

Tandem Visible Light-Mediated Radical Cyclization-Divinylcyclopropane Rearrangement to Tricyclic Pyrrolidinones

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Supporting Information

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General Information:

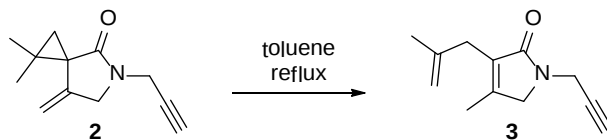
Chemicals were either used as received or purified according to *Purification of Common Laboratory Chemicals*. All reactions were performed using common dry, inert atmosphere techniques. Reactions were monitored by TLC and visualized by a dual short wave/long wave UV lamp and stained with an ethanolic solution of potassium permanganate or p-anisaldehyde. Column flash chromatography was performed using 230-400 mesh silica gel. NMR spectra were recorded on Varian Mercury 300, Varian Unity Plus 400, and Varian Mercury 400 spectrometers. Chemical shifts for ^1H NMR were reported as δ , parts per million, relative to the signal of CHCl_3 at 7.26 ppm. Chemical shifts for ^{13}C NMR were reported as δ , parts per million, relative to the center line signal of the CDCl_3 triplet at 77.0 ppm. Proton and carbon assignments were established using spectral data of similar compounds. The abbreviations s, br. s, d, dd, br. d, ddd, t, q, br. q, m, and br. m stand for the resonance multiplicity singlet, broad singlet, doublet, doublet of doublets, broad doublet, doublet of doublet of doublets, triplet, quartet, broad quartet, multiplet and broad multiplet, respectively. IR spectra were recorded on an Avatar 360 FT-IR spectrometer. Mass spectra were recorded at the Mass Spectrometry Facility at the Department of Chemistry of the Boston University in Boston, MA on a Waters Q-ToF API-US with ESI high resolution mass spectrometer. Concentration refers to removal of solvent under reduced pressure (house vacuum at ca. 20 mmHg).

Reaction Apparatus:

Photoredox catalyzed reactions were carried out under visible light irradiation by a commercially available 14W compact fluorescent lamp (CFL) in a hand held work light clamped ~10 cm from the reaction flask. The bulb and flask were then surrounded by a layer of aluminium foil in order to heat the reaction medium.



4-methyl-3-(2-methylallyl)-1-(prop-2-yn-1-yl)-1H-pyrrol-2(5H)-one, **3** (Scheme 2):



A flame dried 10 mL round bottom flask, equipped with a magnetic stir bar and fitted with a reflux condenser, was charged with **2** (0.61 g, 0.32 mmol), toluene (10 mL) and heated to reflux. After completion of the reaction (as judged by TLC analysis) the mixture was poured into a separatory funnel containing 25 mL of Et₂O and 25 mL of H₂O. The layers were separated and the aqueous layer was extracted with Et₂O (2 X 30 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. The residue was purified by chromatography on silica gel (7:3, hexanes/EtOAc) to afford **3** (0.61 g, 99%) as a colorless oil (8 h reaction time).

R_f (EtOAc/hexane 1:4): 0.18;

IR (neat): 3292, 3225, 3077, 2972, 2717, 1680, 1457, 1408, 1350, 1295, 1155 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): δ 4.75 (d, J = 0.5 Hz, 1 H), 4.67 (d, J = 0.5 Hz, 1 H), 4.27 (d, J = 2.0 Hz, 2 H), 3.90 (s, 2 H), 3.00 (s, 2 H), 2.25 (t, J = 2.0 Hz, 1 H), 2.02 (s, 3 H), 1.76 (s, 3 H);

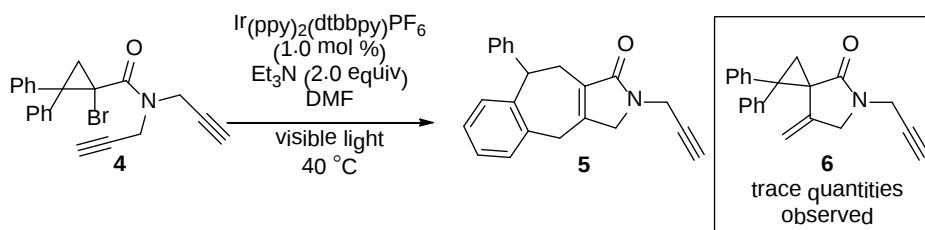
¹³C NMR (CDCl₃, 75 MHz): δ 171.6, 148.7, 142.4, 130.2, 111.0, 78.6, 72.1, 53.4, 31.5, 31.5, 22.6, 13.2;

HRMS (ESI) m/z calculated for C₁₂H₁₆NO⁺ ($[M+1]^+$) 190.1232, found 190.1224.

General Procedure A: Typical Visible Light-Mediated Rearrangement

A 25 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with bromocyclopropane (1.0 mmol, 1.0 equiv), Et₃N (2.0 mmol, 2.0 equiv), DMF (15 mL), Ir(ppy)₂(dtbbpy)PF₆ (0.010 mmol, 0.010 equiv). The mixture was then shielded from light and degassed by Ar sparging for 10 min. The mixture was then irradiated by a 14 W CFL under an atmosphere of Ar for 6 – 24h while the light and flask were surrounded by a layer of aluminium foil. After the reaction was complete (as judged by TLC analysis), the mixture was poured into a separatory funnel containing 25 mL of EtOAc and 50 mL of H₂O. The layers were separated and the aqueous layer was extracted with EtOAc (2 X 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. The residue was purified by chromatography on silica gel, using the solvent system indicated, to afford the desired rearranged product.

9-phenyl-2-(prop-2-yn-1-yl)-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **5** (Table 1, entry 1):



According to General Procedure A, **4** (0.19 g, 0.48 mmol), Et₃N (0.13 mL, 0.96 mmol), and Ir(ppy)₂(dtbbpy)PF₆ (4.4 mg, 4.8 μmol) in DMF (10 mL) afforded **5** (0.10 g, 69%) as a colorless solid after purification by chromatography on SiO₂ (17:3 to 3:1, hexanes/EtOAc) (10 h reaction time).

R_f (EtOAc/hexane 1:3): 0.20;

IR (neat): 2393, 3229, 3061, 3027, 2904, 1674m 1453, 1405, 1296, 1261, 1150 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 7.31 – 7.35 (m, 2 H), 7.24 – 7.27 (m, 4 H), 7.14 – 7.19 (m, 2 H), 7.10 – 7.11 (m, 1 H), 6.93 – 6.95 (m, 1 H), 4.62 (dd, *J* = 9.5, 3.5 Hz, 1 H), 4.31 (dd, *J* = 17.5, 2.5 Hz, 1 H), 4.25 (dd, *J* = 17.5, 2.5 Hz, 1 H), 4.02 (dt, *J* = 18.5, 2.5 Hz, 1 H), 3.92 (dt, *J* = 18.5, 2.5 Hz, 1 H), 3.85 (br d, *J* = 17.0 Hz, 1 H), 3.28 (br t, *J* = 17.0 Hz, 1 H), 3.05 – 3.12 (m, 1 H), 2.91 – 2.98 (m, 1 H), 2.26 (t, *J* = 2.5 Hz, 1 H);

¹³C NMR (CDCl₃, 75 MHz): δ 171.6, 147.2, 143.9, 142.0, 137.6, 130.7, 129.1, 128.6, 128.3, 127.8, 127.3, 126.5, 126.4, 78.4, 72.2, 53.0, 45.4, 34.0, 31.3, 28.5;

HRMS (ESI) *m/z* calculated for C₂₂H₂₀NO⁺ ([M+1]⁺) 314.1545, found 314.1530.

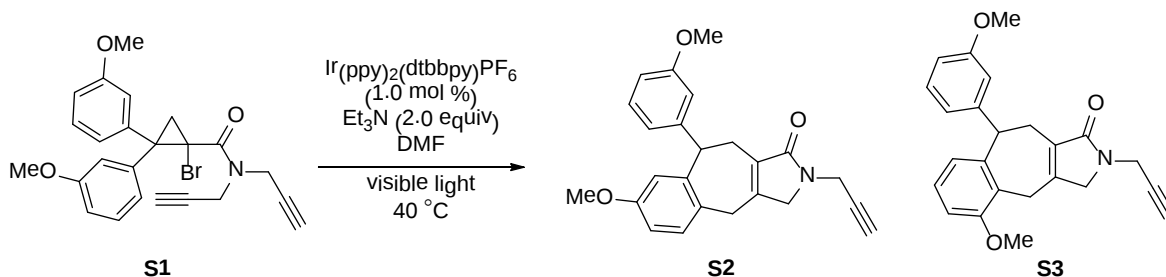
7-methylene-1,1-diphenyl-5-(prop-2-yn-1-yl)-5-azaspiro[2.4]heptan-4-one, **6**

According to General Procedure A, **4** (0.99 g, 2.5 mmol), Et₃N (0.68 mL, 5.0 mmol), and Ir(ppy)₂(dtbbpy)PF₆ (23 mg, 25 μmol) in DMF (52 mL) afforded **5** (0.36 g, 46%) as a colorless solid along with **6** (15 mg, 2%) as a colorless solid after purification by chromatography on SiO₂ (17:3 to 3:1, hexanes/EtOAc) (10 h reaction time).

R_f (EtOAc/hexane 3:7): 0.30;

¹H NMR (CDCl₃, 500 MHz): 7.30 – 7.34 (m, 4 H), 7.01 – 7.26 (m, 4 H), 7.12 – 7.16 (m, 2 H), 4.73 (t, *J* = 1.8 Hz, 1 H), 4.40 (dt, *J* = 13.5, 2.5 Hz, 1 H), 4.32 (dd, *J* = 17.5, 2.5 Hz, 1 H), 4.06 – 4.12 (m, 2 H), 3.77 (t, *J* = 2.0 Hz, 1 H), 2.45 (d, *J* = 5.0 Hz, 1 H), 2.30 (t, *J* = 2.5 Hz, 1 H), 1.93 (d, *J* = 5.0 Hz, 1 H).

7-methoxy-9-(3-methoxyphenyl)-2-(prop-2-yn-1-yl)-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S2**;
 5-methoxy-9-(3-methoxyphenyl)-2-(prop-2-yn-1-yl)-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S3** (Table 1, entry 2):



According to General Procedure A, **S1** (0.16 g, 0.36 mmol), Et_3N (0.10 mL, 0.72 mmol), and $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (17 mg, 3.6 μmol) in DMF (15 mL) afforded **S2** and **S3** (0.10 g, 80%) as a 1:1 mixture of regioisomers after purification by chromatography on SiO_2 (17:3 to 3:1, hexanes/ EtOAc) (12 h reaction time).

Data for compound **S2**:

R_f (EtOAc /hexane 2:3): 0.34;

IR (neat): 3289, 2936 1680, 1606, 1491, 1454, 1262, 1154, 1042 cm^{-1} ;

^1H NMR (CDCl_3 , 500 MHz): δ 7.23 - 7.26 (m, 1H), 7.02 (d, $J = 8.5$ Hz, 1H), 6.86 (br d, $J = 7.0$ Hz, 1 H), 6.80 (br d, $J = 7.0$ Hz, 1 H), 6.78 (s, 1 H), 6.67 (dd, $J = 8.5$, 2.5 Hz, 1 H), 6.53 (d, $J = 2.5$ Hz, 1 H), 4.54 (dd, $J = 9.5$, 3.0 Hz, 1 H), 4.29 (dd, $J = 17.5$, 2.0 Hz, 1 H), 4.24 (dd, $J = 17.5$, 2.0 Hz, 1 H), 4.00 (br d, $J = 18.5$ Hz, 1 H), 3.90 (br d, $J = 18.5$ Hz, 1 H), 3.82 – 3.85 (m, 1 H), 3.79 (s, 3 H), 3.72 (s, 3 H), 3.25 (d, $J = 17.5$ Hz, 1 H), 3.03 (dd, $J = 17.5$, 9.0, 1 H), 2.93 (d, $J = 18.0$ Hz, 1 H), 2.25 (t, $J = 2.5$ Hz, 1 H);

^{13}C NMR (CDCl_3 , 100 MHz): δ 171.7, 159.7, 158.8, 147.9, 145.2, 143.5, 130.6, 129.9, 129.5, 129.4, 120.3, 115.8, 113.8, 111.8, 110.5, 78.5, 72.2, 55.2, 53.1, 45.7, 33.3, 31.4, 28.7;

HRMS (ESI) m/z calculated for $\text{C}_{24}\text{H}_{24}\text{NO}_3^+$ ($[\text{M}+1]^+$) 374.1756, found 374.1748.

Data for compound **S3**:

R_f (EtOAc /hexane 2:3): 0.29;

IR (neat): 3289, 2924, 2837, 1679, 1582, 1470, 1404, 1260, 1153, 1083, 1061 cm^{-1} ;

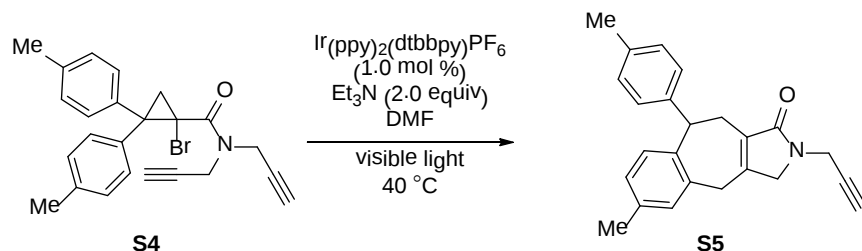
^1H NMR (CDCl_3 , 500 MHz): 7.23 (d, $J = 9.0$ Hz, 1 H), 7.10 (t, $J = 7.5$ Hz, 1 H), 6.86 (d, $J = 7.5$ Hz, 1 H), 6.77 – 6.81 (m, 3 H), 6.55 (d, 8.0 Hz, 1 H), 4.61 (dd, $J = 9.5$, 3.5 Hz, 1 H), 4.29 (dd, $J = 17.5$, 2.5 Hz, 1 H), 4.24 (dd, $J = 17.5$, 2.5 Hz, 1 H), 4.03 (br d, $J = 18.5$

Hz, 1 H), 3.93 (br d, $J = 18.5$ Hz, 1 H), 3.82 – 3.85 (m, 4 H), 3.79 (s, 3 H), 3.66 (br d, $J = 17.5$ Hz, 1 H), 2.92 – 3.03 (m, 2 H), 2.25 (t, $J = 2.5$ Hz, 1 H);

^{13}C NMR (CDCl_3 , 100 MHz): δ 171.7, 159.6, 155.7, 148.0, 145.6, 144.0, 131.0, 129.3, 127.4, 126.2, 121.3, 120.4, 113.9, 111.7, 109.0, 78.5, 72.1, 55.7, 55.2, 53.4, 45.5, 31.3, 28.5, 23.1;

HRMS (ESI) m/z calculated for $\text{C}_{24}\text{H}_{24}\text{NO}_3^+$ ($[\text{M}+1]^+$) 374.1756, found 374.1761.

6-methyl-2-(prop-2-yn-1-yl)-9-(p-tolyl)-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S5** (Table 1, entry 3):



According to General Procedure A, **S4** (95 mg, 0.23 mmol), Et_3N (63 μL , 0.45 mmol), and $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (2.1 mg, 2.3 μmol) in DMF (6.0 mL) afforded **S5** (71 mg, 91%) as a colorless solid after purification by chromatography on SiO_2 (4:1, hexanes/EtOAc) (6 h reaction time).

R_f (EtOAc/hexane 1:4): 0.20;

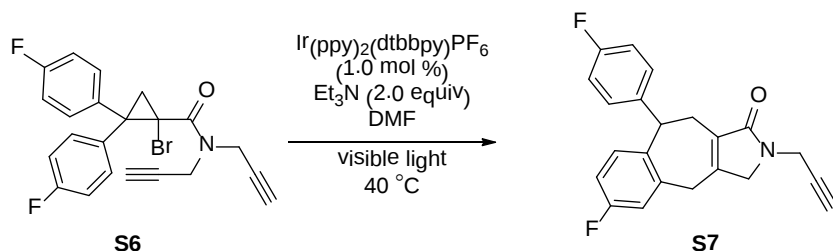
IR (neat): 3301, 2919, 1675, 1513, 1453, 1404, 1349, 1290, 1251, 1150 cm^{-1} ;

^1H NMR (CDCl_3 , 500 MHz): 7.12 – 7.15 (m, 4 H), 6.97 (d, $J = 7.5$ Hz, 1 H), 6.92 (s, 2 H), 6.83 (d, $J = 7.5$ Hz, 1 H), 4.54 (dd, $J = 9.5, 3.5$ Hz, 1 H), 4.30 (dd, $J = 17.5, 2.5$ Hz, 1 H), 4.24 (dd, $J = 17.5, 2.5$ Hz, 1 H), 4.00 (br d, $J = 18.5$ Hz, 1 H), 3.91 (br d, $J = 19.0$ Hz, 1 H), 3.81 (br d, $J = 17.5$ Hz, 1 H), 3.24 (br d, $J = 17.5$ Hz, 1 H), 3.03 (dd, $J = 18.0, 9.5$ Hz, 1 H), 2.91 (br d, $J = 18.0$ Hz, 1 H), 2.37 (s, 3 H), 2.32 (s, 2 H), 2.25 (t, $J = 2.5$ Hz, 1 H);

^{13}C NMR (CDCl_3 , 75 MHz): δ 171.7, 147.3, 141.2, 139.2, 137.5, 136.1, 135.9, 130.8, 129.5, 129.1, 129.0, 127.8, 127.7, 78.5, 72.1, 53.1, 44.7, 34.0, 31.3, 28.7, 21.0, 20.8;

HRMS (ESI) m/z calculated for $\text{C}_{24}\text{H}_{24}\text{NO}^+$ ($[\text{M}+1]^+$) 342.1858, found 342.1851.

6-fluoro-9-(4-fluorophenyl)-2-(prop-2-yn-1-yl)-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S7** (Table 1, entry 4):



According to General Procedure A, **S6** (0.11 g, 0.25 mmol), Et_3N (71 μL , 0.51 mmol), and $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (2.3 mg, 2.5 μmol) in DMF (9.0 mL) afforded **S7** (76 mg, 89%) as a colorless solid after purification by chromatography on SiO_2 (4:1, hexanes/ EtOAc) (8 h reaction time).

R_f (EtOAc /hexane 1:3): 0.16;

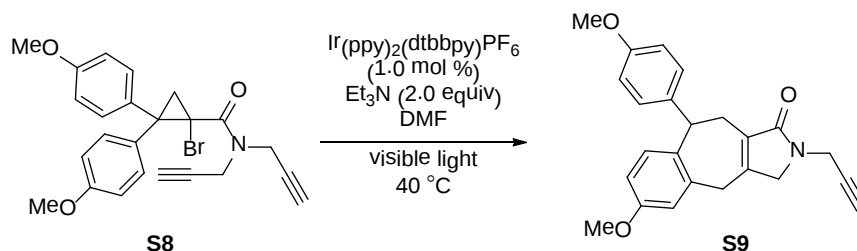
IR (neat): 3302, 2904, 1676, 1508, 1493, 1454, 1405, 1249, 1224, 1160 cm^{-1} ;

^1H NMR (CDCl_3 , 500 MHz): 7.18 – 7.21 (m, 2 H), 7.03 (t, $J = 8.5$ Hz, 2 H), 6.83 – 6.86 (m, 3 H), 4.56 (dd, $J = 9.0, 3.0$ Hz, 1 H), 4.31 (dd, $J = 17.5, 3.0$ Hz, 1 H), 4.23 (dd, $J = 17.5, 3.0$ Hz, 1 H), 4.02 (br d, $J = 19.0$ Hz, 1 H), 3.92 (br d, $J = 19.0$ Hz, 1 H), 3.82 (br d, $J = 17.5$ Hz, 1 H), 3.24 (br d, $J = 17.5$ Hz, 1 H), 3.00 (dd, $J = 18.0, 2.0$ Hz, 1 H), 2.91 (br d, $J = 18.0$ Hz, 1 H), 2.27 (t, $J = 2.5$ Hz, 1 H);

^{13}C NMR (CDCl_3 , 100 MHz): δ 171.4, 161.6 (d, $^1J_{\text{C-F}} = 250.0$ Hz), 161.2 (d, $^1J_{\text{C-F}} = 240.0$ Hz), 146.5, 139.4 (d, $^3J_{\text{C-F}} = 3.0$ Hz), 137.5 (d, $^3J_{\text{C-F}} = 3.0$ Hz), 130.9, 130.5, 130.4, 129.3, 129.2, 116.0, 115.76, 115.3 (d, $^2J_{\text{C-F}} = 21.6$ Hz), 113.6 (d, $^2J_{\text{C-F}} = 20.1$ Hz), 78.3, 72.3, 53.1, 44.2, 33.9, 31.4, 28.8;

HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{NO}^+$ ($[\text{M}+1]^+$) 350.1356, found 350.1349.

6-methoxy-9-(4-methoxyphenyl)-2-(prop-2-yn-1-yl)-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S9** (Table 1, entry 5):



According to General Procedure A, **S8** (0.15 g, 0.32 mmol), Et_3N (90 μL , 0.65 mmol), and $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (2.9 mg, 3.2 μmol) in DMF (7.0 mL) afforded **S9** (94 mg, 79%) as a colorless solid after purification by chromatography on SiO_2 (99:1, DCM/MeOH) (8 h reaction time).

R_f (EtOAc/hexane 2:3): 0.26;

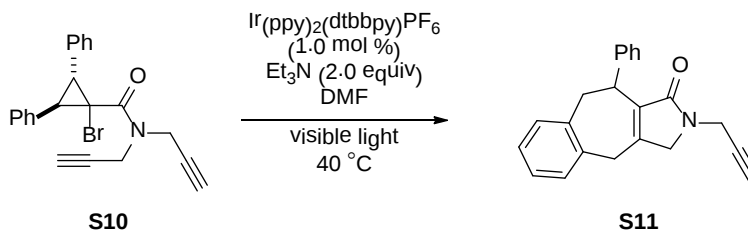
IR (neat): 3285, 3000, 2906, 2835, 1677, 1608, 1511, 1250, 1180 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz): 7.16 (d, J = 8.8 Hz, 2 H), 6.83 – 6.89 (m, 3 H), 6.67 – 6.72 (m, 2 H), 4.49 (dd, J = 9.2, 3.2 Hz, 1 H), 4.29 (dd, J = 17.6, 2.4 Hz, 1 H), 4.22 (dd, J = 17.6, 2.4 Hz, 1 H), 4.00 (br d, J = 18.8 Hz, 1 H), 3.89 (br d, J = 18.8 Hz, 1 H), 2.81 – 3.85 (m, 4 H), 3.77 (s, 3 H), 3.23 (d, J = 17.2 Hz, 1 H), 2.98 (dd, J = 17.8, 9.6 Hz, 1 H), 2.87 (br d, J = 17.8 Hz, 1 H), 2.23 (t, J = 2.4 Hz, 1 H);

^{13}C NMR (CDCl_3 , 125 MHz): 171.7, 158.1, 158.0, 147.0, 138.8, 136.5, 134.4, 130.9, 130.1, 128.8, 115.1, 113.7, 111.4, 78.5, 72.2, 55.2, 53.2, 44.0, 34.2, 31.4, 29.1;

HRMS (ESI) m/z calculated for $\text{C}_{24}\text{H}_{24}\text{NO}_3^+$ ($[\text{M}+1]^+$) 374.1756, found 374.1750.

