Supporting Information

Engaging Sulfinate Salts via Ni/Photoredox Dual Catalysis Enables Facile C–SO_2R Coupling

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Key to Abbreviated Terms:

4CzIPN: 2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile
bpy: 2,2′-bipyridyl
diOMebpy: 4,4′-dimethoxy-2,2′-dipyridyl
dtbbpy: 4,4′-di-*tert*-butyl-2,2′-dipyridyl
LED: Light-emitting diode
phen: 1,10-phenanthroline

General Considerations:

General: All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 4- or 5-port dual-bank manifold. Argon or nitrogen was used to provide such an atmosphere. LED irradiation was accomplished using the LED reactors described in our previous reports or the new reactor design outlined here.[1] NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K. ^{1}H NMR spectra were referenced to residual non-deuterated chloroform (δ 7.26) in $CDCl_3$, residual DMSO-d_5 (δ 2.50) in DMSO-d_6, acetone-d_5 (δ 2.09) in acetone-d_6, and residual MeCN-d_2 (δ 1.94) in MeCN-d_3. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.3), DMSO-d_6 (δ 39.5), the carbonyl carbon of acetone (δ 205.9), or the nitrile carbon of MeCN-d_3 (δ 118.3), respectively ^{19}F NMR spectra were referenced to hexafluorobenzene (δ –164.9)[2] as an internal standard and are run with C-F/C-H decoupling. Reactions were monitored by HPLC, GC/MS, ^{1}H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluant and visualized using permanganate stain, Seebach's stain,[3] ninhydrin stain, and/or UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32-63 μm). Flash chromatography was accomplished using an automated system (monitoring at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 μm). Solvents were purified with drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected.

Chemicals: Deuterated NMR solvents were either used as purchased (MeCN-d_3, acetone-d_6, DMSO-d_6) or stored over 4Å molecular sieves and/or K_2CO_3 ($CDCl_3$). Na_2SO_4, $MgSO_4$, CH_2Cl_2, $CHCl_3$, EtOAc, pentane, hexanes, MeOH, Et_2O, and toluene were used as purchased. Et_3N was purchased from commercial suppliers and distilled from CaH_2 prior to use. THF was purchased and dried *via* a solvent delivery system. DMSO and DMF (99.8%, extra dry) were stored over 4

[1] For information on these reactors and their construction see the supporting information of: (a) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764. (b) Jouffroy, M.; Kelly, C. B.; Molander, G. *Org. Lett.* **2016**. *18*. 876.
[2] Ravikumar, I.; Saha, S.; Ghosh, P. *Chem. Commun*. **2011**, *47*, 4721.
[3] Seebach, D.; Imwinkelried, R; Stucky, G. *Helv. Chim. Acta* **1987**, *70*, 448.

Å molecular sieves. The transition metal photocatalysts $Ru(bpy)_3(PF_6)_2$ and $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ were prepared in-house by the procedure outlined in our previous publications.[4] The organic photocatalyst 4CzIPN was prepared in-house by the procedure outlined in our previous publication.[5] The nickel complexes used in these studies were prepared according to the procedures outlined here from $NiCl_2 \bullet 6H_2O$. Bromo- or iodoarenes were either purchased from commercial suppliers, received as generous donations from industry (e.g. Merck & Co for **1ad**), or prepared in-house using the procedures outlined here. Sodium sulfinate salts were either purchased commercially or prepared in house from their commercially available sulfonyl chlorides.[6] Organobis(catecholate)silicates were prepared as described in our previous publications.[7]

Photochemistry: Irradiation of reaction vessels was accomplished using blue LEDs. LEDs were configured as outlined in the *Photochemical Reactor Design* section of our previous articles[1b,c] or using a second generation reactor design outlined here. A fan was employed to ensure reactions remained at or near rt when using LEDs.

Information for LED-based Photoreactor Components:

- *Blue LEDs*: 39.4 inch strips, 470 nm blue light, 32918 mcd ft^{-1}
- *Power Supply*: 12V DC CPS series Power Supply - 15 Watt
- *Connectors*: LC2 Locking Male Connector CPS Adapter Cable
- *Clip Fan*: 2-Speed Clip Fan, 6-Inch
- Pyrex crystallizing dishes (125 X 65 mm)
- Aluminum foil
- Duct tape
- Polarized film[8]

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[4] (a) Tellis, J. C.; Primer, D. P.; Molander, G. A. *Science* **2014**, *345*, 433; (b) Kelly, C. B.; Patel, N. R.; Primer, D. N.; Jouffroy, M.; Tellis, J. C.; Molander, G. A. Nat. Protoc. 2017, 12, 472.

[5] Patel, N. P.; Kelly, C. B.; Siegenfeld, A. P.; Molander, G. A. *ACS Catal.* **2017**, *7*, 1766.

[6] ***Typical procedure:*** To a round bottom flask equipped with a stir bar was added Na_2SO_3 (2 equiv) and $NaHCO_3$ (2 equiv) followed by deionized H_2O (1 M in sulfonyl chloride). After stirring for 5 min, the sulfonyl chloride (1 equiv) was added portionwise to the flask. The mixture was heated to 80 °C in an oil bath for 12 h. After this time, the reaction mixture was cooled to rt, and the solvent was removed *in vacuo* by rotary evaporation, affording the crude sulfinate salt. The impurities were triturated with EtOH and removed by filtration. The solvent was removed from the filtrate *in vacuo* by rotary evaporation, giving the pure sulfinate salt.

[7] Lin, K.; Kelly, C. B.; Jouffroy, M. *Org. Synth.* **2017**, *94*, 16.

[8] Example (type used in construction of this reactor):
https://www.amazon.com/gp/product/B01N1IUUIY?ref_=psdc_517834_t2_B00FQO48U8&pldnSite=1

- Recycling container

Photochemical Reactor Design

Protocol for Second Generation Reactor Setup

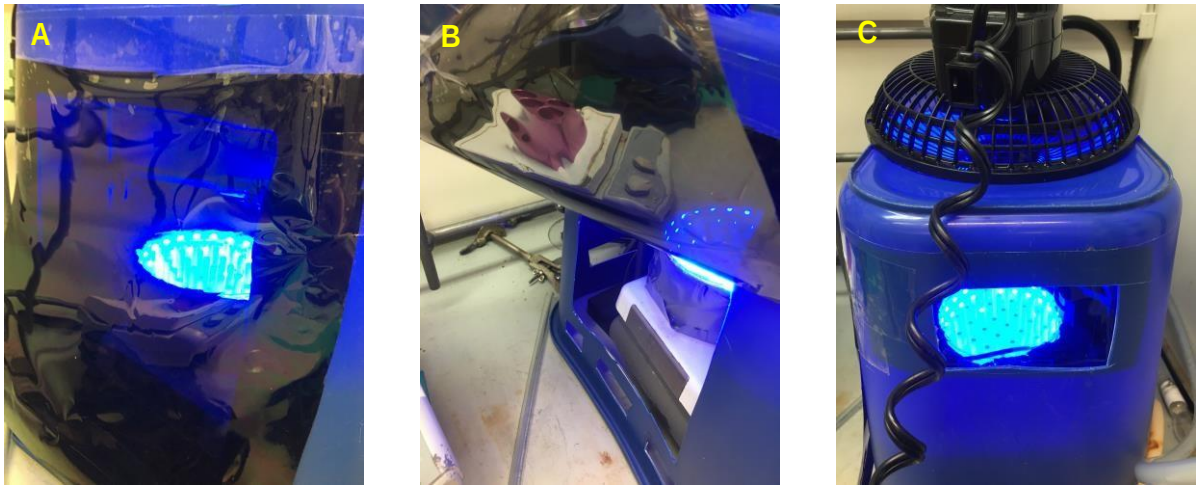
Remove the protective layer on the sticky side of the LED strip and carefully wrap the LED strips on the inside of a clean Pyrex dish.[9] Four bands of LEDs can fit into a 125 X 65 mm Pyrex crystallizing dish.[10] Once the LEDs are securely wrapped, place a layer of aluminum foil around the outside of the dish (including the bottom). Tape the connector wires as well as the foil with duct tape to secure both in place. For vial-scale reactions, cut a sample vial rack to the appropriate size using a saw and place it inside. Place the reactor on top of a 5 x 7 stirring place with a small ring stand underneath it.

Next, modifications to a standard office recycling bin (14.4 x 10.2 x 15 inches) are made. Using a box cutter or similar object, a circular hole is cut in the base of the bin that is smaller than the requisite clip fan such that the clip fan can rest on the top of the bin without falling (~7.5 inch diameter). Next, an additional rectangular hole ~9.5 × 6.5 inches) is cut into the center of the long side of the bin to serve as an entrance. Near the base of the bin, a total of six rectangular air vent holes (~1 × 4 inches) are cut just below the top of the bin (~2 inches). A viewing port (~2 × 4 inches) is cut just above the

[9] Starting from the bottom upward affords the easiest approach.
[10] If smaller lengths of LED strips are used, they can be linked together. Most LED strips are able to be cut (at specified locations) and powered by either end. The appropriate connector is required (male or female) for each end.

base (~1.5 inches). A small square hole (~0.5 × 0.5 inches) is cut at the base of the bin behind the fan port to allow the bar of the ring stand bar to fit through. Polarized film is next cut to fit over the entrance and viewing port. For the viewing port, the film is placed inside and taped. For the entrance, the film is taped to the outside and a small segment of the cut-out piece of the bin is taped to the inside of the film to act as a weight. The bin is next inverted and placed over the stirring plate, and the clip fan is placed atop the inverted bin. The reactor is now ready for use. Turn on the lights and fan (set it to its maximum setting). Allow 15 min to pass for temperature equilibration. Temperature should be monitored in real time using a temperature probe (or thermometer) to determine the ambient temperature within the reactor. Although typically used for vial-scale reactions, this reactor can be used for scale up. For larger vessels (e.g., round bottom flasks), simply lower the flask into the irradiation bay and use the ring stand bar for clamps to hold the flask.[11]

Additional Pictures:

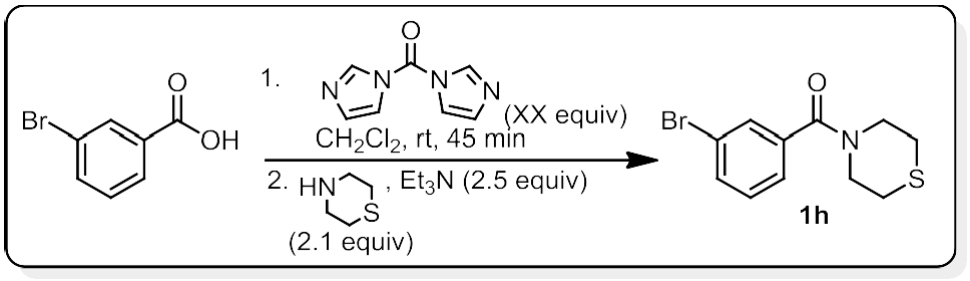


A & B. Entrance flap to photoreactor with polarized film; C. Viewing port with polarized film

[11] This design can accommodate up to a 250 mL round bottom flask. However, if desired, a larger reactor can be assembled by using larger variants of the necessary components and additional LEDs.

Synthesis of Aryl Halides

Amide Synthesis using CDI



(3-Bromophenyl)(thiomorpholino)methanone (1h)

To a 150 mL round bottom flask equipped with stir bar was added 3-bromobenzoic acid (3.01 g, 0.015 mol, 1 equiv) and CH_2Cl_2 (50 mL). To this stirred soln was added 1,1'-carbonyldiimidazole (2.92 g, 0.018 mol, 1.2 equiv) in one portion, turning the soln a clear, pale-yellow and resulting in the evolution of CO_2 gas. The reaction mixture was allowed to stir for 45 min at rt. After this time, thiomorpholine (3.25 g, 3.16 mL, 0.0315 mol, 2.1 equiv) and Et_3N (3.18 g, 4.39 mL, 0.045 mol, 2.5 equiv) were added all at once, and the reaction mixture was stirred overnight. The reaction mixture was then quenched with 50 mL of 2 M aq HCl and stirred vigorously for 10 min. After this time, the soln was transferred to a separatory funnel, and the layers were separated. The aq layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with 2 M aq HCl (150 mL), deionized H_2O (150 mL), saturated aq $NaHCO_3$ (2 × 100 mL), and brine (150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo via* rotary evaporation, affording the pure amide (3.88 g, 90%) as a viscous colorless oil.

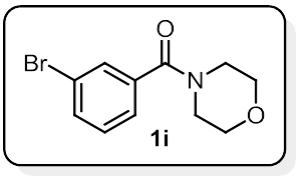
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.56 (br s, 2 H), 2.72 (br s, 2 H), 3.65 (br s, 2 H), 4.01 (br s, 2 H), 7.27 - 7.32 (m, 2 H), 7.50 - 7.53 (m, 1 H), 7.53 - 7.58 (m, 1 H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.5 (CH_2), 28.1 (CH_2), 44.7 (CH_2), 50.2 (CH_2), 122.9 (C), 125.4 (CH), 129.9 (CH), 130.4 (CH), 132.9 (CH), 137.8 (C), 169.0 (C).

FT-IR (cm^{-1}, neat, ATR) 3042 (vw), 2902 (vw), 1628 (vs), 1425 (vs), 1252 (s), 952 (s), 792 (s), 659 (m).

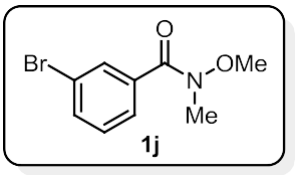
HRMS (ES+) calcd for $C_{11}H_{12}BrNNaOS$ $[M+Na]^+$: 309.9721, found: 307.9740.

(3-Bromophenyl)(morpholino)methanone,[12] 1i (3.67 g, 91%) was prepared according to the above amidation procedure *with the following modification*: 1) morpholine (2.74 g, 2.72 mL, 0.0315 mmol, 2.1 equiv) was used in place of thiomorpholine. The desired amide **1i** was obtained as a viscous colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.39 (br s, 2 H), 3.50 - 3.87 (m, 6 H), 7.21 - 7.32 (m, 2 H), 7.48 - 7.55 (m, 2 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 42.7 (CH_2), 48.3 (CH_2), 66.9 (CH_2), 122.9 (C), 125.8 (CH), 130.3 (CH), 130.4 (CH), 133.1 (CH), 137.4 (C), 168.8 (C).



