Preparation and Applications of Metal Complexes Supported by Fluorene- and Anthrone-Functionalized (Bis)Mesoionic 1,2,3-Triazol-5-ylidenes

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Table S1. Crystallographic Data and Summary of Data Collection and Structure Refinement.

	1a	**1b**	**2a·H$_2$O**
Formula	$C_{38}H_{36}N_6O$	$C_{37}H_{36}N_6$	$C_{42}H_{47}I_2N_7O_2$
Fw	592.73	564.72	935.66
cryst syst	Triclinic	Monoclinic	Monoclinic
Space group	P-1	C2/c	$P2_1/n$
T, K	293(2)	293(2)	293(2)
a, Å	8.0530(3)	15.6174(13)	18.7032(5)
b, Å	12.4053(5)	8.1610(6)	11.9742(3)
c, Å	15.7430(6)	24.7494(19)	20.5670(6)
α, deg	85.589(3)	90	90
β, deg	89.725(3)	101.275(8)	109.161(3)
γ, deg	88.001(3)	90	90
V, Å^3	1567.11(10)	3093.5(4)	4350.9(2)
Z	2	4	4
d_{calc} g.cm^{-3}	1.256	1.213	1.428
μ, mm^{-1}	0.78	0.073	1.487
refl collected	57148	46453	172172
T_{min}/T_{max}	0.952	0.926	0.964
N_{measd}	8287	2726	7653
[R_{int}]	0.0509	0.0693	0.0568
R [*I* > 2sigma(*I*)]	0.0573	0.0459	0.0360
R (all data)	0.0977	0.0647	0.0457
R_w[*I* > 2sigma(*I*)]	0.1374	0.1210	0.0909
R_w (all data)	0.1571	0.1348	0.1016
GOF	1.028	1.029	1.100

	2b·2.5MeCN	**4b**
Formula	$C_{44}H_{49.5}I_2N_{8.5}$	$C_{45}H_{50}Cl_2N_6Pd_2$
Fw	951.22	958.61
cryst syst	Triclinic	Monoclinic
Space group	P-1	$P2_1/n$
T, K	293(2)	293(2)
a, Å	11.9940(6)	15.7938(6)
b, Å	12.5249(10)	9.9184(4)
c, Å	17.3840(11)	27.8711(9)
α, deg	110.940(7)	90
β, deg	105.078(5)	91.812(3)
γ, deg	96.114(5)	90
V, Å^3	2296.7(3)	4363.8(3)
Z	2	4
d_{calc} g.cm^{-3}	1.376	1.459
μ, mm^{-1}	1.408	0.985
refl collected	21403	102569
T_{min}/T_{max}	0.958	0.902
N_{measd}	6367	11695
[R_{int}]	0.1189	0.0497
R [*I* > 2sigma(*I*)]	0.0615	0.0395
R (all data)	0.1062	0.0672
R_w[*I* > 2sigma(*I*)]	0.1415	0.0868
R_w (all data)	0.1757	0.0993
GOF	1.063	1.068

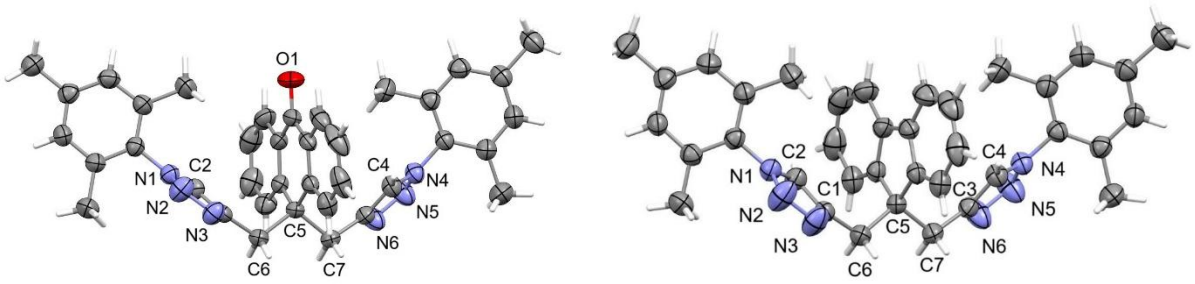
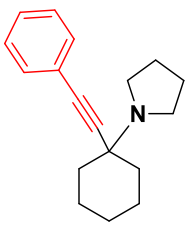


Figure S1. Molecular structures of **1a-b**. Ellipsoids shown at 40% of probability. Counterions and co-crystallization solvents are omitted for clarity.

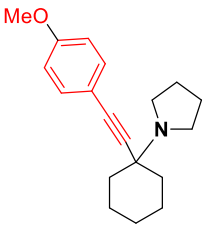
Catalytic trials

General procedure for the KA² coupling reaction

Under argon, a Teflon seal screw-cap pressure tube was charged with the catalyst (1.0 mol%) and the amine substrate (0.1 mmol) and the resulting mixture was stirred for 5 min. The alkyne (0.1 mmol) and the ketone (0.1 mmol) substrates were subsequently added, and the final reaction mixture was stirred at 80°C for 10 h. After reaching room temperature, ethyl acetate was added (2 × 5 mL) and the mixture was stirred for 15 min. The mixture was filtered through a short silica gel plug, concentrated under vacuum and the crude materials were purified by column chromatography (silica gel) with a proper mixture of ethyl acetate/petroleum ether as eluent. The purified products were identified by ^{1}H NMR spectroscopy and they are consistent with the literature data.

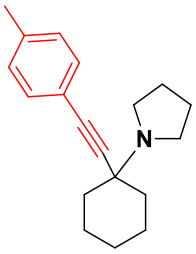


1-(1-(phenylethynyl)cyclohexyl)pyrrolidine (**5a**, Table 2). The general procedure afforded the title compound as a yellow oil in 97% isolated yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.37 (m, 2H), 7.33 – 7.19 (m, 3H), 2.80 (t, *J* = 6.1 Hz, 4H), 2.10 -1.94 (d, *J* = 9.6 Hz, 2H), 1.87 – 1.42 (m, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 131.7, 128.1, 127.6, 123.6, 90.3, 86.1, 59., 47.0, 37.8, 25.7, 23.5, 23.0. The NMR data are consistent with the literature.[1]

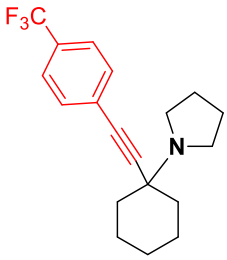


1-(1-((4-methoxyphenyl)ethynyl)cyclohexyl)pyrrolidine (**5b**, Table 2). The general procedure afforded the title compound as a yellow oil in 95% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H), 2.80 (t, *J* = 6.2 Hz, 4H), 2.02 (d, *J* = 9.3 Hz, 2H), 1.84 –

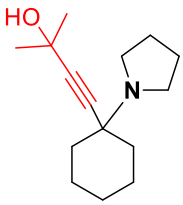
1.47 (m, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.4, 133.2, 115.6, 113.9, 88.0, 86.4, 60.1, 55.4, 47.3, 37.7, 25.6, 23.6, 23.2. The NMR data are consistent with the literature.[1]



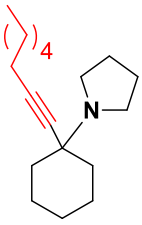
1-(1-(p-tolylethynyl)cyclohexyl)pyrrolidine. (**5c**, Table 2) The general procedure afforded the title compound as a yellow oil in 96% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 2.89 (t, *J* = 6.0 Hz, 4H), 2.34 (s, 3H), 2.03 (s, 2H), 1.84 (m, 4H), 1.73 – 1.55 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 138.1, 131.7, 129.1, 120.3, 88.6, 86.8, 60.3, 47.4, 37.6, 25.6, 23.6, 23.2, 21.5. The NMR data are consistent with the literature.[1]



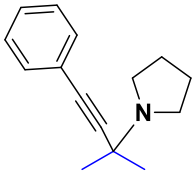
1-(1-((4-(trifluoromethyl)phenyl)ethynyl)cyclohexyl)pyrrolidine (**5d**, Table 2): The general procedure afforded the title compound as a yellow solid in 85% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 4H), 2.82 (t, *J* = 6.0 Hz, 4H), 2.04 (d, *J* = 8.4 Hz, 2H), 1.87 – 1.52 (m, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 132.1, 129.7 (q, *J* = 32.8 Hz), 127.4, 125.2 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.0 Hz), 92.9, 85.4, 60.0, 47.4, 37.6, 25.6, 23.7, 23.1. ^{19}F-NMR (188 MHz, $CDCl_3$): δ -63.2. The NMR data are consistent with the literature.[1]



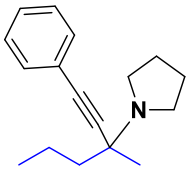
2-methyl-4-(1-(pyrrolidin-1-yl)cyclohexyl)but-3-yn-2-ol (**5e**, Table 2). The general procedure afforded the title compound as an orange liquid in 94% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 – 2.54 (m, 4H), 2.29 – 2.18 (m, 1H), 1.82 – 1.76 (m, 2H), 1.69 – 1.64 (m, 4H), 1.52 (d, *J* = 4.7 Hz, 4H), 1.44 (s, 6H), 1.41 – 1.27 (m, 3H), 1.15 – 1.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 91.3, 81.9, 64.9, 46.8, 37.7, 32.2, 25.6, 23.4, 22.9. The NMR data are consistent with the literature.[2]



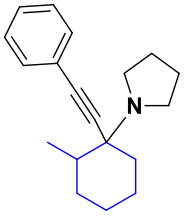
1-(1-(oct-1-yn-1-yl)cyclohexyl)pyrrolidine (**5f**, Table 2). The general procedure afforded the title compound as yellow oil in 91% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77–2.62 (m, 4H), 2.21 (t, *J* = 6.6 Hz, 2H), 1.88 (d, *J* = 12.1 Hz, 2H), 1.79 – 1.70 (m, 4H), 1.62 – 1.21 (m, 17H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.1, 80.0, 59.2, 47.0, 38.1, 31.4, 29.4, 28.6, 25.8, 23.5, 23.2, 22.7, 18.7, 14.2. The NMR data are consistent with the literature.[3]



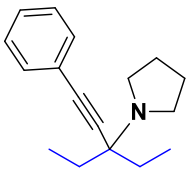
1-(2-methyl-4-phenylbut-3-yn-2-yl)pyrrolidine (**5g**, Table 2). The general procedure afforded the title compound as colourless oil in 98% yield after column chromatography using an ethyl acetate/petroleum ether (1:99) mixture as eluent. ^{1}H NMR (400 MHz, CDCl3) δ 7.43 – 7.39 (m, 2H), 7.31 – 7.27 (m, 3H), 2.89 – 2.80 (m, 4H), 1.87 – 1.81 (m, 4H), 1.52 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 131.9, 128.3, 128.0, 123.4, 91.1, 84.3, 48.5, 29.6, 23.9. The NMR data are consistent with the literature.[1]



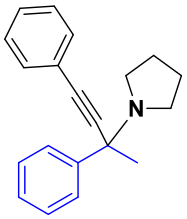
1-(3-methyl-1-phenylhex-1-yn-3-yl)pyrrolidine (**5h**, Table 2). The general procedure afforded the title compound as yellow oil in 93% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.36 (m, 2H), 7.33 – 7.23 (m, 3H), δ 2.82 (t, *J* = 6.3 Hz, 4H), 1.89 – 1.40 (m, 11H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 131.8, 128.2, 127.7, 123.6, 91.3, 84.5, 58.1, 47.9, 43.8, 25.9, 23.7, 17.9, 14.6. The NMR data are consistent with the literature.[1]



1-(2-methyl-1-(phenylethynyl)cyclohexyl)pyrrolidine (**5i**, Table 2): The general procedure afforded the title compound as yellow oil in 94% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47−7.38 (m, 4H), 7.33−7.22 (m, 6H), 2.74 (m, 8H), 2.19−1.29 (m, 26H),1.15 (d, *J* = 6.8 Hz, 3H, major diastereoisomer), 1.03 (d, *J* = 7.2 Hz, 3H, minor diastereoisomer). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 131.8, 131.7, 128.2, 128.2, 127.6, 124.0,91.8, 91.7, 86.1, 85.3, 62.2, 61.5, 46.8, 46.1, 37.4, 36.7, 31.6,30.0, 29.5, 29.2, 24.0, 23.6, 22.8, 22.3, 19.7, 16.8, 13.0. The NMR data are consistent with the literature.[3]

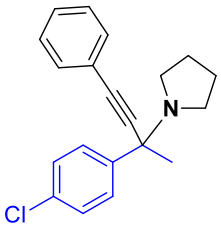


1-(3-ethyl-1-phenylpent-1-yn-3-yl)pyrrolidine (**5j**, Table 2, entry 9): The general procedure afforded the title compound as yellow oil in 90% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.37 (m, 2H), 7.33 – 7.23 (m, 3H), 2.78 (t, *J* = 6.2 Hz, 4H), 1.92 – 1.63 (m, 8H), 0.96 (t, *J* = 7.4 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 131.9, 128.3, 127.7, 123.8, 91.5, 84.9, 62.1, 47.6, 29.0, 23.7, 8.30. The NMR data are consistent with the literature.[1]

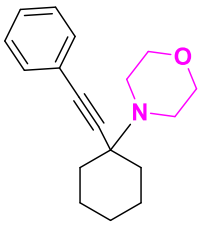


1-(2,4-diphenylbut-3-yn-2-yl)pyrrolidine (**5k**, Table 2, entry 12). The general procedure afforded the title compound as brown oil in 71% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.75 (m, 2H), 7.60 – 7.49 (m, 2H), 7.43 – 7.23 (m, 6H), 2.87 – 2.56 (m, 4H), 1.88 – 1.70 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$):

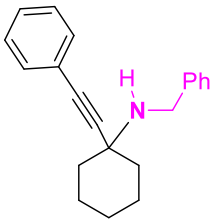
δ 145.8, 131.9, 128.4, 128.2, 128.1, 127.1, 126.5, 89.5, 62.7, 48.5, 32.5, 23.9. The NMR data are consistent with the literature.[3]



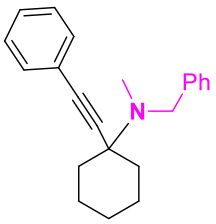
1-(2-(4-chlorophenyl)-4-phenylbut-3-yn-2-yl)pyrrolidine (**5l**, Table 2). The general procedure afforded the title compound as brown oil in 75% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.57 – 7.46 (m, 2H), 7.39 – 7.23 (m, 5H), 2.84 – 2.48 (m, 4H), 1.85–1.64 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 132.9, 132.1, 128.5, 128.4, 128,3 128.1, 123.4, 89.0, 87.7, 62.5, 48.6, 32.6, 24.0. The NMR data are consistent with the literature.[3]



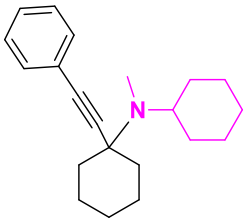
4-(1-(phenylethynyl)cyclohexyl)morpholine (**5m**, Table 2): The general procedure afforded the title compound as yellow oil in 86% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.49 – 7.35 (m, 2H), 7.34 – 7.20 (m, 3H), 3.76 (t, *J* = 5.0 Hz, 4H), 2.76 (t, *J* = 4.6 Hz, 4H), 2.08 – 1.96 (m, 2H), 1.79 – 1.45 (m, 8H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 131.5, 128.0, 127.6, 123.2, 89.6, 86.3, 67.3, 58.7, 46.5, 3520, 25.5, 22.5. The NMR data are consistent with the literature.[1]



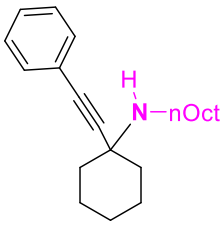
N-benzyl-1-(phenylethynyl)cyclohexan-1-amine (**5n**, Table 2). The general procedure afforded the title compound as yellow oil in 92% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56−7.16 (m, 10H), 3.97 (s, 2H), 2.01−1.95 (m, 2H), 1.77−1.41 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 131.6, 128.5, 128.4, 128.3, 127.8, 126.8, 123.7, 93.6, 84.7, 55.2, 48.0, 38.2, 25.9, 23.0. The NMR data are consistent with the literature.[3]



N-benzyl-N-methyl-1-(phenylethynyl)cyclohexan-1-amine (**5o**, Table 2). The general procedure afforded the title compound as yellow oil in 84% yield after column chromatography using an ethyl acetate/petroleum ether (5:95) mixture as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.44 – 7.40 (m, 2H), 7.37 – 7.32 (m, 5H), 7.27 – 7.23 (m, 1H), 3.72 (s, 2H), 2.25 (s, 3H), 2.14 (dd, J = 9.9, 5.6 Hz, 2H), 1.90 – 1.58 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 131.9, 128.9, 128.8, 128.4, 128.3, 128.3, 127.8, 126.66, 123.9, 90.9, 85.7, 59.3, 55.8, 36.8, 35.4, 25.9, 22.9. The NMR data are consistent with the literature.[4]



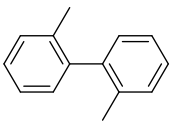
N-(cyclohexylmethyl)-N-methyl-1-(phenylethynyl)cyclohexan-1-amine (**5p**, Table 2). The general procedure afforded the title compound as yellow oil in 58% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.36 (m,2H), 7.33−7.25 (m, 3H), 3.03 (td, *J* = 10.9, 3.3 Hz, 1H), 2.40 (s, 3H), 2.12−1.91 (m, 4H), 1.69 (m, 11H), 1.32 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.5, 128.3, 127.7,124.0, 93.4, 85.8, 58.9, 57.0, 37.1, 30.9, 29.9, 26.7, 26.4, 25.8, 23.2. The NMR data are consistent with the literature.[3]



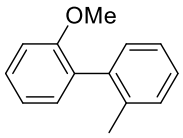
N-octyl-1-(phenylethynyl)cyclohexan-1-amine (**5q**, Table 2). The general procedure afforded the title compound as orange oil in 91% yield after column chromatography using an ethyl acetate/petroleum ether (1:9) mixture as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.35−7.21 (m, 3H), 2.79 (t, *J* = 7.1 Hz, 2H), 1.93 (d, *J* = 11.6 Hz, 2H), 1.74−1.05 (m, 20H), 0.89 (dd, *J* = 9.7, 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.6, 128.1, 127.7, 123.6, 93.3, 84.6, 55.2, 43.2, 38.1, 31.8, 30.5, 29.5, 29.3, 27.5, 25.9, 23.1, 22.7, 14.1. The NMR data are consistent with the literature.[3]

General procedure for the Suzuki-Miyaura coupling of aryl chlorides and boronic acids.