10-phenyl-2-(prop-2-yn-1-yl)-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S11** (Table 1, entry 6):



According to General Procedure A, **S10** (0.16 g, 0.42 mmol), Et₃N (0.12 mL, 0.84 mmol), and Ir(ppy)₂(dtbbpy)PF₆ (4.0 mg, 4.2 μmol) in DMF (12 mL) afforded **S11** (0.11 g, 85%) as a colorless solid after purification by chromatography on SiO₂ (19:1, DCM/EtOAc) (10 h reaction time).

R_f (EtOAc/DCM 1:9): 0.65;

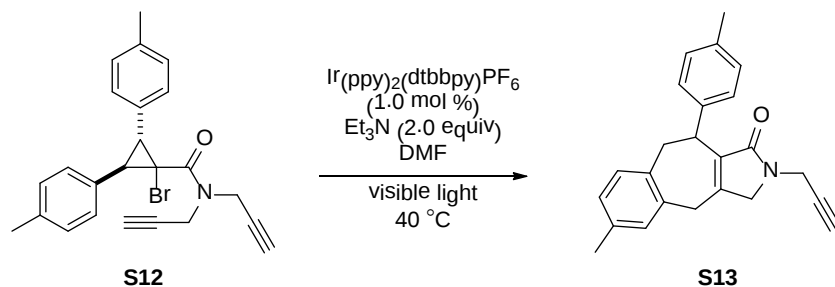
IR (neat): 3290, 3060, 3026, 2925, 1679, 1492, 1453, 1404, 1350, 1263, 1150 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 7.11 – 7.17 (m, 5 H), 7.02 – 7.06 (m, 1 H), 6.90 (d, *J* = 8.5 Hz, 2 H), 6.78 (d, *J* = 7.0 Hz, 1 H), 4.26 (dd, *J* = 18.0, 2.5 Hz, 1 H), 4.05 – 4.14 (m, 4 H), 3.88 (d, *J* = 17.0 Hz, 1 H), 3.76 (d, *J* = 17.0 Hz, 1 H), 3.42 (dd, *J* = 13.5, 3.5 Hz, 1 H), 3.08 (dd, *J* = 13.5, 7.0 Hz, 1 H), 2.25 (t, *J* = 2.5 Hz, 1 H);

¹³C NMR (CDCl₃, 125 MHz): 170.7, 148.9, 142.1, 138.3, 138.1, 138.4, 130.7, 127.9, 127.8, 127.7, 126.9, 126.4, 126.2, 78.5, 72.2, 53.2, 41.7, 40.6, 33.9, 31.2;

HRMS (ESI) *m/z* calculated for C₂₂H₂₀NO⁺ ([M+1]⁺) 314.1545, found 314.1548.

6-methyl-2-(prop-2-yn-1-yl)-10-(p-tolyl)-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S13** (Table 1, entry 7):



According to General Procedure A, **S12** (59 mg, 0.14 mmol), Et_3N (39 μL , 0.28 mmol), and $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (1.3 mg, 1.4 μmol) in DMF (3.0 mL) afforded **S13** (39 mg, 82%) as a colorless solid after purification by chromatography on SiO_2 (7:3, hexanes/EtOAc) (6 h reaction time).

R_f (EtOAc/hexanes 1:3): 0.21;

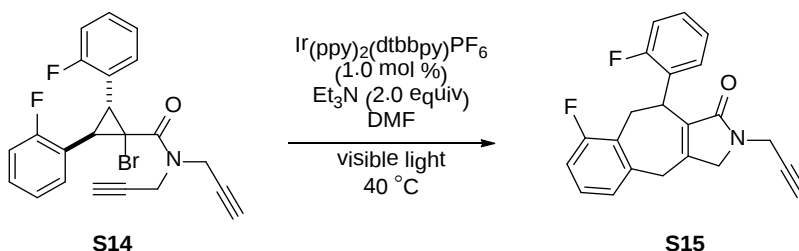
IR (neat): 3286, 3018, 2921, 2857, 1683, 1512, 1454, 1402, 1347, 1306, 1263 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz): 6.95 – 6.98 (m, 2 H), 6.88 (d, $J = 7.6$ Hz, 1 H), 6.83 (d, $J = 8.0$ Hz, 2 H), 6.75 (d, $J = 7.6$ Hz, 1 H), 4.22 (dd, $J = 17.6, 2.4$ Hz, 1 H), 4.04 – 4.11 (m, 2 H), 3.94 – 3.96 (m, 1 H), 3.74 (s, 2 H), 3.29 (dd, $J = 13.8, 4.4$ Hz, 1 H), 3.04 (dd, $J = 13.8, 8.4$ Hz, 1 H), 2.30 (s, 3 H), 2.25 (s, 3 H), 2.21 (t, $J = 2.4$ Hz, 1 H);

^{13}C NMR (CDCl_3 , 125 MHz): 170.8, 148.7, 139.4, 138.4, 136.0, 135.6, 135.2, 133.7, 130.7, 129.1, 128.8, 128.7, 127.6, 127.5, 78.6, 72.9, 53.2, 41.7, 40.3, 33.8, 31.2, 21.1, 20.9;

HRMS (ESI) m/z calculated for $\text{C}_{24}\text{H}_{23}\text{NNaO}^+$ ($[\text{M}+\text{Na}]^+$) 364.1677, found 364.1675.

8-fluoro-10-(2-fluorophenyl)-2-(prop-2-yn-1-yl)-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S15** (Table 1, entry 8):



According to General Procedure A, **S14** (0.10 g, 0.23 mmol), Et_3N (65 μL , 0.47 mmol), and $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (2.1 mg, 2.3 μmol) in DMF (9.0 mL) afforded **S15** (71 mg, 88%) as a colorless solid after purification by chromatography on SiO_2 (2:3, hexanes/EtOAc) (14 h reaction time).

R_f (EtOAc/hexanes 2:3): 0.39;

IR (neat): 3301, 3234, 2924, 1676, 1585, 1488, 1453, 1405, 1246, 1192, 1014 cm^{-1} ;

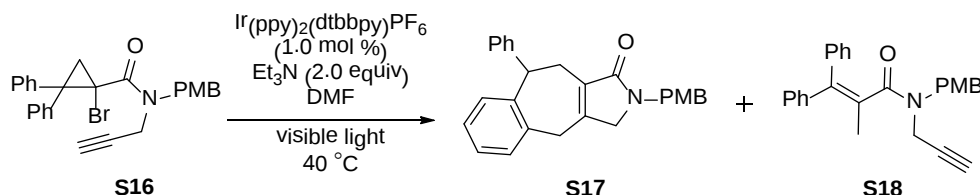
^1H NMR (CDCl_3 , 400 MHz): 7.00 – 7.14 (m, 3 H), 6.93 (d, $J = 7.6$ Hz, 1 H), 6.73 – 6.79 (m, 2 H), 6.41 (t, $J = 7.6$ Hz, 1 H), 4.45 (br s, 1 H), 4.25 (dd, $J = 18.0, 2.8$ Hz, 1 H), 4.10 – 4.15 (m, 3 H), 3.95 (d, $J = 17.2$ Hz, 1 H), 3.67 (d, $J = 17.2$ Hz, 1 H), 3.45 (dd, $J = 14.0, 6.8$ Hz, 1 H), 3.24 (dd, $J = 14.0, 2.8$ Hz, 1 H), 2.25 (t, $J = 2.8$ Hz, 1 H);

^{13}C NMR (CDCl_3 , 100 MHz): 170.2 161.2 (d, $^1J_{\text{C-F}} = 243.9$ Hz), 160.6 (d, $^1J_{\text{C-F}} = 244.6$ Hz), 149.2, 140.8 (d, $^3J_{\text{C-F}} = 3.8$ Hz), 132.9, 128.6 (d, $^3J_{\text{C-F}} = 4.5$ Hz), 127.8 (d, $^2J_{\text{C-F}} = 55.7$ Hz), 127.7 (d, $^2J_{\text{C-F}} = 56.5$ Hz), 125.0, 124.8, 123.4 (d, $^3J_{\text{C-F}} = 3.7$ Hz), 123.3 (d, $^1J_{\text{C-F}} = 3.7$ Hz), 115.1 (d, $^2J_{\text{C-F}} = 21.6$ Hz), 113.9 (d, $^2J_{\text{C-F}} = 23.0$ Hz), 78.3, 72.3, 53.2, 33.9, 33.6, 31.2, 28.3;

HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{NO}^+$ ($[\text{M}+1]^+$) 350.4356, found 350.1355.

2-(4-methoxybenzyl)-9-phenyl-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S17**

N-(4-methoxybenzyl)-2-methyl-3,3-diphenyl-N-(prop-2-yn-1-yl)acrylamide, **S18** (Table 1, entry 9):



According to General Procedure A, **S16** (0.35 g, 0.73 mmol), Et₃N (200 μ L, 1.5 mmol), and Ir(ppy)₂(dtbbpy)PF₆ (6.7 mg, 2.3 μ mol) in DMF (10 mL) afforded **S17** (92 mg, 32%) and **S18** (120 mg, 41%) as a colorless solids after purification by chromatography on SiO₂ (1:9 to 4:6, hexanes/EtOAc) (12 h reaction time).

Data for compound **S17**:

R_f (EtOAc/hexanes 1:3): 0.21;

IR (neat): cm⁻¹ 3432, 3060, 3028, 2911, 2836, 1675, 1611, 1512, 1454, 1246, 1175;

¹H NMR (CDCl₃, 500 MHz): 7.28 (d, *J* = 8.0 Hz, 2 H), 7.22 – 7.24 (m, 3 H), 7.08 – 7.14 (m, 4 H), 7.01 (dd, *J* = 7.0, 2.0 Hz, 1 H), 6.90 (dd, *J* = 7.0, 2.0 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 2 H); 4.59 (dd, *J* = 8.0, 3.0 Hz, 1 H), 4.57 (d, *J* = 14.5 Hz, 1 H), 4.49 (d, *J* = 14.5 Hz, 1 H), 3.77 (s, 3 H), 3.76 – 3.70 (m, 2 H), 3.63 (dt, *J* = 18.5, 2.0 Hz, 1 H), 3.15 (d, *J* = 17.0 Hz, 1 H), 3.11 – 3.05 (m, 1 H), 2.95 (dd, *J* = 17.0, 2.0 Hz, 1 H);

¹³C NMR (CDCl₃, 125 MHz): 172.0, 159.0, 146.5, 144.1, 142.1, 137.8, 131.1, 129.5, 129.4, 129.1, 128.7, 128.4, 127.9, 127.3, 126.5, 126.4, 114.0, 55.2, 53.3, 45.7, 45.4, 34.0, 38.6;

HRMS (ESI) *m/z* calculated for C₂₇H₂₆NO₂⁺ ([M+1]⁺) 396.1964, found 396.1971.

Data for compound **S18** (3:2 mixture of conformational isomers):

R_f (EtOAc/hexanes 1:3): 0.48;

IR (neat): cm⁻¹ 3288, 3237, 3056, 2997, 2835, 1632, 1612, 1453, 1441, 1412, 1302, 1245, 1174, 1134, 1033;

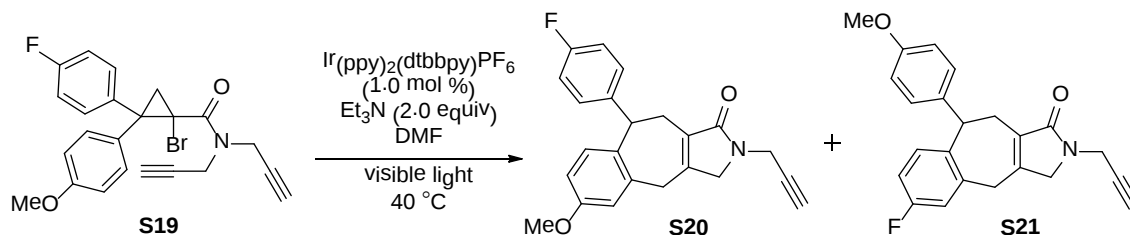
¹H NMR (CDCl₃, 500 MHz): 7.32 – 7.28 (m, 4 H), 7.26 – 7.20 (m, 9 H), 7.19 – 7.15 (m, 5 H), 7.12 – 7.10 (m, 2 H), 6.86 (d, *J* = 8.5 Hz, 2 H), 6.77 (d, *J* = 8.5 Hz, 2 H), 6.65 (br s, 4 H), 5.10 (d, *J* = 15.5 Hz, 1 H), 4.64 (d, *J* = 15.5 Hz, 1 H), 4.29 (d, *J* = 18.0 Hz, 1 H), 4.25 (d, *J* = 18.0 Hz, 1 H), 4.03 – 3.98 (m, 2 H), 3.77 (s, 3 H), 3.75 (s, 3 H), 3.65 (br d, *J*

= 18.0 Hz, 1 H), 3.35 (d, J = 18.0 Hz, 1 H), 2.25 (t, J = 2.5 Hz, 1 H), 2.09 (s, 3 H), 1.98 (s, 3 H), 1.98 (t, J = 2.5 Hz, 1 H);

^{13}C NMR (CDCl_3 , 125 MHz): 172.7, 172.4, 159.2, 158.8, 140.8, 140.7, 140.6, 140.4, 140.2, 139.7, 130.3, 129.7, 129.6, 129.5, 129.2, 129.1, 129.0, 128.3, 128.2, 128.2, 128.2, 127.8, 127.8, 127.5, 127.4, 127.4, 127.3, 114.1, 113.8, 78.4, 77.9, 72.7, 71.7, 55.3, 55.2, 50.1, 45.7, 36.1, 32.3, 19.6, 18.9;

HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{26}\text{NO}_2^+$ ($[\text{M}+1]^+$) 396.1964, found 396.1958.

9-(4-fluorophenyl)-6-methoxy-2-(prop-2-yn-1-yl)-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S20**
 6-fluoro-9-(4-methoxyphenyl)-2-(prop-2-yn-1-yl)-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S21** (Table 1, entry 10):



According to General Procedure A, **S19** (56 mg, 0.13 mmol), Et₃N (35 μ L, 0.25 mmol), and Ir(ppy)₂(dtbbpy)PF₆ (1.2 mg, 1.3 μ mol) in DMF (2.0 mL) afforded **S17** and **S21** (31 mg, 66%) as an inseparable mixture of colorless solids after purification by chromatography on SiO₂ (1:9 to 2:8, hexanes/acetone) (10 h reaction time).

R_f (acetone/hexanes 2:8): 0.23;

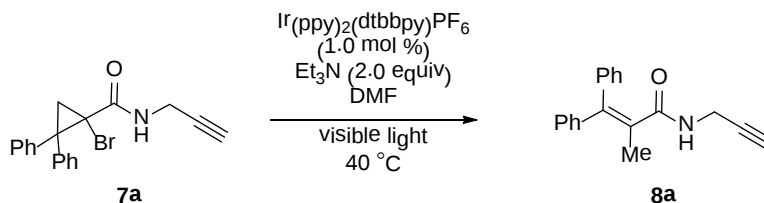
IR (neat): cm⁻¹ 3297, 3229, 2908, 2837, 1677, 1610, 1511, 1454, 1430, 1250, 1181, 1100;

¹H NMR (CDCl₃, 500 MHz): 7.22 – 7.19 (m, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 7.01 (t, *J* = 9.0 Hz, 2 H), 6.88 – 6.85 (m, 3 H), 6.84 – 6.82 (m, 3 H), 6.71 – 6.68 (m, 2 H), 4.55 – 4.51 (m, 2 H), 4.33 – 4.22 (m, 4 H), 4.02 (br d, *J* = 18.5 Hz, 2 H), 3.91 (br d, *J* = 18.5 Hz, 2 H), 3.85 – 3.76 (m, 2 H), 3.83 (s, 3 H), 3.79 (s, 3 H), 3.27 – 3.21 (m, 2 H), 3.05 – 2.97 (m, 2 H), 2.92 – 2.88 (m, 2 H), 2.27 – 2.26 (m, 2 H);

¹³C NMR (CDCl₃, 125 MHz): 171.6, 171.5, 161.5 (d, ¹*J*_{C-F} = 432.9 Hz), 161.12 (d, ¹*J*_{C-F} = 244.3 Hz), 158.3, 158.1, 147.0, 146.4, 146.0 (d, ⁴*J*_{C-F} = 3.3 Hz), 139.5 (d, ³*J*_{C-F} = 7.4 Hz), 138.8, 138.1 (d, ⁴*J*_{C-F} = 3.3 Hz), 135.9, 133.9, 115.7 (d, ²*J*_{C-F} = 21.8 Hz), 115.3, 115.2 (d, ²*J*_{C-F} = 21.3 Hz), 113.9, 113.5 (d, ²*J*_{C-F} = 20.4 Hz), 111.5, 131.1, 130.8, 130.5 (d, ³*J*_{C-F} = 8.3 Hz), 130.1, 129.3 (d, ³*J*_{C-F} = 7.9 Hz), 128.8, 78.4, 78.4, 72.3, 72.2, 55.2, 53.1, 53.1, 44.2, 44.1, 34.2, 33.9, 31.4, 29.0, 28.9;

HRMS (ESI) *m/z* calculated for C₂₃H₂₁FNO₂⁺ ([M+1]⁺) 362.1556, found 362.1559.

2-methyl-3,3-diphenyl-N-(prop-2-yn-1-yl)acrylamide, **8a** (Figure 1,A):



According to General Procedure A, **7a** (0.10 g, 0.28 mmol), Et_3N (79 μL , 0.57 mmol), and $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (2.7 mg, 2.8 μmol) in DMF (10 mL) afforded **8a** (72 mg, 94%) as a colorless solid after purification by chromatography on SiO_2 (1:3, hexanes/EtOAc) (14 h reaction time).

R_f (EtOAc/hexanes 1:3): 0.38;

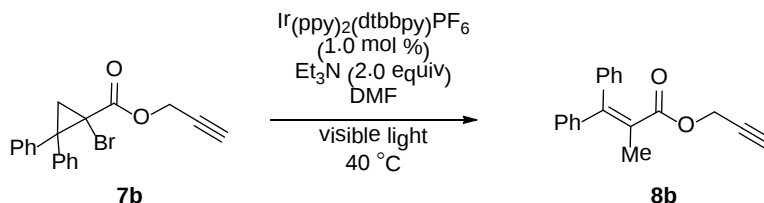
IR (neat): 3296, 3055, 2920, 1645, 1529, 1492, 1442 cm^{-1} ;

^1H NMR (CDCl_3 , 500 MHz): 7.30 – 7.33 (m, 2 H), 7.22 – 7.27 (m, 4 H), 7.15 (d, $J = 7.0$ Hz, 2 H), 7.11 (d, $J = 7.0$ Hz, 2 H), 5.25 (br s, 1 H), 3.79 (dd, $J = 5.5, 2.5$ Hz, 2H), 2.04 (t, $J = 2.5$ Hz, 1 H), 2.02 (s, 3 H);

^{13}C NMR (CDCl_3 , 100 MHz): 171.3, 142.7, 141.1, 140.7, 132.1, 129.5, 128.9, 128.4, 128.2, 127.8, 127.5, 78.9, 71.4, 29.1, 18.6;

HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{14}\text{NNaO}^+$ ($[\text{M}+\text{Na}]^+$) 276.1388, found 276.1391.

Prop-2-yn-1-yl 2-methyl-3,3-diphenylacrylate, **8b** (Figure 1,A):



According to General Procedure A, **7a** (0.87 g, 2.5 mmol), Et_3N (1.3 mL, 4.9 mmol), and $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (22 mg, 25 μmol) in DMF (10 mL) afforded **8a** (0.55 g, 88%) as a colorless solid after purification by chromatography on SiO_2 (98:2 to 9:1, hexanes/ EtOAc) (8 h reaction time).

R_f (EtOAc /hexanes 1:9): 0.44;

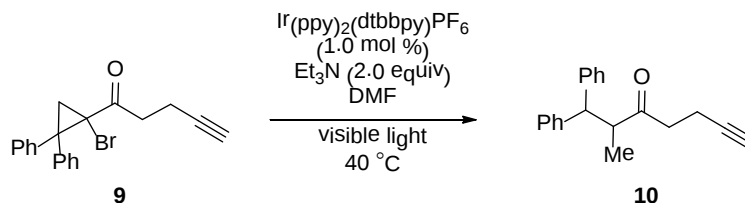
IR (neat): 3290, 3057, 3025, 2946, 1717, 1492, 1443, 1332, 1242, 1116 cm^{-1} ;

^1H NMR (CDCl_3 , 500 MHz): 7.34 (t, $J = 7.0$ Hz, 2 H), 7.25 – 7.31 (m, 4 H), 7.17 (d, $J = 7.0$ Hz, 2 H), 7.13 (d, $J = 6.0$ Hz, 2 H), 4.52 (d, $J = 2.5$ Hz, 2 H), 2.39 (t, $J = 2.5$ Hz, 1 H), 2.08 (s, 3 H);

^{13}C NMR (CDCl_3 , 125 MHz): 170.1, 148.0, 142.1, 140.6, 129.5, 128.7, 128.4, 128.1, 128.0, 127.7, 127.6, 77.3, 76.7, 74.7, 51.9, 18.4;

HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{17}\text{O}_2^+$ ($[\text{M}+1]^+$) 277.1229, found 277.1232.

2-methyl-1,1-diphenylhept-6-yn-3-one, **10** (Figure 1,B):



According to General Procedure A, **9** (99 mg, 0.28 mmol), Et_3N (78 μL , 0.56 mmol), and $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (2.6 mg, 2.8 μmol) in DMF (8.0 mL) afforded **10** (56 mg, 74%) as a colorless oil after purification by chromatography on SiO_2 (19:1, hexanes/ EtOAc) (24 h reaction time).

