Supporting Information for

N-heterocyclic carbene gold(I) and silver(I) complexes bearing functional groups for bio-conjugation.

Mary E. Garner, Weijia Niu, Ion Ghiviriga, and Adam S. Veige*

University of Florida, Department of Chemistry, Center for Catalysis, P.O. Box 117200, Gainesville, FL, 32611.

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1. General Considerations.

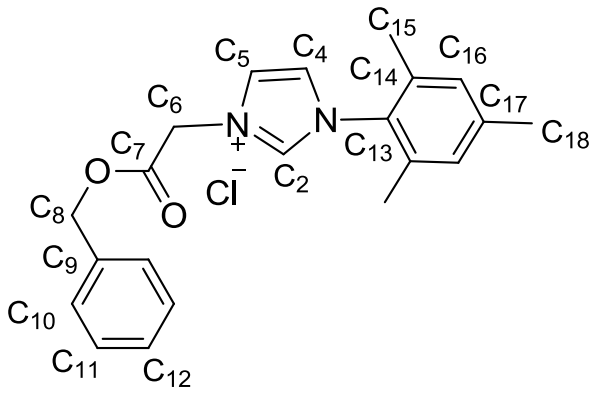
Compounds 1-mesityl-1*H*-imidazole, 1-tert-butyl-1*H*-imidazole, and **3** were prepared according to previously reported procedures.[22,43-44] Unless stated otherwise all syntheses and manipulations were performed under aerobic conditions. $(CH_3)_2SAu^{I}Cl$ and Ag_2O were obtained from Sigma Aldrich and used without further purification.

All NMR spectra were collected on either a Varian Mercury Broad Band 300 MHz or Varian Inova 500 MHz spectrometer. ^{1}H and ^{13}C chemical shifts are reported in δ (ppm) with the solvent peak referenced as an internal reference ($CDCl_3$ δ = 7.26 ppm for ^{1}H and 77.00 ppm for ^{13}C, DMSO-d_6 δ = 2.54 ppm for ^{1}H and 39.54 ppm for ^{13}C).

Electrospray Ionization Mass Spectrometry (ESI-MS) data for positive mode were obtained according to the following procedure. Depending on solubility, the sample was dissolved in methylene chloride, chloroform, or water and then directly injected into an auto-sampler. After injection, it was subjected to ESI with methanol as the mobile phase. The ions were detected with an Agilent 6210 TOF-MS instrument and the data were processed using MassHunterTMsoftware.

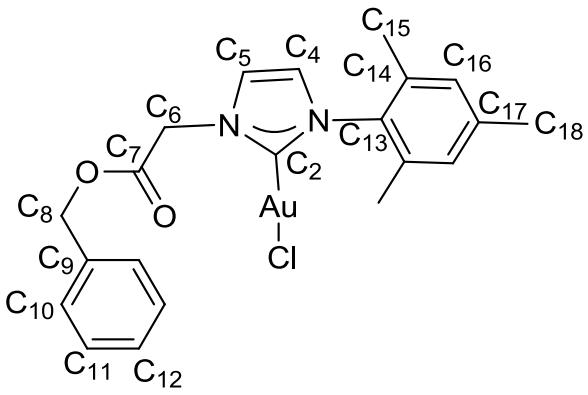
2. Syntheses

1-mesityl-3-(2-benzylacetyl) imidazolium chloride (**1**) was prepared by adding 1-mesityl-1*H*-imidazole (0.640 g, 3.44 mmol), a magnetic stir bar, and 4 mL of dry toluene to a 250 mL round bottom flask. The mixture was allowed to stir for 2 min followed by the dropwise addition of benzyl 2-chloroacetate (0.53 mL, 3.44 mmol). The system was placed under Ar and heated to 110 °C for 6 h while stirring and then stirred for an additional 12 h at room temperature. The solvent was removed in vacuo and the resulting colorless solid was triturated with ether (1.02 g, 79.9%).



^{1}H NMR(500 MHz, $CDCl_3$) δ = 10.41 (s, 1H, *H*C_2), 7.94 (s, 1H, *H*C_5), 7.34 (m, 5H, *H*C_{10}, *H*C_{11}, *H*C_{12}), 7.08 (s, 1H, *H*C_4), 6.95 (s, 2H, *H*C_{16}), 5.98 (s, 2H, H_2C_8), 5.18 (s, 2H, H_2C_6), 2.32 (s, 3H, H_3C_{18}), 2.01 (s, 6H, H_3C_{15}). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 166.4 (C_7), 141.3 (C_2), 139.7 (C_{13}), 139.7 (C_{17}), 134.3 (C_{14}), 134.3 (C_9), 130.6 (C_{16}), 129.7 (C_{10}), 128.7 (C_{12}), 128.6 (C_{11}), 124.4 (C_4), 122.3 (C_5), 68.4 (C_8), 50.6 (C_6), 21.1 (C_{18}), 17.4 (C_{15}). Anal. Calcd. for $C_{21}H_{23}ClN_2O_2$ (370.88 g/mol): C: 68.01%; H: 6.25%; N: 7.55%, Found; C: 67.99%; H: 6.43 N: 7.61%.

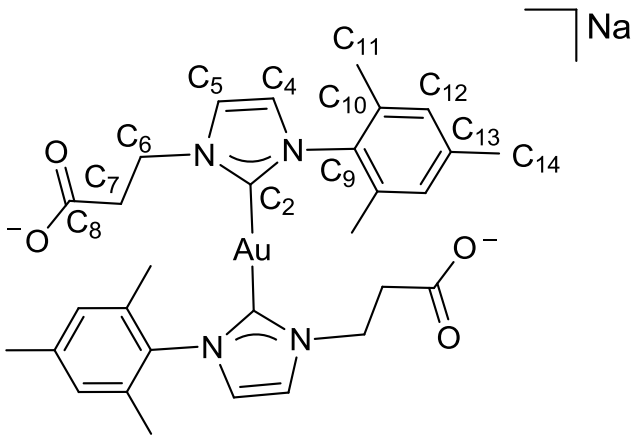
Synthesis of 1-mesityl-3-(2-benzylacetyl)imidazole-2-ylidene gold(I) chloride (2).



1-mesityl-3-(2-benzyleacetyl)imidazolium gold(I) chloride **2** was prepared via an in situ transmetalation from silver(I). Proligand 1 (0.201 g, 0.543 mmol) and Ag_2O (0.150 g, 0.647 mmol) were suspended in 5 mL of dichloromethane and allowed to stir for 24 h in the absence of light. The resulting suspension was passed through a Celite® pad and fine frit filter directly into a stirring suspension of $(CH_3)_2SAu^ICl$ (0.075 g, 0.255 mmol) in 5 mL of dicholoromethane. The reaction mixture was allowed to stir at room temperature for 3.5 h in darkness. The mixture was then passed through a Celite® pad and medium fritted funnel to yield an amber colored filtrate. The solvent was concentrated and then treated with an excess of pentanes to precipitate **2** as a fine off-white powder (0.032 g, 22.2%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38 (m, 5H, HC_{10}, HC_{11}, HC_{12}), 7.23 (s, 1H, HC_5), 6.95 (s, 2H, HC_{16}), 6.92 (s, 1H, HC_4), 5.24 (s, 2H, H_2C_8), 5.14 (s, 2H, H_2C_6), 2.33 (s, 3H, H_3C_{18}), 2.00 (s, 6H, H_3C_{15}). ^{13}C NMR (126 MHz $CDCl_3$) δ = 174.1 (C_2), 166.7 (C_7), 139.8 (C_{13}), 139.8 (C_{17}), 134.8 (C_{14}), 134.4 (C_9), 129.4 (C_{16}), 128.8 (C_{10}), 128.8 (C_{12}), 128.7 (C_{11}), 122.5 (C_4), 121.7 (C_5), 68.2 (C_8), 51.9 (C_6), 21.1 (C_{18}), 17.7 (C_{15}). ESI-MS (positive ion, calculated for M = $C_{21}H_{22}AuClN_2O_2$) Theor: 1155.1963 m/z $[2M+Na]^+$, 1097.2377 m/z $[2M-Cl]^+$, 589.0928 m/z $[M+Na]^+$, 531.1341 m/z $[M-Cl]^+$. Found: 1155.1945 m/z $[2M+Na]^+$, 1097.2374 m/z $[2M-Cl]^+$, 589.0926 m/z $[M+Na]^+$,

531.1339 m/z $[M\text{-}Cl]^+$.

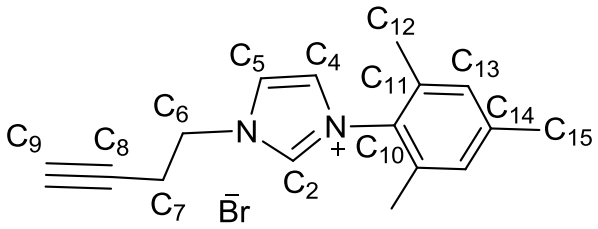
Synthesis of sodium *bis*-(1-mesityl-3-(2-carboxylatoethyl)imidazol-2-ylidene)gold(I) (4).



Bis(1-mesityl-3-(2-carboxylatoethyl)imidazol-2-ylidene) gold(I) sodium salt **4** was prepared via an in situ transmetalation reaction. To a 100 mL Schlenk flask under an atmosphere of Ar, 138.0 mg (0.534 mmol) of **3**, 130.0 mg (0.561 mmol) of Ag_2O, a magnetic stir bar, and 20 mL of deoxygenated water were added and left to stir for 24 h at 50 °C in darkness. After 24 h, the reaction mixture was allowed to cool to ambient temperature whereupon 32.0 mg (0.548 mmol) of NaCl was added and allowed to stir for an additional 30 min at room temperature. The solution was passed through a Celite® pad and fine fritted funnel. To the filtrate, 160.0 mg (0.543 mmol) of $(CH_3)_2SAu^ICl$ was added and allowed to stir for 24 h at room temperature in the absence of light, under an atmosphere of Ar. After 24 h the reaction mixture was passed through a pad of Celite® and fine fritted funnel. The filtrate volume was reduced to 5 mL whereupon the dark purple solution was filtered to remove any gold particles. The remaining solvent was removed from the filtrate in vacuo to give **4** as an off-white residue (62.8 mg, 30.1%). ^1H

NMR (500 MHz, DMSO-d_6) δ = 7.79 (d, 2H, J = 1.9 Hz, HC_5), 7.38 (d, 2H, J = 1.9 Hz, HC_4), 6.95 (s, 4H, HC_{12}), 4.38 (t, J = 7.6 Hz, 4H, H_2C_6), 2.59 (t, J = 7.7, 4H, H_2C_7), 2.41 (s, 6H, H_3C_{14}), 1.67 (s, 12H, H_3C_{11}). ^{13}C NMR (126 MHz, DMSO-d_6) δ = 182.8 (C_2), 174.1 (C_8), 138.2 (C_{13}), 134.4 (C_9), 134.1 (C_{10}), 128.4 (C_{12}), 122.5 (C_5), 122.5 (C_4), 48.2 (C_6), 40.2 (C_7), 20.6 (C_{14}), 16.8 (C_{11}). ESI-MS (positive ion, calculated for M = $C_{30}H_{34}N_4O_4Au$). Theor: 757.2036 m/z$[M+2Na]^+$, 735.2216 m/z $[M-H+Na]^+$, 713.2397 m/z $[M+2H]^+$. Found: 757.2023 m/z $[M+2Na]^+$, 735.2215 m/z $[M-H+Na]^+$, 713. 2386 m/z $[M+2H]^+$.

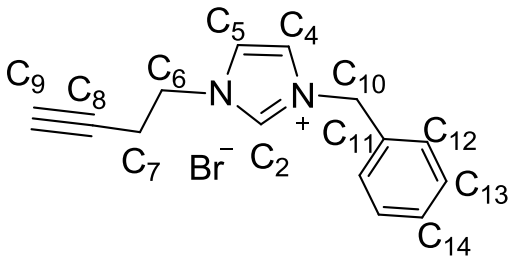
Synthesis of 3-(but-3-yn-1-yl)-1-mesityl-1*H*-imidazol-3-ium bromide (5).



Compound 3-(but-3-yn-1-yl)-1-mesityl-1*H*-imidazol-3-ium bromide (**5**) was prepared by dissolving 1.11 g (5.95 mmol) of 1-mesityl-1*H*-imidazole in 10 mL of toluene in a 100 mL round bottom flask. To this stirring solution, 0.84 mL (8.92 mmol) of cold 4-bromobut-1-yne was added dropwise. The reaction mixture was allowed to reflux at 120 °C for 3 d, during which time an off-white film formed on the inside of the reaction vessel. Approximately 20 mL of diethyl ether was added directly to the reaction mixture and the contents were stirred vigorously for 3 h at room temperature. The suspension was filtered and the solid was washed with 3 x 10 mL of diethyl ether and dried under vacuum for 24 h to provide **5** as an off-white solid (0.70 g, 63.4%). gHMBC was used to determine C-H connectivities and confirm peak assignments. ^{1}H NMR (500 MHz,

$CDCl_3$) δ = 10.15 (s, 1H, *H*C_2), 8.23 (s, 1H, *H*C_5), 7.17 (s, 1H, *H*C_4), 6.98 (s, 2H, *H*C_{13}), 4.89 (t, *J* = 6.0 Hz, 2H, *H*C_6), 2.99 (td, *J* = 6.3, 2.5 Hz, 2H, *H*C_7), 2.31 (s, 3H, *H*C_{15}), 2.06 (t, *J* = 3.4, *H*C_9), 2.05 (s, 6H, *H*C_{12}).^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3 (C_{14}), 137.9 (C_2), 134.2 (C_9), 130.6 (C_{10}), 129.8 (C_{13}), 123.9 (C_5), 122.7 (C_4), 79.1 (C_8), 72.5 (C_9), 48.6 (C_6), 21.1 (C_7), 21.1 (C_{15}), 17.6 (C_{12}). Anal. Calcd. for $C_{16}H_{19}BrN_2$ (319.25 g/mol): C: 60.20%; H: 6.00%; N: 8.78%, Found; C: 60.03%; H: 6.01 N: 8.86%.

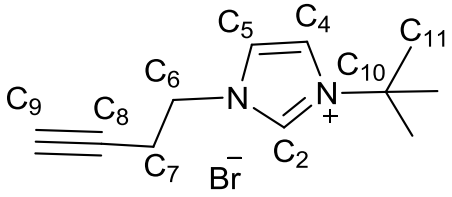
Synthesis of 1-benzyl-3-(but-3-yn-1-yl)-1*H*-imidazol-3-ium bromide (6).



Compound 1-benzyl-3-(but-3-yn-1-yl)-1*H*-imidazol-3-ium bromide (**6**) was prepared by a similar synthetic procedure as **5** using 1.00 g (6.32 mmol) of 1-benzyl-1*H*-imidazole, 0.71 mL (7.59 mmol) of 4-bromobut-1-yne, and 15 mL of toluene. Compound **6** was isolated as an off-white powder (1.48 g, 80.2%). gHMBC was used to determine C-H connectivities and confirm peak assignments. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.45 (t, *J* = 1.5 Hz, 1H, *H*C_2), 7.75 (t, *J* = 1.7 Hz, 1H, *H*C_5), 7.45 (m, 2H, *H*C_{12}), 7.42 (t, *J* = 1.5 Hz, 1H, *H*C_4), 7.34 (m, 3H, *H*C_{13}, *H*C_{14}), 5.56 (s, 2H, H_2C_{10}) 4.51 (t, *J* = 6.4 Hz, 2H, H_2C_6), 2.84 (td, *J* = 6.1 Hz, 2.5 Hz, 2H, H_2C_7), 2.08 (t, *J* = 2.6 Hz, 1H, *H*C_9). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 137.1 (C_2), 132.8 (C_{11}), 129.5 (C_{14}), 129.4 (C_{13}), 128.9 (C_{12}), 122.9 (C_5), 121.6 (C_4), 78.7 (C_8), 72.9 (C_9), 53.4 (C_{10}), 48.4 (C_6), 20.8 (C_7). ESI-MS (positive ion, calculated for M = $C_{14}H_{15}BrN_2$). 327.0070 m/z [M+Cl]+, 291.0484 m/z

[M+H]+, 211.1238 m/z [M+Br]+. Anal. Calcd. for $C_{14}H_{15}BrN_2$ (291.19 g/mol): C: 57.75%; H: 5.19%; N: 9.62%, Found; C: 57.67%; H: 5.13 N: 9.57%.

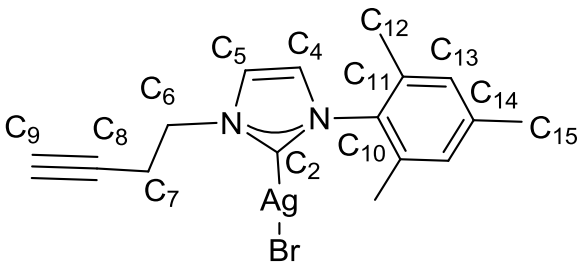
Synthesis of 3-(but-3-yn-1-yl)-1-(*tert*-butyl)-1*H*-imidazol-3-ium bromide (7).



Compound 3-(but-3-yn-1-yl)-1-(*tert*-butyl)-1*H*-imidazol-3-ium bromide (**7**) was prepared by a similar synthetic procedure as **5** but with a slightly modified work-up. The synthesis was performed using 1.11 mL (8.05 mmol) of 1-(*tert*-butyl)-1*H*-imidazole, 1.13 mL (12.1 mmol) of 4-bromobut-1-yne, and 10 mL of toluene. After the reaction was complete, the mixture was allowed to cool to room temperature and 20 mL of diethyl ether was added directly to the reaction vessel. The mixture was stirred for 10 min and the supernatant was decanted. This process was repeated three more times using 10 mL of fresh diethyl ether each time. After the final decanting, the solid was suspended in 2 mL of diethyl ether and transferred directly to a vial. The remaining solvent was removed in vacuo and the resulting off-white, very hygroscopic solid **7** was dried under vacuum for 24 h before transferring to an Ar filled glovebox for storage (0.453 g, 21.9%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.47 (s, 1H, *H*C_2), 7.75 (s, 1H, *H*C_5), 7.55 (s, 1H, *H*C_4), 4.62 (t, *J* = 6.2 Hz, 2H, *H*$_2$$C_6$), 2.88 (td, *J* = 6.4, 1.7 Hz, 2H, *H*$_2$$C_7$), 2.07 (t, *J* = 1.9 Hz,1H, *H*C_9), 1.68 (s, 9H, *H*$_3$$C_{11}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 135.7 (C_2), 122.9 (C_5), 119.2 (C_4), 79.1 (C_8), 72.4 (C_9), 60.4 (C_{10}), 48.0 (C_6), 30.0 (C_{11}), 20.8 (C_7). Anal.

Calcd. for $C_{11}H_{17}BrN_2$ (257.17 g/mol): C: 51.37%; H: 6.66%; N: 10.89%, Found; C: 51.03%; H: 6.88 N: 11.11%.

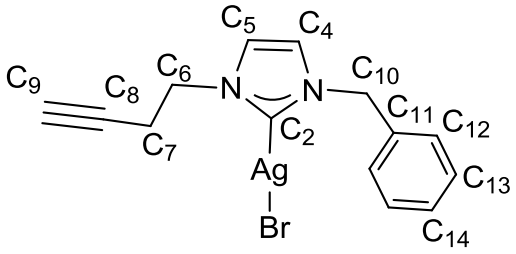
Synthesis of 1-(but-3-yn-1-yl)-3-mesityl-1*H*-imidazol-2(3*H*)-ylidene)silver(I) bromide (8).