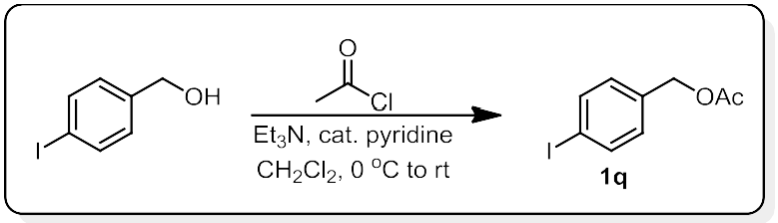
1i

3-Bromo-*N*-methoxy-*N*-methylbenzamide,[13] 1j (11.21 g, 92%) was prepared according to the above amidation procedure *with the following modification*: 1) *N*,*O*-dimethylhydroxylamine hydrochloride (5.85 g, 0.060 mmol, 1.2 equiv) was used in place of thiomorpholine. The desired amide **1i** was obtained as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.35 (s, 3 H) 3.55 (s, 3 H) 7.24-7.32 (t, *J* = 7.88 Hz, 1H) 7.55-7.63 (m, 2H) 7.82 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 33.7 (CH_3) 61.4 (CH_3) 122.2 (C) 127.0 (CH) 129.8 (CH) 131.4 (CH) 133.7 (CH) 136.1 (C) 168.3 (C).



1j

Synthesis of 1q from 4-Iodobenzyl alcohol



1q

4-Iodobenzyl Acetate (1q)[14]

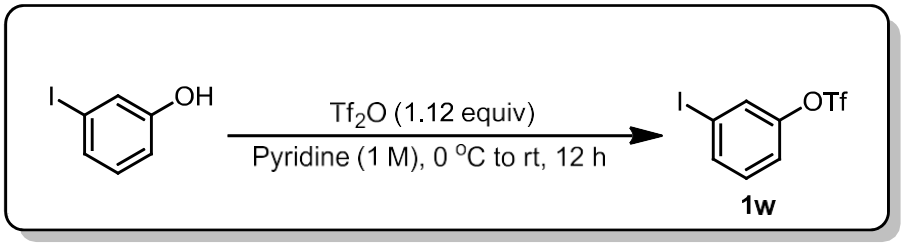
To a 50 mL round bottom flask equipped with a stir bar was added the 4-iodobenzyl alcohol (1.99 g, 8.5 mmol, 1 equiv), Et_3N (1.89 g, 2.61 mL, 18.7 mol, 2.2 equiv), pyridine (0.067 g,

[12] Cederbalk, A.; Lysén, M.; Kehler, J.; Kristensen, J. L. *Tetrahedron* **2017**, *73*, 1576.
[13] Rudzinski, D. M.; Kelly, C. B.; Leadbeater, N. E. *Chem. Commun*. **2012**, *48*, 9610.
[14] Watson, J. K.; Park, S.-J.; Im, J.-H.; Nguyen, S. T.; Mirkin, C. A. *J. Am. Chem. Soc*. **2001**, *123*, 5592.

0.068 mL, 0.85 mol, 0.1 equiv) and CH_2Cl_2 (17 mL). The reaction vessel was sealed with a rubber septum and placed under argon *via* an Ar inlet needle. The flask was cooled to 0 ºC *via* an ice-water bath. After cooling for 5 min, AcCl (0.801 g, 0.730 mL, 12 mmol, 1.2 equiv) was added dropwise *via* a syringe. The reaction mixture was allowed to stir at 0 ºC for 5 min then warmed to rt. The soln was stirred at this temperature overnight. After this time, the reaction mixture was carefully quenched with 2 M aq HCl (40 mL) and transferred to a separatory funnel. Et_2O (100 mL) was added, and the layers were separated. The aq layer was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with 2 M aq HCl (100 mL), deionized H_2O (100 mL) and finally brine (150 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, the crude acetate (**1q**). Further purification was accomplished by vacuum distillation (bp 87-89 ºC @ 0.1 mmHg) as a clear colorless oil (1.50 g, 64%).

^{1}H NMR 2.10 (s, 3 H), 5.04 (s, 2 H), 7.10 (d, *J* = 8.1 Hz, 2 H), 7.70 (d, *J* = 8.2 Hz, 2 H).
^{13}C NMR δ 21.23 (CH_3), 65.81 (CH_2), 94.19 (C), 130.35 (CH), 135.84 (C), 137.93 (CH), 170.99 (C).

Triflation of 3-Iodophenol



3-Iodophenyl Trifluoromethanesulfonate (1w)[15]

To a 50 mL round bottom flask equipped with a stir bar was added pyridine (10 mL) and 3-iodophenol (2.20 g, 10 mmol, 1 equiv). The reaction vessel was sealed with a rubber septum and placed under argon *via* an Ar inlet needle. The flask was cooled to 0 ºC *via* an ice-water bath. After cooling for 5 min, Tf_2O (3.16 g, 1.88 mL, 11.2 mmol, 1.12 equiv) was added dropwise *via* a syringe. The reaction mixture was allowed to stir at 0 ºC for 30 min then warmed to rt. The soln was stirred at this temperature overnight. After this time, the reaction mixture was carefully

[15] Harada, T.; Chiba, M.; Oku, A. *J. Org. Chem.* **1999**, *64*, 8210.

quenched with 2 M HCl (50 mL) and transferred to a separatory funnel. Et_2O (50 mL) was added, and the layers were separated. The aq layer was extracted with Et_2O (2 × 25 mL). The combined organic layers were washed with 2 M aq HCl (50 mL), 2 M aq NaOH (2 × 100 mL), deionized H_2O (100 mL), and finally brine (100 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation, affording the pure triflate (**1w**) (3.44 g, 98%) as a clear yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.17 (t, *J* = 8.1 Hz, 1H), 7.27 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.64 (t, *J* = 1.8 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 94.1 (s, 7 C), 118.9 (q, J_{C-F} = 321.5 Hz, CF_3), 121.0 (CH), 130.6 (CH), 131.6 (CH), 137.8 (CH), 149.4 (C).

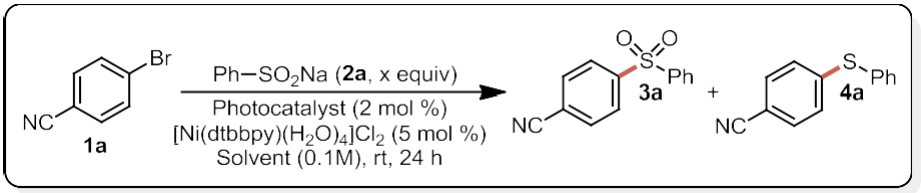
^{19}F NMR ($CDCl_3$, 471 MHz) δ -75.90 (s, 3F).

Optimization and Control Studies

Procedure for optimization and control studies:

To a 4 mL reaction vial equipped with a stir bar was added 4-bromobenzonitrile, **1a** (18.2 mg, 0.1 mmol, 1 equiv), the appropriate photocatalyst (0.002 mmol, 0.02 equiv), the appropriate nickel complex (0.005 mmol, 0.05 equiv), and the appropriate amount of sulfinate salt **2a**. The vial was sealed with a cap containing a TFE-lined silicone septa and was evacuated and purged with argon three times *via* an inlet needle. The vial was then charged with the appropriate anhyd solvent (1 mL). After this, the cap was sealed with Parafilm,® and the vial was irradiated in the aforementioned LED reactor for 24 h. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. After 24 h, an aliquot of a solution of 4,4′-di-*tert*-butylbiphenyl in MeCN with a known concentration (10 mol % relative to the aryl halide) was added to each vial. Product to internal standard ratios as well as thioether to internal standard ratios were determined by HPLC integration.

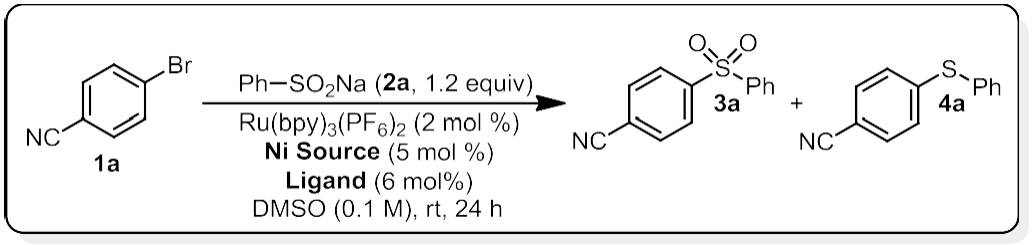
Table S1: Initial Screen of Cross-Coupling



Entry	Photocatalyst	2a loading (equiv)	Solvent	3a/IS Ratio	4a/IS Ratio
1	$Ru(bpy)_3(PF_6)_2$	2.0	1,4-dioxane	–	–
2	$Ru(bpy)_3(PF_6)_2$	2.0	acetone	–	–
3	$Ru(bpy)_3(PF_6)_2$	2.0	MeOH	–	–
4	$Ru(bpy)_3(PF_6)_2$	2.0	MeCN	–	–
5	$Ru(bpy)_3(PF_6)_2$	2.0	DMF	3.10	0.30
5	$Ru(bpy)_3(PF_6)_2$	2.0	DMA	2.91	0.29
6	**$Ru(bpy)_3(PF_6)_2$**	**2.0**	**DMSO**	**3.37**	**0.26**
7[a]	$Ru(bpy)_3(PF_6)_2$	2.0	DMF/H_2O (9:1)	2.57	–
8	$[Ir\{dFCF_3ppy\}2(bpy)]PF_6$	2.0	DMF	1.67	0.24
9	$[Ir\{dFCF_3ppy\}2(bpy)]PF_6$	2.0	DMSO	1.98	0.26
10	$Ru(bpz)_3(PF_6)_2$	2.0	DMF	–	–
11	MesAcr+ClO_4-	2.0	DMF	–	–
12 [a]	4CzIPN	2.0	DMF	0.44	0.32
13	$Ru(bpy)_3(PF_6)_2$	1.0	DMF	2.82	0.24
14	$Ru(bpy)_3(PF_6)_2$	1.2	DMF	2.98	0.24
15	$Ru(bpy)_3(PF_6)_2$	1.5	DMF	3.25	0.26
16	$Ru(bpy)_3(PF_6)_2$	3.0	DMF	3.48	0.21

[a] Multiple unknown side products observed in HPLC trace.

Optimization of Reaction Conditions with High Throughput Experimentation



High throughput experimentation (HTE) was performed at the Penn/Merck Center for High Throughput Experimentation at the University of Pennsylvania. All solvents used in the screening center were dry and degassed. The screen was analyzed by UPLC with addition of an internal standard. The areas for the internal standard (IS), aryl halide (SM), and product (P) from each of the screens are shown in the tables below. The ratios calculated are pertinent only to that specific screen; the ratios from one screen should not be quantitatively compared to those from a different screen. The results of the screens are summarized in two tables shown below, the first representing the ratio of product to internal standard and the second representing the ratio of starting material to internal standard both as determined by UPLC.

General procedure for Screening

To a 96 well plate reactor containing 1 mL reaction vials equipped with a Teflon-coated magnetic stir bar in a glovebox was added a solution of the appropriate ligand (0.6 μmol, 0.06 equiv) dissolved in MeCN (6 μL) to the appropriate vials. Next, a soln of the appropriate Ni source (0.5 μmol, 0.05 equiv) dissolved in MeCN (5 μL) was added to the appropriate vials. The solvent was removed from the vials using a Genevac. To the appropriate vials was added a soln containing the appropriate aryl halide (10 μmol, 1 equiv), sodium benzenesulfinate (12 μmol, 1.2 equiv), $Ru(bpy)_3(PF_6)_2$ (0.02 μmol, 0.02 equiv), 4,4′-di-*tert*-butylbiphenyl (1 μmol, 0.1 equiv) in DMSO (100 μL). The vials were sealed and stirred at rt under blue light irradiation for 24 h. After 24 h the reactions were opened to air, and diluted with 500 μL of MeCN. After stirring the diluted soln on a stirring block for 15 min, 25 μL aliquots were then taken from the reaction vials and dosed into a 96-well UPLC block. These aliquots were further diluted by the addition of 700 μL of MeCN. The reaction mixtures were then analyzed by UPLC.

Table S2: Relevant HTE Data[a]

Sulfonylation

	$Ni(COD)_2$	$NiBr_2(dme)$	$[Ni(py)_4]Cl_2$
bpy	3.01	5.31	5.72
dtbbpy	3.69	4.21	5.61
diOMebpy	4.37	5.35	5.55
Phen	4.12	4.87	**6.03**
BPhen	3.71	3.18	5.06
4,7-OHPhen	4.12	4.14	2.95
2,2'-BOX	3.82	3.99	4.88
^{t}BuBOX	2.07	2.62	4.81

Thioetherification

	$Ni(COD)_2$	$NiBr_2(dme)$	$[Ni(py)_4]Cl_2$
bpy	0.46	1.23	1.23
dtbbpy	0.60	0.85	1.35
diOMebpy	0.72	1.21	1.44
Phen	0.55	0.32	**1.33**
BPhen	0.18	2.04	1.46
4,7-OHPhen	0.84	1.73	2.40
2,2'-BOX	0.94	1.49	1.69
^{t}BuBOX	1.13	2.43	1.69

[a]Values are product to internal standard ratios determined by UPLC analysis; 4,4′-di-*tert*-butylbiphenyl was used as an internal standard for these screens.

