Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Deep eutectic solvents promoting 1,3-Dipolar Cycloaddition Between Azide and β-enaminones

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Supporting Information

TGA Analysis: thermogravimetric analysis was carried out on a TGA Q5000 (TA Instruments Inc., USA). The heating rate was 10°C min^{-1} and the N_2 flow rate was 50 mL min^{-1} from 298.15 to 973.15 K. The sample mass was 2 to 5 mg. The TGA equipment was calibrated by $CaC_2O_4H_2O$ (99.9%).

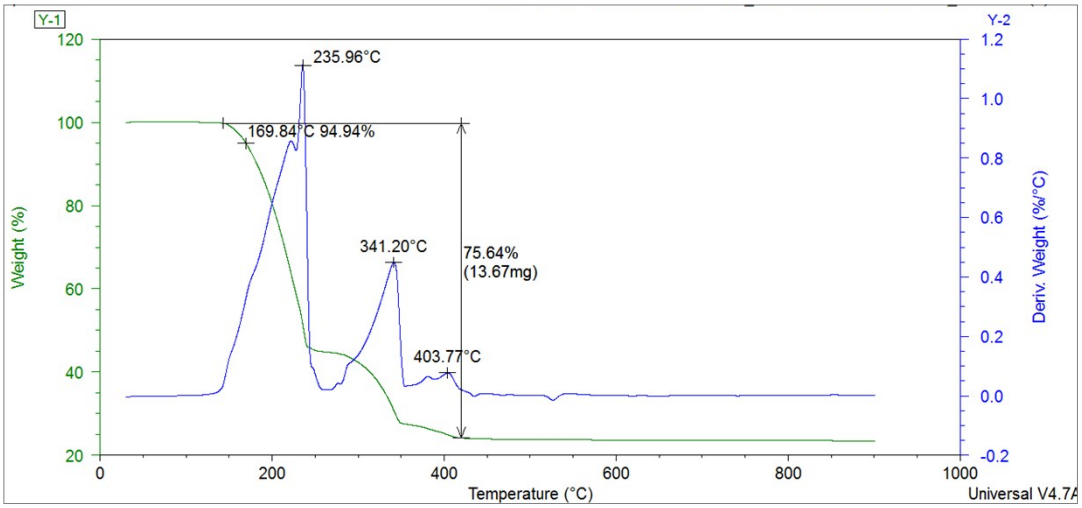


Figure S1. Thermogram TGA of pure urea (10°C/min)

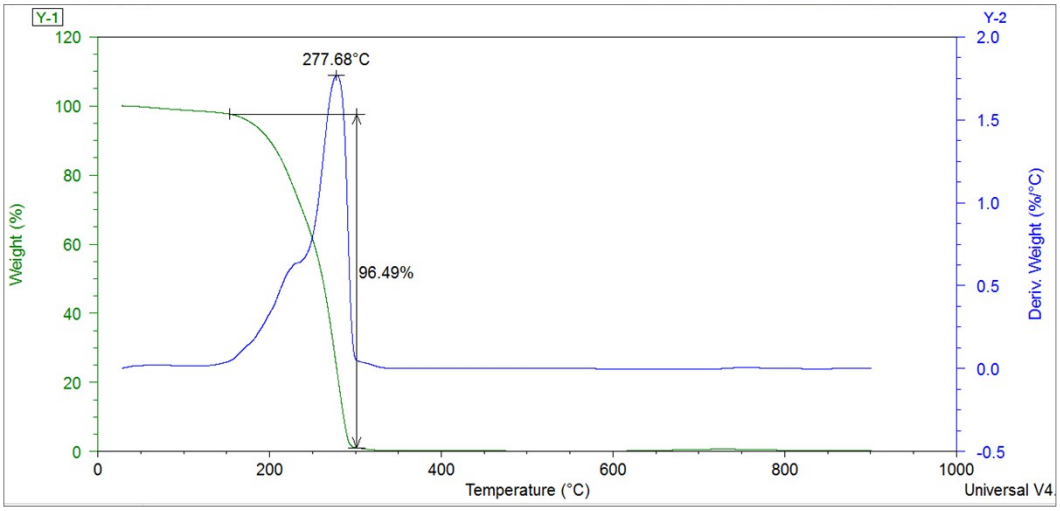
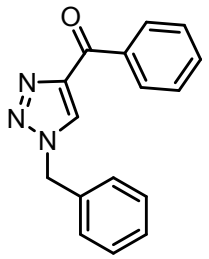


Figure S2. Thermogram TGA of ClCh/urea (10°C/min).

Synthesis and Characterization of Products: Unless otherwise indicated, all common reactants and solvents were used as obtained from commercial supplies without further purifications. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 (^{1}H at 400.13 MHz and ^{13}C at 100.62 MHz) in 5ppm sample tubes at 303 K in $CDCl_3$/TMS solutions. Chemical shifts (δ) are given in ppm. The general reproducibility of chemical shift data was estimated to be not greater than ± 0.01 ppm. J values are given in Hz. The melting points were measured using a Microquímica MQAPF 301 device. Mass spectra were obtained for all compounds on a LTQ Orbitrap Discovery mass spectrometer (Thermo Fisher Scientific). This hybrid system meets the LTQ XL linear ion trap mass spectrometer and an Orbitrap mass analyzer. The experiments were performed via direct infusion of sample (flow: 10 μL/min) in the positive-ion mode using electrospray ionization. Elemental composition calculations for comparison were executed using the specific tool included in the Qual Browser module of Xcalibur (Thermo Fisher Scientific, release 2.0.7) software.

(1-benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone **(6a)**[1]

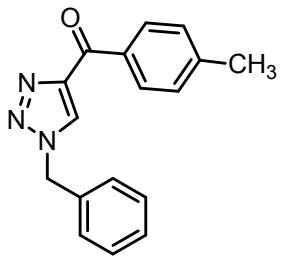


$C_{16}H_{13}N_3O$; m.w. 263.11, m.p. 115-117°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (*J*, Hz) 5.60 (s, 2H), 7.32-7.42 (m, 5H), 7.49 (t, 2H, J^3 = 7.6), 7.59 (t, 1H, J^3 = 7.3), 8.21 (s, 1H), 8.41(d, 2H, J^3 = 7.5).

^{13}C NMR (100 MHz, $CDCl_3$): δ 54.41, 128.35, 128.36, 129.10, 129.29, 130.57, 133.23, 133.87, 136.61, 148.36, 185.60.

(1-benzyl-1*H*-1,2,3-triazol-4-yl)(*p*-tolyl)methanone **(6b)**



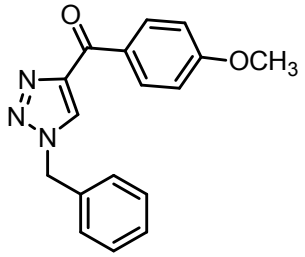
$C_{17}H_{15}N_3O$; m.w. 277.12, m.p. 130°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (*J*, Hz) 2.45 (s, 3H), 5.62 (s, 2H), 7.30-7.42 (m, 7H), 8.18 (s, 1H), 8.37 (d, 2H, J^3 = 8.3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 21.72, 54.37, 128.30, 128.35, 129.06, 129.11, 129.27, 130.73, 133.91, 134.03, 144.17, 148.51, 185.22.

HRMS (ESI+) calcd for $C_{17}H_{15}N_3O$ [M + H]+ 278.1280, found 278.1288

(1-benzyl-1*H*-1,2,3-triazol-4-yl)(4-methoxyphenyl)methanone **(6c)**[2]

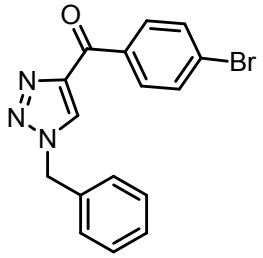


$C_{17}H_{15}N_3O_2$;m.w.293.12, m.p. 129-131°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (*J*, Hz) 3.89 (s, 3H), 5.61 (s, 2H), 7.00 (d, 2H, J^3 = 9.0), 7.32-7.41 (m, 5H), 8.17 (s, 1H), 8.52 (d, 2H, J^3 = 9.0).

^{13}C NMR (100 MHz, $CDCl_3$): δ 54.37, 55.49, 113.69, 128.25, 128.35, 129.06, 129.27, 129.42, 133.09, 133.92, 148.73, 163.84, 183.89.

(1-benzyl-1*H*-1,2,3-triazol-4-yl)(4-bromophenyl)methanone **(6d)**



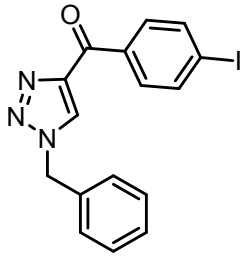
$C_{16}H_{12}BrN_3O$; m.w. 341.02, m.p. 149-151 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (*J*, Hz), 5.62 (s, 2H), 7.34-7.45 (m, 5H), 7.66 (d, 2H, J^3 = 8.6), 8.20 (s, 1H), 8.37 (d, 2H, J^3 = 8.6).

^{13}C NMR (100 MHz, $CDCl_3$): δ 54.50, 128.38, 128.47, 128.65, 129.20, 129.35, 131.70, 132.19, 133.69, 135.18, 148.17, 184.33.

HRMS (ESI+) calcd for $C_{16}H_{12}BrN_3O$ [M + H]+ 342.0228, found 342.0237

(1-benzyl-1*H*-1,2,3-triazol-4-yl)(4-iodophenyl)methanone **(6e)**



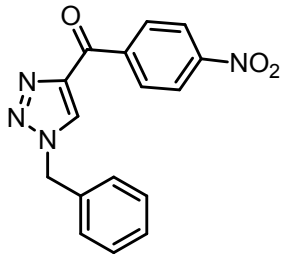
$C_{16}H_{12}IN_3O$; m.w. 389.00, m.p. 156-158 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (*J*, Hz) 5.62 (s, 1H), 7.34-7.43 (m, 5H), 7.89 (d, 2H, J^3 = 8.3), 8.20 (d, 3H, J^3 = 9.3).

^{13}C NMR (100 MHz, $CDCl_3$): δ 54.50, 101.50, 128.35, 128.38, 129.18, 129.33, 132.01, 133.71, 135.78, 137.70, 148.19, 184.58.

HRMS (ESI+) calcd for $C_{16}H_{12}IN_3O$ [M + H]+ 390.0086, found 390.0098

(1-benzyl-1*H*-1,2,3-triazol-4-yl)(4-nitrophenyl)methanone **(6f)**[2]

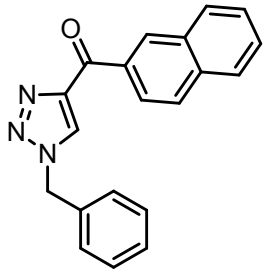


$C_{16}H_{12}N_4O_3$; m.w. 308.09, m.p. 137-139°C.

^{1}HNMR (400 MHz, $CDCl_3$): δ (*J*, Hz) 5.63 (s, 2H), 7.34-7.44 (m, 5H), 8.27 (s, 1H), 8.30 (d, 2H, J^3 = 8.9), 8.60 (d, 2H, J^3 = 8.9).

^{13}C NMR (100 MHz, $CDCl_3$): δ 54.61, 123.40, 128.41, 128.79, 129.29, 129.39, 131.62, 133.53, 141.12, 147.67, 150.29, 183.75.

