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Palladium-Catalyzed Intramolecular Oxypalladation-Initiated Cascade: Solvent-Dependent Chemodivergent Approach to Functionalized Benzazepines and Tetrahydroquinolines

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Supporting Information

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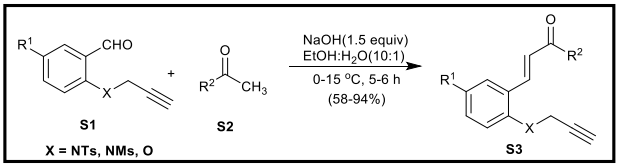
1. General Information

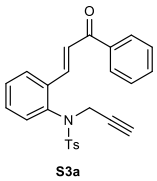
All reagents and solvents used in the experiment were obtained from commercial suppliers (Alfa Aesar, Sigma, Merck etc.) and were used without further purification. The reactions were carried out in oven dried glassware. The reactions were monitored by thin layer chromatography using Merck silica gel 60 F254 and visualized by UV detection or using molecular iodine or *p*-anisaldehyde stain. Silica gel (230-400 mesh) was used for flash column chromatography. Melting points were recorded on a melting point apparatus in capillaries and are uncorrected.^{1}H and ^{13}C{^{1}H}-NMR spectra were recorded in $CDCl_3$ at room temperature on a BruckerAC-400 or 500 spectrometers operating at 400 or 500 MHz for ^{1}H and 101 or 126 MHz for ^{13}C{^{1}H}. Chemical shifts (δ) are expressed in ppm using TMS as an internal standard and coupling constants (*J*) are given in Hz. Infrared (IR) spectra were obtained using an Affinity 1S Spectrophotometer with a diamond ATR accessory for solid and liquid samples, requiring no sample preparation and the major frequencies were reported in cm^{-1}. Elemental analyses were determined at the CAI de Microanálisis Elemental, Universidad Complutense, by using a Leco 932 CHNS combustion microanalyzer.

2. General Procedure for the Synthesis of Enones S3



Compounds **S1** were prepared using the literature procedure reported by our group earlier.[1,2] To a solution of methyl ketone **S2** (11 mmol, 1.1 equiv) in 10:1 EtOH/H_2O mixture (50 mL) was added NaOH (15 mmol, 1.5 equiv) at 0 °C. After stirring for 10 min., aryl aldehyde **S1** (10 mmol , 1.0 equiv) was added and stirring was continued at 10-15 °C for 5-6 h. After completion of the reaction, the reaction mixture was poured into ice water and acidified with 1.5N HCl. The aqueous suspension was extracted with DCM (2 x 100 mL), washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using petroleum ether and ethyl acetate mixture as eluent (90:10, v/v) to deliver the desired products **S3a-f, S3h-k**.

(*E*)-4-Methyl-*N*-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)-*N*-(prop-2-yn-1-yl)benzene sulfonamide (S3a)



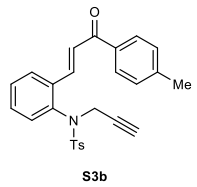
S3a

Colourless solid (3.90 g, 94%); mp: 124-126 °C; IR (neat): 3300, 2112, 1710, 1602, 1549, 1329, 1312, 1277, 1156, 1092 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (m, 2H), 7.90 (d, *J* = 16 Hz, 1H), 7.80 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.62-7.57 (m, 3H), 7.54-7.50 (m, 2H), 7.34 (td, *J* = 7.6, 0.8 Hz, 1H), 7.38-7.34 (m, 2H), 7.22 (d, *J* = 8.0, 2.0 Hz, 2H), 7.13 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.52 (brs, 1H), 4.32 (brs, 1H), 2.33 (s, 3H), 2.17 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 144.1, 140.3, 138.5, 137.9, 136.0, 135.5, 132.8, 130.7, 130.4, 129.6, 129.4, 128.8, 128.6, 128.2, 127.6, 124.9, 77.5, 74.3, 41.7, 21.5. Anal Calcd for $C_{25}H_{21}NO_3S$: C, 72.27; H, 5.09; N, 3.37. Found: C, 71.95; H, 5.01; N, 3.27.

[1] P. Vinoth, M. Karuppasamy, B. S. Vachan, I. Muthukrishnan, C. U. Maheswari, S. Nagarajan, V. Pace, A. Roller, N. Bhuvanesh, V. Sridharan, *Org. Lett.,* 2019, **21**, 3465−3469.

[2] M. Karuppasamy, B. S. Vachan, P. Vinoth, I. Muthukrishnan, S. Nagarajan, L. Ielo, V. Pace, S. Banik, C. U. Maheswari and V. Sridharan, *Org. Lett.,* 2019, **21**, 5784−5788.

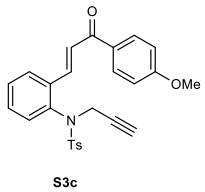
(*E*)-4-Methyl-*N*-(2-(3-oxo-3-(*p*-tolyl)prop-1-en-1-yl)phenyl)-*N*-(prop-2-yn-1-yl)benzene sulfonamide (S3b)



S3b

Colourless solid (3.43 g, 80%); mp: 131-133 °C; IR (neat): 3250, 2142, 1597, 1410, 1342, 1183, 1158, 1090 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 16.0 Hz, 1H), 7.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.43 (td, *J* = 7.6, 0.8 Hz, 1H), 7.37-7.35 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.15 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.54 (brs, 1H), 4.30 (brs, 1H), 2.44 (s, 3H), 2.32 (s, 3H), 2.18 (t, *J* = 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 144.1, 143.7, 139.7, 138.4, 136.1, 135.6, 135.3, 130.6, 130.5, 129.6, 129.4, 129.4, 128.9, 128.2, 127.6, 124.9, 77.5, 74.3, 41.7, 21.7, 21.5. Anal Calcd for $C_{26}H_{23}NO_3S$: C, 72.70; H, 5.40; N, 3.26. Found: C, 72.44; H, 5.36; N, 3.18.

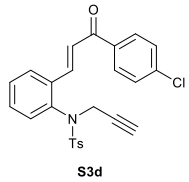
(*E*)-*N*-(2-(3-(4-Methoxyphenyl)-3-oxoprop-1-en-1-yl)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (S3c)



S3c

Colourless solid (3.87 g, 87%); mp: 141-143 °C; IR (neat): 3274, 2174, 1656, 1607, 1594, 1310, 1266, 1117, 1087 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01-8.04 (m, 2H), 7.86 (d, *J* = 15.9 Hz, 1H), 7.78 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.63-7.60 (m, 2H), 7.42 (td, *J* = 7.6, 0.8 Hz, 1H), 7.39-7.33 (m, 2H), 7.22 (d, *J* = 7.6, 2H), 7.14 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.00-6.98 (m, 2H), 4.55 (brs, 1H), 4.30 (brs, 1H), 3.90 (s, 3H), 2.33 (s, 3H), 2.18 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2, 163.4, 144.1, 139.3, 138.3, 136.1, 135.6, 131.1, 130.8, 130.5, 130.4, 129.6, 129.4, 128.2, 127.6, 124.8, 113.9, 77.5, 74.3, 55.5, 41.6, 21.5. Anal Calcd for $C_{26}H_{23}NO_4S$: C, 70.09; H, 5.20; N, 3.14. Found: C, 69.87; H, 5.13; N, 3.07.

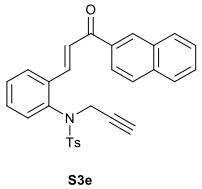
(*E*)-*N*-(2-(3-(4-Chlorophenyl)-3-oxoprop-1-en-1-yl)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide (S3d)



S3d

Colourless solid (4.01 g, 89%); mp: 154-156 °C; IR (neat): 3235, 2197, 1629, 1340, 1294, 1155, 1089, 1070 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99-7.92 (m, 3H), 7.80 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.51-7.47 (m, 2H), 7.45-7.42 (m, 1H), 7.38-7.31 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.08 (dd, *J* = 8.0, 0.8, 1H), 4.48 (brs, 1H), 4.35 (brs, 1H), 2.36 (s, 3H), 2.16 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 144.2, 140.9, 139.2, 138.6, 136.2, 135.9, 135.4, 130.8, 130.3, 130.1, 129.6, 129.4, 128.9, 128.2, 127.6, 124.5, 77.3, 74.3, 41.7, 21.6. Anal Calcd for $C_{25}H_{20}ClNO_3S$: C, 66.74; H, 4.48; N, 3.11. Found: C, 66.53; H, 4.42; N, 3.10.

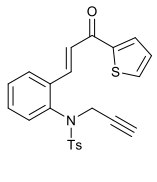
(*E*)-4-Methyl-*N*-(2-(3-(naphthalen-2-yl)-3-oxoprop-1-en-1-yl)phenyl)-*N*-(prop-2-yn-1-yl) benzenesulfonamide (S3e)



S3e

Yellow solid (4.32 g, 93%); mp: 68-70 °C; IR (neat): 3149, 2207, 1519, 1390, 1254, 1165, 1149, 1070 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.11-8.07 (m, 1H), 8.03 (d, *J* = 17.2 Hz, 1H), 7.98-7.96 (m, 2H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.63-7.57 (m, 4H), 7.53-7.46 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 1H), 4.53 (brs, 1H), 4.36 (brs, 1H), 2.33 (s, 3H), 2.18 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 144.1, 140.3, 138.5, 136.1, 135.5, 135.1, 132.6, 130.6, 130.3, 129.7, 129.6, 129.4, 128.6, 128.4, 128.2, 127.8, 127.7, 126.8, 125.2, 124.7, 77.5, 74.3, 41.7, 21.5. Anal Calcd for $C_{29}H_{23}NO_3S$: C, 74.82; H, 4.98; N, 3.01. Found C, 74.53; H, 4.86; N, 2.92. *Two aromatic carbons merged with others.

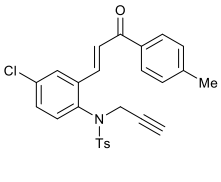
(*E*)-4-Methyl-*N*-(2-(3-oxo-3-(thiophen-2-yl)prop-1-en-1-yl)phenyl)-*N*-(prop-2-yn-1-yl) benzenesulfonamide (S3f)



S3f

Colourless solid (2.86 g, 68%); mp: 137-139 ºC; IR (neat): 3150, 2172, 1507, 1430, 1312, 1209, 1101 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 15.9 Hz, 1H), 7.80 (d, *J* = 7.6 Hz 1H), 7.67-7.62 (m, 3H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.40-7.36 (m, 2H), 7.34 (d, *J* = 16.0 Hz, 1H), 7.28-7.24 (m, 3H), 7.19 (d, *J* = 7.8 Hz, 1H), 6.62-6.61 (m, 1H), 4.56 (brs, 1H), 4.33 (brs, 1H), 2.35 (s, 3H), 2.21 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.3, 145.2, 144.2, 139.3, 138.5, 135.8, 135.6, 133.9, 132.3, 130.7, 130.6, 129.6, 129.4, 128.3, 128.2, 127.8, 124.4, 77.5, 74.3, 41.7, 21.5. Anal Calcd for $C_{23}H_{19}NO_3S_2$: C, 65.54; H, 4.54; N, 3.32. Found: C, 65.37; H, 4.43; N, 3.31.

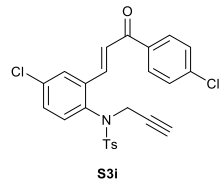
(*E*)-*N*-(4-Chloro-2-(3-oxo-3-(*p*-tolyl)prop-1-en-1-yl)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (S3h)



S3h

Colourless solid (4.64 g, 90%); mp: 130-132 ºC; IR (neat): 3301, 2143, 1713, 1619, 1509, 1309, 1333, 1217, 1106, 1064 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0, 2H), 7.81-7.86 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.37-7.32 (m, 4H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 18.5 Hz, 1H), 4.53 (brs, 1H), 4.30 (brs, 1H), 2.46 (s, 3H), 2.33 (s, 3H), 2.22 (t, *J* = 2.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 144.3, 143.9, 138.2, 137.9, 136.7, 135.4, 135.3, 135.0, 131.9, 130.4, 129.7, 129.4, 128.9, 128.1, 127.4, 125.6, 77.4, 74.6, 41.6, 21.7, 21.5. Anal Calcd for $C_{26}H_{22}ClNO_3S$: C, 67.31; H, 4.78; N, 3.02. Found: C, 66.98; H, 4.77; N, 2.94.

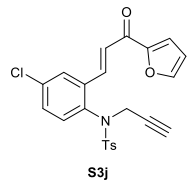
(*E*)-*N*-(4-Chloro-2-(3-(4-chlorophenyl)-3-oxoprop-1-en-1-yl)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (S3i)



S3i

Off-white solid (3.12 g, 58%); mp: 151-153 ºC; IR (neat): 3210, 2149, 1702, 1623, 1514, 1342, 1325, 1261, 1113, 1063 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 15.9 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.35-7.31 (m, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 1H), 4.48 (brs, 1H), 4.33 (brs, 1H), 2.37 (s, 3H), 2.20 (t, *J* = 1.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 144.4, 139.5, 139.3, 137.7, 136.9, 135.9, 135.4, 135.1, 131.4, 130.6, 130.3, 129.7, 129.0, 128.2, 127.5, 125.2, 77.3, 74.6, 41.6, 21.6. Anal Calcd for $C_{25}H_{19}Cl_2NO_3S$: C, 61.99; H, 3.95; N, 2.89. Found: C, 61.73; H, 3.91; N, 2.81.

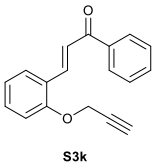
(*E*)-*N*-(4-Chloro-2-(3-(furan-2-yl)-3-oxoprop-1-en-1-yl)phenyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (S3j)



S3j

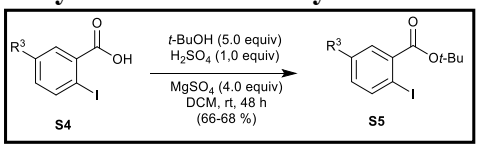
Colourless solid (3.50 g, 78%); mp: 138-140 ºC; IR (neat): 3216, 2132, 1678, 1642, 1532, 1351, 1309, 1297, 1139, 1062 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 15.9 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.68-7.67 (m, 1H), 7.63-7.59 (m, 2H), 7.36-7.35 (m, 1H), 7.33 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.26-7.24 (m, 3H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.62-6.61 (m, 1H), 4.54 (brs, 1H), 4.28 (brs, 1H), 2.34 (s, 3H), 2.21 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.4, 153.3, 146.8, 144.4, 137.7, 137.6, 136.8, 135.4, 135.3, 131.9, 130.6, 129.7, 128.2, 127.5, 124.7, 118.2, 77.2, 74.6, 41.6, 21.5. Anal Calcd for $C_{23}H_{18}ClNO_4S$: C, 62.80; H, 4.12; N, 3.18. Found: C, 62.71; H, 4.11; N, 3.09. *One aromatic carbon merged with others.

(*E*)-1-Phenyl-3-(2-(prop-2-yn-1-yloxy)phenyl)prop-2-en-1-one (S3k)


S3k

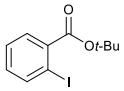
Pale yellow solid (2.12 g, 81%); mp: 69-71 °C; IR (neat): 3312, 2022, 1712, 1623, 1574, 1341, 1307, 1277, 1134, 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 15.8 Hz, 1H), 8.08-8.04 (m, 2H), 7.71-7.66 (m, 2H), 7.60 (t, *J* = 7.2, 1.3 Hz, 1H), 7.53-7.50 (m, 2H), 7.41 (td, *J* = 8.5, 1.6 Hz, 1H), 7.07-7.05 (m, 2H), 4.82 (s, 1H), 4.83 (s, 1H), 2.58 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 156.7, 140.1, 138.4, 132.6, 131.5, 129.5, 128.6, 128.6, 124.5, 123.3, 121.7, 112.8, 78.2, 76.0, 56.2. Anal Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.21; H, 5.31.

3. General Procedure for the Synthesis of *tert*-Butyl 2-iodobenzoates S5[3]



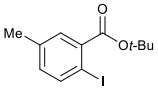
To a stirred suspension of $MgSO_4$ (80 mmol, 4.0 equiv) in DCM (100 mL) at room temperature was added H_2SO_4 (20 mmol, 1.0 equiv) under N_2 atmosphere. After 15 min., 2-iodobenzoic acid **S4** (20 mmol, 1.0 equiv) and *tert*-butanol (100 mmol, 5.0 equiv) were added, and the resulting mixture was stirred at room temperature for 48 h. After completion of the reaction, the mixture was quenched by using saturated $NaHCO_3$ solution and extracted with DCM (2 x 140 mL), washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using petroleum ether-ethyl acetate mixture as eluent (95:05, v/v) to obtain *tert*-butyl 2-iodobenzoates **S5**.

tert-Butyl 2-iodobenzoate (S5a)[3]


S5a

Colourless liquid; yield: 4.136 g, 68%

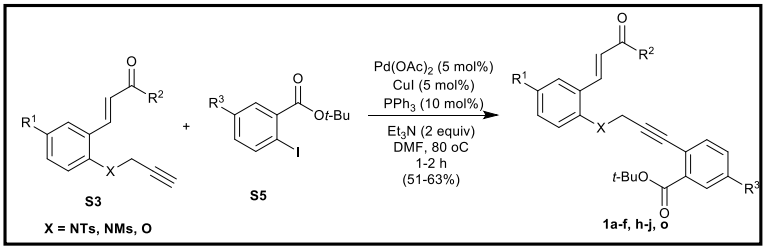
tert-Butyl 2-iodo-5-methylbenzoate (S5b)[3]


S5b

Colourless liquid; yield: 4.198 g, 66%

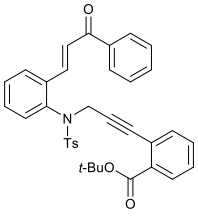
[3] M. Karuppasamy, P. Vinoth, N. Pradeep, S. Nagarajan, C. U. Maheswari and V. Sridharan, *Org. Biomol. Chem.,* 2020, **18**, 8474−8485. (b) M. Karuppasamy, B. S. Vachan, T. Jandial, S. B. Annes, N. Bhuvanesh, C. U. Maheswari and V. Sridharan, *Adv. Synth. Catal.,* 2020, **362**, 2716−2724.

4. General Procedure for the Synthesis of Compounds 1a-f, h-j and o



To a stirred solution of compound S**3** (5 mmol, 1.0 equiv) in DMF (15 mL) were added *tert*-butyl 2-iodobenzoate **S5** (6 mmol, 1.2 equiv), $Pd(OAc)_2$ (0.05 mmol, 5 mol%), PPh_3 (0.1 mmol, 10 mol%), CuI (0.05 mmol, 5mol %), and Et_3N (2 mmol, 2.0 equiv) successively. The resulting mixture was stirred at 80 °C for 1-2 h. After the completion of the reaction, as indicated by TLC, the reaction mixture was quenched by pouring into ice-cold water and extracted with ethyl acetate (2 × 80 mL). The organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated to dryness under reduced pressure and the crude mixture was chromatographed over silica using the petroleum ether and ethyl acetate mixture (85:15 to 80:20, v/ v) as the eluent to access the desired compounds **1a-f, h-j**.

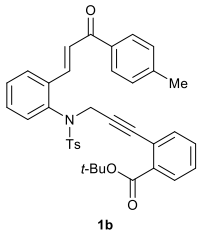
tert-Butyl(*E*)-2-(3-((4-methyl-*N*-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)phenyl)sulfonamido)prop-1-yn-1-yl)benzoate (1a)



1a

Off-white solid (1.86 g, 63%); mp: 130-132 °C; IR (neat): 3012, 2154, 1732, 1595, 1482, 1351, 1308, 1295, 1250, 1180, 1161, 1132 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06-8.01 (m, 3H), 7.84-7.81 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.54-7.50 (m, 2H), 7.45-7.42 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.34-7.31 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.16-7.14 (m, 1H), 4.89 (d, *J* = 17.6 Hz, 1H), 4.53 (d, *J* = 16.9 Hz, 1H), 2.32 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 165.0, 143.9, 140.6, 138.8, 137.9, 136.1, 135.9, 134.3, 133.5, 132.7, 131.0, 130.6, 130.4, 130.1, 129.5, 129.3, 128.9, 128.6, 128.3, 128.1, 127.6, 125.0, 122.3, 87.5, 85.1, 81.6, 42.9, 28.1, 21.5. Anal Calcd for $C_{36}H_{33}NO_5S$: C, 73.07; H, 5.62; N, 2.37. Found: C, 72.88; H, 5.58; N, 2.31.

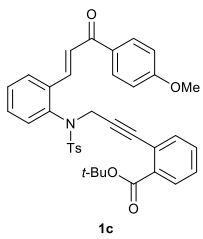
tert-Butyl(*E*)-2-(3-((4-methyl-*N*-(2-(3-oxo-3-(*p*-tolyl)prop-1-en-1-yl)phenyl)phenyl)sulfonamido)prop-1-yn-1-yl)benzoate (1b)



1b

Pale yellow solid (1.72 g, 57%); mp: 176-178 °C; IR (neat): 3021, 2197, 1729, 1634, 1602, 1483, 1350, 1297, 1281, 1182, 1162, 1132 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 16.0 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.38-7.37 (m, 1H), 7.32-7.30 (m, 4H), 7.28-7.26 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 1H), 4.91 (d, *J* = 16.7 Hz, 1H), 4.52 (d, *J* = 16.7 Hz, 1H), 2.45 (s, 3H), 2.31 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 165.1, 143.9, 143.6, 139.9, 138.8, 136.2, 135.9, 135.3, 134.3, 133.5, 131.0, 130.5, 130.4, 130.1, 129.5, 129.3, 129.2, 128.9, 128.3, 128.1, 127.6, 125.1, 122.3, 87.6, 85.0, 81.6, 42.9, 28.1, 21.7, 21.5. Anal Calcd for $C_{37}H_{35}NO_5S$: C, 73.36; H, 5.82; N, 2.31. Found: C, 73.08; H, 5.77; N, 2.29. *Two aromatic carbons merged with others.

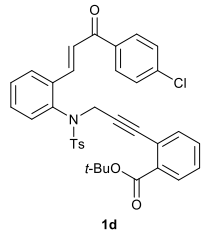
***tert*-Butyl(*E*)-2-(3-((*N*-(2-(3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)phenyl)-4-methyl phenyl)sulfonamido)prop-1-yn-1-yl)benzoate (1c)**



1c

Light brown solid (1.86 g, 60%); mp: 159-161 °C; IR (neat): 2969, 2313, 1723, 1633, 1597, 1568, 1483, 1360, 1352, 1297, 1253, 1175, 1163 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.97 (d, *J* = 16.0 Hz, 1H), 8.80-8.77 (m, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.40-7.36 (m, 2H), 7,34-7.27 (m, 3H), 7.22 (dd, *J* = 12.0, 7.9 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.13-7.11 (m, 1H), 6.96 (dd, *J* = 6.9, 1.9 Hz, 2H), 4.88 (d, *J* = 17.4 Hz, 1H), 4.48 (d, *J* = 17.8 Hz, 1H), 3.87 (s, 3H), 2.28 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.6, 165.1, 163.4, 143.9, 139.6, 138.8, 136.4, 135.9, 134.4, 133.5, 131.3, 131.1, 130.9, 130.5, 130.6, 130.2, 129.6, 129.3, 128.4, 128.1, 127.7, 125.0, 122.4, 113.9, 87.6, 85.1, 81.7, 55.6, 42.9, 28.2, 21.6. Anal Calcd for $C_{37}H_{35}NO_6S$: C, 71.48; H, 5.67; N, 2.25. Found: C, 71.29; H, 5.62; N, 2.23.

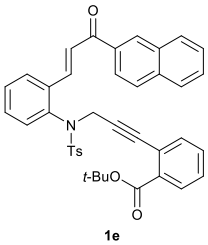
***tert*-Butyl(*E*)-2-(3-((*N*-(2-(3-(4-chlorophenyl)-3-oxoprop-1-en-1-yl)phenyl)-4-methylphen yl)sulfonamido)prop-1-yn-1-yl)benzoate (1d)**



1d

Light brown solid (1.88 g, 60%); mp: 186-188 °C; IR (neat): 2991, 2249, 1728, 1638, 1593, 1482, 1350, 1297, 1281, 1251, 1176, 1133, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 16.1 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.84-7.81 (m, 2H), 7.67 (d, *J* = 8.1 Hz. 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.39-7.35 (m, 2H), 7.33-7.31 (m, 2H), 7.23-7.21 (m, 3H), 7.13-7.11 (m, 1H), 4.84 (d, *J* = 17.2 Hz, 1H), 4.55 (d, *J* = 17.3 Hz, 1H), 2.34 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 164.9, 143.9, 141.2, 139.1, 138.9, 136.2, 136.1, 135.7, 134.2, 133.5, 131.0, 130.8, 130.3, 130.2, 130.1, 129.5, 129.3, 128.9, 128.3, 128.1, 127.6, 124.7, 122.3, 87.4, 85.1, 81.6, 42.9, 28.1, 21.5. Anal Calcd for $C_{36}H_{32}ClNO_5S$: C, 69.05; H, 5.15; N, 2.24. Found C, 68.75; H, 5.06; N, 2.19.

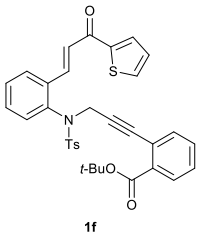
***tert*-Butyl(*E*)-2-(3-((4-methyl-*N*-(2-(3-(naphthalen-2-yl)-3-oxoprop-1-en-1-yl)phenyl)phe nyl)sulfonamido)prop-1-yn-1-yl)benzoate (1e)**



1e

Colourless solid (1.79 g, 56%); mp: 150-152 °C; IR (neat): 3109, 2209, 1724, 1631, 1482, 1364, 1281, 1255, 1162, 1133, 1107 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.14-8.06 (m, 3H), 7.97-7.89 (m, 3H), 7.82-7.80 (m, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.63-7.58 (m, 2H), 7.52 (d, *J* = 16.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.31-7.27 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13-7.11 (m, 1H), 4.88 (d, *J* = 18.9 Hz, 1H), 4.55 (d, *J* = 17.4 Hz, 1H), 2.31 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 165.0, 143.9, 140.5, 138.8, 136.3, 135.8, 135.5, 135.1, 134.3, 133.4, 132.6, 131.0, 130.7, 130.6, 130.3, 130.1, 129.8, 129.5, 129.3, 128.5, 128.4, 128.3, 128.1, 127.8, 127.7, 126.7, 125.3, 124.8, 122.3, 87.5, 85.1, 81.6, 42.9, 28.1, 21.5. Anal Calcd for $C_{40}H_{35}NO_5S$: C, 74.86; H, 5.50; N, 2.18. Found: C, 74.75; H, 5.53; N, 2.21.

***tert*-Butyl(*E*)-2-(3-((4-methyl-*N*-(2-(3-oxo-3-(thiophen-2-yl)prop-1-en-1-yl)phenyl)pheny yl)sulfonamido)prop-1-yn-1-yl)benzoate (1f)**

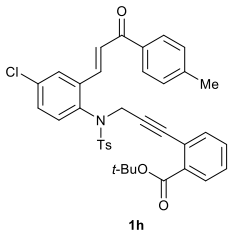


1f

Light brown solid (1.50 g, 51%); mp: 145-147 °C; IR (neat): 2950, 2231, 1721, 1659, 1652, 1567, 1483, 1463, 1393, 1304, 1281, 1249, 1158, 1132 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 16.0 Hz, 1H), 7.83-7.81 (m, 2H), 7.70-7.66 (m, 3H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.38-7.35 (m, 3H), 7.33-7.30 (m, 2H), 7.28 (s, 1H), 7.23-7.18 (m, 3H), 6.61-6.60 (m, 1H), 4.93 (d, *J* = 17.9 Hz, 1H), 4.53 (d, *J* = 17.4 Hz, 1H), 2.32 (s, 3H), 1.52 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 165.1, 153.4, 146.6, 143.9, 139.4, 138.8, 135.9, 135.8, 134.3, 133.4, 131.1, 130.7, 130.5, 130.1,

129.5, 129.3, 128.3, 128.1, 127.7, 124.0, 122.3, 118.0, 112.5, 87.5, 85.1, 81.6, 42.9, 28.1, 21.5. Anal Calcd for $C_{34}H_{31}NO_5S_2$: C, 68.32; H, 5.23; N, 2.34. Found: C, 68.04; H, 5.15; N, 2.31.

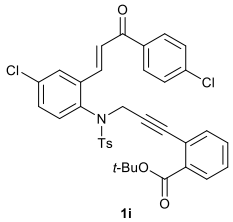
***tert*-Butyl(*E*)-2-(3-((*N*-(4-chloro-2-(3-oxo-3-(*p*-tolyl)prop-1-en-1-yl)phenyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)benzoate (1h)**



1h

Pale yellow solid (1.73 g, 54%); mp: 79-81 °C; IR (neat): 2987, 2209, 1735, 1603, 1562, 1481, 1379, 1268, 1251, 1173, 1157 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94-7.89 (m, 3H), 7.84-7.78 (m, 2H), 7.71-7.65 (m, 2H), 7.37-7.34 (m, 5H), 7.28-7.25 (m, 2H), 7.21-7.19 (m, 3H), 4.91 (d, *J* = 15.4 Hz, 1H), 4.48 (d, *J* = 18.3 Hz, 1H), 2.46 (s, 3H), 2.30 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 164.9, 144.1, 143.9, 138.5, 137.9, 137.1, 135.3, 134.3, 133.4, 131.9, 131.1, 130.4, 130.2, 129.6, 129.4, 129.1, 128.9, 128.4, 128.3, 128.2, 127.4, 125.7, 122.3, 87.2, 85.2, 81.6, 42.8, 28.1, 21.7, 21.5. Anal Calcd for $C_{37}H_{34}ClNO_5S$: C, 69.42; H, 5.35; N, 2.19. Found: C, 69.23; H, 5.31; N, 2.10.

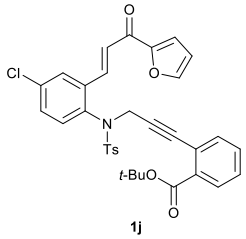
***tert*-Butyl(*E*)-2-(3-((*N*-(4-chloro-2-(3-(4-chlorophenyl)-3-oxoprop-1-en-1-yl)phenyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)benzoate (1i)**



1i

Colourless solid (2.04 g, 62%); mp: 135-137 °C; IR (neat): 2979, 2219, 1742, 1739, 1638, 1612, 1593, 1462, 1314, 1107 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96-7.92 (m, 3H), 7.81-7.79 (m, 1H), 7.75 (d, *J* = 2.5 Hz, 1H), 7.63-7.62 (m, 2H), 7.46-7.44 (m, 2H), 7.32-7.28 (m, 4H), 7.19-7.17 (m, 3H), 7.12 (dd, *J* = 7.5, 1.7 Hz, 1H), 4.82 (d, *J* = 17.2 Hz, 1H), 4.49 (d, *J* = 17.3 Hz, 1H), 2.30 (s, 3H), 1.50 (s, 9H); $^{13}CNMR$ (126 MHz, $CDCl_3$) δ 189.7, 164.9, 144.3, 139.7, 139.4, 137.9, 137.4, 135.9, 135.5, 135.4, 134.4, 133.5, 131.6, 131.2, 130.7, 130.4, 130.3, 129.7, 129.1, 128.4, 128.3, 127.5, 125.4, 122.3, 87.1, 85.4, 81.6, 42.9, 28.2, 21.6. Anal Calcd for $C_{36}H_{31}Cl_2NO_5S$: C, 65.45; H, 4.73; N, 2.12. Found: C, 65.38; H, 4.71; N, 2.09.

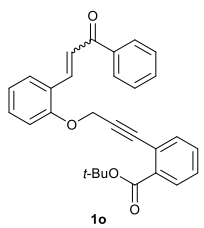
***tert*-Butyl(*E*)-2-(3-((*N*-(4-chloro-2-(3-(furan-2-yl)-3-oxoprop-1-en-1-yl)phenyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)benzoate (1j)**



1j

Colourless solid (1.81 g, 59%); mp: 129-131 °C; IR (neat): 2941, 2201, 1721, 1623, 1642, 1536, 1403, 1373, 1307, 1242, 1126 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 15.9 Hz, 1H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.77 (s, 1H), 7.68-7.66 (m, 3H). 7.38-7.33 (m, 4H), 7.29-7.27 (m, 2H), 7.23-7.21 (m, 3H), 6.62-6.61 (m, 1H), 4.92 (d, *J* = 17.3 Hz, 1H), 4.50 (d, *J* = 17.4 Hz, 1H), 2.31 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 164.9, 153.3, 146.8, 144.2, 137.9, 137.7, 137.2, 135.5, 135.3, 134.3, 133.4, 131.9, 131.1, 130.6, 130.2, 129.6, 128.3, 128.2, 127.5, 124.8, 122.2, 118.2, 112.7, 87.2, 85.3, 81.6, 42.8, 28.1, 21.5. Anal Calcd for $C_{34}H_{30}ClNO_6S$: C, 66.28; H, 4.91; N, 2.27. Found: C, 65.99; H, 4.90; N, 2.22.

***tert*-Butyl (E/Z)-2-(3-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenoxy)prop-1-yn-1-yl)benzoate (1o)**

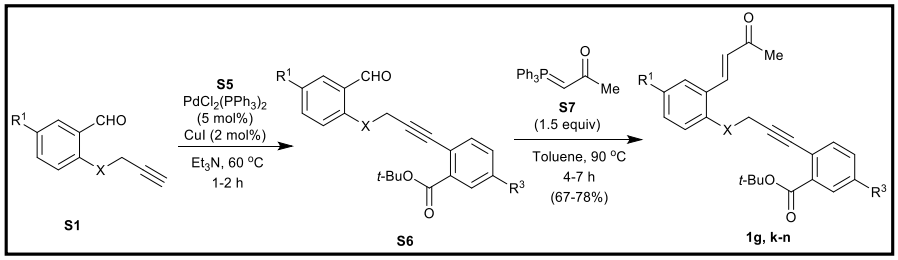


1o

Trans:*cis* = 1:0.19; Yellow viscous liquid (1.37 g, 63%); IR (neat): 3042, 2139, 1741, 1560, 1402, 1348, 1308, 1215, 1260, 1163, 1133 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 15.8 Hz, *trans*, 1H), 8.05 (dd, *J* = 7.2, 1.6 Hz, *trans*, 2H), 7.95 (dd, *J* = 7.4, 1.5 Hz, *cis*, 2H), 7.89 (dd, *J* = 7.3, 1.3 Hz, *trans*, 1H), 7.87 (d, *J* = 1.8 Hz, *cis*, 1H), 7.76 (d, *J* = 15.8 Hz, *trans*, 1H), 7.67 (d, *J* = 7.7, 1.4 Hz, *trans*, 1H), 7.57-7.52 (m, *trans*, 2H), 7.50 (dd, *J* = 8.1, 2.0 Hz, *cis*, 2H), 7.46 (d, *J* = 1.2 Hz, *trans*, 1H), 7.44-

7.43 (m, *cis*, 2H), 7.42-7.31 (m, *trans* & *cis*, 8H), 7.22 (d, J = 8.2 Hz, *trans* & *cis*, 2H), 7.08-7.05 (m, *trans* & *cis* 2H), 6.81 (t, J = 7.6 Hz, *cis*, 1H), 6.67 (d, J = 12.7 Hz, *cis*, 1H), 5.10 (s, *trans*, 2H), 4.95 (s, *cis*, 2H), 1.61 (s, *cis*, 9 H), 1.58 (s, *trans*, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.6, 191.1, 165.4, 157.1, 155.3, 140.4, 138.5, 137.4, 135.6, 134.5, 134.4, 134.0, 133.9, 132.8, 132.6, 131.6, 131.2, 131.1, 130.9, 130.8, 130.2, 130.1, 130.0, 129.9, 128.9, 128.6, 128.6, 128.4, 128.4, 128.3, 126.8, 125.5, 124.5, 123.3, 122.2, 122.5, 121.6, 120.9, 113.0, 112.3, 88.3, 87.9, 86.6, 86.2, 81.9, 81.8, 57.3, 57.1, 29.7, 28.2. Anal Calcd for $C_{29}H_{26}O_4$: C, 79.43; H, 5.98. Found: C, 79.34; H, 5.95. * Four aromatic carbons merged with others.

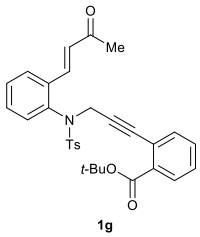
5. General Procedure for the Synthesis of Compounds 1g and 1k-n



To a stirred solution of compound **S1** (5 mmol, 1.0 equiv) in Et_3N (40 mL) were added *tert*-butyl 2-iodobenzoate **S5** (6 mmol, 1.2 equiv), $PdCl_2(PPh_3)_2$ (0.25 mmol, 5 mol%) and CuI (0.25 mmol, 5 mol%) and the resulting mixture was stirred at 60 °C for 1-2 h. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with water and extracted with ethyl acetate (2 × 80 mL). The extract was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated to dryness under reduced pressure. The crude product obtained was taken to the next step without further purification.

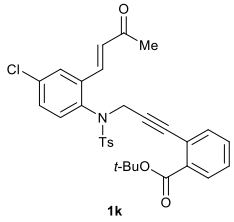
A mixture of crude product **S6** and Wittig ylide **S7** (7.5 mmol, 1.5 equiv) in toluene (40 mL) was heated at 90 °C for 4-7 h. After cooling, the solvent was evaporated to dryness and the residue was treated with ether. The solidified $OPPh_3$ was removed by filtration and the filtrate was concentrated to afford the crude product. The crude was purified by flash column chromatography eluting with petroleum ether-ethyl acetate mixture (85:15, v/v) to obtain compounds **1g, 1k-n**.

tert-Butyl(*E*)-2-(3-((4-methyl-*N*-(2-(3-oxobut-1-en-1-yl)phenyl)phenyl)sulfonamido)prop-1-yn-1-yl)benzoate (1g)



Yellow viscous liquid (2.06 g, 78%); IR (neat): 2994, 2213, 1593, 1476, 1358, 1307, 1278, 1239, 1171 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 16.6 Hz, 1H), 7.84 (d, J = 6.9 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1 H), 7.66 (d, J = 8.0 Hz, 2H), 7.57-7.52 (m, 1H), 7.36-7.32 (m, 3H), 7.24 (d, J = 8.1 Hz, 2H), 7.15-7.14 (m, 2H), 6.62 (d, J = 16.6 Hz, 1H), 4.80 (d, J = 16.7 Hz, 1H), 4.64 (d, J = 16.3 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 164.9, 144.1, 139.6, 138.7, 135.8, 135.7, 134.2, 133.5, 131.1, 130.8, 130.2, 129.9, 129.6, 129.5, 129.4, 128.2, 127.3, 127.2, 122.2, 87.4, 85.0, 81.6, 43.1, 28.1, 26.6, 21.6. Anal Calcd for $C_{31}H_{31}NO_5S$: C, 70.30; H, 5.90; N, 2.64. Found: C, 70.03; H, 5.81; N, 2.55.

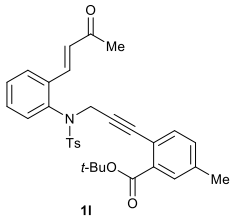
***tert*-Butyl(*E*)-2-(3-((*N*-(4-chloro-2-(3-oxobut-1-en-1-yl)phenyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)benzoate (1k)**



1k

Colourless solid (1.79g, 73%); mp: 111-113 °C; IR (neat): 2986, 1703, 1673, 1597, 1475, 1362, 1345, 1274, 1243, 1214, 1156, 1132, 1087 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88-7.84 (m, 2H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.40-7.35 (m, 2H), 7.30 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 6.59 (d, *J* = 16.5 Hz, 1H), 4.77 (brs, 1H), 4.62 (brs, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 164.8, 144.3, 138.1, 137.7, 137.1, 135.4, 135.4, 134.2, 133.5, 131.2, 131.1, 130.6, 130.3, 130.2, 129.7, 128.3, 128.2, 127.2, 122.1, 87.0, 85.3, 81.6, 42.9, 28.1, 26.9, 21.6. Anal Calcd for $C_{31}H_{30}ClNO_5S$: C, 66.01; H, 5.36; N, 2.48. Found: C, 65.74; H, 5.31; N, 2.44.

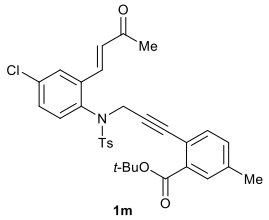
***tert*-Butyl(*E*)-5-methyl-2-(3-((4-methyl-*N*-(2-(3-oxobut-1-en-1-yl)phenyl)phenyl)sulfonamido)prop-1-yn-1-yl)benzoate (1l)**



1l

Colourless solid (1.81 g, 67%); mp: 152-154 °C; IR (neat): 2991, 2223, 1562, 1457, 1362, 1302, 1269, 1257, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 16.6 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.68-7.63 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.18-7.12 (m, 2H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 16.6 Hz, 1H), 4.77 (d, *J* = 15.9 Hz, 1H), 4.64 (d, *J* = 16.1 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 1.53 (s, 9H): ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 165.2, 144.0, 139.7, 138.8, 138.6, 135.9, 135.8, 134.1, 133.4, 131.9, 130.8, 130.7, 129.9, 129.6, 129.5, 129.3, 128.2, 127.2, 119.2, 86.4, 85.1, 81.5, 43.1, 28.1, 26.5, 21.6, 21.3. Anal Calcd for$C_{32}H_{33}NO_5S$: C, 70.69; H, 6.12; N, 2.58. Found: C, 70.44; H, 6.06; N, 2.53.

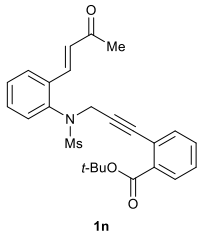
***tert*-Butyl(*E*)-2-(3-((*N*-(4-chloro-2-(3-oxobut-1-en-1-yl)phenyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)-5-methylbenzoate (1m)**



1m

Colourless solid (2.10 g, 73%); mp: 123-125 °C; IR (neat): 2993, 2313, 1703, 1670, 1363, 1346, 1303, 1275, 1242, 1216, 1158, 1145, 1086 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 16.6 Hz, 1H), 7.66 (d, *J* = 2.5 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 1.4 Hz, 1H), 7.26 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.22 (dd, *J* = 8.4, 1.0 Hz, 2H), 7.16-7.14 (m, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.55 (d, *J* = 16.6 Hz, 1H), 4.73 (d, *J* = 16.4 Hz, 1H), 4.56 (d, *J* = 16.9 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H), 1.50 (s, 9H); $^{13}CNMR$ (126 MHz, $CDCl_3$) δ 220.2, 198.6, 165.1, 144.3, 138.8, 138.2, 137.8, 137.2, 135.5, 135.4, 134.2, 133.5, 132.0, 131.3, 130.8, 130.7, 130.2, 129.7, 128.3, 127.2, 119.2, 86.1, 85.5, 81.6, 43.1, 28.2, 26.9, 21.6, 21.4. Anal Calcd for $C_{32}H_{32}ClNO_5S$: C, 66.48; H, 5.58; N, 2.42. Found C, 66.26; H, 5.52; N, 2.30.* One aromatic carbon merged with others.

***tert*-Butyl(*E*)-2-(3-(*N*-(2-(3-oxobut-1-en-1-yl)phenyl)methylsulfonamido)prop-1-yn-1-yl)benzoate (1n)**

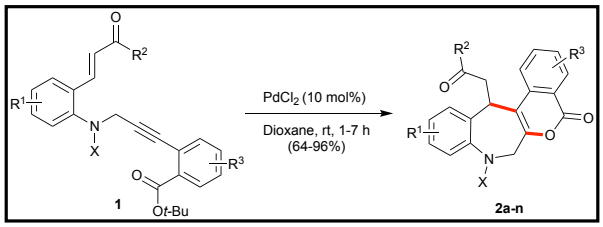


1n

Colourless solid (1.70 g, 75%); mp: 103-105 °C; IR (neat): 2989, 2319, 1797, 1759, 1693, 1678, 1662, 1469, 1120, 1103 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 16.5 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 6.9 Hz, 1H), 7.51-7.38 (m, 5H), 6.69 (d, *J* = 16.5 Hz, 1H), 5.07 (brs, 1H), 4.31 (brs, 1H), 3.30 (s, 3H), 2.42 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 164.8, 139.4, 139.3, 135.3, 134.5, 133.3, 131.5, 131.2, 130.4, 129.7, 129.5, 128.4, 127.5, 122.5, 88.1,

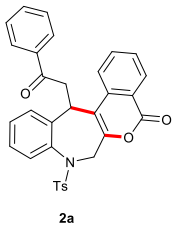
85.2, 81.6, 42.7, 39.8, 28.2, 26.9. Anal Calcd for $C_{25}H_{27}NO_5S$: C, 66.21; H, 6.00; N, 3.09. Found: C, 65.94; H, 5.96; N, 3.01. *One aromatic carbon merged with others.

6. General Procedure for the Synthesis of Benzo[*b*]isochromeno[4,3-*e*]azepin-5(7*H*)-ones 2a-n



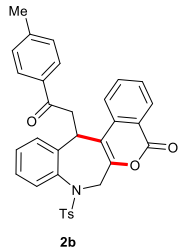
To a solution of compound **1** (0.5 mmol, 1.0 equiv) in dioxane (6 mL) was added $PdCl_2$ (0.1 mmol, 10 mol%) and the resulting mixture was stirred at room temperature for 1-7 h under N_2 atmosphere. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with water and the aqueous suspension was extracted with EtOAc (2 x 20 mL), washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using petroleum ether and ethyl acetate mixture as eluent (85:15 to 80:20, v/v) to obtain the desired products **2**.

13-(2-Oxo-2-phenylethyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]azepin-5(7*H*)-one (2a)


2a

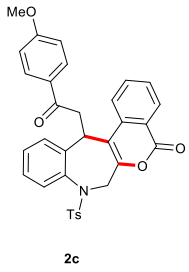
Colourless solid (0.248 g, 93%); mp: 202-204 °C; IR (neat): 2970, 1761, 1738, 1674, 1596, 1481, 1449, 1339, 1248, 1158, 1130 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 7.7 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.60-7.57 (m, 2H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.48-7.42 (m, 4H), 7.28-7.18 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 1H), 5.32 (d, *J* = 8.6 Hz, 1H), 5.24 (d, *J* = 17.8Hz, 1H), 4.75 (dd, *J* = 18.6, 9.6 Hz, 1H), 4.18 (d, *J* = 17.8 Hz, 1H), 3.39 (dd, *J* = 18.6, 1.8 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 161.3, 149.9, 144.4, 140.9, 139.2, 138.4, 137.1, 136.4, 135.6, 133.4, 132.4, 130.4, 130.3, 128.9, 128.6, 128.5, 128.3, 127.2, 125.4, 122.4, 120.8, 113.7, 50.7, 45.2, 36.4, 21.7. Anal Calcd for $C_{32}H_{25}NO_5S$: C, 71.76; H, 4.70; N, 2.62. Found: C, 71.45; H, 4.65; N, 2.60. *One aromatic carbon merged with others.

13-(2-Oxo-2-(*p*-tolyl)ethyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]azepin-5(7*H*)-one (2b)


2b

Colourless solid (0.28 g, 87%); mp: 243-245 °C; IR (neat): 2964, 1752, 1725, 1645, 1584, 1494, 1427, 1326, 1259, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.95-7.92 (m, 4H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.59-7.55 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.24-7.22 (m, 4H), 6.99 (d, *J* = 7.6 Hz, 1H), 5.32 (d, *J* = 8.9 Hz, 1H), 5.23 (d, *J* = 17.9 Hz, 1H), 4.71 (dd, *J* = 18.4, 9.7 Hz, 1H), 4.17 (d, *J* = 17.8 Hz, 1H), 3.35 (d, *J* = 18.4 Hz, 1H), 2.53 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 161.3, 149.9, 144.4, 144.2, 140.9, 139.2, 138.4, 137.1, 135.6, 133.9, 132.4, 130.4, 130.3, 129.3, 128.8, 128.6, 128.5, 128.3, 127.2, 125.3, 122.4, 120.8, 113.8, 50.7, 44.9, 36.5, 29.7, 21.7. Anal Calcd for $C_{33}H_{27}NO_5S$: C, 72.11; H, 4.95; N, 2.55. Found: C, 71.88; H, 4.84; N, 2.51.

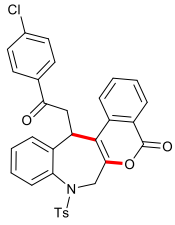
13-(2-(4-Methoxyphenyl)-2-oxoethyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*] azepin-5(7*H*)-one (2c)



2c

Light brown solid (0.270 g, 96%); mp: 244-246 °C; IR (neat): 2971, 1723, 1670, 1600, 1339, 1307, 1257, 1182, 1158, 1138, 1106 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.8 Hz, 1H), 8.04-8.02 (m, 3H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.58-7.55 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.25-7.17 (m, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.31 (d, *J* = 8.6 Hz, 1H), 5.23 (d, *J* = 17.8 Hz, 1H), 4.69 (dd, *J* = 18.2, 9.6 Hz, 1H), 4.17 (d, *J* = 17.8 Hz, 1H), 3.83 (s, 3H), 3.31 (d, *J* = 18.2 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 163.7, 161.3, 149.8, 139.2, 138.4, 137.2, 135.6, 132.4, 130.8, 130.4, 130.3, 129.6, 128.8, 128.5, 128.3, 127.19, 125.3, 122.5, 120.8, 113.8, 113.7, 55.5, 50.7, 44.7, 36.7, 21.7. Anal Calcd for $C_{33}H_{27}NO_6S$: C, 70.07; H, 4.81; N, 2.48. Found: C, 69.87; H, 4.72; N, 2.43. *Two aromatic carbons merged with others.

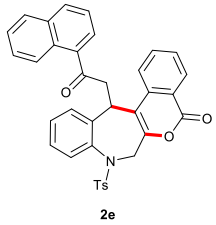
13-(2-(4-Chlorophenyl)-2-oxoethyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]aze pin-5(7*H*)-one (2d)



2d

Pale yellow solid (0.236 g, 83%); mp: 163-167 °C; IR (neat): 2990, 1769, 1747, 1672, 1600, 1473, 1454, 1364, 1249, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.8 Hz, 1H), 7.99-7.91 (m, 5H), 7.88 (td, *J* = 8.2, 1.0 Hz, 1H), 7.60-7.54 (m, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.24-7.20 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 5.29-5.21 (m, 2H), 4.73 (dd, *J* = 18.5, 9.8 Hz, 1H), 4.61 (d, *J* = 17.6 Hz, 1H), 3.33 (dd, *J* = 18.4, 1.9 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 161.2, 149.9, 144.5, 140.6, 139.9, 139.2, 138.3, 137.0, 135.6, 134.8, 132.4, 130.4, 129.9, 128.9, 128.5, 128.4, 127.2, 125.4, 122.3, 120.8, 113.5, 50.6, 44.9, 36.7, 21.7. Anal Calcd for $C_{32}H_{24}ClNO_5S$: C, 67.42; H, 4.24; N, 2.46. Found C, 67.13; H, 4.21; N, 2.37.* Two aromatic carbons merged with others.

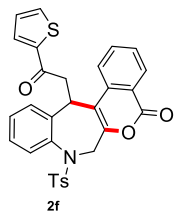
13-(2-(Naphthalen-1-yl)-2-oxoethyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]aze pin-5(7*H*)-one (2e)



2e

Colourless solid (0.195 g, 67%); mp: 251-253 °C; IR (neat): 2983, 1778, 1743, 1670, 1544, 1473, 1469, 1323, 1256, 1167, 1141 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.33 (dd, *J* = 7.8, 1.3 Hz, 1H), 8.06-8.03 (m, 2H), 7.95-7.91 (m, 3H), 7.86 (td, *J* = 7.4, 1.4 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.56-7.53 (m, 2H), 7.52 (t, *J* = 2.0 Hz, 1H), 7.47 (td, *J* = 8.1, 1.2 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.20-7.13 (m, 2H), 7.00 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.31 (dd, *J* = 9.5, 1.6 Hz, 1H), 5.23 (d, *J* = 17.8 Hz, 1H), 4.86 (dd, *J* = 18.1, 9.8 Hz, 1H), 4.17 (d, *J* = 17.8 Hz, 1H), 3.42 (dd, *J* = 18.1, 2.3 Hz, 1H), 2.49 (s, 3H); ^{13}CNMR (126 MHz, $CDCl_3$) δ 198.7, 161.4, 150.0, 144.5,140.7, 139.4, 138.4, 137.2, 135.8, 135.7, 133.9, 132.7, 132.4, 131.2, 130.5, 130.4, 130.1, 128.9, 128.6, 128.6, 128.4, 127.6, 127.3, 126.7, 125.5, 123.9, 122.5, 120.9, 113.7, 50.8, 45.1, 37.3, 21.7. Anal Calcd for $C_{36}H_{27}NO_5S$: C, 73.83; H, 4.65; N, 2.39. Found: C, 73.68; H, 4.55; N, 2.32.

13-(2-Oxo-2-(thiophen-2-yl)ethyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]azepi n-5(7*H*)-one (2f)

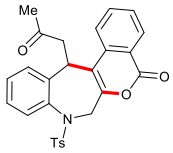


2f

Light brown solid (0.189 g, 70%); mp: 145-147 °C; IR (neat): 3092, 2992, 1752, 1745, 1681, 1598, 1469, 1321, 1251, 1173, 1141 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 7.9, 1.1 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.87-7.84 (m, 2H), 7.58-7.57 (m, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.44 (d, *J* = 8.2 Hz,

2H), 7.21-7.15 (m, 2H), 7.04 (t, J = 4.1 Hz, 1H), 6.97 (dd, J = 7.3, 1.5 Hz, 1H), 5.33-5.17 (m, 2H), 4.58 (dd, J = 17.8, 9.9 Hz, 1H), 4.13 (d, J = 17.8 Hz, 1H), 3.32 (dd, J = 17.7, 2.2 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 161.3, 150.0, 144.5, 143.9, 140.5, 139.3, 138.4, 137.1, 135.7, 134.4, 133.8, 132.3, 130.5, 130.4, 129.0, 128.6, 128.5, 128.4, 127.3, 125.4, 122.5, 120.9, 113.5, 93.2, 50.7, 45.5, 37.1, 29.8, 21.8. Anal Calcd for $C_{30}H_{23}NO_5S_2$: C, 66.53; H, 4.28; N, 2.59. Found: C, 66.41; H, 4.25; N, 2.56.

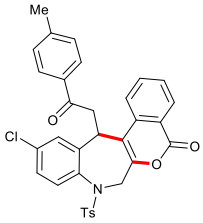
13-(2-Oxopropyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]azepin-5(7*H*)-one (2g)



2g

Colourless solid (0.195 g, 83%); mp: 231-233 °C; IR (neat): 2965, 1713, 1694, 1581, 1462, 1449, 1339, 1228, 1150, 1130 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 8.3 Hz, 2H), 7.87 (d, J = 3.6 Hz, 2H), 7.59-7.55 (m, 1H), 7.48-7.45 (m, 3H), 7.28-7.22 (m, 2H), 7.01 (dd, J = 7.2, 1.3 Hz, 1H), 5.19 (d, J = 17.8 Hz, 1H), 4.96 (dd, J = 10.4, 2.1 Hz, 1H), 4.13 (d, J = 17.8 Hz, 1H), 4.02 (dd, J = 17.8, 10.5 Hz, 1H), 2.92 (dd, J = 17.8, 2.4 Hz, 1H), 2.53 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 161.1, 149.8, 144.4, 140.2, 139.2, 138.5, 136.9, 135.5, 132.4, 130.4, 128.9, 128.4, 128.2, 127.1, 125.3, 122.0, 120.8, 113.2, 50.6, 48.9, 36.9. 30.9, 21.7. Anal Calcd for $C_{27}H_{23}NO_5S$: C, 68.48; H, 4.90; N, 2.96. Found: C, 68.23; H, 4.82; N, 2.92. *One aromatic carbon merged with others.

