Supporting Information

A new cascade halosulfonylation of 1,7-enynes toward 3,4-dihydroquinolin-2(1*H*)-ones *via* sulfonyl radical-triggered addition/6-*exo*-*dig* cyclization

Yi-Long Zhu,[a,b] Bo Jiang,*[,a,c] Wen-Juan Hao,[a] Ai-Fang Wang,[a] Jiang-Kai Qiu,[a,b] Ping Wei,*[,b] De-Cai Wang,[b] Guigen Li,[c,d] and Shu-Jiang Tu*[,a]

[a] *School of Chemistry and Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou, 211116, P. R. China; E-mail: jiangchem@jsnu.edu.cn (B. Jiang); laotu@jsnu.edu.cn (S.-J. Tu); Tel./fax: +86 516 83500065 ;*

[b] *Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing, 210009, Jiangsu, P. R. China, E-mail: weiping@njtech.edu.cn;*

[c] *Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061, USA;*

[d] *Institute of Chemistry & BioMedical Sciences, Nanjing University, Nanjing 210093, P. R. China;*

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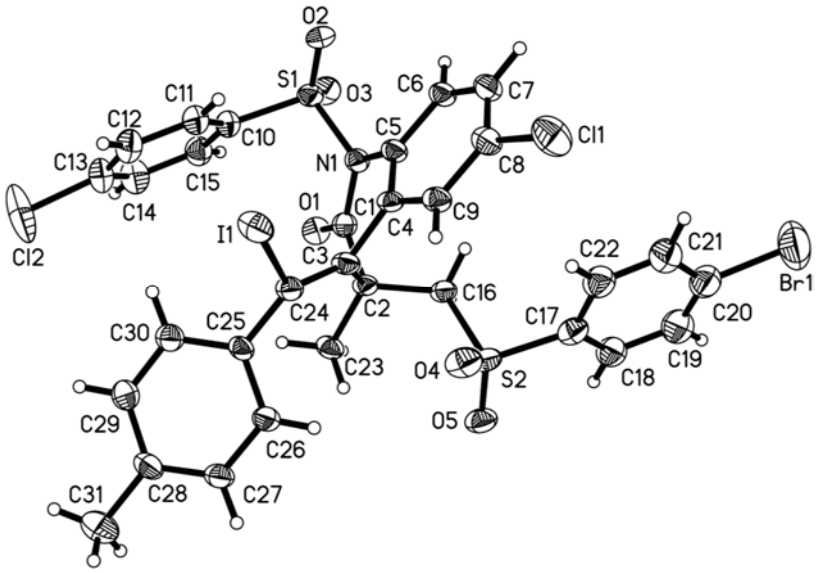


Figure 1. X-Ray Structure of Product **3y**

General Information

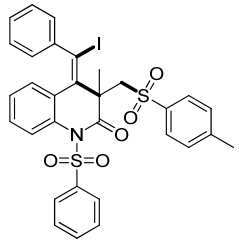
All one-pot reactions were carried out in a 10-mL Schlenk tube equipped with a magnetic stir bar under air. All melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 MHz instrument with TMS as internal standard. Chemical shifts (δ) were reported in ppm with respect to TMS. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiples), coupling constant (J, Hz) and integration. HRMS analyses were carried out using a TOF-MS instrument with an ESI source. X-Ray crystallographic analysis was performed with a SMART CCD and a P4 diffractometer.

Typical Experimental Procedure

General Procedure for the Synthesis of Products 3

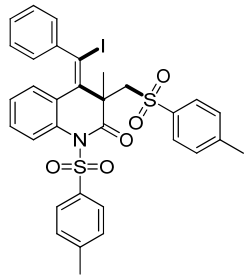
A mixture of 1,7-Enynes (**1**, 1.0 equiv., 0.5 mmol), arylsulfonyl hydrazid (**2**, 2.0 equiv., 1.0 mmol), NIS (1.2 equiv., 0.6 mmol) and anhydrous TBHP (2.0 equiv. 1.0 mmol, 5.5 M in decane) in acetonitrile (2.0 mL) was heated at 60 °C for 8 hours. After completion of the reaction as indicated by TLC, the mixture was evaporated under vacuum and washed by methanol to afford the desired product **3** as a white solid.

4-(Iodo(phenyl)methylene)-3-methyl-1-(phenylsulfonyl)-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3a)



white solid, mp 267-269 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.11-8.05 (m, 1H), 8.04-7.99 (m, 2H), 7.82-7.75 (m, 1H), 7.72-7.64 (m, 3H), 7.61 (d, *J* =7.6 Hz, 1H), 7.57-7.48 (m, 2H), 7.41 (d, *J* =8.4 Hz, 2H), 7.37-7.30 (m, 1H), 7.28-7.11 (m, 4H), 6.45 (d, *J* =7.6 Hz, 1H), 2.79 (s, 2H), 2.41 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 167.8, 145.0, 144.9, 138.5, 137.7, 136.4, 135.5, 134.1, 132.9, 132.4, 129.9, 129.3, 128.9, 128.4, 128.0, 127.8, 127.3, 127.0, 126.7, 124.5, 103.4, 60.7, 53.0, 21.6, 21.4. IR (film, ν, cm^{-1}) 3058, 2938, 1713, 1596, 1480, 1389, 1267, 1197, 1174, 1085, 963, 779. HR-MS (ESI) m/z calcd for $C_{31}H_{26}INO_5S_2$ $[M+Na]^+$ 706.5661, found 706.5654.

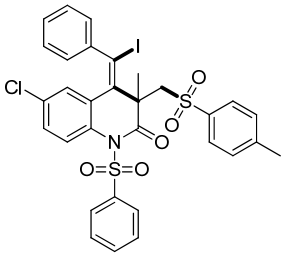
4-(Iodo(phenyl)methylene)-3-methyl-1-tosyl-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3b)



white solid, mp 281-283 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.12-8.02 (m, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.71-7.64 (m, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.55-7.49 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.37-7.31 (m, 1H), 7.27-7.18 (m, 3H), 7.18-7.10 (m, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 2.78 (s, 2H), 2.55 (s, 3H), 2.41 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 167.9, 145.4, 145.0, 137.7, 136.5, 135.6, 133.0, 132.3, 129.9, 129.5, 129.3, 129.1, 128.3, 128.1, 128.0, 127.7, 127.3, 126.9, 126.6, 124.6, 103.3, 60.7, 53.0, 21.7, 21.6, 21.4. IR (film, ν, cm^{-}

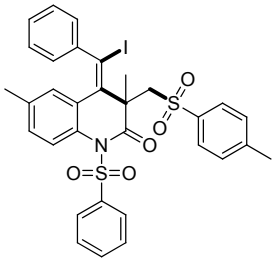
[1]) 3058, 3011 1723, 1596, 1489, 1371, 1267, 1198, 1085, 1042, 963, 813. HR-MS (ESI) m/z calcd for $C_{32}H_{28}INO_5S_2$ $[M+Na]^+$ 720.0352, found 720.0356.

6-Chloro-4-(iodo(phenyl)methylene)-3-methyl-1-(phenylsulfonyl)-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3c)



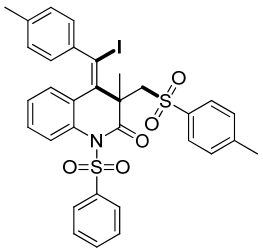
white solid, mp 270-272 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09-7.97 (m, 3H), 7.85-7.77 (m, 1H), 7.73-7.66 (m, 2H), 7.65-7.56 (m, 2H), 7.52-7.42 (m, 3H), 7.38-7.29 (m, 3H), 7.26-7.19 (m, 1H), 7.18-7.11 (m, 1H), 6.36 (d, J = 7.6 Hz, 1H), 2.83 (d, J = 14.0 Hz, 1H), 2.72 (d, J = 13.6 Hz, 1H), 2.43 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.5, 145.2, 144.5, 138.2, 137.7, 137.2, 135.4, 134.3, 132.6, 132.0, 131.4, 130.1, 129.3, 129.0, 128.5, 128.1, 127.8, 127.3, 126.8, 126.0, 104.4, 60.8, 52.9, 21.6, 21.2. IR (film, ν, cm^{-1}) 3078, 3065, 1722, 1596, 1470, 1447, 1377, 1287, 1222, 1174, 1083, 891, 835. HR-MS (ESI) m/z calcd for $C_{31}H_{25}ClINO_5S_2$ $[M+Na]^+$ 739.9805, found 739.9803.

4-(Iodo(phenyl)methylene)-3,6-dimethyl-1-(phenylsulfonyl)-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3d)



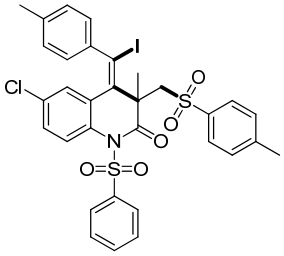
white solid, mp 261-263 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.06-7.97 (m, 2H), 7.85 (d, J = 1.2 Hz, 1H), 7.82-7.75 (m, 1H), 7.72-7.64 (m, 2H), 7.59 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.36-7.29 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.23-7.18 (m, 1H), 7.16-7.10 (m, 1H), 6.38 (d, J = 7.6 Hz, 1H), 2.82 (d, J = 14.0 Hz, 1H), 2.78 (d, J = 14.0 Hz, 1H), 2.58 (s, 3H), 2.42 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.8, 145.0, 144.9 138.5, 137.8, 136.9, 136.5, 135.5, 134.0, 132.4, 130.5, 129.9, 128.9, 128.3, 128.0, 127.9, 127.8, 127.3, 127.0, 124.6, 103.1, 60.9, 53.0, 21.6, 21.3, 21.2. IR (film, ν, cm^{-1}) 3056, 3028, 1712, 1594, 1489, 1382, 1288, 1197, 1084, 963, 850. HR-MS (ESI) m/z calcd for $C_{32}H_{28}INO_5S_2$ $[M+Na]^+$ 720.0352, found 720.0348.

4-(Iodo(p-tolyl)methylene)-3-methyl-1-(phenylsulfonyl)-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3e)



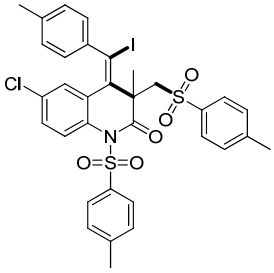
white solid, mp 275-277 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.10-7.98 (m, 3H), 7.82-7.74 (m, 1H), 7.73-7.63 (m, 3H), 7.57-7.46 (m, 3H), 7.41 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.2 Hz, 1H), 6.97 (d, J = 7.6 Hz, 1H), 6.34 (d, J = 6.4 Hz, 1H), 2.78 (s, 2H), 2.41 (s, 3H), 2.33 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.9, 145.0, 142.2, 138.6, 138.4, 137.7, 136.2, 134.0, 132.9, 132.5, 129.9, 129.3, 129.0, 128.9, 128.6, 128.5, 127.9, 127.3, 126.9, 126.7, 124.5, 104.0, 60.7, 52.9, 21.6, 21.4, 21.3. IR (film, ν, cm^{-1}) 3063, 3001, 716, 1596, 1506, 1478, 1369, 1191, 1085, 817, 784. HR-MS (ESI) m/z calcd for $C_{32}H_{28}INO_5S_2$ $[M+Na]^+$ 720.0352, found 720.0348.

6-Chloro-4-(iodo(p-tolyl)methylene)-3-methyl-1-(phenylsulfonyl)-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3f)



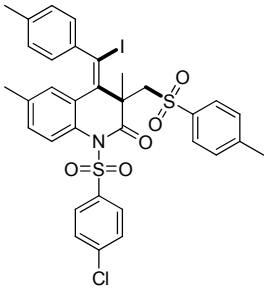
white solid, mp 276-278 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.06-7.97 (m, 3H), 7.84-7.75 (m, 1H), 7.73-7.65 (m, 2H), 7.61 (d, J = 8.8 Hz, 1H), 7.52-7.42 (m, 4H), 7.30 (s, 2H), 7.14 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.26 (d, J = 8.0 Hz, 1H), 2.82 (d, J = 14.0 Hz, 1H), 2.71 (d, J = 13.6 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.5, 145.2, 141.7, 138.6, 138.2, 137.7, 137.3, 135.2, 134.2, 132.5, 132.0, 131.4, 130.1, 129.2, 129.0, 128.7, 128.6, 127.7, 127.3, 126.7, 126.0, 105.0, 60.8, 52.9, 21.6, 21.3. IR (film, ν, cm^{-1}) 3108, 3053, 1723, 1595, 1468, 1368, 1192, 1083, 961, 892, 833, 815. HR-MS (ESI) m/z calcd for $C_{32}H_{27}ClINO_5S_2$ $[M+Na]^+$ 753.9962, found 753.9966.

6-Chloro-4-(iodo(p-tolyl)methylene)-3-methyl-1-tosyl-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3g)



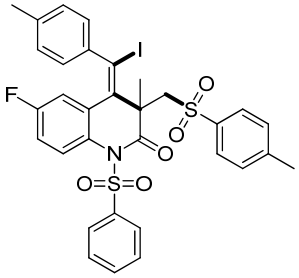
white solid, mp 265-267 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.01 (d, J = 2.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.8 Hz, 1H), 7.52-7.41 (m, 6H), 7.30 (s, 1H), 7.26 (s, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.29-6.21 (m, 1H), 2.81 (d, J = 13.6 Hz, 1H), 2.70 (d, J = 13.6 Hz, 1H), 2.56 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.5, 145.6, 145.2, 141.8, 138.5, 137.7, 137.3, 135.2, 132.4, 131.9, 131.4, 130.0, 129.5, 129.1, 128.8, 128.5, 127.7, 127.3, 126.6, 126.0, 104.8, 60.9, 52.9, 21.8, 21.6, 21.3, 21.2. IR (film, ν, cm^{-1}) 3027, 2998, 1720, 1596, 1505, 1470, 1368, 1272, 1193, 1083, 961, 829. HR-MS (ESI) m/z calcd for $C_{33}H_{29}ClINO_5S_2$ $[M+Na]^+$ 768.0118, found 768.0115.

1-((4-Chlorophenyl)sulfonyl)-4-(iodo(p-tolyl)methylene)-3,6-dimethyl-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3h)



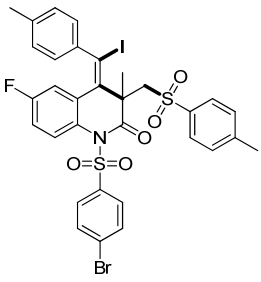
white solid, mp 239-241 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.99-7.90 (m, 2H), 7.83 (d, J = 1.2 Hz, 1H), 7.70-7.61 (m, 2H), 7.54-7.45 (m, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.32-7.29 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.36-6.28 (m, 1H), 2.81 (d, J = 14.0 Hz, 1H), 2.76 (d, J = 14.0 Hz, 1H), 2.57 (s, 3H), 2.42 (s, 3H), 2.34 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 168.0, 145.1, 142.0, 140.9, 138.5, 137.8, 137.1, 136.7, 136.2, 135.7, 132.4, 130.5, 130.2, 123.0, 129.9, 129.1, 128.7, 127.8, 127.3, 126.8, 124.7, 104.0, 60.9, 53.0, 21.6, 21.4, 21.3, 21.2. IR (film, ν, cm^{-1}) 3094, 2922, 1717, 1583, 1505, 1489, 1374, 1321, 11171, 1014, 965, 824. HR-MS (ESI) m/z calcd for $C_{33}H_{29}ClINO_5S_2$ $[M+Na]^+$ 768.0118, found 768.0117.

6-Fluoro-4-(iodo(p-tolyl)methylene)-3-methyl-1-(phenylsulfonyl)-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3i)



white solid, mp 274-276 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.05-7.96 (m, 2H), 7.83-7.72 (m, 2H), 7.72-7.62 (m, 3H), 7.46 (d, J = 8.0 Hz, 3H), 7.29 (s, 1H), 7.27 (s, 1H), 7.24-7.17 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.27 (d, J = 6.4, 1H), 2.81 (d, J = 14.0 Hz, 1H), 2.74 (d, J = 14.0, 1H), 2.43 (s, 3H), 2.33 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.6, 160.6 (J_{CF} = 247.4 Hz), 145.2, 141.8, 138.6, 138.3, 137.6, 135.4, 134.2, 130.0, 129.0 (J_{CF} = 4.9 Hz), 128.7, 128.6 (J_{CF} = 13.3 Hz), 127.7, 127.3, 126.7, 126.52 (J_{CF} = 8.6 Hz), 119.1 (J_{CF} = 24.1 Hz), 116.3 (J_{CF} = 22.8 Hz), 105.0, 60.8, 53.0, 21.6, 21.4, 21.3. IR (film, ν, cm^{-1}) 3089, 3026, 1725, 1594, 1481, 1449, 1320, 1260, 1196, 1084, 888. HR-MS (ESI) m/z calcd for $C_{32}H_{27}FINO_5S_2$ $[M+Na]^+$ 738.0257, found 738.0251.

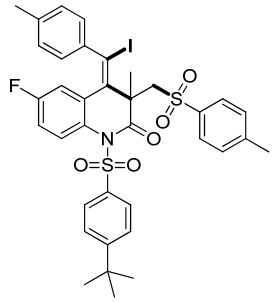
1-((4-Bromophenyl)sulfonyl)-6-fluoro-4-(iodo(p-tolyl)methylene)-3-methyl-3-(tosylmethyl)-3,4-dihydroquinolin-2(1H)-one (3j)



white solid, mp 273-275 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.90-7.79 (m, 4H), 7.78-7.70 (m, 1H), 7.61 (dd, J = 9.2 Hz, 4.8 Hz, 1H), 7.46 (d, J = 8.0 Hz, 3H), 7.29 (s, 1H), 7.27 (s, 1H), 7.24-7.12 (m, 2H), 7.05 (d, J = 8.0 Hz, 1H),

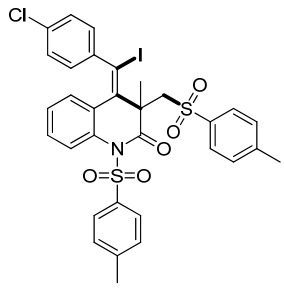
6.34-6.27 (m, 1H), 2.81 (d, J = 14.0 Hz, 1H), 2.72 (d, J = 13.6 Hz, 1H), 2.43 (s, 3H), 2.35 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.7, 160.7 (J_{CF} = 247.8 Hz), 145.3, 141.7, 138.8, 137.8, 137.7, 137.6, 136.9, 135.3, 132.2, 130.6, 130.0, 129.8, 128.8 (J_{CF} = 10.4 Hz), 128.7 (J_{CF} = 3.0 Hz), 127.3, 126.6 (J_{CF} = 8.2 Hz), 119.2 (J_{CF} = 23.9 Hz), 116.4 (J_{CF} = 23.0 Hz), 105.4, 60.7, 53.0, 21.6, 21.5, 21.3. IR (film, ν, cm^{-1}) 3102, 3031, 1725, 1593, 1573, 1482, 1447, 1393, 1262, 1192, 1084, 1013, 827. HR-MS (ESI) m/z calcd for $C_{32}H_{26}BrFINO_5S_2$ $[M+Na]^+$ 815.9362, found 815.9363.

1-((4-(*tert*-Butyl)phenyl)sulfonyl)-6-fluoro-4-(iodo(p-tolyl)methylene)-3-methyl-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3k)



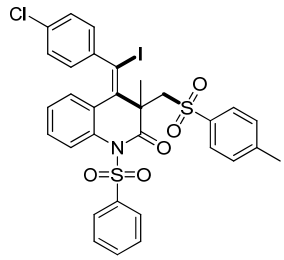
white solid, mp 275-277 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.91 (d, J = 8.4 Hz, 2H), 7.78-7.61 (m, 4H), 7.46 (d, J = 8.0 Hz, 3H), 7.29 (s, 1H), 7.27 (s, 1H), 7.24-7.10 (m, 2H), 6.89 (d, J = 8.0 Hz, 1H), 6.26 (d, J = 7.2 Hz, 1H), 2.81 (d, J = 14.0 Hz, 1H), 2.74 (d, J = 13.6 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 3H), 1.44 (s, 9H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.6, 160.6 (J_{CF} =247.5 Hz), 158.4, 145.2, 141.9, 138.5, 137.7 (J_{CF} =4.2 Hz), 137.6, 135.5, 135.1, 130.0, 129.1 (J_{CF} =2.9 Hz), 128.9, 128.7, 128.3, 127.8, 127.3, 126.7, 126.6 (J_{CF} =2.6 Hz), 126.0, 119.0 (J_{CF} =24.1 Hz), 116.3 (J_{CF} = 22.8 Hz), 104.7, 60.8, 53.0, 35.5, 31.1, 21.6, 21.4, 21.3. IR (film, ν, cm^{-1}) 3026, 3009, 2959, 1717, 1595, 1505, 1485, 1370, 1299, 1195, 1172, 1086, 822. HR-MS (ESI) m/z calcd for $C_{36}H_{35}FINO_5S_2$ $[M+Na]^+$ 794.0883, found 794.0876.

4-((4-Chlorophenyl)iodomethylene)-3-methyl-1-tosyl-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3l)



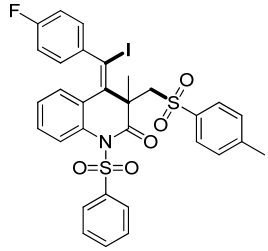
white solid, mp 272-274 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.08-8.02 (m, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.70-7.63(m, 1H), 7.58 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.55-7.48 (m, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.33 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.15 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 6.40 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 2.79 (d, J = 14.0 Hz, 1H), 2.75 (d, J = 14.0 Hz, 1H), 2.55 (s, 3H), 2.41 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.7, 145.4, 145.1, 143.5, 137.7, 137.4, 135.5, 135.3, 134.3, 132.9, 132.2, 129.9, 129.5, 129.1, 128.4, 128.3, 128.1, 127.3, 126.6, 124.6, 101.3, 60.6, 53.1, 21.7, 21.6. IR (film, ν, cm^{-1}) 3058, 2958, 1723, 1595, 1486, 1393, 1299, 1193, 1086, 963, 828. HR-MS (ESI) m/z calcd for $C_{32}H_{27}ClINO_5S_2$ $[M+Na]^+$ 754.0378, found 754.0372.

4-((4-Chlorophenyl)iodomethylene)-3-methyl-1-(phenylsulfonyl)-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3m)



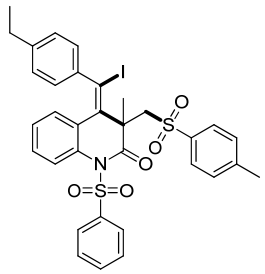
white solid, mp 275-277 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.13-7.95 (m, 3H), 7.82-7.74 (m, 1H), 7.72-7.63 (m, 3H), 7.62-7.48 (m, 3H), 7.40 (d, J = 8.4 Hz, 2H), 7.36-7.30 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.19-7.12 (m, 1H), 6.40 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 2.80 (d, J = 14.0 Hz, 1H), 2.76 (d, J = 14.0 Hz, 1H), 2.41 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.7, 145.1, 143.4, 138.5, 137.6, 137.3, 135.3, 134.3, 134.1, 132.9, 132.4, 129.9, 129.5, 129.0, 128.9, 128.5, 128.3, 127.3, 126.8, 124.5, 101.5, 60.6, 53.1, 21.7, 21.6. IR (film, ν, cm^{-1}) 3097, 3030, 1719, 1596, 1583, 1485, 1367, 1262, 1191, 1084, 1015, 962, 886, 835. HR-MS (ESI) m/z calcd for $C_{31}H_{25}ClINO_5S_2$ $[M+Na]^+$ 739.9805, found 739.9808.

4-((4-Fluorophenyl)iodomethylene)-3-methyl-1-(phenylsulfonyl)-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3n)



white solid, mp 268-270 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.10-8.04 (m, 1H), 8.04-7.98 (m, 2H), 7.81-7.74 (m, 1H), 7.72-7.59 (m, 4H), 7.56-7.49 (m, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.06-6.98 (m, 1H), 6.92-6.83 (m, 1H), 6.49-6.43 (m, 1H), 2.80 (d, J = 14.0 Hz, 1H), 2.76 (d, J = 14.0 Hz, 1H), 2.40 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.7, 162.3 (J_{CF} = 248.0 Hz), 145.1, 141.0 (J_{CF} = 3.0 Hz), 138.5, 137.7, 137.2, 135.4, 134.1, 132.9, 132.4, 130.1 (J_{CF} = 8.2 Hz), 129.9, 129.5, 129.0, 128.9, 127.3, 126.8, 124.5, 115.2 (J_{CF} = 13.4 Hz), 102.0, 60.6, 53.0, 21.6. IR (film, ν, cm^{-1}) 3066, 3031, 1712, 1596, 1481, 1378, 1266, 1197, 1084, 1040, 963, 832, 810. HR-MS (ESI) m/z calcd for $C_{31}H_{25}FINO_5S_2$ $[M+Na]^+$ 724.0101, found 724.0109.

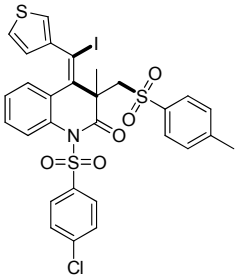
4-((4-Ethylphenyl)iodomethylene)-3-methyl-1-(phenylsulfonyl)-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3o)



white solid, mp 276-278 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09-7.99 (m, 3H), 7.81-7.74 (m, 1H), 7.71-7.64 (m, 3H), 7.55-7.47 (m, 3H), 7.44-7.38 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 1H), 7.01-6.96 (m, 1H), 6.36 (dd, J = 8.0, 1.6 Hz, 1H), 2.78 (s, 2H), 2.64 (d, J = 7.6 Hz, 1H), 2.61 (d, J = 7.2 Hz, 1H), 2.41 (s, 3H), 1.23 (t, J = 7.6 Hz, 3H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.9, 145.0, 144.7, 142.3, 138.6, 137.7, 136.1, 135.7,

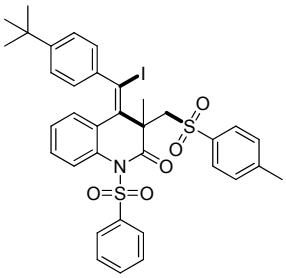
134.0, 132.9, 132.5, 129.9, 129.3, 129.0, 128.9, 127.9, 127.3, 127.0, 126.7, 124.5, 104.1, 60.7, 52.9, 28.6, 21.6, 21.4, 15.2. IR (film, ν, cm^{-1}) 3057, 3027, 1719, 1596, 1447, 1367, 1264, 1191, 1084, 962, 829, 815. HR-MS (ESI) m/z calcd for $C_{33}H_{30}INO_5S_2$ $[M+Na]^+$ 734.0508, found 734.0506.

1-((4-Chlorophenyl)sulfonyl)-4-(iodo(thiophen-3-yl)methylene)-3-methyl-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3p)



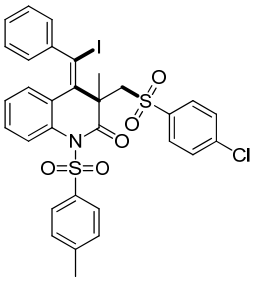
white solid, mp 258-260 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09-8.01 (m, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.68-7.60 (m, 4H), 7.56-7.48 (m, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.28-7.22 (m, 3H), 6.50 (d, J = 4.4 Hz, 1H), 2.83 (d, J = 13.6 Hz, 1H), 2.77 (d, J = 13.2 Hz, 1H), 2.41 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.8, 145.1, 143.5, 140.9, 137.8, 137.7, 136.8, 135.2, 132.9, 132.5, 130.4, 129.9, 129.5, 129.1, 127.3, 126.9, 125.7, 125.0, 124.4, 97.8, 60.3, 53.2, 21.6, 20.7. IR (film, ν, cm^{-1}) 3026, 2992, 1709, 1595, 1477, 1392, 1267, 1195, 1143, 1082, 1041, 1015, 961, 830. HR-MS (ESI) m/z calcd for $C_{29}H_{23}ClINO_5S_3$ $[M+Na]^+$] 745.9370, found 745.9366.

4-((4-(*tert*-Butyl)phenyl)iodomethylene)-3-methyl-1-(phenylsulfonyl)-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (3q)



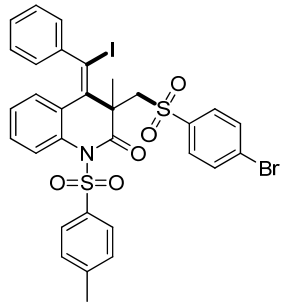
white solid, mp 250-252 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.10-7.98 (m, 3H), 7.84-7.76 (m, 1H), 7.73-7.64 (m, 3H), 7.56-7.47 (m, 3H), 7.41 (d, J = 8.4 Hz, 2H), 7.36-7.30 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.18-7.12 (m, 1H), 6.42-6.33 (m, 1H), 2.78 (s, 2H), 2.41 (s, 3H), 1.30 (s, 9H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.9, 151.6, 145.0, 141.9, 138.6, 137.7, 136.1, 135.7, 134.1, 132.9, 132.5, 129.9, 129.2, 128.9, 127.6, 127.3, 126.7, 124.8, 124.8, 124.6, 104.1, 60.7, 52.9, 34.7, 31.2, 21.6, 21.3. IR (film, ν, cm^{-1}) 3063, 3029, 1723, 1597, 1500, 1480, 1379, 1266, 1191, 1084, 961, 827. HR-MS (ESI) m/z calcd for $C_{35}H_{34}INO_5S_2$ $[M+Na]^+$ 762.0821, found 762.0816.

3-(((4-Chlorophenyl)sulfonyl)methyl)-4-(iodo(phenyl)methylene)-3-methyl-1-tosyl-3,4-dihydroquinolin-2(1*H*)-one (3r)



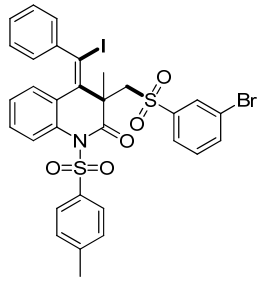
white solid, mp 260-262 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09-8.00 (m, 1H), 7.94-7.87 (m, 2H), 7.71-7.64 (m, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.55-7.40 (m, 8H), 7.37-7.30 (m, 1H), 7.26-7.19 (m, 1H), 7.18-7.12 (m, 1H), 6.42 (d, J = 7.6 Hz, 1H), 2.81 (d, J = 14.0 Hz, 1H), 2.77 (d, J = 14.0 Hz, 1H), 2.56 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.6, 145.4, 144.9, 140.8, 139.0, 135.4, 133.0, 132.2, 129.7, 129.5, 129.4, 129.1, 128.8, 128.4, 128.1, 127.9, 127.8, 126.9, 126.6, 124.7, 103.5, 60.9, 52.9, 21.7, 21.5. IR (film, ν, cm^{-1}) 3059, 3032, 1723, 1595, 1476, 1371, 1199, 1090, 1016, 963, 832. HR-MS (ESI) m/z calcd for $C_{31}H_{25}ClINO_5S_2$ $[M+Na]^+$ 739.9805, found 739.9801.

