Supporting Information

C–H Arylations of 1,2,3-Triazoles by Reusable Heterogenous Palladium Catalysis in Biomass-Derived γ-Valerolactone

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Contents

General remarks

Catalytic reactions were carried out under a N_2 atmosphere using pre-dried glassware. Triazoles **1** were prepared in analogy to previously described methodologies.[1-4] Additional starting materials were obtained from commercial sources, and were used without further purification. γ-Valerolactone was purchased from Acros Organics (98%), dried over CaH_2, distilled and stored over molecular sieve (4 Å) or purchased from Sigma Aldrich (99%) and used without further purification. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H-NMR and GC, unless otherwise indicated. Flash chromatography: Macherey-Nagel silica gel 60 (70-230 mesh). NMR: Spectra were recorded on Varian-NMR 300, 400 or 500 instruments in the solvent indicated; chemical shifts (δ) are given in ppm. All IR spectra were recorded on a Bruker FT-IR Alpha device. MS: EI-MS- and ESIMS-spectra were recorded with Finnigan MAT 95, 70 eV; High resolution mass spectrometry (HRMS) with APEX IV 7T FTICR, Bruker Daltonic. M. p.: Stuart melting point apparatus SMP3, Barloworld Scientific, values are uncorrected.

General Procedures for the palladium-catalyzed C–H arylation of 1,2,3-triazoles

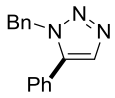
Representative Procedure A:

A suspension of Pd/C (13.3 mg, 5.0 mol %), $MesCO_2H$ (12.3 mg, 30 mol %), KTFA (114 mg, 0.75 mmol), **1a** (40.0 mg, 0.25 mmol) and **2a** (118.0 mg, 0.75 mmol) in GVL (1.0 mL) was stirred under N_2 for 16 h at 150 ^{o}C. After cooling to ambient temperature, the mixture was diluted with EtOAc (2.0 mL) and filtered, then NaOH (2M, 20 mL) was added to the filtrate and stirred for 20 min, the crude mixture was extracted with EtOAc (3 × 30 mL), the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The remaining residue was purified by column chromatography (*n*-hexane/EtOAc) to afford the desired product **3aa**.

Representative Procedure B:

A suspension of Pd/C (15.9 mg, 5.0 mol %), $MesCO_2H$ (14.8 mg, 30 mol %), K_2CO_3 (83.0 mg, 0.6 mmol), **1l** (64.5 mg, 0.3 mmol) and **2f** (103 mg, 0.45 mmol) in GVL (2.0 mL) was stirred under N_2 for 24 h at 120 ^{o}C. After cooling to ambient temperature, the mixture was filtered, NaOH (2M, 25 mL) was added to the filtrate and stirred for 20 min, the crude mixture was extracted with EtOAc (3 × 30 mL), the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The remaining residue was purified by column chromatography (*n*-hexane/EtOAc) to afford the desired

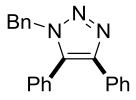
product **3lf**. Procedure for recovery of Pd/C: To the remaining material (Pd/C and inorganic salts) H_2O (1.0 mL) and EtOH (0.5 mL) were added and the mixture was stirred for 10 min. After centrifugation, the solvents were removed. To the remaining residue (Pd/C), EtOH (1.0 mL) was added, the vial containing the mixture was treated with ultrasound in a sonication bath for 3 h. The solvent was removed after centrifugation and the residual Pd/C was dried in vacuum at 60 °C overnight. The recovered material was used for the subsequent run.



3aa

1-Benzyl-5-phenyl-1*H*-1,2,3-triazole (3aa)

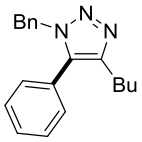
The general procedure A was followed using 1-benzyl-1*H*-1,2,3-triazole (**1a**) (40 mg, 0.25 mmol) and bromobenzene (**2a**) (118 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 5/1) yielded **3aa** (36 mg, 63%) as a colourless solid and **4aa** (6 mg, 8%) as a colourless solid. M.p. = 70–72 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.71 (s, 1H), 7.43–7.34 (m, 3H), 7.28–7.20 (m, 5H), 7.09–7.02 (m, 2H), 5.52 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 138.2 (C_q), 135.6 (C_q), 133.3 (CH), 129.6 (CH), 129.0 (CH), 129.0 (CH), 128.9 (CH), 128.2 (CH), 127.2 (CH), 126.9 (C_q), 51.9 (CH_2). IR (ATR): 2960, 1484, 1210, 835, 730, 694, 528, 462 cm^{-1}. MS (EI) *m/z* (relative intensity) 235 (20) [M^+], 206 (40), 116 (20), 104 (25), 91 (100), 89 (15), 65 (20). HR-MS (ESI) *m/z* calcd for $C_{15}H_{14}N_3$ [M+H$^+$] 236.1182, found: 236.1180. The analytical data are in accordance with those reported in the literature.[5]



4aa

1-Benzyl-4,5-diphenyl-1*H*-1,2,3-triazole (4aa)

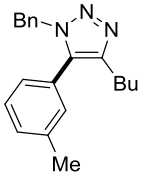
M.p. = 108–110 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.59–7.49 (m, 2H), 7.49–7.33 (m, 3H), 7.30–7.17 (m, 6H), 7.16–7.09 (m, 2H), 7.06–6.96 (m, 2H), 5.39 (s, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 144.6 (C_q), 135.4 (C_q), 133.9 (C_q), 131.0 (C_q), 130.2 (CH), 129.7 (CH), 129.2 (CH), 128.7 (CH), 128.5 (CH), 128.2 (CH), 127.9 (C_q), 127.7 (CH), 127.6 (CH), 126.8 (CH), 52.2 (CH_2). IR (ATR): 3060, 1602, 1498, 1246, 983, 730, 691, 558, 457 cm^{-1}. MS (EI) *m/z* (relative intensity) 311 (20) [M^+], 282 (5), 192 (95), 165 (30), 91 (100), 65 (20). HR-MS (ESI) *m/z* calcd for $C_{21}H_{18}N_3$ [M+H$^+$]: 312.1495, found: 312.1496. The analytical data are in accordance with those reported in the literature.[5]



3ba

1-Benzyl-4-*n*-butyl-5-phenyl-1*H*-1,2,3-triazole (3ba)

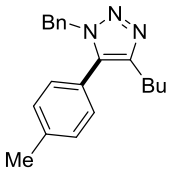
The general procedure A was followed using 1-benzyl-4-*n*-butyl-1*H*-1,2,3-triazole (**1b**) (54 mg, 0.25 mmol) and bromobenzene (**2a**) (118 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 12/1) yielded **3ba** (57 mg, 80%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.46–7.30 (m, 3H), 7.29–7.18 (m, 3H), 7.13–7.04 (m, 2H), 7.02–6.94 (m, 2H), 5.37 (s, 2H), 2.70–2.51 (t, J = 7.3 Hz, 2H), 1.73–1.49 (m, 2H), 1.33–1.20 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.2 (C_q), 135.8 (C_q), 134.5 (C_q), 129.8 (CH), 129.3 (CH), 128.9 (CH), 128.8 (CH), 128.1 (CH), 127.8 (C_q), 127.5 (CH), 52.1 (CH_2), 31.8 (CH_2), 24.9 (CH_2), 22.5 (CH_2), 13.9 (CH_3). IR (ATR): 2955, 2930, 1494, 1455, 1217, 1013, 762, 698, 547 cm^{-1}. MS (EI) *m/z* (relative intensity) 291 (5) [M^+], 249 (35), 172 (10), 91 (100). HR-MS (EI) *m/z* calcd for $C_{19}H_{22}N_3$, [M^+] 291.1735, found: 291.1734. The analytical data are in accordance with those reported in the literature.[5]



3bb

1-Benzyl-4-*n*-butyl-5-(*m*-tolyl)-1*H*-1,2,3-triazole (3bb)

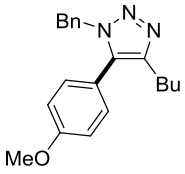
The general procedure A was followed using 1-benzyl-4-*n*-butyl-1*H*-1,2,3-triazole (**1b**) (54 mg, 0.25 mmol) and 1-bromo-3-methylbenzene (**2b**) (128 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 12/1) yielded **3bb** (47 mg, 62%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.31–7.18 (m, 5H), 7.03–6.97 (m, 2H), 6.89 (d, J = 7.3 Hz, 1H), 6.84 (s, 1H), 5.36 (s, 2H), 2.59 (t, J = 7.3 Hz, 2H), 2.30 (s, 3H), 1.68–1.52 (m, 2H), 1.33–1.20 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 146.0 (C_q), 138.6 (C_q), 135.9 (C_q), 134.6 (C_q), 130.5 (CH), 130.0 (CH), 128.8 (CH), 128.7 (CH), 128.1 (CH), 127.6 (C_q), 127.5 (CH), 126.9 (CH), 52.1 (CH_2), 31.8 (CH_2), 24.9 (CH_2), 22.5 (CH_2), 21.4 (CH_3), 13.9 (CH_3). IR (ATR): 2954, 2929, 1455, 1218, 786, 732, 702, 456 cm^{-1}. MS (EI) *m/z* (relative intensity) 305 (5) [M^+], 263 (20), 186 (10), 130 (15), 91 (100), 65 (15). HR-MS (ESI) *m/z* calcd for $C_{20}H_{24}N_3$ [M+H^+]: 306.1965, found: 306.1964.



3bc

1-Benzyl-4-*n*-butyl-5-(*p*-tolyl)-1*H*-1,2,3-triazole (3bc)

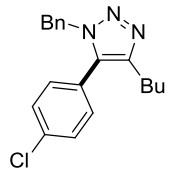
The general procedure A was followed using 1-benzyl-4-*n*-butyl-1*H*-1,2,3-triazole (**1b**) (54 mg, 0.25 mmol) and 1-bromo-4-methylbenzene (**2c**) (128 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 12/1) yielded **3bc** (56 mg, 74%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.30–7.12 (m, 5H), 7.11–6.87 (m, 4H), 5.36 (s, 2H), 2.67–2.44 (t, J = 7.3 Hz, 2H). 2.38 (s, 3H), 1.72–1.46 (m, 2H), 1.33–1.20 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 146.1 (C_q), 139.3 (C_q), 136.0 (C_q), 134.5 (C_q), 129.7 (CH), 129.65 (CH), 128.8 (CH), 128.0 (CH), 127.4 (CH), 124.7 (C_q), 51.9 (CH_2), 31.9 (CH_2), 25.0 (CH_2), 22.5 (CH_2), 21.5 (CH_3), 13.9 (CH_3). IR (ATR): 2954, 2929, 1497, 1454, 1217, 1012, 831, 715, 547 cm^{-1}. MS (EI) *m/z* (relative intensity) 305 (5) [M^+], 263 (30), 186 (25), 130 (40), 91 (100). HR-MS (EI) *m/z* calcd for $C_{20}H_{23}N_3$, [M^+] 305.1892, found 305.1885.



3bd

1-Benzyl-4-*n*-butyl-5-(4-methoxyphenyl)-1*H*-1,2,3-triazole (3bd)

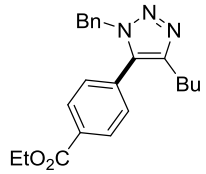
The general procedure A was followed using 1-benzyl-4-*n*-butyl-1*H*-1,2,3-triazole (**1b**) (54 mg, 0.25 mmol) and 1-bromo-4-methoxybenzene (**2d**) (140 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 11/1) yielded **3bd** (44 mg, 55%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.25–7.20 (m, 3H), 7.02–6.97 (m, 4H), 6.94–6.86 (m, 2H), 5.35 (s, 2H), 3.82 (s, 3H), 2.57 (t, J = 7.3 Hz, 2H), 1.64–1.54 (m, 2H), 1.37–1.15 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 160.2 (C_q), 146.0 (C_q), 135.9 (C_q), 134.2 (C_q), 131.1 (CH), 128.7 (CH), 128.0 (CH), 127.4 (CH), 119.6 (C_q), 114.4 (CH), 55.5 (CH_3), 52.0 (CH_2), 31.9 (CH_2), 25.0 (CH_2), 22.6 (CH_2), 14.0 (CH_3). IR (ATR): 2954, 2931, 1505, 1248, 1020, 838, 721, 607, 553 cm^{-1}. MS (EI) *m/z* (relative intensity) 321 (25) [M^+], 279 (65), 202 (80), 146 (100), 133 (30), 91 (85). HR-MS (ESI) *m/z* calcd for $C_{20}H_{24}N_3O$ [$M+H^+$]: 322.1914, found: 322.1919.



3be

1-Benzyl-4-*n*-butyl-5-(4-chlorophenyl)-1*H*-1,2,3-triazole (3be)

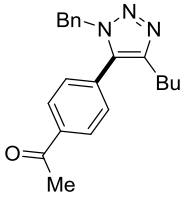
The general procedure A was followed using 1-benzyl-4-*n*-butyl-1*H*-1,2,3-triazole (**1b**) (54 mg, 0.25 mmol) and 1-bromo-4-chlorobenzene (**2e**) (142 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 15/1) yielded **3be** (54 mg, 67%) as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, J = 8.0 Hz, 2H), 7.29–7.16 (m, 3H), 7.0 (d, J = 8.0 Hz, 2H), 6.98–6.95 (m, 2H), 5.36 (s, 2H), 2.56 (t, J = 7.3 Hz, 2H), 1.68–1.47 (m, 2H), 1.30–1.21 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 146.4 (C_q), 135.6 (C_q), 135.6 (C_q), 133.3 (C_q), 131.1 (CH), 129.3 (CH), 128.9 (CH), 128.2 (CH), 127.4 (CH), 126.2 (C_q), 52.2 (CH_2), 31.8 (CH_2), 24.9 (CH_2), 22.5 (CH_2), 13.9 (CH_3). IR (ATR): 2955, 2930, 1488, 1091, 1009, 838, 733, 712, 508 cm^{-1}. MS (EI) *m/z* (relative intensity) 325 (5) [M^+], 285 (5), 283 (20), 206 (10), 91 (100), 65 (15). HR-MS (ESI) *m/z* calcd for $C_{19}H_{21}N_3Cl$ [M+H^+]: 326.1419, found: 326.1421.



3bf

Ethyl 4-(1-benzyl-4-*n*-butyl-1*H*-1,2,3-triazol-5-yl)benzoate (3bf)

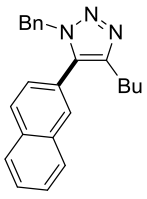
The general procedure A was followed using 1-benzyl-4-*n*-butyl-1*H*-1,2,3-triazole (**1b**) (54 mg, 0.25 mmol) and ethyl 4-bromobenzoate (**2f**) (172 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 12/1) yielded **3bf** (74 mg, 82%) as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, J = 8.6 Hz, 2H), 7.23–7.15 (m, 5H), 6.99–6.92 (m, 2H), 5.39 (s, 2H), 4.38 (q, J = 7.3 Hz, 2H), 2.58 (t, J = 7.3 Hz, 2H), 1.63–1.52 (m, 2H), 1.38 (t, J = 7.3 Hz, 3H), 1.30–1.20 (m, 2H), 0.80 (t, J = 7.3 Hz, 3H).^{13}C-NMR (100 MHz, $CDCl_3$) δ = 166.0 (C_q), 146.6 (C_q), 135.5 (C_q), 133.5 (C_q), 132.3 (C_q), 131.3 (C_q), 130.1 (CH), 129.8 (CH), 128.9 (CH), 128.3 (CH), 127.4 (CH), 61.5 (CH_2), 52.3 (CH_2), 31.8 (CH_2), 24.9 (CH_2), 22.5 (CH_2), 14.4 (CH_3), 13.8 (CH_3). IR (ATR): 2956, 2932, 1715, 1271, 1103, 1011, 772, 704, 456 cm^{-1}. MS (EI) *m/z* (relative intensity) 363 (5) [M^+], 321 (25), 244 (10), 91 (100). HR-MS (ESI) *m/z* calcd for $C_{22}H_{25}N_3O_2$ [M+H^+]: 364.2020, found: 364.2022.



3bg

1-[4-(1-Benzyl-4-*n*-butyl-1*H*-1,2,3-triazol-5-yl)phenyl]ethan-1-one (3bg)

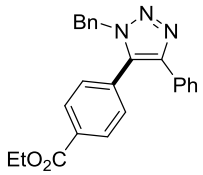
The general procedure A was followed using 1-benzyl-4-*n*-butyl-1*H*-1,2,3-triazole (**1b**) (54 mg, 0.25 mmol) and 1-(4-bromophenyl)ethan-1-one (**2g**) (149 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 8/1) yielded **3bg** (54 mg, 65%) as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, J = 8.6 Hz, 2H), 7.24–7.19 (m, 5H), 6.98–6.95 (m, 2H), 5.39 (s, 2H), 2.61 (s, 3H), 2.59 (d, J = 7.3 Hz, 2H), 1.63–1.55 (m, 2H), 1.30–1.21 (m, 2H), 0.81 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 197.4 (C_q), 146.6 (C_q), 137.5 (C_q), 135.5 (C_q), 133.4 (C_q), 132.6 (C_q), 130.0 (CH), 128.9 (CH), 128.8 (CH), 128.3 (CH), 127.3 (CH), 52.3 (CH_2), 31.8 (CH_2), 26.8 (CH_3), 24.9 (CH_2), 22.5 (CH_2), 13.9 (CH_3). IR (ATR): 2955, 2930, 1683, 1610, 1261, 846, 726, 599 cm^{-1}. MS (EI) *m/z* (relative intensity) 333 (5) [M^+], 291 (25), 214 (10), 91 (100). HR-MS (ESI) *m/z* calcd for $C_{21}H_{24}N_3O$ [$M+H^+$]: 334.1914, found: 334.1914.



3bh

1-Benzyl-4-*n*-butyl-5-(naphthalen-1-yl)-1*H*-1,2,3-triazole (3bh)

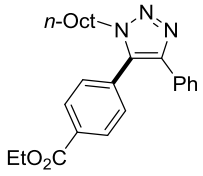
The general procedure A was followed using 1-benzyl-4-*n*-butyl-1*H*-1,2,3-triazole (**1b**) (54 mg, 0.25 mmol) and 2-bromonaphthalene (**2h**) (154 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 12/1) yielded **3bh** (65 mg, 76%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.79 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.53–7.41 (m, 3H), 7.18–7.09 (m, 4H), 6.99–6.90 (m, 2H), 5.35 (s, 2H), 2.58 (t, J = 8.0 Hz, 2H), 1.63–1.51 (m, 2H), 1.32–1.23 (m, 2H), 0.75 (t, J = 7.3 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 146.4 (C_q), 135.9 (C_q), 134.5 (C_q), 133.3 (C_q), 133.1 (C_q), 129.7 (CH), 129.0 (CH), 128.8 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.5 (CH), 127.2 (CH), 127.0 (CH), 126.8 (CH), 125.0 (C_q), 52.2 (CH_2), 31.9 (CH_2), 25.0 (CH_2), 22.5 (CH_2), 13.9 (CH_3). IR (ATR): 2954, 2929, 1455, 1216, 861, 823, 730, 477 cm^{-1}. MS (EI) *m/z* (relative intensity) 341 (15) [M^+], 299 (55), 222 (40), 195 (40), 166 (70), 153 (30), 91 (100). HR-MS (ESI) *m/z* calcd for $C_{23}H_{24}N_3$ [$M+H^+$]: 342.1965, found: 342.1965.



