Reductive Cyclization of *β*-substituted Trifluoromethylated-Acrylamides.



Scheme S4. Reductive Cyclization of Fluorinated-Acrylamides.

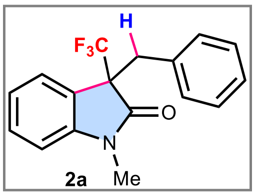


Scheme S5. Reductive Cyclization of Methyl-methacrylamides.

General Procedure III (GP III): An oven-dried reaction vial (7.0 mL) equipped with a magnetic stir bar was charged with *o*-halo acrylamide (**1, 6, 7, 8, 10**, 1 equiv) and $NaBH_4$ (3 equiv). Then, the reaction vial was introduced into the glove box, and THF solvent (0.1 M) was added. The reaction vial was capped, taken outside, and stirred at 100 °C (using a heating block) for 12 hours. After the reaction time was completed, the vial was cooled to room temperature, quenched with water, and extracted with DCM (3 times). The mixture was then concentrated under vacuum. The crude mixture was then purified by column chromatography on silica gel (Hexane/Ethyl Acetate/Dichloromethane) to afford the desired products.

3.3 Characterization of products:

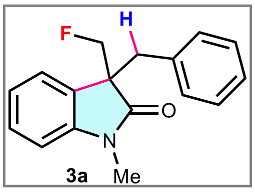
3-Benzyl-1-methyl-3-(trifluoromethyl) indolin-2-one (2a):[3]



According to **GP-III**, the reaction of (*Z*)-*N*-(2-iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide (**1a**; 86.2 mg, 0.2 mmol) with $NaBH_4$ (22.7 mg, 0.6 mmol), afforded **2a** (43.0 mg) in 70% yield as a white solid along with **3a** (5.6 mg) in 10% yield as a colorless semi-solid; R_f (**3a**) = 0.50 (3% EtOAc, 30% DCM in hexane).

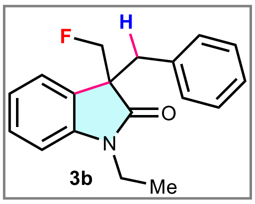
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.27 (td, *J* = 7.8, 1.2 Hz, 1H), 7.12 (td, *J* = 7.6, 1.0 Hz, 1H), 7.08 – 6.98 (m, 3H), 6.86 – 6.80 (m, 2H), 6.58 (d, *J* = 7.8 Hz, 1H), 3.61 (d, *J* = 12.9 Hz, 1H), 3.31 (d, *J* = 12.9 Hz, 1H), 2.94 (s, 3H); **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -71.5.

3-Benzyl-3-(fluoromethyl)-1-methylindolin-2-one (3a):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (bd, *J* = 7.4 Hz, 1H), 7.23 (td, *J* = 7.8, 1.2 Hz, 1H), 7.14 – 7.02 (m, 4H), 6.90 – 6.81 (m, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 4.72 (d, *J* = 46.8 Hz, 2H), 3.17 (bs, 2H), 2.99 (s, 3H); **^{13}C{^{1}H} (101 MHz, $CDCl_3$)** δ 175.9 (d, *J* = 6.4 Hz), 143.8, 134.6, 129.8, 128.6, 128.4 (d, *J* = 1.1 Hz), 127.7, 126.7, 124.2, 122.4, 108.0, 85.6 (d, *J* = 177.3 Hz), 55.2 (d, *J* = 18.9 Hz), 38.8 (d, *J* = 5.4 Hz), 26.0; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -225.8 (t, *J* = 47.0 Hz); **HRMS (ESI−TOF) *m/z***: $[M+Na]^+$ calcd. for $C_{17}H_{16}FNONa$: 292.1108, found 292.1125.

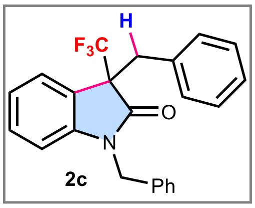
3-Benzyl-1-ethyl-3-(fluoromethyl)indolin-2-one (3b):



According to **GP-III**, the reaction of (*Z*)-*N*-ethyl-*N*-(2-iodophenyl)-3-phenyl-2-(trifluoromethyl)acrylamide (**1b**; 89.0 mg, 0.2 mmol) with $NaBH_4$ (22.7 mg, 0.6 mmol), afforded **2b** (trace) along with **3b** (13.0 mg) in 23% yield as a white solid; R_f (**3b**) = 0.50 (3% EtOAc, 30% DCM in hexane); Melting point (**3b**): 135−137 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, J = 7.4 Hz, 1H), 7.23 (td, J = 7.8, 1.3 Hz, 1H), 7.09 (td, J = 7.6, 0.9 Hz, 1H), 7.06 – 7.00 (m, 3H), 6.86 – 7.82 (m, 2H), 6.64 (d, J = 7.9 Hz, 1H), 4.78 (q, J = 8.8 Hz, 1H), 4.66 (q, J = 8.8 Hz, 1H), 3.70 (ddt, J = 11.7, 7.3, 5.9 Hz, 1H), 3.37 (ddt, J = 10.3, 7.1, 5.2 Hz, 1H), 3.17 (bs, 2H), 0.85 (t, J = 7.2 Hz, 3H); **^{13}C{^{1}H} (101 MHz, CDCl$_3$)** δ 175.4 (d, J = 6.6 Hz), 143.0, 134.5, 129.9, 128.7 (d, J = 0.6 Hz), 128.6, 127.7, 126.7, 124.3, 122.2, 108.2, 85.8 (d, J = 177.3 Hz), 55.1 (d, J = 18.7 Hz), 38.8 (d, J = 5.5 Hz), 34.4, 12.0; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -226.0 (t, J = 47.2 Hz); **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{18}H_{19}FNO$: 284.1445, found 284.1454.

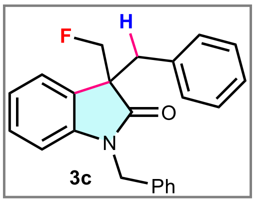
1,3-Dibenzyl-3-(trifluoromethyl)indolin-2-one (2c):[3]



According to **GP-II**, the reaction of (*Z*)-*N*-benzyl-*N*-(2-iodophenyl)-3-phenyl-2-(trifluoromethyl)acrylamide (**1c**; 101.5 mg, 0.2 mmol) with $NaBH_4$ (22.7 mg, 0.6 mmol), afforded **2c** (14.3 mg) in 19% yield as a white solid along with **3c** (15.7 mg) in 23% yield as a white solid; R_f (**3c**) = 0.56 (3% EtOAc, 30% DCM in hexane); Melting point (**3c**): 148−150 °C.

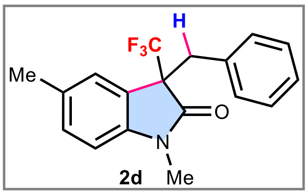
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, J = 7.3 Hz, 1H), 7.20 – 7.09 (m, 6H), 7.05 (t, J = 7.6 Hz, 2H), 6.90 (d, J = 7.1 Hz, 2H), 6.64 (d, J = 6.7 Hz, 2H), 6.41 (d, J = 8.2 Hz, 1H), 4.88 (d, J = 16.0 Hz, 1H), 4.57 (d, J = 16.0 Hz, 1H), 3.70 (d, J = 13.0 Hz, 1H), 3.41 (d, J = 13.0 Hz, 1H); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -71.8.

1,3-Dibenzyl-3-(fluoromethyl)indolin-2-one (3c):



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 (d, J = 8.0 Hz, 1H), 7.17 – 7.11 (m, 4H), 7.10 – 7.04 (m, 4H), 6.91 (d, J = 7.4 Hz, 2H), 6.67 (d, J = 6.4 Hz, 2H), 6.43 (d, J = 8.5 Hz, 1H), 4.97 (d, J = 16.0 Hz, 1H), 4.77 (d, J = 47.0 Hz, 2H), 4.53 (d, J = 16.0 Hz, 1H), 3.26 (bs, 2H); **^{13}C{^{1}H} (101 MHz, CDCl$_3$)** δ 175.8 (d, J = 6.3 Hz), 143.1, 135.0, 134.7, 130.1, 128.61, 128.58, 128.4, 128.0, 127.2, 126.8, 126.5, 124.1, 122.5, 109.4, 86.2 (d, J = 178.3 Hz), 55.5 (d, J = 18.5 Hz), 43.5, 38.4 (d, J = 5.3 Hz); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -225.1 (t, J = 47.0 Hz); **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{23}H_{21}FNO$: 346.1602, found 346.1606.

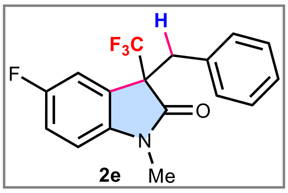
3-Benzyl-1,5-dimethyl-3-(trifluoromethyl) indolin-2-one (2d):[4]



According to **GP-III**, the reaction of (*Z*)-*N*-(2-iodo-4-methylphenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide (**1d**; 89.0 mg, 0.2 mmol) with $NaBH_4$ (22.7 mg, 0.6 mmol), afforded **2d** (33.2 mg) in 52% yield as a semi-solid along with **3d** in trace amount.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.10 – 6.98 (m, 4H), 6.83 (bd, *J* = 6.2 Hz, 2H), 6.47 (d, *J* = 7.4 Hz, 1H), 3.59 (d, *J* = 12.8 Hz, 1H), 3.29 (d, *J* = 12.8 Hz, 1H), 2.91 (s, 3H), 2.39 (s, 3H); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -71.4.

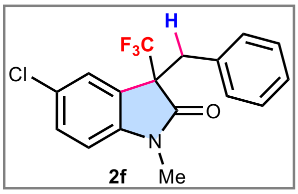
3-Benzyl-5-fluoro-1-methyl-3-(trifluoromethyl) indolin-2-one (2e):[5]



According to **GP-II**, the reaction of (*Z*)-*N*-(4-fluoro-2 iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl) acrylamide (**1e**; 44.9 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **2e** (13.1 mg) in 41% yield as a white solid along with **3e** in trace amount.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.02 (m, 3H), 6.98 (t, *J* = 8.7 Hz, 1H), 6.85 (d, *J* = 7.3 Hz, 2H), 6.51 (dd, *J* = 8.5, 4.0 Hz, 1H), 3.62 (d, *J* = 13.0 Hz, 1H), 3.28 (d, *J* = 13.0 Hz, 1H), 2.94 (s, 3H); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -71.4, -119.4 (td, *J* = 8.5, 4.2 Hz).

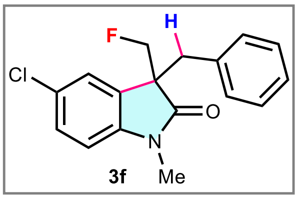
3-Benzyl-5-chloro-1-methyl-3-(trifluoromethyl) indolin-2-one (2f):[3]



According to **GP-II**, the reaction of (*Z*)-*N*-(4-chloro-2 iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl) acrylamide (**1f**; 46.6 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **2f** (15.2 mg) in 45% yield as a white solid along with **3f** (6.8 mg) in 22% yield as a white solid; R_f (**3f**) = 0.46 (3% EtOAc, 30% DCM in hexane); Melting point (**3f**): 82–84 °C for **3f**.

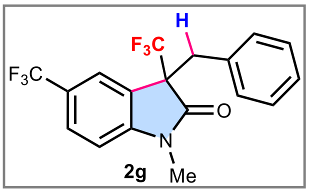
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.27 (bs, 1H), 7.14 – 7.03 (m, 3H), 6.86 (bd, *J* = 6.7 Hz, 2H), 6.52 (d, *J* = 8.2 Hz, 1H), 3.63 (d, *J* = 13.0 Hz, 1H), 3.30 (d, *J* = 13.0 Hz, 1H), 2.94 (s, 3H); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -71.3.

3-Benzyl-5-chloro-3-(fluoromethyl)-1-methylindolin-2-one (3f):



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, J = 2.0 Hz, 1H), 7.21 (dd, J = 8.3, 2.1 Hz, 1H), 7.11 – 7.06 (m, 3H), 6.90 – 6.82 (m, 2H), 6.55 (d, J = 8.3 Hz, 1H), 4.76 (dd, J = 12.0, 8.9 Hz, 1H), 4.64 (dd, J = 12.0, 8.9 Hz, 1H), 3.17 (bd, J = 13.1 Hz, 1H), 3.13 (bd, J = 13.2 Hz, 1H), 2.97 (s, 3H); **^{13}C{^{1}H} (101 MHz, CDCl$_3$)** δ 175.4 (d, J = 6.7 Hz), 142.4, 134.1, 132.6, 129.8, 128.6, 127.8, 126.9, 124.7, 108.9, 96.1, 85.3 (d, J = 177.8 Hz), 55.5 (d, J = 18.8 Hz), 38.8 (d, J = 5.2 Hz), 26.1; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -225.8 (t, J = 46.9 Hz); **HRMS (ESI−TOF) *m/z***: [M+H]$^+$ calcd. for $C_{17}H_{16}ClFNO$: 304.0899, found 304.0914.

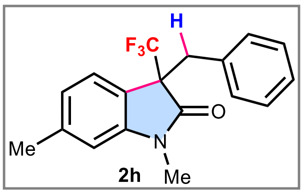
3-Benzyl-1-methyl-3,5-bis(trifluoromethyl)indolin-2-one (2g):[3]



According to **GP-III**, the reaction of (*Z*)-*N*-(2-iodo-4-(trifluoromethyl)phenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide (**1g**; 100.0 mg, 0.2 mmol) with NaBH$_4$ (22.7 mg, 0.6), afforded **2g** (41.7 mg) in 56% yield as a white solid along with **3g** in trace amount.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (s, 1H), 7.56 (ddd, J = 8.2, 1.8, 0.8 Hz, 1H), 7.10 – 7.00 (m, 3H), 6.83 – 6.77 (m, 2H), 6.66 (d, J = 8.2 Hz, 1H), 3.64 (d, J = 13.0 Hz, 1H), 3.34 (d, J = 13.0 Hz, 1H), 2.98 (s, 3H); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -61.6, -71.2.

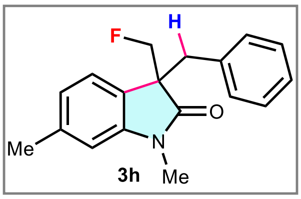
3-Benzyl-1,6-dimethyl-3-(trifluoromethyl)indolin-2-one (2h):[5]



According to **GP-III**, the reaction of (*Z*)-*N*-(5-methyl-2 iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl) acrylamide (**1h**; 89.0 mg, 0.2 mmol) with NaBH$_4$ (22.7 mg, 0.6 mmol), afforded **2h** (30.2 mg) in 47% yield and as a white solid along with **3h** (9.8 mg) in 17% yield as a white solid; R_f (**3h**) = 0.44 (3% EtOAc, 30% DCM in hexane); Melting point (**3h**): 76–78 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, J = 7.4 Hz, 1H), 7.10 – 7.00 (m, 3H), 6.92 (d, J = 7.5 Hz, 1H), 6.87 – 6.82 (m, 2H), 6.42 (s, 1H), 3.58 (d, J = 12.9 Hz, 1H), 3.29 (d, J = 12.9 Hz, 1H), 2.92 (s, 3H), 2.33 (s, 3H); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -71.6.

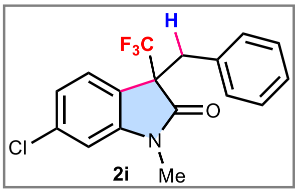
3-Benzyl-3-(fluoromethyl)-1,6-dimethylindolin-2-one (3h):



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.14 (d, J = 7.5 Hz, 1H), 7.10 – 7.05 (m, 3H), 6.90 – 6.86 (m, 3H), 6.47 (bs, 1H), 4.68 (d, J = 47.1 Hz, 2H), 3.16 (d, J = 13.1 Hz, 1H), 3.12 (d, J = 13.1 Hz, 1H), 2.98 (s, 3H), 2.33 (s, 3H); **^{13}C{^{1}H} (101 MHz, CDCl$_3$)** δ 176.3 (d, J = 6.3

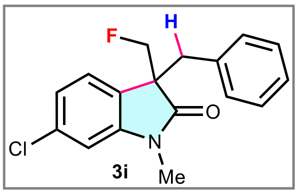
Hz), 143.9, 138.7, 134.8, 129.9, 127.7, 126.6, 125.3 (d, J = 1.4 Hz), 123.9, 122.9, 109.0, 85.7 (d, J = 177.3 Hz), 54.9 (d, J = 18.7 Hz), 38.7 (d, J = 5.3 Hz), 26.0, 21.8; **^{19}F NMR (377 MHz, CDCl₃)** δ -225.6 (t, J = 47.0 Hz); **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{18}H_{19}FNO$: 284.1445, found 284.1453.

3-Benzyl-6-chloro-1-methyl-3-(trifluoromethyl)indolin-2-one (2i)[5]:



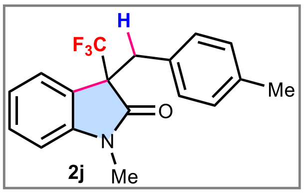
According to **GP-III**, the reaction of (*Z*)-*N*-(5-chloro-2-iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide (**1i**; 93.1 mg, 0.2 mmol) with $NaBH_4$ (22.7 mg, 0.6 mmol), afforded **2i** (5.0 mg) in 7% yield and as a white solid along with **3i** (15.5 mg) in 26% yield as a white solid; R_f (**3i**)= 0.46 (3% EtOAc, 30% DCM in hexane); Melting point (**3i**): 71–73 ºC.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 1H), 7.12 – 7.02 (m, 4H), 6.86 – 6.81 (m, 2H), 6.60 (d, J = 1.8 Hz, 1H), 3.60 (d, J = 13.0 Hz, 1H), 3.29 (d, J = 13.0 Hz, 1H), 2.93 (s, 3H); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -71.4.

3-Benzyl-6-chloro-3-(fluoromethyl)-1-methylindolin-2-one (3i):



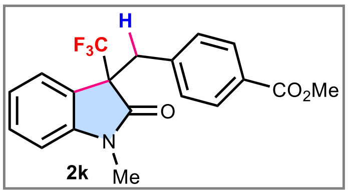
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 7.9 Hz, 1H), 7.11 – 7.03 (m, 4H), 6.88 – 6.83 (m, 2H), 6.64 (d, J = 1.8 Hz, 1H), 4.75 (dd, J = 12.0, 8.9 Hz, 1H), 4.64 (dd, J = 12.0, 8.9 Hz, 1H), 3.15 (bs, 2H), 2.98 (s, 3H); **^{13}C{^{1}H} (101 MHz, $CDCl_3$)** δ 175.9 (d, J = 6.5 Hz), 145.0, 134.4, 134.2, 129.8, 127.9, 126.9, 126.7 (d, J = 1.2 Hz), 125.1, 122.2, 108.8, 85.4 (d, J = 177.8 Hz), 55.0 (d, J = 18.8 Hz), 38.7 (d, J = 5.3 Hz), 26.1; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -225.7 (t, J = 47.0 Hz); **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{17}H_{15}ClFNNaO$: 326.0718, found 326.0736.

3-Benzyl-1,6-dimethyl-3-(trifluoromethyl)indolin-2-one (2j):[6]



According to **GP-III**, the reaction of (*Z*)-*N*-(2-iodophenyl)-*N*-methyl-3-(*p*-tolyl)-2-(trifluoromethyl)acrylamide (**1j**; 44.52 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **2j** (20.4 mg) in 64% yield as a white solid along with **3j** in trace amount.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.5 Hz, 1H), 7.28 (td, J = 7.8, 1.3 Hz, 1H; part of peaks merged with $CDCl_3$), 7.11 (td, J = 7.6, 1.0 Hz, 1H), 6.82 (d, J = 7.9 Hz, 2H), 6.71 (bd, J = 8.1 Hz, 2H), 6.60 (d, J = 7.8 Hz, 1H), 3.57 (d, J = 13.0 Hz, 1H), 3.28 (d, J = 13.0 Hz, 1H), 2.96 (s, 3H), 2.18 (s, 3H); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -71.4.

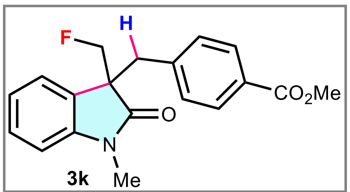
Methyl 4-((1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)methyl)benzoate (2k):



According to **GP-III**, the reaction of Methyl (*Z*)-4-(3,3,3-trifluoro-2-((2-iodophenyl)(methyl)carbamoyl)prop-1-en-1-yl)benzoate (**1k**; 48.9 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **2k** (11.5 mg) in 32% yield and as a white solid R_f (**2k**) = 0.30 (3% EtOAc, 30% DCM in hexane); Melting point (**2k**): 129–131 ºC, along with **3k** (11 mg) in 34% yield as a white solid; R_f (**3k**) = 0.28 (3% EtOAc, 30% DCM in hexane); Melting point (**3k**): 79–81 ºC.

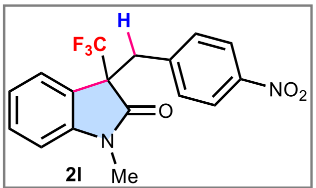
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.27 (td, *J* = 7.8, 1.2 Hz, 1H), 7.12 (td, *J* = 7.6, 1.0 Hz, 1H), 6.91 (dt, *J* = 8.5, 1.9 Hz, 2H), 6.59 (d, *J* = 7.8 Hz, 1H), 3.83 (s, 3H), 3.66 (d, *J* = 12.8 Hz, 1H), 3.36 (d, *J* = 12.8 Hz, 1H), 2.94 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 170.5 (bq, *J* = 2.4 Hz), 166.8, 144.0, 138.2, 130.2, 130.0, 129.01, 128.97, 125.2, 124.5 (q, *J* = 281.9 Hz), 123.1, 122.9, 108.5, 57.9 (q, *J* = 26.6 Hz), 52.0, 37.1 (q, *J* = 2.4 Hz), 26.2; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -71.6; **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{19}H_{17}F_3NO_3$: 364.1155, found 364.1161.

Methyl 4-((3-(fluoromethyl)-1-methyl-2-oxoindolin-3-yl)methyl)benzoate (3k):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.23 (td, *J* = 7.7, 1.1 Hz, 1H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 6.93 (td, *J* = 8.4, 1.2 Hz, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 4.76 (dd, *J* = 25.9, 8.8 Hz, 1H), 4.65 (dd, *J* = 25.8, 8.8 Hz, 1H), 3.84 (s, 3H), 3.26 (d, *J* = 12.9 Hz, 1H), 3.22 (d, *J* = 12.9 Hz, 1H), 2.97 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 175.4 (d, *J* = 7.0 Hz), 166.9, 143.6, 140.1, 129.8, 129.0, 128.8, 128.6, 127.9 (d, *J* = 1.0 Hz), 124.1, 122.6, 108.2, 85.6 (d, *J* = 178.2 Hz), 55.1 (d, *J* = 18.9 Hz), 52.0, 38.6 (d, *J* = 5.4 Hz), 26.0; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -226.0 (d, *J* = 47.0 Hz); **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{19}H_{19}FNO_3$: 328.1343, found 328.1346.

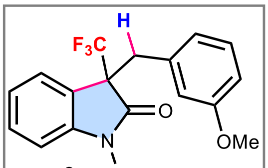
1-Methyl-3-(4-nitrobenzyl)-3-(trifluoromethyl)indolin-2-one (2l):[3]



According to **GP-III**, the reaction of (*Z*)-*N*-(2-iodophenyl)-*N*-methyl-3-(4-nitrophenyl)-2-(trifluoromethyl)acrylamide (**1l**; 95.2 mg, 0.2 mmol) with $NaBH_4$ (22.7 mg, 0.6 mmol), afforded **2l** (17.4 mg) in 25% yield as a white solid along with **3l** in trace amount.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (td, J = 9.2, 3.1 Hz, 2H), 7.49 (d, J = 7.5 Hz, 1H), 7.32 (td, J = 7.8, 1.3 Hz, 1H), 7.16 (td, J = 7.6, 1.0 Hz, 1H), 7.02 (dt, J = 8.8, 2.2 Hz, 2H), 6.64 (d, J = 7.8 Hz, 1H), 3.72 (d, J = 12.8 Hz, 1H), 3.41 (d, J = 12.8 Hz, 1H), 2.98 (s, 3H); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -71.7.

3-(3-Methoxybenzyl)-1-methyl-3-(trifluoromethyl)indolin-2-one (2m):[5]

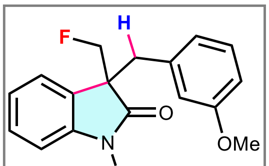


2m

According to **GP-III**, the reaction of (*Z*)-*N*-(2-iodophenyl)-3-(3-methoxyphenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (**1m**; 92.2 mg, 0.2 mmol) with NaBH$_4$ (22.7 mg, 0.6 mmol), afforded **2m** (12.8 mg) in 19% yield and as a white solid along with **3m** (19 mg) in 32% yield as a colorless liquid; R$_f$ (**3m**) = 0.35 (3% EtOAc, 30% DCM in hexane).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 (d, J = 7.6 Hz, 1H), 7.29 (td, J = 7.8, 1.3 Hz, 1H), 7.13 (td, J = 7.6, 1.0 Hz, 1H), 6.94 (t, J = 8.0 Hz, 1H), 6.64 – 6.59 (m, 2H), 6.47 (d, J = 7.6 Hz, 1H; looks dt, but peaks are not split clearly), 6.32 (t, J = 2.0 Hz, 1H), 3.59 (d, J = 12.9 Hz, 1H), 3.57 (s, 3H), 3.29 (d, J = 12.9 Hz, 1H), 2.96 (s, 3H); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -71.5.

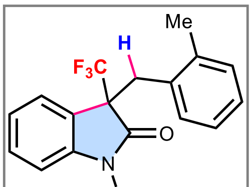
3-(Fluoromethyl)-3-(3-methoxybenzyl)-1-methylindolin-2-one (3m):



3m

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, J = 7.4 Hz, 1H), 7.24 (td, J = 8.0, 1.2 Hz, 1H), 7.08 (td, J = 7.6, 1.0 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 6.68 – 6.61 (m, 2 H), 6.50 (d, J = 7.6 Hz, 1H), 6.35 (t, J = 2.0 Hz, 1H), 4.78 (dd, J = 12.0, 8.9 Hz, 1H), 4.66 (dd, J = 12.0, 8.9 Hz, 1H), 3.59 (s, 3H), 3.15 (bs, 2H), 3.00 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 175.9 (q, J = 6.3 Hz), 158.9, 143.9, 136.1, 128.6 (d, J = 2.2 Hz), 128.44 (d, J = 1.1 Hz), 128.42, 124.2, 122.3, 122.0, 114.6, 113.0, 108.1, 85.6 (d, J = 177.4 Hz), 55.1 (d, J = 19.0 Hz), 55.0, 38.8 (d, J = 5.4 Hz), 26.0; **^{19}F NMR (377 MHz, CDCl$_3$)** δ -225.8 (t, J = 47.1 Hz); **HRMS (ESI–TOF) *m/z*:** [M+H]$^+$ calcd. for $C_{18}H_{19}FNO_2$: 300.1394, found 300.1401.

1-Methyl-3-(2-methylbenzyl)-3-(trifluoromethyl)indolin-2-one (2n):

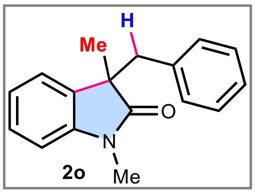


2n

According to **GP-II**, the reaction of (*Z*)-*N*-(2-iodophenyl)-*N*-methyl-3-(o-tolyl)-2-(trifluoromethyl)acrylamide (**1n**; 44.5 mg, 0.1 mmol) with NaBH$_4$ (11.35 mg, 0.3 mmol), afforded **2n** (5.6 mg) in 18% yield as a colorless liquid; R$_f$ (**2n**) = 0.35 (3% EtOAc, 30% DCM in hexane); along with **3n** in trace amount; R$_f$ (**3n**) = 0.68 (3% EtOAc, 30% DCM in hexane).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, J = 7.5 Hz, 1H), 7.30 (td, J = 7.8, 1.0 Hz, 1H), 7.07 (td, J = 7.6, 1.0 Hz, 1H), 7.01 – 6.94 (m, 2H), 6.85 (td, J = 7.6, 2.0 Hz, 1H), 6.73 (d, J = 7.7 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H), 3.62 (d, J = 13.7 Hz, 1H), 3.45 (d, J = 13.7 Hz, 1H), 3.01 (s, 3H), 2.18 (s, 3H); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -71.3; **HRMS (ESI−TOF) *m/z***: $[M+H]^+$ calcd. for $C_{18}H_{17}F_3NO$: 320.1257, found 320.1261.

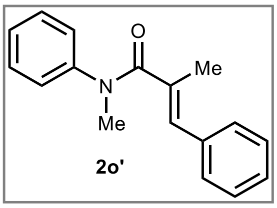
3-Benzyl-1,3-dimethylindolin-2-one (2o):[4]



According to **GP-III**, the reaction of (*Z*)-*N*-(2-iodophenyl)-*N*,2-dimethyl-3-phenylacrylamide (**1o**, 37.7 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **2o** (11.2 mg) in 45% yield as a white solid along with **2o'** (10.5 mg) in 42% yield as a white solid.

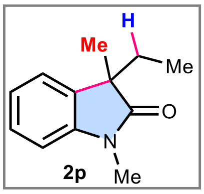
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 (td, J = 7.7, 1.2 Hz, 1H), 7.13 (dd, J = 5.6, 1.1 Hz, 1H), 7.09 – 7.00 (m, 4H), 6.88–6.82 (m, 2H), 6.62 (d, J = 7.7 Hz, 1H), 3.12 (d, J = 13.0 Hz, 1H), 3.01 (d, J = 13.0 Hz, 1H), 2.99 (s, 3H), 1.48 (s, 3H).

(*E*)-*N*,2-dimethyl-*N*,3-diphenylacrylamide (2o'):[11]



^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35 (t, J = 6.9 Hz, 2H), 7.29 – 7.17 (m, overlapping $CDCl_3$, 6H), 7.03 (d, J = 7.1 Hz, 2H), 6.60 (s, 1H), 3.42 (s, 3H), 1.82 (s, 3H).

3-Ethyl-1,3-dimethylindolin-2-one (2p):[9]



According to **GP-III**, the reaction of (*E*)-*N*-(2-iodophenyl)-*N*,2-dimethylbut-2-enamide (**1p**, 63.0 mg, 0.2 mmol) with $NaBH_4$ (22.7 mg, 0.6 mmol), afforded **2p** (20.2 mg) in 54% yield as a white solid.

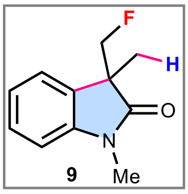
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 (td, J = 7.8, 1.4 Hz, 1H), 7.16 (ddd, J = 5.6, 1.2, 0.4 Hz, 1H), 7.06 (td, J = 7.5, 1.0 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 3.21 (s, 3H), 1.93 (dq, J = 13.6, 7.4 Hz, 1H), 1.77 (dq, J = 13.6, 7.4 Hz, 1H), 1.35 (s, 3H), 0.58 (t, J = 7.4 Hz, 3H).

3-(Fluoromethyl)-1,3-dimethylindolin-2-one (9):[4]

According to **GP-III**, the reaction of *N*-(2-iodophenyl)-*N*-methyl-2-(trifluoromethyl)acrylamide (**6**, 35.5 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **9** (7.4 mg) in 38% yield as a white solid.

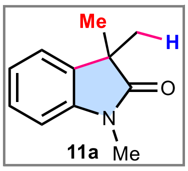
According to **GP-II**, the reaction of 3,3-difluoro-*N*-(2-iodophenyl)-*N*,2-dimethylacrylamide (**7**, 33.7 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **9** (7.6 mg) in 39% yield as a white solid.

According to **GP-III**, the reaction of 3-fluoro-*N*-(2-iodophenyl)-*N*,2-dimethylacrylamide (**8**, 31.9 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **9** (7.2 mg) in 38% yield as a white solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.88 (dt, *J* = 8.0, 0.8 Hz, 1H), 4.56 (d, *J* = 47.0 Hz, 2H), 3.23 (s, 3H), 1.40 (d, *J* = 1.6 Hz, 3H); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -223.7 (t, *J* = 47.0 Hz).

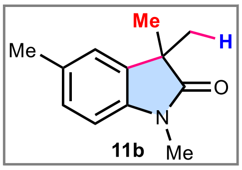
1,3,3-Trimethylindolin-2-one (11a):[7]



According to **GP-III**, the reaction of *N*-(2-iodophenyl)-*N*-methylmethacrylamide (**10a**, 30.1 mg, 0.1 mmol) using $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **11a** (12.0 mg) in 69% yield as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (td, *J* = 6.4, 1.3 Hz, 1H), 7.20 (dd, *J* = 7.1, 0.8 Hz, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.21 (s, 3H), 1.37 (s, 6H).

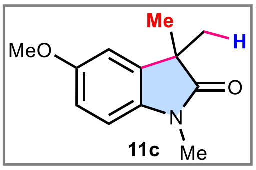
1,3,3,5-Tetramethylindolin-2-one (11b):[7]



According to **GP-III**, the reaction of *N*-(2-iodo-4-methylphenyl)-*N*-methylmethacrylamide (**10b**, 31.5 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **11b** (13.9 mg) in 74% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.8 Hz, 1H), 7.02 (s, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 3.19 (s, 3H), 2.35 (s, 3H), 1.36 (s, 6H).

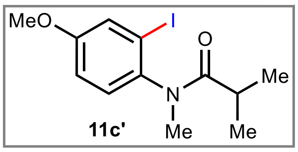
5-Methoxy-1,3,3-trimethylindolin-2-one (11c):[7a]



According to **GP-II**, the reaction of *N*-(2-iodo-4-methoxyphenyl)-*N*-methylmethacrylamide (**10c**, 33.1 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 3 equiv), afforded a mixture of **11c** (11.7 mg) in 57% yield and **11c'** (3.5 mg) in 10% yield (77:23 ratio, according to ^{1}H-NMR) as a colorless liquid.

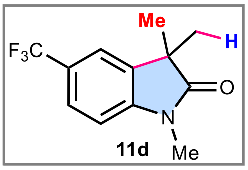
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (dd, J = 2.4, 0.5 Hz, 1H), 6.80 – 6.72 (m, 2H), 3.80 (s, 3H), 3.19 (s, 3H), 1.36 (s, 6H).

***N*-(2-iodo-4-methoxyphenyl)-*N*-methylisobutyramide (11c'):**[7b]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 2.8 Hz, 1H), 7.15 (d, J = 8.6 Hz, 1H), 6.93 (dd, J = 8.7, 2.8 Hz, 1H), 3.82 (s, 3H), 3.13 (s, 3H), 2.25 (sept, J = 6.8 Hz, 1H), 1.12 (d, J = 6.6 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H).

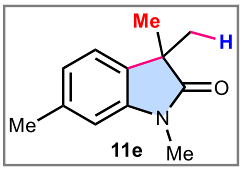
1,3,3-Trimethyl-5-(trifluoromethyl)indolin-2-one (11d):[7]



According to **GP-III**, the reaction of *N*-(2-iodo-4-(trifluoromethyl)phenyl)-*N*-methylmethacrylamide (**10d**, 36.9 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **11d** (8.0 mg) in 33% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (ddd, J = 8.2, 1.8, 0.8 Hz, 1H; looks like dq, but peaks are not split clearly), 7.42 (d, J = 1.6 Hz, 1H; peaks not split clearly), 6.91 (d, J = 8.2 Hz, 1H), 3.25 (s, 3H), 1.40 (s, 6H); **^{19}F NMR (377 MHz, $CDCl_3$)** δ -61.3.

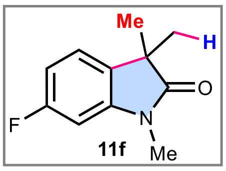
1,3,3,6-Tetramethylindolin-2-one (11e):[7]



According to **GP-III**, the reaction of *N*-(2-iodo-5-methylphenyl)-*N*-methylmethacrylamide (**10e**, 31.5 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **11e** (7.2 mg) in 38% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 7.4 Hz, 1H), 6.87 (ddd, J = 7.4, 1.4, 0.7 Hz, 1H), 6.68 – 6.67 (m, 1H), 3.20 (s, 3H), 2.39 (s, 3H), 1.35 (s, 6H).

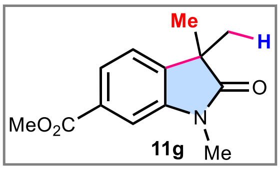
6-Fluoro-1,3,3-trimethylindolin-2-one (11f):[7]



According to **GP-III**, the reaction of *N*-(5-fluoro-2-iodophenyl)-*N*-methylmethacrylamide (**10f**, 31.9 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **11f** (12.3 mg) in 64% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, J = 8.1, 5.3 Hz, 1H), 6.73 (ddd, J = 9.8, 8.1, 2.4 Hz, 1H), 6.58 (dd, J = 8.9, 2.3 Hz, 1H), 3.19 (s, 3H), 1.35 (s, 6H); **^{19}F NMR (377 MHz, $CDCl_3$)** δ –113.1 to –113.2(m).

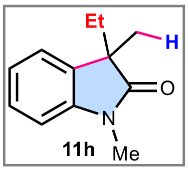
Methyl 1,3,3-trimethyl-2-oxoindoline-6-carboxylate (11g):[8]



According to **GP-III**, the reaction of Methyl 4-iodo-3-(*N*-methylmethacrylamido)benzoate (**10g**, 35.9 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **11g** (7.5 mg) in 32% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 7.7, 1.5 Hz, 1H), 7.49 (d, J = 1.3 Hz, 1H), 7.28–7.24 (m, 1H), 3.93 (s, 3H), 3.26 (s, 3H), 1.38 (s, 6H).

3-Ethyl-1,3-dimethylindolin-2-one (11h):[9]

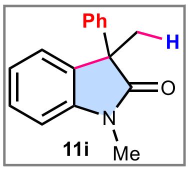


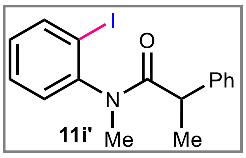
According to **GP-III**, the reaction of *N*-(2-iodophenyl)-*N*-methyl-2-methylenebutanamide (**10h**, 31.5 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **11h** (8.0 mg) in 42% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (td, J = 7.7, 1.3 Hz, 1H), 7.16 (ddd, J = 5.6, 1.2, 0.4 Hz, 1H), 7.07 (td, J = 7.5, 1.0 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 3.21 (s, 3H), 1.93 (dq, J = 13.6, 7.4 Hz, 1H), 1.77 (dq, J = 13.6, 7.4 Hz, 1H), 1.35 (s, 3H), 0.59 (t, J = 7.4 Hz, 3H).

1,3-Dimethyl-3-phenylindolin-2-one (11i):[10]

According to **GP-III**, the reaction of *N*-(2-iodophenyl)-*N*-methyl-2-phenylacrylamide (**10i**, 36.3 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol) afforded a mixture of **11i** (10.45 mg) in 44% yield along with **11i'** (10.45 mg) in 29% yield (50:50 ratio, according to ^{1}H-NMR) as a colorless liquid.



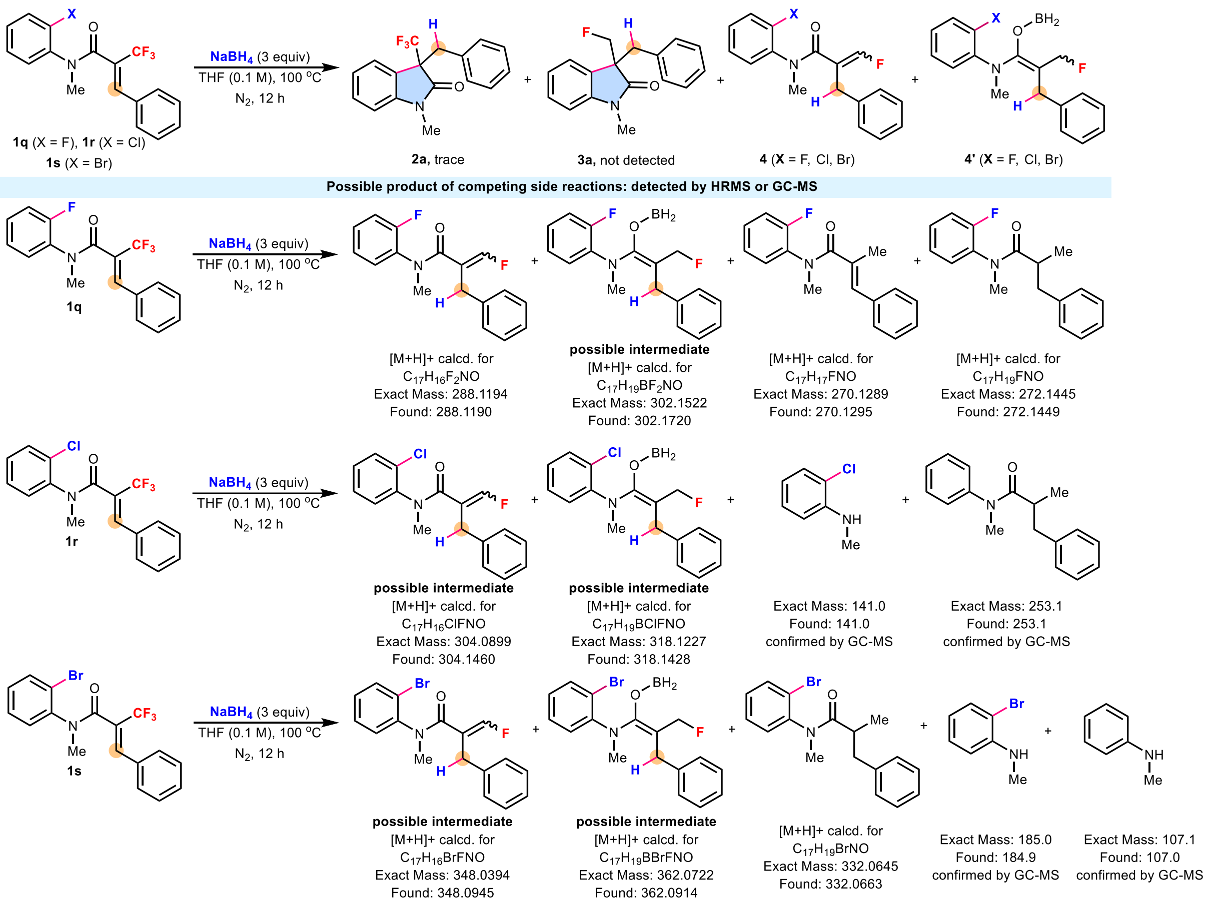


4. Mechanistic Studies:

4.1 Control Experiment (CE):

CE 1 To investigate the nucleophilic aromatic substitution (S_NAr) reaction pathway by using various *o*-halo acrylamides:

According to **GP-III**, the reaction of (*Z*)-*N*-(2-halophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide (**1q**; ***o*-F**, **1r**; ***o*-Cl**, and **1s**; ***o*-Br**, 1 equiv) with $NaBH_4$ (3 equiv), afforded a trace amount of desired products along with several products of competing side reactions. All the side products identified by HRMS or GC-MS analysis.



Scheme S6. Reaction with various *o*-halo trifluoromethylated acrylamides.

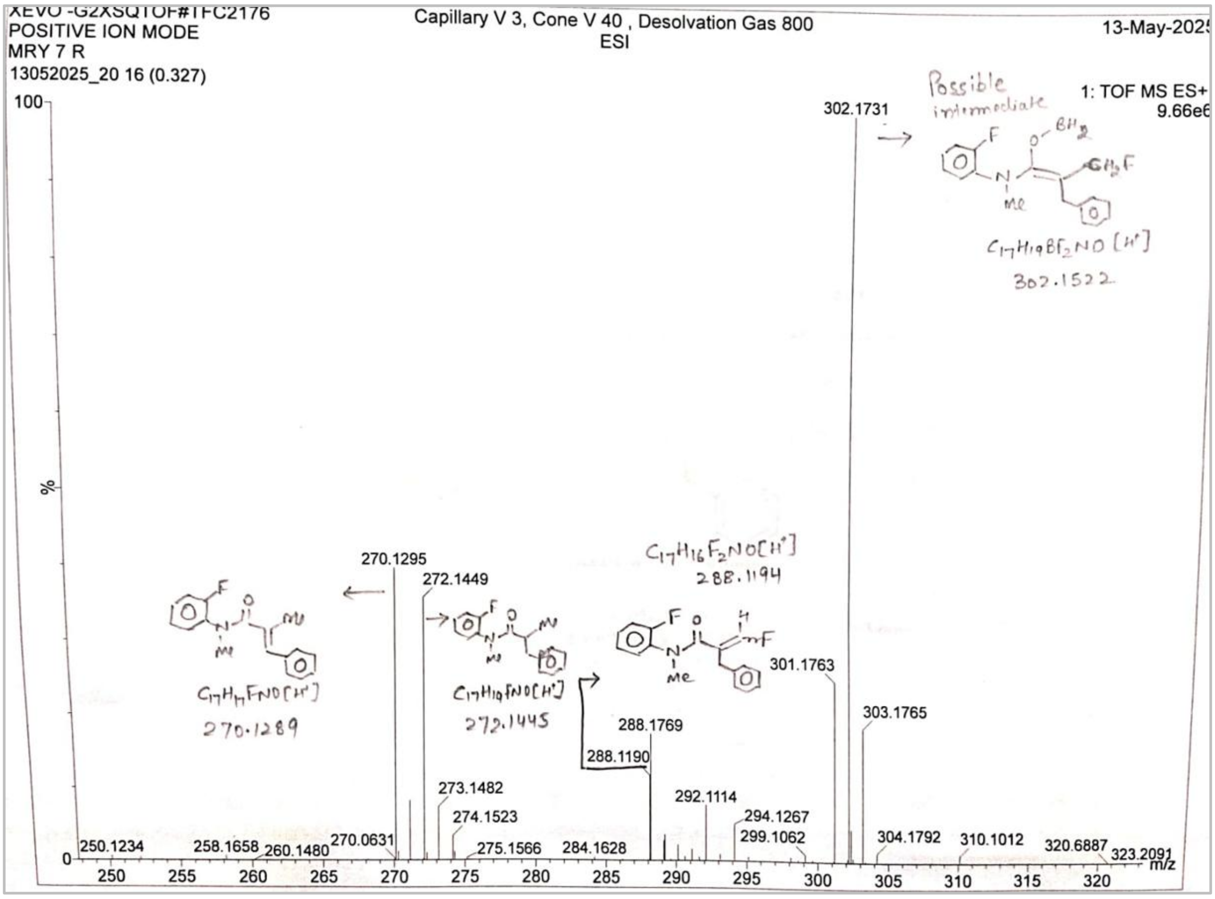


Figure S3. HRMS data for the reaction of **1q** with $NaBH_4$.

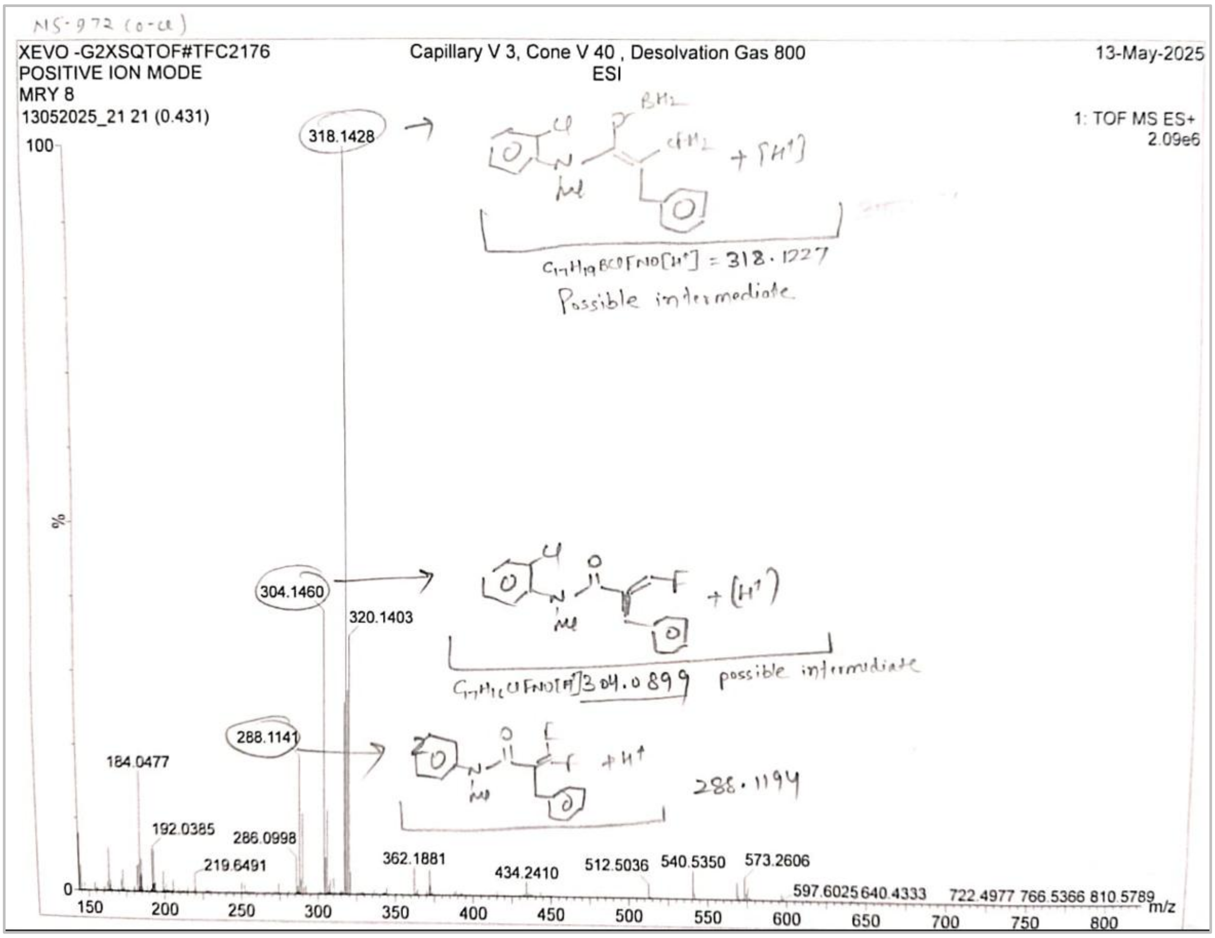


Figure S4. HRMS data for the reaction of **1r** with $NaBH_4$.

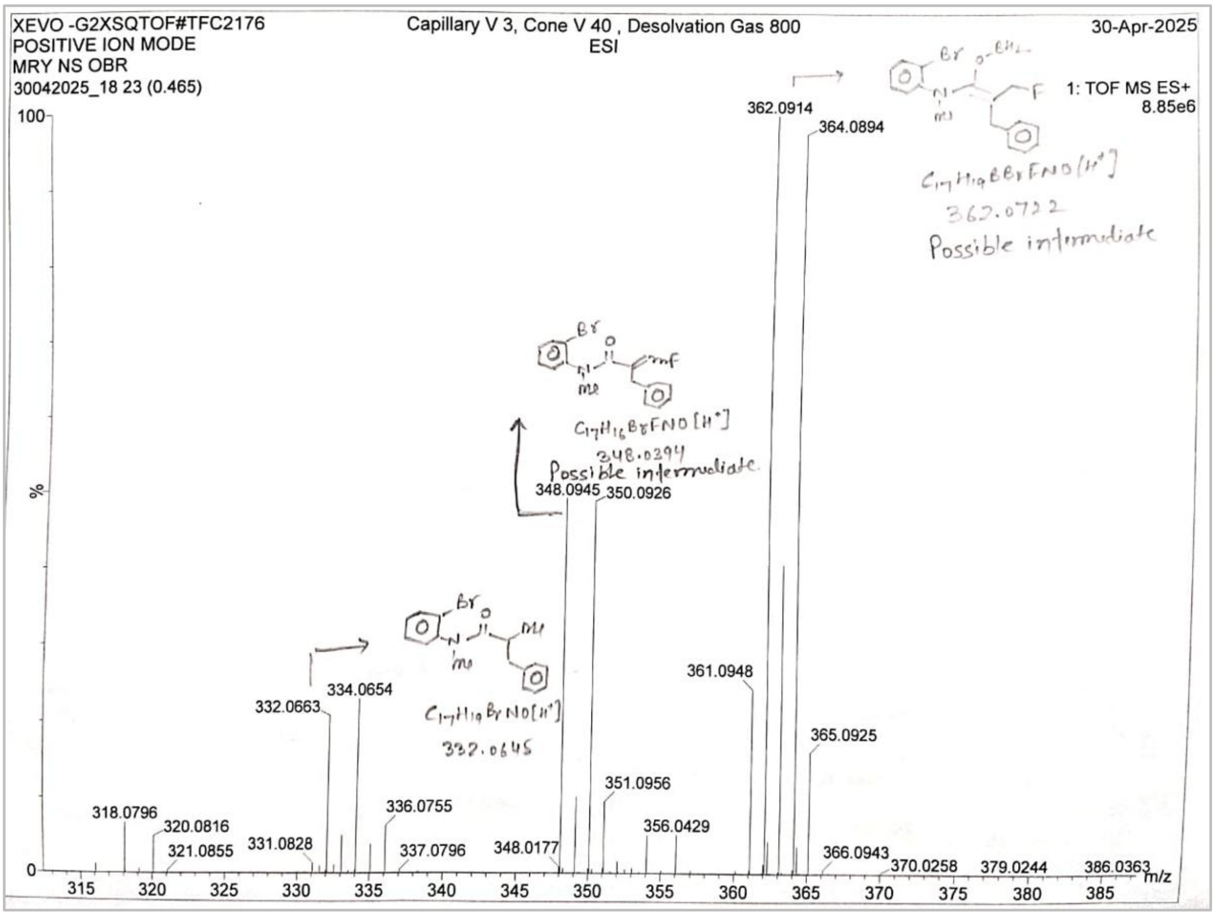
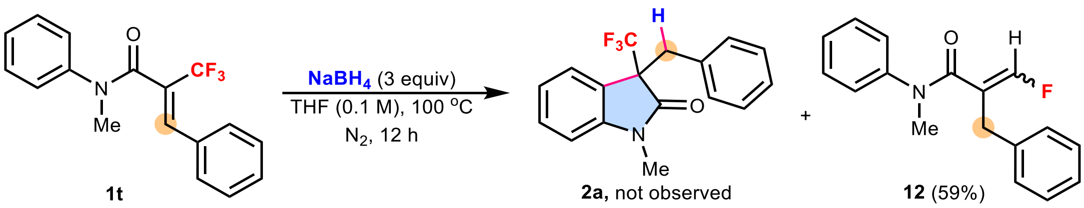


Figure S5. HRMS data for the reaction of **1s** with $NaBH_4$.

Result: *Under these control conditions, the defluorinated olefin (mono-fluorinated) derived from the starting material was observed, rather than the expected oxindole cyclization. The negligible amount of desired product excludes the possibility of an intramolecular* S_NAr *mechanism.*

CE 2 To understand the role of $C(sp^2)$–I bond:

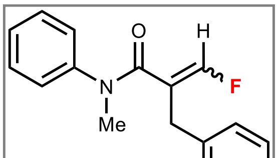
According to **GP-III**, the reaction of (*Z*)-*N*-methyl-*N*,3-diphenyl-2-(trifluoromethyl)acrylamide (**1t**, 30.5 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **12** (16.0 mg) in 59% yield as a colorless liquid; R_f = 0.40 (3% EtOAc, 30% DCM in hexane).



1t **2a,** not observed **12** (59%)

Scheme S7. Reaction with trifluoromethylated acrylamides lacking halide.

2-Benzyl-3-fluoro-*N*-methyl-*N*-phenylacrylamide (12):



12

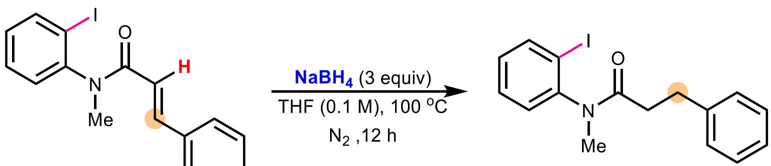
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 – 7.18 (m, 3H; peak merged in CDCl$_3$), 7.22 – 7.18 (m, 3H), 7.15 (d, J = 6.8 Hz, 2H), 6.65 – 6.60 (m, 2H), 6.58 (d, J = 83.3 Hz, 1H), 3.53 (d, J = 2.4 Hz, 2H), 3.24 (s, 3H); **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)** δ 167.4 (d, J = 14.3 Hz), 152.8 (d, J = 270.8 Hz), 144.2, 137.8 (d, J = 2.4 Hz), 129.3, 129.1, 128.5, 127.0, 126.6, 126.5, 120.2 (d, J = 7.8 Hz), 38.2, 30.8 (d, J = 4.1 Hz); **^{19}F NMR (377 MHz, CDCl$_3$)** δ -124.0 (d, J = 83.9 Hz) ppm; **HRMS (ESI−TOF) *m/z***: [M+H]$^+$ calcd. for $C_{17}H_{17}FNO$: 270.1289, found 270.1299.

Result: *Under these control conditions, the defluorinated olefin (mono-fluorinated), originating from the starting material, was observed in place of the anticipated oxindole cyclization. This outcome suggests that the C(sp²)–I bond plays a crucial role in facilitating the cyclization process.*

CE 3 To understand the role of α– & β–substitution in the cyclization process:

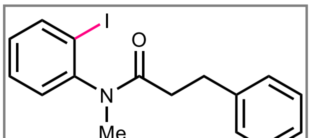
Reactivity with α-hydrogen substitution:

According to **GP-III**, the reaction of *N*-(2-iodophenyl)-*N*-methylcinnamamide (**1u**, 36.3 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **13** (16.0 mg) in 44% yield as a white solid.



Scheme S8. Reaction of **1u** with $NaBH_4$.

***N*-(2-iodophenyl)-*N*-methyl-3-phenylpropanamide (13):**[10]



13

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, J = 7.9, 1.4 Hz, 1H), 7.34 (td, J = 7.6, 1.4 Hz, 1H), 7.23 (t, J = 7.2 Hz, 2H), 7.15 (bt, J = 7.3 Hz, 1H), 7.10 – 6.93 (m, 4H), 3.17 (s, 3H), 2.98 – 2.88 (m, 2H), 2.29 – 2.19 (m, 2H).