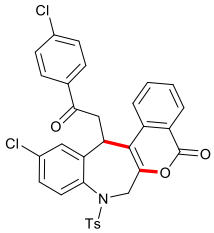
11-Chloro-13-(2-oxo-2-(*p*-tolyl)ethyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]azepin-5(7*H*)-one (2h)



2h

Colourless solid (0.186 g, 64%); mp: 292-294 °C; IR (neat): 2971, 1724, 1722, 1632, 1591, 1482, 1427, 1305, 1259, 1125 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 7.9 Hz, 1H), 7.92-7.89 (m, 3H), 7.86 (d, J = 8.3 Hz, 2H), 7.84-7.81 (m, 1H), 7.56 (d, J = 2.3 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.14 (dd, J = 8.5, 2.4 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 5.28-5.17 (m, 2H), 4.65 (dd, J = 18.7, 9.5 Hz, 1H), 4.09 (d, J = 17.8 Hz, 1H), 3.32 (dd, J = 18.6, 2.0 Hz, 1H), 2.49 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 161.2, 149.7, 144.7, 144.5, 142.8, 138.1, 137.8, 136.9, 135.7, 134.1, 133.9, 132.4, 130.5, 130.5, 129.4, 128.9, 128.7, 128.5, 127.2, 126.7, 122.4, 120.9, 113.5, 50.6, 44.9, 36.2, 21.8. Anal Calcd for $C_{33}H_{26}ClNO_5S$: C, 67.86; H, 4.49; N, 2.40. Found: C, 67.61; H, 4.44; N, 2.36. *One aromatic carbon merged with others.

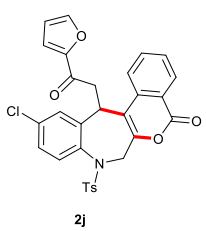
11-Chloro-13-(2-(4-chlorophenyl)-2-oxoethyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]azepin-5(7*H*)-one (2i)



2i

Colourless solid (0.235 g, 78%); mp: 269-271 °C; IR (neat): 2962, 1751, 1654, 1573, 1432, 1339, 1357, 1269, 1103 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.98-7.89 (m, 5H), 7.59 (s, 2H), 7.46-7.43 (m, 4H), 7.28 (s, 1H), 7.17 (s, 1H), 6.89 (s, 1H), 5.21 (s, 1H), 4.69 (s, 1H), 4.12 (d, J = 16.0 Hz, 1H), 3.68 (s, 1H), 3.34 (d, J = 18.2 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR could not be run due to the poor solubility of the compound in common NMR solvents. Anal Calcd for $C_{32}H_{23}Cl_2NO_5S$: C, 63.58; H, 3.84; N, 2.32. Found: C, 63.29; H, 3.77; N, 2.29.

11-Chloro-13-(2-(furan-2-yl)-2-oxoethyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]azepin-5(7*H*)-one (2j)

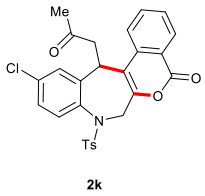


2j

Off-white solid (0.184 g, 66%); mp: 258-260 °C; IR (neat): 2980, 1754, 1731, 1692, 1594, 1476, 1432, 1345, 1209, 1150 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (dd, J = 7.9, 1.1 Hz, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.85 (dd, J = 7.2, 1.2 Hz, 1H), 7.58 (d, J = 1.6 Hz, 1H), 7.55 (d,

J = 7.4 Hz, 1H), 7.48 (d, *J* = 2.4 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.35-7.34 (m, *1*H), 7.15 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.47-6.46 (m, 1H), 5.28-5.13 (m, 2H), 4.38 (dd, *J* = 17.9, 10.0 Hz, 1H), 4.09 (d, *J* = 17.8 Hz, 1H), 3.23 (dd, *J* = 17.9, 2.4 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.3, 161.1, 151.9, 149.8, 147.5, 144.8, 142.2, 137.9, 137.8, 136.8, 135.8, 134.1, 132.2, 130.6, 130.5, 129.1, 128.6, 127.3, 126.7, 122.4, 120.9, 119.9, 113.0, 112.5, 50.6, 44.5, 36.4, 21.8. Anal Calcd for $C_{30}H_{22}ClNO_6S$: C, 64.34; H, 3.96; N, 2.50. Found: C, 64.09; H, 3.91; N, 2.55.

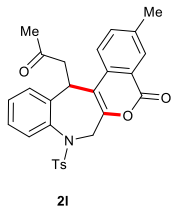
10-Chloro-13-(2-oxopropyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]azepin-5 (7*H*)-one (2k)



2k

Colourless solid (0.202 g, 80%); mp: 264-266 °C; IR (neat): 2969, 1723, 1687, 1575, 1454, 1450, 1321, 1207, 1149, 1137 cm^{-1}; ^{1}H NMR (400 MHz $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.80-7.70 (m, 4H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.41-7.37 (m, 3H), 7.11 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.09 (d, *J* = 17.6 Hz, 1H), 4.83 (d, *J* = 9.6 Hz, 1H), 4.01 (d, *J* = 18.0 Hz, 1H), 3.90 (dd, *J* = 18.4, 10.4 Hz, 1H), 2.84 (dd, *J* = 18.4, 2.0 Hz, 1H), 2.44 (s, 3H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 206.9, 161.0, 149.6, 144.7, 142.1, 138.1, 137.6, 136.6, 135.6, 133.9, 132.4, 130.4, 128.9, 128.5, 127.1, 126.6, 121.9, 120.8, 112.9, 50.4, 48.8, 36.3, 30.6, 21.7. Anal Calcd for $C_{27}H_{22}ClNO_5S$: C, 63.84; H, 4.37; N, 2.76. Found: C, 63.71; H, 4.32; N, 2.65. *One aromatic carbon merged with others.

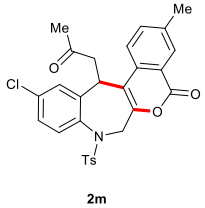
3-Methyl-13-(2-oxopropyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]azepin-5 (7*H*)-one (2l)



2l

Colourless solid (0.218 g, 90%); mp: 269-271 °C; IR (neat): 2968, 1731, 1714, 1618, 1494, 1345, 1248, 1161, 1113, 1089 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.48-7.46 (m, 3H), 7.25-7.22 (m, 2H), 7.00 (d, *J* = 7.2 Hz, 1H), 5.18 (d, *J* = 17.8 Hz, 1H), 4.94 (d, *J* = 9.2 Hz, 1H), 4.12 (d, *J* = 17.8 Hz, 1H), 4.00 (dd, *J* = 17.9, 10.6 Hz, 1H), 2.91 (dd, *J* = 17.8, 1.9 Hz, 1H), 2.53 (s, 3H), 2.50 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 161.4, 148.8, 144.4, 140.3, 139.2, 138.6, 138.5, 136.7, 134.4, 132.4, 130.4, 130.2, 128.8, 128.4, 127.1, 125.3, 122.0, 120.7, 113.2, 50.5, 48.9, 37.0, 30.9, 21.7, 21.1. Anal Calcd for $C_{28}H_{25}NO_5S$: C, 68.98; H, 5.17; N, 2.87. Found: C, 68.77; H, 5.10; N, 2.78.

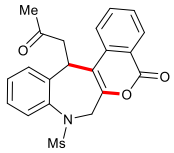
11-Chloro-3-methyl-13-(2-oxopropyl)-8-tosyl-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*] azepin-5(7*H*)-one (2m)



2m

Colourless solid (0.229 g, 88%); mp: 182-184 °C; IR (neat): 2970, 1732, 1712, 1344, 1250, 1132, 1160, 1102, 1088 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H) 7.66 (d, *J* = 8.4 Hz, 1H), 7.63 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.46 (d, *J* = 2.5 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.16 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 5.13 (d, *J* = 17.7 Hz, 1H), 4.86 (dd, *J* = 10.4, 2.5 Hz, 1H), 4.04 (d, *J* = 17.7 Hz, 1H), 3.94 (dd, *J* = 18.4, 10.5 Hz, 1H), 2.87 (dd, *J* = 18.4, 2.6 Hz, 1H), 2.49 (s, 3H), 2.46 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.1, 161.3, 148.7, 144.7, 142.3, 138.9, 138.2, 137.7, 136.9, 134.2, 134.0, 132.4, 130.5, 130.3, 128.9, 127.2, 126.7, 121.9, 120.7, 112.9, 50.4, 48.9, 36.4, 30.7, 21.8, 21.2. Anal Calcd for $C_{28}H_{24}ClNO_5S$: C, 64.43; H, 4.63; N, 2.68. Found: C, 64.14; H, 4.55; N, 2.66.

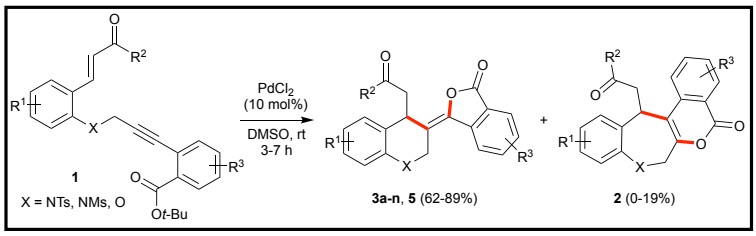
8-(Methylsulfonyl)-13-(2-oxopropyl)-8,13-dihydrobenzo[*b*]isochromeno[4,3-*e*]azepin-5(7*H*)-one (2n)



2n

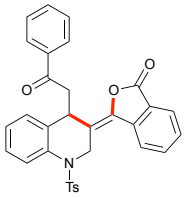
Colourless solid (0.140 g, 71%); mp: 214-216 °C; IR (neat): 2963, 1721, 1713, 1343, 1306, 1164, 1151, 1138, 1092 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.85-7.81 (m, 2H), 7.55-7.52 (m, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.34-7.33 (m, 1H), 7.28 (d, *J* = 7.2 Hz, 2H), 4.96-4.91 (m, 2H), 4.21 (d, *J* = 17.9 Hz, 1H), 3.80 (dd, *J* = 17.9, 10.6 Hz, 1H), 3.31 (s, 3H), 2.84 (dd, *J* = 17.9, 2.6 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.5, 161.1, 149.4, 140.3, 138.7, 136.8, 135.6, 132.8, 130.5, 129.3, 128.7, 128.5, 125.9, 122.1, 120.9, 113.2, 49.8, 49.0, 42.1, 37.0, 30.9. Anal Calcd for $C_{21}H_{19}NO_5S$: C, 63.46; H, 4.82; N, 3.52. Found: C, 63.29; H, 4.71; N, 3.50.

7. General Procedure for the Synthesis of 3-(Quinolin-3(2*H*)-ylidene)isobenzofuran-1(3*H*)-ones 3a-n and 5



To a solution of compound **1** (0.5 mmol, 1.0 equiv) in DMSO (6 mL) was added $PdCl_2$ (0.1 mmol, 10 mol%) and the resulting mixture was stirred at room temperature for 3-7 h under N_2 atmosphere. After completion of the reaction, as indicated by TLC, the reaction mixture was quenched with ice cold water and the aqueous suspension was extracted with EtOAc (2 x 20 mL), washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using petroleum ether and ethyl acetate mixture as eluent (85:15 to 80:20, v/v) to obtain the desired product **3/5**.

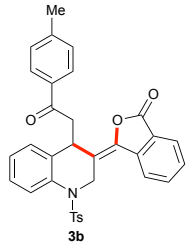
(*E*)-3-(4-(2-Oxo-2-phenylethyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)isobenzofuran-1(3*H*)-one (3a)



3a

Colourless solid (0.208 g, 78%); mp: 170-172 °C; IR (neat): 2962, 1768, 1683, 1454, 1355, 1311, 1164, 1158, 1031 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.4 Hz, 2H), 7.78 (t, *J* = 7.4 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.60-7.59 (m, 1H), 7.55 (t, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 3H), 4.94 (dd, *J* = 9.1, 3.2 Hz, 1H), 4.85 (d, *J* = 17.1 Hz, 1H), 4.81 (d, *J* = 17.0 Hz, 1H), 3.79 (dd, *J* = 17.4, 9.1 Hz, 1H), 3.17 (dd, *J* = 17.4, 3.3 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 165.9, 143.9, 140.6, 137.2, 137.0, 136.9, 136.4, 134.9, 133.7, 133.3, 129.8, 129.6, 128.8, 128.7, 128.3, 127.8, 127.1, 126.5, 125.8, 125.5, 125.4, 123.2, 120.9, 46.4, 46.1, 34.2, 21.3. Anal Calcd for $C_{32}H_{25}NO_5S$: C, 71.76; H, 4.70; N, 2.62. Found: C, 71.55; H, 4.65; N, 2.56.

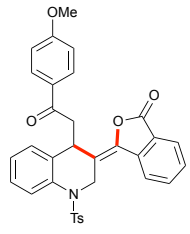
(*E*)-3-(4-(2-Oxo-2-(*p*-tolyl)ethyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)isobenzofuran-1(3*H*)-one (3b)



3b

Colourless solid (0.238 g, 87%); mp: 149-151 °C; IR (neat): 2997, 1702, 1695, 1634, 1591, 1479, 1401, 1334, 1271, 1169 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.77 (td, *J* = 8.3, 1.1 Hz, 1H), 7.75 (dd, *J* = 6.7, 1.8 Hz, 2H), 7.59-7.56 (m, 3H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.26 (dd, *J* = 7,7, 1.6 Hz, 1H), 7.23 (dd, *J* = 7,6, 1.6 Hz, 1H), 7.17 (d, *J* = 8 Hz, 2 H), 7.10-7.07 (m, 3H), 4.88 (dd, *J* = 9.3. 3.3 Hz, 1 H), 4.83-4.76 (m, 2H), 3.69 (dd, *J* = 17.3, 9.1 Hz, 1H), 3.07 (dd, *J* = 17.4, 3.3 Hz, 1H), 2.35 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 166.1, 144.7, 143.9, 140.6, 138.4, 137.2, 136.9, 135.0, 133.9, 133.3, 129.8, 129.5, 129.3, 128.7, 128.4, 127.7, 127.3, 127.1, 126.5, 125.7, 125.4, 123.3, 120.9, 46.3, 45.9, 34.1, 21.7, 21.3. Anal Calcd for: $C_{33}H_{27}NO_5S$: C, 72.11; H, 4.95; N, 2.55. Found: C, 71.87; H, 4.89; N, 2.48.

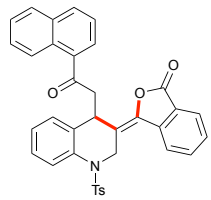
(*E*)-3-(4-(2-(4-Methoxyphenyl)-2-oxoethyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene) isobenzofuran-1(3*H*)-one (3c)



3c

Pale yellow solid (0.188 g, 67%); mp: 81-83 °C; IR (neat): 2961, 1732, 1676, 1622, 1548, 1456, 1481, 1365, 1278, 1171 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.77 (dd, *J* = 8.9, 2.8 Hz, 2H), 7.74 (td, *J* = 8.1, 1.8 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 2H,), 7.56-7.51 (m, 2H,), 7.25-7.19 (m, 2H), 7.10-7.06 (m, 3H), 6.83 (dd, *J* = 8.8, 2.4 Hz, 2H), 4.86 (dd, *J* = 9.1, 3.3 Hz, 1H), 4.84-4.75 (m, 2H), 3.81 (s, 3H), 3.72 (dd, *J* = 17.0, 9.2 Hz, 1H), 3.04 (dd, *J* = 17.0, 3.45 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 166.1, 164.0, 144.0, 140.6, 137.1, 137.2, 136.9, 135.1, 133.4, 130.8, 129.8, 129.6, 129.6, 128.8, 127.7, 127.2, 126.5, 125.8, 125.5, 125.4, 123.4, 121.1, 113.9, 55.6, 46.2, 45.9, 34.4, 21.4. Anal Calcd for: $C_{33}H_{27}NO_6S$: C, 70.07; H, 4.81; N, 2.48. Found: C, 69.79; H, 4.80; N, 2.55.

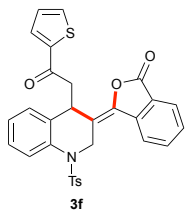
(*E*)-3-(4-(2-(Naphthalen-1-yl)-2-oxoethyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)iso benzofuran-1(3*H*)-one (3e)



3e

Pale yellow solid (0.198 g, 68%); mp: 98-100 °C; IR (neat): 2964, 1769, 1703, 1657, 1541, 1423, 1311, 1247, 1107 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.95-7.90 (m, 3H), 7.84-7.77 (m, 4H) 7.66 (d, *J* = 8.2 Hz, 2H), 7.58-7.56 (m, 3H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.20 (td, J = 7.8, 1.3 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.05 (td, *J* = 7.9, 1.9 Hz, 1H), 4.95-4.90 (m, 2H), 4.78 (d, *J* = 17.0 Hz, 1H), 3.99 (dd, *J* = 17.0, 9.4 Hz, 1H), 3.25 (dd, *J* = 16.8, 3.5 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 166.1, 144.0, 140.6, 137.2, 137.1, 136.9, 135.7, 135.1, 133.8, 132.4, 130.7, 129.9, 129.8, 129.7, 129.6, 128.9, 128.8, 128.5, 127.8, 127.7, 127.1, 126.9, 126.5, 125.8, 125.5, 125.2, 123.5, 123.3, 121.1, 46.2, 46.1, 34.9, 21.4. Anal Calcd for: $C_{36}H_{27}NO_5S$: C, 73.83; H, 4.65; N, 2.39. Found: C, 73.63; H, 4.58; N, 2.44.

(*E*)-3-(4-(2-Oxo-2-(thiophen-2-yl)ethyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)iso benzofuran-1(3*H*)-one (3f)

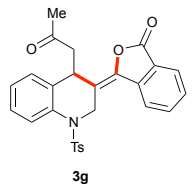


3f

Pale yellow solid (0.173 g, 64%); mp: 196-198 °C; IR (neat): 2945, 1787, 1758, 1621, 1479, 1357, 1268, 1191, 1093 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.63-7.56 (m, 5H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.14-7.12 (m, 4H), 6.48-6.47 (m, 1H), 4.88-4.77 (m, 3H), 3.59 (dd, *J* = 16.4, 9.2 Hz, 1H), 3.10 (dd, *J* = 16.8, 4.4 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.5, 166.0, 152.1, 144.0, 140.7, 137.1, 137.0, 136.9, 135.0, 132.8, 129.8,

129.5, 128.6, 127.8,127.1, 126.4, 125.7, 125.5, 125.3, 123.4, 120.2, 119.2, 112.6, 45.9, 45.8, 34.5, 21.3. Anal Calcd for $C_{30}H_{23}NO_5S_2$: C, 66.53; H, 4.28; N, 2.59. Found: C, 66.25; H, 4.21; N, 2.58. *One aromatic carbon merged with others.

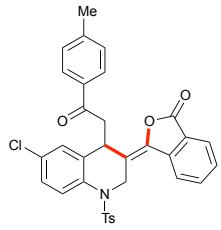
(*E*)-3-(4-(2-Oxopropyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)isobenzofuran-1-(3*H*)-one (3g)



3g

Colourless solid (0.210 g, 89%); mp: 163-165 °C; IR (neat): 2968, 1764, 1716, 1473, 1351, 1276, 1164, 1102, 1091 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.59-7.55 (m, 3H), 7.32-7.28 (m, 1H), 7.24-7.18 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.78 (s, 2H), 4.66 (dd, *J* = 9.0, 2.9 Hz, 1H), 2.93 (dd, *J* = 17.9, 9.1 Hz, 1H), 2.65 (dd, *J* = 17.9, 3.1 Hz, 1H), 2.17 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 165.9, 143.9, 140.4, 137.2, 136.8, 136.7, 134.9, 133.2, 129.8, 129.5, 128.5, 127.8, 127.1, 126.5, 125.8, 125.6, 125.5, 123.1, 120.6, 51.0, 45.9, 33.5, 30.9, 21.3. Anal Calcd for $C_{27}H_{23}NO_5S$: C, 68.48; H, 4.90; N, 2.96. Found: C, 68.24; H, 4.89; N, 2.87.

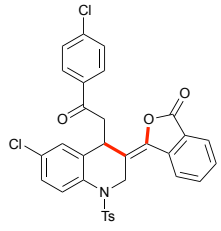
(*E*)-3-(6-Chloro-4-(2-oxo-2-(*p*-tolyl)ethyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)isobenzofuran-1(3*H*)-one (3h)



3h

Colourless solid (0.189 g, 65%); mp: 174-176 °C; IR (neat): 2967, 1778, 1770, 1675, 1480, 1475, 1352, 1277, 1161, 1086 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (t, *J* = 8.2 Hz, 2H), 7.78-7.73 (m, 3H), 7.60-7.55 (m, 4H), 7.33 (d, *J* = 2.2 Hz, 1H), 7.24-7.22 (m, 3H), 7.11 (d, *J* = 8.1 Hz, 2H), 4.90-4.85 (m, 2H), 4.74 (d, *J* = 16.9 Hz, 1H), 3.67 (dd, *J* = 17.6, 8.8 Hz, 1H), 3.16 (dd, *J* = 17.7, 3.4 Hz, 1H), 2.40 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 165.8, 144.9, 144.1, 140.9, 137.1, 136.5, 135.4, 135.0, 133.7, 131.8, 129.9, 129.6, 129.4, 128.6, 128.4, 127.9, 127.1, 126.9, 125.8, 125.6, 123.2, 119.6, 46.3, 45.7, 33.6, 21.7, 21.3. Anal Calcd for $C_{33}H_{26}ClNO_5S$: C, 67.86; H, 4.49; N, 2.40. Found: C, 67.55; H, 4.36; N, 2.29. *One aromatic carbon merged with others.

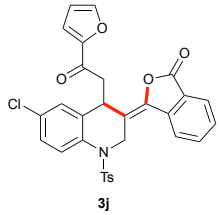
(*E*)-3-(6-Chloro-4-(2-(4-chlorophenyl)-2-oxoethyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)isobenzofuran-1(3*H*)-one (3i)



3i

Off-white solid (0.220 g, 73%); mp: 164-165 °C; IR (neat): 2969, 1774, 1718, 1614, 1484, 1367, 1268, 1151, 1093 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (t, *J* = 8.3 Hz, 2H), 7.77-7.73 (m, 3H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.55 (t, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.38 (dd, *J* = 8.5, 2.6 Hz, 2H), 7.27 (d, *J* = 2.6 Hz, 1H), 7.20 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.86-4.70 (m, 3H), 3.68 (dd, *J* = 17.7, 9.0 Hz, 1H), 3.15 (dd, *J* = 17.5, 3.7 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 165.8, 144.3, 140.9, 140.4, 137.0, 136.6, 135.5, 135.1, 134.9, 134.5, 131.8, 130.0, 129.7, 129.1, 128.6, 128.0, 127.1, 127.4, 126.7, 125.9, 125.5, 123.1, 119.6, 46.0, 45.9, 33.9, 21.4. Anal Calcd for $C_{32}H_{23}Cl_2NO_5S$: C, 63.58; H, 3.84; N, 2.32. Found: C, 63.33; H, 3.81; N, 2.30.

(*E*)-3-(6-Chloro-4-(2-(furan-2-yl)-2-oxoethyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)isobenzofuran-1(3*H*)-one (3j)

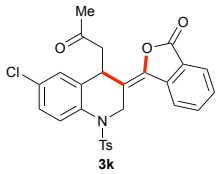


3j

Colourless solid (0.173 g, 62%); mp: 187-189 °C; IR (neat): 2973, 1774, 1762, 1658, 1492, 1348, 1251, 1151, 1056 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$ δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.74 (td, *J* = 8.3, 1.2 Hz, 1H), 7.56-7.52 (m, 5H), 7.25 (d, *J* = 2.4 Hz, 1H), 7.20 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.12 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.06 (d, *J* = 8.0 Hz,

2H), 6.48-6.47 (m, 1H), 4.82 (d, *J* = 16.8 Hz, 1H), 4.74-4.68 (m, 2H), 3.47 (dd, *J* = 16.9, 8.7 Hz, 1H), 3.06 (dd, *J* = 16.9, 4.2 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.1, 165.9, 152.1, 147.5, 144.2, 141.1, 137.1, 136.5, 135.5, 135.1, 134.5, 131.9, 130.1, 129.6, 128.5, 128.0, 127.2, 126.9, 125.9, 125.6, 123.3, 119.1, 118.8, 112.8, 45.9, 45.6, 33.9, 21.4. Anal Calcd for $C_{30}H_{22}ClNO_6S$: C, 64.34; H, 3.96; N, 2.50. Found: C, 64.01; H, 3.90; N, 2.44.

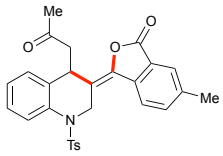
(*E*)-3-(6-Chloro-4-(2-oxopropyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)isobenzofuran-1(3*H*)-one (3k)



3k

Off-white solid (0.202 g, 80%); mp: 185-187 °C; IR (neat): 2987, 1778, 1731, 1467, 1361, 1254, 1132, 1102, cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.24-7.21 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 4.81 (d, *J* = 17.0 Hz, 1H), 4.64 (d, *J* = 17.0 Hz, 1H), 4.56 (dd, *J* = 8.7, 2.8 Hz, 1H), 2.83 (dd, *J* = 18.4, 8.9 Hz, 1H), 2.62 (dd, *J* = 18.3, 3.1 Hz, 1H), 2.11 (s, 3H), 2.02 (s, 3H); ^{13}CNMR (126 MHz, $CDCl_3$) δ 206.0, 165.8, 144.2, 140.8, 137.1, 136.5, 135.3, 135.1, 134.9, 131.9, 130.1, 129.6, 128.4, 128.0, 127.3, 127.2, 125.9, 125.7, 123.1, 119.3, 51.1, 45.7, 33.0, 30.7, 21.3. Anal Calcd for $C_{27}H_{22}ClNO_5S$: C, 63.84; H, 4.37; N, 2.76. Found: C, 63.61; H, 4.33; N, 2.71.

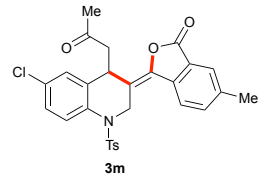
(*E*)-6-Methyl-3-(4-(2-oxopropyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)isobenzofuran-1(3*H*)-one (3l)



3l

Colourless solid (0.214 g, 71%); mp: 181-183 °C; IR (neat): 2967, 1763, 1717, 1490, 1353, 1339, 1285, 1159, 1091 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.1 Hz, 3H), 7.29-7.28 (m, 1H), 7.24-7.18 (m, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 4.76 (s, 2H), 4.63 (d, *J* = 6.9 Hz, 1H), 2.90 (dd, *J* = 17.9, 9.1 Hz, 1H), 2.64 (dd, *J* = 17.6, 1.8 Hz, 1H), 2.50 (s, 3H), 2.18 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 166.1, 143.8, 140.6, 140.5, 136.8, 136.7, 136.1, 134.8, 133.3, 129.5, 128.5, 127.8, 127.1, 126.5, 125.8, 125.7, 125.6, 122.8, 119.3, 51.0, 45.8, 33.5, 30.9, 21.4, 21.3. Anal Calcd for $C_{28}H_{25}NO_5S$: C, 68.98; H, 5.17; N, 2.87. Found: C, 68.79; H, 5.11; N, 2.76.

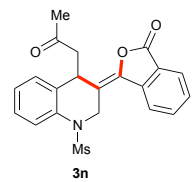
(*E*)-3-(6-Chloro-4-(2-oxopropyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)-6-methylisobenzofuran-1(3*H*)-one (3m)



3m

Colourless solid (0.180 g, 69%); mp: 217-219 °C; IR (neat): 2967, 1734, 1711, 1665, 1491, 1236, 1307, 1275, 1279, 1102 cm^{-1}; ^{1}H NMR (400 MHz $CDCl_3$) δ 7.72-7.71 (m, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.53-7.49 (m, 3H), 7.24-7.21 (m, 2H), 7.08-7.06 (m, 2H), 4.78 (d, *J* = 17.0 Hz, 1H), 4.64 (d, *J* = 17.0 Hz, 1H), 4.56 (dd, *J* = 8.8, 2.6 Hz, 1H), 2.81 (dd, *J* = 18.3, 8.8 Hz, 1H), 2.68 (dd, *J* = 18.8, 3.3 Hz, 1H), 2.47 (s, 3H), 2.13 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.1, 165.9, 144.1, 140.9, 140.8, 136.5, 136.2, 135.3, 135.0, 134.7, 131.9, 129.6, 128.4, 127.9, 127.3, 127.2, 125.9, 125.9, 122.8, 118.1, 51.1, 45.6, 33.0, 30.7, 21.5, 21.3. Anal Calcd for $C_{28}H_{24}ClNO_5S$: C, 64.43; H, 4.63; N, 2.68. Found: C, 64.16; H, 4.55; N, 2.59.

(*E*)-3-(4-(2-Oxopropyl)-1-tosyl-1,4-dihydroquinolin-3(2*H*)-ylidene)isobenzofuran-1(3*H*)-one (3n)

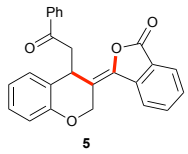


3n

Colourless solid (0.142 g, 72%); mp: 181-183 °C; IR (neat): 2974, 1703, 1694, 1489, 1278, 1337, 1230, 1278, 1154, 1102 cm^{-1}; ^{1}H NMR (400 MHz $CDCl_3$) δ 8.10 (d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 5.06 (d, *J* = 17.1 Hz, 1H), 4.95 (dd, *J* =

9.4, 2.8 Hz, 1H), 4.52 (d, *J* = 17.3 Hz, 1H), 3.28 (dd, *J* = 17.7, 9.7 Hz, 1H) 3.19 (s, 3H), 2.89 (dd, *J* = 17.6, 3.0 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 165.9, 140.1, 137.3, 137.1, 135.2, 133.1, 129.9, 129.3, 128.1, 126.1, 126.0, 125.4, 123.3, 123.1, 121.6, 49.9, 46.6, 40.91, 34.6, 31.0. Anal Calcd for $C_{21}H_{19}NO_5S$: C, 63.46; H, 4.82; N, 3.52. Found: C, 63.15; H, 4.79; N, 3.44.

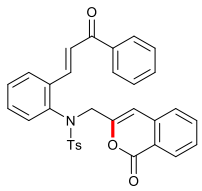
(*E*)-3-(4-(2-Oxo-2-phenylethyl)chroman-3-ylidene)isobenzofuran-1(3*H*)-one (5)



5

Colourless solid (0.166 g, 87%); mp: 151-153 °C; IR (neat): 2912, 1753, 1691, 1432, 1313, 1301, 1198, 1132, 1062 cm^{-1}; ^{1}H NMR (400 MHz $CDCl_3$) δ 8.27 (d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.60-7.54 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.29-7.27 (m, 1H), 7.17 (td, *J* = 7.7, 1.6 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 5.30 (d, *J* = 14.7 Hz, 1H), 5,16-5.14 (m, 1H), 5.04 (d, *J* = 14.7 Hz, 1H), 3.85 (dd, *J* = 17.0, 8.6 Hz, 1H), 3.35 (dd, *J* = 17.0, 4.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 166.2, 154.6, 140.8, 137.5, 136.6, 135.0, 133.6, 129.9, 129.0, 128.7, 128.5, 128.2, 126.1, 125.8, 125.7, 123.7, 122.0, 120.1, 117.6, 64.4, 46.4, 32.8. Anal Calcd for $C_{25}H_{18}O_4$: C, 78.52; H, 4.74. Found: C, 78.44; H, 4.71.

(*E*)-4-Methyl-*N*-((1-oxo-1*H*-isochromen-3-yl)methyl)-*N*-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)benzenesulfonamide (5)

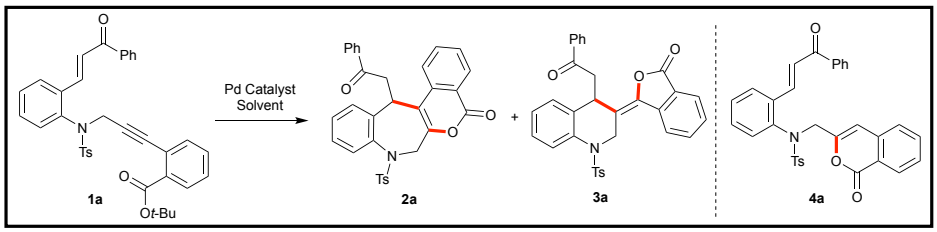


4a

Colourless solid; mp: 81-83 °C; IR (neat): 2891, 1737, 1725, 1674, 1668, 1482, 1339, 1241, 1163, 1133 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,) δ 8.14 (d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 16.1 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.66-7.57 (m, 4H), 7.52-7.49 (m, 2H), 7.44-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.27 (d, *J* = 2.5 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.62 (s, 1H), 4.66-4.59 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 161.6, 151.5, 144.3, 140.2, 139.0, 137.7, 136.4, 135.7, 135.3, 134.8, 132.8, 131.0, 130.5, 129.8, 129.5, 129.4, 128.7, 128.6, 128.5, 127.9, 127.6, 126.0, 124.8, 120.5, 106.3, 53.6, 21.5. Anal Calcd for $C_{32}H_{25}NO_5S$: C, 71.76; H, 4.70; N, 2.62. Found: C, 71.41; H, 4.61; N, 2.55.

8. Optimization of the Reaction Conditions

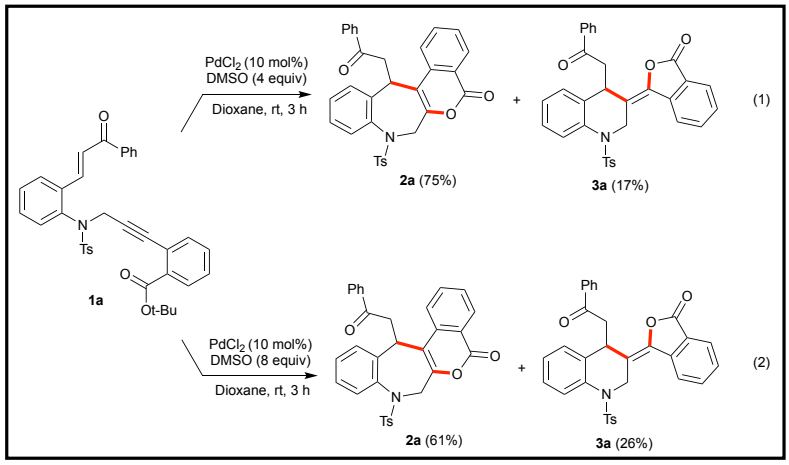
Table S1. Optimization of the reaction conditions for the chemodivergent syntheses of benzazepine **2a** and tetrahydroquinoline **3a**[a]



Entry	Catalyst (10 mol%)	Solvent	Time (h)	Yield of **2a** (%)[b]	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]
1	$Pd(OAc)_2$	MeCN	14	trace	trace	61
2	$Pd(OAc)_2$	Dioxane	48	trace	trace	73
3	$Pd(OAc)_2$	DMSO	14	trace	trace	-
4	$Pd(OAc)_2$	THF	25	trace	trace	60
5	$Pd(OAc)_2$	Toluene	25	trace	trace	74
6	$Pd(OAc)_2$	DCM	25	trace	trace	76
7	$Pd(OAc)_2$	DCE	25	trace	trace	79
8	$Pd(OAc)_2$	DME	25	trace	trace	75
9	$Pd(OAc)_2$	DMF	25	trace	trace	42
10	$Pd(OAc)_2$	EtOH	25	trace	trace	71
11	$PdCl_2$	MeCN	2	37	55	-
12	$PdCl_2$	Toluene	3	38	33	-
13	$PdCl_2$	THF	7	62	trace	-
14	$PdCl_2$	DCM	2	87	0	-
15	$PdCl_2$	DCE	2	90	trace	-
16[c]	**$PdCl_2$**	**Dioxane**	**2**	**93**	**0**	**-**
17	$PdCl_2$	DME	2	81	trace	-
18[d]	**$PdCl_2$**	**DMSO**	**3**	**14**	**78**	**-**
19[e]	$PdCl_2$	DMSO	0.5	18	70	-
20[f]	$PdCl_2$	DMSO	0.5	29	56	-
21[g]	$PdCl_2$	DMSO	2	10	71	-
22[h]	$PdCl_2$	DMSO	6	14	77	
23	$PdCl_2$	DMF	4	43	45	-
24	$PdCl_2$	EtOH	10	34	38	-
25[i]	$PdCl_2$	DMSO	16	trace	trace	-
26	$PdCl_2(MeCN)_2$	DCM	2	88	trace	-
27	$PdCl_2(MeCN)_2$	DCE	2	90	0	-
28	$PdCl_2(MeCN)_2$	Dioxane	2	91	0	-
29	$PdCl_2(MeCN)_2$	DMSO	3	15	76	-
30[j]	$Pd(PPh_3)_2Cl_2$	Dioxane	24	-	-	-
31[j]	$Pd(PPh_3)_2Cl_2$	DMSO	24	-	-	-
32[j]	$Pd(OTf)_2$	Dioxane	24	-	-	-
33[j]	$Pd(OTf)_2$	DMSO	24	-	-	-
34[k]	$Sc(OTf)_3$	Dioxane	48	-	-	-
35[k]	$Yb(OTf)_3$	Dioxane	48	-	-	-
36[k]	$Sc(OTf)_3$	DMSO	48	-	-	-
37[k]	$Yb(OTf)_3$	DMSO	48	-	-	-

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.5 mmol), catalyst (10 mol%) in 6 mL of solvent at room temperature. [b]Isolated yield. [c]Optimized reaction condition to access **2a**. [d]Optimized reaction condition to access **3a**. [e]Reaction was carried out at 50 °C. [f]Reaction was carried out at 80 °C. [g]Reaction was carried out with 3 mL of solvent. [h]Reaction was carried out with 9 mL of solvent. [i]Bipyridine was used as a ligand. [j]No reaction was observed and starting material was recovered. [k]No reaction.

9. Control Experiments



10. Crystallographic Data of Compound 2a

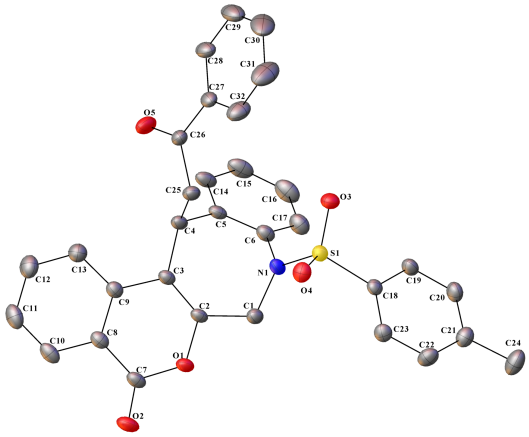


Figure S1: Thermal ellipsoids plot of compound **2a**. Hydrogen atoms are not shown for clarity.

Data Collection

A Leica MZ 75 microscope was used to identify a suitable colorless block with very well defined faces with dimensions (max, intermediate, and min) 0.205 x 0.183 x 0.102 mm^3 from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER Quest X-ray (fixed-Chi geometry) diffractometer with a PHOTON III detector was employed for crystal screening, unit cell determination, and data collection.The goniometer was controlled using the APEX3 software suite.[1] The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal

was rotated through all positions. The X-ray radiation employed was generated from a Mo-IμsX-ray tube (K_α= 0.71073Å). 45 data frames were taken at widths of 1°. These reflections were used to determine the unit cell. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed.
After careful examination of the unit cell, an extended data collection procedure (7sets) was initiated using omega and phi scans.

Data Reduction, Structure Solution, and Refinement

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.[1]The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS[2] was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group *P*-1. A solution was obtained readily using XT/XS in APEX3.[1,3]Half a molecule of ethyl acetate was found solvated per molecule of the compound. Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Residual electron density peaks near the solvent suggested it sits on a symmetry position and was modeled with PART -1 and half occupancy. Appropriate restraints were used to keep the thermal ellipsoids of the disordered solvent meaningful. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).[#]The structure was refined (weighted least squares refinement on F^2) to convergence.[3,4]
Olex2 was employed for the final data presentation and structure plots.[4]

[1] APEX3 "Program for Data Collection on Area Detectors" BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA

[2]SADABS, Sheldrick, G.M. "Program for Absorption Correction of Area Detector Frames", BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

[3]Sheldrick, G.M. (2008). ActaCryst. A64, 112-122. Sheldrick, G. M. (2015), ActaCryst. A71, 3-8. Sheldrick, G. M. (2015). ActaCryst. C71, 3-8. XT, XS, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

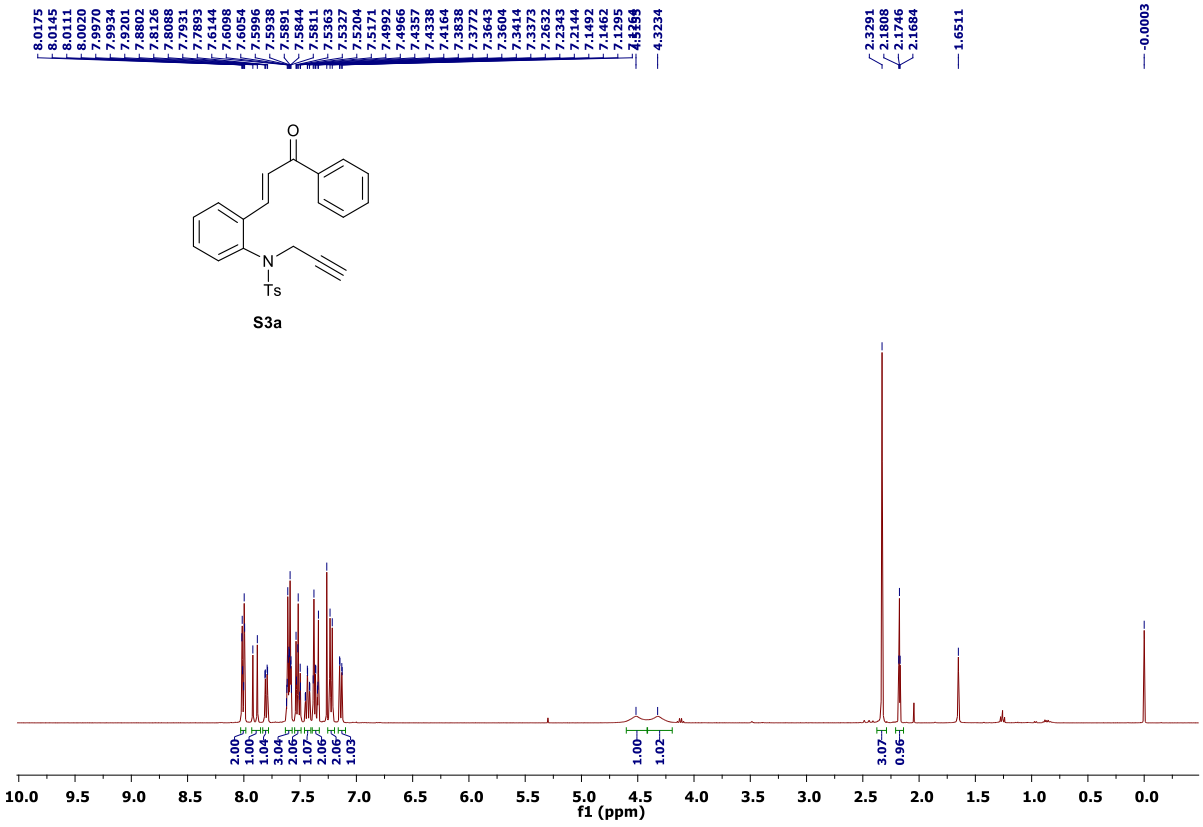
[4] Dolomanov, O. V, Bourhis, L. J., Gildea, R. J., Howard, J. A. K., and Puschmann, H. "OLEX2: A Complete Structure Solution, Refinement and Analysis Program", *J. Appl. Cryst.***2009***, 42*, 339-341.

Table S1. Crystal data and structure refinement for compound 2a

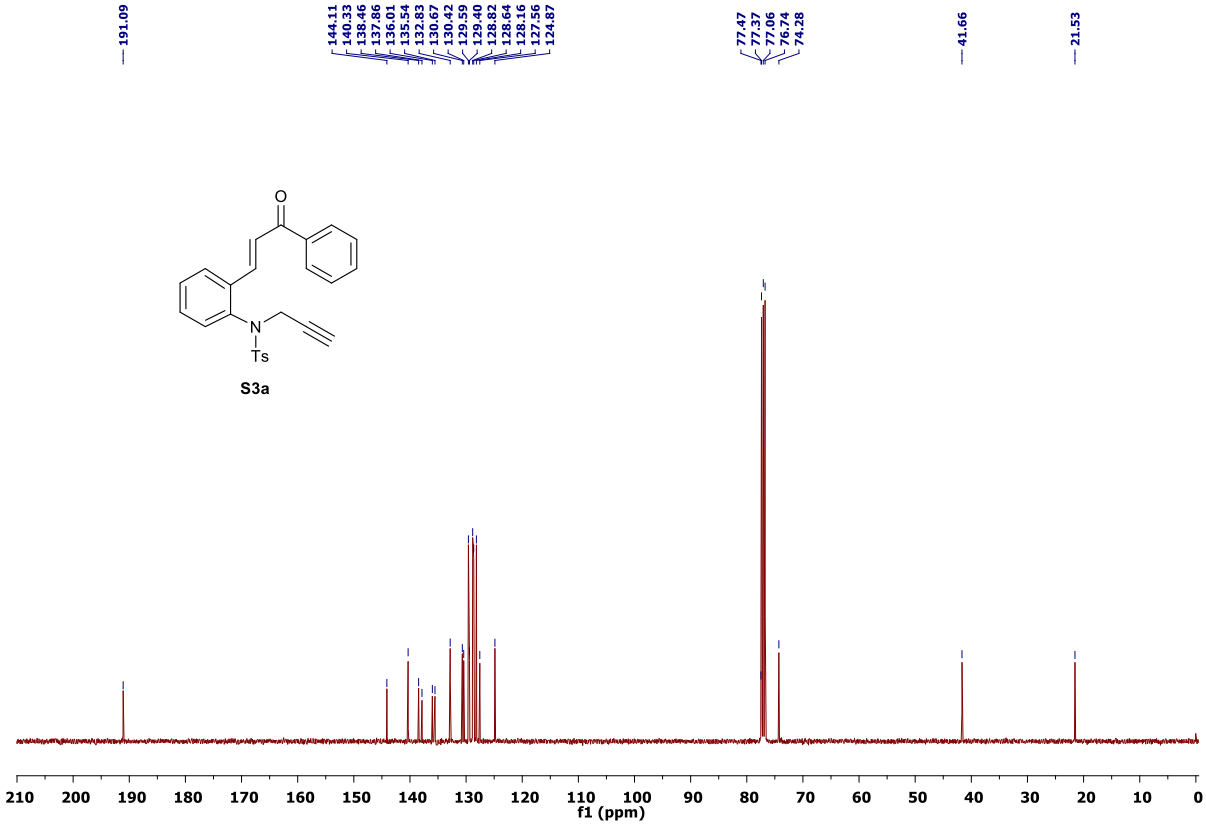
Identification code	2a	
Empirical formula	C34 H29 N O6 S	
Formula weight	579.64	
Temperature	110.00 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.5669(6) Å	□= 90.682(2)°.
	b = 11.3682(6) Å	□= 99.416(2)°.
	c = 11.9934(6) Å	□ = 97.172(2)°.
Volume	1409.43(13) $Å^3$	
Z	2	
Density (calculated)	1.366 Mg/m^3	
Absorption coefficient	0.164 mm^{-1}	
F(000)	608	
Crystal size	0.205 x 0.183 x 0.102 mm^3	
Theta range for data collection	1.806 to 29.914°.	
Index ranges	-14<=h<=14, -15<=k<=15, -16<=l<=16	
Reflections collected	46933	
Independent reflections	8098 [R(int) = 0.0453]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.7191	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8098 / 60 / 409	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.0436, wR2 = 0.1220	
R indices (all data)	R1 = 0.0642, wR2 = 0.1292	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.476 and -0.304 $e.Å^{-3}$	

11. ^{1}H and ^{13}C NMR Spectra of all the New Compounds

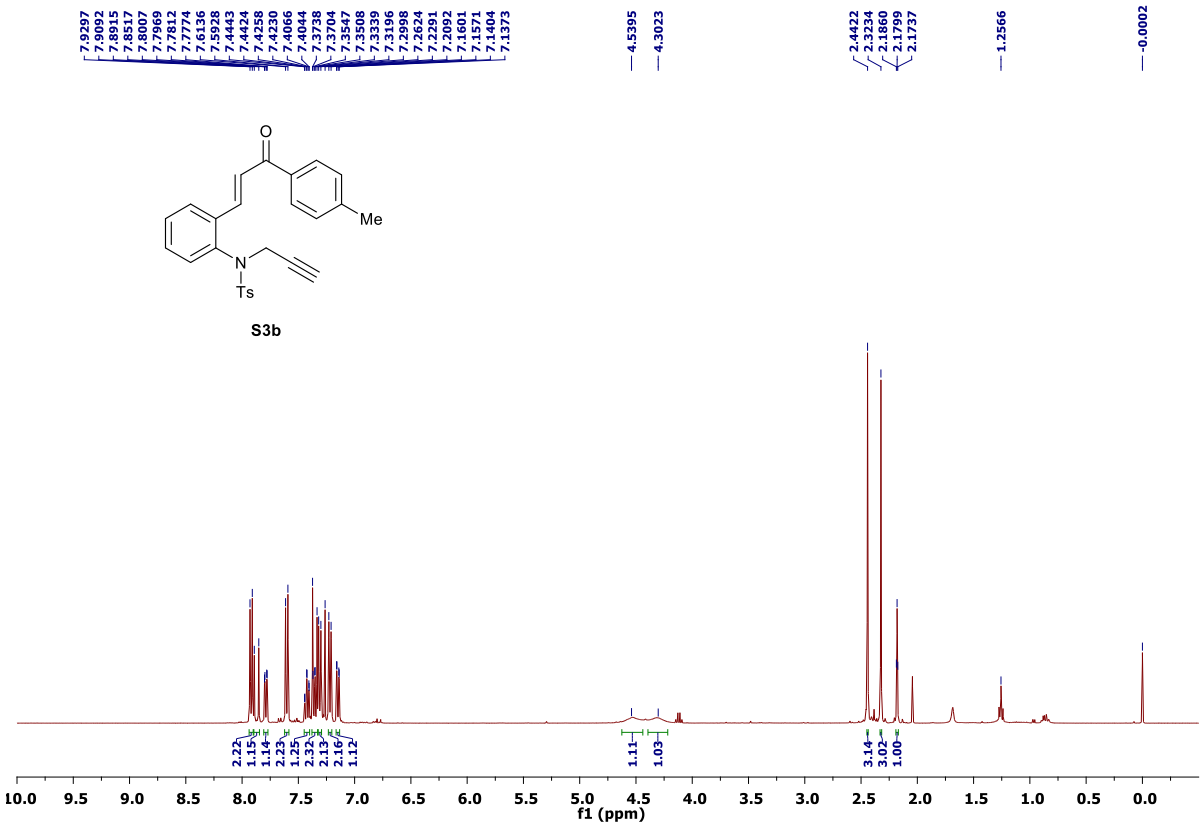
^{1}H NMR spectra of compound **S3a** ($CDCl_3$, 400 MHz)



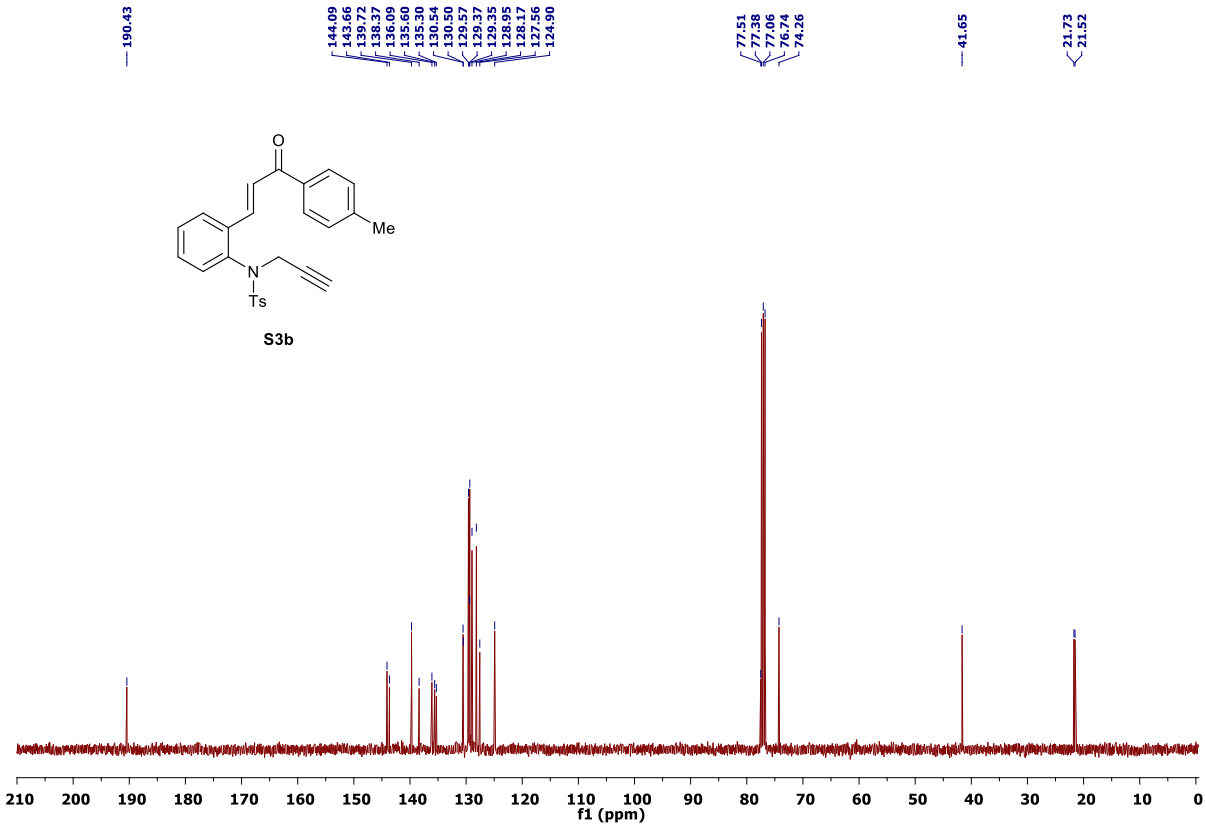
^{13}C{^{1}H} NMR spectra of compound **S3a**($CDCl_3$, 101 MHz)