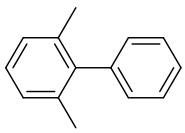
Sodium *tert*-butoxide (1.5 mmol) and boronic acid (1.2 mmol) were charged in a 10 mL screw capped vial equipped with a magnetic bar. The catalyst (1.0 mol%) and 4 mL of anhydrous dioxane were added and the mixture was stirred for 15 minutes. The aryl chloride (1.0 mmol) was added in one portion, and the reaction mixture was stirred at room temperature for 2 hours and monitored by ^{1}H NMR spectroscopy. Water was added to the reaction mixture, the organic layer was extracted with ethyl acetate, dried with magnesium sulfate, and the solvent was evaporated under vacuum. When necessary the product was purified by column chromatography on silica gel using a proper mixture of ethyl acetate/hexanes as eluent.



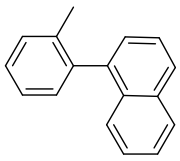
2,2-dimethyl-1,1´-biphenyl (**6a**, Table 4, entry 1): The general procedure afforded the title compound in 98% isolated yield (colorless liquid) after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.19-7.26 (m, 6H, Ar*H*), 7.09 (d, *J* = 6.8 Hz, 2H, Ar*H*), 2.05 (s, 6H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 19.8, 125.5, 127.1, 129.3, 129.8, 135.8, 141.6. Spectroscopy data is consistent with the literature.[5]



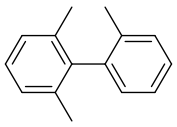
2-methoxy-2´-methyl-1,1´-biphenyl (**6b**, Table 4, entry 2): The general procedure afforded the title compound in 94% isolated yield (colorless liquid) after column chromatography using a mixture of 15:85 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.30-7.32 (m, 1H, Ar*H*), 7.14-7.23 (m, 5H, ArH), 6.94-7.02 (m, 2H, ArH), 3.73 (s, 3H, OCH_3), 2.13 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 19.9, 55.4, 110.7, 120.5, 125.5, 127.3, 128.6, 129.6, 130.0, 130.9 131.0, 136.8, 138.7, 156.5. Spectroscopy data is consistent with the literature.[5]



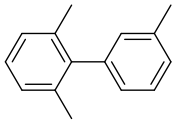
2,6-dimethyl-biphenyl (**6c**, Table 4, entry 3): The general procedure afforded the title compound in 96% isolated yield (colorless liquid) after column chromatography using a mixture of 10:90 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.39 (t, *J* = 7.4 Hz, 2H, ArH), 7.31 (d, *J* = 6.8 Hz, 1H, ArH), 7.07-7.13 (m, 5H, ArH), 2.01 (s, 6H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 20.9, 126.5, 127.1, 127.3, 128.5, 129.1, 136.1, 141.1, 141.9. Spectroscopy data is consistent with the literature.[5]



1-(o-tolyl)naphthalene (**6d**, Table 4, entry 4): The general procedure afforded the title compound in 92% isolated yield (while solid) after column chromatography using a mixture of 15:85 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.89 (d, *J* = 8.0 Hz, 1H, Ar*H*) ,7.85 (d, *J* = 8.4 Hz, 1H, ArH),7.51 (dt, *J* = 1.5, 7.7 Hz, 1H, Ar*H*) ,7.44-7.48 (m, 2H, ArH), 7.23-7.39 (m, 6H, ArH), 2.02 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 20.0, 125.4, 125.6, 125.7, 125.9, 126.1, 126.6, 127.4, 127.5, 128.2, 129.8, 130.4, 132.0, 133.5, 136.8, 139.8, 140.2. Spectroscopy data is consistent with the literature.[6]

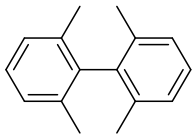


2,2´,6-trimethyl-biphenyl (**6e**, Table 4, entry 5): The general procedure (reaction carried out for 12 h) afforded the title compound in 87% isolated yield (colorless liquid) after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.09-7.29 (m, 6H, Ar*H*), 6.99-7.02 (m, 1H, ArH), 1.96 (s, 3H, CH_3), 1.92 (s, 6H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 19.4 20.3, 126.0, 126.9, 127.0, 127.2, 128.8, 130.0, 135.6, 135.8 140.5, 141.1. Spectroscopy data is consistent with the literature.[5]

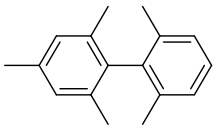


2,3´,6-trimethyl-biphenyl (**6f**, Table 4, entry 6): The general procedure (reaction carried out for 12 h) afforded the title compound in 90% isolated yield (colorless liquid) after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.13-7.17 (m, 1H, Ar*H*), 6.96-7.01 (m, 4H, ArH), 6.78-6.83 (m, 2H, Ar*H*), 2.22 (s, 3H, CH_3), 1.90 (s, 6H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 20.9, 21.6,

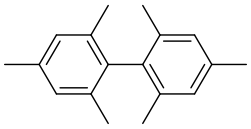
126.1, 127.0, 127.3, 127.4, 128.4, 129.8, 136.1, 138.0, 141.1, 142.1. Spectroscopy data is consistent with the literature.[5]



2,2',6,6'-tetramethyl-1,1'-biphenyl (**6g**, Table 4, entry 7): The general procedure (reaction carried out for 12 h) afforded the title compound in 88% isolated yield (colorless solid) after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.24-7.12 (m, 6H, Ar*H*), 1.92 (s, 12H, C*H*$_3$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 140.1, 135.6, 127.6, 126.9, 20.0. Spectroscopy data is consistent with the literature.[7]



2,2',4,6,6'-pentamethyl-1,1'-biphenyl (**6h**, Table 4, entry 8): The general procedure afforded (reaction carried out for 12 h) the title compound in 85% isolated yield (white solid) after column chromatography using a mixture of 5:95 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.17-7.05 (m, 3H, Ar*H*), 6.94 (s, 2H, Ar*H*), 2.33 (s, 3H, CH_3), 1.90 (s, 6H, CH_3), 1.85 (s, 6H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 140.0, 136.9, 136.1, 135.7, 135.2, 128.2, 127.3, 126.7, 21.1, 19.9, 19.7. Spectroscopy data is consistent with the literature.[7]



2,2',4,4,6,6'-hexamethylbiphenyl (**6i**, Table 4, entry 9): The general procedure (reaction carried out for 12 h) afforded the title compound in 83% isolated yield (while solid) after column chromatography using a mixture of 15:85 ethyl acetate/hexane as eluent. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 6.94 (s, 4H, Ar*H*), 2.32 (s, 6H, CH_3), 1.87 (s, 12H, CH_3); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 137.0, 136.0, 135.5, 128.2, 21.1, 19.8. Spectroscopy data is consistent with the literature.[7]

Mercury poisoning test

Under argon, an NMR tube with J-Young valve was charged with the catalyst (1.0 mol%), ketone (0.1 mmol), amine (0.1 mmol) and the alkyne (0.1 mmol). Afterward, an excess amount of Hg (0.05 mmol) was added (at the proper reaction time = 0, 30, 60, 120 min), and the reaction mixture was heated to 80ºC. Reaction controls by ^{1}H NMR spectroscopy were performed every 30 min in a period of 10 h.

DCT poisoning test

Under argon, the ketone (0.1 mmol), amine (0.1 mmol) and alkyne (0.1 mmol) were added to a Schlenk flask and the mixture stirred for 5 min. After, the catalyst (1 mol%) and a slight exces of DCT (1.5 mol%) were added to the mixture and the reaction heated at 60°C for 12h. Aliquots (aprox. 10 μL) were removed every hour and analyzed by gas chromatography.

References:

1) S. G. Chalkidis, G. C. Vougioukalakis, *Eur. J. Inorg. Chem.*, **2023**, *26*, e2023010965.
2) M. Mateus, L. Rycek, *ChemPlusChem*, **2024**, *89*, e202400365.
3) N. V. Tzouras, S. P. Neofotistos, G. C. Vougioukalakis, *ACS Omega*, **2019**, *4*, 10279.
4) O. P. Pereshivko, V. A. Peshkov, E. V. Van der Eycken, *Org. Lett.*, **2012**, *12*, 2638.
5) Chen, M.-T; Kao, Z.-L. *Dalton Trans.*, **2017**, *46*, 16394.
6) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550.
7) M. Lesieur, A. M. Z. Slawin, C. S. J. Cazin, *Org. Biomol. Chem.*, **2014**, *12*, 5586.

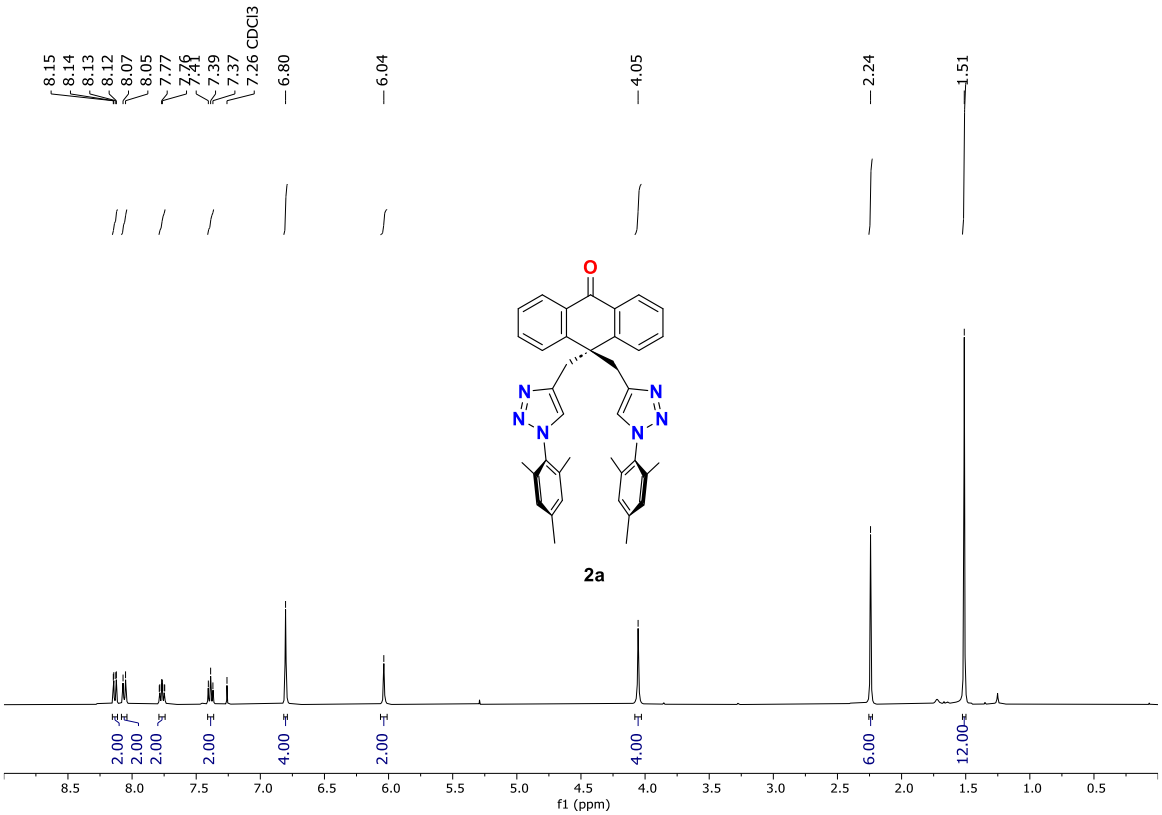


Figure S2. ^{1}H NMR spectrum (400 MHz) of triazole **1a** in $CDCl_3$.

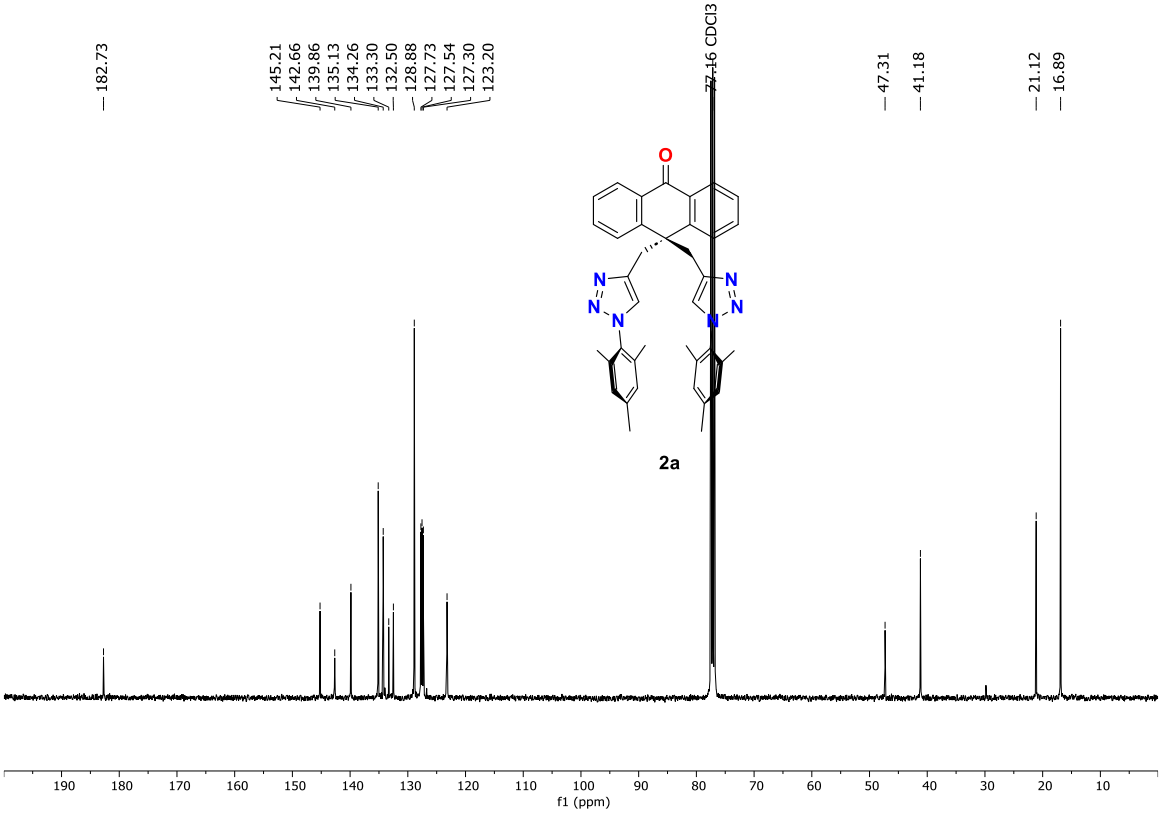


Figure S3. ^{13}C NMR spectrum (100 MHz) of triazole **1a** in $CDCl_3$.

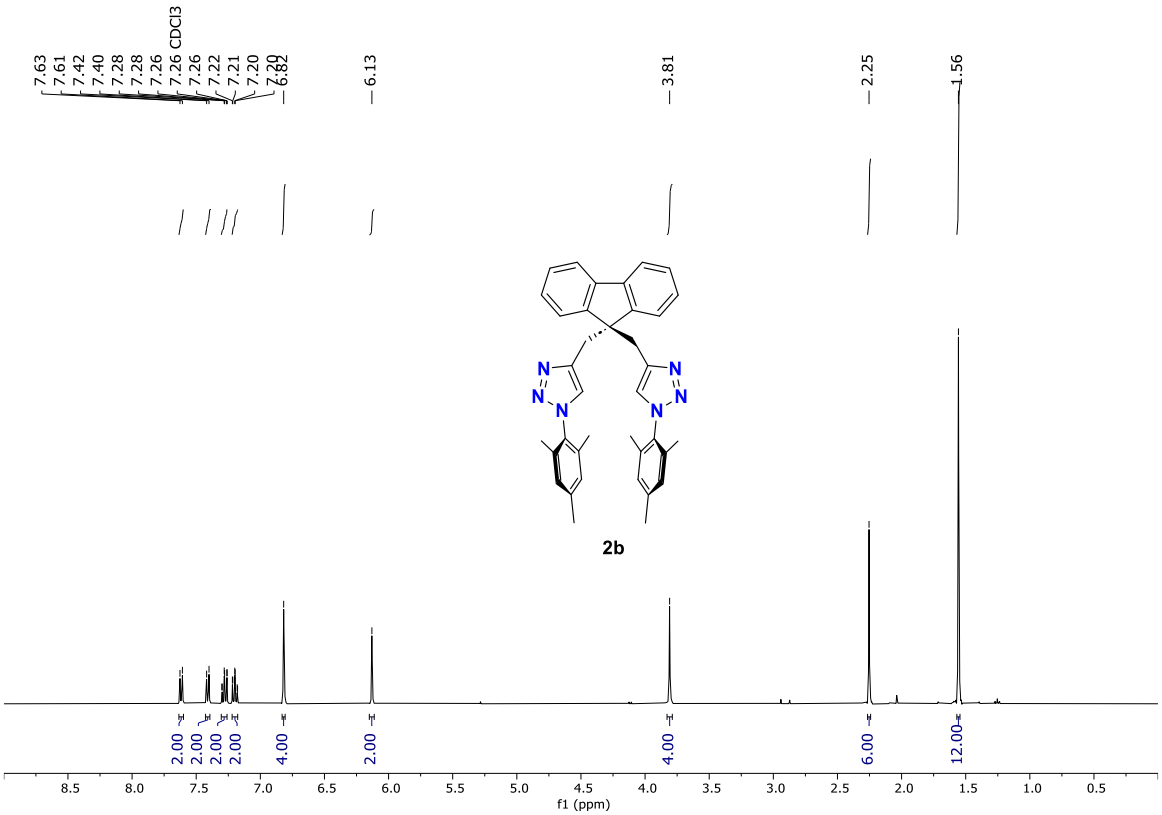


Figure S4. ^{1}H NMR spectrum (400 MHz) of triazole **1b** in $CDCl_3$.