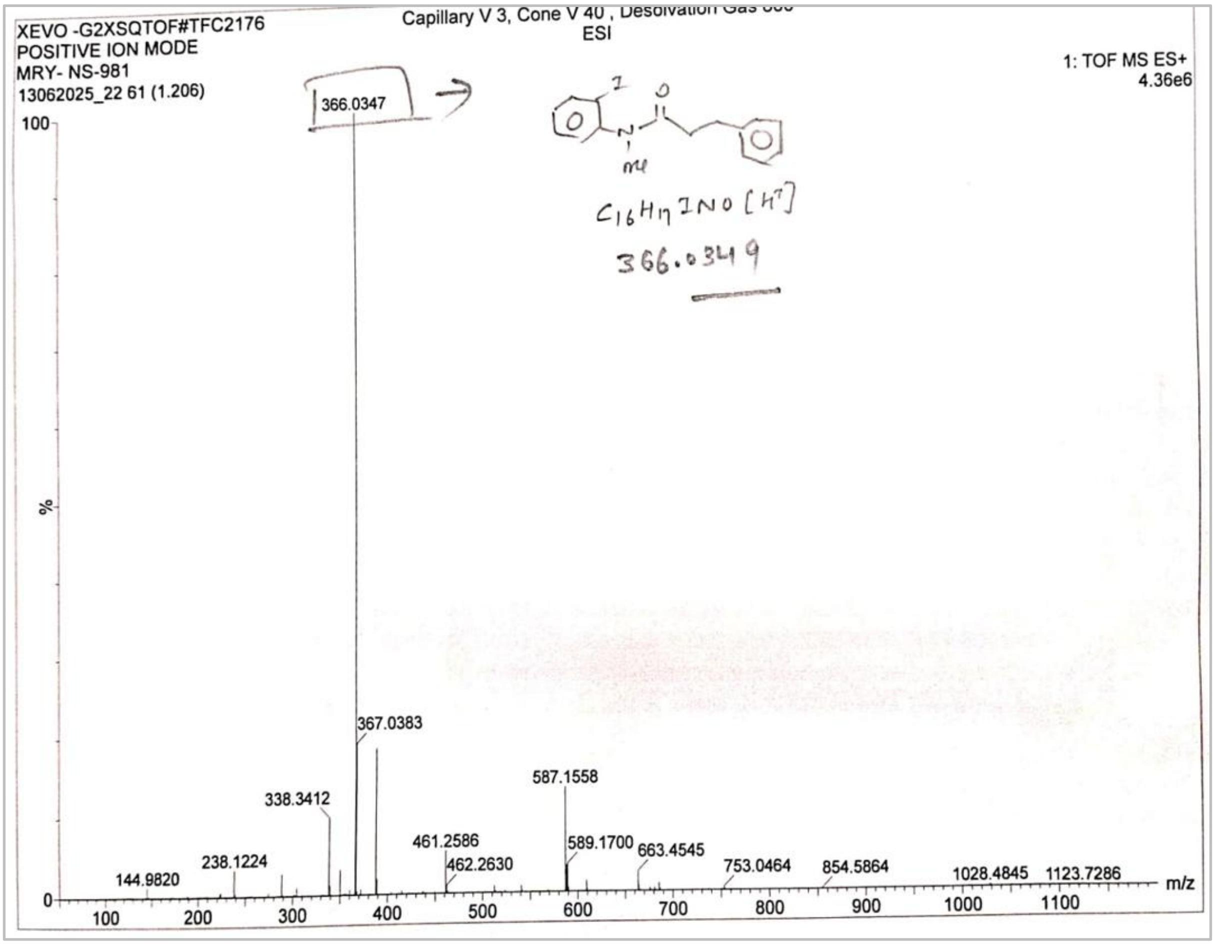
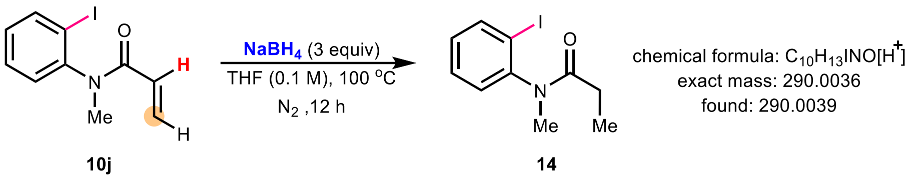


Figure S6. HRMS data for the reaction of **1u** with NaBH4.

Reactivity with *α* and *β*-hydrogen substitution:

According to **GP-III**, the reaction of *N*-(2-iodophenyl)-*N*-methylacrylamide (**10j**, 28.7 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **14** confirmed by HRMS.



Scheme S9. Reaction of **10j** with $NaBH_4$.

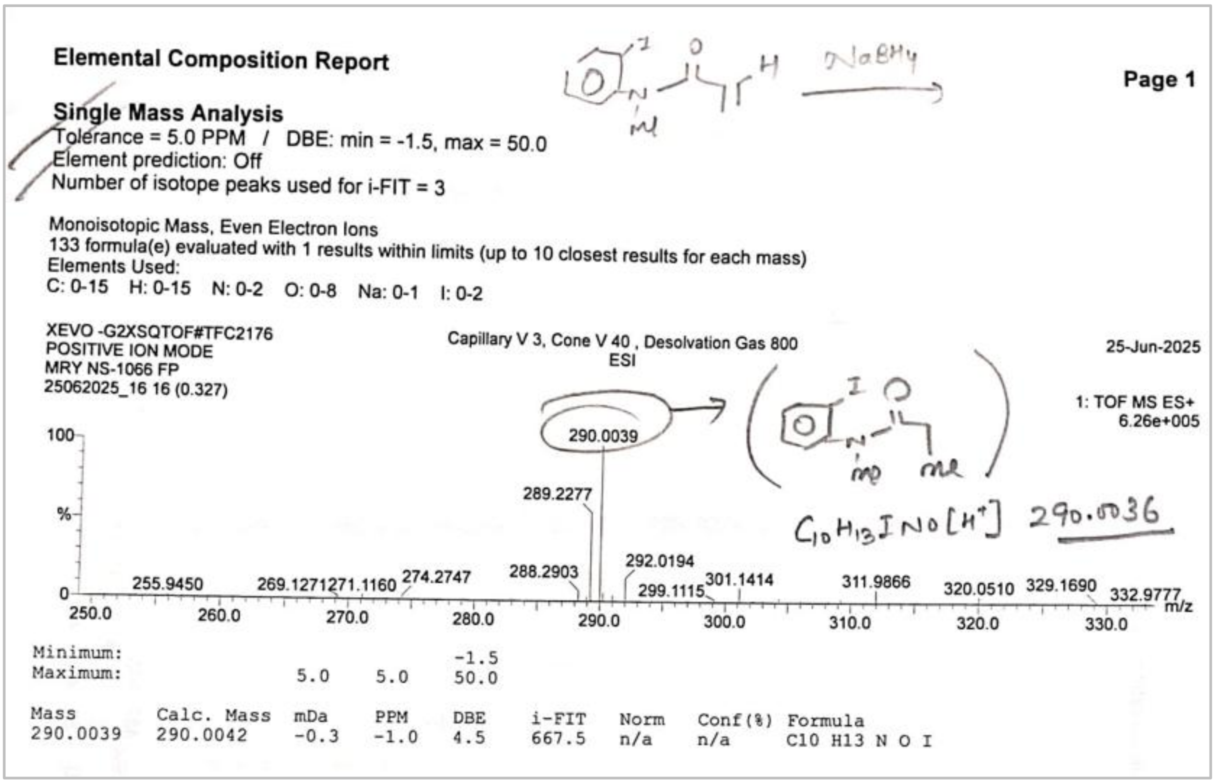
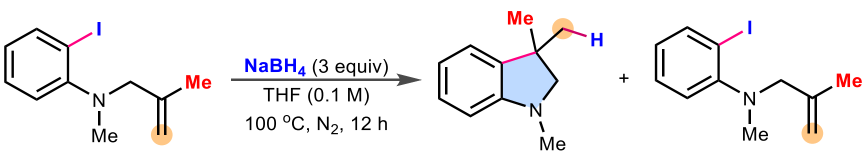


Figure S7. HRMS data for the reaction of **10j** with $NaBH_4$.

Result: *When the α-(trifluoro)methyl and β-phenyl group was replaced by hydrogen, the olefin-reduced product was obtained, suggesting that the α-substitution is essential to enable cyclization.*

CE 4 To understand the role of the carbonyl group:

According to **GP-III**, the reaction of 2-iodo-*N*-methyl-*N*-(2-methylallyl)aniline (**10k**, 28.7 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 0.3 mmol) did not afford the desired product **11k**.



10k **11k**, not observed only starting material recovered

Scheme S10. Reaction of **10k** with $NaBH_4$.

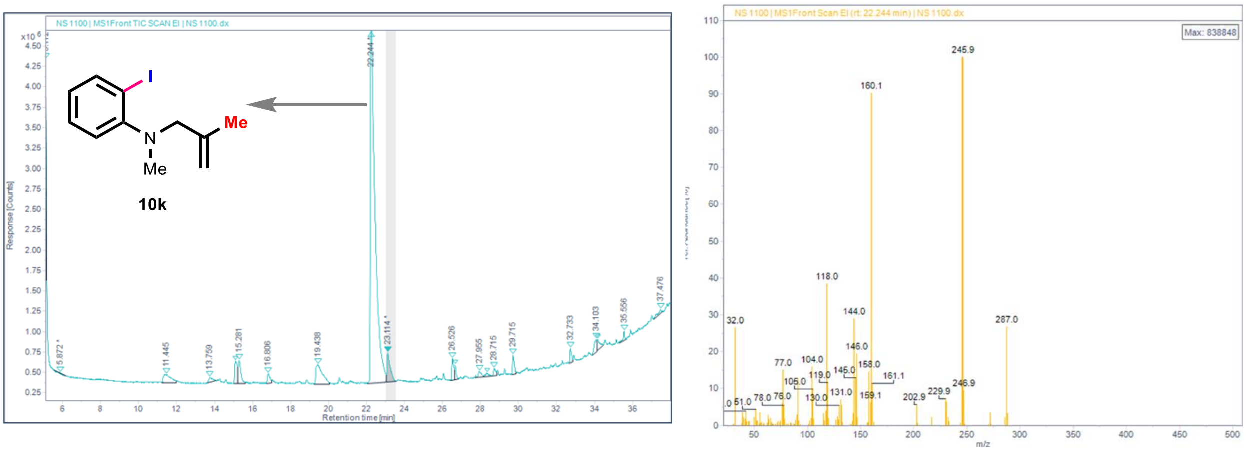
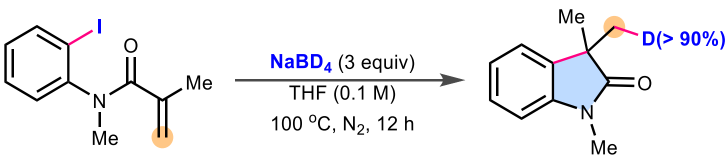


Figure S8. GC-MS data for the reaction of **10k** with $NaBH_4$.

Result: *Without a carbonyl group, the reaction does not work, emphasizing the importance of the carbonyl group, which may help in the initial attack of hydride at the β-position and carbanion stabilization in the molecule.*

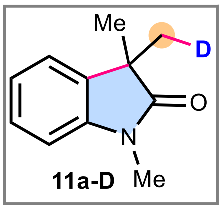
CE 5 Deuterium labeling experiment:

According to **GP-III**, the reaction of *N*-(2-iodophenyl)-*N*-methylmethacrylamide (**10a**, 30.1 mg, 0.1 mmol) with $NaBD_4$ (12.6 mg, 0.3 mmol), afforded **11a-D** (8.0 mg) in 45% yield as a colorless semi-solid.



Scheme S11. Reaction with **10a** with $NaBD_4$.

1,3-Dimethyl-3-(methyl-*d*)indolin-2-one (11a-D):[12]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 7.7, 1.3 Hz, 1H; peaks are merged with $CDCl_3$), 7.20 (ddd, J = 7.4, 0.6 Hz, 1H), 7.06 (td, J = 7.5, 1.0 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 3.22 (s, 3H), 1.37 (s, 3H), 1.35 (t, J = 2.0 Hz, 2H).

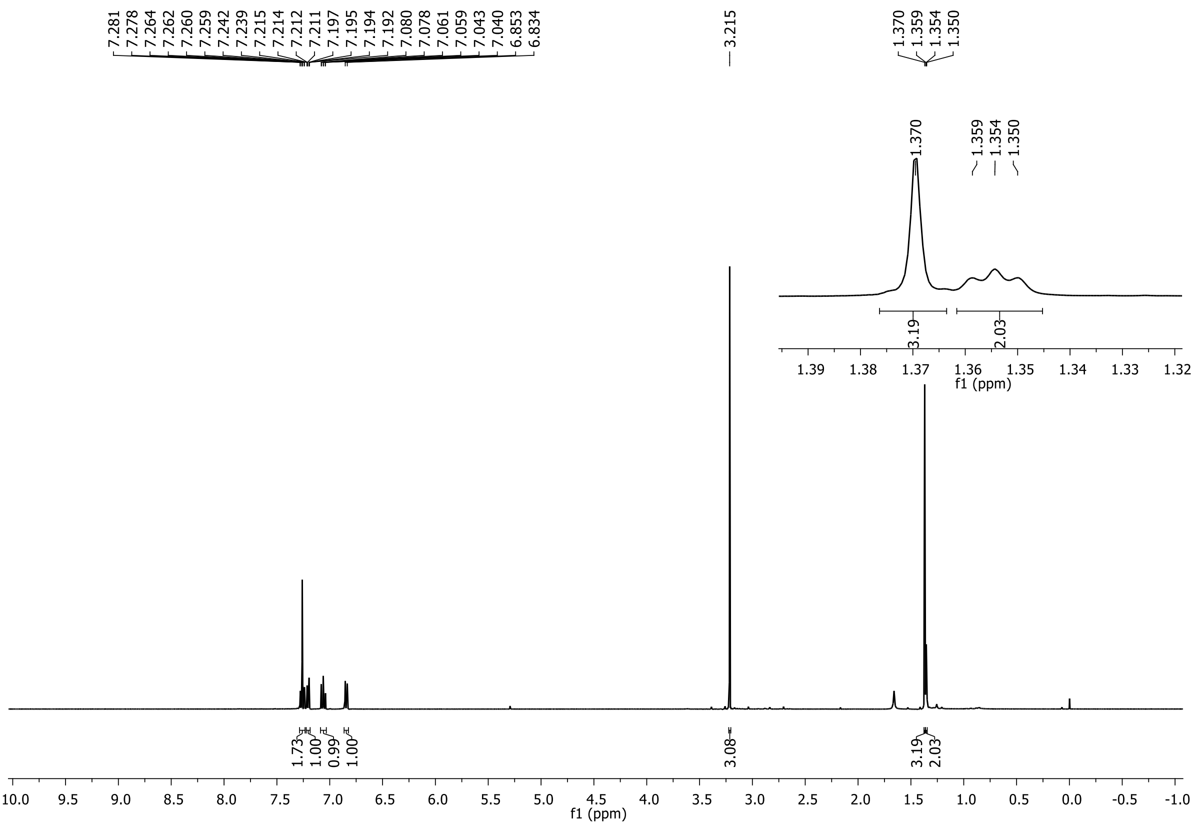
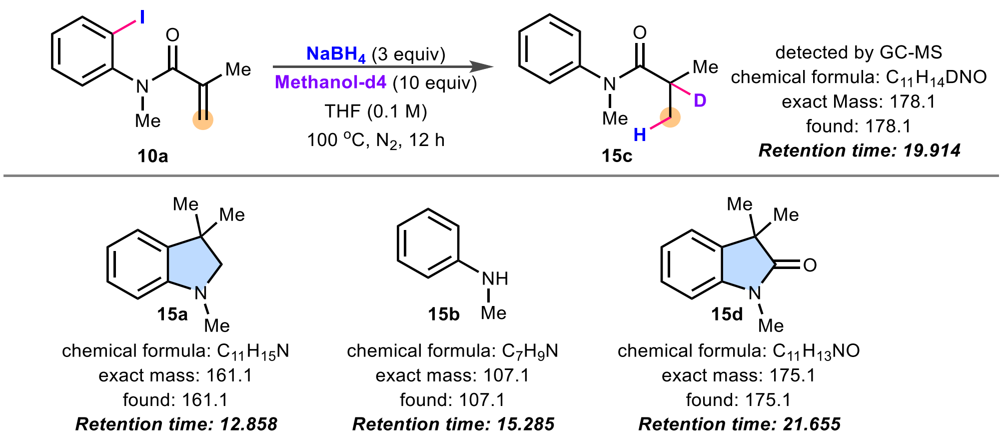


Figure S9. [1]H-NMR data for the reaction of **10a** with $NaBD_4$.

Result: The result of the deuterium labelling experiment indicates that the Hydrogen source is from $NaBH_4$, not from the solvent.

CE 6 Trapping of electrophile at α-position:

According to **GP-III**, the reaction of *N*-(2-iodophenyl)-*N*-methylmethacrylamide (**10a**, 30.1 mg, 0.1 mmol) with $NaBH_4$ (11.35 mg, 3 equiv) and methanol-D4 (40 µL, 10 equiv) afforded **15**, detected by GC-MS.



Scheme S12. Trapping of the electrophile from methanol-D4.

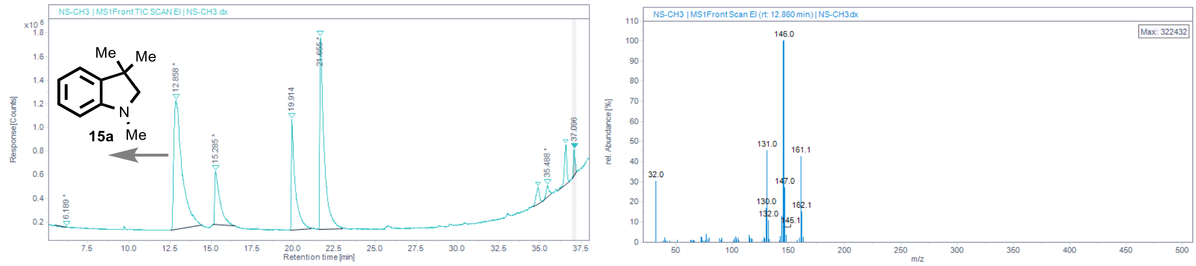


Figure S10. Detection of **15a** from GC-MS.

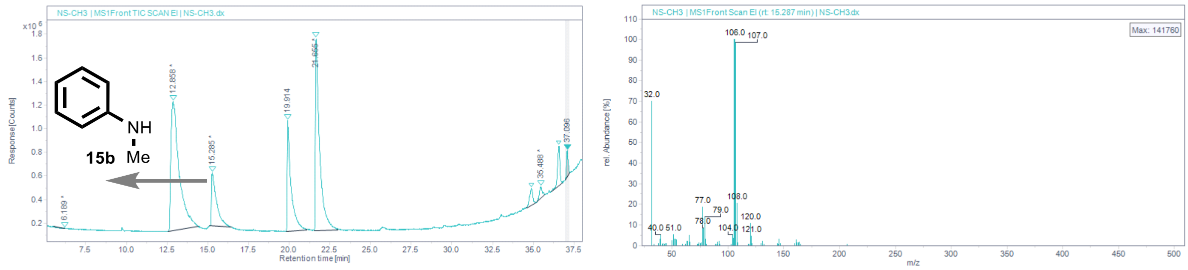


Figure S11. Detection of **15b** from GC-MS.

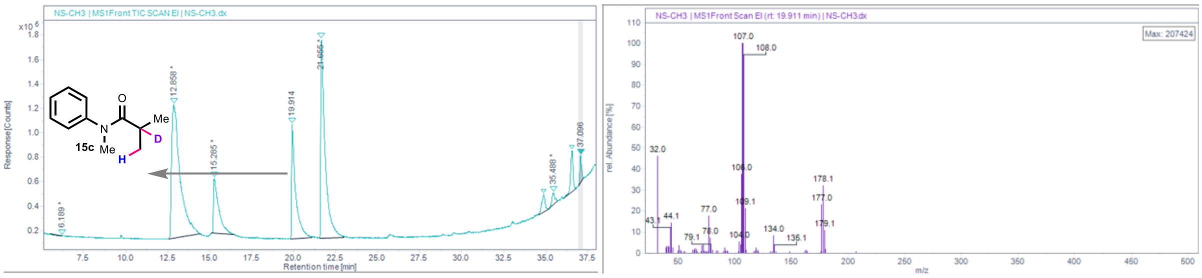


Figure S12. Detection of **15c** from GC-MS.

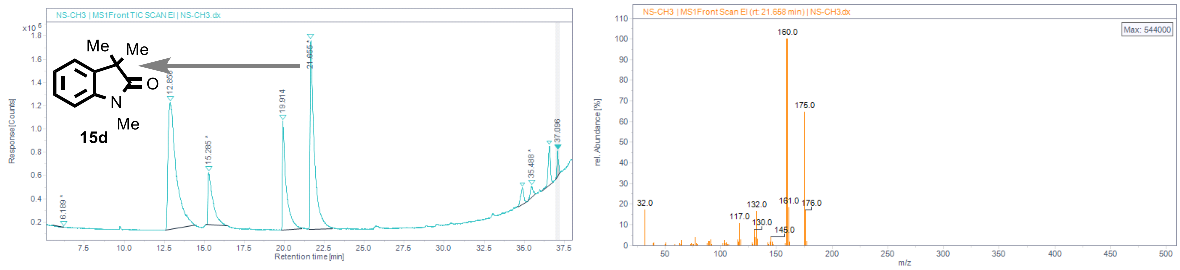


Figure S13. Detection of **15d** from GC-MS.

Result: The result of the deuterium labelling experiment indicates the possibility of the existence of α–carbanion.

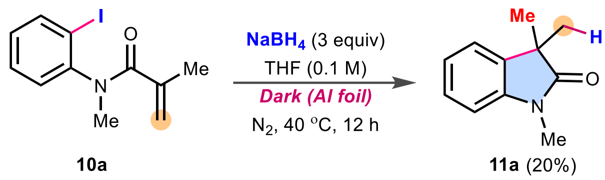
CE 7 To understand the role of light irradiation and radical initiator on the reaction profile:

CE 7.1 To understand the role of the light irradiation on the reaction profile:

According to **GP-III**, the reaction of *N*-(2-iodophenyl)-*N*-methylmethacrylamide (**10a**, 15.1 mg, 0.05 mmol) with $NaBH_4$ (5.7 mg, 0.15 mmol) under 390 nm blue LED at 40 °C (temperature measured under light by thermometer), which afforded **11a** in 11% yield (Crude yields were measured with the help of ^{1}H-NMR by adding 1,3,5-trimethoxybenzene as internal standard).

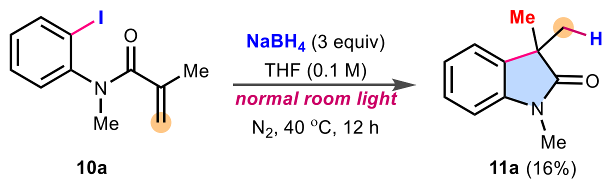
Scheme S13. Reaction of **10a** under 390 nm blue LED.

The same reaction was performed in the dark at 40 °C by covering the reaction vial with aluminum foil, which afforded **11a** in 20% yield (Crude yields were measured using ^{1}H NMR by adding 1,3,5-trimethoxybenzene as an internal standard).



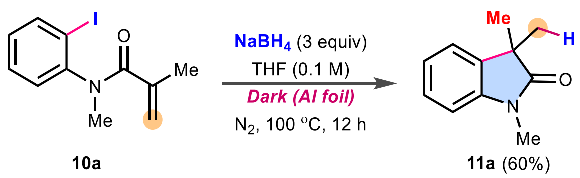
Scheme S14. Reaction of **10a** at 40 °C in the dark (Al foil).

The same reaction was performed under normal room light at 40 °C, which afforded **11a** in 16% yield (Crude yields were measured with the help of ^{1}H NMR by adding 1,3,5-trimethoxybenzene as an internal standard).



Scheme S15. Reaction of **10a** in the normal room light 40 °C.

The same reaction was performed in the dark by covering the reaction vial with aluminum foil at 100°C, which afforded **11a** in 60% yield (Crude yields were measured with the help of ^{1}H NMR by adding 1,3,5-trimethoxybenzene as an internal standard).

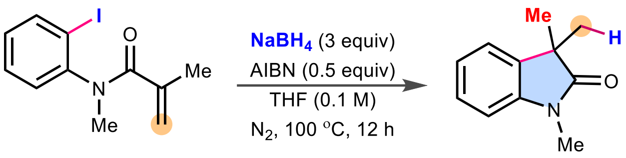


Scheme S16. Reaction of **10a** in the dark (Al foil) at 100 °C.

Result: The diminished yield with or without light at 40 °C, excluding any special role of light on the reaction profile. Raising the reaction temperature from 40 °C to 100 °C further excludes the role of light on the reaction profile, as evidenced by the enhanced product yield.

CE 7.2 To understand the role of the radical initiator on the reaction profile:

According to **GP-III**, the reaction of *N*-(2-iodophenyl)-*N*-methylmethacrylamide (**10a**, 15.1 mg, 0.05 mmol) with $NaBH_4$ (5.7 mg, 0.15 mmol) with AIBN (8.2 mg, 0.05 mmol) at 100 °C afforded **11a** in traces (Crude yields were measured with the help of ^{1}H-NMR by adding 1,3,5-trimethoxybenzene as internal standard).



10a **11a** (trace)

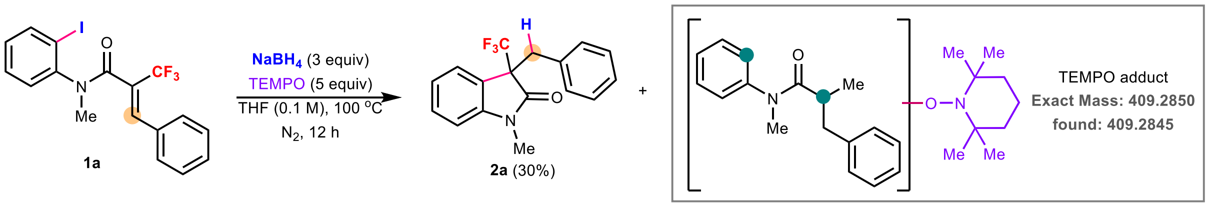
Scheme S17. Reaction of **10a** with AIBN.

Result: Only traces of product with AIBN, excluding the role of any radical initiator.

CE 8 Radical trapping experiment:

TEMPO trapping experiment with 1a:

According to **GP-III**, the reaction of (*Z*)-*N*-(2-iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide (**1a**, 43.1 mg, 0.1 mmol), TEMPO (78.1 mg, 5 equiv) with $NaBH_4$ (11.35 mg, 0.3 mmol), afforded **2a** (9.0 mg) in 30% yield as a white solid.

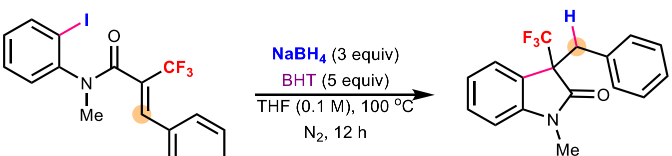


1a **2a** (30%)

Scheme S18. Reaction of **1a** with $NaBH_4$ in the presence of TEMPO.

BHT trapping experiment with 1a:

According to **GP-III**, the reaction of (*Z*)-*N*-(2-iodophenyl)-*N*-methyl-3-phenyl-2-(trifluoromethyl)acrylamide (**1a,** 43.1 mg, 0.1 mmol), BHT (110.2 mg, 5 equiv) with $NaBH_4$ (11.35 mg, 3 equiv), afforded **2a** (13.8 mg) in 45% yield as a white solid.



1a **2a** (45%)

Scheme S19. Reaction of **1a** with NaBH4 in the presence of BHT.

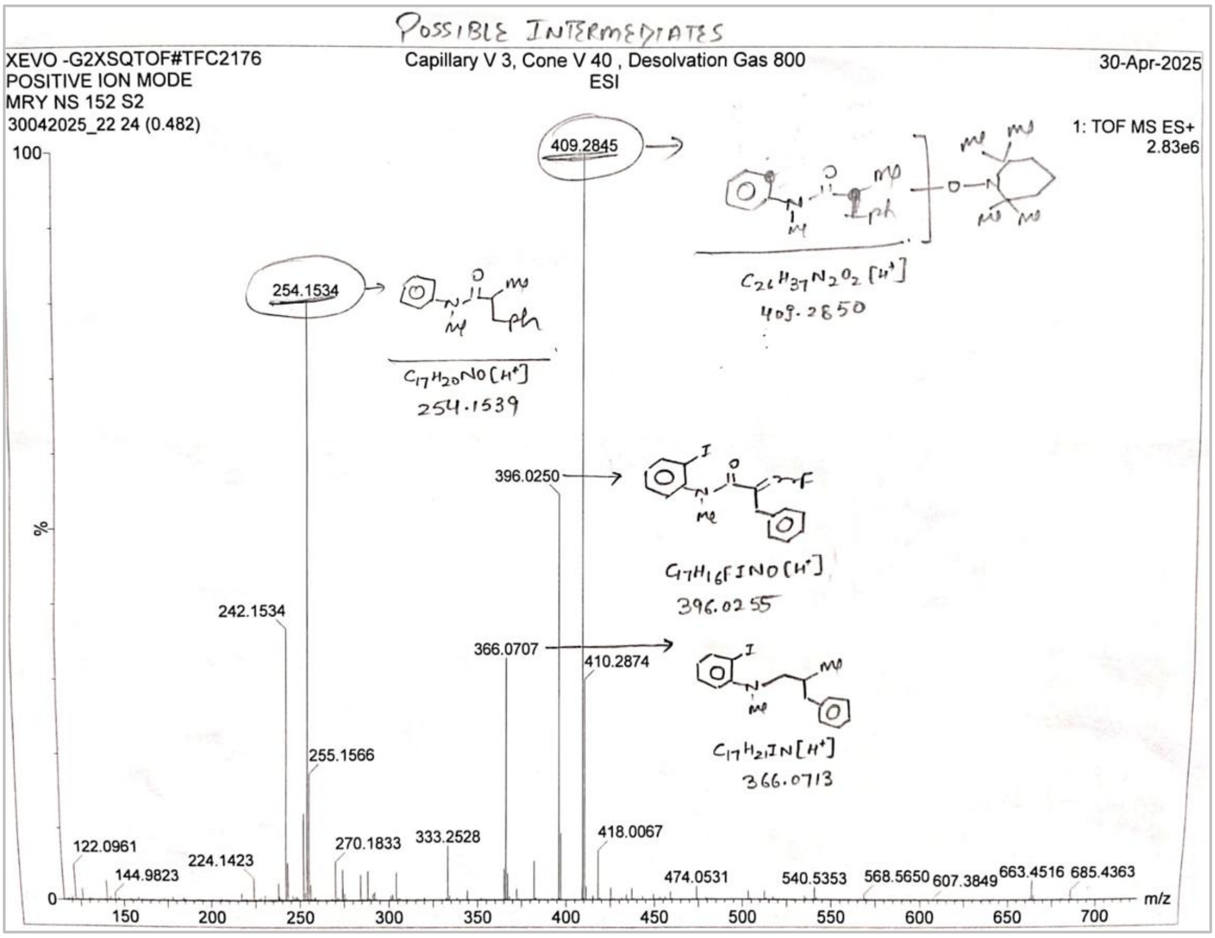
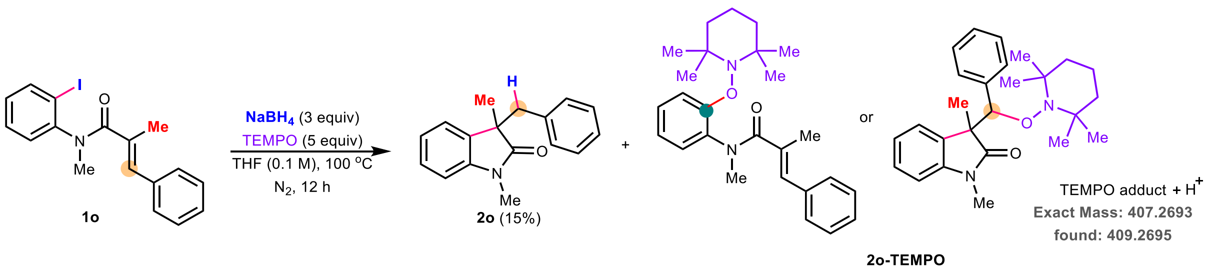


Figure S14. HRMS data for TEMPO trapping experiments with **1a**.

Result: *Under this control experiment, the TEMPO adduct was detected for* ***1a*** *(Figure S14); the presence of TEMPO or BHT was found to reduce the conversion efficiency toward the desired product (Scheme S18 and S19). These findings suggest that a radical pathway may be involved as one of the mechanistic routes for this transformation.*

TEMPO trapping experiment with 1o:

According to **GP-III**, the reaction of (*Z*)-*N*-(2-iodophenyl)-*N*,2-dimethyl-3-phenylacrylamide (**1o**, 37.7 mg, 0.1 mmol), TEMPO (78.1 mg, 5 equiv) with NaBH4 (11.35 mg, 0.3 mmol), afforded **2o** (3.8 mg) in 15% yield as a white solid.



Scheme S20. Reaction of **1o** with NaBH4 in the presence of TEMPO.

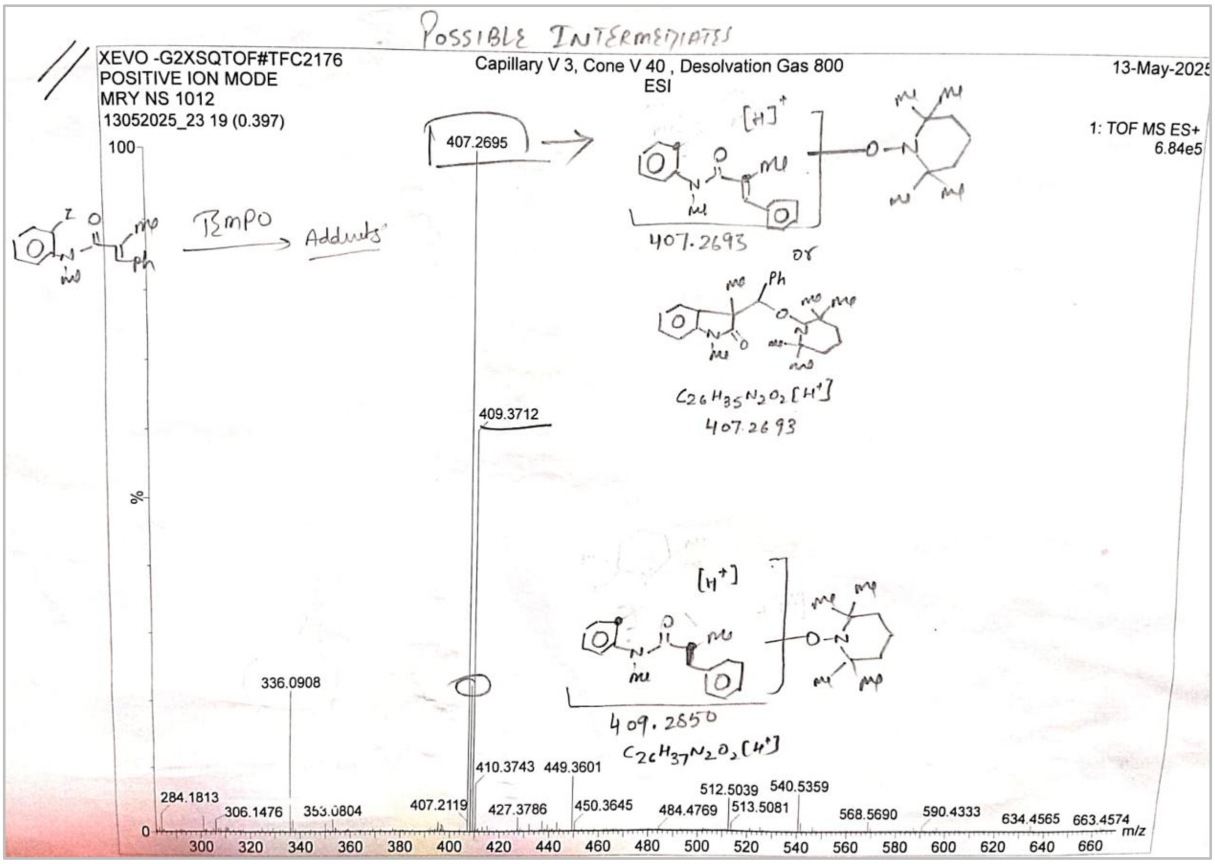
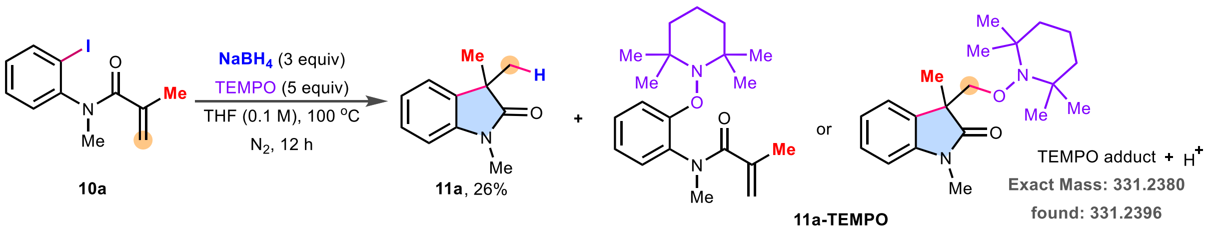


Figure S15. HRMS data for TEMPO trapping experiments with **1o**.

TEMPO trapping experiment with 10a:

According to **GP-III**, the reaction of *N*-(2-iodophenyl)-*N*-methylmethacrylamide (**10a**, 30.1 mg, 0.1 mmol), TEMPO (78.1 mg, 5 equiv), with $NaBH_4$ (11.35 mg, 3 equiv), afforded **11a** (4.5 mg) in 26% yield as a colorless liquid.



Scheme S21. Reaction of **10a** with $NaBH_4$ in the presence of TEMPO.

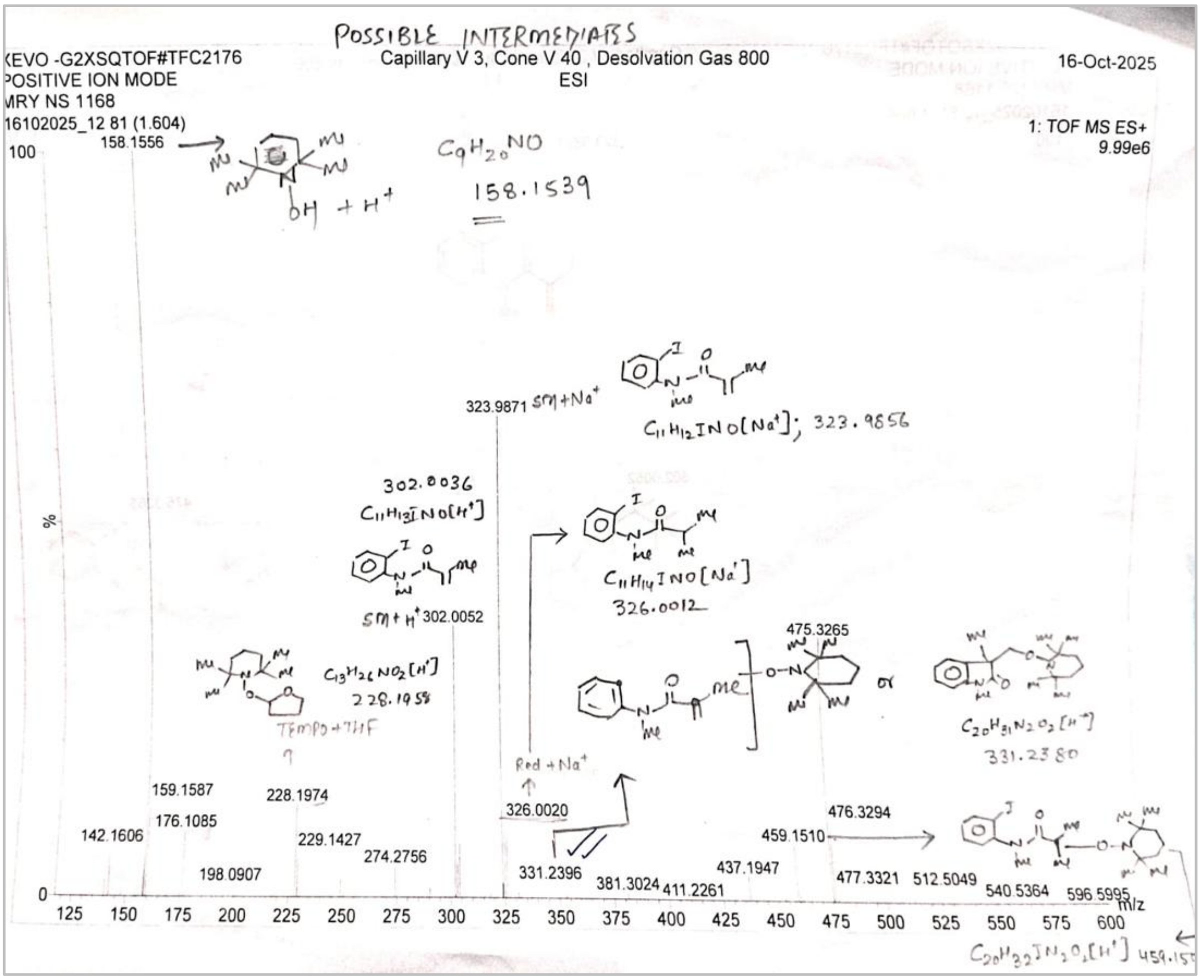


Figure S16. HRMS data for TEMPO trapping experiments with **10a**.

Result: *Substrates **1o** and **10a**, in the presence of TEMPO, gave lower yields of products, hence confirming the possibility of a radical mechanism. Also, they afforded the corresponding TEMPO adducts (Schemes 20 and 21).*

CE 9 Trace Metal Analysis by ICP-MS:

Trace metal analysis was performed by ICP-MS (Agilent 7900). The parameters used during sample preparation are provided below:

Nebulizer Gas flow: ~ 1 L/min, Auxiliary Gas flow: ~ 1 L/min, Plasma Gas flow: ~15 L/min, He Gas flow in Reaction Cell: ~ 0.2 mL/min, Reflected Power: ~ 45 W, Forward Power: ~ 1500 W, Analyzer vacuum: ~6x10^{-5}.

Microwave Digestion: Samples ($NaBH_4$ powder, >98.0%, purchased from Sigma-Aldrich) were digested in a microwave reaction system (Anton Paar make model: Multiwave PRO), concentrated HCl (6 mL), concentrated HNO_3 (2 mL), internal temperature limit (ºC): 200, max. microwave power (Watt): 1200, max. pressure (bar): 60, volume make up: 40 mL of Milli-Q water, filtration of samples: 0.2-micron membrane.

Sample preparation:

Sample weight = 0.0962 g, Volume makeup = 40 mL, Concentration = 2.405 g/L

Table S2. Residual metal content in the $NaBH_4$:

Element	Isotope monitored	Mean conc. (ppb)	RSD (%)	SD (ppb)	LOD (ppb)	LOD%
Boron	^{11}B [no gas]	58494.556	3.5	2047.31	6141.93	10.5
Boron	^{11}B [He]	52770.517	1.2	633.25	1899.75	3.6
Cobalt	^{59}Co [He]	<0.000	N/A	N/A	N/A	N/A
Nickel	^{60}Ni [He]	<0.000	N/A	N/A	N/A	N/A
Copper	^{63}Cu [He]	0.825	4.6	0.03795	0.114	13.8
Zinc	^{66}Zn [He]	0.648	1.2	0.007776	0.0233	3.6
Rhodium	^{103}Rh [He]	<0.000	N/A	N/A	N/A	N/A
Palladium	^{105}Pd [He]	0.469	6.6	0.03095	0.093	19.8
Silver	^{107}Ag [He]	0.105	10.2	0.01071	0.0321	30.6
Iridium	^{193}Ir [He]	<0.000	N/A	N/A	N/A	N/A
Gold	^{197}Au [He]	2.347	18.1	0.4245	1.274	54.3

RSD = Relative Standard Deviation, SD = Standard Deviation, LOD = Limit of Detection.

5. Computational Details and Results:

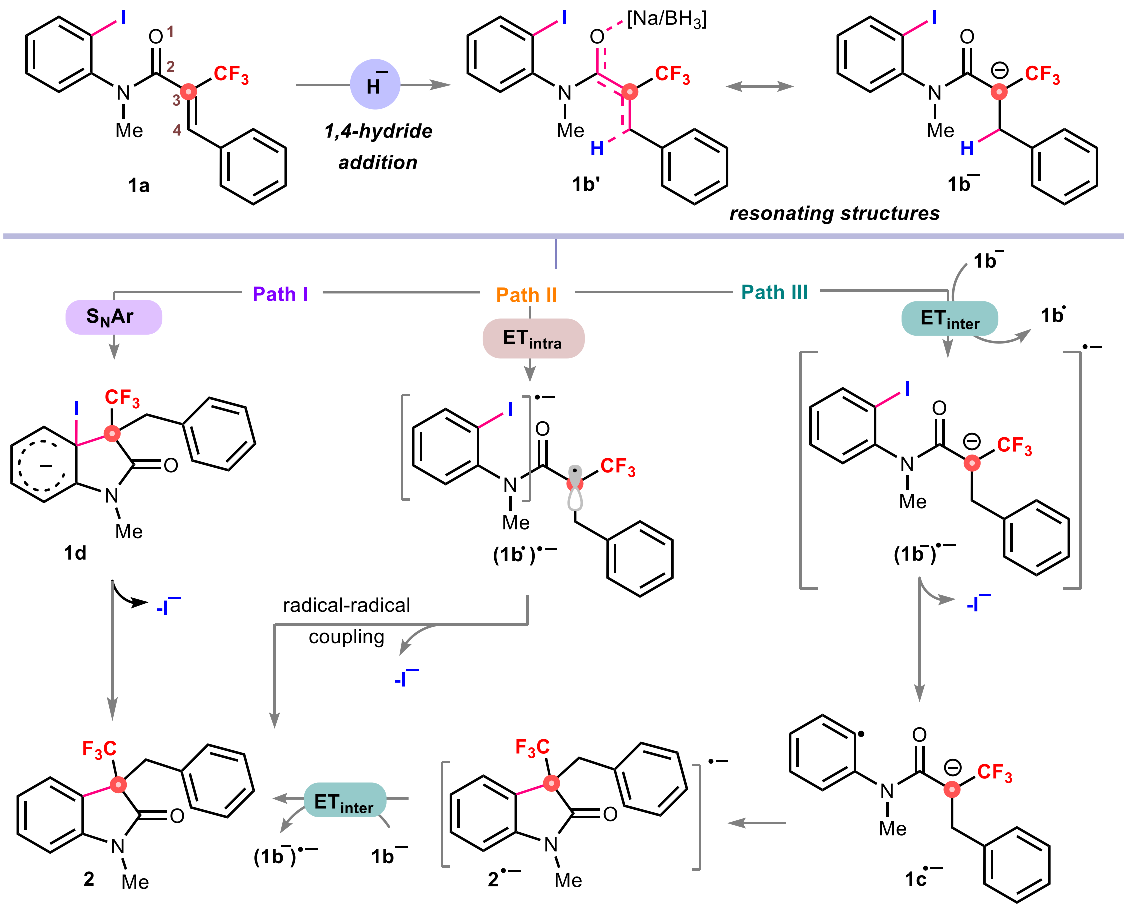


Figure S17. Plausible reaction paths

Based on literature precedents,[13] three plausible mechanistic pathways were considered (Figure S17): (i) a concerted S_NAr-type pathway (**Path I**), (ii) an intramolecular electron transfer (ET) process (**Path II**), and (iii) an intermolecular electron transfer process (**Path III**). In all three pathways, the reaction is most likely initiated by a 1,4-hydride addition to the *o*-iodo-trifluoromethylated acrylamide, generating a resonance-stabilized carbanion (**1b**$^-$/**1b′**). **Path I** (Concerted S_NAr): From **1b**$^-$, cyclization proceeds *via* a concerted S_NAr mechanism, accompanied by the elimination of iodide to afford the product.[14] **Path II** (Intramolecular ET): Alternatively, **1b**$^-$ can undergo intramolecular electron transfer to form **(1b˙)**$^{\bullet-}$. The loss of iodide from **(1b˙)**$^{\bullet-}$ yields a diradical species, which can recombine *via* radical–radical coupling to form the cyclized product.[15,16] **Path III** (Intermolecular ET): In this scenario, two molecules of **1b**$^-$ undergo intermolecular electron transfer, generating the radical dianion **(1b**$^-$**)**$^{\bullet-}$. Subsequent iodide elimination furnishes radical anion species **1c**$^{\bullet-}$, which undergoes cyclization to afford **2**$^{\bullet-}$. This intermediate can then participate in an intermolecular ET with another molecule of **1b**$^-$, ultimately producing the desired product **2** along with regeneration of

(1b⁻)•⁻, thereby sustaining the reaction.[15,16] The first path is an S_NAr mechanism, and the latter two are likely to follow the $S_{RN}1$-type mechanism. To differentiate between these possible pathways, we undertook density functional theory (DFT) calculations. These investigations were designed to probe the energetic feasibility of each pathway and to identify the most likely operative mechanism under the reaction conditions.

Computational Details: The geometries of all species were optimised by the DFT method employing the B3LYP functional[17] with the BSI basis set. In BSI, 6-31+G(d,p)[18-25] basis sets were employed for H, C, N, O, F, Cl, B, and Na atoms, and the aug-cc-pVDZ-PP[26,27] basis set was employed for I and Br atoms with the effective core potentials (ECPs) for their core electrons. The solvent effects of THF were evaluated by the polarizable continuum model (PCM).[28] The vibrational frequencies were calculated with the B3LYP/BSI to check whether the optimized species is in an equilibrium structure or a transition state. The intrinsic reaction coordinate (IRC) calculation was carried out to confirm that each transition state connects a corresponding reactant and a product of each elementary step.

Single-point calculations with the B3LYP functional were performed to refine the potential energies with a better basis set system named BSII, where the geometries optimized by the B3LYP/BSI were employed. The PCM method was used to incorporate the solvent effects of THF, too. In BSII, 6-311++G(d)[21,24,25,29,30] basis sets for H, C, N, O, F, Cl, B, and Na atoms, and aug-cc-pVDZ-PP basis set were employed for I and Br atoms with the effective core potentials (ECPs) for their core electrons. Thermal corrections and entropy contributions of vibrational movements to the Gibbs energy change were evaluated at the B3LYP/BSI level at 373.15 K and 1 atm in THF. The Gibbs energy was calculated with the B3LYP functional using BSII, where the translational entropy was corrected with the method developed by Whitesides et al.[31] The calculated Gibbs energy was used for the discussion. All these calculations were carried out using the Gaussian 16 program.[32]

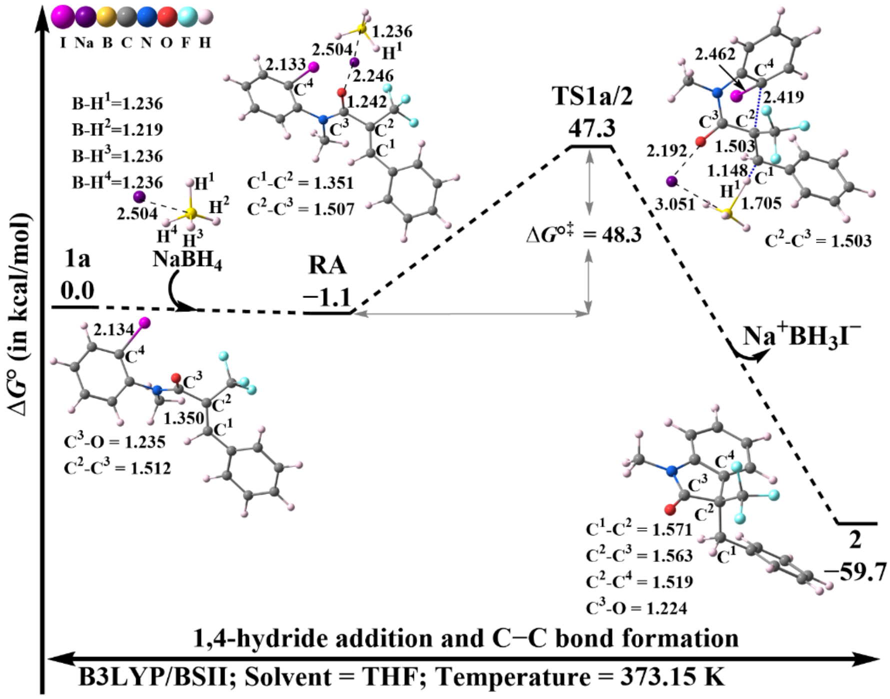


Figure S18. Gibbs energy changes (in kcal/mol) and geometry changes with several important bond distances (in Å unit) in a concerted single-step 1,4-hydride addition and C-C bond formation to produce **2** from **1a** and $NaBH_4$.

The first step of this conversion is the formation of an energetically stable ($\Delta G°$ = −1.1 kcal/mol) reactant adduct **RA**. In the **RA**, $NaBH_4$ interacts through the Na atom with the O atom of **1a** with a bond distance of 2.246 Å; see Figure S18 in supporting information (SI) for the geometry and Gibbs energy changes. In both $NaBH_4$ and **RA**, the Na···B distance is 2.504 Å. However, the C^3–O bond distance slightly increased from 1.235 Å to 1.242 Å. The **RA** undergoes the 1,4-hydride addition of the B–H^1 bond to the C^1–C^2 bond by transfer of H^1 to the C^1 atom. Here, we investigated two possibilities: (i) A single-step involving simultaneous 1,4-hydride addition and C–C bond formation and (ii) a stepwise 1,4-hydride addition followed by C–C bond formation. The simultaneous 1,4-hydride addition and C–C bond formation occur *via* transition states **TS1a/2**, which subsequently lead to product **2** with the elimination of $NaBH_3^+I^-$. However, this pathway requires a significantly high Gibbs free energy barrier ($\Delta G^{\circ\ddagger}$) of 48.3 kcal/mol, with an exergonic Gibbs free energy of reaction ($\Delta G°$) of −58.7 kcal/mol, suggesting that this pathway is kinetically unfavourable and is therefore ruled out (Figure S18 in SI).

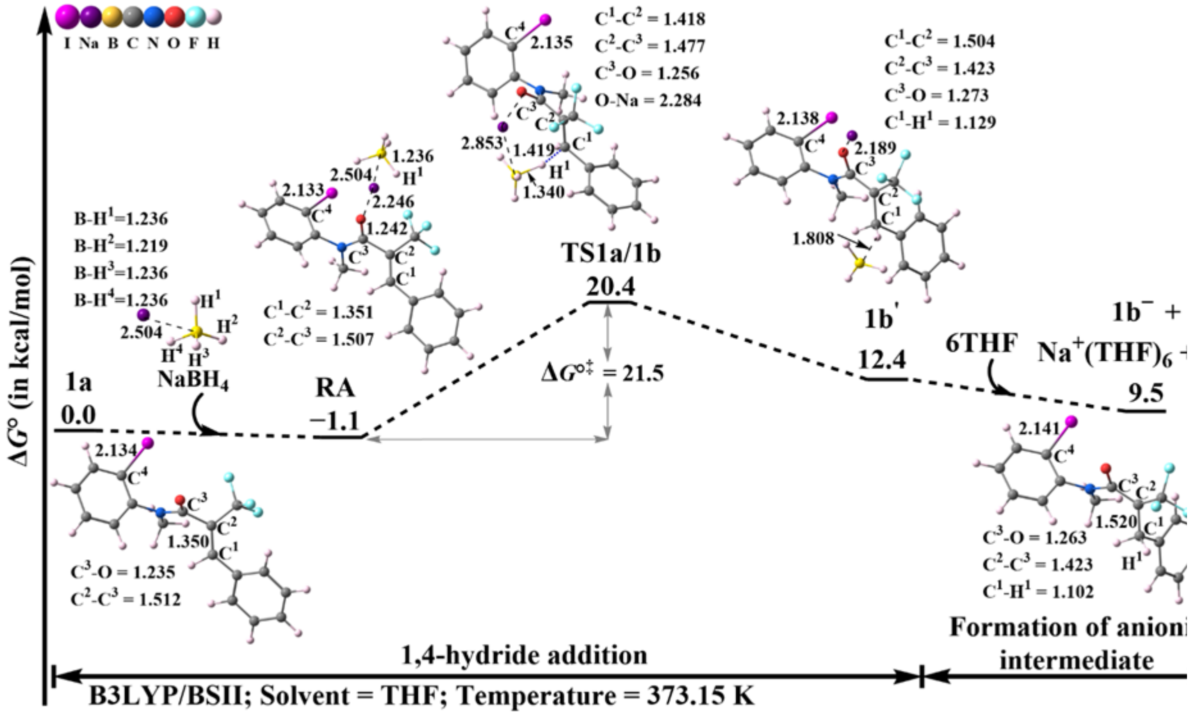


Figure S19. Gibbs energy changes (in kcal/mol) and geometry changes with several important bond distances (in Å) in the 1,4-hydride addition. The numbers below the name of the species are Gibbs free energies (in kcal/mol) relative to the sum of **1a** and $NaBH_4$ **R1**.

A stepwise, 1,4-hydride addition occurs *via* **TS1a/1b** (Figure S19 in SI). In **TS1a/1b**, the B–H^1 bond elongates from 1.236 Å to 1.340 Å, accompanied by an increase in B···Na distance to 2.853 Å. The Na···O distance also moderately increases to 2.284 Å. The C^1−H^1 bond distance is 1.419 Å, and the C^1−C^2 bond distance increases from 1.351 Å to 1.418 Å. All these geometry changes indicate that the hydride transfer from $NaBH_4$ to the β-carbon (C^1) of **1a** is in progress at the **TS1a/1b**. The **TS1a/1b** stabilizes to the endergonic intermediate species **1b′** ($\Delta G°$ = 13.5 kcal/mol). This intermediate **1b′** is converted to moderately stable enolate anion **1b⁻** along with $Na^+(THF)_n$ and BH_3 ($\Delta G°$ = 10.6 kcal/mol). This moderate stabilization is attributed to the release of Na^+ ion, which is stabilized by a polar coordinating solvent like THF. The stabilization of Na^+ by solvent molecules seems to be progressively increasing with an increase in the number of THF molecules but saturates up to six THF molecules (Figure S20 in SI). We also investigated the role of the solvent in the stabilization of the Na^+ ion. For instance, in contrast to the polar THF solvent, the non-polar 1,4-dioxane solvent destabilizes the Na^+ ion (Table S3 in SI). This is consistent with the experimental fact that 1,4-dioxane produced no **2a** product and low **3a** (Table S1 in SI, entry 6). In **1b⁻**, the C^1−H^1 bond distance is 1.102 Å, suggesting that this C−H bond is completely established. The C^2−C^3 bond distance decreases from 1.507 Å to 1.423 Å, and the C^3−O bond distance increases slightly from 1.242 Å to 1.263 Å, confirming enolate formation. The overall formation of **1b⁻** starting from the **RA** *via* **TS1a/1b** and intermediate **1b′** has a moderate $\Delta G^{\circ\ddagger}$ (21.5 kcal/mol) and ΔG° (10.6 kcal/mol) values, suggesting that this 1,4-hydride transfer occurs easily (Figure S19 in SI).

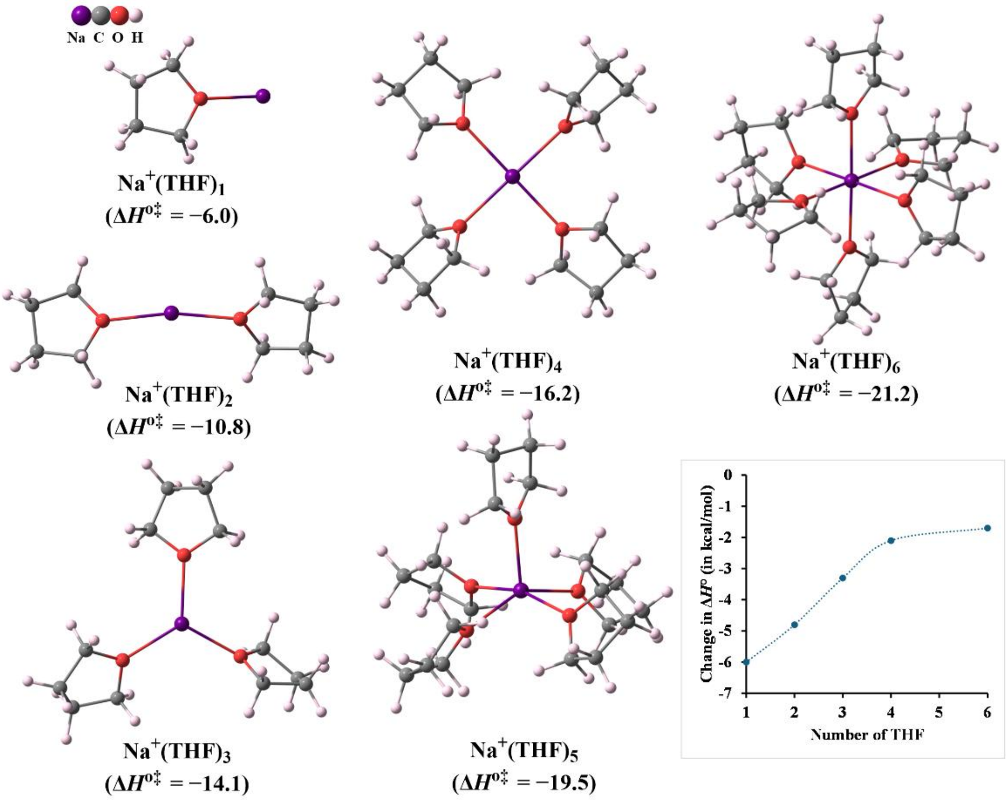


Figure S20. Relative Stability of $Na^{+}(THF)_{n}$ Complexes.

