Supporting Information

Metal-free Alkynylation of α-C-H Bonds of Ethers with Ethynylbenziodoxolones

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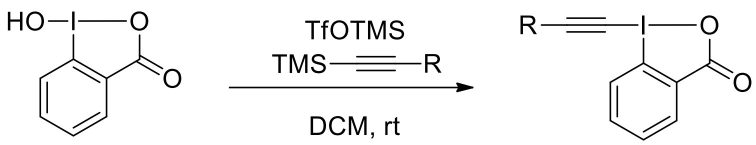
General information.

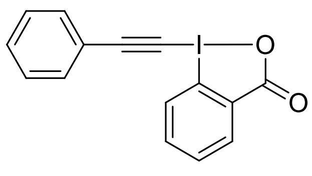
^{1}H-NMR, ^{13}C-NMR spectra were measured on a Bruker AM400 NMR spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz) with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane (TMS) standard. APCI-MS spectral data were recorded on Waters APCI-Quattrro Ptemier XE. All reagents were purchased from commercial suppliers and used without further purification. Ethynylbenziodoxolones were prepared according to the literature procedure.

General procedure for the aromatic ethynylbenziodoxolones[1]



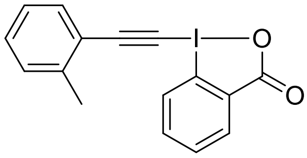
R = o-MePh (**1b**)
R = m-MePh (**1c**)
R = p-MePh (**1d**)
R = p-ClPh (**1e**)

Following a reported procedure, trimethylsilyl triflate (7.50 mL, 41.5 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (10.0 g, 37.7 mmol, 1 equiv) in DCM (100 mL) at rt. The resulting yellow mixture was stirred for 1 h, followed by the dropwise addition of the appropriate alkynyltrimethylsilane (41.5 mmol, 1.1 equiv) (slightly exothermic). The resulting suspension was stirred for 6 h at rt, during this time a white solid was formed. A saturated solution of $NaHCO_3$ (100 mL) was then added and the mixture was stirred vigorously. The resulting suspension was filtered on porosity 4 glass filter. The two layers of the mother liquors were separated and the organic layer was washed with sat. $NaHCO_3$, dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting mixture was combined with the solid obtained by filtration and boiled in CH_3CN (300 mL). The mixture was cooled down, the formed solid was collected and dried under high vacuum to afford the product.



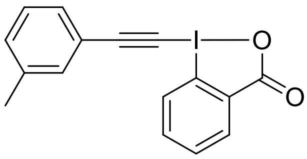
1a

1-(Phenylethynyl)-1,2-benziodoxol-3(1*H*)-one (Ph-EBX). White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41-8.40 (m, 1H), 8.26-8.24 (m, 1H), 7.79-7.72 (m, 2H), 7.60-7.58 (m, 2H), 7.50-7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.77, 135.02, 132.97, 132.57, 131.69, 131.49, 130.88, 128.88, 126.44, 120.67, 116.32, 106.68, 50.28. MS (APCI) calcd for $C_{15}H_{10}IO_2^+$ $[M + H]^+$: 348.97, found : 348.97.



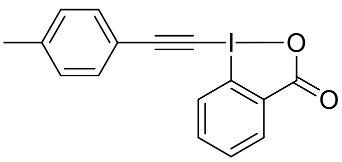
1b

1-(1-methyl-2-phenylethynyl)-1,2-benziodoxol-3(1*H*)-one (*o*-MePh-EBX). White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44-8.41 (m, 1H), 8.30-8.27 (m, 1H), 7.80-7.74 (m, 2H), 7.58-7.56 (m, 1H), 7.40-7.36 (m, 1H), 7.32-7.30 (m, 1H), 7.27-7.23 (m, 1H), 2.54, (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.79, 142.01, 134.97, 133.52, 132.57, 131.67, 131.54, 130.85, 130.05, 126.36, 126.11, 120.55, 116.47, 105.85, 53.25, 20.94. MS (APCI) calcd for $C_{16}H_{12}IO_2^+$ [M + H]$^+$: 362.99, found : 362.99.



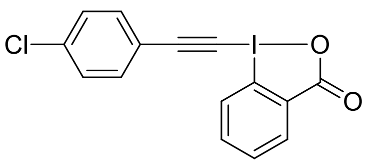
1c

1-(1-methyl-3-phenylethynyl)-1,2-benziodoxol-3(1*H*)-one (*m*-MePh-EBX). White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42-8.40 (m, 1H), 8.25-8.23 (m, 1H), 7.80-7.73 (m, 2H), 7.41-7.39 (m, 2H), 7.34-7.28 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.74, 138.79, 135.01, 133.44, 132.58, 131.84, 131.70, 131.50, 130.11, 128.78, 126.40, 120.44, 116.32, 107.08, 49.69, 21.36. MS (APCI) calcd for $C_{16}H_{12}IO_2^+$ [M + H]$^+$: 362.99, found : 362.99.



1d

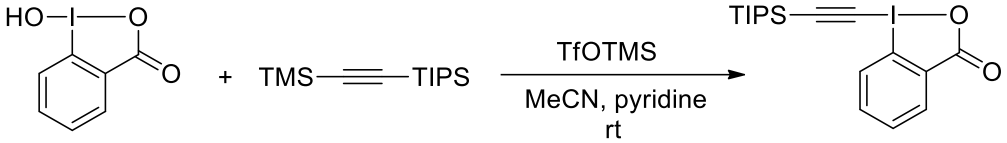
1-(1-methyl-4-phenylethynyl)-1,2-benziodoxol-3(1*H*)-one (*p*-MePh-EBX). White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.41 (m, 1H), 8.26-8.24 (m, 1H), 7.80-7.74 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.75, 141.67, 135.00, 132.97, 132.59, 131.70, 131.51, 129.66, 126.39, 117.54, 116.36, 107.33, 49.29, 21.88. MS (APCI) calcd for $C_{16}H_{12}IO_2^+$ [M + H]$^+$: 362.99, found : 362.99.



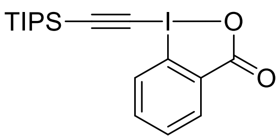
1e

1-(1-Chloro-4-phenylethynyl)-1,2-benziodoxol-3(1*H*)-one (*p*-ClPh-EBX). White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41-8.39 (m, 1H), 8.23-8.21 (m, 1H), 7.80-7.73 (m, 2H), 7.54-7.51 (m, 2H), 7.42-7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.85, 137.19, 135.07, 134.16, 132.61, 131.73, 131.47, 129.29, 126.48, 119.16, 116.32, 105.21, 51.80. MS (APCI) calcd for $C_{15}H_9ClIO_2^+$ [M + H]$^+$: 382.93, found : 382.93.

General procedure for silyl ethynylbenziodoxolones[1]



2-iodosylbenzoic acid (21.7 g, 82.0 mmol, 1.0 equiv) was charged in oven-dried three-neck 1L flask equipped with a magnetic stirred. After 3 vacuum/nitrogen cycles, anhydrous acetonitrile (500 mL) was added via canula and cooled to 4 ℃. Trimethylsilyltriflate (16.4 mL, 90.0 mmol, 1.1 equiv) was added dropwise via a dropping funnel over 30 min (no temperature increase was observed). After 15 min, (trimethylsilyl)(tri*iso*propylsilyl)acetylene (23.0 g, 90.0 mmol, 1.1 equiv) was added via canula over 15 min (no temperature increase was observed). After 30 min, the suspension became an orange solution. After 10 min, pyridine (7.0 mL, 90 mmol, 1.1 equiv) was added via syringe. After 15 min, the reaction mixture was transferred in a one-neck 1L flask and reduced under vacuum until a solid was obtained. The solid was dissolved in CH_2Cl_2 (200 mL) and transferred in a 1L separatory funnel. The organic layer was added and washed with 1 M HCl (200 mL) and the aqueous layer was extracted with CH_2Cl_2 (200 mL). The organic layers were combined, washed with a saturated solution of $NaHCO_3$ (2 x 200 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. Recrystallization from acetonitrile (120 mL) afforded the product.



1f

1-[(Tri*iso*propyllsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX). colorless cristals ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42-8.40 (m, 1H), 8.30-8.28 (m, 1H), 7.77-7.74 (m, 2H), 1.15-1.14 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.51, 134.85, 132.64, 131.71, 131.56, 126.18, 115.75, 114.43, 64.87, 18.64, 11.33. MS (APCI) calcd for $C_{18}H_{26}IO_2Si^+$ [M + H]$^+$: 429.07, found : 429.07.

General procedure for alkynylation of α-C-H bonds

A sealed 25 mL Schlenk tube with a magnetic stir bar charged with ethynylbenziodoxolones (0.2 mmol), TBHP (anhydrous, 5.5M in decane, 3.0 equiv), solvent (1 mL), and the reaction mixture was heated under argon atmosphere for 16 h.

The reaction mixture was then allowed to cool to ambient temperature, and diluted with 20 mL of ethyl acetate, and washed with brine (15 mL), water (15 mL), and then the organic layer was dried over Na_2SO_4. After concentrated in vacuo, the crude product was purified by column chromatography. The identity and purity of the known product was confirmed by ^{1}H-NMR, ^{13}C-NMR and GC-MS.

General procedure for the kinetic isotope experiment

A sealed 25 mL Schlenk tube with a magnetic stir bar charged with Ph-EBX (0.2 mmol), TBHP (anhydrous, 5.5M in decane, 3.0 equiv), mixture of THF (0.5 mL) and its deuterated derivative THF-d8 (0.5 mL), and the reaction mixture was heated at 60℃under argon atmosphere for 16 h. The reaction mixture was then allowed to cool to ambient temperature, and diluted with 20 mL of ethyl acetate, and washed with brine (15 mL), water (15 mL), and then the organic layer was dried over Na_2SO_4. After concentrated in vacuo, the crude product was purified by column chromatography. The identity and purity of the known product was confirmed by ^{1}H-NMR and GC-MS.

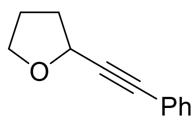
General procedure for the radical inhibition experiments

A sealed 25 mL Schlenk tube with a magnetic stir bar charged with Ph-EBX (0.2 mmol), TBHP (anhydrous, 5.5M in decane, 3.0 equiv), THF (1 mL), the radical scavenger (1.0 equiv), and the reaction mixture was heated at 60℃under argon atmosphere for 16 h. The reaction mixture was then allowed to cool to ambient temperature, and diluted with 20 mL of ethyl acetate, and washed with brine (15 mL), water (15 mL), and then the organic layer was dried over Na_2SO_4. After concentrated in vacuo, the crude product was purified by column chromatography.

Reference

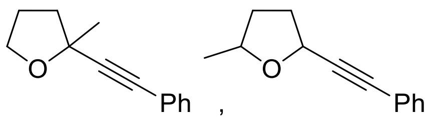
1. (a) C. A. Panetta, S. M. Garlick, H . D. Durst, F. R. Longo, and J. R. Ward, *J. Org. Chem.*, 1990, **55**, 5202; (b) S. Nicolai, C. Piemontesi, and J. Waser, *Angew. Chem., Int. Ed.*, 2011, **50**, 468.

Spectroscopic data of products



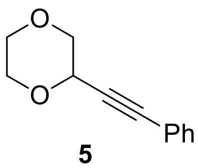
3

2-(phenylethynyl)tetrahydrofuran Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.30-7.28 (m, 3H), 4.83-4.80 (m, 1H), 4.04-3.99 (m, 1H), 3.89-3.83 (m, 1H), 2.20-2.19 (m, 1H), 2.12-2.05 (m, 1H), 1.97-1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.86, 128.38, 128.35, 122.98, 89.22, 84.62, 68.76, 68.08, 33.57, 25.64. MS (APCI) calcd for $C_{12}H_{13}O^+$ $[M + H]^+$: 173.10, found : 173.10.



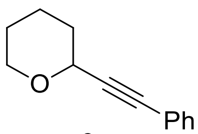
4a, 4b

2-methyl-2-(phenylethynyl)tetrahydrofuran, 2-methyl-5-(phenylethynyl)tetrahydrofuran Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.30-7.28 (m, 3H), 4.94-4.91 (m, 0.12H), 4.31-4.26 (m, 0.12H), 4.50-3.96 (m, 1.77H), 2.33-2.27 (m, 1H), 2.19-2.13 (m, 1H), 2.02-1.98 (m, 1H), 1.90-1.85 (m, 1H), 1.64 (s, 2.48H), 1.36 (d, *J* = 6.4 Hz, 0.36H). The ratio of **4a** and **4b** was 7.4 : 1, which was judged by δ 4.50 : (δ 4.94 + δ 4.31). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.81, 128.30, 128.20, 123.10, 92.45, 82.84, 76.53, 67.79, 40.29, 27.84, 25.84. MS (APCI) calcd for $C_{13}H_{15}O^+$ $[M + H]^+$: 187.11, found : 187.11.



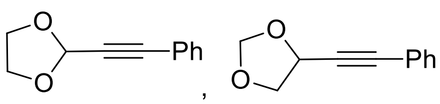
5

2-(phenylethynyl)-1,4-dioxane Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 2H), 7.33-7.30 (m, 3H), 4.59-4.56 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.96-3.92 (m, 2H), 3.78-3.67 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.01, 128.85, 128.41, 122.16, 86.69, 84.39, 70.54, 66.59, 66.53, 65.97. MS (APCI) calcd for $C_{12}H_{13}O_2^+$ $[M + H]^+$: 189.09, found : 189.09.



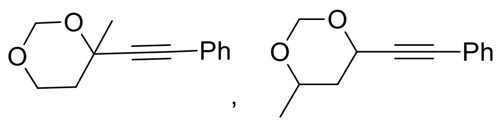
6

2-(phenylethynyl)tetrahydro-2*H*-pyran Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.44 (m, 2H), 7.31-7.29 (m, 3H), 4.52-4.50 (dd, *J* = 7.6, 2.8 Hz, 1H), 4.08-4.03 (m, 1H), 3.62-3.56 (m, 1H), 1.96-1.88 (m, 2H), 1.83-1.78 (m, 1H), 1.65-1.61 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.91, 128.42, 128.35, 122.91, 88.27, 85.35, 67.60, 66.78, 32.33, 25.83, 21.97. MS (APCI) calcd for $C_{13}H_{15}O^+$ $[M + H]^+$: 187.11, found : 187.11.



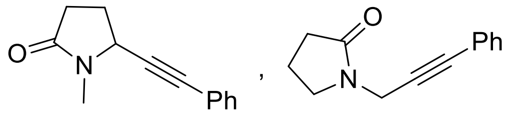
7a, 7b

2-(Phenylethynyl)-1,3-dioxolane, 4-(Phenylethynyl)-1,3-dioxolane Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.34-7.31 (m, 3H), 5.89 (s, 0.79H), 5.09 (s, 0.15H), 5.07 (s, 0.15H), 4.93 (t, *J* = 6.4 Hz, 0.15H), 4.21-4.10 (m, 2H), 4.03-3.91 (m, 2H). The ratio of **7a** and **7b** was 5.3 : 1, which was judged by δ 5.89 : δ 5.09. ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.06, 131.94, 129.10, 128.90, 128.44, 128.42, 121.71, 95.34, 93.57, 85.75, 85.34, 84.53, 70.72, 65.92. MS (APCI) calcd for $C_{11}H_{11}O_2^+$ $[M + H]^+$: 175.08, found : 175.07.



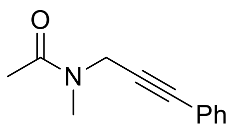
8a, 8b

4-methyl-4-(phenylethynyl)-1,3-dioxane, 4-methyl-6-(phenylethynyl)-1,3-dioxane Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.35-7.31 (m, 3H), 5.34 (d, *J* = 6.4 Hz, 0.3H), 5.26 (d, *J* = 6.8 Hz, 0.74H), 5.06 (d, *J* = 4.4 Hz, 0.28H), 4.94 (d, *J* = 6.8 Hz, 0.83H), 4.16-4.00 (m, 1.85H), 2.12-1.99 (m, 1H), 1.74-1.71 (m, 1H), 1.62 (s, 2.22H), 1.26 (d, *J* = 6.4 Hz, 1.16H). The ratio of **8a** and **8b** was 1.9 : 1, which was judged by δ 1.62 : δ 1.26. ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.87, 128.78, 128.71, 128.51, 128.49, 122.51, 90.05, 88.88, 88.66, 87.07, 70.17,69.02, 64.34, 64.24, 38.30, 38.21, 29.91, 21.53. MS (APCI) calcd for $C_{13}H_{14}NaO_2^+$ $[M + Na]^+$: 225.09, found : 225.09.



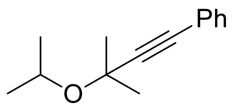
9a, 9b

1-methyl-5-(phenylethynyl)pyrrolidin-2-one, 1-(3-phenylprop-2-yn-1-yl)pyrrolidin-2-one Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.35-7.30 (m, 3H), 4.50-4.46 (m, 0.87H), 4.33 (s, 0.28H), 3.56 (t, *J* = 6.8 Hz, 0.31H), 2.94 (s, 2.67H), 2.59-2.53 (m, 1H), 2.47-2.36 (m, 2.22H), 2.23-2.17 (m, 1H), 2.08 (t, *J* = 7.6 Hz, 0.31H). The ratio of **9a** and **9b** was 6.2 : 1, which was judged by δ 4.50 : 1/2 δ 4.33. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.46, 131.89, 128.83, 128.52, 122.30, 86.57, 85.47, 51.99, 29.98, 28.19, 26.37. MS (APCI) calcd for $C_{13}H_{14}NO^+$ $[M + H]^+$: 200.11, found : 200.11.



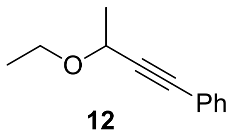
10

N-methyl-N-(3-phenylprop-2-yn-1-yl)acetamide Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.34-7.28 (m, 3H), 4.46 (s, 1.26H), 4.26 (s, 1.75H), 3.14 (s, 1.86H), 3.05 (s, 1.14H), 2.22 (s, 1.10H), 2.13 (s, 1.91H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.47, 131.93, 131.84, 128.79, 128.52, 128.48, 128.41, 122.89, 84.30, 83.77, 83.22, 77.36, 41.28, 36.85, 35.30, 33.47, 21.85, 21.65. MS (APCI) calcd for $C_{12}H_{14}NO^+$ $[M + H]^+$: 188.11, found : 188.11.



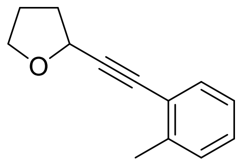
11

(3-isopropoxy-3-methylbut-1-yn-1-yl)benzene Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.31-7.29 (m, 3H), 4.15-4.09 (m, 1H), 1.53 (s, 6H), 1.23 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.39, 128.19, 126.80, 125.53, 123.29, 92.82, 83.12, 67.24, 30.02, 24.65. MS (APCI) calcd for $C_{14}H_{19}O^+$ $[M + H]^+$: 203.14, found : 203.14.



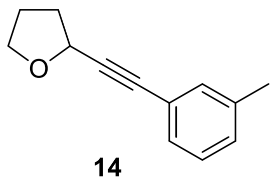
12

(3-ethoxybut-1-yn-1-yl)benzene Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.31-7.29 (m, 3H), 4.42-4.37 (q, *J* = 6.8 Hz, 1H), 3.90-3.82 (m, 1H), 3.55-3.48 (m, 1H), 1.54-1.52 (d, *J* = 6.4 Hz, 3H), 1.28-1.25 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.87, 128.38, 123.01, 89.59, 84.81, 65.67, 64.36, 22.43, 15.39. MS (APCI) calcd for $C_{12}H_{15}O^+$ $[M + H]^+$: 175.11, found : 175.09.



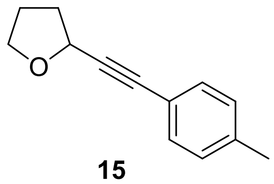
13

2-(*o*-tolylethynyl)tetrahydrofuran Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 1H), 7.20-7.17 (m, 2H), 7.13-7.09 (m, 1H), 4.88-4.85 (m, 1H), 4.05-4.00 (m, 1H), 3.90-3.85 (m, 1H), 2.42 (s, 3H), 2.25-2.21 (m, 1H), 2.13-2.07 (m, 1H), 2.00-1.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.34, 132.14, 129.47, 128.40, 125.58, 122.70, 93.21, 83.48, 68.85, 67.95, 33.73, 25.54, 20.77. MS (APCI) calcd for $C_{13}H_{15}O^+$ $[M + H]^+$: 187.11, found : 187.10.



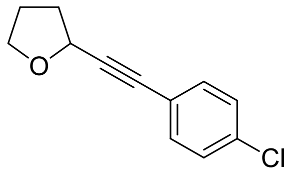
14

2-(*m*-tolylethynyl)tetrahydrofuran Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12-7.10 (m, 1H), 4.82-4.79 (m, 1H), 4.03-3.98 (m, 1H), 3.88-3.83 (m, 1H), 2.31 (s, 3H), 2.25-2.18 (m, 1H), 2.12-2.05 (m, 2H), 1.96-1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.00, 132.45, 129.27, 128.90, 128.24, 122.75, 88.84, 84.77, 68.76, 68.04, 33.58, 25.62, 21.31. MS (APCI) calcd for $C_{13}H_{15}O^+$ $[M + H]^+$: 187.11, found : 187.11.



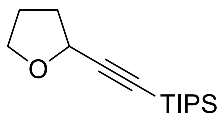
15

2-(*p*-tolylethynyl)tetrahydrofuran Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 4.82-4.79 (m, 1H), 4.04-3.98 (m, 1H), 3.88-3.83 (m, 1H), 2.33 (s, 3H), 2.25-2.18 (m, 1H), 2.12-2.03 (m, 2H), 1.96-1.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.47, 131.75,129.10, 119.88, 88.46, 84.74, 68.81, 68.04, 33.58, 25.64, 21.59. MS (APCI) calcd for $C_{13}H_{15}O^+$ $[M + H]^+$: 187.11, found : 187.11.



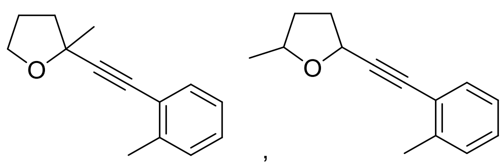
16

2-((4-chlorophenyl)ethynyl)tetrahydrofuran Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 2H), 7.28-7.25 (m, 2H), 4.81-4.78 (m, 1H), 4.03-3.98 (m, 1H), 3.89-3.83 (m, 1H), 2.26-2.19 (m, 1H), 2.11-2.04 (m, 2H), 1.97-1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.45, 133.09, 128.71, 131.47, 90.23, 83.52, 68.67, 68.16, 33.50, 25.66. MS (APCI) calcd for $C_{12}H_{12}ClO^+$ $[M + H]^+$: 207.06, found : 207.06.



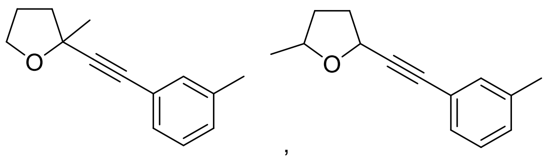
17

triisopropyl((tetrahydrofuran-2-yl)ethynyl)silane Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64-4.61 (m, 1H), 3.98-3.93 (m, 1H), 3.85-3.80 (m, 1H), 2.16-2.10 (m, 1H), 2.08-1.95 (m, 2H), 1.92-1.86 (m, 1H), 1.07-1.06 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.93, 85.20, 68.73, 67.72, 33.84, 25.27, 18.73, 11.29. MS (APCI) calcd for $C_{15}H_{29}OSi^+$ $[M + H]^+$: 253.20, found : 253.09.



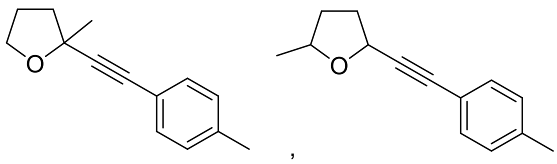
18a, 18b

2-methyl-2-(*o*-tolylethynyl)tetrahydrofuran, 2-methyl-5-(*o*-tolylethynyl)tetrahydrofuran Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 1H), 7.20-7.17 (m, 2H), 7.14-7.09 (m, 1H), 4.98-4.95 (m, 0.11H), 4.33-4.28 (m, 0.12H), 4.06-3.95 (m, 1.80H), 2.41 (s, 1H), 2.33-2.27 (m, 1H), 2.21-2.12 (m, 1H), 2.03-2.00 (m, 1H), 1.90-1.83 (m, 1H), 1.66 (s, 2.56H), 1.36 (d, *J* = 6.4 Hz, 0.30H). The ratio of **18a** and **18b** was 7.4 : 1, which was judged by δ 4.06 : (δ 4.98 + δ 4.33). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.24, 132.00, 129.45, 128.25, 125.58, 122.90, 96.56, 81.82, 76.70, 67.71, 40.45, 27.83, 25.83, 20.77. MS (APCI) calcd for $C_{14}H_{17}O^+$ $[M + H]^+$: 201.13, found : 201.13.



