

Supporting Information

Microwave assisted azide-alkyne cycloaddition reaction using polymer supported Cu(I) as a catalytic species: A solvent less approach

Abu Taher, Debkumar Nandi, Rafique Ul Islam, Meenakshi Choudhary, Kaushik Mallick

Department of Chemistry, University of Johannesburg, P.O. Box: 524, Auckland Park 2006, South Africa.

*Corresponding author: kaushikm@uj.ac.za (K. Mallick)

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Characterization of cycloadducts:

1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (3aa):^{2,3} White solid, (233 mg and 226mg; 99% and 96% yields for table 1 and table 2 respectively) mp: 136-138°C (lit.² mp: 128-130°C). Synthesized following the general procedure from azidomethylbenzene **1a** (133 mg, 1.0 mmol), phenylacetylene **2a** (102 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). For multicomponent click reaction: synthesized following the general procedure from benzylbromide **4a** (171 mg, 1.0 mmol), NaN₃ (65 mg, 1.0 mmol), phenylacetylene **2a** (102 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). ¹H NMR (400 MHz, CDCl₃): δ 5.54(s, 2H, -NCH₂), 7.27-7.39(m, 9H, ArH), 7.83(bs, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 54.41, 125.52, 128.04, 128.10, 128.75, 128.79, 129.08, 134.59.

1-Benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (3ab):^{2,3} White solid, (257 mg and 244 mg; 97% and 92% yields for table 1 and table 2 respectively) mp: 154-156°C (lit.² mp: 143-144°C). Synthesized following the general procedure from azidomethylbenzene **1a** (133 mg, 1.0 mmol), 1-ethynyl-4-methoxybenzene **2b** (132 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). For multicomponent click reaction: synthesized following the general procedure from benzylbromide **4a** (171 mg, 1.0 mmol), NaN₃ (65 mg, 1.0 mmol), phenylacetylene 1-ethynyl-4-methoxybenzene **2b** (132 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). ¹H NMR (400 MHz, CDCl₃): δ 4.19(bs, 1H, -OH), 4.74(bs, 2H, -OCH₂), 5.41(s, 2H, -NCH₂), 7.18-7.32(m, 5H, ArH), 7.71(bs, 1H, -C=CH); ¹³C NMR (100 MHz, CDCl₃): δ 54.17, 55.23, 114.15, 118.79, 123.00, 126.98, 127.99, 128.68, 129.06, 134.64, 147.88, 159.59.

(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methanol (3ac):^{1a} White solid, (174 mg, and 163 mg; 92% and 86% yields for table 1 and table 2 respectively) mp: 81-83°C (lit.^{1a} mp: 76-78°C). Synthesized following the general procedure from azidomethylbenzene **1a** (133 mg, 1.0 mmol), prop-2-yn-1-ol **2c** (56 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). For multicomponent click reaction: synthesized following the general procedure from benzylbromide **4a** (171 mg, 1.0 mmol), NaN₃ (65 mg, 1.0 mmol), prop-2-yn-1-ol **2c** (56 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). ¹H NMR (400 MHz, CDCl₃): δ 3.79(s, 3H, -OCH₃), 5.51(s, 2H, -NCH₂), 6.90(d, *J* = 8.8 Hz, 2H, ArH), 7.25-7.28(m, 2H, ArH), 7.32-7.35(m, 3H, ArH), 7.58(bs, 1H, -C=CH), 7.70(d, *J* = 8.4 Hz, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ 54.37, 55.55, 128.01, 128.61, 128.70, 128.92, 129.00, 134.31.

2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)ethanol (3ad):^{1a} White solid, (179 mg, 88% yield) mp: 81-83°C (lit.^{1a} mp: 76-78°C). Synthesized following the general procedure from azidomethylbenzene **1a** (133 mg, 1.0 mmol), but-3-yn-1-ol **2d** (70 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). ¹H NMR (400 MHz, CDCl₃): δ

2.88(t, $J = 6.4$ Hz, 2H), 3.84(bs, 2H) 4.00(s, 1H, -OH), 5.43(s, 2H, -NCH₂), 7.21-7.24(m, 2H, ArH), 7.29-7.34(m, 3H, ArH), 7.38(bs, 1H, -C=CH); ¹³C NMR (100 MHz, CDCl₃): δ 28.60, 33.82, 61.01, 121.17, 127.83, 128.44, 128.83, 134.48, 149.64.

Methyl 1-benzyl-1*H*-1,2,3-triazole-4-carboxylate (3ae): White solid, (195 mg and 185 mg; 90% and 85% yields for table 1 and table 2 respectively) mp: 113-115°C. Synthesized following the general procedure from azidomethylbenzene **1a** (133 mg, 1.0 mmol), methyl propiolate **2e** (84 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). For multicomponent click reaction: synthesized following the general procedure from benzylbromide **4a** (171 mg, 1.0 mmol), NaN₃ (65 mg, 1.0 mmol), methyl propiolate **2e** (84 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). ¹H NMR (400 MHz, CDCl₃): δ 3.89(s, 3H, -OCH₃), 5.55(s, 2H, -NCH₂), 7.25-7.27(m, 2H, ArH), 7.35-7.37(m, 3H, ArH), 7.95(s, 1H, -C=CH); ¹³C NMR (100 MHz, CDCl₃): δ 52.15, 54.46, 127.33, 128.24, 129.13, 129.29, 133.59, 140.28, 161.04.

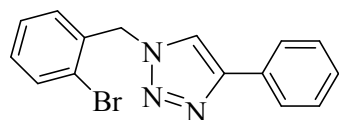
Ethyl 1-benzyl-1*H*-1,2,3-triazole-4-carboxylate (3af): ^{1c,2} White solid, (210 mg; 91% yield) mp: 92-94°C (lit.² mp: 83-85°C). Synthesized following the general procedure from azidomethylbenzene **1a** (133 mg, 1.0 mmol), ethyl propiolate **2f** (98 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). ¹H NMR (400 MHz, CDCl₃): δ 1.30(t, $J = 6.8$ Hz, 3H, CH₃), 4.31(q, $J = 7.2$ Hz, 2H, -CH₂), 5.52(s, 2H, -NCH₂), 7.21-7.25(m, 2H, ArH), 7.29-7.32(m, 3H, ArH), 7.98(s, 1H, -C=CH); ¹³C NMR (100 MHz, CDCl₃): δ 14.07, 54.18, 61.04, 127.25, 128.03, 128.84, 129.04, 133.65, 140.30, 160.46.

1-Benzyl-4-propyl-1*H*-1,2,3-triazole (3ag): ⁴ Light yellow liquid, (185 mg and 161 mg; 92% and 80% yields for table 1 and table 2 respectively). Synthesized following the general procedure from azidomethylbenzene **1a** (133 mg, 1.0 mmol), methyl pent-1-yne **2g** (68 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). For multicomponent click reaction: synthesized following the general procedure from benzylbromide **4a** (171 mg, 1.0 mmol), NaN₃ (65 mg, 1.0 mmol), methyl pent-1-yne **2g** (68 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). ¹H NMR (400 MHz, CDCl₃): δ 0.91(t, $J = 7.2$ Hz, 3H, -CH₃), 1.63 (q, $J = 7.6$ Hz, 2H, -CH₂), 2.63(t, $J = 7.2$ Hz, 2H, -CH₂), 5.44(s, 2H, -NCH₂), 7.20-7.24(m, 3H, ArH), 7.28-7.31(m, 3H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ 13.47, 22.34, 27.36, 53.59, 120.51, 127.60, 128.23, 128.69, 134.77, 148.26.

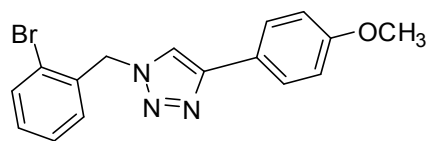
1-Benzyl-4-butyl-1*H*-1,2,3-triazole (3ah): ⁴ Light yellow liquid, (204 mg; 95% yield). Synthesized following the general procedure from azidomethylbenzene **1a** (133 mg, 1.0 mmol), methyl hex-1-yne **2h** (82 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). ¹H NMR (400 MHz, CDCl₃): δ 0.84(t, $J = 7.2$ Hz, 3H, -CH₃), 1.28-1.32(m, 2H, -CH₂), 1.54-1.57(m, 2H, -CH₂), 2.62(t, $J = 8.0$ Hz, 2H, -CH₂), 5.41(s, 2H, -NCH₂), 7.16-7.19(m, 3H,

ArH), 7.26-7.28(m, 3H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ 13.58, 22.09, 25.15, 32.28, 53.02, 120.44, 127.71, 128.34, 128.80, 134.82, 148.57.

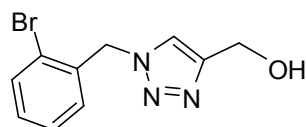
1-(2-Bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole (3ba):^{1c,5} White solid, (308 mg and 295mg; 98% and 94% yields for table1 and table 2 respectively) mp: 110-112°C (lit.^{1c} mp: 103-104°C). Synthesized following the general procedure from 1-(azidomethyl)-2-bromobenzene **1b** (212 mg, 1.0 mmol), phenylacetylene **2a** (102 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). For multicomponent click reaction: synthesized following the general procedure from *o*-bromobenzylbromide (249 mg, 1.0 mmol), NaN_3 (65 mg, 1.0 mmol), phenylacetylene **2a** (102 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). ^1H NMR (400 MHz, CDCl_3): δ 5.01(s, 2H, N- CH_2), 6.88-6.93(m, 2H, ArH), 6.98-7.00(m, 1H, ArH), 7.15-7.20(m, 3H, ArH), 7.24-7.26(m, 1H, ArH), 7.37-7.39(m, 3H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ 52.06, 119.86, 123.27, 125.83, 127.72, 128.77, 128.82, 129.06, 130.05, 130.17, 132.28, 132.92, 148.16.



1-(2-Bromobenzyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (3bb): White solid, (337 mg and 313 mg; 98% and 91% yields for table1 and table 2 respectively) mp: 156-158°C. Synthesized following the general procedure from 1-(azidomethyl)-2-bromobenzene **1b** (212 mg, 1.0 mmol), 1-ethynyl-4-methoxybenzene **2b** (132 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). For multicomponent click reaction: synthesized following the general procedure from *o*-bromobenzylbromide **4b** (249 mg, 1.0 mmol), NaN_3 (65 mg, 1.0 mmol), 1-ethynyl-4-methoxybenzene **2b** (132 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). ^1H NMR (400 MHz, CDCl_3): δ 3.80(s, 3H, - OCH_3), 5.66(s, 2H, - NCH_2), 6.91(d, J = 8.4 Hz, 2H, ArH), 7.13(dd, J = 1.6, 7.6 Hz, 1H, ArH), 7.17-7.22(m, 1H, ArH), 7.26-7.30(m, 1H, ArH), 7.59(dd, J = 1.2, 8.0 Hz, 1H, ArH), 7.68(s, 1H, - $\text{C}=\text{CH}$), 7.72(d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ 53.75, 55.26, 114.14, 119.01, 123.08, 123.29, 126.96, 128.18, 130.12, 130.30, 133.11, 134.25, 159.54.