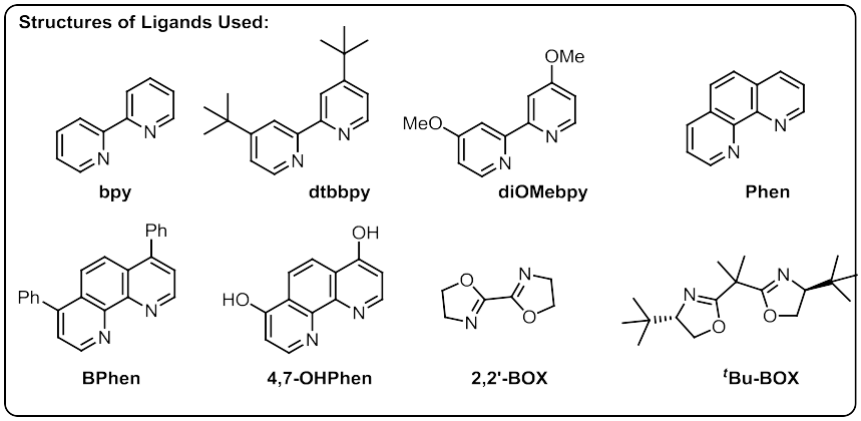
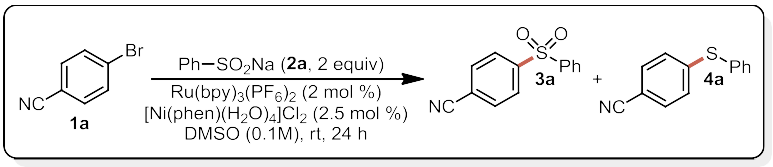


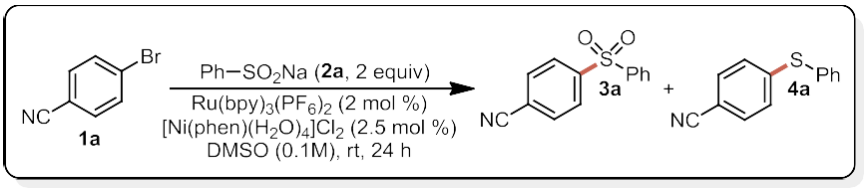
Table S3: Control Studies Using Optimized Conditions



Entry	Deviation from procedure	**3a**/IS Ratio	**4a**/IS Ratio
1	*None*	3.79	0.24
2	*No $Ru(bpy)_3(PF_6)_2$*	n.d.	n.d.
3	*No $[Ni(phen)(H_2O)_4]Cl_2$*	n.d.	n.d.
5	*No $Ru(bpy)_3(PF_6)_2$ and no $[Ni(phen)(H_2O)_4]Cl_2$*	n.d.	n.d.
6	*No light*	n.d.	n.d.
7	*No sulfinate salt,* ***2a***	n.d.	n.d.
8	*Reaction performed at 50 °C*	2.69	0.23

[a]Values are product to internal standard ratios determined by HPLC analysis; 4,4′-di-*tert*-butylbiphenyl was used as an internal standard for these experiments.

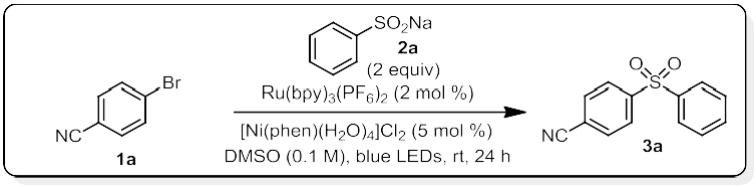
Table S4: Reaction Monitoring



Entry	Time	**1a**/IS Ratio	**3a**/IS Ratio	**4a**/IS Ratio
1	*1 h*	3.12	0.22	n.d.
2	*3 h*	1.31	1.47	0.10
3	*6 h*	0.72	2.89	0.16
5	*12 h*	0.10	3.70	0.23
6	*24 h*	n. d.	3.79	0.24
7	*48 h*	n. d.	3.80	0.24

[a]Values are product to internal standard ratios determined by HPLC analysis; 4,4′-di-*tert*-butylbiphenyl was used as an internal standard for these experiments.

Representative Procedure for Ni/Photoredox C–SO_2R Cross-Coupling



4-(Phenylsulfonyl)benzonitrile[16] (3a)

To an 8 mL reaction vial equipped with a stir bar were added $Ru(bpy)_3(PF_6)_2$ (8.6 mg, 0.01 mmol, 0.02 equiv), bromoarene **1a** (91.0 mg, 0.5 mmol, 1 equiv), $[Ni(phen)(H_2O)_4]Cl_2$ (4.8 mg, 0.025 mmol, 0.025 equiv)[17] and sodium benzenesulfinate, **2a** (164.2 mg, 0.6 mmol, 2 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa and placed under an Ar atmosphere through evacuating and purging with Ar three times *via* an inlet needle. The vial was then charged with anhyd DMSO (5 mL) *via* a syringe. The cap was sealed with Parafilm®, and the now bright red soln was irradiated with blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. The soln was stirred vigorously while being irradiated. Reaction progress was monitored by HPLC and/or GC/MS. Once complete,[18] the now dark red-brown soln was transferred to a separatory funnel and diluted with deionized H_2O (20 mL) and EtOAc (~20 mL). The layers were separated, and the aq layer was extracted with EtOAc (3 × ~20 mL). The combined organic layers were washed with deionized H_2O (2 × ~50 mL) followed by brine (~100 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hex/EtOAc)[19] to give the desired sulfone, **3a**, (101 mg, 83%) as a powdery white solid (mp = 123-124 °C).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (t, *J* = 8.2 Hz, 2H), 7.63 (tt, *J* = 7.3, 2.0 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.93 - 7.98 (m, 2H), 8.06 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 117.2 (C), 117.4 (C), 128.3 (CH), 128.6 (CH), 129.9 (CH), 133.3 (CH), 134.3 (CH), 140.4 (C), 146.2 (C).

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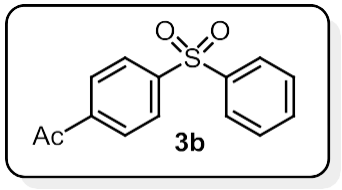
[16] Ulman, A.; Urankar, E. *J. Org. Chem.* **1989**, *54*, 4691.

[17] Although the reaction may be performed without pre-complexation, we found using this pre-complex to provide more consistent results and simplifies the process entirely. This complex can easily be prepared by reacting phen (1.05 equiv) with $NiCl_2 \bullet 6H_2O$ in refluxing EtOH (0.1 M) for 12 h. Once cooled to rt, the solvent can be removed *in vacuo* by rotary evaporation, and the resulting mint green solid can be washed with Et_2O followed by pentane to remove any residual ligand. This complex can be stored on the bench for an indefinite period of time.

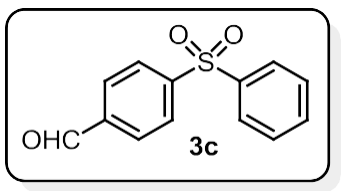
[18] The reaction was complete in 24 h for most substrates. In certain cases, the reaction time was extended to 48 h.

[19] Alternatively, for certain substrates CH_2Cl_2/MeOH was used as the eluent.

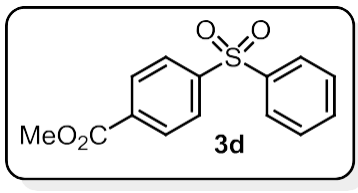
1-(4-(Phenylsulfonyl)phenyl)ethanone,[20] 3b (102.1 mg, 78%) was prepared according to the general procedure from 4′-bromoacetophenone, **1b,** (99.5 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3b** was isolated as a powdery white solid (mp = 133-134 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.62 (s, 3H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.57 - 7.63 (m, 1H), 7.96 (dd, *J* = 8.2, 1.1 Hz, 2H), 8.01-8.07 (m, *J* = 1.8 Hz, 4H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.1 (CH_3), 128.1 (CH), 128.3 (CH), 129.3 (CH), 129.7 (CH), 133.9 (CH), 140.6 (C), 141.1 (C), 145.7 (C), 196.9 (C).



4-(Phenylsulfonyl)benzaldehyde,[20] 3c (65.9 mg, 54%) was prepared according to the general procedure from 4-bromobenzaldehyde, **1c,** (92 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3c** was isolated as a powdery white solid (mp = 131-132 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.54 (t, *J* = 7.5 Hz, 2H), 7.61 (tt, *J* = 7.9, 2.1 Hz, 1H), 7.96 - 7.99 (m, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 2H), 10.08 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 128.2 (CH), 128.6 (CH), 129.8 (CH), 130.6 (CH), 134.1 (CH), 139.4 (C), 140.8 (C), 146.9 (C), 191.0 (CH).

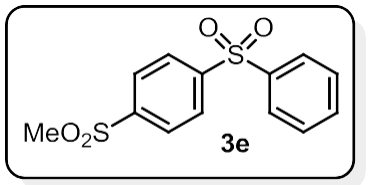


Methyl 4-(Phenylsulfonyl)benzoate,[21] 3d (103.3 mg, 75%) was prepared according to the general procedure from methyl 4-bromobenzoate, **1d,** (107.5 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3c** was isolated as a powdery white solid (mp = 144-145 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.94 (s, 3H), 7.53 (tt, *J* = 7.6, 1.4 Hz, 2H), 7.60 (tt, *J* = 7.2, 2.1 Hz, 1H), 7.93 - 7.98 (m, 2H), 8.01 (dt, *J* = 8.5, 1.8 Hz, 2H), 8.15 (dt, *J* = 8.7, 1.8 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 53.0 (CH_3), 128.0 (CH), 128.2 (CH), 129.7 (CH), 130.7 (CH), 133.9 (CH), 134.6 (C), 141.1 (C), 145.8 (C), 165.8 (C).

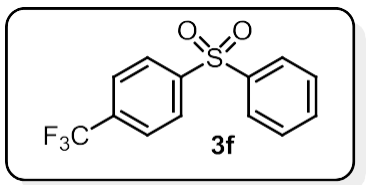


[20] Ulman, A.; Urankar, E. *J. Org. Chem.* **1989**, *54*, 4691
[21] Yang, H.; Li, Y.; Jiang, M.; Wang, J.; Fu, H. *Chem. – Eur. J.* **2011**, *17*, 5652.

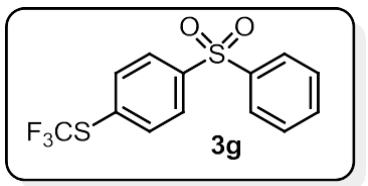
1-(Methylsulfonyl)-4-(phenylsulfonyl)benzene, 3e (90.9 mg, 61%) was prepared according to the general procedure from 1-bromo-4-(methylsulfonyl)benzene, **1e,** (117.5 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (246.2 mg, 1.5 mmol, 3 equiv). The desired sulfone **3e** was isolated as a powdery off-white solid (mp = 149-150 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.07 (s, 3H), 7.57 (t, *J* = 7.3 Hz, 2H), 7.65 (tt, *J* = 7.3, 2.0 Hz, 1H), 7.96 - 8.00 (m, 2H), 8.09 (d, *J* = 8.6 Hz, 2H), 8.16 (d, *J* = 8.3 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 44.5 (CH_3), 128.3 (CH), 128.8 (CH), 129.0 (CH), 129.9 (CH), 134.3 (CH), 140.4 (C), 145.0 (C), 147.1 (C). **FT-IR** (cm^{-1}, neat, ATR) 3089 (w, br), 3024 (w, br), 2926 (w, br), 1309 (s), 1286 (s), 1146 (vs), 956 (m), 738 (s), 604 (vs), 569 (vs). **HRMS** (EI) calcd for $C_{13}H_{12}O_4S_2$ $[M]^+$: 296.0177, found: 296.0168.



1-(Phenylsulfonyl)-4-(trifluoromethyl)benzene,[22] 3f (110.0 mg, 77%) was prepared according to the general procedure from 4-bromobenzotrifluoride, **1f,** (112.5 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (246.2 mg, 1.5 mmol, 3 equiv). The desired sulfone **3f** was isolated as a powdery white solid (mp = 90-91 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.54 (t, *J* = 7.9 Hz, 2H), 7.62 (tt, *J* = 7.2, 2.0 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 123.4 (q, $J_{C\text{-}C\text{-}F}$ = 273.1 Hz, CF_3), 126.7 (q, $J_{C\text{-}C\text{-}C\text{-}F}$ 3.7 Hz, CH), 128.2 (CH), 128.5 (CH), 129.8 (CH), 134.1 (CH), 135.1 (q, $J_{C\text{-}C\text{-}F}$ =33.0 Hz, C), 140.9 (C), 145.5 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -66.35 (s, 3F).



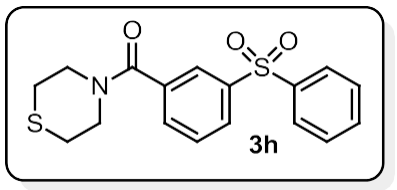
(4-(Phenylsulfonyl)phenyl)(trifluoromethyl)sulfane[23], 3g (120.7 mg, 76%) was prepared according to the general procedure from 4-(trifluoromethylthio)bromobenzene, **1g,** (128.5 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3g** was isolated powdery white solid



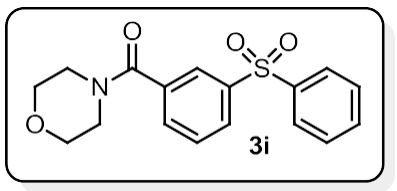
[22] Umierski, N.; Manolikakes, G. *Org. Lett.* **2013**, *15*, 188.
[23] Desbois, M. US Patent: US 4552984 A, **1985**.

(mp = 77-78 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.55 (tt, *J* = 7.8, 1.8 Hz, 2H), 7.62 (tt, *J* = 7.5, 2.0 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.94 - 8.00 (m, 4H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 129.3 (q, J_{C-F} = 309.8 Hz, CF_3), 128.9 (CH), 128.8 (CH), 129.8 (CH), 131.1 (q, $J_{C-S-C-F}$ = 2.7 Hz, C), 134.0 (CH), 136.4 (CH), 141.0 (C), 144.2 (C).**^{19}F NMR** ($CDCl_3$, 471 MHz) δ -44.58 (3F).

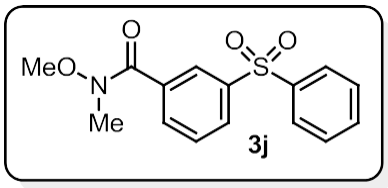
(3-(Phenylsulfonyl)phenyl)(thiomorpholino)methanone, 3h (68.8 mg, 40%) was prepared according to the general procedure from (3-bromophenyl)(thiomorpholino)methanone, **1h,** (143.1 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (246.2 mg, 1.5 mmol, 3 equiv). The desired sulfone **3g** was isolated as a white foam. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.56 (br s, 2H), 2.74 (br s, 2H), 3.61 (br s, 2H), 4.02 (br s, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.55 - 7.64 (m, 3H), 7.92 - 7.96 (m, 3H), 7.96 - 8.04 (m, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 27.6 (CH_2), 28.2 (CH_2), 45.0 (CH_2), 50.4 (CH_2), 126.1 (CH), 128.0 (CH), 129.0 (CH), 129.7 (CH), 130.2 (CH), 131.7 (CH), 133.8 (CH), 137.2 (C), 141.0 (C), 142.6 (C), 168.8 (C). **FT-IR** (cm^{-1}, neat, ATR) 3061 (vw), 2932 (w), 1628 (s), 1412 (m), 1300 (m), 1156 (s), 1099 (m), 717 (m), 687 (m), 581 (vs). **HRMS** (ES+) calcd for $C_{17}H_{17}NNaO_3S_2$ $[M+Na]^+$: 370.0572, found: 370.0545.