Table S3. Changes in Gibbs free reaction energy (ΔG°_{ET}) and Gibbs free energy barrier ($\Delta G^{\circ\ddagger}_{ET}$) for 1,4-hydride addition, aromatic nucleophilic substitution mechanism (S_NAr, **Path I**), intramolecular ET (ET_{intra}, **Path II**), and intermolecular ET (ET_{inter}, **Path III**) using Marcus−Hush theory with **1b⁻** as acceptor.

Halogen	**1,4-hydride addition**				**S_NAr, Path I**		**ET_{intra}, Path II**		**ET_{inter}, Path III**	
	RA ($\Delta G°$)	**TS1a/1b ($\Delta G^{\circ\ddagger}$)**	**1b′ ($\Delta G°$)**	**$1b^-$ ($\Delta G°$)**	**$TS1b^-/2$ ($\Delta G^{\circ\ddagger}$)**	**2 ($\Delta G°$)**	**$TS1b^-/(1b^{\bullet})^{\bullet-}$ ($\Delta G^{\circ\ddagger}_{ET}$)**	**$(1b^{\bullet})^{\bullet-}$ (ΔG°_{ET})**	**$TS1b^-/(1b^-)^{\bullet-}$ ($\Delta G^{\circ\ddagger}_{ET}$)**	**$(1b^-)^{\bullet-}$ (ΔG°_{ET})**
THF (373.15 K)										
F	-1.6	22.2	13.1	9.3	33.6	-25.4	118.7	70.0	188.3	90.4
Cl	-1.9	20.4	15.0	10.3	37.7	-49.3	125.3	70.7	188.2	88.1
Br	-4.7	23.1	16.3	12.9	34.2	-50.2	42.0	37.8	32.3	31.1
I	-1.1	21.5	13.4	10.5	32.1	-56.9	34.8	32.2	18.2	17.9
1,4-dioxane										
I (373.15)	-8.2	19.6	14.8	54.0	-	-	-	-	-	-
I (403.15)	-7.0	19.9	14.9	52.9	-	-	-	-	-	-

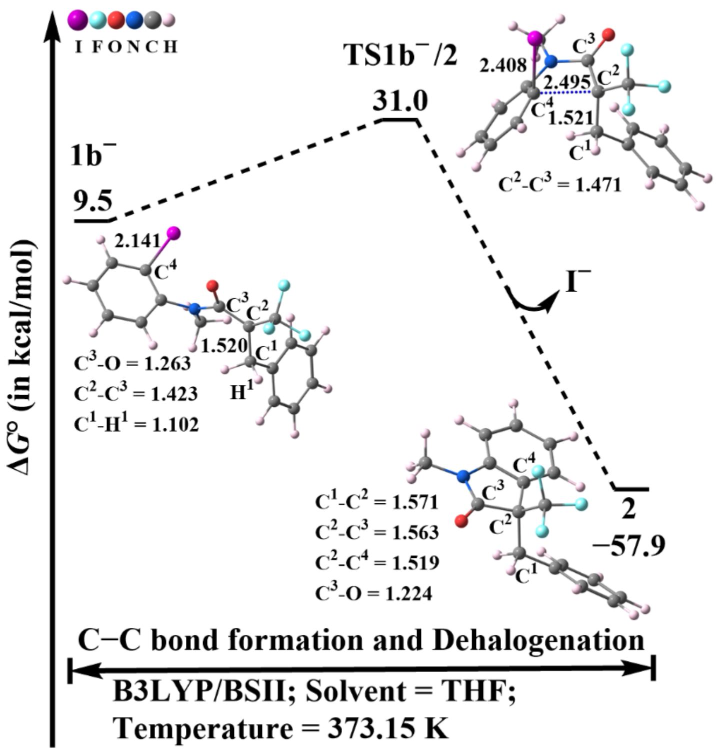


Figure S21. Gibbs energy changes (in kcal/mol) and geometry changes with several important bond distances (in Å unit) in the Nucleophilic Aromatic Substitution (S_NAr) reaction starting from **1b⁻ (Path I)**.

Starting from enolate anion **1b⁻**, three possible reaction pathways (**Paths I-III**) can occur depending on the initiation step. The feasibility of all these proposed pathways was examined through detailed computational investigation as discussed below. Although **Path-I** is less likely from a mechanistic investigation, we still performed it to understand the energetics involved in this path and compare it with the latter two paths. In **Path I**, starting from **1b⁻** anion, a nucleophilic aromatic substitution (S_NAr) occurs in which anion **1b⁻** attacks the aromatic ring through C^2−C^4 bond formation *via* transition state **TS1b⁻/2** and subsequent dehalogenation afford the product **2** (cf. Figure S21 in SI.). The respective $\Delta G^{\circ\ddagger}$ and ΔG° values for this step are 32.1 kcal/mol and −56.8 kcal/mol with respect to the most stable reactant species **RA** (−1.1 kcal/mol); see Figure S19 in SI.

In **Path II**, an intramolecular electron transfer (ET_{intra}) from 1b⁻ anion to the C−X bond may take place to give diradical anion $(1b^{\bullet})^{\bullet-}$ (Figure S22 in SI) with ΔG° of 32.3 kcal/mol with respect to the most stable species RA (Figure S19 in SI), suggesting that this step is endergonic. In this mechanism, the single **1b⁻** anion acts as both a donor and an acceptor. The $\Delta G^{\circ\ddagger}$ value of this step,

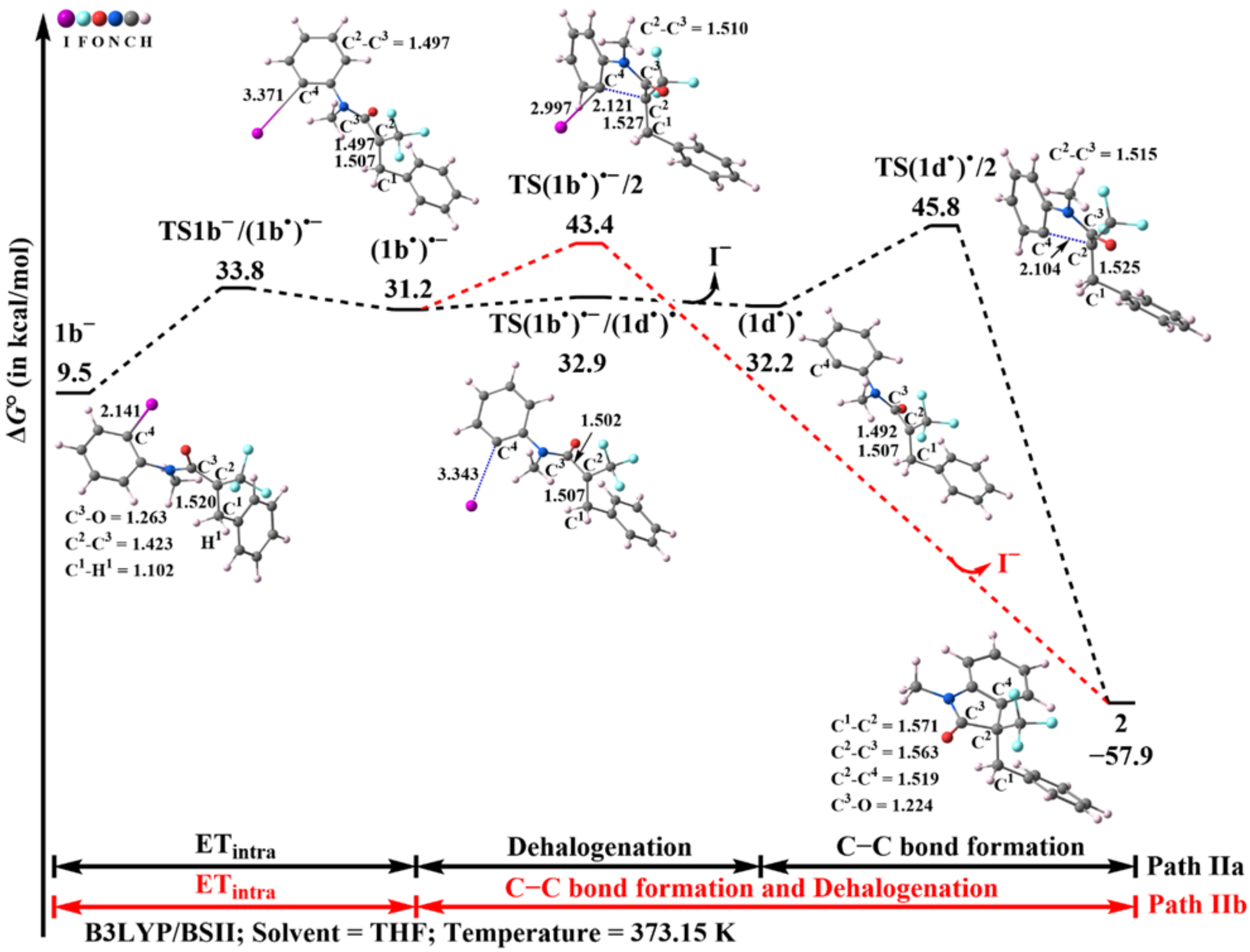


Figure S22. Gibbs energy changes (in kcal/mol) and geometry changes with several important bond distances (in Å unit) in Intramolecular Electron Transfer (ET_{intra}) reaction starting from **1b⁻** (**Path II**).

calculated using the Marcus-Hush theory for this ET_{intra}, is 34.9 kcal/mol (Table S4 in SI). Starting from the diradical anion **(1b•)•⁻** two possible reaction routes can occur: **Path IIa** and **Path IIb**. In **Path IIa**, a rapid dehalogenation of the radical anion moiety generates the biradical species **(1d•)•** *via* **TS(1b•)•⁻/(1d•)•** with a $\Delta G^{\circ\ddagger}$ value of 34.0 kcal/mol and ΔG° value of 33.3 kcal/mol with respect to the most stable species RA (cf. Figure S19 and S22 in SI). The biradical **(1d•)•** then forms product **2** through intramolecular C^4−C^2 bond coupling of two radical centers *via* **TS(1d•)•/2**. As shown in Figure S22 in SI, in **TS(1d•)•/2**, the C^2−C^3 distance increases slightly from 1.492 Å to 1.515 Å. The C^4−C^2 distance in **TS(1d•)•/2** is 2.104 Å, which reduces to 1.519 Å in **2**, confirming the completion of radical cyclization (ΔG° = −56.8 kcal/mol). However, the large $\Delta G^{\circ\ddagger}$ value of 46.9 kcal/mol for radical-radical coupling indicates that **Path IIa** is difficult. **In Path IIb**, starting from diradical anion **(1b•)•⁻**, the product **2** is produced through transition state **TS(1b•)•⁻/2** *via* simultaneous nucleophilic aromatic substitution involving $C^4{-}C^2$ bond formation and the dehalogenation. Despite large exergonicity ($\Delta G°$ = −56.6 kcal/mol with respect to the most stable species RA), this $C^4{-}C^2$ bond coupling is also difficult due to the high $\Delta G^{°‡}$ value (44.5 kcal/mol with respect to the most stable RA).

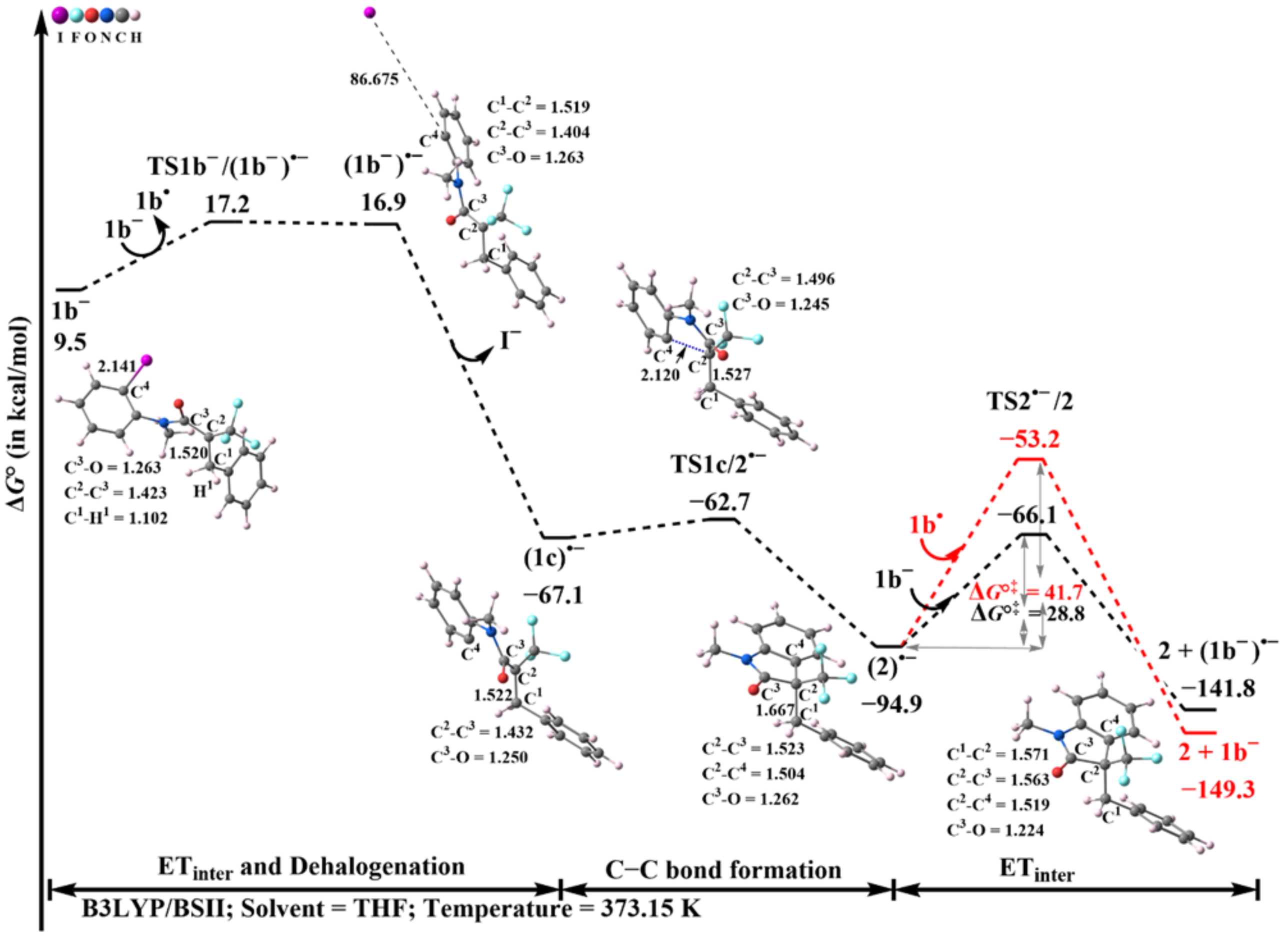


Figure S23. Gibbs energy changes (in kcal/mol) and geometry changes with several important bond distances (in Å unit) in the Intermolecular Electron Transfer (ET_{inter}) reaction starting from **1b**⁻ (**Path III**).

Starting from **1b**⁻, an intermolecular electron transfer (ET_{inter}) may take place *via* **Path III**, which requires an electron donor. In this mechanism, **1b**⁻ anion acts as both the electron donor and electron acceptor. Therefore, two **1b**⁻ species react with each other to produce the radical dianion **(1b⁻)**$^{•-}$ and radical **1b**$^{•}$ (Figure S23 in SI or Figure 2b in main text). This ET_{inter} is moderately endergonic ($\Delta G°$ of 7.4 kcal with respective **1b**⁻ or 18.0 kcal/mol with respect to **RA**; Figure S19). For this ET_{inter} mechanism, we also calculated the $\Delta G^{°‡}$ value by employing the Marcus-Hush theory, considering it to be an outer-sphere ET process. The calculated $\Delta G^{°‡}$ for this ET_{inter} is 18.3 kcal/mol with respect to the most stable species **RA** (Figures S19 and S23 in SI). We also investigated the effect of different halogen species on this intermolecular electron transfer process. The calculated $\Delta G°$ and $\Delta G^{°‡}$ values (Table S3 in SI) suggest that the ET_{inter} becomes difficult with an increase in the electron affinity of the halogen in the order F > Cl > Br >> I. This radical dianion **(1b⁻)**$^{•-}$ undergoes the exergonic dehalogenation to give distonic radical anion **1c**$^{•-}$ ($\Delta G°$ = −66.0 kcal/mol with respective to **RA**). The next step, starting from **1c**$^{•-}$ is the intramolecular C^4−C^2 bond formation to give the cyclized radical anion **2**$^{•-}$ via **TS1c**$^{•-}$**/2**$^{•-}$ (Figure S23 in SI or Figure 2b in main text). The small $\Delta G^{°‡}$ (4.4 kcal/mol) and moderate exergonicity ($\Delta G°$ = −27.8 kcal/mol) suggest that this step occurs easily. In **TS1c**$^{•-}$**/2**$^{•-}$, the C^2−C^3 distance increases slightly from 1.432 Å to 1.496 Å and becomes 1.523 Å in **2**$^{•-}$. The C^2−C^4 distance in **TS1c**$^{•-}$**/2**$^{•-}$ is 2.120 Å, which shortens to 1.504 Å, indicating that this radical cyclization is complete in **2**$^{•-}$. The formation of product **2** can occur in two distinct ways. The first case is intermolecular electron transfer between **2**$^{•-}$ and radical **1b**$^{•}$ form in the first step of Figure S23 in SI or Figure 2b in main text. Although this step is exergonic ($\Delta G°$ = −54.4 kcal/mol), the large $\Delta G^{°‡}$ value (41.4 kcal/mol) suggests that this intermolecular electron transfer is difficult. The other possible intermolecular electron transfer occurs between **2**$^{•-}$ and **1b**$^{-}$ to afford product **2**. This step is also exergonic ($\Delta G°$ = −46.9 kcal/mol) but it has a moderate value of $\Delta G^{°‡}$ (28.8 kcal/mol) estimated by employing the Marcus-Hush theory. This moderate $\Delta G^{°‡}$ turns out to be smaller than the ones for the other two possible paths (Table S3 in SI).

Based on these studies, among the three possible pathways (**Path I**, **II**, and **III**) proposed above for the generation of **2** from **1b**$^{-}$, due to the high $\Delta G^{°‡}$ values, the nucleophilic aromatic substitution (**Path I**; 32.1 kcal/mol) as well as intramolecular ET (**Path II**; 34.9 kcal/mol) may be ruled out. The intermolecular ET *via* the generation of radical dianion **(1b⁻)**$^{•-}$ followed by dehalogenation and radical cyclization (**Path III**; 18.3 kcal/mol) is the most favourable pathway.

MARCUS-HUSH CALCULATIONS

We employed the Marcus−Hush theory to calculate the activation free energy ($\Delta G^{\circ\ddagger}_{ET}$) associated with outer-sphere electron transfer (ET) in both ET_{inter} and ET_{intra} pathways.

$$\Delta G^{\circ\ddagger}_{ET} = \frac{\lambda}{4}\,(1 + \frac{\Delta G_{rel}}{\lambda})^2 \; \ldots(1)$$

where ΔG_{rel} represents the relative free energy difference between the reactants and products, while λ denotes the reorganization energy defined as the vertical energy difference between the minimum of the product potential energy surface and the point where it intersects with the reactant surface.

In this study, the ET reactions were evaluated in THF solvent. The solvent reorganization energy (λ_o) was determined using Equation (2):

$$\lambda_0 = 331.2 \text{ kcal/mol}\,(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{2a_1 + 2a_2}) + (\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon}) \; \ldots(2)$$

where a_1 and a_2 are the radii of the species involved in the ET, obtained from the optimized geometries used in the SCRF calculations (in angstroms). The optical dielectric constant (ε_{op} = 1.974025) and static dielectric constant (ε = 7.4257) correspond to those of THF solvent. For the intermolecular and intramolecular ET process, the anion **1b**⁻ serves as both the electron donor and acceptor. The calculated results for both intermolecular and intramolecular ET processes are summarized in Table S3 in SI.

Table S4. Details for the calculations of activation free energy ($\Delta G^{\circ\ddagger}_{ET}$) for intermolecular and intramolecular ET using Marcus−Hush theory with **1b⁻** as acceptor.

Species	SCRF a_0 (Å)	λ_0 (kcal/mol)	($\Delta G^{\circ\ddagger}_{ET}$) kcal/mol)	(ΔG°_{ET}) kcal/mol)
Acceptor				
1b⁻	5.60	11.00	-	-
Donor				
1b⁻ (inter)	5.60	11.00	18.2	17.9
1b⁻ (intra)	5.60	11.00	34.8	32.2
2•⁻radical anion	5.46	11.14	28.8	-47.0

For THF solvent, the ε_{op} and ε values are 1.974025 and 7.4257, respectively.

Table S5: Cartesian Coordinates of the optimized geometries.

1a

E(scf done): -1380.98019511 a.u.

C	-0.101722000	-3.910295000	-3.860726000
C	0.558096000	-2.756333000	-4.292507000
C	-1.451960000	-3.856409000	-3.505896000
H	1.604880000	-2.801535000	-4.571605000
H	-1.968744000	-4.750858000	-3.172666000
C	-0.137521000	-1.546253000	-4.368523000
C	-2.138630000	-2.644352000	-3.581168000
H	-3.188714000	-2.586150000	-3.310738000
C	-1.492491000	-1.478909000	-4.012388000
H	0.444339000	-4.847181000	-3.806092000
I	0.906603000	0.184765000	-5.052431000
N	-2.234641000	-0.247309000	-4.038539000
C	-2.982455000	0.026250000	-5.150090000
O	-2.920684000	-0.656118000	-6.177070000
C	-3.952158000	1.185612000	-5.106995000
C	-4.992702000	1.152648000	-4.247024000
H	-4.937523000	0.358623000	-3.502637000
C	-2.149112000	0.588812000	-2.831737000
H	-2.501665000	1.595825000	-3.047128000
H	-2.741375000	0.162032000	-2.014774000
H	-1.104665000	0.647133000	-2.516858000
C	-3.723499000	2.225398000	-6.175238000
F	-4.065933000	3.473717000	-5.765323000
F	-2.412934000	2.286656000	-6.522489000
F	-4.414922000	1.993505000	-7.326471000
C	-6.199052000	1.983531000	-4.110990000
C	-6.761515000	2.097822000	-2.822759000
C	-6.853869000	2.612739000	-5.187583000
C	-7.909918000	2.859257000	-2.606467000
C	-8.011828000	3.359932000	-4.971524000
C	-8.538375000	3.495241000	-3.682054000
H	-6.285635000	1.592820000	-1.986229000
H	-6.478743000	2.499615000	-6.197386000
H	-8.318807000	2.946746000	-1.604283000
H	-8.508729000	3.831378000	-5.814224000
H	-9.439059000	4.079925000	-3.519744000

NaBH4 (R1)

E(scf done): -189.608463630 a.u.

Na	-2.524713000	-1.957279000	-7.819164000
B	-4.298177000	-2.765806000	-9.352387000
H	-4.666493000	-2.859831000	-8.175814000
H	-4.051639000	-1.581078000	-9.603639000
H	-5.171454000	-3.179063000	-10.095415000
H	-3.265717000	-3.427975000	-9.502446000

RA (Reactant Adduct)
E(scf done): -1570.60124864 a.u.

C	-4.280647000	-0.839530000	2.629520000
C	-4.284922000	-0.694682000	1.239368000
C	-3.077653000	-1.032859000	3.312984000
H	-5.219955000	-0.540806000	0.712487000
H	-3.070484000	-1.143358000	4.392593000
C	-3.080315000	-0.743444000	0.531917000
C	-1.878696000	-1.083667000	2.601334000
H	-0.935095000	-1.231087000	3.117934000
C	-1.867898000	-0.939064000	1.208949000
H	-5.220338000	-0.798505000	3.171733000
N	-0.607726000	-1.031172000	0.516158000
C	0.135475000	0.097975000	0.391994000
O	-0.306025000	1.210703000	0.723766000
C	1.547372000	0.009266000	-0.127081000
C	2.463384000	-0.720992000	0.546831000
H	2.046987000	-1.357492000	1.326611000
C	-0.234234000	-2.365999000	0.019270000
H	0.554454000	-2.281916000	-0.725891000
H	0.101271000	-3.007228000	0.840979000
H	-1.109758000	-2.820460000	-0.448773000
C	1.826540000	0.905691000	-1.308228000
F	2.766453000	0.394355000	-2.138053000
F	0.708918000	1.083072000	-2.057852000
F	2.253048000	2.154077000	-0.957430000
C	3.924987000	-0.828889000	0.440700000
C	4.510453000	-2.047847000	0.842259000
C	4.770261000	0.220296000	0.029274000
C	5.891268000	-2.232962000	0.782377000
C	6.152267000	0.038444000	-0.012169000
C	6.716972000	-1.189009000	0.352616000
H	3.874159000	-2.856352000	1.192381000
H	4.357152000	1.186786000	-0.232233000
H	6.322017000	-3.183874000	1.080995000
H	6.790506000	0.860122000	-0.322828000
H	7.793708000	-1.325274000	0.315945000
Na	-0.317699000	3.437507000	1.019650000
B	-0.539704000	5.854370000	1.637360000
H	-0.943586000	5.671942000	0.483698000
H	-0.662904000	7.029444000	1.941808000
H	-1.197097000	5.146176000	2.408431000
H	0.649005000	5.522422000	1.704232000
I	-3.134445000	-0.498464000	-1.586759000

TS1a/2
E(scf done): -1570.53055104 a.u.

C	2.064108000	-2.680137000	2.000344000
C	1.225560000	-2.319256000	0.927654000
C	2.994153000	-1.777456000	2.513334000

H	0.550570000	-3.049832000	0.496332000
H	3.656136000	-2.068067000	3.322930000
C	1.347416000	-1.048023000	0.385107000
C	3.049143000	-0.469528000	2.001324000
H	3.700184000	0.270707000	2.457476000
C	2.214366000	-0.100980000	0.949642000
H	2.003469000	-3.690611000	2.395698000
I	1.346242000	-1.128499000	-2.075161000
N	2.083220000	1.223864000	0.469107000
C	0.822707000	1.633537000	0.105471000
O	0.661211000	2.699956000	-0.527974000
C	-0.299574000	0.722750000	0.456761000
C	-1.446383000	0.720246000	-0.515399000
H	-1.036010000	0.579850000	-1.517924000
C	3.236862000	2.113166000	0.394697000
H	2.972088000	2.973308000	-0.217814000
H	3.534771000	2.461175000	1.391073000
H	4.077519000	1.585263000	-0.063226000
C	-0.676152000	0.700498000	1.894271000
F	-1.182310000	-0.489315000	2.335529000
F	0.342754000	1.009782000	2.743858000
F	-1.676897000	1.622945000	2.207078000
C	-2.573134000	-0.274348000	-0.283645000
C	-2.445061000	-1.594844000	-0.742334000
C	-3.761937000	0.095939000	0.360858000
C	-3.472587000	-2.522797000	-0.550323000
C	-4.792382000	-0.829253000	0.554192000
C	-4.651127000	-2.144331000	0.101062000
H	-1.535661000	-1.895054000	-1.254030000
H	-3.884996000	1.114350000	0.716149000
H	-3.352828000	-3.539717000	-0.914324000
H	-5.704925000	-0.520139000	1.056690000
H	-5.451412000	-2.864099000	0.248889000
Na	-0.110478000	4.607684000	-1.283584000
B	-2.682587000	2.976506000	-1.466910000
H	-2.636211000	3.712899000	-0.521596000
H	-3.688905000	2.381593000	-1.694188000
H	-1.862995000	3.070103000	-2.334167000
H	-1.918188000	1.765928000	-0.541836000

2

E(scf done): -1085.84923677 a.u.

C	-0.634722000	-3.488119000	-0.623017000
C	0.191091000	-2.354131000	-0.555221000
C	-1.776872000	-3.582959000	0.176216000
H	1.073648000	-2.285306000	-1.180139000
H	-2.405780000	-4.465954000	0.114832000
C	-0.145281000	-1.327844000	0.319590000
C	-2.132973000	-2.550697000	1.056549000
H	-3.025602000	-2.623259000	1.668101000

C	-1.304887000	-1.433992000	1.105318000
H	-0.381144000	-4.295137000	-1.302912000
N	-1.468825000	-0.277733000	1.889246000
C	-0.471710000	0.631785000	1.657218000
O	-0.354507000	1.728681000	2.188631000
C	0.528769000	-0.004366000	0.638315000
C	1.901203000	-0.113505000	1.394274000
H	1.688190000	-0.671925000	2.311032000
C	-2.564898000	-0.055863000	2.819084000
H	-2.417876000	0.918283000	3.284490000
H	-3.522473000	-0.064681000	2.289565000
H	-2.571640000	-0.831201000	3.591070000
C	0.606458000	0.898401000	-0.600785000
F	1.264017000	0.307698000	-1.628363000
F	-0.633380000	1.210551000	-1.065301000
F	1.237879000	2.070736000	-0.357177000
C	3.066589000	-0.768583000	0.680144000
C	3.297583000	-2.147385000	0.804424000
C	3.976006000	-0.003955000	-0.067420000
C	4.393743000	-2.750879000	0.181358000
C	5.072890000	-0.602909000	-0.691888000
C	5.283330000	-1.980376000	-0.573015000
H	2.619363000	-2.752543000	1.399663000
H	3.828891000	1.068679000	-0.158068000
H	4.555440000	-3.819342000	0.292041000
H	5.765350000	0.007222000	-1.264702000
H	6.137926000	-2.446488000	-1.054720000
H	2.170168000	0.901527000	1.699255000

$Na^+BH_3I^-$

E(scf done): -484.861014822 a.u.

Na	1.330074000	0.116484000	0.116974000
B	-1.434545000	0.083321000	0.081511000
H	-0.940745000	1.089569000	-0.371171000
H	-2.632909000	0.053995000	0.065214000
H	-0.927971000	-0.324987000	1.100763000
I	-0.776574000	-1.611528000	-1.552902000

TS1a/1b

E(scf done): -1570.57017428 a.u.

C	4.458323000	2.489376000	-0.857765000
C	4.477504000	1.124312000	-0.556907000
C	3.245668000	3.134026000	-1.114985000
H	5.419037000	0.625943000	-0.354347000
H	3.225788000	4.193786000	-1.349504000
C	3.278543000	0.407209000	-0.511739000
C	2.054175000	2.408802000	-1.073619000
H	1.103272000	2.894443000	-1.271825000
C	2.053744000	1.040981000	-0.769588000

H	5.392788000	3.041518000	-0.889336000
I	3.352785000	-1.669748000	-0.024103000
N	0.805442000	0.331679000	-0.775172000
C	0.045819000	0.333576000	0.367645000
O	0.550488000	0.750264000	1.439967000
C	-1.357283000	-0.122830000	0.301707000
C	-2.249962000	0.586472000	-0.541265000
H	-1.755906000	1.020197000	-1.409761000
C	0.439818000	-0.332274000	-2.031848000
H	-0.326641000	-1.080442000	-1.832843000
H	0.070653000	0.385200000	-2.774108000
H	1.322274000	-0.830890000	-2.440656000
C	-1.830696000	-0.809656000	1.518106000
F	-2.980040000	-1.511893000	1.354025000
F	-0.919821000	-1.678729000	2.034446000
F	-2.125483000	0.054655000	2.603388000
C	-3.649100000	0.120124000	-0.873982000
C	-3.802285000	-0.784699000	-1.937497000
C	-4.789183000	0.562768000	-0.193608000
C	-5.069489000	-1.246103000	-2.302085000
C	-6.057986000	0.099191000	-0.556122000
C	-6.203476000	-0.806367000	-1.610667000
H	-2.927732000	-1.133822000	-2.479480000
H	-4.683048000	1.272064000	0.620630000
H	-5.169319000	-1.945975000	-3.127038000
H	-6.931794000	0.450693000	-0.014654000
H	-7.189370000	-1.163636000	-1.894085000
Na	-0.791779000	2.149343000	2.647380000
B	-2.493679000	3.079677000	0.554953000
H	-2.930154000	2.874518000	1.671997000
H	-3.180629000	3.788387000	-0.139209000
H	-1.301586000	3.310371000	0.503857000
H	-2.559599000	1.858850000	0.005317000

1b′

E(scf done): -1570.58036042 a.u.

C	4.031935000	2.722418000	1.110157000
C	3.884288000	1.363419000	0.817226000
C	2.904648000	3.543308000	1.198261000
H	4.757751000	0.723572000	0.754889000
H	3.011407000	4.599996000	1.424547000
C	2.607001000	0.832259000	0.615996000
C	1.636306000	3.002144000	0.983624000
H	0.751728000	3.629985000	1.040209000
C	1.459947000	1.640428000	0.691569000
H	5.025956000	3.130264000	1.268162000
I	2.440934000	-1.263528000	0.227051000
N	0.141500000	1.150526000	0.440873000
C	-0.661820000	0.828690000	1.544387000
O	-0.043045000	0.617709000	2.637129000

C	-2.075975000	0.736050000	1.419151000
C	-2.900582000	1.532404000	0.445170000
H	-2.250078000	2.231236000	-0.084598000
C	-0.236858000	1.004990000	-0.965126000
H	-1.071162000	0.309281000	-1.052556000
H	-0.514487000	1.960833000	-1.428557000
H	0.606823000	0.591004000	-1.525510000
C	-2.773734000	0.134859000	2.543261000
F	-4.118508000	0.043081000	2.360754000
F	-2.354589000	-1.125957000	2.922384000
F	-2.680040000	0.839029000	3.803294000
C	-3.777164000	0.813930000	-0.583069000
C	-3.718747000	-0.572452000	-0.772524000
C	-4.648048000	1.560775000	-1.393876000
C	-4.504688000	-1.198704000	-1.747210000
C	-5.433793000	0.941299000	-2.368680000
C	-5.365321000	-0.445420000	-2.549965000
H	-3.050876000	-1.161759000	-0.151089000
H	-4.712486000	2.637971000	-1.259408000
H	-4.443463000	-2.276237000	-1.875392000
H	-6.099992000	1.539413000	-2.984745000
H	-5.976989000	-0.930310000	-3.305679000
Na	-0.521325000	0.504262000	4.770654000
B	-4.066535000	3.892929000	1.458707000
H	-5.165750000	3.479267000	1.680487000
H	-3.845180000	4.454672000	0.428442000
H	-3.253659000	3.922273000	2.333010000
H	-3.604513000	2.200110000	1.022809000

1b^{-} anion

E(scf done): -1381.69960920 a.u.

C	4.275152000	2.271916000	-1.262309000
C	4.154355000	0.910901000	-1.556081000
C	3.170669000	2.977806000	-0.776826000
H	5.012240000	0.355381000	-1.919268000
H	3.255549000	4.034541000	-0.540413000
C	2.929795000	0.265001000	-1.360085000
C	1.951503000	2.322651000	-0.604644000
H	1.084030000	2.862559000	-0.236262000
C	1.797370000	0.954728000	-0.891135000
H	5.229770000	2.769011000	-1.408209000
I	2.845041000	-1.840878000	-1.738389000
N	0.518674000	0.351272000	-0.734535000
C	0.070805000	0.082683000	0.592881000
O	0.981331000	-0.052859000	1.458276000
C	-1.324700000	-0.027078000	0.851174000
C	-2.390944000	0.778820000	0.128274000
H	-1.902442000	1.510602000	-0.524509000
C	-0.249414000	0.128897000	-1.955457000
H	-1.029780000	-0.607447000	-1.764344000

H	-0.717068000	1.045809000	-2.342797000
H	0.405487000	-0.268730000	-2.737851000
C	-1.700565000	-0.504121000	2.175673000
F	-3.054116000	-0.772245000	2.274742000
F	-1.077055000	-1.647719000	2.613754000
F	-1.504211000	0.390114000	3.264191000
C	-3.459102000	0.059015000	-0.703158000
C	-3.490745000	-1.331554000	-0.863855000
C	-4.459787000	0.818033000	-1.334913000
C	-4.484809000	-1.948728000	-1.633330000
C	-5.454946000	0.210689000	-2.105283000
C	-5.471734000	-1.181440000	-2.259072000
H	-2.725898000	-1.927902000	-0.374158000
H	-4.458607000	1.900804000	-1.218627000
H	-4.487785000	-3.030744000	-1.740563000
H	-6.216794000	0.821166000	-2.583900000
H	-6.244831000	-1.658598000	-2.855442000
H	-2.936875000	1.399732000	0.856440000

BH_3

E(scf done): -26.6178336582 a.u.

B	-0.466166000	0.000000000	-2.024693000
H	-0.466166000	0.869287000	-2.840779000
H	-0.791355000	-1.105433000	-2.331168000
H	-0.140978000	0.236146000	-0.902132000

$Na^+(THF)_6$

E(scf done): -1557.10936248 a.u.

Na	-0.006757000	-0.006272000	0.012484000
O	-1.397400000	0.853113000	-1.801451000
C	-2.590133000	0.220778000	-2.323968000
H	-3.376988000	0.274407000	-1.560395000
H	-2.365017000	-0.831687000	-2.518363000
C	-2.972752000	1.009015000	-3.579432000
H	-2.453947000	0.609089000	-4.457892000
H	-4.047887000	0.979316000	-3.776000000
C	-2.452889000	2.416516000	-3.245905000
H	-3.161234000	2.942389000	-2.595732000
H	-2.277577000	3.034368000	-4.130805000
C	-1.160994000	2.103943000	-2.489185000
H	-0.890221000	2.856217000	-1.743662000
H	-0.315323000	1.974205000	-3.177748000
O	1.388794000	-0.863968000	1.832943000
C	2.481910000	-0.136578000	2.440453000
H	2.069765000	0.606896000	3.136217000
H	3.020213000	0.388880000	1.647589000
C	3.320151000	-1.181736000	3.177510000
H	4.037222000	-1.650727000	2.494213000
H	3.876442000	-0.753702000	4.015921000

C	2.248996000	-2.194981000	3.611920000
H	1.737590000	-1.844565000	4.515468000
H	2.651427000	-3.191378000	3.813692000
C	1.293635000	-2.186739000	2.414964000
H	0.250304000	-2.370751000	2.686101000
H	1.591787000	-2.922139000	1.656926000
O	-1.387149000	-2.026760000	0.154774000
C	-2.591044000	-2.166522000	0.947112000
H	-3.353282000	-1.488599000	0.542681000
H	-2.366863000	-1.864400000	1.974348000
C	-3.017366000	-3.632412000	0.820823000
H	-2.537585000	-4.241213000	1.595349000
H	-4.099691000	-3.758029000	0.911766000
C	-2.474585000	-4.009326000	-0.567070000
H	-3.152594000	-3.657902000	-1.353129000
H	-2.328472000	-5.085145000	-0.696950000
C	-1.157871000	-3.233265000	-0.609108000
H	-0.843809000	-2.942688000	-1.614857000
H	-0.344078000	-3.802407000	-0.139336000
O	1.404521000	2.003351000	-0.108443000
C	2.546922000	2.163798000	-0.982609000
H	2.186525000	2.295070000	-2.011443000
H	3.143781000	1.248765000	-0.937441000
C	3.285685000	3.408394000	-0.486270000
H	3.988889000	3.145109000	0.312020000
H	3.845115000	3.905056000	-1.283703000
C	2.134633000	4.260364000	0.071958000
H	1.618953000	4.784998000	-0.740387000
H	2.461205000	5.003435000	0.804521000
C	1.222948000	3.197458000	0.689349000
H	0.162337000	3.462985000	0.672647000
H	1.510847000	2.974596000	1.725141000
O	1.434424000	-1.097666000	-1.639730000
C	1.304622000	-0.983997000	-3.077356000
H	1.584370000	0.035249000	-3.373786000
H	0.256390000	-1.147494000	-3.342511000
C	2.258812000	-2.022770000	-3.672642000
H	1.759653000	-2.993655000	-3.768403000
H	2.626798000	-1.730213000	-4.659760000
C	3.363717000	-2.092340000	-2.606392000
H	4.062656000	-1.256381000	-2.723562000
H	3.936335000	-3.023346000	-2.636169000
C	2.561810000	-1.943688000	-1.312507000
H	3.117028000	-1.470673000	-0.498098000
H	2.185173000	-2.914163000	-0.962289000
O	-1.460087000	1.109243000	1.634127000
C	-1.260491000	1.079338000	3.066829000
H	-0.435526000	1.757581000	3.323388000
H	-0.975741000	0.062440000	3.348952000
C	-2.578741000	1.549990000	3.682921000
H	-3.275619000	0.710751000	3.788452000

H	-2.438942000	2.003837000	4.667828000
C	-3.086067000	2.540783000	2.622919000
H	-2.586957000	3.509602000	2.737411000
H	-4.165870000	2.706927000	2.666102000
C	-2.654438000	1.864273000	1.318834000
H	-2.415943000	2.569442000	0.517570000
H	-3.420951000	1.168374000	0.954152000

THF

E(scf done): -232.473407288 a.u.

O	-1.287173000	-0.000005000	-1.640786000
C	-0.222704000	0.514618000	-0.811449000
H	-0.226226000	1.612033000	-0.869044000
H	0.730325000	0.148384000	-1.206573000
C	-0.519091000	0.030765000	0.611465000
H	-0.096629000	-0.967545000	0.772836000
H	-0.112073000	0.701407000	1.373473000
C	-2.055287000	-0.030724000	0.611446000
H	-2.477756000	0.967594000	0.772752000
H	-2.462325000	-0.701327000	1.373478000
C	-2.351628000	-0.514650000	-0.811450000
H	-3.304667000	-0.148481000	-1.206609000
H	-2.348052000	-1.612069000	-0.868994000

TS1b⁻/2

E(scf done): -1381.66515578 a.u.

C	-0.672269000	4.058881000	0.610899000
C	-1.009548000	3.799774000	-0.715018000
C	-0.460506000	2.982631000	1.494778000
H	-1.157509000	4.617596000	-1.415906000
H	-0.092079000	3.167318000	2.500322000
C	-1.225818000	2.477026000	-1.155817000
C	-0.652187000	1.670488000	1.064062000
H	-1.565190000	2.295514000	-2.170216000
C	-1.109647000	1.429228000	-0.249398000
H	-0.537642000	5.078499000	0.959040000
N	-0.288848000	0.535639000	1.814163000
C	0.290059000	-0.531226000	1.110705000
C	-0.394367000	0.515490000	3.264885000
H	-0.236428000	-0.508881000	3.600658000
H	0.354796000	1.164956000	3.738482000
H	-1.390883000	0.847030000	3.573032000
C	0.680316000	-0.207777000	-0.269722000
C	0.699149000	-1.335058000	-1.219388000
F	0.673245000	-0.900118000	-2.529994000
F	1.836483000	-2.151216000	-1.183628000
F	-0.335305000	-2.206131000	-1.094075000
C	1.735690000	0.859337000	-0.544977000
H	1.631732000	1.200559000	-1.581548000

H	1.519236000	1.729981000	0.080435000
C	3.191901000	0.468350000	-0.308899000
C	3.668853000	0.180627000	0.980829000
C	4.102251000	0.420698000	-1.374923000
C	5.009333000	-0.147706000	1.197466000
C	5.446622000	0.091973000	-1.165431000
C	5.906170000	-0.195135000	0.123110000
H	2.985127000	0.213307000	1.825217000
H	3.754089000	0.640522000	-2.381667000
H	5.354561000	-0.366036000	2.204757000
H	6.131650000	0.059565000	-2.008801000
H	6.948708000	-0.451743000	0.290112000
I	-2.946527000	-0.127688000	-0.489471000
O	0.408973000	-1.641570000	1.657832000

I$^-$ anion

E(scf done): -295.979563362 a.u.

I	-0.062619000	0.000000000	-1.982947000

(1b$^{\bullet}$)$^{\bullet-}$ diradical anion

E(scf done): -1381.65776363 a.u.

C	-3.783848000	3.201421000	-1.212154000
C	-4.002774000	1.861743000	-0.850663000
C	-2.524781000	3.780256000	-1.009051000
H	-4.971930000	1.396088000	-1.005574000
H	-2.352539000	4.816856000	-1.283811000
C	-2.950549000	1.151162000	-0.302623000
C	-1.483553000	3.038241000	-0.446697000
H	-0.510118000	3.491229000	-0.284787000
C	-1.690792000	1.692959000	-0.090013000
H	-4.591162000	3.784780000	-1.647814000
I	-3.991511000	-2.039417000	0.014500000
N	-0.639246000	0.928467000	0.522774000
C	0.560314000	0.797400000	-0.103333000
O	0.796933000	1.227139000	-1.244476000
C	1.675987000	0.078798000	0.590240000
C	2.260068000	-1.162515000	-0.033971000
H	1.573168000	-1.492423000	-0.819027000
C	-0.980242000	0.233712000	1.771285000
H	-1.145772000	0.957239000	2.575254000
H	-1.885821000	-0.357644000	1.612465000
H	-0.171437000	-0.441281000	2.052579000
C	2.400176000	0.741357000	1.713618000
F	3.506012000	1.435906000	1.303375000
F	1.631670000	1.637888000	2.385870000
F	2.851369000	-0.160554000	2.631739000
C	3.666642000	-1.025930000	-0.616090000
C	3.910030000	-0.167857000	-1.699973000
C	4.726802000	-1.780329000	-0.096931000

C	5.188534000	-0.072900000	-2.254520000
C	6.008875000	-1.685471000	-0.650773000
C	6.243184000	-0.831258000	-1.731736000
H	3.092762000	0.426928000	-2.098226000
H	4.551261000	-2.448974000	0.742309000
H	5.361985000	0.593450000	-3.095172000
H	6.819646000	-2.279119000	-0.237429000
H	7.237087000	-0.756259000	-2.163994000
H	2.273774000	-1.955239000	0.725643000

TS(1b$^{\bullet}$)$^{\bullet-}$/(1d$^{\bullet}$)$^{\bullet}$

E(scf done): -1381.65738135 a.u.

C	4.038282000	2.757287000	1.607561000
C	4.058785000	1.436993000	1.128284000
C	2.907879000	3.557372000	1.400037000
H	4.928952000	0.805457000	1.285556000
H	2.890100000	4.579616000	1.766740000
C	2.943824000	0.960909000	0.460297000
C	1.797849000	3.052818000	0.717689000
H	0.921773000	3.673237000	0.554010000
C	1.809076000	1.729267000	0.243435000
H	4.900067000	3.155344000	2.137689000
I	3.418214000	-2.212829000	-0.304685000
N	0.683029000	1.207234000	-0.487071000
C	-0.542056000	1.162061000	0.092914000
O	-0.782754000	1.552972000	1.245800000
C	-1.683003000	0.565787000	-0.681715000
C	-2.029331000	-0.894248000	-0.540922000
H	-1.162781000	-1.407048000	-0.110892000
C	0.955741000	0.720894000	-1.845645000
H	1.337746000	1.541965000	-2.460380000
H	1.694588000	-0.084047000	-1.805930000
H	0.036155000	0.341219000	-2.292729000
C	-2.643631000	1.507513000	-1.318197000
F	-3.605722000	1.983952000	-0.470002000
F	-2.017923000	2.609603000	-1.821240000
F	-3.314295000	0.928226000	-2.352237000
C	-3.269365000	-1.191741000	0.302922000
C	-3.312503000	-0.840080000	1.661325000
C	-4.371217000	-1.846408000	-0.263002000
C	-4.434606000	-1.143333000	2.435993000
C	-5.496048000	-2.151564000	0.512053000
C	-5.530593000	-1.800814000	1.864391000
H	-2.469472000	-0.318408000	2.105731000
H	-4.350313000	-2.123506000	-1.314108000
H	-4.453317000	-0.865933000	3.486379000
H	-6.340946000	-2.661919000	0.057893000
H	-6.402395000	-2.036270000	2.468368000
H	-2.179726000	-1.319403000	-1.541508000

(1d•)• diradical

E(scf done): -1085.69417380 a.u.

C	-0.711621000	-4.400281000	-6.445307000
C	-1.212079000	-4.114698000	-7.727352000
C	-1.005794000	-3.535737000	-5.384787000
H	-0.996778000	-4.761760000	-8.572880000
H	-0.612225000	-3.745684000	-4.394988000
C	-1.987451000	-2.985956000	-7.852782000
C	-1.791842000	-2.395890000	-5.567329000
H	-2.000626000	-1.740432000	-4.731473000
C	-2.319276000	-2.095674000	-6.842007000
H	-0.099340000	-5.283123000	-6.286184000
N	-3.085883000	-0.929256000	-7.126228000
C	-3.936338000	-0.385908000	-6.197518000
O	-4.214179000	-0.933684000	-5.121836000
C	-4.586581000	0.928464000	-6.471729000
C	-6.081204000	1.052803000	-6.325047000
H	-6.495007000	0.040716000	-6.299207000
C	-3.050005000	-0.463140000	-8.519890000
H	-2.054765000	-0.092350000	-8.775931000
H	-3.306948000	-1.293301000	-9.184289000
H	-3.783530000	0.327350000	-8.668349000
C	-3.775829000	2.172299000	-6.660616000
F	-3.835997000	3.006351000	-5.584922000
F	-2.459480000	1.926046000	-6.874267000
F	-4.218452000	2.906531000	-7.724826000
C	-6.581953000	1.833137000	-5.108972000
C	-6.329456000	1.370115000	-3.808738000
C	-7.330584000	3.004470000	-5.279333000
C	-6.820116000	2.067408000	-2.702417000
C	-7.822520000	3.703761000	-4.171844000
C	-7.567639000	3.237291000	-2.879676000
H	-5.745323000	0.464768000	-3.672022000
H	-7.532980000	3.373255000	-6.281766000
H	-6.618765000	1.697092000	-1.701087000
H	-8.402824000	4.609838000	-4.321305000
H	-7.947854000	3.778627000	-2.018202000
H	-6.473404000	1.534425000	-7.230377000

TS(1d•)• /2

E(scf done): -1085.67270663 a.u.

C	3.751243000	0.290742000	1.315396000
C	3.251407000	-1.020687000	1.116936000
C	3.133373000	1.403740000	0.728186000
H	3.747133000	-1.855051000	1.606331000
H	3.531989000	2.402319000	0.874236000
C	2.181306000	-1.259469000	0.258948000
C	1.990724000	1.183006000	-0.037530000
H	1.879583000	-2.272431000	0.011097000

C	1.483390000	-0.138396000	-0.236343000
H	4.634111000	0.433666000	1.929730000
N	1.133703000	2.149639000	-0.549215000
C	-0.216914000	1.787329000	-0.586184000
O	-1.062905000	2.493731000	-1.120549000
C	1.552878000	3.515393000	-0.851266000
H	1.661560000	4.099085000	0.069267000
H	2.504629000	3.494052000	-1.384669000
H	0.787192000	3.973973000	-1.475661000
C	-0.508420000	0.458827000	0.080901000
C	-0.768692000	0.537549000	1.547093000
F	-1.979063000	1.107690000	1.878285000
F	-0.779983000	-0.694674000	2.125343000
F	0.157563000	1.281373000	2.218304000
C	-1.321796000	-0.562974000	-0.707027000
H	-1.049314000	-0.442481000	-1.760625000
H	-0.967444000	-1.557163000	-0.410609000
C	-2.842416000	-0.543361000	-0.574801000
C	-3.495789000	-1.556780000	0.141072000
C	-3.619648000	0.448739000	-1.192629000
C	-4.890593000	-1.578732000	0.246221000
C	-5.012786000	0.428889000	-1.090981000
C	-5.654548000	-0.584143000	-0.369633000
H	-2.910136000	-2.337603000	0.619773000
H	-3.127454000	1.245016000	-1.741640000
H	-5.376361000	-2.373355000	0.805698000
H	-5.597834000	1.205233000	-1.576421000
H	-6.737913000	-0.598495000	-0.291681000

TS(1b')$^{\bullet-}$/2

E(scf done): -1381.64179987 a.u.

C	3.760138000	0.332010000	1.359604000
C	3.250988000	-0.976278000	1.250474000
C	3.134505000	1.407802000	0.698262000
H	3.746343000	-1.788261000	1.778347000
H	3.513404000	2.418366000	0.818254000
C	2.175410000	-1.245890000	0.403884000
C	1.996294000	1.147025000	-0.056288000
H	1.872886000	-2.274035000	0.220959000
C	1.506069000	-0.181893000	-0.259055000
H	4.638079000	0.520480000	1.970619000
N	1.133611000	2.132725000	-0.558015000
C	-0.199797000	1.770796000	-0.649327000
O	-1.034670000	2.470561000	-1.229866000
C	1.586600000	3.473613000	-0.901130000
H	1.848565000	4.040713000	-0.000235000
H	2.461207000	3.414993000	-1.554649000
H	0.775271000	3.982431000	-1.420170000
C	-0.503326000	0.443835000	0.003579000
C	-0.758374000	0.505380000	1.463910000

F	-1.967727000	1.097220000	1.820987000
F	-0.808019000	-0.735460000	2.033298000
F	0.170157000	1.219865000	2.165553000
C	-1.356328000	-0.549216000	-0.783267000
H	-1.120042000	-0.393467000	-1.840101000
H	-0.993021000	-1.554855000	-0.542792000
C	-2.869520000	-0.534918000	-0.594927000
C	-3.507630000	-1.609678000	0.042380000
C	-3.664165000	0.513646000	-1.087752000
C	-4.899068000	-1.639315000	0.192108000
C	-5.053554000	0.487577000	-0.942088000
C	-5.678450000	-0.588817000	-0.300092000
H	-2.909781000	-2.433961000	0.424396000
H	-3.180197000	1.356485000	-1.571437000
H	-5.370362000	-2.482911000	0.689817000
H	-5.650409000	1.308794000	-1.330853000
H	-6.759134000	-0.607968000	-0.187624000
I	2.065032000	-0.818899000	-3.1333950000

1b˙ radical
E(scf done): -1381.55451468 a.u.

C	-0.812559000	-4.283663000	-6.161434000
C	-2.050162000	-4.466414000	-6.784711000
C	-0.364008000	-2.997087000	-5.852518000
H	-2.397757000	-5.466405000	-7.018987000
H	0.595458000	-2.851493000	-5.366437000
C	-2.839760000	-3.356592000	-7.098735000
C	-1.156118000	-1.893887000	-6.171436000
H	-0.822342000	-0.887346000	-5.938120000
C	-2.398812000	-2.059483000	-6.796096000
H	-0.205434000	-5.150528000	-5.918854000
I	-4.731511000	-3.686396000	-8.029940000
N	-3.162828000	-0.891227000	-7.136929000
C	-3.989403000	-0.352451000	-6.191340000
O	-4.211301000	-0.901968000	-5.103312000
C	-4.610997000	0.974806000	-6.459783000
C	-3.800877000	2.225167000	-6.691933000
H	-2.780168000	1.936198000	-6.957564000
C	-2.981409000	-0.351050000	-8.490461000
H	-2.012639000	0.149847000	-8.590181000
H	-3.032536000	-1.169970000	-9.212142000
H	-3.782778000	0.351577000	-8.720886000
C	-6.076860000	1.096072000	-6.176939000
F	-6.628213000	2.113167000	-6.897243000
F	-6.757728000	-0.030363000	-6.508575000
F	-6.371974000	1.355820000	-4.872840000
C	-3.757149000	3.170345000	-5.490276000
C	-4.375000000	4.426275000	-5.548430000
C	-3.081958000	2.799265000	-4.317177000
C	-4.316830000	5.299784000	-4.456947000

C	-3.023641000	3.669323000	-3.226005000
C	-3.642019000	4.923111000	-3.292409000
H	-4.902011000	4.725733000	-6.450630000
H	-2.600154000	1.827098000	-4.253991000
H	-4.798667000	6.271427000	-4.518962000
H	-2.496443000	3.368242000	-2.325197000
H	-3.596715000	5.599623000	-2.443857000
H	-4.212790000	2.767953000	-7.551578000

$(1b^{-})^{\bullet-}$ radical dianion

E(scf done): -1381.81211186 a.u.

C	-13.069869000	0.082672000	-1.132883000
C	-13.229976000	-1.253453000	-0.720786000
C	-14.153309000	0.961376000	-0.988463000
H	-12.417680000	-1.970212000	-0.817745000
H	-14.049313000	1.996142000	-1.305019000
C	-14.446066000	-1.611253000	-0.185519000
C	-15.373035000	0.548669000	-0.451057000
H	-16.189203000	1.254745000	-0.347795000
C	-15.566289000	-0.792258000	-0.017750000
H	-12.125977000	0.420213000	-1.551819000
I	72.208525000	0.284845000	-0.170323000
N	-16.764376000	-1.284583000	0.469741000
C	-17.811752000	-0.392324000	0.937252000
O	-17.463330000	0.555828000	1.696193000
C	-19.139229000	-0.639708000	0.551076000
C	-20.258552000	0.072534000	1.290729000
H	-19.859838000	0.349063000	2.274844000
C	-16.809340000	-2.704017000	0.808806000
H	-16.687734000	-3.333242000	-0.081517000
H	-16.009540000	-2.958236000	1.519398000
H	-17.769951000	-2.932023000	1.268148000
C	-19.567117000	-1.598782000	-0.459596000
F	-20.686136000	-1.173628000	-1.154953000
F	-18.654804000	-1.937503000	-1.417292000
F	-20.002125000	-2.858053000	0.034632000
C	-20.832942000	1.333969000	0.652737000
C	-20.001183000	2.288015000	0.044474000
C	-22.211719000	1.590907000	0.694835000
C	-20.530413000	3.462339000	-0.498615000
C	-22.748905000	2.763311000	0.149656000
C	-21.908614000	3.706321000	-0.450045000
H	-18.932831000	2.098772000	0.004711000
H	-22.875586000	0.861040000	1.154235000
H	-19.866676000	4.187751000	-0.962841000
H	-23.821784000	2.935051000	0.188914000
H	-22.320789000	4.616871000	-0.876821000
H	-21.092260000	-0.617210000	1.479663000

$1c^{\bullet-}$ radical anion

E(scf done): -1085.85117356 a.u.

C	4.964761000	0.353275000	0.602857000
C	4.720953000	-1.014328000	0.732864000
C	3.950231000	1.234752000	0.198491000
H	5.512951000	-1.691253000	1.045057000
H	4.172631000	2.294550000	0.122022000
C	3.427023000	-1.505285000	0.451341000
C	2.660474000	0.740032000	-0.085469000
H	3.225185000	-2.570933000	0.557743000
C	2.436490000	-0.638682000	0.031894000
H	5.952354000	0.752781000	0.819718000
N	1.608955000	1.576937000	-0.505258000
C	0.403056000	0.971373000	-0.944133000
O	-0.106256000	1.374359000	-2.020361000
C	1.913507000	2.922979000	-0.969537000
H	2.326590000	3.523588000	-0.151602000
H	2.635470000	2.921281000	-1.798326000
H	0.991833000	3.385142000	-1.318816000
C	-0.108375000	-0.132454000	-0.188470000
C	-0.210164000	-0.140176000	1.275464000
F	-1.481253000	0.250902000	1.743313000
F	-0.073768000	-1.397889000	1.838389000
F	0.635909000	0.672012000	1.962701000
C	-0.992388000	-1.142436000	-0.906363000
H	-0.681045000	-1.135568000	-1.956724000
H	-0.770056000	-2.145793000	-0.523686000
C	-2.506094000	-0.949856000	-0.858751000
C	-3.338417000	-1.958725000	-0.352436000
C	-3.106923000	0.222050000	-1.349707000
C	-4.730372000	-1.807489000	-0.330566000
C	-4.495048000	0.376907000	-1.331905000
C	-5.315286000	-0.637232000	-0.821308000
H	-2.893090000	-2.873098000	0.033809000
H	-2.465104000	1.005619000	-1.741827000
H	-5.353697000	-2.602603000	0.070667000
H	-4.939606000	1.290911000	-1.718070000
H	-6.394964000	-0.514952000	-0.806597000

TS1c•−/2•−
E(scf done): -1085.84585407 a.u.