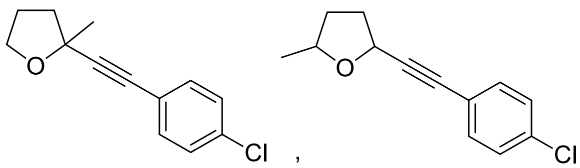
19a, 19b

2-methyl-2-(*m*-tolylethynyl)tetrahydrofuran, 2-methyl-5-(*m*-tolylethynyl)tetrahydrofuran Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.21 (m, 2H), 7.19-7.15 (m, 1H), 7.11-7.09 (m, 1H), 4.93-4.90 (m, 0.12H), 4.31-4.26 (m, 0.13H), 4.04-3.95 (m, 1.86H), 2.31 (s, 3H), 2.29-2.26 (m, 1H), 2.29-2.11 (m, 1H), 2.02-1.98 (m, 1H), 1.89-1.82 (m, 1H), 1.63 (s, 2.57H), 1.35 (d, *J* = 6.0 Hz, 0.32H). The ratio of **19a** and **19b** was 7.4 : 1, which was judged by δ 4.04 : (δ 4.93 + δ 4.31). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.97, 132.44, 129.09, 128.87, 128.22, 122.95, 92.12, 83.02, 76.56, 67.77, 40.34, 27.86, 25.85, 21.32. MS (APCI) calcd for $C_{14}H_{17}O^+$ $[M + H]^+$: 201.13, found : 201.12.



20a, 20b

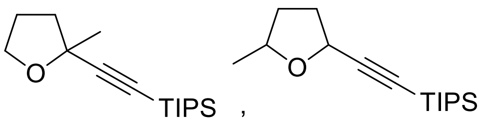
2-methyl-2-(*p*-tolylethynyl)tetrahydrofuran, 2-methyl-5-(*p*-tolylethynyl)tetrahydrofuran Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.93-4.90 (m, 0.13H), 4.31-4.26 (m, 0.14H), 4.04-3.93 (m, 1.80H), 2.33 (s, 3H), 2.31-2.26 (m, 1H), 2.19-2.12 (m, 1.24H), 2.04-1.97 (m, 1H), 1.89-1.82 (m, 0.87H), 1.63 (s, 2.48H), 1.35 (d, *J* = 6.0 Hz, 0.32H). The ratio of **20a** and **20b** was 6.7 : 1, which was judged by δ 4.04 : (δ 4.93 + δ 4.31). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.25, 131.71, 129.06, 120.07, 91.74, 82.97, 76.58, 67.75, 40.34, 27.90, 25.86, 21.58. MS (APCI) calcd for $C_{14}H_{17}O^+$ $[M + H]^+$: 201.13, found : 201.12.



21a, 21b

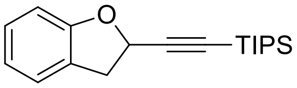
2-((4-chlorophenyl)ethynyl)-2-methyltetrahydrofuran, 2-((4-

chlorophenyl)ethynyl)-5-methyltetrahydrofuran Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 2H), 7.27-7.25 (m, 2H), 4.92-4.89 (m, 0.17H), 4.30-4.25 (m, 0.19H), 4.02-3.95 (m, 1.59H), 2.32-2.26 (m, 1H), 2.18-2.09 (m, 1.22H), 2.03-1.98 (m, 1H), 1.90-1.83 (m, 0.81H), 1.62 (s, 2.40H), 1.35 (d, *J* = 6.0Hz, 0.47H). The ratio of **21a** and **21b** was 4.4 : 1, which was judged by δ 4.04 : (δ 4.92 + δ 4.30). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.23, 133.06, 128.65, 121.66, 93.54, 81.78, 76.50, 67.87, 40.26, 27.82, 25.87. MS (APCI) calcd for $C_{13}H_{14}ClO^+$ $[M + H]^+$: 221.07, found : 221.07.



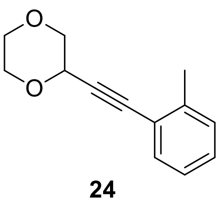
22a, 22b

tri*iso*propyl((2-methyltetrahydrofuran-2-yl)ethynyl)silane, triisopropyl((5-methyltetrahydrofuran-2-yl)ethynyl)silane Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73-4.70 (m, 0.26H), 4.57-4.54 (m, 0.13H), 4.26-4.21 (m, 0.25H), 4.06-3.92 (m, 1.27H), 2.21-1.93 (m, 3H), 1.78-1.71 (m, 0.66H), 1.55 (s, 1.48H), 1.47-1.40 (m, 0.53H), 1.25-1.23 (d, *J* = 6.0 Hz, 1.48H), 1.06-1.05 (m, 21H). The ratio of **22a** and **22b** was 1 : 1, which was judged by 1/2 δ 4.73 : δ 4.57. ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.19, 108.52, 84.93, 82.85, 76.44, 74.84, 68.57, 67.45, 40.52, 34.52, 34.19, 33.12, 32.78, 27.48, 25.59, 21.95, 21.02, 18.74, 11.29. MS (APCI) calcd for $C_{16}H_{31}OSi^+$ $[M + H]^+$: 267.21, found : 267.11.



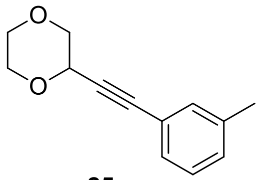
23

((2,3-dihydrobenzofuran-2-yl)ethynyl)tri*iso*propylsilane Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.31 (m, 0.28H), 7.17-7.11 (m, 1.71H), 6.94-6.80 (m, 2H), 5.38-5.33 (m, 0.71H), 4.82-4.77 (m, 0.28H), 4.46-4.35 (m, 0.57H), 3.54-3.48 (m, 0.76H), 3.34-3.28 (m, 0.74H), 1.07-1.06 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.36, 124.81, 120.92, 109.91, 105.72, 72.00, 58.64, 38.29, 35.15, 29.85, 18.69, 11.23. MS (APCI) calcd for $C_{19}H_{29}OSi^+$ $[M + H]^+$: 301.20, found : 301.09.



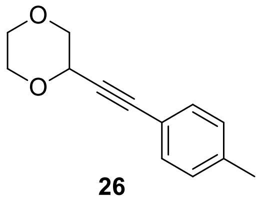
24

2-(*o*-tolylethynyl)-1,4-dioxane Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 1H), 7.25-7.18 (m, 2H), 7.14-7.10 (m, 1H), 4.62-4.60 (dd, *J* = 8.4, 3.2 Hz, 1H), 3.98-3.93 (m, 2H), 3.79-3.68 (m, 4H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.56, 132.38, 129.55, 128.85, 125.65, 122.02, 88.38, 85.60, 70.71, 66.73, 66.58, 65.87, 20.79. MS (APCI) calcd for $C_{13}H_{15}O_2^+$ $[M + H]^+$: 203.11, found : 203.10.



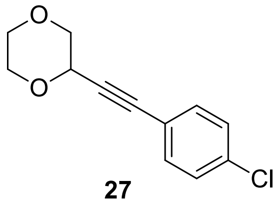
25

2-(*m*-tolylethynyl)-1,4-dioxane Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.14-7.13 (m, 1H), 4.57-4.55 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.96-3.91 (m, 2H), 3.78-3.66 (m, 4H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.11, 132.62, 129.73, 129.08, 128.31, 122.02, 86.91, 84.09, 70.61, 66.64, 66.56, 65.94, 21.31. MS (APCI) calcd for $C_{13}H_{15}O_2^+$ $[M + H]^+$: 203.11, found : 203.11.



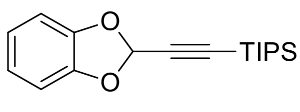
26

2-(*p*-tolylethynyl)-1,4-dioxane Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.57-4.54 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.95-3.91 (m, 2H), 3.78-3.66 (m, 4H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.02, 131.93, 129.18, 119.14, 86.89, 83.73, 70.63, 66.70, 66.55, 65.99, 21.62. MS (APCI) calcd for $C_{13}H_{15}O_2^+$ $[M + H]^+$: 203.11, found : 203.10.



27

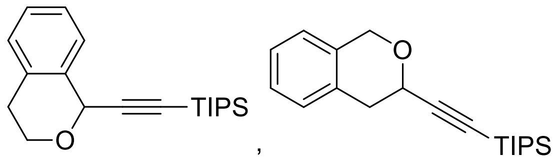
2-((4-chlorophenyl)ethynyl)-1,4-dioxane Yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2H), 7.29-7.26 (m, 2H), 4.57-4.54 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.96-3.90 (m, 2H), 3.78-3.66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.98, 133.25, 128.81, 120.72, 85.60, 85.50, 70.46, 66.56, 66.52, 65.92. MS (APCI) calcd for $C_{12}H_{12}ClO_2^+$ $[M + H]^+$: 223.05, found : 223.06.



28

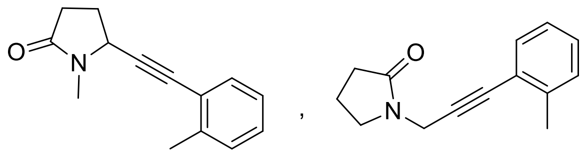
(benzo[*d*][1,3]dioxol-2-ylethynyl)triisopropylsilane Colorless oil. ^1H NMR (400

MHz, $CDCl_3$) δ 6.85 (s, 6.85H), 6.58 (s, 1H), 1.08 (s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.85, 122.01, 109.007, 99.81, 98.26, 91.03, 18.61, 11.10. MS (APCI) calcd for $C_{18}H_{27}O_2Si^+$ $[M + H]^+$: 303.18, found : 303.14.



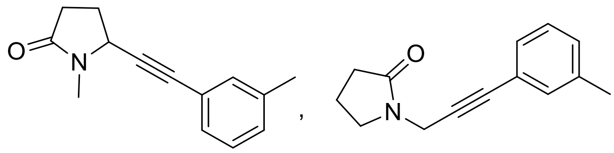
29a, 29b

(isochroman-1-ylethynyl)triisopropylsilane, (isochroman-3-ylethynyl)triisopropylsilane Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 0.55H), 7.20-7.09 (m, 3H), 6.99-6.97 (m, 0.51H), 5.03-4.99 (m, 0.25H), 4.82 (s, 0.30H), 4.78 (s, 0.41H), 4.72-4.69 (m, 0.23H), 4.28-4.22 (m, 0.66H), 4.10-4.06 (m, 0.12H), 4.00-3.94 (m, 0.86H), 3.89-3.85 (m, 0.11H), 3.15-2.82 (m, 2H), 1.17-1.01 (m, 21H). The ratio of **29a** and **29b** was 3.1 : 1, which was judged by (δ 4.82 + δ 4.78) : δ 4.72. ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.31, 132.76, 128.97, 127.18, 126.32, 126.15, 106.42, 87.14, 67.53, 62.67, 28.15, 18.74, 11.31. MS (APCI) calcd for $C_{20}H_{31}OSi^+$ $[M + H]^+$: 315.21, found : 315.19.



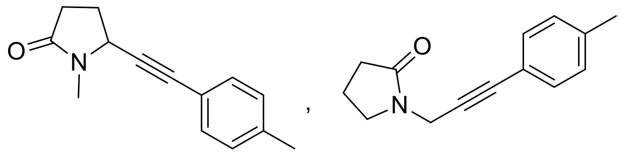
30a, 30b

1-methyl-5-(*o*-tolylethynyl)pyrrolidin-2-one, 1-(3-(*o*-tolyl)prop-2-yn-1-yl)pyrrolidin-2-one Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.38 (m, 1H), 7.24-7.20 (m, 2H), 7.16-7.12 (m, 1H), 4.54-4.51 (m, 0.82H), 4.37 (s, 0.32H), 3.58 (t, J = 7.2 Hz, 0.31H), 2.96 (s, 2.51H), 2.59-2.53 (m, 0.85), 2.47-2.39 (m, 5H), 2.24-2.18 (m, 0.88H), 2.08 (t, J = 7.6 Hz, 0.34H). The ratio of **30a** and **30b** was 5.1 : 1, which was judged by δ 4.54 : 1/2 δ 4.37. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.45, 140.31, 132.14, 129.66, 128.83, 125.76, 122.07, 90.51, 84.33, 52.12, 29.98, 28.20, 20.82. MS (APCI) calcd for $C_{14}H_{16}NO^+$ $[M + H]^+$: 214.12, found: 214.12.



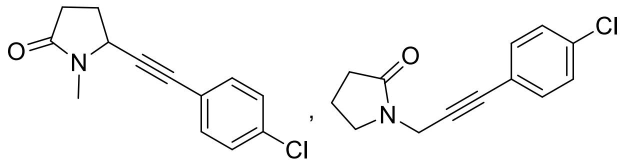
31a, 31b

1-methyl-5-(*m*-tolylethynyl)pyrrolidin-2-one, 1-(3-(*m*-tolyl)prop-2-yn-1-yl)pyrrolidin-2-one Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.24 (m, 1H), 7.22-7.19 (m, 2H), 7.16-7.14 (m, 1H), 4.49-4.46 (m, 0.93H), 4.32 (s, 0.25H), 3.56 (t, J = 6.8 Hz, 0.28H), 2.94 (s, 2.82H), 2.58-2.52 (m, 1H), 2.47-2.38 (m, 2.28H), 2.33 (s, 2.81H), 2.32 (s, 0.46H), 2.23-2.16 (m, 1H), 2.10-2.06 (m, 0.32H). The ratio of **31a** and **31b** was 7.4 : 1, which was judged by δ 4.49 : 1/2 δ 4.32. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.46, 138.26, 132.44, 129.71, 128.91, 128.42, 122.08, 86.18, 85.63, 52.00, 29.97, 28.18, 26,39, 21.32. MS (APCI) calcd for $C_{14}H_{16}NO^+$ $[M + H]^+$: 214.12, found: 214.12.



32a, 32b

1-methyl-5-(*p*-tolylethynyl)pyrrolidin-2-one, 1-(3-(*p*-tolyl)prop-2-yn-1-yl)pyrrolidin-2-one Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.6 Hz), 4.48-4.45 (m, 0.90H), 4.32 (s, 0.18H), 3.56 (t, J = 7.2 Hz, 0.19H), 2.94 (s, 2.70H), 2.58-2.52 (m, 1H), 2.46-2.37 (m, 2H), 2.35 (s, 3H), 2.22-2.15 (m, 1H), 2.09-2.05 (m, 0.22H). The ratio of **32a** and **32b** was 10 : 1, which was judged by δ 4.48 : 1/2 δ 4.32. ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.46, 139.01, 131.79, 131.74, 129.27, 129.19, 119.20, 85.86, 85.59, 52.02, 29.98, 28.17, 26.41, 21.62. MS (APCI) calcd for $C_{14}H_{16}NO^+$ $[M + H]^+$: 214.12, found: 214.12.

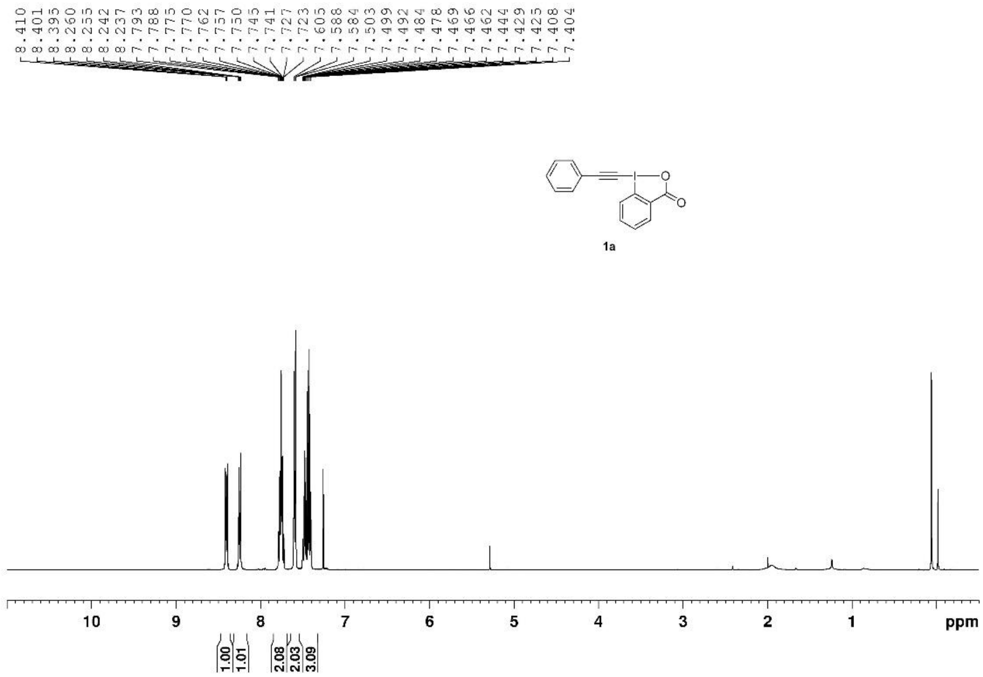


33a, 33b

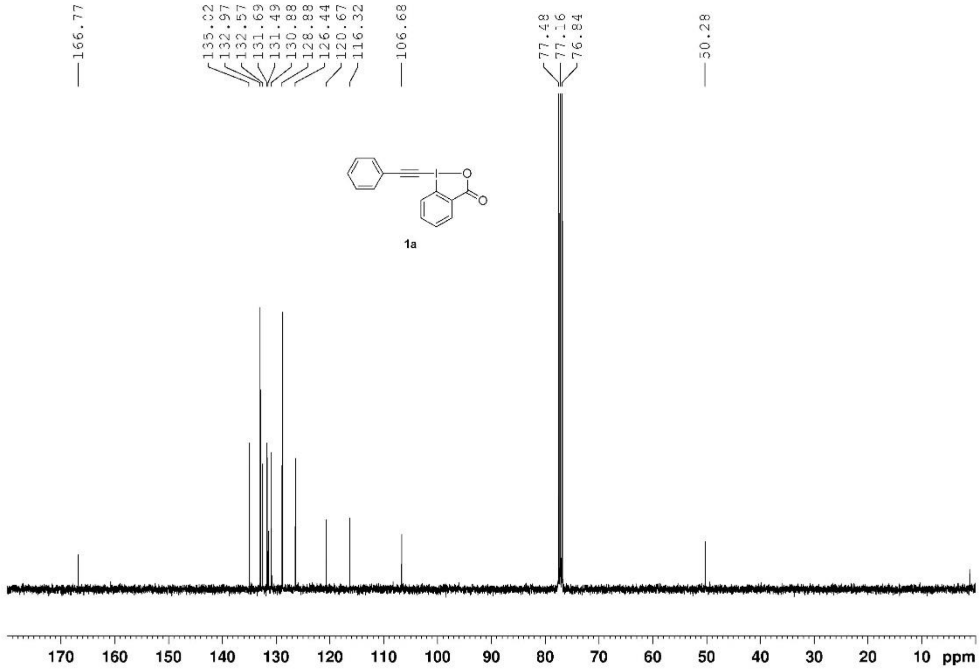
5-((4-chlorophenyl)ethynyl)-1-methylpyrrolidin-2-one, 1-(3-(4-chlorophenyl)prop-2-yn-1-yl)pyrrolidin-2-one Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.33 (m, 2H), 7.31-7.26 (m, 2H), 4.48-4.45 (m, 0.85H), 4.32 (s, 0.33H), 3.55 (t, J = 7.2 Hz, 0.38H), 2.93 (s, 2.56H), 2.61-2.52 (m, 1H), 2.47-2.36 (m, 2.34H), 2.22-2.16 (m, 1H), 2.10-2.07 (m, 0.38H). The ratio of **33a** and **33b** was 5.2 : 1, which was judged by δ 4.48 : 1/2 δ 4.32. ^{13}C NMR (100 MHz, $CDCl_3$) δ 17443, 134.96, 133.09, 128.89, 120.77, 87.59, 84.37, 51.94, 29.89, 28.22, 26.28. MS (APCI) calcd for $C_{13}H_{13}ClNO^+$ $[M + H]^+$: 234.07, found: 234.07.