Inside an Ar filled glovebox, 303.0 mg (0.949 mmol) of compound **5** was added to a vial and dissolved in 4 mL of chloroform. Silver(I) oxide (151.1 mg, 0.652 mmol) was added directly as a solid to the stirring solution of **5**. The reaction vessel was wrapped in aluminum foil and allowed to stir for 3 d at room temperature. The reaction mixture was passed through a pad of Celite® atop a filter paper fitted glass pipette to remove any insoluble gray particulates. The amber colored filtrate was reduced in vacuo to 1 mL whereupon an excess of diethyl ether (~5 mL) was added to precipitate an off-white solid. The supernatant was decanted, the solid was suspended in 2 mL of diethyl ether, and the supernatant was decanted again (this was repeated 2 more times with 2 x 2 mL of diethyl ether). The solid was dried completely under vacuum to give an **8** as an off-white solid (264.5 mg, 65.4%). Heteronuclear multiple bond coherence (gHMBC) was applied to determine C-H connectivities and confirm peak assignments. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.36 (d, 1H, *J* = 1.6 Hz, *H*C$_5$), 6.94 (s, 2H, *H*C$_{13}$), 6.92 (d, 1H, *J* = 1.6 Hz, *H*C$_4$), 4.38 (t, *J* = 6.2 Hz, 2H, *H*C$_6$), 2.76 (td, *J* = 6.7, 2.4 Hz, 2H, *H*C$_7$), 2.33 (s, 3H, *H*C$_{15}$), 2.04 (t, *J* = 2.9, *H*C$_9$), 1.94 (s, 6H, *H*C$_{12}$).^{13}C NMR (126 MHz, $CDCl_3$) δ 182.5

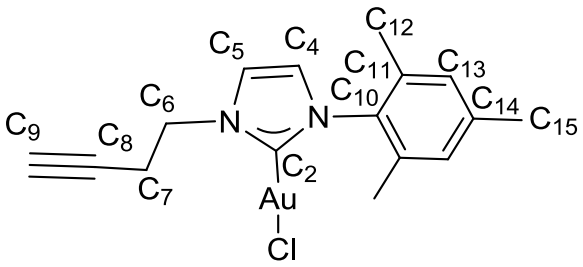
(C_2), 139.2 (C_{14}), 135.1 (C_{10}), 134.6 (C_{11}), 129.1 (C_{13}), 122.3 (C_4), 121.2 (C_5), 79.2 (C_8), 71.8 (C_9), 49.9 (C_6), 21.6 (C_7), 20.8 (C_{15}), 17.5 (C_{12}). Anal. Calcd. for $C_{16}H_{18}AgBrN_2$ (426.11 g/mol): C: 45.10%; H: 4.26%; N: 6.57%, Found; C: 45.26%; H: 4.13 N: 6.89%.

Synthesis of 1-(but-3-yn-1-yl)-3-benzyl-1*H*-imidazol-2(3*H*)-ylidene)silver(I) bromide (9).



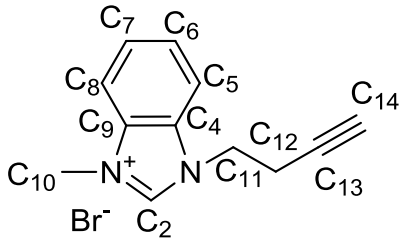
Compound **9** was prepared in a similar procedure to **8** using 300 mg (1.03 mmol) of **6**, 167.1 mg (0.72 mmol) of Ag_2O, and 4 mL of chloroform to yield an off-white powder (82.3 mg, 40.1%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.34 (m, 3H, *H*C_{13}, *H*C_{14}), 7.23 (m, 2H, *H*C_{12}), 7.14 (d, *J* = 1.8 Hz, 1H, *H*C_5), 6.90 (d, *J* = 1.7 Hz, 1H, *H*C_4), 5.32 (s, 2H, H_2C_{10}), 4.32 (t, *J* = 6.4 Hz, 2H, H_2C_6), 2.71 (dt, *J* = 6.3, 2.4 Hz, 2H, H_2C_7), 2.07 (t, *J* = 2.6 Hz, 1H, *H*C_9). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 181.9 (C_2), 135.6 (C_{11}), 129.1 (C_{14}), 128.6 (C_{13}), 127.8 (C_{12}), 121.9 (C_5), 120.9 (C_4), 80.1 (C_8), 72.1 (C_9), 55.8 (C_{10}), 50.3 (C_6), 21.8 (C_7).

In situ preparation of 1-(but-3-yn-1-yl)-3-mesityl-1*H*-imidazol-2(3*H*)-ylidene)gold(I) bromide (10).



Inside an Ar filled glovebox, 1-(but-3-yn-1-yl)-3-mesityl-1*H*-imidazol-2(3*H*)-ylidene)gold(I) bromide (**10**) was prepared directly in a sealable NMR tube by dissolving 30 mg (0.0704 mmol) of complex **8** in 0.5 mL of $CDCl_3$ and then adding 15.9 mg (0.054 mmol) of solid $(CH_3)_2SAuCl$ directly to the solution. The tube was capped and inverted several times to thoroughly mix the reagents. The progress of the reaction was monitored by ^1H and ^{13}C NMR spectroscopy. gHMBC was used to determine C-H connectivities and confirm peak assignments. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.31 (d, 1H, *J* = 1.9 Hz, *H*C_5), 6.94 (d, 1H, *J* = 1.9 Hz, *H*C_4), 6.87 (s, 2H, *H*C_{13}), 4.41 (t, *J* = 6.4 Hz, 2H, *H*C_6), 2.85 (td, *J* = 6.4, 2.6 Hz, 2H, *H*C_7), 2.31 (s, 3H, *H*C_{15}), 2.07 (t, *J* = 2.5, *H*C_9), 2.00 (s, 6H, *H*C_{12}).^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0 (C_2), 139.7 (C_{14}), 134.7 (C_{10}), 134.7 (C_{11}), 129.4 (C_{13}), 121.8 (C_4), 121.4 (C_5), 79.5 (C_8), 72.0 (C_9), 49.7 (C_6), 21.4 (C_7), 21.1 (C_{15}), 17.8 (C_{12}). Isolation of complex **10** was hampered by decomposition. Solution phase NMR characterization is provided.

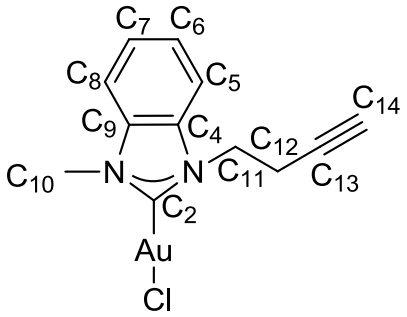
Synthesis of 1-methyl-3-(prop-2-yn-1-yl)-1*H*-benzo[d]imidazol-3-ium bromide (11).



Compound 1-methyl-3-(prop-2-yn-1-yl)-1*H*-benzo[d]imidazol-3-ium bromide (**11**) was

prepared by a similar synthetic procedure as **5** using 1.06 g (8.00 mmol) of 1-methyl-1H-benzo[d]imidazole, 1.58 g (12.00 mmol) of 4-bromobut-1-yne, and 10 mL of toluene. Compound **11** was isolated as an off-white powder (1.56 g, 78%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 11.11 (s, 1H, *H*C_2), 7.66-7.90(m, 4H, *H*C_5, *H*C_6, *H*C_7, *H*C_8), 4.86 (t, J=6.5 Hz, 2H, *H*C_{11}), 4.31 (s, 3H, *H*C_{10}), 3.04 (dt, J = 6.5 Hz, J = 2.6 Hz, 2H, *H*C_{12}), 2.08 (t, J = 2.6 Hz, 1H, *H*C_{14}). ^{13}C{^{1}H} NMR ($CDCl_3$, 500 MHz): δ = 143.2 (C_2), 131.8 (C_9), 131.3 (C_4), 127.3 (C_6), 127.3 (C_7), 113.4 (C_5), 113.0 (C_8), 78.9 (C_{13}), 73.1 (C_{14}), 46.1 (C_{11}), 34.1 (C_{10}), 20.4 (C_{12}). Anal. Calcd. for $C_{12}H_{13}BrN_2$ (265.15 g/mol): C: 54.36%; H: 4.94%; N: 10.57%, Found: C: 54.25%; H: 5.18 N: 10.61%.

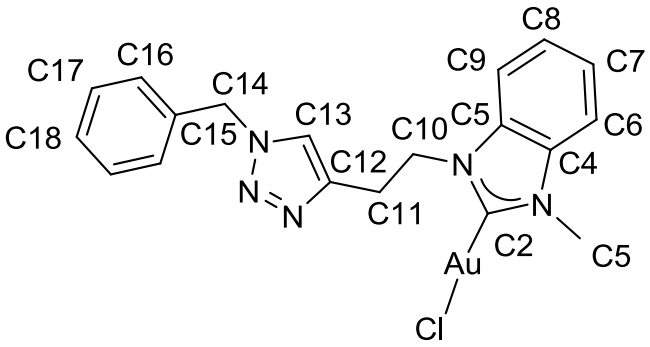
Synthesis of 1-methyl-3-(prop-2-yn-1-yl)-1*H*-benzo[d]imidazol-2(3H)-ylidene)gold(I) chloride (13).



In a glovebox, solid ligand 1-methl-3-(prop-2-yn-1-yl)-1*H*-benzoimidazole-3-ium bromide (**11**) (159.09 mg, 6.00 mmol., 1 equiv.) and Ag_2O (97.32 mg, 4.00 mmol., 0.7 equiv.) was dissolved in chloroform (10 mL) and stirred for 2 days to provide the NHC-Ag^{I} complex **12** in-situ. To the reaction mixture was added $(CH_3)_2SAuCl$ (176.73mg, 6.00 mmol, 1 equiv.) and stirred for 1 h. Then the reaction mixture was filtrated through Celite®. The filtrate was collected and reduced under vacuum to 1 ml of solution. Diethyl ether was added to precipitate an off-white powder. The solid was collected by filtration

and dried under vacuum for 2 h to provide the NHC-Au^{I} complex **13** (112.5 mg, Yield = 45%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44-7.57 (m, 4H, HC_5, HC_6, HC_7, HC_8), 4.69 (t, 2H, ^{3}J = 7.0 Hz, HC_{11}), δ4.03 (s, 3H, HC_{10}), 2.85 (dt, 2H, ^{3}J = 7.0 Hz, ^{4}J = 2.0 Hz, HC_{12}), and 1.97 (t, 1H, ^{4}J = 2.0 Hz, HC_{14}) ppm. $^{13}C\{^{1}H\}$ NMR (500 MHz, $CDCl_3$): δ= 178.6 (C_2) , 133.6 (C_9), 131.1 (C_4), 124.8 (C_6) , 124.8 (C_7), 111.6 (C_5), 111.4 (C_8), 76.9 (C_{13}), 72.2 (C_{14}), 46.9 (C_{11}), 35.4 (C_{10}) and 20.5 (C_9) ppm. Anal. Calcd. for $C_{12}H_{12}AuClN_2$ (416.66 g/mol): C: 34.59%; H: 2.90%; N: 6.72%, Found; C: 33.98%; H: 2.92%; N: 6.49%.

NMR tube conjugation test reaction between benzyl azide and 13.



In an NMR tube, **13** (42 mg, 0.1 mmol, 1 equiv) and benzyl azide (15 mg, 0.11mmol, 1.1equiv) were dissolved in 1 ml of $CDCl_3$. To the mixture was 10% mol catalyst $PPh_3Cu(OAc)$ was added. The NMR tube was placed in anaerobic environment for 48 h to generate **14** in situ. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.72 (s, 1H, HC_{13}), 7.33-7.42 (m, 4H, HC_6, HC_7, HC_8, HC_9), 6.85-7.16 (m, 5H, HC_{16}, HC_{17}, HC_{18}), 5.49 (s, 2H, HC_{14}), 4.77 (t, J = 7.0 Hz, 2H, HC_{10}), 3.62 (t, J = 7.0 Hz, 2H, HC_{11}), 3.49 (s, 3H, HC_4).

4. ^{1}H and ^{13}C NMR Spectra for 1-13.