3-(((4-Bromophenyl)sulfonyl)methyl)-4-(iodo(phenyl)methylene)-3-methyl-1-tosyl-3,4-dihydroquinolin-2(1*H*)-one (3s)



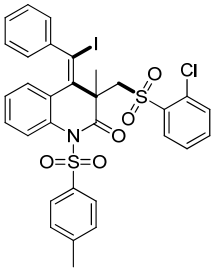
white solid, mp 256-258 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.08-8.01 (m, 1H), 7.93-7.87 (m, 2H), 7.73-7.65 (m, 1H), 7.65-7.55 (m, 3H), 7.54-7.43 (m, 4H), 7.43-7.37 (m, 2H), 7.36-7.30 (m, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.18-7.11 (m, 1H), 6.42 (d, J = 7.6 Hz, 1H), 2.81 (d, J = 13.6 Hz, 1H), 2.77 (d, J = 14.0 Hz, 1H), 2.56 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.6, 145.4, 144.9, 136.2, 135.4, 133.0, 132.7, 132.2, 129.5, 129.4, 129.4, 129.1, 128.9, 128.4, 128.1, 127.9, 127.8, 126.9, 126.6, 124.7, 103.5, 60.8, 52.9, 21.7, 21.5. IR (film, ν, cm^{-1}) 3060, 3012, 1723, 1596, 1575, 1454, 1384, 1172, 1083, 1067, 1012, 763. HR-MS (ESI) m/z calcd for $C_{31}H_{25}BrINO_5S_2$ $[M+Na]^+$ 783.9300, found 783.9306.

3-(((3-Bromophenyl)sulfonyl)methyl)-4-(iodo(phenyl)methylene)-3-methyl-1-tosyl-3,4-dihydroquinolin-2(1*H*)-one (3t)



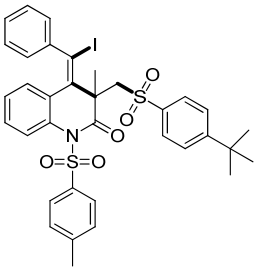
white solid, mp 261-263 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09-8.01 (m, 1H), 7.93-7.87 (m, 2H), 7.75-7.65 (m, 2H), 7.65-7.61 (m, 1H), 7.60-7.44 (m, 6H), 7.39-7.31 (m, 2H), 7.25-7.19 (m, 1H), 7.15 (t, J = 7.2 Hz, 1H), 6.40 (d, J = 7.6 Hz, 1H), 2.83 (d, J = 14.0 Hz, 1H), 2.79 (d, J = 14.4 Hz, 1H), 2.56 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.5, 145.4, 144.9, 142.2, 137.0, 136.1, 135.4, 133.0, 132.1, 130.8, 130.3, 129.5, 129.1, 128.4, 128.1, 127.9, 127.8, 126.9, 126.8, 125.9, 124.8, 123.3, 103.5, 60.9, 52.9, 21.7, 21.4. IR (film, ν, cm^{-1}) 3054, 2927, 1722, 1595, 1453, 1372, 1295, 1197, 1085, 1041, 962, 813. HR-MS (ESI) m/z calcd for $C_{31}H_{25}BrINO_5S_2$ $[M+Na]^+$ 783.9300, found 783.9306.

3-(((2-Chlorophenyl)sulfonyl)methyl)-4-(iodo(phenyl)methylene)-3-methyl-1-tosyl-3,4-dihydroquinolin-2(1*H*)-one (3u)



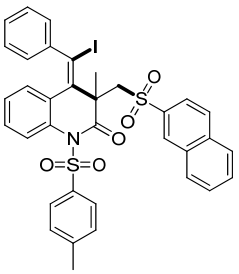
white solid, mp 259-261 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.99-7.92 (m, 2H), 7.92-7.87 (m, 2H), 7.70-7.65 (m, 1H), 7.59-7.53 (m, 1H), 7.53-7.37 (m, 7H), 7.36-7.30 (m, 1H), 7.24-7.18 (m, 1H), 7.17-7.12 (m, 1H), 6.47 (d, J = 7.6 Hz, 1H), 3.18 (s, 2H), 2.55 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.9, 145.4, 145.1, 138.1, 136.5, 135.5, 135.0, 132.8, 132.6, 132.4, 131.9, 130.8, 129.5, 129.4, 129.1, 128.4, 128.0, 127.8, 127.5, 127.0, 126.7, 124.5, 103.8, 59.1, 53.0, 21.9, 21.7. IR (film, ν, cm^{-1}) 3053, 3006, 1719, 1596, 1488, 1373, 1298, 1195, 1086, 962, 780. HR-MS (ESI) m/z calcd for $C_{31}H_{25}ClINO_5S_2$ $[M+Na]^+$ 739.9805, found 739.9806.

3-(((4-(*tert*-Butyl)phenyl)sulfonyl)methyl)-4-(iodo(phenyl)methylene)-3-methyl-1-tosyl-3,4-dihydroquinolin-2(1*H*)-one (3v)



white solid, mp 262-263 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09-8.00 (m, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.70-7.64 (m, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.55-7.49 (m, 2H), 7.49-7.41 (m, 6H), 7.38-7.31 (m, 1H), 7.25-7.19 (m, 1H), 7.18-7.11 (m, 1H), 6.43 (d, J = 7.6 Hz, 1H), 2.82 (d, J = 14.0 Hz, 1H), 2.77 (d, J = 14.0 Hz, 1H), 2.55 (s, 3H), 1.33 (s, 9H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.9, 158.0, 145.3, 145.0, 137.5, 136.5, 135.5, 133.0, 132.4, 129.5, 129.3, 129.1, 128.3, 128.1, 128.0, 127.7, 127.2, 127.0, 126.6, 126.3, 124.6, 103.3, 60.7, 53.0, 43.5, 35.3, 31.0, 21.7, 21.5. IR (film, ν, cm^{-1}) 3052, 1715, 1593, 1477, 1368, 1296, 1192, 1082, 962, 735. HR-MS (ESI) m/z calcd for $C_{35}H_{34}INO_5S_2$ $[M+Na]^+$ 762.0821, found 762.0818.

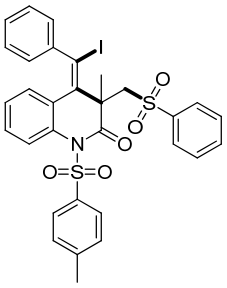
4-(Iodo(phenyl)methylene)-3-methyl-3-((naphthalen-2-ylsulfonyl)methyl)-1-tosyl-3,4-dihydroquinolin-2(1*H*)-one (3w)



white solid, mp 255-257 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.17 (d, J = 1.2 Hz, 1H), 8.12 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.95-7.84 (m, 5H), 7.72-7.61 (m, 4H), 7.59-7.54 (m, 1H), 7.53-7.41 (m, 4H), 7.40-7.33 (m, 1H), 7.27-7.20 (m, 1H), 7.19-7.12 (m, 1H), 6.44 (d, J = 7.6 Hz, 1H), 2.89 (s, 2H), 2.55 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.8, 145.4, 145.0, 137.4, 136.4, 135.6, 135.5, 135.2, 133.0, 132.3, 132.0, 129.7, 129.5, 129.4, 129.3, 129.1,

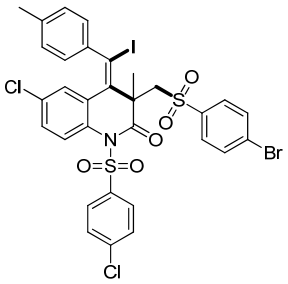
128.4, 128.1, 128.0, 127.9, 127.7, 127.0, 126.6, 124.7, 121.8, 103.4, 60.8, 53.1, 21.8, 21.5. IR(film, ν, cm^{-1}) 3056, 1719, 1625, 1595, 1487, 1369, 1265, 1196, 1130, 1087, 1071, 963, 817. HR-MS (ESI) m/z calcd for $C_{35}H_{28}INO_5S_2$ $[M+Na]^+$ 756.0352, found 756.0356.

4-(Iodo(phenyl)methylene)-3-methyl-3-((phenylsulfonyl)methyl)-1-tosyl-3,4-dihydroquinolin-2(1*H*)-one (3x)



white solid, mp 264-266 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09-8.02 (m, 1H), 7.94-7.87 (m, 2H), 7.70-7.64 (m, 1H), 7.63-7.56 (m, 2H), 7.56-7.49 (m, 4H), 7.49-7.43 (m, 4H), 7.38-7.31 (m, 1H), 7.25-7.19 (m, 1H), 7.19-7.11 (m, 1H), 6.43 (d, J = 7.6 Hz, 1H), 2.80 (s, 2H), 2.55 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.8, 145.4, 145.0, 140.6, 136.4, 135.5, 133.9, 133.0, 132.3, 129.5, 129.3, 129.1, 128.4, 128.1, 128.0, 127.7, 127.3, 126.9, 126.6, 124.6, 103.4, 60.7, 53.0, 21.7, 21.5. IR (film, ν, cm^{-1}) 3058, 3010, 1723, 1595, 1488, 1372, 1298, 1173, 1085, 1041, 962, 813. HR-MS (ESI) m/z calcd for $C_{31}H_{26}INO_5S_2$ $[M+Na]^+$ 706.0195, found 706.0198.

3-(((4-Bromophenyl)sulfonyl)methyl)-6-chloro-1-((4-chlorophenyl)sulfonyl)-4-(iodo(*p*-tolyl)methylene)-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (3y)

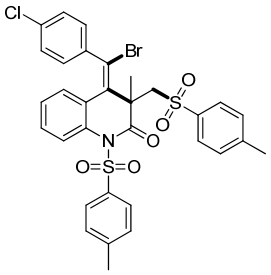


white solid, mp 274-276 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.01 (d, J = 2.0 Hz, 1H), 7.97-7.91 (m, 2H), 7.70-7.63 (m, 4H), 7.59 (d, J = 8.8 Hz, 1H), 7.50-7.41 (m, 4H), 7.15 (d, J = 7.6 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.30 (d, J = 7.2 Hz, 1H), 2.84 (d, J = 14.0 Hz, 1H), 2.69 (d, J = 13.6 Hz, 1H), 2.35 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.3, 141.5, 141.3, 139.4, 138.9, 137.3, 136.3, 134.8, 132.8, 131.9, 131.1, 130.6, 129.6, 129.4, 129.3, 128.9, 128.8, 127.6, 126.6, 126.1, 105.5, 60.8, 52.8, 21.4, 21.3. IR (film, ν, cm^{-1}) 3102, 2930, 1722, 1572, 1474, 1375, 1286, 1176, 1091, 962, 896, 830. HR-MS (ESI) m/z calcd for $C_{31}H_{23}BrCl_2INO_5S_2$ $[M+Na]^+$ 851.8521, found 851.8518.

(b) General Procedure for the Synthesis of Products 4

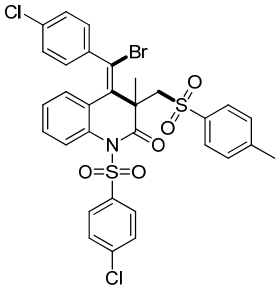
A mixture of 1,7-enynes (**1**, 1.0 equiv., 0.5 mmol), sulfonyl hydrazid (**2**, 2.0 equiv., 1.0 mmol), NBS (1.2 equiv., 0.6 mmol) and anhydrous TBHP (2.0 equiv. 1.0 mmol, 5.5 M in decane) in acetonitrile (2.0 mL) was heated at 60 °C for 6 hours. After completion of the reaction as indicated by TLC, the mixture was evaporated under vacuum and washed with methanol to afford the desired product **4** as a white solid.

4-(Bromo(4-chlorophenyl)methylene)-3-methyl-1-tosyl-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (4a)



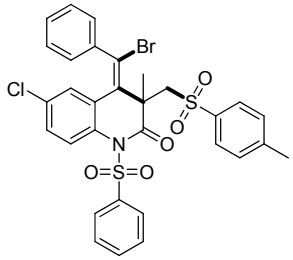
white solid, mp 272-274 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.10-8.03 (m, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.71-7.61 (m, 2H), 7.55-7.47 (m, 2H), 7.46-7.34 (m, 5H), 7.24 (d, J = 8.4 Hz, 2H), 7.21-7.16 (m, 1H), 6.48 (d, J = 7.6 Hz, 1H), 2.77 (s, 2H), 2.54 (s, 3H), 2.41 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.9, 145.4, 145.1, 139.3, 137.7, 135.6, 134.9, 133.0, 132.1, 131.9, 130.5, 129.9, 129.4, 129.3, 128.9, 128.5, 128.3, 127.3, 126.7, 124.6, 122.9, 60.0, 53.1, 21.7, 21.6, 21.6. IR (film, ν, cm^{-1}) 3059, 2987, 1723, 1596, 1488, 1321, 1288, 1193, 1086, 1039, 1016, 964, 830. HR-MS (ESI) m/z calcd for $C_{32}H_{27}BrClNO_5S_2$ $[M+Na]^+$ 706.0101, found 706.0109.

4-(Bromo(4-chlorophenyl)methylene)-1-((4-chlorophenyl)sulfonyl)-3-methyl-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (4b)



white solid, mp 238-240 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09-8.04 (m, 1H), 7.94-7.88 (m, 2H), 7.68-7.59 (m, 4H), 7.56-7.48 (m, 2H), 7.42-7.34 (m, 3H), 7.28-7.22 (m, 3H), 6.52 (d, J = 6.8 Hz, 1H), 2.77 (s, 2H), 2.41 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 168.0, 145.2, 141.0, 139.1, 137.6, 136.7, 135.1, 132.7, 132.4, 132.1, 130.5, 130.4, 130.0, 129.4, 129.1, 128.6, 128.5, 127.3, 127.0, 124.6, 123.3, 59.8, 53.2, 21.6, 21.6. IR (film, ν, cm^{-1}) 3094, 2998, 1723, 1597, 1583, 1478, 1377, 1192, 1089, 964, 842. HR-MS (ESI) m/z calcd for $C_{31}H_{24}BrCl_2NO_5S_2$ $[M+Na]^+$ 725.9554, found 725.9558.

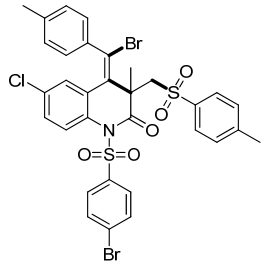
4-(Bromo(phenyl)methylene)-6-chloro-3-methyl-1-(phenylsulfonyl)-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (4c)



white solid, mp 285-287 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.05 (d, J = 2.4 Hz, 1H), 8.00-7.94 (m, 2H), 7.82-7.75 (m, 1H), 7.71-7.59 (m, 4H), 7.51-7.44 (m, 3H), 7.42-7.34 (m, 1H), 7.33-7.29 (m, 2H), 7.23-7.15 (m, 1H), 6.44 (d, J = 7.6 Hz, 1H), 2.82 (d, J = 14.0 Hz, 1H), 2.74 (d, J = 14.0 Hz, 1H), 2.43 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.7, 145.3, 140.4, 138.3, 137.7, 134.3, 133.9, 132.7, 131.6, 130.6, 130.1, 129.1, 129.0, 128.9, 128.8,

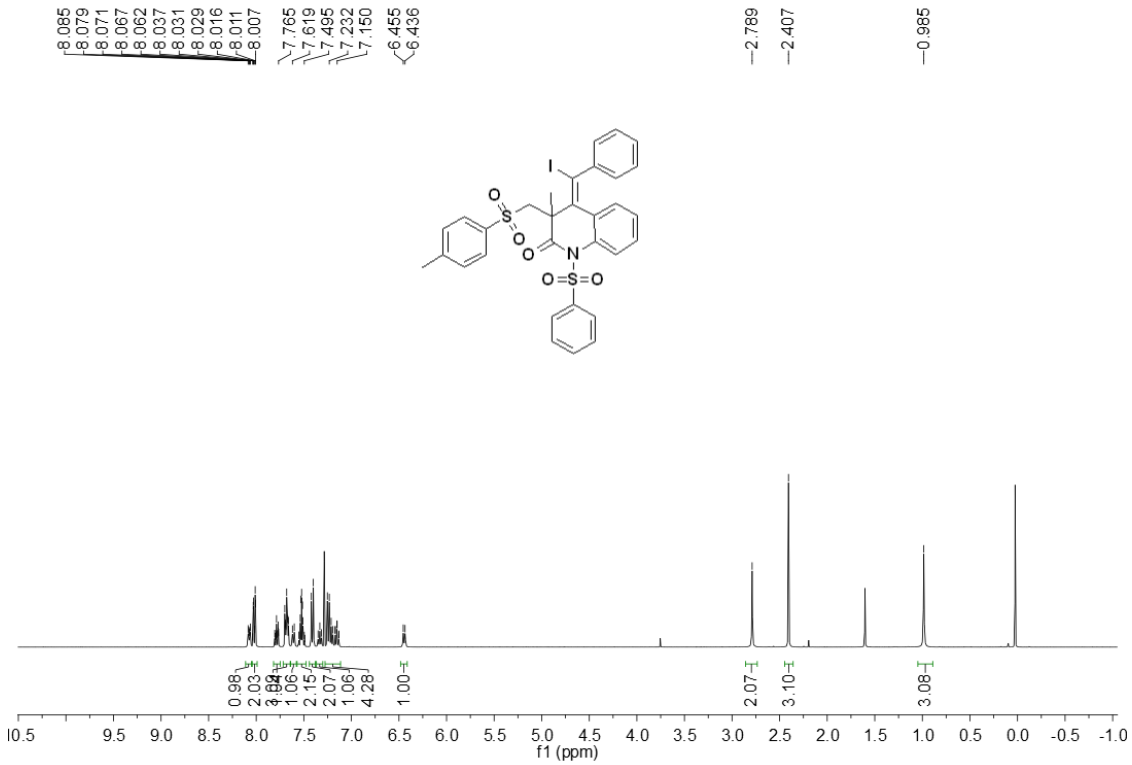
128.3, 128.0, 127.6, 127.3, 126.0, 125.6, 60.2, 52.9, 21.6, 21.1. IR (film, ν, cm^{-1}) 3080, 2938 1724, 1595, 1471, 1375, 1289, 1173, 1085, 960, 893, 841. HR-MS (ESI) m/z calcd for $C_{31}H_{25}BrClNO_5S_2[M+Na]^+$ 691.9944, found 691.9948.

4-(Bromo(*p*-tolyl)methylene)-1-((4-bromophenyl)sulfonyl)-6-chloro-3-methyl-3-(tosylmethyl)-3,4-dihydroquinolin-2(1*H*)-one (4d)

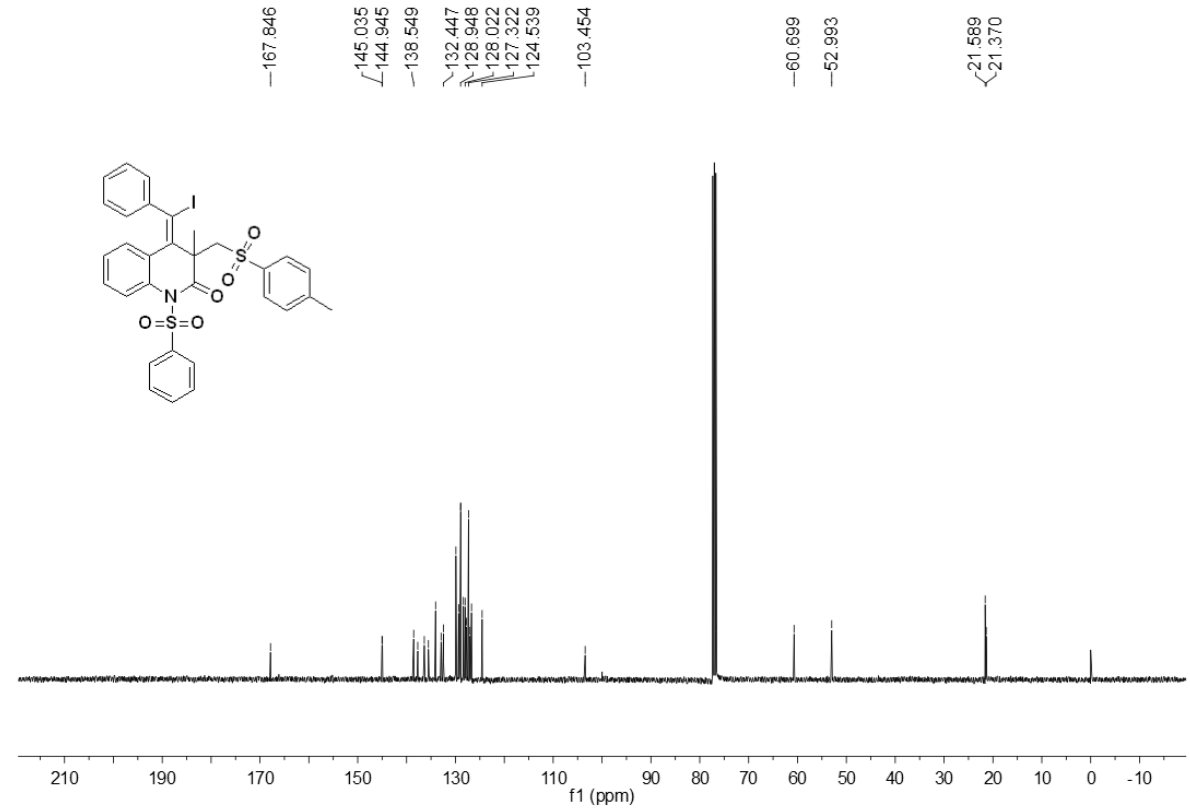


white solid, mp 278-280 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.03 (d, J = 2.4 Hz, 1H), 7.85-7.76 (m, 4H), 7.61-7.51 (m, 2H), 7.50-7.42 (m, 3H), 7.29 (d, J = 6.0 Hz, 2H), 7.19 (d, J = 7.6 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.37 (d, J = 7.6 Hz, 1H), 2.81 (d, J = 13.6, 1H), 2.72 (d, J = 14.0, 1H), 2.43 (s, 3H), 2.37 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 167.8, 145.3, 139.3, 137.6, 137.3, 137.0, 134.2, 132.9, 132.2, 131.6, 131.2, 130.3, 130.1, 129.8, 129.1, 128.9, 128.8, 127.4, 127.3, 126.3, 126.0, 60.1, 53.0, 21.6, 21.4, 21.3. IR (film) ν (cm^{-1}) 3097, 2934, 1723, 1595, 1470, 1393, 1289, 1191, 1171, 1083, 962, 892, 830. HR-MS (ESI) m/z calcd for $C_{32}H_{26}Br_2ClNO_5S_2$ $[M+Na]^+$ 783.9206, found 783.9208.

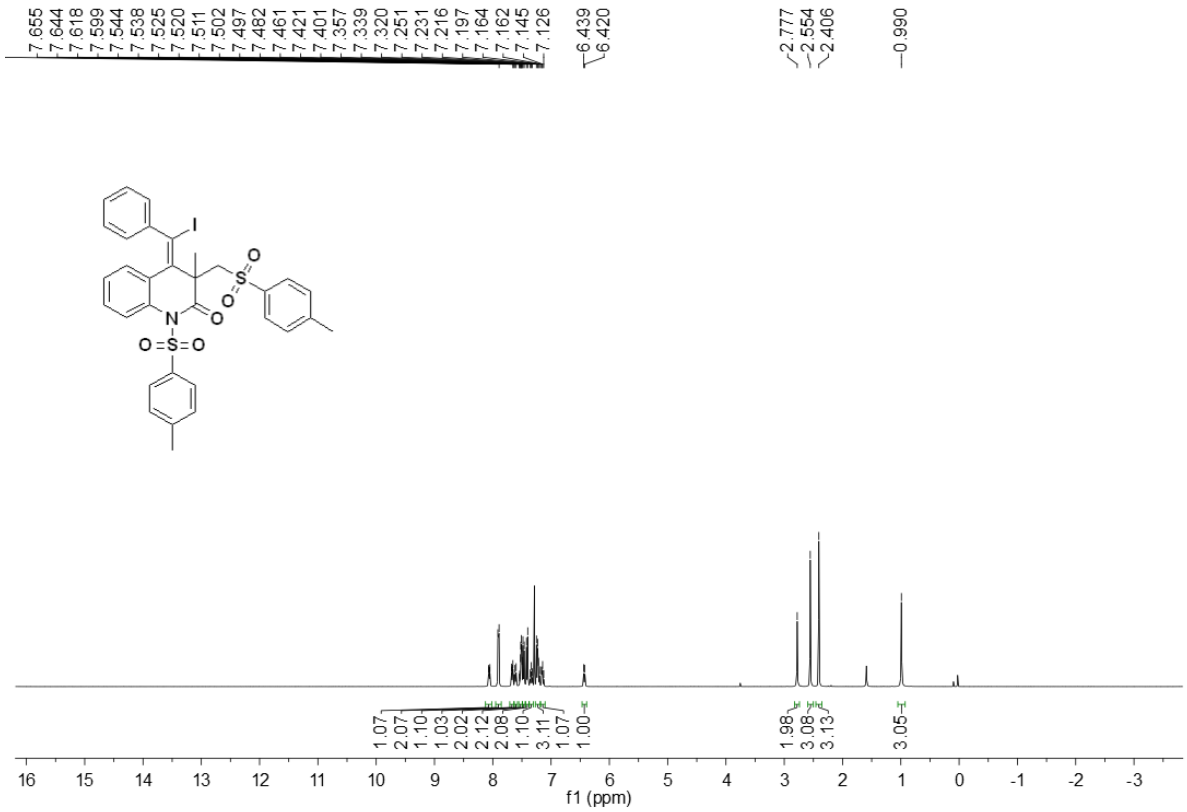
Copies of ^{1}H and ^{13}C NMR Spectra of Products