R_f (EtOAc /hexanes 1:9): 0.38;

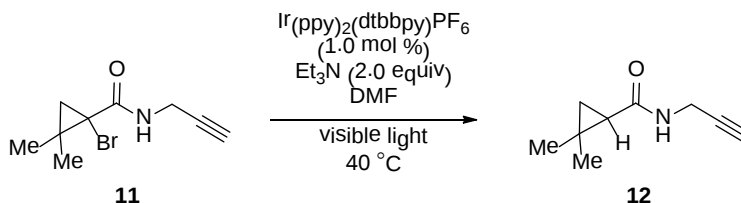
IR (neat): 3291, 3061, 3027, 2967, 2929, 2875, 1712, 1597, 1493, 1451, 1373, 1079 cm^{-1} ;

^1H NMR (CDCl_3 , 500 MHz): 7.26 – 7.29 (m, 4 H), 7.23 – 7.25 (m, 4 H), 7.17 – 7.20 (m, 1 H), 7.12 – 7.15 (m, 1 H), 4.12 (d, J = 12 Hz, 1 H), 3.48 – 3.54 (m, 1 H), 2.67 (ddd, J = 14.5, 8.5, 6.0 Hz, 1 H), 2.39 (ddd, J = 18.0, 8.5, 6.0 Hz, 1 H), 2.26 – 2.32 (m, 1 H), 2.18 – 2.24 (m, 1 H), 1.89 (t, J = 2.5 Hz, 1 H), 1.07 (d, J = 7.0 Hz, 3 H);

^{13}C NMR (CDCl_3 , 125 MHz): 211.4, 143.1, 142.2, 128.7, 128.1, 127.7, 126.6, 126.6, 83.1, 68.4, 54.6, 50.7, 41.2, 16.4, 12.6;

HRMS (ESI) m/z calculated for $\text{C}_{20}\text{H}_{21}\text{O}^+$ ($[\text{M}+1]^+$) 277.1592, found 277.1589.

2,2-dimethyl-N-(prop-2-yn-1-yl)cyclopropanecarboxamide, **12** (Figure 1,C):



According to General Procedure A, **9** (0.15 g, 0.41 mmol), Et_3N (0.11 mL, 0.82 mmol), and $\text{Ir(ppy)}_2(\text{dtbbpy})\text{PF}_6$ (3.7 mg, 4.1 μmol) in DMF (15 mL) afforded **12** (56 mg, 94%) as a colorless oil after purification by chromatography on SiO_2 (2:1, hexanes/ EtOAc) (11 h reaction time).

R_f (EtOAc /hexanes 3:17): 0.13;

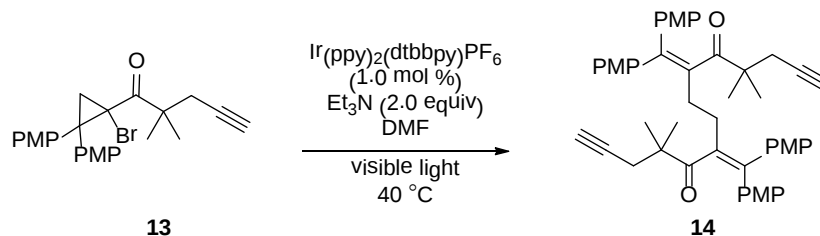
IR (neat): 3296, 3071, 2998, 2949, 2870, 1643, 1534, 1436, 1404, 1276, 1221, 1122 cm^{-1} ;

^1H NMR (CDCl_3 , 400 MHz): 5.74 (br s, 1 H), 4.00 – 4.12 (m, 2 H), 2.22 (t, J = 2.4 Hz, 1H), 1.25 (dd, J = 8.0, 5.6 Hz, 1 H), 1.18 (s, 3 H), 1.11 – 1.13 (m, 4 H), 0.76 (dd, J = 8.0, 4.4 Hz, 1 H);

^{13}C NMR (CDCl_3 , 75 MHz): 171.2, 80.0, 71.3, 29.3, 28.7, 27.0, 21.9, 20.4, 18.6;

HRMS (ESI) m/z calculated for $\text{C}_9\text{H}_{14}\text{NO}^+$ ($[\text{M}+1]^+$) 152.1075, found 152.1077.

Dimer **14** (Figure 1,D):



According to General Procedure A, **13** (0.20 g, 0.44 mmol), Et₃N (0.12 mL, 0.89 mmol), and Ir(ppy)₂(dtbbpy)PF₆ (4.1 mg, 4.4 μmol) in DMF (15 mL) afforded **14** (94 mg, 79%) as a colorless solid after purification by chromatography on SiO₂ (4:1, hexanes/EtOAc) (11 h reaction time).

R_f (EtOAc/hexanes 1:3): 0.36;

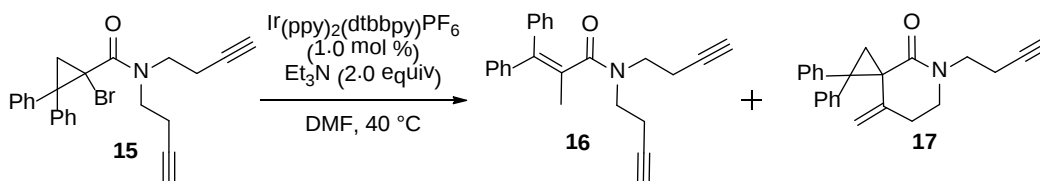
IR (neat): 3296, 2966, 2934, 2836, 1479, 1605, 1508, 1464, 1280, 1244, 1173, 1033 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 6.93 (d, *J* = 8.5 Hz, 4 H), 6.92 (d, *J* = 8.5 Hz, 4 H), 6.77 (d, *J* = 8.5 Hz, 4 H), 6.70 (d, *J* = 8.5 Hz, 4 H), 3.83 (s, 6 H), 3.75 (s, 6 H), 2.39 (br s, 4 H), 2.03 (br d, *J* = 2.5 Hz, 4 H), 1.95 (t, *J* = 2.5 Hz, 2 H);

¹³C NMR (CDCl₃, 100 MHz): 215.4, 159.0, 158.6, 138.8, 137.5, 134.3, 132.8, 131.5, 130.3, 113.6, 113.3, 81.5, 70.6, 55.1, 46.9, 31.6, 29.0, 24.4;

HRMS (ESI) *m/z* calculated for C₄₈H₅₁O₆⁺ ([M+1]⁺) 723.3686, found 723.3689.

N,N-di(but-3-yn-1-yl)-2-methyl-3,3-diphenylacrylamide, **16**;
 5-(but-3-yn-1-yl)-8-methylene-1,1-diphenyl-5-azaspiro[2.5]octan-4-one, **17** (Figure 1,E):



According to General Procedure A, **15** (0.12 g, 0.28 mmol), Et₃N (80 μ L, 0.57 mmol), and Ir(ppy)₂(dtbbpy)PF₆ (2.5 mg, 2.8 μ mol) in DMF (7.0 mL) afforded **16** (41 mg, 44%) and **17** (34 mg, 36%) as a colorless solids after purification by chromatography on SiO₂ (9:1 to 7:3, hexanes/EtOAc) (12 h reaction time).

Data for compound 16:

R_f (EtOAc/hexanes 3:7): 0.45;

IR (neat): 3293, 3055, 3027, 2919, 1615, 1492, 1442, 1418, 1370, 1254, 1152, 1058 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 7.34 – 7.37 (m, 2 H), 7.28 – 7.31 (m, 2 H), 7.21 – 7.25 (m, 4 H), 7.16 – 7.18 (m, 2 H), 3.64 – 3.76 (m, 2 H), 3.09 – 3.14 (m, 2 H), 2.26 – 2.34 (m, 2 H), 2.06 (s, 3 H), 1.99 – 2.10 (m, 3 H), 1.90 (t, *J* = 3.0 Hz, 1 H);

¹³C NMR (CDCl₃, 125 MHz): 172.8, 140.8, 140.5, 139.9, 130.1, 129.6, 129.2, 128.2, 128.1, 127.7, 127.4, 81.6, 80.7, 70.6, 69.6, 47.5, 43.5, 19.8, 18.6, 16.6;

HRMS (ESI) *m/z* calculated for C₂₄H₂₄NO⁺ ([M+1]⁺) 342.1858, found 342.1852.

Data for compound 17:

R_f (EtOAc/hexanes 3:7): 0.43;

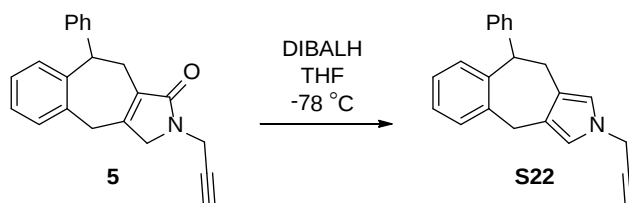
IR (neat): 3294, 3058, 3022, 2939, 1641, 1476, 1418, 1368, 1251, 1161 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 7.48 – 7.49 (m, 2 H), 7.26 – 7.32 (m, 4 H), 7.18 – 7.23 (m, 3 H), 7.12 – 7.14 (m, 1 H), 5.65 – 5.69 (m, 1 H), 4.86 (dt, *J* = 11.0, 2.0 Hz, 1 H), 4.47 (t, *J* = 14.0 Hz, 1 H), 3.78 – 3.84 (m, 1 H), 3.4 (d, *J* = 11.0 Hz, 1 H), 3.06 (d, *J* = 5.0 Hz, 1 H), 2.91 – 2.96 (m, 1 H), 2.47 – 2.55 (m, 1 H), 2.34 – 2.41 (m, 1 H), 1.95 (t, *J* = 2.0 Hz, 1 H), 1.90 – 1.94 (m, 1 H), 1.77 – 1.84 (m, 1 H), 1.56 (d, *J* = 5.0 Hz, 1 H);

¹³C NMR (CDCl₃, 125 MHz): 170.4, 142.3, 139.9, 130.5, 130.0, 128.7, 128.4, 128.2, 128.1, 126.7, 126.5, 82.3, 69.5, 47.2, 46.6, 44.8, 39.2, 28.8, 27.4, 17.3;

HRMS (ESI) *m/z* calculated for C₂₄H₂₄NO⁺ ([M+1]⁺) 342.1858, found 342.1855.

9-phenyl-2-(prop-2-yn-1-yl)-2,4,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrole, **S22** (Scheme 5):



A flame dried 25 mL round bottom flask, equipped with a magnetic stir bar was charged with **5** (0.15 g, 0.48 mmol), THF (9 mL) and cooled to -78 °C. The mixture was then treated dropwise with DIBAL-H (0.17 mL, 0.96 mmol). After completion of the reaction (as judged by TLC analysis) the mixture was quenched by the addition of 2 N aq. NaOH (1.0 mL) at -78 °C and allowed to warm to room temperature. The mixture was poured into a separatory funnel containing 25 mL of Et₂O and 25 mL of H₂O. The layers were separated and the aqueous layer was extracted with Et₂O (2 X 30 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. The residue was purified by chromatography on silica gel (19:1, hexanes/EtOAc) to afford **S22** (0.11 g, 80%) as a colorless oil (2.5 h reaction time).

R_f (EtOAc/hexane 1:9): 0.54;

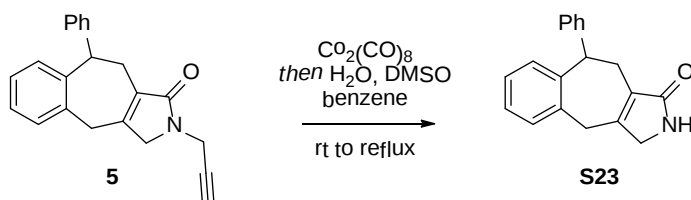
IR (neat): 3282, 3060, 3026, 2903, 2843, 1708, 1600, 1528, 1495, 1448, 1390, 1145 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): δ 7.33 - 7.38 (m, 3 H), 7.26 - 7.29 (m, 1 H), 1.17 (dd, J = 7.0, 1.5 Hz, 1 H), 7.03 - 7.10 (m, 2 H), 6.78 (dd, J = 7.5, 2.0 Hz, 1 H), 6.55 (d, J = 2.5 Hz, 1 H), 6.51 (d, J = 2.5 Hz, 1 H), 4.76 (dd, J = 11.0, 3.5 Hz, 1 H), 4.57 (d, J = 2.5 Hz, 1 H), 4.56 - 4.23 (d, J = 15.0 Hz, 1 H), 3.61 (d, J = 15.0 Hz, 1 H), 3.24 - 3.47 (m, 2 H), 2.42 (t, J = 2.5 Hz, 1 H), ;

¹³C NMR (CDCl₃, 100 MHz): δ 144.4, 144.0, 140.8, 128.5, 128.3, 128.0, 128.0, 126.4, 126.2, 126.2, 119.9, 119.7, 119.0, 116.7, 78.3, 73.4, 45.7, 38.4, 32.6, 30.2;

HRMS (ESI) m/z calculated for C₂₂H₂₀N⁺ ($[M+1]^+$) 298.1596, found 298.1589.

9-phenyl-2,3,9,10-tetrahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-1(4H)-one, **S23** (Scheme 5):



A flame dried 25 mL round bottom flask, equipped with a magnetic stir bar and fitted with a reflux condenser was charged with **5** (0.27 g, 0.85 mmol), benzene (17 mL) and treated with $\text{Co}_2(\text{CO})_8$. After consumption of **5** (as judged by TLC analysis) H_2O (46 μL , 2.6 mmol) and DMSO (0.18 mL, 2.6 mmol) was added and the mixture heated to reflux. After completion of the reaction, the solvent was evaporated and the residue was purified by chromatography on silica gel (19:1, DCM/MeOH) to afford **S23** (0.16 g, 62%) as a colorless solid (12 h reaction time).

R_f (MeOH/DCM 5:95): 0.28;

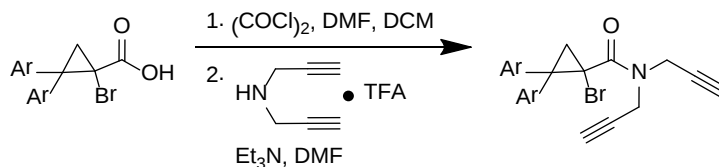
IR (neat): 3315, 3060, 2919, 1679, 1449, 1408 cm^{-1} ;

^1H NMR (CDCl_3 , 500 MHz): δ 7.31 – 7.24 (m, 2 H), 7.25 – 7.27 (m, 3 H), 7.16 – 7.23 (m, 2 H), 7.09 – 7.11 (m, 1 H), 6.95 – 6.96 (m, 1 H), 5.98 (br s, 1 H), 4.63 (dd, J = 9.5, 3.5 Hz, 1 H), 3.95 (d, J = 18.5 Hz, 1 H), 3.87 (d, J = 15.5 Hz, 1 H), 3.84 (d, J = 15.5 Hz, 1 H), 3.27 (d, J = 17.5 Hz, 1 H), 3.09 (dd, J = 17.5, 9.0 Hz, 1 H), 2.95 (d, J = 17.5 Hz, 1 H), ;

^{13}C NMR (CDCl_3 , 125 MHz): δ 175.3, 149.7, 144.0, 142.0, 137.6, 129.2, 128.8, 128.4, 127.9, 127.4, 126.6, 126.5, 49.5, 45.6, 34.3, 28.2;

HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{18}\text{NO}^+$ ($[\text{M}+1]^+$) 276.1388, found 276.1389.

General Procedure B: Typical Substrate Synthesis

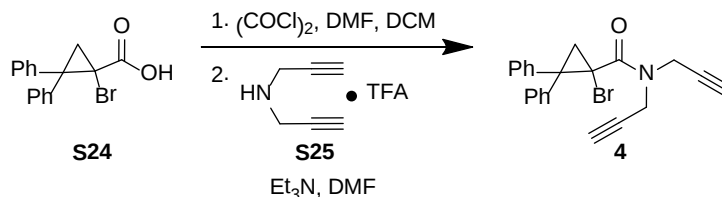


A flame dried 25 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with bromocyclopropyl carboxylate (1.0 mmol, 1.0 equiv), DMF (5 – 10 drops), DCM (8 mL) and cooled to 0 °C. The mixture is then treated with oxalyl chloride (1.5 mmol, 1.5 equiv) and stirred for 15 min at 0 °C then warmed to room temperature and stirred for another 2 h. The solvent was then removed and the acyl chloride used immediately.

A separate flame dried 25 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with dipropargylamine TFA salt (1.5 mmol, 1.5 equiv),¹ DMF (5 mL), and Et₃N (2.5 mmol, 2.5 equiv). This mixture was treated with a solution of the acyl chloride in DMF (5 mL) at room temperature. After the reaction was complete (as judged by TLC analysis), the mixture was poured into a separatory funnel containing 25 mL of EtOAc and 50 mL of H₂O. The layers were separated and the aqueous layer was extracted with EtOAc (2 X 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. The residue was purified by chromatography on silica gel, using the solvent system indicated, to afford the desired bromocyclopropyl amide.

¹ Krasia, T. C.; Steinke, J. H. G. *Chem. Commun.* **2002**, 1, 22.

1-bromo-2,2-diphenyl-N,N-di(prop-2-yn-1-yl)cyclopropanecarboxamide, **4**:



According to General Procedure B, **S24** (1.3 g, 4.2 mmol), DMF (10 drops), oxalyl chloride (0.54 mL, 6.4 mmol) in DCM (31 mL) afforded the acyl chloride. Treatment of this acyl chloride with **S25** (1.3 g, 6.3 mmol) and Et₃N (1.5 mL, 11 mmol) in DMF (40 mL) afforded **4** (1.4 g, 82%) as a yellow solid after purification by chromatography on SiO₂ (17:3 to 3:1, hexanes/EtOAc) (12 h reaction time).

R_f (EtOAc/hexanes 3:17): 0.33;

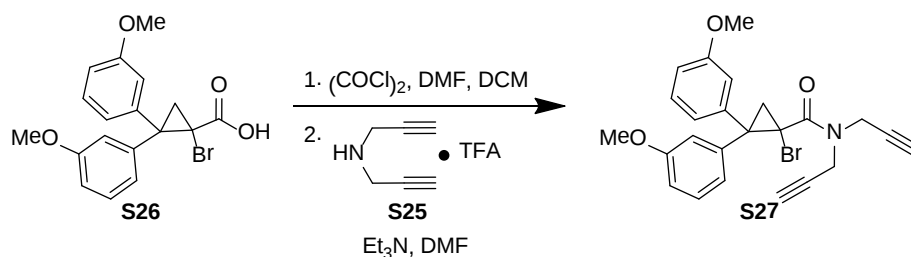
IR (neat): 2395, 3059, 1653, 1495, 1445, 1414, 1230 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 7.51 (d, *J* = 5.0 Hz, 2 H), 7.43 (t, *J* = 7.5 Hz, 2 H), 7.38 (t, *J* = 7.0 Hz, 1 H), 7.12 – 7.21 (m, 5 H), 4.77 (d, *J* = 17.5 Hz, 1 H), 4.42 (d, *J* = 17.0 Hz, 1 H), 4.09 (dd, *J* = 17.5, 2.5 Hz, 1 H), 3.97 (dd, *J* = 17.5, 2.5 Hz, 1 H), 2.99 (d, *J* = 7.5 Hz, 1 H), 2.33 (t, *J* = 2.5 Hz, 1 H), 2.03 (t, *J* = 2.5 Hz, 1 H), 2.02 (d, *J* = 7.5 Hz, 1 H);

¹³C NMR (CDCl₃, 100 MHz): 165.1, 140.5, 137.4, 130.4, 128.4, 128.3, 127.5, 127.4, 127.0, 77.0, 76.6, 73.7, 72.0, 42.0, 38.8, 37.3, 33.6, 37.7;

HRMS (ESI) *m/z* calculated for C₂₂H₁₉BrNO⁺ ([M+1]⁺) 392.0650, found 392.0651.

1-bromo-2,2-bis(3-methoxyphenyl)-N,N-di(prop-2-yn-1-yl)cyclopropanecarboxamide, **S27**:



According to General Procedure B, **S26** (1.3 g, 3.4 mmol), DMF (10 drops), oxalyl chloride (0.44 mL, 5.2 mmol) in DCM (21 mL) afforded the acyl chloride. Treatment of this acyl chloride with **S25** (1.1 g, 5.2 mmol) and Et₃N (1.4 mL, 10 mmol) in DMF (22 mL) afforded **S27** (1.0 g, 66%) as a yellow solid after purification by chromatography on SiO₂ (17:3 to 4:1, hexanes/EtOAc) (12 h reaction time).

R_f (EtOAc/hexanes 1:4): 0.29;

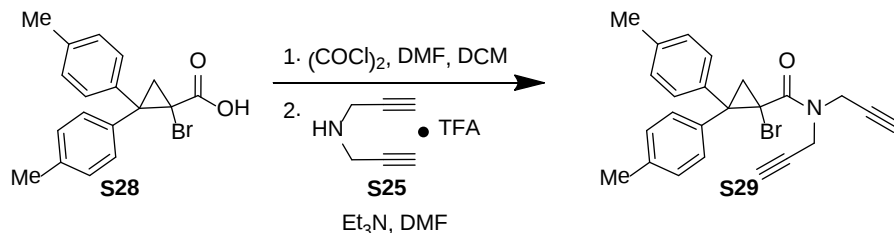
IR (neat): 3293, 3054, 3000, 2835, 1651, 1598, 1431, 1287, 1215 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 7.35 (t, *J* = 7.5 Hz, 1 H), 7.10 (t, *J* = 8.0 Hz, 2 H), 7.01 (t, *J* = 2.0 Hz, 1 H), 6.89 (dd, *J* = 8.5, 3.0 Hz, 1 H), 6.74 (d, *J* = 8.5 Hz, 1 H), 6.68 – 6.69 (m, 2 H), 4.74 (d, *J* = 17.5 Hz, 1 H), 4.45 (d, *J* = 17.5 Hz, 1 H), 4.05 (dd, *J* = 17.5, 2.5 Hz, 1 H), 3.96 (dd, *J* = 17.5, 2.5 Hz, 1 H), 3.85 (s, 3 H), 3.73 (s, 3 H), 2.94 (d, *J* = 7.5 Hz, 1 H), 2.33 (t, *J* = 2.5 Hz, 1 H), 2.05 (t, *J* = 2.5 Hz, 1 H), 2.00 (d, *J* = 7.5 Hz, 1 H);

¹³C NMR (CDCl₃, 100 MHz): 165.0, 159.3, 159.3, 141.7, 138.8, 129.2, 129.1, 122.6, 119.7, 116.5, 113.1, 112.6, 112.4, 76.9, 76.5, 73.7, 71.9, 55.0, 54.8, 41.8, 38.8, 37.2, 33.5, 33.5, 27.9;

HRMS (ESI) *m/z* calculated for C₂₄H₂₃BrNO₃⁺ ([*M*+1]⁺) 452.0861, found 452.0857.

