Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

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- **General Remarks**

Methods

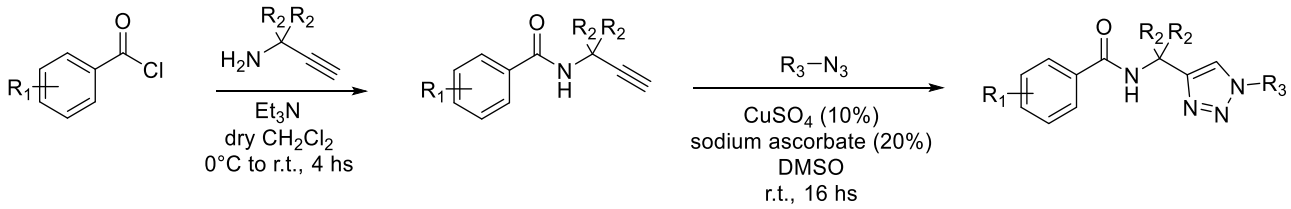
All reactions were carried out in Schlenk tubes under a N_2 atmosphere using pre-dried glassware. THF was dried using a solvent purification system (SPS) from Inert. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR. Column chromatography was performed on silica gel 60 (40-63 mesh). Melting points were measured with an Electrothermal apparatus and are uncorrected. NMR spectra were recorded on a Bruker 400 MHz and JEOL 600 MHz using solvents as internal standards (7.26 ppm for ^{1}H NMR and 77.00 ppm for ^{13}C NMR for $CDCl_3$). The terms m, s, d, t, q, and quint represent multiplet, singlet, doublet, triplet, quadruplet, and quintuplet respectively, and the term bs means a broad signal. ^{13}C DEPTQ NMR spectra are reported for all compounds. Mass spectra were recorded in the ESI mode. Exact masses were recorded on a LTQ ORBITRAP XL Thermo Mass Spectrometer (ESI source).

Materials

PhMgBr (1.0 M in THF) was freshly prepared from Bromobenzene ≥99.5% (GC) and magnesium turnings in anhydrous THF and titrated prior to use using I_2 in THF. The solution of $ZnCl_2$ in THF (1.0 mol/L) was prepared in a Schlenk tube by melting anhydrous $ZnCl_2$ at 230 °C under vacuum for 3 hours. Then, dry THF was added and the solution was stirred until all the $ZnCl_2$ was dissolved. Anhydrous $ZnBr_2$ for catalytic reactions was weighted under air (90 mg, 0.06 mmol) and then transferred in a 1 ml Eppendorf vial. The Eppendorf vial was then placed in a BUCHI glass oven for drying under vacuum at 110 °C for 3 hours prior to use. Vinylferrocene (**2n**), 2-Vinylthiophene (**2l**), 2-Vinyl-1-benzothiophene (**2m**), 4-Fluorostyrene (**2g**), 3-(Trifluoromethyl) styrene (**2i**), 3-fluoro-4-methoxystyrene (**2j**), 2-Fluorostyrene (**xx**) and 4-vinyl-1,1'-biphenyl (**2d**) were synthesized according to known procedures.[1,2] 3-(Trifluoromethyl)benzoic acid and 4-(Trifluoromethyl)benzoic acid were obtained according to previously described methods.[3] Other chemicals were obtained from commercial sources and were used without further purification.

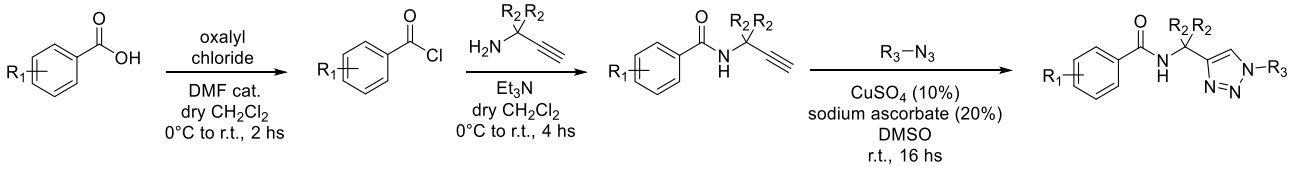
- **Synthesis and Characterisation of benzamides 1**

Procedure A



Acyl chloride (1.0 equiv) was added dropwise to a solution of propargylamine (1.5 equiv), NEt_3 (3.0 equiv) in dry CH_2Cl_2 (10 ml) at 0 °C under a nitrogen atmosphere. The mixture was initially stirred at the same temperature and then at ambient temperature for 4 hs. To the reaction was added sat. aqueous $NaHCO_3$ (20 ml). The aqueous layers were extracted with CH_2Cl_2 (3x20 ml). The combined organic extracts were washed with HCl (1.0 M, 20 ml), brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure. The crude product was further submitted to the corresponding azide (1.5 equiv), $CuSO_4 \cdot 5H_2O$ (10 mol %), sodium ascorbate (20 mol %) in DMSO (10 ml). After 16 hs, the reaction was quenched with sat. aqueous NH_4Cl (40 ml). The aqueous layers were extracted with EtOAc (3x40 ml). The combined organic extracts were dried over Na_2SO_4 and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

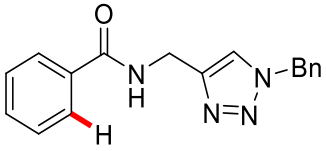
Procedure B



Oxalyl chloride (1.1 equiv) was added dropwise to a mixture of the carboxylic acid (1.0 equiv), DMF (cat.) in dry CH_2Cl_2 under a N_2 atmosphere at 0 °C. The mixture was stirred at the same temperature for 2 hs upon which it was allowed to warm up to ambient temperature. The crude acyl chloride was cooled to 0 °C and it was added dropwise to a solution of propargylamine (1.5 equiv), NEt_3 (3.0 equiv) in dry CH_2Cl_2 (10 ml) at 0 °C under a nitrogen atmosphere. The mixture was initially stirred at the same temperature and then at ambient temperature for 4 hs. To the reaction was added sat. aqueous $NaHCO_3$ (20 ml). The aqueous layers were extracted with CH_2Cl_2 (3x20 ml). The combined organic extracts were washed with HCl (1.0 M, 20 ml), brine and dried over Na_2SO_4. The filtrate was

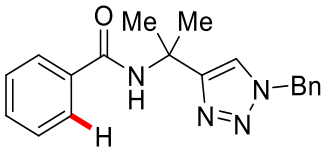
concentrated under reduced pressure. The crude product was further submitted to the corresponding azide (1.5 equiv), $CuSO_4 \cdot 5H_2O$ (10 mol %), sodium ascorbate (20 mol %) in DMSO (10 ml). After 16 hs, the reaction was quenched with sat. aqueous NH_4Cl (40 ml). The aqueous layers were extracted with EtOAc (3x40 ml). The combined organic extracts were dried over Na_2SO_4 and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]benzamide (1a)



Representative procedure **A** was followed using Benzoyl chloride (420 mg, 3.0 mmol) and benzyl azide (598 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1a** (744 mg, 85%) as a white solid. M.p. = 122-123 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.82 – 7.77 (m, 2H), 7.58 – 7.49 (m, 2H), 7.48 – 7.37 (m, 5H), 7.33 – 7.29 (m, 2H), 6.90 (bs, 1H), 5.53 (s, 2H), 4.72 (d, *J* = 5.6 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.5 (C_q), 134.5 (C_q), 134.0 (2 x C_q), 131.6 (CH), 129.1 (CH), 128.8 (CH), 128.5 (CH), 128.2 (2 x CH), 127.1 (CH), 54.3 (CH_2), 35.4 (CH_2). MS (ESI) *m/z* (relative intensity): 331 (15) $[M+K]^+$, 325 (20), 315 (100) $[M+Na]^+$, 293 (57) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{17}H_{17}N_4O$ $[M+H]^+$ 293.1397, found 293.1392.

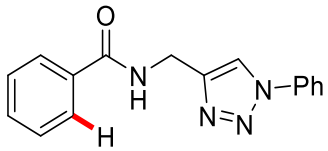
_N_-[2-(1-Benzyl-1_H_-1,2,3-triazol-4-yl)propan-2-yl]benzamide (1b)



Representative procedure **A** was followed using Benzoyl chloride (420 mg, 3.0 mmol), 1,1-Dimethylpropargylamine (373 mg, 4.5 mmol) and benzyl azide (598 mg, 4.50 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 8:2→ 6:4) yielded **1b** (768 mg, 82%) as a white solid. M.p. = 152-153 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.76 (m, 2H), 7.53 – 7.47 (m, 2H), 7.46 – 7.38 (m, 5H), 7.32-7.30 (m, 2H), 7.03 (bs, 1H), 5.54 (s, 2H), 1.88 (s, 6H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 166.7 (C_q), 154.0 (C_q), 135.3 (C_q), 134.6 (C_q), 131.3 (CH), 129.1 (CH), 128.8 (CH), 128.5 (CH), 128.1 (CH), 126.9 (CH), 120.3 (CH), 54.2 (CH_2), 51.9 (C_q), 28.0 (CH_3). MS (ESI) *m/z* (relative

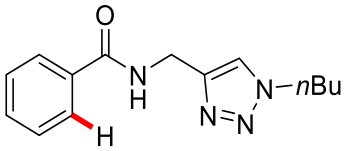
intensity): 358 (12) $[M+K]^+$, 343 (100) $[M+Na]^+$, 321 (37) $[M+H]^+$, 200 (20), 172 (16). HR-MS (ESI) *m/z* calcd for $C_{19}H_{21}N_4O$ $[M+H]^+$ 321.1710, found 321.1716.

_N_-[(1-Phenyl-1_H_-1,2,3-triazol-4-yl)methyl]benzamide (1c)



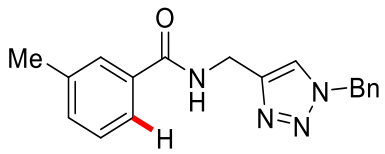
Representative procedure **A** was followed using Benzoyl chloride (366 mg, 3.0 mmol) and azidobenzene (535 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 6:4→ 4:6) yielded **1c** (625 mg, 75%) as a white solid. M.p. = 167-168 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1H), 7.87 – 7.81 (m, 2H), 7.79 – 7.72 (m, 2H), 7.59 – 7.50 (m, 3H), 7.49-7.44 (m, 3H), 6.97 (s, 1H), 4.85 (d, *J* = 5.7 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.6 (C_q), 145.4 (C_q), 137.0 (C_q), 133.9 (C_q), 131.8 (CH), 129.8 (CH), 128.9 (CH), 128.6 (CH), 127.1 (CH), 120.9 (CH), 120.6 (CH), 35.4 (CH_2). MS (ESI) *m/z* (relative intensity): 301 (100) $[M+Na]^+$, 279 (60) $[M+H]^+$, 130 (12). HR-MS (ESI) *m/z* calcd for $C_{16}H_{15}N_4O$ $[M+H]^+$ 279.1240, found 279.1245.

_N_-[(1-Butyl-1_H_-1,2,3-triazol-4-yl)methyl]benzamide (1d)



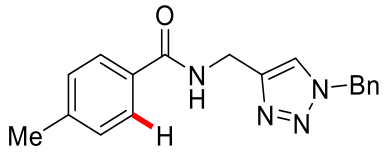
Representative procedure **A** was followed using Benzoyl chloride (420 mg, 3.0 mmol) and 1-azidobutane (445 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1d** (642 mg, 83%) as a white solid. M.p. = 84-85 °C. ^{1}H-NMR (400 MHz, CDCl3): δ = 7.83 – 7.81 (m, 2H), 7.64 (s, 1H), 7.53 – 7.49 (m, 1H), 7.46 – 7.41 (m, 2H), 7.07 (bs, 1H), 4.74 (d, *J* = 5.6 Hz, 2H), 4.36 (t, *J* = 7.3 Hz, 2H), 1.98 – 1.85 (quint, *J* = 7.6 Hz, 2H), 1.45 – 1.33 (sest, , *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.4 (C_q), 144.5 (C_q), 134.0 (C_q), 131.7 (CH), 128.6 (CH), 127.0 (CH), 122.3 (CH), 50.2 (CH_2), 35.4 (CH_2), 32.2 (CH_2), 19.7 (CH_2), 13.4 (CH_3)**.** MS (ESI) *m/z* (relative intensity): 297 (15) $[M+K]^+$, 281 (100) $[M+Na]^+$, 259 (53) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{14}H_{19}N_4O$ $[M+H]^+$ 259.1553, found 259.1561.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-3-methylbenzamide (1e)



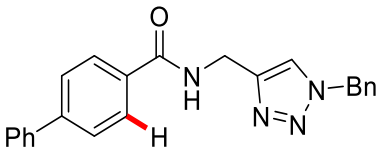
Representative procedure **A** was followed using *m*-Toluoyl chloride (464 mg, 3.0 mmol) and benzyl azide (598 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1e** (744 mg, 85%) as a white solid. M.p. = 143-144 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.62 (s, 1H), 7.59 – 7.54 (m, 2H), 7.42 – 7.36 (m, 3H), 7.32 – 7.30 (m, 4H), 6.94 (bs, 1H), 5.53 (s, 2H), 4.71 (d, *J* = 4.9 Hz, 2H), 2.40 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.7 (C_q), 138.4 (C_q), 134.5 (C_q), 133.9 (2 x C_q), 132.4 (CH), 129.2 (CH), 128.8 (CH), 128.4 (CH), 128.2 (2 x CH), 127.8 (CH), 124.1 (CH), 54.3 (CH_2), 35.3 (CH_2), 21.3 (CH_3). MS (ESI) *m/z* (relative intensity): 345 (16) $[M+K]^+$,329 (100) $[M+Na]^+$, 307 (78) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{18}H_{19}N_4O$ $[M+H]^+$ 307.1553, found 307.1550.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-4-methylbenzamide (1f)



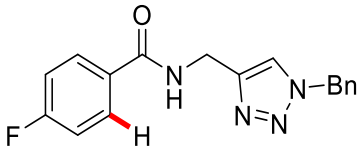
Representative procedure **B** was followed using 4-Methylbenzoic acid (408 mg, 3.0 mmol) and benzyl azide (598 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1f** (678 mg, 74%) as a white solid. M.p. = 164-165 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.2 Hz, 2H), 7.56 (s, 1H), 7.39 – 7.36 (m, 3H), 7.30 – 7.29 (m, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.96 (bs, 1H), 5.52 (s, 2H), 4.70 (d, *J* = 5.6 Hz, 2H), 2.40 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.3 (C_q), 145.2 (C_q), 142.1 (C_q), 134.5 (C_q), 131.1 (C_q), 129.2, (CH) 129.1 (CH), 128.8 (CH), 128.2 (CH), 127.0 (CH), 122.4 (CH), 54.3 (CH_2), 35.4 (CH_2), 21.5 (CH_3). ESI-MS calcd for $C_{18}H_{19}N_4O$ $[M+H]^+$ 307.15, found 307.18. MS (ESI) *m/z* (relative intensity): 329 (100) $[M+Na]^+$, 307 (69) $[M+H]^+$, 143 (229, 119 (39). HR-MS (ESI) *m/z* calcd for $C_{18}H_{19}N_4O$ $[M+H]^+$ 307.1553, found 307.1557.

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-[1,1'-biphenyl]-4-carboxamide (1g)**



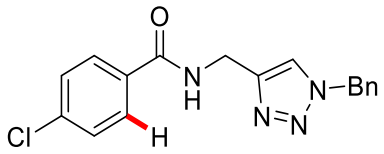
Representative procedure **B** was followed using [1,1'-Biphenyl]-4-carboxylic acid (594 mg, 3.0 mmol) and benzyl azide (598 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1g** (770 mg, 70%) as a white solid. M.p. = 212-213 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.61 (m, 2H), 7.59 (s, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.43 – 7.37 (m, 4H), 7.31 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.00 (bs, 1H), 5.54 (s, 2H), 4.75 (d, *J* = 5.1 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.1 (C_q), 144.5 (C_q), 140.0 (C_q), 134.4 (C_q), 132.6 (2 x C_q), 129.2 (CH), 128.9 (CH), 128.8 (CH), 128.2 (CH), 128.0 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 122.3 (CH), 54.3 (CH_2), 35.5 (CH_2). MS (ESI) *m/z* (relative intensity): 759 $[2M+Na]^+$ (100), 391 (48) $[M+Na]^+$, 269 (30) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{23}H_{21}N_4O$ $[M+H]^+$ 369.1710, found 369.1706.

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-4-fluorobenzamide (1h)**



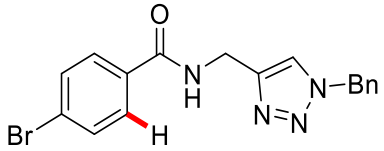
Representative procedure **B** was followed using 4-Fluorobenzoic acid (420 mg, 3.0 mmol) and benzyl azide (598 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1g** (650 mg, 70%) as a light-yellow solid. M.p. = 133-135 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.88 – 7.81 (m, 2H), 7.60 (s, 1H), 7.45 (bs, 1H), 7.39 – 7.37 (m, 3H), 7.30 – 7.29 (m, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 5.51 (s, 2H), 4.68 (d, *J* = 5.6 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 166.4 (C_q), 164.8 (d, $^{1}J_{C\text{-}F}$ = 251 Hz, C_q), 145.01 (C_q), 134.35 (C_q), 130.1 (d, $^{4}J_{C\text{-}F}$ = 4 Hz, C_q), 129.5 (d, $^{3}J_{C\text{-}F}$ = 9 Hz, CH), 129.2 (CH), 128.9 (CH), 128.2 (CH), 122.53 (CH), 115.5 (d, $^{2}J_{C\text{-}F}$ = 22 Hz, CH), 54.33 (CH_2), 35.29 (CH_2). ^{19}F-NMR (565 MHz, $CDCl_3$): δ = -107.85 (ddd, *J* = 13.6, 8.5, 5.1 Hz). MS (ESI) *m/z* (relative intensity): 349 (34) $[M+K]^+$, 333 (100) $[M+Na]^+$, 311 (60) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{17}H_{16}FN_4O$ $[M+H]^+$ 311.1303, found 311.1308.

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-4-chlorobenzamide (1i)**



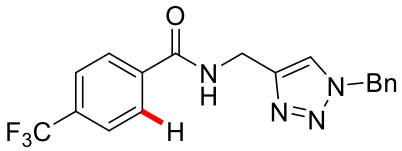
Representative procedure **B** was followed using 4-Chlorobenzoic acid (468 mg, 3.0 mmol) and benzyl azide (598 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1i** (782 mg, 80%) as a white solid. M.p. = 172-173 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.5 Hz, 2H), 7.60 (bs, 1H), 7.41 – 7.38 (m, 5H), 7.34 – 7.29 (m, 2H), 7.16 (bs, 1H), 5.52 (s, 2H), 4.69 (d, *J* = 4.4 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 166.4 (C_q), 137.9 (C_q), 134.3 (C_q), 132.3 (2 x C_q), 129.2 (CH), 128.9 (CH), 128.8 (CH), 128.5 (2 x CH), 128.2 (CH), 54.4 (CH_2), 35.4 (CH_2). MS (ESI) *m/z* (relative intensity): 349 (100) $[M+Na]^+$, 327 (54) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{17}H_{16}ClN_4O$ $[M+H]^+$ 327.1007, found 327.1012.

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-4-bromobenzamide (1j)**



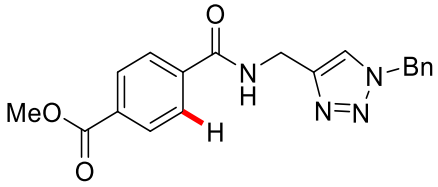
Representative procedure **B** was followed using 4-Bromobenzoic acid (603 mg, 3.0 mmol) and benzyl azide (598 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1j** (790 mg, 71%) as a white solid. M.p. = 176-178 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.6 Hz, 2H), 7.57 (s, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.40 – 7.37 (m, 3H), 7.31 – 7.29 (m, 3H), 5.52 (s, 2H), 4.68 (d, *J* = 5.6 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 166.5 (C_q), 144.8 (C_q), 134.3 (C_q), 132.8 (C_q), 131.8 (CH), 129.2 (CH), 128.9 (CH), 128.7 (CH), 128.2 (CH), 126.4 (C_q), 122.4 (CH), 54.3 (CH_2), 35.4 (CH_2). MS (ESI) *m/z* (relative intensity): 409 (13) $[M+K]^+$, 393 (100) $[M+Na]^+$, 371 (29) $[M+H]^+$, 144 (49). HR-MS (ESI) *m/z* calcd for $C_{17}H_{16}BrN_4O$ $[M+H]^+$ 371.0502, found 371.0510.

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-4-(trifluoromethyl)benzamide (1k)**



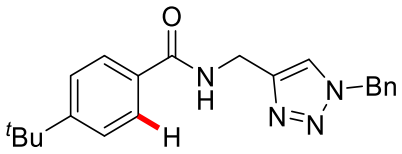
Representative procedure **B** was followed using 4-(Trifluoromethyl) benzoic acid (570 mg, 3.0 mmol) and benzyl azide (598 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1j** (702 mg, 65%) as a white solid. M.p. = 173-174 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.57 (s, 1H), 7.41 – 7.38 (m, 3H), 7.32 – 7.29 (m, 2H), 7.24 (bs, 1H), 5.54 (s, 2H), 4.72 (d, *J* = 5.6 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 166.1 (C_q), 144.7 (C_q), 137.2 (C_q), 134.3 (C_q), 133.3 (q, $^{2}J_{C\text{-}F}$ = 32 Hz, C_q), 129.2 (CH), 129.0 (CH), 128.2 (CH), 127.6 (CH), 125.6 (q, $^{4}J_{C\text{-}F}$ = 4 Hz, CH), 123.7 (q, $^{1}J_{C\text{-}F}$ = 273 Hz, C_q), 122.5 (CH), 54.4 (CH_2), 35.4 (CH_2). ^{19}F-NMR (565 MHz, $CDCl_3$): δ = -62.9 (s). MS (ESI) *m/z* (relative intensity): 383 (100) $[M+Na]^+$, 361 (55) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{18}H_{16}F_3N_4O$ $[M+H]^+$ 361.1271, found 361.1268.

Methyl 4-{[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]carbamoyl}benzoate (1l)



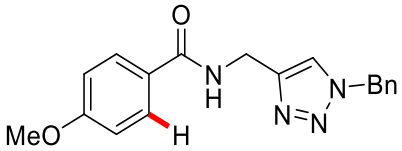
Representative procedure **B** was followed using 4-(Methoxycarbonyl)benzoic acid (540 mg, 3.0 mmol) and benzyl azide (598 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1l** (690 mg, 66%) as a white solid. M.p. = 174-176 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.56 (s, 1H), 7.42 – 7.37 (m, 3H), 7.31 – 7.29 (m, 2H), 6.99 (s, 1H), 5.54 (s, 2H), 4.72 (d, *J* = 5.4 Hz, 2H), 3.96 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 166.6 (C_q), 166.3 (C_q), 137.9 (C_q), 134.4 (C_q), 132.8 (2 x C_q), 129.8 (2 x CH), 129.2 (CH), 128.9 (CH), 128.2 (CH), 127.2 (CH), 54.4 (CH_2), 52.4 (CH_3), 35.4 (CH_2). MS (ESI) *m/z* (relative intensity): 723 (23) $[2M+Na]^+$, 545 (12), 351(100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{19}H_{19}N_4O_3$ $[M+H]^+$ 351.1452, found 351.1458.

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-4-(tert-butyl)benzamide (1m)**



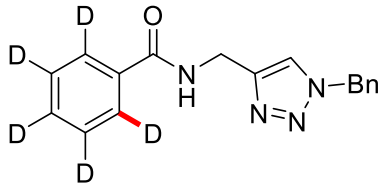
Representative procedure **B** was followed using 4-(*tert*-Butyl)benzoic acid (534 mg, 3.0 mmol) and benzyl azide (598 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1m** (616 mg, 59%) as a white solid. M.p. = 167–169 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 7.7 Hz, 2H), 7.55 (s, 1H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.40 – 7.37 (m, 3H), 7.30 – 7.27 (m, 2H), 6.94 (s, 1H), 5.52 (s, 2H), 4.70 (d, *J* = 5.6 Hz, 2H), 1.34 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.3 (C_q), 155.2 (C_q), 145.2 (C_q), 134.5 (C_q), 131.1 (C_q), 129.2 (CH), 128.8 (CH), 128.2 (CH), 126.8 (CH), 125.5 (CH), 122.3 (CH), 54.3 (CH_2), 35.4 (CH_2), 34.9 (C_q), 31.2 (CH_3). MS (ESI) *m/z* (relative intensity): 719 $[2M+Na]^+$ (53), 542 (37), 387 (30) $[M+K]^+$, 371 (92) $[M+Na]^+$, 349 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{21}H_{25}N_4O$ $[M+H]^+$ 349.2023, found 349.2027.

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-4-methoxybenzamide (1n)**



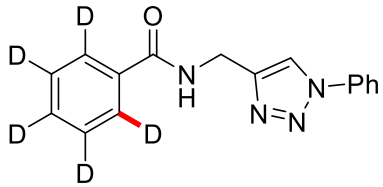
Representative procedure **B** was followed using 4-Methoxybenzoic acid (456 mg, 3.0 mmol) and benzyl azide (598 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded **1n** (589 mg, 61 %) as a white solid. M.p. = 134-136 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.8 Hz, 2H), 7.56 (s, 1H), 7.39 – 7.35 (m, 3H), 7.30 – 7.27 (m, 2H), 6.95 (bs, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.51 (s, 2H), 4.68 (d, *J* = 5.6 Hz, 2H), 3.85 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 166.9 (C_q), 162.3 (C_q), 145.3 (C_q), 134.5 (C_q), 129.2 (CH), 128.9 (CH), 128.8 (CH), 128.2 (CH), 126.3 (C_q), 122.3 (CH), 113.8 (CH), 55.4 (CH_3), 54.3 (CH_2), 35.4 (CH_2). MS (ESI) *m/z* (relative intensity): 667 $[2M+Na]^+$ (51), 503 (30), 361 (25) $[M+K]^+$, 345 (100) $[M+Na]^+$, 323 (68) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{18}H_{19}N_4O_2$ $[M+H]^+$ 323.1502, found 323.1507.

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]benzamide-d_5 ([D]$_5$-1a)**



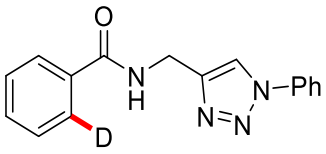
Representative procedure **B** was followed using d_5-Benzoic acid (381 mg, 3.0 mmol) and benzyl azide (686 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded [D]$_5$-**1a** (702 mg, 70%) as a white solid. M.p. = 128-129 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 1H), 7.41 – 7.36 (m, 3H), 7.30 – 7.28 (m, 2H), 6.97 (bs, 1H), 5.52 (s, 2H), 4.71 (d, *J* = 5.6 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.4 (C_q), 145.0 (C_q), 134.4 (C_q), 133.8 (C_q), 131.2 (t, *J* = 24 Hz, CD), 129.2 (CH), 128.9 (CH), 128.1 (t, *J* = 24 Hz, CD), 128.2 (CH), 126.6 (t, *J* = 25 Hz, CD), 122.3 (CH), 54.3 (CH_2), 35.4 (CH_2). MS (ESI) *m/z* (relative intensity): 466 (35), 320 (53) $[M+Na]^+$, 298 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{17}H_{12}D_5N_4O$ $[M+H]^+$ 298.1711, found 298.1718.

***N*-[(1-Phenyl-1*H*-1,2,3-triazol-4-yl)methyl]benzamide-d_5 ([D]$_5$-1c)**



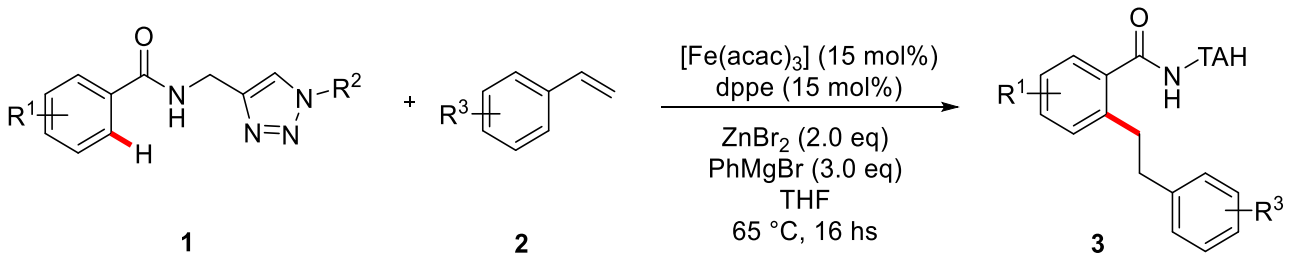
Representative procedure **B** was followed using d_5-Benzoic acid (381 mg, 3.0 mmol) and azidobenzene (535 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded [D]$_5$-**1c** (577 mg, 68%) as a white solid. M.p. = 167-168 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1H), 7.76 – 7.73 (m, 2H), 7.57 – 7.51 (m, 2H), 7.49 – 7.44 (m, 1H), 7.09 (bs, 1H), 4.84 (d, *J* = 5.8 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.6 (C_q), 145.4 (C_q), 137.0 (C_q), 133.8 (C_q), 131.2 (t, *J* = 24 Hz, CD), 129.8 (CH), 128.9 (CH), 128.1 (t, *J* = 24 Hz, CD), 126.7 (t, *J* = 25 Hz, CD), 120.9 (CH), 120.6 (CH), 35.4 (CH_2). MS (ESI) *m/z* (relative intensity): 445 (16), 306 (30) $[M+Na]^+$, 284 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{16}H_{10}D_5N_4O$ $[M+H]^+$ 284.1481, found 284.1486.

***N*-[(1-Phenyl-1*H*-1,2,3-triazol-4-yl)methyl]benzamide-2-d ([D]$_1$-1c)**



Representative procedure **B** was followed using Benzoic-2-[d] acid (369 mg, 3.0 mmol) and azidobenzene (535 mg, 4.5 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1→ 3:7) yielded [D]$_1$-**1c** (510 mg, 61%) as a white solid. M.p. = 169-170 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1H), 7.84 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.76 – 7.73 (m, 2H), 7.54 (dtd, *J* = 7.6, 6.0, 1.2 Hz, 3H), 7.46 (ddt, *J* = 7.1, 6.0, 1.7 Hz, 3H), 7.08 (s, 1H), 4.83 (d, *J* = 5.7 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 167.5 (C_q), 145.4 (C_q), 134.0 (C_q), 133.9 (C_q), 131.8 (CH), 129.8 (CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 127.0 (d, *J* = 1 Hz, CH), 126.5 (t, *J* = 25 Hz, CD), 120.8 (CH), 120.6 (CH), 35.4 (CH_2). MS (ESI) *m/z* (relative intensity): 302 (26) $[M+Na]^+$, 280 (100) $[M+H]^+$, 130 (34). HR-MS (ESI) *m/z* calcd for $C_{16}H_{14}DN_4O$ $[M+H]^+$ 280.1230, found 284.1227.

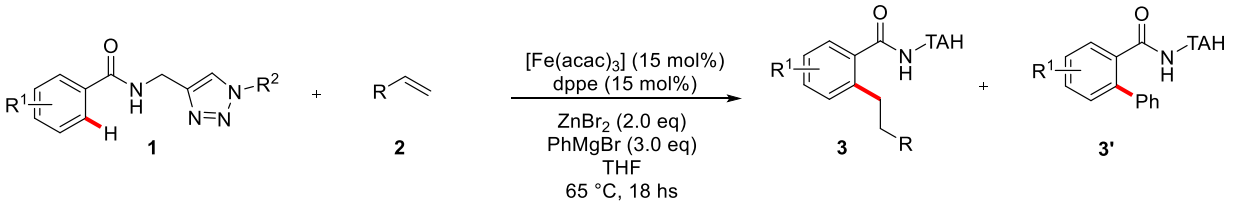
- **Representative procedure for iron-catalyzed C–H alkylation with vinylarenes**

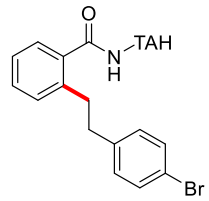


1 **2** **3**

To a stirred solution of $Fe(acac)_3$ (10.6 mg, 0.03 mmol), dppe (11.9 mg, 0.03 mmol), zinc bromide (90.0 mg, 0.40 mmol, 2.0 equiv) and **1** (0.20 mmol) in THF (0.4 ml) under N_2 atmosphere, PhMgBr (1.0 M in THF, 600 µl, 0.60 mmol, 3.0 equiv) was added in a single portion. Then, **2** (0.60 mmol, 3.0 equiv) was added and the mixture was placed in a pre-heated oil bath at 65 °C. After stirring for 16 hs, the reaction was cooled to room temperature and quenched by the addition of an aqueous solution of HCl (1.0 M, 5 ml). The reaction was extracted with CH_2Cl_2 (3x15 ml), and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc).

- **Substrate scope limitations for C–H alkylation with vinylarenes**

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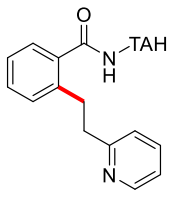
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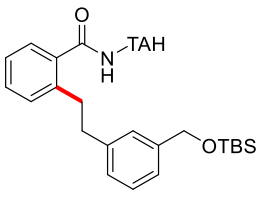
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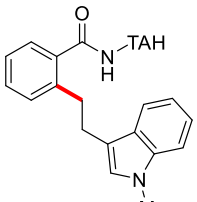
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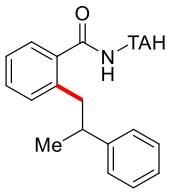
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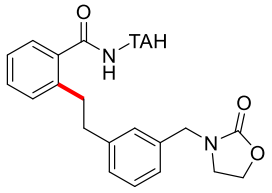
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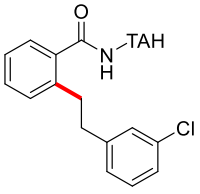
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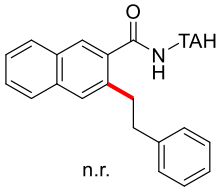
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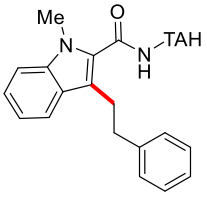
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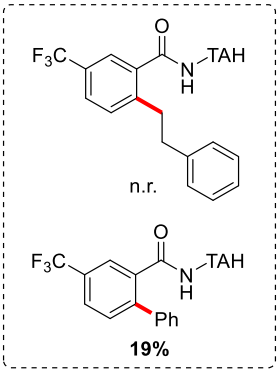
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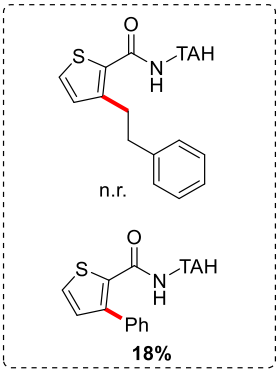
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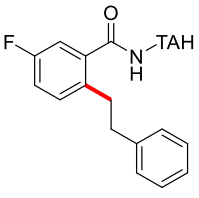
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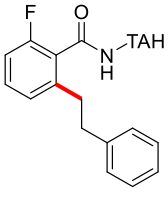
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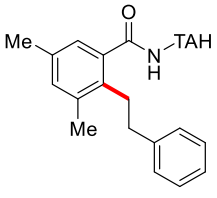
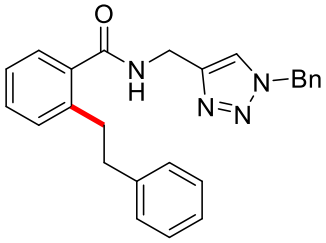

n.r.

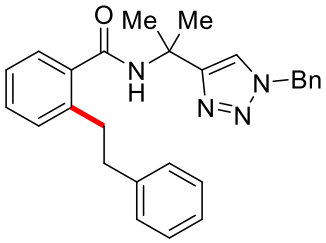
- **Characterisation data for compounds 3**

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-2-phenethylbenzamide (3aa)**



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and styrene **2a** (69 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3aa** (56.3 mg, 71%) as a white solid. M.p. = 125-127 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.37 – 7.30 (m, 5H), 7.26 – 7.17 (m, 7H), 7.08 – 7.06 (m, 2H), 6.15 (bs, 1H), 5.45 (s, 2H), 4.59 (d, *J* = 5.8 Hz, 2H), 3.04 (dd, *J* = 9.1, 6.5 Hz, 2H), 2.86 (dd, *J* = 9.2, 6.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.1 (C_q), 144.9 (C_q), 141.6 (C_q), 139.8 (C_q), 136.0 (C_q), 134.4 (C_q), 130.4 (CH), 130.1 (CH), 129.2 (CH), 128.8 (CH), 128.6 (CH), 128.3 (CH), 128.1 (CH), 126.9 (CH), 126.1 (CH), 125.9 (CH), 122.2 (CH), 54.2 (CH_2), 37.9 (CH_2), 35.4 (CH_2), 35.1 (CH_2). MS (ESI) *m/z* (relative intensity): 815 (24) $[2M+Na]^+$, 435 (32) $[M+K]^+$, 419 (49) $[M+Na]^+$, 397 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{25}H_{25}N_4O$ $[M+H]^+$ 397.2023, found 397.2018.

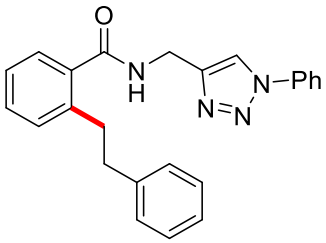
***N*-[2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-yl]-2-phenethylbenzamide (3ba)**



To a stirred solution of $Fe(acac)_3$ (7.0 mg, 0.02 mmol), bpy (3.4 mg, 0.022 mmol), $ZnBr_2$ (90 mg, 0.40 mmol, 2.00 equiv) and **1b** (64.1 mg, 0.20 mmol) in THF (0.4 ml) under N_2 atmosphere, PhMgBr (1.0 M in THF, 600 µl, 0.6 mmol, 3.0 equiv) was added in a single portion. Then, styrene **2a** (69 µl, 0.60 mmol, 3.0 equiv) was added and the mixture was placed in a pre-heated oil bath at 65 °C. After stirring for 18 h, the reaction was cooled to room temperature and quenched by the addition of an aqueous solution of HCl (1.0 M, 5 ml). The reaction was extracted with CH_2Cl_2 (3x15 ml) and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated. Purification by column chromatography on silica gel (*n*-hexane/EtOAc 6:4) yielded **3ba** (16.1 mg, 19%) as a white

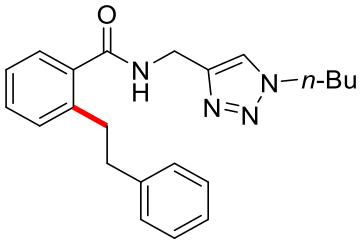
solid. M.p. = 128-130 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 7.41 – 7.36 (m, 4H), 7.34 – 7.29 (m, 3H), 7.28 – 7.17 (m, 6H), 7.17 – 7.12 (m, 2H), 5.48 (s, 2H), 3.05 (dd, *J* = 9.8, 6.3 Hz, 2H), 2.89 (dd, *J* = 9.8, 6.3 Hz, 2H), 1.87 (s, 6H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.7 (C_q), 153.5 (C_q), 141.9 (C_q), 139.7 (C_q), 137.1 (C_q), 134.5 (C_q), 130.3 (CH), 129.7 (CH), 129.2 (CH), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 126.9 (CH), 126.1 (CH), 125.9 (CH), 120.6 (CH), 54.3 (CH_2), 51.8 (C_q), 37.9 (CH_2), 35.3 (CH_2), 27.9 (CH_3). (ESI) *m/z* (relative intensity): 871 (10) $[2M+Na]^+$, 463 (16) $[M+K]^+$, 447 (29) $[M+Na]^+$, 425 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{27}H_{29}N_4O$ $[M+H]^+$ 425.2336, found 425.2340.

2-Phenethyl-*N*-[(1-phenyl-1*H*-1,2,3-triazol-4-yl)methyl]benzamide (3ca)



The representative procedure was followed using **1c** (55.7 mg, 0.20 mmol) and styrene **2a** (69 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ca** (45.1 mg, 59%) as a white solid. M.p. = 132-134 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 7.70 – 7.68 (m, 2H), 7.55 – 7.50 (m, 2H), 7.48 – 7.44 (m, 1H), 7.39 – 7.35 (m, 2H), 7.26 – 7.13 (m, 5H), 7.10 – 7.07 (m, 2H), 6.23 (bs, 1H), 4.70 (d, *J* = 5.9 Hz, 2H), 3.10 (dd, *J* = 9.2, 6.5 Hz, 2H), 2.91 (dd, *J* = 9.2, 6.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.2 (C_q), 145.3 (C_q), 141.6 (C_q), 139.9 (C_q), 137.0 (C_q), 135.9 (C_q), 130.4 (CH), 130.2 (CH), 129.8 (CH), 128.8 (CH), 128.6 (CH), 128.3 (CH), 126.9 (CH), 126.1 (CH), 125.9 (CH), 120.6 (CH), 120.5 (CH), 38.1 (CH_2), 35.4 (CH_2), 35.2 (CH_2). MS (ESI) *m/z* (relative intensity): 787 (27) $[2M+Na]^+$, 593 (43), 405 (66) $[M+Na]^+$, 383 (100) $[M+H]^+$, 208 (12). HR-MS (ESI) *m/z* calcd for $C_{24}H_{23}N_4O$ $[M+H]^+$ 383.1866, found 383.1871.

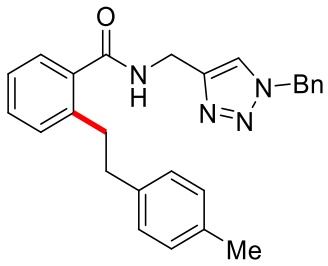
***N*-[(1-Butyl-1*H*-1,2,3-triazol-4-yl)methyl]-2-phenethylbenzamide (3da)**



The representative procedure was followed **1d** (51.7 mg, 0.20 mmol) and styrene **2a** (69 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3da** (41.3

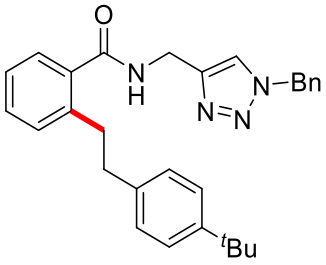
mg, 57%) as a white solid. M.p. = 91-93 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.59 (s, 1H), 7.37 – 7.32 (m, 2H), 7.27 – 7.16 (m, 5H), 7.12 – 7.09 (m, 2H), 6.24 (bs, 1H), 4.62 (d, *J* = 5.8 Hz, 2H), 4.28 (t, *J* = 7.2 Hz, 2H), 3.07 (dd, *J* = 9.3, 6.5 Hz, 2H), 2.89 (dd, *J* = 9.3, 6.5 Hz, 2H), 1.84 (quint, *J* = 7.2 Hz, 2H), 1.34 (sest, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.2 (C_q), 144.1 (C_q), 141.6 (C_q), 140.0 (C_q), 135.8 (C_q), 130.4 (CH), 130.2 (CH), 128.6 (CH), 128.3 (CH), 127.0 (CH), 126.2 (CH), 126.0 (CH), 122.7 (CH), 50.5 (CH_2), 38.0 (CH_2), 35.2 (CH_2), 34.9 (CH_2), 32.1 (CH_2), 19.7 (CH_2), 13.4 (CH_3). MS (ESI) *m/z* (relative intensity): 747 (18) $[2M+Na]^+$, 385 (44) $[M+Na]^+$, 363 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{22}H_{27}N_4O$ $[M+H]^+$ 363.2179, found 363.2183.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-(4-methylphenethyl)benzamide (3ab)



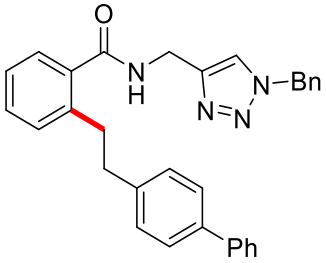
The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 4-methylstyrene **2b** (79 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ab** (53.4 mg, 65%) as a white solid. M.p. = 138-140 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.39 – 7.29 (m, 5H), 7.27 – 7.18 (m, 4H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.18 (t, *J* = 5.9 Hz, 1H), 5.44 (s, 2H), 4.57 (d, *J* = 5.8 Hz, 2H), 3.01 (dd, *J* = 9.1, 6.5 Hz, 2H), 2.82 (dd, *J* = 9.1, 6.5 Hz, 2H), 2.31 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.2 (C_q), 145.0 (C_q), 139.9 (C_q), 138.5 (C_q), 136.0 (C_q), 135.4 (C_q), 134.5 (C_q), 130.3 (CH), 130.1 (CH), 129.1 (CH), 129.0 (CH), 128.8 (CH), 128.5 (CH), 128.1 (CH), 126.9 (CH), 126.1 (CH), 122.2 (CH), 54.2 (CH_2), 37.5 (CH_2), 35.4 (CH_2), 35.2 (CH_2), 21.0 (CH_3). (ESI) *m/z* (relative intensity): 843 (30) $[2M+Na]^+$, 449 (13) $[M+K]^+$, 433 (52) $[M+Na]^+$, 411 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{26}H_{27}N_4O$ $[M+H]^+$ 411.2179, found 411.2181.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-[4-(tert-butyl)phenethyl]benzamide (3ac)



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 4-tert-Butylstyrene **2c** (110 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ac** (39.8 mg, 44%) as a white solid. M.p. = 129-131 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 1H), 7.43 – 7.29 (m, 7H), 7.28 – 7.19 (m, 4H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.20 (bs, 1H), 5.44 (s, 2H), 4.60 (d, *J* = 5.8 Hz, 2H), 3.02 (dd, *J* = 9.6, 6.4 Hz, 2H), 2.83 (dd, *J* = 9.6, 6.4 Hz, 2H), 1.32 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.2 (C_q), 148.8 (C_q), 145.0 (C_q), 140.0 (C_q), 138.6 (C_q), 135.9 (C_q), 134.4 (C_q), 130.3 (CH), 130.1 (CH), 129.2 (CH), 128.8 (CH), 128.2 (CH), 128.0 (CH), 126.9 (CH), 126.1 (CH), 125.2 (CH), 122.3 (CH), 54.2 (CH_2), 37.4 (CH_2), 35.4 (CH_2), 35.0 (CH_2), 34.9 (C_q), 31.4 (CH_3). (ESI) *m/z* (relative intensity): 927 (37) $[2M+Na]^+$, 491 (20) $[M+K]^+$, 475 (39) $[M+Na]^+$, 453 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{29}H_{33}N_4O$ $[M+H]^+$ 453.2649, found 453.2647.

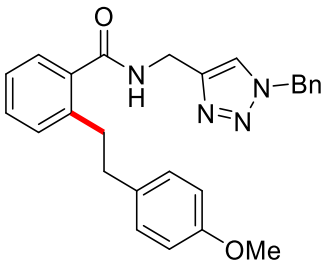
2-{2-[(1,1'-Biphenyl)-4-yl]ethyl}-_N_-((1-benzyl-1_H_-1,2,3-triazol-4-yl)methyl)benzamide (3ad)



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 4-vinyl-1,1'-biphenyl **2d** (108.2 mg, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ad** (70.0 mg, 74%) as a white solid. M.p. = 155-156 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.51 – 7.49 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.33 (m, 6H), 7.27 (bs, 1H), 7.26 – 7.20 (m, 4H), 7.16 (d, *J* = 8.2 Hz, 2H), 5.42 (s, 2H), 4.61 (d, *J* = 5.7 Hz, 2H), 3.09 (dd, *J* = 9.2, 6.4 Hz, 2H), 2.91 (dd, *J* = 9.3, 6.4 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.1 (C_q), 144.9 (C_q), 140.9 (C_q), 140.8 (C_q), 139.9 (C_q), 138.8 (C_q), 135.9 (C_q), 134.5 (C_q), 130.4 (CH), 130.2 (CH), 129.1 (2 x CH), 128.8 (2 x CH), 128.1 (CH), 127.1 (CH), 127.0 (2 x CH), 126.9 (CH), 126.2 (CH), 122.1 (CH), 54.2

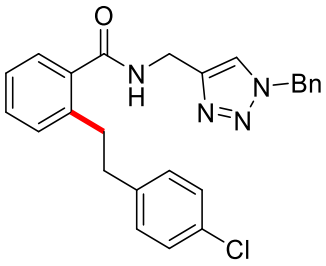
(CH_2), 37.6 (CH_2), 35.5 (CH_2), 35.1 (CH_2). (ESI) *m/z* (relative intensity): 495 (28) $[M+Na]^+$, 473 (100) $[M+H]^+$**.** HR-MS (ESI) *m/z* calcd for $C_{31}H_{29}N_4O$ $[M+H]^+$ 473.2336, found 473.2333.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-(4-methoxyphenethyl)benzamide (3ae)



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 4-methoxystyrene **2e** (80 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ae** (38.4 mg, 45%) as a white solid. M.p. = 114-116 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.37 – 7.30 (m, 5H), 7.26 – 7.18 (m, 4H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.18 (t, *J* = 5.8 Hz, 1H), 5.46 (s, 2H), 4.59 (d, *J* = 5.7 Hz, 2H), 3.78 (s, 3H), 3.01 (dd, *J* = 8.9, 6.6 Hz, 2H), 2.80 (dd, *J* = 9.0, 6.6 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.1 (C_q), 157.9 (C_q), 145.0 (C_q), 139.9 (C_q), 136.0 (C_q), 134.5 (C_q), 133.6 (C_q), 130.4 (CH), 130.1 (CH), 129.5 (CH), 129.2 (CH), 128.8 (CH), 128.1 (CH), 126.9 (CH), 126.1 (CH), 122.2 (CH), 113.7 (CH), 55.3 (CH_3), 54.2 (CH_2), 37.0 (CH_2), 35.4 (CH_2), 35.3 (CH_2). (ESI) *m/z* (relative intensity): 875 (28) $[2M+Na]^+$, 465 (16) $[M+K]^+$, 449 (100) $[M+Na]^+$, 427 (88) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{26}H_{27}N_4O_2$ $[M+H]^+$ 427.2129, found 427.2124.

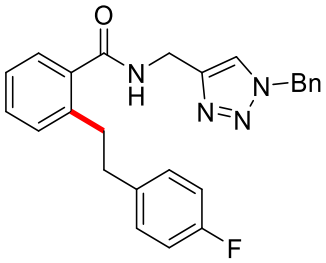
_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-(4-chlorophenethyl)benzamide (3af)



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 4-chlorostyrene **2f** (76 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3af** (56.9 mg, 66%) as a white solid. M.p. = 131-132 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.38 – 7.32 (m, 5H), 7.28 – 7.23 (m, 3H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.17 (m, 1H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.32 (t, *J* = 5.5 Hz, 1H), 5.48 (s, 2H), 4.63 (d, *J* = 5.6 Hz, 2H), 3.03 (dd, *J* = 9.2, 6.5 Hz, 2H), 2.83 (dd, *J* = 9.2, 6.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.0 (C_q), 144.8 (C_q), 140.1 (C_q),

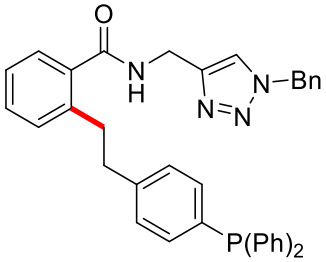
139.8 (C_q), 135.7 (C_q), 134.4 (C_q), 131.6 (C_q), 130.5 (CH), 130.2 (CH), 130.0 (CH), 129.2 (CH), 128.9 (CH), 128.3 (CH), 128.1 (CH), 127.0 (CH), 126.3 (CH), 122.1 (CH), 54.3 (CH_2), 37.2 (CH_2), 35.4 (CH_2), 35.1 (CH_2). (ESI) *m/z* (relative intensity): 883 (23) $[2M+Na]^+$, 453 (32) $[M+Na]^+$, 431 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{25}H_{24}ClN_4O$ $[M+H]^+$ 431.1633, found 431.1630.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-(4-fluorophenethyl)benzamide (3ag)



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 4-fluorostyrene **2g** (72 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ag** (51.4 mg, 62%) as a white solid. M.p. = 121-122 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 1H), 7.40 – 7.30 (m, 5H), 7.28 – 7.16 (m, 4H), 7.04 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.92 (t, *J* = 8.7 Hz, 2H), 6.36 (t, *J* = 5.7 Hz, 1H), 5.48 (s, 2H), 4.63 (d, *J* = 5.7 Hz, 2H), 3.02 (dd, *J* = 9.2, 6.5 Hz, 2H), 2.83 (dd, *J* = 9.3, 6.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.0 (C_q), 161.3 (d, $^1J_{C-F}$ = 245 Hz, C_q), 139.8 (2 x C_q), 137.3 (d, $^4J_{C-F}$ = 3 Hz, C_q), 135.8 (C_q), 134.4 (C_q), 130.5 (CH), 130.2 (CH), 129.9 (d, $^3J_{C-F}$ = 7 Hz, CH), 129.2 (CH), 128.9 (CH), 128.6 (CH), 128.1 (CH), 127.0 (CH), 126.2 (CH), 122.1 (CH), 115.0 (d, $^2J_{C-F}$ = 21 Hz, CH), 54.3 (CH_2), 37.1 (CH_2), 35.4 (CH_2), 35.3 (CH_2). ^{19}F-NMR (565 MHz, $CDCl_3$): δ = -117.4 (ddd, *J* = 14.2, 8.9, 5.4 Hz). (ESI) *m/z* (relative intensity): 453 (77) $[M+K]^+$, 437 (81) $[M+Na]^+$, 415 (100) $[M+H]^+$**.** HR-MS (ESI) *m/z* calcd for $C_{25}H_{24}FN_4O$ $[M+H]^+$ 415.1929, found 415.1926.

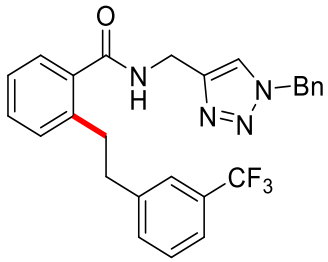
_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-[4-(diphenylphosphanyl)phenethyl]benzamide (3ah)



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 4-(Diphenylphosphino) styrene **2h** (80 µL, 0.60 mmol). Purification by column chromatography on

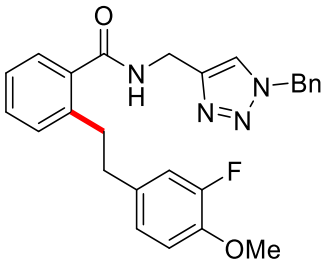
silica gel (*n*-hexane/EtOAc 1:1) yielded **3ah** (40.6 mg, 35%) as pale yellow waxy solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.38 – 7.29 (m, 15H), 7.26 – 7.18 (m, 6H), 7.11 (dd, *J* = 8.0, 1.5 Hz, 2H), 6.44 (bs, *J* = 5.2 Hz, 1H), 5.41 (s, 2H), 4.62 (d, *J* = 5.8 Hz, 2H), 3.03 (dd, *J* = 9.7, 6.4 Hz 2H), 2.85 (dd, *J* = 9.8, 6.3 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.0 (C_q), 144.8 (C_q), 142.6 (C_q), 140.0 (C_q), 137.4 (d, $J_{C\text{-}P}$ = 11 Hz, C_q), 135.7 (C_q), 134.4 (C_q), 134.2 (d, $J_{C\text{-}P}$ = 10 Hz, C_q), 133.9 (d, $J_{C\text{-}P}$ = 19 Hz, CH), 133.7 (d, $J_{C\text{-}P}$ = 19 Hz, CH), 130.4 (CH), 130.1 (CH), 129.2 (CH), 128.9 (CH), 128.8 (d, $J_{C\text{-}P}$ = 7 Hz, CH), 128.7 (CH), 128.5 (d, $J_{C\text{-}P}$ = 7 Hz, CH), 128.1 (CH), 127.0 (CH), 126.2 (CH), 122.2 (CH), 54.3 (CH_2), 37.7 (CH_2), 35.3 (CH_2), 35.1 (CH_2). ^{31}P-NMR (162 MHz, $CDCl_3$): δ = -6.29. (ESI) *m/z* (relative intensity): 603 (76) $[M+Na]^+$, 581 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{37}H_{34}N_4OP$ $[M+H]^+$ 581.2465, found 581.2461.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-[3-(trifluoromethyl)phenethyl]benzamide (3ai)



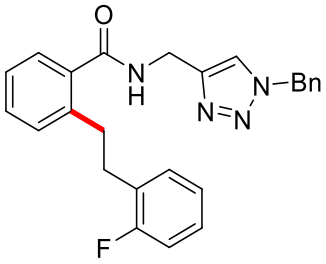
The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 3-(Trifluoromethyl)styrene **2i** (89 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ai** (62.2 mg, 67%) as a white solid. M.p. = 149-150 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.58 (bs, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.29 (m, 8H), 7.26 – 7.21 (m, 3H), 7.18 (d, *J* = 7.6, 1H), 6.42 (s, 1H), 5.49 (s, 2H), 4.65 (s, 2H), 3.08 – 3.04 (m, 2H), 2.95-2.91 (m, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.9 (C_q), 142.6 (C_q), 139.7 (C_q), 135.7 (C_q), 134.4 (C_q), 132.1 (2 x CH), 130.6 (C_q), 130.5 (CH), 130.5 (q, $^{2}J_{C\text{-}F}$ = 4 Hz, C_q), 130.3 (CH), 129.1 (CH), 128.9 (CH), 128.7 (CH), 128.1 (CH), 127.1 (CH), 126.4 (CH), 125.3 (q, $^{4}J_{C\text{-}F}$ = 4 Hz, CH), 124.3 (q, $^{1}J_{C\text{-}F}$ = 272 Hz, C_q), 122.8 (q, $^{3}J_{C\text{-}F}$ = 4 Hz, CH), 54.6 (CH_2), 37.7 (CH_2), 35.21 (CH_2), 29.7 (CH_2). ^{19}F-NMR (565 MHz, $CDCl_3$): δ = -62.3 (s). (ESI) *m/z* (relative intensity): 951 (14) $[2M+Na]^+$, 487 (100) $[M+Na]^+$, 465 (33) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{26}H_{24}F_3N_4O$ $[M+H]^+$ 465.1897, found 465.1900.

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-2-(3-fluoro-4-methoxyphenethyl)benzamide (3aj)**



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 3-fluoro-4-methoxystyrene **2j** (91.1 mg, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3aj** (49.8 mg, 56%) as a white solid. M.p. = 87-89 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 1H), 7.38 – 7.32 (m, 6H), 7.27 – 7.26 (m, 1H), 7.24 – 7.18 (m, 2H), 6.86 – 6.81 (m, 2H), 6.76 (dd, *J* = 8.0 Hz, *J* = 4 Hz, 1H), 6.33 (bs, 1H), 5.50 (s, 2H), 4.64 (d, *J* = 5.7 Hz, 2H), 3.86 (s, 3H), 3.01 (dd, *J* = 9.2, 6.5 Hz, 2H), 2.79 (dd, *J* = 9.2, 6.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.0 (C_q), 153.4 (d, $^{1}J_{C\text{-}F}$ = 245 Hz C_q), 151.0 (C_q), 144.8 (C_q), 139.8 (C_q), 135.8 (C_q), 134.8 (d, $^{3}J_{C\text{-}F}$ = 7 Hz, C_q), 134.5 (C_q), 130.4 (CH), 130.2 (CH), 129.2 (CH), 128.8 (CH), 128.1 (CH), 126.9 (CH), 126.2 (CH), 124.1 (d, $^{4}J_{C\text{-}F}$ = 3 Hz, CH), 122.1 (CH), 116.2 (d, $^{2}J_{C\text{-}F}$ = 18 Hz, CH) 113.2 (d, $^{5}J_{C\text{-}F}$ = 2 Hz, CH), 56.3 (CH_3), 54.2 (CH_2), 37.0 (CH_2), 35.4 (CH_2), 35.2 (CH_2). ^{19}F-NMR (565 MHz, $CDCl_3$): δ= -135.53 (dd, *J* = 12.5, 8.7 Hz). (ESI) *m/z* (relative intensity): 445 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{26}H_{26}FN_4O_2$ $[M+H]^+$ 445.2034, found 445.2037.

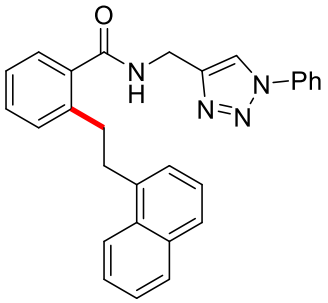
***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-2-(2-fluorophenethyl)benzamide (3ak)**



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 2-fluorostyrene **2k** (73.3 mg, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ak** (53.9 mg, 65%) as a white solid. M.p.= 128-130 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 1H), 7.37 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.26 (dd, *J* = 4.5, 1.7 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.17 – 7.13 (m, 1H), 7.06 (td, *J* = 7.5, 2.1 Hz, 1H), 7.01 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.29 (bs, 1H), 5.50 (s, 2H), 4.64 (d, *J* = 5.7 Hz, 2H), 3.05 (dd, *J* = 9.2, 6.4 Hz, 2H), 2.90 (dd, *J* = 9.3, 6.4 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.0 (C_q), 161.1 (d, $^{1}J_{C\text{-}F}$ = 244 Hz C_q), 145.0 (C_q),

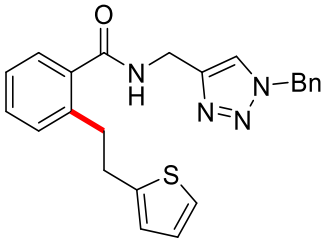
139.7 (C_q), 135.9 (C_q), 134.5 (C_q), 130.9 (d, $^4J_{C-F}$ = 5 Hz , CH), 130.5 (CH), 130.1 (CH), 129.1 (CH), 128.8 (CH), 128.3 (d, $^3J_{C-F}$ = 16 Hz C_q), 128.1 (CH), 127.7 (d, $^6J_{C-F}$ = 8 Hz , CH) , 126.9 (CH), 126.2 (CH), 123.9 (d, $^5J_{C-F}$ = 3 Hz , CH), 122.2 (CH), 115.1 (d, $^2J_{C-F}$ = 22 Hz , CH), 54.2 (CH_2), 35.4 (CH_2), 33.7 (CH_2), 31.0 (d, $^7J_{C-F}$ = 2 Hz, CH_2). ^{19}F-NMR (565 MHz, $CDCl_3$): δ = -118.75 (q, *J* = 8.8, 7.9 Hz). (ESI) *m/z* (relative intensity): 851 (16) $[2M+Na]^+$, 437 (27) $[M+Na]^+$, 415 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{25}H_{24}FN_4O$ $[M+H]^+$ 415.1929, found 415.1933.

2-[2-(Naphthalen-1-yl)ethyl]-*N*-[(1-phenyl-1*H*-1,2,3-triazol-4-yl)methyl]benzamide (3cl)



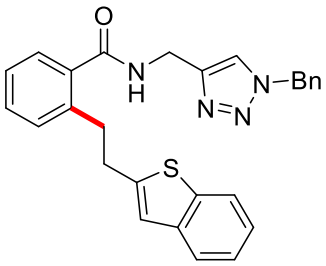
The representative procedure was followed using **1c** (55.6 mg, 0.20 mmol) and 1-vinylnaphthalene **2l** (89 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3cl** (51.0 mg, 59%) as a white solid. M.p. = 143-145 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.8 Hz, 1H), 8.00 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.57 (m, 2H), 7.56 – 7.51 (m, 1H), 7.50 – 7.37 (m, 5H), 7.35 – 7.30 (m, 3H), 7.24 (td, *J* = 7.4, 1.2 Hz, 1H), 7.17 (d, *J* = 6.8 Hz, 1H), 6.16 (t, *J* = 5.9 Hz, 1H), 4.52 (d, *J* = 5.8 Hz, 2H), 3.40 (dd, *J* = 9.3, 6.4 Hz, 2H), 3.24 (dd, *J* = 9.3, 6.4 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.2 (C_q), 145.3 (C_q), 140.3 (C_q), 137.7 (C_q), 136.9 (C_q), 136.0 (C_q), 133.8 (C_q), 131.9 (C_q), 130.5 (CH), 130.3 (CH), 129.7 (CH), 128.8 (CH), 128.7 (CH), 126.8 (CH), 126.8 (CH), 126.3 (CH), 126.2 (CH), 126.0 (CH), 125.6 (CH), 125.5 (CH), 124.0 (CH), 120.6 (CH), 120.4 (CH), 35.4 (CH_2), 35.1 (CH_2), 34.6 (CH_2). (ESI) *m/z* (relative intensity): 455 (100) $[M+Na]^+$, 433 (47) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{28}H_{25}N_4O$ $[M+H]^+$ 433.2023, found 433.2025.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-[2-(thiophen-2-yl)ethyl]benzamide (3am)



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 2-vinylthiophene **2m** (66.1 mg, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3am** (33.8 mg, 42%) as a white solid. M.p. = 101-103 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 1H), 7.39 – 7.32 (m, 5H), 7.27 – 7.20 (m, 4H), 7.09 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.88 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.66 (dd, *J* = 3.4, 1.1 Hz, 1H), 6.29 (s, 1H), 5.48 (s, 2H), 4.64 (d, *J* = 5.8 Hz, 2H), 3.09 (s, 4H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.0 (C_q), 145.0 (C_q), 144.2 (C_q), 139.3 (C_q), 136.0 (C_q), 134.5 (C_q), 130.3 (CH), 130.2 (CH), 129.2 (CH), 128.8 (CH), 128.1 (CH), 126.9 (CH), 126.8 (CH), 126.3 (CH), 124.6 (CH), 123.2 (CH), 122.2 (CH), 54.2 (CH_2), 35.4 (CH_2), 35.4 (CH_2), 31.8 (CH_2). (ESI) *m/z* (relative intensity): 827 (20) $[2M+Na]^+$, 452 (17), 441 (30) $[M+K]^+$, 425 (100) $[M+Na]^+$, 403 (44) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{23}H_{23}N_4OS$ $[M+H]^+$ 403.1587, found 403.1595.

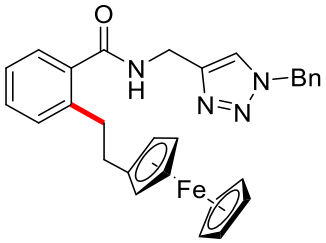
2-[2-(Benzo[b]thiophen-2-yl)ethyl]-_N_-[(1-benzyl-1_H_-1,2,3-triazol-4-yl)methyl]benzamide (3an)



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and 2-vinylbenzo[b]thiophene **2n** (96.1 mg, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3an** (40.7 mg, 45%) as a white solid. M.p. = 94-96 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.51 (s, 1H), 7.36 – 7.31 (m, 6H), 7.27 – 7.23 (m, 3H), 7.22 – 7.17 (m, 2H), 6.93 (s, 1H), 6.40 (bs, 1H), 5.39 (s, 2H), 4.60 (d, *J* = 5.8 Hz, 2H), 3.22 – 3.12 (m, 4H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.0 (C_q), 145.3 (C_q), 144.9 (C_q), 140.1 (C_q), 139.4 (C_q), 139.3 (C_q), 135.8 (C_q), 134.4 (C_q), 130.4 (CH), 130.3 (CH), 129.1 (CH), 128.8 (CH), 128.1 (CH), 127.0 (CH), 126.4 (CH), 125.8 (CH), 124.1 (CH), 123.6 (CH), 122.8 (CH), 122.1 (CH), 121.0 (CH),

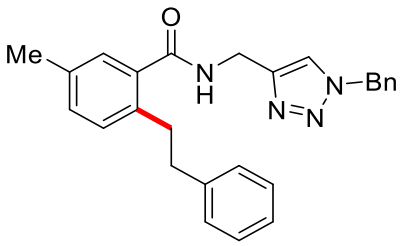
54.2 (CH_2), 35.3 (CH_2), 34.8 (CH_2), 32.6 (CH_2). (ESI) *m/z* (relative intensity): 927 (43) $[2M+Na]^+$, 475 (100) $[M+Na]^+$. HR-MS (ESI) *m/z* calcd for $C_{27}H_{24}N_4NaOS$ $[M+Na]^+$ 475.1743, found 475.1748.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-(2-(ferocenyl)ethyl)benzamide (3ao)



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and vinylferrocene **2o** (127.2 mg, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ao** (37.3 mg, 37%) as an orange viscous oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 1H), 7.42 – 7.33 (m, 5H), 7.26 – 7.18 (m, 4H), 6.13 (bs, 1H), 5.48 (s, 2H), 4.58 (d, *J* = 5.7 Hz, 2H), 4.18 (s, 1H), 4.11 (s, 4H), 4.01 (s, 2H), 3.91 (s, 2H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.2 (C_q), 145.0 (C_q), 139.9 (C_q), 136.2 (C_q), 134.6 (C_q), 130.1 (CH), 130.0 (CH), 129.2 (CH), 128.8 (CH), 128.2 (CH), 126.9 (CH), 126.0 (CH), 122.3 (CH), 88.3 (C_q), 68.8 (CH), 68.7 (CH), 68.4 (CH), 67.4 (CH), 54.2 (CH_2), 35.4 (CH_2), 34.5 (CH_2), 31.9 (CH_2). (ESI) *m/z* (relative intensity): 1031 (12) $[2M+Na]^+$, 543 (18) $[M+K]^+$, 527 (41) $[M+Na]^+$, 505 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{29}H_{29}FeN_4O$ $[M+H]^+$ 505.1686, found 505.1682.