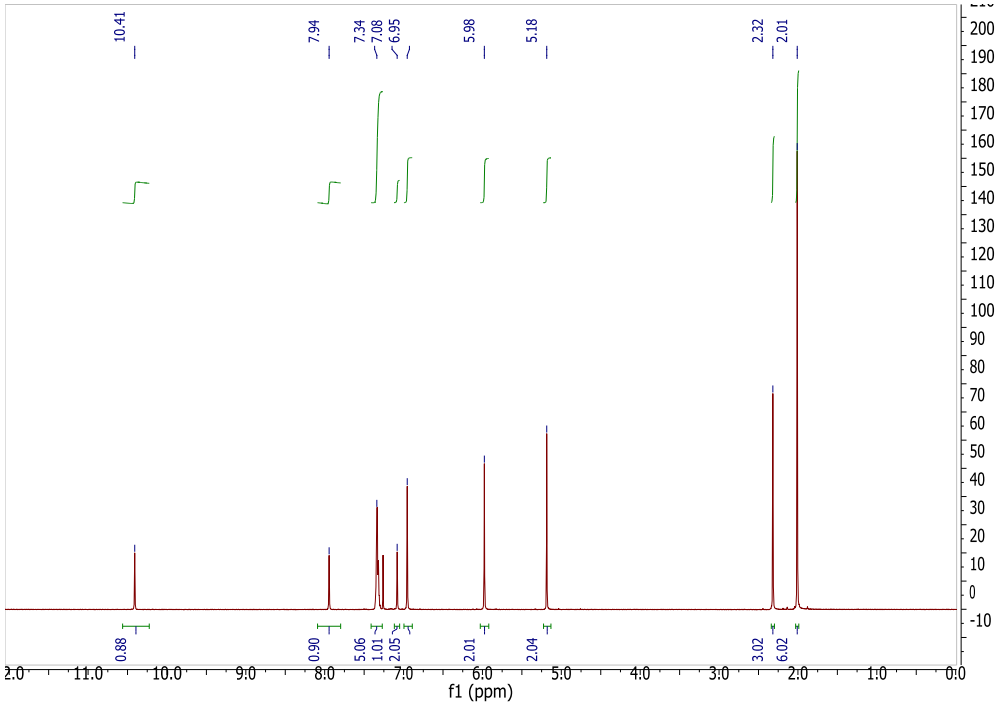


Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$

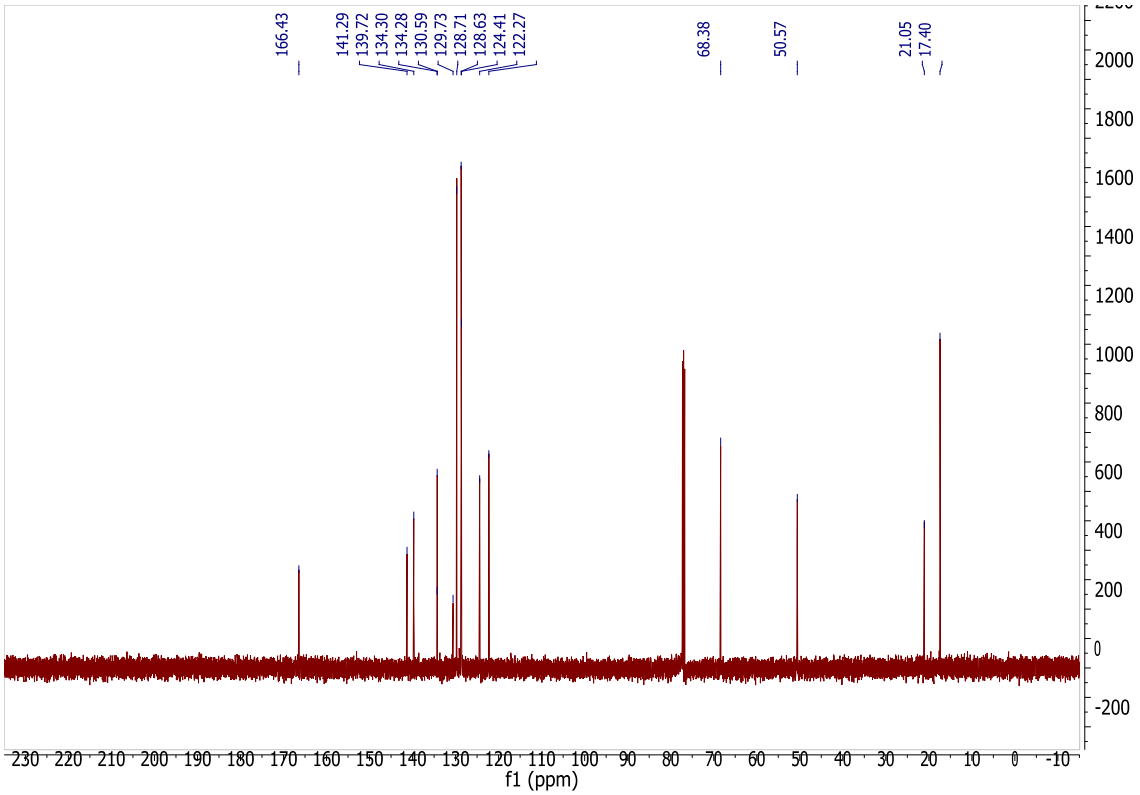


Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$

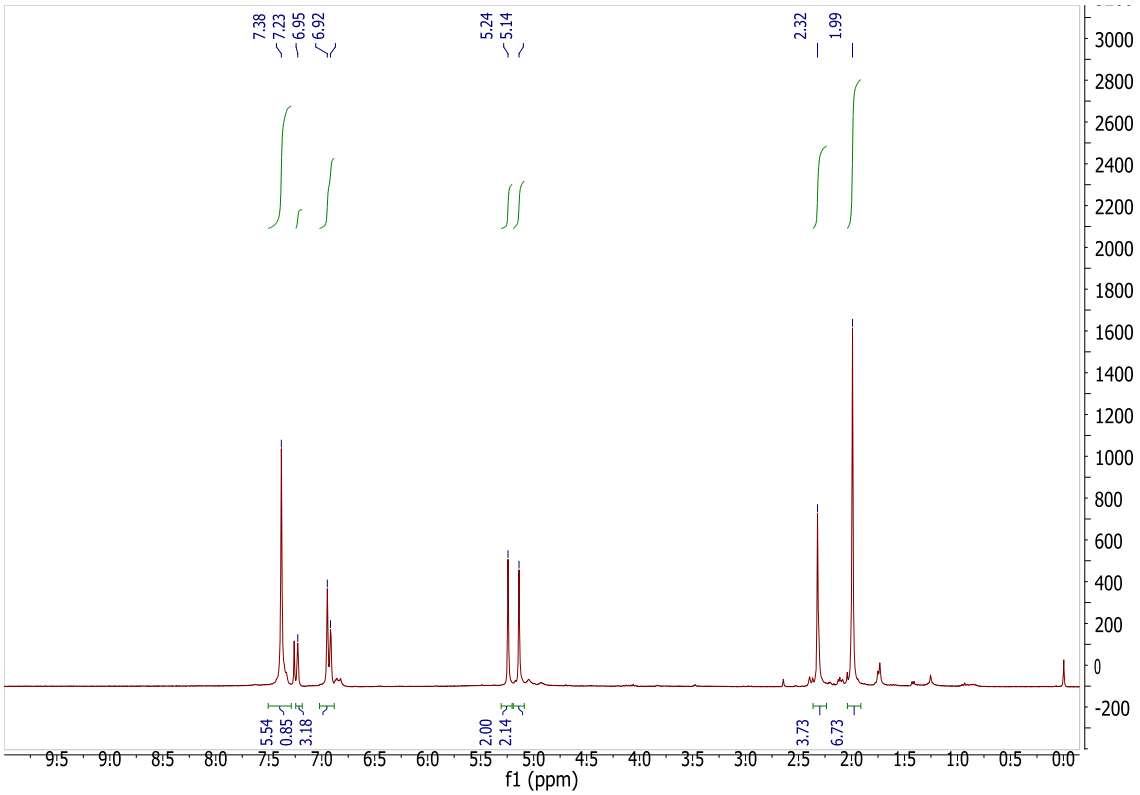


Figure S3. ^{1}H NMR spectrum of **2** in $CDCl_3$

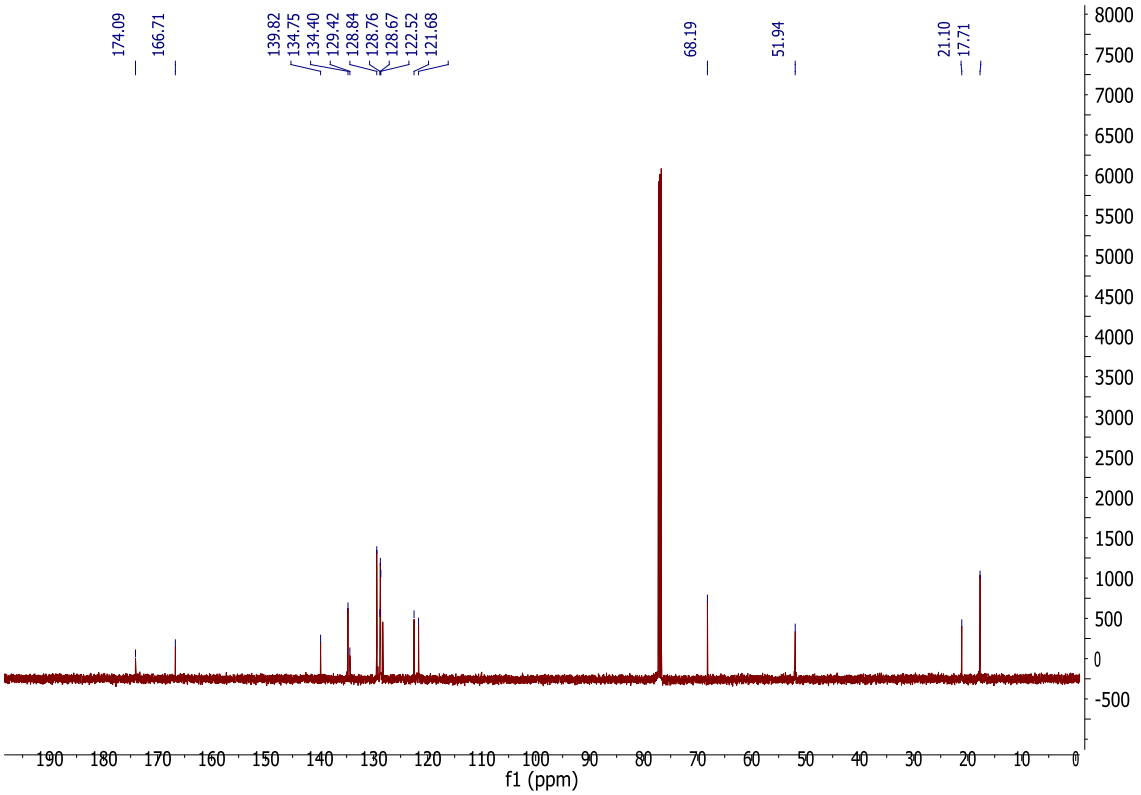


Figure S4. ^{13}C NMR spectrum of **2** in $CDCl_3$

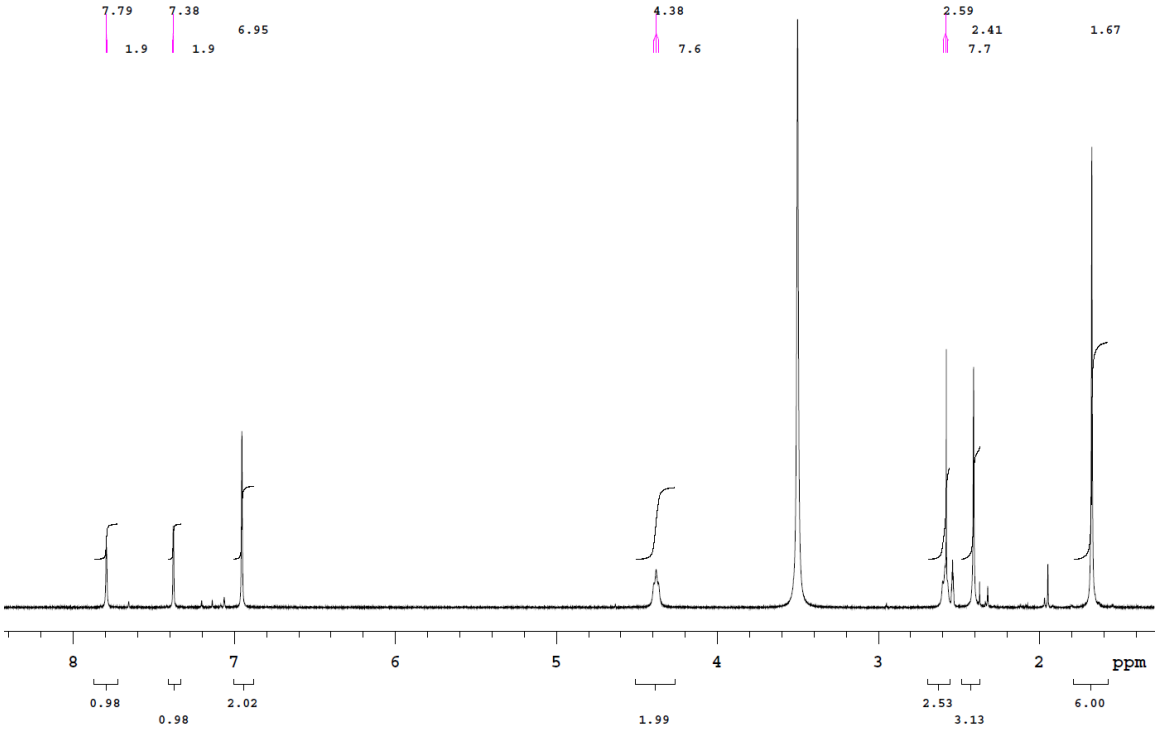


Figure S5. ^{1}H NMR spectrum of **4** in DMSO-d_6

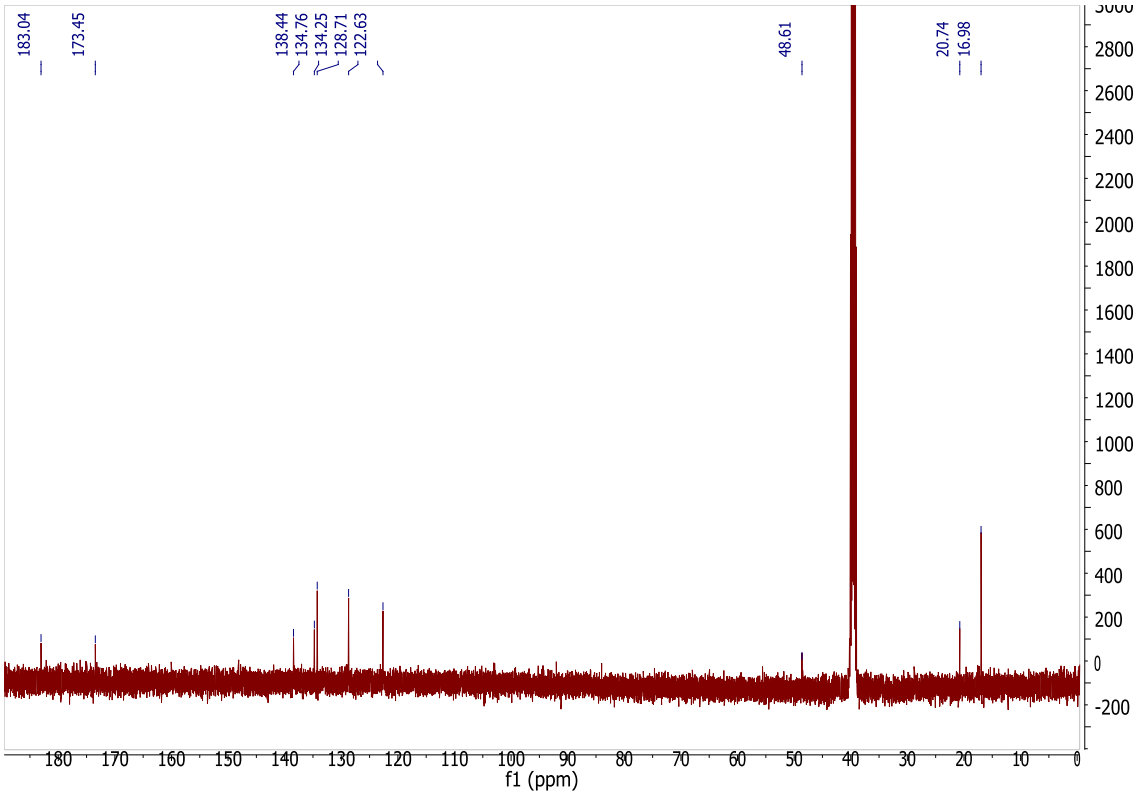


Figure S6. ^{13}C NMR spectrum of **4** in DMSO-d_6

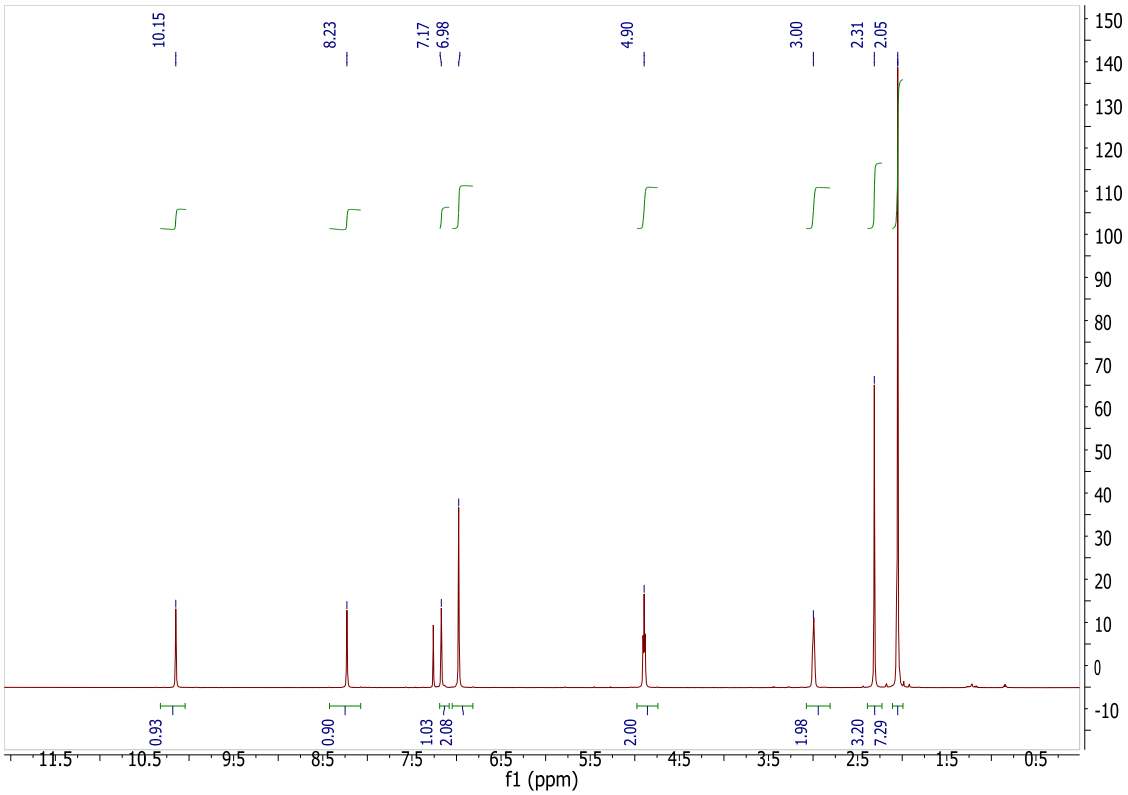


Figure S7. ^{1}H NMR spectrum of **5** in $CDCl_3$

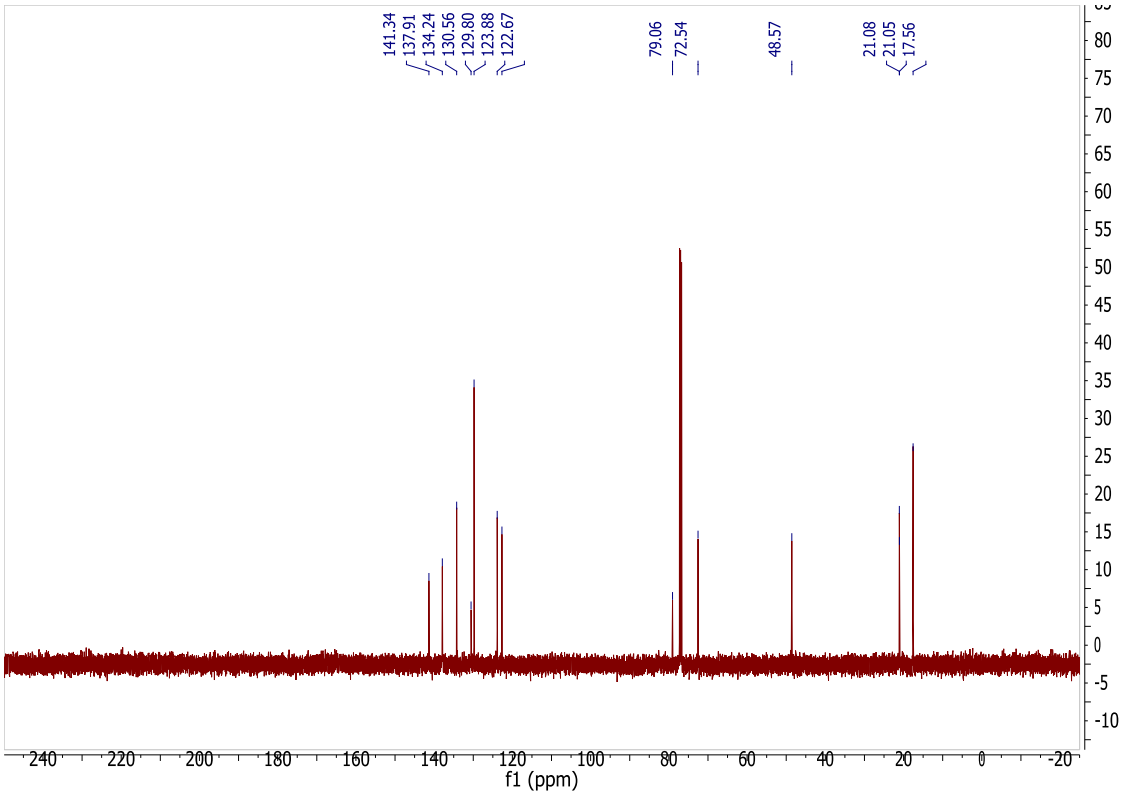


Figure S8. ^{13}C NMR spectrum of **5** in $CDCl_3$

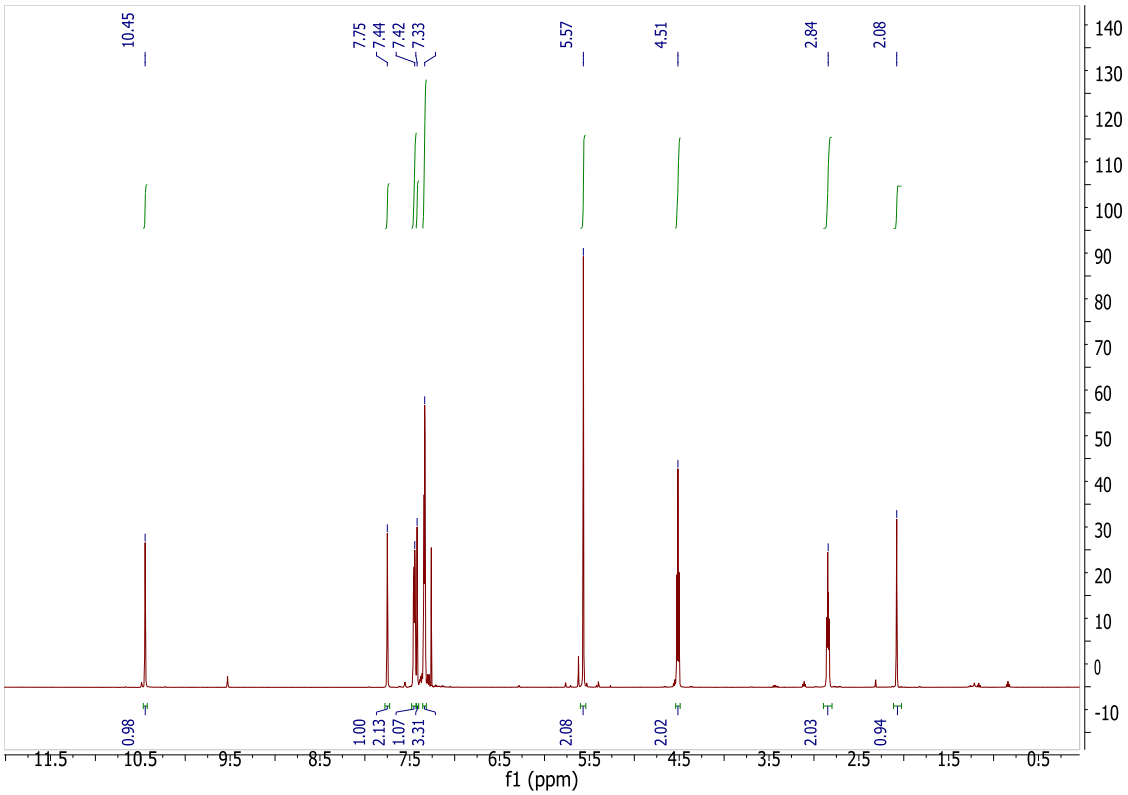