1-bromo-N,N-di(prop-2-yn-1-yl)-2,2-di-p-tolylcyclopropanecarboxamide, **S9**:



According to General Procedure B, **S28** (0.79 g, 2.3 mmol), DMF (5 drops), oxalyl chloride (0.29 mL, 3.4 mmol) in DCM (15 mL) afforded the acyl chloride. Treatment of this acyl chloride with **S25** (0.80 g, 4.6 mmol) and Et₃N (1.3 mL, 9.2 mmol) in DMF (20 mL) afforded **S29** (0.74 g, 77%) as a yellow solid after purification by chromatography on SiO₂ (19:1 to 17:3, hexanes/EtOAc) (8 h reaction time).

R_f (EtOAc/hexanes 1:4): 0.51;

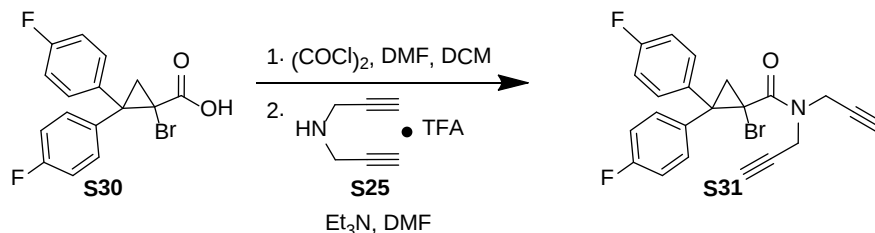
IR (neat): 3299, 3027, 2921, 1651, 1513, 1439, 1414, 1230, 1182, 1011 cm⁻¹

¹H NMR (CDCl₃, 500 MHz): 7.38 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.99 (d, *J* = 8.0 Hz, 2 H); 4.77 (d, *J* = 17.5 Hz, 1 H), 4.44 (d, *J* = 17.5 Hz, 1 H), 4.05 (dd, *J* = 17.5, 2.0 Hz, 1 H), 3.95 (dd, *J* = 17.5, 2.0 Hz, 1 H), 2.93 (d, *J* = 7.5 Hz, 1 H), 2.40 (s, 3 H), 2.33 (t, *J* = 2.0 Hz, 1 H), 2.25 (s, 3 H), 2.01 (t, *J* = 3.0 Hz, 1 H), 1.96 (d, *J* = 7.0 Hz, 1 H);

¹³C NMR (CDCl₃, 125 MHz): 165.4, 137.9, 137.1, 136.6, 134.7, 130.1, 129.1, 129.0, 127.3, 77.2, 76.8, 73.7, 71.7, 41.5, 39.0, 37.4, 33.6, 27.7, 21.1, 20.8;

HRMS (ESI) *m/z* calculated for C₂₄H₂₃BrNO⁺ ([M+1]⁺) 420.0963, found 420.0974.

1-bromo-2,2-bis(4-fluorophenyl)-N,N-di(prop-2-yn-1-yl)cyclopropanecarboxamide, **S31**:



According to General Procedure B, **S30** (1.0 g, 2.8 mmol), DMF (5 drops), oxalyl chloride (0.36 mL, 4.3 mmol) in DCM (17 mL) afforded the acyl chloride. Treatment of this acyl chloride with **S25** (0.88 g, 4.3 mmol) and Et_3N (1.2 mL, 8.5 mmol) in DMF (25 mL) afforded **S31** (0.86 g, 71%) as a yellow solid after purification by chromatography on SiO_2 (17:3 to 3:1, hexanes/ EtOAc) (8 h reaction time).

R_f (EtOAc /hexanes 3:17): 0.30;

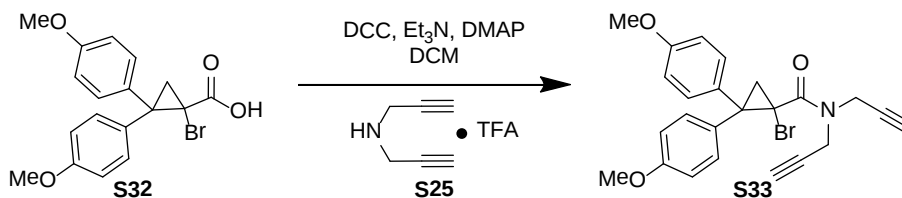
IR (neat): 3299, 1650, 1602, 1508, 1414, 1225, 1161 cm^{-1}

^1H NMR (CDCl_3 , 500 MHz): 7.46 (dd, $J = 9.0, 5.0$ Hz, 2 H), 7.10 – 7.14 (m, 4 H), 6.89 (t, $J = 8.5$ Hz, 2 H), 4.69 (d, $J = 17.5$ Hz, 1 H), 4.42 (d, $J = 17.5$ Hz, 1 H), 4.09 (dd, $J = 17.5, 2.5$ Hz, 1 H), 3.95 (dd, $J = 17.5, 2.5$ Hz, 1 H); 2.96 (d, $J = 7.0$ Hz, 1 H), 2.35 (t, $J = 2.5$ Hz, 1 H), 2.07 (t, $J = 2.5$ Hz, 1 H), 1.97 (d, $J = 7.0$ Hz, 1 H);

^{13}C NMR (CDCl_3 , 100 MHz): 164.7, 161.8 (d, $^1J_{\text{C-F}} = 246.1$ Hz), 161.7 (d, $^1J_{\text{C-F}} = 235.2$ Hz), 136.3 (d, $^3J_{\text{C-F}} = 2.9$ Hz), 133.0 (d, $^3J_{\text{C-F}} = 3.0$ Hz), 131.9 (d, $^3J_{\text{C-F}} = 8.1$ Hz), 129.2 (d, $^3J_{\text{C-F}} = 8.1$ Hz), 115.44 (d, $^2J_{\text{C-F}} = 30.5$ Hz), 115.23 (d, $^2J_{\text{C-F}} = 29.7$ Hz), 77.0, 76.4, 73.9, 72.0, 40.6, 38.5, 37.3, 33.7, 28.0;

HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{17}\text{BrF}_2\text{NO}^+$ ($[\text{M}+1]^+$) 428.0462, found 428.0462.

1-bromo-2,2-bis(4-methoxyphenyl)-N,N-di(prop-2-yn-1-yl)cyclopropanecarboxamide, **S27**:



A flame dried 50 mL round bottom flask, equipped with a magnetic stir bar was charged with **S32** (1.1 g, 2.9 mmol), **S25** (0.73 g, 3.5 mmol), Et₃N (1.0 mL, 7.3 mmol), DMAP (35 mg, 0.29 mmol) and DCM (25 mL). The mixture was then treated with DCC (640 mg, 3.0 mmol). After consumption of the reaction (as judged by TLC analysis) the mixture was filtered into a separatory funnel containing 25 mL of DCM and 50 mL of H₂O. The layers were separated and the aqueous layer was extracted with DCM (2 X 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. The residue was purified by chromatography on silica gel (17:3 to 3:1, hexanes/EtOAc) to afford **S33** (0.50 g, 38%) as a colorless solid (12 h reaction time).

R_f (EtOAc/hexanes 35:65): 0.47;

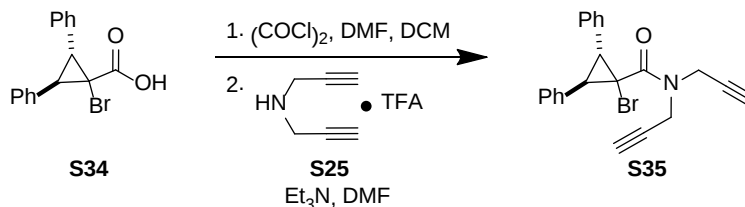
IR (neat): 3291, 3005, 2934, 2836, 1651, 1511, 1440, 1413, 1247, 1034 cm⁻¹

¹H NMR (CDCl₃, 500 MHz): 7.40 (d, *J* = 9.0 Hz, 2 H), 7.05 (d, *J* = 9.0 Hz, 2 H), 6.95 (d, *J* = 9.0 Hz, 2 H), 6.71 (d, *J* = 9.0 Hz, 2 H), 4.74 (d, *J* = 18.5 Hz, 1 H), 4.42 (d, *J* = 17.5 Hz, 1 H), 4.02 (dd, *J* = 17.5, 2.0 Hz, 1 H), 3.92 (dd, *J* = 17.5, 2.0 Hz, 1 H), 3.83 (s, 3 H), 3.71 (s, 3 H), 2.89 (d, *J* = 7.5 Hz, 1 H), 2.31 (t, *J* = 2.0 Hz, 1 H), 2.00 (t, *J* = 2.0 Hz, 1 H), 1.90 (d, *J* = 7.5 Hz, 1 H);

¹³C NMR (CDCl₃, 100 MHz): 165.3, 158.6, 158.4, 133.0, 131.3, 129.7, 128.5, 113.7, 113.6, 77.2, 76.7, 73.7, 71.8, 55.1, 55.0, 40.7, 39.1, 37.3, 33.5, 27.7;

HRMS (ESI) *m/z* calculated for C₂₄H₂₃BrNO₃⁺ ([M+1]⁺) 452.0861, found 452.0847.

1-bromo-trans-2,3-diphenyl-N,N-di(prop-2-yn-1-yl)cyclopropanecarboxamide, **S35**:



According to General Procedure B, **S34** (2.5 g, 8.0 mmol), DMF (10 drops), oxalyl chloride (1.0 mL, 12 mmol) in DCM (45 mL) afforded the acyl chloride. Treatment of this acyl chloride with **S25** (2.5 g, 12 mmol) and Et_3N (3.4 mL, 24 mmol) in DMF (66 mL) afforded **S35** (2.5 g, 81%) as a yellow solid after purification by chromatography on SiO_2 (3:1, hexanes/ EtOAc) (12 h reaction time).

R_f (EtOAc /hexanes 1:9): 0.35;

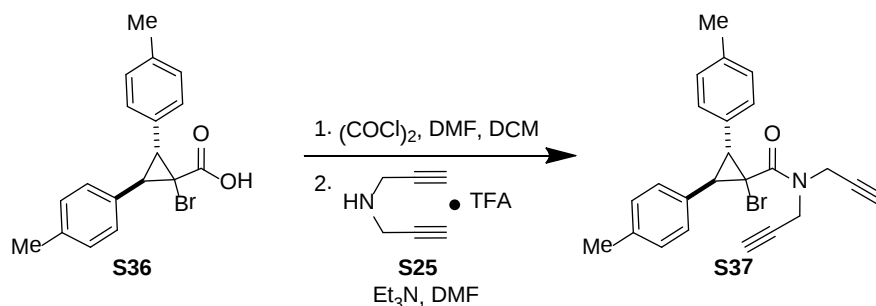
IR (neat): 3295, 3087, 3062, 3032, 2926, 1650, 1603, 1497, 1447, 1335, 1283, 1223, 1178 cm^{-1}

^1H NMR (CDCl_3 , 500 MHz): 7.37 – 7.43 (m, 4 H), 7.30 – 7.35 (m, 3 H), 7.24 – 7.27 (m, 1 H), 7.19 (d, $J = 7.0$ Hz, 2 H), 4.46 (dd, $J = 17.0, 9.5$ Hz, 2 H), 4.00 (dd, $J = 17.0, 2.0$ Hz, 1 H), 3.63 (dd, $J = 17.0, 2.0$ Hz, 1 H), 3.52 (d, $J = 8.5$ Hz, 1 H), 3.20 (d, $J = 8.5$ Hz, 1 H), 2.18 (t, $J = 2.0$ Hz, 1 H), 2.05 (t, $J = 2.0$ Hz, 1 H);

^{13}C NMR (CDCl_3 , 100 MHz): 165.0, 136.0, 134.7, 129.2, 128.9, 128.2, 127.5, 127.4, 126.8, 77.0, 76.5, 73.3, 71.9;

HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{19}\text{BrNO}^+$ ($[\text{M}+1]^+$) 392.0650, found 392.0646.

1-bromo-N,N-di(prop-2-yn-1-yl)-trans-2,3-di-p-tolylcyclopropanecarboxamide, **S37**:



According to General Procedure B, **S36** (0.32 g, 0.93 mmol), DMF (5 drops), oxalyl chloride (0.12 mL, 1.4 mmol) in DCM (6 mL) afforded the acyl chloride. Treatment of this acyl chloride with **S25** (0.33 g, 1.9 mmol) and Et₃N (0.52 mL, 3.7 mmol) in DMF (10 mL) afforded **S37** (0.33 g, 85%) as a yellow solid after purification by chromatography on SiO₂ (19:1, hexanes/EtOAc) (12 h reaction time).

R_f (EtOAc/hexanes 1:9): 0.38;

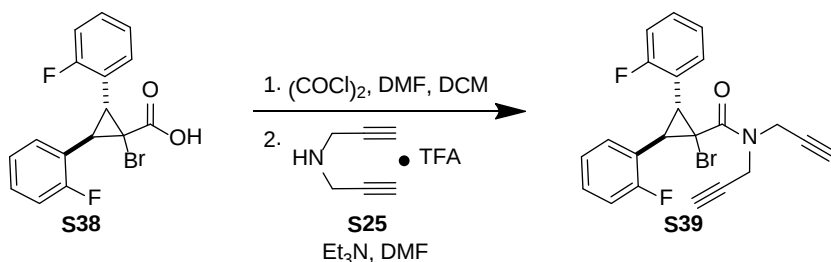
IR (neat): 3296, 3023, 2921, 1650, 1516, 1443, 1416, 1282, 1252, 1027, 1180, 1125 cm⁻¹

¹H NMR (CDCl₃, 500 MHz): 7.29 (d, *J* = 8.0 Hz, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 4.48 (dd, *J* = 17.5, 11.5 Hz, 2 H), 3.97 (d, *J* = 17.0 Hz, 1 H), 3.62 (d, *J* = 18.0 Hz, 1 H), 3.43 (d, *J* = 8.5 Hz, 1 H), 3.13 (d, *J* = 8.5 Hz, 1 H), 2.39 (s, 3 H), 2.33 (s, 3 H), 2.195 (br s, 1 H), 2.03 (br s, 1 H);

¹³C NMR (CDCl₃, 100 MHz): 165.2, 137.1, 137.0, 133.1, 131.7, 129.5, 129.0, 128.9, 126.7, 77.2, 76.7, 73.2, 71.8, 41.5, 38.3, 37.0, 33.4, 33.0, 21.1, 21.0;

HRMS (ESI) *m/z* calculated for C₂₄H₂₃BrNO⁺ ([M+1]⁺) 420.0963, found 420.0959.

1-bromo-trans-2,3-bis(2-fluorophenyl)-N,N-di(prop-2-yn-1-yl)cyclopropanecarboxamide, **S39**:



According to General Procedure B, **S38** (0.38 g, 1.1 mmol), DMF (5 drops), oxalyl chloride (0.14 mL, 1.7 mmol) in DCM (10 mL) afforded the acyl chloride. Treatment of this acyl chloride with **S25** (0.46 g, 2.2 mmol) and Et₃N (0.46 mL, 3.3 mmol) in DMF (15 mL) afforded **S39** (0.34 g, 72%) as a colorless solid after purification by chromatography on SiO₂ (9:1, hexanes/EtOAc) (14 h reaction time).

R_f (EtOAc/hexanes 1:9): 0.26;

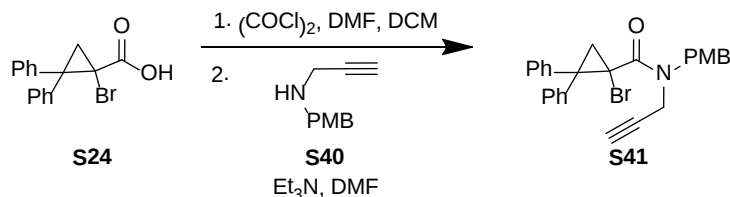
IR (neat): 3298, 3045, 2924, 1654, 1584, 1493, 1452, 1431, 1286, 1235, 1185, 1120, 1095 cm⁻¹

¹H NMR (CDCl₃, 400 MHz): 7.23 – 7.36 (m, 3 H), 7.05 – 7.19 (m, 4 H), 6.95 (t, *J* = 8.0 Hz, 1 H), 4.58 (d, *J* = 17.4 Hz, 1 H), 4.38 (d, *J* = 17.4 Hz, 1 H); 3.99 (dd, *J* = 17.4, 2.0 Hz, 1 H), 3.85 (dd, *J* = 17.4, 2.0 Hz, 1 H), 3.65 (d, *J* = 8.6 Hz, 1 H), 3.54 (d, 8.6 Hz, 1 H), 2.17 (br s, 1 H), 1.97 (br s, 1 H);

¹³C NMR (CDCl₃, 125 MHz): 164.2, 162.1 (d, ¹*J*_{C-F} = 247.1 Hz), 161.9 (d, ¹*J*_{C-F} = 244.3 Hz), 130.2 (d, ⁴*J*_{C-F} = 2.8 Hz), 129.3 (d, ²*J*_{C-F} = 38.8 Hz), 129.2 (d, ²*J*_{C-F} = 39.4 Hz), 126.1 (d, ⁴*J*_{C-F} = 2.8 Hz), 124.6 (d, ³*J*_{C-F} = 3.6 Hz), 123.7 (d, ³*J*_{C-F} = 3.8 Hz), 123.3 (d, ³*J*_{C-F} = 13.8 Hz), 121.4 (d, ³*J*_{C-F} = 13.5 Hz), 115.5 (d, ²*J*_{C-F} = 21.3 Hz), 115.3 (d, ²*J*_{C-F} = 21.3 Hz), 77.0, 76.5, 73.2, 71.8, 40.2, 36.7, 33.5, 30.9 (d, ³*J*_{C-F} = 5.1 Hz), 27.1 (d, ³*J*_{C-F} = 2.3 Hz);

HRMS (ESI) *m/z* calculated for C₂₂H₁₇BrF₂NO⁺ ([M+1]⁺) 428.0462, found 428.0456.

1-bromo-N-(4-methoxybenzyl)-2,2-diphenyl-N-(prop-2-yn-1-yl)cyclopropanecarboxamide, **S41**:



According to General Procedure B, **S24** (0.60 g, 1.9 mmol), DMF (10 drops), oxalyl chloride (0.24 mL, 2.9 mmol) in DCM (11 mL) afforded the acyl chloride. Treatment of this acyl chloride with **S40** (0.50 g, 2.9 mmol) and Et_3N (0.79 mL, 5.7 mmol) in DMF (16 mL) afforded **S41** (0.57 g, 62%) as a pale yellow solid containing a mixture of conformational isomers after purification by chromatography on SiO_2 (8:2 to 1:1, hexanes/ EtOAc) (12 h reaction time).

R_f (EtOAc /hexanes 15:85): 0.30;

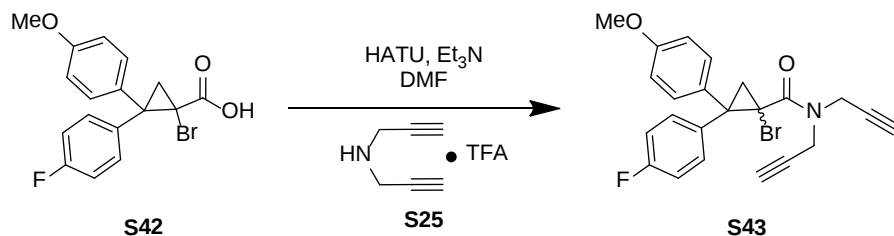
IR (neat): 3303, 3009, 2933, 2836, 1644, 1611, 1440, 1415, 1247, 1229, 1175, 1033 cm^{-1} ;

^1H NMR (CDCl_3 , 500 MHz): 7.47 – 7.45 (m, 4 H), 7.38 – 7.34 (m, 4 H), 7.31 – 7.27 (m, 1 H), 7.28 – 7.11 (m, 10 H), 6.76 (d, $J = 8.5$ Hz, 2 H), 6.78 (d, $J = 8.5$ Hz, 2 H), 6.71 (d, $J = 8.5$ Hz, 2 H), 6.66 (d, $J = 8.5$ Hz, 2 H), 5.18 (d, $J = 14.5$ Hz, 1 H), 4.81 (d, $J = 14.5$ Hz, 1 H), 4.59 (d, $J = 17.5$ Hz, 1 H), 4.21 (d, $J = 14.5$ Hz, 1 H), 4.16 – 4.09 (m, 2 H), 3.79 – 3.75 (m, 1 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 3.51 (dd, $J = 17.0, 2.0$ Hz, 1 H), 3.04 (d, $J = 7.0$ Hz, 1 H), 3.00 (d, $J = 7.5$ Hz, 1 H), 2.30 (t, $J = 2.5$ Hz, 1 H), 2.02 (d, $J = 7.5$ Hz, 1 H), 1.96 (d, $J = 7.0$ Hz, 1 H), 1.93 (t, $J = 2.5$ Hz, 1 H);

^{13}C NMR (CDCl_3 , 125 MHz): 165.9, 165.5, 159.1, 158.6, 140.9, 140.5, 137.7, 137.2, 130.5, 130.1, 129.3, 128.3, 128.2, 127.5, 127.3, 127.2, 126.8, 126.7, 126.1, 113.8, 133.6, 77.2, 77.0, 73.7, 71.5, 54.9, 54.9, 50.0, 46.5, 41.9, 41.7, 39.8, 39.2, 36.9, 32.9, 28.3, 27.4;

HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{25}\text{BrNO}_2^+$ ($[\text{M}+1]^+$) 474.1069, found 474.1078.

1-bromo-2-(4-fluorophenyl)-2-(4-methoxyphenyl)-N,N-di(prop-2-yn-1-yl)cyclopropanecarboxamide, **43**:



A flame dried 25 mL round bottom flask, equipped with a magnetic stir bar was charged with **S42** (1.5 g, 4.0 mmol), **S25** (0.63 g, 4.9 mmol), Et₃N (1.7 mL, 12 mmol) and DMF (15 mL). The mixture was then treated with HATU (1.7 g, 4.4 mmol). After consumption of the starting material (as judged by TLC analysis) the mixture was filtered into a separatory funnel containing 25 mL of EtOAc and 50 mL of H₂O. The layers were separated and the aqueous layer was extracted with EtOAc (2 X 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. The residue was purified by chromatography on silica gel (9:1 to 7:3, hexanes/EtOAc) to afford both diastereoisomers of **S43** (0.31 g, 18%) as a colorless solids (12 h reaction time).