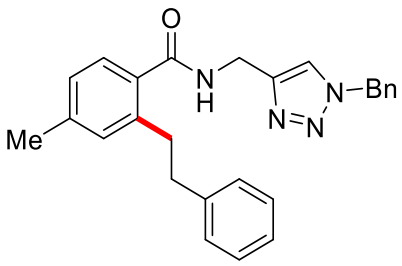
_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-5-methyl-2-phenethylbenzamide (3ea)



The representative procedure was followed using **1e** (61.3 mg, 0.20 mmol) and styrene **2a** (69 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ea** (54.2 mg, 66%) as a white solid. M.p. = 153-155 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.37 – 7.35 (m, 3H), 7.26 – 7.22 (m, 4H), 7.18 – 7.14 (m, 2H), 7.12 – 7.10 (m, 2H), 7.09 – 7.05 (m, 2H), 6.09 (s, 1H), 5.46 (s, 2H), 4.58 (d, *J* = 5.7 Hz, 2H), 2.99 (dd, *J* = 9.1, 6.5 Hz, 2H), 2.84 (dd, *J* = 9.2, 6.4 Hz, 2H), 2.32 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.2 (C_q), 145.0 (C_q), 141.7 (C_q), 136.7 (C_q), 135.8 (C_q), 135.7 (C_q), 134.5 (C_q), 130.8 (CH), 130.3 (CH), 129.2 (CH), 128.8 (CH), 128.6 (CH), 128.3 (CH),

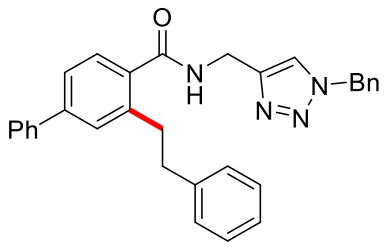
128.1 (CH), 127.4 (CH), 125.9 (CH), 122.2 (CH), 54.2 (CH_2), 38.0 (CH_2), 35.4 (CH_2), 34.7 (CH_2), 20.9 (CH_3). (ESI) *m/z* (relative intensity): 843 (60) $[2M+Na]^+$, 433 (62) $[M+Na]^+$, 411 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{26}H_{27}N_4O$ $[M+H]^+$ 411.2179 found 411.2184.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-4-methyl-2-phenethylbenzamide (3fa)



The representative procedure was followed using **1f** (61.3 mg, 0.20 mmol) and styrene **2a** (69 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3fa** (52.5 mg, 64%) as a white solid. M.p. = 125-127. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 1H), 7.37 – 7.35 (m, 3H), 7.26 – 7.23 (m, 4H), 7.21 – 7.15 (m, 2H), 7.10 (d, *J* = 6.5 Hz, 2H), 7.05 – 7.01 (m, 2H), 6.12 (s, 1H), 5.45 (s, 2H), 4.58 (d, *J* = 5.7 Hz, 2H), 3.02 (dd, *J* = 9.4, 6.4 Hz, 2H), 2.85 (dd, *J* = 9.5, 6.4 Hz, 2H), 2.35 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.2 (C_q), 145.1 (C_q), 141.8 (C_q), 140.2 (C_q), 140.0 (C_q), 134.5 (C_q), 133.0 (C_q), 131.2 (CH), 129.1 (CH), 128.8 (CH), 128.6 (CH), 128.3 (CH), 128.1 (CH), 127.0 (CH), 126.7 (CH), 125.9 (CH), 122.2 (CH), 54.2 (CH_2), 38.1 (CH_2), 35.4 (CH_2), 35.2 (CH_2), 21.3 (CH_3). (ESI) *m/z* (relative intensity): 843 (27) $[2M+Na]^+$, 433 (40) $[M+Na]^+$, 411 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{26}H_{27}N_4O$ $[M+H]^+$ 411.2179 found 411.2181.

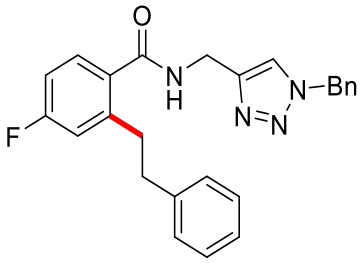
_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-3-phenethyl-[1,1'-biphenyl]-4-carboxamide (3ga)



The representative procedure was followed using **1g** (73.7 mg, 0.20 mmol) and styrene **2a** (69 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 6:4) yielded **3ga** (58.6 mg, 62%) as a white solid. M.p. = 163-165 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.57 – 7.52 (m, 3H), 7.49 – 7.40 (m, 6H), 7.40 – 7.35 (m, 4H), 7.27 – 7.25 (m, 3H), 7.22 – 7.17 (m, 1H), 7.13 – 7.08

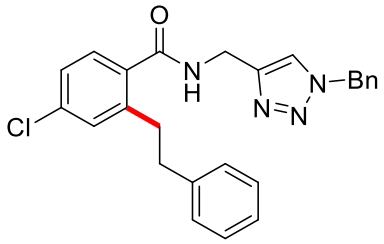
(m, 2H), 6.27 (bs, 1H), 5.46 (s, 2H), 4.62 (d, *J* = 5.7 Hz, 2H), 3.12 (dd, *J* = 9.1, 6.5 Hz, 2H), 2.92 (dd, *J* = 9.0, 6.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.9 (C_q), 145.0 (C_q), 142.9 (C_q), 141.6 (C_q), 140.5 (C_q), 140.3 (C_q), 134.7 (C_q), 134.5 (C_q), 129.3 (CH), 129.2 (CH), 128.8 (2 x CH), 128.7 (CH), 128.4 (CH), 128.1 (CH), 127.8 (CH), 127.5 (CH), 127.2 (CH), 126.0 (CH), 124.8 (CH), 122.2 (CH), 54.2 (CH_2), 38.0 (CH_2), 35.5 (CH_2), 35.4 (CH_2). (ESI) *m/z* (relative intensity): 495 (47) $[M+Na]^+$, 473 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{31}H_{29}N_4O$ $[M+H]^+$ 473.2336 found 473.2339.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-4-fluoro-2-phenethylbenzamide (3ha)



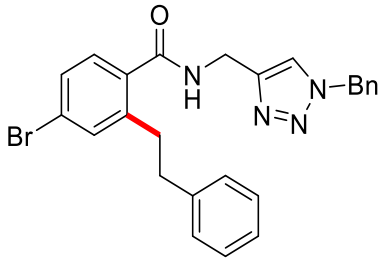
The representative procedure was followed using **1h** (62.1 mg, 0.20 mmol) and styrene **2a** (69 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ha** (47.3 mg, 57%) as a white solid. M.p. = 110-112 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 1H), 7.38-7.36 (m, 4H), 7.27 – 7.23 (m, 4H), 7.19 – 7.16 (m, 1H), 7.07 (d, *J* = 6.9 Hz, 2H), 6.94 – 6.87 (m, 2H), 6.15 (t, *J* = 5.7 Hz, 1H), 5.46 (s, 2H), 4.57 (d, *J* = 5.7 Hz, 2H), 3.05 (dd, *J* = 8.9, 6.6 Hz, 2H), 2.86 (dd, *J* = 9.0, 6.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.2 (C_q), 163.4 (d, $^1J_{C\text{-}F}$ = 250 Hz C_q), 144.7 (C_q), 143.2 (d, $^5J_{C\text{-}F}$ = 9 Hz, C_q), 141.1 (C_q), 134.3 (C_q), 132.1 (d, $^6J_{C\text{-}F}$ = 3 Hz, C_q), 129.2 (CH), 129.0 (d, $^4J_{C\text{-}F}$ = 8 Hz, CH), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 126.1 (CH), 122.2 (CH), 117.1 (d, $^2J_{C\text{-}F}$ = 21 Hz CH), 113.1 (d, $^3J_{C\text{-}F}$ = 21 Hz CH), 54.3 (CH_2), 37.6 (CH_2), 35.3 (CH_2), 35.0 (CH_2). ^{19}F-NMR (565 MHz, $CDCl_3$): δ= -110.28 – -110.36 (m). (ESI) *m/z* (relative intensity): 437 (39) $[M+Na]^+$, 415 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{25}H_{24}FN_4O$ $[M+H]^+$ 415.1929, found 415.1932.

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-4-chloro-2-phenethylbenzamide (3ia)**



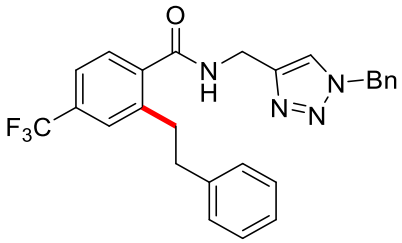
The representative procedure was followed using **1i** (65.4 mg, 0.20 mmol) and styrene **2a** (69 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ia** (43.1 mg, 50%) as a white solid. M.p. = 127-129 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 7.38 – 7.36 (m, 3H), 7.27 – 7.23 (m, 6H), 7.19 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.07 (d, *J* = 7.3 Hz, 2H), 6.14 (bs, 1H), 5.46 (s, 2H), 4.56 (d, *J* = 5.7 Hz, 2H), 3.02 (dd, *J* = 9.1, 6.5 Hz, 2H), 2.85 (dd, *J* = 9.1, 6.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.1 (C_q), 144.7 (C_q), 142.1 (C_q), 141.1 (C_q), 135.9 (C_q), 134.4 (C_q), 134.4 (C_q), 130.4 (CH), 129.2 (CH), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 126.3 (CH), 126.1 (CH), 122.1 (CH), 54.3 (CH_2), 37.7 (CH_2), 35.4 (CH_2), 34.9 (CH_2). (ESI) *m/z* (relative intensity): 453 (36) $[M+Na]^+$, 431 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{25}H_{24}ClN_4O$ $[M+H]^+$ 431.1633, found 431.1635.

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-4-bromo-2-phenethylbenzamide (3ja)**



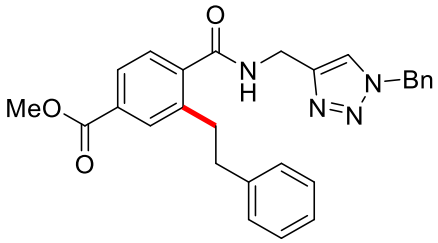
The representative procedure was followed using **1j** (74.2 mg, 0.20 mmol) and styrene **2a** (69 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ja** (43.7 mg, 46%) as a white solid. M.p. = 99-101 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 7.39 – 7.33 (m, 5H), 7.26 – 7.23 (m, 4H), 7.19 – 7.17 (m, 2H), 7.06 (d, *J* = 6.8 Hz, 2H), 6.17 (s, 1H), 5.46 (s, 2H), 4.55 (d, *J* = 5.7 Hz, 2H), 3.00 (dd, *J* = 9.1, 6.4 Hz, 2H), 2.85 (dd, *J* = 9.2, 6.4 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.1 (C_q), 144.7 (C_q), 142.3 (C_q), 141.1 (C_q), 134.8 (C_q), 134.4 (C_q), 133.3 (CH), 129.2 (2 x CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 126.1 (CH), 124.3 (C_q), 122.1 (CH), 54.2 (CH_2), 37.7 (CH_2), 35.4 (CH_2), 34.9 (CH_2). (ESI) *m/z* (relative intensity): 497 (86) $[M+Na]^+$, 475 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{25}H_{24}BrN_4O$ $[M+H]^+$ 475.1128, found 475.1132.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-phenethyl-4-(trifluoromethyl)benzamide (3ka)



The representative procedure was followed using **1k** (61.3 mg, 0.20 mmol) and styrene **2a** (69 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3ka** (30.7 mg, 33%) as a white solid. M.p. = 135-137 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.48 – 7.45 (m, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.36 (m, 3H), 7.27 – 7.23 (m, 4H), 7.20 – 7.16 (m, 1H), 7.04 (d, *J* = 6.7 Hz, 2H), 6.21 (bs, 1H), 5.47 (s, 2H), 4.59 (d, *J* = 5.7 Hz, 2H), 3.07 (dd, *J* = 9.0, 6.6 Hz, 2H), 2.88 (dd, *J* = 8.9, 6.6 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 168.8 (C_q), 144.5 (C_q), 140.9 (C_q), 140.8 (C_q), 139.3 (C_q), 134.4 (C_q), 131.9 (q, $^{2}J_{C\text{-}F}$ = 33 Hz C_q), 129.2 (CH), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.1 (CH), 127.4 (CH), 127.1 (q, $^{3}J_{C\text{-}F}$ = 4 Hz, CH), 126.2 (CH), 123.6 (q, $^{1}J_{C\text{-}F}$ = 273 Hz, C_q), 123.0 (q, $^{4}J_{C\text{-}F}$ = 4 Hz, CH), 122.2 (CH), 54.3 (CH_2), 37.7 (CH_2), 35.4 (CH_2), 35.0 (CH_2). ^{19}F-NMR (565 MHz, $CDCl_3$): δ= -62.8 (s). (ESI) *m/z* (relative intensity): 487 (56) $[M+Na]^+$, 465 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{26}H_{24}F_3N_4O$ $[M+H]^+$ 465.1897 found 465.1901.

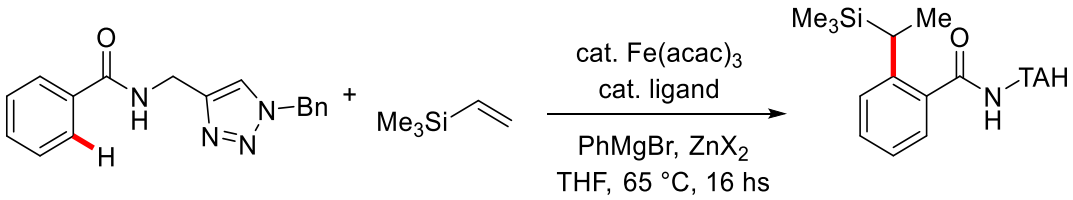
Methyl 4-{[(1-benzyl-1_H_-1,2,3-triazol-4-yl)methyl]carbamoyl}-3-phenethylbenzoate (3la)



The representative procedure was followed using **1l** (70.1 mg, 0.20 mmol) and styrene **2a** (69 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **3la** (31.8 mg, 35%) as a white solid. M.p. = 84-85 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 1.7 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.52 (s, 1H), 7.39 – 7.33 (m, 5H), 7.28 – 7.21 (m, 3H), 7.20 – 7.15 (m, 1H), 7.05 (d, *J* = 6.8 Hz, 2H), 6.20 (bs, 1H), 5.45 (s, 2H), 4.56 (d, *J* = 5.7 Hz, 2H), 3.95 (s, 3H), 3.05 (dd, *J* = 9.2, 6.4 Hz, 2H), 2.88 (dd, *J* = 9.0, 6.5 Hz, 2H).^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.3 (C_q), 166.5 (C_q), 144.7 (C_q), 141.2 (C_q), 140.2 (C_q), 140.1 (C_q), 134.4 (C_q), 131.4 (C_q), 131.4 (CH), 129.2 (CH), 128.9 (CH), 128.6 (CH), 128.4 (CH), 128.1 (CH), 127.3 (CH), 127.0 (CH), 126.1 (CH), 122.2 (CH), 54.2 (CH_2),

52.3 (CH_3), 37.8 (CH_2), 35.4 (CH_2), 35.0 (CH_2). (ESI) *m/z* (relative intensity): 931 (68) $[2M+Na]^+$, 477 (100) $[M+Na]^+$, 455 (70) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{27}H_{27}N_4O_3$ $[M+H]^+$ 455.2078 found 455.2081.

- **Variation of key parameters for iron-catalyzed C–H alkylation with vinylsilanes**

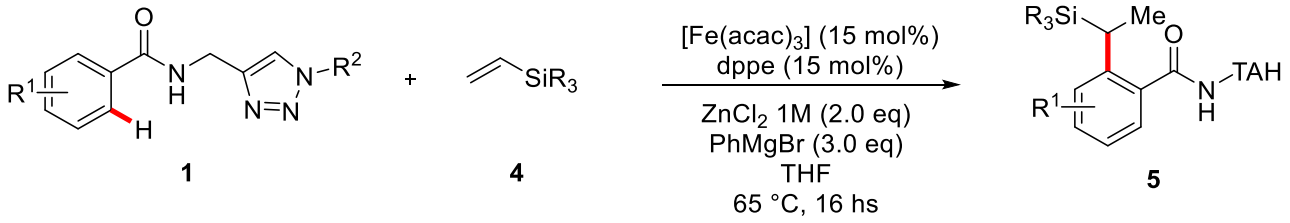


1a **4a** **5aa**

Entry[a]	ligand	ZnX_2	**5aa** (%)[b]
1	dppen	$ZnBr_2$	25
2	dppe	$ZnBr_2$	53 (45)
3	dppe	$ZnCl_2$	73 (64)
4	dppe	--	--

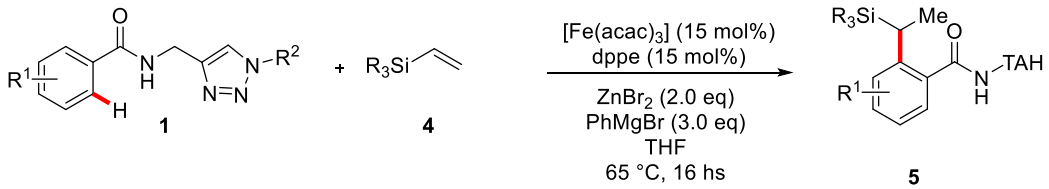
[a] Reaction conditions: **1a** (0.20 mmol), **4a** (0.60 mmol), $Fe(acac)_3$ (0.03 mmol), ligand (0.03 mmol), PhMgBr (0.60 mmol), ZnX_2 (0.40 mmol), THF (0.5 ml), 65 °C. [b] Yields determined using 1,3,5-trimethoxybenzene as the internal standard. In parenthesis, isolated yields.

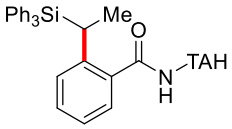
- **Representative procedure for iron-catalyzed C–H alkylation with vinylsilanes**



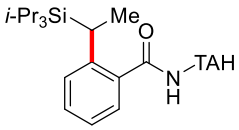
To a stirred solution of $Fe(acac)_3$ (10.6 mg, 0.03 mmol), dppe (11.9 mg, 0.03 mmol) zinc chloride (1 M in THF, 400 µl, 0.4 mmol, 2.0 equiv) and **1** (0.20 mmol) under N_2 atmosphere, PhMgBr (1.0 M in THF, 600 µl, 0.6 mmol, 3.0 equiv) was added in a single portion. Then, **4** (0.6 mmol, 3.0 equiv) was added and the mixture was placed in a pre-heated oil bath at 65 °C. After stirring for 16 hs, the reaction was cooled to room temperature and quenched by the addition of an aqueous solution of HCl (1.0 M, 5 ml). The reaction was extracted with CH_2Cl_2 (3x15 ml) and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc).

- **Substrate scope limitations for C–H alkylation with vinylsilanes**

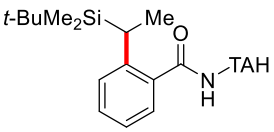




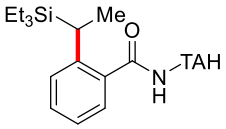
n.r



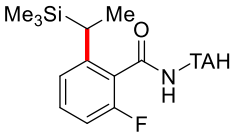
n.r.



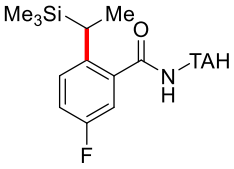
trace



16%



n.r



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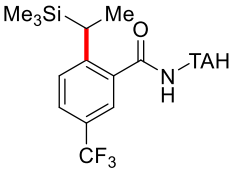

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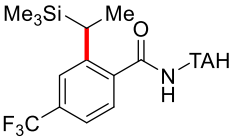
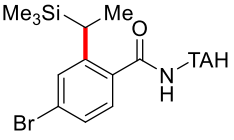


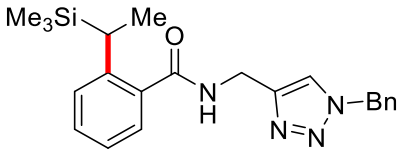
n.r



n.r

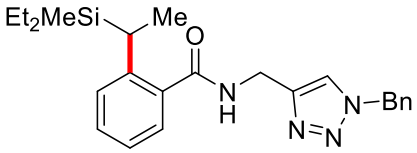
- **Characterization data for compounds 5**

***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-2-[1-(trimethylsilyl)ethyl]benzamide (5aa)**



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and vinyltrimethylsilane **4a** (88 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 6:4) yielded **5aa** (50.1 mg, 64%, *b:l* = 20:1) as a white solid. M.p. = 84-85 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 1H), 7.42 – 7.26 (m, 7H), 7.17 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.08 (td, *J* = 7.4, 1.2 Hz, 1H), 6.49 (s, 1H), 5.52 (s, 2H), 4.66 (d, *J* = 5.7 Hz, 2H), 2.81 (q, *J* = 7.4 Hz, 1H), 1.34 (d, *J* = 7.4 Hz, 3H), -0.10 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.5 (C_q), 145.3 (C_q), 144.9 (C_q), 134.8 (C_q), 134.4 (C_q), 129.9 (CH), 129.2 (CH), 128.9 (CH), 128.1 (CH), 127.5 (CH), 126.9 (CH), 124.1 (CH), 122.2 (CH), 54.3 (CH_2), 35.3 (CH_2), 24.6 (CH), 16.1 (CH_3), -2.9 (CH_3). (ESI) *m/z* (relative intensity): 807 (39) $[2M+Na]^+$, 415 (46) $[M+Na]^+$, 393(100) $[M+H]^+$, 144 (33). HR-MS (ESI) *m/z* calcd for $C_{22}H_{29}N_4OSi$ $[M+H]^+$ 393.2105, found 393.2109.

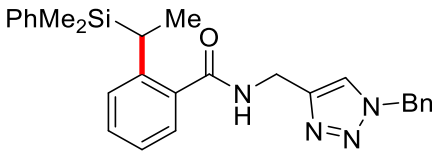
***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-2-{1-[diethyl(methyl)silyl]ethyl}benzamide (5ab)**



The representative procedure was followed using **1a** (58.5 mg, 0.2 mmol) and diethylmethylvinylsilane **4b** (77.0 mg, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **5ab** (40.4 mg, 48%, *b:l* = 17:1) as a white solid. M.p. = 86-88 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 1H), 7.44 – 7.37 (m, 3H), 7.36 – 7.29 (m, 3H), 7.28 – 7.25 (m, 1H), 7.21 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.08 (td, *J* = 7.5, 1.3 Hz, 1H), 6.42 (s, 1H), 5.53 (s, 2H), 4.67 (dd, *J* = 5.7, 4.6 Hz, 2H), 2.87 (q, *J* = 7.5 Hz, 1H), 1.35 (d, *J* = 7.5 Hz, 3H), 0.84 (t, *J* = 7.9 Hz, 3H), 0.78 (t, *J* = 7.9 Hz, 3H), 0.53 – 0.35 (m, 4H), -0.12 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.5 (C_q), 145.4 (C_q), 144.9 (C_q), 134.8 (C_q), 134.3 (C_q), 129.9 (CH), 129.2 (CH), 128.9 (CH), 128.2 (CH), 127.9 (CH), 127.0 (CH), 124.1 (CH), 122.2 (CH), 54.4 (CH_2), 35.2 (CH_2), 22.9 (CH), 16.6 (CH_3), 7.4 (CH_3), 7.4 (CH_3), 3.9 (CH_2),

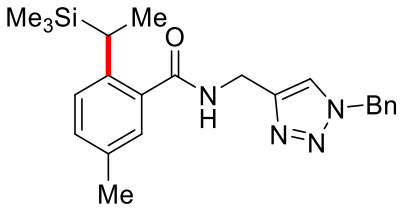
3.8 (CH_2), -7.6 (CH_3). (ESI) *m/z* (relative intensity): 863 (25) $[2M+Na]^+$, 443 (100) $[M+Na]^+$, 421 (67) $[M+H]^+$, 377 (28). HR-MS (ESI) *m/z* calcd for $C_{24}H_{33}N_4OSi$ $[M+H]^+$ 421.2418, found 421.2427.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-{1-[dimethyl(phenyl)silyl]ethyl}benzamide (5ac)



The representative procedure was followed using **1a** (58.5 mg, 0.20 mmol) and dimethylphenylvinylsilane **4c** (88 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 6:4) yielded **5ac** (45.5 mg, 50%, *b:l* = 8:1) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 7.39 – 7.37 (m, 4H), 7.33 – 7.29 (m, 3H), 7.26 – 7.22 (m, 2H), 7.19 – 7.12 (m, 4H), 7.08 (td, *J* = 7.4, 1.2 Hz, 1H), 5.62 – 5.55 (m, 1H), 5.50 (d, *J* = 3.9 Hz, 2H), 4.49 (dd, *J* = 15.1, 5.9 Hz, 1H), 4.32 (dd, *J* = 15.1, 5.6 Hz, 1H), 2.96 (q, *J* = 7.4 Hz, 1H), 1.37 (d, *J* = 7.4 Hz, 3H), 0.28 (s, 3H), 0.19 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.6 (C_q), 145.0 (C_q), 144.0 (C_q), 137.7 (C_q), 135.3 (C_q), 134.5 (C_q), 134.2 (CH), 129.7 (CH), 129.2 (CH), 129.1 (CH), 128.8 (CH), 128.2 (CH), 128.1 (CH), 127.6 (CH), 126.9 (CH), 124.3 (CH), 122.3 (CH), 54.3 (CH_2), 35.4 (CH_2), 24.7 (CH), 15.9 (CH_3), -4.9 (CH_3), -5.1 (CH_3). (ESI) *m/z* (relative intensity): 931 (89) $[2M+Na]^+$, 493 (20) $[M+K]^+$, 477 (100) $[M+Na]^+$, 455 (34) $[M+H]^+$, 377 (28). HR-MS (ESI) *m/z* calcd for $C_{27}H_{31}N_4OSi$ $[M+H]^+$ 455.2262, found 455.2266.

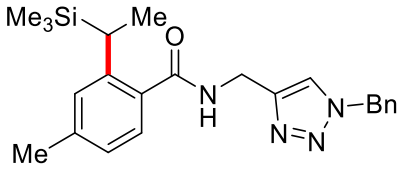
_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-5-methyl-2-[1-(trimethylsilyl)ethyl]benzamide (5ea)



The representative procedure was followed using **1e** (61.3 mg, 0.20 mmol) and vinyltrimethylsilane **4a** (88 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **5ea** (42.5 mg, 52%, *b:l* = 15:1) as a white solid. M.p. = 157-159 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 1H), 7.41 – 7.37 (m, 3H), 7.31 – 7.29 (m, 2H), 7.15 – 7.13 (m, 1H), 7.08 – 7.05 (m, 2H), 6.38 (bs, 1H), 5.53 (s, 2H), 4.66 (d, *J* = 5.7 Hz, 2H), 2.75 (q, *J* = 7.5 Hz, 1H), 2.29 (s, 3H), 1.32 (d, *J* = 7.5 Hz, 3H), -0.10 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.6 (C_q), 145.0 (C_q), 142.0 (C_q), 134.7 (C_q), 134.5 (C_q), 133.6 (C_q), 130.7 (CH), 129.2 (CH), 128.9 (CH), 128.2 (CH), 127.5 (CH), 127.4 (CH), 122.1 (CH), 54.3 (CH_2), 35.3 (CH_2), 24.1 (CH), 20.7 (CH_3), 16.2 (CH_3), -3.0 (CH_3). (ESI) *m/z* (relative intensity):

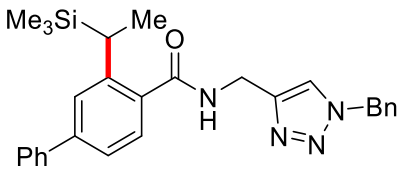
835 (48) $[2M+Na]^+$, 445 (14) $[M+K]^+$, 429 (53) $[M+Na]^+$, 407 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{23}H_{31}N_4OSi$ $[M+H]^+$ 407.2262, found 407.2265.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-4-methyl-2-[1-(trimethylsilyl)ethyl]benzamide (5fa)



The representative procedure was followed using **1f** (61.3 mg, 0.20 mmol) and vinyltrimethylsilane **4a** (88 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **5fa** (41.5 mg, 51%, *b:l* = 15:1) as a white solid. M.p.= 106-108 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 1H), 7.40 – 7.37 (m, 3H), 7.30 (dd, *J* = 4.4, 2.4 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 6.97 (s, 1H), 6.88 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.38 (bs, 1H), 5.53 (s, 2H), 4.65 (d, *J* = 5.7 Hz, 2H), 2.87 (q, *J* = 7.4 Hz, 1H), 2.34 (s, 3H), 1.34 (d, *J* = 7.5 Hz, 3H), -0.10 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.6 (C_q), 145.4 (C_q), 145.1 (C_q), 139.8 (C_q), 134.4 (C_q), 131.9 (C_q), 129.2 (CH), 128.9 (CH), 128.2 (CH), 128.1 (CH), 127.0 (CH), 124.8 (CH), 122.1 (CH), 54.3 (CH_2), 35.3 (CH_2), 24.3 (CH), 21.6 (CH_3), 16.0 (CH_3), -3.0 (CH_3). (ESI) *m/z* (relative intensity): 835 (81) $[2M+Na]^+$, 429 (48) $[M+Na]^+$, 407 (100) $[M+H]^+$, 143 (14). HR-MS (ESI) *m/z* calcd for $C_{23}H_{31}N_4OSi$ $[M+H]^+$ 407.2262, found 407.2268.

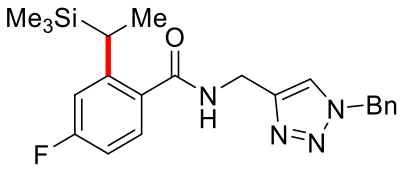
_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-3-[1-(trimethylsilyl)ethyl]-[1,1'-biphenyl]-4-carboxamide (5ga)



The representative procedure was followed using **1g** (73.7 mg, 0.20 mmol) and vinyltrimethylsilane **4a** (88 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **5ga** (42.2 mg, 45%, *b:l* = 167: 1) as a white solid. M.p. = 171-172 °C.^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.58 – 7.56 (m, 3H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.41 – 7.38 (m, 5H), 7.36 (s, 1H), 7.33 – 7.29 (m, 3H), 6.47 (t, *J* = 5.7 Hz, 1H), 5.54 (s, 2H), 4.69 (d, *J* = 5.7 Hz, 2H), 2.94 (q, *J* = 7.4 Hz, 1H), 1.41 (d, *J* = 7.5 Hz, 3H), -0.05 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.3 (C_q), 146.0 (C_q), 144.9 (C_q), 142.7 (C_q), 140.7 (C_q), 134.4 (C_q), 133.6 (C_q), 129.2 (CH), 128.9 (CH), 128.8 (CH), 128.2 (CH), 127.7 (CH), 127.5 (CH),

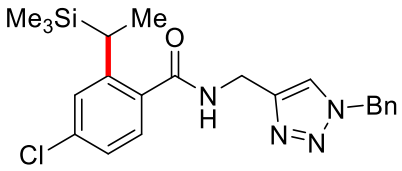
127.2 (CH), 126.3 (CH), 123.0 (CH), 122.1 (CH), 54.3 (CH_2), 35.3 (CH_2), 24.6 (CH), 16.1 (CH_3), -2.9 (CH_3). (ESI) *m/z* (relative intensity): 469 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{28}H_{33}N_4OSi$ $[M+H]^+$ 469.2418, found 469.2423.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-4-chloro-2-(1-(trimethylsilyl)ethyl)benzamide (5ha)



The representative procedure was followed using **1h** (62.1 mg, 0.20 mmol) and vinyltrimethylsilane **4a** (88 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **5ha** (27.9 mg, 34%, *b:l* =21:1) as a white solid. M.p. = 155-156 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 1H), 7.40 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.33 – 7.29 (m, 3H), 6.85 (dd, *J* = 10.9, 2.6 Hz, 1H), 6.77 (td, *J* = 8.2, 2.6 Hz, 1H), 6.55 (s, 1H), 5.53 (s, 2H), 4.65 (d, *J* = 5.5 Hz, 2H), 2.94 (qd, *J* = 7.4, 1.8 Hz, 1H), 1.33 (d, *J* = 7.4 Hz, 3H), -0.09 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.7 (C_q), 163.7 (d, $^1J_{C-F}$ = 249 Hz, C_q), 149.2 (d, $^5J_{C-F}$ = 8.0 Hz, C_q), 149.14 (CH), 134.3 (2 x C_q) 130.7 (d, $^6J_{C-F}$ = 3 Hz, C_q), 129.2 (CH), 129.0 (d, $^4J_{C-F}$ = 9 Hz, CH), 129.0 (CH), 128.2 (CH), 122.2 (CH), 114.2 (d, $^2J_{C-F}$ = 22 Hz, CH), 111.0 (d, $^3J_{C-F}$ = 22 Hz, CH), 54.4 (CH_2), 35.2 (CH_2), 24.9 (d, J_{C-F} = 2 Hz CH), 15.8 (CH_3), -3.1 (CH_3). ^{19}F-NMR (565 MHz, $CDCl_3$): δ= -110.2 – -110.3 (m). (ESI) *m/z* (relative intensity): 483 (10) $[2M+Na]^+$, 449 (27) $[M+K]^+$, 433 (100) $[M+Na]^+$, 411 (40) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{22}H_{28}FN_4OSi$ $[M+H]^+$ 411.2011, found 411.2016.

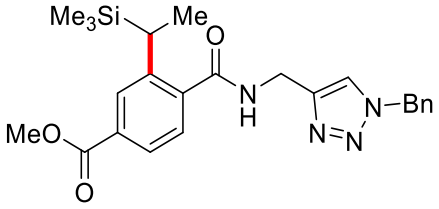
_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-4-chloro-2-[1-(trimethylsilyl)ethyl]benzamide (5ia)



The representative procedure was followed using **1i** (65.4 mg, 0.20 mmol) and vinyltrimethylsilane **4a** (88 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **5ha** (25.6 mg, 30%, *b:l* = 22.: 1) as a white solid. M.p. = 121-122 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.40 – 7.38 (m, 3H), 7.31 – 7.29 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 2.1 Hz, 1H), 7.07 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.44 (bs, 1H), 5.53 (s, 2H), 4.65 (d, *J* = 5.7 Hz, 2H), 2.86 (q, *J* = 7.4

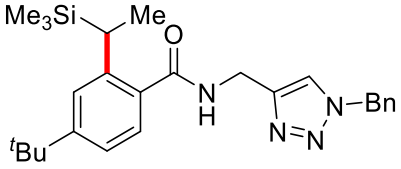
Hz, 1H), 1.33 (d, *J* = 7.4 Hz, 3H), -0.08 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.5 (C_q), 147.9 (C_q), 144.7 (C_q), 136.1 (C_q), 134.4 (C_q), 133.1 (C_q), 129.2 (CH), 128.9 (CH), 128.3 (CH), 128.2 (CH), 127.5 (CH), 124.3 (CH), 122.0 (CH), 54.3 (CH_2), 35.3 (CH_2), 24.8 (CH), 15.9 (CH_3), -3.1 (CH_3). (ESI) *m/z* (relative intensity): 875 (27) $[2M+Na]^+$, 449 (21) $[M+Na]^+$, 427 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{22}H_{28}ClN_4OSi$ $[M+H]^+$ 427.1715, found 427.1719.

Methyl-4-{[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]carbamoyl}-3-(1-(trimethylsilyl)ethyl)benzoate (5la)



The representative procedure was followed using **1l** (70.1 mg, 0.20 mmol) and vinyltrimethylsilane **4a** (88 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **5la** (37.0 mg, 41%, *b:l* =17:1) as a white solid. M.p. = 161-162 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.85 (s, 1H), 7.73 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.57 (s, 1H), 7.40 – 7.38 (m, 3H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.29 (m, 2H), 6.66 (bs, 1H), 5.52 (s, 2H), 4.66 (d, *J* = 5.6 Hz, 2H), 3.92 (s, 3H), 2.78 (q, *J* = 7.4 Hz, 1H), 1.37 (d, *J* = 7.5 Hz, 3H), -0.09 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.7 (C_q), 166.7 (C_q), 145.8 (C_q), 138.8 (C_q), 134.3 (2 x C_q), 131.2 (C_q). 129.2 (CH), 128.9 (CH), 128.6 (CH), 128.2 (CH), 127.1 (CH), 125.3 (CH), 122.2 (CH), 54.3 (CH_2), 52.3 (CH_3), 35.2 (CH_2), 24.9 (CH), 16.0 (CH_3), -3.0 (CH_3). (ESI) *m/z* (relative intensity): 489 (65) $[M+K]^+$, 473 (53) $[M+Na]^+$, 451 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{24}H_{31}N_4O_3Si$ $[M+H]^+$ 451.2160, found 451.2166.

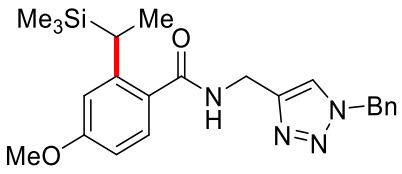
***N*-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-4-(*tert*-butyl)-2-[1-(trimethylsilyl)ethyl]benzamide (5ma)**



The representative procedure was followed using **1m** (69.7 mg, 0.20 mmol) and vinyltrimethylsilane **4a** (88 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1)

yielded **5ma** (33.2 mg, 37%, *b:l* =13:1) as a white solid. M.p. = 142-143 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 1H), 7.40 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.31 (d, *J* = 2.8 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.09 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.47 (bs, 1H), 5.53 (s, 2H), 4.67 (d, *J* = 5.6 Hz, 2H), 2.88 (q, *J* = 7.4 Hz, 1H), 1.36 (d, *J* = 7.3 Hz, 3H), 1.31 (s, 9H), -0.10 (s, 9H).^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.6 (C_q), 152.9 (C_q), 144.9 (C_q), 134.2 (C_q), 131.8 (C_q), 129.2 (CH), 128.9 (CH), 128.6 (C_q), 128.2 (CH), 126.8 (CH), 124.8 (CH), 122.3 (CH), 121.0 (CH), 54.4 (CH_2), 35.1 (CH_2), 34.7 (C_q), 31.2 (CH_3), 24.5 (CH), 16.1 (CH_3), -3.0 (CH_3). (ESI) *m/z* (relative intensity): 487 (60) $[M+K]^+$, 471 (100) $[M+Na]^+$, 449 (20) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{26}H_{37}N_4OSi$ $[M+H]^+$ 449.2731, found 449.2737.

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-4-methoxy-2-[1-(trimethylsilyl)ethyl]benzamide (5na)

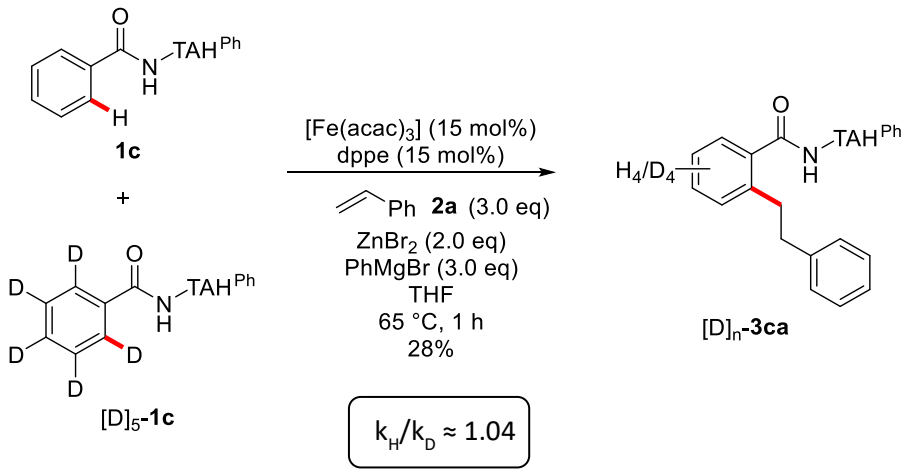


The representative procedure was followed using **1n** (64.5 mg, 0.20 mmol) and vinyltrimethylsilane **4a** (88 µL, 0.60 mmol). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded **5na** (38.9 mg, 46%, *b:l* = 22:1) as a colourless waxy solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 1H), 7.42 – 7.29 (m, 5H), 7.27 (d, *J* = 8.6 Hz, 1H), 6.69 (d, *J* = 2.5 Hz, 1H), 6.60 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.40 (bs, 1H), 5.52 (s, 2H), 4.64 (d, *J* = 5.7 Hz, 2H), 3.81 (s, 3H), 3.01 (q, *J* = 7.4 Hz, 1H), 1.33 (d, *J* = 7.5 Hz, 3H), -0.09 (s, 9H).^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.2 (C_q), 160.8 (C_q), 148.1 (C_q), 145.1 (C_q), 134.5 (C_q), 129.2 (CH), 128.9 (CH), 128.7 (CH), 128.2 (CH), 127.3 (C_q), 122.1 (CH), 113.3 (CH), 108.9 (CH), 55.1 (CH_3), 54.3 (CH_2), 35.3 (CH_2), 24.4 (CH), 15.9 (CH_3), -3.0 (CH_3). (ESI) *m/z* (relative intensity): 445 (86) $[M+Na]^+$, 423 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{23}H_{31}N_4O_2Si$ $[M+H]^+$ 423.2211, found 423.2218.

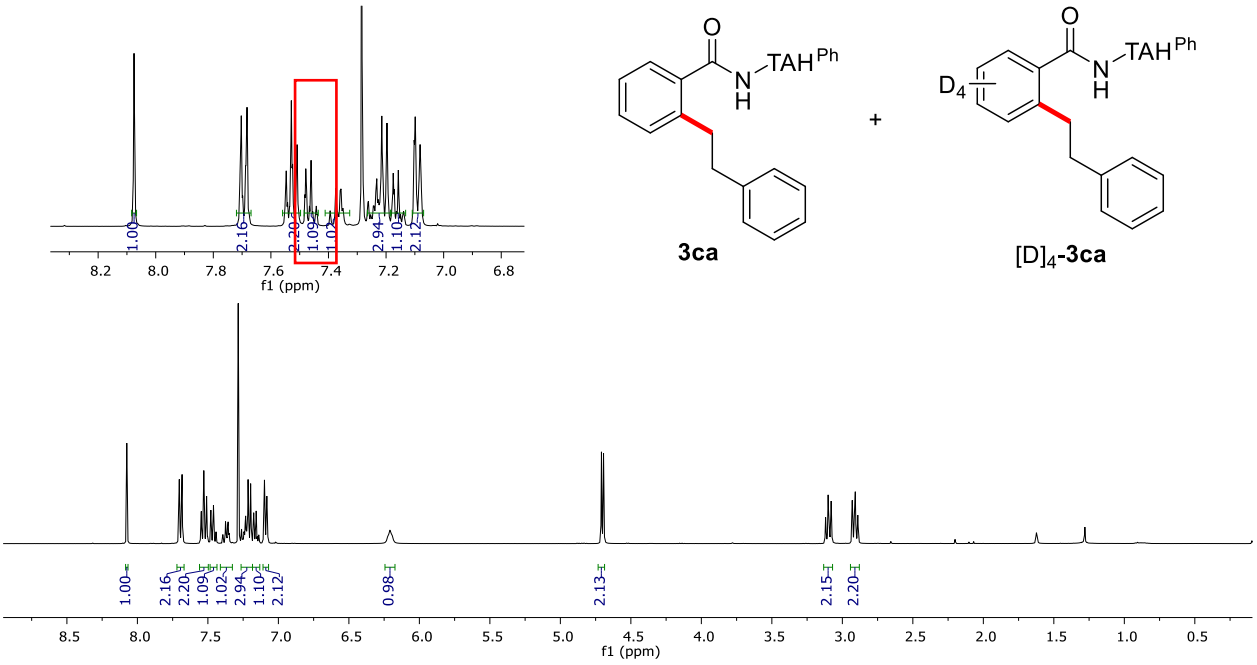
- **Key Mechanistic Findings**

KIE Experiments

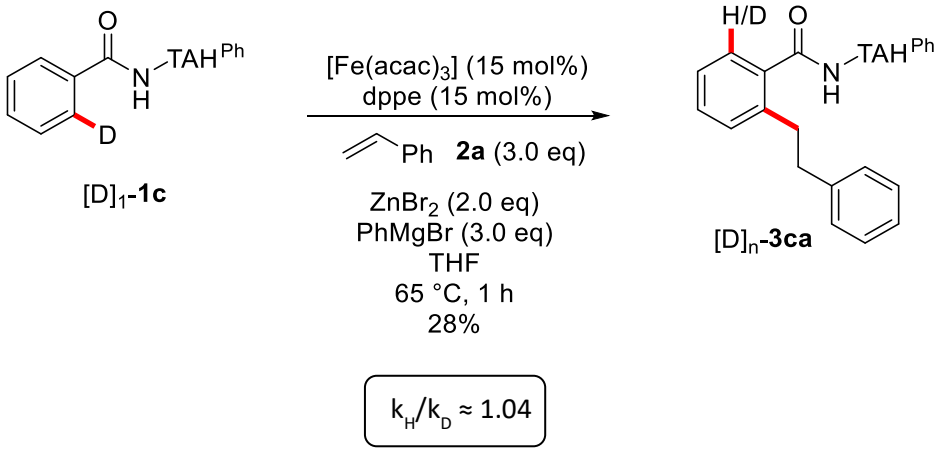
Intermolecular KIE



To a stirred solution of $Fe(acac)_3$ (10.6 mg, 0.03 mmol), dppe (11.9 mg, 0.03 mmol), zinc bromide (90.0 mg, 0.40 mmol), **1c** (27.8 mg, 0.10 mmol) and $[D]_5$-**1c** (28.3 mg, 0.10 mmol) in THF (0.4 ml) under N_2 atmosphere, PhMgBr (1.0 M in THF, 600 µl, 0.60 mmol) was added in a single portion. Then, styrene **2a** (69 µL, 0.60 mmol) was added and the mixture was placed in a pre-heated oil bath at 65 °C. After stirring for 1 h, the reaction was cooled to room temperature and quenched by the addition of an aqueous solution of HCl (1.0 M, 5 ml). The reaction was extracted with CH_2Cl_2 (3x15 ml) and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography (*n*-hexane/EtOAc). The mixture was analysed by 400 MHz ^{1}H-NMR spectroscopy to determine the ratio of **3ca**/$[D]_4$-**3ca** [(1.02/0.98 = 1.04)].

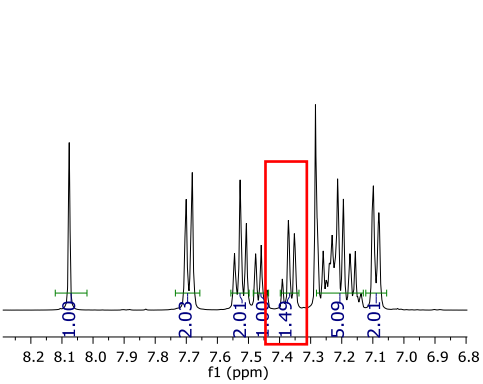

O
N
H
TAH^Ph
3ca
+
D4
[D]4-3ca
1.00
2.16
2.20
1.09
1.02
2.94
1.10
2.12
0.98
2.13
2.15
2.20
f1 (ppm)

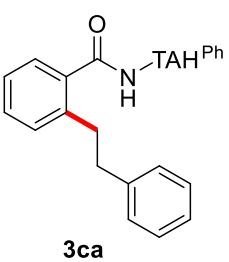
Intramolecular KIE



$k_H/k_D \approx 1.04$

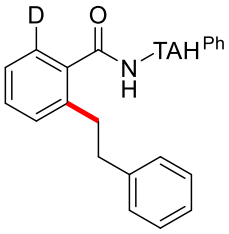
To a stirred solution of $Fe(acac)_3$ (10.6 mg, 0.03 mmol), dppe (11.9 mg, 0.03 mmol), zinc bromide (90.0 mg, 0.40 mmol) and [D]-**1c** (55.9 mg, 0.20 mmol) in THF (0.4 ml) under N_2 atmosphere, PhMgBr (1.0 M in THF, 600 µl, 0.60 mmol) was added in a single portion. Then, styrene **2a** (69 µL, 0.60 mmol) was added and the mixture was placed in a pre-heated oil bath at 65 °C. After stirring for 1 h, the reaction was cooled to room temperature and quenched by the addition of an aqueous solution of HCl (1.0 M, 5 ml). The reaction was extracted with CH_2Cl_2 (3x15 ml), and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography (*n*-hexane/EtOAc). The mixture was analysed by 400 MHz ^{1}H-NMR spectroscopy to determine the ratio of **3ca**/[D]-**3ca** [(1.0-0.49/0.49) = 1.04].


1.00
2.03
2.01
1.00
1.49
5.09
2.01
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)

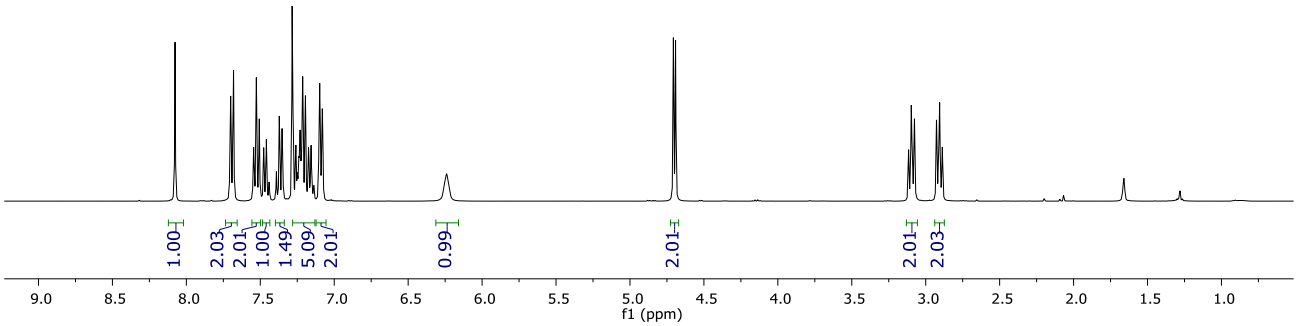

O
N
H
TAH
Ph

3ca

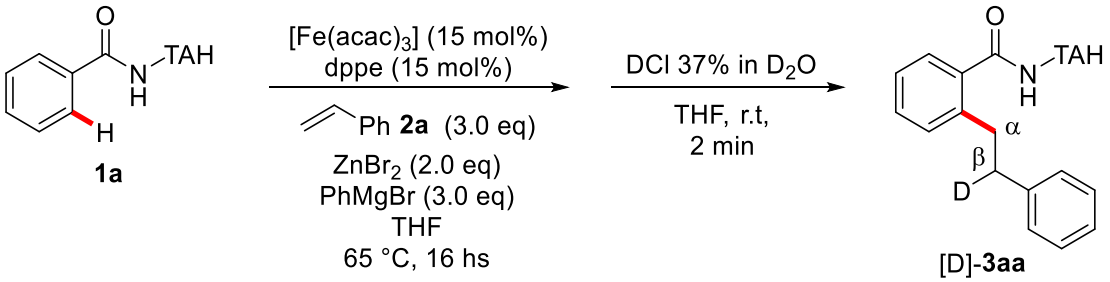
+


D
O
N
H
TAH
Ph

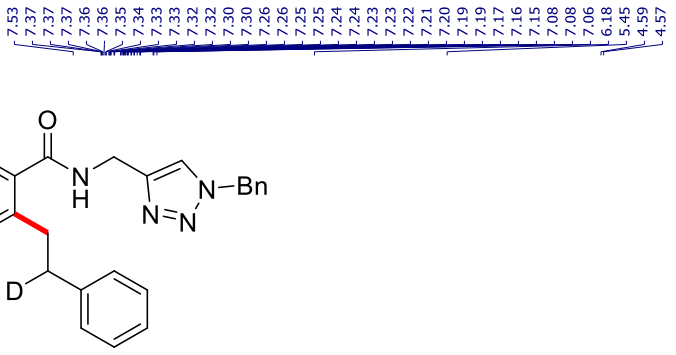
[D]-**3ca**


1.00
2.03
2.01
1.00
1.49
5.09
2.01
0.99
2.01
2.01
2.03
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
f1 (ppm)

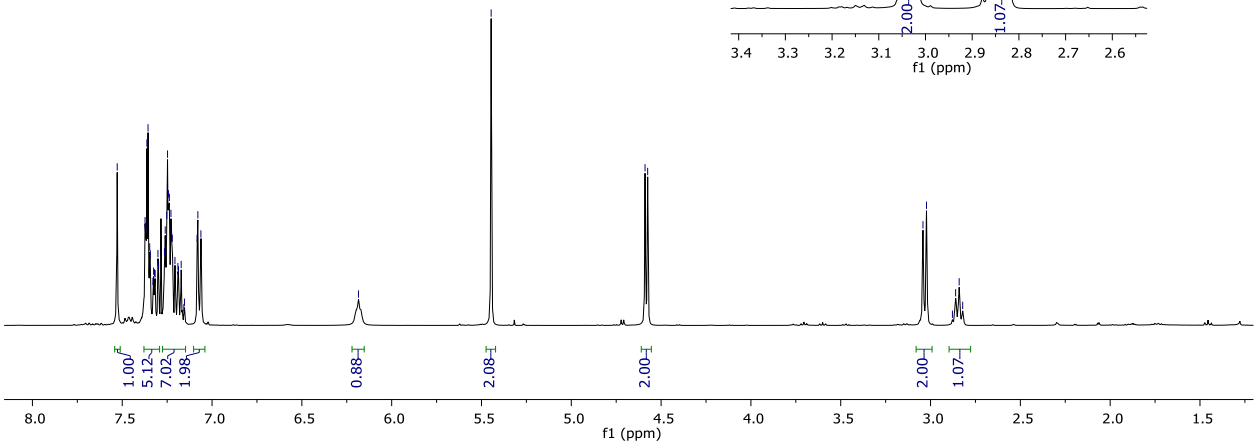
Reaction with DCl

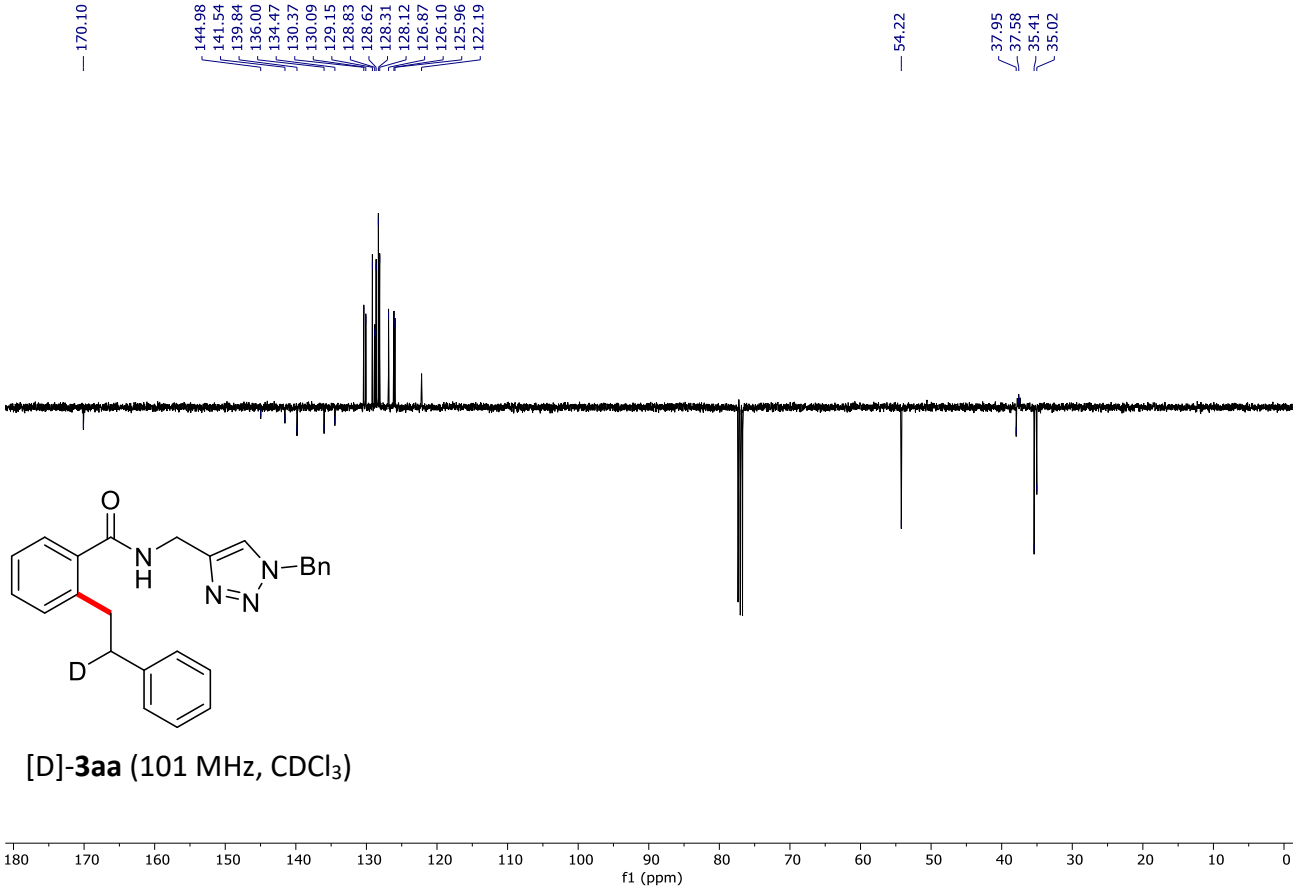


To a stirred solution of $Fe(acac)_3$ (10.6 mg, 0.03 mmol), dppe (11.9 mg, 0.03 mmol), zinc bromide (90.0 mg, 0.4 mmol) and **1a** (58.5 mg, 0.20 mmol) in THF (0.4 ml) under N_2 atmosphere, PhMgBr (1 M in THF, 600 µl, 0.60 mmol) was added in a single portion. Then, styrene **2a** (69 µl, 0.60 mmol) was added and the mixture was placed in a pre-heated oil bath at 65 °C. After stirring for 16 hs, the reaction was cooled to room temperature and quenched by the addition of 37% DCl in D_2O (1.5 ml). The reaction was extracted with CH_2Cl_2 (3x15 ml) and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated. Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded [D]-**3aa** (53.8 mg, 68%) as a white solid. The amount of deuterium incorporation was determined by ^{1}H NMR. M.p. = 127-129 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 7.37 – 7.30 (m, 5H), 7.26 – 7.15 (m, 7H), 7.07 (d, *J* = 6.7 Hz, 2H), 6.14 (s, 1H), 5.45 (s, 2H), 4.59 (d, *J* = 5.7 Hz, 2H), 3.03 (d, *J* = 7.9 Hz, 2H), 2.85 (q, *J* = 7.9 Hz, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.1 (C_q), 145.0 (C_q), 141.5 (C_q), 139.8 (C_q), 136.0 (C_q), 134.5 (C_q), 130.4 (CH), 130.1 (CH), 129.2 (CH), 128.8 (CH), 128.6 (CH), 128.3 (CH), 128.1 (CH), 126.9 (CH), 126.1 (CH), 126.0 (CH), 122.2 (CH), 54.2 (CH_2), 38.0 (CH_2), 37.6 (t, *J* = 20 Hz, CDH), 35.4 (CH_2), 35.0 (CH_2). (ESI) *m/z* (relative intensity): 420 (20) $[M+Na]^+$, 398 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{25}H_{24}DN_4O$ $[M+H]^+$ 398.2086, found 398.2088.

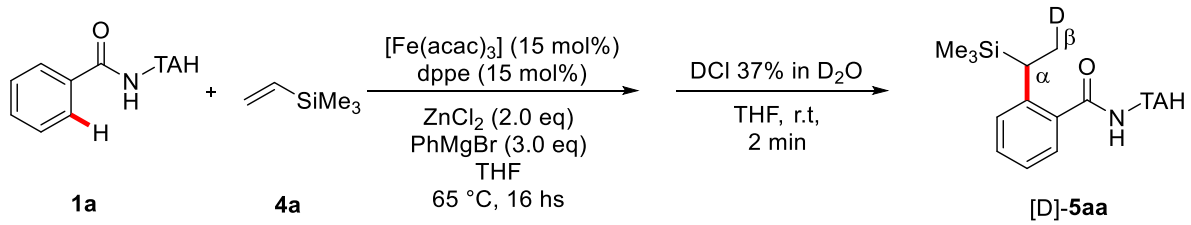


[D]-**3aa** (400 MHz, $CDCl_3$)

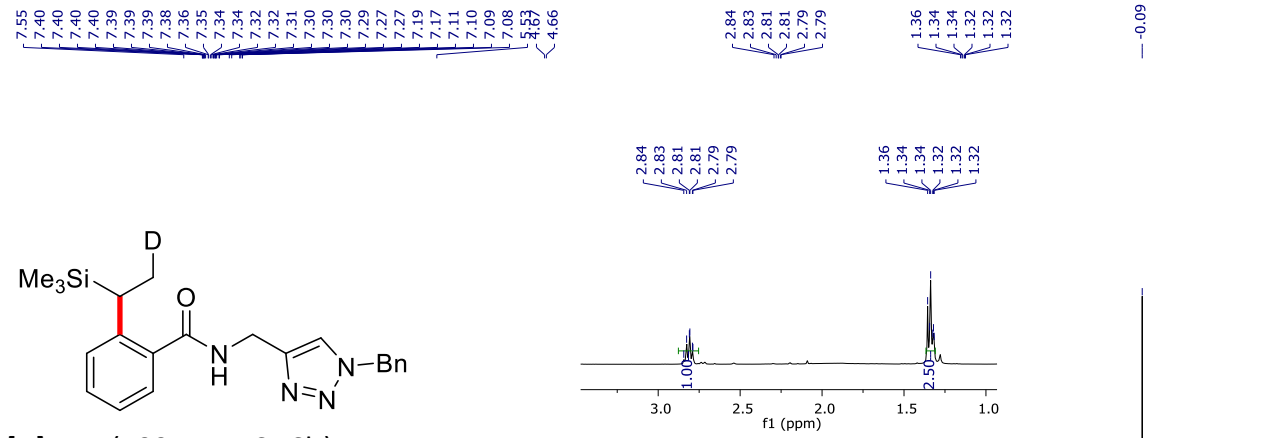




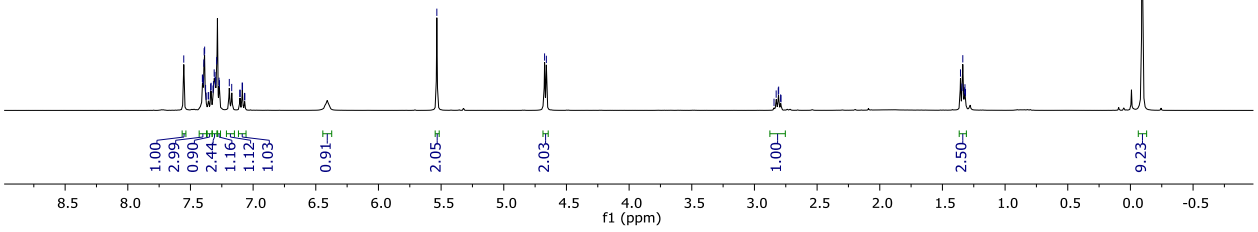
[D]-**3aa** (101 MHz, $CDCl_3$)

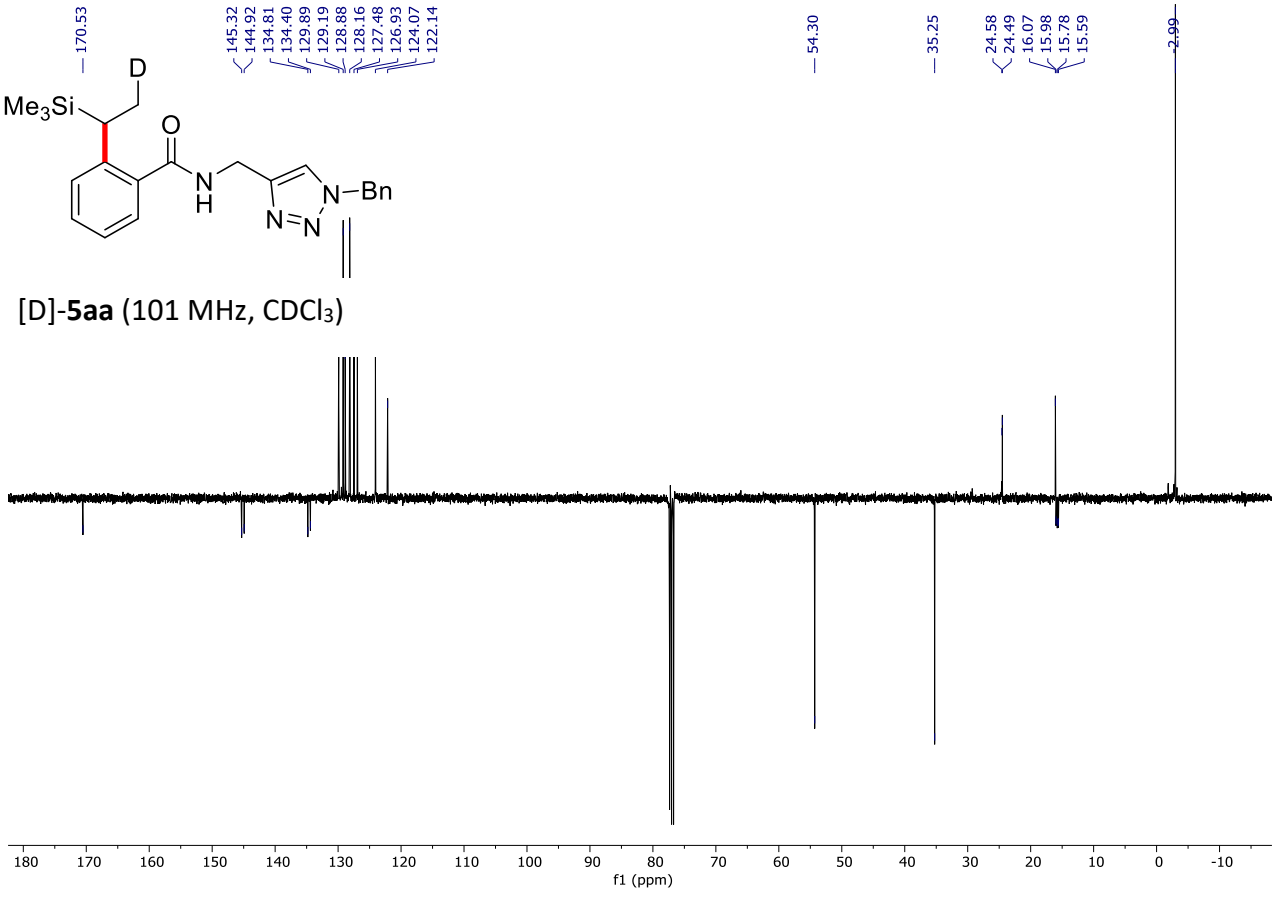


To a stirred solution of $Fe(acac)_3$ (10.6 mg, 0.03 mmol), dppe (11.9 mg, 0.03 mmol) zinc chloride (1 M in THF, 400 µl, 0.4 mmol, 2.0 equiv) and **1** (0.20 mmol) under N_2 atmosphere, PhMgBr (1.0 M in THF, 600 µl, 0.6 mmol, 3.0 equiv) was added in a single portion. Then, vinyltrimethylsilane **4a** (88 µL, 0.6 mmol) was added and the mixture was placed in a pre-heated oil bath at 65 °C. After stirring for 16 hs, the reaction was cooled to room temperature and quenched by the addition of 37% DCl in D_2O (1.5 ml). The reaction was extracted with CH_2Cl_2 (3x15 ml) and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated. Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded [D]-**5aa** (44.9 mg, 57%) as a white solid. The amount of deuterium incorporation was determined by ^{1}H NMR. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 1H), 7.43 – 7.37 (m, 3H), 7.35 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.27 (d, *J* = 1.4 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.09 (td, *J* = 7.5, 1.2 Hz, 1H), 6.41 (t, *J* = 5.8 Hz, 1H), 5.53 (s, 2H), 4.67 (d, *J* = 5.7 Hz, 2H), 2.86 – 2.77 (m, 1H), 1.34 (t, *J* = 7.2 Hz, 2H), -0.09 (s, 9H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.5 (C_q), 145.3 (C_q), 144.9 (C_q), 134.8 (C_q), 134.4 (C_q), 129.9 (CH), 129.2 (CH), 128.9 (CH), 128.2 (CH), 127.5 (CH), 126.9 (CH), 124.1 (CH), 122.1 (CH), 54.3 (CH_2), 35.3 (CH_2), 24.5 (d, *J*= 8 Hz CH), 16.1 (CH_3), 15.8 (t, *J*= 19 Hz CH_2D) -3.0 (CH_3). (ESI) *m/z* (relative intensity): 416 (32) $[M+Na]^+$, 394 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{22}H_{28}DN_4OSi$ $[M+H]^+$ 394.2095, found 394.2098.