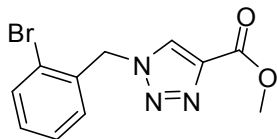


1-(2-Bromobenzyl)-1*H*-1,2,3-triazol-4-yl) methanol (3bc): White solid, (241 mg, and 222 mg; 90% and 83% yields for table1 and table 2 respectively) mp: 124-126°C. Synthesized following the general procedure from 1-(azidomethyl)-2-bromobenzene **1b** (212 mg, 1.0 mmol), prop-2-yn-1-ol **2c** (56 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). For multicomponent click reaction: synthesized following the general procedure from *o*-bromobenzylbromide **4b** (249 mg, 1.0 mmol), NaN_3 (65 mg, 1.0 mmol), prop-2-yn-1-ol **2c** (56 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-pPDA catalyst (5mg of 0.05 mol% Cu). ^1H NMR (400 MHz, CDCl_3): δ 4.01(bs, 1H, -OH), 4.72(s, 2H, - OCH_2), 5.59(s, 2H, - NCH_2), 7.11(d, J = 7.2 Hz,



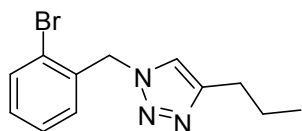
¹H, ArH), 7.16-7.19(m, 1H, ArH), 7.24-7.27(m, 1H, ArH), 7.55-7.58(m, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ 53.89, 56.00, 123.45, 128.19, 130.13, 133.15, 133.85.

Methyl 1-(2-bromobenzyl)-1*H*-1,2,3-triazole-4-carboxylate (3be): White solid, (263 mg and 248 mg; 89% and 84% yields for table 1 and table 2 respectively) mp: 120-122°C. Synthesized following the general



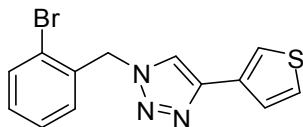
procedure from 1-(azidomethyl)-2-bromobenzene **1b** (212 mg, 1.0 mmol), methyl propiolate **2e** (84 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). For multicomponent click reaction: synthesized following the general procedure from *o*-bromobenzylbromide **4b** (249 mg, 1.0 mmol), NaN₃ (65 mg, 1.0 mmol), methyl propiolate **2e** (84 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). ¹H NMR (400 MHz, CDCl₃): δ 3.90(s, 3H, -CH₃), 5.68(s, 2H, -NCH₂), 7.20-7.24(m, 2H, ArH), 7.28-7.33(m, 1H), 7.59-7.61(m, 1H, ArH), 8.06 (s, 1H, -C=CH); ¹³C NMR (100 MHz, CDCl₃): δ 52.21, 54.16, 123.77, 127.64, 128.35, 130.55, 130.80, 130.88, 133.10, 133.41, 161.03.

1-(2-Bromobenzyl)-4-propyl-1*H*-1,2,3-triazole (3bg): Light yellow liquid, (258 mg and 218 mg; 92% and 78% yields for table 1 and table 2 respectively).



Synthesized following the general procedure from 1-(azidomethyl)-2-bromobenzene **1b** (212 mg, 1.0 mmol), methyl pent-1-yne **2g** (68 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). For multicomponent click reaction: synthesized following the general procedure from *o*-bromobenzylbromide **4b** (249 mg, 1.0 mmol), NaN₃ (65 mg, 1.0 mmol), methyl pent-1-yne **2g** (68 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). ¹H NMR (400 MHz, CDCl₃): δ 0.78(t, *J* = 7.6 Hz, 3H, -CH₃), 1.46-1.56 (m, 2H, -CH₂-CH₂-CH₃), 2.51 (t, *J* = 7.6 Hz, 2H, -CH₂-CH₂-CH₃), 5.43 (s, 2H, -NCH₂), 6.88(dd, *J* = 1.2, 7.6 Hz, 1H, ArH), 7.02(dt, *J* = 1.6, 7.6 Hz, 1H, ArH), 7.10 (dt, *J* = 1.2, 7.6 Hz, 1H, ArH), 7.24 (bs, 1H, C=CH), 7.41 (dd, *J* = 1.2, 8.0 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ 13.35, 22.21, 27.21, 53.10, 120.85, 122.73, 127.67, 129.48, 129.71, 132.58, 134.12, 148.08.

1-(2-Bromobenzyl)-4-(thiophen-3-yl)-1*H*-1,2,3-triazole (3bi): White solid, (307 mg 96% yield) mp: 104-106°C. Synthesized following the general



procedure from 1-(azidomethyl)-2-bromobenzene **1b** (212 mg, 1.0 mmol), 3-ethynylthiophene **2i** (108 mg, 1.0 mmol), triethylamine (0.14 mL, 1 mmol) and Cu(I)-*p*PDA catalyst (5mg of 0.05 mol% Cu). ¹H NMR (400 MHz, CDCl₃): δ 5.65(s, 2H, -NCH₂), 7.12(dd, *J* = 1.6, 7.6 Hz, 1H, ArH), 7.20(dt, *J* = 1.6, 7.6 Hz, 1H, ArH), 7.27(dt, *J* = 1.2, 7.6 Hz, 1H, ArH), 7.33(dd, *J* = 2.8, 5.2 Hz, 1H, ArH), 7.40(dd, *J* = 1.2, 5.2 Hz, 1H, ArH), 7.59(dd, *J* = 1.2, 7.6 Hz, 1H, ArH), 7.65(dd, *J* = 1.2, 2.8 Hz, 1H, ArH), 7.66(s, 1H, -C=CH); ¹³C NMR (100 MHz, CDCl₃): δ 53.73, 119.62, 121.14, 123.29, 125.70, 126.29, 128.18, 130.11, 130.33, 131.54, 133.11, 134.10, 144.19.

Experimental References:

- (1) (a) F. Alonso, Y. Moglie, G. Radivoy, M. Yus, *Eur. J. Org. Chem.*, **2010**, 1875–1884;
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NMR Spectra

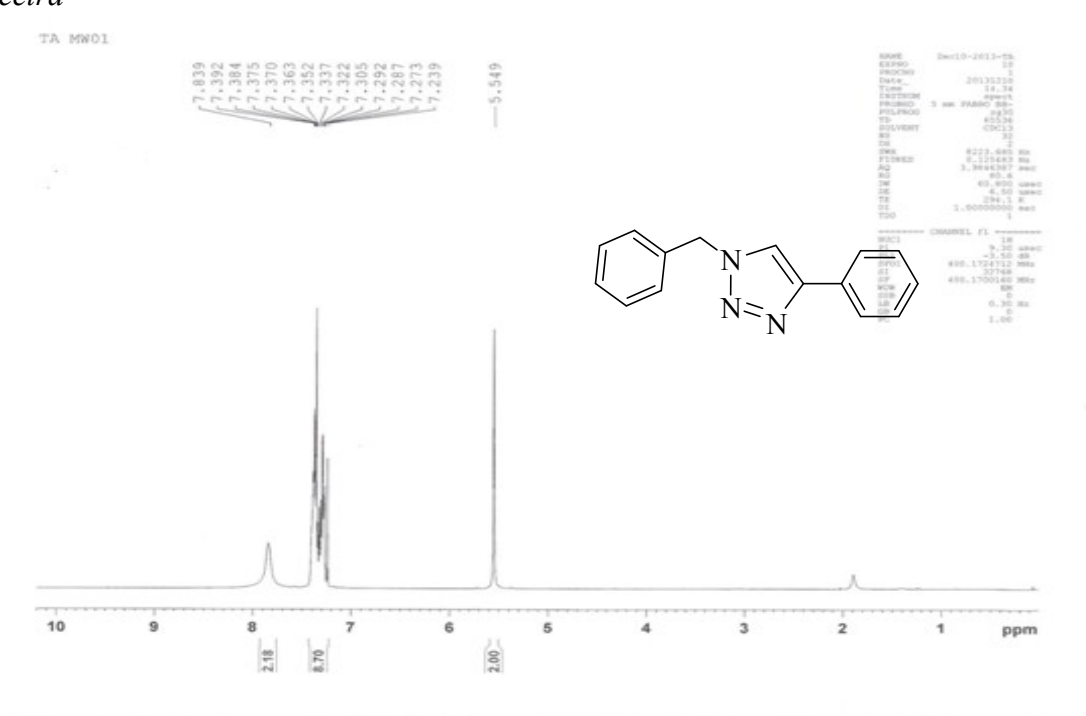


Figure S1. ¹H NMR spectrum of 3aa.

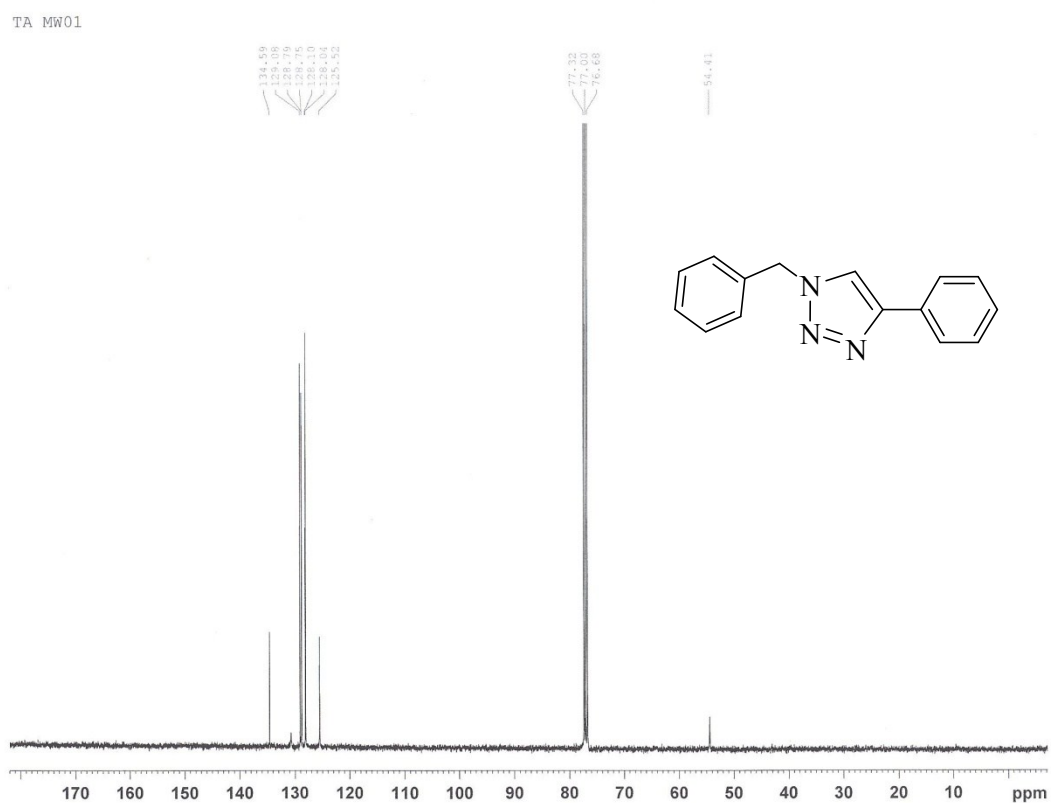


Figure S2. ^{13}C NMR spectrum of **3aa**.

