

Supplementary Materials for

**Organic-Photoredox-Catalyzed Three-Component
Sulfonylative Pyridylation of Styrenes**

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1. General Information

General Considerations: Commercial reagents were purchased from Adamas, Aldrich, TCI, Energy Chemical, Bide, Leyan and J&K chemical, and were used as received. All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen unless otherwise noted. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on Bruker 400 (400, 100 and 375 MHz) and Bruker 600 (600, 150 and 565 MHz), and are internally referenced to residual solvent signals (for CDCl_3 , 7.26 and 77.0 ppm, and for DMSO-d_6 , 2.50, 39.5 ppm). Data for ^1H NMR and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. High resolution mass spectra were obtained at Shanghai Institute of Organic Chemistry mass spectrometry facility. Photochemical experiments have been performed using 90 W Blue LED light (commercialized from WATTCASTM).

2. General Procedures

2.1. General procedure for the sulfonylative pyridylation of alkenes: To a flame-dried 10 mL reaction vial was charged with 9, 10-diphenylanthracene (0.01 mmol, 5 mol %), Cyanopyridine (0.4 mmol, 2.0 equiv), and Sodium methyl sulfinate (0.3 mmol, 1.5 equiv), Olefins (0.2 mmol, 1.0 equiv, if solid) and Ammonium chloride (0.4 mmol, 2.0 equiv). The vial was capped. MeCN/EtOH (1:1) [0.025 M] was added via a syringe. It was bubbled with nitrogen for 15 minutes, followed by the addition of Olefins (0.2 mmol, 1.0 equiv., if liquid). The reaction mixture was then irradiated with a 90 W Blue LED lamp for 4 h at room temperature. After reaction completed, the mixture was evaporated on rotary evaporator. Then, the residue was dilute with ethyl acetate and wash with H₂O. The combined organic layers were dried with MgSO₄, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography to afford the product.

2.2. The gram-scale synthesis of β -pyridyl sulfone **3**



To a 250 mL oven-dried round bottom flask containing a magnetic stir bar was added 9, 10-diphenylanthracene (66.1 mg, 0.2 mmol, 5 mol %), Cyanopyridine (832 mg, 8.0 mmol, 2.0 equiv), Sodium methyl sulfinate (612 mg, 6.0 mmol, 1.5 equiv) and Ammonium chloride (428 mg, 8.0 mmol, 2.0 equiv). The vial was capped and MeCN/EtOH (80 mL/80 mL) was added via a syringe. It was bubbled with nitrogen for 30 minutes, followed by the addition of 1-(tert-butyl)-4-vinylbenzene (0.73 mL, 4.0 mmol, 1.0 equiv.). The reaction mixture was then irradiated with a 90 W Blue

LED lamp for 4 h at room temperature. After reaction completed, the mixture was evaporated on rotary evaporator. Then, the residue was dilute with ethyl acetate and wash with H₂O. The combined organic layers were dried with MgSO₄, filtered, and concentrated in vacuo. The product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a pale-yellow oil (1.13 g, 89 %)

3. Optimization of the Reaction Conditions

General procedure for the optimization studies: To a flame-dried 10 mL reaction vial was charged with 9, 10-diphenylanthracene (0.005 mmol, 5 mol %), Cyanopyridine (0.2 mmol, 2.0 equiv), and Sodium methyl sulfinate (0.15 mmol, 1.5 equiv), Ammonium chloride (0.2 mmol, 2.0 equiv) and MeCN/EtOH (1:1) [0.025 M] was added via a syringe. It was bubbled with nitrogen for 15 minutes, followed by the addition of 1-(tert-butyl)-4-vinylbenzene (0.1 mmol, 1.0 equiv). The reaction mixture was then irradiated with a 90 W Blue LED lamp for 4 h at room temperature. The reaction mixtures were analyzed by ^1H NMR with an internal standard.

Table S1.Catalyst effect.

The reaction scheme illustrates the coupling of alkene 1 and pyridine 2 to form β -pyridyl sulfone 3. Alkene 1 (1-(tert-butyl)-4-vinylbenzene) reacts with pyridine 2 (Cyanopyridine) under the specified conditions to yield the product 3.

Entry	Catalyst	Yields of 3
1	DPA	94%
2	Eosin-Y	82%
3	4CzIPN	45%
4	DCA	23%
5	DMA	5%
6	Benzophenone	8%
7	9-Fluorenone	Tr
8	4,4'-Biphenyldicarbonitrile	Tr
9	Anthraquinone	43%
10	Pyrene	67%

Table S2. Solvent effect

The reaction scheme illustrates the coupling of alkene 1 and pyridine 2 to form β -pyridyl sulfone 3. Alkene 1 (4-*t*Bu-phenyl substituted alkene) reacts with pyridine 2 (pyridine substituted with a cyano group) under the following conditions: DPA (5 mol%), MeSO_2Na , NH_4Cl , Sol. [0.025 M], 90 W Blue LED, 4h. The product is β -pyridyl sulfone 3, where the alkene carbon is bonded to a *t*Bu group, a phenyl ring, and a pyridine ring substituted with a cyano group, while also bearing a SO_2Me group.

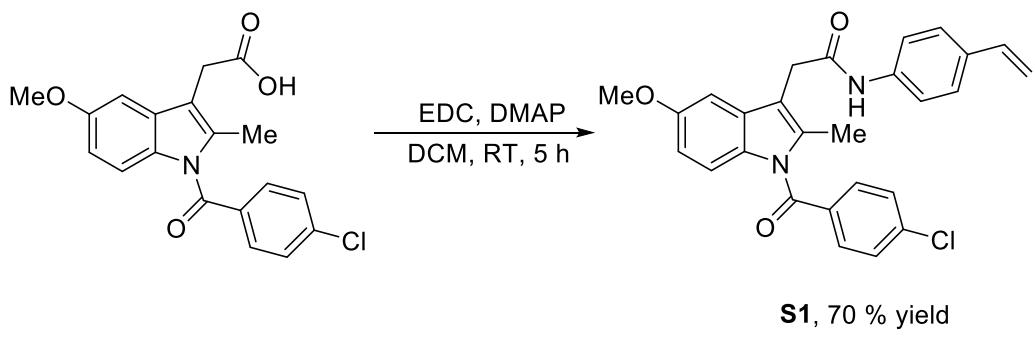
Entry	Solvent	Yields of 3
1	MeCN/EtOH	94%
2	MeCN	83%
3	Acetone	79%
4	THF	7%
5	DCM	<5%
6	DMSO	0%
7	Toluene	0%
8	DCE	25%
9	EtOH	63%

Table S3. Additive effect

The reaction scheme illustrates the formation of β -pyridyl sulfone (3) from alkene 1 and pyridine 2. Alkene 1 (4-*t*Bu-phenyl substituted alkene) reacts with pyridine 2 (4-cyano-pyridine) under the following conditions: DPA (5 mol%), MeSO_2Na , MeCN/EtOH (1:1), 90 W Blue LED, 4 h. The product is β -pyridyl sulfone 3 (4-(4-*t*Bu-phenyl)-4-methylsulfonyl-pyridine).

Entry	Additive	Yields of 3
1	NH_4Cl	94%
2	NH_4OAc	49%
3	TBAI	51%
4	NH_4PF_6	54%
5	NH_4HCO_3	73%
6	HOAc	53%
7	TFA	88%
8	AlCl_3	0%

4. Preparation of Substrates

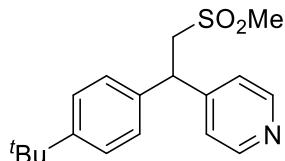


To a 250 mL oven-dried round bottom flask containing a magnetic stir bar was charged with Indometacin (3.0 mmol, 1.0 equiv), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (4.5 mmol, 1.5 equiv), and 4-Dimethylaminopyridine (0.3 mmol, 1.5 equiv). After it was evacuated and backfilled nitrogen three times, CH₂Cl₂ (60 mL) was added via a syringe, followed by the addition of 4-Vinylbenzenamine (3.06 mmol, 1.02 equiv.). The reaction mixture was stirred at room temperature for 5 hours and then quenched with 15 mL H₂O. The resulting mixture was extracted with CH₂Cl₂ and the combined extracts were dried with Na₂SO₄, filtered, concentrated in vacuo and purified by silica gel chromatography (petroleum ether: ethyl acetate = 5:1) to give target product as pale-yellow solid. (700 mg, 70%).

¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.36 – 7.19 (m, 5H), 6.87 (d, J = 1.6 Hz, 1H), 6.80 (d, J = 9.0 Hz, 1H), 6.64 (dd, J = 9.0, 1.8 Hz, 1H), 6.56 (dd, J = 17.6, 10.9 Hz, 1H), 5.58 (d, J = 17.6 Hz, 1H), 5.10 (d, J = 10.9 Hz, 1H), 3.73 (s, 5H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.29, 168.07, 156.37, 139.63, 136.90, 136.64, 135.97, 134.01, 133.46, 131.19, 130.92, 130.11, 129.22, 126.72, 120.02, 115.19, 113.20, 112.44, 112.29, 100.70, 55.74, 33.31, 13.32. HRMS (ESI+): calcd for C₂₇H₂₄ClN₂O₃⁺ (M+H) 459.1470, found 459.1466.

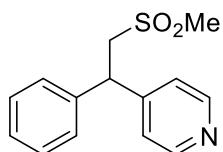
5. Characterizations Date for Products

4-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)pyridine (3)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a pale-yellow oil (59.7 mg, 94%). ^1H NMR (400 MHz, CDCl_3) δ 8.55 (d, J = 6.0 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 7.22 (m, 4H), 4.62 (t, J = 7.2 Hz, 1H), 3.75 (m, 2H), 2.42 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.17, 150.90, 150.15, 136.47, 127.42, 126.26, 122.83, 59.70, 44.95, 42.06, 34.47, 31.16. HRMS (ESI+): calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 318.1522, found 318.1520.

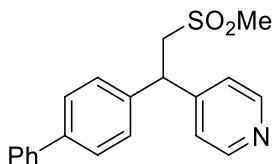
4-(2-(methylsulfonyl)-1-phenylethyl)pyridine (4)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5.0 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34.0 mg, 0.3 mmol, 1.5 equiv.), Styrene (23.0 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a pale-yellow oil (47.0 mg, 90%). ^1H NMR (400 MHz, CDCl_3) δ 8.48 (d, J = 5.6 Hz, 2H), 7.33 – 7.27 (m,

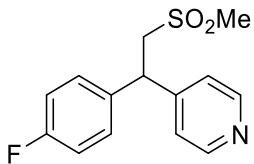
2H), 7.25 – 7.20 (m, 3H), 7.16 (d, J = 5.6 Hz, 2H), 4.64 – 4.55 (m, 1H), 3.78 – 3.62 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.57, 150.11, 139.64, 129.39, 128.06, 127.84, 122.70, 59.63, 45.35, 42.12.¹

4-(1-([1,1'-biphenyl]-4-yl)-2-(methylsulfonyl)ethyl)pyridine (5)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 4-vinyl-1,1'-biphenyl (36.0 mg, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a yellow solid (57.4 mg, 85%). ^1H NMR (400 MHz, CDCl_3) δ 8.57 (d, J = 5.2 Hz, 2H), 7.57 (m, 4H), 7.43 (t, J = 7.6 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.27 (d, J = 4.7 Hz, 2H), 4.71 (t, J = 7.1 Hz, 1H), 3.81 (m, 2H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.88, 149.89, 141.02, 139.85, 138.51, 128.84, 128.26, 128.01, 127.69, 126.94, 122.88, 59.58, 45.02, 42.25. HRMS (ESI+): calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 338.1209, 338.1205.

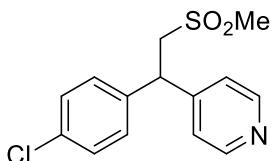
4-(1-(4-fluorophenyl)-2-(methylsulfonyl)ethyl)pyridine (6)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-fluoro-4-vinylbenzene (23.9 μL , 0.2 mmol,

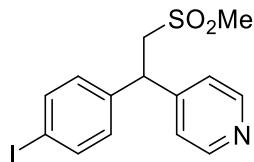
1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a pale-yellow oil (49.1 mg, 88%). ^1H NMR (400 MHz, CDCl_3) δ 8.50 (d, J = 5.8 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.15 (d, J = 5.8 Hz, 2H), 6.99 (t, J = 8.6 Hz, 2H), 4.61 (t, J = 7.2 Hz, 1H), 3.69 (d, J = 7.2 Hz, 2H), 2.45 (s, 3H). ^{19}F NMR (377 MHz, CDCl_3) δ -113.42 – -113.49 (m). ^{13}C NMR (101 MHz, CDCl_3) δ 162.18 (d, J = 248.1 Hz), 150.55, 150.09, 135.49 (d, J = 3.3 Hz), 129.51 (d, J = 8.1 Hz), 122.70, 116.36 (d, J = 21.7 Hz), 59.57, 44.48, 42.27. HRMS (ESI+): calcd for $\text{C}_{14}\text{H}_{15}\text{FNO}_2\text{S}^+$ ($\text{M}+\text{H}$) 280.0802, found 280.0800.

4-(1-(4-chlorophenyl)-2-(methylsulfonyl)ethyl)pyridine (7)



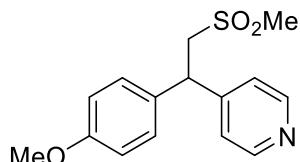
According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-chloro-4-vinylbenzene (24.0 μL , 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a white solid (47.9 mg, 81%). ^1H NMR (600 MHz, CDCl_3) δ 8.55 (d, J = 5.2 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.22 (m, 4H), 4.65 (t, J = 7.1 Hz, 1H), 3.75 (d, J = 7.1 Hz, 2H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.31, 150.07, 138.18, 134.06, 129.56, 129.19, 122.73, 59.34, 44.57, 42.32. HRMS (ESI+): calcd for $\text{C}_{14}\text{H}_{15}\text{ClNO}_2\text{S}^+$ ($\text{M}+\text{H}$) 296.0507, found 296.0505.

4-(1-(4-iodophenyl)-2-(methylsulfonyl)ethyl)pyridine (8)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-iodo-4-vinylbenzene (46.1 mg, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a brown oil (53.4 mg, 69%). ^1H NMR (400 MHz, CDCl_3) δ 8.54 (d, J = 5.4 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 5.4 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H), 4.61 (t, J = 7.2 Hz, 1H), 3.74 (d, J = 7.2 Hz, 2H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.28, 150.05, 139.36, 138.50, 129.72, 122.77, 93.66, 59.25, 44.76, 42.37. HRMS (ESI+): calcd for $\text{C}_{14}\text{H}_{15}\text{INO}_2\text{S}^+$ ($\text{M}+\text{H}$) 387.9863, found 387.9859.

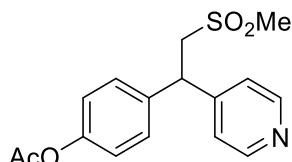
4-(1-(4-methoxyphenyl)-2-(methylsulfonyl)ethyl)pyridine (9)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-methoxy-4-vinylbenzene (26.6 μL , 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (55.3 mg, 95%). ^1H NMR (400 MHz, CDCl_3) δ 8.55 (d, J = 5.5 Hz, 2H), 7.26 – 7.15 (m, 4H), 6.89 (d, J = 8.6 Hz, 2H), 4.62 (dd, J = 8.3, 5.9 Hz, 1H), 3.85 – 3.75 (m, 4H), 3.70 (dd, J = 14.6, 5.9 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.22,

151.17, 149.89, 131.40, 128.97, 122.66, 114.74, 59.77, 55.25, 44.60, 42.17. HRMS (ESI+): calcd for $C_{15}H_{18}NO_3S^+$ ($M+H$) 292.1002, found 292.1001.

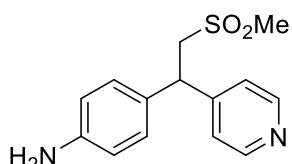
4-(2-(methylsulfonyl)-1-(pyridin-4-yl)ethyl)phenyl acetate (10)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 4-vinylphenyl acetate (30.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (59.4 mg, 93%).

¹H NMR (400 MHz, CDCl₃) δ 8.49 (d, J = 5.8 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.17 (d, J = 5.8 Hz, 2H), 7.06 – 7.00 (m, 2H), 4.61 (t, J = 7.2 Hz, 1H), 3.69 (d, J = 7.2 Hz, 2H), 2.43 (s, 3H), 2.21 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.16, 150.43, 150.20, 149.94, 137.15, 128.85, 122.84, 122.54, 59.54, 44.67, 42.22, 21.02. HRMS (ESI+): calcd for $C_{16}H_{18}NO_4S^+$ ($M+H$) 320.0951, found 320.0948.

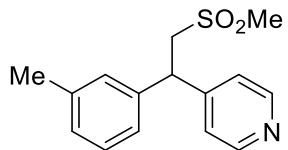
4-(2-(methylsulfonyl)-1-(pyridin-4-yl)ethyl)aniline (11)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 4-vinylaniline (23.5 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a yellow solid (49.2 mg, 89%). ¹H NMR (400

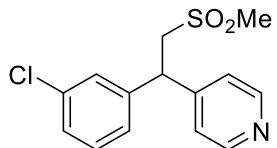
MHz, CDCl₃) δ 8.52 (d, J = 6.0 Hz, 2H), 7.19 (d, J = 6.0 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 4.53 (dd, J = 8.8, 5.6 Hz, 1H), 4.08 – 3.77 (brs, 2H), 3.77 – 3.71 (m, 1H), 3.63 (dd, J = 14.6, 5.6 Hz, 1H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151.35, 149.92, 146.26, 128.87, 128.85, 122.59, 115.63, 59.90, 44.70, 42.14. HRMS (ESI+): calcd for C₁₄H₁₇N₂O₂S⁺ (M+H) 277.1005, found 277.1001.

4-(2-(methylsulfonyl)-1-(m-tolyl)ethyl)pyridine (12)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-methyl-3-vinylbenzene (26.2 μL, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow solid (48.5 mg, 88%). ¹H NMR (400 MHz, CDCl₃) δ 8.48 (d, J = 5.9 Hz, 2H), 7.24 – 7.12 (m, 3H), 7.03 (d, J = 8.0 Hz, 3H), 4.59 – 4.51 (m, 1H), 3.69 (ddd, J = 20.9, 14.6, 7.2 Hz, 2H), 2.37 (s, 3H), 2.26 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.75, 150.04, 139.56, 139.26, 129.25, 128.82, 128.61, 124.71, 122.73, 59.67, 45.33, 42.12, 21.37. HRMS (ESI+): calcd for C₁₅H₁₈NO₂S⁺ (M+H) 276.1053, found 276.1047.

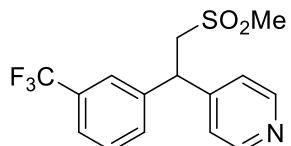
4-(1-(3-chlorophenyl)-2-(methylsulfonyl)ethyl)pyridine (13)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl

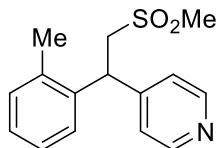
sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-chloro-3-vinylbenzene (25.4 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (41.4 mg, 70%). 1 H NMR (400 MHz, CDCl₃) δ 8.51 (d, J = 5.4 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.16 (d, J = 5.4 Hz, 2H), 7.12 (dt, J = 7.1, 1.6 Hz, 1H), 4.59 (t, J = 7.1 Hz, 1H), 3.69 (d, J = 7.1 Hz, 2H), 2.48 (s, 3H). 13 C NMR (101 MHz, CDCl₃) δ 150.19, 149.98, 141.74, 135.26, 130.65, 128.32, 127.93, 126.04, 122.79, 59.26, 44.85, 42.33. HRMS (ESI+): calcd for C₁₄H₁₅ClNO₂S⁺ (M+H) 296.0507, found 296.0505.

4-(2-(methylsulfonyl)-1-(3-(trifluoromethyl)phenyl)ethyl)pyridine (14)



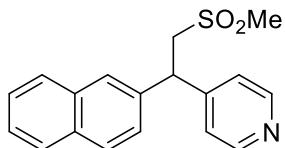
According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(trifluoromethyl)-3-vinylbenzene (34.4 mg, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (53.3 mg, 81%). 1 H NMR (400 MHz, CDCl₃) δ 8.60 (d, J = 5.2 Hz, 2H), 7.60 – 7.47 (m, 4H), 7.24 (d, J = 5.2 Hz, 2H), 4.77 (t, J = 7.1 Hz, 1H), 3.85 – 3.74 (m, 2H), 2.57 (s, 3H). 13 C NMR (101 MHz, CDCl₃) δ 150.49, 149.55, 140.90, 131.70 (q, J = 32.3 Hz), 131.31, 129.91, 124.91 (q, J = 3.0 Hz), 124.38 (q, J = 3.6 Hz), 123.62 (q, J = 273.7 Hz), 122.72, 59.17, 44.85, 42.31. 19 F NMR (377 MHz, CDCl₃) δ -62.64. HRMS (ESI+): calcd for C₁₅H₁₅F₃NO₂S⁺ (M+H) 330.0770, found 330.0767.

4-(2-(methylsulfonyl)-1-(o-tolyl)ethyl)pyridine (15)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-methyl-2-vinylbenzene (25.7 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (50.7 mg, 92%). ^1H NMR (600 MHz, CDCl_3) δ 8.52 (d, J = 4.9 Hz, 2H), 7.25 – 7.16 (m, 6H), 4.92 (t, J = 7.1 Hz, 1H), 3.75 (ddd, J = 20.9, 14.6, 7.1 Hz, 2H), 2.44 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.35, 149.94, 137.66, 136.33, 131.42, 127.85, 126.77, 126.74, 122.99, 59.68, 42.09, 40.59, 19.72. HRMS (ESI $+$): calcd for $\text{C}_{15}\text{H}_{18}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 276.1053, found 276.1046.

4-(2-(methylsulfonyl)-1-(naphthalen-2-yl)ethyl)pyridine (16)

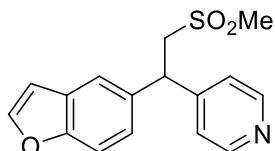


According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (48.0 mg, 77%).

^1H NMR (400 MHz, CDCl_3) δ 8.57 (d, J = 6.0 Hz, 2H), 7.88 – 7.77 (m, 4H), 7.57 – 7.47 (m, 2H), 7.34 (m, 1H), 7.30 – 7.25 (m, 2H), 4.90 – 4.81 (m, 1H), 3.88 (ddd, J = 20.8, 14.6, 7.1 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.39, 150.28,

136.88, 133.32, 132.65, 129.51, 127.84, 127.73, 126.92, 126.91, 126.68, 125.17, 122.81, 59.57, 45.44, 42.25. HRMS (ESI+): calcd for $C_{18}H_{18}NO_2S^+$ ($M+H$) 312.1053, found 312.1048.

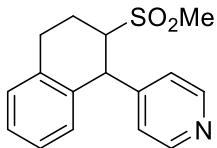
4-(1-(benzofuran-5-yl)-2-(methylsulfonyl)ethyl)pyridine (17)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 5-vinylbenzofuran (27.7 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (51.8 mg, 86%).

1H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, $J = 5.8$ Hz, 2H), 7.63 (d, $J = 2.1$ Hz, 1H), 7.54 (d, $J = 1.3$ Hz, 1H), 7.48 (d, $J = 8.5$ Hz, 1H), 7.25 – 7.16 (m, 3H), 6.73 (d, $J = 2.1$ Hz, 1H), 4.76 (dd, $J = m$, 1H), 3.81 (ddd, $J = 20.6, 14.6, 7.2$ Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.21, 151.25, 149.83, 146.19, 134.21, 128.27, 123.87, 122.74, 120.61, 112.32, 106.50, 59.91, 45.23, 42.16. HRMS (ESI+): calcd for $C_{16}H_{16}NO_3S^+$ ($M+H$) 302.0845, found 302.0843.

4-(2-(methylsulfonyl)-1,2,3,4-tetrahydronaphthalen-1-yl)pyridine (18)



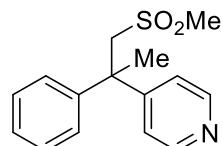
According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 2-(methylsulfonyl)-1,2,3,4-tetrahydronaphthalen-1-yl (27.7 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (51.8 mg, 86%).

sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1,2-dihydronaphthalene (26.1 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (45.4 mg, 79%).

^1H NMR (400 MHz, CDCl_3) δ 8.62 – 8.51 (m, 2H), 7.19 (m, 2H), 7.17 – 7.05 (m, 3H), 6.88 – 6.76 (m, 1H), 4.78 – 4.66 (m, 1H), 3.49 (m, 1H), 3.09 (m, 1H), 3.04 – 2.92 (m, 1H), 2.71 (s, 1H), 2.60 (d, J = 3.5 Hz, 3H), 2.54 – 2.45 (m, 1H), 2.21 – 2.09 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 153.41, 150.14, 135.59, 134.63, 129.99, 128.71, 127.20, 126.99, 124.13, 66.32, 43.98, 40.25, 27.22, 21.51. HRMS (ESI $+$): calcd for $\text{C}_{16}\text{H}_{18}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 288.1053, found 288.1051.

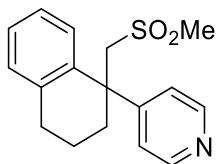
4-(1-(methylsulfonyl)-2-phenylpropan-2-yl)pyridine (19)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), prop-1-en-2-ylbenzene (26.0 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (53.9 mg, 98%).

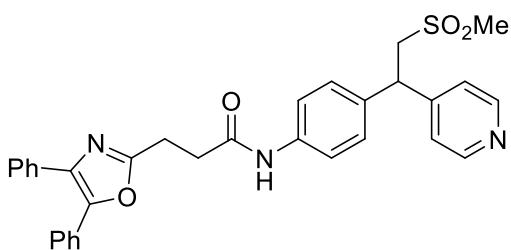
^1H NMR (600 MHz, CDCl_3) δ 8.52 (d, J = 5.9 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 7.6 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.09 (m, 2H), 3.84 (dd, J = 38.7, 14.6 Hz, 2H), 2.09 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.47, 149.88, 143.72, 128.71, 127.59, 127.55, 121.81, 64.87, 45.36, 42.61, 26.73.¹

4-(1-((methylsulfonyl)methyl)-1,2,3,4-tetrahydronaphthalen-1-yl)pyridine (20)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 4-cyanopyridine (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-methylene-1,2,3,4-tetrahydronaphthalene (28.5 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (43.9 mg, 73%). ^1H NMR (600 MHz, CDCl_3) δ 8.49 (d, $J = 4.7$ Hz, 2H), 7.23 (dd, $J = 7.9, 1.5$ Hz, 2H), 7.20 – 7.15 (m, 1H), 7.04 (d, $J = 7.9$ Hz, 1H), 6.98 (d, $J = 6.0$ Hz, 2H), 3.95 – 3.85 (m, 2H), 2.97 – 2.86 (m, 2H), 2.77 (dt, $J = 16.6, 3.5$ Hz, 1H), 2.35 (s, 3H), 2.07 (dd, $J = 13.0, 3.5$ Hz, 1H), 1.80 (ddd, $J = 17.1, 8.6, 5.2$ Hz, 1H), 1.53 – 1.42 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.87, 149.70, 139.40, 136.02, 130.22, 129.23, 127.62, 126.09, 122.24, 64.50, 45.79, 43.61, 35.33, 29.63, 18.76. HRMS (ESI+): calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 302.1209, found 302.1206.

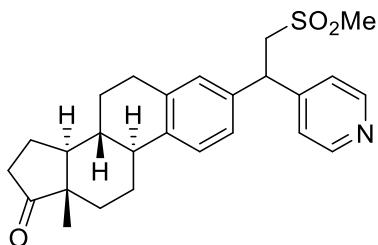
3-(4,5-diphenyloxazol-2-yl)-N-(4-(2-(methylsulfonyl)-1-(pyridin-4-yl)ethyl)phenyl)propanamide (21)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium methanesulfinate (30.6 mg, 0.3 mmol, 1.5 equiv.),

3-(4,5-diphenyloxazol-2-yl)-N-(4-vinylphenyl)propanamide (78.9 mg, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a white solid (107.0 mg, 97%). ¹H NMR (600 MHz, CDCl₃) δ 9.15 (s, 1H), 8.48 (d, J = 5.1 Hz, 2H), 7.57 (dd, J = 7.6, 1.4 Hz, 2H), 7.51 (d, J = 8.0 Hz, 4H), 7.35 – 7.28 (m, 6H), 7.15 (t, J = 7.1 Hz, 4H), 4.62 – 4.51 (m, 1H), 3.74 (dd, J = 14.5, 8.3 Hz, 1H), 3.65 (dd, J = 14.5, 6.1 Hz, 1H), 3.22 (t, J = 7.0 Hz, 2H), 2.90 (t, J = 7.0 Hz, 2H), 2.45 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.14, 162.44, 150.69, 150.21, 145.72, 138.19, 134.98, 134.75, 132.21, 128.72, 128.68, 128.61, 128.45, 128.32, 127.83, 126.47, 122.72, 120.43, 59.55, 44.80, 42.30, 33.93, 23.90. HRMS (ESI+): calcd for C₃₂H₃₀N₃O₄S⁺ (M+H) 552.1952, found 552.1949.

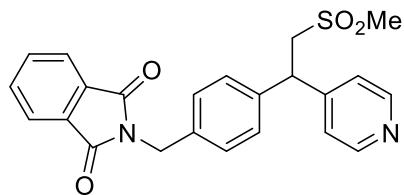
(8R,9S,13S,14S)-13-methyl-3-(2-(methylsulfonyl)-1-(pyridin-4-yl)ethyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta²phenanthren-17-one (22)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium methanesulfinate (30.6 mg, 0.3 mmol, 1.5 equiv.), (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta²phenanthren-17-one (56.1 mg, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a white solid (59.5 mg, 68%). ¹H NMR (400 MHz, CDCl₃) δ 8.55 (d, J = 5.4 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.06 (d, J = 8.1 Hz, 1H), 7.00 (d, J = 5.4 Hz, 1H),

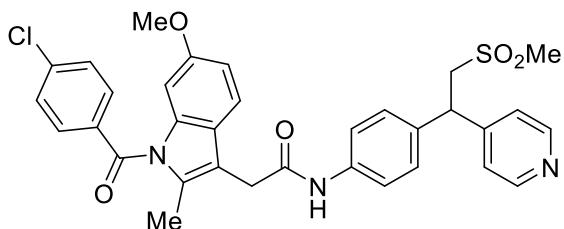
4.60 (t, $J = 7.0$ Hz, 1H), 3.83 – 3.68 (m, 2H), 2.96 – 2.81 (m, 2H), 2.58 – 2.45 (m, 4H), 2.43 – 2.35 (m, 1H), 2.26 (m, 1H), 2.15 (m, 1H), 2.06 (m, 2H), 1.97 – 1.92 (m, 1H), 1.67 – 1.41 (m, 6H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 219.56, 149.93, 149.13, 138.76 (d, $J = 2.3$ Hz), 136.74, 136.05 (d, $J = 6.4$ Hz), 127.38 (d, $J = 20.4$ Hz), 125.36 (d, $J = 3.6$ Hz), 123.82 (d, $J = 20.1$ Hz), 121.82, 58.67, 49.43, 46.87, 43.99 (d, $J = 3.8$ Hz), 43.18, 41.23, 36.92, 34.76, 30.49, 28.33, 25.28, 24.55, 20.51, 12.79. HRMS (ESI+): calcd for $\text{C}_{26}\text{H}_{32}\text{NO}_3\text{S}^+$ ($\text{M}+\text{H}$) 438.2097, found 438.2096.

2-(4-(2-(methylsulfonyl)-1-(pyridin-4-yl)ethyl)benzyl)isoindoline-1,3-dione (23)



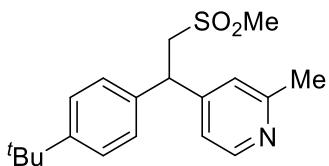
According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium methanesulfinate (30.6 mg, 0.3 mmol, 1.5 equiv.), 2-(4-vinylbenzyl)isoindoline-1,3-dione (52.6 mg, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a white solid (60.5 mg, 72%). ^1H NMR (400 MHz, DMSO-d6) δ 8.44 (s, 2H), 7.85 (ddd, $J = 7.7, 5.0, 2.1$ Hz, 4H), 7.48 – 7.34 (m, 4H), 7.29 – 7.22 (m, 2H), 4.71 (s, 2H), 4.58 (d, $J = 4.9$ Hz, 1H), 4.11 (m, 1H), 4.01 (m, 1H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6) δ 167.69, 151.32, 149.69, 140.86, 135.50, 134.55, 131.53, 127.95, 127.81, 123.22, 122.94, 56.89, 43.82, 41.37, 40.46. HRMS (ESI+): calcd for $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_4\text{S}^+$ ($\text{M}+\text{H}$) 421.1217, found 421.1212.

2-(1-(4-chlorobenzoyl)-6-methoxy-2-methyl-1H-indol-3-yl)-N-(4-(methylsulfonyl)-1-(pyridin-4-yl)ethyl)phenylacetamide (24)



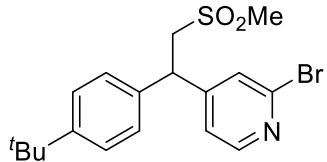
According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium methanesulfinate (30.6 mg, 0.3 mmol, 1.5 equiv.), 2-(1-(4-chlorobenzoyl)-6-methoxy-2-methyl-1H-indol-3-yl)-N-(4-vinylphenyl)acetamide (91.6 mg, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a white solid (73.8 mg, 60 %). ¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, J = 5.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 7.5 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.17 (t, J = 6.8 Hz, 4H), 6.92 (d, J = 2.4 Hz, 1H), 6.85 (d, J = 9.0 Hz, 1H), 6.69 (dd, J = 9.0, 2.5 Hz, 1H), 4.65 – 4.55 (m, 1H), 3.78 (s, 3H), 3.77 (s, 2H), 3.75 – 3.62 (m, 2H), 2.46 (s, 3H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.42, 168.36, 156.37, 150.63, 150.22, 139.75, 137.36, 136.74, 135.62, 133.41, 131.24, 130.99, 130.15, 129.28, 128.45, 122.70, 120.91, 115.21, 112.22, 112.16, 100.98, 59.52, 55.81, 44.76, 42.33, 33.27, 13.33. HRMS (ESI+): calcd for C₃₃H₃₁ClN₃O₅S⁺ (M+H)⁺ 616.1667, found 616.1666.

4-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)-2-methylpyridine (25)



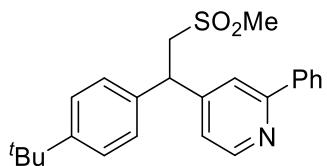
According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 2-methylisonicotinonitrile (47.3 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a yellow solid (55.4 mg, 84%). 1 H NMR (600 MHz, CDCl₃) δ 8.41 (d, J = 5.2 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.09 (s, 1H), 7.03 (d, J = 5.2 Hz, 1H), 4.56 (t, J = 7.1 Hz, 1H), 3.80 – 3.64 (m, 2H), 2.51 (s, 3H), 2.40 (s, 3H), 1.26 (s, 9H). 13 C NMR (101 MHz, CDCl₃) δ 158.98, 151.00, 150.93, 149.41, 136.71, 127.35, 126.17, 122.33, 119.68, 59.78, 44.98, 42.00, 34.43, 31.14, 24.27. HRMS (ESI+): calcd for C₁₉H₂₆NO₂S⁺ (M+H) 332.1679, found 332.1679.

2-bromo-4-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)pyridine (26)



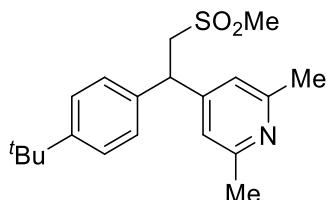
According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 2-bromoisonicotinonitrile (73.2 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (65.8 mg, 83%). 1 H NMR (400 MHz, CDCl₃) δ 8.31 (d, J = 5.1 Hz, 1H), 7.47 – 7.31 (m, 3H), 7.21 – 7.11 (m, 3H), 4.61 (t, J = 7.1 Hz, 1H), 3.72 (ddd, J = 20.6, 14.5, 7.1 Hz, 2H), 2.48 (s, 3H), 1.30 (s, 9H). 13 C NMR (101 MHz, CDCl₃) δ 153.57, 151.55, 150.55, 142.89, 135.84, 127.46, 126.90, 126.49, 121.90, 59.45, 44.60, 42.18, 34.57, 31.20. HRMS (ESI+): calcd for C₁₈H₂₃BrNO₂S⁺ (M+H) 396.0627, found 396.0624.

4-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)-2-phenylpyridine (27)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 2-phenylisonicotinonitrile (72.0 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (70.8 mg, 90%). ^1H NMR (400 MHz, CDCl_3) δ 8.63 (d, $J = 5.1$ Hz, 1H), 7.99 – 7.90 (m, 2H), 7.66 (s, 1H), 7.49 – 7.36 (m, 5H), 7.28 – 7.24 (m, 2H), 7.16 (dd, $J = 5.1, 1.5$ Hz, 1H), 4.70 (t, $J = 7.1$ Hz, 1H), 3.89 – 3.72 (m, 2H), 2.44 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.23, 151.29, 151.16, 150.20, 138.93, 136.68, 129.21, 128.75, 127.44, 126.99, 126.30, 120.93, 119.73, 59.92, 45.28, 42.12, 34.51, 31.20. HRMS (ESI+): calcd for $\text{C}_{24}\text{H}_{28}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 394.1835, found 394.1831.

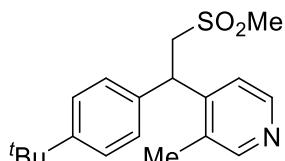
4-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)-2-methoxypyridine (28)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 2,6-dimethylisonicotinonitrile (52.8 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (ethyl acetate) as a pale-yellow oil (61.8 mg, 89%). ^1H NMR (600 MHz, CDCl_3) δ 7.36 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J =$

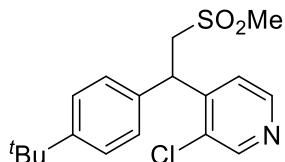
8.4 Hz, 2H), 6.89 (s, 2H), 4.53 (t, J = 7.2 Hz, 1H), 3.72 (qd, J = 14.7, 7.2 Hz, 2H), 2.49 (s, 6H), 2.39 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.50, 150.99, 150.96, 136.93, 127.37, 126.21, 119.18, 60.01, 45.08, 42.05, 34.51, 31.23, 24.53. HRMS (ESI+): calcd for $\text{C}_{20}\text{H}_{28}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 346.1835, found 346.1832.

4-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)-3-methylpyridine (29)



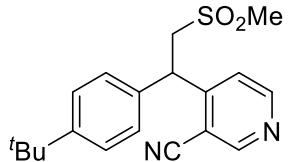
According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 3-methylisonicotinonitrile (47.3 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μL , 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1:2) as a colorless oil (58.1 mg, 88%). ^1H NMR (600 MHz, CDCl_3) δ 8.45 (d, J = 4.9 Hz, 1H), 8.37 (s, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.21 (dd, J = 13.2, 6.7 Hz, 3H), 4.81 (t, J = 7.1 Hz, 1H), 3.72 (ddd, J = 21.1, 14.6, 7.1 Hz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.42, 150.97, 148.54, 147.70, 135.75, 131.69, 127.73, 126.07, 120.81, 59.93, 42.11, 40.92, 34.42, 31.14, 16.49. HRMS (ESI+): calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 332.1679, found 332.1673.