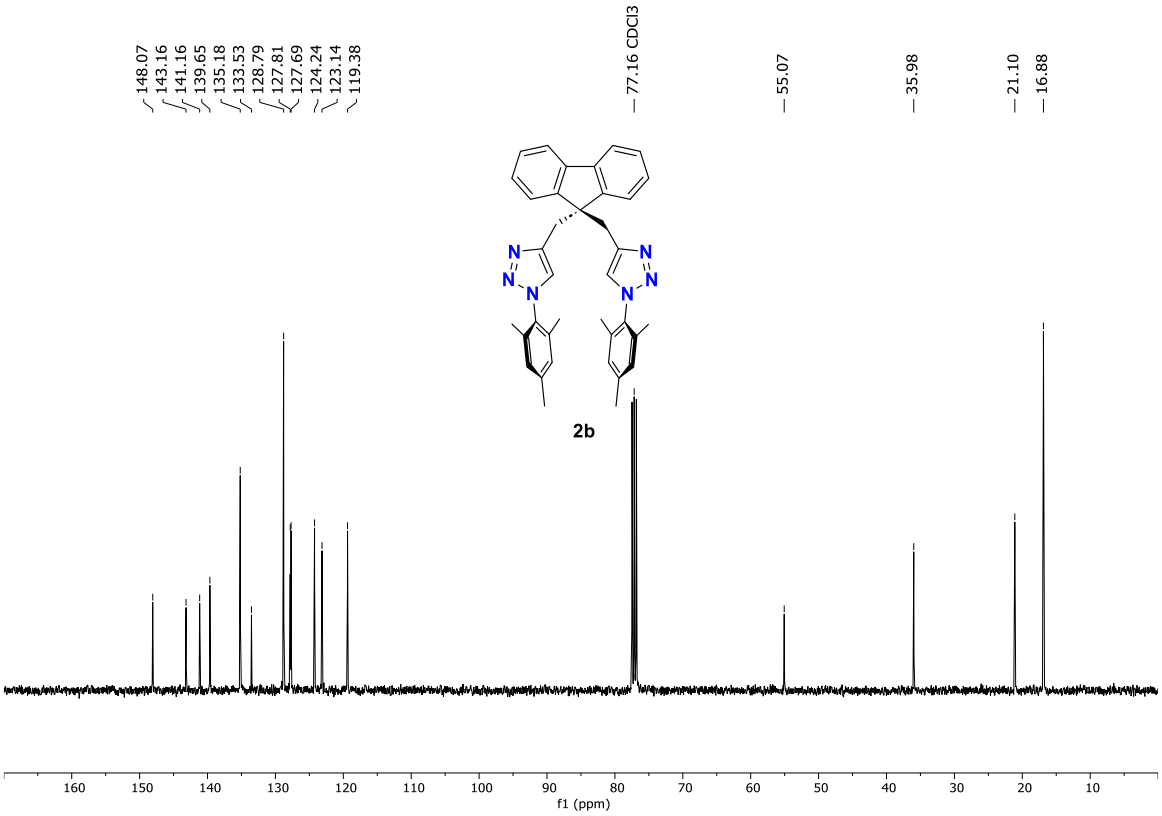


Figure S5. ^{13}C NMR spectrum (100 MHz) of triazole **1b** in $CDCl_3$.

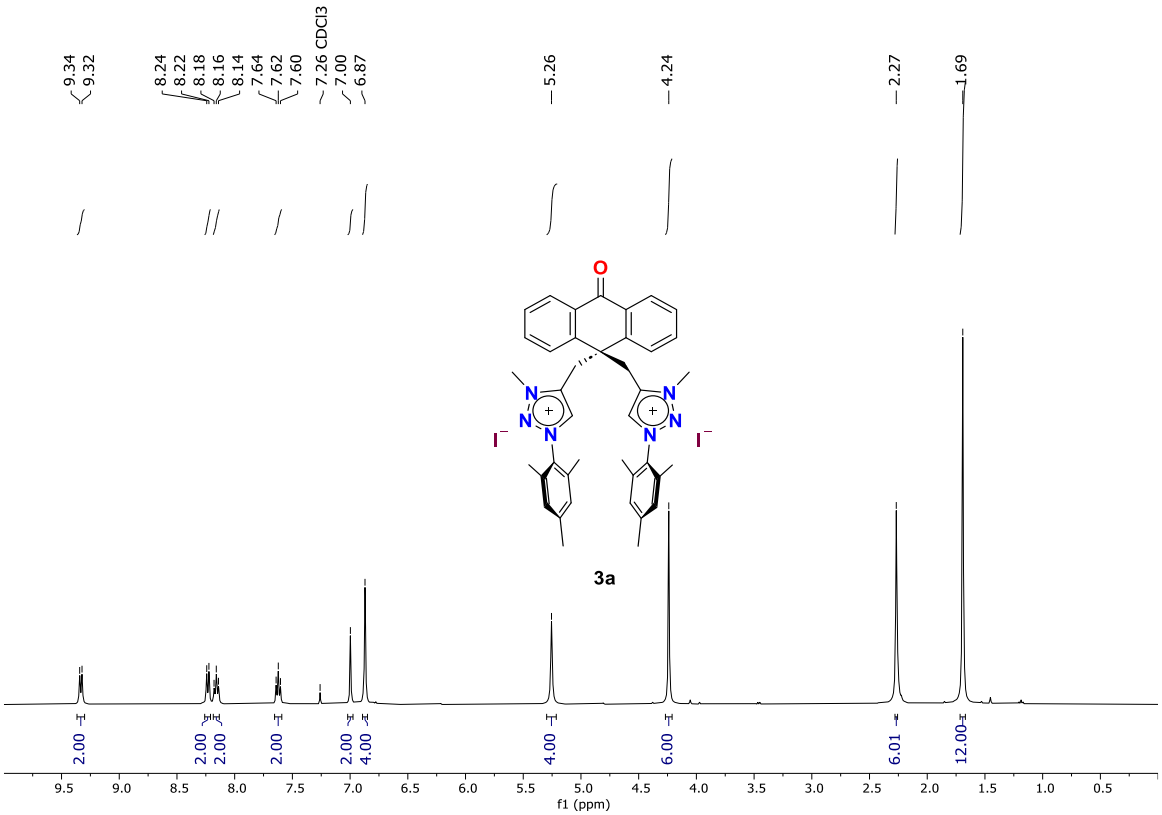


Figure S6. ^{1}H NMR spectrum (400 MHz) of triazole **2a** in $CDCl_3$.

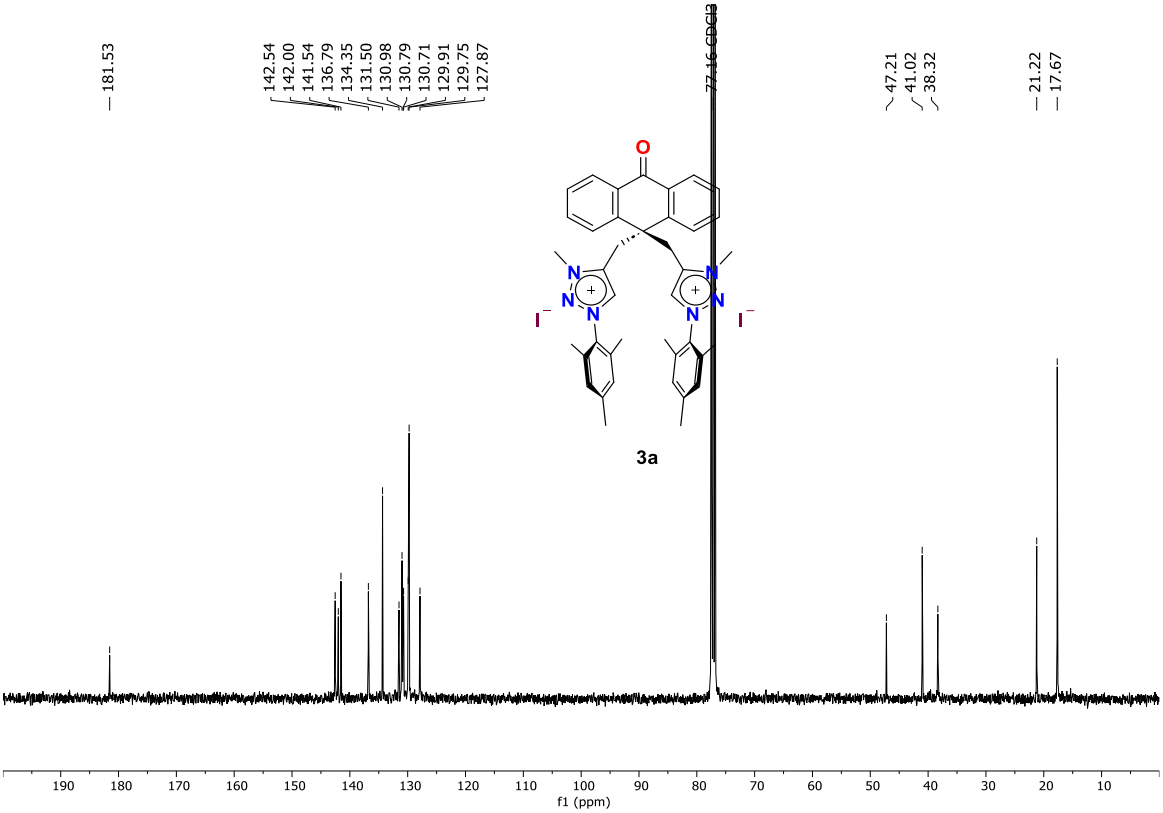


Figure S7. ^{13}C NMR spectrum (100 MHz) of triazole **2a** in $CDCl_3$.

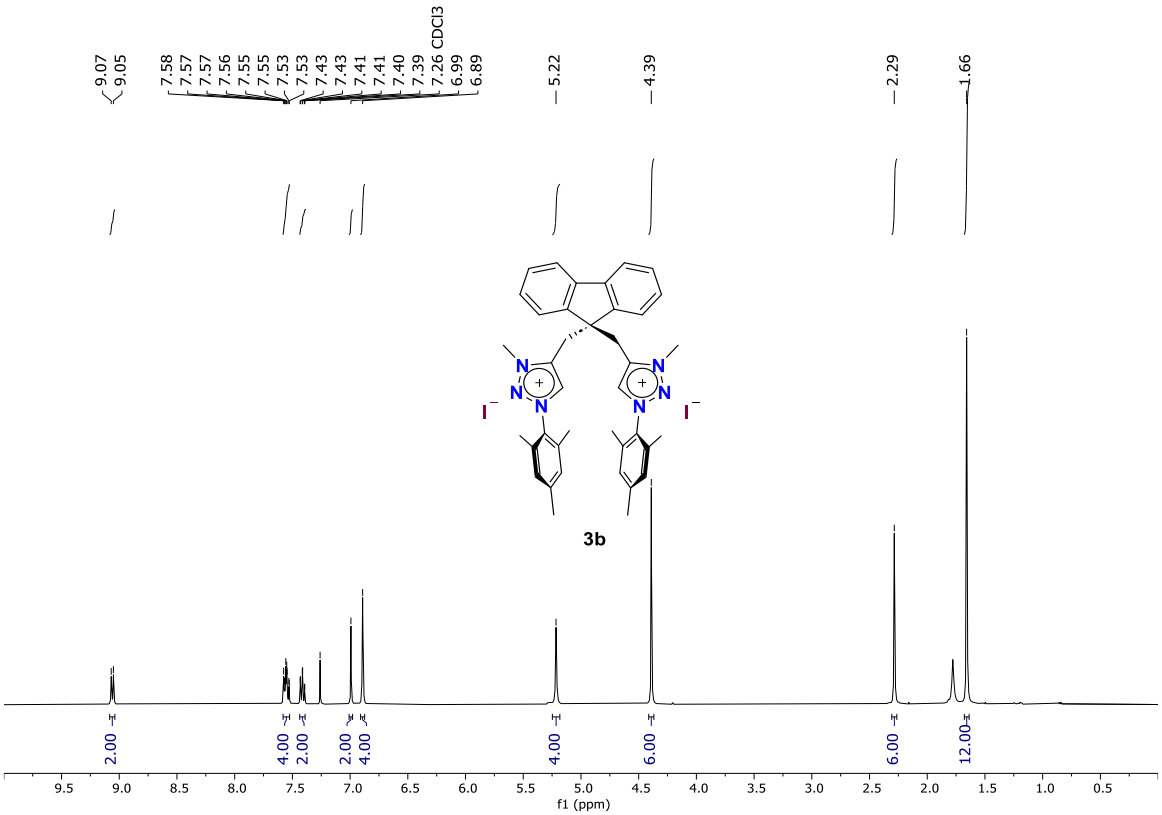


Figure S8. ^{1}H NMR spectrum (400 MHz) of triazole **2b** in $CDCl_3$.

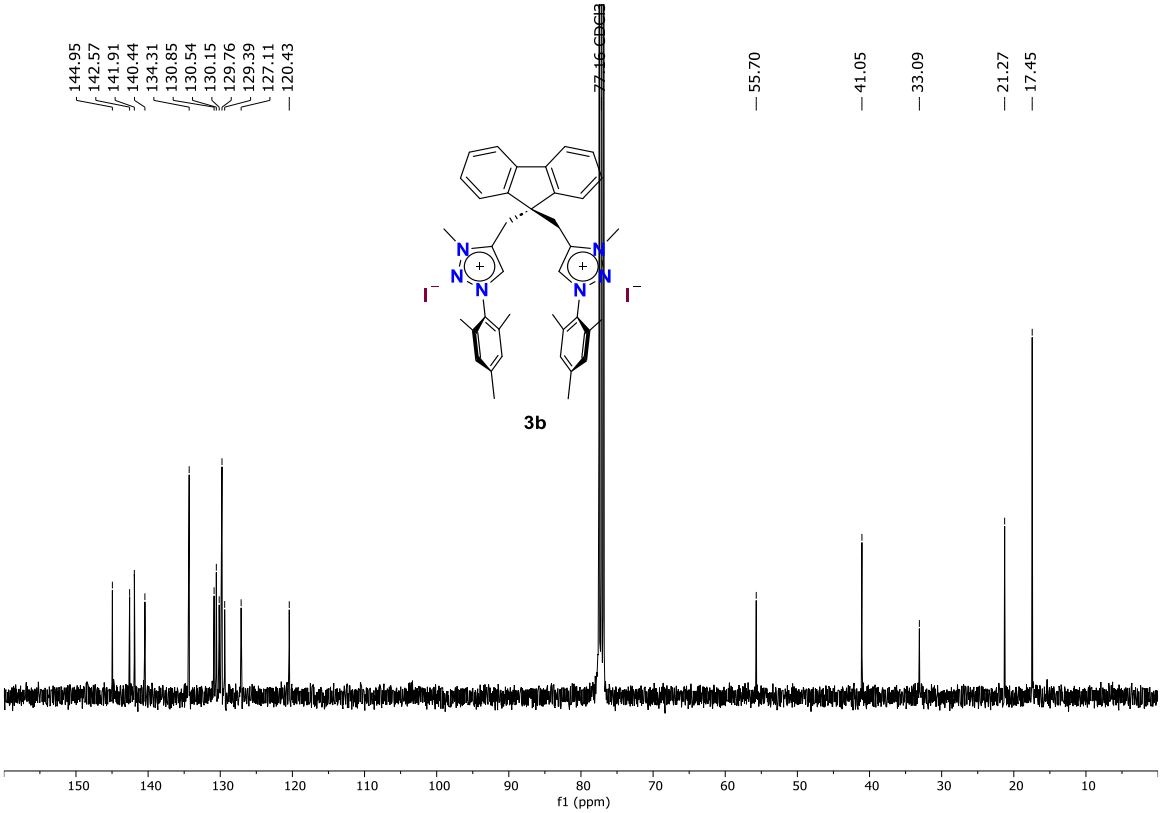


Figure S9. ^{13}C NMR spectrum (100 MHz) of triazole **2b** in $CDCl_3$.

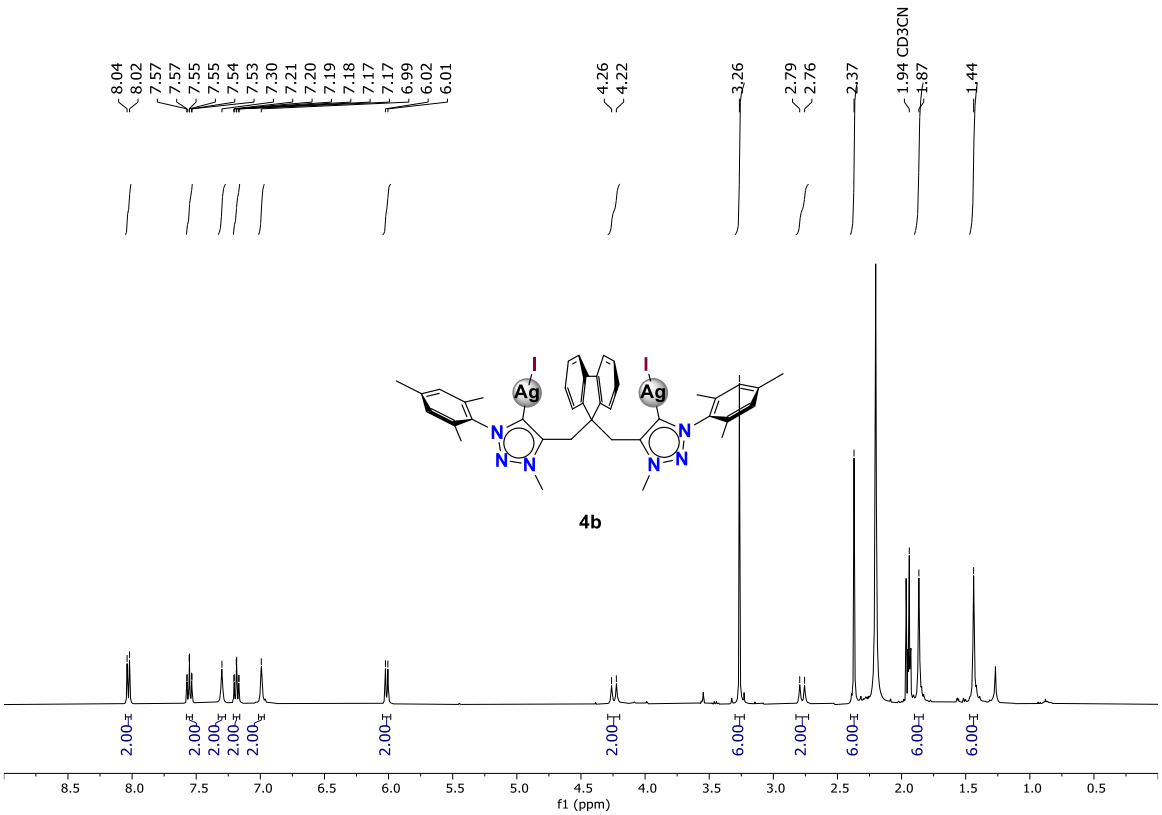


Figure S10. ^{1}H NMR spectrum (400 MHz) of triazole **3b** in $CDCl_3$.