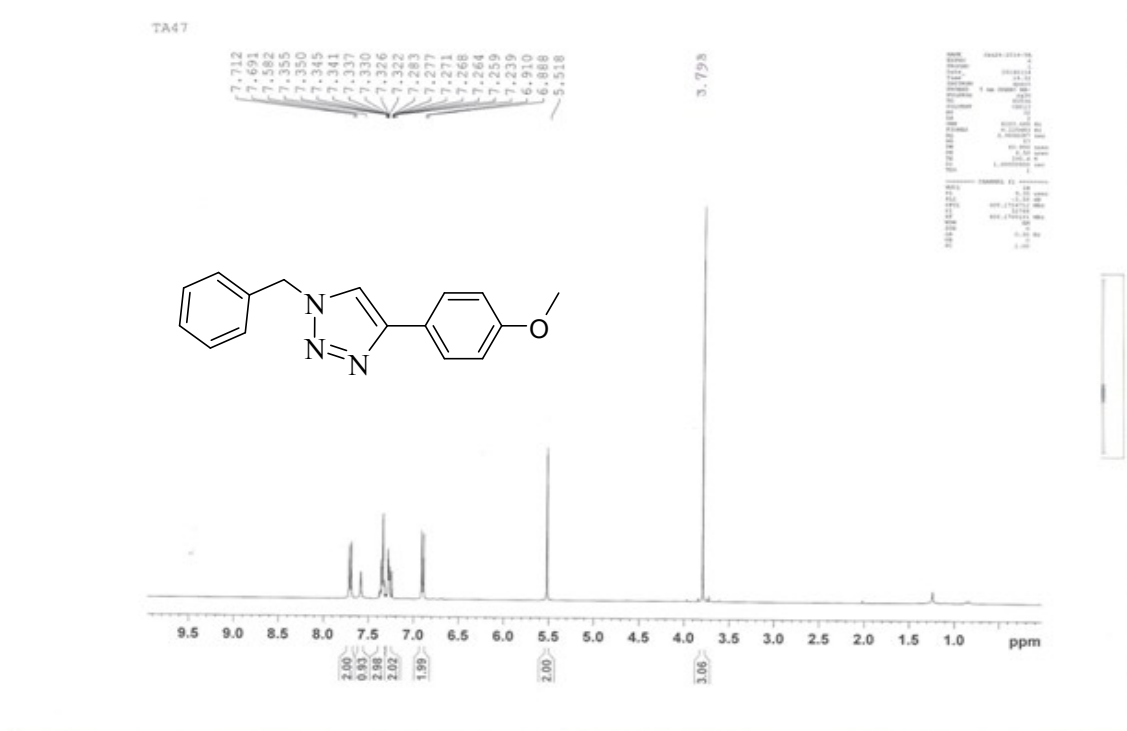
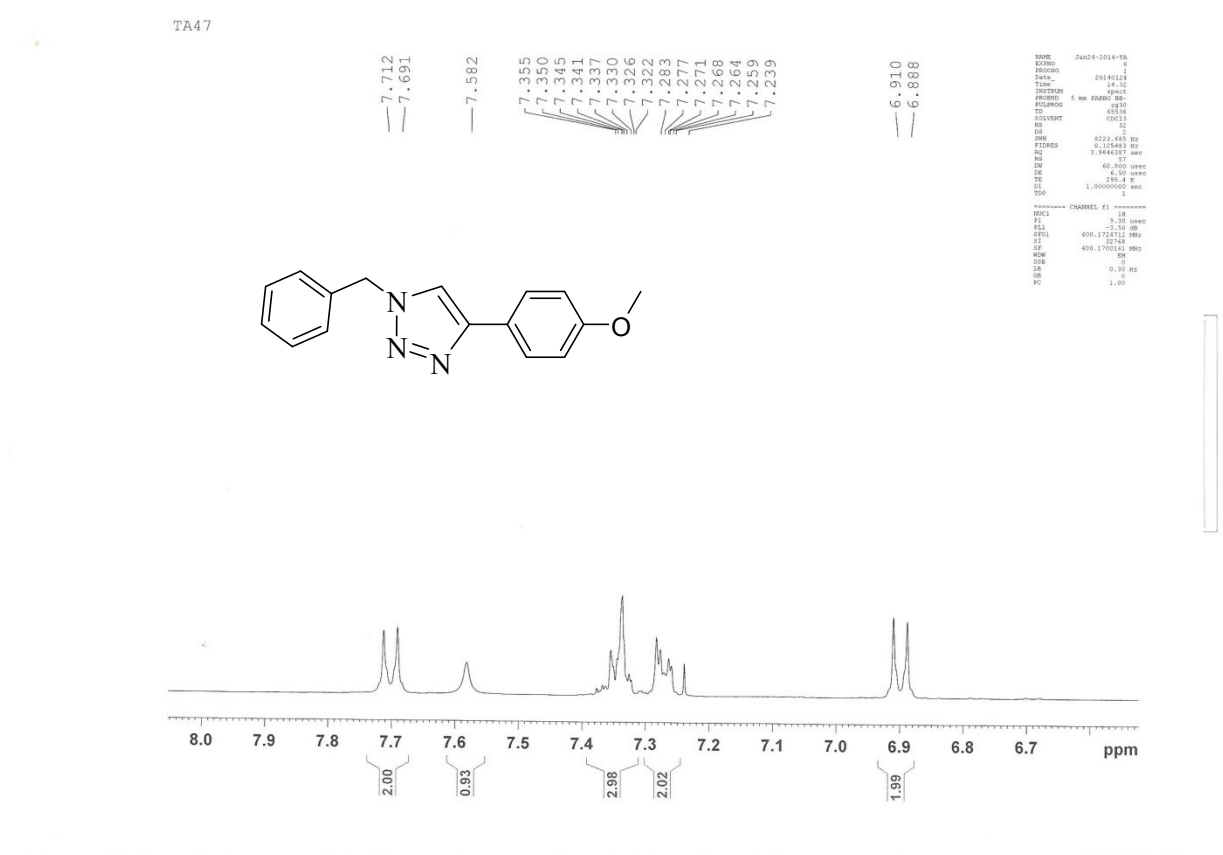


Figure S3. ^1H NMR spectrum of **3ab**.



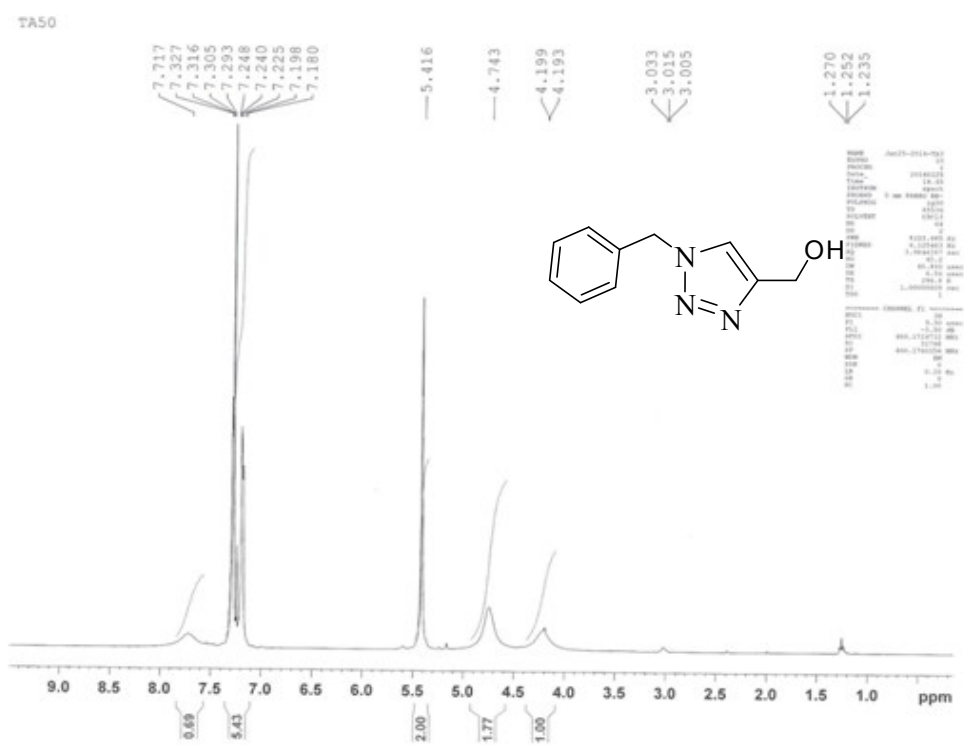


Figure S5. ^1H NMR spectrum of **3ac**.

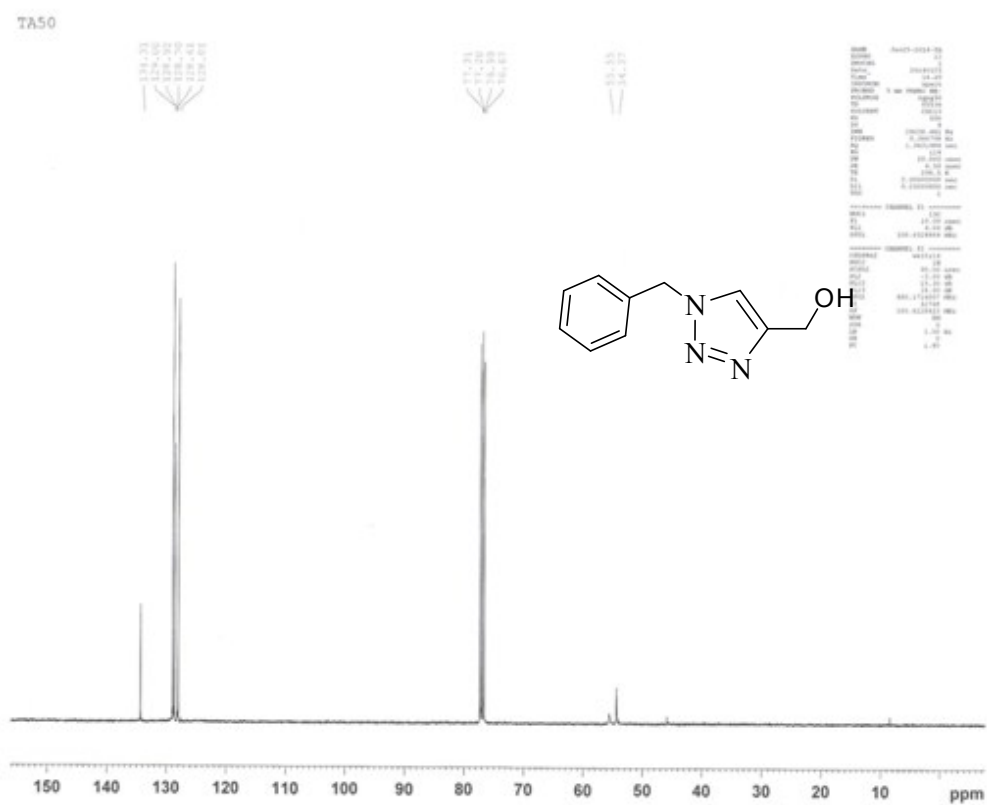


Figure S6. ^{13}C NMR spectrum of **3ac**.

