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Supporting Information

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Supporting Information

Catalyst-Free Radical Dearomatization of Phenols with Aryldiazonium Tetrafluoroborates, and DABCO • $(SO_2)_2$

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1. Supplementary Notes

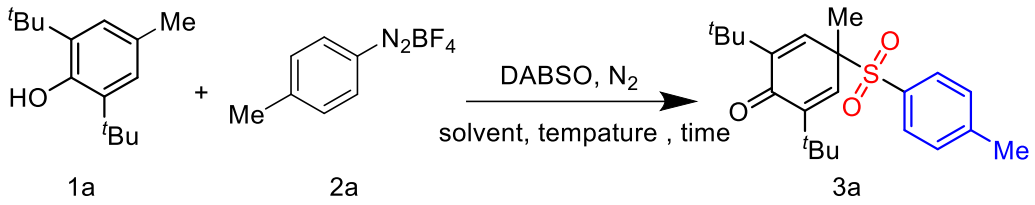
Chemicals were purchased from commercial suppliers((Adamas-beta, Leyan, J&K Scientific, TCl, Aldrich, Energy Chemical, Alfa Aesar, Bidepharm)and used without further purification unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm). ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; p = pentet; m = multiplet; brs = broad singlet), coupling constant (Hz), integration. Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). ESI-HRMS data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source. Collection of XRD data was performed on a Rigaku Smartlab diffractometer equipped. All heating reaction heat sources are oil bath.

2. Supplementary Methods

2.1 General procedure for preparation of aryl diazonium salts

Add aniline (10 mmol), tetrafluoroboric acid solution (45 wt % in H_2O, 3.4 mL, 26 mmol) to 50 ml flask and cool to 0 °C, followed by distilled water added until precipitation was completely dissolved. Then Sodium nitrite solution (0.7 g, 10 mmol) of distilled water (2 mL) was added dropwise and the reaction was stirred for 30 minutes at 0 °C. Then thick precipitate was generated which was separated by filtration. The crude product was washed with diethyl ether (40 mL) three times. Then the resulting solid was recrystallized with acetonitrile/diethyl ether to furnish expected aryldiazonium tetrafluoroborate as a crystalline solid.

2.2 Condition optimization

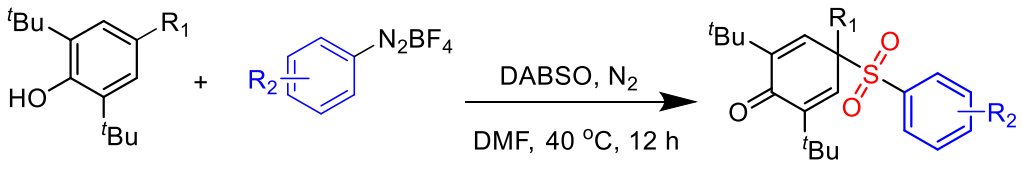


1a 2a 3a

Entry[a]	solvent	SO_2 surrogates	Temp (°C)	Yield[b] (%)
1	DCM	DABSO	25	58
2	DCE	DABSO	25	59
3	MeCN	DABSO	25	65
4	acetone	DABSO	25	trace
5	THF	DABSO	25	n.d.
6	DMF	DABSO	25	72
7	DMSO	DABSO	25	61
8	DMF	DABSO	10	65
9	DMF	DABSO	40	84
10	DMF	DABSO	60	83
11	DMF	Na_2SO_3	40	38
12	DMF	$Na_2S_2O_5$	40	10

[a] Reaction conditions: **1a** (0.20 mmol), **DABSO** (0.3 mmol，1.5 equiv.) and **2a** (0.4 mmol, 2 equiv.) in solvent (2 mL) under N_2, [b] Isolated yield based on phenol **1a.**

2.3 General procedures for the preparation of products 3

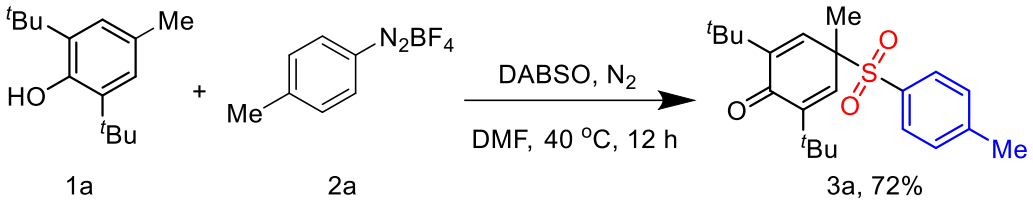


1 2 3

2,6-di-*tert*-butyl-4-methylphenol **1** (0.2 mmol), DABSO (72 mg, 0.3 mmol) and aryldiazonium salt **2** (0.4 mmol) were added to a 10 ml oven-dried reaction vial equipped with a magnetic stirring bar. The reaction vessel was sealed with a rubber stopper, evacuated and refilled three times with N_2. DMF (2.0 mL) were then added sequentially via syringe to the above system. The reaction mixture was stirred at 40 °C for 12 hours. After completion of the reaction monitored by TLC. The reaction solution was diluted with 10 mL of water and extracted with EA (15 mL x 3). The combined organic phase was concentrated, and the resulting residue was purified flash chromatography on silica gel eluted with PE/EA (v/v = 10/1) to afford the

corresponding products **3**.

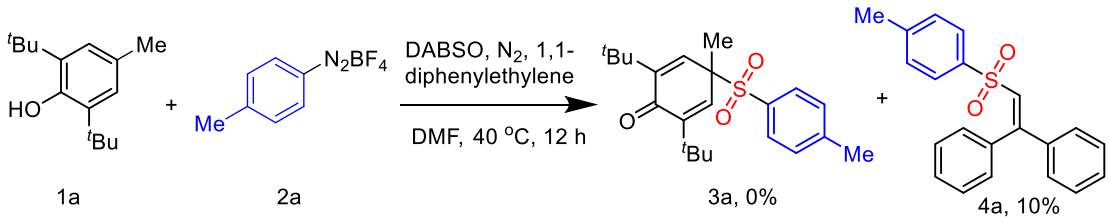
2.4 Gram-scale reaction



1a 2a 3a, 72%

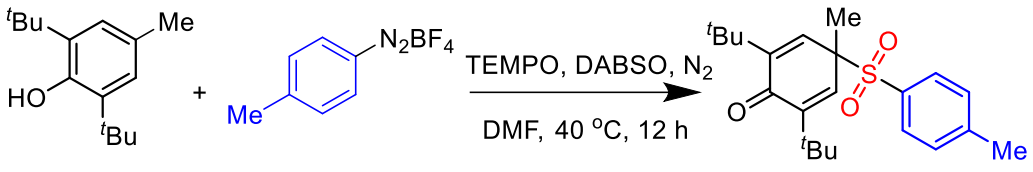
2,6-di-*tert*-butyl-4-methylphenol **1a** (2.2 g, 10 mmol), DABSO (3.6 g, 15 mmol) and aryldiazonium salt **2a** (4.12 g, 20 mmol) were added to an 100ml oven-dried reaction vial equipped with a magnetic stirring bar. The reaction vessel was sealed with a rubber stopper, evacuated and refilled three times with N_2. DMF (50 mL) were then added sequentially via syringe to the above system. The reaction mixture was stirred at 40 °C for 12 hours. After completion of the reaction monitored by TLC. The reaction solution was diluted with 150 mL of water and extracted with EA (50 mL x 3). The combined organic phase was concentrated, and the resulting residue was purified flash chromatography on silica gel eluted with PE/EA (v/v = 10/1) to afford the corresponding products **3a** (2.69 g, 72%).

2.5. Mechanistic studies



1a 2a 3a, 0% 4a, 10%

Radical trapping agent (1,1-diphenyletylene 3.0 equiv.) is added under the conditions of preparing the product according to the general procedure under general procedures for the preparation of products conditions (**2.3**). When the reaction is completed (monitored by TLC), the mixture is purified by flash chromatography on silica gel to afford the product **4a** (10% Yield).

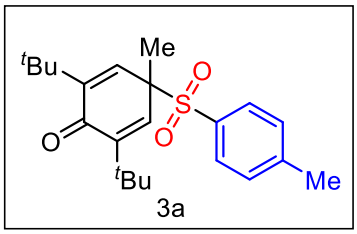


1a 2a 3a, 0%

Free radical trapping agent (TEMPO, 3.0 equiv.) is added under the conditions of preparing the product according to the general procedure under general procedures for the preparation of products conditions (**2.3**). When the reaction was complete, neither TLC nor ^{1}H NMR detected the target product **3a.**

2.6 Characterization data of products 3

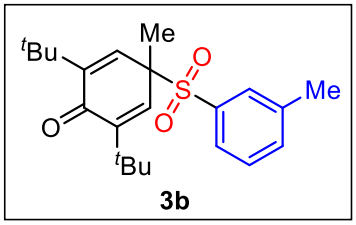
2,6-di-*tert*-butyl-4-methyl-4-tosylcyclohexa-2,5-dien-1-one (3a)



3a

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 15/1 – 10/1, v/v, R_f=0.4) to afford **3a** as white solid (63 mg, 84% yield). **M.p.** = 142–143 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 7.0 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.63 (s, 2H), 2.35 (s, 3H), 1.80 (s, 3H), 1.09 (s, 18H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.7, 151.2, 145.3, 135.7, 130.6, 130.3, 128.8, 65.8, 35.2, 29.0, 21.6, 18.5. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{22}H_{31}O_3S^+$ calcd for 375.1989; found 375.1988.

2,6-di-*tert*-butyl-4-methyl-4-(m-tolylsulfonyl)cyclohexa-2,5-dien-1-one (3b)

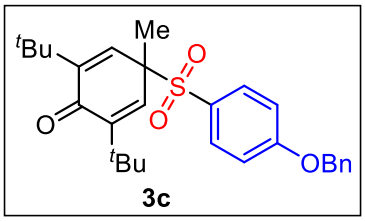


3b

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 7/1, v/v, R_f=0.4) to afford **3b** as white solid (48 mg, 64% yield). **M.p.** = 109–111 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 6.64 (s, 2H), 2.33 (s, 3H), 1.81 (s, 3H), 1.09 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.8, 151.3, 138.3, 135.6, 135.0, 133.5, 130.5, 128.1, 127.6, 65.8, 35.2, 29.0, 21.3, 18.5. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{22}H_{31}O_3S^+$ calcd for 375.1989; found 375.1984.

4-((4-(benzyloxy)phenyl)sulfonyl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dien-1-

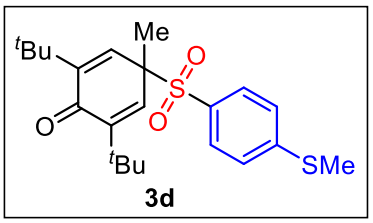
one (3c)



3c

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 8/1, v/v, R_f=0.4) to afford **3c** as yellow solid (65 mg, 70% yield). **M.p.** = 72–74 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.27 (m, 6H), 7.24 (t, *J* = 2.1 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.63 (s, 2H), 5.00 (s, 2H), 1.81 (s, 3H), 1.10 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.7, 158.3, 151.4, 135.8, 135.5, 134.7, 129.3, 128.7, 128.4, 127.6, 122.7, 120.2, 116.9, 70.5, 65.9, 35.2, 29.1, 18.5. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{28}H_{35}O_4S^+$ calcd for 467,2251; found 467.2256.

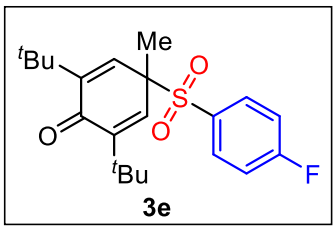
2,6-di-*tert*-butyl-4-methyl-4-((4-(methylthio)phenyl)sulfonyl)cyclohexa-2,5-dien-1-one (3d)



3d

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 8/1, v/v, R_f=0.4) to afford **3d** as white solid (53 mg, 65% yield). **M.p.** = 122–124 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.62 (s, 2H), 2.44 (s, 3H), 1.80 (s, 3H), 1.10 (s, 18H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.7, 151.4, 148.1, 135.6, 130.4, 129.1, 124.4, 65.9, 35.2, 29.0, 18.6, 14.9. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{22}H_{31}O_3S_2^+$ calcd for 407.1710; found 407.1706.

2,6-di-*tert*-butyl-4-((4-fluorophenyl)sulfonyl)-4-methylcyclohexa-2,5-dien-1-one (3e)

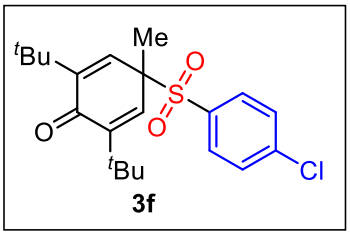


3e

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 15/1, v/v, R_f=0.4) to afford **3e** as white solid (48 mg, 63% yield). **M.p.** = 126–128 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (dd, *J* = 8.8, 5.1 Hz, 2H), 7.08 (t, *J* = 8.5 Hz, 2H), 6.64 (s, 2H), 1.83 (s, 3H), 1.11 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.6, 166.1 (d, *J* = 258.0 Hz), 151.7, 135.3, 133.2 (d, *J* = 9.5 Hz), 129.5 (d, *J* = 3.0 Hz), 115.6 (d, *J* = 22.6 Hz), 65.9, 35.3, 29.0, 18.5. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -102.16. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$

$C_{21}H_{28}FO_3S$ calcd for 379.1738; found 379.1739.

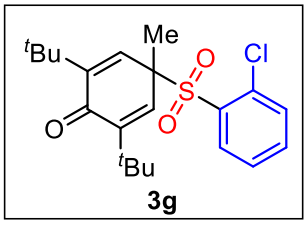
2,6-di-*tert*-butyl-4-((4-chlorophenyl)sulfonyl)-4-methylcyclohexa-2,5-dien-1-one (3f)



3f

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 15/1, v/v, R_f=0.4) to afford **3f** as white solid (51 mg, 65% yield). **M.p.** = 154–156 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 8.6 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 6.61 (s, 2H), 1.10 (s, 10H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.6, 151.7, 141.1, 135.2, 132.1, 131.7, 128.5, 65.9, 35.3, 29.0, 18.5. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{21}H_{28}ClO_3S^+$ calcd for 395.1443; found 395.1441.

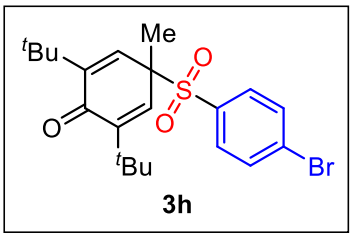
2,6-di-*tert*-butyl-4-((2-chlorophenyl)sulfonyl)-4-methylcyclohexa-2,5-dien-1-one (3g)



3g

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 13/1, v/v, R_f=0.4) to afford **3g** as white solid (41 mg, 52% yield). **M.p.** = 160–162 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 6.71 (s, 2H), 1.84 (s, 3H), 1.12 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.9, 151.2, 135.2, 135.0, 134.9, 134.78, 132.4, 130.6, 126.6, 67.5, 35.3, 28.8, 18.7. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{21}H_{28}ClO_3S^+$ calcd for 395.1443; found 395.1450.

4-((4-bromophenyl)sulfonyl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dien-1-one (3h)

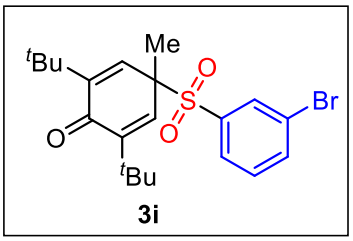


3h

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 10/1, v/v, R_f=0.4) to afford **3h** as white solid (48 mg, 55% yield). **M.p.** = 149–150 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 6.61

(s, 2H), 1.82 (s, 3H), 1.11 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.6, 151.8, 135.2, 132.6, 131.7, 131.6, 129.7, 65.9, 35.3, 29.0, 18.5. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{21}H_{28}BrO_3S^+$ calcd for 439.0938; found 439.0932.

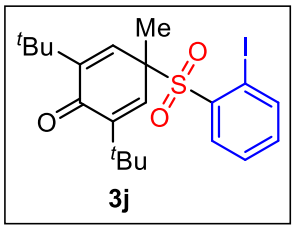
4-((3-bromophenyl)sulfonyl)-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dien-1-one (3i)



3i

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 15/1, v/v, R_f=0.4) to afford **3i** as yellow solid (63mg, 71% yield). **M.p.** = 111–113 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.24 (m, 1H), 6.62 (s, 2H), 1.82 (s, 3H), 1.11 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.7, 151.9, 137.2, 135.3, 135.1, 133.0, 129.6, 128.9, 122.4, 66.0, 35.3, 29.1, 18.4. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{21}H_{28}BrO_3S$ calcd for 439.0938; found 439.0936.

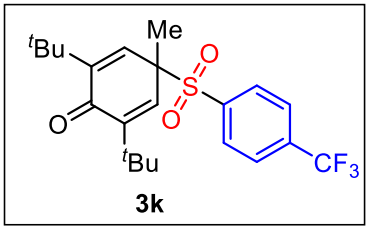
2,6-di-*tert*-butyl-4-((2-iodophenyl)sulfonyl)-4-methylcyclohexa-2,5-dien-1-one (3j)



3j

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 10/1, v/v, R_f=0.4) to afford **3j** as white solid (38 mg, 39% yield). **M.p.** = 166–167 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.73 (s, 2H), 1.83 (s, 3H), 1.15 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 184.1, 151.4, 143.4, 134.9, 134.8, 134.7, 134.0, 127.9, 94.6, 67.5, 35.3, 28.8, 19.1. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{21}H_{28}IO_3S$ calcd for 487.0779; found 487.0791.

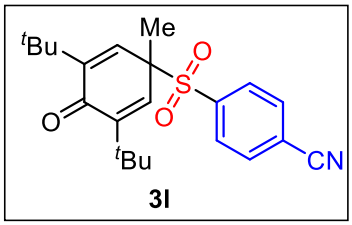
2,6-di-*tert*-butyl-4-methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)cyclohexa-2,5-dien-1-one (3k)



3k

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 10/1 – 8/1, v/v, R_f=0.4) to afford **3k** as white solid (64 mg, 75% yield). **M.p.** = 149–152 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 6.62 (s, 2H), 1.84 (s, 3H), 1.09 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.4, 152.0, 137.0, 135.8 (q, *J* = 33.4 Hz), 134.9, 130.9, 125.3 (q, *J* = 3.8 Hz), 122.9 (q, *J* = 273.2 Hz), 66.0, 35.3, 28.9, 18.3. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -63.41.**HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{22}H_{28}F_3O_3S$ calcd for 429.1706; found 429.1709.

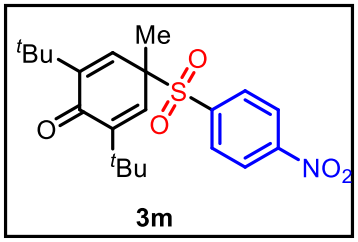
4-((3,5-di-*tert*-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)sulfonyl)benzonitrile (3l)



3l

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 8/1, v/v, R_f=0.4) to afford **3l** as white solid (55 mg, 72% yield). **M.p.** = 189–191 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 6.61 (s, 2H), 1.86 (s, 3H), 1.10 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.5, 152.2, 137.7, 134.6, 131.8, 131.0, 117.8, 116.9, 66.0, 35.4, 29.0, 18.3. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{22}H_{28}NO_3S^+$ calcd for 386.1785; found 386.1787.

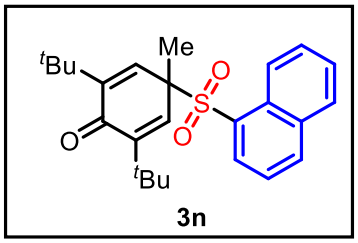
2,6-di-*tert*-butyl-4-methyl-4-((4-nitrophenyl)sulfonyl)cyclohexa-2,5-dien-1-one (3m)



3m

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 10/1, v/v, R_f=0.4) to afford **3m** as white solid (56 mg, 69% yield). **M.p.** = 176–178 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.29 – 8.14 (m, 2H), 7.89 – 7.76 (m, 2H), 6.63 (s, 2H), 1.87 (s, 3H), 1.11 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.6, 152.4, 150.9, 139.2, 134.5, 131.8, 123.2, 66.1, 35.4, 29.0, 18.3. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{21}H_{28}NO_5S^+$ calcd for 406.1683; found 406.1685.

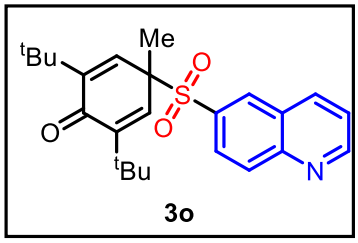
2,6-di-*tert*-butyl-4-methyl-4-(naphthalen-1-ylsulfonyl)cyclohexa-2,5-dien-1-one (3n)



3n

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 10/1, v/v, R_f=0.4) to afford **3n** as white solid (50 mg, 61% yield). **M.p.** = 141–143 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.99 (d, *J* = 8.7 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 6.8 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 6.68 (s, 2H), 1.89 (s, 3H), 0.88 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.4, 151.1, 136.0, 135.4, 134.0, 133.7, 130.7, 129.2, 128.9, 128.7, 126.8, 125.5, 123.5, 67.2, 35.0, 28.6, 19.1. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{25}H_{31}O_3S^+$ calcd for 411.1989; found 411.1985.

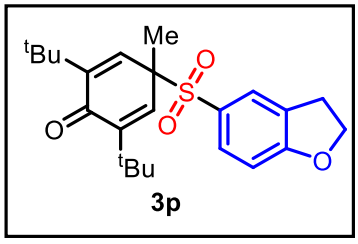
2,6-di-*tert*-butyl-4-methyl-4-(quinolin-6-ylsulfonyl)cyclohexa-2,5-dien-1-one (3o)



3o

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc =5/1, v/v, Rf=0.3) to afford **3o** as white solid (42.0 mg, 51% yield). M.p. = 154–155 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.03 (s, 1H), 8.17 (d, *J* = 10.1 Hz, 2H), 8.08 (d, *J* = 8.9 Hz, 1H), 7.85 (d, *J* = 10.9 Hz, 1H), 7.50 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.69 (s, 2H), 1.86 (s, 3H), 1.01 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.5, 153.8, 151.7, 149.7, 137.1, 135.2, 132.3, 131.6, 130.0, 128.5, 126.3, 122.8, 66.1, 35.2, 29.0, 18.6. **HRMS (ESI-ion trap)** m/z: [M+H]+ $C_{24}H_{30}NO_3S^+$ calcd for 412.1941; found 412.1940.