(1-benzyl-1*H*-1,2,3-triazol-4-yl)(naphtalen-2-yl)methanone **(6g)**[1]

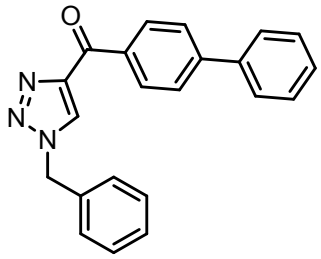


$C_{20}H_{15}N_3O$; m.w. 313.12, m.p. 156-158 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ5.64 (s, 2H), 7.36-7.45 (m, 5H), 7.56 (t, 1H, J^3 = 7.5), 7.62 (t, 1H, J^3 = 7.3), 7.90 (d, 1H, J^3 = 8.0), 7.95 (d, 1H, J^3 = 8.6), 8.06 (d, 1H, J^3 = 8.0), 8.24 (s, 1H), 8.35-8.37 (dd, 1H, J^3 = 8.6 J^1 = 1.6), 9.26 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (*J*, Hz) 54.47, 125.54, 126.60, 127.71, 128.14, 128.37, 128.4, 128.62, 129.13, 129.32, 130.09, 132.57, 133.41, 133.82, 133.84, 135.75, 148.66, 185.3.

[1,1'-biphenyl]-4-yl(1-benzyl-1*H*-1,2,3-triazol-4-yl)methanone **(6h)**



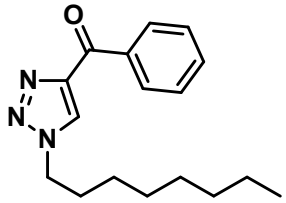
$C_{22}H_{17}N_3O$; m.w. 339.14, m.p. 146-147 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (*J*, Hz) 5.64 (s, 2H), 7.35-7.38 (m, 2H), 7.40-7.46 (m, 4H), 7.48-7.52 (m, 2H), 7.66-7.69 (m, 2H), 7.74-7.75 (m, 1H), 7.77- 7.78 (m, 1H), 8.22 (s, 1H), 8.54-8.55 (m, 1H), 8.56-8.57 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 54.48, 127.07, 127.36, 128.24, 128.34, 128.41, 128.96, 129.18, 129.36, 131.24, 133.79, 135.27, 140.04, 145.94, 148.53, 185.14.

HRMS (ESI+) calcd for $C_{22}H_{17}N_3O$ [M + H]+ 340.1435, found 340.1444

(1-octyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone **(7a)**[3]

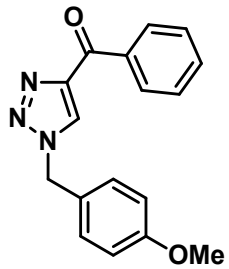


$C_{17}H_{23}N_3O$; m.w. 285.18, m.p. 35-37 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (*J*, Hz) 0.90 (t, 3 Hz, J^3 = 6.9), 1.29-1.38 (m, 10H), 1.96-2.03 (m, 2H), 4,46 (t, 2H, J^3 = 7.2), 7.52-7.56 (m, 2H), 7,61-7,65 (m, 1H), 8,26 (s, 1H), 8,28 (ddd, 2H, J^1 = 1.6, J^2 = 3.0, J^3 = 7.2.

^{13}C NMR (100 MHz, $CDCl_3$): δ13.96, 22.53, 26.42, 28.87, 28.96, 30.12, 31.65, 50.63, 128.06, 128.33, 130.61, 133.16, 136.65, 148.15, 185.71.

(1-(4-methoxybenzyl)-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone **(8a)**[4]

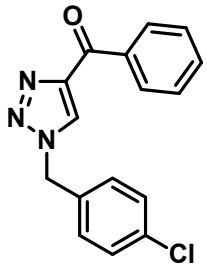


$C_{17}H_{15}N_3O$; m.w. 293.12, m.p. 118-119 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (*J*, Hz) 3.81 (s,3H), 5.54 (s, 2H), 6,92 (d, 2H, J^3 = 8.2), 7.29 (d, 2H, J^3 = 8), 7.50 (t, 2H, J^3 = 7.4), 7.60 (t, 1H, J^3 = 7.4), 8.13 (s, 1H), 8.4 (d, 2H J^3 = 8.2).

^{13}C NMR (100 MHz, $CDCl_3$): δ 54.03, 55.40, 114,72, 125.62, 128.08, 128.38, 130.03, 130.59, 133.26, 136.54, 148.27, 160.25, 185.73.

(1-(4-chlorobenzyl)-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone **(9a)**



$C_{16}H_{12}ClN_3O$; m.w. 297.74, m.p. 150-152 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (*J*, Hz) 5.57 (s, 2H), 7.27-7.28 (m, 2H), 7.36-7.38 (m, 2H,), 7.49-7.52 (m, 2H), 7.60 (ddd, 1H, J^1 = 1.2, J^2 = 2.4, J^3 = 8.5), 8.18 (s, 1H), 8.40-8.42 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 53.69, 128.20, 128.38, 129.55, 129.64, 130.58, 132.29, 133.31, 135.33, 136.48, 148.53, 185.50.

HRMS (ESI+) calcd for $C_{16}H_{12}ClN_3O$ [M + H]+ 298.0733, found 298.0742

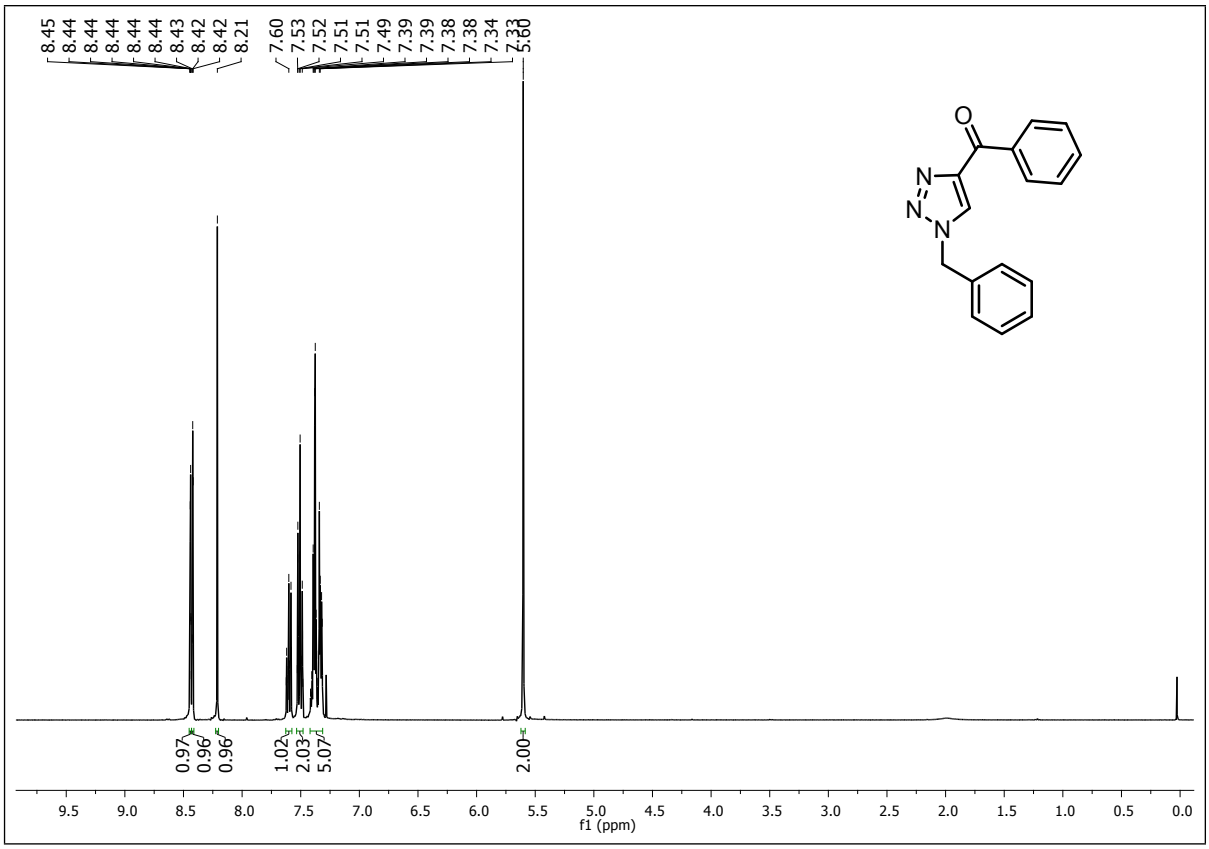


Figure S3. ^{1}H NMR spectrum of compound **6a** in $CDCl_3$ at 399.73 MHz.

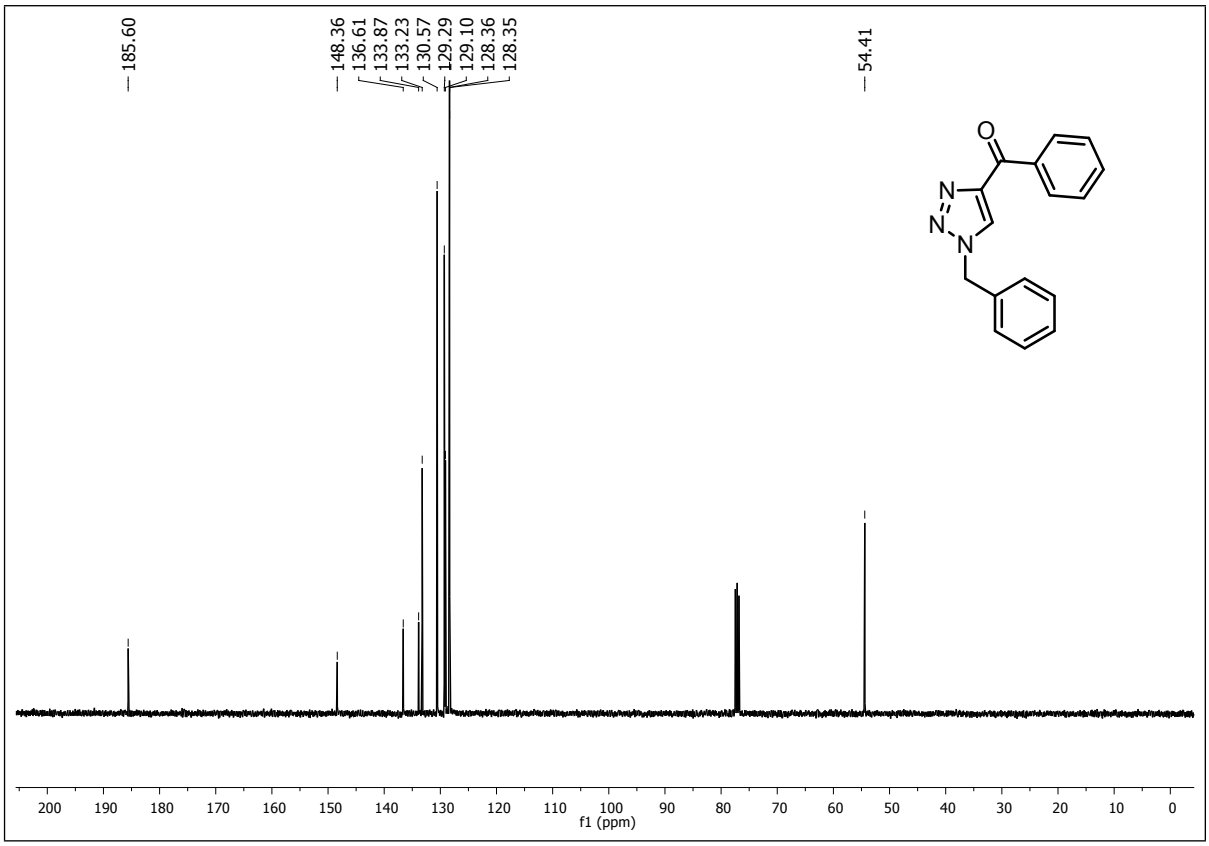


Figure S4. ^{13}C NMR spectrum of compound **6a** in $CDCl_3$ at 100.51 MHz.