^{1}H NMR and ^{13}C NMR spectra of the products

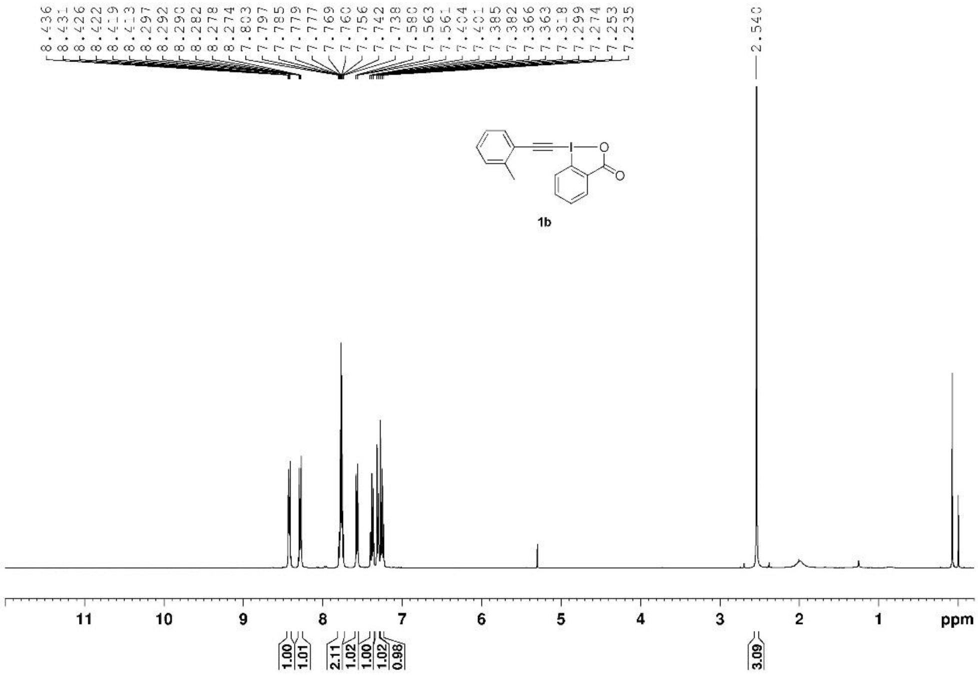
^{1}H NMR of **1a**



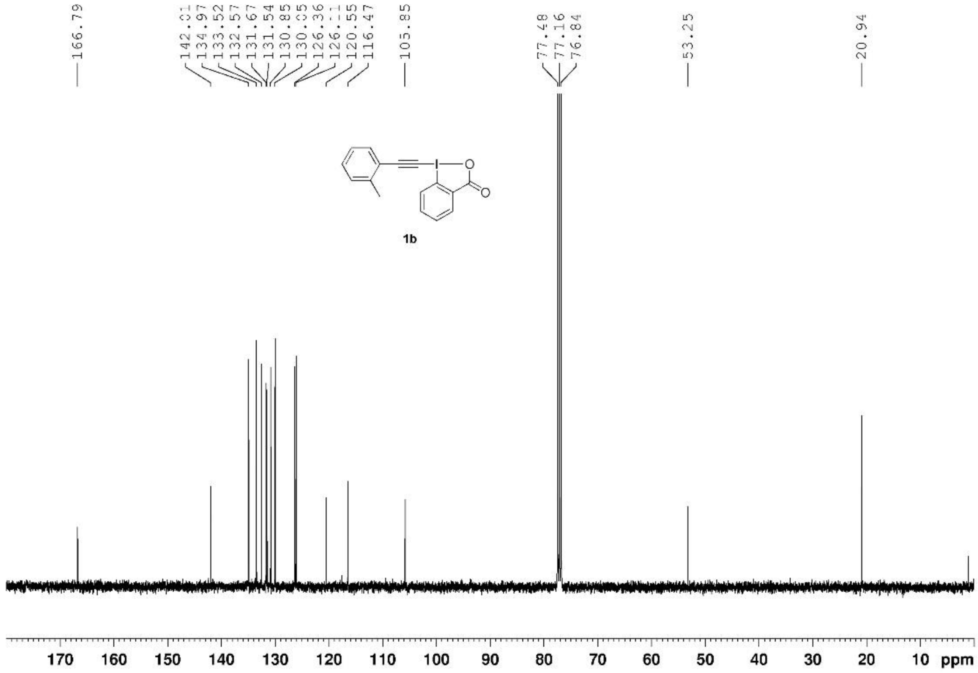
^{13}C NMR of **1a**



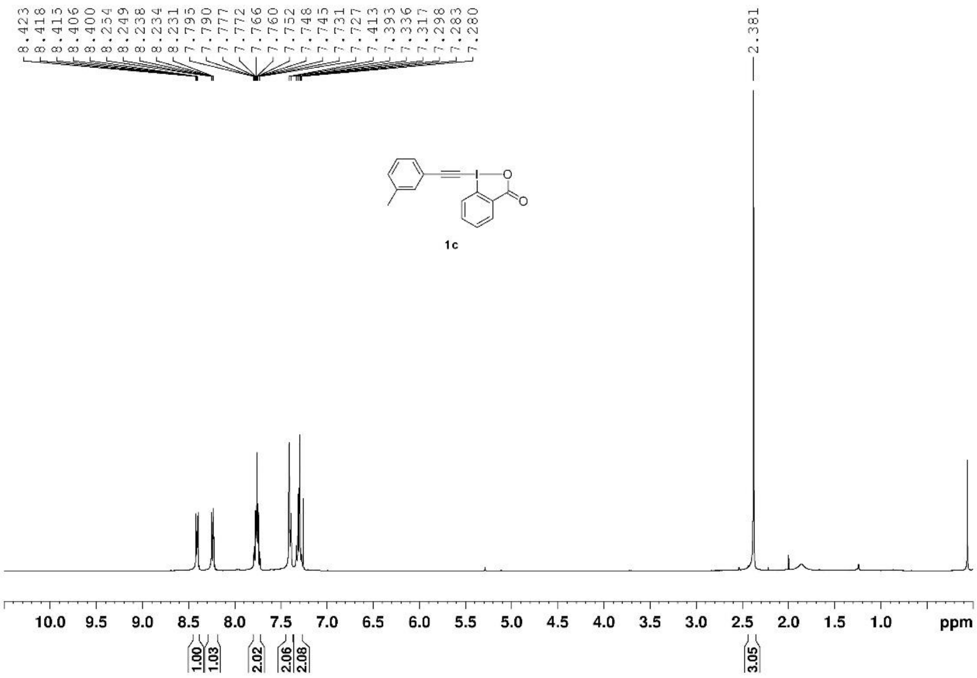
^{1}H NMR of **1b**



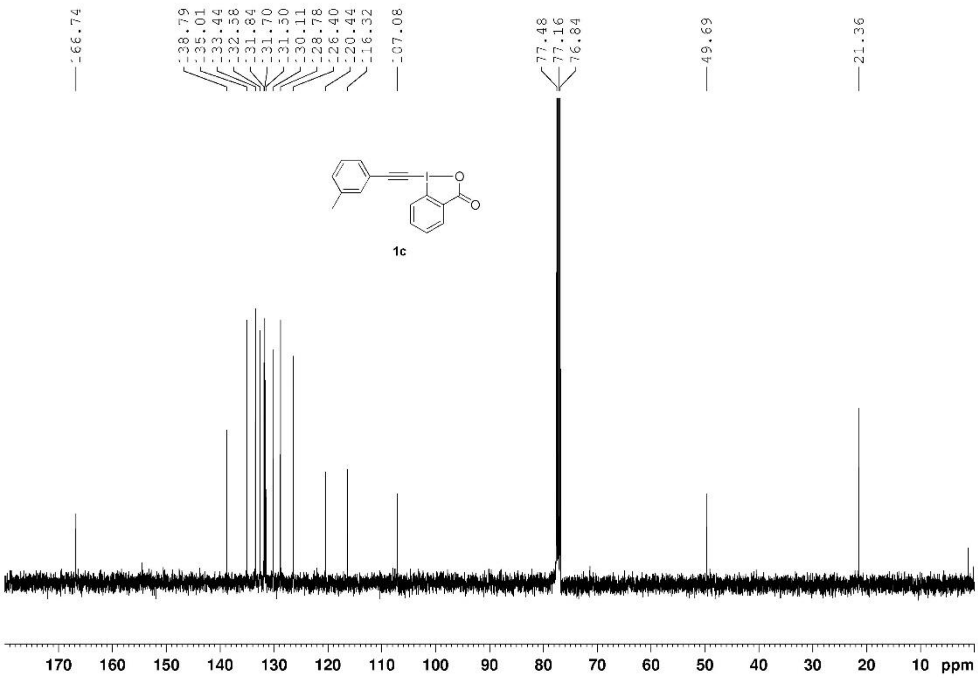
^{13}C NMR of **1b**



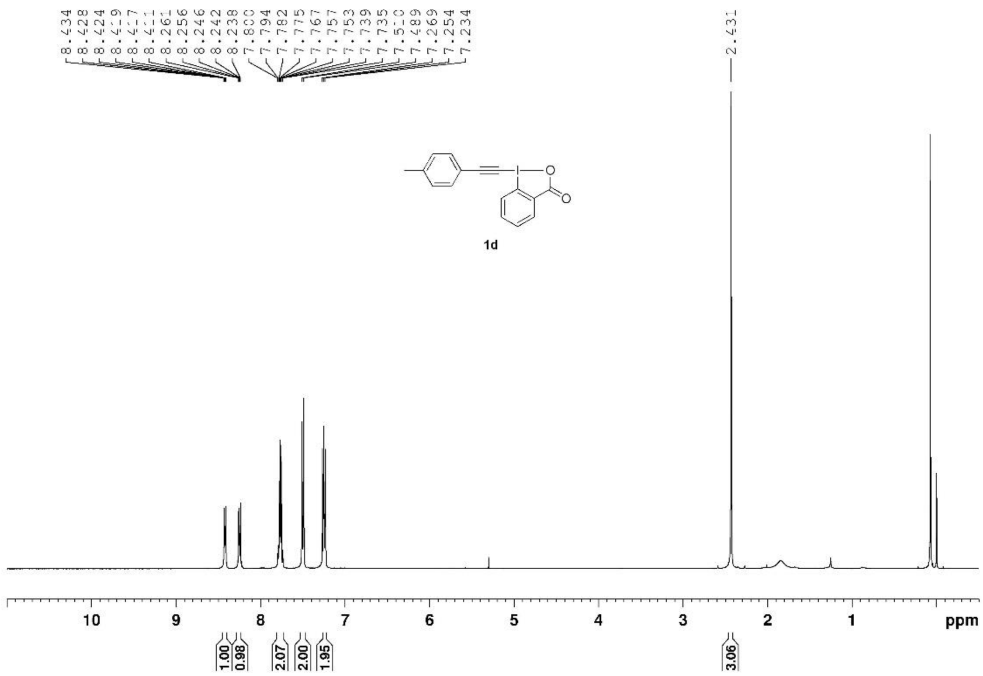
^{1}H NMR of **1c**



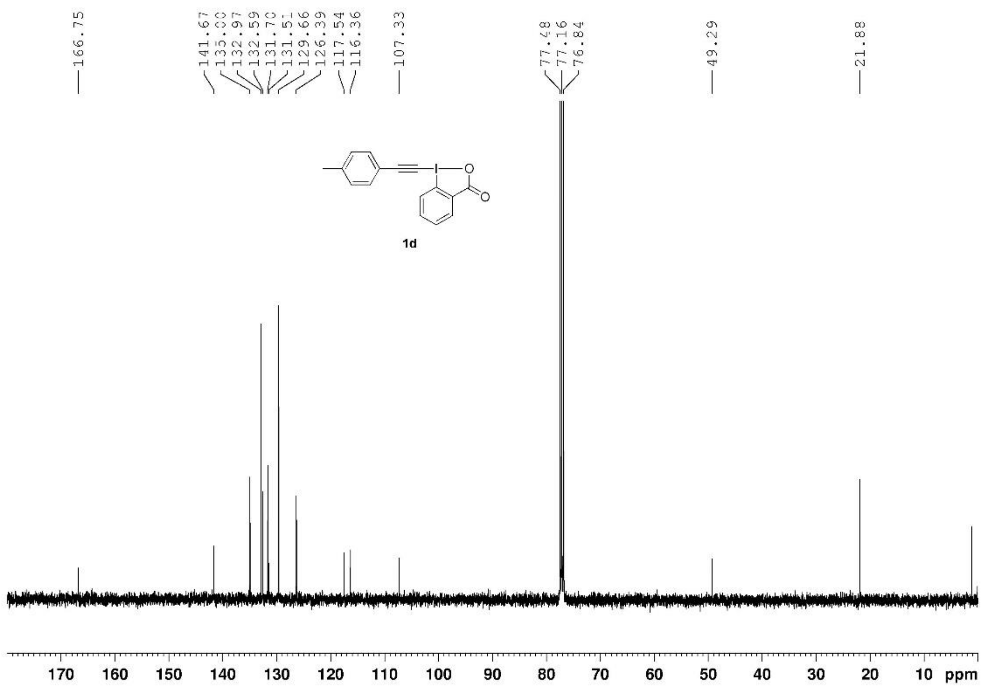
^{13}C NMR of **1c**



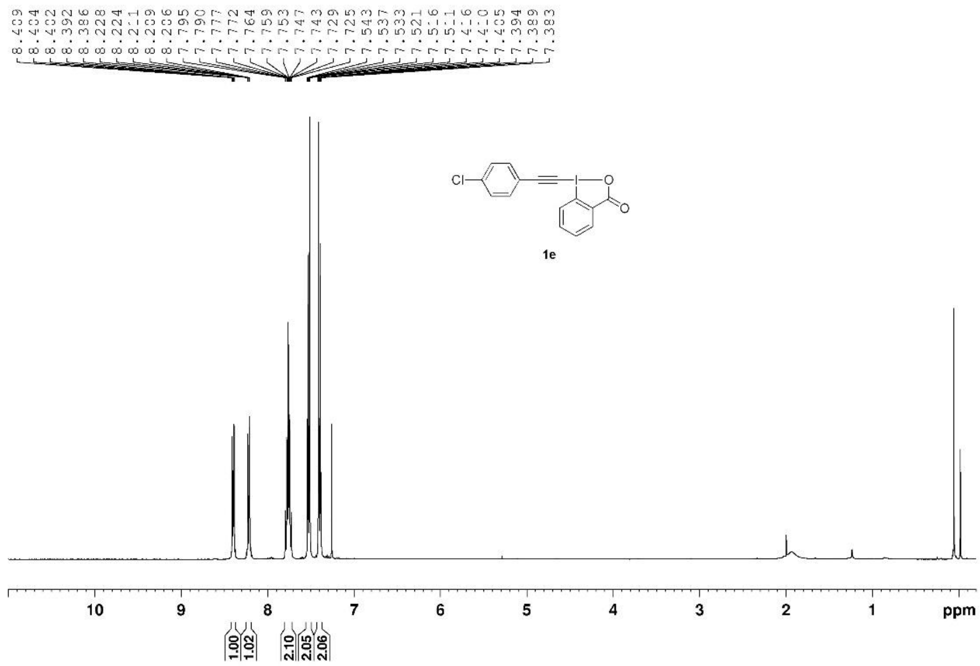
^{1}H NMR of **1d**



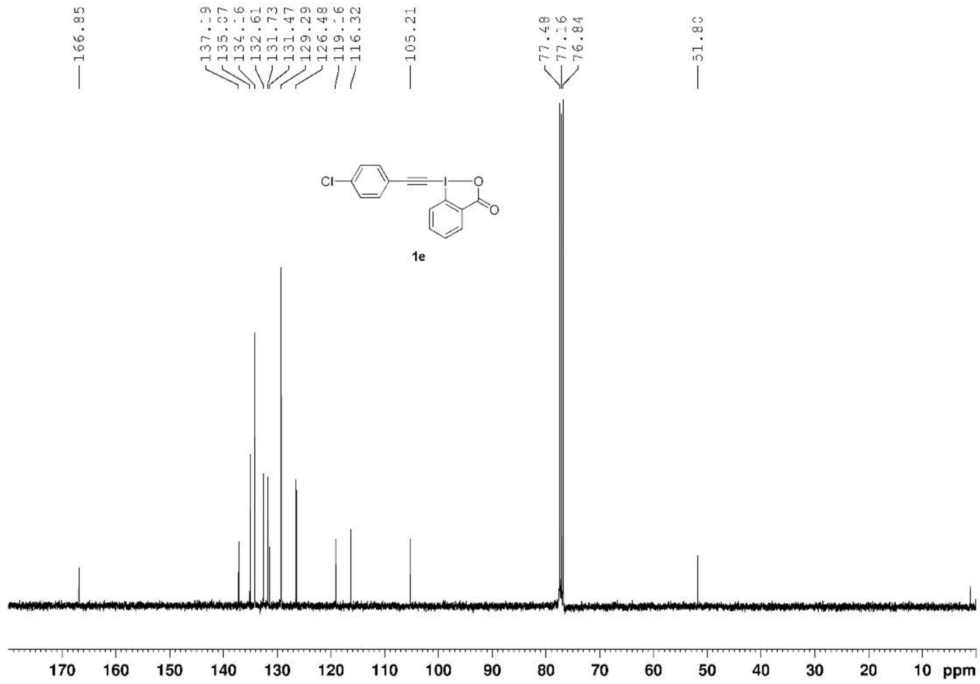
^{13}C NMR of **1d**



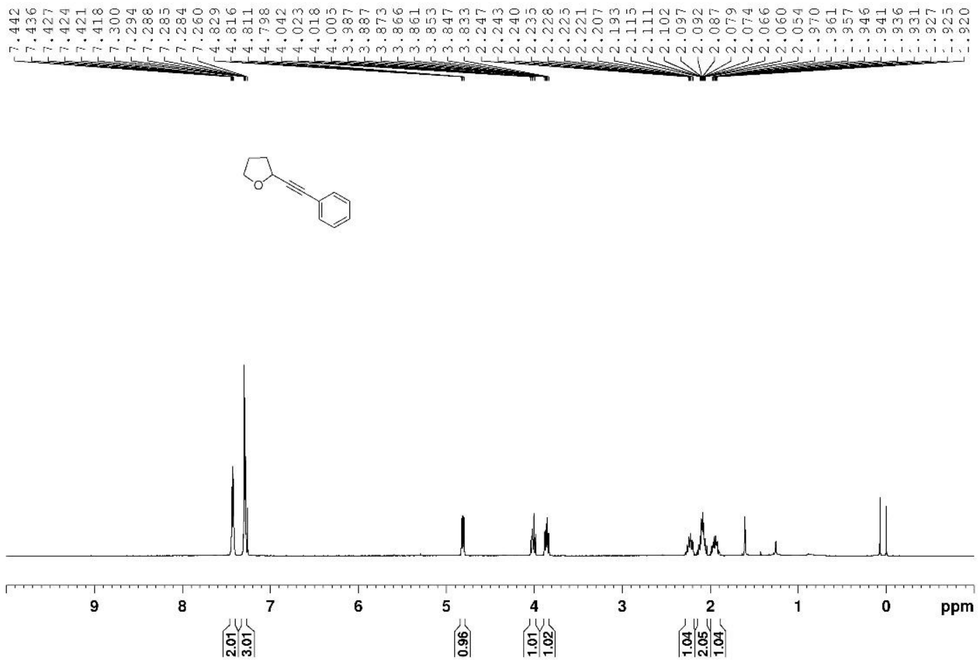
^{1}H NMR of **1e**



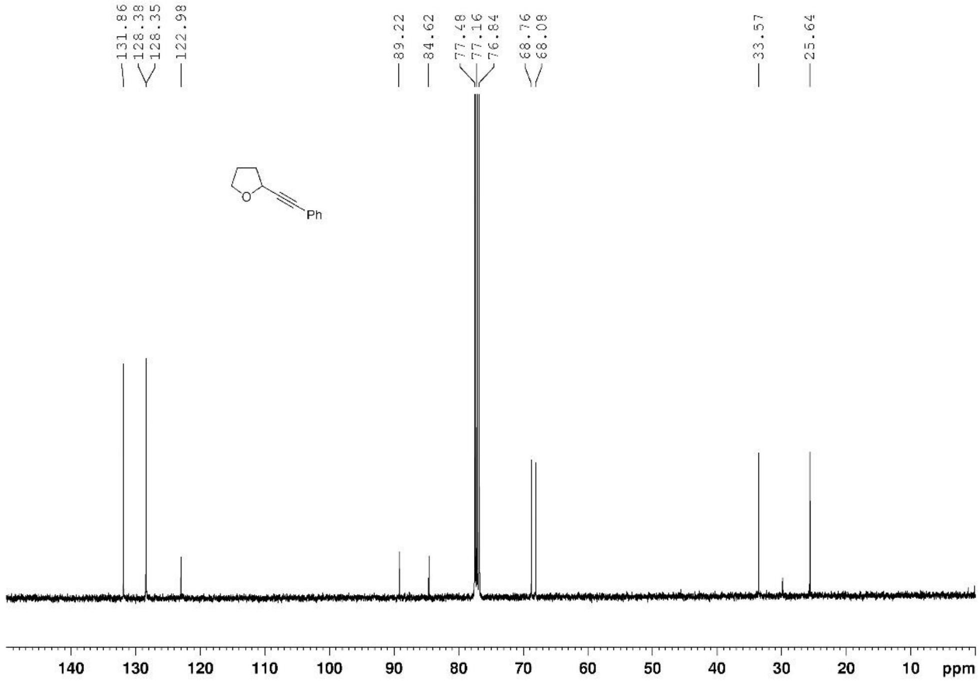
^{13}C NMR of **1e**



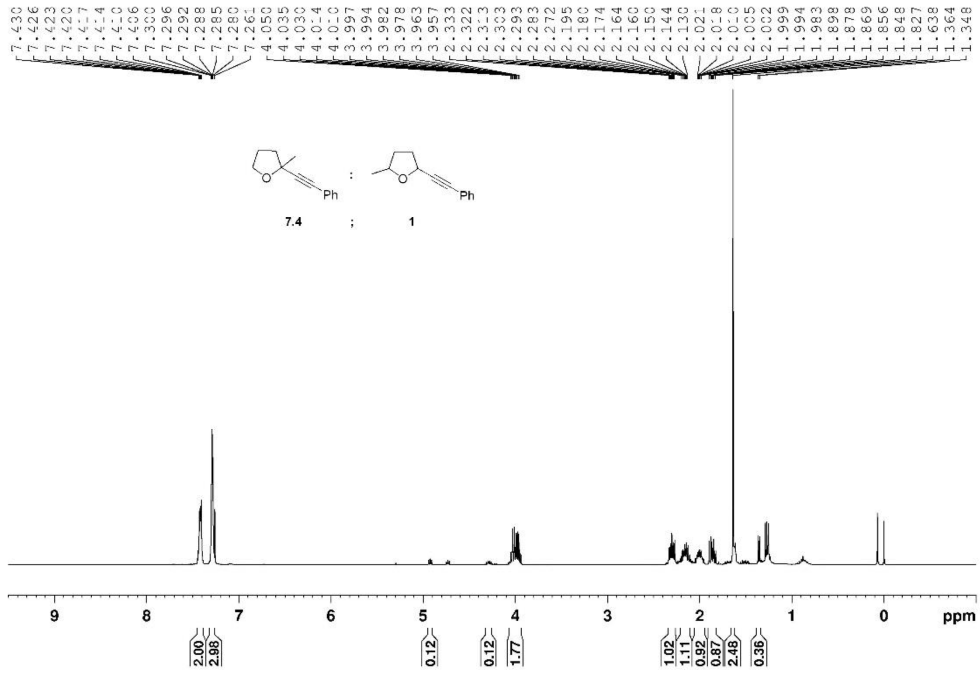
^{1}H NMR of **3**



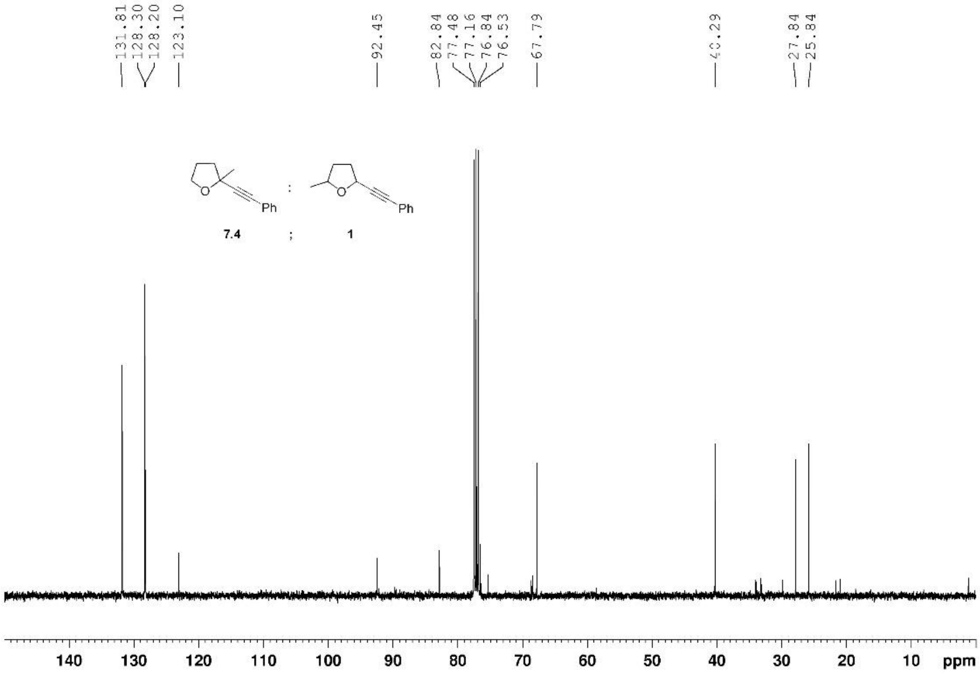
^{13}C NMR of **3**