3cf

Ethyl 4-(1-benzyl-4-phenyl-1*H*-1,2,3-triazol-5-yl)benzoate (3cf)

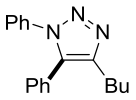
The general procedure A was followed using 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (**1c**) (59 mg, 0.25 mmol) and ethyl 4-bromobenzoate (**2f**) (172 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 12/1) yielded **3cf** (57 mg, 60%) as a colourless solid. M.p. = 114–116 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, J = 8.0 Hz, 2H), 7.54–7.45 (m, 2H), 7.29–7.16 (m, 8H), 7.03–6.95 (m, 2H), 5.41 (s, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 165.9 (C_q), 145.1 (C_q), 135.2 (C_q), 133.0 (C_q), 132.6 (C_q), 131.7 (C_q), 130.6 (C_q), 130.3 (CH), 130.3 (CH), 128.9 (CH), 128.7 (CH), 128.4 (CH), 128.1 (CH), 127.5 (CH), 126.9 (CH), 61.6 (CH_2), 52.4 (CH_2), 14.4 (CH_3). IR (ATR): 2984, 1714, 1275, 1128, 1017, 854, 732, 694, 567 cm^{-1}. MS (EI) *m/z* (relative intensity) 383 (15) [M^+], 264 (85), 236 (25), 190 (15), 165 (15), 91 (100). HR-MS (EI) *m/z* calcd for $C_{24}H_{22}N_3O_2$, [M^+] 383.1634, found 383.1621. The analytical data are in accordance with those reported in the literature.[4]



3df

Ethyl 4-(1-*n*-octanoyl-4-phenyl-1*H*-1,2,3-triazol-5-yl)benzoate (3df)

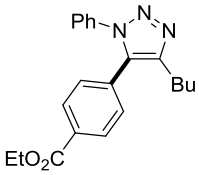
The general procedure A was followed using 1-(4-phenyl-1*H*-1,2,3-triazol-1-yl)octan-1-one (**1d**) (64 mg, 0.25 mmol) and ethyl 4-bromobenzoate (**2f**) (172 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 15/1) yielded **3df** (52 mg, 50%) as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, J = 8.6 Hz, 2H), 7.51–7.45 (m, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.27–7.20 (m, 3H), 4.41 (q, J = 7.1 Hz, 2H), 4.18 (t, J = 7.4 Hz, 2H), 1.82–1.69 (m, 2H), 1.40 (t, J = 7.1 Hz, 3H), 1.27–1.11 (m, 10H), 0.82 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 165.9 (C_q), 144.7 (C_q), 133.0 (C_q), 132.8 (C_q), 131.8 (C_q), 130.8 (C_q), 130.6 (CH), 130.2 (CH), 128.6 (CH), 128.0 (CH), 127.0 (CH), 61.6 (CH_2), 48.6 (CH_2), 31.8 (CH_2), 30.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 26.5 (CH_2), 22.7 (CH_2), 14.4 (CH_3), 14.2 (CH_3). IR (ATR): 2926, 1716, 1269, 1099, 1018, 776, 694 cm^{-1}. MS (EI) *m/z* (relative intensity) 405 (20) [M^+], 377 (10), 265 (100), 237 (20), 165 (25). HR-MS (ESI) *m/z* calcd for $C_{25}H_{32}N_3O_2$ [$M+H^+$]: 406.2489, found: 406.2492. The analytical data are in accordance with those reported in the literature.[4]



3ea

4-*n*-Butyl-1,5-diphenyl-1*H*-1,2,3-triazole (3ea)

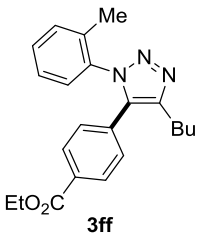
The general procedure A was followed using 4-*n*-butyl-1-phenyl-1*H*-1,2,3-triazole (**1e**) (50 mg, 0.25 mmol) and bromobenzene (**2a**) (118 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 12/1) yielded **3ea** (55 mg, 79%) as a colourless solid. M.p. = 106–108 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.36–7.30 (m, 6H), 7.28–7.24 (m, 2H), 7.15–7.11 (m, 2H), 2.77–2.66 (m, 2H), 1.76–1.61 (m, 2H), 1.41–1.26 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 146.4 (C_q), 137.0 (C_q), 133.9 (C_q), 129.7 (CH), 129.2 (CH), 129.0 (CH), 128.9 (CH), 128.7 (CH), 127.8 (C_q), 124.9 (CH), 31.9 (CH_2), 24.9 (CH_2), 22.6 (CH_2), 13.9 (CH_3). IR (ATR): 2952, 2926, 1502, 1448, 1117, 991, 755, 700, 579 cm^{-1}. MS (EI) *m/z* (relative intensity) 277 (5) [M^+], 249 (25), 207 (20), 206 (100), 104 (35), 77 (40). HR-MS (ESI) *m/z* calcd for $C_{18}H_{20}N_3$ [$M+H^+$]: 278.1652, found: 278.1654. The analytical data are in accordance with those reported in the literature.[6]



3ef

Ethyl 4-(4-*n*-butyl-1-phenyl-1*H*-1,2,3-triazol-5-yl)benzoate (3ef)

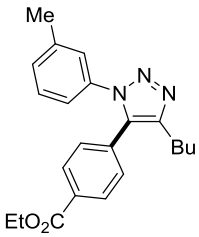
The general procedure A was followed using 4-*n*-butyl-1-phenyl-1*H*-1,2,3-triazole (**1e**) (50 mg, 0.25 mmol) and ethyl 4-bromobenzoate (**2f**) (172 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 15/1) yielded **3ef** (68 mg, 79%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.97 (d, J = 8.4 Hz, 2H), 7.38–7.32 (m, 3H), 7.25–7.11 (m, 4H), 4.32 (q, J = 7.1 Hz, 2H), 2.68 (t, J = 8.0 Hz, 2H), 1.70–1.60 (m, 2H), 1.35–1.25 (m, 5H), 0.82 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 166.0 (C_q), 146.8 (C_q), 136.7 (C_q), 133.0 (C_q), 132.3 (C_q), 130.9 (C_q), 130.0 (CH), 129.6 (CH), 129.4 (CH), 129.1 (CH), 125.0 (CH), 61.4 (CH_2), 31.8 (CH_2), 25.0 (CH_2), 22.6 (CH_2), 14.4 (CH_3), 13.9 (CH_3). IR (ATR): 2957, 2932, 1713, 1498, 1269, 1097, 994, 760, 694 cm^{-1}. MS (EI) *m/z* (relative intensity) 321 (30) [M-Et^+], 279 (20), 278 (100), 175, (35), 147 (15), 77 (20) HR-MS (ESI) *m/z* calcd for $C_{21}H_{24}N_3O_2$ [$M+H^+$]: 350.1863, found: 350.1863. The analytical data are in accordance with those reported in the literature.[4]



3ff

Ethyl 4-[4-*n*-butyl-1-(*o*-tolyl)-1*H*-1,2,3-triazol-5-yl]benzoate (3ff)

The general procedure A was followed using 4-*n*-butyl-1-(*o*-tolyl)-1*H*-1,2,3-triazole (**1f**) (54 mg, 0.25 mmol) and ethyl 4-bromobenzoate (**2f**) (172 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 15/1) yielded **3ff** (73 mg, 81%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.95 (d, J = 8.6 Hz, 2H), 7.36–7.28 (m, 1H), 7.26–7.12 (m, 5H), 4.33 (q, J = 7.1 Hz, 2H), 2.78 (t, J = 7.3 Hz, 2H), 1.92 (s, 3H), 1.81–1.65 (m, 2H), 1.30–1.20 (m, 5H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.0 (C_q), 145.8 (C_q), 135.9 (C_q), 135.1 (C_q), 134.2 (C_q), 132.0 (C_q), 131.3 (CH), 130.7 (C_q), 130.1 (CH), 129.9 (CH), 129.0 (CH), 127.8 (CH), 126.9 (CH), 61.4 (CH_2), 31.8 (CH_2), 25.2 (CH_2), 22.6 (CH_2), 17.7 (CH_3), 14.4 (CH_3), 13.9 (CH_3). IR (ATR): 2957, 2930, 1714, 1270, 1105, 994, 762, 454 cm^{-1}. MS (EI) *m/z* (relative intensity) 335 (30) [M-Et$^+$], 292 (100), 175 (25). HR-MS (ESI) *m/z* calcd for $C_{22}H_{26}N_3O_2$ [M+H$^+$]: 364.2020, found: 364.2020. The analytical data are in accordance with those reported in the literature.[4]

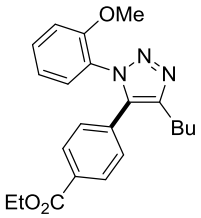


3gf

Ethyl 4-[4-*n*-butyl-1-(*m*-tolyl)-1*H*-1,2,3-triazol-5-yl]benzoate (3gf)

The general procedure A was followed using 4-*n*-butyl-1-(*m*-tolyl)-1*H*-1,2,3-triazole (**1g**) (54 mg, 0.25 mmol) and ethyl 4-bromobenzoate (**2f**) (172 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 15/1) yielded **3gf** (73 mg, 88%) as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.01 (d, J = 8.1 Hz, 2H), 7.27–7.14 (m, 5H), 6.91 (d, J = 7.5 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.72 (t, J = 7,6 Hz, 2H), 2.30 (s, 3H), 1.75–1.62 (m, 2H), 1.35–1.23 (m, 5H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 166.0 (C_q), 146.7 (C_q), 139.7 (C_q), 136.6 (C_q), 133.0 (C_q), 132.4 (C_q), 130.8 (C_q), 130.0 (CH), 129.8 (CH), 129.6 (CH), 129.0 (CH), 125.7 (CH), 122.0 (CH), 61.4 (CH_2), 31.8 (CH_2), 25.0 (CH_2), 22.6 (CH_2), 21.4 (CH_3), 14.4 (CH_3), 13.9 (CH_3). IR (ATR): 2956, 2930, 1714, 1270, 1099, 865, 775, 693 cm^{-1}. MS (EI) *m/z* (relative intensity) 335 (30) [M-Et$^+$], 293 (25), 292 (100), 175 (25). HR-MS (ESI) *m/z*

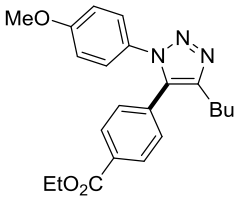
calcd for $C_{22}H_{26}N_3O_2$ [M+H$^+$]: 364.2020, found: 364.2021. The analytical data are in accordance with those reported in the literature.[4]



3hf

Ethyl 4-[4-*n*-butyl-1-(2-methoxyphenyl)-1*H*-1,2,3-triazol-5-yl]benzoate (3hf)

The general procedure A was followed using 4-*n*-butyl-1-(2-methoxyphenyl)-1*H*-1,2,3-triazole (**1h**) (58 mg, 0.25 mmol) and ethyl 4-bromobenzoate (**2f**) (172 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 12/1) yielded **3hf** (46 mg, 50%) as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.7 Hz, 2H), 7.43 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.36 (ddd, *J* = 8.3, 7.6, 1.7 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.02 (td, *J* = 7.7, 1.2 Hz, 1H), 6.82 (dd, *J* = 8.4, 1.2 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.40 (s, 3H), 2.75 (t, *J* = 7.3 Hz, 2H), 1.77–1.64 (m, 2H), 1.36–1.23 (m, 5H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 166.1 (C_q), 153.4 (C_q), 145.5 (C_q), 134.7 (C_q), 133.0 (C_q), 131.3 (CH), 130.4 (C_q), 129.6 (CH), 128.6 (CH), 128.5 (CH), 125.8 (C_q), 121.1 (CH), 112.3 (CH), 61.3 (CH_2), 55.4 (CH_3), 31.8 (CH_2), 25.1 (CH_2), 22.6 (CH_2), 14.4 (CH_3), 13.9 (CH_3). IR (ATR): 2956, 2931, 1712, 1505, 1270, 1104, 1015, 861, 753, 699 cm^{-1}. MS (EI) *m/z* (relative intensity) 351 (30) [M-Et$^+$], 308 (100), 280 (10), 175 (20), 134 (15), 77 (10). HR-MS (ESI) *m/z* calcd for $C_{22}H_{26}N_3O_3$ [M+H$^+$]: 380.1969, found: 380.1969. The analytical data are in accordance with those reported in the literature.[4]

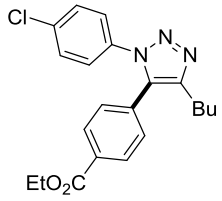


3if

Ethyl 4-[4-*n*-butyl-1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-5-yl]benzoate (3if)

The general procedure A was followed using 4-*n*-butyl-1-(2-methoxyphenyl)-1*H*-1,2,3-triazole (**1i**) (58 mg, 0.25 mmol) and ethyl 4-bromobenzoate (**2f**) (172 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1) yielded **3if** (75 mg, 79%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 2.72 (t, *J* = 8.0 Hz, 2H), 1.77–1.59 (m, 2H), 1.36–1.27 (m, 5H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 165.9 (C_q), 159.9 (C_q), 146.4 (C_q),

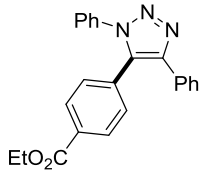
133.0 (C_q), 132.4 (C_q), 130.8 (C_q), 129.9 (CH), 129.7 (C_q), 129.6 (CH), 126.3 (CH), 114.5 (CH), 61.4 (CH_2), 55.7 (CH_3), 31.9 (CH_2), 25.1 (CH_2), 22.7 (CH_2), 14.5 (CH_3), 14.0 (CH_3). IR (ATR): 2956, 2932, 1714, 1514, 1270, 1249, 1097, 832, 775 cm^{-1}. MS (EI) *m/z* (relative intensity) 379 (5) [M+], 351.2 (45), 309 (30), 308 (100), 235 (10), 175 (25), 134 (25), 77 (10). HR-MS (ESI) *m/z* calcd for $C_{22}H_{26}N_3O_3$ [$M+H^+$]: 380.1969, found: 380.1972.



3jf

Ethyl 4-[4-*n*-butyl-1-(4-chlorophenyl)-1*H*-1,2,3-triazol-5-yl]benzoate (3jf)

The general procedure A was followed using 4-*n*-butyl-1-(4-chlorophenyl)-1*H*-1,2,3-triazole (**1j**) (58 mg, 0.25 mmol) and ethyl 4-bromobenzoate (**2f**) (172 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 13/1) yielded **3jf** (60 mg, 63%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.26–7.14 (m, 4H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.75–1.59 (m, 2H), 1.39–1.26 (m, 5H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 165.9 (C_q), 147.0 (C_q), 135.2 (C_q), 135.0 (C_q), 133.0 (C_q), 132.0 (C_q), 131.2 (C_q), 130.2 (CH), 129.64 (CH), 129.61 (CH), 126.0 (CH), 61.5 (CH_2), 31.8 (CH_2), 24.9 (CH_2), 22.5 (CH_2), 14.4 (CH_3), 13.9 (CH_3). IR (ATR): 2957, 2931, 1714, 1469, 1270, 1090, 992, 831, 705 cm^{-1}. MS (EI) *m/z* (relative intensity) 384 (5) [$M+H^+$], 355 (40), 314 (35), 312 (100), 175 (60), 147 (30), 75 (15). HR-MS (ESI) *m/z* calcd for $C_{21}H_{23}N_3O_2Cl$ [$M+H^+$]: 384.1473, found: 384.1476.

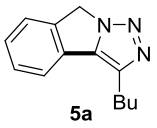


3kf

Ethyl 4-(1,4-diphenyl-1*H*-1,2,3-triazol-5-yl)benzoate (3kf)

The general procedure A was followed using 1,4-diphenyl-1*H*-1,2,3-triazole (**1k**) (55 mg, 0.25 mmol) and ethyl 4-bromobenzoate (**2f**) (172 mg, 0.75 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 15/1) yielded **3kf** (67 mg, 73%) as a colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.6 Hz, 2H), 7.58–7.52 (m, 2H), 7.39–7.35 (m, 3H), 7.31–7.23 (m, 7H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.0 (C_q), 145.3 (C_q), 136.4 (C_q), 132.8 (C_q), 132.3 (C_q), 131.4 (C_q), 130.5 (C_q), 130.3 (CH), 130.2 (CH), 129.4 (CH), 129.4 (CH), 128.7 (CH), 128.3 (CH), 127.6 (CH), 125.3 (CH), 61.5 (CH_2), 14.4 (CH_3). IR (ATR): 2976, 1716, 1497, 1269, 1108, 778,

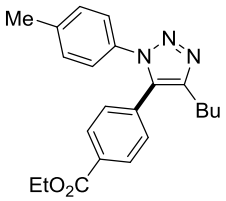
728, 602 cm^{-1}. MS (EI) *m/z* (relative intensity) 369 (5) [M^+], 341 (50), 313 (30), 268 (10), 190 (10), 165 (55). HR-MS (EI) *m/z* calcd for $C_{23}H_{19}N_3O_2$, [M^+] 369.1477, found 369.1479.



5a

3-*n*-Butyl-8*H*-[1,2,3]triazolo[5,1-a]isoindole (5a)

The general procedure A was followed using 1-(2-bromobenzyl)-4-*n*-butyl-1*H*-1,2,3-triazole (**1k**) (73.3 mg, 0.25 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 10/1) yielded **5a** (40 mg, 75%) as a colourless solid. M.p. = 71–72 °C ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 8.3 Hz, 1H), 7.48–7.39 (m, 2H), 7.34 (dd, *J* = 7.5, 1.3 Hz, 1H), 5.25 (s, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 1.85–1.65 (m, 2H), 1.52–1.30 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 140.7 (C_q), 139.4 (C_q), 139.3 (C_q), 128.7 (CH), 128.6 (C_q), 127.7 (CH), 124.2 (CH), 120.9 (CH), 51.1 (CH_2), 31.8 (CH_2), 25.8 (CH_2), 22.5 (CH_2), 14.0 (CH_3). IR (ATR): 2928, 2868, 1475, 1165, 1007, 908, 768, 725, 416 cm^{-1}. MS (EI) *m/z* (relative intensity) 213 (10) [M^+], 184 (25), 170 (55), 156 (40), 115 (35), 89 (25), 58 (25). HR-MS (ESI) *m/z* calcd for $C_{13}H_{16}N_3$ [M+H^+]: 214.1339, found: 214.1340.



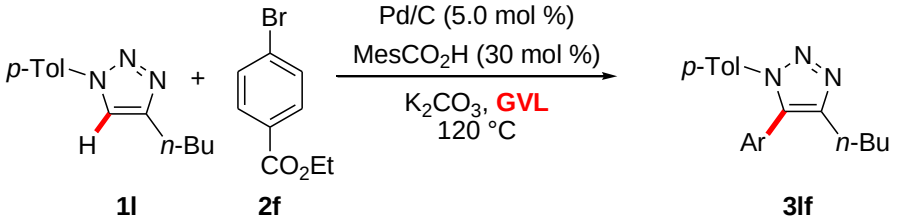
Ethyl 4-[4-*n*-butyl-1-(*p*-tolyl)-1*H*-1,2,3-triazol-5-yl]benzoate (3lf)

The general procedure B was followed using 4-*n*-butyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**1l**) (64.5 mg, 0.3 mmol) and ethyl 4-bromobenzoate (**2f**) (103 mg, 0.45 mmol). Purification by column chromatography (*n*-hexane/EtOAc: 15/1) yielded **3lf** (100 mg, 90%) as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.11 (s, 4H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 1.63–1.71 (m, 2H), 1.41–1.24 (m, 5H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 166.0 (C_q), 146.6 (C_q), 139.1 (C_q), 134.2 (C_q), 132.9 (C_q), 132.4 (C_q), 130.8 (C_q), 130.0 (CH), 129.9 (CH), 129.6 (CH), 124.8 (CH), 61.3 (CH_2), 31.8 (CH_2), 25.0 (CH_2), 22.5 (CH_2), 21.2 (CH_3), 14.4 (CH_3), 13.8 (CH_3). IR (ATR): 2956, 2930, 1714, 1515, 1269, 1098, 818, 708 cm^{-1}. MS (EI) *m/z* (relative intensity) 364 (30) [M+H^+], 335 (45), 293 (25), 292 (100), 175 (25). HR-MS (ESI) *m/z* calcd for $C_{22}H_{26}N_3O_2$ [M+H^+]: 364.2020, found: 364.2018.

Hg-Poisoning Tests

Two representative reactions with **1l** and **2f** as substrates were run in parallel.

Reaction conditions: **1l** (64.5 mg, 0.3 mmol), **2f** (103 mg, 1.5 equiv), Pd/C (16 mg, 5.0 mol %), $MesCO_2H$ (14.8 mg, 30 mol %), K_2CO_3 (83 mg, 2 equiv), GVL (2.0 mL), 120 °C. After 2.5 h at 120 °C, conversion to product **3lf** was measured as being 21% by GC-analysis. Then, to only one of the two reaction mixtures 100 equivalents (relative to the catalyst) of Hg(0) were added. Both mixtures were left to react for overall 20 h at 120 °C, and then conversion to product was measured by GC-analysis.

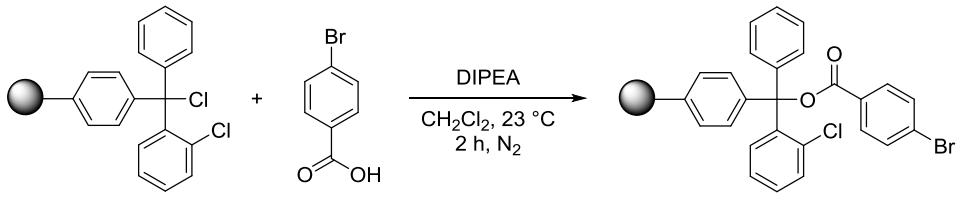


1l **2f** **3lf**

Time		Conversion, %
2.5 h		21
20 h	control	64
	test	21

Three-phase test

Immobilization of 4-bromobenzoic acid onto trityl-resin



I **II**

Commercially available trityl-resin **I** (100-200 mesh, 1.0-1.6 mmol Cl-/g, 1% cross-linked with divinylbenzene) was washed with CH_2Cl_2 prior to use. To Trityl-resin **I** (2.00 g, 3.2 mmol, 1.0 equiv) was added a solution of 4-bromobenzoic acid (1.29 g, 6.4 mmol, 2.0 equiv), DIPEA (2.2 mL, 13 mmol, 4.0 equiv) in CH_2Cl_2 (8 mL). N_2 was bubbled through the reaction mixture for 2 h, then the resin was washed with CH_2Cl_2 (2x5 mL). The loading was repeated with a freshly prepaired solution of 4-bromobenzoic acid (1.29 g, 6.4 mmol, 2.0 equiv) and DIPEA (2.2 mL, 13 mmol, 4.0 equiv) in CH_2Cl_2

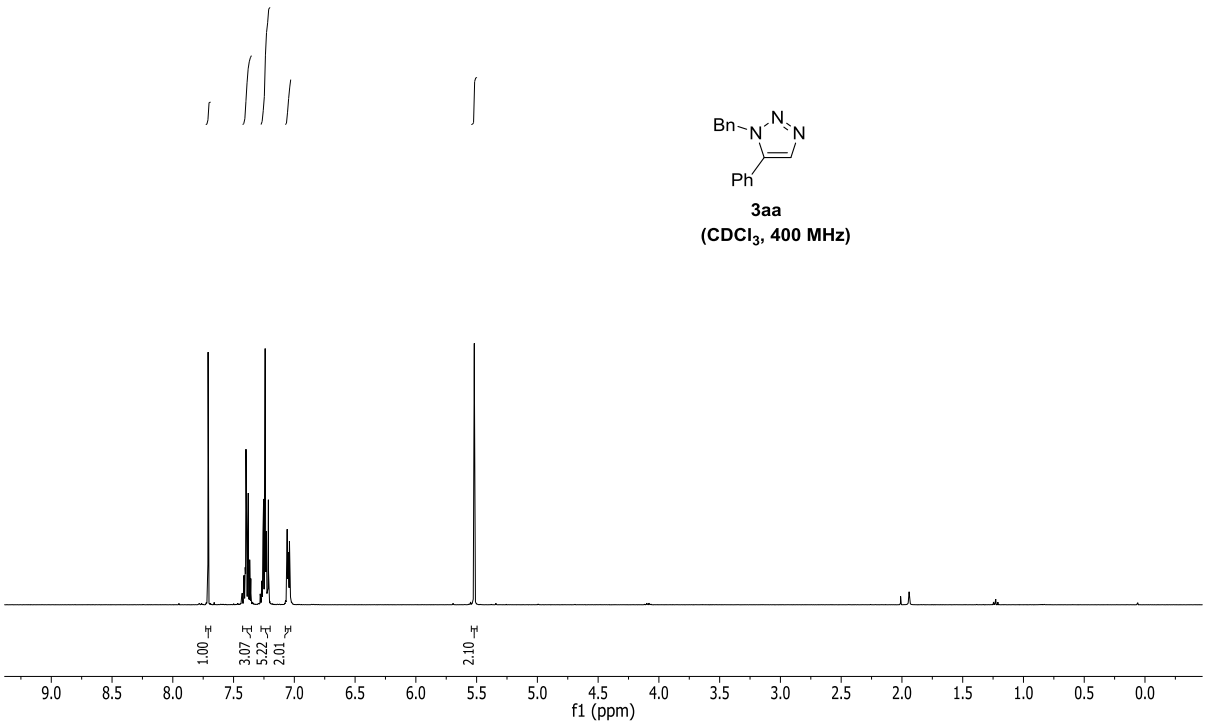
(8 mL). After washing three times with CH_2Cl_2 (5 mL) and DMF (5 mL), the capping solution (CH_2Cl_2:MeOH:DIPEA, 80:15:5, 2x5 mL, 2x30 minutes) was added to the resin. Finally the resin was washed with DMF, MeOH and CH_2Cl_2 three times (5-10 mL each) and dried under high vacuum overnight. To determine the loading, 50 mg of trityl-resin **II** were stirred with a freshly prepared solution of CH_2Cl_2:HFIP (4:1, 5 mL) for 30 minutes at ambient temperature. The reaction mixture was filtered off, the resin washed with CH_2Cl_2:HFIP (4:1, 5 mL) and CH_2Cl_2 (5 mL) and the filtrate evaporated to dryness. The loading was determined to be 0.87 mmol/g.