2,6-di-*tert*-butyl-4-((2,3-dihydrobenzofuran-5-yl)sulfonyl)-4-methylcyclohexa-2,5-dien-1-one (3p)

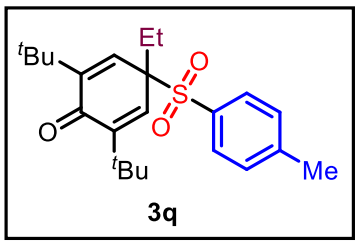


3p

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc =10/1, v/v, Rf=0.3) to afford **3p** as yellow solid (50.7 mg, 63% yield). M.p. = 132–134 ℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43-7.40 (m, 2H), 6.73 (d, *J* = 8.3 Hz, 1H), 6.64 (s, 2H),

4.63 (t, J = 8.8 Hz, 2H), 3.14 (t, J = 8.8 Hz, 2H), 1.82 (s, 3H), 1.12 (s, 18H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 183.9, 165.1, 151.3, 136.0, 132.2, 127.4, 127.3, 124.6, 108.9, 72.4, 65.9, 35.2, 29.1, 28.9, 18.6. **HRMS (ESI-ion trap)** m/z: [M+H]+ $C_{23}H_{31}O_4S^+$ calcd for 403.1938; found 403.1935.

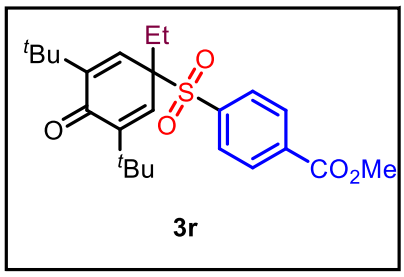
2,6-di-*tert*-butyl-4-ethyl-4-tosylcyclohexa-2,5-dien-1-one (3q)



3q

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 8/1, v/v, R_f=0.4) to afford **3q** as white solid (58 mg, 75% yield). **M.p.** = 97–99 ℃. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.50 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 6.58 (s, 2H), 2.40 (q, J = 7.5 Hz, 2H), 2.35 (s, 3H), 1.10 (s, 18H), 0.78 (t, J = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 184.0, 153.0, 145.3, 134.8, 131.4, 130.1, 128.8, 70.2, 35.4, 29.1, 24.6, 21.6, 8.3. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{23}H_{33}O_3S^+$ calcd for 389.2145; found 389.2142.

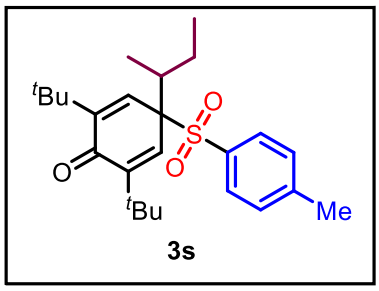
methyl4-((3,5-di-*tert*-butyl-1-ethyl-4-oxocyclohexa-2,5-dien-1-yl)sulfonyl)benzoate (3r)



3r

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 8/1, v/v, R_f=0.4) to afford **3r** as white solid (44 mg, 51% yield). **M.p.** = 116–118 ℃. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.05 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.5 Hz, 2H), 6.60 (s, 2H), 3.93 (s, 3H), 2.43 (q, J = 7.5 Hz, 2H), 1.10 (s, 18H), 0.81 (t, J = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 183.8, 165.3, 153.6, 138.3, 135.0, 134.2, 130.3, 129.2, 70.2, 52.8, 35.5, 29.1, 24.5, 8.1. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{24}H_{33}O_5S$ calcd for 433.2044; found 433.2045.

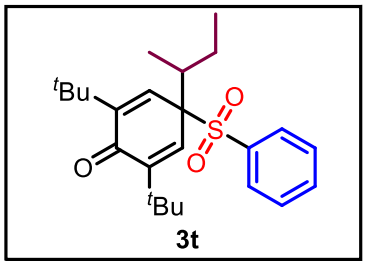
4-(sec-butyl)-2,6-di-*tert*-butyl-4-tosylcyclohexa-2,5-dien-1-one (3s)



3s

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 10/1, v/v, R_f=0.4) to afford **3s** as yellow solid (59 mg, 71% yield). **M.p.** = 113–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 3.0 Hz, 1H), 6.67 (d, *J* = 3.0 Hz, 1H), 2.67 – 2.57 (m, *J* = 10.5, 6.7, 3.2 Hz, 1H), 2.35 (s, 3H), 1.95 – 1.79 (m, 1H), 1.15 (d, *J* = 6.8 Hz, 3H), 1.08 (s, 9H), 1.07 (s, 9H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 184.0, 152.1, 151.8, 145.0, 135.0, 134.5, 133.2, 129.6, 128.7, 72.4, 39.5, 35.4, 35.4, 29.0, 29.0, 25.3, 21.6, 14.8, 12.1. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{25}H_{37}O_3S^+$ calcd for 417.2458; found 417.2455.

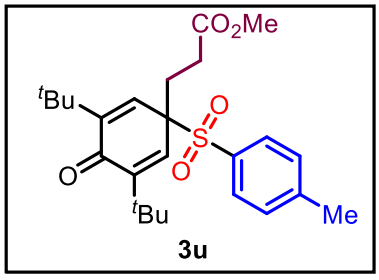
4-(sec-butyl)-2,6-di-tert-butyl-4-(phenylsulfonyl)cyclohexa-2,5-dien-1-one (3t)



3t

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 8/1, v/v, R_f=0.4) to afford **3t** as white solid (56 mg, 70% yield). **M.p.** = 93–95 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.60 (m, 2H), 7.58 – 7.52 (m, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 3.0 Hz, 1H), 6.69 (d, *J* = 3.0 Hz, 1H), 2.65 (dqd, *J* = 9.8, 6.7, 2.7 Hz, 1H), 1.87 (dtd, *J* = 14.1, 7.1, 2.6 Hz, 1H), 1.17 (d, *J* = 6.8 Hz, 3H), 1.11 (s, 3H), 1.08 (s, 3H) , 1.02 (dd, *J* = 8.4, 4.4 Hz, 1H), 0.96 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 183.9, 152.3, 152.0, 136.1, 134.8, 134.2, 133.9, 129.7, 128.1, 72.4, 39.5, 35.4, 35.4, 29.0, 29.0, 25.3, 14.8, 12.1. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{24}H_{35}O_3S^+$ calcd for 403.2302; found 403.2298.

methyl 3-(3,5-di-*tert*-butyl-4-oxo-1-tosylcyclohexa-2,5-dien-1-yl)propanoate (3u)

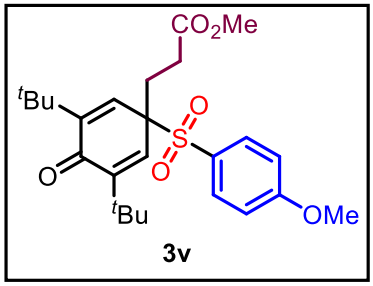


3u

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 10/1, v/v, R_f=0.4) to afford **3u** as white solid (74 mg, 83% yield). **M.p.** = 171–173 °C. **^{1}H NMR (400 MHz,**

CDCl$_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.58 (s, 2H), 3.65 (s, 3H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.35 (s, 3H), 2.14 (t, *J* = 7.7 Hz, 2H), 1.08 (s, 18H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 183.5, 172.3, 153.3, 145.5, 134.1, 130.9, 130.2, 128.9, 69.0, 52.0, 35.5, 29.0, 28.8, 26.5, 21.6. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{25}H_{35}O_5S^+$ calcd for 447.2200; found 447.2207.

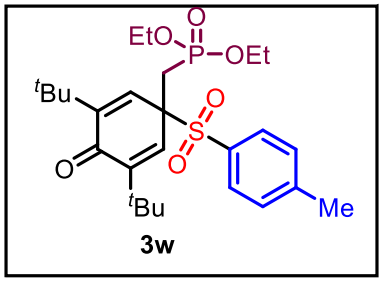
Methyl 3-(3,5-di-*tert*-butyl-1-((4-methoxyphenyl)sulfonyl)-4-oxocyclohexa-2,5-dien-1-yl)propanoate (3v)



3v

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 15/1, v/v, R_f=0.3) to afford **3v** as white solid (60 mg, 65% yield). **M.p.** = 149–151 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.55 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.59 (s, 2H), 3.79 (s, 3H), 3.65 (s, 3H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.14 (t, *J* = 7.7 Hz, 2H), 1.10 (s, 18H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 183.6, 172.3, 164.2, 153.3, 134.2, 132.4, 125.4, 113.5, 69.2, 55.8, 52.0, 35.5, 29.0, 28.8, 26.6. **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{25}H_{35}O_6S^+$ calcd for 463.2149; found 463.2150.

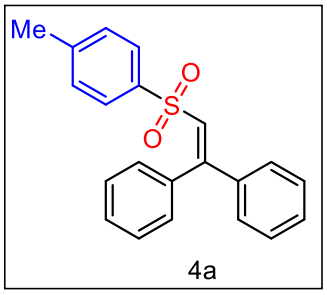
Diethyl ((3,5-di-*tert*-butyl-4-oxo-1-tosylcyclohexa-2,5-dien-1-yl)methyl)phosphonate (3w)



3w

According to the general procedure, Flash column chromatography on silica gel (eluent: PE/EtOAc = 5/1, v/v, R_f=0.4) to afford **3w** as white solid (52 mg, 51% yield). **M.p.** = 142–144 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.64 (s, 2H), 4.09 – 3.90 (m, 4H), 2.89 (s, 1H), 2.85 (s, 1H), 2.36 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 6H), 1.11 (s, 18H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 183.9, 151.7, 145.8, 134.1 (d, *J* = 2.0 Hz), 130.9, 129.1 (d, *J* = 2.1 Hz), 128.9, 66.8 (d, *J* = 2.4 Hz), 62.1 (d, *J* = 6.6 Hz), 35.4, 29.2 (d, *J* = 70.2 Hz), 28.9, 21.7, 16.5 (d, *J* = 5.6 Hz). **HRMS (ESI-ion trap)** m/z: $[M+H]^+$ $C_{26}H_{40}O_6PS^+$ calcd for 511.2278; found 511.2269.

(2-tosylethene-1,1-diyl)dibenzene (4a)[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.38-7.35 (m, 2H), 7.32-7.28 (m, 4H), 7.21-7.19 (m, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.11-7.08 (m, 2H), 6.99 (s, 1H), 2.38 (s, 3H).

2.7 Crystal data and structure refinement for 3a Experimental method:

2,6-di-*tert*-butyl-4-methyl-4-tosylcyclohexa-2,5-dien-1-one (**3a**) was crystallized from ethyl alcohol /hexane mixture (1/1, v/v), under the condition of room temperature.

The crystallographic data are summarized in the following table.

The crystal structure of compound **3a** has been deposited at the Cambridge Crystallographic Data Centre (CCDC: 2395276).

The data is available free of charge at https://www.ccdc.cam.ac.uk/News/List/2018-07-new-joint-services/

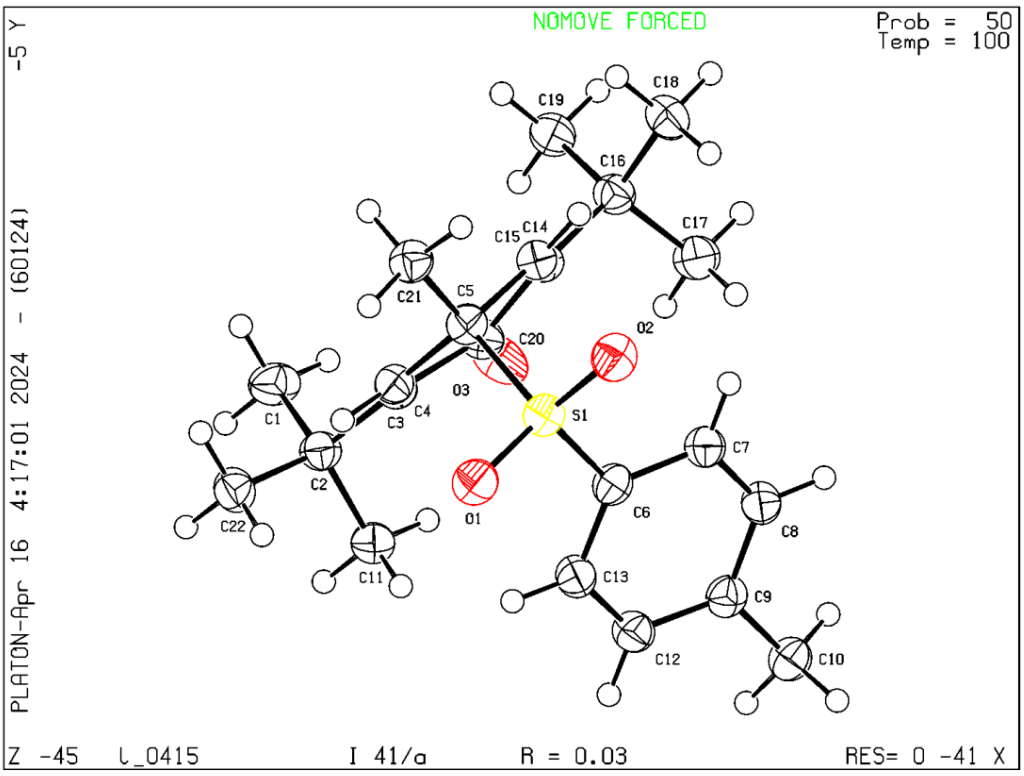


Table 1 Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{22}H_{30}O_3S$
Formula weight	374.52
Temperature/K	100.0(2)
Crystal system	tetragonal
Space group	$I4_1/a$
a/Å	25.1999(4)
b/Å	25.1999(4)
c/Å	12.8113(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	8135.6(3)
Z	16
ρ_{calc}g/cm^3	1.223
μ/mm^{-1}	1.550
F(000)	3232.0
Crystal size/mm^3	0.43 × 0.41 × 0.4
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.016 to 136.462
Index ranges	$-29 \le h \le 30$, $-22 \le k \le 29$, $-15 \le l \le 15$
Reflections collected	36710

Independent reflections	3717 [R_{int} = 0.0290, R_{sigma} = 0.0110]
Data/restraints/parameters	3717/0/243
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0342, wR_2 = 0.0936
Final R indexes [all data]	R_1 = 0.0347, wR_2 = 0.0939
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.41

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	3565.6(2)	6866.8(2)	5710.9(2)	30.51(12)
O1	3040.3(4)	7022.8(4)	6028.3(8)	36.8(2)
O2	4013.0(4)	7061.7(4)	6297.9(8)	37.5(2)
O3	3780.1(4)	5846.3(4)	2305.5(9)	46.5(3)
C1	2859.3(6)	6349.8(6)	1202.4(11)	41.3(3)
C2	2742.0(5)	6316.5(5)	2378.3(10)	30.5(3)
C3	3222.6(5)	6512.1(5)	3004.1(10)	29.1(3)
C4	3189.6(5)	6886.0(5)	3740.3(10)	29.4(3)
C5	3653.7(5)	7087.7(5)	4345.5(10)	29.7(3)
C6	3600.3(5)	6166.7(5)	5673.0(10)	30.1(3)
C7	4094.7(5)	5922.6(5)	5743.9(10)	32.1(3)
C8	4122.0(5)	5374.0(6)	5759.7(10)	32.8(3)
C9	3662.2(5)	5065.1(5)	5710.6(10)	31.0(3)
C10	3693.7(6)	4469.0(5)	5770.9(11)	34.3(3)
C11	2612.7(5)	5740.7(5)	2684.5(11)	34.2(3)
C12	3173.5(5)	5321.0(6)	5628.2(11)	33.6(3)
C13	3136.9(5)	5869.8(5)	5608.2(10)	32.9(3)
C14	4177.0(5)	6889.4(5)	3975.1(10)	30.2(3)
C15	4236.8(5)	6515.0(5)	3245.1(10)	29.9(3)
C16	4779.1(5)	6324.2(5)	2854.5(11)	31.4(3)
C17	4868.0(6)	5739.3(6)	3161.6(12)	39.2(3)
C18	5230.4(5)	6650.3(6)	3333.9(12)	36.4(3)
C19	4809.0(6)	6391.8(6)	1660.5(11)	35.8(3)
C20	3749.7(5)	6257.7(5)	2807.9(11)	32.7(3)
C21	3647.5(5)	7698.0(5)	4400.9(11)	33.4(3)
C22	2251.1(5)	6655.1(5)	2603.3(12)	36.2(3)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 3a. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U_{11}+2hka*b*U_{12}+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	33.40(18)	30.54(18)	27.60(18)	-1.67(11)	0.31(11)	0.94(11)
O1	39.8(5)	36.3(5)	34.2(5)	-1.0(4)	5.6(4)	4.7(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	43.5(5)	36.3(5)	32.8(5)	-3.7(4)	-5.4(4)	-2.0(4)
O3	33.7(5)	46.3(6)	59.5(7)	-22.9(5)	5.2(5)	-1.9(4)
C1	44.3(8)	49.9(8)	29.5(7)	1.2(6)	-0.1(6)	-12.7(6)
C2	30.4(6)	32.3(6)	28.8(6)	1.3(5)	0.3(5)	-3.1(5)
C3	29.2(6)	29.5(6)	28.5(6)	3.3(5)	1.4(5)	-1.9(5)
C4	28.9(6)	30.0(6)	29.3(6)	2.9(5)	1.0(5)	1.3(5)
C5	31.5(6)	29.4(6)	28.4(6)	-0.6(5)	1.2(5)	0.6(5)
C6	33.2(7)	31.4(6)	25.8(6)	0.7(5)	-0.6(5)	0.4(5)
C7	30.8(6)	35.4(7)	30.0(7)	2.2(5)	-1.9(5)	-2.3(5)
C8	30.1(6)	36.4(7)	32.1(7)	2.7(5)	-1.1(5)	2.3(5)
C9	34.2(7)	34.2(7)	24.6(6)	0.5(5)	0.1(5)	0.3(5)
C10	36.7(7)	34.5(7)	31.7(7)	0.9(5)	0.1(5)	0.5(5)
C11	33.2(7)	32.4(7)	36.8(7)	1.0(5)	-0.3(5)	-2.7(5)
C12	30.8(7)	36.6(7)	33.5(7)	1.3(5)	-1.1(5)	-2.6(5)
C13	29.7(6)	36.7(7)	32.2(7)	1.2(5)	-0.4(5)	1.6(5)
C14	29.0(6)	30.3(6)	31.2(6)	2.5(5)	-0.4(5)	-1.0(5)
C15	29.4(6)	28.8(6)	31.7(7)	2.4(5)	1.5(5)	-0.4(5)
C16	28.9(6)	30.8(6)	34.7(7)	-0.5(5)	2.2(5)	0.3(5)
C17	37.2(7)	33.2(7)	47.2(8)	2.6(6)	8.4(6)	4.3(6)
C18	28.8(7)	38.6(7)	41.8(8)	-2.5(6)	0.4(5)	1.4(5)
C19	33.2(7)	38.4(7)	35.9(7)	-1.9(6)	4.1(5)	0.8(5)
C20	32.4(7)	32.7(7)	33.0(7)	-2.6(5)	3.2(5)	-1.6(5)
C21	35.6(7)	29.4(7)	35.1(7)	-1.3(5)	1.5(5)	0.3(5)
C22	31.7(7)	34.8(7)	42.2(7)	0.4(6)	-5.7(6)	-0.7(5)

Table 4 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.4396(10)	C6	C7	1.3925(19)
S1	O2	1.4414(10)	C6	C13	1.3893(19)
S1	C5	1.8490(13)	C7	C8	1.384(2)
S1	C6	1.7670(13)	C8	C9	1.398(2)
O3	C20	1.2227(17)	C9	C10	1.5062(19)
C1	C2	1.5374(19)	C9	C12	1.3942(19)
C2	C3	1.5337(18)	C12	C13	1.386(2)
C2	C11	1.5382(18)	C14	C15	1.3370(19)
C2	C22	1.5302(19)	C15	C16	1.5327(18)
C3	C4	1.3357(19)	C15	C20	1.4968(18)
C3	C20	1.4963(18)	C16	C17	1.5420(19)
C4	C5	1.4926(18)	C16	C18	1.5316(19)
C5	C14	1.4879(18)	C16	C19	1.5410(19)

Table 4 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C5	C21	1.5399(18)			

Table 5 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	O2	118.61(6)	C13	C6	S1	119.85(10)
O1	S1	C5	107.18(6)	C13	C6	C7	121.20(12)
O1	S1	C6	109.02(6)	C8	C7	C6	119.13(12)
O2	S1	C5	107.28(6)	C7	C8	C9	120.96(13)
O2	S1	C6	108.41(6)	C8	C9	C10	120.63(12)
C6	S1	C5	105.58(6)	C12	C9	C8	118.57(13)
C1	C2	C11	110.00(11)	C12	C9	C10	120.79(12)
C3	C2	C1	110.06(11)	C13	C12	C9	121.44(13)
C3	C2	C11	109.70(10)	C12	C13	C6	118.70(12)
C22	C2	C1	108.04(11)	C15	C14	C5	124.05(12)
C22	C2	C3	111.14(11)	C14	C15	C16	123.38(12)
C22	C2	C11	107.86(11)	C14	C15	C20	118.36(12)
C4	C3	C2	123.14(12)	C20	C15	C16	118.24(11)
C4	C3	C20	118.43(12)	C15	C16	C17	110.25(11)
C20	C3	C2	118.39(11)	C15	C16	C19	109.45(11)
C3	C4	C5	123.93(12)	C18	C16	C15	111.28(11)
C4	C5	S1	107.15(9)	C18	C16	C17	107.63(11)
C4	C5	C21	110.86(11)	C18	C16	C19	107.61(11)
C14	C5	S1	107.88(9)	C19	C16	C17	110.59(11)
C14	C5	C4	114.49(11)	O3	C20	C3	120.48(12)
C14	C5	C21	111.05(11)	O3	C20	C15	120.86(12)
C21	C5	S1	104.82(9)	C3	C20	C15	118.66(11)
C7	C6	S1	118.91(10)				

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C5	C14	C15	111.65(13)	C6	S1	C5	C4	64.61(10)
S1	C6	C7	C8	177.25(10)	C6	S1	C5	C14	-59.14(10)
S1	C6	C13	C12	-177.06(10)	C6	S1	C5	C21	-177.55(8)
O1	S1	C5	C4	-51.52(10)	C6	C7	C8	C9	-0.31(19)
O1	S1	C5	C14	-175.26(9)	C7	C6	C13	C12	0.79(19)
O1	S1	C5	C21	66.32(10)	C7	C8	C9	C10	-177.57(12)
O1	S1	C6	C7	-158.03(10)	C7	C8	C9	C12	1.01(19)
O1	S1	C6	C13	19.87(12)	C8	C9	C12	C13	-0.8(2)
O2	S1	C5	C4	-179.92(8)	C9	C12	C13	C6	-0.1(2)