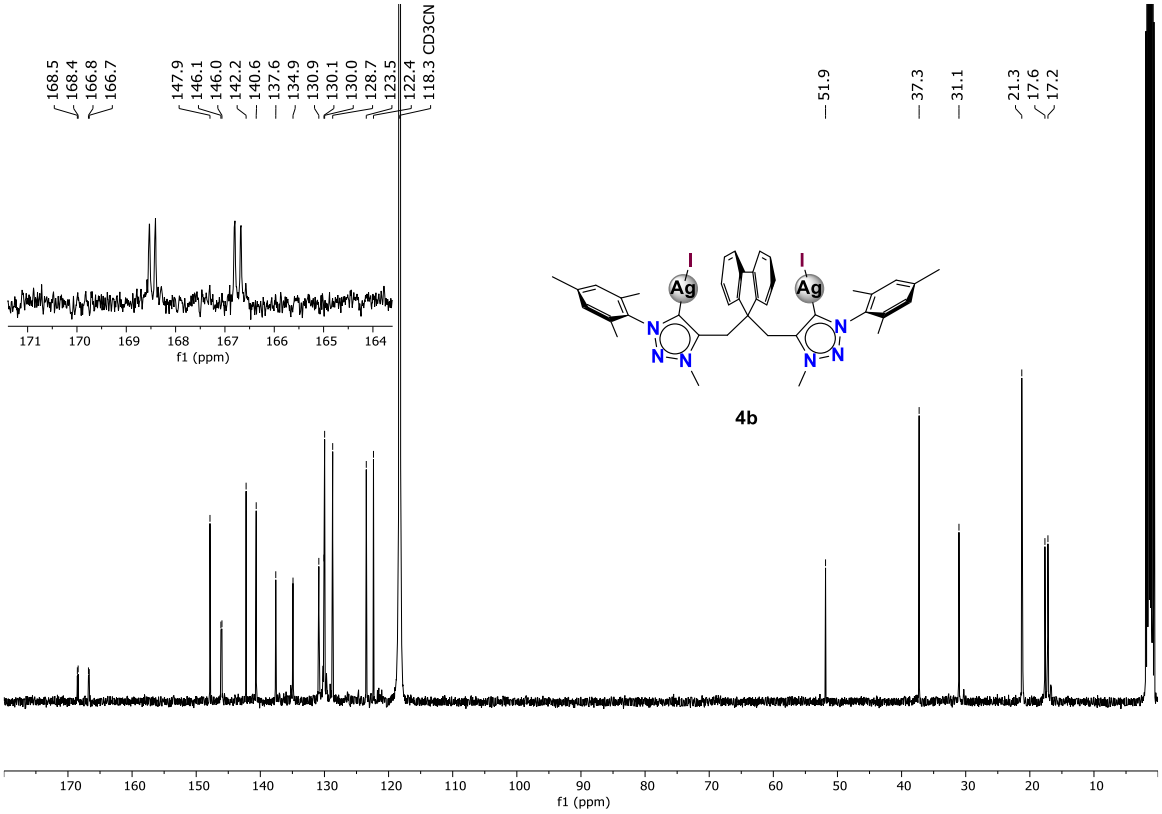


Figure S11. ^{13}C NMR spectrum (100 MHz) of triazole **3b** in $CDCl_3$.

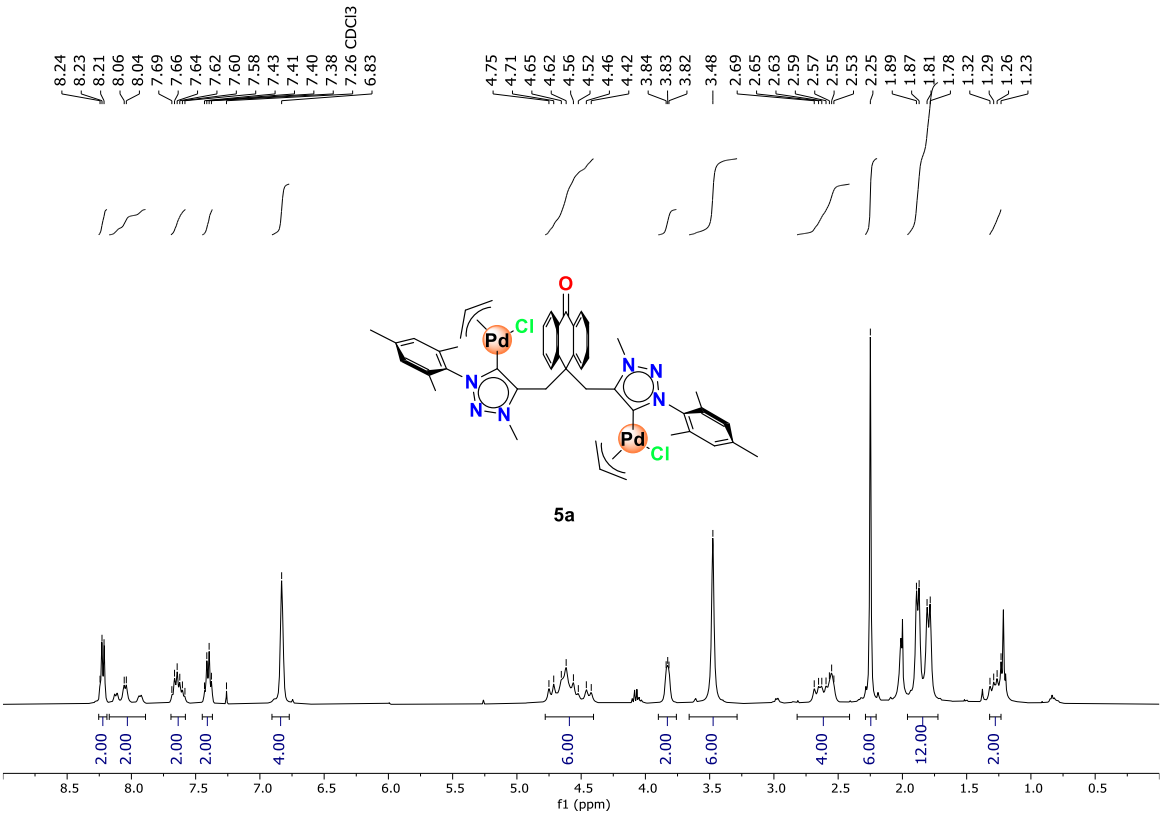


Figure S12. ^{1}H NMR spectrum (400 MHz) of triazole **4a** in $CDCl_3$.

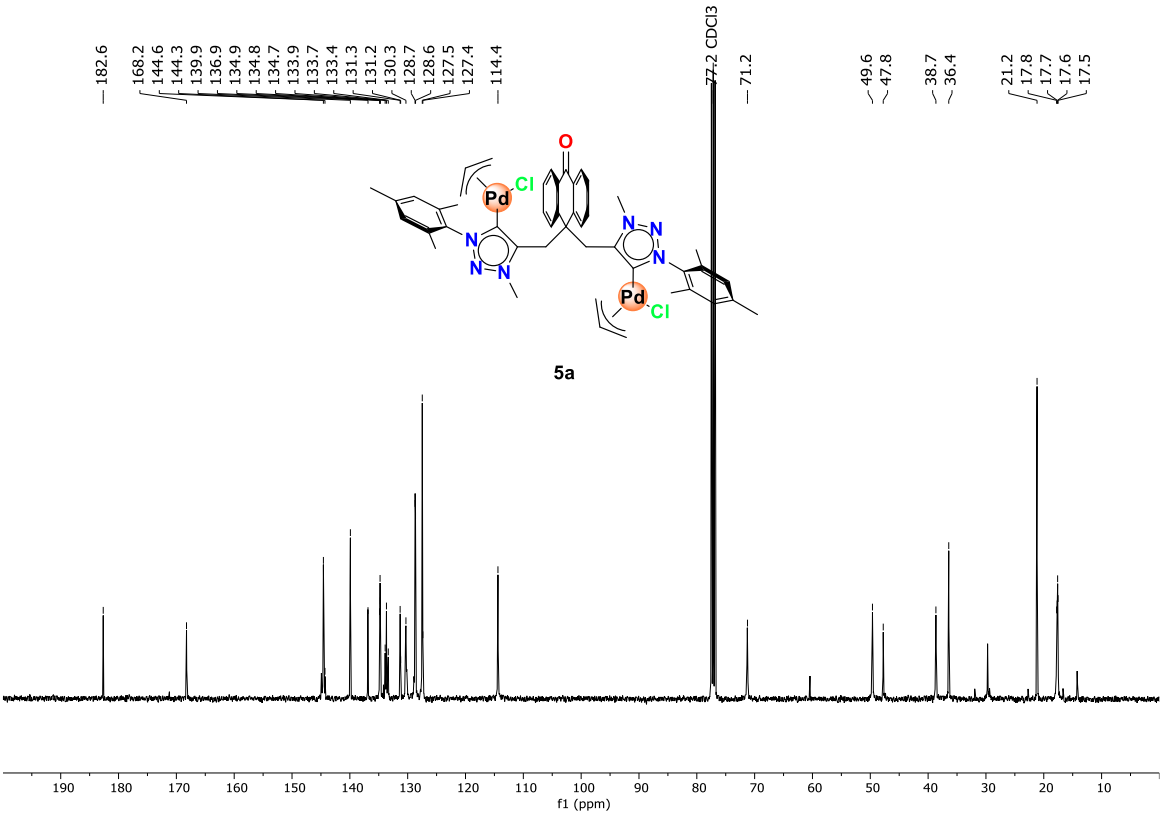


Figure S13. ^{13}C NMR spectrum (100 MHz) of triazole **4a** in $CDCl_3$.

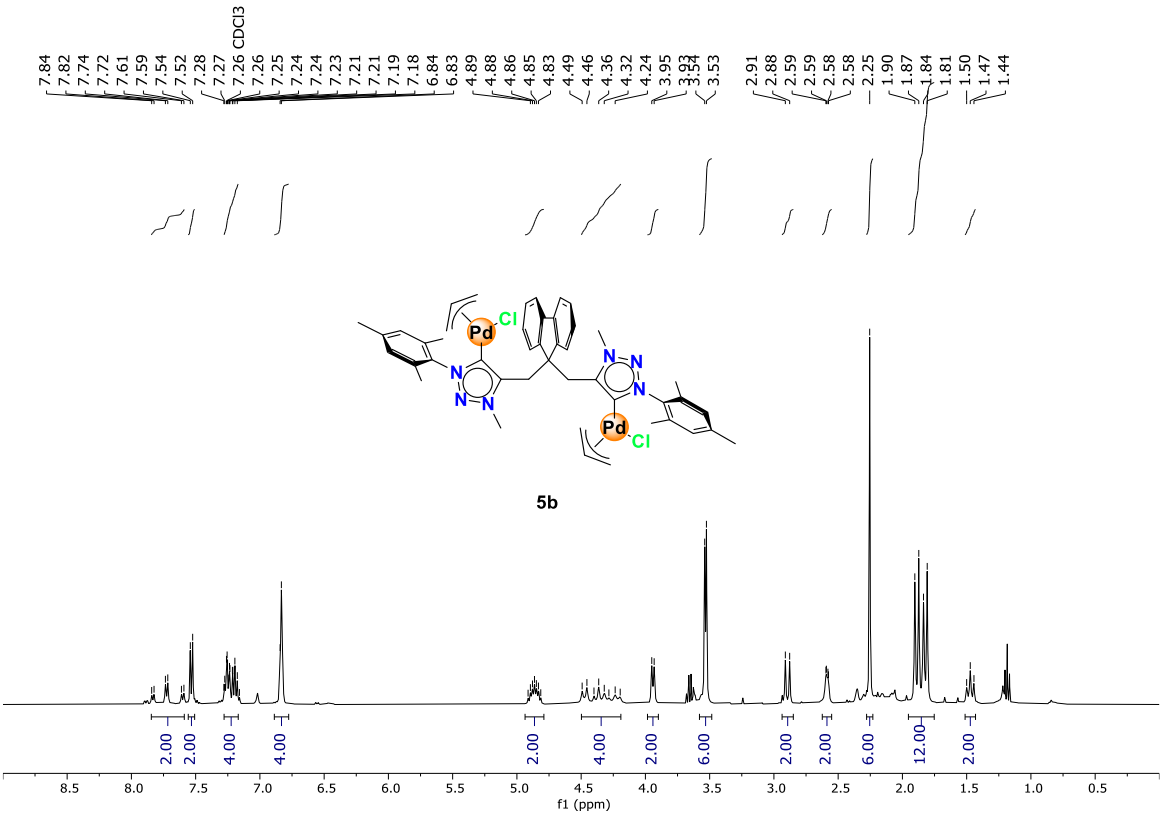


Figure S14. ^{1}H NMR spectrum (400 MHz) of triazole **4b** in $CDCl_3$.

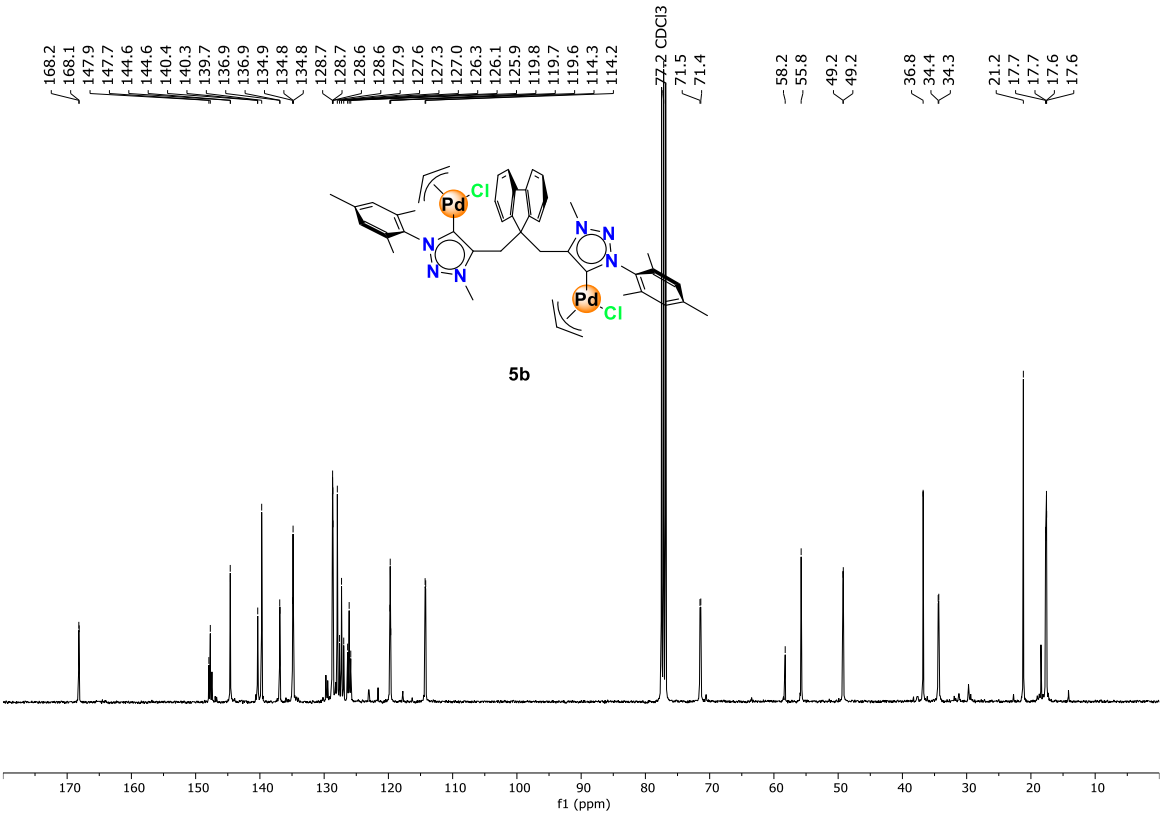


Figure S15. ^{13}C NMR spectrum (100 MHz) of triazole **4b** in $CDCl_3$.

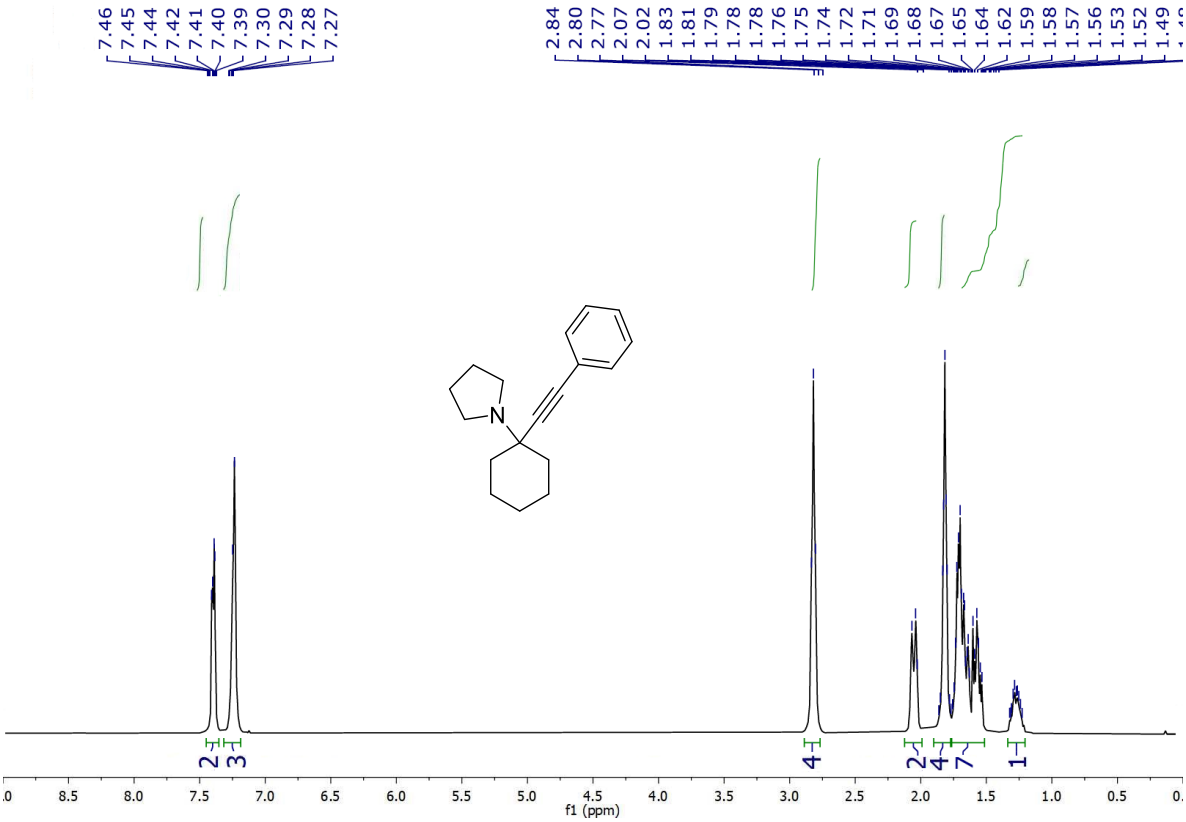


Figure S16. ^{1}H NMR spectrum (400 MHz) of 1-(1-(phenylethynyl)cyclohexyl)pyrrolidine (**5a**) in $CDCl_3$.