Reactions were undertaken as per general procedure **A**, substituting **1a** for the immobilized analogue **II**. To cleave the substrate from the support after the reaction, the reaction residue was washed with EtOAc, then treated with CH_2Cl_2:HFIP (4:1, 5 mL) as reported above. Yields were determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard.

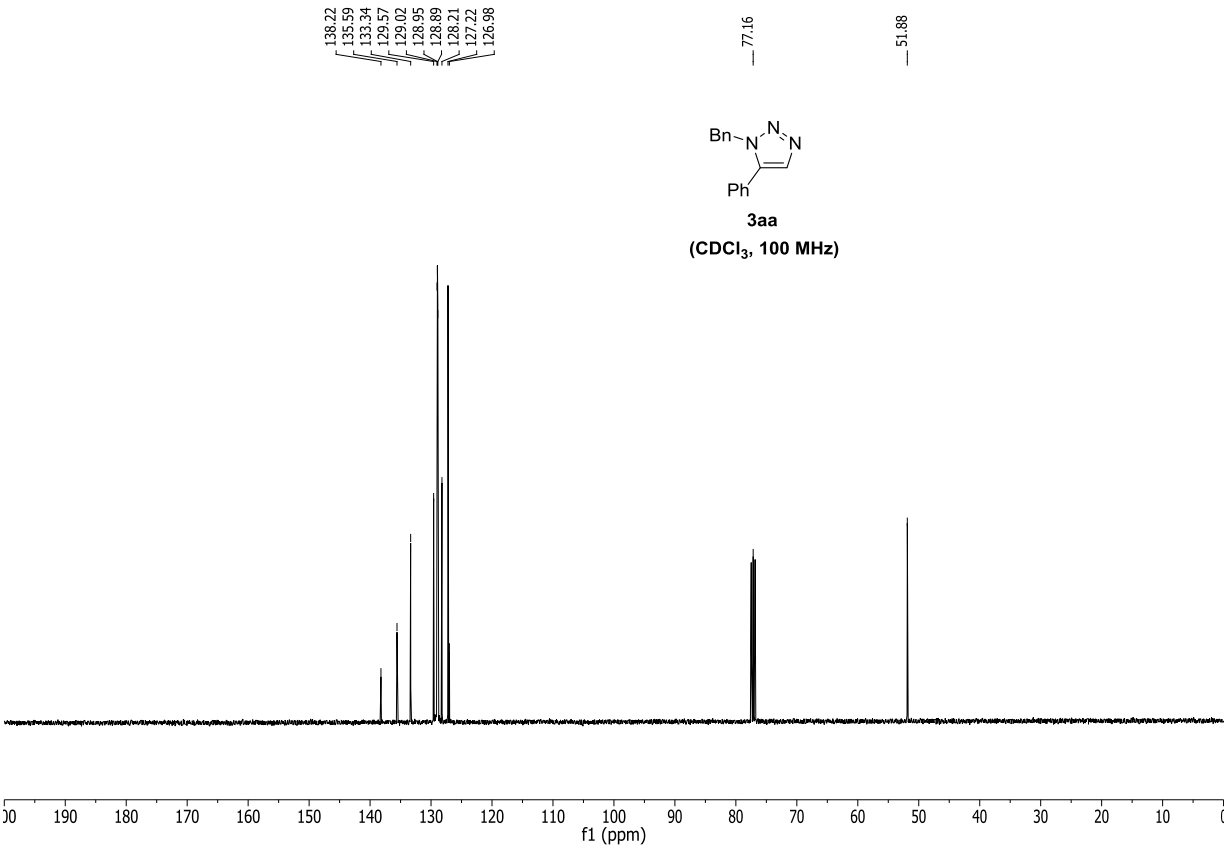
1. The standard reaction of triazole **1b** and bromobenzene **2a** in the presence of 50 mg unmodified trityl-resin **I** resulted in the formation of **3ba** in a slightly lower yield (44%).
2. The reaction of immobilized substrate **II** with triazole **1b** in GVL (1.6 mL) under standard conditions was utilized in place of ethyl 4-bromobenzoate **3f** in the reaction, using. Result: No product was detected in solution or on the support. This experiment suggests that no active homogeneous catalyst species is formed during the reaction and that the immobilized substrate is not cleaved from the trityl-resin under the reaction conditions.
3. The standard reaction with triazol **1b** and ethyl 4-bromobenzoate **2f** in the presence of immobilized substrate **II** yielded **3bf** (50%) in the solution but not on the solid support. The absence of product on the solid support strongly suggests that the active catalyst species is heterogeneous in nature.

Reference:

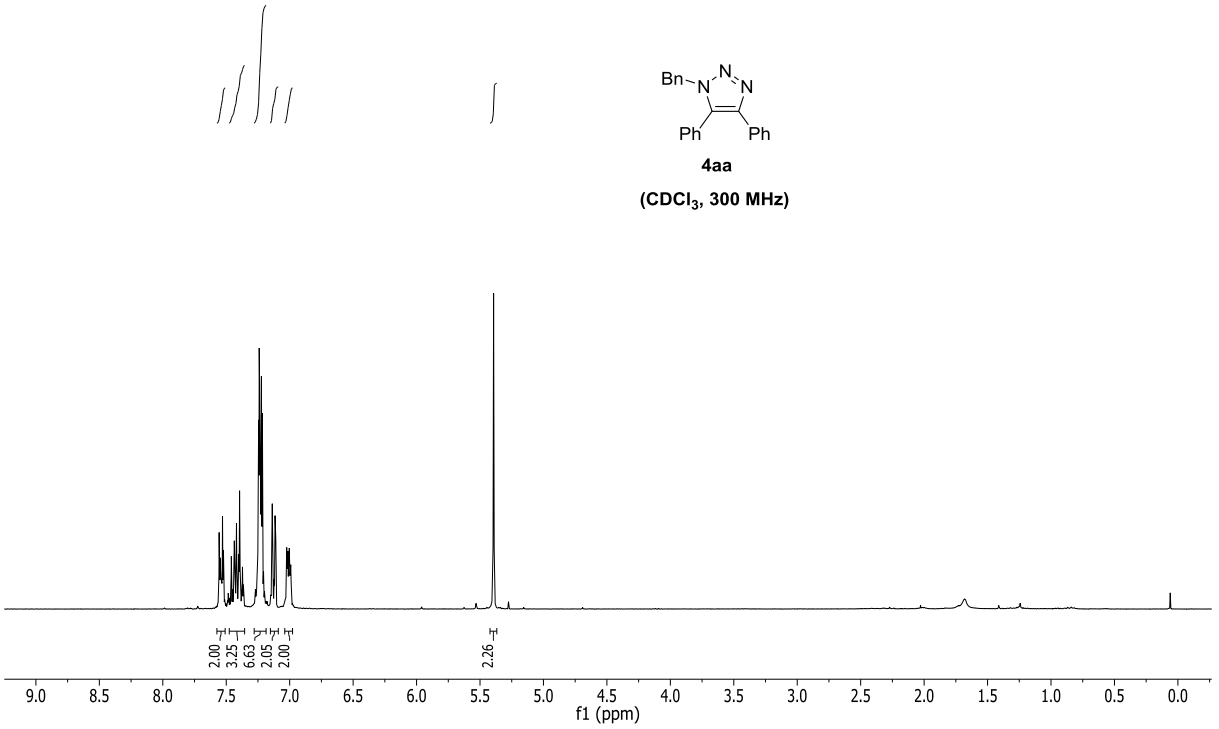
1) J. Andersen, S. Bolving and X. Liang, *Synlett* 2005, 2941-2947.
2) K. Kacprzak, *Synlett* 2005, 943-946.
3) J. T. Fletcher, M. E. Keeney and S. E. Walz, *Synthesis* 2010, 3339-3345.
4) (a) L. Ackermann, R. Vicente and R. Born, *Adv. Synth. Catal.*, 2008, **350**, 741-748 (b) L. Ackermann and R. Vicente, *Org. Lett*., 2009, **11**, 4922-4925.
5) J. Thomas, J. John, N. Parekh and W Dehaen, *Angew. Chem. Int. Ed*. 2014, **53**, 10155-10159.
6) L. Ackermann, A. Althammer and S. Fenner, *Angew. Chem. Int. Ed*. 2009, **48**, 201-204.



3aa
($CDCl_3$, 400 MHz)

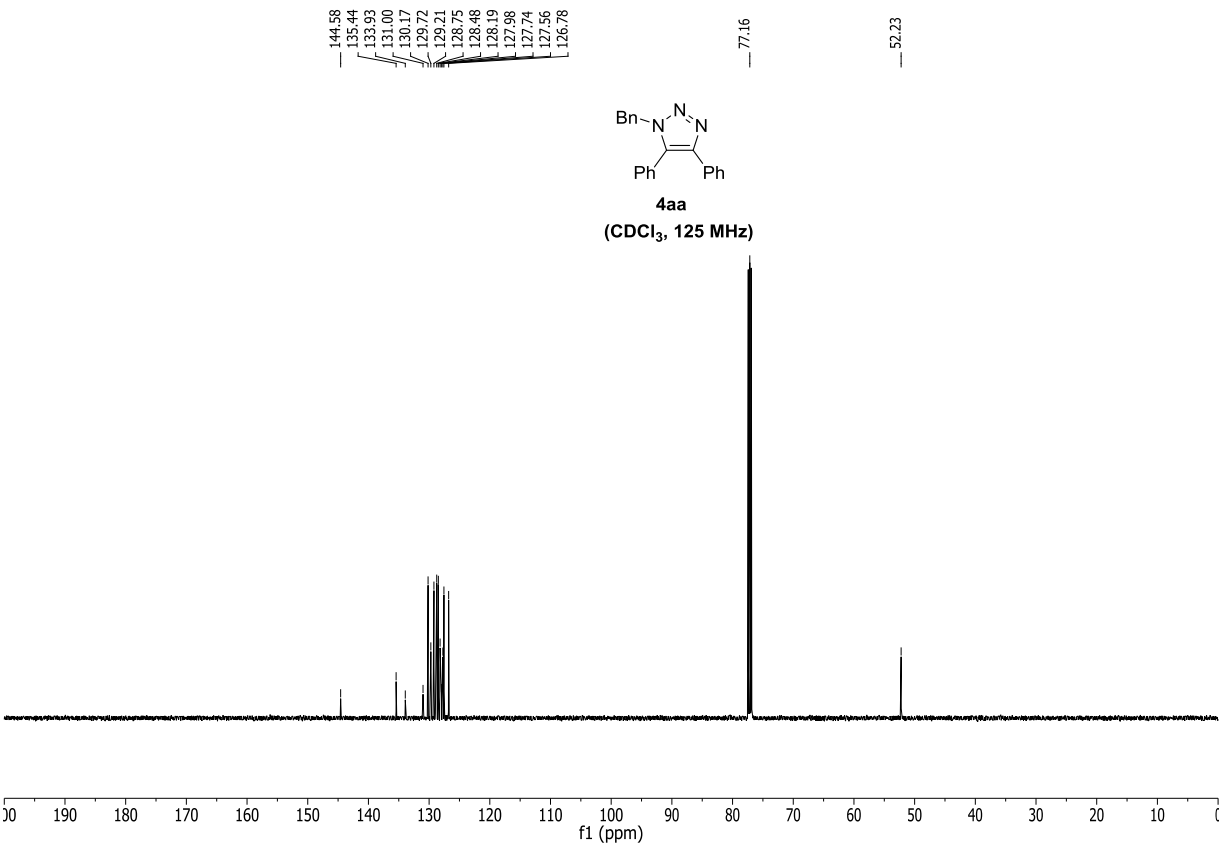


3aa
($CDCl_3$, 100 MHz)



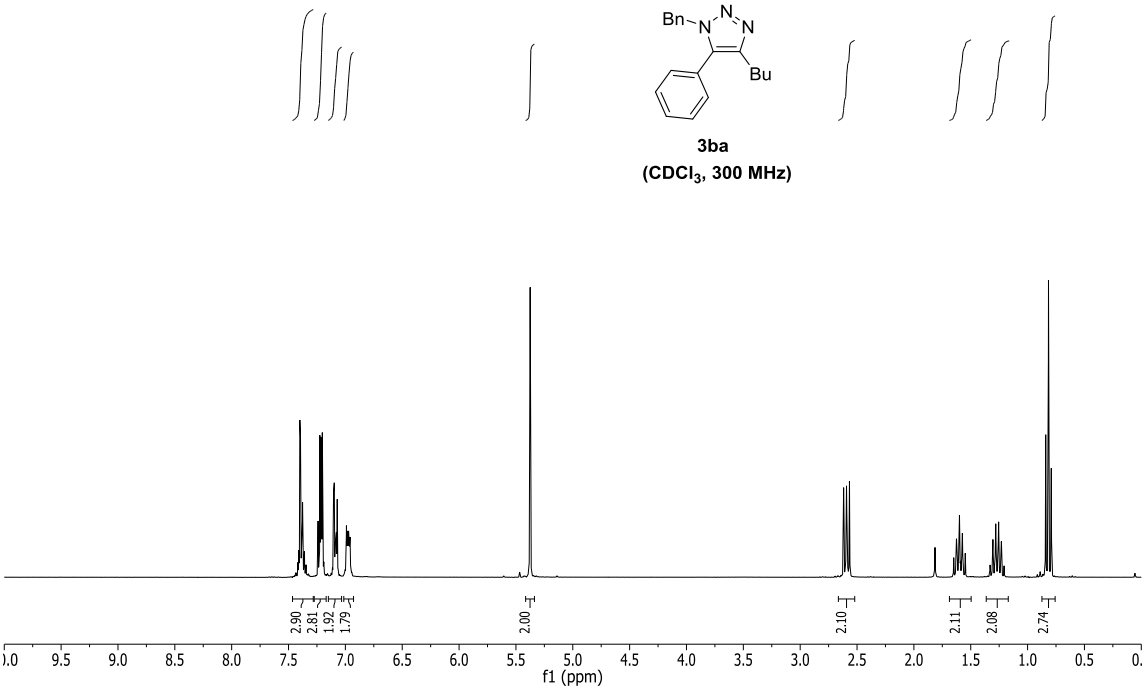
4aa

($CDCl_3$, 300 MHz)

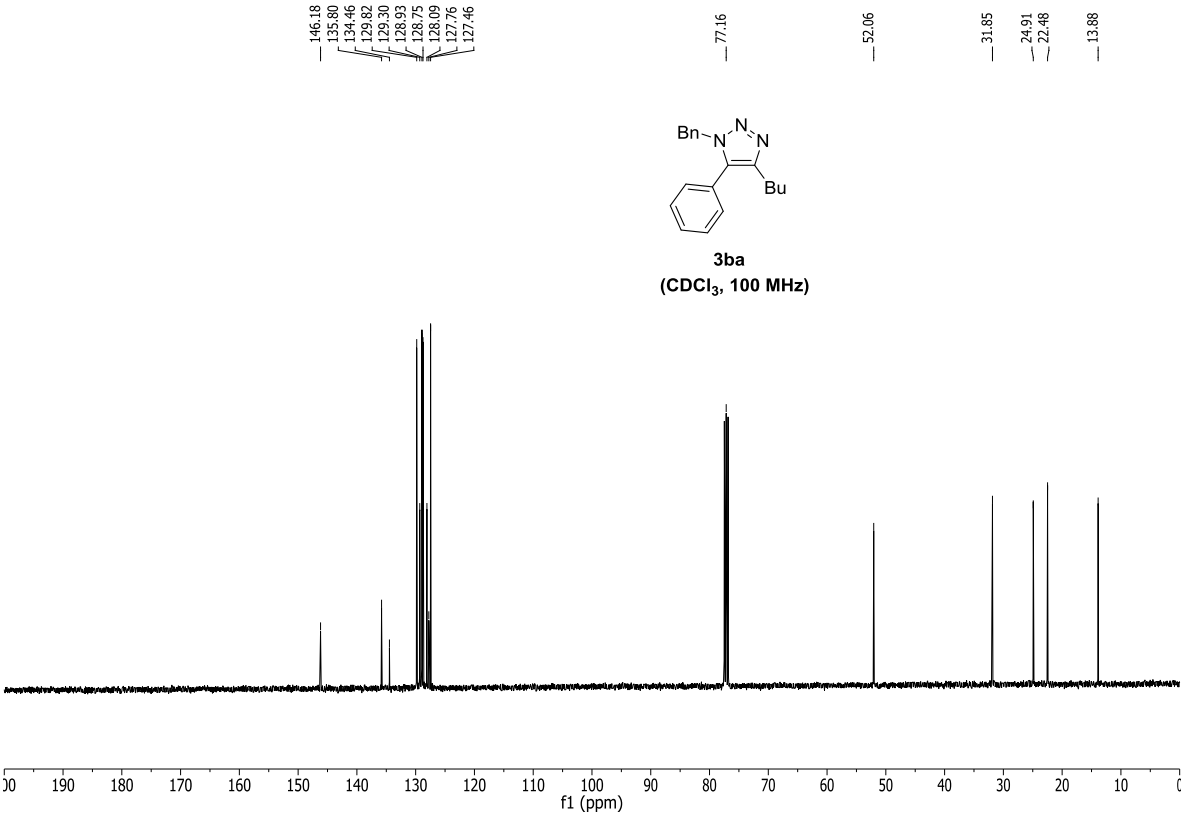


4aa

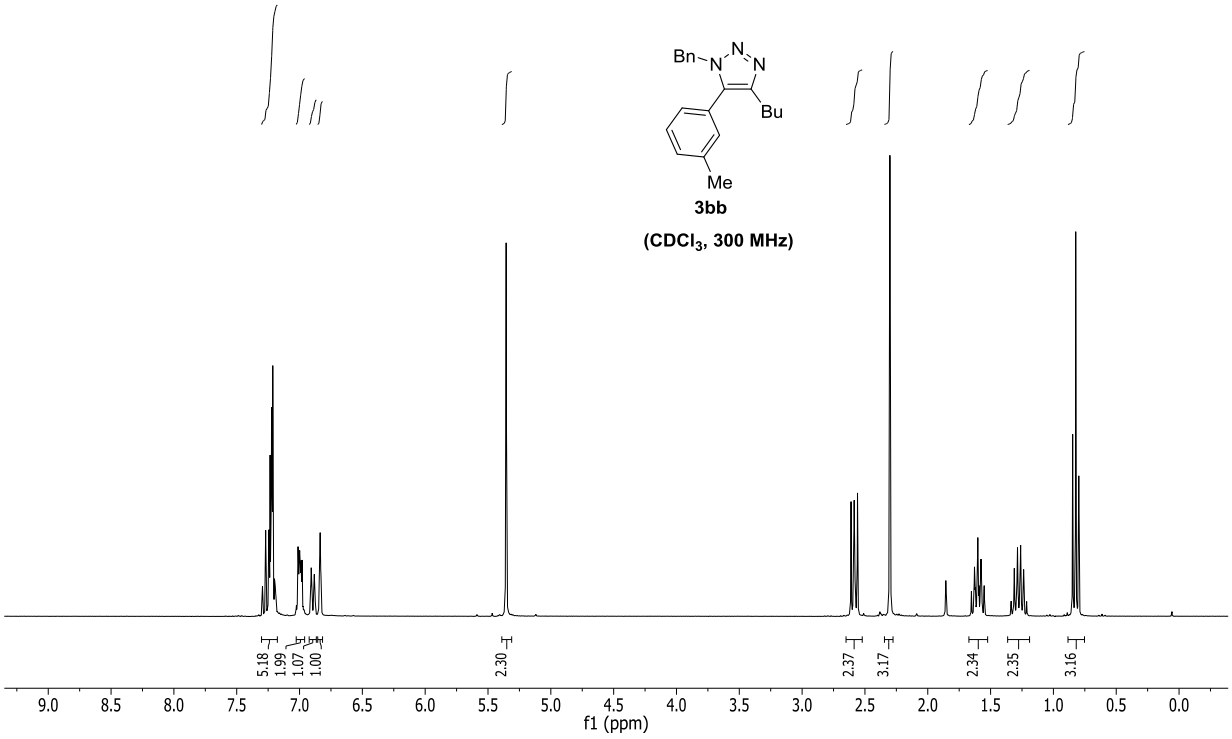
($CDCl_3$, 125 MHz)



3ba
($CDCl_3$, 300 MHz)

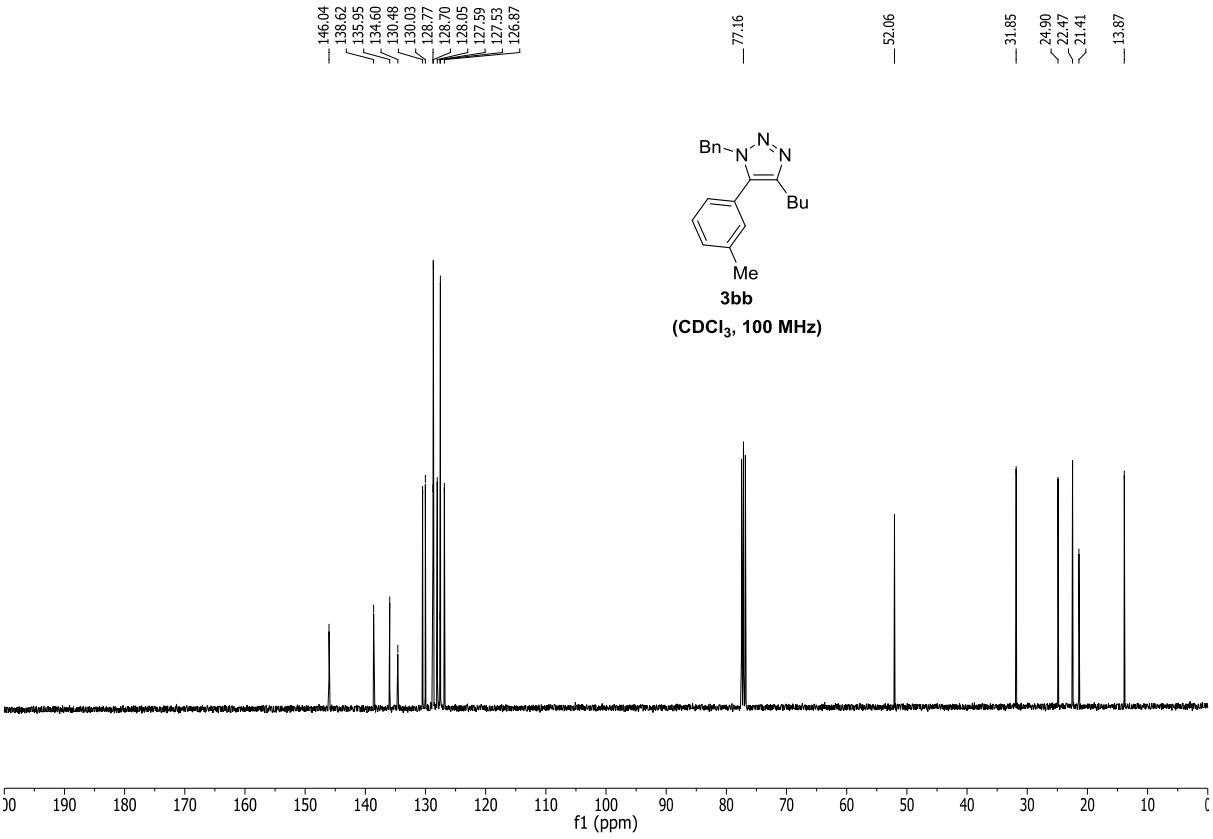


3ba
($CDCl_3$, 100 MHz)