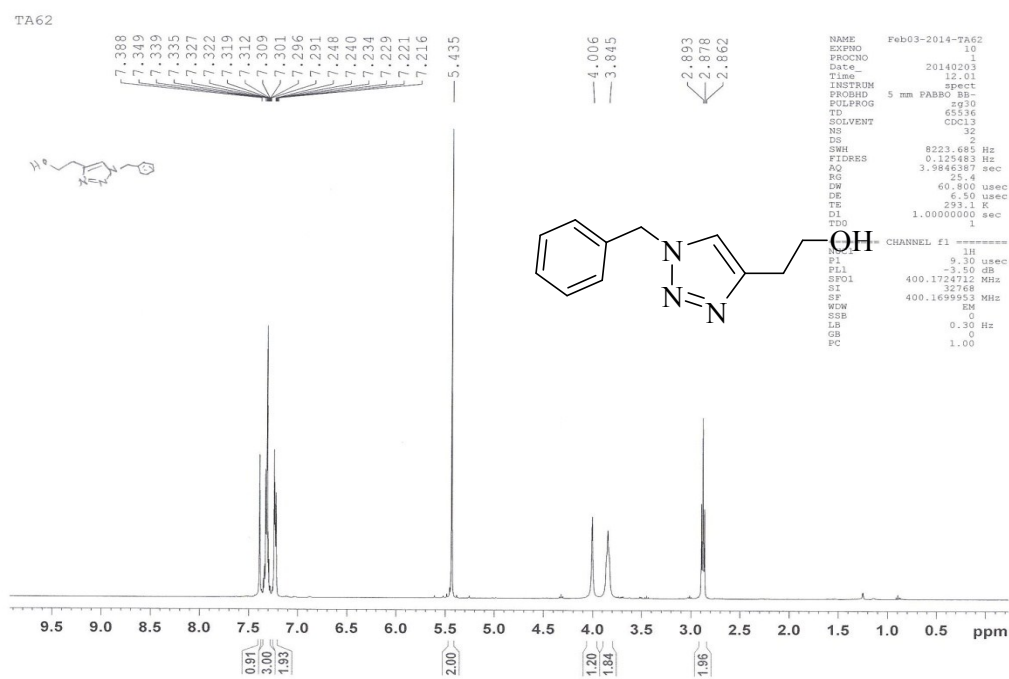


Figure S7. ¹H NMR spectrum of 3ad.

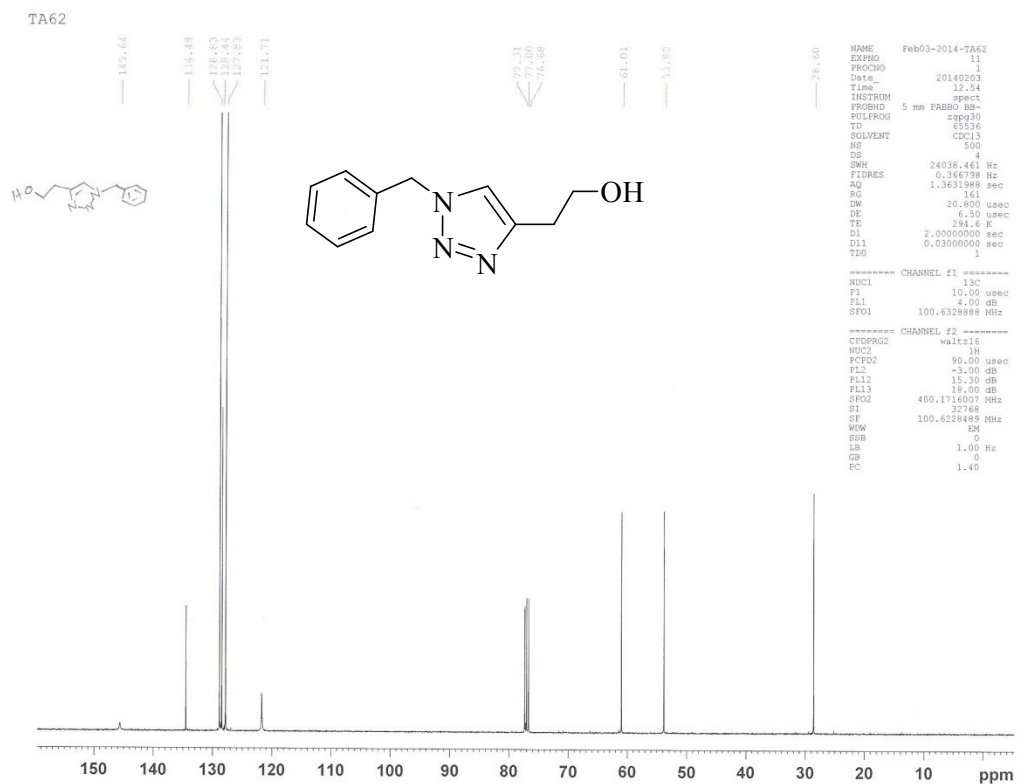


Figure S8. ^{13}C NMR spectrum of **3ad**.

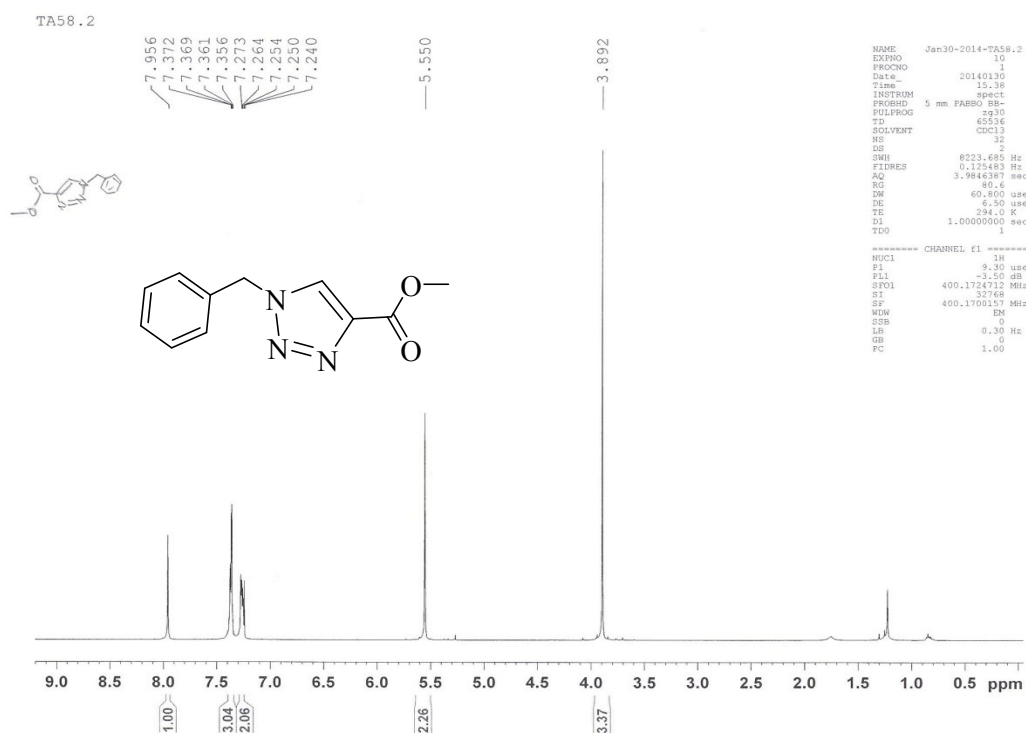


Figure S9. ^1H NMR spectrum of **3ae**.

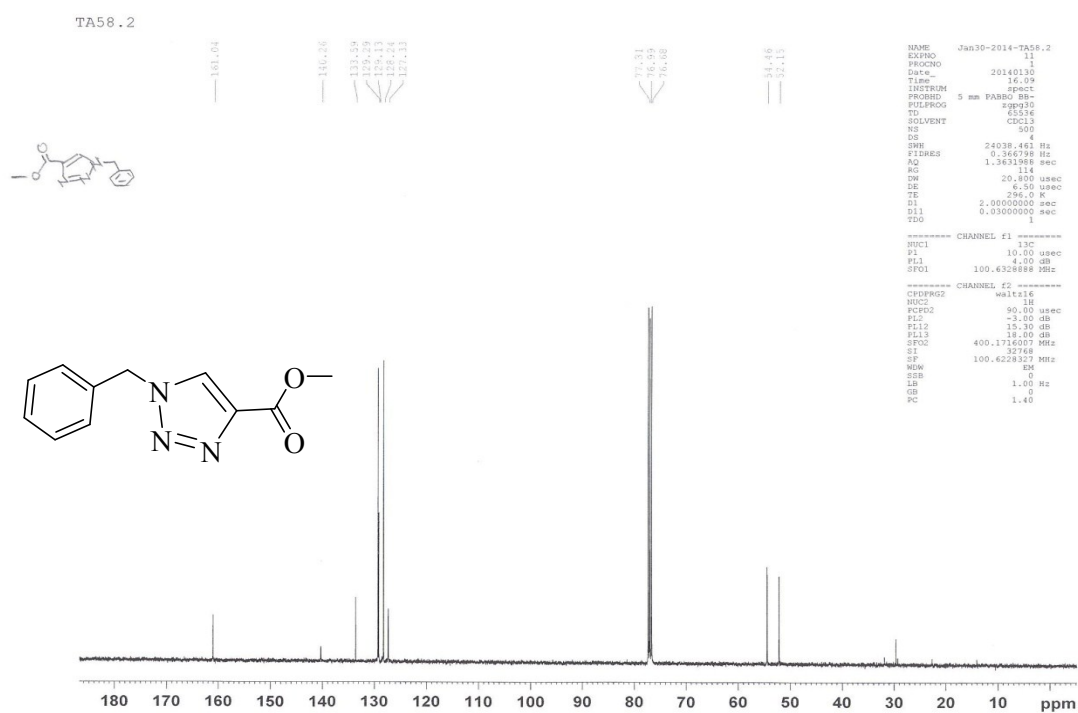


Figure S10. ^{13}C NMR spectrum of **3ae**.