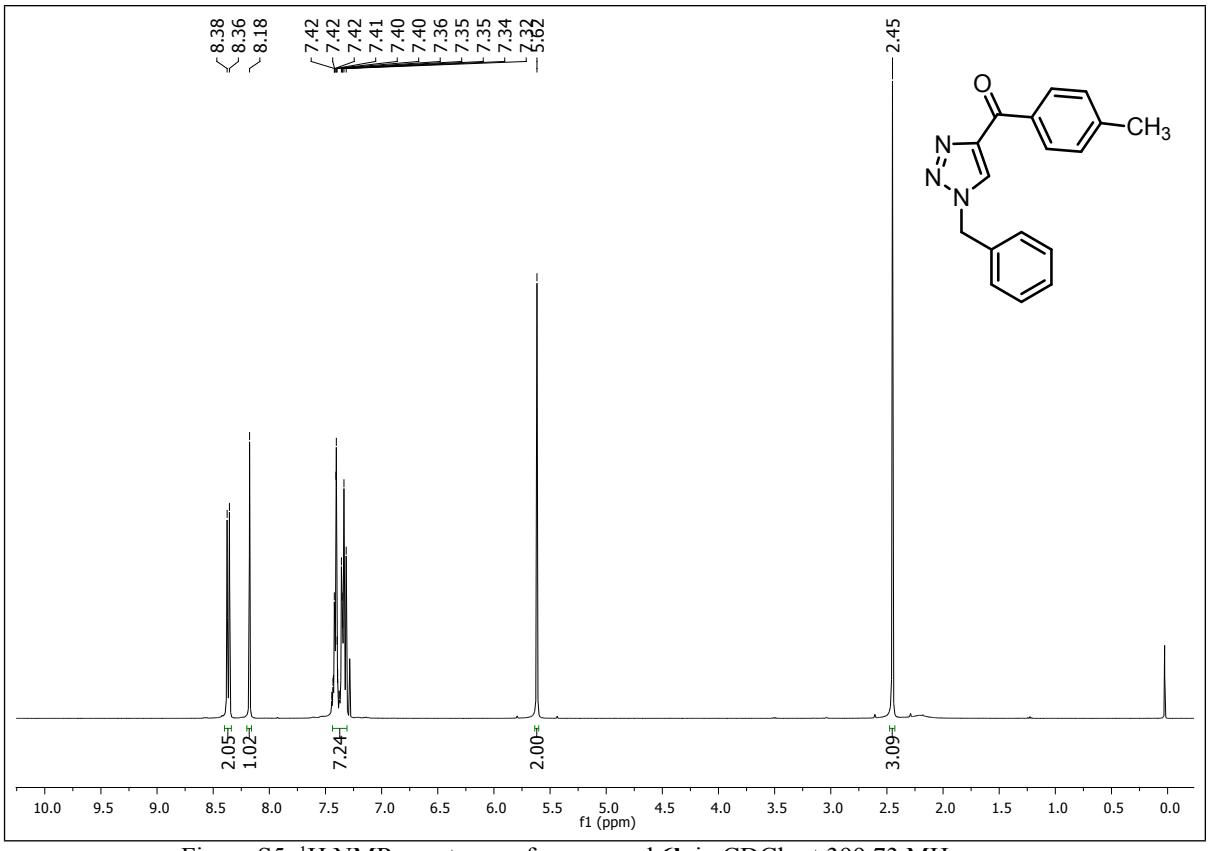


Figure S5. ^{1}H NMR spectrum of compound **6b** in $CDCl_3$ at 399.73 MHz.

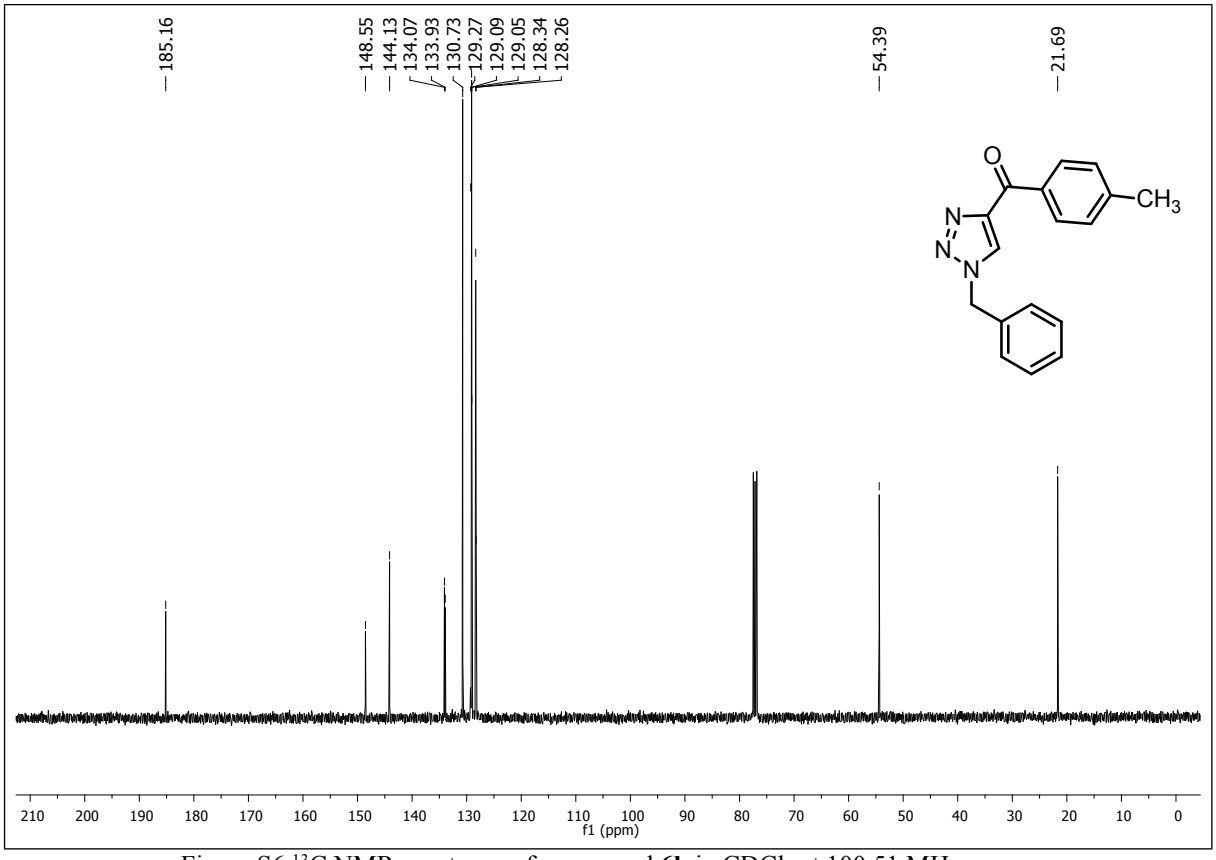


Figure S6. ^{13}C NMR spectrum of compound **6b** in $CDCl_3$ at 100.51 MHz.

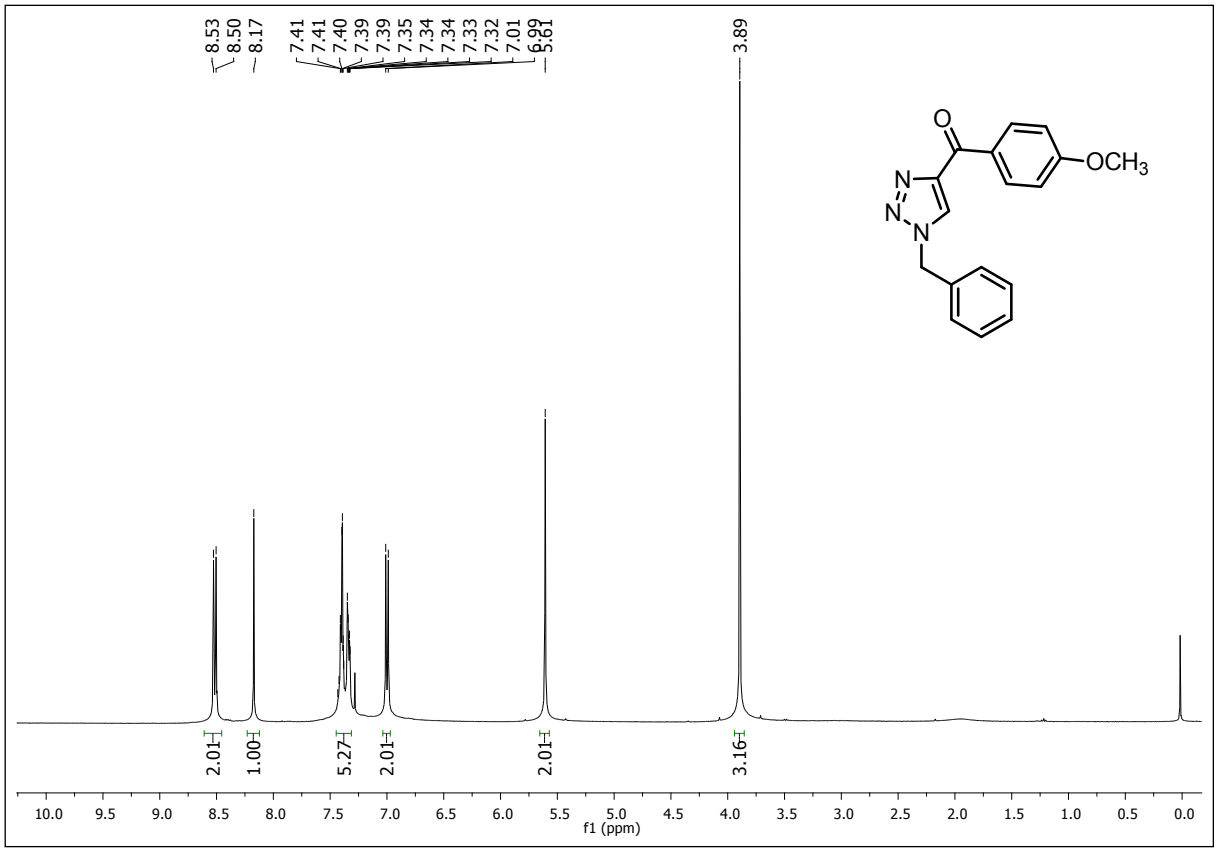


Figure S7.^{1}H NMR spectrum of compound **6c** in $CDCl_3$ at 399.73 MHz.