Data for undefined diastereoisomer **S43a**:

R_f (EtOAc/hexanes 35:65): 0.53;

IR (neat): 3296, 3041, 3001, 2934, 2837, 1652, 1608, 1510, 1441, 1414, 1248, 1232 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 7.36 (d, *J* = 8.5 Hz, 2 H), 7.08 (dd, *J* = 9.0, 5.5 Hz, 2 H), 6.92 (d, *J* = 8.5 Hz, 2 H), 6.84 (t, *J* = 9.0 Hz, 2 H), 4.67 (d, *J* = 17.5 Hz, 1 H), 4.38 (d, *J* = 17.5 Hz, 1 H), 4.03 (dd, *J* = 17.5, 2.5 Hz, 1 H), 3.92 (dd, *J* = 17.5, 2.5 Hz, 1 H), 3.82 (s, 3 H), 2.89 (d, *J* = 7.0 Hz, 1 H), 2.30 (t, *J* = 2.5 Hz, 1 H), 2.02 (t, *J* = 2.5 Hz, 1 H), 1.93 (d, *J* = 7.0 Hz, 1 H);

¹³C NMR (CDCl₃, 125 MHz): 165.2, 161.8 (d, ¹*J*_{C-F} = 245.5 Hz), 158.9, 133.7 (d, ⁴*J*_{C-F} = 3.1 Hz), 132.7, 131.5, 129.2 (d, ³*J*_{C-F} = 8.3 Hz), 115.2 (d, ²*J*_{C-F} = 21.8 Hz), 114.0, 77.2, 76.6, 73.8, 71.9, 55.3, 40.8, 39.1, 37.4, 33.7, 28.1;

HRMS (ESI) *m/z* calculated for C₂₃H₂₀BrFNO₂⁺ ([M+1]⁺) 440.0661, found 440.0660.

Data for undefined diastereoisomer **S43b**:

R_f (EtOAc/hexanes 35:65): 0.50;

IR (neat): 3298, 3043, 2934, 2837, 1650, 1606, 1510, 1441, 1414, 1289, 1250, 1229, 1182, 1161 cm⁻¹;

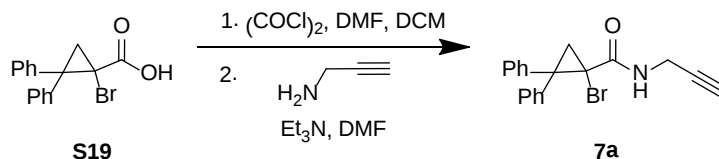
¹H NMR (CDCl₃, 500 MHz): 7.46 (dd, *J* = 9.0, 5.5 Hz, 2 H), 7.11 (t, *J* = 9.0 Hz, 2 H), 7.05 (d, *J* = 9.0 Hz, 2 H), 6.73 (d, *J* = 9.0 Hz, 2 H), 4.73 (d, *J* = 17.5 Hz, 1 H), 4.43 (d, *J*

= 17.5 Hz, 1 H), 4.45 (dd, $J = 17.5, 2.5$ Hz, 1 H), 3.94 (dd, $J = 17.5, 2.5$ Hz, 1 H), 3.73 (s, 3 H), 2.94 (d, $J = 7.0$ Hz, 1 H), 2.35 (t, $J = 2.5$ Hz, 1 H), 2.03 (t, $J = 2.5$ Hz, 1 H), 1.92 (d, $J = 7.0$ Hz, 1 H);

^{13}C NMR (CDCl_3 , 125 MHz): 165.2, 161.9 (d, $^1J_{\text{C-F}} = 245.8$ Hz), 158.7, 136.8 (d, $^4J_{\text{C-F}} = 3.3$ Hz), 132.0 (d, $^3J_{\text{C-F}} = 7.9$ Hz), 129.3, 128.7, 115.5 (d, $^2J_{\text{C-F}} = 21.3$ Hz), 113.8, 77.3, 76.7, 73.8, 71.9, 55.1, 40.8, 38.7, 37.4, 33.7, 27.9;

HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{20}\text{BrFNO}_2^+$ ($[\text{M}+1]^+$) 440.0661, found 440.0672.

1-bromo-2,2-diphenyl-N-(prop-2-yn-1-yl)cyclopropanecarboxamide, **7a**:



According to General Procedure B, **S19** (0.25 g, 0.79 mmol), DMF (5 drops), oxalyl chloride (0.10 mL, 1.2 mmol) in DCM (5 mL) afforded the acyl chloride. Treatment of this acyl chloride with propargyl amine (76 μ L, 1.2 mmol) and Et₃N (0.33 mL, 2.4 mmol) in DMF (10 mL) afforded **7a** (0.25 g, 89%) as a colorless solid after purification by chromatography on SiO₂ (17:3 to 4:1, hexanes/EtOAc) (18 h reaction time).

R_f (EtOAc/hexanes 1:3): 0.43;

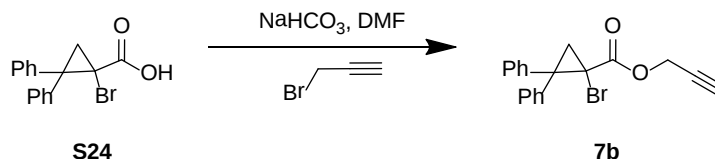
IR (neat): 3304, 3059, 3026, 1658, 1510, 1493, 1447, 1417, 1308, 1268 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 7.45 (dd, J = 8.5, 1.5 Hz, 2 H), 7.30 – 7.36 (m, 3 H), 7.20 – 7.24 (m, 3 H), 7.13 – 7.17 (m, 1 H), 6.94 (br s, 1 H), 4.05 (ddd, J = 17.5, 5.5, 2.5 Hz, 1 H), 3.94 (ddd, J = 17.5, 5.0, 2.5 Hz, 1 H), 2.90 (d, J = 6.3 Hz, 1 H), 2.3 (t, J = 2.5 Hz, 1 H), 2.09 (d, J = 6.3 Hz, 1 H);

¹³C NMR (CDCl₃, 100 MHz): 166.2, 141.9, 140.2, 129.2, 128.4, 128.3, 128.3, 127.2, 127.0, 79.0, 71.8, 45.5, 42.0, 30.3, 27.0;

HRMS (ESI) m/z calculated for C₁₉H₁₇BrNO⁺ ([M+1]⁺) 354.0494, found 354.0510.

prop-2-yn-1-yl 1-bromo-2,2-diphenylcyclopropanecarboxylate, **7b**:



A flame dried 25 mL round bottom flask, equipped with a magnetic stir bar was charged with **S24** (0.33 g, 1.0 mmol), DMF (15 mL) and treated with NaHCO_3 (180 mg, 2.1 mmol). The mixture was then stirred at room temperature for 20 min and then treated with an 80% solution of propargyl bromide in toluene (2.3 mL, 2.1 mmol). After completion of the reaction (as judged by TLC analysis) the mixture was poured into a separatory funnel containing 25 mL of EtOAc and 50 mL of H_2O . The layers were separated and the aqueous layer was extracted with EtOAc (2 X 50 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by chromatography on silica gel (95:5, hexanes/EtOAc) to afford **7b** (0.30 g, 79%) as a colorless solid (19 h reaction time).

R_f (EtOAc/hexanes 1:9): 0.38;

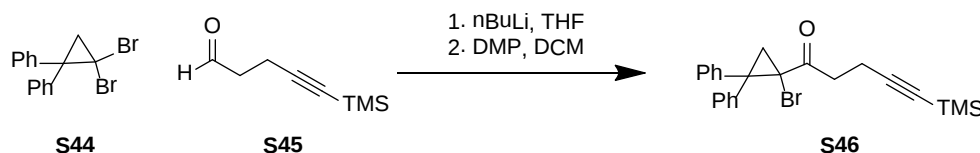
IR (neat): 3301, 3085, 3060, 3028, 2942, 2251, 2131, 1734, 1493, 1448, 1233 cm^{-1} ;

^1H NMR (CDCl_3 , 500 MHz): 7.49 (d, $J = 7.5$ Hz, 2 H), 7.39 (d, $J = 7.5$ Hz, 2 H), 7.32 (t, $J = 7.0$ Hz, 2 H), 7.23 (t, $J = 7.0$ Hz, 2 H), 7.16 (t, $J = 7.5$ Hz, 1 H), 4.58 (dd, $J = 16.0, 2.5$ Hz, 1 H), 4.36 (dd, $J = 16.0, 2.5$ Hz, 1 H), 2.83 (d, $J = 6.5$ Hz, 1 H), 2.42 (t, $J = 2.5$ Hz, 1 H), 2.10 (d, $J = 6.5$ Hz, 1 H);

^{13}C NMR (CDCl_3 , 125 MHz): 167.0, 141.1, 140.0, 129.3, 128.5, 128.4, 128.3, 128.3, 127.3, 127.2, 76.6, 75.3, 53.4, 45.4, 37.9, 27.7;

HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{15}\text{BrNaO}_2^+$ ($[\text{M}+\text{Na}]^+$) 377.0153, found 377.0153.

1-(1-bromo-2,2-diphenylcyclopropyl)-5-(trimethylsilyl)pent-4-yn-1-one, **S46**:



A flame dried 50 mL round bottom flask, equipped with a magnetic stir bar was charged with **S44**² (0.33 g, 1.0 mmol), THF (28 mL) and cooled to -78 °C. The mixture was then treated dropwise with a 2.5 M solution of nBuLi in hexanes (1.3 mL, 3.4 mmol). This mixture was then stirred at -78 °C for 20 min. A solution of **S45**³ (0.43 g, 2.8 mmol) in THF (5 mL) is then added dropwise. After 1 h the reaction was warmed to rt and quenched by the addition of 10 mL of sat. aq. NH₄Cl. The mixture was then poured into a separatory funnel containing 25 mL of EtOAc and 50 mL of H₂O. The layers were separated and the aqueous layer was extracted with EtOAc (2 X 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated to afford a mixture of diastereotopic alcohols, which were used without further purification.

A 25 mL flask, equipped with a magnetic stir bar was charged with the mixture of alcohols (0.48 g, 1.1 mmol) and DCM (12 mL). The mixture was then treated with DMP (720 mg, 1.7 mmol). After completion of the reaction (as judged by TLC analysis) the mixture was poured into a separatory funnel containing 25 mL of DCM and 50 mL of 1:1 aq. Na₂S₂O₃/NaHCO₃. The layers were separated and the aqueous layer was extracted with DCM (2 X 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. The residue was purified by chromatography on silica gel (95:5, hexanes/EtOAc) to afford **S46** (0.88 g, 67% over two steps) as a colorless oil (1.5 h reaction time).

R_f (EtOAc/hexanes 1:9): 0.64;

IR (neat): 3062, 3028, 2958, 2176, 1705, 1493, 1448, 1249, 1180, 1067 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 7.49 (d, *J* = 8.0 Hz, 2 H), 7.35 (t, *J* = 7.5 Hz, 2 H), 7.20 – 7.28 (m, 5 H), 7.13 – 7.16 (m, 1 H), (3.35 (ddd, *J* = 18.0, 9.5, 5.0 Hz, 1 H), 2.96 (ddd, *J* = 18.0, 9.5, 5.0 Hz, 1 H), 2.96 (d, *J* = 6.5 Hz, 1 H), 2.42 (ddd, *J* = 17.5, 10.5, 5.0 Hz, 1 H), 2.15 (ddd, *J* = 17.5, 10.5, 5.0 Hz, 1 H), 2.00 (d, *J* = 6.5 Hz, 1 H), 0.20 (s, 9 H);

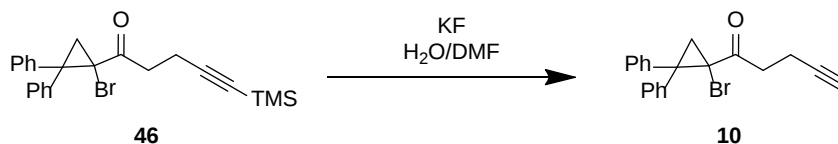
¹³C NMR (CDCl₃, 125 MHz): 200.1, 141.3, 139.0, 129.5, 128.6, 128.5, 128.3, 127.4, 127.2, 105.4, 85.0, 47.1, 46.9, 40.8, 26.9, 15.1, 0.0;

HRMS (ESI) *m/z* calculated for C₂₃H₂₆BrOSi⁺ ([M+1]⁺) 425.0936, found 425.0946.

² Kramer, K.; Leong, P.; Lautens, M. *Org. Lett.* **2011**, *13*, 819.

³ Makabe, H.; Kimura, Y.; Higuchi, M.; Konno, H.; Murai, M.; Miyoshi, H. *Bioorg. Med. Chem.* **2006**, *14*, 3119.

1-(1-bromo-2,2-diphenylcyclopropyl)pent-4-yn-1-one, **10**:



A flame dried 50 mL round bottom flask, equipped with a magnetic stir bar was charged with **S46** (0.57 g, 1.3 mmol), DMF (10 mL) and water (0.5 mL). The mixture was then treated KF (120 mg, 2.0 mmol) at rt. After completion of the reaction (as judged by TLC analysis) the mixture was poured into a separatory funnel containing 25 mL of DCM and 50 mL of 1:1 aq. Na₂S₂O₃/NaHCO₃. The layers were separated and the aqueous layer was extracted with DCM (2 X 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. The residue was purified by chromatography on silica gel (95:5, hexanes/EtOAc) to afford **10** (0.40 g, 85%) as a colorless oil (4 h reaction time).

R_f (EtOAc/hexanes 1:9): 0.45;

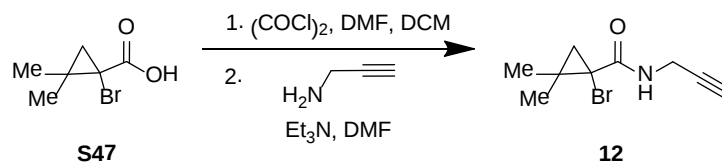
IR (neat): 3292, 3083, 3025, 2922, 1703, 1597, 1493, 1447, 0405, 1361, 1305, 1181, 1122, 1181 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 7.47 (d, *J* = 8.5 Hz, 2 H), 7.34 (t, *J* = 7.5 Hz, 2 H), 7.19 – 7.27 (m, 5 H), 7.12 – 7.15 (m, 1 H), 3.35 (ddd, *J* = 18.5, 9.5, 6.0 Hz, 1 H), 2.97 (ddd, *J* = 18.5, 9.5, 6.0 Hz, 1 H), 2.96 (d, *J* = 6.5 Hz, 1 H), 2.31 – 2.39 (m, 1 H), 2.12 – 2.18 (m, 1 H), 1.99 (d, *J* = 6.5 Hz, 1 H), 1.95 (t, *J* = 2.5 Hz, 1 H);

¹³C NMR (CDCl₃, 100 MHz): 200.2, 141.4, 139.0, 129.6, 128.7, 128.6, 128.4, 127.5, 127.3, 82.9, 68.8, 47.4, 46.9, 40.7, 27.1, 13.6;

HRMS (ESI) *m/z* calculated for C₂₀H₁₈BrO⁺ ([*M*+1]⁺) 353.0541, found 353.0718.

1-bromo-2,2-dimethyl-N-(prop-2-yn-1-yl)cyclopropanecarboxamide, **12**:



According to General Procedure B, **S47**⁴ (1.0 g, 5.3 mmol), DMF (10 drops), oxalyl chloride (0.67 mL, 7.9 mmol) in DCM (10 mL) afforded the acyl chloride. Treatment of this acyl chloride with propargyl amine (0.51 mL, 1.2 mmol) and Et₃N (2.2 mL, 16 mmol) in DMF (25 mL) afforded **12** (1.1 g, 60%) as a colorless solid after purification by chromatography on SiO₂ (17:3 to 4:1, hexanes/EtOAc) (18 h reaction time).

R_f (EtOAc/hexanes 3:17): 0.43;

IR (neat): 3254, 2986, 2966, 2871, 1639, 1523, 1456, 1422, 1345, 1273 cm⁻¹;

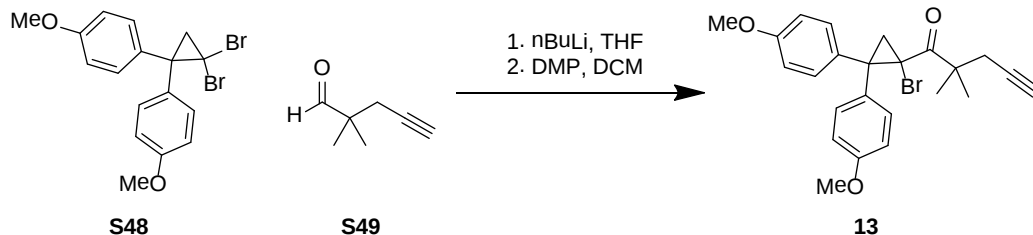
¹H NMR (CDCl₃, 400 MHz): 6.64 (br s, 1 H), 4.09 (ddd, *J* = 17.6, 5.4, 2.6 Hz, 1 H), 4.03 (ddd, *J* = 17.6, 5.4, 2.6 Hz, 1 H), 2.24 (t, *J* = 2.6 Hz, 1 H), 1.88 (d, *J* = 6.0 Hz, 1 H), 1.41 (s, 3 H), 1.17 (s, 3 H), 0.99 (d, *J* = 6.0 Hz, 1 H);

¹³C NMR (CDCl₃, 100 MHz): 167.8, 79.2, 71.6, 43.1, 30.1, 28.2, 16.4, 26.0, 19.4;

HRMS (ESI) *m/z* calculated for C₉H₁₃BrNO⁺ ([*M*+1]⁺) 230.0181, found 230.0190.

⁴ Hoffmann, H. M. R.; Wulff, J. M.; Kuetz, A.; Wartchow, R. *Angew. Chem.* **1982**, 94, 79.

1-(1-bromo-2,2-bis(4-methoxyphenyl)cyclopropyl)-2,2-dimethylpent-4-yn-1-one, **13**:



A flame dried 50 mL round bottom flask, equipped with a magnetic stir bar was charged with **S48**⁵ (1.7 g, 4.1 mmol), THF (35 mL) and cooled to -78 °C. The mixture was then treated dropwise with a 2.5 M solution of nBuLi in hexanes (1.8 mL, 4.1 mmol). This mixture was then stirred at -78 °C for 20 min. A solution of **S49**⁶ (0.40 g, 3.6 mmol) in THF (5 mL) is then added dropwise. After 1 h the reaction was warmed to rt and quenched by the addition of 10 mL of sat. aq. NH₄Cl. The mixture was then poured into a separatory funnel containing 25 mL of EtOAc and 50 mL of H₂O. The layers were separated and the aqueous layer was extracted with EtOAc (2 X 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated to afford a mixture of diastereotopic alcohols, which were used without further purification.

A 50 mL flask, equipped with a magnetic stir bar was charged with the mixture of alcohols and DCM (20 mL). The mixture was then treated with DMP (1.8 g, 4.3 mmol). After completion of the reaction (as judged by TLC analysis) the mixture was poured into a separatory funnel containing 25 mL of DCM and 50 mL of 1:1 aq. Na₂S₂O₃/NaHCO₃. The layers were separated and the aqueous layer was extracted with DCM (2 X 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. The residue was purified by chromatography on silica gel (95:5, hexanes/EtOAc) to afford **13** (0.84 g, 51% over two steps) as a colorless solid (1.5 h reaction time).

R_f (EtOAc/hexanes 5:95): 0.24;

IR (neat): 3293, 2970, 2935, 2836, 1687, 1608, 1511, 1464, 1440, 1286, 1247, 1176, 1040 cm⁻¹;

¹H NMR (CDCl₃, 500 MHz): 7.44 (d, *J* = 8.5 Hz, 2 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 6.93 (d, *J* = 8.5 Hz, 2 H), 6.73 (d, *J* = 8.5 Hz, 2 H), 3.84 (s, 3 H), 3.74 (s, 3 H), 3.01 (d, *J* = 7.0 Hz, 1 H), 2.45 (dd, *J* = 16.5, 2.5 Hz, 1 H), 2.07 (dd, *J* = 16.5, 2.5 Hz, 1 H), 1.97 (t, *J* = 2.5 Hz, 1 H), 1.78 (d, *J* = 7.0 Hz, 1 H), 1.38 (s, 3 H), 1.27 (s, 3 H);

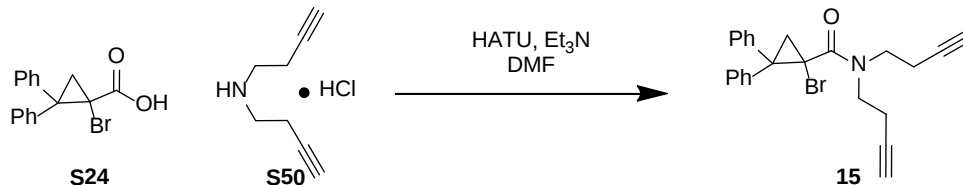
¹³C NMR (CDCl₃, 125 MHz): 204.2, 158.6, 158.5, 133.8, 131.7, 129.6, 129.3, 113.7, 113.5, 80.9, 70.7, 55.1, 55.1, 46.9, 44.5, 41.7, 30.1, 26.9, 25.1, 23.5;

HRMS (ESI) *m/z* calculated for C₂₄H₂₆BrO₃⁺ ([*M*+1]⁺) 441.1065, found 441.1044.

⁵ Yarnazak, S.; Yamamoto, Y.; Fukushima, Y.; Takebayashi, M.; Ukai, T.; Mikata, Y. *J. Org. Chem.* **2010**, 75, 5216.

⁶ Rigby, J. H.; Laxmisha, M. S.; Hudson, A. R.; Heap, C. H.; Heeg, M. J. *J. Org. Chem.* **2004**, 69, 6751.

1-bromo-N,N-di(but-3-yn-1-yl)-2,2-diphenylcyclopropanecarboxamide, **15**:



A flame dried 25 mL round bottom flask, equipped with a magnetic stir bar was charged with **S24** (0.30 g, 0.95 mmol), **S50** (0.15 g, 0.95 mmol), Et₃N (0.40 mL, 15 mmol) and DMF (15 mL). The mixture was then treated with HATU (0.40 g, 1.05 mmol). After consumption of the starting material (as judged by TLC analysis) the mixture was filtered into a separatory funnel containing 25 mL of EtOAc and 50 mL of H₂O. The layers were separated and the aqueous layer was extracted with EtOAc (2 X 50 mL). The combined organic layers were dried (Na₂SO₄) and concentrated. The residue was purified by chromatography on silica gel (17:3 to 3:1, hexanes/EtOAc) to afford **15** (0.25 g, 62%) as a colorless solid (14 h reaction time).