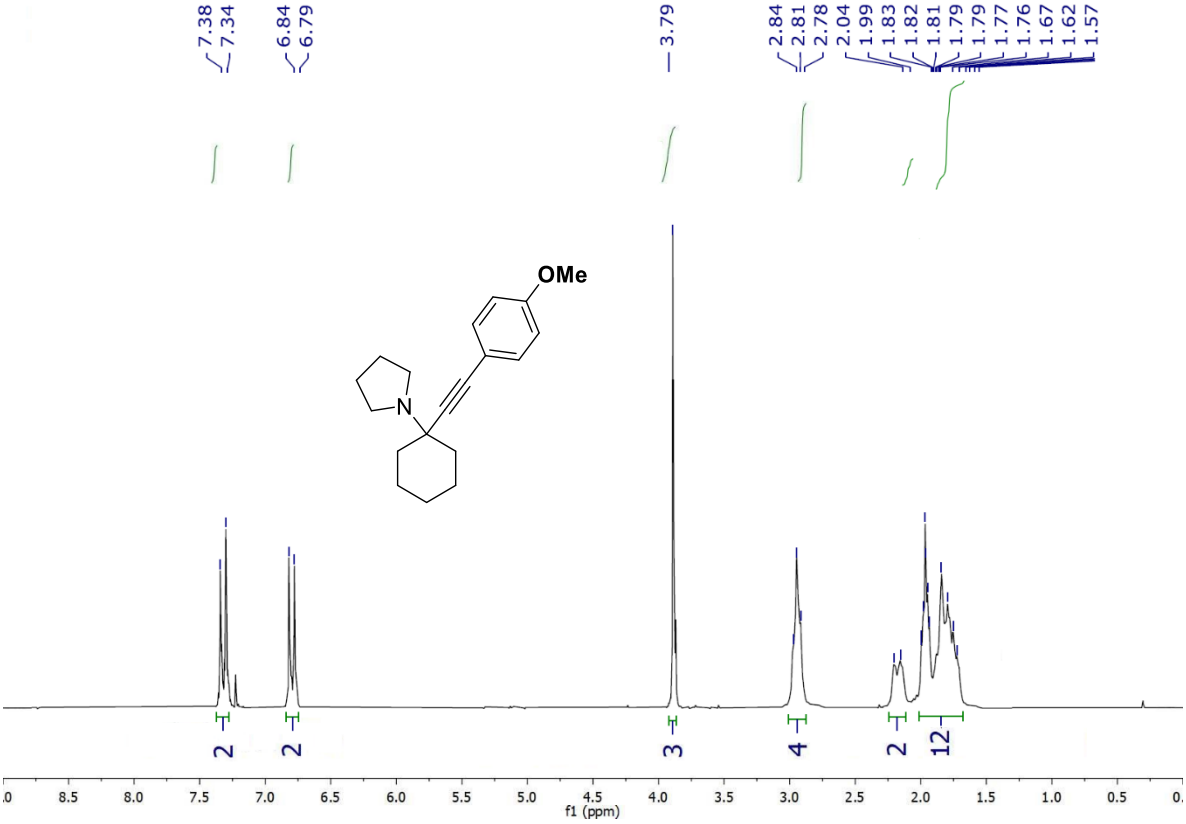


Figure S17. ^{1}H NMR spectrum (400 MHz) of 1-(1-((4-methoxyphenyl)ethynyl)cyclohexyl)pyrrolidine (**5b**) in $CDCl_3$.

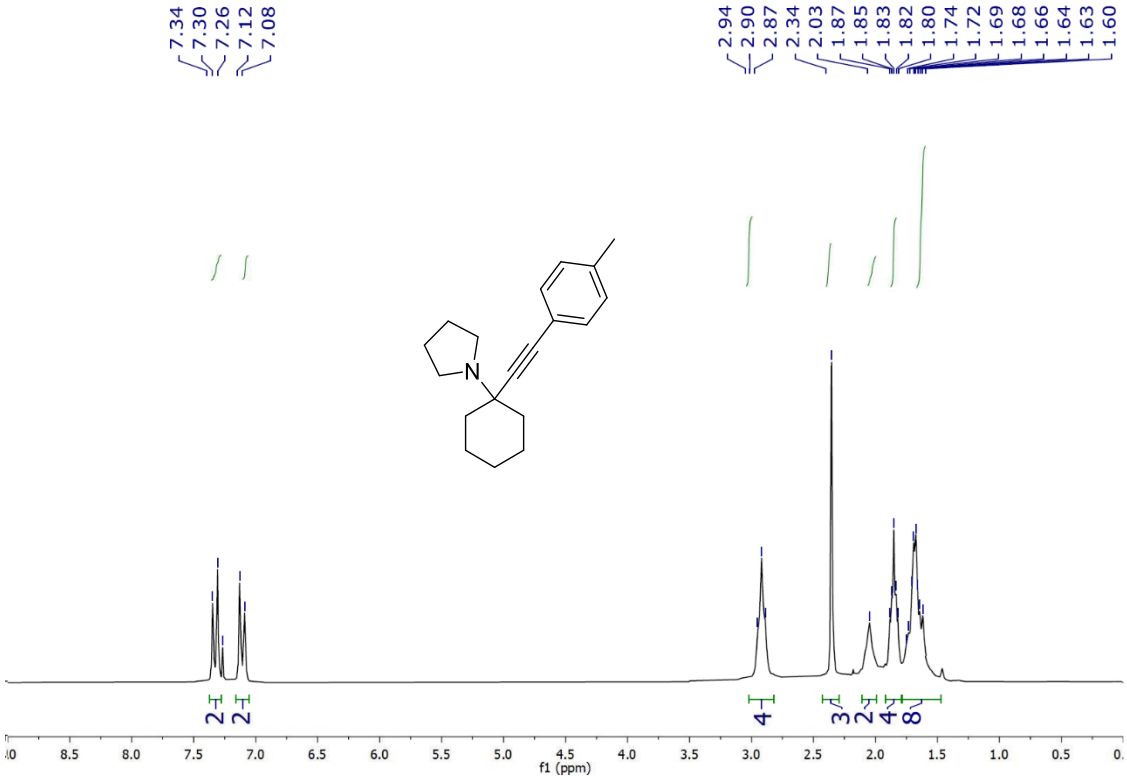


Figure S18. ^{1}H NMR spectrum (400 MHz) of 1-(1-(p-tolylethynyl)cyclohexyl)pyrrolidine (**5c**) in $CDCl_3$.

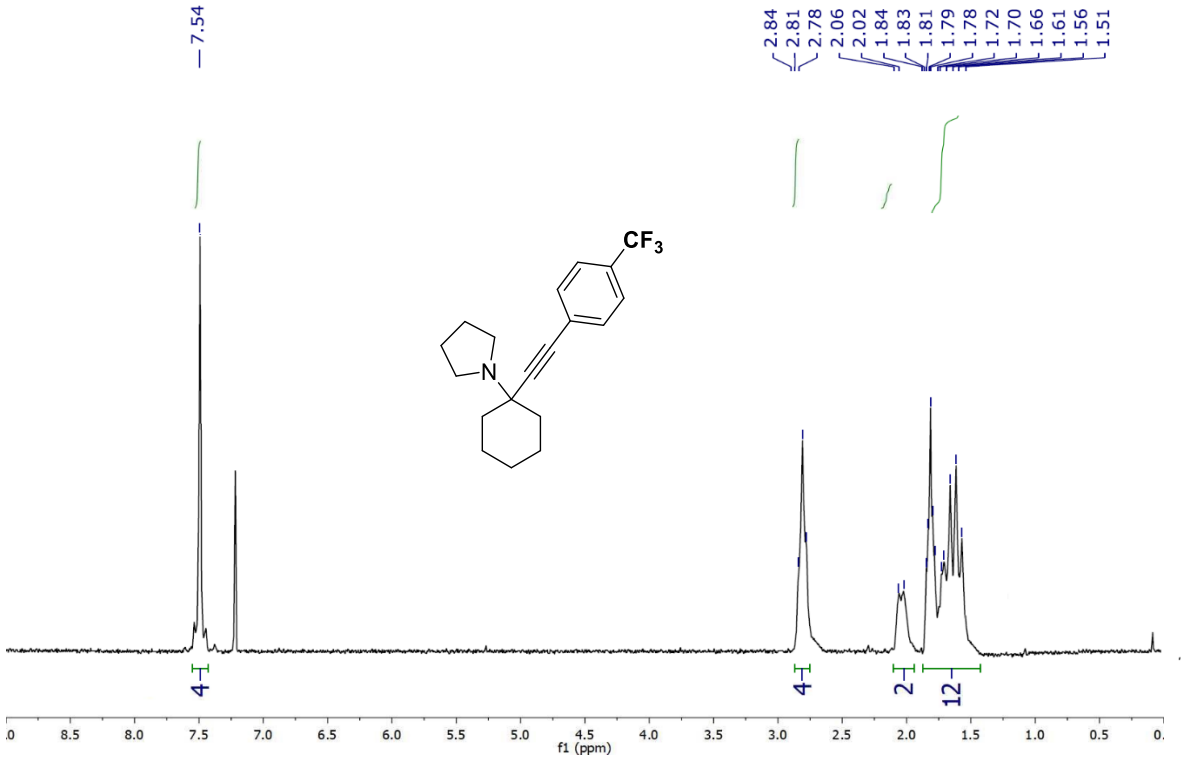


Figure S19. ^{1}H NMR spectrum (400 MHz) of 1-(1-((4-(trifluoromethyl)phenyl)ethynyl)cyclohexyl)pyrrolidine (**5d**) in $CDCl_3$.

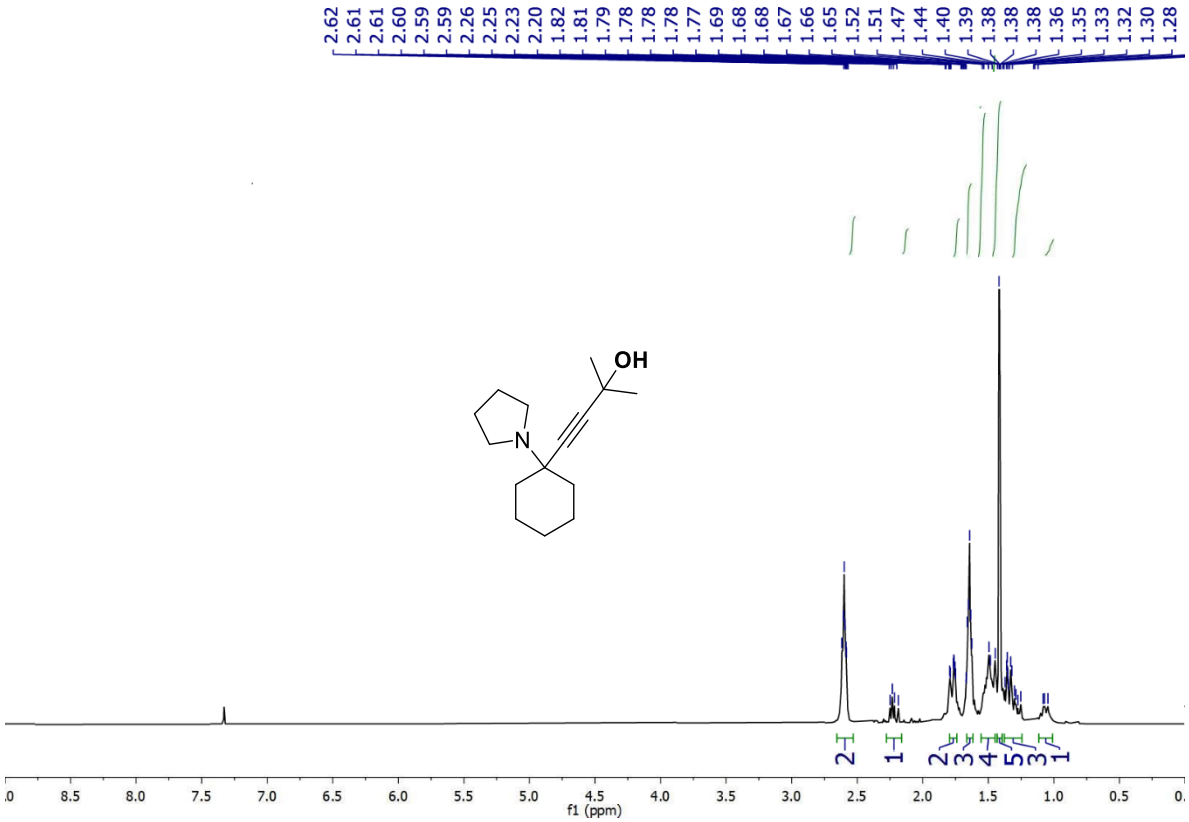


Figure S20. ^{1}H NMR spectrum (400 MHz) of 2-methyl-4-(1-(pyrrolidin-1-yl)cyclohexyl)but-3-yn-2-ol **(5e)** in $CDCl_3$.

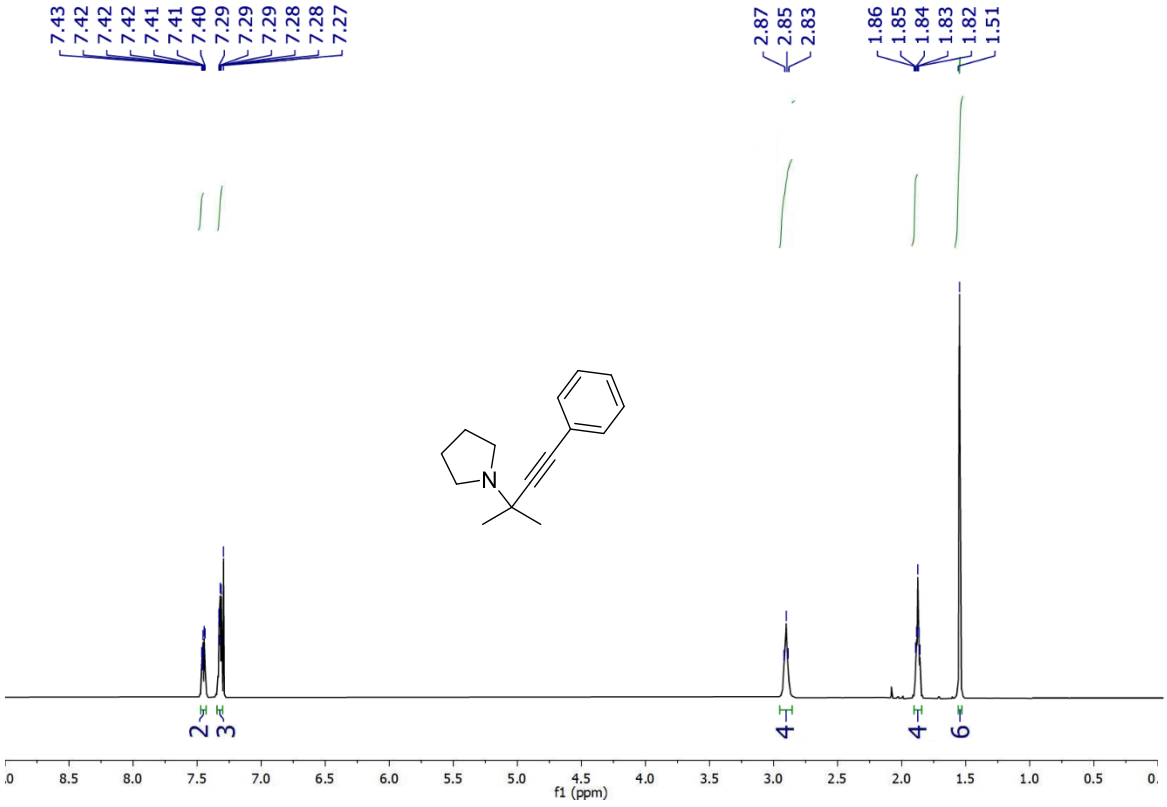


Figure S21. ^{1}H NMR spectrum (400 MHz) of 1-(2-methyl-4-phenylbut-3-yn-2-yl)pyrrolidine (**5g**) in $CDCl_3$.

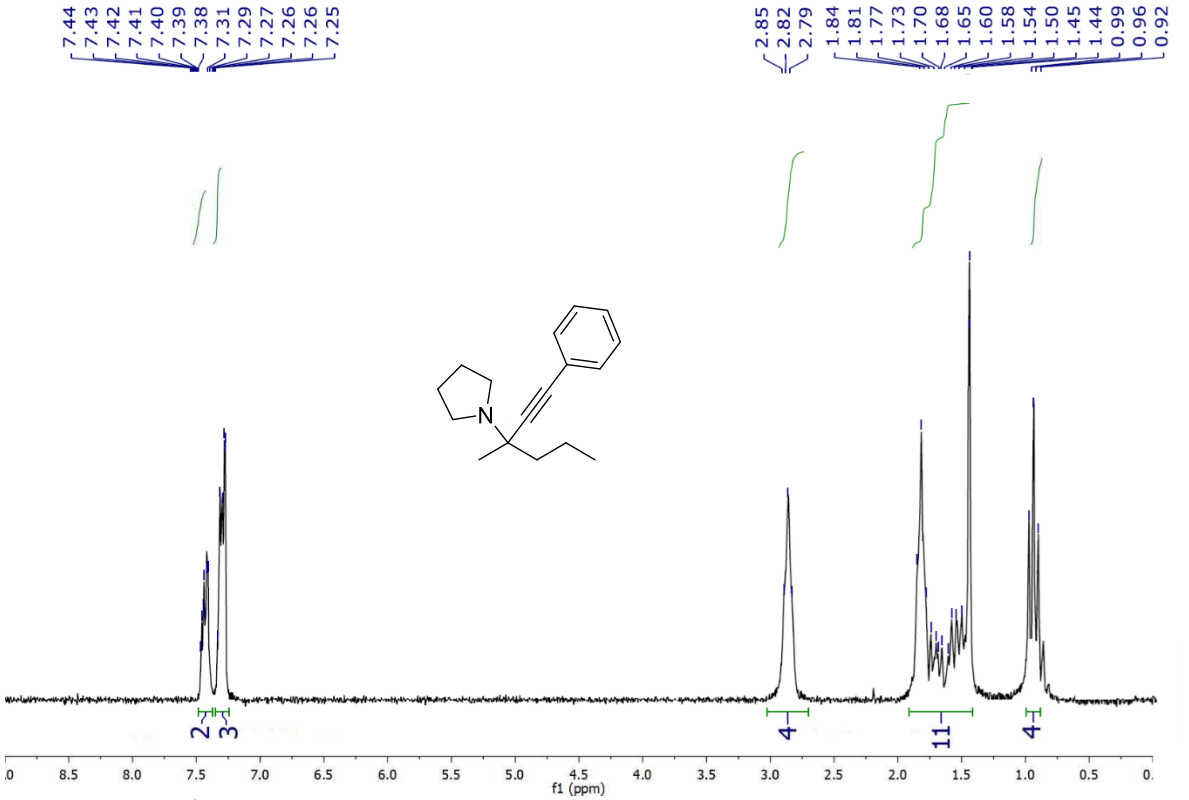


Figure S22. ^{1}H NMR spectrum (400 MHz) of 1-(3-methyl-1-phenylhex-1-yn-3-yl)pyrrolidine **(5h)** in $CDCl_3$.