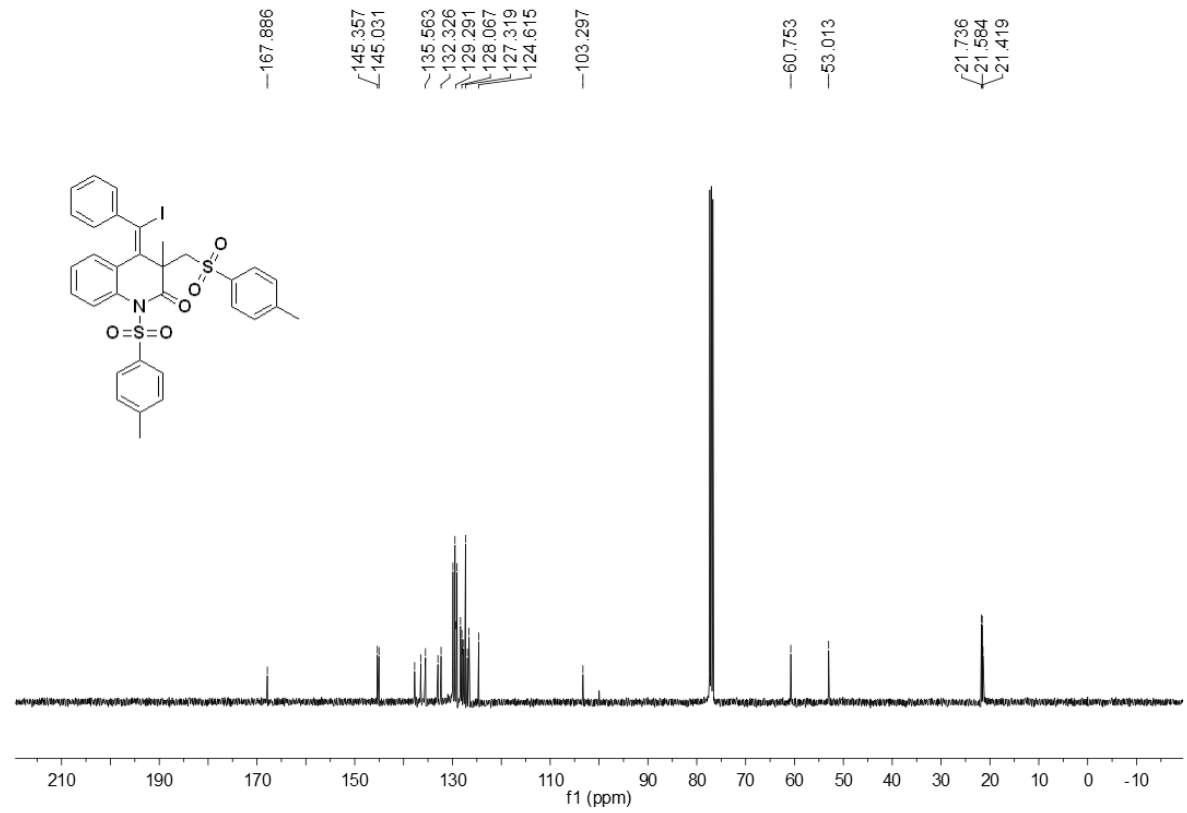
^{1}H NMR Spectrum of Compound 3a



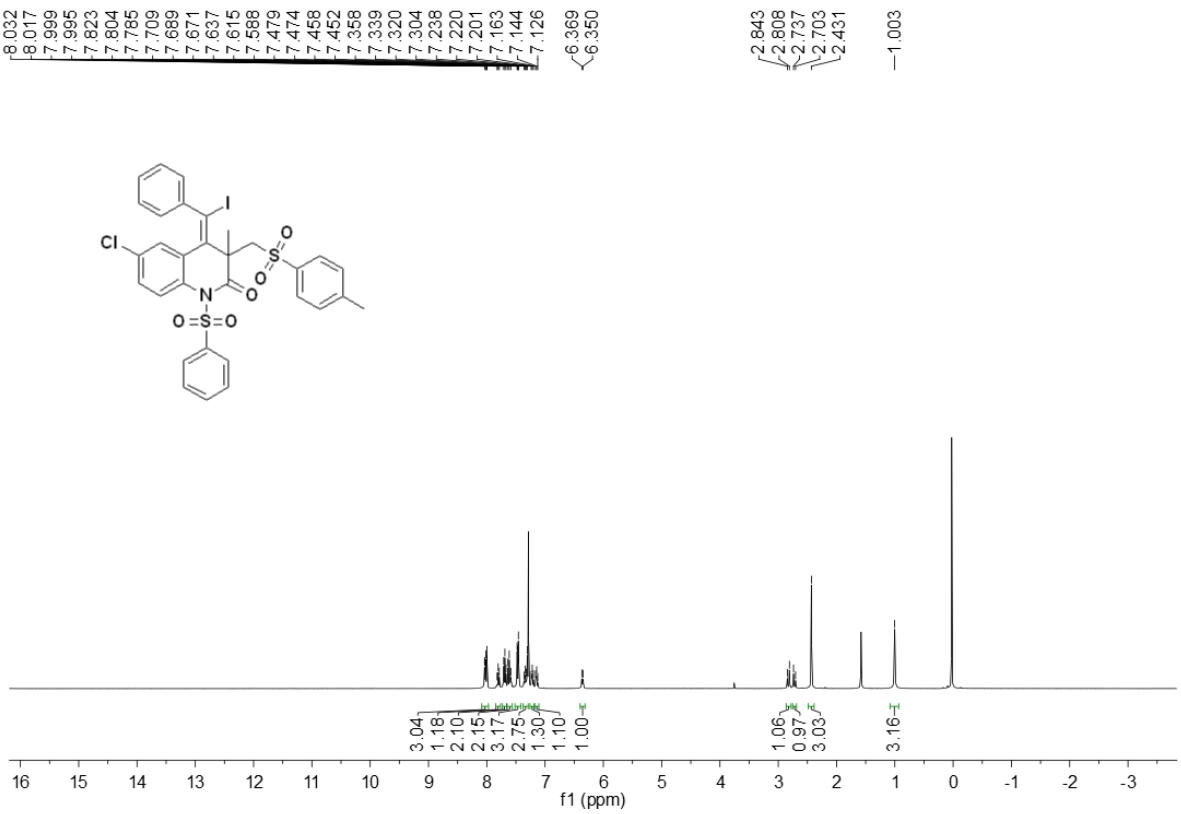
^{13}C NMR Spectrum of Compound 3a



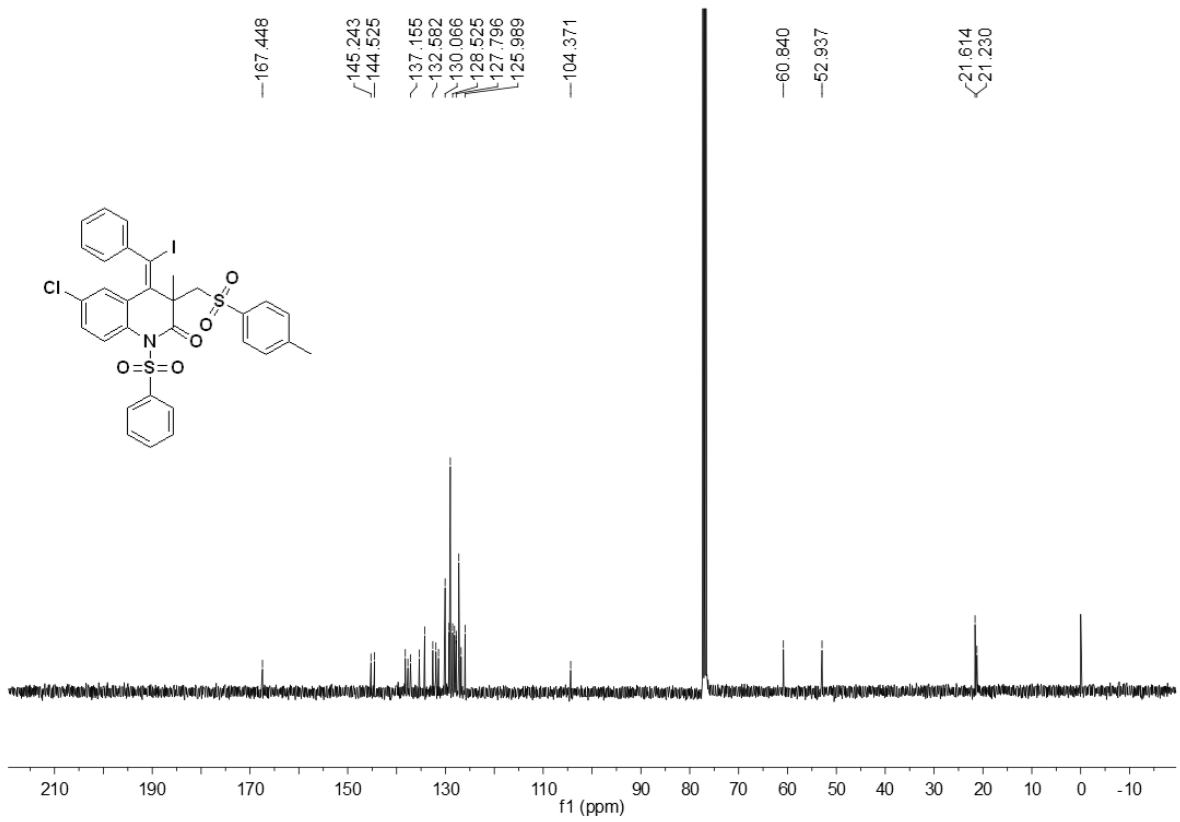
[1]H NMR Spectrum of Compound 3b



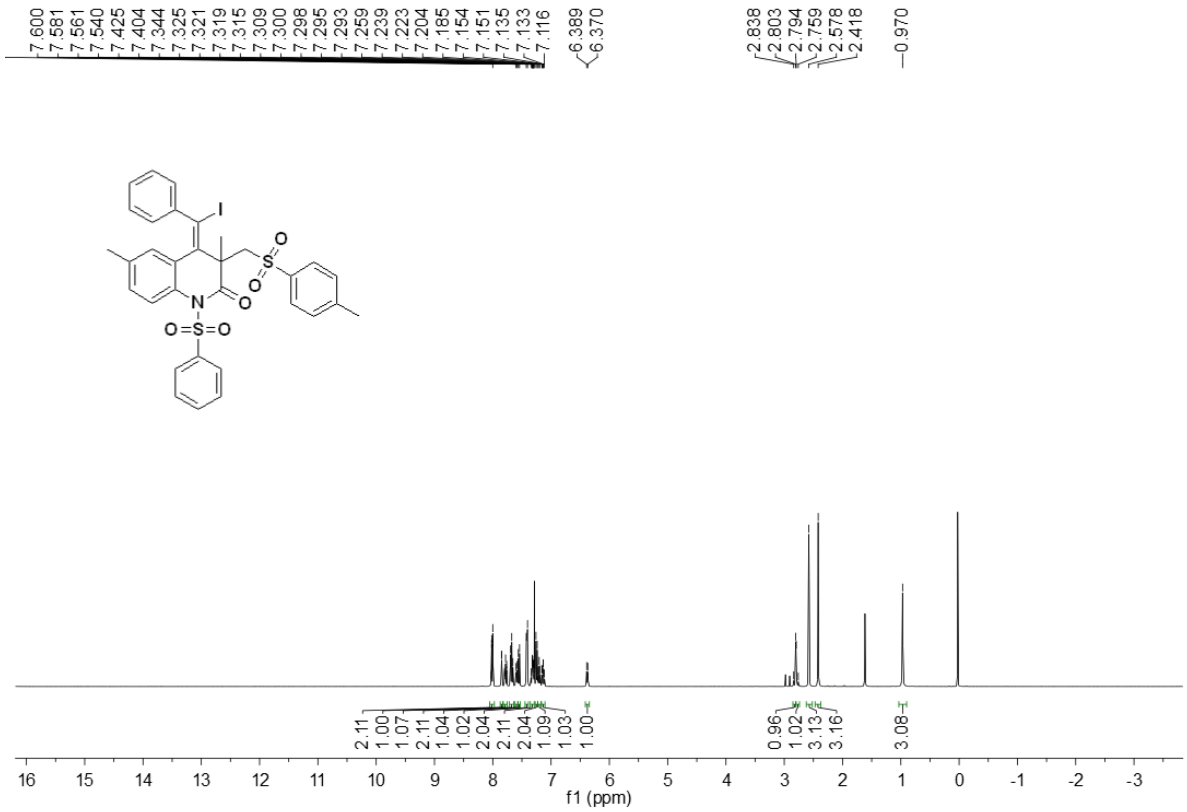
[13]C NMR Spectrum of Compound 3b



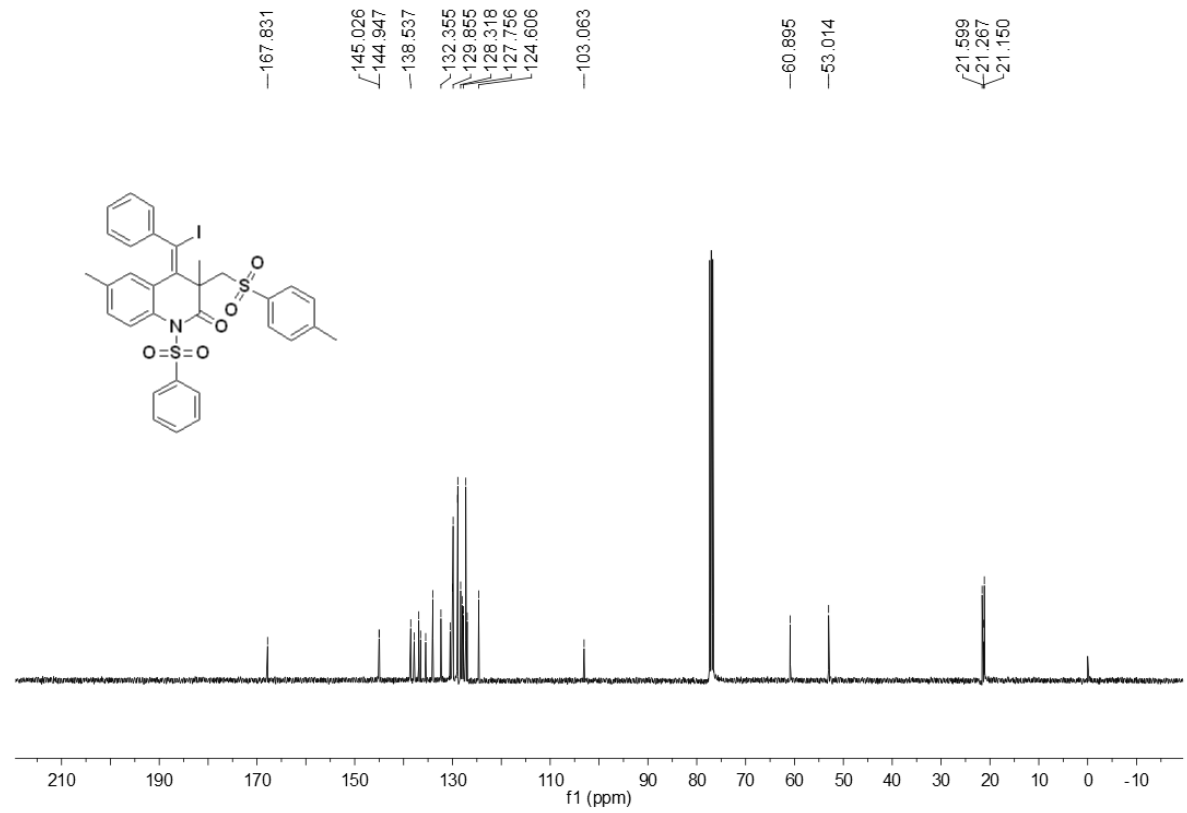
^{1}H NMR Spectrum of Compound 3c



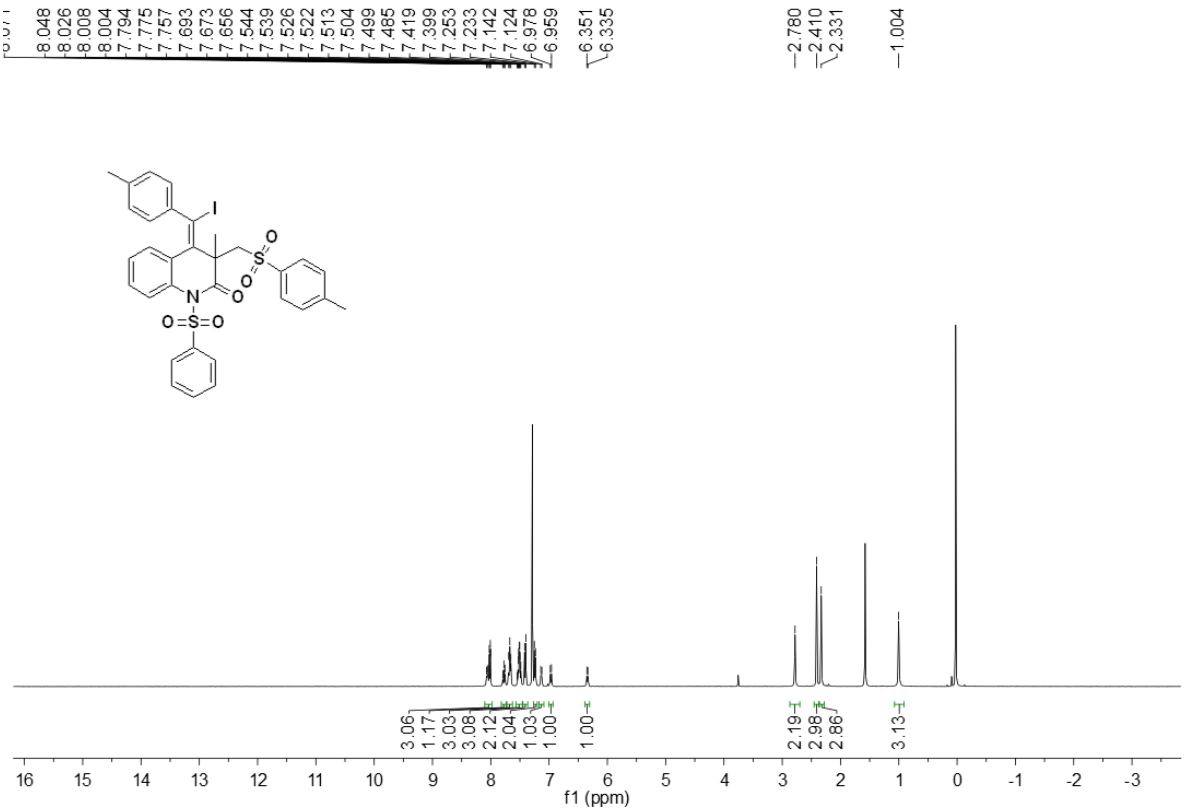
^{13}C NMR Spectrum of Compound 3c



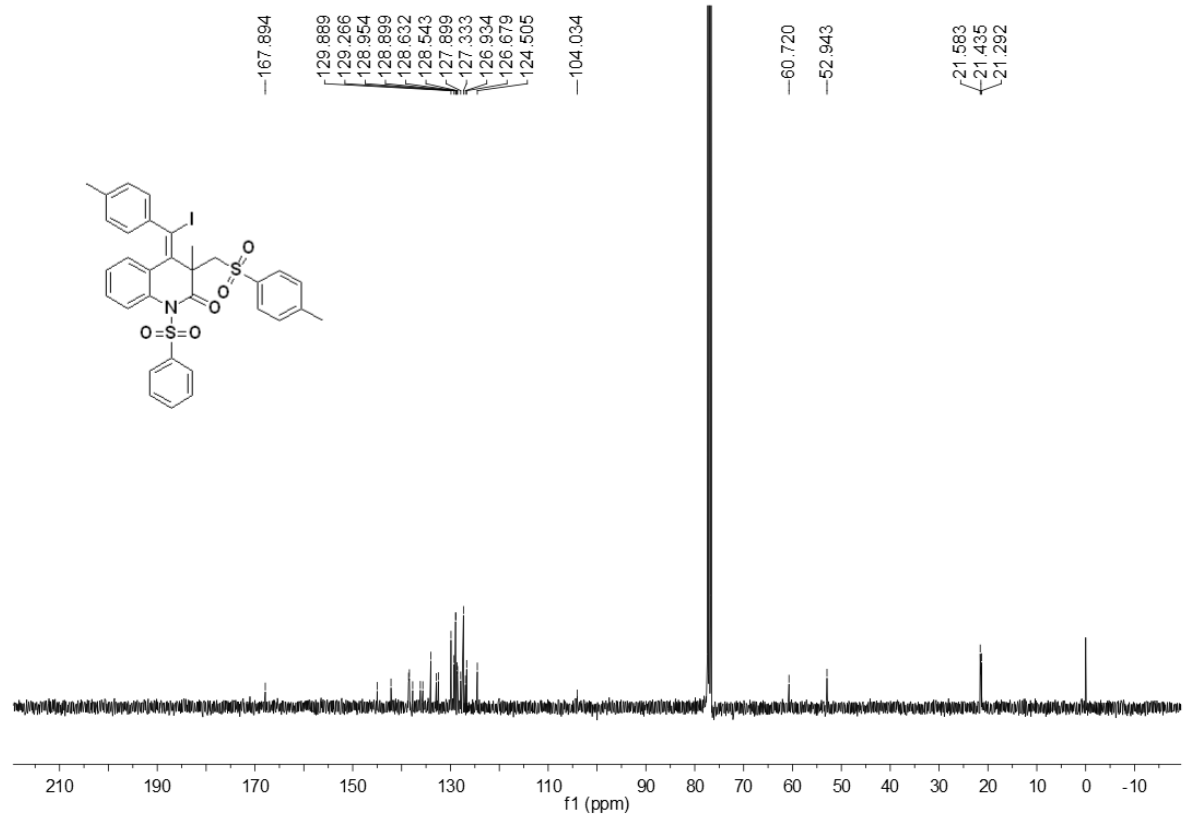
^{1}H NMR Spectrum of Compound 3d



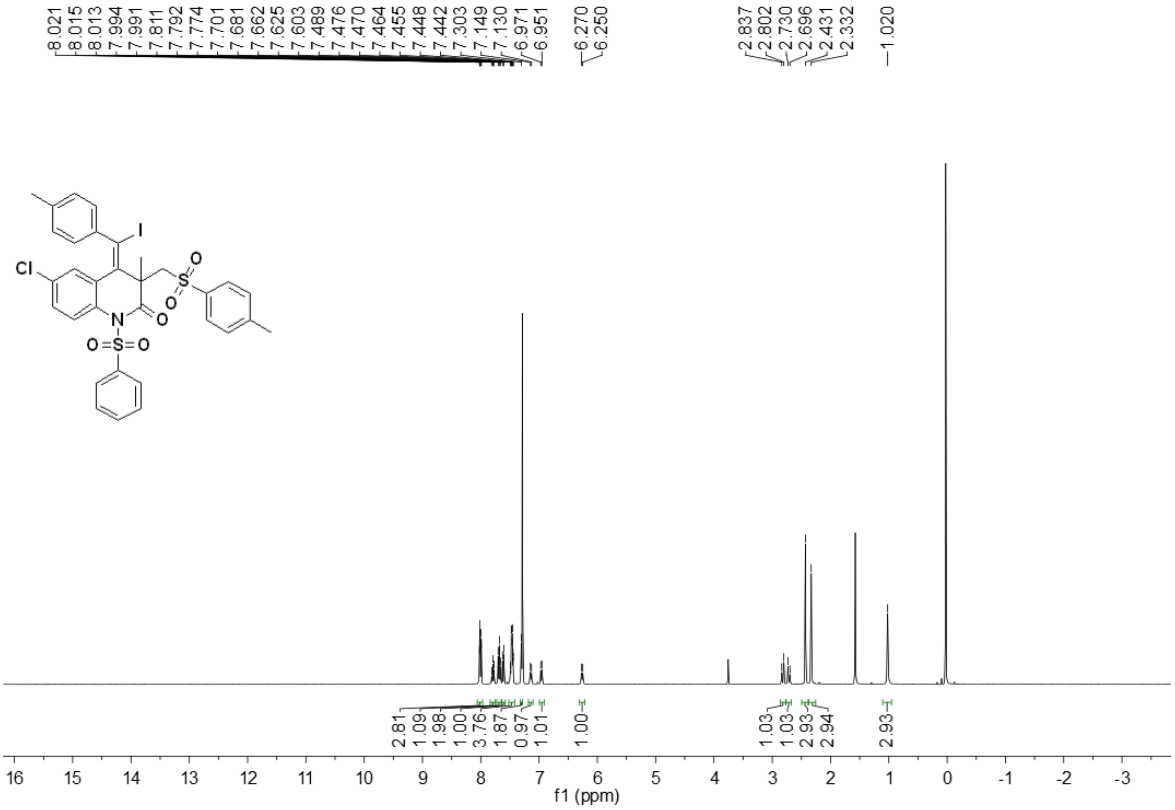
^{13}C NMR Spectrum of Compound 3d



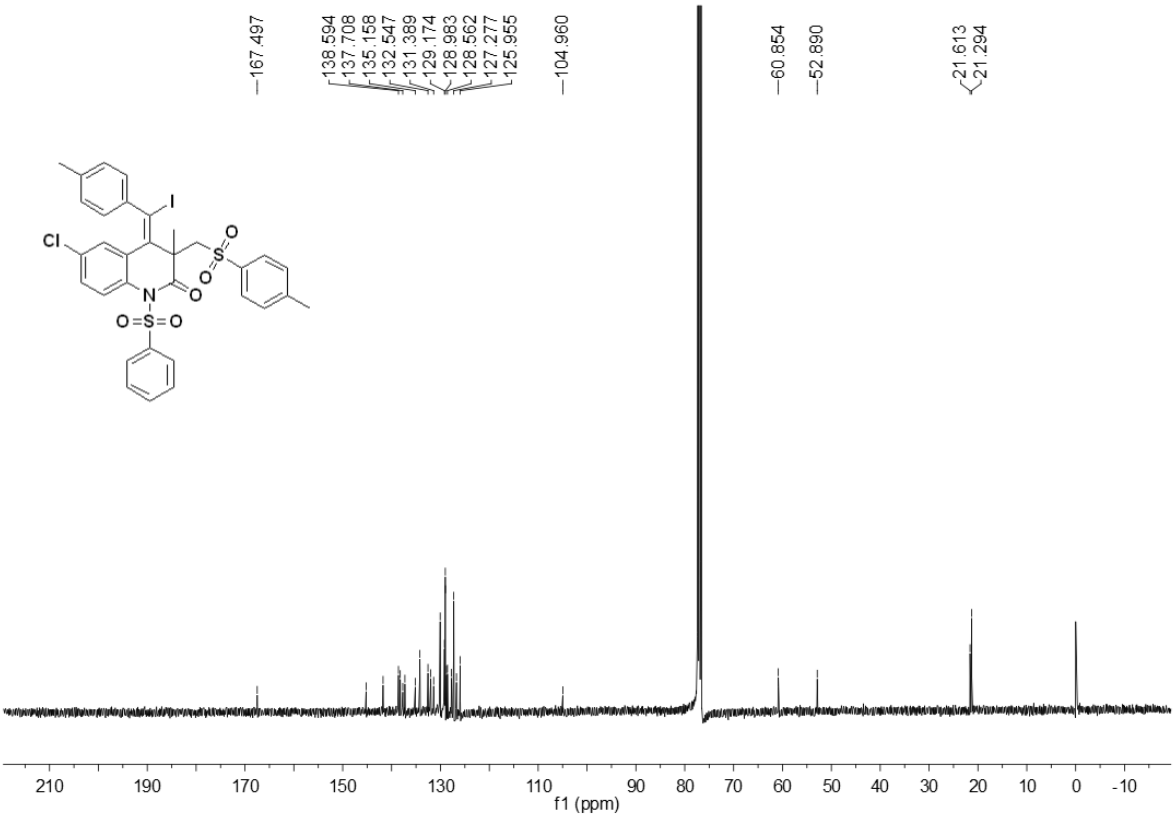
[1]H NMR Spectrum of Compound 3e



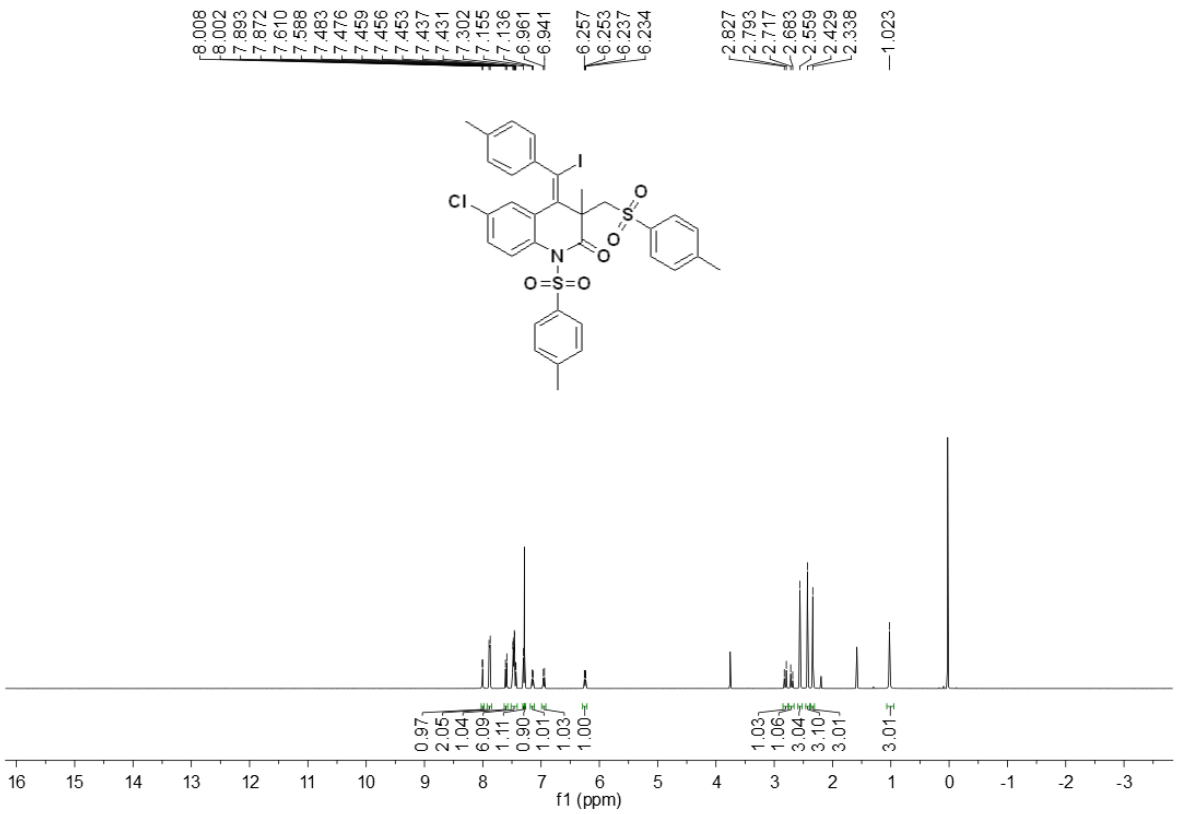
[13]C NMR Spectrum of Compound 3e



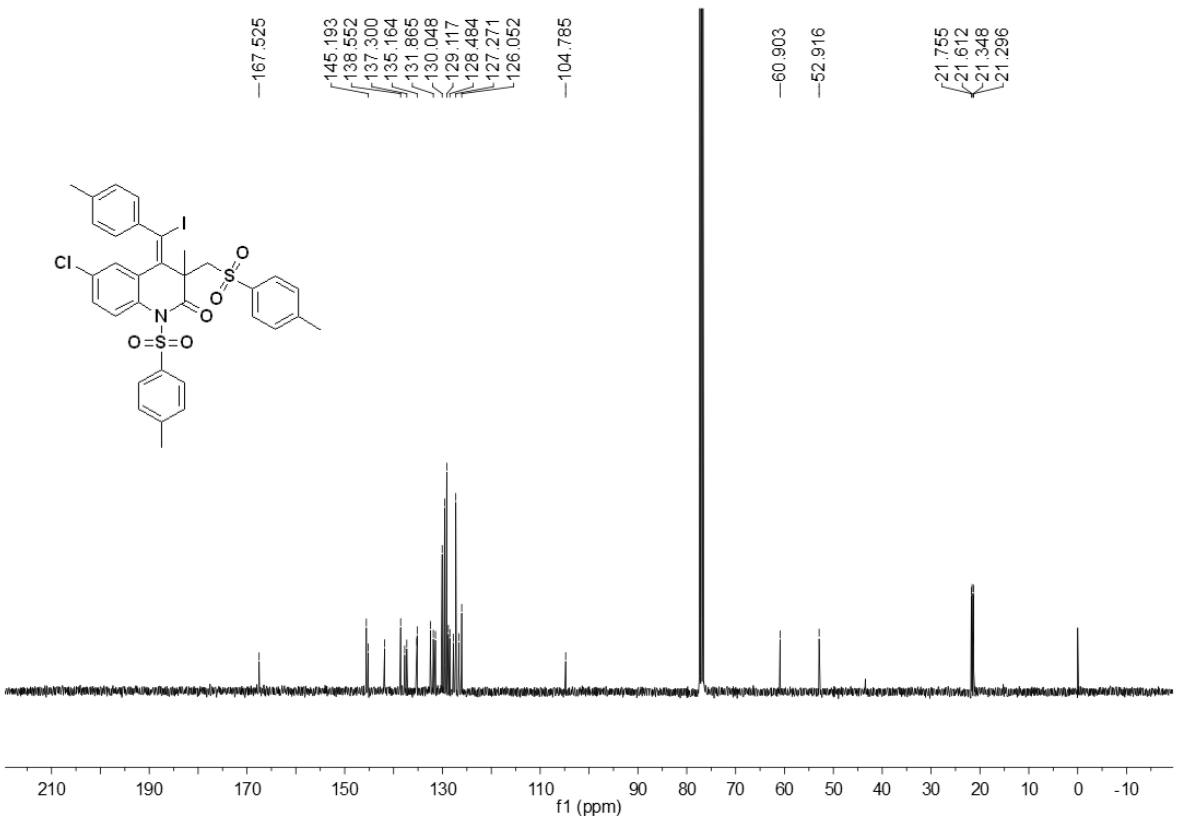