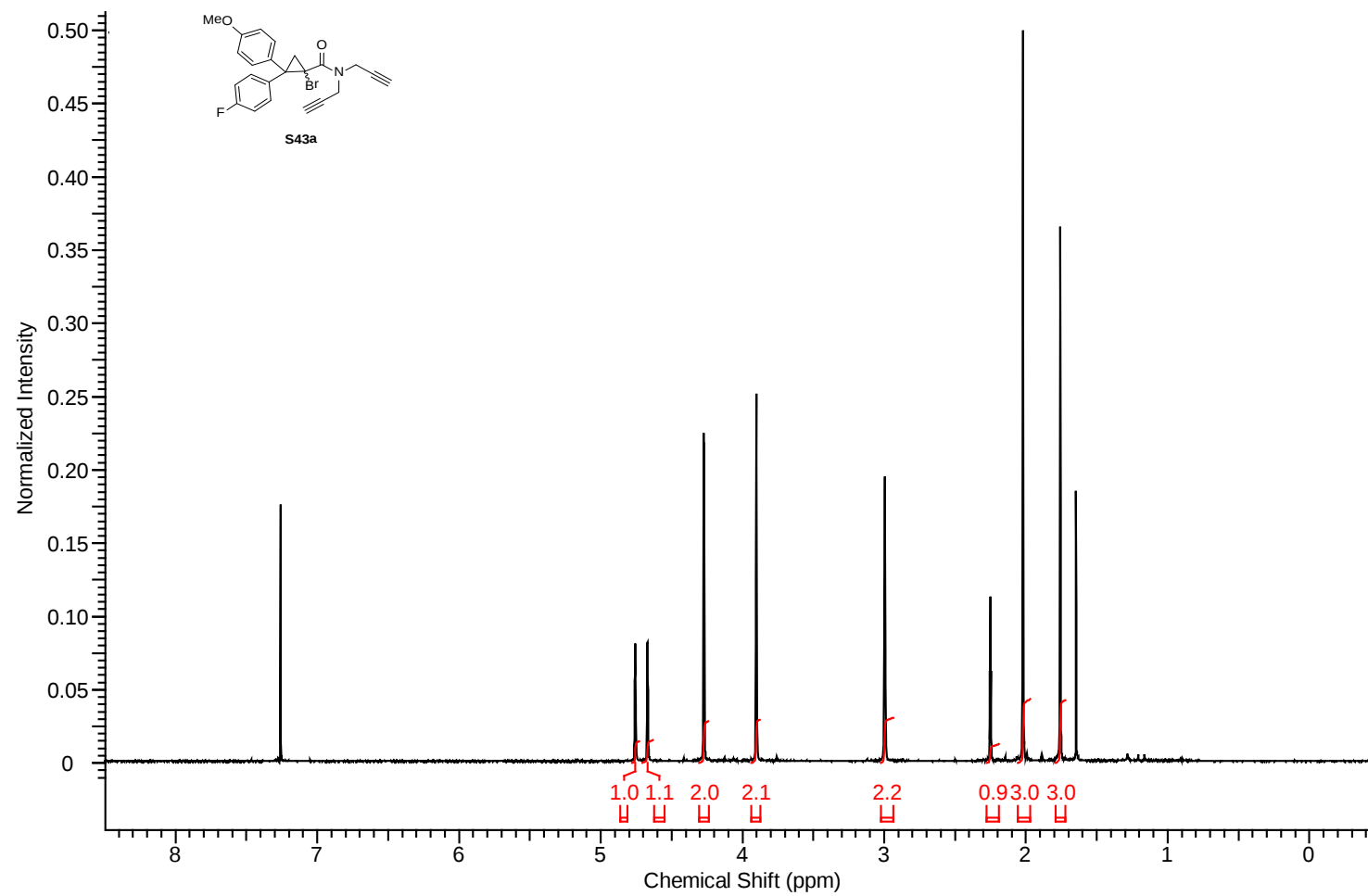
R_f (EtOAc/hexanes 3:7): 0.57;

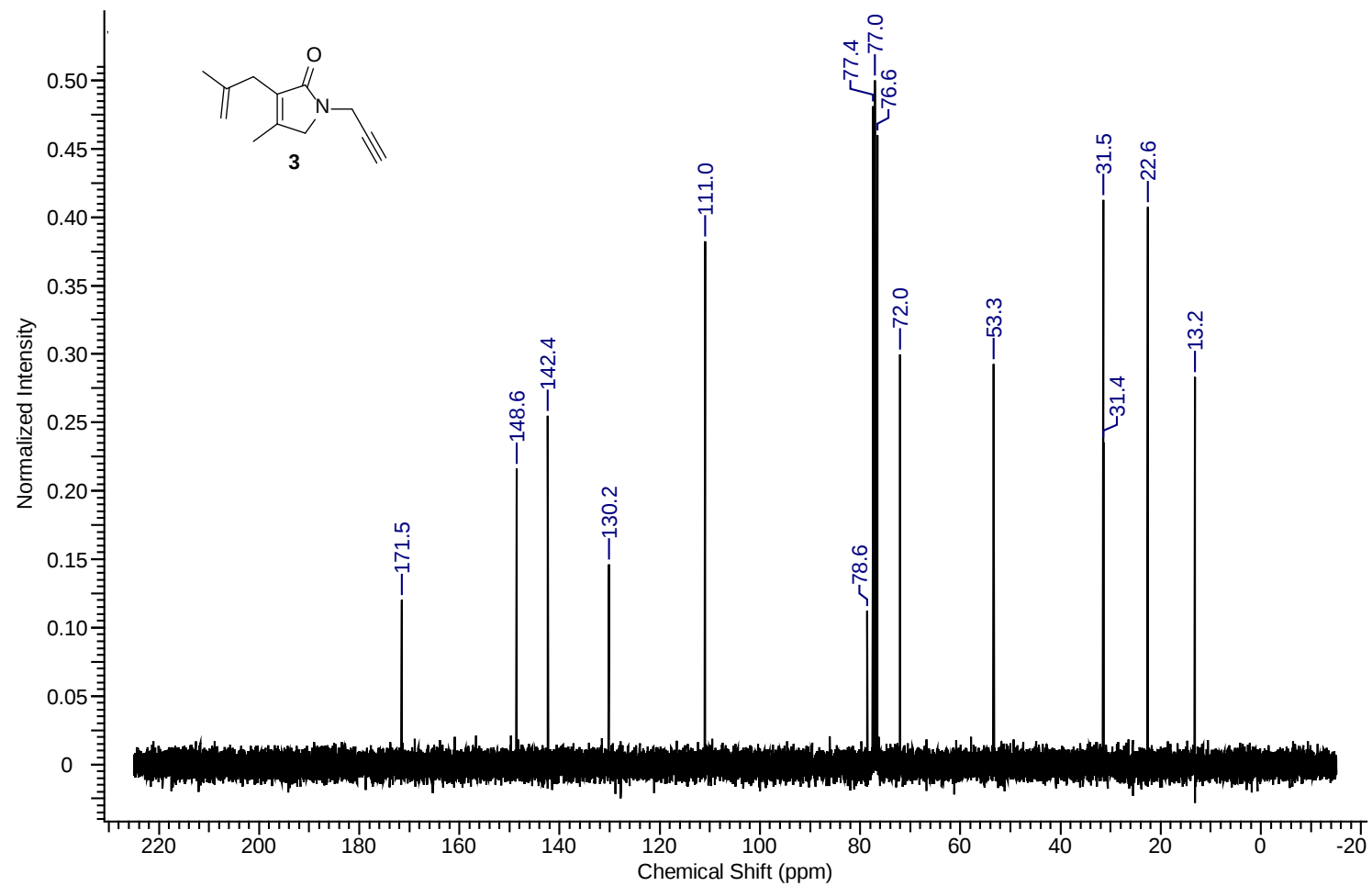
IR (neat): 3296 3059, 2949, 2119, 1642, 1497, 1448, 1423, 1371, 1331, 1254, 1170, 1056 cm⁻¹

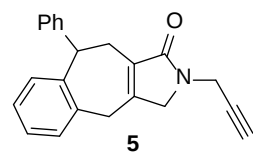
¹H NMR (CDCl₃, 500 MHz): 7.55 (d, *J* = 7.0 Hz, 2 H), 7.43 (t, *J* = 7.0 Hz, 2 H), 7.34 – 7.37 (m, 1 H), 7.15 – 7.24 (m, 5 H), 4.08 (ddd, *J* = 15.5, 11.0, 5.5 Hz, 1 H), 3.52 (ddd, *J* = 14.0, 8.5, 5.0 Hz, 1 H), 3.33 (ddd, *J* = 16.0, 10.5, 5.0 Hz, 1 H), 3.08 (ddd, *J* = 14.5, 9.0, 6.0 Hz, 1 H), 3.00 (d, *J* = 7.5 Hz, 1 H), 2.54 – 2.61 (m, 1 H), 2.16 (t, *J* = 3.0 Hz, 1 H), 2.07 – 2.15 (m, 2 H), 1.97 (d, *J* = 7.5 Hz, 1 H), 1.93 (t, *J* = 3.0 Hz, 1 H), 1.76 – 1.83 (m, 1 H);

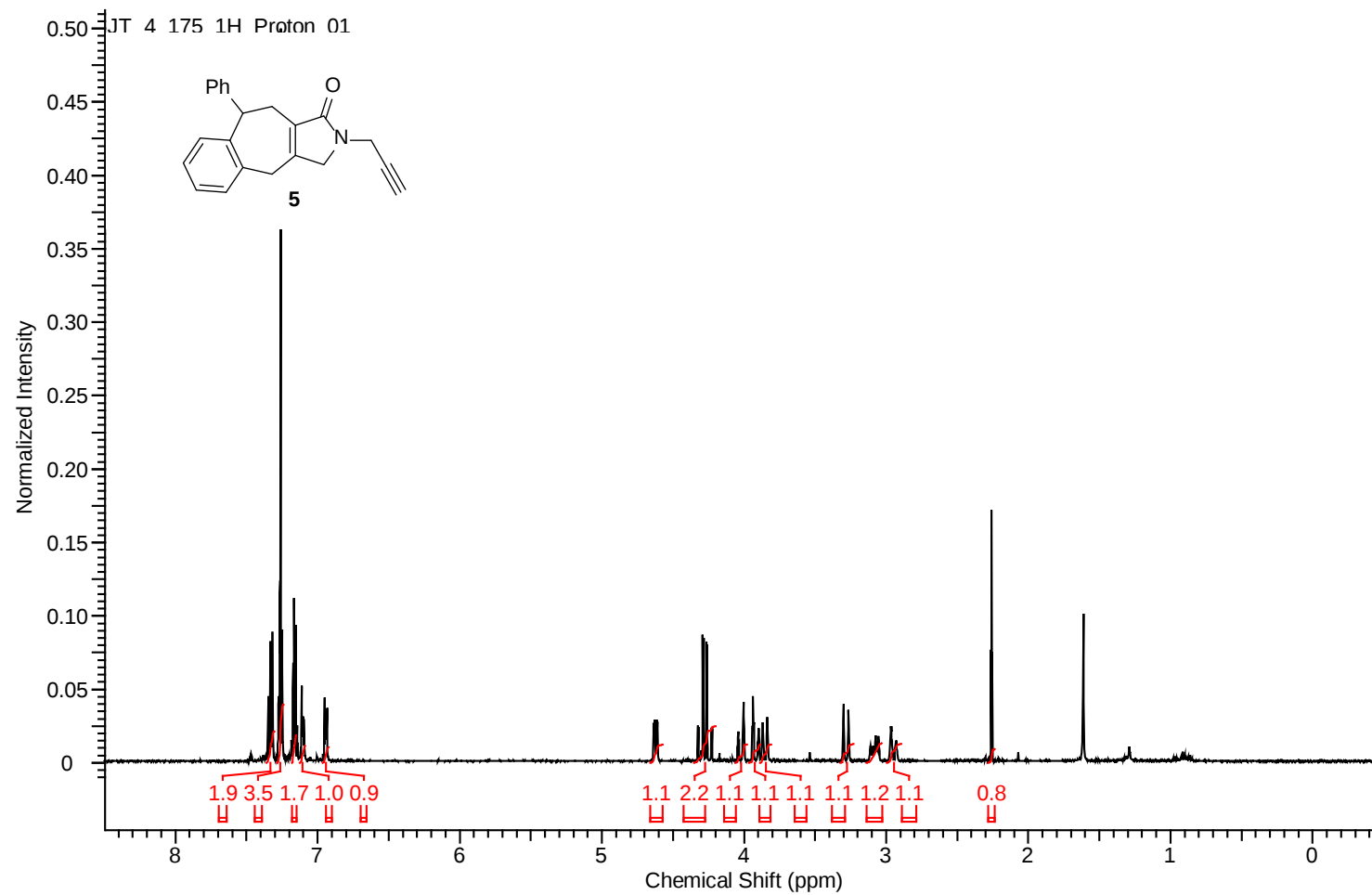
¹³C NMR (CDCl₃, 125 MHz): 166.0, 140.6, 137.4, 130.7, 128.4, 128.3, 127.6, 127.4, 127.2, 81.4, 80.4, 70.6, 69.7, 47.2, 44.3, 41.6, 39.6, 27.9, 17.7, 16.0;

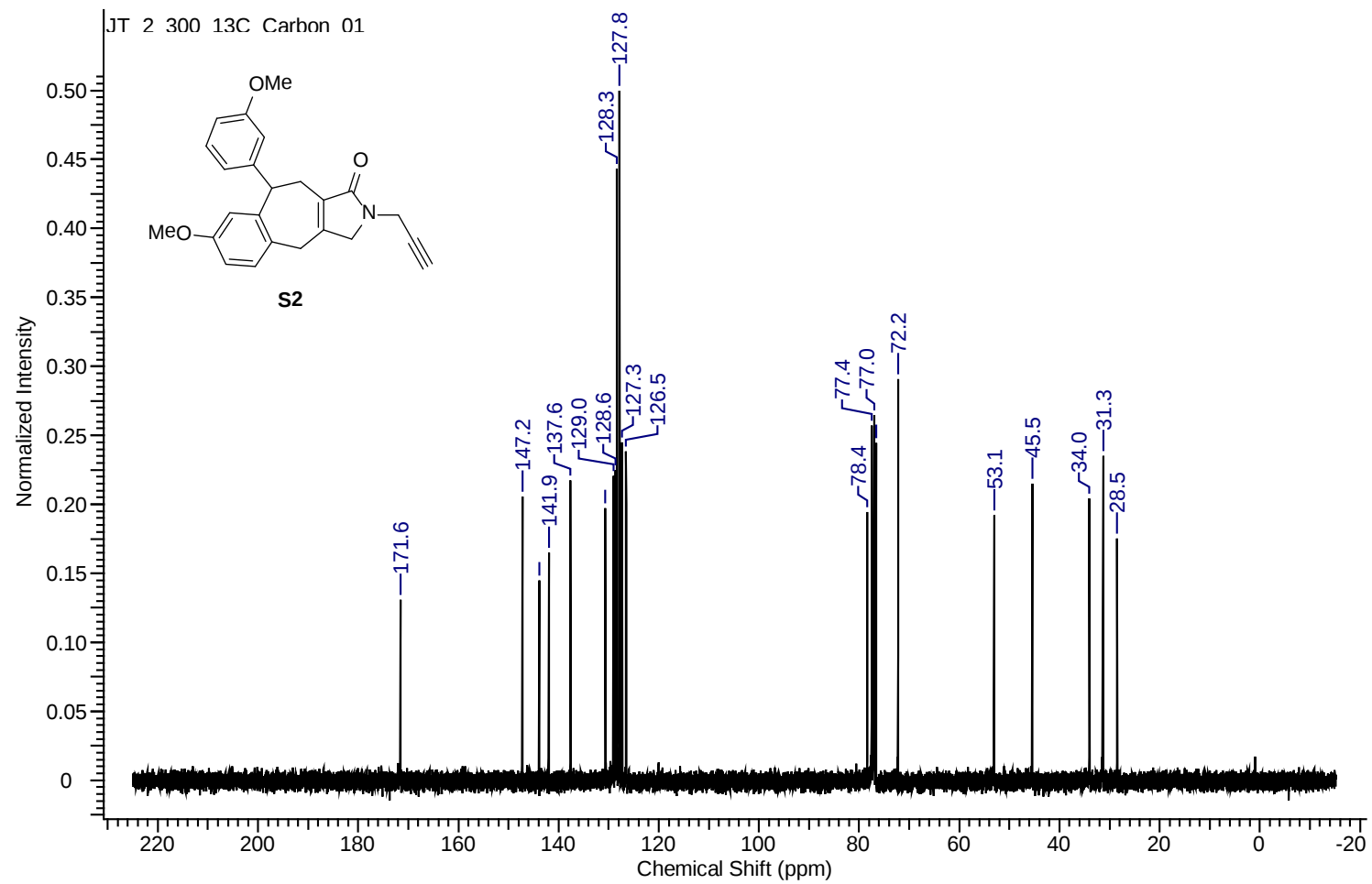
HRMS (ESI) *m/z* calculated for C₂₄H₂₃BrNO⁺ ([M+1]⁺) 420.0963, found 420.0974.