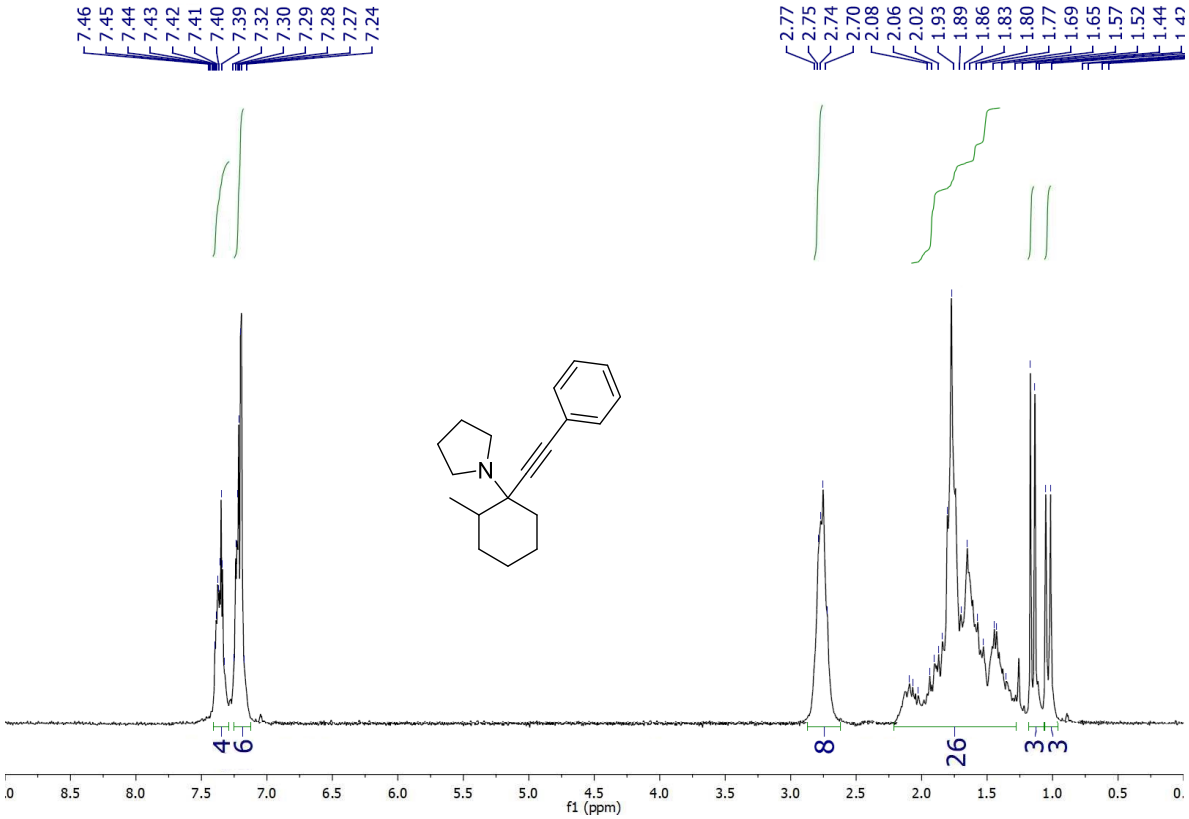


Figure S23. ^{1}H NMR spectrum (400 MHz) of 1-(2-methyl-1-(phenylethynyl)cyclohexyl)pyrrolidine (**5i**) in $CDCl_3$.

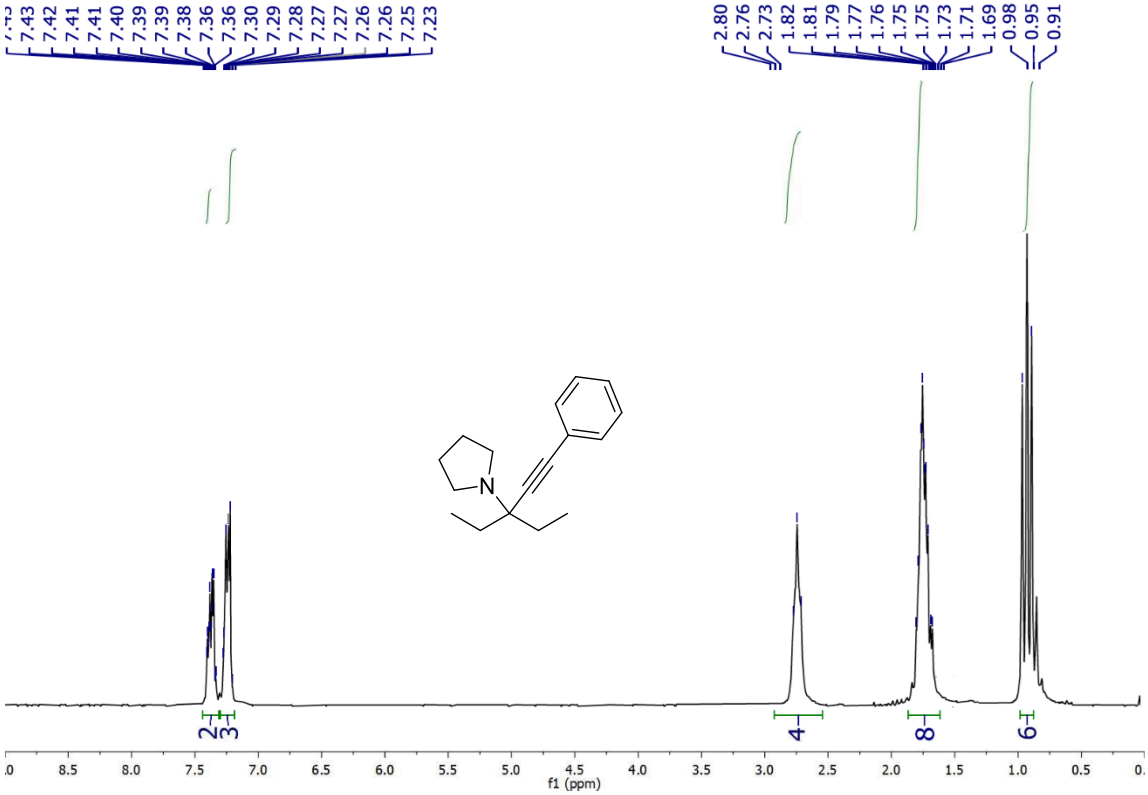


Figure S24. ^{1}H NMR spectrum (400 MHz) of 1-(3-ethyl-1-phenylpent-1-yn-3-yl)pyrrolidine pyrrolidine (**5j**) in $CDCl_3$.

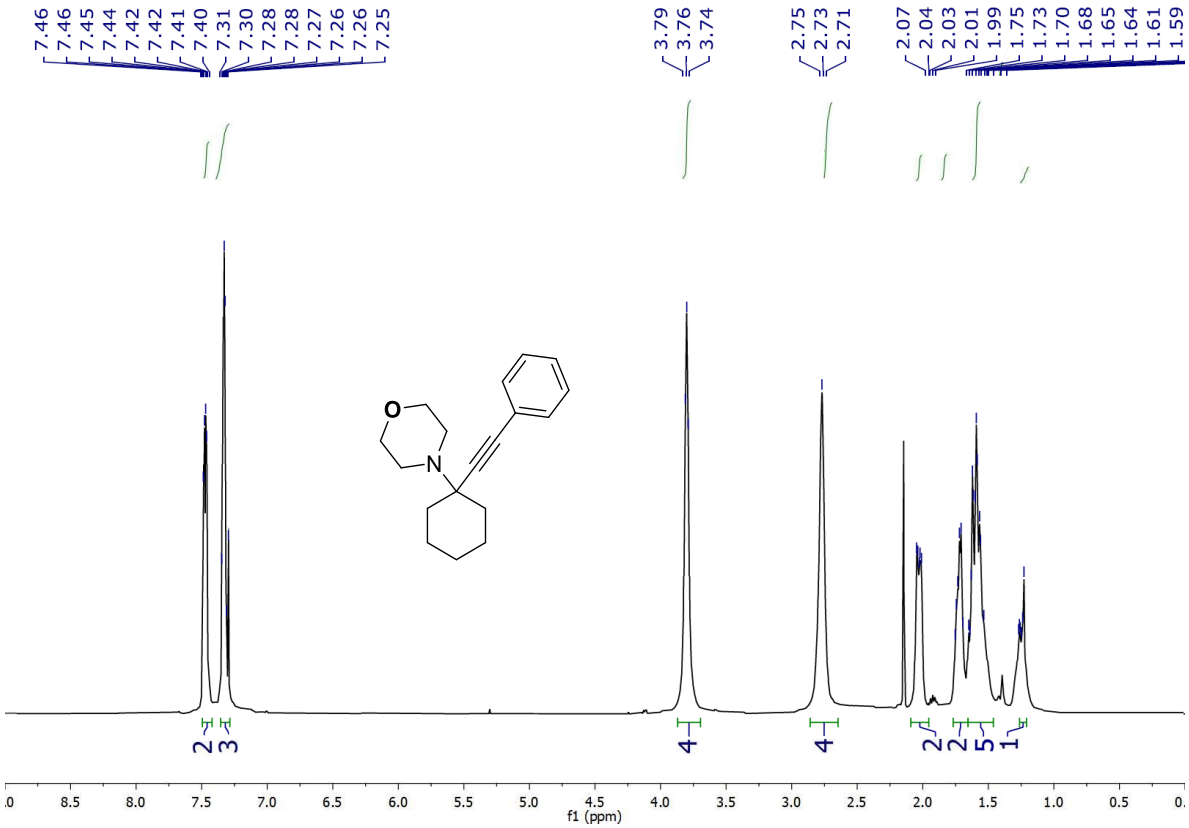


Figure S25. ^{1}H NMR spectrum (400 MHz) of 4-(1-(phenylethynyl)cyclohexyl)morpholine (**5q**) in $CDCl_3$.

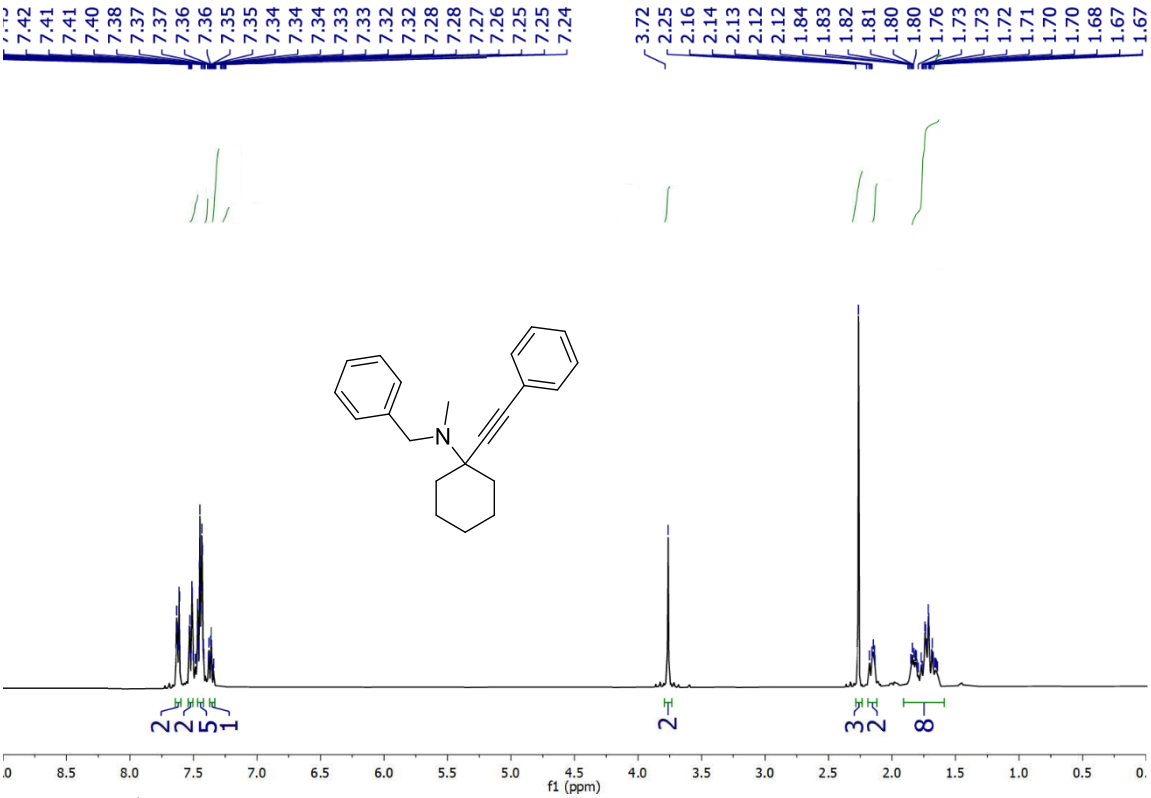


Figure S26. ^{1}H NMR spectrum (400 MHz) of N-benzyl-N-methyl-1-(phenylethynyl)cyclohexan-1-amine (**5o**) in $CDCl_3$.

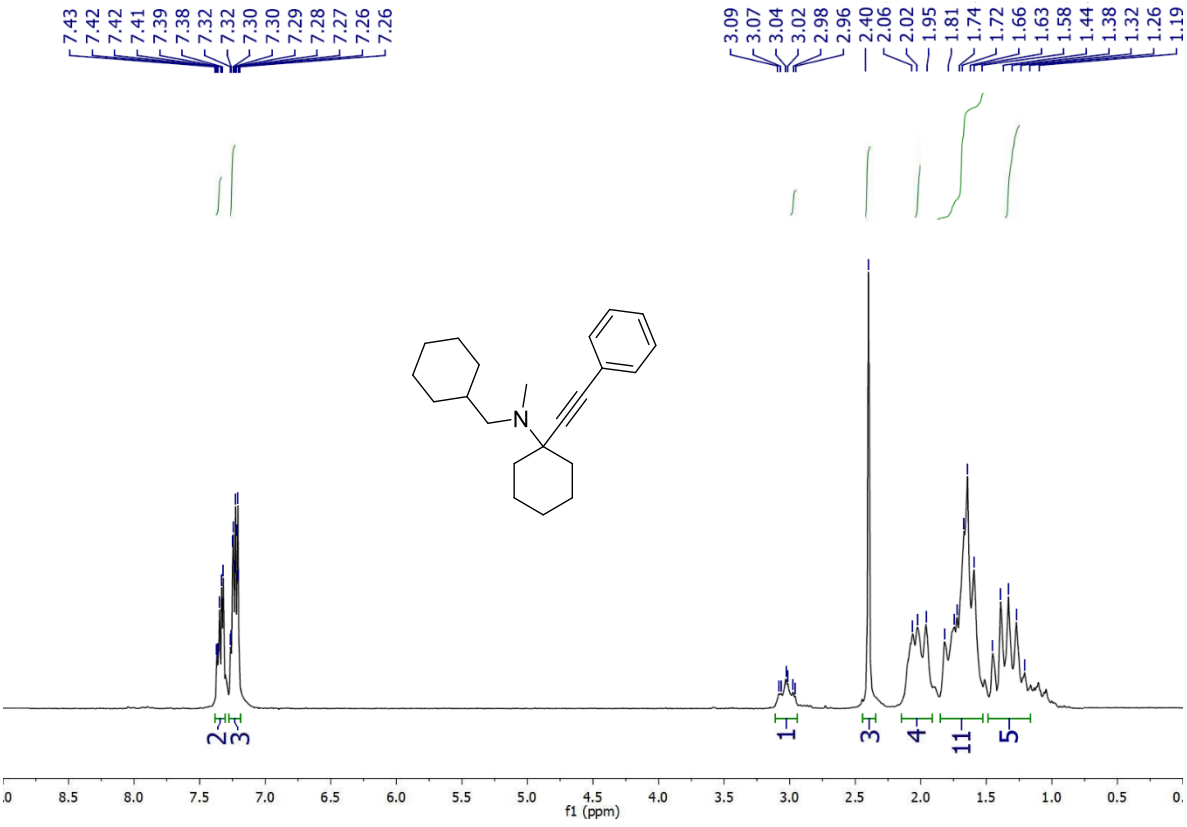


Figure S27. ^{1}H NMR spectrum (400 MHz) of N-(cyclohexylmethyl)-N-methyl-1-(phenylethynyl)cyclohexan-1-amine (**5p**) in $CDCl_3$.

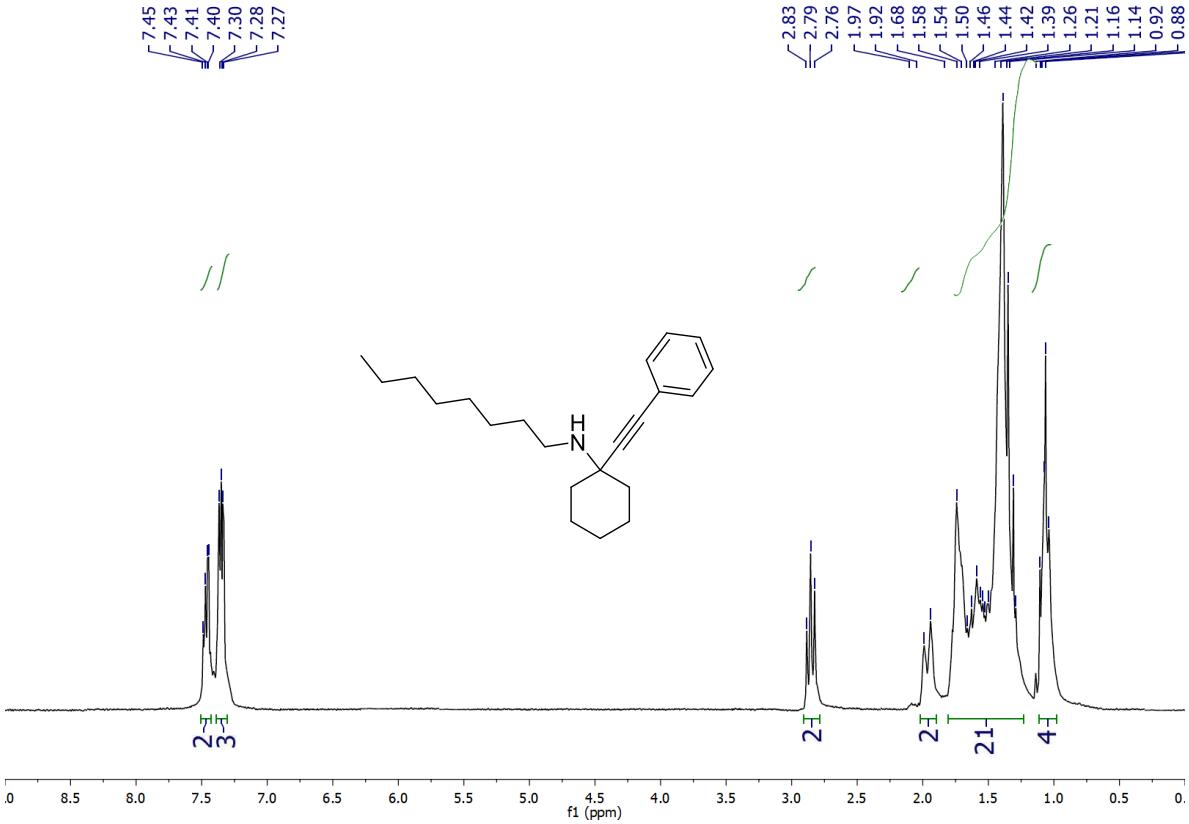


Figure S28. ^{1}H NMR spectrum (400 MHz) of N-octyl-1-(phenylethynyl)cyclohexan-1-amine (**5m**) in $CDCl_3$.