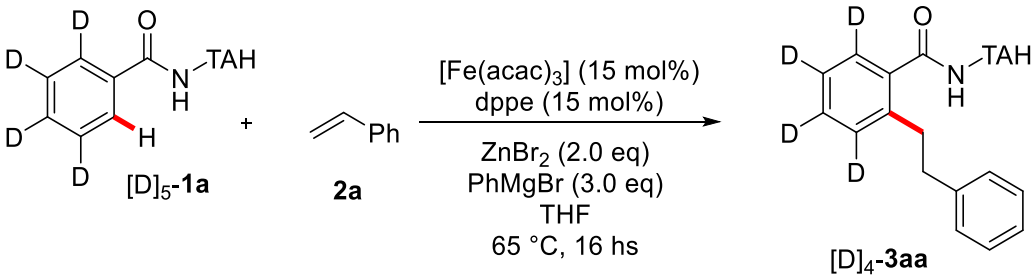
[D]-**5aa** (400 MHz, $CDCl_3$)



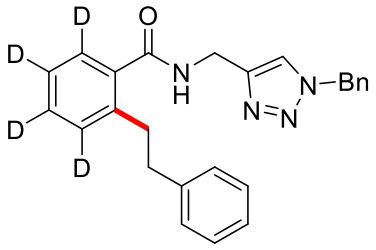


[D]-**5aa** (101 MHz, $CDCl_3$)

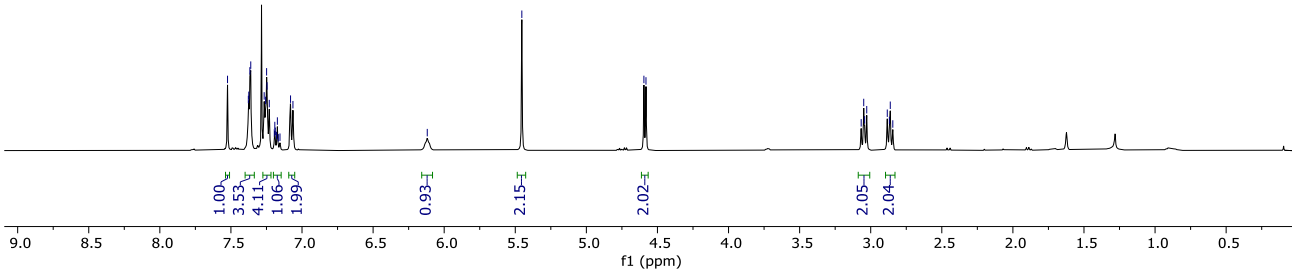
Reaction of $[D]_5$-1a

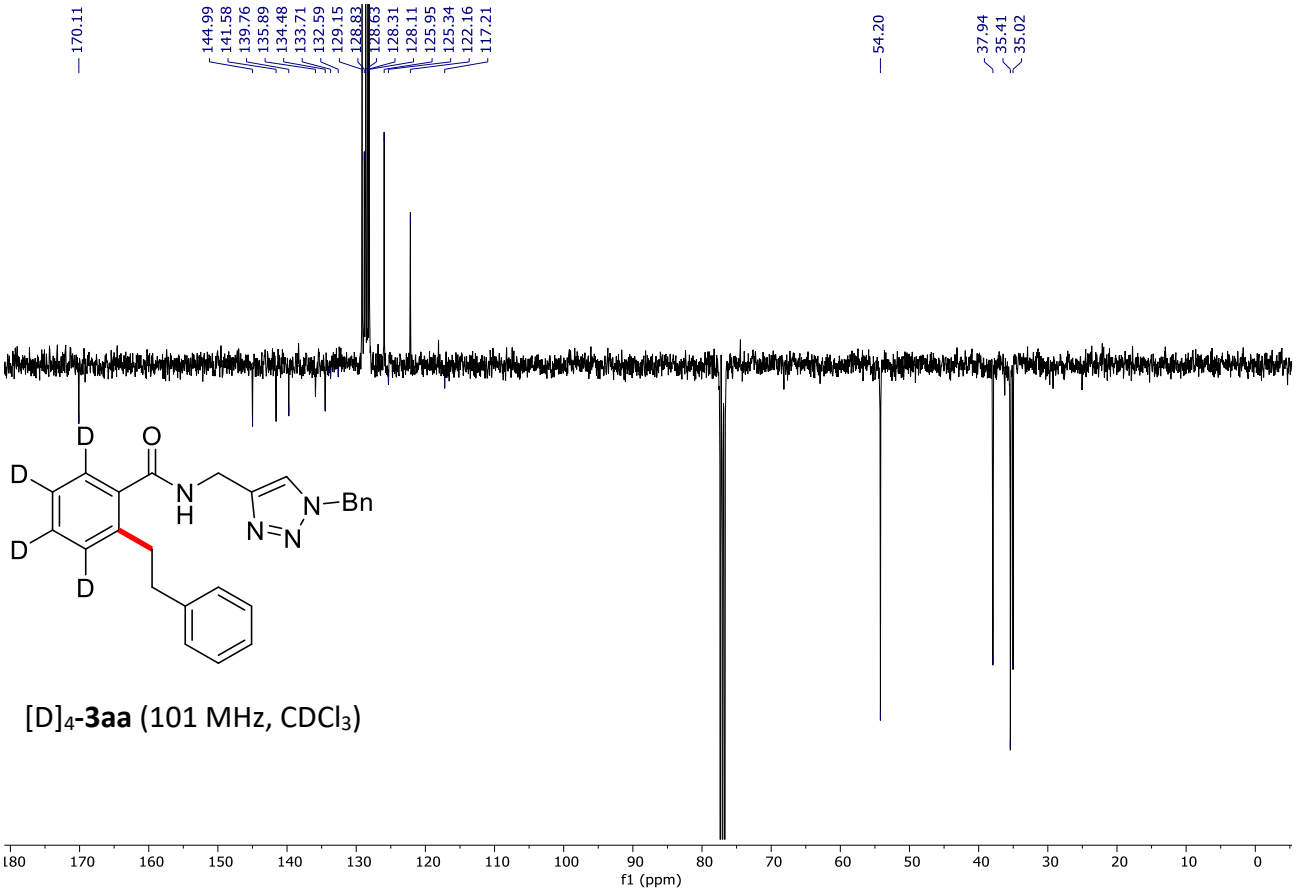


To a stirred solution of $Fe(acac)_3$ (10.6 mg, 0.03 mmol), dppe (11.9 mg, 0.03 mmol), zinc bromide (90.0 mg, 0.40 mmol) and $[D]_5$-**1a** (59.5 mg, 0.02 mmol) in THF (0.4 ml) under N_2 atmosphere, PhMgBr (1.0 M in THF, 600 µl, 0.60 mmol) was added in a single portion. Then, styrene **2a** (69 µL, 0.60 mmol) was added and the mixture was placed in a pre-heated oil bath at 65 °C. After stirring for 16 hs, the reaction was cooled to room temperature and quenched by the addition of an aqueous solution of HCl (1.0 M, 5 ml). The reaction was extracted with CH_2Cl_2 (3x15 ml), and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated. Purification by column chromatography on silica gel (*n*-hexane/EtOAc 1:1) yielded $[D]_4$-**3aa** (51.2 mg, 65 %) as a white solid. No hydrogen scrambling was observed by ^{1}H-NMR spectroscopy. M.p. = 128-129 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 1H), 7.37 – 7.36 (m, 3H), 7.26 – 7.23 (m, 4H), 7.20 – 7.15 (m, 1H), 7.07 (d, *J* = 6.8 Hz, 2H), 6.12 (bs, 1H), 5.45 (s, 2H), 4.59 (d, *J* = 5.8 Hz, 2H), 3.05 (dd, *J* = 9.1, 6.5 Hz, 2H), 2.86 (dd, *J* = 9.1, 6.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.1 (C_q), 145.0 (C_q), 141.6 (C_q), 139.8 (C_q), 135.9 (C_q), 134.5 (C_q), 133.7 (CD), 132.6 (CD), 129.2 (CH), 128.8 (CH), 128.6 (CH), 128.3 (CH), 128.1 (CH), 125.3 (CD), 126.0 (CH), 122.2 (CH), 117.2 (CD), 54.2 (CH_2), 37.9 (CH_2), 35.4 (CH_2), 35.0 (CH_2). (ESI) *m/z* (relative intensity): 439 (10) $[M+K]^+$, 423 (24) $[M+Na]^+$,401 (100) $[M+H]^+$. HR-MS (ESI) *m/z* calcd for $C_{25}H_{21}D_4N_4O$ $[M+H]^+$ 401.2201, found 401.2206.



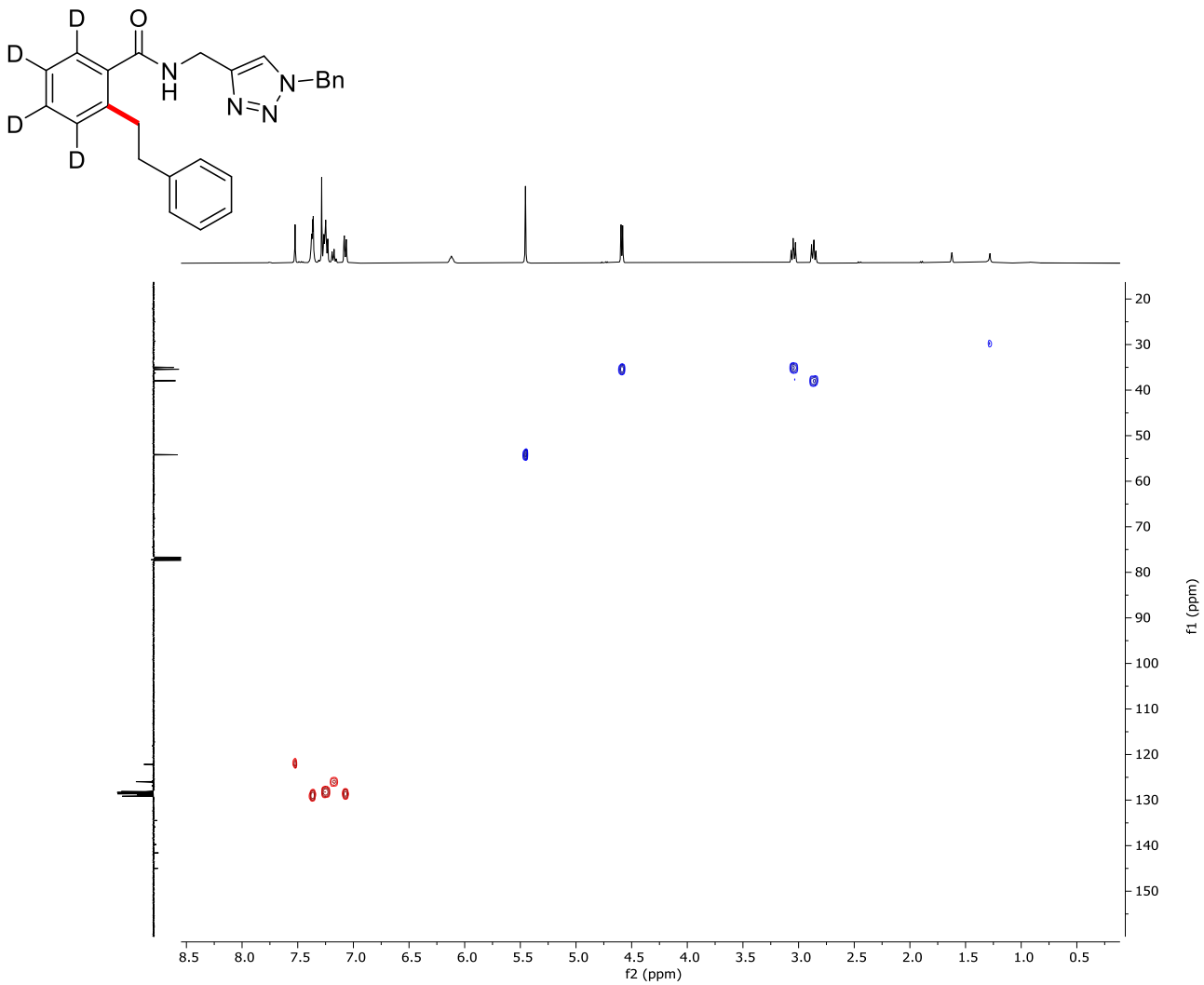
[D]$_4$-**3aa** (400 MHz, $CDCl_3$)





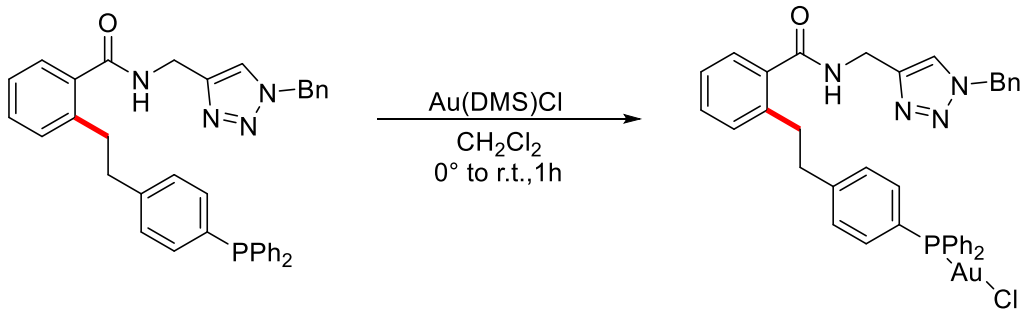
[D]$_4$-**3aa** (101 MHz, $CDCl_3$)

HSQC $[D]_4$-**3aa**


D
O
D
N
H
N
N
N–Bn
D
D
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
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
f2 (ppm)

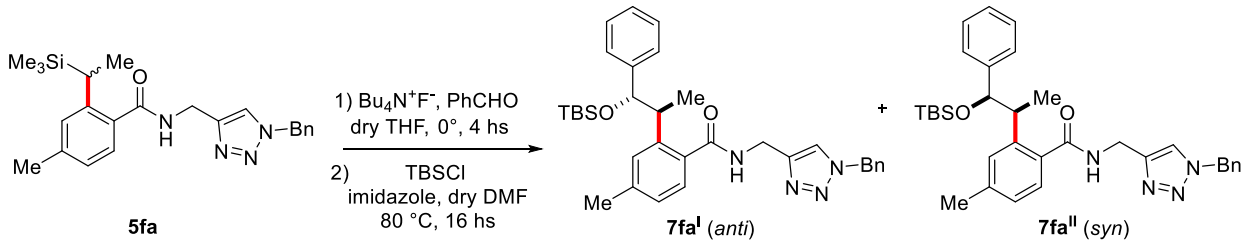
- **Late-stage synthetic manipulations**

_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-[4-(diphenylphosphanyl)phenethyl]benzamide-AuCl (6ah)



In a two-necked round bottom flask, under N_2 atmosphere, Au(DMS)Cl (10.7 mg, 0.036 mmol, 1.1 equiv.) was added to solution of **3ah** (19.1 mg, 0.032 mmol) in CH_2Cl_2 (3.0 ml) at 0 °C. The reaction was stirred at the same temperature for 30 min and then allowed to reach room temperature. After 1h, the mixture was filtered through celite, washed with EtOAc (10 ml) and additional CH_2Cl_2 (20 ml). The volatiles were concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc 3:7) to yield **6ah** (18.5 mg, 71%) as a white waxy solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55 – 7.46 (m, 12H), 7.41 – 7.33 (m, 6H), 7.27 – 7.24 (m, 5H), 7.18 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.48 (bs, 1H), 5.48 (s, 2H), 4.66 (d, *J* = 5.6 Hz, 2H), 3.07 (dd, *J* = 9.8, 6.0 Hz, 2H), 2.95 (dd, *J* = 9.9, 6.1 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.8 (C_q), 146.5 (d, $J_{C\text{-}P}$ = 3 Hz, C_q), 144.6 (C_q), 139.7 (C_q), 135.5 (C_q), 134.3 (CH), 134.2 (CH), 134.0 (CH), 131.9 (d, $J_{C\text{-}P}$ = 3 Hz, CH), 130.4 (d, $J_{C\text{-}P}$ = 17 Hz, CH), 129.5 (d, $J_{C\text{-}P}$ = 17 Hz, CH), 129.2 (d, $J_{C\text{-}P}$ = 12 Hz, CH), 129.1 (CH), 128.9 (CH), 128.7 (C_q), 128.1 (CH), 127.1 (CH), 126.4 (CH), 125.9 (C_q), 125.3 (C_q), 122.0 (CH), 54.3 (CH_2), 37.7 (CH_2), 35.4 (CH_2), 35.1 (CH_2). ^{31}P-NMR (162 MHz, $CDCl_3$): δ = 32.5. (ESI) *m/z* (relative intensity): 813 (100) $[M+H]^+$, 777 (54) $[M\text{-}Cl]^+$. HR-MS (ESI) *m/z* calcd for $C_{37}H_{34}AuNOP$ $[M\text{-}Cl]^+$ 777.2058, found 777.2064.

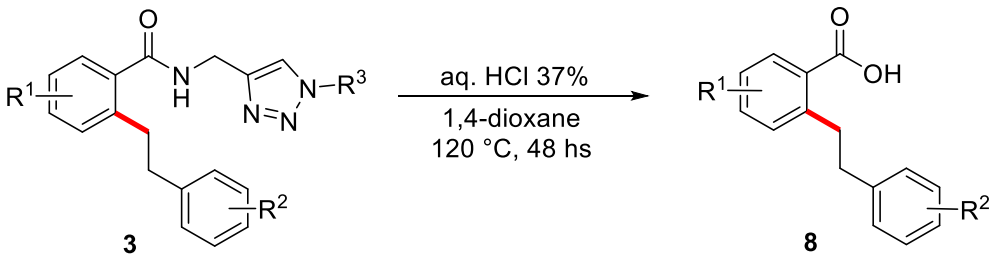
_N_-[(1-Benzyl-1_H_-1,2,3-triazol-4-yl)methyl]-2-(1-[(*tert*-butyldimethylsilyl)oxy]-1-phenylpropan-2-yl)-4-methylbenzamide (7fa)



Tetra-*n*-butylammonium fluoride (75 µl, 1 M solution in THF, dried over molecular sieves, 0.422 mmol) was added to a solution of **5fa** (20.3 mg, 0.050 mmol) and freshly distilled benzaldehyde (27

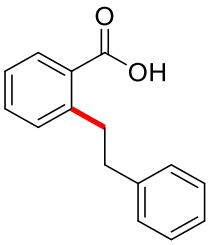
µl, 0.165 mmol) in dry THF (2 ml), in an ice-bath and under N_2. The solution was stirred at 0 °C for 4 hs and saturated aqueous ammonium chloride solution (10 ml) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 ml). The combined organic extracts were washed with brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure. The crude product was further submitted to *tert*-Butyldimethylsilyl chloride (11.3 mg, 0.075 mmol) in anhydrous DMF (2 ml) with imidazole (5.1 mg, 0.075 mmol). The solution was stirred at 70 °C. After 16 hs, the reaction was diluted with water and extracted with EtOAc (3x10 ml). The combined organic extracts were dried over Na_2SO_4 and the filtrate was concentrated under reduced pressure. Purification by column chromatography on silica gel (*n*-hexane/EtOAc 2:8) yielded **7fa** as mixture of diastereoisomer (14.7 mg, 53% for two steps, *anti:syn* = 2.9:1) as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$, *anti*): δ = 8.28 (bs, 1H), 7.60 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.28 – 7.22 (m, 4H), 7.21 – 7.15 (m, 3H), 7.15 – 7.06 (m, 3H), 5.57 – 5.44 (m, 2H), 4.89 – 4.82 (m, 1H), 4.65 – 4.59 (m, 1H), 4.53 (d, *J* = 9.5 Hz, 1H), 3.31 (dq, *J* = 9.5, 6.9 Hz, 1H), 2.39 (s, 3H), 0.84 (d, *J* = 6.9 Hz, 3H), 0.52 (s, 9H), -0.31 (s, 6H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.3 (C_q), 146.1 (C_q), 142.9 (C_q), 141.4 (C_q), 139.9 (C_q), 134.7 (C_q), 134.6 (C_q), 129.0 (CH), 128.6 (CH), 128.4 (2 x CH), 128.0 (CH), 127.8 (CH), 127.5 (CH), 127.2 (CH), 126.8 (CH), 122.7 (CH), 83.3 (CH), 54.2 (CH_2), 43.0 (CH), 35.5 (CH_2), 25.3 (CH_3), 21.5 (CH_3), 18.6 (CH_3), 17.9 (C_q), -5.6 (CH_3). ^{1}H-NMR (400 MHz, $CDCl_3$, *syn*): δ = 7.52 (s, 1H), 7.37 – 7.29 (m, 3H), 7.28 – 7.22 (m, 4H), 7.21 – 7.15 (m, 3H), 7.15 – 7.06 (m, 3H), 7.00 (d, *J* = 8.6 Hz, 1H), 5.77 (bs, 1H), 5.57 – 5.44 (m, 2H), 4.83 (d, *J* = 4.7 Hz, 1H), 4.65 – 4.59 (m, 1H), 4.50 – 4.45 (m, 1H), 3.42 (dq, *J* = 6.9, 4.7 Hz, 1H), 2.38 (s, 3H), 1.21 (d, *J* = 7.0 Hz, 3H), 0.90 (s, 9H), -0.42 (s, 6H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.5 (C_q), 145.1 (C_q), 144.7 (C_q), 142.7 (C_q), 139.4 (C_q), 134.5 (C_q), 133.5 (C_q), 129.4 (CH), 129.2 (CH), 128.8 (CH), 128.1 (CH), 126.9 (CH), 126.7 (CH), 126.6 (2 X CH), 126.4 (CH), 122.2 (CH), 78.4 (CH), 54.2 (CH_2), 43.6 (CH), 35.4 (CH_2), 25.9 (CH_3), 21.5 (CH_3), 18.2 (C_q), 14.6 (CH_3), -5.0 (CH_3). (ESI) *m/z* (relative intensity): 1154 (35) $[2M+Na]^+$, 577 (100) $[M+Na]^+$. HR-MS (ESI) *m/z* calcd for $C_{33}H_{43}N_4O_2Si$ $[M+H]^+$ 554.3077, found 554.3083.

- **Removal of the TAH directing group**



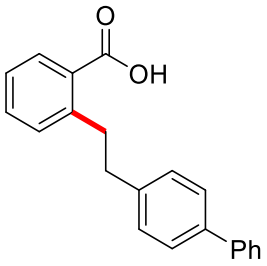
A solution of benzamide **3** (0.10 mmol) in aqueous HCl (3.0 ml, 37%) and 1,4-dioxane (1.5 ml) was stirred at 120 °C for 48 hs. Then, the reaction mixture was diluted with water (15 ml) and extracted with CH_2Cl_2 (3 x 10 ml). The combined organic extracts were dried over Na_2SO_4, and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc).

2-Phenethylbenzoic acid (8aa)



The representative procedure was followed using **3aa** (0.10 mmol, 39.6 mg). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 7:3) yielded **8aa** (15.4 mg, 68%) as a white solid. M.p. = 128-130 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.72 (bs, 1H), 8.10 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.28 – 7.19 (m, 4H), 3.41 – 3.30 (m, 2H), 3.02 – 2.92 (m, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 172.3 (C_q), 144.8 (C_q), 141.9 (C_q), 133.0 (CH), 131.8 (CH), 131.5 (CH), 128.6 (CH), 128.4 (CH), 128.0 (C_q), 126.3 (CH), 125.9 (CH), 38.1 (CH_2), 37.1 (CH_2). (ESI) *m/z* (relative intensity): 473 (100) $[2M+Na]^-$. HR-MS (ESI) *m/z* calcd for $C_{15}H_{15}O_2$ $[M+H]^+$ 227.1067, found 427.1072. The spectral data were in accordance with those reported in the literature.[4]

2-{2-[(1,1'-biphenyl)-4-yl]ethyl}benzoic acid (8ad)



The representative procedure was followed using **3ad** (0.10 mmol, 47.2 mg). Purification by column chromatography on silica gel (*n*-hexane/EtOAc 7:3) yielded **8ad** (22.1 mg, 73%) as a white solid. M.p. = 149-151 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.13 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.60 – 7.57 (m, 2H), 7.55 – 7.49 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.29 (m, 5H), 3.42 – 3.37 (m, 2H), 3.03 – 2.99 (m, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 171.9 (C_q), 144.8 (C_q), 141.1 (C_q), 141.0 (C_q), 138.9 (C_q), 133.1 (CH), 131.9 (CH), 131.6 (CH), 129.0 (CH), 128.7 (CH), 127.9 (C_q), 127.1 (CH), 127.0 (CH), 126.9 (CH), 126.3 (CH), 37.8 (CH_2), 37.1 (CH_2). (ESI) *m/z* (relative intensity): 625 (93) $[2M+Na]^+$, 325 (100) $[M+Na]^+$. HR-MS (ESI) *m/z* calcd for $C_{21}H_{19}O_2$ $[M+H]^+$ 303.1380, found 303.1384.

- **References**

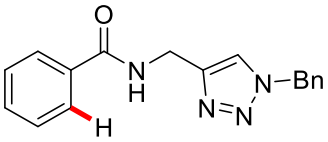
[1] N. Camedda, A. Serafino, R. Maggi, F. Bigi, G. Cera and G. Maestri, *Synthesis*, 2020, **52**, 1762.

[2] X. Ma, Y. Liu, P. Liu, J. Xie, B. Dai and Z. Liu, *Appl. Organometal. Chem.*, 2013, **27**, 707.

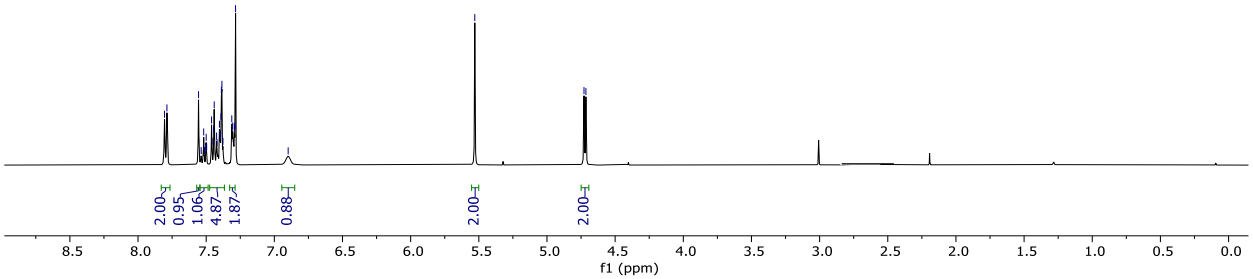
[3] L. Sancineto, C. Tidei, L. Bagnoli, F. Marini, E. J. Lenardão and C. Santi, *Molecules*, 2015, **20**, 10496.

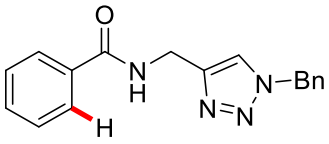
[4] R. Zhu, J. Jiang, X. Li, J. Deng and Y. Fu, *ACS Catal.*, 2017, **7**, 7520.

- **^{1}H-, ^{13}C-, ^{19}F and ^{31}P-NMR Spectra**



1a (400 MHz, $CDCl_3$)





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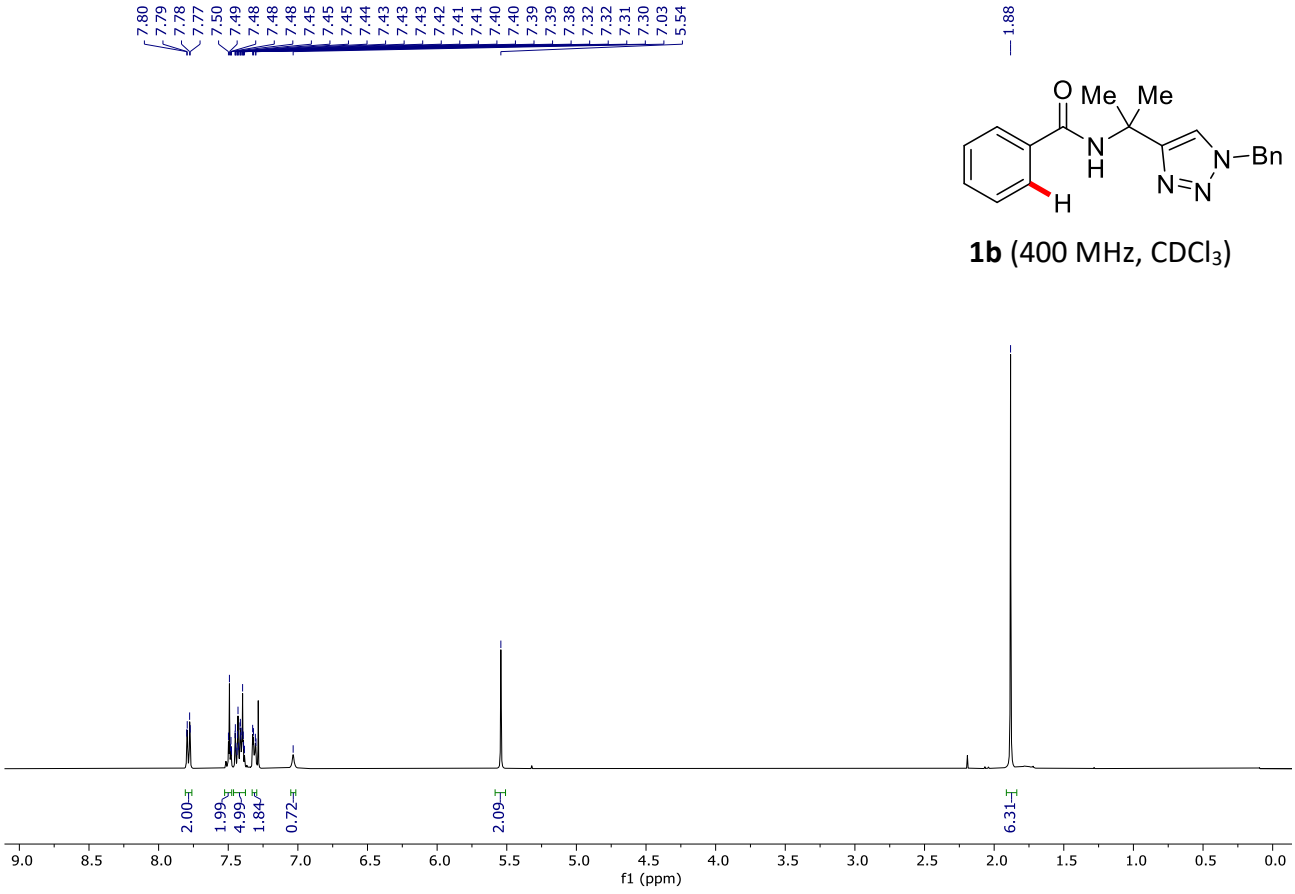

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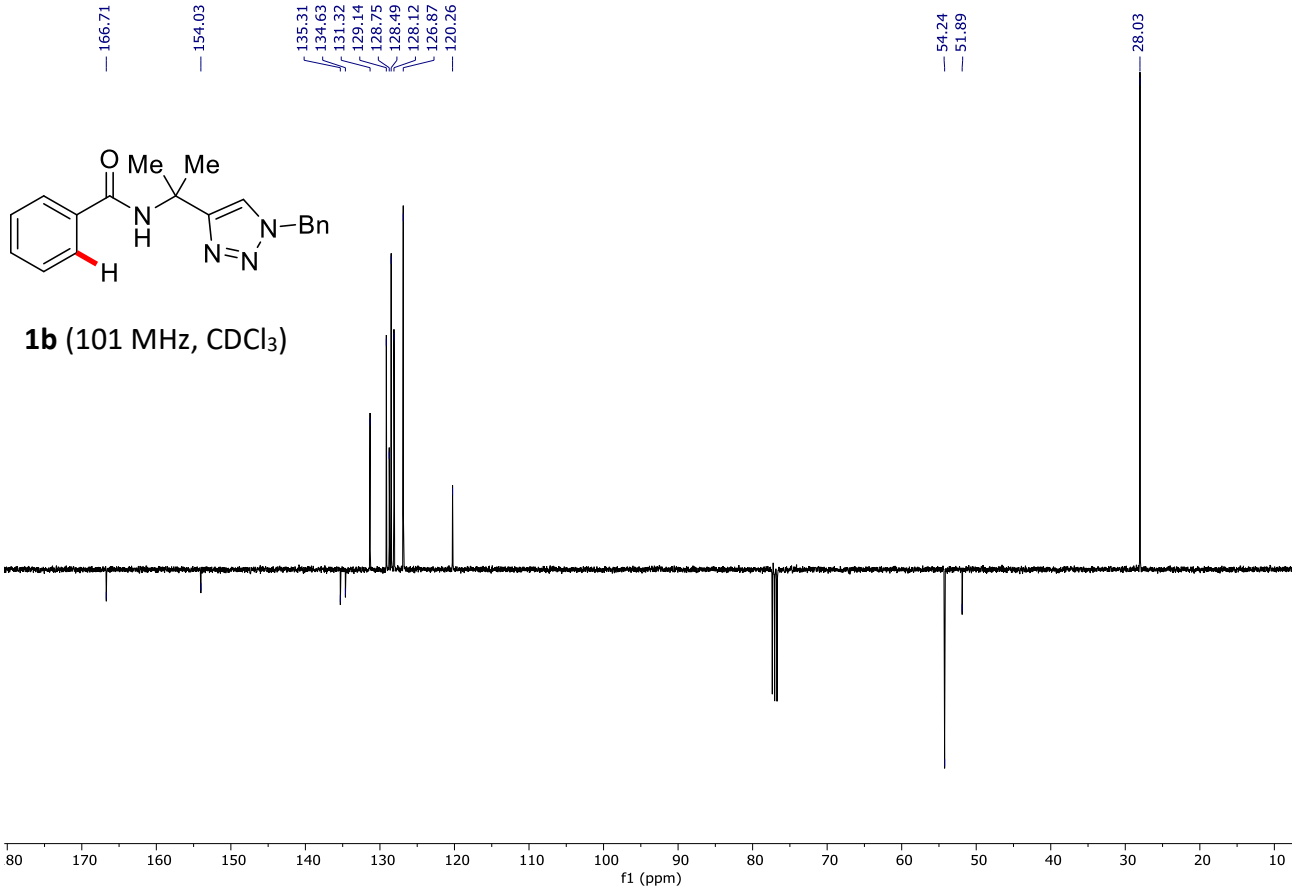

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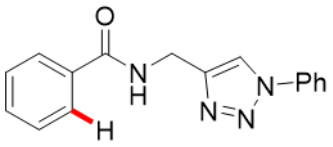

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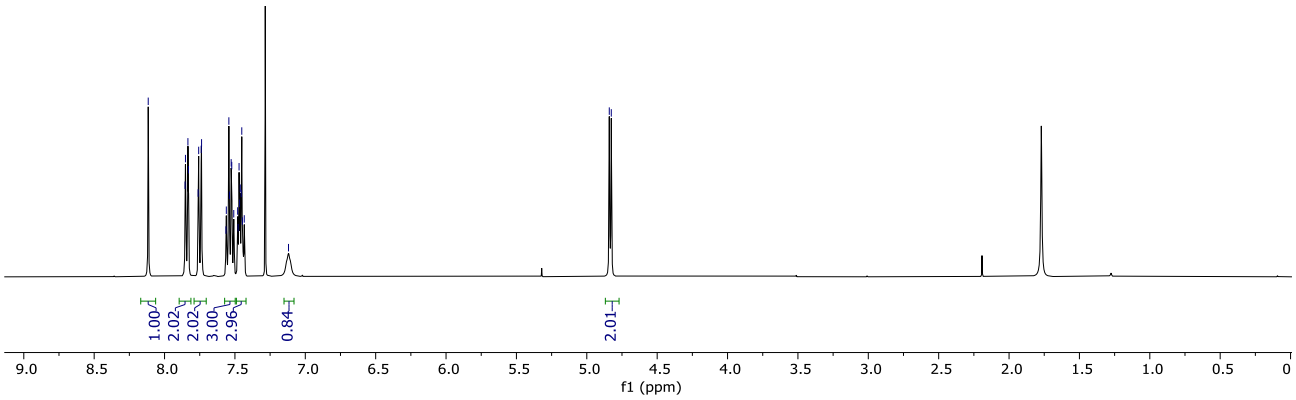

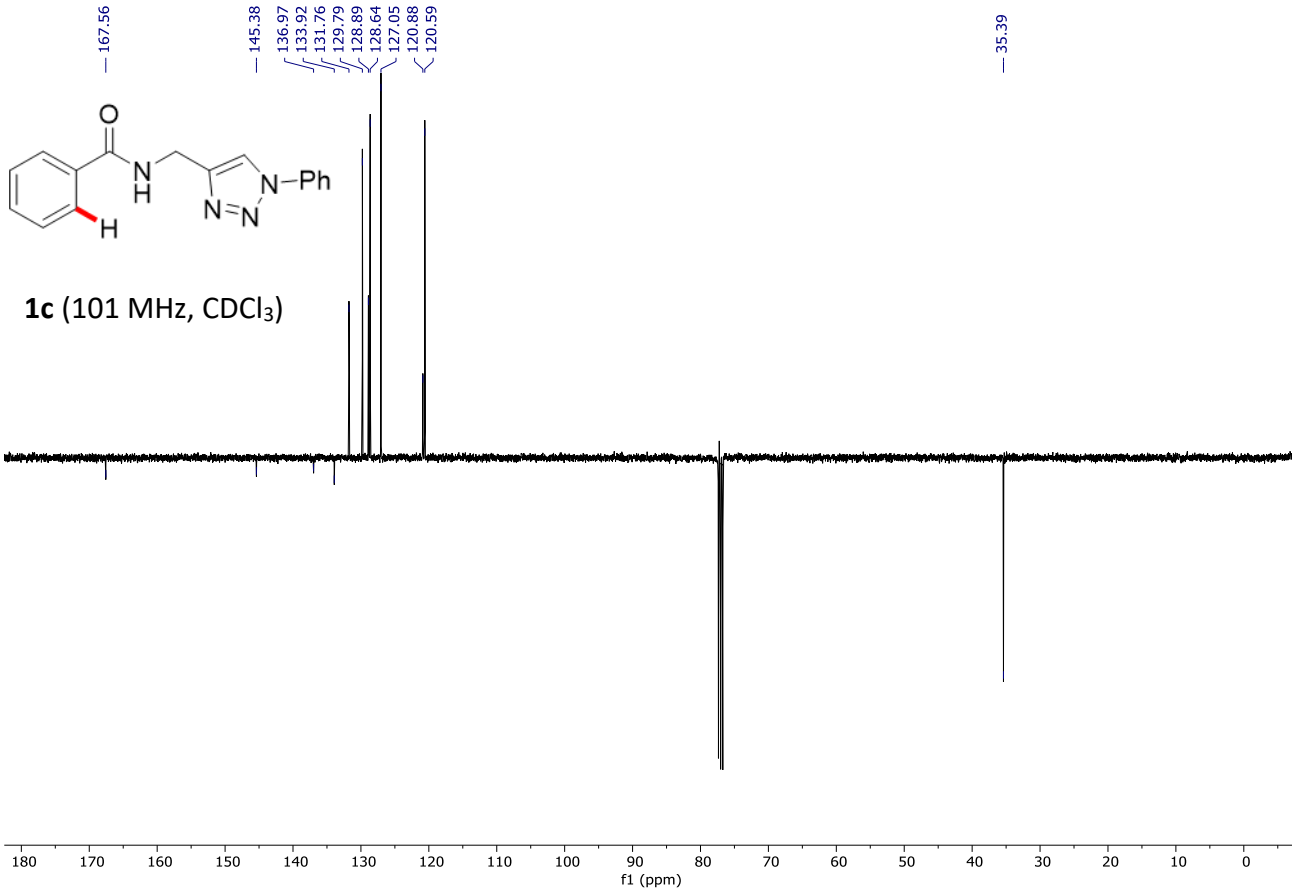

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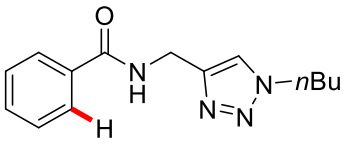

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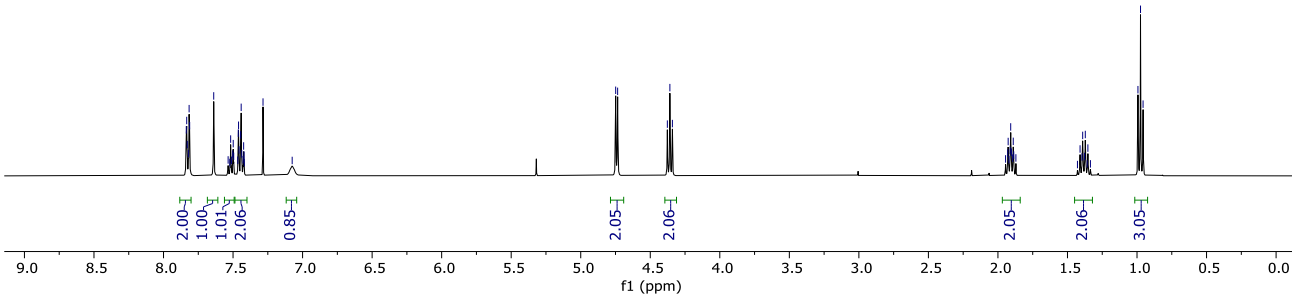

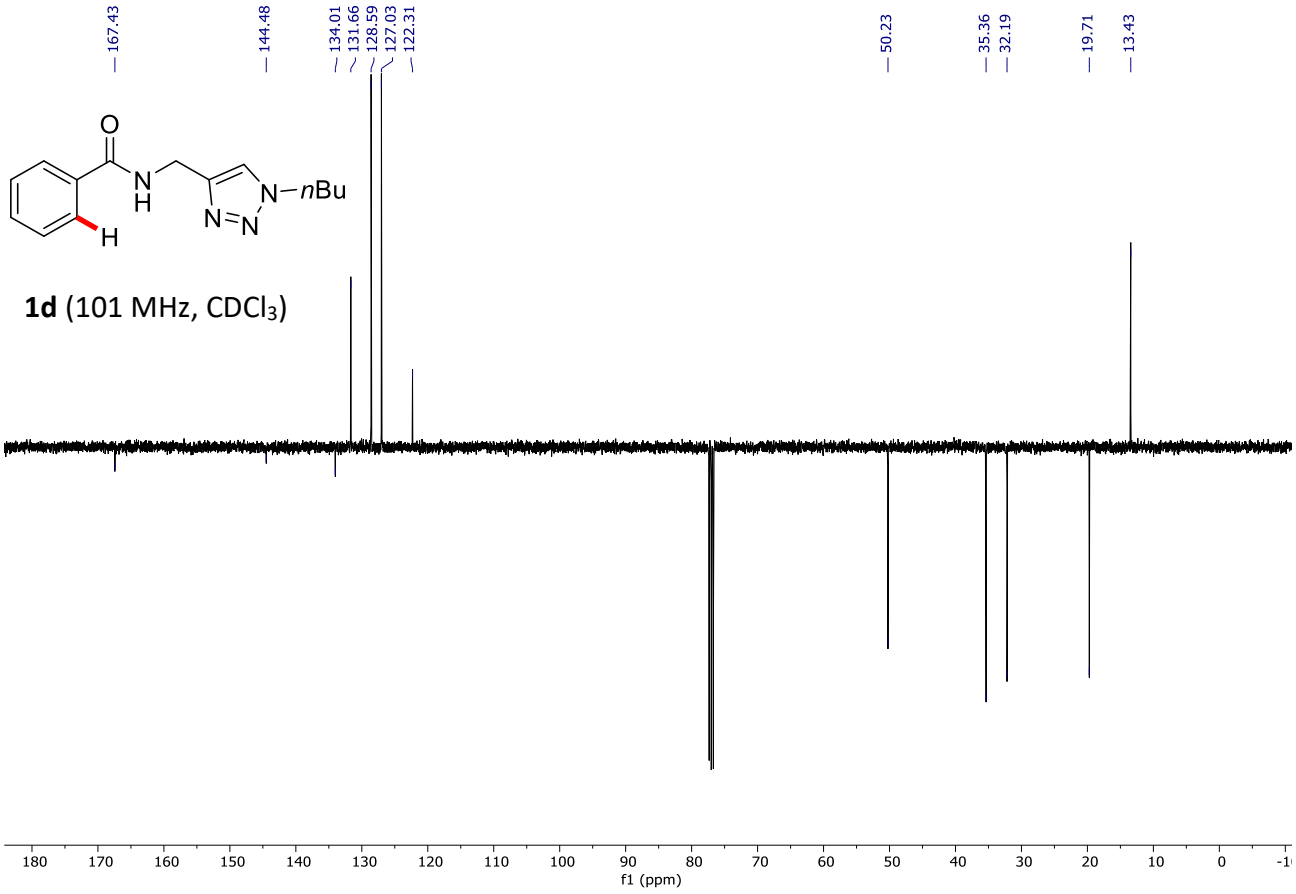

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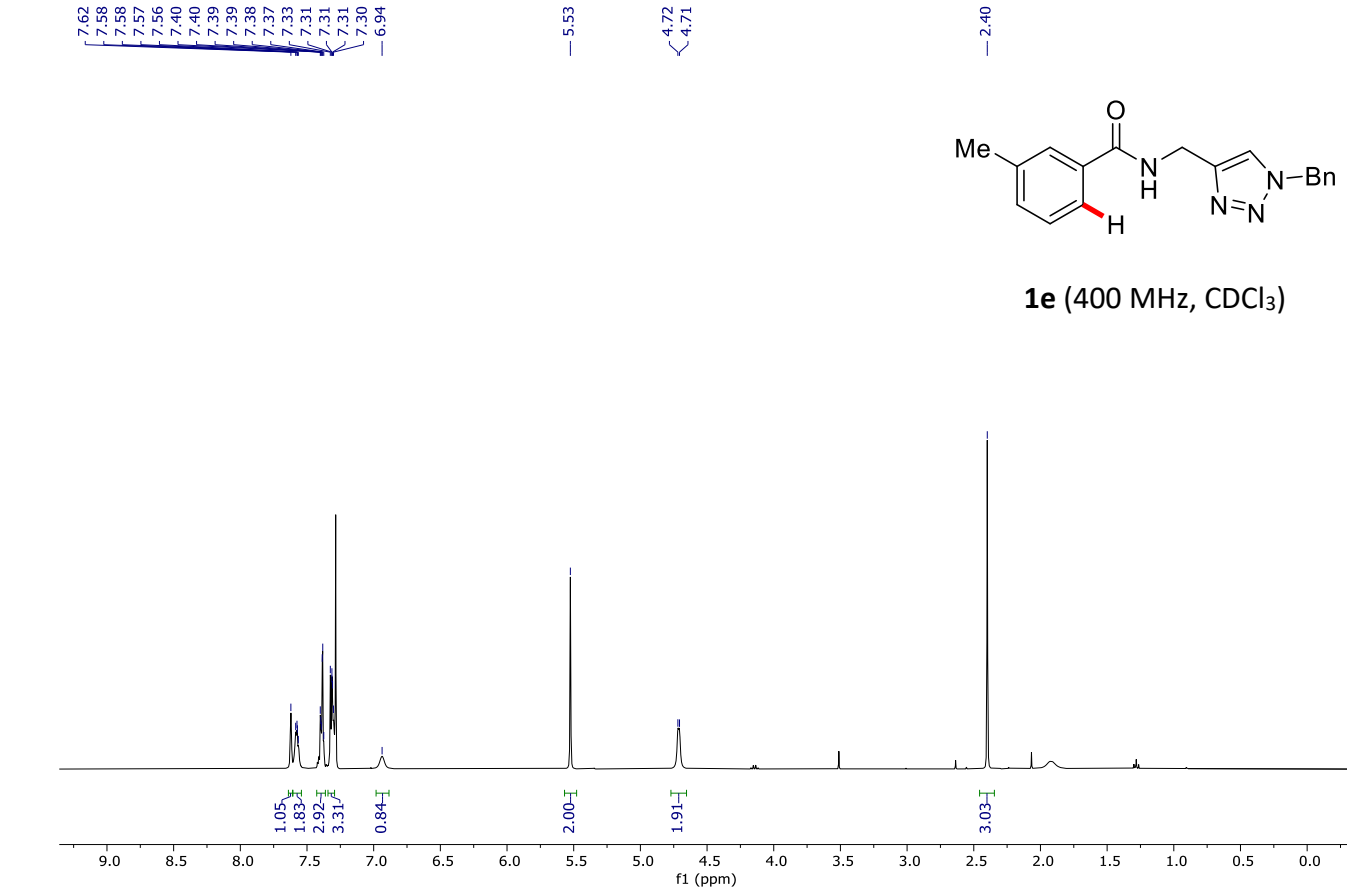

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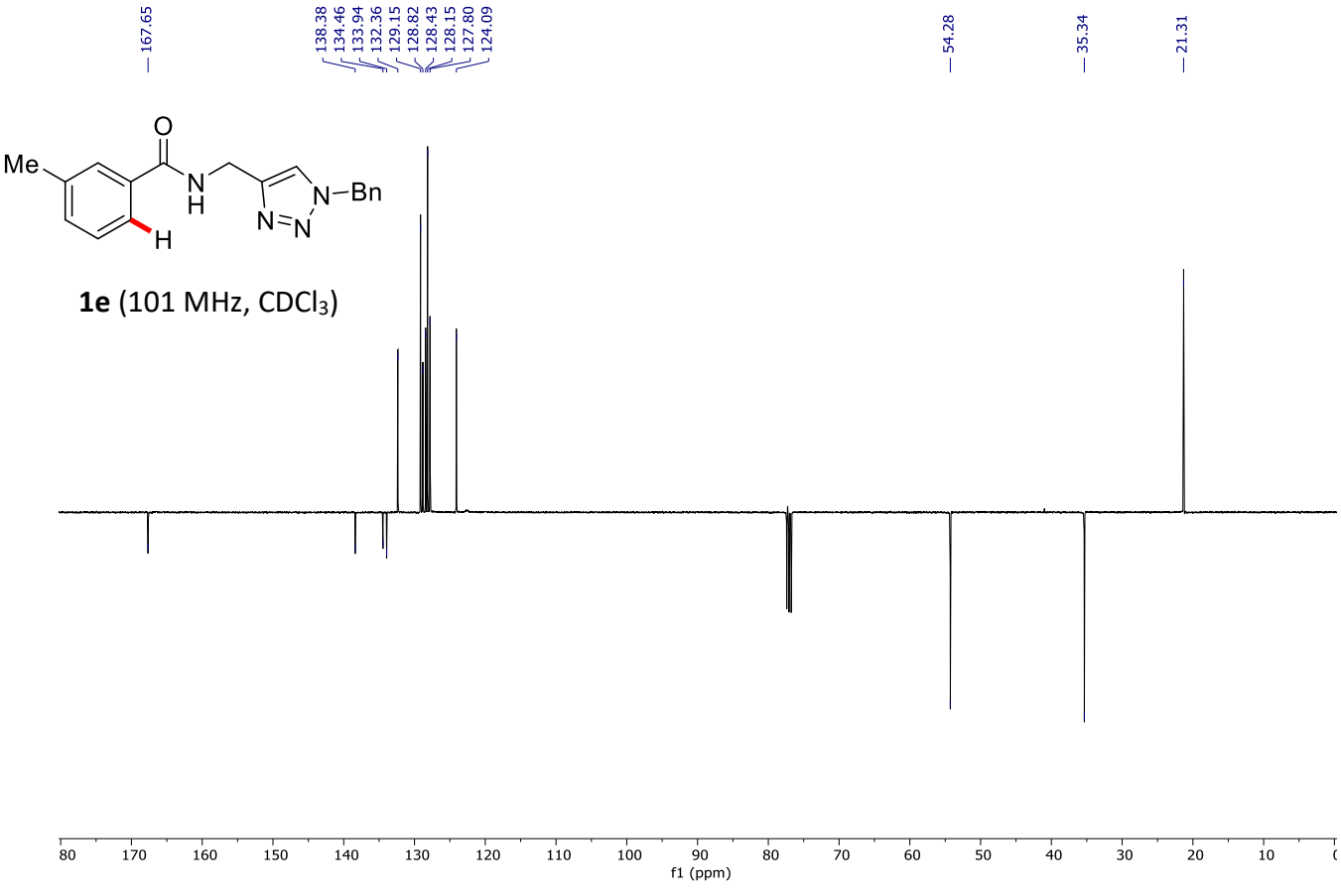

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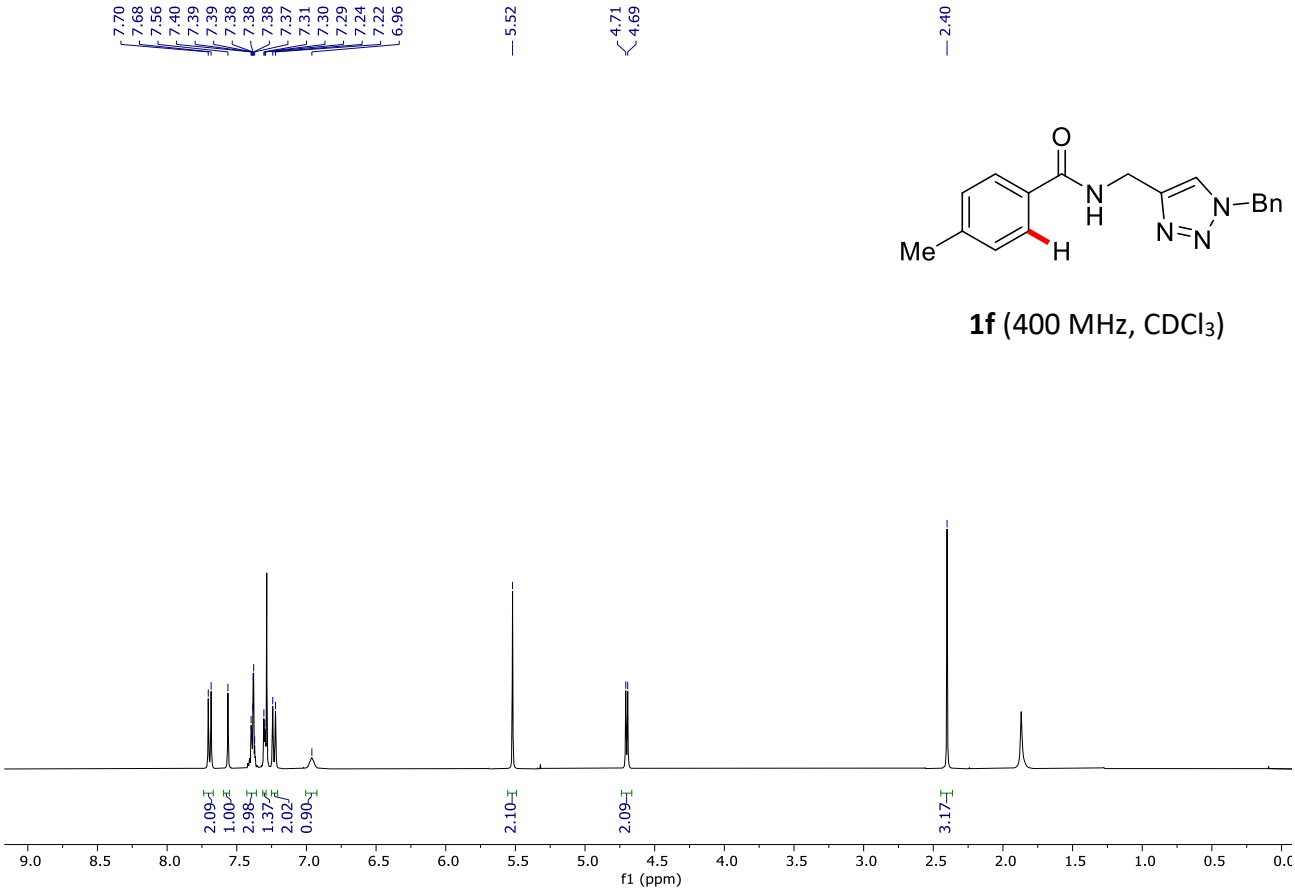

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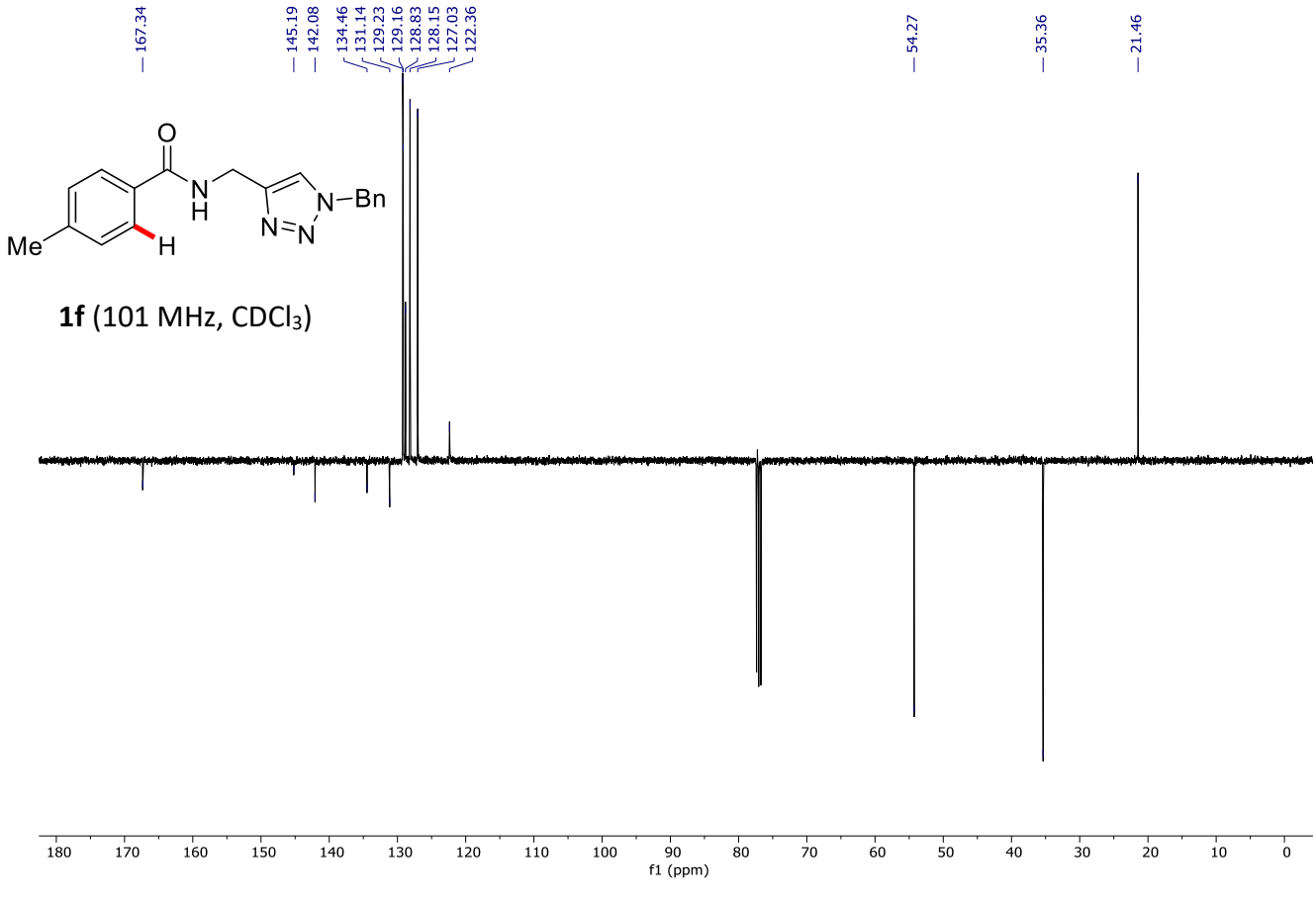

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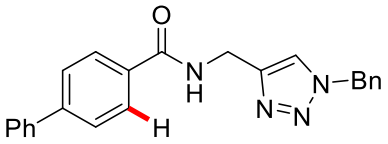

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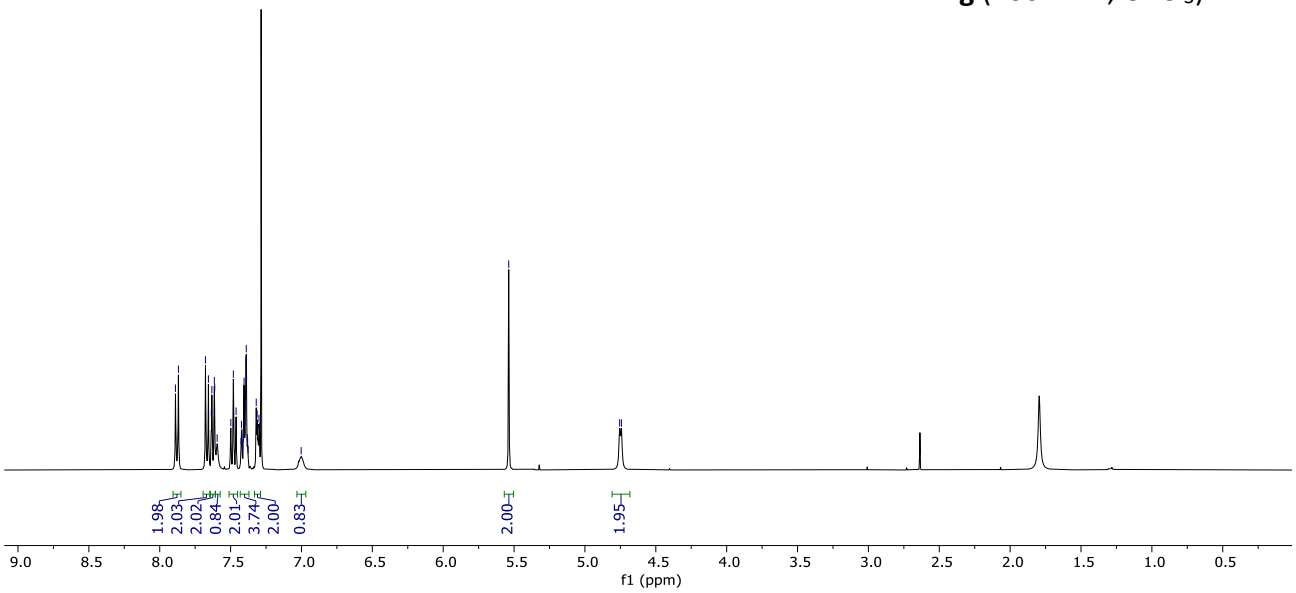

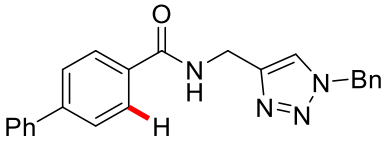

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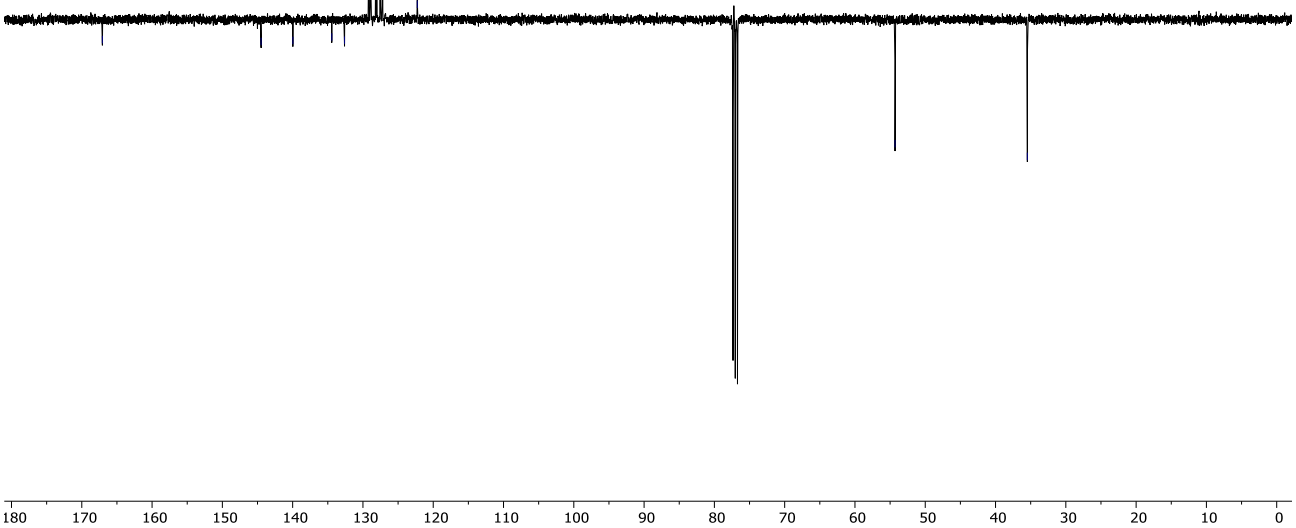

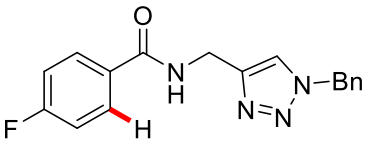

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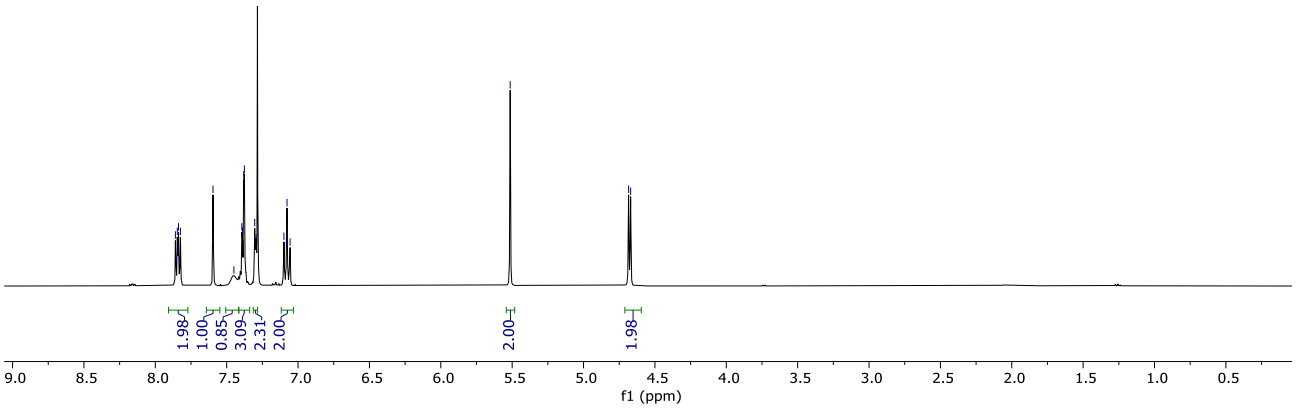

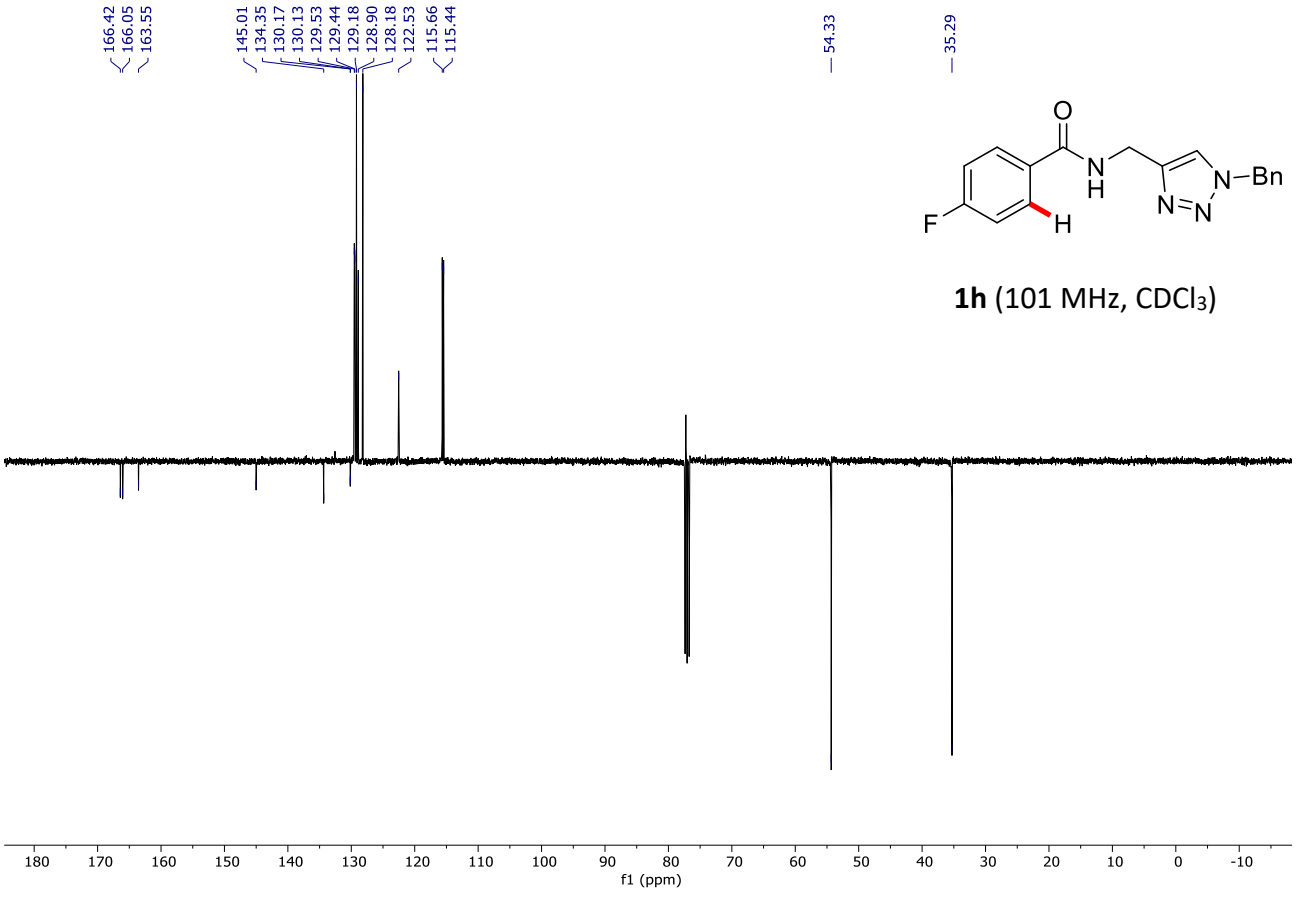

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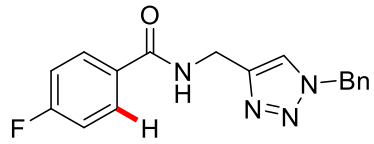