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	S1	C5	C14	56.34(10)	C10	C9	C12	C13	177.75(12)
O2	S1	C5	C21	-62.07(10)	C11	C2	C3	C4	-111.42(14)
O2	S1	C6	C7	-27.60(12)	C11	C2	C3	C20	66.25(15)
O2	S1	C6	C13	150.30(10)	C13	C6	C7	C8	-0.61(19)
C1	C2	C3	C4	127.42(14)	C14	C15	C16	C17	114.27(14)
C1	C2	C3	C20	-54.91(15)	C14	C15	C16	C18	-5.07(18)
C2	C3	C4	C5	-178.98(11)	C14	C15	C16	C19	-123.87(14)
C2	C3	C20	O3	-12.74(19)	C14	C15	C20	O3	-165.10(13)
C2	C3	C20	C15	167.69(11)	C14	C15	C20	C3	14.47(18)
C3	C4	C5	S1	-112.12(12)	C16	C15	C20	O3	13.2(2)
C3	C4	C5	C14	7.47(18)	C16	C15	C20	C3	-167.23(11)
C3	C4	C5	C21	134.05(13)	C20	C3	C4	C5	3.35(19)
C4	C3	C20	O3	165.05(13)	C20	C15	C16	C17	-63.93(15)
C4	C3	C20	C15	-14.52(18)	C20	C15	C16	C18	176.73(11)
C4	C5	C14	C15	-7.52(18)	C20	C15	C16	C19	57.93(15)
C5	S1	C6	C7	87.11(11)	C21	C5	C14	C15	-134.00(13)
C5	S1	C6	C13	-95.00(11)	C22	C2	C3	C4	7.77(17)
C5	C14	C15	C16	178.56(12)	C22	C2	C3	C20	-174.56(11)
C5	C14	C15	C20	-3.24(19)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	*x*	*y*	*z*	U(eq)
H1A	2549.26	6226.83	809.1	62
H1B	3165.48	6125.44	1035.85	62
H1C	2937.97	6718.23	1012.85	62
H4	2850.29	7032.34	3887.47	35
H7	4409.08	6129.77	5781.02	38
H8	4458.3	5205.12	5804.57	39
H10A	4020.78	4347.47	5433.04	51
H10B	3386.7	4313.44	5414.7	51
H10C	3694.18	4358.19	6504.13	51
H11A	2530.78	5724.34	3431.55	51
H11B	2919.21	5513.81	2534.24	51
H11C	2305.78	5616.97	2282.67	51
H12	2858.64	5114.79	5584.9	40
H13	2801.52	6039.61	5551.22	39
H14	4487.91	7038.02	4275.93	36
H17A	4853.07	5704.67	3922.91	59
H17B	5216.5	5622.66	2911.3	59
H17C	4590.91	5518.68	2845.58	59

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	*x*	*y*	*z*	U(eq)
H18A	5180.91	7025.96	3161.34	55
H18B	5570.72	6527.64	3053.13	55
H18C	5228.35	6606.07	4093.84	55
H19A	4529.6	6179.68	1330.17	54
H19B	5156.57	6271.96	1411.07	54
H19C	4759.82	6766.56	1480.89	54
H21A	3937.34	7820.25	4850.67	50
H21B	3307.63	7817.57	4689.05	50
H21C	3693.45	7844.77	3698.31	50
H22A	2160.73	6629.04	3345.57	54
H22B	1952.61	6527.08	2182.56	54
H22C	2325.52	7026	2425.99	54

Table 8 Solvent masks information for 3a.

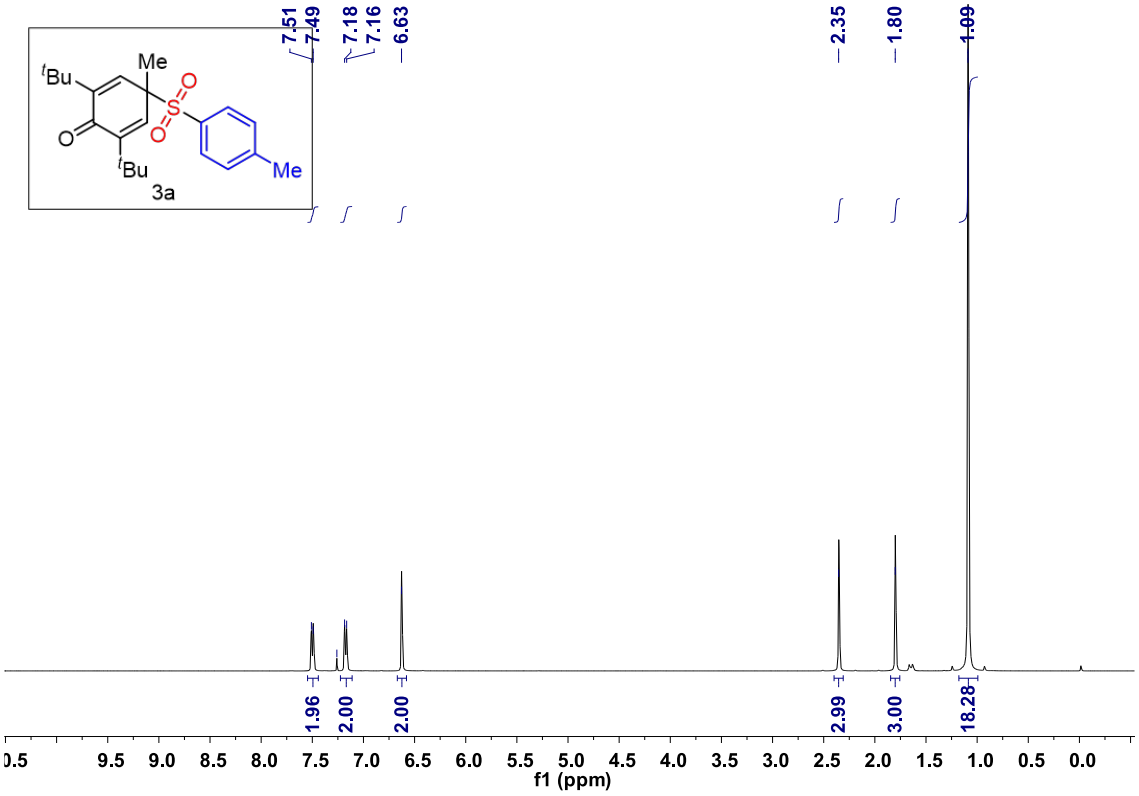
Number	X	Y	Z	Volume	Electron count	Content
1	0.000	0.250	0.125	16.7	3.0	0.18 CH4O
2	0.000	0.750	0.875	16.7	3.0	0.18 CH4O
3	0.500	0.250	0.375	16.7	3.0	0.18 CH4O
4	0.500	0.750	0.625	16.7	3.0	0.18 CH4O

3. Reference

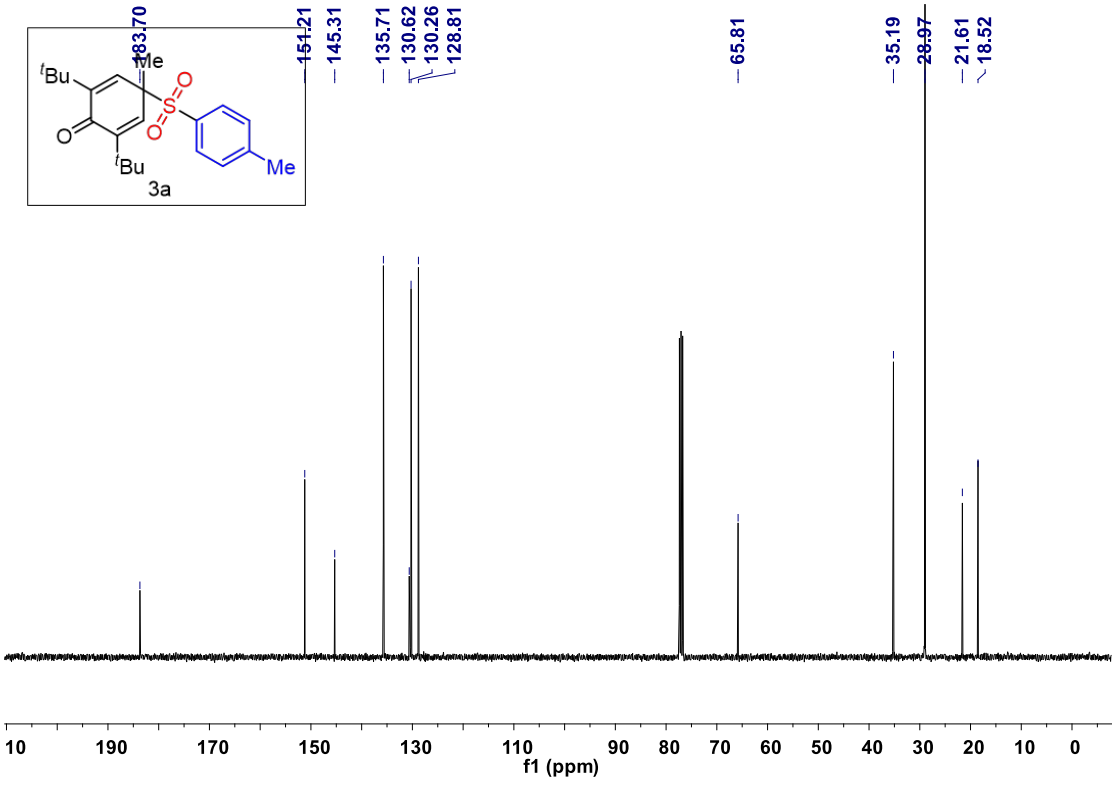
1. Zhang, G; Fu, J.-G.; Zhao, Q.; Zhang, G.-S.; Li, M.-Y.; Feng, C.-G.; Lin, G.-Q. *Chem. Commun*., **2020**, *56*, 4688-4691.

4. Copies of NMR spectra

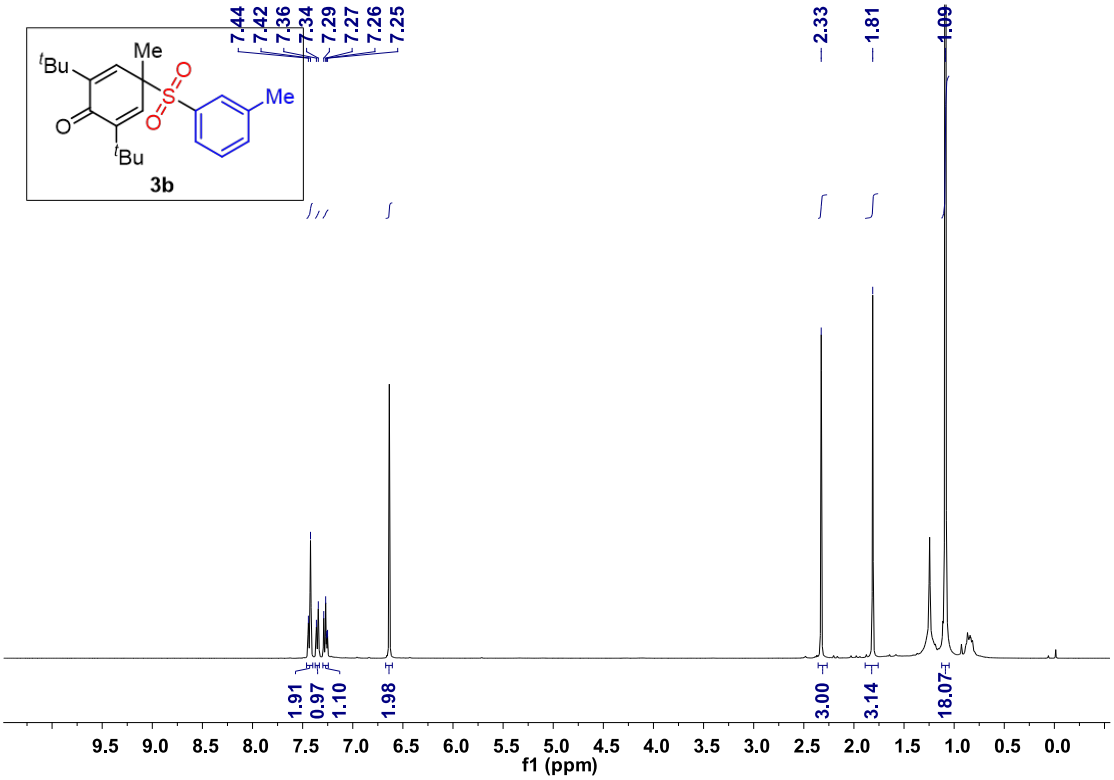
^{1}H NMR of 3a (400 MHz, $CDCl_3$)



^{13}C NMR of 3a (101 MHz, $CDCl_3$)



^{1}H NMR of 3b (400 MHz, $CDCl_3$)



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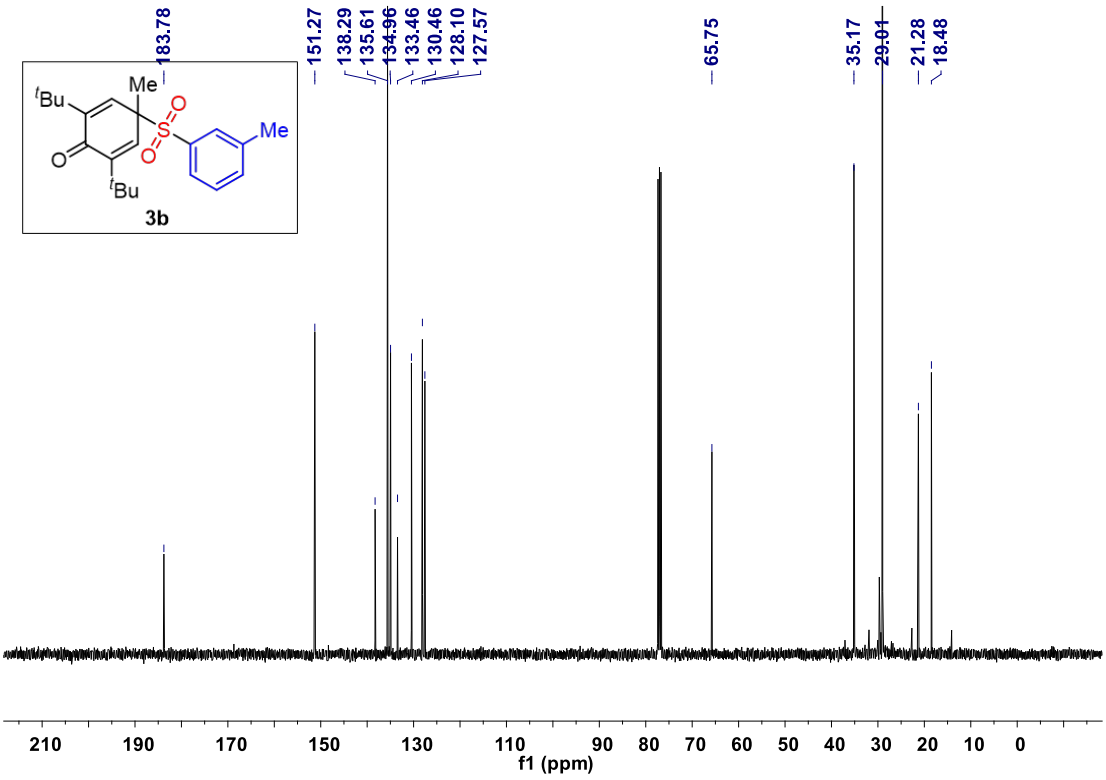

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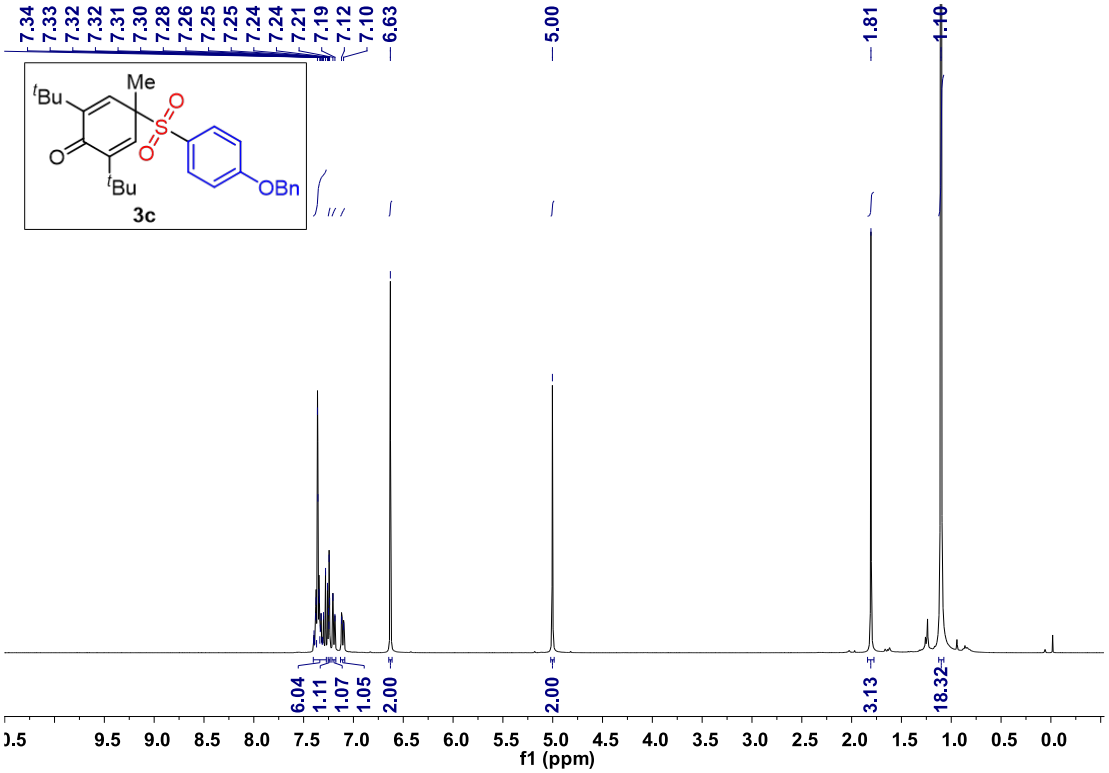
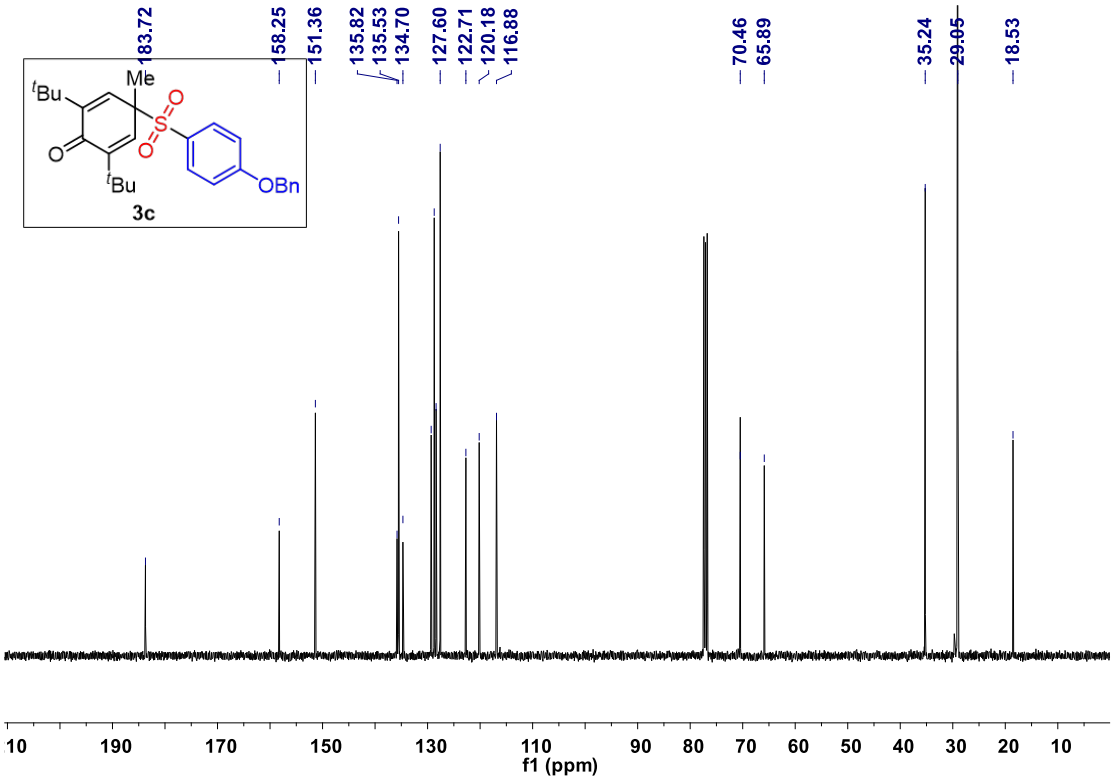
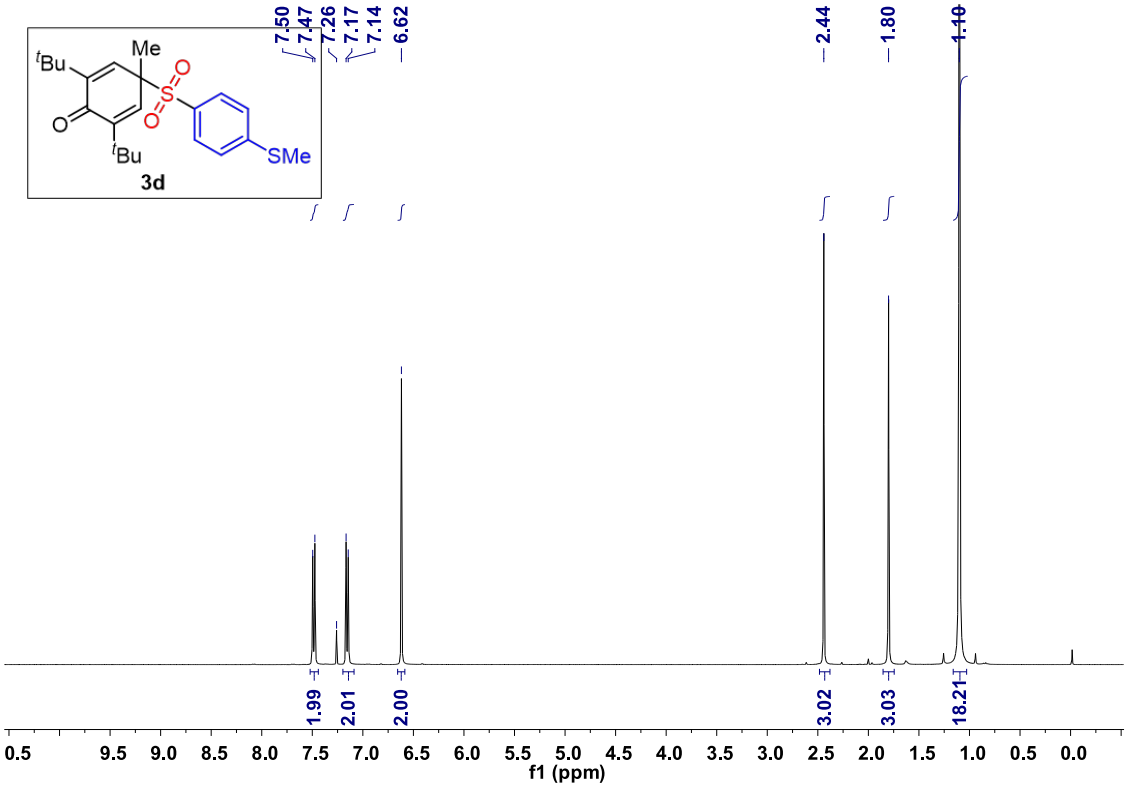