Figure S9. ^{1}H NMR spectrum of **6** in $CDCl_3$

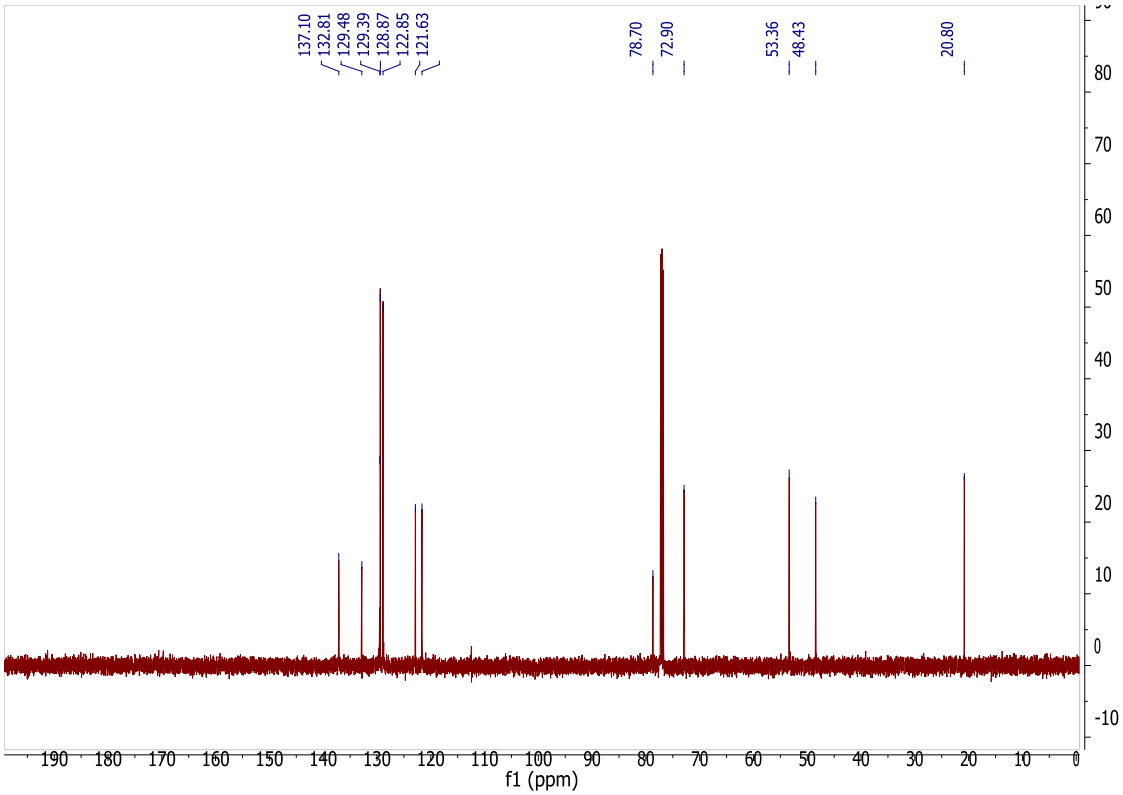


Figure S10. ^{13}C NMR spectrum of **6** in $CDCl_3$

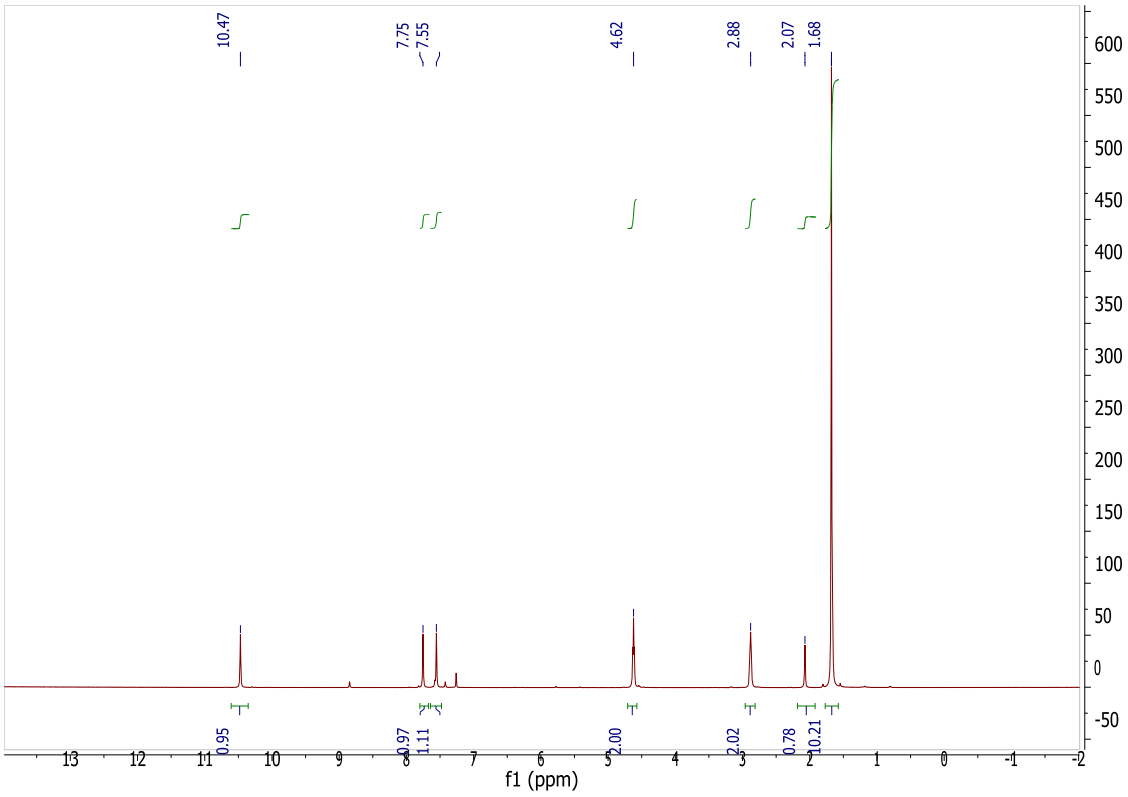


Figure S11. ^{1}H NMR spectrum of **7** in $CDCl_3$

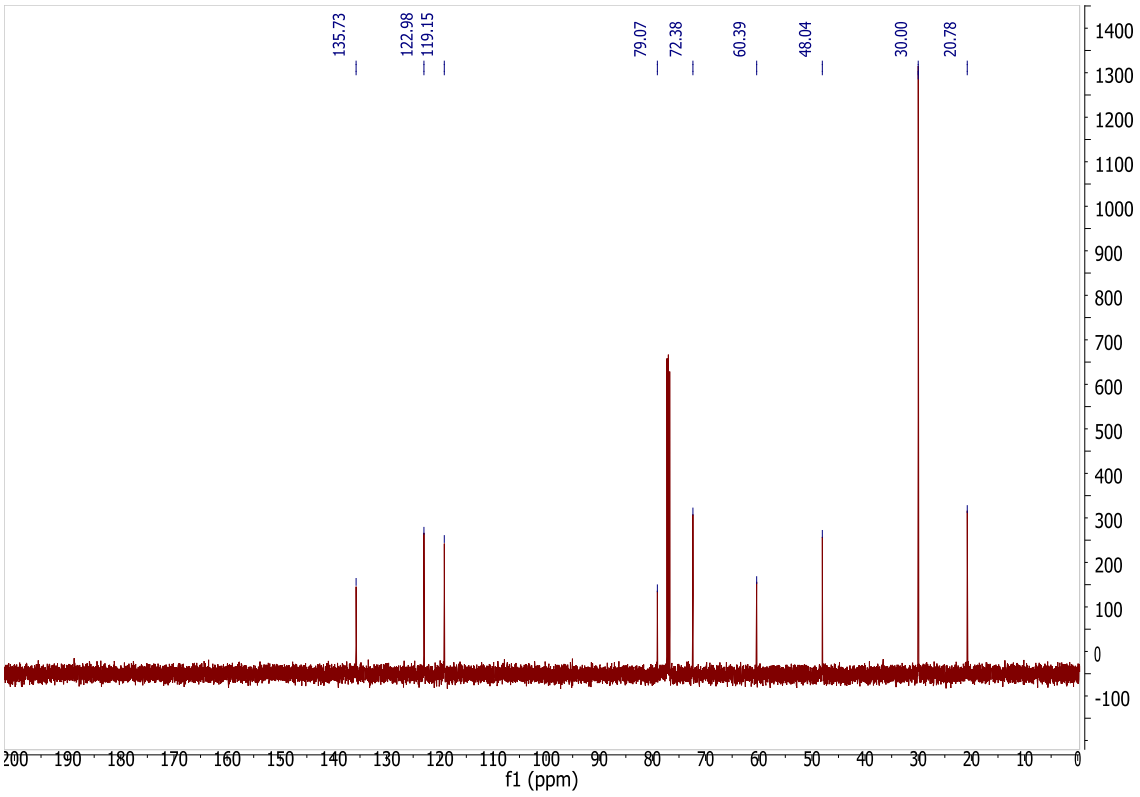


Figure S12. ^{13}C NMR spectrum of **7** in $CDCl_3$

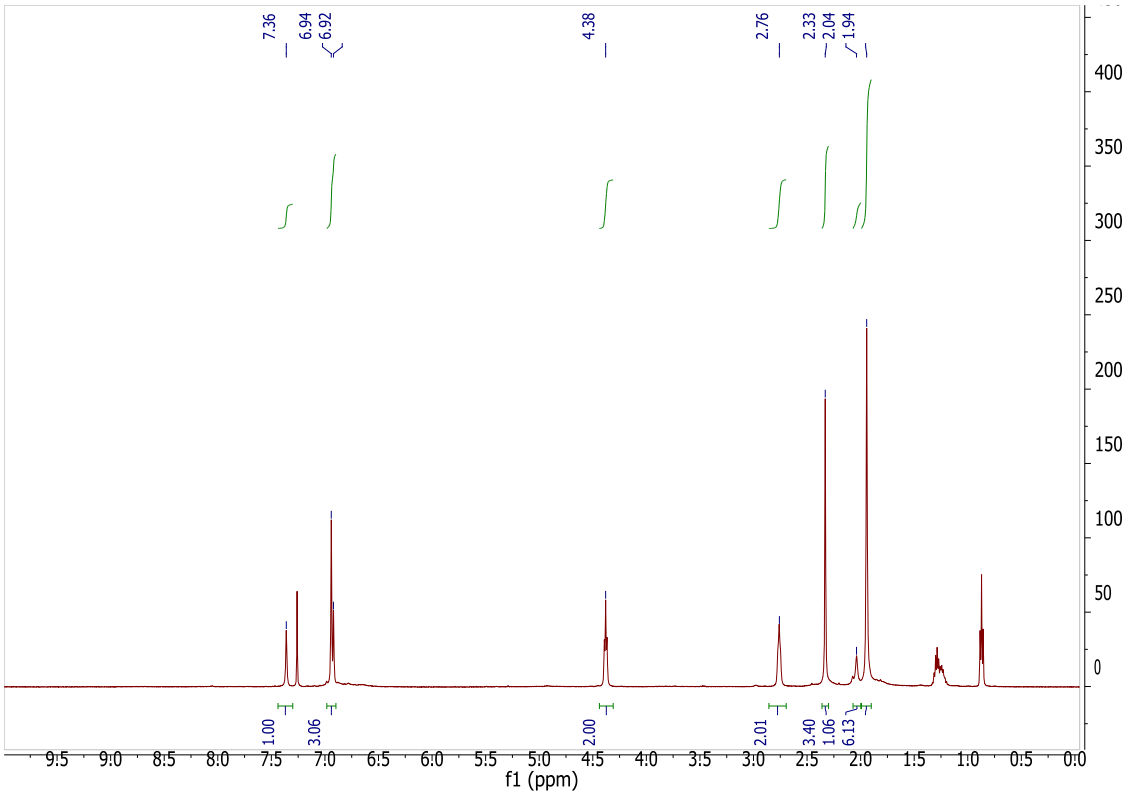


Figure S13. ^{1}H NMR spectrum of **8** in $CDCl_3$

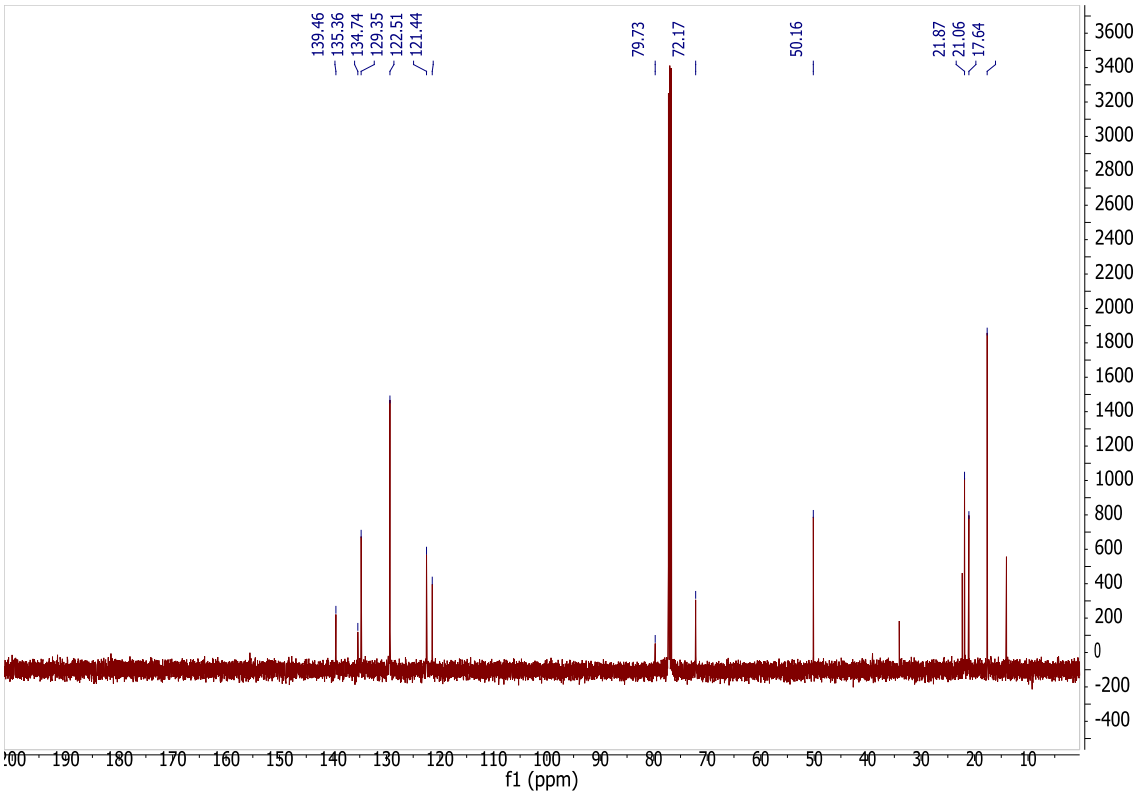


Figure S14. ^{13}C NMR spectrum of **8** in $CDCl_3$

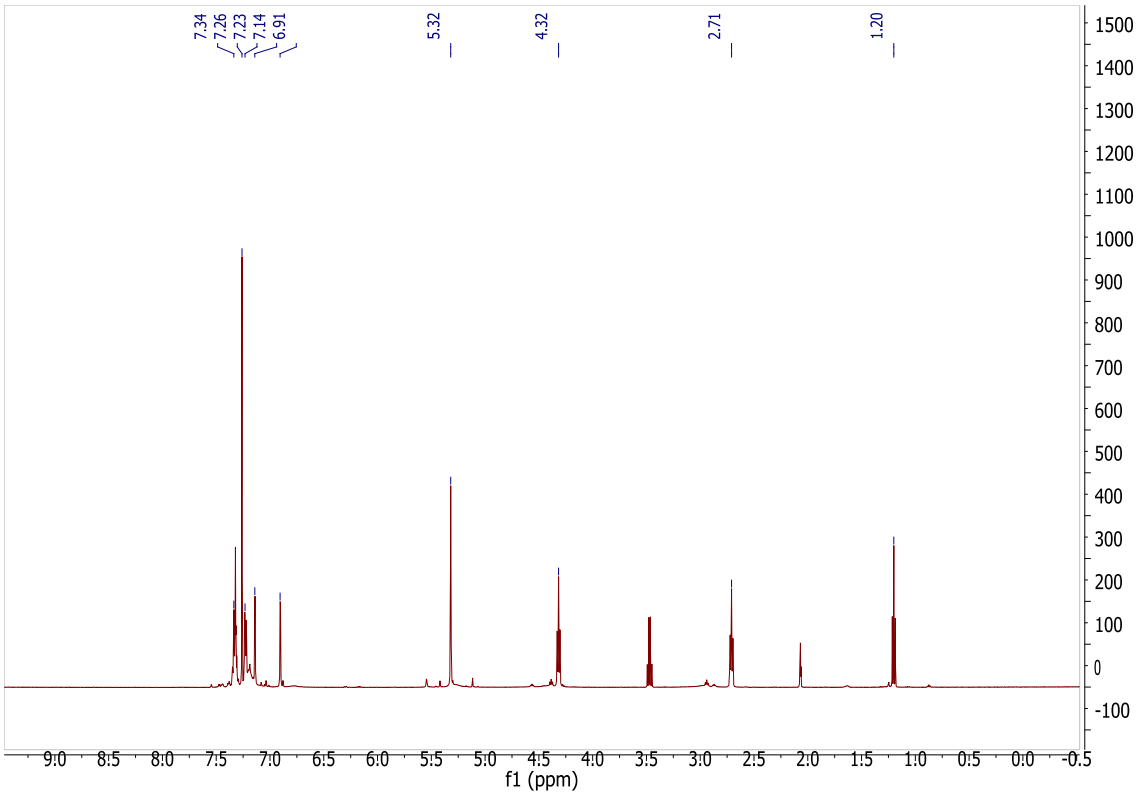


Figure S15. ^{1}H NMR spectrum of **9** in $CDCl_3$

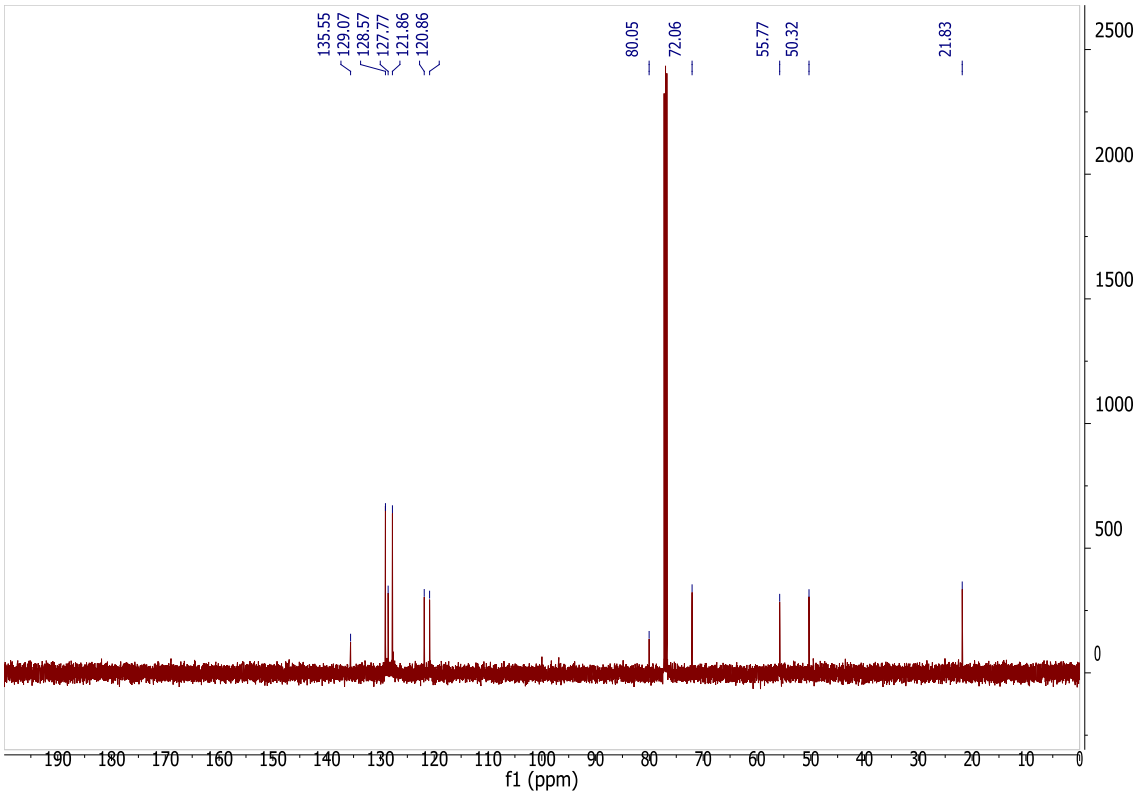


Figure S16. ^{13}C NMR spectrum of **9** in $CDCl_3$

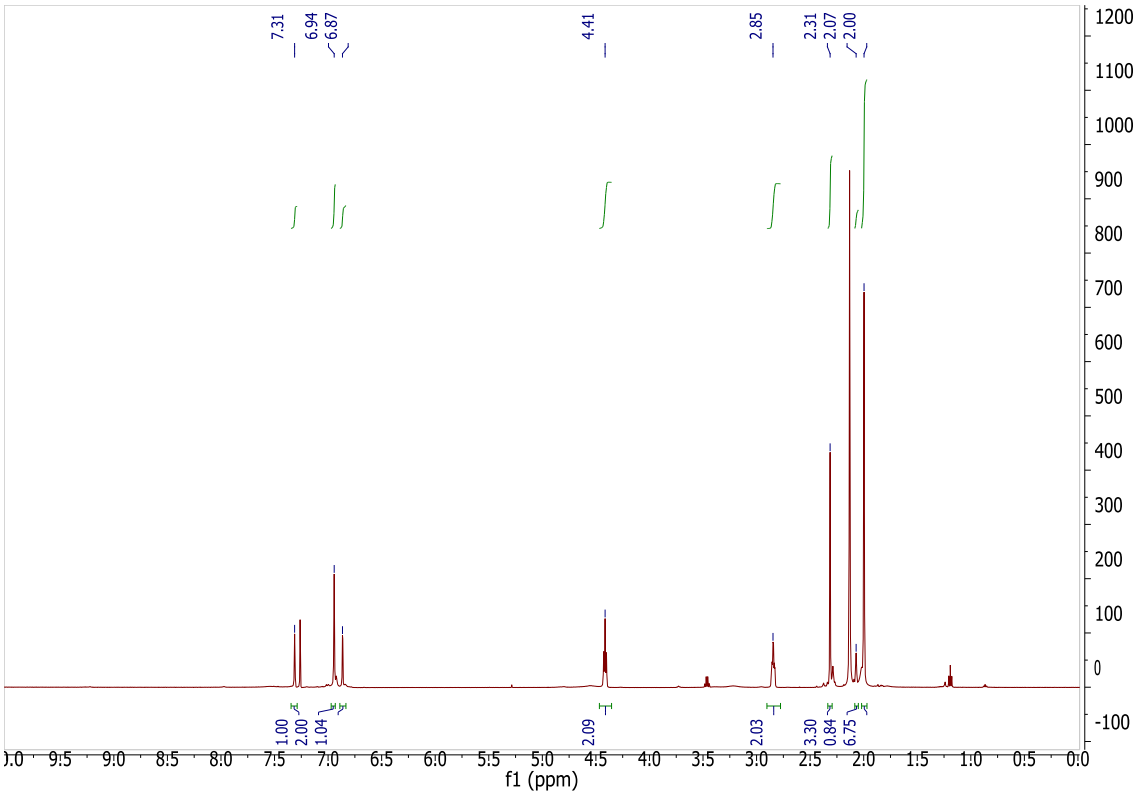


Figure S17. ^{1}H NMR spectrum of **10** in $CDCl_3$

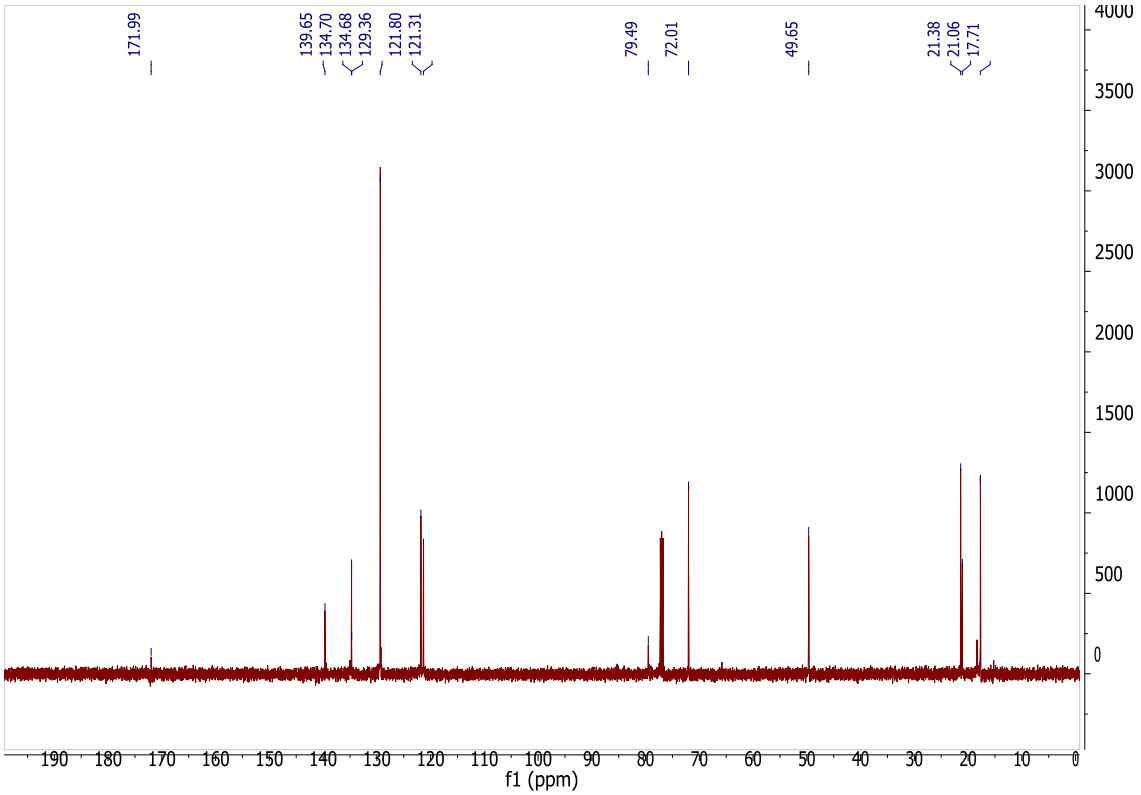