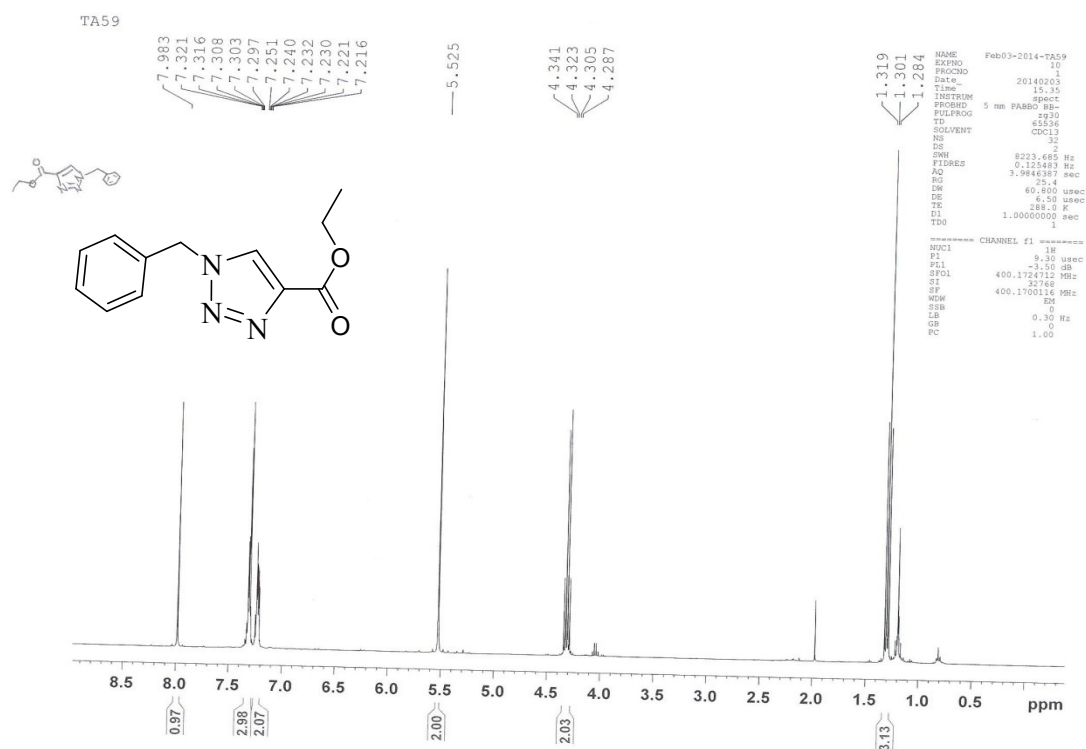


Figure S11. ^1H NMR spectrum of **3af**.

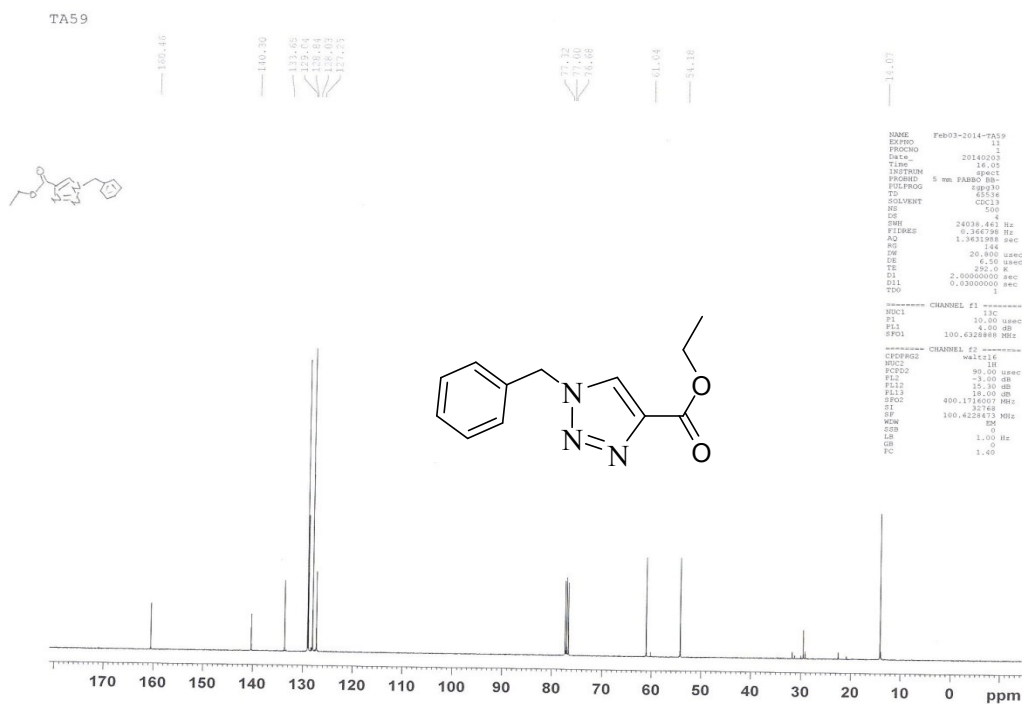


Figure S12. ^{13}C NMR spectrum of **3af**.

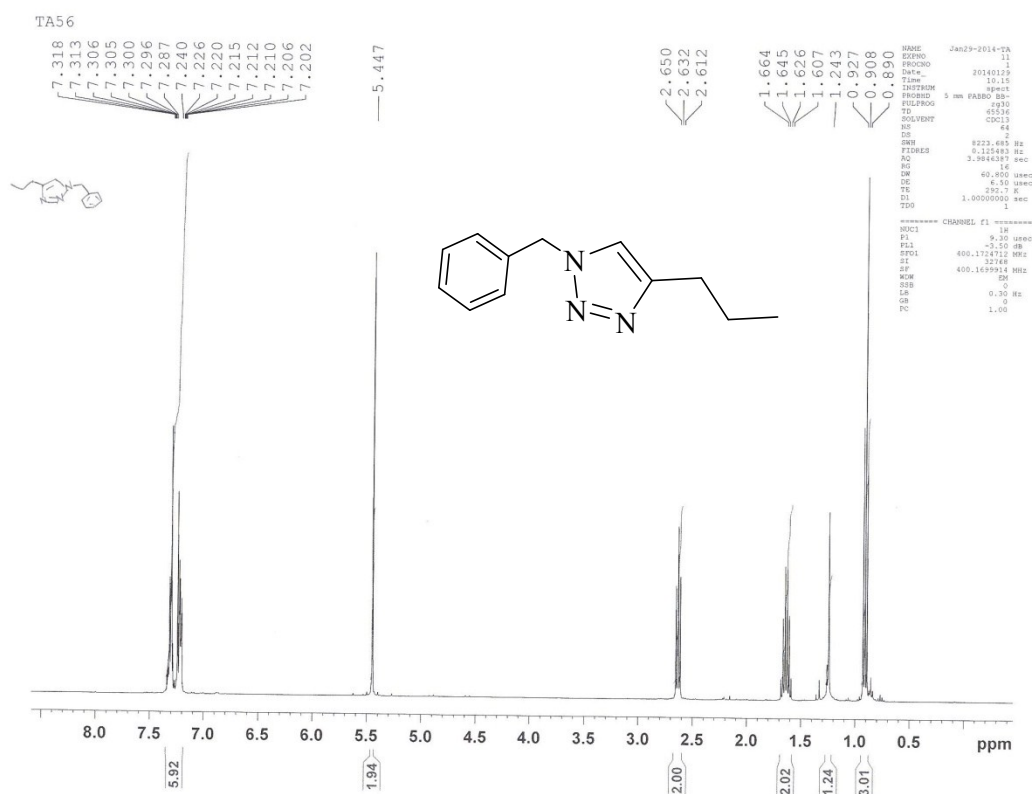


Figure S13. ^1H NMR spectrum of **3ag**.

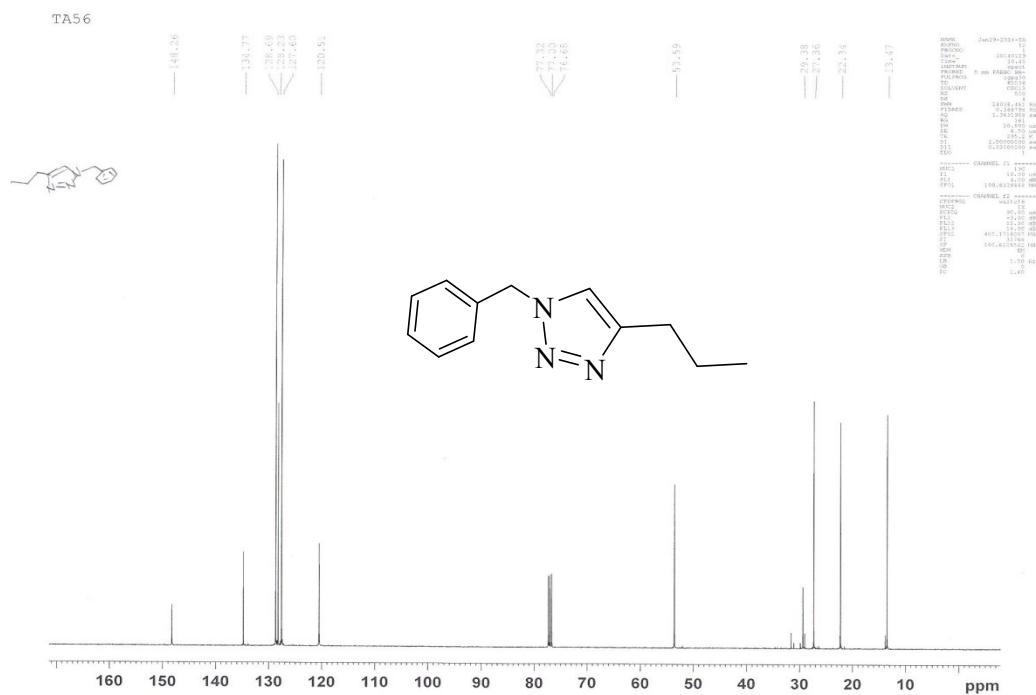


Figure S14. ^{13}C NMR spectrum of **3ag**.