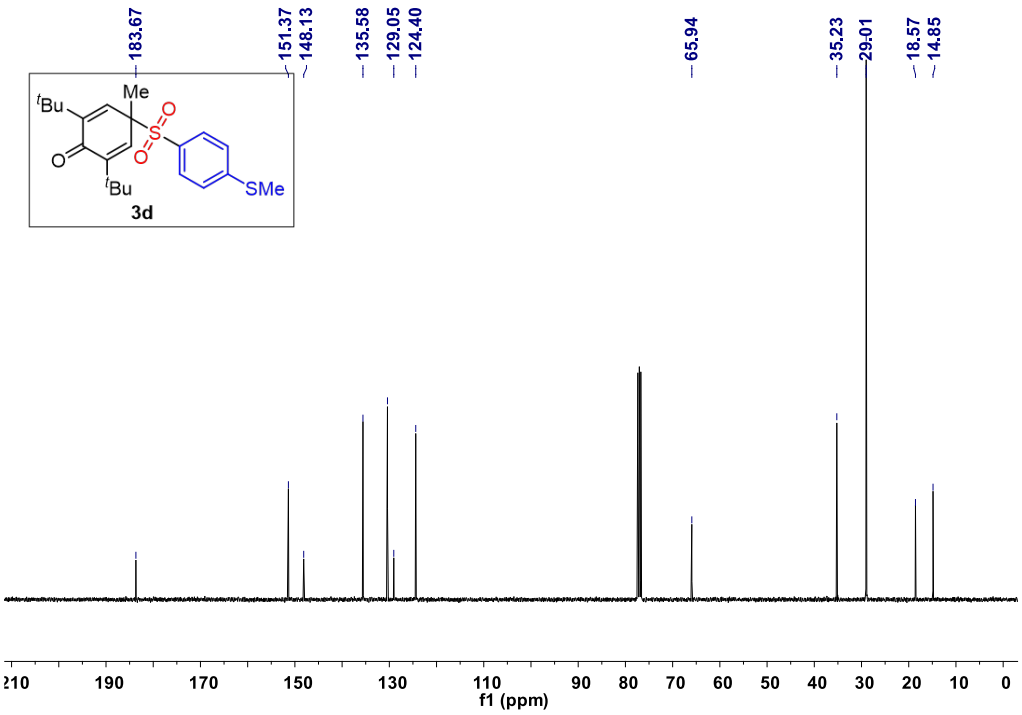
^{13}C NMR of 3c (101 MHz, $CDCl_3$)



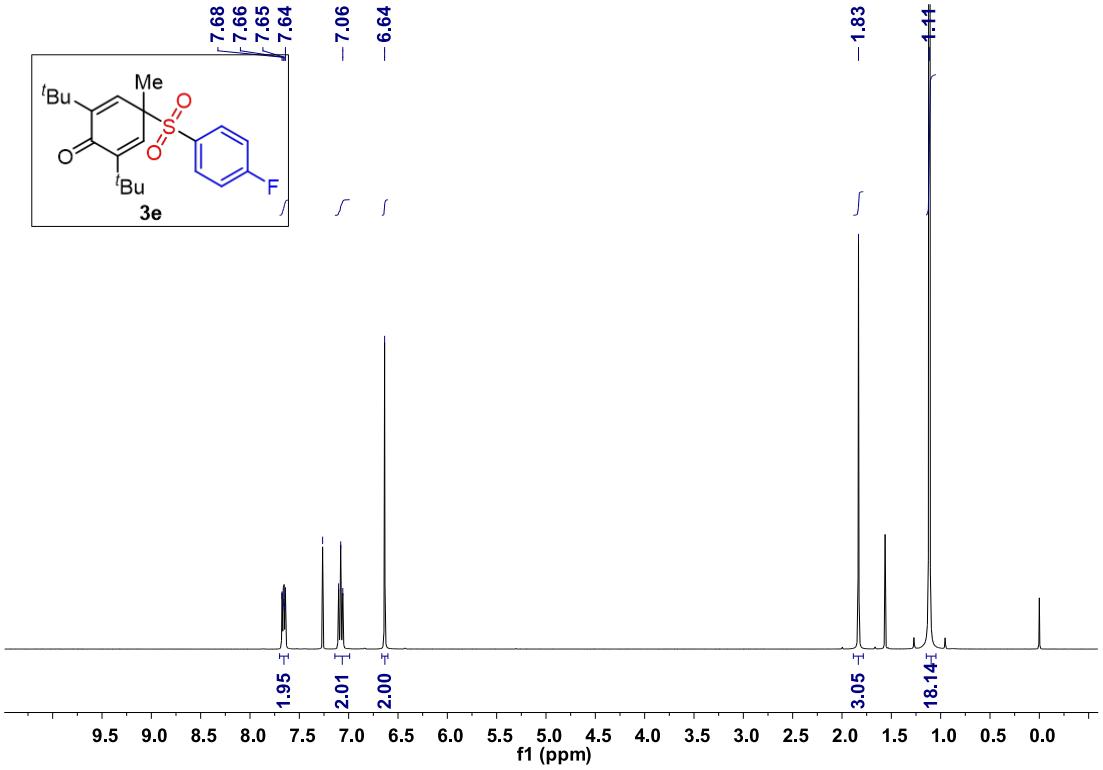
^{1}H NMR of 3d (400 MHz, $CDCl_3$)



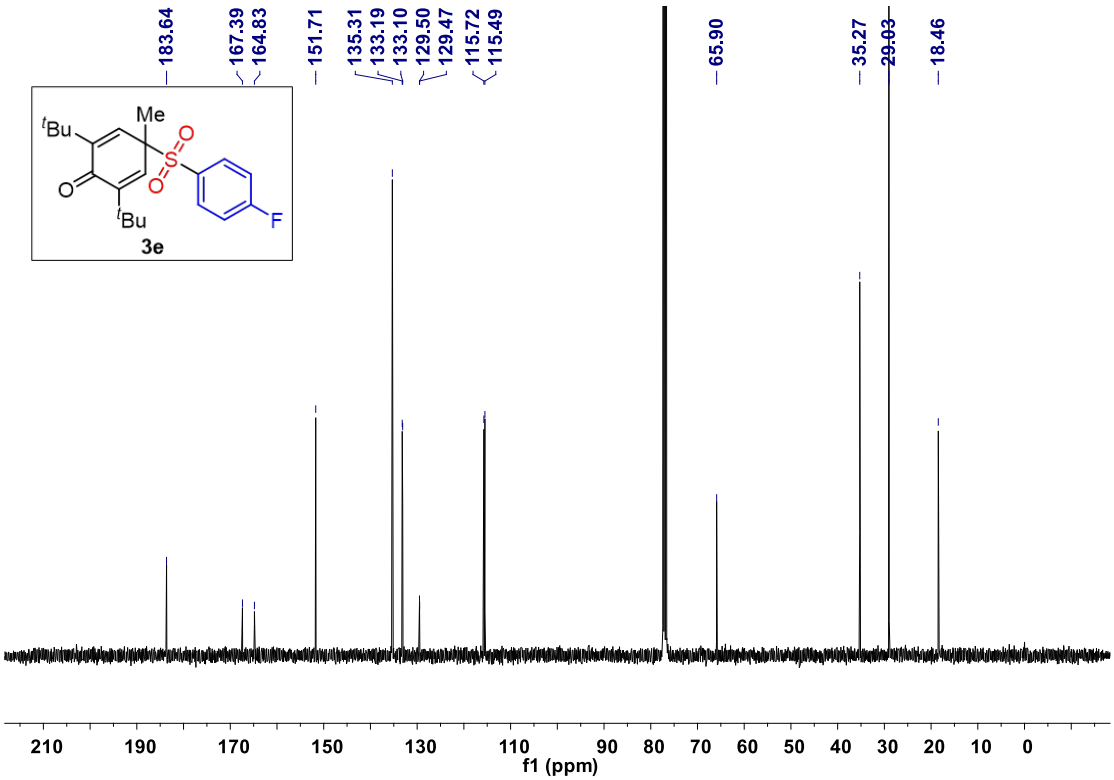
^{13}C NMR of 3d (101 MHz, $CDCl_3$)



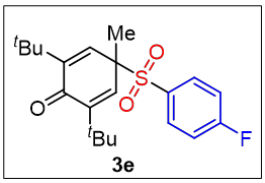
^{1}H NMR of 3e (400 MHz, $CDCl_3$)



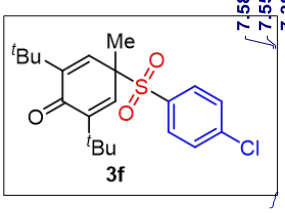
^{13}C NMR of 3e (101 MHz, $CDCl_3$)



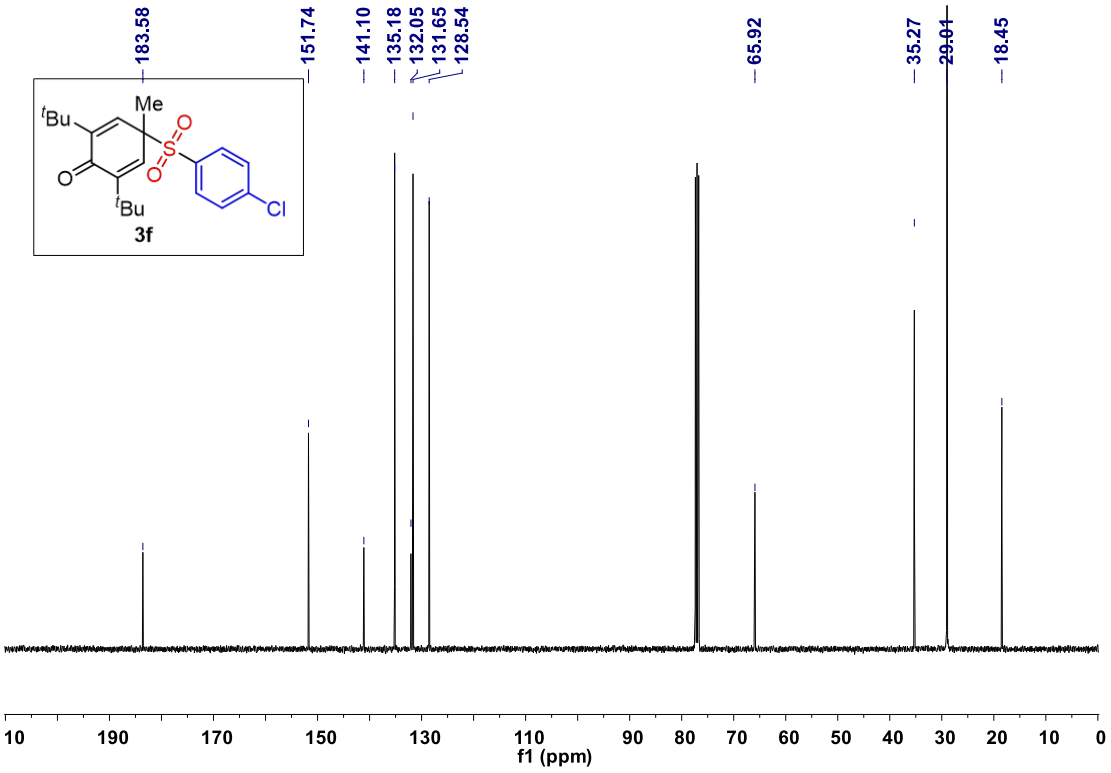
^{19}F NMR of 3e (377 MHz, $CDCl_3$)



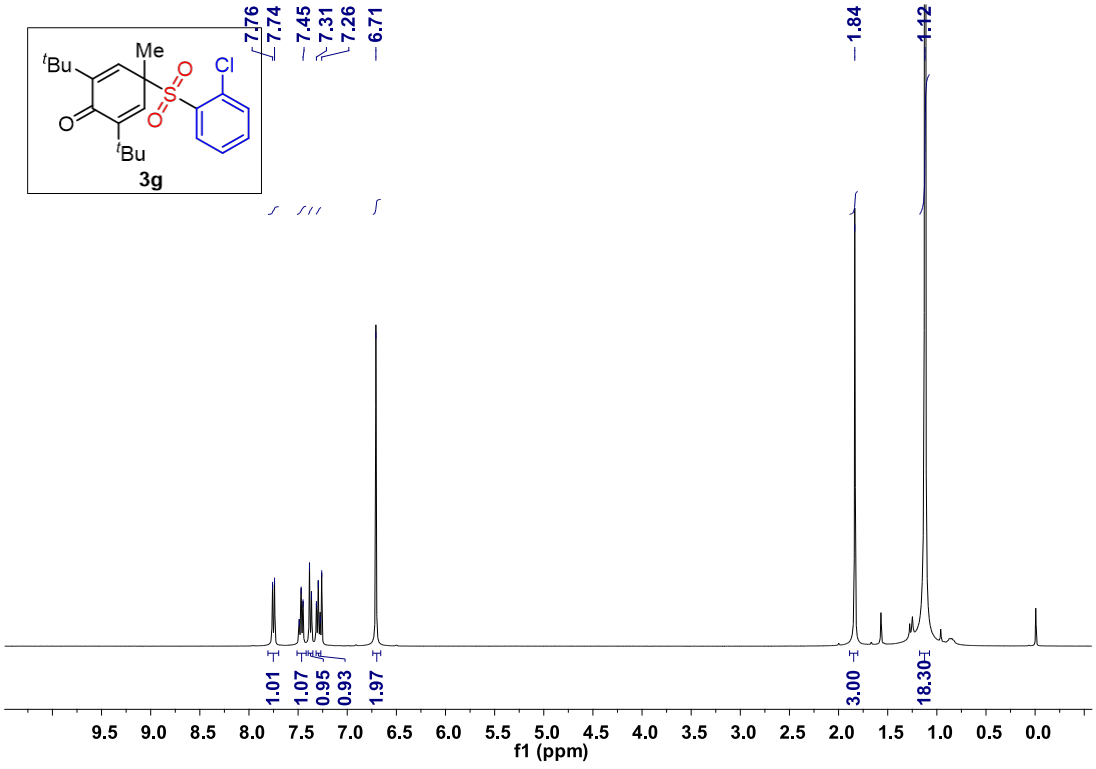
^{1}H NMR of 3f (400 MHz, $CDCl_3$)



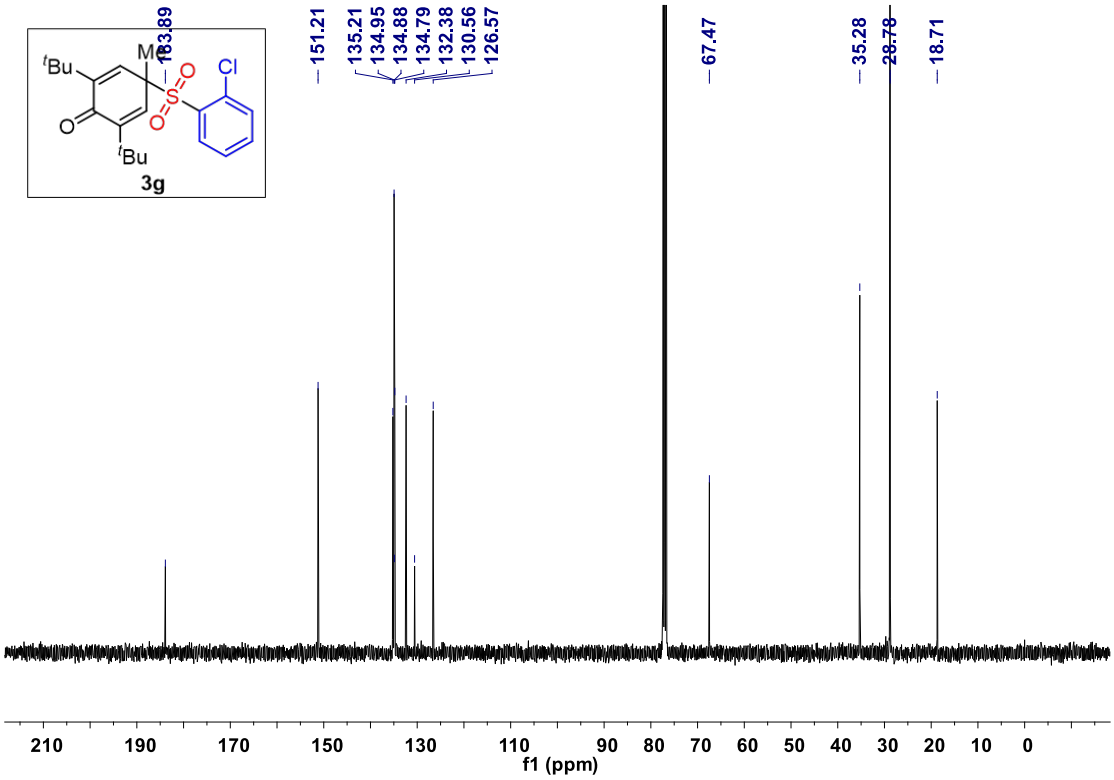
^{13}C NMR of 3f (101 MHz, $CDCl_3$)



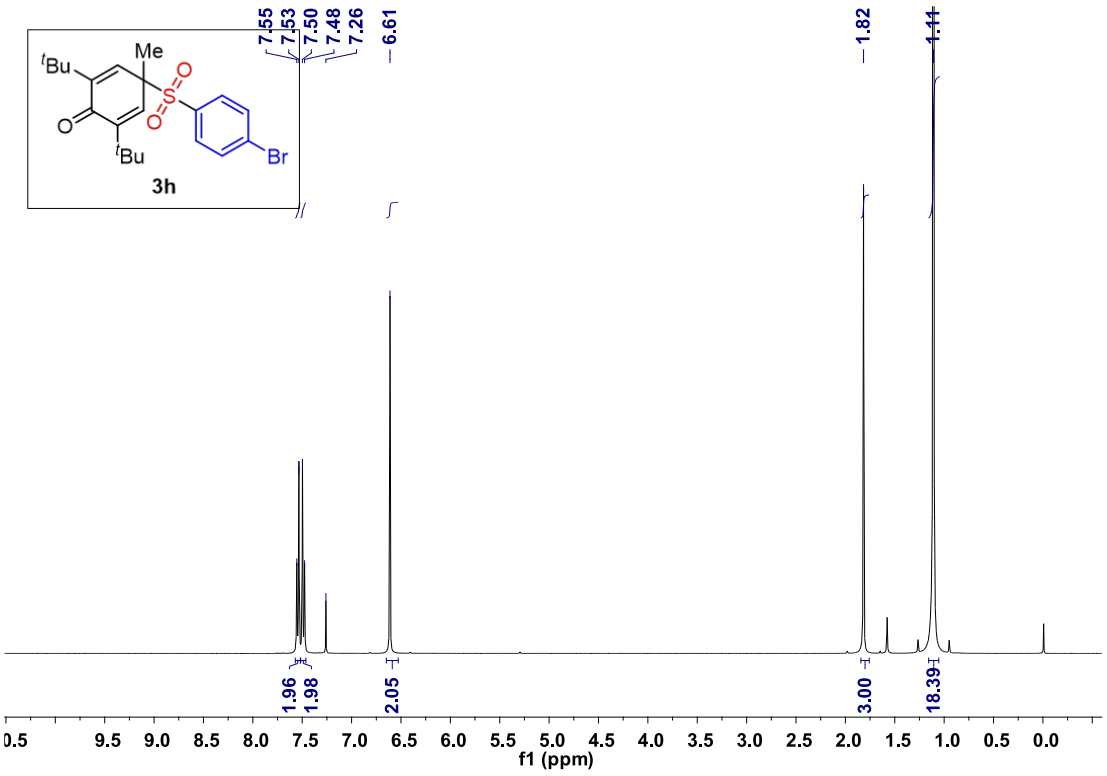
^{1}H NMR of 3g (400 MHz, $CDCl_3$)