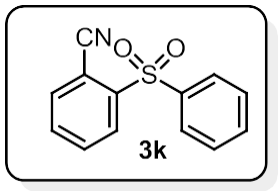
(3-Bromophenyl)(morpholino)methanone, 3i (83.1 mg, 50%) was prepared according to the general procedure from (3-bromophenyl)(morpholino)methanone, **1i,** (143.1 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3i** was isolated as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.35 (br s, 2H), 3.59 (br s, 2H), 3.74 (br s, 4H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.52 - 7.62 (m, 3H), 7.85 - 8.02 (m, 4H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 42.8 (CH_2), 48.4 (CH_2), 66.9 (CH_2), 126.4 (CH), 128.0 (CH), 129.1 (CH), 129.7 (CH), 130.1 (CH), 132.0 (CH), 133.8 (CH), 136.8 (C), 141.0 (C), 142.5 (C), 168.5 (C). **FT-IR** (cm^{-1}, neat, ATR) 3052 (vw), 1629 (vs), 1435 (m), 1301 (m), 1148 (vs), 1112 (vs), 1024 (m), 718 (vs), 689 (s), 575 (vs). **HRMS** (ES+) calcd for $C_{17}H_{18}NO_4S$ $[M+H]^+$: 332.0957, found: 332.0941.



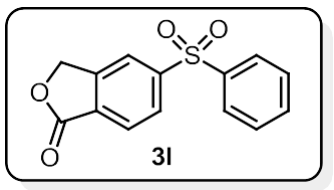
***N*-Methoxy-*N*-methyl-3-(phenylsulfonyl)benzamide, 3j** (69.7 mg, 46%) was prepared according to the general procedure from 3-bromo-*N*-methoxy-*N*-methylbenzamide, **1j,** (122.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3j** was isolated as a clear yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.35 (br s, 3H), 3.48 (br s, 3H), 7.39 - 7.64 (m, 4H), 7.80 - 7.97 (m, 3H), 8.02 (br s, 1H), 8.26 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 33.6 (CH_3), 61.5 (CH_3), 127.8 (CH), 128.0 (CH), 129.5 (CH), 129.6 (CH), 129.7 (CH), 133.2 (CH), 133.7 (CH), 135.5 (C), 141.4 (C), 141.9 (C), 168.0 (C). **FT-IR** (cm^{-1}, neat, ATR) 3061 (vw), 2943 (vw), 1641 (s), 1303 (s), 1150 (vs), 1100 (s), 718 (s), 580 (vs). **HRMS** (EI) calcd for $C_{15}H_{15}NO_4S$ $[M]^+$: 305.0722, found: 305.0719.



2-(Phenylsulfonyl)benzonitrile,[24] 3k (49.1 mg, 40%) was prepared according to the general procedure from 2-bromobenzonitrile, **1k,** (122.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3j** was isolated as powdery white solid (mp = 97-98 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.57 (tt, *J* = 7.3, 1.4 Hz, 2H), 7.65 (tt, *J* = 7.5, 2.0 Hz, 1H), 7.67 - 7.72 (m, 1H), 7.81 (t, *J* = 7.5 Hz, 2H), 8.06 - 8.12 (m, 2H), 8.33 - 8.38 (m, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 111.7 (C), 115.9 (C), 128.9 (CH), 129.7 (CH), 130.1 (CH), 133.5 (CH), 133.6 (CH), 134.5 (CH), 135.9 (CH), 139.8 (C), 143.9 (C).



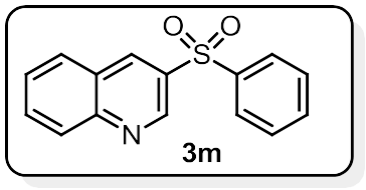
5-(Phenylsulfonyl)isobenzofuran-1(3*H*)-one, 3l (103.2 mg, 75%) was prepared according to the general procedure from 5-bromoisobenzofuran-1(3*H*)-one, **1l,** (106.5 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3l** was isolated as a powdery white solid (mp = 167-168 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 5.39 (s, 2H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.64 (tt, *J* = 7.3, 1.2 Hz, 1H), 7.97 - 8.01 (m, 2H), 8.05 (d, *J* = 8.1 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.13 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 69.8 (CH_2), 122.2 (CH), 127.2 (CH), 128.3 (CH), 128.8 (CH), 129.9 (CH), 130.1 (C), 134.3 (CH), 140.6 C), 147.4 (C), 147.6 (C), 169.3 (C). **FT-IR** (cm^{-1}, neat, ATR) 3085 (vw), 2924 (vw),



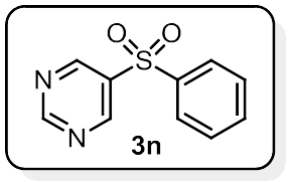
[24] Perumal, S.; Chandrasekaran, R.; Vijayabaskar, V.; Wilson, D. A. *Magn. Reson. Chem.* **1995**, *33*, 779.

1759 (vs), 1305 (s), 1150 (vs), 1000 (m), 723 (vs), 590 (s). **HRMS** (EI) calcd for $C_{14}H_{10}O_4S$ $[M]^+$: 274.0300, found: 274.0289.

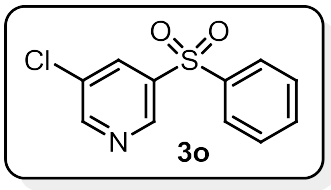
3-(Phenylsulfonyl)quinoline,[25] **3m** (77.0 mg, 70%) was prepared according to the general procedure from 3-bromoquinoline, **1m,** (104.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2mg, 1.0 mmol, 2 equiv). The desired sulfone **3m** was isolated as a powdery off-white solid (mp = 149-150 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.55 (tt, *J* = 7.9, 1.2 Hz, 2H), 7.61 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.69 (ddd, *J* = 8.0, 7.0, 1.4 Hz, 1H), 7.89 (ddd, *J* = 8.5, 7.0, 1.4 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 8.02 - 8.06 (m, 2H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.83 (d, *J* = 2.3 Hz, 1H), 9.28 (d, *J* = 2.3 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 126.7 (C), 128.1 (CH), 128.7 (CH), 129.5 (CH), 129.9 (CH), 129.9 (CH), 133.0 (CH), 134.0 (CH), 135.0 (C), 137.2 (CH), 141.3 (C), 147.4 (CH), 149.7 (C).



5-(Phenylsulfonyl)pyrimidine, 3n (45.1 mg, 41%) was prepared according to the general procedure from 5-bromopyrimidine, **1n,** (79.5 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (246.2 mg, 1.5 mmol, 3 equiv). The desired sulfone **3n** was isolated as a powdery white solid (mp = 125-126 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.61 (t, *J* = 7.3 Hz, 2H), 7.69 (tt, *J* = 7.3, 1.2 Hz, 1H), 7.98 - 8.04 (m, 2H), 9.22 (s, 2H), 9.37 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 128.2 (CH), 130.2 (CH), 134.7 (CH), 137.3 (CH), 140.2 (CH), 156.2 (CH), 161.7 (C). **FT-IR** (cm^{-1}, neat, ATR) 3056 (w), 1558 (vs), 1317 (s), 1144 (vs), 715 (m), 565 (s). **HRMS** (ES+) calcd for $C_{10}H_9N_2O_2S$ $[M+H]^+$: 221.0385, found: 221.0390.



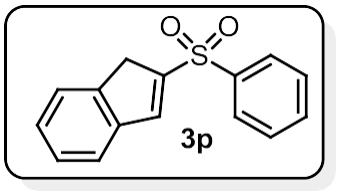
3-Chloro-5-(phenylsulfonyl)pyridine, 3o (62.5 mg, 49%) was prepared according to the general procedure from 3-bromo-5-chloropyridine, **1o,** (96.2 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (246.2 mg, 1.5 mmol, 3 equiv). The desired sulfone **3o** was isolated as a powdery white solid (mp = 125-126 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.59 (t, *J* = 7.3 Hz, 2H), 7.66 (tt, *J* = 7.3, 2.2 Hz, 1H), 7.97 - 8.01 (m, 2H), 8.20 (t, *J* =



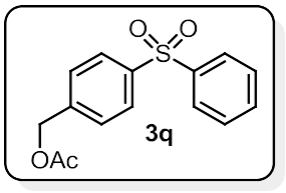
[25] Padwa, A.; Kline, D. N.; Norman, B. H. *J. Org. Chem.* **1989**, *54*, 810.

2.1 Hz, 1H), 8.74 (d, *J* = 2.2 Hz, 1H), 9.01 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 128.1 (CH), 129.9 (CH, C), 134.4 (CH, C), 134.9 (CH), 140.3 (C), 146.4 (CH), 152.9 (CH). **FT-IR** (cm^{-1}, neat, ATR) 3051 (vw), 1329 (m), 1156 (vs), 1079 (m), 721 (s), 688 (vs), 571 (vs). **HRMS** (EI) calcd for $C_{11}H_8ClNO_2S$ $[M]^+$: 252.9964, found: 252.9973.

2-(Phenylsulfonyl)-1*H*-indene,[26] 3p (99.4 mg, 77%) was prepared according to the general procedure from 2-bromo-1H-indene, **1p,** (96.2 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (246.2 mg, 1.5 mmol, 3 equiv) ***with the following modification:*** the nickel catalyst was not added to the reaction mixture. The desired sulfone **3p** was isolated as a powdery light yellow solid (mp = 119-120 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.65 (s, 2H), 7.32 - 7.38 (m, 2H), 7.42 - 7.47 (m, 1H), 7.51 - 7.57 (m, 3H), 7.61 (tt, *J* = 7.5, 2.0 Hz, 1H), 7.71 (t, *J* = 1.8 Hz, 1H), 7.99 (d, *J* = 7.3 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 38.1 (CH_2), 124.3 (CH), 124.7 (CH), 127.7 (CH), 128.0 (CH), 128.6 (CH), 129.6 (CH), 133.6 (CH), 140.9 (C), 141.2 (C), 141.3 (CH), 144.6 (C), 145.6 (C).

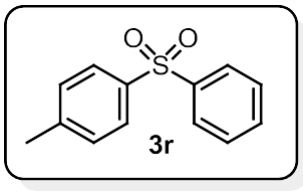


4-(Phenylsulfonyl)benzyl acetate, 3q (79.9 mg, 55%) was prepared according to the general procedure from 4-iodobenzyl acetate, **1q** (138.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3q** was isolated as a powdery white solid (mp = 86-87 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.11 (s, 3H), 5.13 (s, 2H), 7.45 - 7.54 (m, 4H), 7.57 (t, *J* = 7.0 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 4H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.0 (CH_3), 65.2 (CH_2), 127.9 (CH), 128.2 (CH), 128.7 (CH), 129.5 (CH), 133.5 (CH), 141.5 (C), 141.7 (C), 141.8 (C), 170.7 (C). **FT-IR** (cm^{-1}, neat, ATR) 2951 (vw), 1725 (s), 1236 (s), 1151 (m), 963 (m), 722 (s), 571 (vs). **HRMS** (EI) calcd for $C_{15}H_{14}O_4S$ $[M]^+$: 290.0613, found: 290.0622.

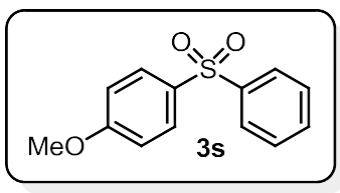


[26] Nenajdenko, V. G.; Denisenko, D. I.; Balenkova, E. S. *Russ. Chem. Bull.* **2002**, 51, 2090.

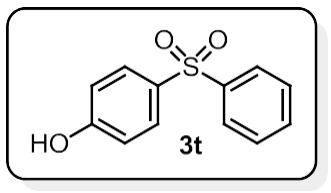
1-Methyl-4-(phenylsulfonyl)benzene,[27] **3r** (86.0 mg, 74%) was prepared according to the general procedure from 4-iodotoluene, **1r** (109.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3r** was isolated as a powdery white solid (mp = 124-125 °C. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.39 (s, 3 H), 7.29 (d, *J*=8.1 Hz, 2 H), 7.48 (t, *J*=7.8 Hz, 2 H), 7.54 (tt, *J*=7.2, 1.7 Hz, 1 H), 7.83 (d, *J*=8.4 Hz, 2 H), 7.93 (d, *J*=7.3 Hz, 2 H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.8 (CH_3), 127.8 (CH C), 128.0 (CH), 129.5 (CH), 130.2 (CH), 133.3 (CH), 138.9 (C), 142.3 (C), 144.4 (C)**.**



1-Methoxy-4-(phenylsulfonyl)benzene,[28] **3s** (79.7 mg, 64%) was prepared according to the general procedure from 4-iodoanisole, **1s** (117.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (246.2 mg, 1.5 mmol, 3 equiv). The desired sulfone **3s** was isolated as a powdery white solid (mp = 89-90 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.84 (s, 3H), 6.96 (d, *J* = 8.9 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.54 (tt, *J* = 7.2, 2.4 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.90 - 7.94 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 55.9 (CH_3), 114.7 (CH), 127.5 (CH), 129.4 (CH), 130.1 (CH), 133.1 (CH), 133.3 (C), 142.6 (C), 163.6 (C).

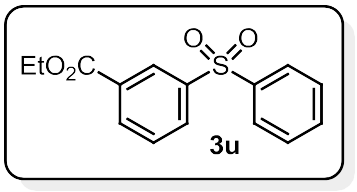


4-(Phenylsulfonyl)phenol,[29] **3t** (87.0 mg, 74%) was prepared according to the general procedure from 4-iodophenol, **1t** (117.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (246.2 mg, 1.5 mmol, 3 equiv). The desired sulfone **3t** was isolated as a a powdery white solid (mp = 136-137 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 5.77 (br s, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 6.6 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR** (acetone-d_6, 125 MHz) δ 116.5 (CH), 127.6 (CH), 129.8 (CH), 130.6 (CH), 133.0 (C), 133.3 (CH), 143.6 (C), 162.3 (C)**.**

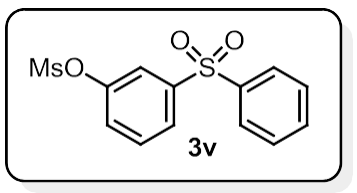


[27] Emmett, E. J.; Hayter, B. R.; Willis, M. C. *Angew. Chem., Int. Ed.* **2013**, *52*, 12679.
[28] Deeming, A. S.; Russell, C. J.; Hennessy, A. J.; Willis, M. C. *Org. Lett.* **2014**, *16*, 150.
[29] Zhu, W.; Ma, D. *J. Org. Chem.* **2005**, *70*, 2696.