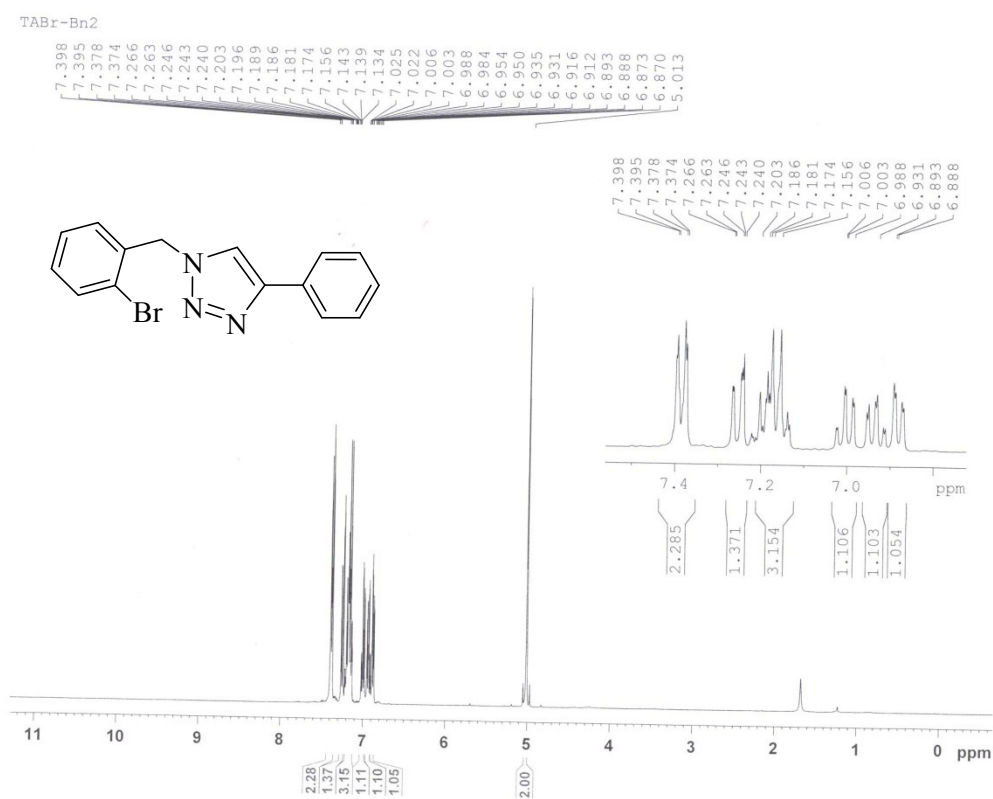


Figure S17. ¹H NMR spectrum of 3ba.

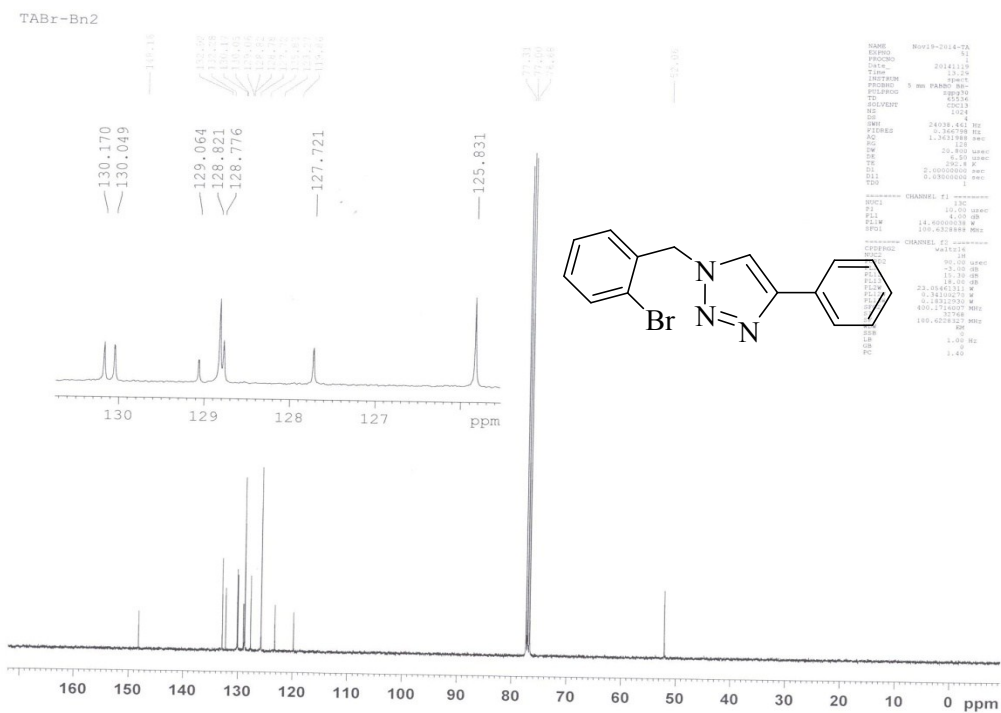


Figure S18. ^{13}C NMR spectrum of **3ba**.

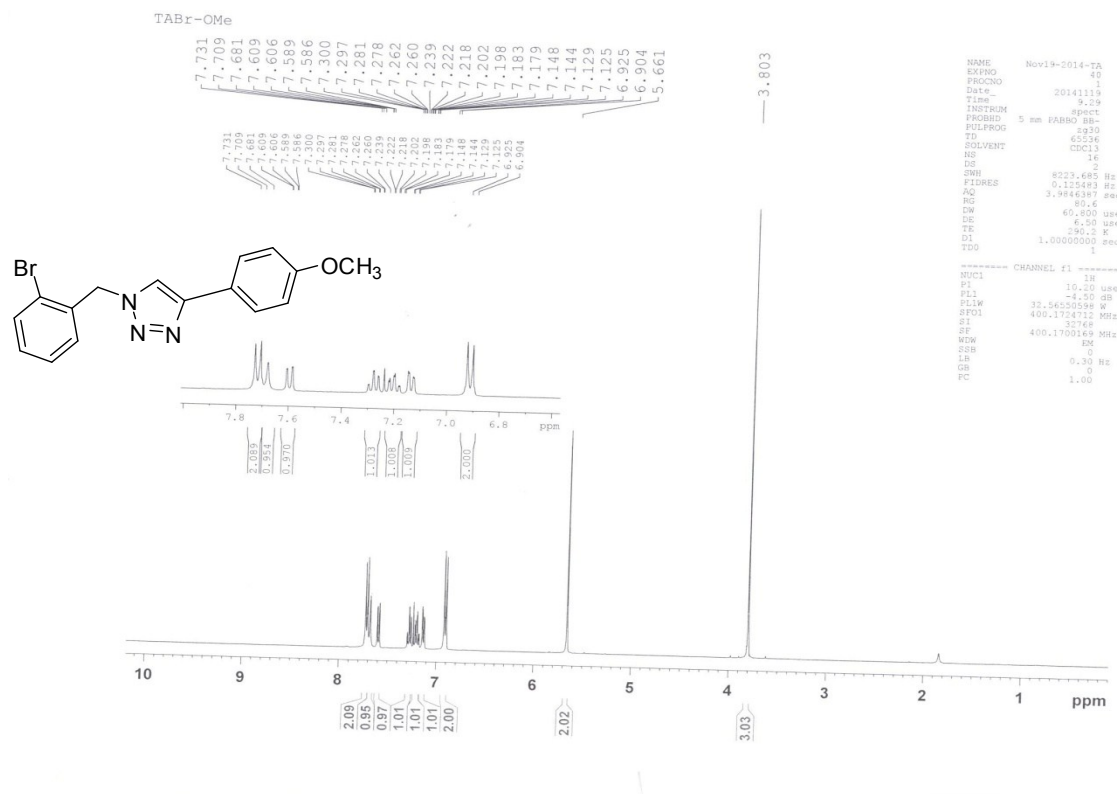


Figure S19. ^1H NMR spectrum of **3bb**.

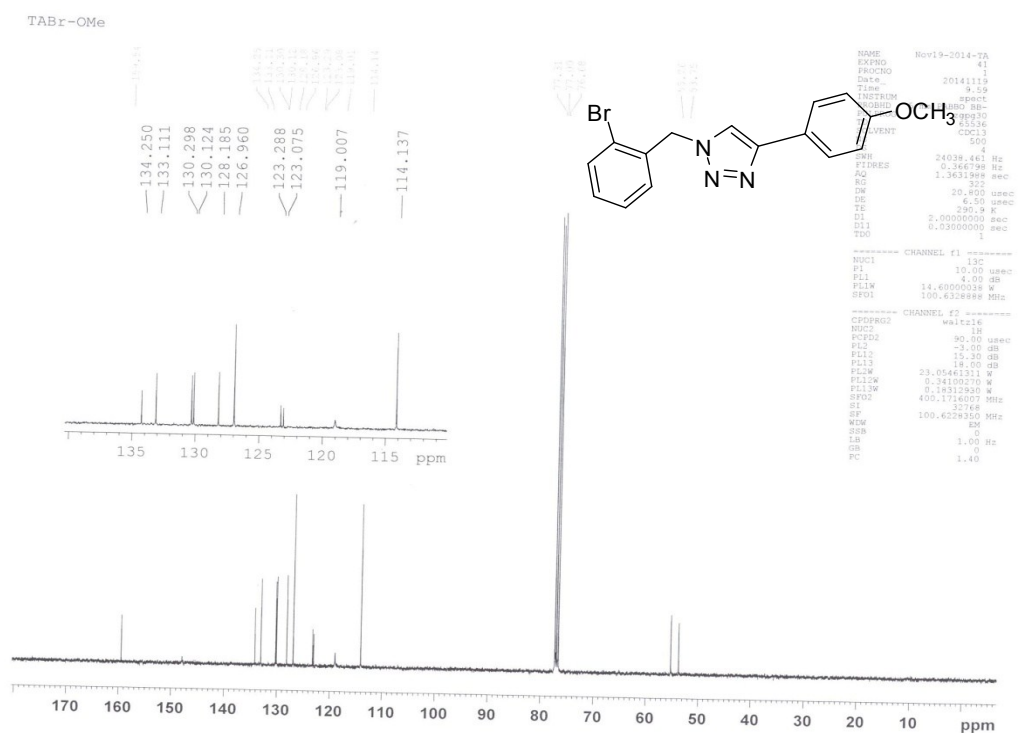


Figure S20. ^{13}C NMR spectrum of **3bb**.