4-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)-3-chloropyridine (30)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 3-chloroisonicotinonitrile (55.4 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography(petroleum ether: ethyl acetate = 3:1) as a pale-yellow oil (68.6 mg, 97%). ^1H NMR (600 MHz, CDCl_3) δ 8.56 (s, 1H), 8.47 (d, J = 5.0 Hz, 1H), 7.37 (d, J = 8.2 Hz, 2H), 7.32 – 7.25 (m, 3H), 5.16 – 5.07 (m, 1H), 3.77 (ddd, J = 20.8, 14.6, 7.2 Hz, 2H), 2.53 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.21, 150.05, 148.03, 147.53, 134.77, 131.50, 127.78, 126.08, 122.62, 58.76, 41.89, 41.32, 34.43, 31.11. HRMS (ESI+): calcd for $\text{C}_{18}\text{H}_{23}\text{ClNO}_2\text{S}^+$ ($\text{M}+\text{H}$) 352.1133, found 352.1130.

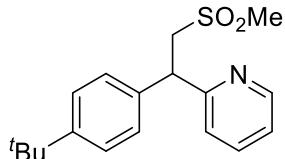
4-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)nicotinonitrile (31)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), pyridine-3,4-dicarbonitrile (51.7 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1:1) as a white solid (65.9mg, 96%). ^1H NMR (600 MHz, CDCl_3) δ 8.80 (s, 1H), 8.76 (d, J = 5.3 Hz, 1H), 7.49 (d, J = 5.3 Hz, 1H), 7.39 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 5.01 (t, J = 7.3 Hz, 1H), 3.88 (d, J = 7.3 Hz, 2H), 2.69 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.50, 153.13, 151.66, 134.72, 127.43, 126.39, 121.81,

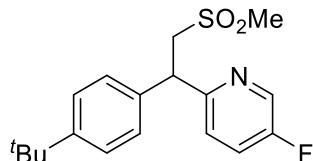
115.71, 109.95, 58.21, 43.29, 41.85, 34.47, 31.07. HRMS (ESI+): calcd for $C_{19}H_{23}N_2O_2S^+$ ($M+H$) 343.1475, found 343.1471.

2-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)pyridine (32)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), picolinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a pale-yellow oil (45.7mg, 72%). 1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 4.6 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.31 (q, J = 8.4 Hz, 4H), 7.24 (d, J = 7.8 Hz, 1H), 7.19 – 7.14 (m, 1H), 4.76 – 4.65 (m, 1H), 4.42 (dd, J = 14.6, 8.0 Hz, 1H), 3.62 (dd, J = 14.6, 5.7 Hz, 1H), 2.41 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.81, 150.51, 149.16, 137.98, 136.99, 127.54, 125.94, 123.95, 122.24, 59.59, 47.38, 42.02, 34.44, 31.25. HRMS (ESI+): calcd for $C_{18}H_{24}NO_2S^+$ ($M+H$) 318.1522, found 318.1519.

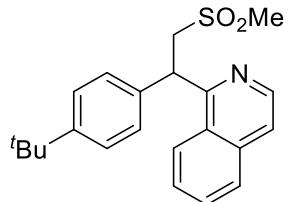
2-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)-5-fluoropyridine (33)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 5-fluoropicolinonitrile (48.8 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the

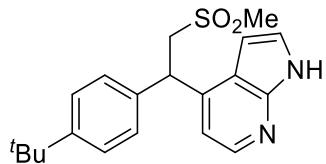
product was isolated by flash chromatography (petroleum ether: ethyl acetate = 5: 1) as a pale-yellow oil (47.6mg, 71%). ^1H NMR (400 MHz, CDCl_3) δ 8.44 (d, J = 2.4 Hz, 1H), 7.40 – 7.29 (m, 3H), 7.28 – 7.20 (m, 3H), 4.73 (m, 1H), 4.35 (dd, J = 14.6, 7.9 Hz, 1H), 3.62 (dd, J = 14.6, 5.8 Hz, 1H), 2.46 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.56 (d, J = 255.8 Hz), 155.87 (d, J = 3.7 Hz), 150.74, 137.57 (d, J = 45.2 Hz), 137.11, 127.52, 126.06, 124.74 (d, J = 4.2 Hz), 123.90 (d, J = 18.4 Hz), 59.67, 46.58, 42.12, 34.50, 31.27. ^{19}F NMR (377 MHz, CDCl_3) δ -129.11 (dd, J = 8.1, 4.3 Hz). HRMS (ESI+): calcd for $\text{C}_{18}\text{H}_{23}\text{FNO}_2\text{S}^+$ ($\text{M}+\text{H}$) 336.1428, found 336.1422.

1-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)isoquinoline (34)



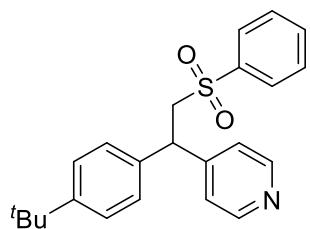
According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isoquinoline-1-carbonitrile (61.7 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μL , 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 4: 1) as a pale-yellow oil (61.8mg, 84%). ^1H NMR (400 MHz, CDCl_3) δ 8.53 (d, J = 5.7 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.64 – 7.51 (m, 3H), 7.36 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 5.60 (dd, J = 7.7, 5.7 Hz, 1H), 4.65 (m, 1H), 3.76 (m, 1H), 2.42 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.47, 150.38, 141.10, 137.59, 136.58, 130.05, 127.67, 127.43, 126.53, 125.89, 124.71, 120.50, 60.22, 43.29, 42.20, 34.35, 31.15. HRMS (ESI+): calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 368.1679, found 368.1676.

4-(1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethyl)-1H-pyrrolo[2,3-b]pyridine (35)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), 1H-pyrrolo[2,3-b]pyridine-4-carbonitrile (57.3 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a white solid (52.8 mg, 74%). 1 H NMR (400 MHz, CDCl₃) δ 11.44 (s, 1H), 8.29 (d, J = 5.0 Hz, 1H), 7.39 – 7.31 (m, 5H), 7.02 (d, J = 5.0 Hz, 1H), 6.66 (d, J = 3.5 Hz, 1H), 5.08 (m, 1H), 3.93 (dd, J = 6.8, 4.0 Hz, 2H), 2.35 (s, 3H), 1.26 (s, 9H). 13 C NMR (101 MHz, CDCl₃) δ 150.72, 148.88, 143.00, 142.68, 136.67, 127.49, 125.99, 125.66, 119.15, 113.58, 99.11, 59.84, 43.23, 41.81, 34.42, 31.18. HRMS (ESI+): calcd for C₂₀H₂₅N₂O₂S⁺ (M+H) 357.1631, found 357.1630.

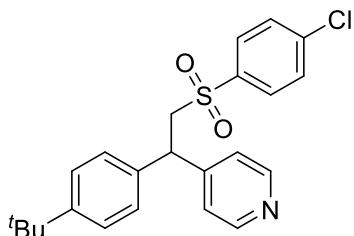
4-(1-(4-(tert-butyl)phenyl)-2-(phenylsulfonyl)ethyl)pyridine (36)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium benzenesulfinate hydrate (60.1 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium

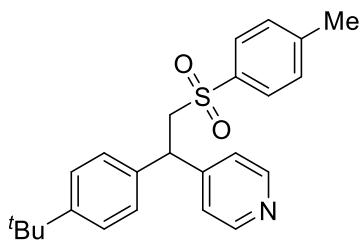
chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 1) as a pale-yellow oil (66.0 mg, 87%). ^1H NMR (600 MHz, CDCl_3) δ 8.39 (d, J = 5.7 Hz, 2H), 7.63 (dd, J = 8.3, 1.1 Hz, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.32 (q, J = 7.5 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 5.7 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 4.57 (t, J = 7.1 Hz, 1H), 3.89 (m, 2H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.71, 150.27, 149.38, 139.13, 136.37, 133.39, 128.86, 127.75, 127.01, 125.75, 122.84, 60.32, 45.08, 34.22, 31.05. HRMS (ESI+): calcd for $\text{C}_{23}\text{H}_{26}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 380.1679, found 380.1675.

4-(1-(4-(tert-butyl)phenyl)-2-((4-chlorophenyl)sulfonyl)ethyl)pyridine (37)



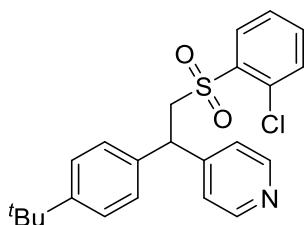
According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium 4-chlorobenzenesulfinate (59.6 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μL , 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 1) as a pale-yellow oil (69.1 mg, 83%). ^1H NMR (600 MHz, CDCl_3) δ 8.45 (d, J = 5.4 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.27 – 7.24 (m, 2H), 7.19 – 7.14 (m, 2H), 7.10 (d, J = 6.0 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 4.57 (t, J = 7.2 Hz, 1H), 3.89 (ddd, J = 21.2, 14.8, 7.2 Hz, 2H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.09, 150.78, 149.47, 140.15, 137.69, 135.70, 129.36, 129.15, 127.19, 125.90, 122.87, 60.55, 45.28, 34.37, 31.19.³

4-(1-(4-(tert-butyl)phenyl)-2-tosylethyl)pyridine (38)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium 4-methylbenzenesulfinate hydrate (75.1 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 1) as a pale-yellow oil (63.9 mg, 81%). ^1H NMR (600 MHz, CDCl_3) δ 8.40 (d, J = 5.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 5.9 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 4.55 (t, J = 7.1 Hz, 1H), 3.86 (qd, J = 14.7, 7.1 Hz, 2H), 2.35 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.70, 150.38, 149.59, 144.45, 136.60, 136.29, 129.53, 127.89, 127.08, 125.78, 122.89, 60.60, 45.18, 34.32, 31.16, 21.47.¹

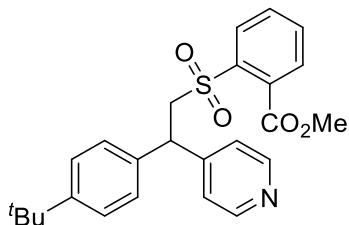
4-(1-(4-(tert-butyl)phenyl)-2-((2-chlorophenyl)sulfonyl)ethyl)pyridine (39)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium 2-chlorobenzenesulfinate (59.6 mg, 0.3 mmol, 1.5 equiv.),

1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a pale-yellow oil (74.5 mg, 90%). 1 H NMR (400 MHz, CDCl₃) δ 8.32 (d, J = 5.0 Hz, 2H), 7.64 (m, 1H), 7.33 – 7.22 (m, 2H), 7.10 (m, 3H), 7.02 (d, J = 5.5 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 4.49 (t, J = 7.3 Hz, 1H), 4.14 (qd, J = 14.9, 7.3 Hz, 2H), 1.14 (s, 9H). 13 C NMR (101 MHz, CDCl₃) δ 150.40, 149.99, 149.79, 136.70, 135.97, 134.51, 132.24, 131.52, 131.36, 127.12, 127.09, 125.77, 122.71, 58.21, 45.36, 34.32, 31.12. HRMS (ESI+): calcd for C₂₃H₂₅ClNO₂S⁺ (M+H) 414.1289, found 414.1288.

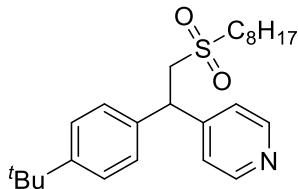
methyl 2-((2-(4-(tert-butyl)phenyl)-2-(pyridin-4-yl)ethyl)sulfonyl)benzoate (40)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium 2-(methoxycarbonyl)benzenesulfinate (66.7 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a pale-yellow oil (75.3 mg, 86%). 1 H NMR (400 MHz, CDCl₃) δ 8.39 (d, J = 5.8 Hz, 2H), 7.57 (t, J = 8.8 Hz, 2H), 7.50 (dd, J = 10.9, 4.2 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.17 (dd, J = 9.0, 7.4 Hz, 4H), 7.09 (d, J = 8.4 Hz, 2H), 4.66 (t, J = 7.4 Hz, 1H), 4.49 – 4.31 (m, 2H), 3.98 (s, 3H), 1.23 (s, 9H). 13 C NMR (101 MHz, CDCl₃) δ 167.61, 150.37, 150.20, 149.87, 138.22,

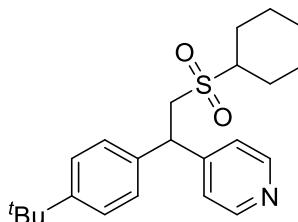
136.45, 133.09, 132.47, 130.66, 130.63, 129.22, 127.31, 125.73, 122.92, 60.56, 53.23, 45.45, 34.34, 31.18. HRMS (ESI+): calcd for $C_{25}H_{28}NO_4S^+$ ($M+H$) 438.1734, found 438.1730.

4-(1-(4-(tert-butyl)phenyl)-2-(octylsulfonyl)ethyl)pyridine (41)



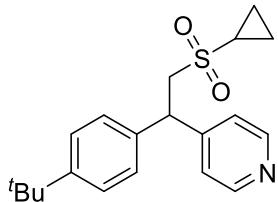
According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium octane-1-sulfinate (60.0 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a pale-yellow oil (69.7 mg, 84%). 1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 6.0 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.25 – 7.13 (m, 4H), 4.77 – 4.47 (m, 1H), 3.68 (ddd, J = 20.7, 14.6, 7.1 Hz, 2H), 2.37 (m, 2H), 1.57 (dd, J = 12.0, 6.7 Hz, 2H), 1.29 (s, 9H), 1.18 (dd, J = 36.0, 12.6 Hz, 10H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.16, 150.71, 150.30, 136.82, 127.55, 126.23, 122.70, 57.57, 54.08, 44.83, 34.53, 31.61, 31.24, 29.68, 28.81, 28.22, 22.55, 21.90, 14.02. HRMS (ESI+): calcd for $C_{25}H_{38}NO_2S^+$ ($M+H$) 416.2618, found 416.2615.

4-(1-(4-(tert-butyl)phenyl)-2-(cyclohexylsulfonyl)ethyl)pyridine (42)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium cyclohexanesulfinate (51.0 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 1) as a pale-yellow oil (52.5 mg, 68%). 1 H NMR (600 MHz, CDCl₃) δ 8.55 (d, J = 5.5 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.22 (d, J = 8.4 Hz, 2H), 4.66 (m, 1H), 3.75 (dd, J = 14.4, 7.8 Hz, 1H), 3.59 (dd, J = 14.4, 6.3 Hz, 1H), 2.09 – 2.00 (m, 2H), 1.84 (m, 2H), 1.77 (d, J = 13.5 Hz, 1H), 1.59 (d, J = 13.3 Hz, 1H), 1.47 – 1.40 (m, 2H), 1.30 (s, 9H), 1.14 – 1.07 (m, 1H), 0.97 m, 1H), 0.90 – 0.85 (m, 1H). 13 C NMR (101 MHz, CDCl₃) δ 151.79, 150.95, 149.28, 136.90, 127.49, 126.07, 123.00, 61.36, 54.08, 44.38, 34.42, 31.16, 25.37, 24.91, 24.77, 24.72, 23.77. HRMS (ESI+): calcd for C₂₃H₃₂NO₂S⁺ (M+H) 386.2148, found 386.2144.

4-(1-(4-(tert-butyl)phenyl)-2-(cyclopropylsulfonyl)ethyl)pyridine (43)



According to the general procedure, 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and sodium cyclopropanesulfinate (38.4 mg, 0.3 mmol, 1.5 equiv.), 1-(tert-butyl)-4-vinylbenzene (36.6 μ L, 0.2 mmol, 1.0 equiv.) and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.), the product was isolated by flash chromatography (petroleum ether: ethyl acetate = 1: 2) as a pale-yellow oil (63.2 mg, 92%). 1 H NMR (400 MHz, CDCl₃) δ 8.47 (d, J = 5.5 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 5.5 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 4.59 (t, J = 7.1 Hz, 1H), 3.72 (d, J = 7.1 Hz, 2H), 1.72 (tt, J = 8.0, 4.8 Hz,

1H), 1.20 (s, 9H), 1.10 – 0.97 (m, 2H), 0.73 – 0.61 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.97, 150.81, 149.98, 137.08, 127.32, 126.02, 122.88, 58.75, 44.85, 34.42, 31.15, 30.71, 5.24, 5.15. HRMS (ESI+): calcd for $\text{C}_{20}\text{H}_{26}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 344.1679, found 344.1675.

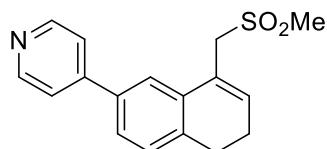
6. Mechanistic Studies

6.1. Radical clock experiments



45, 47% yield

To a flame-dried 10 mL reaction vial was charged with 9,10-diphenylanthracene (3.3 mg, 0.01 mmol, 5 mol%), isonicotinonitrile (41.6 mg, 0.4 mmol, 2.0 equiv.), and Sodium methyl sulfinate (34 mg, 0.3 mmol, 1.5 equiv.), and Ammonium chloride (21.4 mg, 0.4 mmol, 2.0 equiv.). The vial was capped. MeCN/EtOH (1:1) [0.025 M] was added via a syringe. It was bubbled with nitrogen for 15 minutes, followed by the addition of (1-cyclopropylvinyl)benzene (30.8 μ L, 0.2 mmol, 1.0 equiv.). The reaction mixture was then irradiated with a 90 W Blue LED lamp for 4 h at room temperature. After reaction completed, the mixture was evaporated on rotary evaporator. Then, the residue was dilute with ethyl acetate and wash with H₂O. The combined organic layers were dried with MgSO₄, filtered, and concentrated in vacuo. The product was isolated by flash chromatography (petroleum ether: acetone = 1: 1) as a white solid (28.1 mg, 47 %).



4-(8-((methylsulfonyl)methyl)-5,6-dihydronaphthalen-2-yl)pyridine (45)

¹H NMR (400 MHz, CDCl₃) δ 8.66 (d, J = 3.5 Hz, 2H), 7.68 (s, 1H), 7.53 (d, J = 5.4 Hz, 2H), 7.47 (d, J = 7.7 Hz, 1H), 7.28 (d, J = 8.5 Hz, 1H), 6.37 (t, J = 4.5 Hz, 1H),

4.24 (s, 2H), 2.91 (s, 3H), 2.88 (t, $J = 8.1$ Hz, 2H), 2.49 – 2.41 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.99, 148.43, 137.27, 136.44, 135.89, 133.17, 128.67, 126.34, 125.85, 122.40, 121.63, 58.51, 39.80, 27.44, 23.35. HRMS (ESI+): calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) 300.1053, found 300.1049.

6.2. Stern-Volmer fluorescence quenching studies.

The emission intensity at 428 nm was collected with excited wavelength of 373 nm in MeCN/EtOH using a Shimadzu RF-5301pc spectrofluorophotometer. The concentration of DPA is 1×10^{-5} M. After degassing the sample with a stream of argon for 30 minutes, plots were constructed according to the Stern-Volmer equation $I_0 / I = 1 + kq t_0^4$.

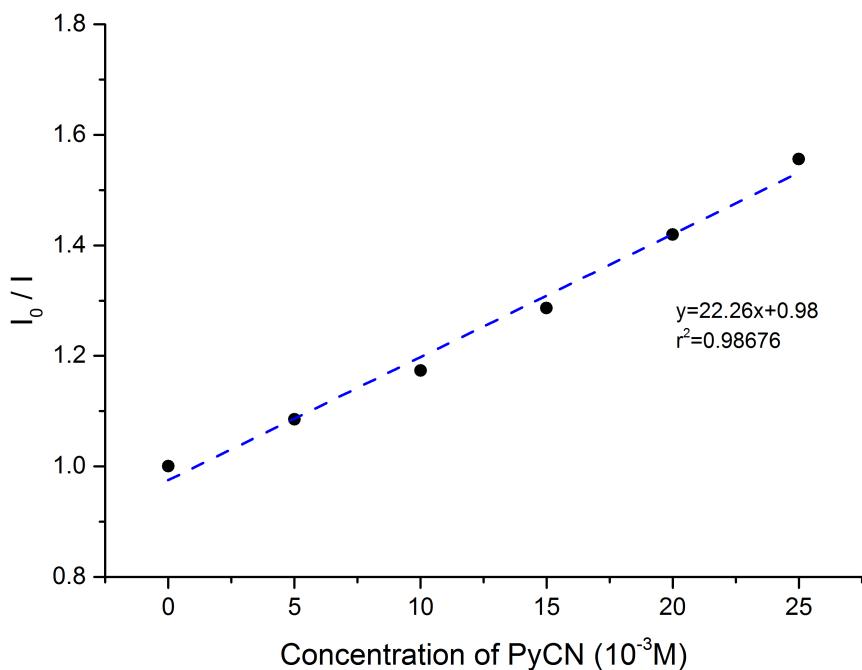


Figure S1. DPA emission quenching with 4-cyanopyridine

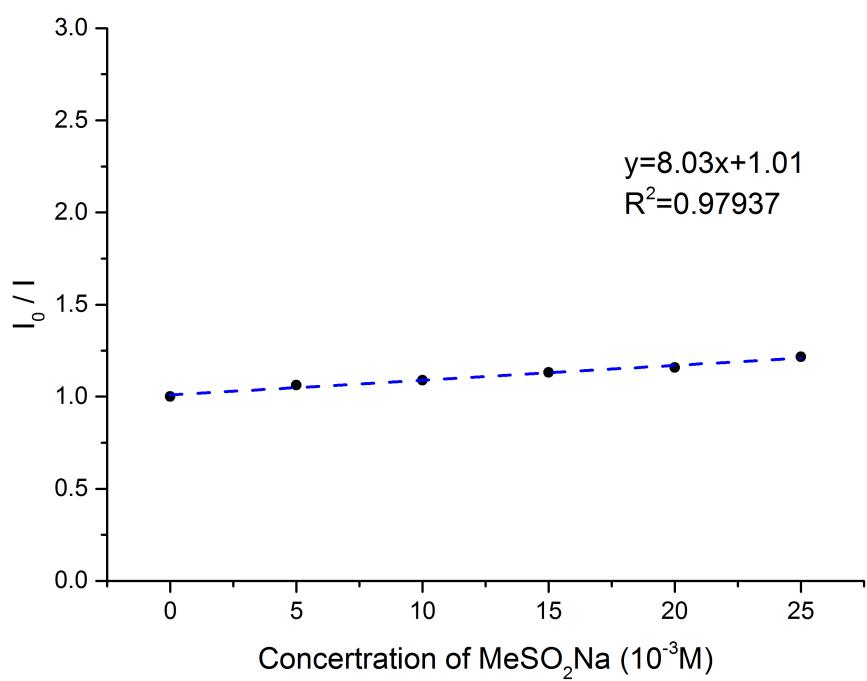


Figure S2. DPA emission quenching with MeSO_2Na

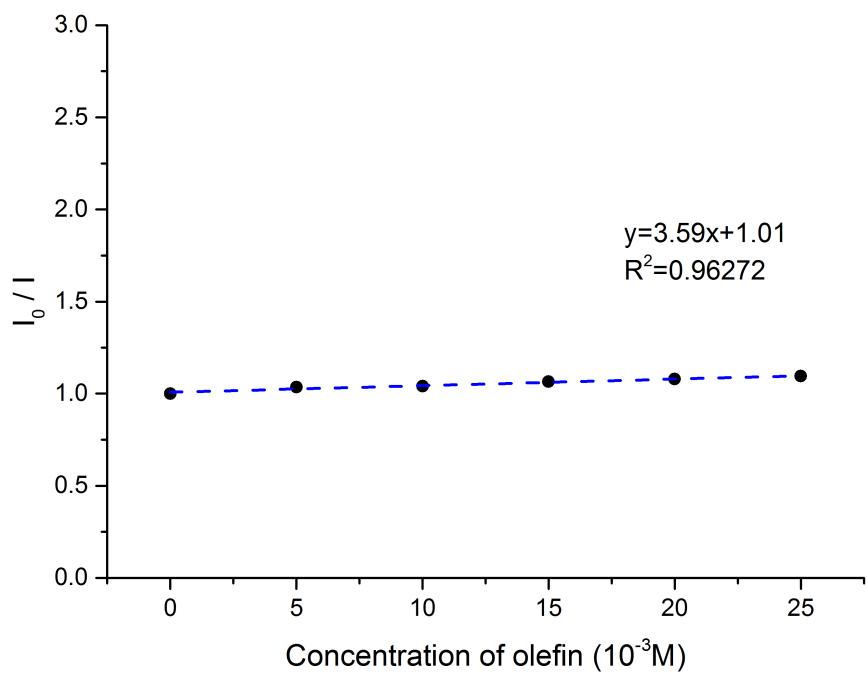
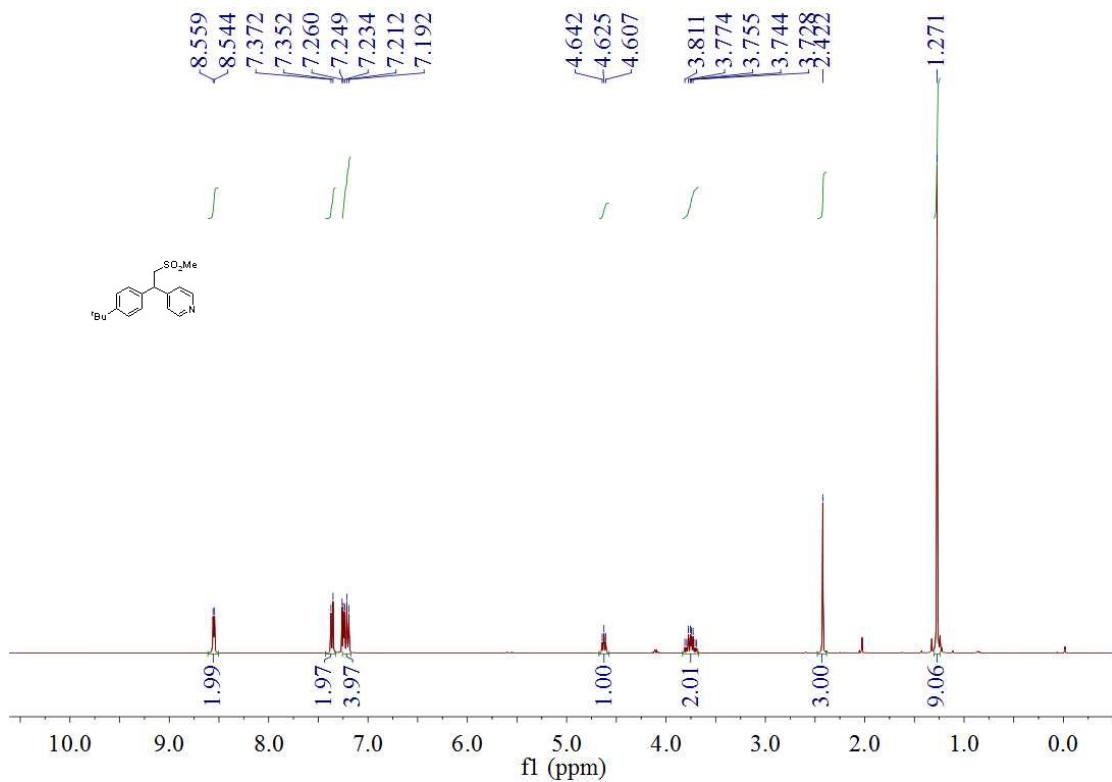


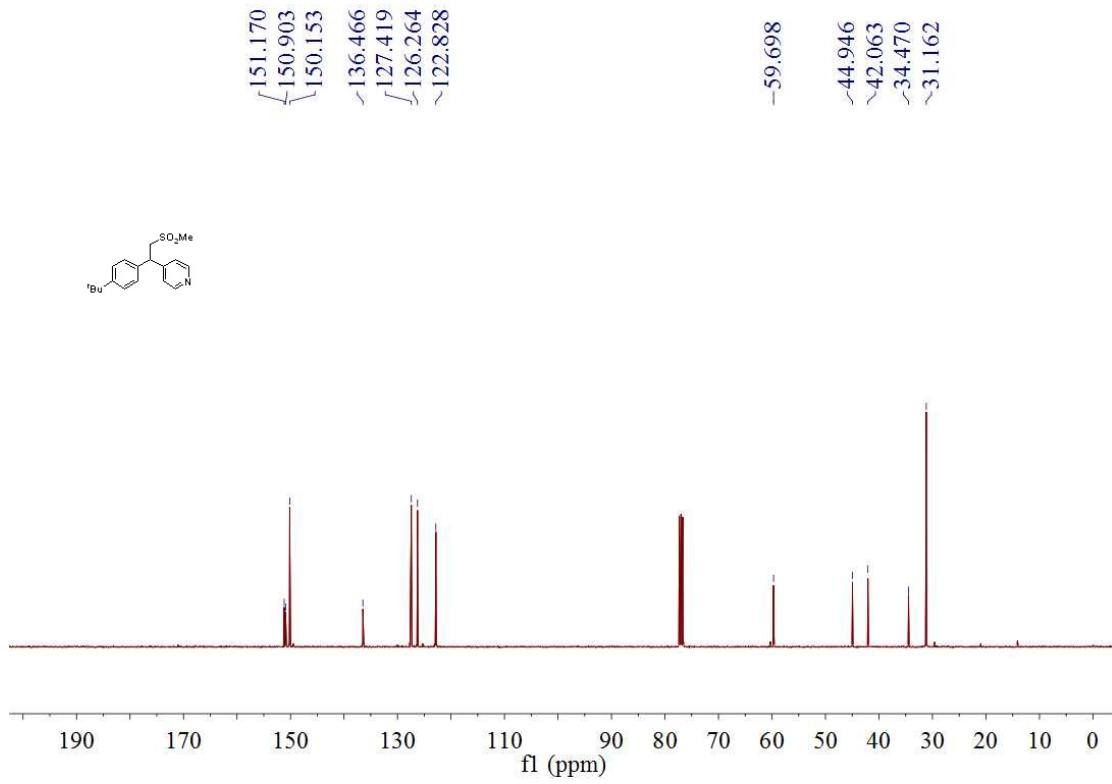
Figure S3. DPA emission quenching with 4-tert-Butylstyrene

7. NMR Spectra

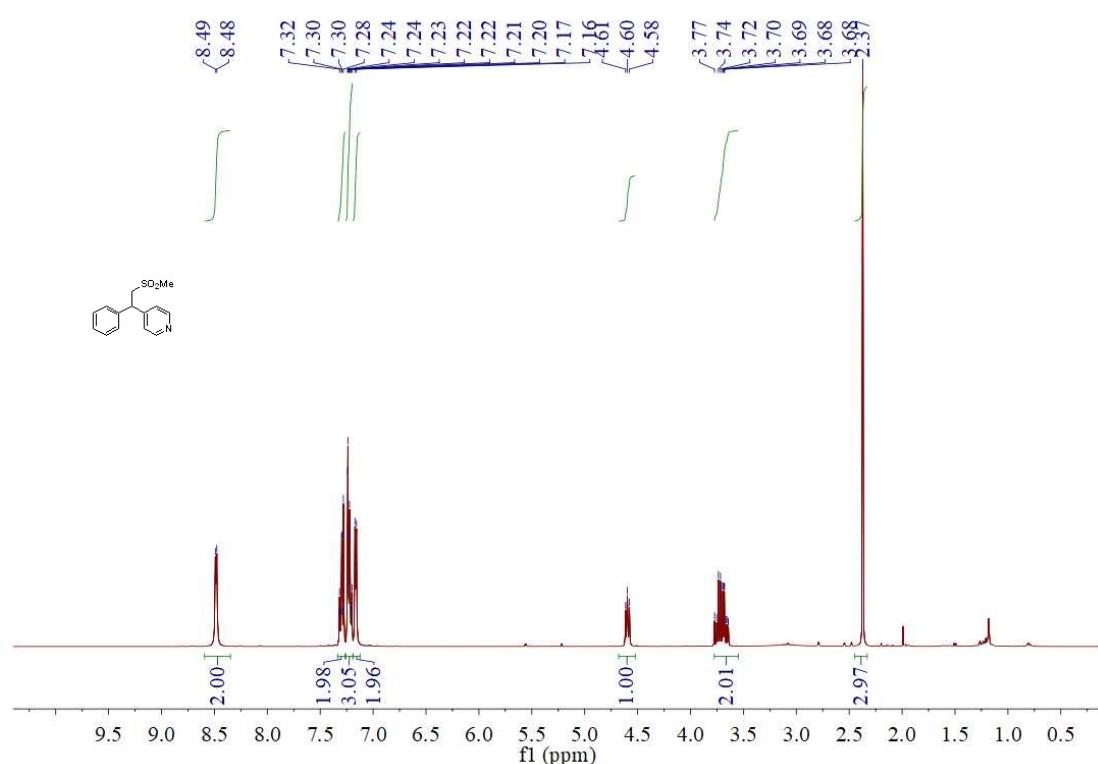
3; ^1H NMR (400 MHz, CDCl_3)



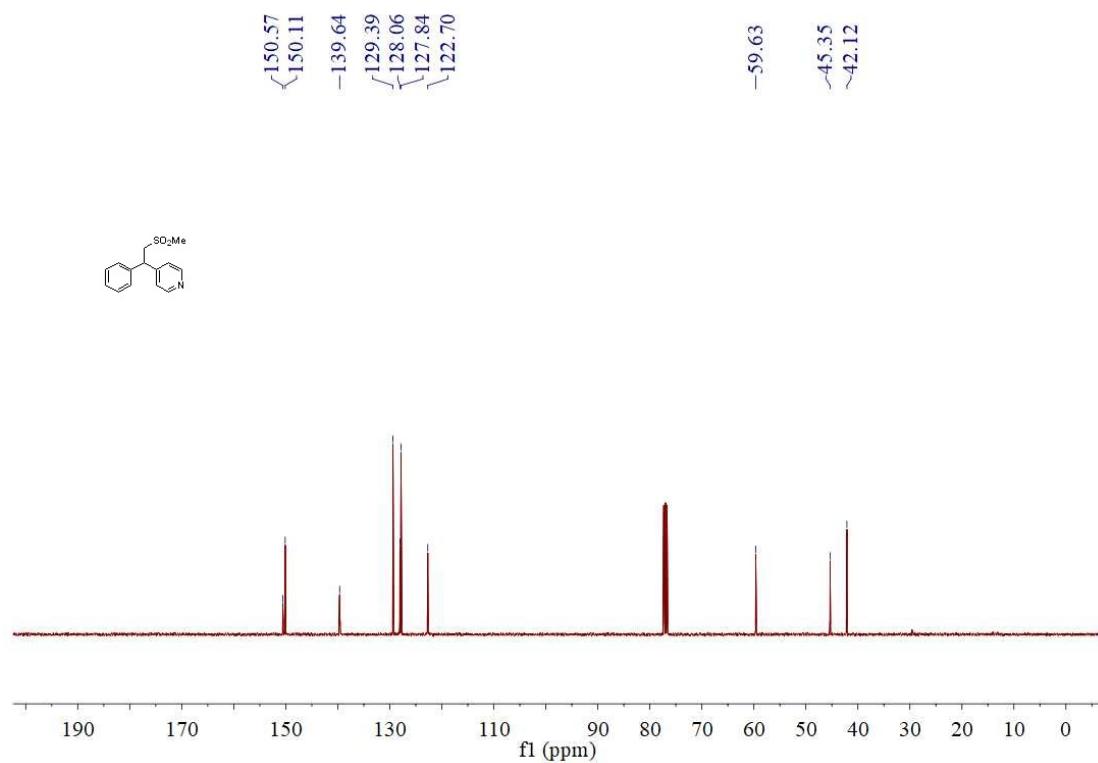
3; ^{13}C NMR (101 MHz, CDCl_3)



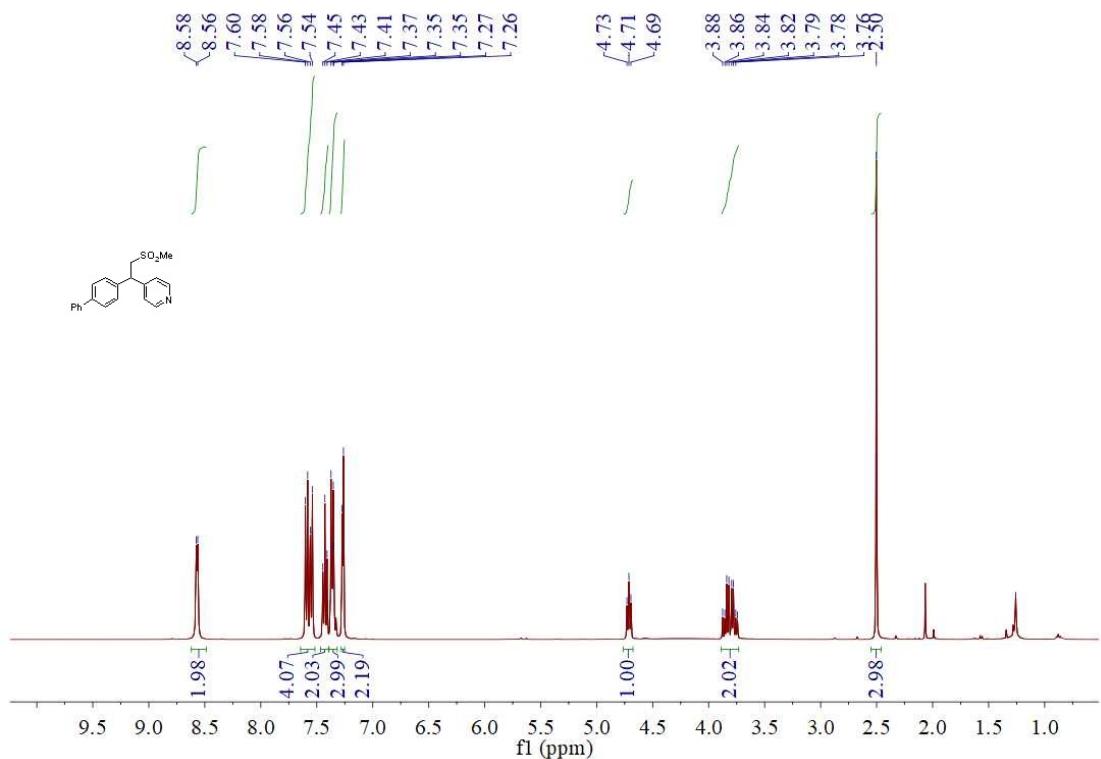
4; ^1H NMR (400 MHz, CDCl_3)