C	3.993071000	0.369117000	1.175658000
C	3.457306000	-0.916207000	1.243256000
C	3.252142000	1.411768000	0.571548000
H	4.022806000	-1.715125000	1.721349000
H	3.660449000	2.418529000	0.543678000
C	2.204876000	-1.195156000	0.650618000
C	1.990630000	1.121877000	0.054813000
H	1.845132000	-2.224677000	0.651649000
C	1.474583000	-0.188657000	0.003927000
H	4.970034000	0.582799000	1.601122000
N	1.095520000	2.121183000	-0.423534000

C	-0.219748000	1.741380000	-0.585800000
O	-1.009478000	2.399138000	-1.287918000
C	1.564397000	3.433669000	-0.831918000
H	1.998108000	3.972376000	0.018957000
H	2.326892000	3.348908000	-1.615340000
H	0.715744000	3.996363000	-1.218492000
C	-0.547954000	0.441878000	0.077716000
C	-0.825736000	0.507599000	1.517513000
F	-2.066546000	1.088959000	1.873336000
F	-0.889148000	-0.731274000	2.106678000
F	0.067852000	1.239658000	2.248577000
C	-1.389265000	-0.549959000	-0.722360000
H	-1.118298000	-0.403545000	-1.774334000
H	-1.045324000	-1.559274000	-0.465196000
C	-2.909018000	-0.529774000	-0.600212000
C	-3.582778000	-1.634126000	-0.056066000
C	-3.678389000	0.551615000	-1.063285000
C	-4.979741000	-1.662644000	0.031346000
C	-5.072419000	0.527017000	-0.980574000
C	-5.731913000	-0.580357000	-0.431940000
H	-3.006929000	-2.483738000	0.304167000
H	-3.165142000	1.417031000	-1.471265000
H	-5.476042000	-2.529849000	0.459432000
H	-5.647382000	1.374970000	-1.344462000
H	-6.816517000	-0.597277000	-0.367289000

2$^{\bullet-}$ radical anion

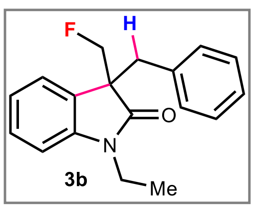
E(scf done): -1085.89747426 a.u.

C	-0.770425000	-3.536777000	-0.556228000
C	0.045448000	-2.398385000	-0.568759000
C	-1.875767000	-3.617707000	0.320162000
H	0.891210000	-2.351058000	-1.247179000
H	-2.503245000	-4.504866000	0.322534000
C	-0.239649000	-1.323007000	0.280958000
C	-2.170727000	-2.561352000	1.195637000
H	-3.022269000	-2.621765000	1.867678000
C	-1.348733000	-1.434803000	1.178488000
H	-0.552743000	-4.360793000	-1.230325000
N	-1.449345000	-0.272116000	1.916159000
C	-0.497015000	0.672615000	1.493861000
O	-0.365220000	1.817986000	2.007448000
C	0.476396000	-0.029704000	0.555826000
C	1.912310000	-0.194104000	1.387155000
H	1.617623000	-0.825796000	2.230645000
C	-2.521334000	0.043063000	2.835272000
H	-2.275676000	0.986026000	3.325536000
H	-3.482137000	0.153523000	2.313609000
H	-2.622713000	-0.741258000	3.592527000
C	0.729994000	0.806436000	-0.701721000
F	1.423332000	0.123354000	-1.657976000

F	-0.424683000	1.209672000	-1.308811000
F	1.438613000	1.944783000	-0.466153000
C	3.113820000	-0.762299000	0.711925000
C	3.329270000	-2.159519000	0.647859000
C	4.085541000	0.069876000	0.106224000
C	4.442522000	-2.694892000	0.000775000
C	5.198729000	-0.464109000	-0.540834000
C	5.388578000	-1.854149000	-0.606411000
H	2.610305000	-2.826358000	1.117251000
H	3.960891000	1.148845000	0.152726000
H	4.578907000	-3.773630000	-0.026288000
H	5.928951000	0.205059000	-0.990131000
H	6.256186000	-2.270611000	-1.110231000
H	2.117435000	0.809500000	1.768826000

6. X-ray Structural Analysis:

Crystal Growth of Compound 3b:



A saturated solution of **3b** in DCM was kept at room temperature to obtain crystals. Colorless crystals were observed after the DCM was evaporated. A suitable crystal was selected and visualized on a Bruker APEX−II CCD diffractometer. The crystal was kept at 150.00 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss−Newton minimization. The crystal structure was drawn on diamond−3 software.

Crystal Structure of Compound 3b:

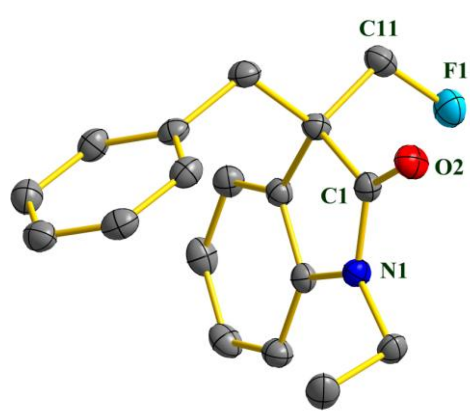


Figure S24. Crystal Structure of compound **3b**. The ellipsoid contour has been drawn at 50% probability levels.

Table S5: Crystal data and structure refinement for 3b:

Empirical formula	**$C_{18}H_{18}FNO$**
CCDC	**2517708**
Formula weight	283.33
Temperature/K	150.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.8231(3)
b/Å	18.1789(6)
c/Å	9.0840(2)
α/°	90
β/°	97.691(1)
γ/°	90
Volume/Å^3	1443.91(8)
Z	4
ρ_{calc}(g/cm^3)	1.303
μ/mm^{-1}	0.089
F(000)	600.0
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.482 to 56.612
Index ranges	$-11 \leq h \leq 11$, $-24 \leq k \leq 24$, $-10 \leq l \leq 12$
Reflections collected	39874
Independent reflections	3579 [R_{int} = 0.0406, R_{sigma} = 0.0190]
Data/restraints/parameters	3579/1/199
Goodness−of−fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0502, wR_2 = 0.1318

7. References:

1. (a) Xiao, P.; Pannecoucke, X.; Bouillon, J.P.; Couve-Bonnaire, S. Ligand-Free Palladium-Catalyzed Synthesis of *α*-Trifluoromethylacrylic Acids and Related Acrylates by Three-Component Reaction. *Adv. Synth. Catal*. **2020**, *362*, 949–954. (b) Sihag, N.; Bhartiya, H.; Jain, S.; Singh, J.; Reddy, S.R.; Yadav, M.R. Pd-catalyzed enantioselective reductive Heck reaction of mono-fluoro, *gem*-difluoro, and trifluoromethyl tethered-alkenes. *Chem. Commun.* **2025**, *61*, 11413–11416. (c) Seashore-Ludlow, B.; Somfai, P. Domino

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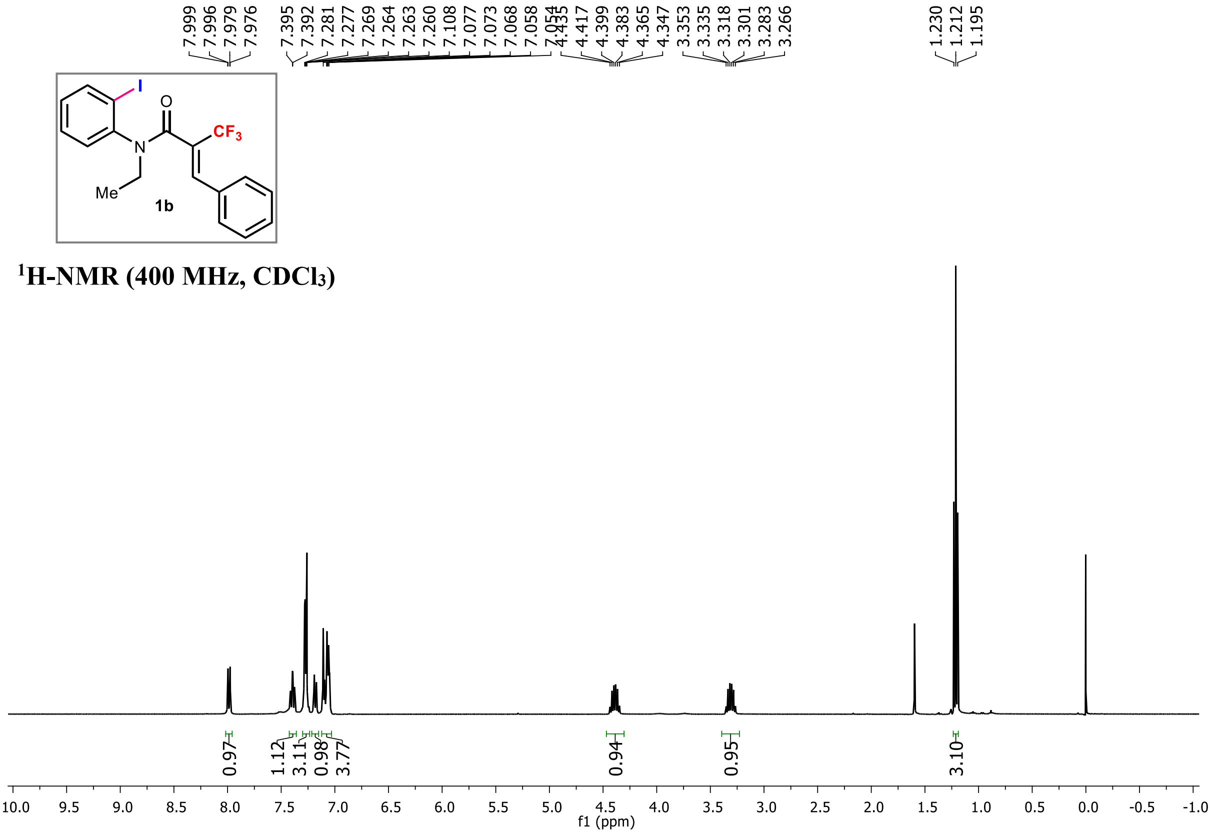
8. NMR Spectra



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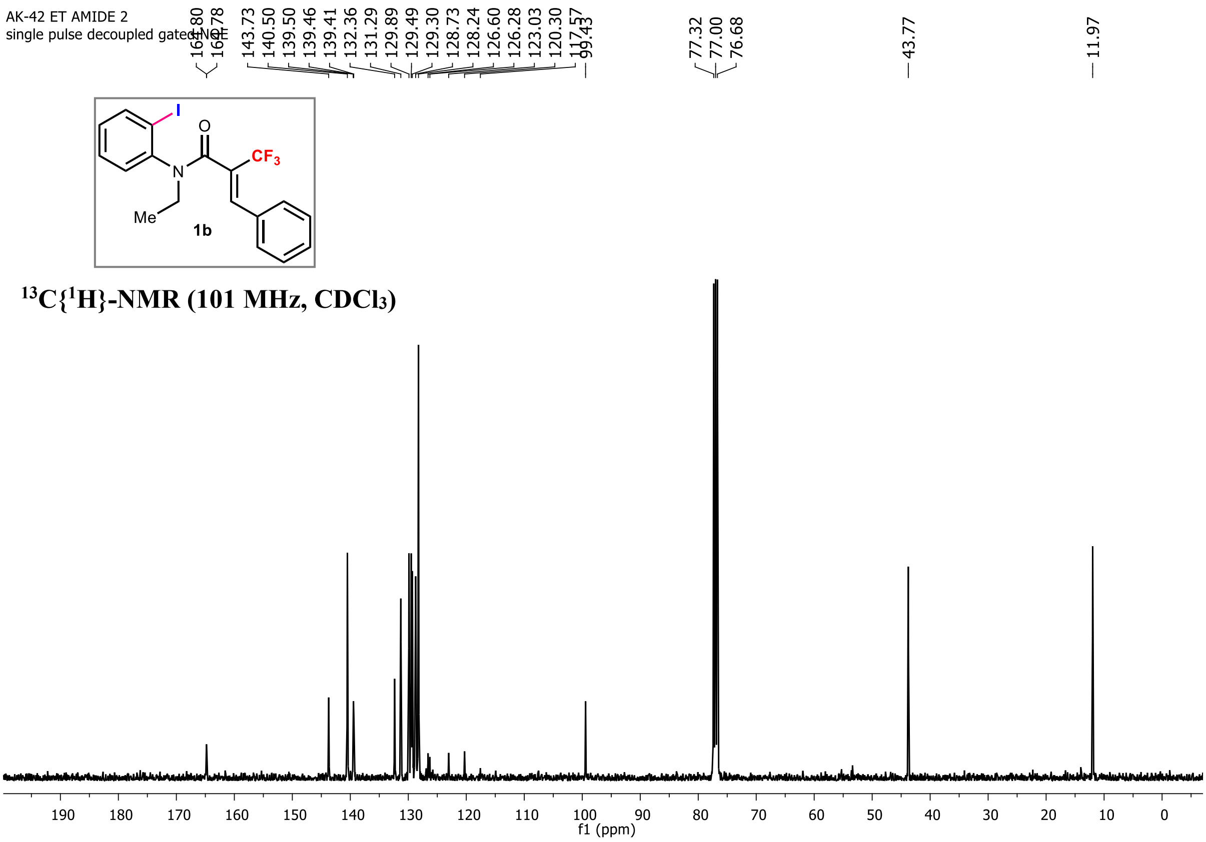

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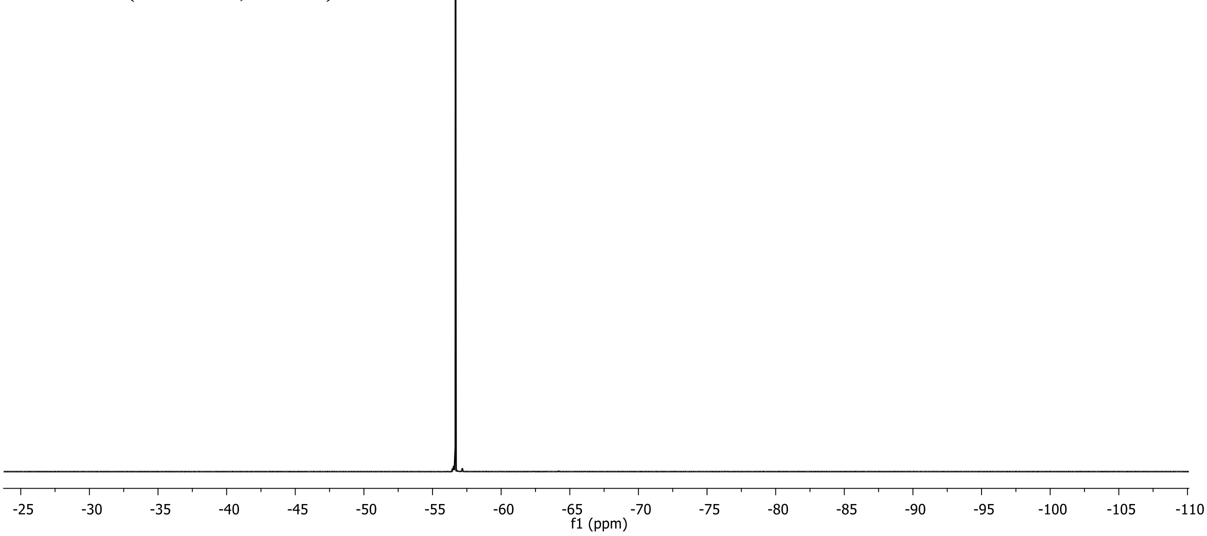

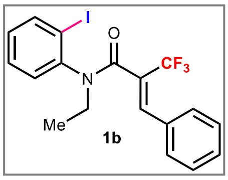

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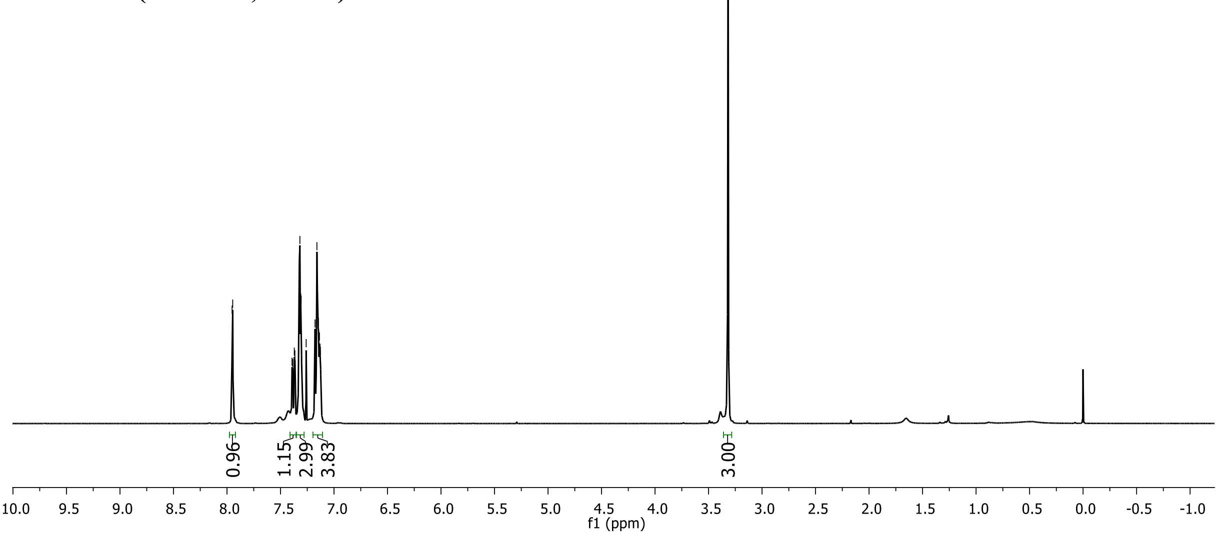

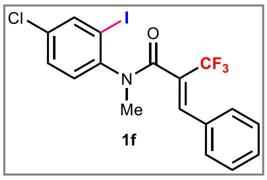

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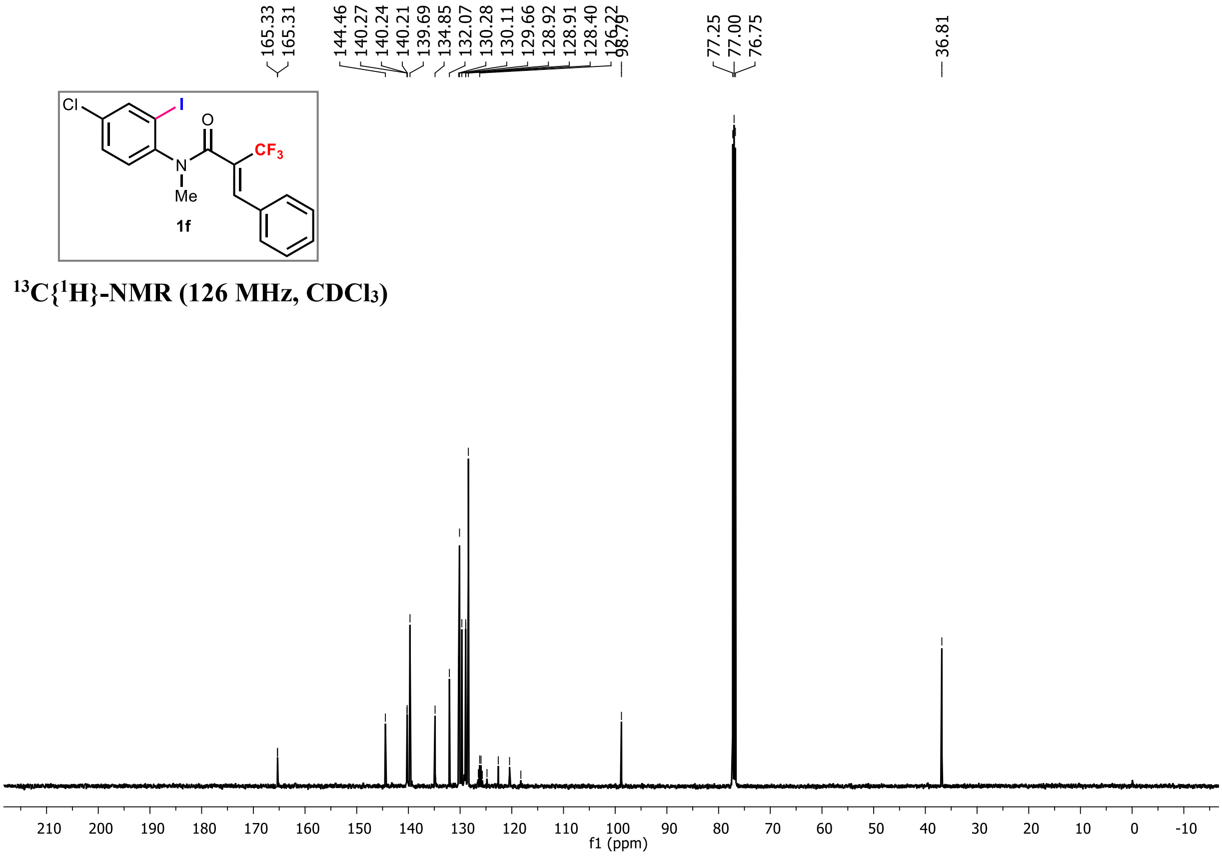
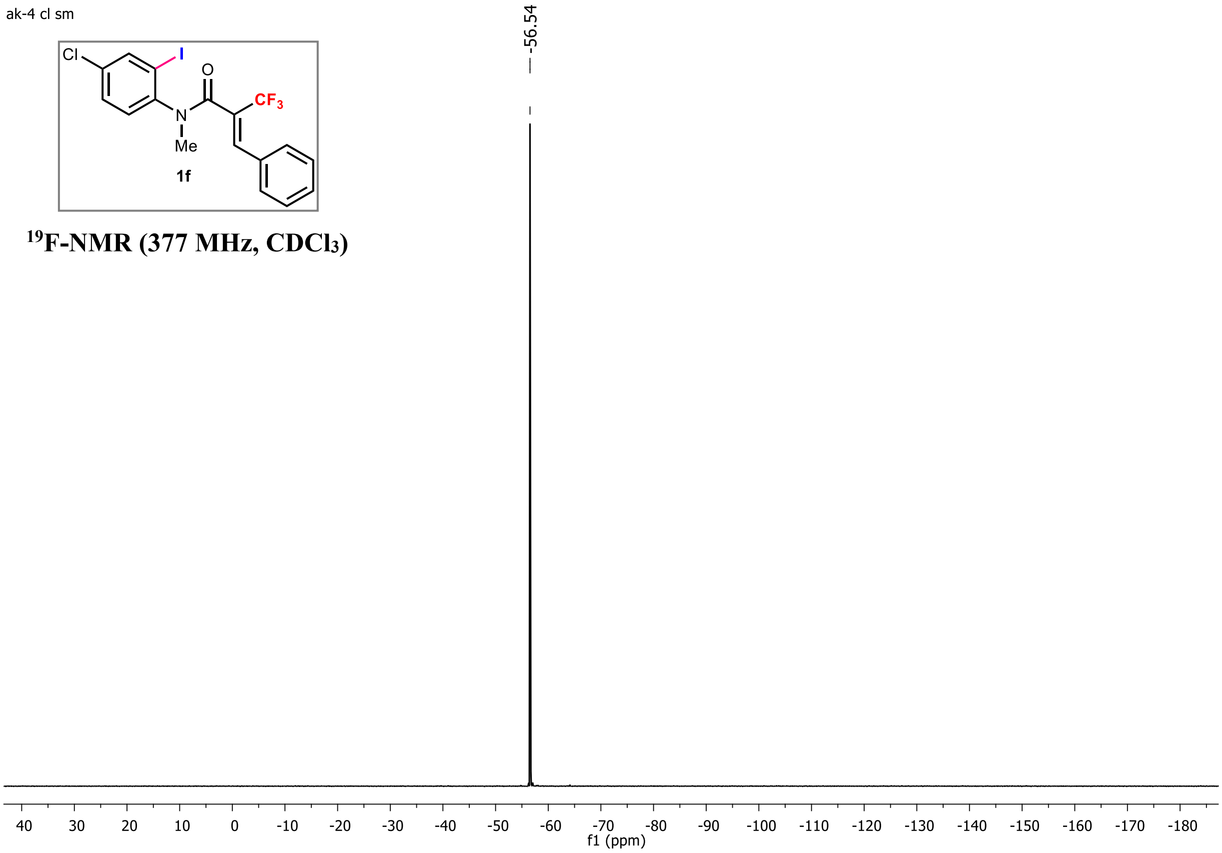


$^{13}C\{^{1}H\}$-NMR (126 MHz, $CDCl_3$)

ak-4 cl sm



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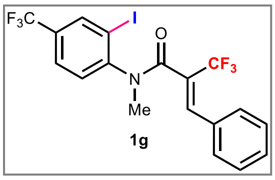

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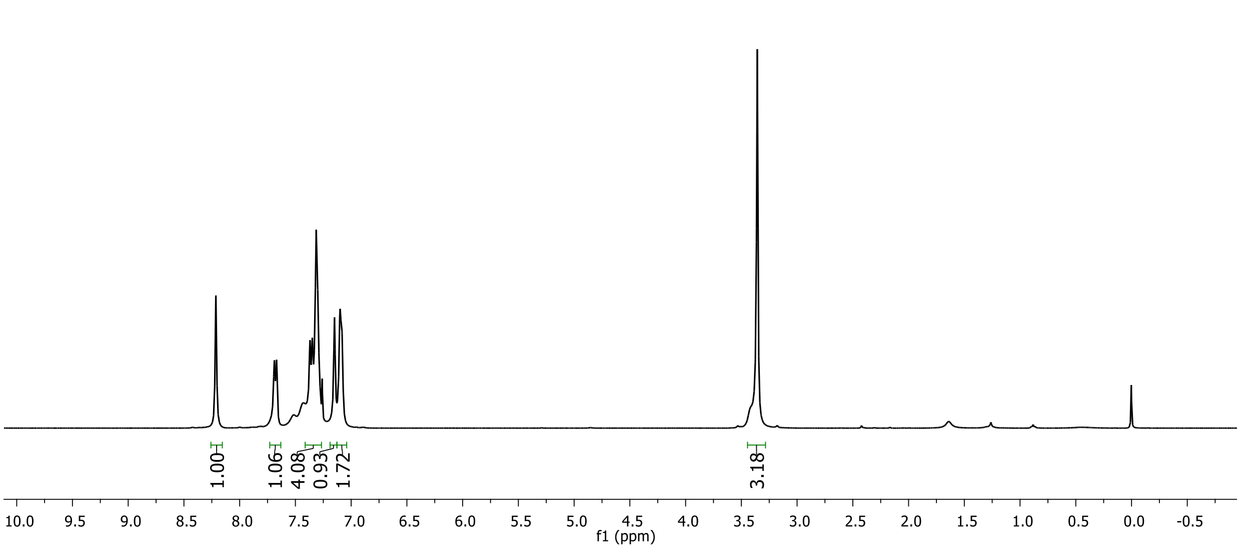

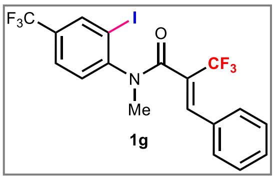

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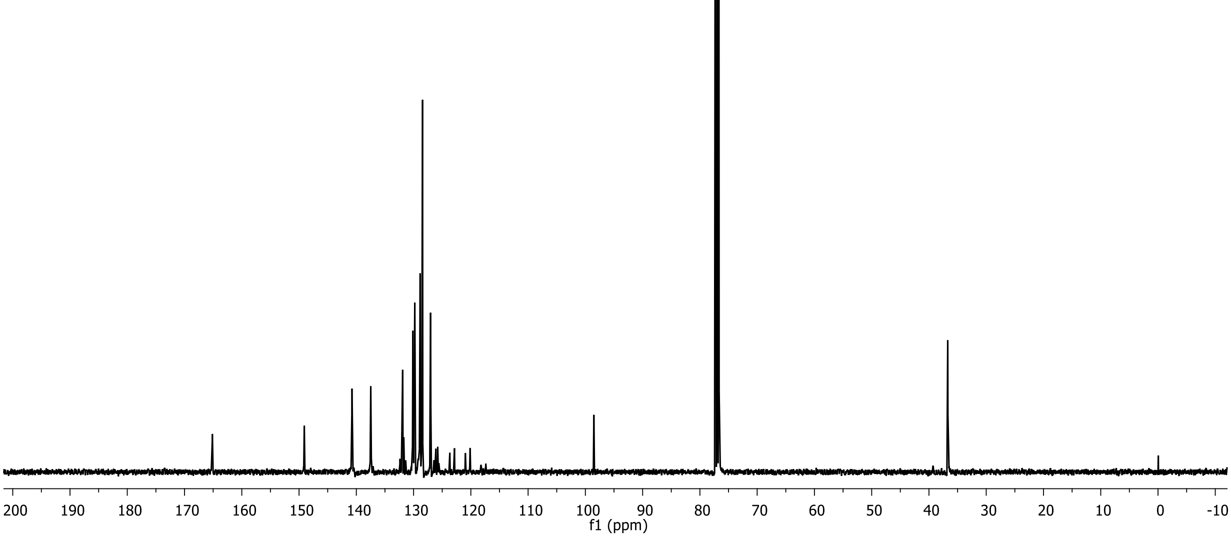

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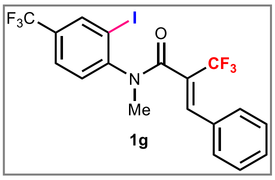

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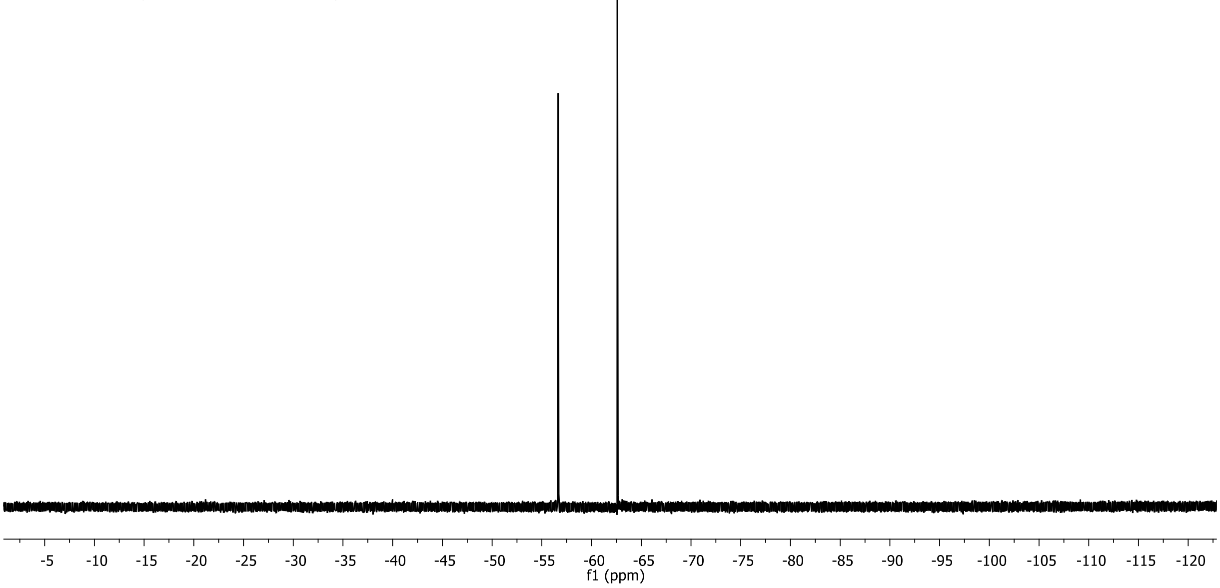

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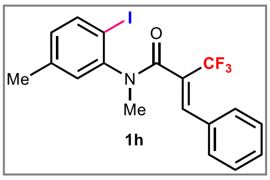

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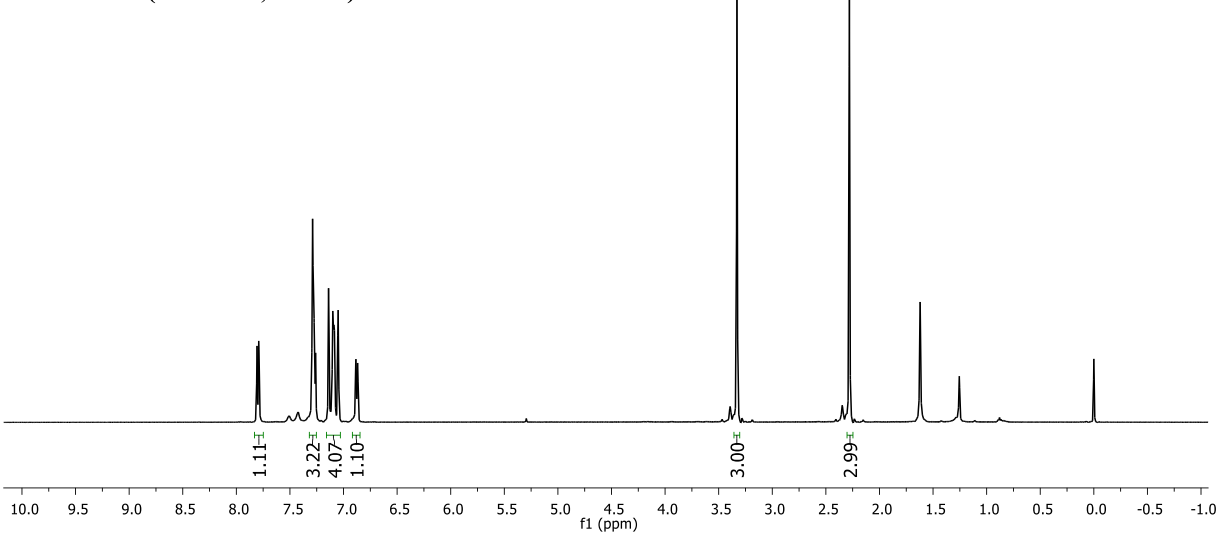

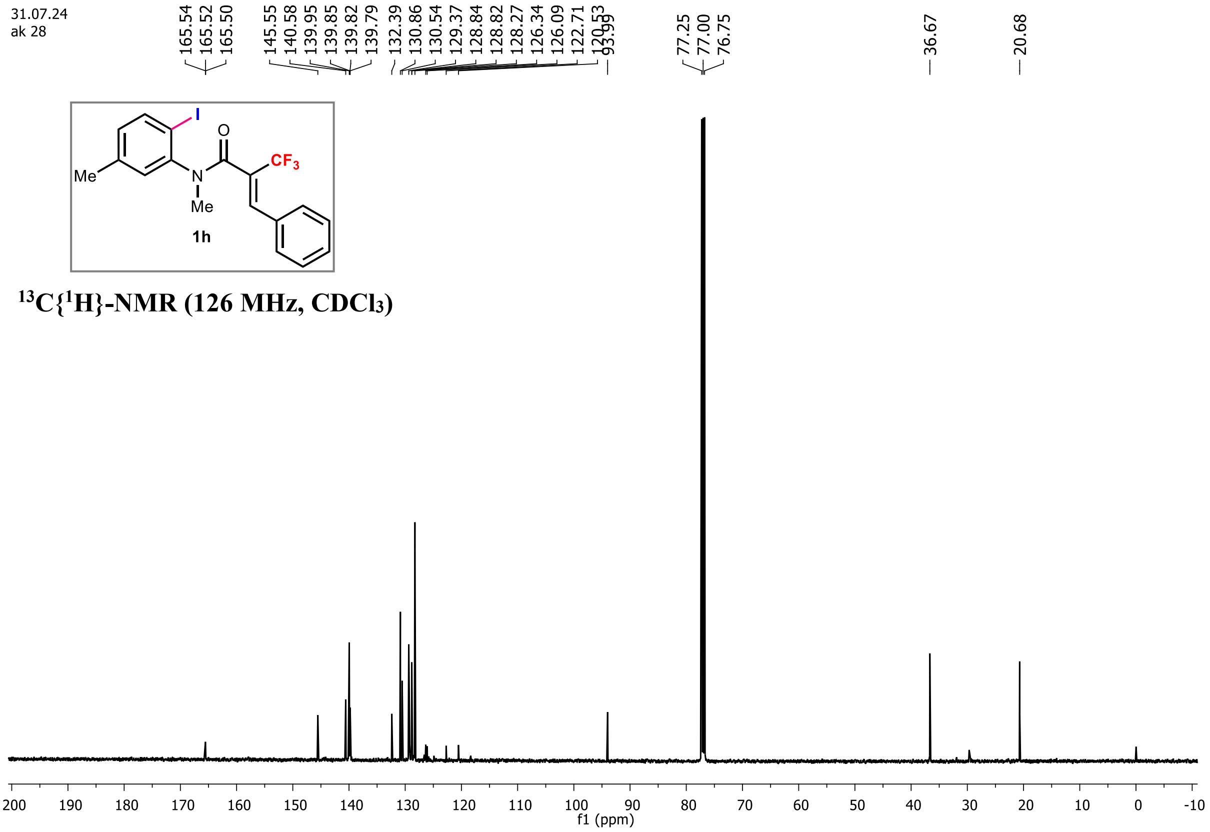

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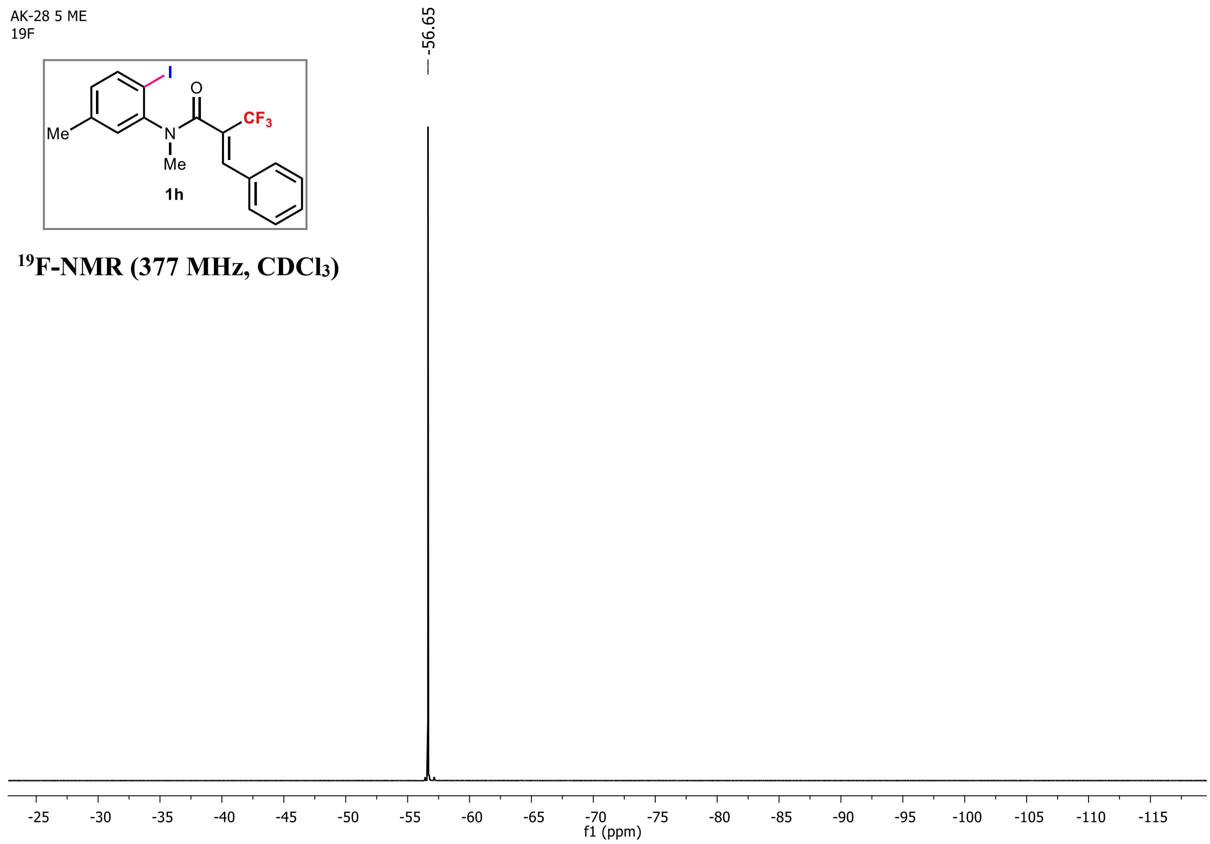

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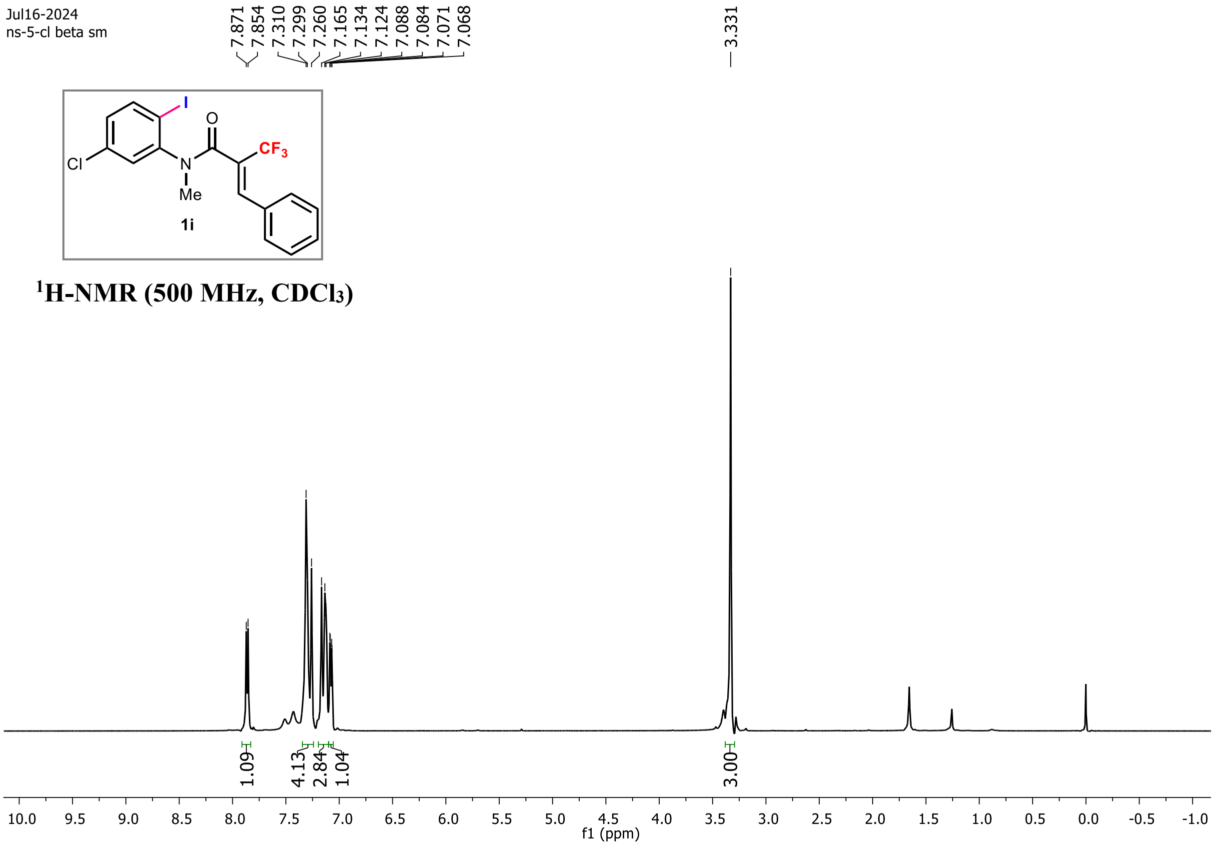
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7.071
7.068
3.331
Cl
I
O
N
CF3
Me
1i
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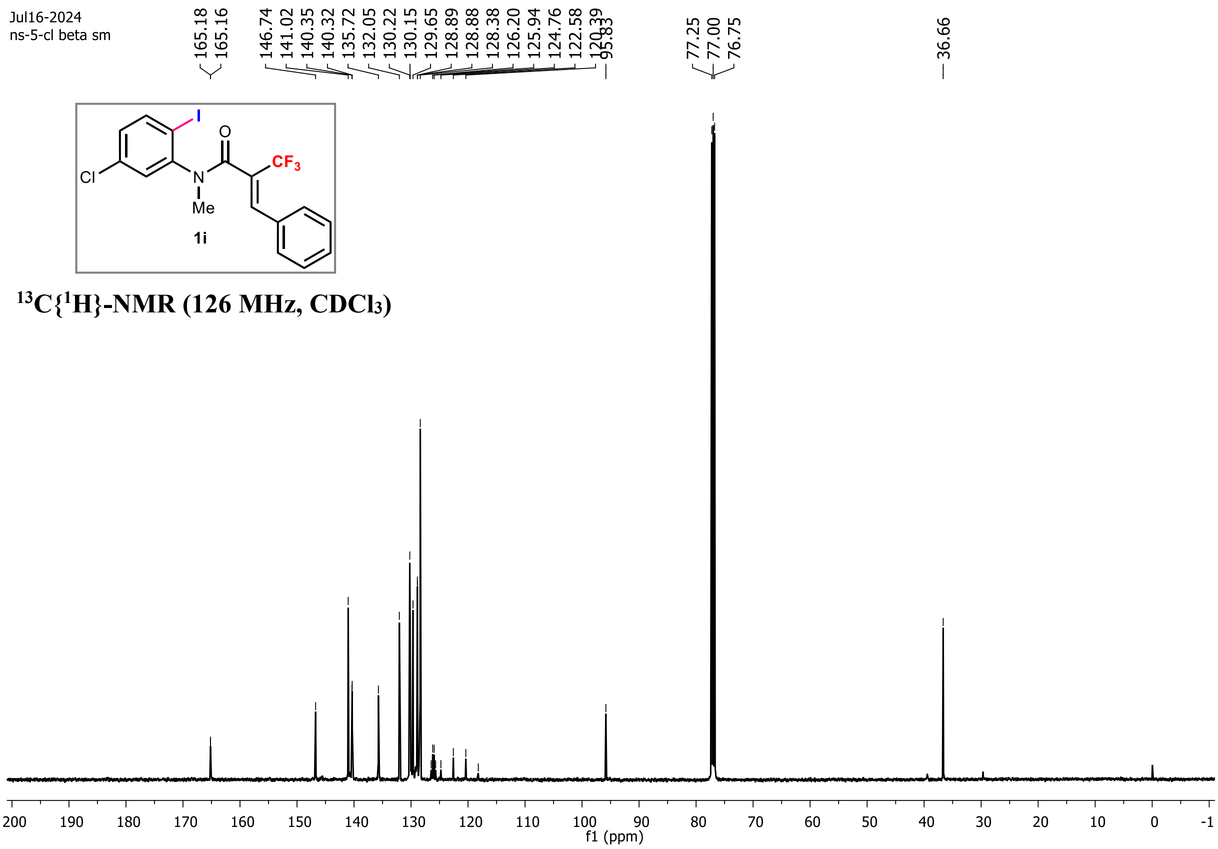
3.00
f1 (ppm)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77.00
76.75
36.66
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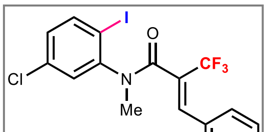
13C{1H}-NMR (126 MHz, CDCl3)
f1 (ppm)

NS-5-CL BETA PH SM
19F



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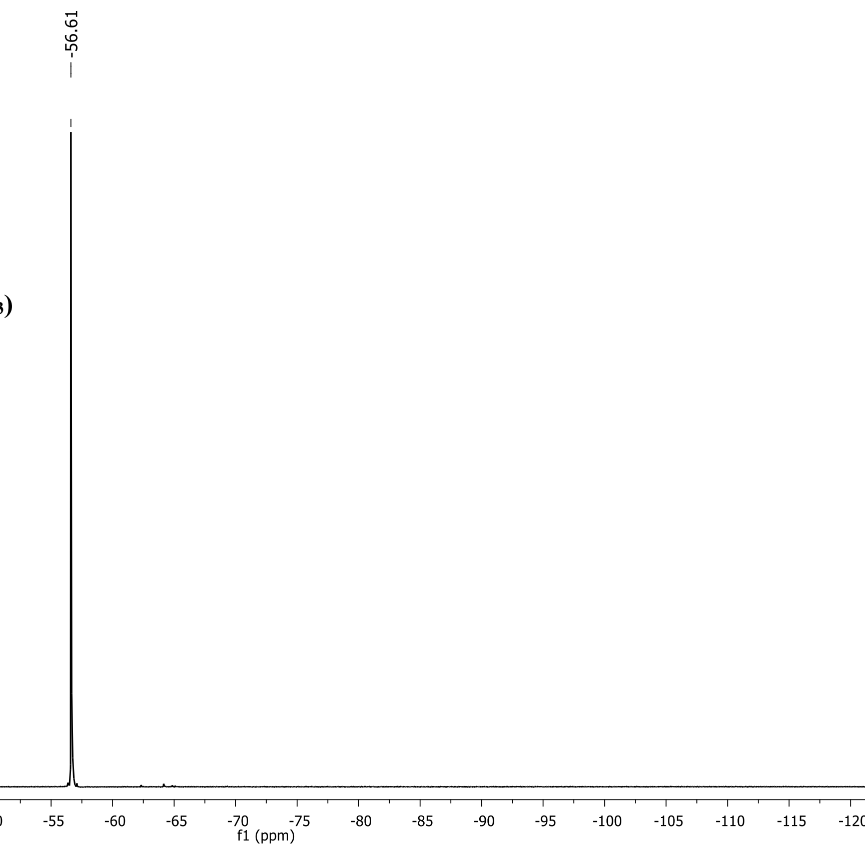

^{19}F-NMR (377 MHz, CDCl$_3$)

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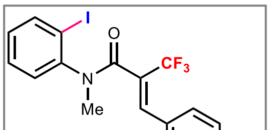

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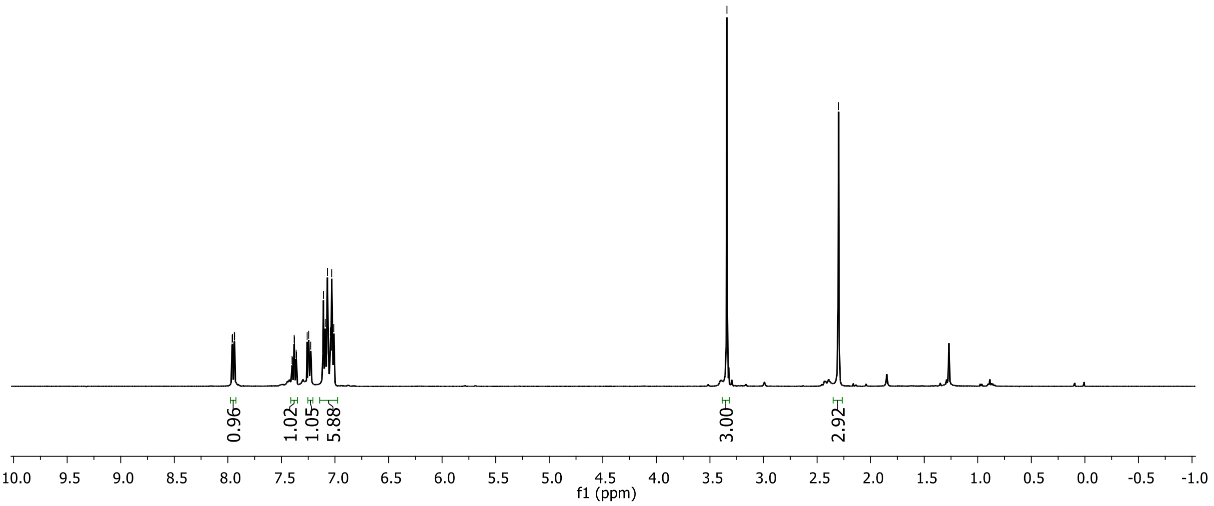

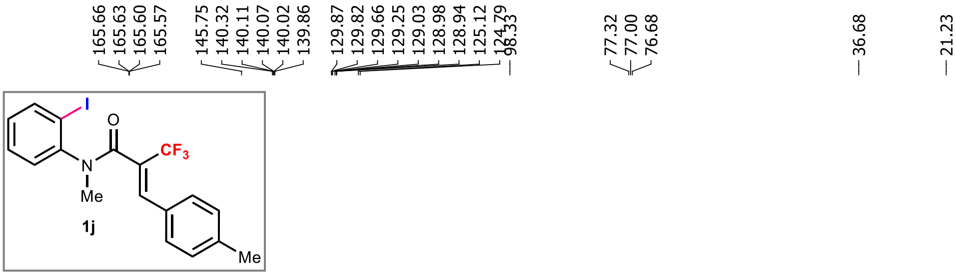

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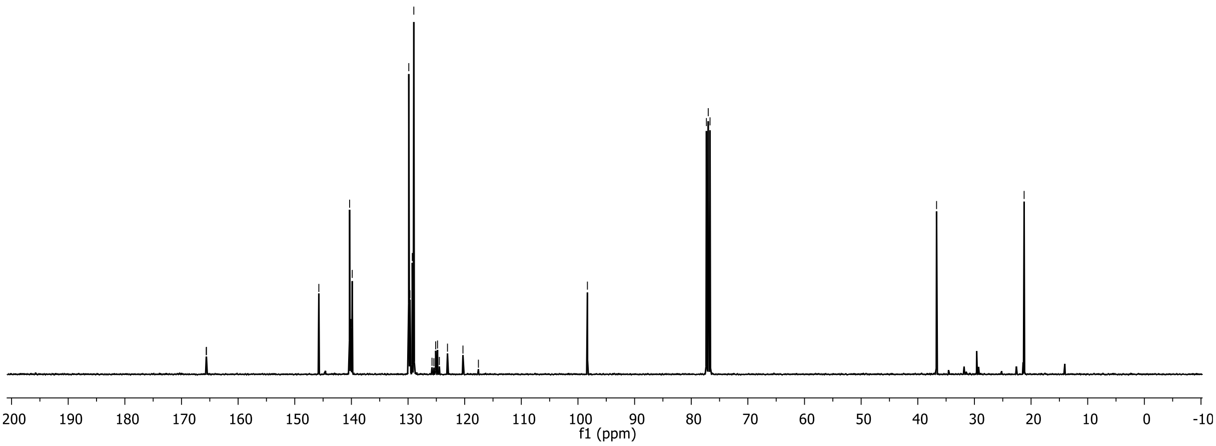

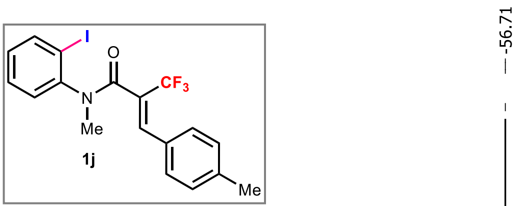

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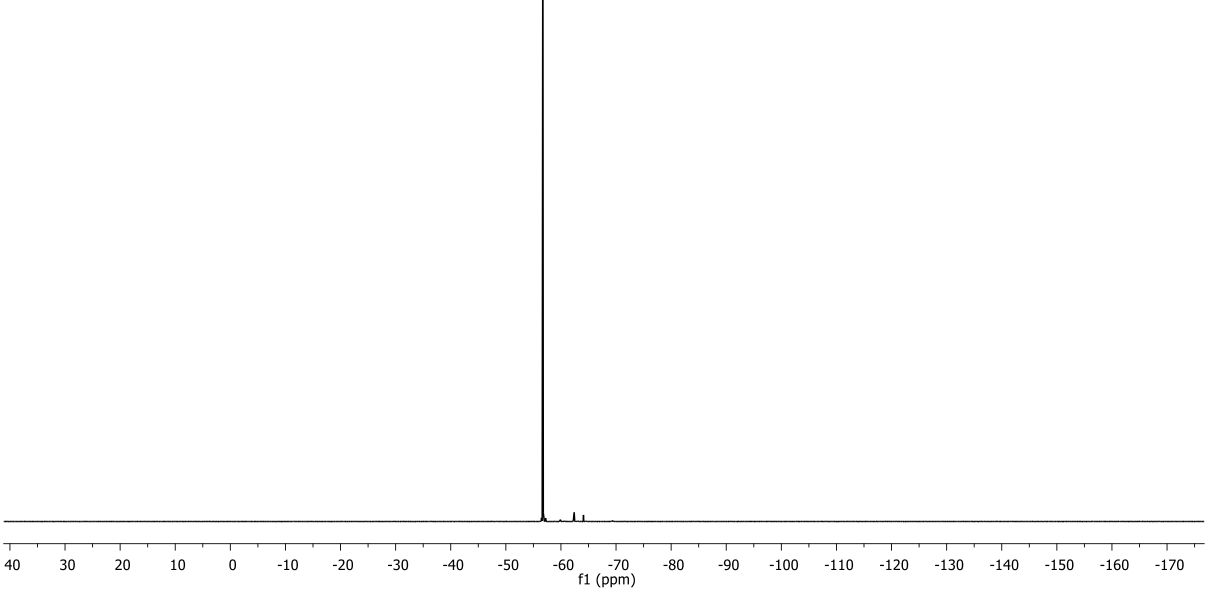

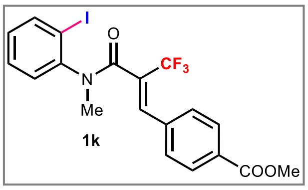

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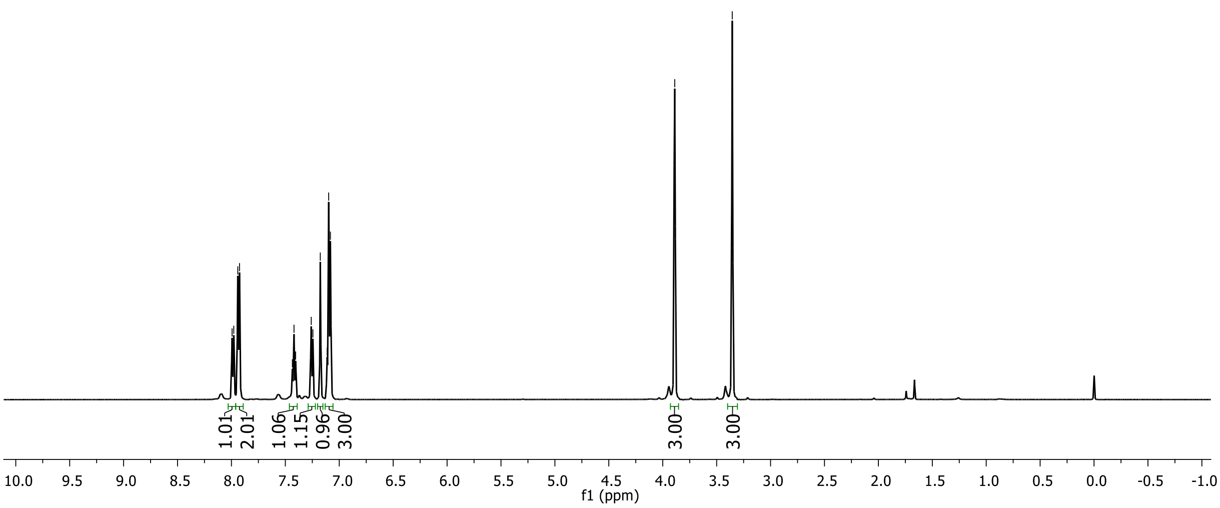