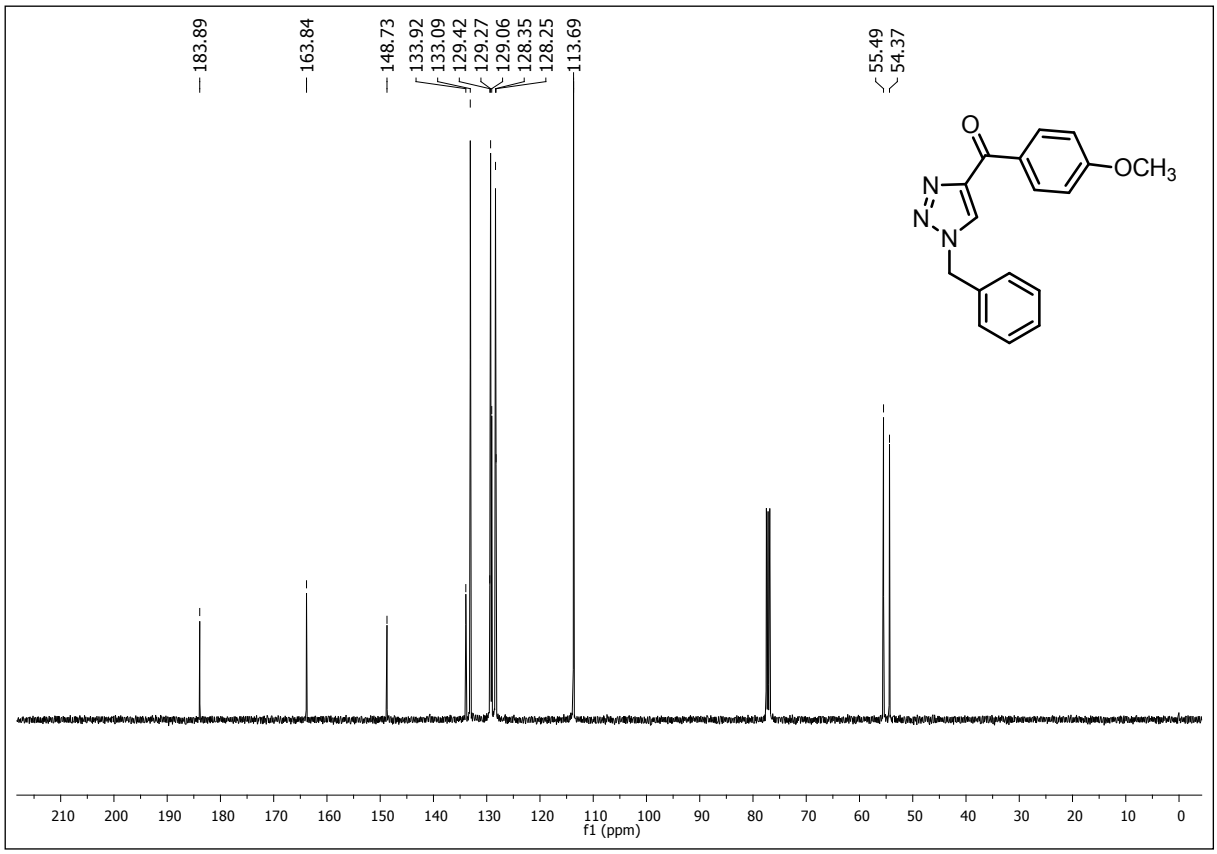


Figure S8. ^{13}C NMR spectrum of compound **6c** in $CDCl_3$ at 100.51 MHz.

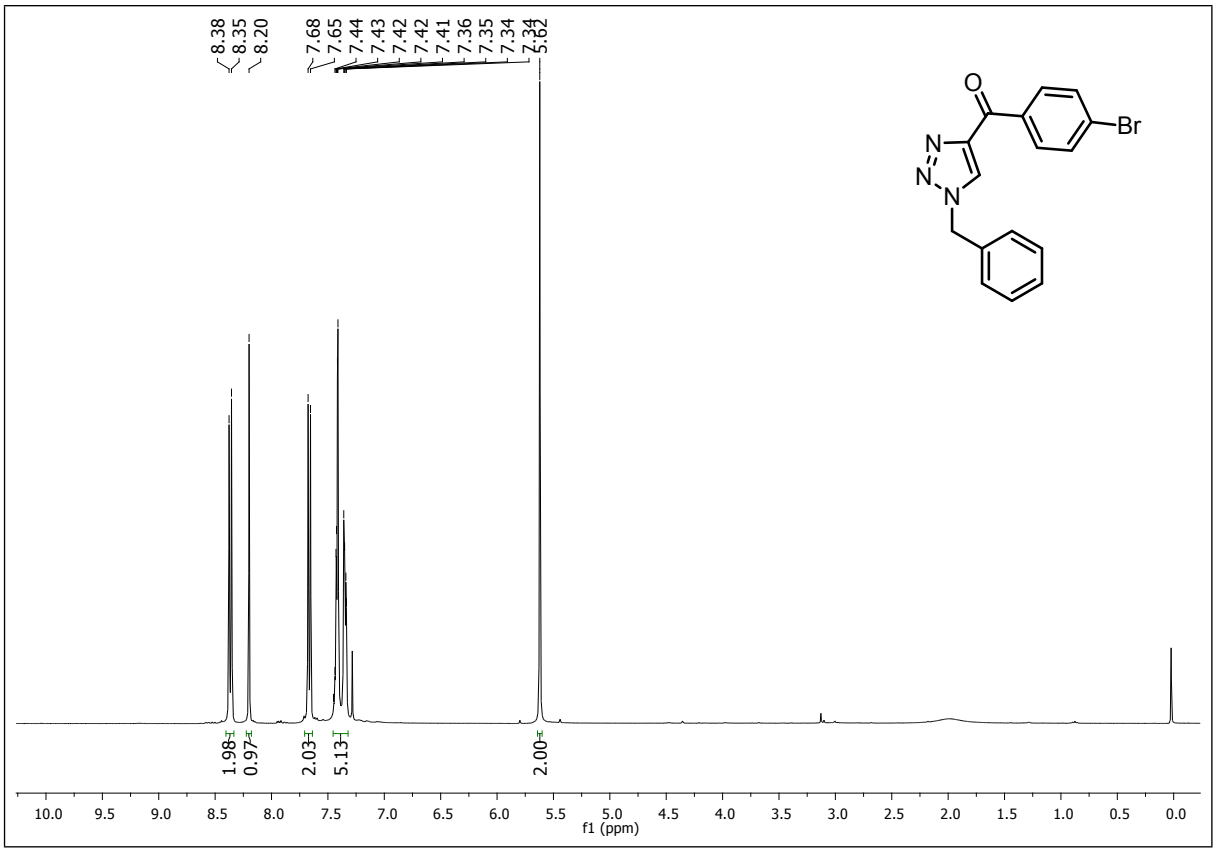


Figure S9.^{1}H NMR spectrum of compound **6d** in $CDCl_3$ at 399.73 MHz.

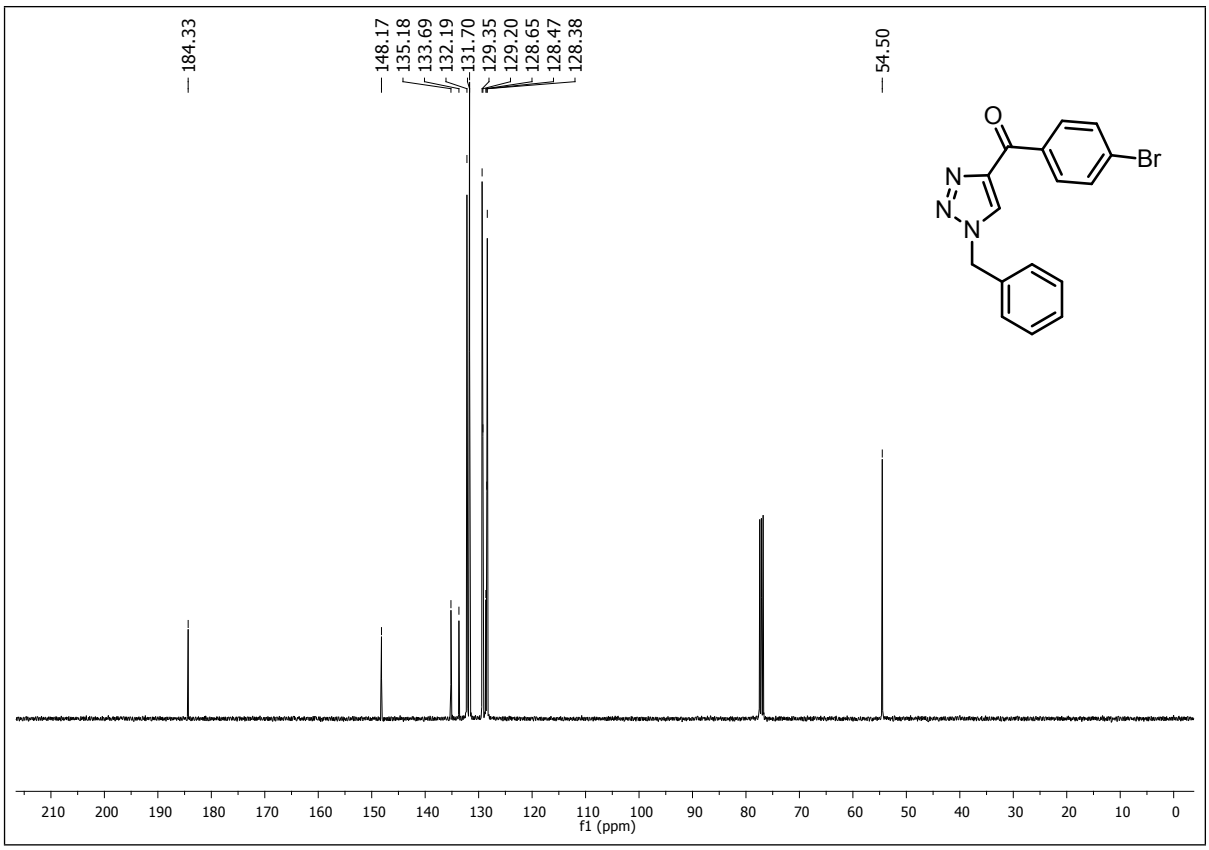


Figure S10.^{13}C NMR spectrum of compound **6d** in $CDCl_3$ at 100.51 MHz.