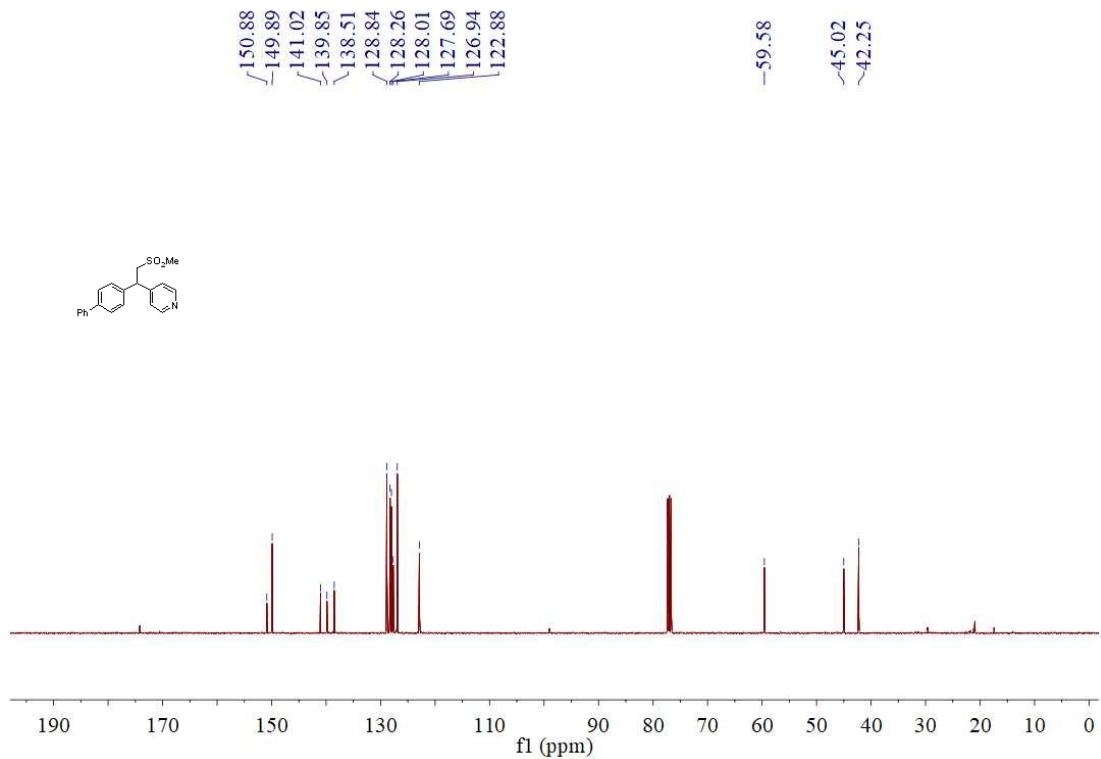
4; ^{13}C NMR (101 MHz, CDCl_3)



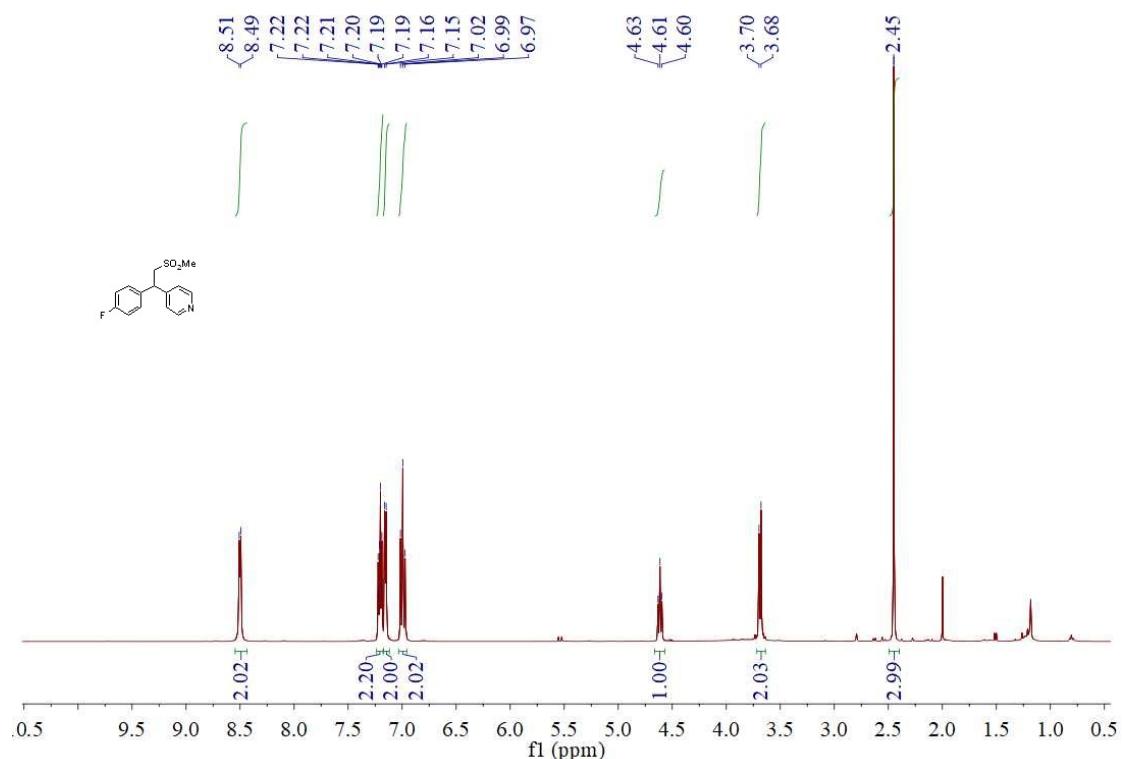
5; ^1H NMR (400 MHz, CDCl_3)



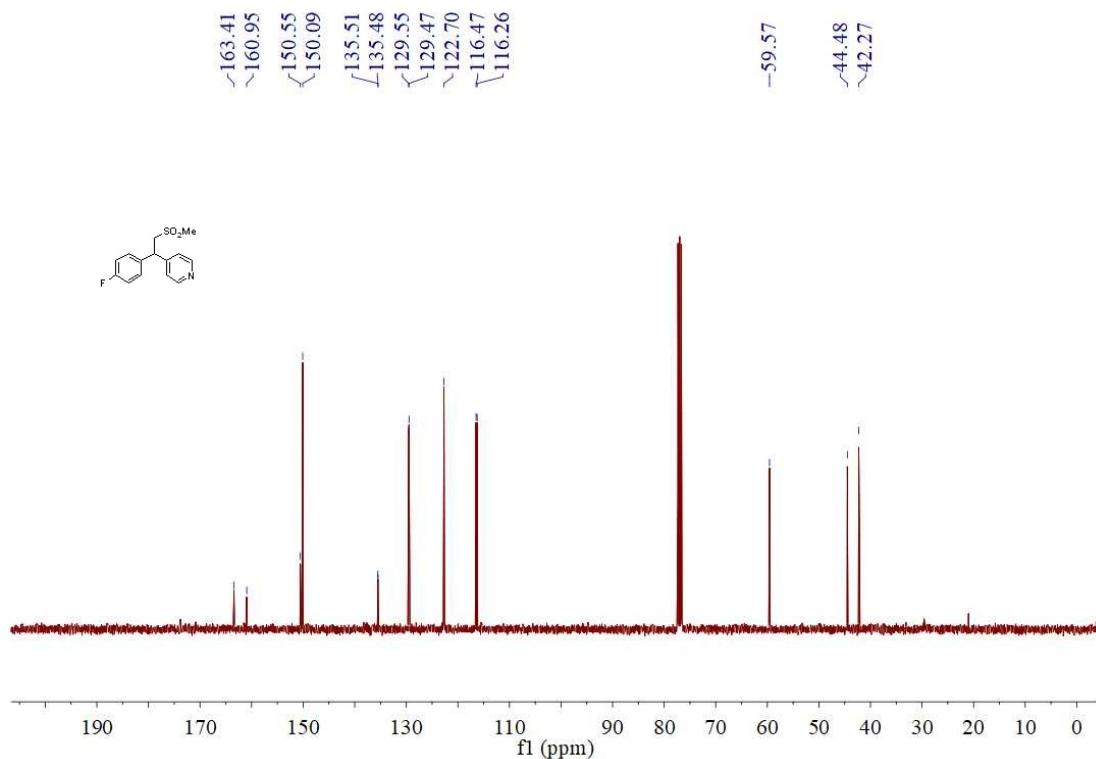
5; ^{13}C NMR (101 MHz, CDCl_3)



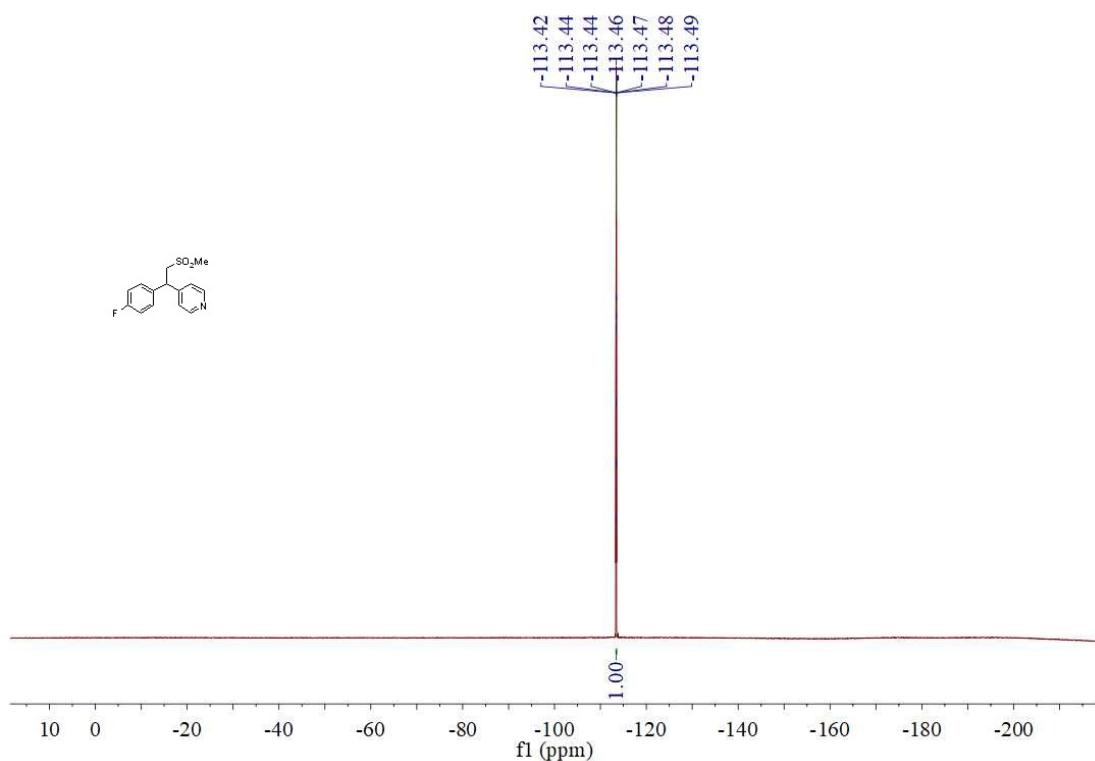
6; ^1H NMR (400 MHz, CDCl_3)



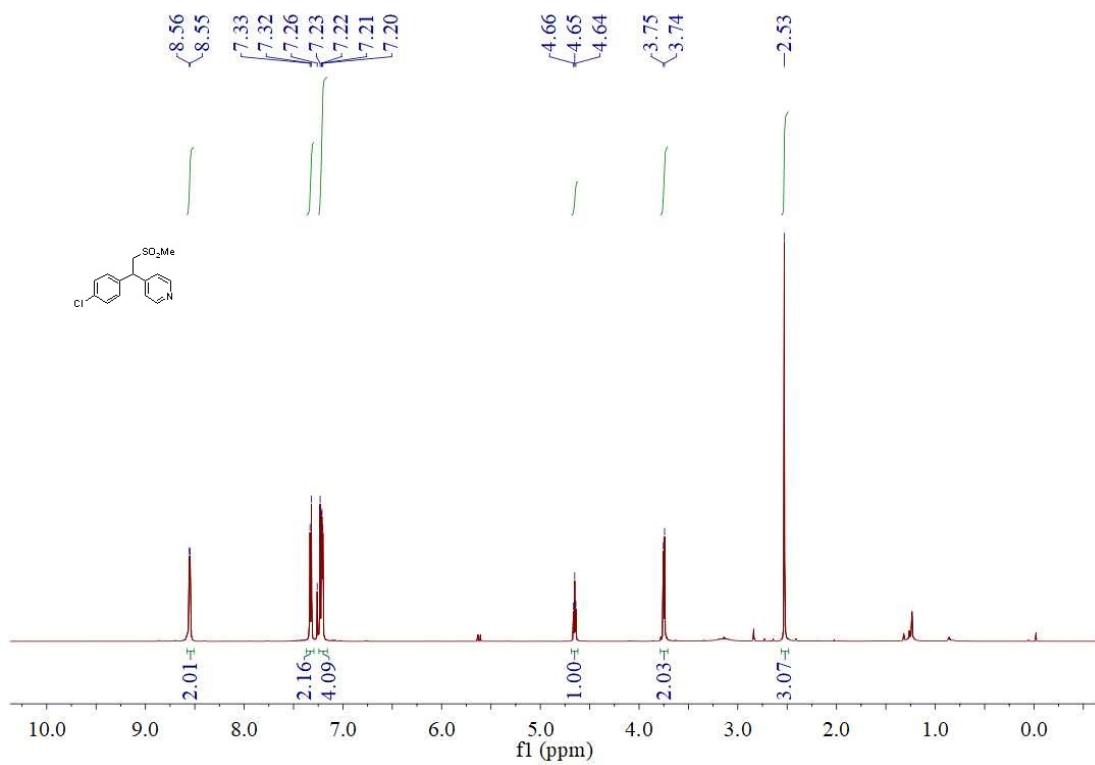
6; ^{13}C NMR (101 MHz, CDCl_3)



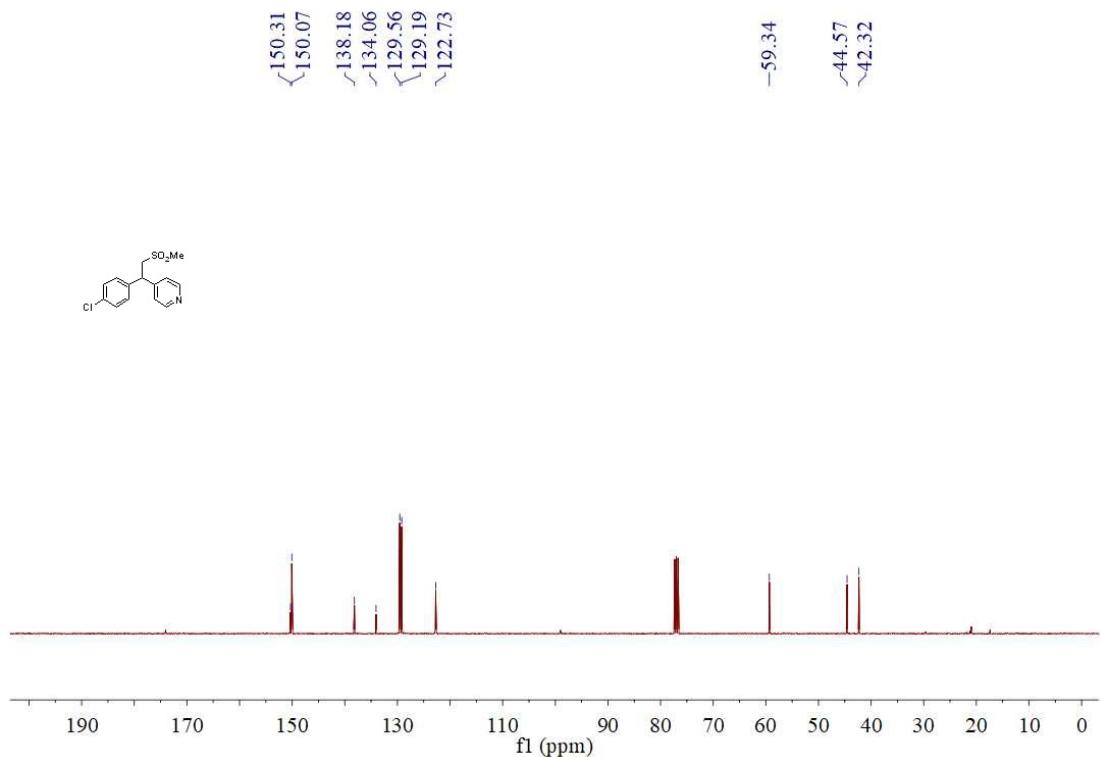
6; ^{19}F NMR (377 MHz, CDCl_3)



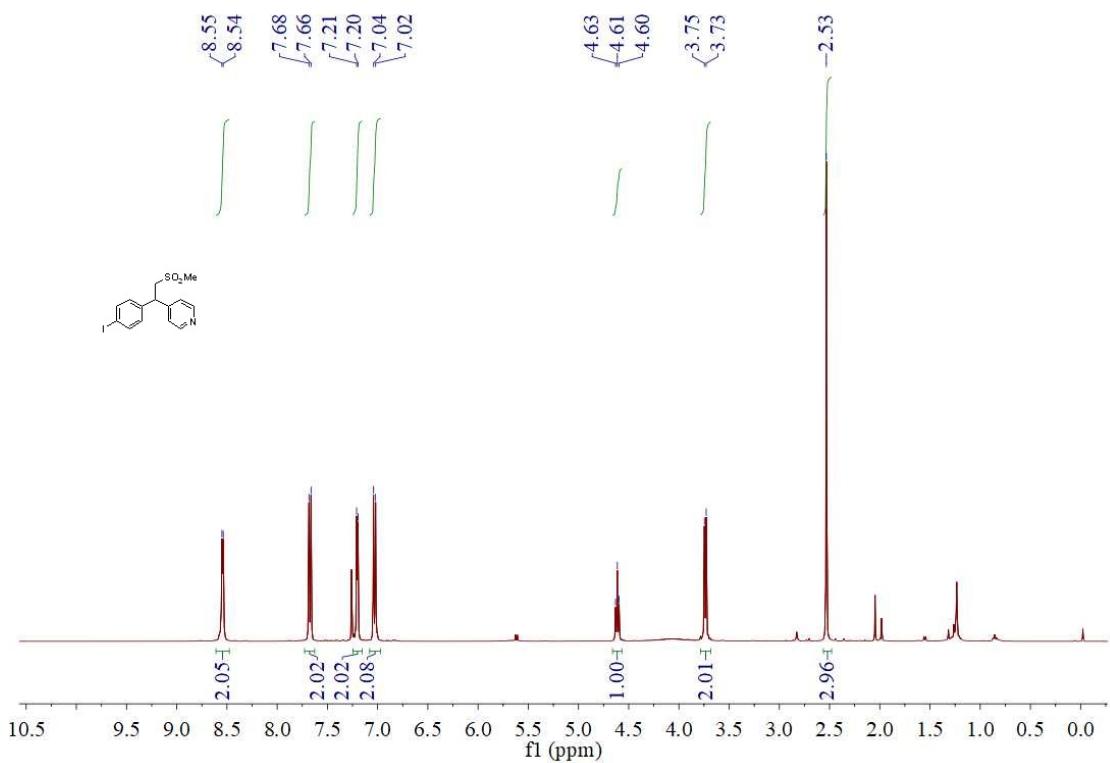
7; ^1H NMR (600 MHz, CDCl_3)



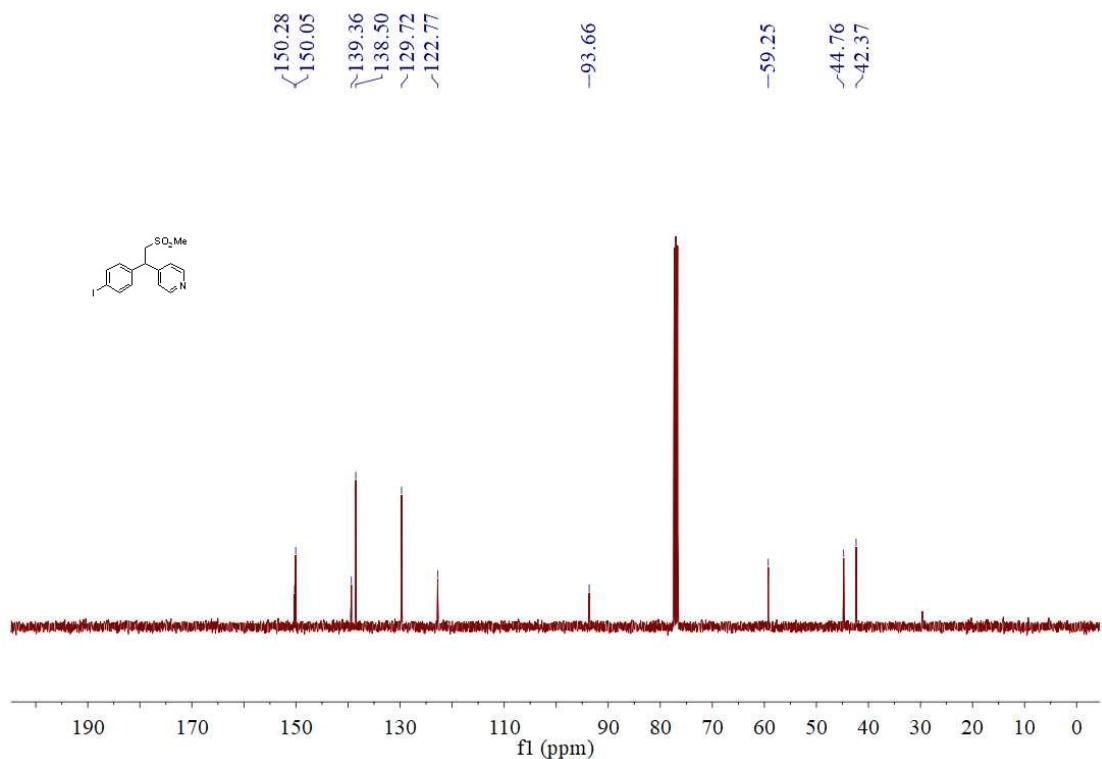
7; ^{13}C NMR (101 MHz, CDCl_3)



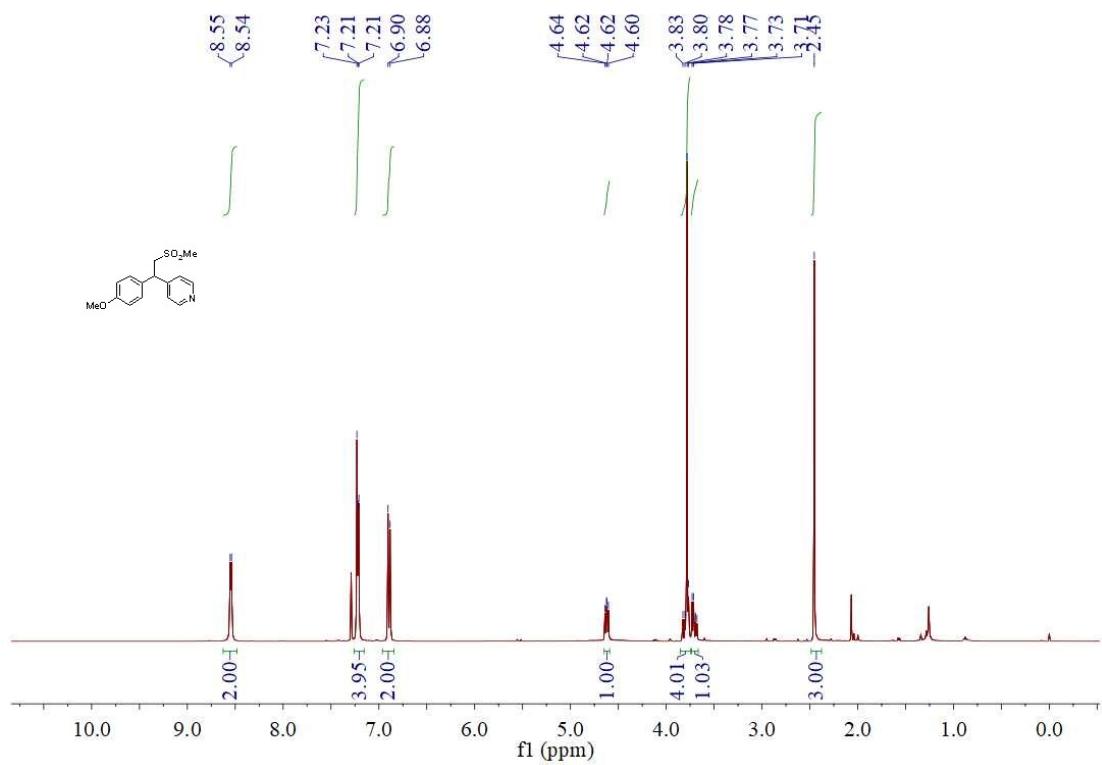
8; ^1H NMR (400 MHz, CDCl_3)



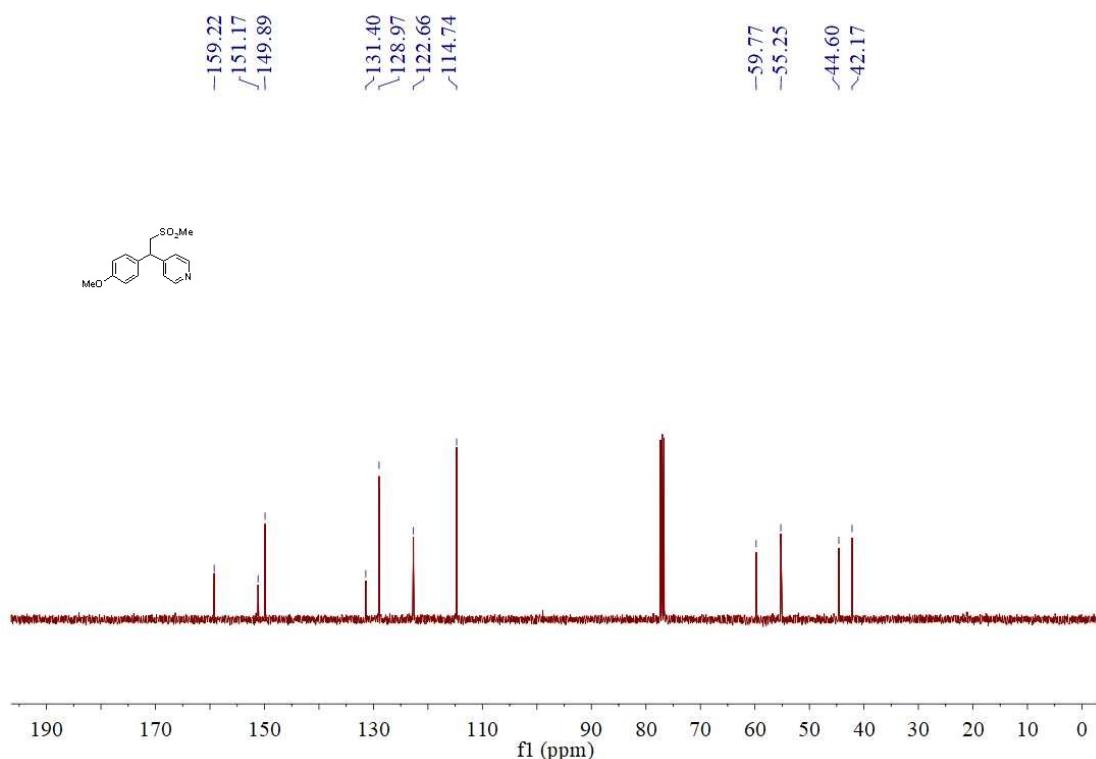
8; ^{13}C NMR (101 MHz, CDCl_3)



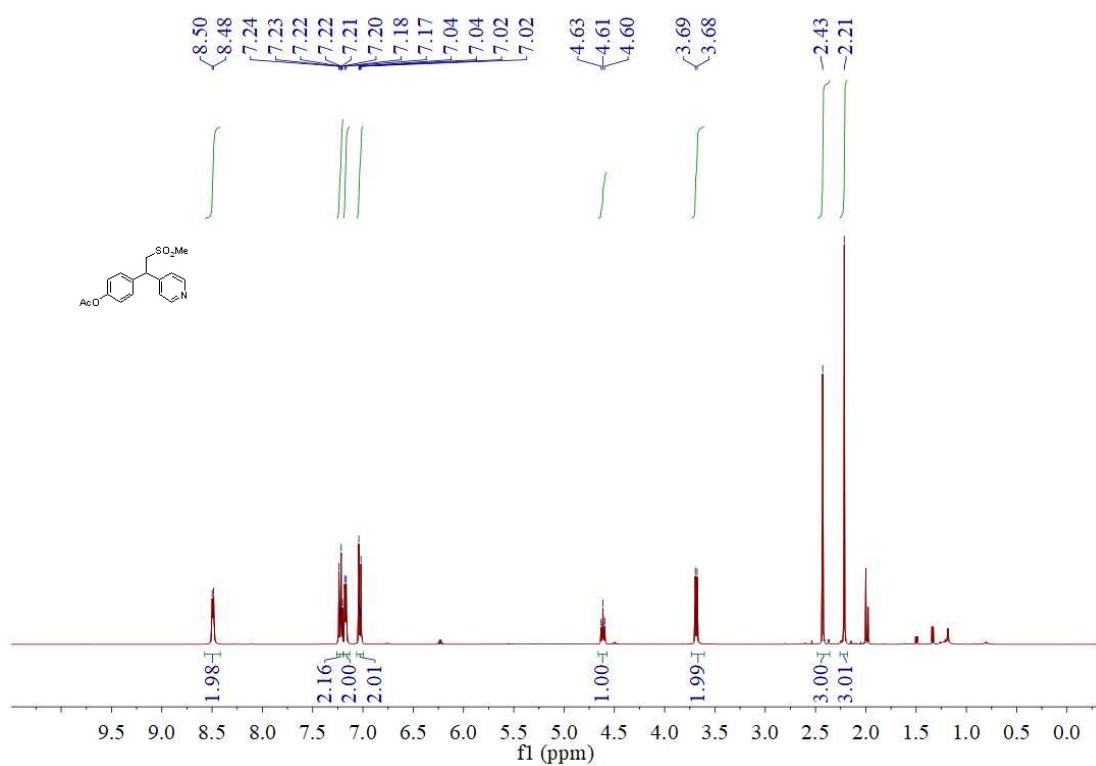
9; ^1H NMR (400 MHz, CDCl_3)



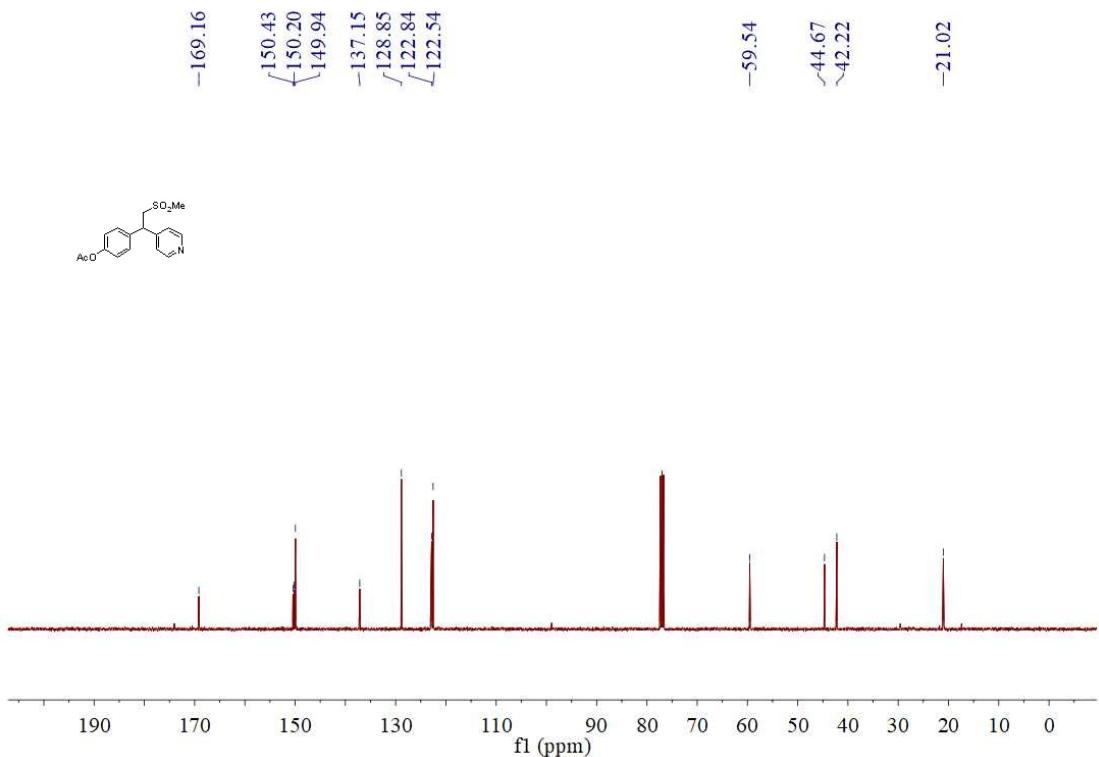
9; ^{13}C NMR (101 MHz, CDCl_3)



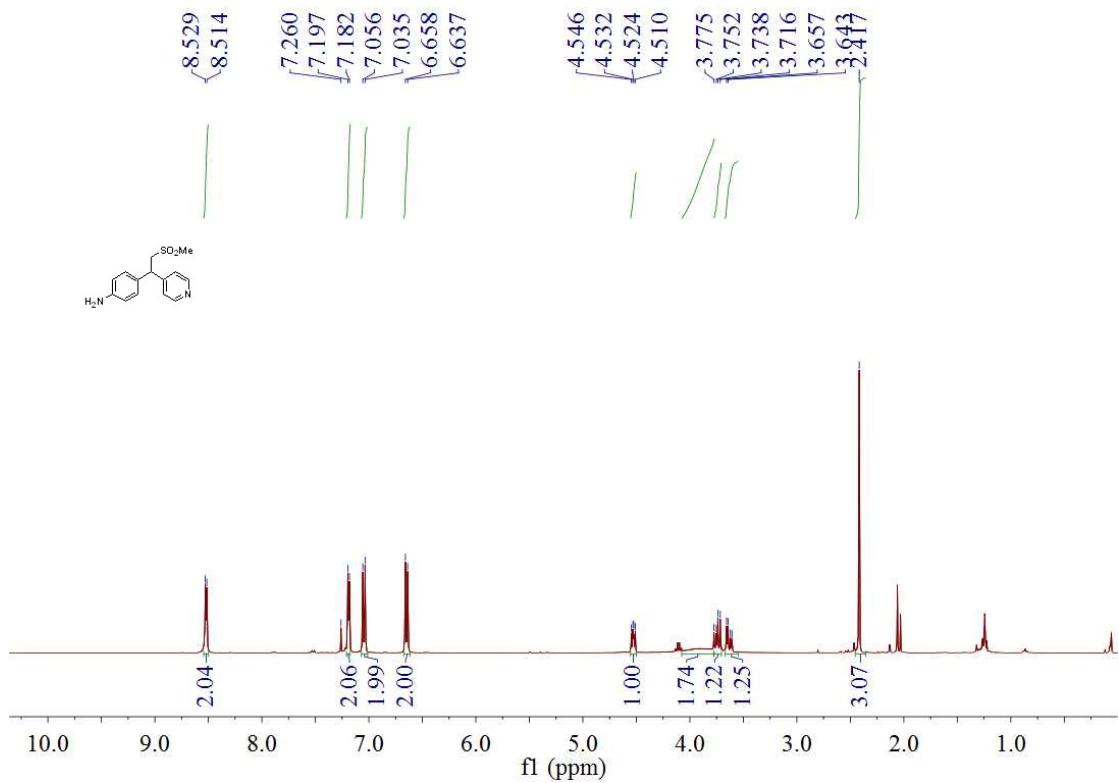
10; ^1H NMR (400 MHz, CDCl_3)



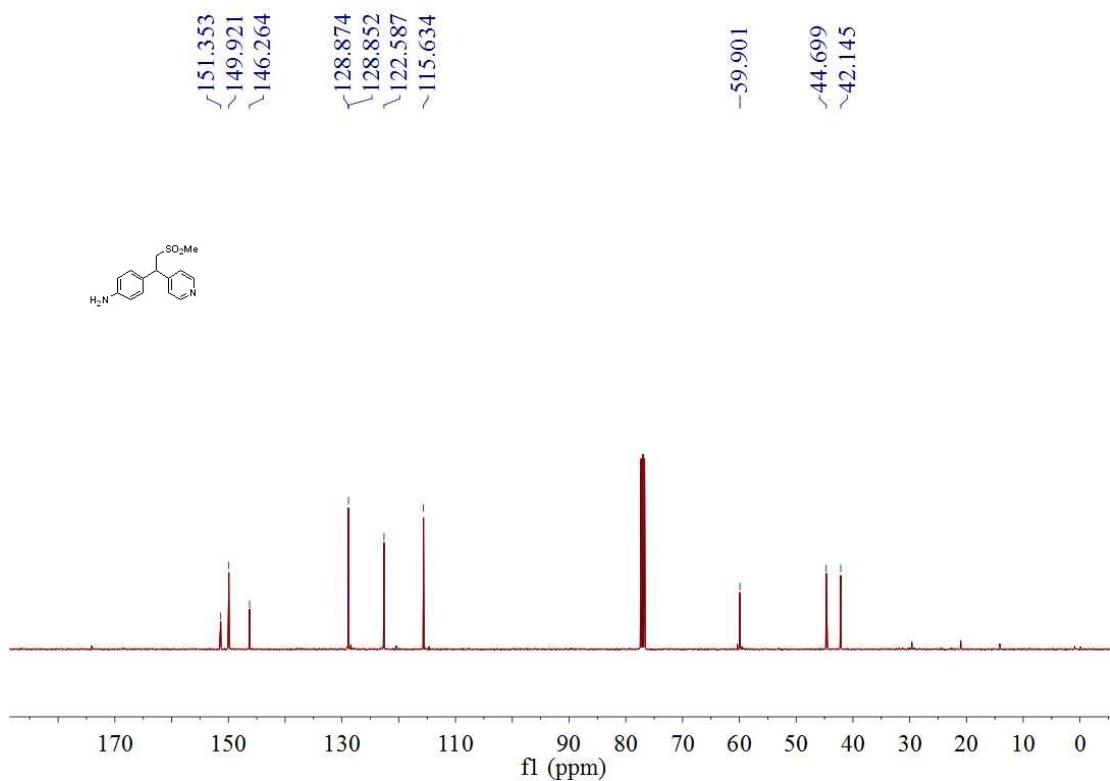
10; ^{13}C NMR (101 MHz, CDCl_3)