^{1}H NMR Spectrum of Compound 3f



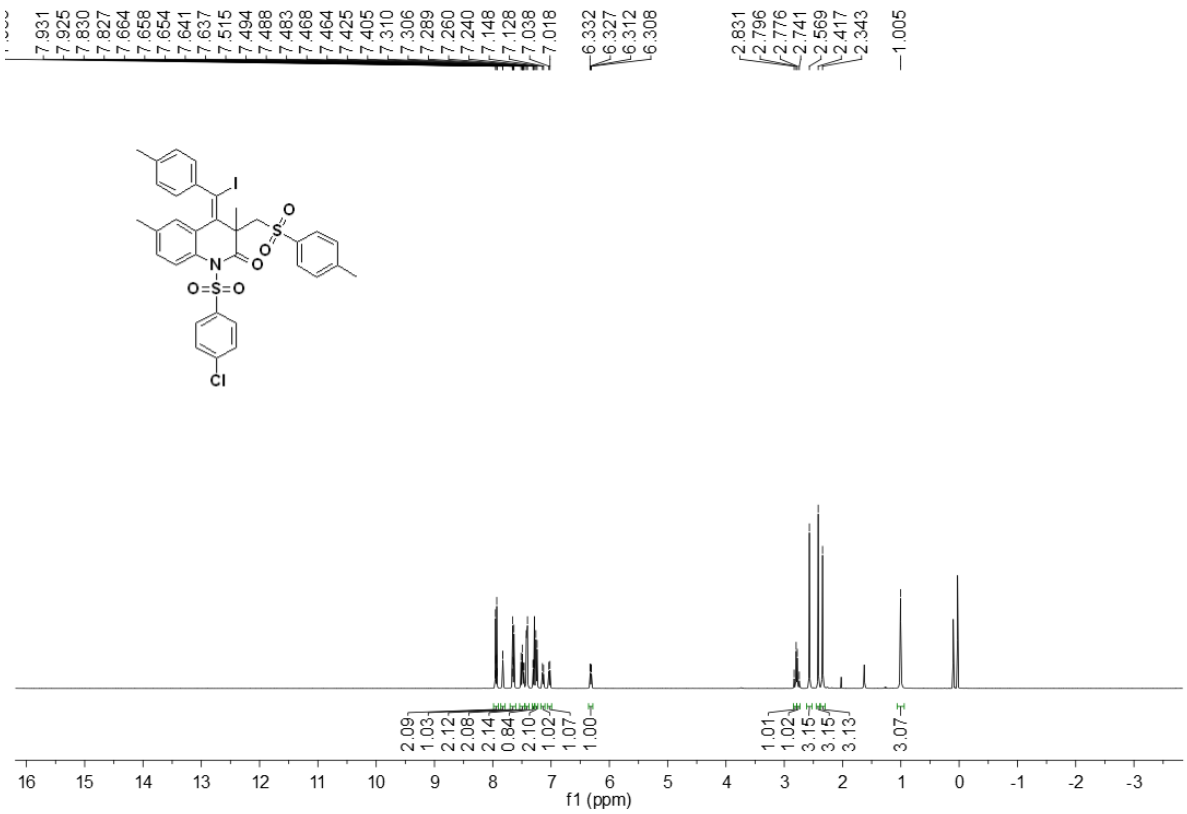
^{13}C NMR Spectrum of Compound 3f



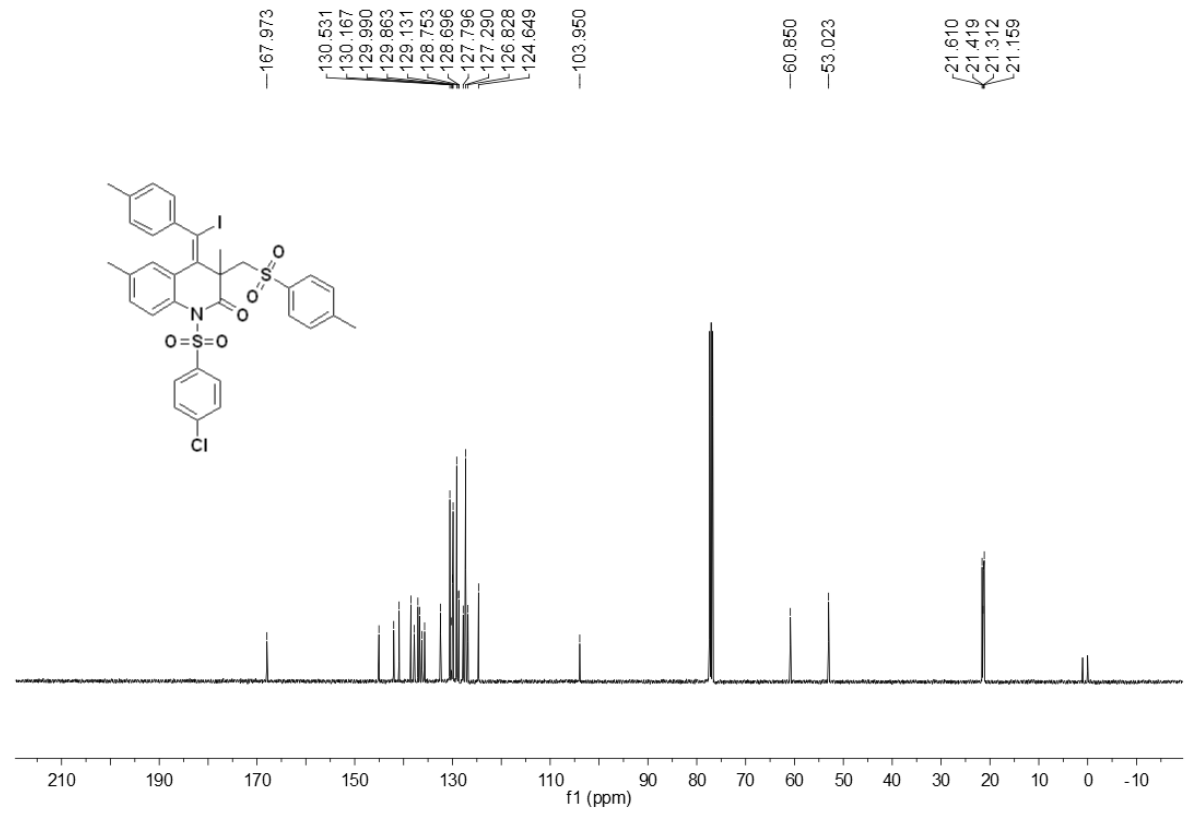
^{1}H NMR Spectrum of Compound 3g



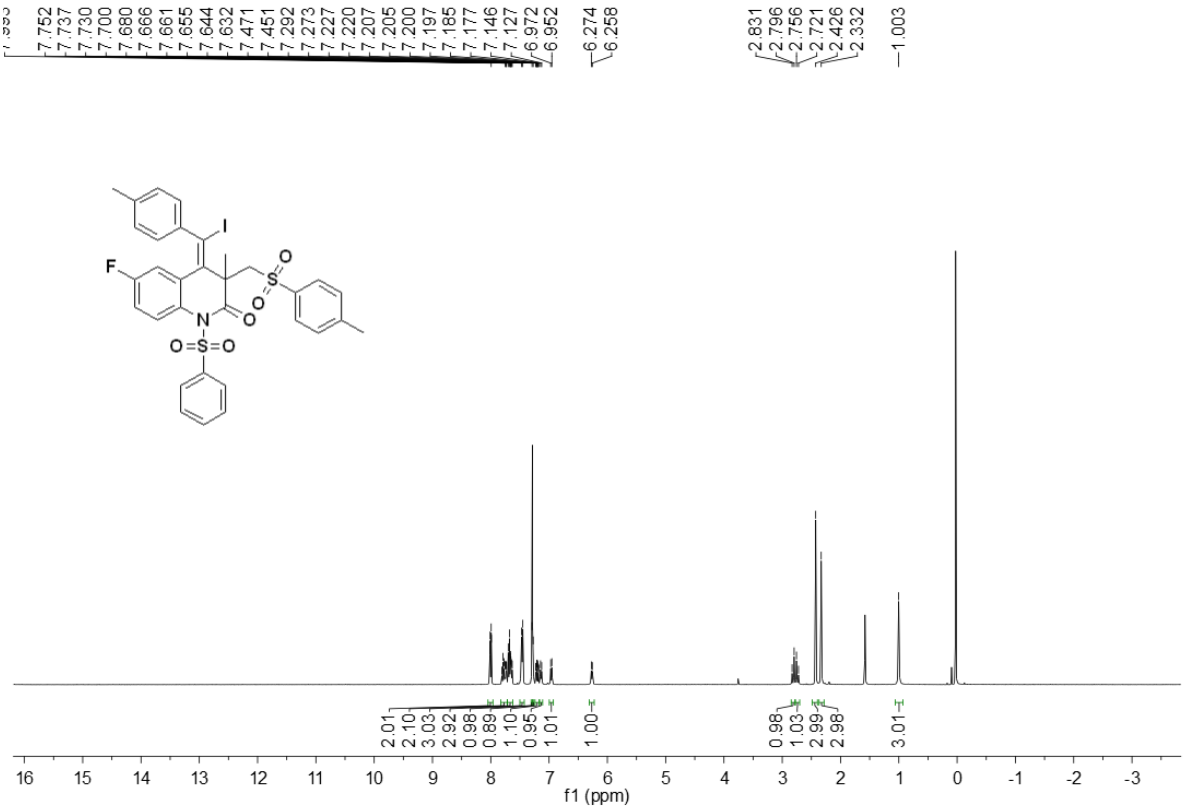
^{13}C NMR Spectrum of Compound 3g



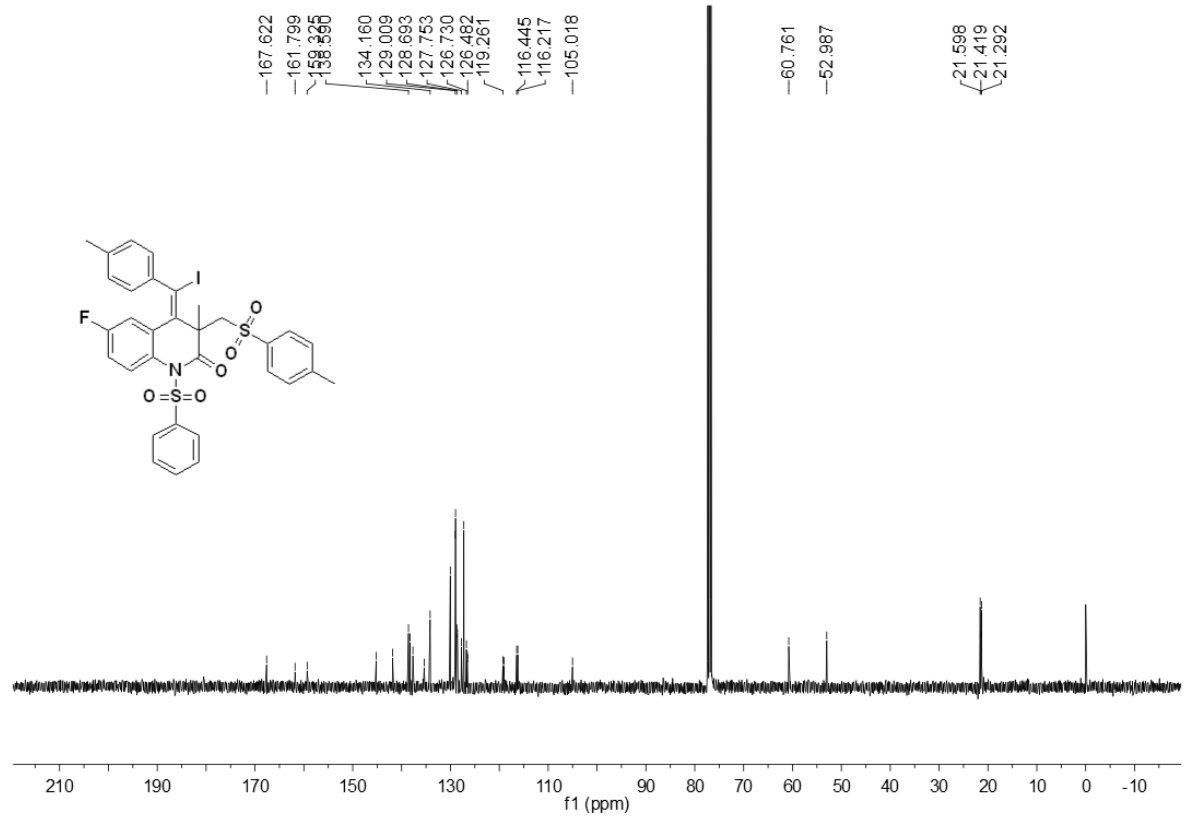
[1]H NMR Spectrum of Compound 3h



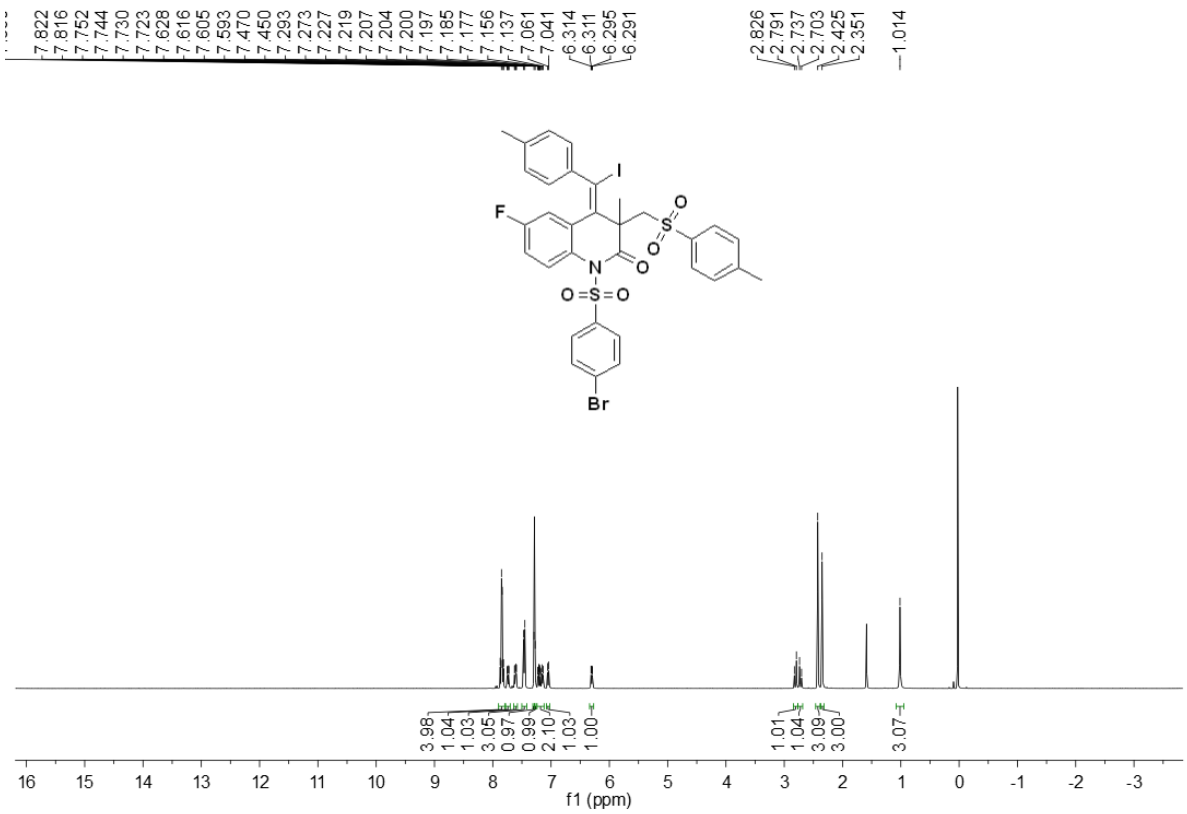
[13]C NMR Spectrum of Compound 3h



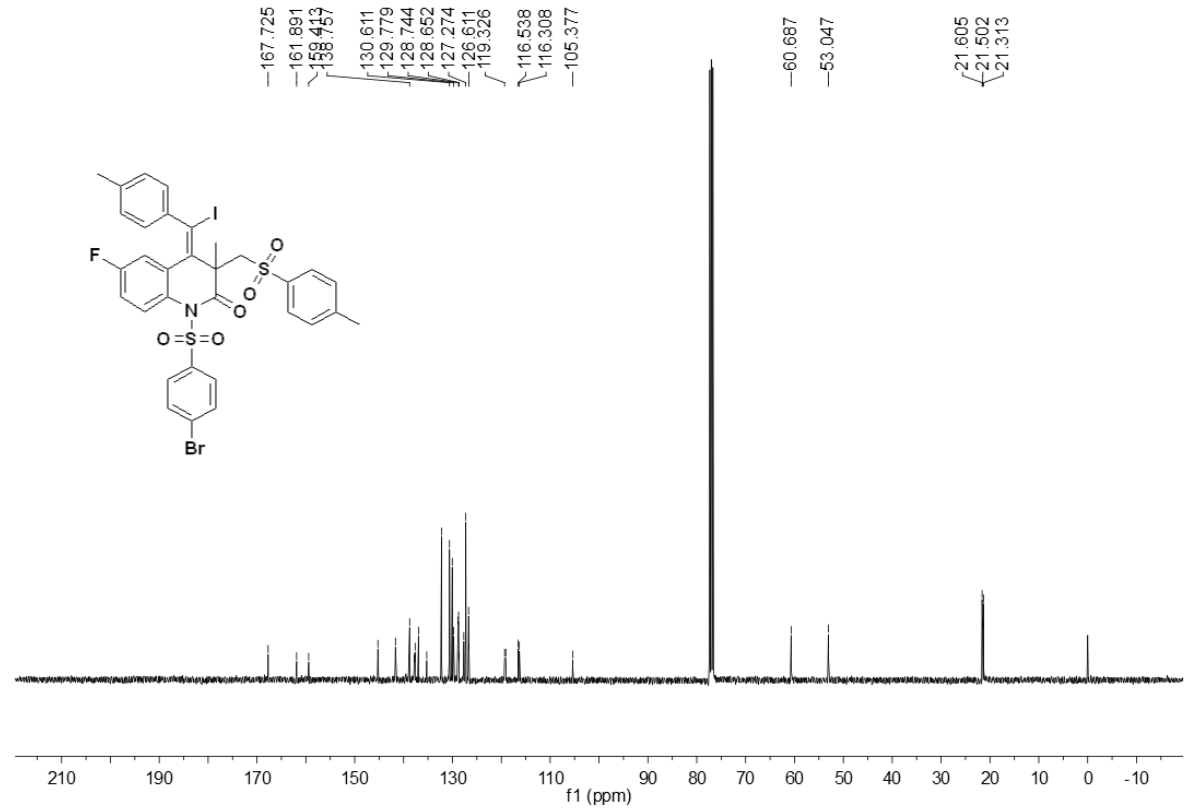
^{1}H NMR Spectrum of Compound 3i



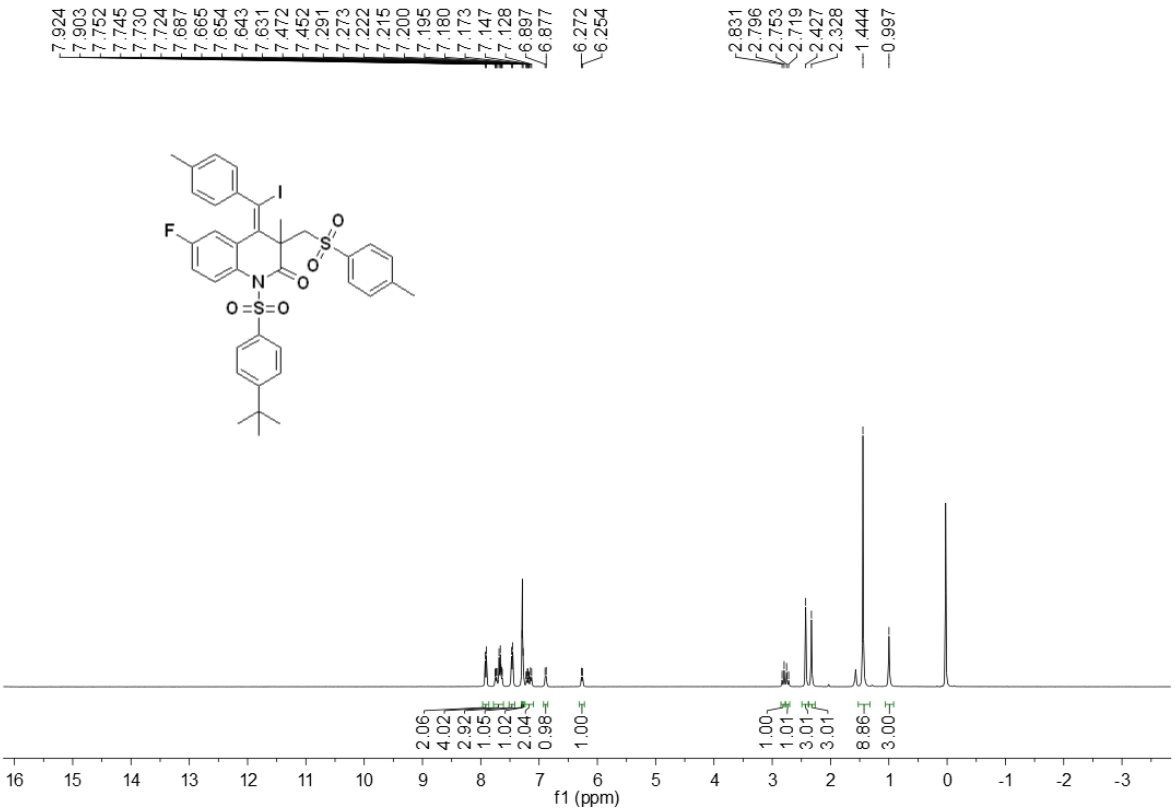
^{13}C NMR Spectrum of Compound 3i



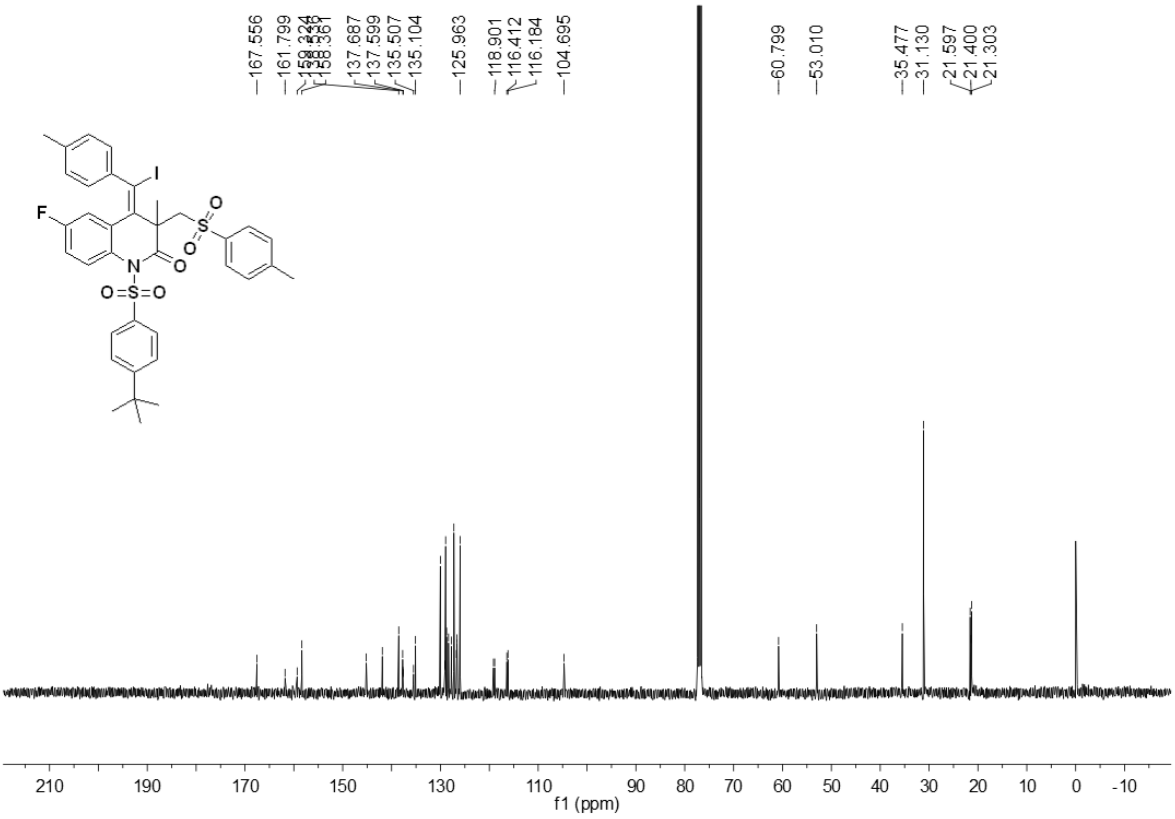
^{1}H NMR Spectrum of Compound 3j



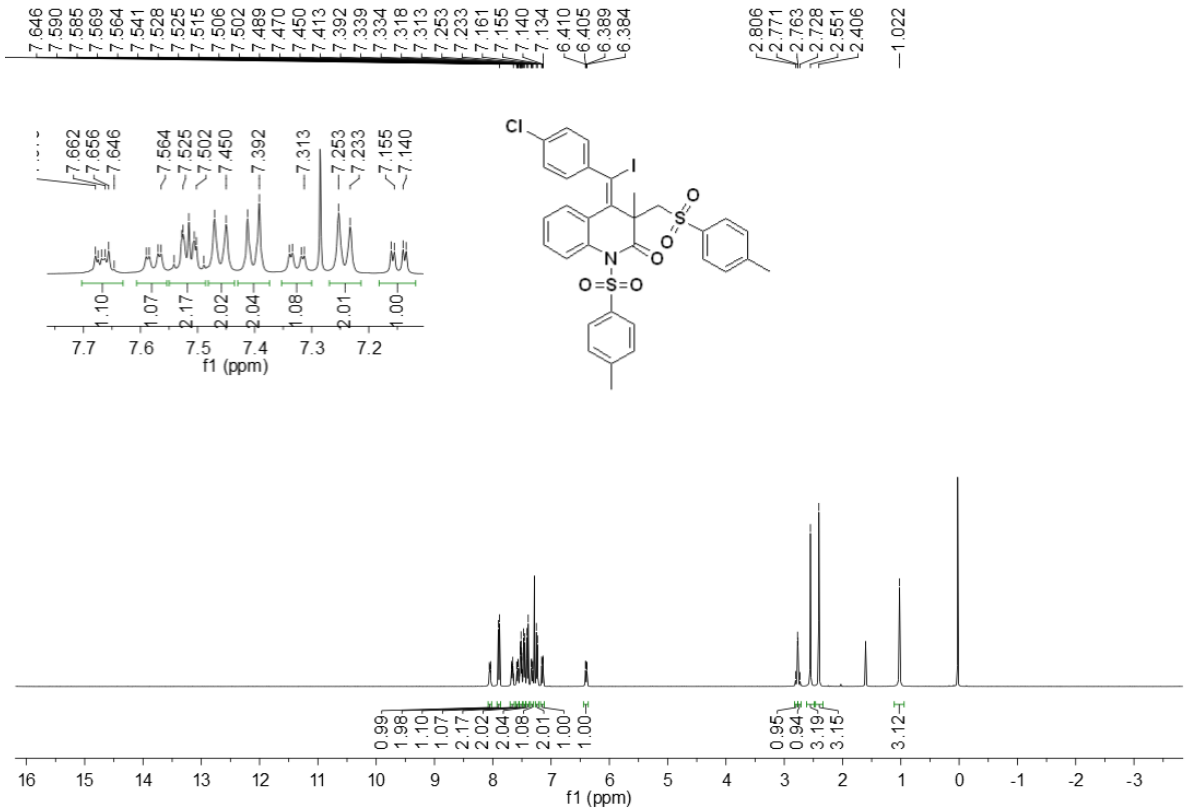
^{13}C NMR Spectrum of Compound 3j



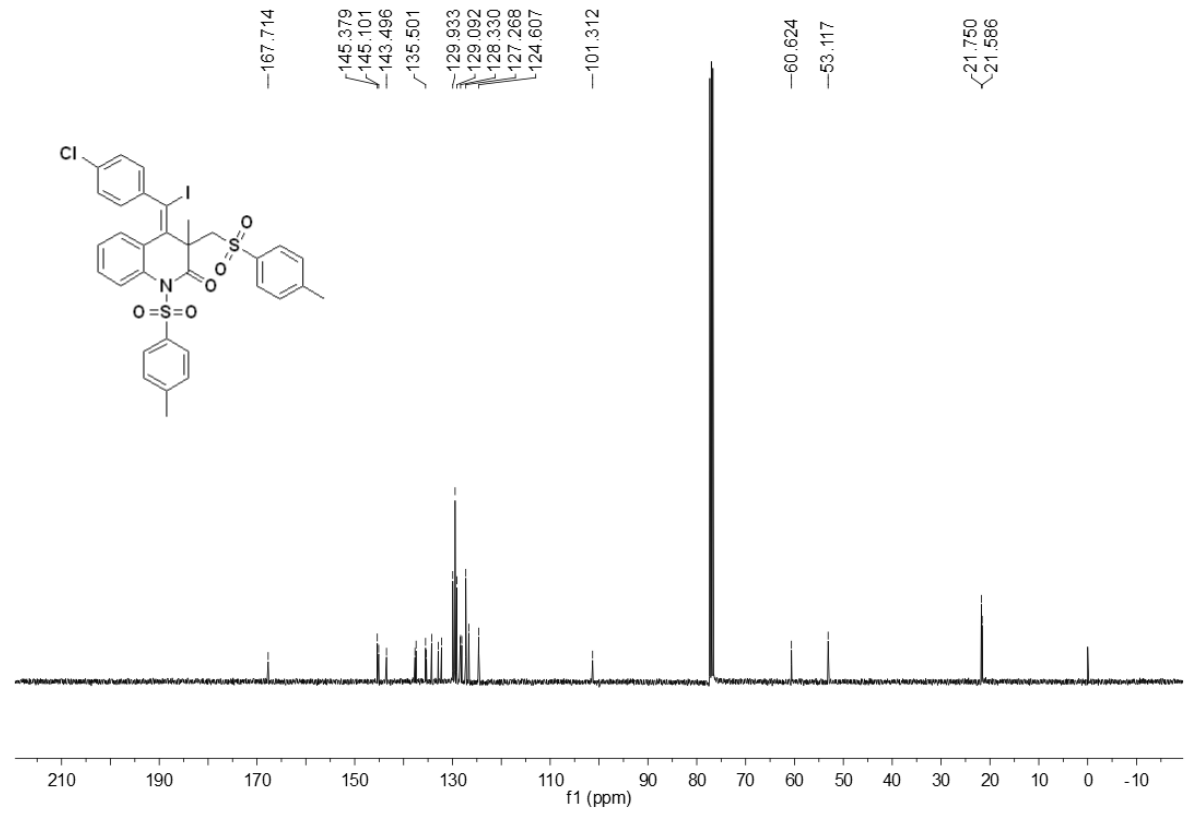
[1]H NMR Spectrum of Compound 3k