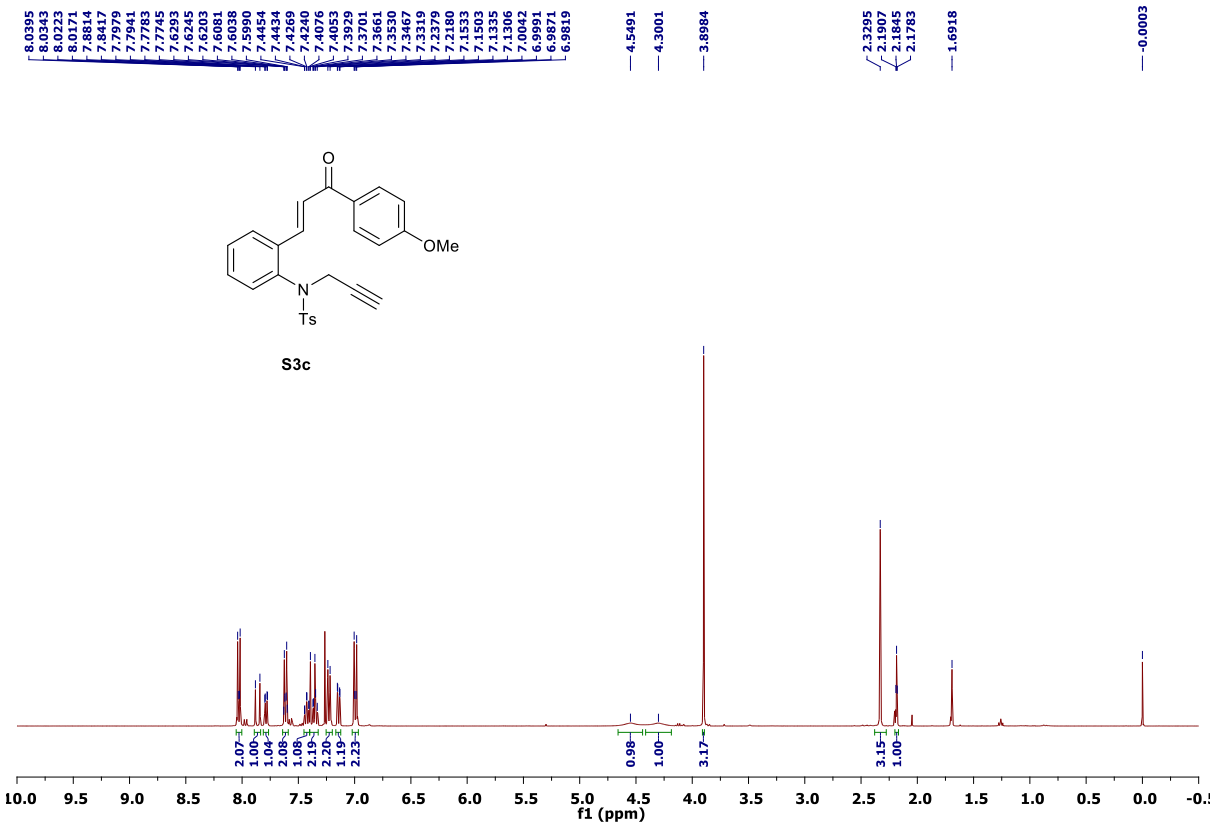
^{1}H NMR spectra of compound **S3b** ($CDCl_3$, 400 MHz)



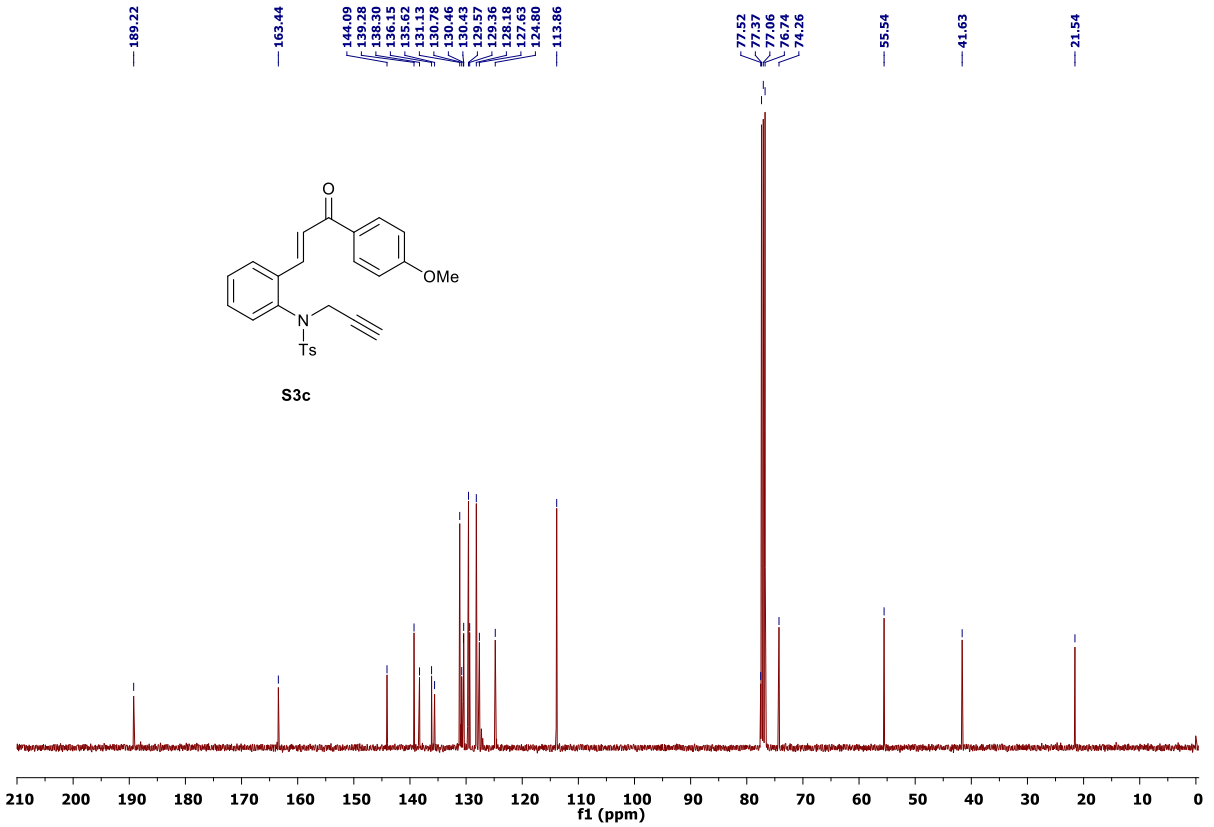
^{13}C{^{1}H} NMR spectra of compound **S3b** ($CDCl_3$, 101 MHz)



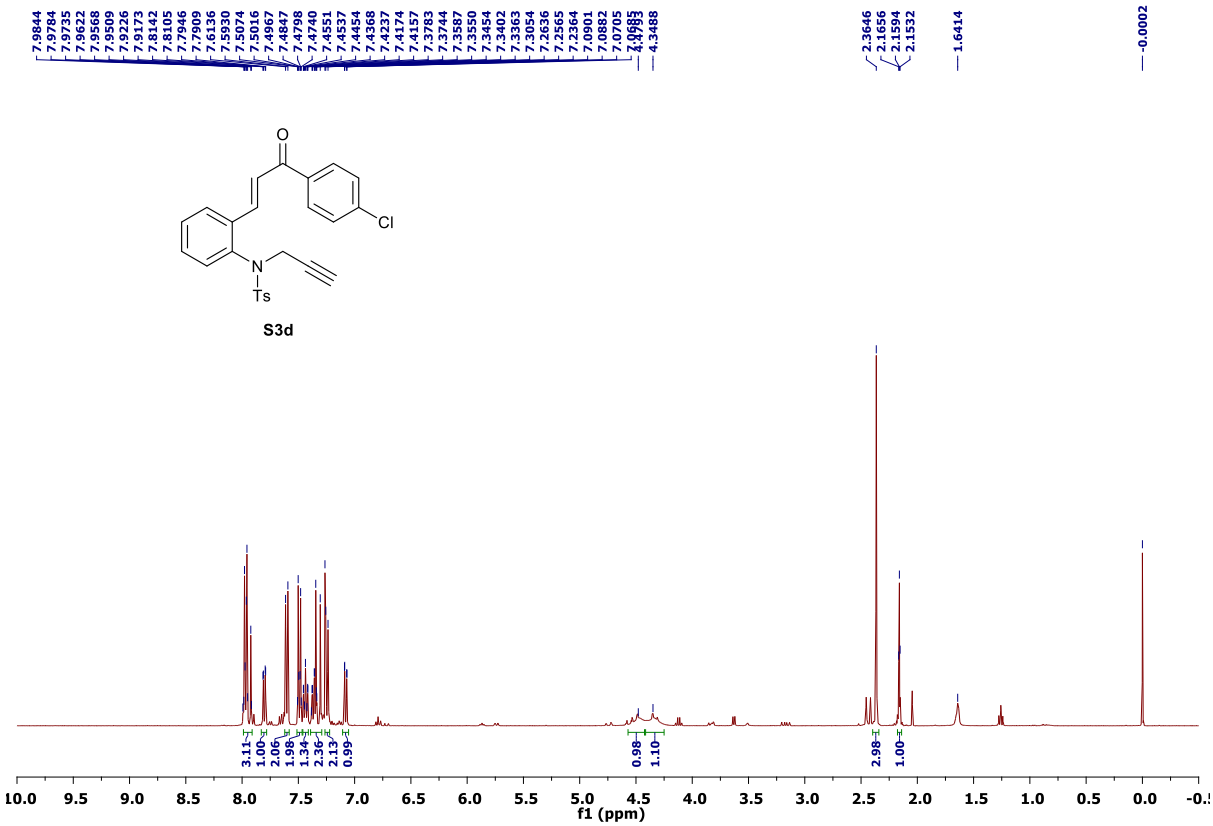
^{1}H NMR spectra of compound **S3c** ($CDCl_3$, 400 MHz)



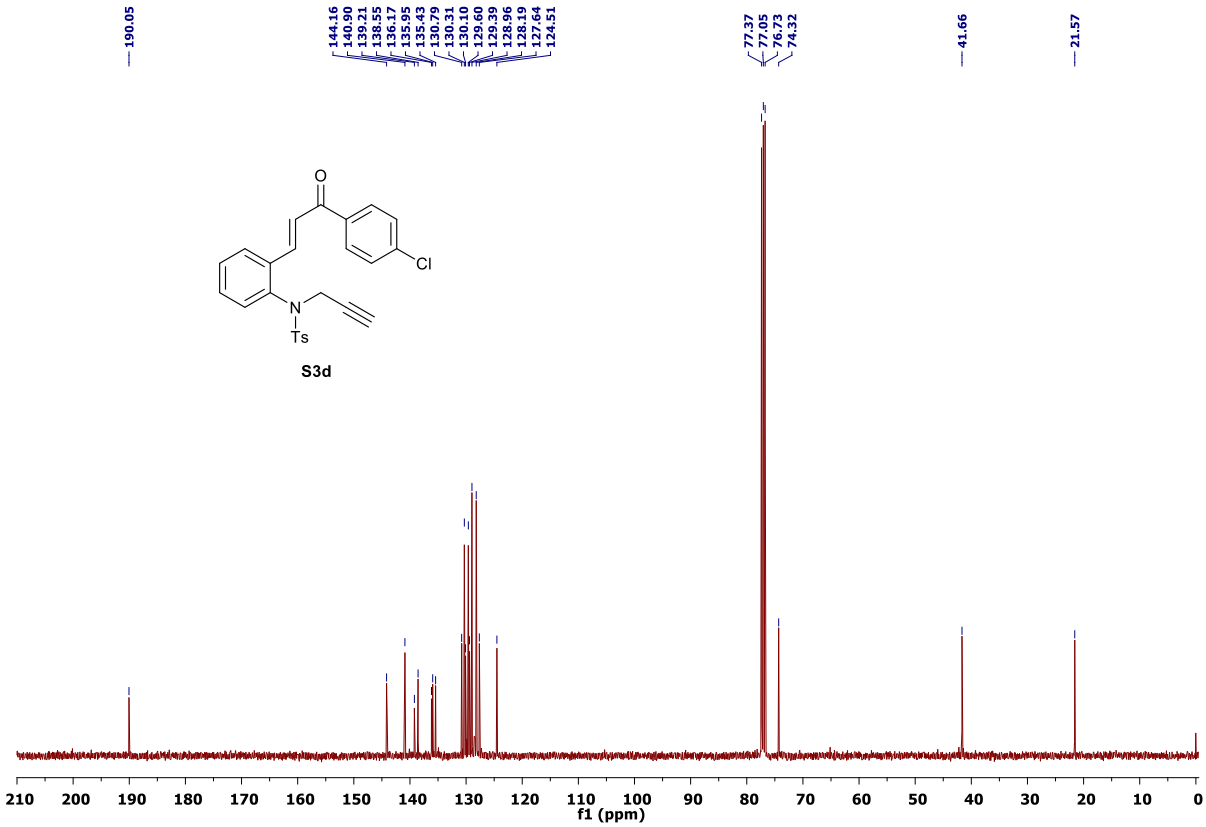
^{13}C{^{1}H} NMR spectra of compound **S3c** ($CDCl_3$, 101 MHz)



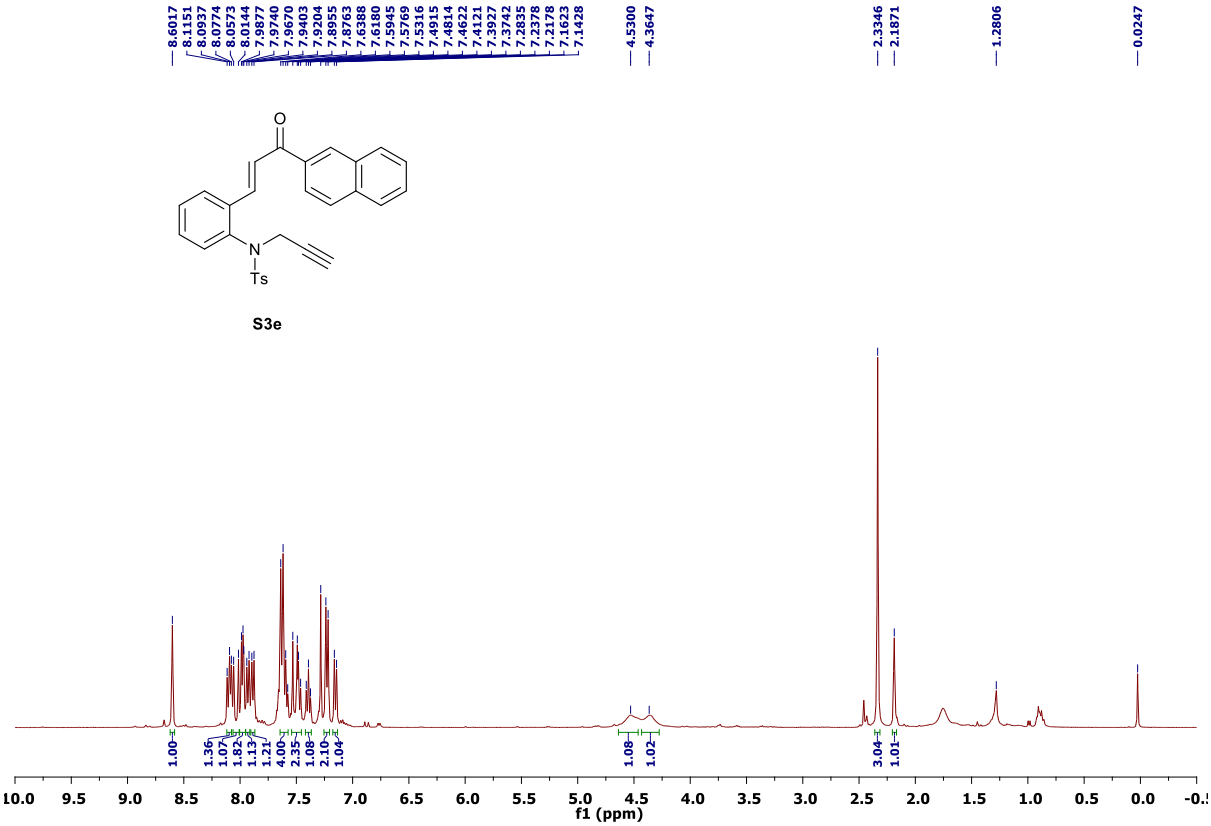
^{1}H NMR spectra of compound **S3d** ($CDCl_3$, 400 MHz)



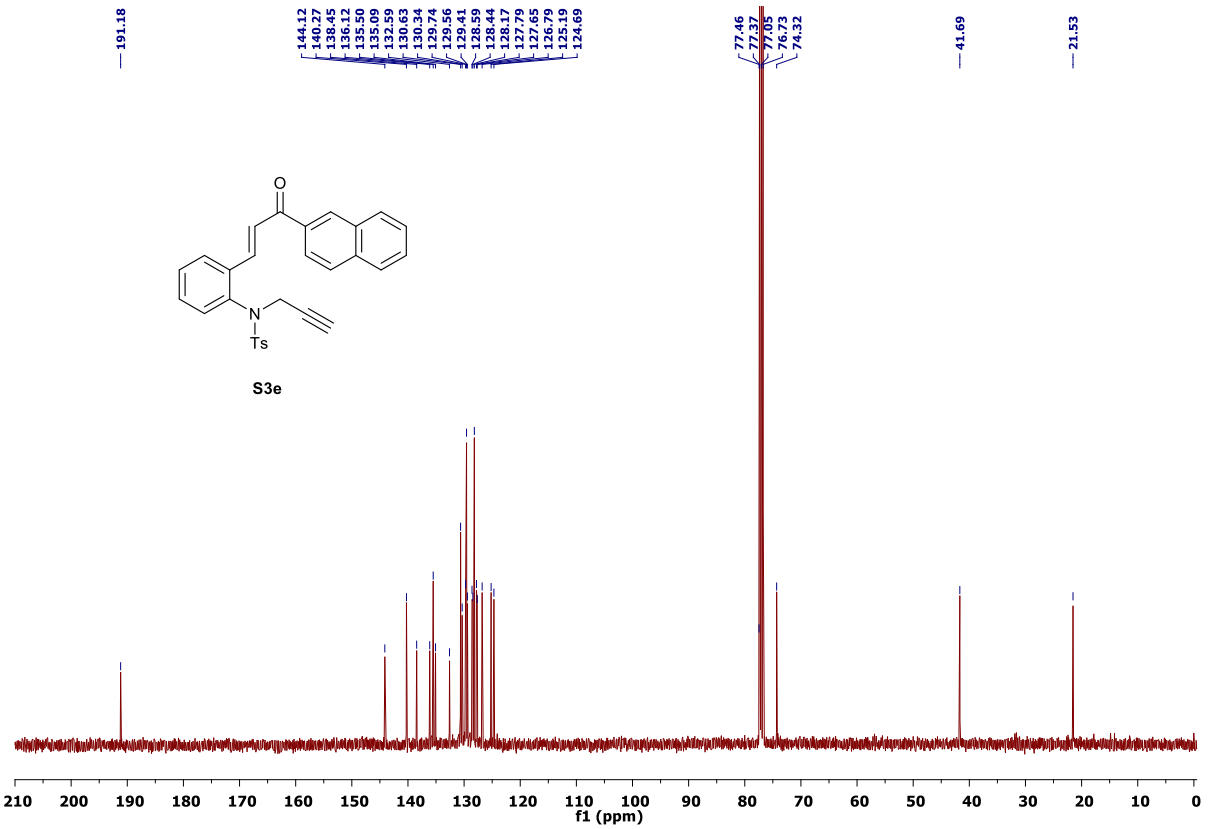
^{13}C{^{1}H} NMR spectra of compound **S3d** ($CDCl_3$, 101 MHz)



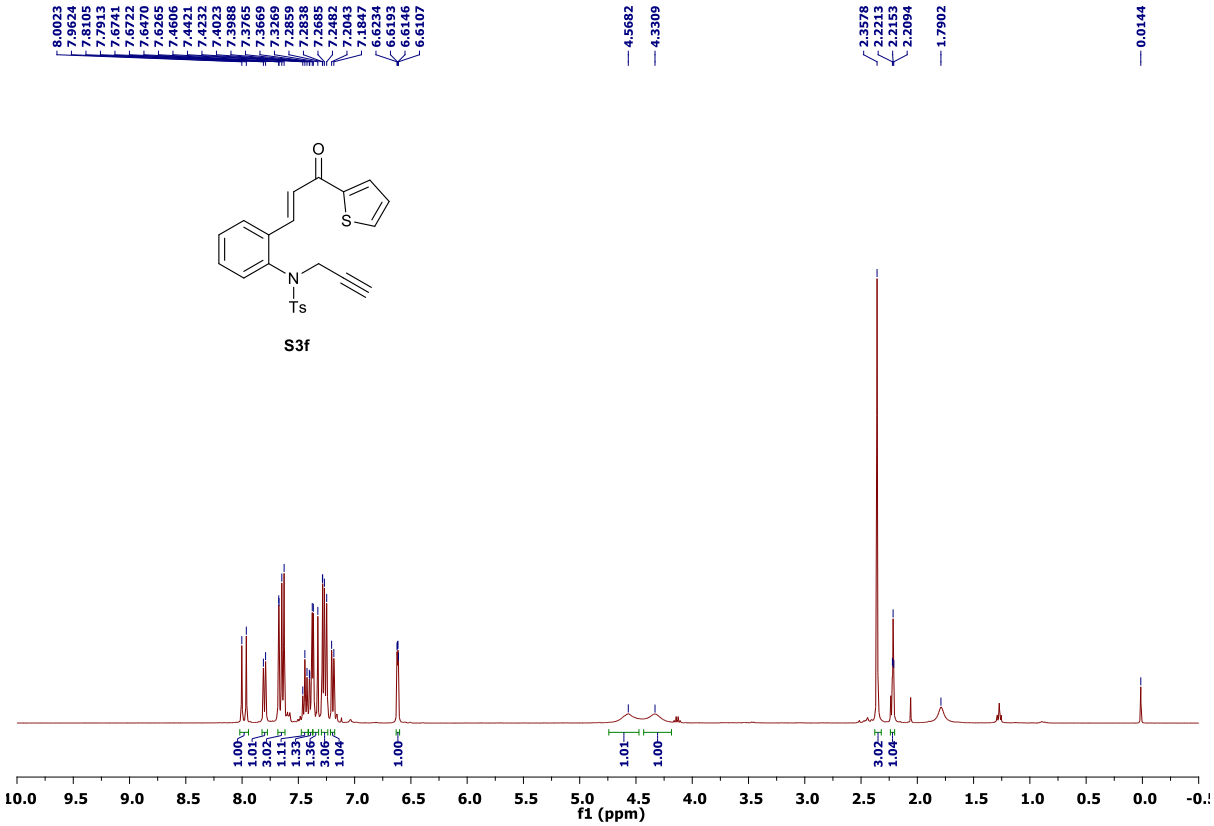
^{1}H NMR spectra of compound **S3e** ($CDCl_3$, 400 MHz)



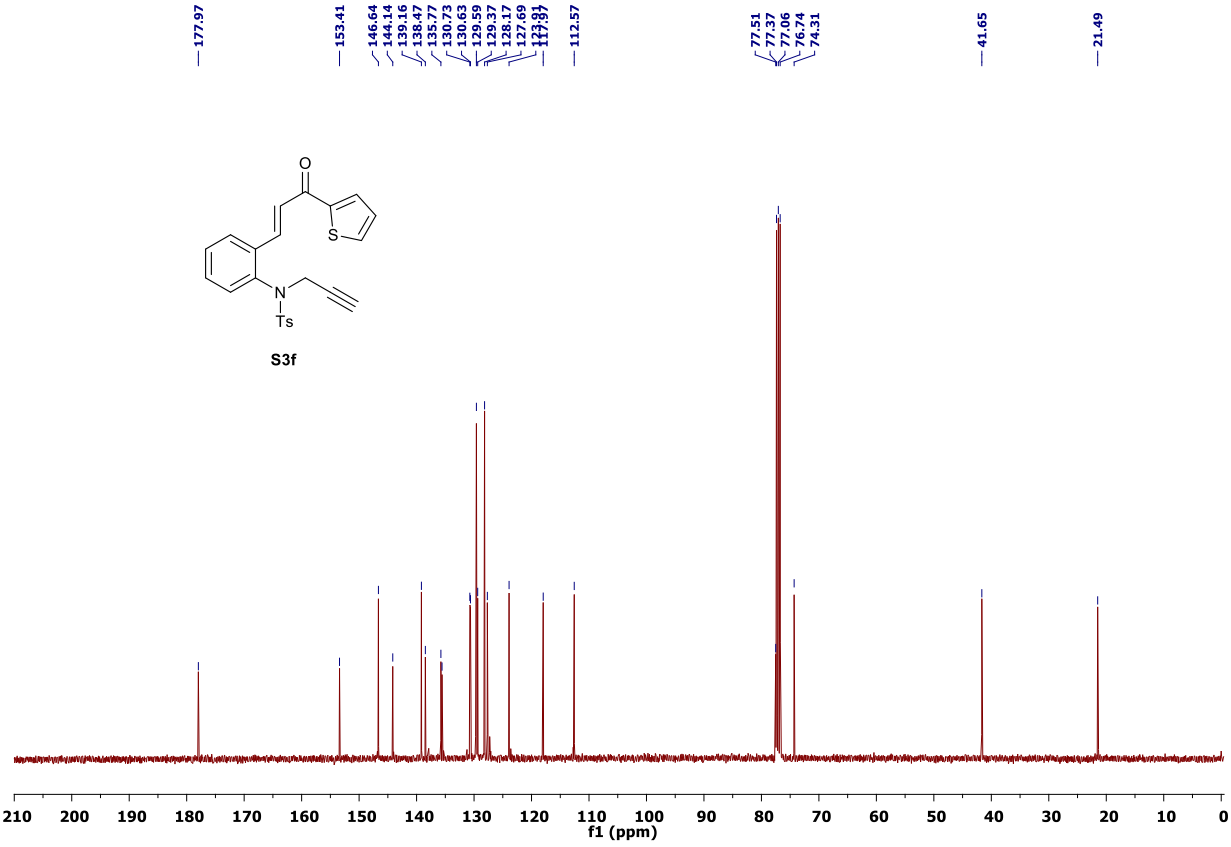
^{13}C{^{1}H} NMR spectra of compound **S3e** ($CDCl_3$, 101 MHz)



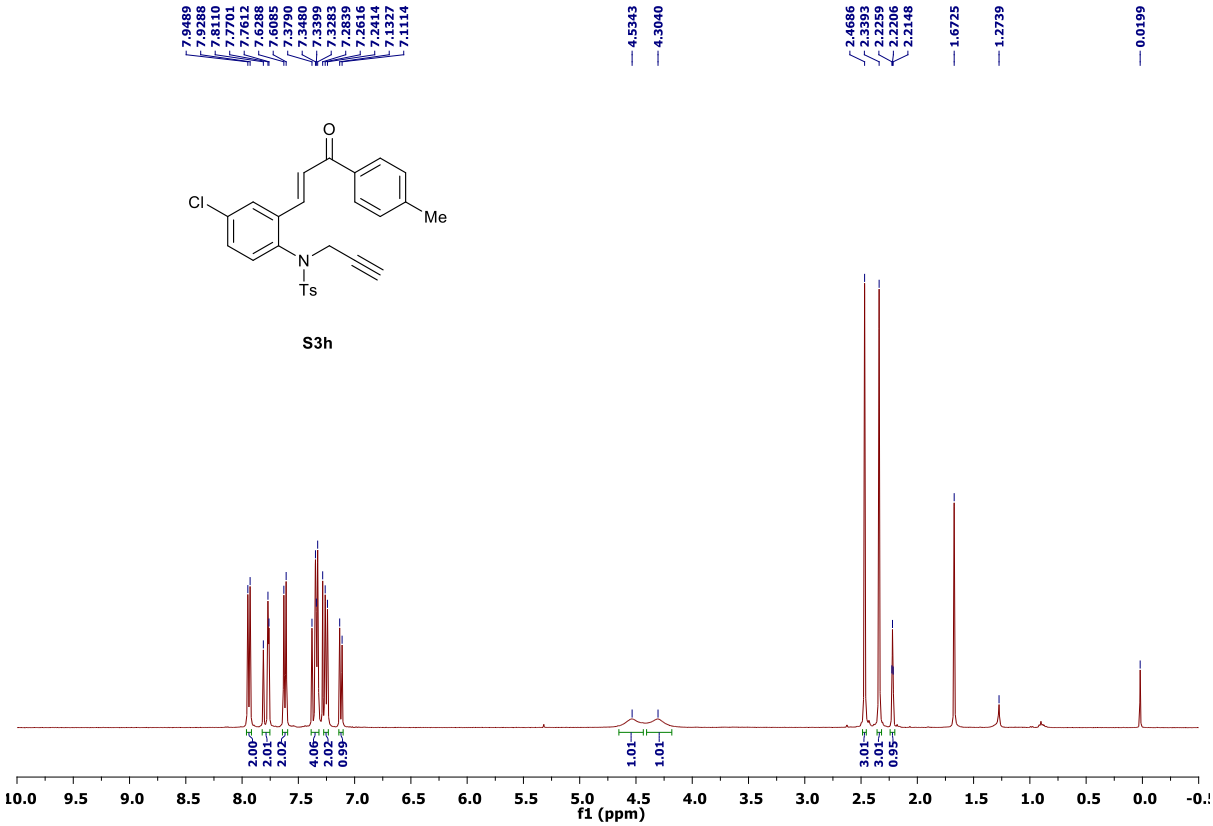
^{1}H NMR spectra of compound **S3f** ($CDCl_3$, 400 MHz)



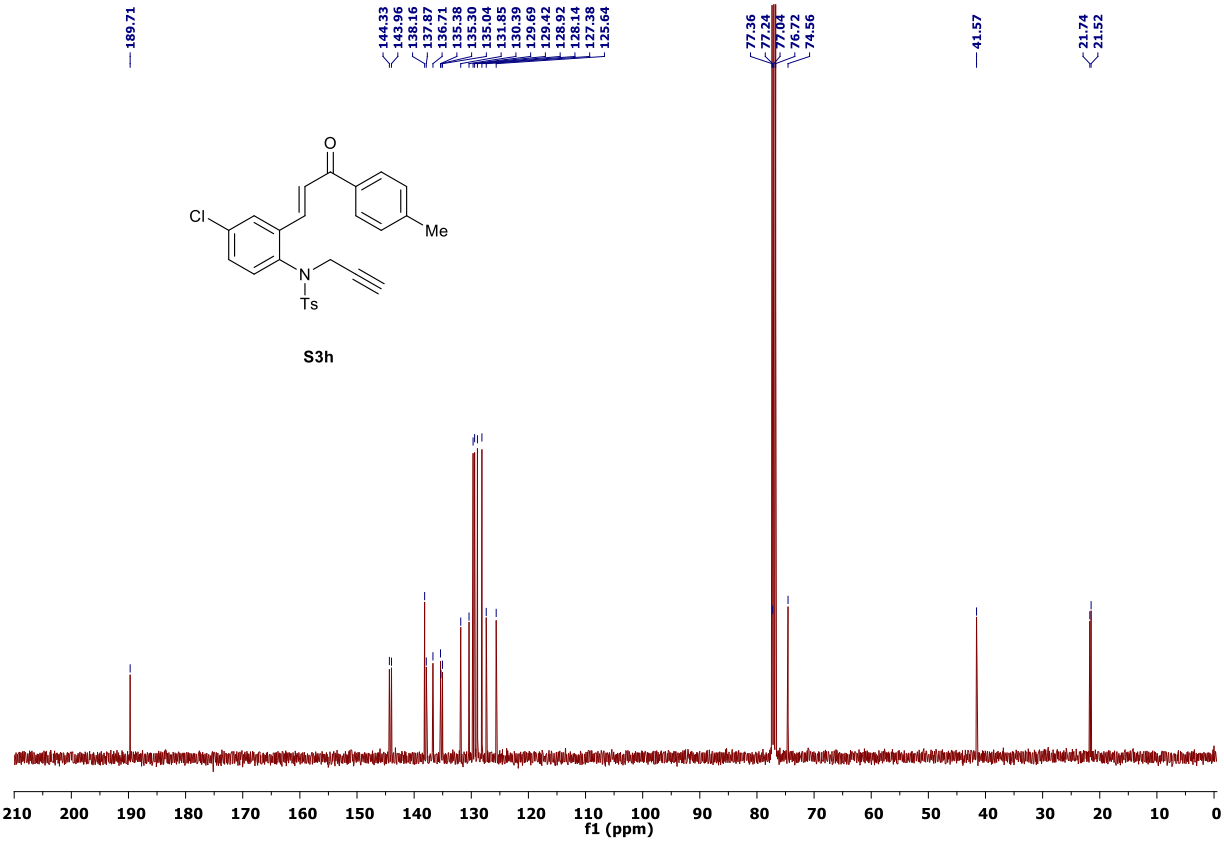
^{13}C{^{1}H} NMR spectra of compound **S3f** ($CDCl_3$, 101 MHz)



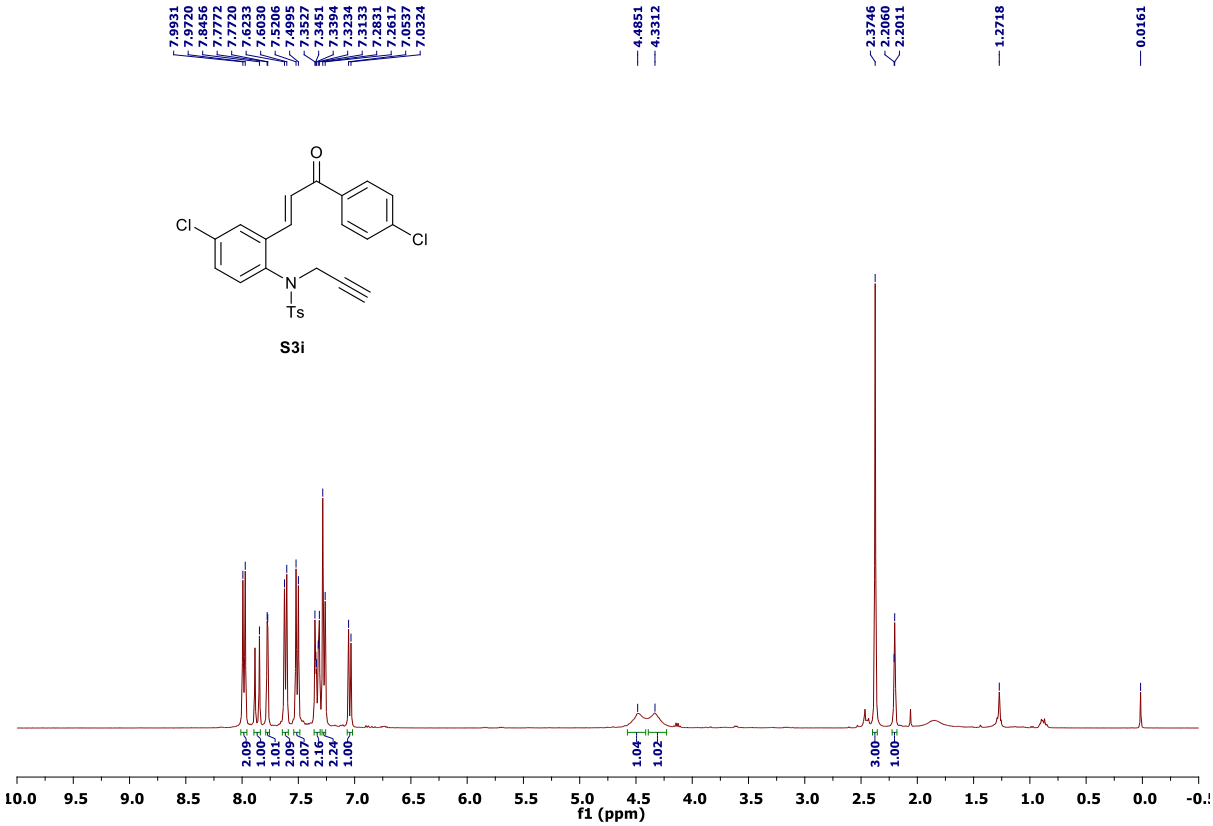
^{1}H NMR spectra of compound **S3h** ($CDCl_3$, 400 MHz)



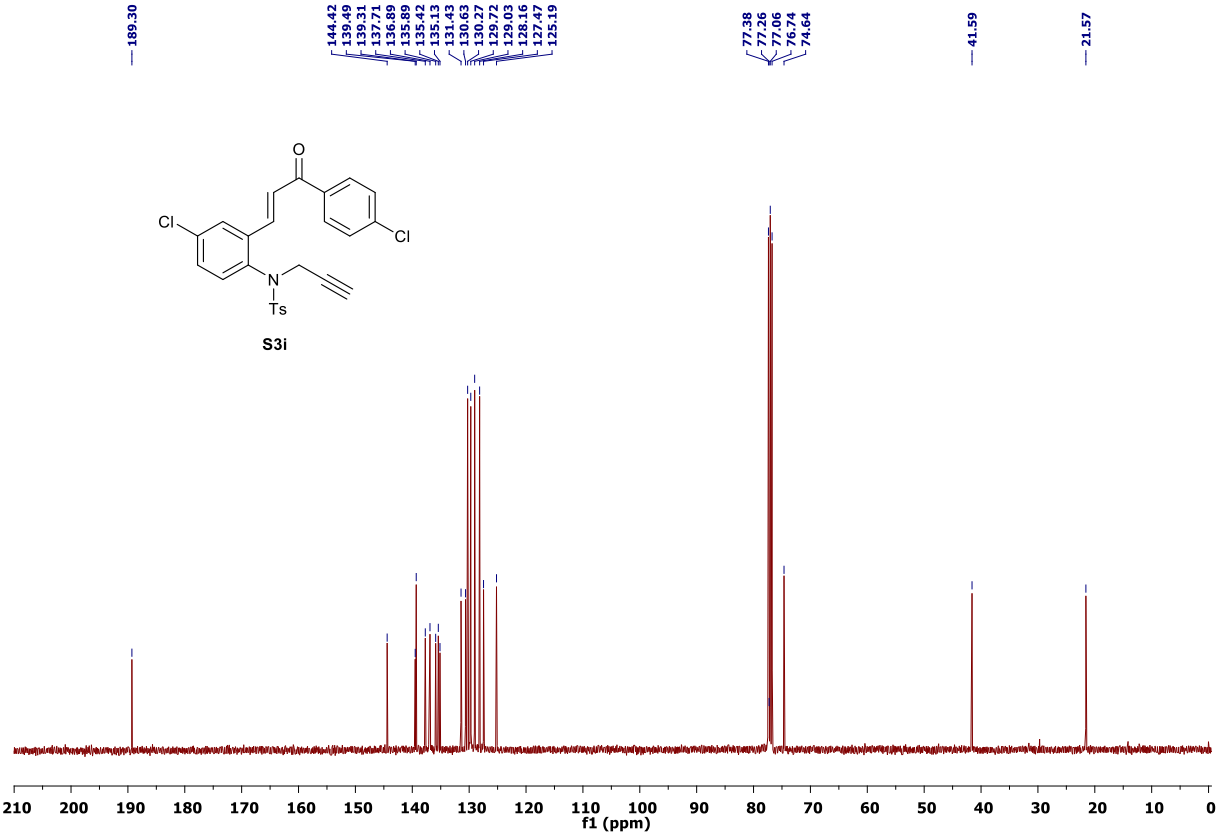
^{13}C{^{1}H} NMR spectra of compound **S3h** ($CDCl_3$, 101 MHz)



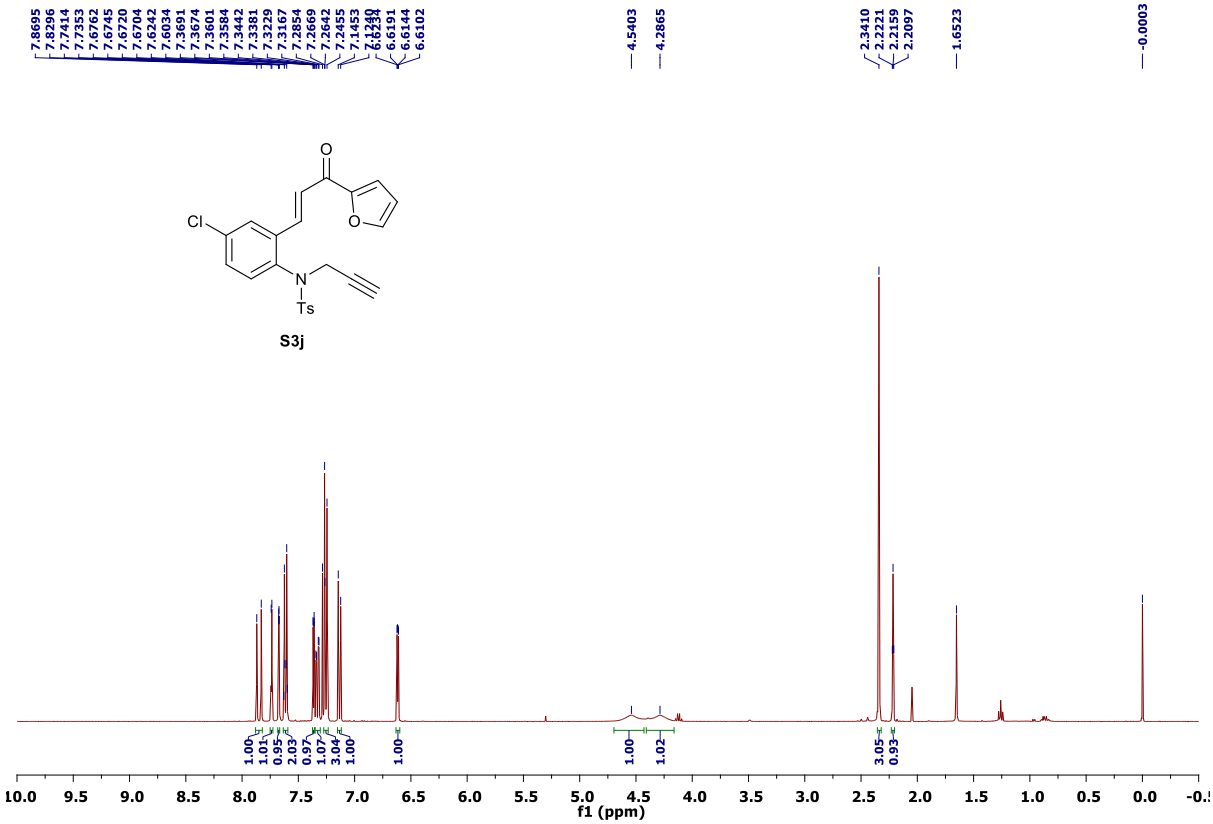
^{1}H NMR spectra of compound **S3i** ($CDCl_3$, 400 MHz)



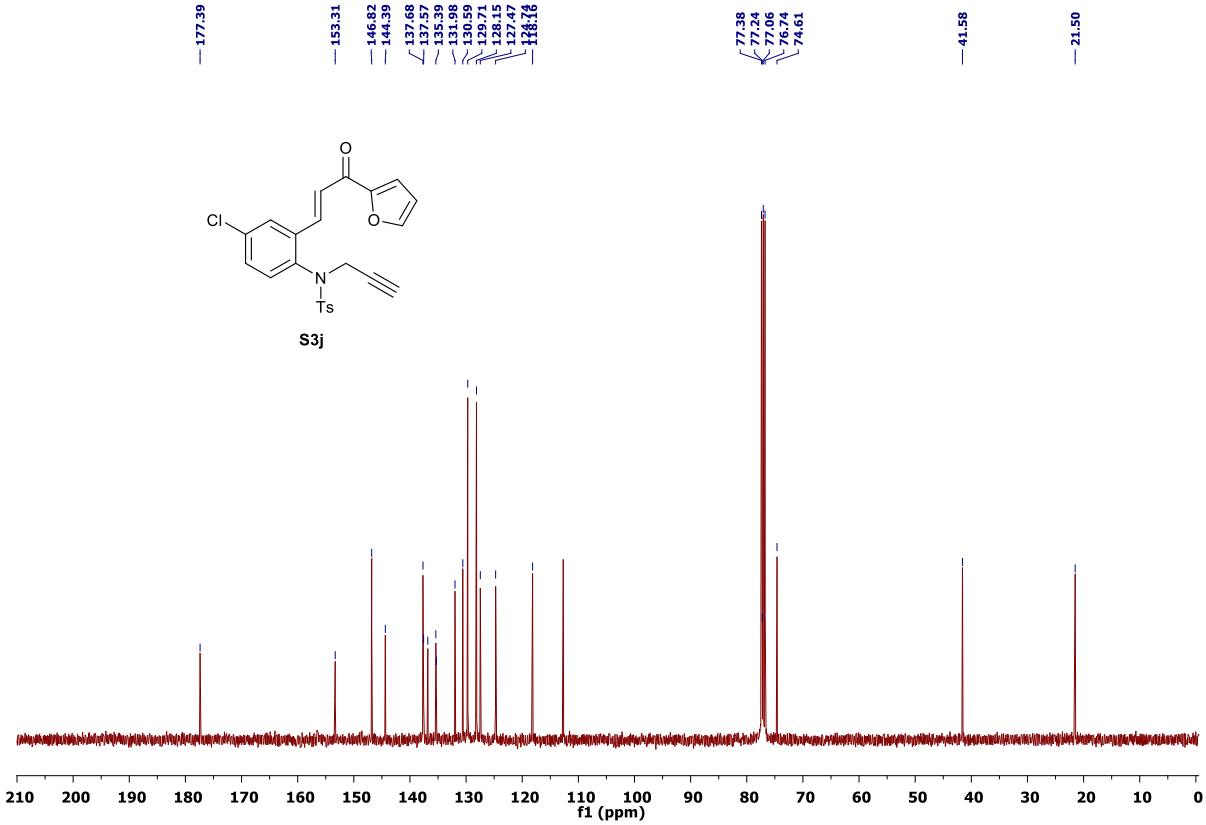
^{13}C{^{1}H} NMR spectra of compound **S3i** ($CDCl_3$, 101 MHz)



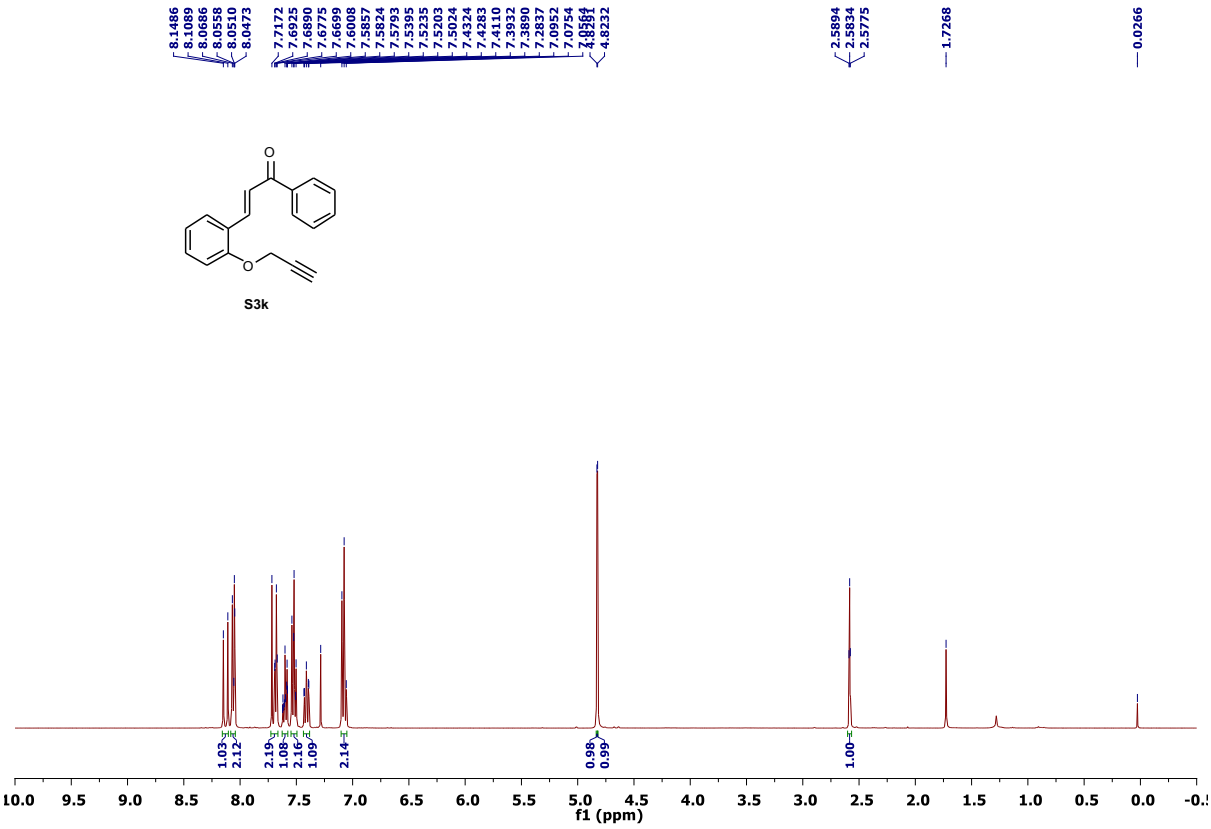
^{1}H NMR spectra of compound **S3j** ($CDCl_3$, 400 MHz)



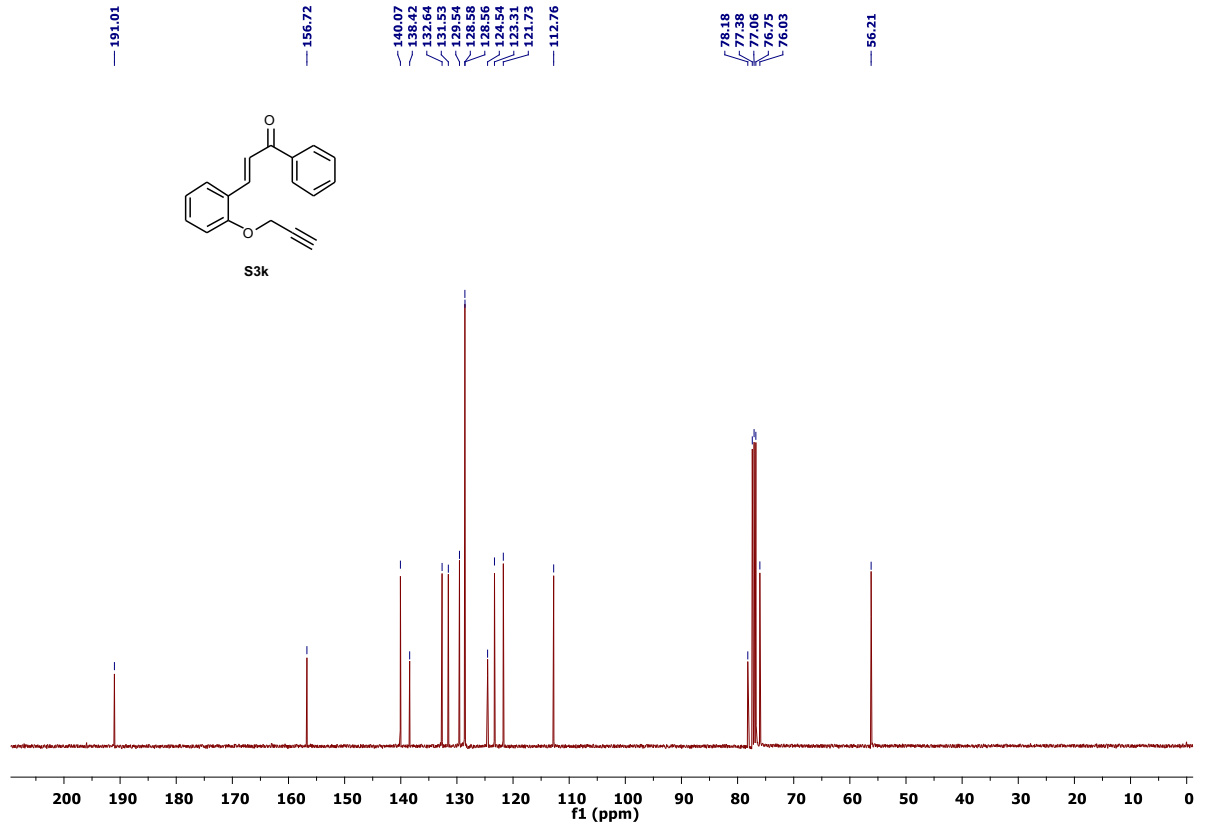
^{13}C{^{1}H} NMR spectra of compound **S3j** ($CDCl_3$, 101 MHz)



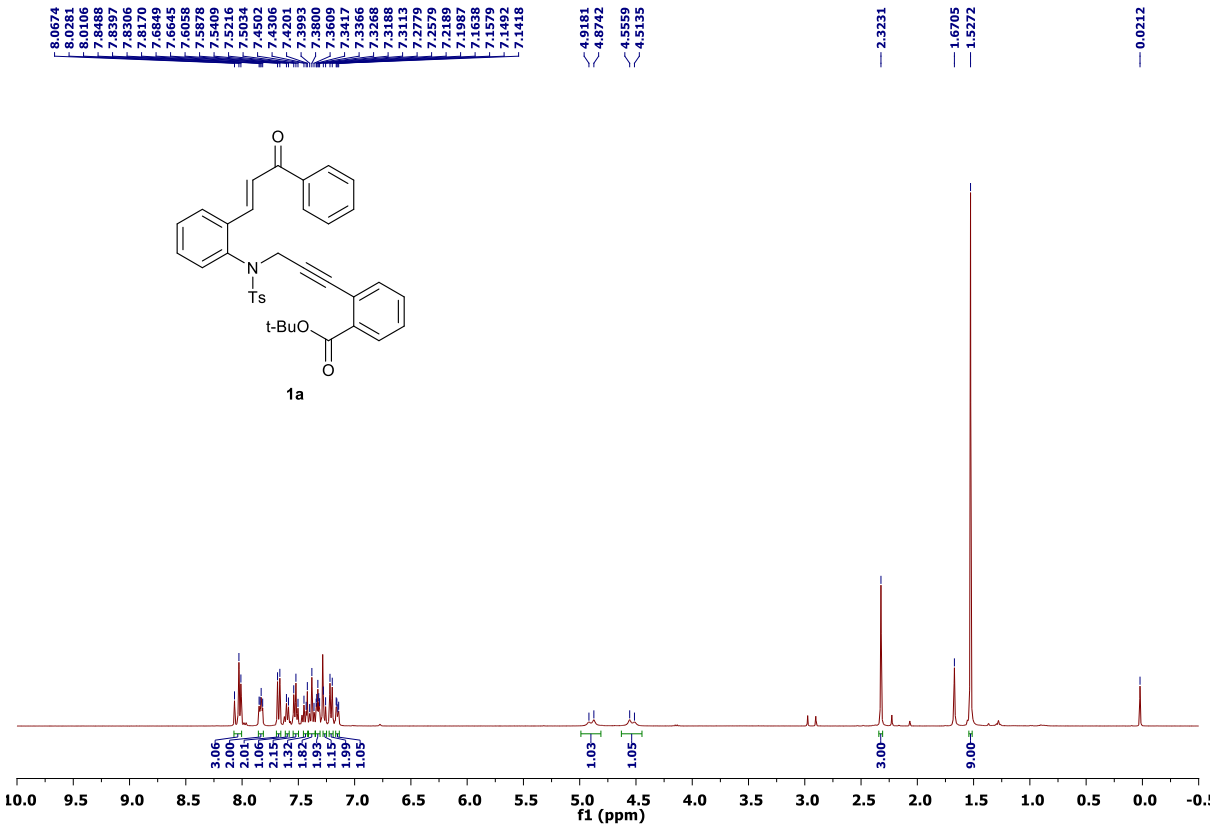
^{1}H NMR spectra of compound **S3k** ($CDCl_3$, 400 MHz)