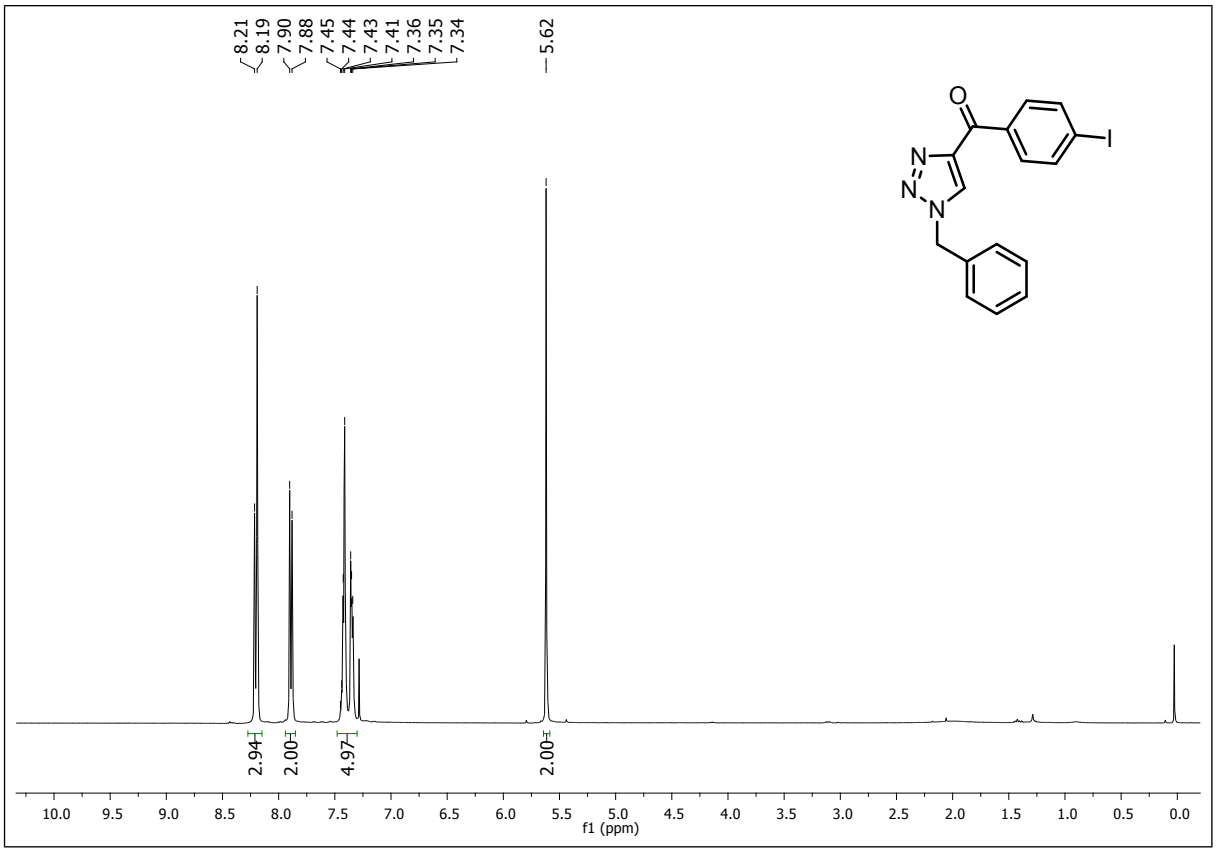


Figure S11. ^{1}H NMR spectrum of compound **6e** in $CDCl_3$ at 399.73 MHz.

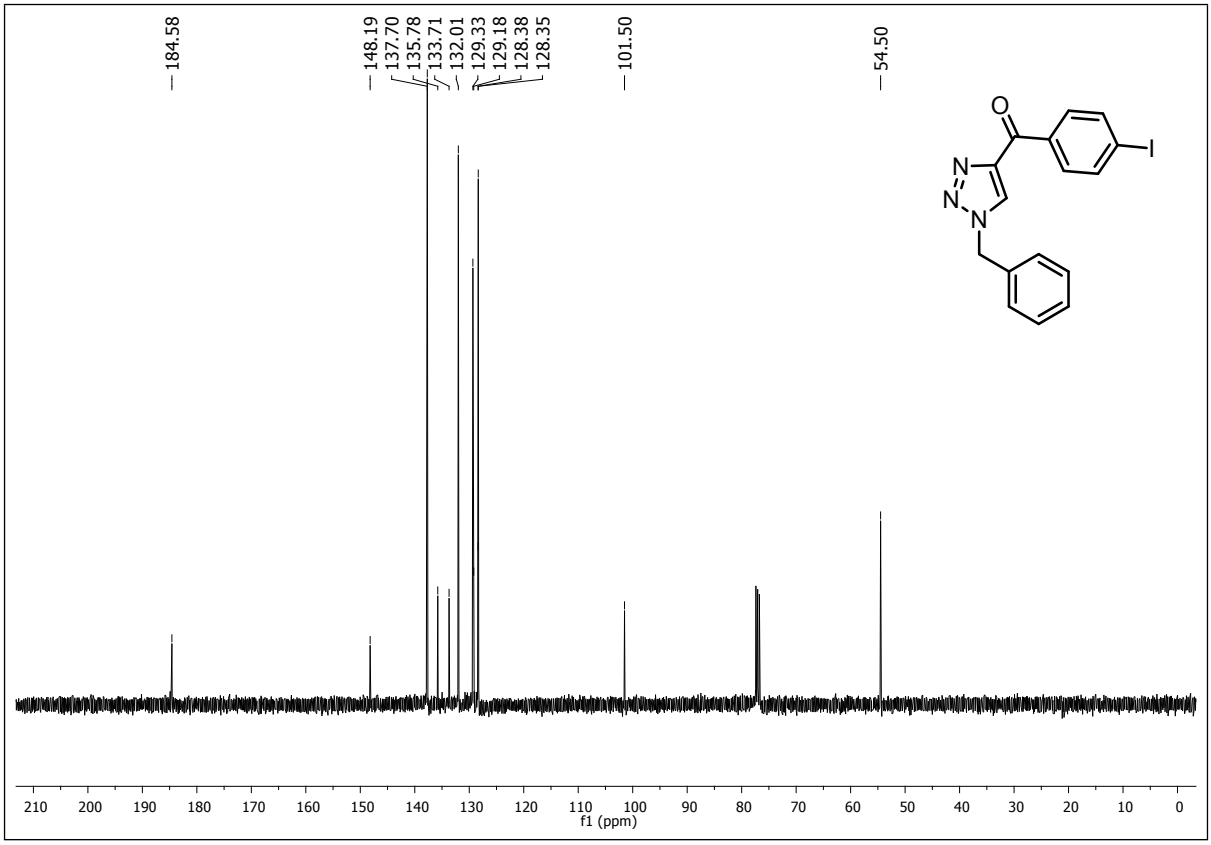


Figure S12. ^{13}C NMR spectrum of compound **6e** in $CDCl_3$ at 100.51 MHz.

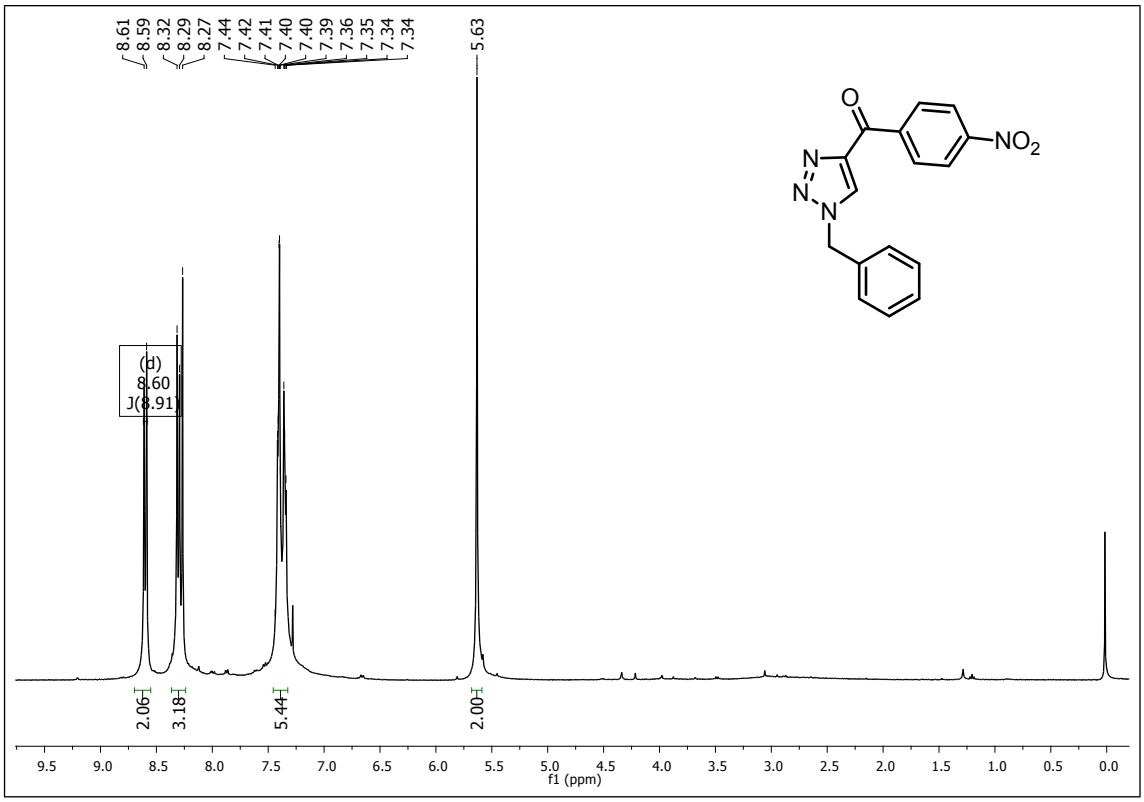


Figure S13.^{1}H NMR spectrum of compound **6f** in $CDCl_3$ at 399.73 MHz.

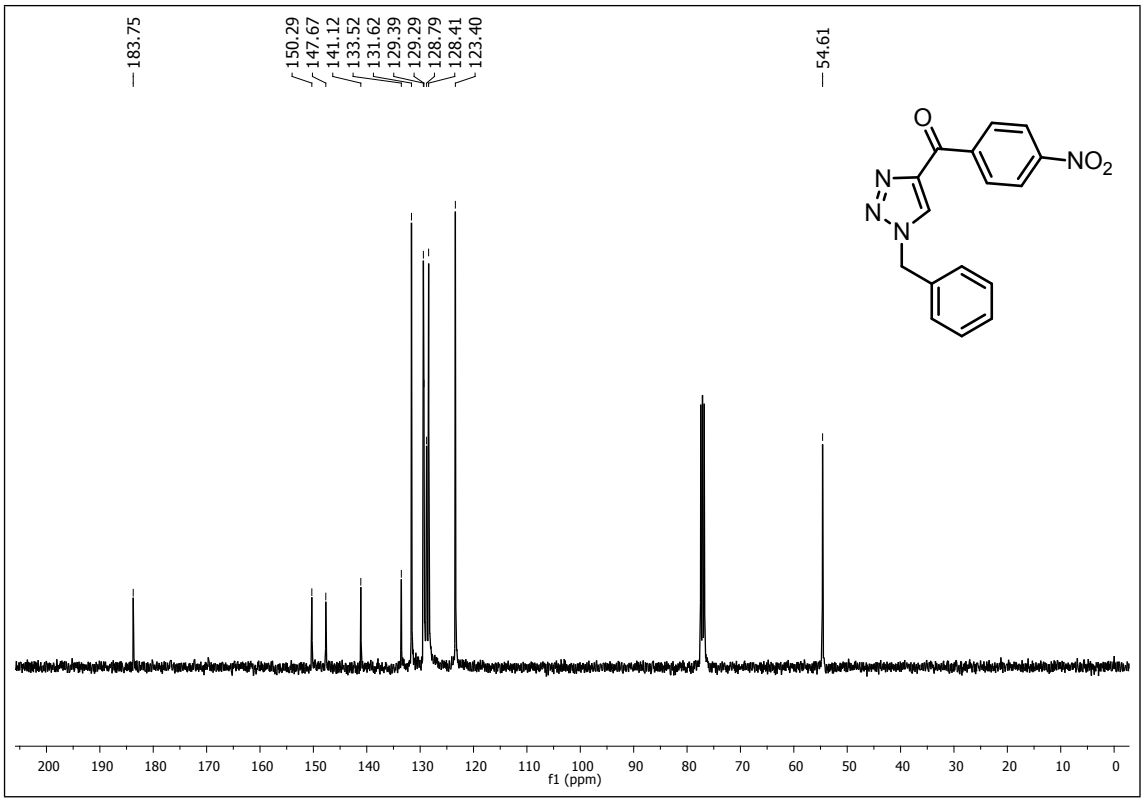


Figure S14.^{13}C NMR spectrum of compound **6f** in $CDCl_3$ at 100.51 MHz.