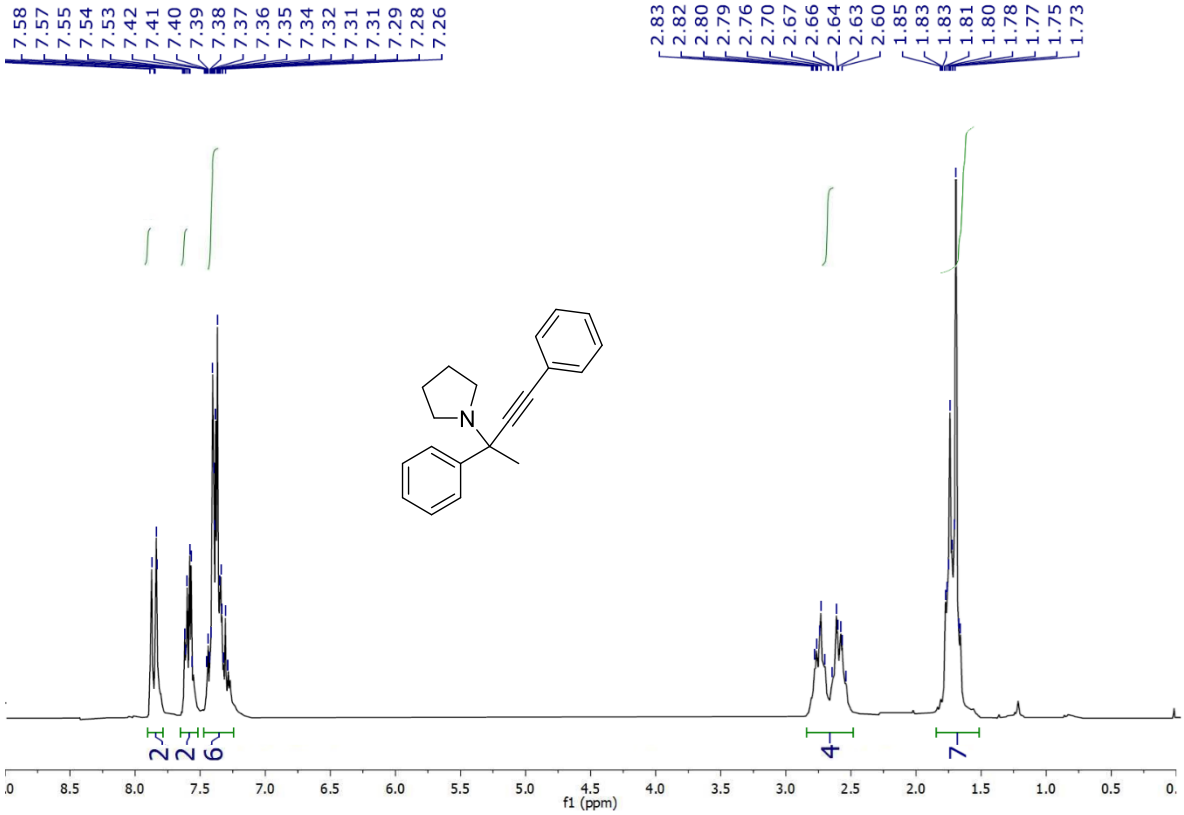


Figure S29. ^{1}H NMR spectrum (400 MHz) of 1-(2,4-diphenylbut-3-yn-2-yl)pyrrolidine (**5k**) in $CDCl_3$.

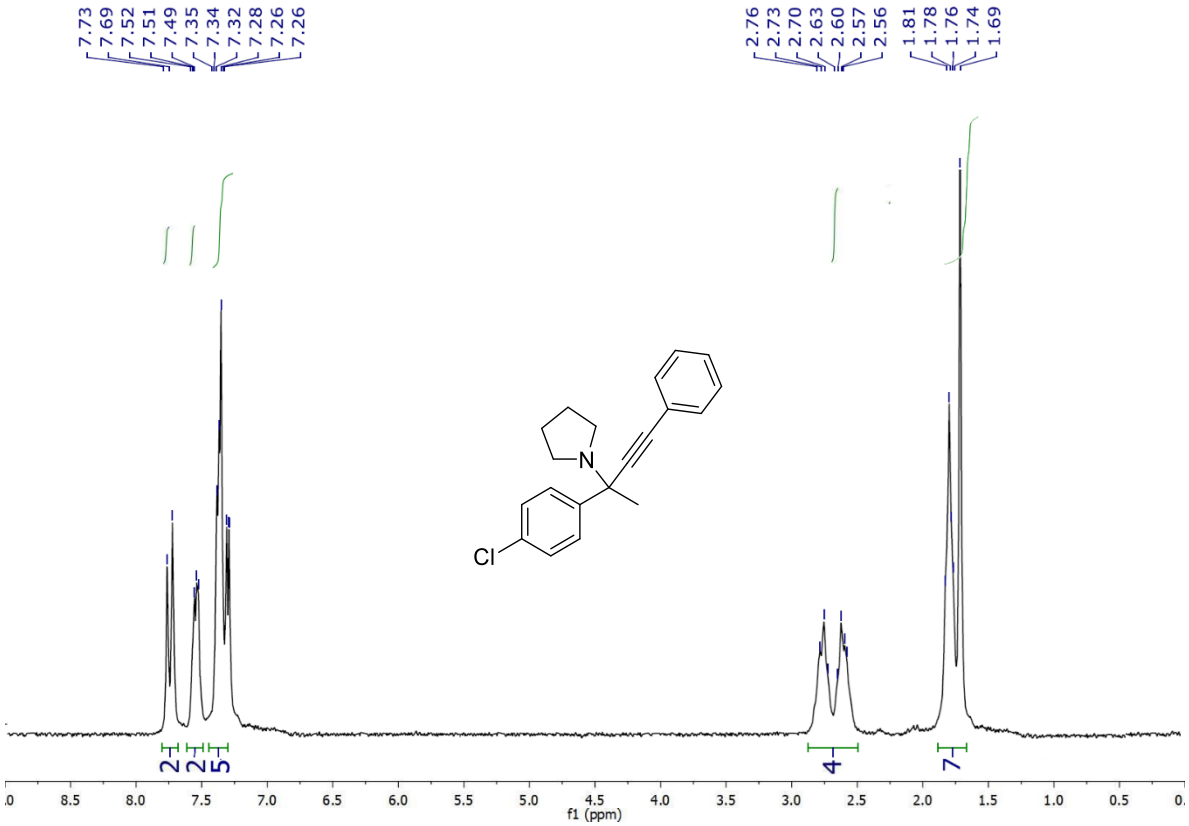


Figure S30. ^{1}H NMR spectrum (400 MHz) of 1-(2-(4-chlorophenyl)-4-phenylbut-3-yn-2-yl)pyrrolidine (**5l**) in $CDCl_3$.

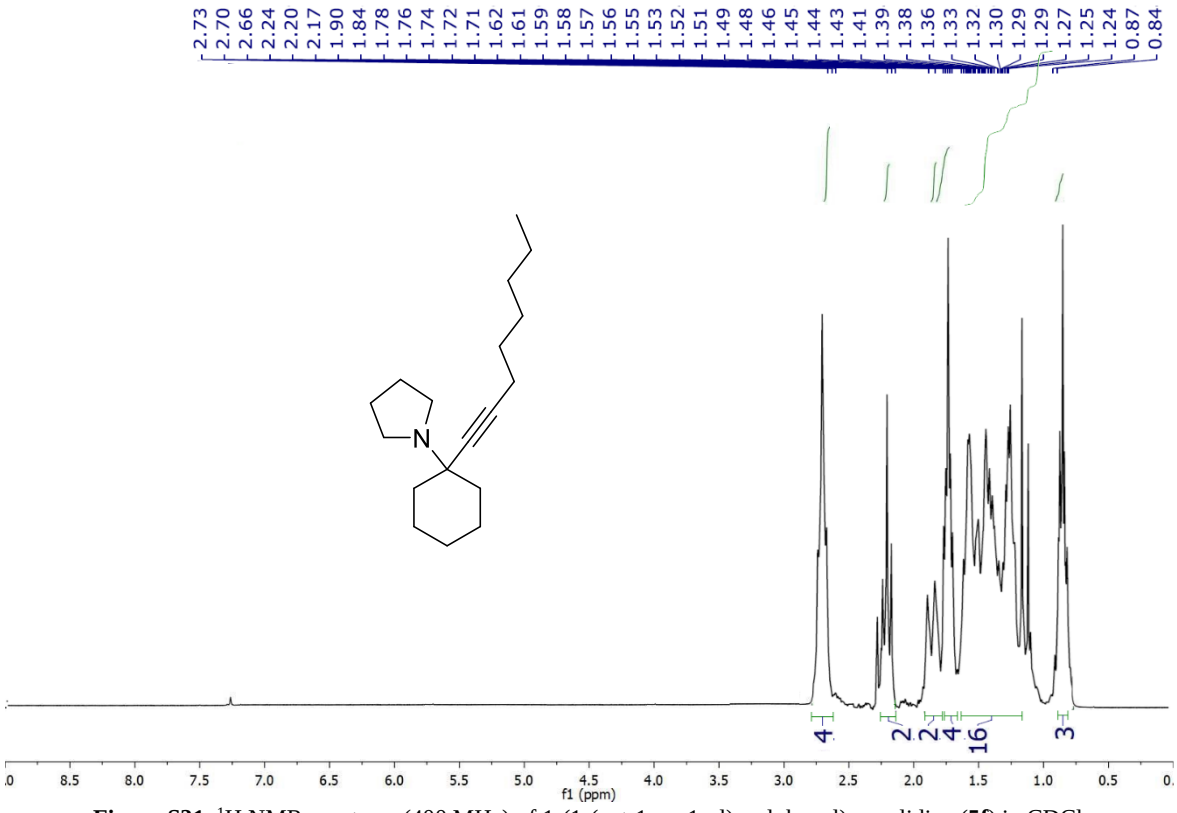


Figure S31. ^{1}H NMR spectrum (400 MHz) of 1-(1-(oct-1-yn-1-yl)cyclohexyl)pyrrolidine (**5f**) in $CDCl_3$.

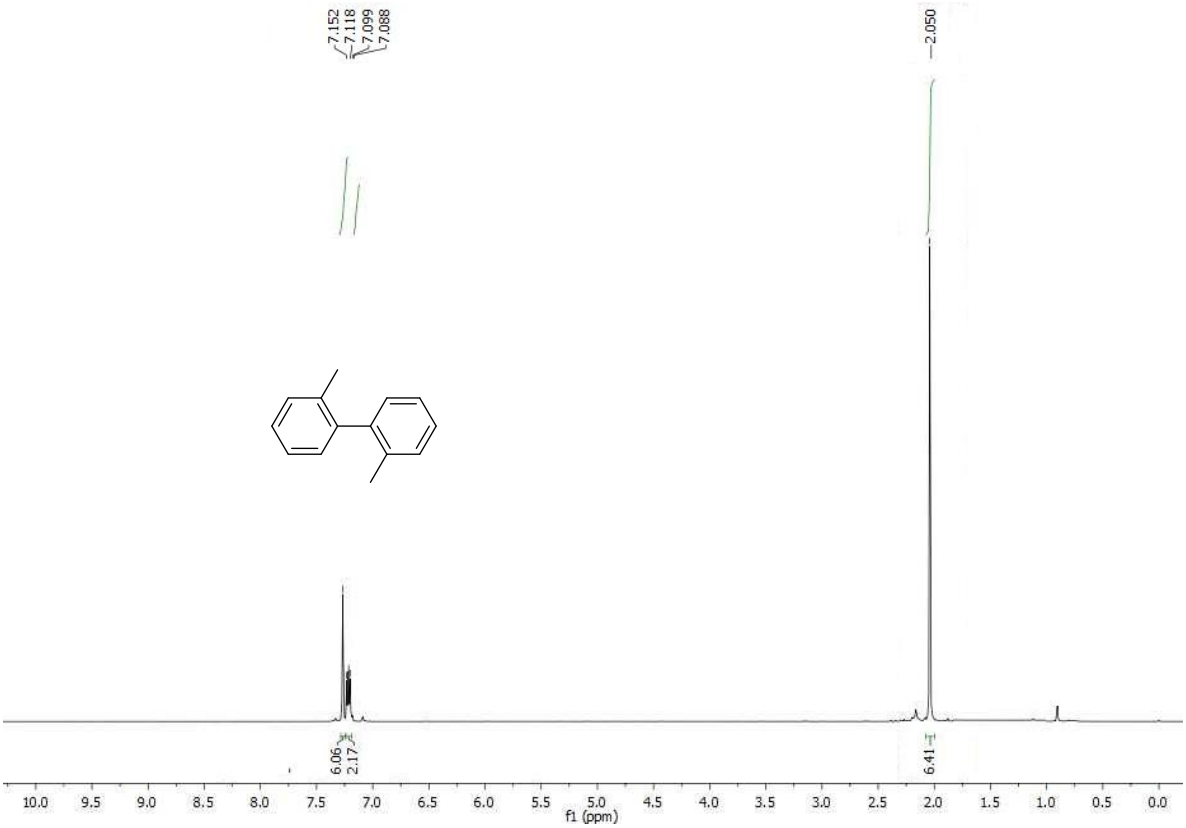


Figure S32. ^{1}H NMR spectrum (400 MHz) of 2,2-dimethyl-1,1´-biphenyl (**6a**) in $CDCl_3$.

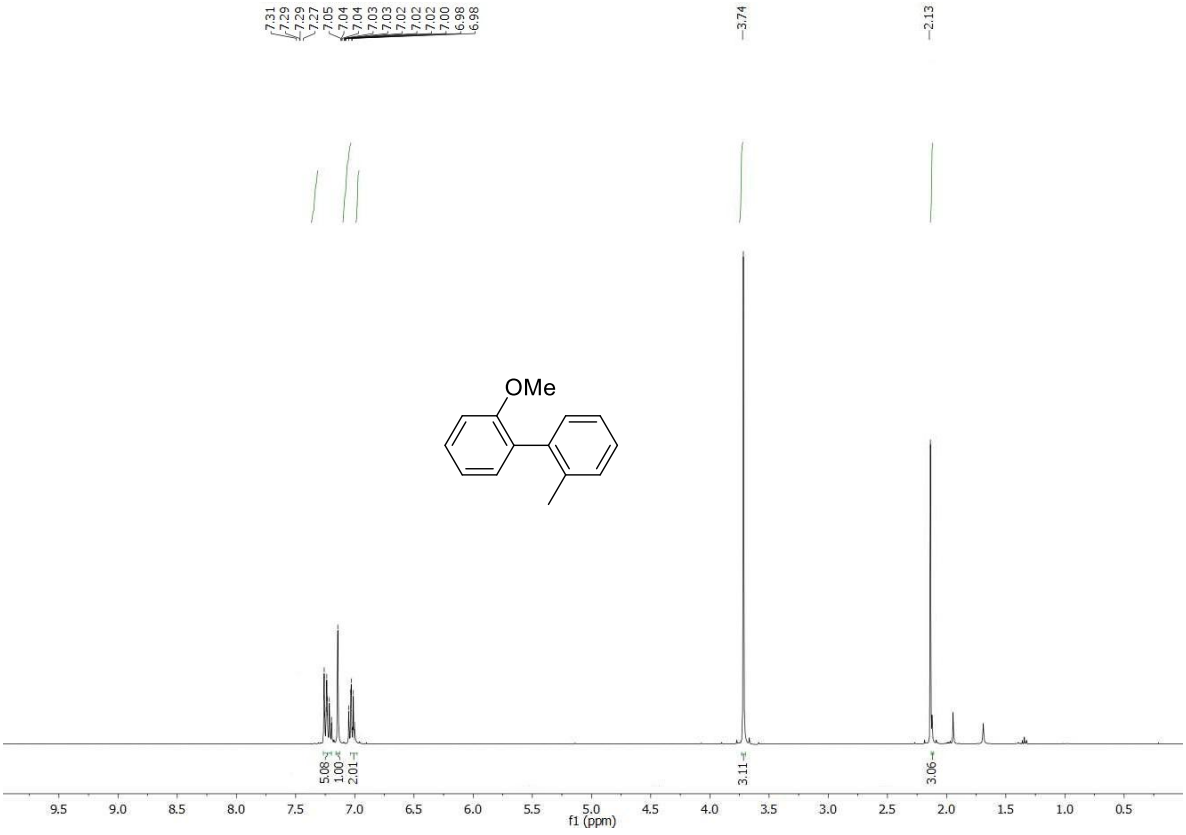


Figure S33. ^{1}H NMR spectrum (400 MHz) of 2-methoxy-2´-methyl-1,1´-biphenyl (**6b**) in $CDCl_3$.