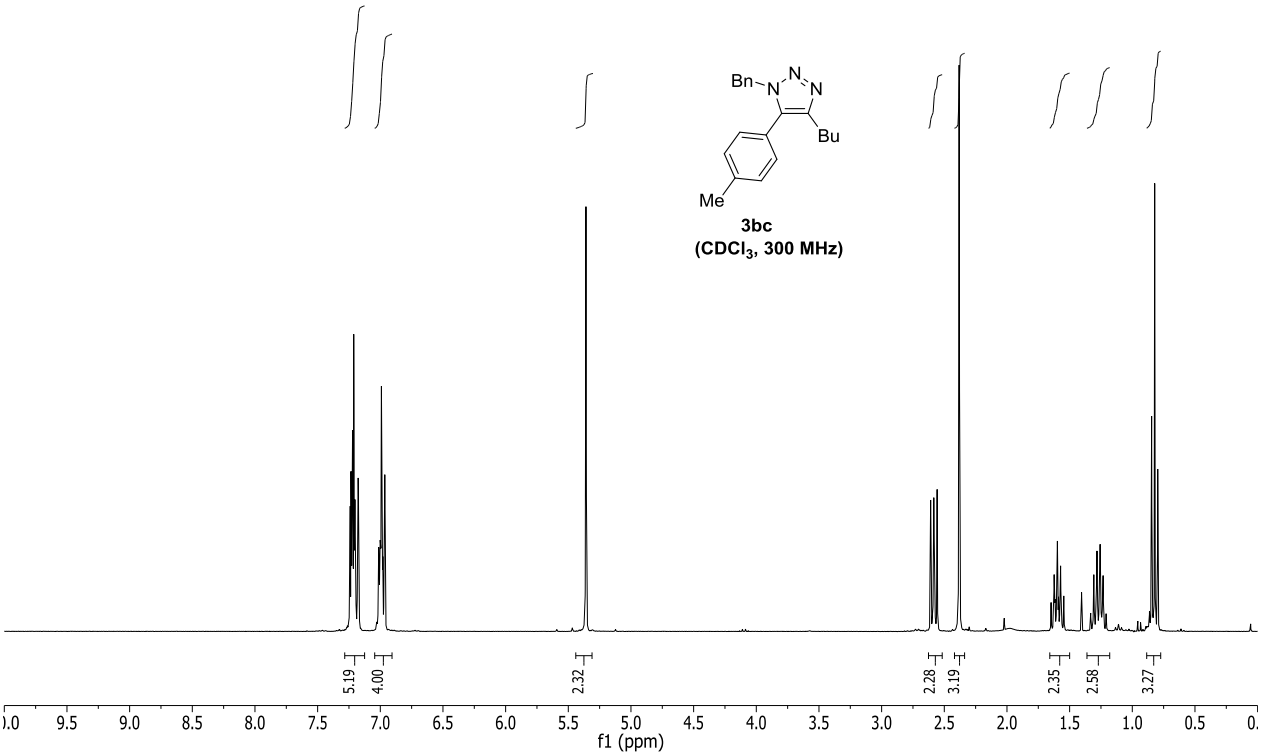
3bb

($CDCl_3$, 300 MHz)

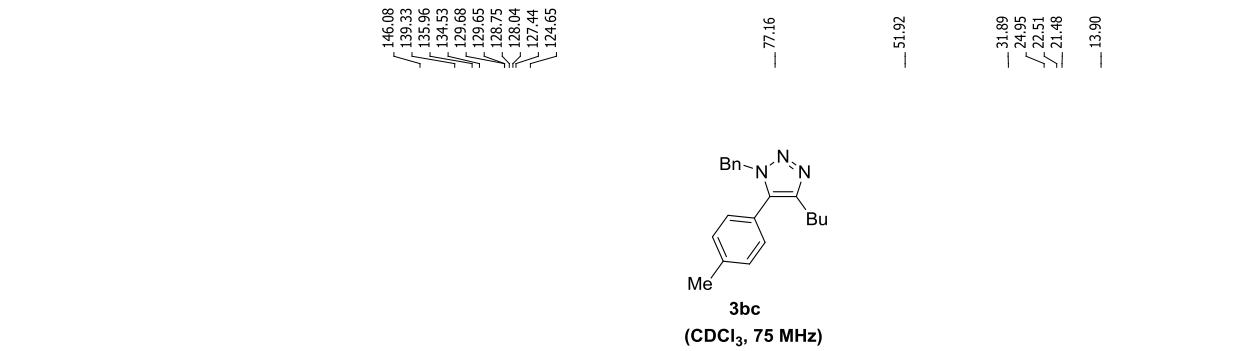


3bb

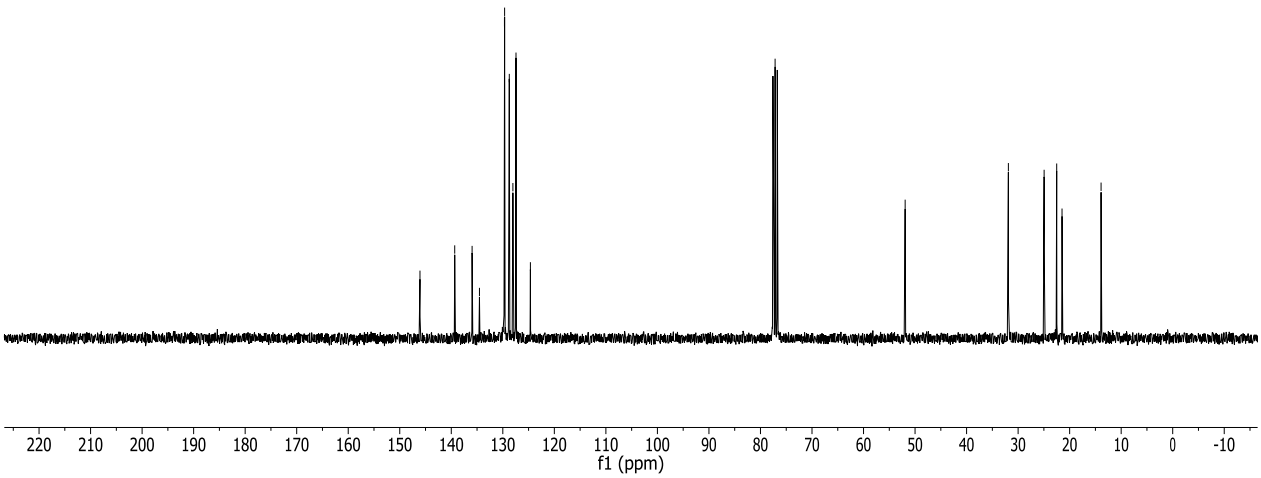
($CDCl_3$, 100 MHz)

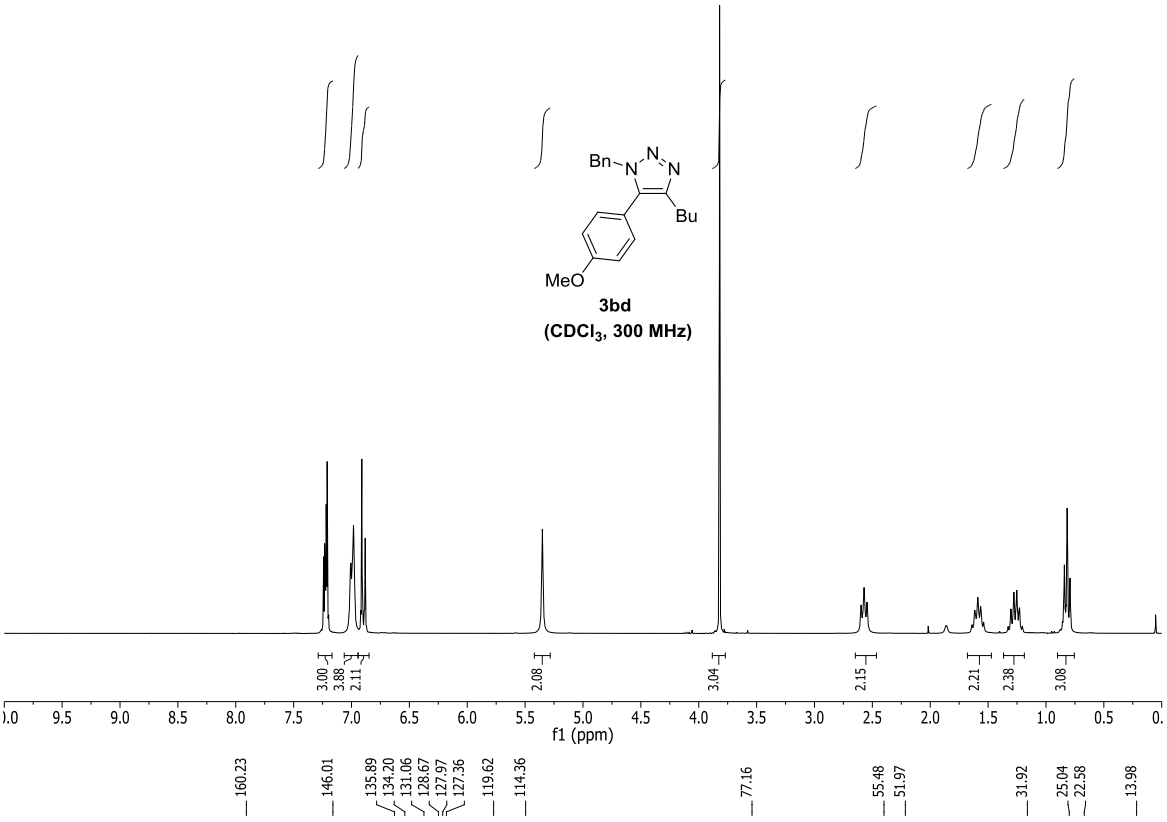


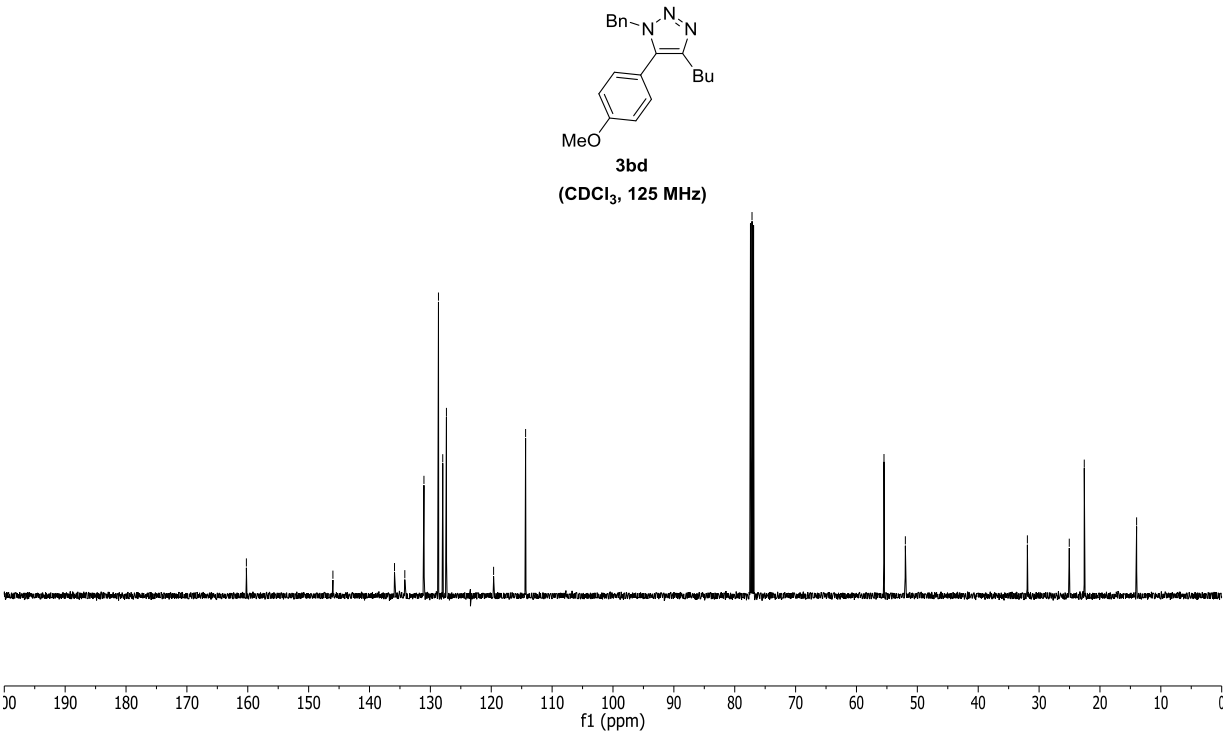
3bc
($CDCl_3$, 300 MHz)

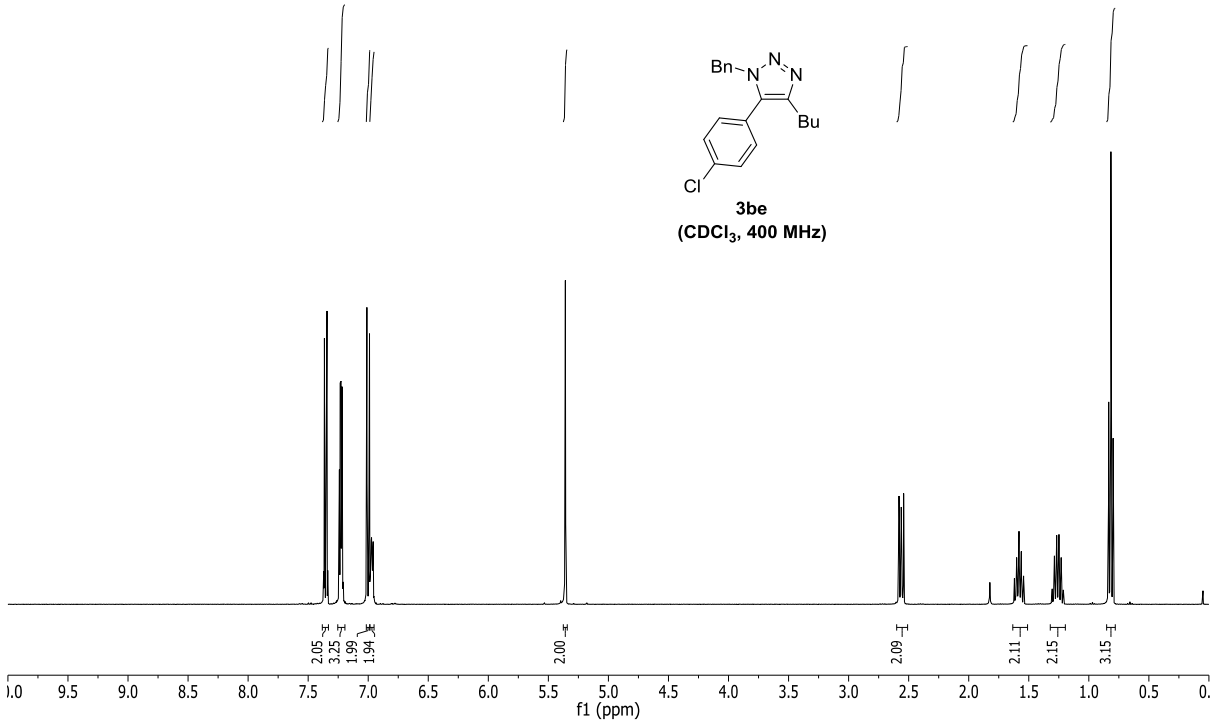


3bc
($CDCl_3$, 75 MHz)



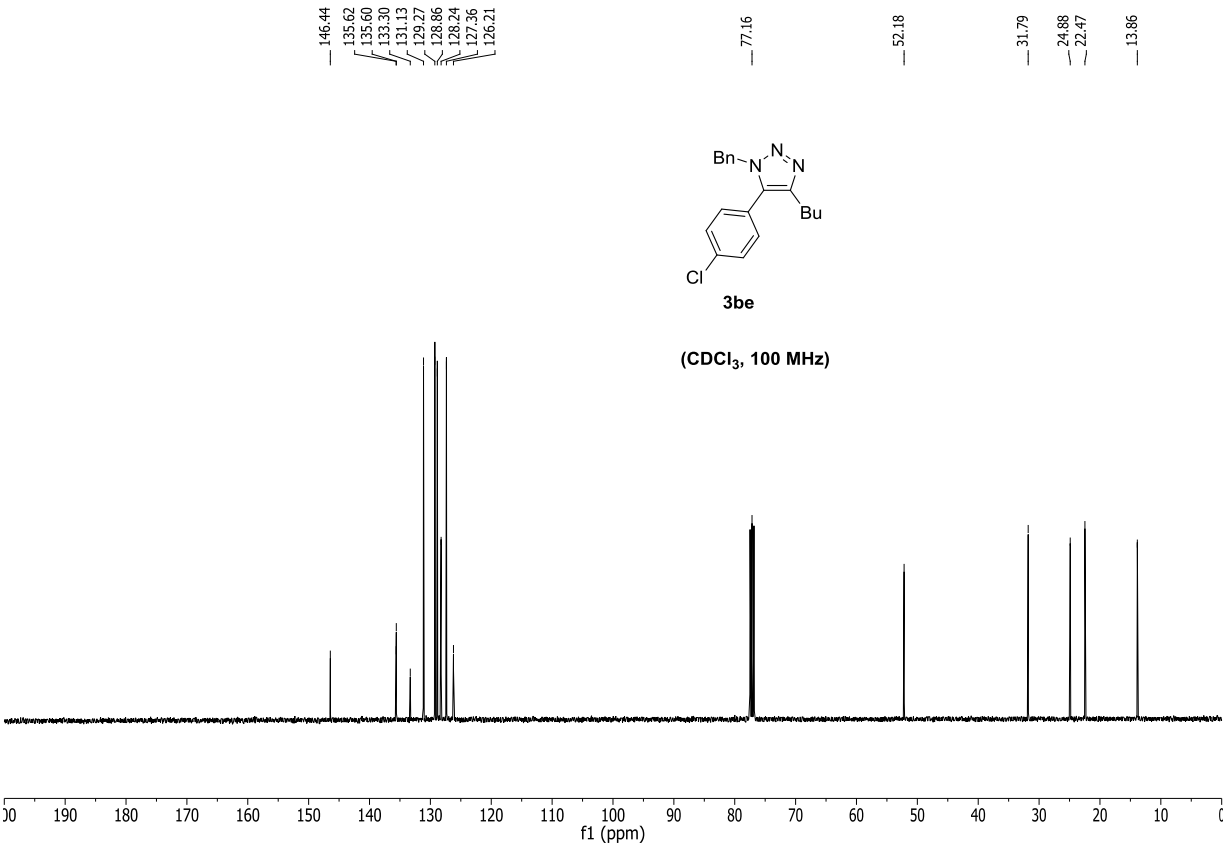

Bn
N
N
N
Bu
MeO
3bd
(CDCl3, 300 MHz)
3.00
3.88
2.11
2.08
3.04
2.15
2.21
2.38
3.08
f1 (ppm)


160.23
146.01
135.89
134.20
131.06
128.67
127.97
127.36
119.62
114.36
77.16
55.48
51.97
31.92
25.04
22.58
13.98
Bn
N
N
N
Bu
MeO
3bd
(CDCl3, 125 MHz)
f1 (ppm)



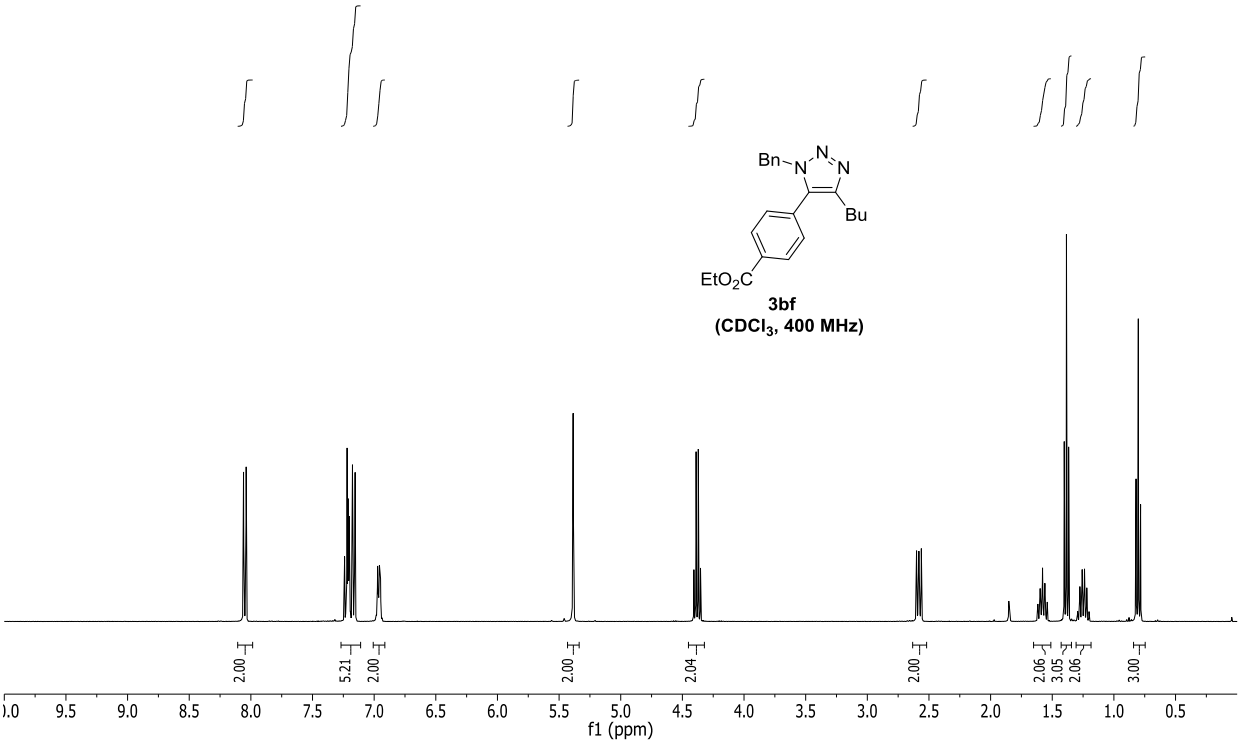
3be

($CDCl_3$, 400 MHz)