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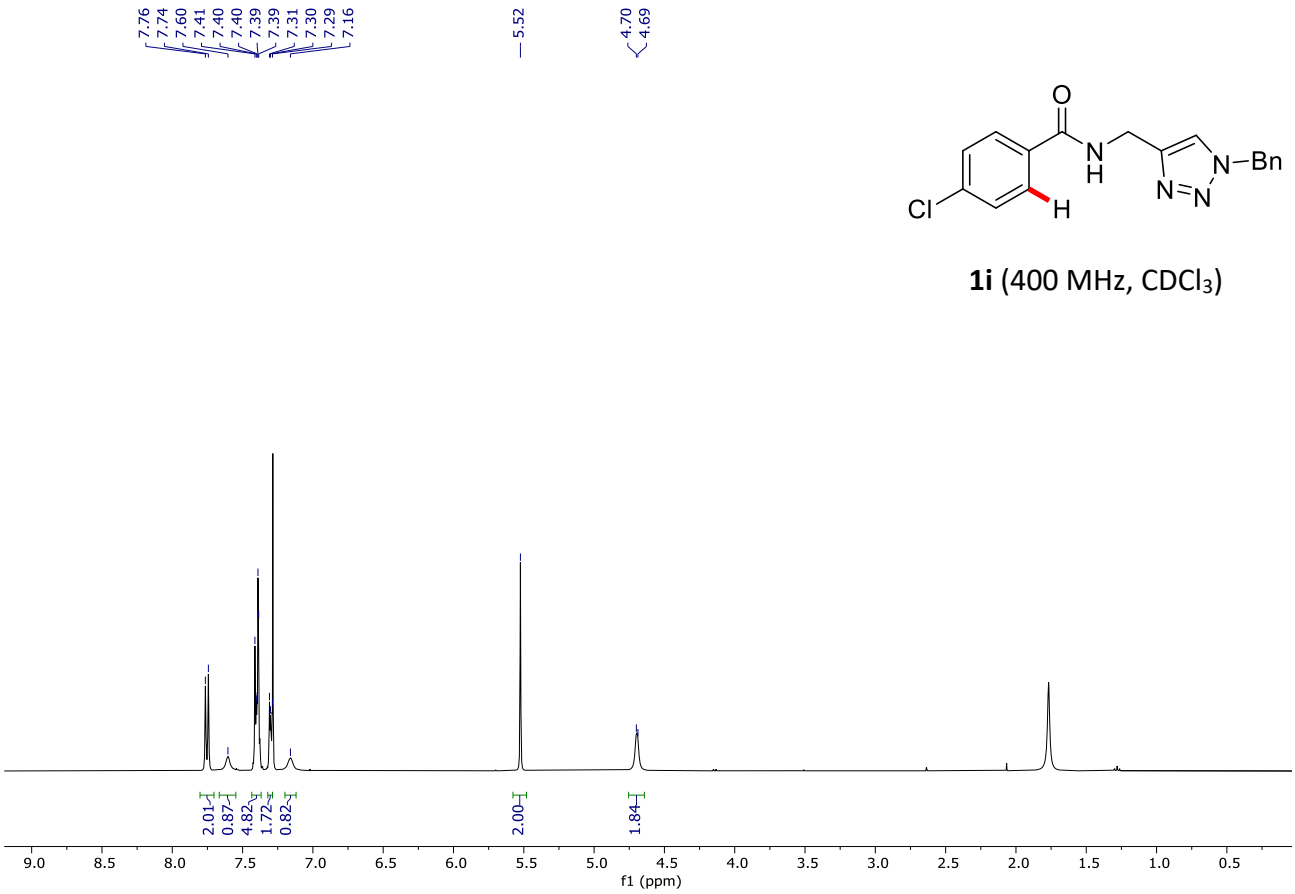

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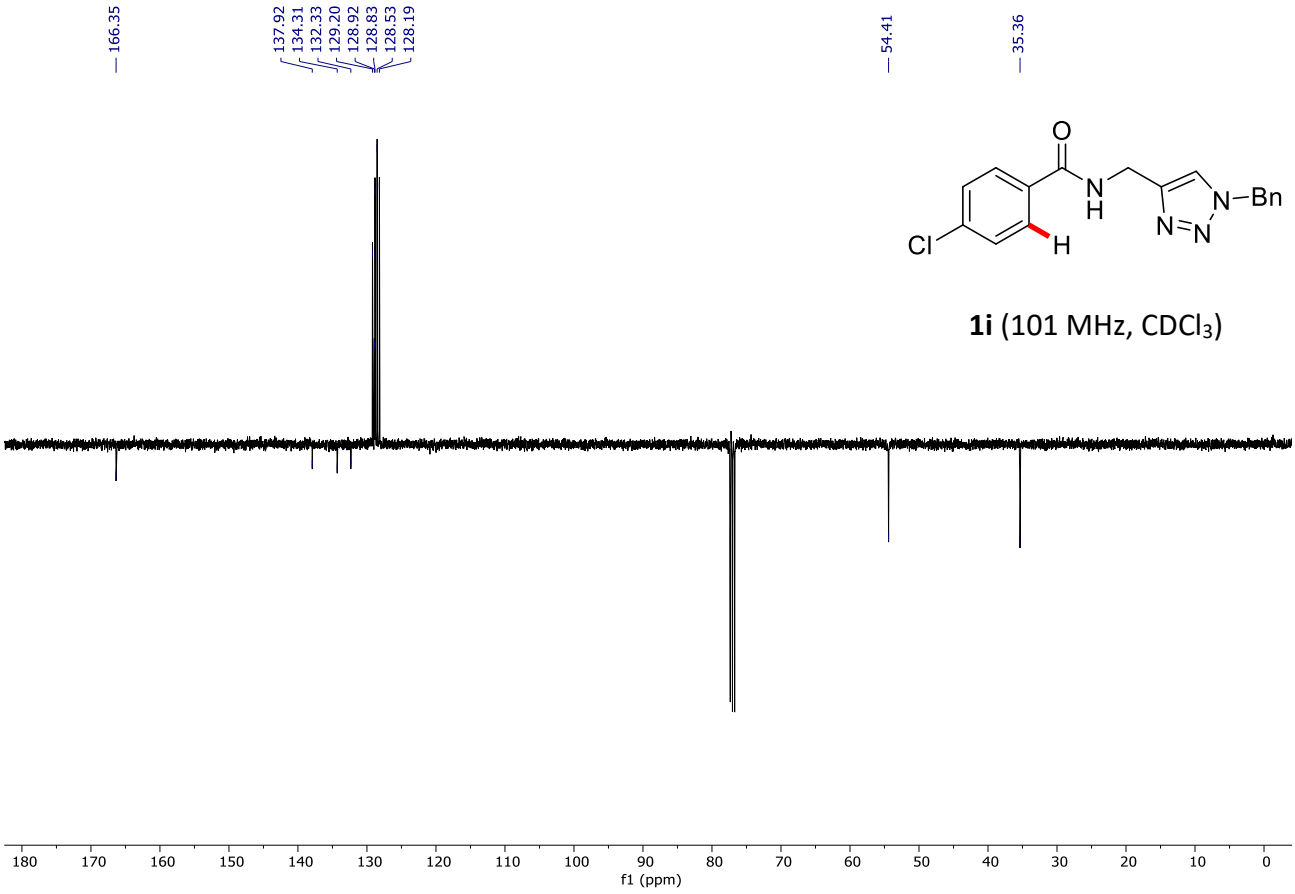

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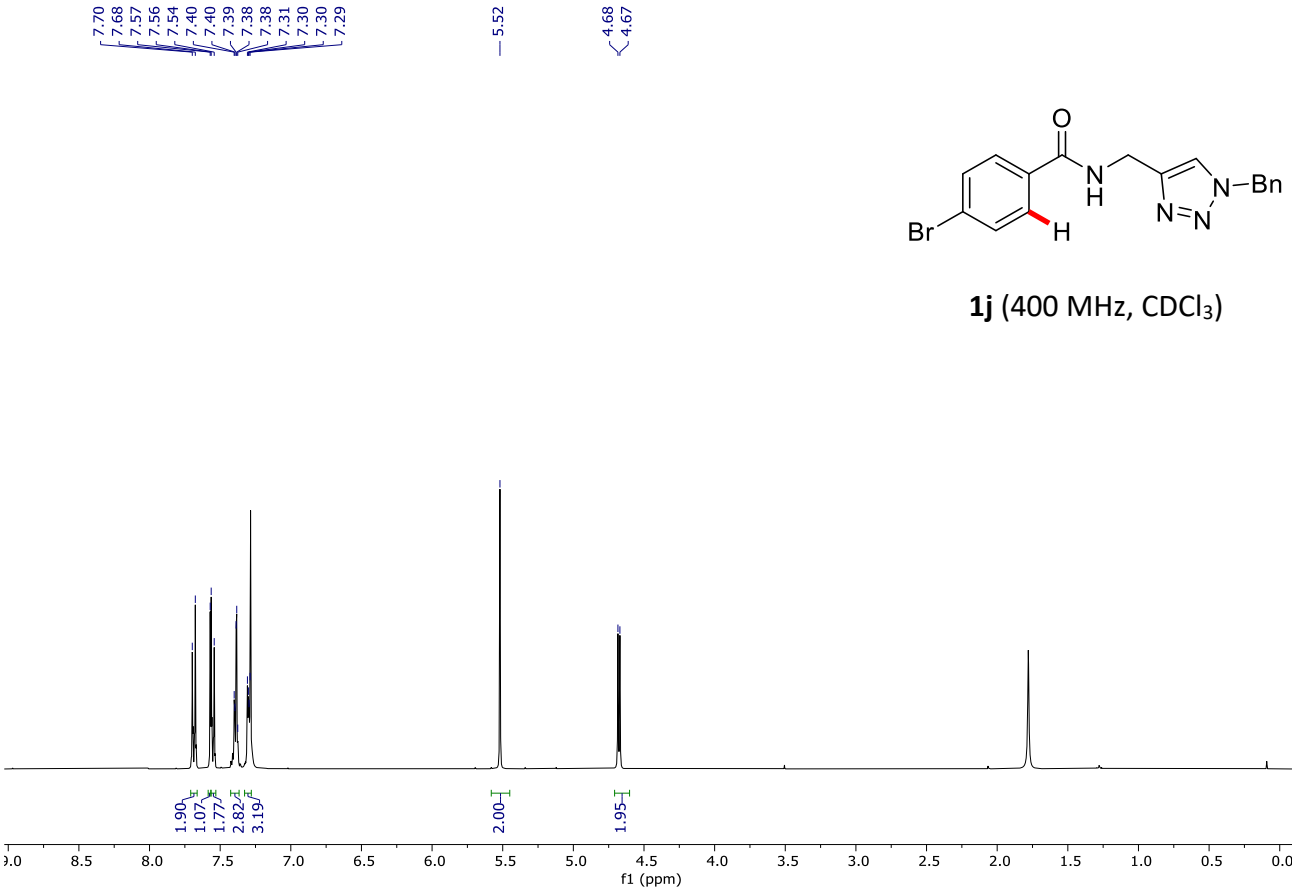

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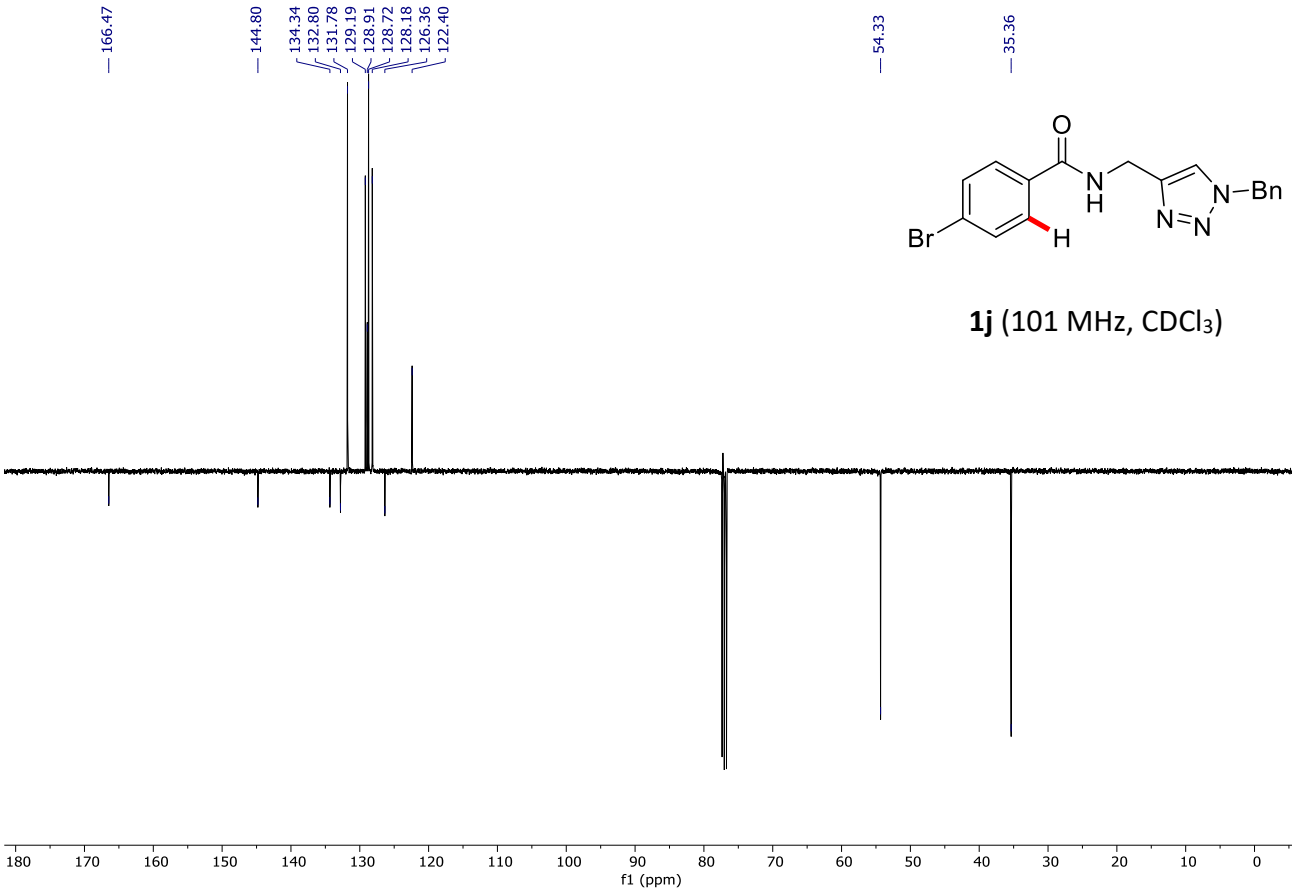

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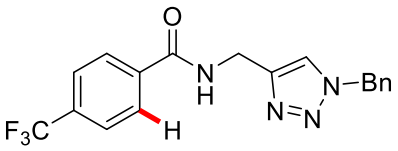

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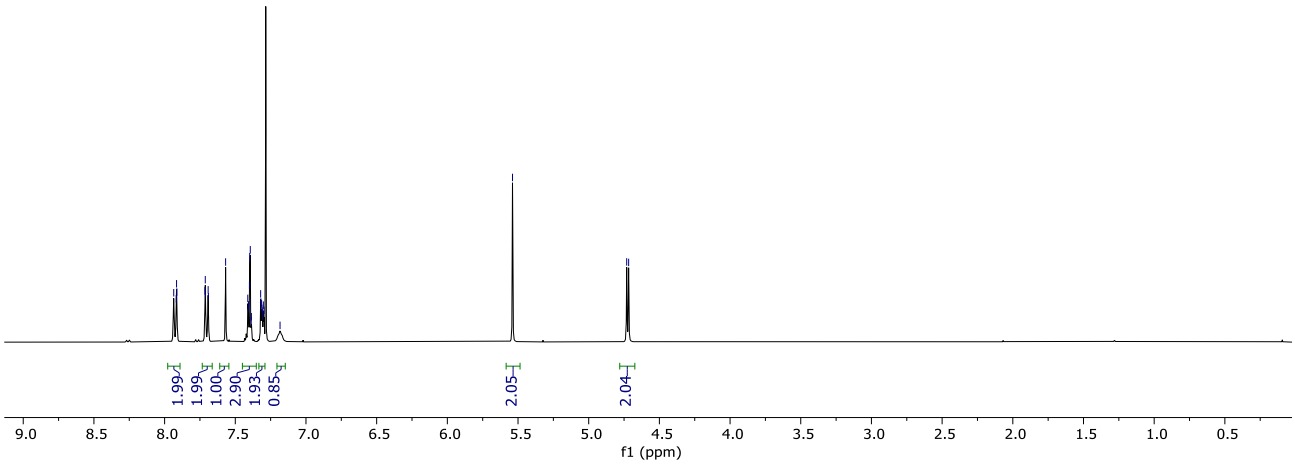

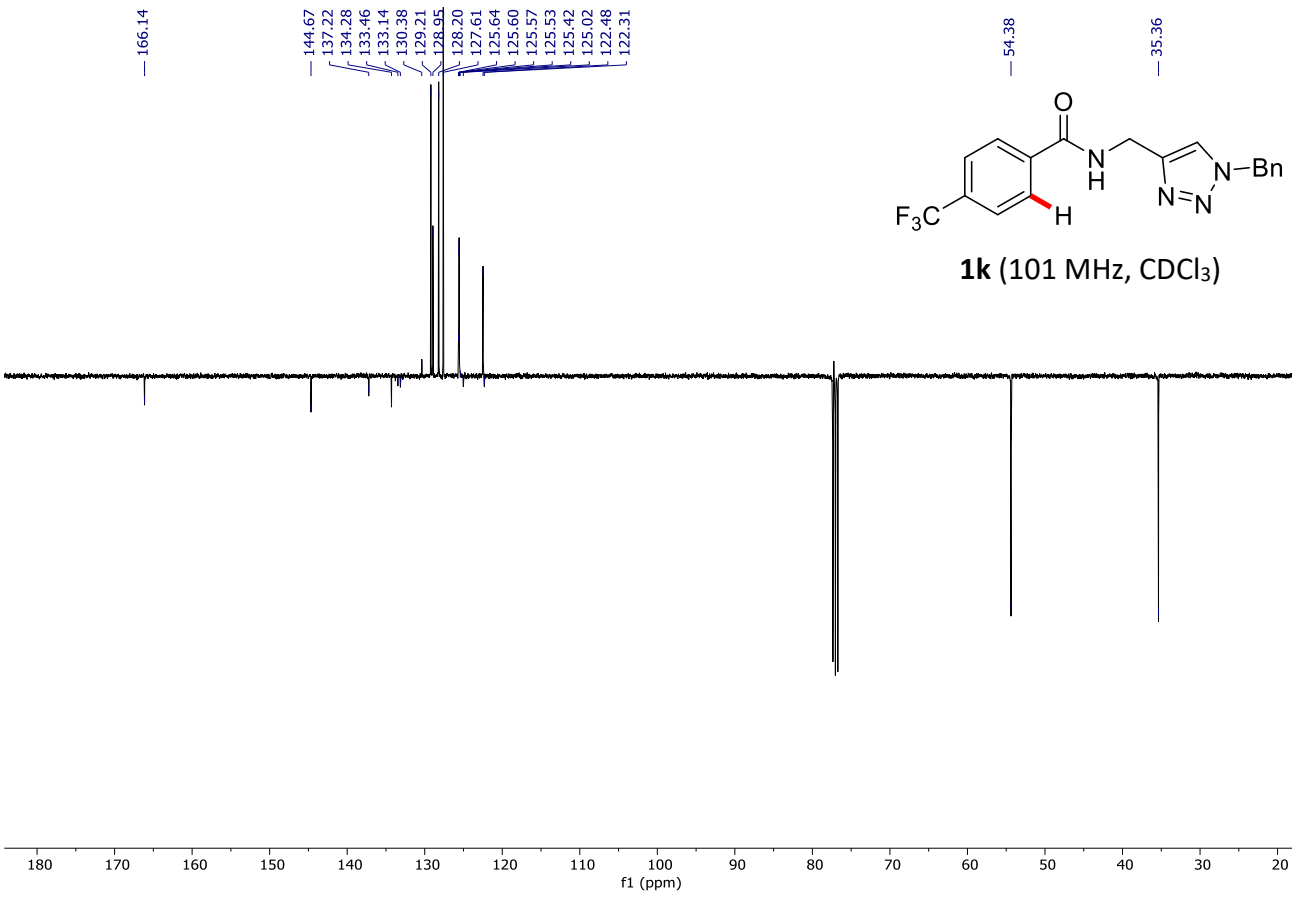

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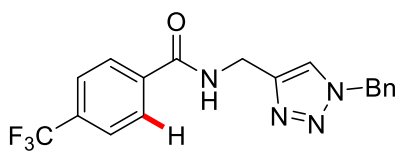

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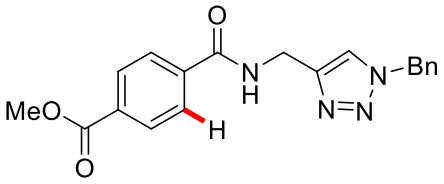
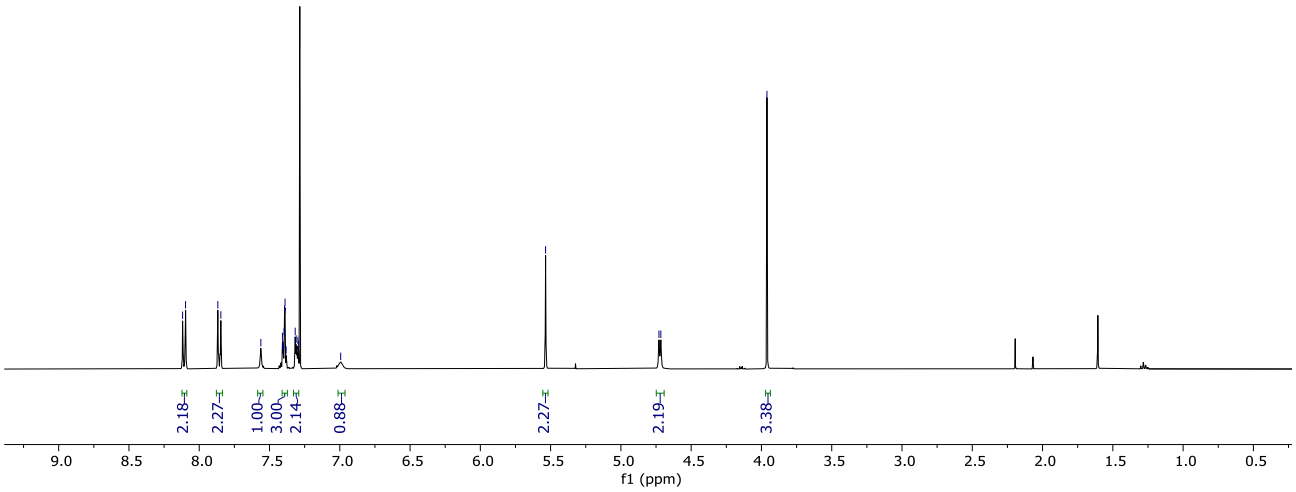
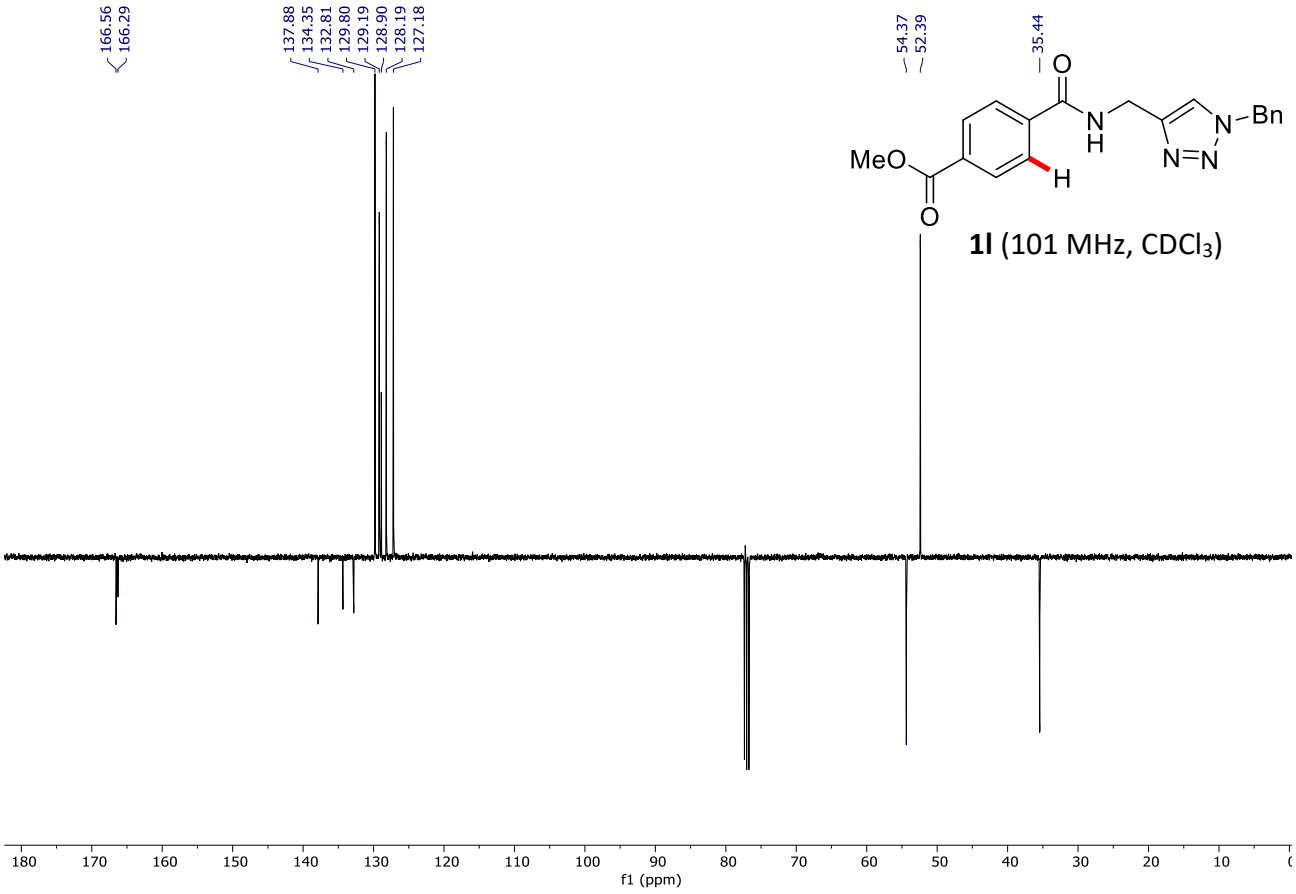


1l (400 MHz, $CDCl_3$)





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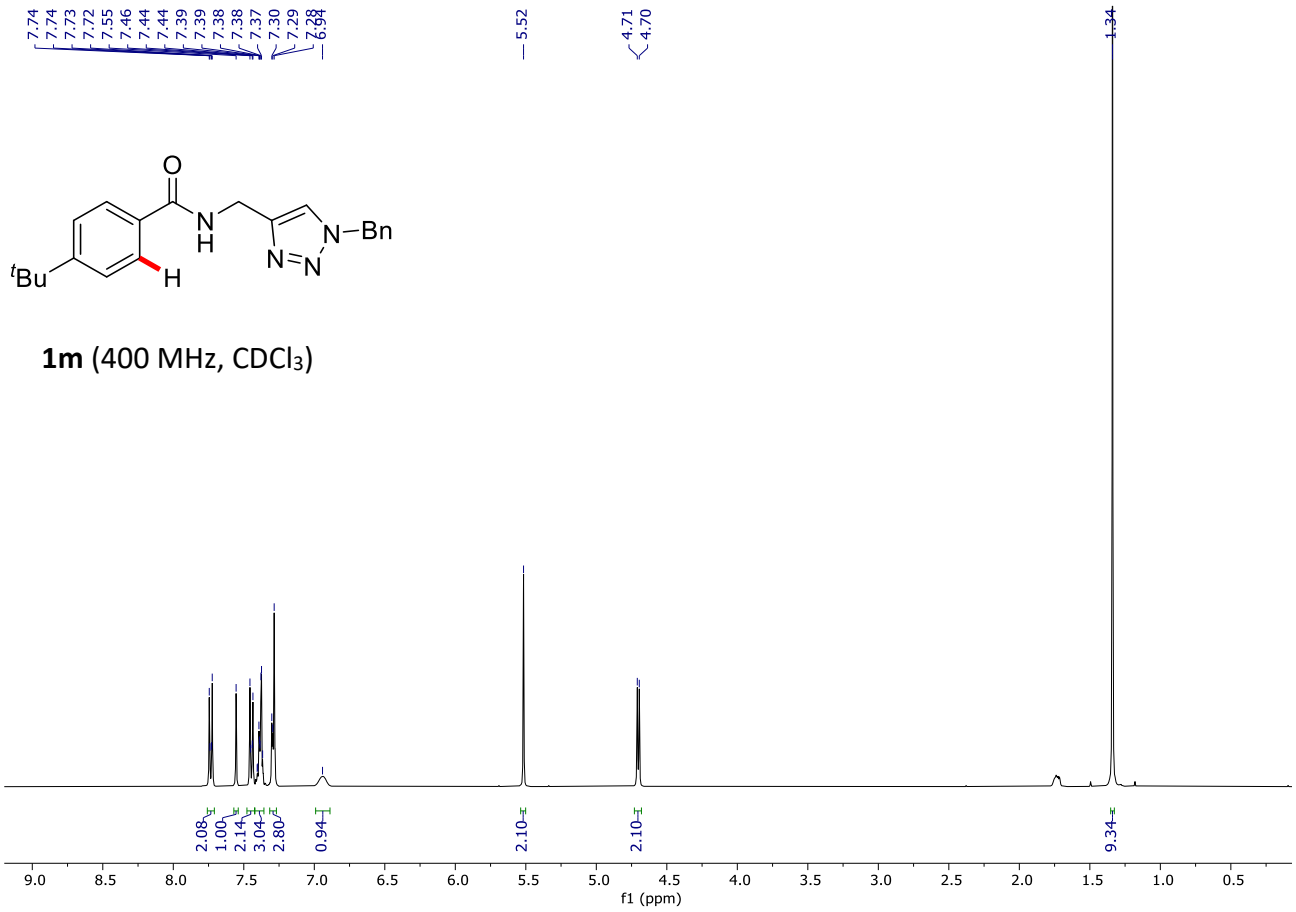

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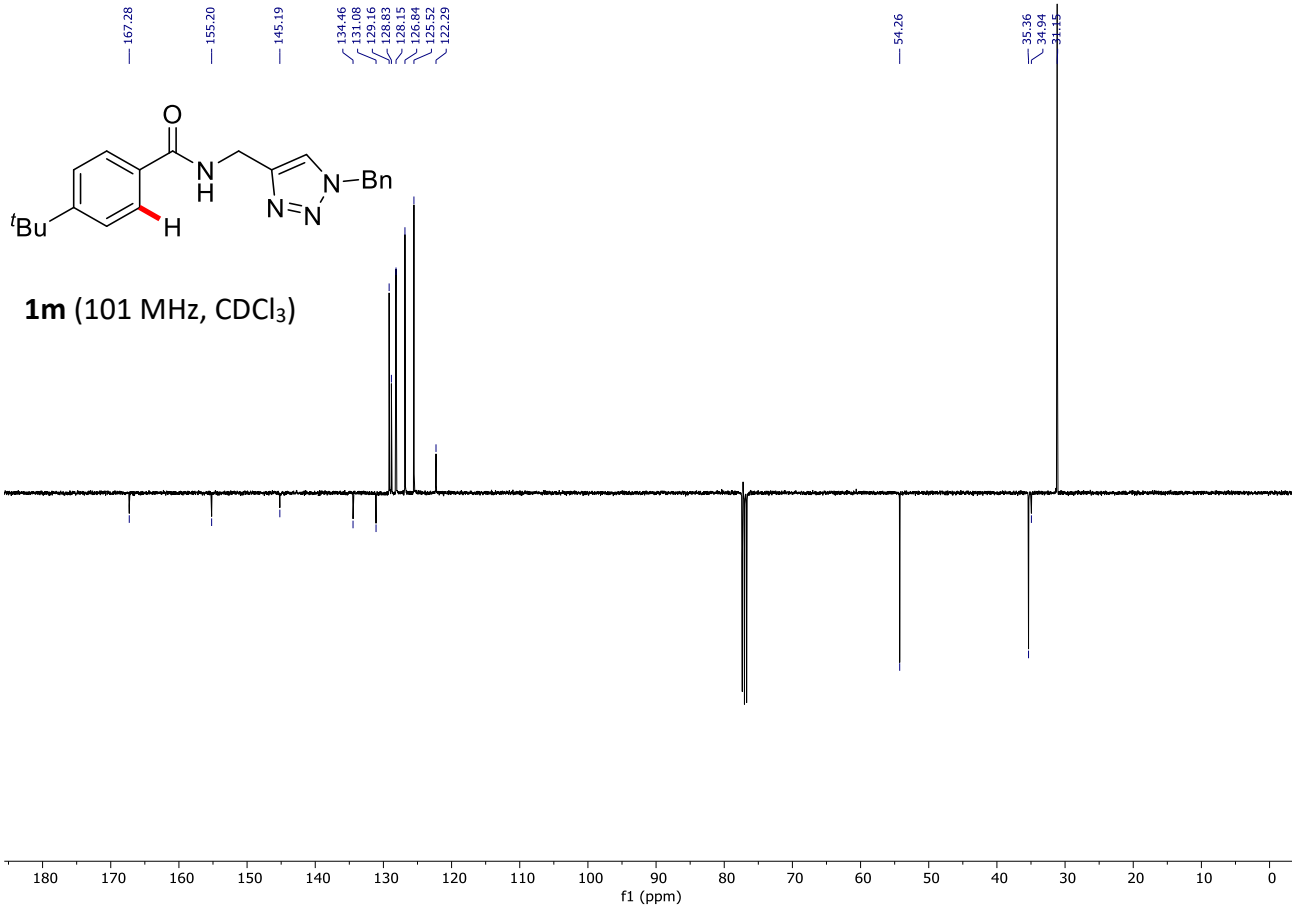

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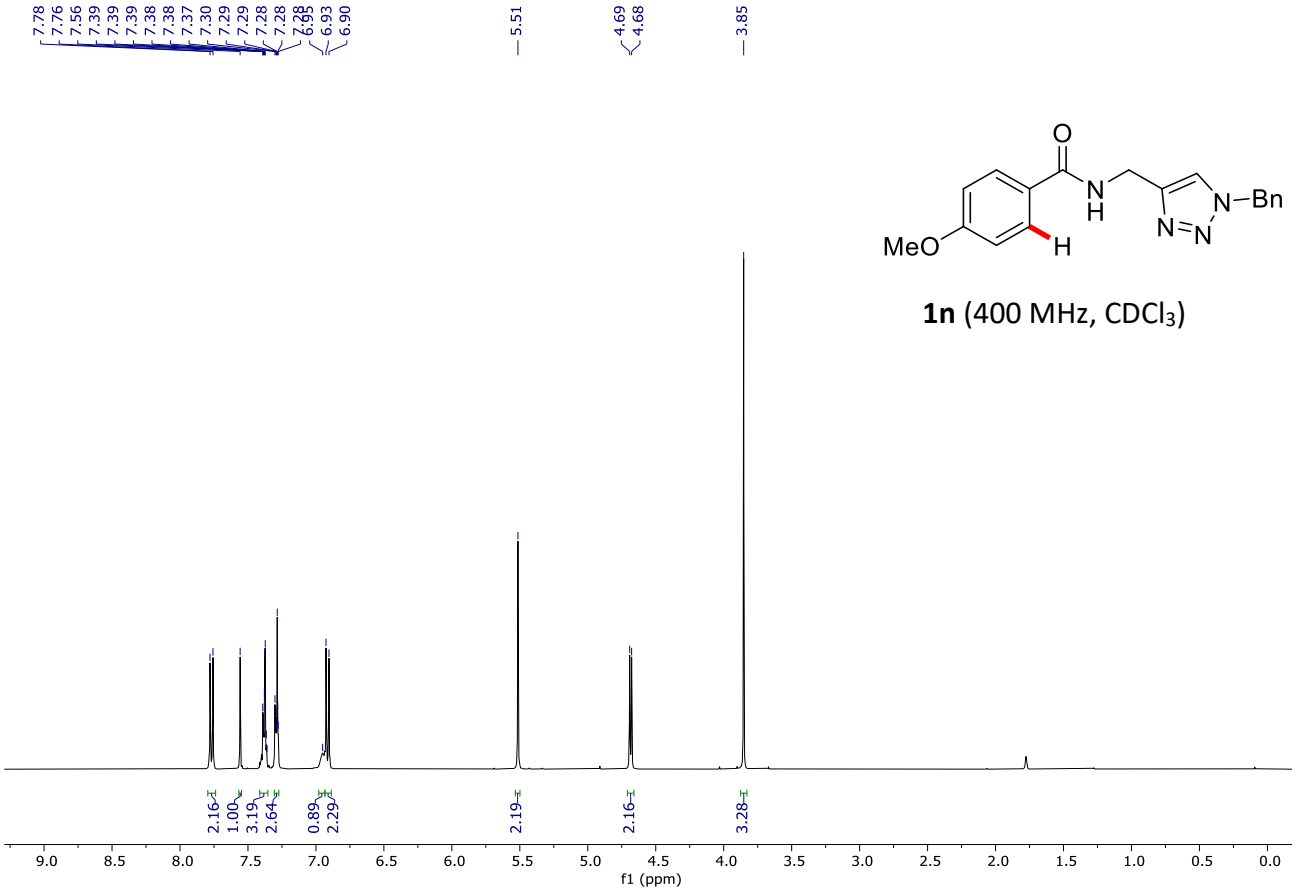
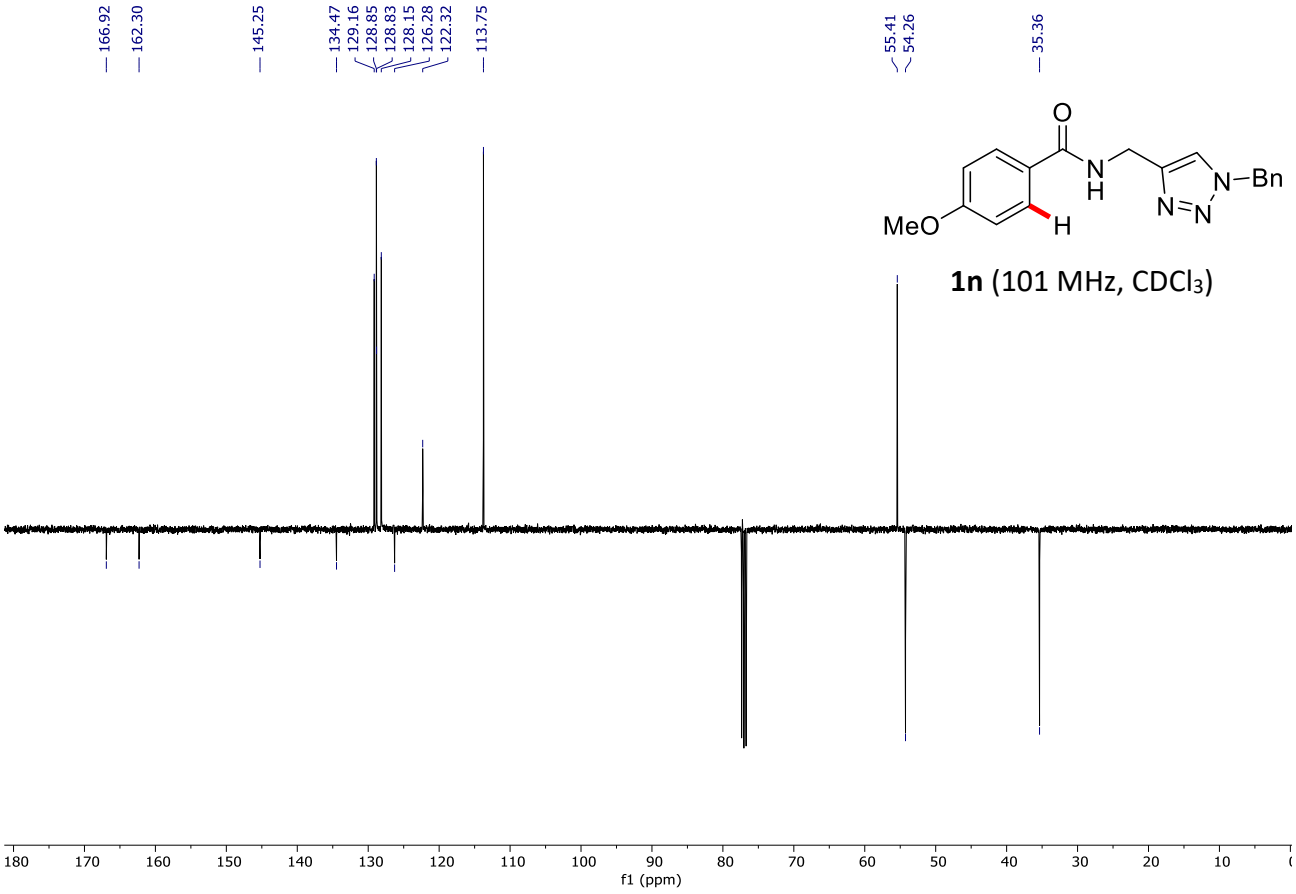
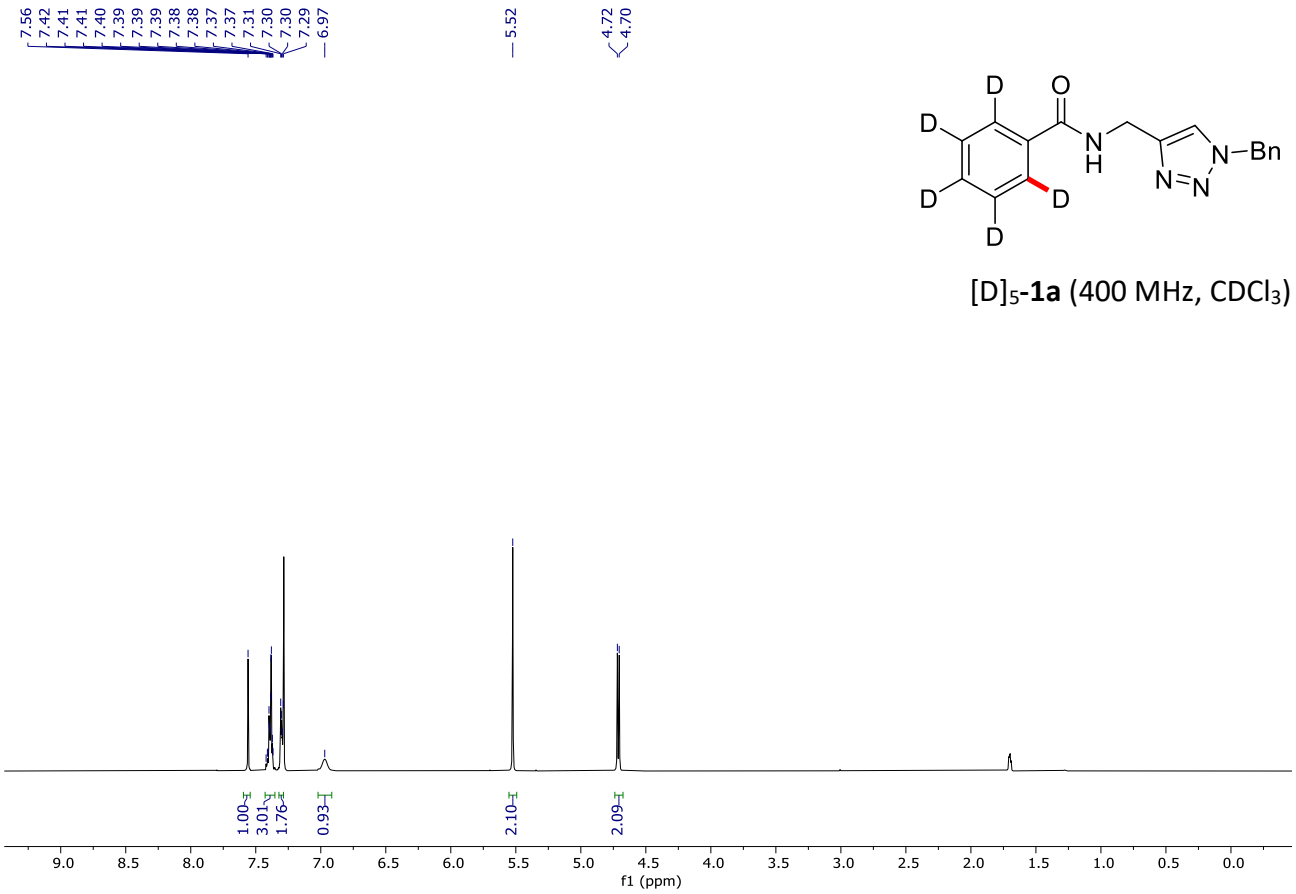


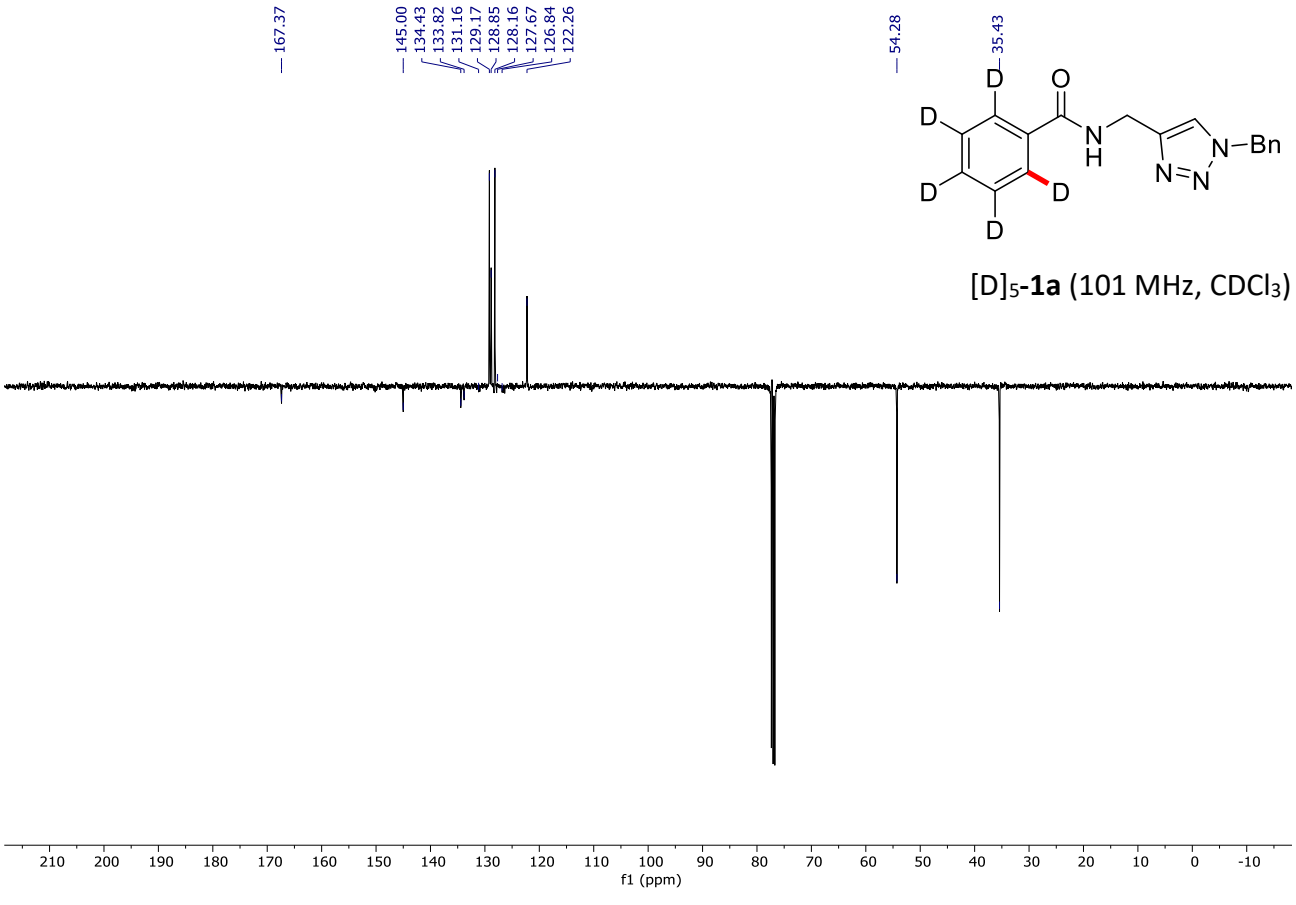
1n (400 MHz, $CDCl_3$)



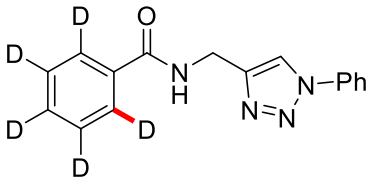
1n (101 MHz, $CDCl_3$)



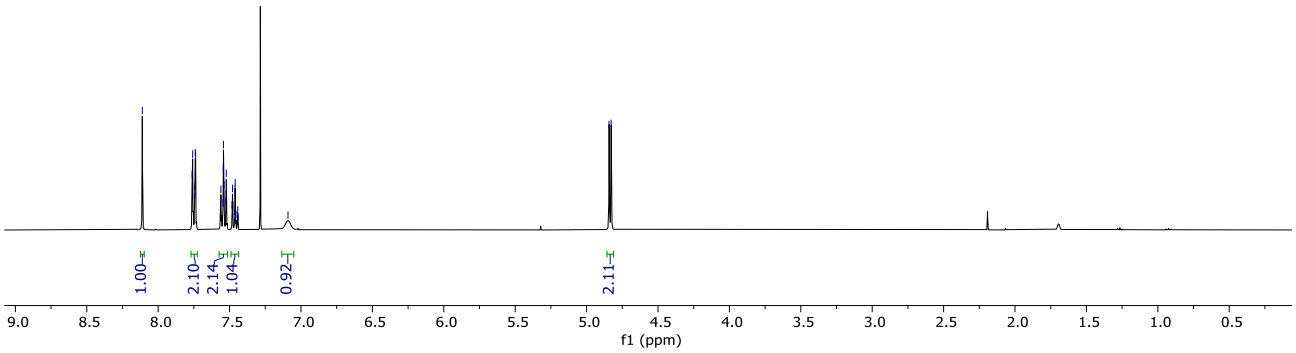
[D]$_5$-**1a** (400 MHz, $CDCl_3$)

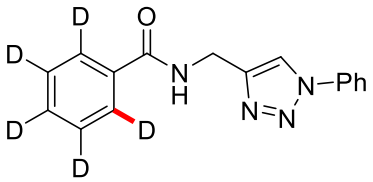


[D]$_5$-**1a** (101 MHz, $CDCl_3$)

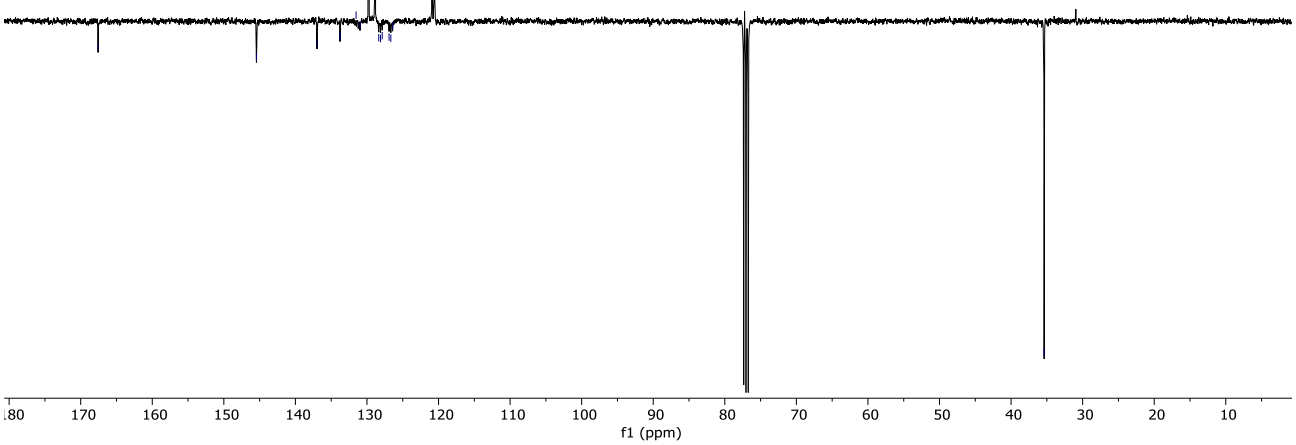


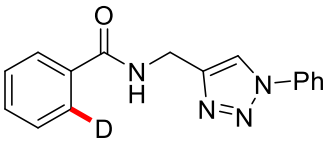
[D]$_5$-**1c** (400 MHz, $CDCl_3$)



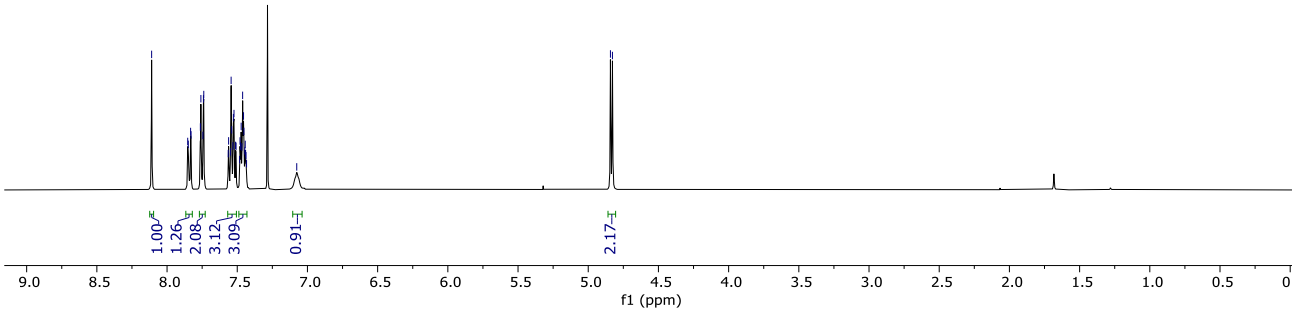


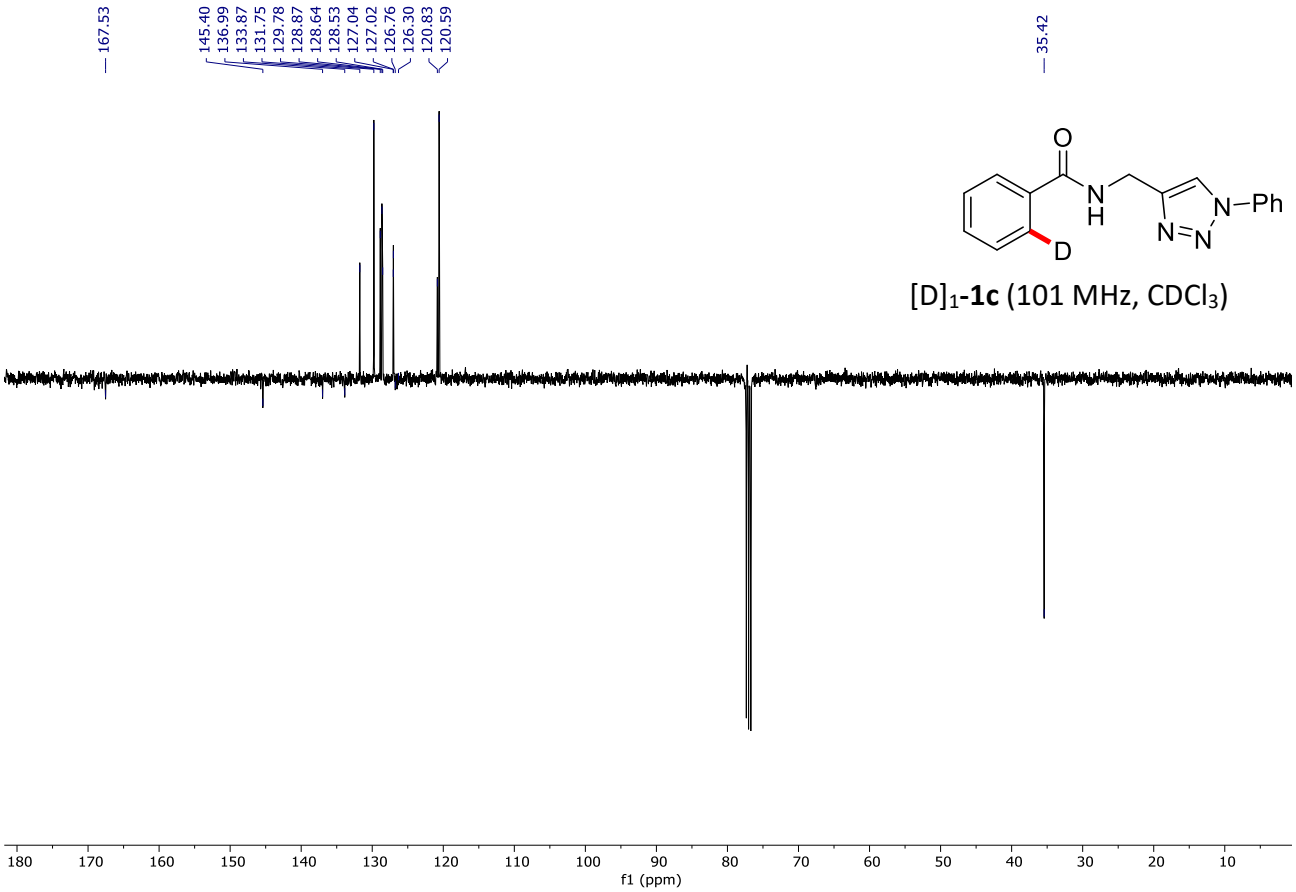
[D]$_5$-**1c** (101 MHz, $CDCl_3$)



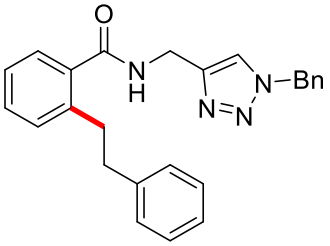


$[D]_1$-**1c** (400 MHz, $CDCl_3$)

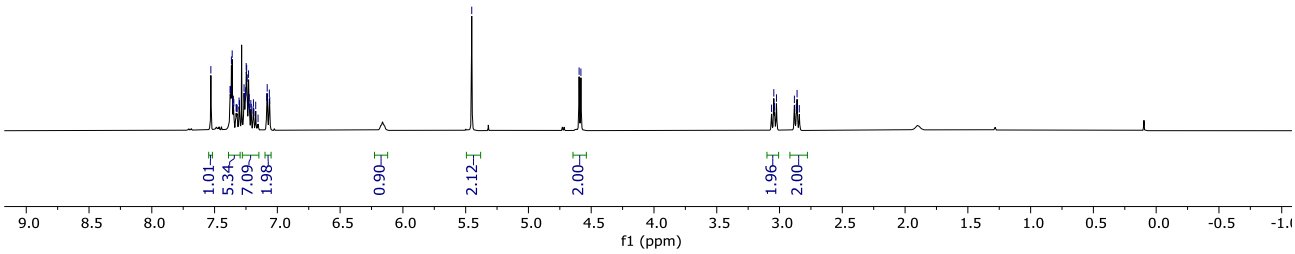


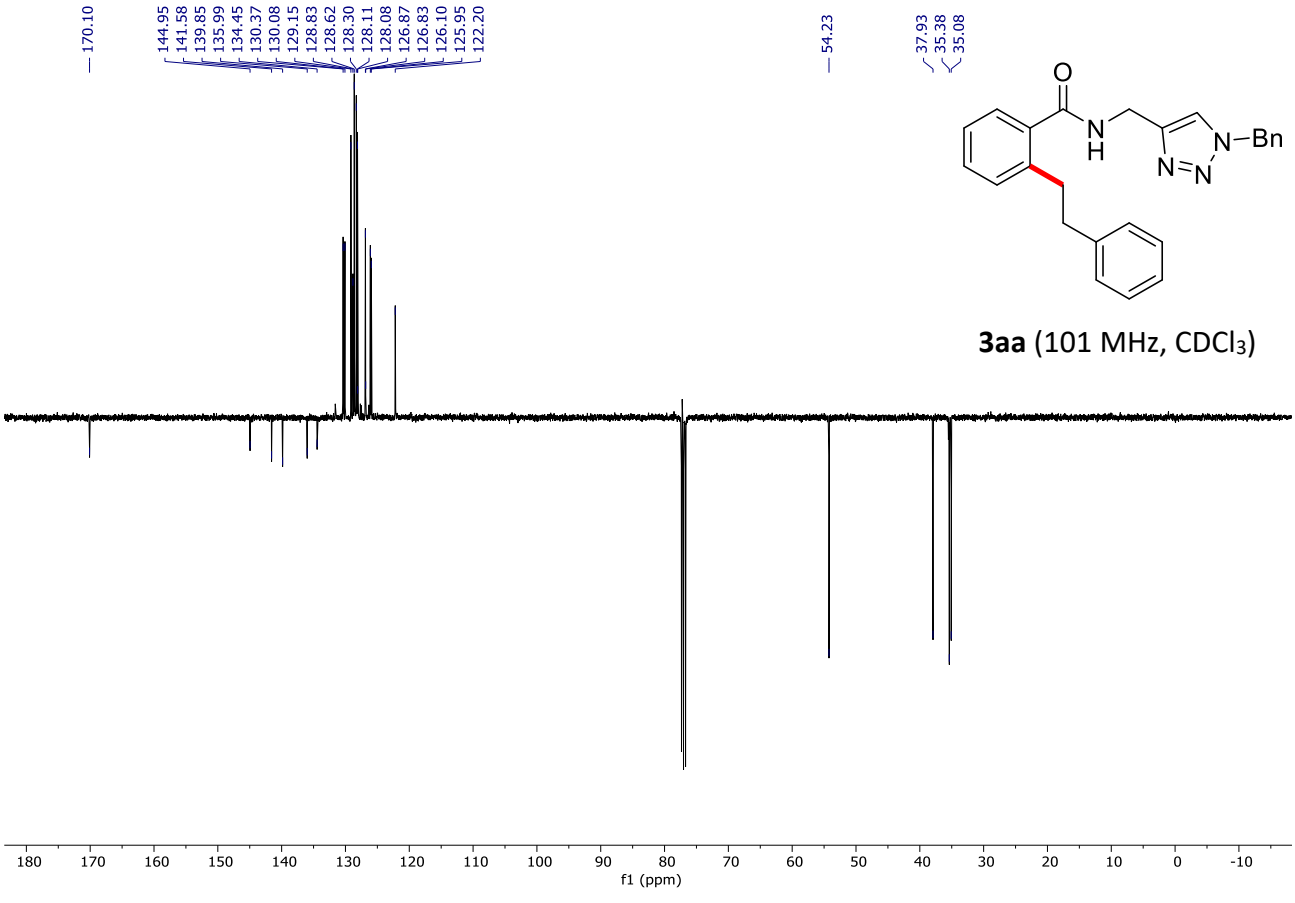


$[D]_1$-**1c** (101 MHz, $CDCl_3$)

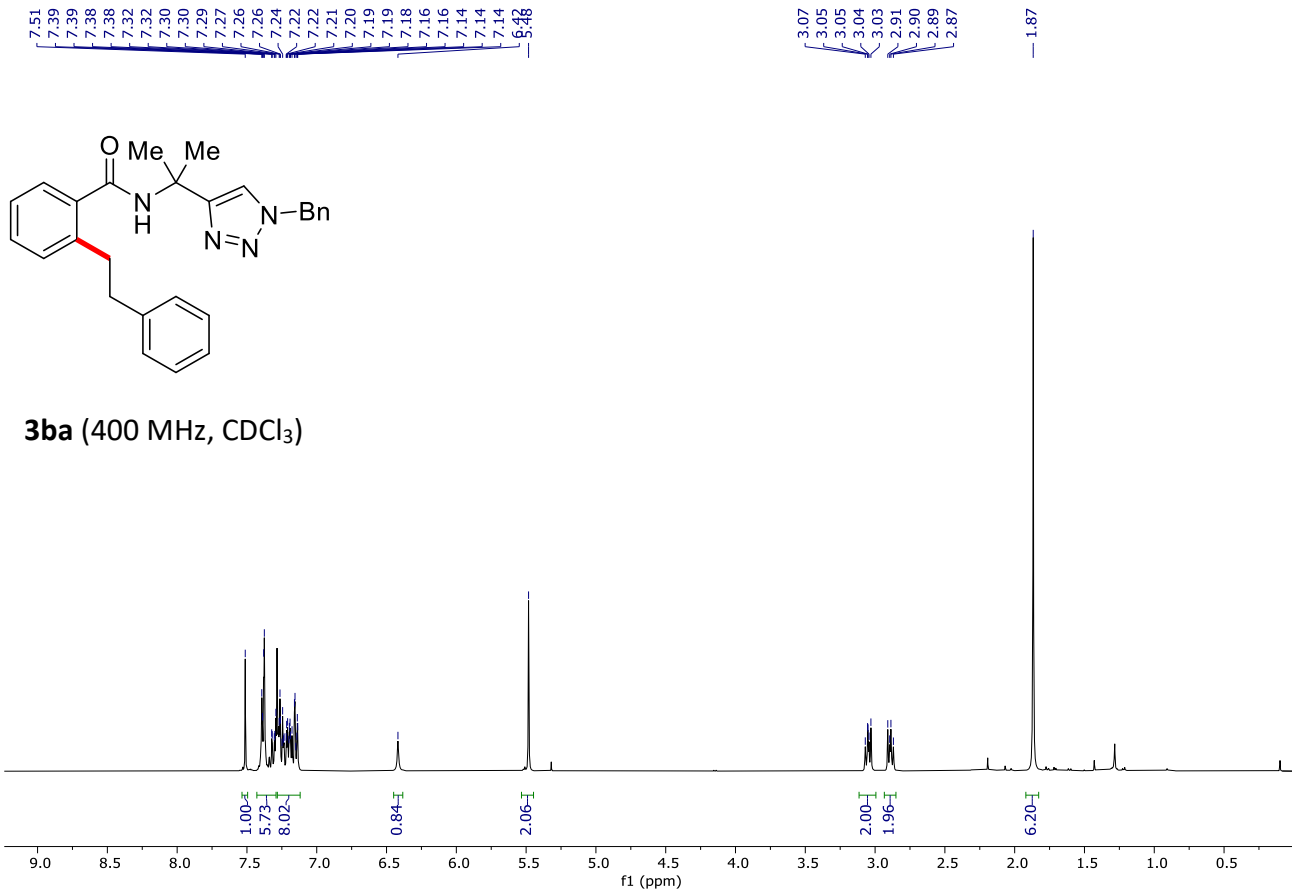


3aa (400 MHz, $CDCl_3$)