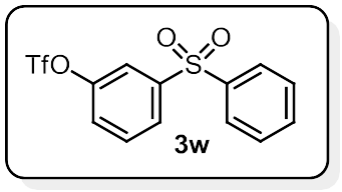
Ethyl 3-(Phenylsulfonyl)benzoate,[30] 3u (124.2 mg, 86%) was prepared according to the general procedure from ethyl 3-iodobenzoate, **1u** (138.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (246.2 mg, 1.5 mmol, 3 equiv). The desired sulfone **3t** was isolated as a powdery white solid (mp = 61-62 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.41 (t, *J* = 7.1 Hz, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 8.2 Hz, 2H), 7.56 - 7.63 (m, 2H), 7.93 - 8.01 (m, 2H), 8.13 (dt, *J* = 7.6, 1.1 Hz, 1H), 8.24 (dt, *J* = 7.9, 1.3 Hz, 1H), 8.60 (t, *J* = 1.7 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.6 (CH_3), 62.0 (CH_2), 128.1 (CH), 129.0 (CH), 129.7 (CH), 129.8 (CH), 131.84 (CH), 132.2 (C), 133.8 (CH), 134.3 (CH), 141.3 (C), 142.6 (C), 165.1 (C).



3-(Phenylsulfonyl)phenyl Methanesulfonate, 3v (129.6 mg, 83%) was prepared according to the general procedure from 3-iodophenyl methanesulfonate, **1u** (149.1 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3t** was isolated as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.19 (s, 3H), 7.47 - 7.63 (m, 5H), 7.84 - 7.86 (m, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 38.2 (CH_3), 121.5 (CH), 126.7 (CH), 127.2 (CH), 128.0 (CH), 129.8 (CH), 131.4 (CH), 134.0 (CH), 140.9 (C), 144.0 (C), 149.4 (C). **FT-IR** (cm^{-1}, neat, ATR) 3065 (vw), 3042(vw), 2939 (vw), 1598 (w), 1301 (s) 1203 (s), 1161 (vs), 1149 (vs), 906 (s), 795 (s), 677 (s), 587 (s). **HRMS** (EI) calcd for $C_{13}H_{12}O_5S_2$ $[M]^+$: 312.0126, found: 312.0130.



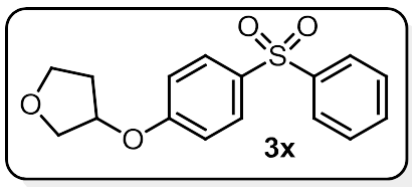
3-(Phenylsulfonyl)phenyl Trifluoromethanesulfonate, 3w (117.0 mg, 64%) was prepared according to the general procedure from 3-iodophenyl trifluoromethanesulfonate, **1w** (176.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3w** was isolated as a clear colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.47 (d, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 6.7 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 2H), 7.87 (br s, 1H), 7.95 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 118.9 (q, $J_{C\text{-}F}$ = 321.5 Hz, CF_3), 121.1 (CH), 126.4 (CH), 127.8 (CH), 128.1 (CH), 129.9 (CH), 131.8 (CH), 134.2



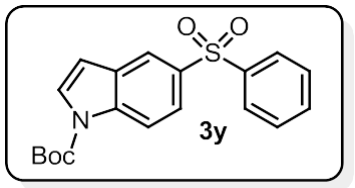
[30] Perumal, S.; Chandrasekaran, R.; Vijayabaskar, V.; Wilson, D. A. *Magn. Reson. Chem.* **1995**, *33*, 779.

(CH), 140.6 (C), 144.6 (CH), 149.7 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -75.74 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 3070 (vw), 1590 (w), 1423 (s), 1209 (vs), 1165 (s), 1136 (vs), 912 (s), 805 (s), 677 (m), 588 (s). **HRMS** (EI) calcd for $C_{13}H_9F_3O_5S_2$ $[M]^+$: 365.9843, found: 365.9855.

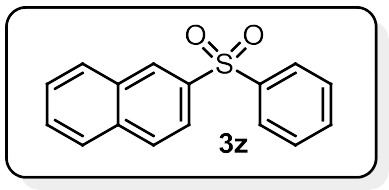
3-(4-(Phenylsulfonyl)phenoxy)tetrahydrofuran, 3x (95.3 mg, 63%) was prepared according to the general procedure from 3-(4-iodophenoxy)tetrahydrofuran, **1x** (145.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3x** was isolated as a powdery white solid (mp = 133-134 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.06 - 2.16 (m, 1H), 2.19 - 2.29 (m, 1H), 3.87 - 4.04 (m, 4H), 4.96 (t, *J* = 5.3 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 7.47 - 7.52 (m, 2H), 7.52 - 7.58 (m, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 37.0 (CH_2), 68.2 (CH_2), 73.4 (CH_2), 78.1 (CH), 112.4 (CH), 123.0 (CH), 124.7 (CH), 125.4 (CH), 128.1 (CH), 128.5 (C), 136.6 (C),153.9 (C). **FT-IR** (cm^{-1}, neat, ATR) 2950 (vw), 1588 (w), 1259 (s), 1148(s) 1107 (m), 1078 (m), 832 (m), 581 (s). **HRMS** (EI) calcd for $C_{16}H_{16}O_4S$ $[M]^+$: 304.0769, found: 304.0776.



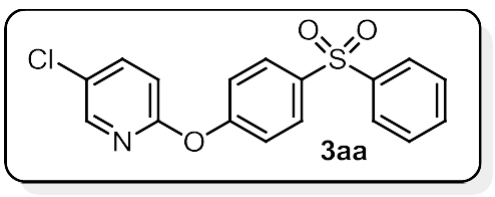
***tert*-Butyl 5-(Phenylsulfonyl)-1H-indole-1-carboxylate, 3y** (77.6 mg, 44%) was prepared according to the general procedure from *tert*-butyl 5-iodo-1H-indole-1-carboxylate, **1y** (145.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3y** was isolated as a clear, yellow oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.66 (s, 9H), 6.65 (d, *J* = 3.6 Hz, 1H), 7.41 - 7.58 (m, 3H), 7.69 (d, *J* = 3.6 Hz, 1H), 7.86 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.90 - 8.00 (m, 2H), 8.17 - 8.31 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 28.3 (CH_3), 85.1 (C), 107.8 (CH), 116.1 (CH), 121.7 (CH), 123.5 (CH), 127.6 (CH), 128.5 (CH), 129.4 (CH), 130.8 (C), 133.1 (CH), 135.8 (C), 137.7 (C), 142.6 (C), 149.3 (C). **FT-IR** (cm^{-1}, neat, ATR) 2981 (vw), 1736 (vs), 1369 (m), 1305 (s), 1283 (s), 1147 (vs), 1135 (vs), 1022 (s), 727 (vs), 687 (s), 573 (vs). **HRMS** (EI) calcd for $C_{14}H_{10}NO_2S$ $[M-C_5O_2H_9]^+$: 256.0432, found: 256.0460.



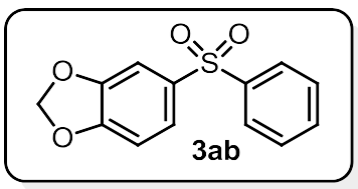
2-(Phenylsulfonyl)naphthalene,[31] **3z** (100.9 mg, 76%) was prepared according to the general procedure from 2-iodonaphthalene, **1z** (127.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3z** was isolated as a powdery white solid (mp = 118-119 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.47 - 7.53 (m, 2H), 7.53 - 7.58 (m, 1H), 7.59 - 7.67 (m, 2H), 7.83 - 7.90 (m, 2H), 7.91 - 7.95 (m, 1H), 7.96 - 8.04 (m, 3H), 8.58 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 122.9 (CH), 127.9 (CH), 127.9 (CH), 128.1 (CH), 129.3 (CH), 129.4 (CH), 129.5 (CH), 129.6 (CH), 129.9 (CH), 132.4 (C), 133.4 (CH), 135.2 (C), 138.6 (C), 141.9 (C).



5-Chloro-2-(4-(phenylsulfonyl)phenoxy)pyridine, 3aa (135.6 mg, 79%) was prepared according to the general procedure from 5-chloro-2-(4-iodophenoxy)pyridine, **1aa** (127.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3aa** was isolated as a powdery white solid (mp = 170-171 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 6.96 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.0 Hz, 2H), 7.57 (d, *J* = 6.9 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.97 (t, *J* = 6.7 Hz, 4H), 8.12 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 113.8 (CH), 121.3 (CH), 127.4 (C), 127.8 (CH), 129.5 (CH), 129.9 (CH), 133.4 (CH), 137.5 (C), 140.0 (CH), 141.8 (C), 146.2 (CH), 158.2 (C), 160.8 (C). **FT-IR** (cm^{-1}, neat, ATR) 3065 (vw), 2932 (w), 1579 (m), 1457 (s), 1265 (s), 1151 (vs), 1104 (vs), 733 (s), 568 (vs). **HRMS** (EI) calcd for $C_{17}H_{12}ClNO_3S$ $[M]^+$: 345.0226, found: 345.0242.



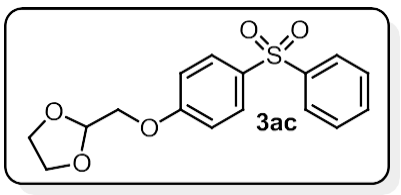
5-(Phenylsulfonyl)benzo[*d*][1,3]dioxole,[32] **3ab** (106.5 mg, 81%) was prepared according to the general procedure from 5-iodobenzo[d][1,3]dioxole, **1ab** (124.0 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (246.2 mg, 1.5 mmol, 3 equiv). The desired sulfone **3ab** was isolated as a powdery white solid (mp = 101-102 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 6.05 (s, 2H), 6.88 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.50 (tt, *J* = 7.9, 1.5 Hz,



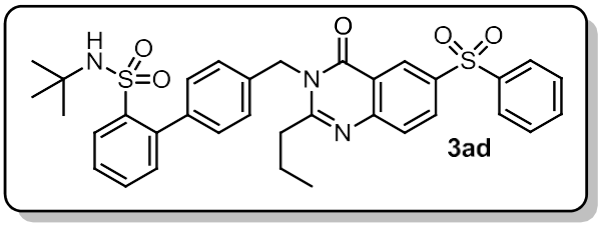
[31] Umierski, N.; Manolikakes, G. *Org. Lett.* **2013**, *15*, 188.
[32] Pandya, V. G.; Mhaske, S. B. *Org. Lett.* **2014**, *16*, 3836.

2H), 7.53 - 7.58 (m, 2H), 7.88 - 7.94 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 102.7 (CH_2), 108.1 (CH), 108.8 (CH), 123.9 (CH), 127.7 (CH), 129.5 (CH), 133.3 (CH), 135.2 (C), 142.3 (C), 148.6 (C), 152.1 (C).

2-((4-(Phenylsulfonyl)phenoxy)methyl)-1,3-dioxolane, 3ac (96.5 mg, 61%) was prepared according to the general procedure from 2-((4-iodophenoxy)methyl)-1,3-dioxolane, **1ab** (153.1 mg, 0.5 mmol, 1 equiv) and sodium benzenesulfinate, **2a** (164.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3ac** was isolated as a powdery white solid (mp = 141-142 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.94 - 4.06 (m, 4H), 4.07 (d, *J* = 3.7 Hz, 2H), 5.28 (t, *J* = 3.9 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 65.5 (CH_2), 69.2 (CH_2), 101.7 (CH), 115.3 (CH), 127.5 (CH), 129.4 (CH), 130.0 (CH), 133.1 (CH), 133.8 (C), 142.4 (C), 162.5 (C). **FT-IR** (cm^{-1}, neat, ATR) 2935 (w), 2887 (w), 1591 (m), 1259 (m), 1148 (vs), 1039 (s), 1022 (m), 732 (s), 561 (vs). **HRMS** (EI) calcd for $C_{16}H_{16}O_5S$ $[M]^+$: 320.0718, found: 320.0745.

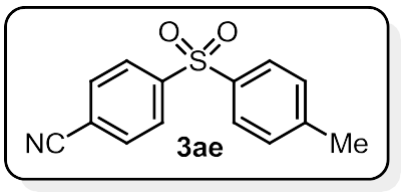


***N*-(*tert*-Butyl)-4'-((4-oxo-6-(phenylsulfonyl)-2-propylquinazolin-3(4*H*)-yl)methyl)-[1,1'-biphenyl]-2-sulfonamide, 3ad** (56.7 mg, 64%) was prepared according to the general procedure from 2 *N*-(*tert*-butyl)-4'-((6-iodo-4-oxo-2-propylquinazolin-3(4H)-yl)methyl)-[1,1'-biphenyl]-2-sulfonamide, **1ad** (92.3 mg, 0.15 mmol, 1 equiv) and sodium benzenesulfinate **2a** (49.2 mg, 0.3 mmol, 2 equiv). The desired sulfone **3ad** was isolated as a white foam. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 0.97 (s, 9H), 1.01 (t, *J* = 7.3 Hz, 3H), 1.74 - 1.94 (m, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 3.50 (s, 1H), 5.44 (br s, 2H), 7.25 (d, *J* = 7.5 Hz, 3H), 7.42 - 7.60 (m, 7H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 2H), 8.14 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.87 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 14.1 (CH_3), 20.6 (CH_2), 30.0 (CH_3), 37.5 (CH_2), 46.8 (CH_2), 54.7 (C), 120.8 (C), 126.5 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 128.9 (CH), 129.7 (CH), 130.8 (CH), 132.1 (CH), 132.5 (CH), 132.6 (CH), 133.7 (s, 2 C), 136.0 (C), 139.4 (C), 139.5 (C), 139.7 (C), 141.5 (C),

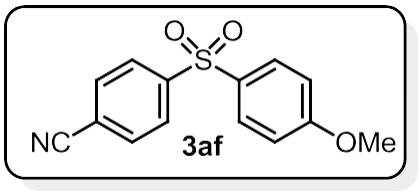


142.3 (C), 150.5 (C), 160.3 (C), 161.8 (C). **FT-IR** (cm^{-1}, neat, ATR) 3305 (w, br), 2962 (w), 2932 (w), 2229 (w), 1671 (s), 1586 (m), 1303 (s), 1158 (vs), 1129 (m), 729 (vs), 583 (vs). **HRMS** (ES+) calcd for $C_{34}H_{36}N_3O_5S_2$ $[M+H]^+$: 630.2096, found: 630.2094.