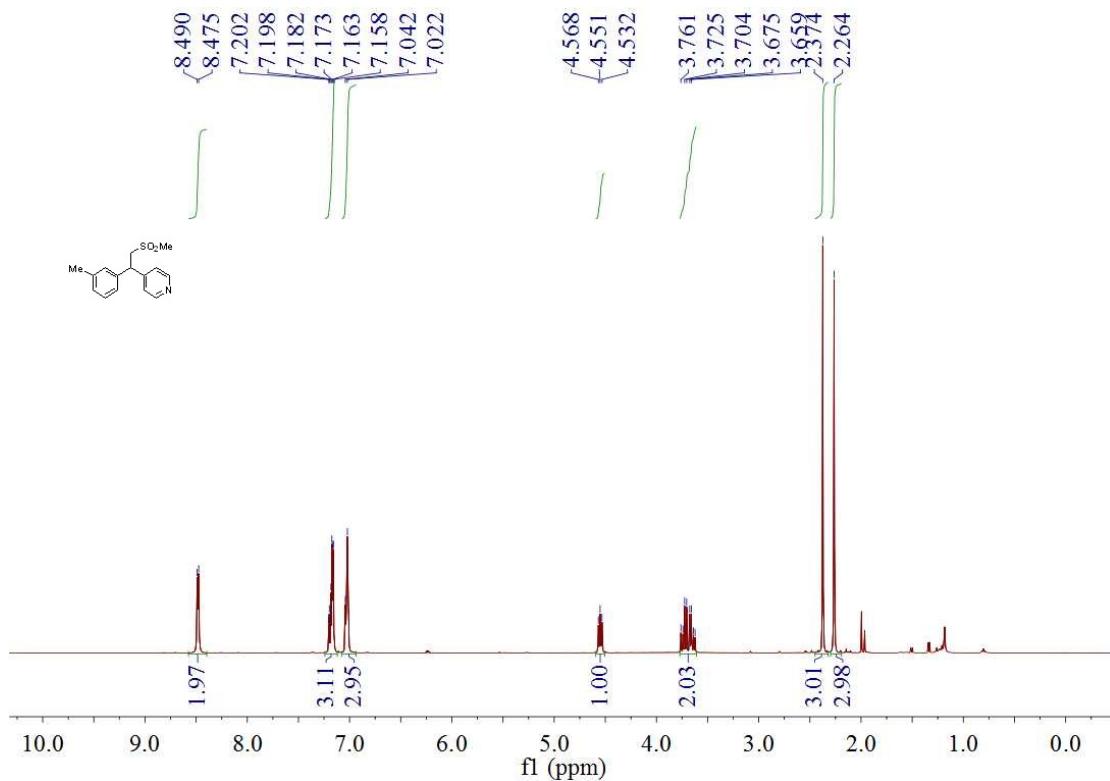
11; ^1H NMR (400 MHz, CDCl_3)



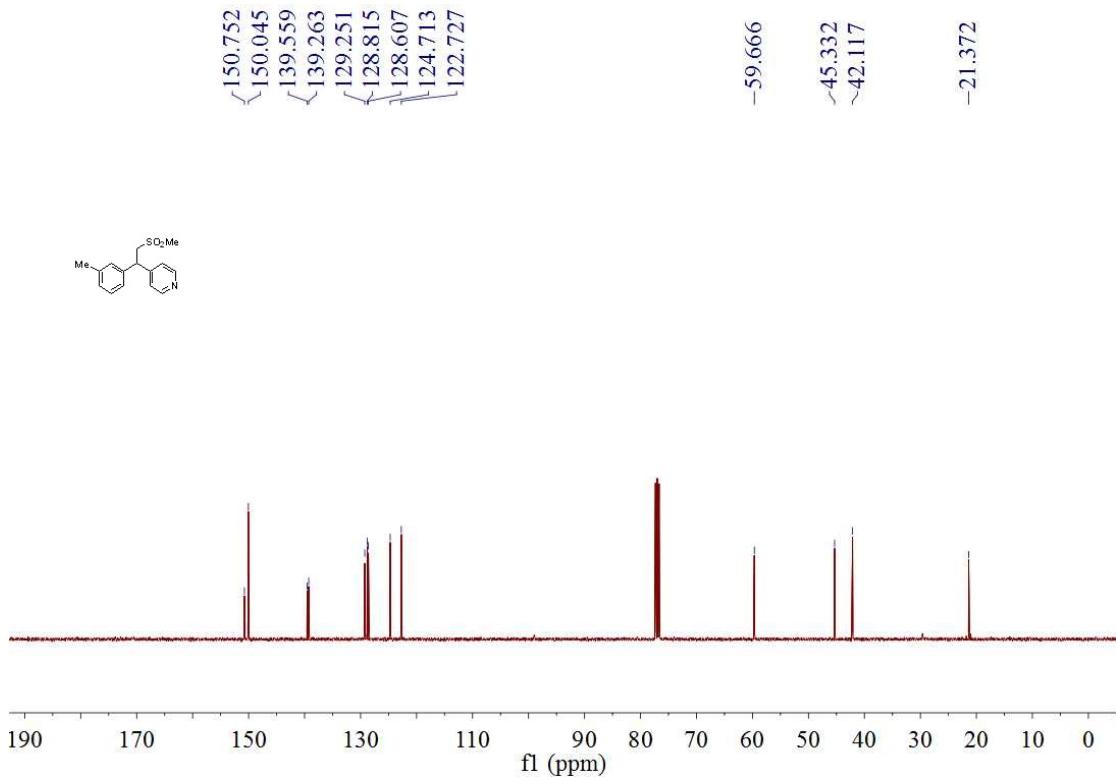
11; ^{13}C NMR (101 MHz, CDCl_3)



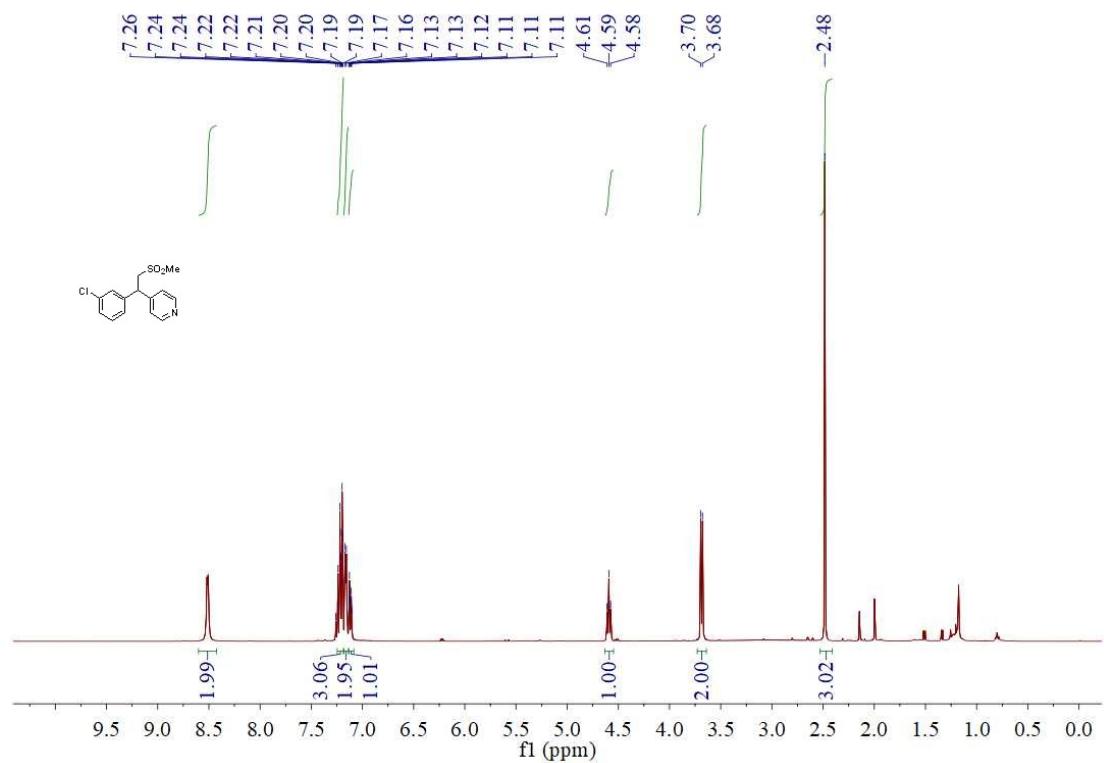
12; ^1H NMR (400 MHz, CDCl_3)



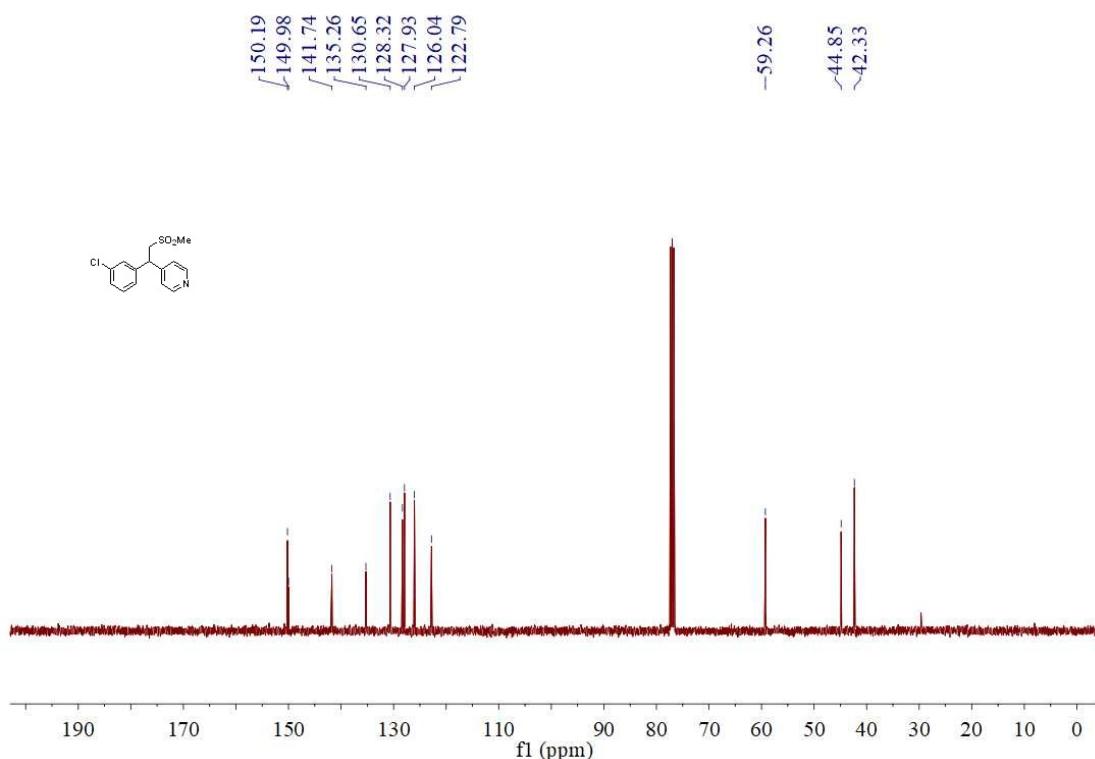
12; ^{13}C NMR (101 MHz, CDCl_3)



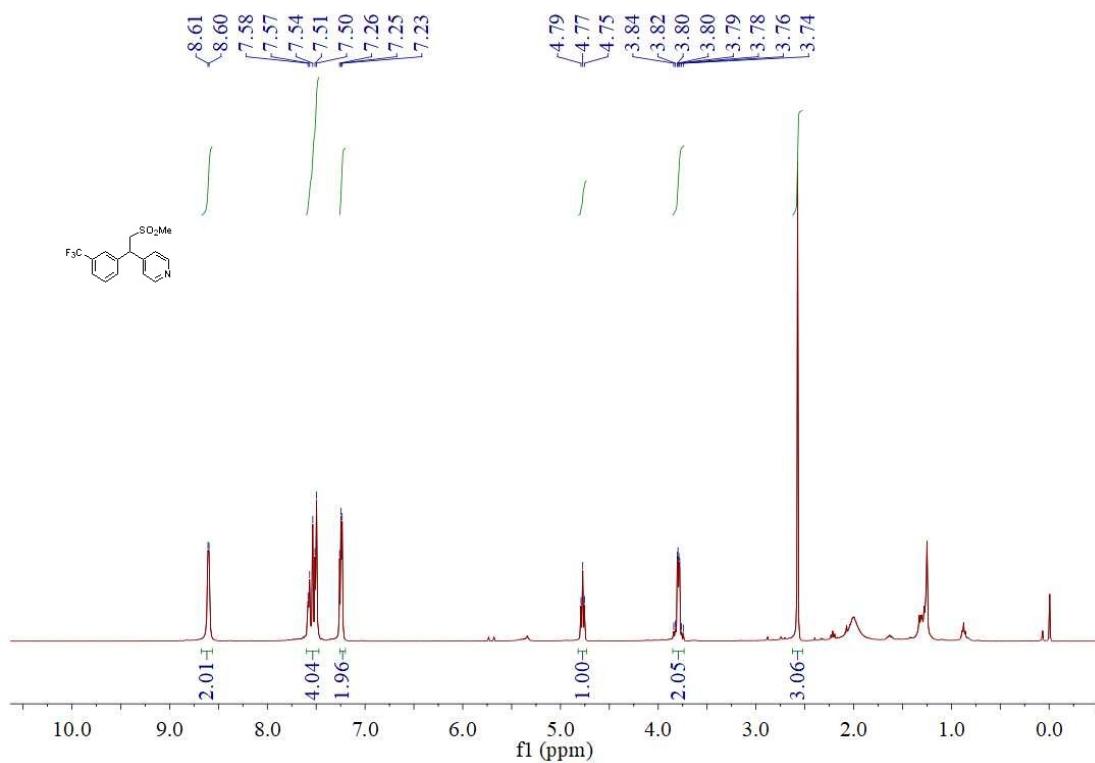
13; ^1H NMR (400 MHz, CDCl_3)



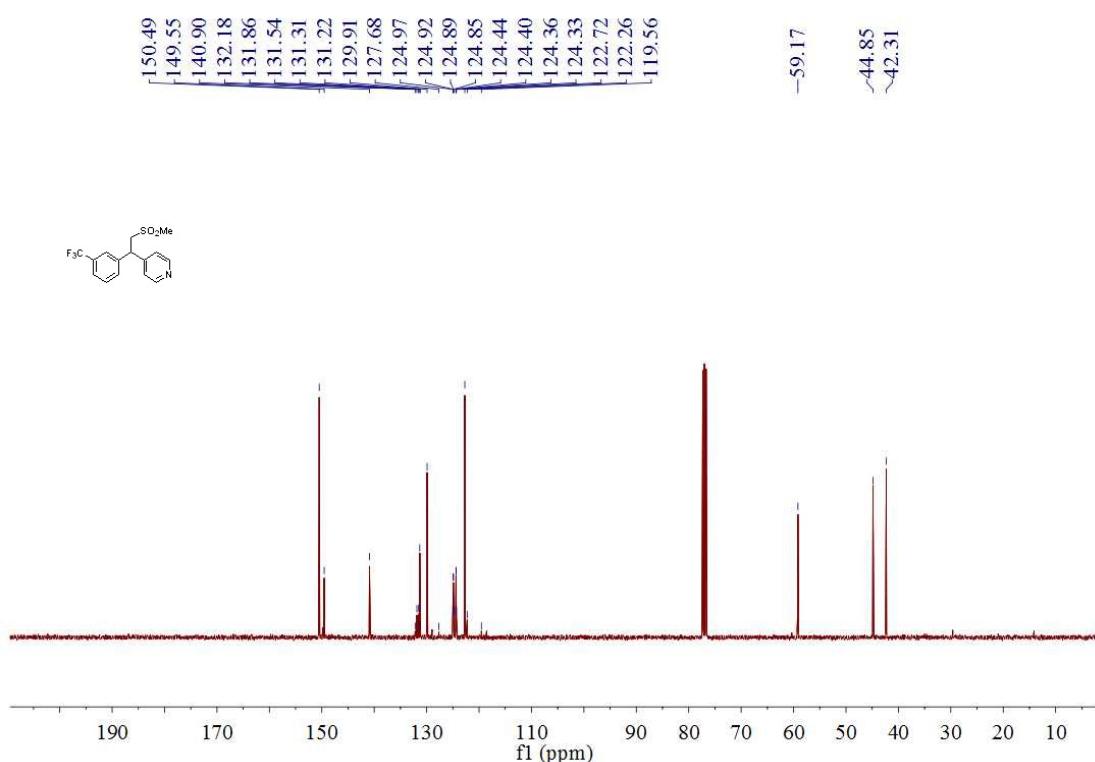
13; ^{13}C NMR (101 MHz, CDCl_3)



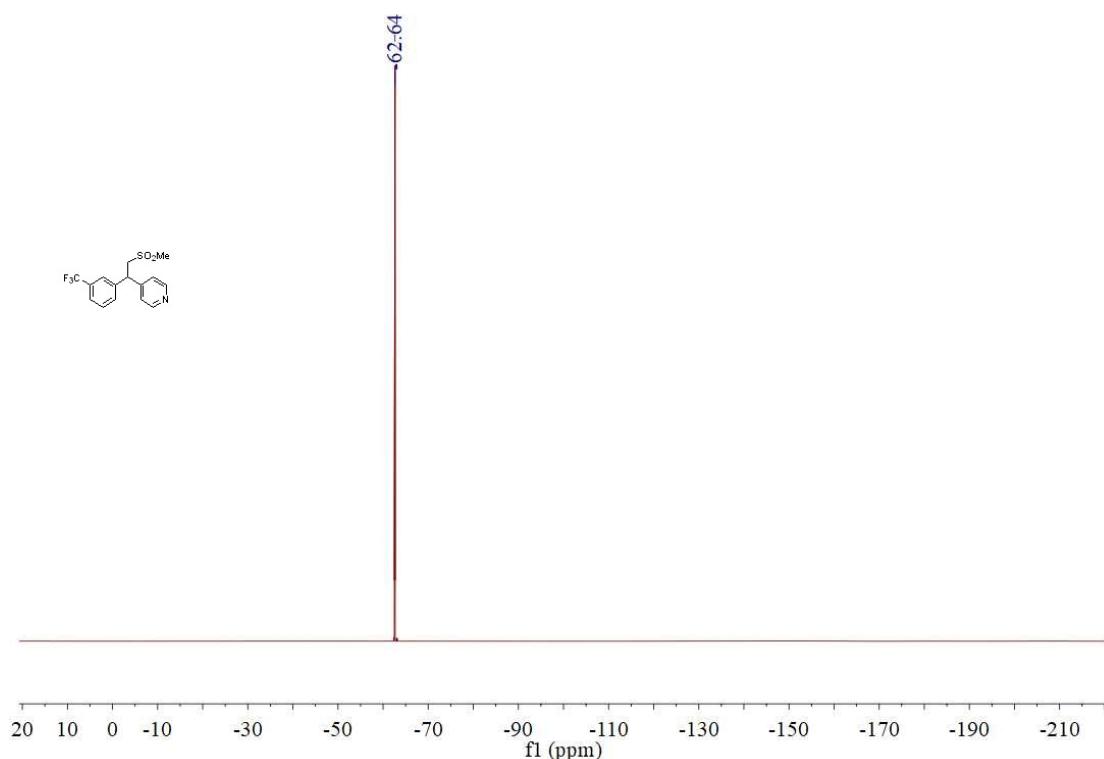
14; ^1H NMR (400 MHz, CDCl_3)



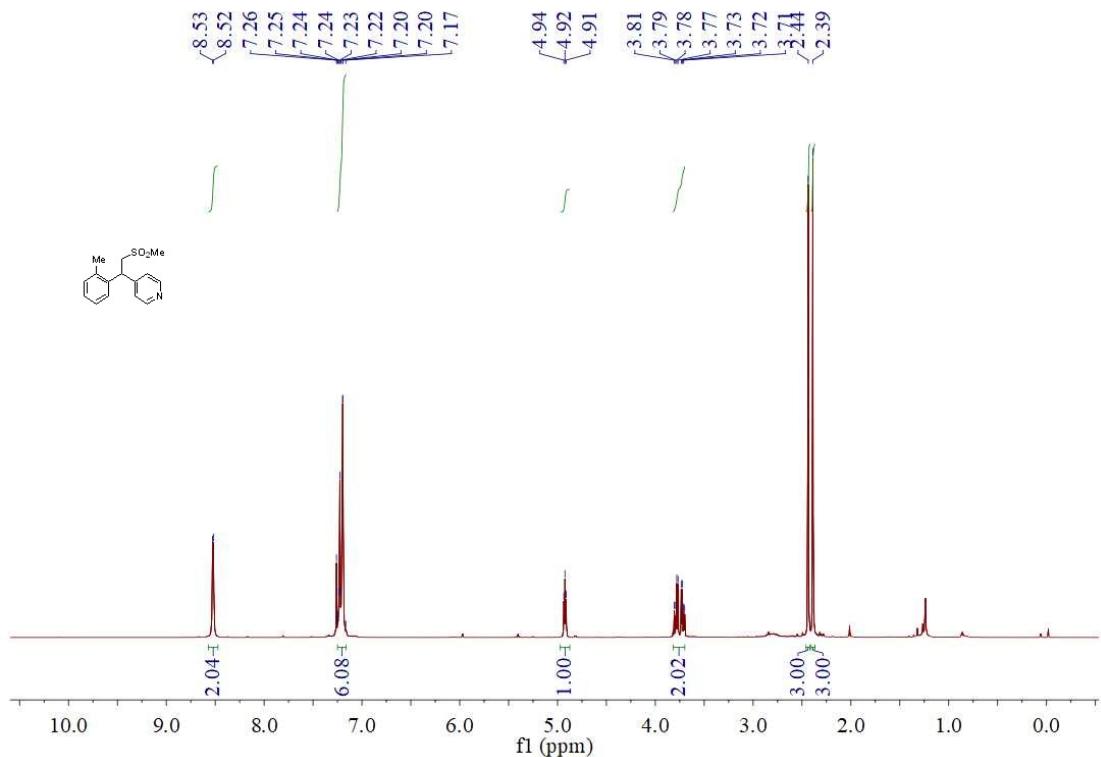
14; ^{13}C NMR (101 MHz, CDCl_3)



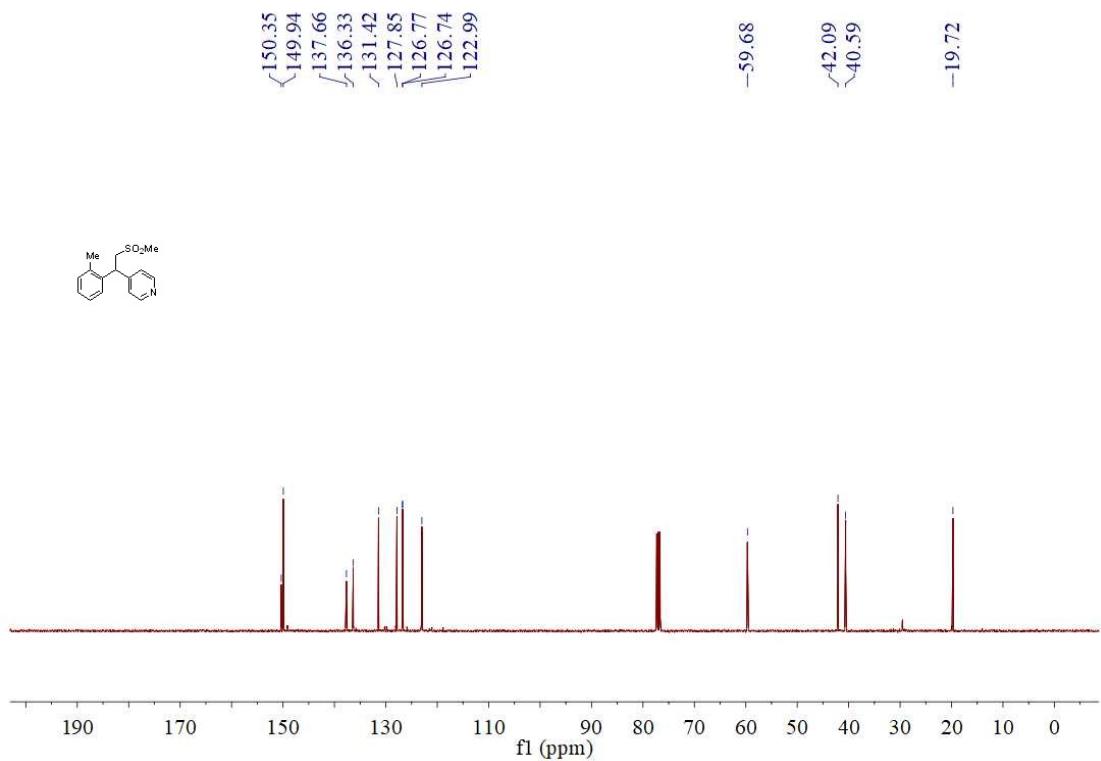
14; ^{19}F NMR (377 MHz, CDCl_3)



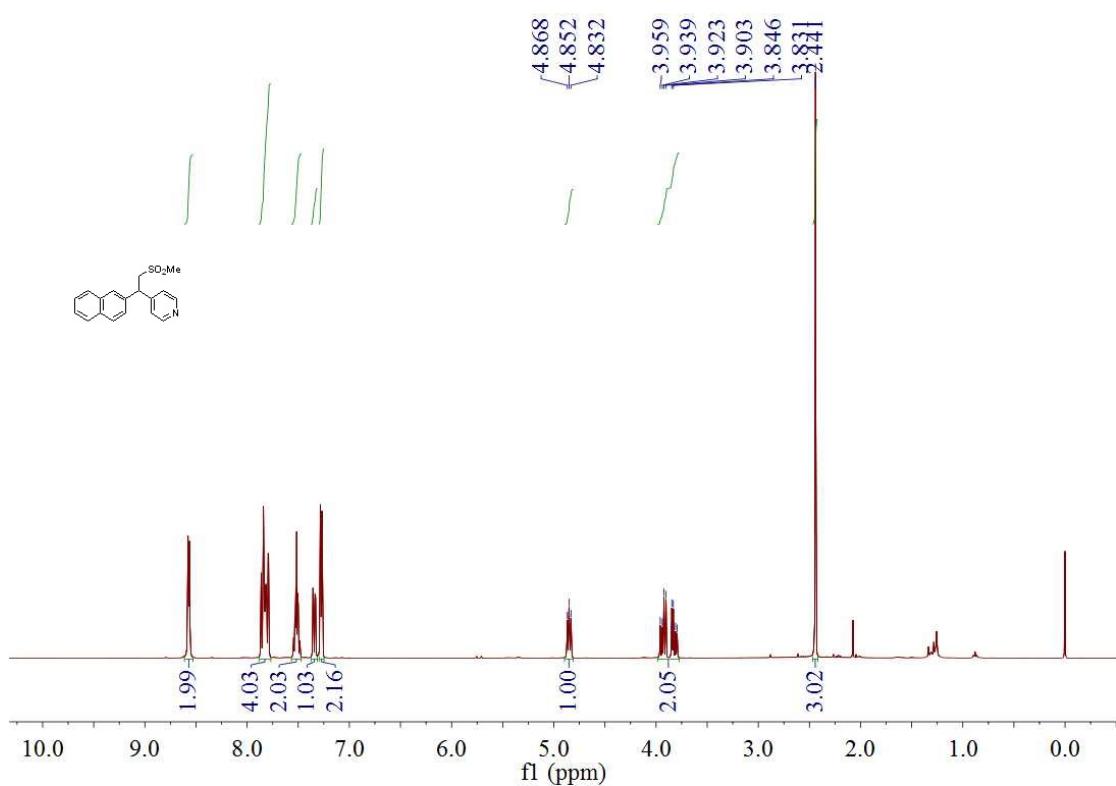
15; ^1H NMR (600 MHz, CDCl_3)



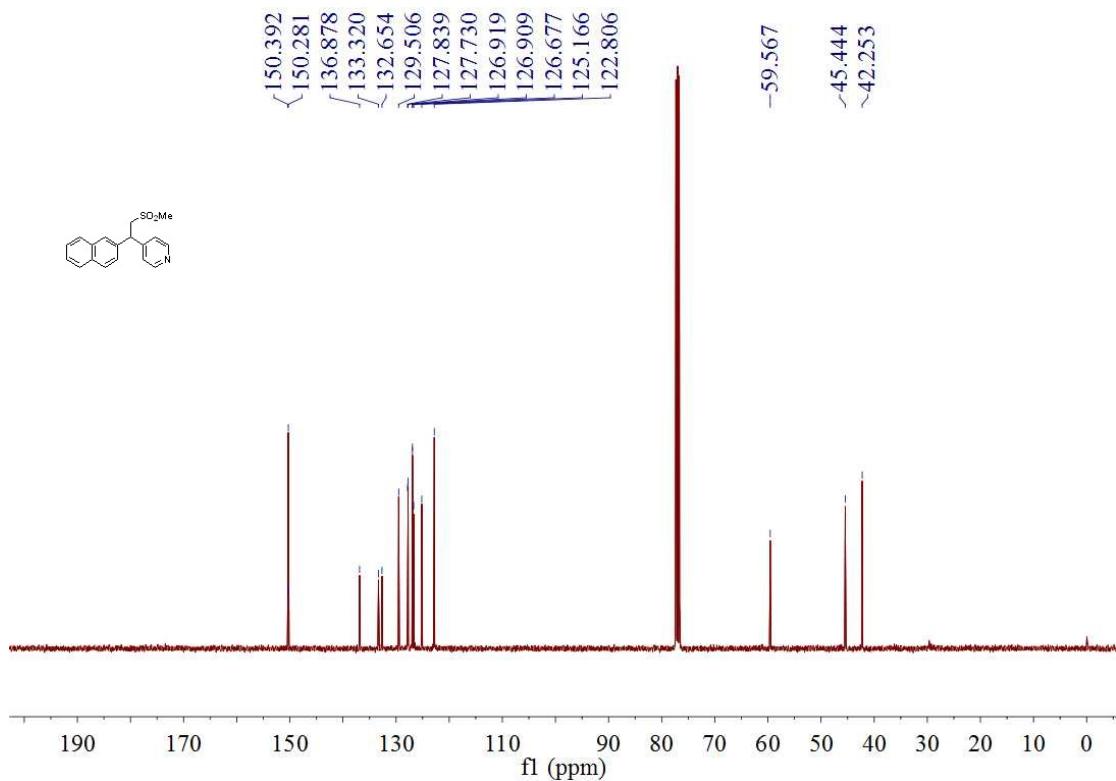
15; ^{13}C NMR (101 MHz, CDCl_3)



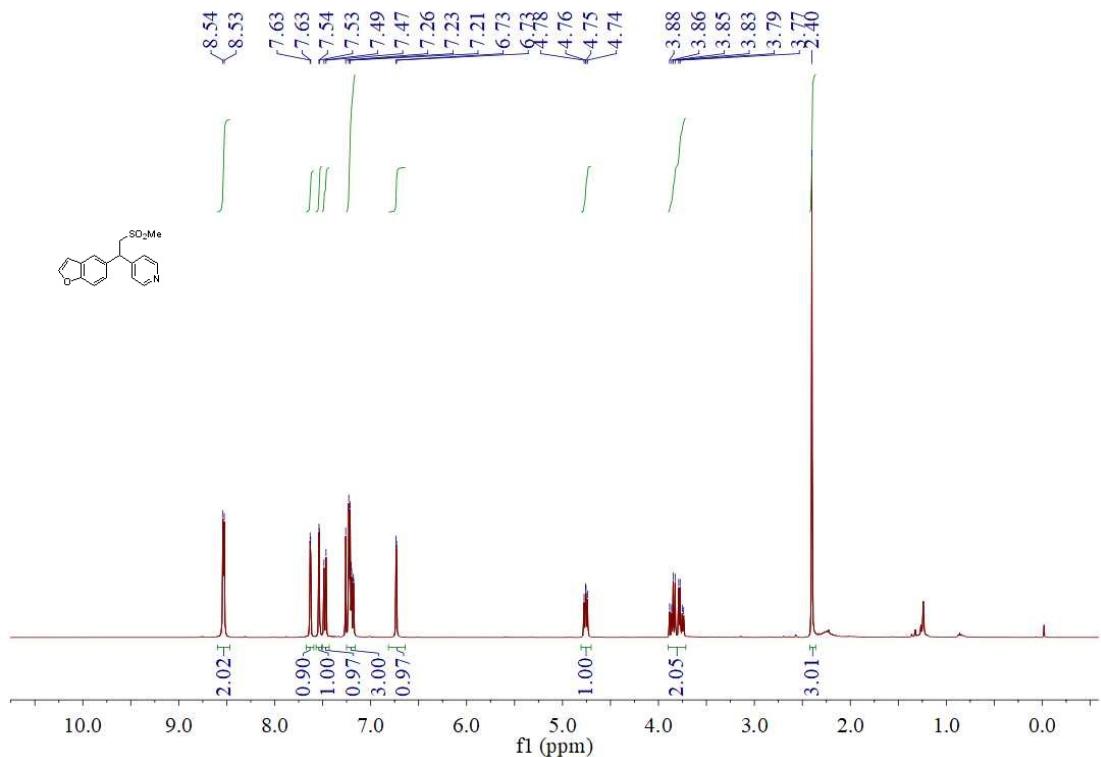
16; ^1H NMR (400 MHz, CDCl_3)



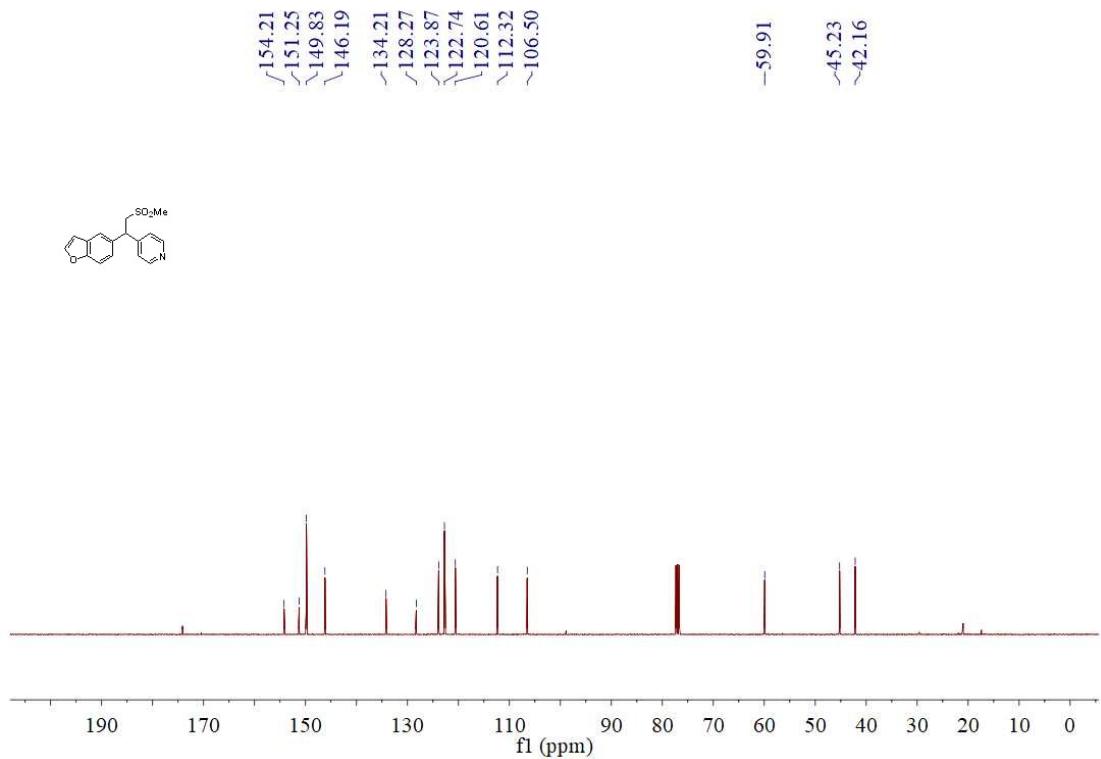
16; ^{13}C NMR (101 MHz, CDCl_3)



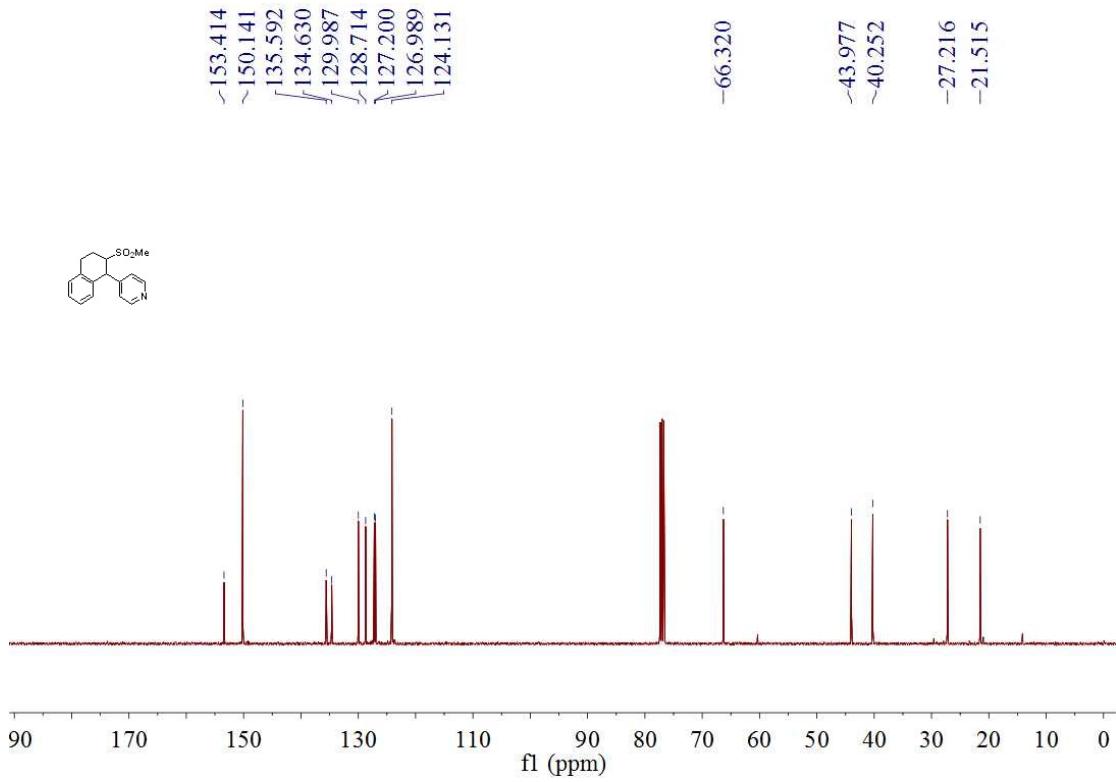
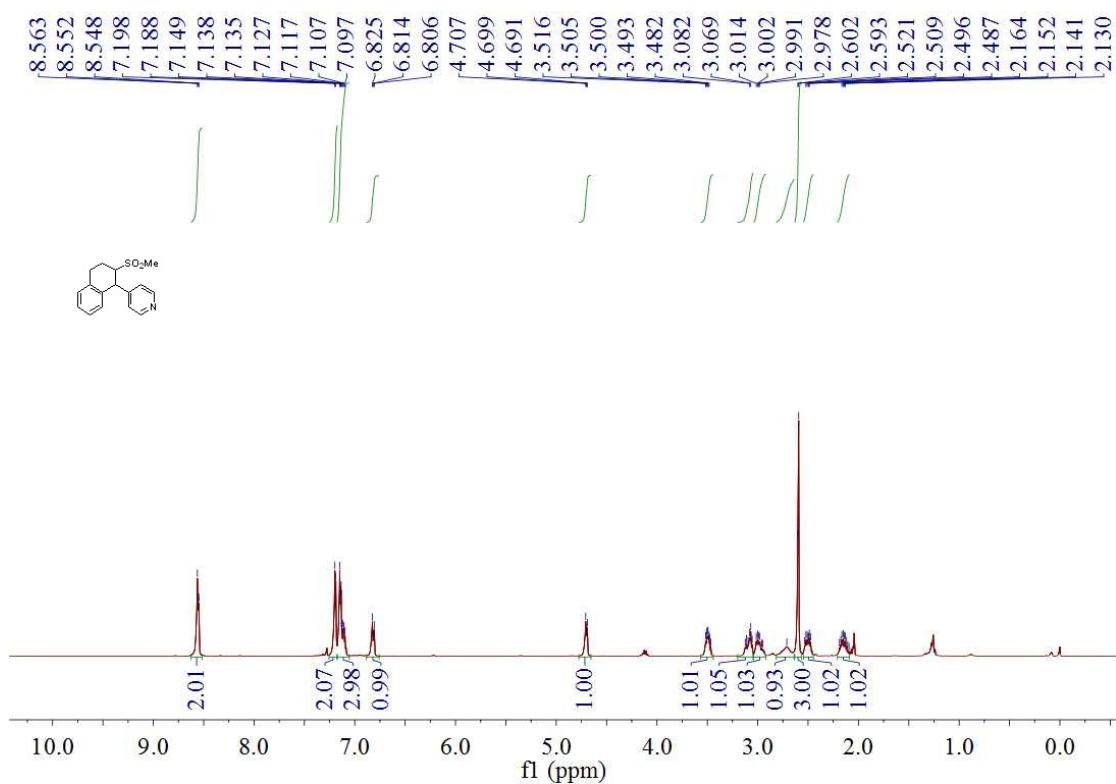
17; ^1H NMR (400 MHz, CDCl_3)