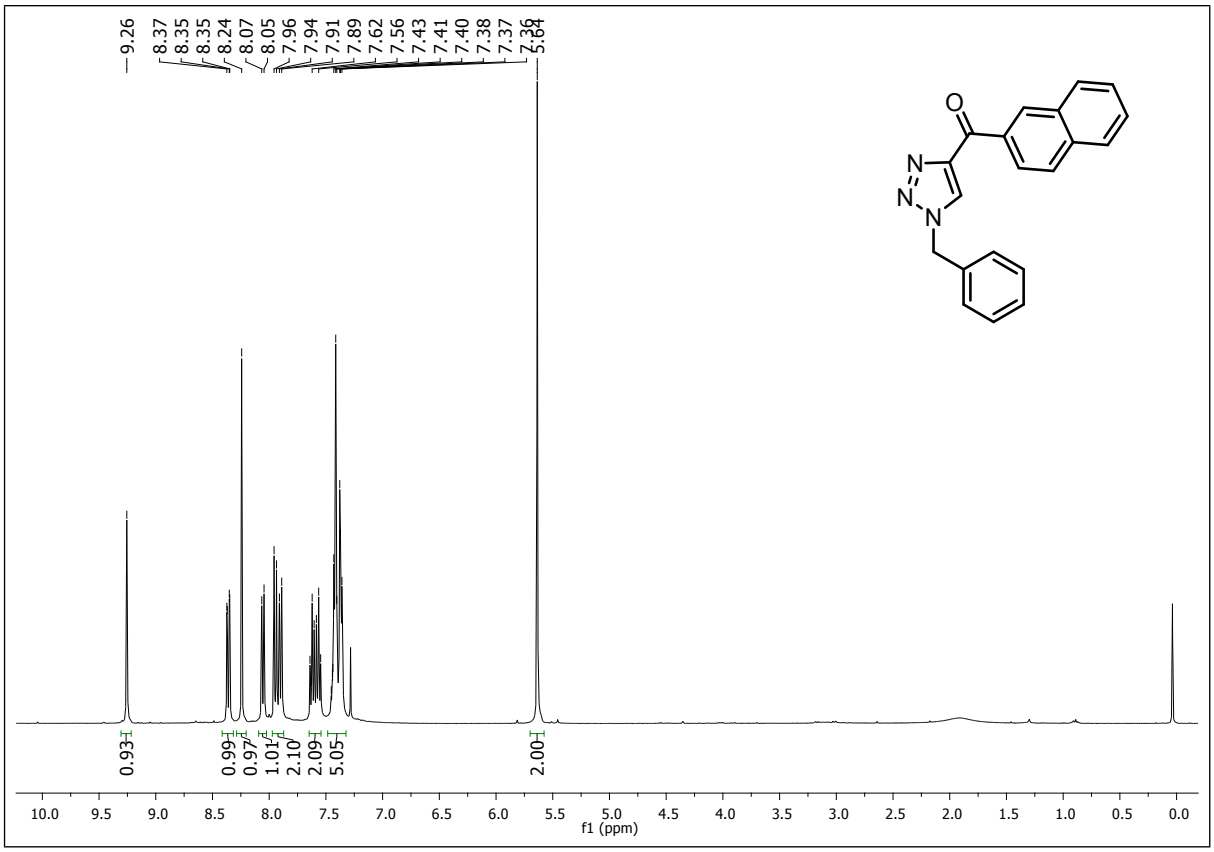


Figure S15.^{1}H NMR spectrum of compound **6g** in $CDCl_3$ at 399.73 MHz.

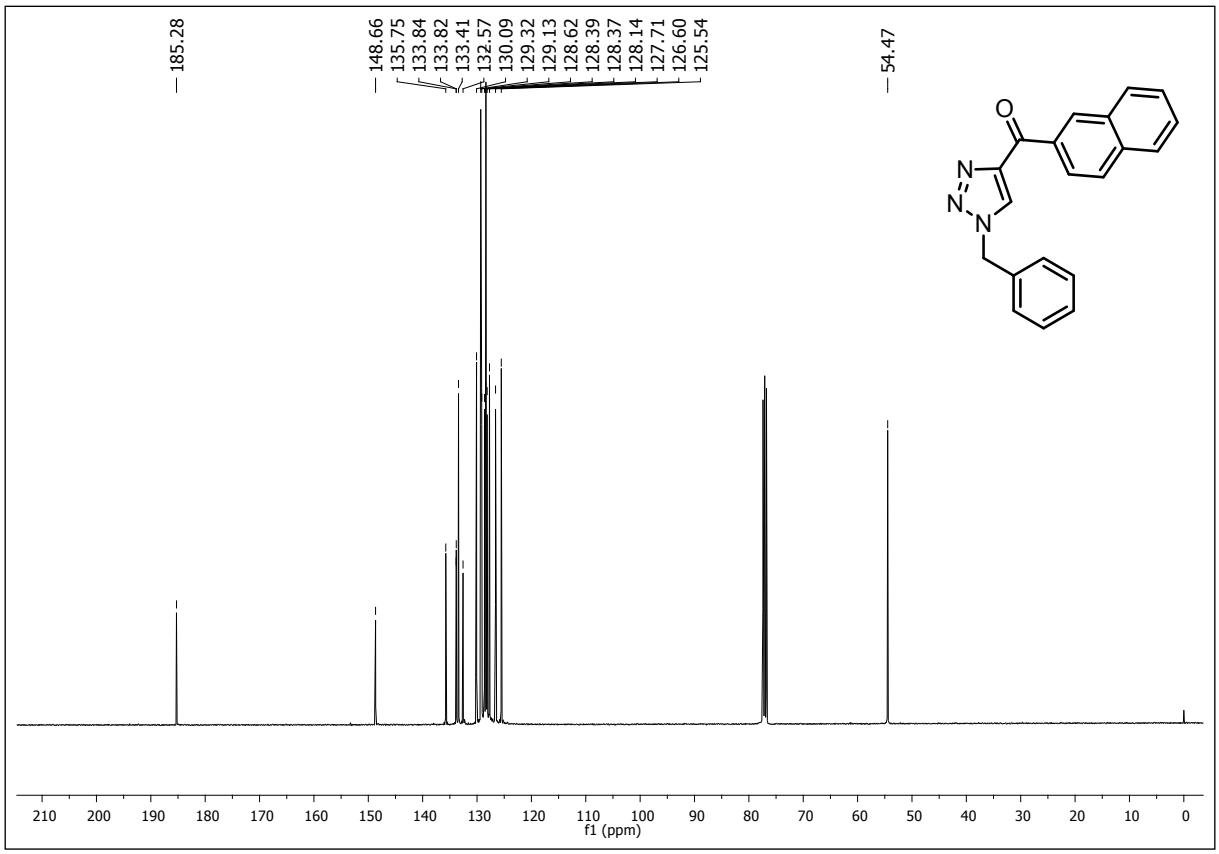


Figure S16.^{13}C NMR spectrum of compound **6g** in $CDCl_3$ at 100.51 MHz.

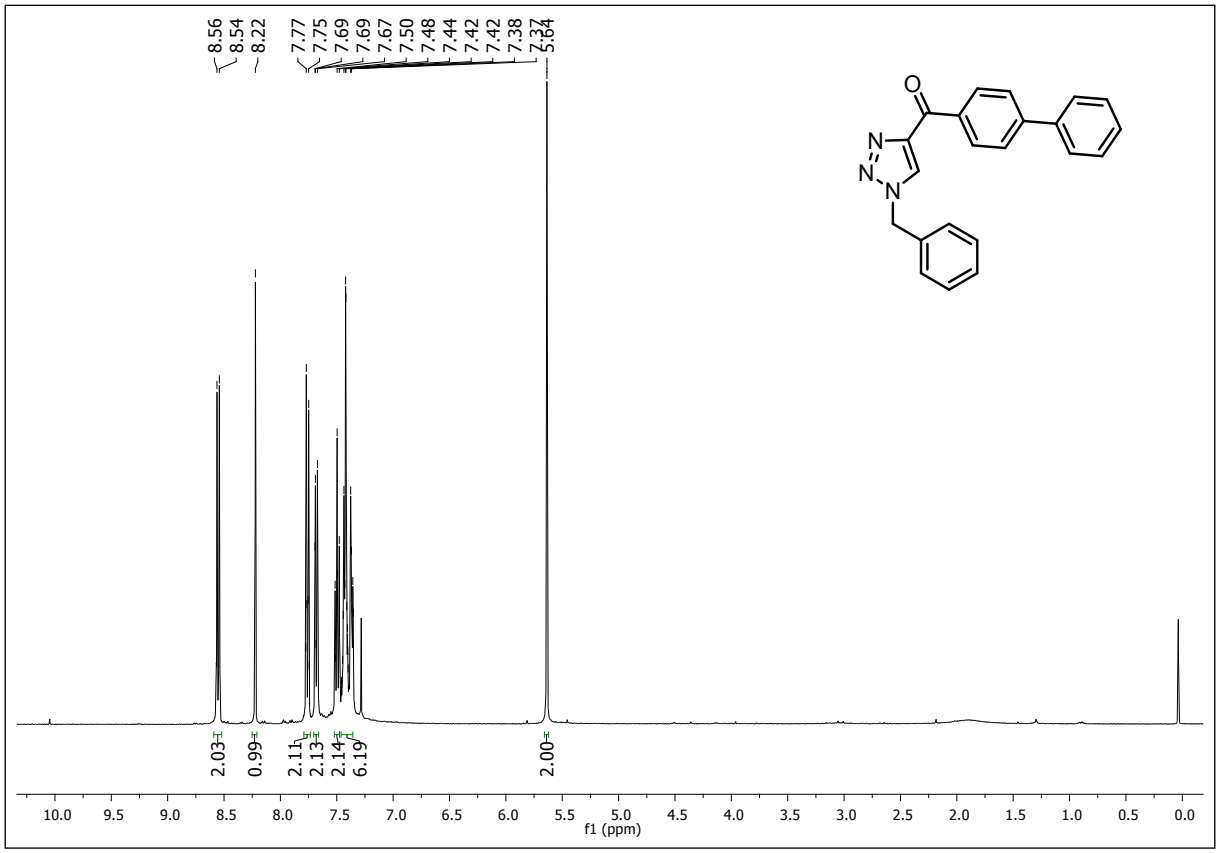


Figure S17.^{1}H NMR spectrum of compound 6**h** in $CDCl_3$ at 399.73 MHz.