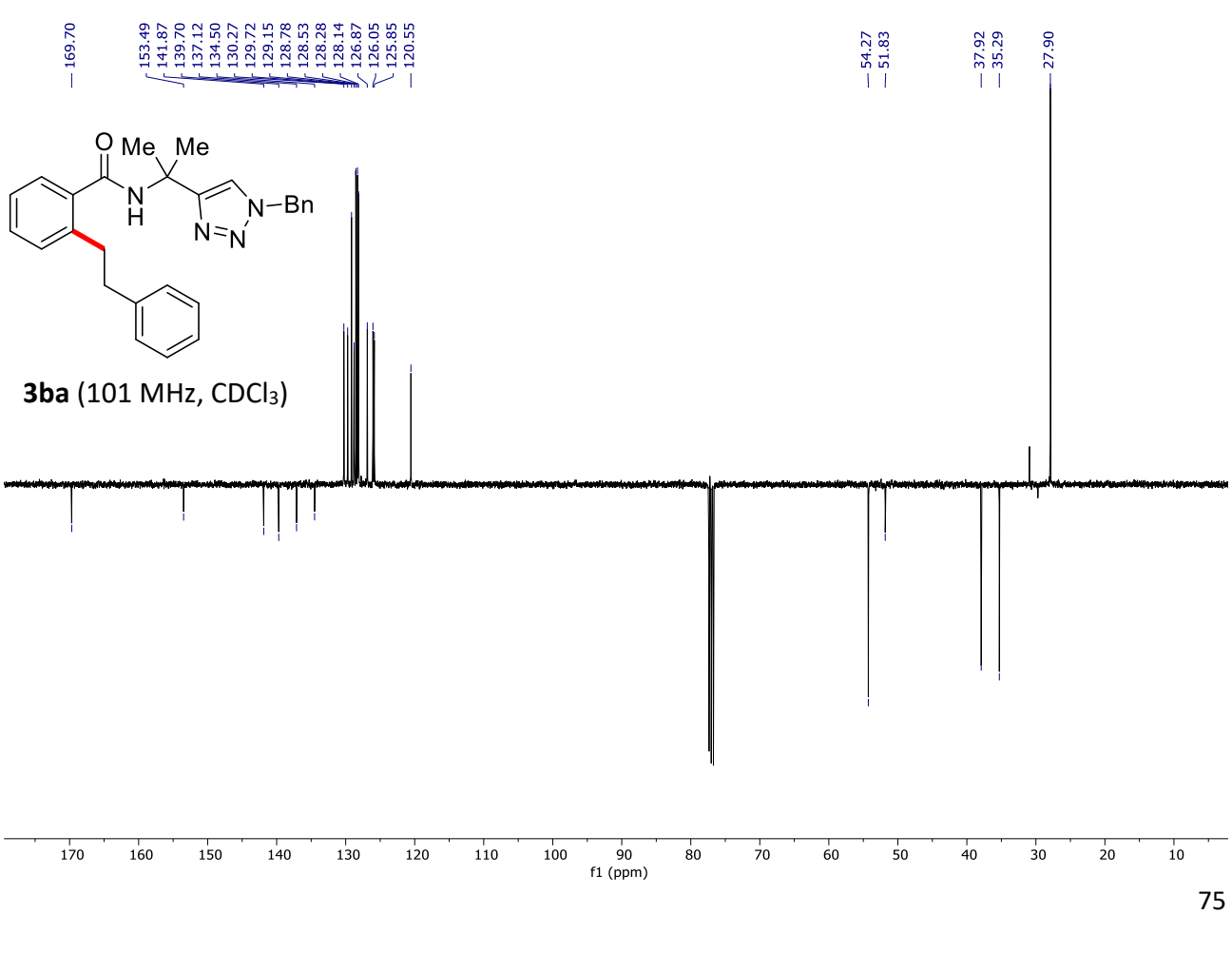




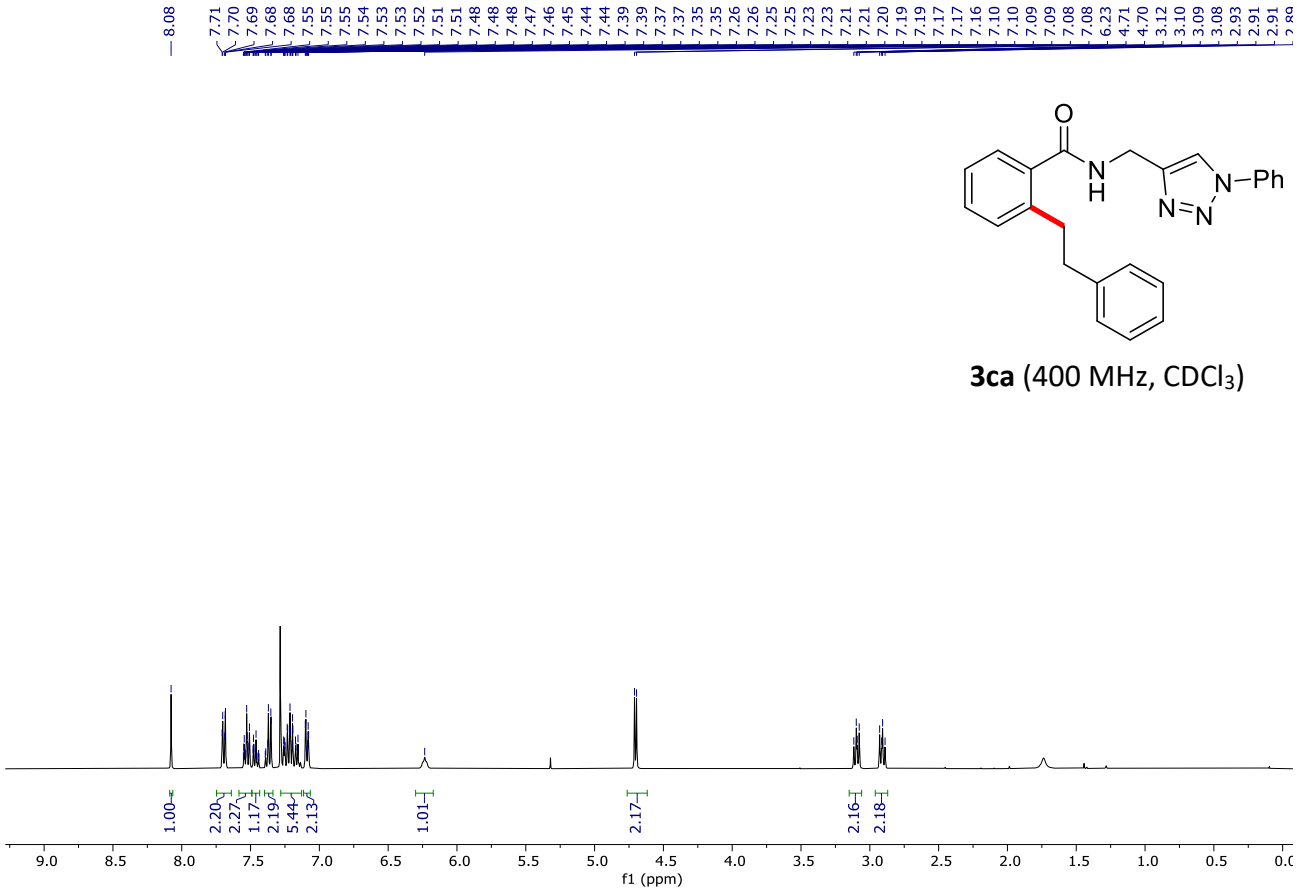
3aa (101 MHz, $CDCl_3$)



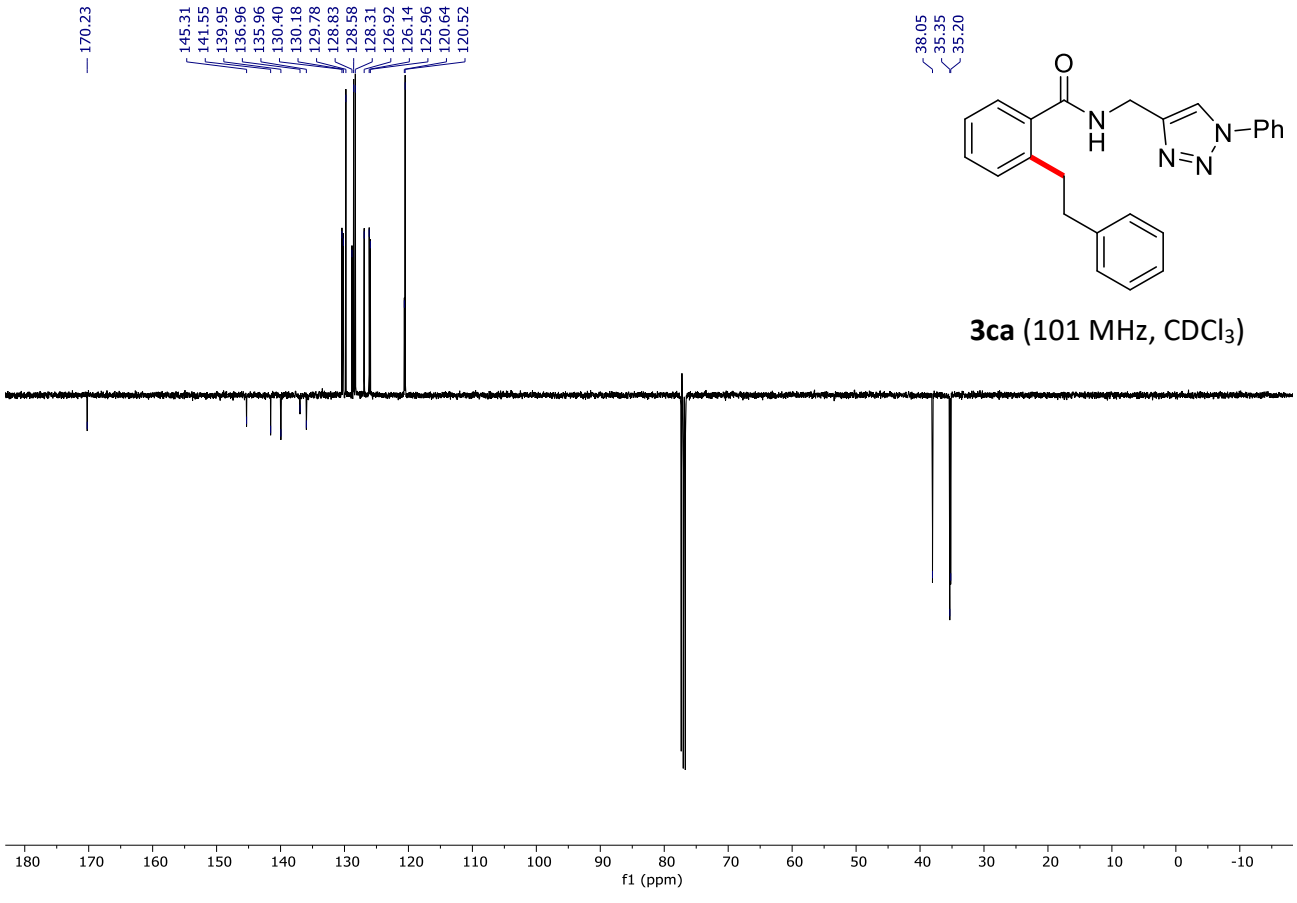
3ba (400 MHz, $CDCl_3$)



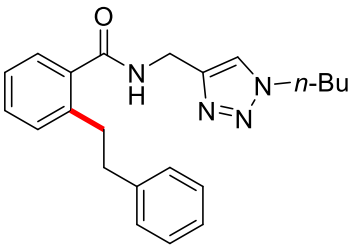
3ba (101 MHz, $CDCl_3$)



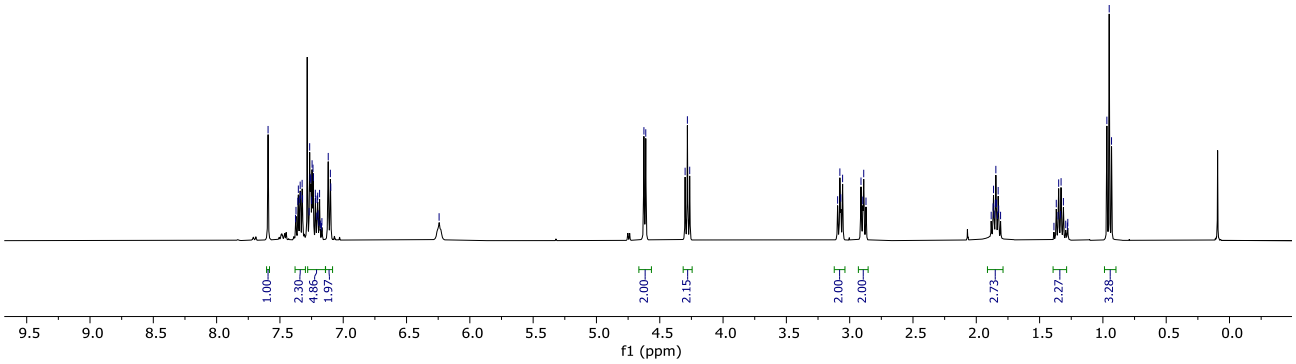
3ca (400 MHz, $CDCl_3$)

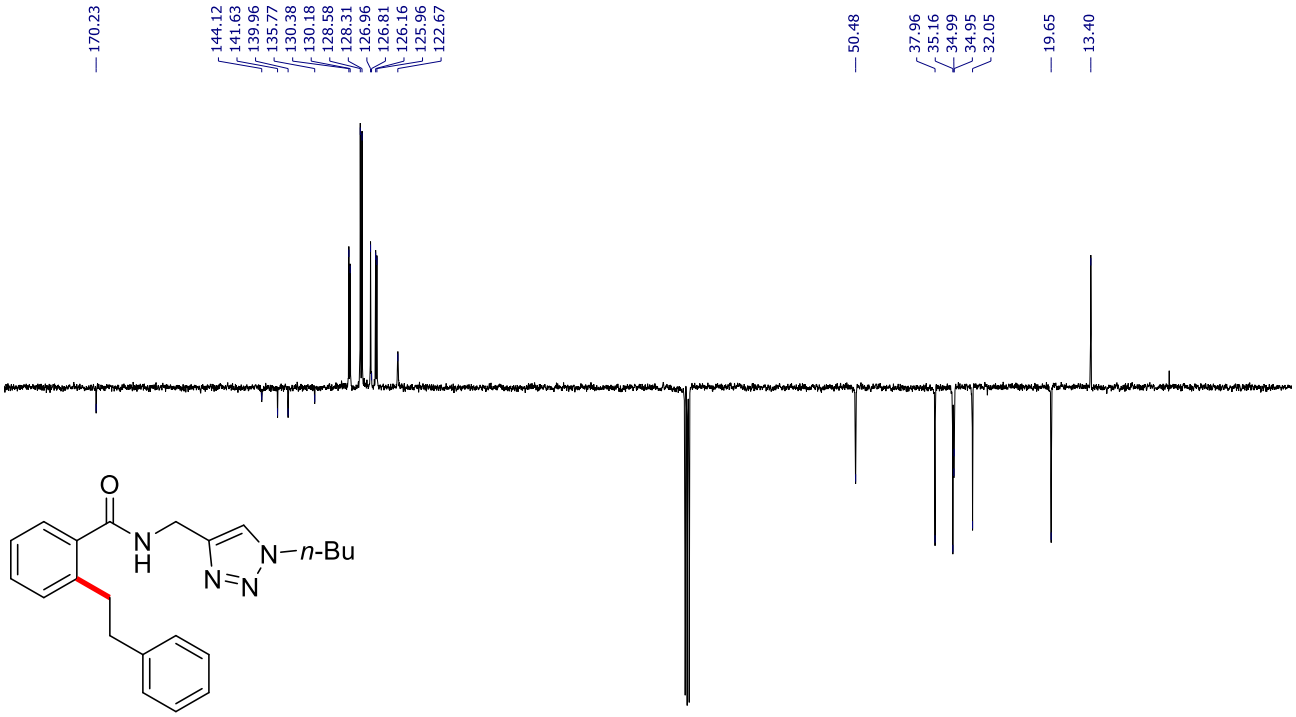


3ca (101 MHz, $CDCl_3$)

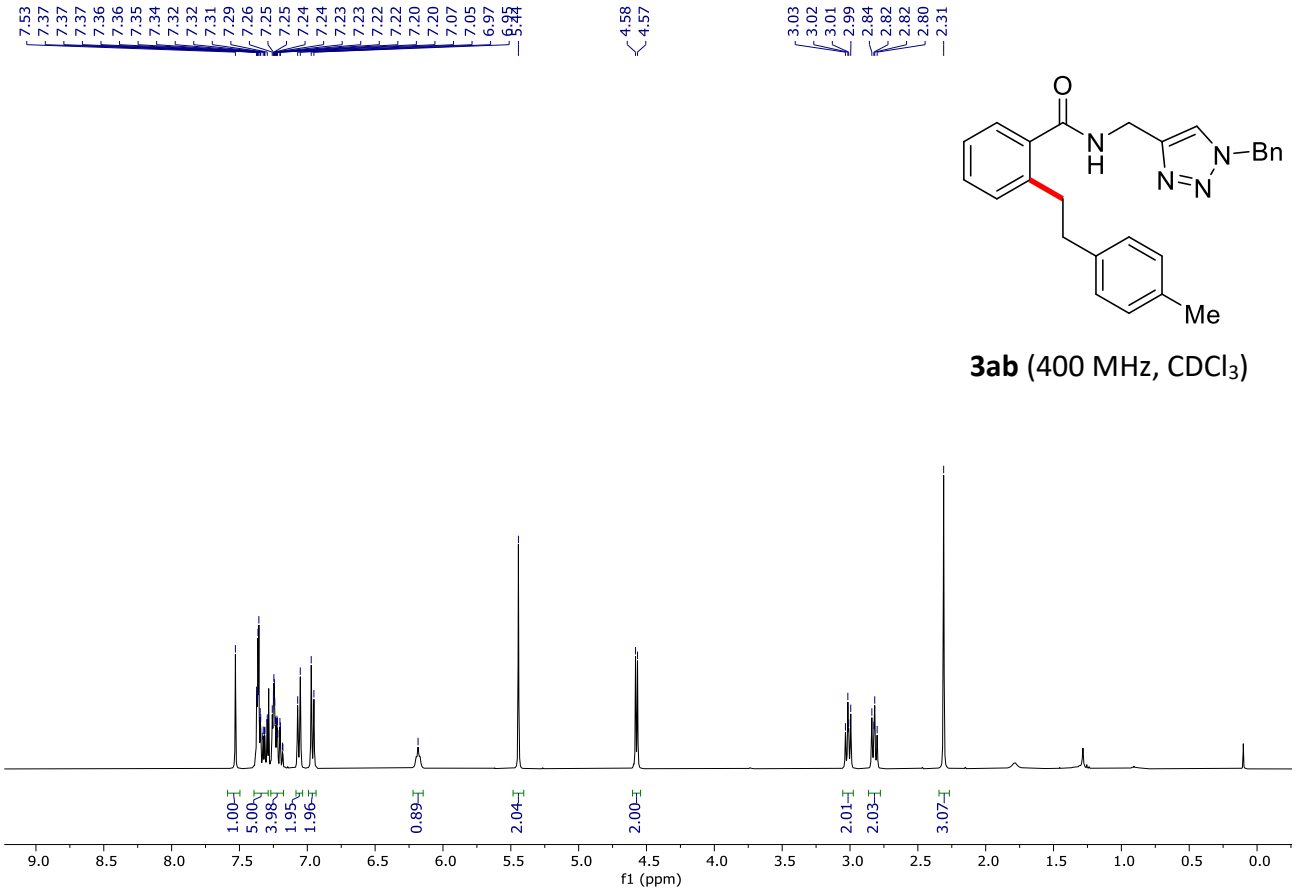


3da (400 MHz, $CDCl_3$)

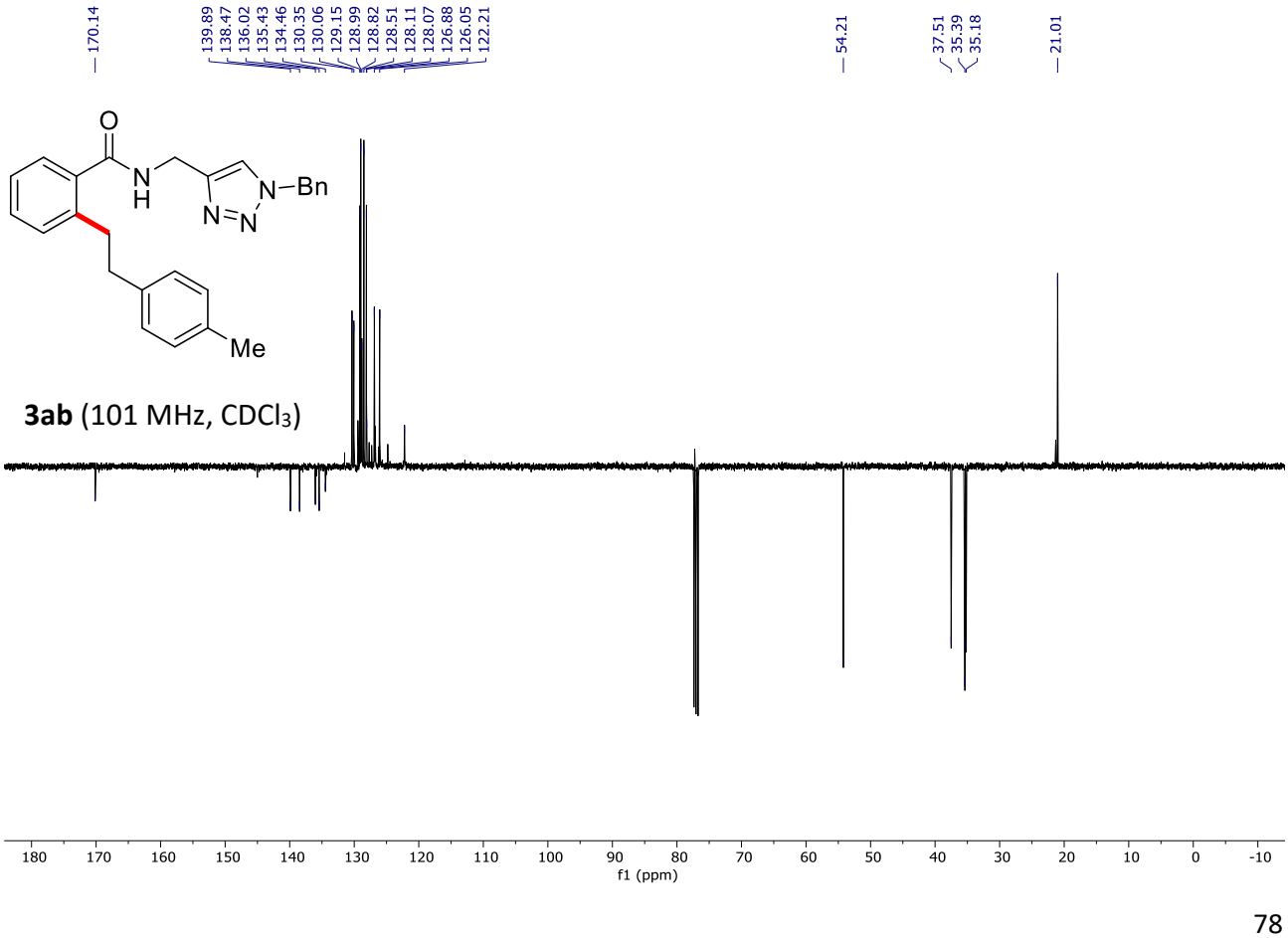




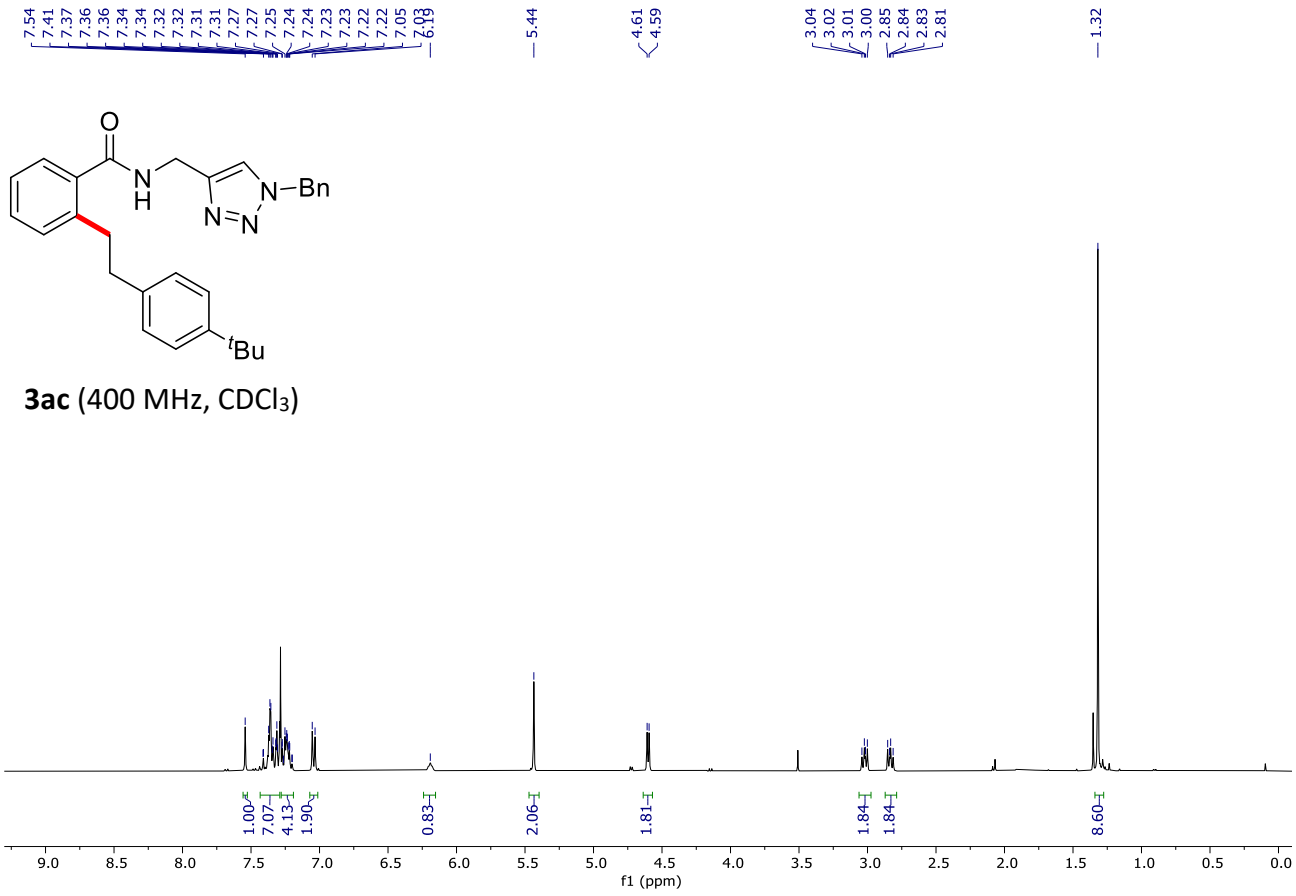
3da (101 MHz, $CDCl_3$)



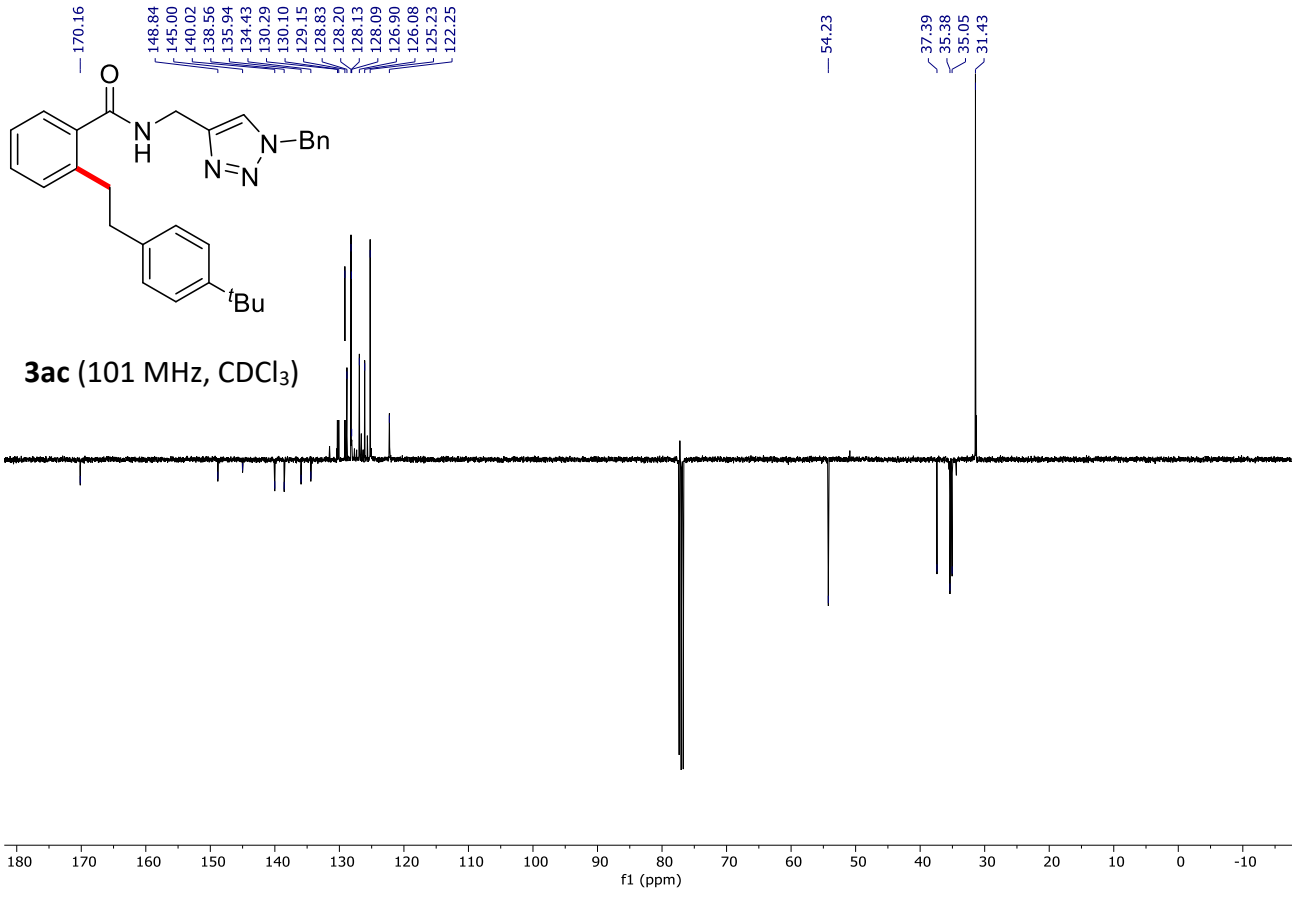
3ab (400 MHz, $CDCl_3$)



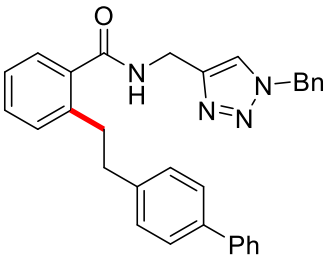
3ab (101 MHz, $CDCl_3$)



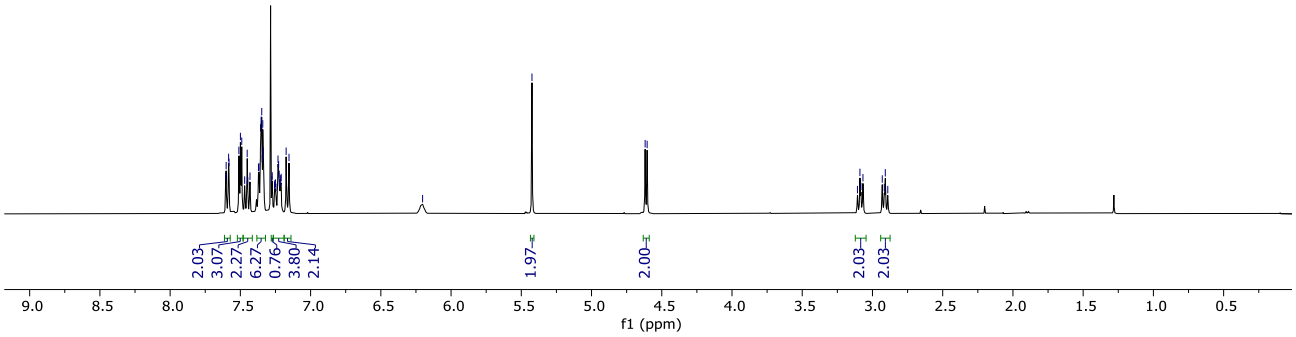
3ac (400 MHz, $CDCl_3$)

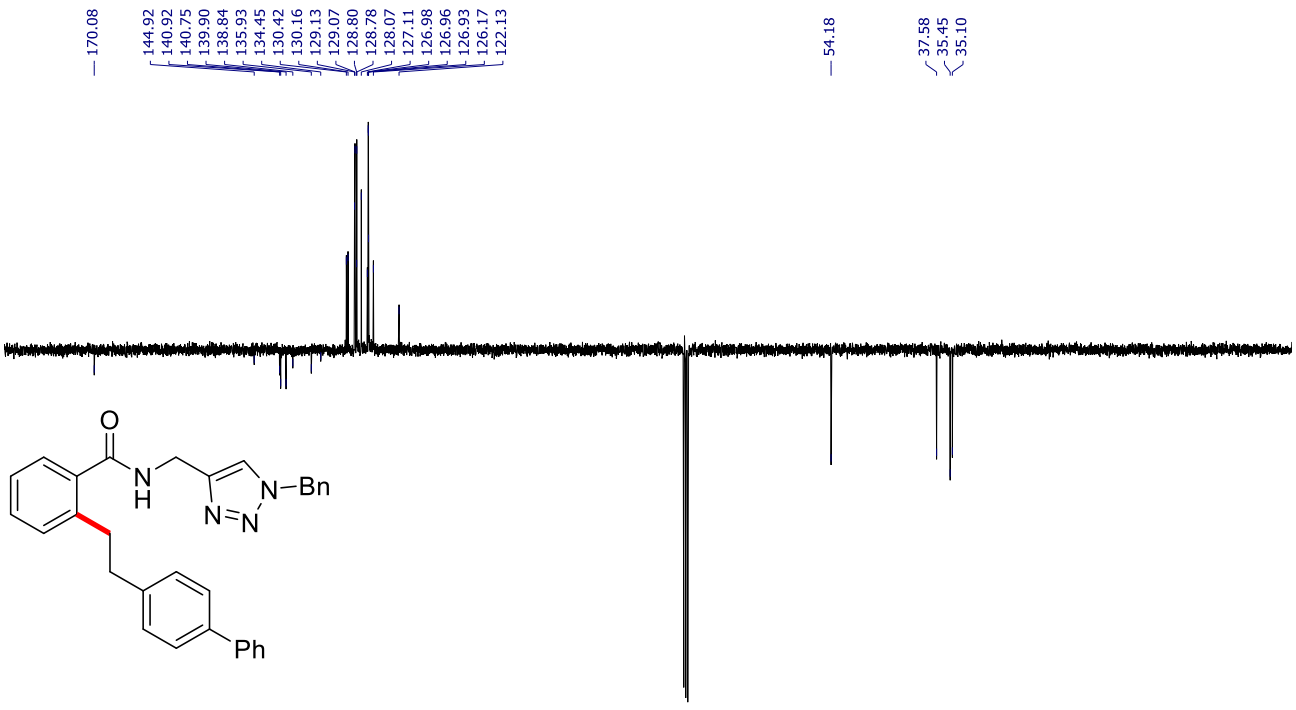


3ac (101 MHz, $CDCl_3$)

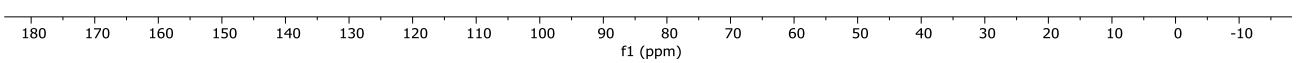


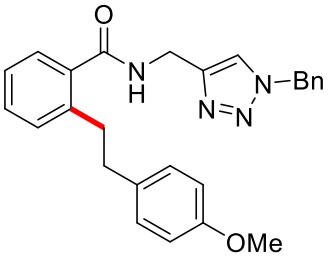
3ad (400 MHz, $CDCl_3$)



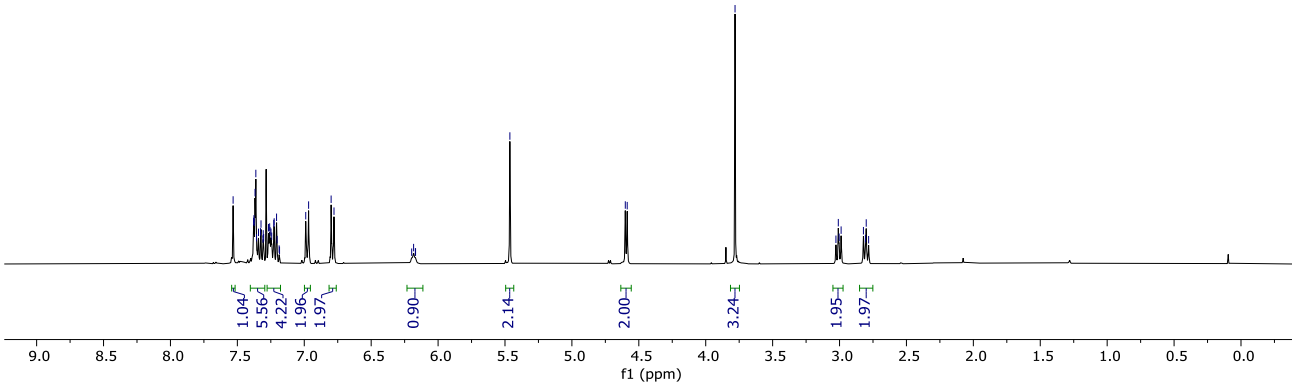


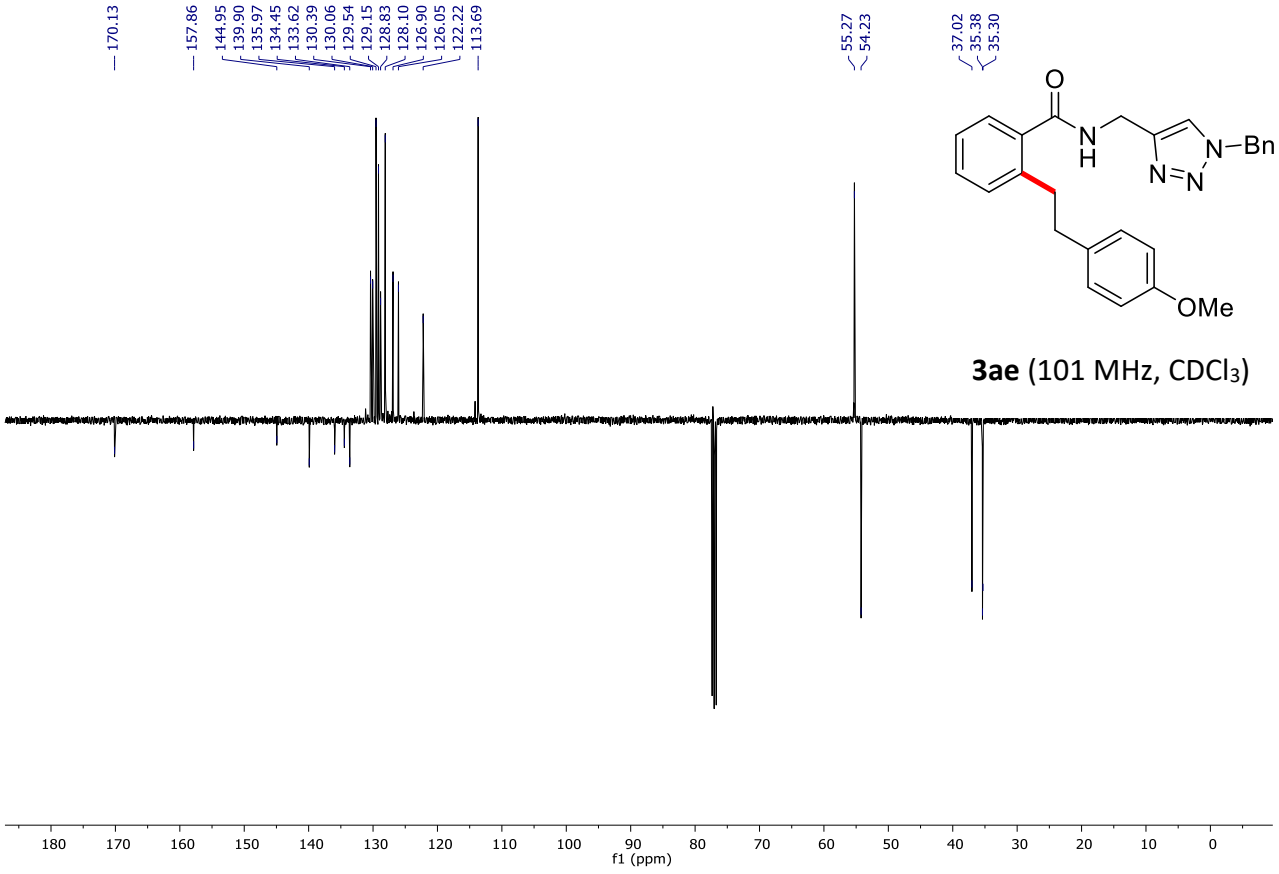
3ad (101 MHz, $CDCl_3$)



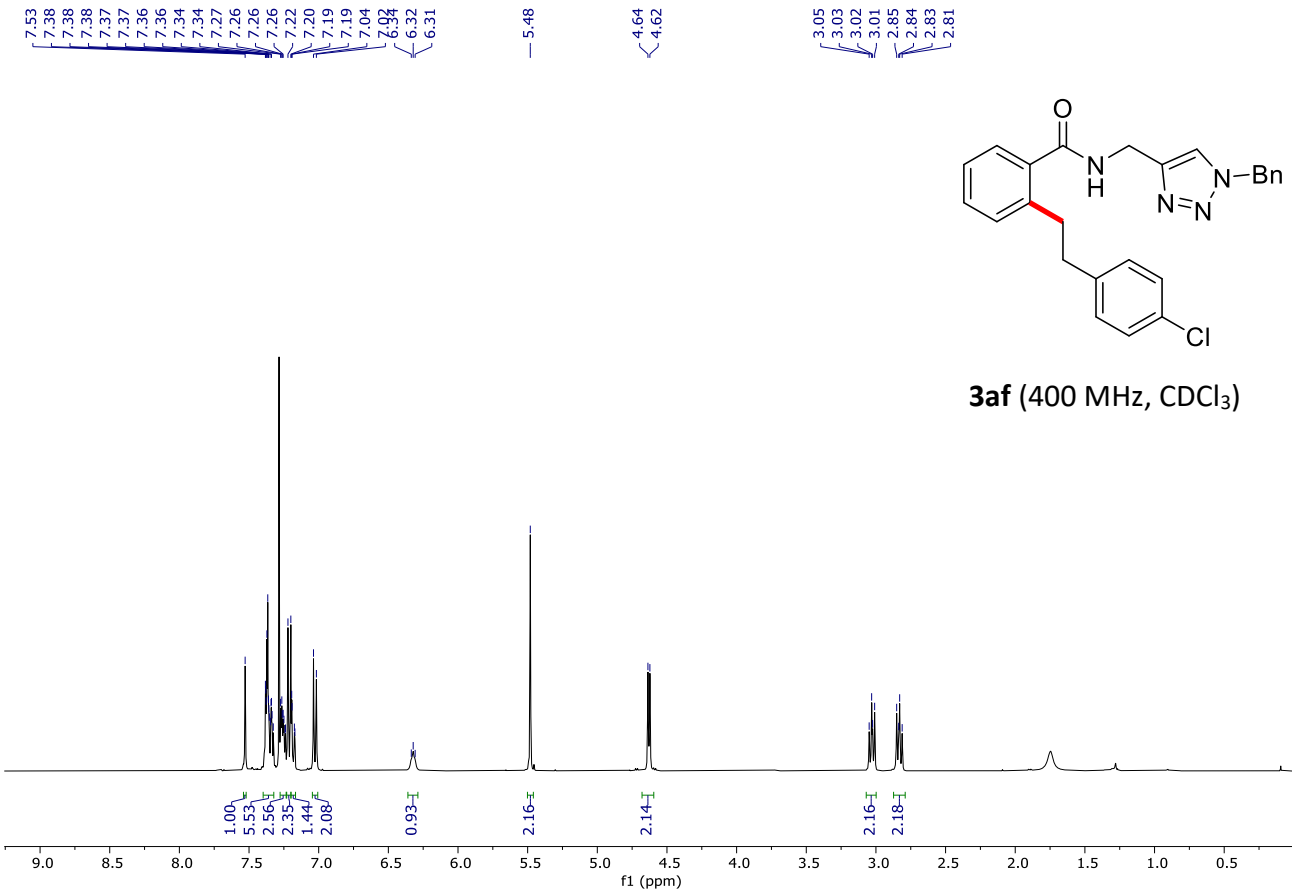


3ae (400 MHz, $CDCl_3$)

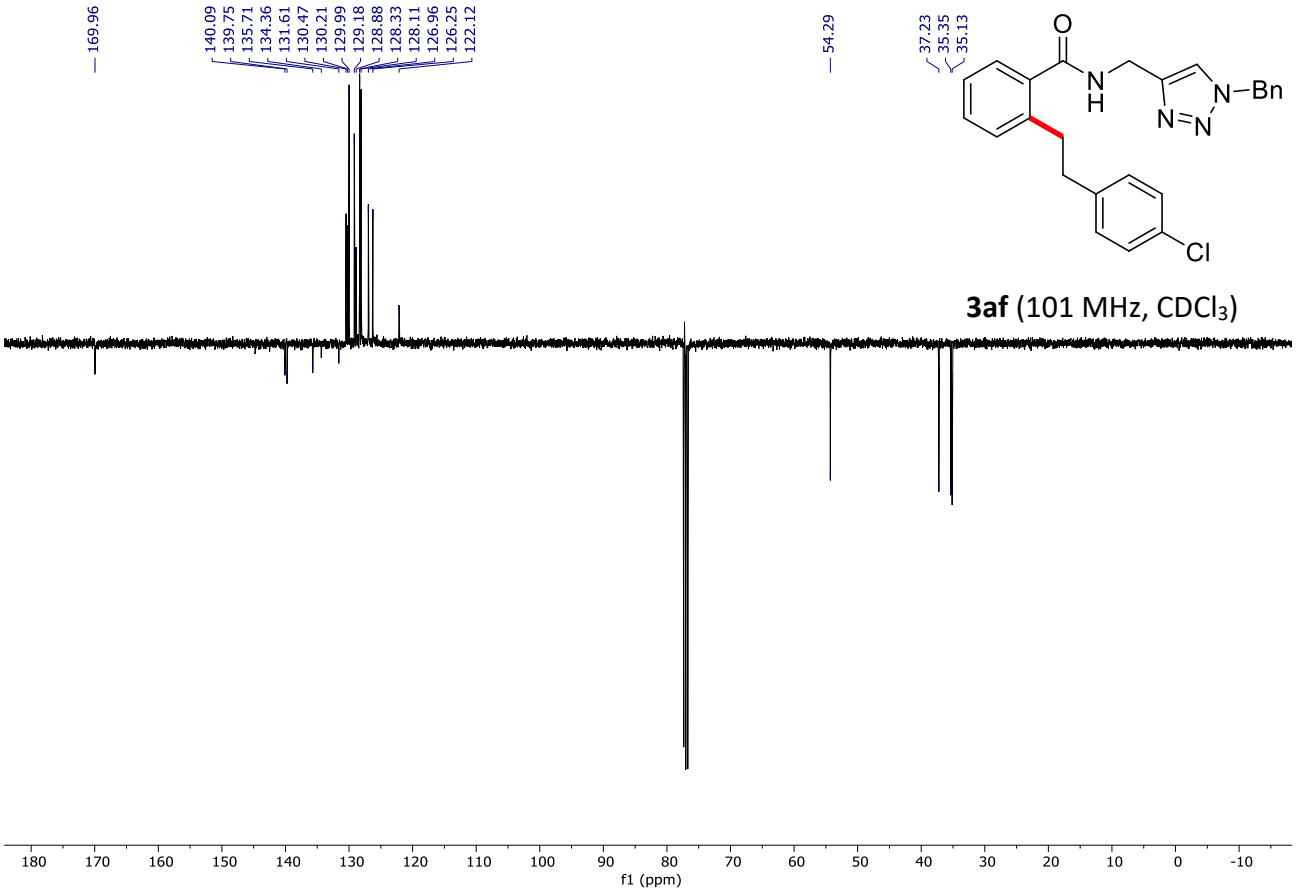




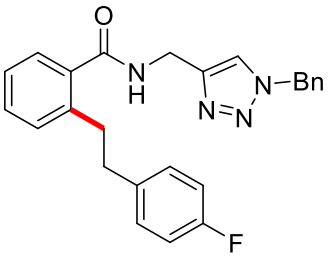
3ae (101 MHz, $CDCl_3$)



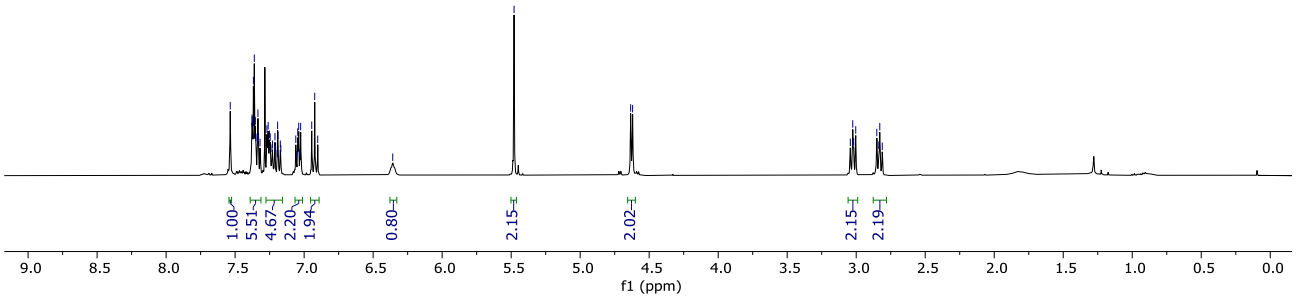
3af (400 MHz, $CDCl_3$)

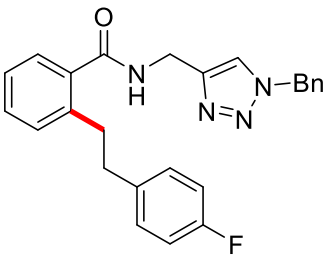


3af (101 MHz, $CDCl_3$)

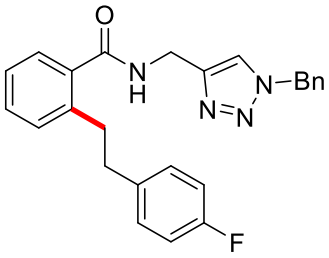


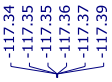
3ag (400 MHz, $CDCl_3$)



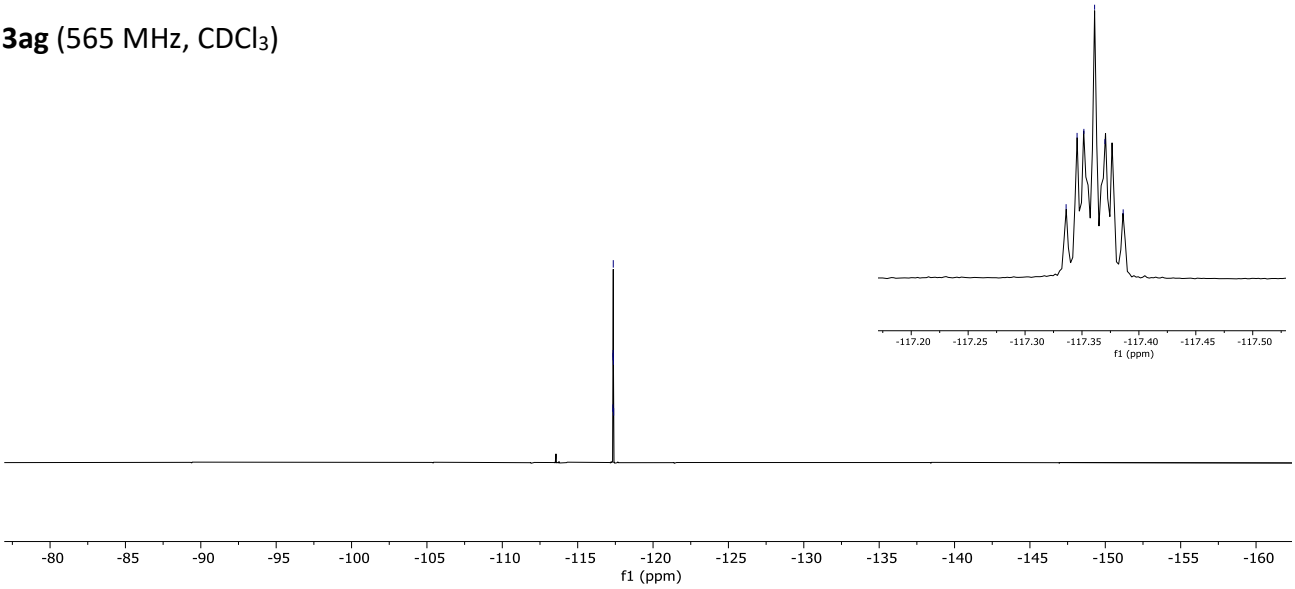


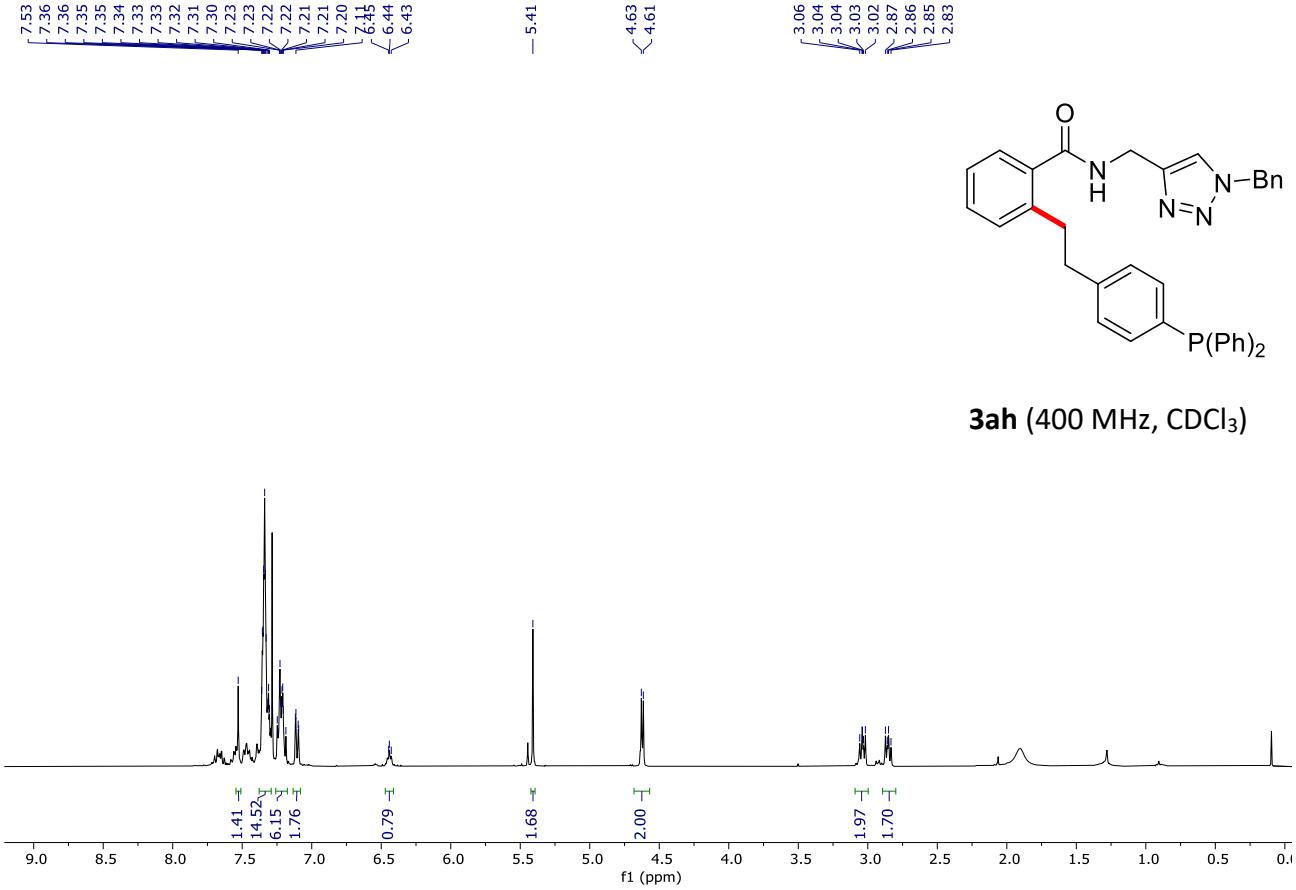
3ag (101 MHz, $CDCl_3$)

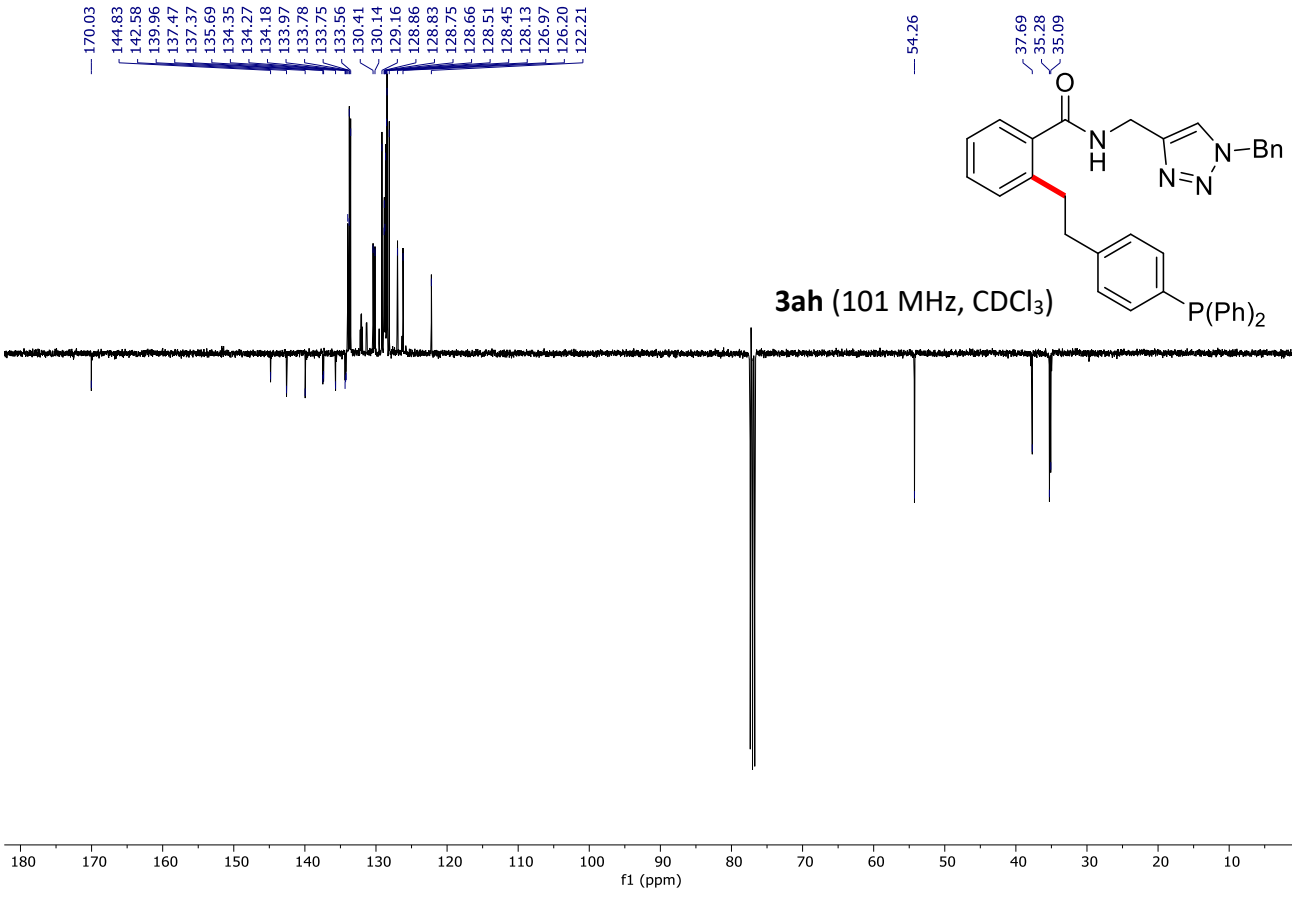


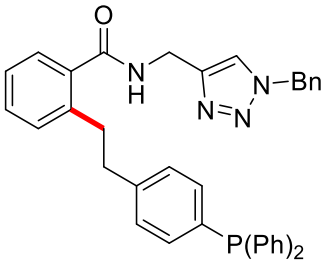


3ag (565 MHz, $CDCl_3$)

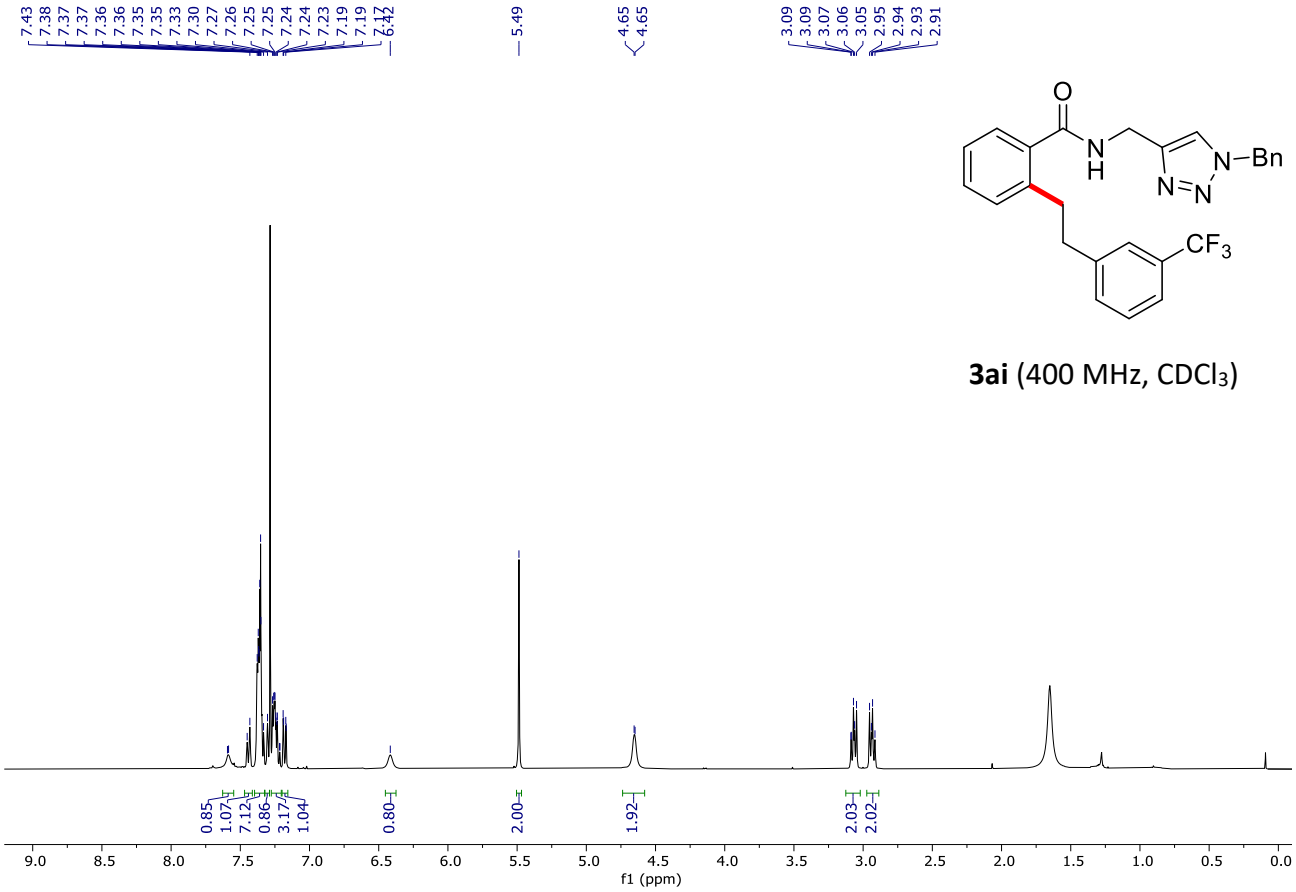



7.53
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.23
7.23
7.22
7.22
7.21
7.21
7.20
6.45
6.44
6.43
5.41
4.63
4.61
3.06
3.04
3.04
3.03
3.02
2.87
2.86
2.85
2.83
O
N
H
N
N=N
N–Bn
P(Ph)2
3ah (400 MHz, CDCl3)
1.41
14.52
6.15
1.76
0.79
1.68
2.00
1.97
1.70
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

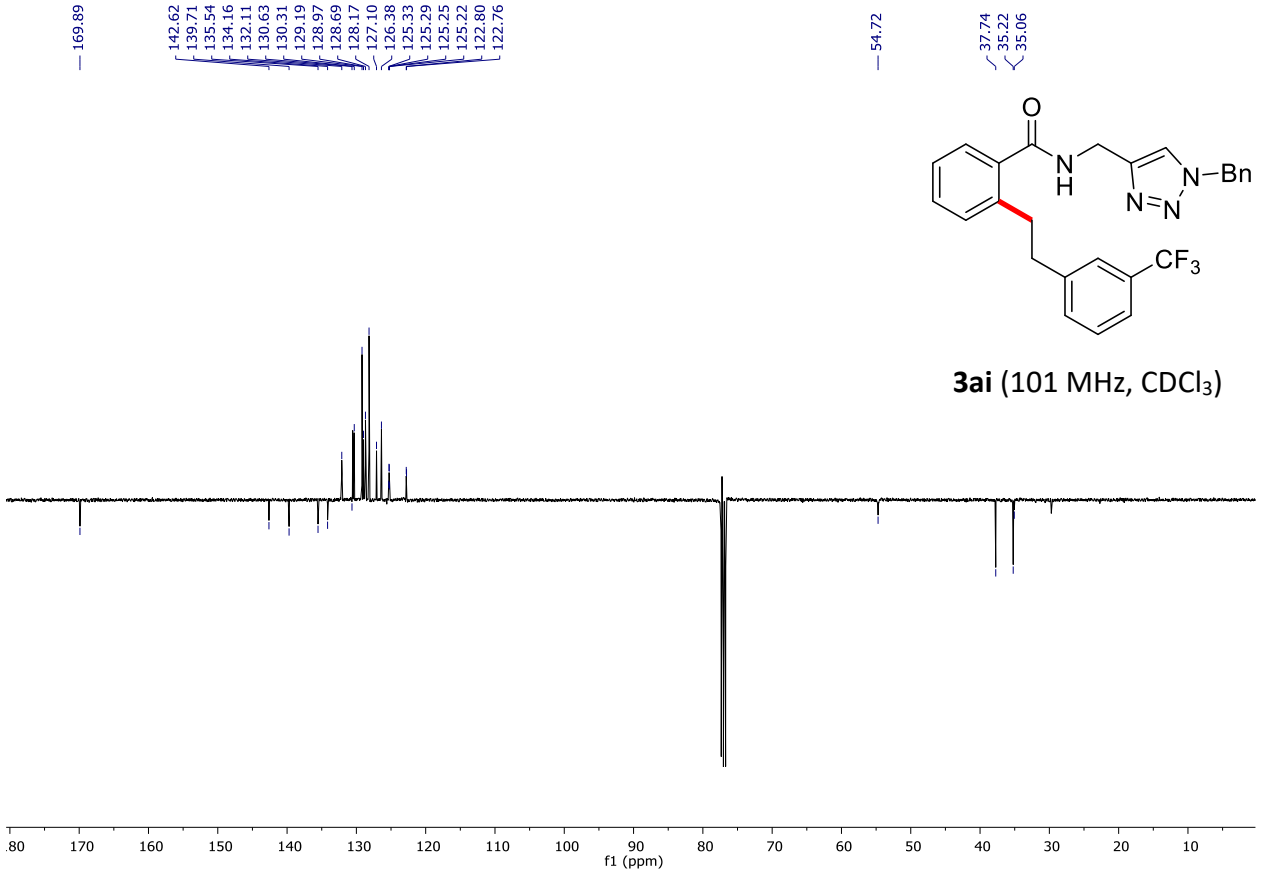

170.03
144.83
142.58
139.96
137.47
137.37
135.69
134.35
134.27
134.18
133.97
133.78
133.75
133.56
130.41
130.14
129.16
128.86
128.83
128.75
128.66
128.51
128.45
128.13
126.97
126.20
122.21
54.26
37.69
35.28
35.09
O
N
H
N
N=N
N–Bn
P(Ph)2
3ah (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



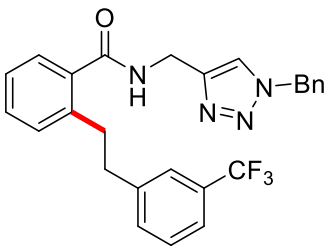
3ah (162 MHz, $CDCl_3$)



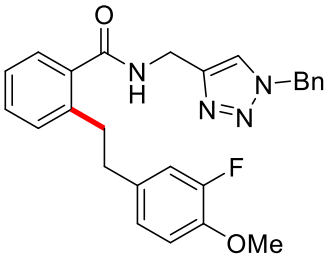
3ai (400 MHz, $CDCl_3$)



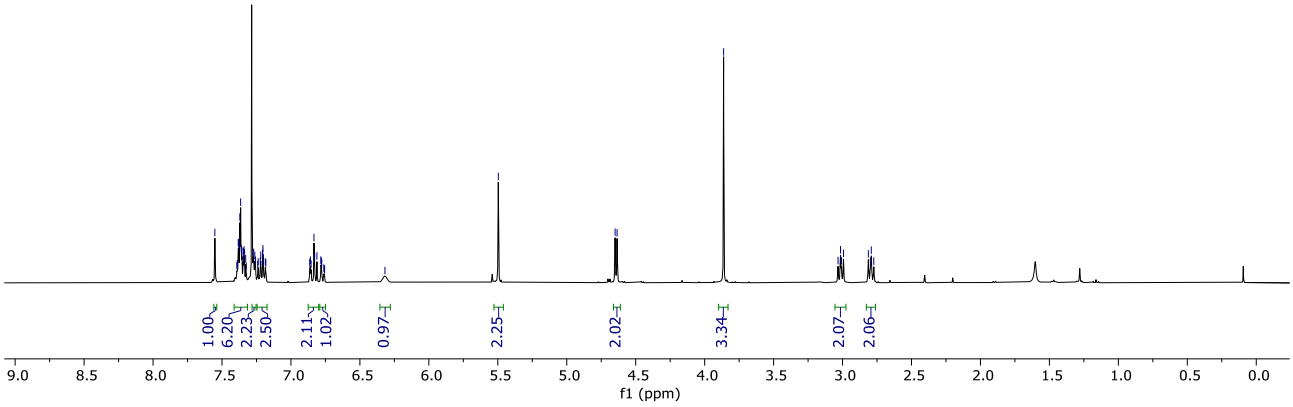
3ai (101 MHz, $CDCl_3$)