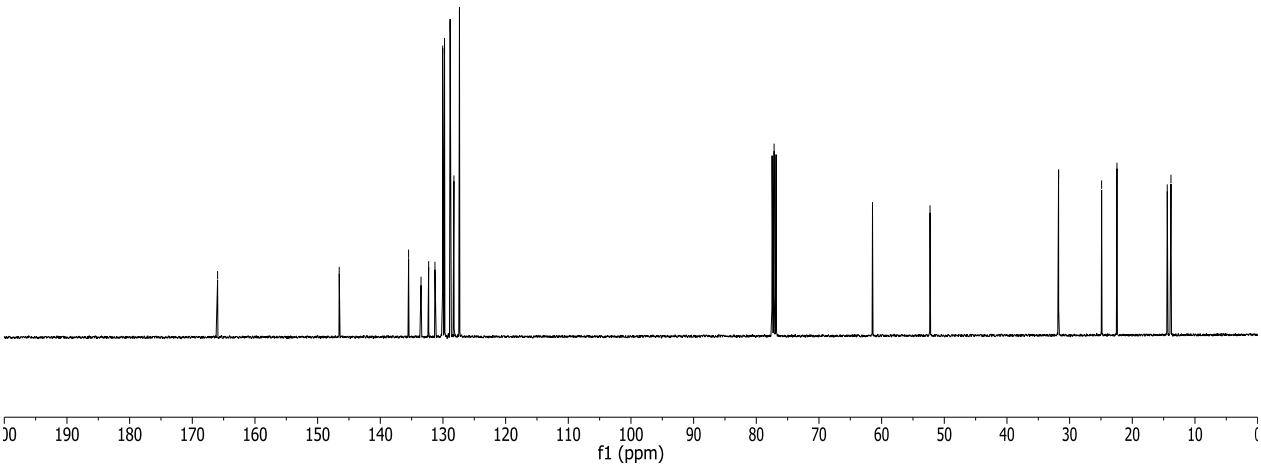
3be

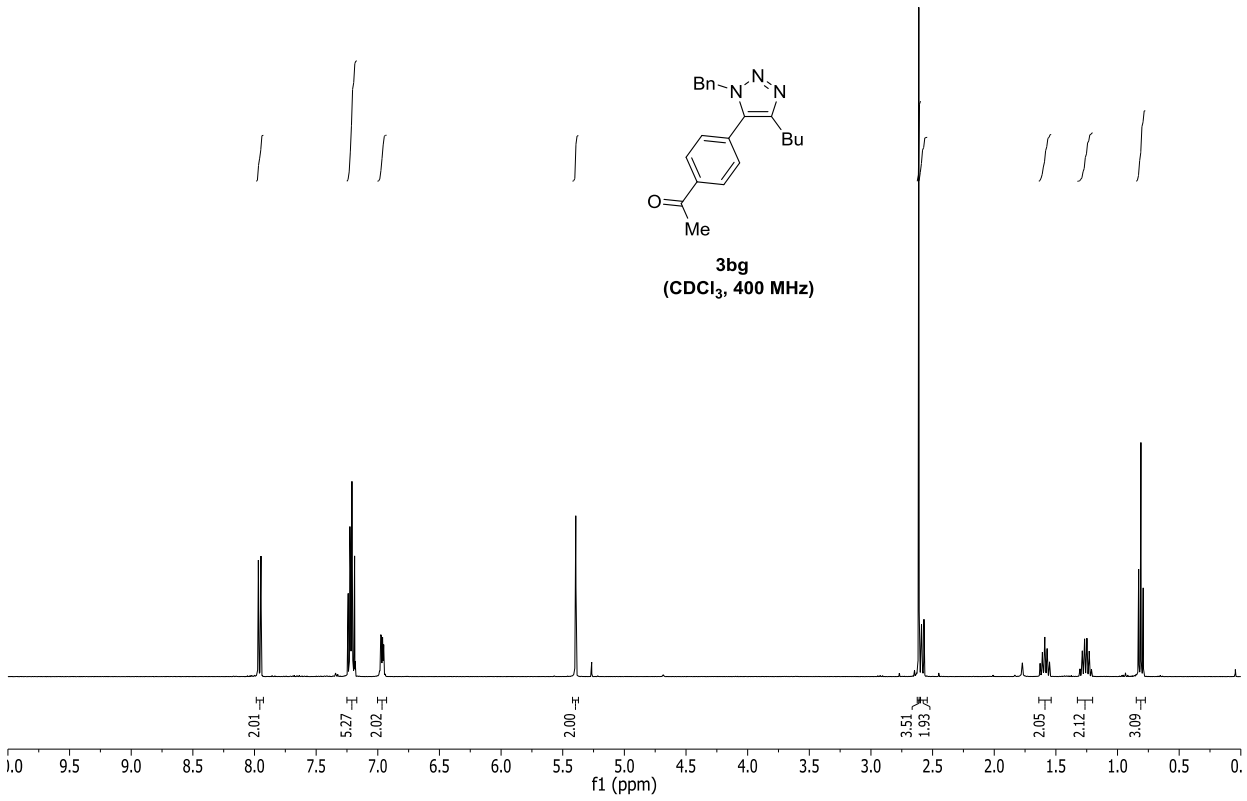
($CDCl_3$, 100 MHz)



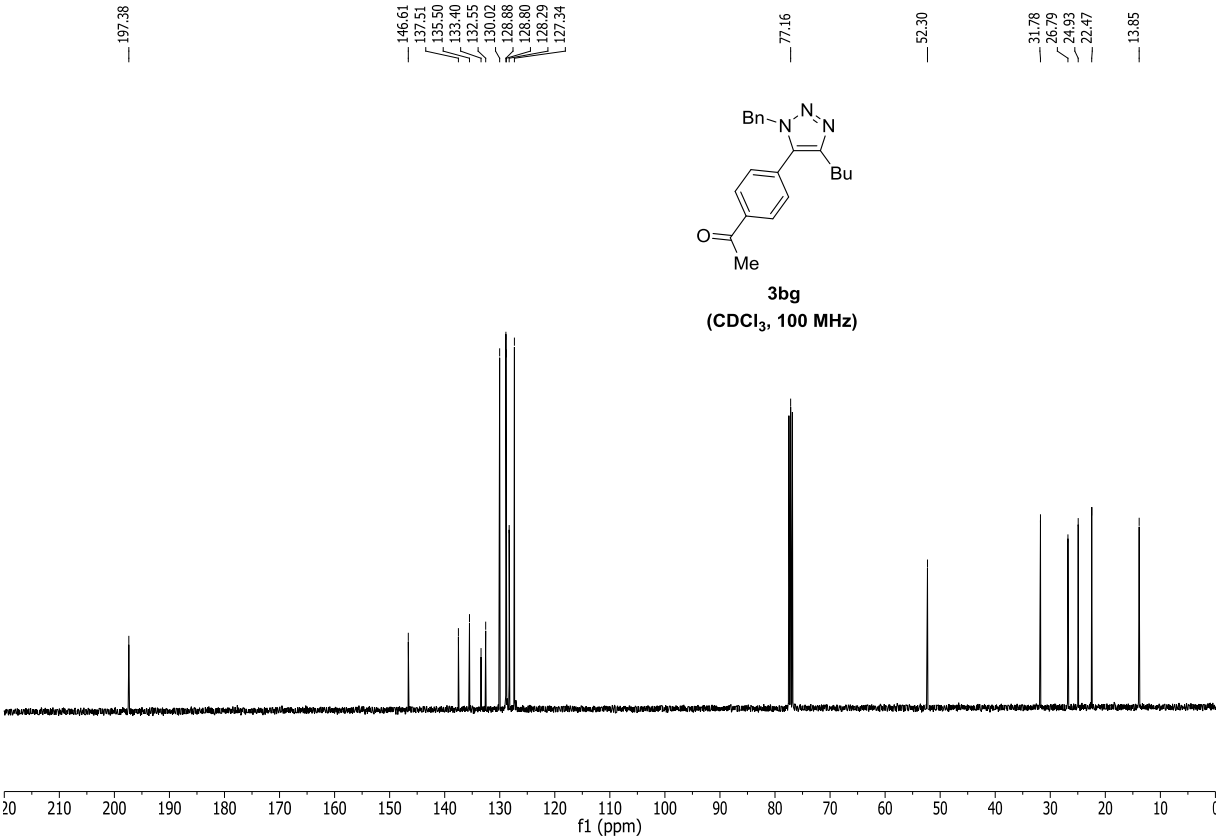
3bf
($CDCl_3$, 400 MHz)

3bf
($CDCl_3$, 100 MHz)

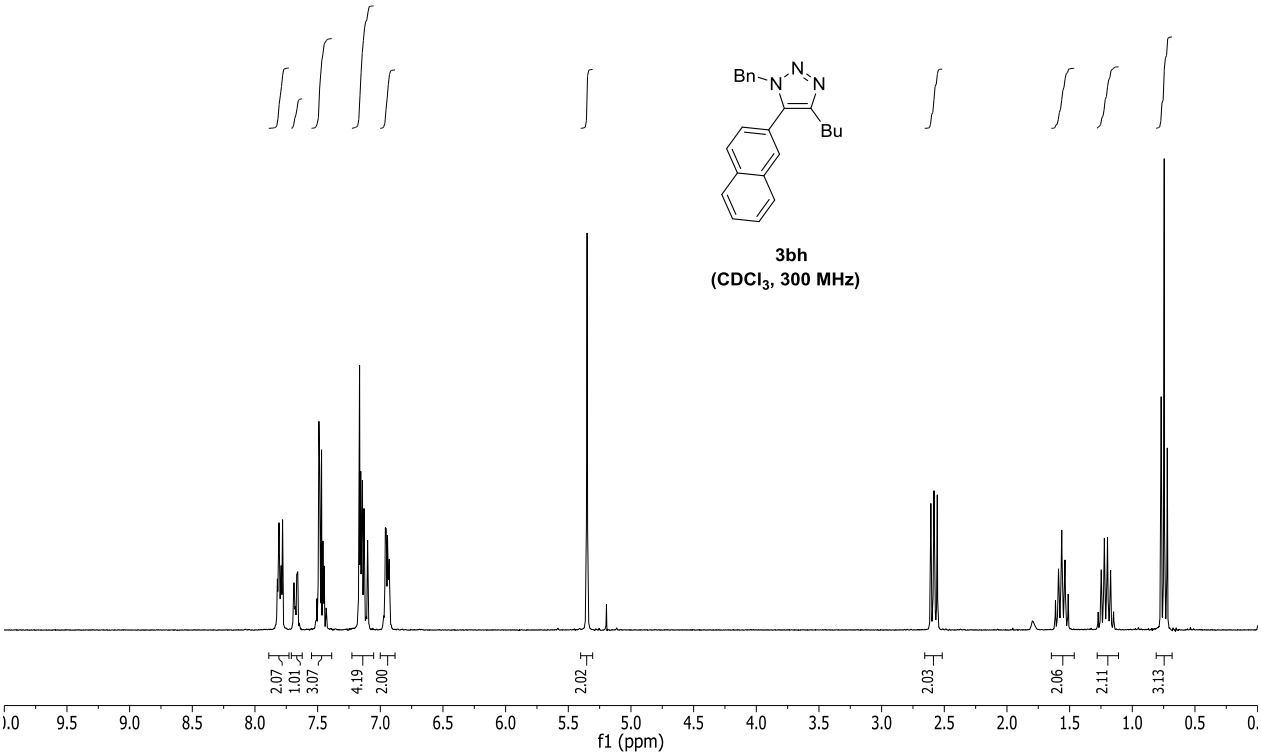




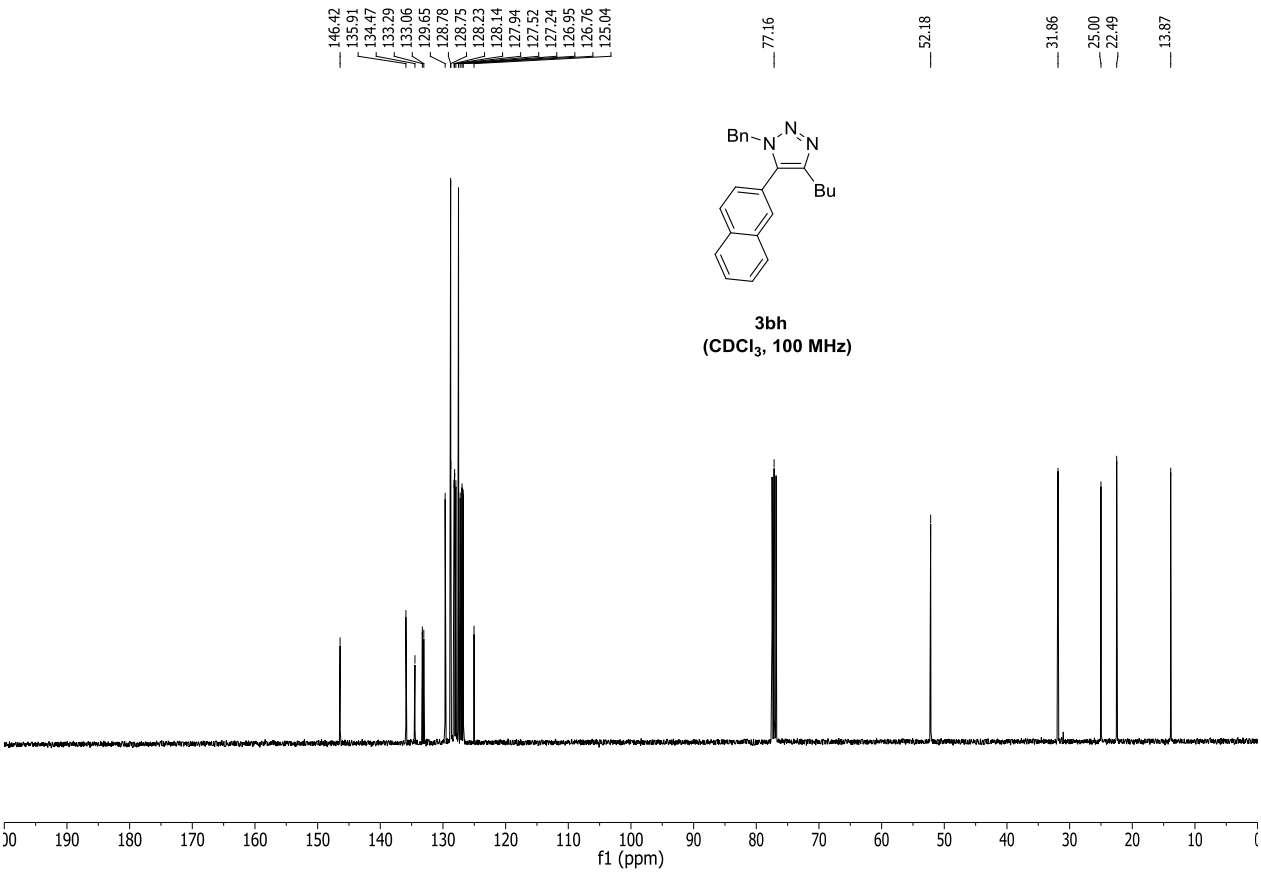
3bg
($CDCl_3$, 400 MHz)



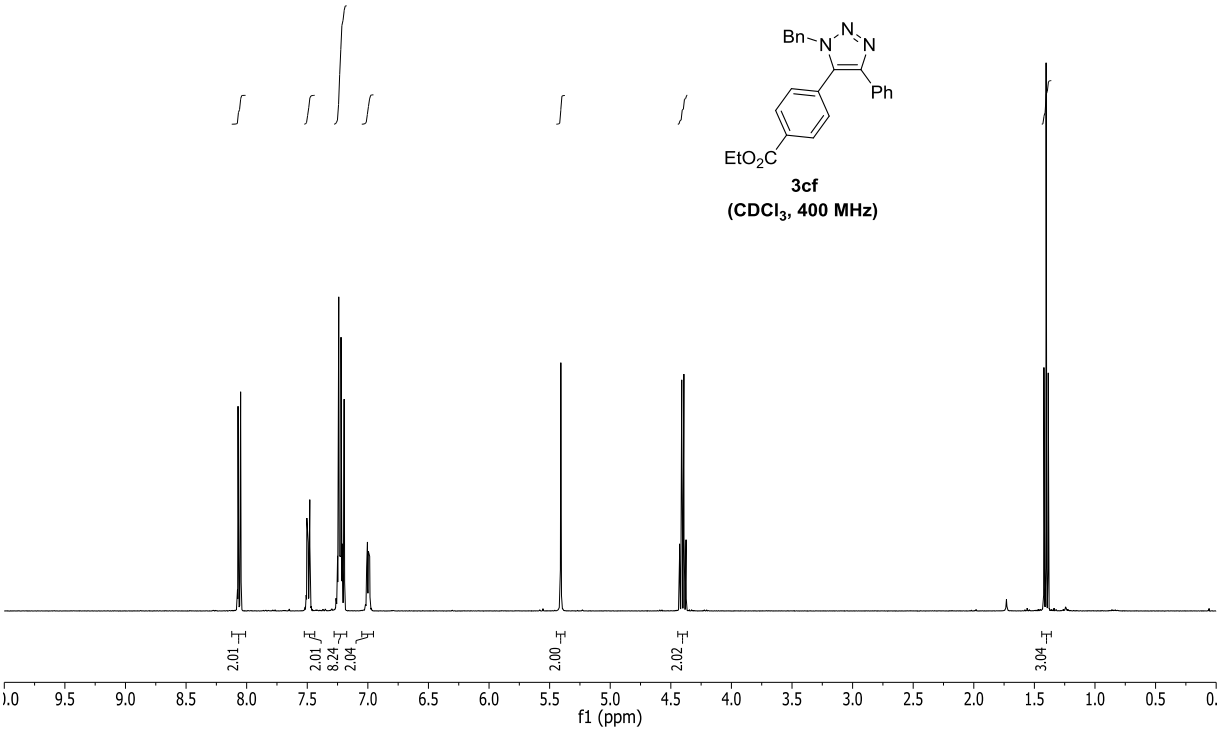
3bg
($CDCl_3$, 100 MHz)

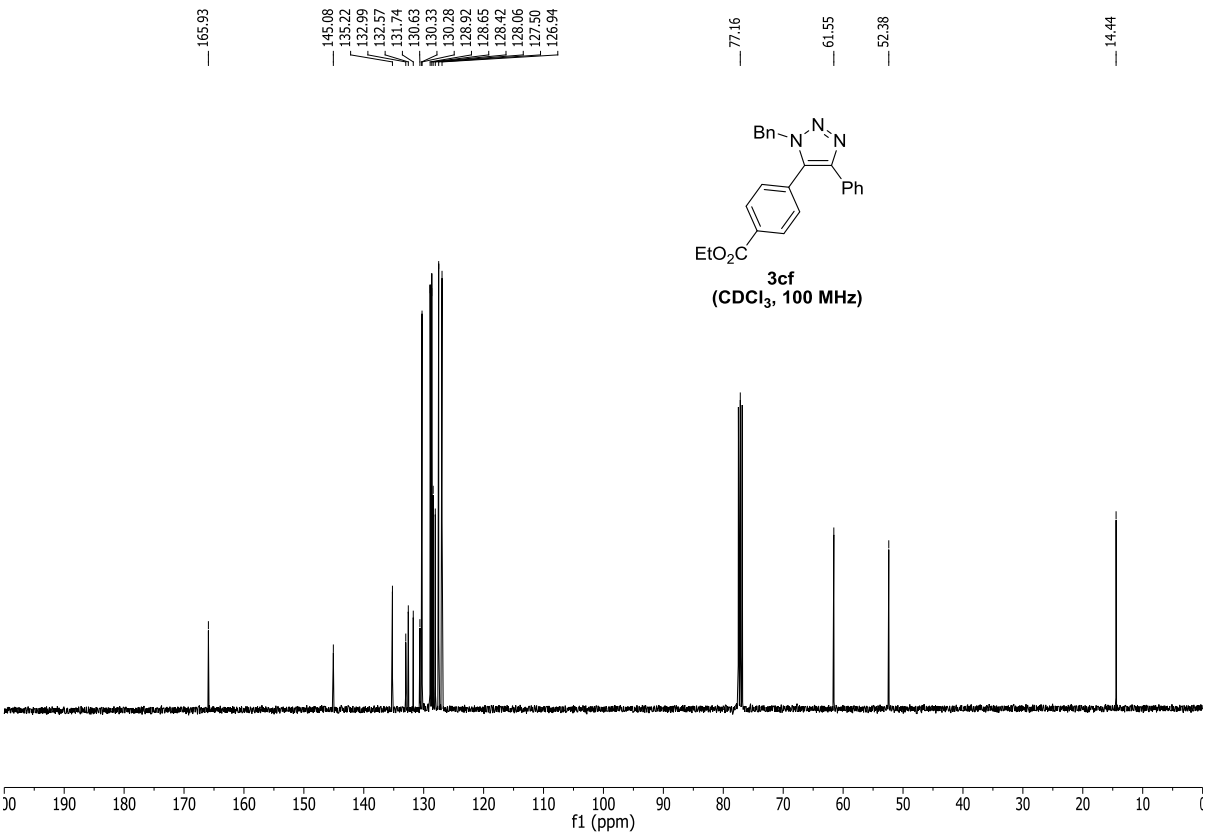


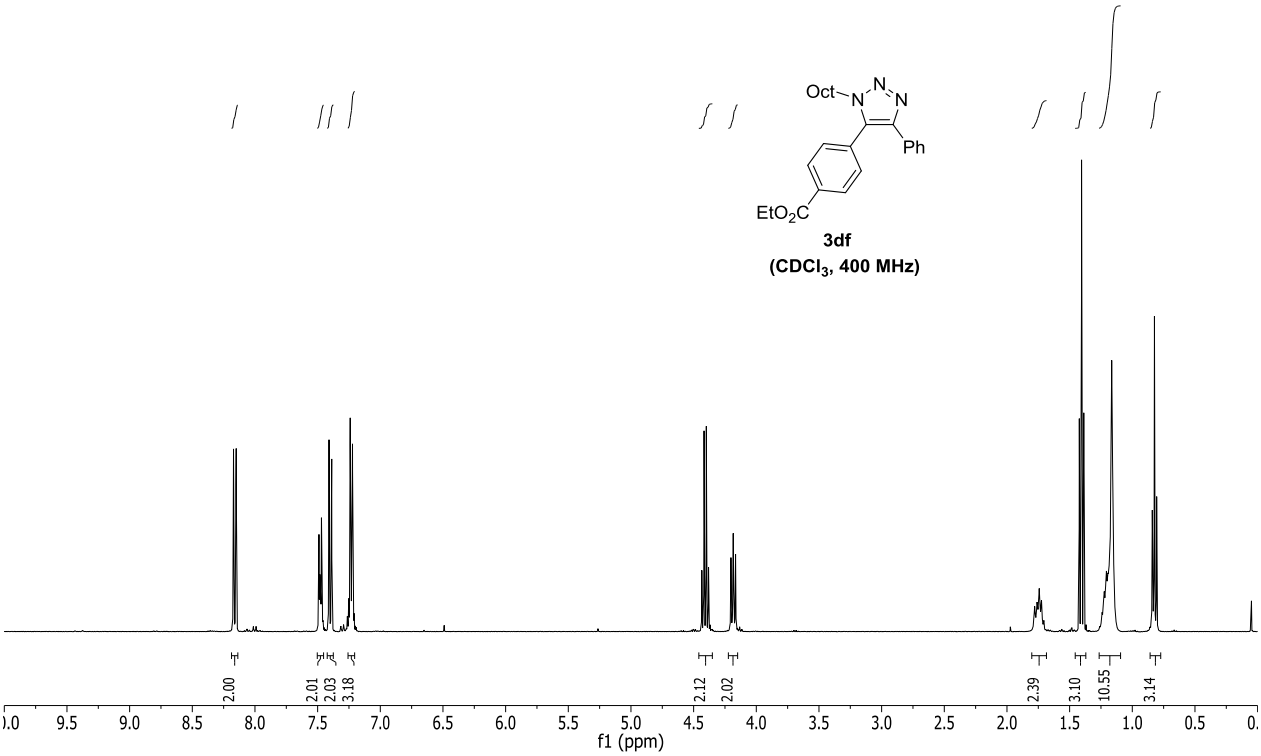
3bh
($CDCl_3$, 300 MHz)