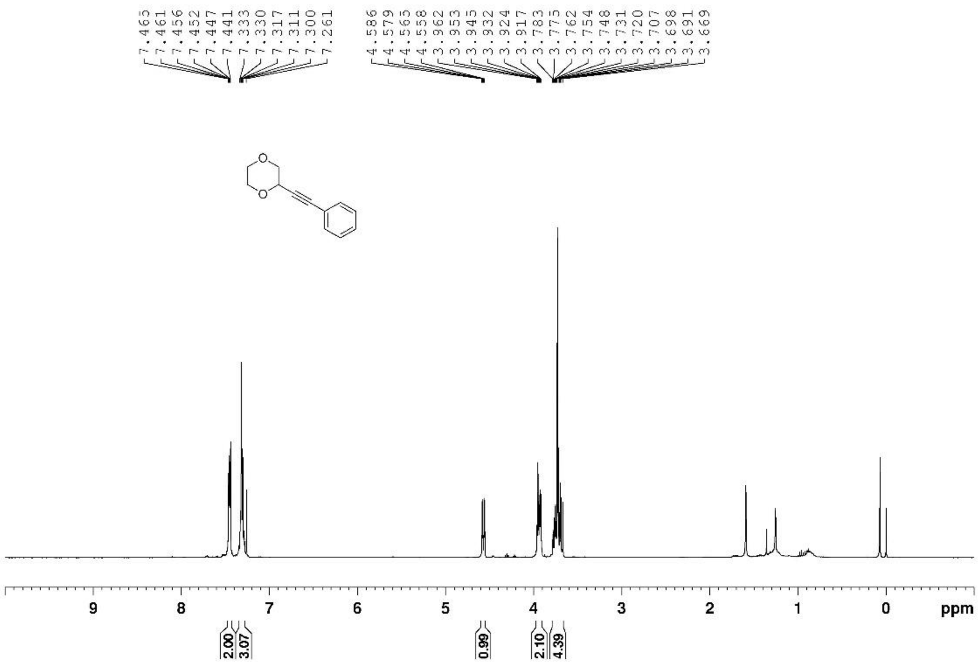
^{1}H NMR of **4a** and **4b**



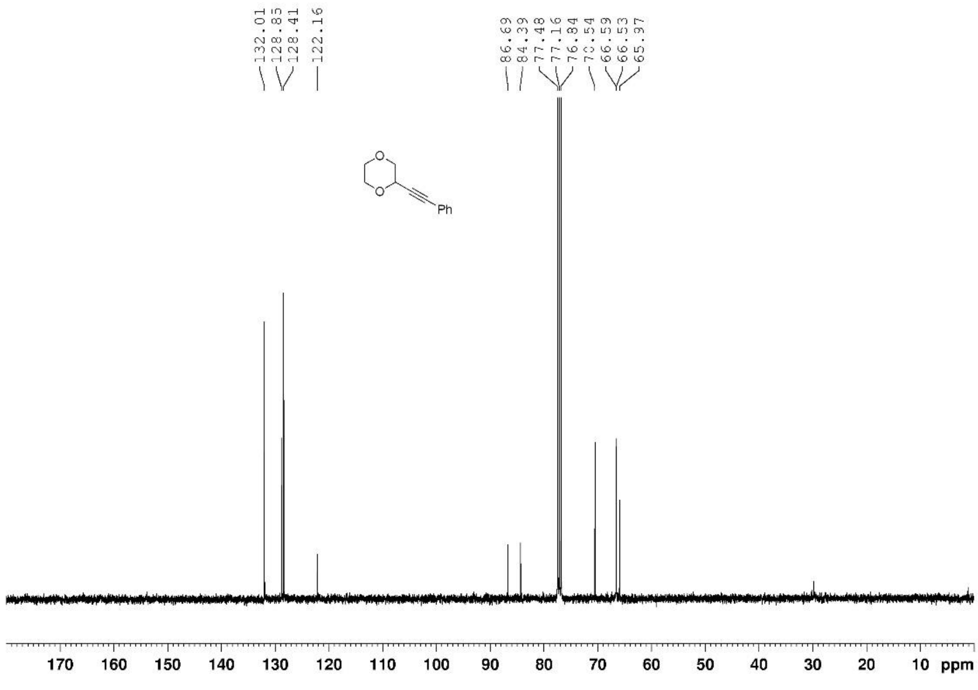
^{13}C NMR of **4a** and **4b**



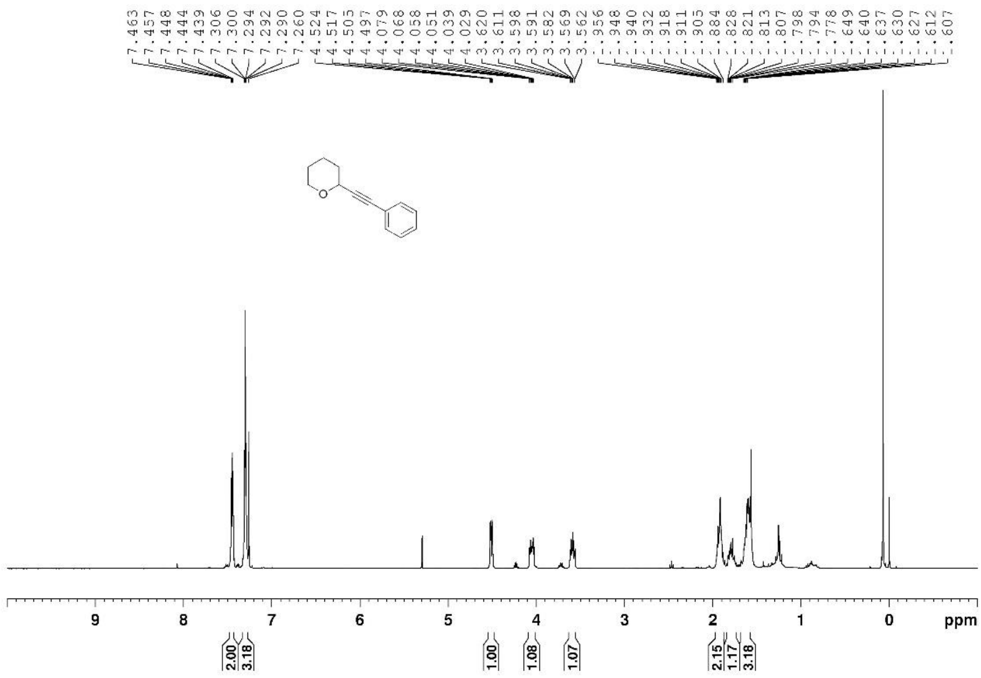
^{1}H NMR of **5**



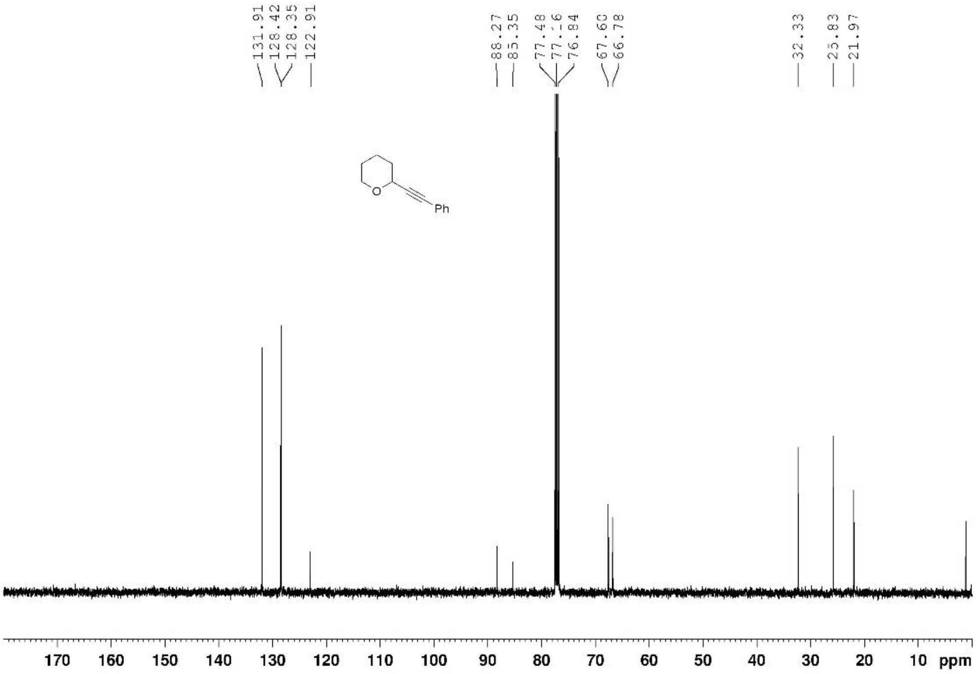
^{13}C NMR of **5**



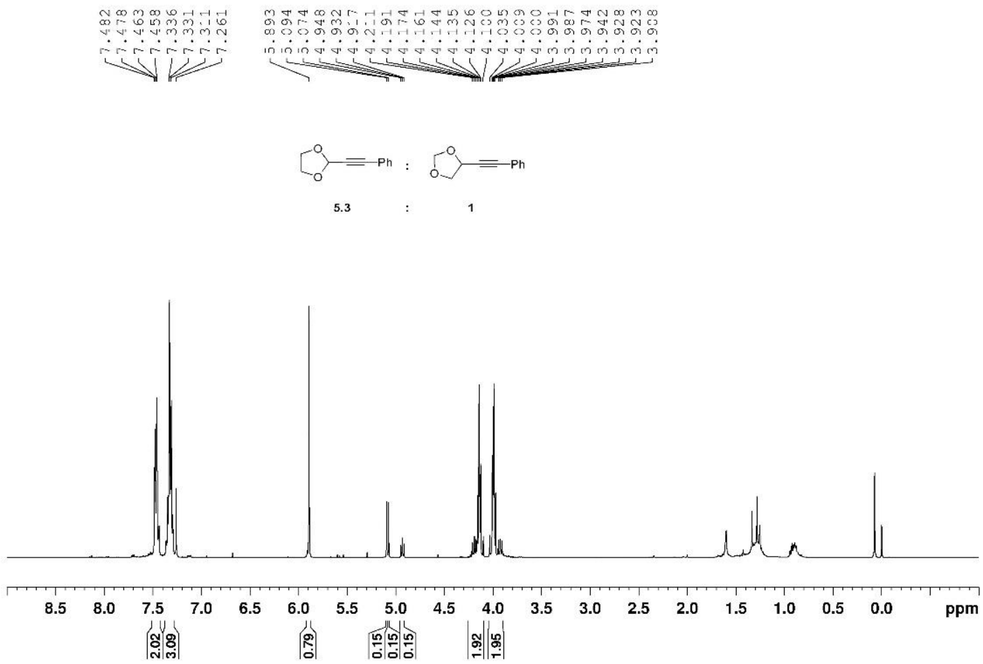
^{1}H NMR of **6**



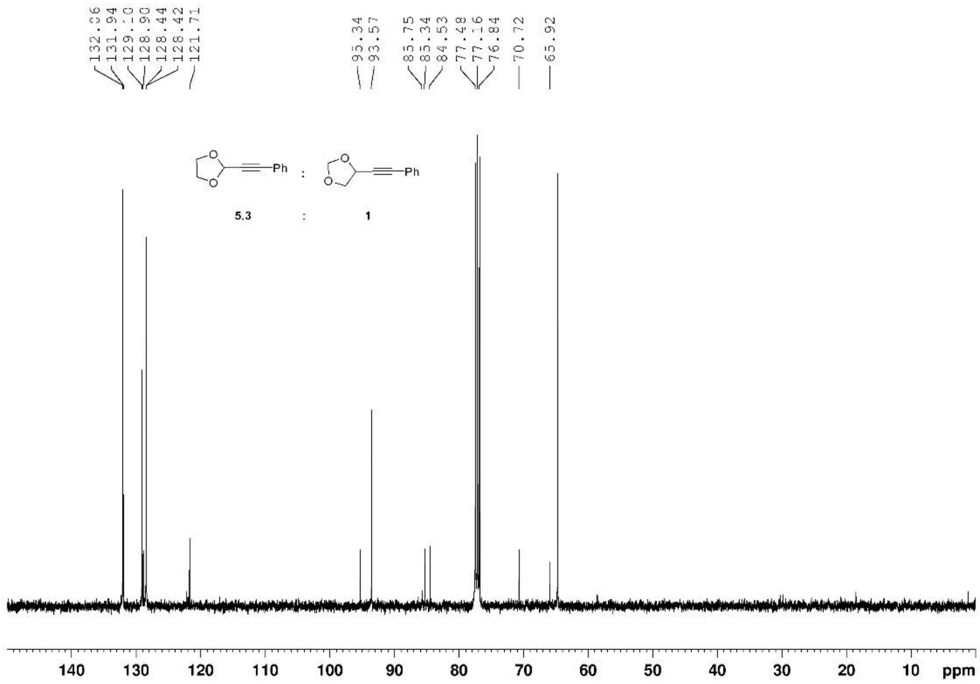
^{13}C NMR of **6**



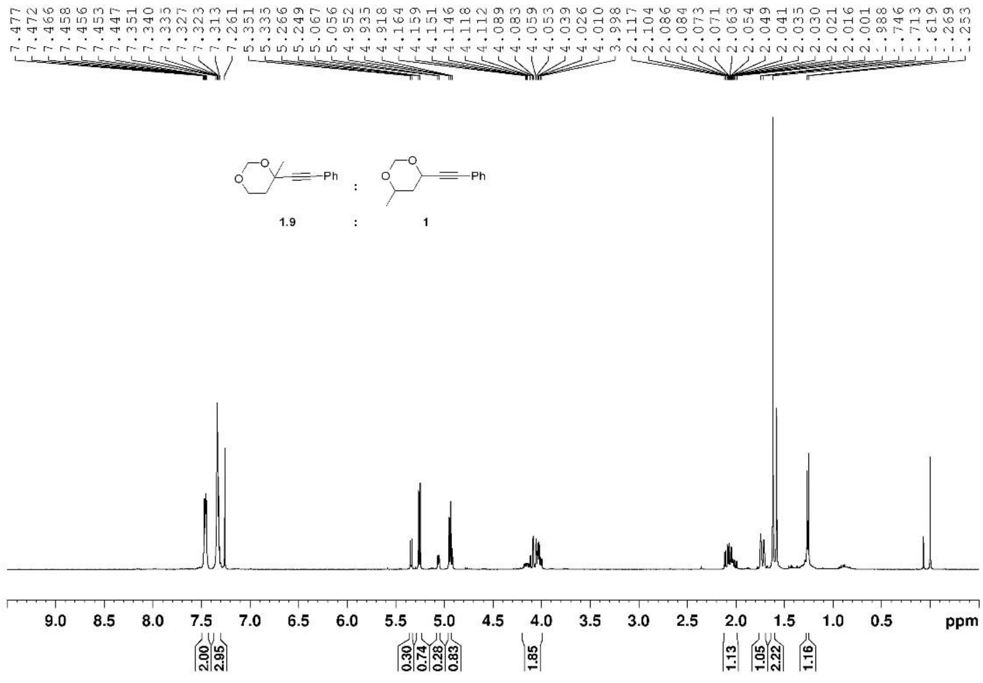
^{1}H NMR of **7a** and **7b**



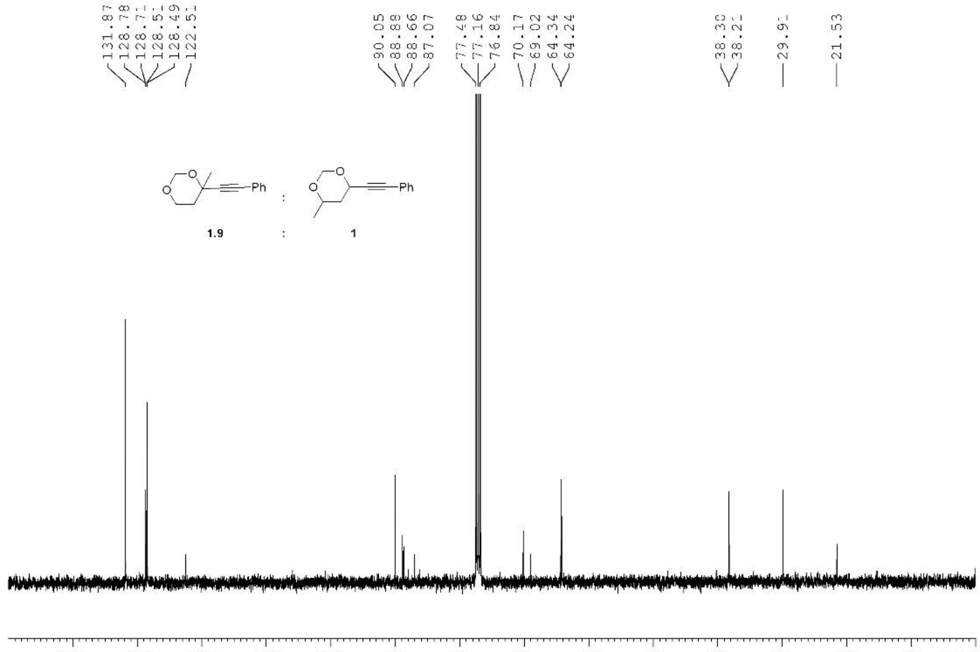
^{13}C NMR of **7a** and **7b**



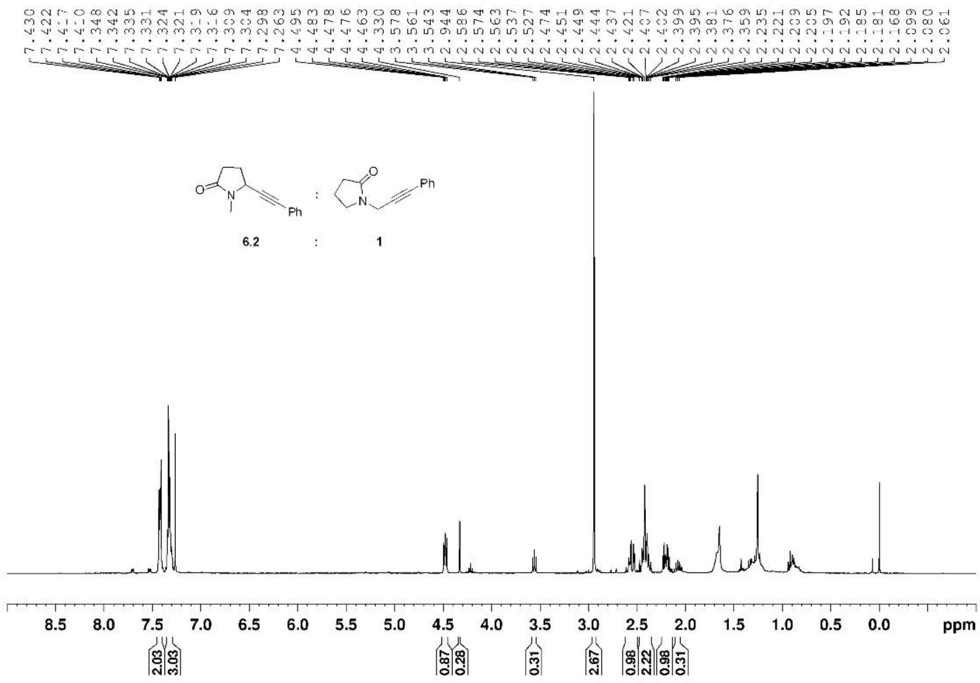
^{1}H NMR of **8a** and **8b**



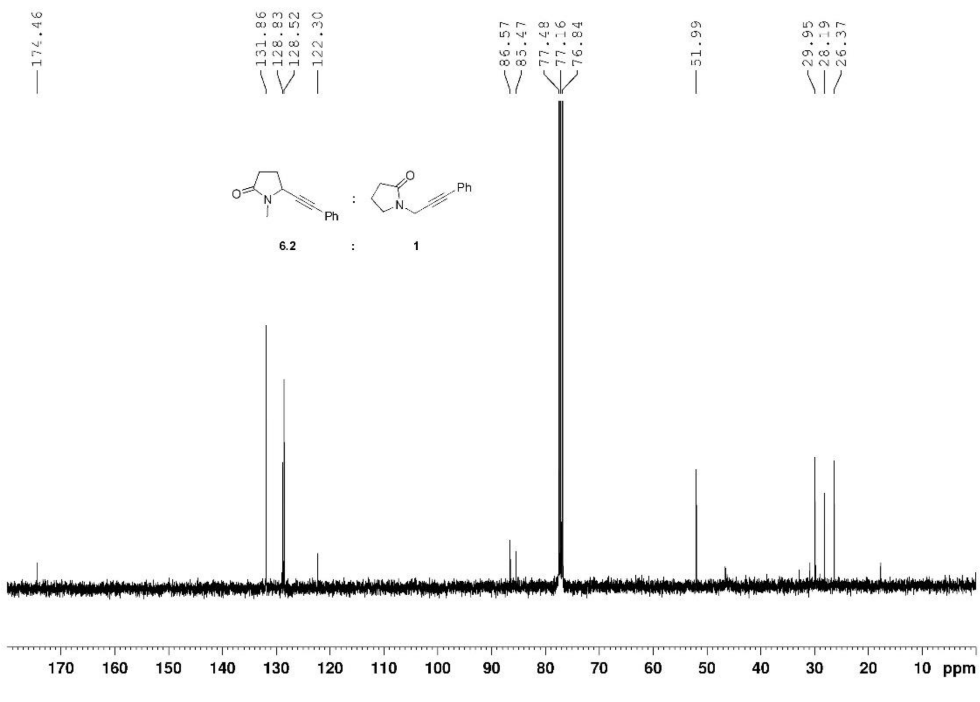
^{13}C NMR of **8a** and **8b**



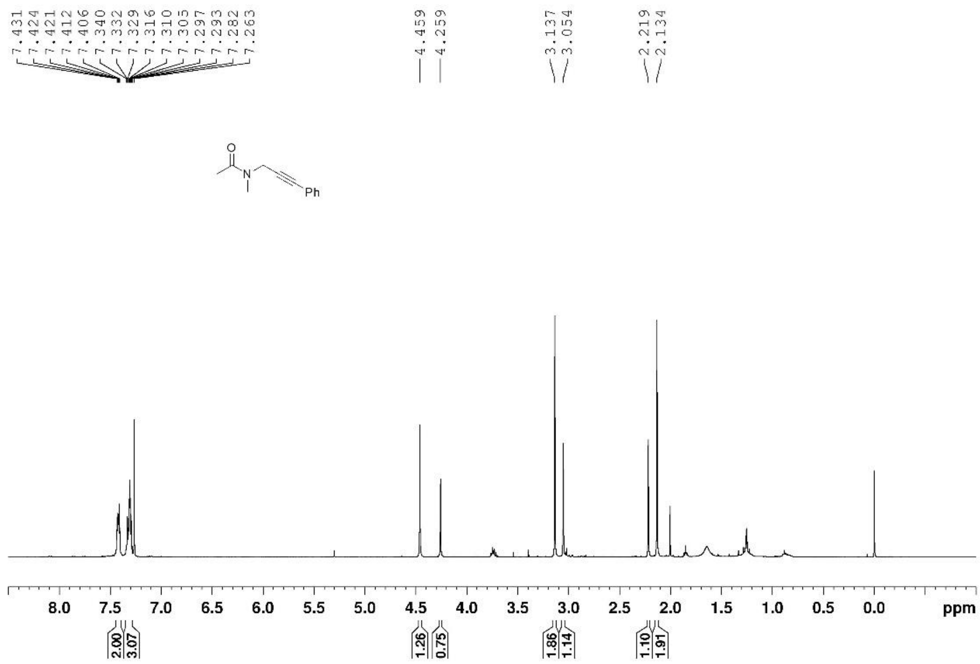
^{1}H NMR of **9**



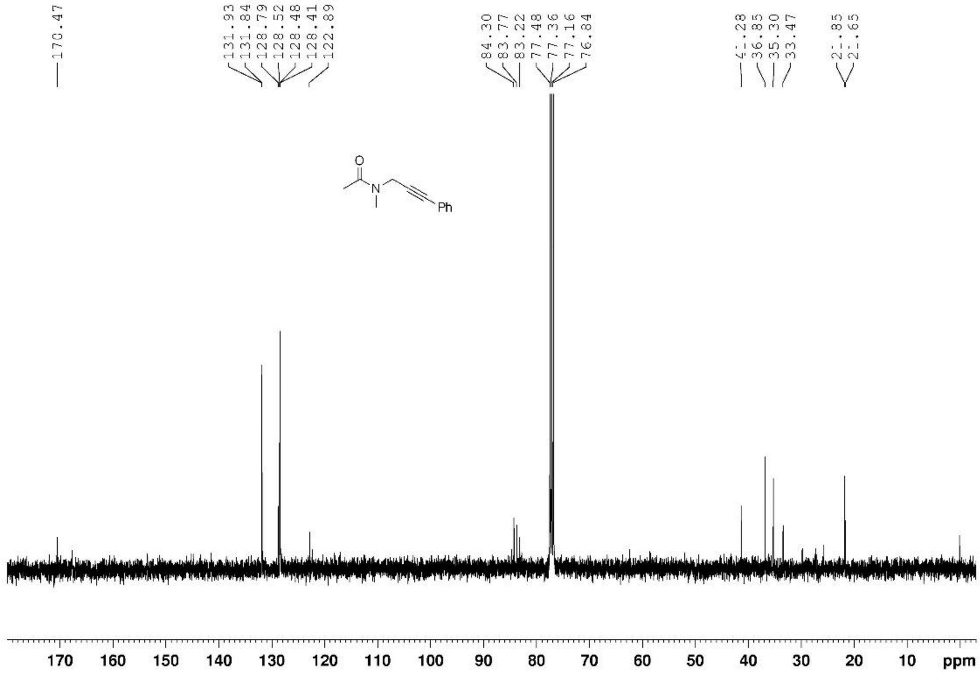
^{13}C NMR of **9**