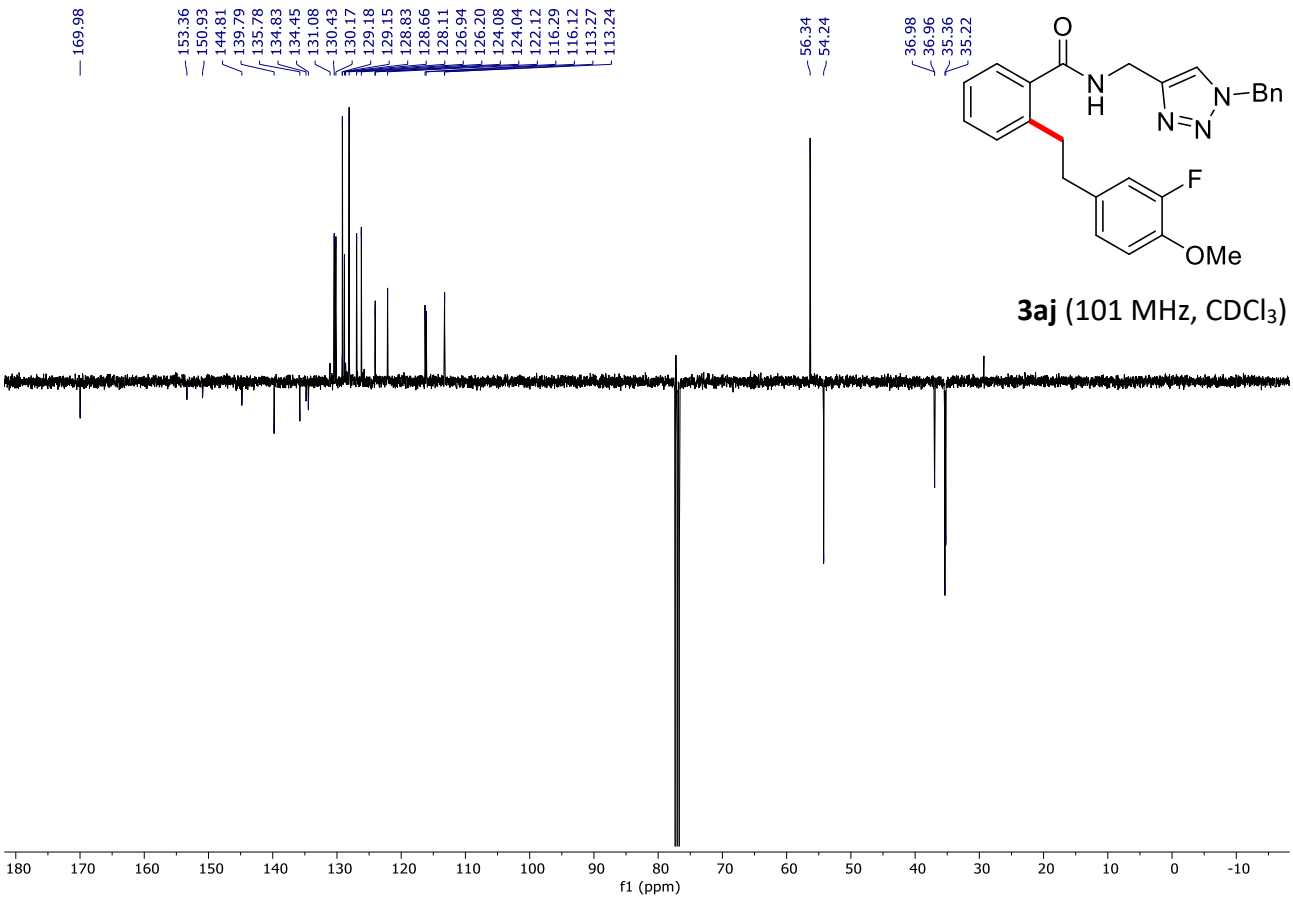


3ai (565 MHz, $CDCl_3$)

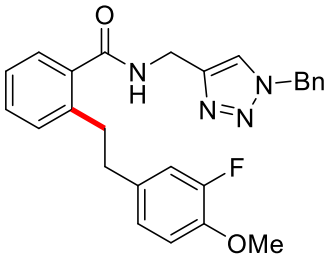


3aj (400 MHz, $CDCl_3$)

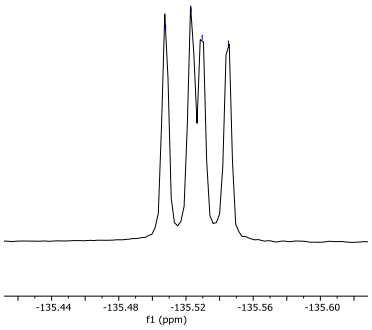


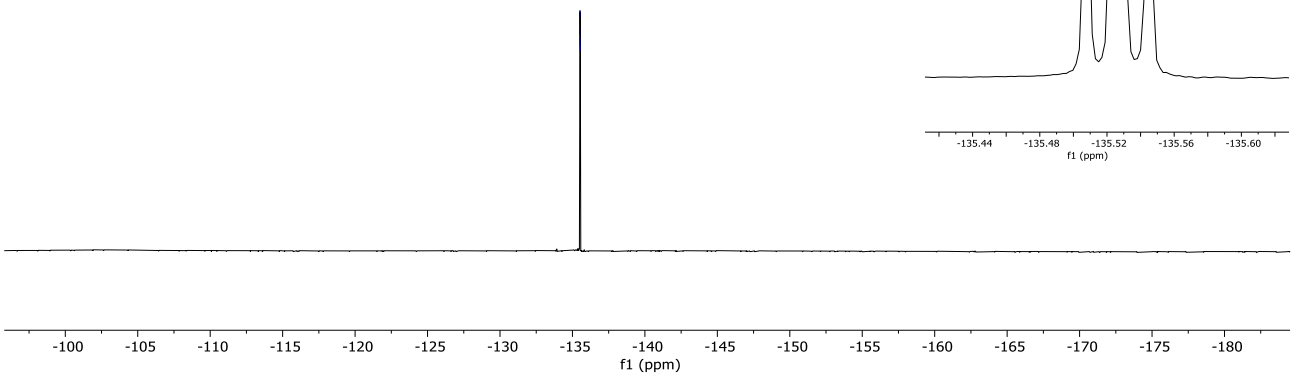


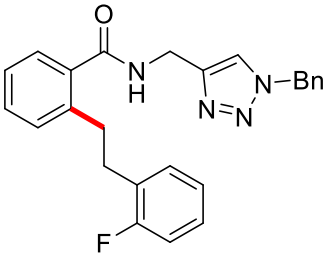
3aj (101 MHz, $CDCl_3$)



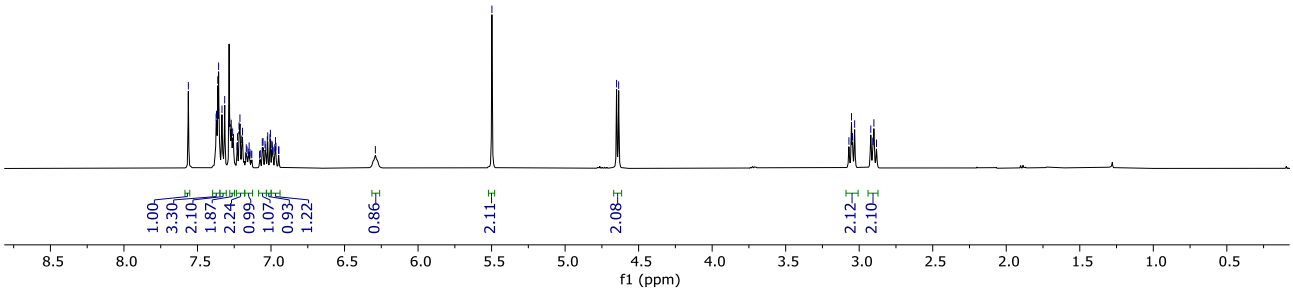
3aj (565 MHz, $CDCl_3$)

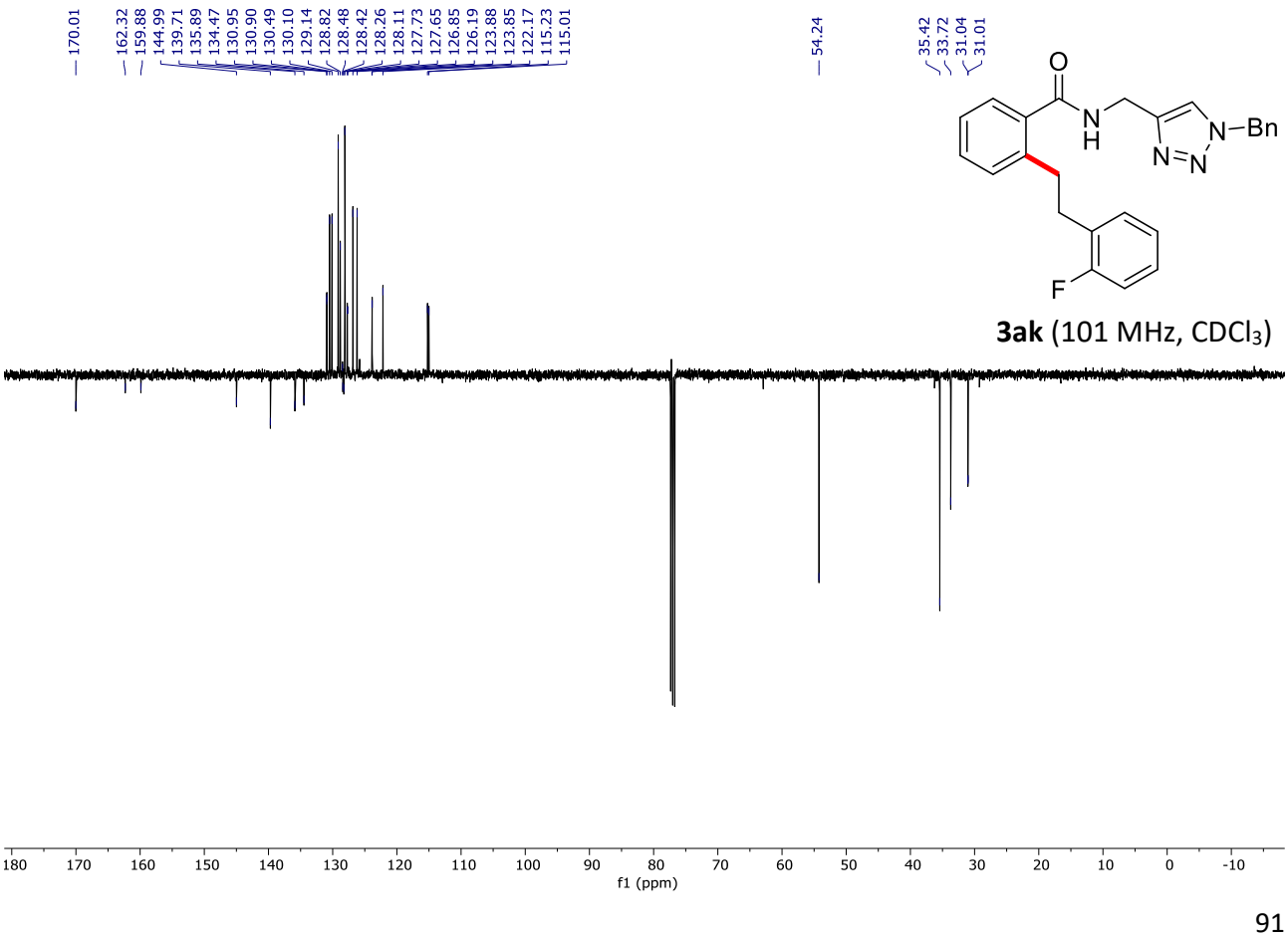




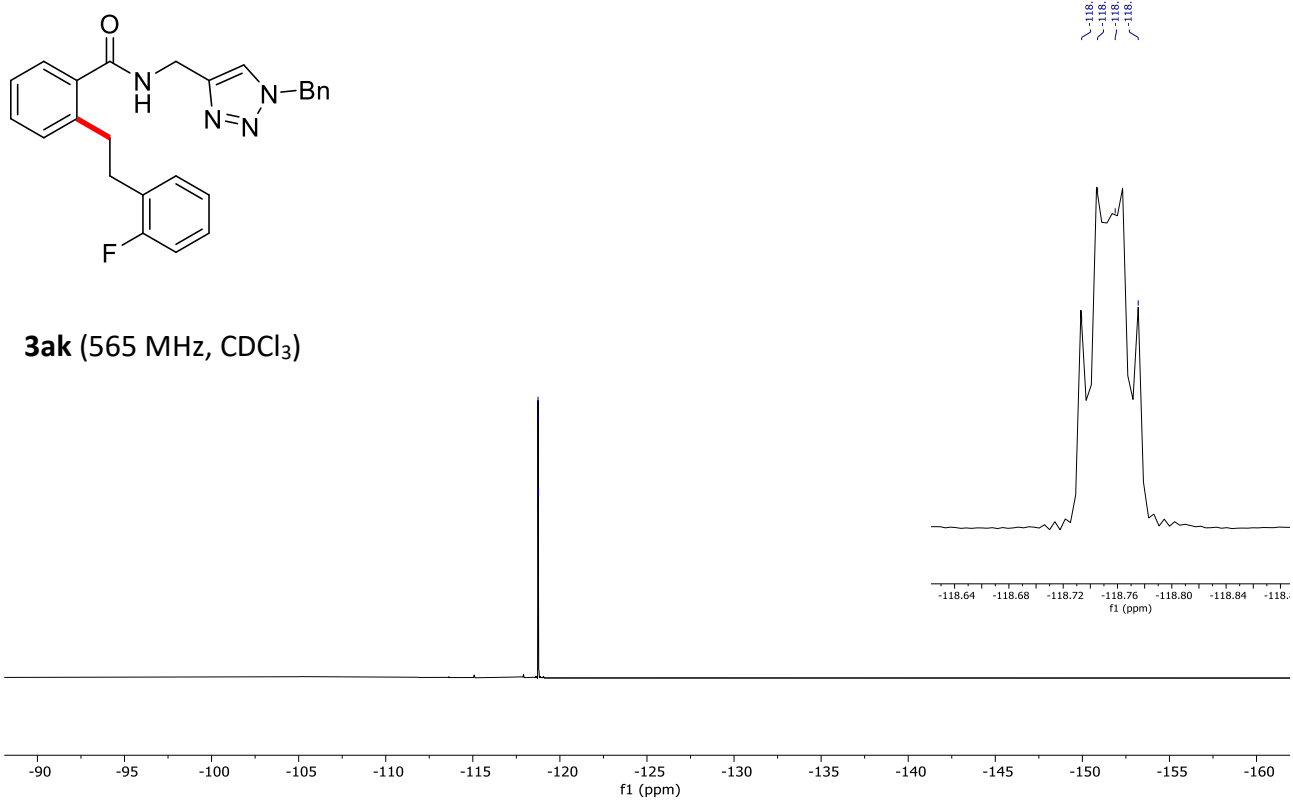


3ak (400 MHz, $CDCl_3$)

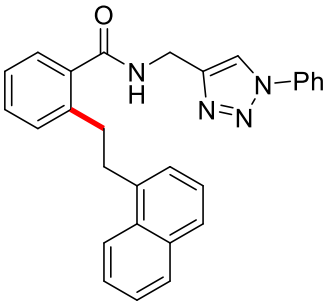




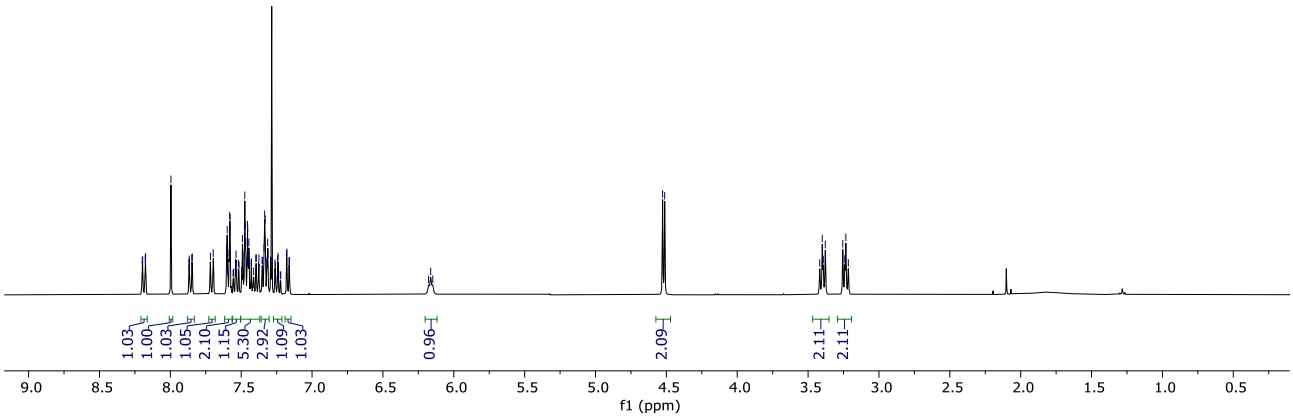
3ak (101 MHz, $CDCl_3$)

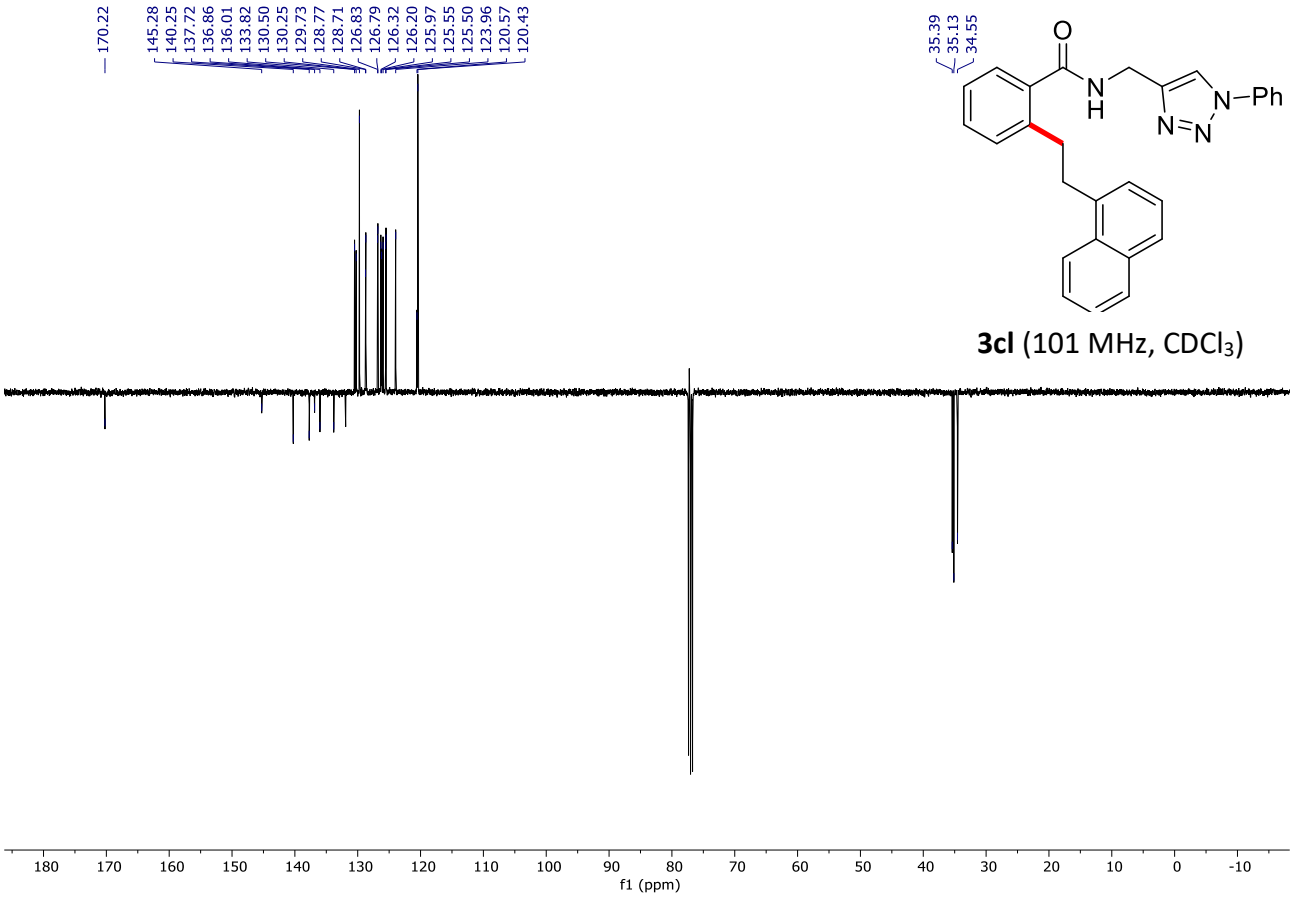


3ak (565 MHz, $CDCl_3$)

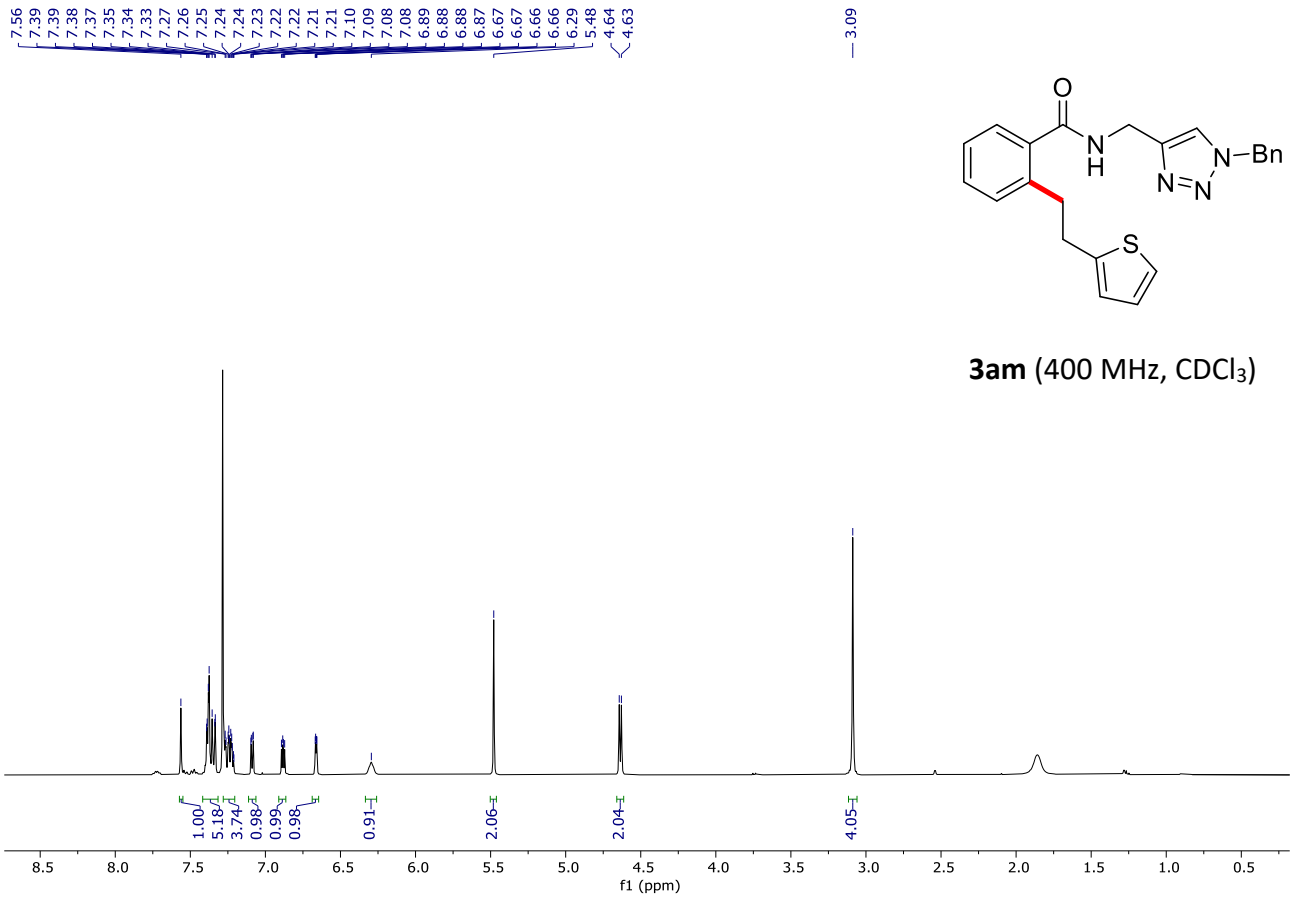


3cl (400 MHz, $CDCl_3$)

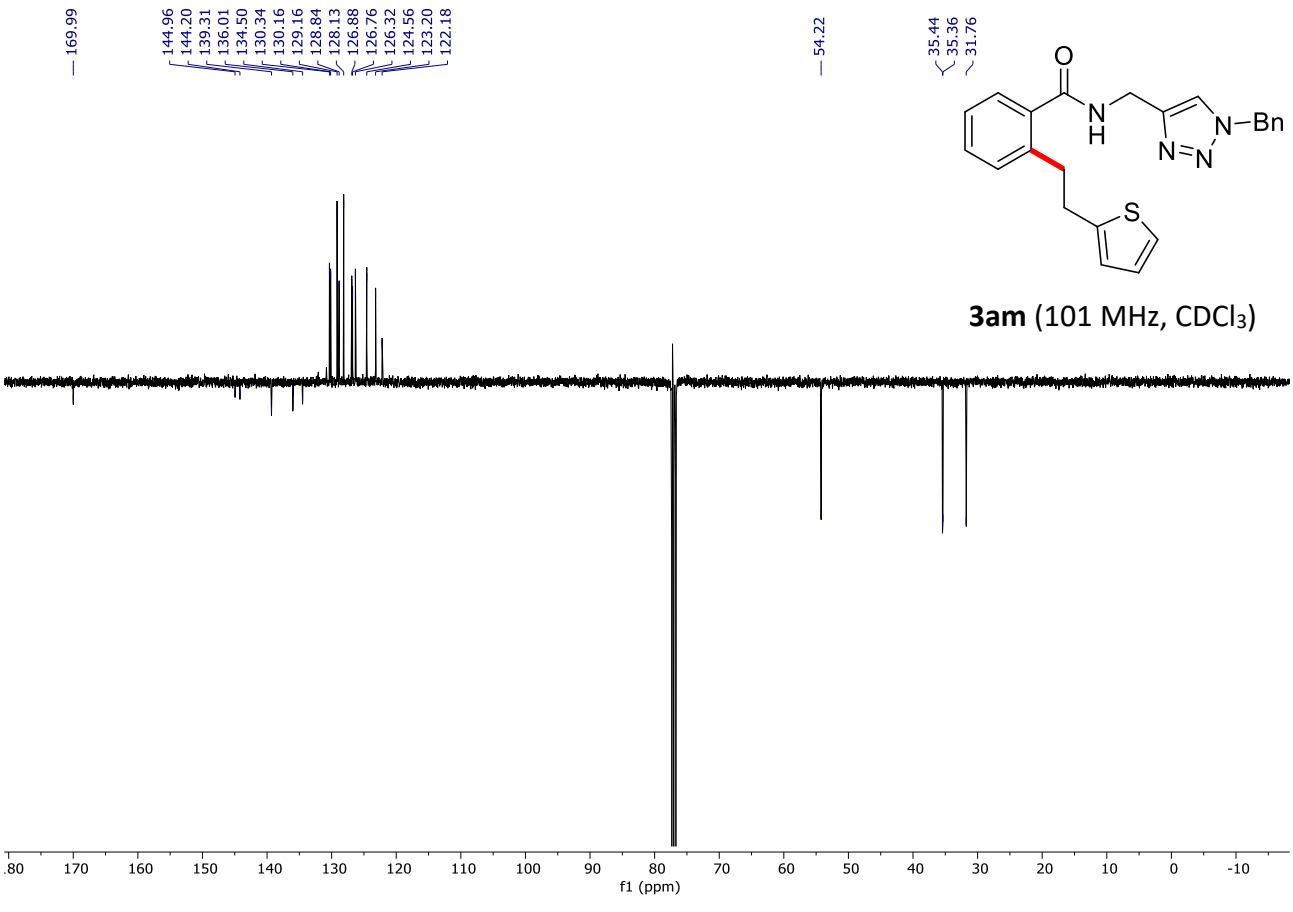




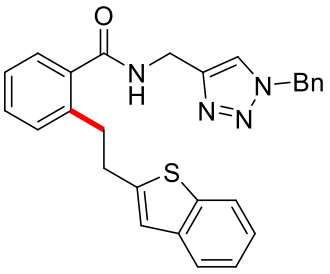
3cl (101 MHz, $CDCl_3$)



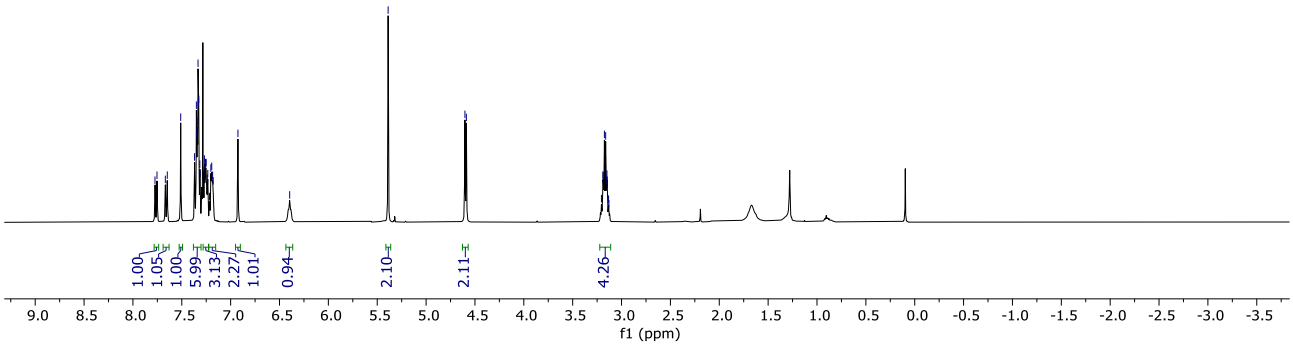
3am (400 MHz, $CDCl_3$)

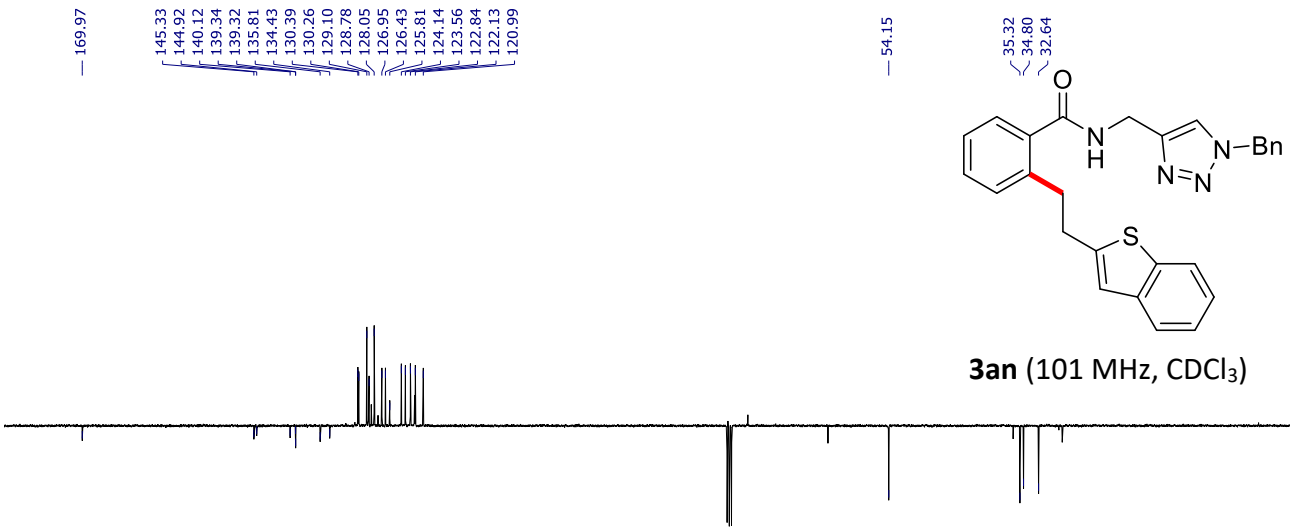


3am (101 MHz, $CDCl_3$)

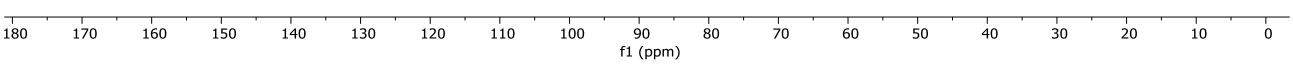


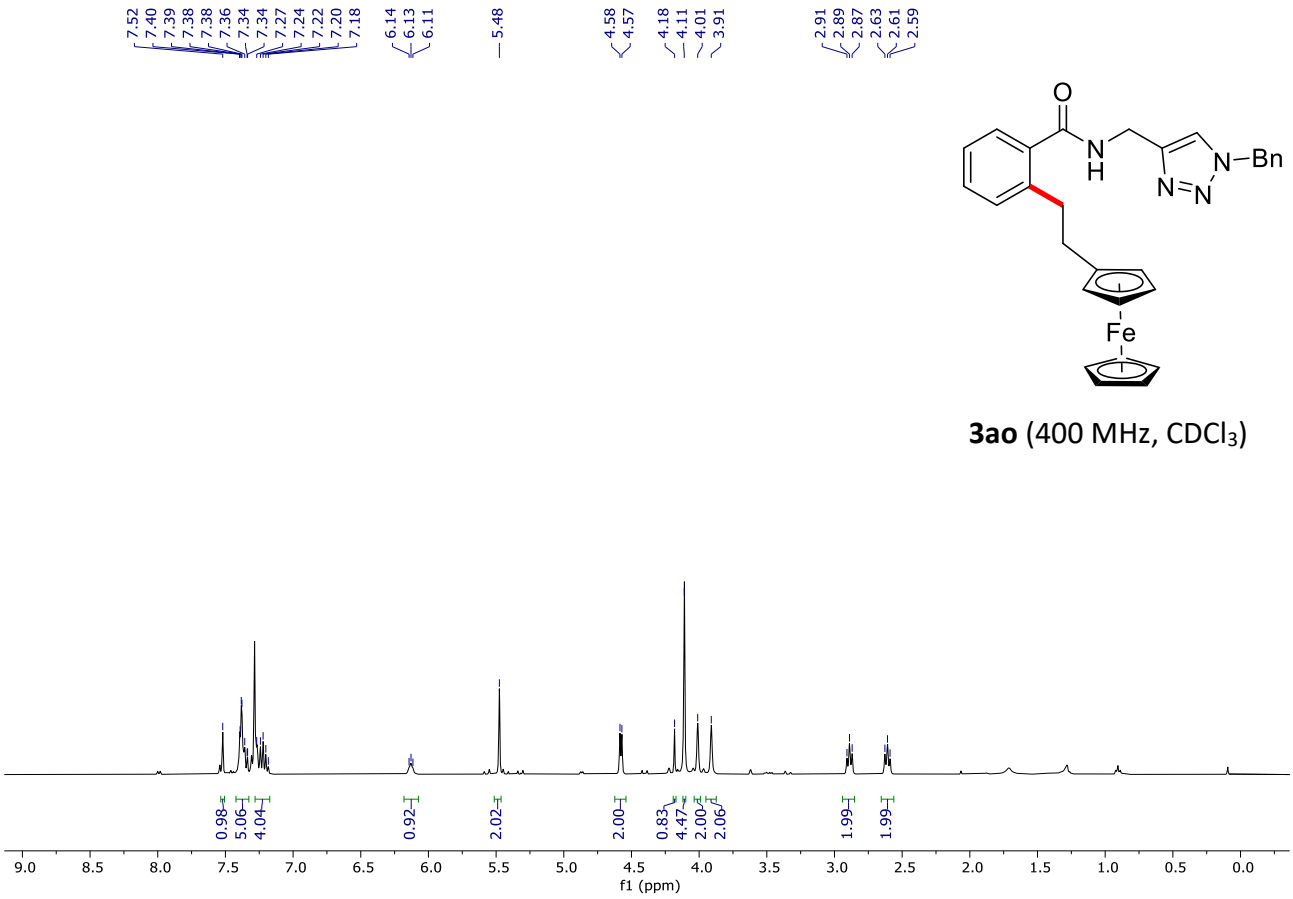
3an (400 MHz, $CDCl_3$)



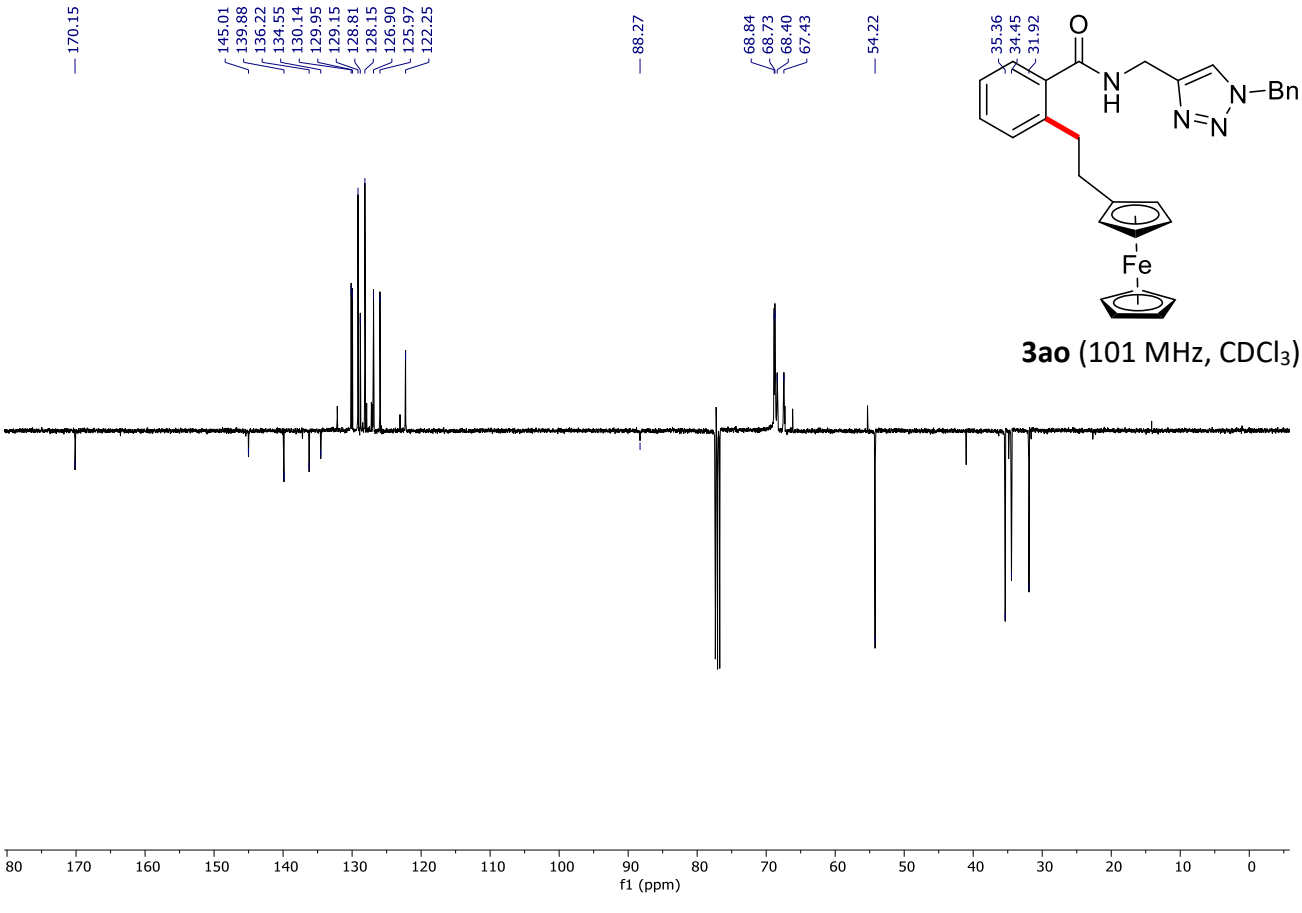


3an (101 MHz, $CDCl_3$)

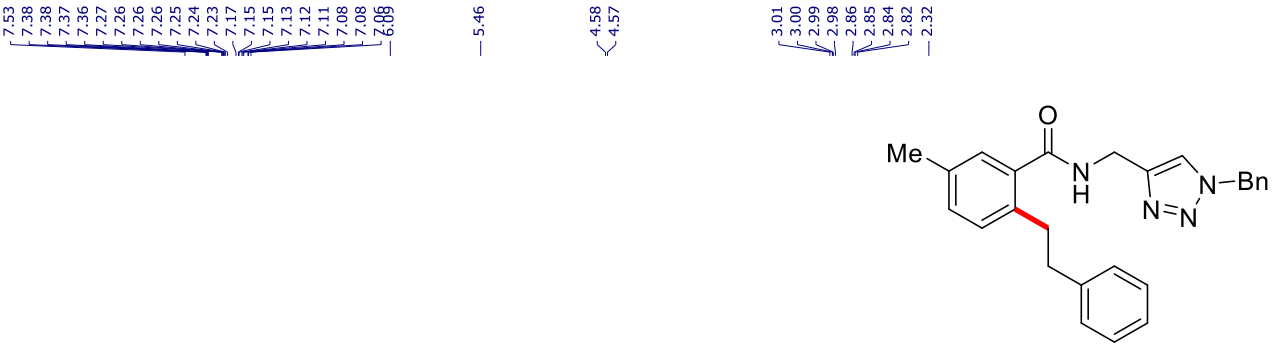




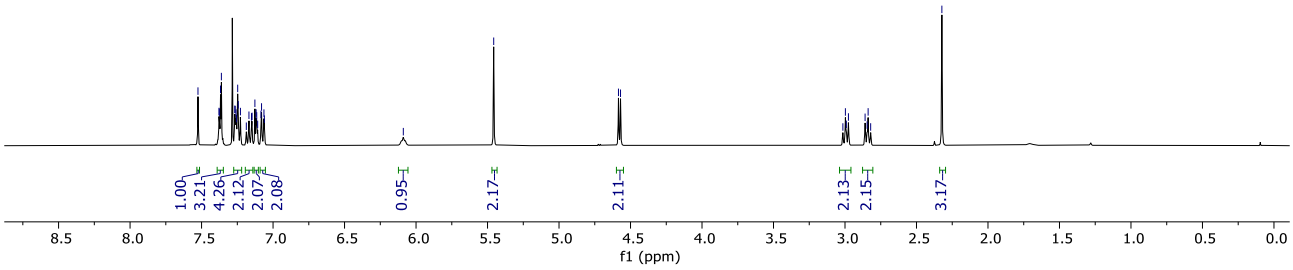
3ao (400 MHz, $CDCl_3$)

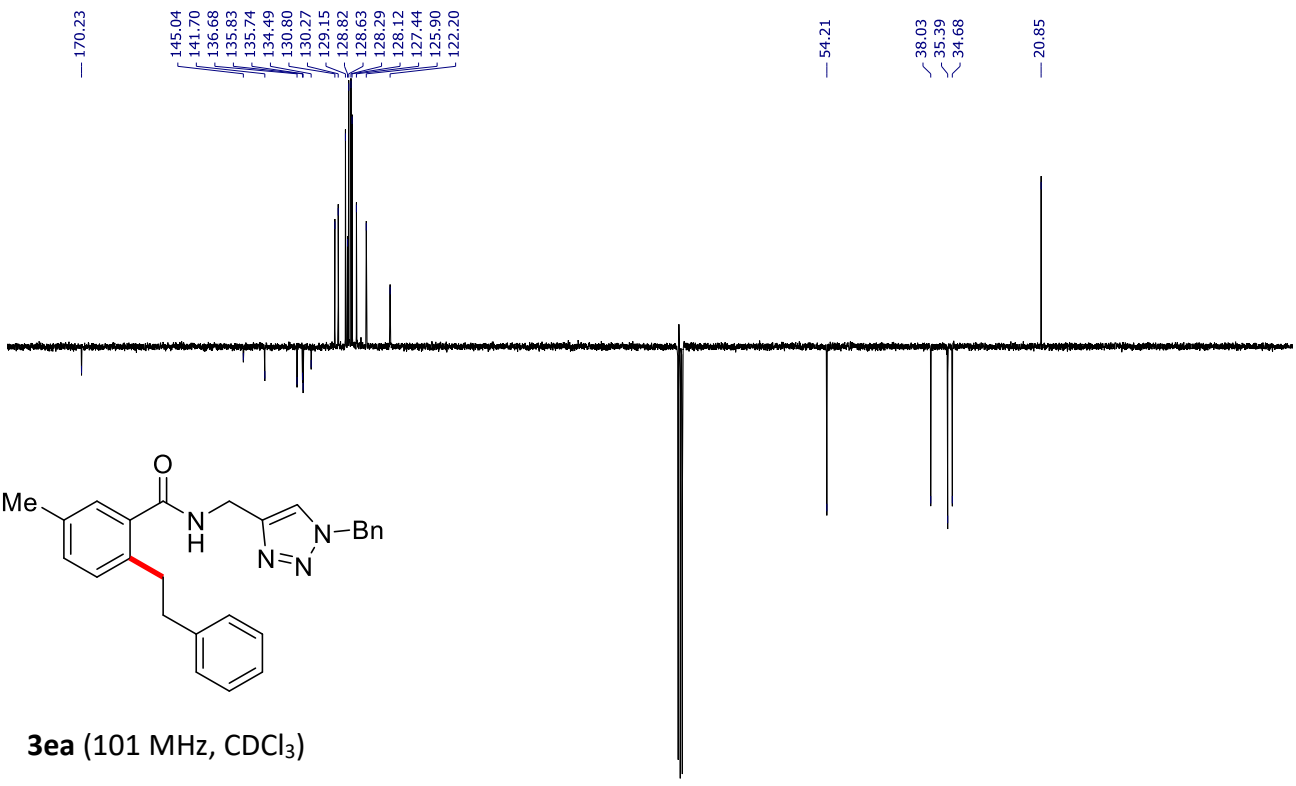


3ao (101 MHz, $CDCl_3$)

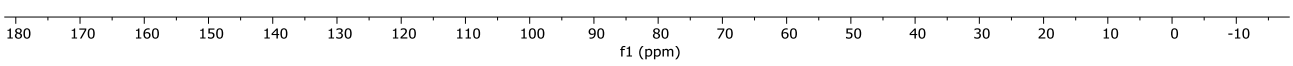


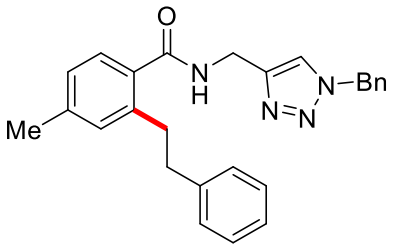
3ea (400 MHz, $CDCl_3$)



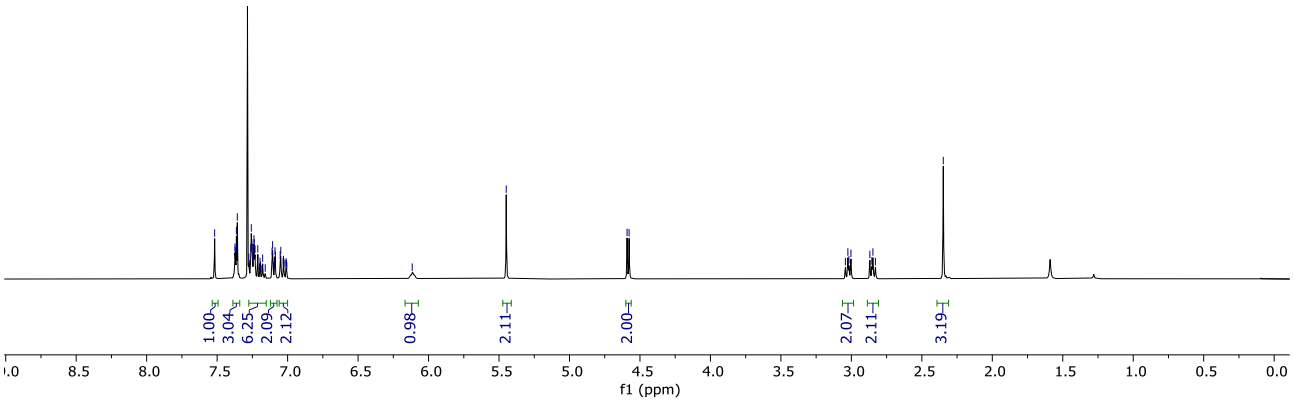


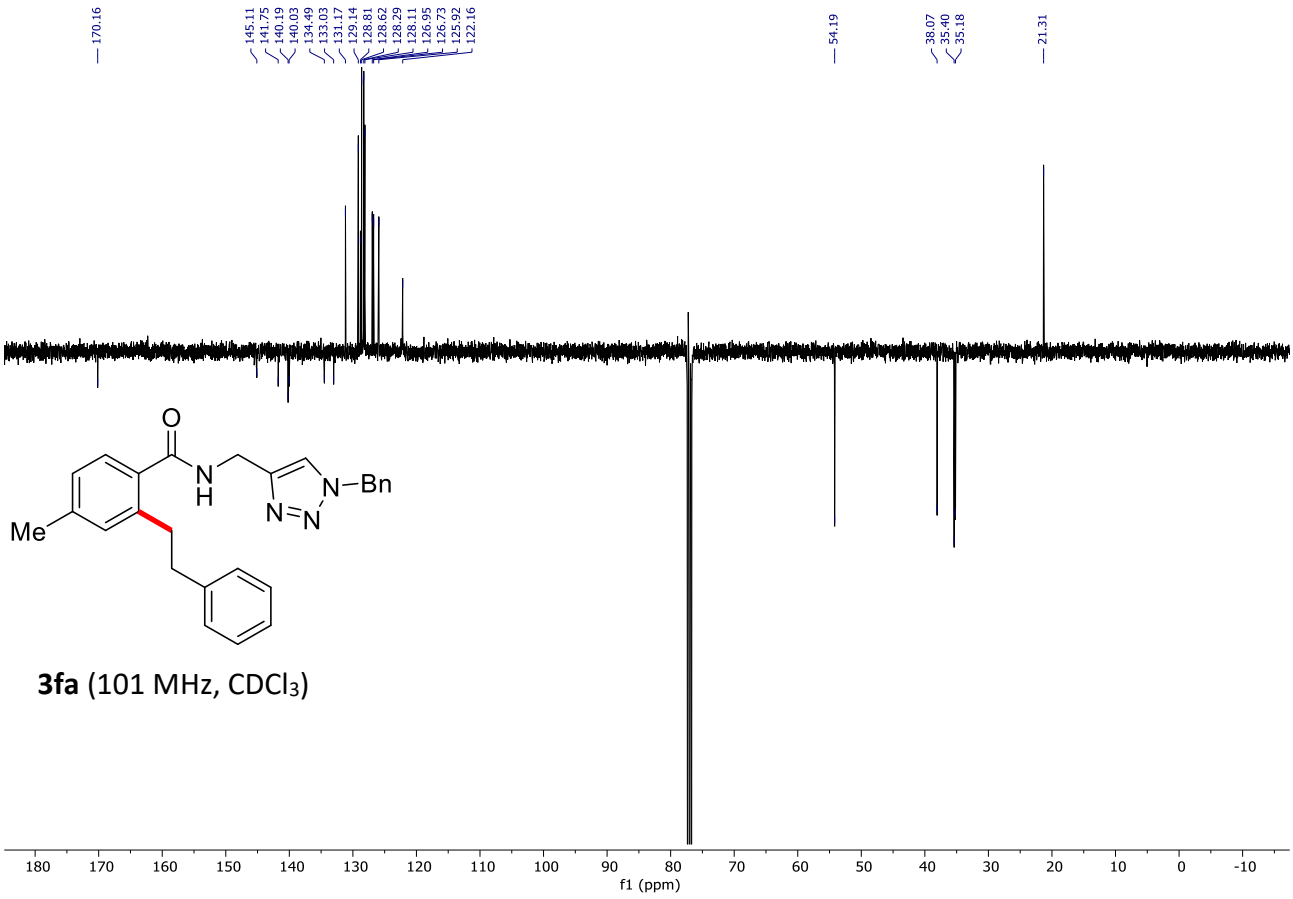
3ea (101 MHz, $CDCl_3$)



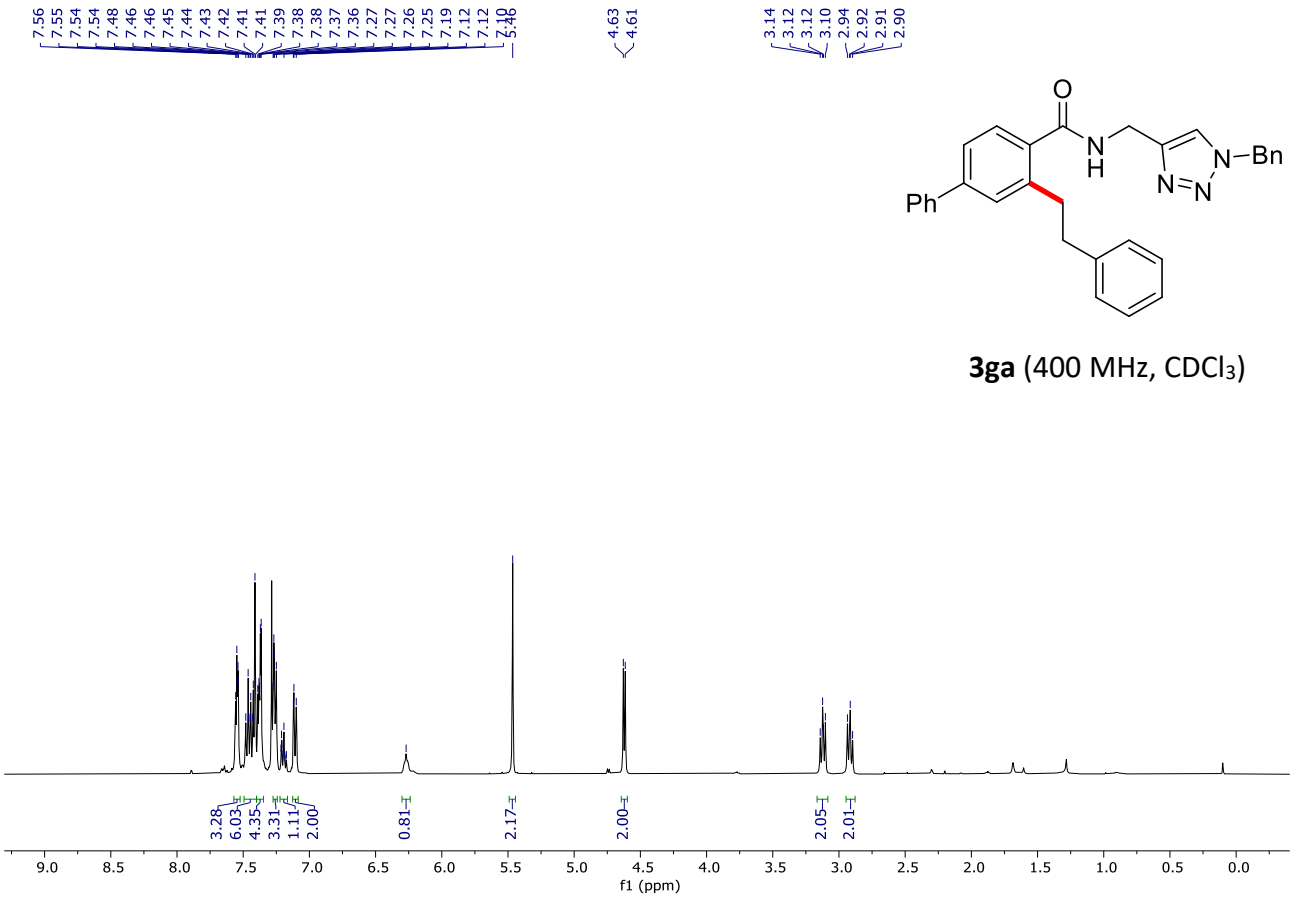


3fa (400 MHz, $CDCl_3$)

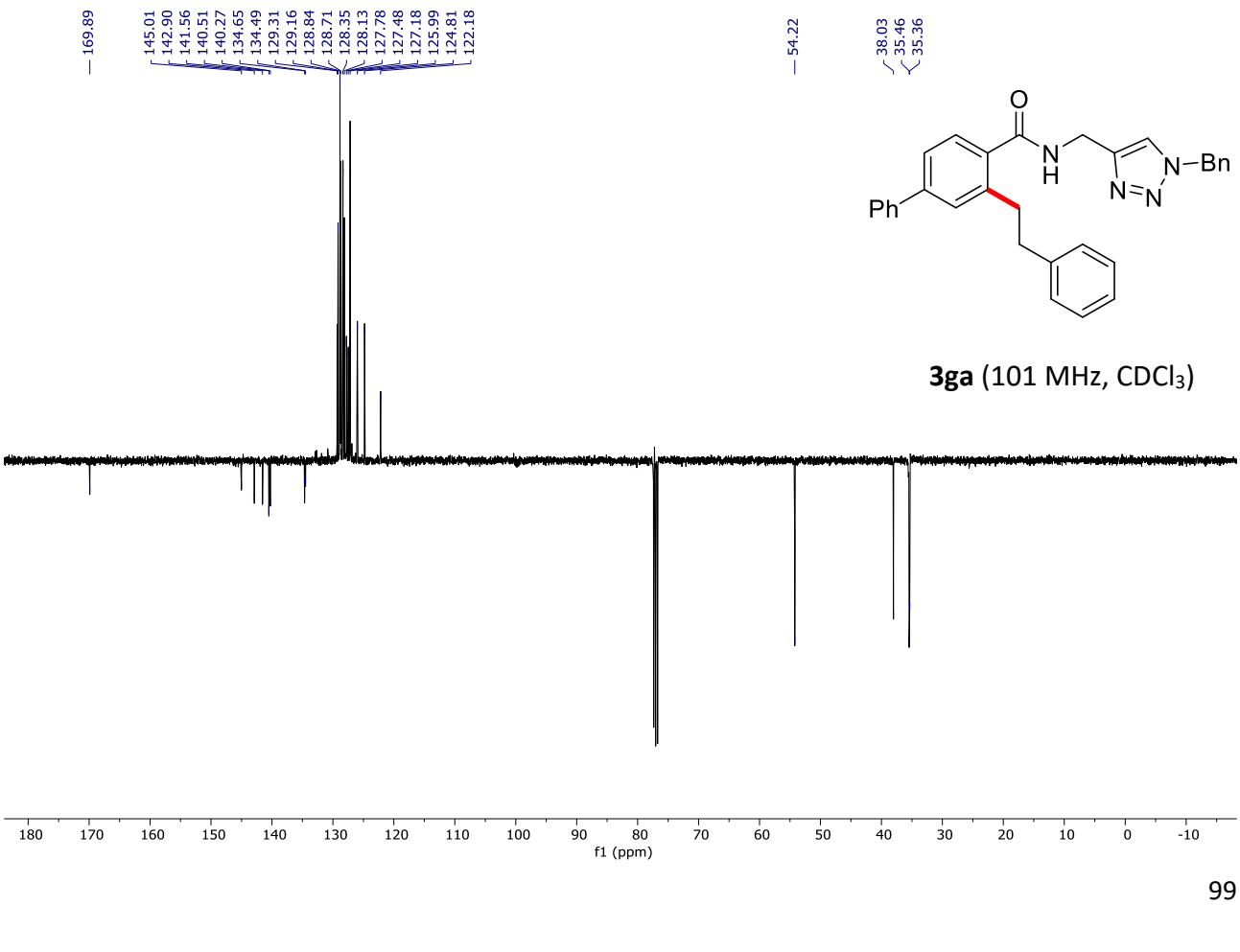




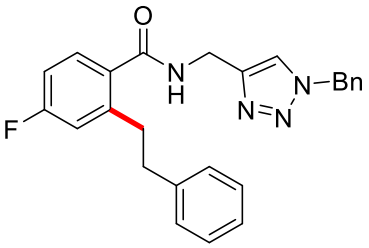
3fa (101 MHz, $CDCl_3$)



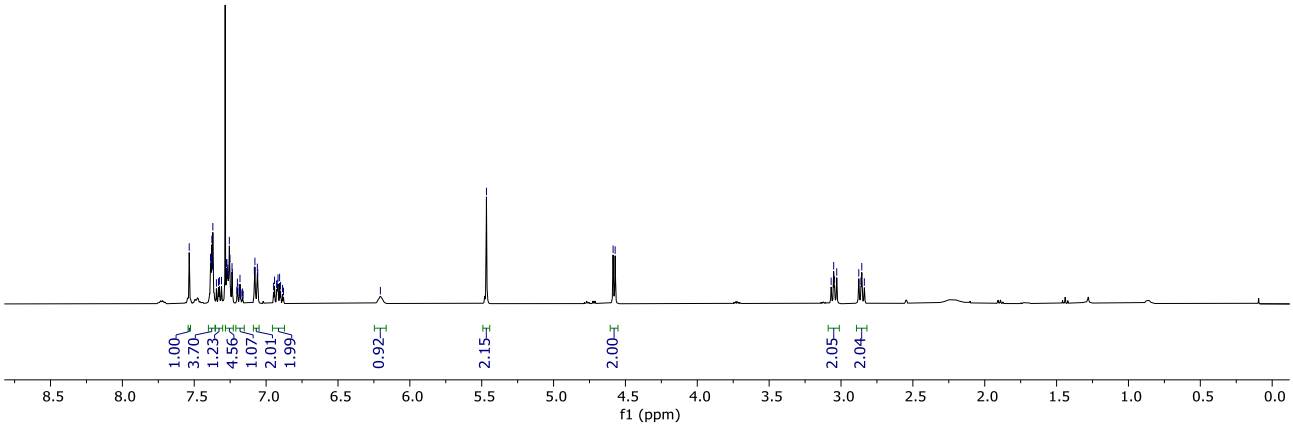
3ga (400 MHz, $CDCl_3$)

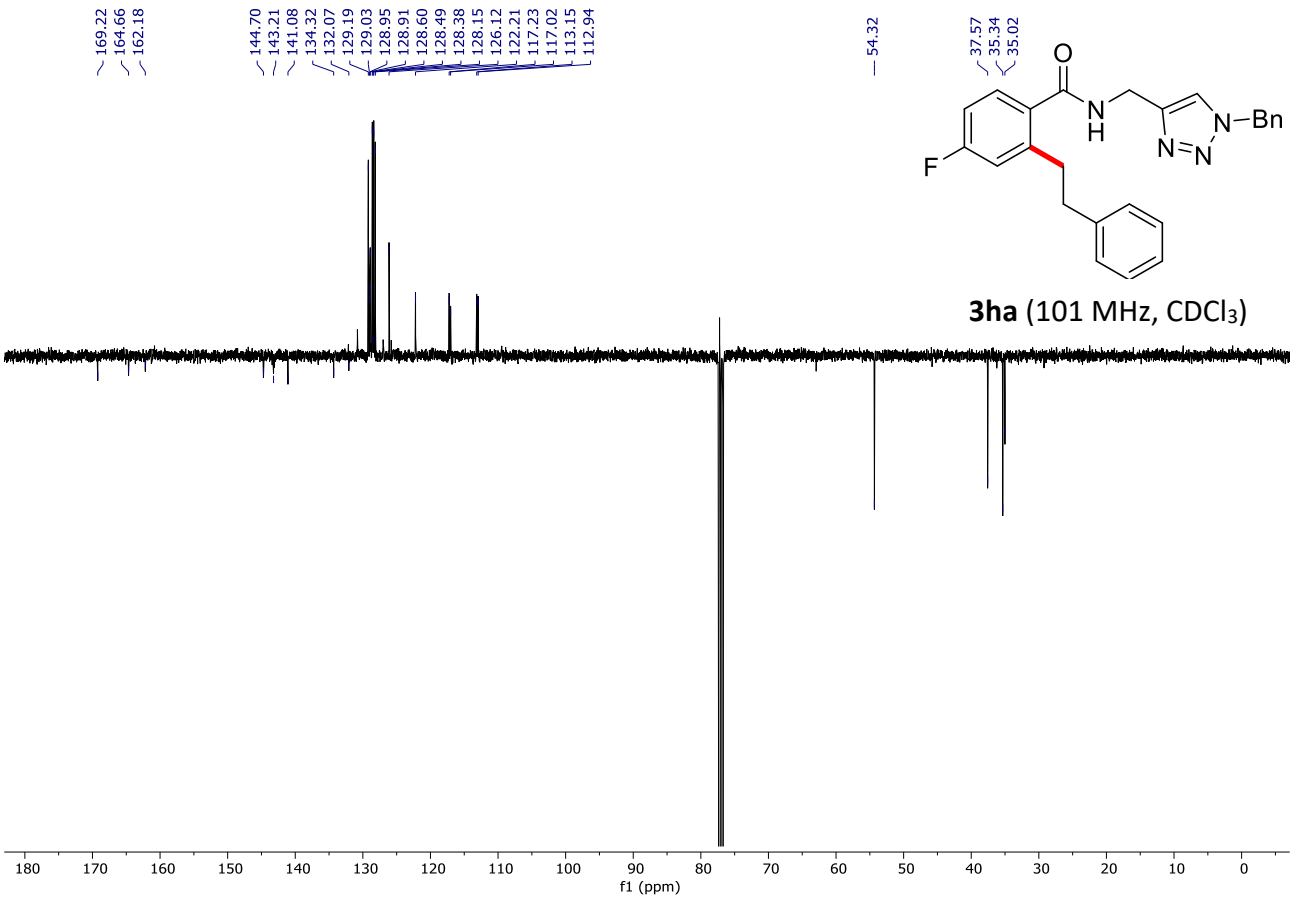


3ga (101 MHz, $CDCl_3$)

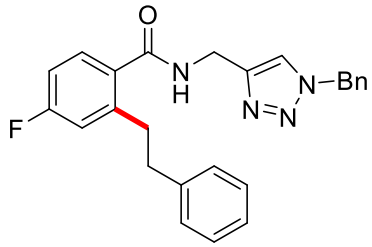


3ha (400 MHz, $CDCl_3$)

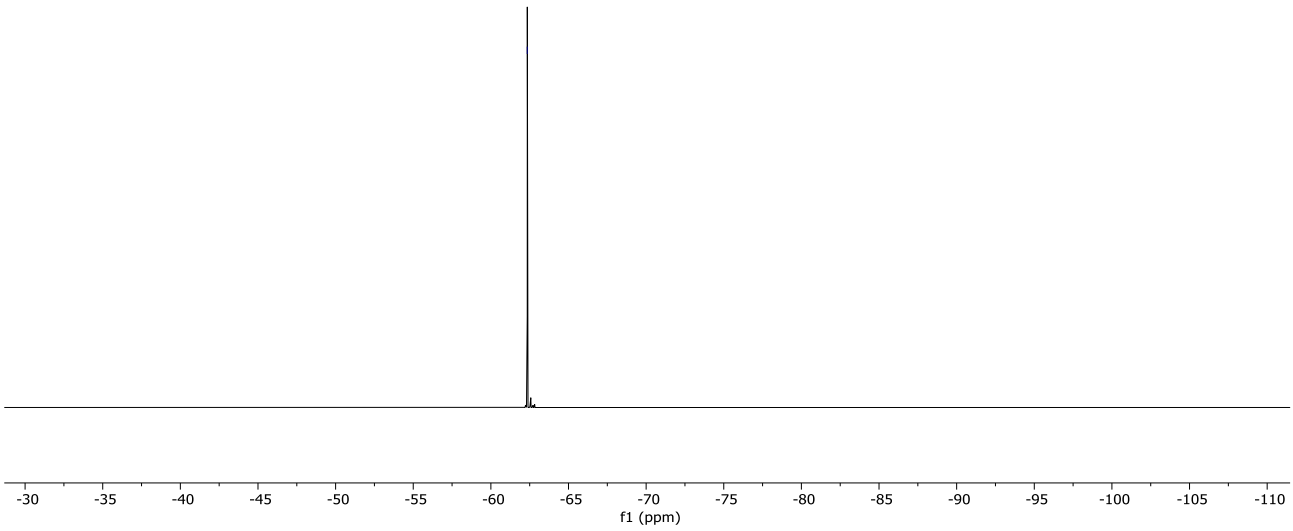


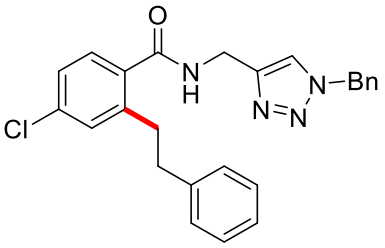


3ha (101 MHz, $CDCl_3$)