4-Tosylbenzonitrile,[33] **3ae** (77.9 mg, 61%) was prepared according to the general procedure from 4-bromobenzonitrile, **1a** (91.0 mg, 0.5 mmol, 1 equiv) and sodium 4-methylbenzenesulfinate, **2b** (178.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3ae** was isolated as a powdery white solid (mp = 130-131 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 2.42 (s, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 21.8 (CH_3), 116.9 (C), 117.4 (C), 128.2 (CH), 128.3 (CH), 130.5 (CH), 133.3 (CH), 137.3 (C), 145.5 (C), 146.4 (C).

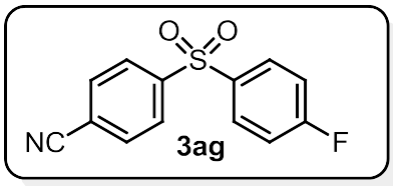


4-((4-Methoxyphenyl)sulfonyl)benzonitrile,[34] **3af** (88.7 mg, 66%) was prepared according to the general procedure from 4-bromobenzonitrile, **1a** (91.0 mg, 0.5 mmol, 1 equiv) and sodium 4-methoxybenzenesulfinate, **2c** (194.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3ae** was isolated as a powdery white solid (mp = 132-133 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.86 (s, 3H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.9 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 55.98 (CH_3), 115.12 (CH), 116.73 (C), 117.47 (C), 128.15 (CH), 130.48 (CH), 131.64 (C), 133.24 (CH), 146.84 (C), 164.27 (C).

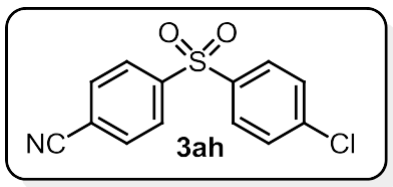


[33] Srinivas; R., Vikas S.; Konda, K.; Sreedhar, B. *Adv. Synth. Catal.* **2014**, *356*, 805.
[34] Samreth, S.; Renaut, P.; Bajgrowicz, J.; Millet, J. US Patent: US5100913 A, **1992**.

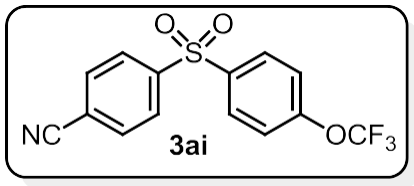
4-((4-Fluorophenyl)sulfonyl)benzonitrile,[35] **3ag** (90.4 mg, 70%) was prepared according to the general procedure from 4-bromobenzonitrile, **1a** (91.0 mg, 0.5 mmol, 1 equiv) and sodium 4-fluorobenzenesulfinate, **2d** (182.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3ag** was isolated as a powdery white solid (mp = 159-160 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.24 (t, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.98 (dd, *J* = 8.4, 5.0 Hz, 2H), 8.05 (d, *J* = 8.3 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 117.2 (d, $J_{C\text{-}C\text{-}F}$ = 22.7 Hz, CH, C), 117.3 (C), 128.4 (CH), 131.1 (d, $J_{C\text{-}C\text{-}C\text{-}F}$ = 10.0 Hz, CH), 133.3 (CH), 136.4 (d, $J_{C\text{-}C\text{-}C\text{-}C\text{-}F}$ = 2.7 Hz, C), 145.8 (C), 166.1 (d, $J_{C\text{-}F}$ = 257.9 Hz, CF). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -105.50 (s, 1F).



4-((4-Chlorophenyl)sulfonyl)benzonitrile,[36] **3ah** (62.5 mg, 45%) was prepared according to the general procedure from 4-bromobenzonitrile, **1a** (91.0 mg, 0.5 mmol, 1 equiv) and sodium 4-chlorobenzenesulfinate, **2e** (198.6 mg, 1.0 mmol, 2 equiv). The desired sulfone **3ah** was isolated as a powdery white solid (mp = 155-156 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.53 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 7.8 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 117.3 (C), 117.4 (C), 128.5 (CH), 129.7 (CH), 130.3 (CH), 133.4 (CH), 138. 9 (C), 141.2 (C), 145.7 (C).



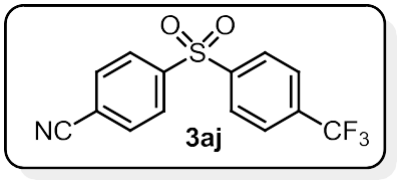
4-((4-(Trifluoromethoxy)phenyl)sulfonyl)benzonitrile, 3ai (53.8 mg, 33%) was prepared according to the general procedure from 4-bromobenzonitrile, **1a** (91.0 mg, 0.5 mmol, 1 equiv) and sodium 4-(trifluoromethoxy)benzenesulfinate, **2f** (284.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3ai** was isolated as a powdery white solid (mp = 117-118 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.38 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.3 Hz, 2H). **^{13}C NMR**



[35] Zheng, X.; Bauer, P.; Baumeister, T.; Buckmelter, A. J.; Caligiuri, M.; Clodfelter, K. H.; Han, B.; Ho, Y.-C.; Kley, N.; Lin, J.; Reynolds, D. J.; Sharma, G.; Smith, C. C.; Wang, Z.; Dragovich, P. S.; Gunzner-Toste, J.; Liederer, B. M.; Ly, J.; O'Brien, T.; Oh, A.; Wang, L.; Wang, W.; Xiao, Y.; Zak, M.; Zhao, G.; Yuen, P.-w.; Bair, K. W. *J. Med. Chem.* **2013**, 56, 6413.
[36] Ahammed, S.; Kundu, D.; Siddiqui, M. N.; Ranu, B. C. *Tetrahedron Lett.* **2015**, 56, 335.

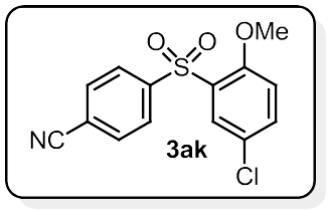
($CDCl_3$, 125 MHz) δ 120.3 (q, J_{C-F} = 258.9 Hz, CF_3), 117.2 (C), 117.4 (C), 121.5 (CH), 128.5 (CH), 130.4 (CH), 133.4 (CH), 138.5 (C), 145.4 (C), 153.3 (C). **^{19}F NMR** ($CDCl_3$, 471 MHz) δ -60.85 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 3101 (vw), 2932 (vw), 2230 (w), 1889 (w), 1495 (w), 1216 (s), 1152 (vs), 632 (s0, 580 (vs). **HRMS** (EI) calcd for $C_{14}H_8F_3NO_3S$ $[M]^+$: 327.0177, found: 327.0191.

4-((4-(Trifluoromethyl)phenyl)sulfonyl)benzonitrile, 3aj (65.1 mg, 42%) was prepared according to the general procedure from 4-bromobenzonitrile, **1a** (91.0 mg, 0.5 mmol, 1 equiv) and sodium 4-(trifluoromethyl)benzenesulfinate, **2g** (232.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3aj** was isolated as a powdery white solid (mp = 142-143 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.84 (t, J = 8.1 Hz, 4H), 8.06 - 8.13 (m, 4H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 117.2 (C), 117.8 (C), 123.2 (q, J_{C-F} = 273.4 Hz, CF_3), 127.1 (CH), 128.8 (CH), 128.8 (CH), 133.6 (CH), 135.9 (q, J_{C-C-F} =34.5 Hz, C), 144.0 (C), 145.1 (C). **^{19}F NMR** ($CDCl_3$, 125 MHz) δ -66.48 (s, 3F). **FT-IR** (cm^{-1}, neat, ATR) 3098 (vw), 2232 (w) 1403 (m), 1298 (s), 1131 (vs0, 1060 (s), 636 (m), 579 (s). **HRMS** (EI) calcd for $C_{14}H_8F_3NO_2S$ $[M]^+$: 311.0228, found: 311.0222.



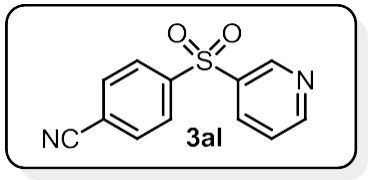
3aj

4-((5-Chloro-2-methoxyphenyl)sulfonyl)benzonitrile, 3ak (65.4 mg, 43%) was prepared according to the general procedure from 4-iodobenzonitrile, **1ae** (114.5 mg, 0.5 mmol, 1 equiv) and sodium 5-chloro-2-methoxybenzenesulfinate, **2h** (232.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3ak** was isolated as a pale yellow solid (mp = 162-163 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.77 (s, 3H), 6.88 (d, J = 8.9 Hz, 1H), 7.54 (dd, J = 8.8, 2.4 Hz, 1H), 7.80 (d, J = 8.2 Hz, 2H), 8.08 (d, J = 8.2 Hz, 2H), 8.14 (d, J = 2.3 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 56.6 (CH_3), 114.3 (CH), 117.2 (C), 117.5 (C), 126.4 (C), 129.2 (C), 129.4 (CH), 129.9 (CH), 132.7 (CH), 136.2 (CH), 145.2 (C), 155.9 (C). **FT-IR** (cm^{-1}, neat, ATR) 3081 (vw), 2936 (vw), 2231 (w), 1595 (w), 1480 (m), 1310 (s), 1275 (m), 1147 (vs), 1013 (m), 819 (m), 627 (s), 588 (s). **HRMS** (EI) calcd for $C_{14}H_{10}ClNO_3S$ $[M]^+$: 307.0070, found: 307.0081.

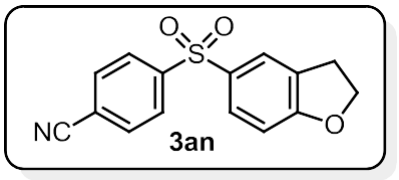


3ak

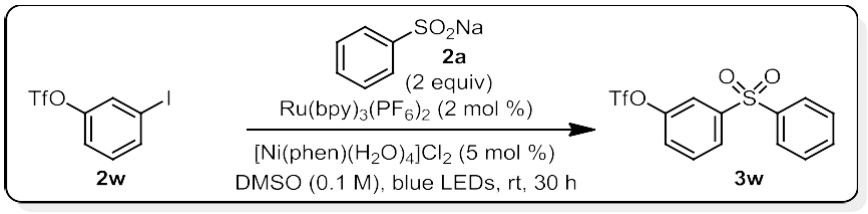
4-(Pyridin-3-ylsulfonyl)benzonitrile, 3al (68.2 mg, 56%) was prepared according to the general procedure from 4-bromobenzonitrile, **1a** (91.0 mg, 0.5 mmol, 1 equiv) and sodium pyridine-3-sulfinate, **2i** (165.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3al** was isolated as a pale yellow solid (mp = 155-156 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.51 (dd, *J* = 7.7, 5.3 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 8.10 (d, *J* = 8.1 Hz, 2H), 8.24 (d, *J* = 7.8 Hz, 1H), 8.86 (d, *J* = 4.2 Hz, 1H), 9.17 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 117.2 (C), 117.8 (C), 124.4 (CH), 128.7 (CH), 133.6 (CH), 135.8 (CH), 137.2 (C), 145.2 (C), 149.2 (CH), 154.7 (CH). **FT-IR** (cm^{-1}, neat, ATR) 3045 (vw), 2931 (vw), 2232 (w), 1578 (w), 1419 (m), 1312 (m), 1157 (s), 1077 (m), 846 (m), 700 (s), 574 (vs). **HRMS** (EI) calcd for $C_{12}H_8N_2O_2S$ $[M]^+$: 244.0306, found: 244.0306.



4-((2,3-Dihydrobenzofuran-5-yl)sulfonyl)benzonitrile, 3am (105.3 mg, 74%) was prepared according to the general procedure from 4-bromobenzonitrile, **1a** (91.0 mg, 0.5 mmol, 1 equiv) and sodium 2,3-dihydrobenzofuran-5-sulfinate, **2j** (206.2 mg, 1.0 mmol, 2 equiv). The desired sulfone **3am** was isolated as a pale brown solid (mp = 136-137 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 3.26 (t, *J* = 8.8 Hz, 2H), 4.68 (t, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 1H), 7.68 - 7.83 (m, 4H), 8.02 (d, *J* = 8.3 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 29.1 (CH_2), 72.8 (CH_2), 110.3 (CH), 116.6 (C), 117.5 (C), 125.4 (CH), 128.0 (CH), 129.5 (C), 130.1 (CH), 131.5 (C), 133.2 (CH), 147.0 (C), 165.3 (C). **FT-IR** (cm^{-1}, neat, ATR) 3082 (vw), 2930 (w), 2230 (w), 1580 (m), 1486 (m), 1246 (s), 1140 (s), 1081 (s), 892 (m), 627 (s), 481 (s). **HRMS** (EI) calcd for $C_{15}H_{11}NO_3S$ $[M]^+$: 285.0460, found: 285.0468.



Representative Procedure for Large Scale Sulfone Synthesis



3-(Phenylsulfonyl)phenyl Trifluoromethanesulfonate (3w)

To an oven dried, 100 mL round bottom flask equipped with a stir bar was added $Ru(bpy)_3(PF_6)_2$ (0.086 g, 0.1 mmol, 0.02 equiv), $[Ni(phen)(H_2O)_4]Cl_2$ (0.048 g, 0.13 mmol, 0.025 equiv), and sodium benzenesulfinate (1.64 g, 10 mmol, 2 equiv). The flask was sealed with a rubber septum and was evacuated and purged with argon three times *via* an inlet needle. The flask was then charged with 3-iodophenyl trifluoromethanesulfonate, **2w** (1.76 g, 5 mmol, 1 equiv) anhyd DMSO (50 mL) *via* a syringe. The now bright red soln was irradiated by blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at ~27 °C *via* a fan, and the soln was stirred vigorously. Reaction progress was monitored by HPLC. Once complete (~30 h), the now dark red-brown soln was transferred to a separatory funnel and diluted with deionized H_2O (125 mL) and EtOAc (~100 mL). The layers were separated, and the aq layer was extracted with EtOAc (2 × ~50 mL). The combined organic layers were washed with deionized H_2O (2 × ~100 mL) followed by brine (~150 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient hexane/EtOAc) to give the desired sulfone, **3w**, (0.971 g, 53%) as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47 (d, J = 7.3 Hz, 1H), 7.54 (t, J = 6.7 Hz, 2H), 7.61 (t, J = 7.5 Hz, 2H), 7.87 (br s, 1H), 7.95 (d, J = 6.9 Hz, 3H).