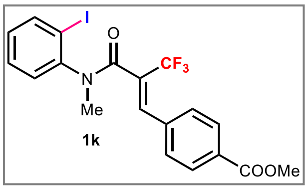

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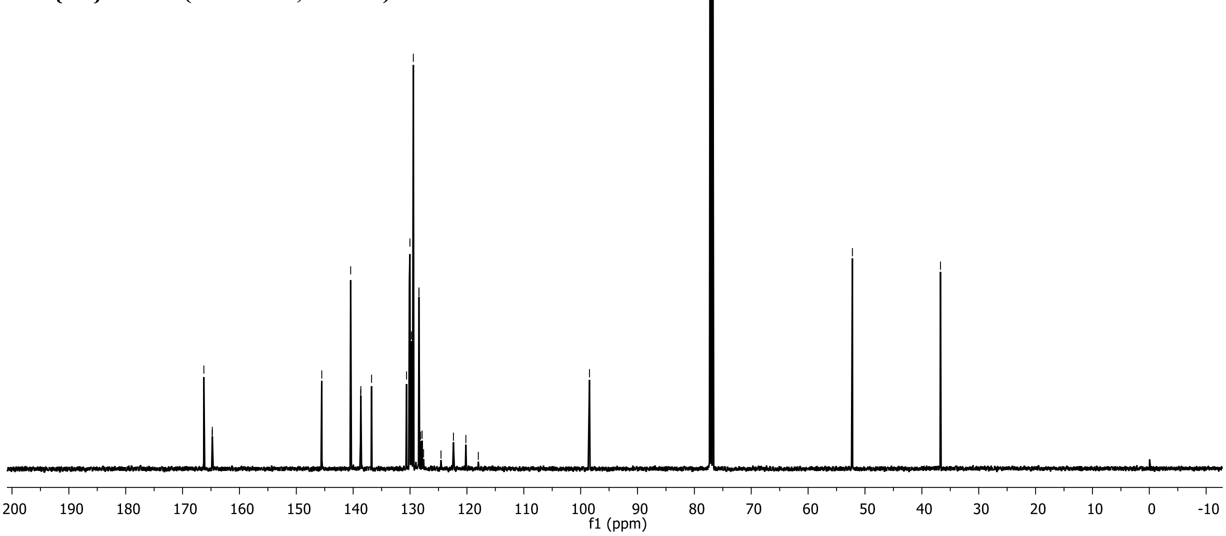

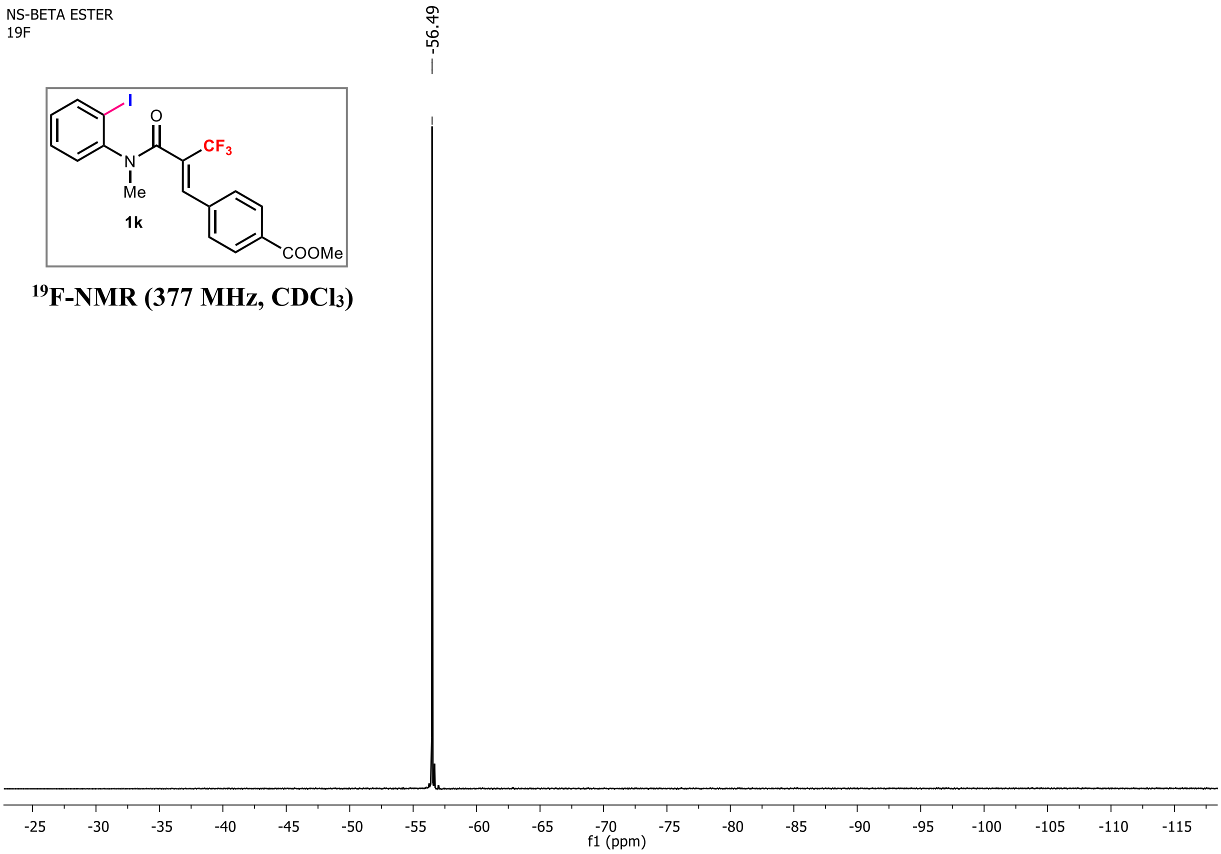

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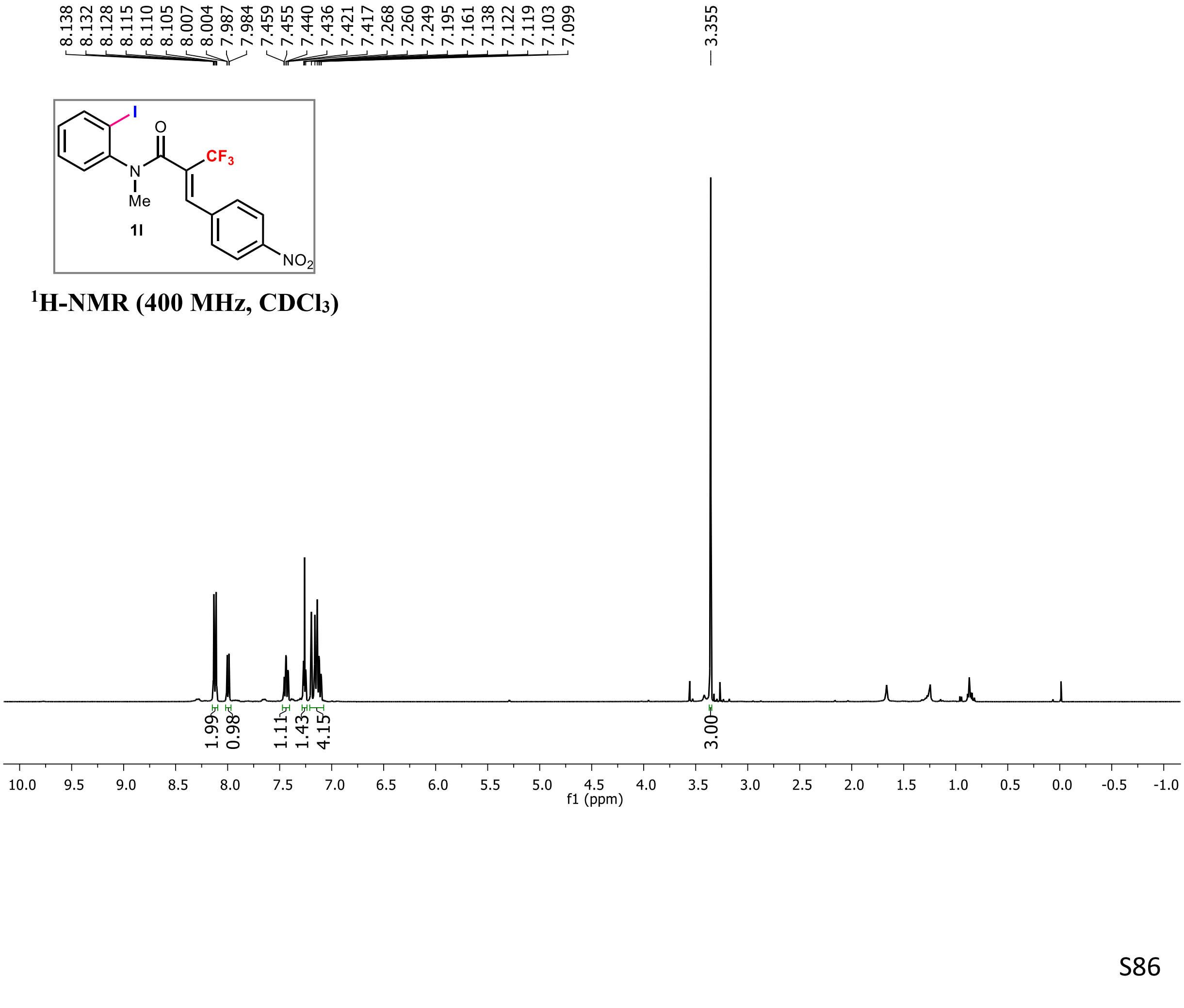

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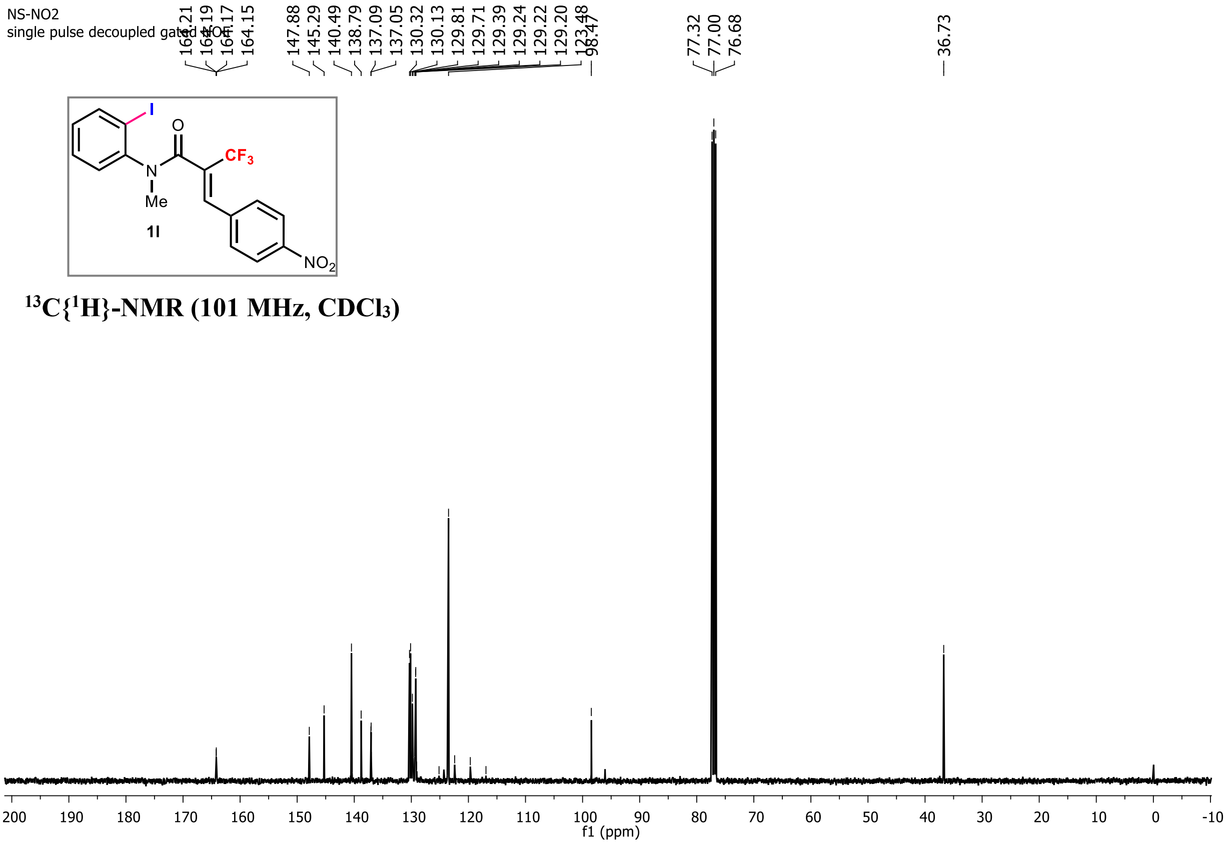
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129.20
123.48
98.47
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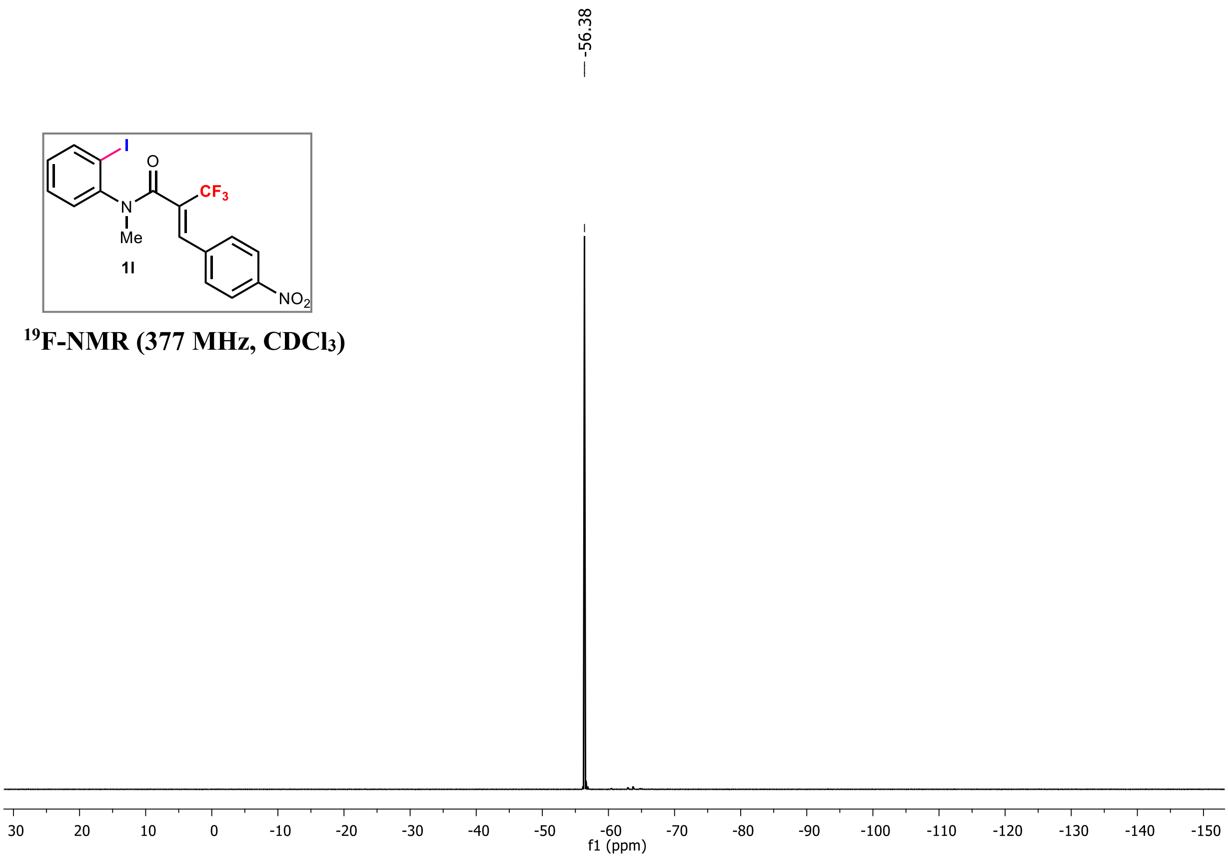
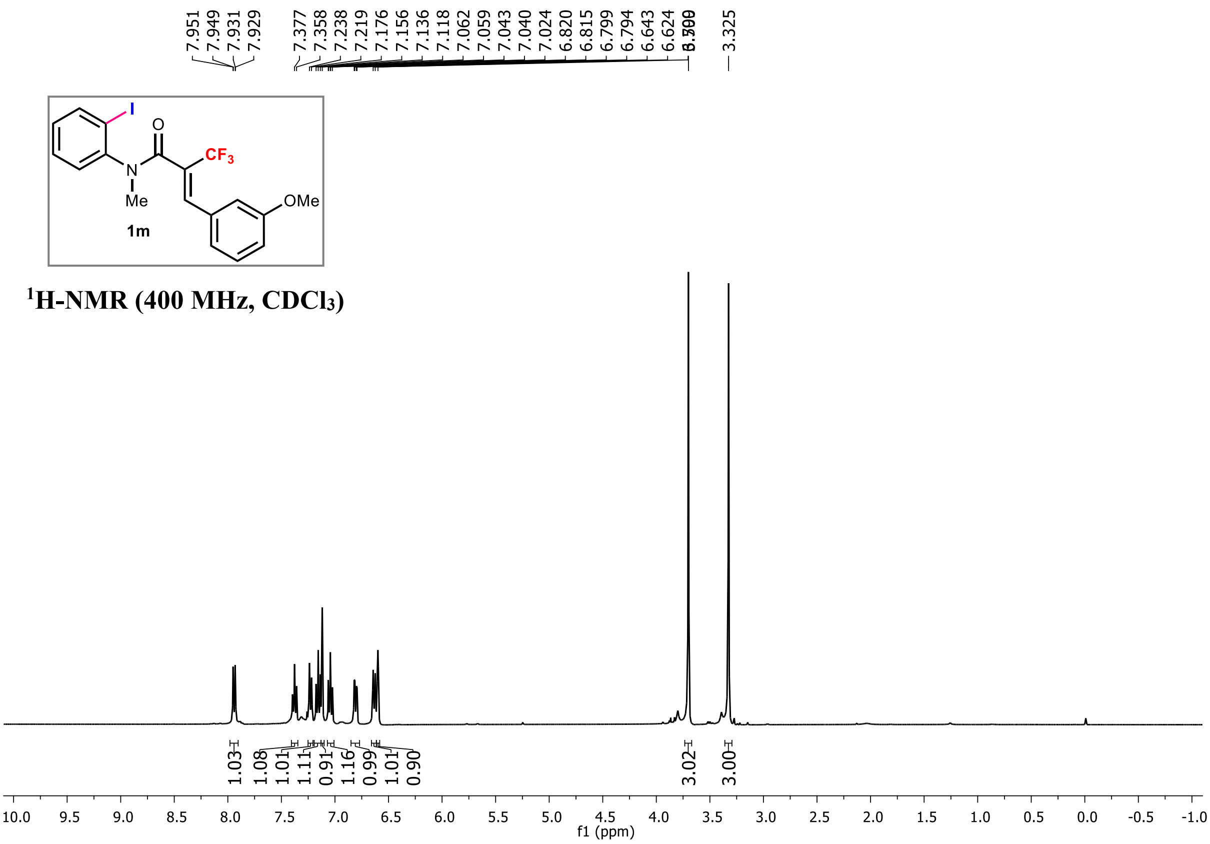
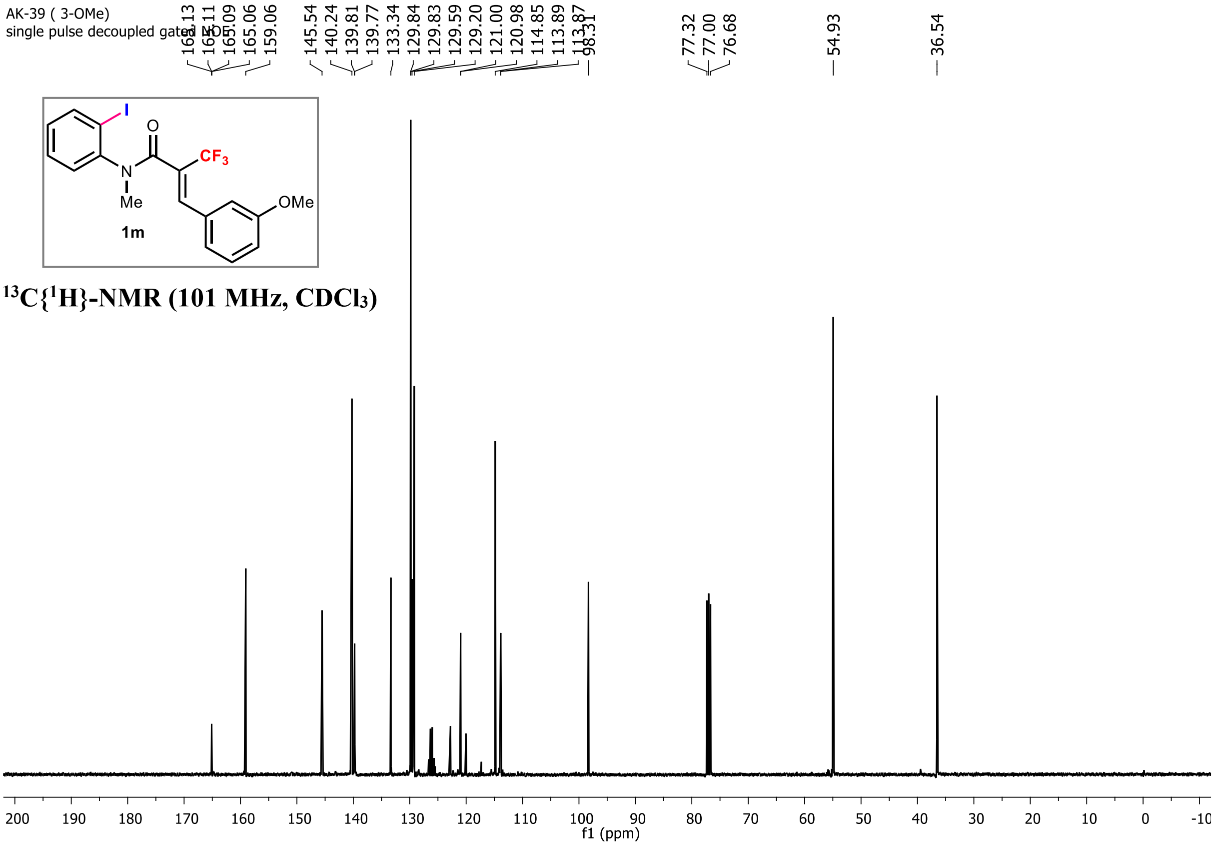
I
O
CF3
N
Me
1l
NO2
13C{1H}-NMR (101 MHz, CDCl3)
f1 (ppm)


-56.38
I
O
CF3
N
Me
1l
NO2
19F-NMR (377 MHz, CDCl3)
f1 (ppm)

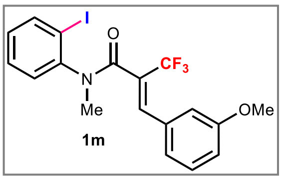


^{1}H-NMR (400 MHz, $CDCl_3$)



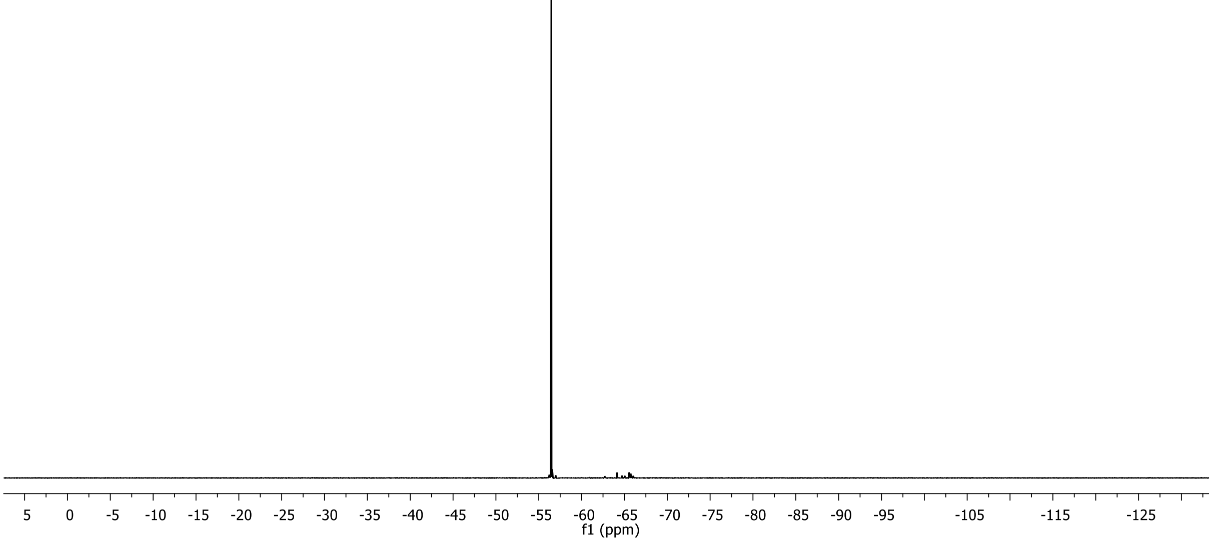
$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$)

AK-39

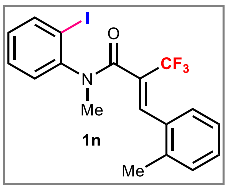


1m

^{19}F-NMR (377 MHz, CDCl$_3$)

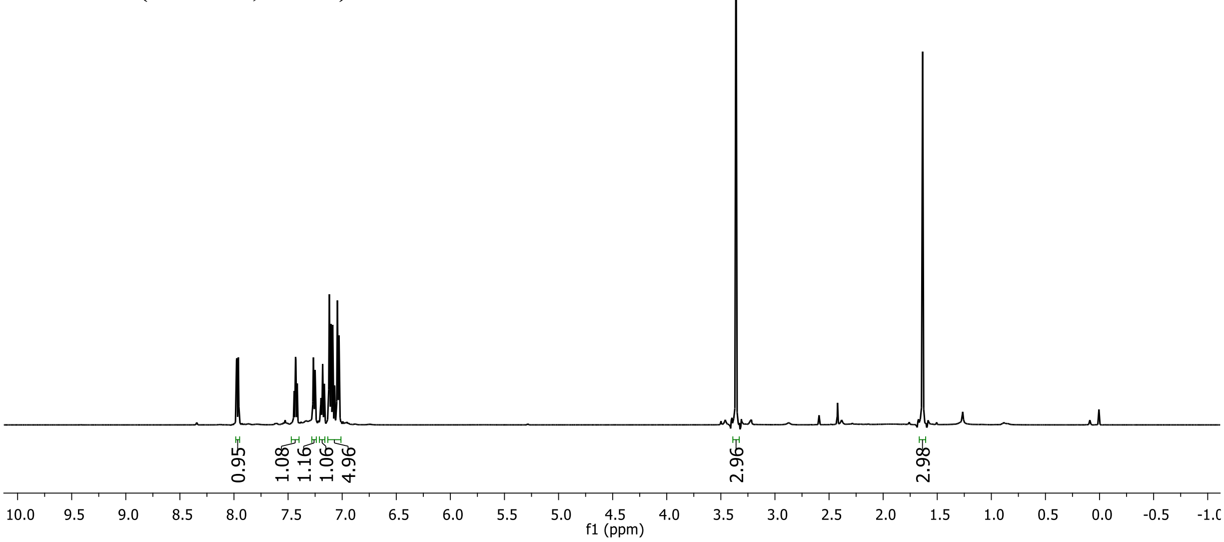


14.02.24
ns-2 me sm beta

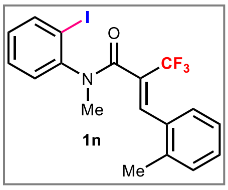


1n

^{1}H-NMR (500 MHz, CDCl$_3$)

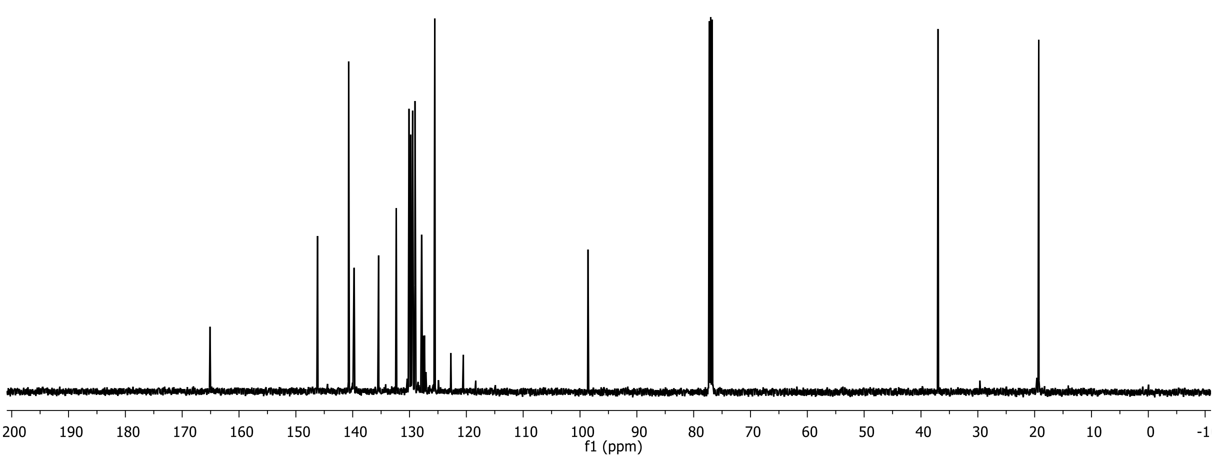


14.02.24
ns-2 me sm beta

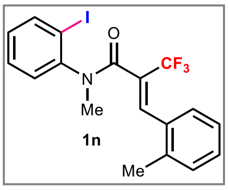


1n

$^{13}C\{^{1}H\}$-NMR (126 MHz, CDCl$_3$)

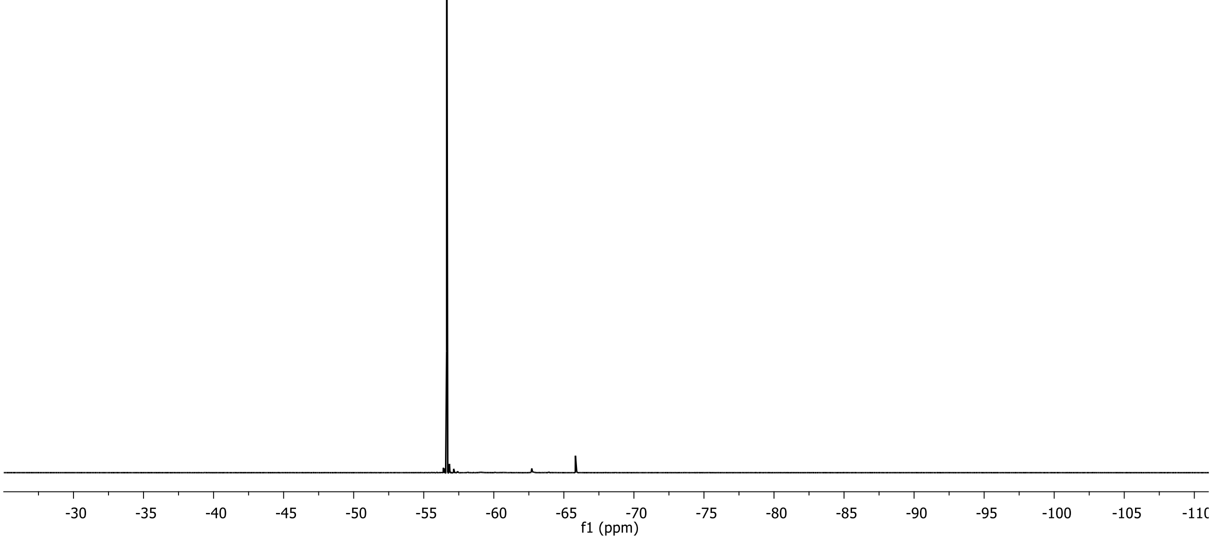


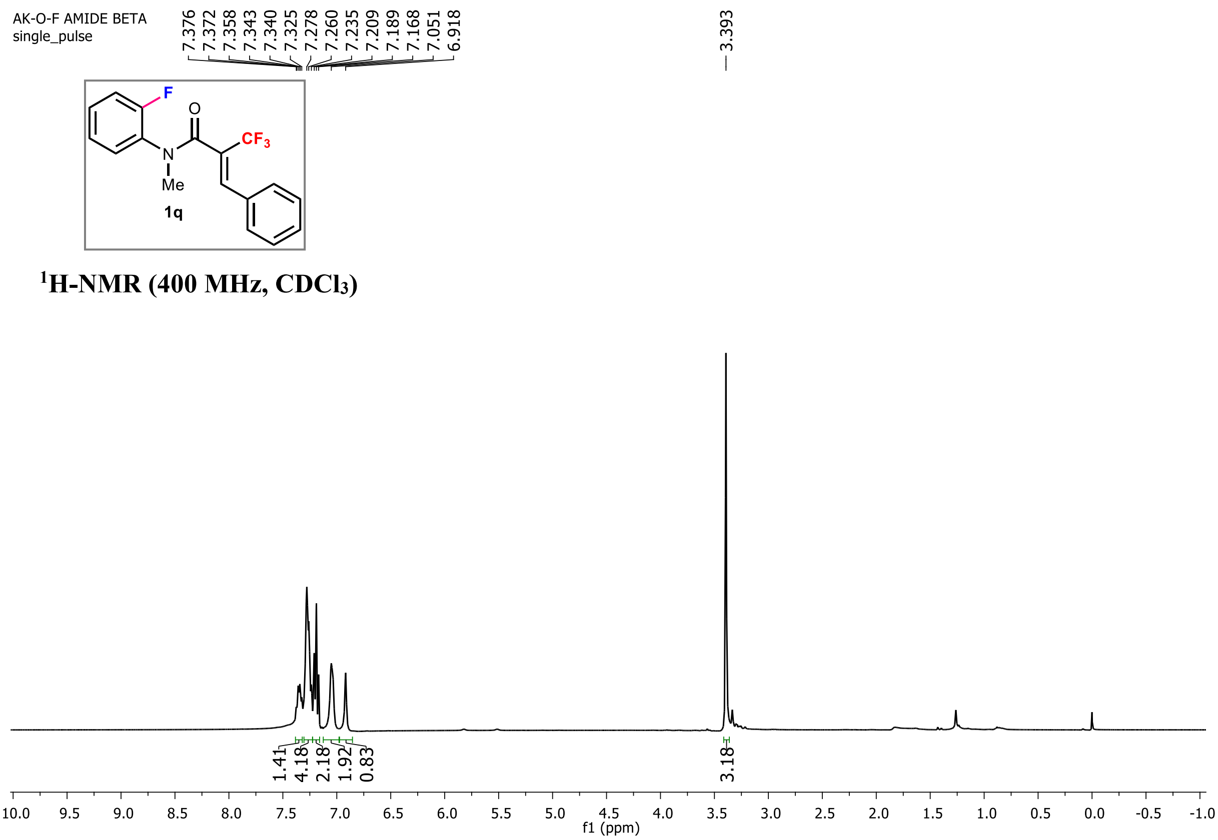
NS-2-Me BETA SM
19F



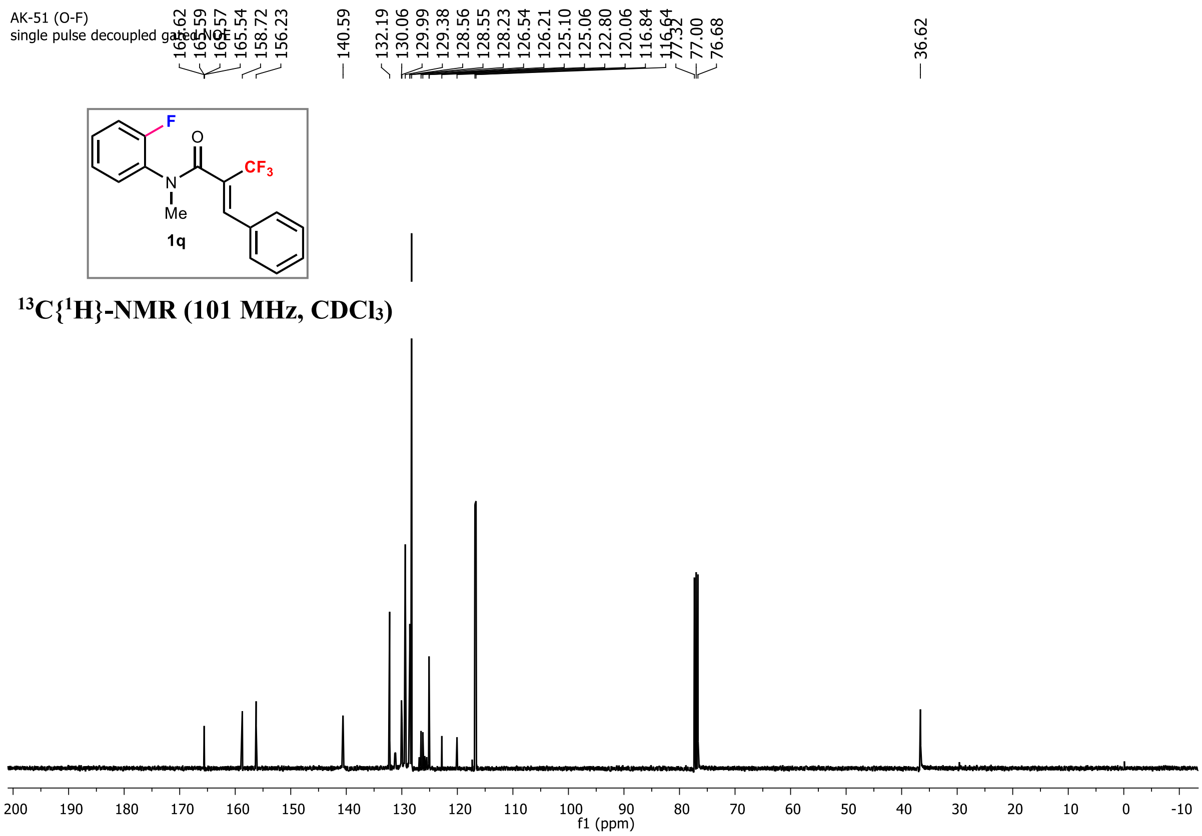
1n

^{19}F-NMR (377 MHz, CDCl$_3$)

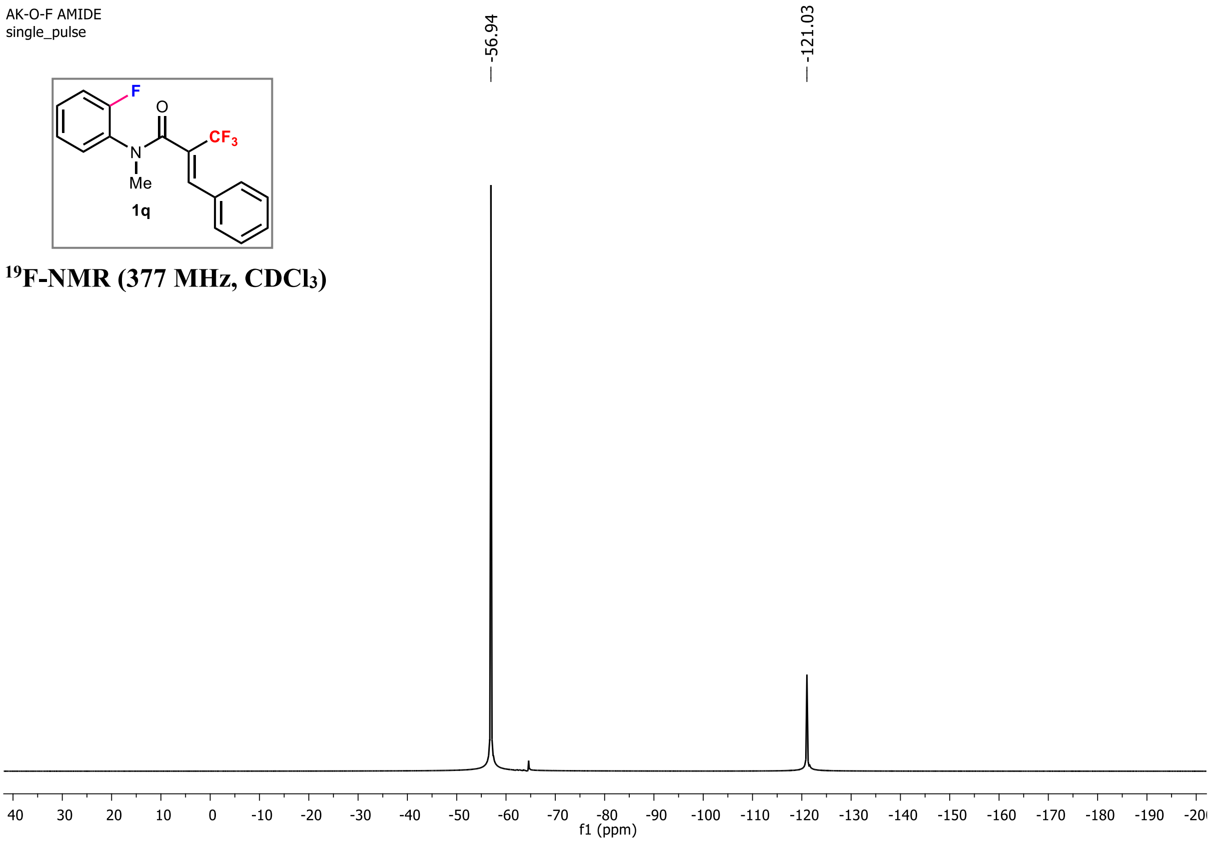




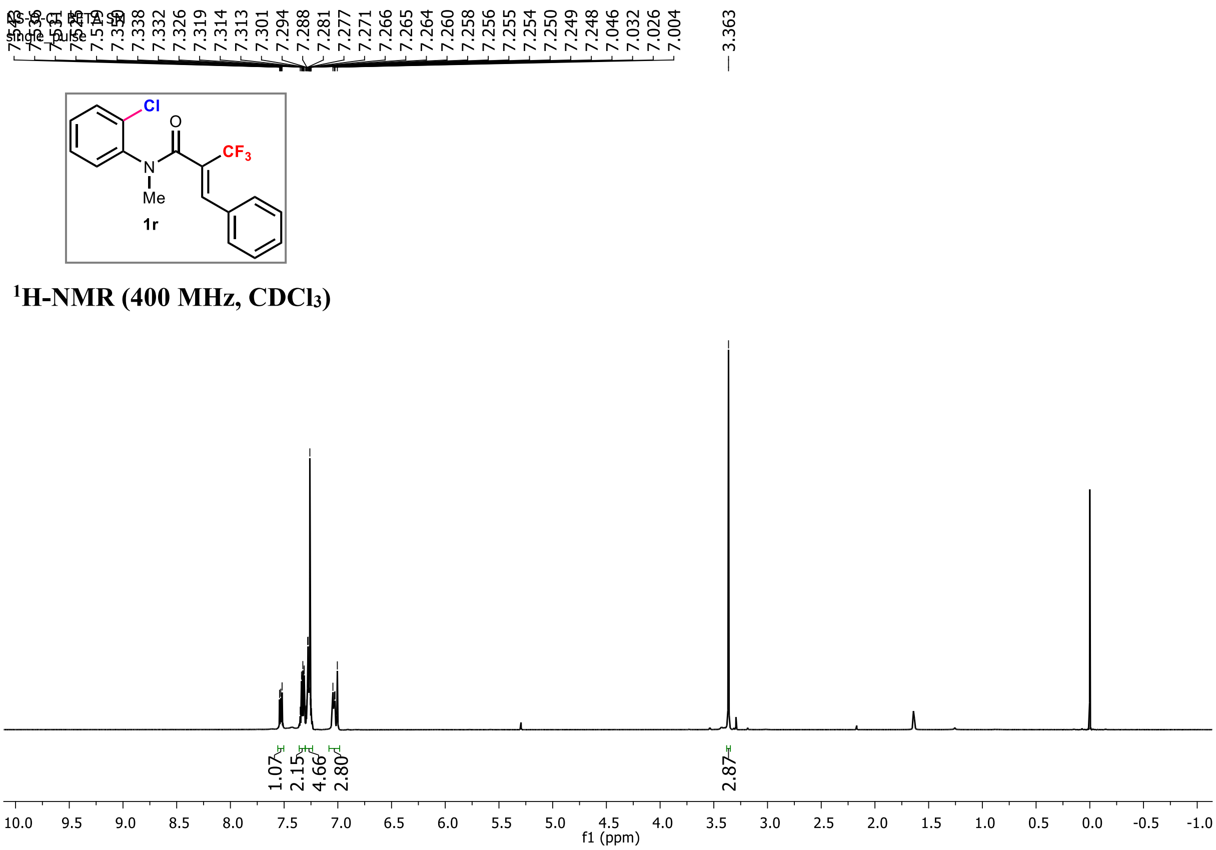
^{1}H-NMR (400 MHz, CDCl$_3$)



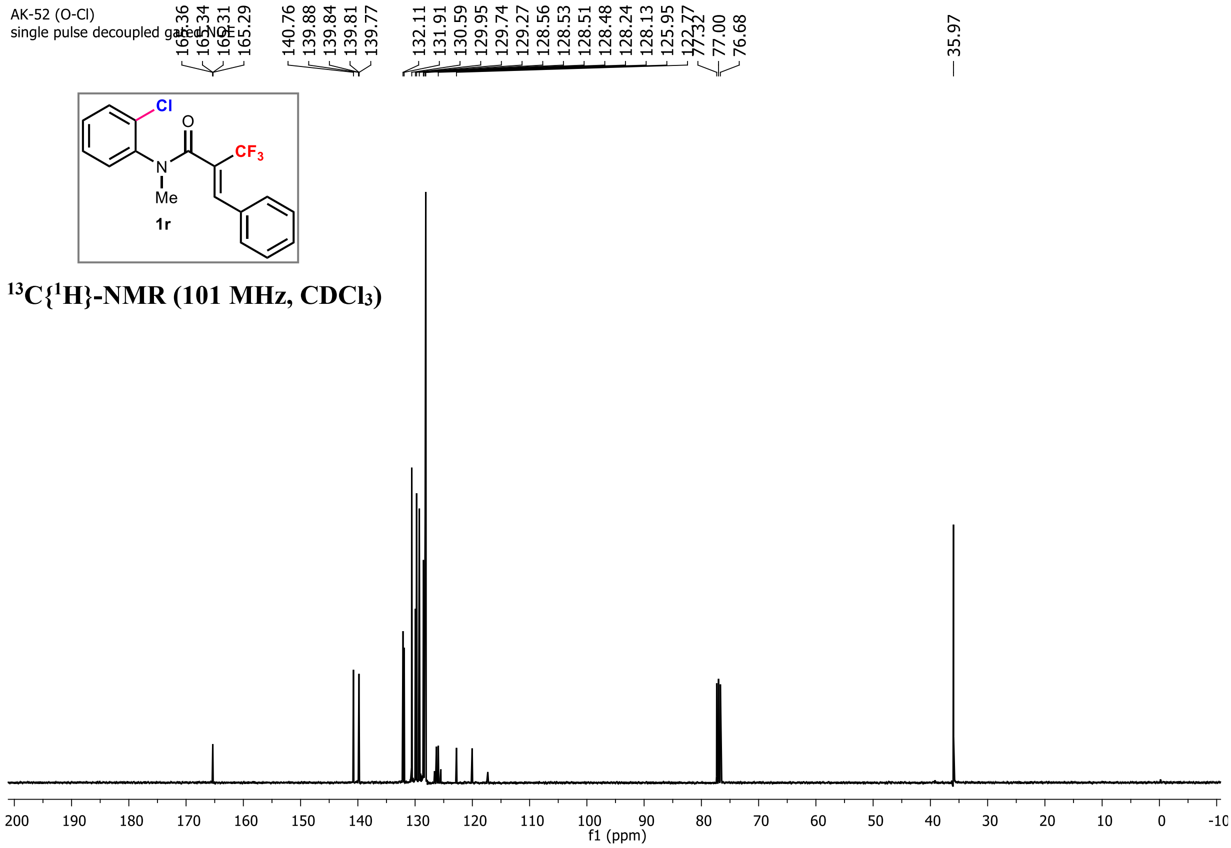
^{13}C{^{1}H}-NMR (101 MHz, CDCl$_3$)



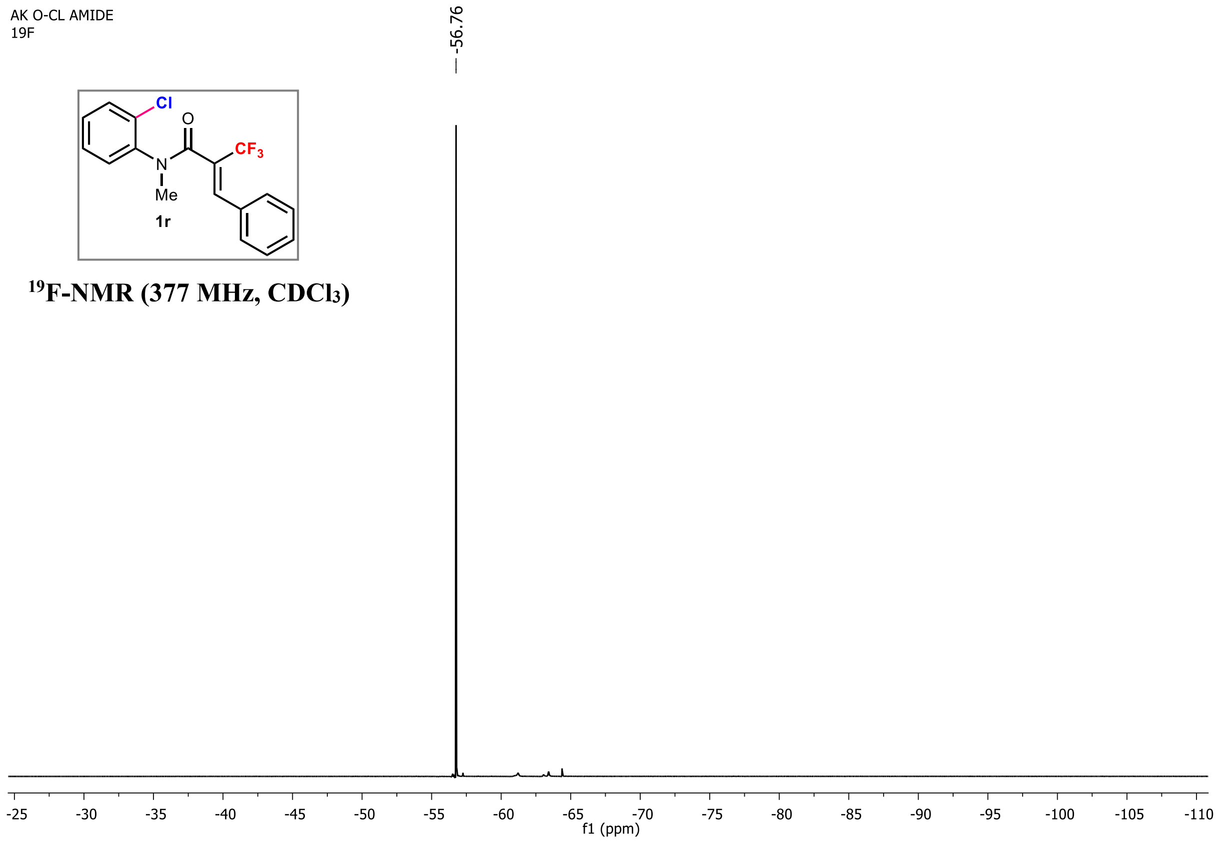
^{19}F-NMR (377 MHz, $CDCl_3$)



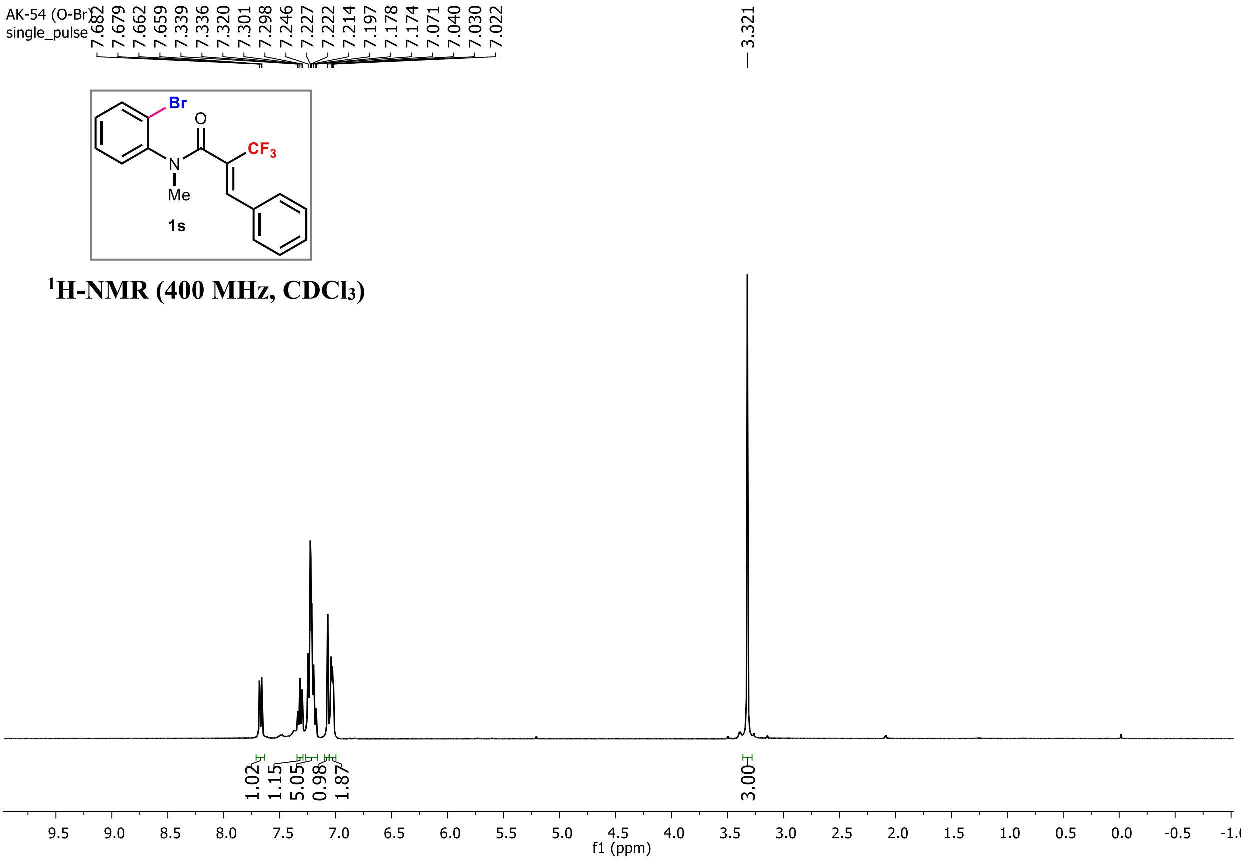
^{1}H-NMR (400 MHz, $CDCl_3$)

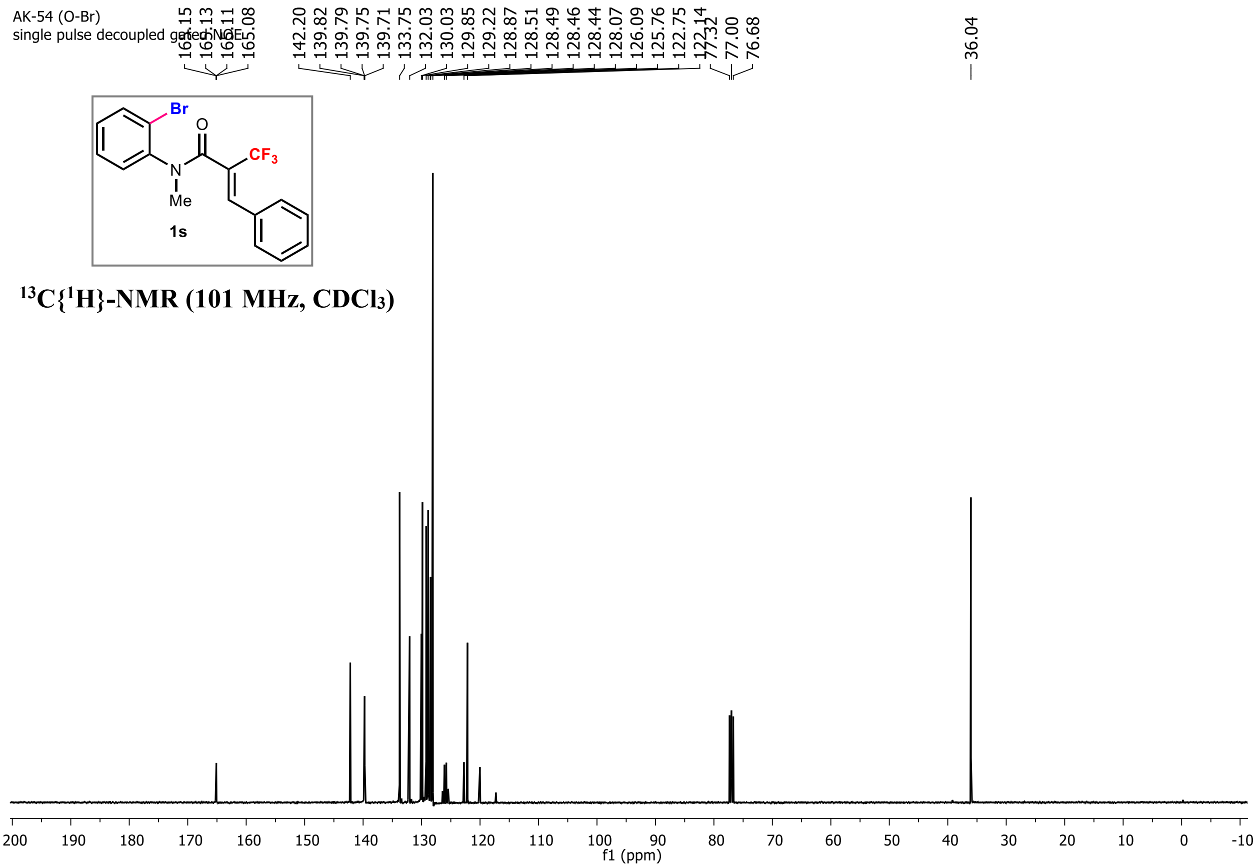


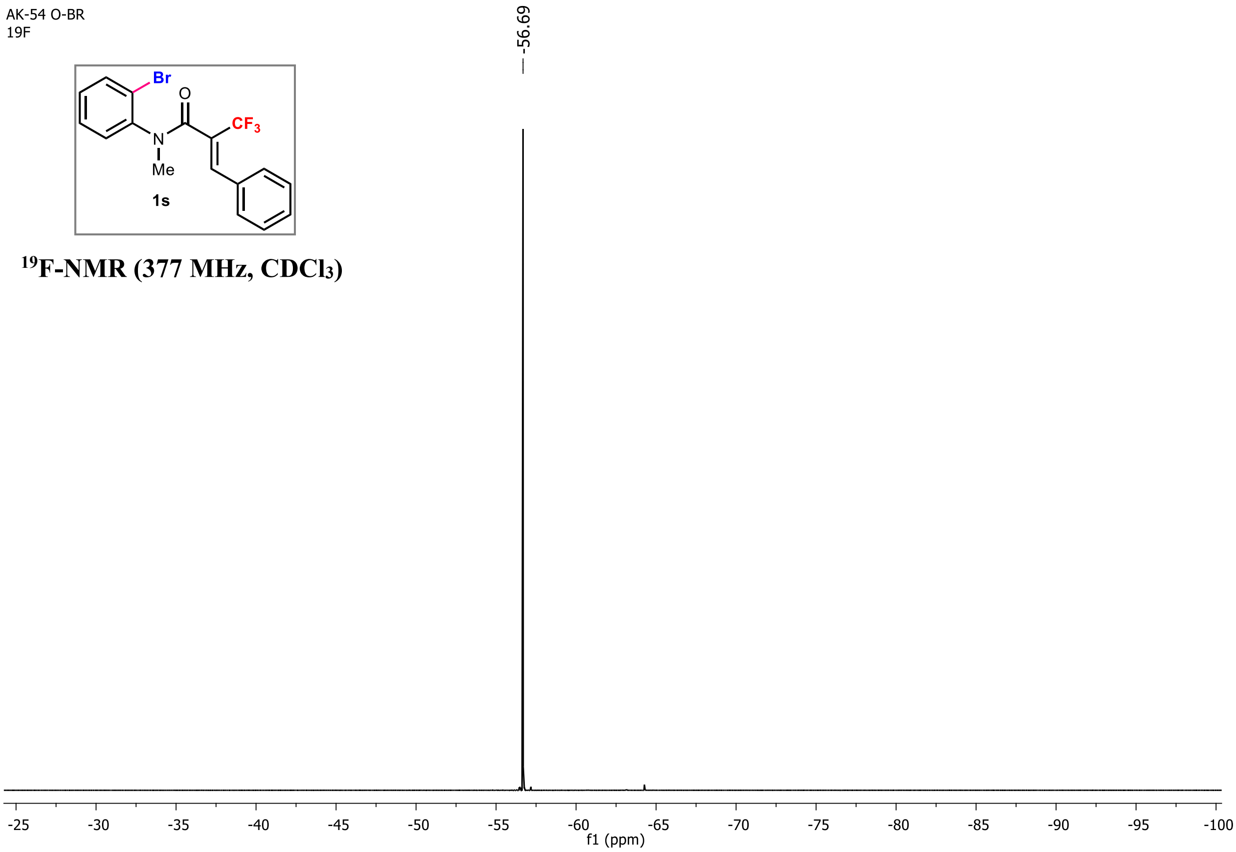
$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$)