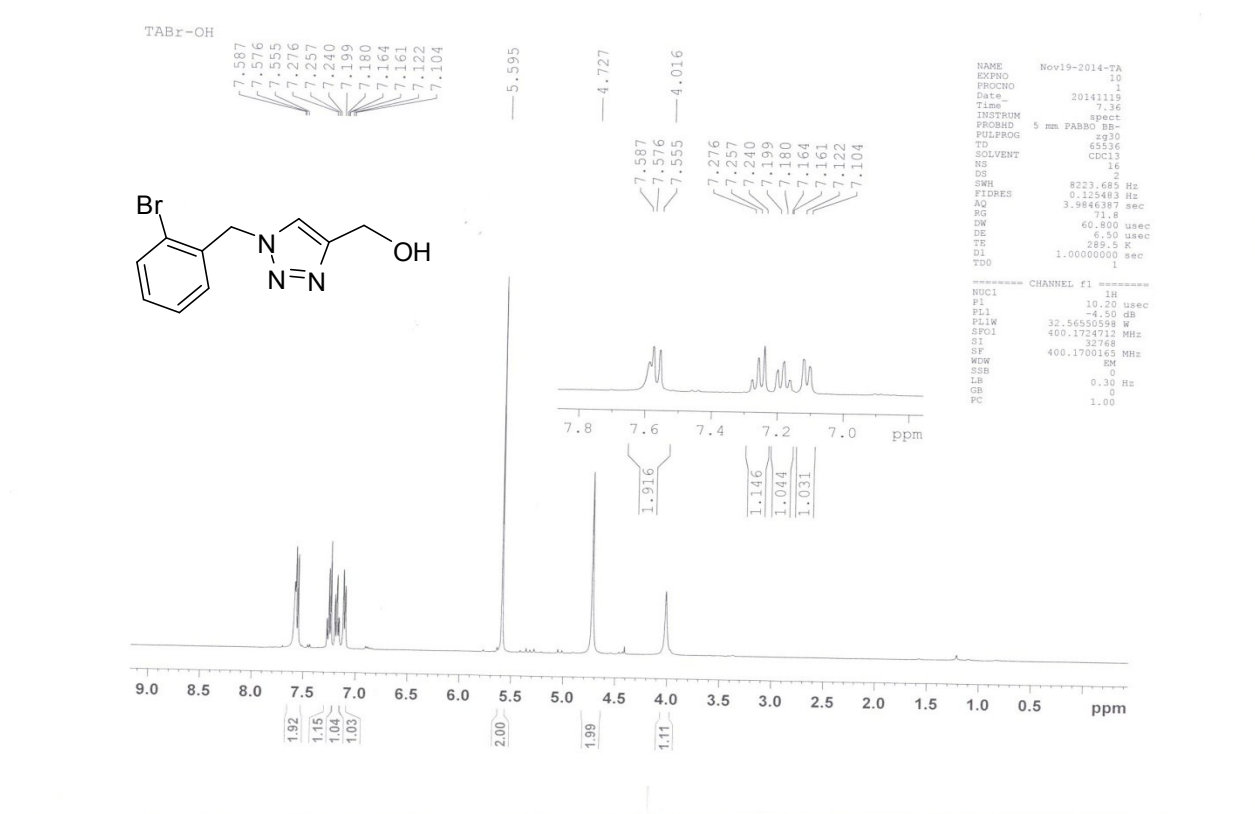


Figure S21. ^1H NMR spectrum of **3bc**.

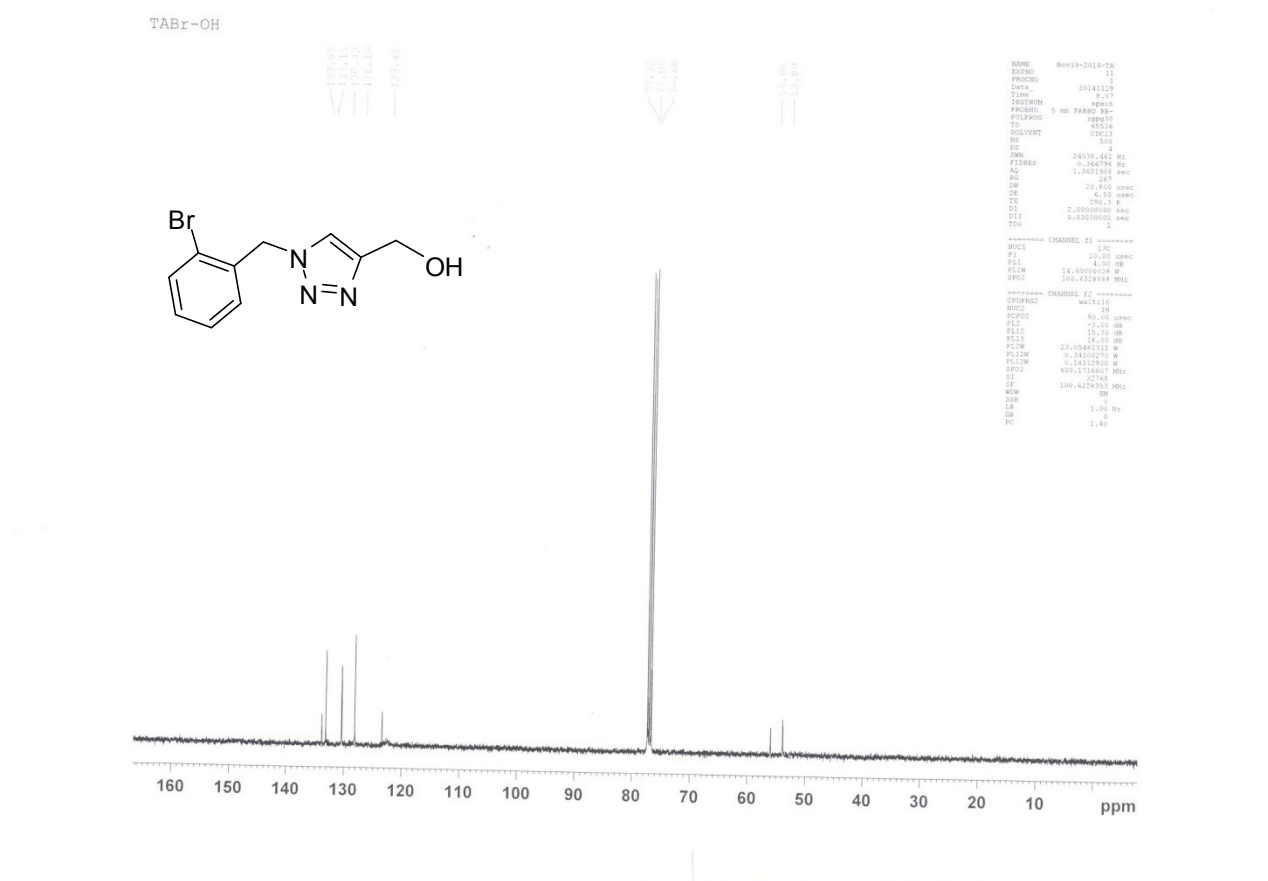


Figure S22. ^{13}C NMR spectrum of **3bc**.

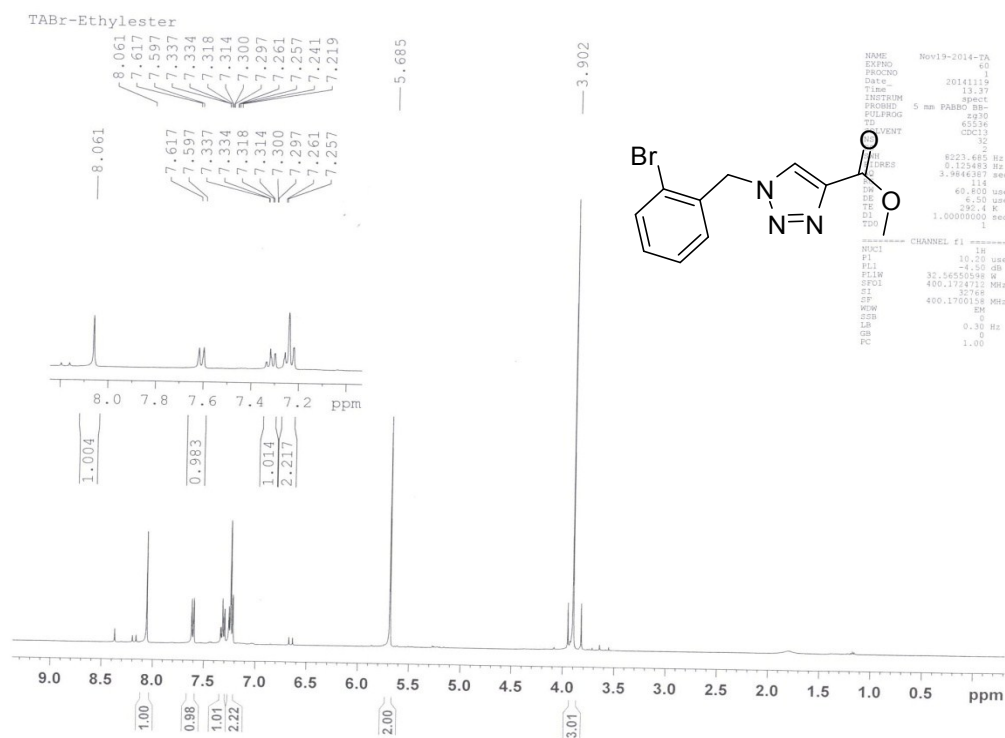


Figure S23. ^1H NMR spectrum of **3be**.

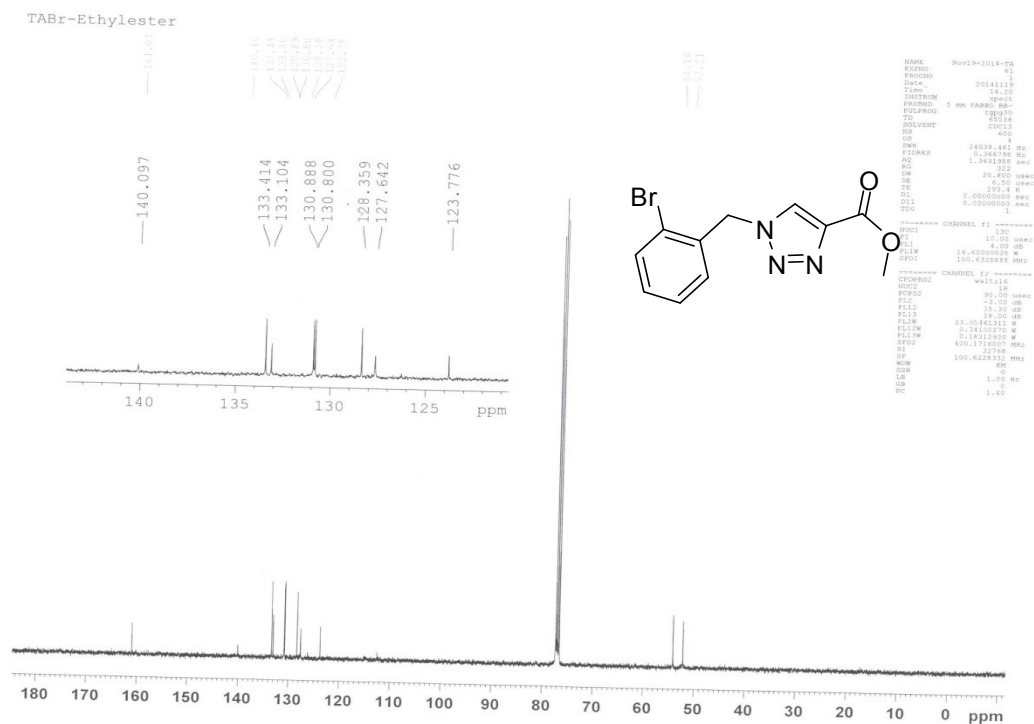


Figure S24. ^{13}C NMR spectrum of **3be**.