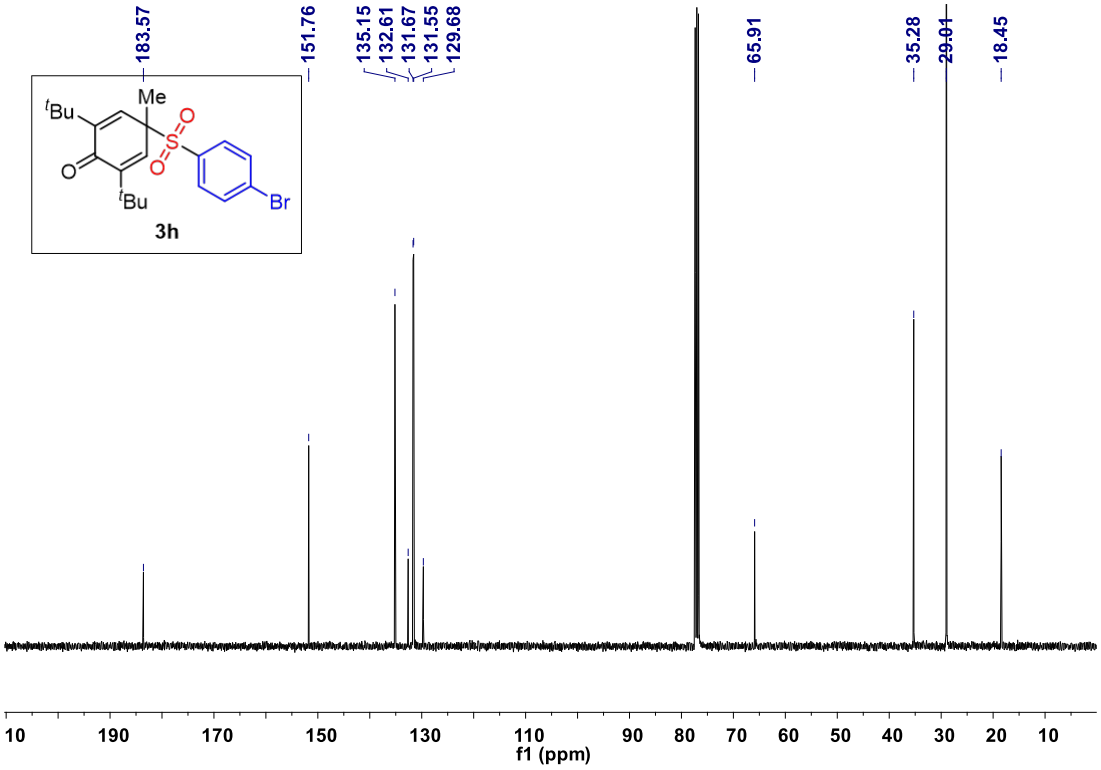
^{13}C NMR of 3g (101 MHz, $CDCl_3$)



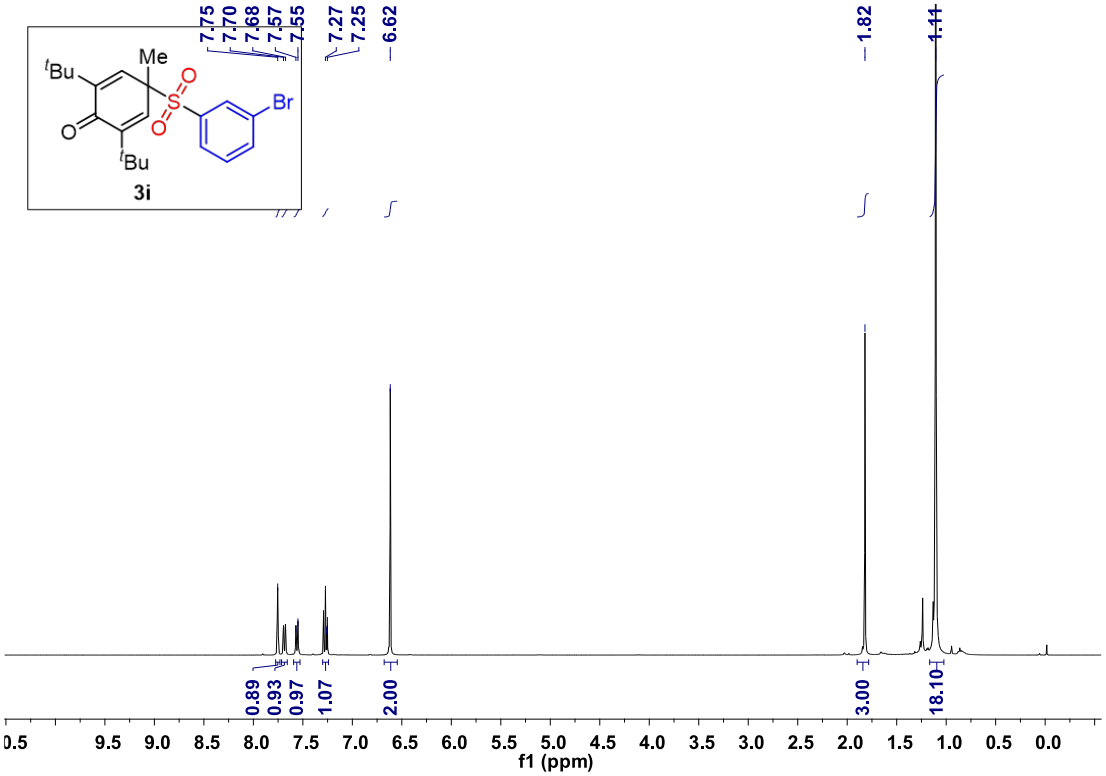
^{1}H NMR of 3h (400 MHz, $CDCl_3$)



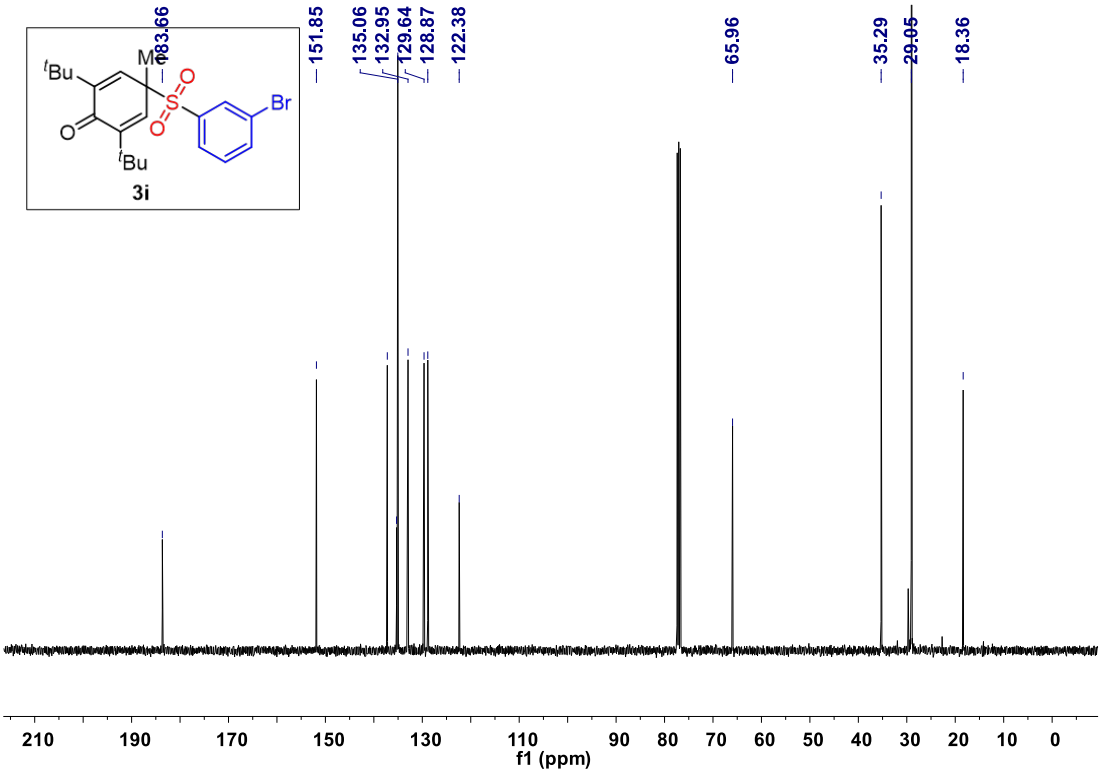
^{13}C NMR of 3h (101 MHz, $CDCl_3$)



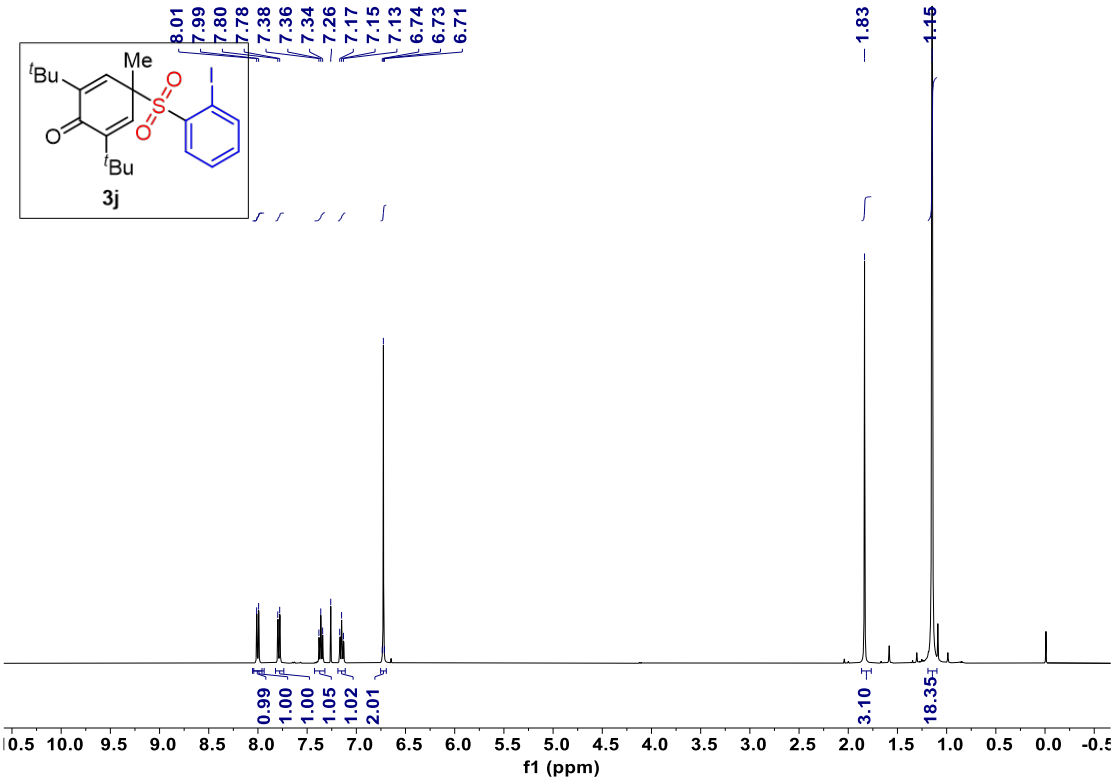
^{1}H NMR of 3i (400 MHz, $CDCl_3$)



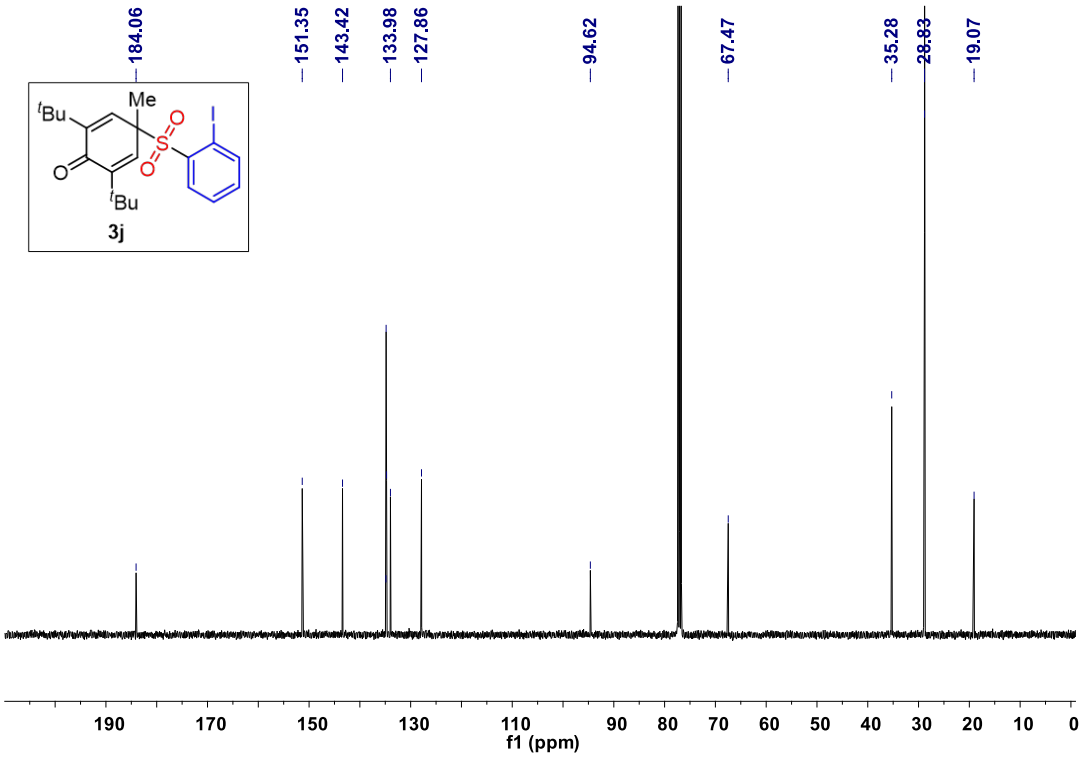
^{13}C NMR of 3i (101 MHz, $CDCl_3$)



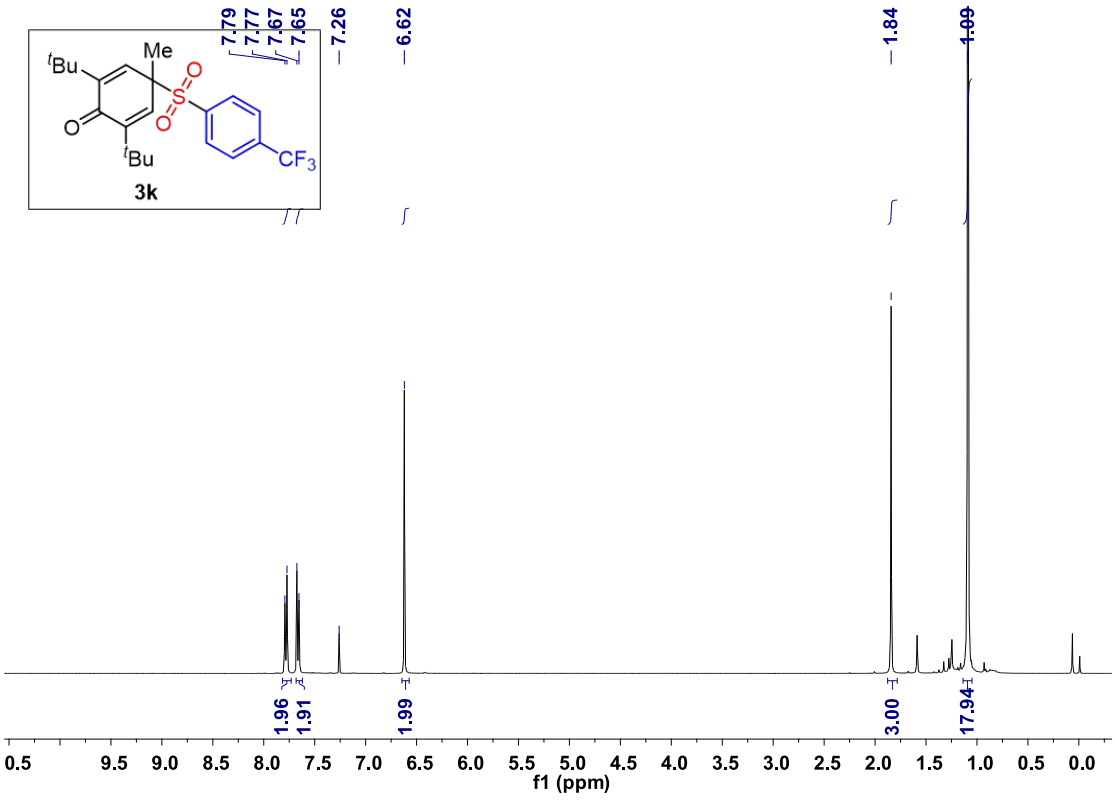
^{1}H NMR of 3j (400 MHz, $CDCl_3$)



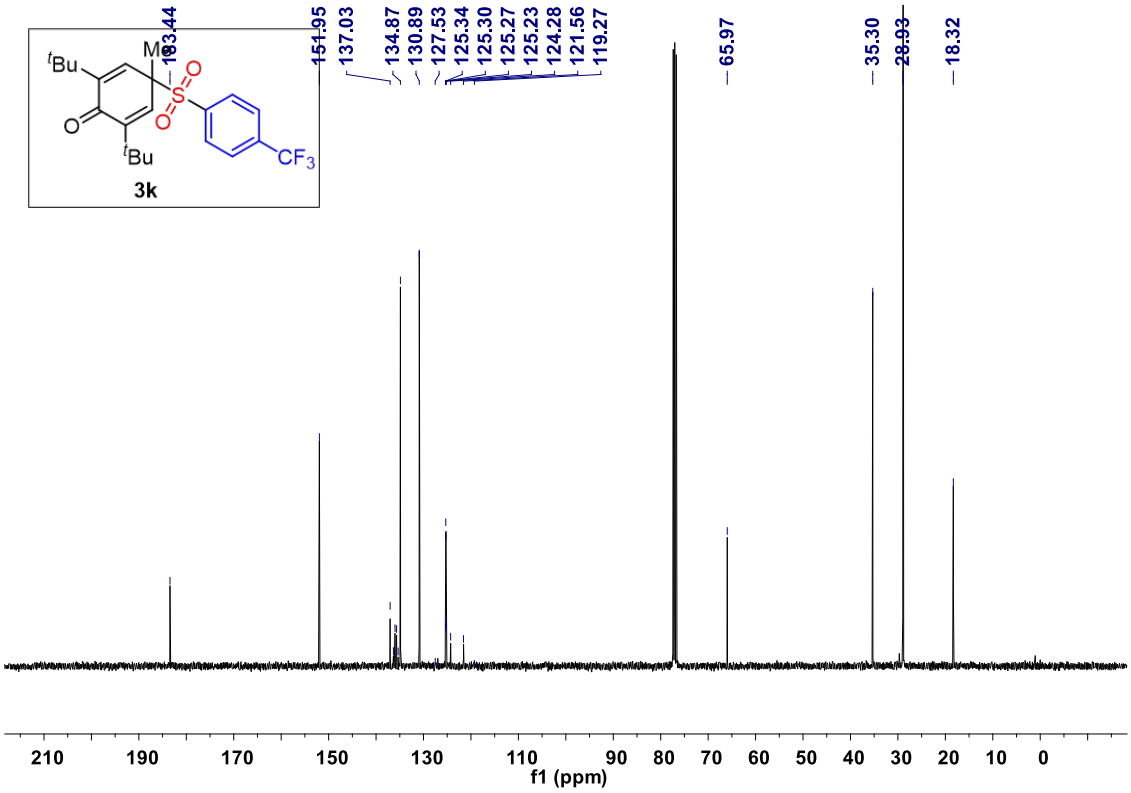
^{13}C NMR of 3j (101 MHz, $CDCl_3$)



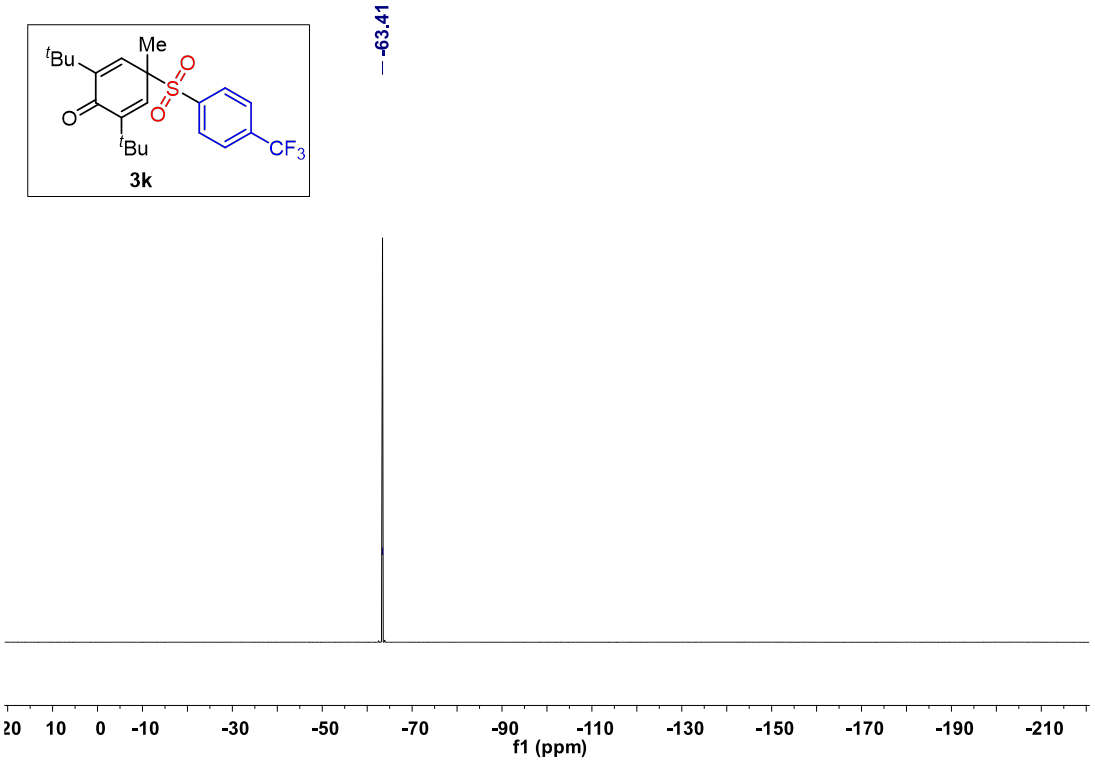
^{1}H NMR of 3k (400 MHz, $CDCl_3$)