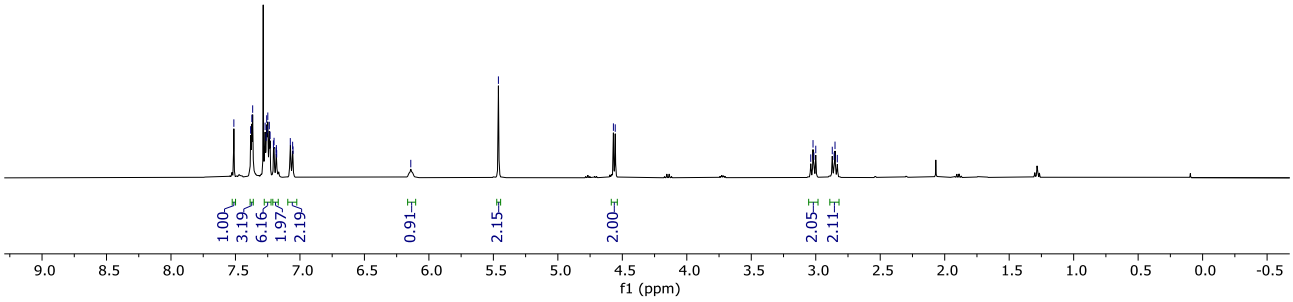


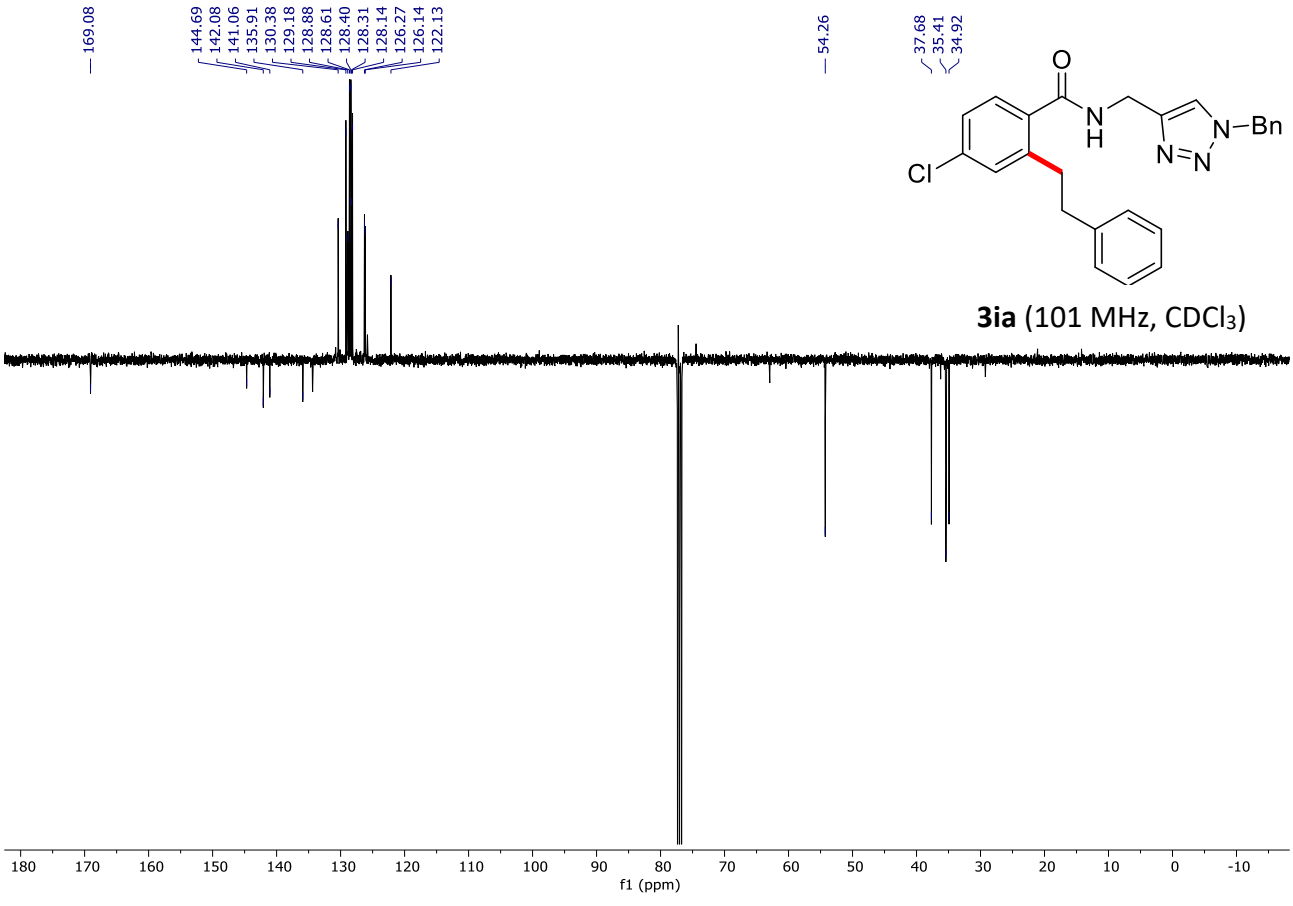
3ha (565 MHz, $CDCl_3$)



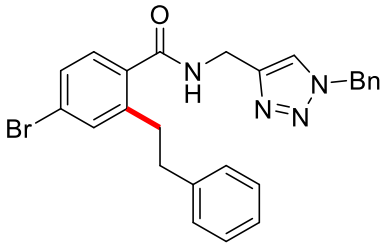


3ia (400 MHz, $CDCl_3$)

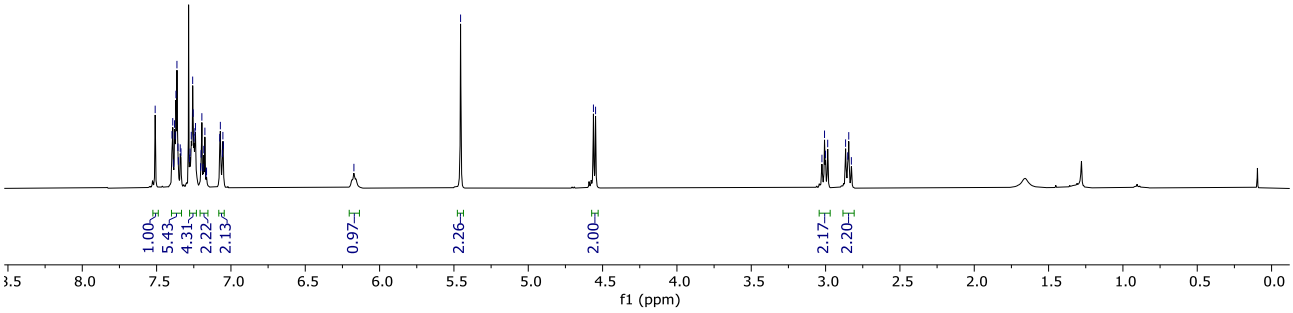


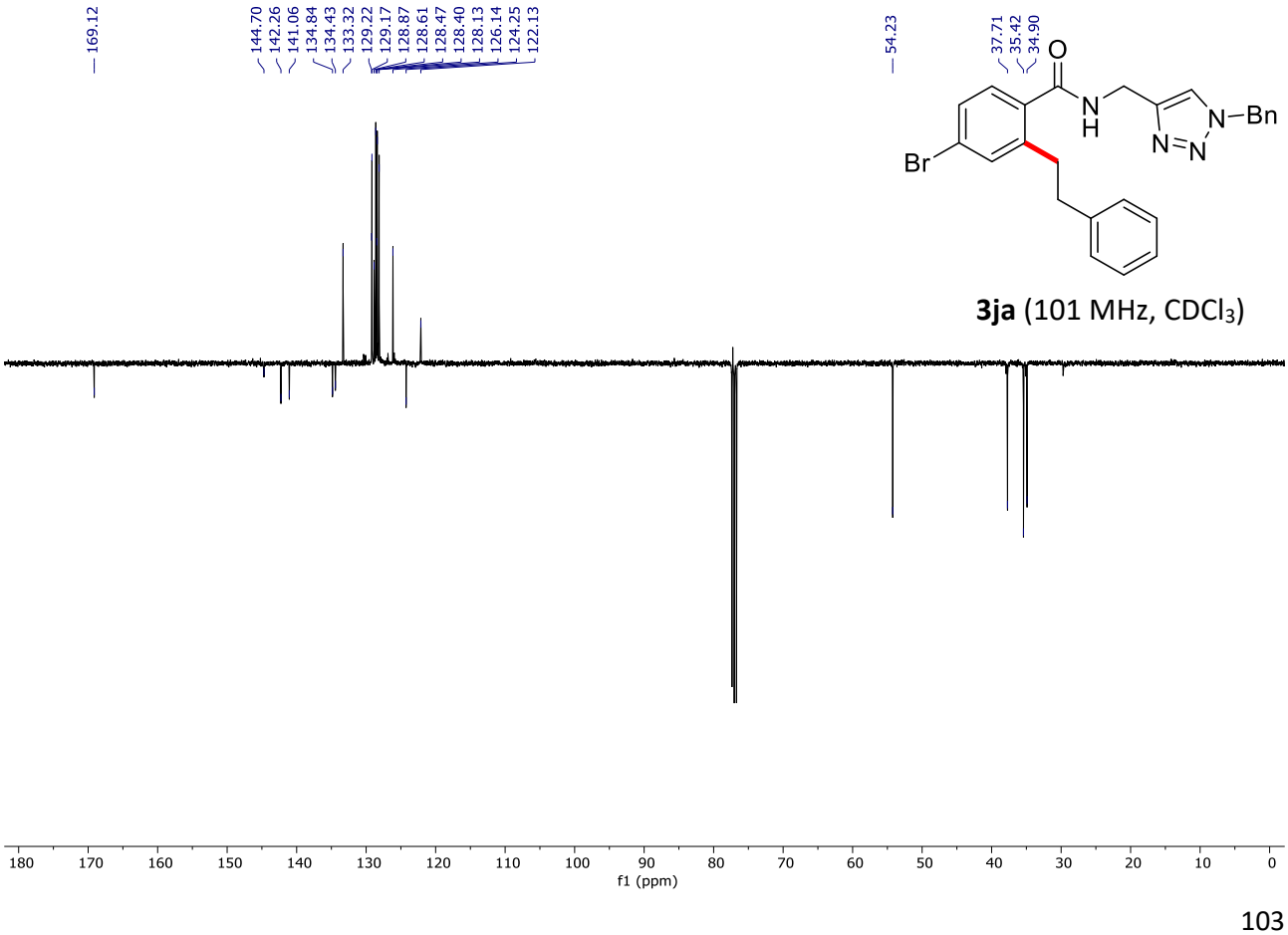


3ia (101 MHz, $CDCl_3$)

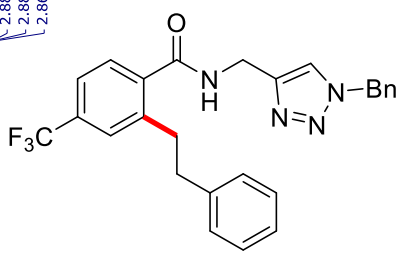


3ja (400 MHz, $CDCl_3$)

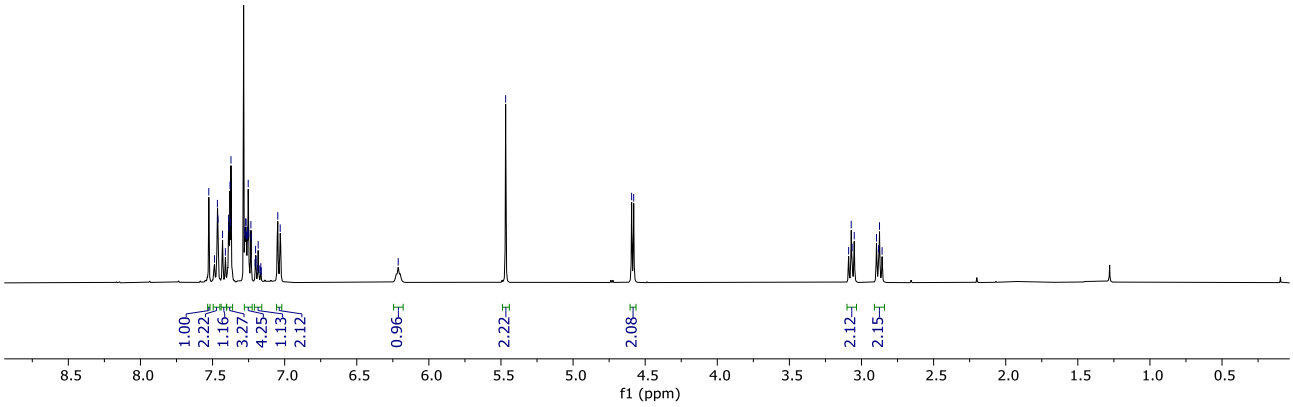


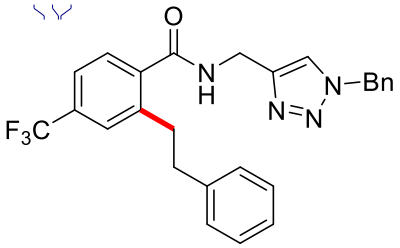


3ja (101 MHz, $CDCl_3$)

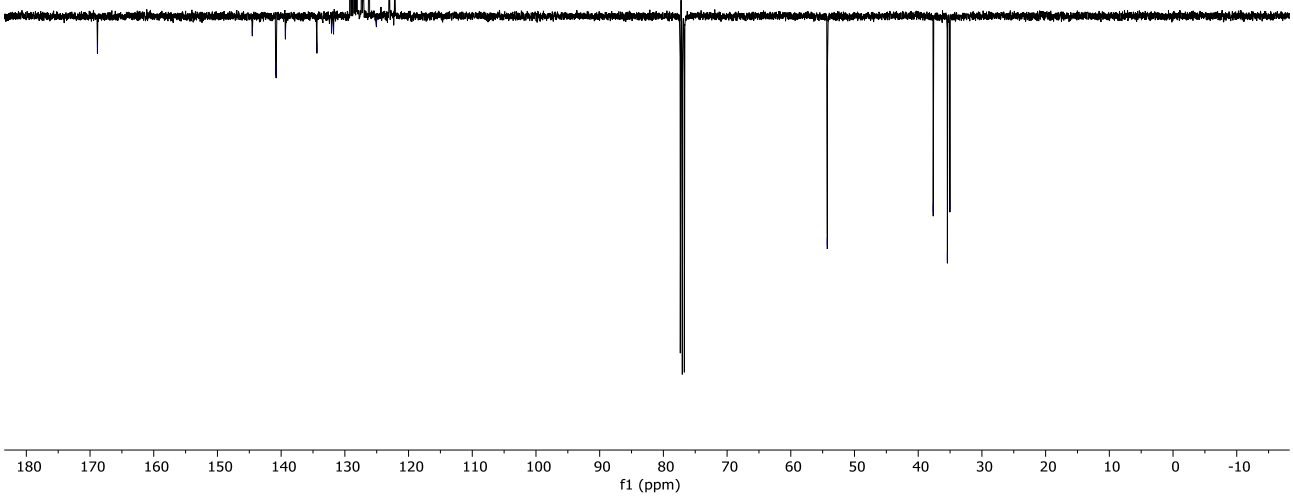


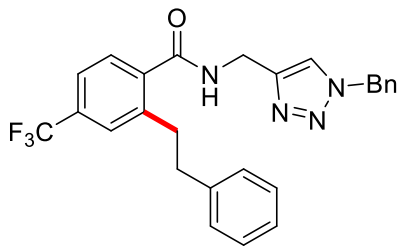
3ka (400 MHz, $CDCl_3$)



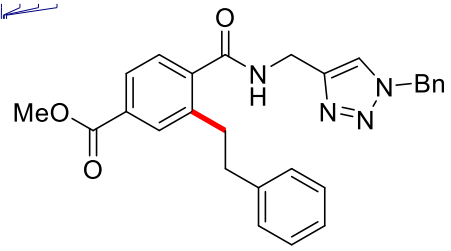


3ka (101 MHz, $CDCl_3$)

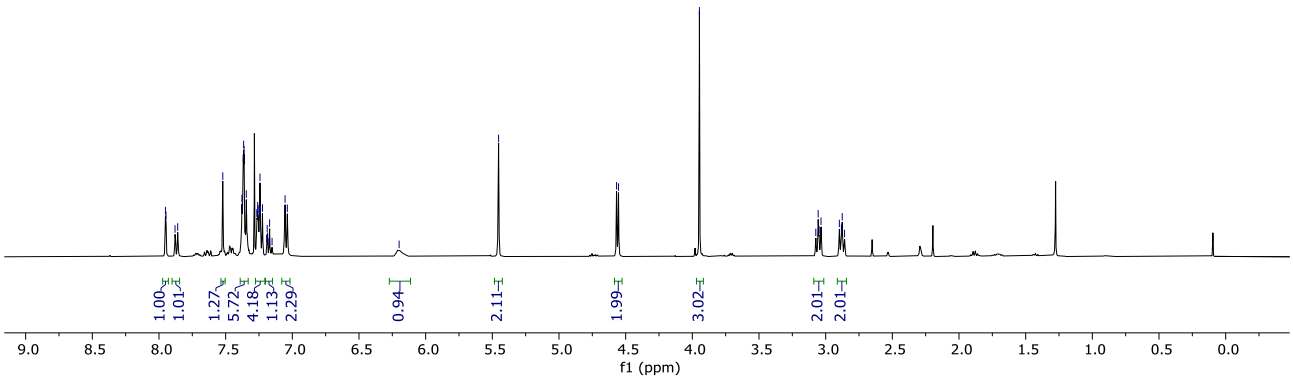


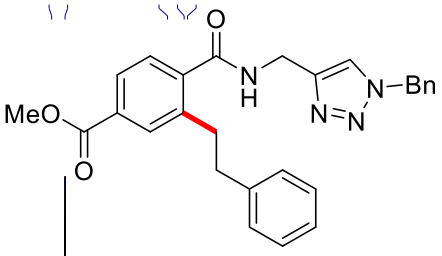


3ka (565 MHz, $CDCl_3$)

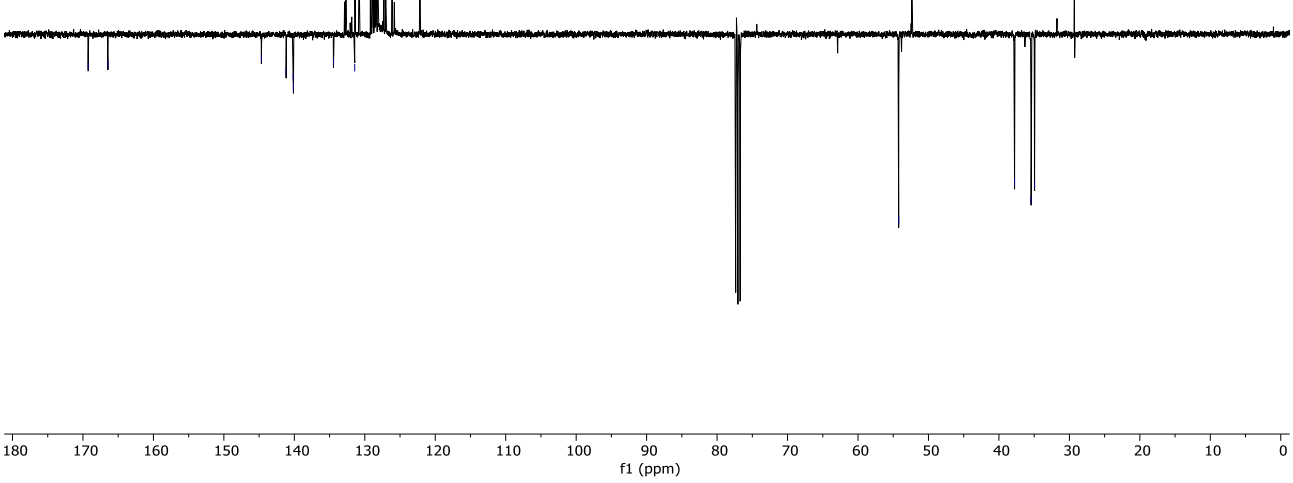


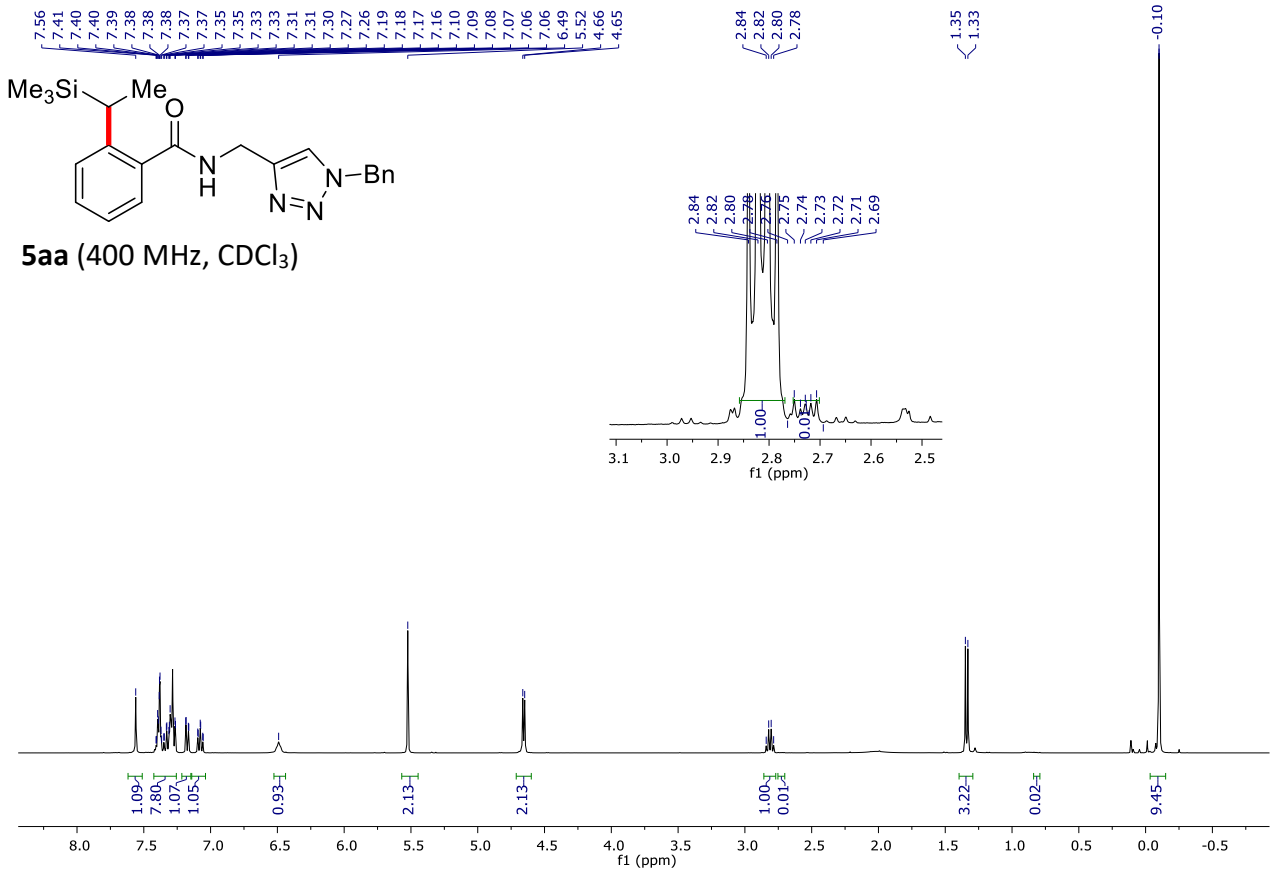
3la (400 MHz, $CDCl_3$)



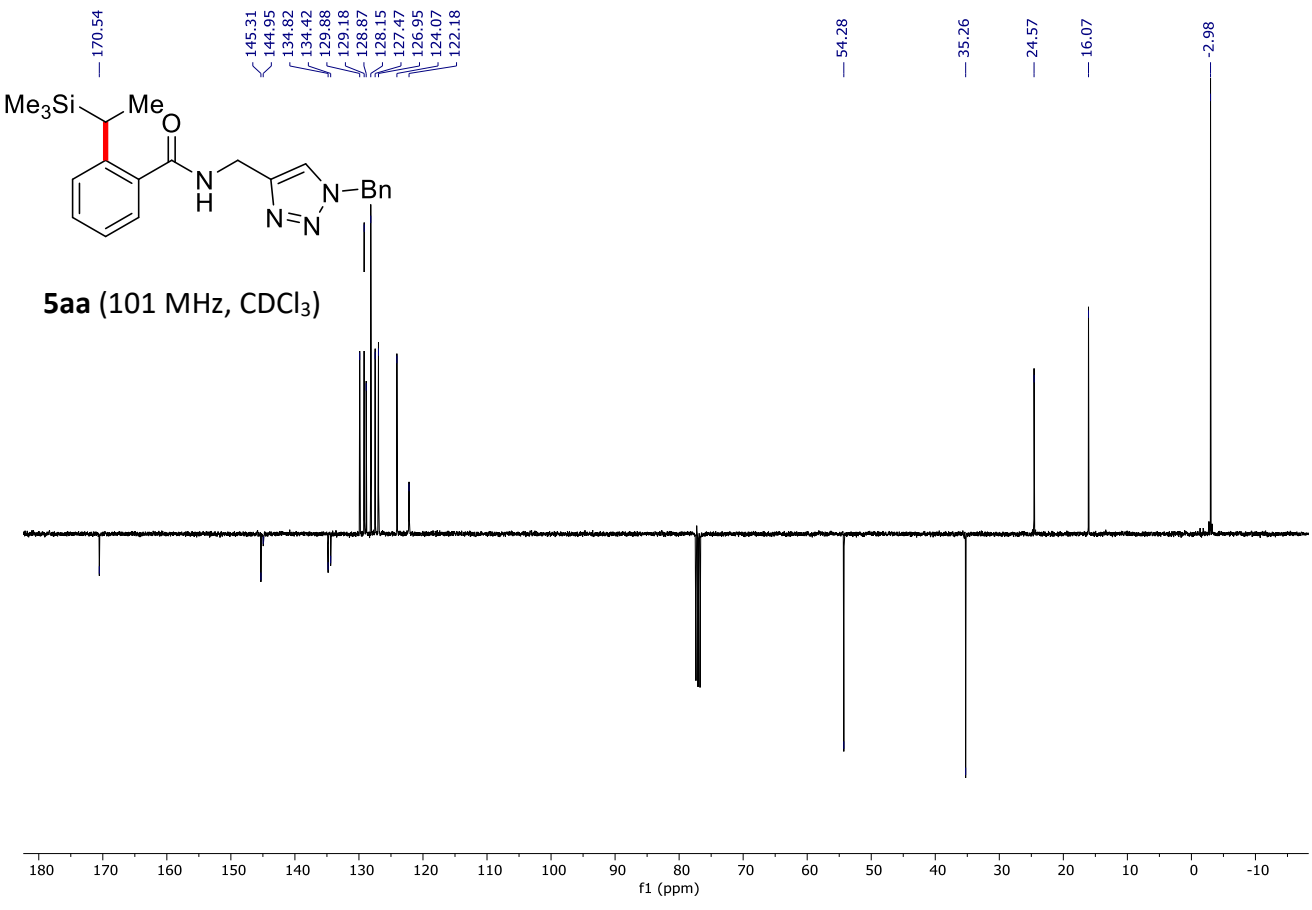


3la (101 MHz, $CDCl_3$)

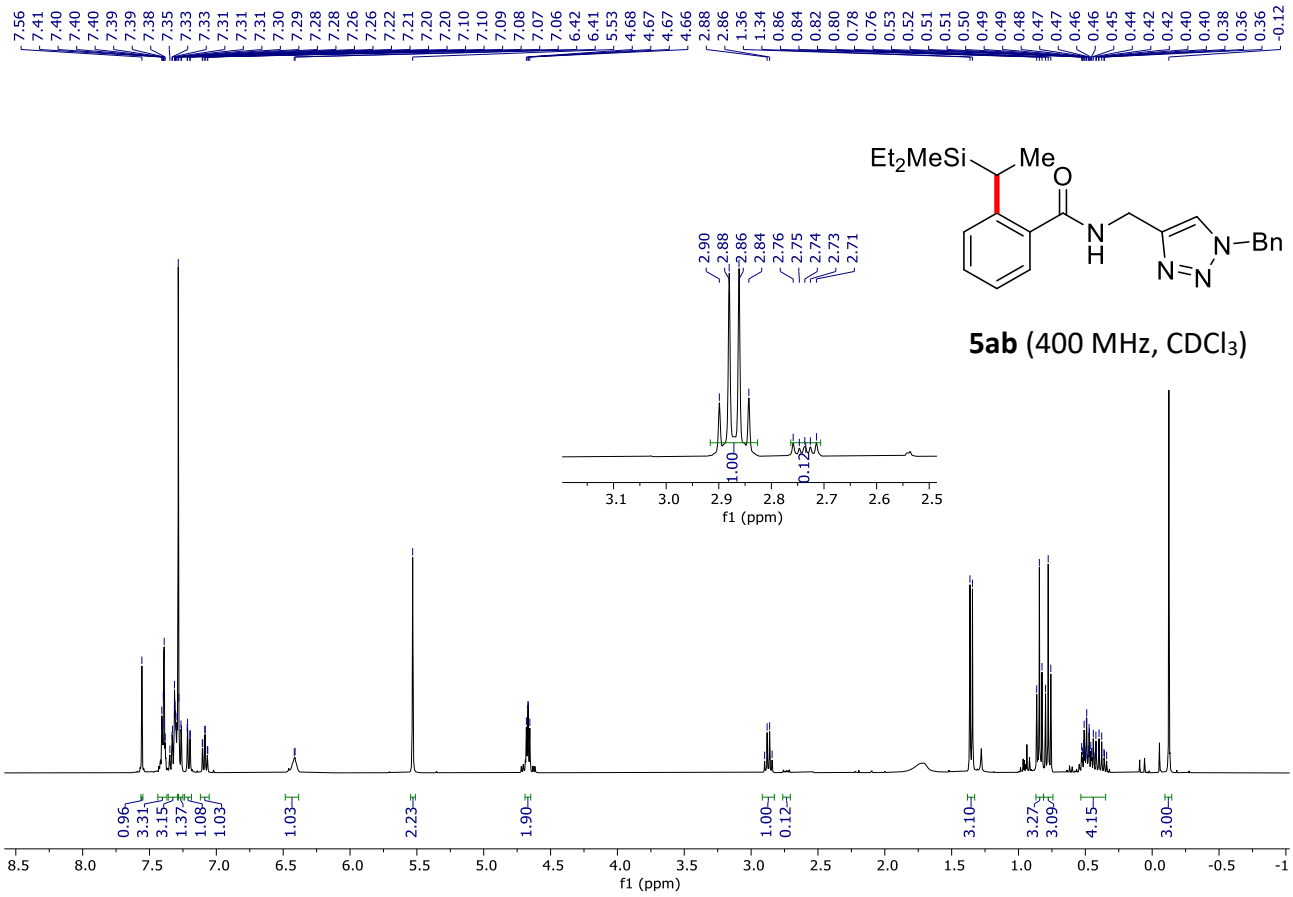


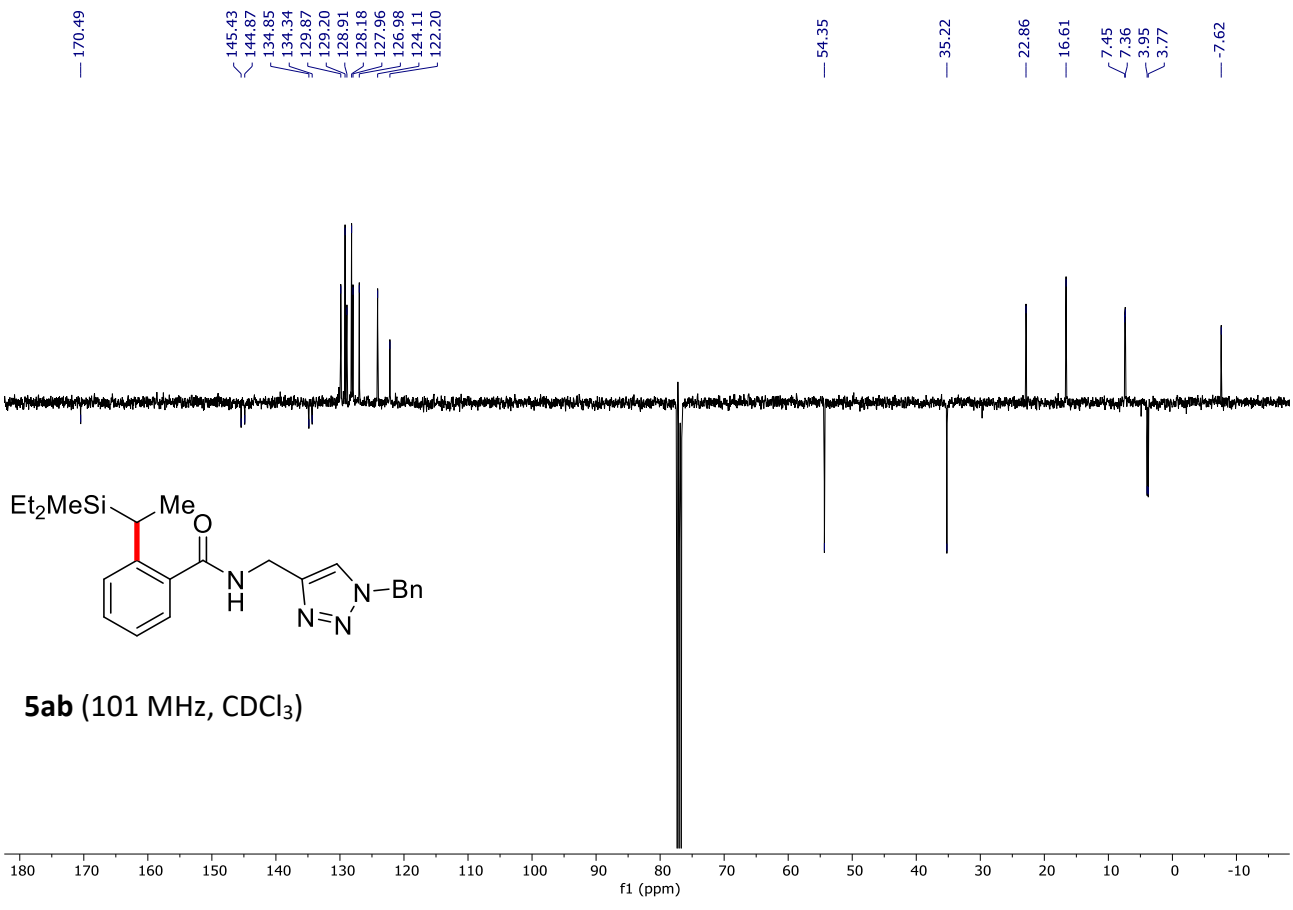


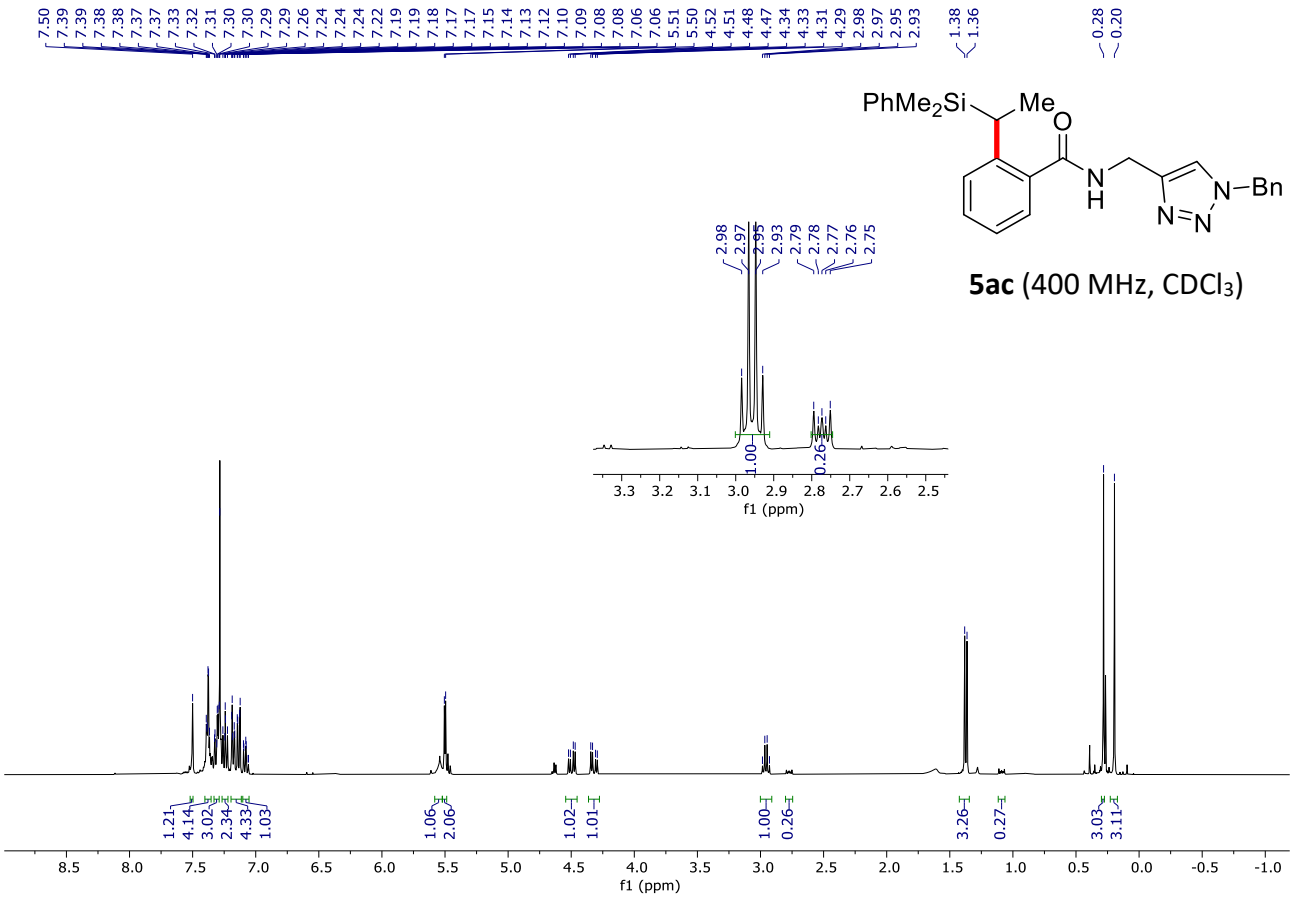
5aa (400 MHz, $CDCl_3$)



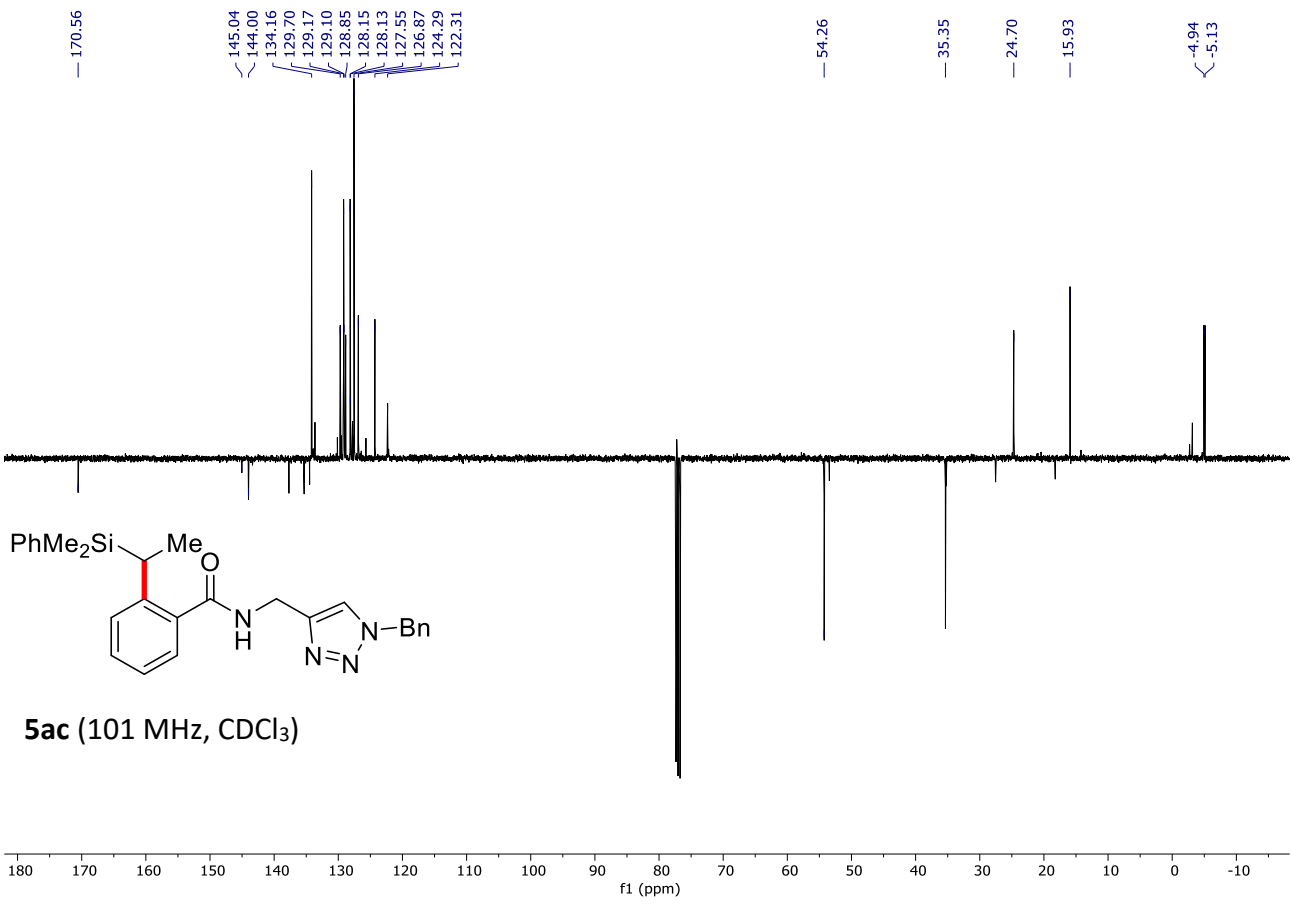
5aa (101 MHz, $CDCl_3$)


Et2MeSi
Me
O
N
H
N–Bn
N=N
5ab (400 MHz, CDCl3)
f1 (ppm)

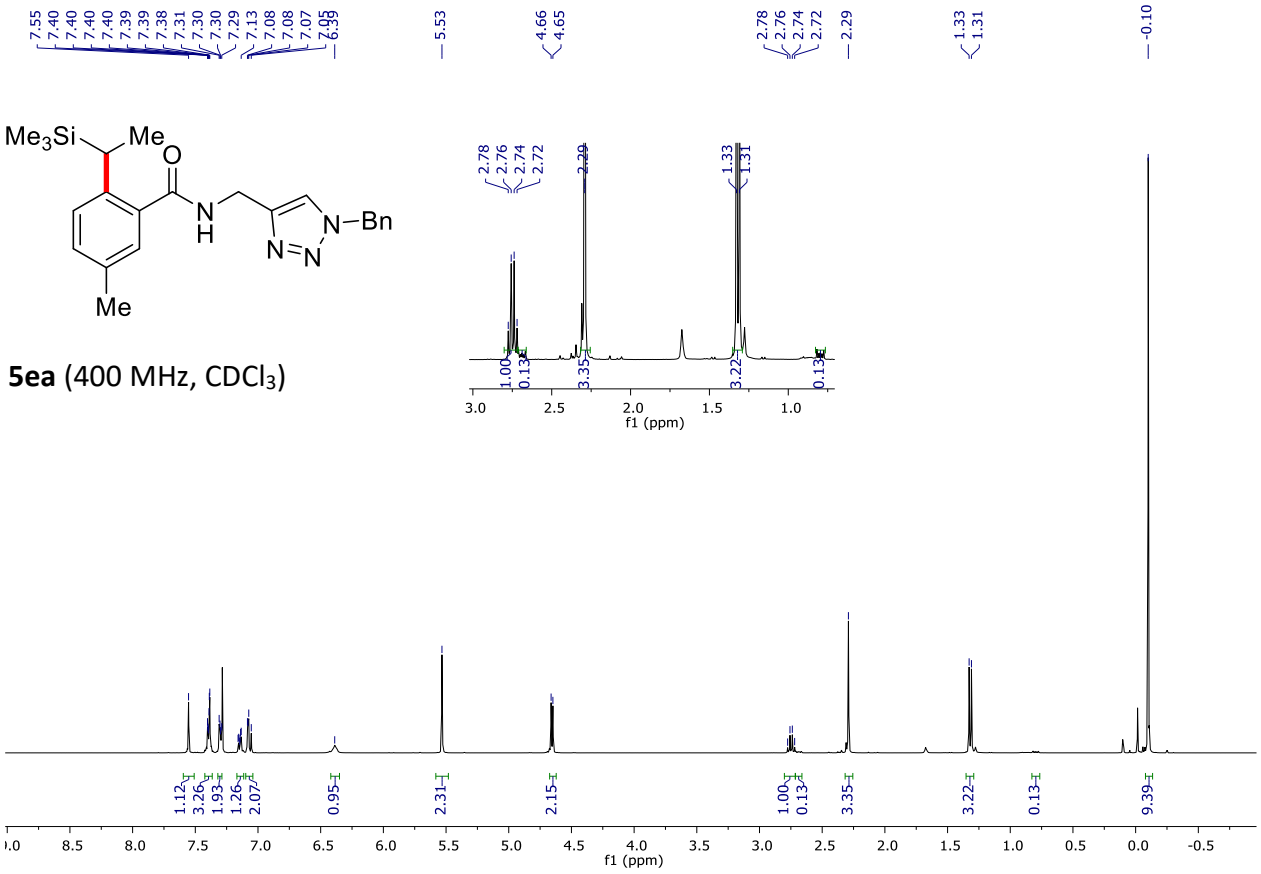

Et2MeSi
Me
O
N
H
N–Bn
N=N
5ab (101 MHz, CDCl3)
f1 (ppm)

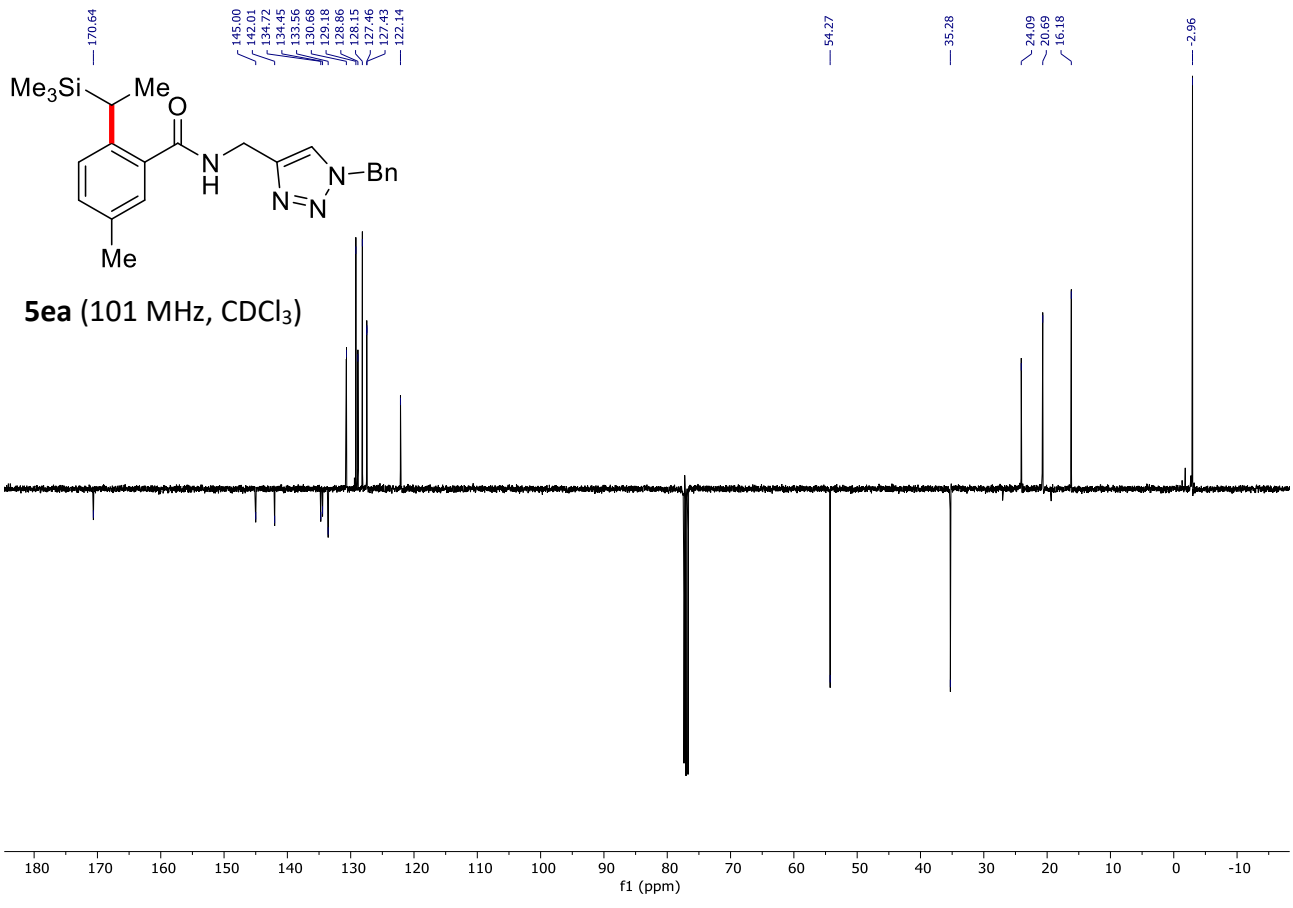


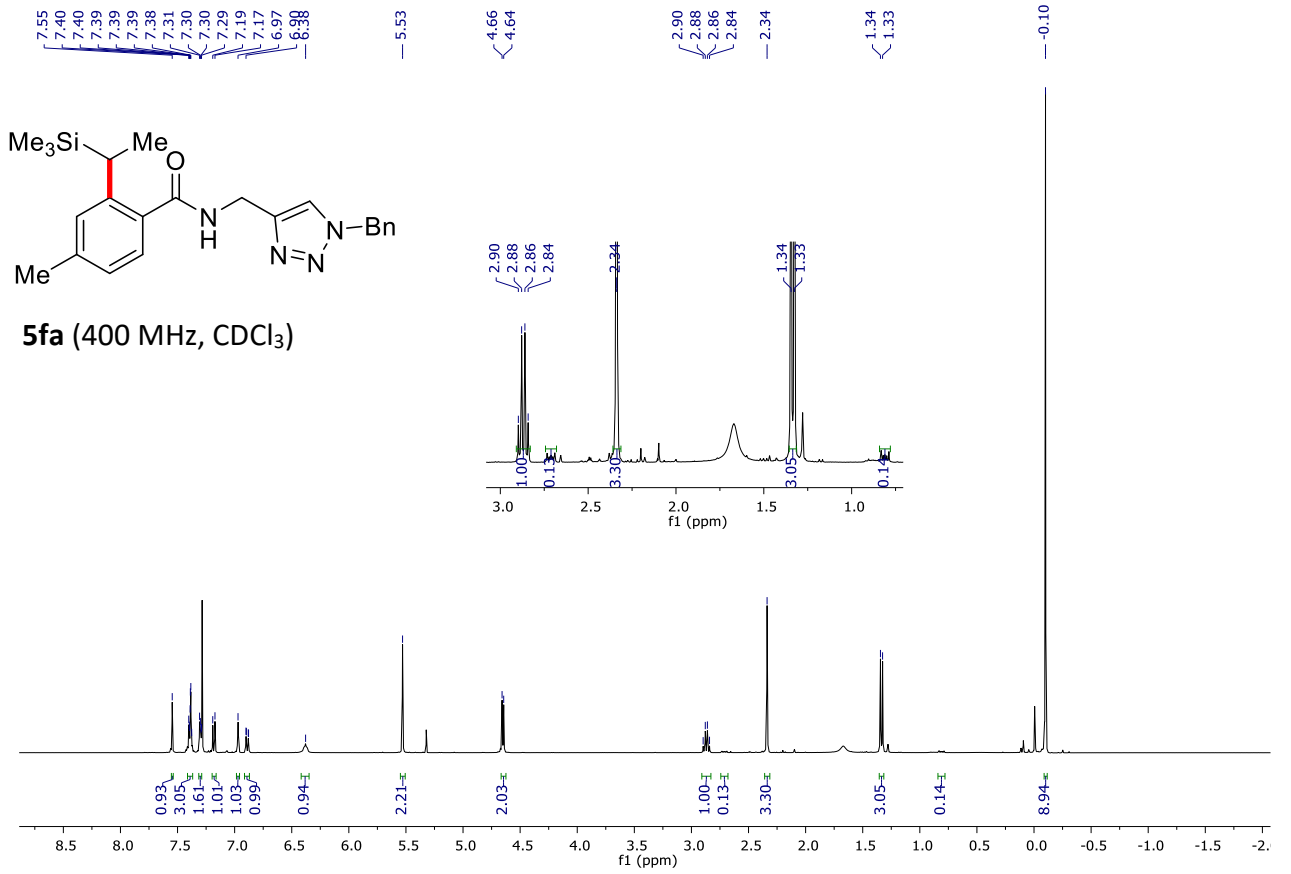
5ac (400 MHz, $CDCl_3$)



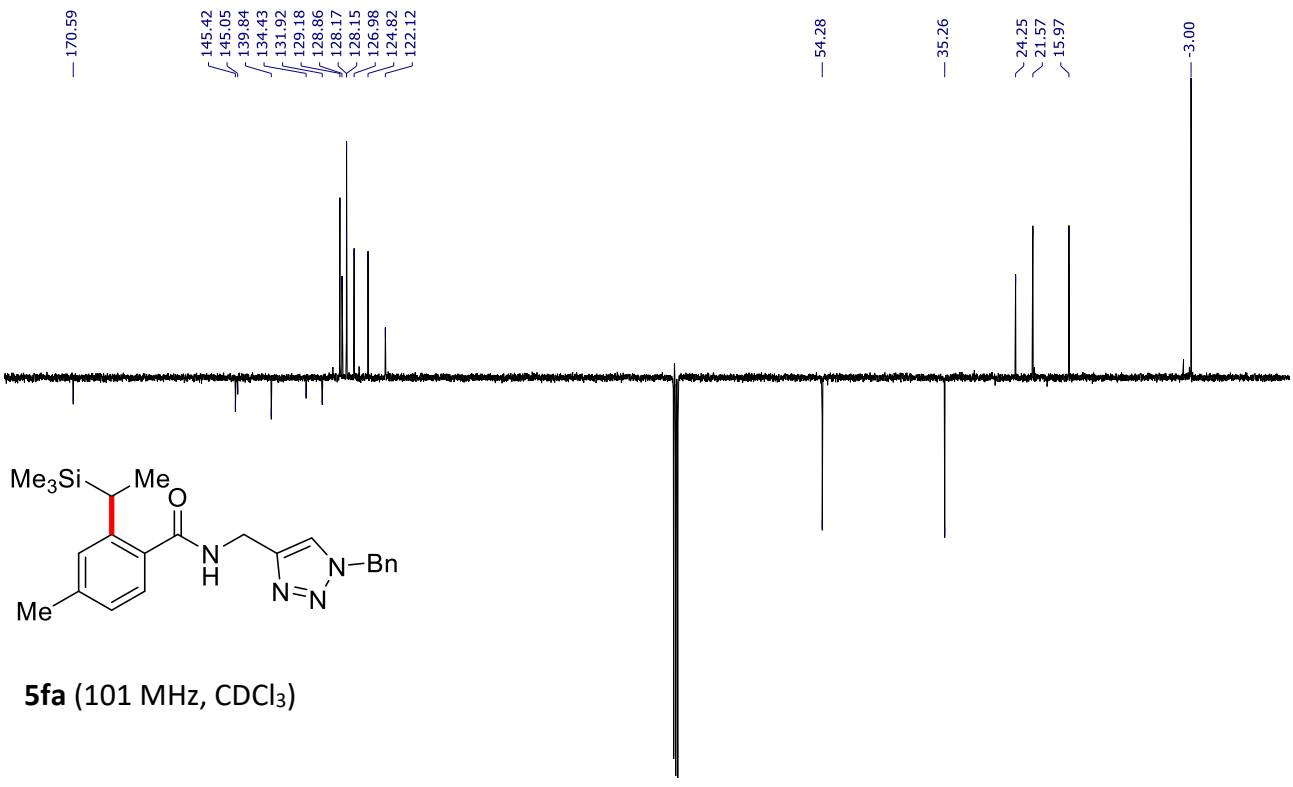
5ac (101 MHz, $CDCl_3$)


Me3Si
Me
O
N
H
N–Bn
N=N
Me
5ea (400 MHz, CDCl3)
f1 (ppm)

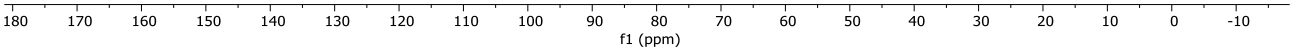

Me3Si
Me
O
N
H
N–Bn
N=N
Me
5ea (101 MHz, CDCl3)
f1 (ppm)

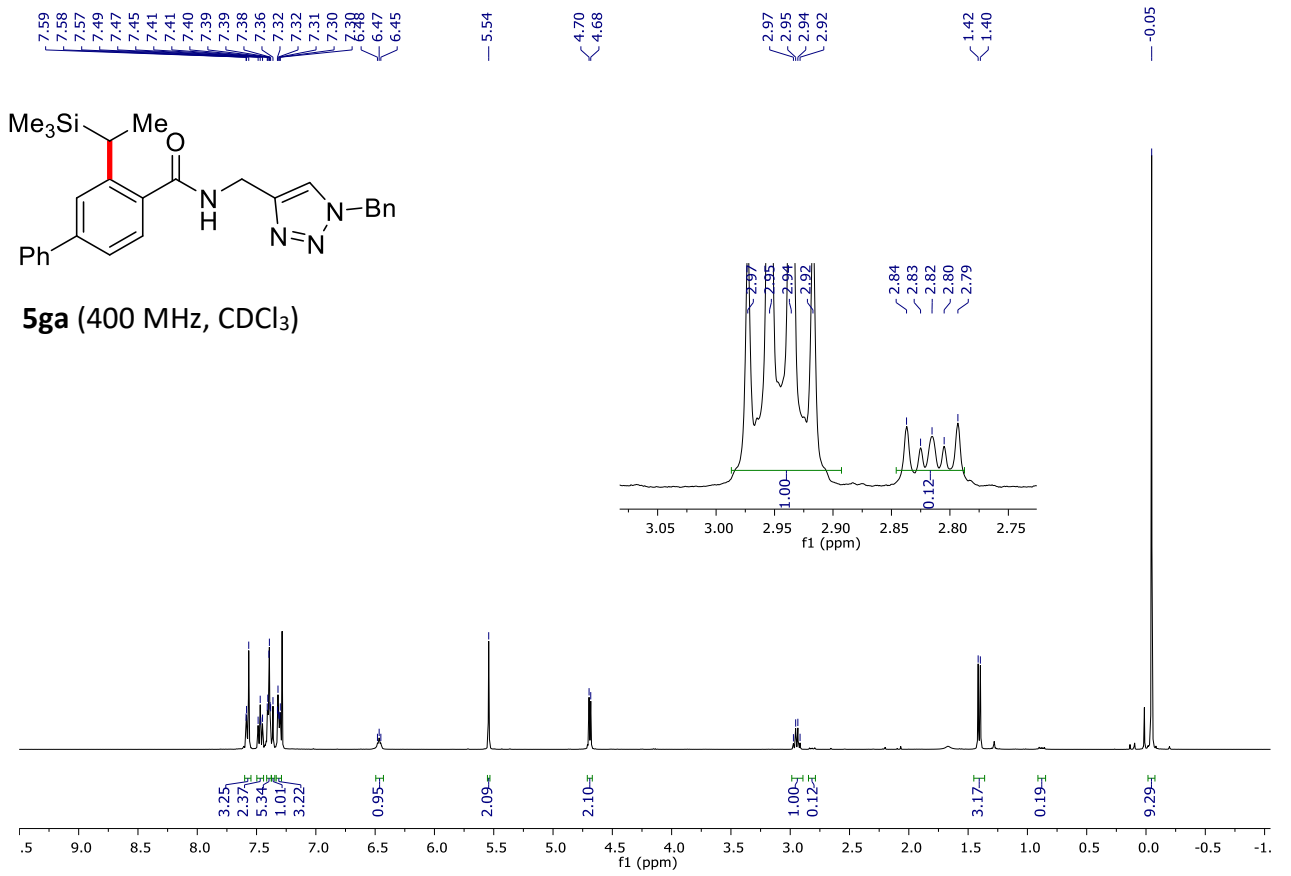


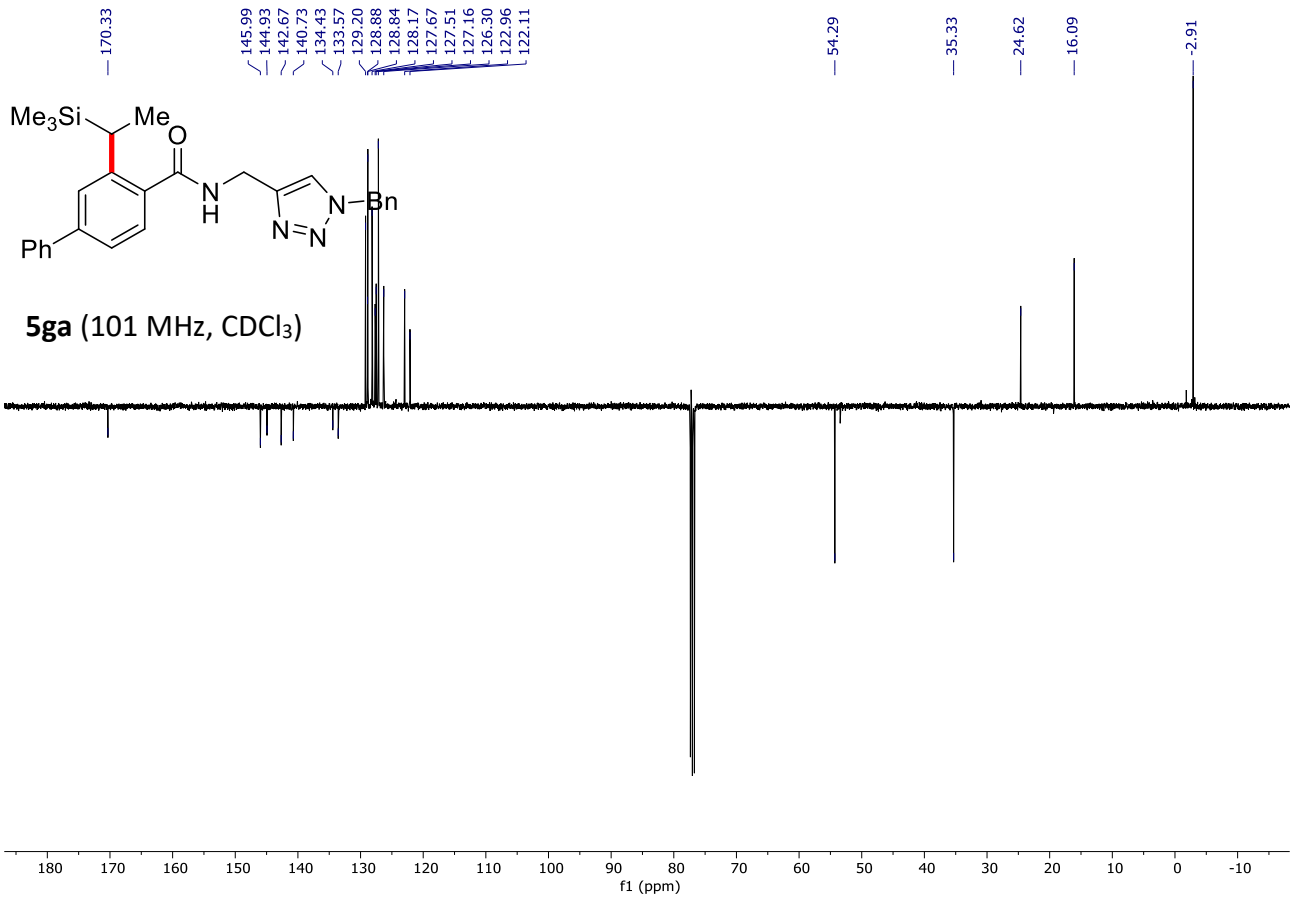
5fa (400 MHz, $CDCl_3$)

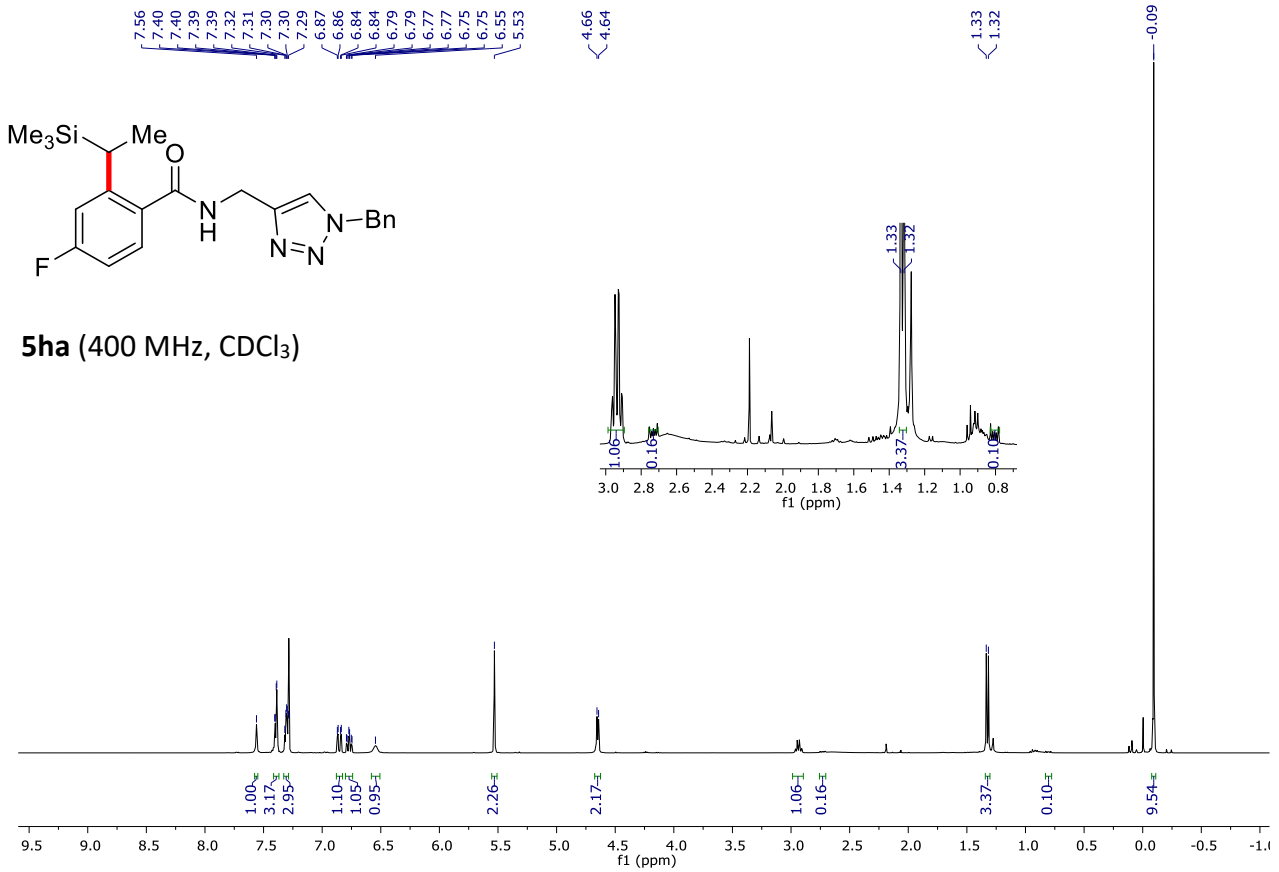


5fa (101 MHz, $CDCl_3$)

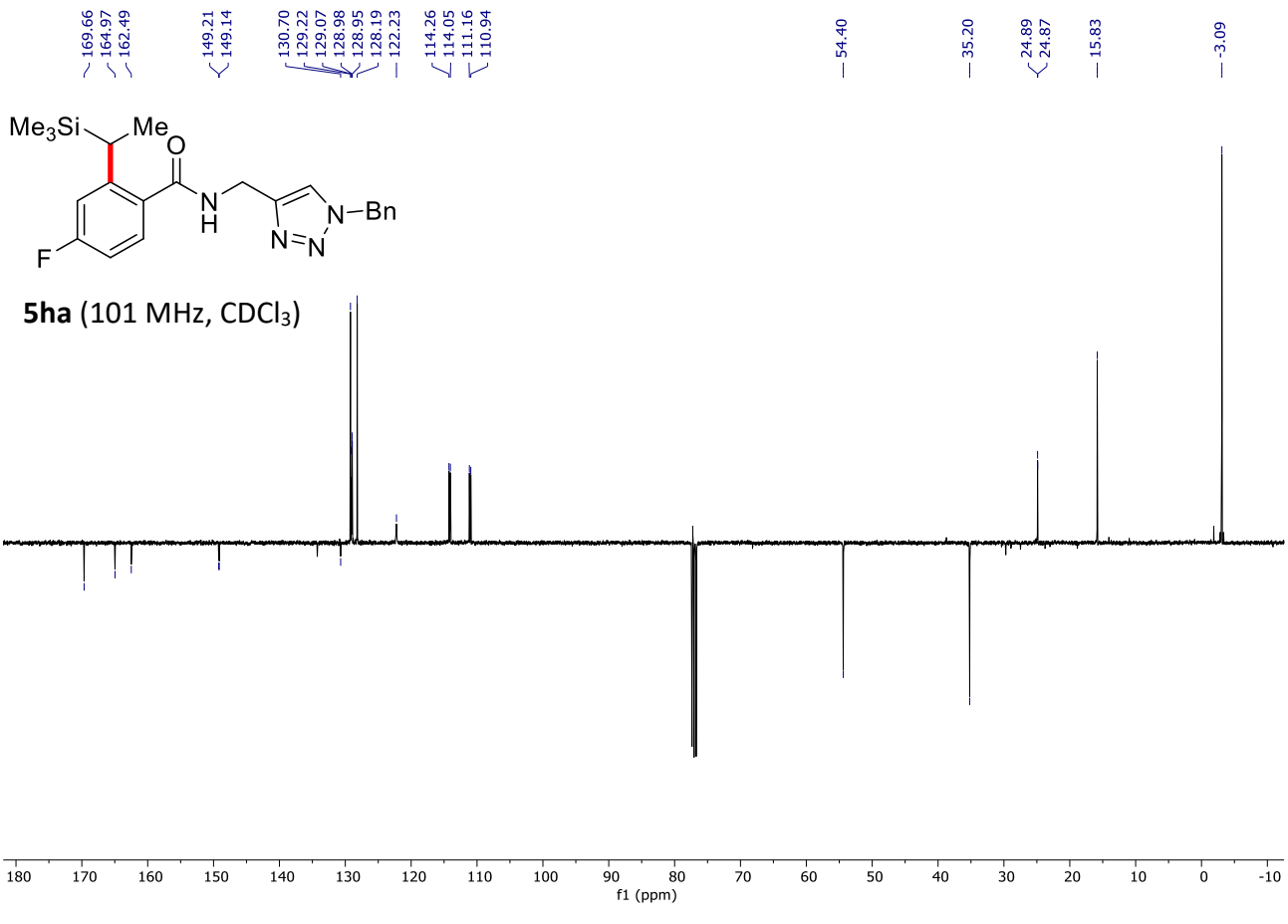



Me3Si
Me
O
N
H
N–Bn
N=N
Ph
5ga (400 MHz, CDCl3)
f1 (ppm)