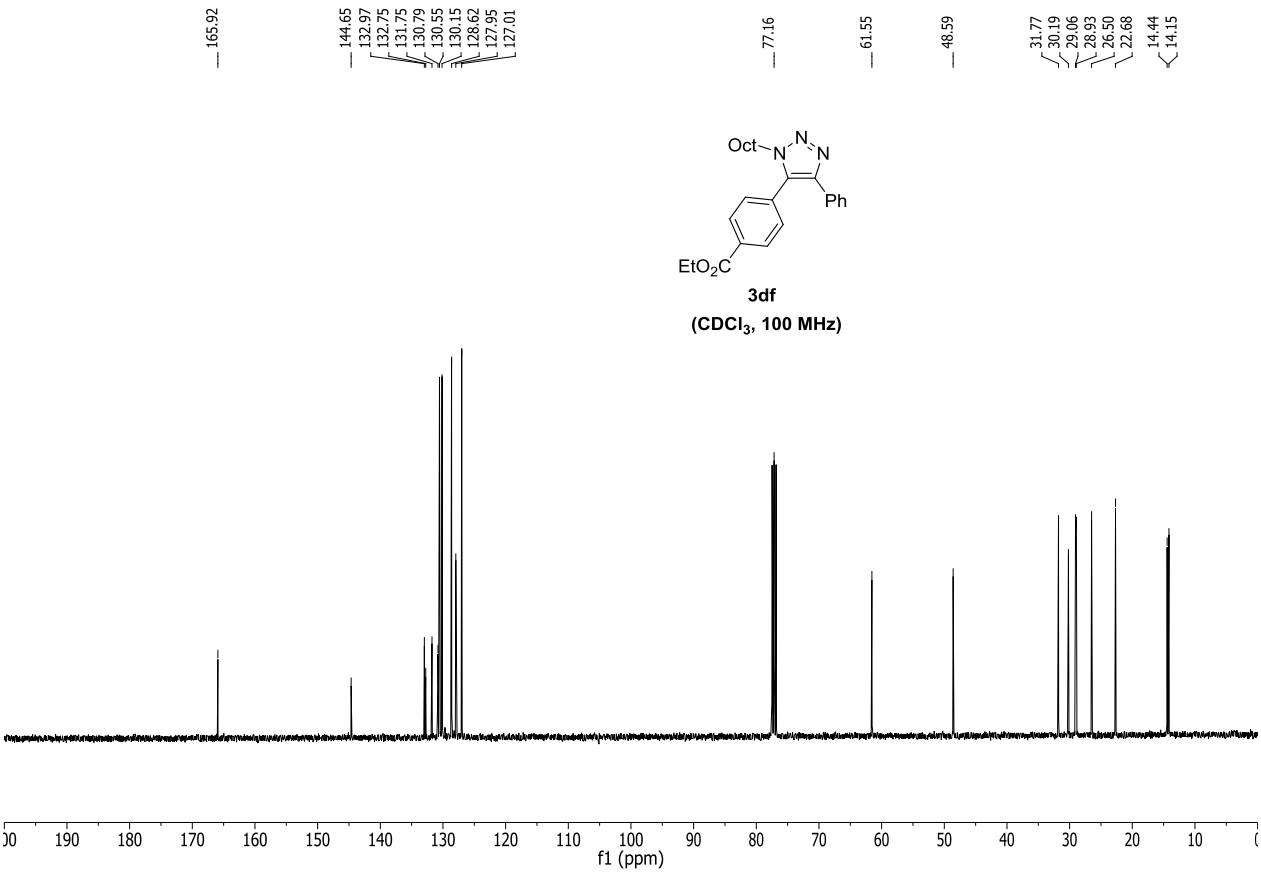
3bh
($CDCl_3$, 100 MHz)


Bn
N
N
N
Ph
EtO2C
3cf
(CDCl3, 400 MHz)
2.01
2.01
8.24
2.04
2.00
2.02
3.04
f1 (ppm)

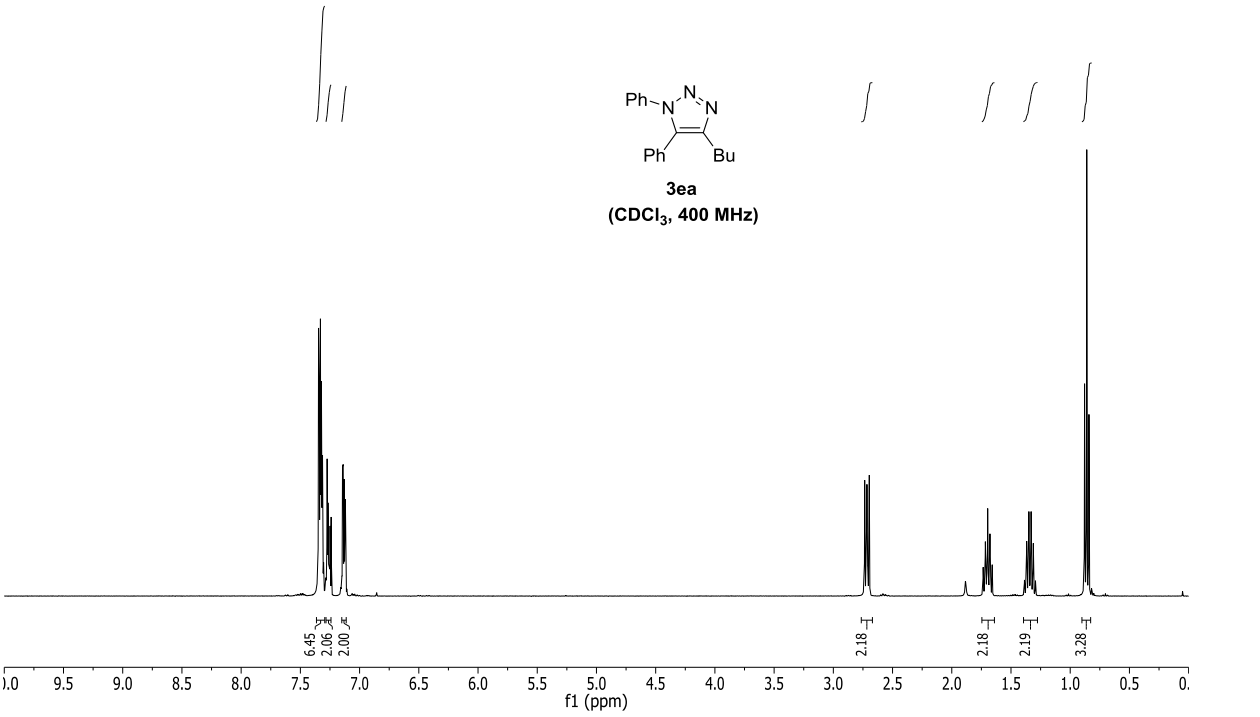

165.93
145.08
135.22
132.99
132.57
131.74
130.63
130.33
130.28
128.92
128.65
128.42
128.06
127.50
126.94
77.16
61.55
52.38
14.44
Bn
N
N
N
Ph
EtO2C
3cf
(CDCl3, 100 MHz)
f1 (ppm)



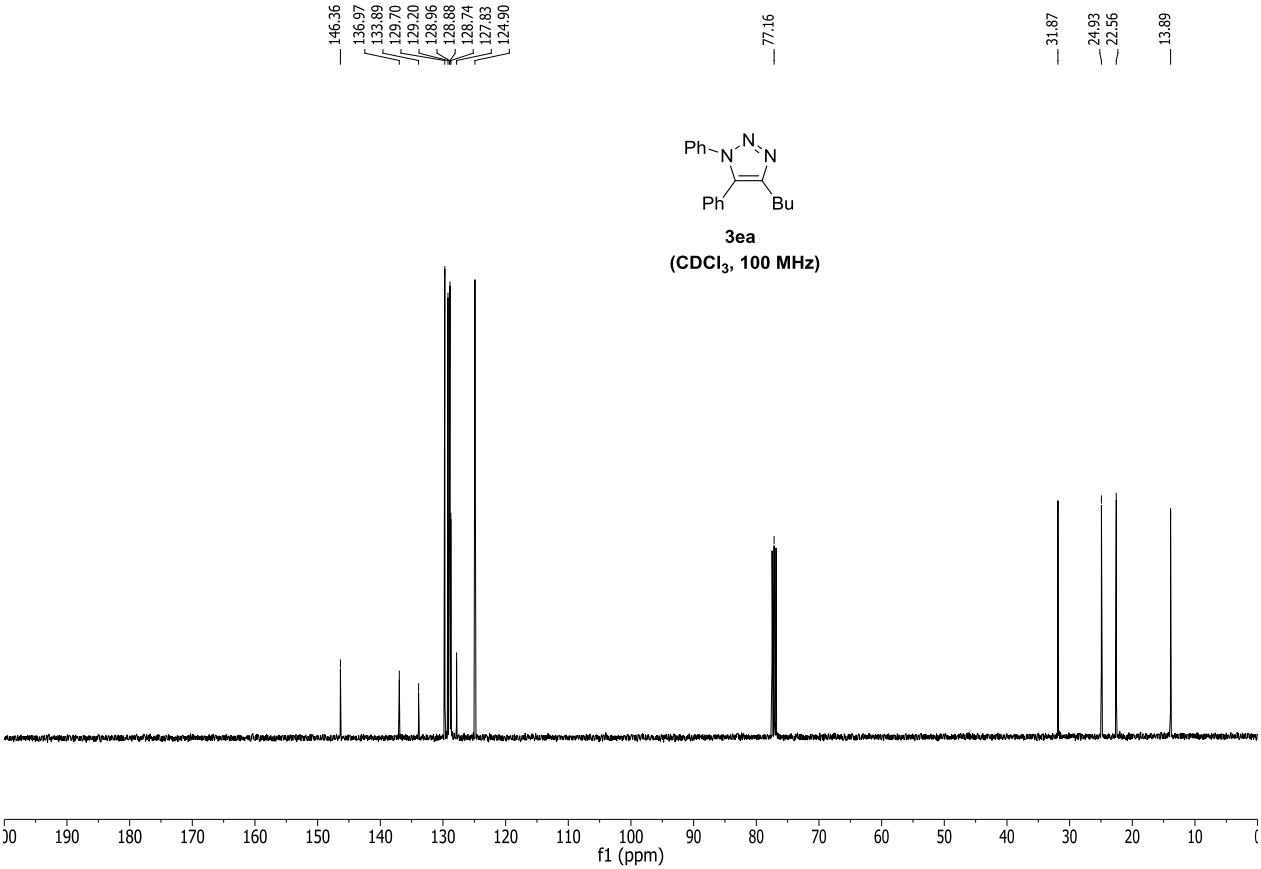
3df
($CDCl_3$, 400 MHz)



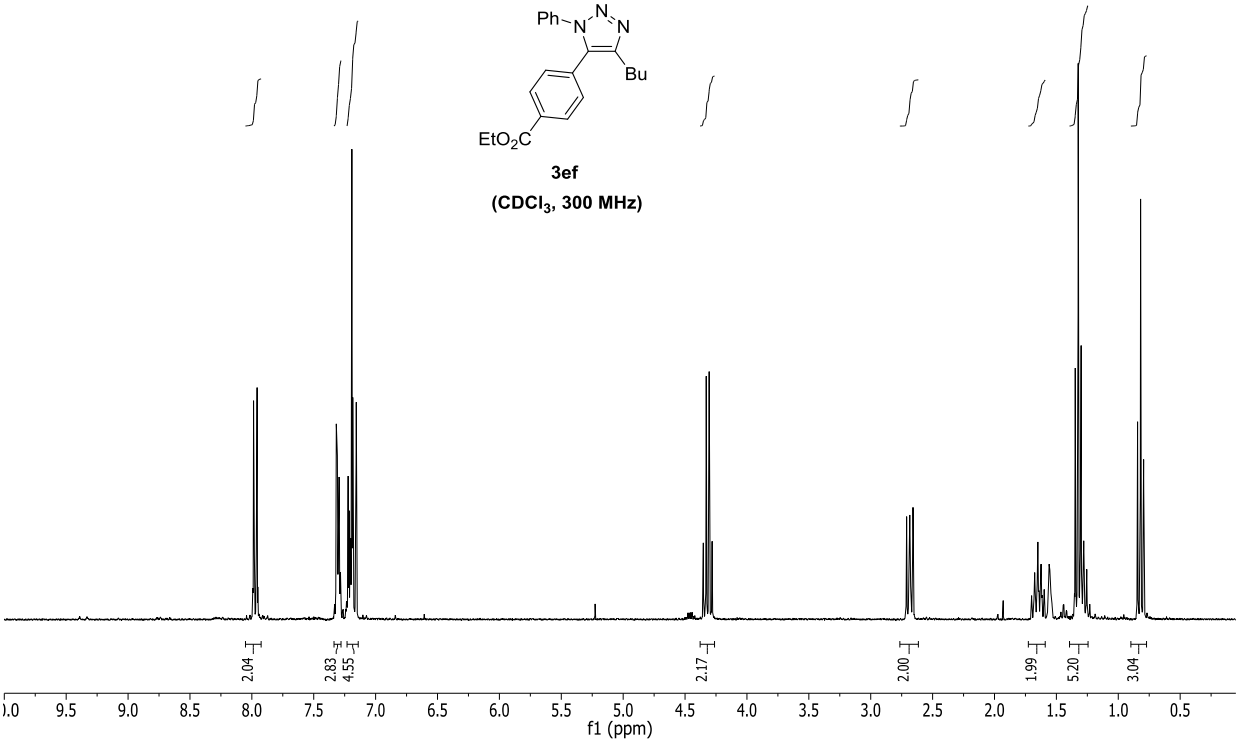
3df
($CDCl_3$, 100 MHz)



3ea
($CDCl_3$, 400 MHz)

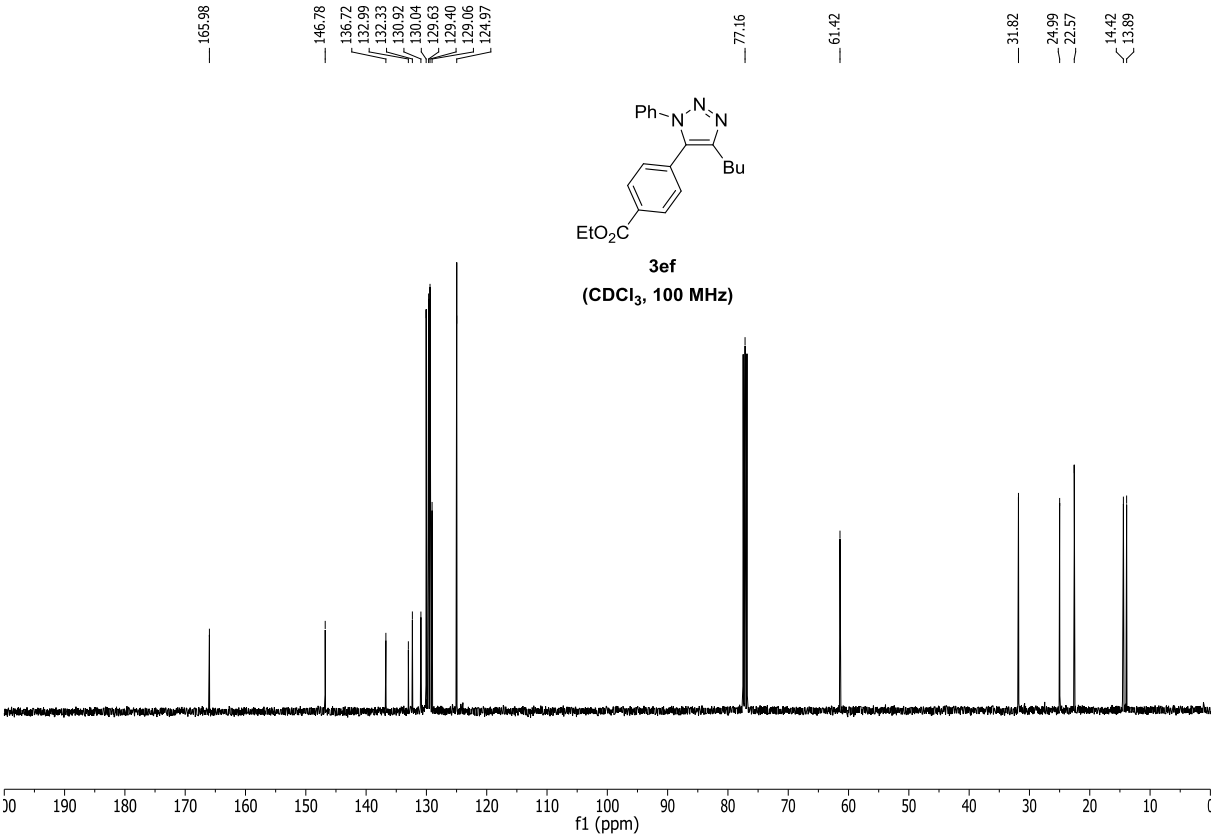


3ea
($CDCl_3$, 100 MHz)



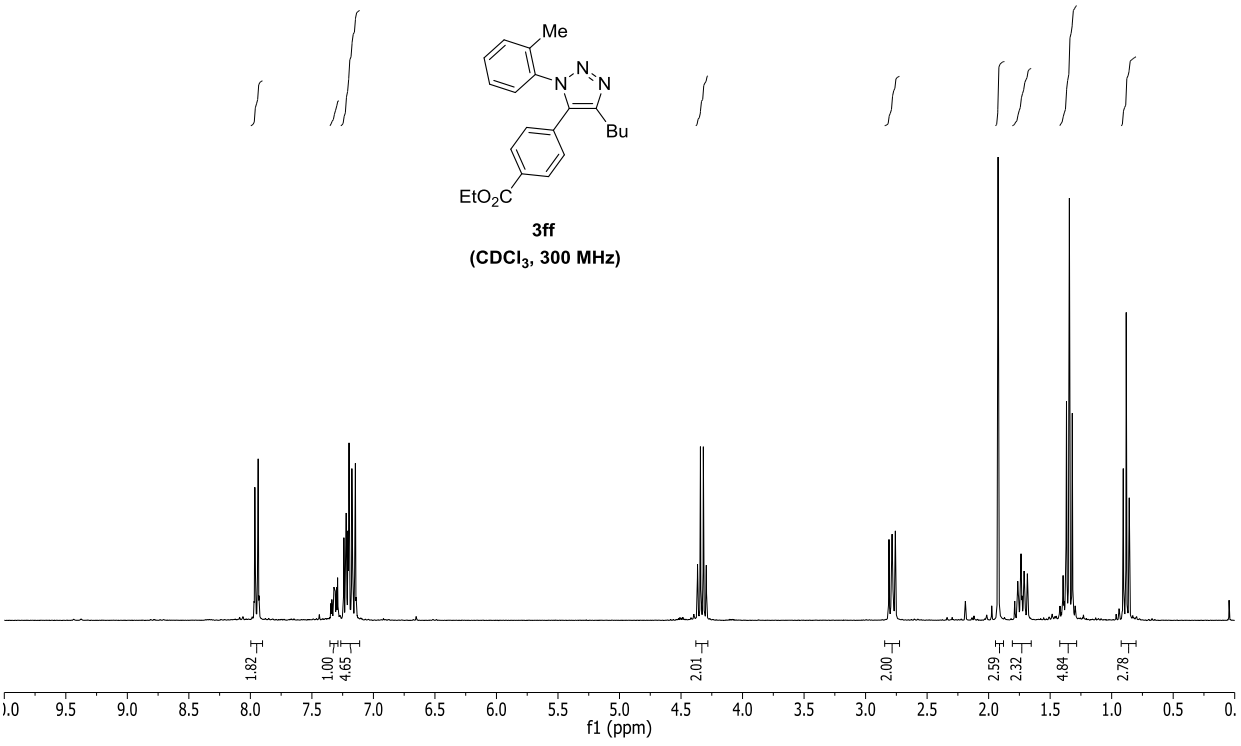
3ef

($CDCl_3$, 300 MHz)