Figure S18. ^{13}C NMR spectrum of **10** in $CDCl_3$

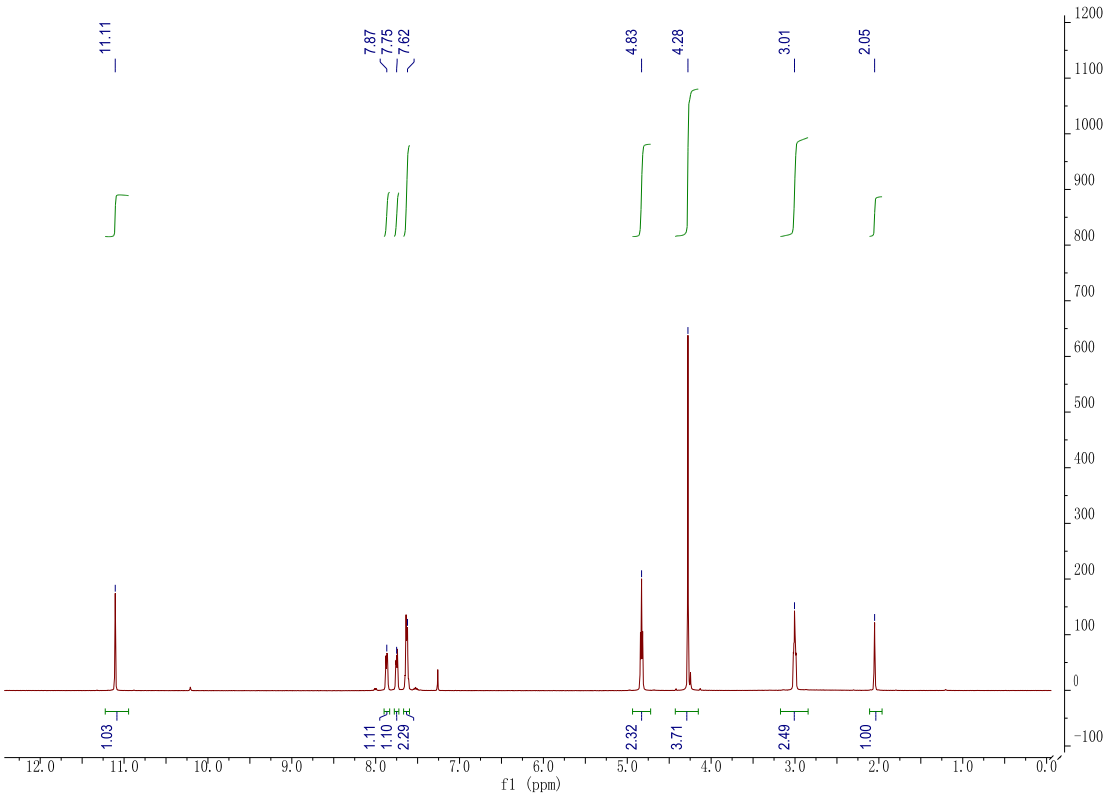


Figure S19. ^{1}H NMR spectrum of **11** in $CDCl_3$

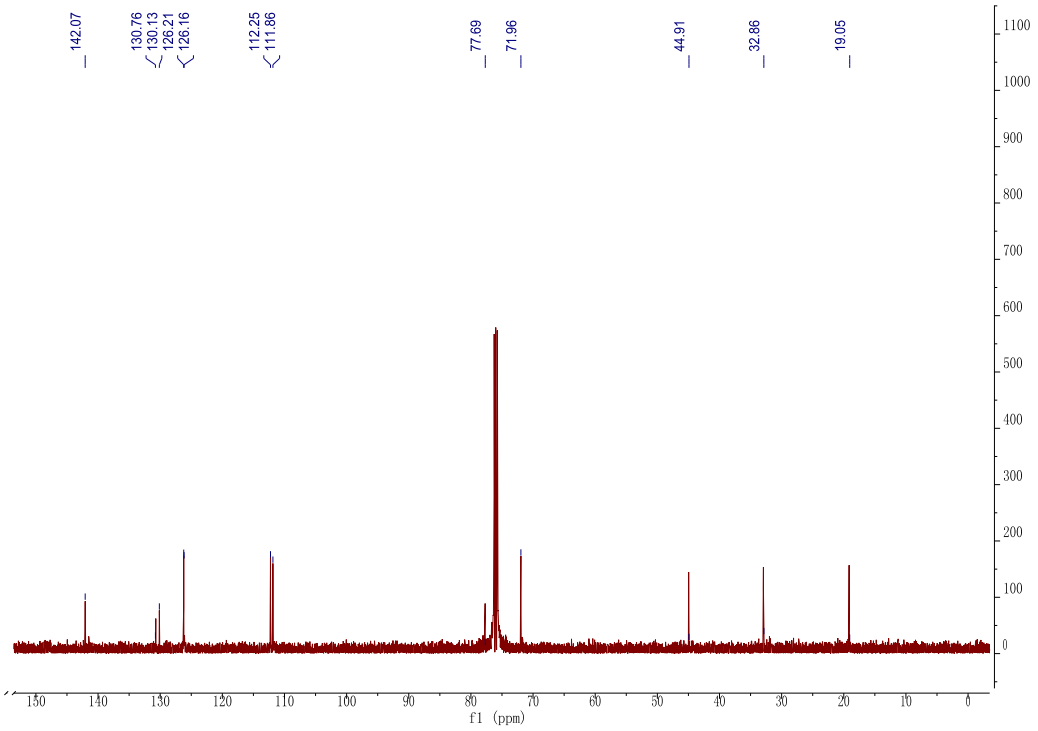


Figure S20. ^{13}C NMR spectrum of **11** in $CDCl_3$

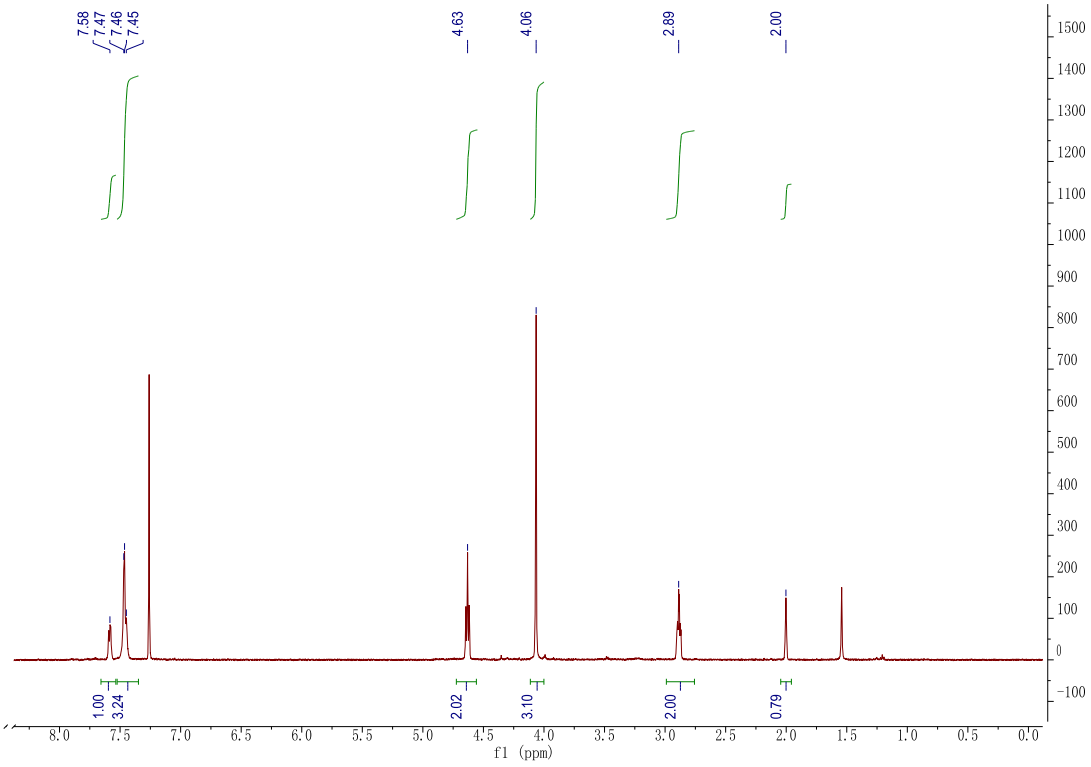


Figure S21. ^{1}H NMR spectrum of **13** in $CDCl_3$

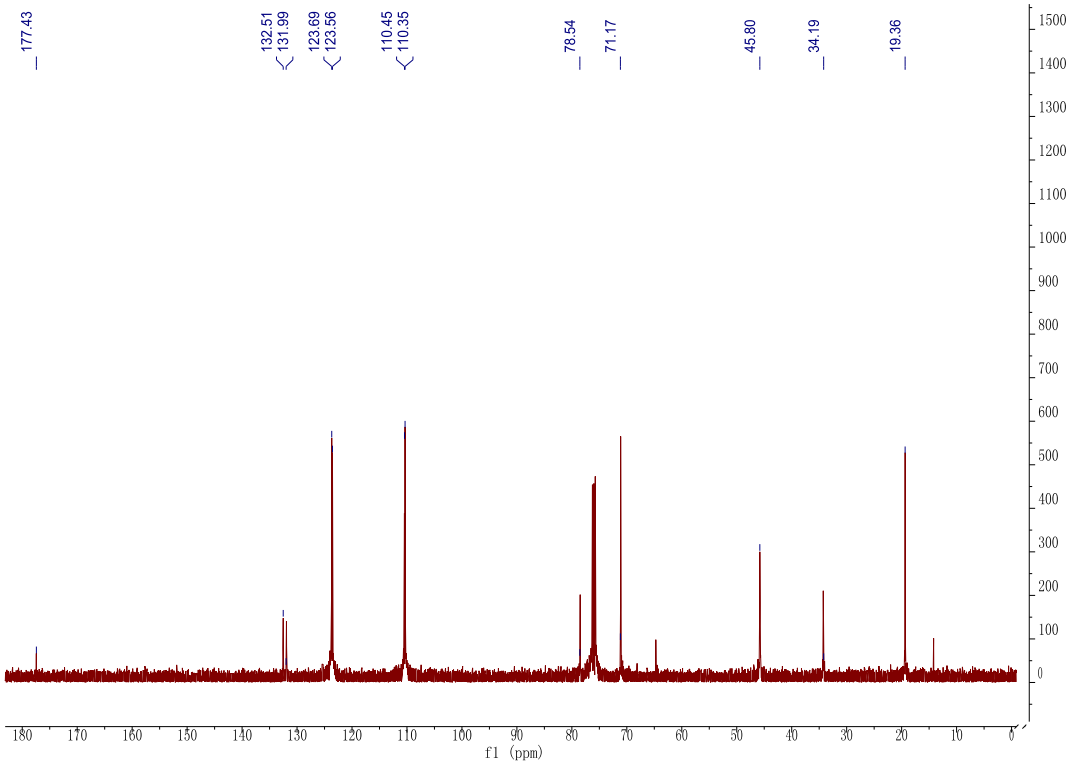


Figure S22. ^{13}C NMR spectrum of **13** in $CDCl_3$

5. 1H NMR Spectra and IR spectra of click reaction.

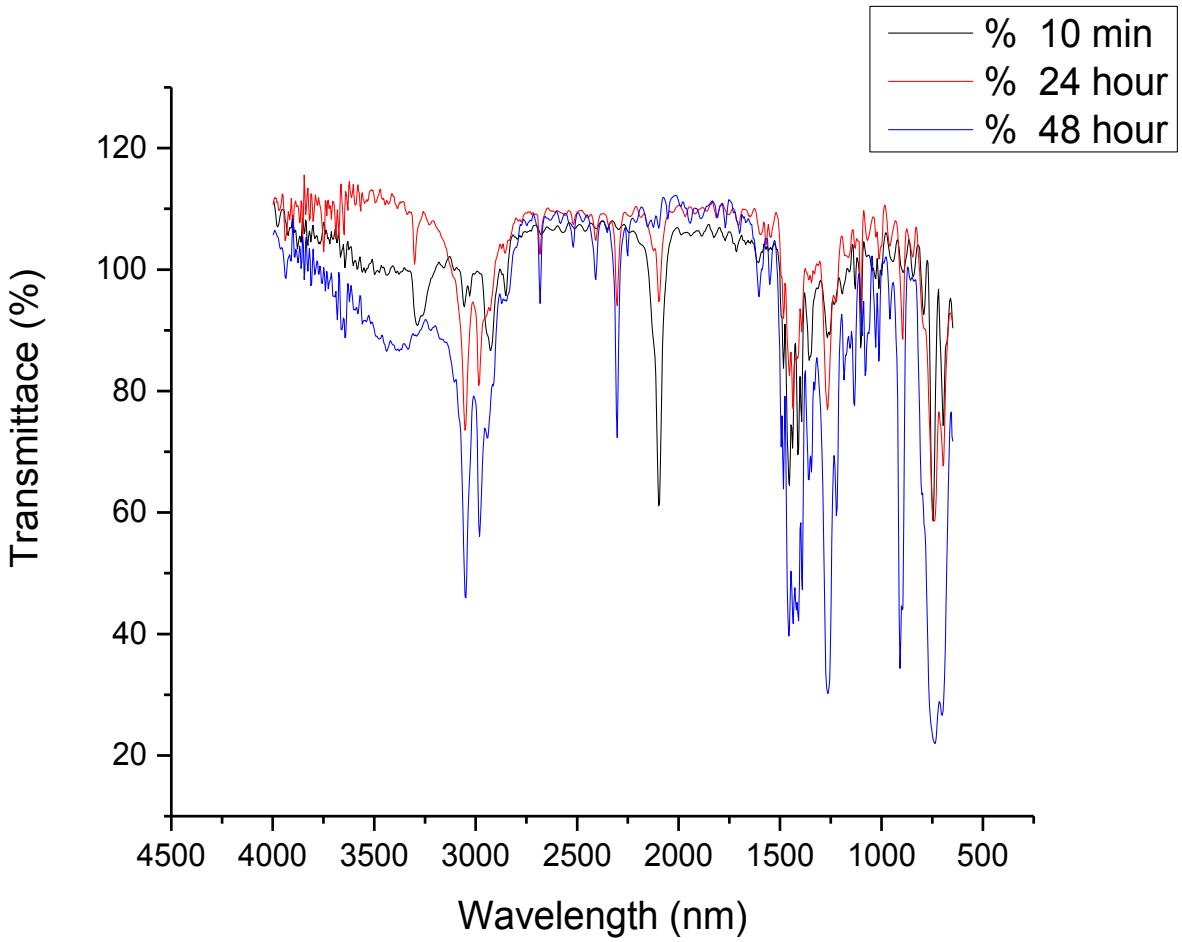


Figure S23. IR Spectra of Click reaction between compound **13** and benzyl azide after 10 min (black), 24 h (red), and 48 h (blue).

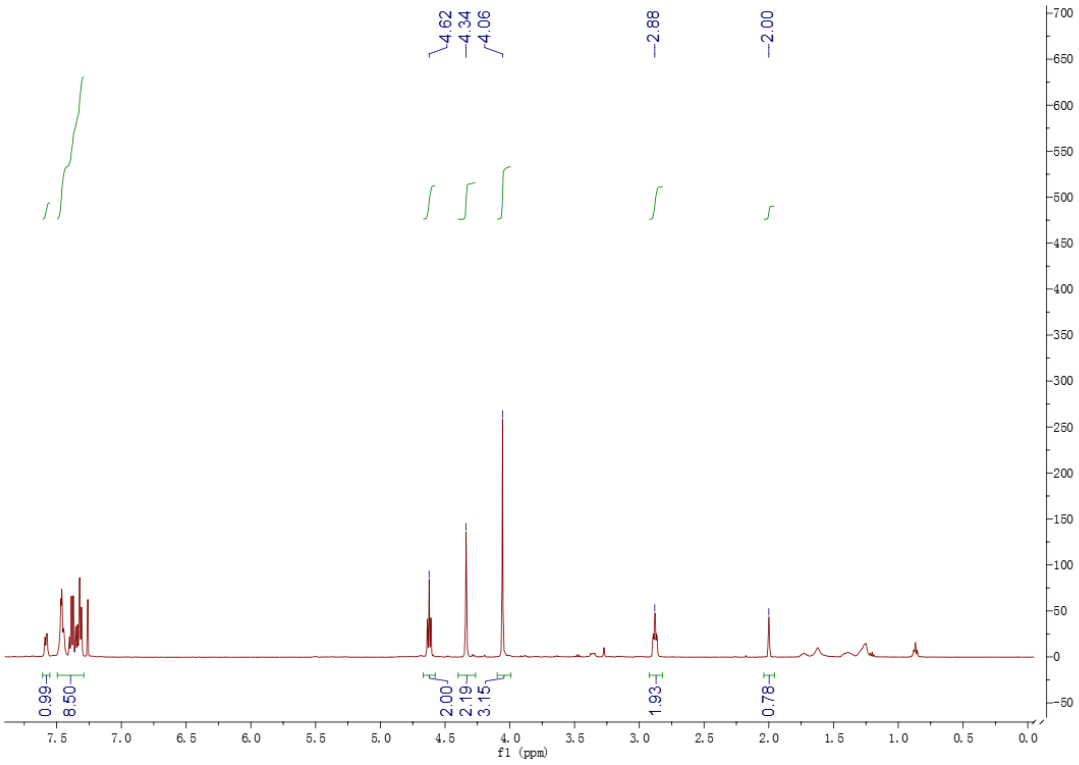


Figure S24. ^{1}H NMR spectrum of Click reaction between Compound **13** and benzyl azide after 10 min.