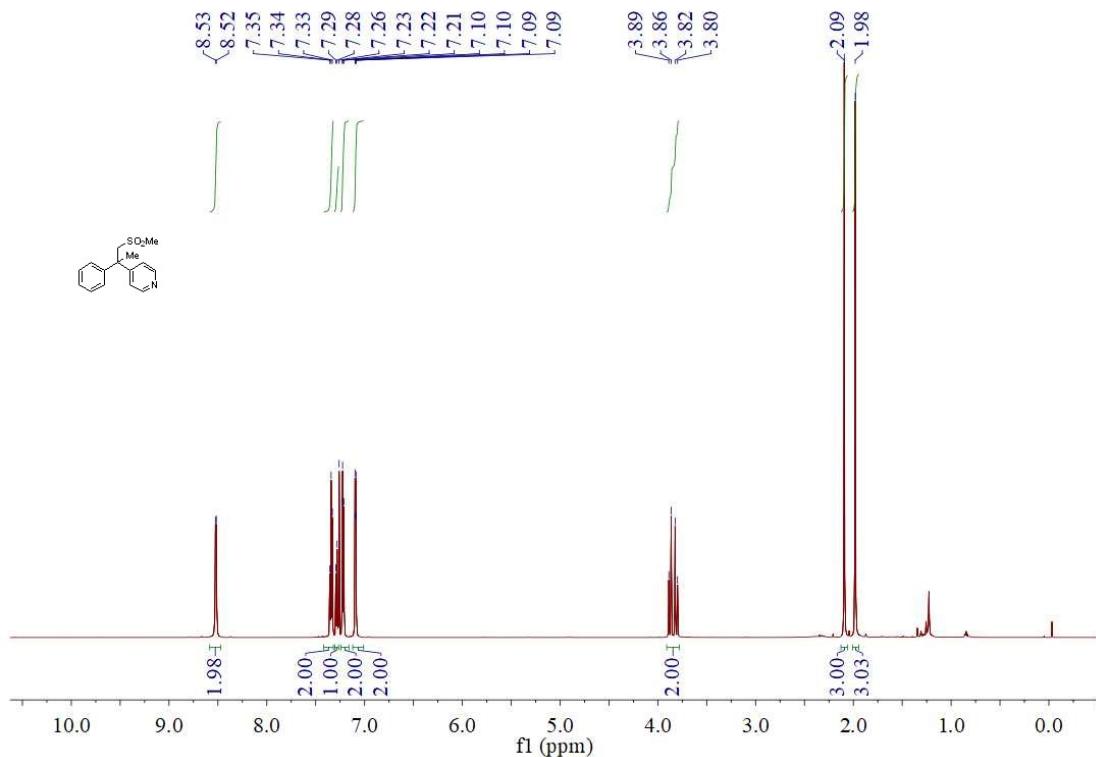
17; ^{13}C NMR (101 MHz, CDCl_3)



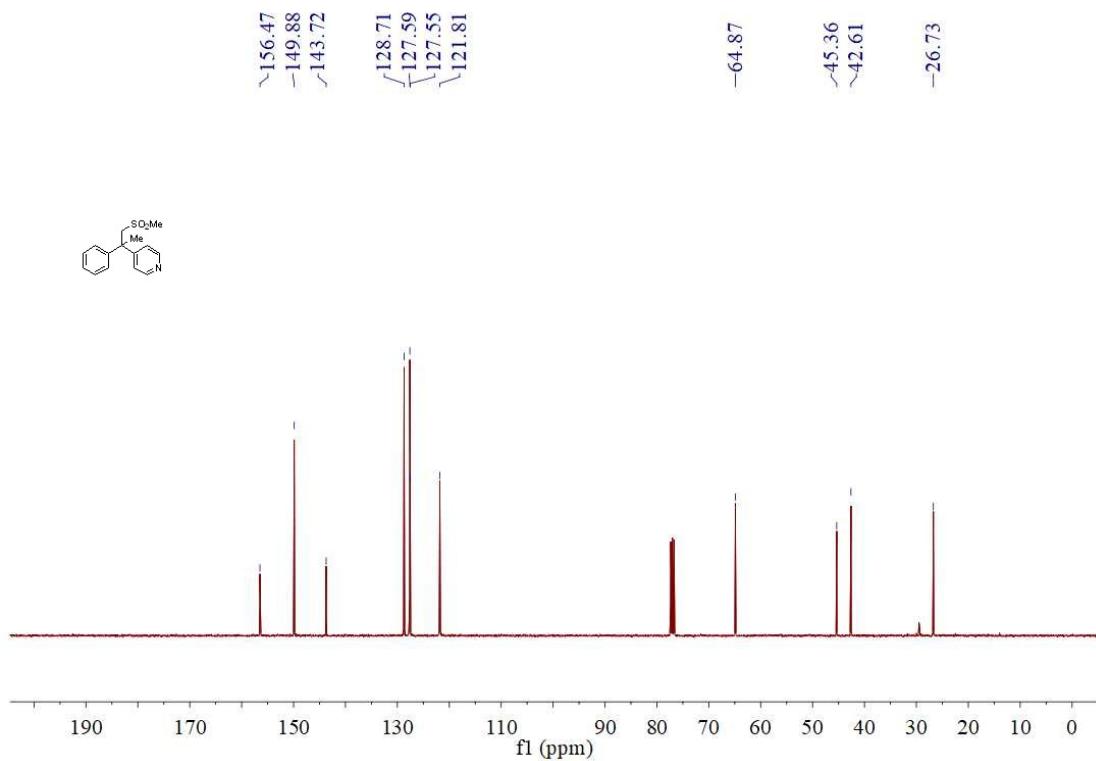
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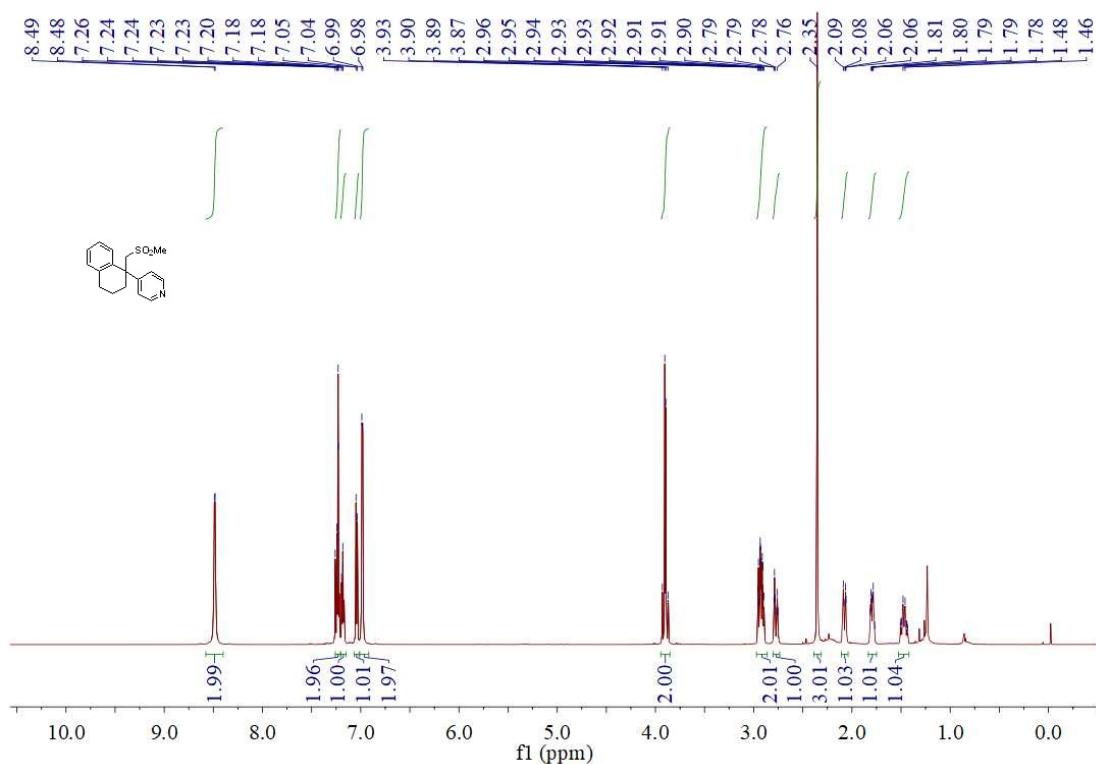
19; ^1H NMR (600 MHz, CDCl_3)



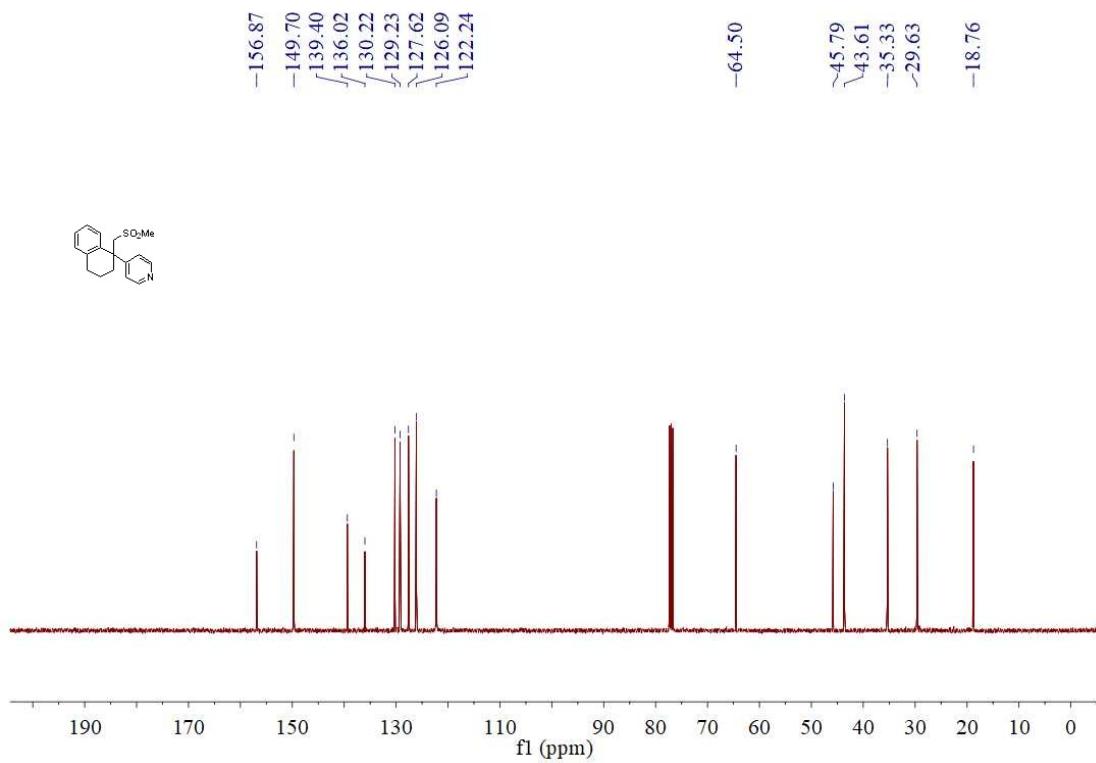
19; ^{13}C NMR (101 MHz, CDCl_3)



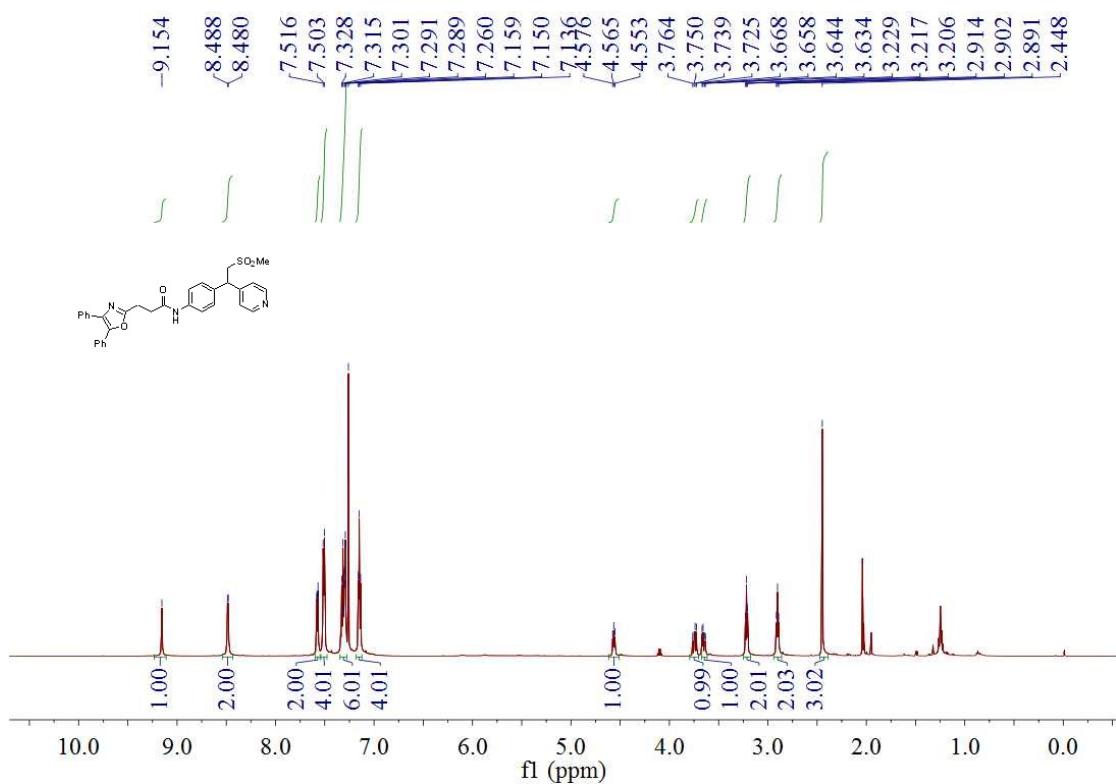
20; ^1H NMR (600 MHz, CDCl_3)



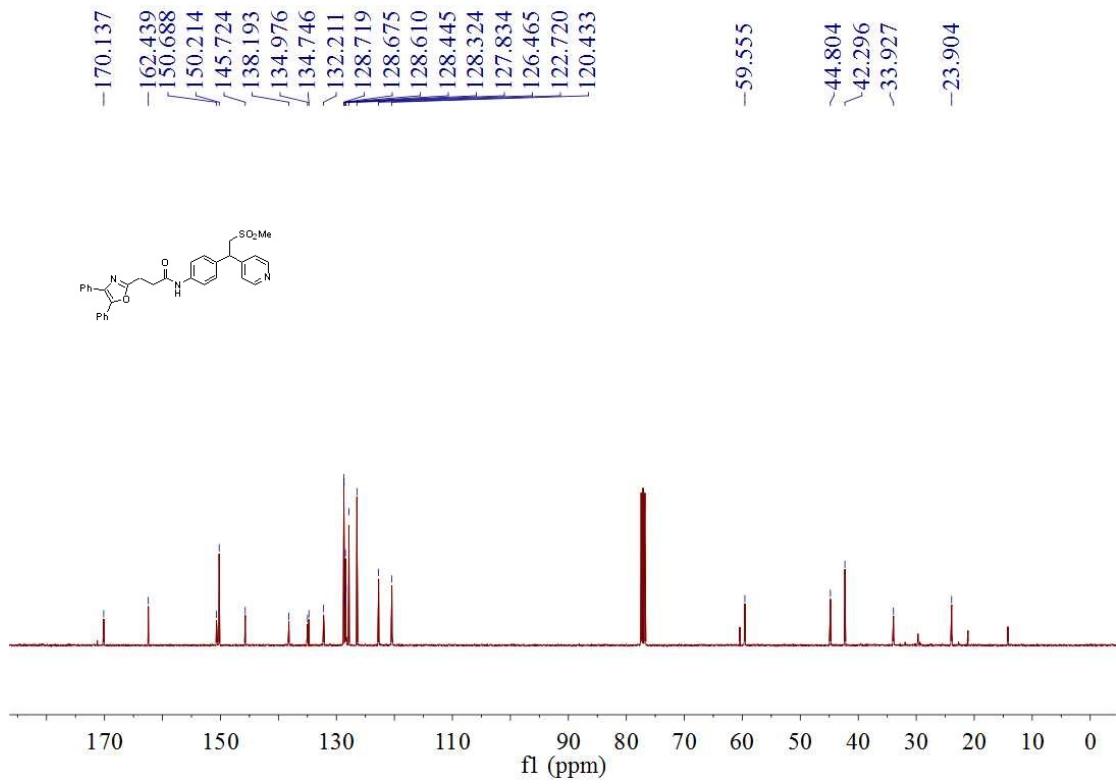
20; ^{13}C NMR (101 MHz, CDCl_3)



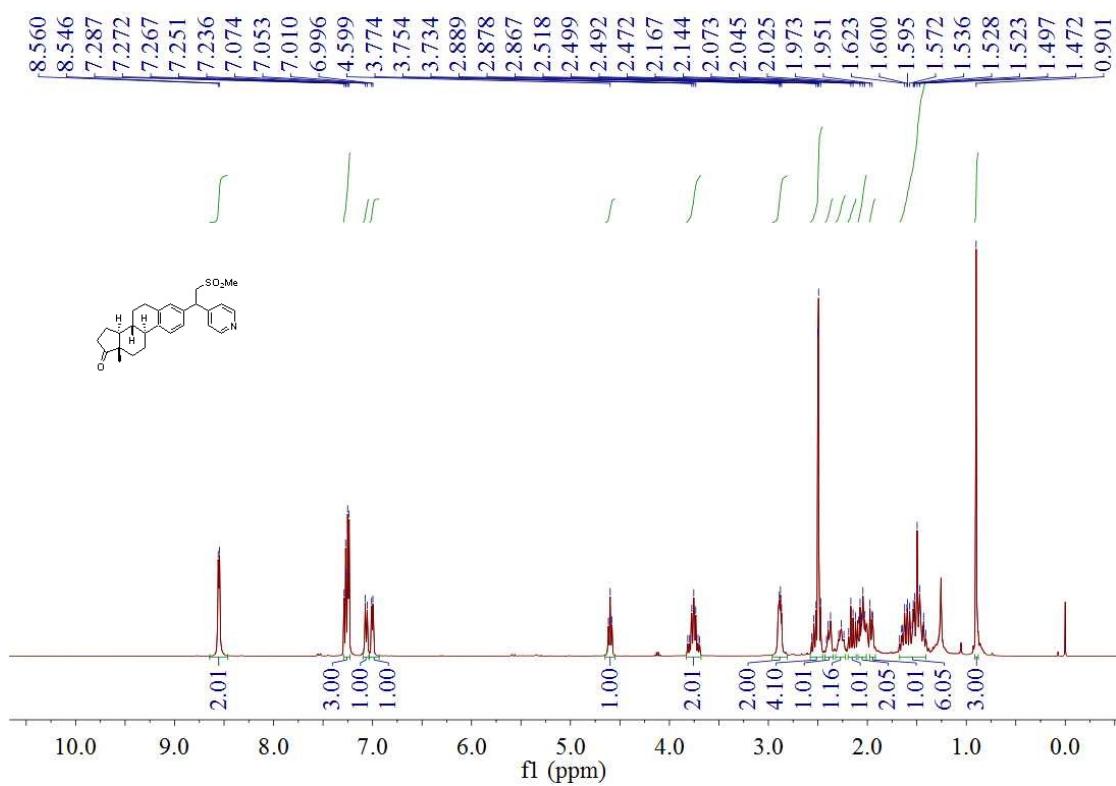
21; ^1H NMR (600 MHz, CDCl_3)



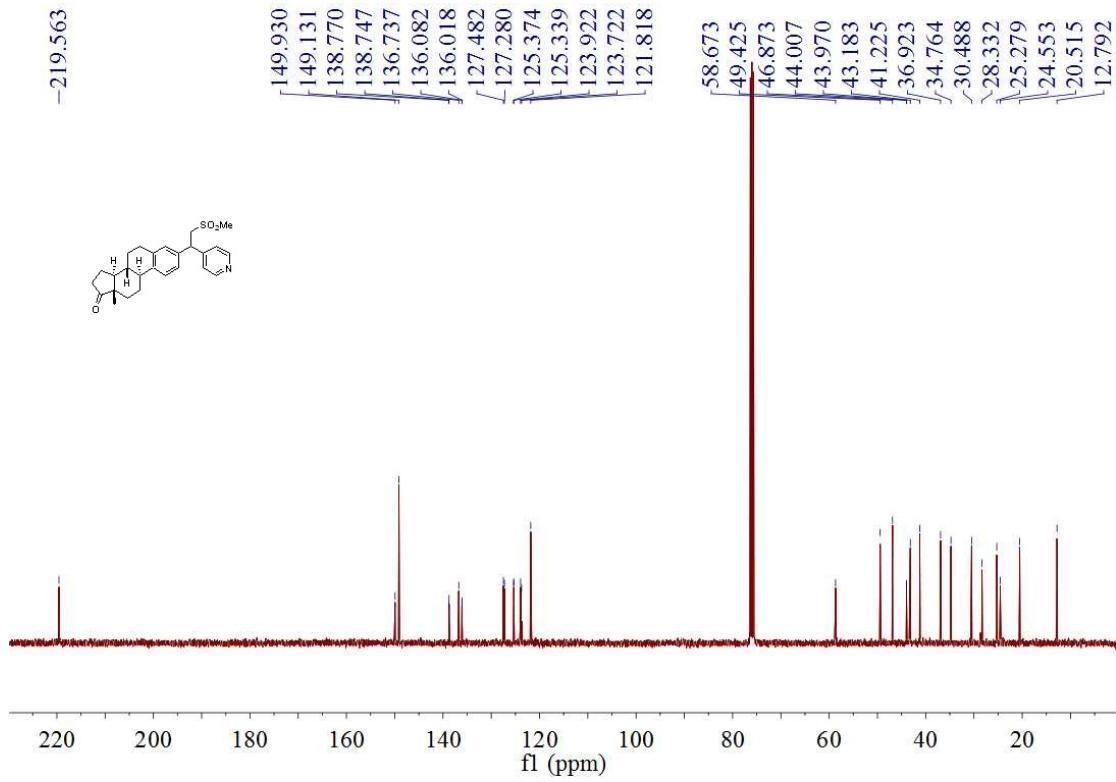
21; ^{13}C NMR (101 MHz, CDCl_3)



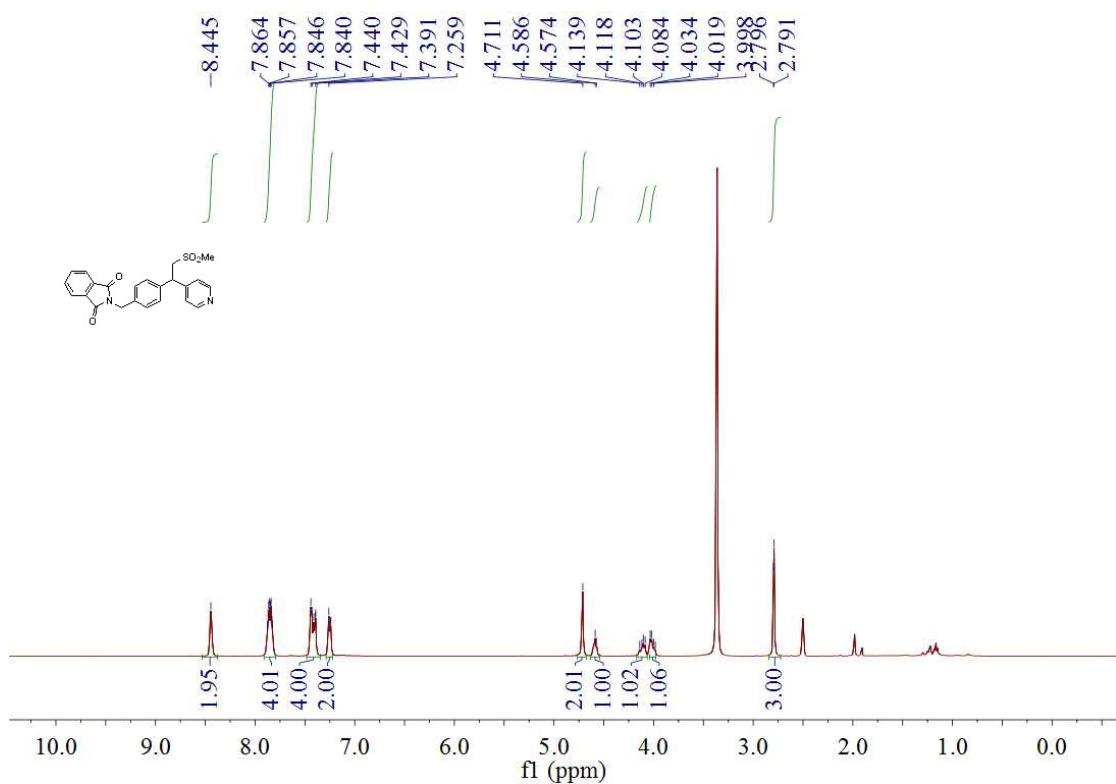
22; ^1H NMR (400 MHz, CDCl_3)



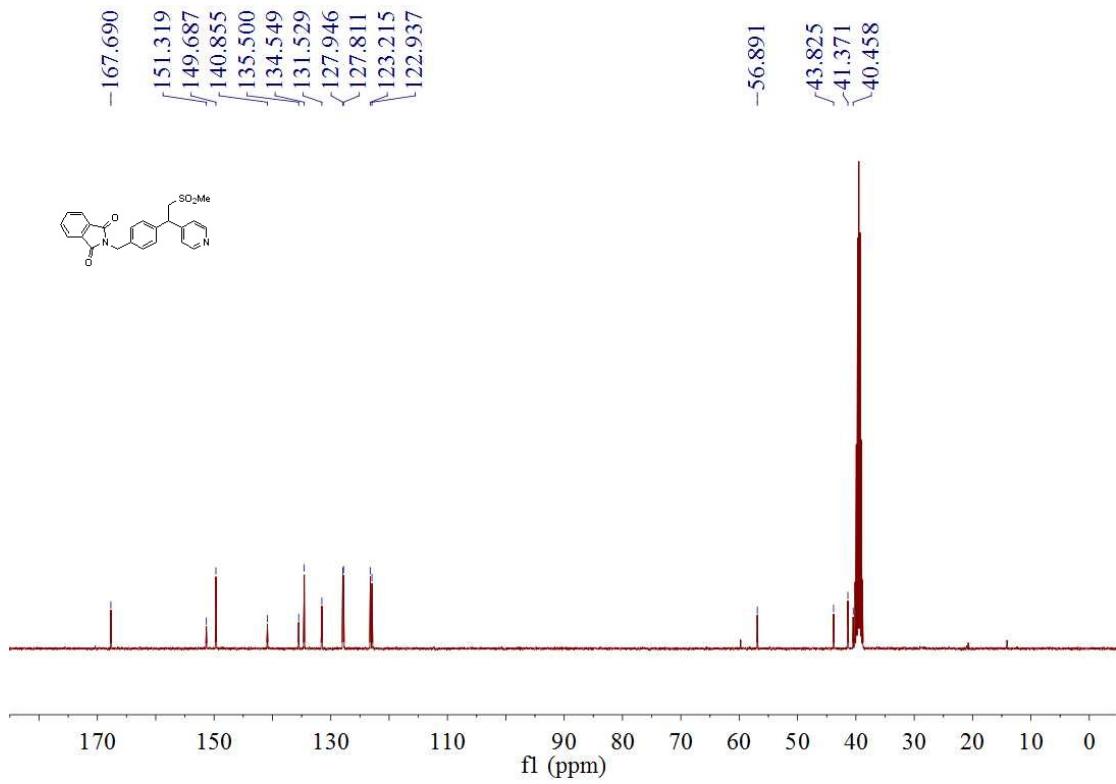
22; ^{13}C NMR (101 MHz, CDCl_3)



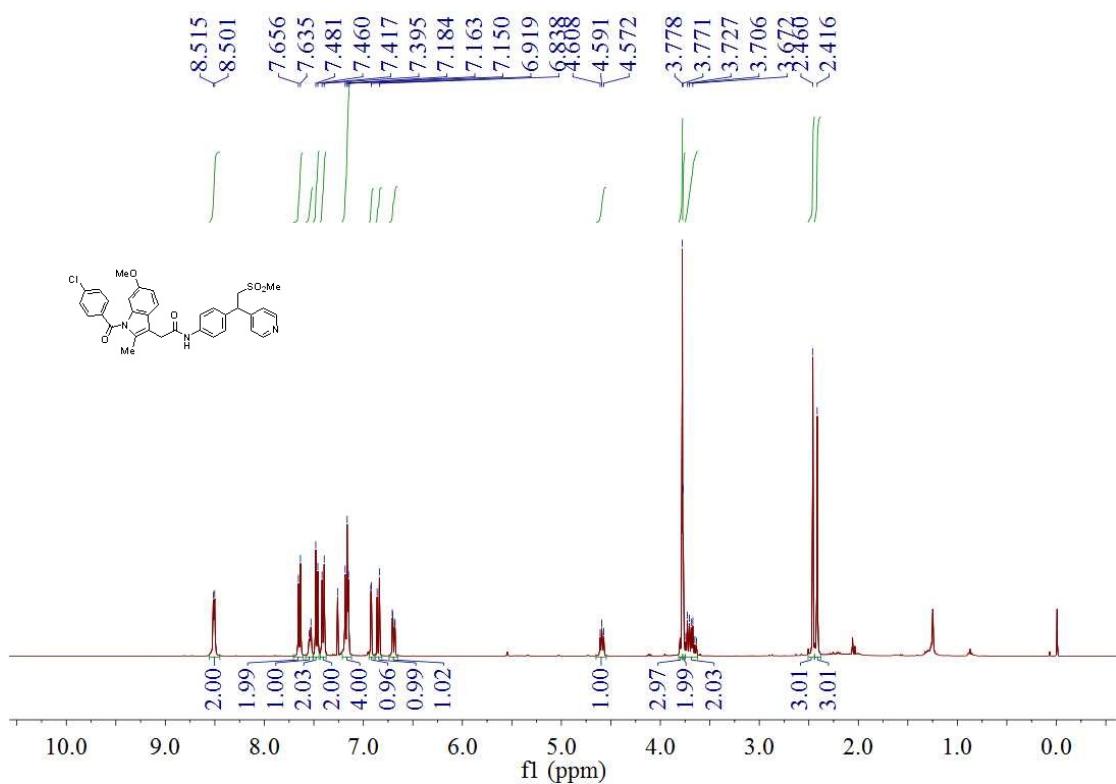
23; ^1H NMR (400 MHz, DMSO-d₆)



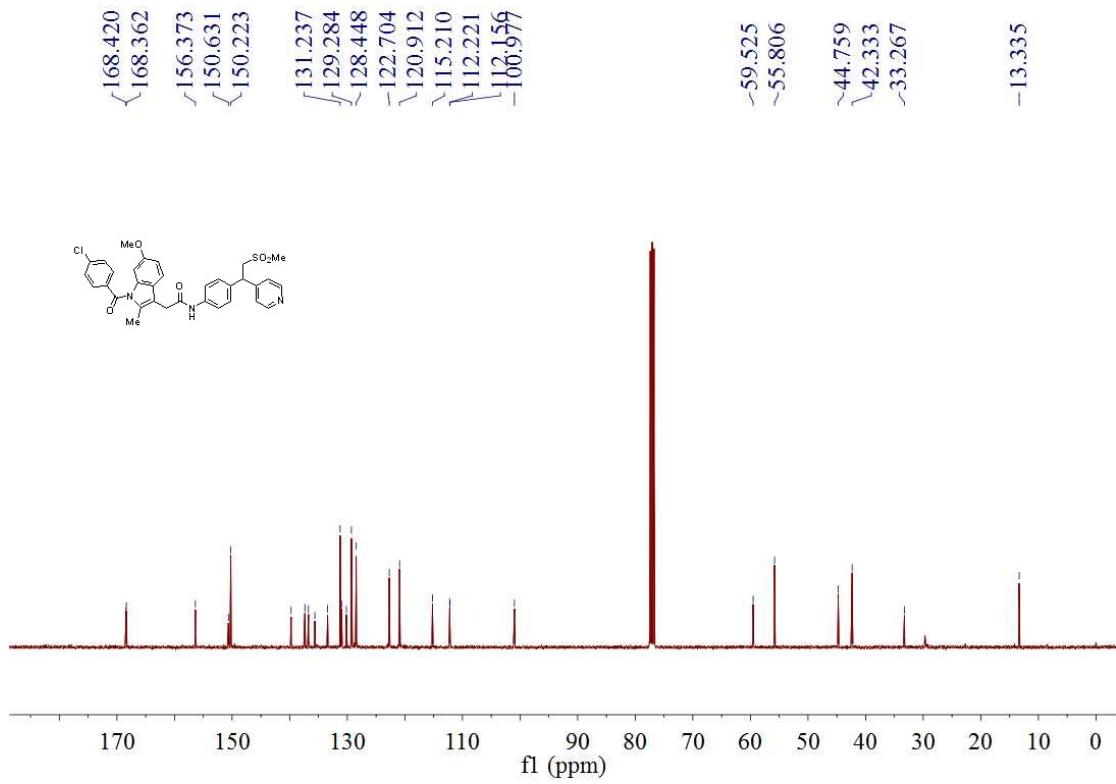
23; ^{13}C NMR (101 MHz, DMSO-d₆)



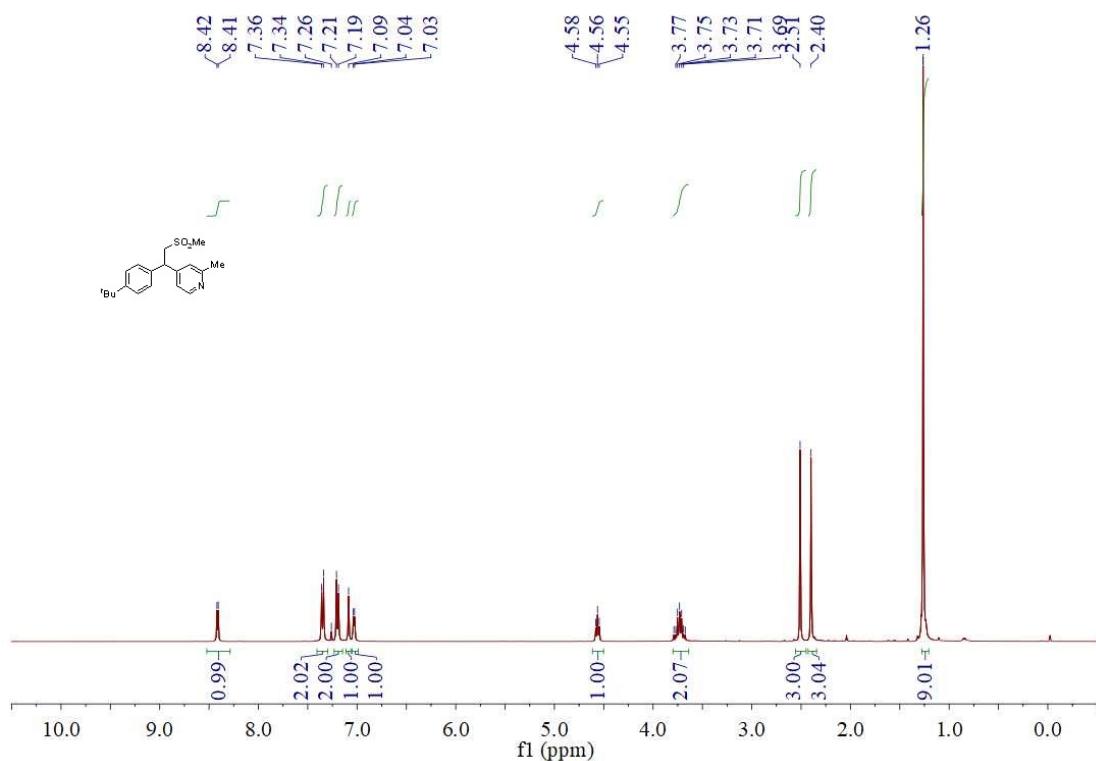
24; ^1H NMR (400 MHz, CDCl_3)