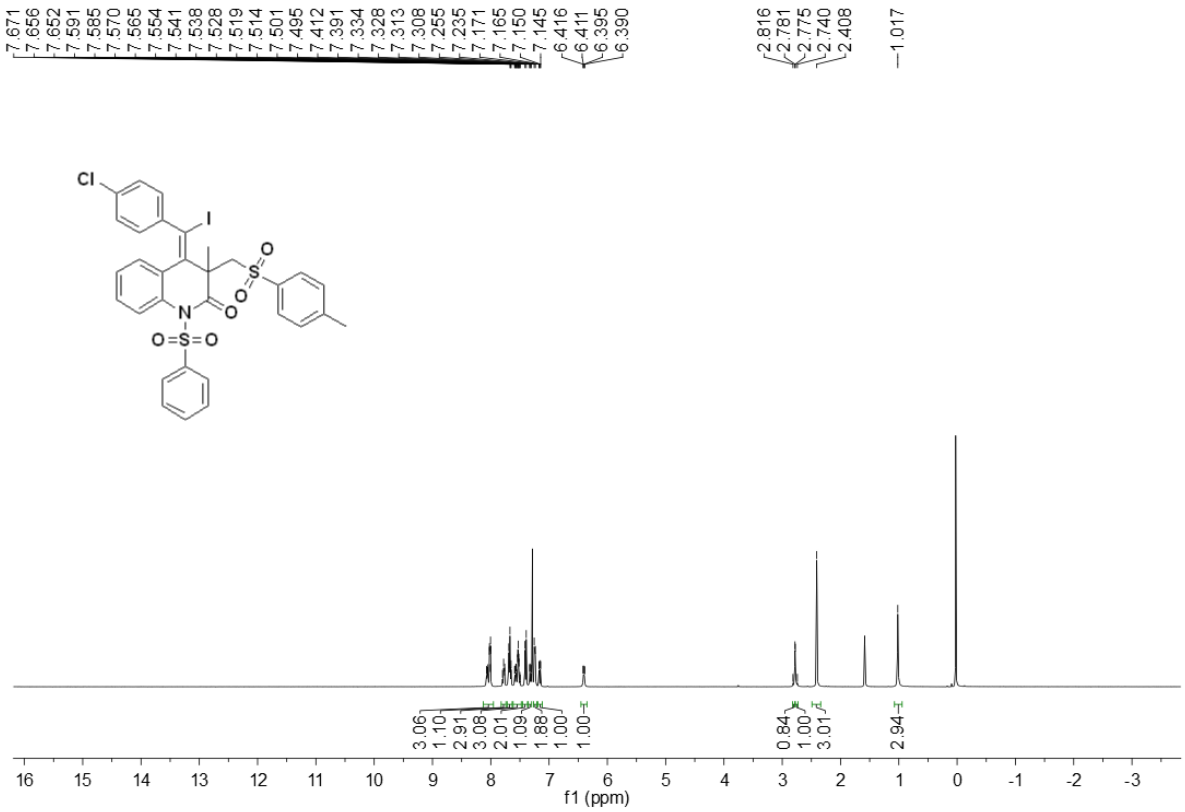
[13]C NMR Spectrum of Compound 3k



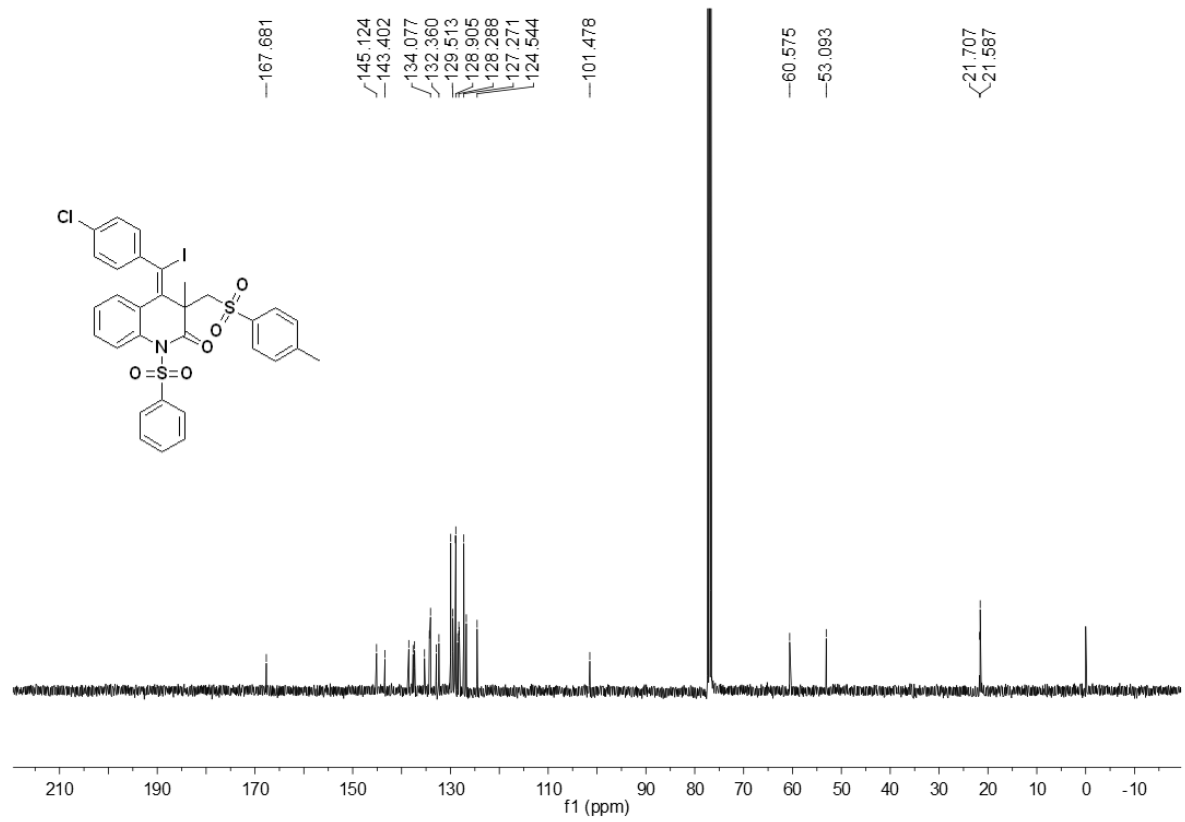
^{1}H NMR Spectrum of Compound 3l



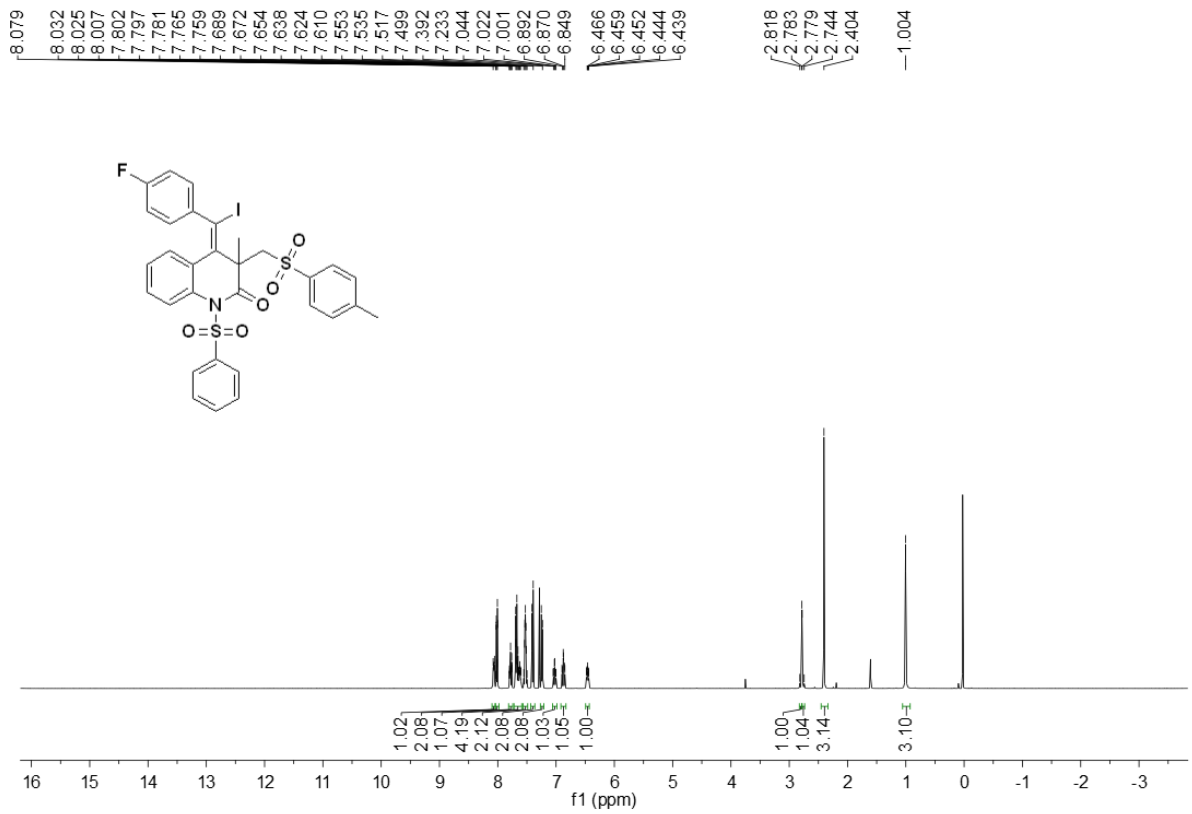
^{13}C NMR Spectrum of Compound 3l



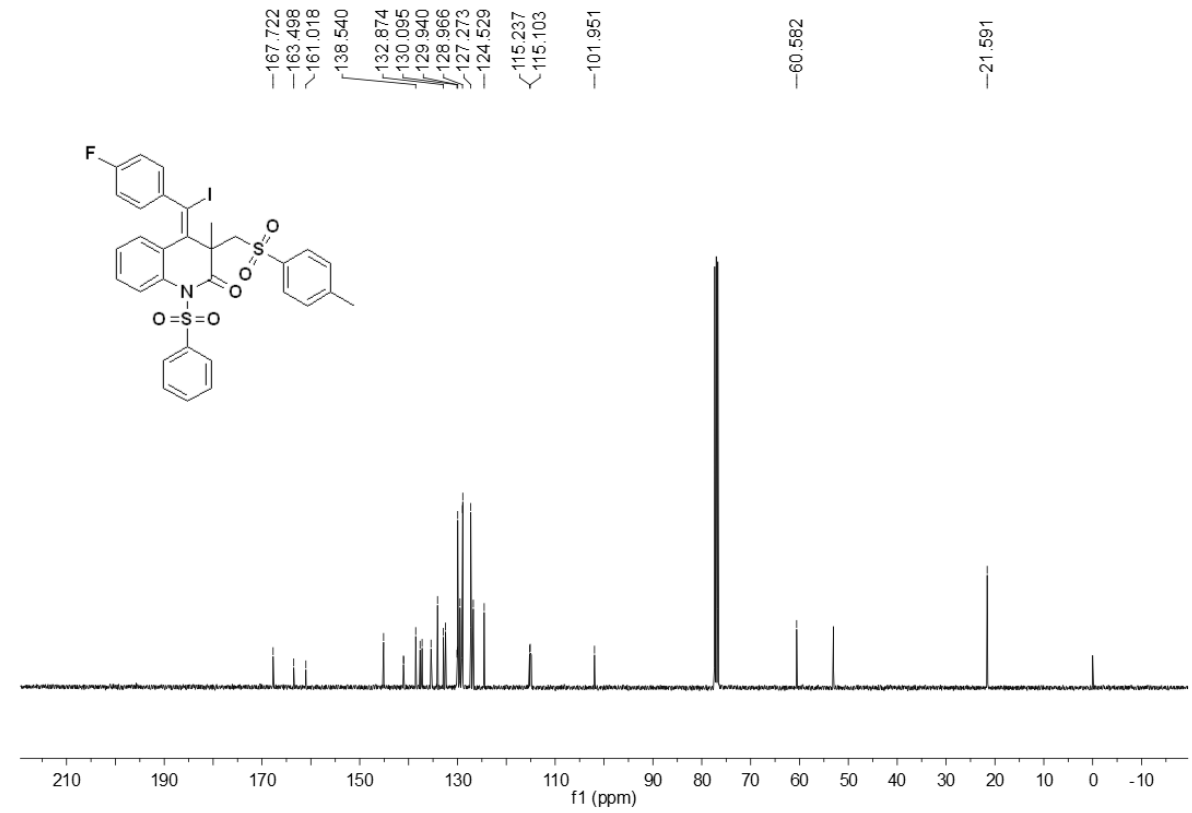
^{1}H NMR Spectrum of Compound 3m



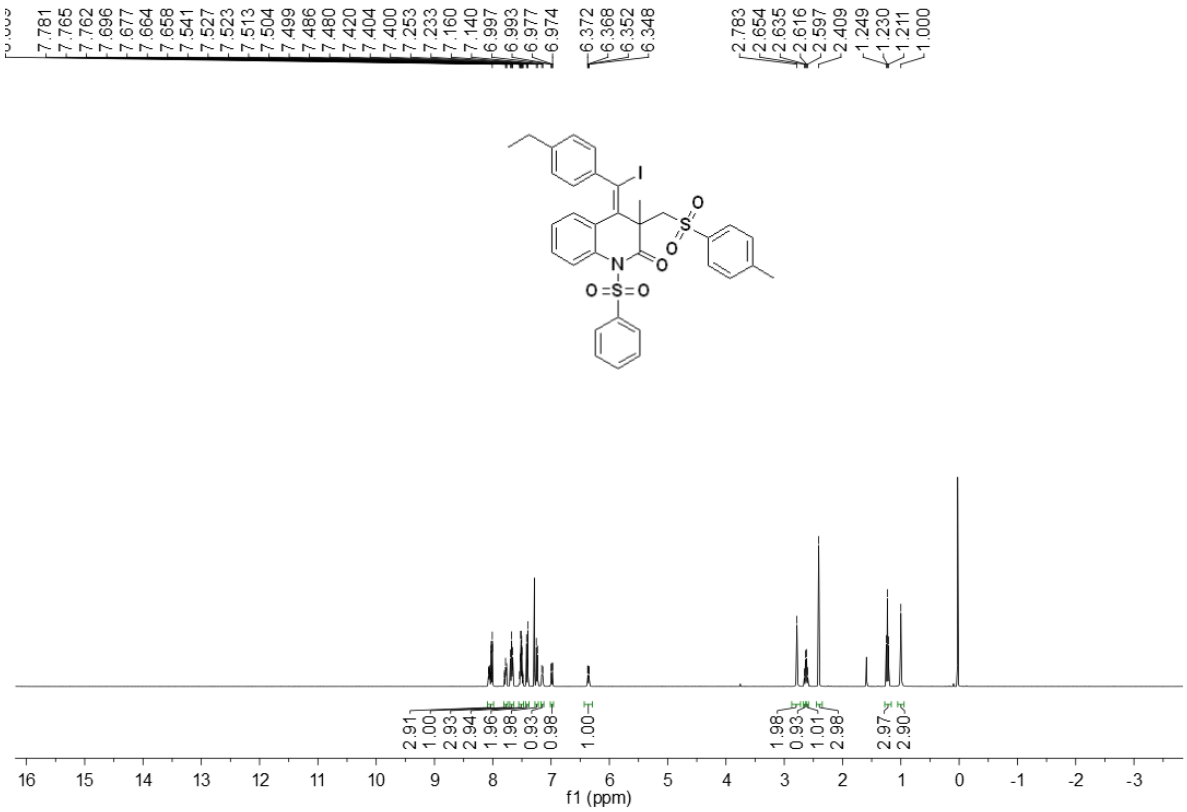
^{13}C NMR Spectrum of Compound 3m



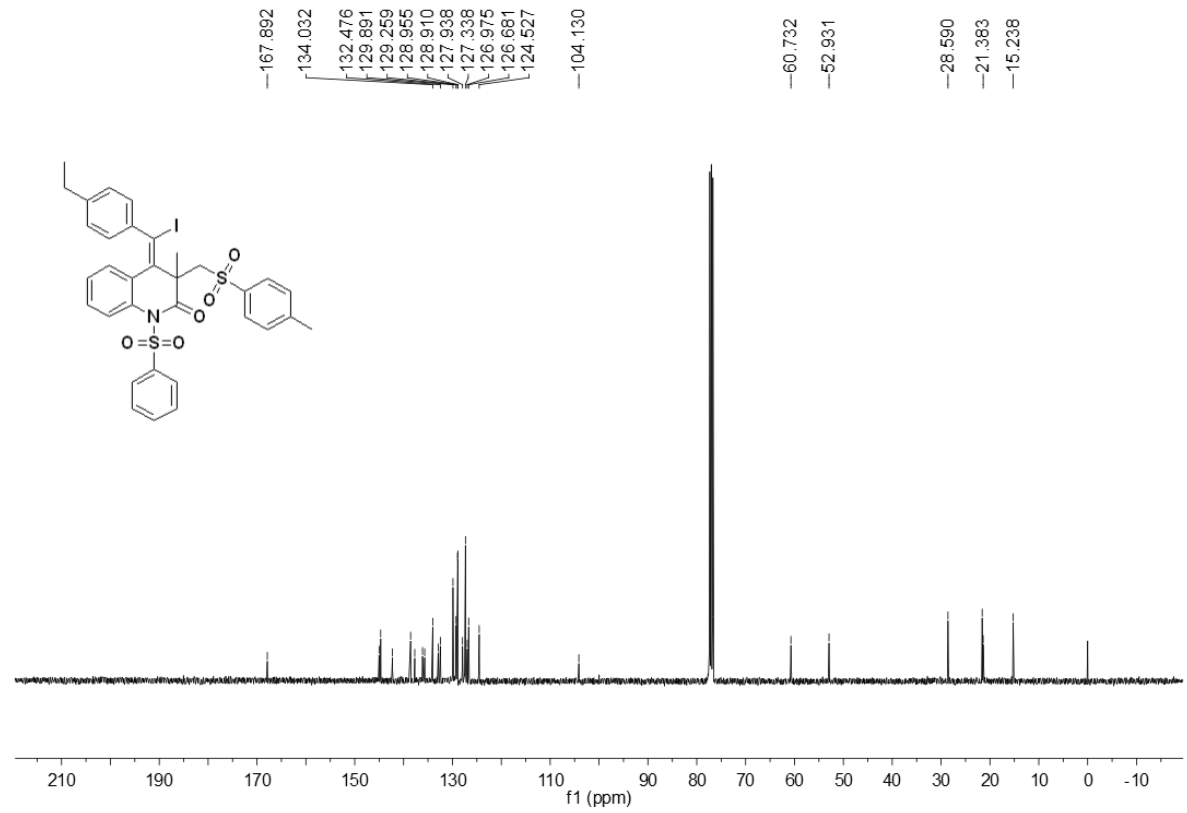
[1]H NMR Spectrum of Compound 3n



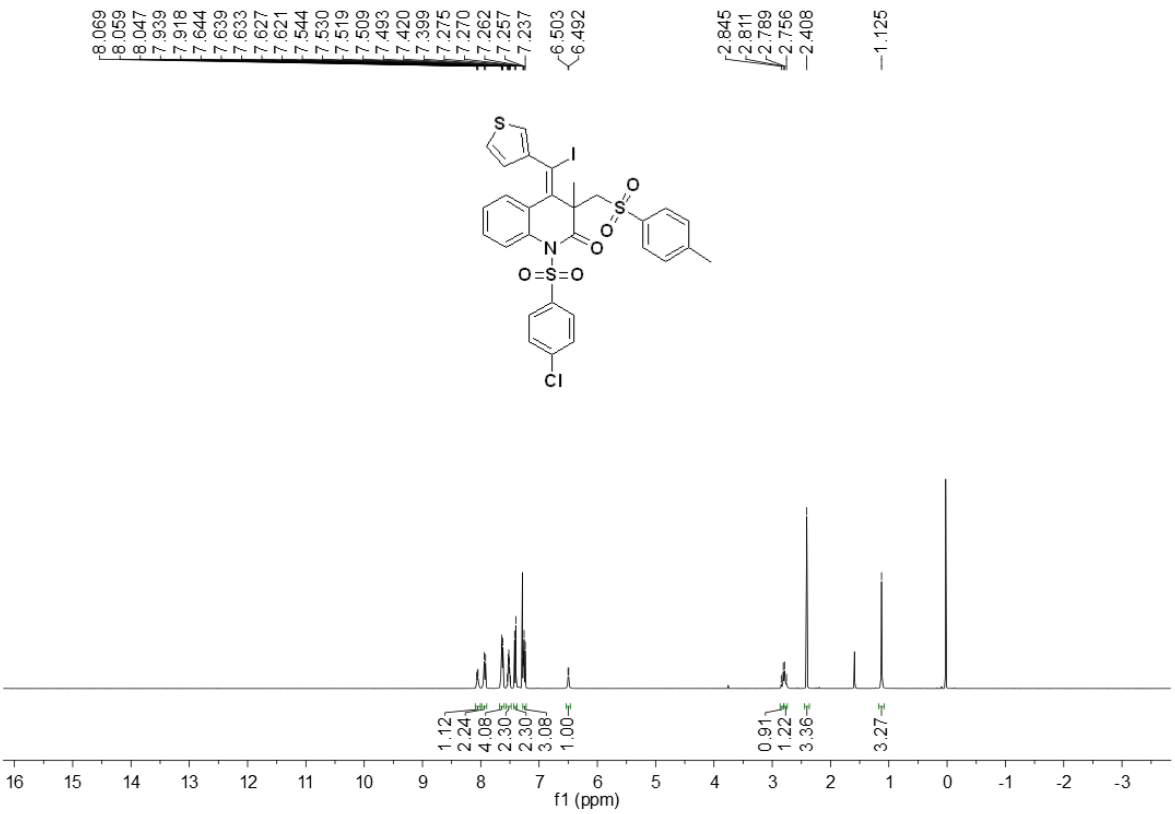
[13]C NMR Spectrum of Compound 3n



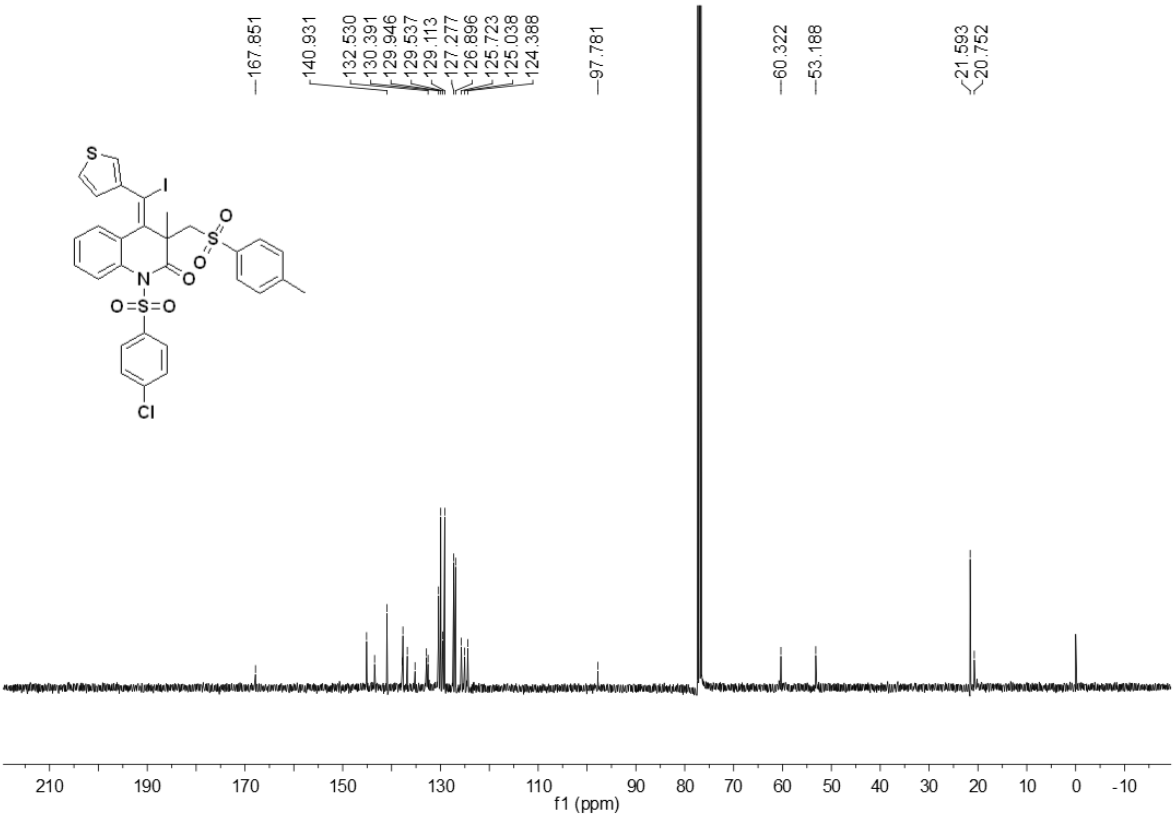
[1]H NMR Spectrum of Compound 3o



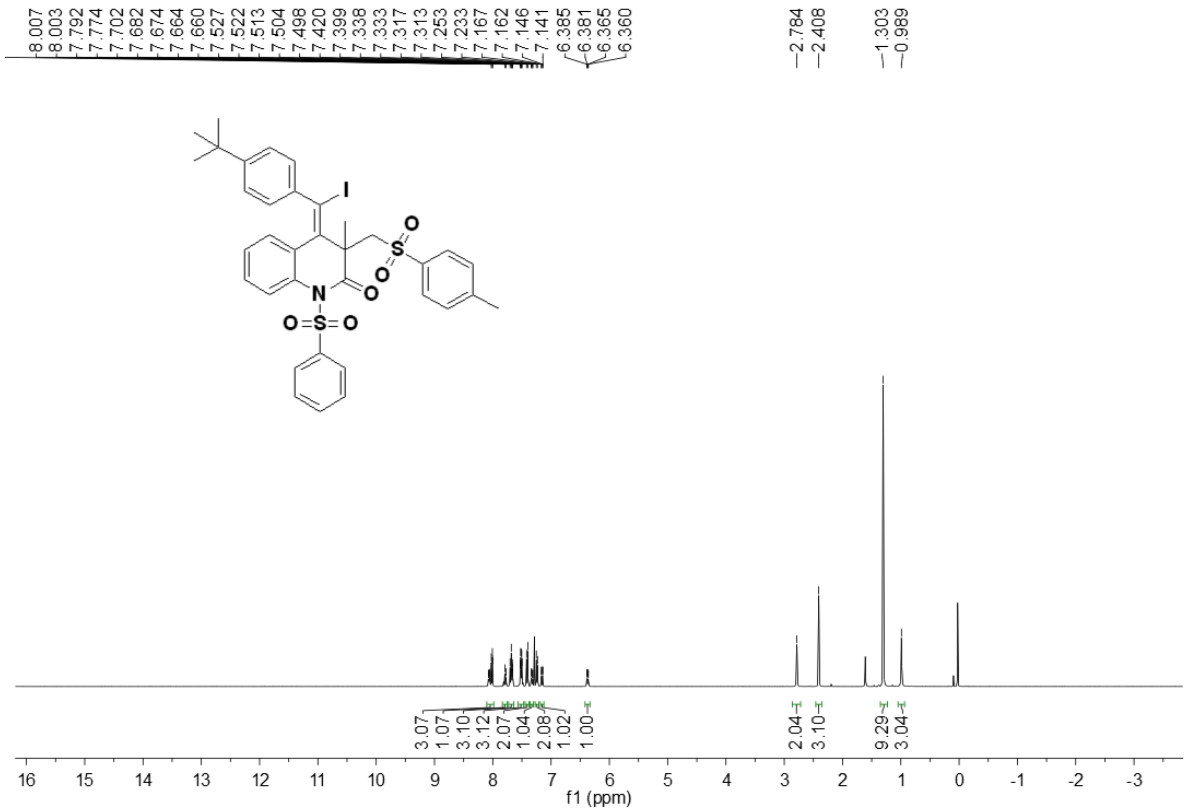
[13]C NMR Spectrum of Compound 3o



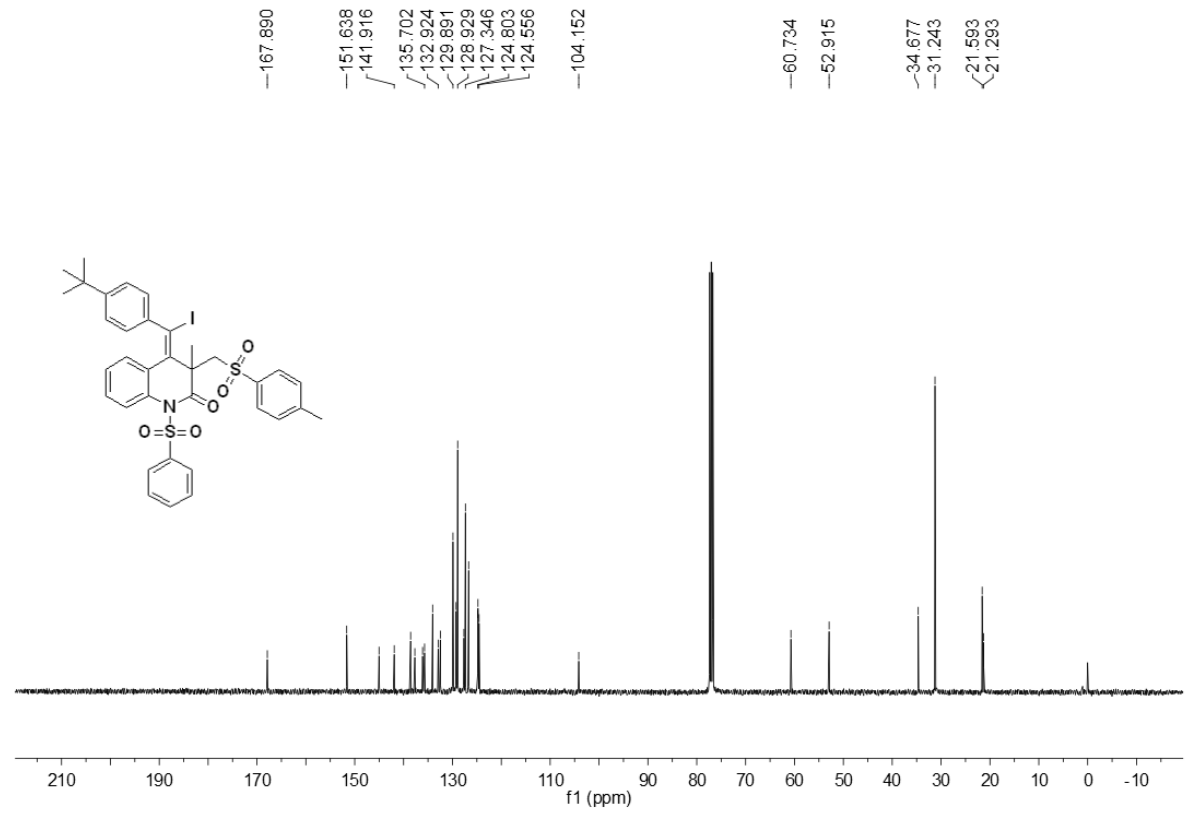
[1]H NMR Spectrum of Compound 3p



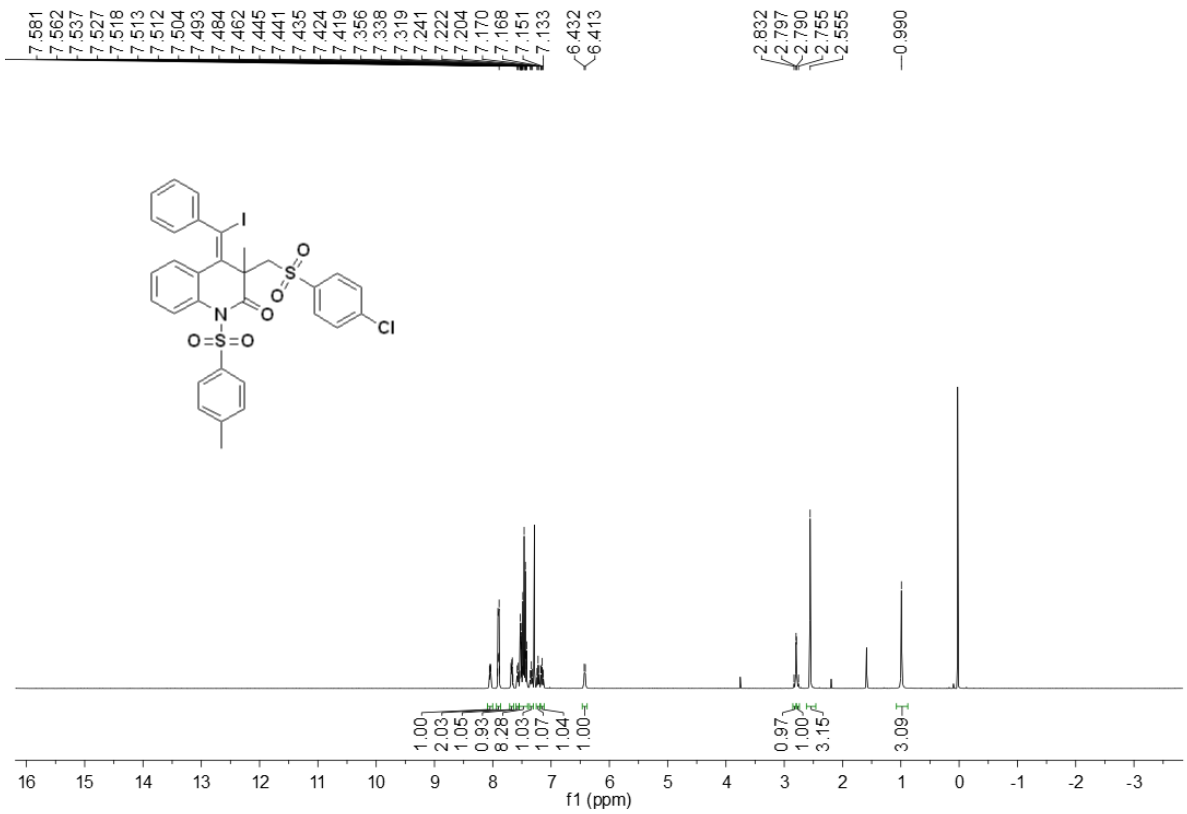