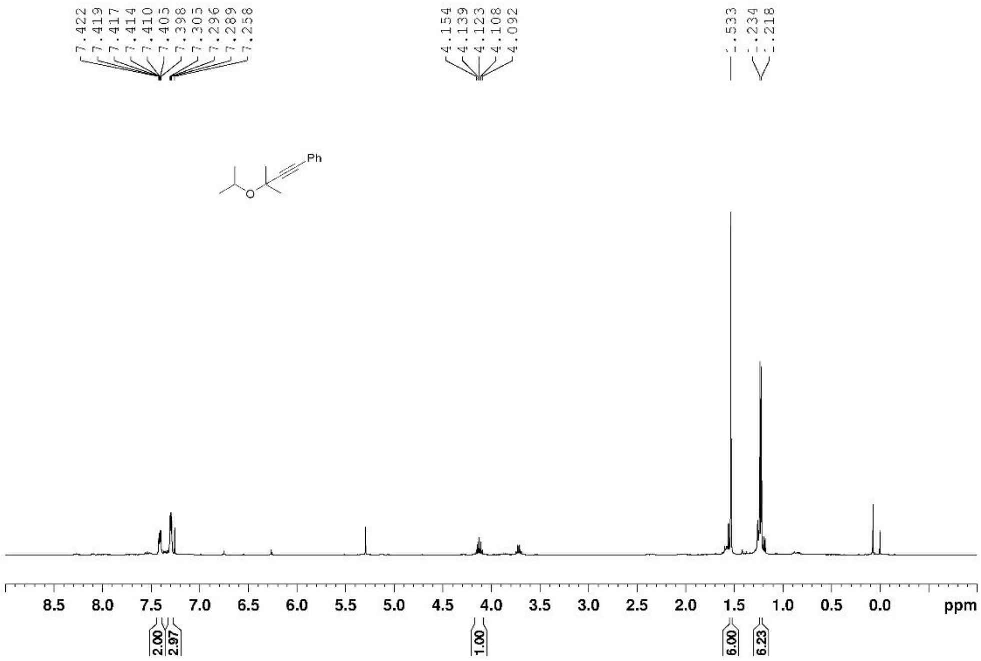
^{1}H NMR of **10**



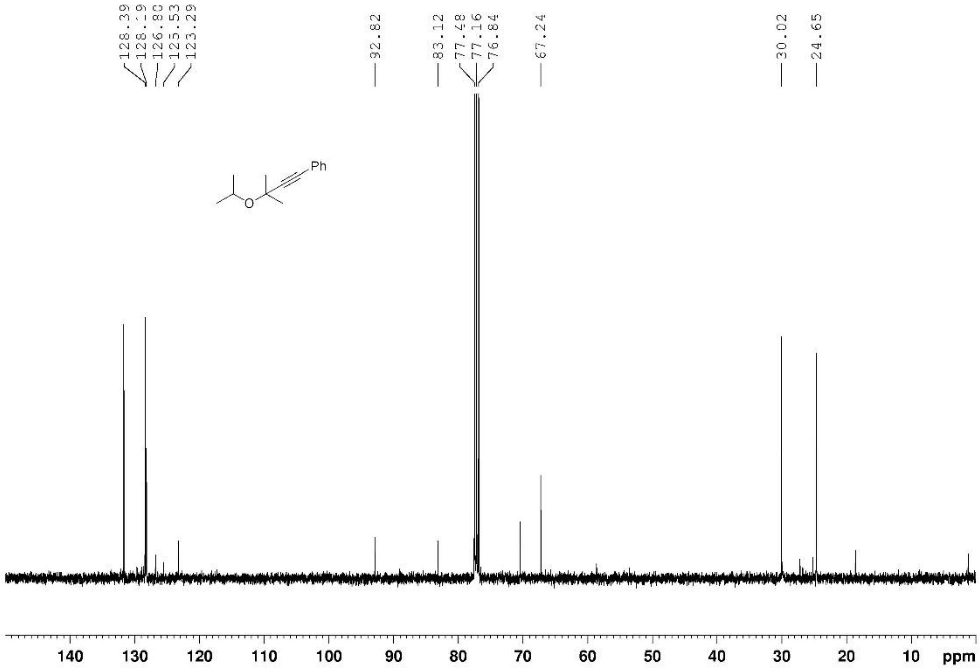
^{13}C NMR of **10**



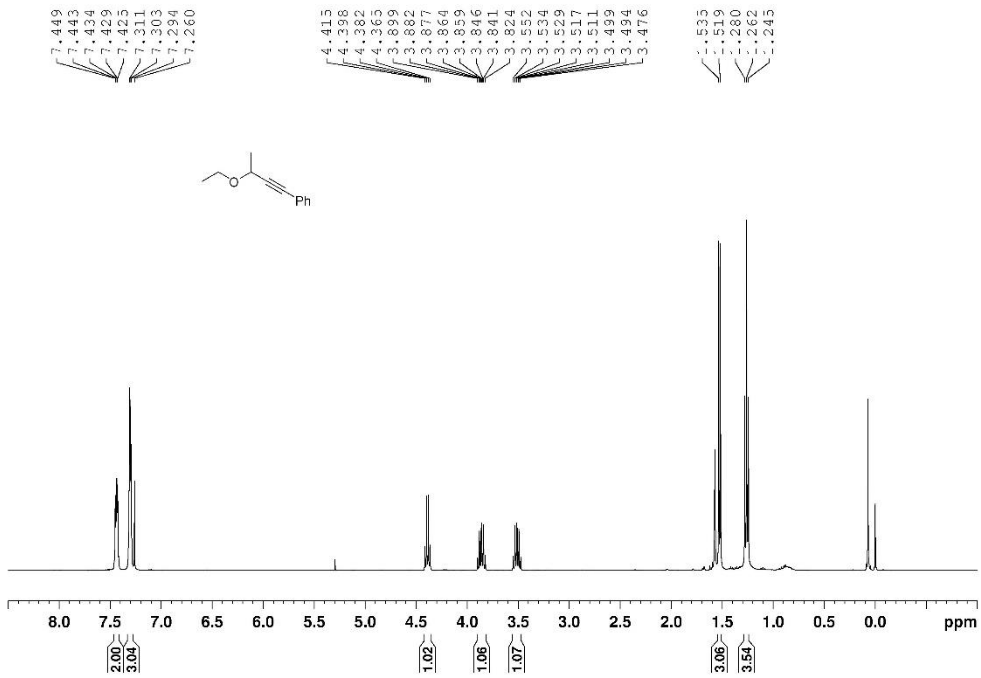
^{1}H NMR of **11**



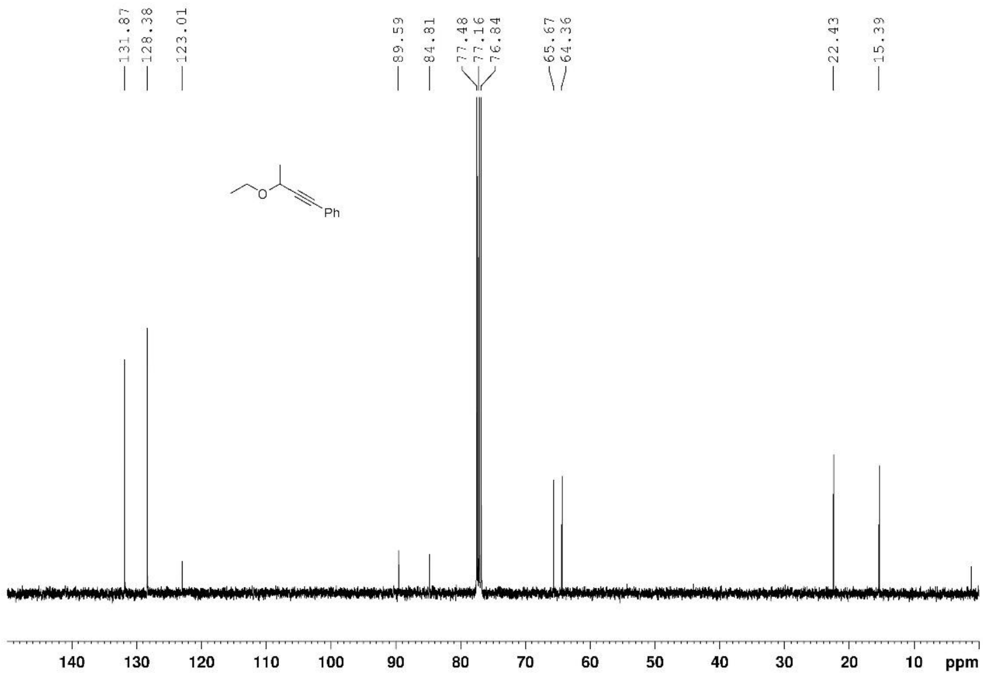
^{13}C NMR of **11**



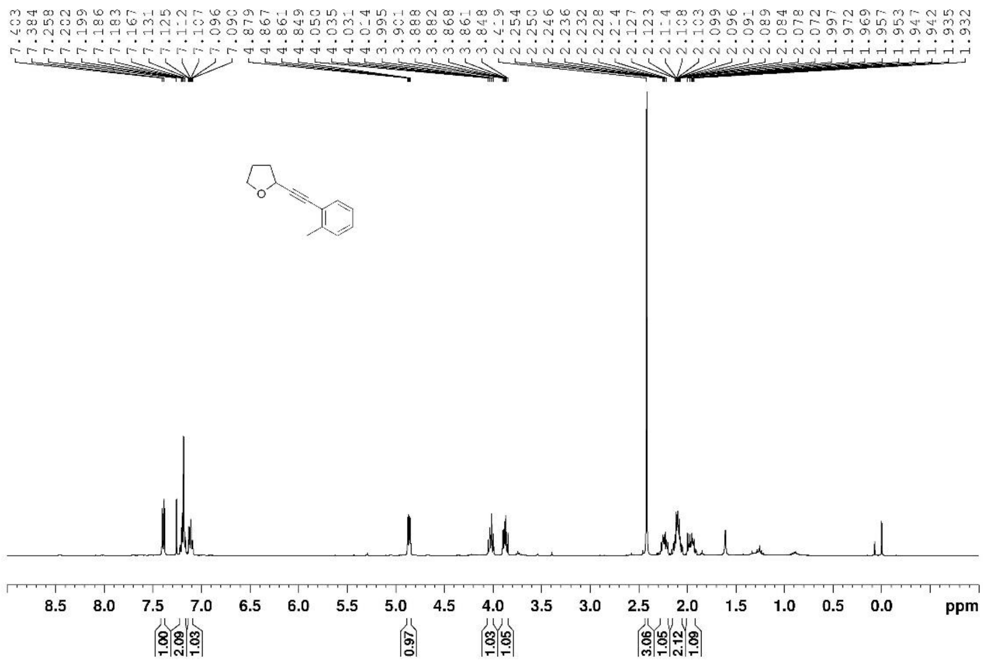
^{1}H NMR of **12**



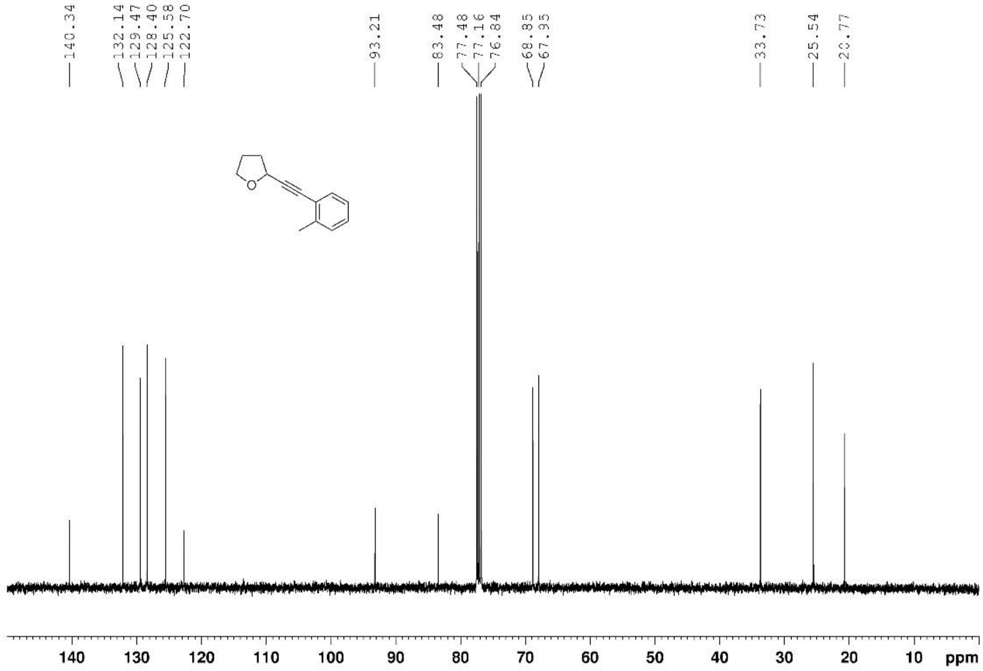
^{13}C NMR of **12**



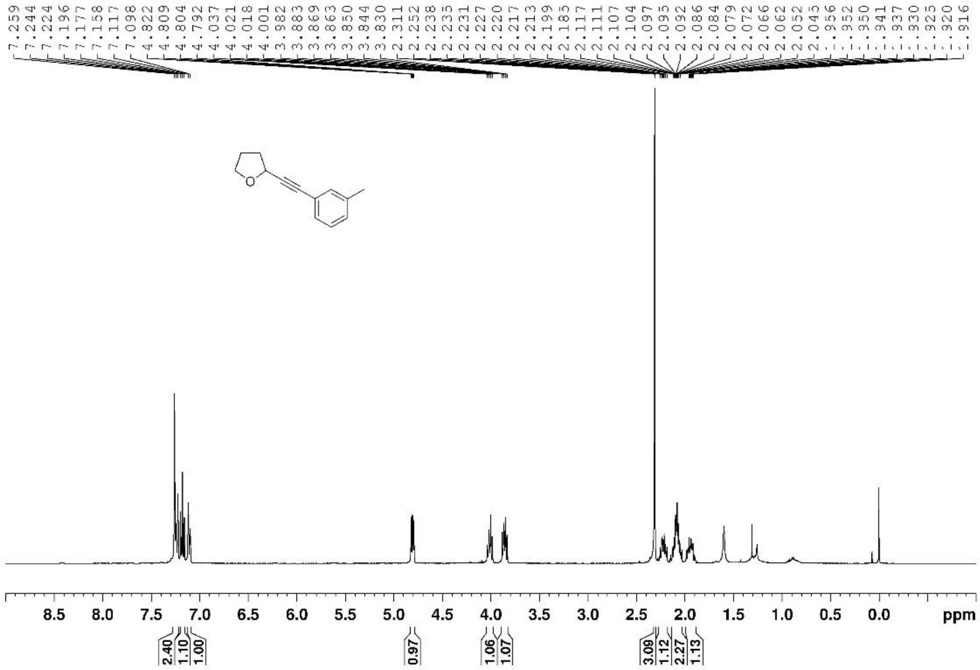
^{1}H NMR of **13**



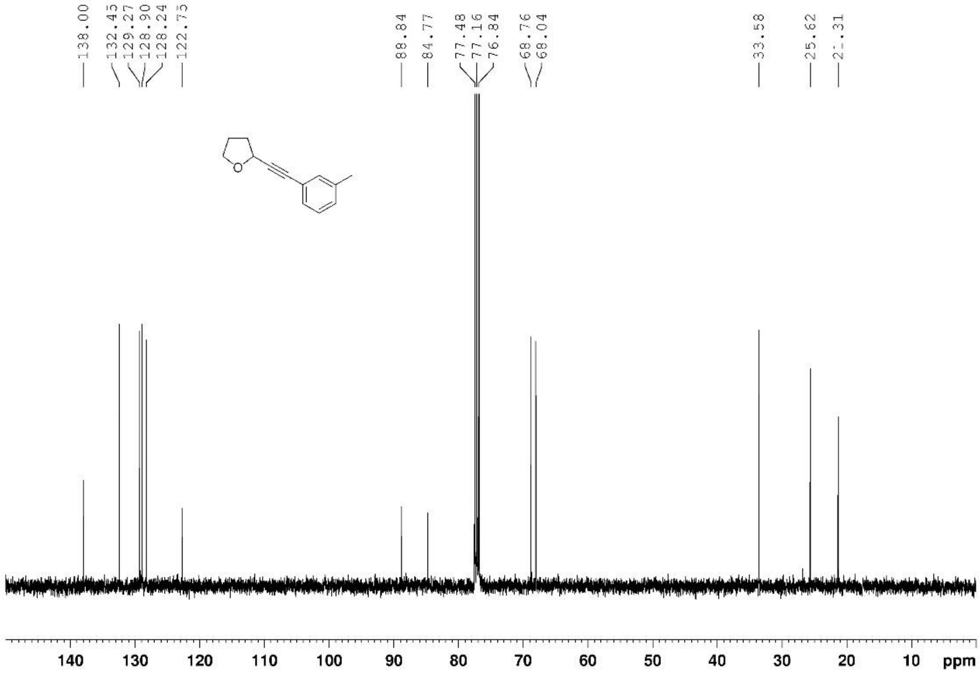
^{13}C NMR of **13**



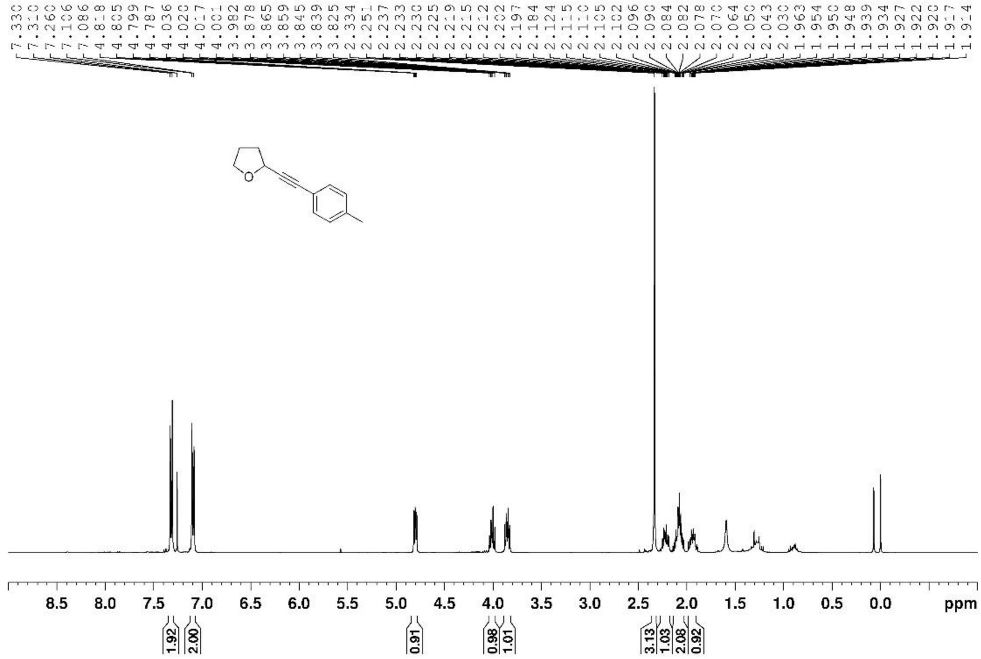
^{1}H NMR of **14**



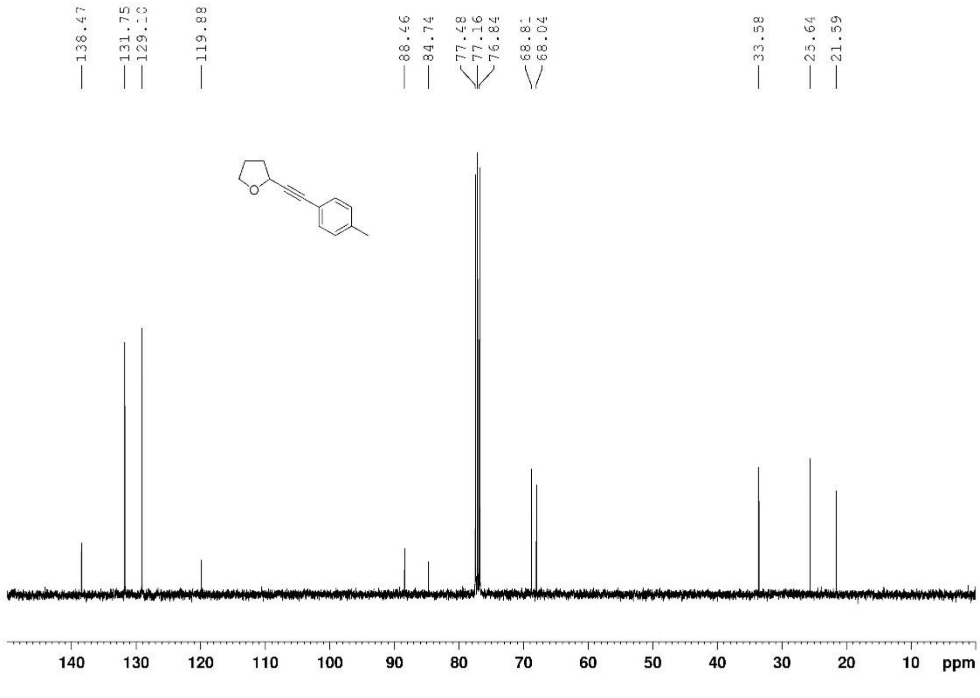
^{13}C NMR of **14**



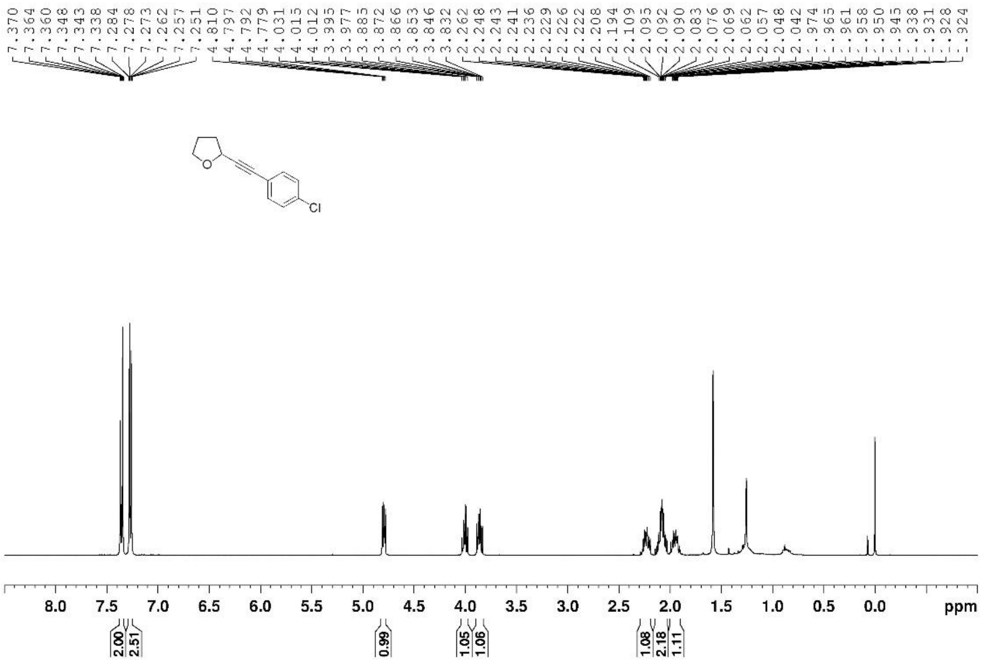
^{1}H NMR of **15**



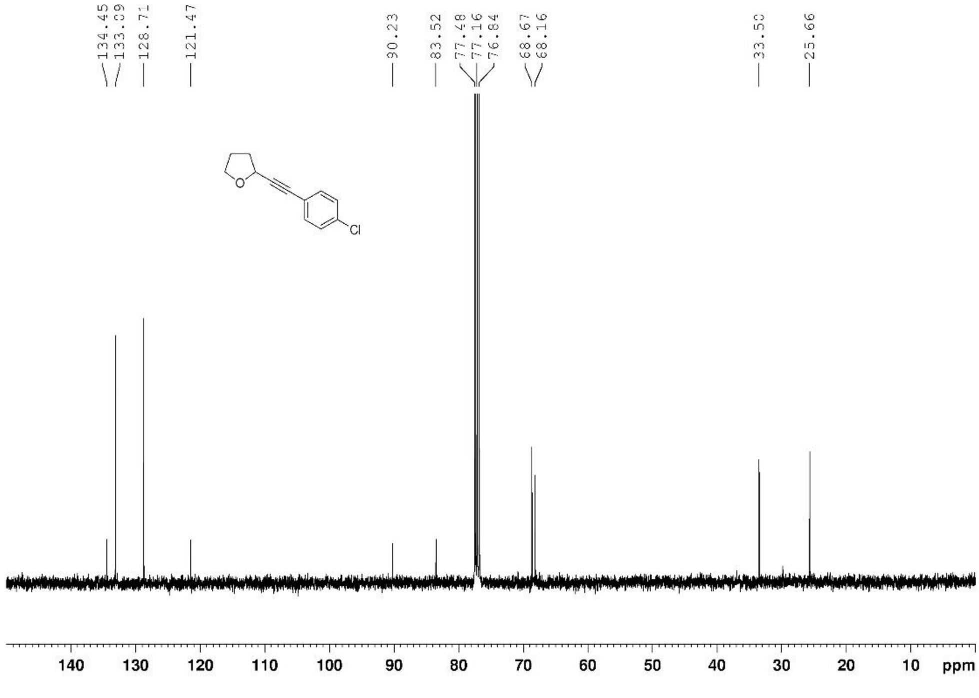
^{13}C NMR of **15**



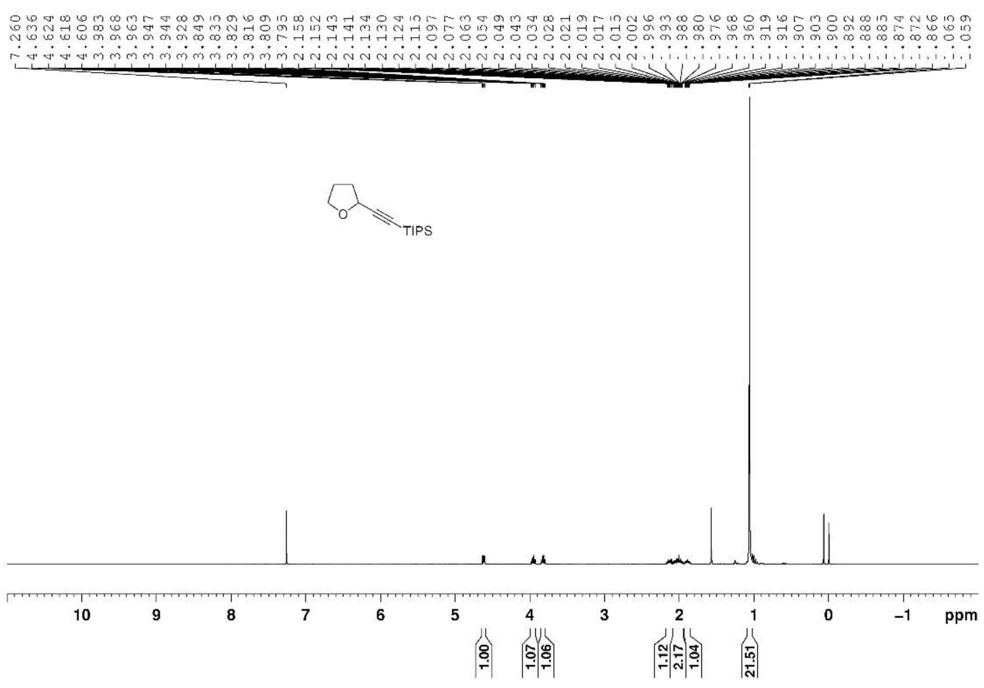
^{1}H NMR of **16**