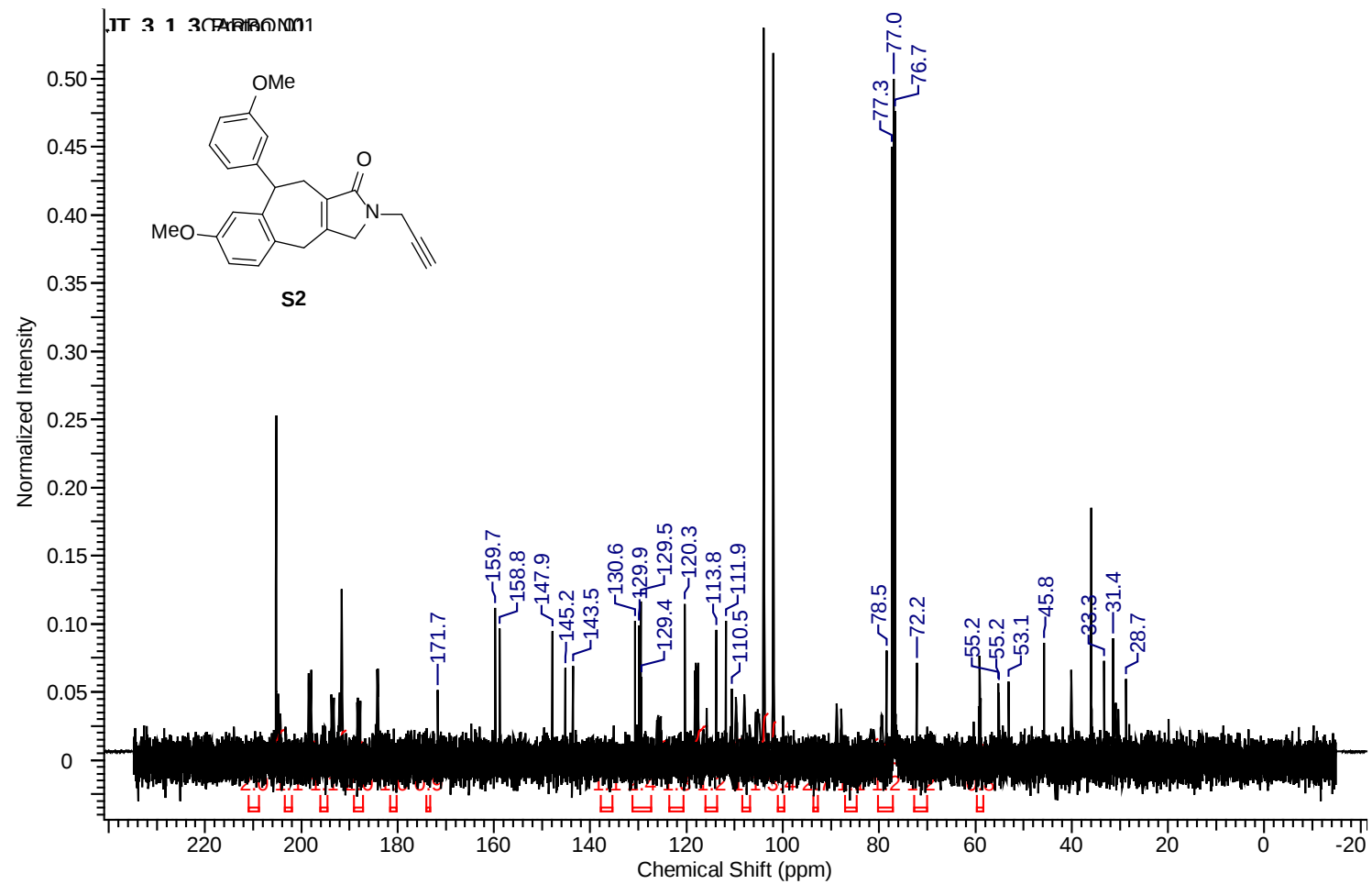


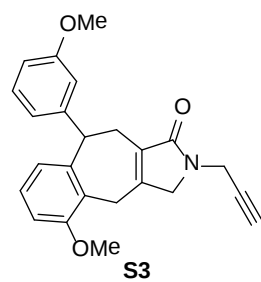


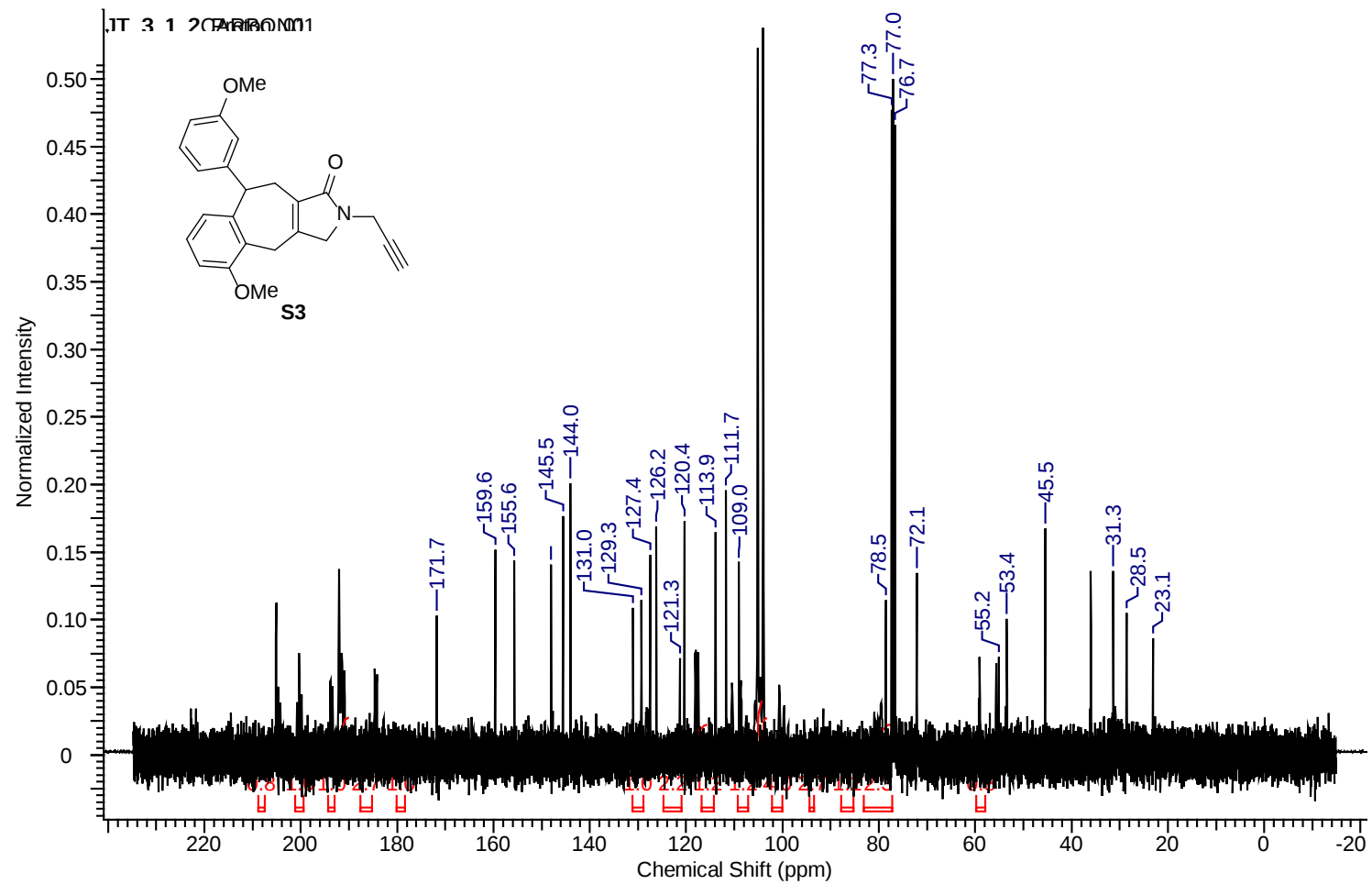


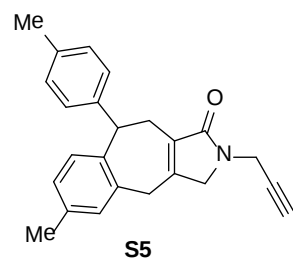


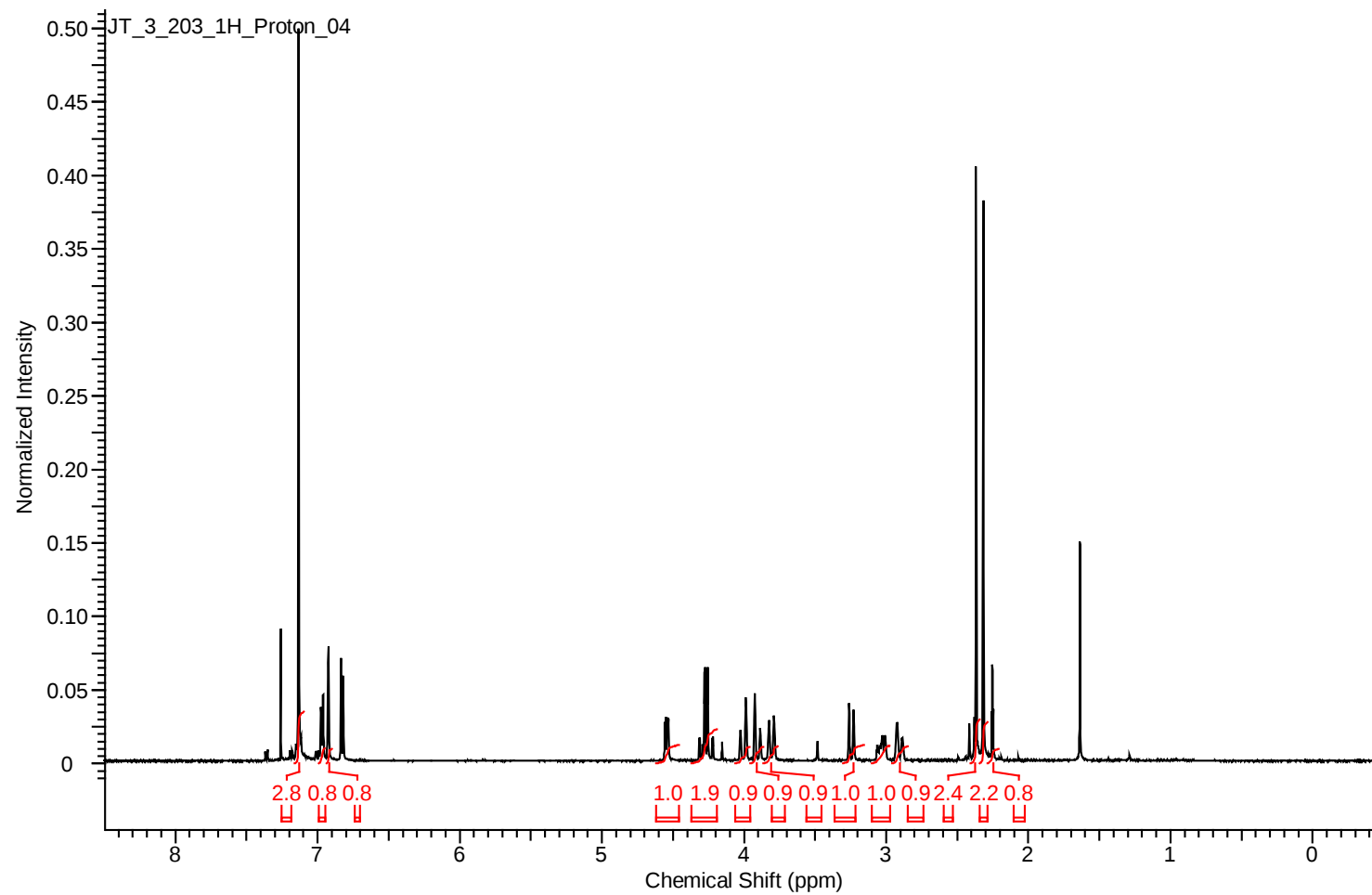


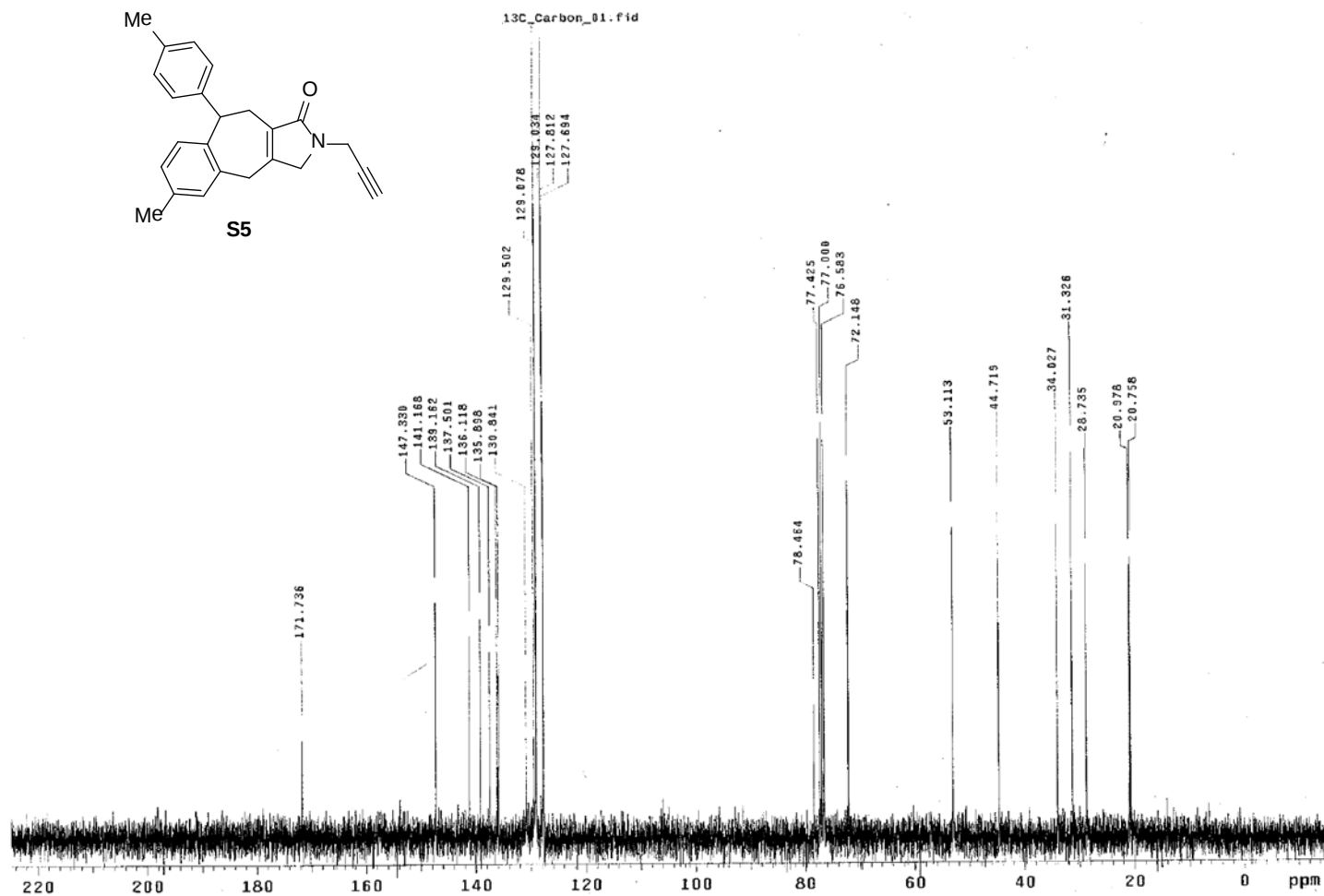


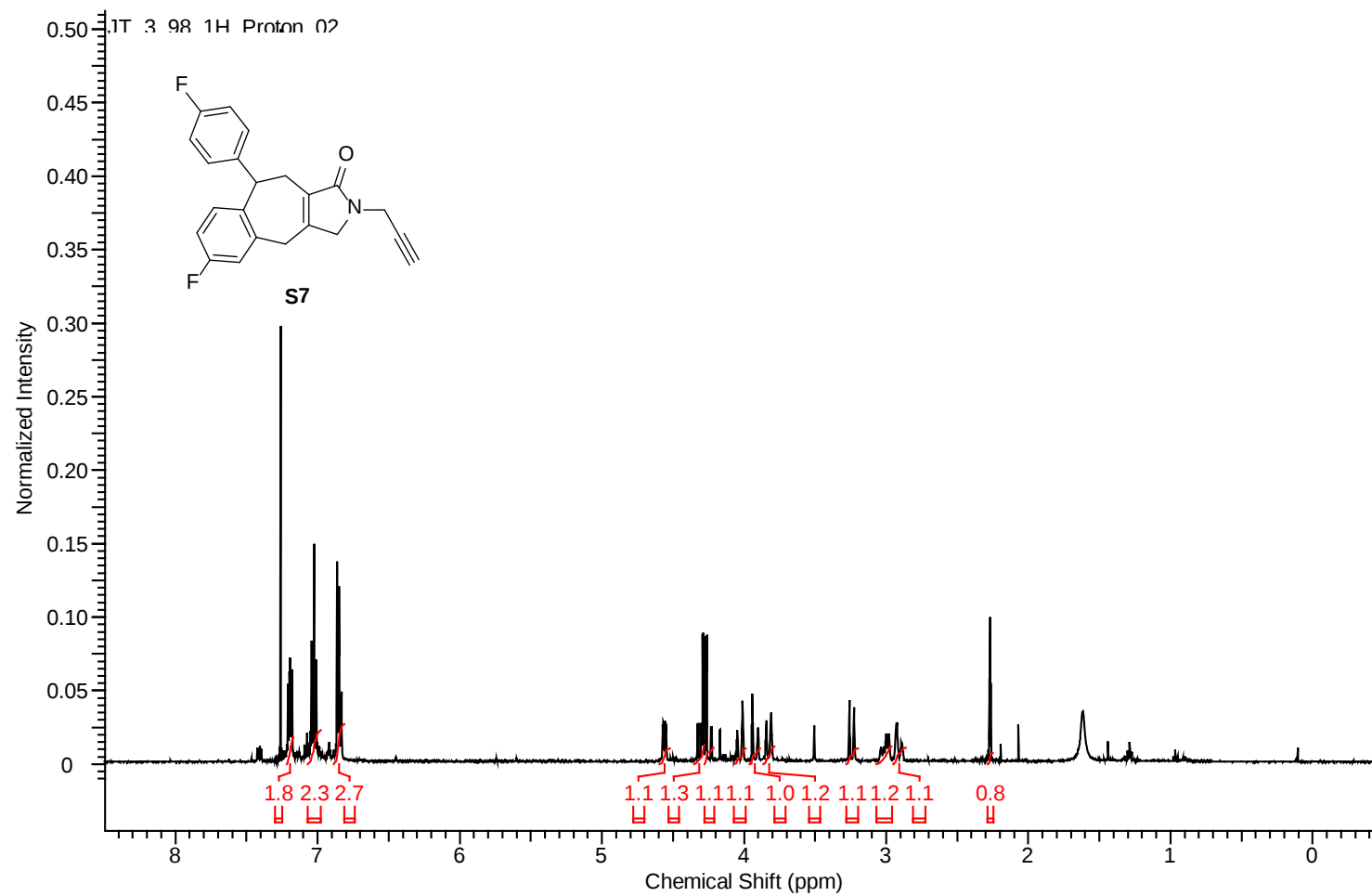


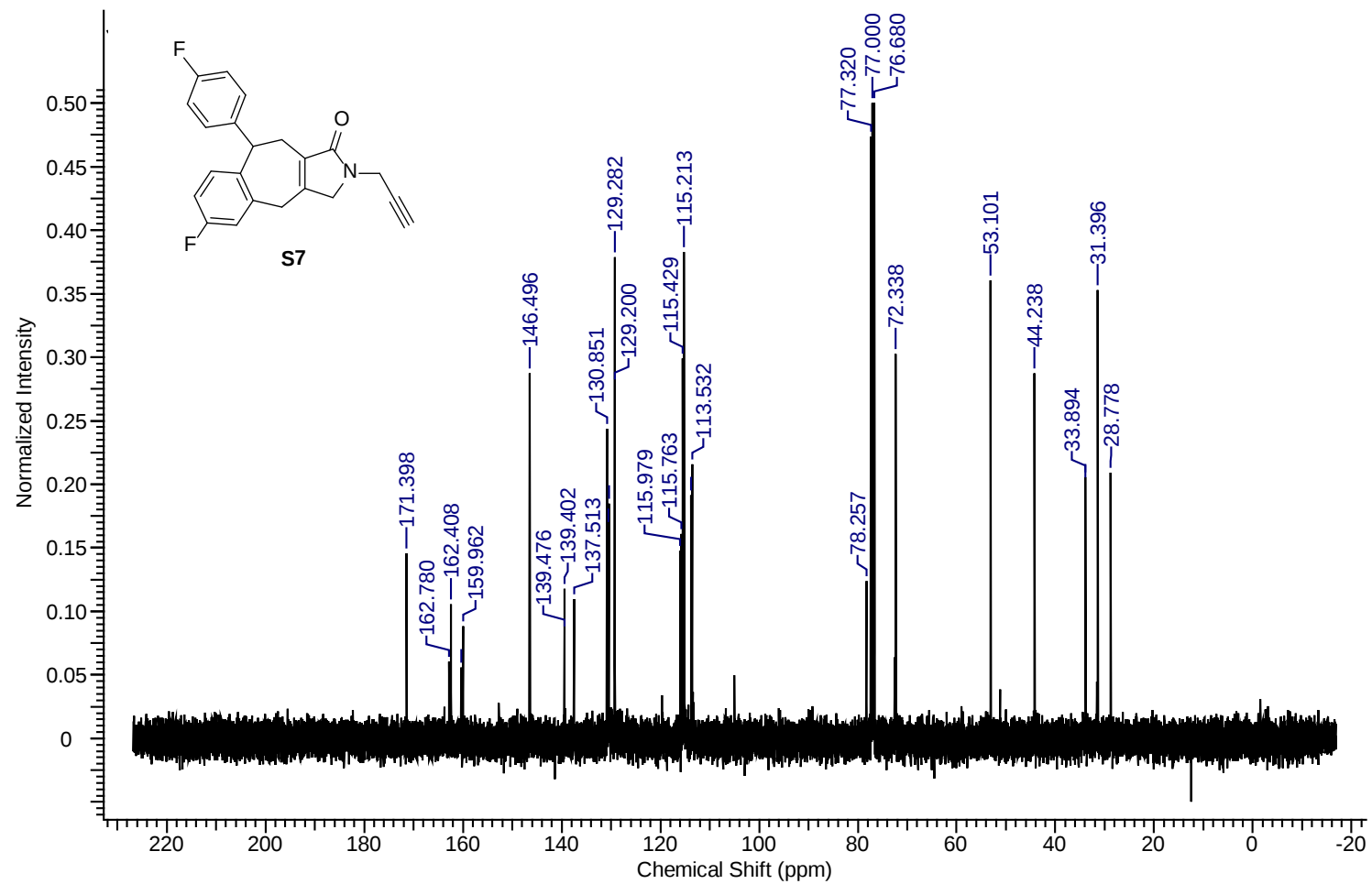