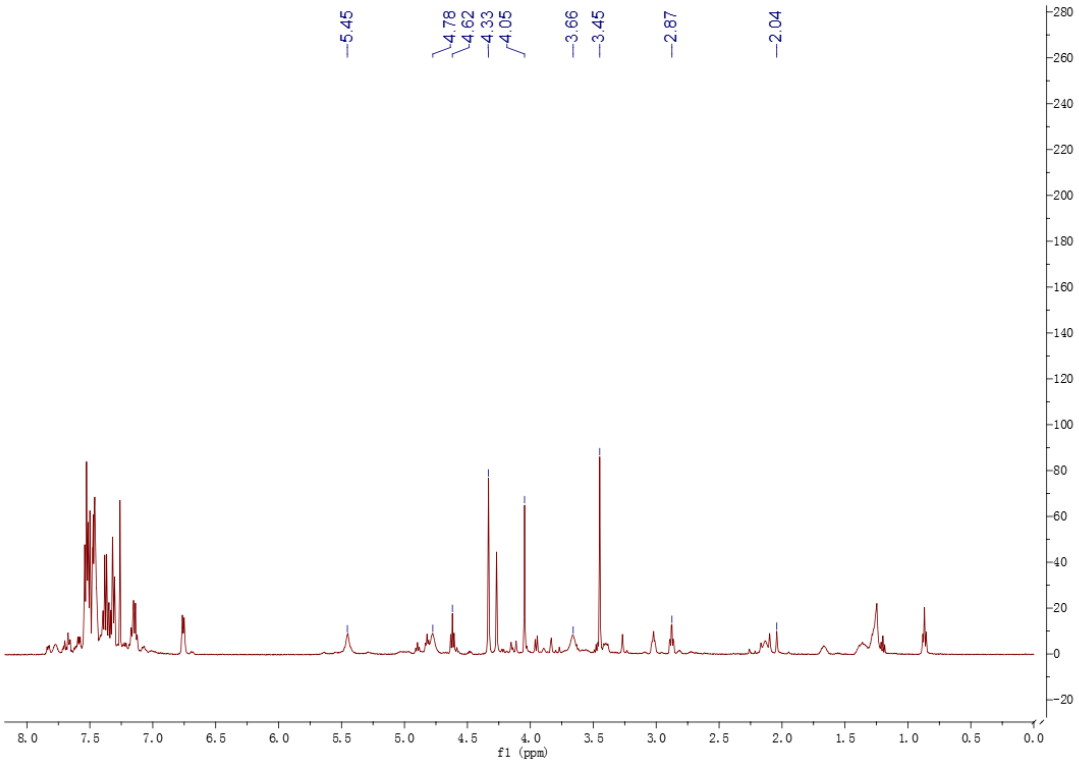


Figure S25. ^{1}H NMR spectrum of Click reaction between Compound **13** and benzyl azide after 24 h.

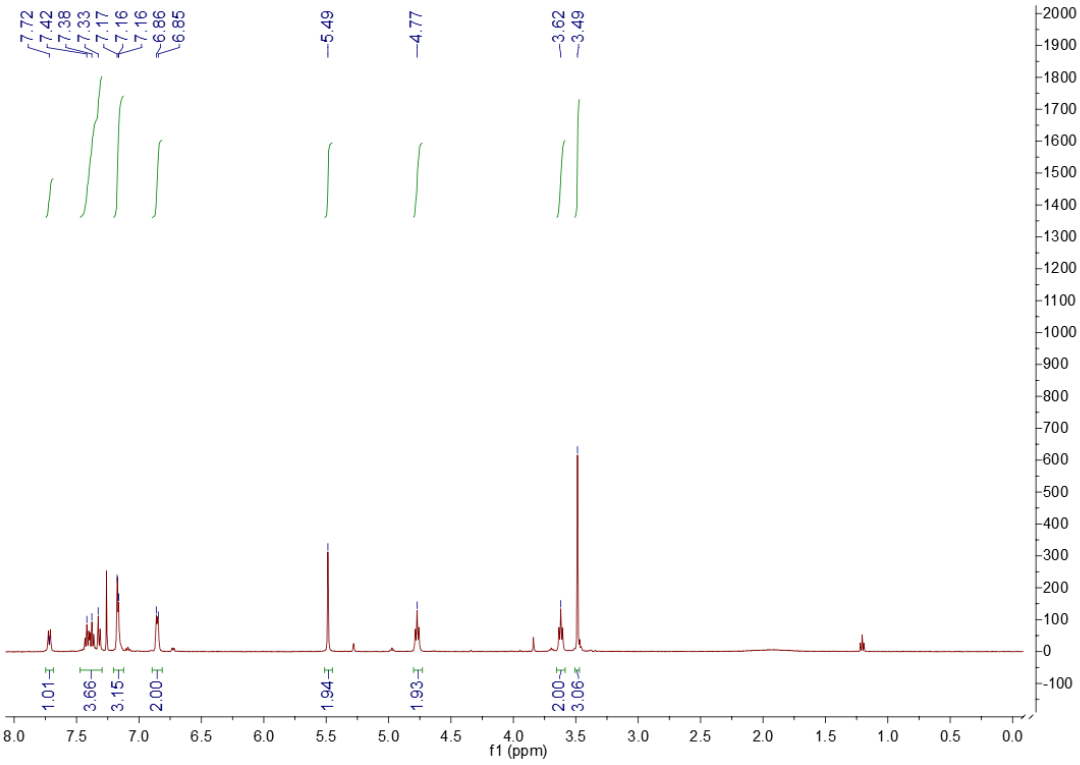


Figure S26. ^{1}H NMR spectrum of Click reaction between Compound **13** and benzyl azide after 48 h. (After work up.)