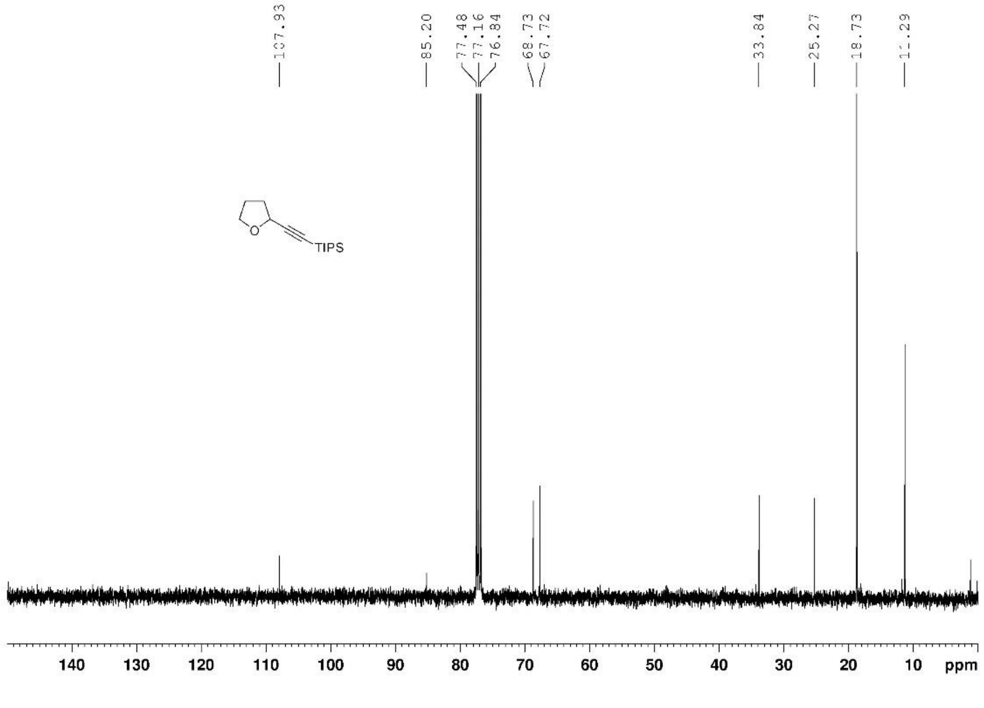
^{13}C NMR of **16**



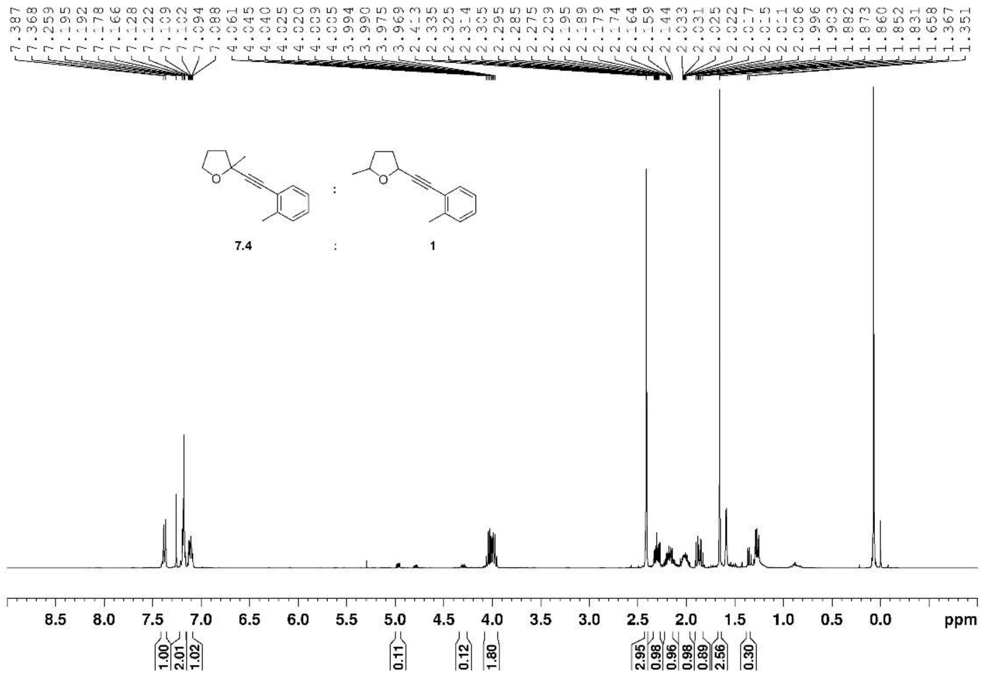
^{1}H NMR of **17**



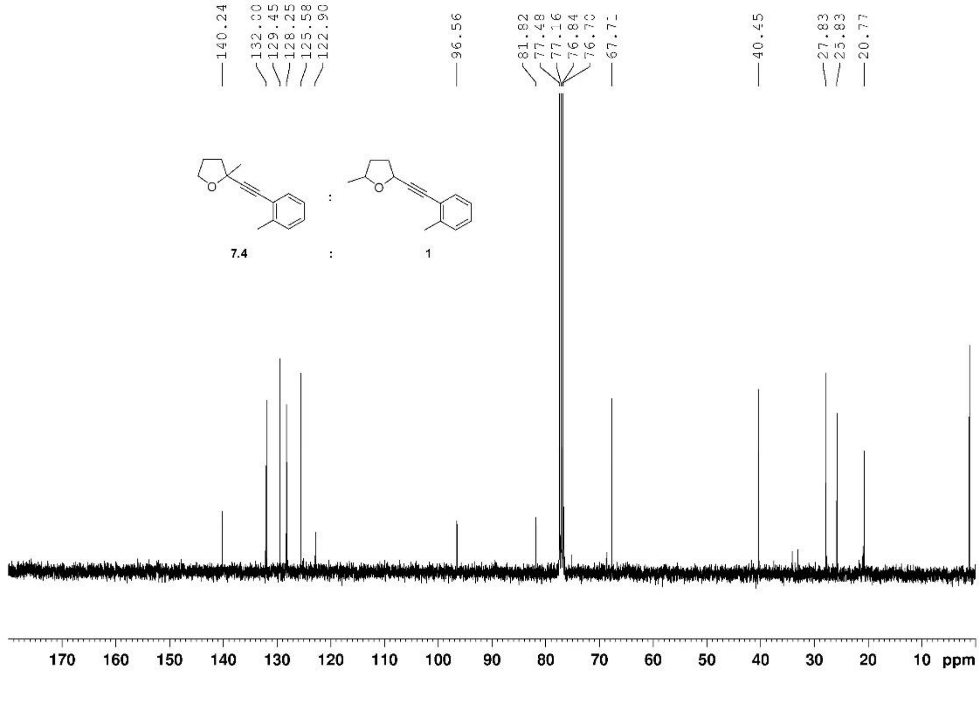
^{13}C NMR of **17**



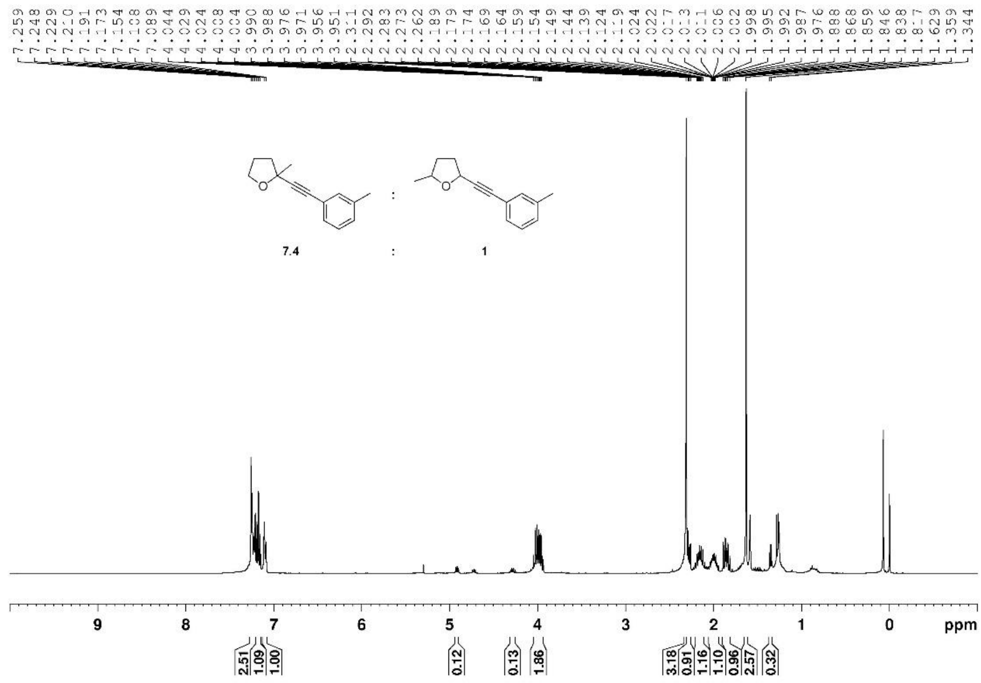
^{1}H NMR of **18a** and **18b**



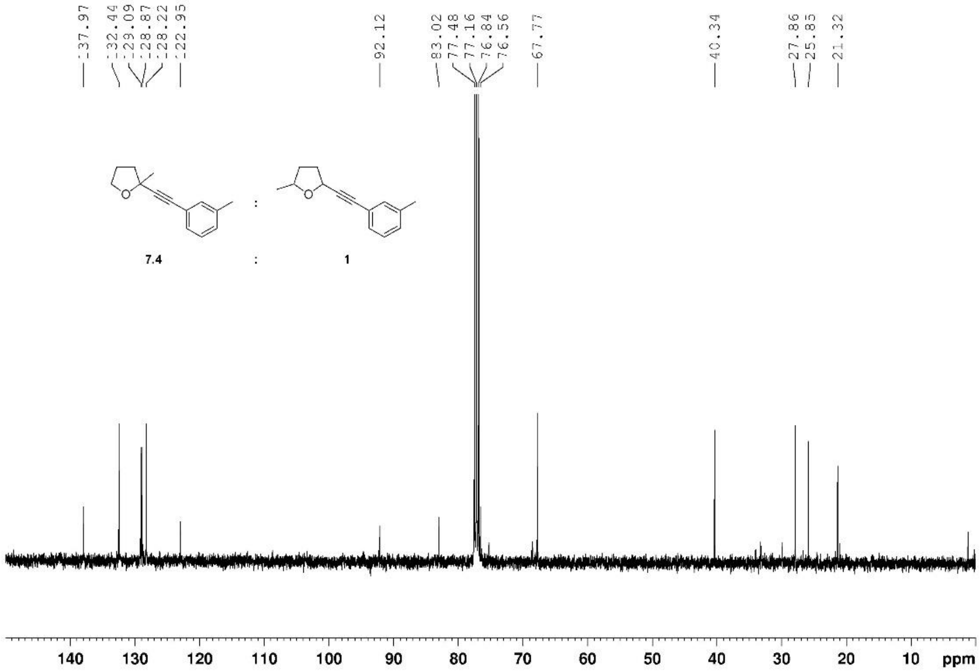
^{13}C NMR of **18a** and **18b**



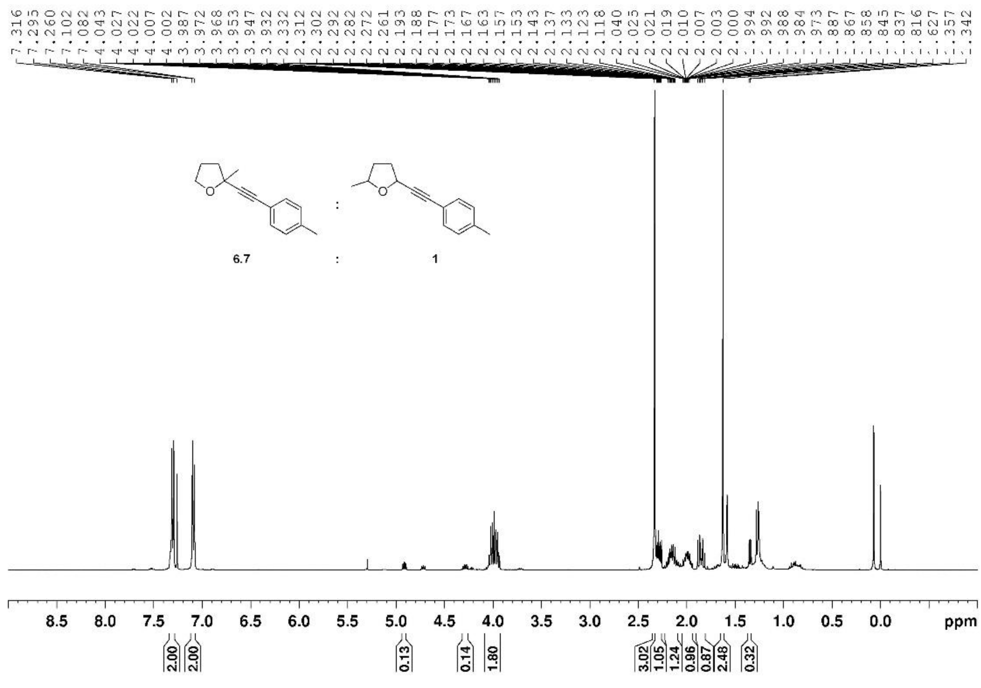
^{1}H NMR of **19a** and **19b**



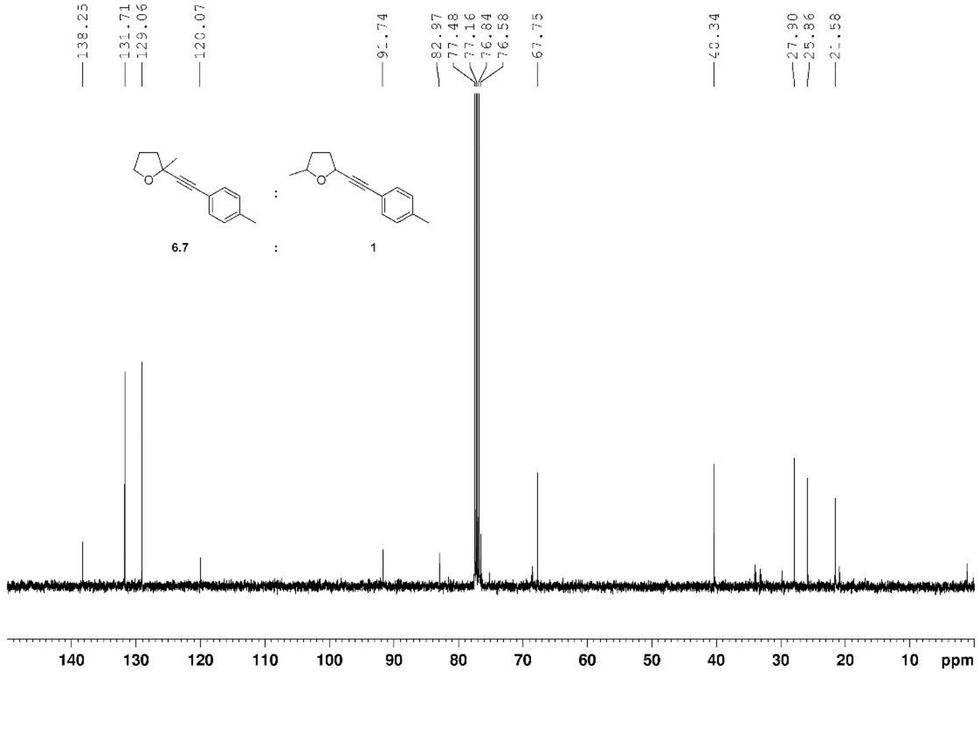
^{13}C NMR of **19a** and **19b**



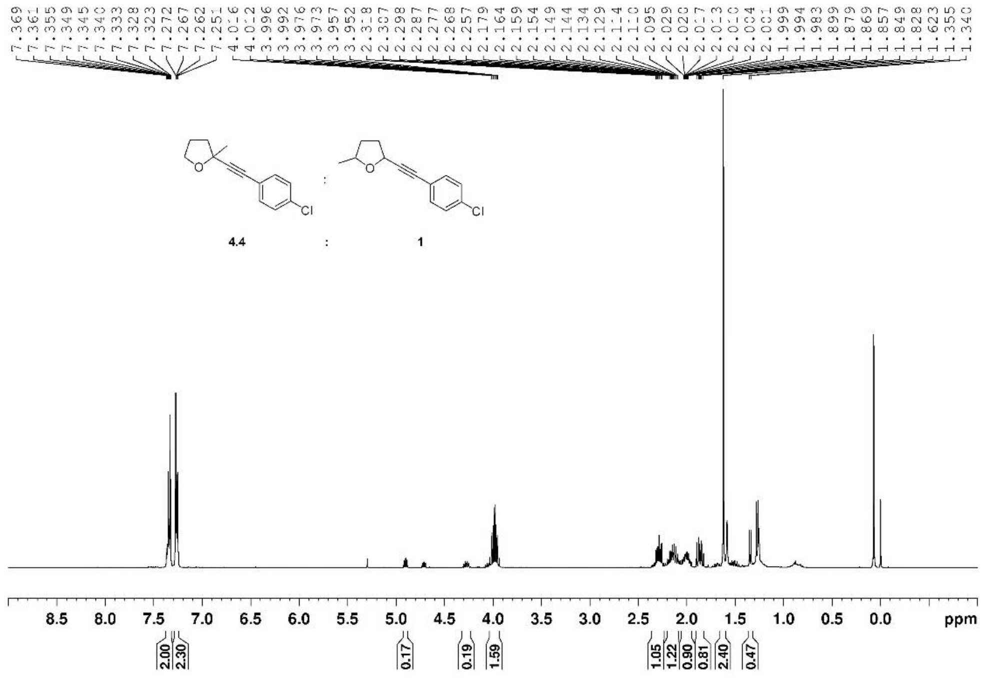
^{1}H NMR of **20a** and **20b**



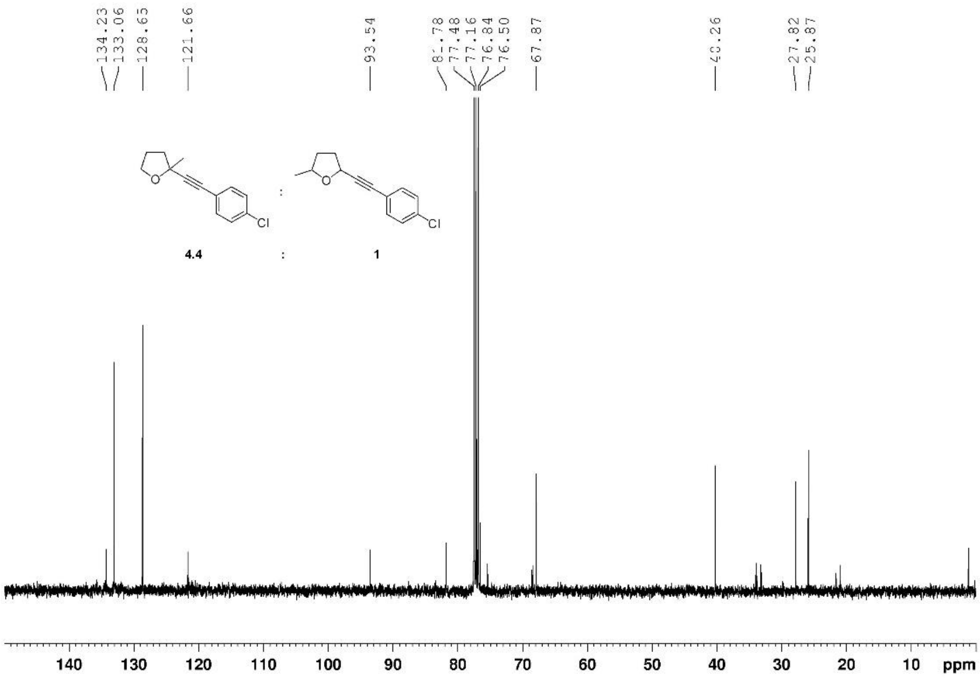
^{13}C NMR of **20a** and **20b**



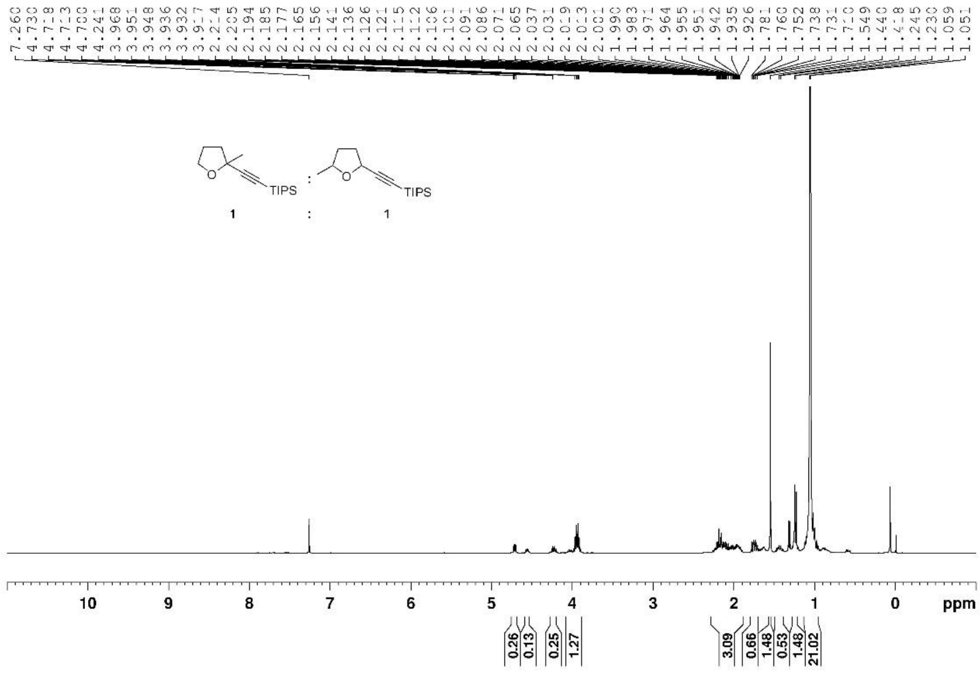
^{1}H NMR of **21a** and **21b**



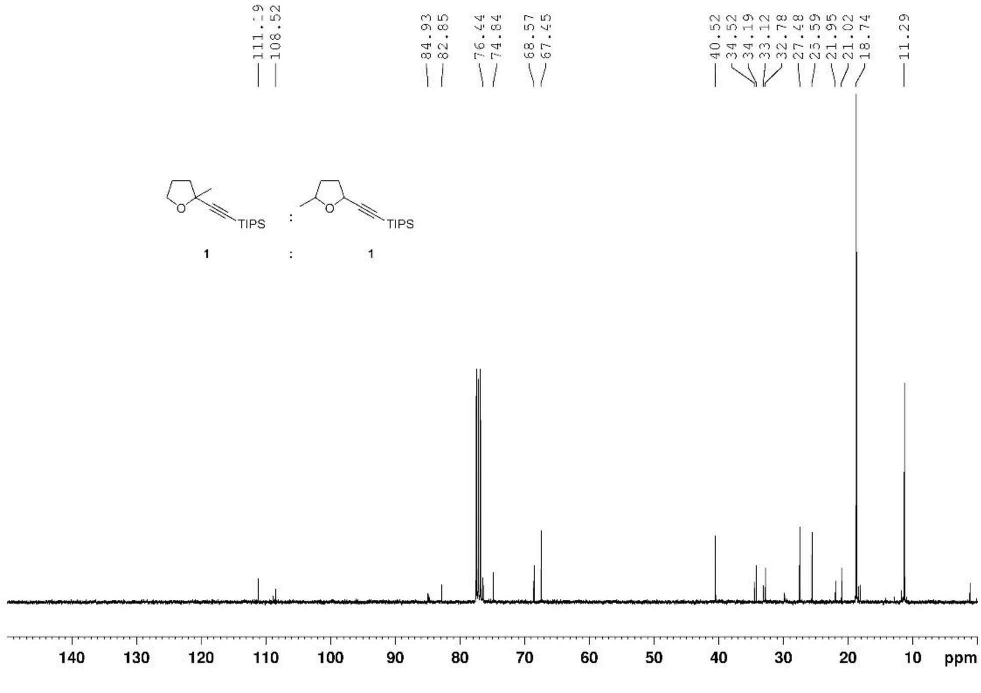
^{13}C NMR of **21a** and **21b**