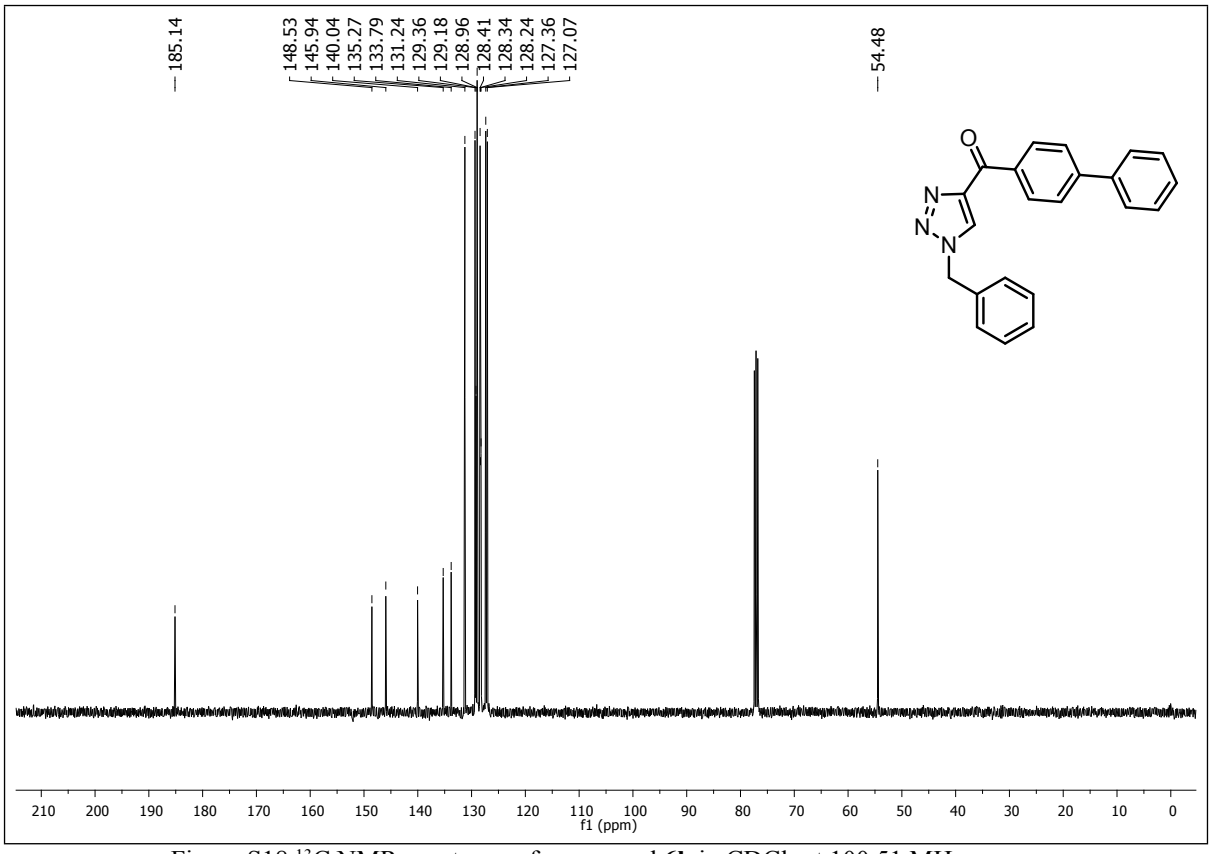


Figure S18.^{13}C NMR spectrum of compound **6h** in $CDCl_3$ at 100.51 MHz.

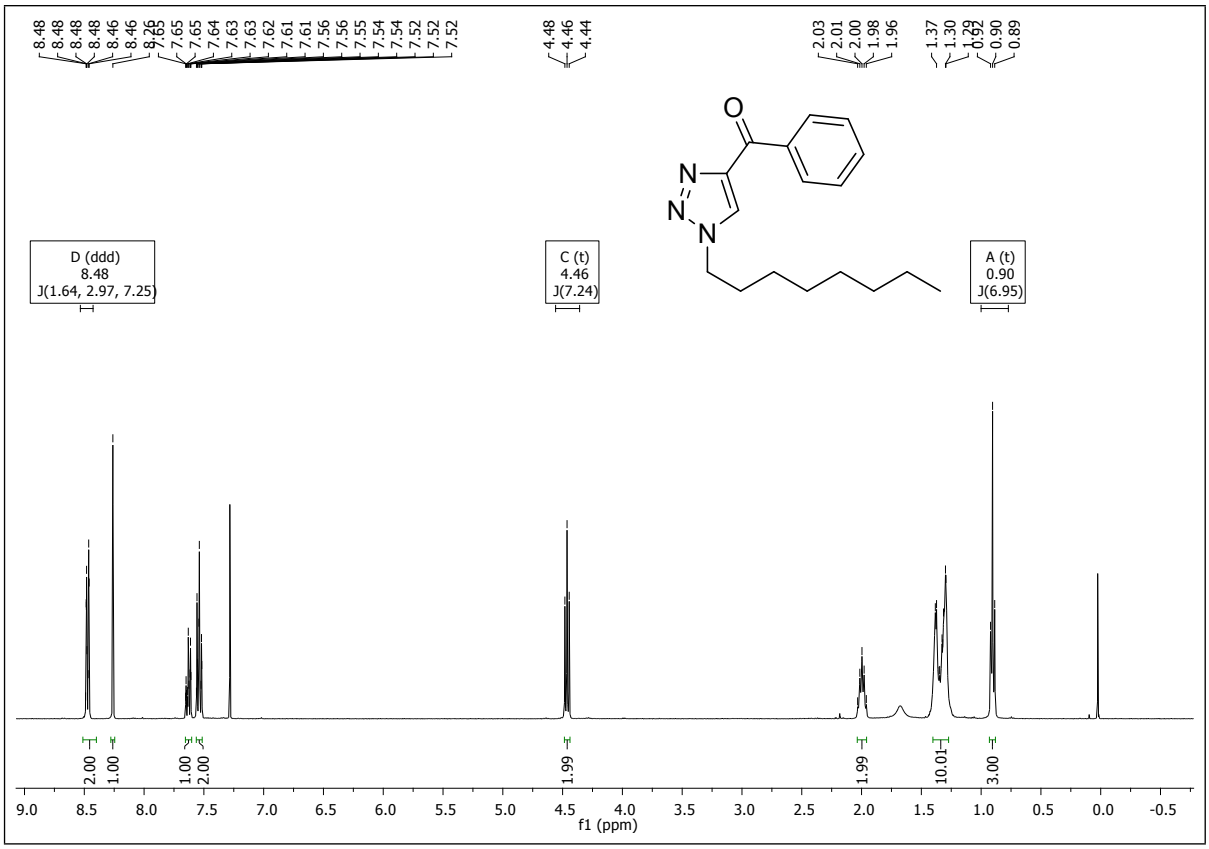


Figure S19.^{1}H NMR spectrum of compound **7a** in $CDCl_3$ at 399.73 MHz.

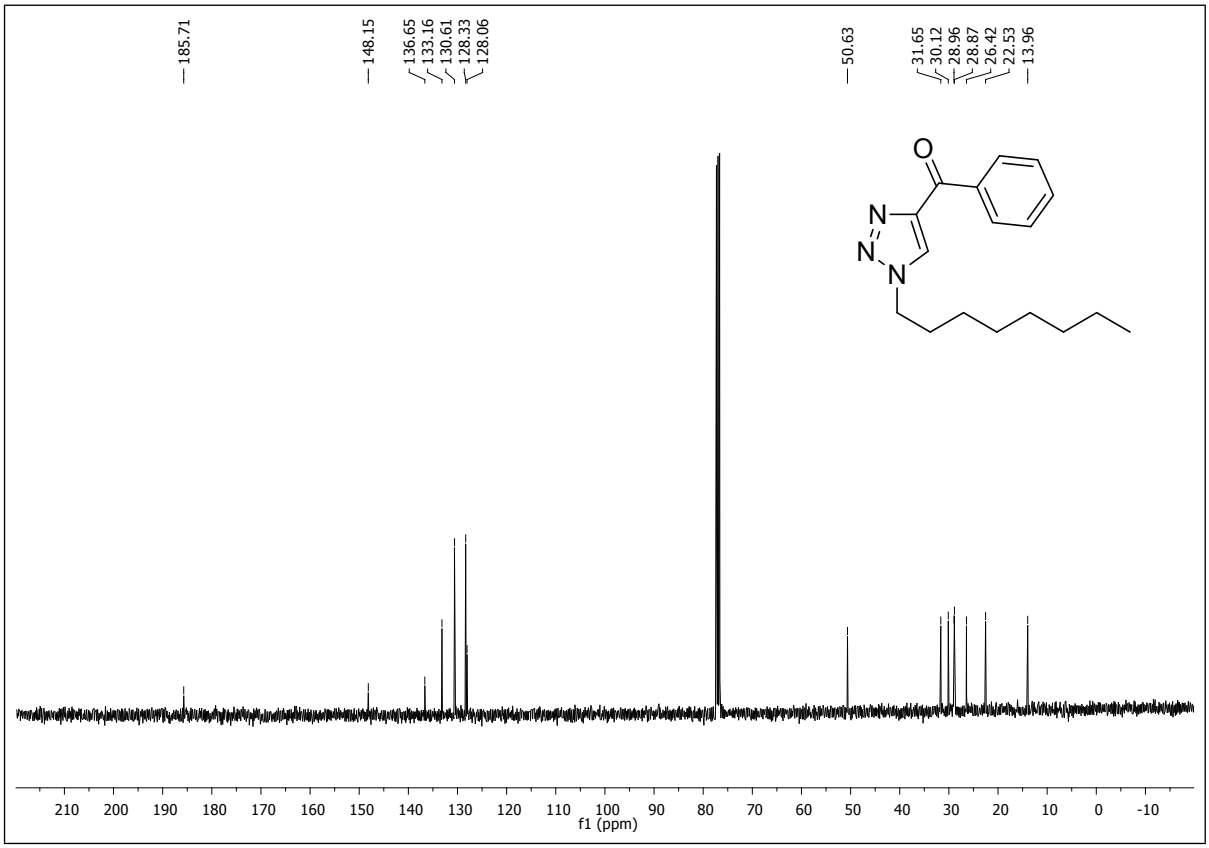


Figure S20.^{13}C NMR spectrum of compound **7a** in $CDCl_3$ at 100.51 MHz.

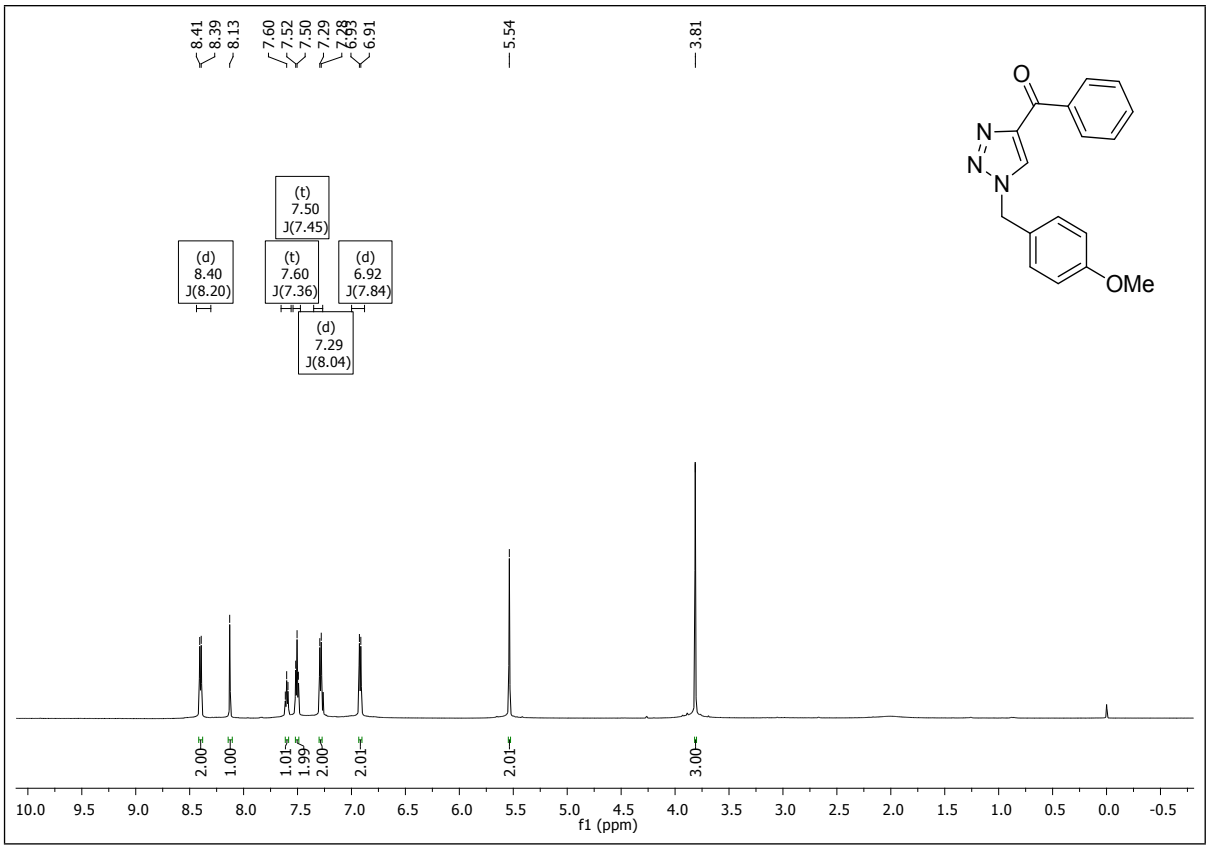


Figure S21.^{1}H NMR spectrum of compound **8a** in $CDCl_3$ at 399.73 MHz.