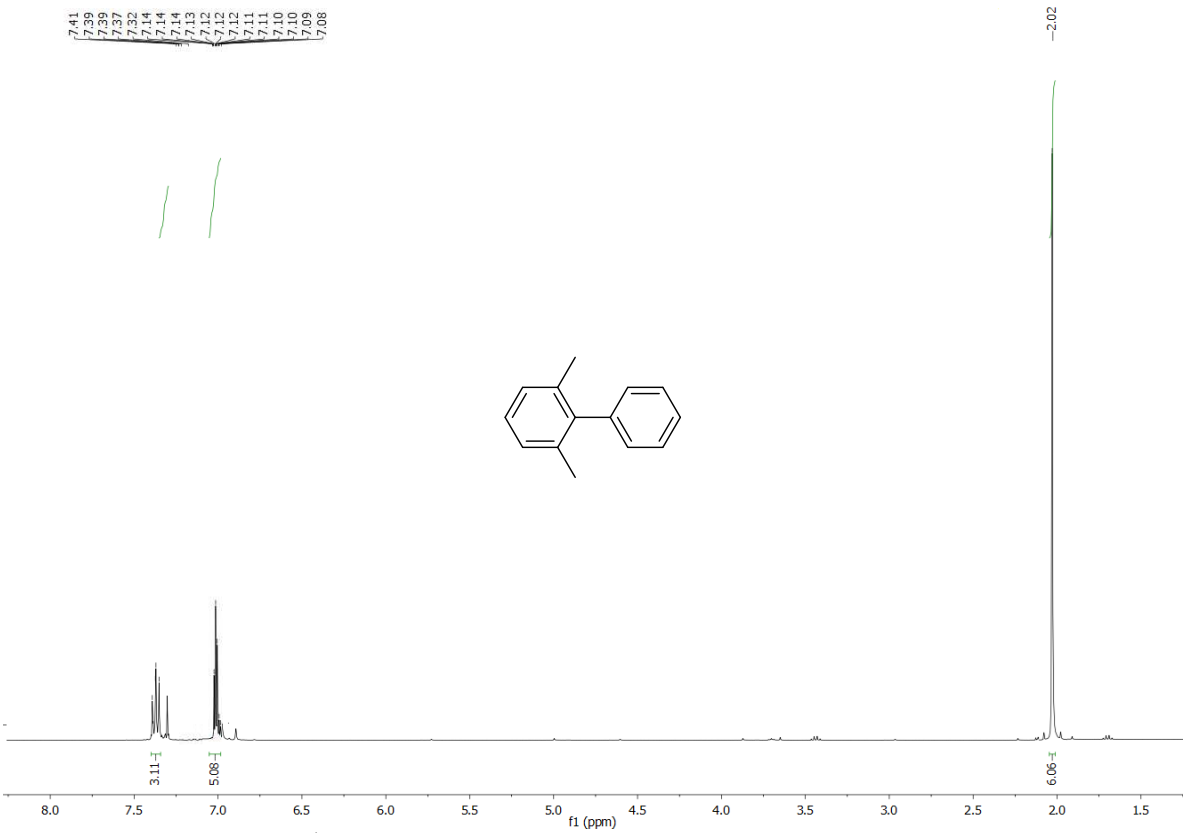


Figure S34. ^{1}H NMR spectrum (400 MHz) of 2,6-dimethyl-biphenyl (**6c**) in $CDCl_3$.

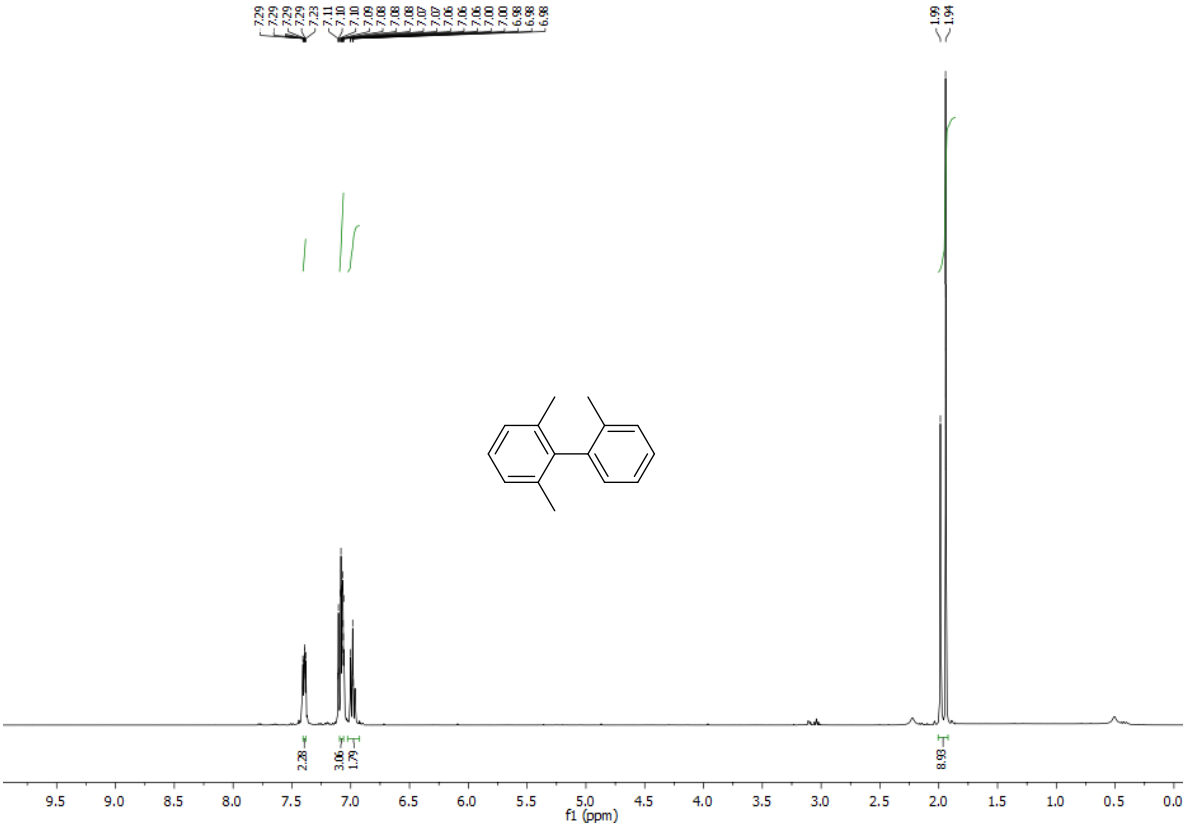


Figure S35. ^{1}H NMR spectrum (400 MHz) of 2,2´,6-trimethyl-biphenyl (**6e**) in $CDCl_3$.

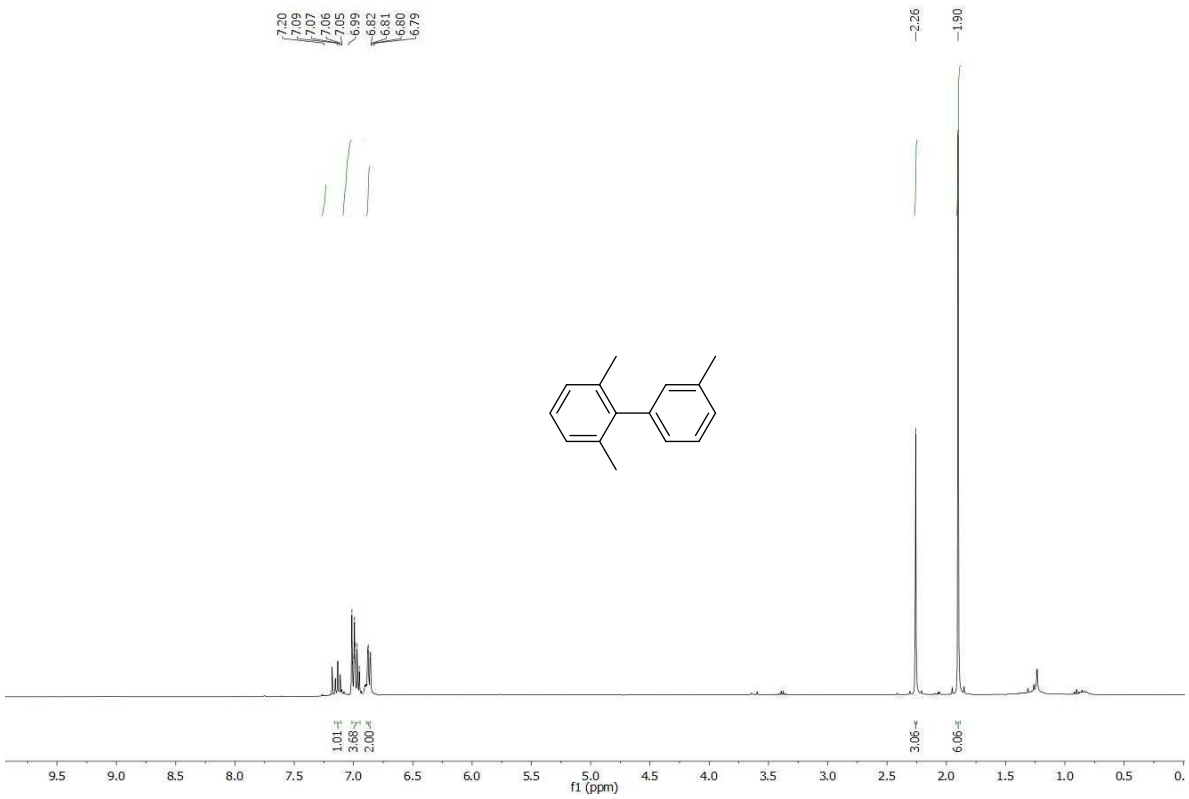


Figure S36. ^{1}H NMR spectrum (400 MHz) of 2,3´,6-trimethyl-biphenyl (**6f**) in $CDCl_3$.

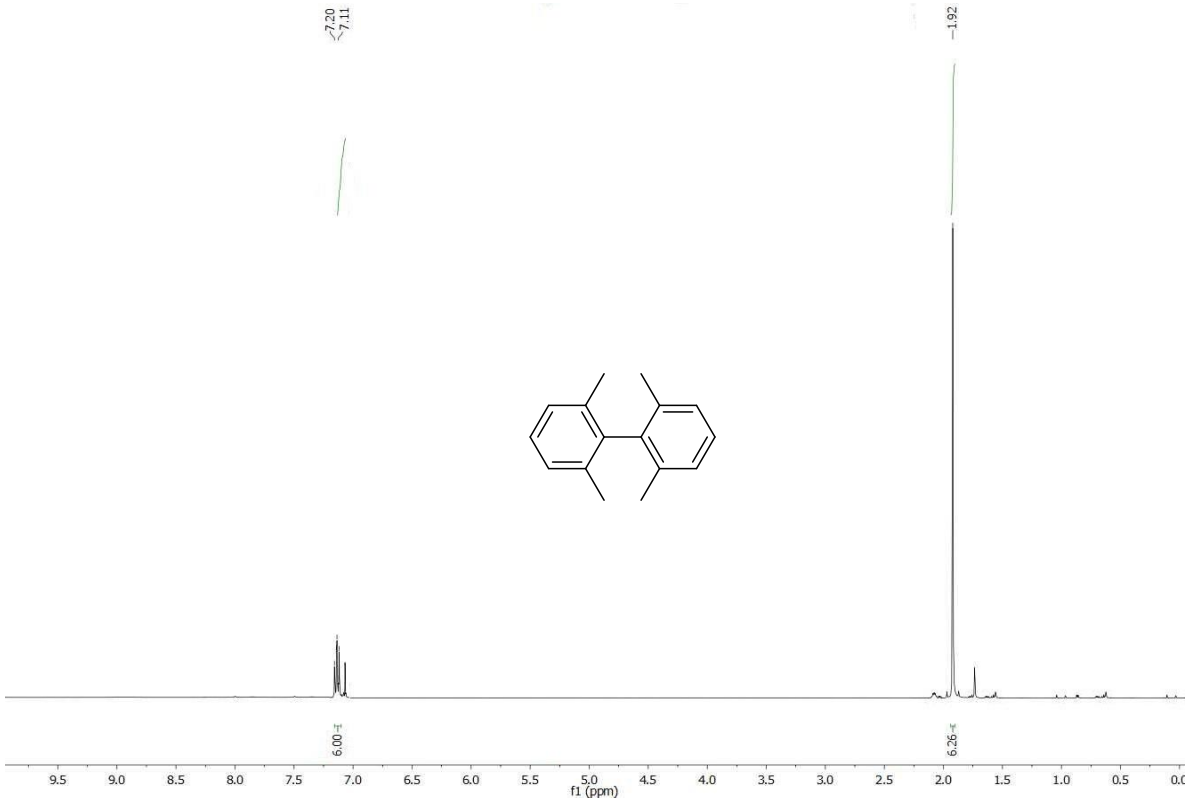


Figure S37. ^{1}H NMR spectrum (400 MHz) of 2,2',6,6'-tetramethyl-1,1'-biphenyl (**6g**) in $CDCl_3$.

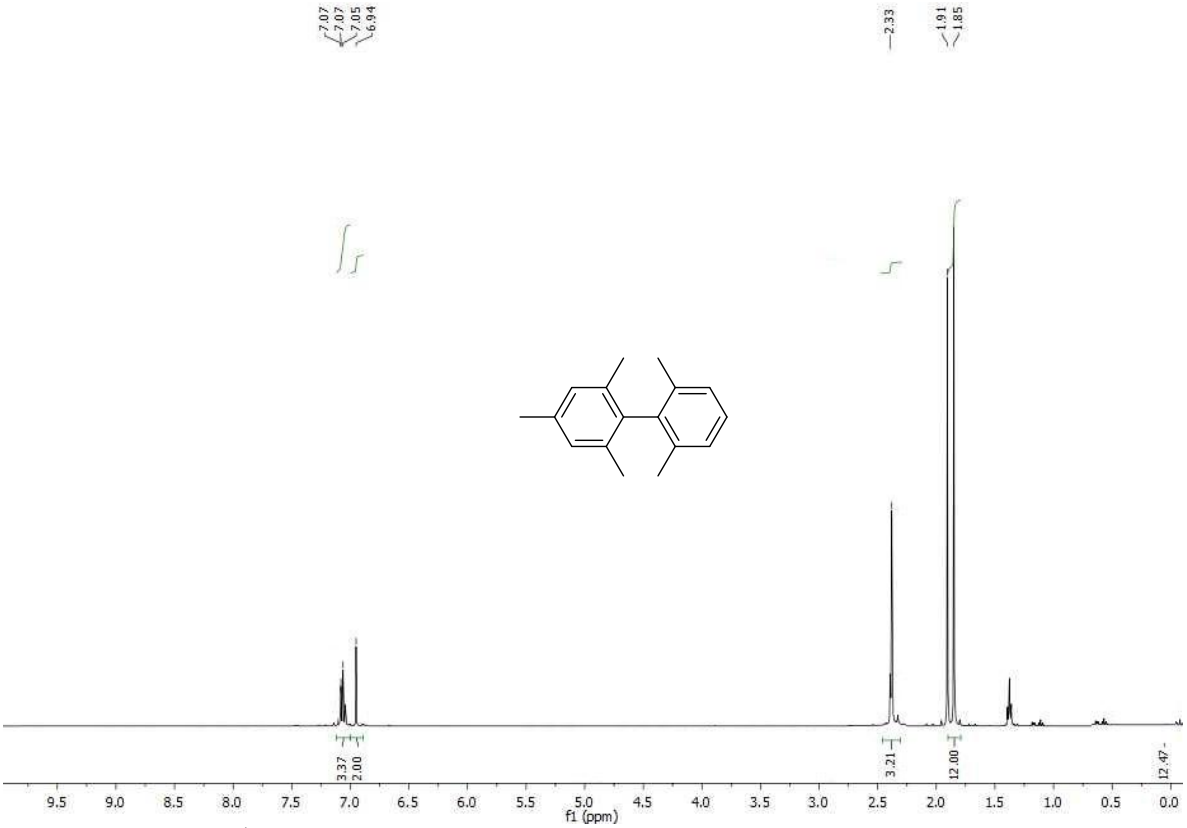


Figure S38. ^{1}H NMR spectrum (400 MHz) of 2,2',4,6,6'-pentamethyl-1,1'-biphenyl (**6h**) in $CDCl_3$.

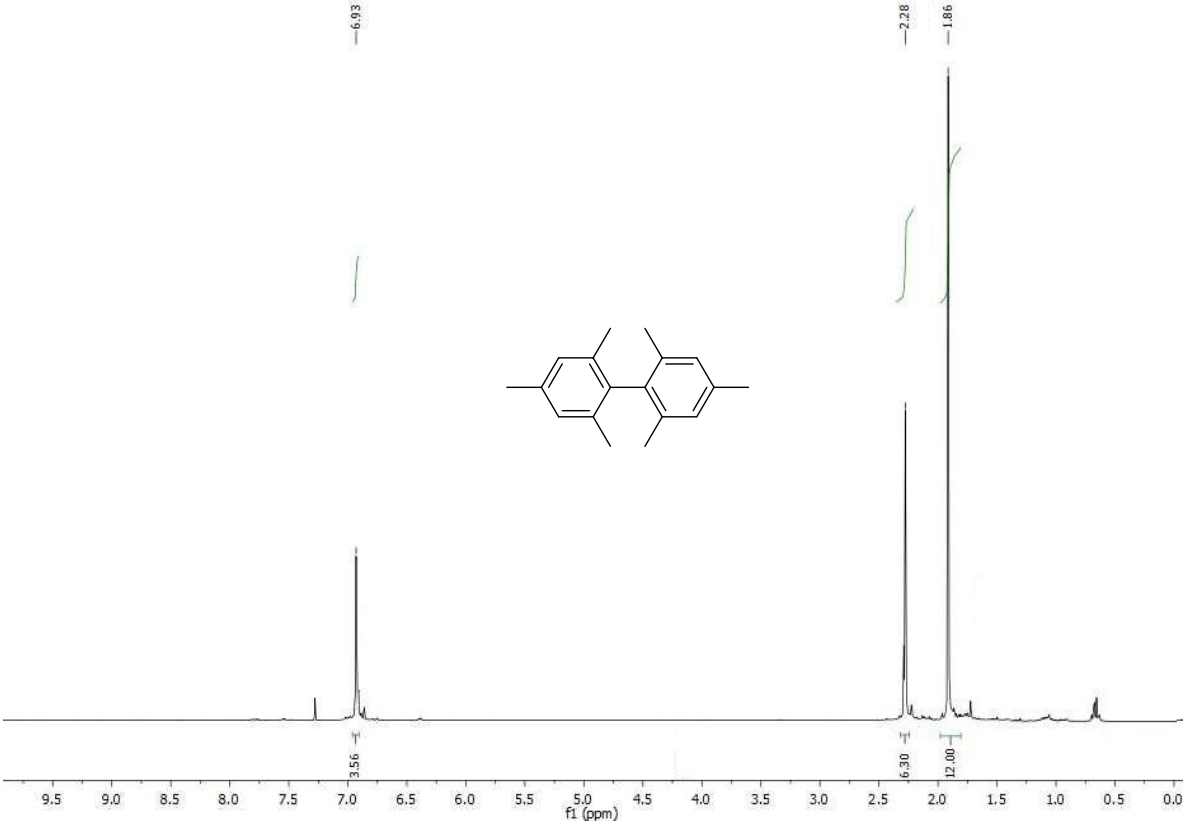


Figure S39. ^{1}H NMR spectrum (400 MHz) of 2,2',4,4,6,6'-hexamethylbiphenyl (**6i**) in $CDCl_3$.