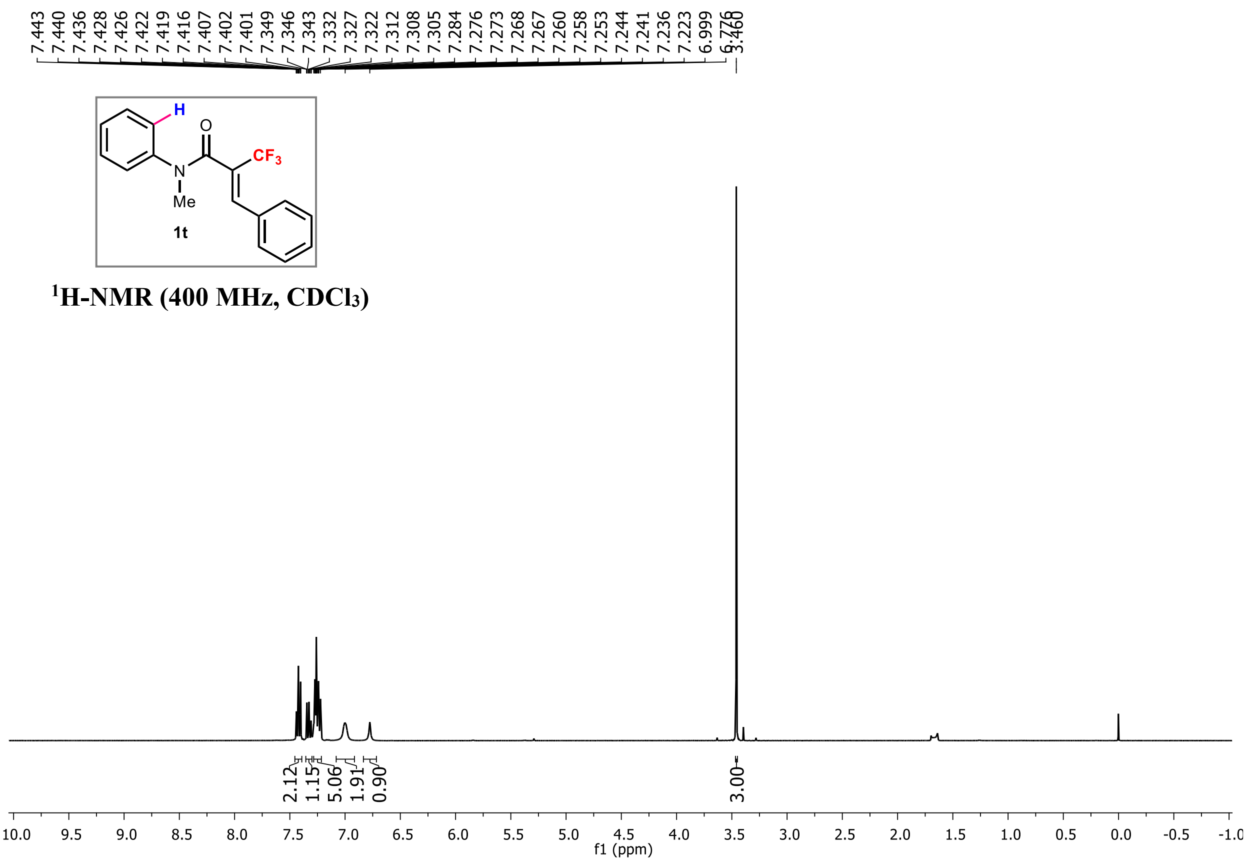


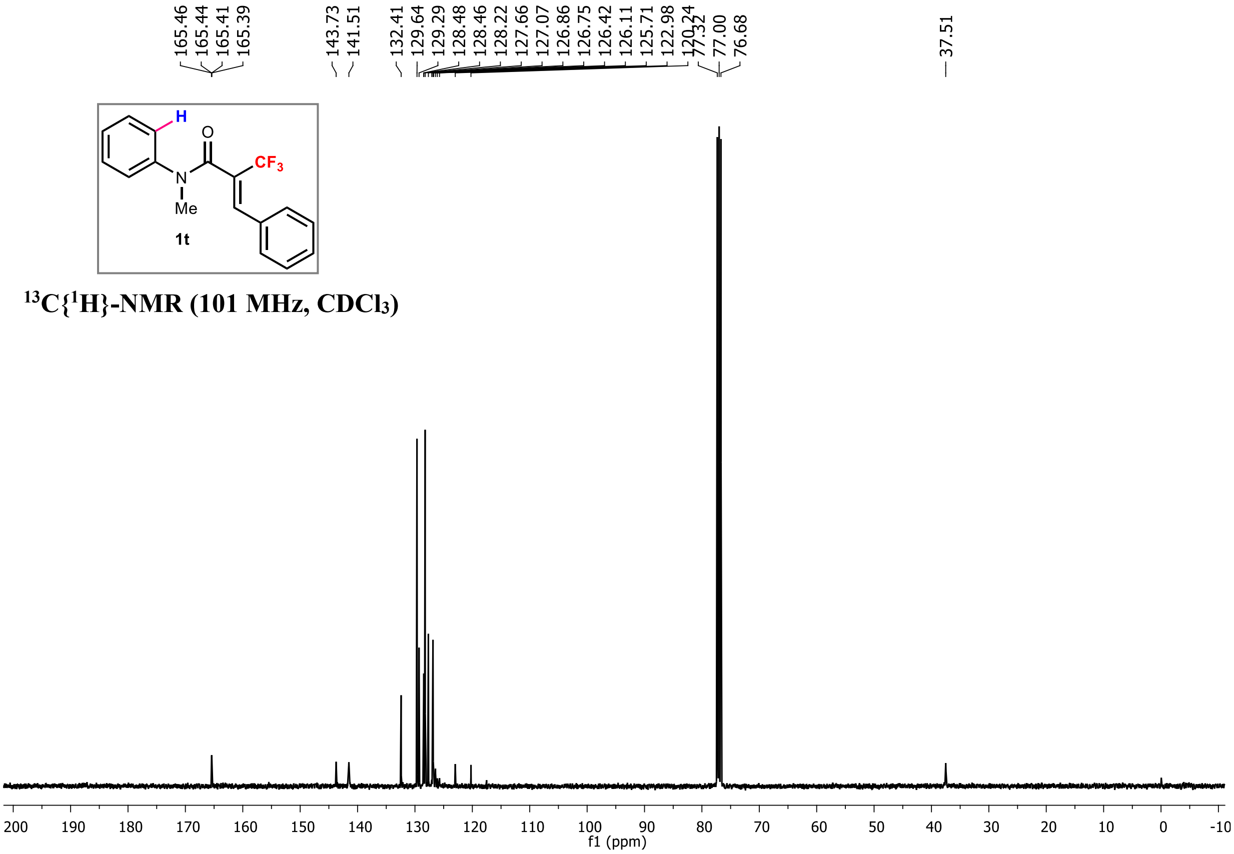
^{19}F-NMR (377 MHz, $CDCl_3$)


AK-54 (O-Br)
single_pulse
7.682
7.679
7.662
7.659
7.339
7.336
7.320
7.301
7.298
7.246
7.227
7.222
7.214
7.197
7.178
7.174
7.071
7.040
7.030
7.022
3.321
Br
O
CF3
N
Me
1s
1H-NMR (400 MHz, CDCl3)
1.02
1.15
5.05
0.98
1.87
3.00
f1 (ppm)

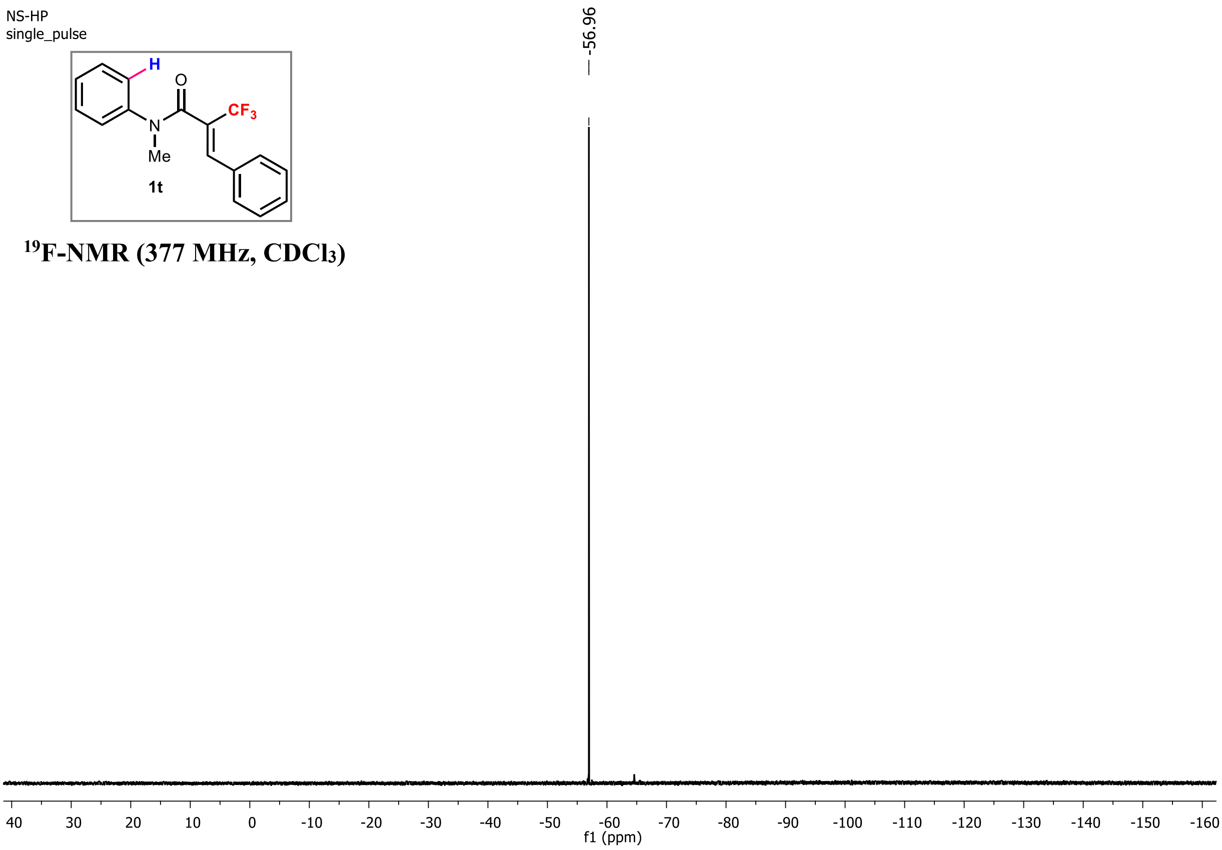

AK-54 (O-Br)
single pulse decoupled gated NOE
165.15
165.13
165.11
165.08
142.20
139.82
139.79
139.75
139.71
133.75
132.03
130.03
129.85
129.22
128.87
128.51
128.49
128.46
128.44
128.07
126.09
125.76
122.75
122.14
77.32
77.00
76.68
36.04
Br
O
CF3
N
Me
1s
13C{1H}-NMR (101 MHz, CDCl3)
f1 (ppm)


AK-54 O-BR
19F
-56.69
Br
O
CF3
N
Me
1s
19F-NMR (377 MHz, CDCl3)
-25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100
f1 (ppm)

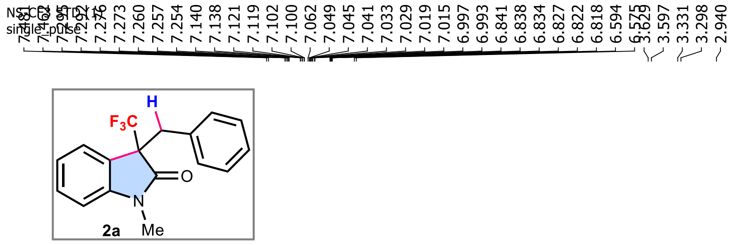

7.443 7.440 7.436 7.428 7.426 7.422 7.419 7.416 7.407 7.402 7.401 7.349 7.346 7.343 7.332 7.327 7.322 7.312 7.308 7.305 7.284 7.276 7.273 7.268 7.267 7.260 7.258 7.253 7.244 7.241 7.236 7.223 6.999
3.460
H
O
CF3
N
Me
1t
1H-NMR (400 MHz, CDCl3)
2.12 1.15 5.06 1.91 0.90
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 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 -0.5 -1.0
f1 (ppm)



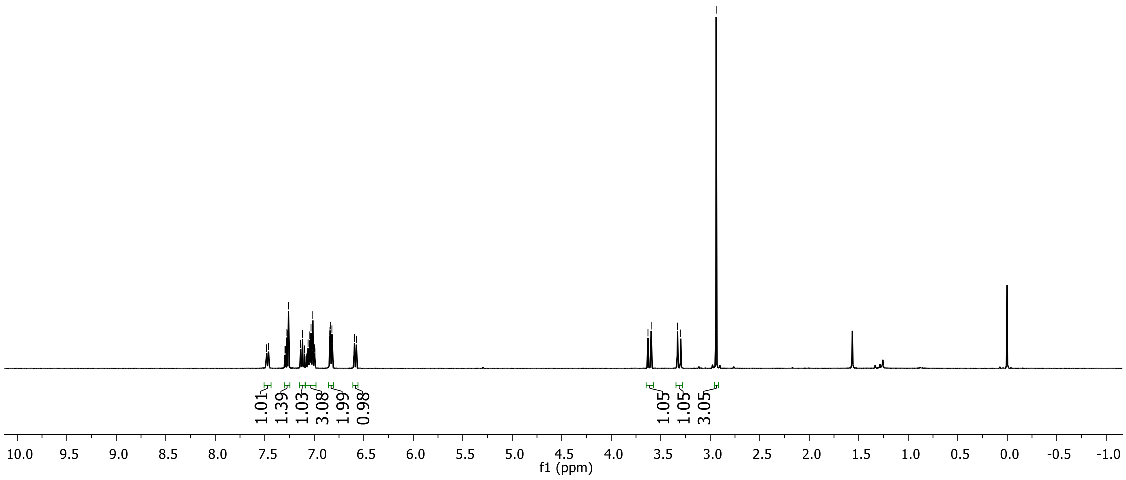
$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$)

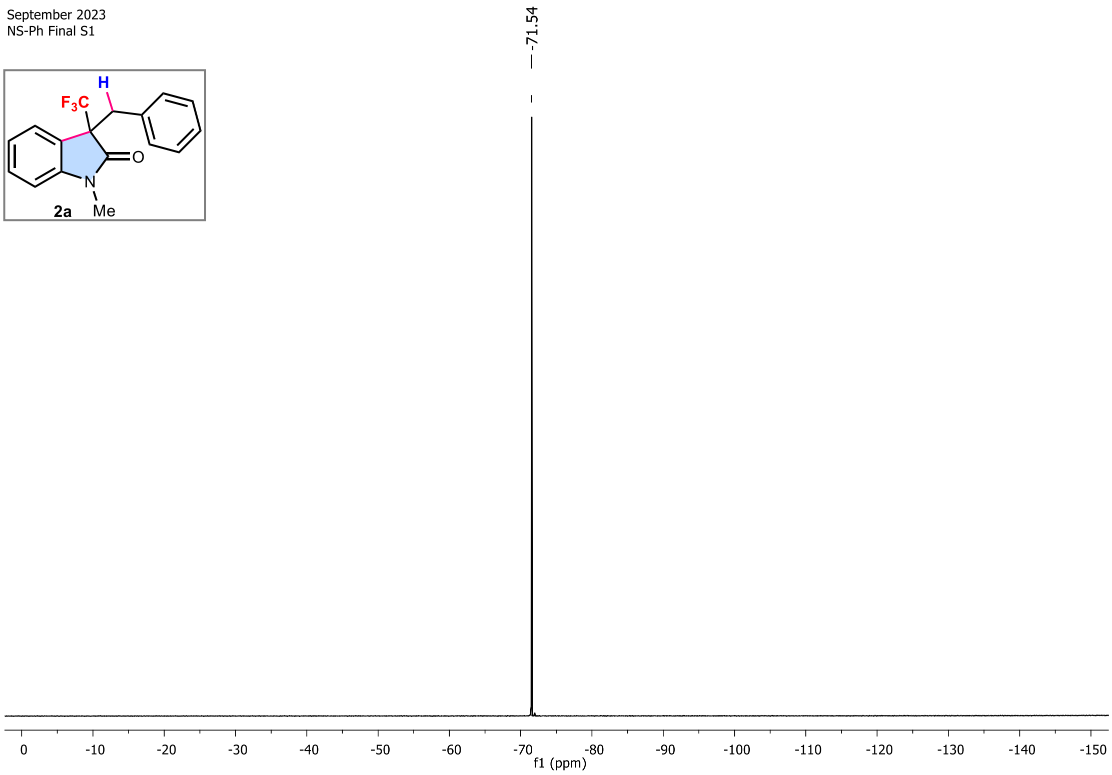


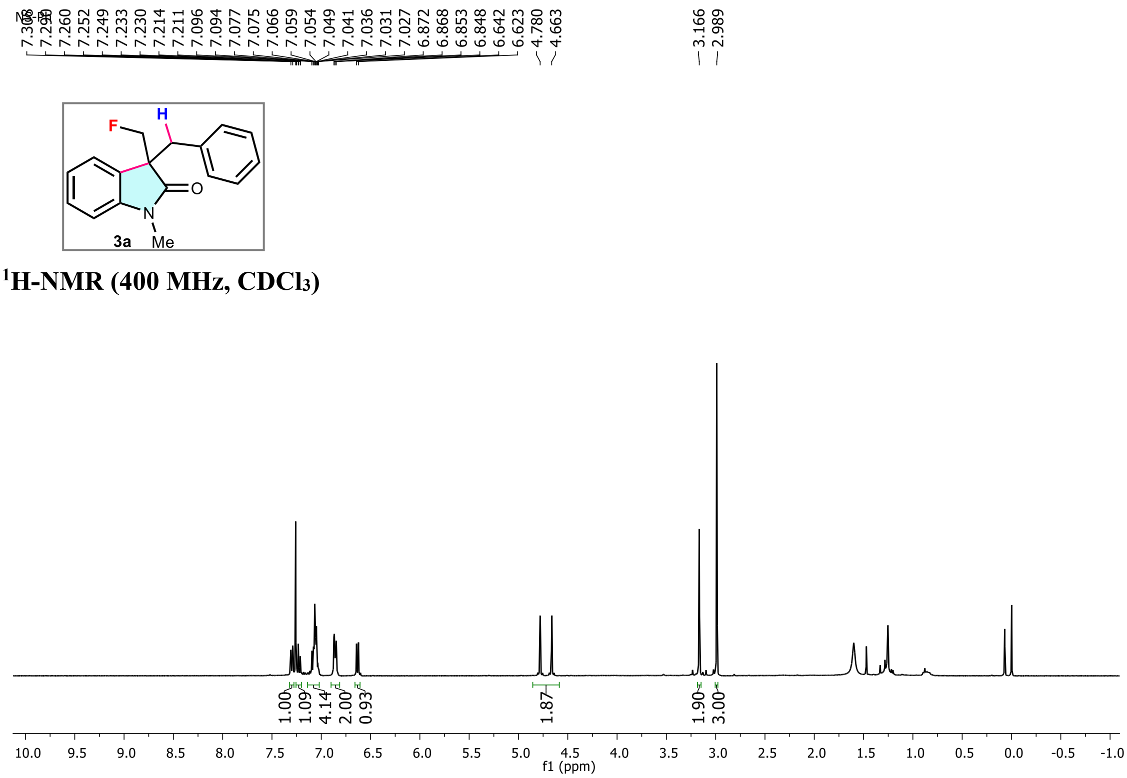
^{19}F-NMR (377 MHz, $CDCl_3$)



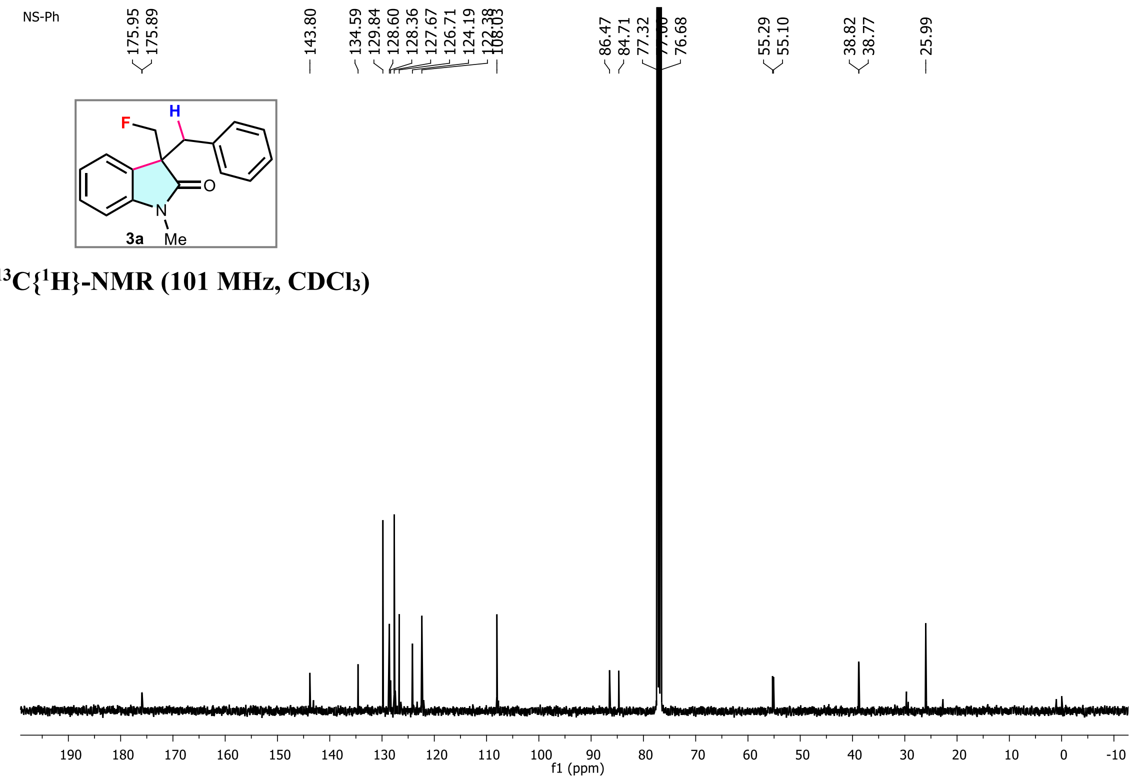
[1]H-NMR (400 MHz, CDCl$_3$)





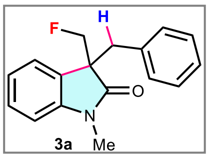


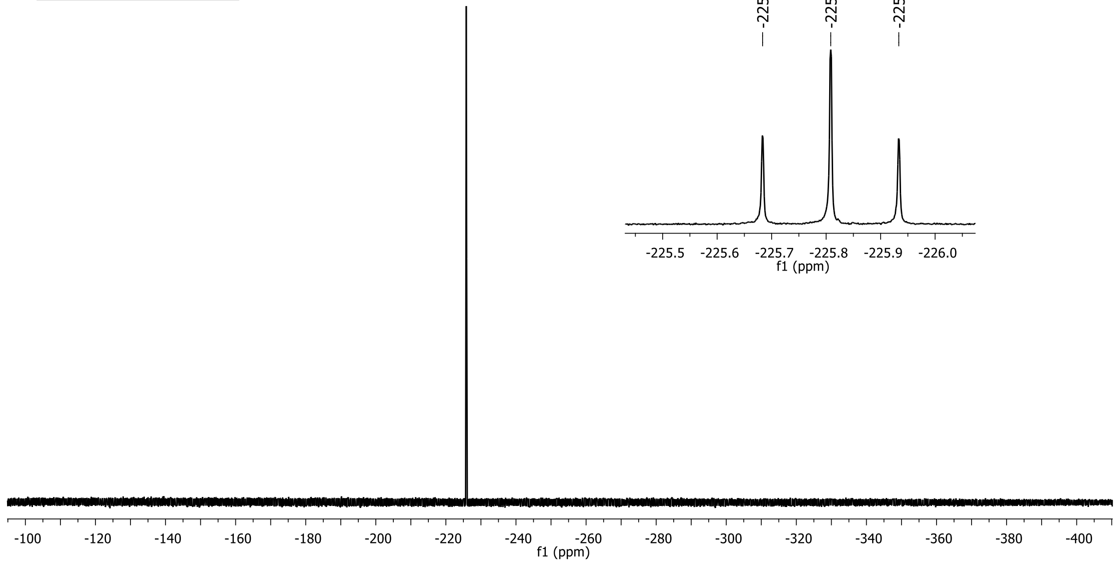
[1]H-NMR (400 MHz, $CDCl_3$)

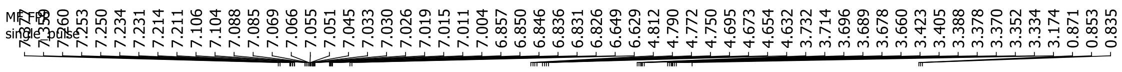


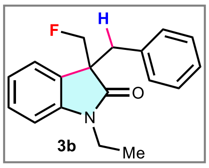
[13]C{[1]H}-NMR (101 MHz, $CDCl_3$)

NS-Ph

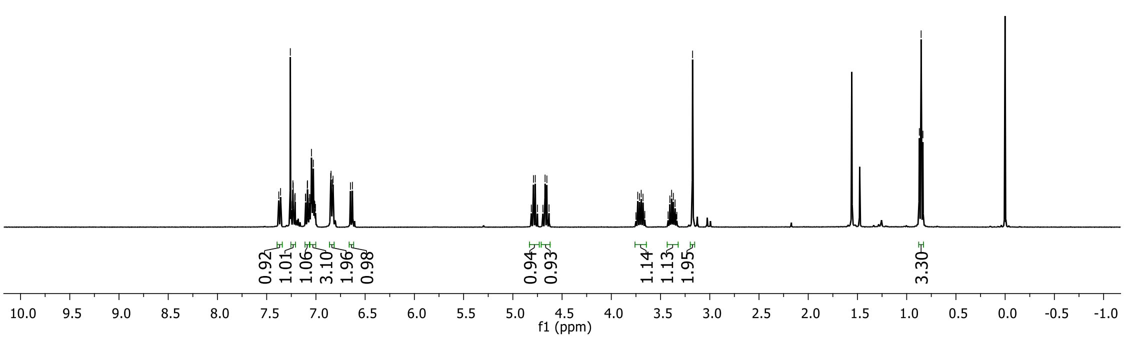


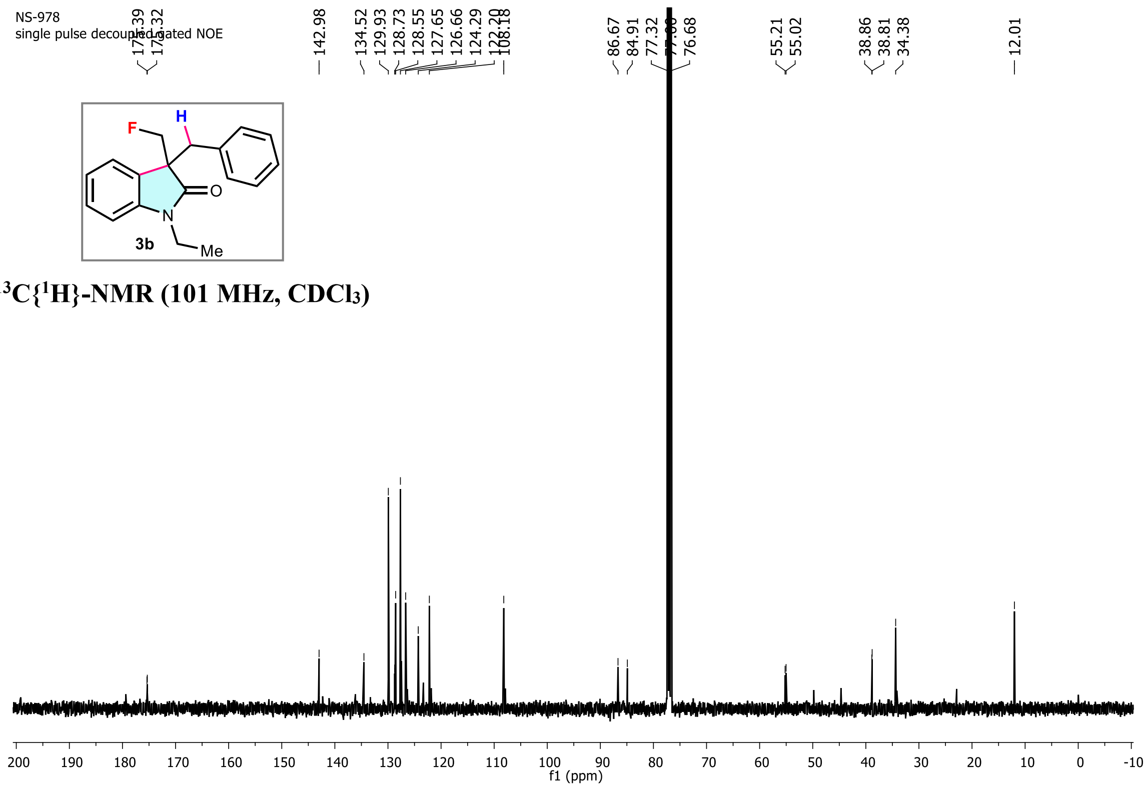




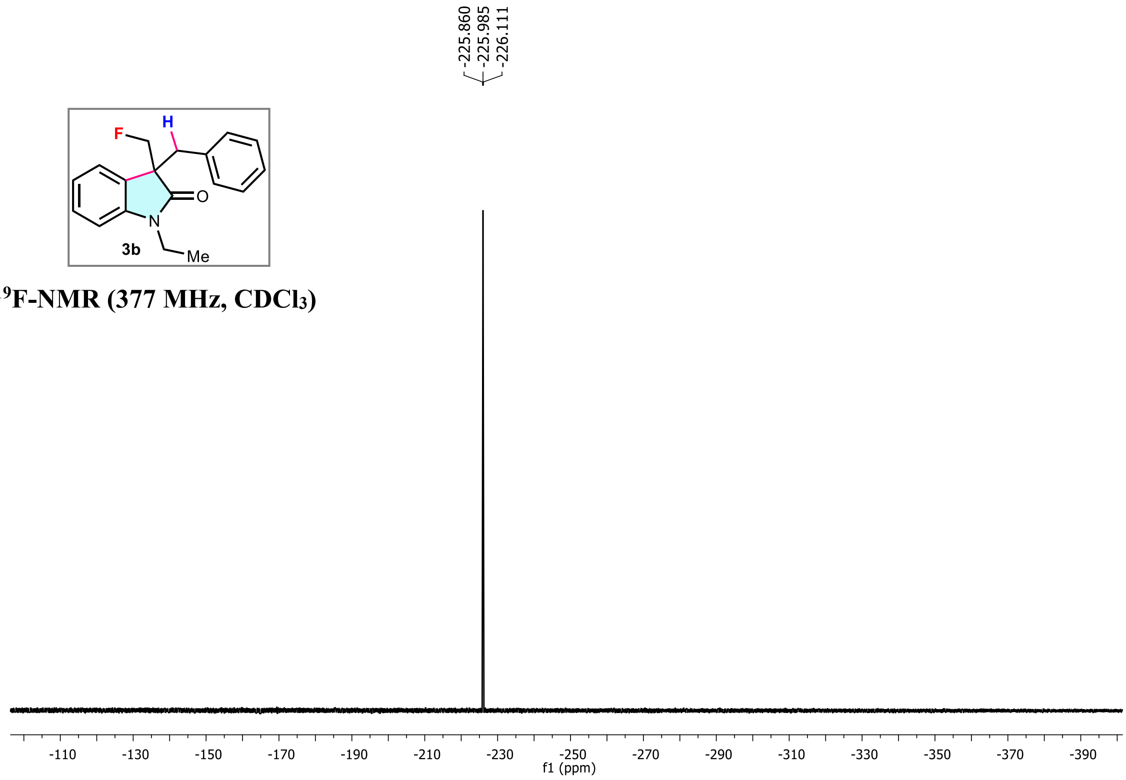


[1]H-NMR (400 MHz, CDCl$_3$)

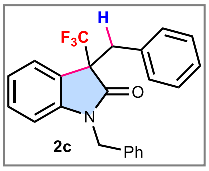




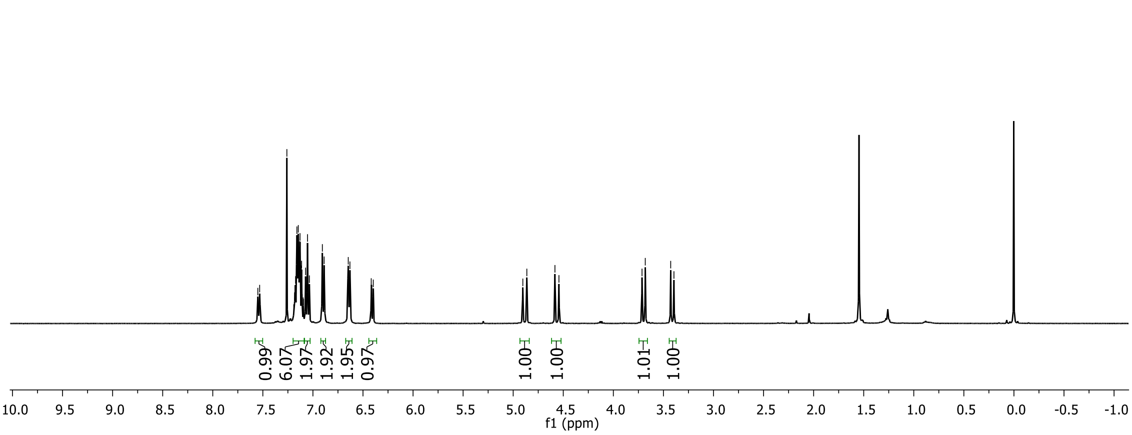
$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$)

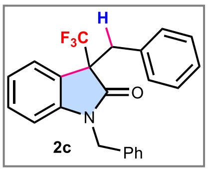


^{19}F-NMR (377 MHz, $CDCl_3$)

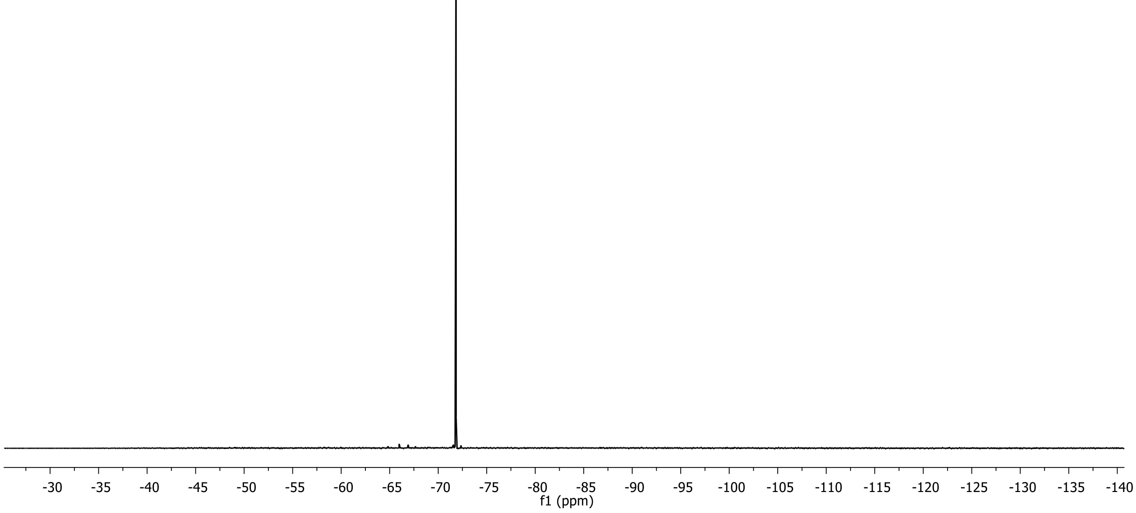


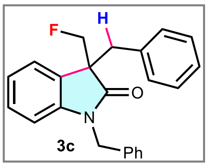
[1]H-NMR (400 MHz, CDCl$_3$)



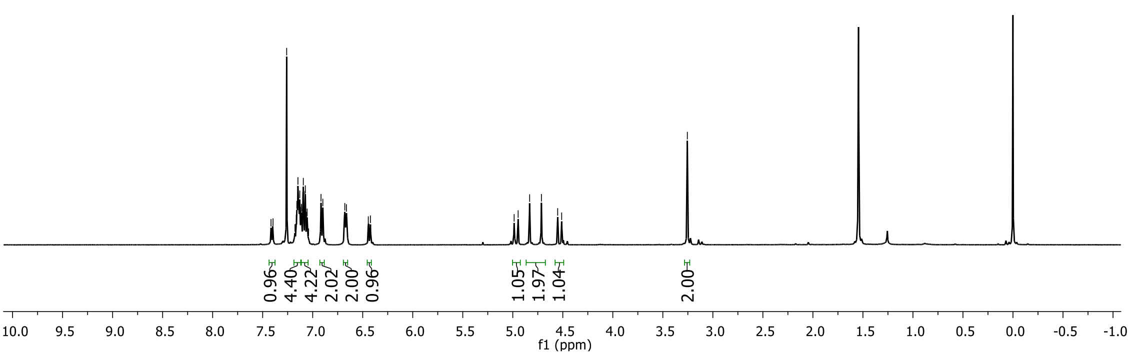


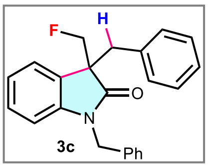
[19]F-NMR (377 MHz, CDCl$_3$)



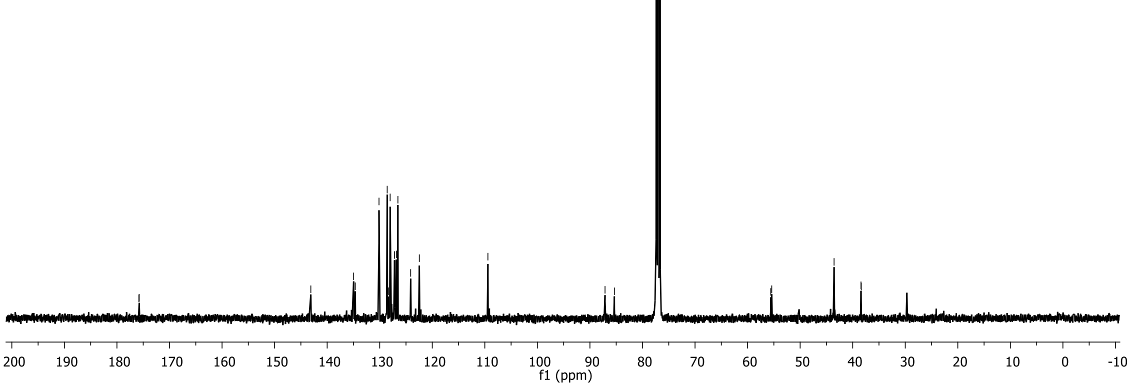


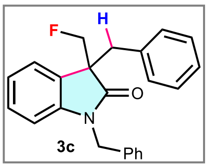
[1]H-NMR (400 MHz, CDCl₃)



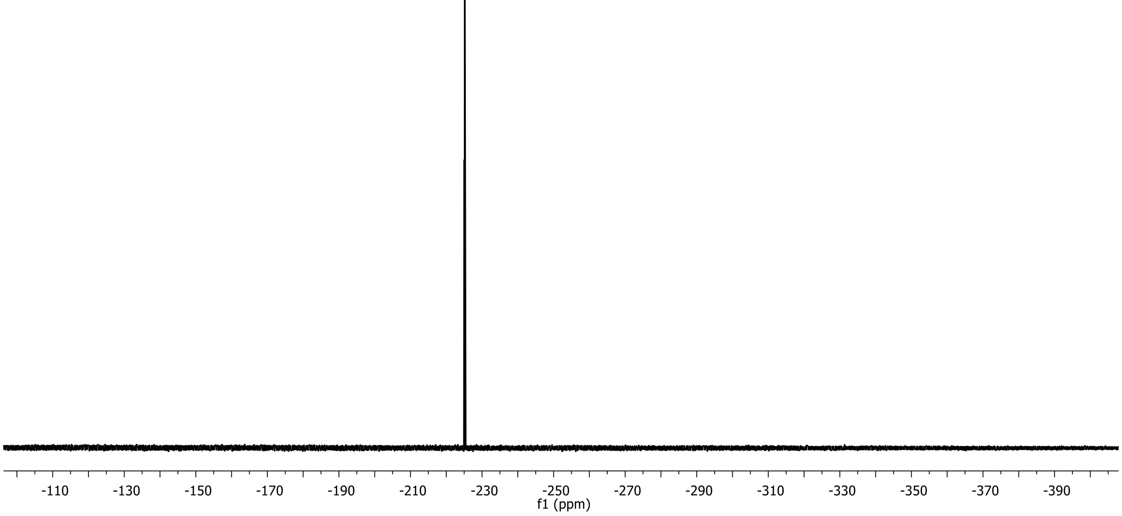


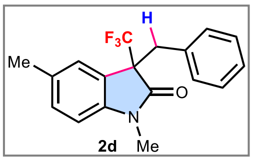
[13]C{[1]H}-NMR (101 MHz, CDCl₃)



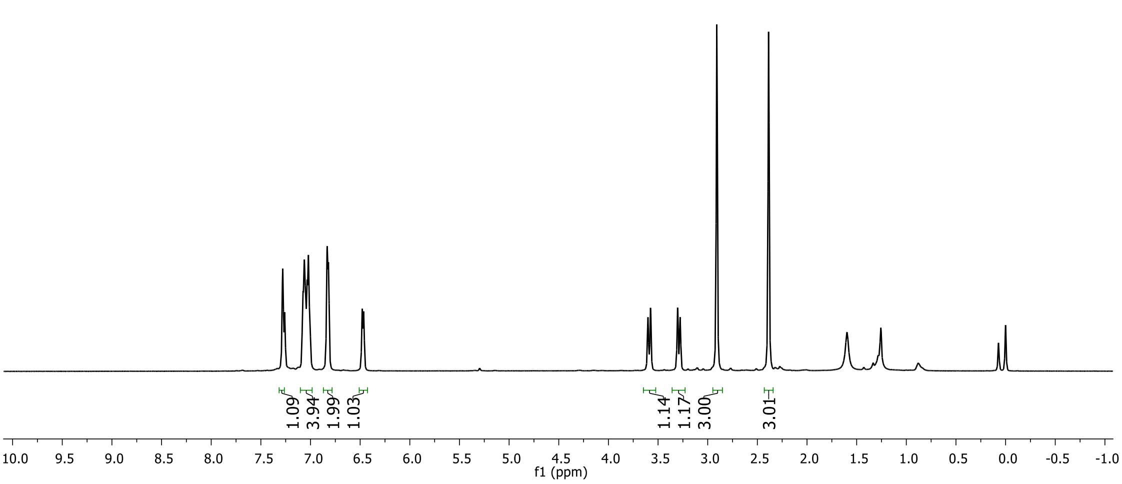


^{19}F-NMR (377 MHz, CDCl$_3$)

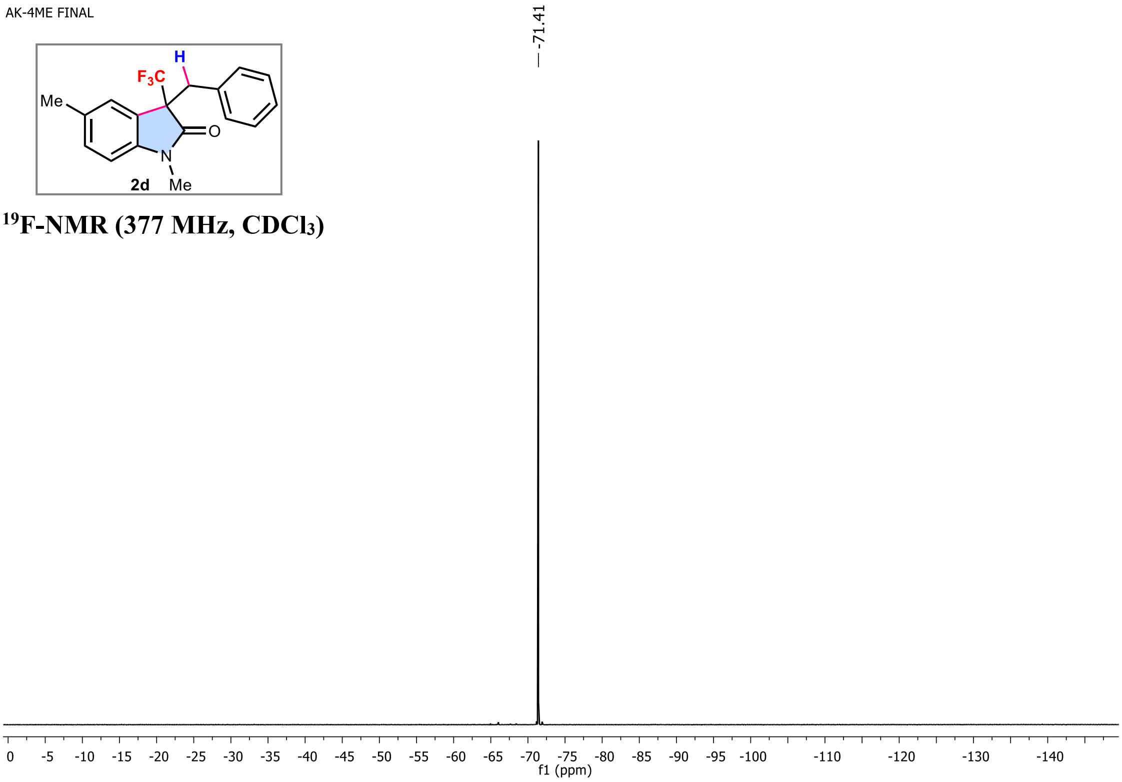




^{1}H-NMR (500 MHz, CDCl$_3$)

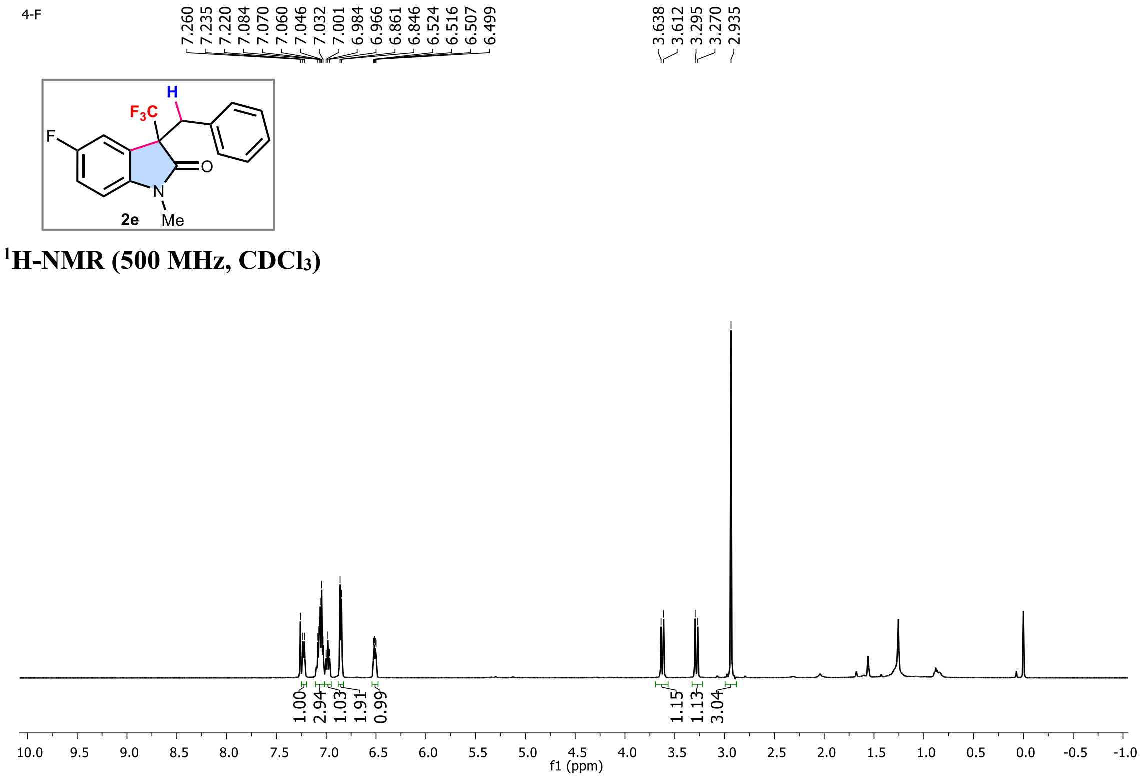


AK-4ME FINAL

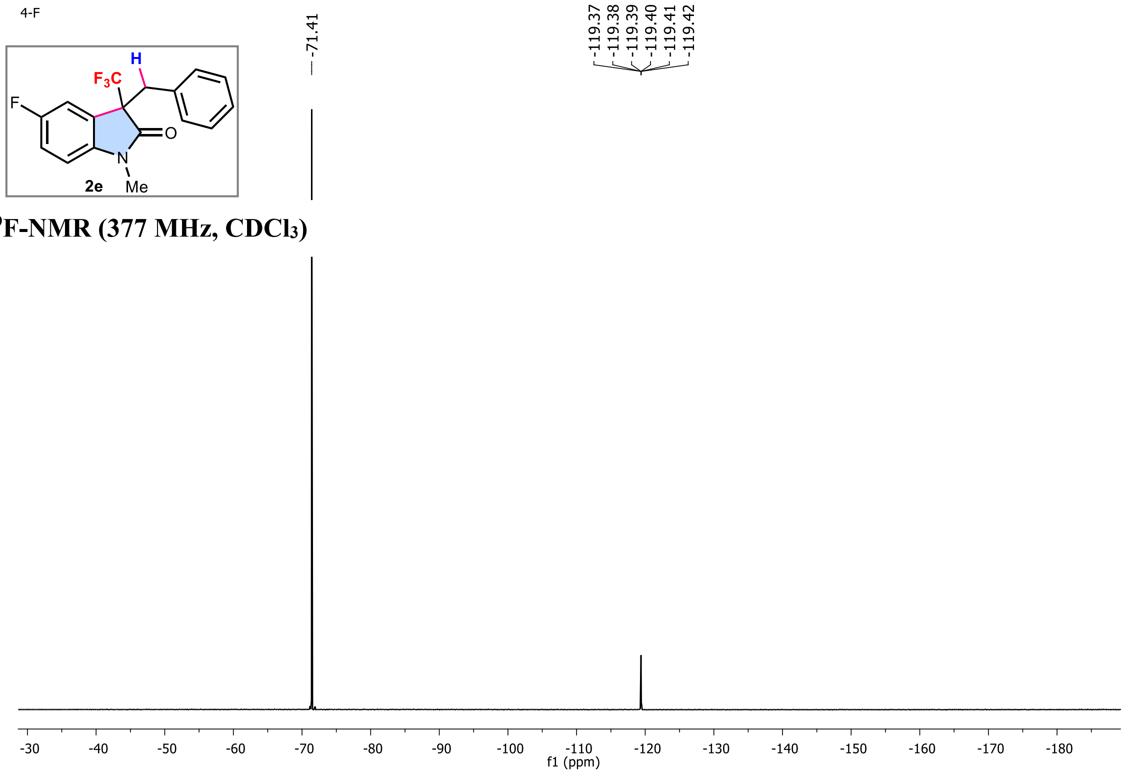


^{19}F-NMR (377 MHz, CDCl$_3$)

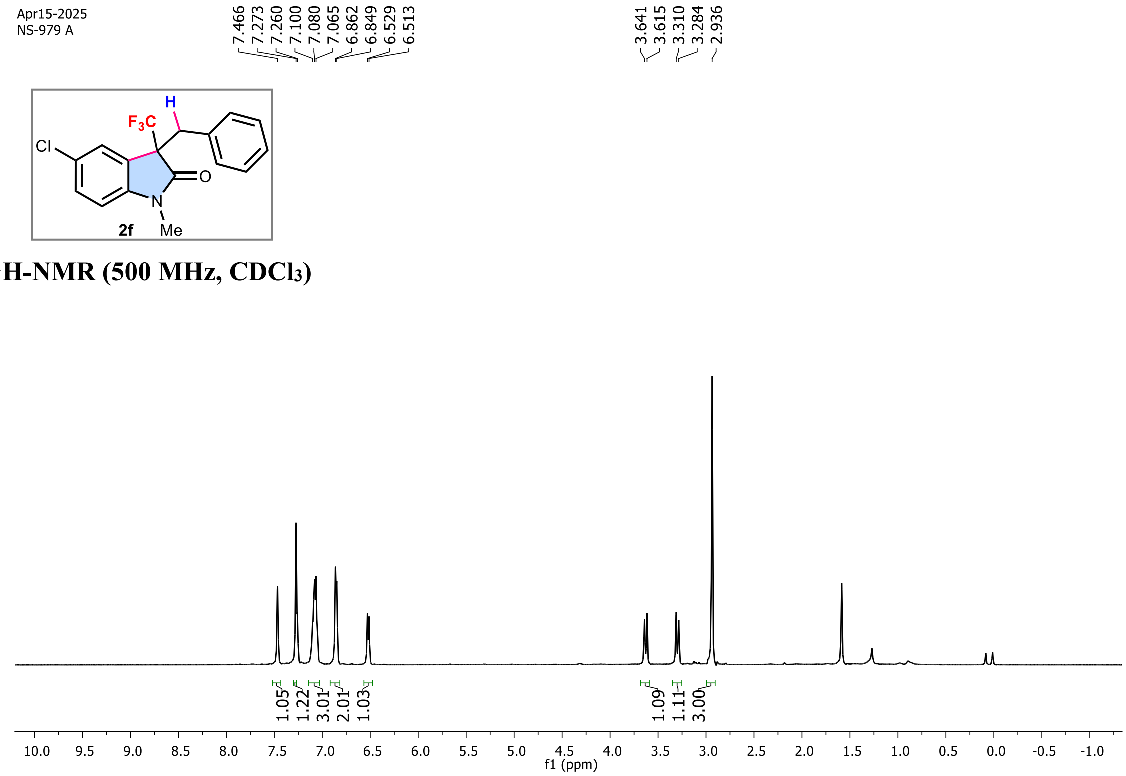
4-F



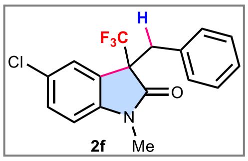
^{1}H-NMR (500 MHz, CDCl$_3$)



[19]F-NMR (377 MHz, $CDCl_3$)

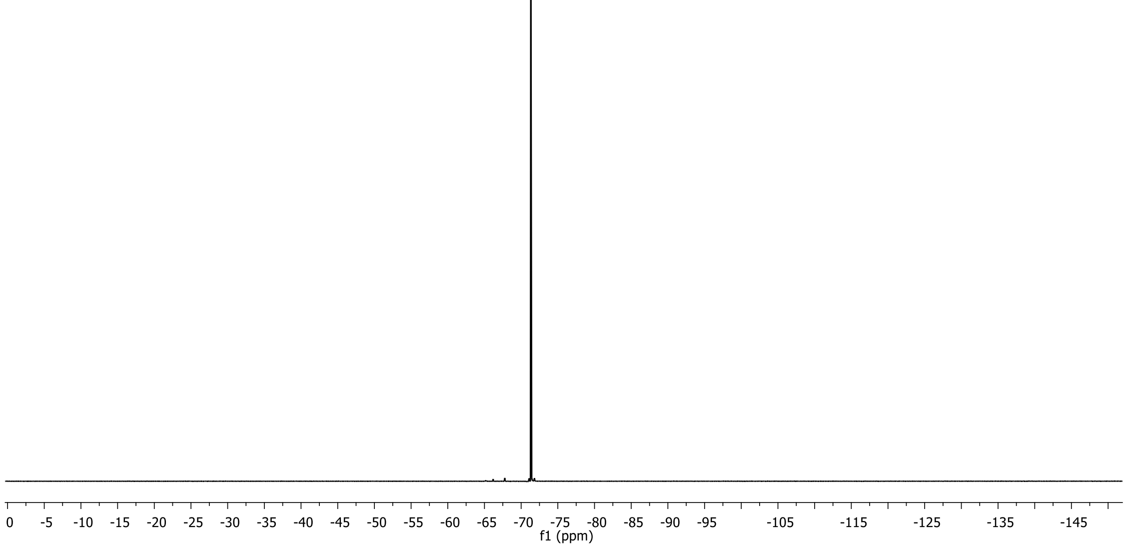


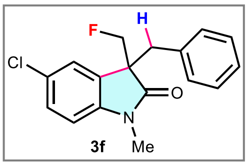
[1]H-NMR (500 MHz, $CDCl_3$)