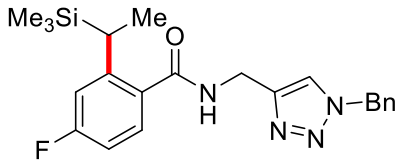

Me3Si
Me
O
N
H
N–Bn
N=N
Ph
5ga (101 MHz, CDCl3)
f1 (ppm)



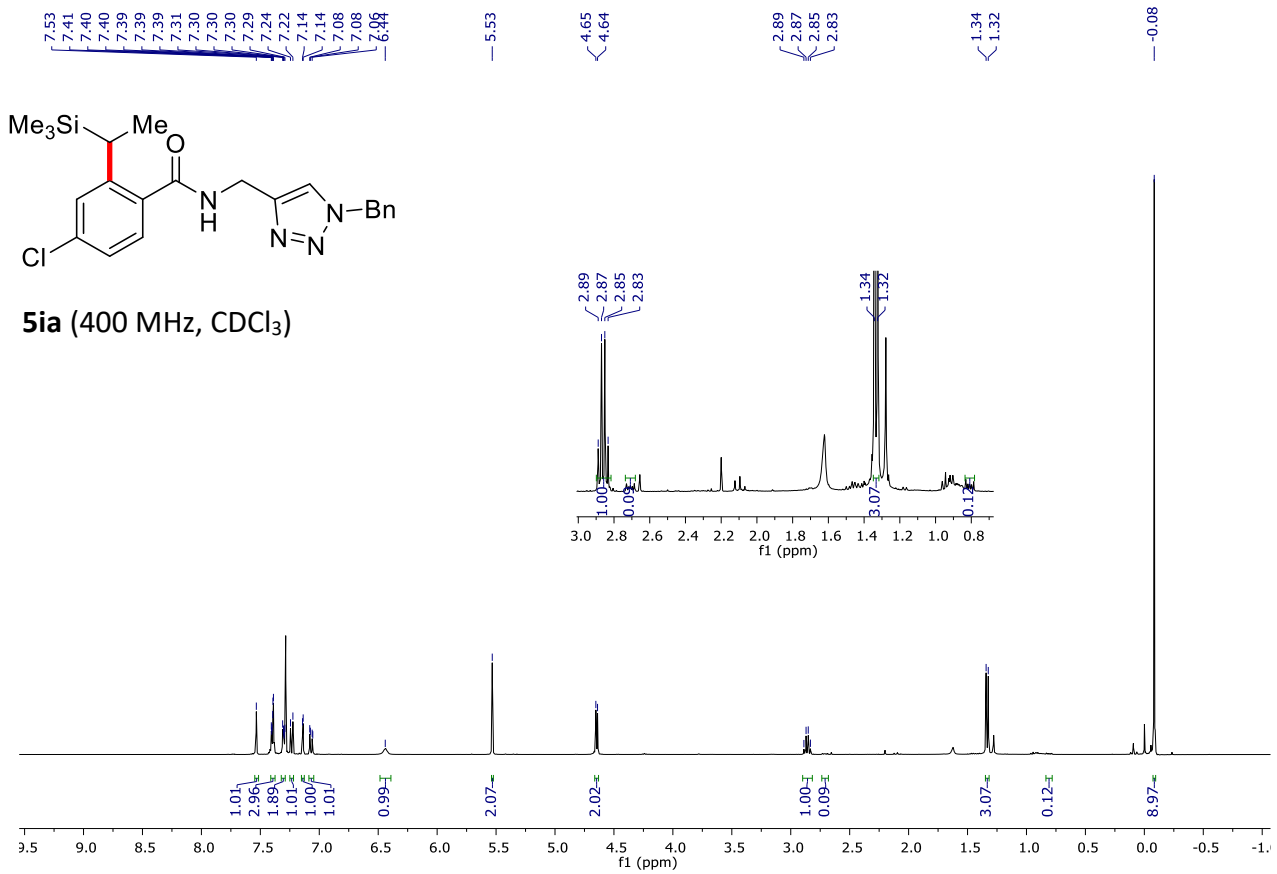
5ha (400 MHz, $CDCl_3$)



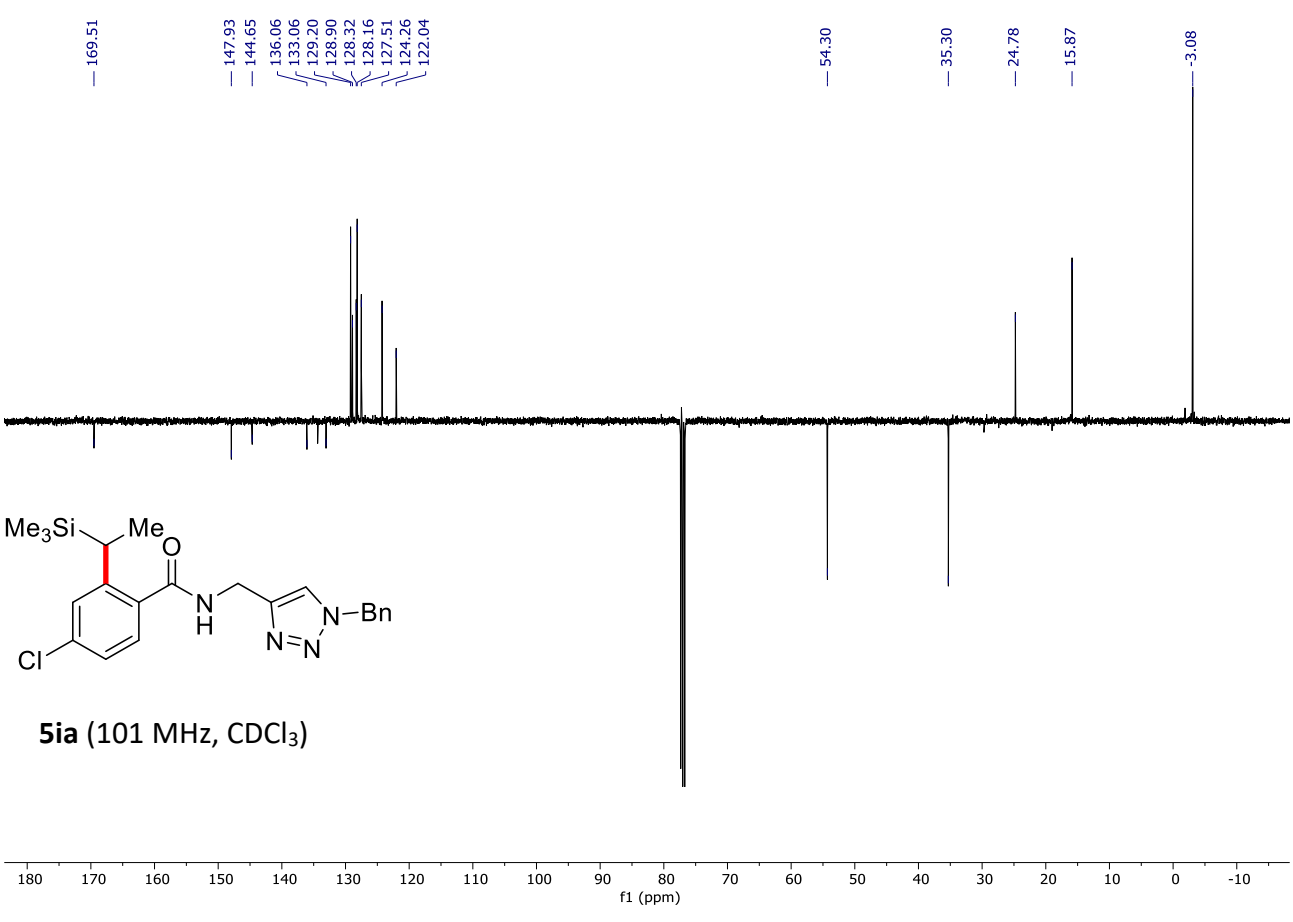
5ha (101 MHz, $CDCl_3$)



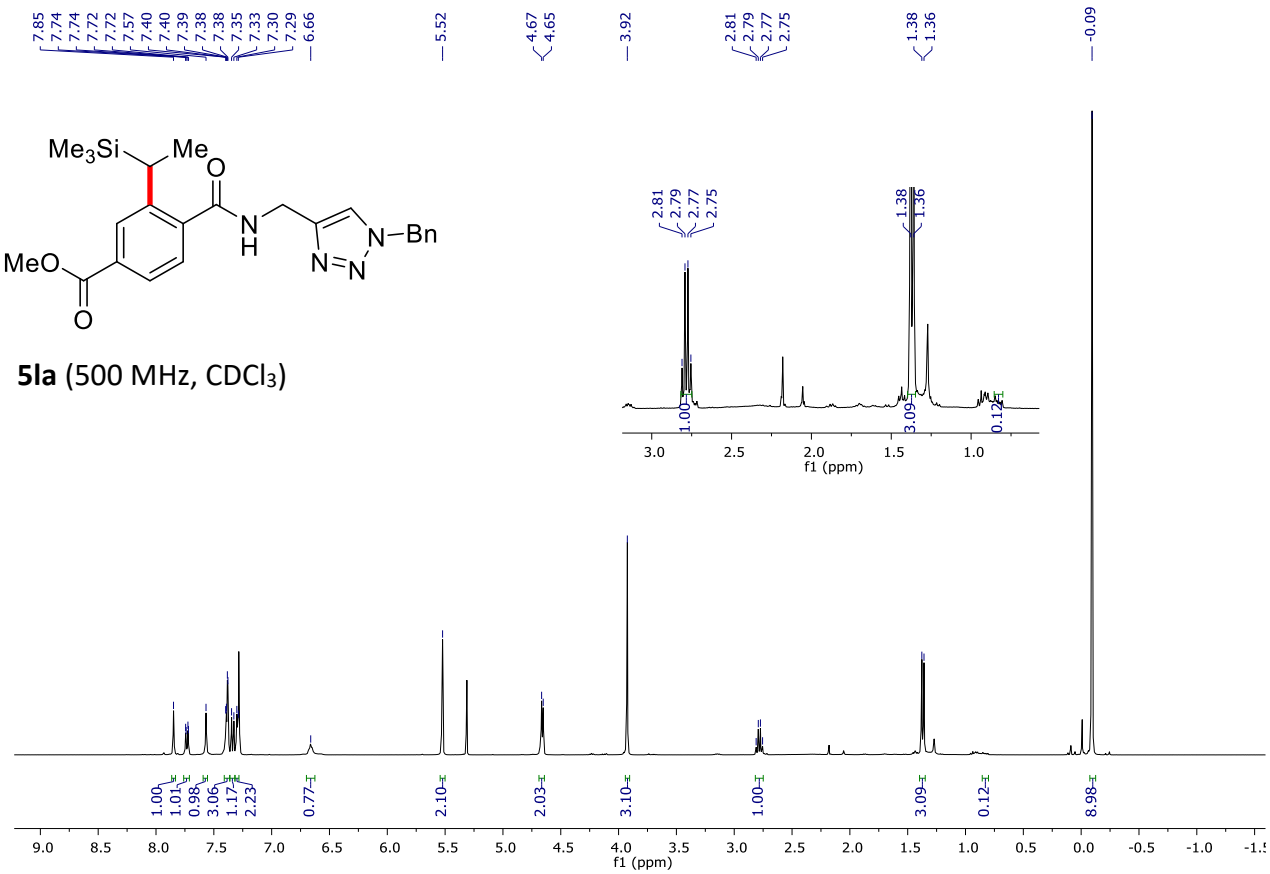
5ha (565 MHz, $CDCl_3$)



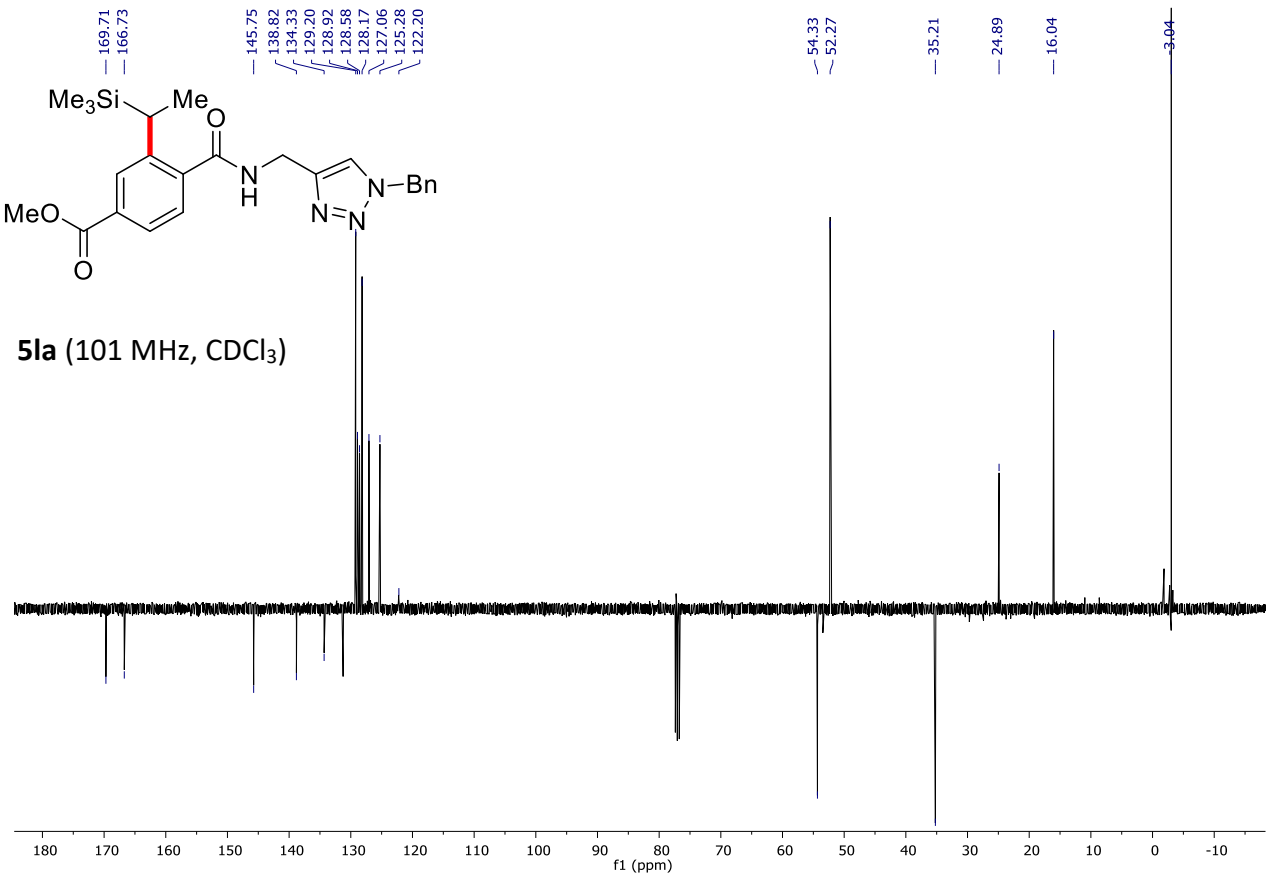
5ia (400 MHz, $CDCl_3$)



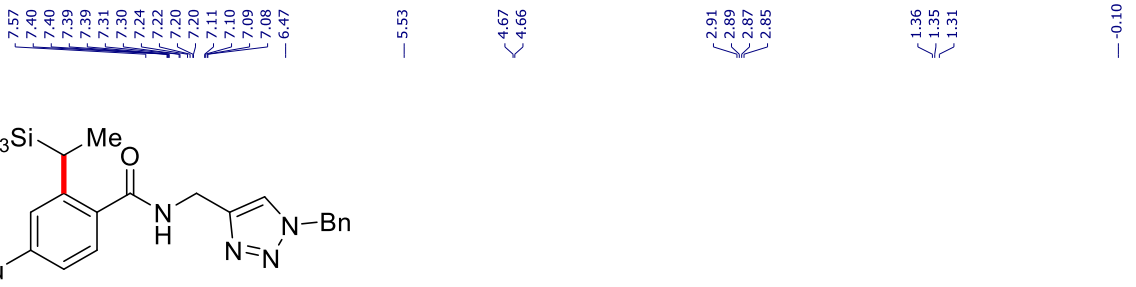
5ia (101 MHz, $CDCl_3$)



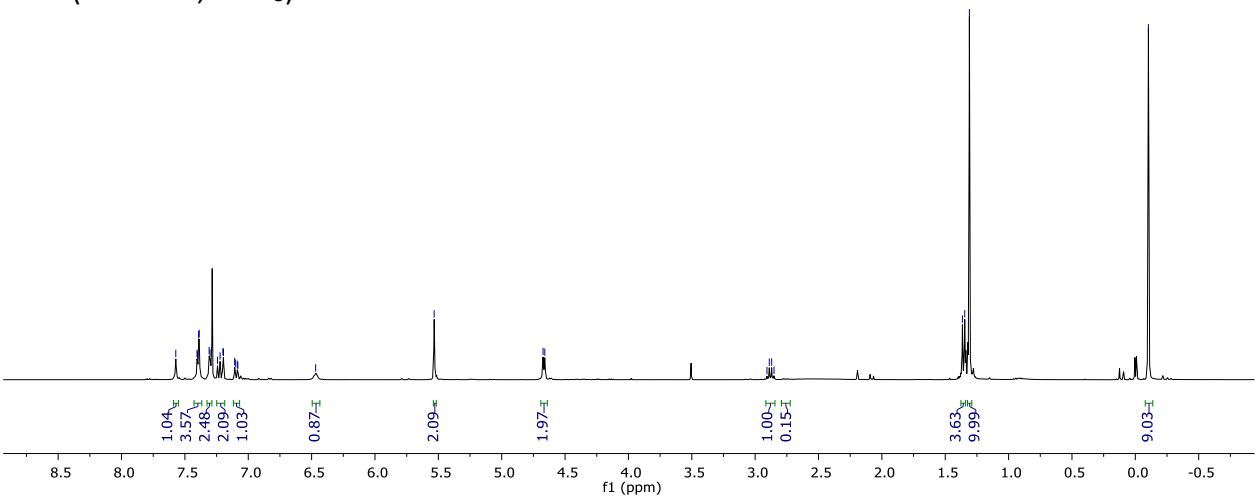
5la (500 MHz, $CDCl_3$)

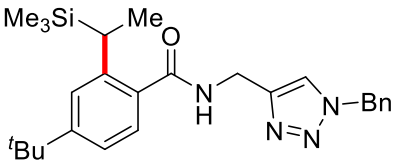


5la (101 MHz, $CDCl_3$)

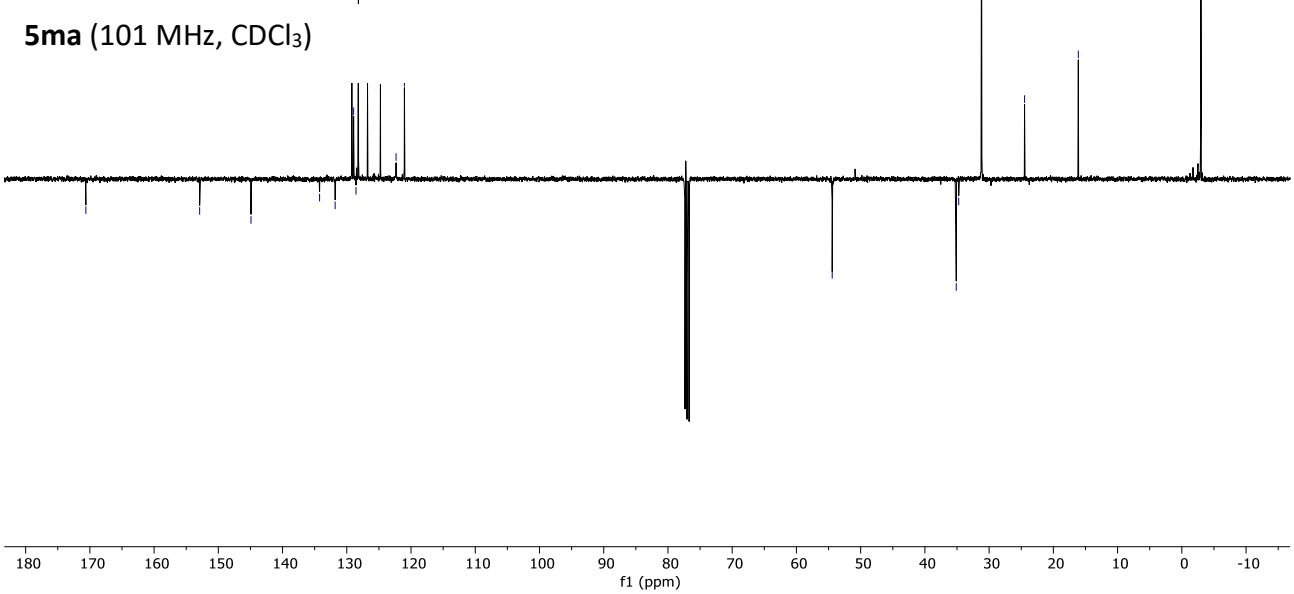


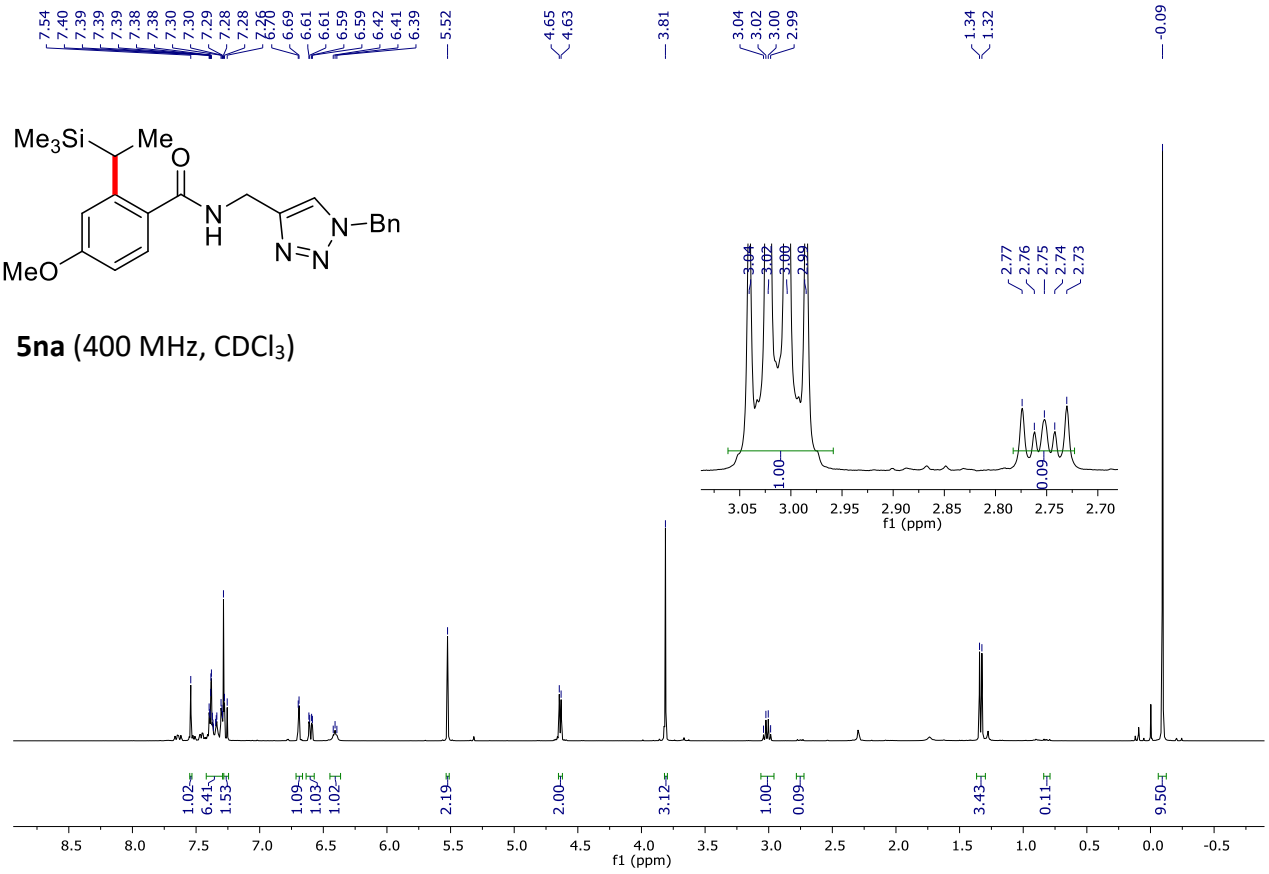
5ma (500 MHz, $CDCl_3$)



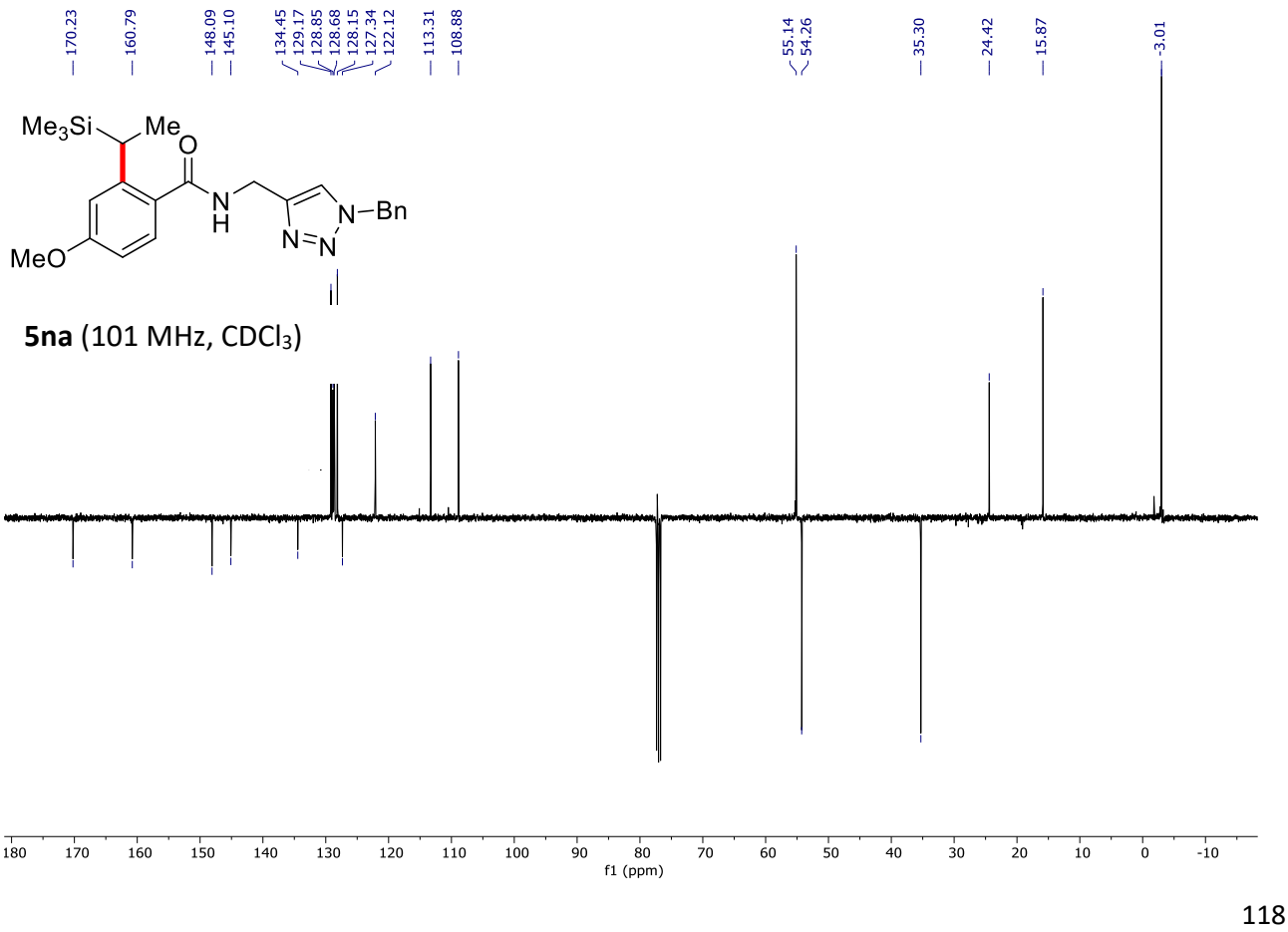


5ma (101 MHz, $CDCl_3$)

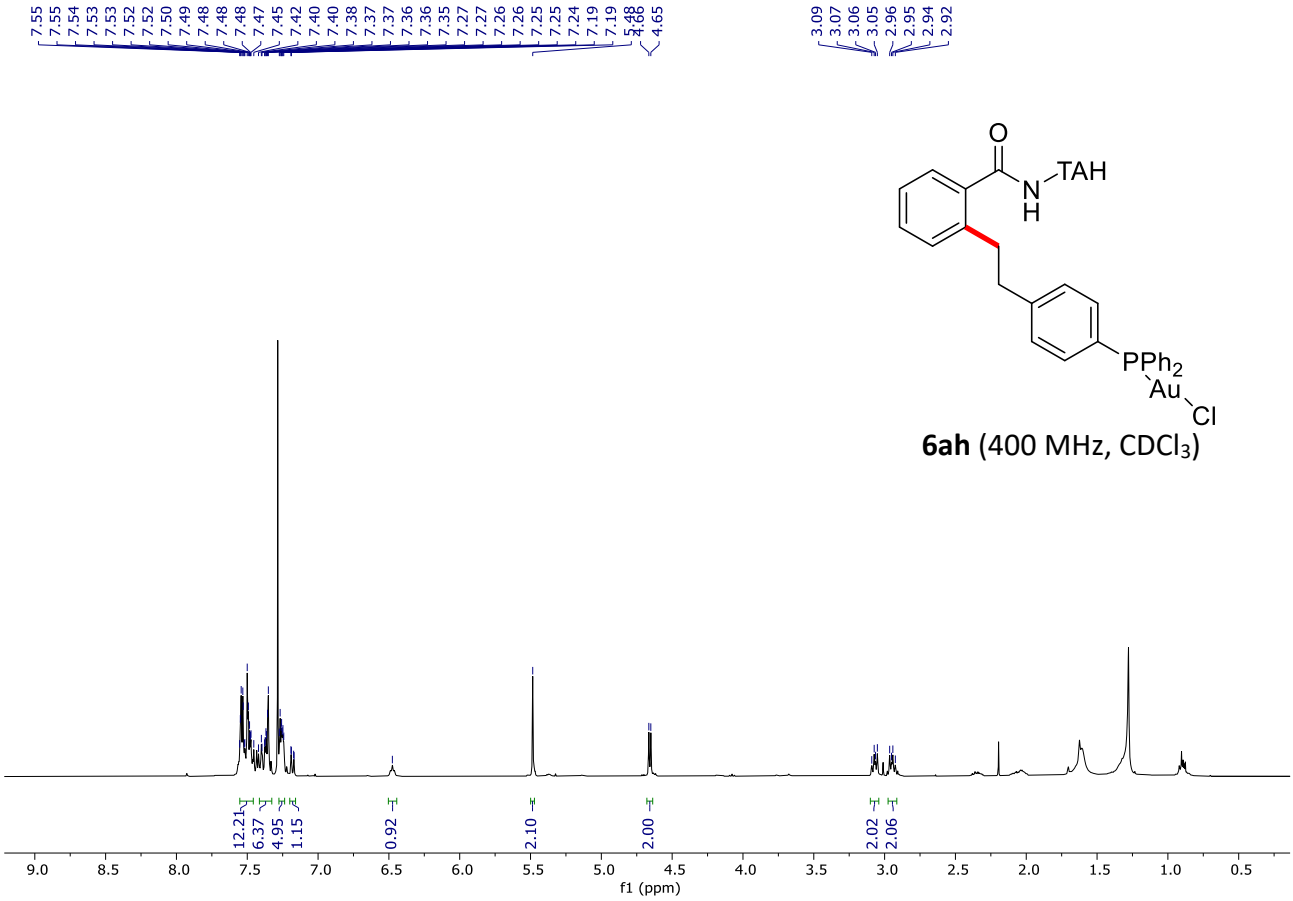




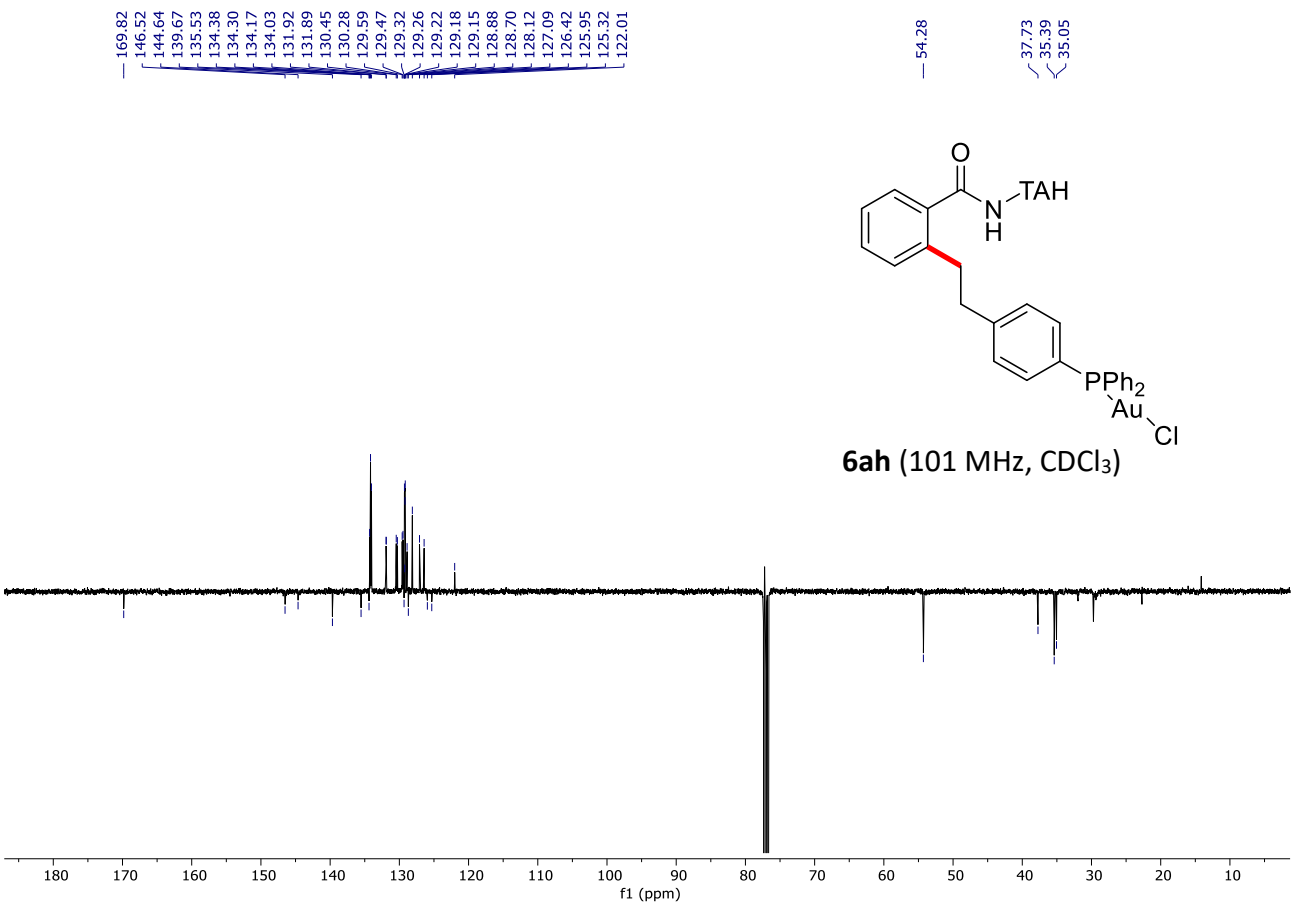
5na (400 MHz, $CDCl_3$)



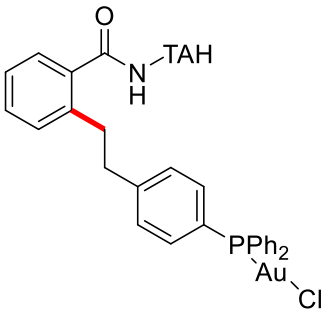
5na (101 MHz, $CDCl_3$)



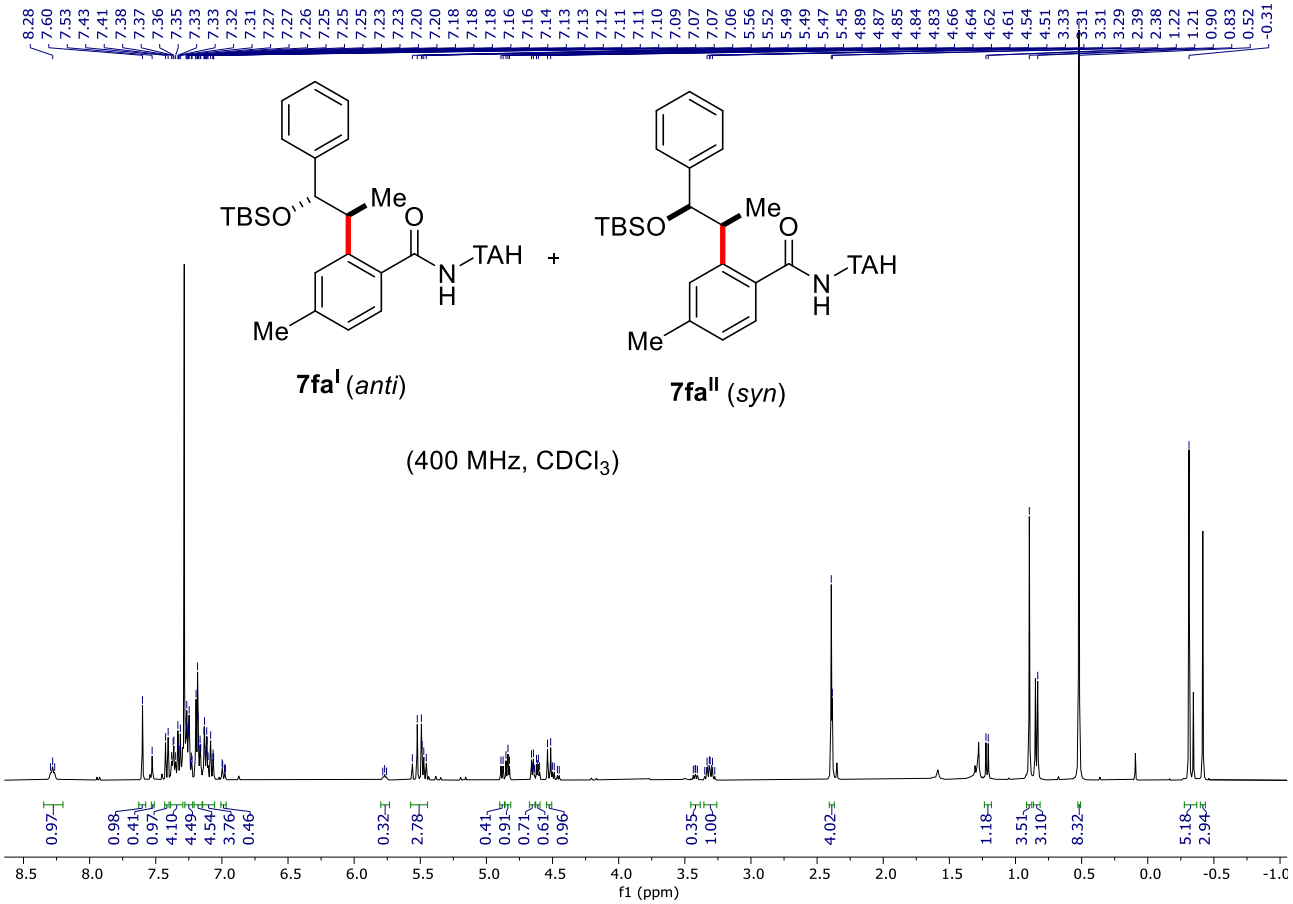
6ah (400 MHz, $CDCl_3$)

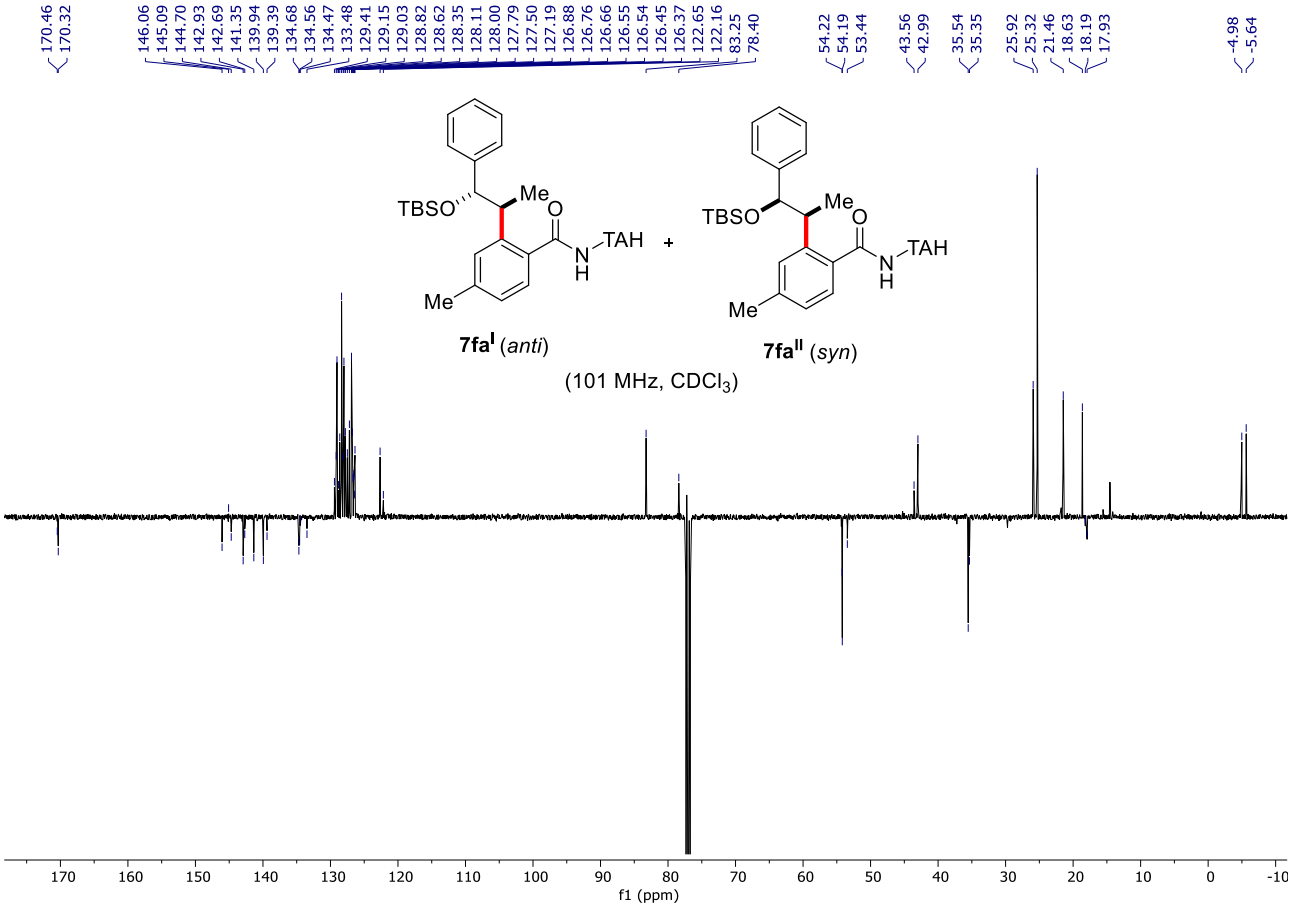


6ah (101 MHz, $CDCl_3$)

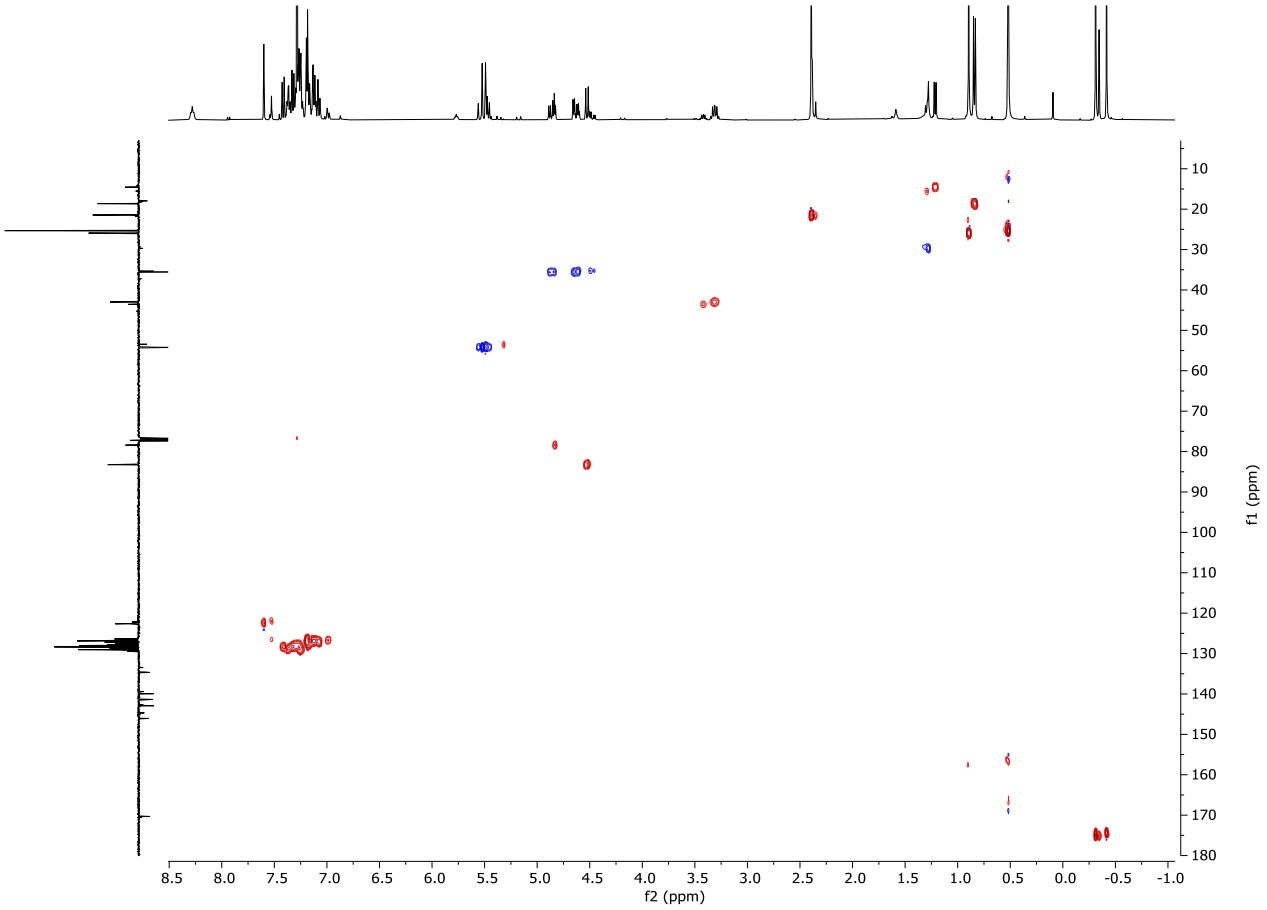


6ha (162 MHz, $CDCl_3$)

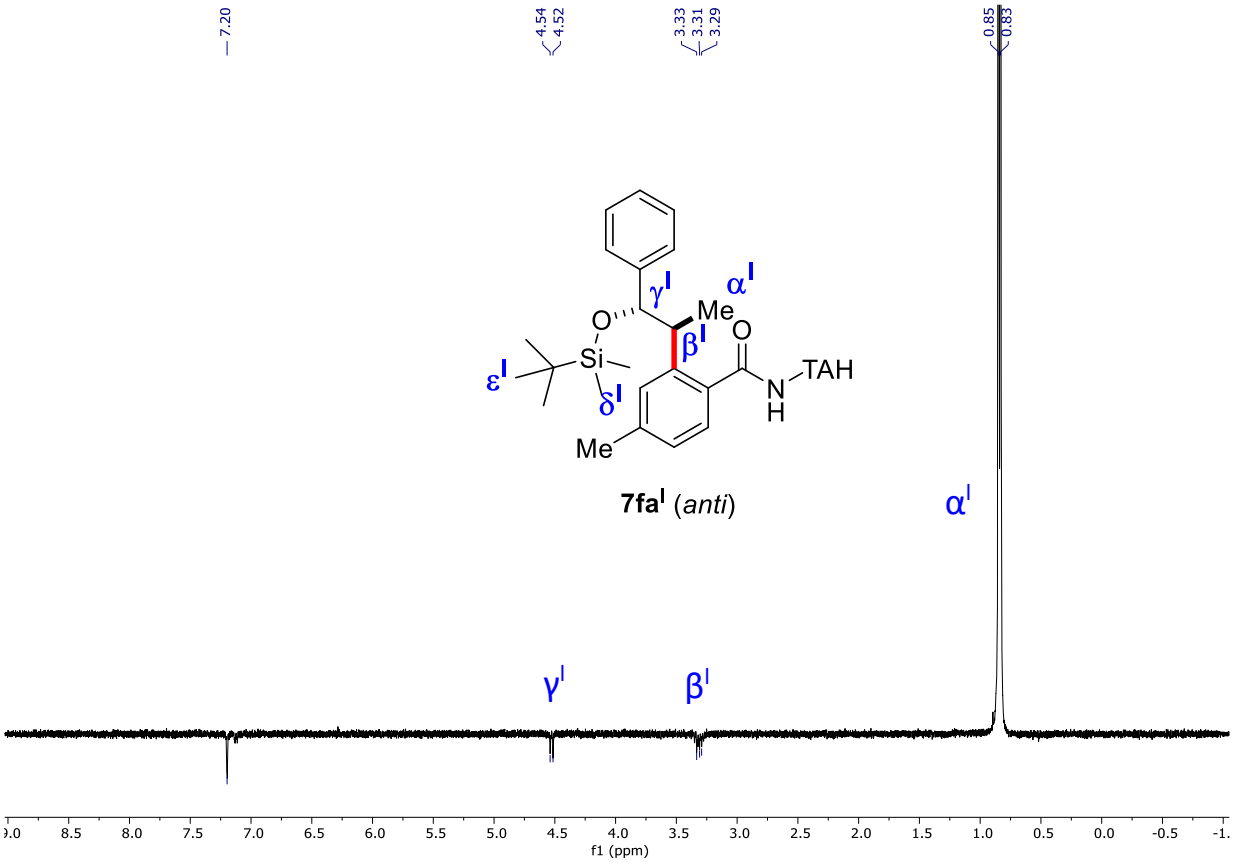

TBSO
Me
O
N
H
TAH
Me
7fa^I (anti)
7fa^II (syn)
(400 MHz, CDCl3)
f1 (ppm)


TBSO
Me
O
N
H
TAH
Me
7fa^I (anti)
7fa^II (syn)
(101 MHz, CDCl3)
f1 (ppm)

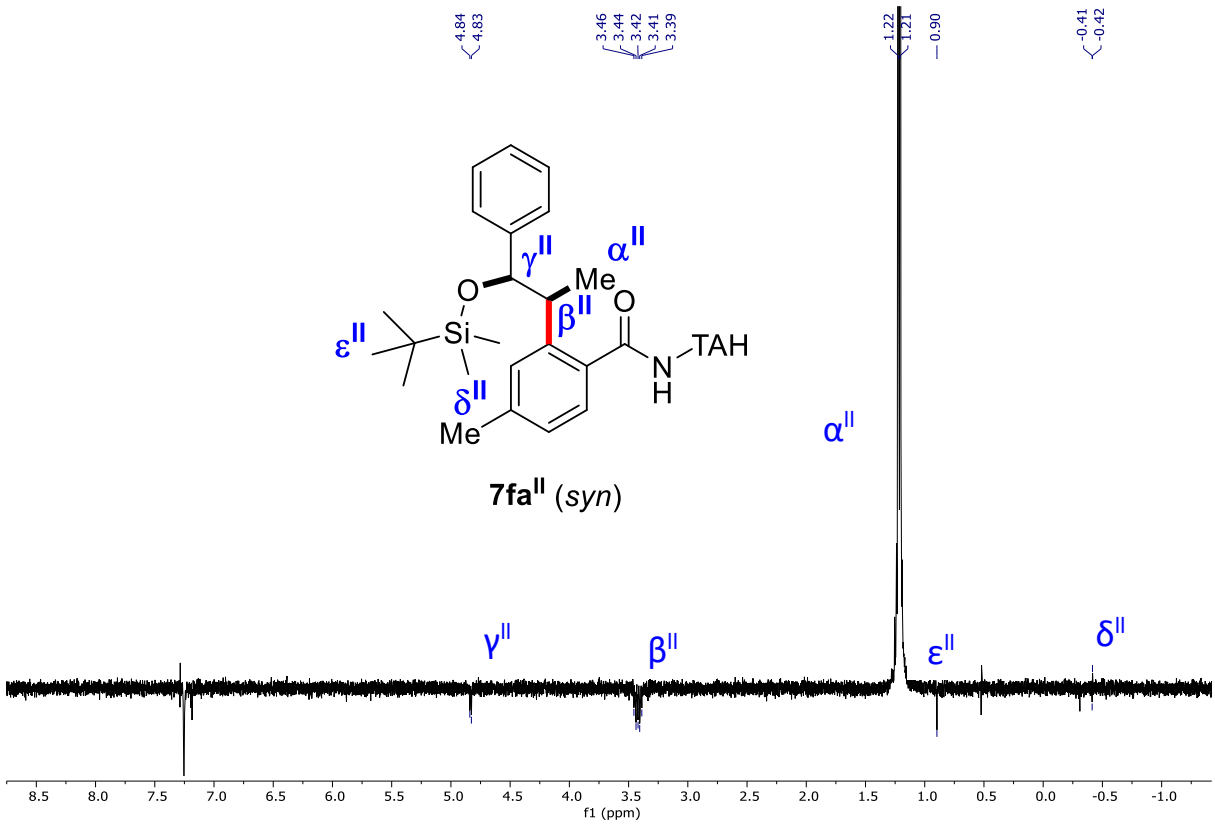
7fa-HSQC

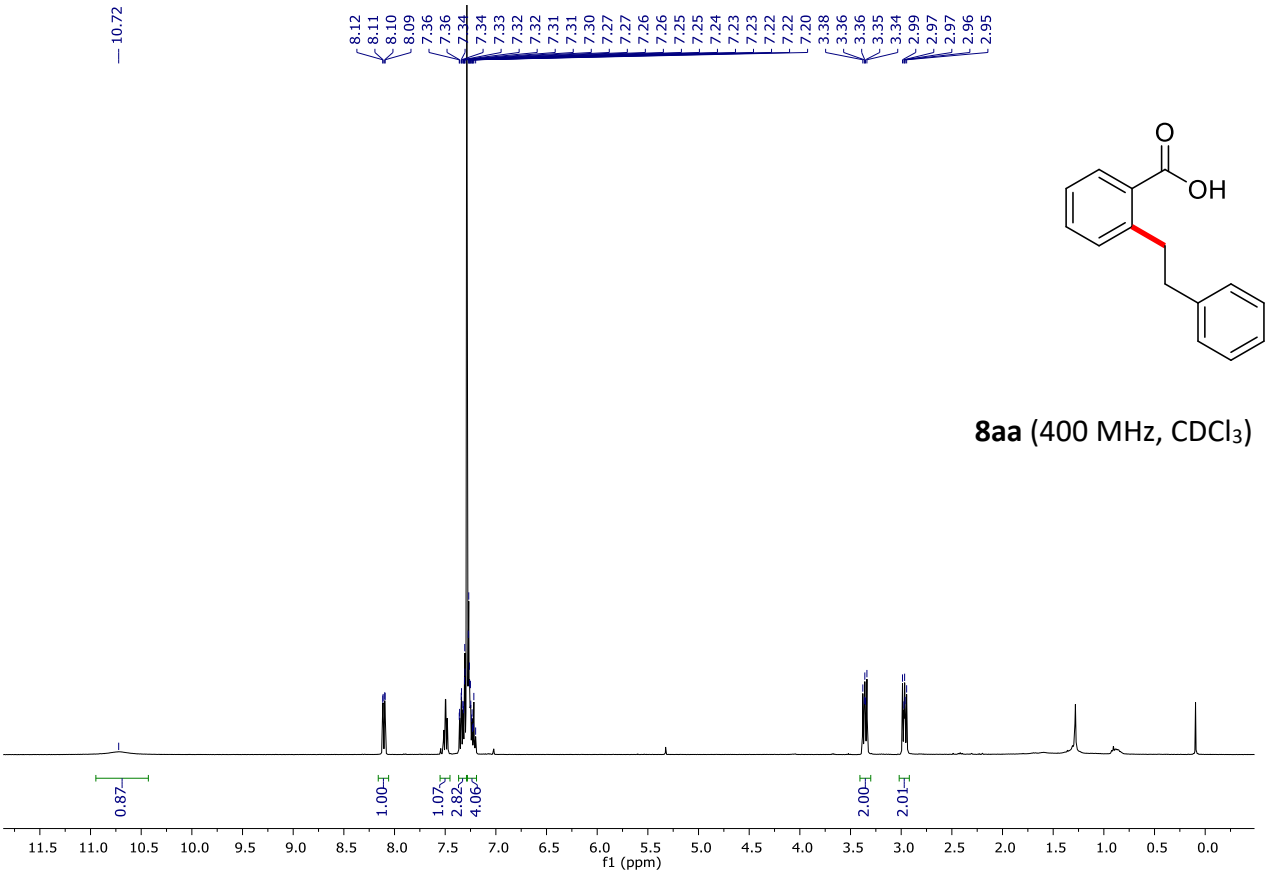


8fa^{I} (anti)-SELECTIVE NOESY by irradiation at 0.84 ppm (α^{I} signal)

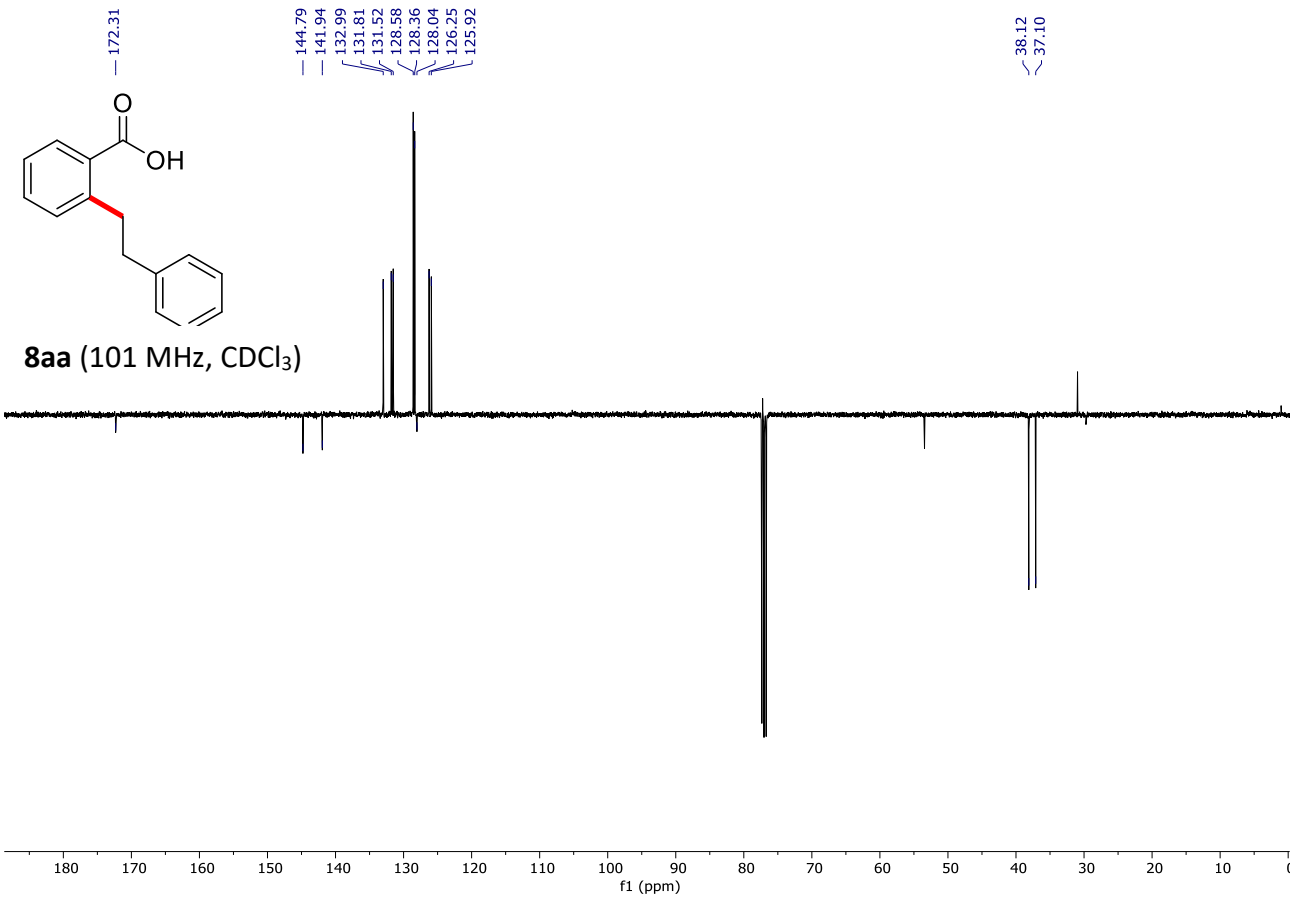


8fa^{II} (syn)-SELECTIVE NOESY by irradiation at 1.21 ppm (α^{II} signal)

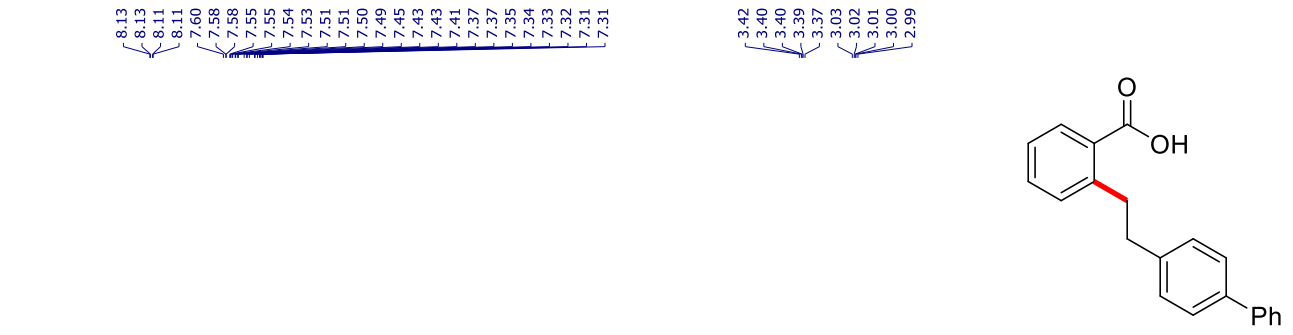




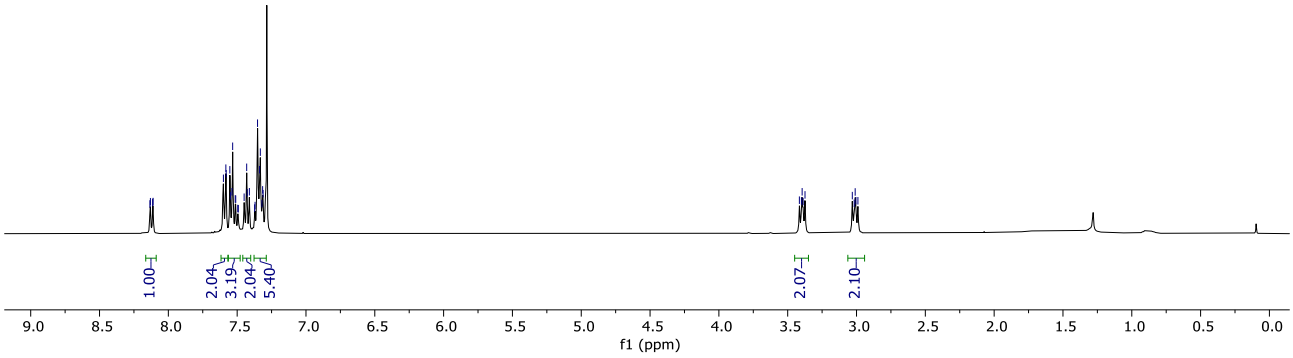
8aa (400 MHz, $CDCl_3$)

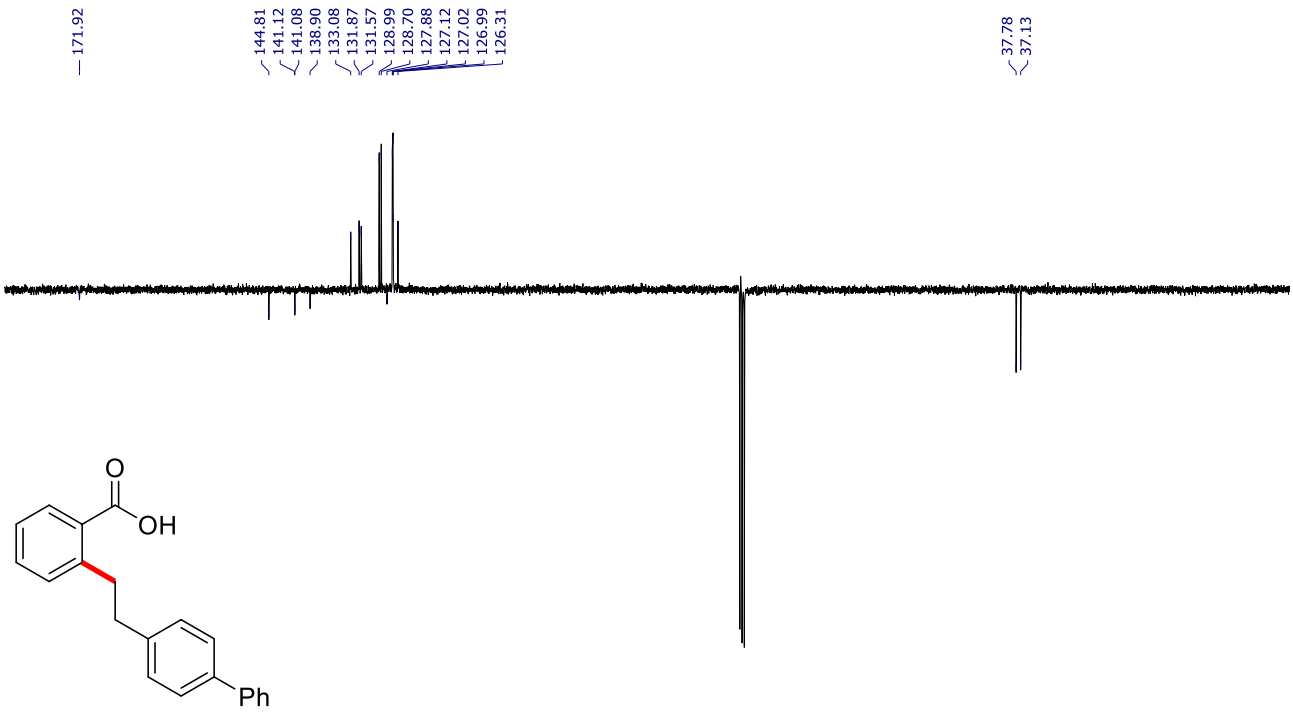


8aa (101 MHz, $CDCl_3$)



8ad (400 MHz, $CDCl_3$)





8ad (101 MHz, $CDCl_3$)