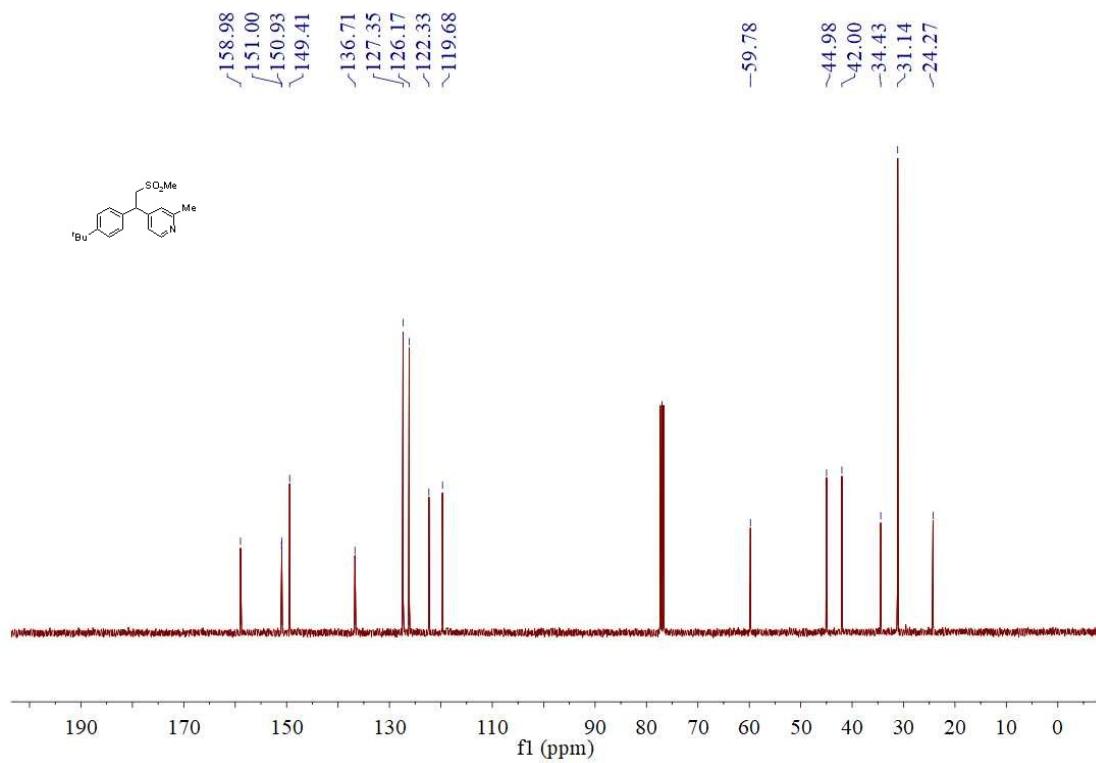
24; ^{13}C NMR (101 MHz, CDCl_3)



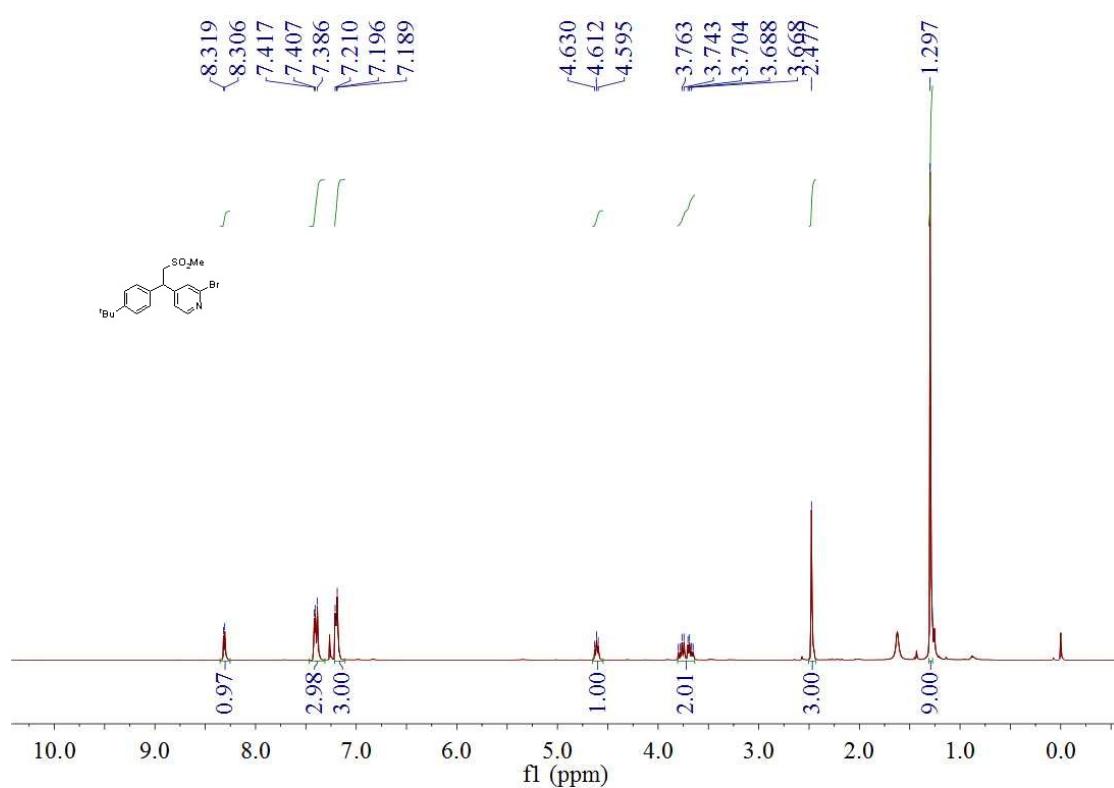
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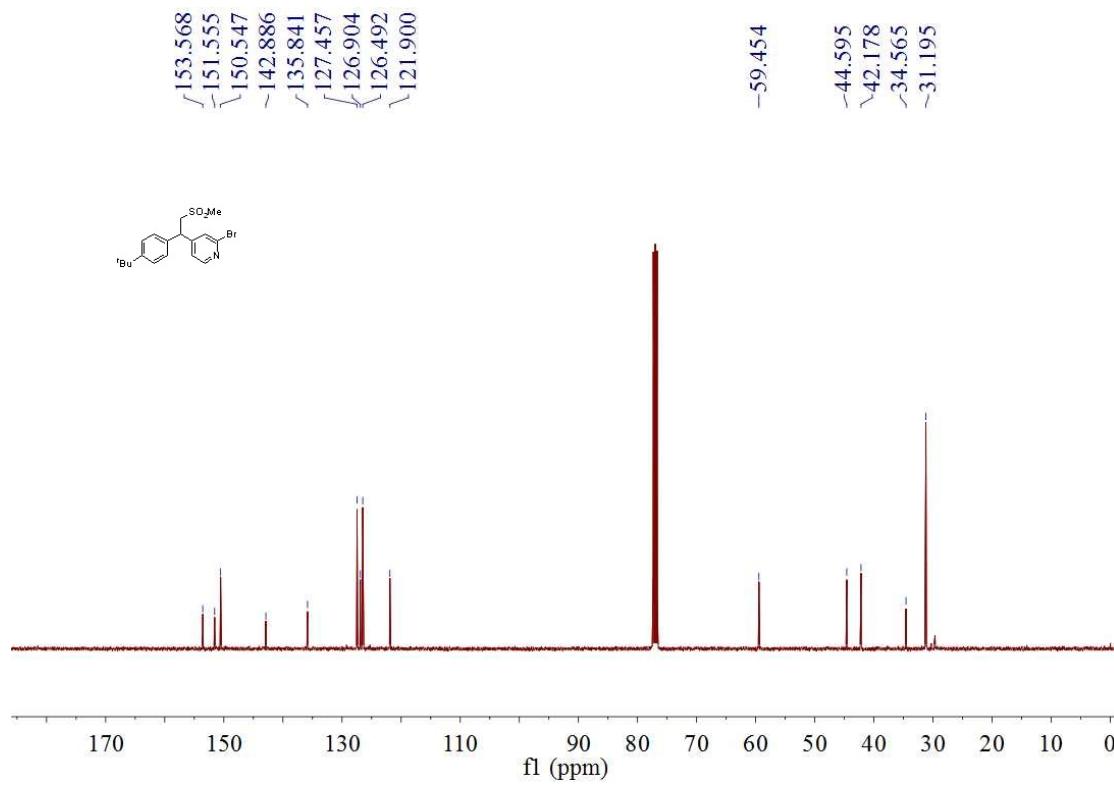
25; ^{13}C NMR (101 MHz, CDCl_3)



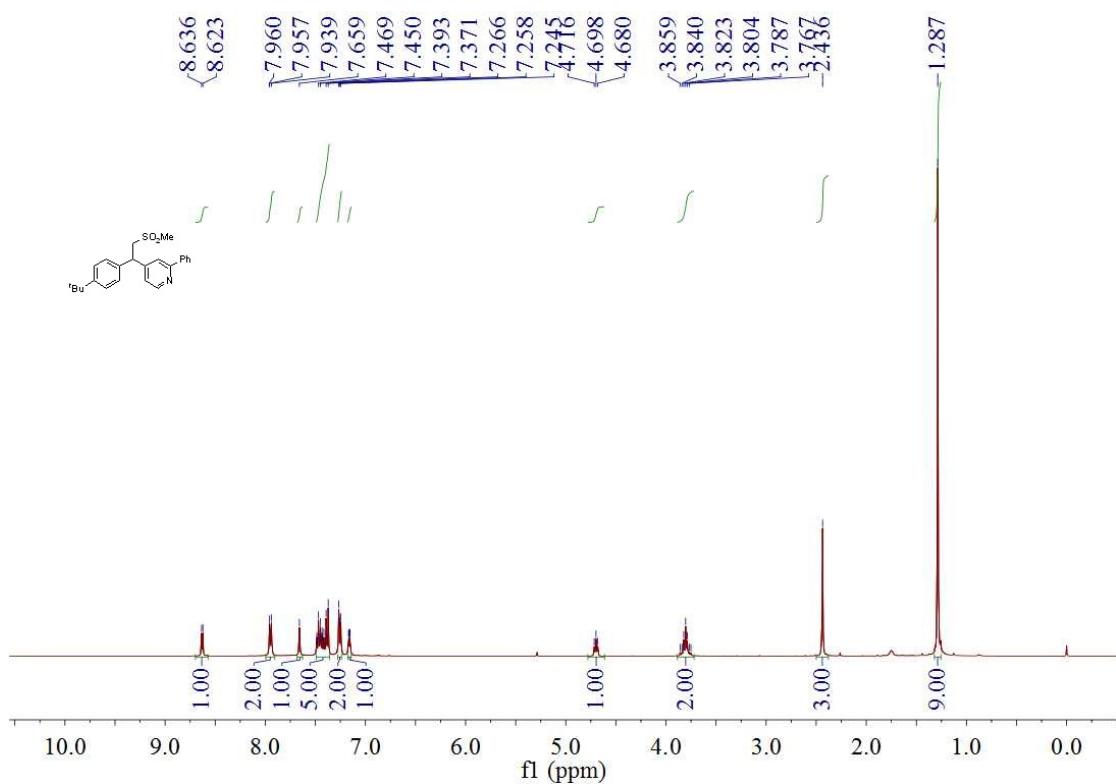
26; ^1H NMR (400 MHz, CDCl_3)



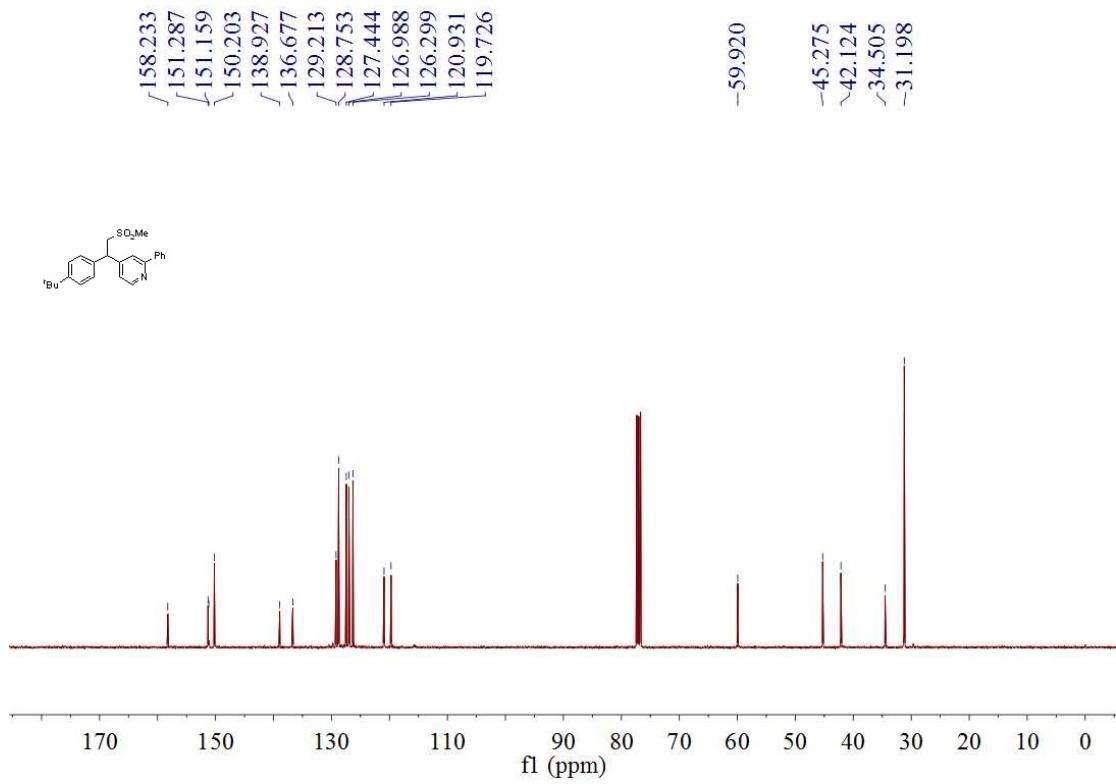
26; ^{13}C NMR (101 MHz, CDCl_3)



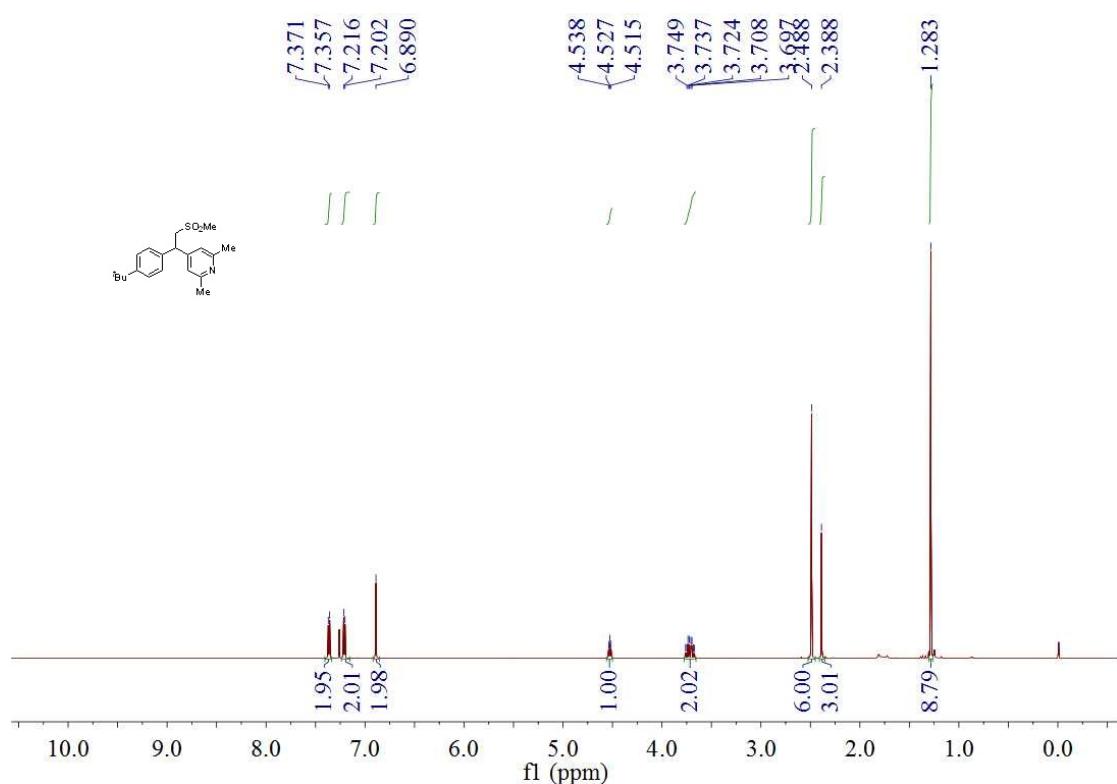
27; ^1H NMR (400 MHz, CDCl_3)



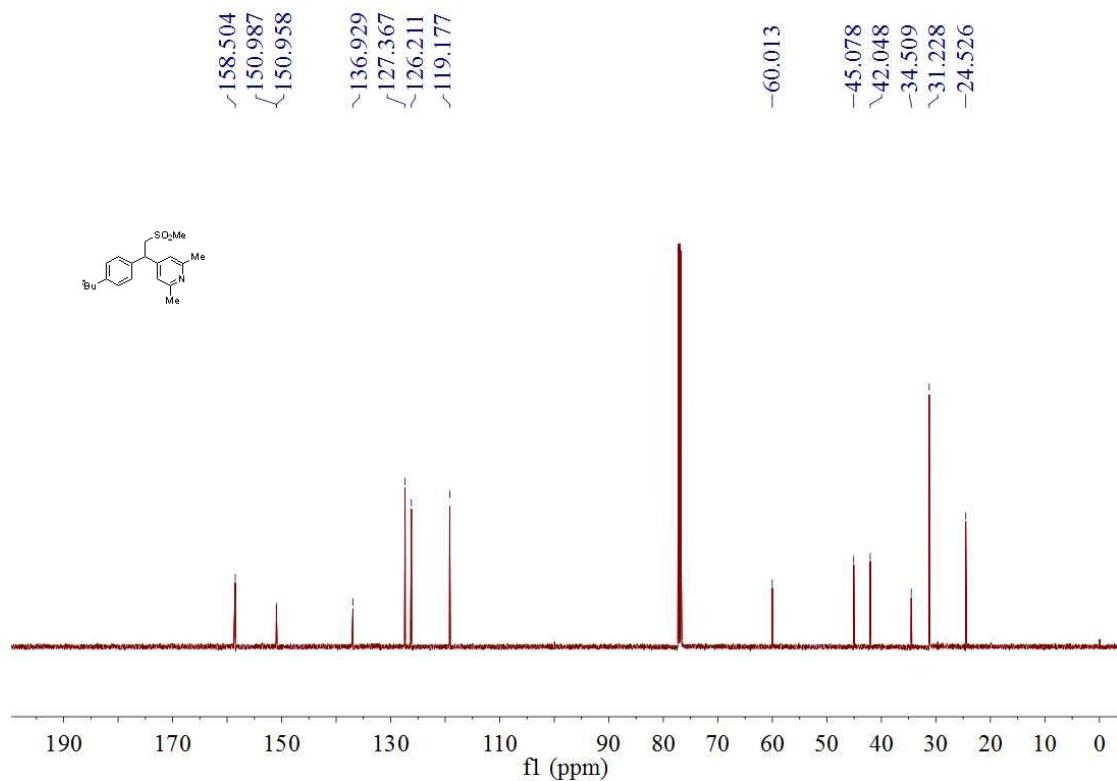
27; ^{13}C NMR (101 MHz, CDCl_3)



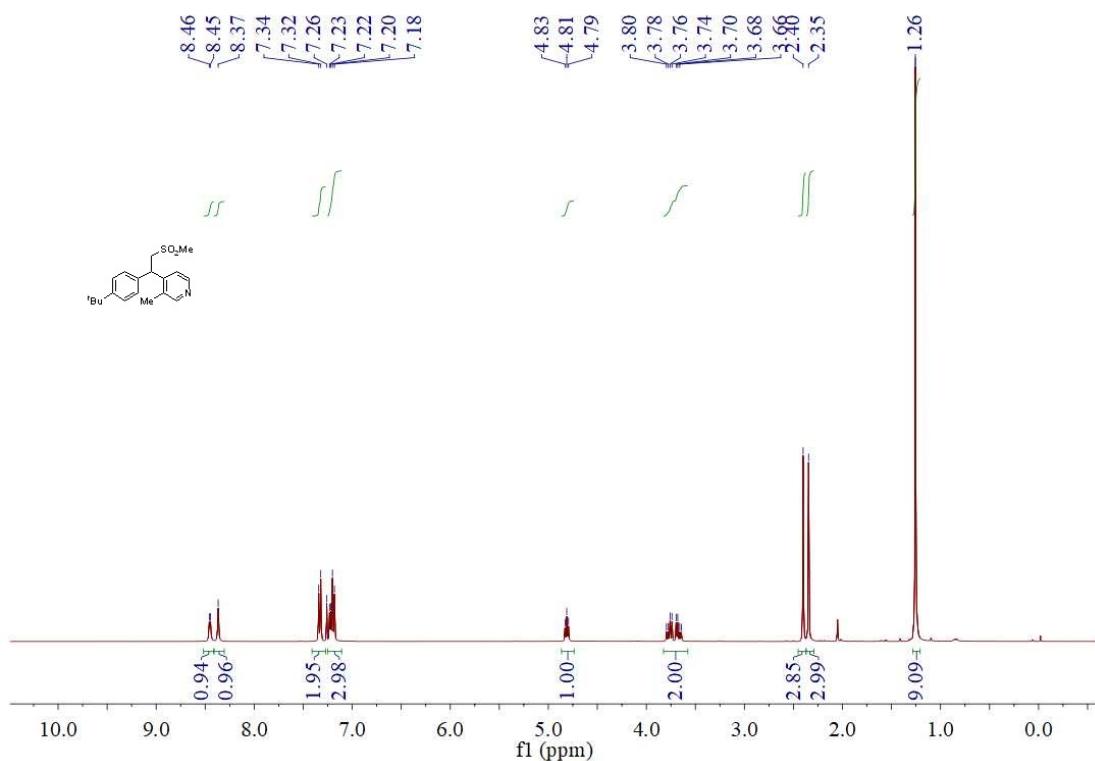
28; ^1H NMR (600 MHz, CDCl_3)



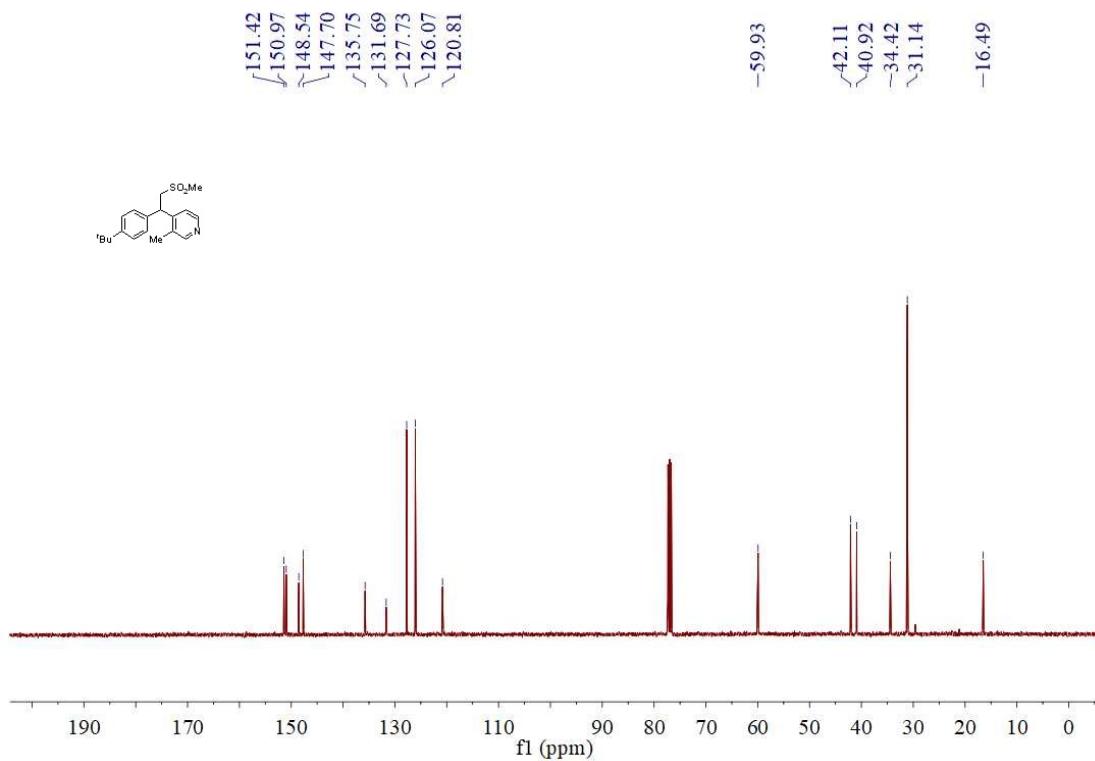
28; ^{13}C NMR (101 MHz, CDCl_3)



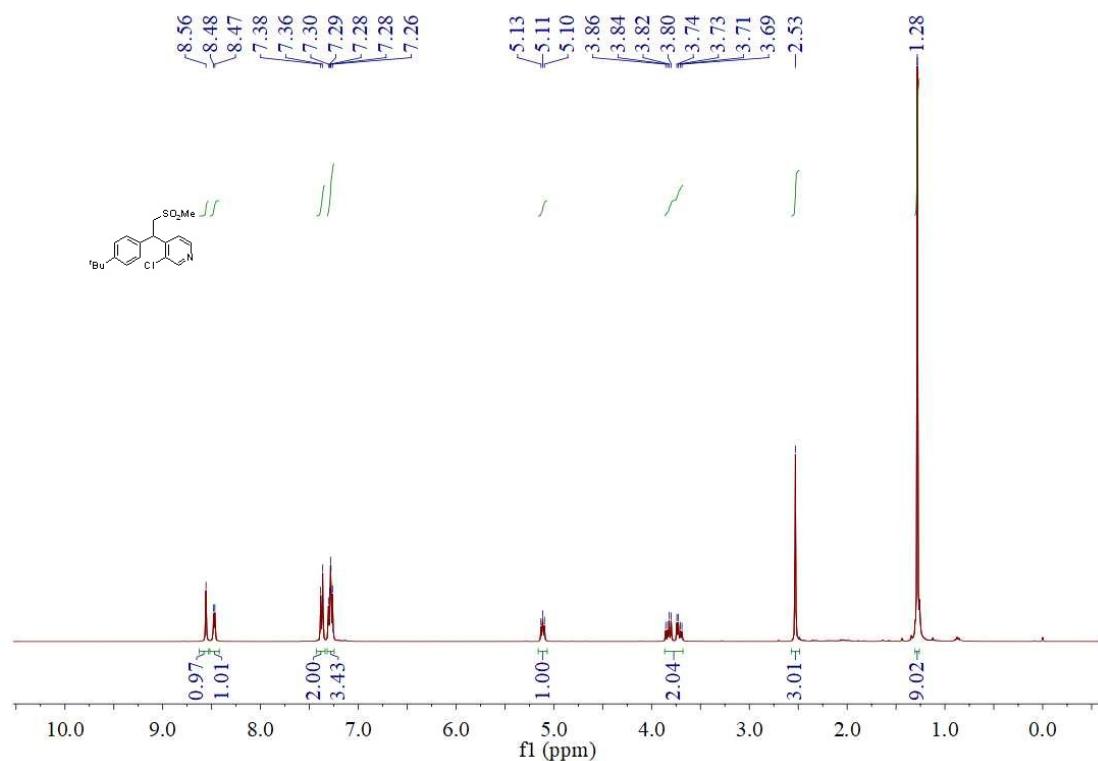
29; ^1H NMR (600 MHz, CDCl_3)



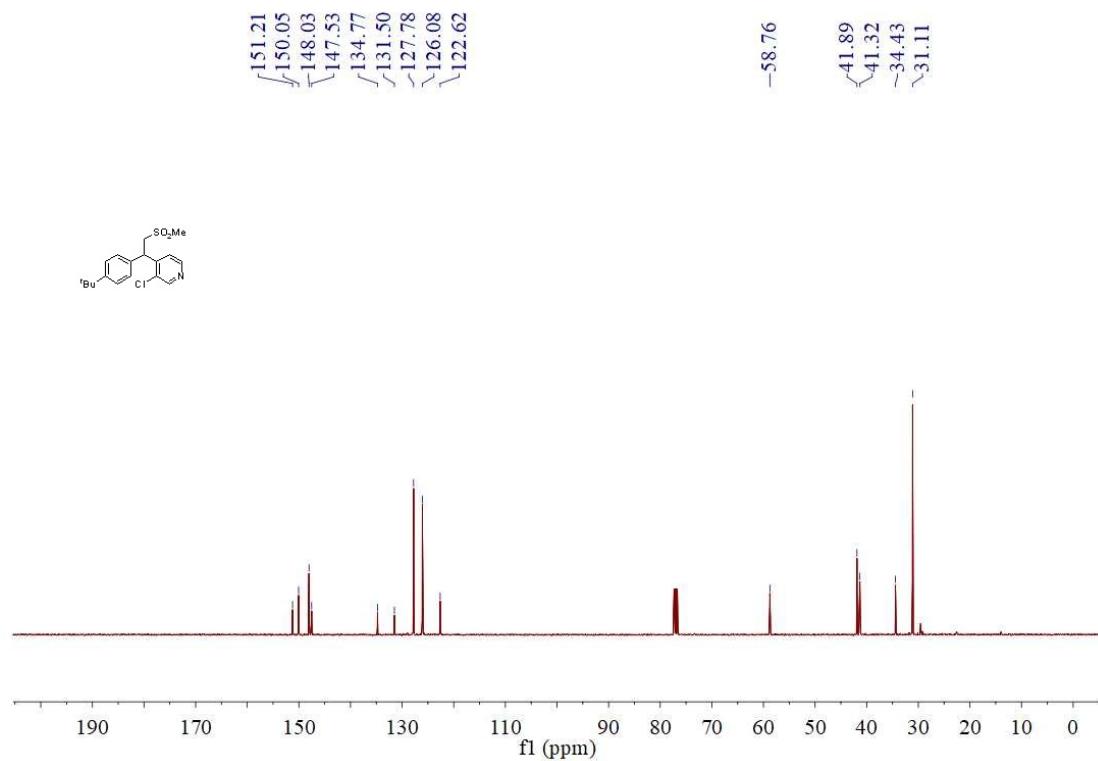
29; ^{13}C NMR (101 MHz, CDCl_3)



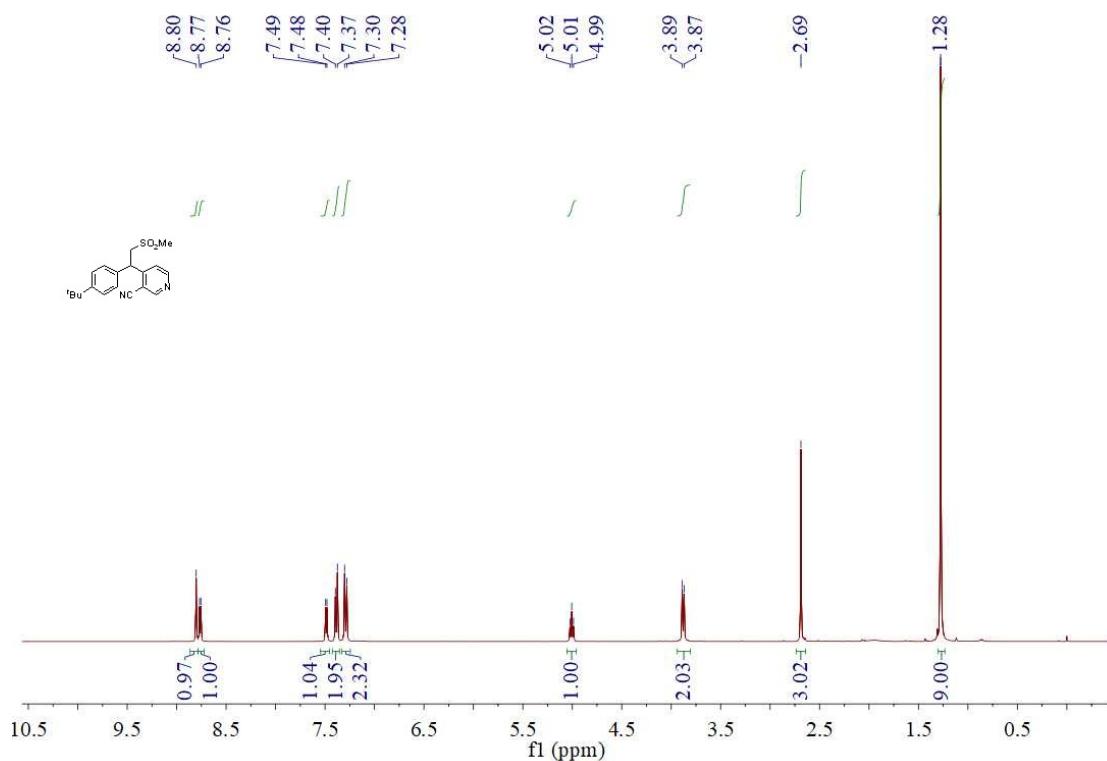
30; ^1H NMR (600 MHz, CDCl_3)



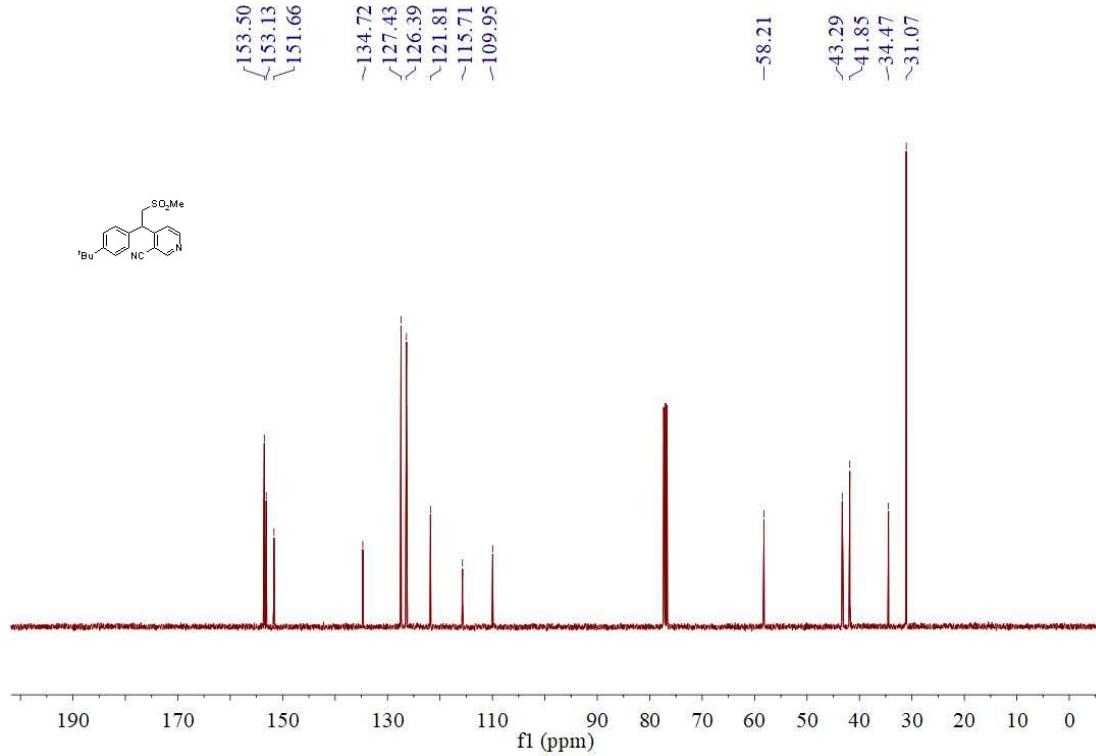
30; ^{13}C NMR (101 MHz, CDCl_3)



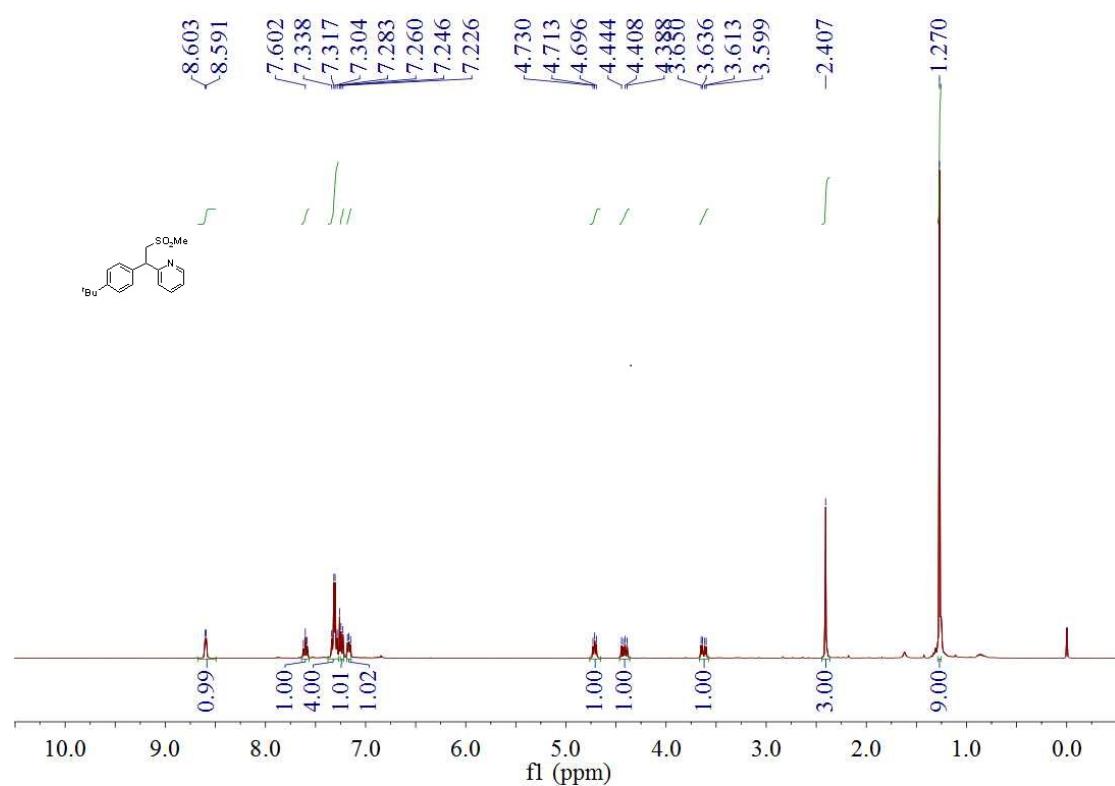
31; ^1H NMR (600 MHz, CDCl_3)