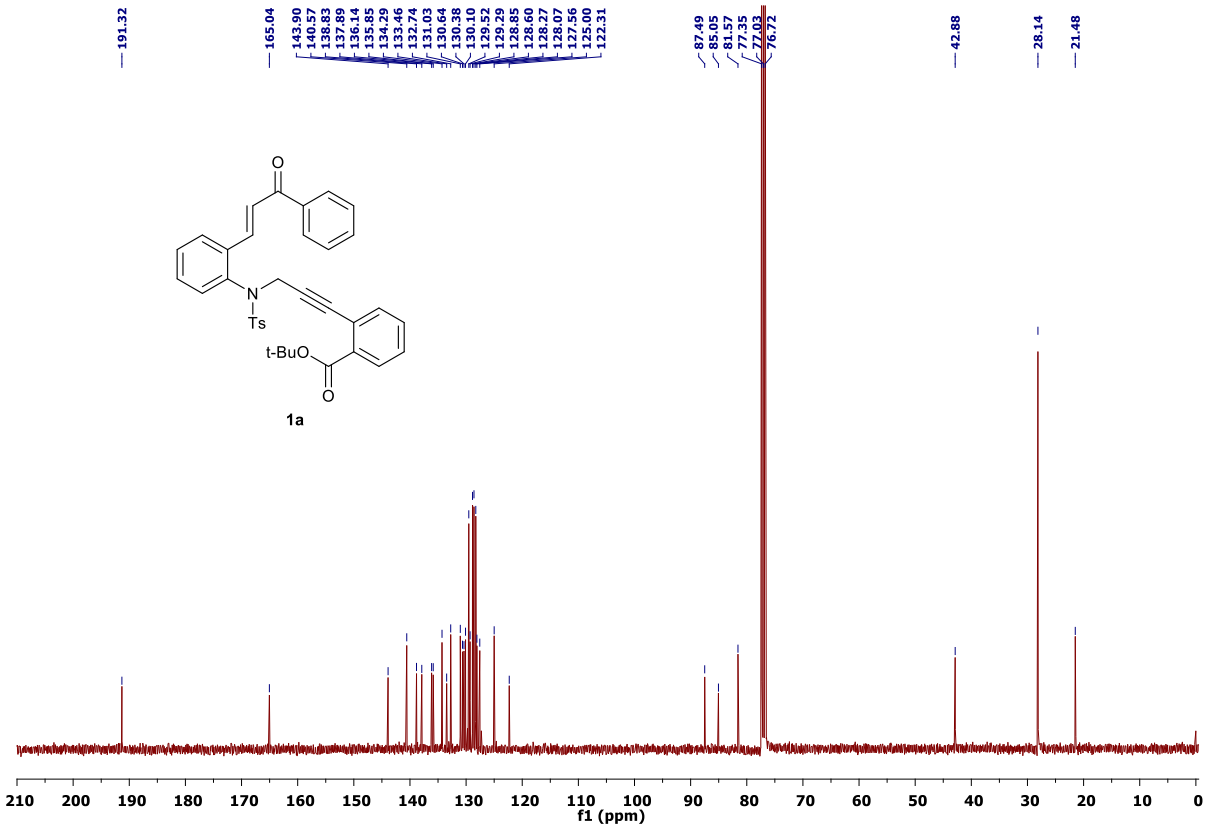
^{13}C{^{1}H} NMR spectra of compound **S3k** ($CDCl_3$, 101 MHz)



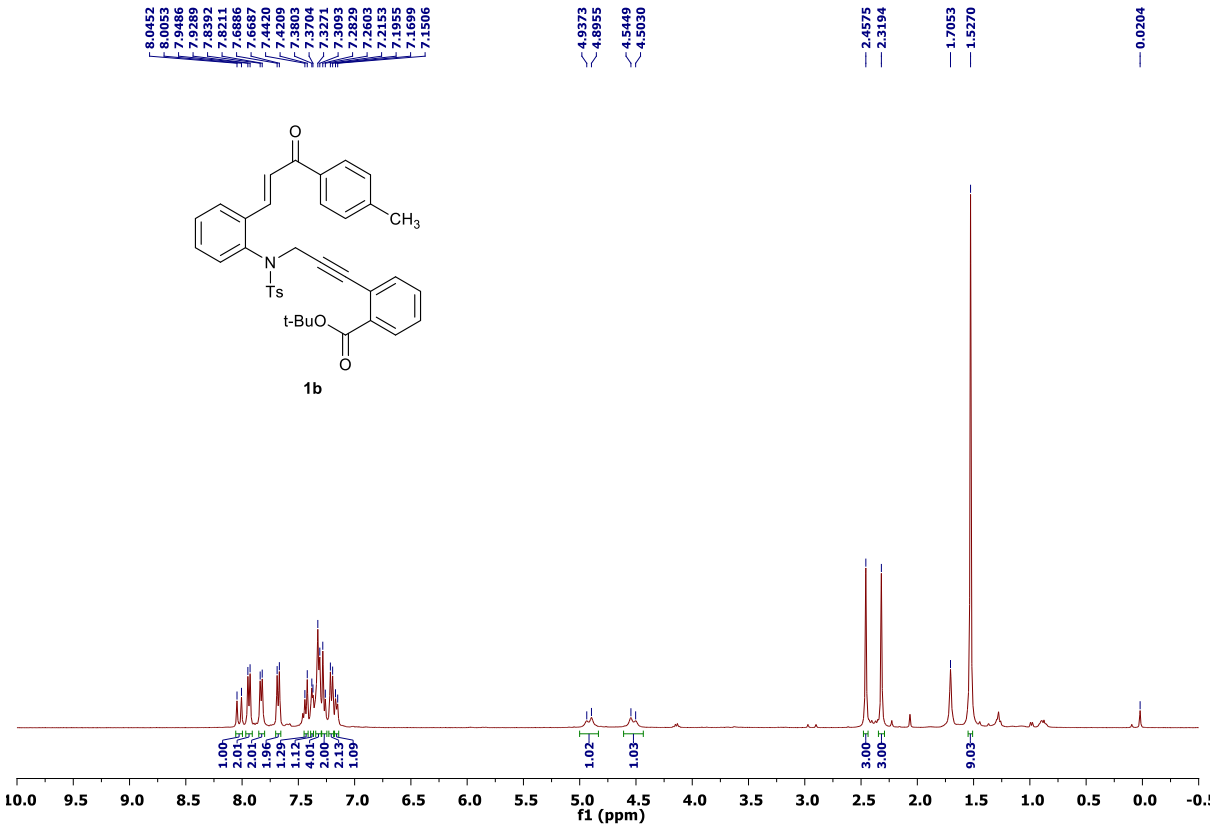
^{1}H NMR spectra of compound **1a** ($CDCl_3$, 400 MHz)



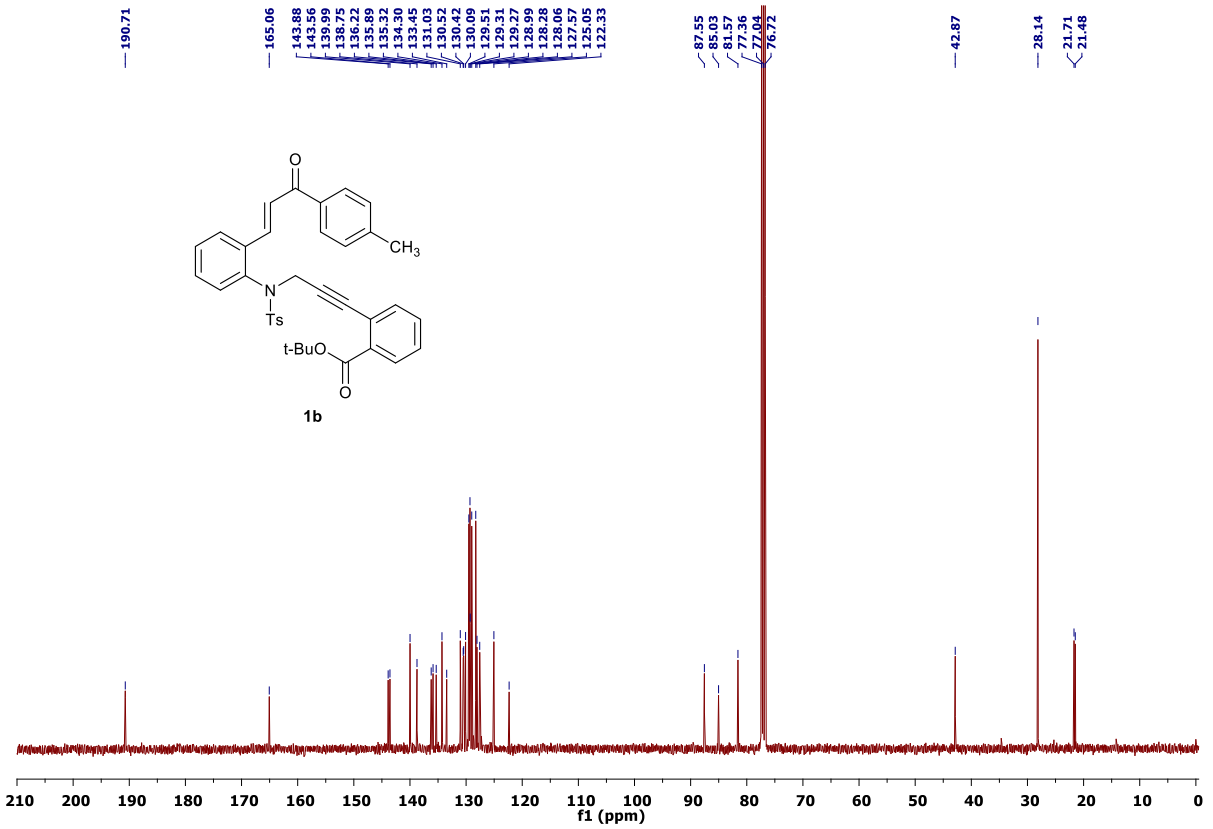
^{13}C{^{1}H} NMR spectra of compound **1a** ($CDCl_3$, 101 MHz)



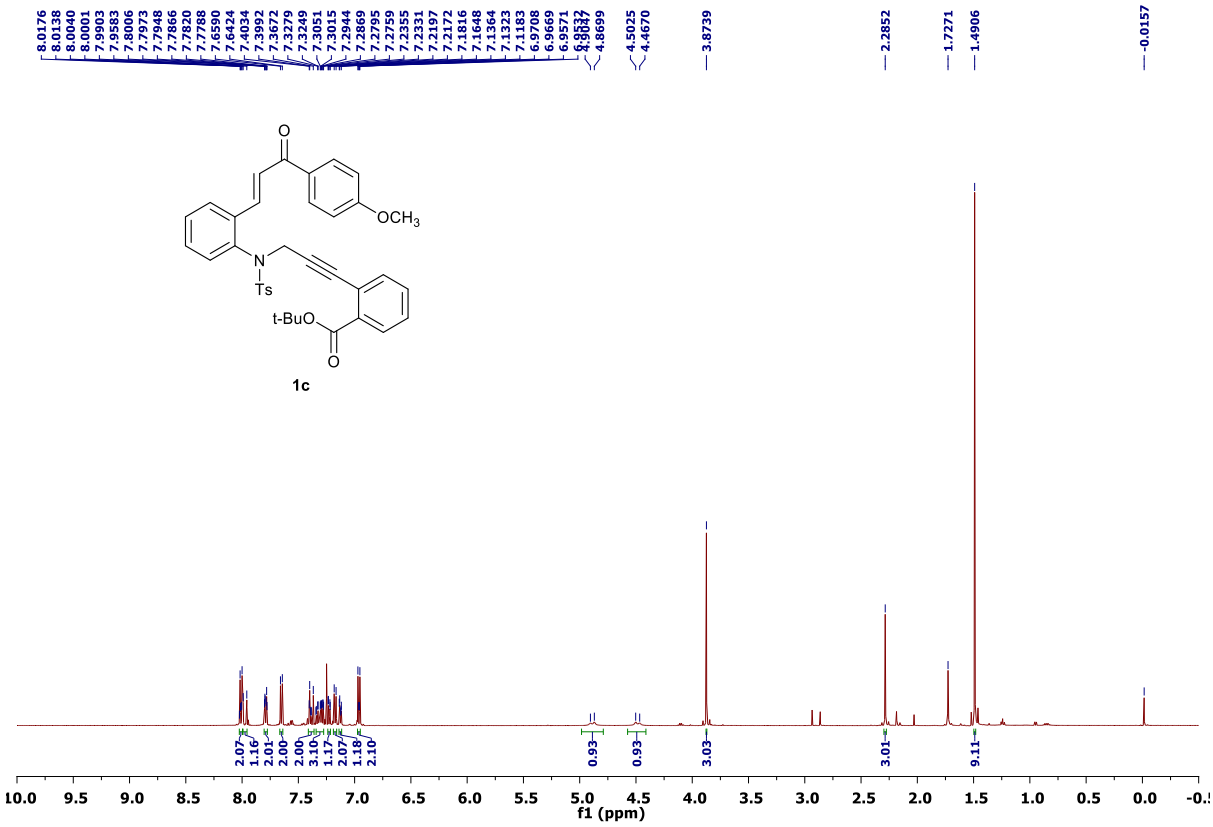
^{1}H NMR spectra of compound **1b** ($CDCl_3$, 400 MHz)



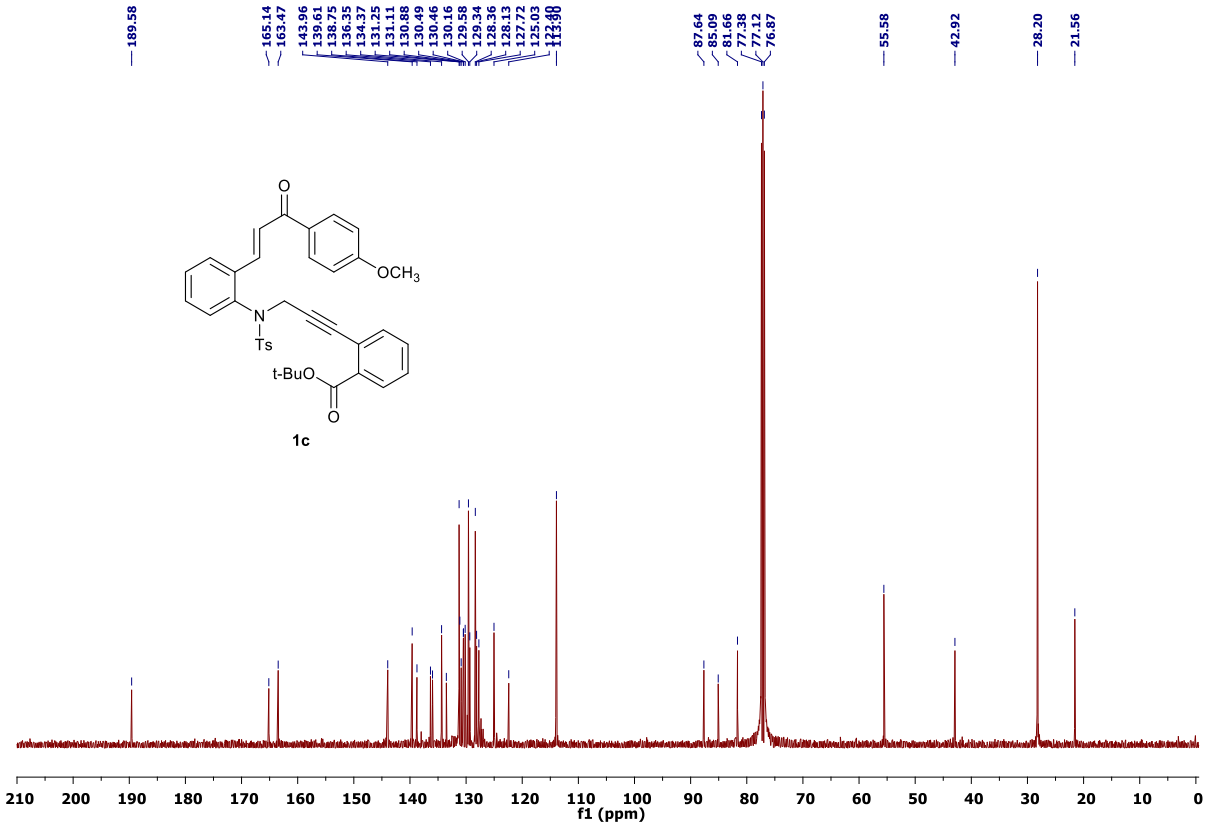
^{13}C{^{1}H} NMR spectra of compound **1b** ($CDCl_3$, 101 MHz)



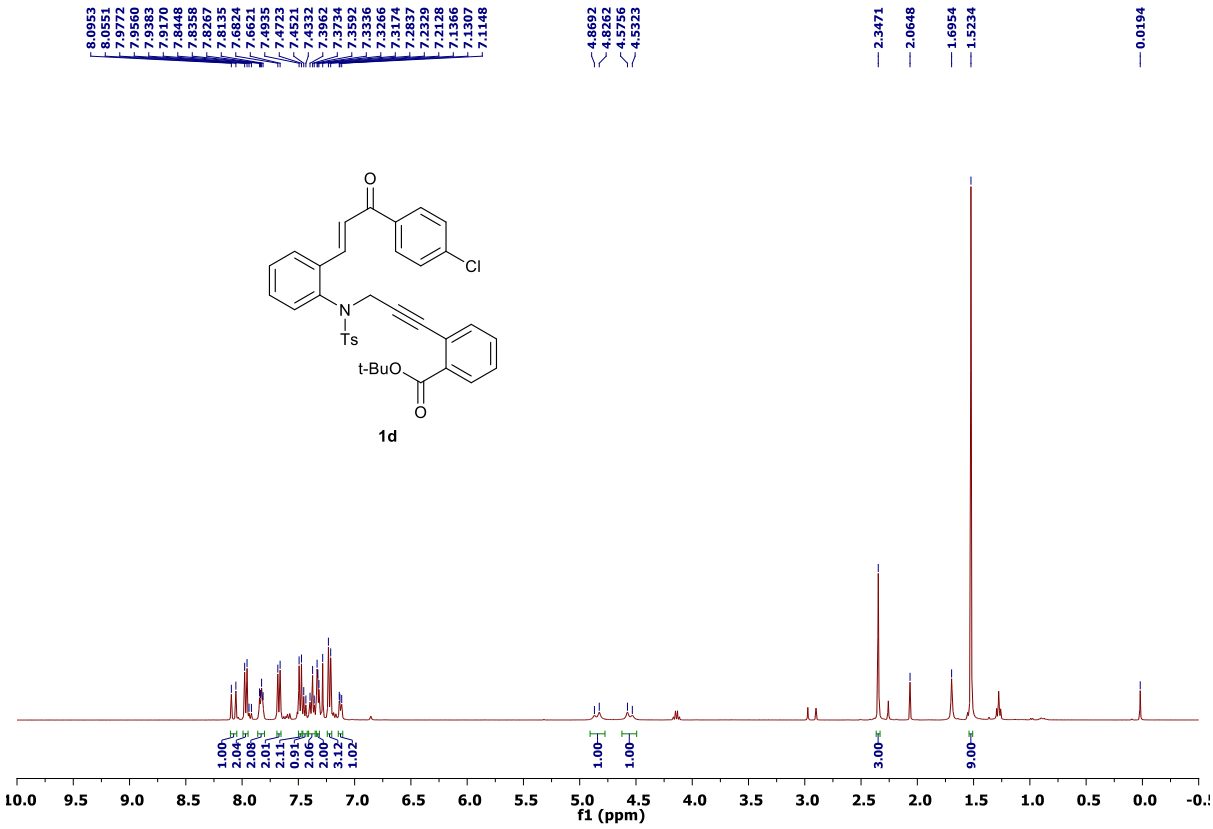
^{1}H NMR spectra of compound **1c** ($CDCl_3$, 500 MHz)



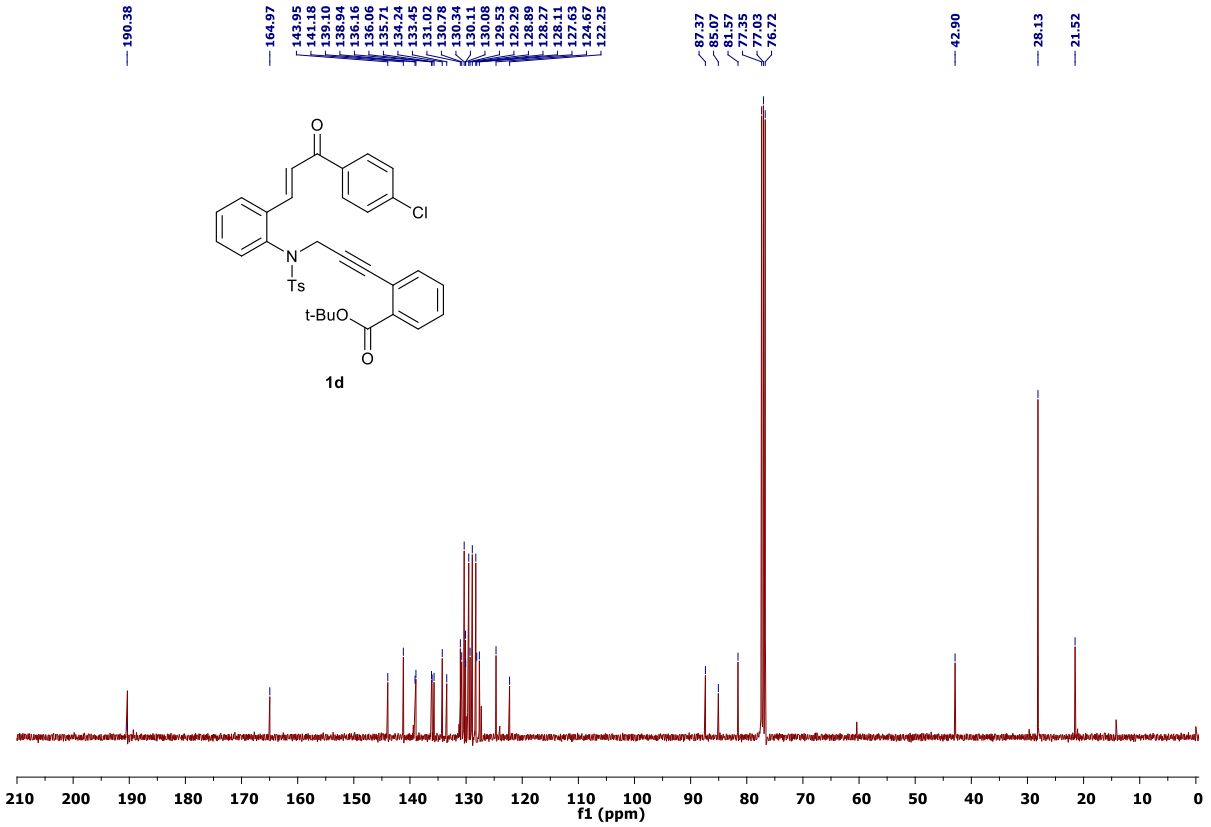
^{13}C{^{1}H} NMR spectra of compound **1c** ($CDCl_3$, 126 MHz)



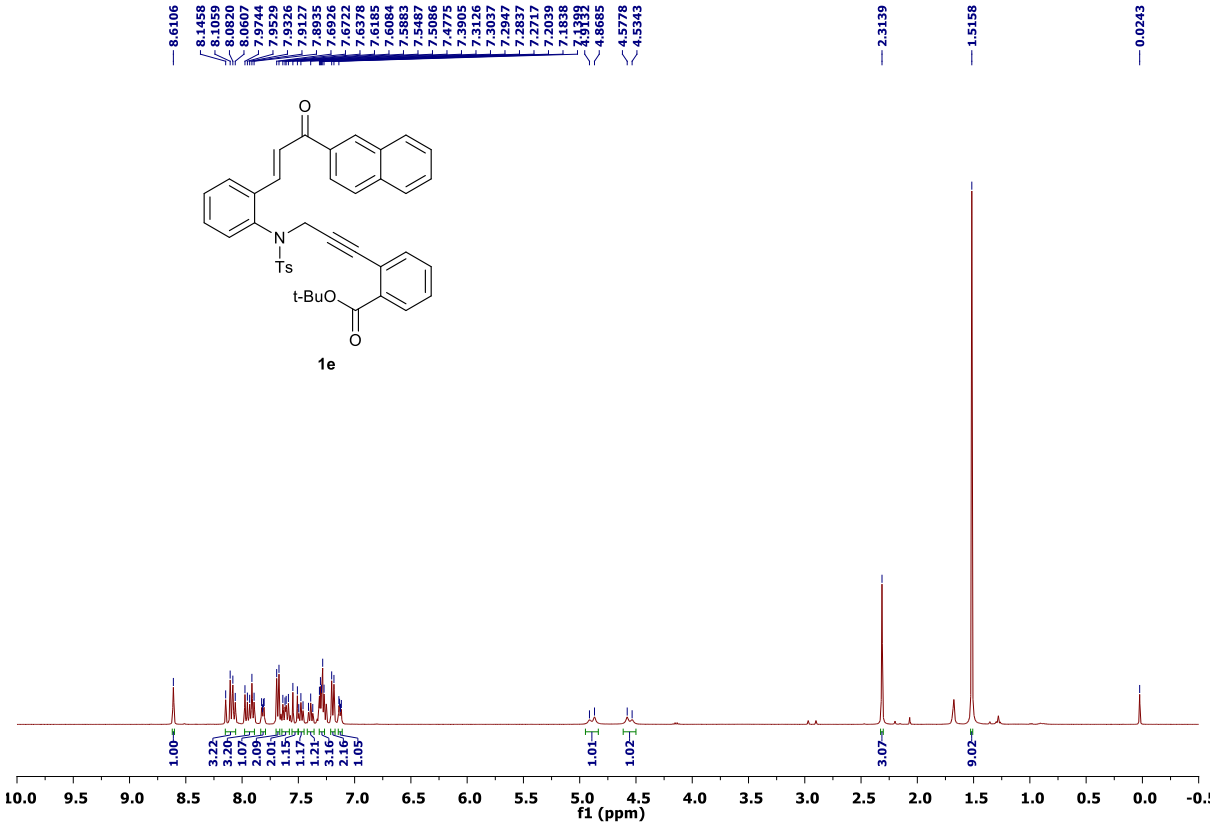
^{1}H NMR spectra of compound **1d** ($CDCl_3$, 400 MHz)



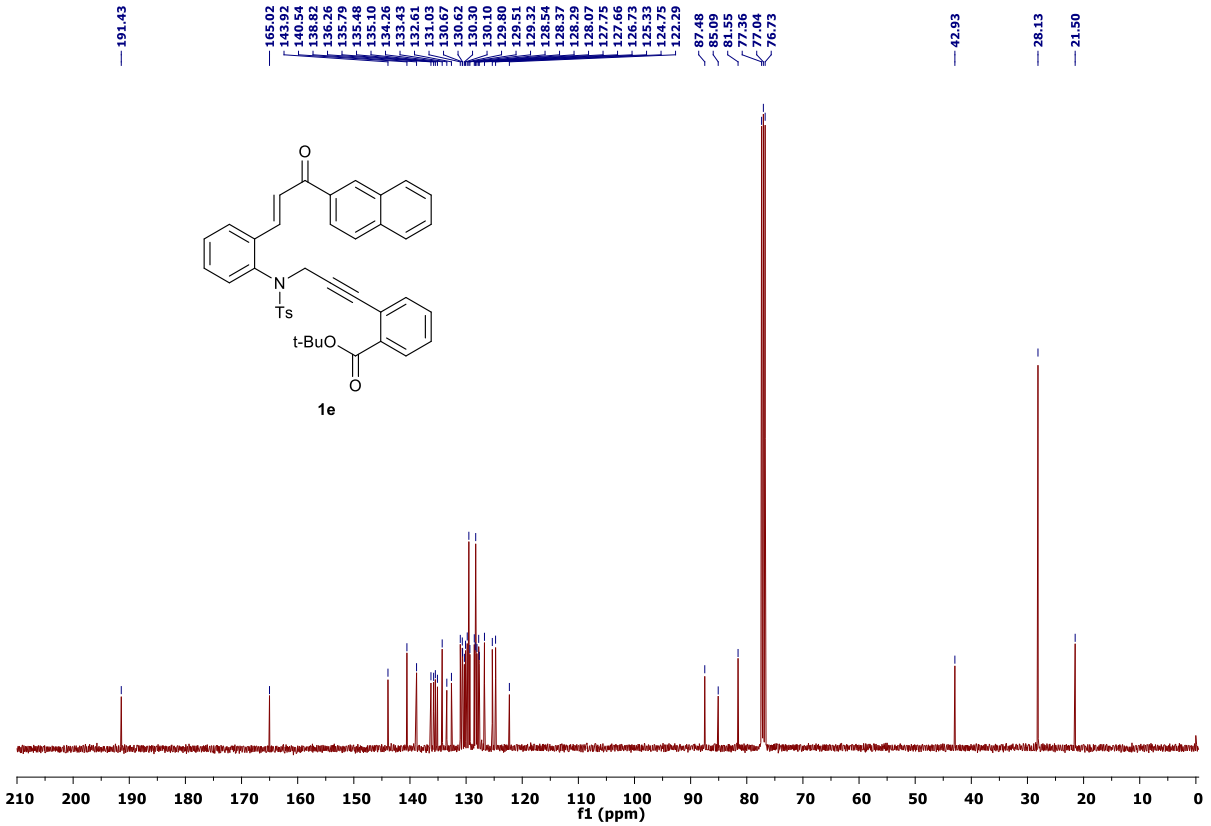
^{13}C{^{1}H} NMR spectra of compound **1d** ($CDCl_3$, 101 MHz)



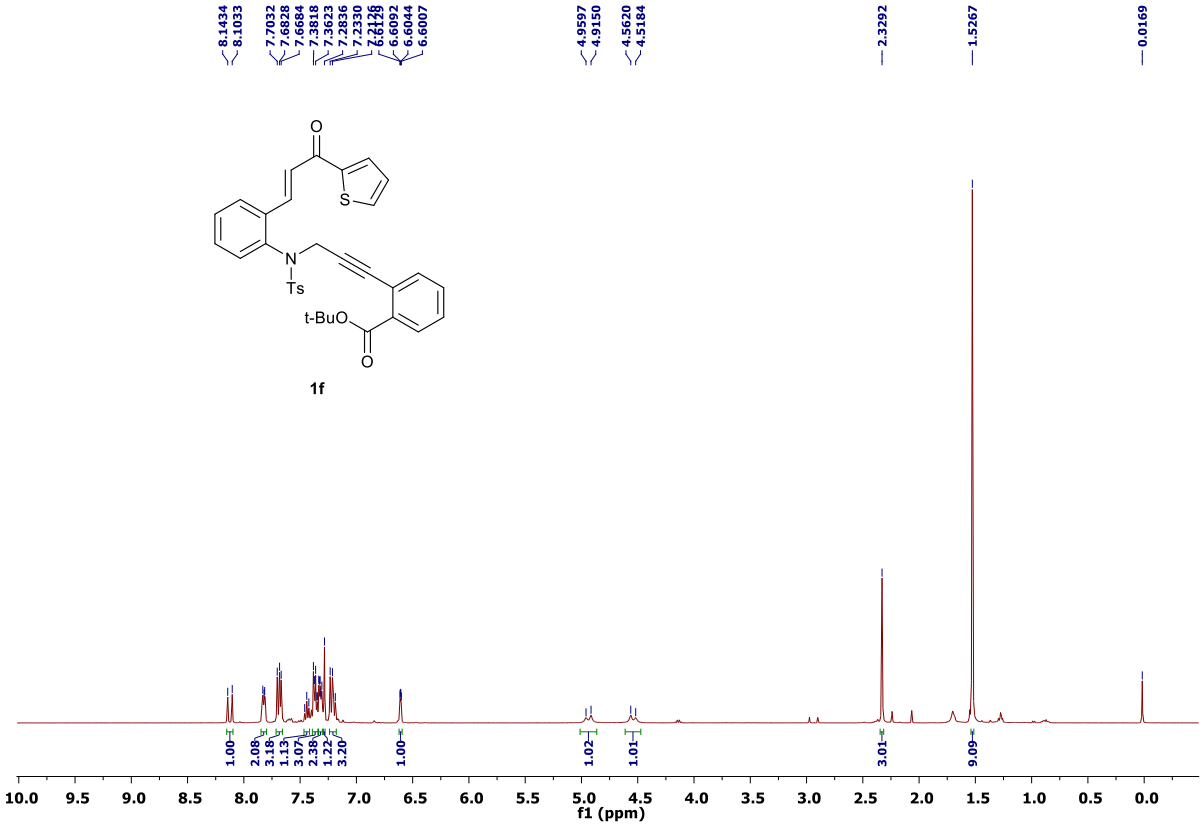
^{1}H NMR spectra of compound **1e** ($CDCl_3$, 400 MHz)



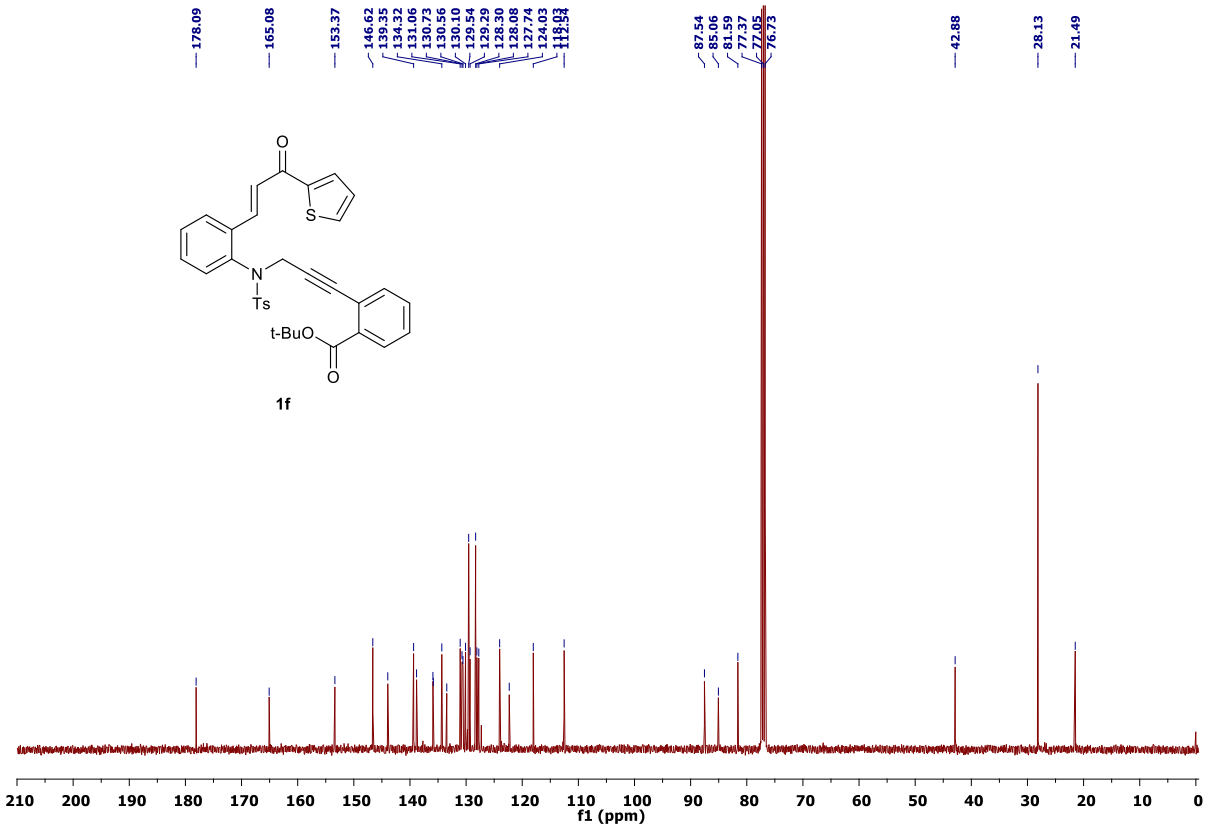
^{13}C{^{1}H} NMR spectra of compound **1e** ($CDCl_3$, 101 MHz)



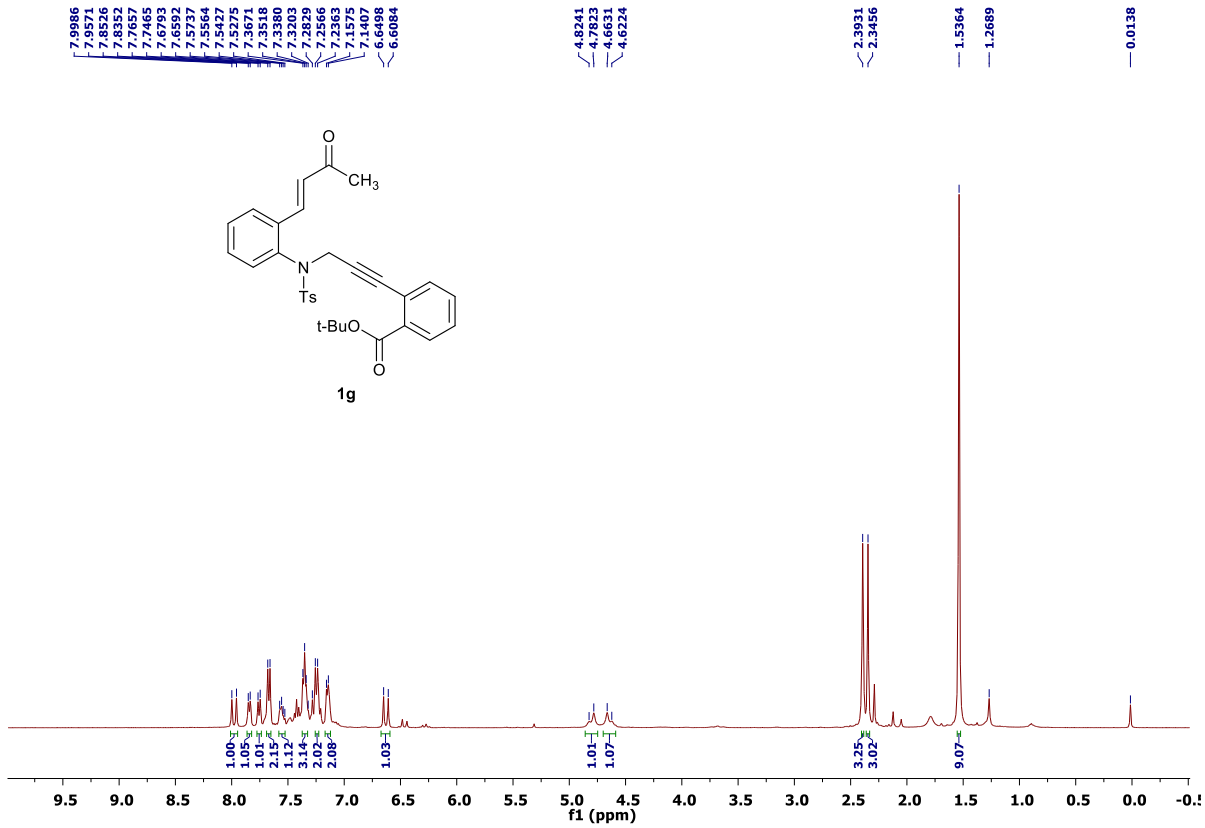
^{1}H NMR spectra of compound **1f** ($CDCl_3$, 400 MHz)



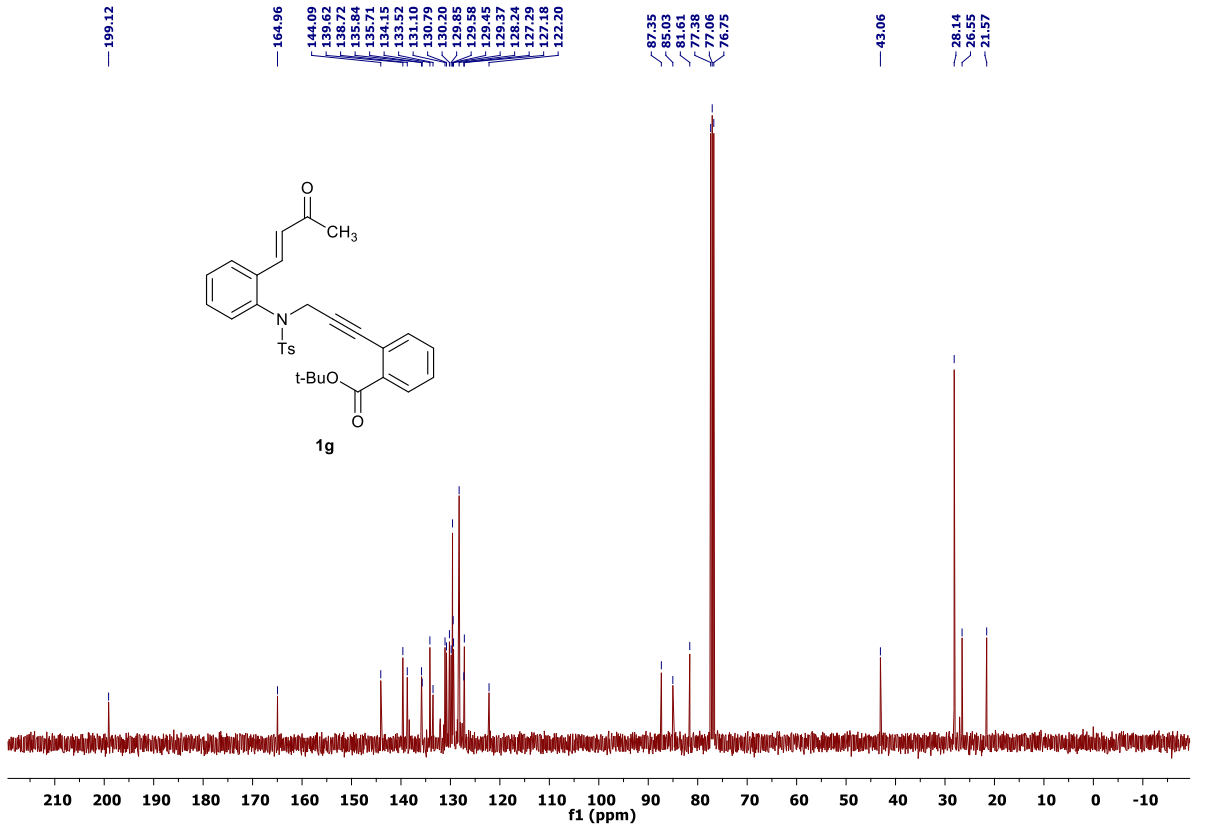
^{13}C{^{1}H} NMR spectra of compound **1f** ($CDCl_3$, 101 MHz)



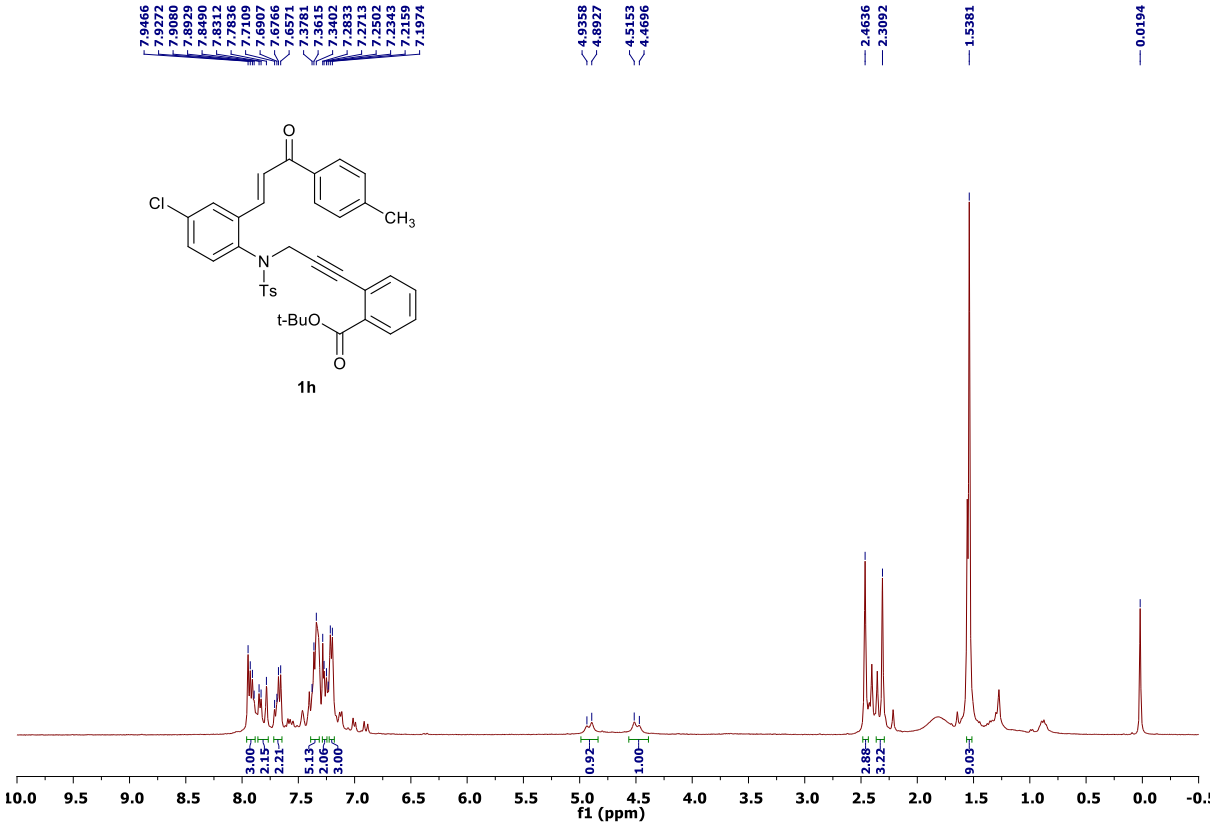
^{1}H NMR spectra of compound **1g** ($CDCl_3$, 400 MHz)



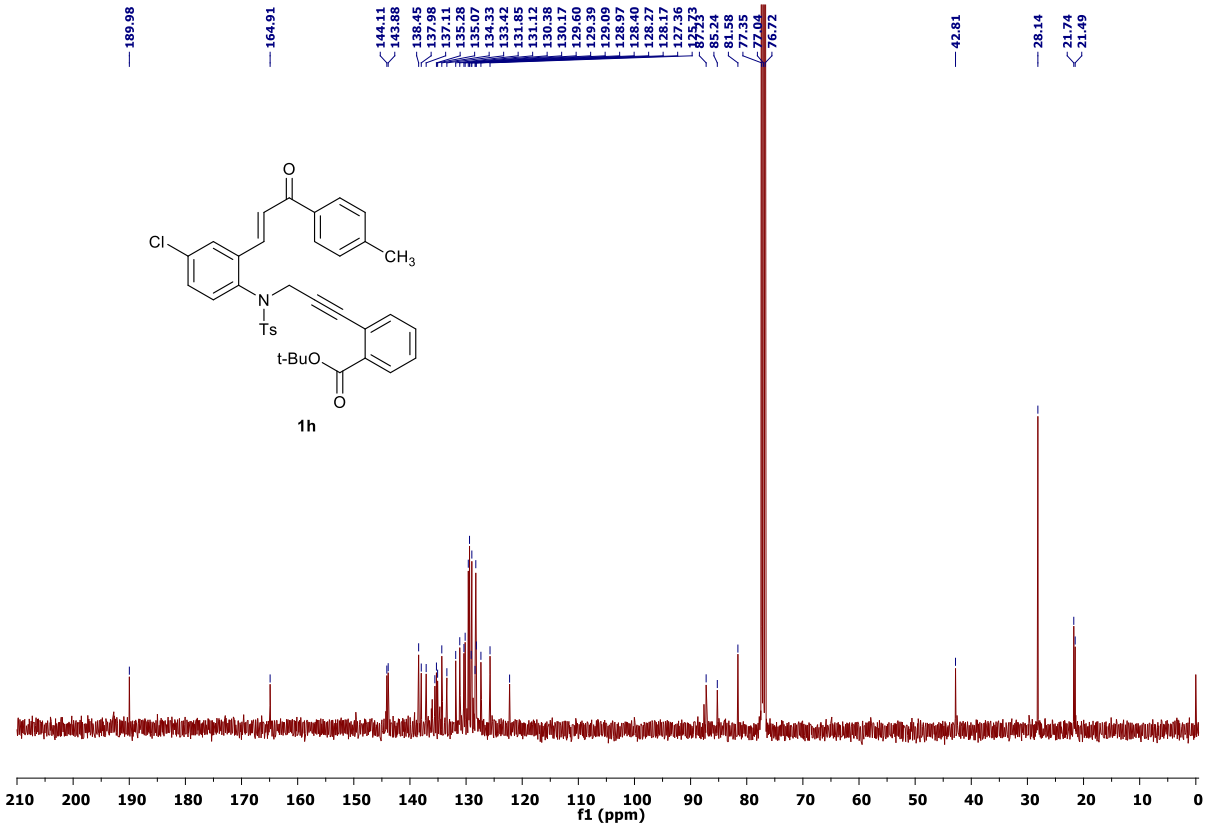
^{13}C{^{1}H} NMR spectra of compound **1g** ($CDCl_3$, 101 MHz)



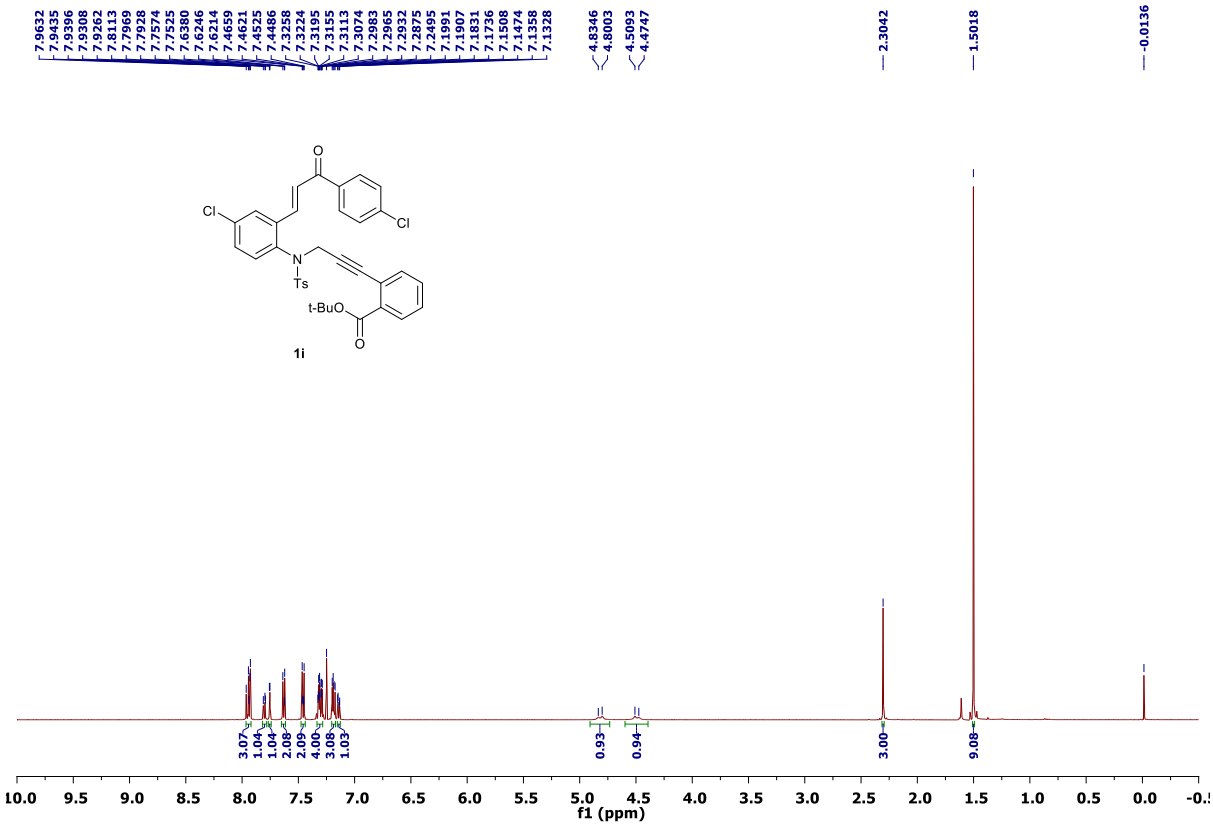
^{1}H NMR spectra of compound **1h** ($CDCl_3$, 400 MHz)



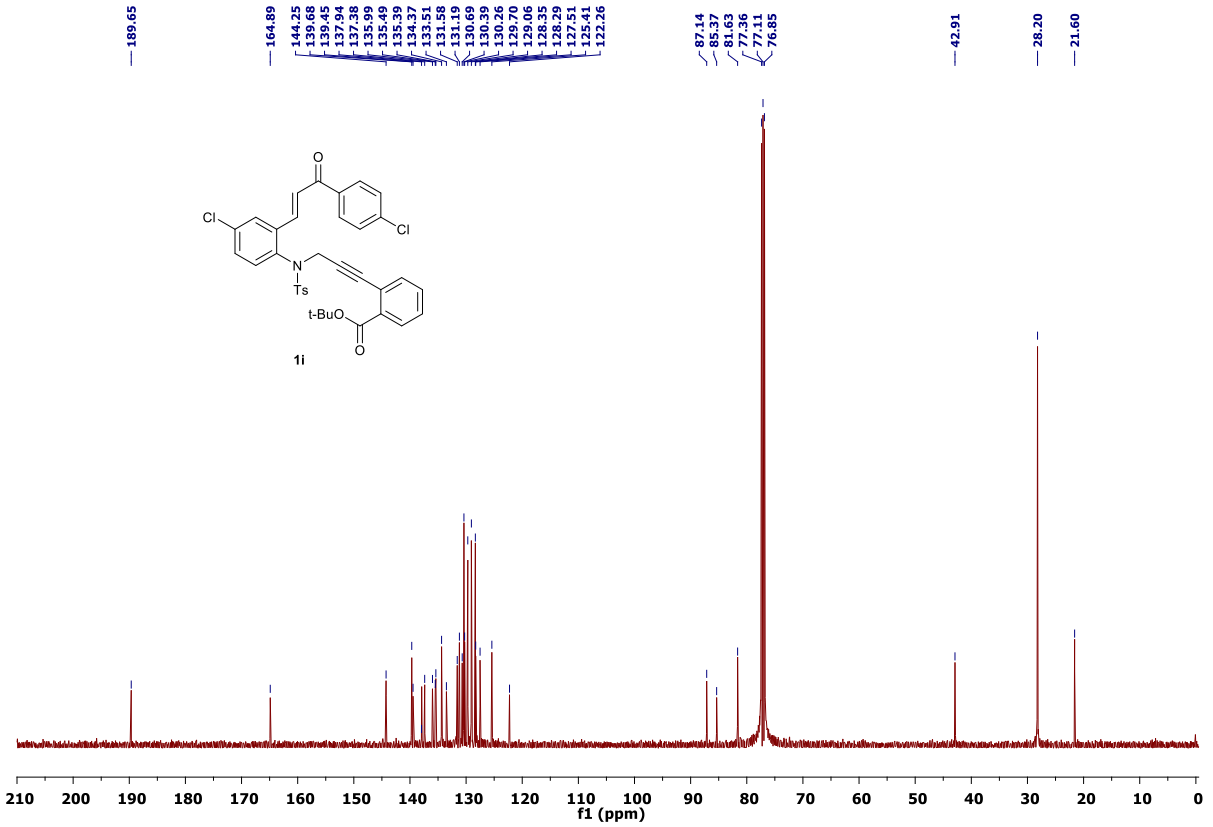
^{13}C{^{1}H} NMR spectra of compound **1h** ($CDCl_3$, 101 MHz)