2f

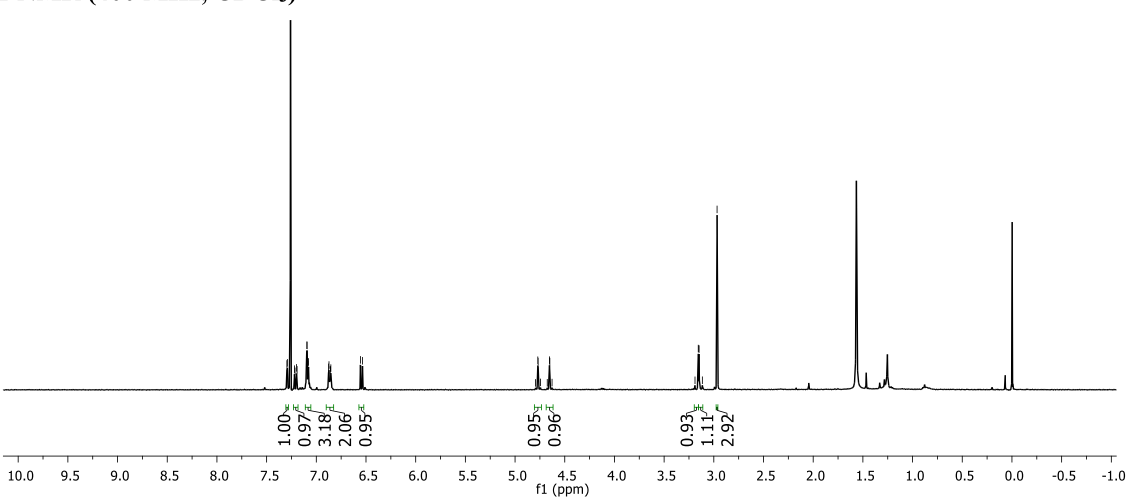
^{19}F-NMR (377 MHz, CDCl$_3$)

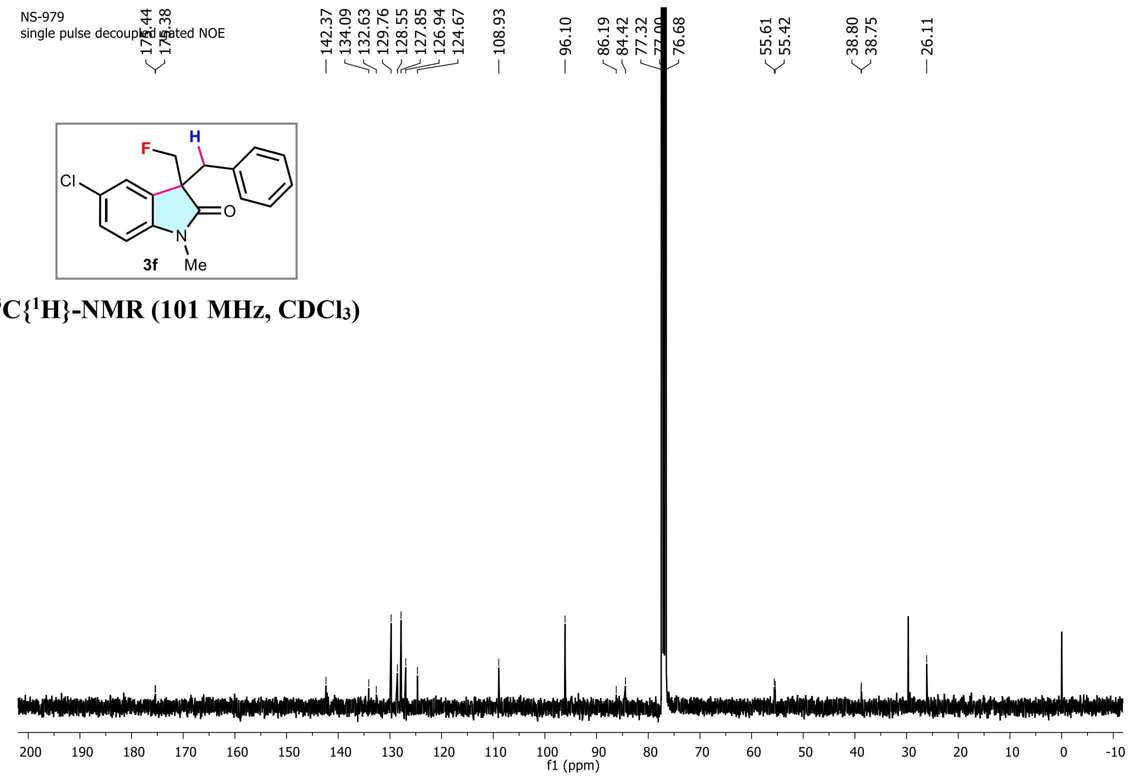




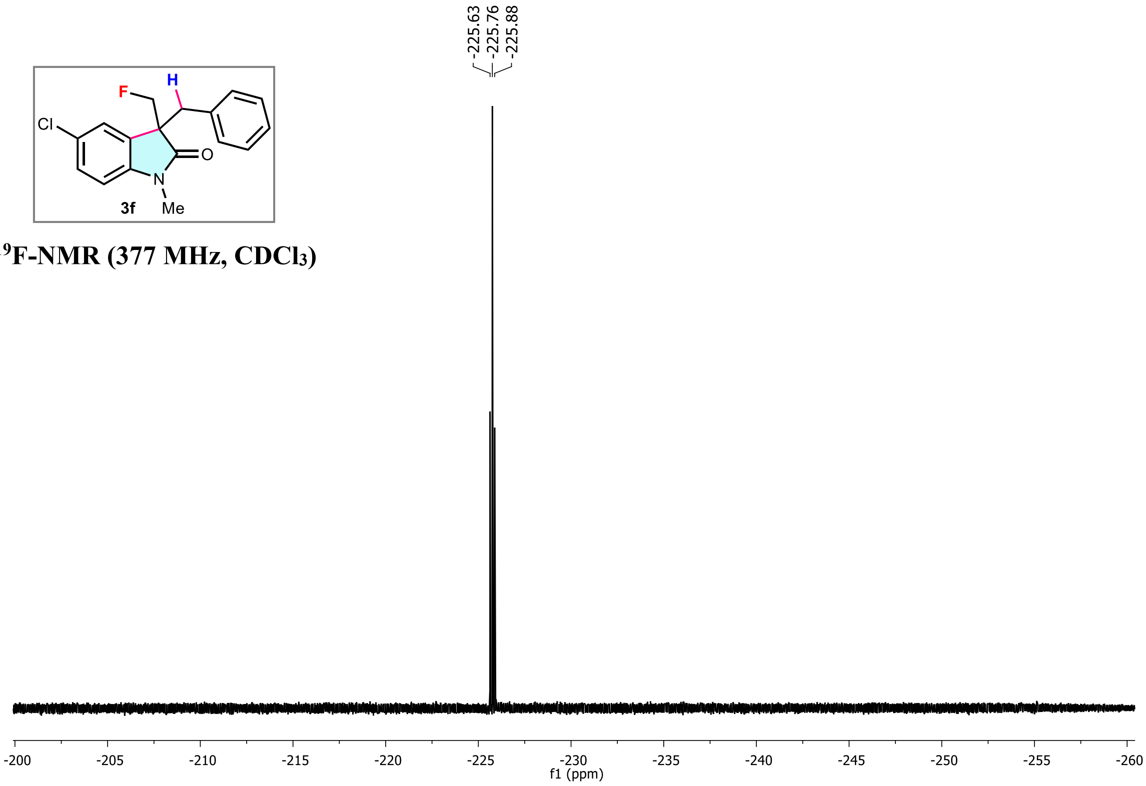
3f

^{1}H-NMR (400 MHz, CDCl$_3$)

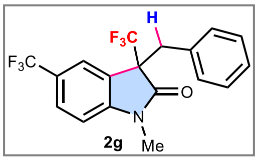




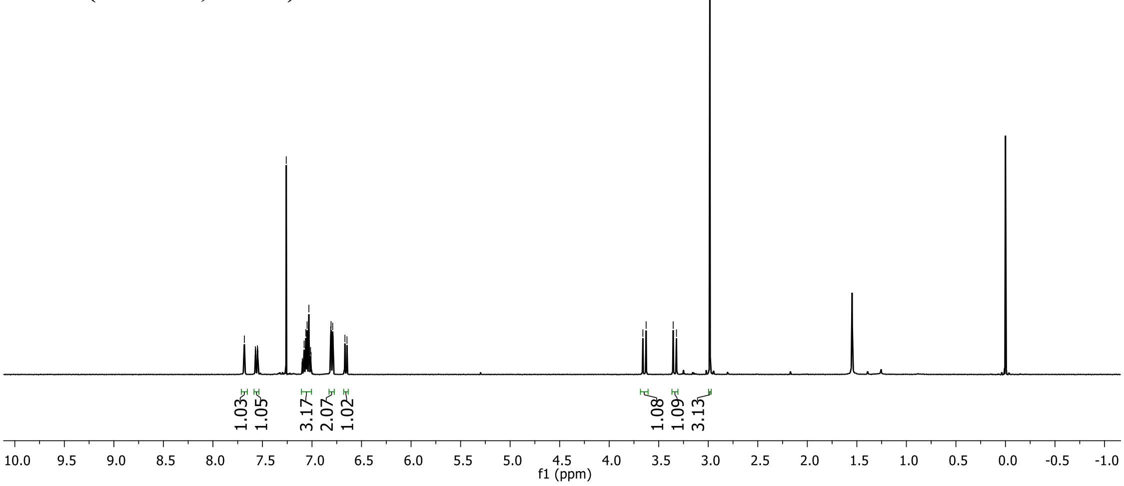
$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$)

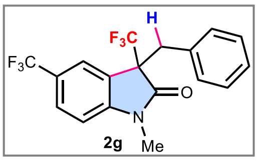


^{19}F-NMR (377 MHz, $CDCl_3$)

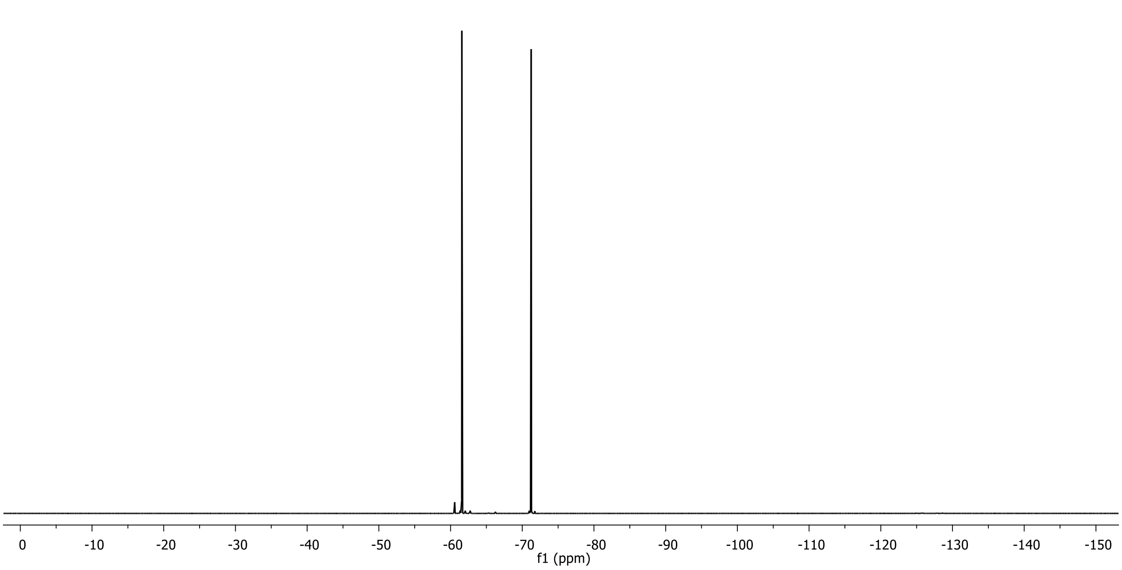


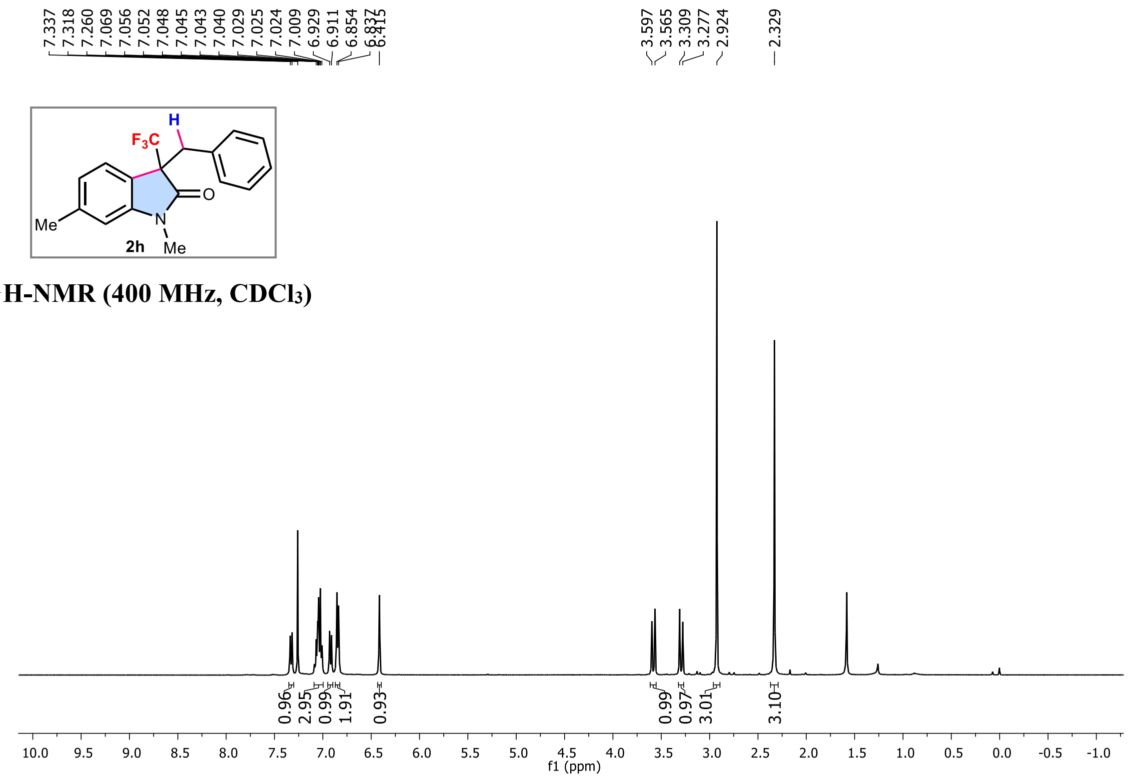
^{1}H-NMR (400 MHz, CDCl$_3$)



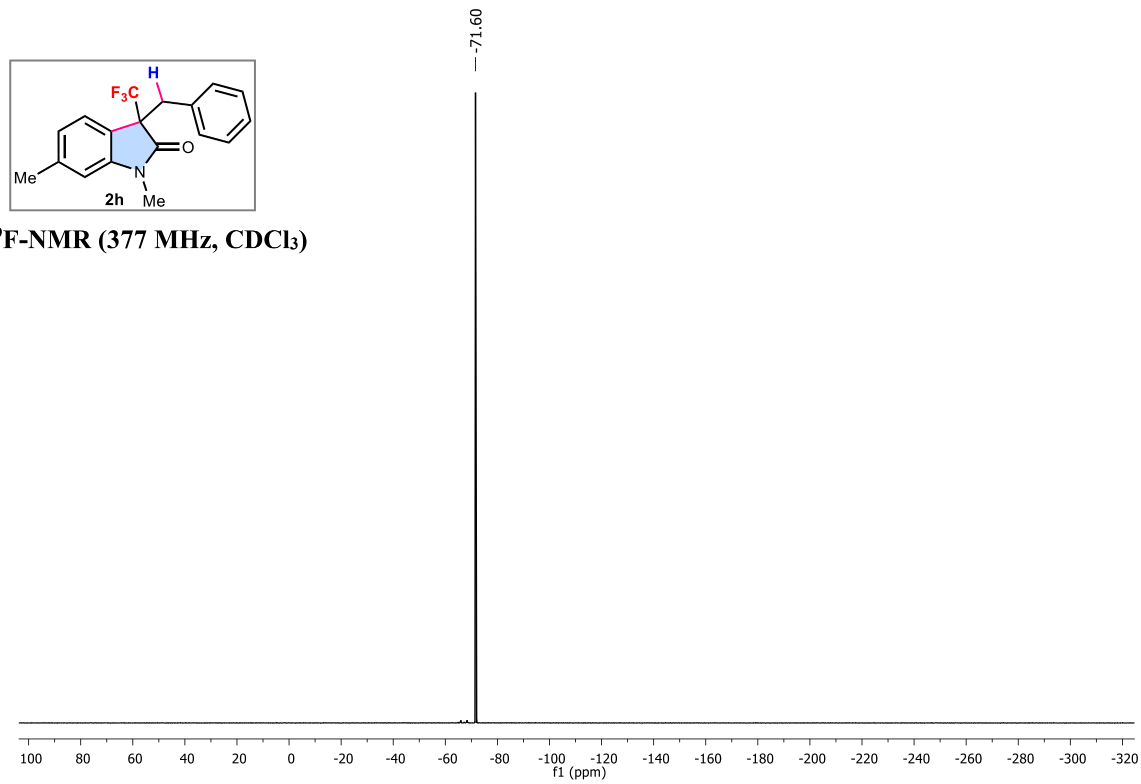


^{19}F-NMR (377 MHz, CDCl$_3$)

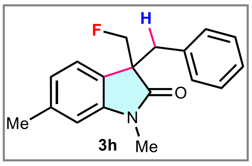


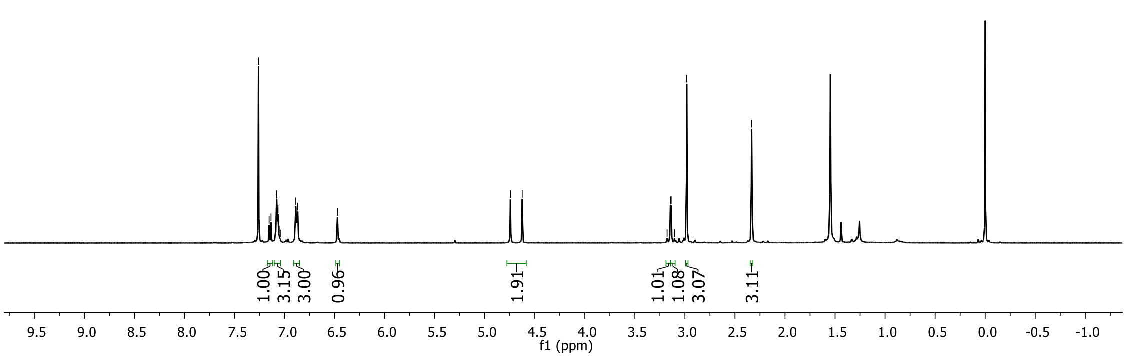


^{1}H-NMR (400 MHz, $CDCl_3$)

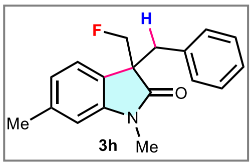


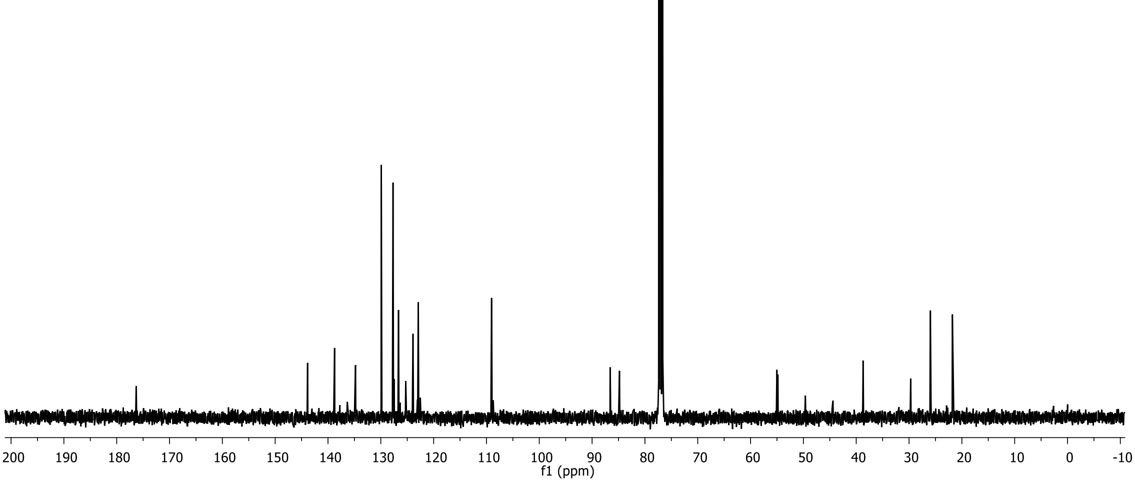
^{19}F-NMR (377 MHz, $CDCl_3$)



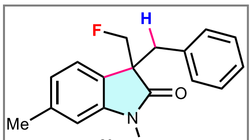


[1]H-NMR (400 MHz, $CDCl_3$)



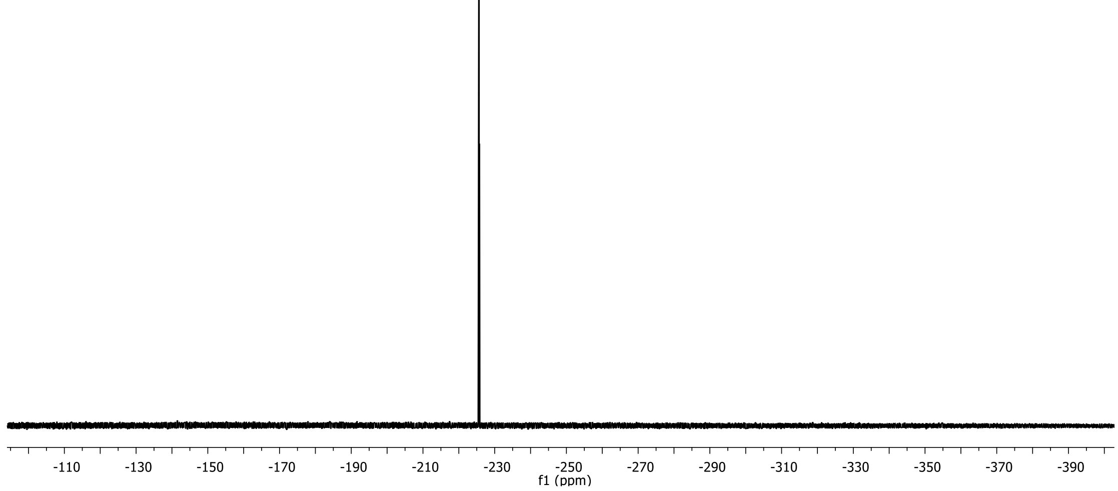


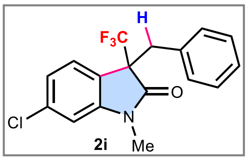
[13]C{[1]H}-NMR (101 MHz, $CDCl_3$)



3h

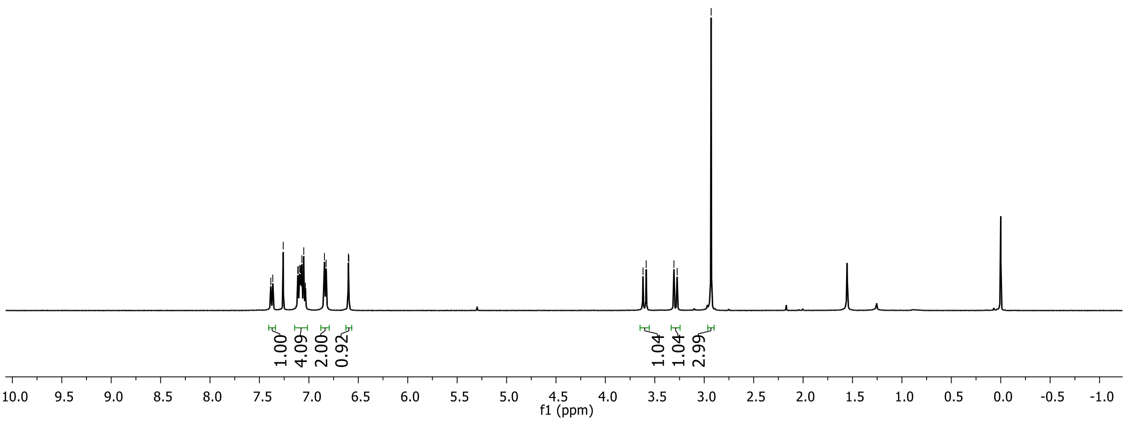
[19]F-NMR (377 MHz, $CDCl_3$)

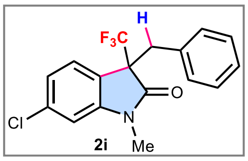


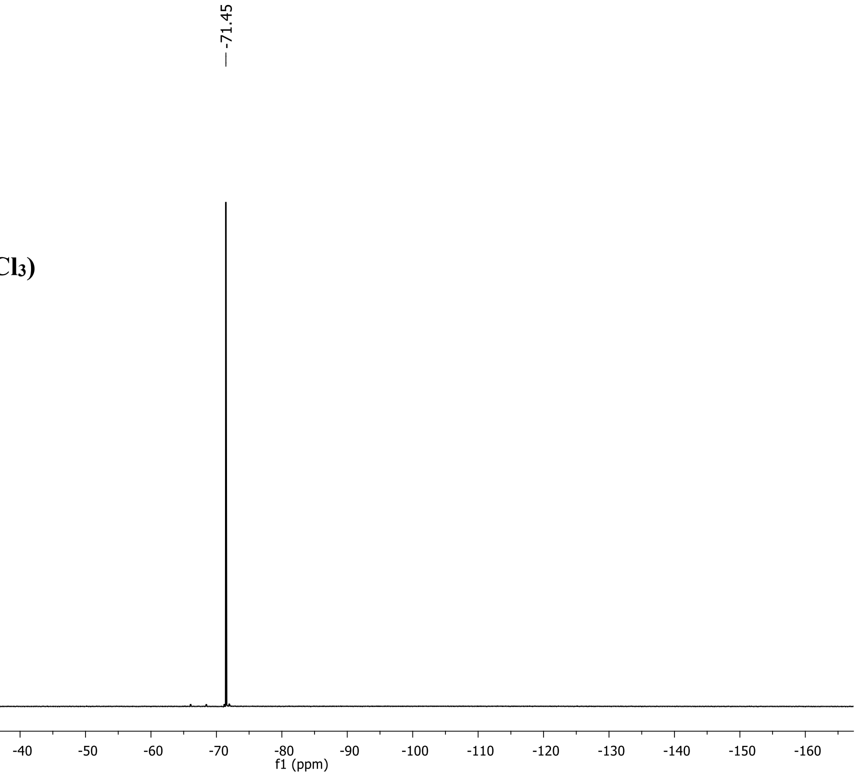


2i

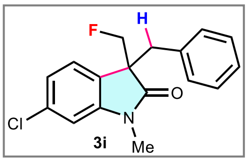
[1]H-NMR (400 MHz, $CDCl_3$)



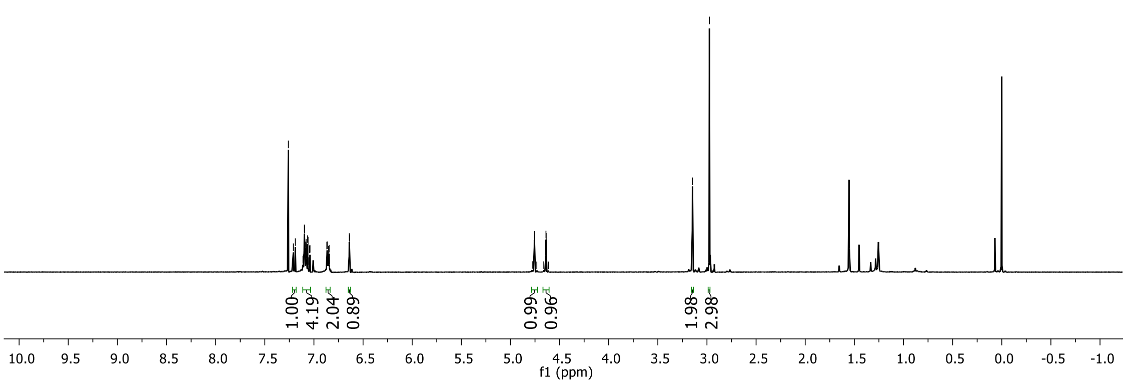


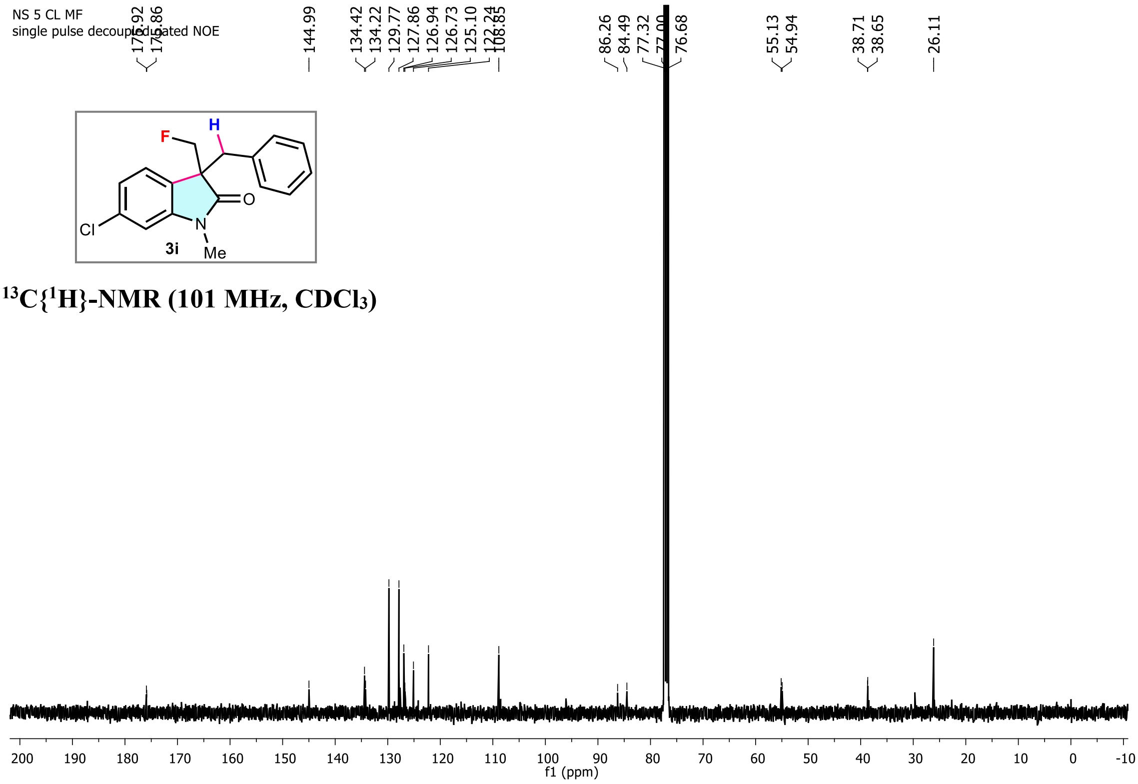


[19]F-NMR (377 MHz, CDCl3)

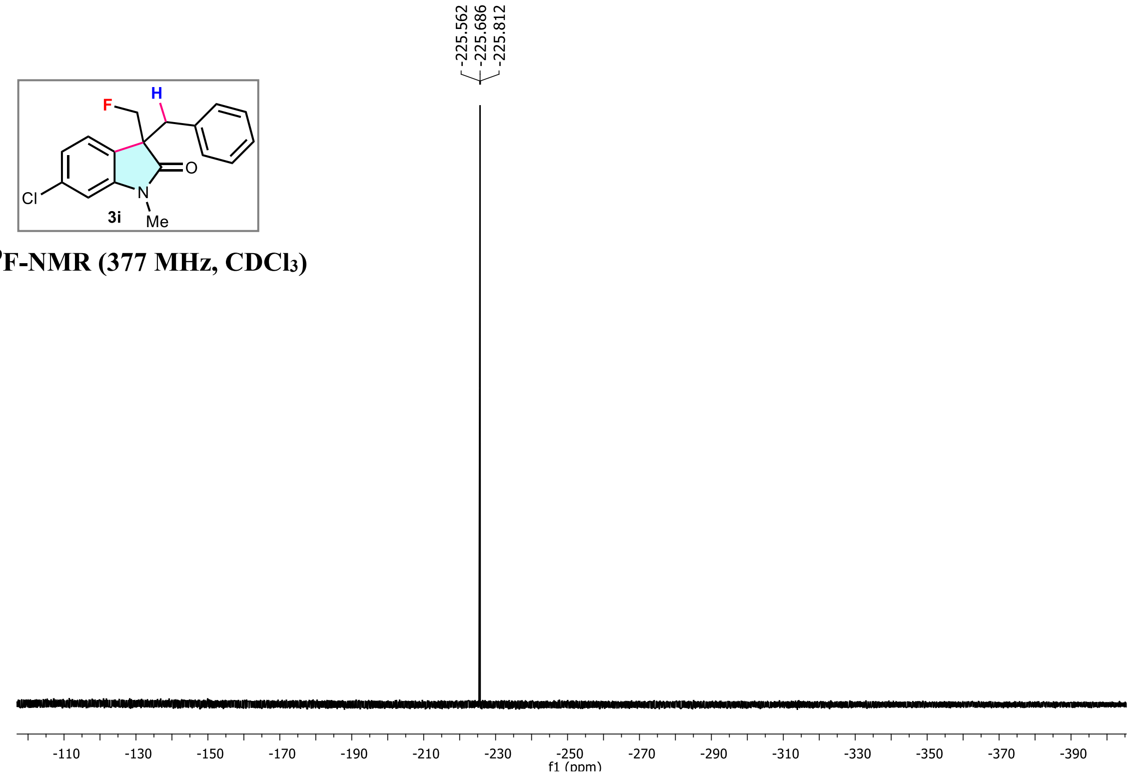


[1]H-NMR (400 MHz, CDCl3)

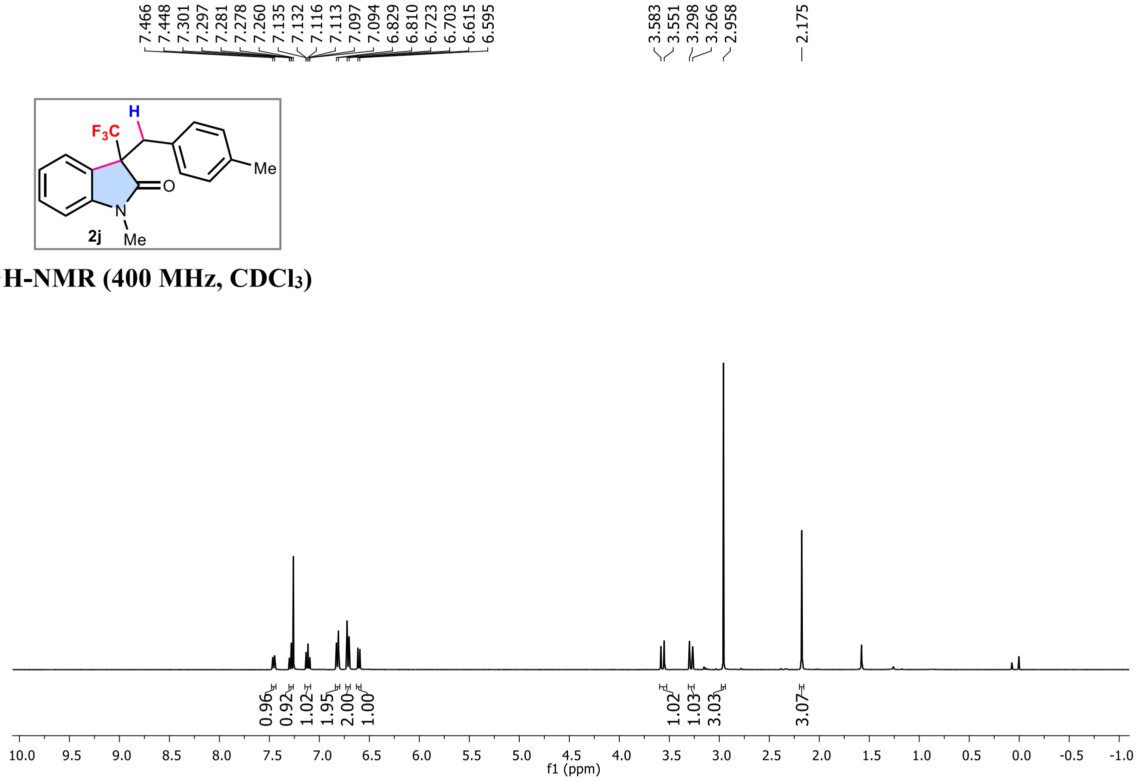




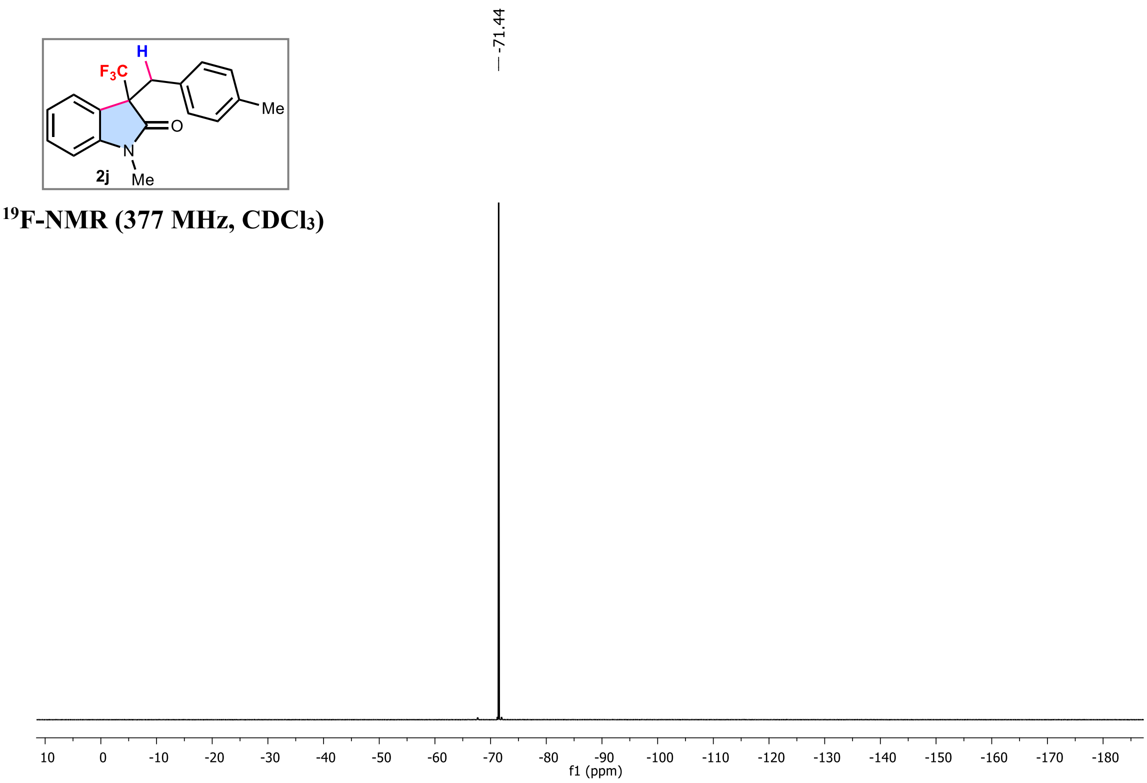
$^{13}C\{^{1}H\}$-NMR (101 MHz, CDCl$_3$)



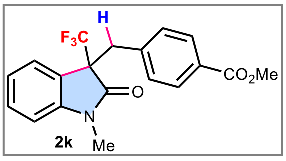
^{19}F-NMR (377 MHz, CDCl$_3$)



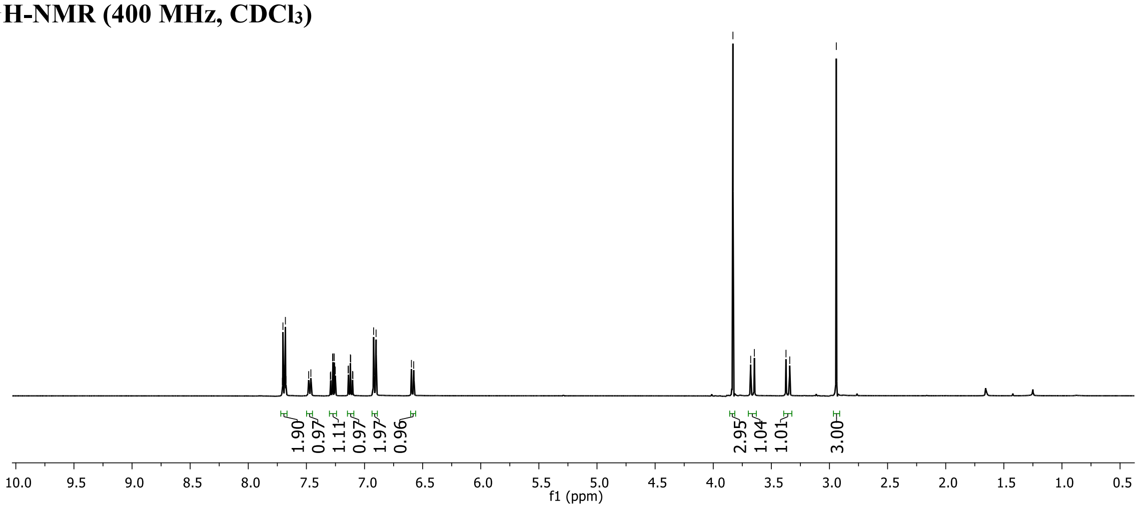
^{1}H-NMR (400 MHz, CDCl$_3$)

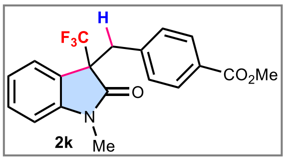


^{19}F-NMR (377 MHz, CDCl$_3$)

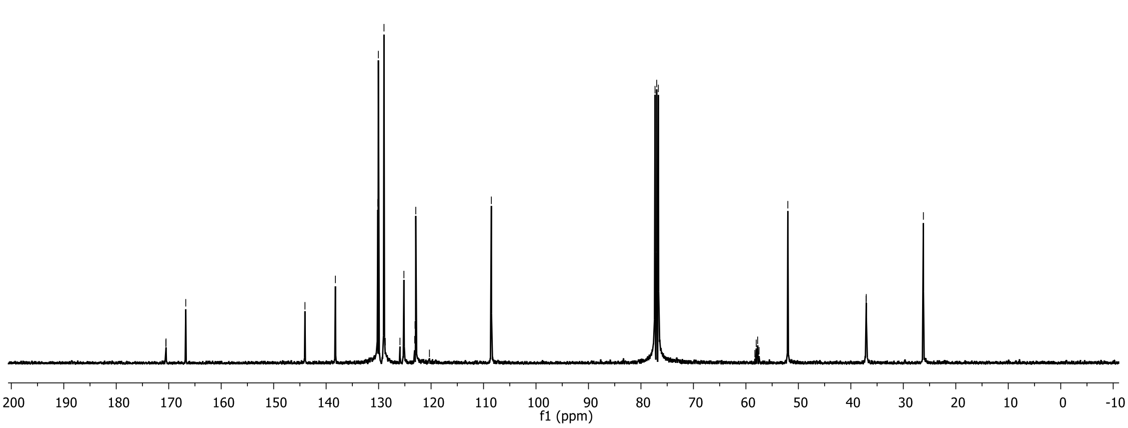


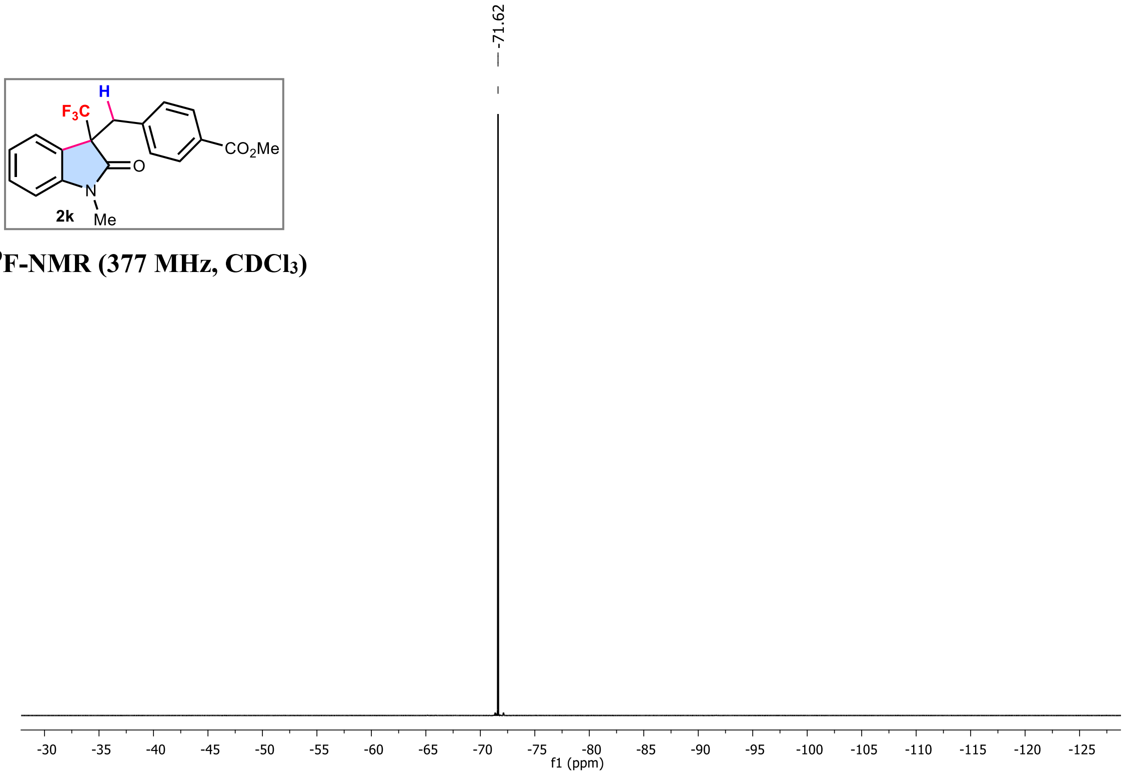
[1]H-NMR (400 MHz, CDCl3)



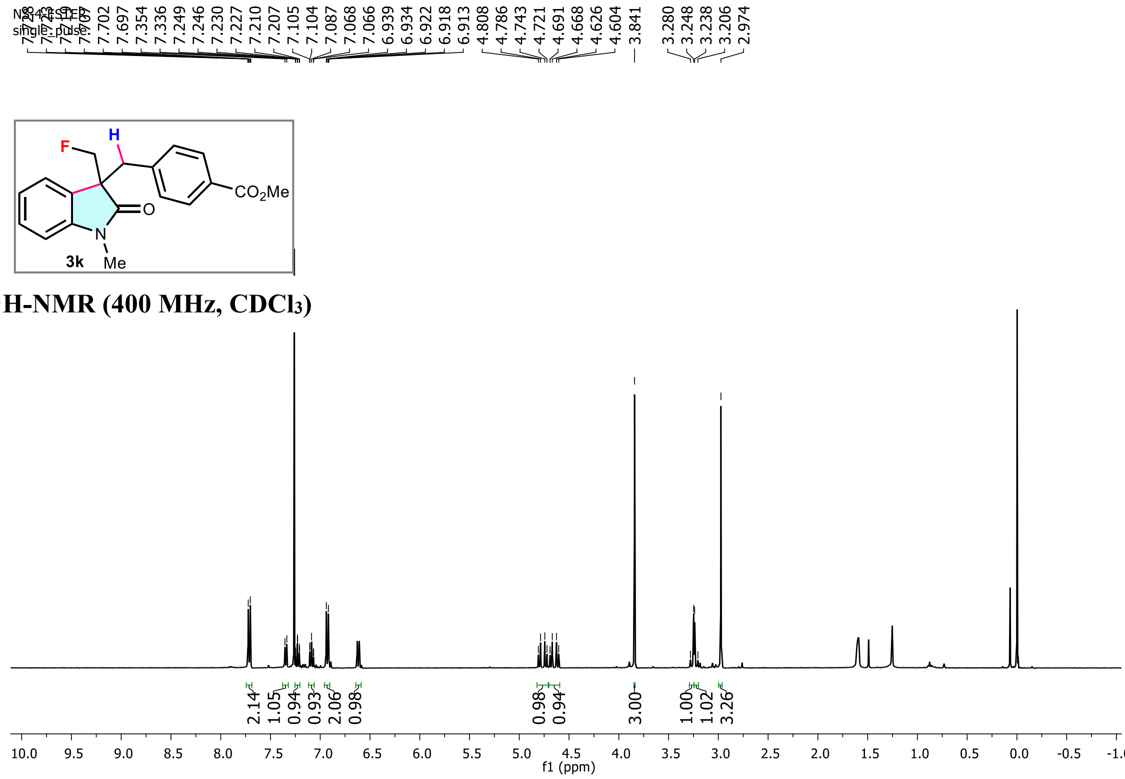


[13]C{[1]H}-NMR (101 MHz, CDCl3)

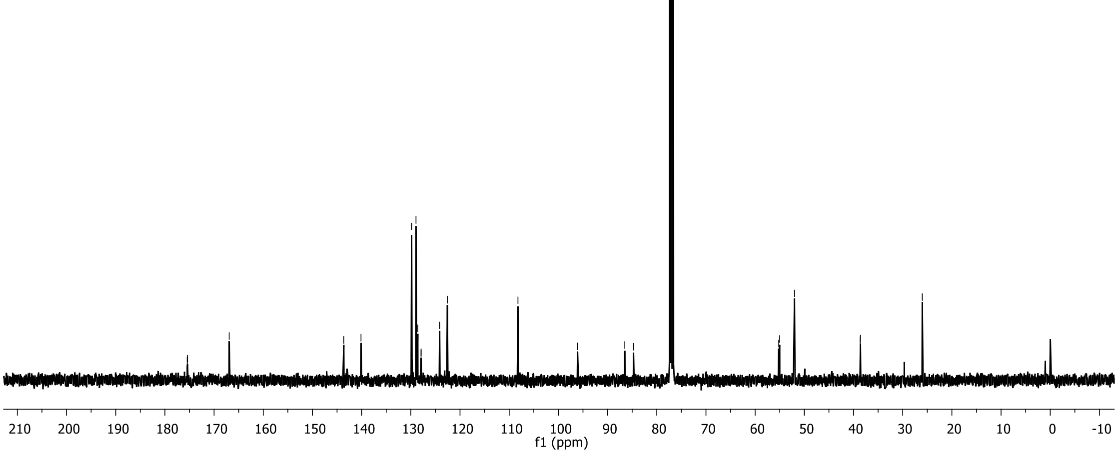


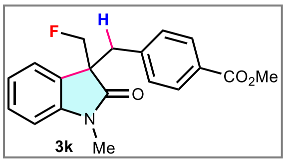


[19]F-NMR (377 MHz, CDCl3)

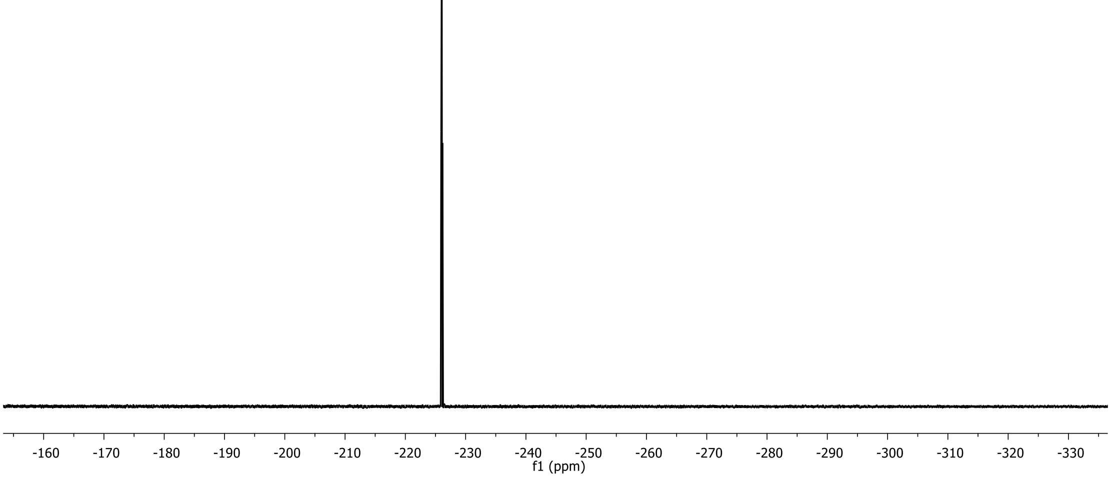


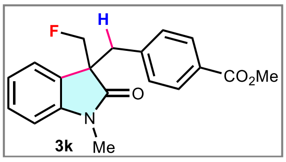
[1]H-NMR (400 MHz, CDCl3)



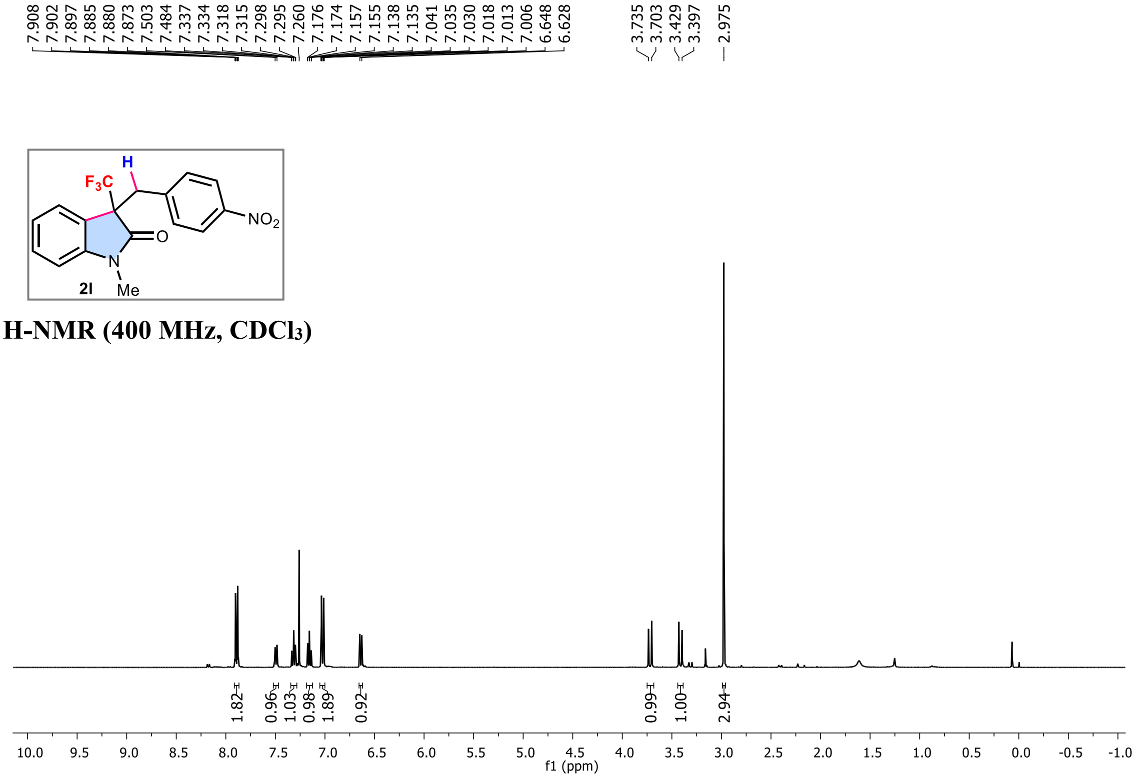


$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$)

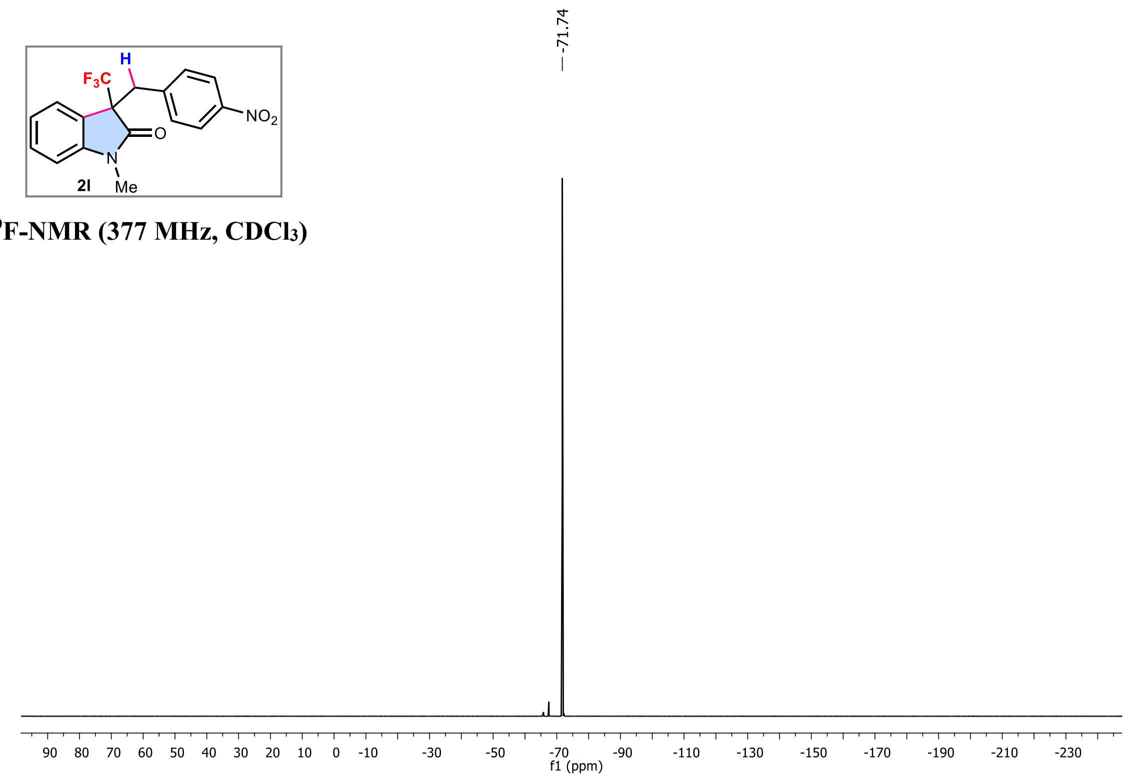




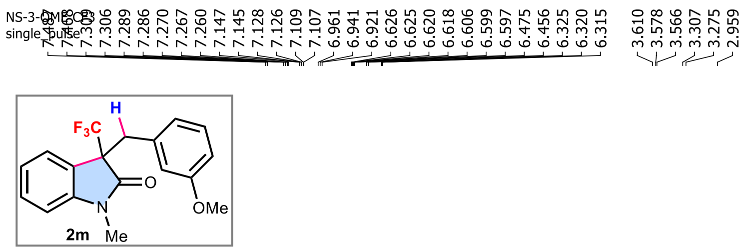
^{19}F-NMR (377 MHz, $CDCl_3$)



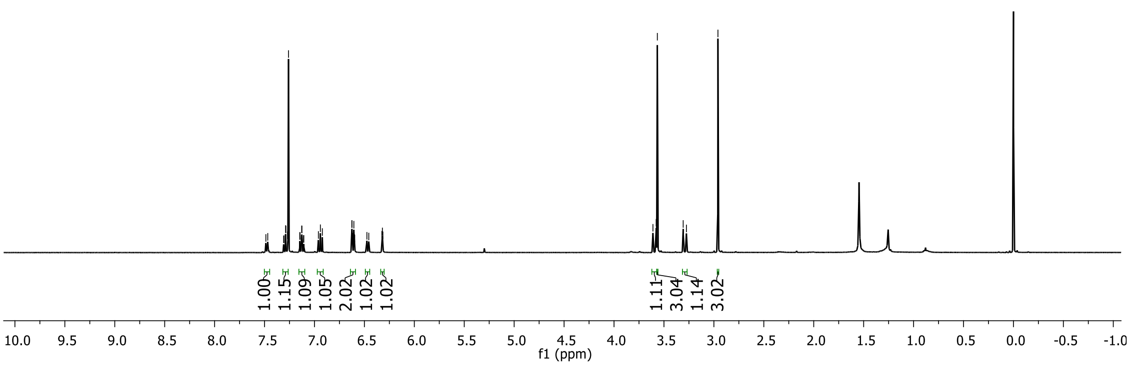
[1]H-NMR (400 MHz, CDCl3)