[13]C NMR Spectrum of Compound 3p



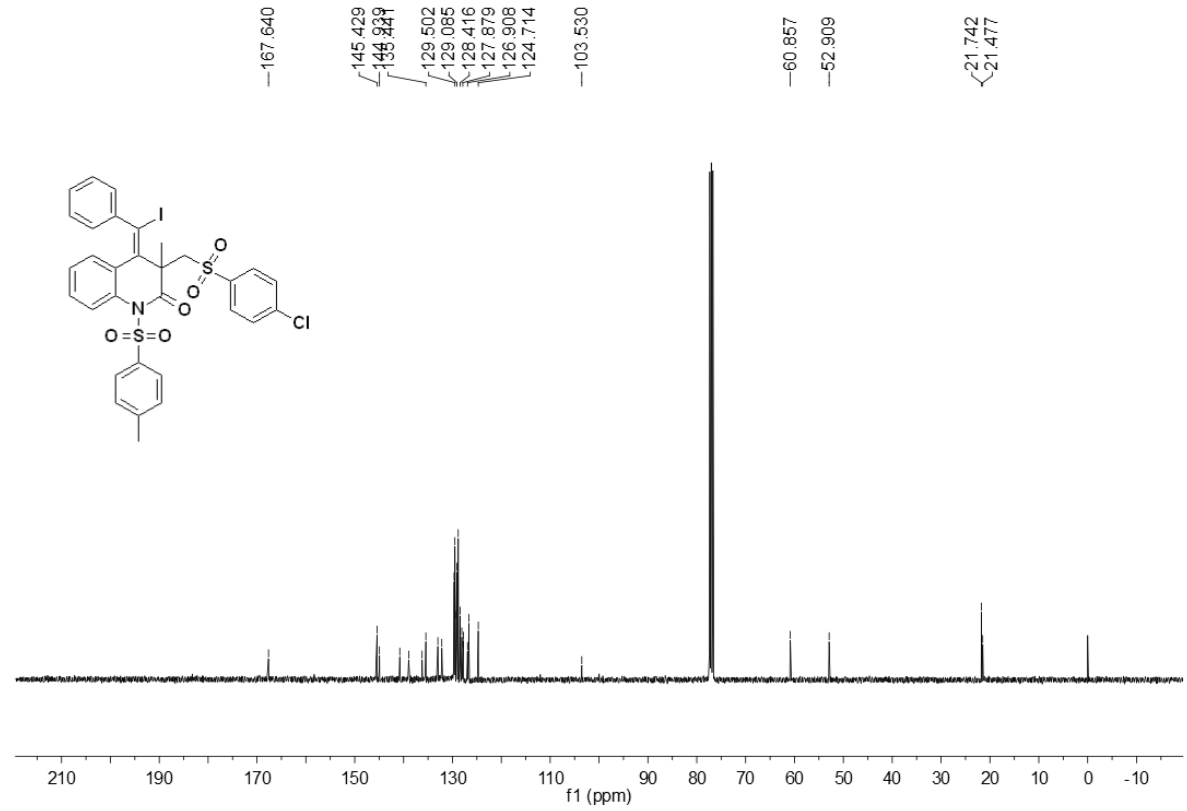
[1]H NMR Spectrum of Compound 3q



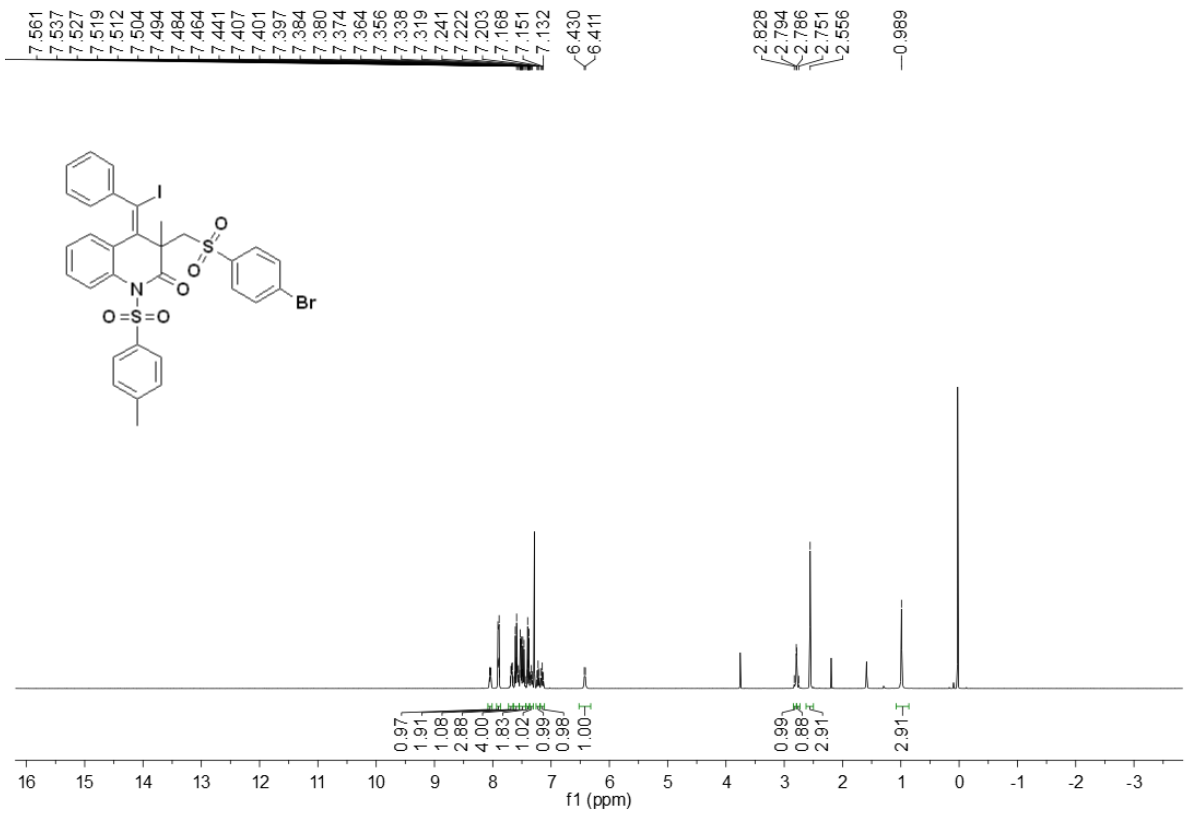
[13]C NMR Spectrum of Compound 3q



^{1}H NMR Spectrum of Compound 3r



^{13}C NMR Spectrum of Compound 3r



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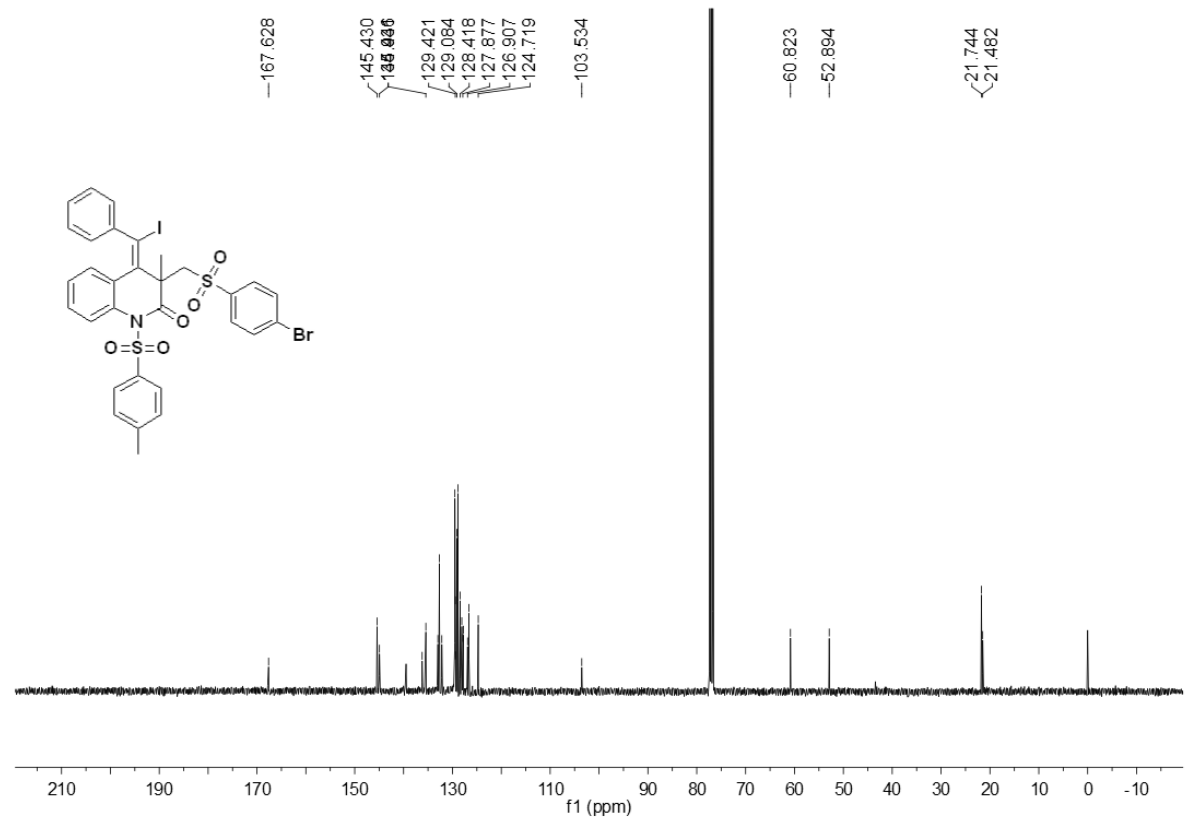
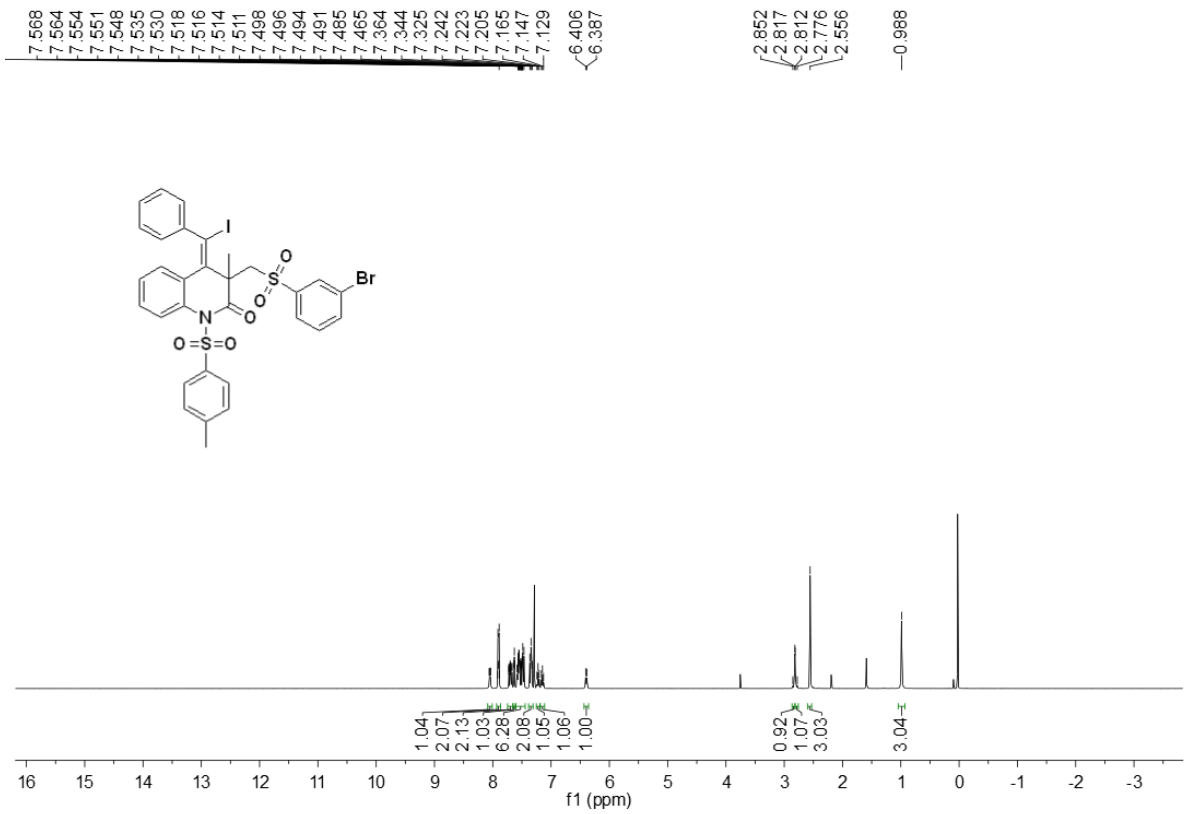


[13]C NMR Spectrum of Compound 3s



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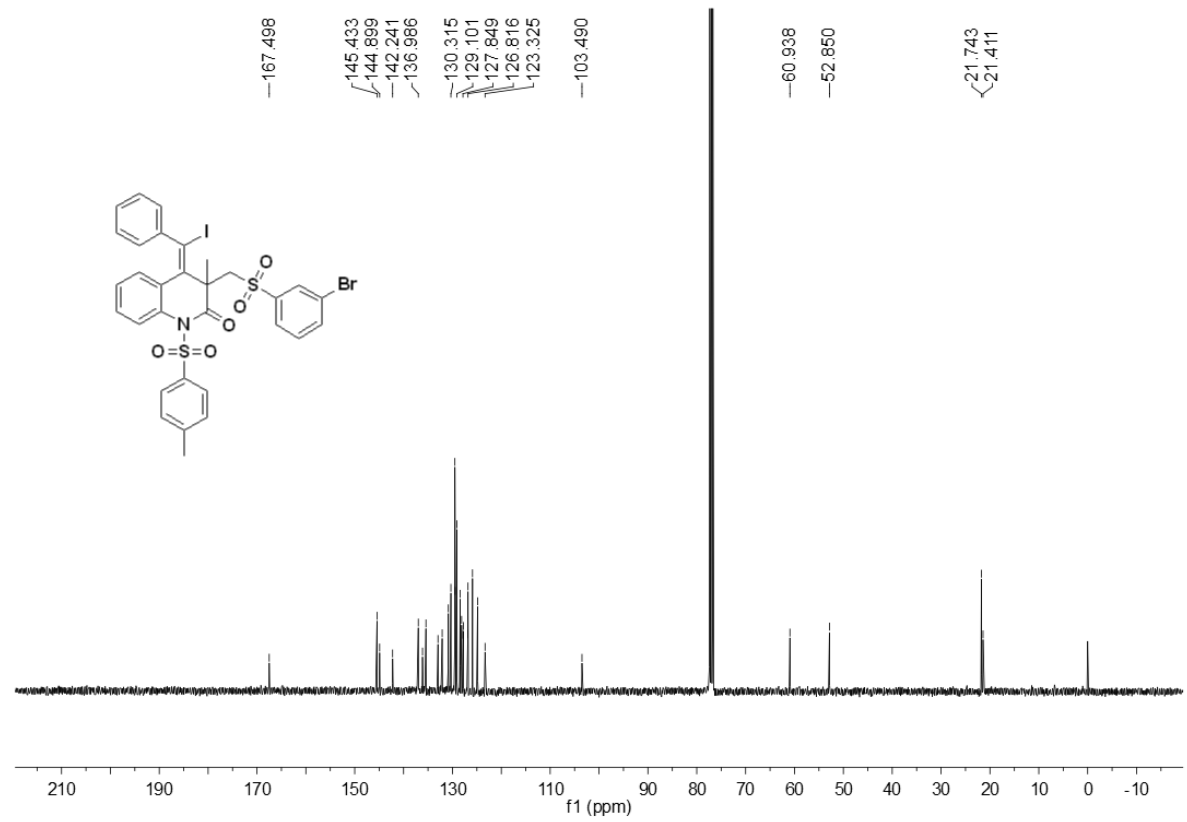
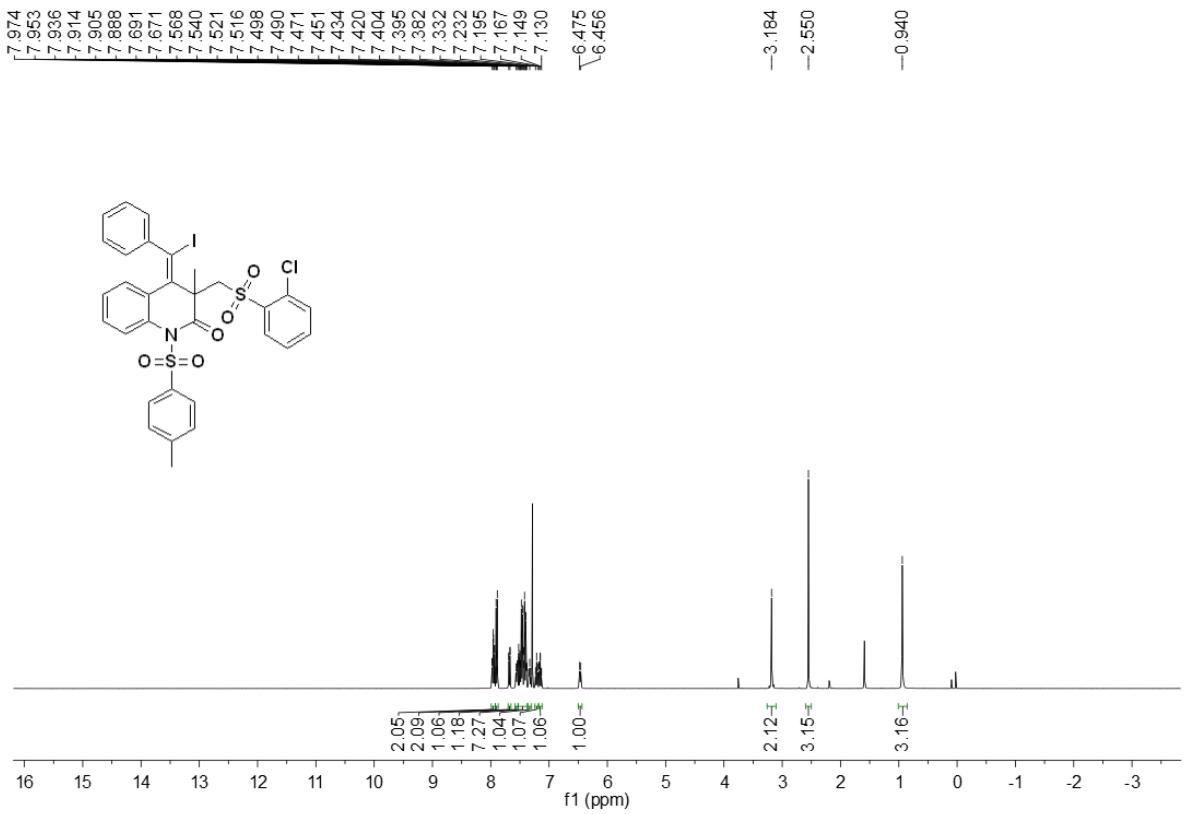


^{13}C NMR Spectrum of Compound 3t



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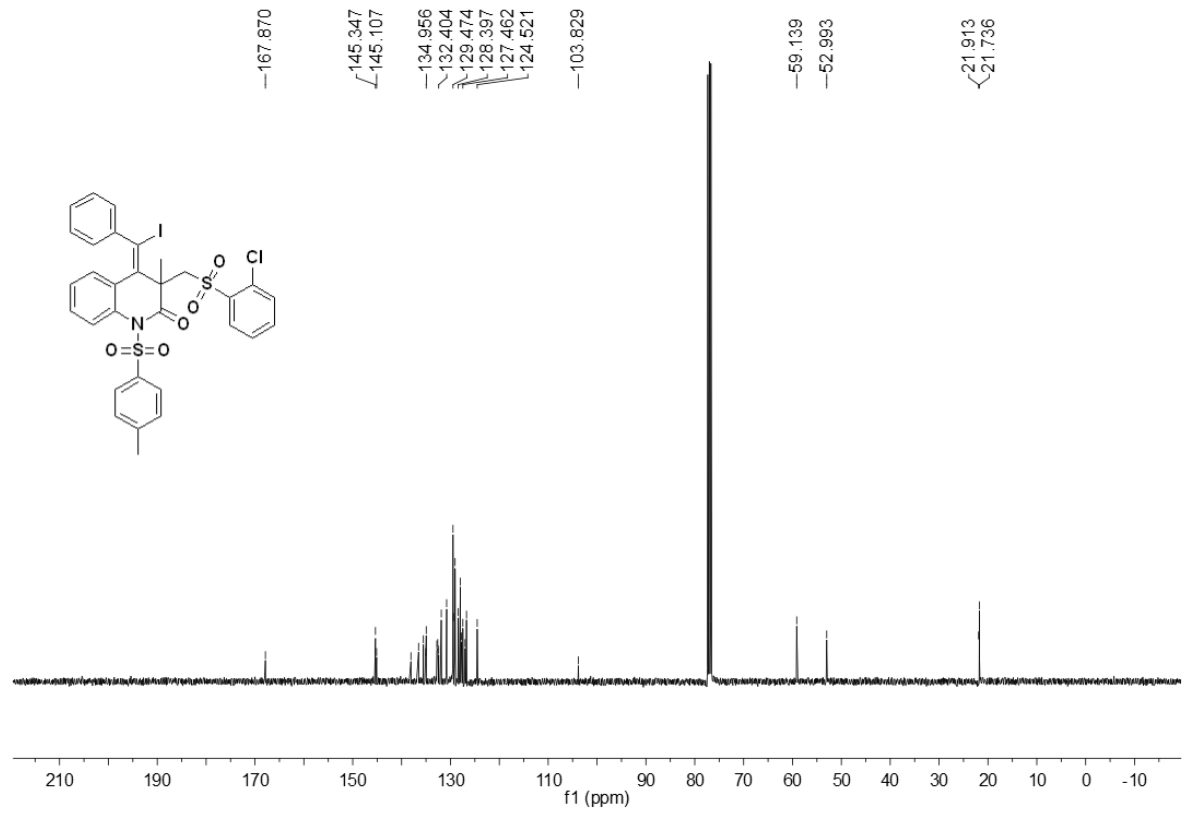
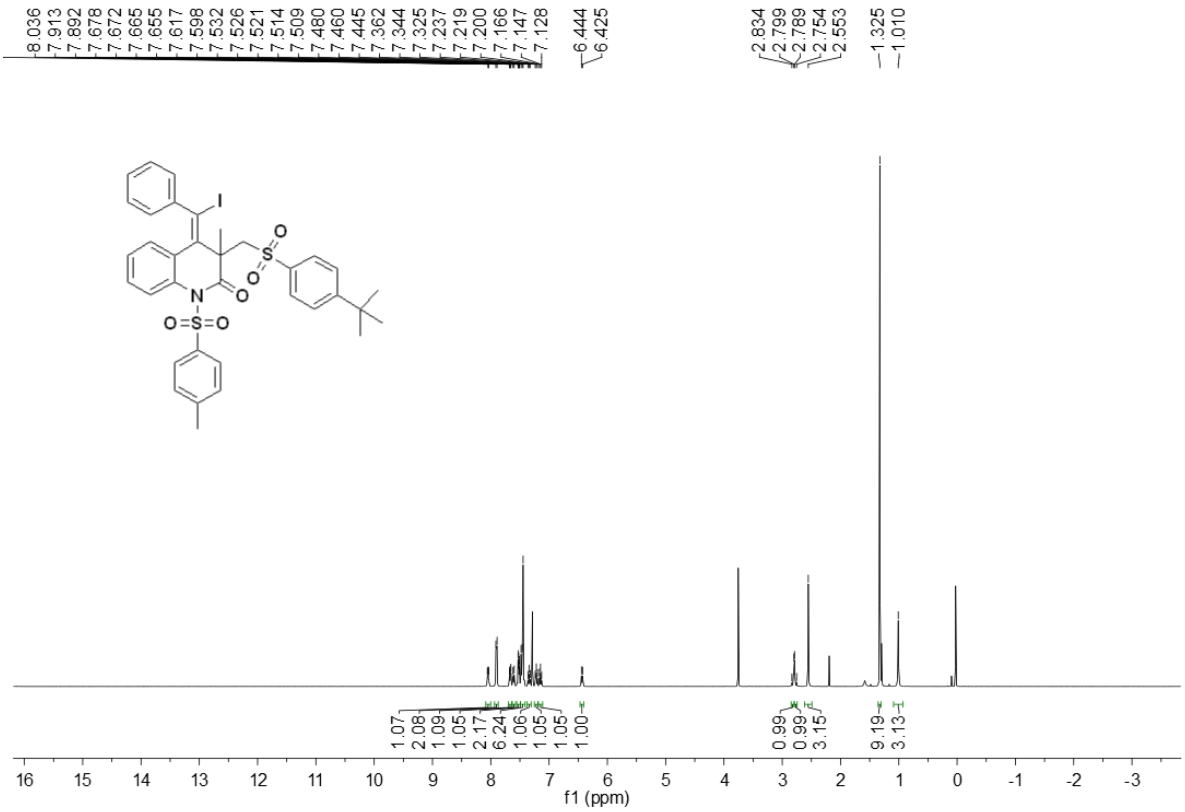
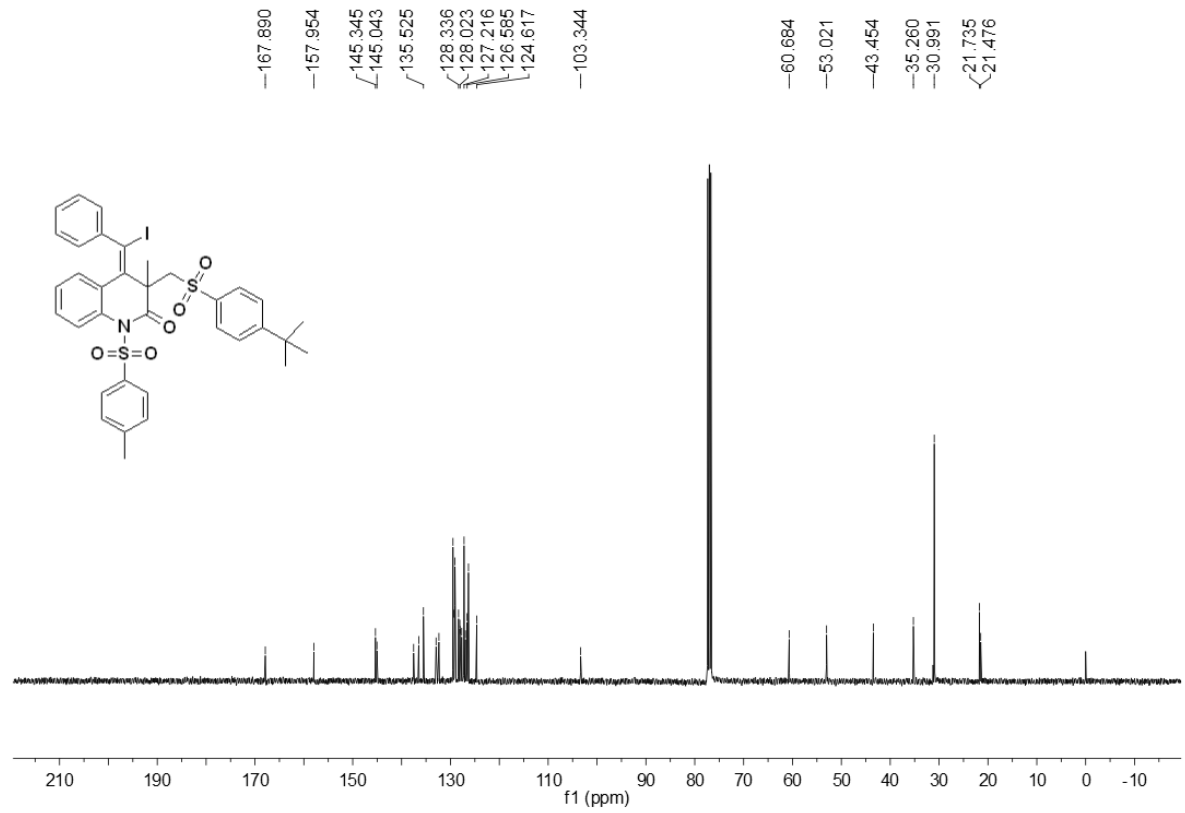