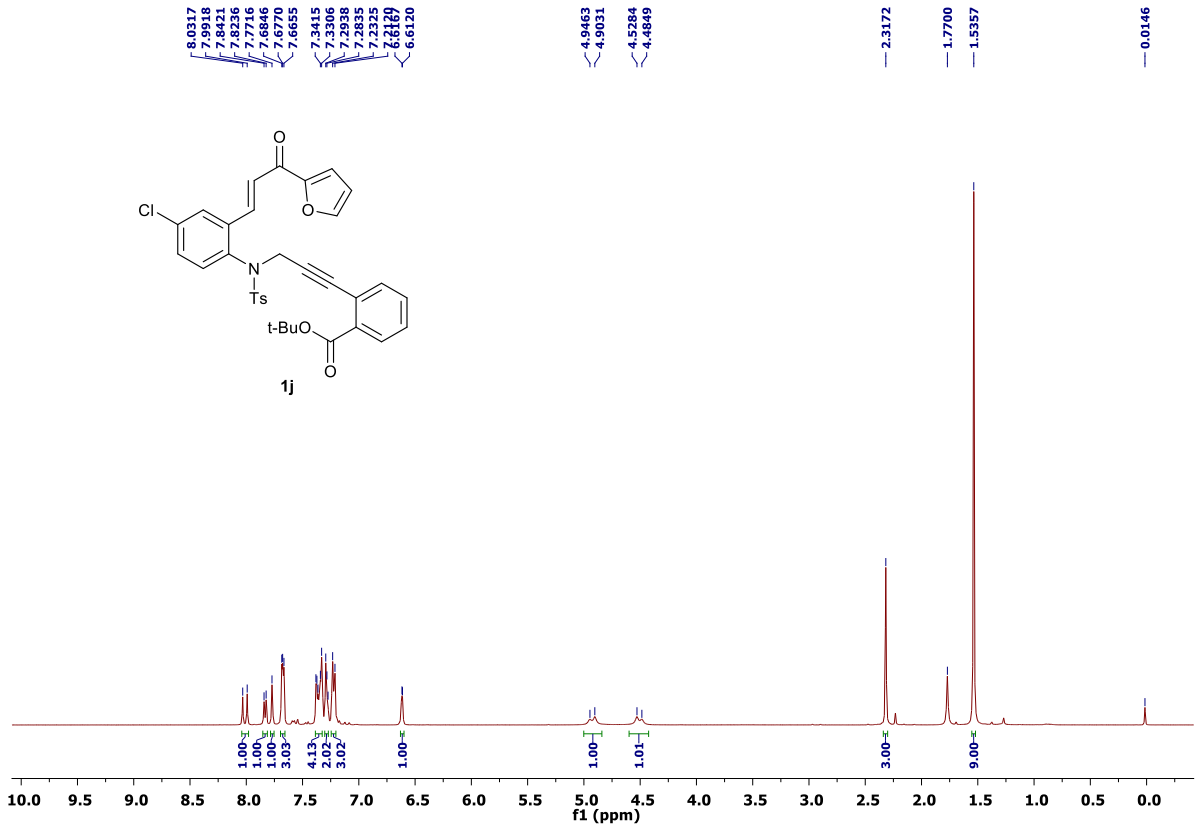
^{1}H NMR spectra of compound **1i** ($CDCl_3$, 500 MHz)



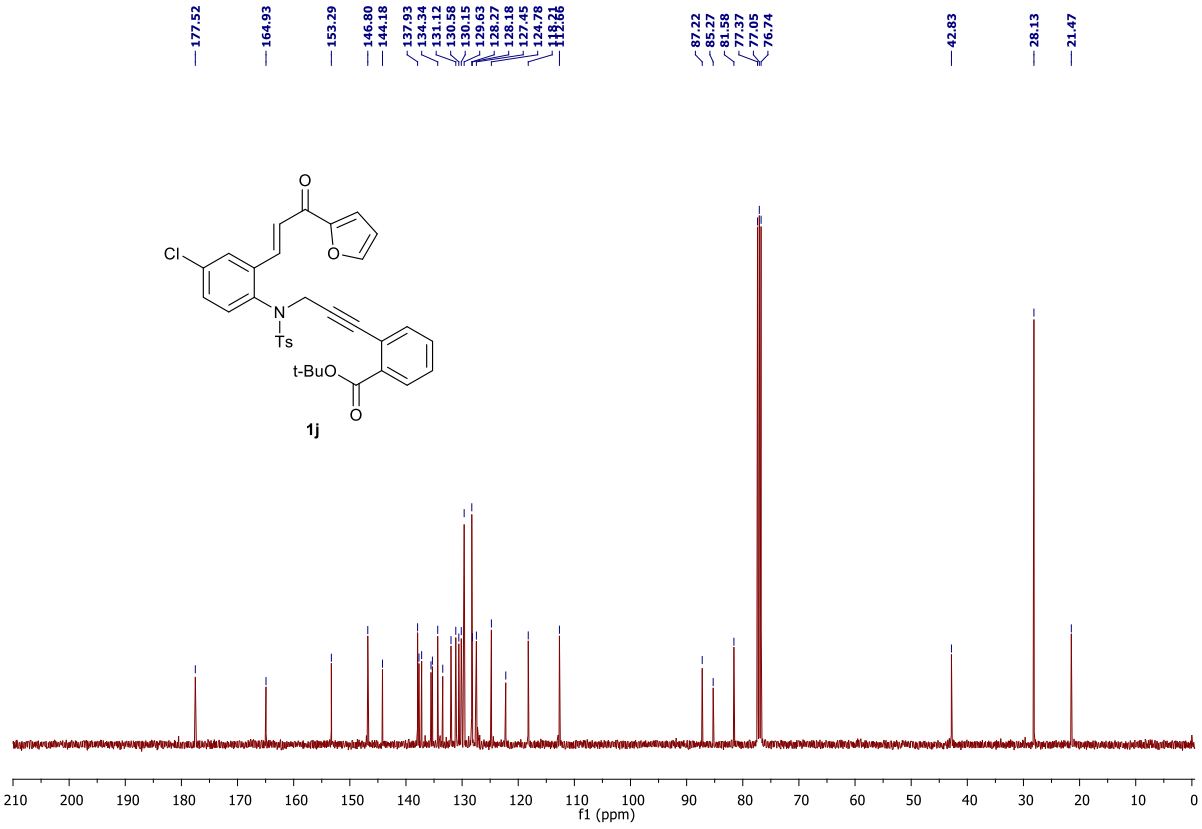
^{13}C{^{1}H} NMR spectra of compound **1i** ($CDCl_3$, 126 MHz)



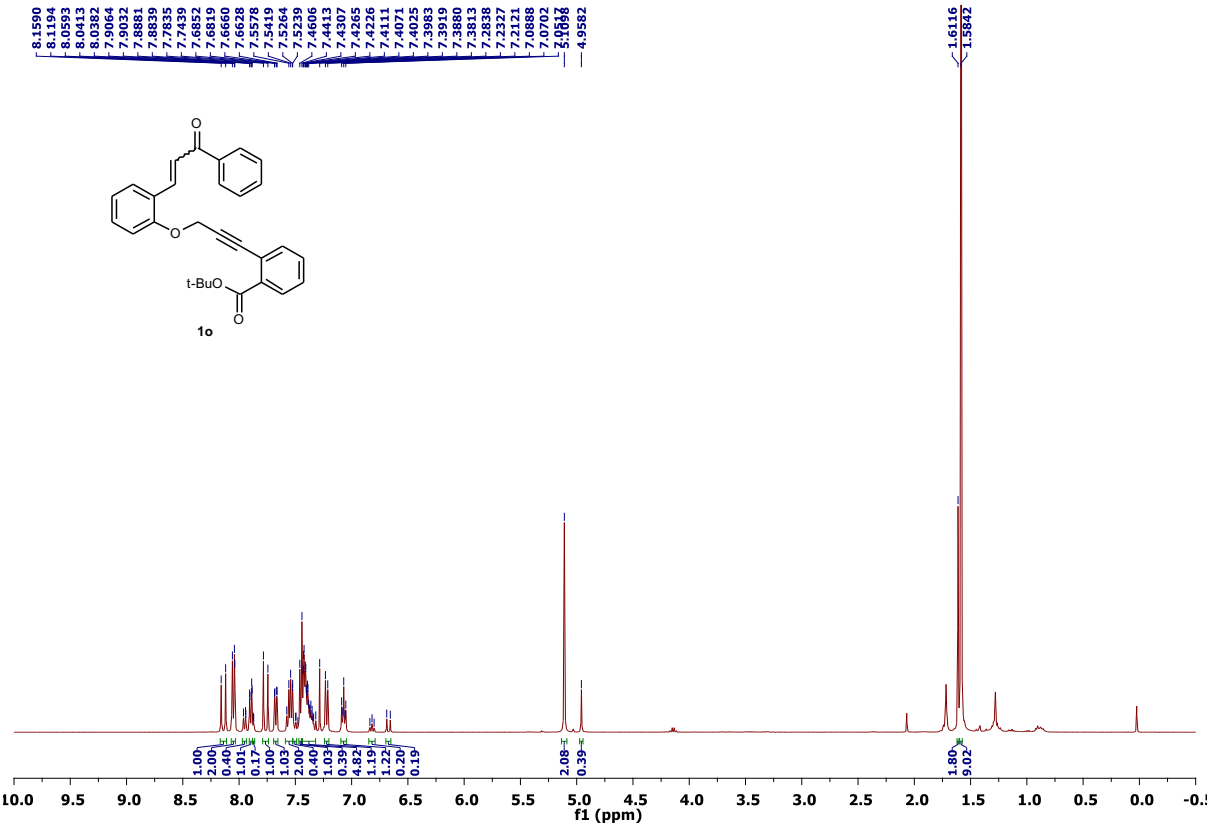
^{1}H NMR spectra of compound **1j** ($CDCl_3$, 400 MHz)



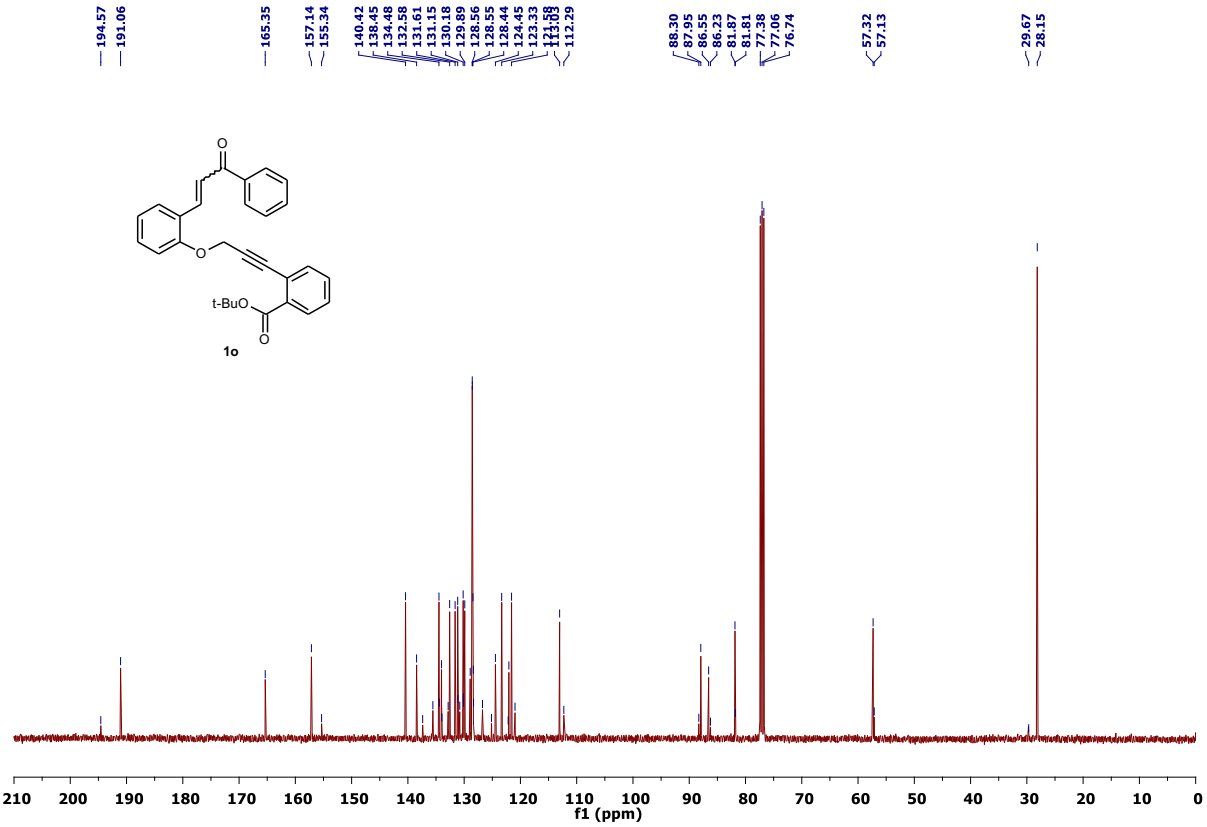
^{13}C{^{1}H} NMR spectra of compound **1j** ($CDCl_3$, 101 MHz)



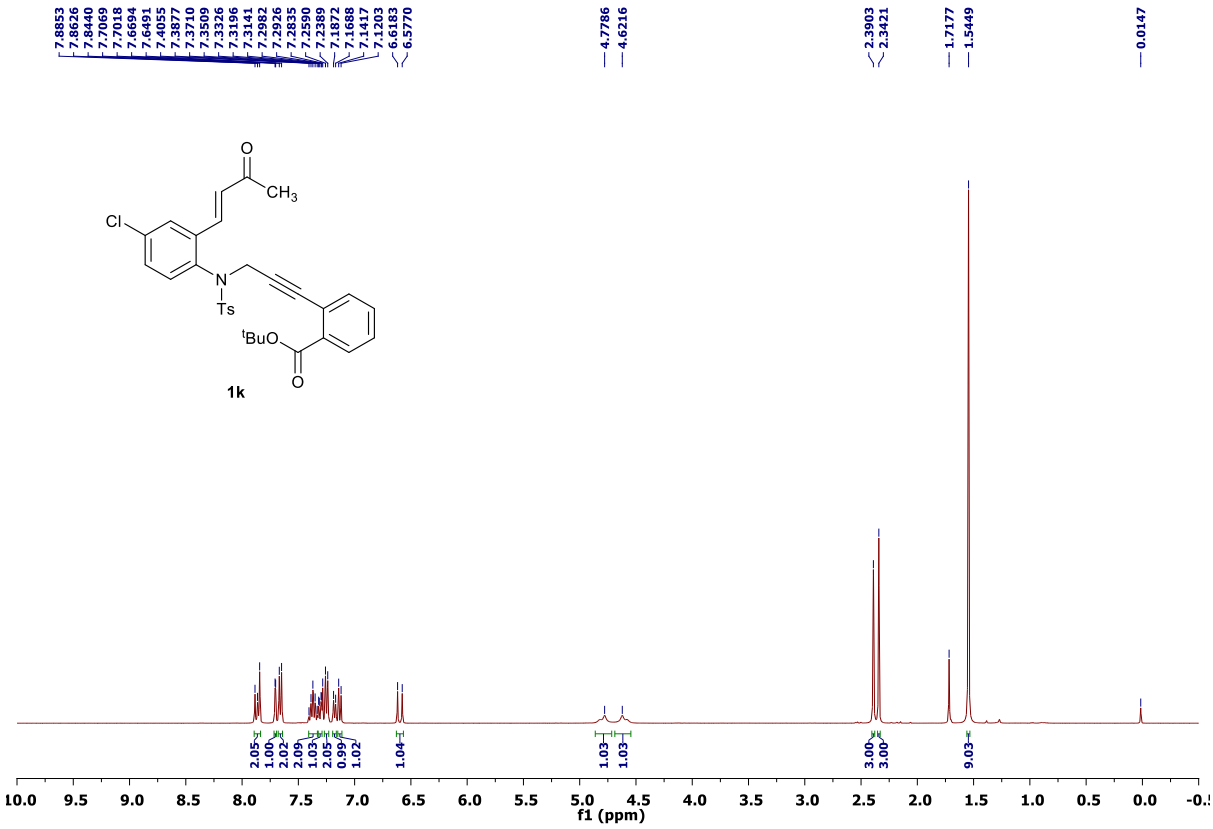
^{1}H NMR spectra of compound **1o** ($CDCl_3$, 400 MHz)



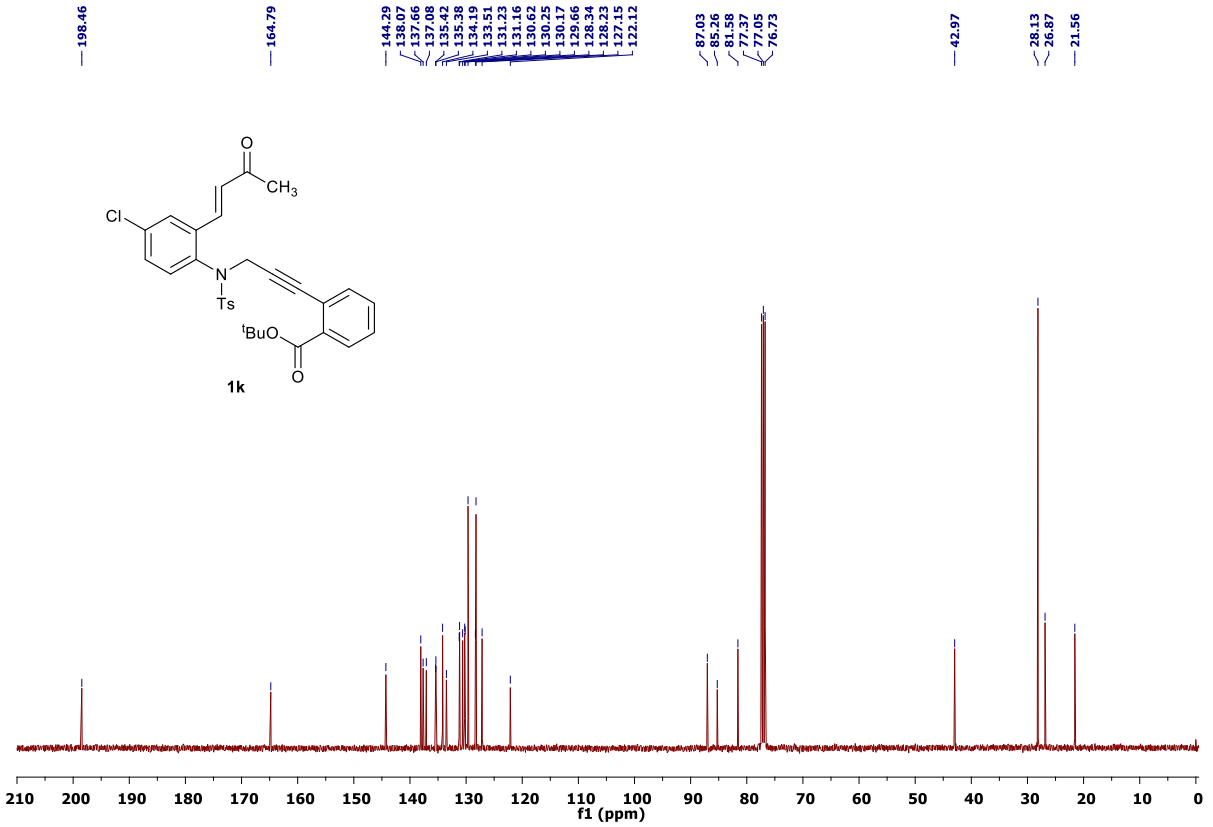
^{13}C{^{1}H} NMR spectra of compound **1o** ($CDCl_3$, 101 MHz)



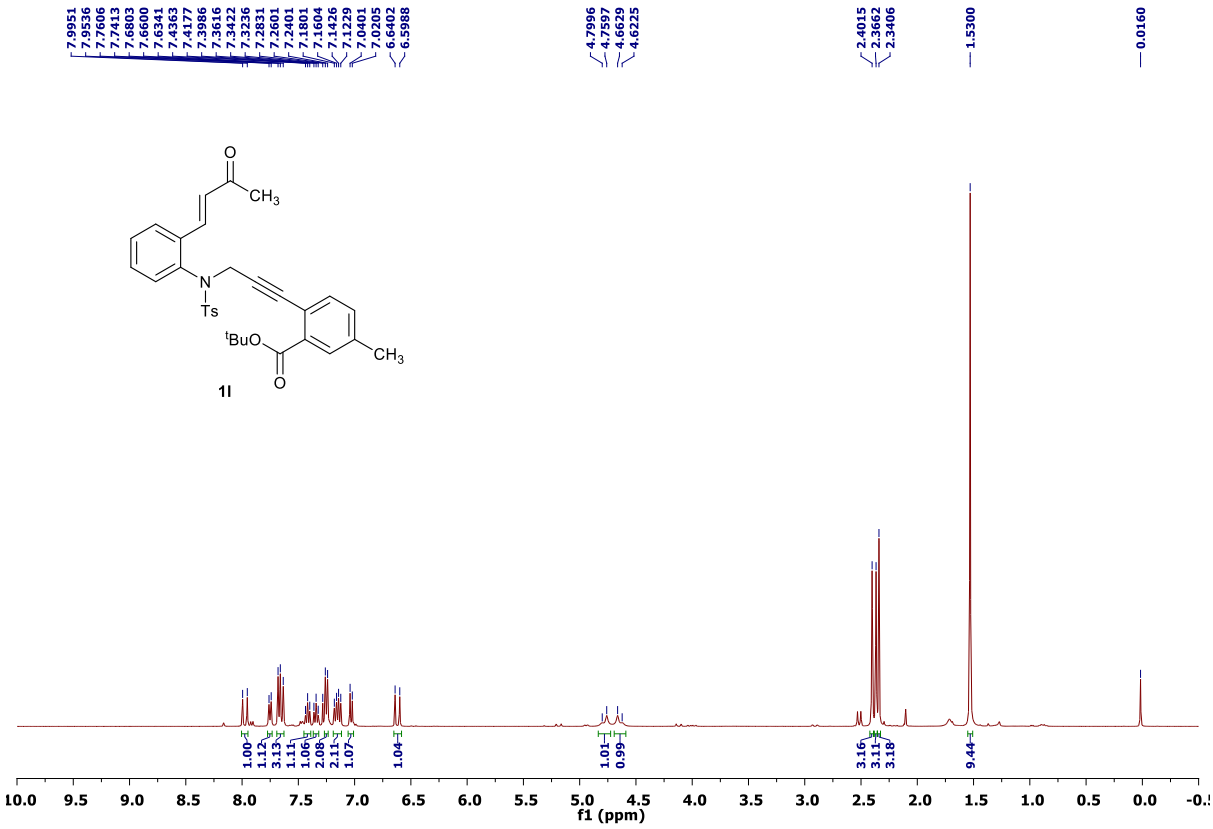
^{1}H NMR spectra of compound **1k** ($CDCl_3$, 400 MHz)



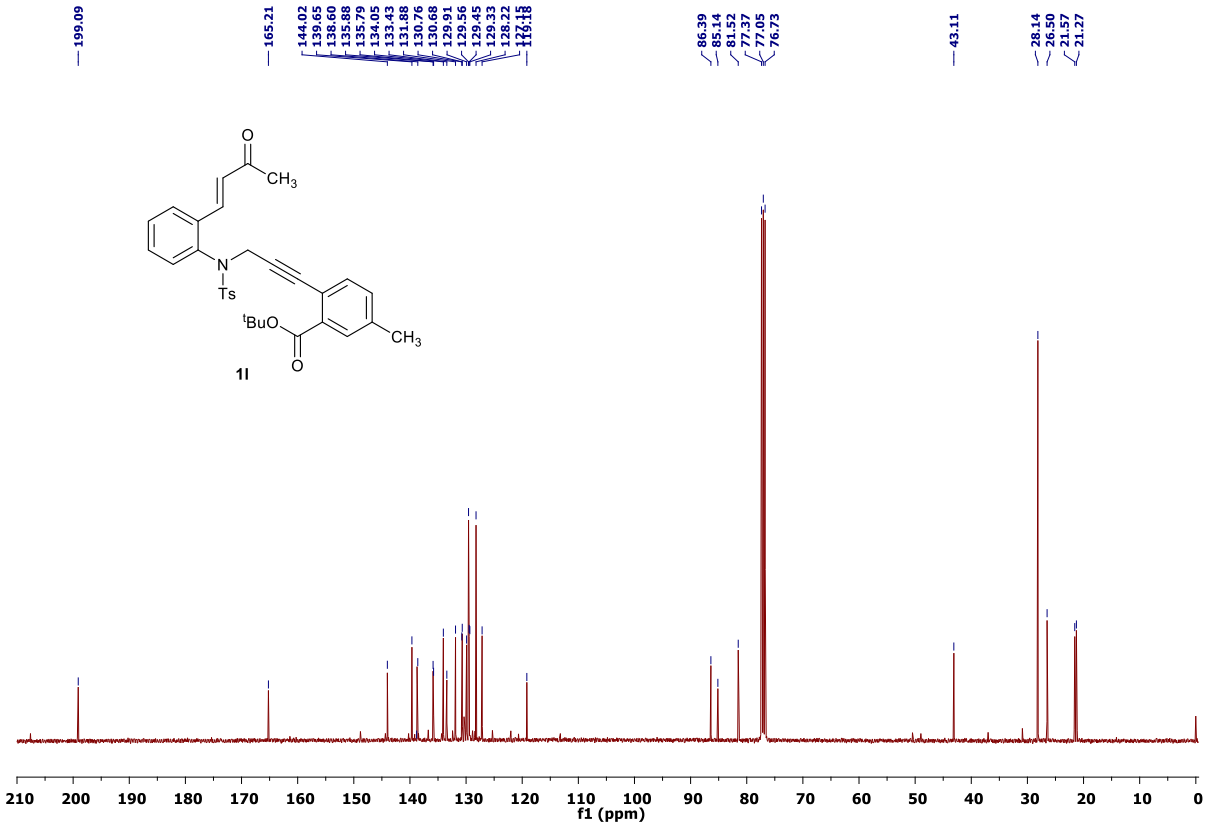
^{13}C{^{1}H} NMR spectra of compound **1k** ($CDCl_3$, 101 MHz)



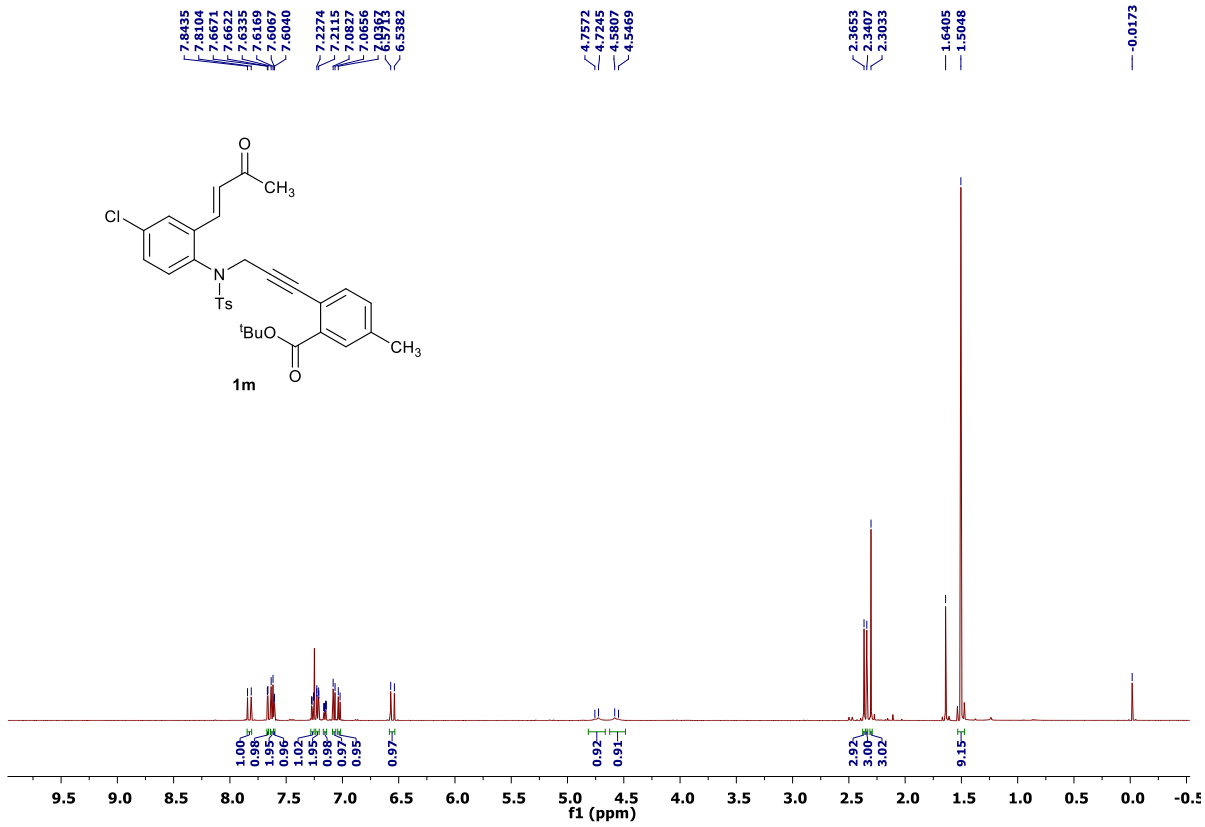
^{1}H NMR spectra of compound **1l** ($CDCl_3$, 400 MHz)



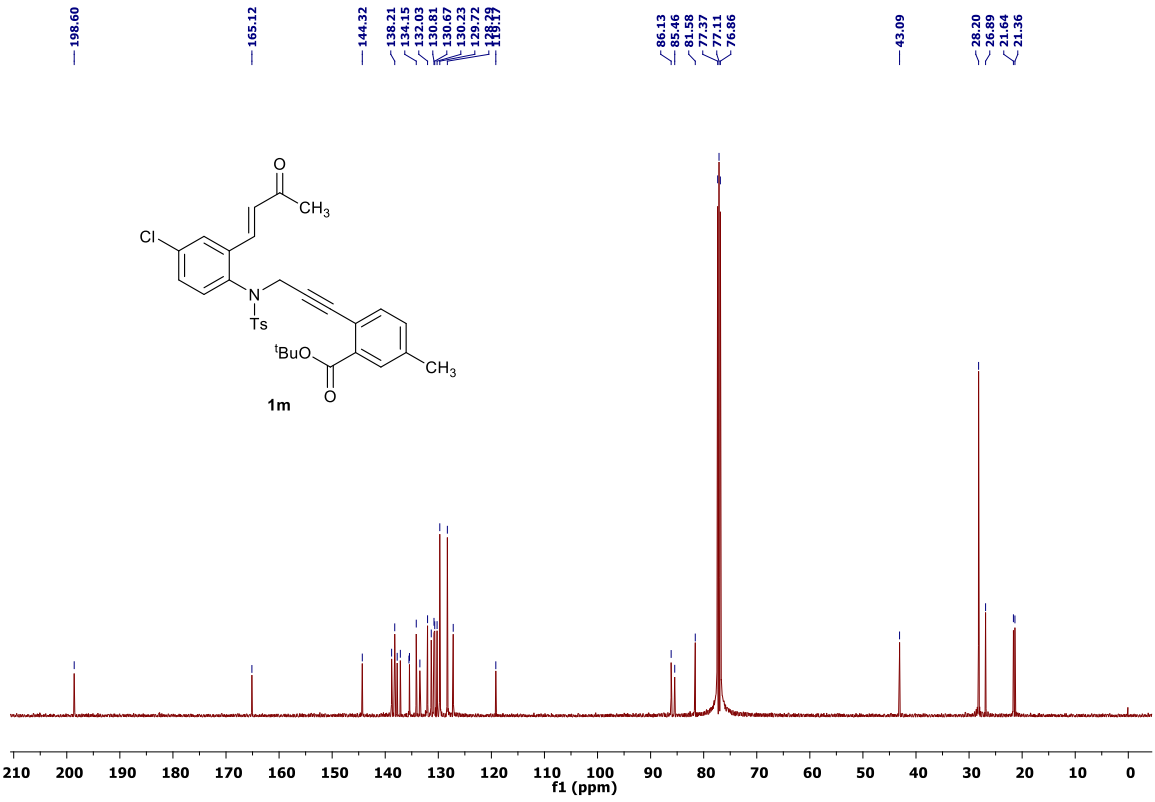
^{13}C{^{1}H} NMR spectra of compound **1l** ($CDCl_3$, 101 MHz)



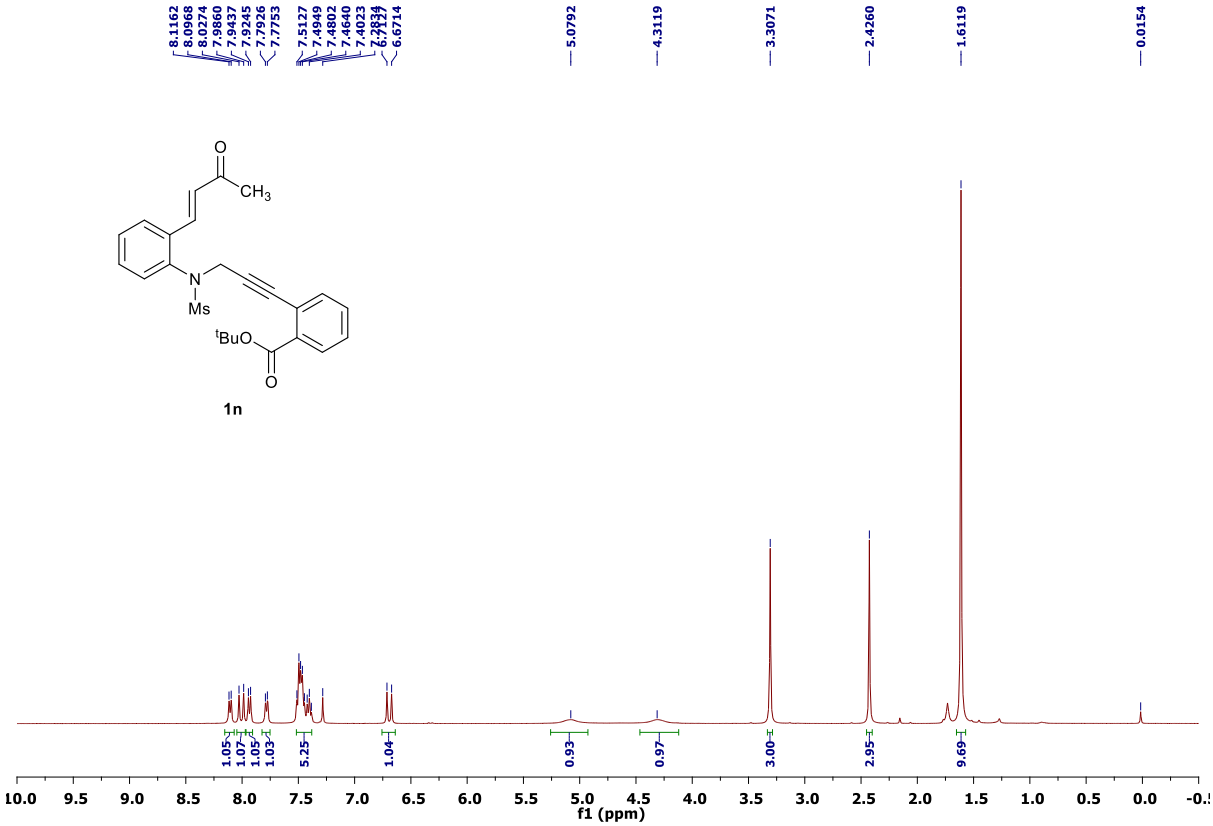
^{1}H NMR spectra of compound **1m** ($CDCl_3$, 500 MHz)



^{13}C{^{1}H} NMR spectra of compound **1m** ($CDCl_3$, 126 MHz)

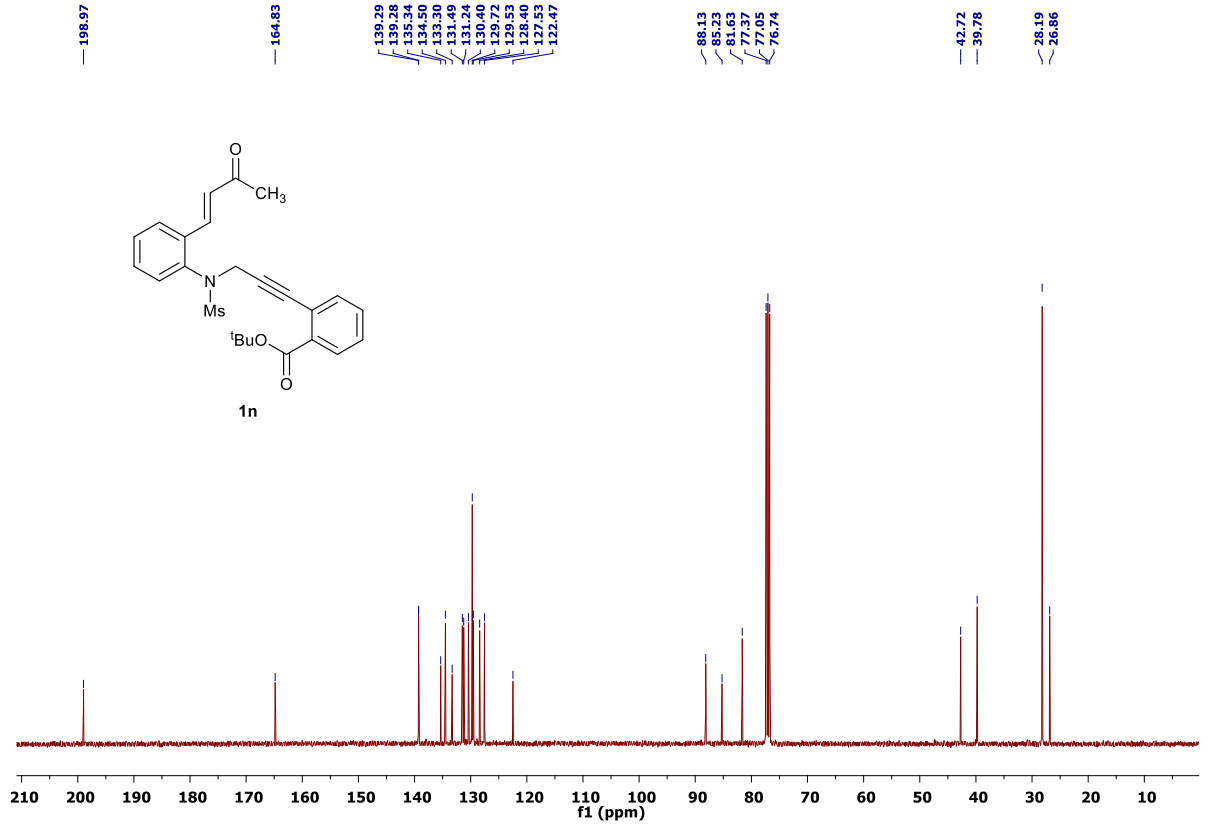


^{1}H NMR spectra of compound **1n** ($CDCl_3$, 400 MHz)



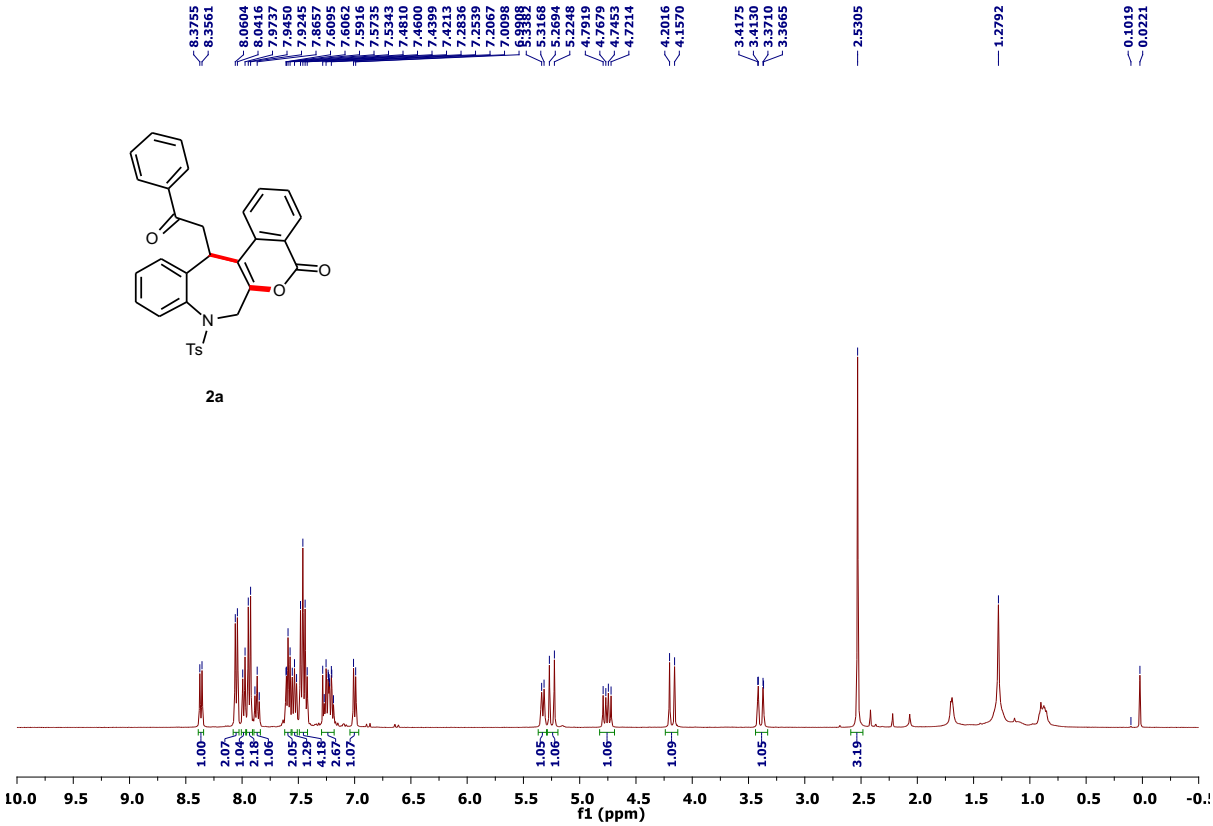
1n

^{13}C{^{1}H} NMR spectra of compound **1n** ($CDCl_3$, 101 MHz)

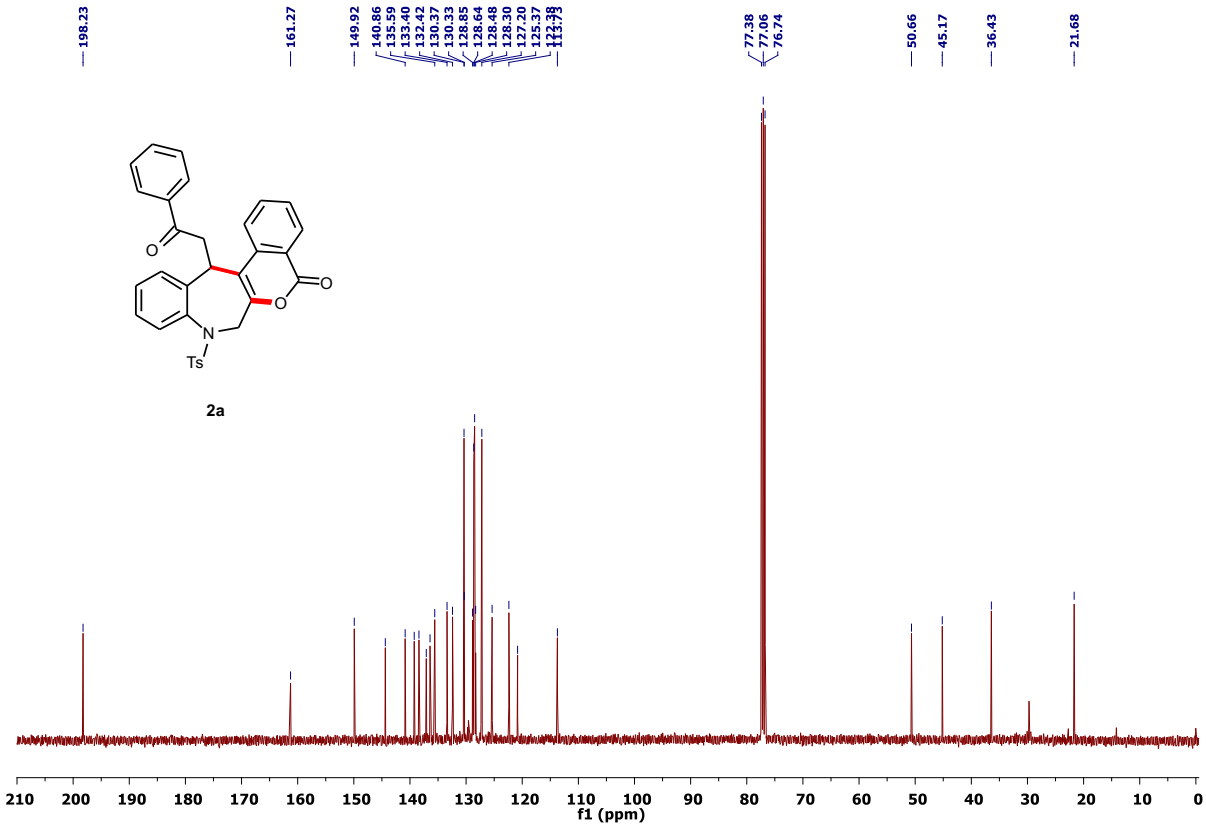


1n

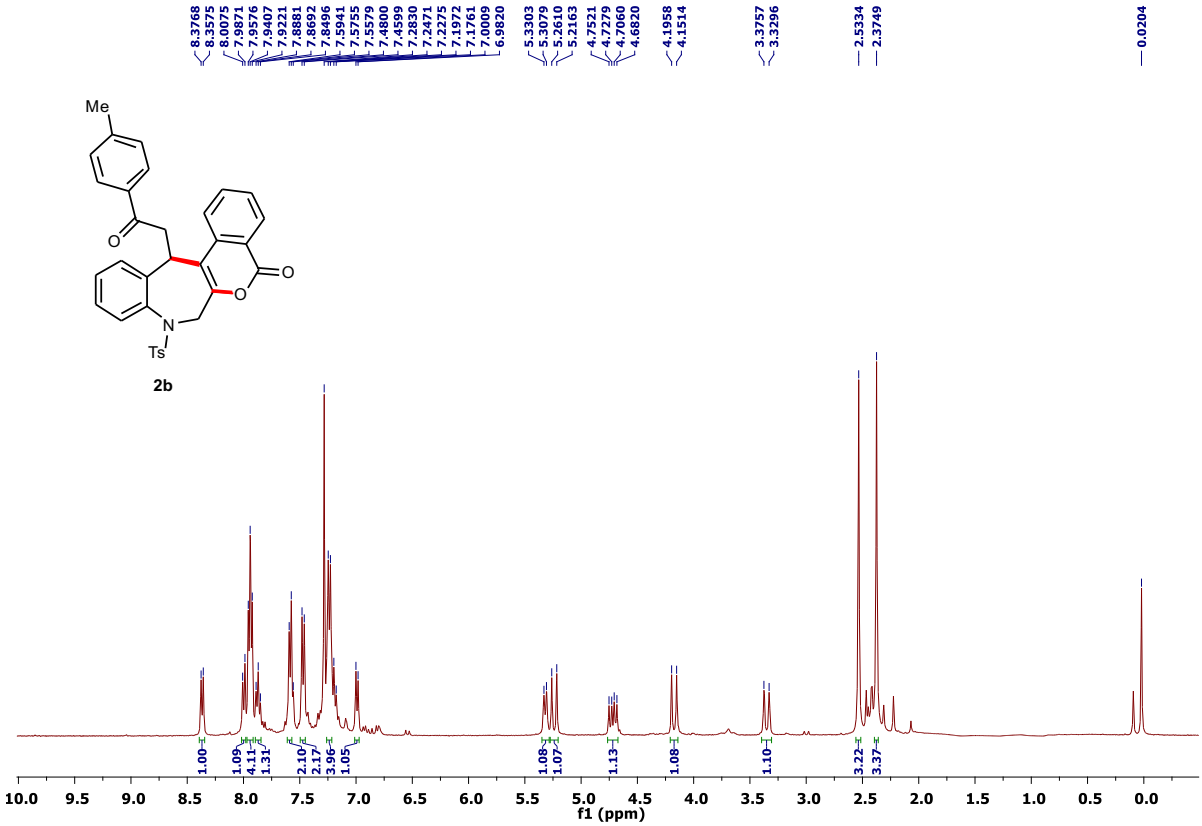
^{1}H NMR spectra of compound **2a** ($CDCl_3$, 400 MHz)



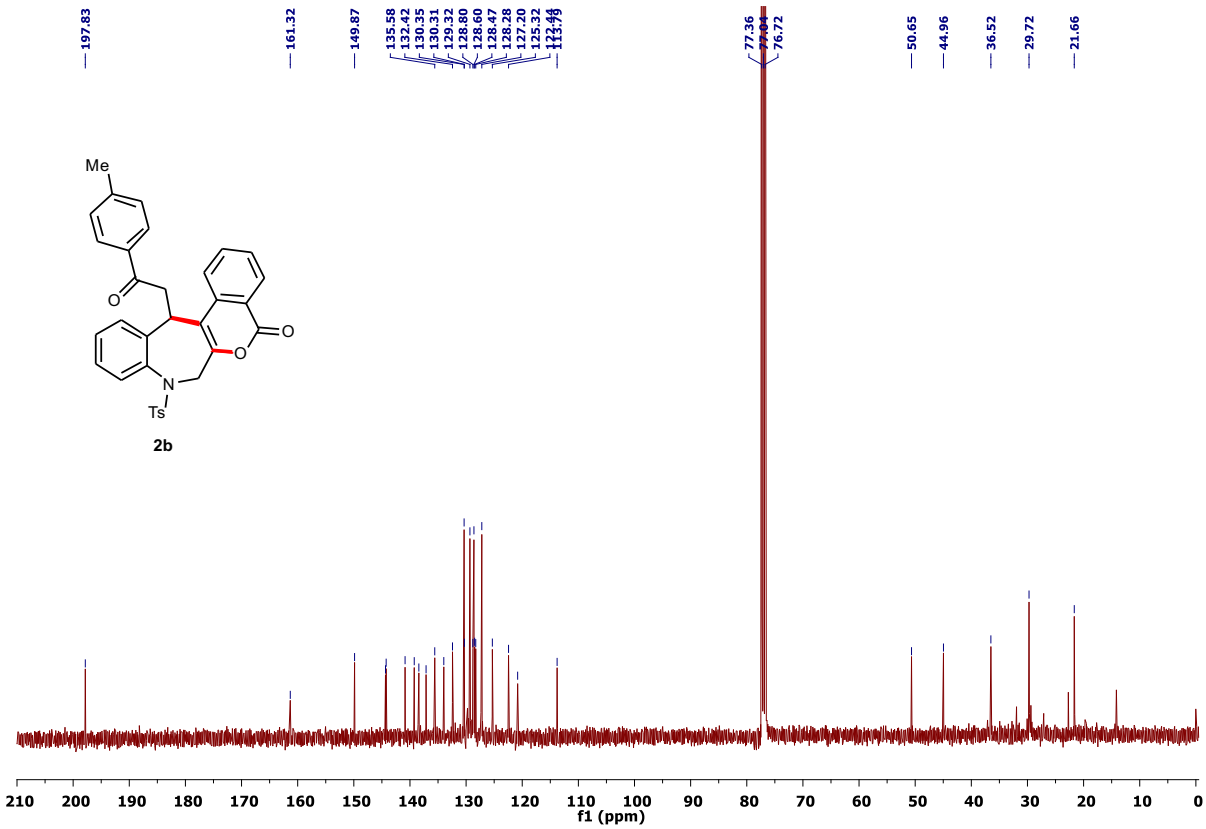
^{13}C{^{1}H} NMR spectra of compound **2a** ($CDCl_3$, 101 MHz)



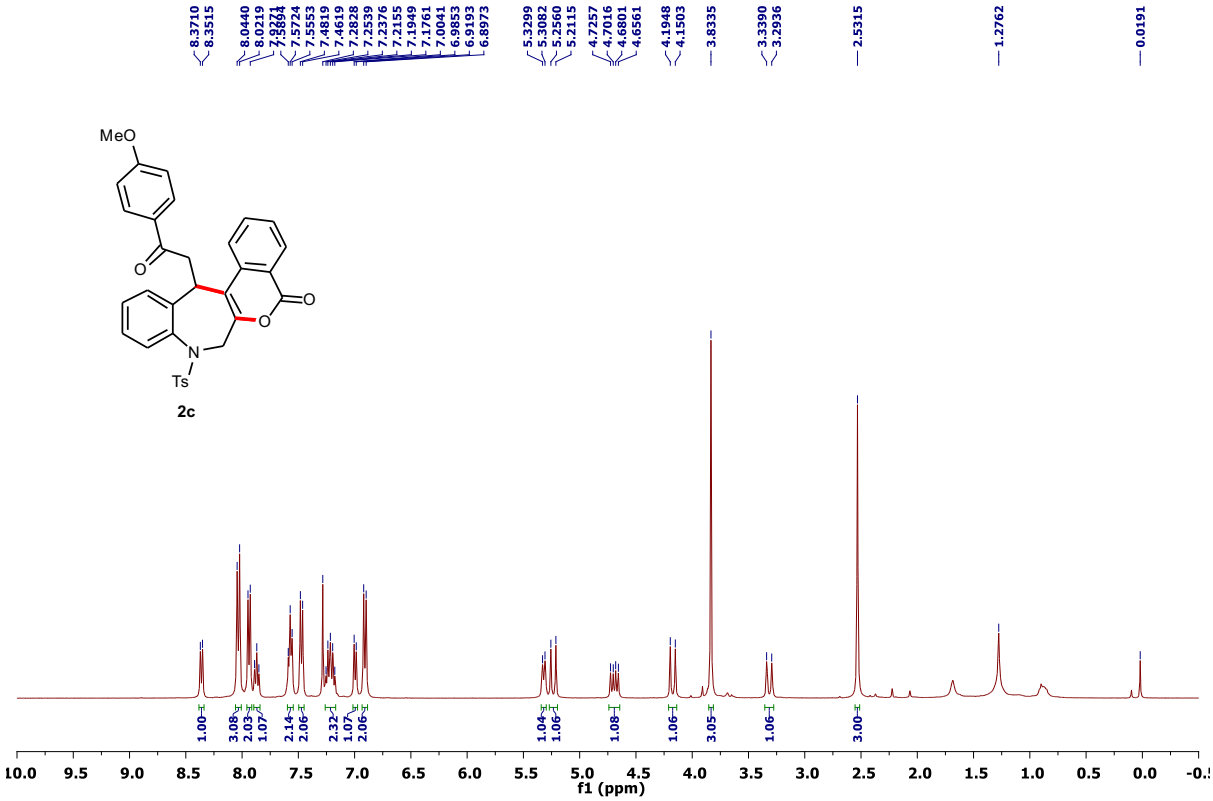
^{1}H NMR spectra of compound **2b** ($CDCl_3$, 400 MHz)



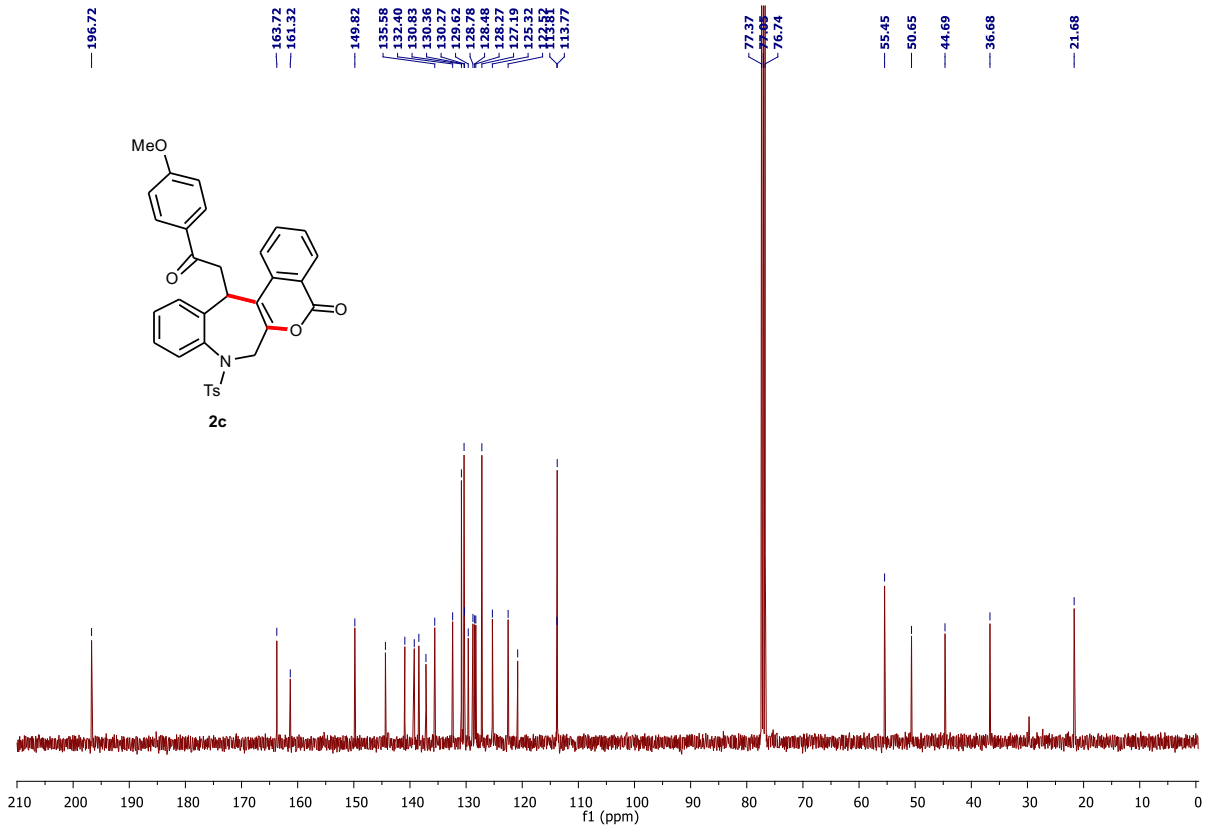
^{13}C{^{1}H} NMR spectra of compound **2b** ($CDCl_3$, 101 MHz)