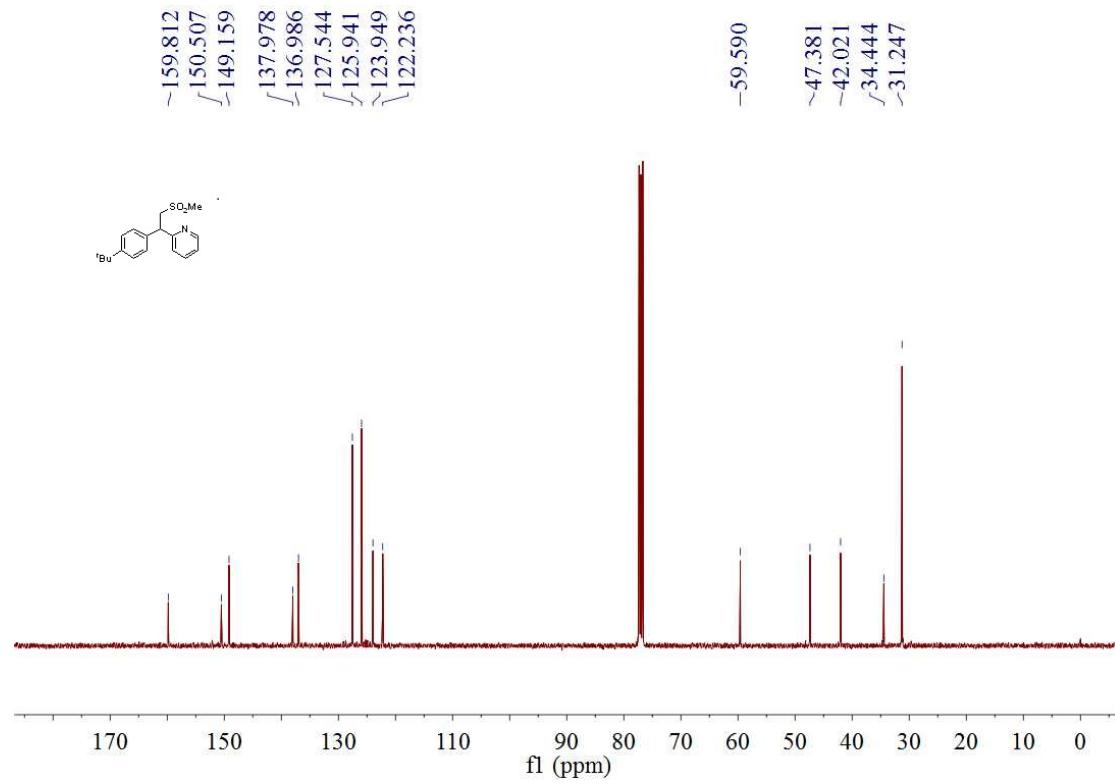
31; ^{13}C NMR (101 MHz, CDCl_3)



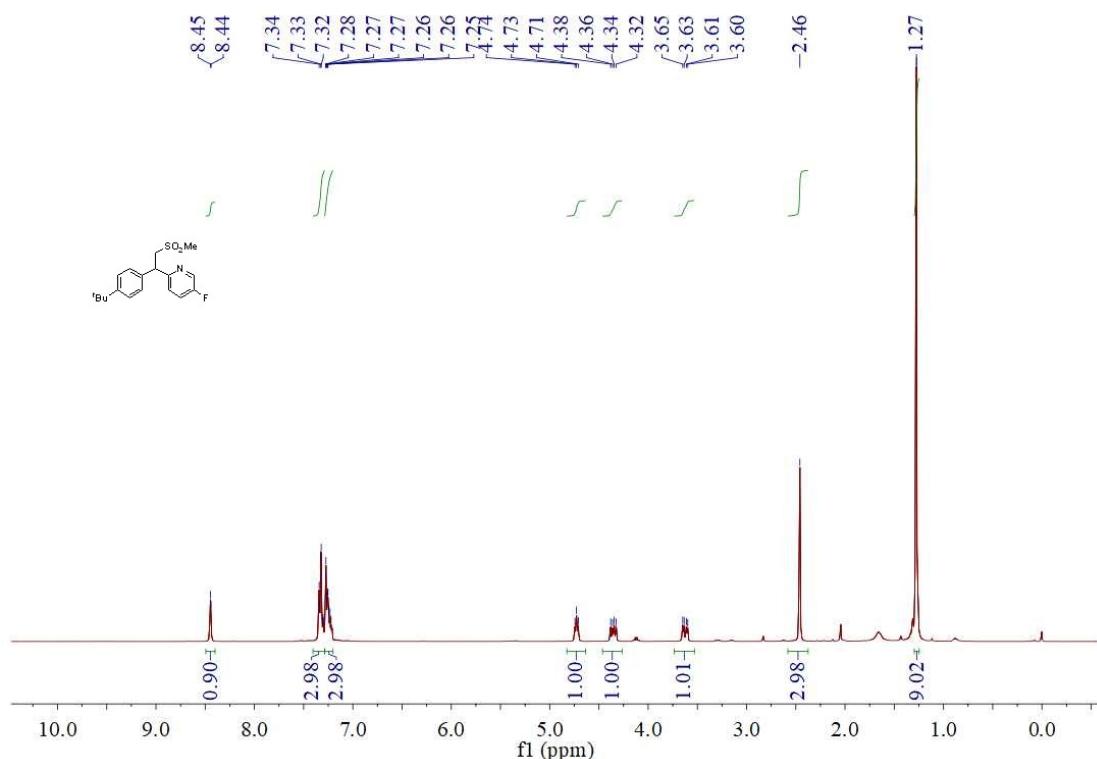
32; ^1H NMR (400 MHz, CDCl_3)



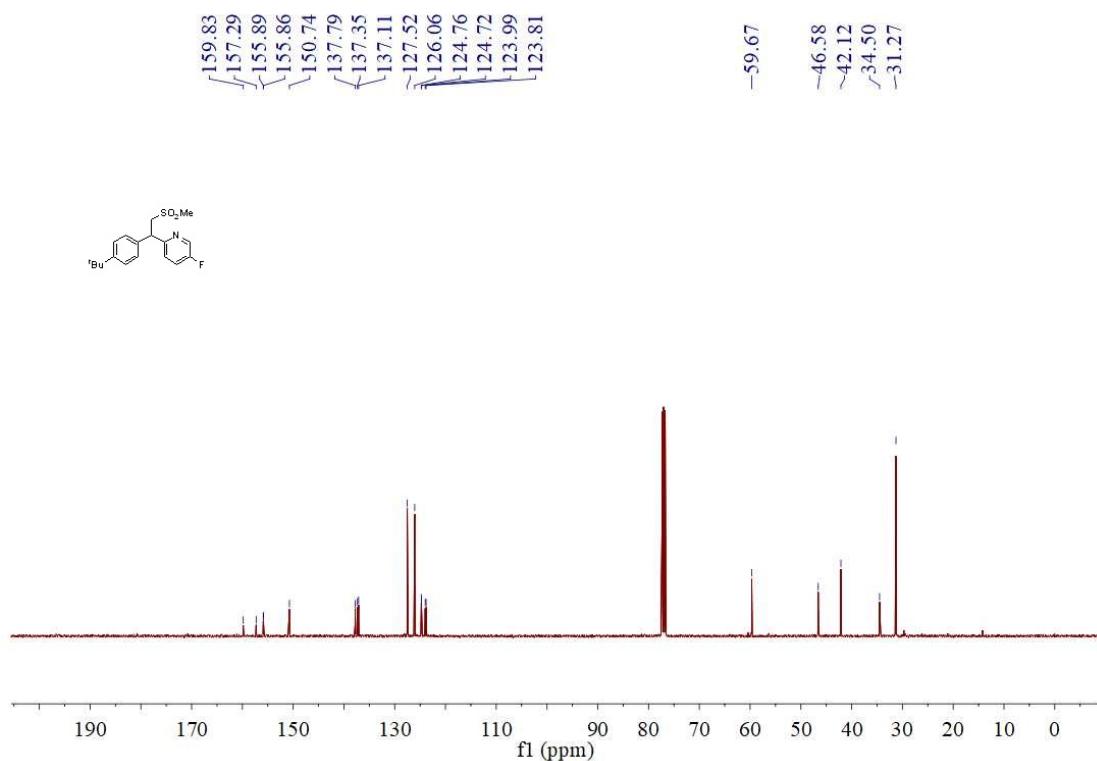
32; ^{13}C NMR (101 MHz, CDCl_3)



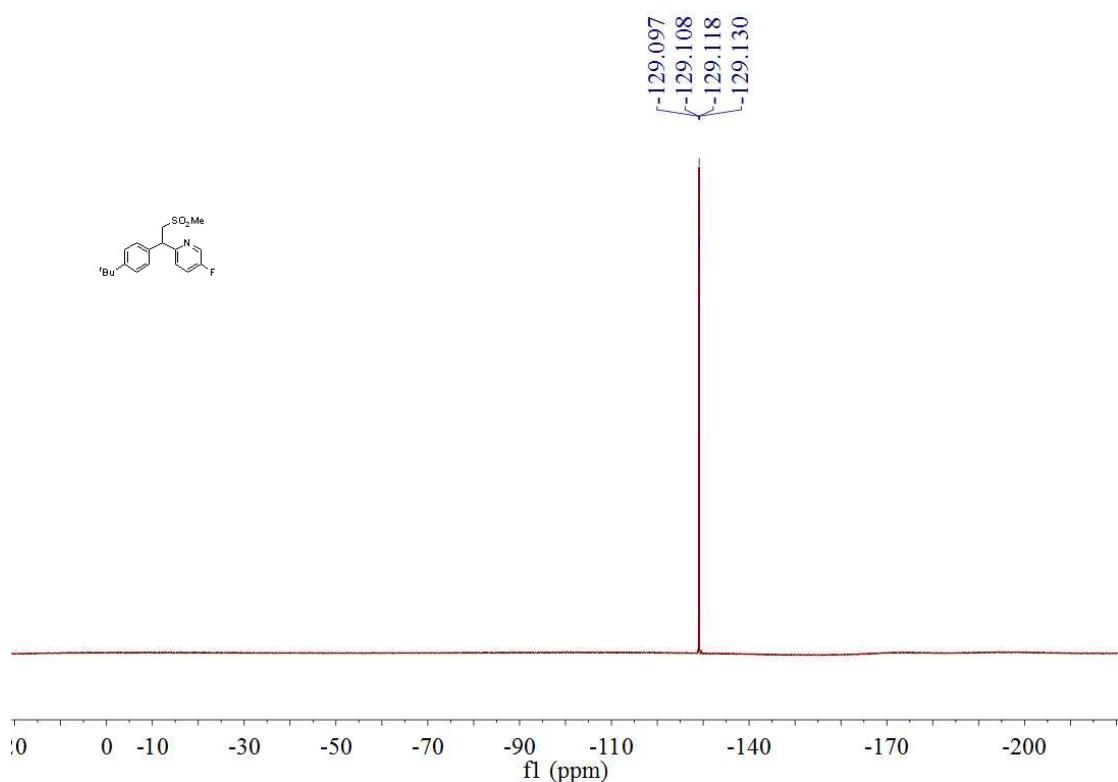
33; ^1H NMR (400 MHz, CDCl_3)



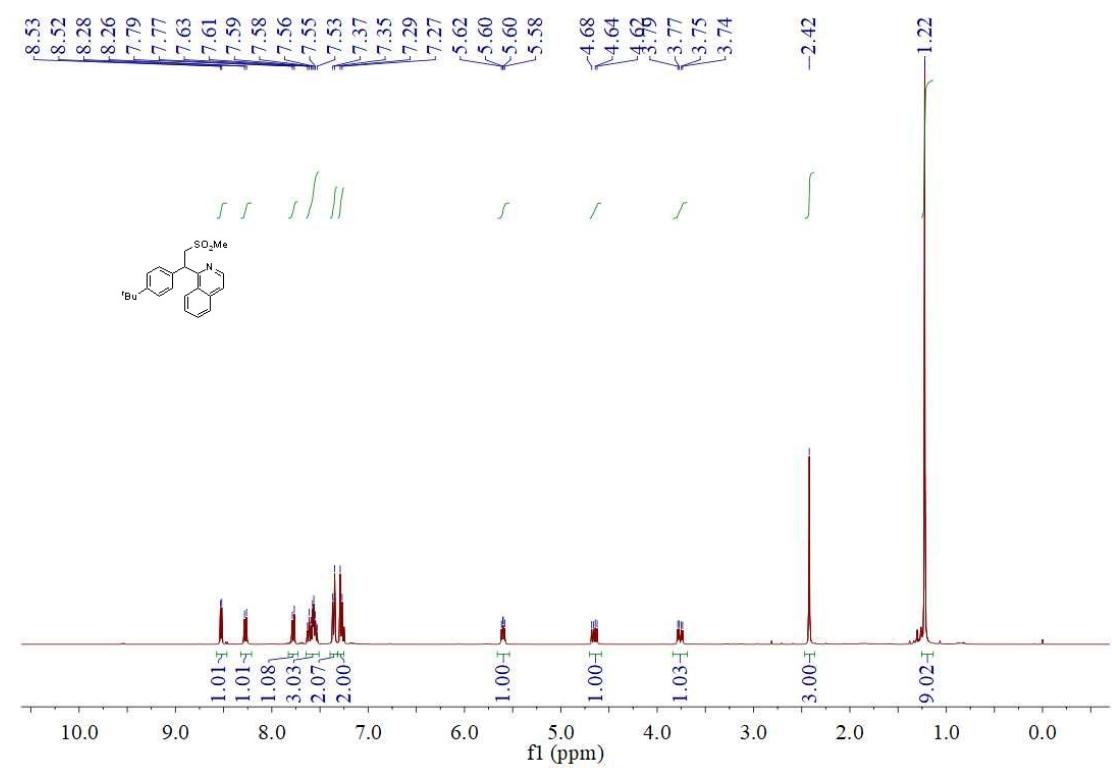
33; ^{13}C NMR (101 MHz, CDCl_3)



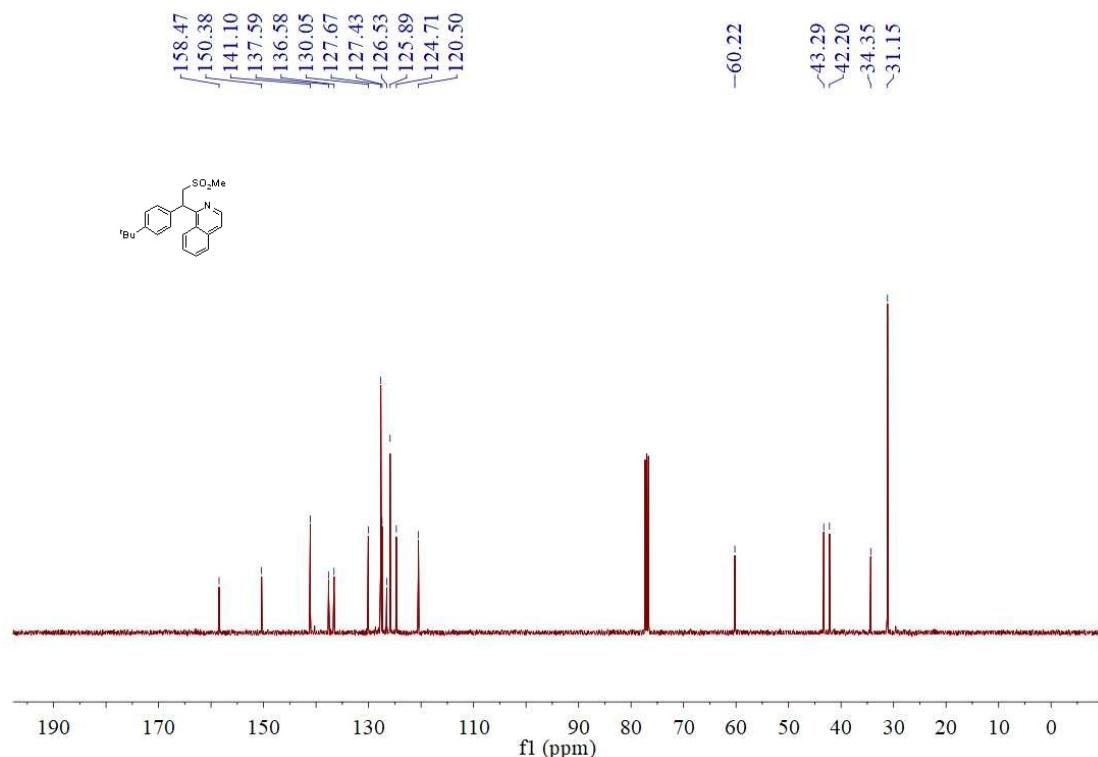
33; ^{19}F NMR (377 MHz, CDCl_3)



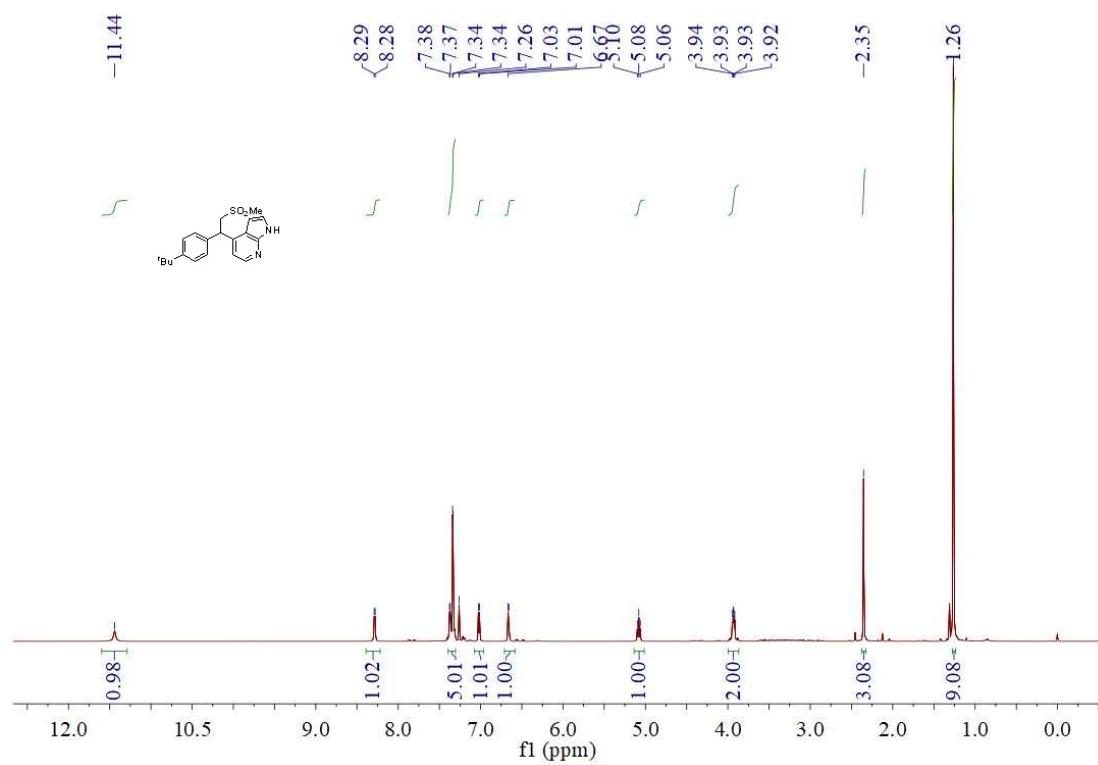
34; ^1H NMR (400 MHz, CDCl_3)



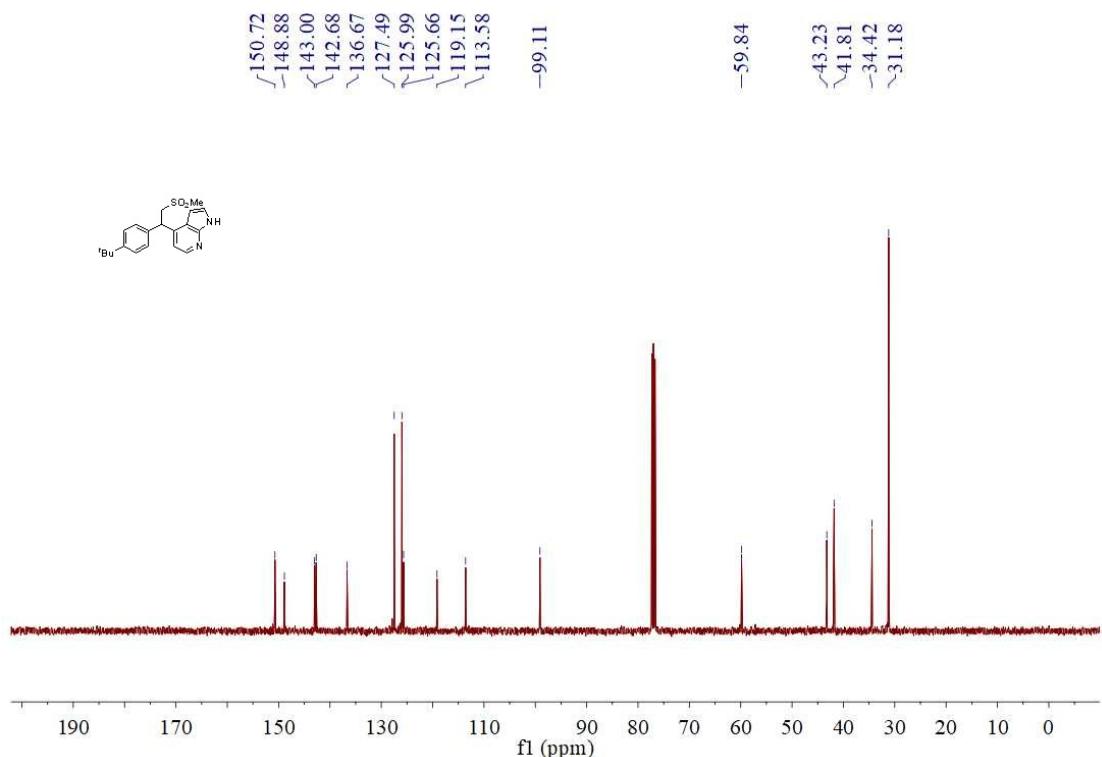
34; ^{13}C NMR (101 MHz, CDCl_3)



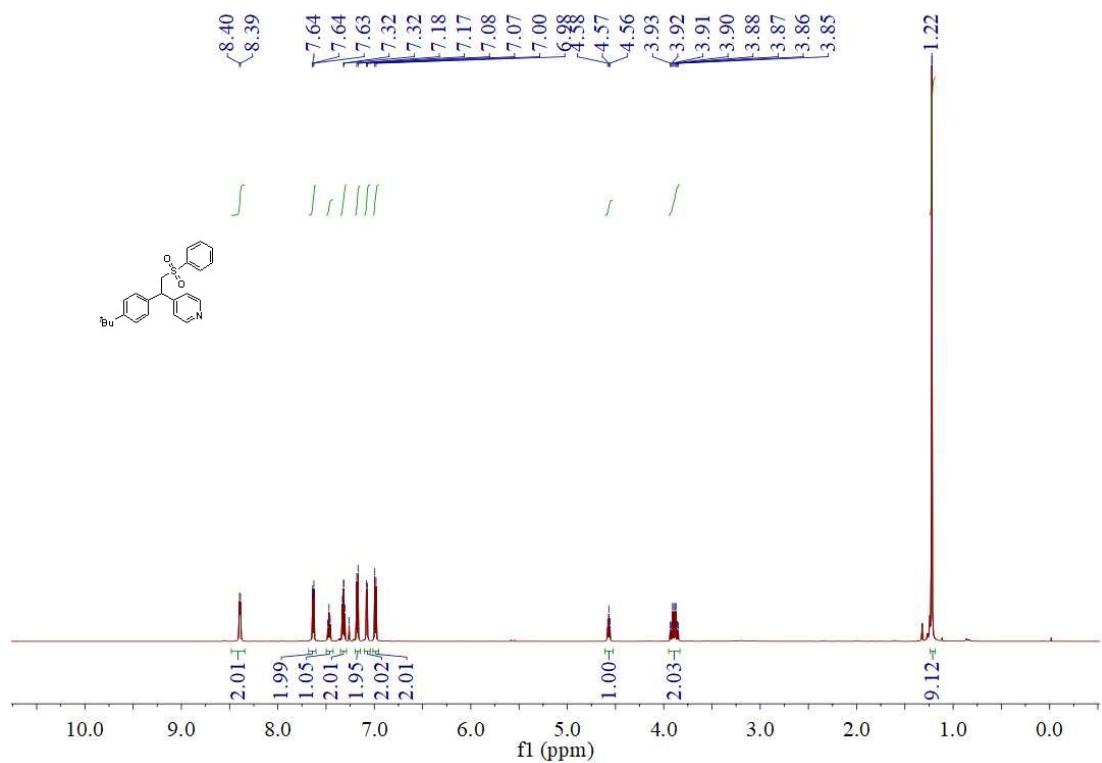
35; ^1H NMR (400 MHz, CDCl_3)



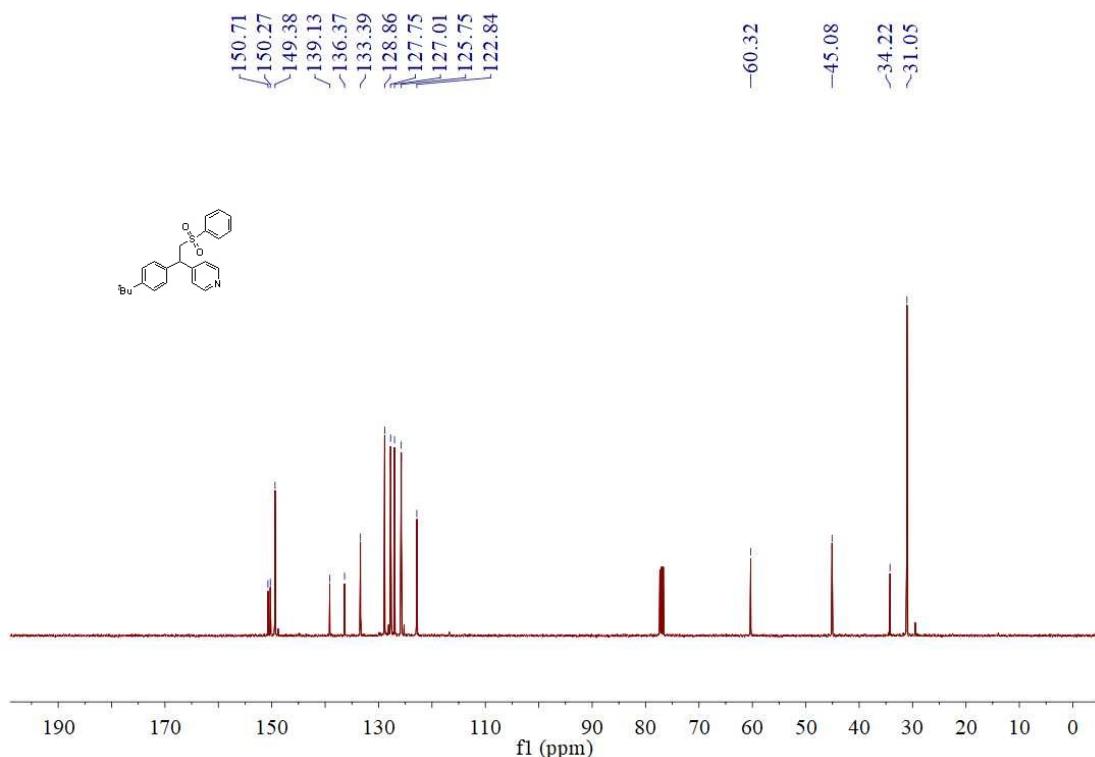
35; ^{13}C NMR (101 MHz, CDCl_3)



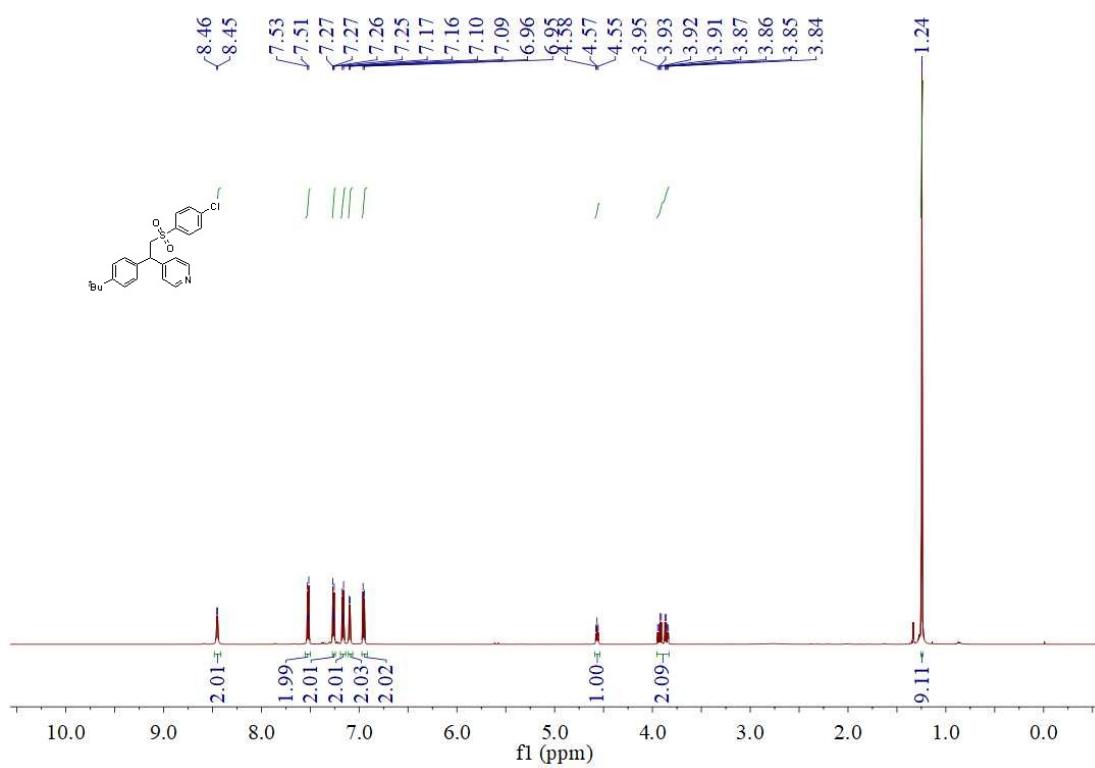
36; ^1H NMR (600 MHz, CDCl_3)



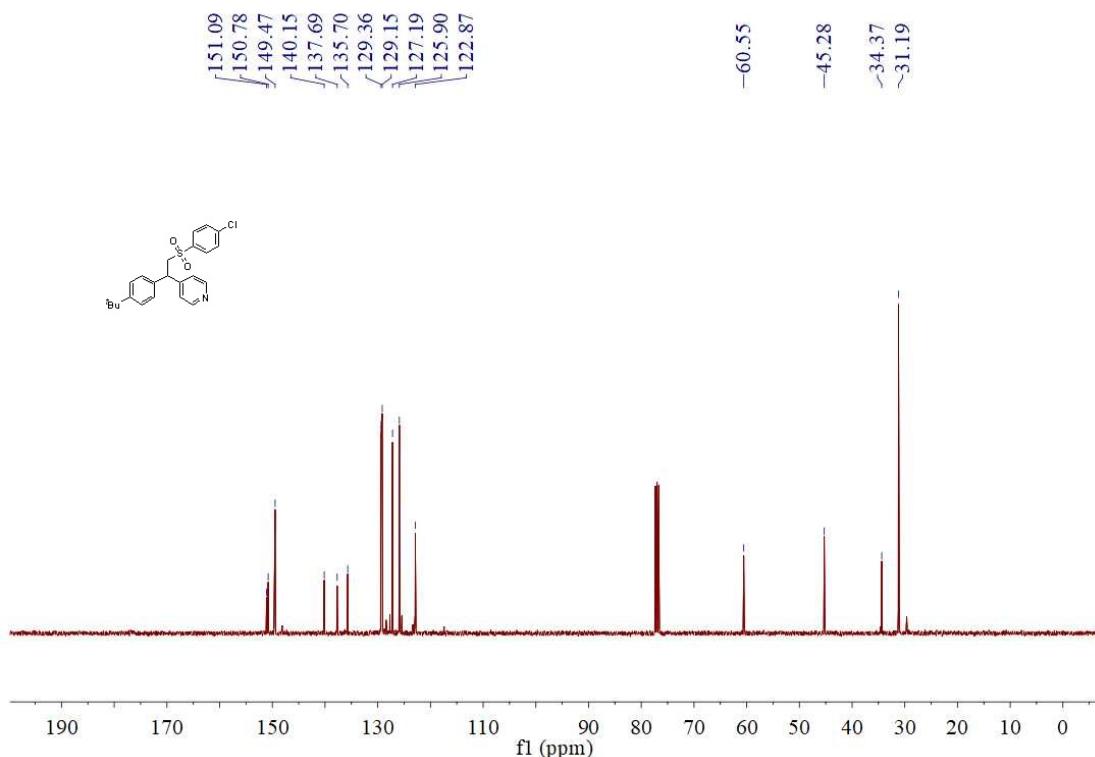
36; ^{13}C NMR (101 MHz, CDCl_3)



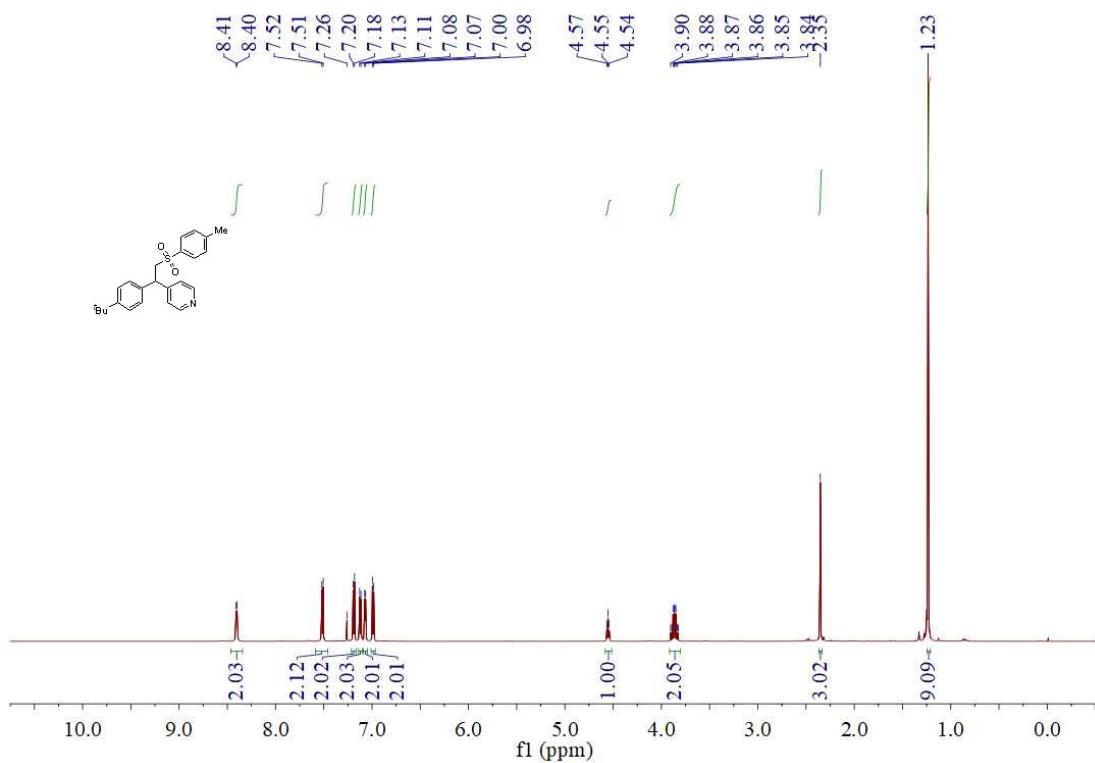
37; ^1H NMR (600 MHz, CDCl_3)



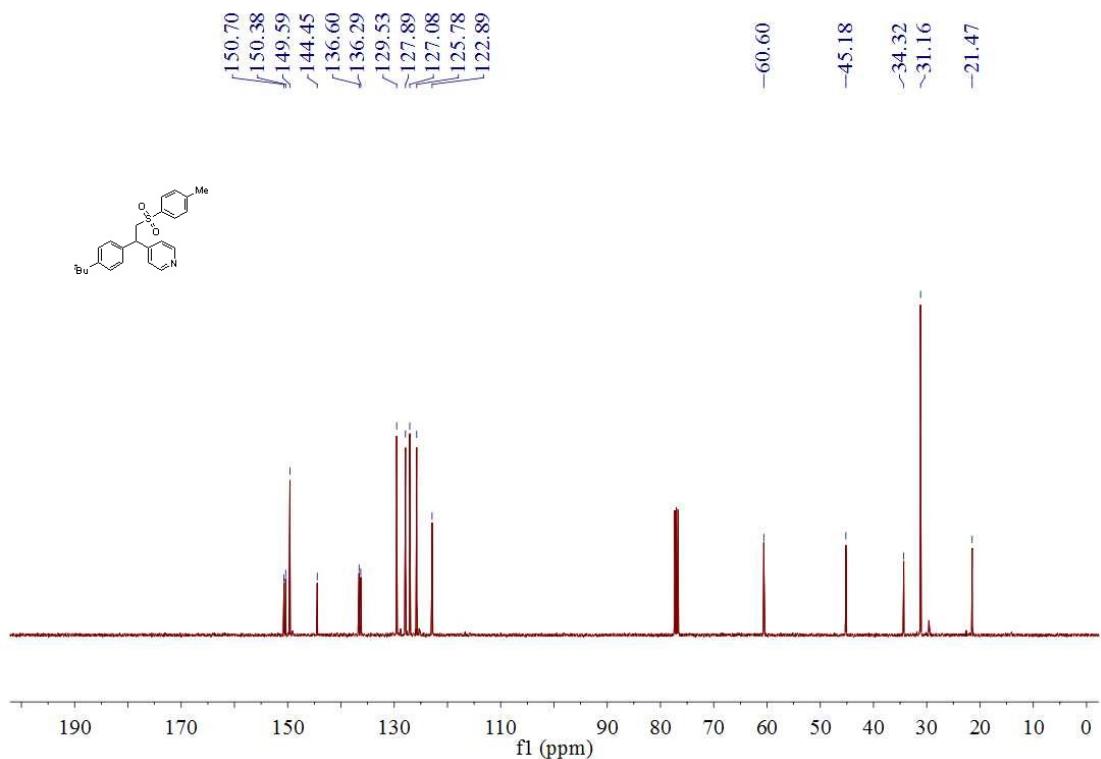
37; ^{13}C NMR (101 MHz, CDCl_3)