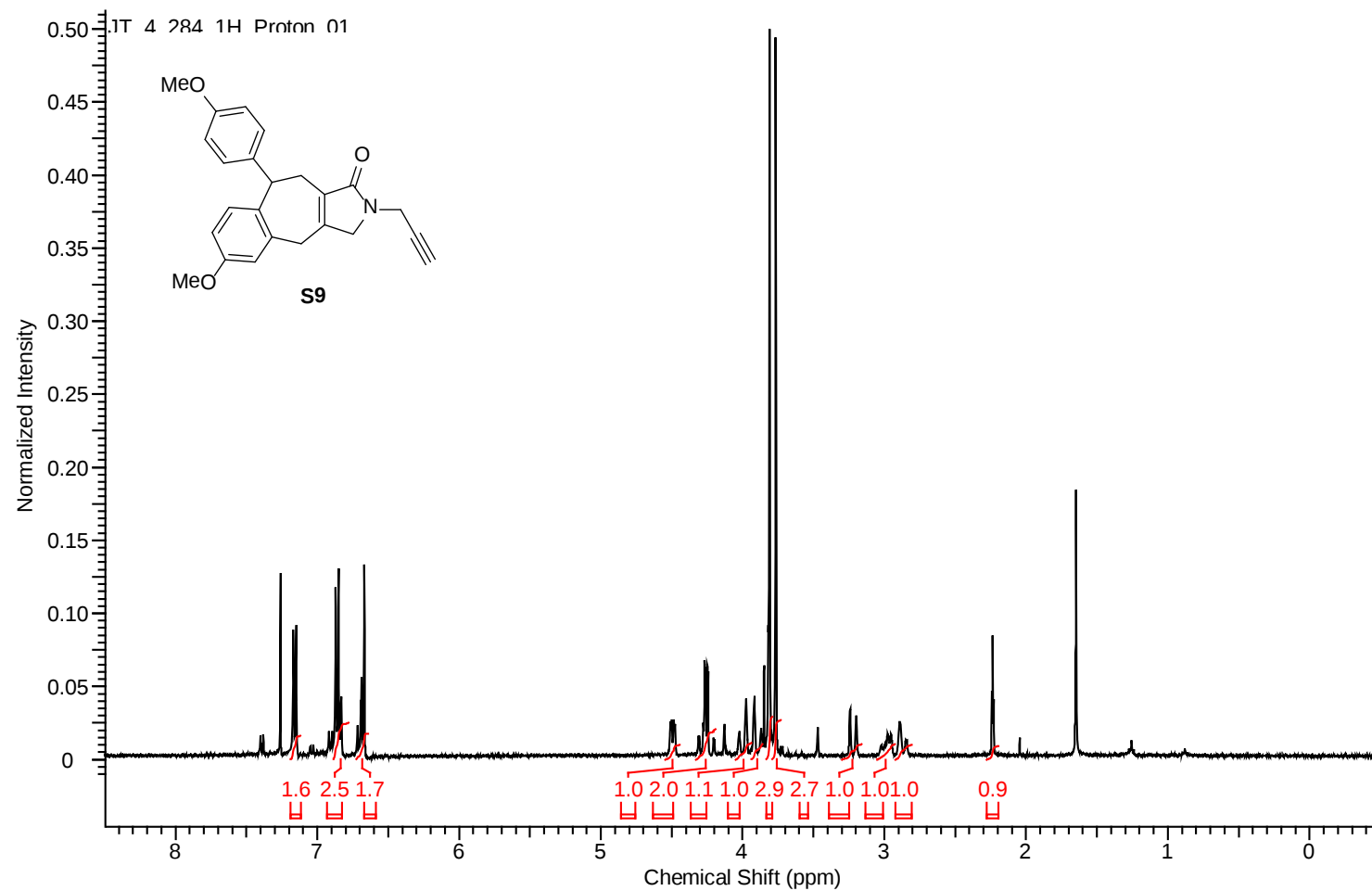


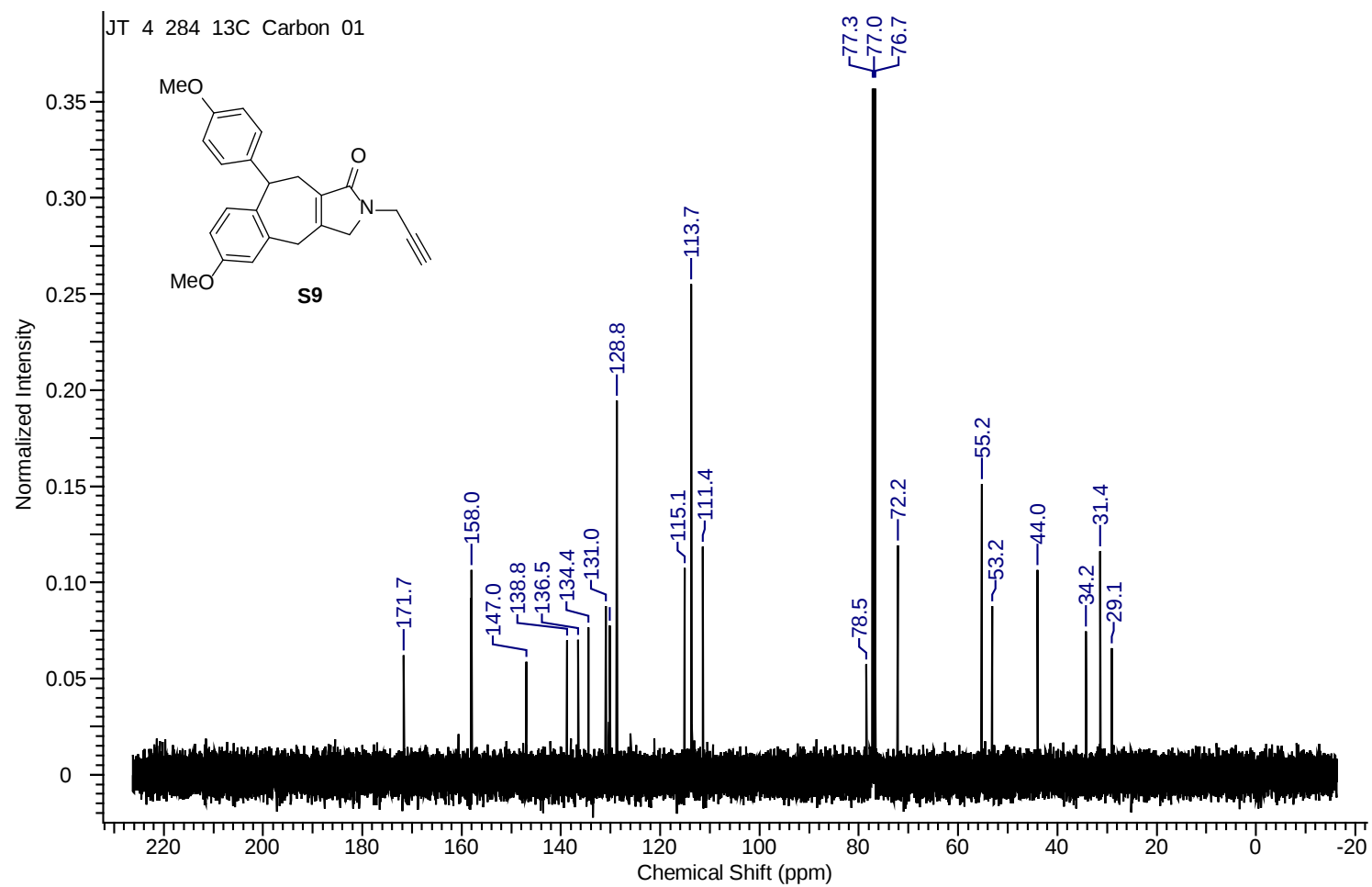


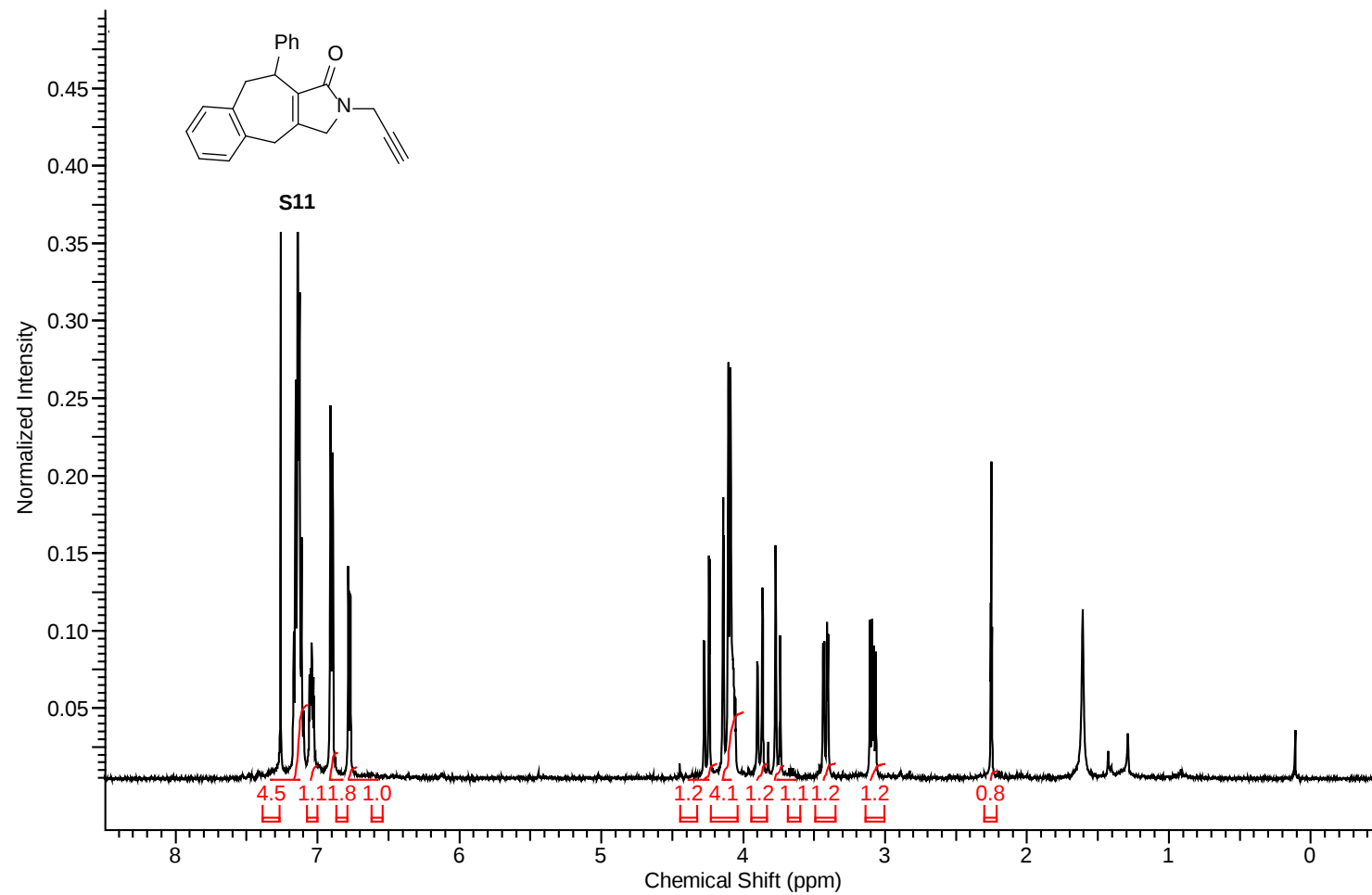


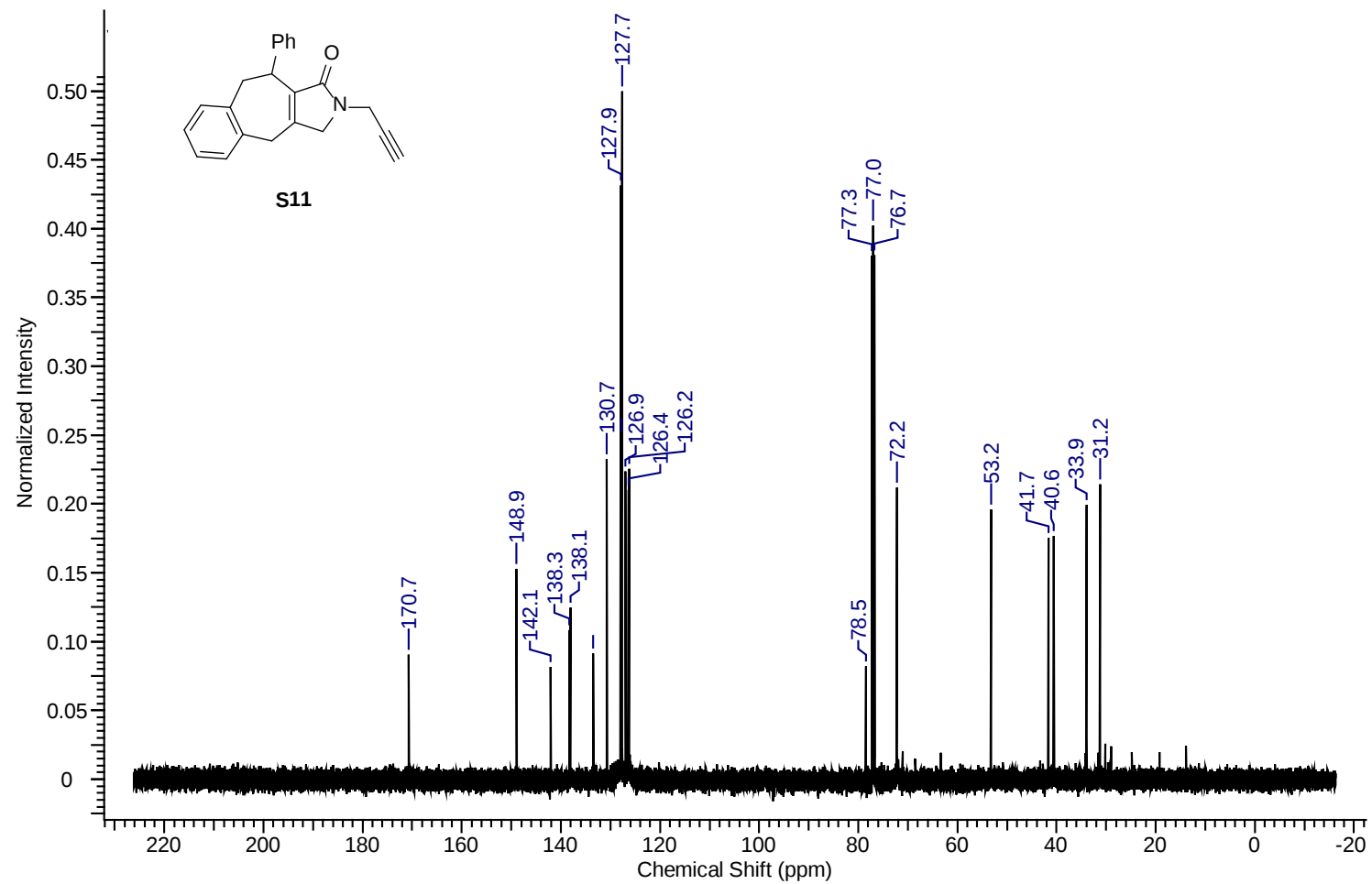


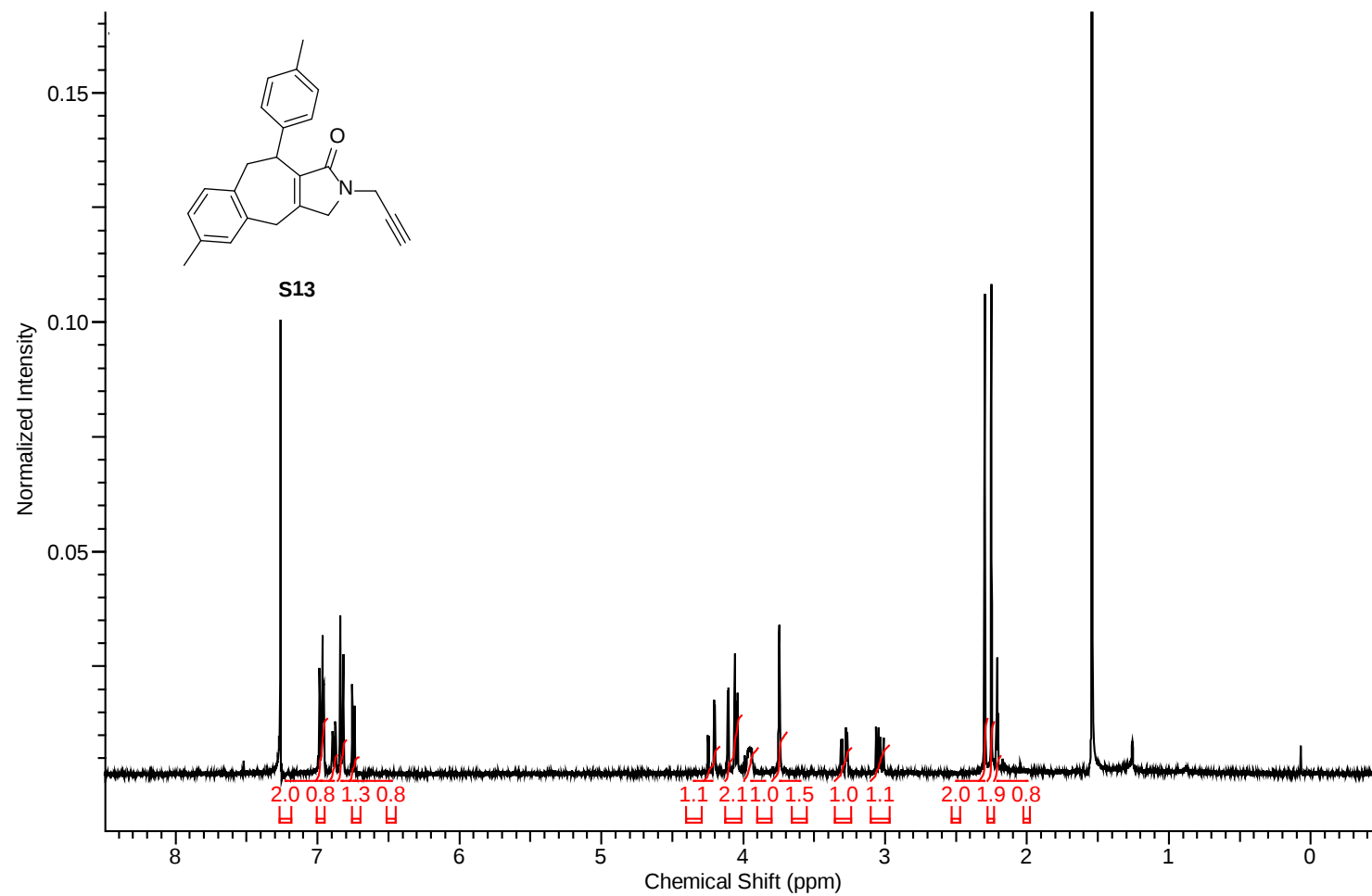


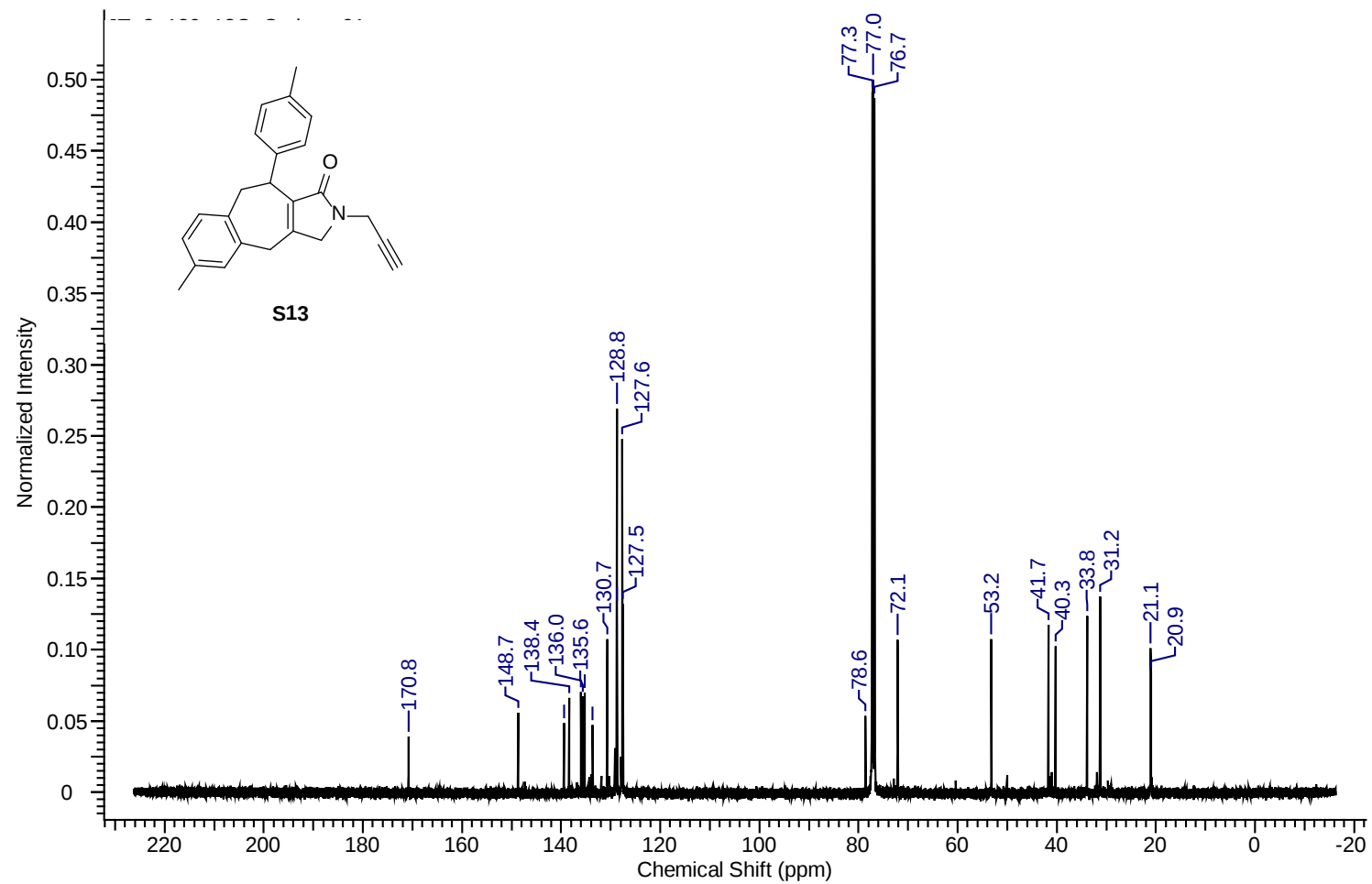


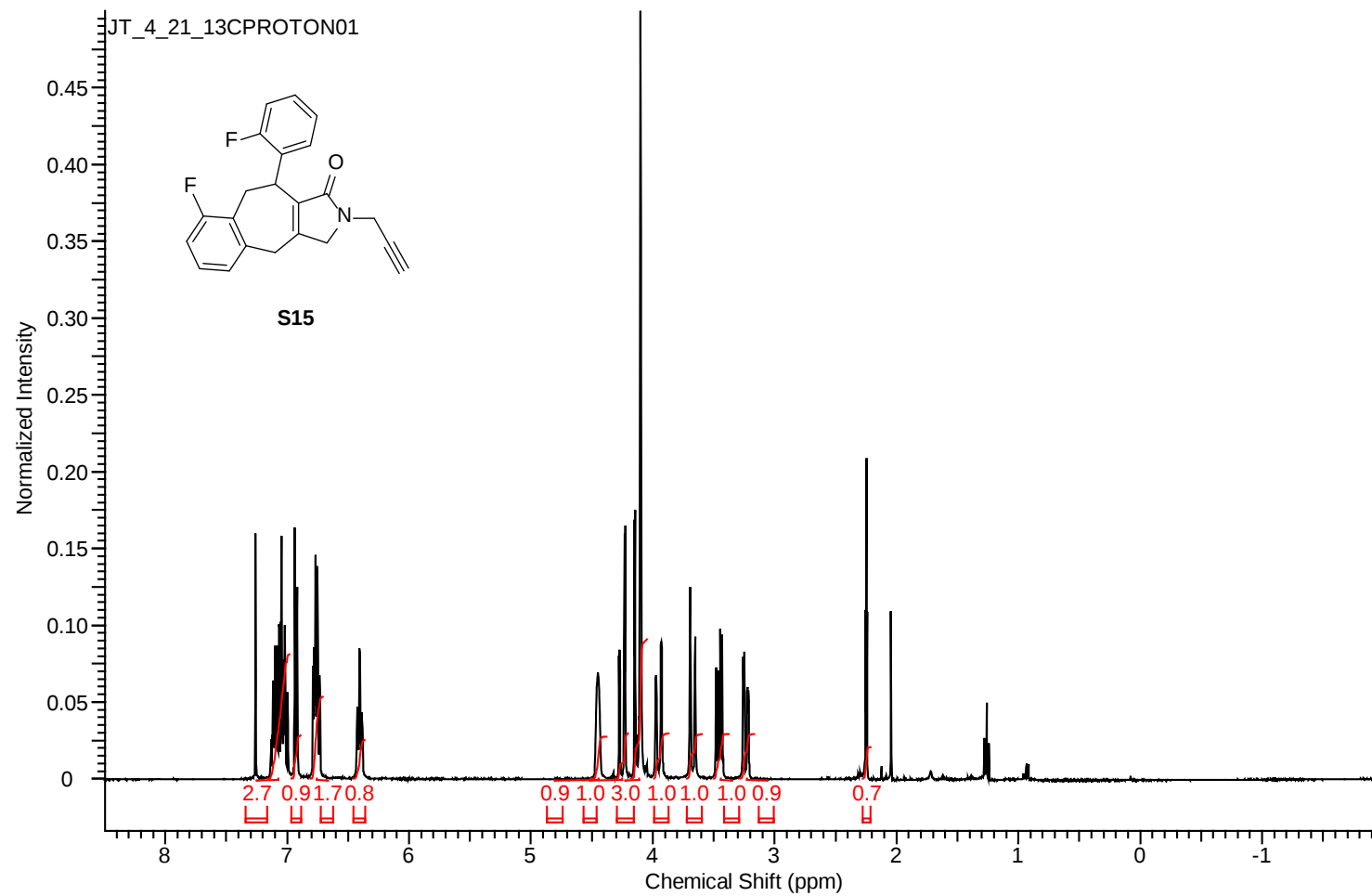












S65