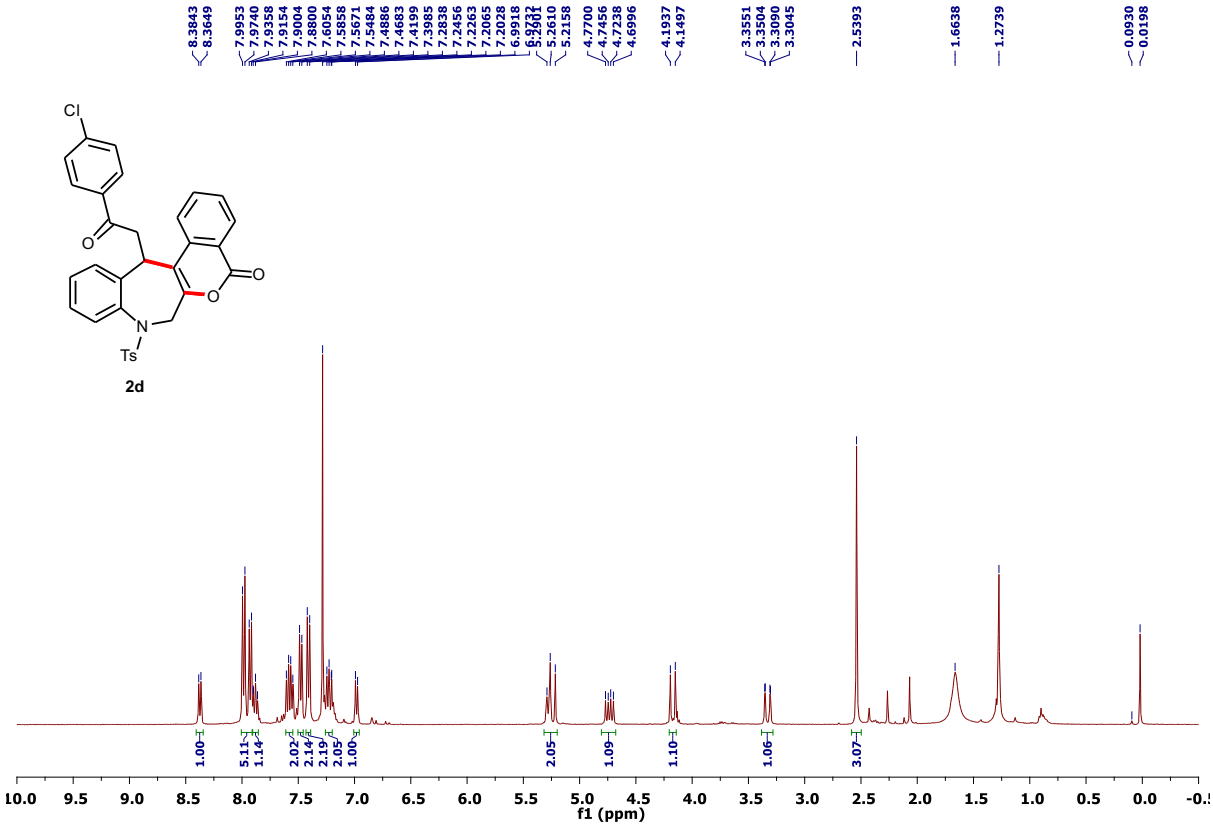
^{1}H NMR spectra of compound **2c** ($CDCl_3$, 400 MHz)



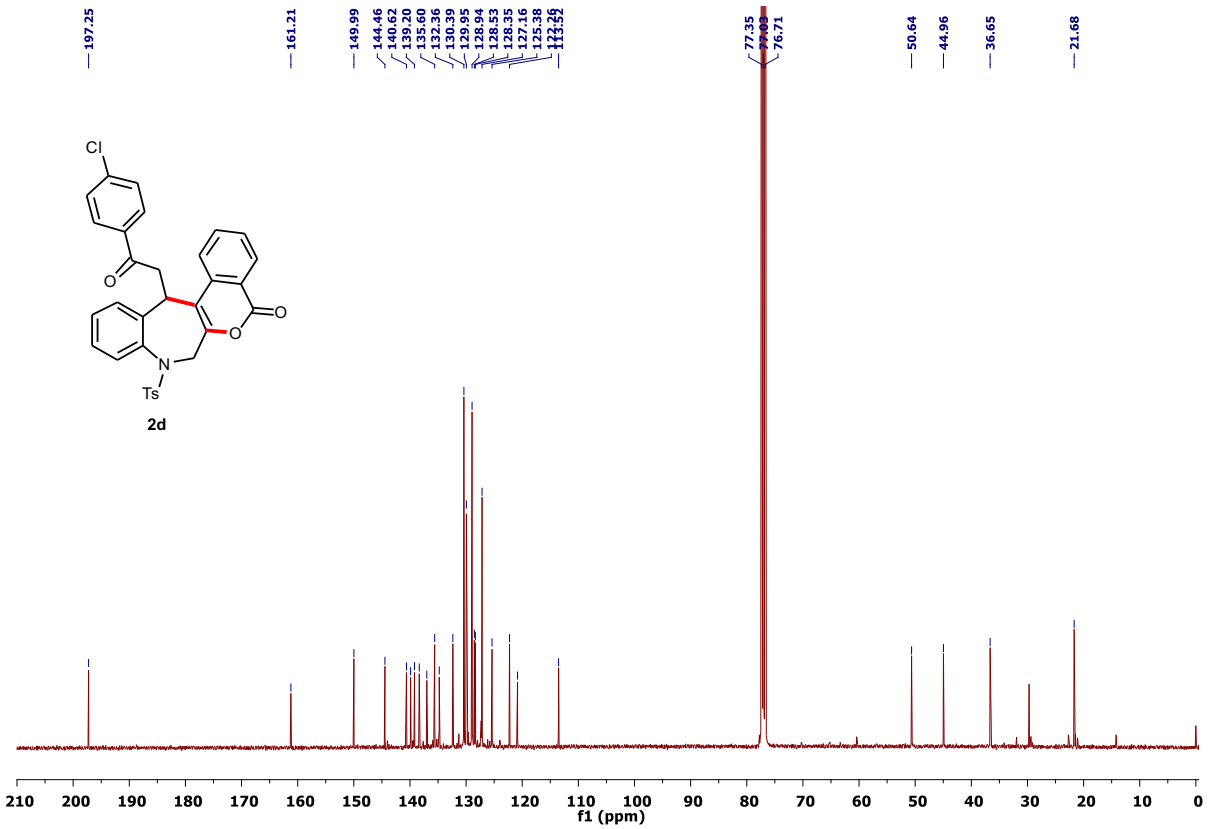
^{13}C{^{1}H} NMR spectra of compound **2c** ($CDCl_3$, 101 MHz)



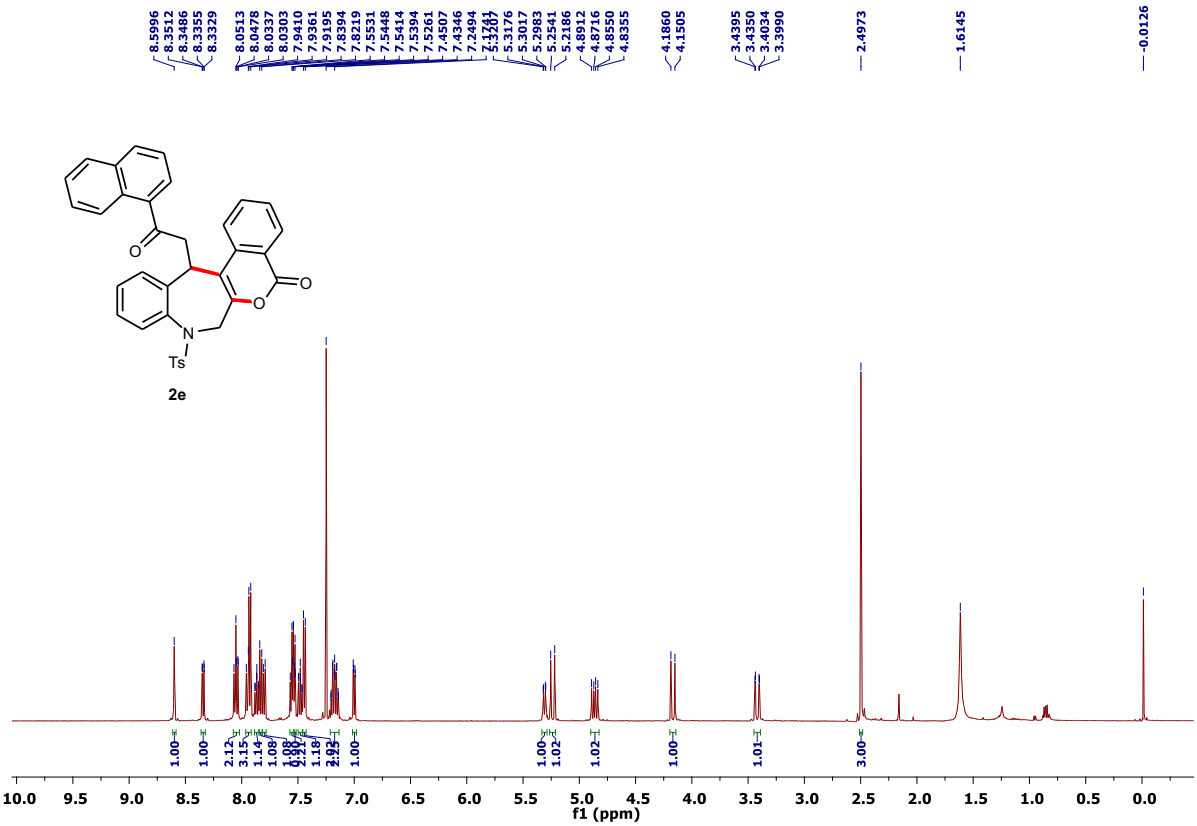
^{1}H NMR spectra of compound **2d** ($CDCl_3$, 400 MHz)



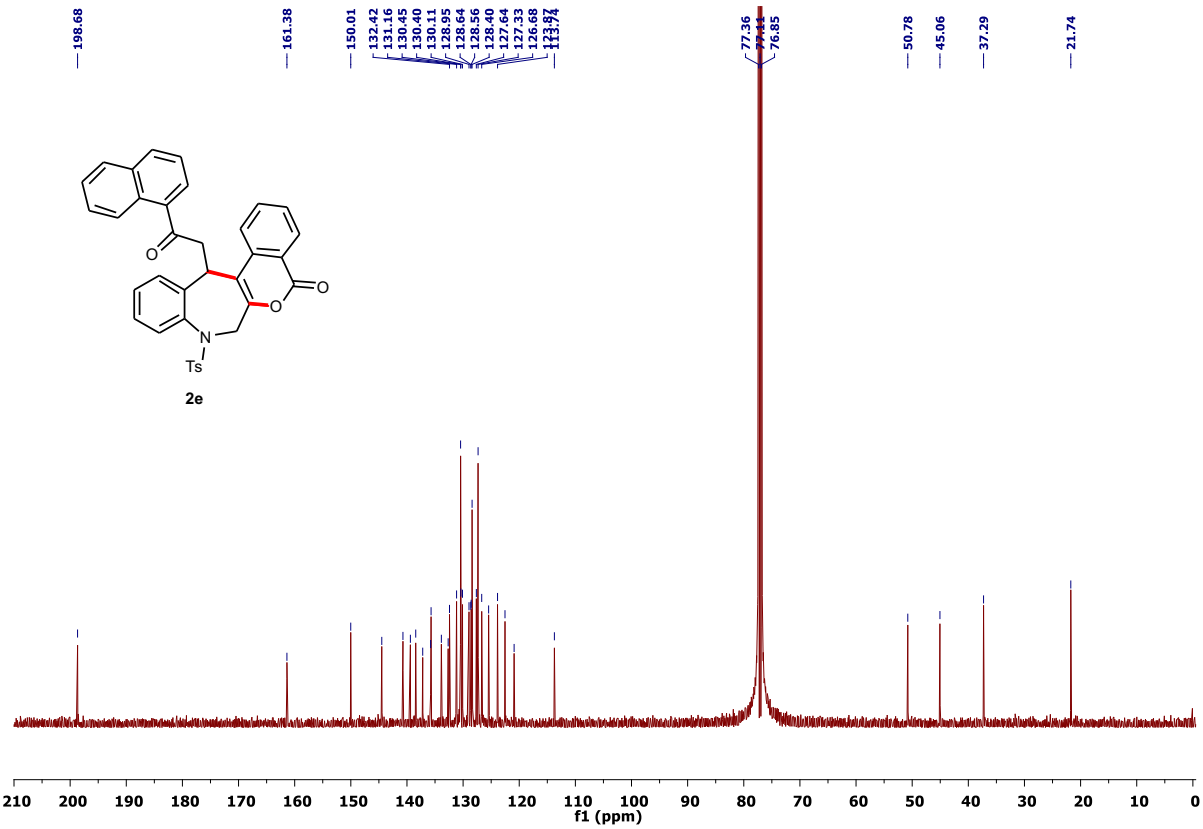
^{13}C{^{1}H} NMR spectra of compound **2d** ($CDCl_3$, 101 MHz)



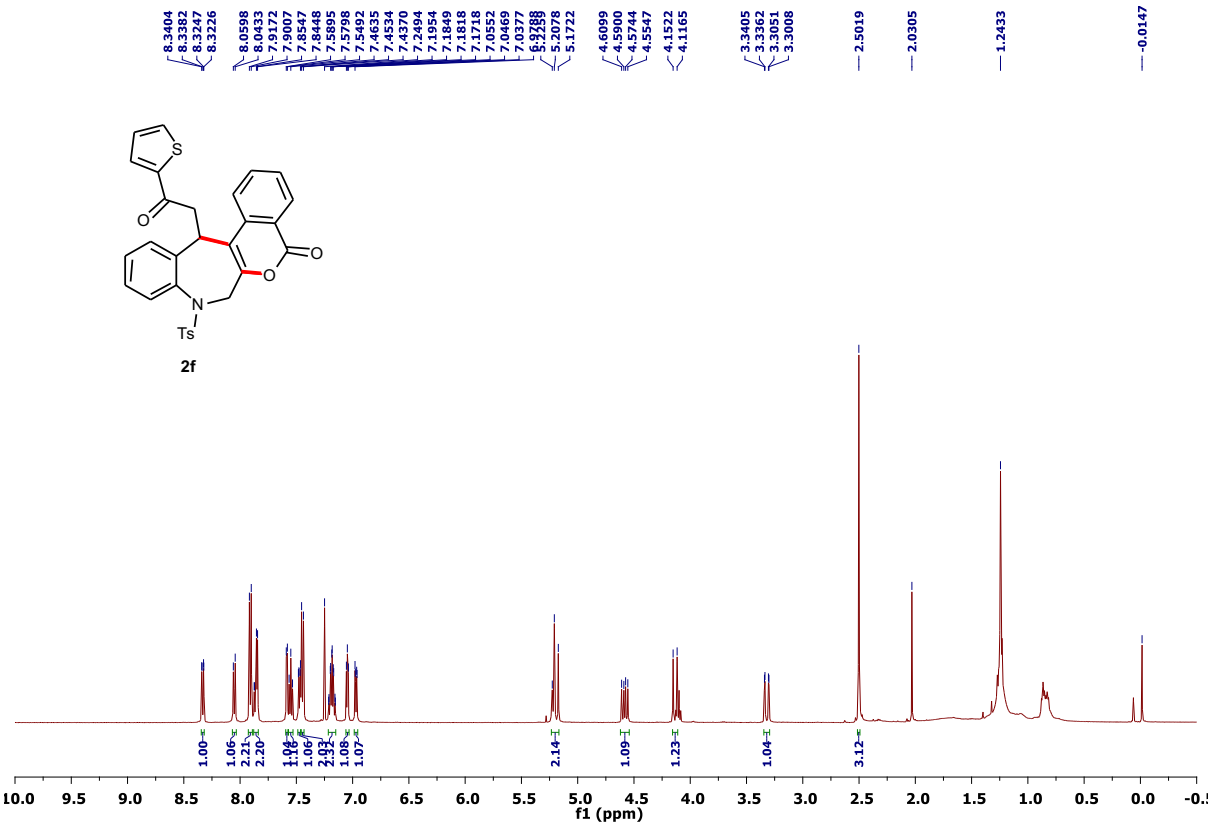
^{1}H NMR spectra of compound **2e** ($CDCl_3$, 500 MHz)



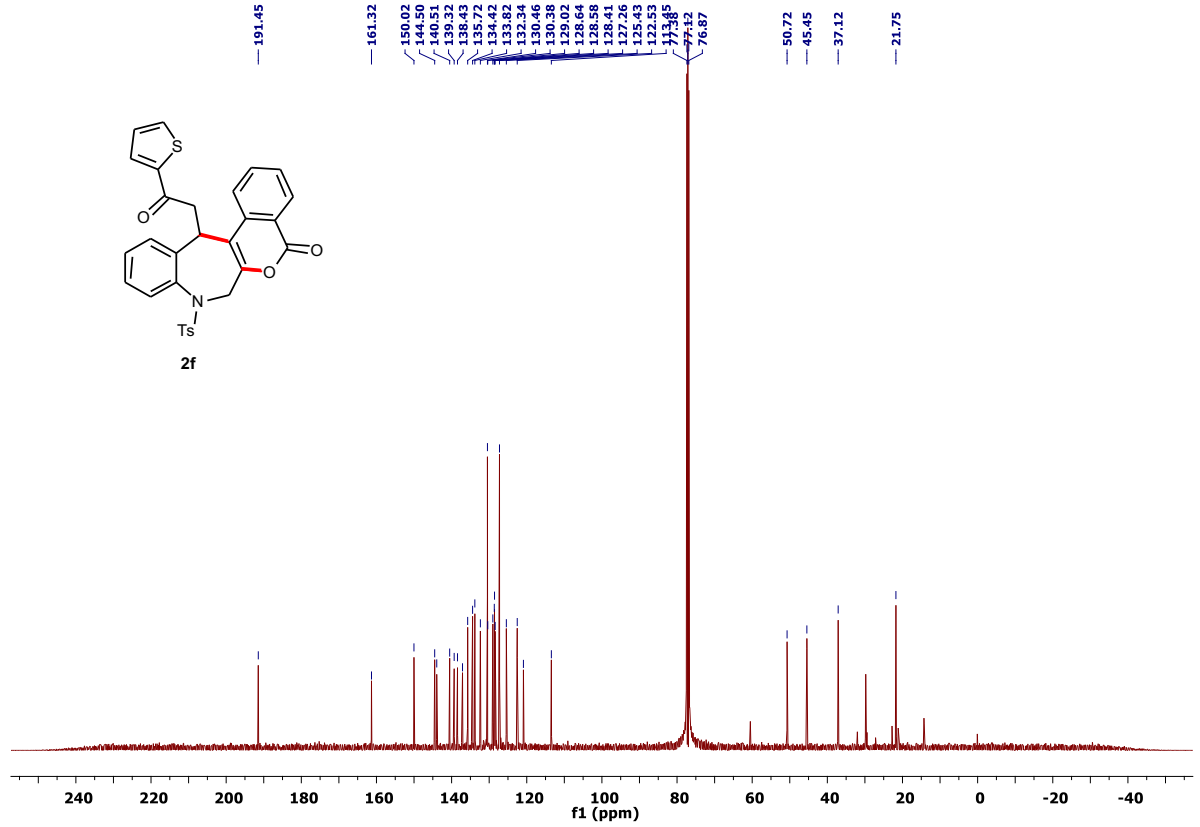
^{13}C{^{1}H} NMR spectra of compound **2e** ($CDCl_3$, 126 MHz)



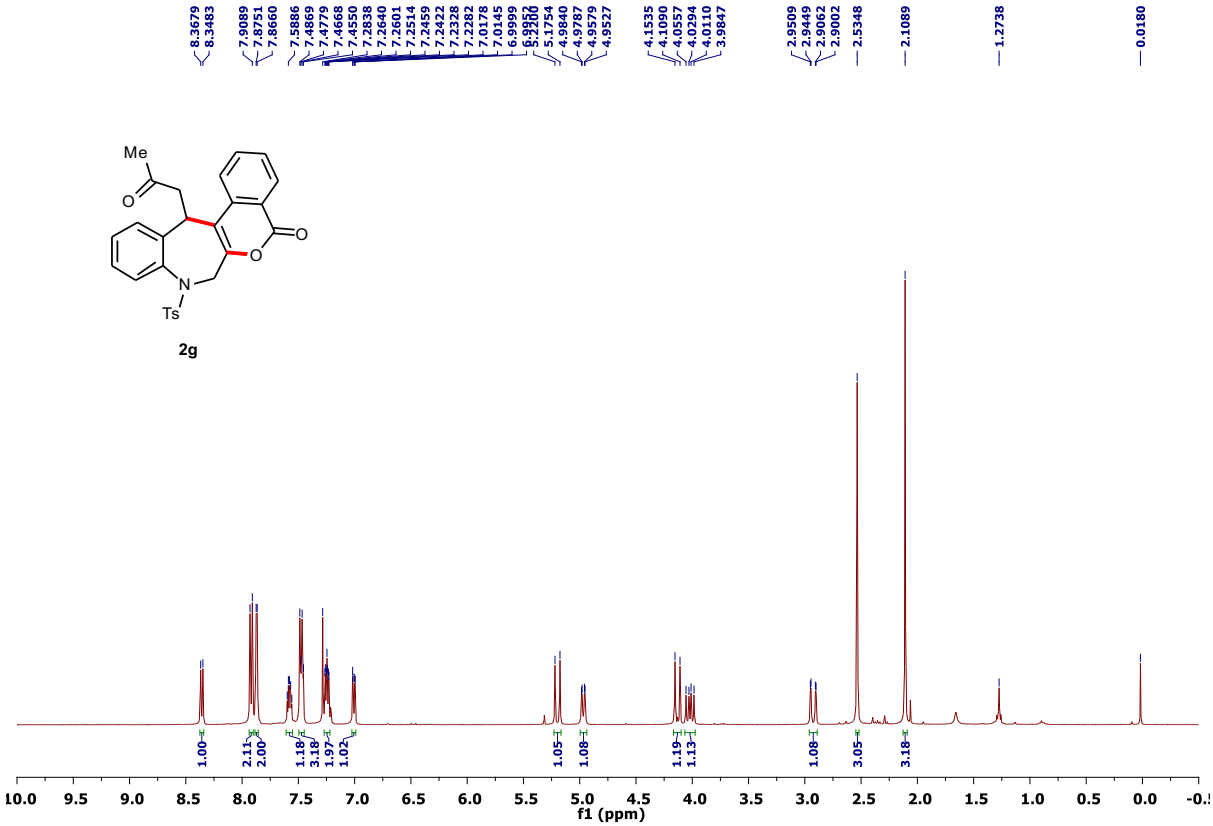
^{1}H NMR spectra of compound **2f** ($CDCl_3$, 500 MHz)



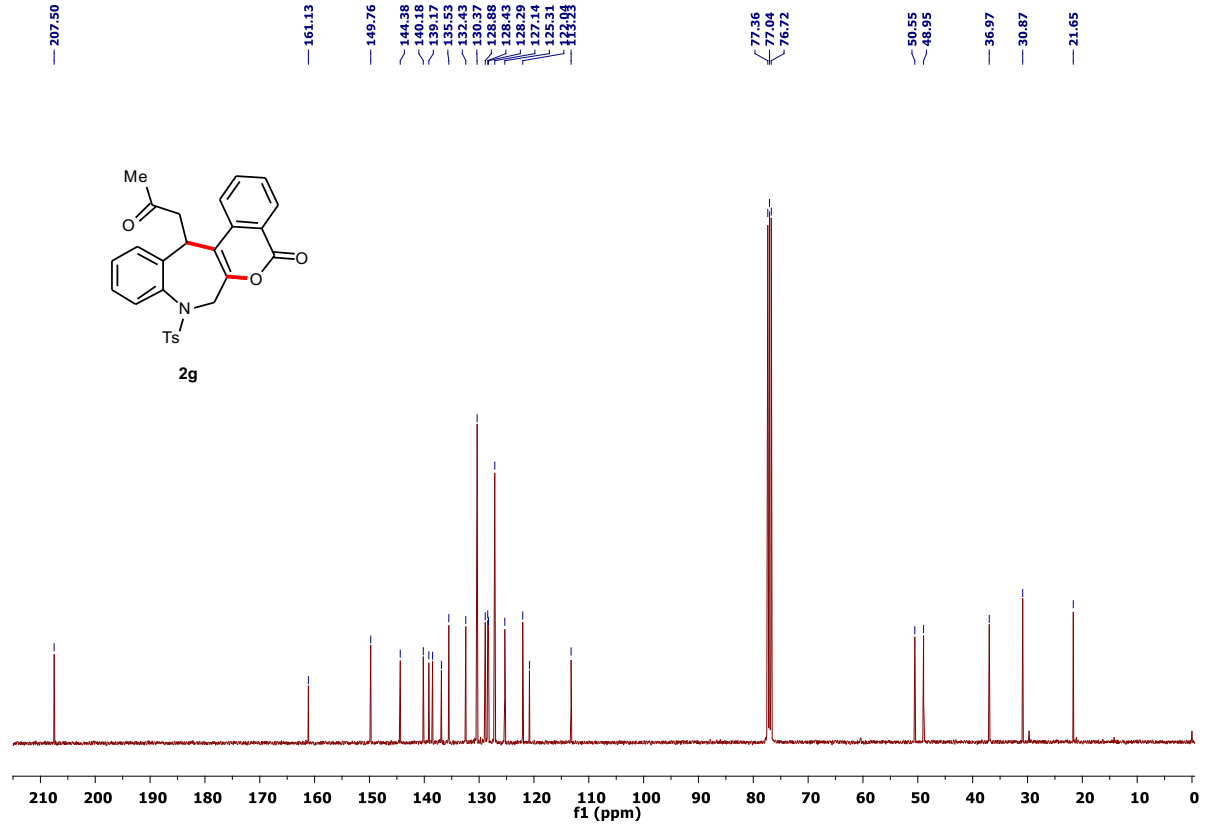
^{13}C{^{1}H} NMR spectra of compound **2f** ($CDCl_3$, 126 MHz)



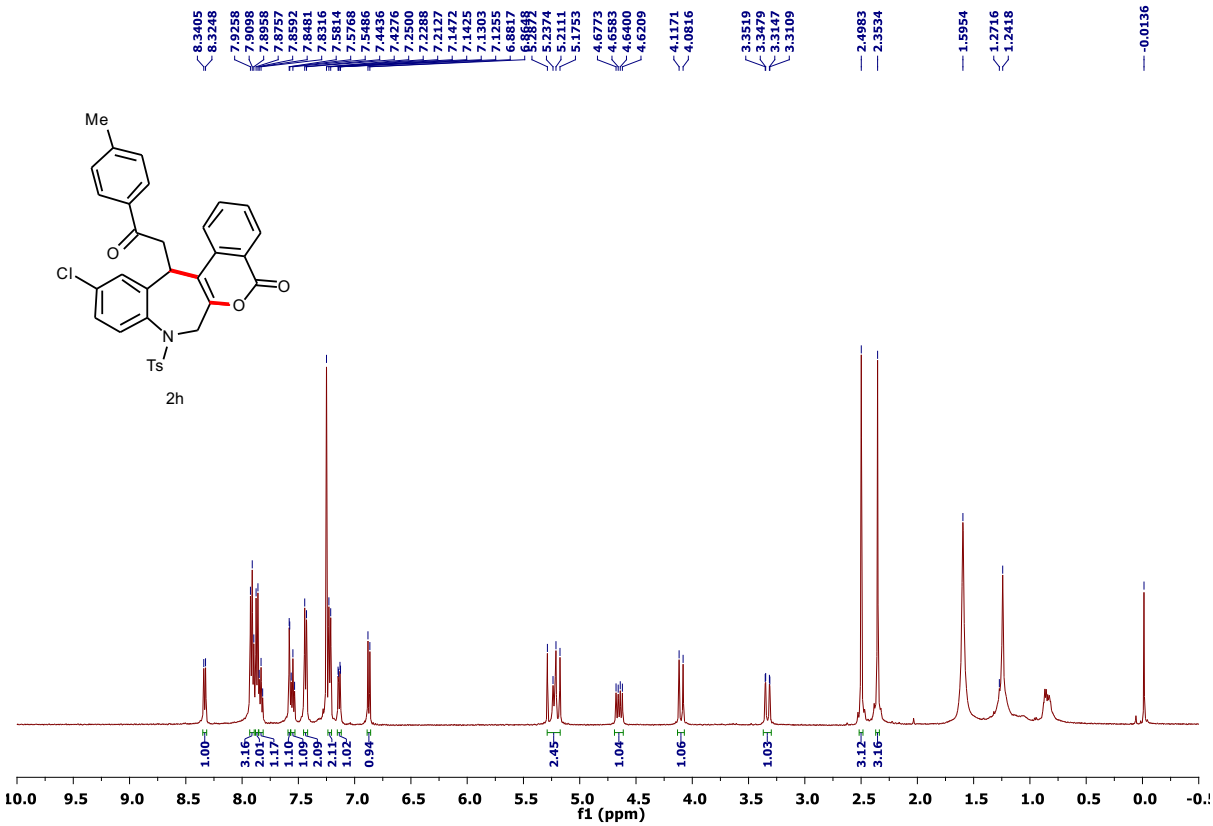
^{1}H NMR spectra of compound **2g** ($CDCl_3$, 400 MHz)



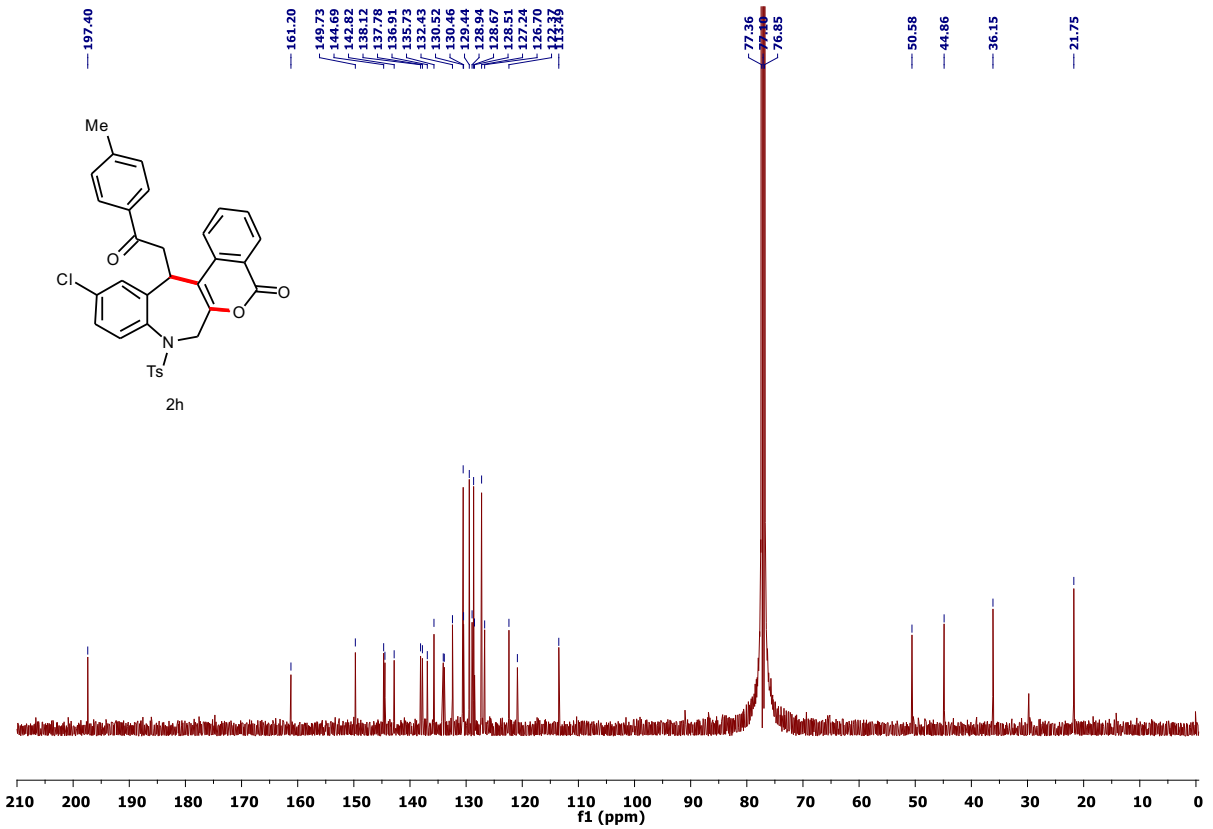
^{13}C{^{1}H} NMR spectra of compound **2g** ($CDCl_3$, 101 MHz)



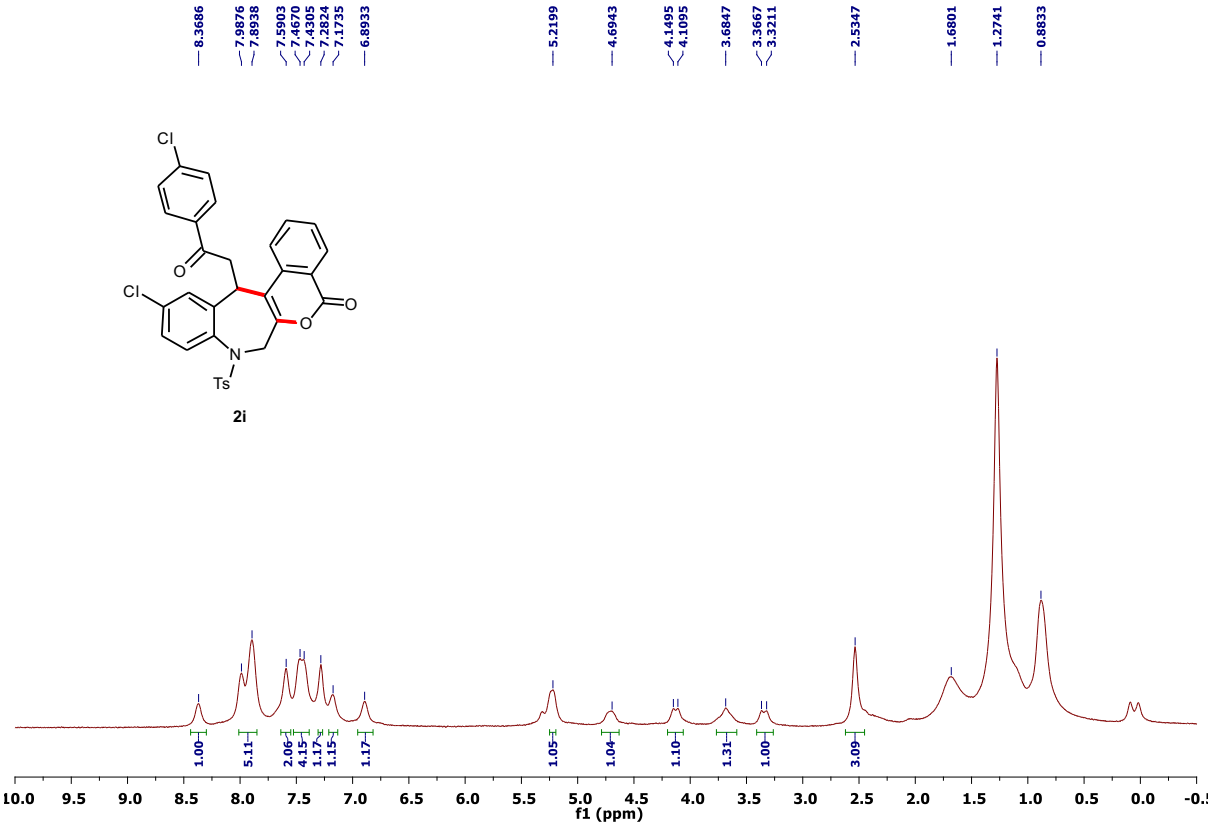
^{1}H NMR spectra of compound **2h** ($CDCl_3$, 500 MHz)



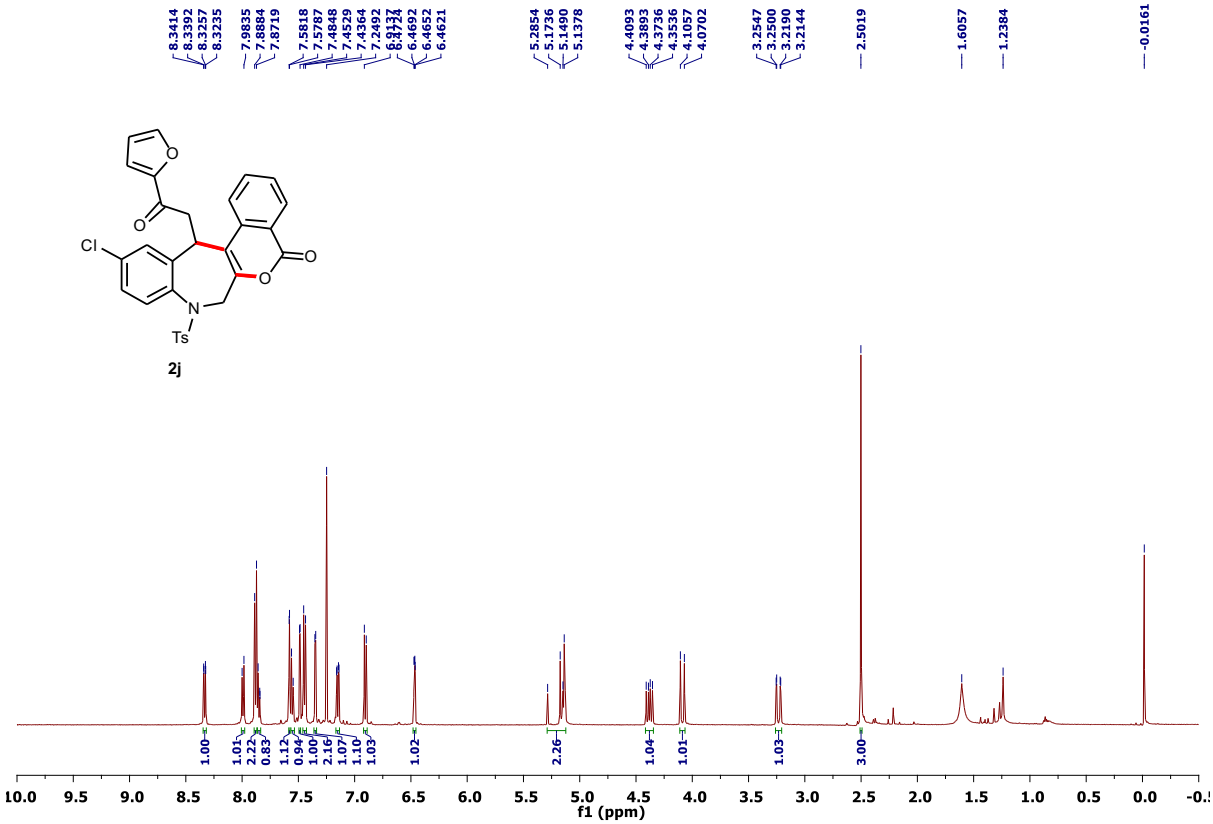
^{13}C{^{1}H} NMR spectra of compound **2h** ($CDCl_3$, 126 MHz)



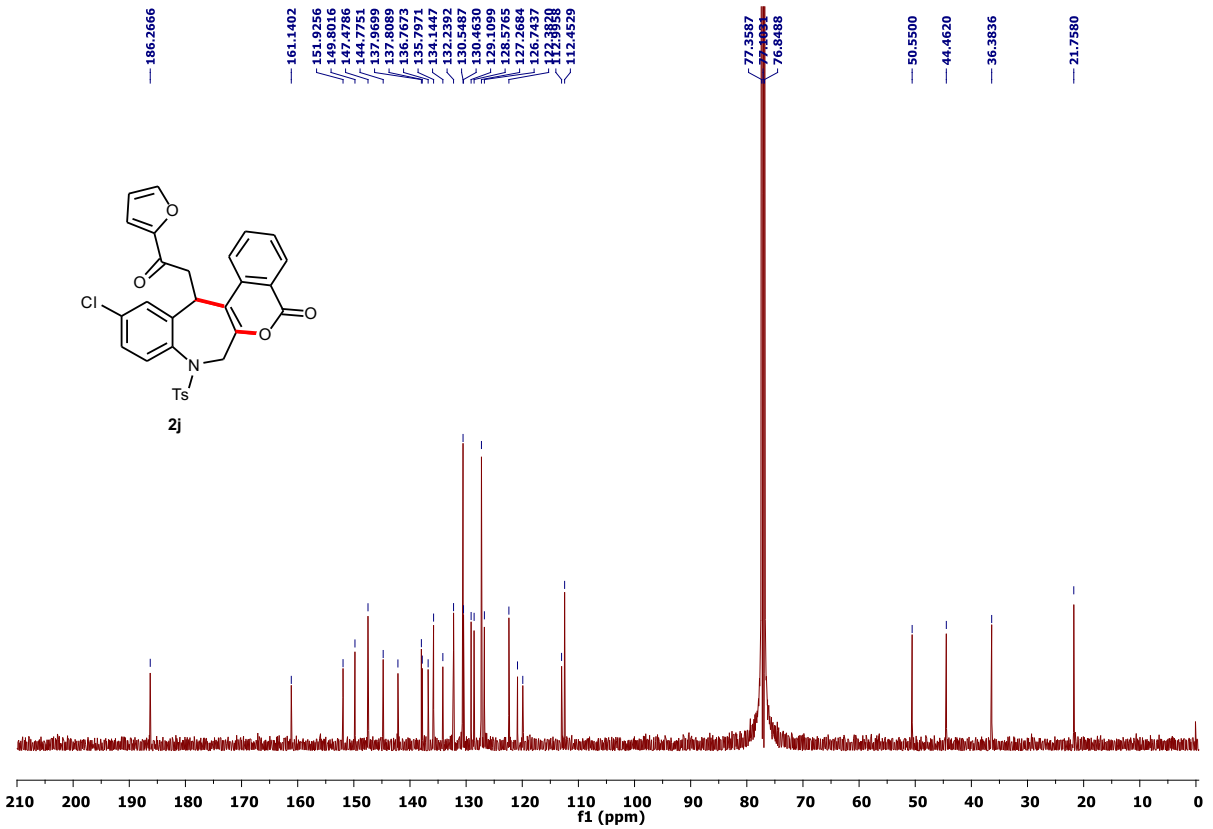
^{1}H NMR spectra of compound **2i** ($CDCl_3$, 400 MHz)



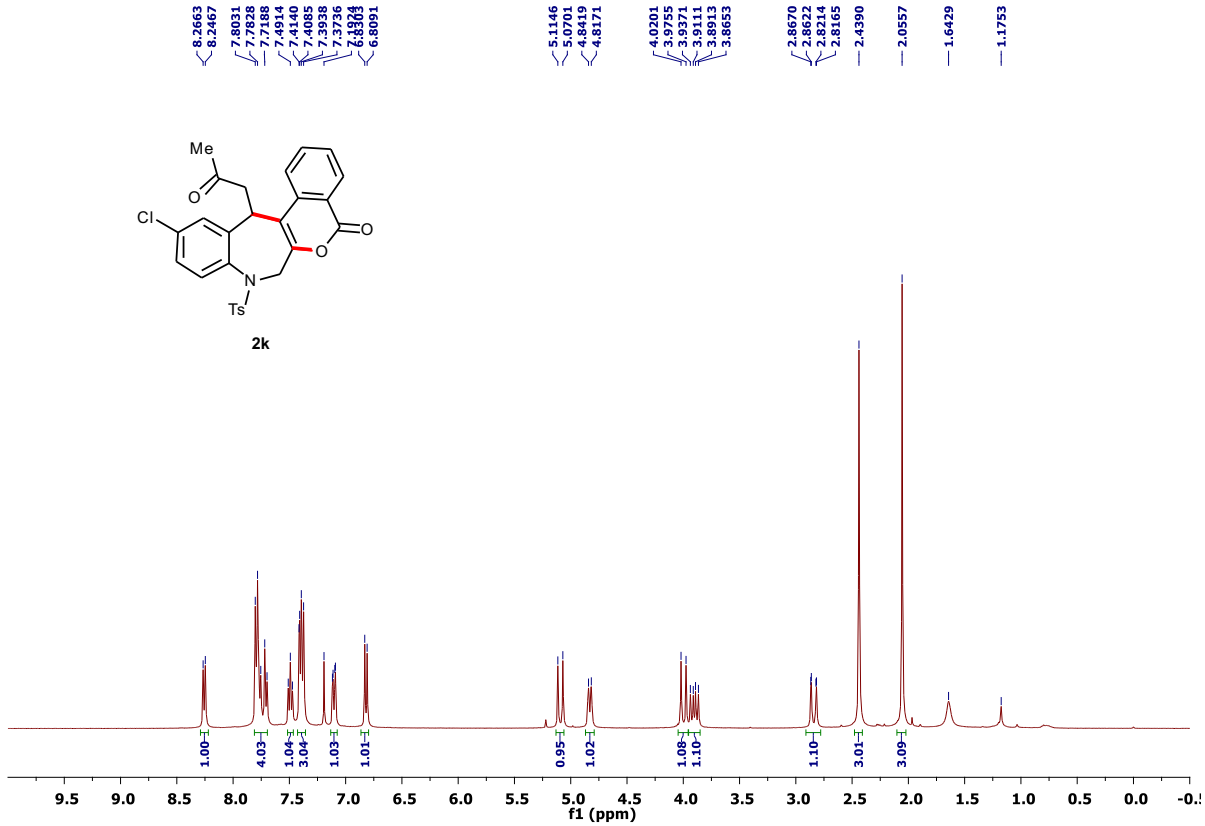
^{1}H NMR spectra of compound **2j** ($CDCl_3$, 500 MHz)



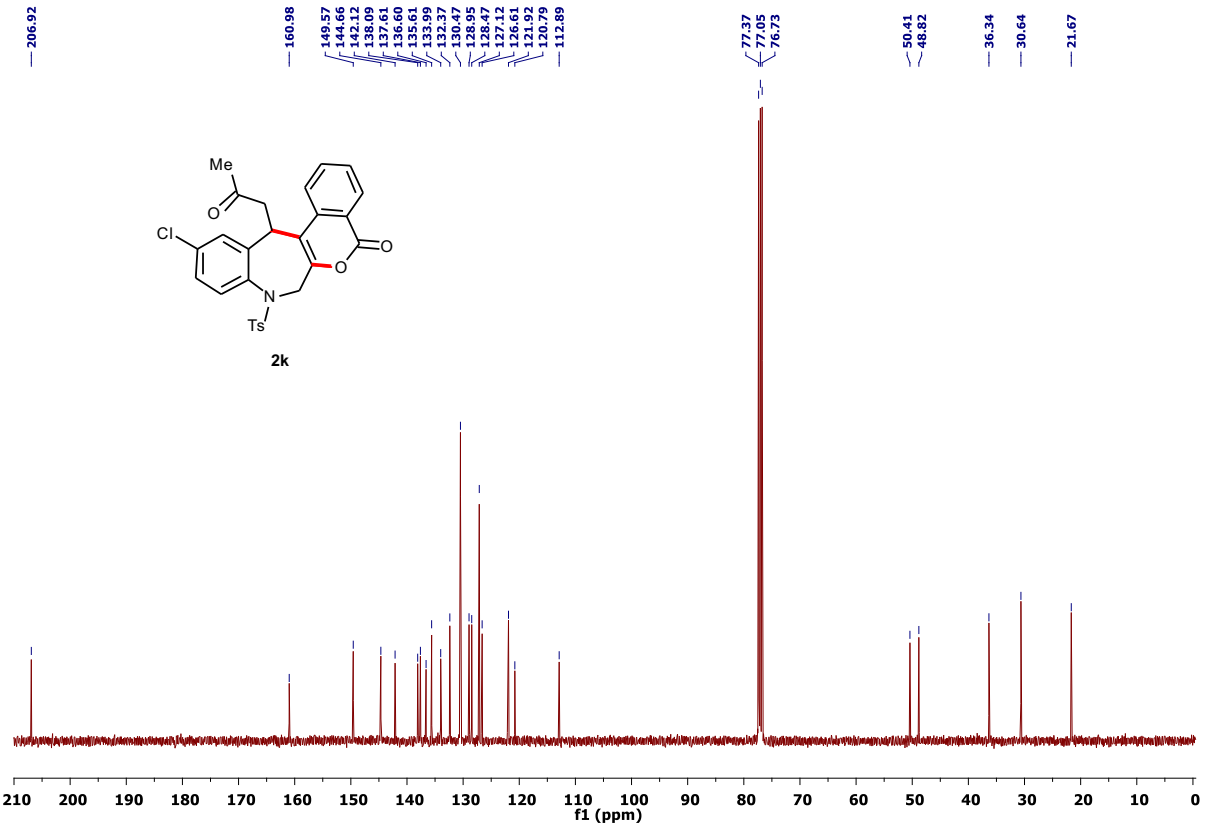
^{13}C{^{1}H} NMR spectra of compound **2j** ($CDCl_3$, 126 MHz)



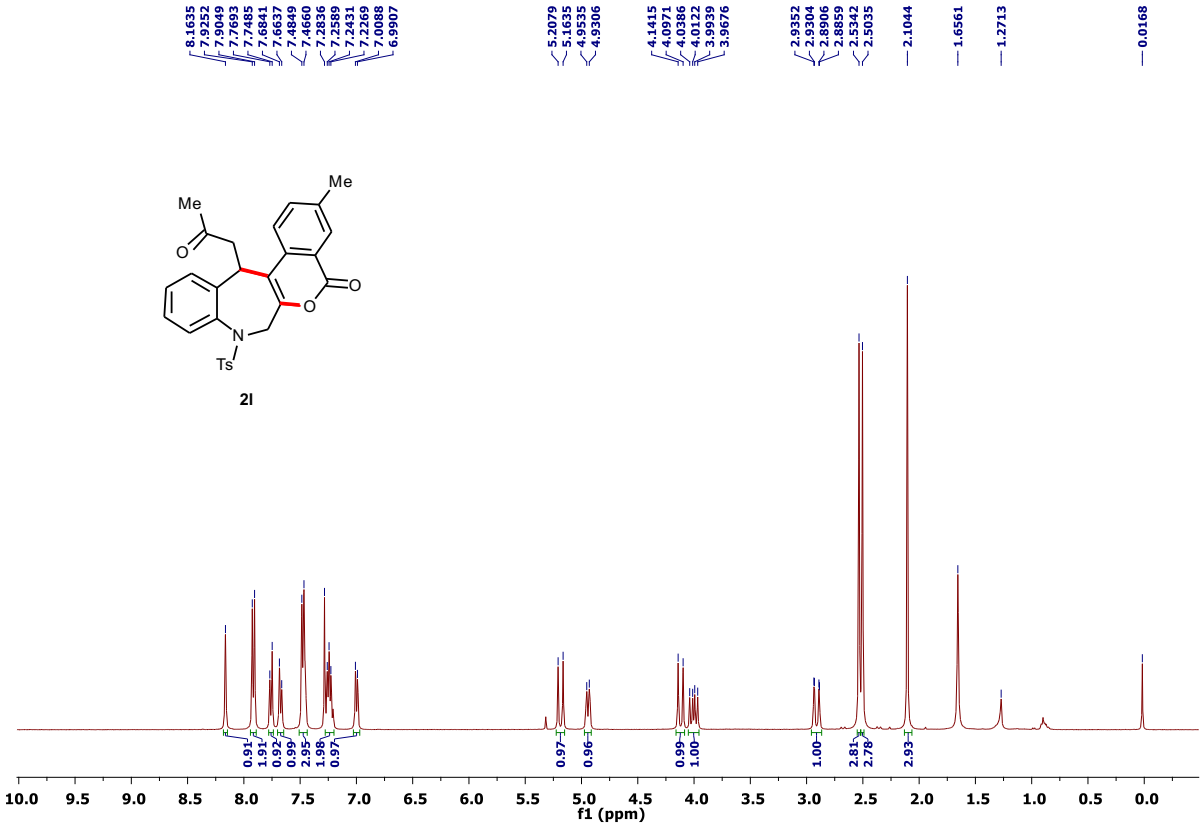
^{1}H NMR spectra of compound **2k** ($CDCl_3$, 400 MHz)



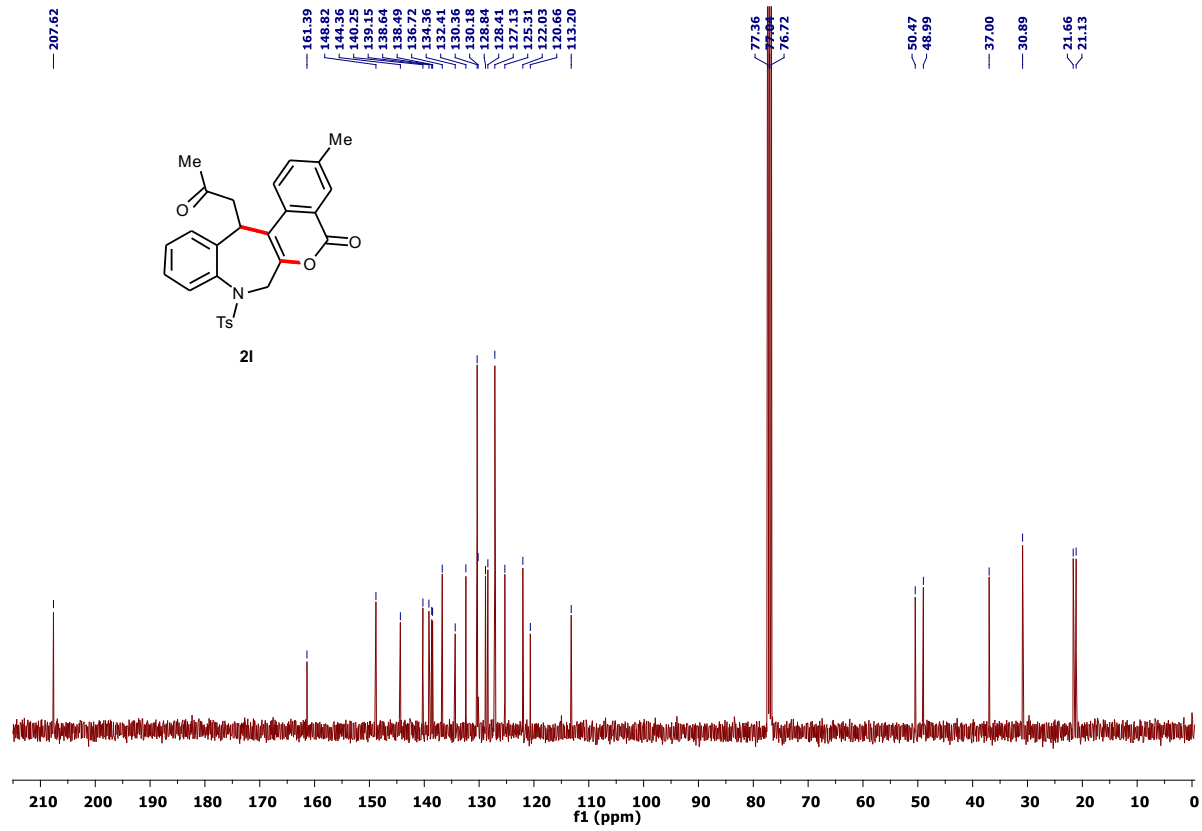
^{13}C{^{1}H} NMR spectra of compound **2k** ($CDCl_3$, 101 MHz)