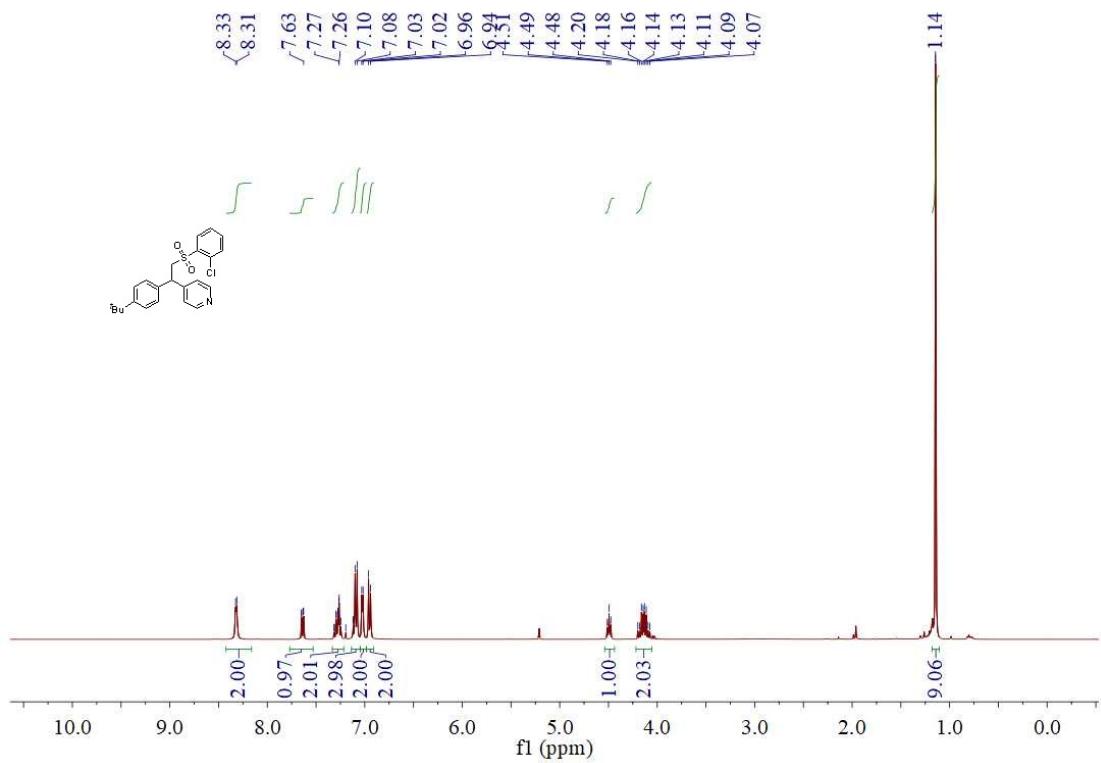
38; ^1H NMR (600 MHz, CDCl_3)



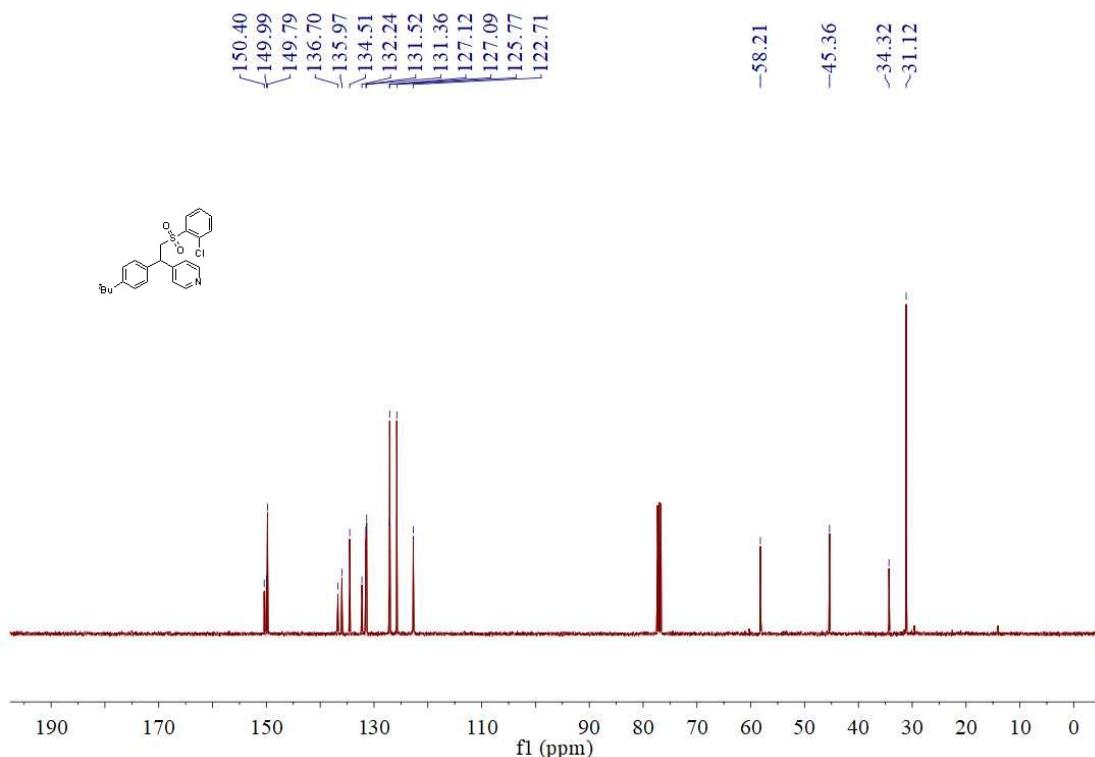
38; ^{13}C NMR (101 MHz, CDCl_3)



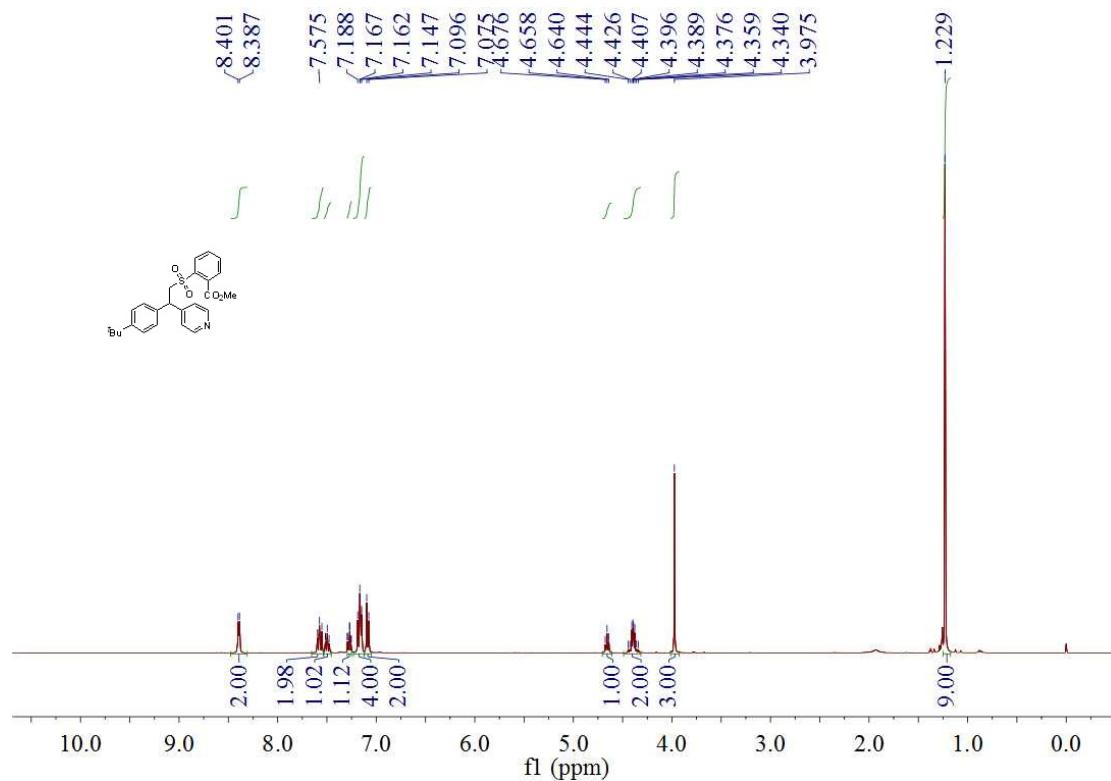
39; ^1H NMR (400 MHz, CDCl_3)



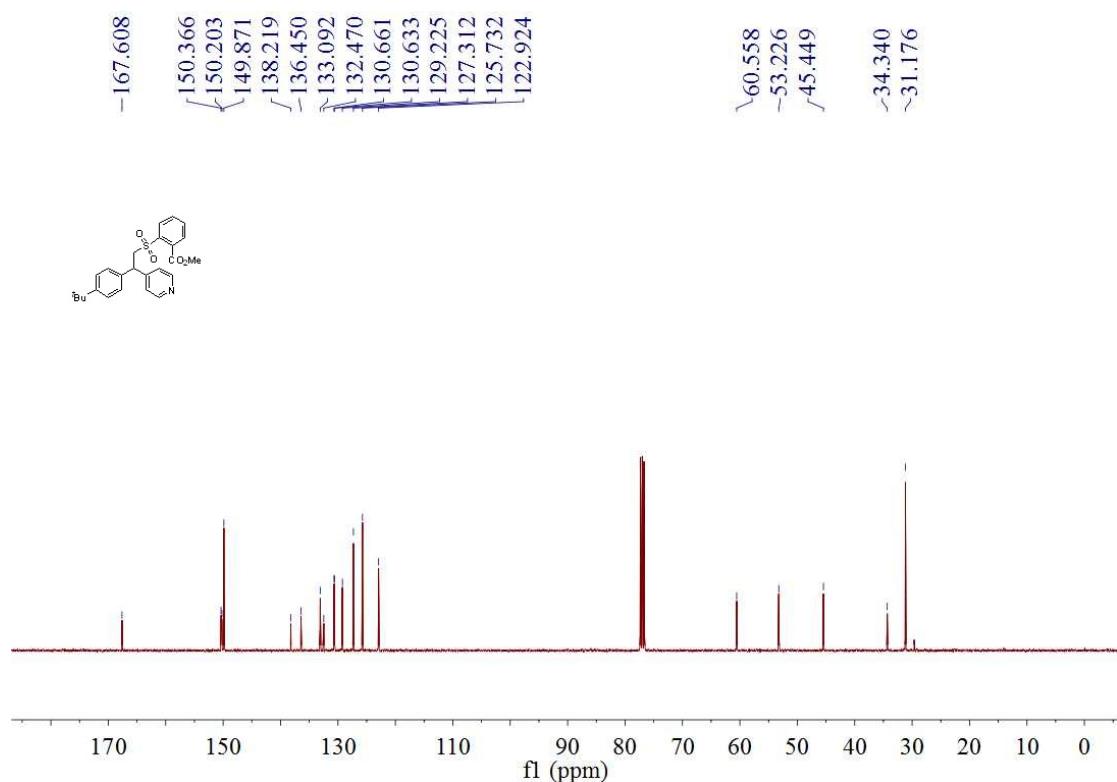
39; ^{13}C NMR (101 MHz, CDCl_3)



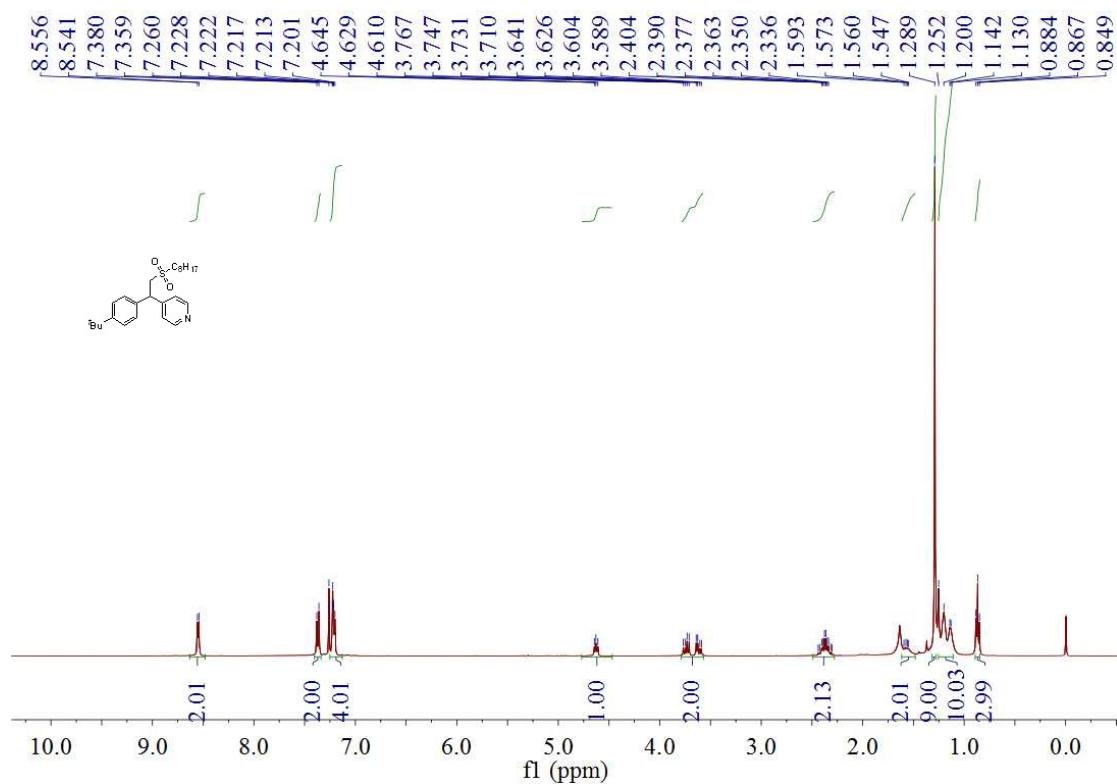
40; ^1H NMR (400 MHz, CDCl_3)



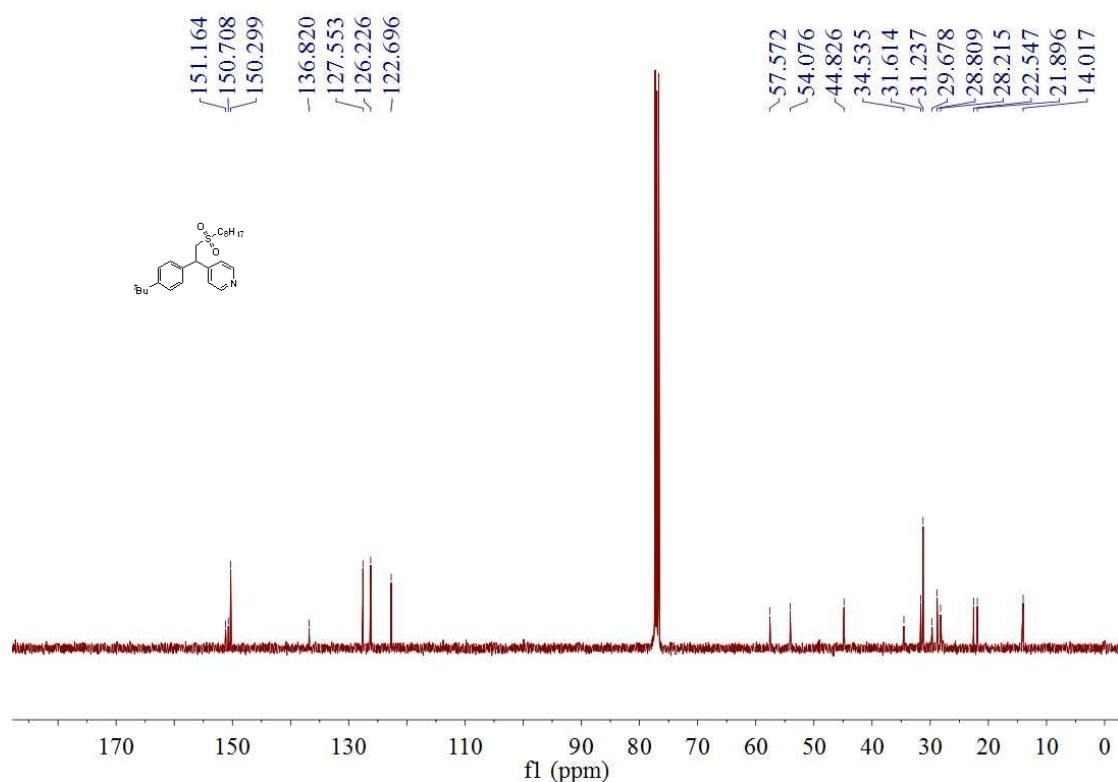
40; ^{13}C NMR (101 MHz, CDCl_3)



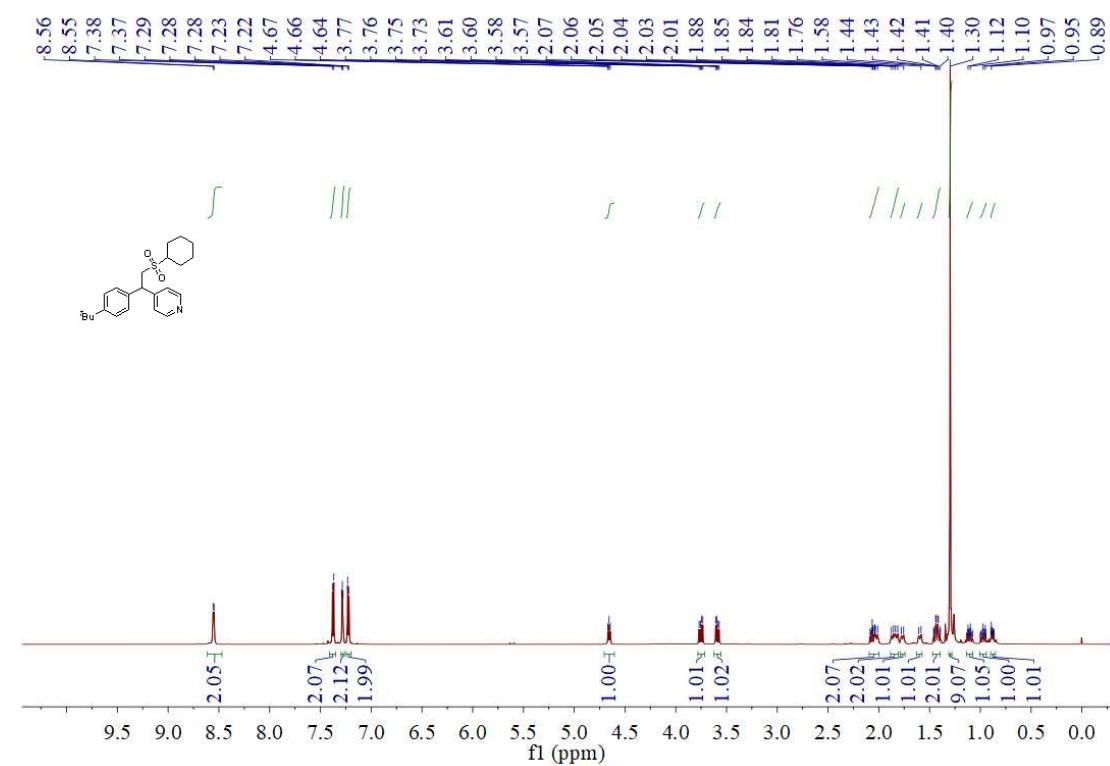
41; ^1H NMR (400 MHz, CDCl_3)



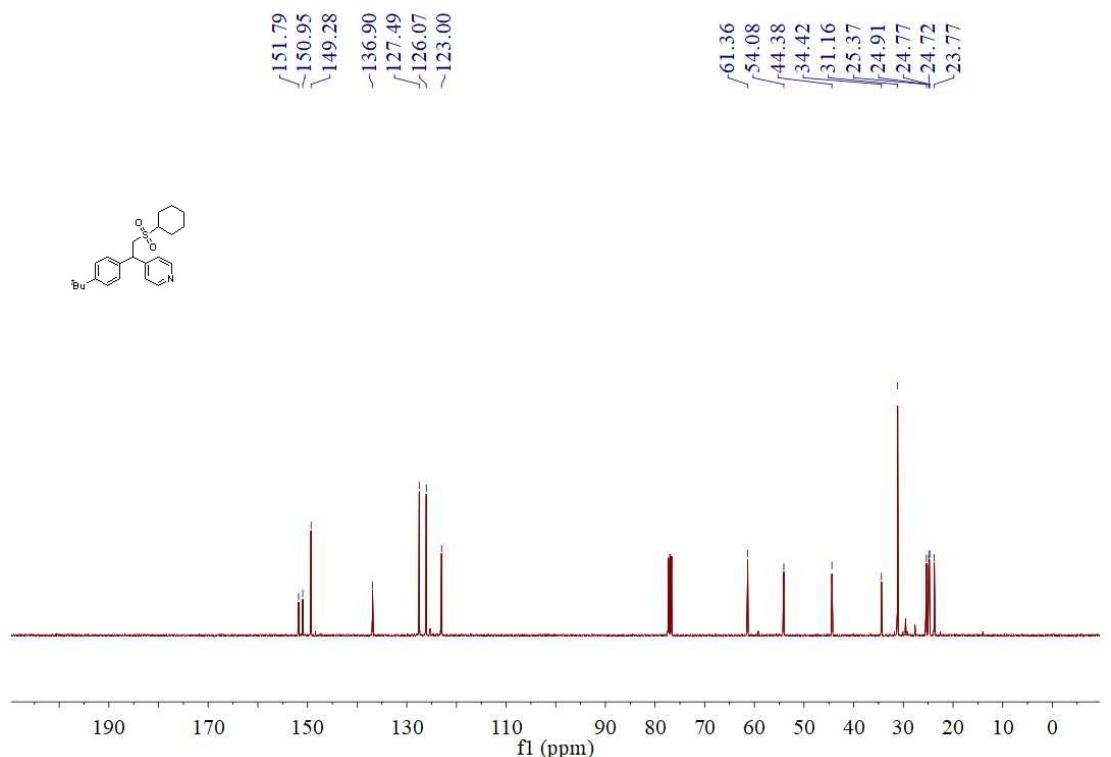
41; ^{13}C NMR (101 MHz, CDCl_3)



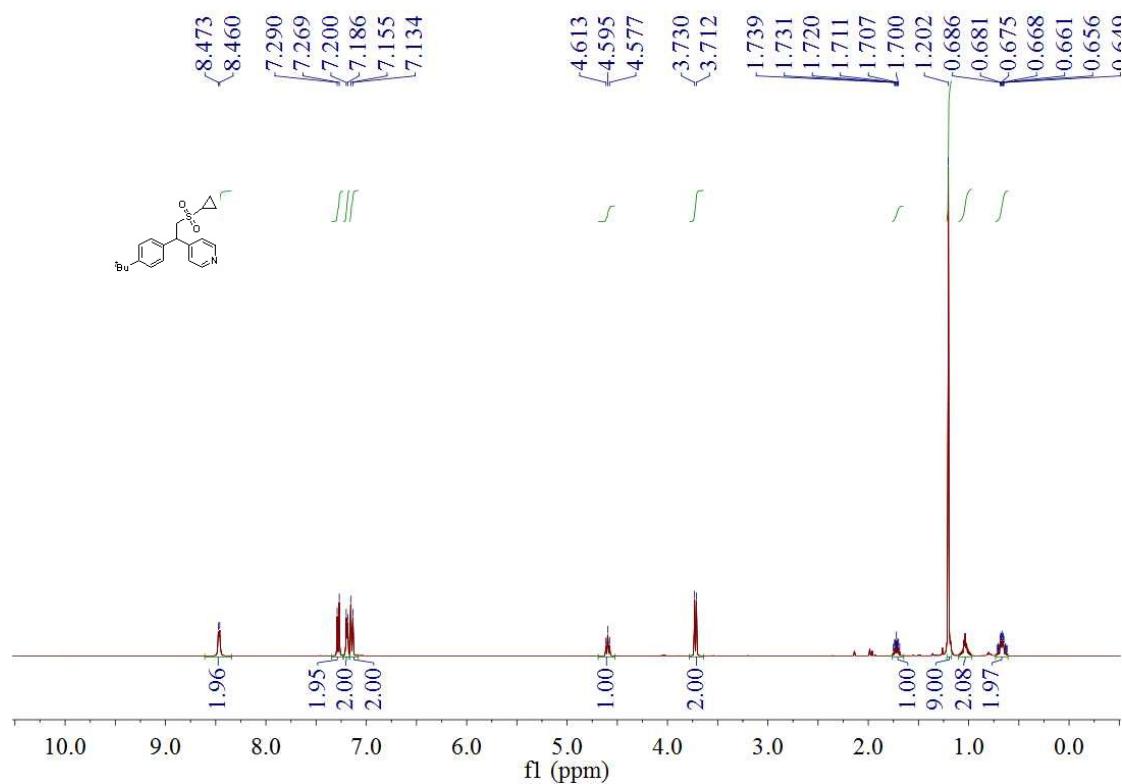
42; ^1H NMR (600 MHz, CDCl_3)



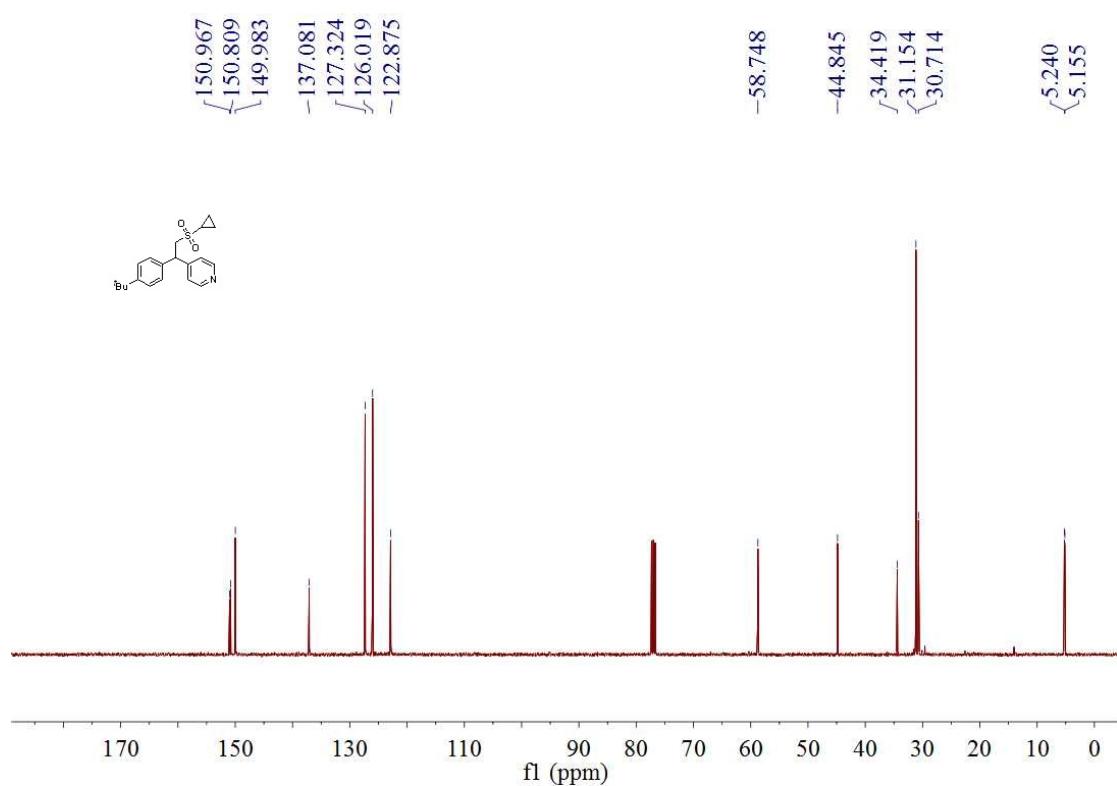
42; ^{13}C NMR (101 MHz, CDCl_3)



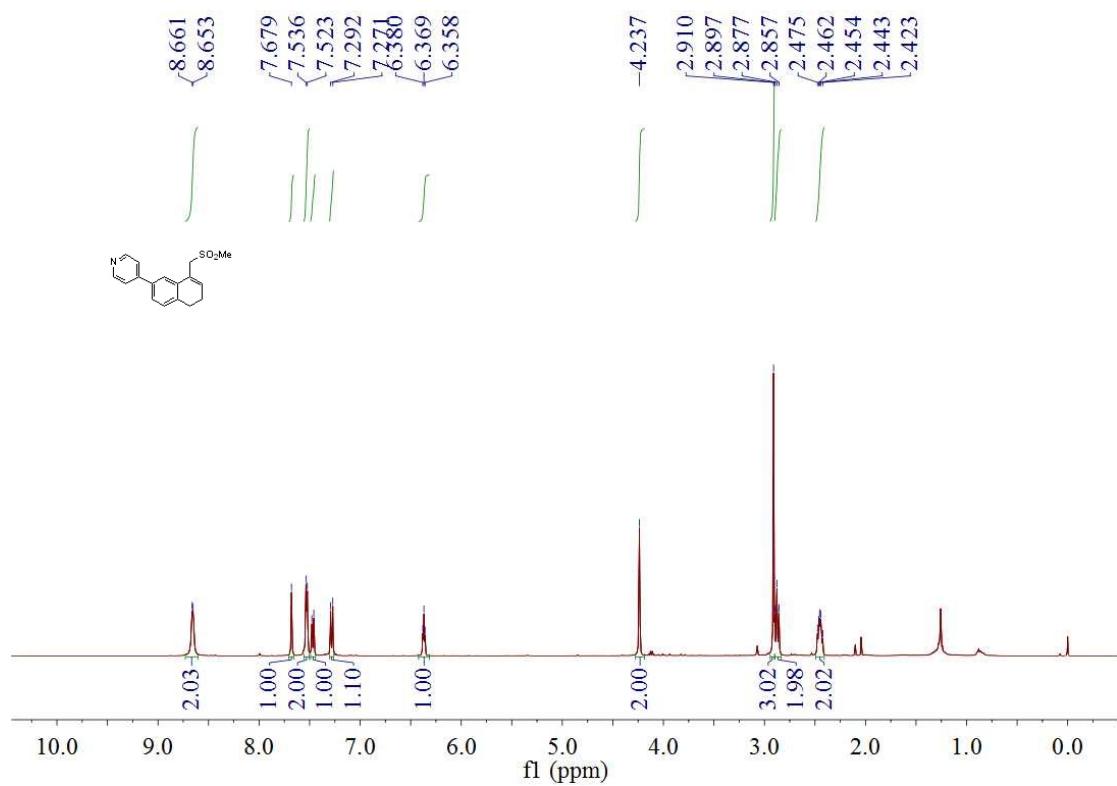
43; ^1H NMR (400 MHz, CDCl_3)



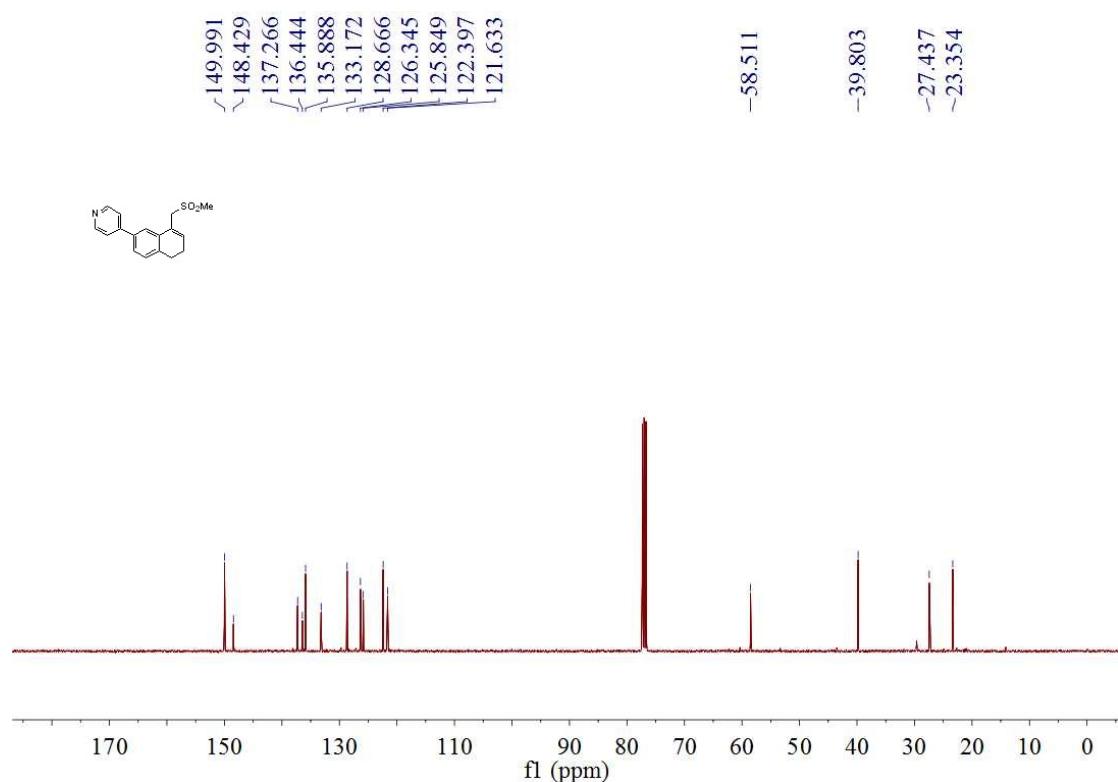
43; ^{13}C NMR (101 MHz, CDCl_3)



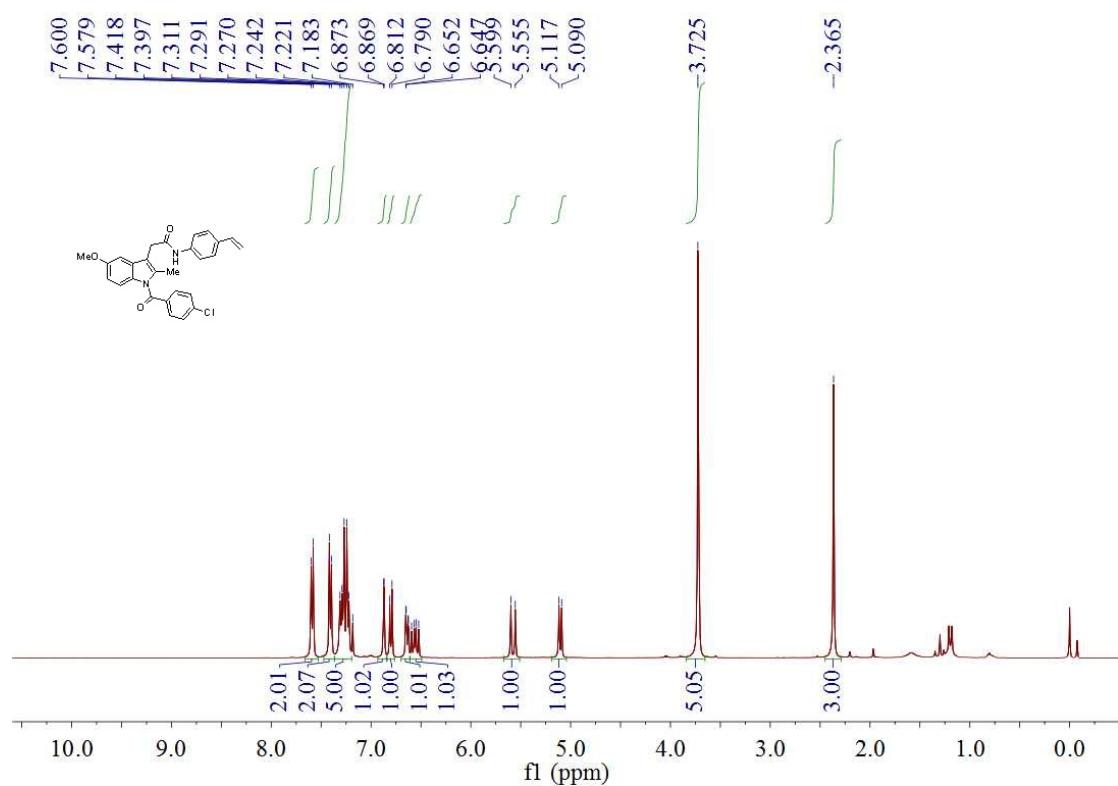
45; ^1H NMR (400 MHz, CDCl_3)



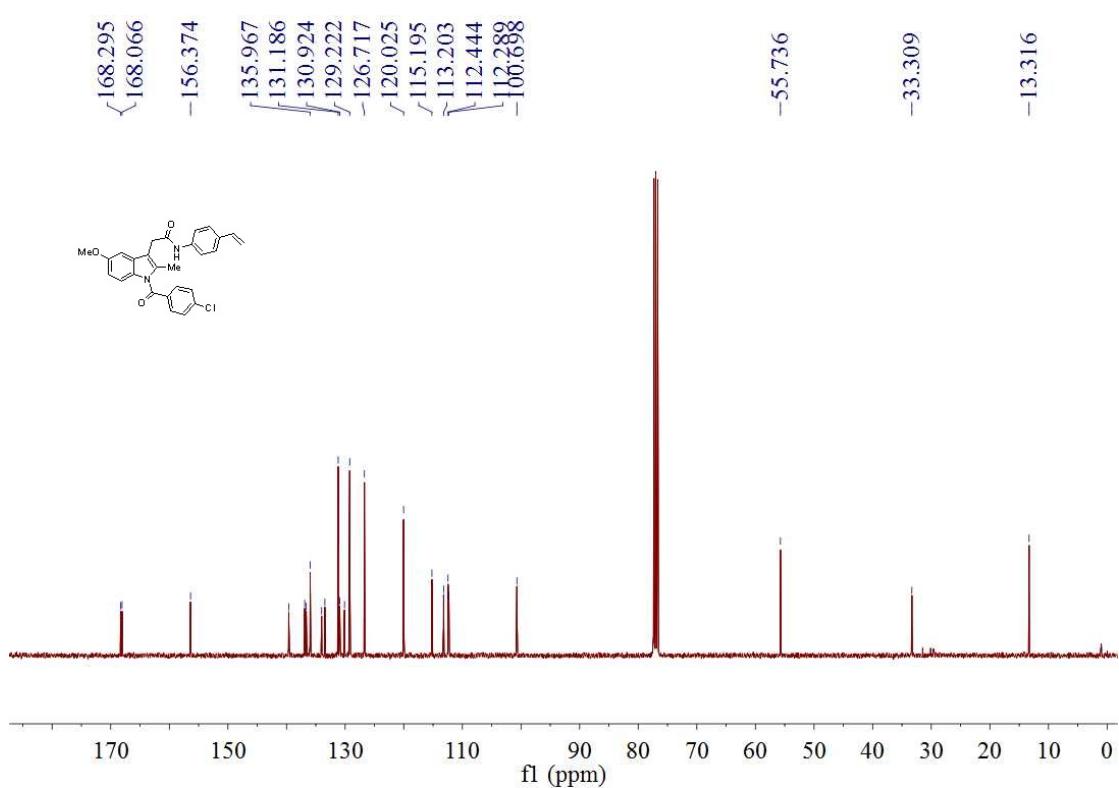
45; ^{13}C NMR (101 MHz, CDCl_3)



S1; ^1H NMR (400 MHz, CDCl_3)



S1; ^{13}C NMR (101 MHz, CDCl_3)



8. References

1. Lipp, B.; Kammer, L. M.; Küçükdisli, M.; Luque, A.; Kühlborn, J.; Pusch, S.; Matulevičiūtė, G.; Schollmeyer, D.; Šačkus, A.; Opatz, T., *Chem. Eur. J.* **2019**, *25*, 8965-8969.
2. Zhou, Y.; Bandar, J. S.; Buchwald, S. L., *J. Am. Chem. Soc.*, **2017**, *139* (24), 8126-8129.
3. Kunitski, M.; Eicke, N.; Huber, P.; Köhler, J.; Zeller, S.; Voigtsberger, J.; Schlott, N.; Henrichs, K.; Sann, H.; Trinter, F.; Schmidt, L. P. H.; Kalinin, A.; Schöffler, M. S.; Jahnke, T.; Lein, M.; Dörner, R., *Nat. Comm.* **2019**, *10*, 1.
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