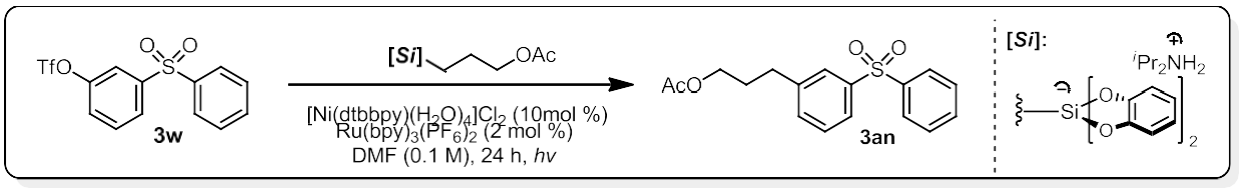
^{13}C NMR ($CDCl_3$, 125 MHz) δ 118.9 (q, $J_{C\text{-}F}$ = 321.5 Hz, CF_3), 121.1 (CH), 126.4 (CH), 127.8 (CH), 128.1 (CH), 129.9 (CH), 131.8 (CH), 134.2 (CH), 140.6 (C), 144.6 (CH), 149.7 (C).

^{19}F NMR ($CDCl_3$, 471 MHz) δ -75.74 (s, 3F).

FT-IR (cm^{-1}, neat, ATR) 3070 (vw), 1590 (w), 1423 (s), 1209 (vs), 1165 (s), 1136 (vs), 912 (s), 805 (s), 677 (m), 588 (s).

HRMS (EI) calcd for $C_{13}H_9F_3O_5S_2$ $[M]^+$: 365.9843, found: 365.9855.

Ni/Photoredox C_{sp^2}-C_{sp^3} Cross-Coupling Reactions of 3w



3-(3-(Phenylsulfonyl)phenyl)propyl Acetate, 3an

To an 8 mL reaction vial equipped with a stir bar were added diisopropylammonium bis(catecholato)(3-acetoxypropyl)silicate (0.336 g, 0.75 mmol, 1.5 equiv, $[Ni(dtbbpy)(H_2O)_4]Cl_2$ (23.5 mg, 0.05 mmol, 0.1 equiv),[37] and $Ru(bpy)_3(PF_6)$ (8.6 mg, 0.01 mmol, 0.02 equiv). The vial was sealed with a cap containing a TFE-lined silicone septum. The vial was evacuated three times *via* an inlet needle, then purged with argon. The vial was then charged *via* a syringe with sulfone **3w** (0.183 g, 0.5 mmol, 1 equiv) dissolved in anhyd DMF (5 mL). The cap was sealed with Parafilm®, and the now bright red soln was irradiated in the aforementioned LED reactor. The temperature of the reaction was maintained at approximately 27 °C *via* a fan and stirred vigorously while irradiated. Reaction progress was monitored by HPLC. Once judged to be complete, the now opaque, milky-brown soln was transferred to a separatory funnel and diluted with deionized H_2O (~ 20 mL) and EtOAc (~ 20 mL). The layers were separated, and the aq layer was extracted with Et_2O (3 × ~20 mL). The combined organic layers were washed with 2 M aq NaOH (2 × ~30 mL), 2 M aq HCl (~30 mL), deionized H_2O (~30 mL), and brine (~50 mL). The organic layer was dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by flash column chromatography (gradient hexane/EtOAc) to give the desired coupling product, **3ao**, (0.110 g, 69%) as a clear, colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.89 - 1.97 (m, 2H), 2.01 (s, 3H), 2.73 (t, *J* = 7.6 Hz, 2H), 4.04 (t, *J* = 6.2 Hz, 2H), 7.34 - 7.42 (m, 2H), 7.48 (t, *J* = 7.0 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.71 - 7.81 (m, 2H), 7.92 (d, *J* = 7.5 Hz, 2H).

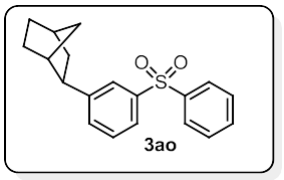
^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.1 (CH_3), 30.0 (CH_2), 32.2 (CH_2), 63.6 (CH_2), 125.7 (CH), 127.5 (CH), 127.8 (CH), 129.5 (CH), 129.6 (CH), 133.4 (CH), 133.5 (CH), 141.8 (C), 141.9 (C), 143.1 (C), 171.2 (C).

[37] To prepare this complex, mix dtbbpy (1.05 equiv) with $NiCl_2 \cdot 6H_2O$ in refluxing EtOH (0.1 M) for 12 h. Once cooled to rt, remove the solvent *in vacuo* by rotary evaporation. Wash the resulting mint green solid with Et_2O then pentane (to remove any residual ligand). This complex can be stored on the bench for an indefinite period of time.

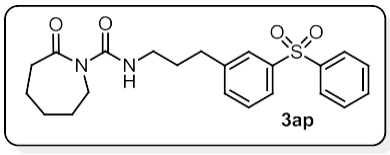
FT-IR (cm^{-1}, neat, ATR) 2952 (w), 1733 (vs), 1447 (m), 1303 (s), 1238 (vs), 1150 (vs), 1038 (m), 725 (vs), 689 (s), 583 (vs).

HRMS (EI) calcd for $C_{17}H_{18}O_4S$ $[M]^+$: 318.0926, found: 318.0940.

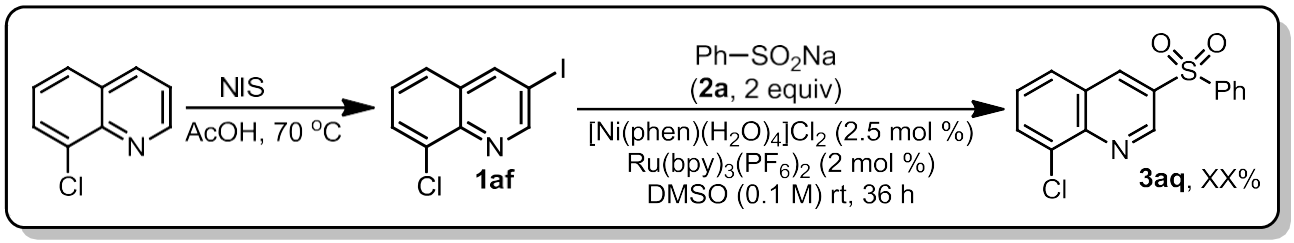
(±)-2-(3-(Phenylsulfonyl)phenyl)bicyclo[2.2.1]heptane, 3ao (114.0 mg, 73%) was prepared according to the general procedure from triflate **3w** (183.2 mg, 0.5 mmol, 1.2 equiv) and diisopropylammonium bis(catecholato)((±)-2-bicyclo[2.2.1]heptyl)silicate (331.2 mg, 0.75 mmol, 1.5 equiv). The cross-coupled product was isolated as a white powdery solid (mp = 91-92 °C). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.17 - 1.23 (m, 1H), 1.24 - 1.30 (m, 1H), 1.32 - 1.39 (m, 1H), 1.45 (dt, *J* = 9.9, 1.8 Hz, 1H), 1.52 - 1.66 (m, 3H), 1.79 (ddd, *J* = 12.2, 9.4, 2.4 Hz, 1 H), 2.32 - 2.40 (m, 2H), 2.78 (dd, *J* = 8.9, 5.6 Hz, 1H), 7.36 - 7.42 (m, 2H), 7.48 - 7.52 (m, 2H), 7.53 - 7.58 (m, 1H), 7.70 (dt, *J* = 6.6, 2.0 Hz, 1H), 7.80 (s, 1H), 7.92 - 7.97 (m, 2H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 29.0 (CH_2), 30.7 (CH_2), 36.3 (CH_2), 37.1 (CH), 39.3 (CH_2), 43.0 (CH), 47.4 (CH), 125.1 (CH), 126.3 (CH), 127.8 (CH), 129.4 (CH), 129.5 (CH), 132.2 (CH), 133.3 (CH), 141.6 (C), 142.1 (C), 149.5 (C). **FT-IR** (cm^{-1}, neat, ATR) 2952 (m), 2866 (w), 1304 (s), 1151 (s), 1104 (m), 723 (s), 574 (vs). **HRMS** (EI) calcd for $C_{19}H_{20}O_2S$ $[M]^+$: 312.1184, found: 312.1187.



2-Oxo-*N*-(3-(3-(phenylsulfonyl)phenyl)propyl)azepane-1-carboxamide, 3ap (130.0 mg, 63%) was prepared according to the general procedure from triflate **3w** (183.2 mg, 0.5 mmol, 1.2 equiv) and diisopropylammonium bis(catecholato)(*N*-propylcarbamoylcaprolactam)silicate (407.8 mg, 0.75 mmol, 1.5 equiv). The cross-coupled product was isolated as a clear, colorless oil. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 1.59 - 1.81 (m, 6H), 1.87 (dt, *J* = 14.7, 7.1 Hz, 2H), 2.63 - 2.78 (m, 4H), 3.30 (q, *J* = 6.4 Hz, 2H), 3.98 (d, *J* = 4.4 Hz, 2H), 7.35 - 7.44 (m, 2H), 7.45 - 7.58 (m, 3H), 7.68 - 7.81 (m, 2H), 7.94 (d, *J* = 7.6 Hz, 2H), 9.33 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 23.4 (CH_2), 28.2 (CH_2), 29.0 (CH_2), 30.7 (CH_2), 32.9 (CH_2), 39.6 (CH_2), 39.8 (CH_2), 43.7 (CH_2), 125.3 (CH), 127.2 (CH), 127.5 (CH), 129.2 (CH), 129.2 (CH), 133.0 (CH), 133.2 (CH), 141.5 (C), 141.6 (C), 143.2 (C), 154.8 (C), 179.4 (C). **FT-IR** (cm^{-1}, neat, ATR) 3265 (w, br), 2941 (w), 1693 (vs), 1527 (s), 1303 (s), 1150 (vs), 725 (vs), 689 (s), 583 (vs). **HRMS** (ES+) calcd for $C_{22}H_{27}N_2O_4S$ $[M+H]^+$: 415.1692, found: 415.1710.



Synthesis of 3aq, a precursor to RVT-101



Iodination

8-Chloro-3-iodoquinoline,[38] 1af

To a 150 mL round bottom flask equipped with a stir bar was added 8-chloroquinoline (5.41 g, 0.0331 mol, 1 equiv) and glacial AcOH (34 mL). The flask was equipped with an air-cooled condenser and placed under argon via a Ar inlet adapter. The reaction mixture was heated to 70 °C. Once at this temperature *N*-iodosuccinimide (7.44 g, 0.0331 mol, 1 equiv) was added in three portions over 15 min. The soln turned from its initial bright yellow to a brownish-red. After complete addition, the reaction was stirred at this temperature overnight. After ~12 h, the reaction was analyzed by NMR and determined to be incomplete. At this time, additional *N*-iodosuccinimide (1.48 g, 0.0066 mol, 0.2 equiv) was added, and the reaction was allowed to stir for an additional 4 h. At this time, the reaction was deemed complete. The solvent was removed carefully *in vacuo* by rotary evaporation to give a thick red-brown liquid. The liquid was dissolved in CH_2Cl_2 (100 mL) and transferred to a separatory funnel. The organic layer was washed with a 1:1 mixture of saturated aq $Na_2S_2O_3$ (50 mL) and saturated aqueous $NaHCO_3$ (50 mL). The layers were separated, and the aqueous was extracted with CH_2Cl_2 (2 × 40 mL). The combined organic layers were washed with saturated aq $Na_2S_2O_3$ (2 × 100 mL), followed by saturated aq $NaHCO_3$ (100 mL), deionized H_2O (100 mL), then and finally brine (150 mL). The organic layer was dried (Na_2SO_4) and the solvent was removed *in vacuo* by rotary evaporation. The resulting crude brown solid was recrystallized from hot EtOAc followed by washing the resulting crystals with cold EtOAc and pentane. The solid was then dried *in vacuo* to give 8-chloro-3-iodoquinoline (3.62 g, 38%) as powdery off-white solid (mp = 97-98 °C).

[38] Emmett, E. J.; Hayter, B. R.; Willis, M. C. *Angew. Chem., Int. Ed.* **2014**, 53, 10204.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.44 (t, *J* = 7.6 Hz, 1H), 7.58 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.80 (dd, *J* = 7.5, 1.2 Hz, 1H), 8.50 (d, *J* = 2.1 Hz, 1H), 9.09 (d, *J* = 2.0 Hz, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 91.3 (C), 126.1 (CH), 127.7 (CH), 130.4 (CH), 131.2 (C), 133.9 (C), 142.9 (C), 144.2 (CH), 156.4 (CH).

Sulfonylation

8-Chloro-3-(phenylsulfonyl)quinoline,[39] 3aq

To an oven dried, 100 mL round bottom flask equipped with a stir bar was added $Ru(bpy)_3(PF_6)_2$ (0.129 g, 0.15 mmol, 0.03 equiv), $[Ni(phen)(H_2O)_4]Cl_2$ (0.067 g, 0.175 mmol, 0.035 equiv), sodium benzenesulfinate (2.46 g, 15 mmol, 3 equiv), and 8-chloro-3-iodoquinoline, **3af** (1.64 g, 10 mmol, 2 equiv). The flask was sealed with a rubber septum and was evacuated and purged with argon three times *via* an inlet needle. The flask was then charged with anhydrous DMSO (50 mL) *via* a syringe. The now bright red soln was irradiated by blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 °C *via* a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by HPLC. Once complete (~36 h), the now dark red-brown soln was transferred to a separatory funnel and diluted with deionized H_2O (100 mL) and CH_2Cl_2 (100 mL).[40] The aquoues layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic layers were washed with deionized water (2 × 100 mL) followed by brine (150 mL). The organic layer was dried (Na_2SO_4) and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO2 column chromatography (CH_2Cl_2/MeOH) to give the desired sulfone, **3aq**, (0.851 g, 56%) as a powdery off-white solid (mp > 200 °C).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (t, *J* =7.9 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 2H), 8.85 (d, *J* = 2.1 Hz, 1H), 9.36 (d, *J* = 2.1 Hz, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 128.1 (C), 128.2 (CH), 128.5 (CH), 128.7 (CH), 130.0 (CH), 133.0 (CH), 134.3 (CH), 134.37 (C), 136.1 (C), 137.5 (CH), 140.9 (C), 145.8 (C), 148.0 (CH).