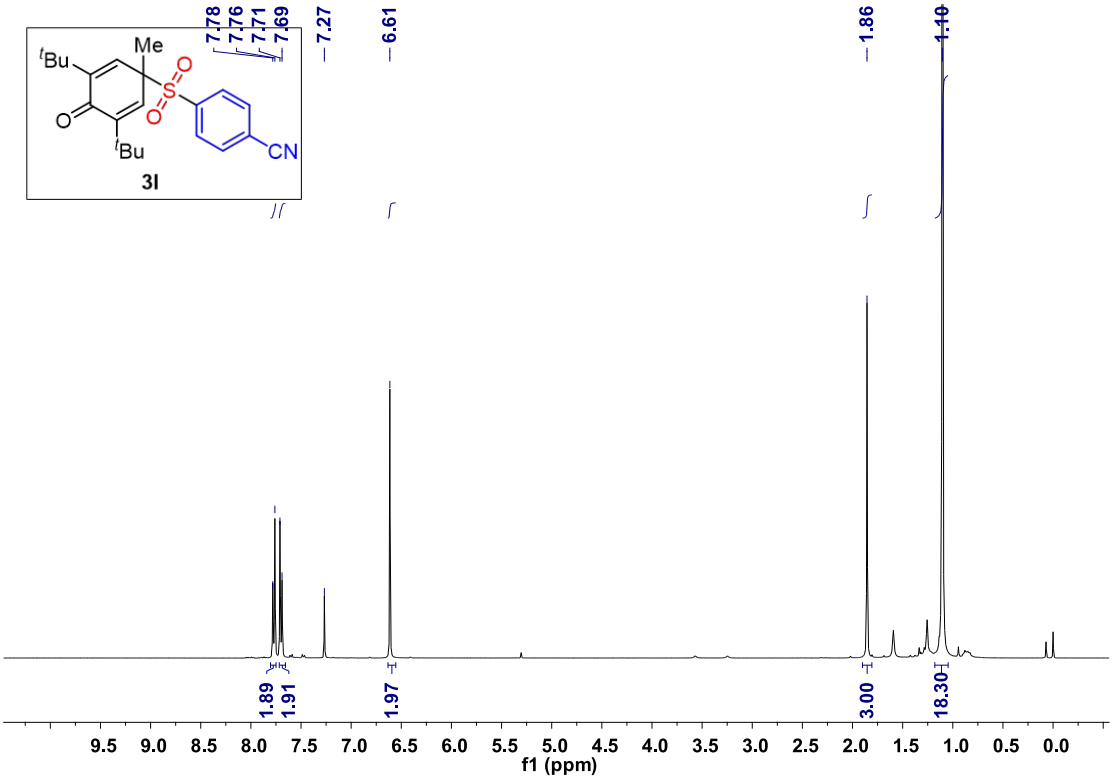
^{13}C NMR of 3k (101 MHz, $CDCl_3$)



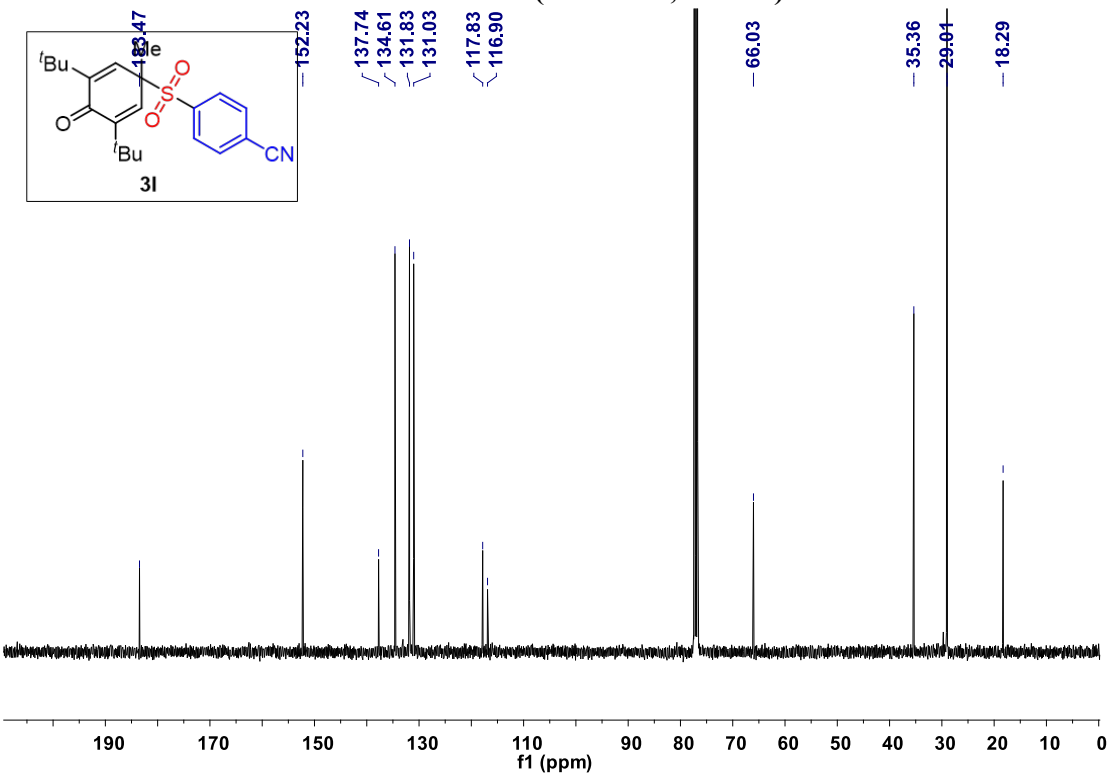
^{19}F NMR of 3k (377 MHz, $CDCl_3$)



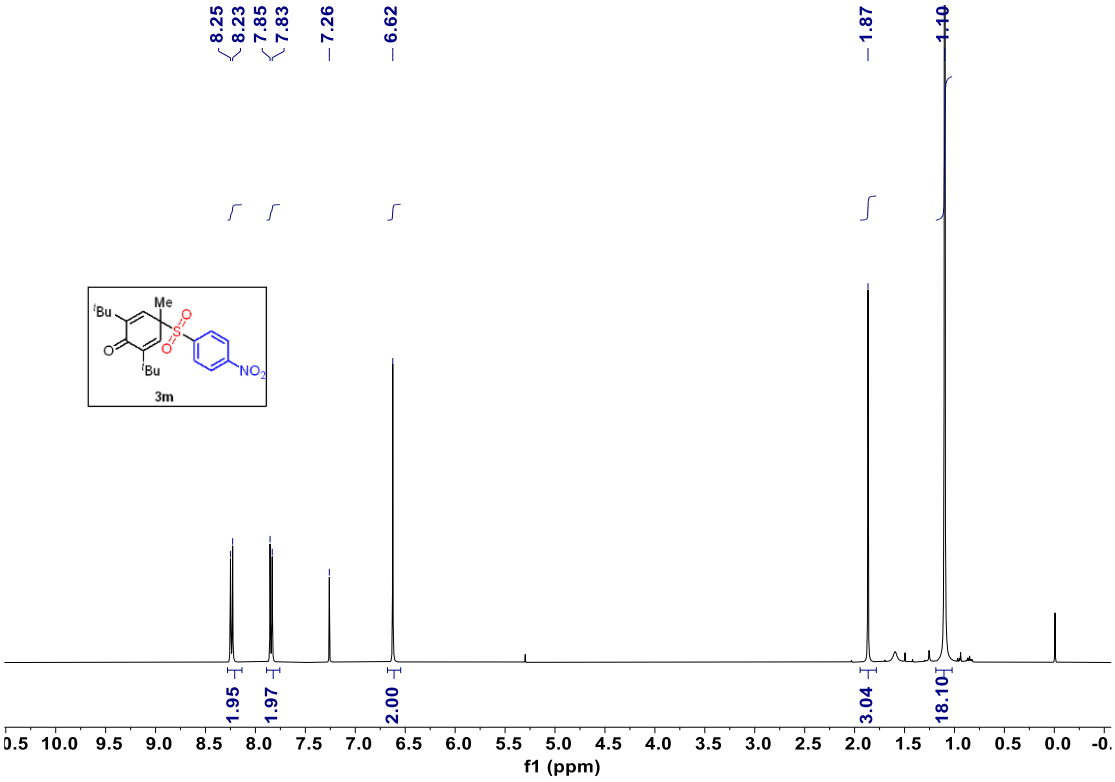
^{1}H NMR of 3l (400 MHz, $CDCl_3$)



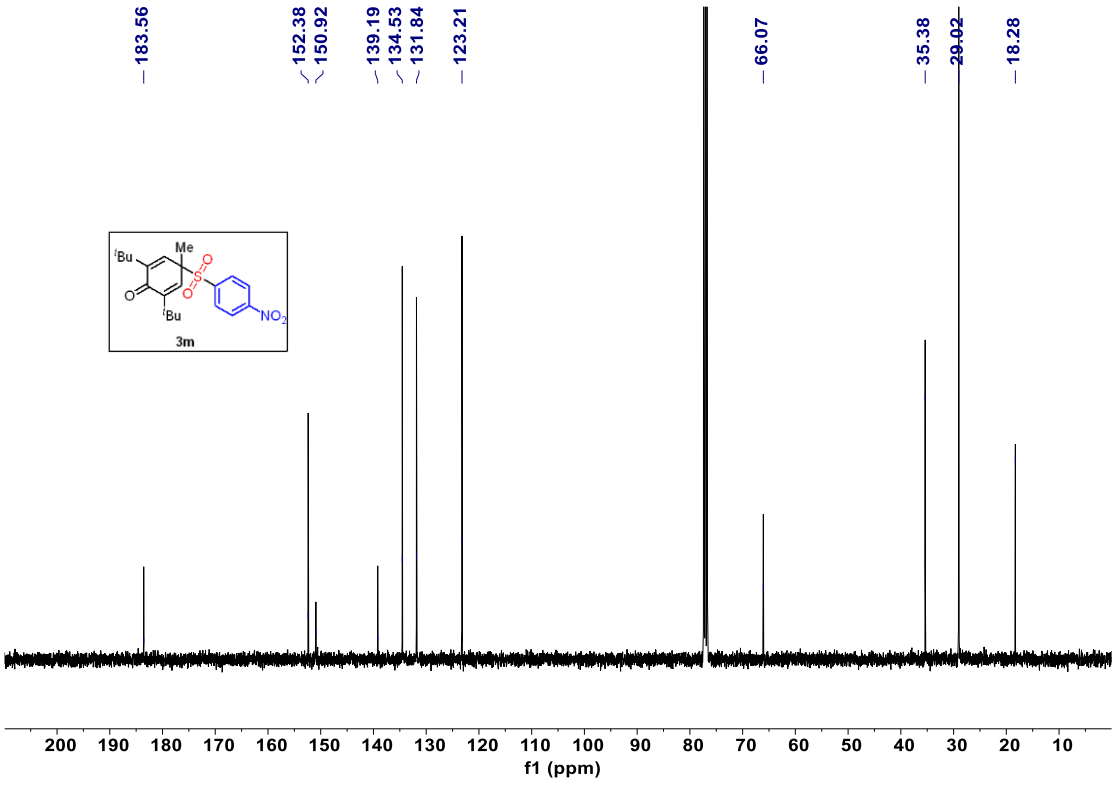
^{13}C NMR of 3l (101 MHz, $CDCl_3$)



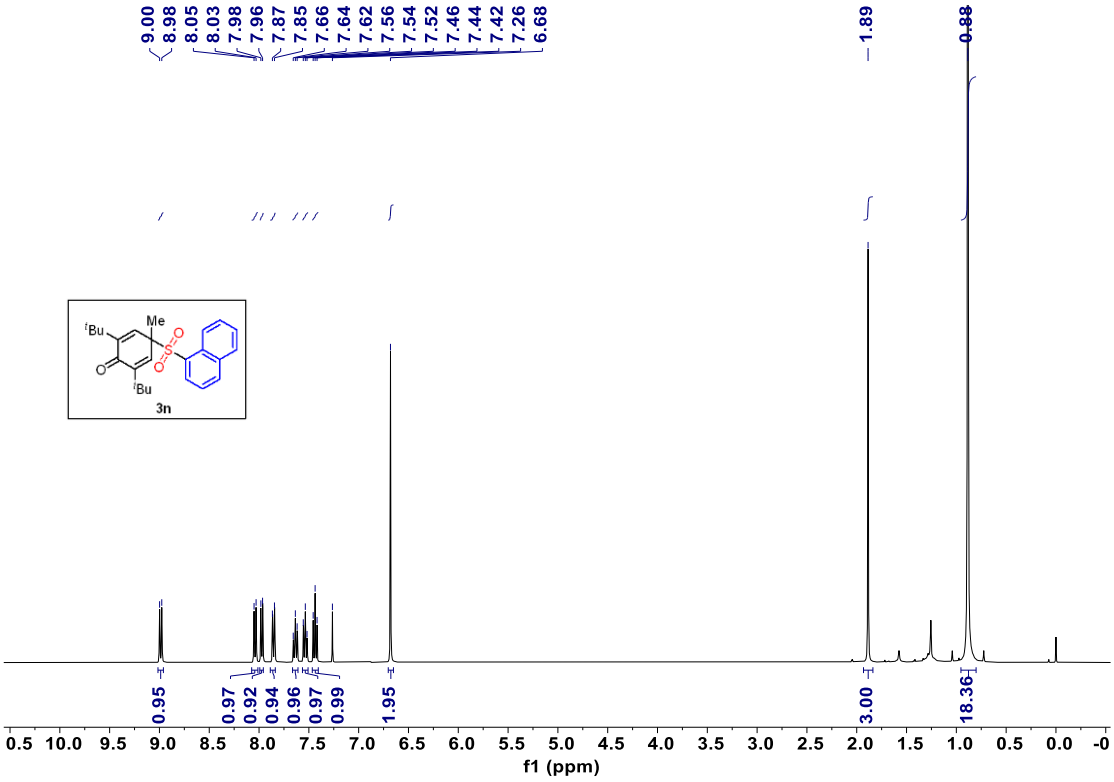
^{1}H NMR of 3m (400 MHz, $CDCl_3$)



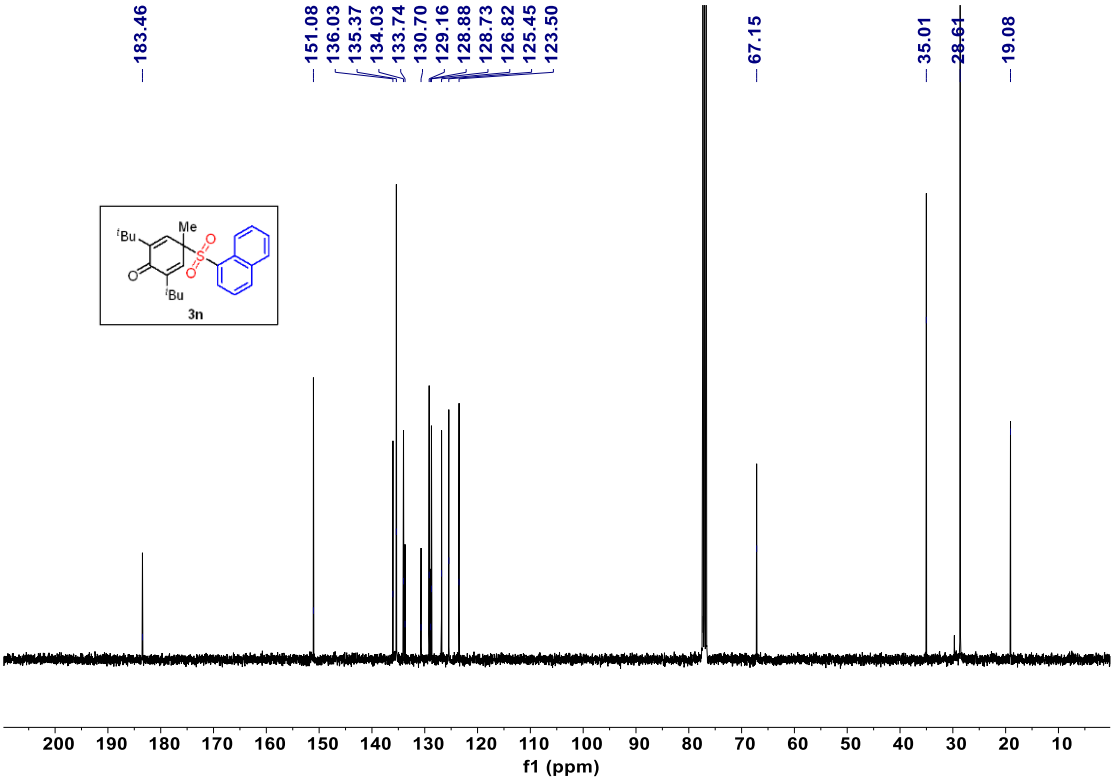
^{13}C NMR of 3m (101 MHz, $CDCl_3$)



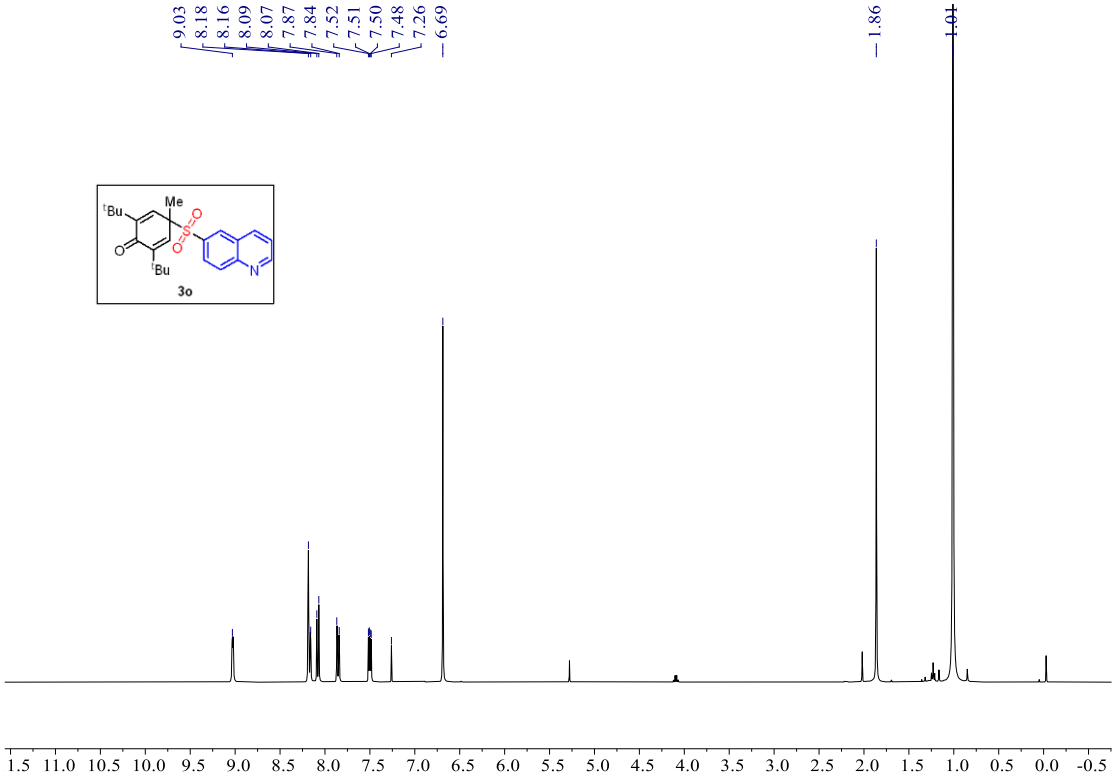
^{1}H NMR of 3n (400 MHz, $CDCl_3$)



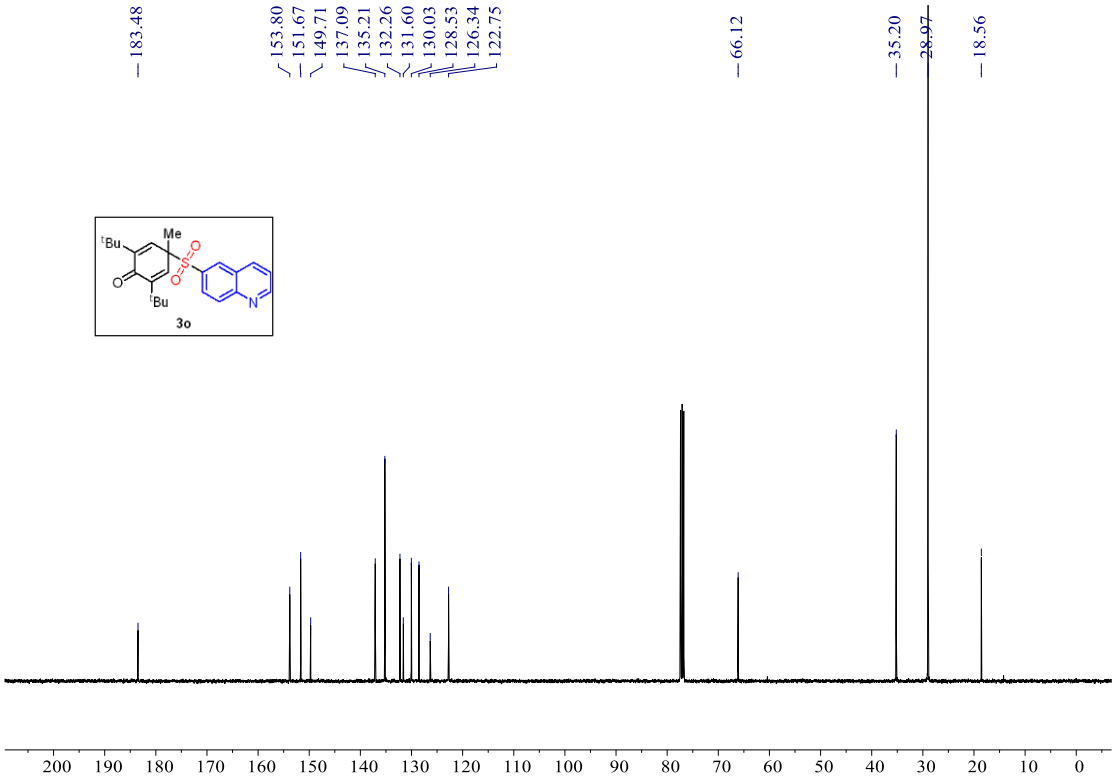
^{13}C NMR of 3n (101 MHz, $CDCl_3$)