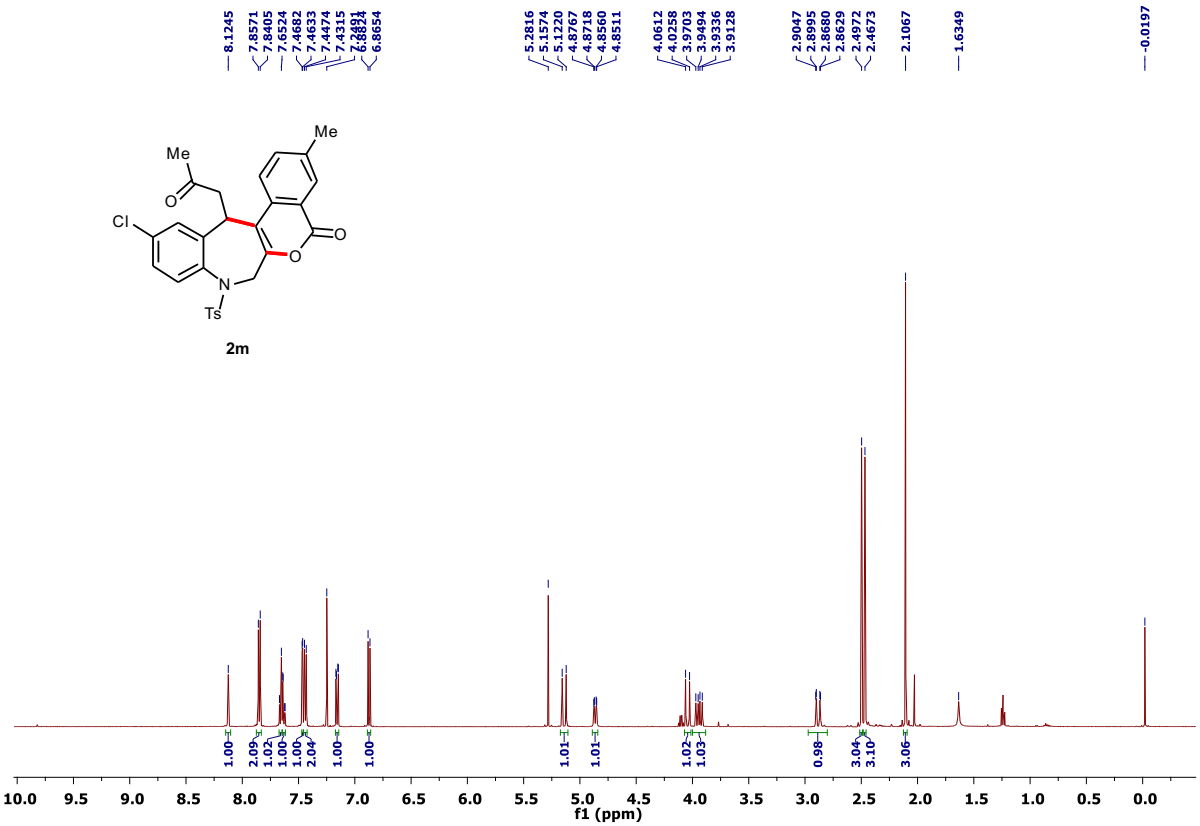
^{1}H NMR spectra of compound **2l** ($CDCl_3$, 400 MHz)



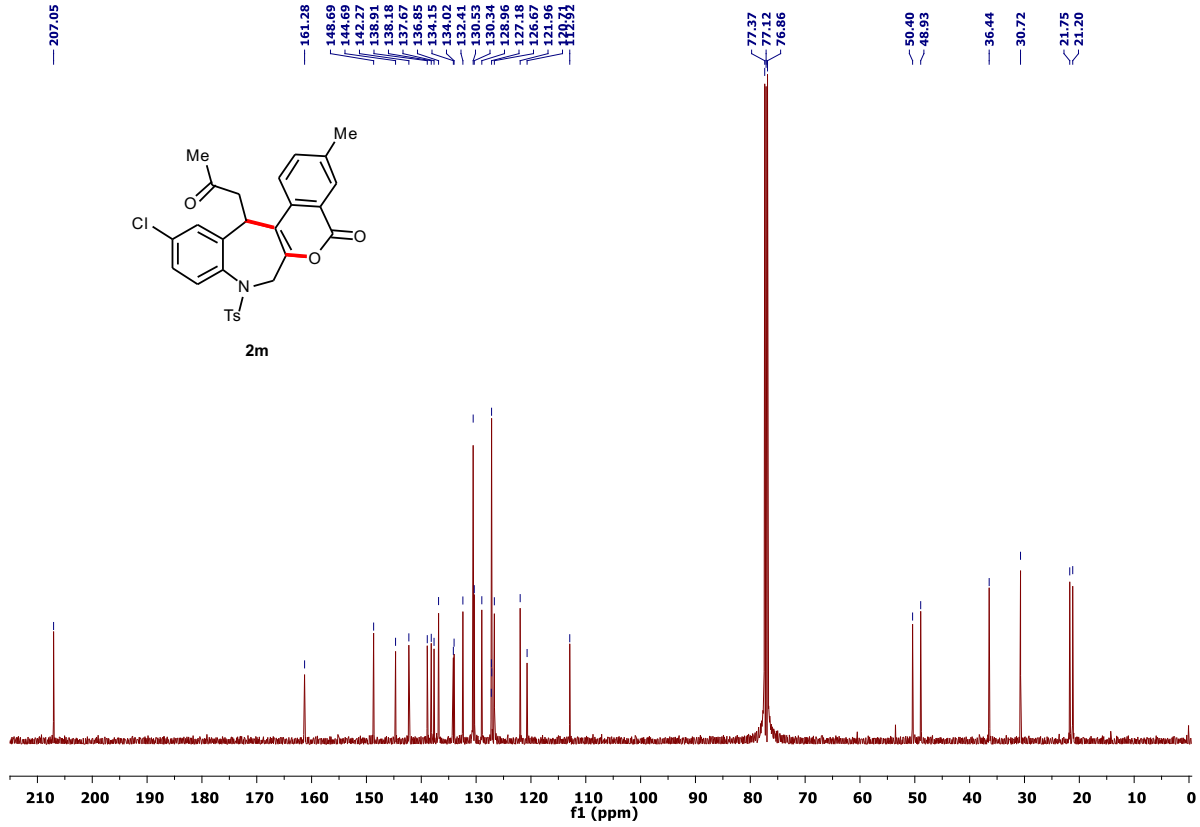
^{13}C{^{1}H} NMR spectra of compound **2l** ($CDCl_3$, 101 MHz)



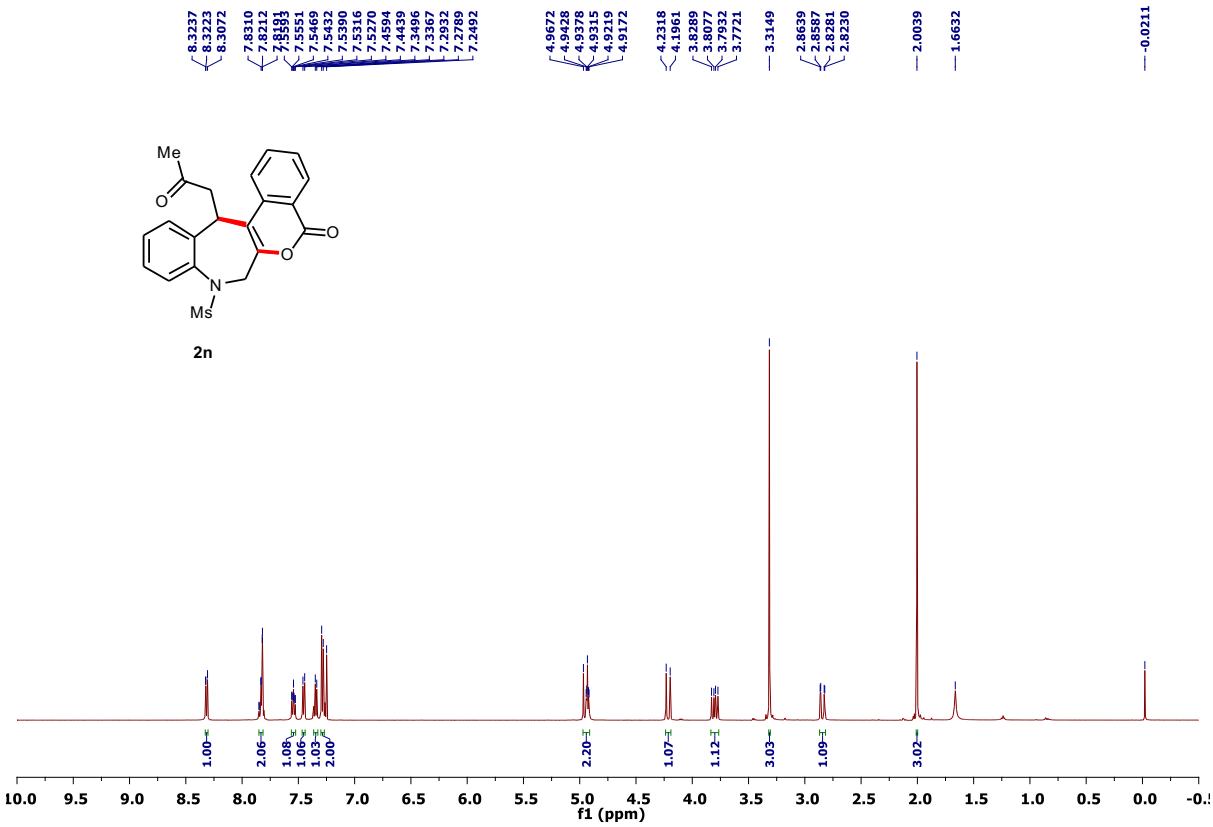
^{1}H NMR spectra of compound **2m** ($CDCl_3$, 500 MHz)



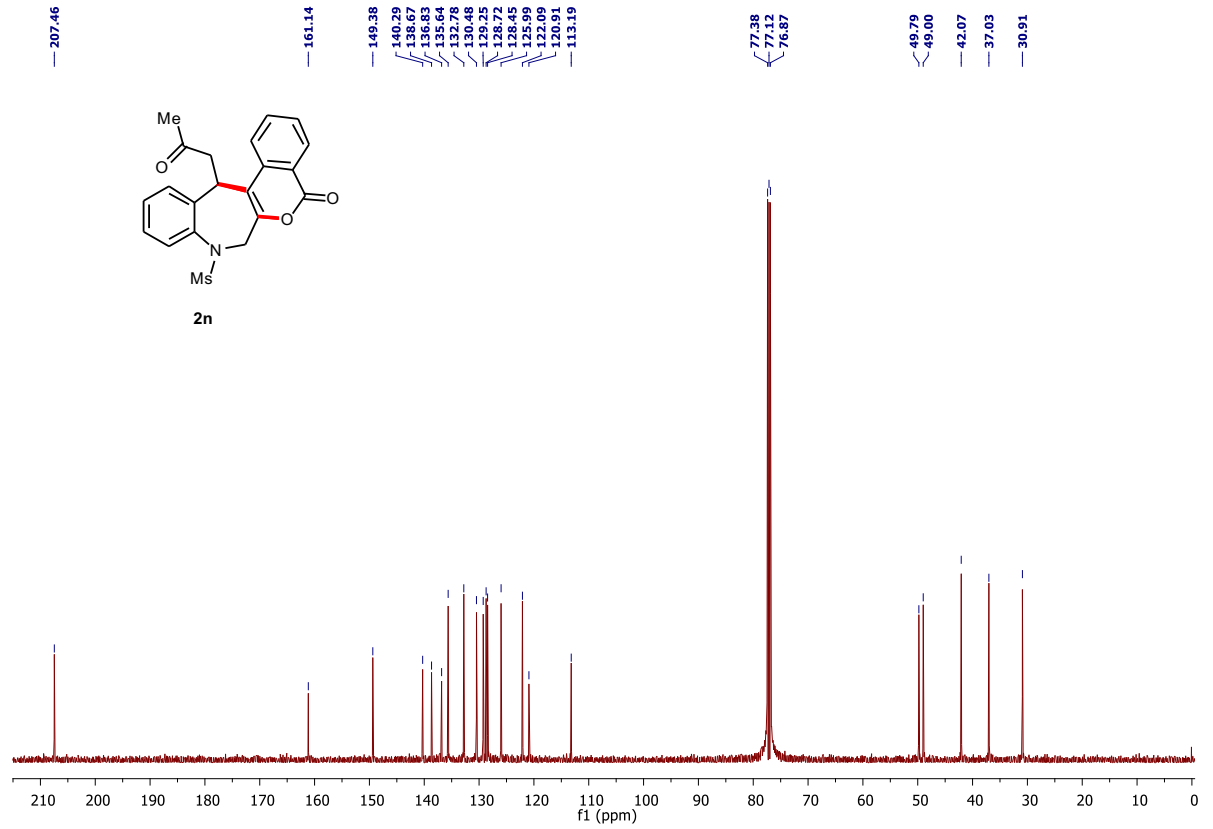
^{13}C{^{1}H} NMR spectra of compound **2m** ($CDCl_3$, 126 MHz)



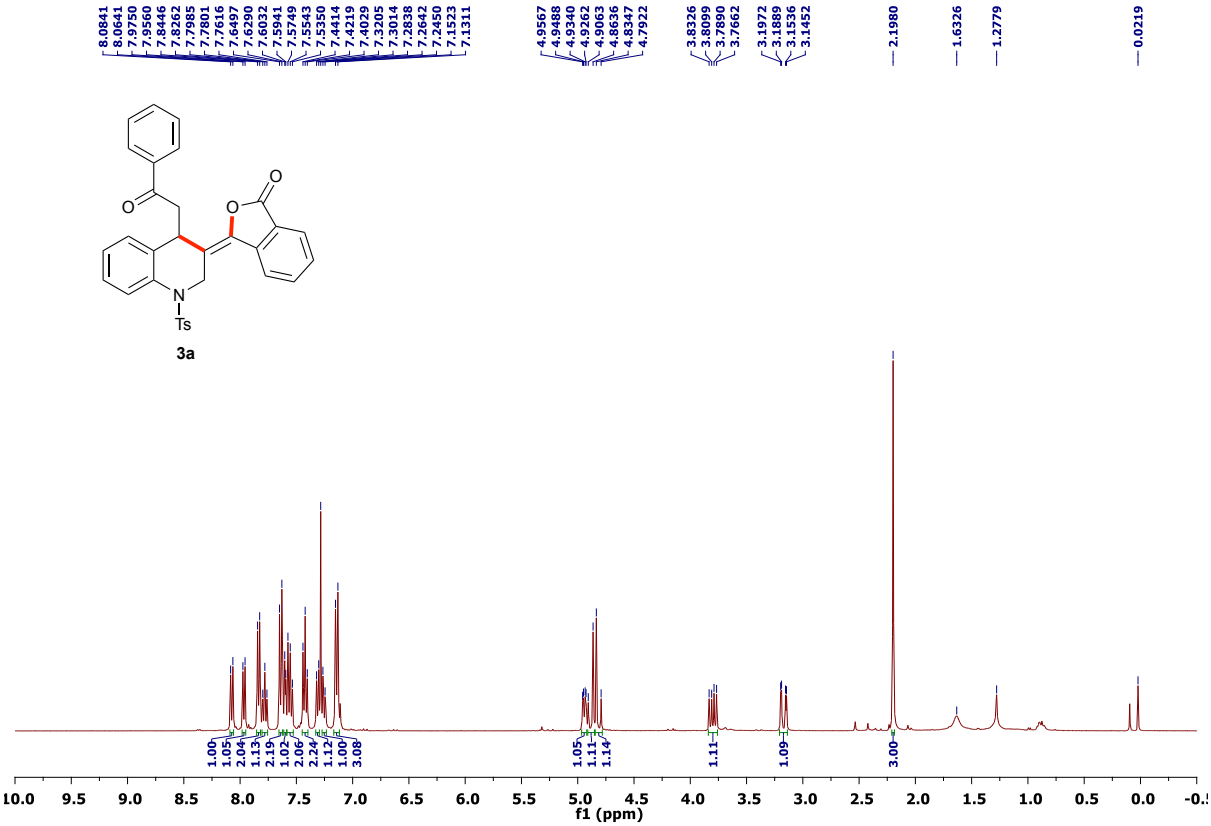
^{1}H NMR spectra of compound **2n** ($CDCl_3$, 500 MHz)



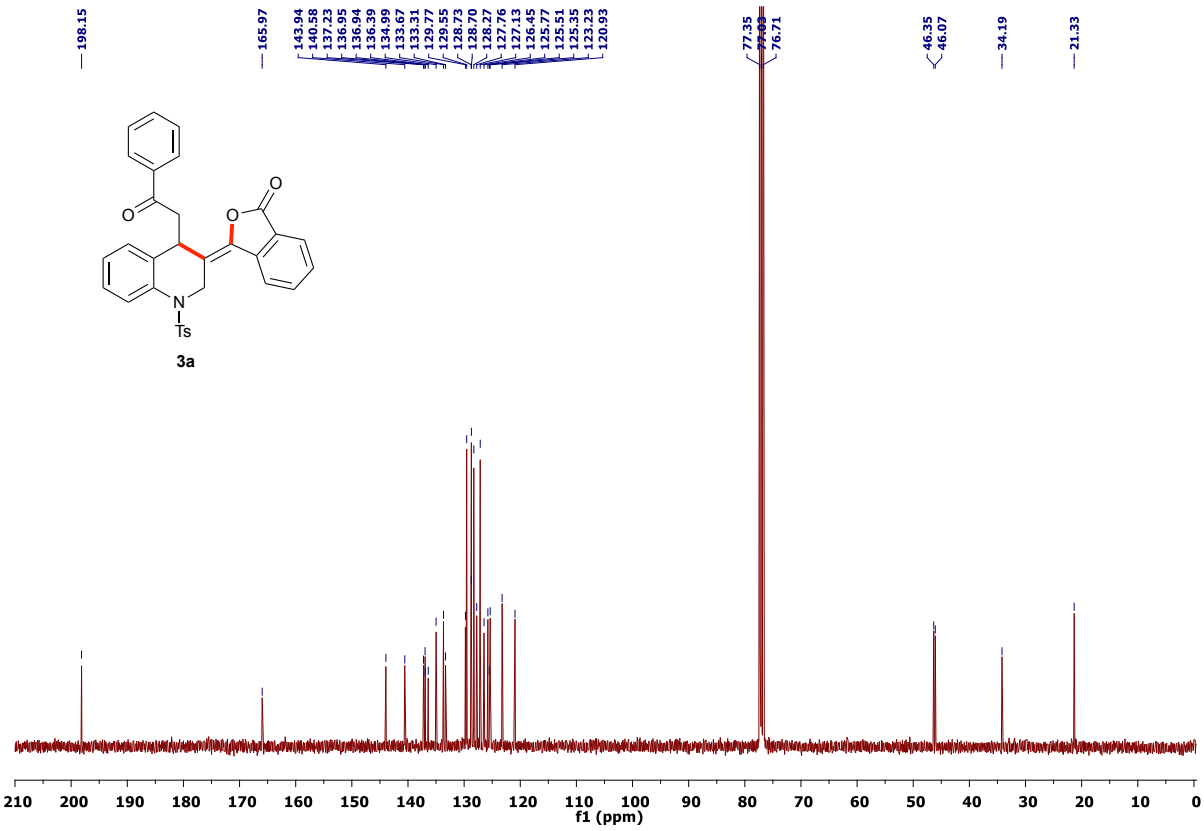
^{13}C{^{1}H} NMR spectra of compound **2n** ($CDCl_3$, 126 MHz)



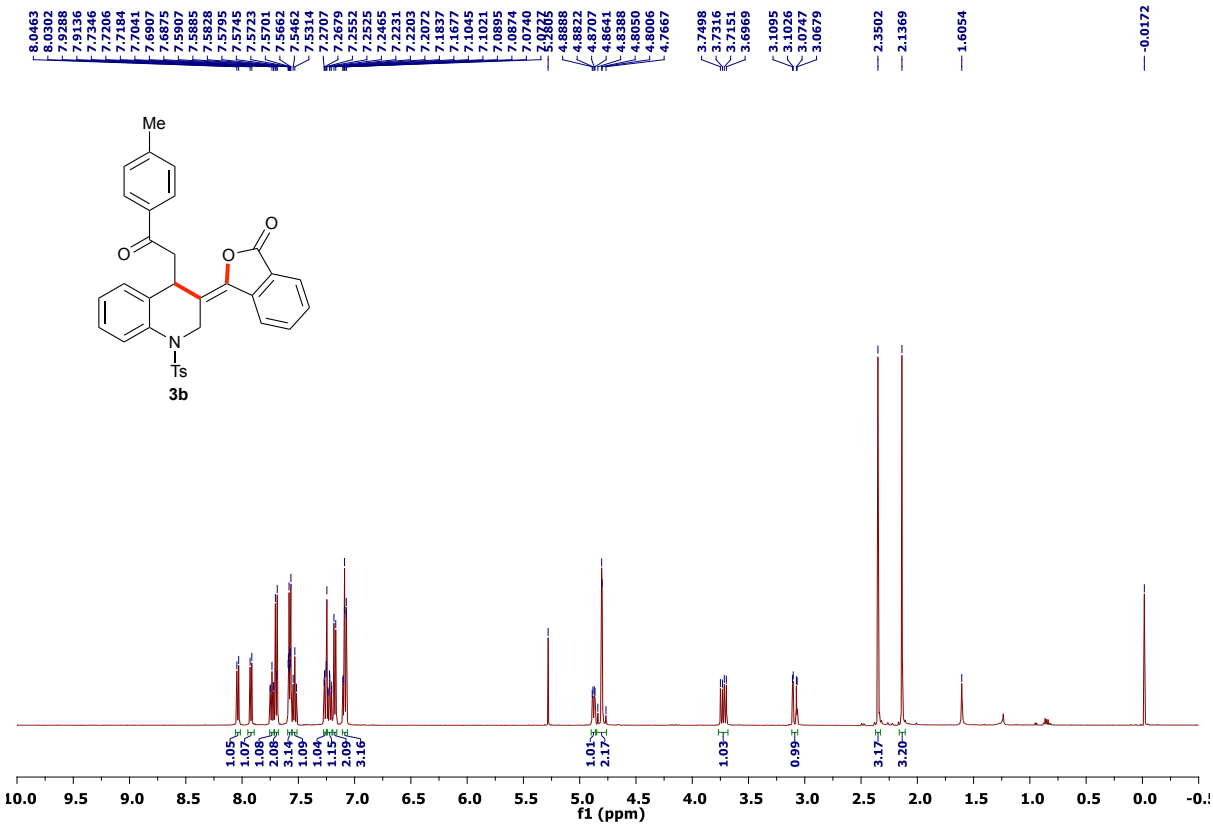
^{1}H NMR spectra of compound **3a** ($CDCl_3$, 400 MHz)



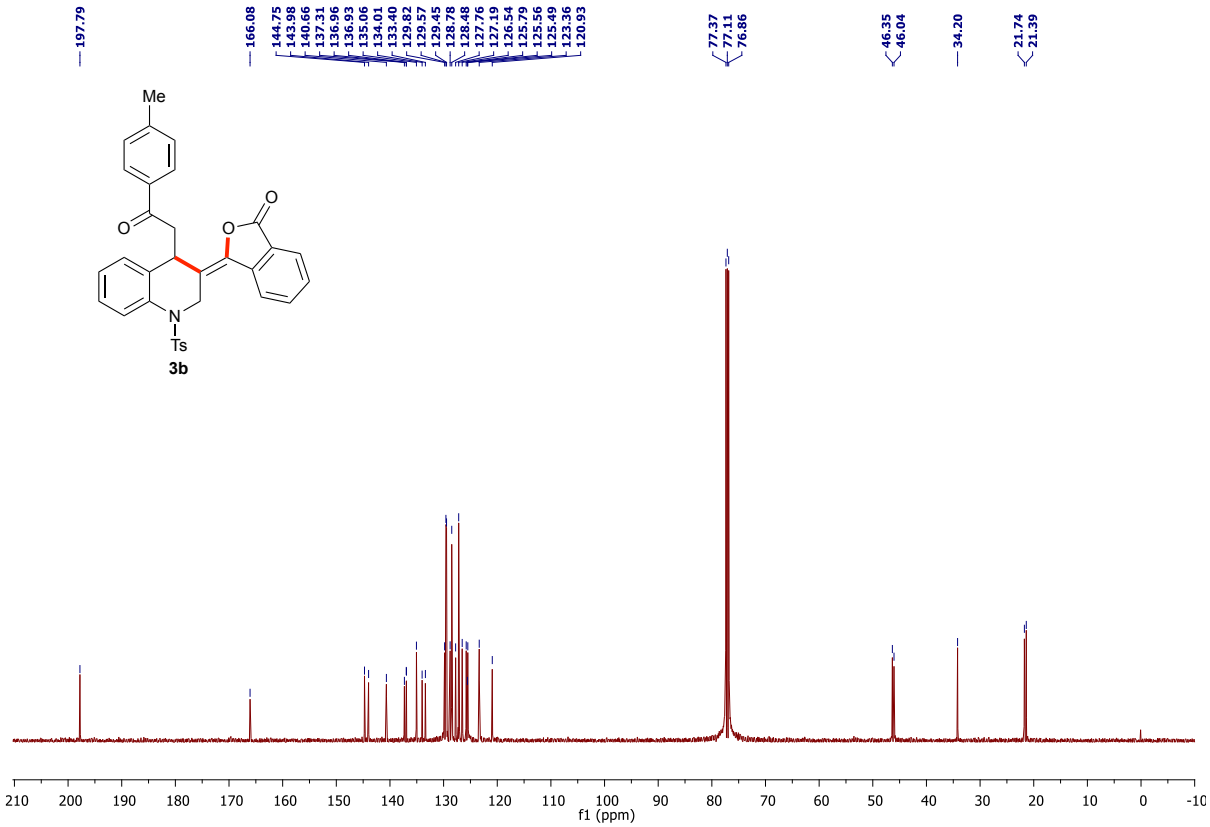
^{13}C{^{1}H} NMR spectra of compound **3a** ($CDCl_3$, 101 MHz)



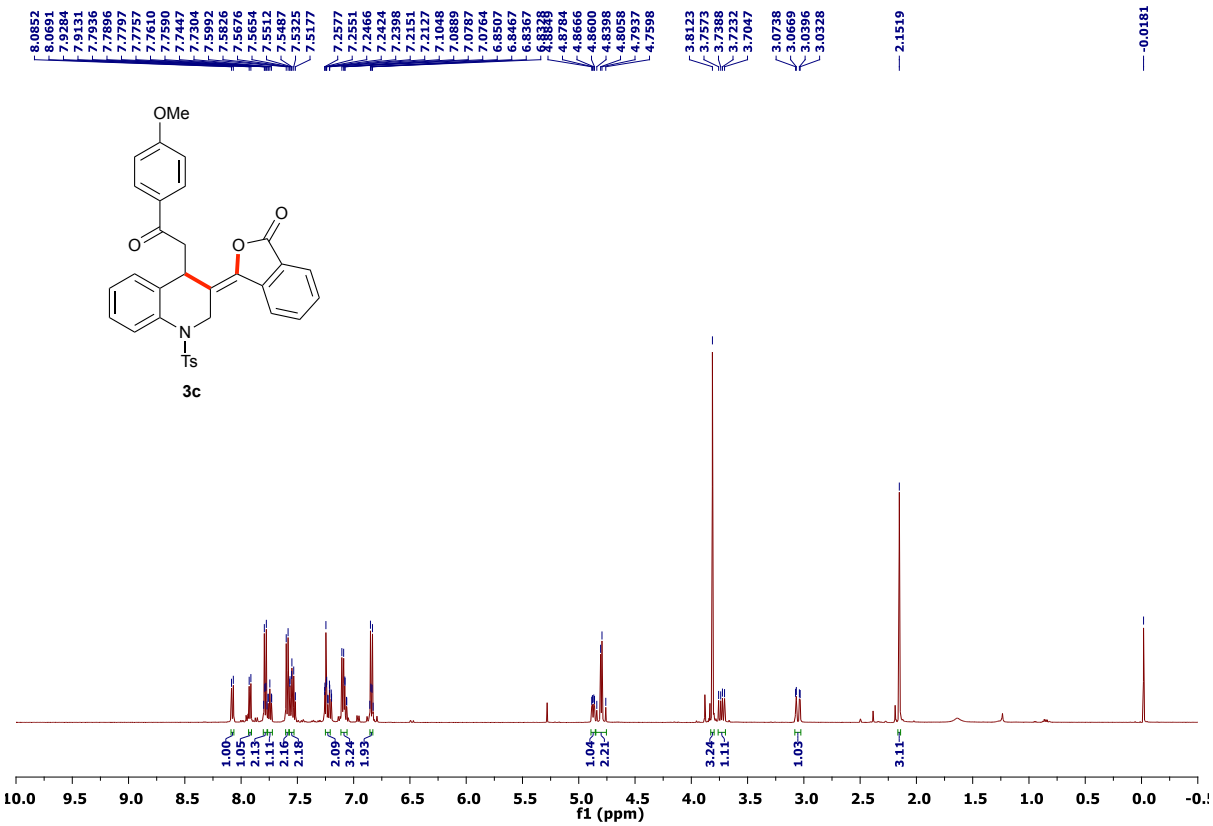
^{1}H NMR spectra of compound **3b** ($CDCl_3$, 500 MHz)



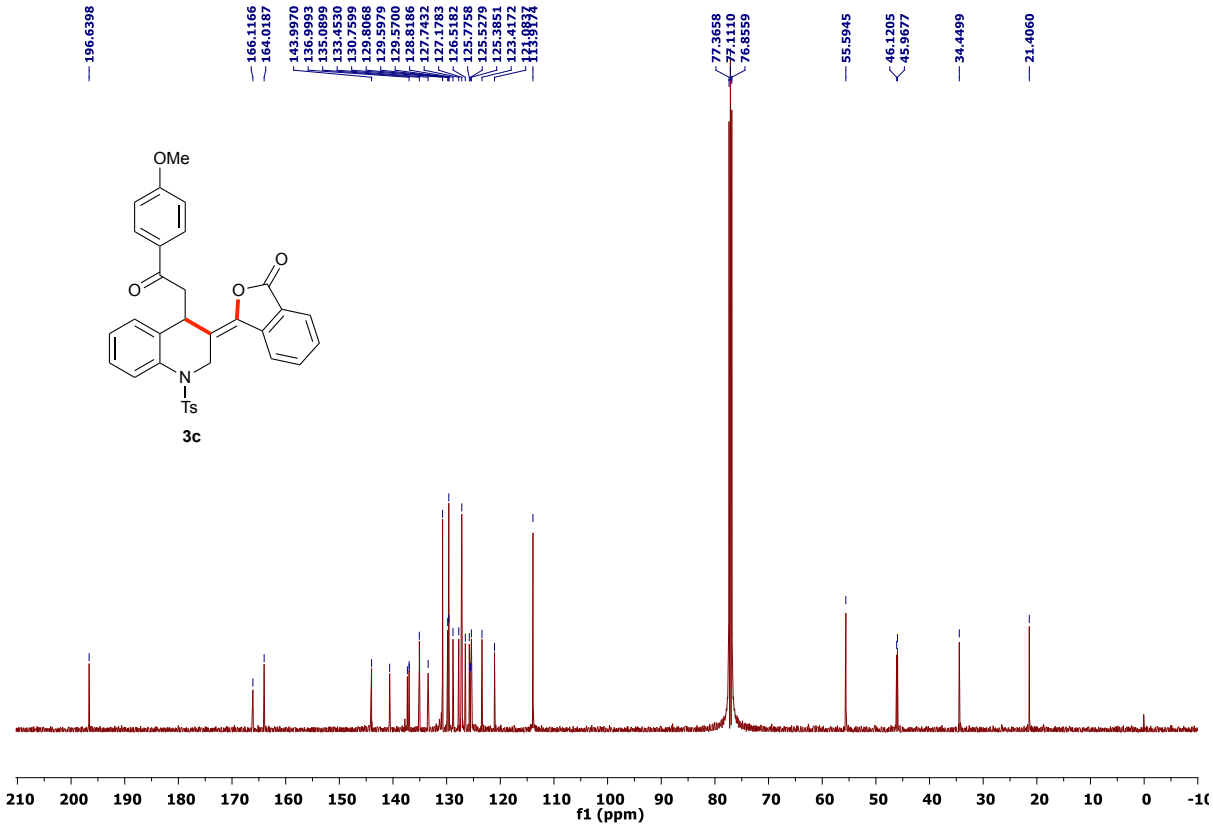
^{13}C{^{1}H} NMR spectra of compound **3b** ($CDCl_3$, 104 MHz)



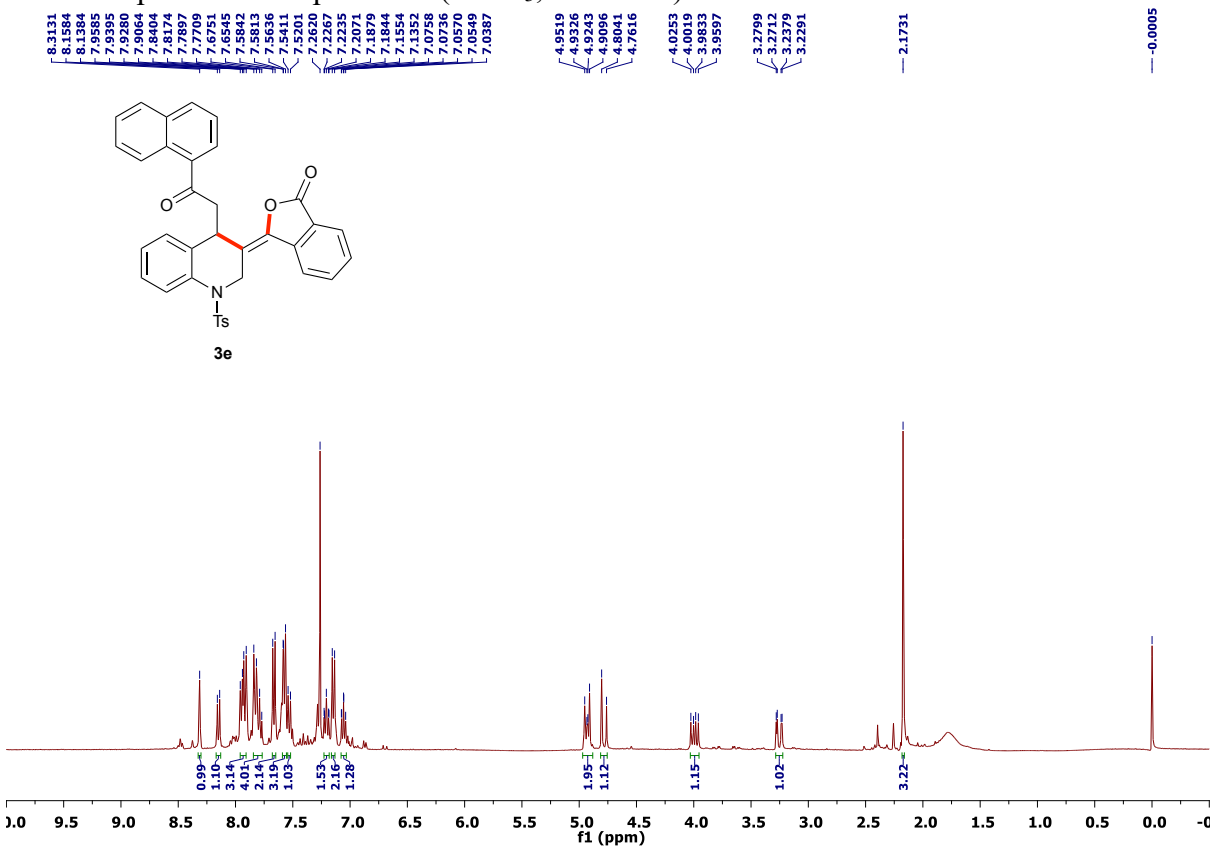
^{1}H NMR spectra of compound **3c** ($CDCl_3$, 500 MHz)



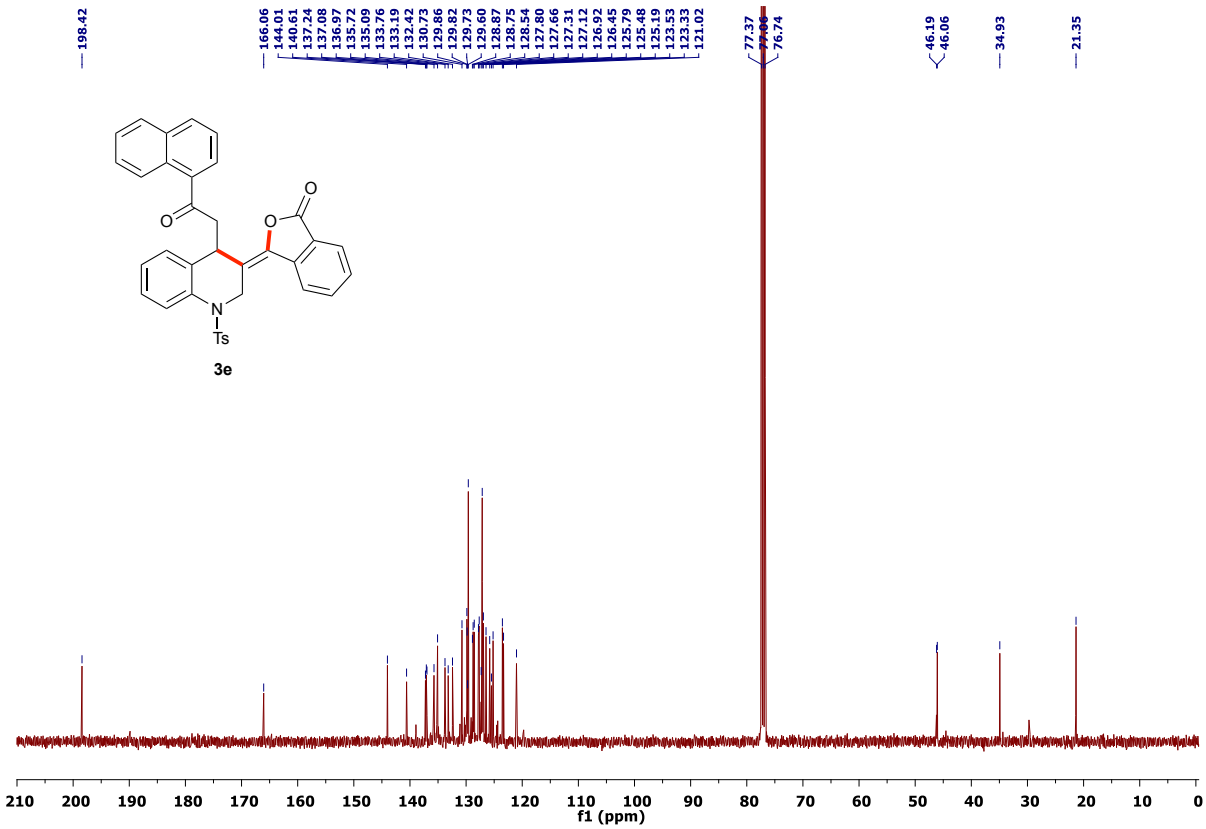
^{13}C{^{1}H} NMR spectra of compound **3c** ($CDCl_3$, 104 MHz)



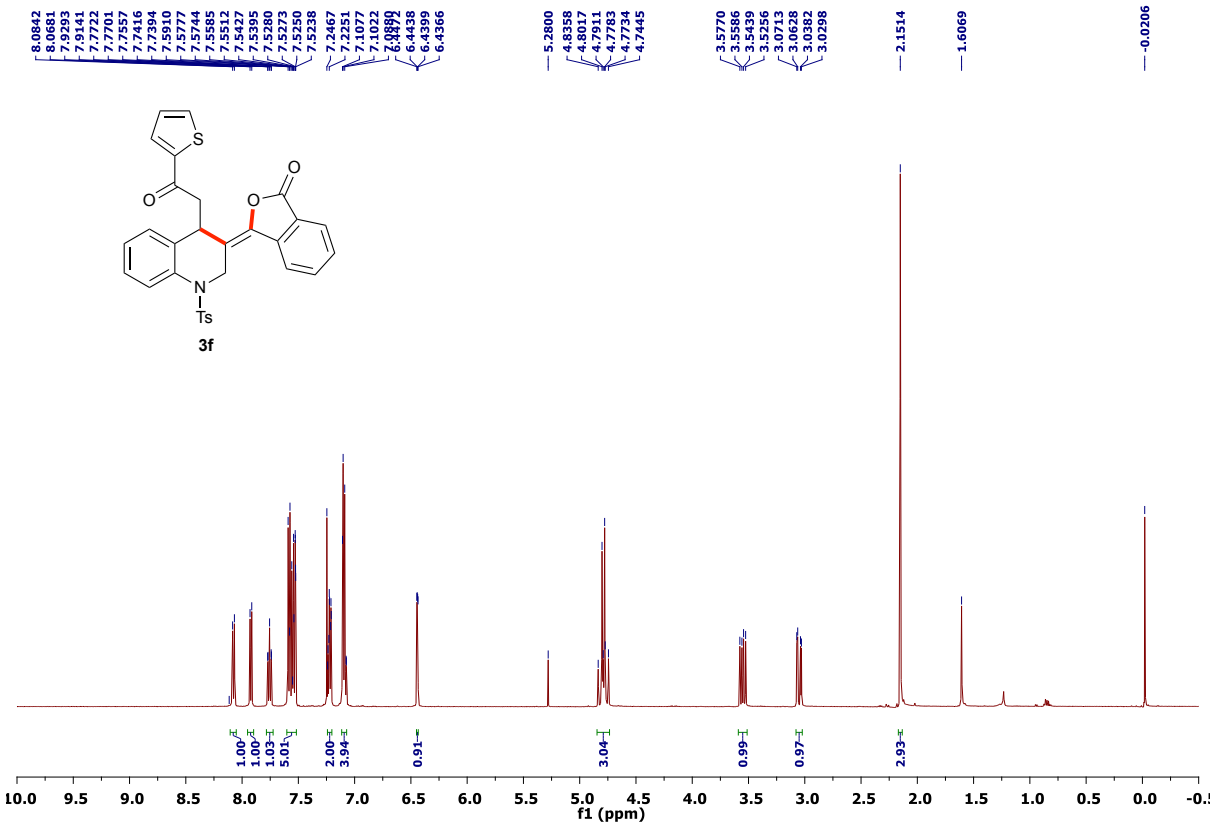
^{1}H NMR spectra of compound **3e** ($CDCl_3$, 400 MHz)



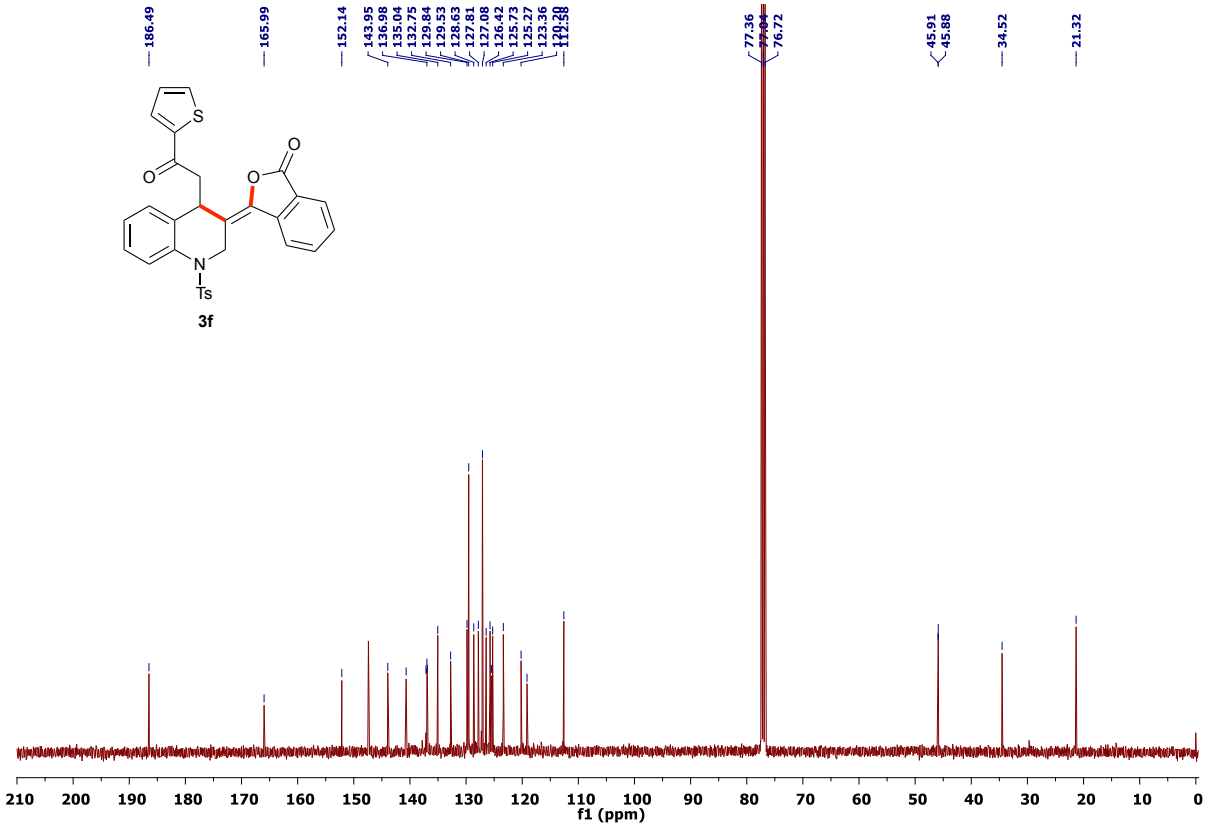
^{13}C{^{1}H} NMR spectra of compound **3e** ($CDCl_3$, 101 MHz)



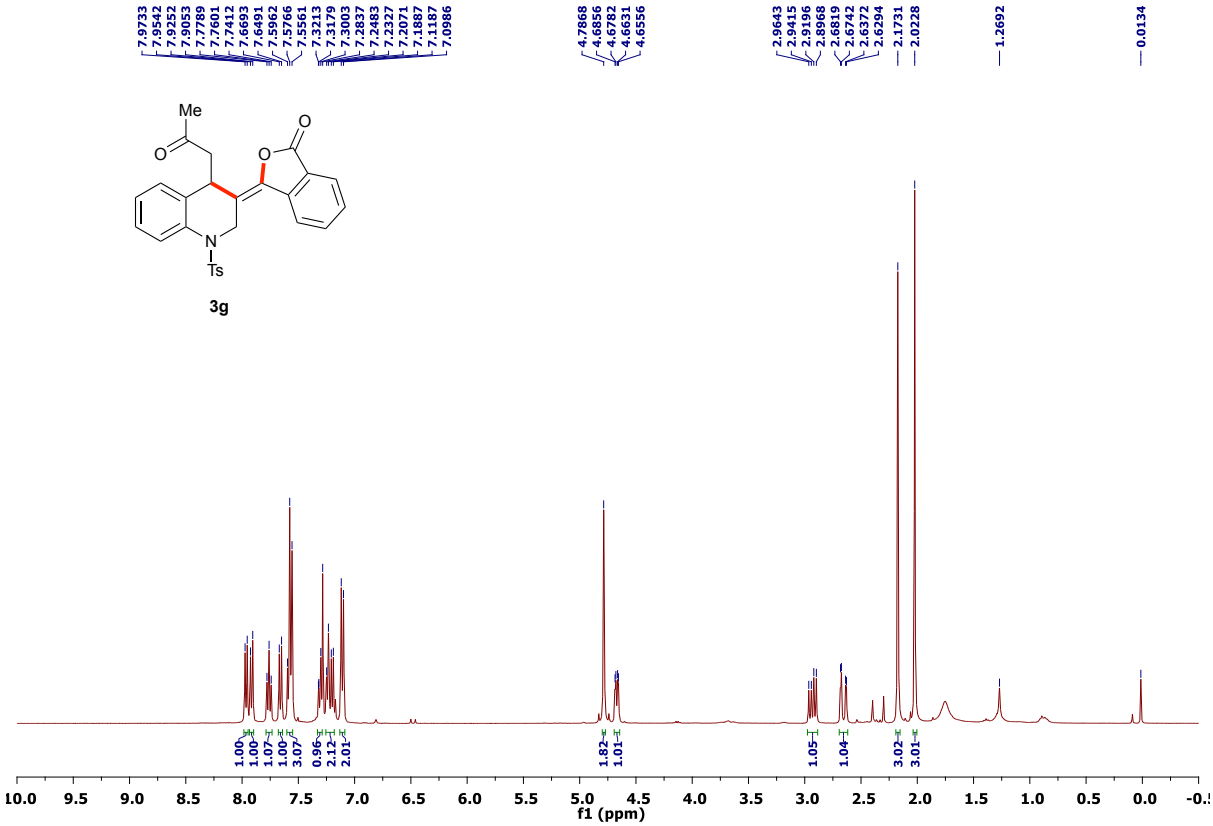
^{1}H NMR spectra of compound **3f** ($CDCl_3$, 500 MHz)



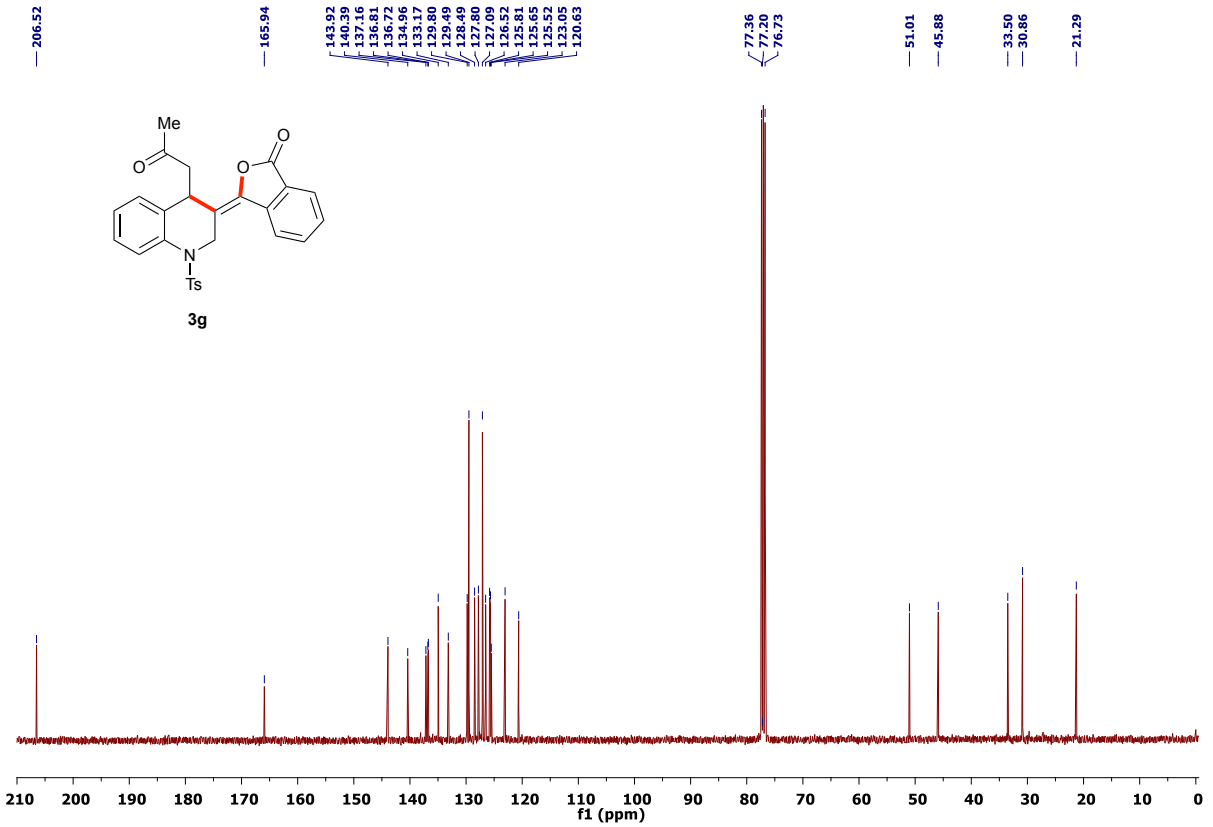
^{13}C{^{1}H} NMR spectra of compound **3f** ($CDCl_3$, 101 MHz)



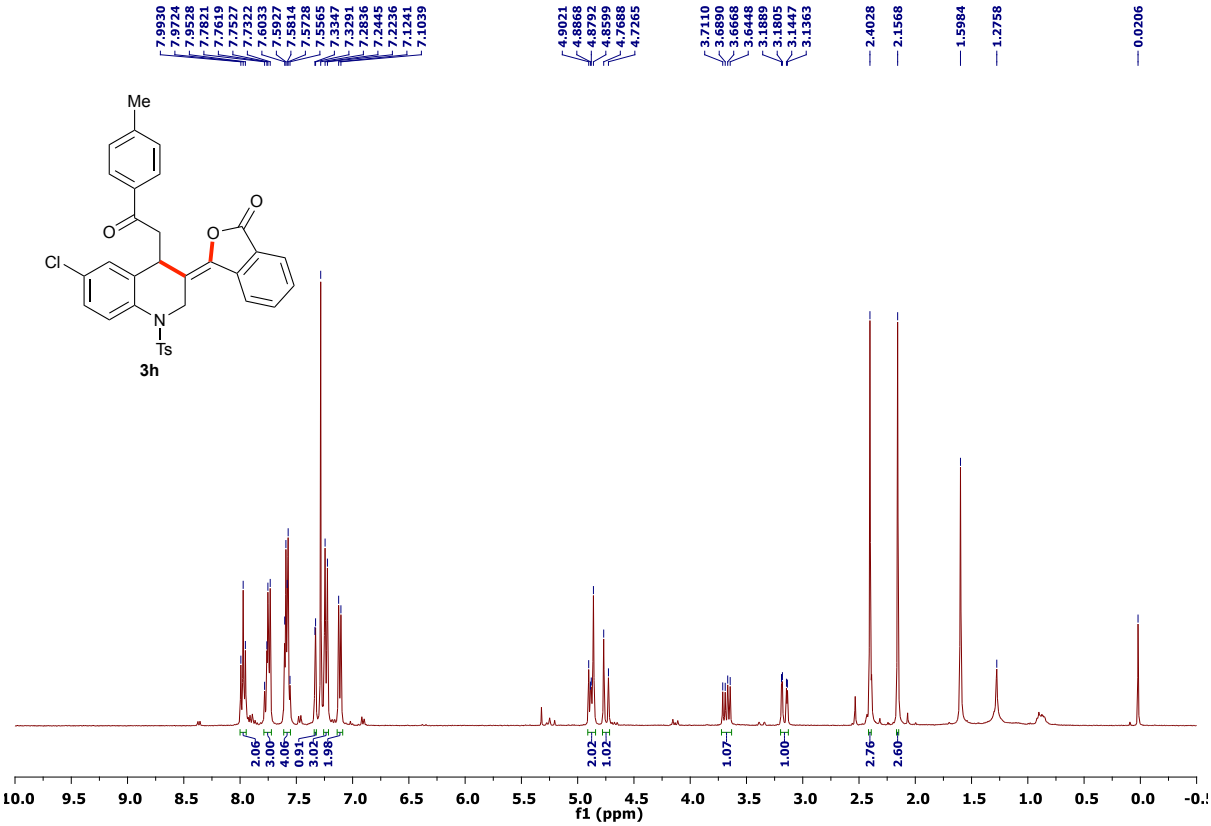
^{1}H NMR spectra of compound **3g** ($CDCl_3$, 400 MHz)