6. Gradient Heteronuclear Multiple Bond Coherence (gHMBC) spectra for compounds 1-13.

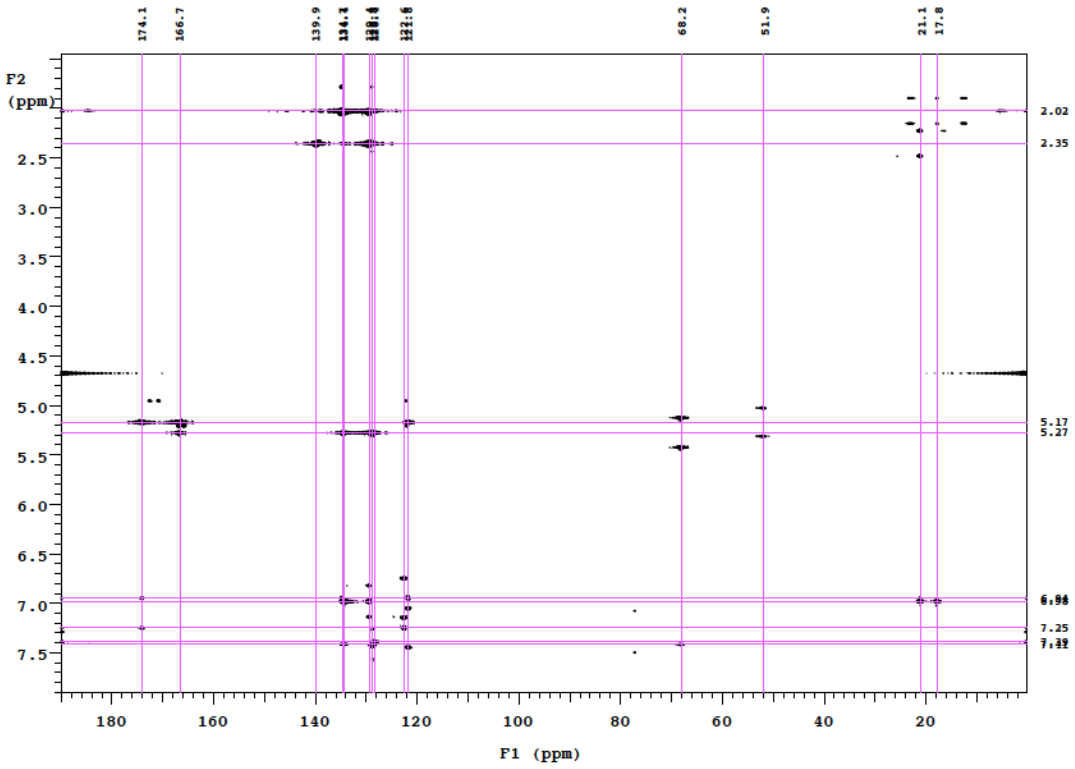


Figure S27. gHMBC spectrum of **2** – 500 MHz, $CDCl_3$

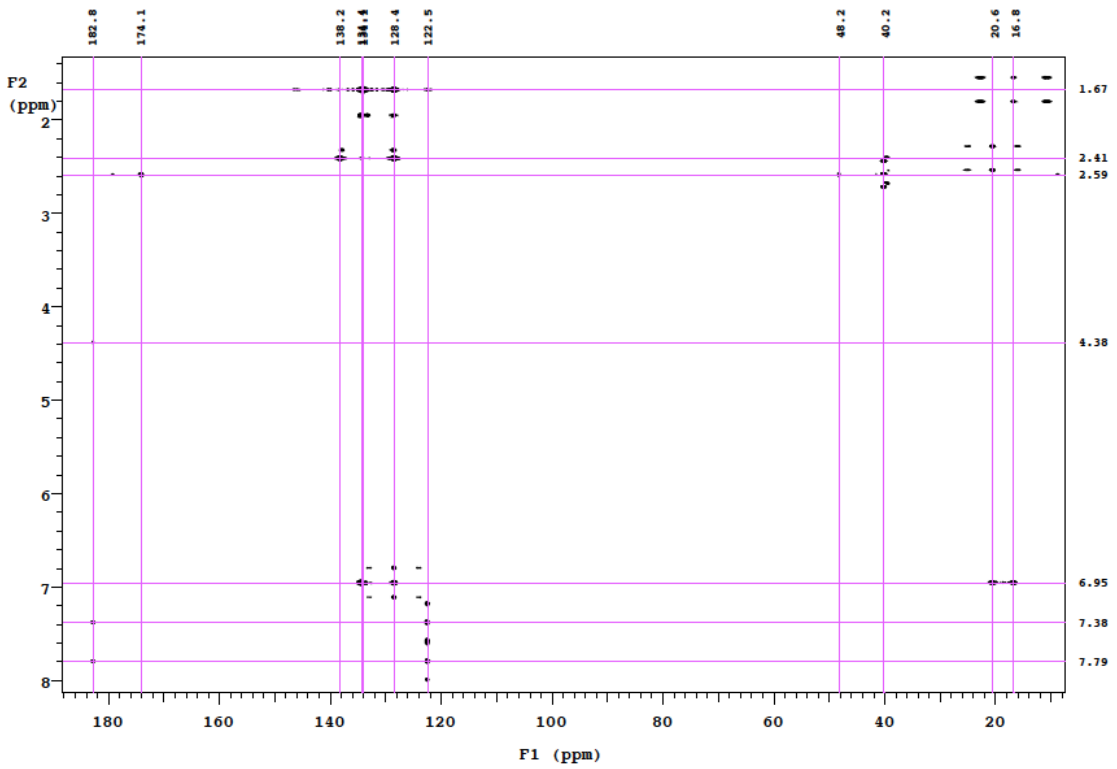


Figure S28. gHMBC spectrum of **4** – 500 MHz, $CDCl_3$

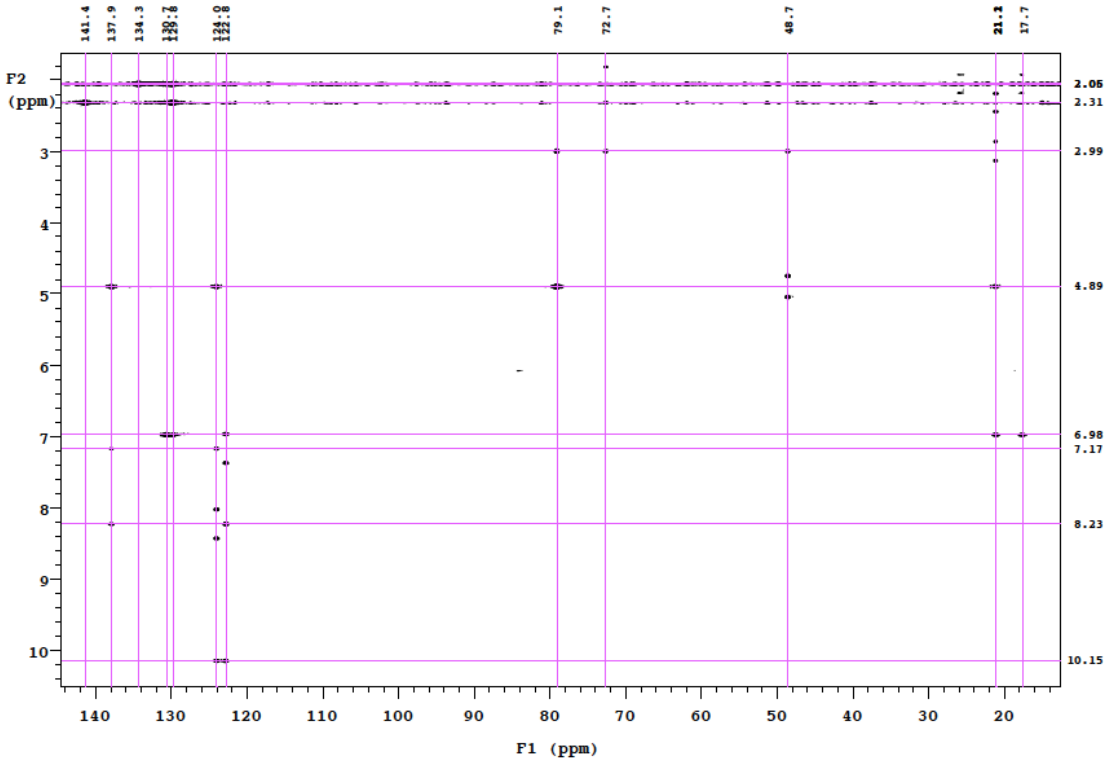


Figure S29. gHMBC spectrum of **5** – 500 MHz, $CDCl_3$

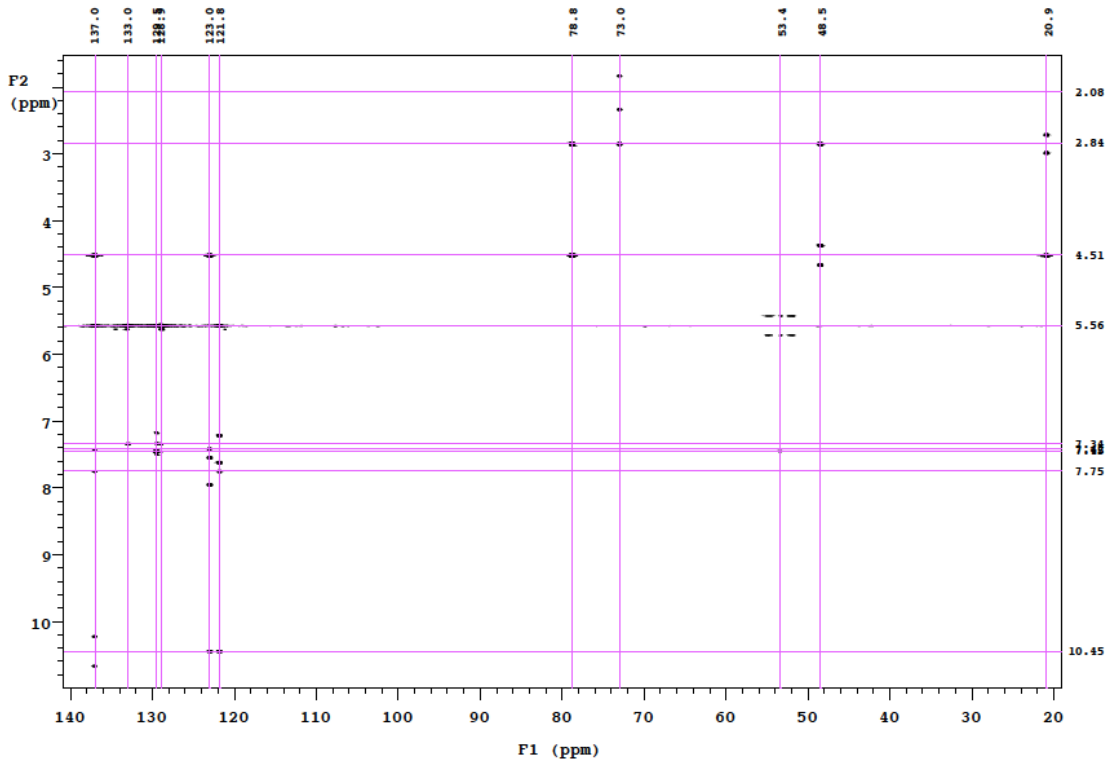


Figure S30. gHMBC spectrum of **6** – 500 MHz, $CDCl_3$

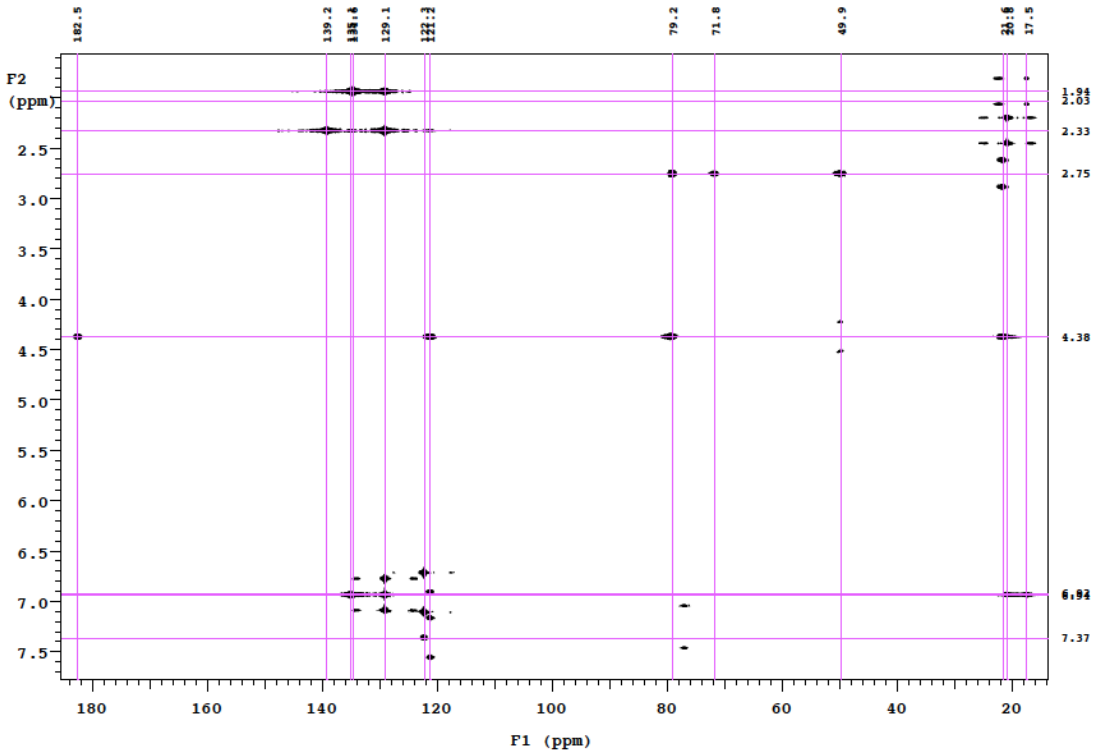


Figure S31. gHMBC spectrum of **8** – 500 MHz, $CDCl_3$

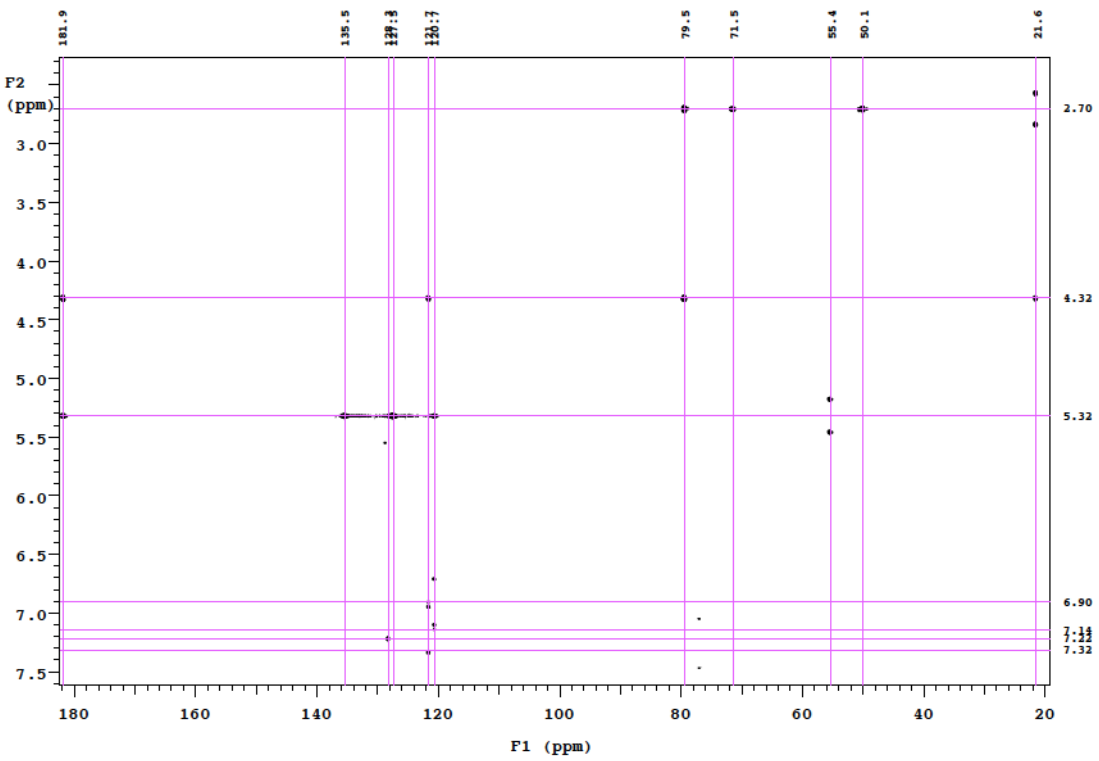


Figure S32. gHMBC spectrum of **9** – 500 MHz, $CDCl_3$

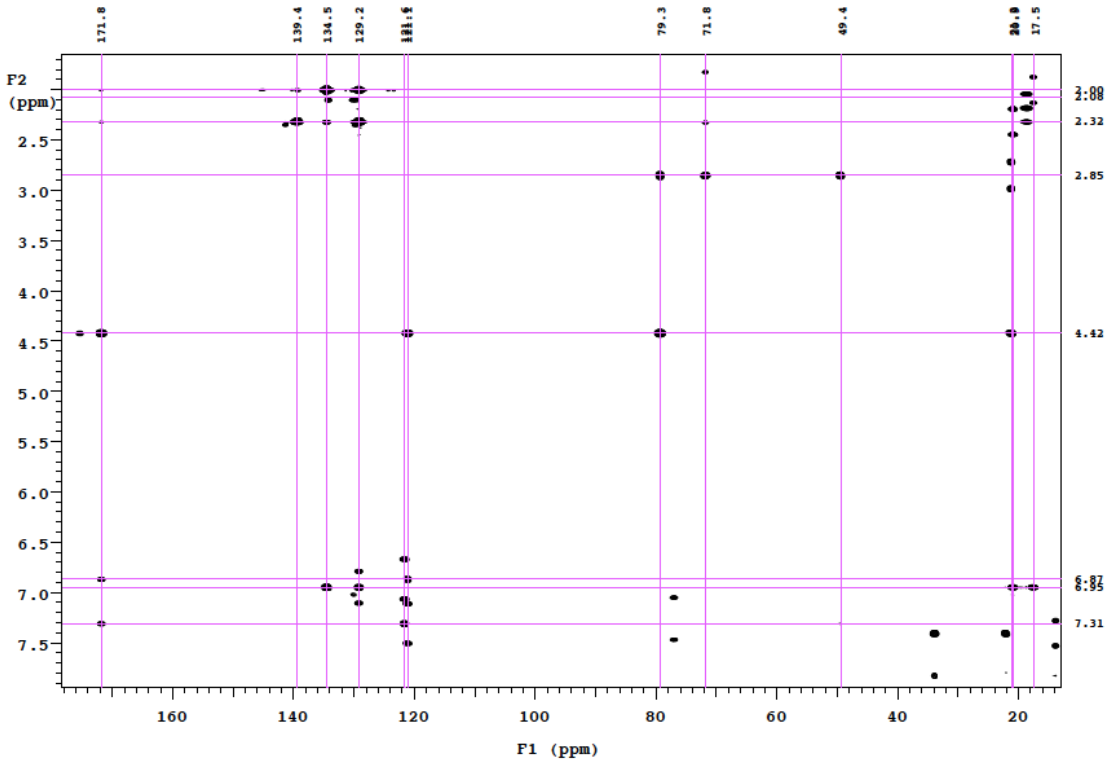


Figure S33. gHMBC spectrum of **10** – 500 MHz, $CDCl_3$

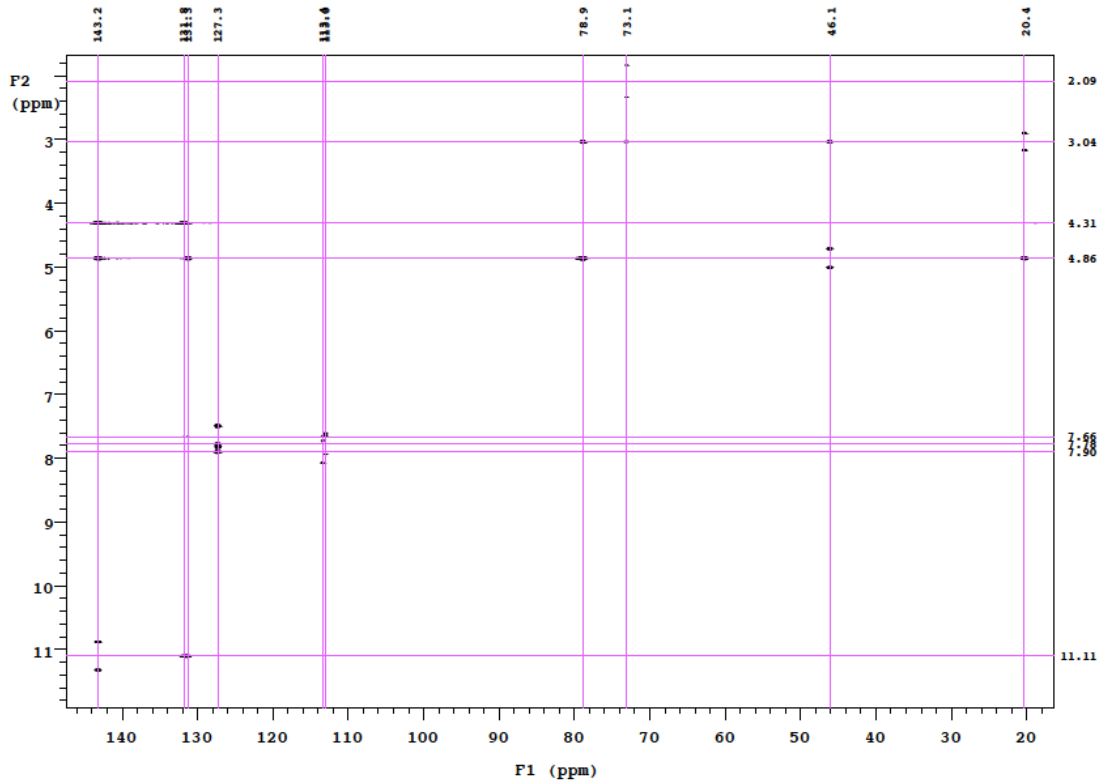


Figure S34. gHMBC spectrum of **11** – 500 MHz, $CDCl_3$

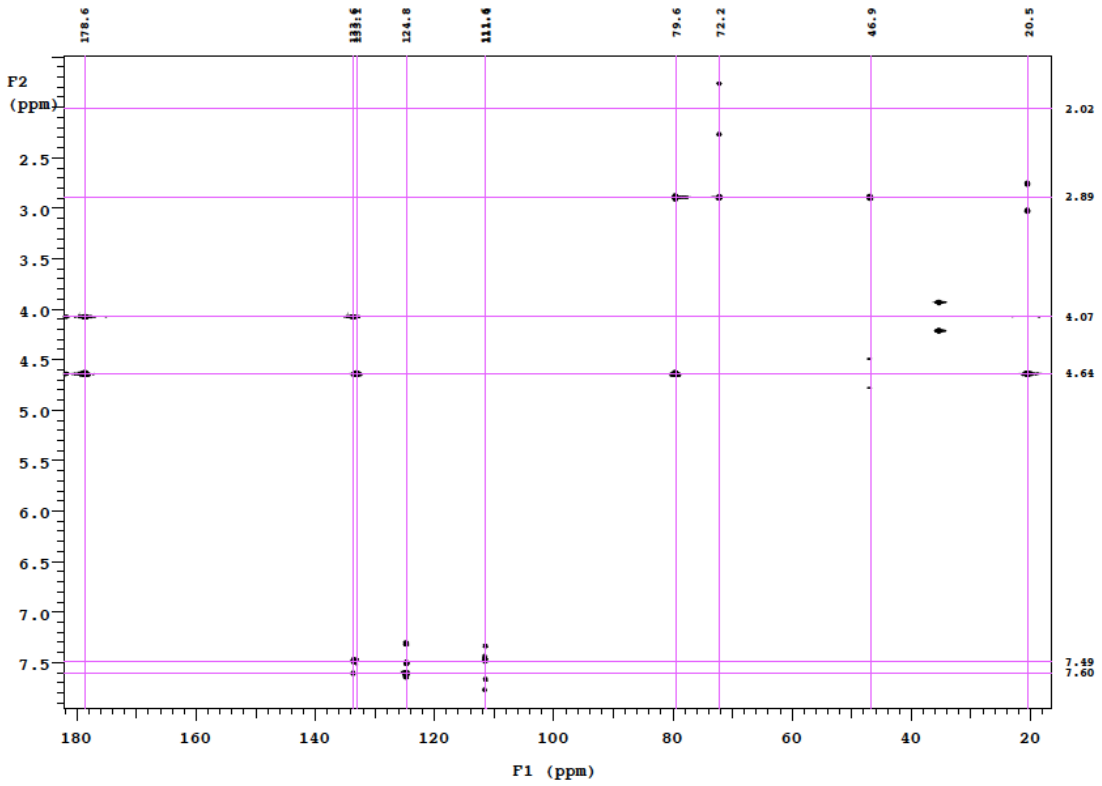


Figure S35. gHMBC spectrum of **13** – 500 MHz, $CDCl_3$

18. Mass Spectrometry Data for 2 and 4-6.

Compound **2**: ESI-MS (positive ion, calculated for M = $C_{21}H_{22}N_2O_2AuCl$). 1155.1945 m/z $[2M+Na]^+$, 1097.2374 m/z $[2M-Cl]^+$, 589.0926 m/z $[M+Na]^+$, 531.1339 m/z $[M-Cl]^+$.

Compound **4**: ESI-MS (positive ion, calculated for M = $C_{30}H_{34}N_4O_4Au$). 757.2023 m/z $[M+2Na]^+$, 735.2215 m/z $[M-H+Na]^+$, 713. 2386 m/z $[M+2H]^+$.

Compound **5**: ESI-MS (positive ion, calculated for M = $C_{16}H_{19}BrN_2$). Theor: 355.0393 m/z $[M+Cl]^+$, 319.0804 m/z $[M+H]^+$, 239.1543 m/z $[M-Br]^+$. Found: 355.0402 m/z $[M+Cl]^+$, 319.0802 m/z $[M+H]^+$, 239.1554 m/z $[M-Br]^+$.

Compound **6**: ESI-MS (positive ion, calculated for M = $C_{14}H_{15}BrN_2$). Theor: 327.0080 m/z $[M+Cl]^+$, 291.0491 m/z $[M+H]^+$, 211.1230 m/z $[M-Br]^+$. Found: 327.0070 m/z $[M+Cl]^+$, 291.0484 m/z $[M+H]^+$, 211.1238 m/z $[M-Br]^+$.

19. Cell Culture

The cell lines DLD-1 (human colorectal adenocarcinoma), CEM (T cell leukemia) and Ramos (Burkitt's Lymphoma) were cultured according to ATCC specifications in RPMI-1640 medium. The cell lines MCF-7 (human breast adenocarcinoma), HEK (human embryonic kidney), and Hep-G2 (human hepatocellular carcinoma) were cultured according to ATCC specifications in DMEM medium. Both media were supplemented with 10% fetal bovine serum (Invitrogen) and the cells were incubated at 37 °C in 5% CO_2.

20. Cytotoxicity studies of **6** and **9** using MTS assay

DLD-1, MCF-7, HEK, and Hep-G2 cell lines were treated at the following concentrations **9** (dissolved in DMSO to obtain a stock concentration of 20 mM): 0.5 μM, 1.0 μM, 2.0 μM, 4.0 μM, 8.0 μM, 16 μM, 32 μM, and 64 μM, respectively, for 48 h at 37 °C. In addition to treatments, cells were treated with two controls: (a) cells in media and (b) DMSO (0.01%). Approximately 100 μL of 2,000-5,000 (depending on the growth characteristics of the cell line) freshly collected cells were added to the inner 60 wells of its own 96-well plate. After 24 h incubation, 80 μL of old media was removed from each well and then 100 uL of each concentration of **9** was added to six wells of each of the 96-well plates. Each of the plates was subjected to this treatment and incubated for 48 h at 37 °C in 5% CO_2. After 48 h, 100 μL of the drug treatment was removed and replaced with 120 uL of MTS dye (MTS = 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium) diluted with PBS buffer (to 15% MTS). The assay was allotted 2 h at 37 °C for development. After incubation with the MTS dye, the 490 nm absorbance of each well was read on a Tecan plate 110 reader. Each cell measurement had the treatment background subtracted before analysis. Quantitative and statistical analyses were performed using the nonlinear dose response curve fitting in Origin 8.5 software. The same procedures were used to study **6**, **11**, and **13**.

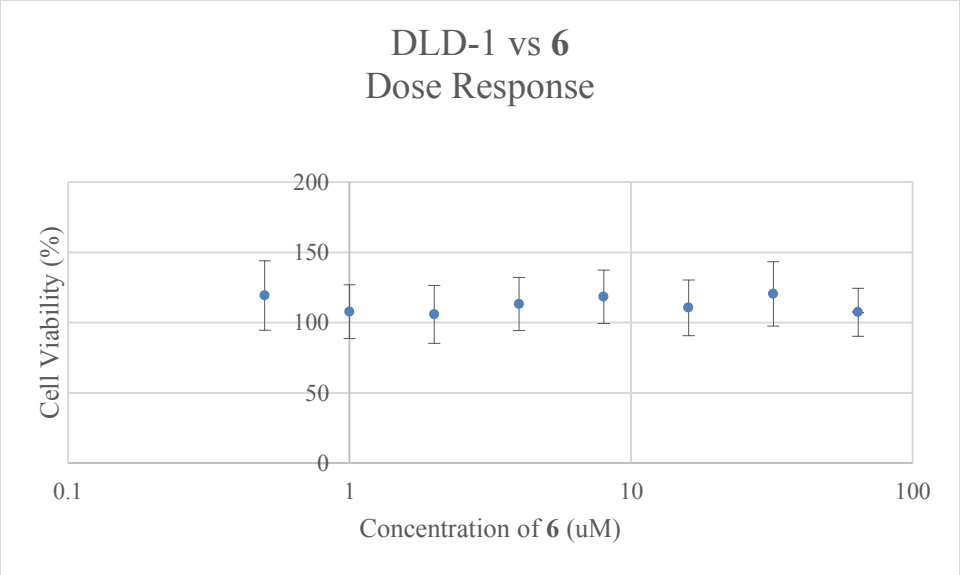


Figure S19. DLD-1 cell viability vs **6**.

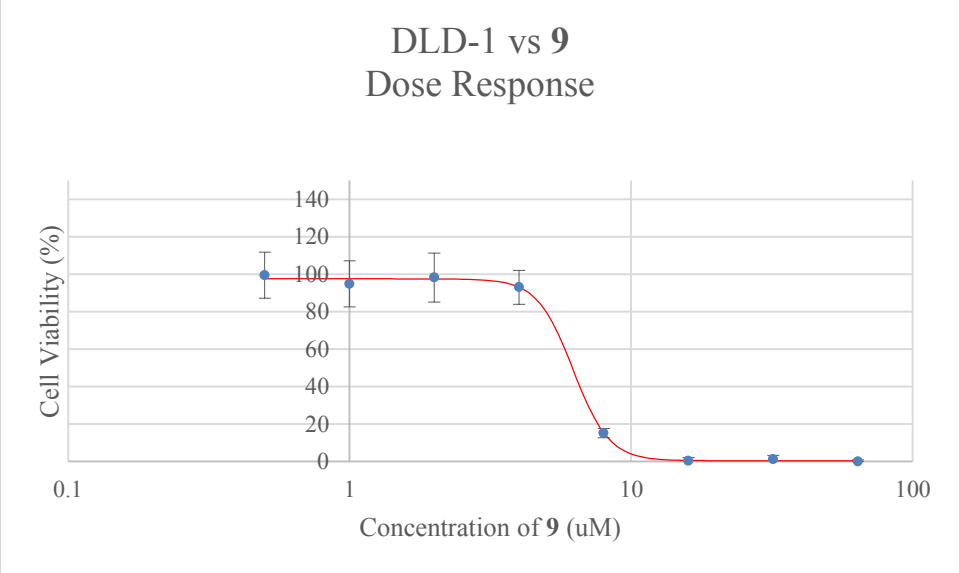


Figure S20. DLD-1 cell viability vs **9**.

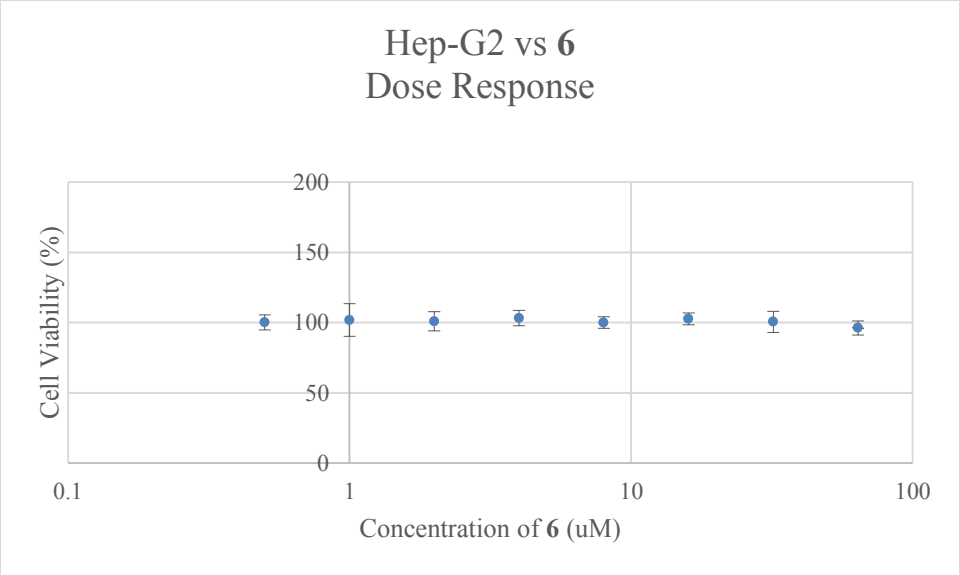


Figure S21. Hep-G2 cell viability vs **6**.

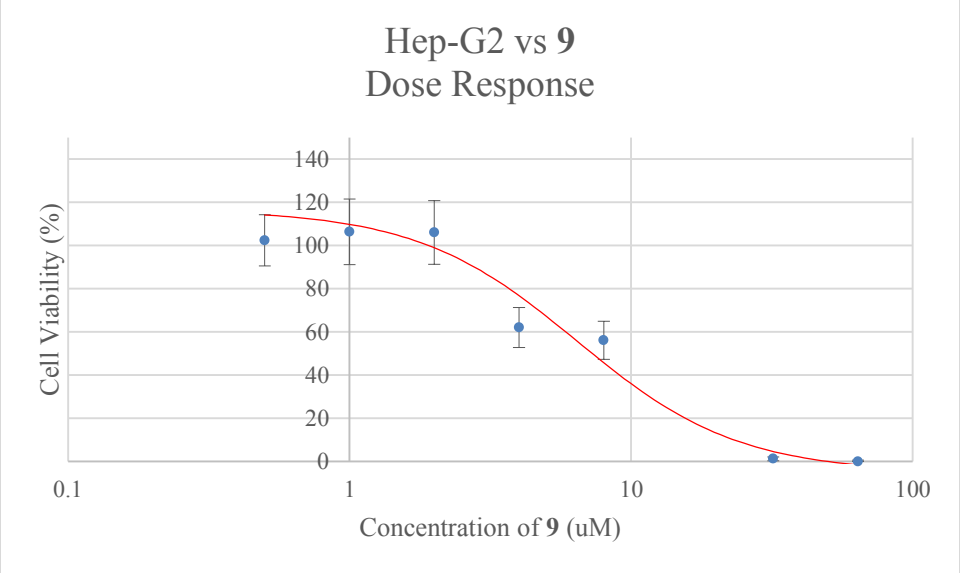


Figure S22. Hep-G2 cell viability vs **9**.