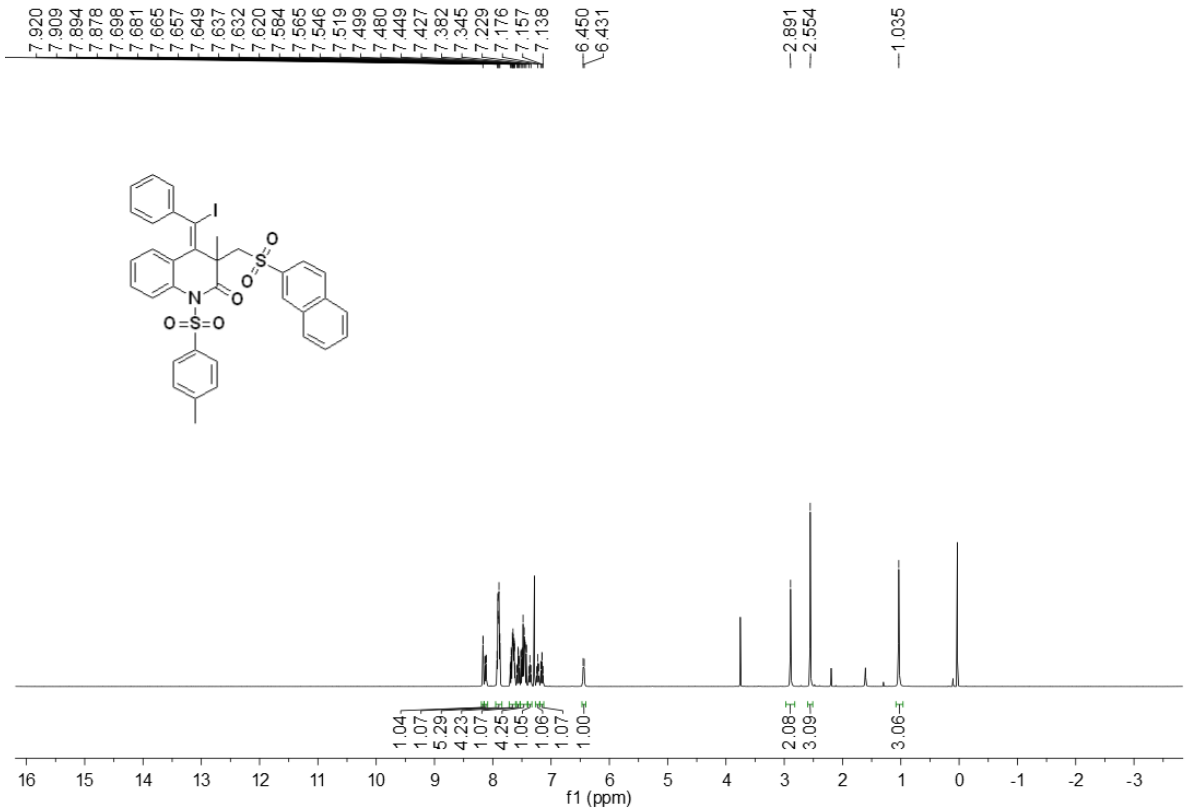
[13]C NMR Spectrum of Compound 3u



^{1}H NMR Spectrum of Compound 3v



^{13}C NMR Spectrum of Compound 3v



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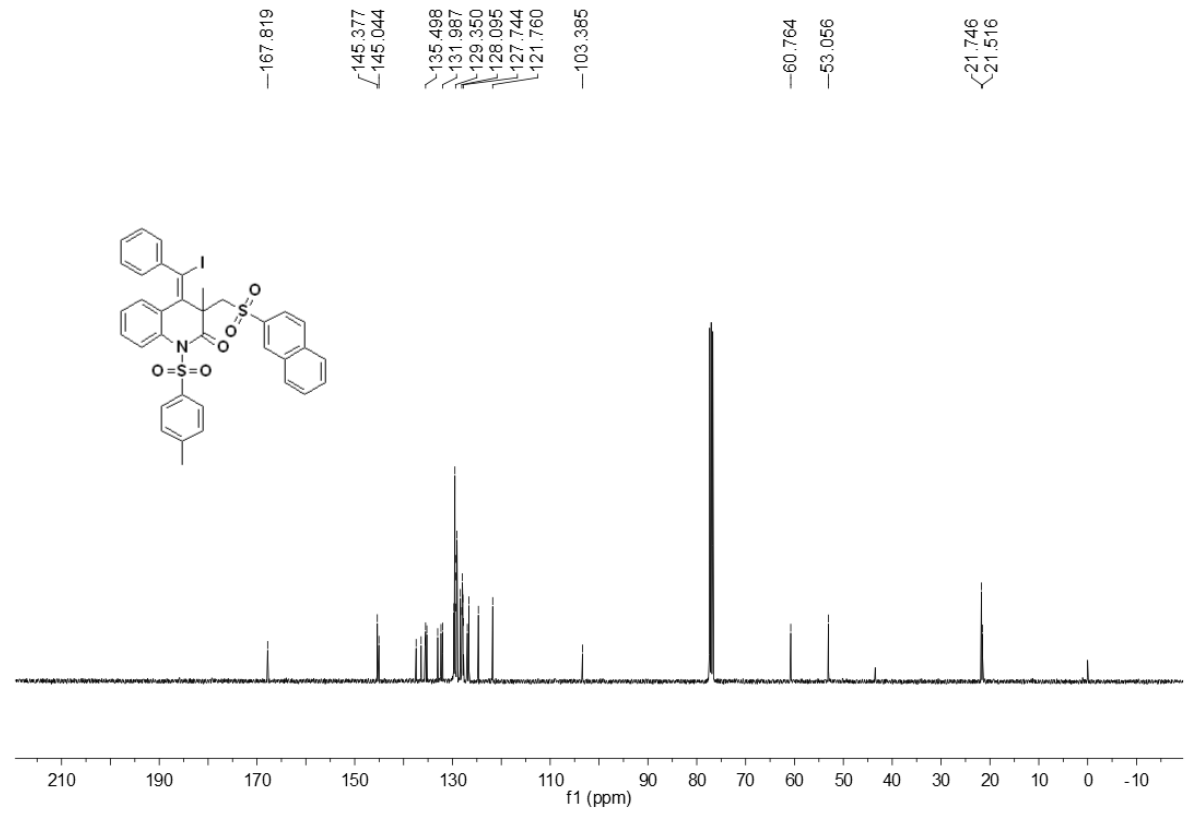

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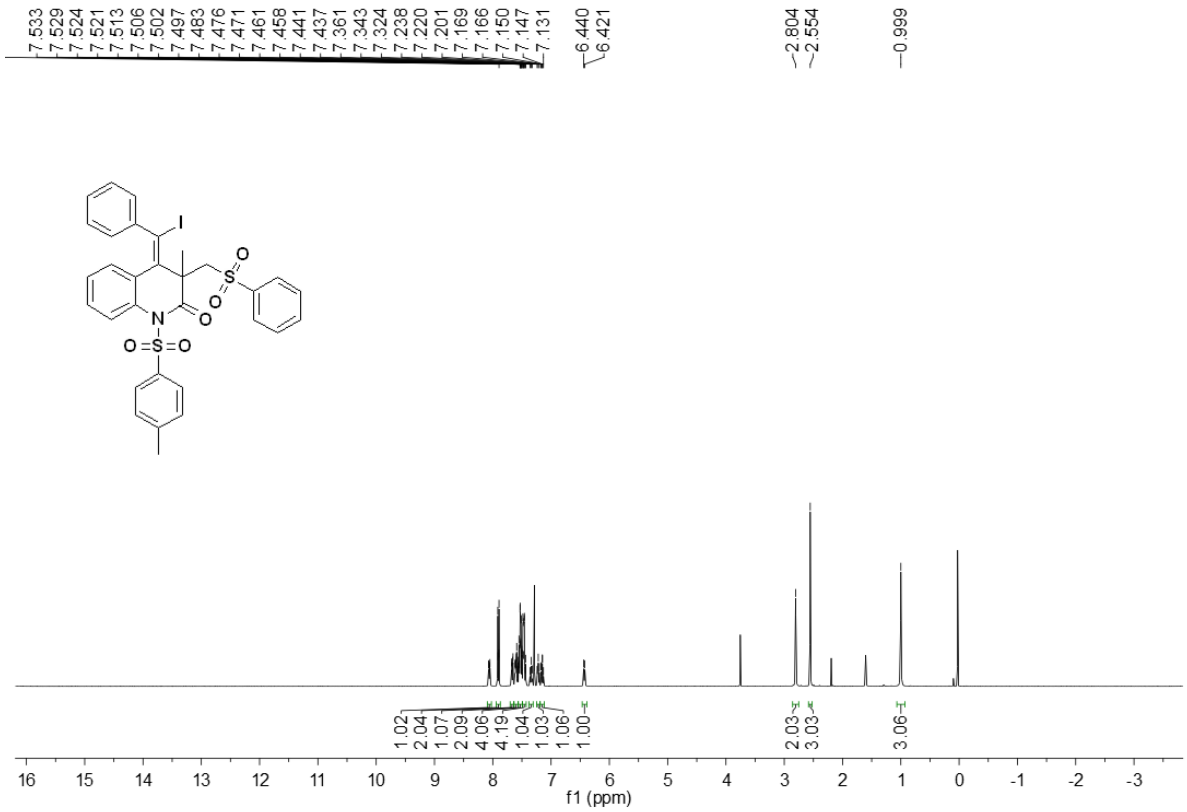

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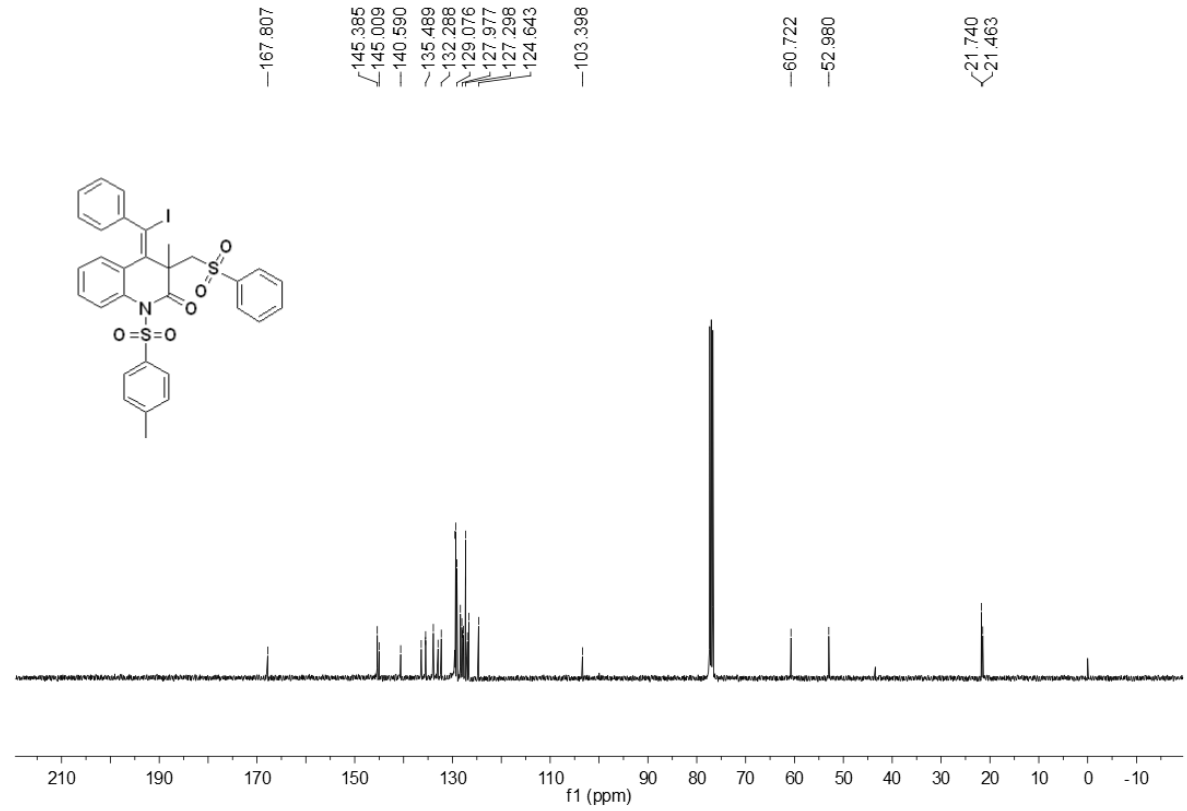

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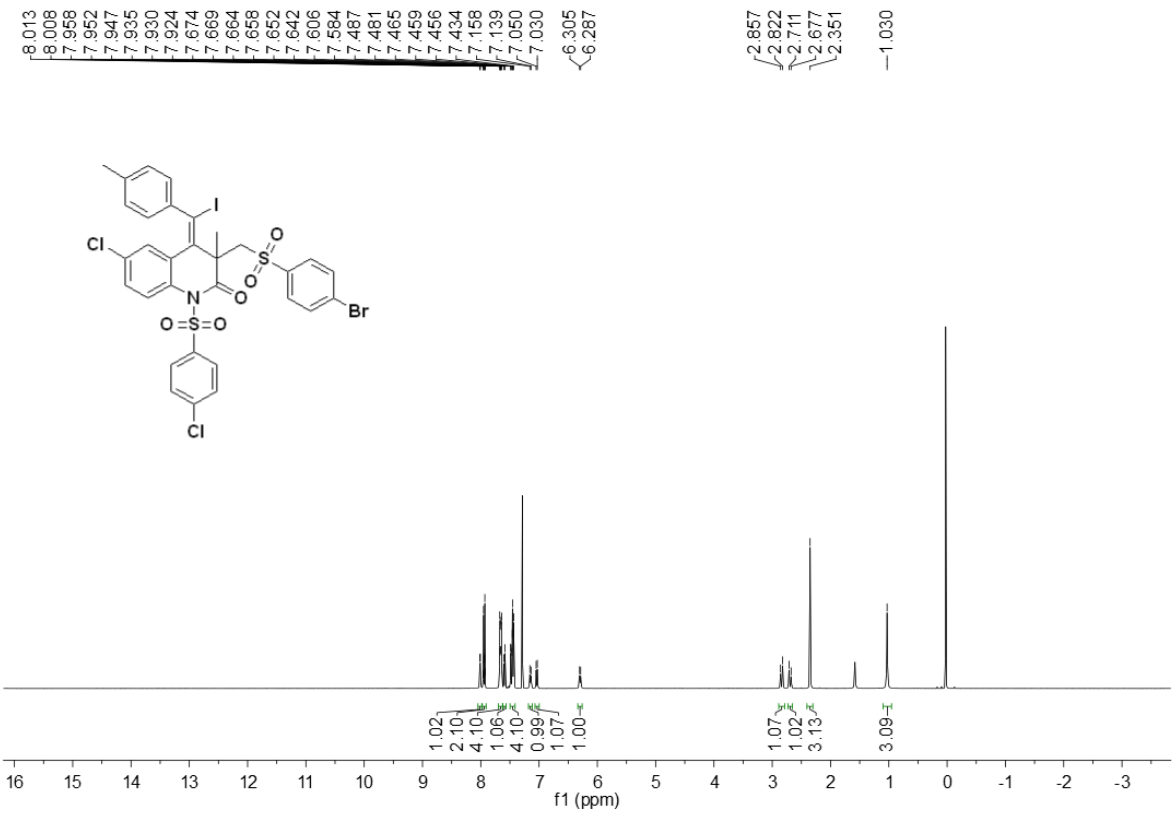
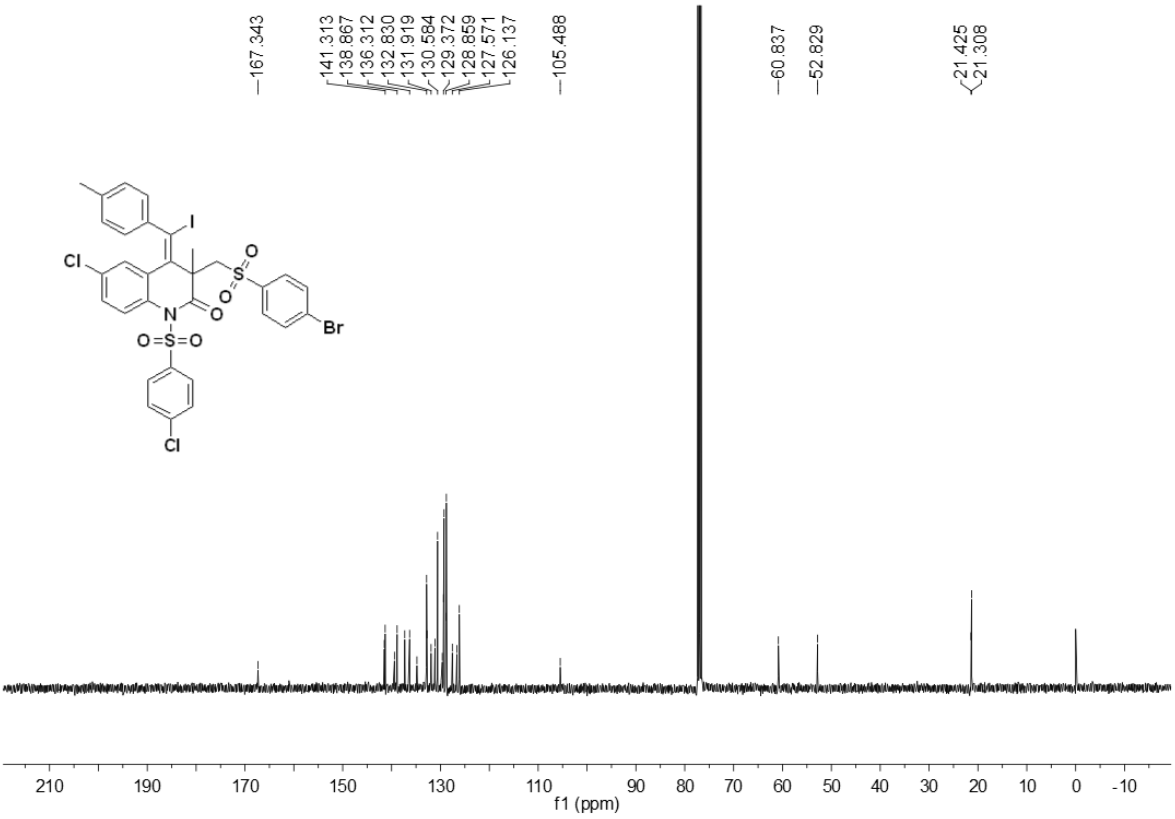


[1]H NMR Spectrum of Compound 3y



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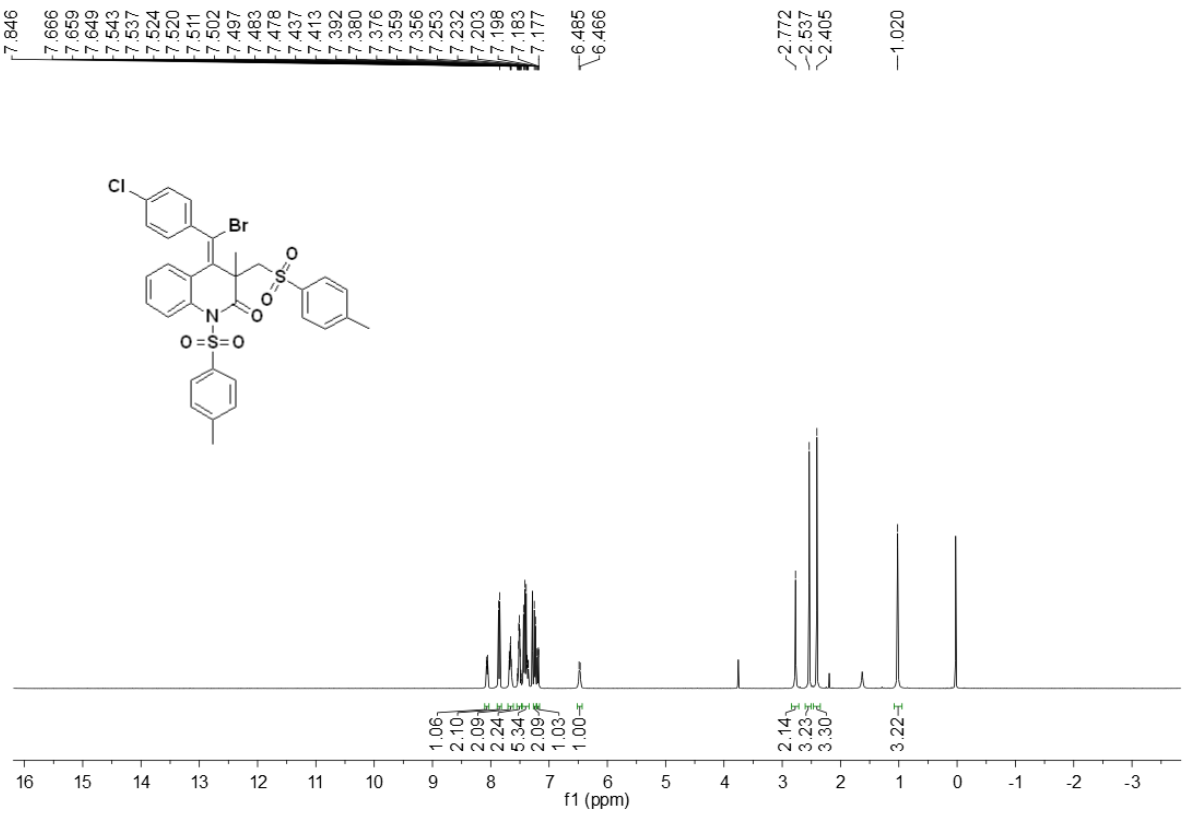
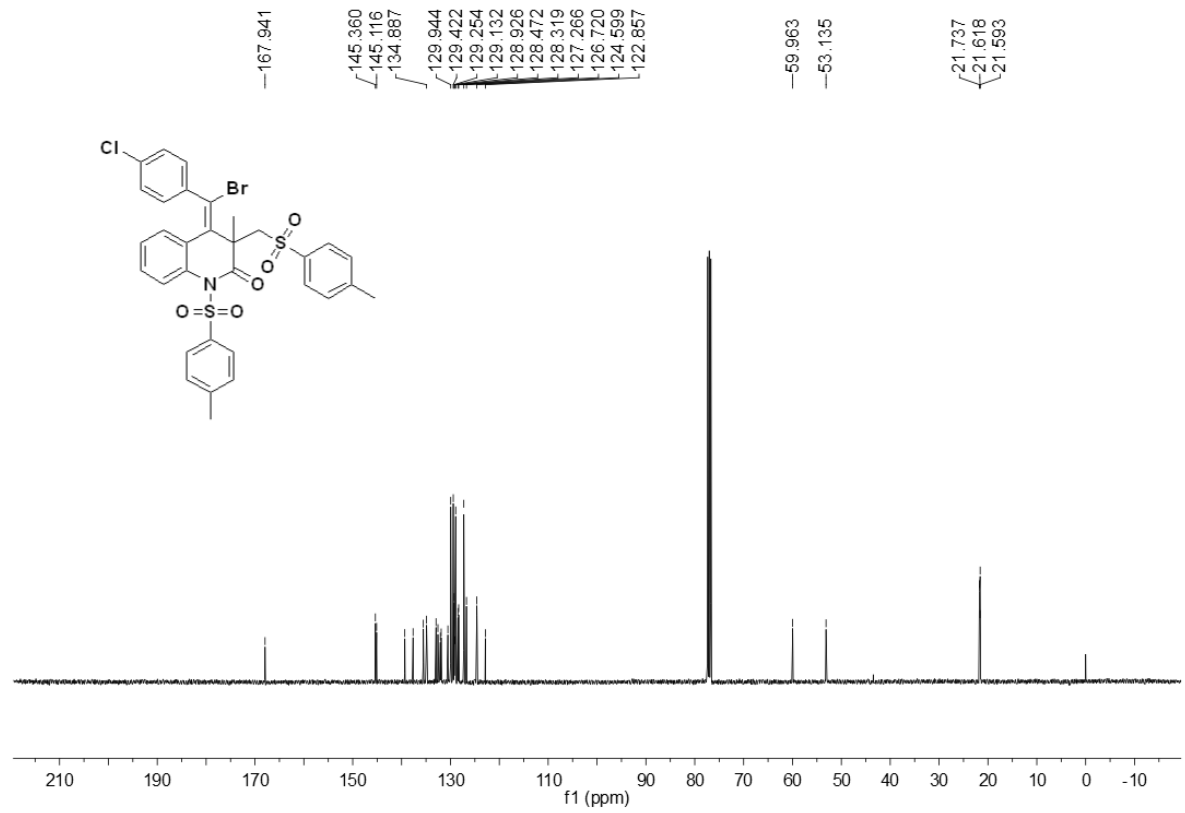
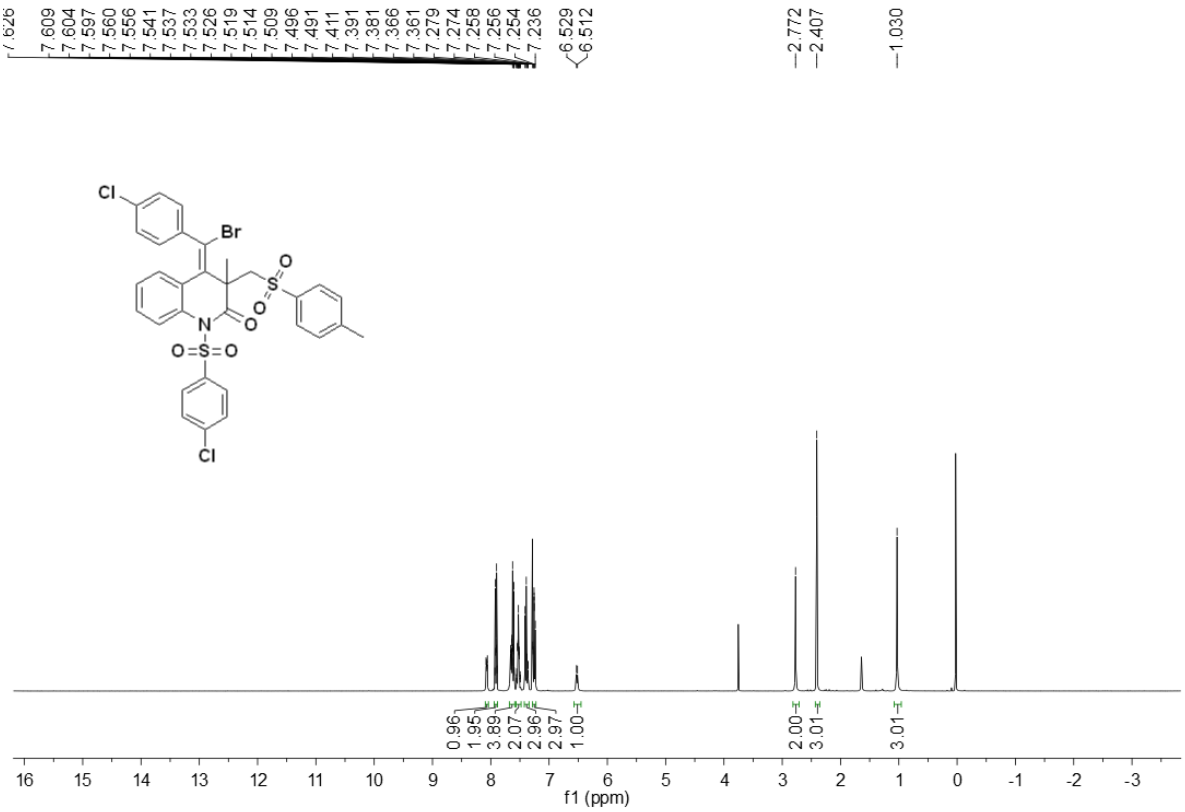