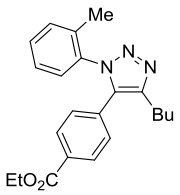


3ef

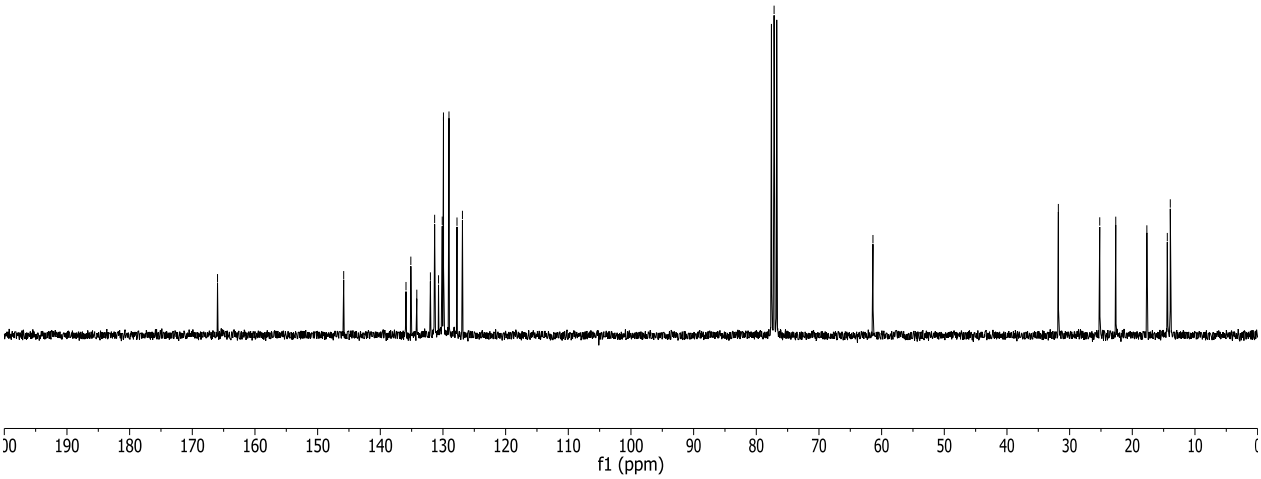
($CDCl_3$, 100 MHz)

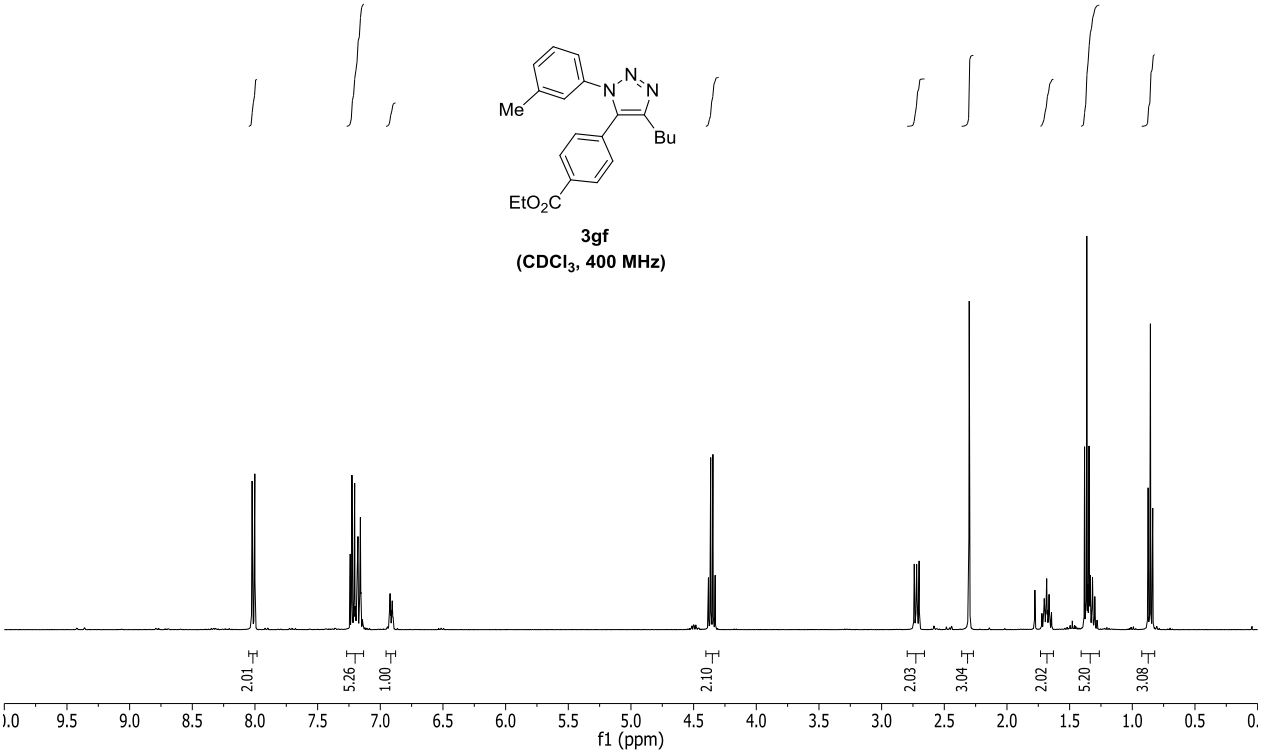


3ff
($CDCl_3$, 300 MHz)

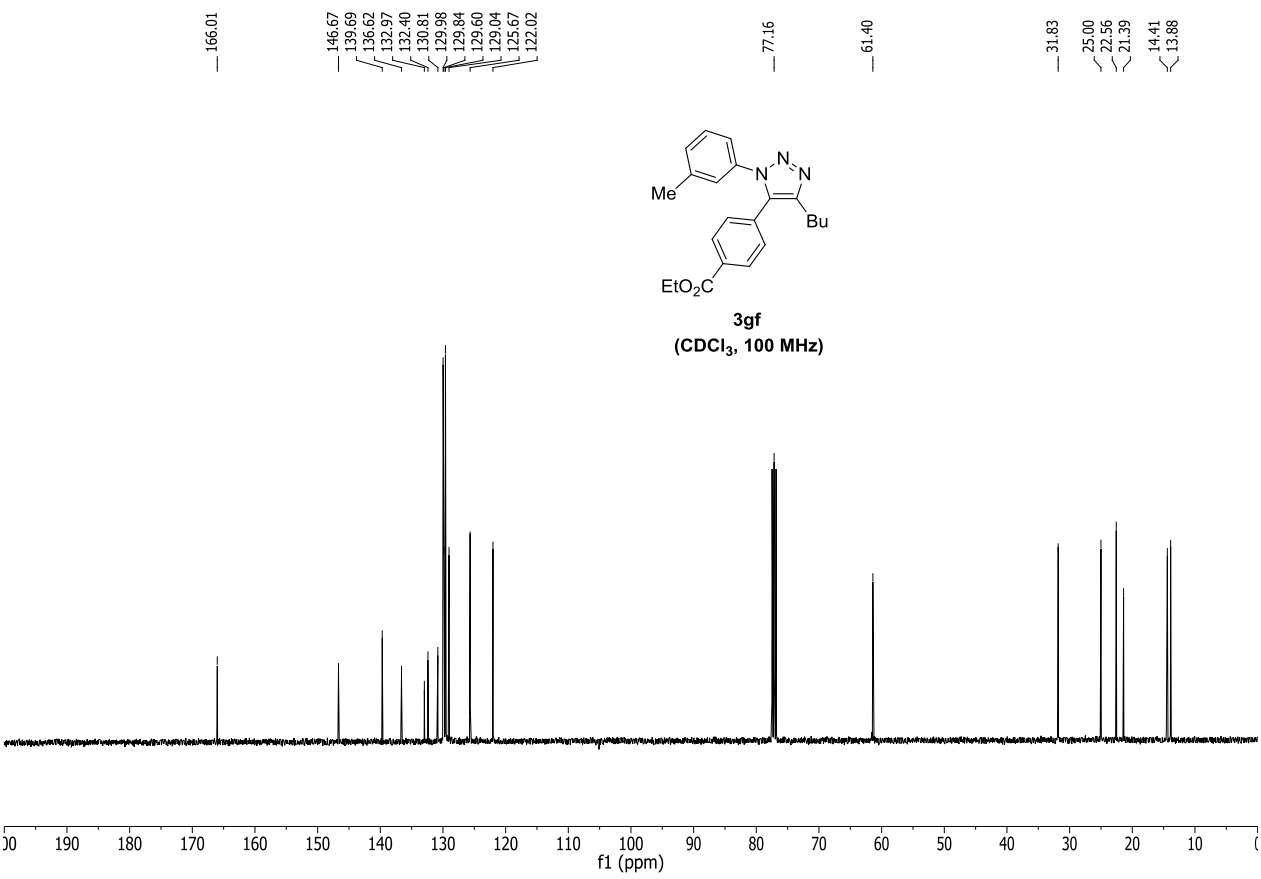


3ff
($CDCl_3$, 75 MHz)

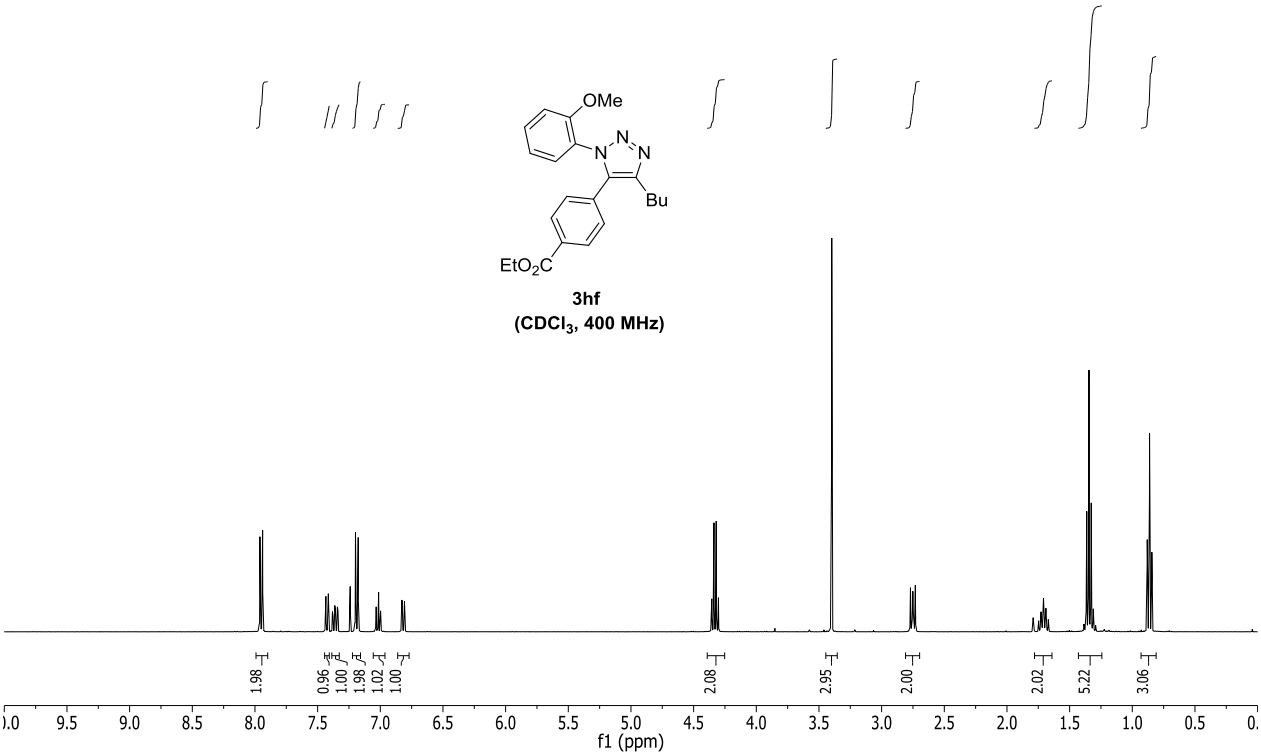




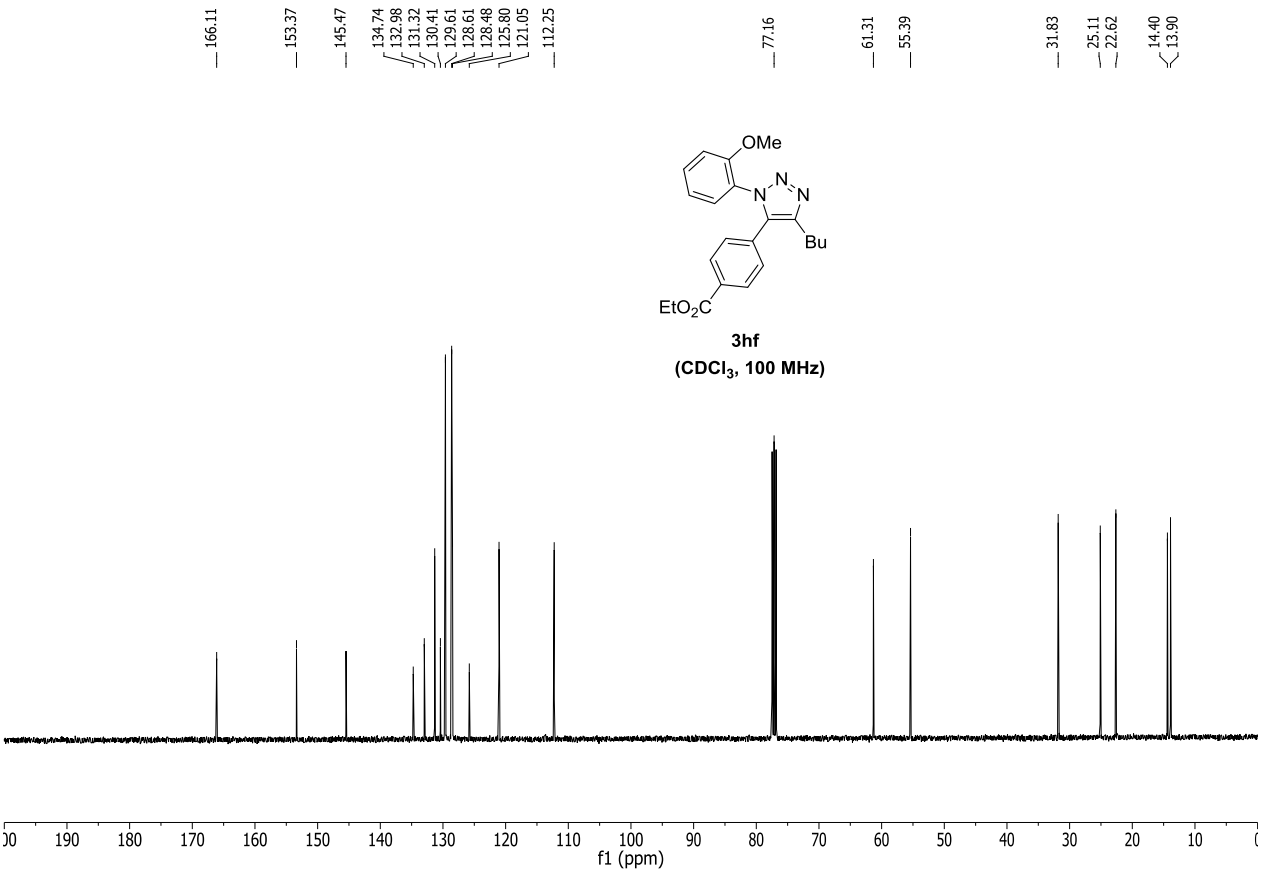
3gf
($CDCl_3$, 400 MHz)



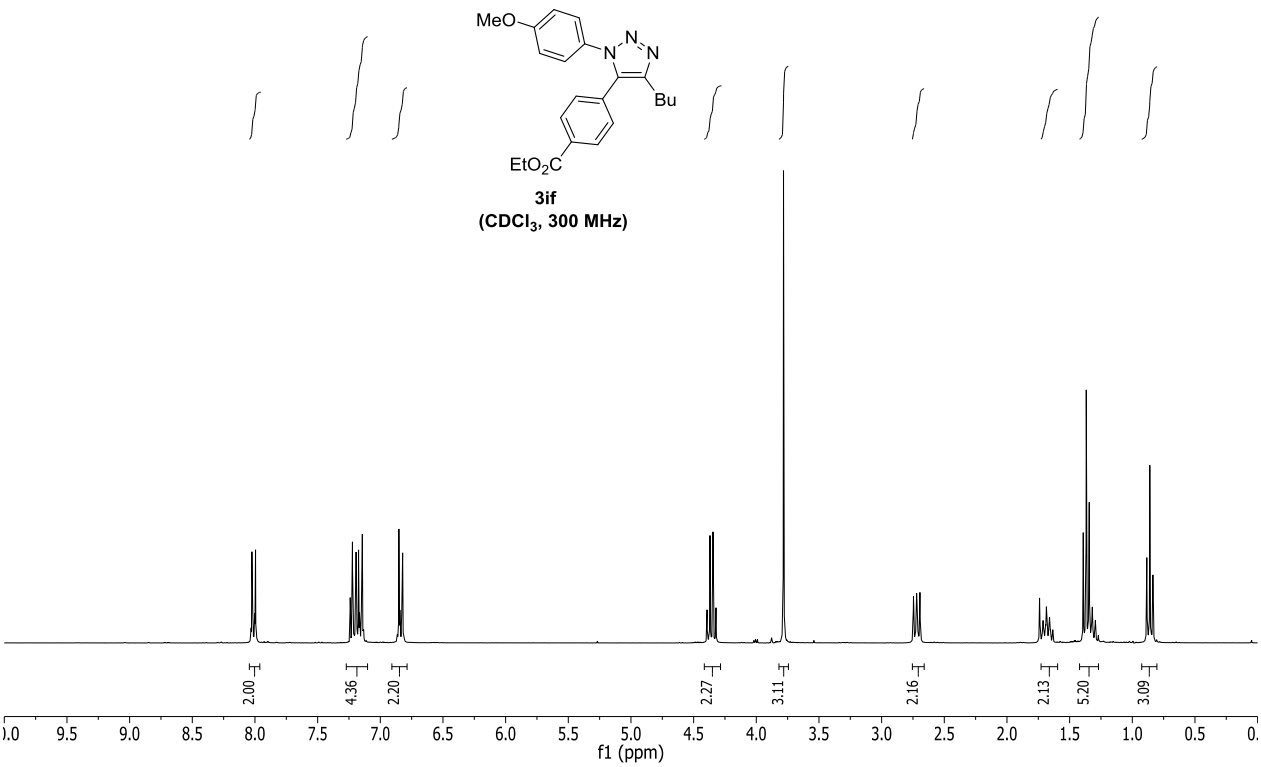
3gf
($CDCl_3$, 100 MHz)



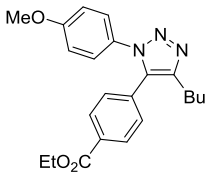
3hf
($CDCl_3$, 400 MHz)



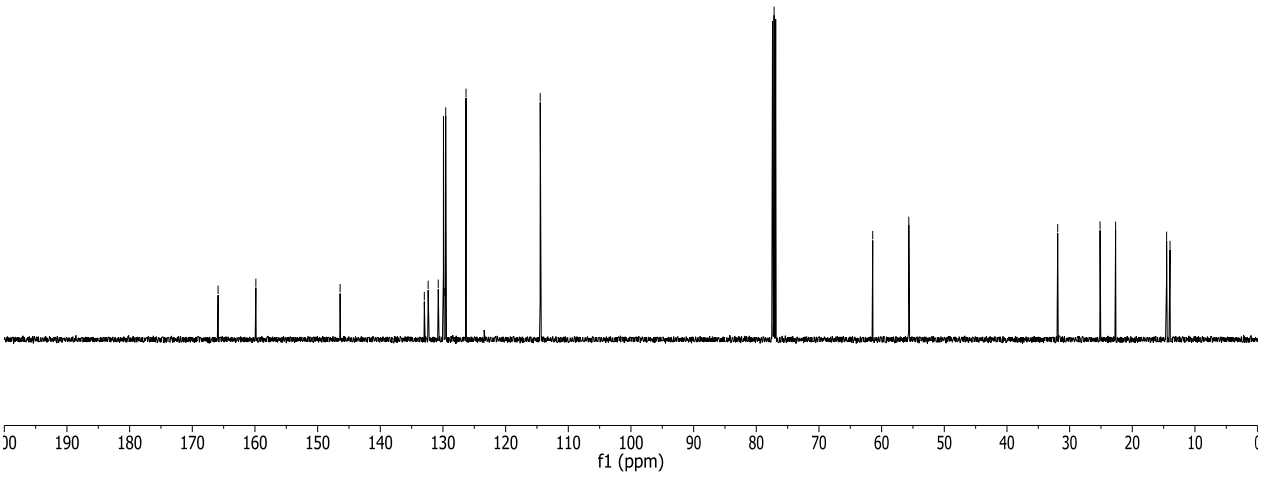
3hf
($CDCl_3$, 100 MHz)

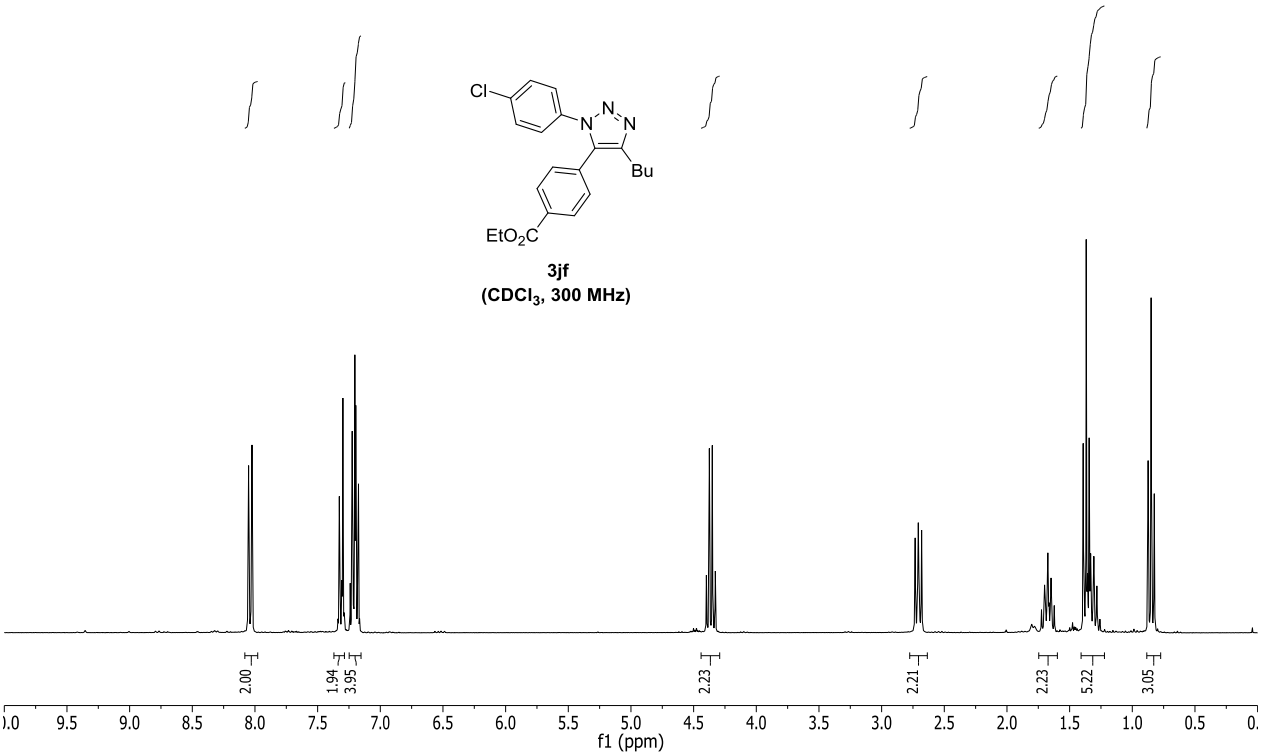


3if
($CDCl_3$, 300 MHz)