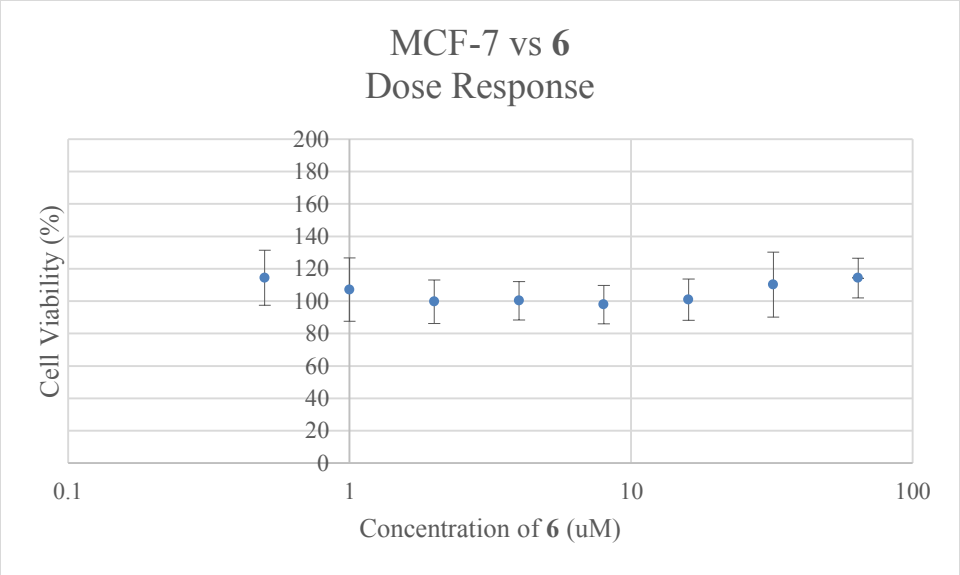


Figure S23. MCF-7 cell viability vs **6**.

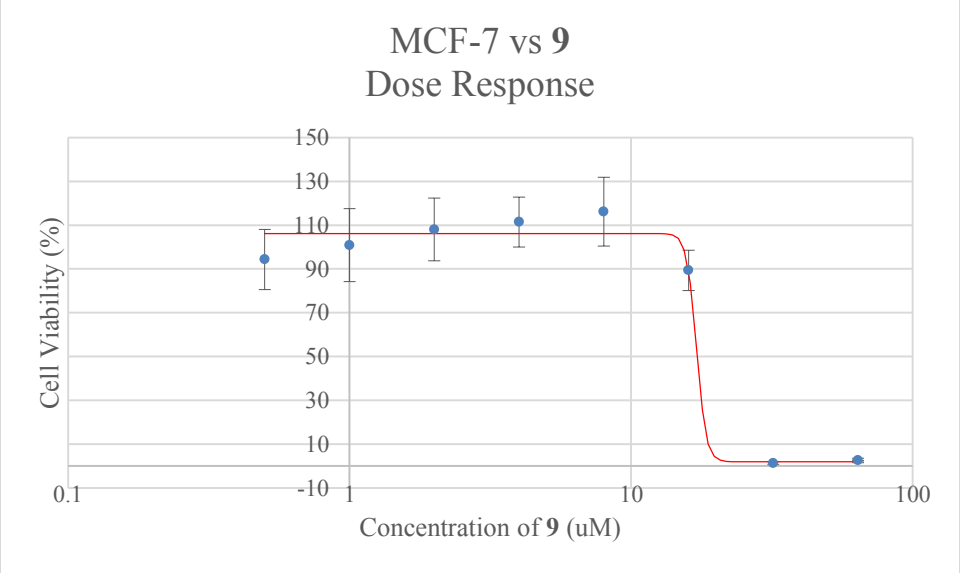


Figure S24. MCF-7 cell viability vs **9**.

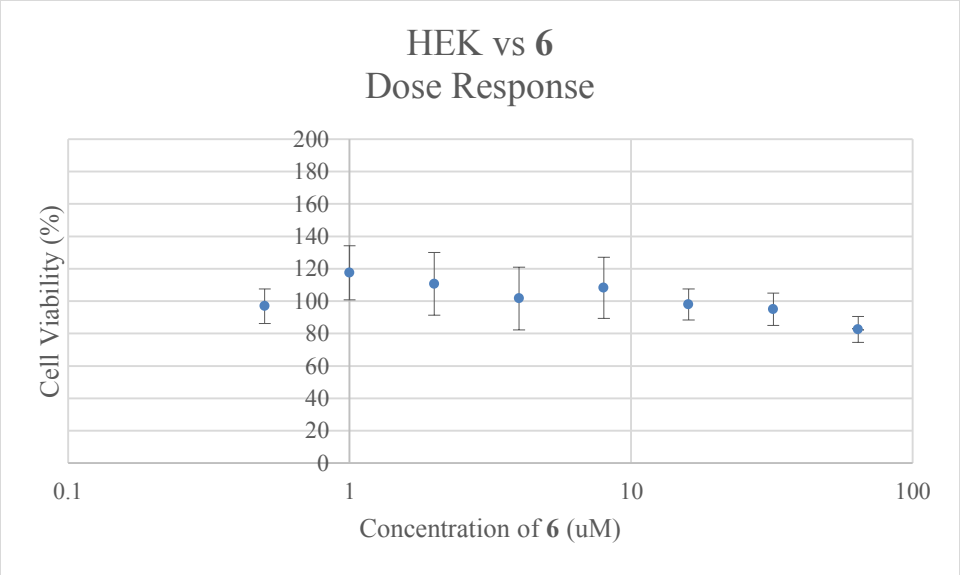


Figure S25. HEK cell viability vs **6**.

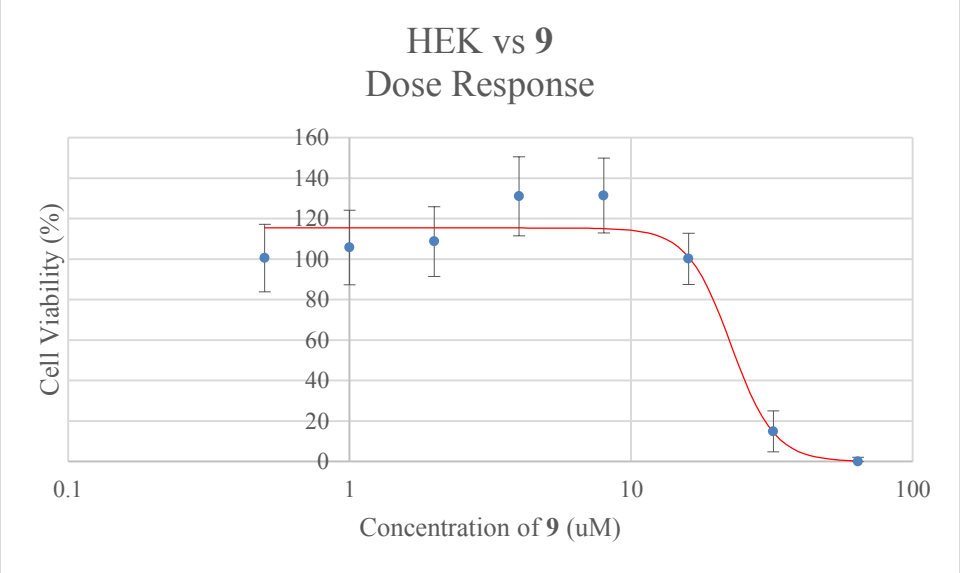


Figure S26. HEK cell viability vs **9**.

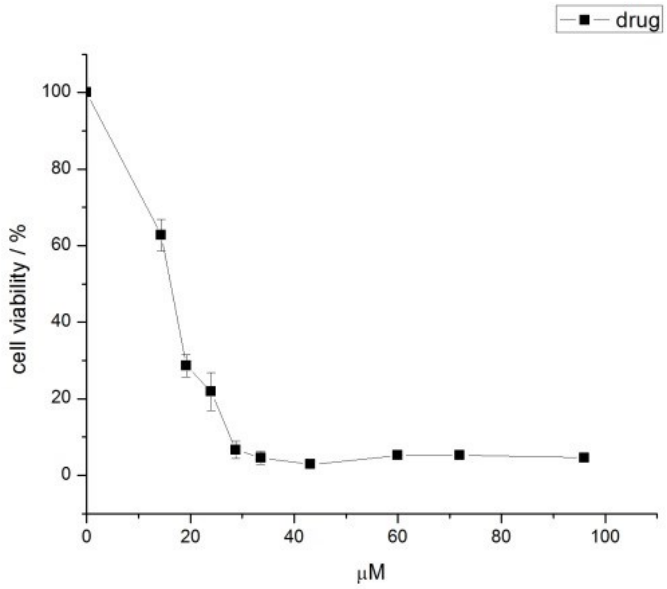


Figure 27. CEM cell viability vs **13**.

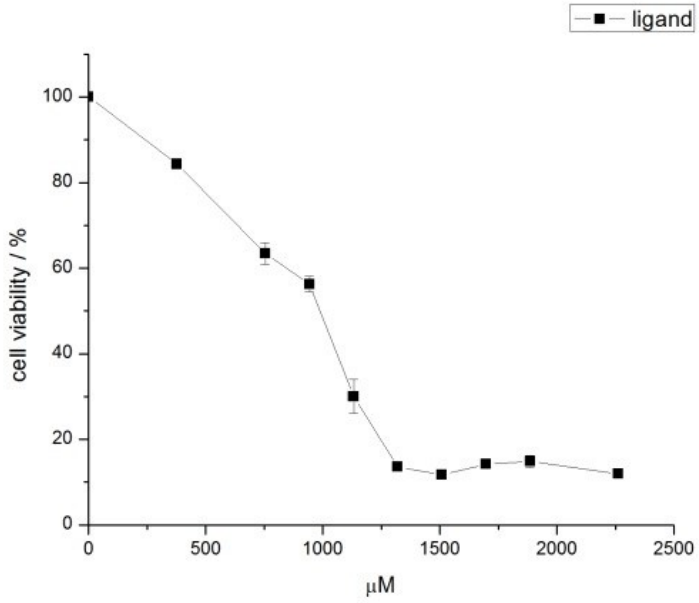


Figure 28. CEM cell viability vs **11**.

Similarly, preliminary cytotoxicity studies were performed with **3** and **4**. CEM and Ramos cells were treated at the following concentrations of compound **4** (dissolved in H_2O to obtain a stock concentration of 20 mM): 0.5 μM, 1.0 μM, 3.5 μM, 5.0 μM, 7.5

μM, 10 μM, 15 μM, and 25 μM, respectively, for 48 h at 37 °C. In addition to treatments, two negative controls: (a) cells in media and (b) water (0.01%) treated cells. Approximately 30 μL of 10,000 freshly collected CEM cells were added to each well of a 96-well plate. Similarly, Ramos cells were added to a separate 96-well plate. Both plates were incubated at 37 °C in 5% CO_2 for 24 h before beginning experiments. After 24 h incubation, 30 μL of each concentration of 4 was added to eight wells of each of the 96-well plates and to a third plate with wells containing no cells (30 μL of media for background measurements). Each of the three plates was subjected to treatment and incubated for 48 h at 37 °C in 5% CO_2. After 48 h, 30 μL of MTS dye were added to each well. The assay was allotted 4 h at 37 °C for development. After incubation with the MTS dye, the 490 nm absorbances of each well were read on a Tecan plate 110 reader. Each cell measurement had the treatment background subtracted before analysis. Quantitative and statistical analyses were done using the Origin 8.5 software using the nonlinear dose response curve fitting function. The same procedures were used to study compound **3** to assess whether the proligand displayed any cytotoxicity.

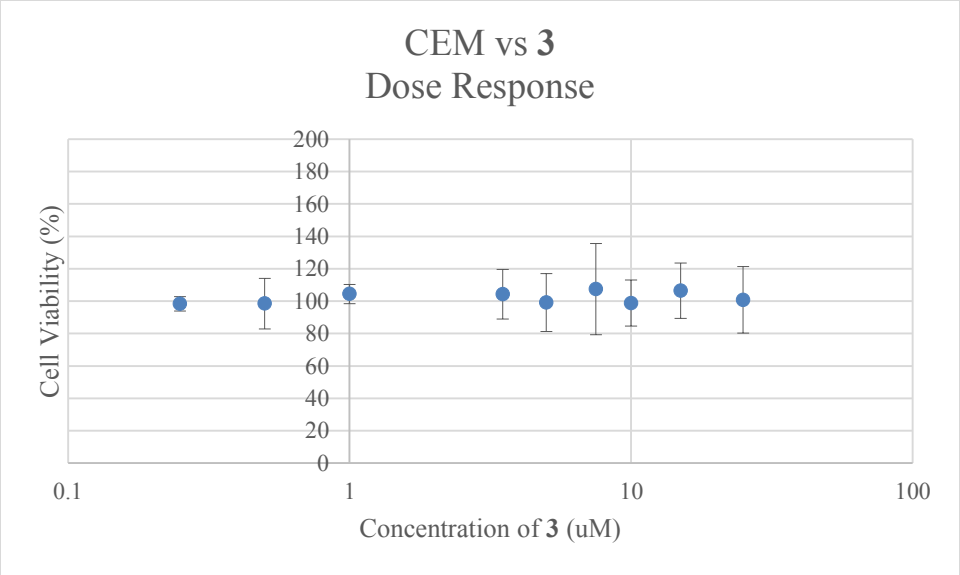


Figure S29. CEM cell viability vs **3**.

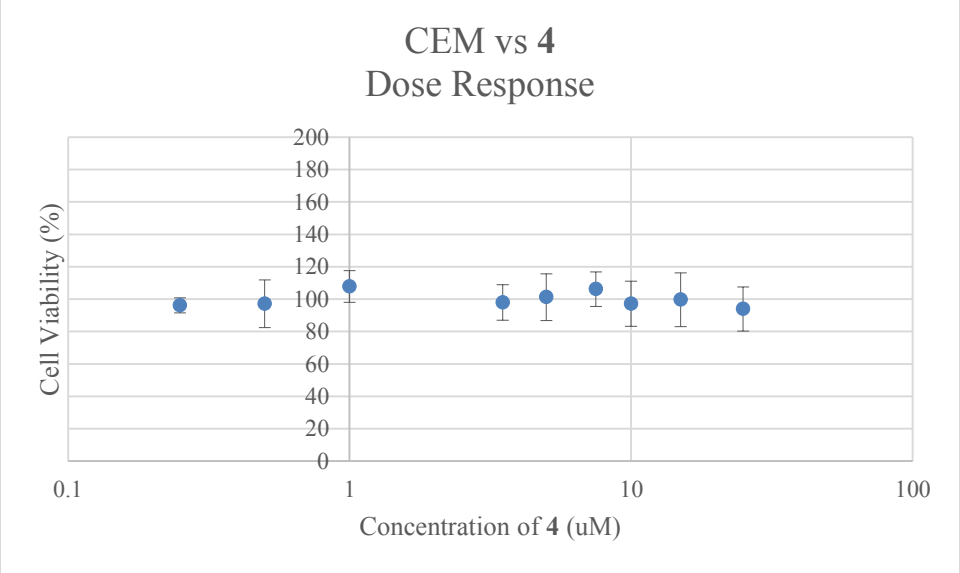


Figure S30. CEM cell viability vs **4**.

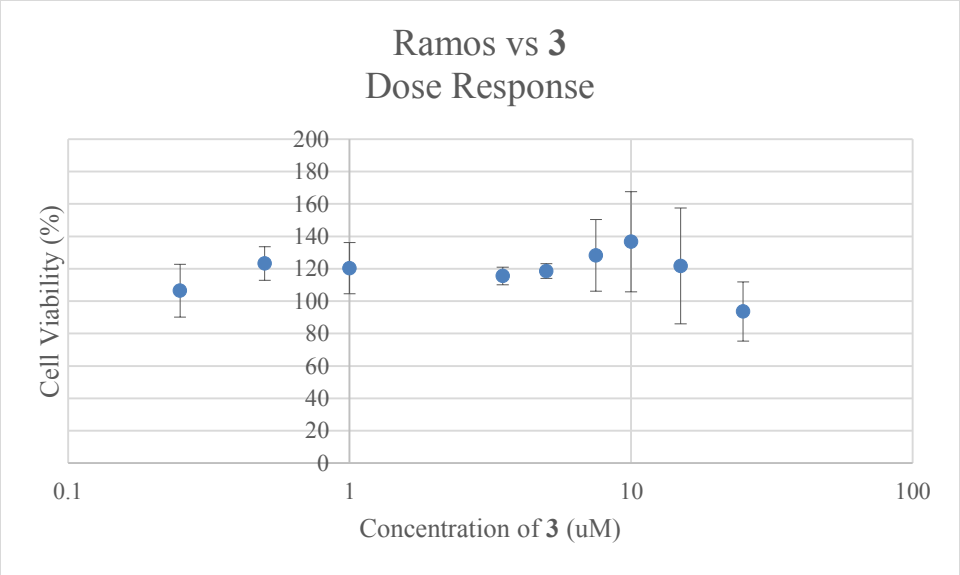


Figure S31. Ramos cell viability vs **3**.

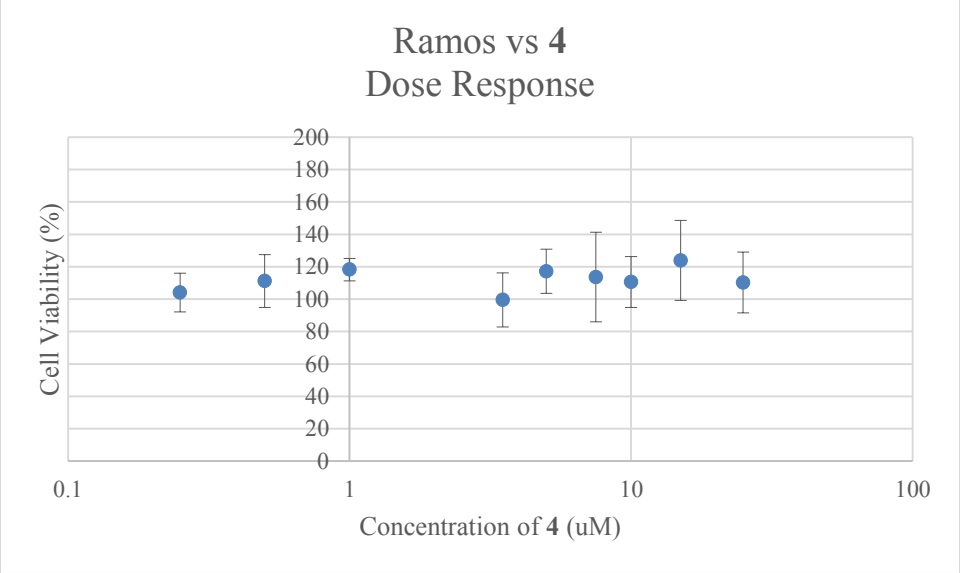


Figure S32. Ramos cell viability vs **4**.

Table S1. Calculated IC_{50} values of **3**, **4**, **6**, **9**, **11**, and **13** against various cell lines.

	3	**4**	**6**	**9**	**11**	**13**
DLD-1	--	--	> 100	6.8 $\pm$ 0.8	-	-
Hep-G2	--	--	> 100	6.9 $\pm$ 0.7	-	-
MCF-7	--	--	> 100	17.1 $\pm$ 0.4	-	-
HEK-293	--	--	> 100	22.6 $\pm$ 0.9	-	-
CEM	> 100	> 100	--	--	>100	16.2
Ramos	> 100	> 100	--	--	--	--