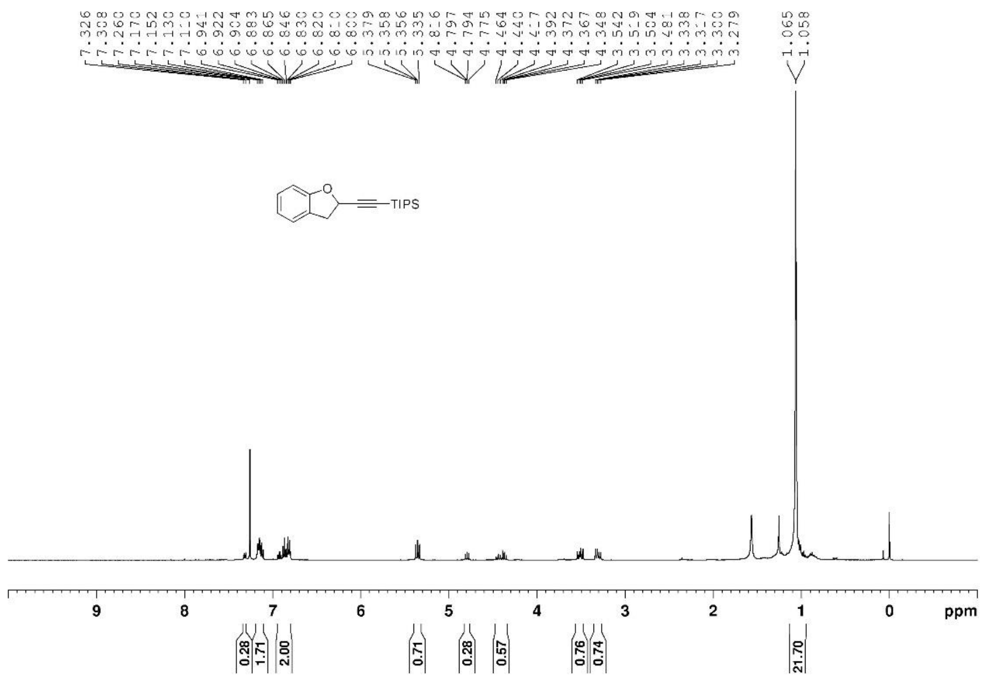
^{1}H NMR of **22a** and **22b**



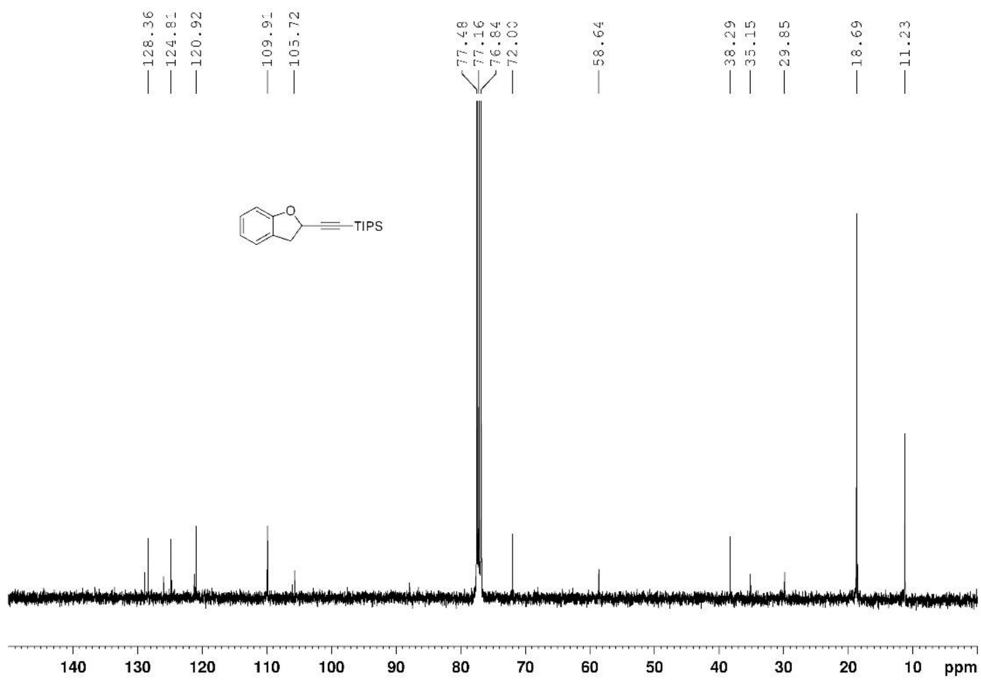
^{13}C NMR of **22a** and **22b**



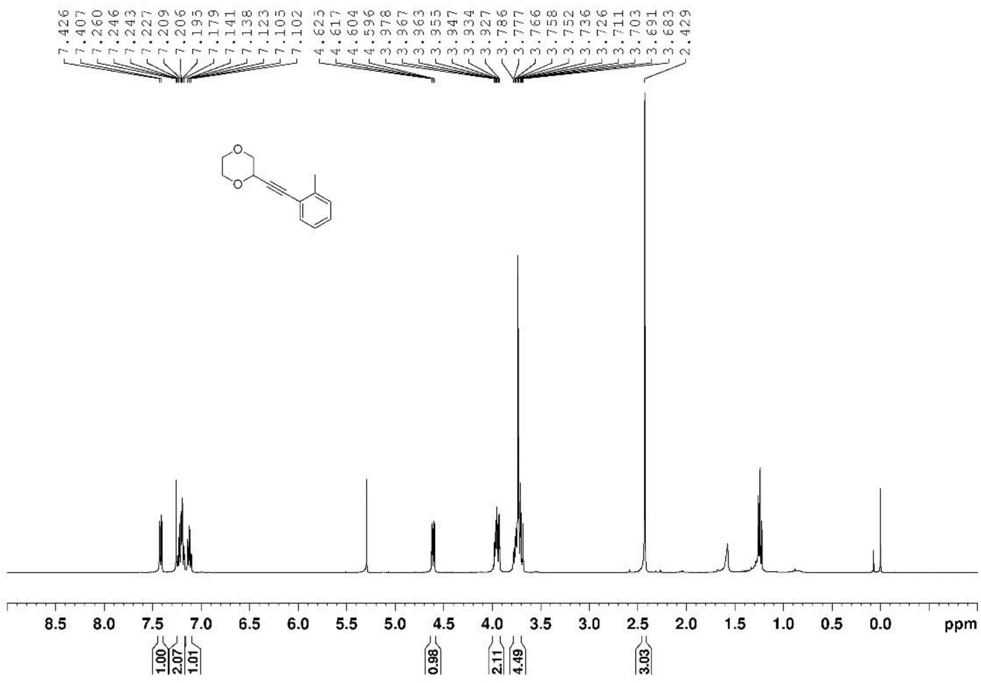
^{1}H NMR of **23**



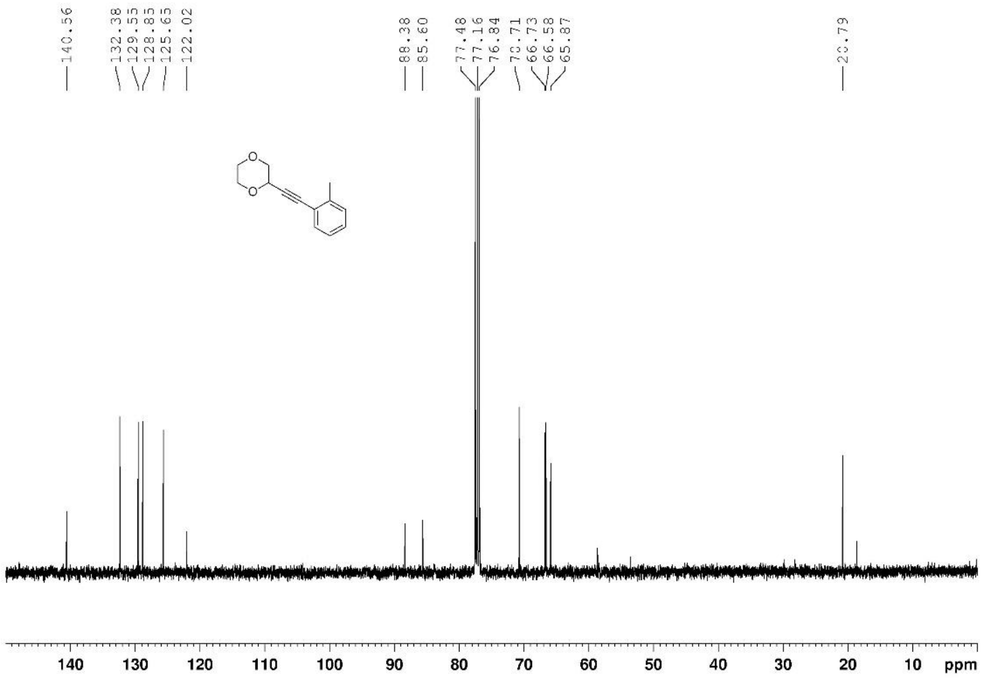
^{13}C NMR of **23**



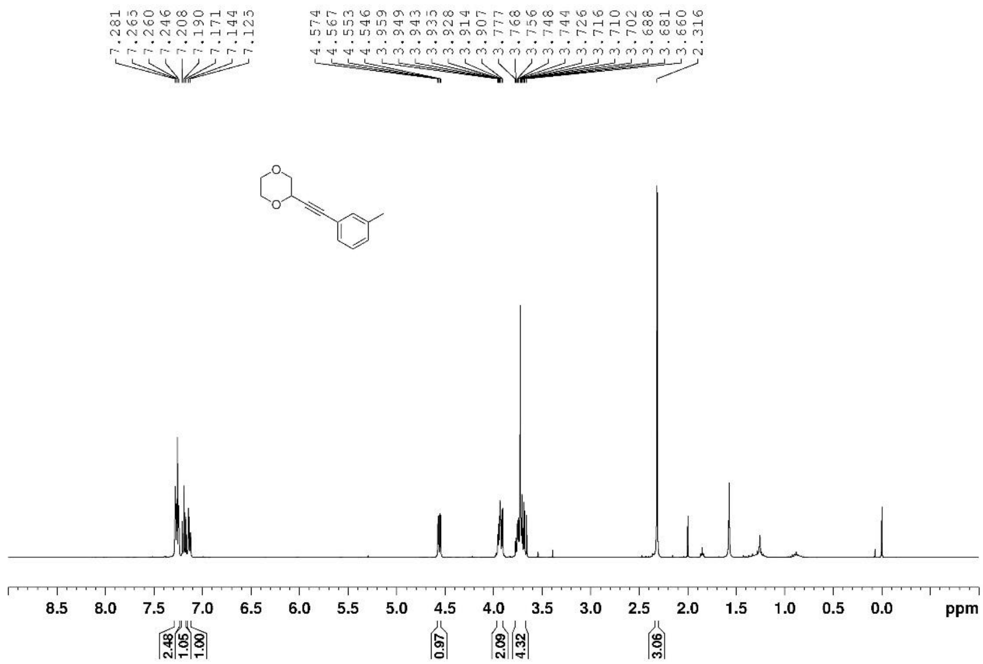
^{1}H NMR of **24**



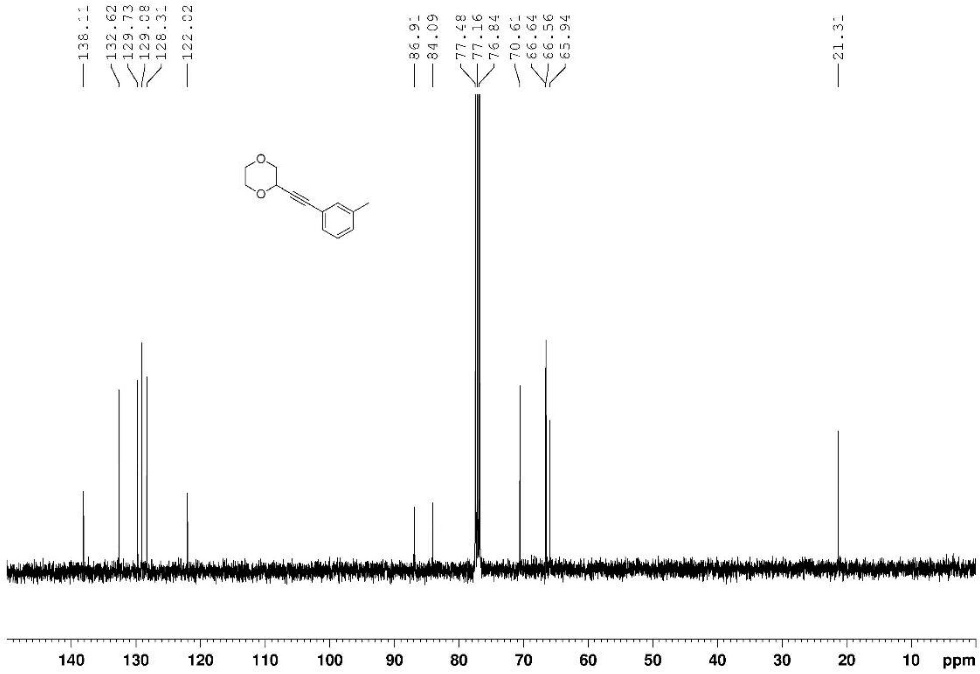
^{13}C NMR of **24**



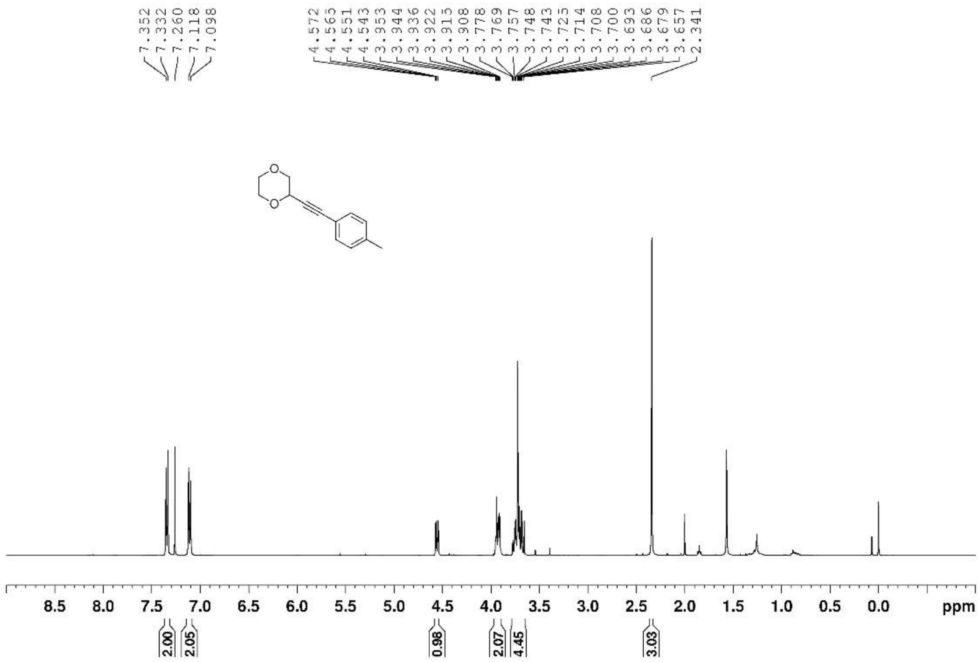
^{1}H NMR of **25**



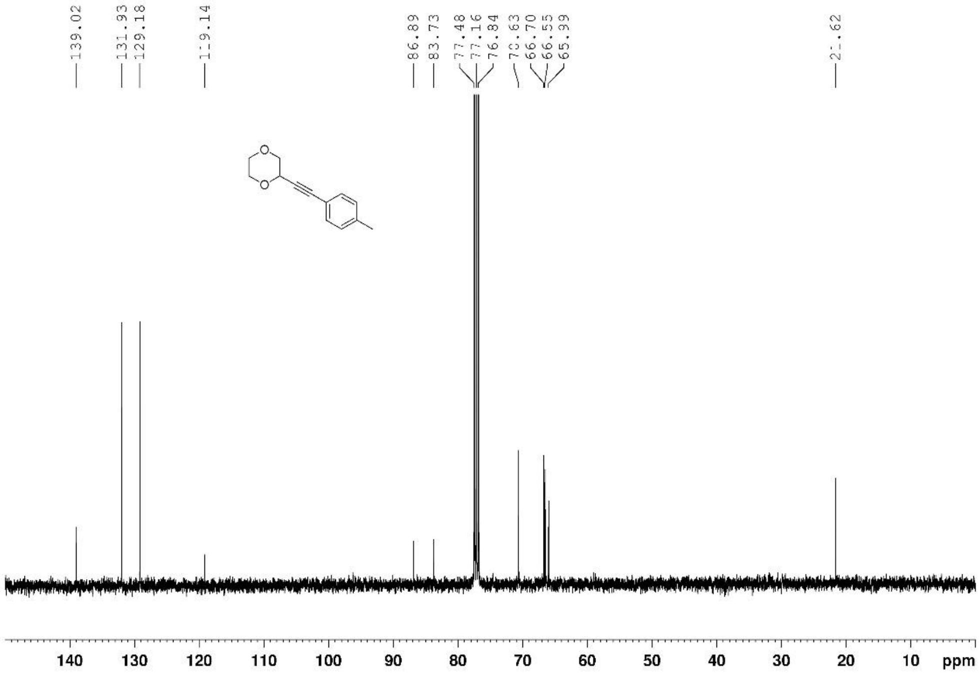
^{13}C NMR of **25**



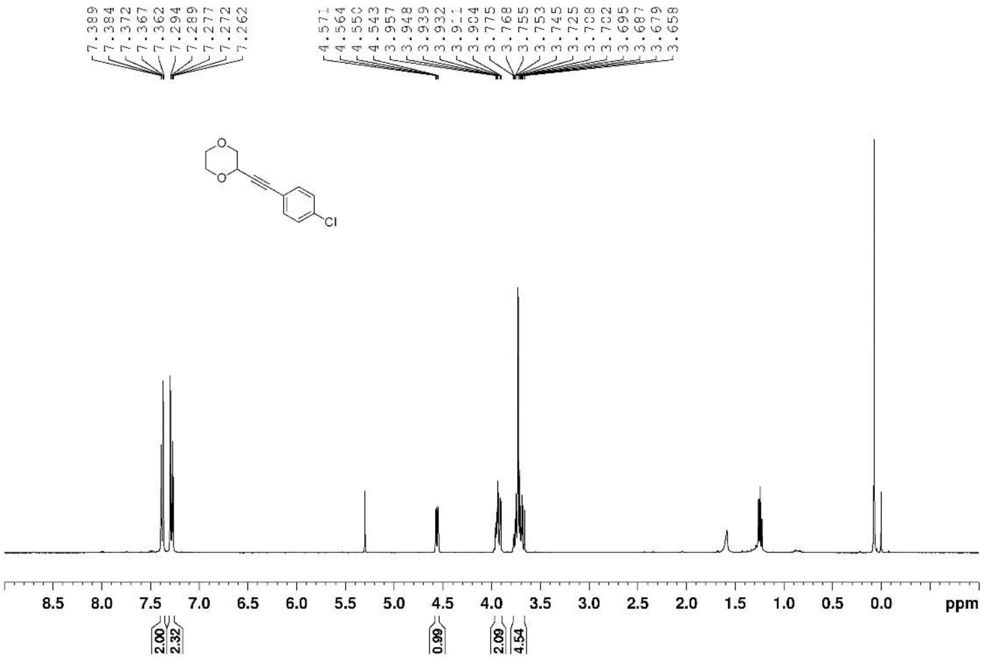
^{1}H NMR of **26**



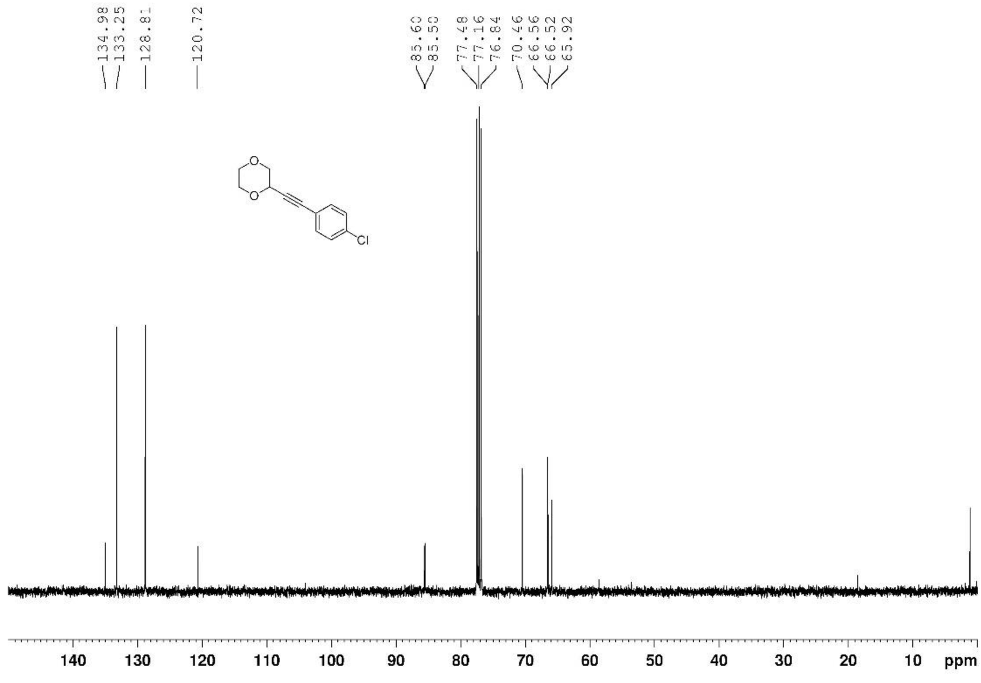
^{13}C NMR of **26**



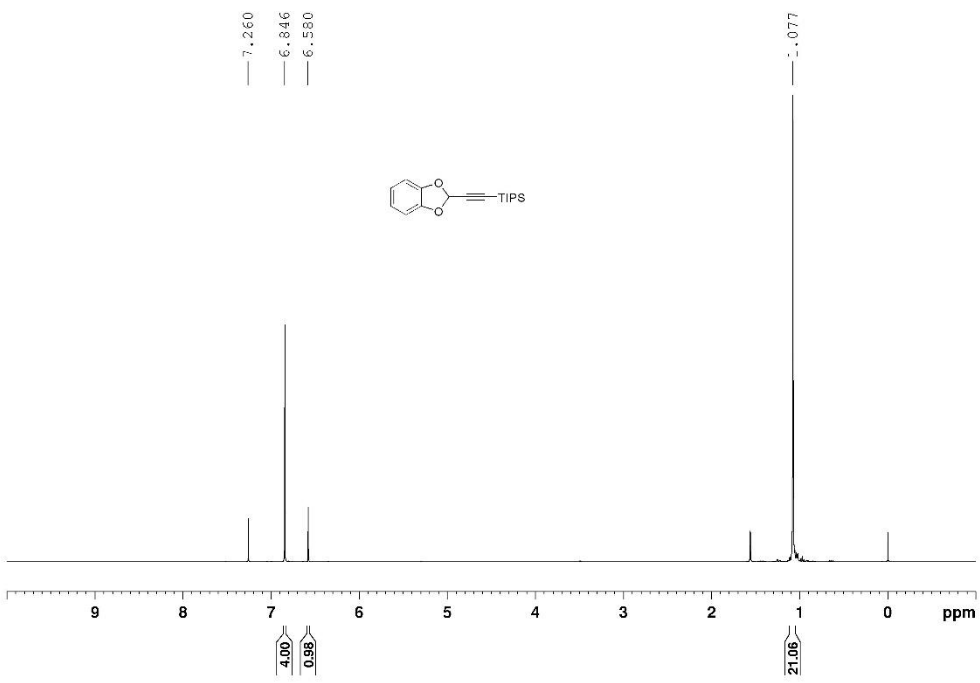
^{1}H NMR of **27**



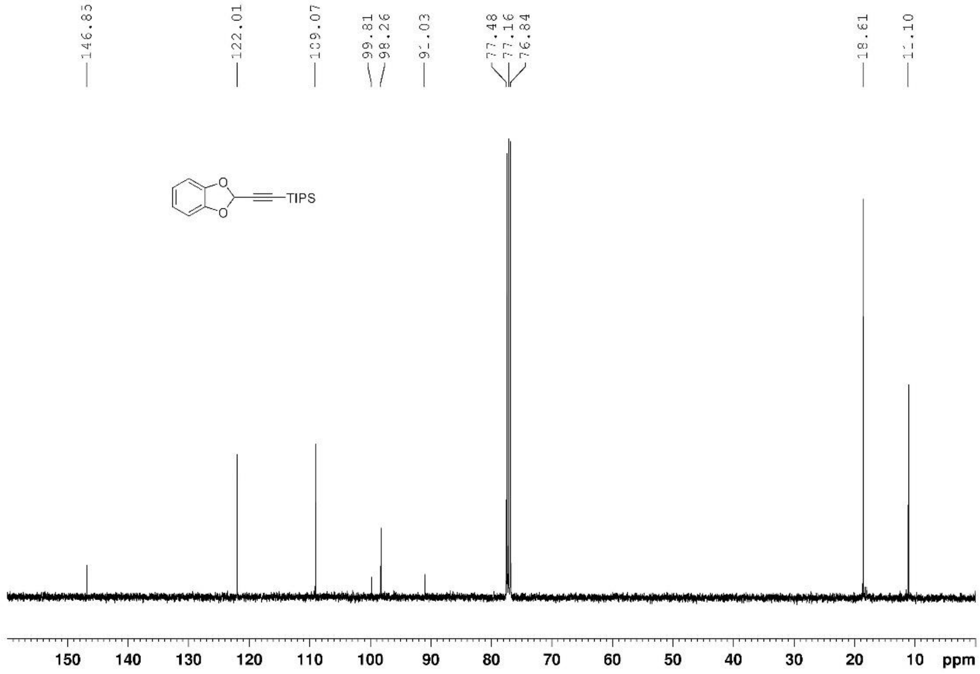
^{13}C NMR of **27**



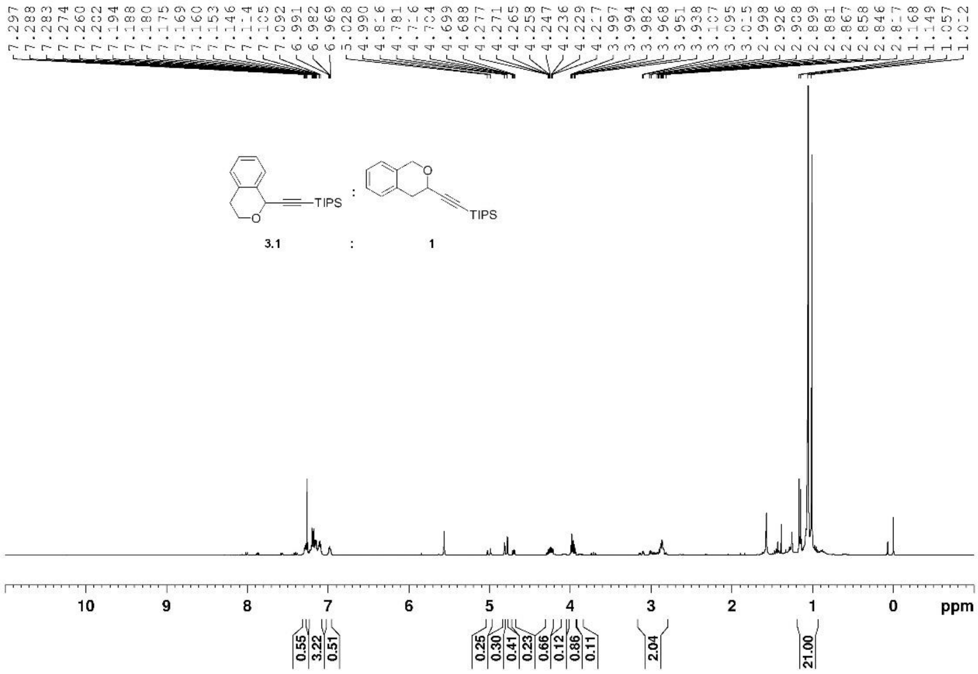