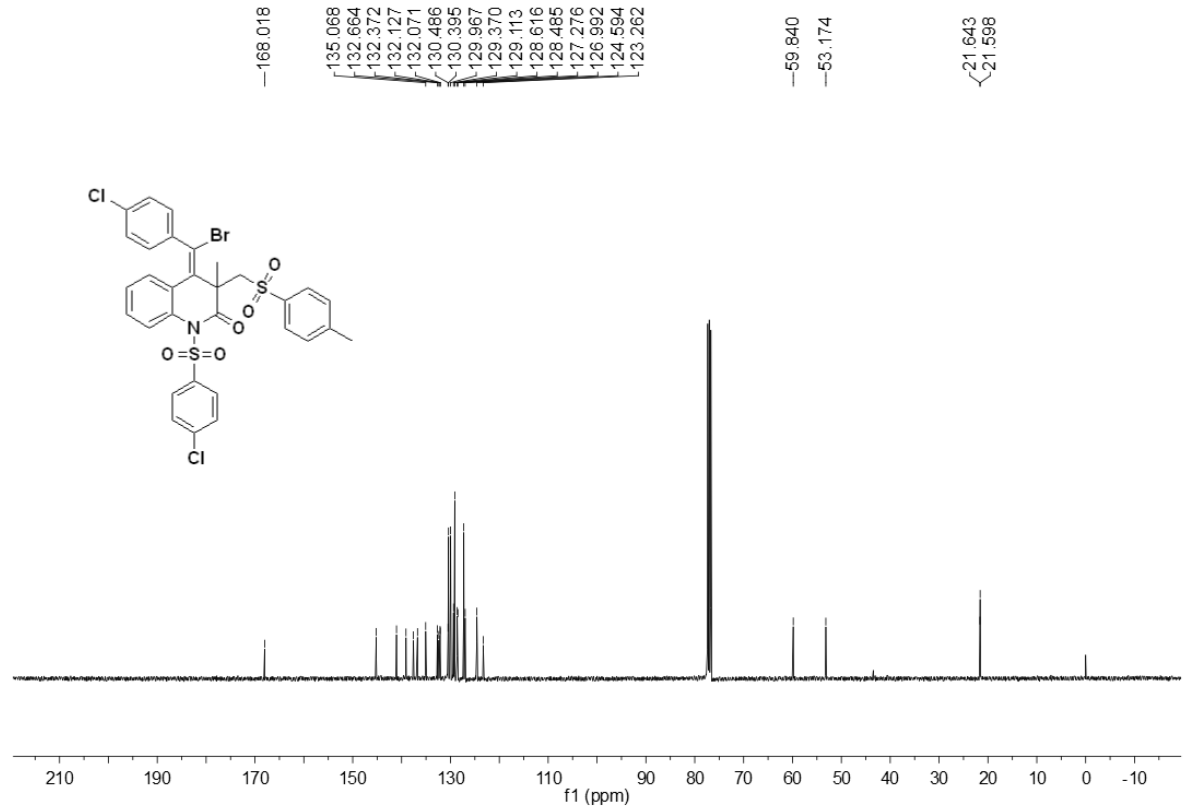
^{1}H NMR Spectrum of Compound 4a



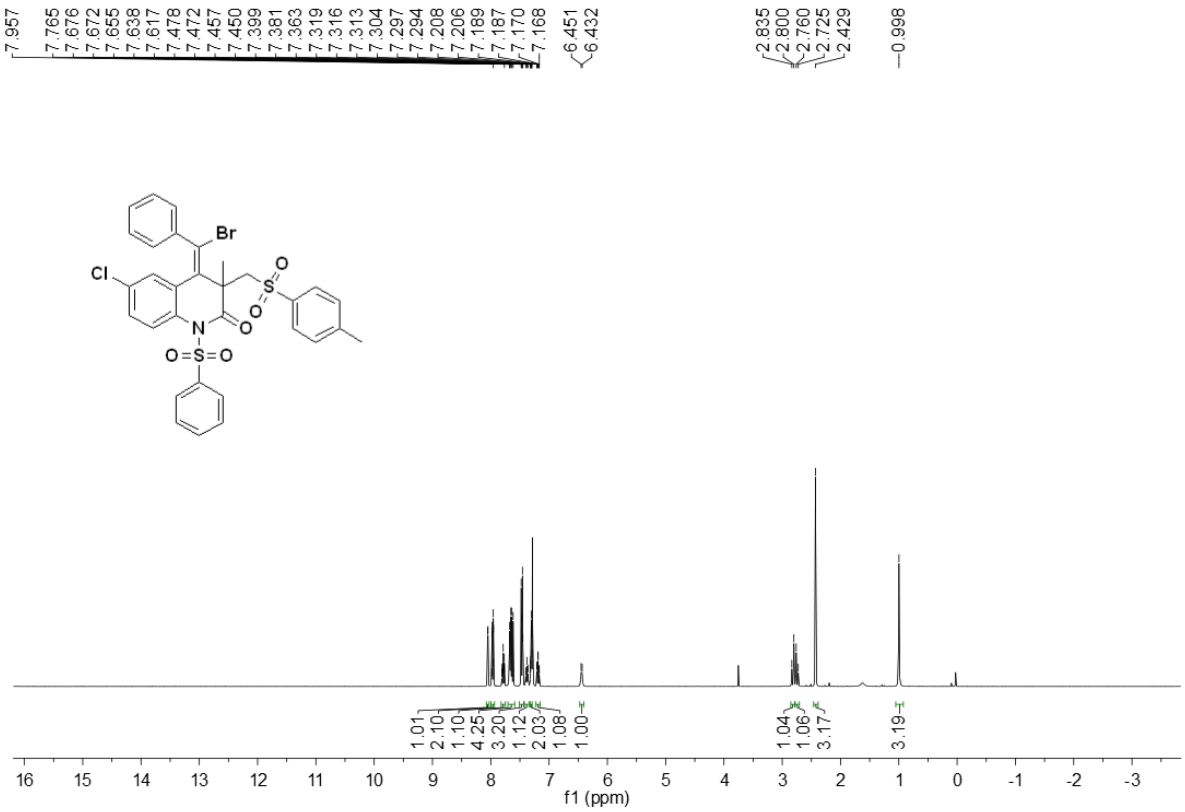
^{13}C NMR Spectrum of Compound 4a



[1]H NMR Spectrum of Compound 4b



[13]C NMR Spectrum of Compound 4b



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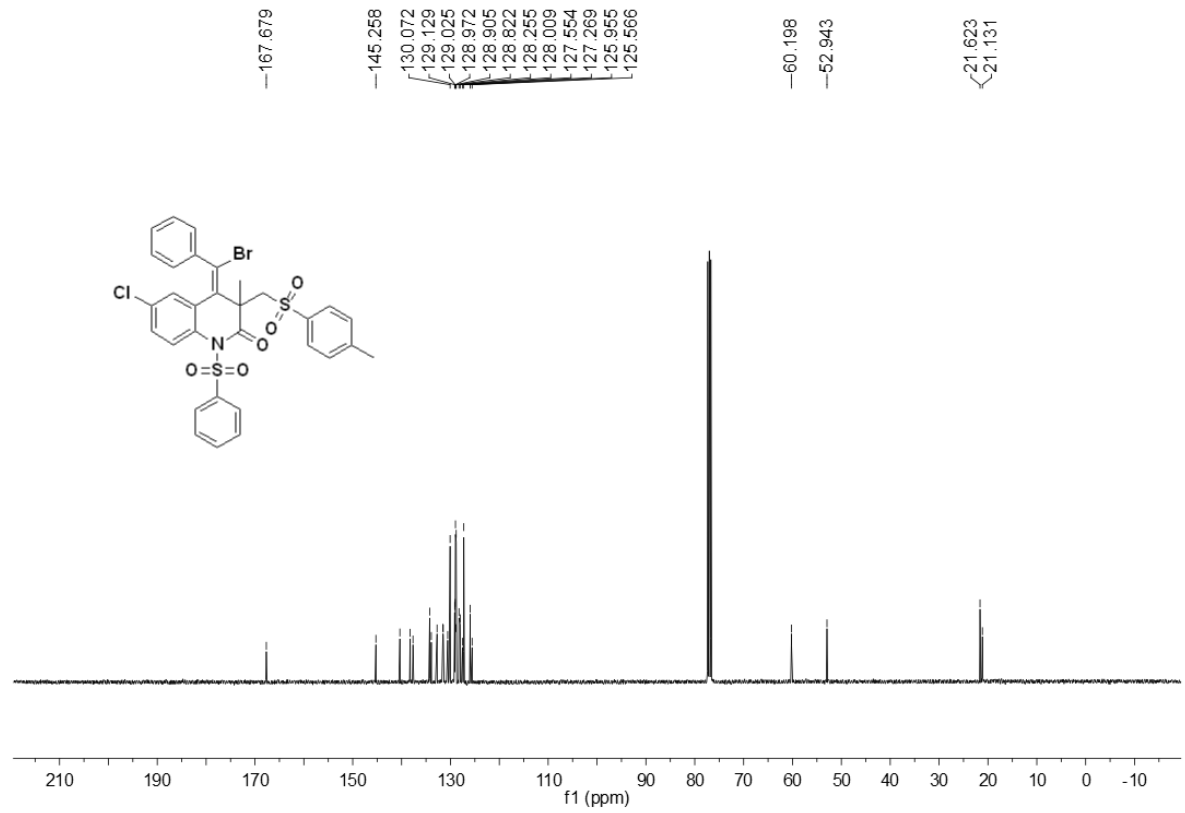
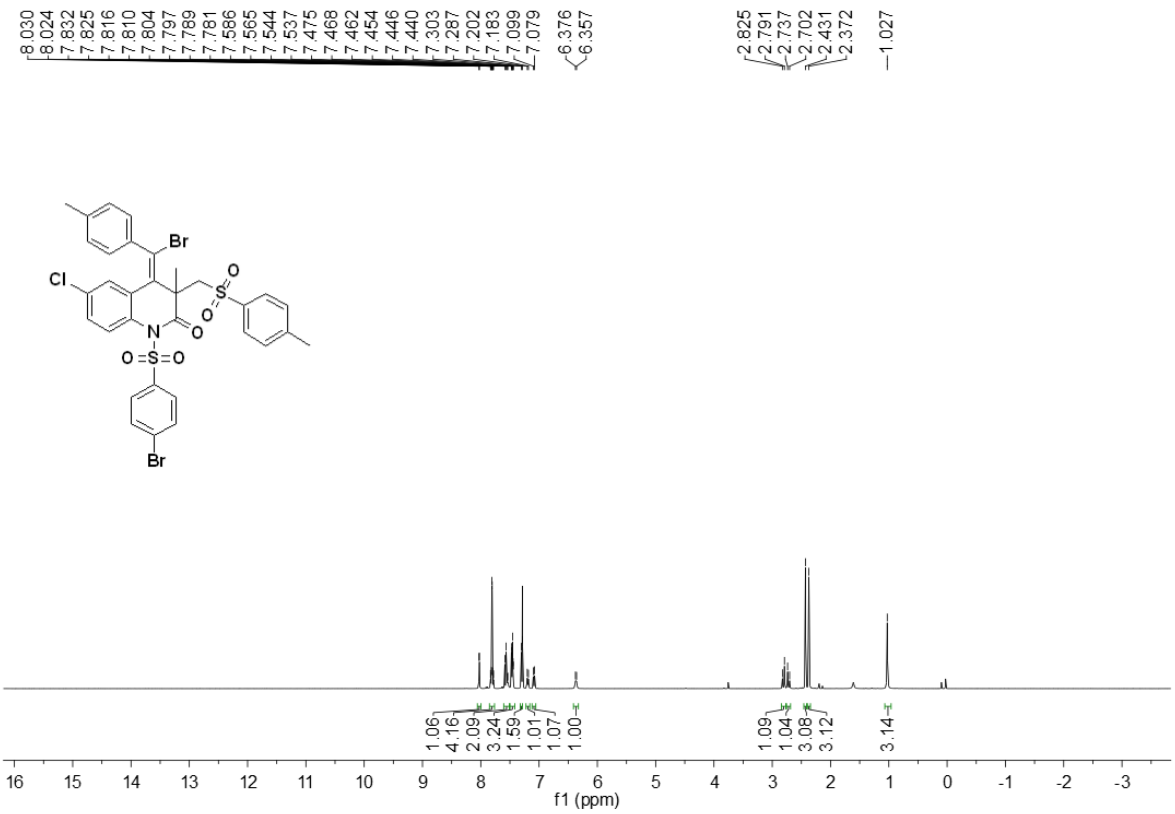


[13]C NMR Spectrum of Compound 4c



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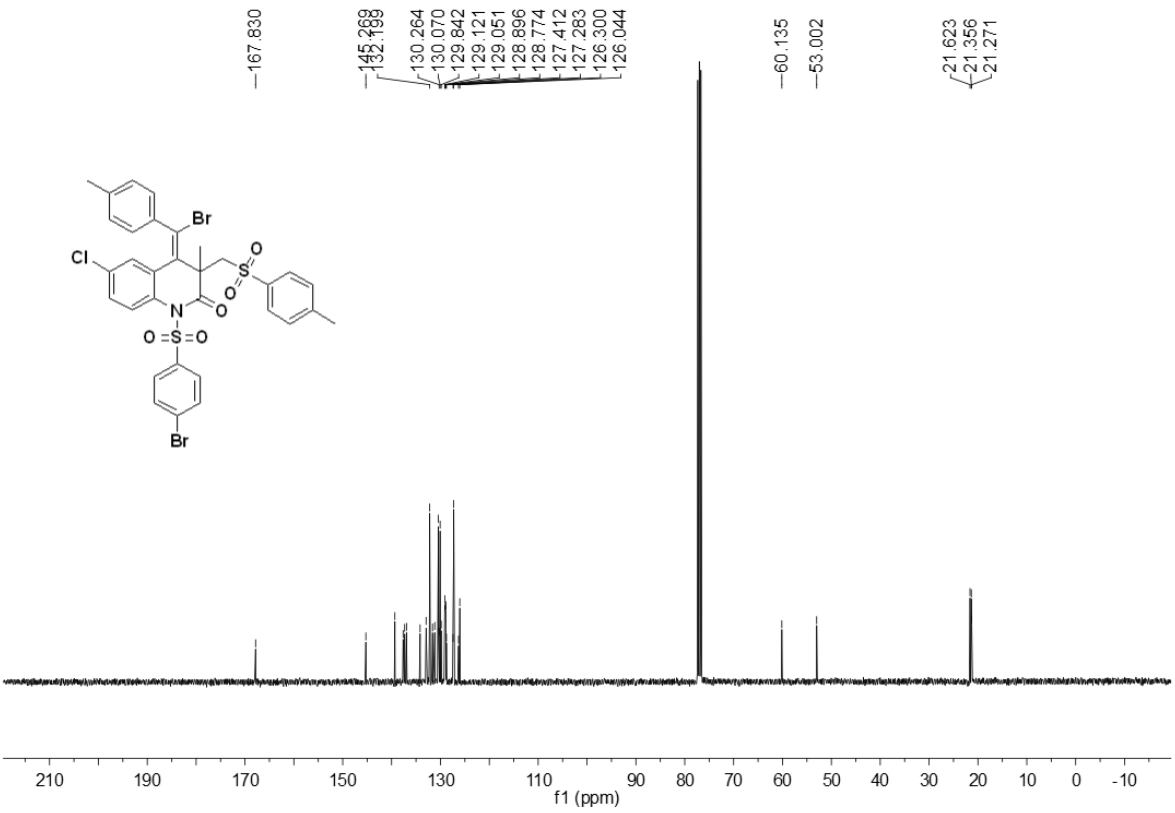

[13]C NMR Spectrum of Compound 4d

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F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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C24 C 0.4607(13) 0.1282(4) 0.4251(16) 0.042(3) Uani 1 1 d . . .
C25 C 0.3734(13) 0.1499(4) 0.3224(15) 0.041(3) Uani 1 1 d . . .
C26 C 0.3869(14) 0.1881(4) 0.3173(17) 0.046(4) Uani 1 1 d . . .
H26 H 0.4500 0.1995 0.3809 0.055 Uiso 1 1 calc R . .
C27 C 0.3043(14) 0.2089(4) 0.2151(17) 0.048(4) Uani 1 1 d . . .
H27 H 0.3130 0.2342 0.2149 0.058 Uiso 1 1 calc R . .
C28 C 0.2104(14) 0.1934(4) 0.1144(18) 0.052(4) Uani 1 1 d . . .
C29 C 0.1997(14) 0.1549(4) 0.1212(18) 0.052(4) Uani 1 1 d . . .
H29 H 0.1370 0.1435 0.0569 0.062 Uiso 1 1 calc R . .
C30 C 0.2798(14) 0.1336(4) 0.2209(17) 0.049(4) Uani 1 1 d . . .
H30 H 0.2713 0.1082 0.2203 0.059 Uiso 1 1 calc R . .
C31 C 0.1227(18) 0.2162(5) 0.005(2) 0.078(6) Uani 1 1 d . . .
H31A H 0.0811 0.2326 0.0716 0.117 Uiso 1 1 calc R . .
H31B H 0.0658 0.2004 -0.0557 0.117 Uiso 1 1 calc R . .
H31C H 0.1654 0.2301 -0.0692 0.117 Uiso 1 1 calc R . .

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I1 0.0868(9) 0.0666(7) 0.0341(6) 0.0003(5) 0.0138(5) 0.0329(6)
Br1 0.115(2) 0.161(3) 0.115(2) 0.0230(19) -0.0435(18) -0.0309(19)
Cl1 0.052(3) 0.099(4) 0.089(4) 0.013(3) 0.010(2) 0.013(2)
Cl2 0.121(6) 0.249(10) 0.072(4) -0.004(5) -0.049(4) 0.008(6)
N1 0.051(8) 0.040(6) 0.033(6) 0.002(5) 0.003(5) 0.003(5)
O1 0.050(7) 0.055(6) 0.055(6) 0.000(5) 0.011(5) -0.001(5)
O2 0.070(7) 0.034(5) 0.067(7) -0.009(5) -0.004(6) 0.014(5)
O3 0.075(7) 0.053(6) 0.047(6) 0.014(5) 0.017(5) -0.014(5)
O4 0.092(9) 0.054(6) 0.047(6) 0.006(5) 0.028(6) -0.005(6)
O5 0.084(8) 0.038(5) 0.060(7) -0.005(5) 0.011(6) 0.008(5)
S1 0.061(2) 0.0355(19) 0.040(2) 0.0071(16) 0.0029(17) 0.0010(17)
S2 0.072(3) 0.0322(18) 0.045(2) 0.0010(16) 0.0137(19) -0.0017(17)
C1 0.051(10) 0.042(8) 0.037(8) -0.001(6) 0.005(7) 0.002(7)
C2 0.058(9) 0.031(7) 0.028(7) 0.004(6) 0.007(6) 0.002(6)
C3 0.057(9) 0.033(7) 0.035(8) 0.006(6) 0.009(7) 0.006(6)
C4 0.051(9) 0.028(7) 0.031(7) 0.000(6) 0.007(6) 0.009(6)
C5 0.052(10) 0.037(7) 0.033(7) 0.005(6) 0.003(6) 0.006(6)
C6 0.058(10) 0.040(8) 0.036(8) 0.006(6) 0.001(7) 0.007(7)
C7 0.054(10) 0.049(9) 0.048(9) 0.000(7) -0.003(7) 0.013(7)
C8 0.055(10) 0.051(9) 0.048(9) 0.005(7) 0.002(7) 0.009(7)
C9 0.058(10) 0.039(7) 0.034(7) 0.003(6) 0.007(7) 0.007(7)
C10 0.055(10) 0.048(9) 0.040(8) -0.002(7) 0.001(7) 0.000(7)
C11 0.065(11) 0.055(9) 0.047(9) -0.001(8) -0.003(8) 0.000(8)
C12 0.073(13) 0.071(11) 0.051(10) -0.011(9) -0.003(9) -0.002(10)
C13 0.079(14) 0.080(13) 0.049(10) -0.007(9) -0.013(9) -0.001(10)
C14 0.071(13) 0.089(14) 0.065(12) -0.004(10) -0.001(10) -0.001(10)
C15 0.061(11) 0.061(10) 0.051(10) 0.000(8) 0.004(8) -0.004(8)
C16 0.060(10) 0.032(7) 0.036(8) 0.001(6) 0.007(7) 0.001(7)
C17 0.067(11) 0.044(8) 0.055(10) -0.005(7) 0.012(8) -0.002(8)
C18 0.078(13) 0.057(10) 0.056(10) -0.008(8) 0.004(9) 0.005(9)
C19 0.093(16) 0.074(12) 0.072(13) -0.010(11) 0.001(11) 0.002(12)
C20 0.083(14) 0.066(11) 0.068(12) -0.003(10) 0.001(10) -0.008(10)
C21 0.075(13) 0.072(12) 0.076(13) -0.006(10) 0.001(11) 0.001(10)
C22 0.075(13) 0.061(10) 0.061(11) -0.007(9) 0.007(10) 0.000(9)
C23 0.056(9) 0.044(8) 0.042(8) 0.001(7) 0.004(7) 0.020(7)
C24 0.057(9) 0.038(7) 0.034(7) 0.001(6) 0.007(6) 0.006(6)
C25 0.057(9) 0.040(7) 0.025(7) 0.002(6) 0.002(6) 0.010(7)
C26 0.059(10) 0.038(8) 0.040(8) 0.004(6) 0.002(7) 0.004(7)

C27 0.061(10) 0.038(7) 0.046(8) 0.005(7) 0.005(8) 0.011(7)
C28 0.061(10) 0.052(9) 0.041(8) 0.010(7) 0.002(7) 0.013(8)
C29 0.057(10) 0.057(10) 0.041(8) 0.000(7) 0.006(7) 0.000(8)
C30 0.060(10) 0.047(8) 0.040(8) 0.000(7) 0.007(7) 0.006(7)
C31 0.074(14) 0.077(13) 0.083(13) 0.016(11) 0.002(10) 0.022(10)

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;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
;

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Cl1 C8 1.754(17) . ?
Cl2 C13 1.731(17) . ?
N1 C1 1.401(17) . ?
N1 C5 1.432(18) . ?
N1 S1 1.723(11) . ?
O1 C1 1.219(17) . ?
O2 S1 1.433(10) . ?
O3 S1 1.423(11) . ?
O4 S2 1.437(11) . ?
O5 S2 1.439(10) . ?
S1 C10 1.754(15) . ?
S2 C17 1.764(17) . ?
S2 C16 1.819(13) . ?
C1 C2 1.538(19) . ?
C2 C23 1.549(18) . ?
C2 C16 1.567(18) . ?
C2 C3 1.581(19) . ?
C3 C24 1.339(18) . ?
C3 C4 1.477(18) . ?
C4 C5 1.349(18) . ?
C4 C9 1.41(2) . ?
C5 C6 1.423(19) . ?

C6 C7 1.38(2) . ?
C6 H6 0.9300 . ?
C7 C8 1.37(2) . ?
C7 H7 0.9300 . ?
C8 C9 1.39(2) . ?
C9 H9 0.9300 . ?
C10 C15 1.38(2) . ?
C10 C11 1.38(2) . ?
C11 C12 1.38(2) . ?
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C12 C13 1.39(3) . ?
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C13 C14 1.41(3) . ?
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C16 H16B 0.9700 . ?
C17 C18 1.37(2) . ?
C17 C22 1.39(2) . ?
C18 C19 1.42(3) . ?
C18 H18 0.9300 . ?
C19 C20 1.35(3) . ?
C19 H19 0.9300 . ?
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C22 H22 0.9300 . ?
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C5 N1 S1 119.0(9) . . ?
O3 S1 O2 119.6(7) . . ?
O3 S1 N1 108.5(6) . . ?
O2 S1 N1 105.9(6) . . ?
O3 S1 C10 109.7(7) . . ?
O2 S1 C10 109.2(7) . . ?
N1 S1 C10 102.6(6) . . ?
O4 S2 O5 118.4(7) . . ?
O4 S2 C17 108.9(8) . . ?
O5 S2 C17 108.3(7) . . ?
O4 S2 C16 109.6(6) . . ?
O5 S2 C16 109.3(7) . . ?
C17 S2 C16 100.9(7) . . ?
O1 C1 N1 120.1(13) . . ?
O1 C1 C2 123.5(13) . . ?
N1 C1 C2 116.3(13) . . ?
C1 C2 C23 107.9(12) . . ?
C1 C2 C16 104.9(10) . . ?
C23 C2 C16 109.9(11) . . ?
C1 C2 C3 104.0(10) . . ?
C23 C2 C3 117.1(11) . . ?
C16 C2 C3 112.1(12) . . ?
C24 C3 C4 126.2(13) . . ?
C24 C3 C2 125.3(13) . . ?
C4 C3 C2 107.6(10) . . ?
C5 C4 C9 120.4(12) . . ?
C5 C4 C3 117.2(13) . . ?
C9 C4 C3 121.7(12) . . ?
C4 C5 C6 120.4(14) . . ?
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C7 C8 C9 122.5(15) . . ?
C7 C8 Cl1 119.2(12) . . ?
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C4 C9 H9 121.0 . . ?
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C12 C11 C10 120.3(16) . . ?
C12 C11 H11 119.9 . . ?
C10 C11 H11 119.9 . . ?
C11 C12 C13 117.4(17) . . ?
C11 C12 H12 121.3 . . ?
C13 C12 H12 121.3 . . ?
C12 C13 C14 123.2(16) . . ?
C12 C13 Cl2 118.5(15) . . ?
C14 C13 Cl2 118.2(16) . . ?
C15 C14 C13 118.1(18) . . ?
C15 C14 H14 120.9 . . ?
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C14 C15 H15 121.0 . . ?
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S2 C16 H16A 108.6 . . ?
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S2 C16 H16B 108.6 . . ?
H16A C16 H16B 107.6 . . ?
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C17 C22 H22 120.9 . . ?
C2 C23 H23A 109.5 . . ?
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H23A C23 H23B 109.5 . . ?
C2 C23 H23C 109.5 . . ?
H23A C23 H23C 109.5 . . ?
H23B C23 H23C 109.5 . . ?
C3 C24 C25 133.4(13) . . ?
C3 C24 I1 116.2(10) . . ?
C25 C24 I1 110.3(9) . . ?
C30 C25 C26 118.8(12) . . ?
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C27 C26 H26 120.4 . . ?
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C28 C27 H27 118.5 . . ?
C26 C27 H27 118.5 . . ?
C27 C28 C29 116.4(13) . . ?
C27 C28 C31 122.3(15) . . ?
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C5 N1 C1 C2 5.2(17) . . . . ?
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O1 C1 C2 C23 -11.1(18) . . . . ?
N1 C1 C2 C23 164.4(11) . . . . ?
O1 C1 C2 C16 106.0(15) . . . . ?
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O1 C1 C2 C3 -136.1(14) . . . . ?
N1 C1 C2 C3 39.3(15) . . . . ?
C1 C2 C3 C24 106.1(15) . . . . ?
C23 C2 C3 C24 -13(2) . . . . ?
C16 C2 C3 C24 -141.1(14) . . . . ?
C1 C2 C3 C4 -64.2(13) . . . . ?
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C16 C2 C3 C4 48.6(14) . . . . ?
C24 C3 C4 C5 -123.1(16) . . . . ?
C2 C3 C4 C5 47.1(15) . . . . ?
C24 C3 C4 C9 66(2) . . . . ?
C2 C3 C4 C9 -124.2(13) . . . . ?
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C3 C4 C5 C6 -172.0(12) . . . . ?
C9 C4 C5 N1 171.4(12) . . . . ?
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C1 N1 C5 C4 -29.1(18) . . . . ?
S1 N1 C5 C4 132.4(11) . . . . ?
C1 N1 C5 C6 142.9(13) . . . . ?
S1 N1 C5 C6 -55.6(16) . . . . ?
C4 C5 C6 C7 -1(2) . . . . ?
N1 C5 C6 C7 -172.9(13) . . . . ?
C5 C6 C7 C8 3(2) . . . . ?
C6 C7 C8 C9 -3(2) . . . . ?
C6 C7 C8 Cl1 177.9(11) . . . . ?
C7 C8 C9 C4 2(2) . . . . ?
Cl1 C8 C9 C4 -179.6(10) . . . . ?
C5 C4 C9 C8 0(2) . . . . ?
C3 C4 C9 C8 171.4(13) . . . . ?

O3 S1 C10 C15 15.0(14) . . . . ?
O2 S1 C10 C15 147.8(12) . . . . ?
N1 S1 C10 C15 -100.2(13) . . . . ?
O3 S1 C10 C11 -167.7(12) . . . . ?
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N1 S1 C10 C11 77.2(13) . . . . ?
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S1 C10 C11 C12 -176.7(12) . . . . ?
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Cl2 C13 C14 C15 -175.6(13) . . . . ?
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S1 C10 C15 C14 176.7(12) . . . . ?
C13 C14 C15 C10 -1(3) . . . . ?
C1 C2 C16 S2 177.3(10) . . . . ?
C23 C2 C16 S2 -66.9(14) . . . . ?
C3 C2 C16 S2 65.2(13) . . . . ?
O4 S2 C16 C2 -44.3(12) . . . . ?
O5 S2 C16 C2 87.0(11) . . . . ?
C17 S2 C16 C2 -159.0(11) . . . . ?
O4 S2 C17 C18 151.8(13) . . . . ?
O5 S2 C17 C18 21.8(15) . . . . ?
C16 S2 C17 C18 -92.9(14) . . . . ?
O4 S2 C17 C22 -33.4(15) . . . . ?
O5 S2 C17 C22 -163.4(13) . . . . ?
C16 S2 C17 C22 81.9(14) . . . . ?
C22 C17 C18 C19 1(3) . . . . ?
S2 C17 C18 C19 176.2(14) . . . . ?
C17 C18 C19 C20 0(3) . . . . ?
C18 C19 C20 C21 -4(3) . . . . ?
C18 C19 C20 Br1 -178.7(14) . . . . ?
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Br1 C20 C21 C22 -179.2(14) . . . . ?
C20 C21 C22 C17 -4(3) . . . . ?
C18 C17 C22 C21 1(3) . . . . ?
S2 C17 C22 C21 -174.2(14) . . . . ?
C4 C3 C24 C25 -178.9(15) . . . . ?
C2 C3 C24 C25 13(3) . . . . ?
C4 C3 C24 I1 3(2) . . . . ?
C2 C3 C24 I1 -165.7(10) . . . . ?
C3 C24 C25 C30 -112.3(19) . . . . ?
I1 C24 C25 C30 66.1(16) . . . . ?
C3 C24 C25 C26 71(2) . . . . ?
I1 C24 C25 C26 -110.1(13) . . . . ?

C30 C25 C26 C27 2(2) . . . . ?
C24 C25 C26 C27 178.4(13) . . . . ?
C25 C26 C27 C28 -2(2) . . . . ?
C26 C27 C28 C29 1(2) . . . . ?
C26 C27 C28 C31 -179.9(16) . . . . ?
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C28 C29 C30 C25 2(2) . . . . ?
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