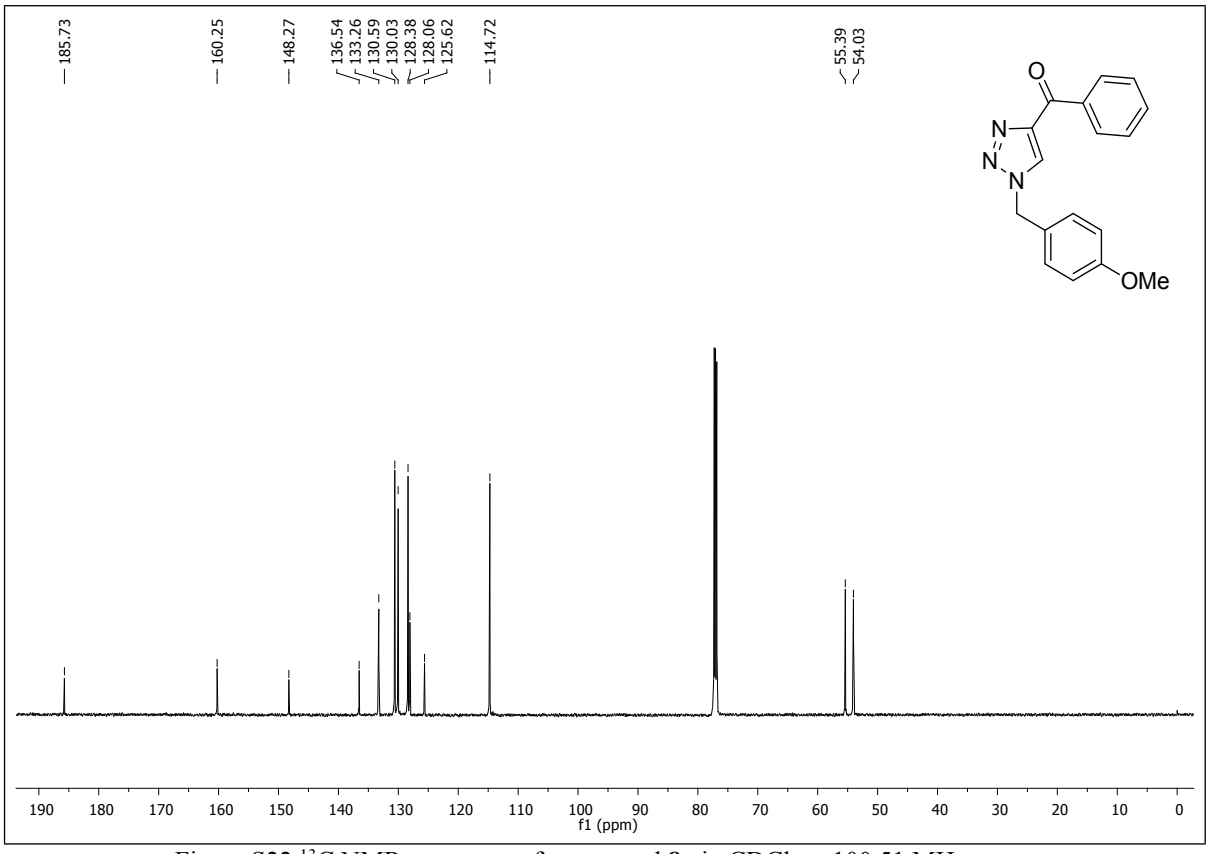


Figure S22.^{13}C NMR spectrum of compound **8a** in $CDCl_3$ at 100.51 MHz.

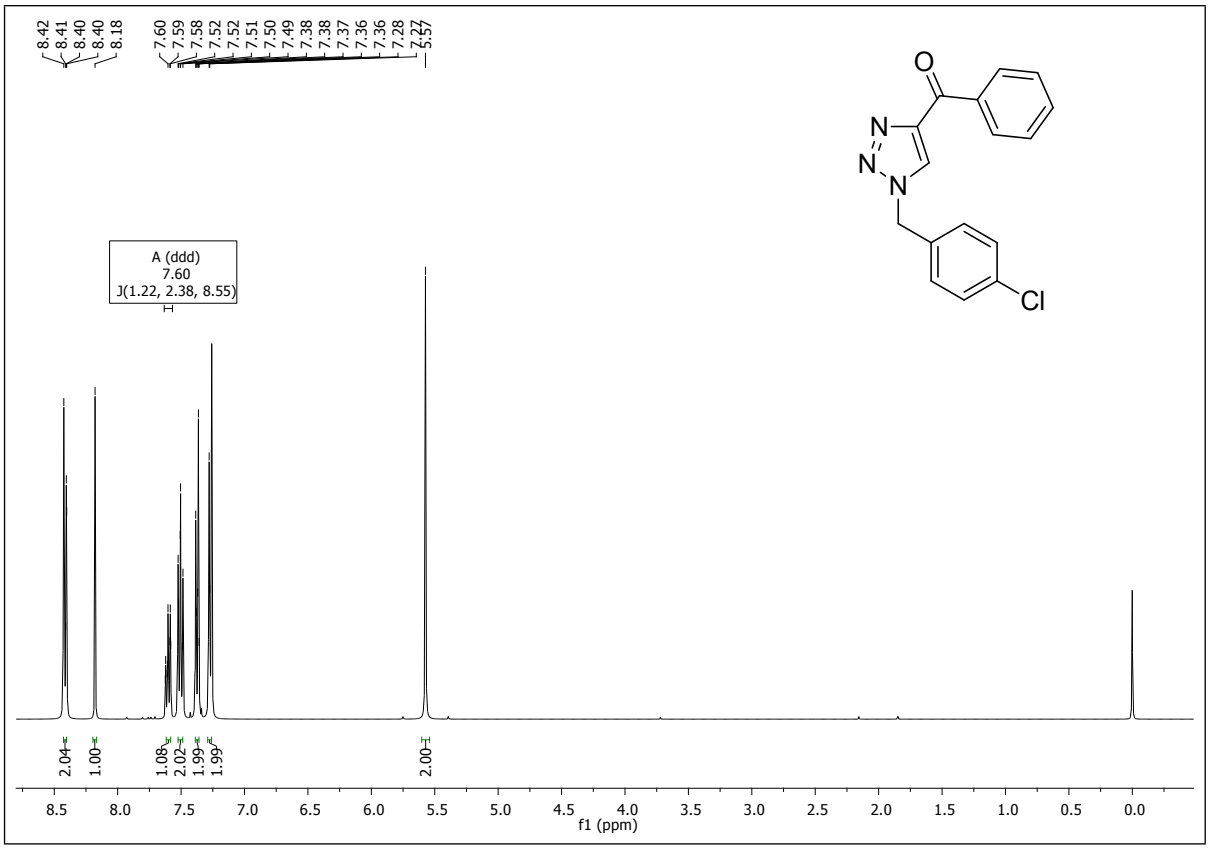


Figure S23.^{1}H NMR spectrum of compound **8a** in $CDCl_3$ at 399.73 MHz.

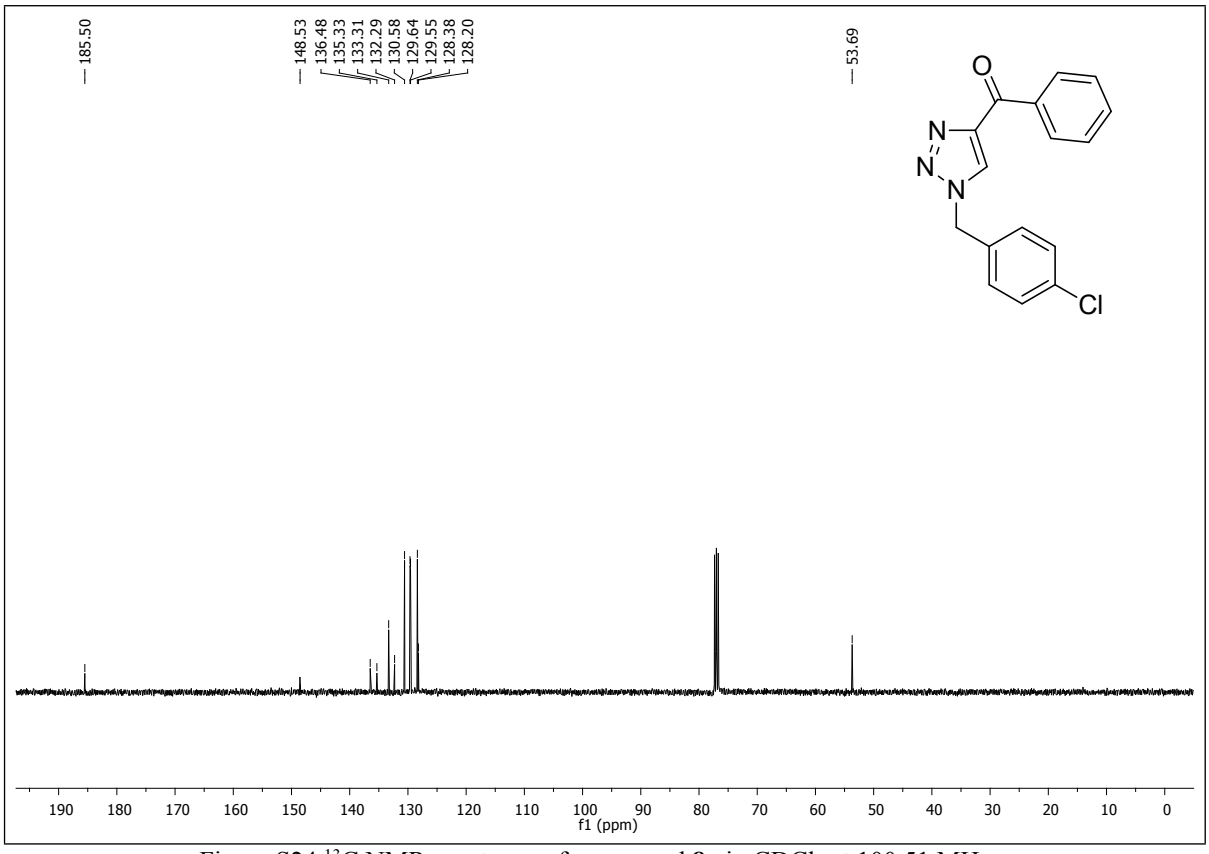


Figure S24.^{13}C NMR spectrum of compound **8a** in $CDCl_3$ at 100.51 MHz.

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