^{1}H NMR of **28**



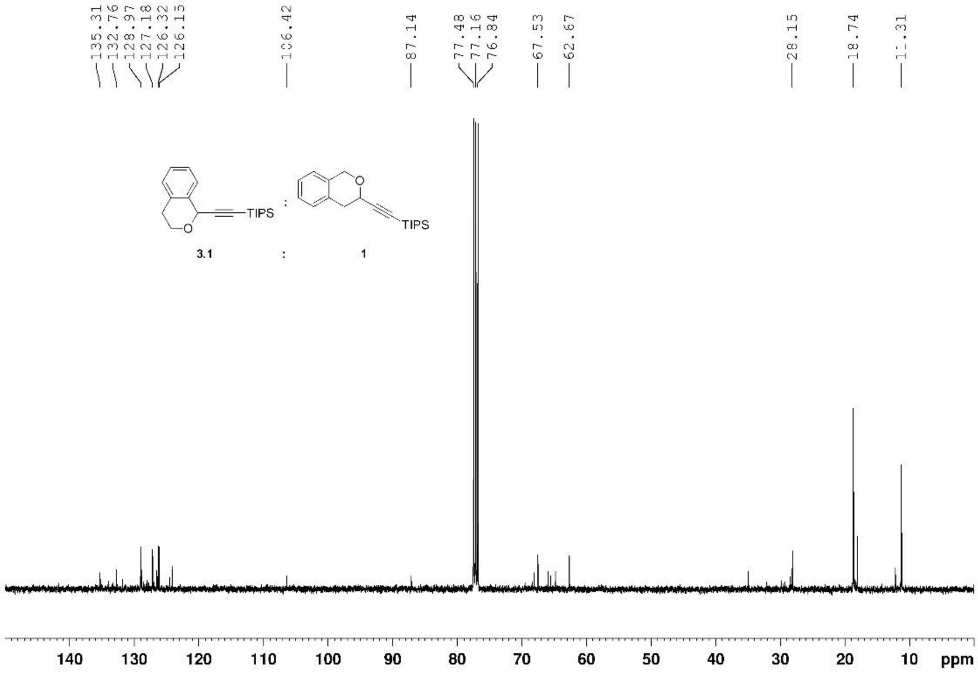
^{13}C NMR of **28**



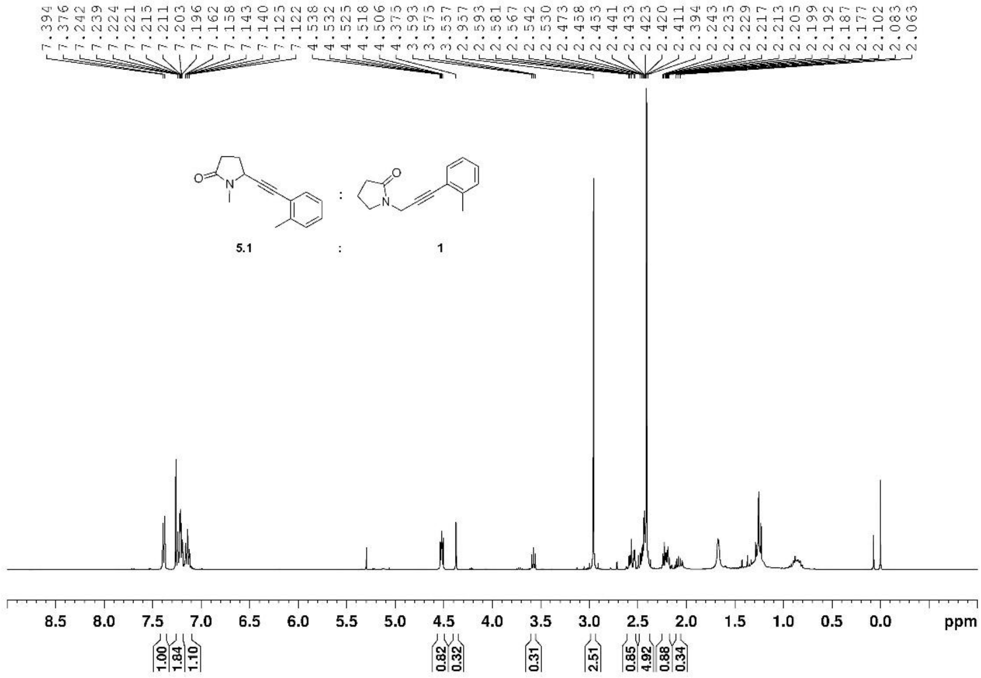
^{1}H NMR of **29a** and **29b**



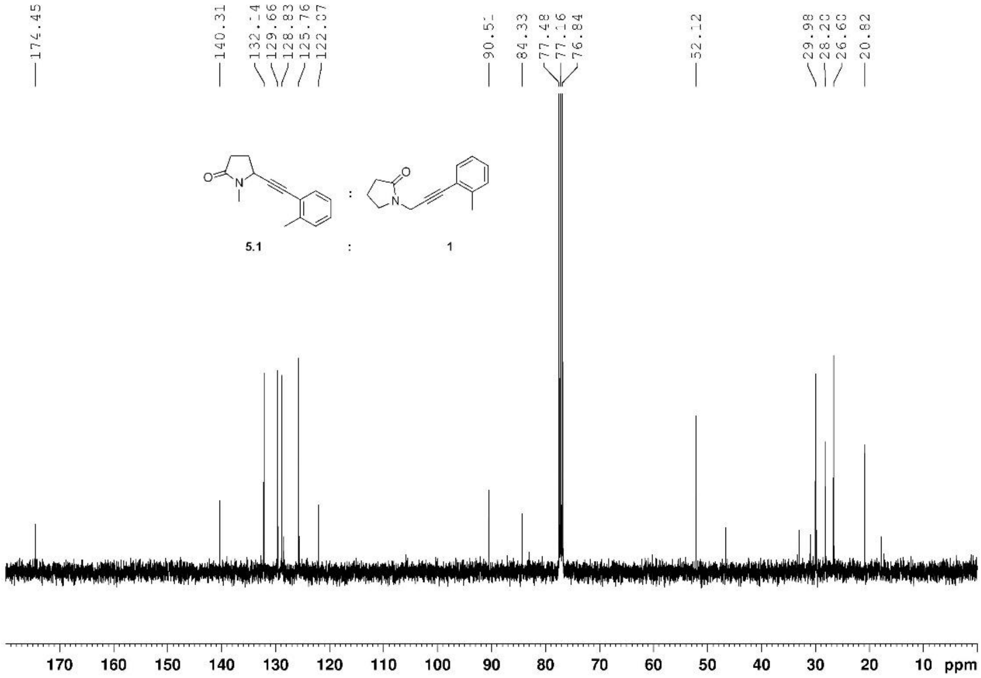
^{13}C NMR of **29a** and **29b**



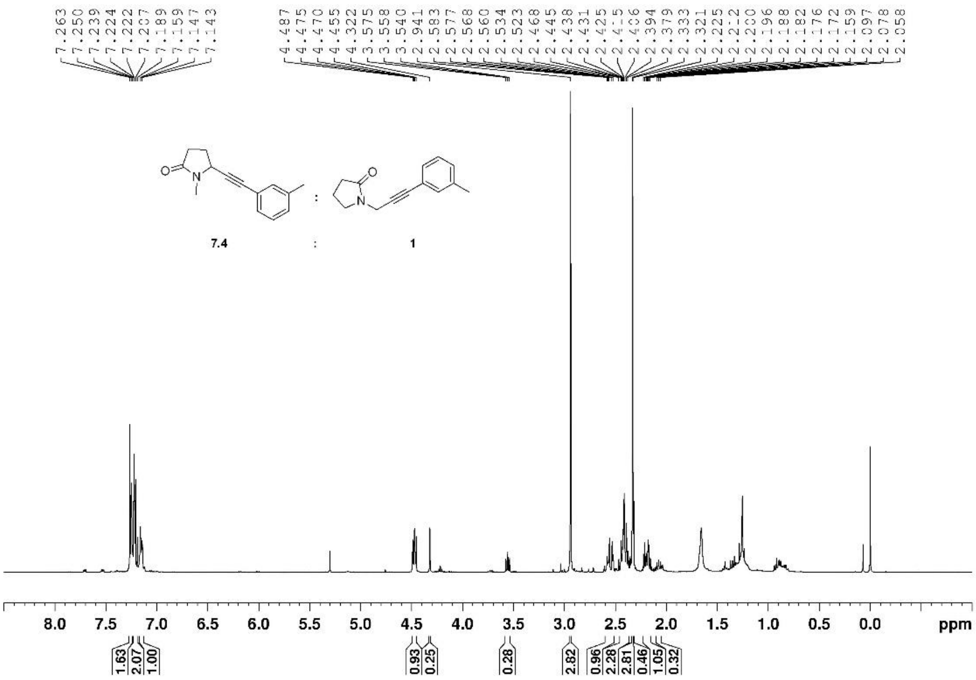
^{1}H NMR of **30a** and **30b**



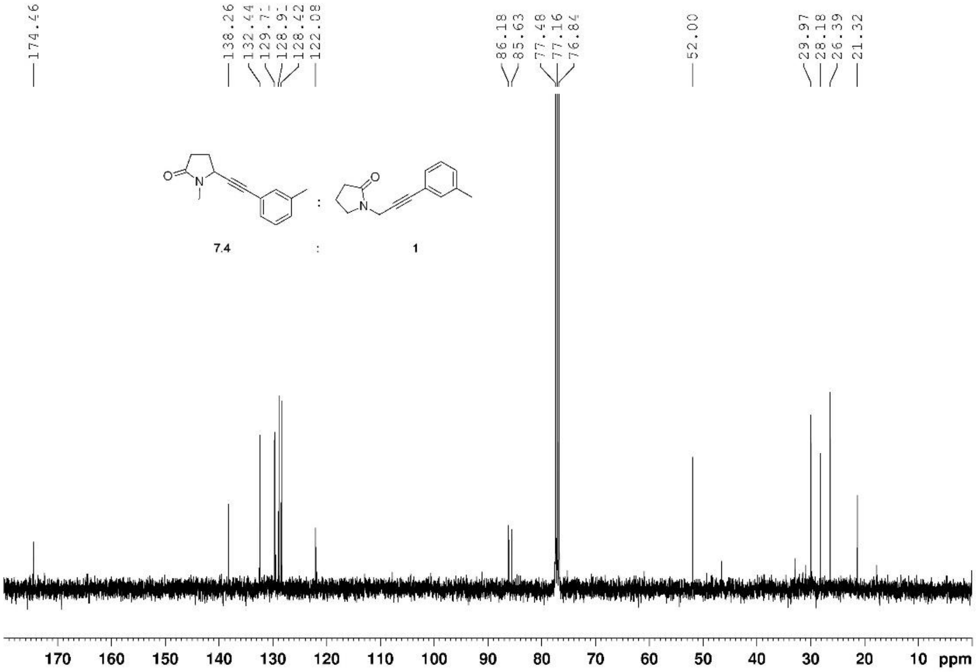
^{13}C NMR of **30a** and **30b**



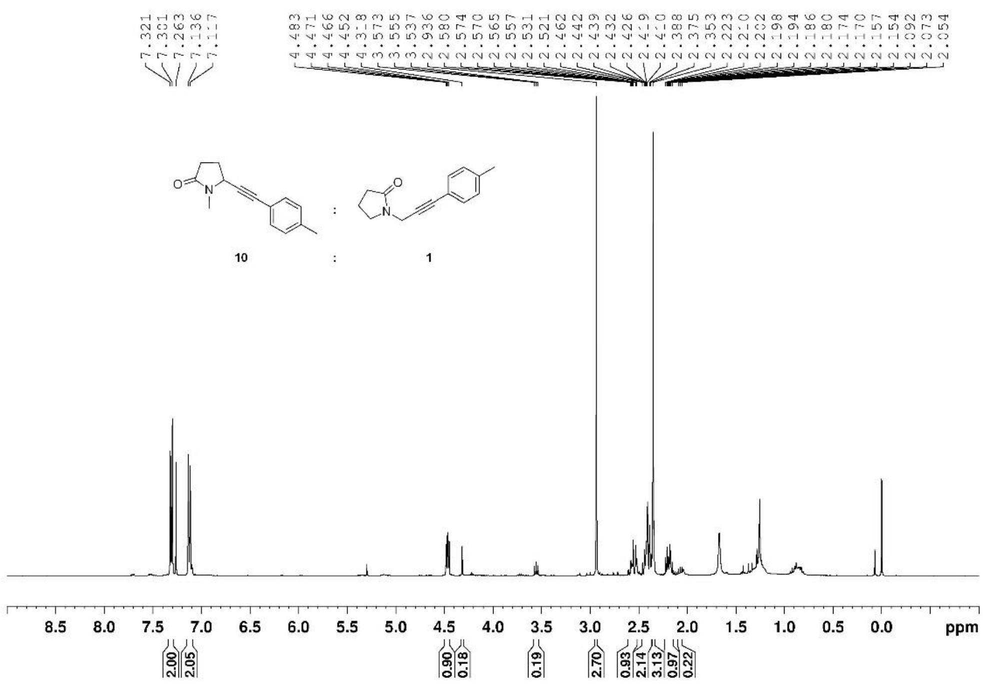
^{1}H NMR of **31a** and **31b**



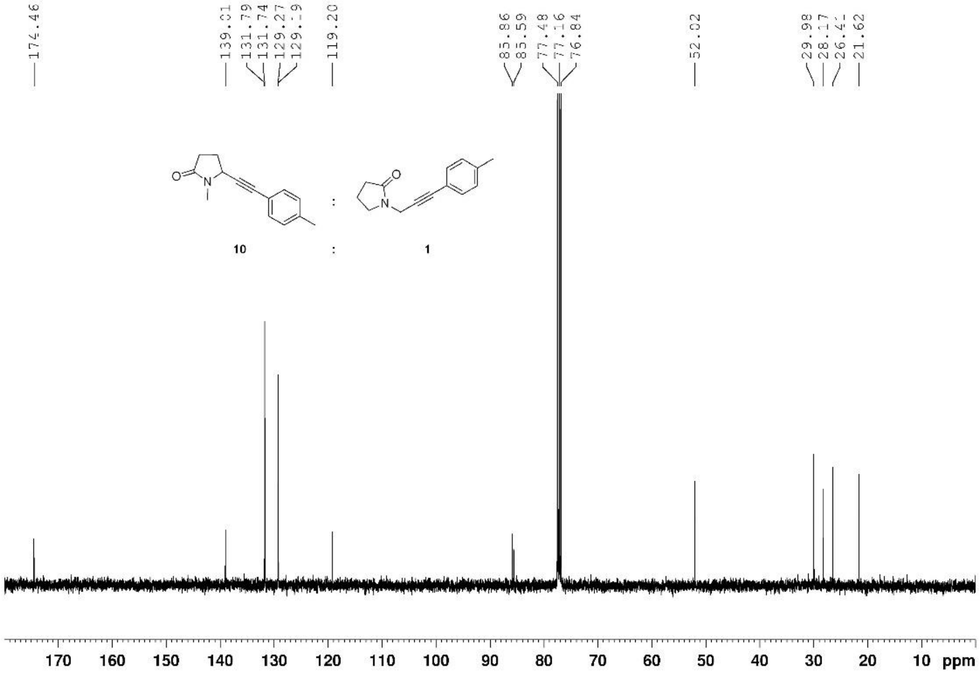
^{13}C NMR of **31a** and **31b**



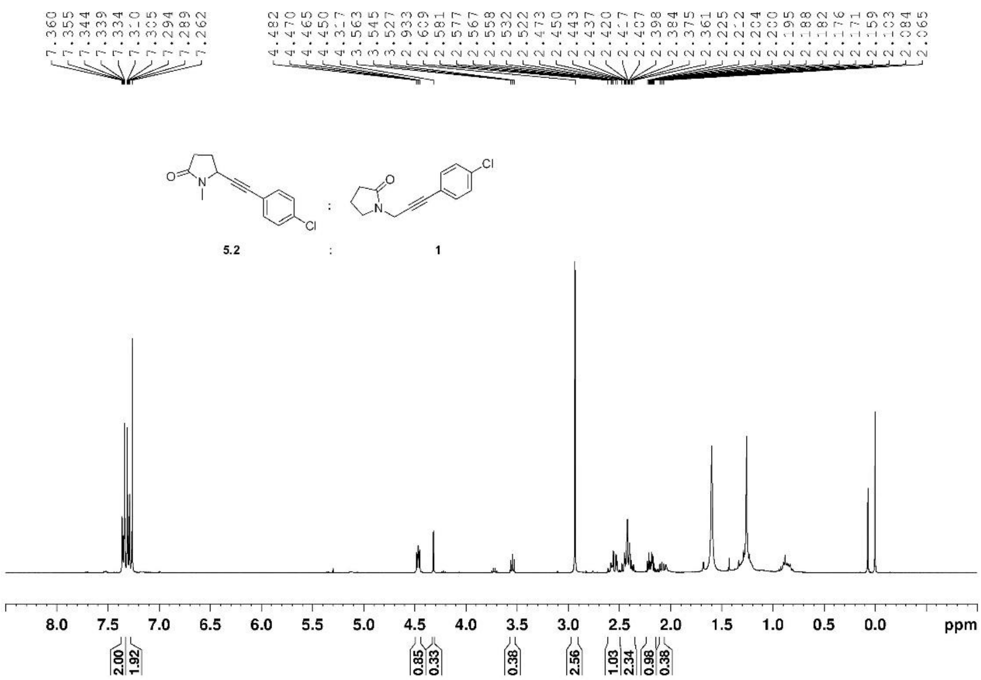
^{1}H NMR of **32a** and **32b**



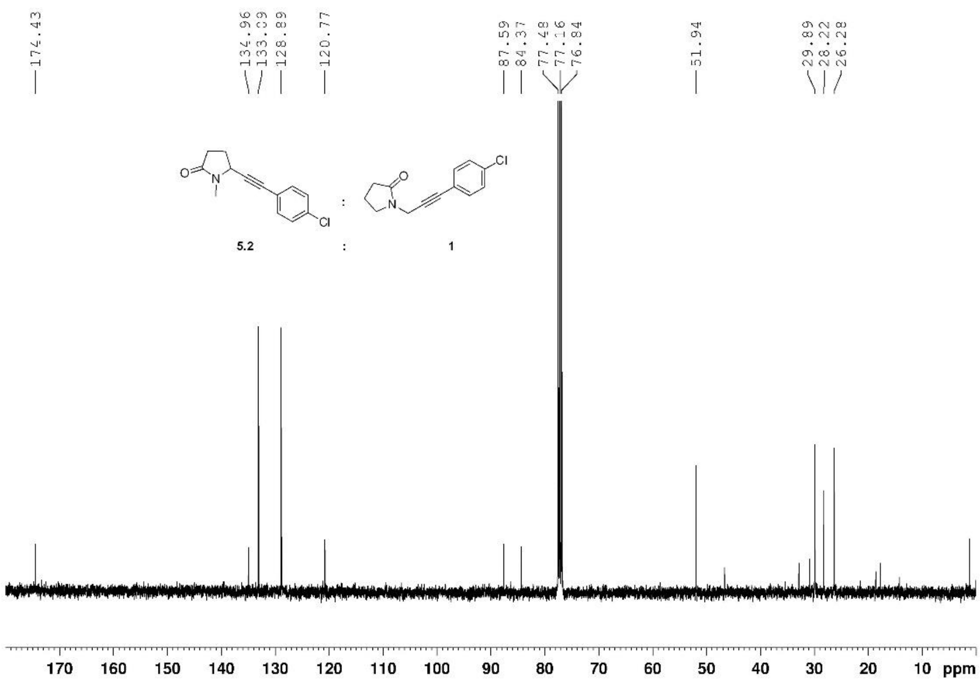
^{13}C NMR of **32a** and **32b**



^{1}H NMR of **33a** and **33b**



^{13}C NMR of **33a** and **33b**



Spectroscopic data of the kinetic isotope experiment