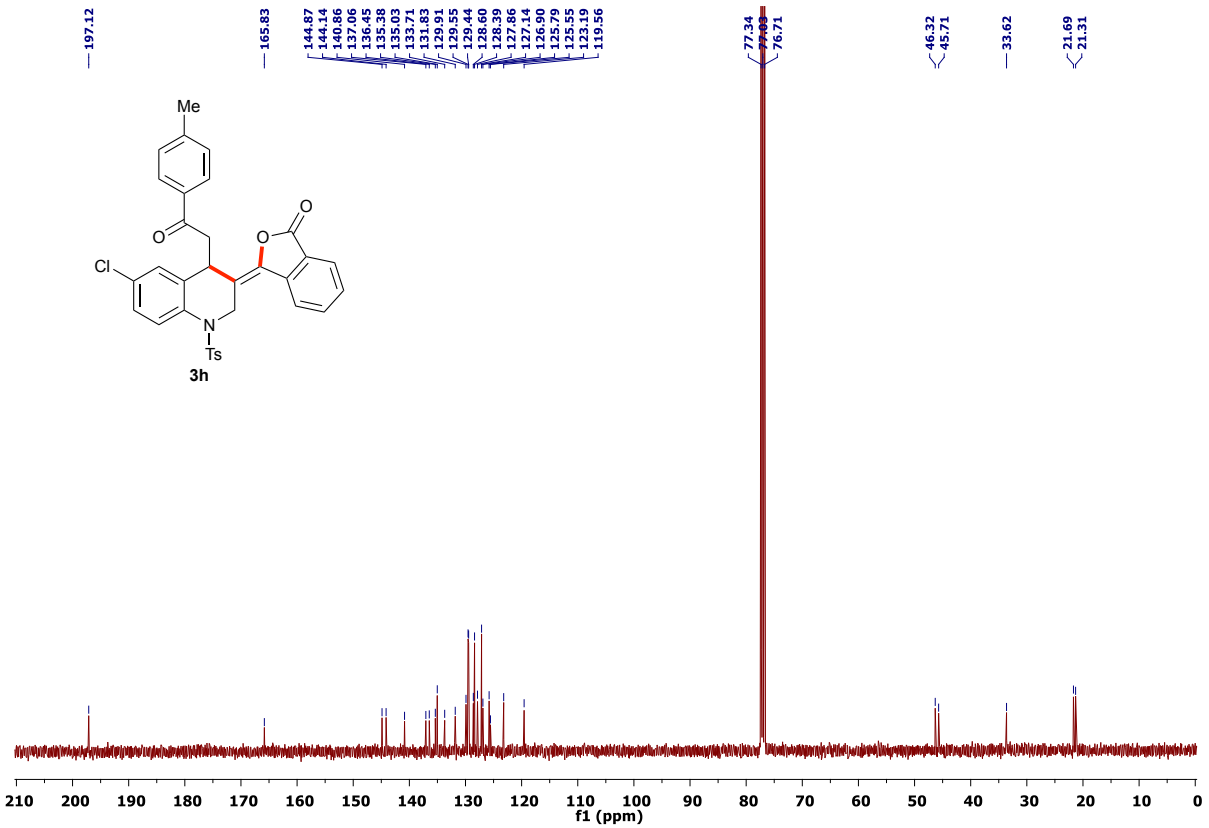
^{13}C{^{1}H} NMR spectra of compound **3g** ($CDCl_3$, 101 MHz)



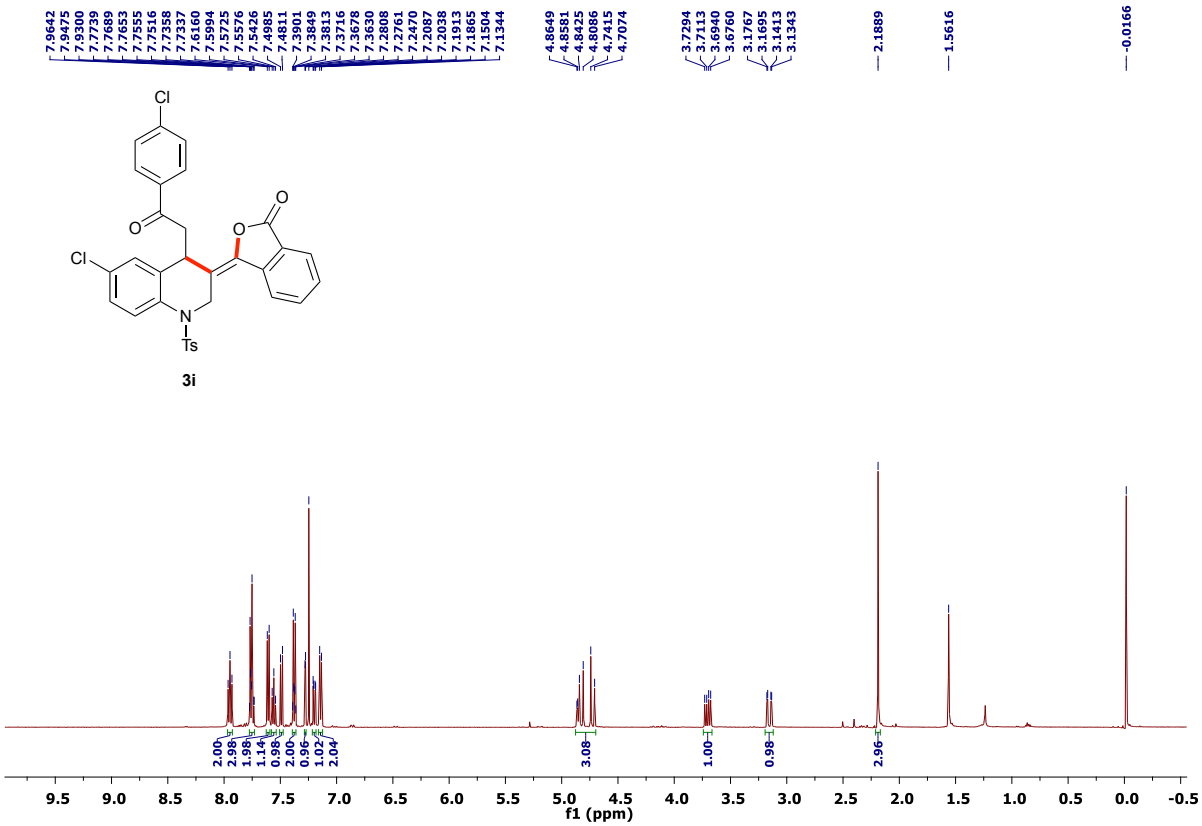
^{1}H NMR spectra of compound **3h** ($CDCl_3$, 400 MHz)



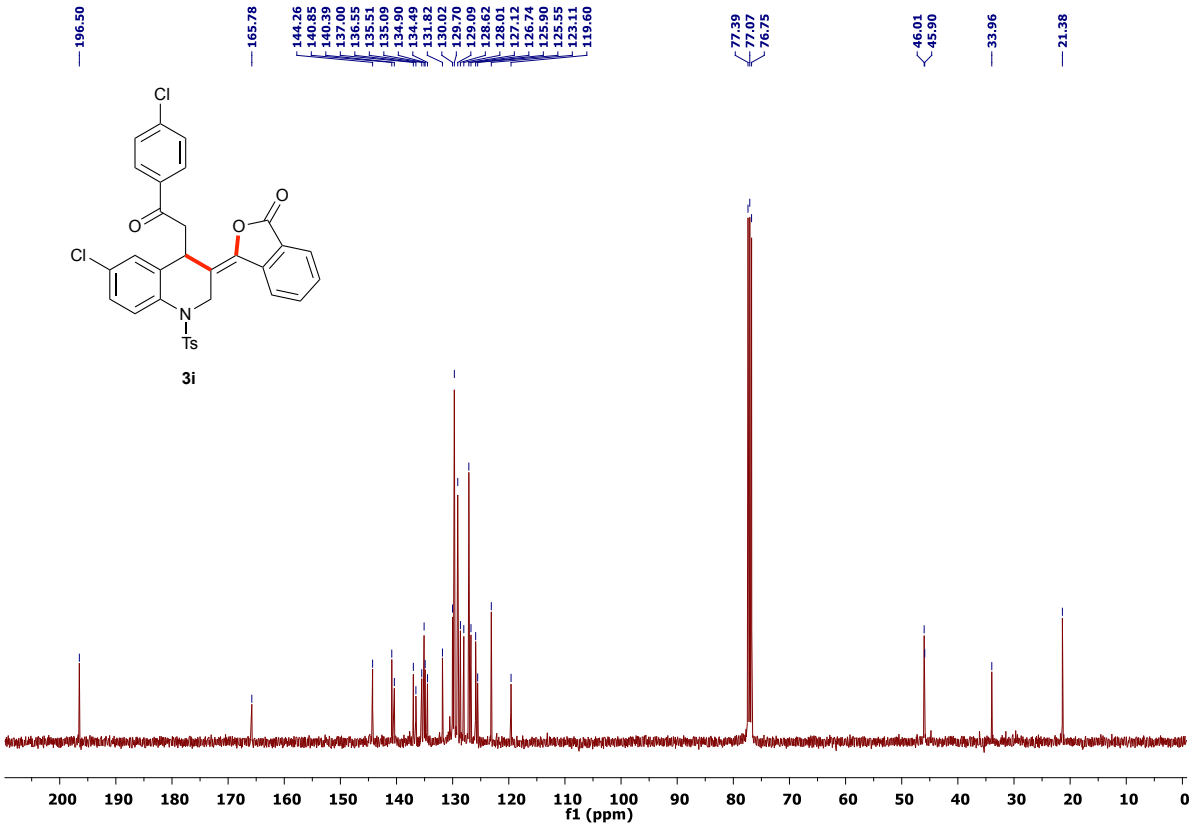
^{13}C{^{1}H} NMR spectra of compound **3h** ($CDCl_3$, 101 MHz)



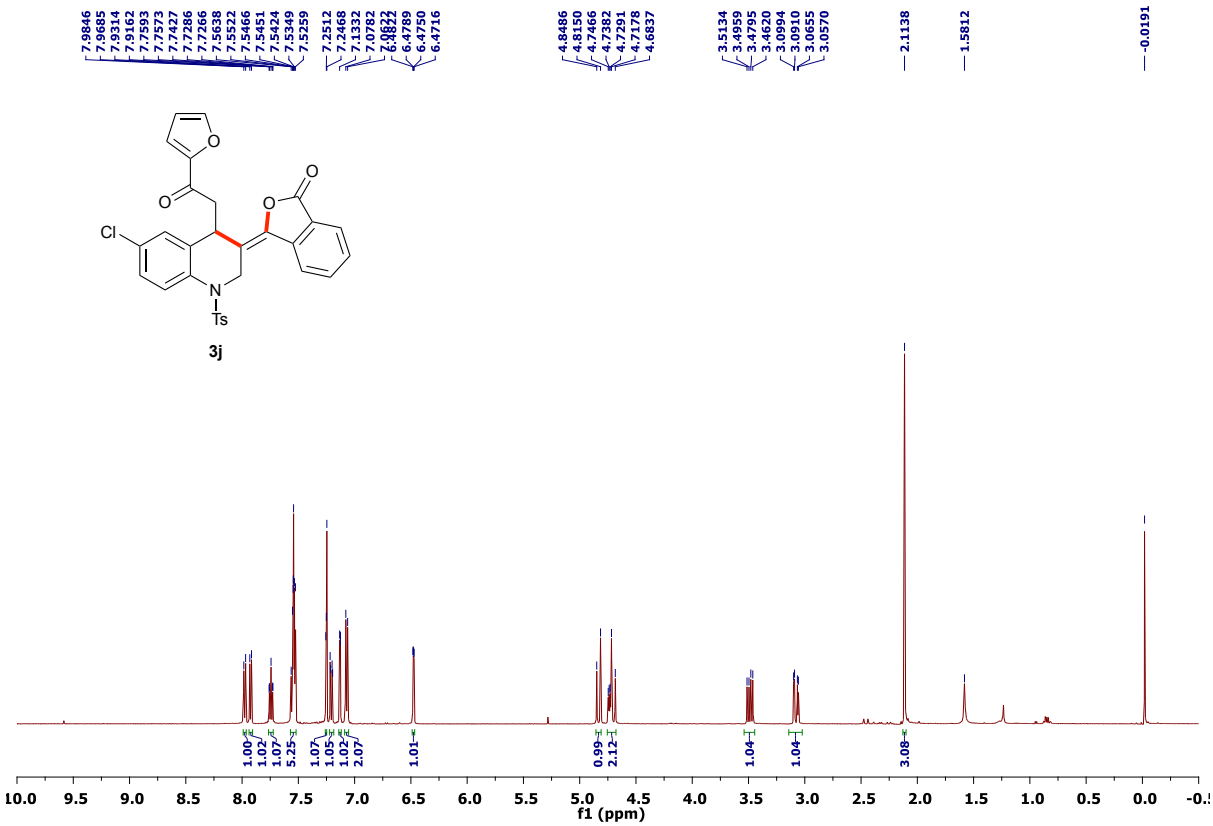
^{1}H NMR spectra of compound **3i** ($CDCl_3$, 500 MHz)



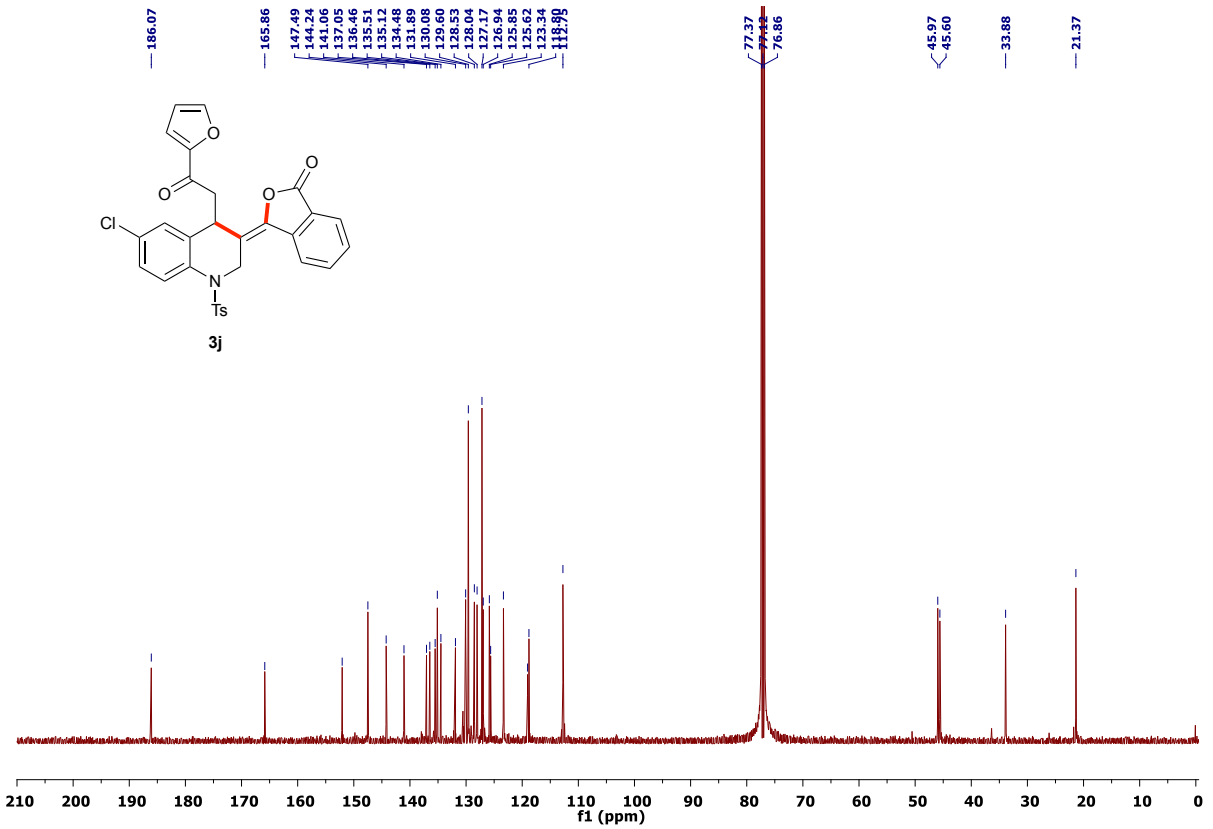
^{13}C{^{1}H} NMR spectra of compound **3i** ($CDCl_3$, 101 MHz)



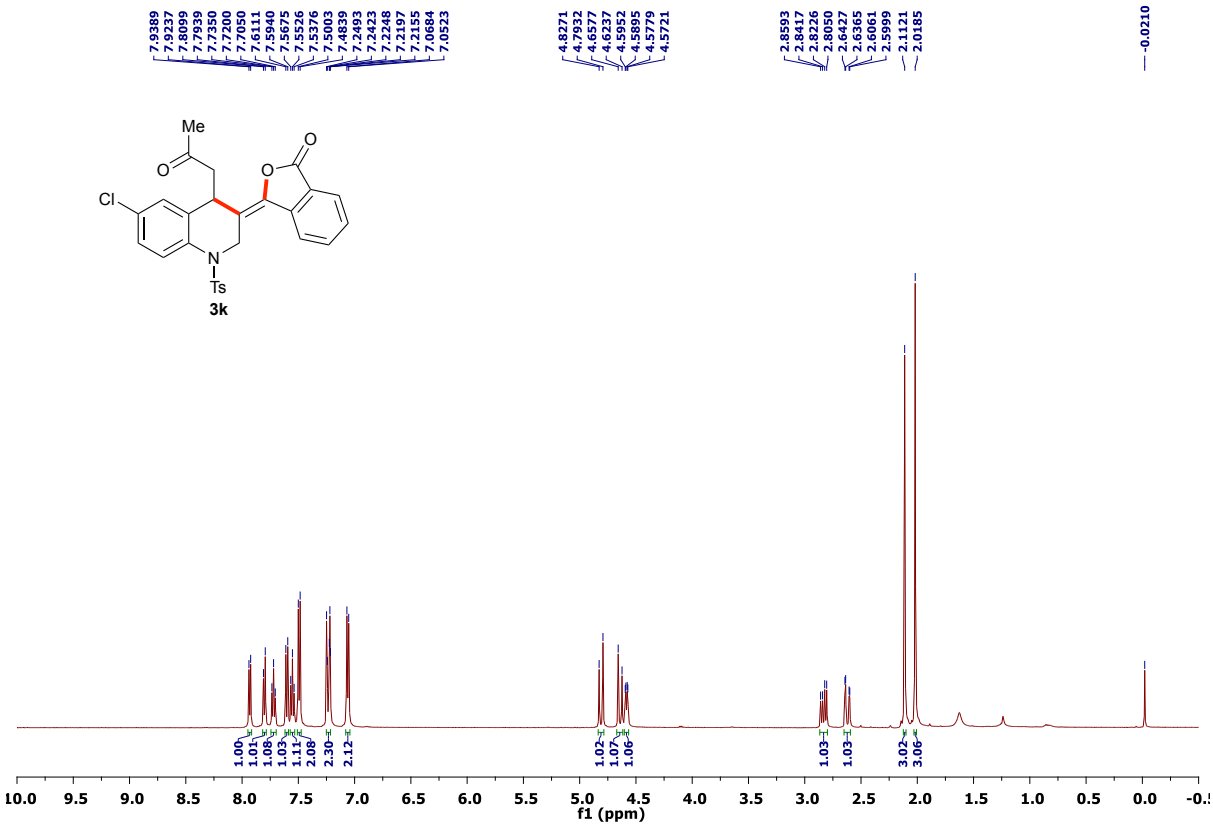
^{1}H NMR spectra of compound **3j** ($CDCl_3$, 500 MHz)



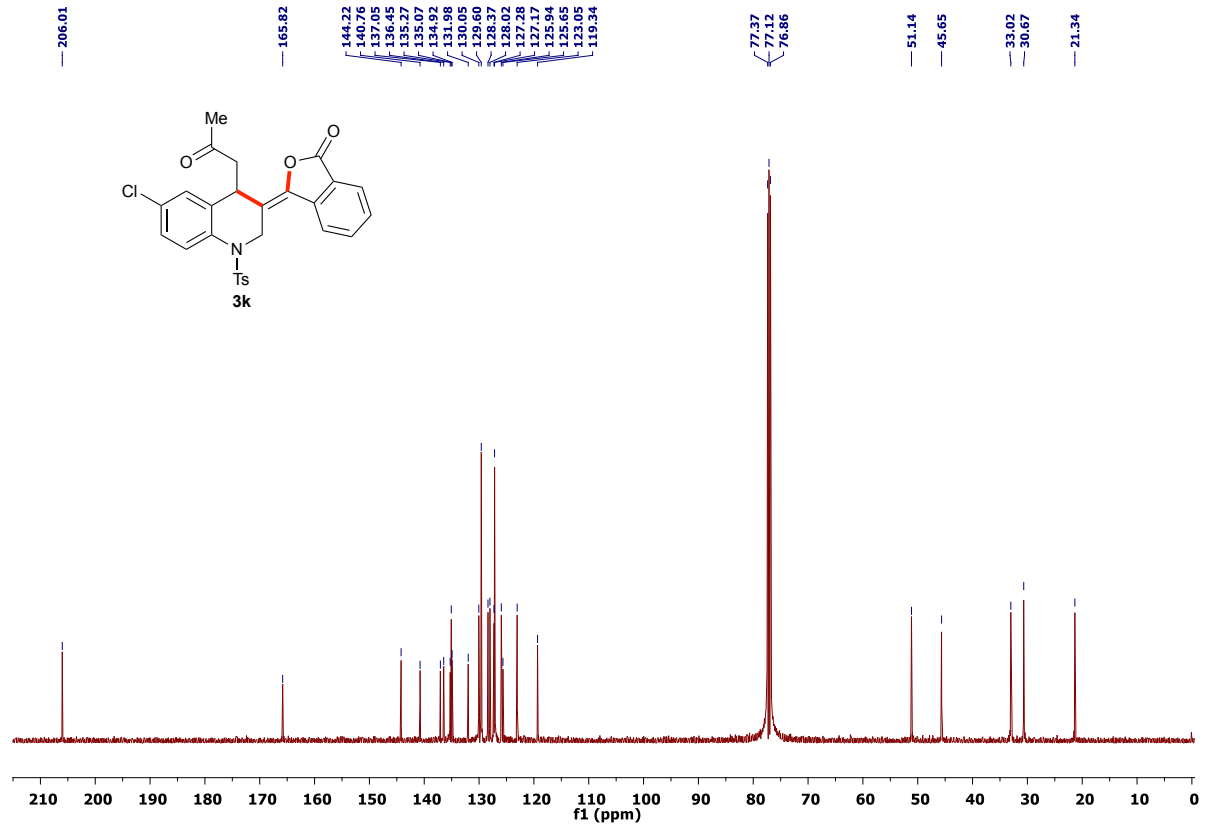
^{13}C{^{1}H} NMR spectra of compound **3j** ($CDCl_3$, 126 MHz)



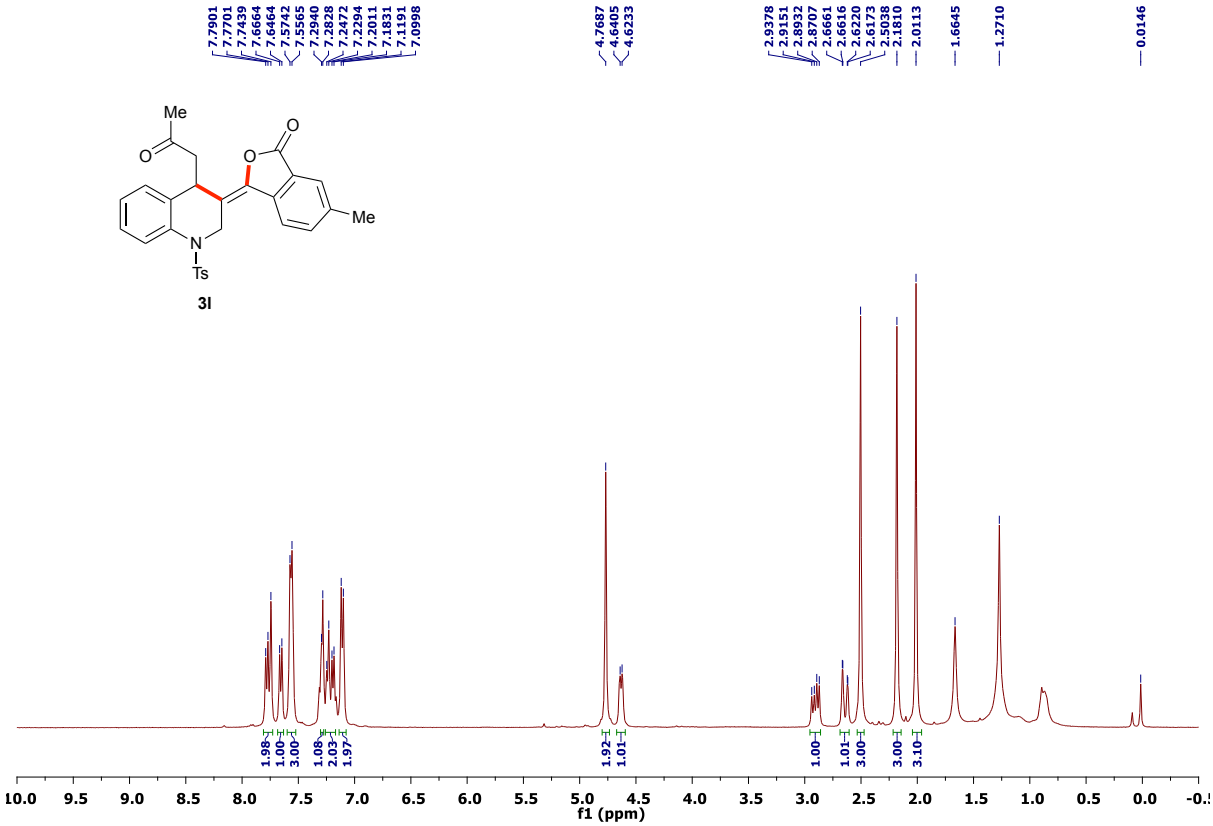
^{1}H NMR spectra of compound **3k** ($CDCl_3$, 500 MHz)



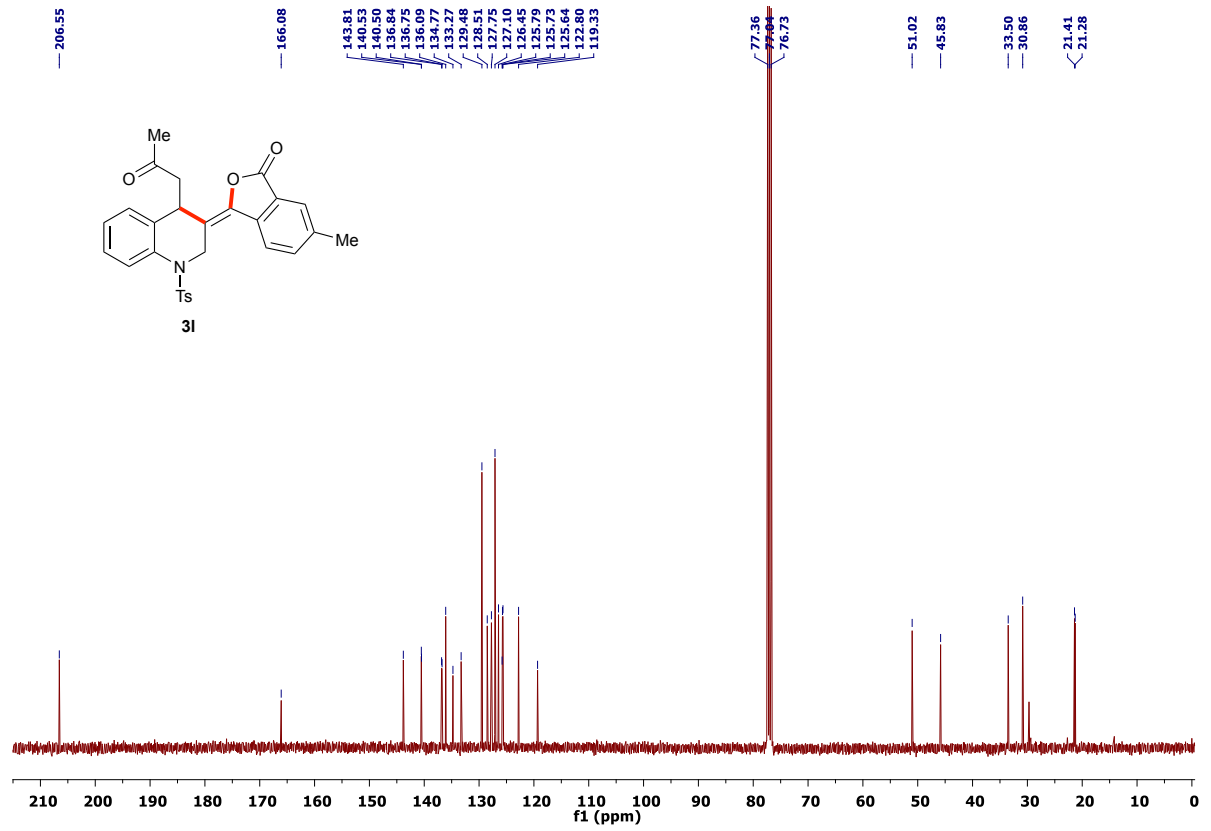
^{13}C{^{1}H} NMR spectra of compound **3k** ($CDCl_3$, 126 MHz)



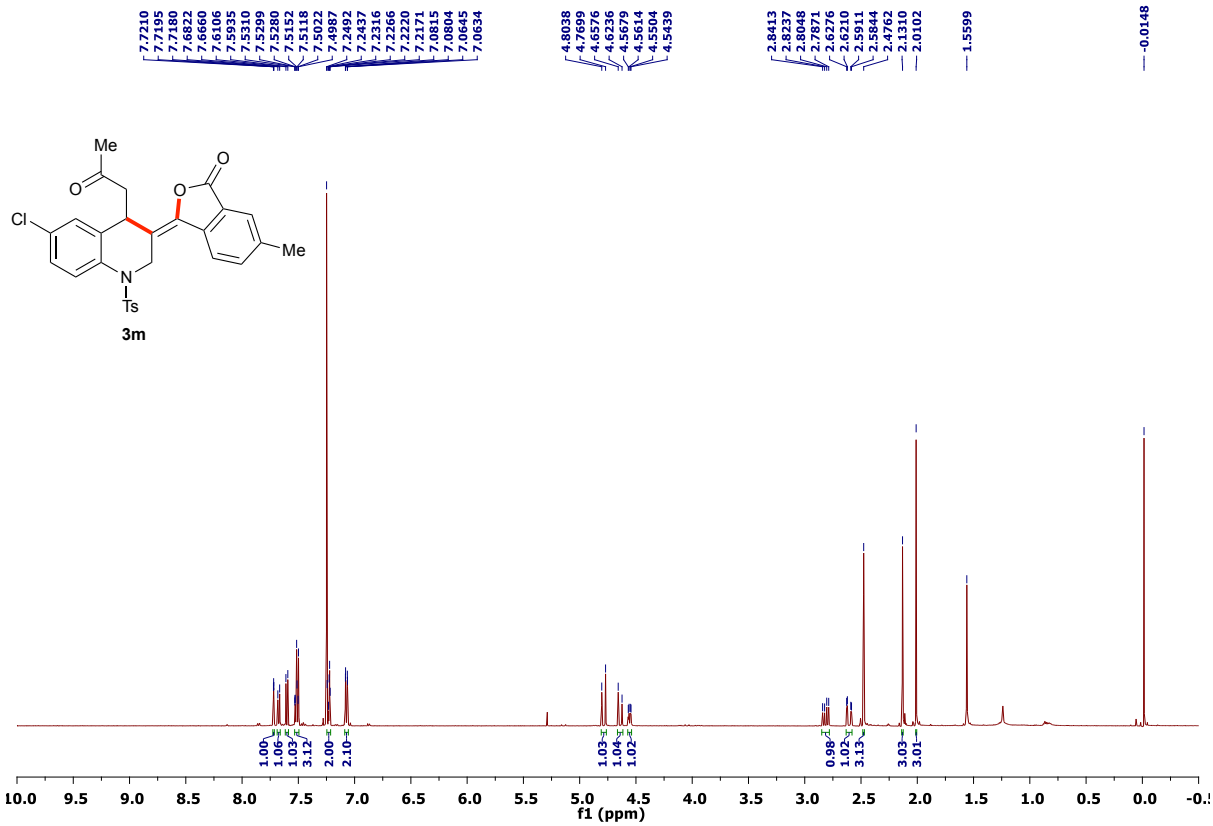
^{1}H NMR spectra of compound **3l** ($CDCl_3$, 400 MHz)



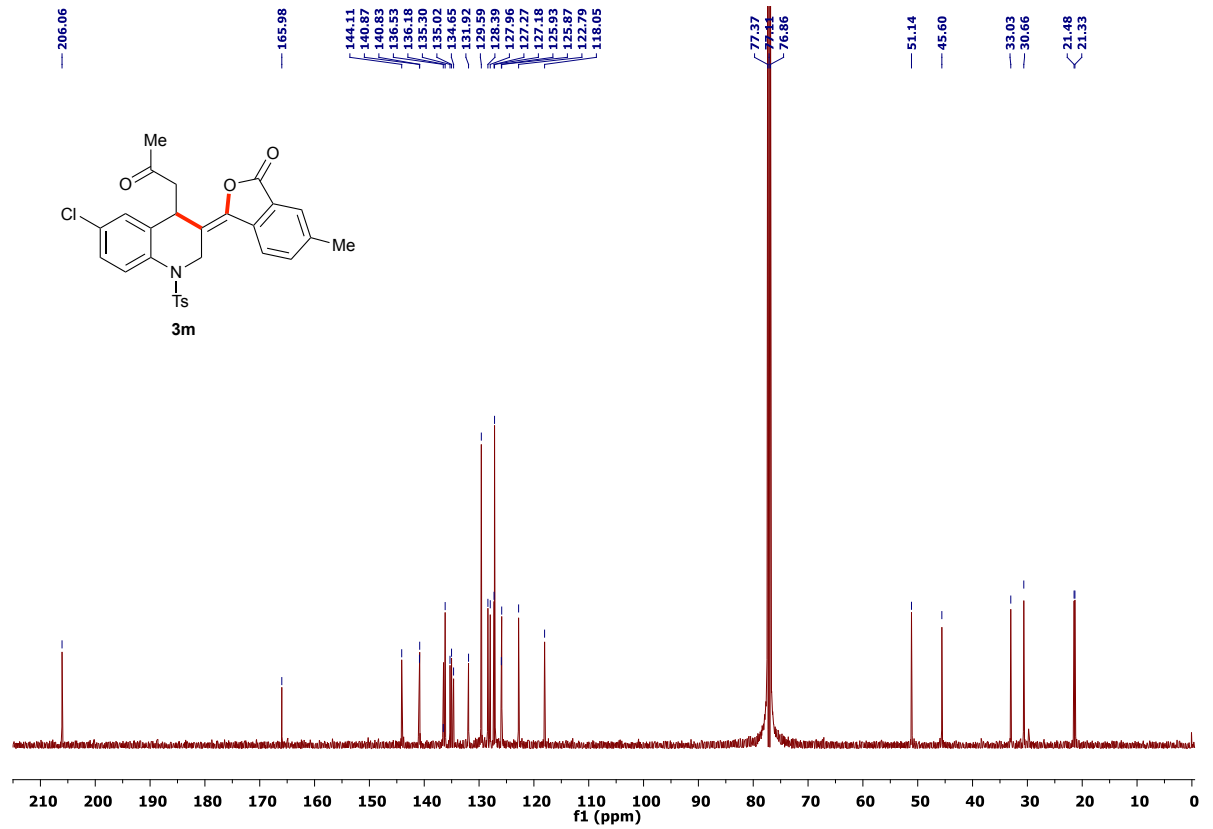
^{13}C{^{1}H} NMR spectra of compound **3l** ($CDCl_3$, 101 MHz)



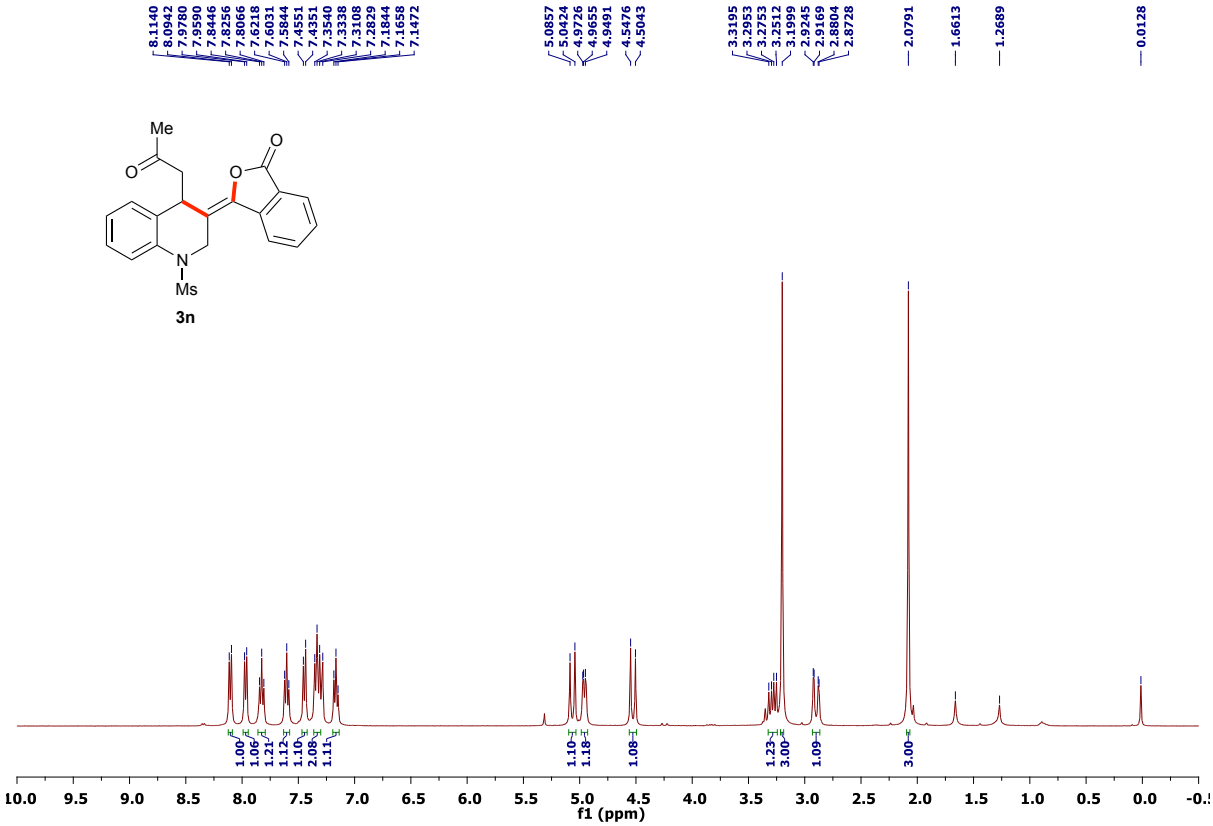
^{1}H NMR spectra of compound **3m** ($CDCl_3$, 500 MHz)



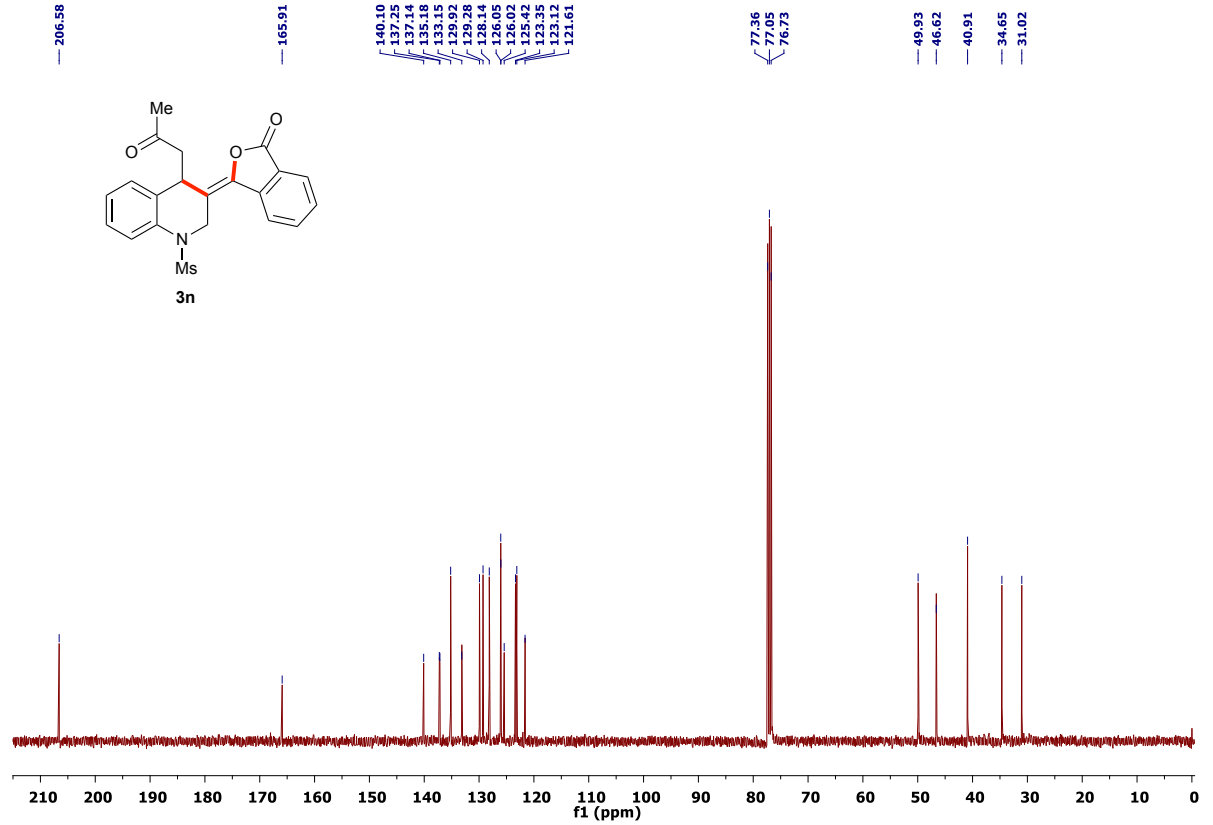
^{13}C{^{1}H} NMR spectra of compound **3m** ($CDCl_3$, 126 MHz)



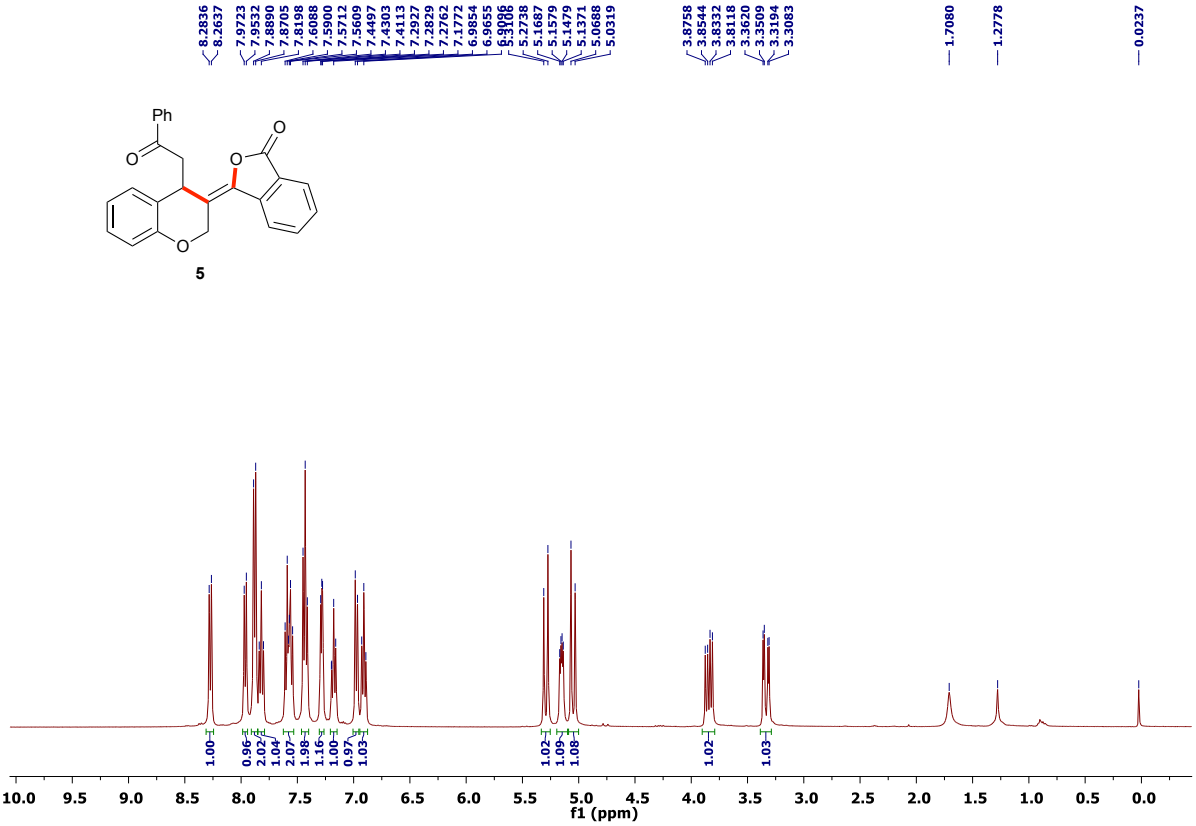
^{1}H NMR spectra of compound **3n** ($CDCl_3$, 400 MHz)



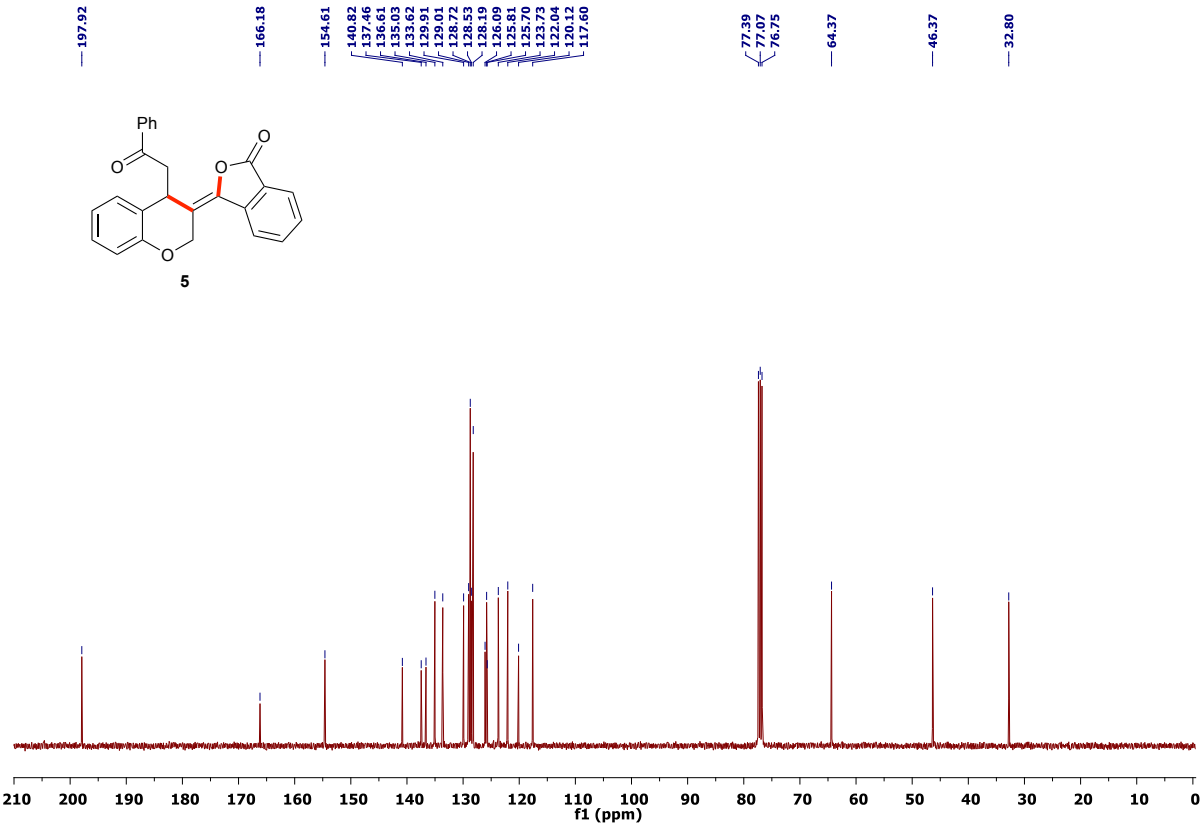
^{13}C{^{1}H} NMR spectra of compound **3n** ($CDCl_3$, 101 MHz)



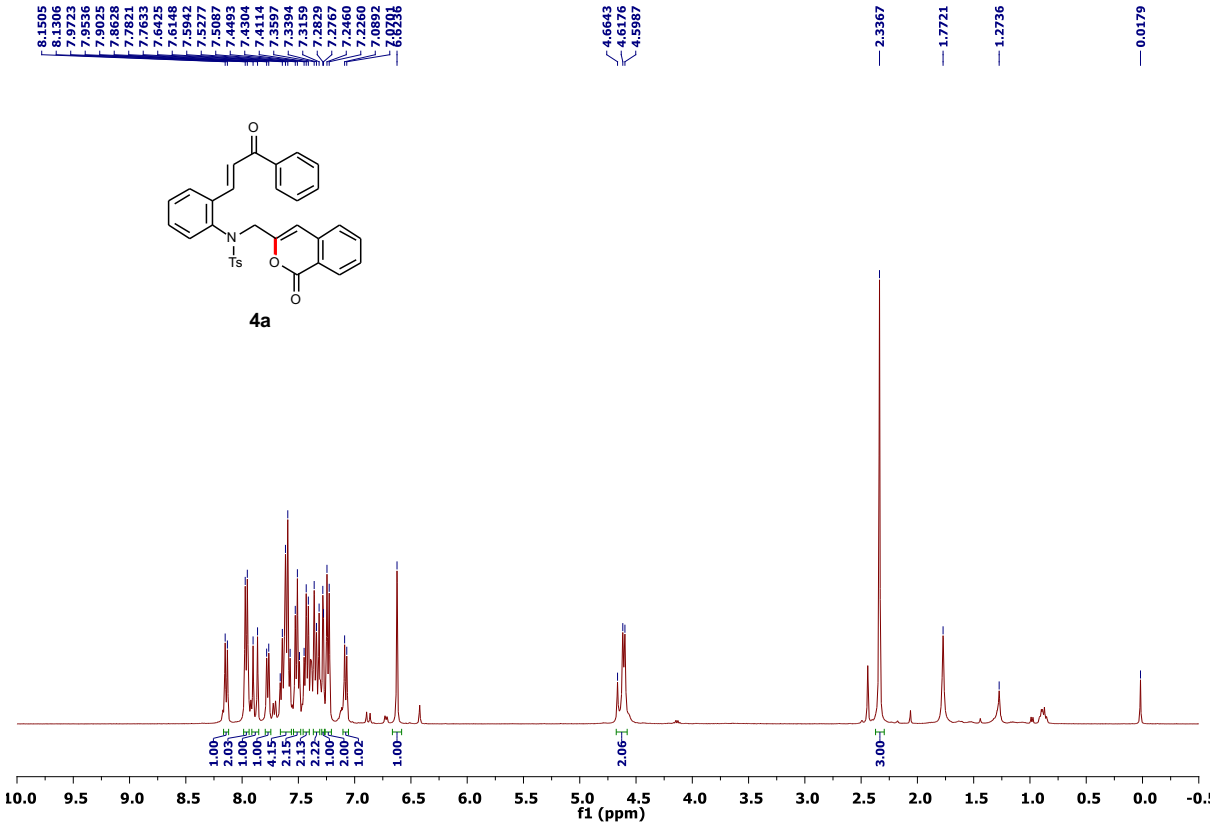
^{1}H NMR spectra of compound **5** ($CDCl_3$, 400 MHz)



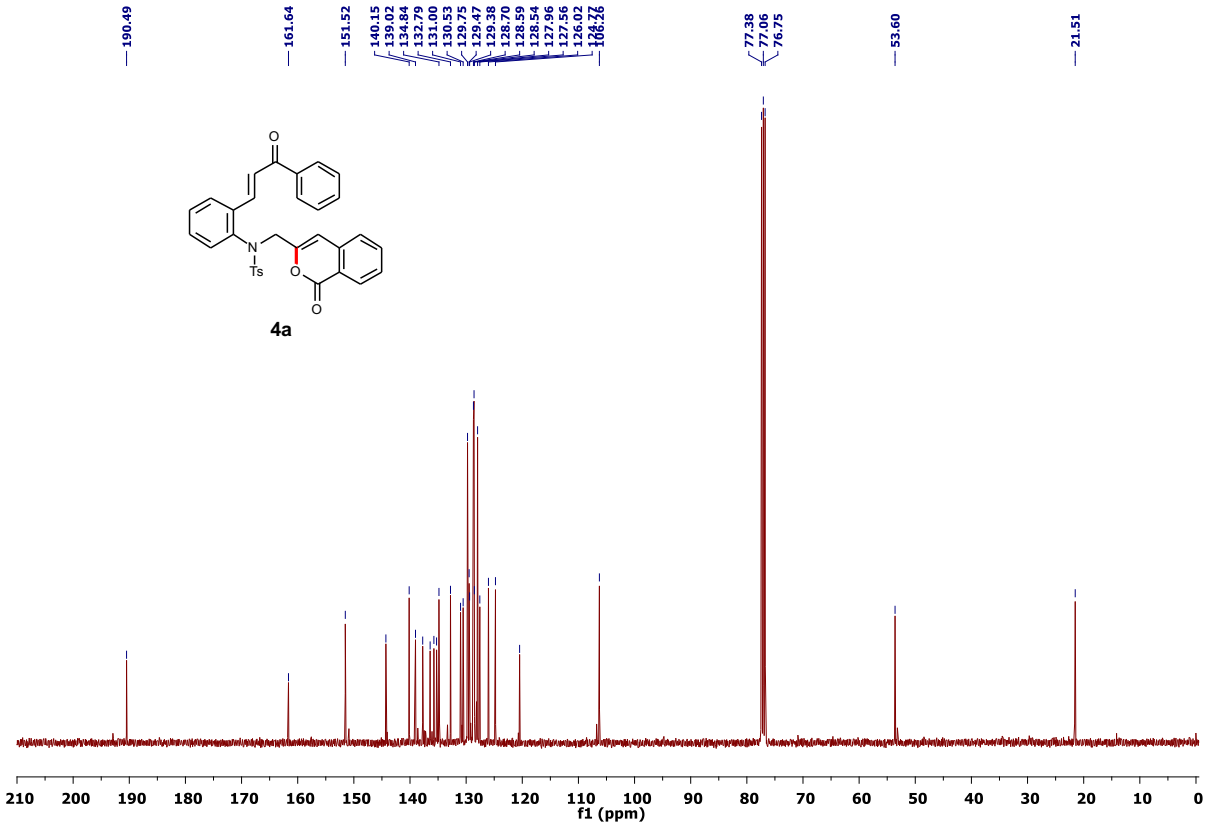
^{13}C{^{1}H} NMR spectra of compound **5** ($CDCl_3$, 101 MHz)



^{1}H NMR spectra of compound **4a** ($CDCl_3$, 400 MHz)



^{13}C{^{1}H} NMR spectra of compound **4a** ($CDCl_3$, 101 MHz)



12. NOESY Spectrum of Compound 3b ($CDCl_3$, 400 MHz)