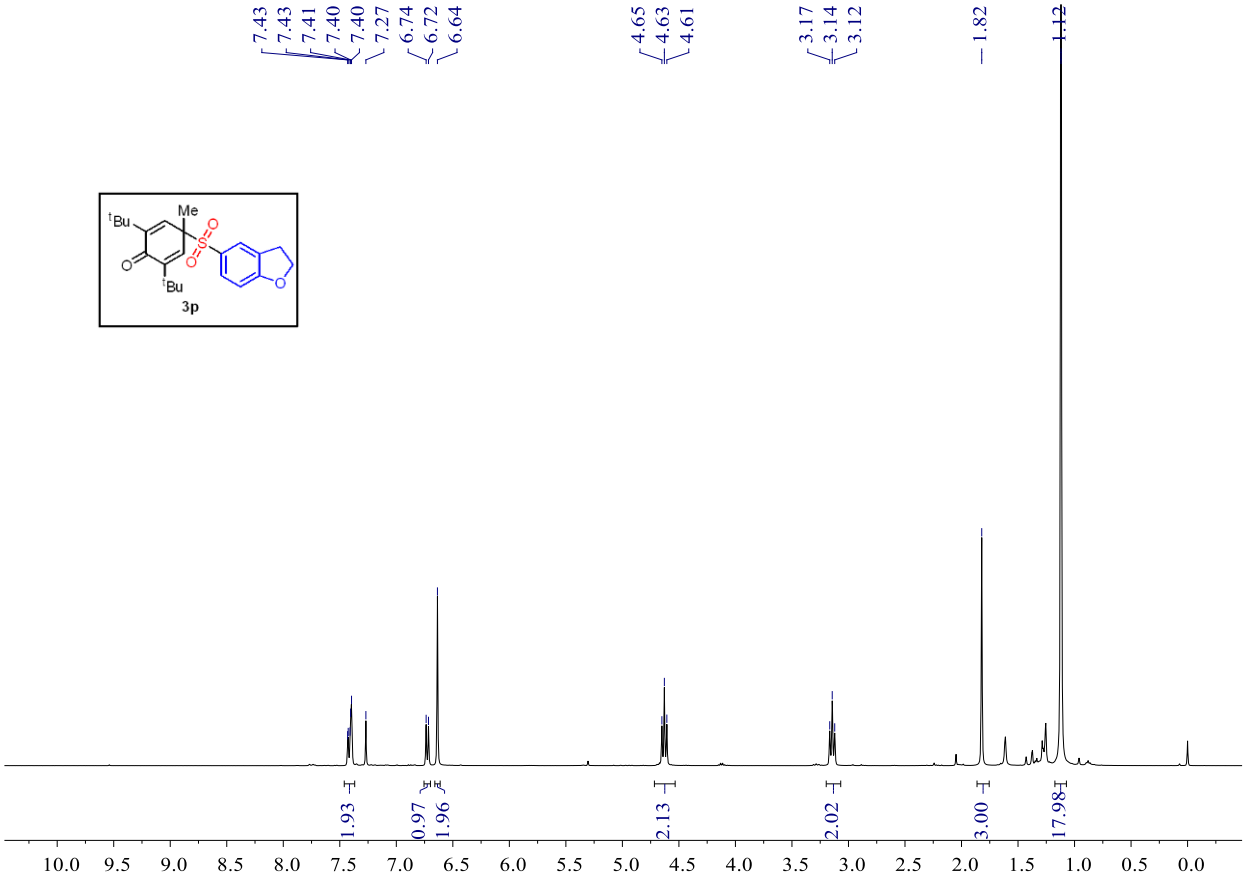
^{1}H NMR of 3o (400 MHz, $CDCl_3$)



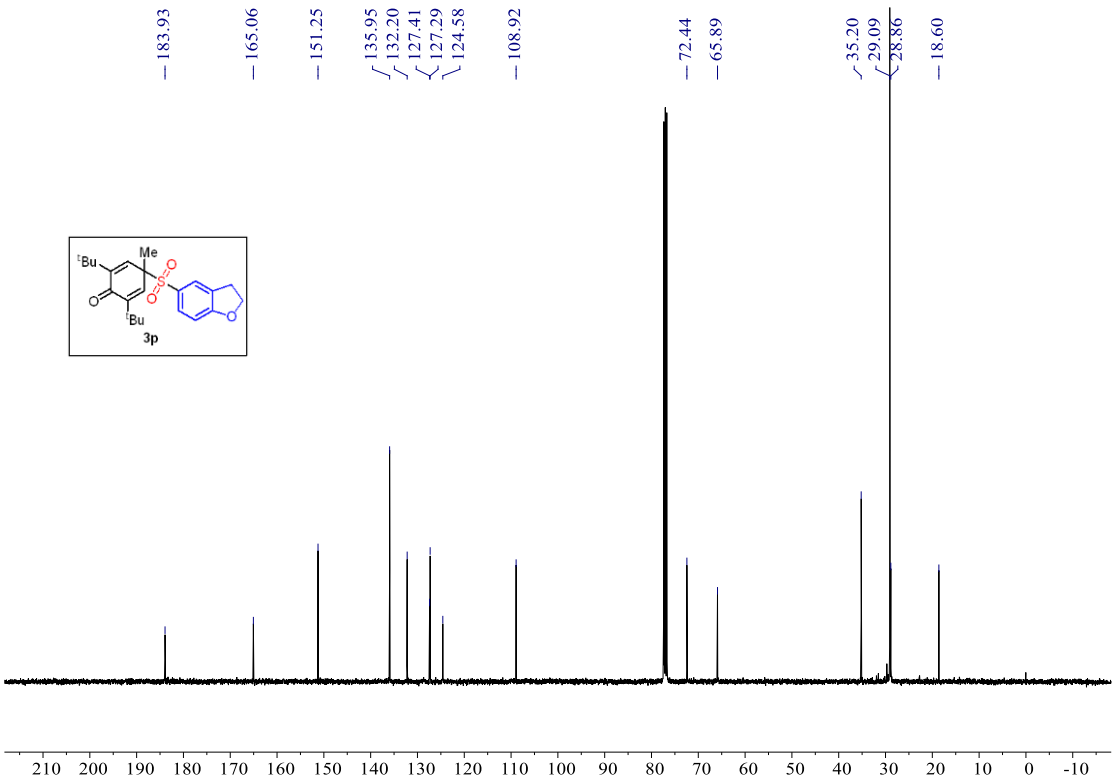
^{13}C NMR of 3o (101 MHz, $CDCl_3$)



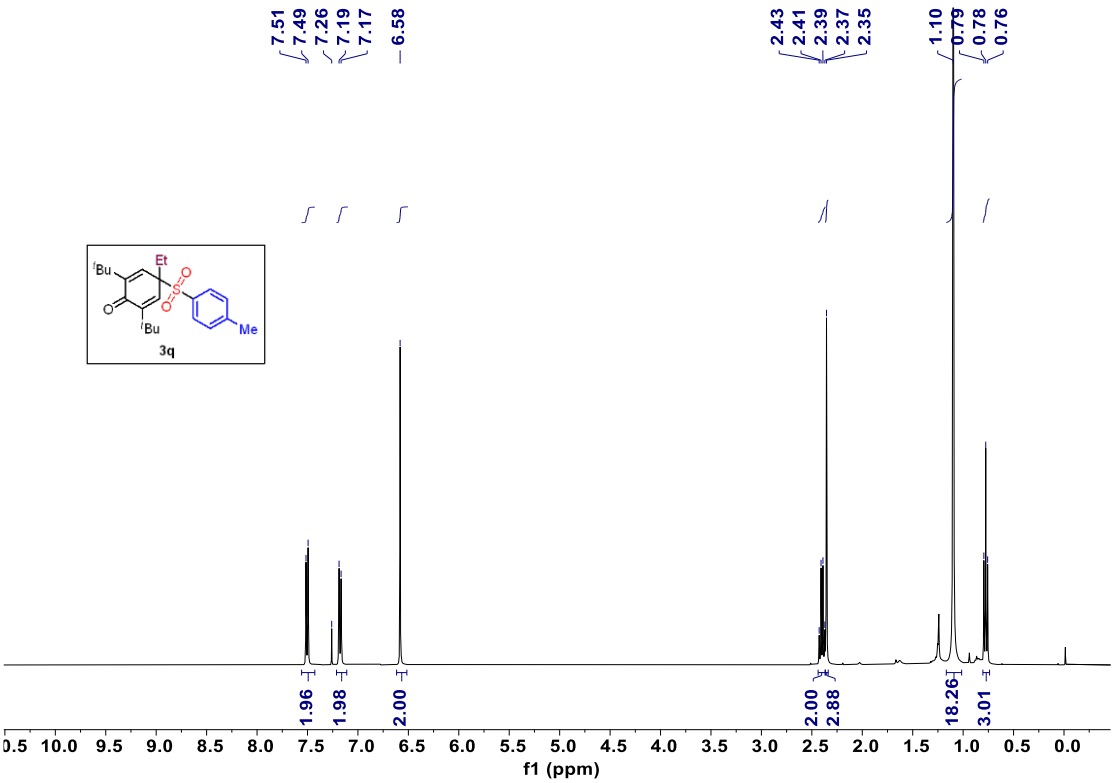
^{1}H NMR of 3p (400 MHz, $CDCl_3$)



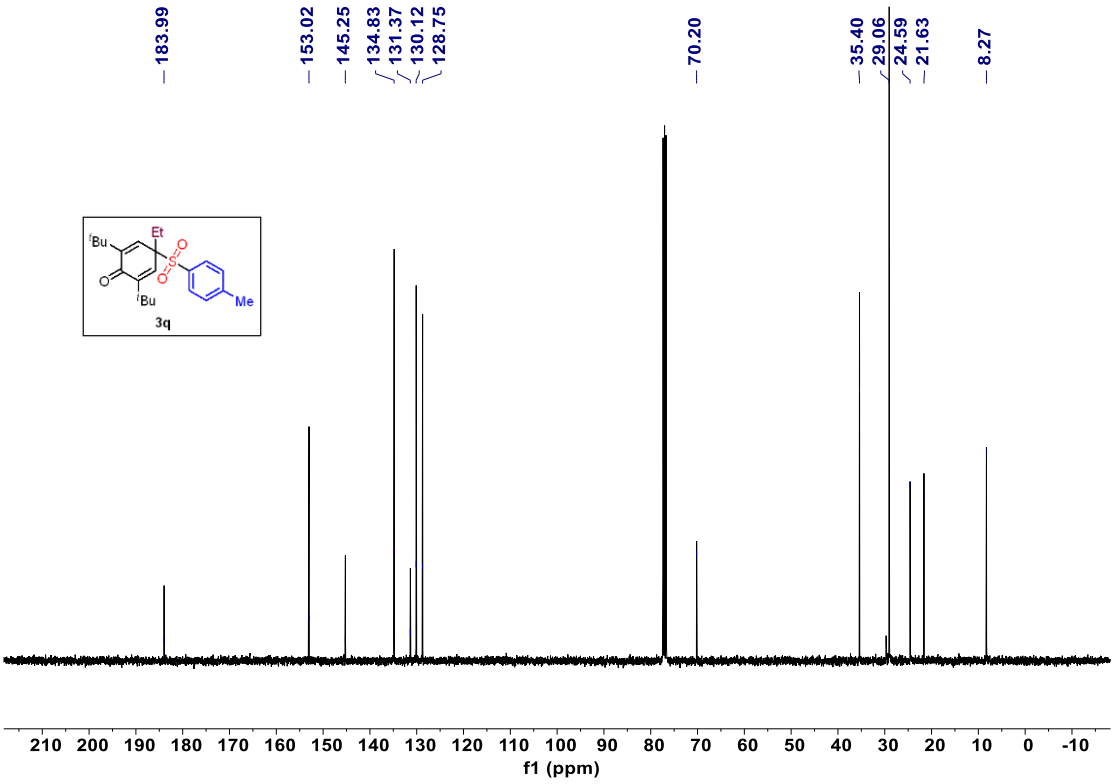
^{13}C NMR of 3p (101 MHz, $CDCl_3$)



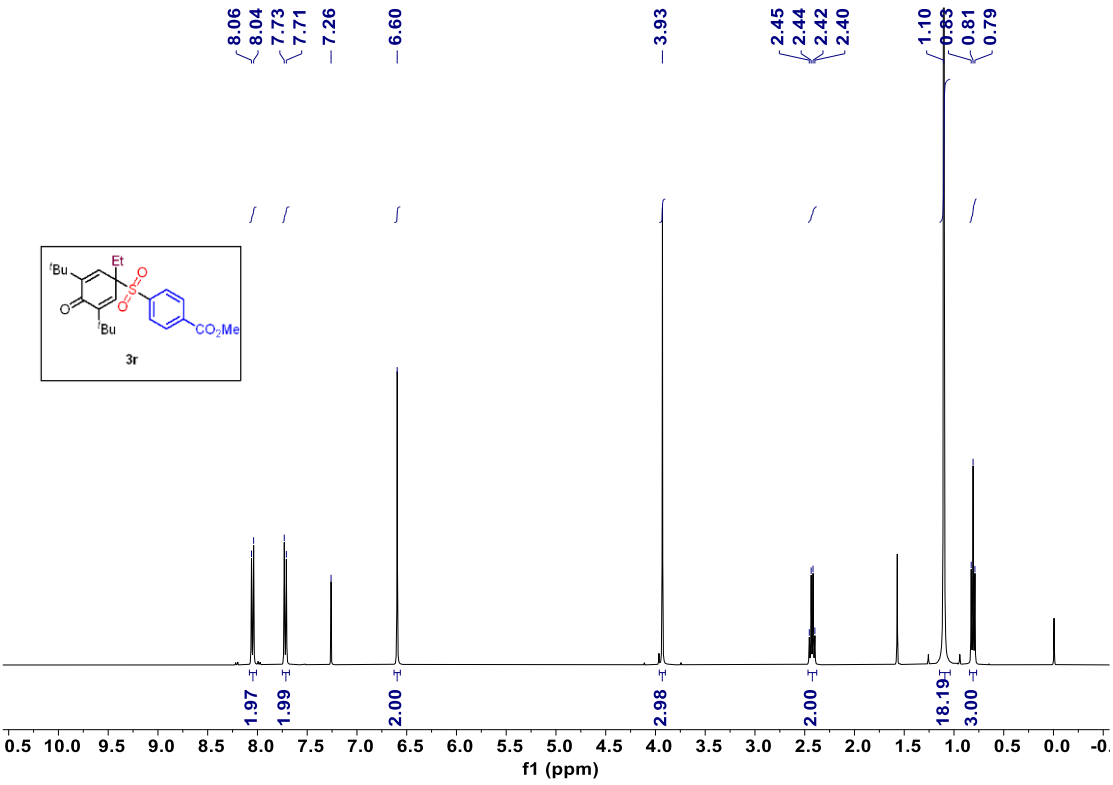
^{1}H NMR of 3q (400 MHz, $CDCl_3$)



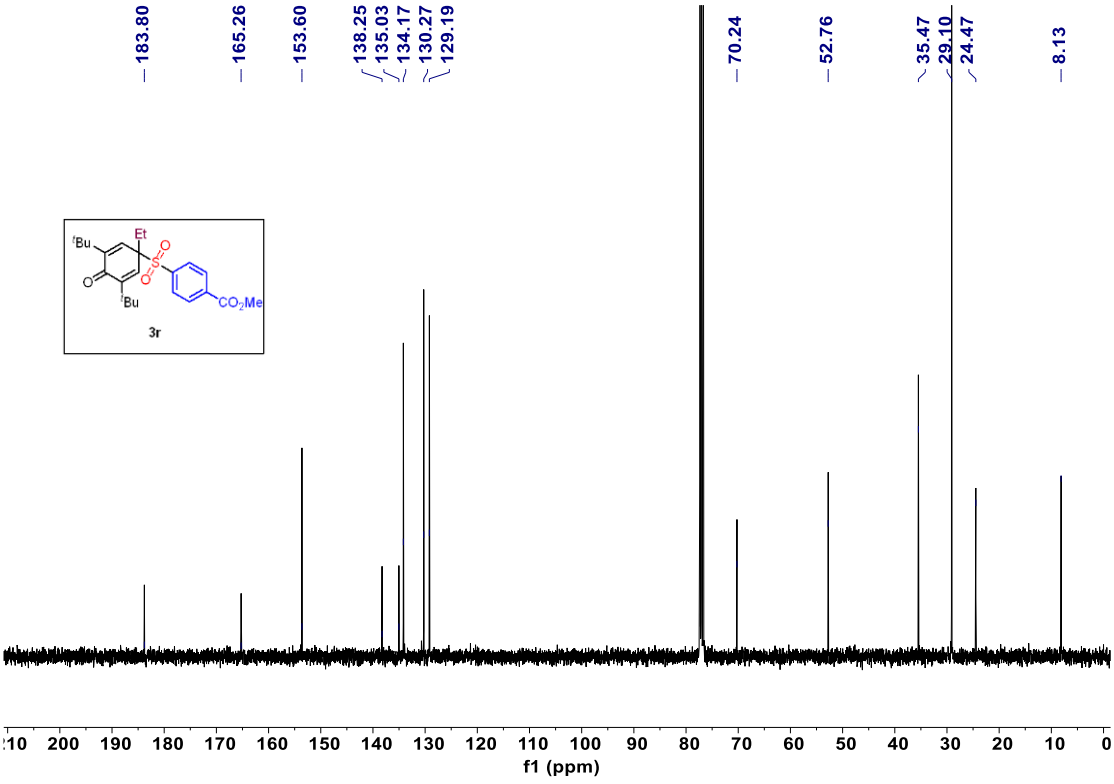
^{13}C NMR of 3q (101 MHz, $CDCl_3$)



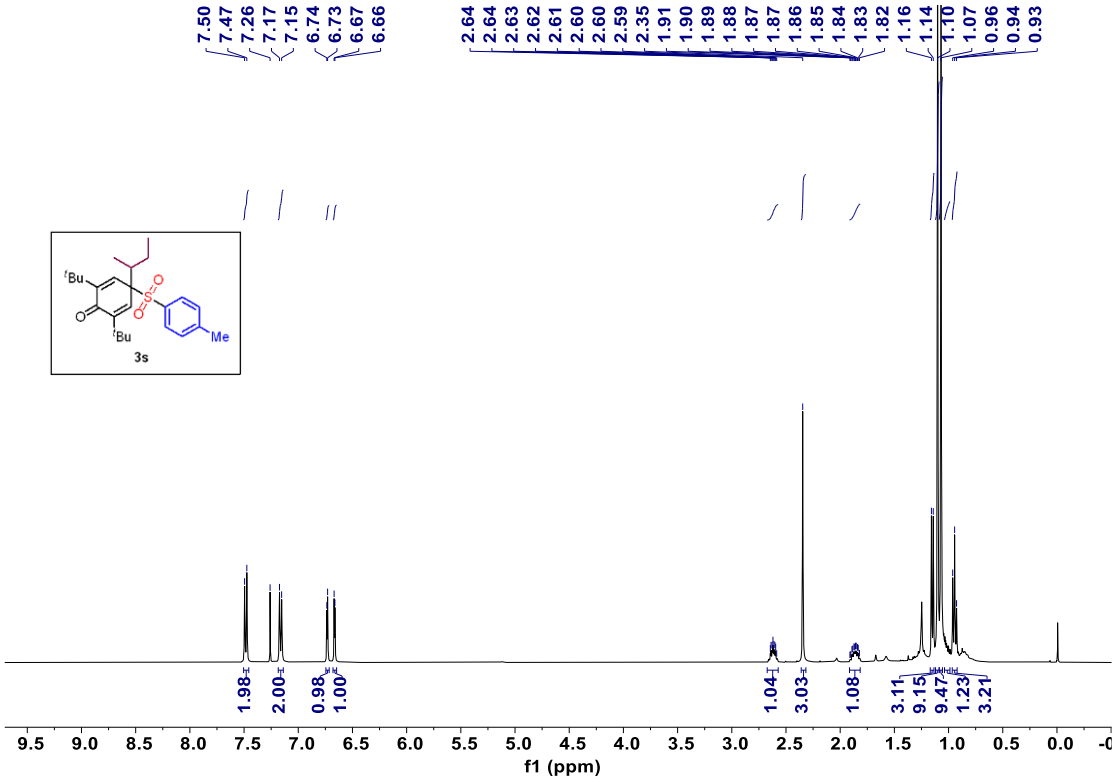
^{1}H NMR of 3r (400 MHz, $CDCl_3$)



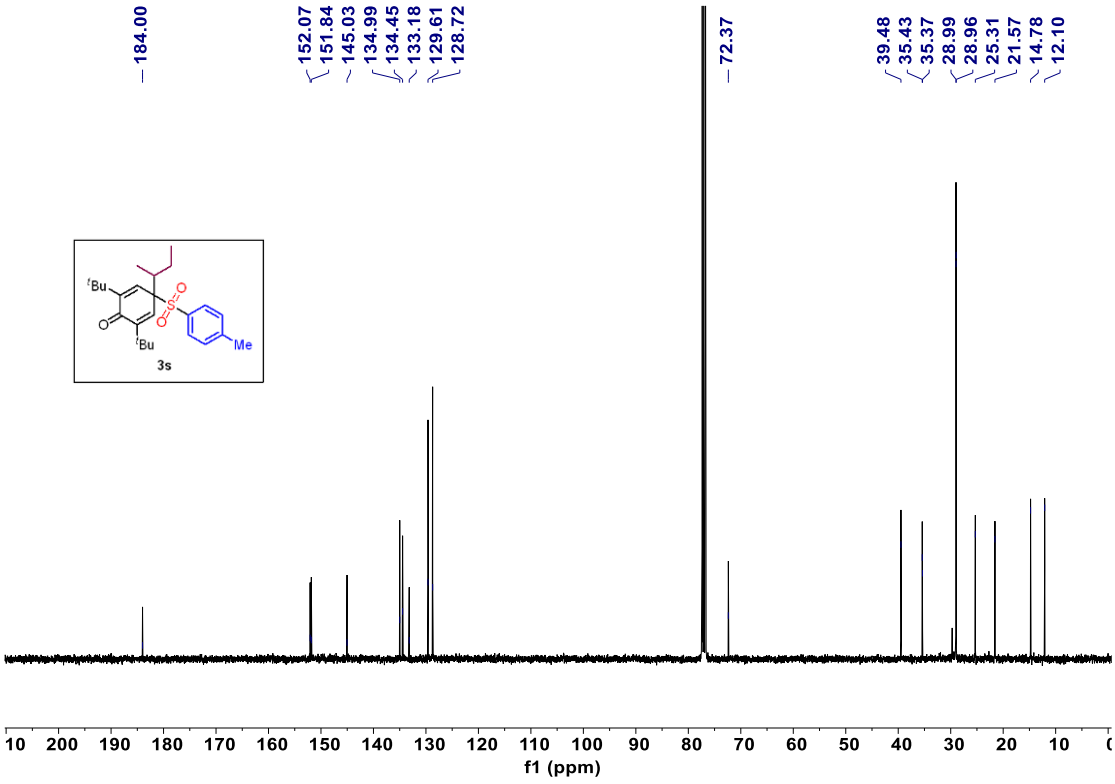
^{13}C NMR of 3r (101 MHz, $CDCl_3$)