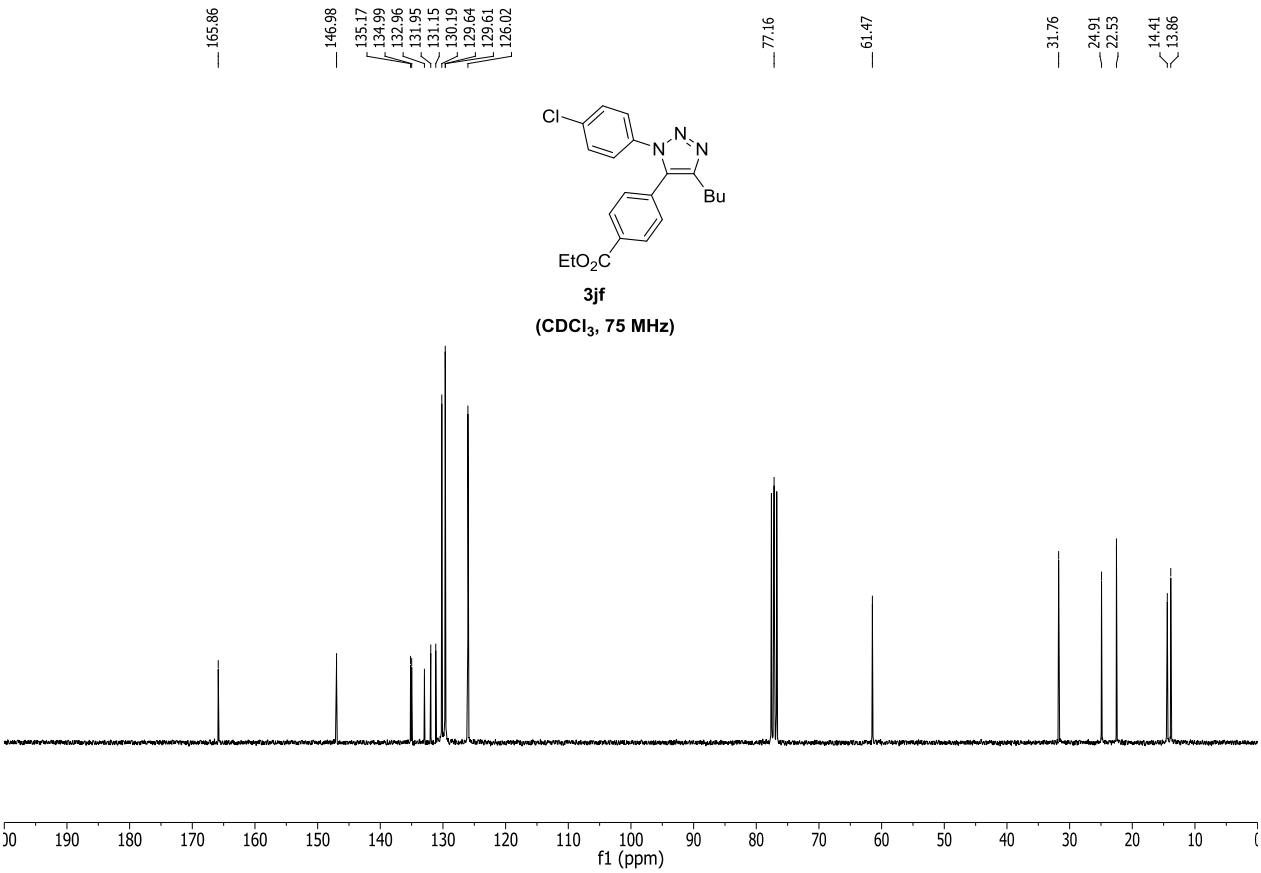


3if
($CDCl_3$, 125 MHz)

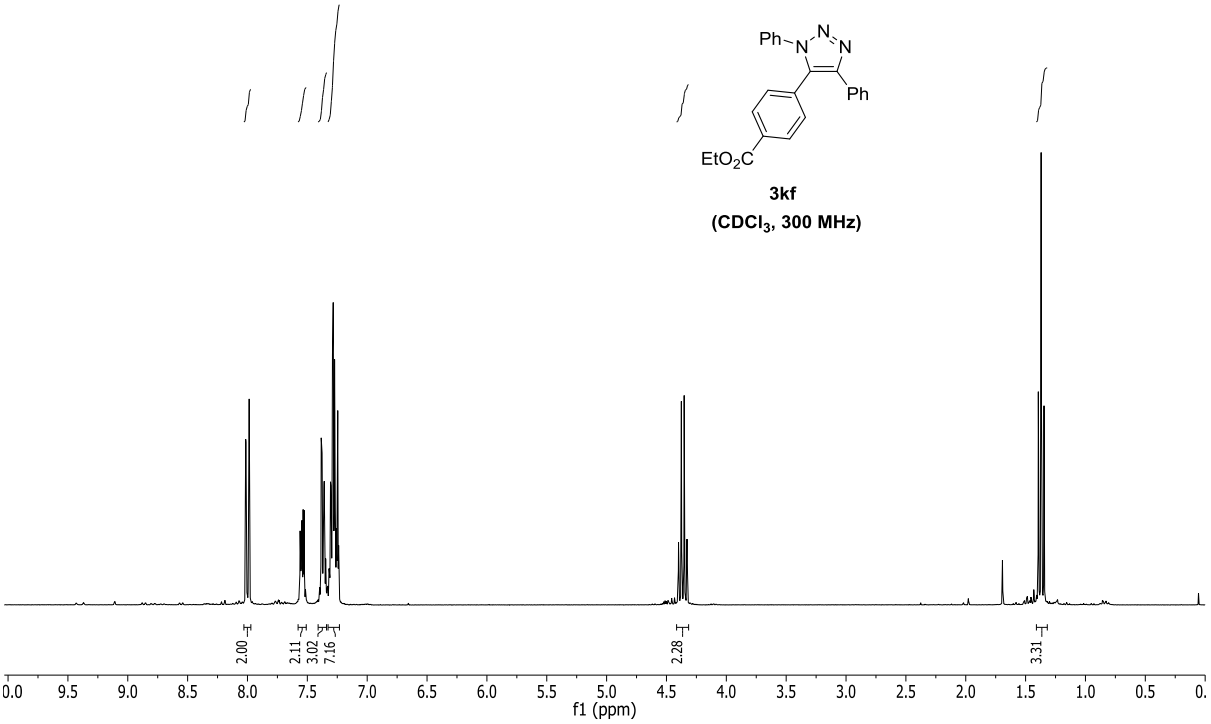




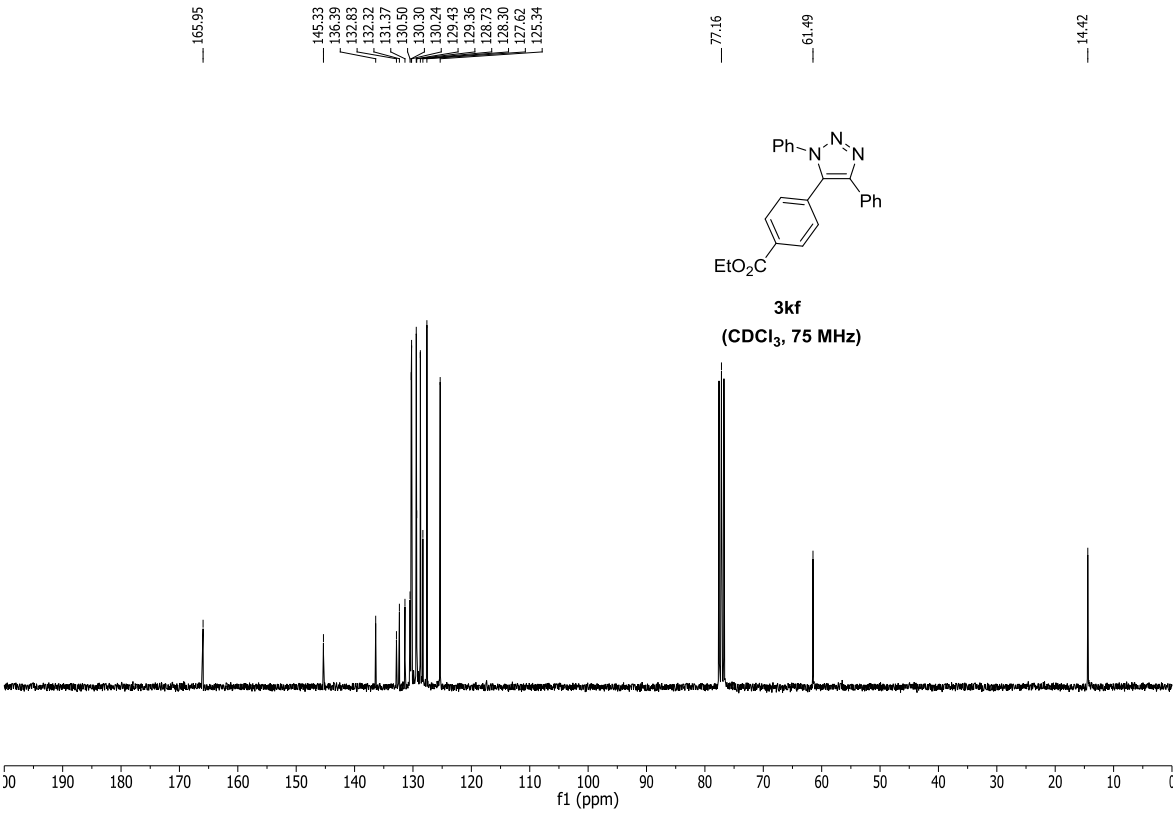
3jf
($CDCl_3$, 300 MHz)



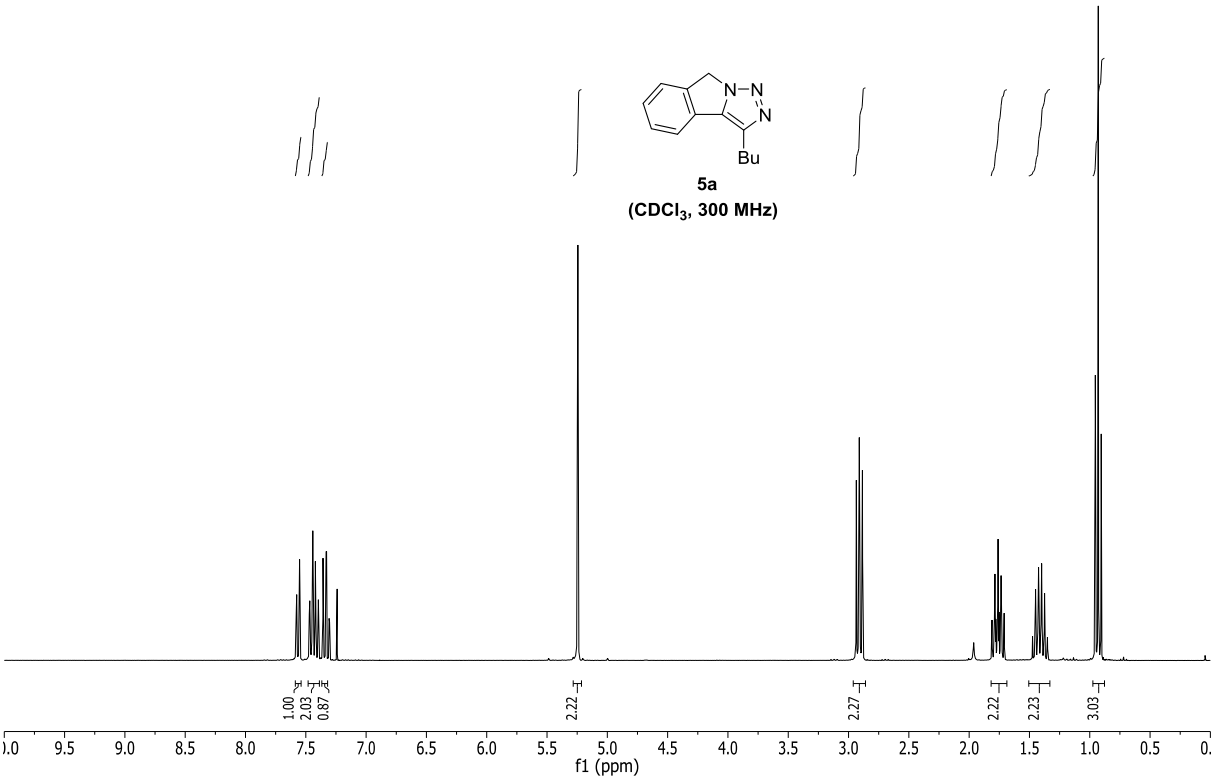
3jf
($CDCl_3$, 75 MHz)



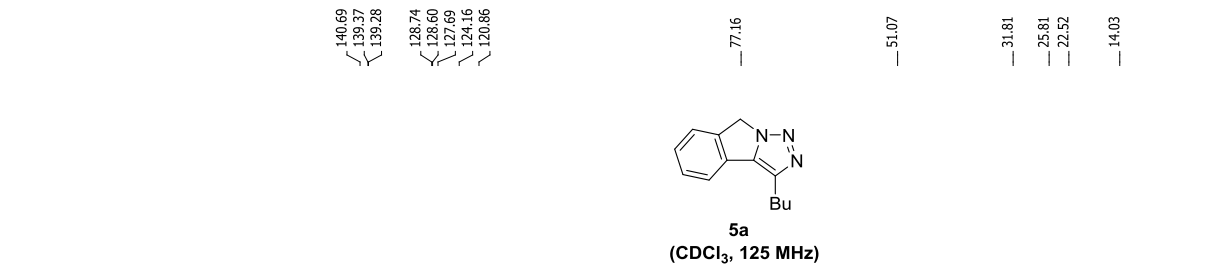
3kf
($CDCl_3$, 300 MHz)



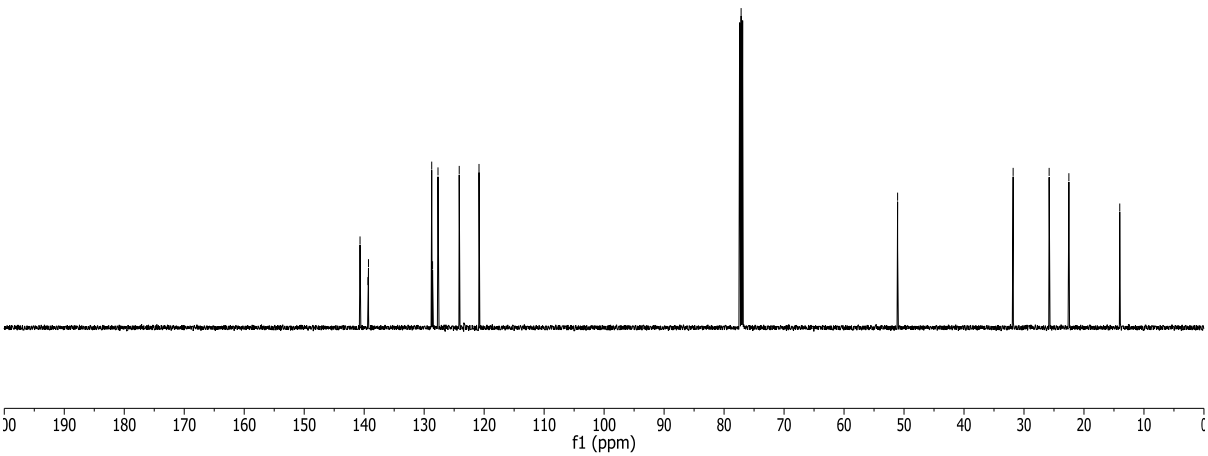
3kf
($CDCl_3$, 75 MHz)

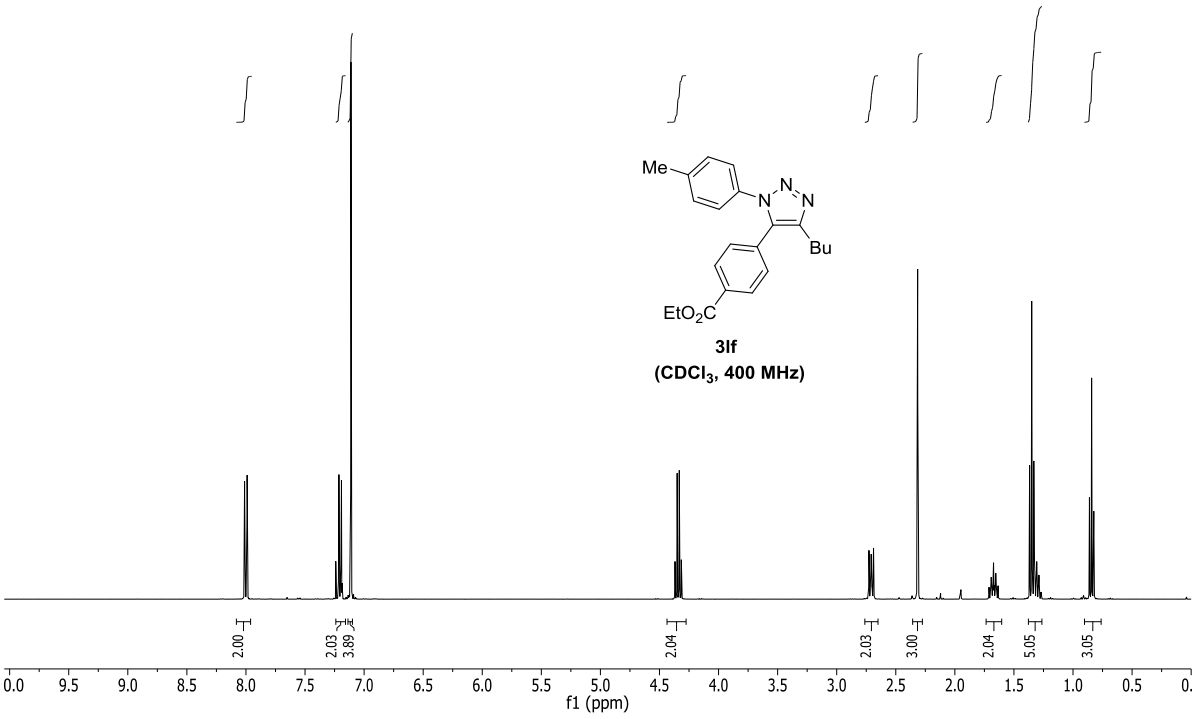


5a
($CDCl_3$, 300 MHz)

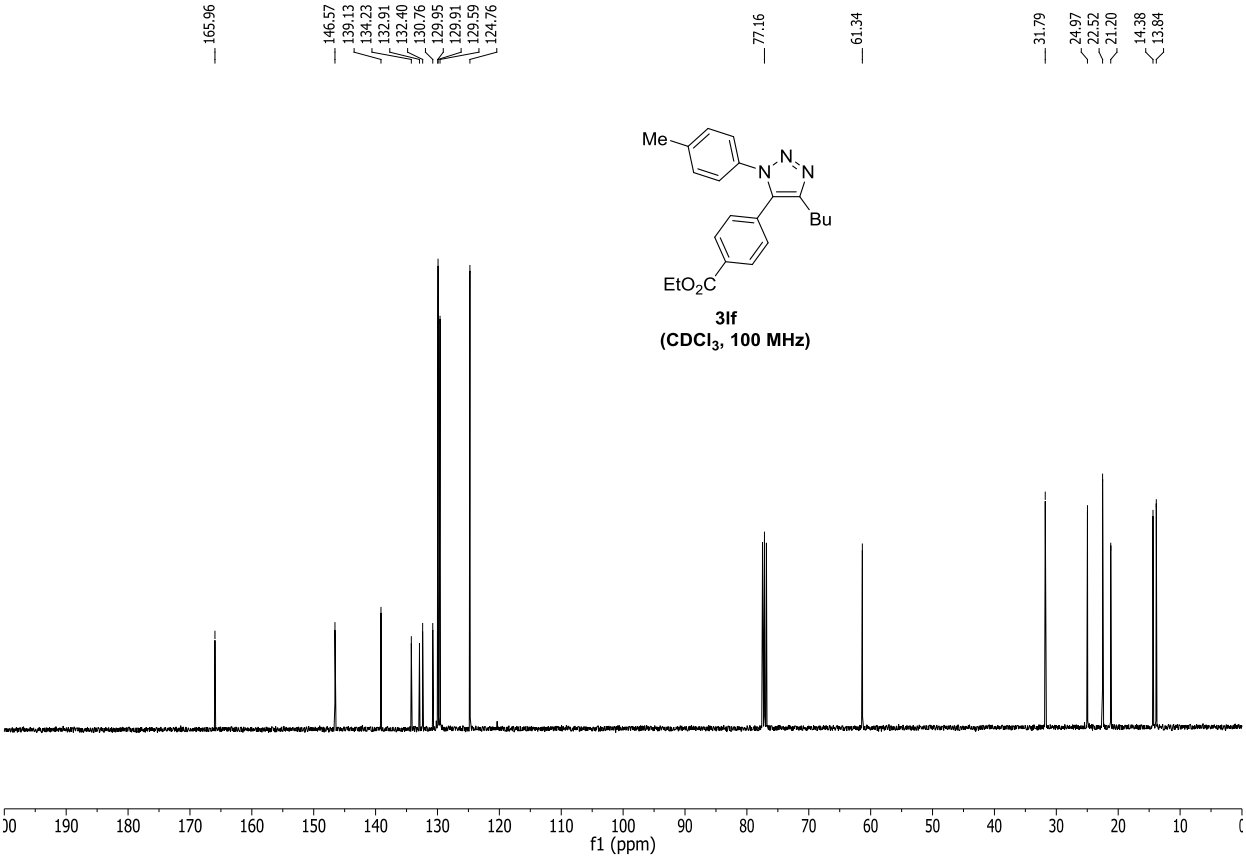


5a
($CDCl_3$, 125 MHz)





3lf
($CDCl_3$, 400 MHz)



3lf
($CDCl_3$, 100 MHz)