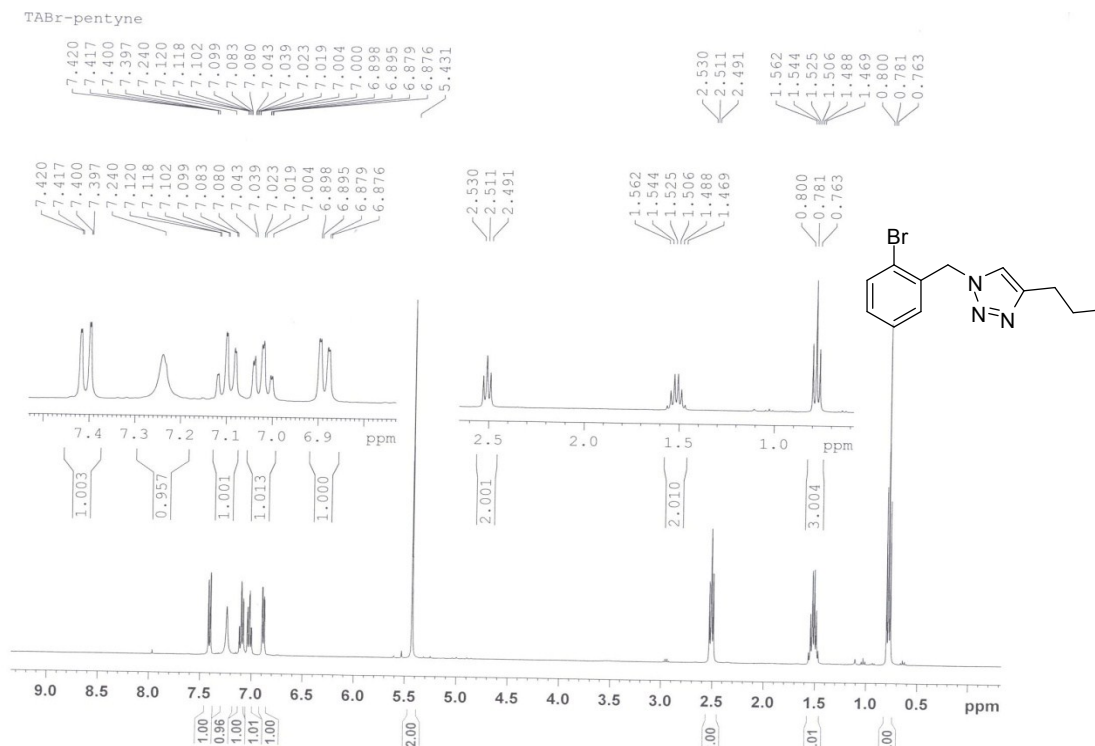


Figure S25. ^1H NMR spectrum of **3bg**.

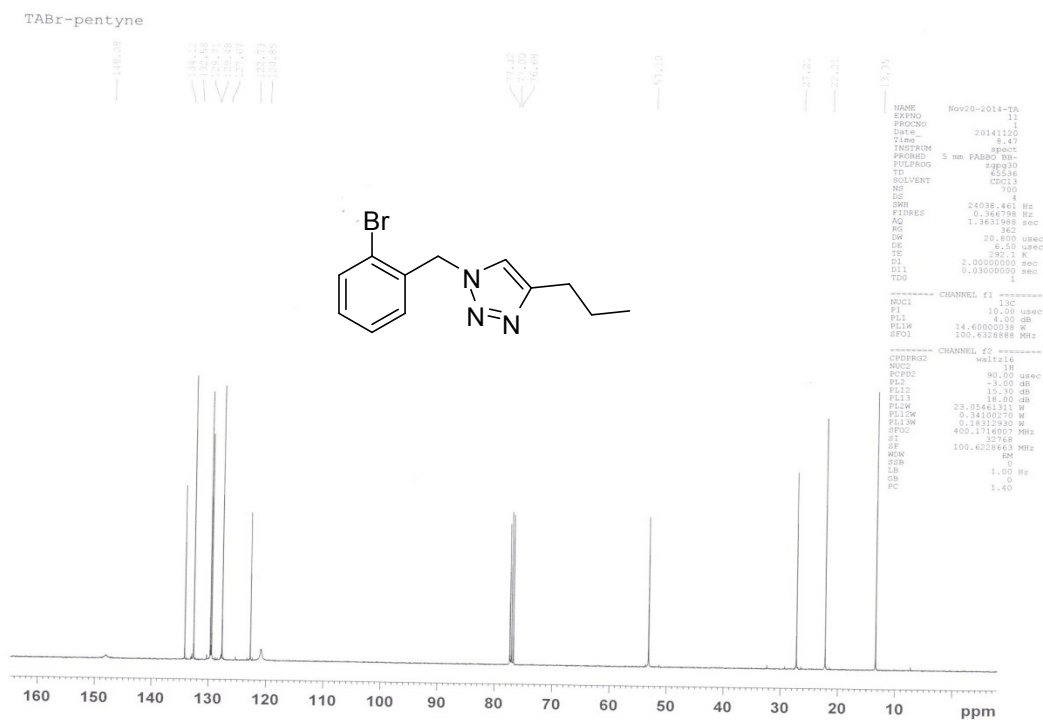


Figure S26. ^{13}C NMR spectrum of **3bg**.

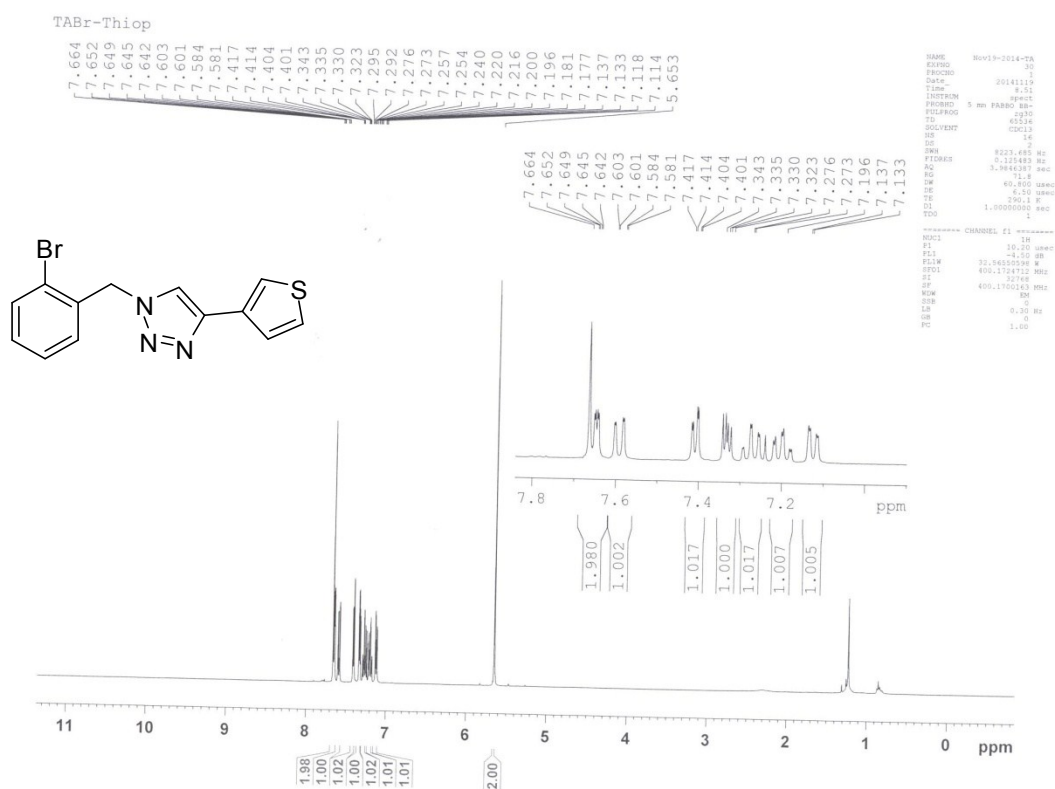


Figure S27. ^1H NMR spectrum of **3bi**.

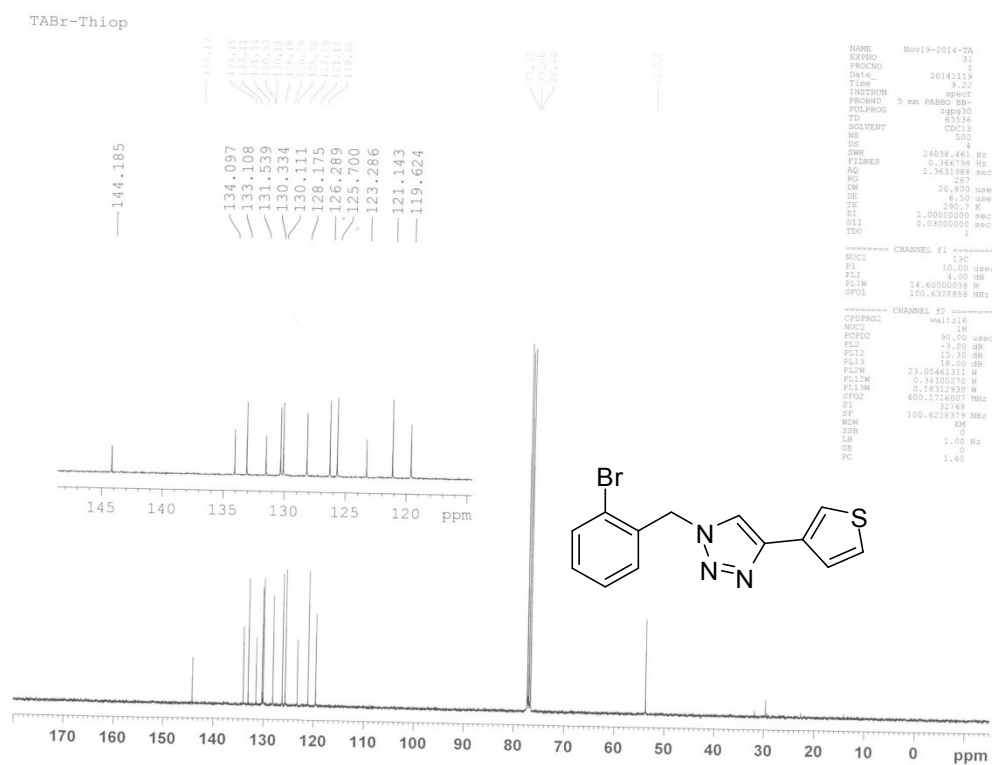


Figure S28. ^{13}C NMR spectrum of **3bi**.