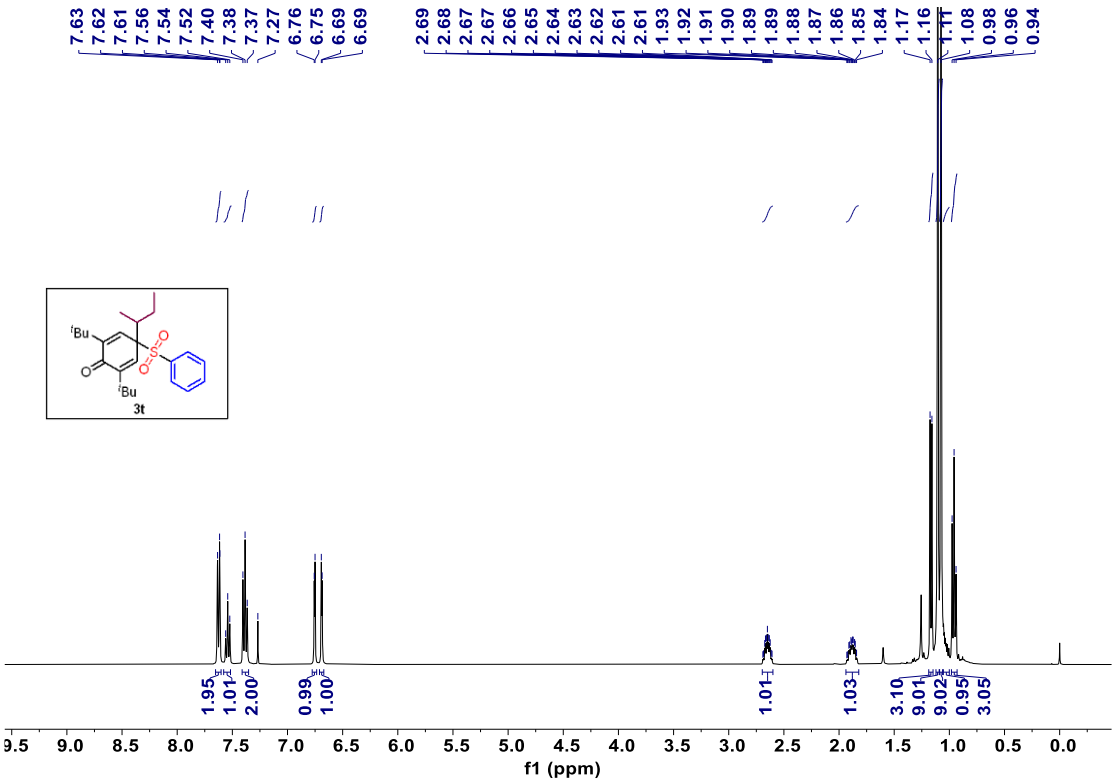
^{1}H NMR of 3s (400 MHz, $CDCl_3$)



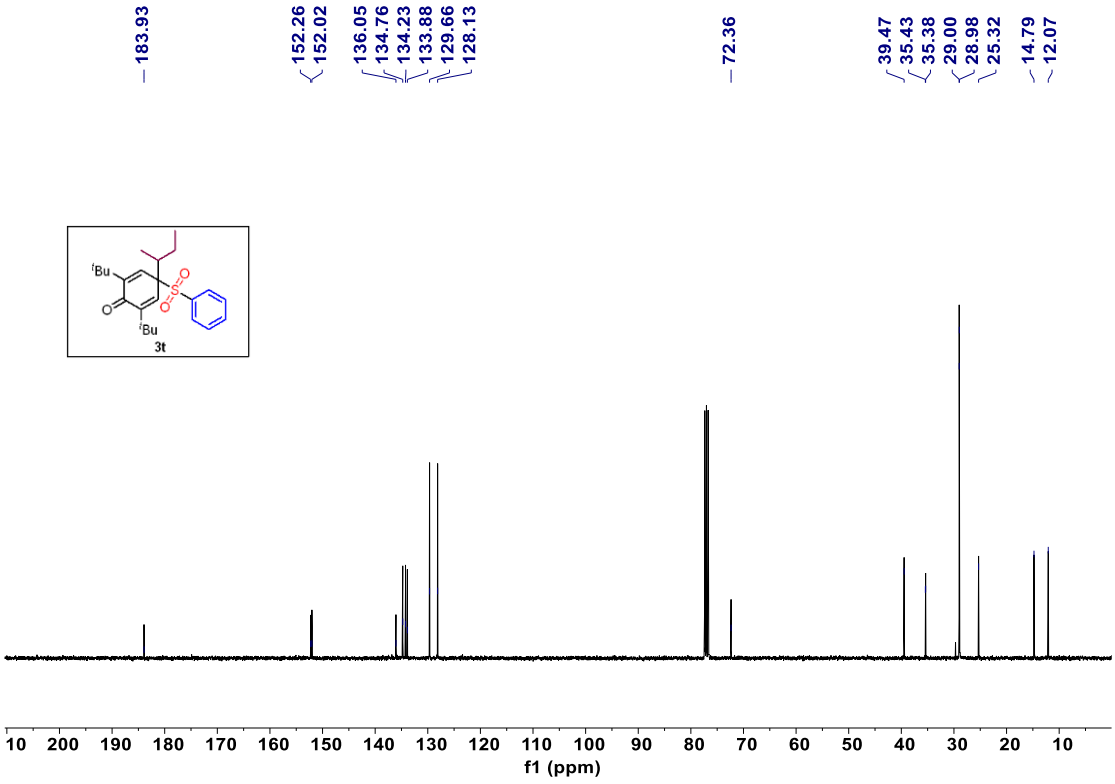
^{13}C NMR of 3s (101 MHz, $CDCl_3$)



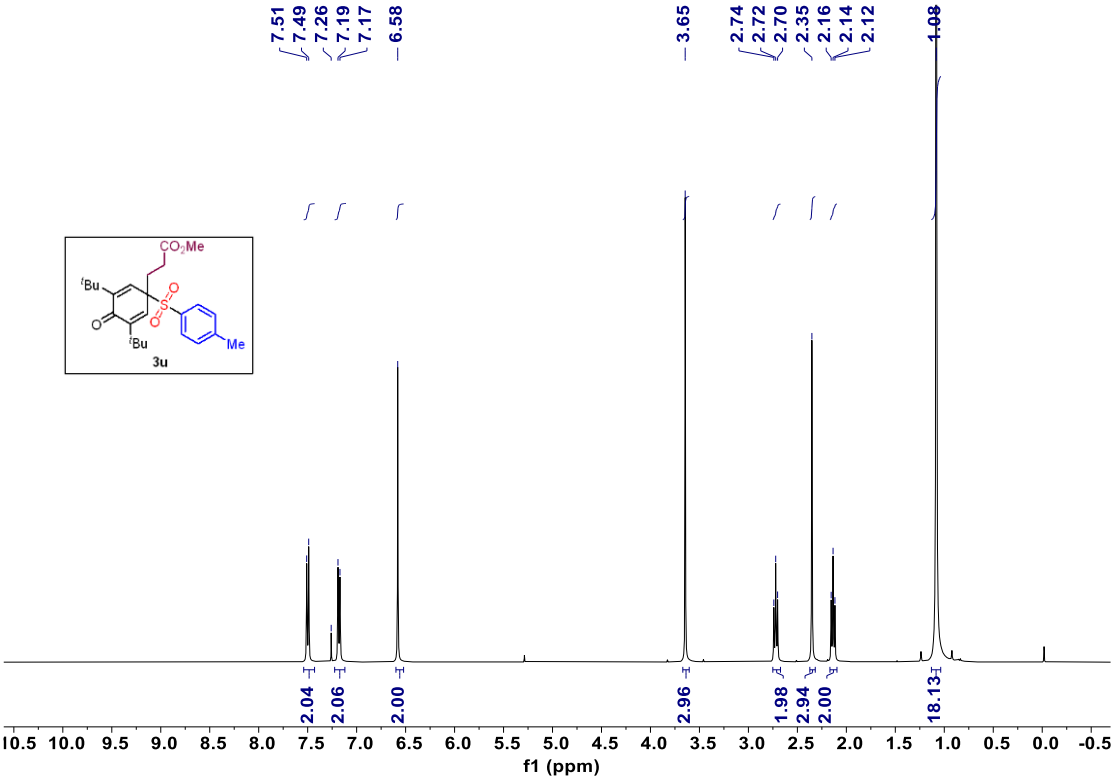
^{1}H NMR of 3t (400 MHz, $CDCl_3$)



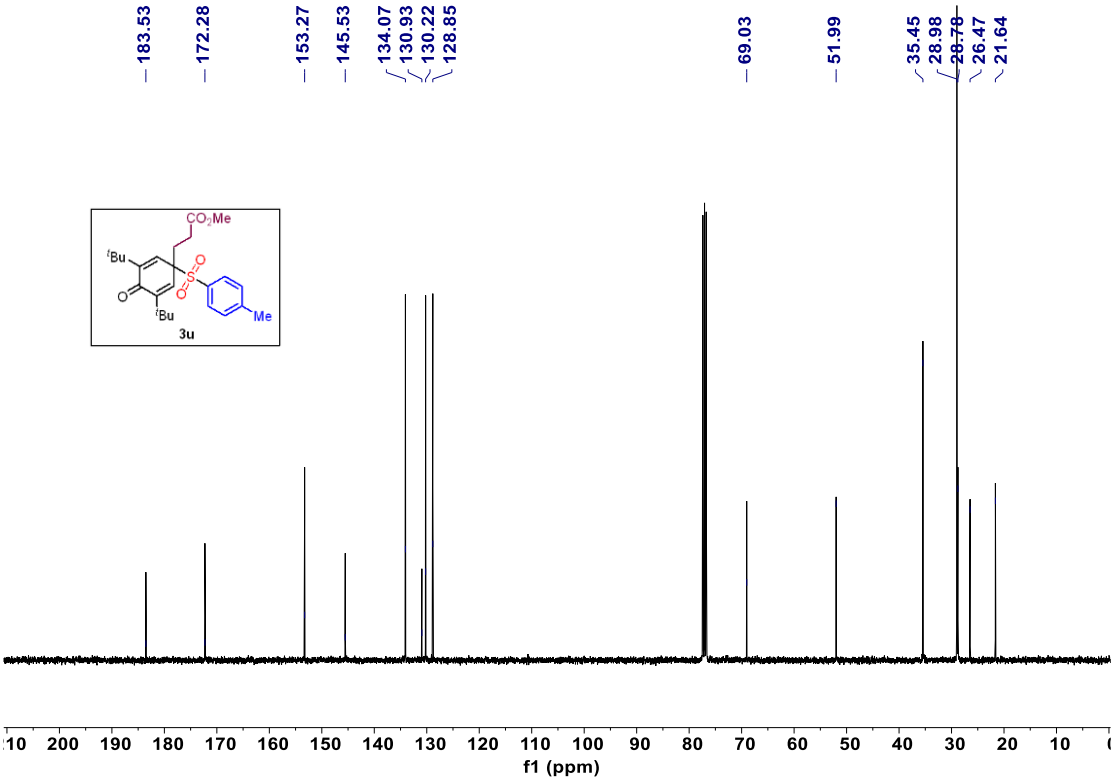
^{13}C NMR of 3t (101 MHz, $CDCl_3$)



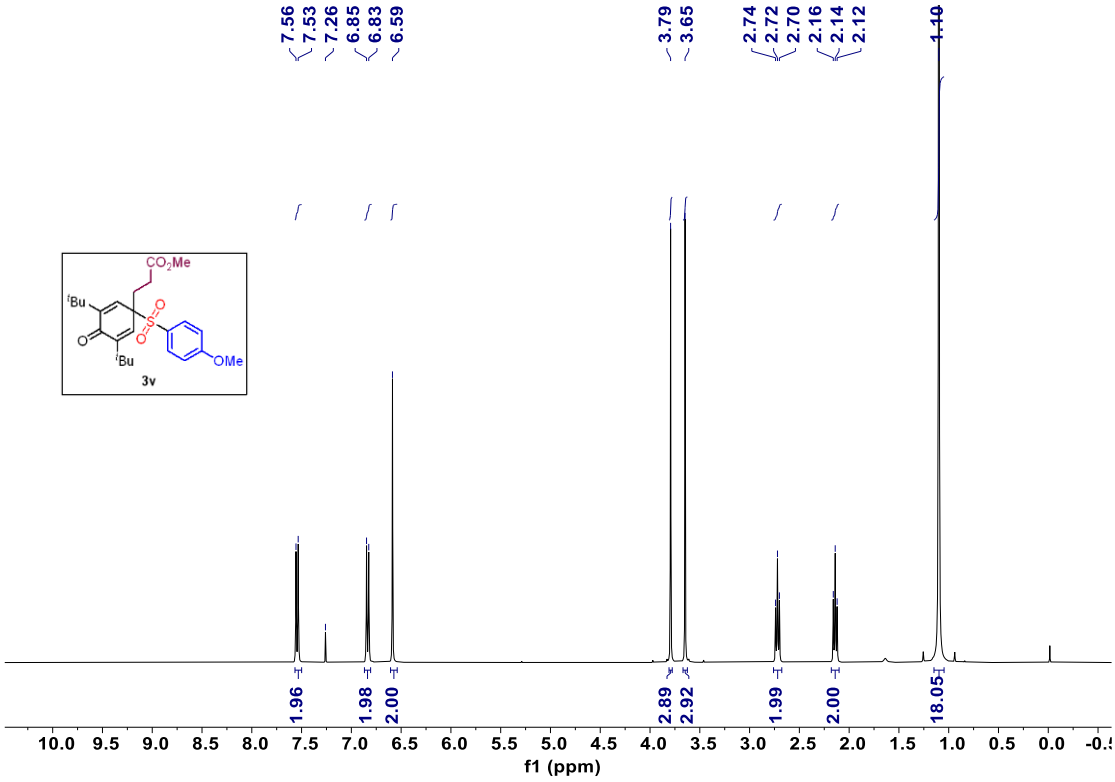
^{1}H NMR of 3u (400 MHz, $CDCl_3$)



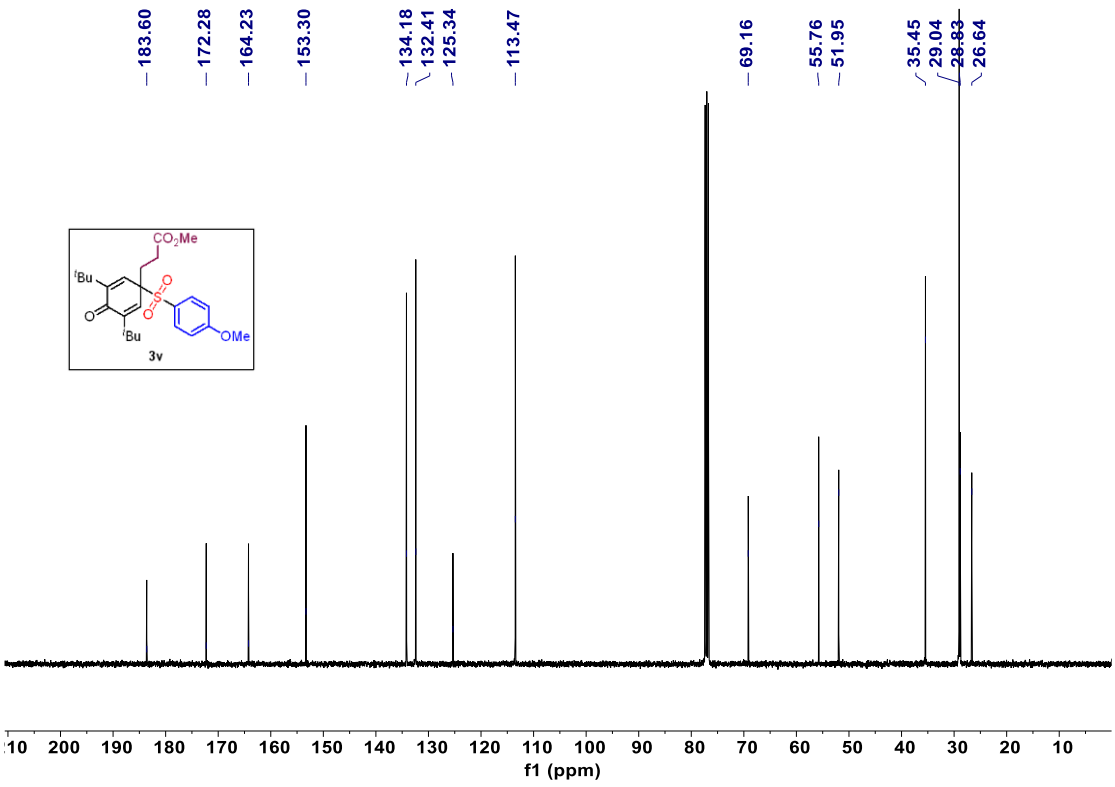
^{13}C NMR of 3u (101 MHz, $CDCl_3$)



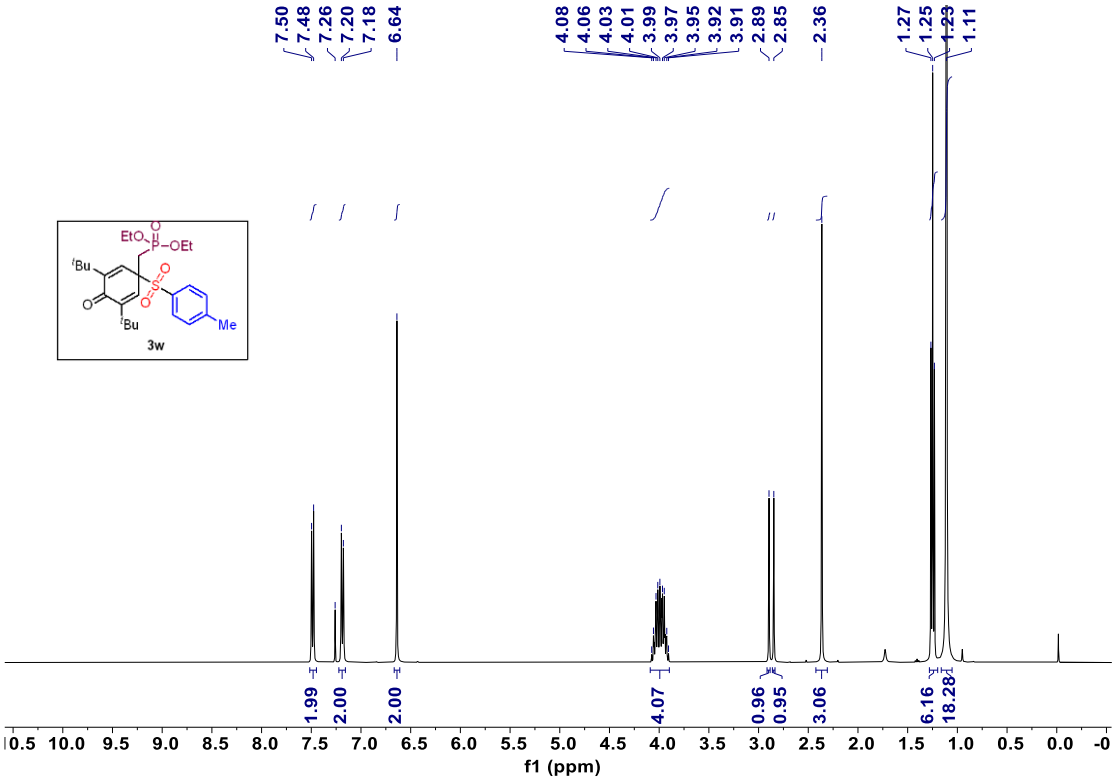
^{1}H NMR of 3v (400 MHz, $CDCl_3$)



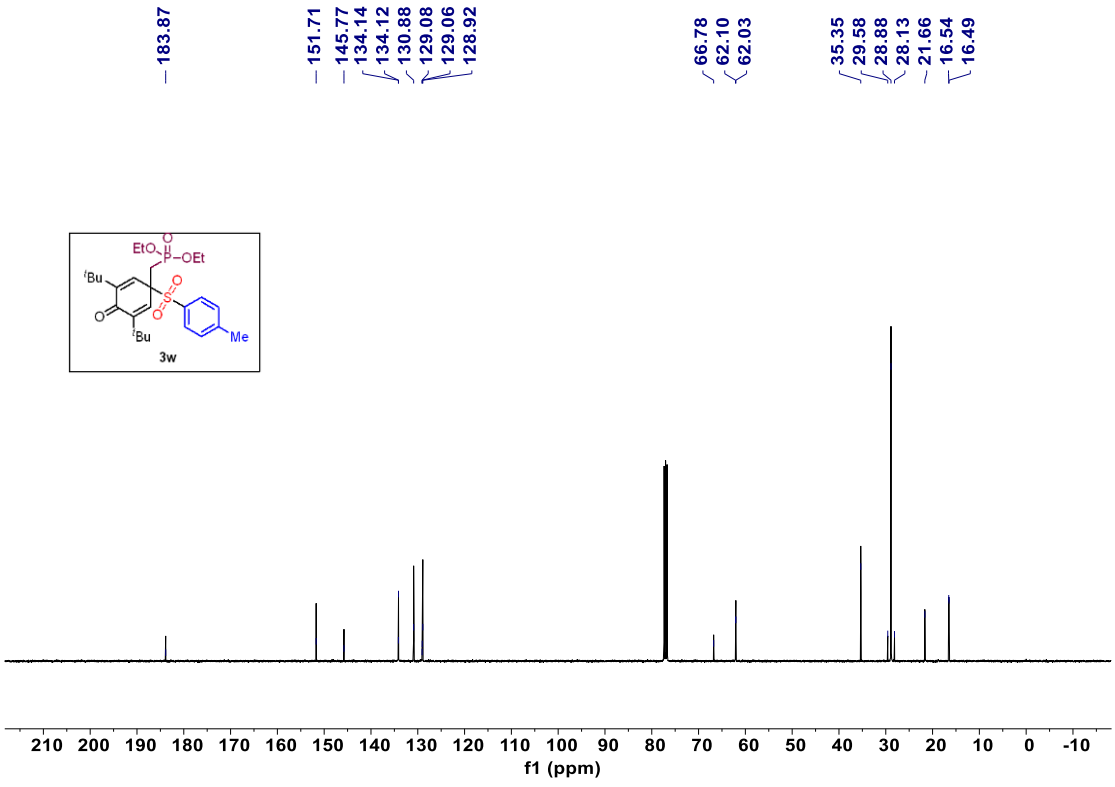
^{13}C NMR of 3v (101 MHz, $CDCl_3$)



^{1}H NMR of 3w (400 MHz, $CDCl_3$)



^{13}C NMR of 3w (101 MHz, $CDCl_3$)



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