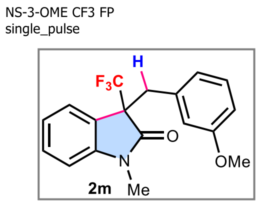


[19]F-NMR (377 MHz, CDCl3)

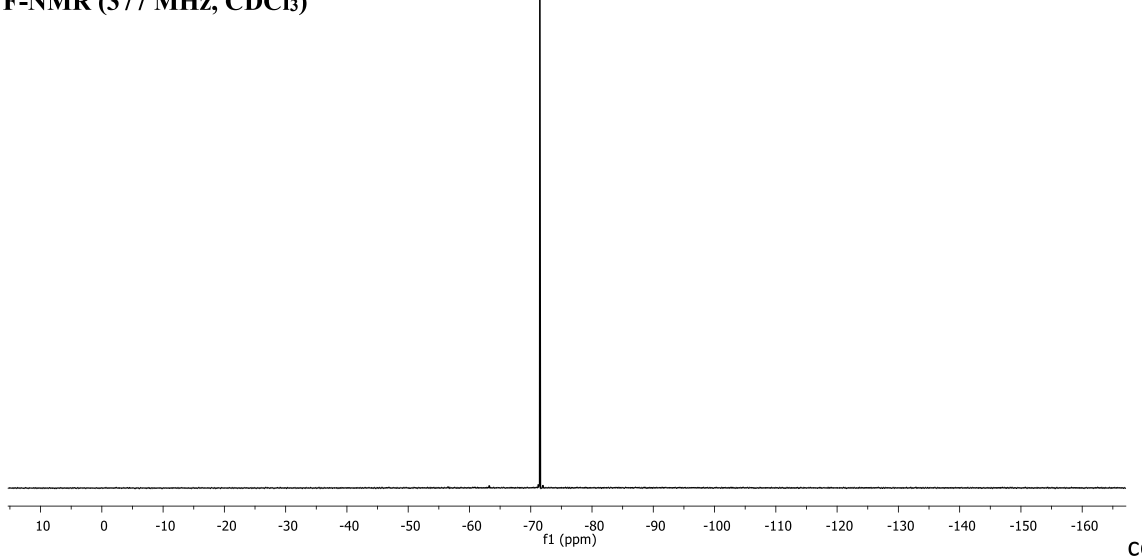


^{1}**H-NMR (400 MHz, CDCl$_3$)**





^{19}**F-NMR (377 MHz, CDCl$_3$)**



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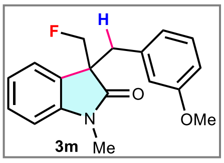
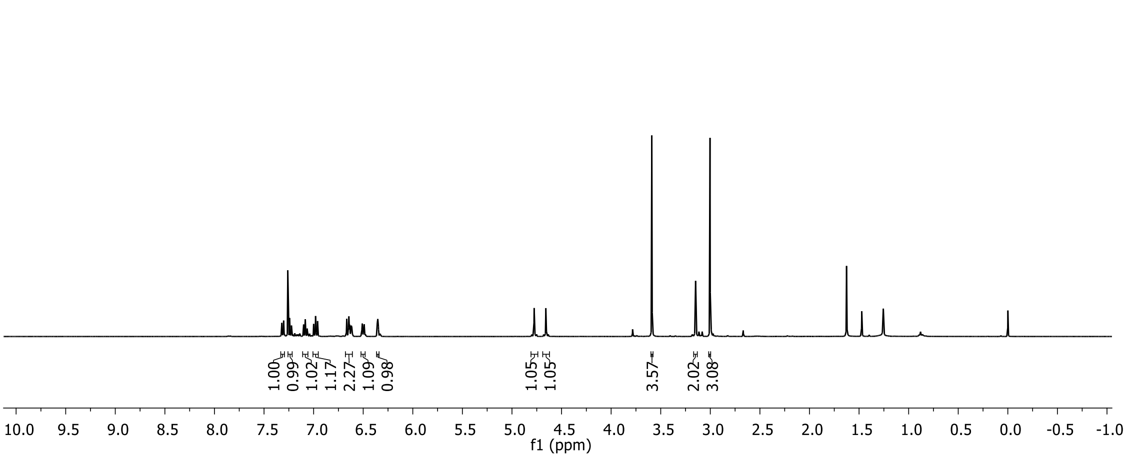
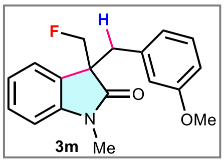
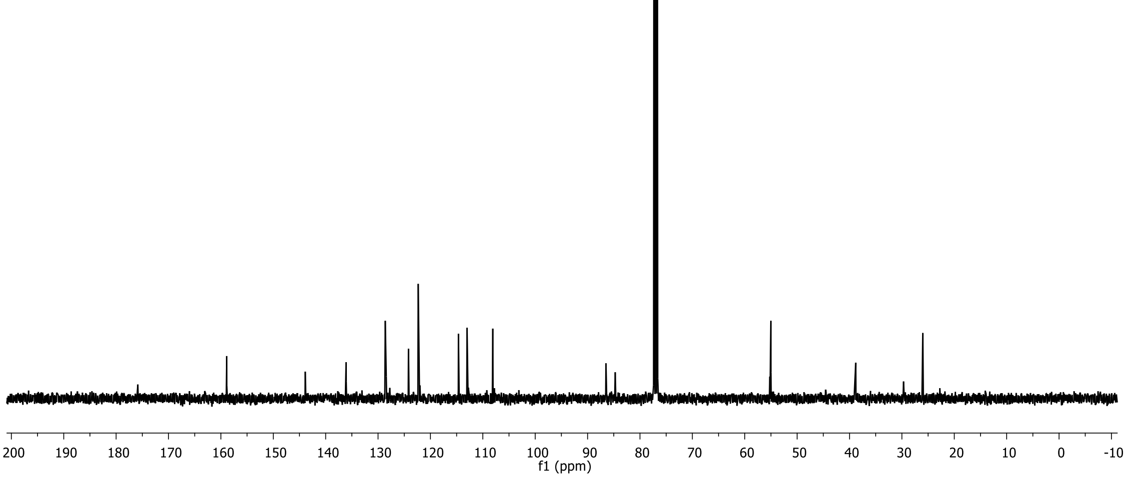


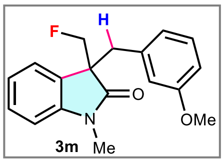
^{1}H-NMR (400 MHz, $CDCl_3$)





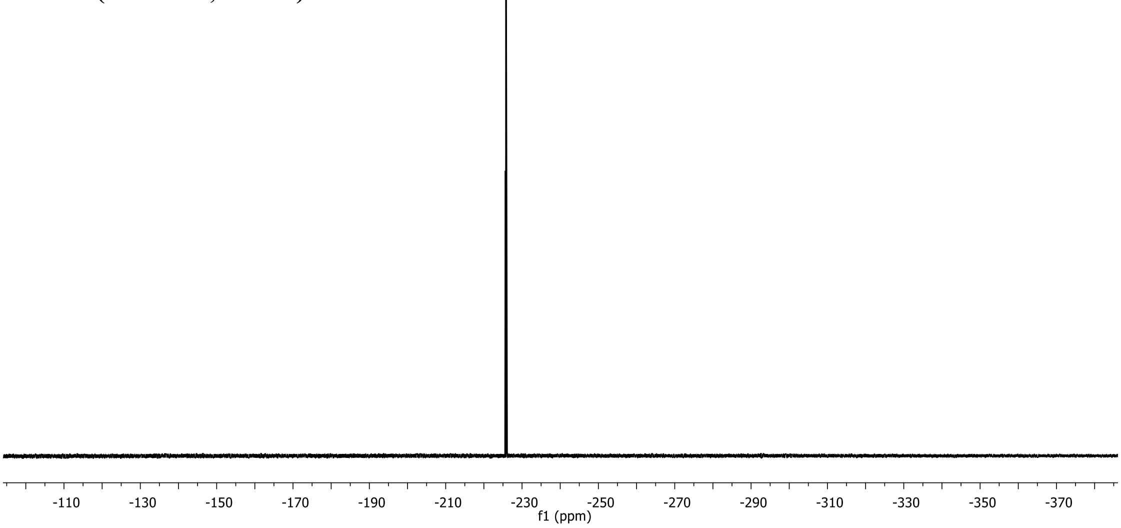
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$)

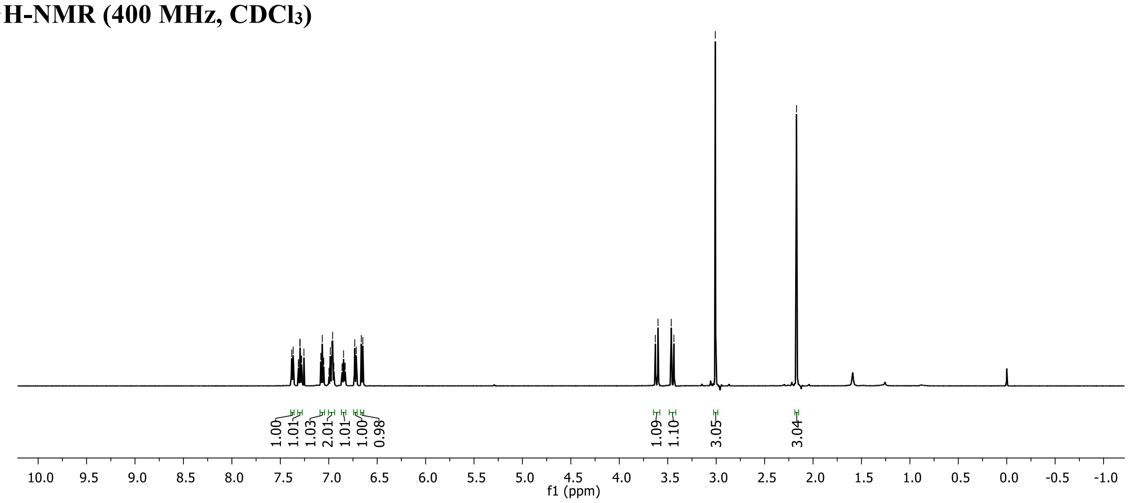


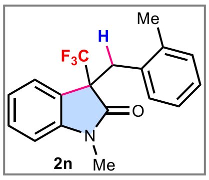


3m

[19]F-NMR (377 MHz, $CDCl_3$)

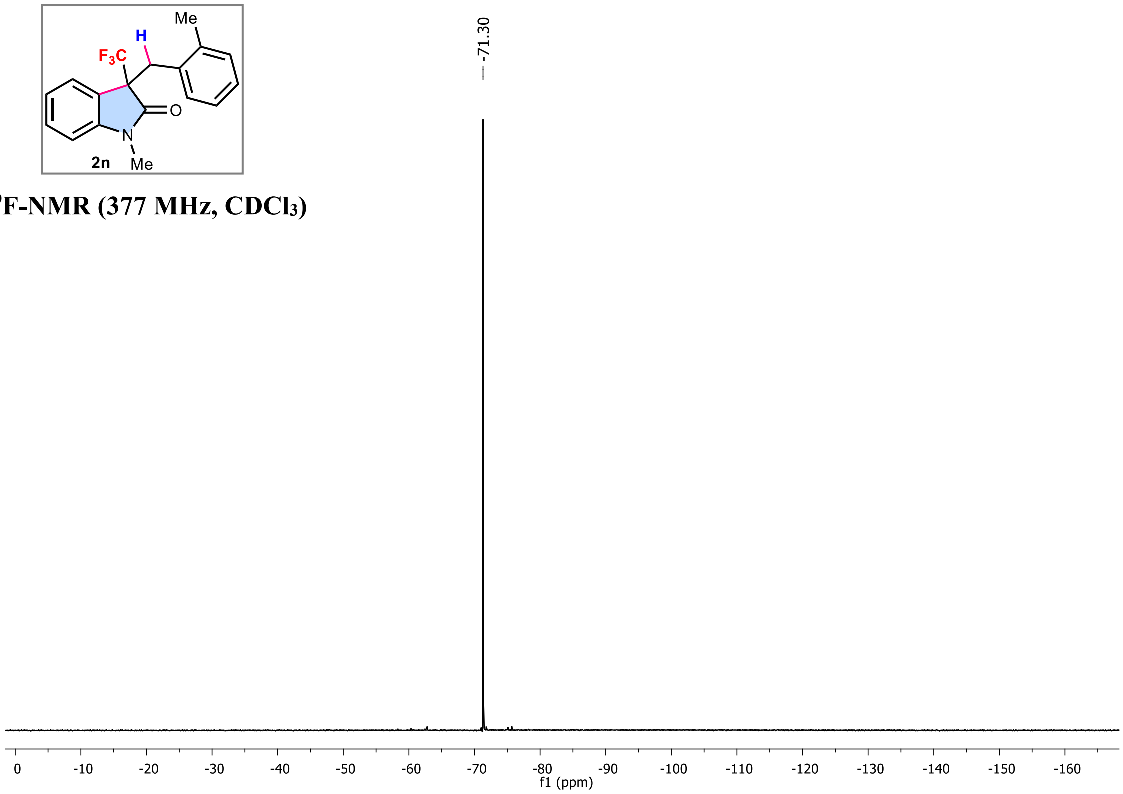




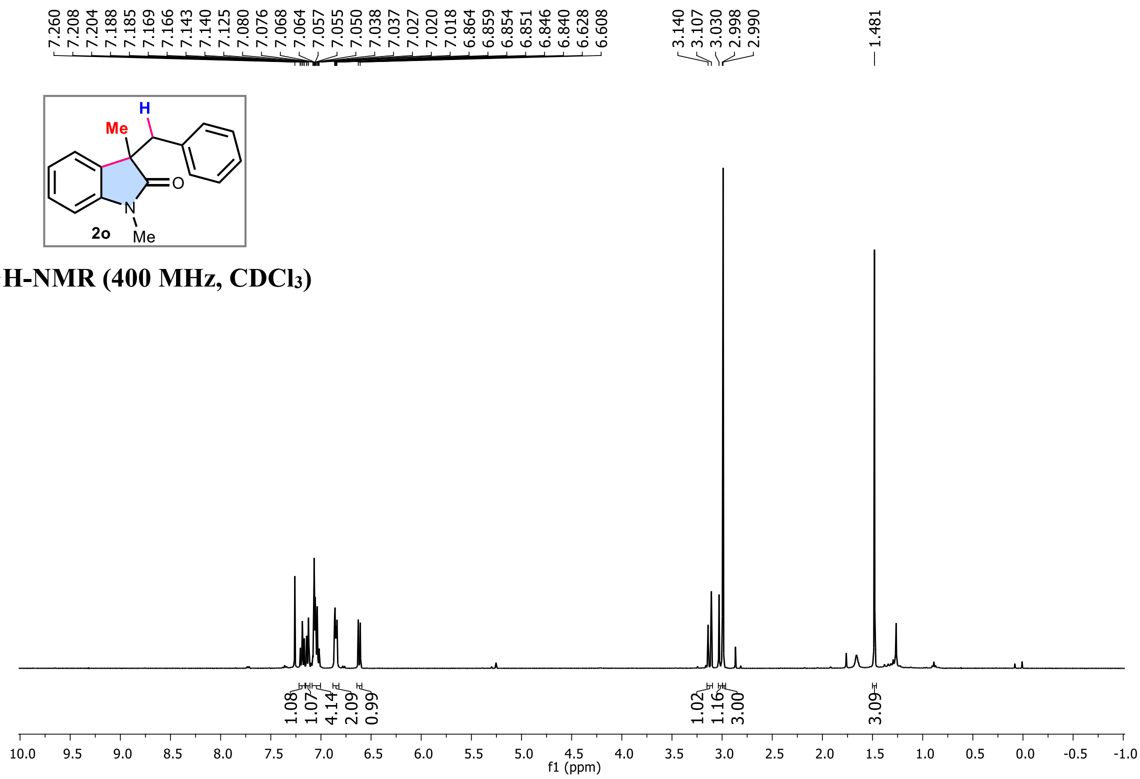


2n

[1]H-NMR (400 MHz, $CDCl_3$)



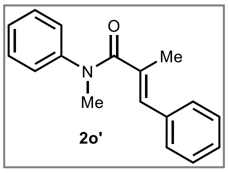
[19]F-NMR (377 MHz, CDCl3)



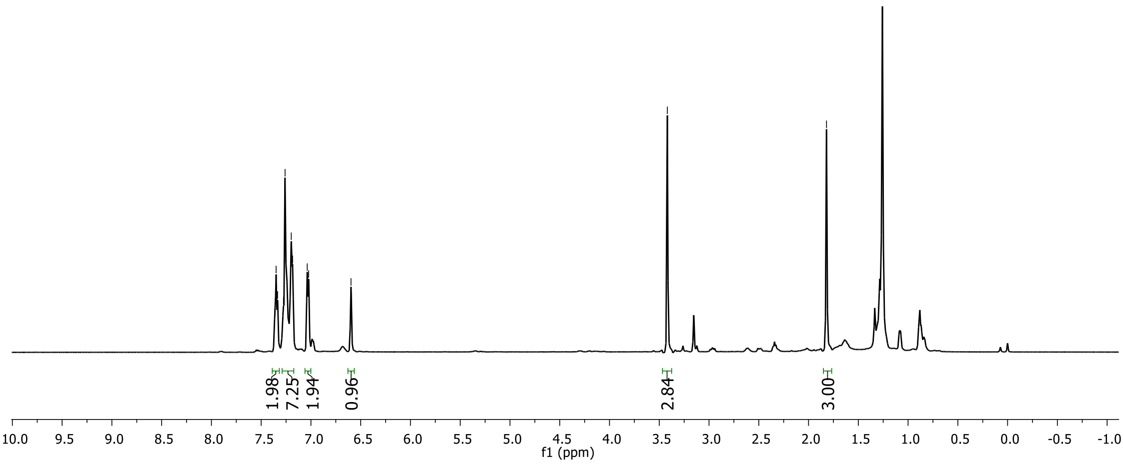
[1]H-NMR (400 MHz, CDCl3)

15.04.2025
ns-ch3 ph s3

7.363, 7.350, 7.335, 7.276, 7.260, 7.197, 7.184, 7.037, 7.023, 6.597, 3.419, 1.819

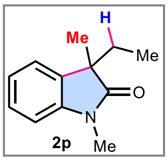


[1]H-NMR (500 MHz, CDCl$_3$)

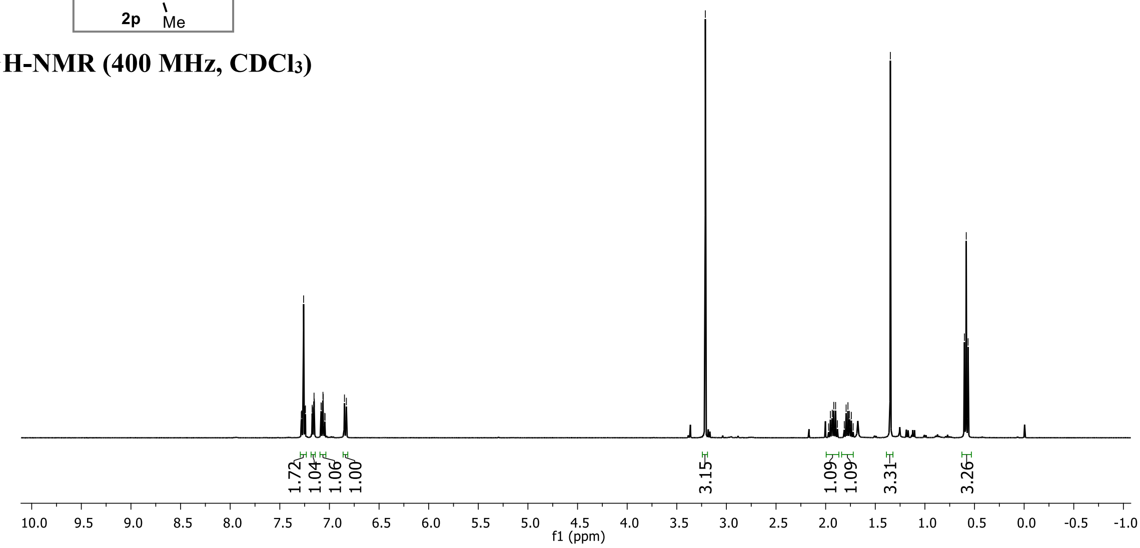


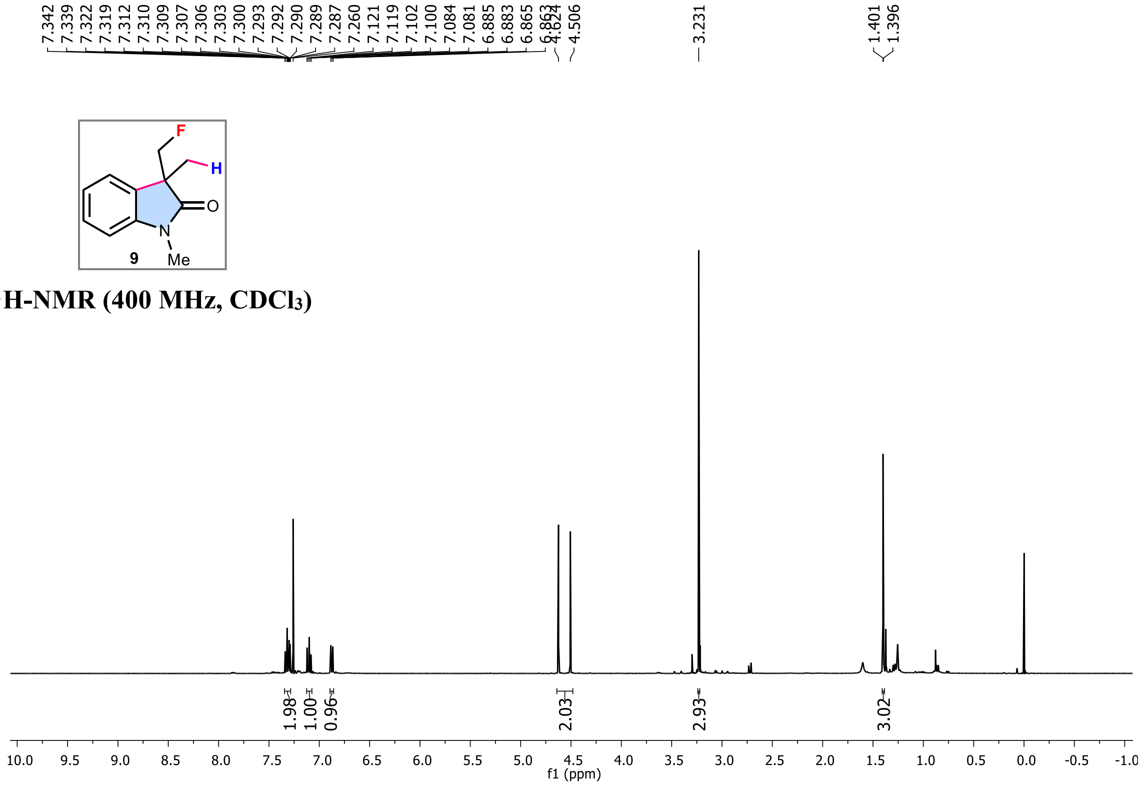
AK-161 A
single_pulse

7.283, 7.280, 7.264, 7.260, 7.245, 7.242, 7.174, 7.172, 7.170, 7.155, 7.153, 7.152, 7.084, 7.082, 7.065, 7.063, 7.047, 7.044, 6.849, 6.829, 3.212, 1.952, 1.937, 1.933, 1.918, 1.900, 1.794, 1.775, 1.760, 1.757, 1.741, 1.348, 0.602, 0.583, 0.565

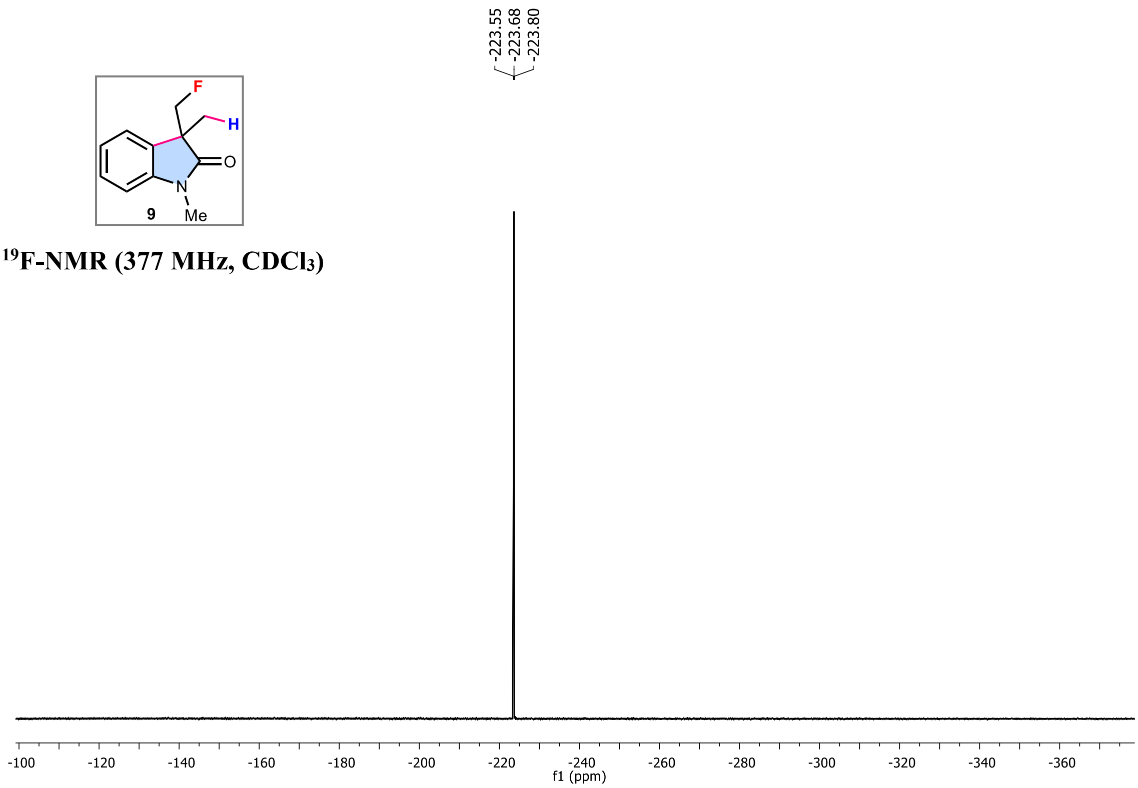


[1]H-NMR (400 MHz, CDCl$_3$)

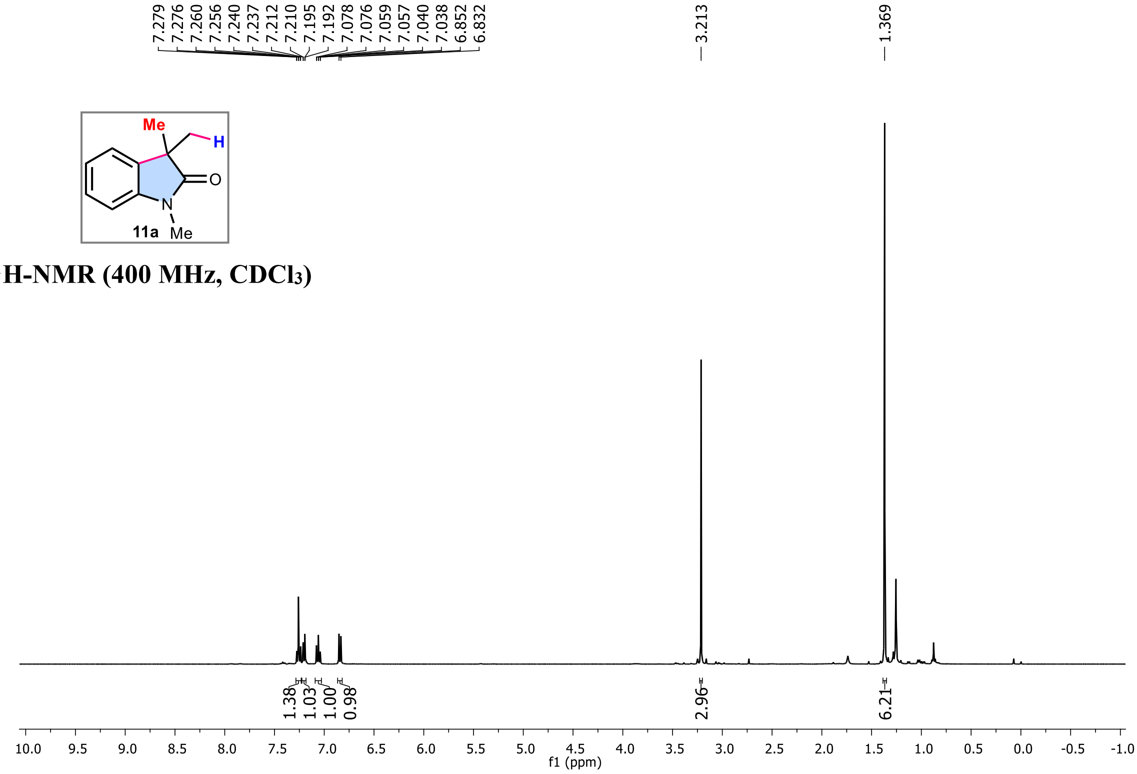




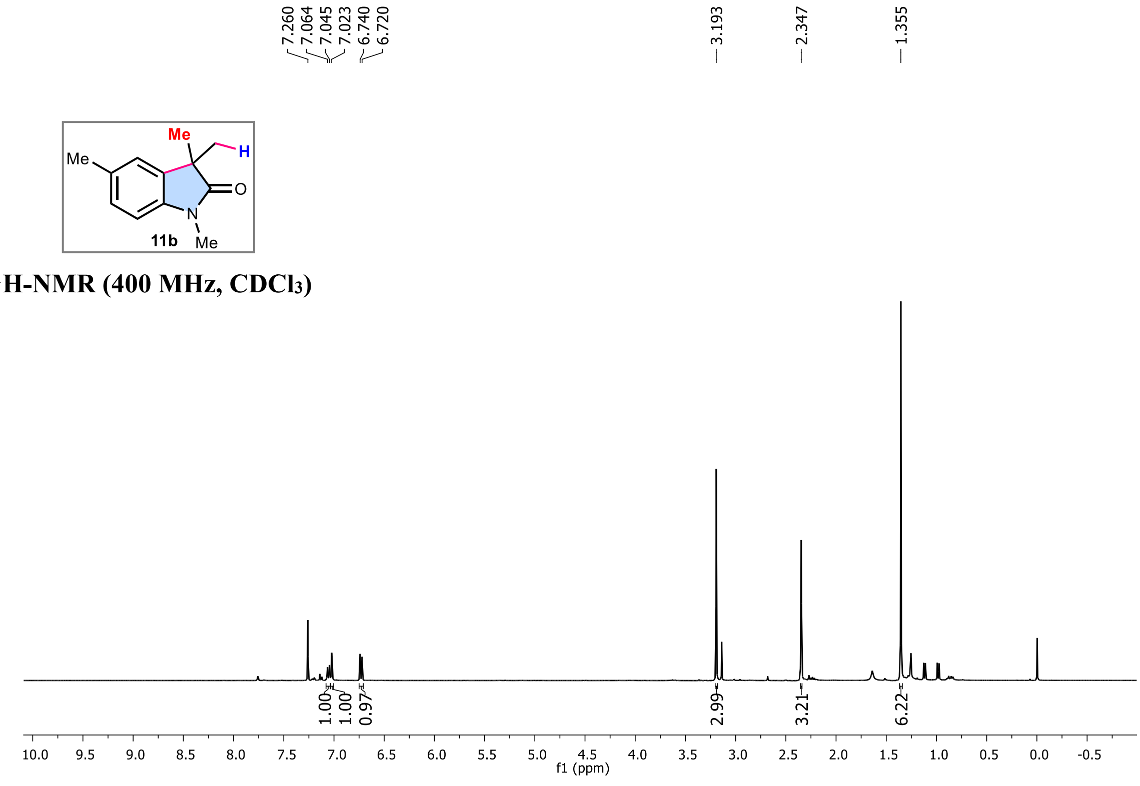
^{1}H-NMR (400 MHz, CDCl$_3$)



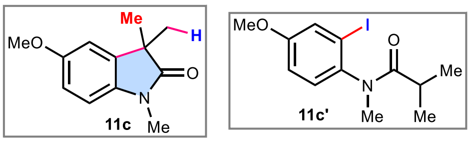
^{19}F-NMR (377 MHz, CDCl$_3$)



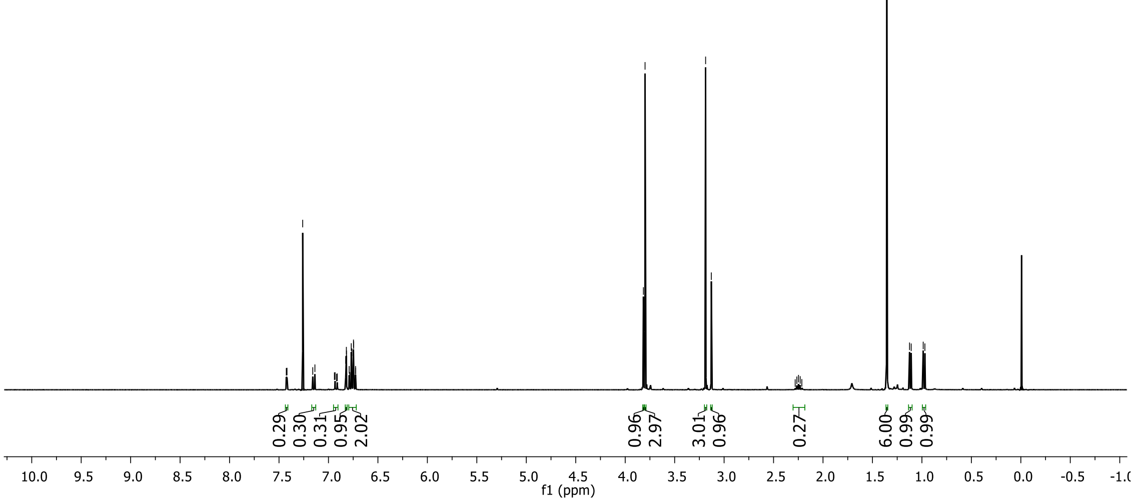
[1]H-NMR (400 MHz, CDCl$_3$)

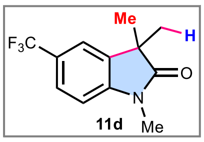


[1]H-NMR (400 MHz, CDCl$_3$)

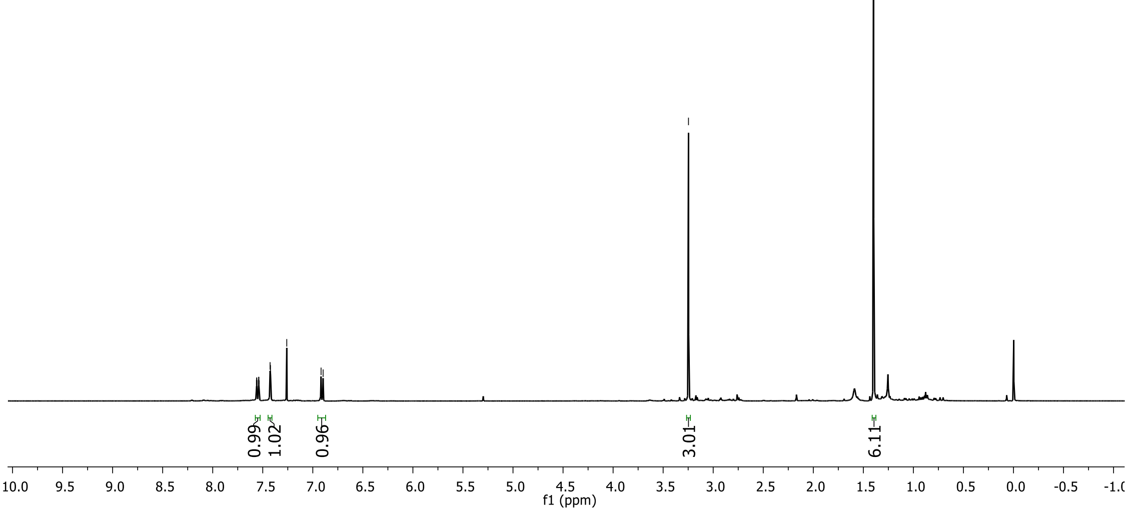


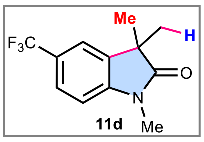
^{1}H-NMR (400 MHz, $CDCl_3$), 11c: 11c' (77:23)



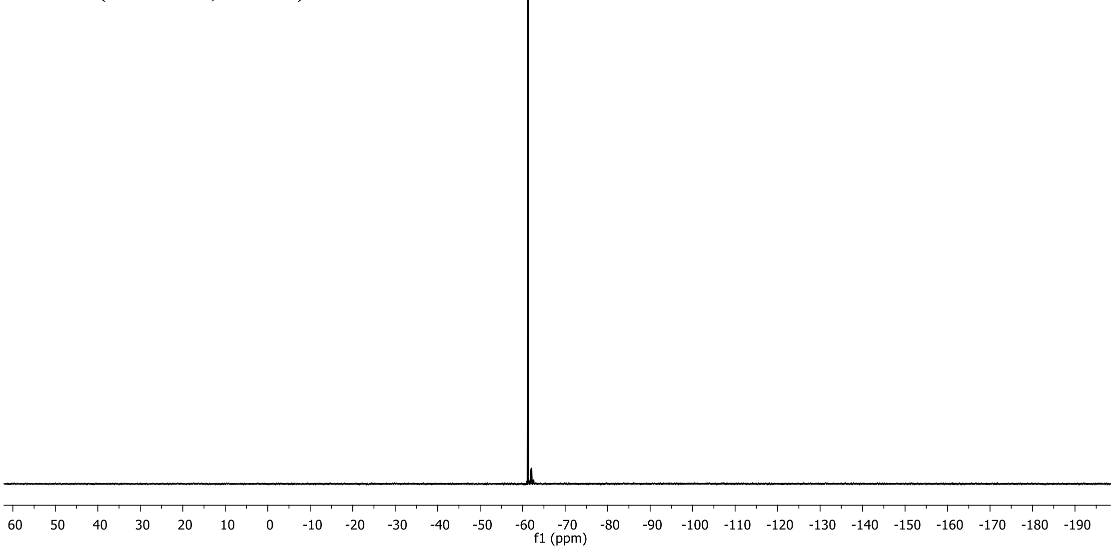


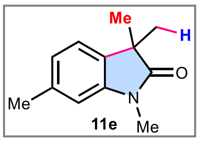
^{1}H-NMR (400 MHz, $CDCl_3$)



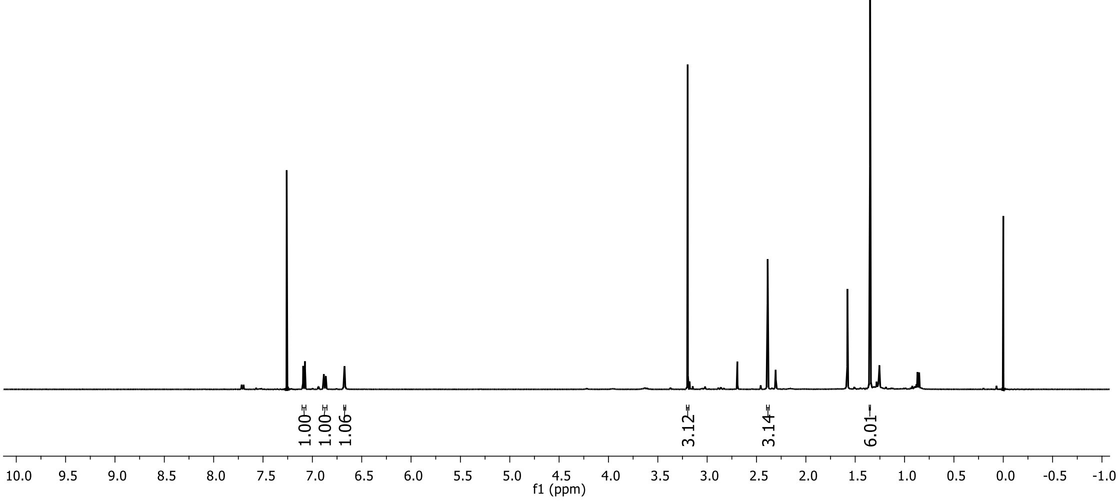


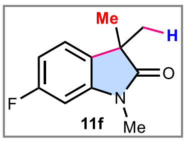
^{19}F-NMR (377 MHz, CDCl$_3$)



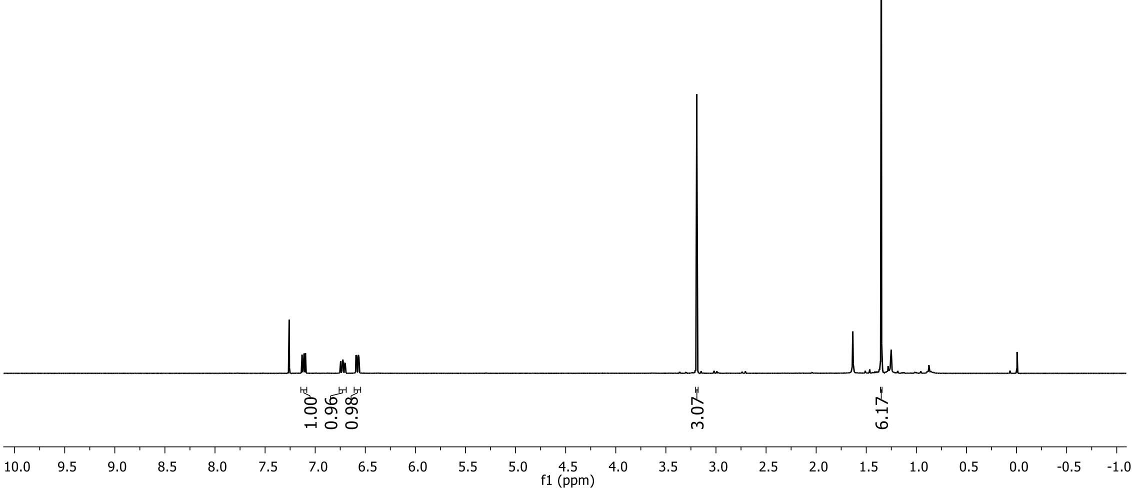


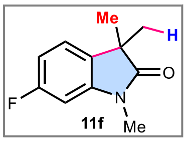
^{1}H-NMR (400 MHz, CDCl$_3$)



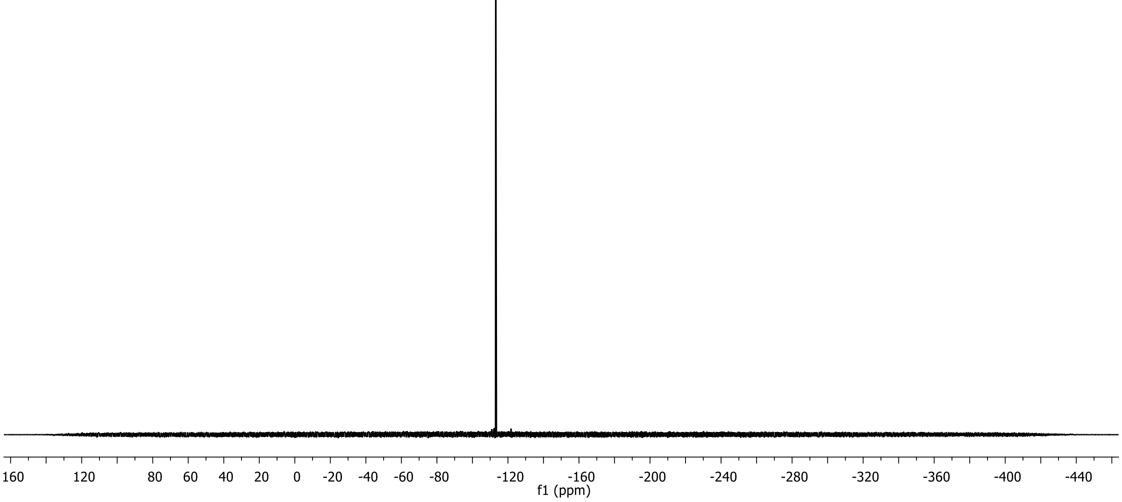


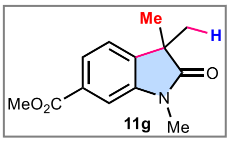
^{1}H-NMR (400 MHz, $CDCl_3$)



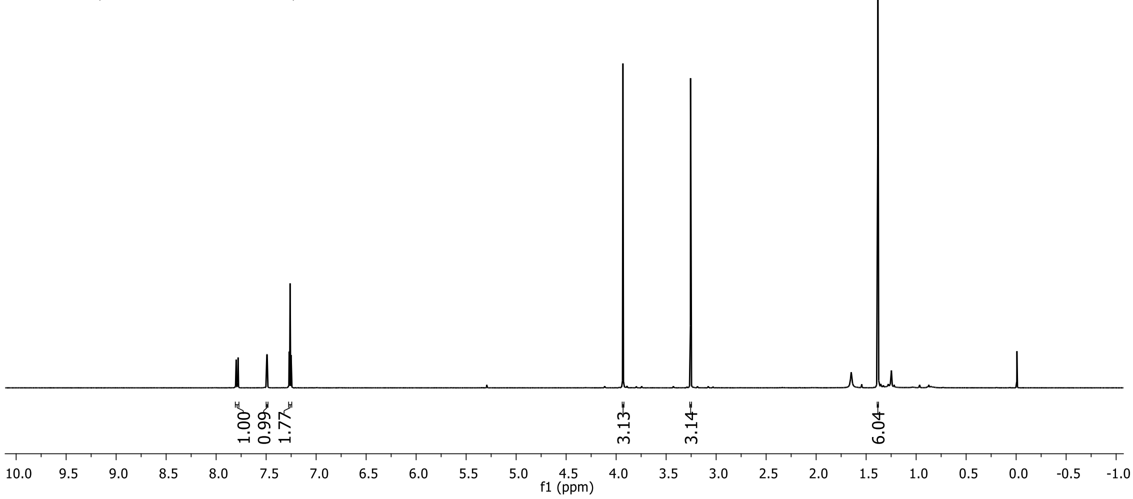


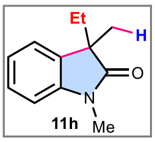
^{19}F-NMR (377 MHz, $CDCl_3$)



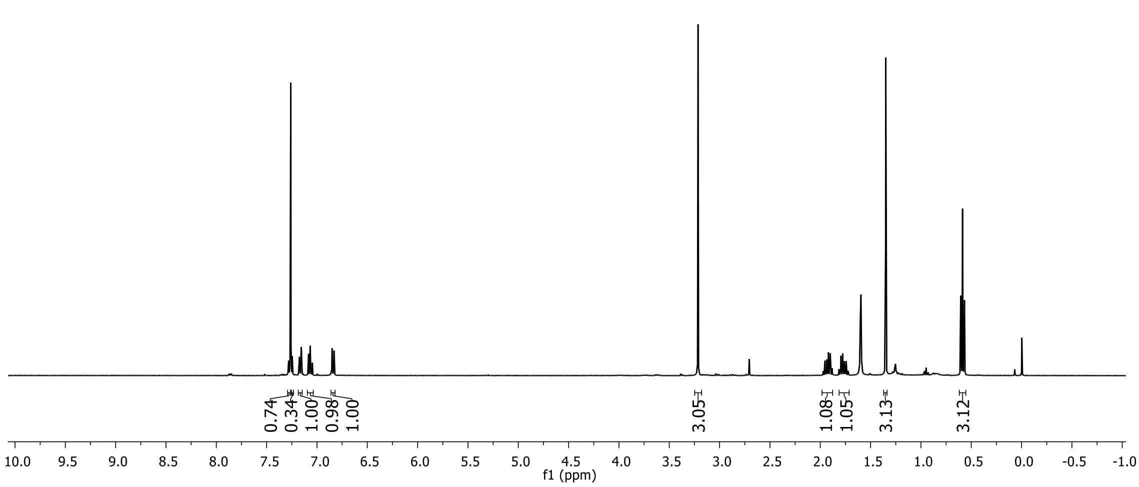


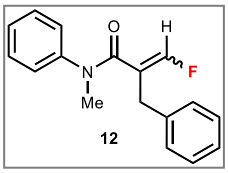
^{1}H-NMR (400 MHz, $CDCl_3$)



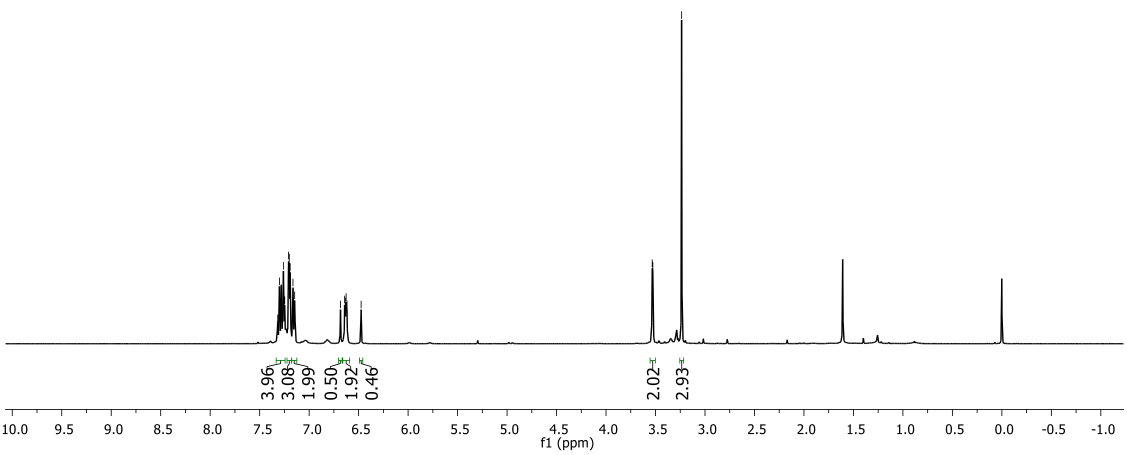


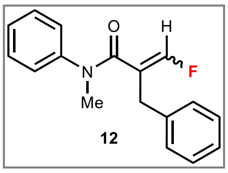
^{1}H-NMR (400 MHz, $CDCl_3$)



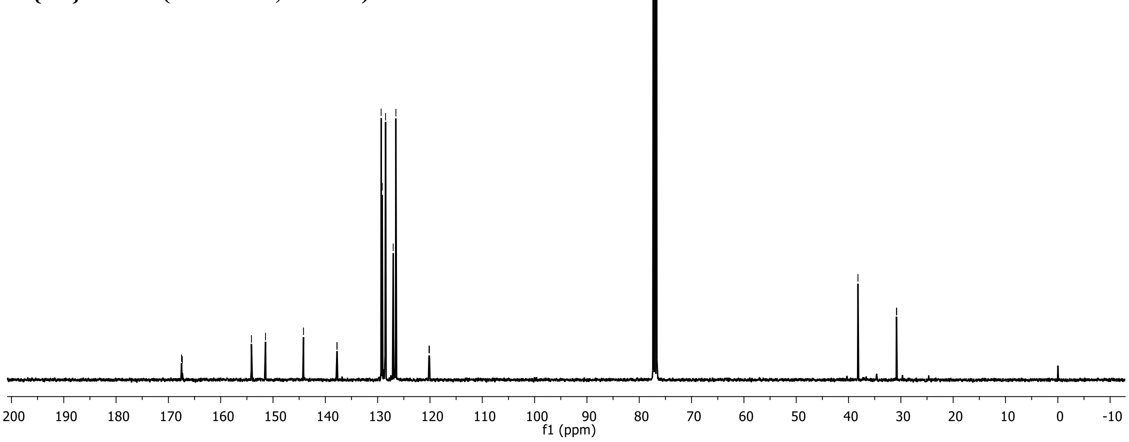


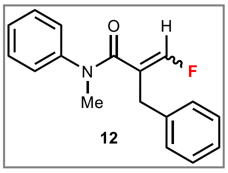
[1]H-NMR (400 MHz, CDCl$_3$)



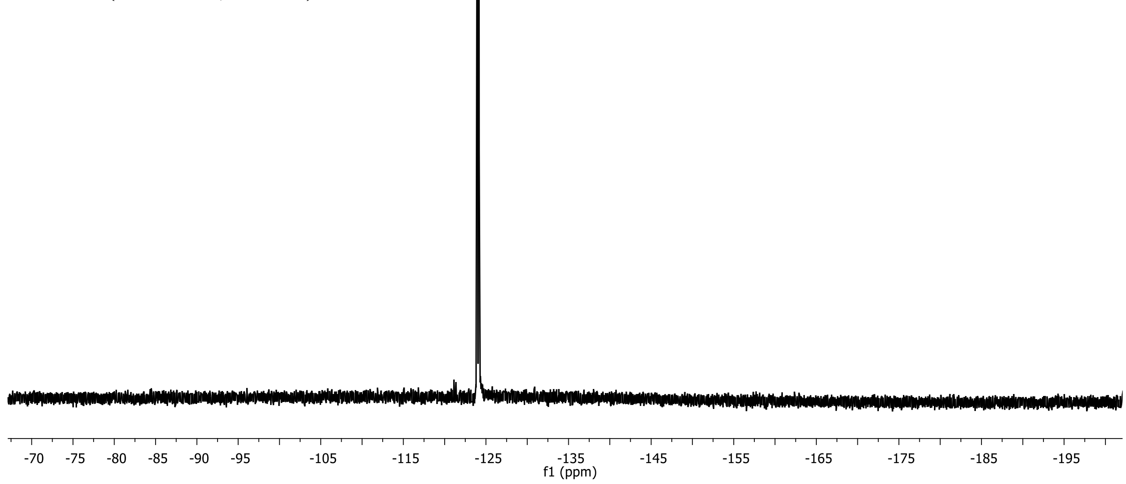


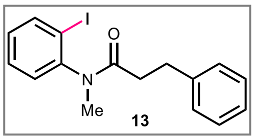
[13]C{[1]H}-NMR (101 MHz, CDCl$_3$)



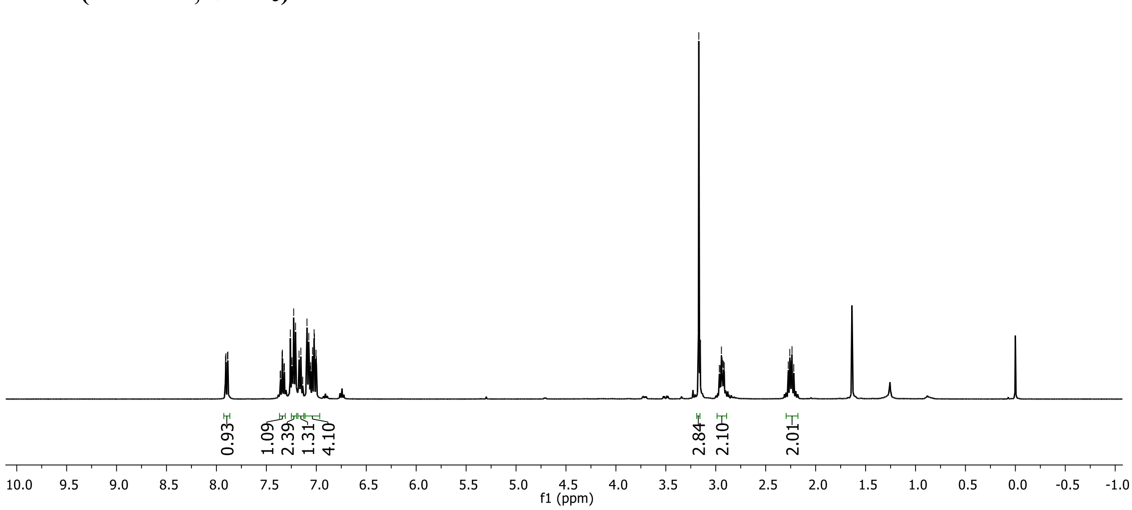


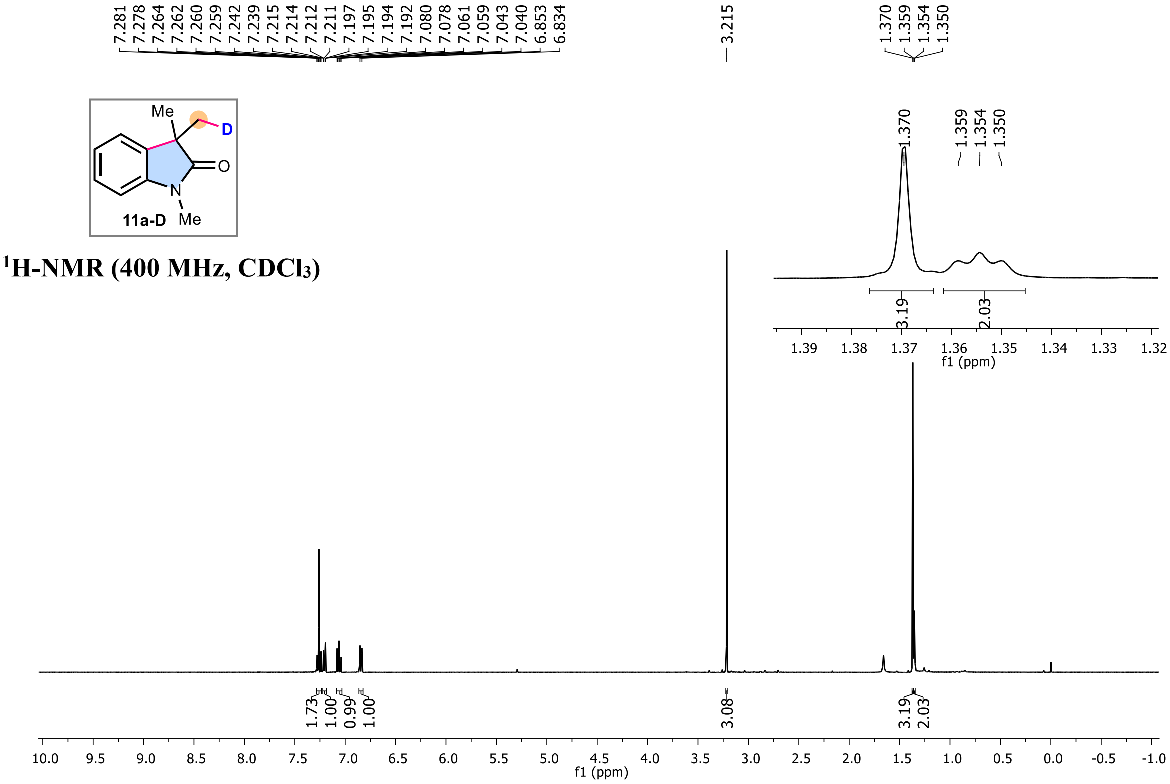
[19]F-NMR (377 MHz, CDCl₃)





[1]H-NMR (400 MHz, $CDCl_3$)





7.281 7.278 7.264 7.262 7.260 7.259 7.242 7.239 7.215 7.214 7.212 7.211 7.197 7.195 7.194 7.192 7.080 7.078 7.061 7.059 7.043 7.040 6.853 6.834
3.215
1.370 1.359 1.354 1.350
Me
D
O
N
Me
11a-D
1H-NMR (400 MHz, CDCl3)
3.19
2.03
1.73
1.00
0.99
1.00
3.08
f1 (ppm)