[39] Emmett, E. J.; Hayter, Barry R.; Willis, Michael C. *Angew. Chem., Int. Ed.* **2013**, *52*, 12679.
[40] **3aq** is poorly soluble in EtOAc but reasonably soluble in CH_2Cl_2. Thus, during workup and column chromatography the latter solvent was used.

Computational Methods and Analyses

Full Reference of Gaussian09:

Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

All optimizations of intermediates and transition states were calculated without constraints using unrestricted B3LYP[41]/6-31G(d)-LANL2DZ[42] (for Br, S, and Ni) with the "guess=mix" keyword as implemented in Gaussian09. Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). To refine the energies calculated, we carried out single point energy calculations using UM06[43]/6-311+G(d,p)-SDD (for Br, S, and Ni) in THF using SMD[44] as the solvation model. Similar methods have been used before to rationalize selectivity and reactivity on related systems.[45] All structural figures were generated using CYLview.[46] Exhaustive conformational searches were performed for all structures to elucidate the lowest energy profiles for each potential reaction pathway.

[41] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
[42] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
[43] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.
[44] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.
[45] (a) Sperger, T.; Sanhueza, I. A.; Kalvet, I.; Schoenebeck, F. *Chem. Rev.* **2015**, *115*, 9532; (b) Sperger, T.; Sanhueza, I. A.; Schoenebeck, F. *Acc. Chem. Res.* **2016**, *49*, 1311.
[46] *CYLview, 1.0b*; Legault, C. Y., Université de Sherbrooke, **2009**, (http://www.cylview.org)

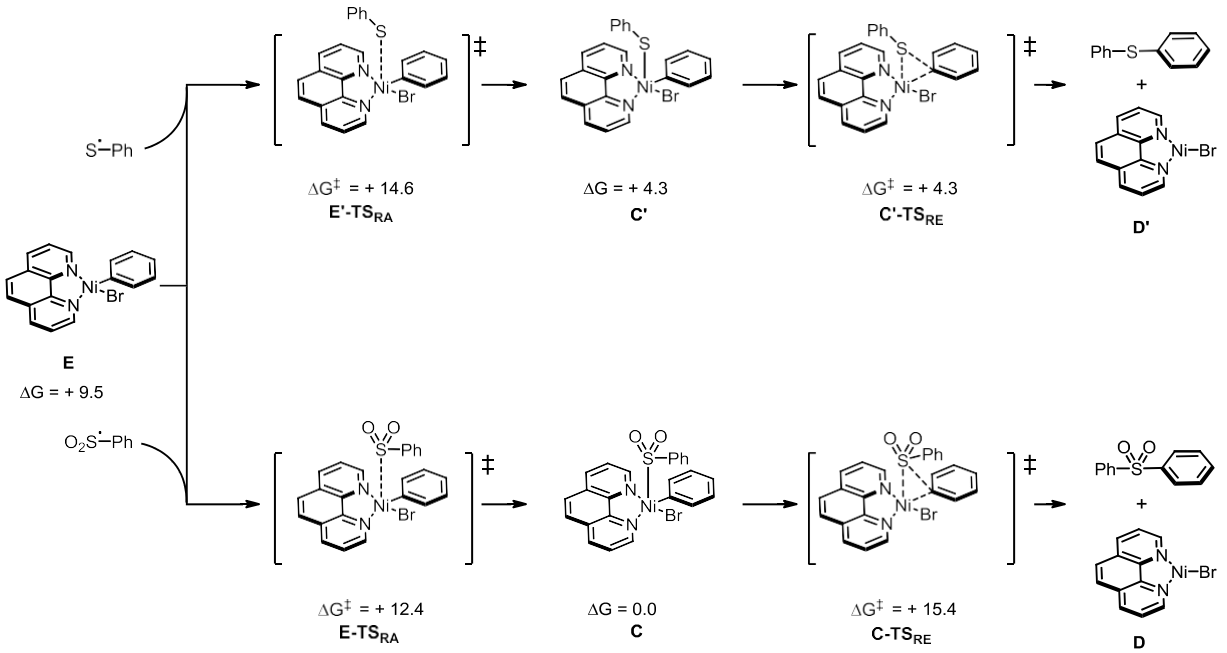


Figure S1. Competing mechanistic pathway (kcal/mol; 298.15 K).

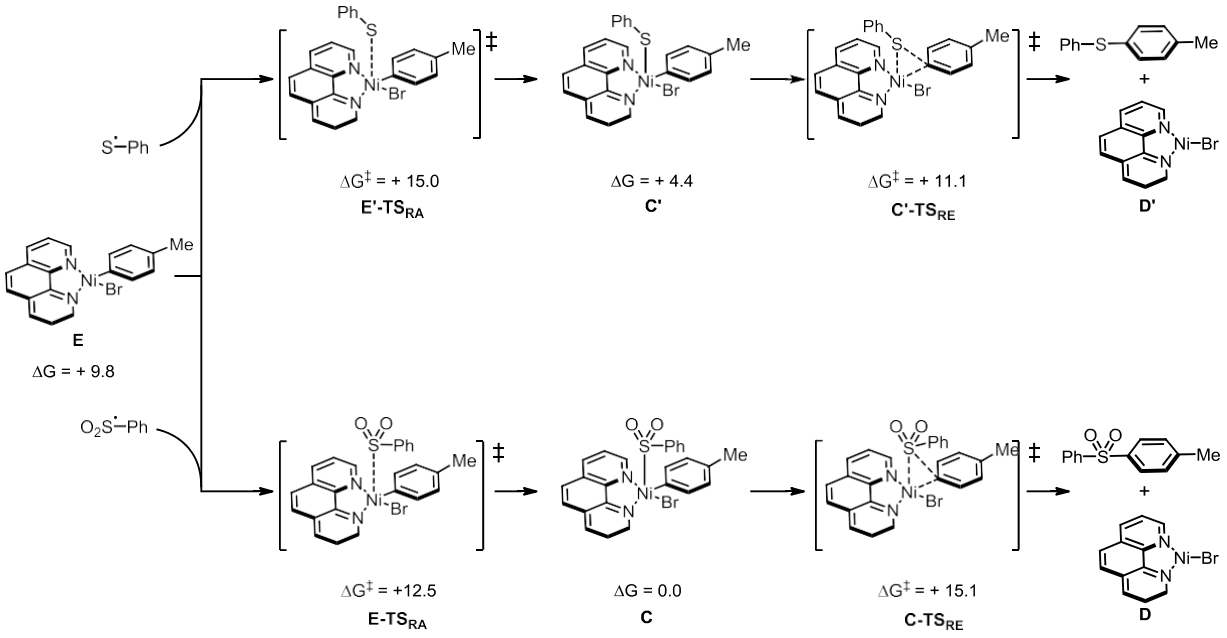


Figure S2. Competing mechanistic pathway (kcal/mol; 298.15 K).

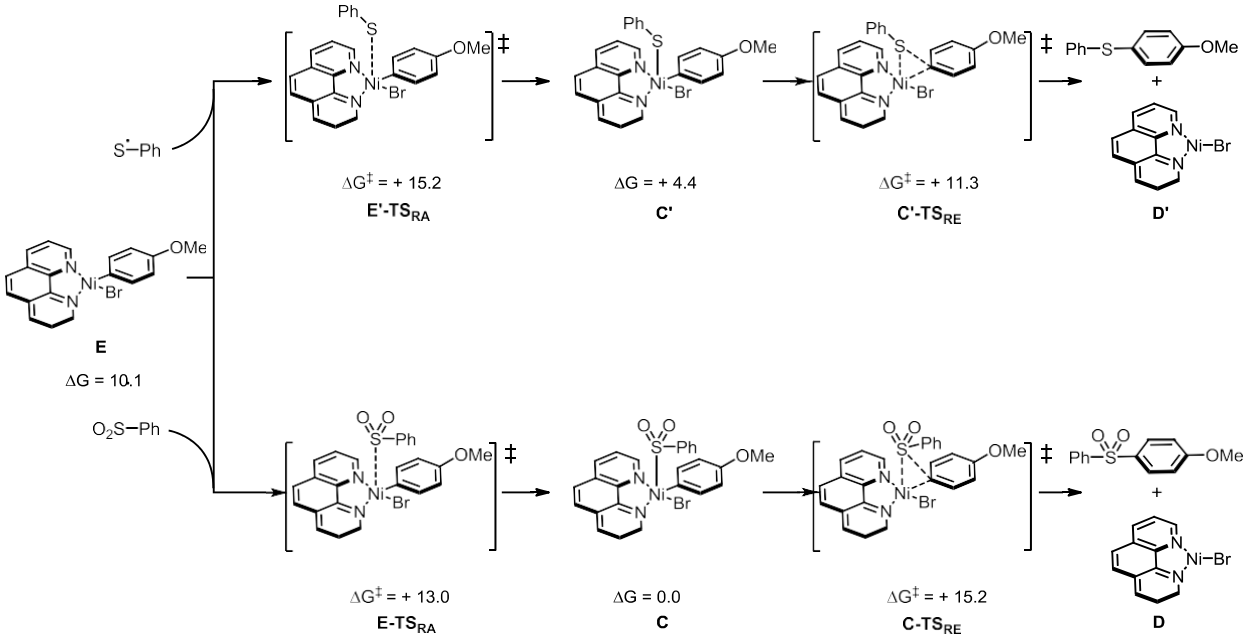


Figure S3. Competing mechanistic pathway (kcal/mol; 298.15 K).

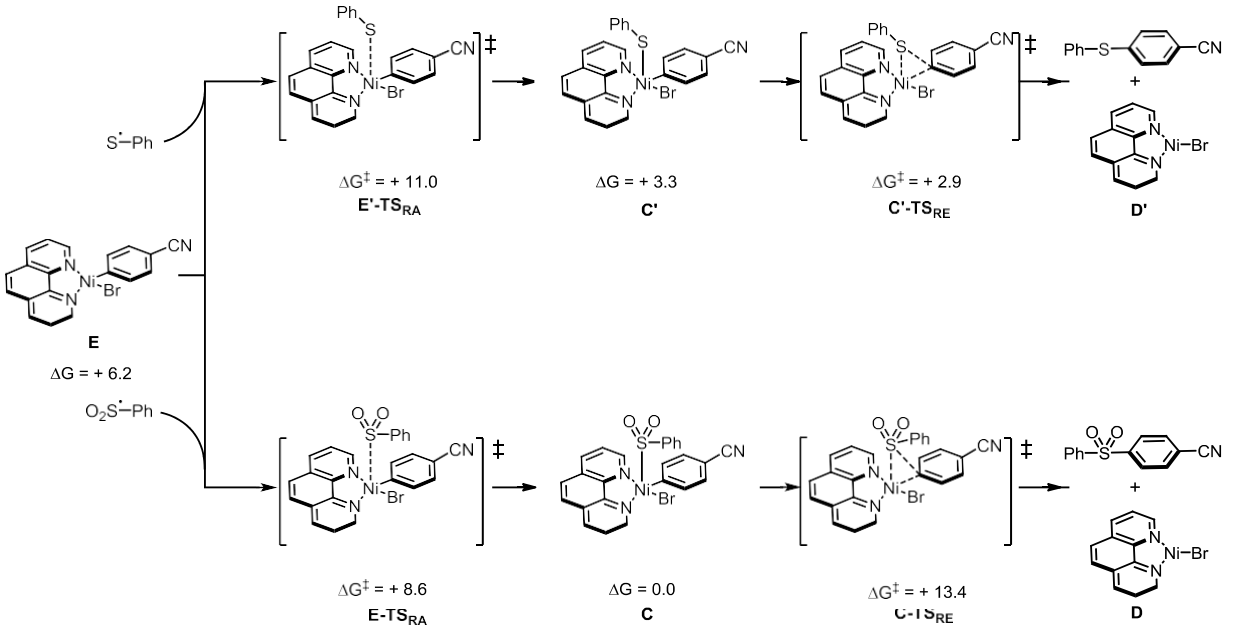


Figure S4. Competing mechanistic pathway (kcal/mol; 298.15 K).

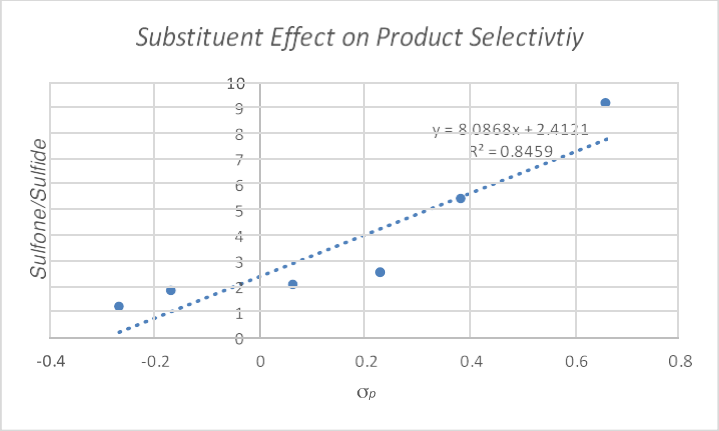
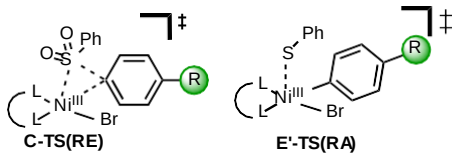


Figure S5. Correlation between experimental product selectivity (sulfone/sulfide) as a function of Hammett σ_p.[47]



R =	σ (para)	ΔG ‡	ΔG ‡
CN	0.66	13.4	11.0
Ac	0.38	13.5	12.7
Cl	0.23	14.8	12.4
F	0.06	15.3	13.1
Me	-0.17	15.1	15.0
OMe	-0.27	15.2	15.2

Figure S6. Correlation between overall free energy barriers (UM06/6-311+G(d,p)-(Br,Ni, Cl, and S-SDD)-TMH(SMD)//UB3LYP/6-31G(d)-(Br, Ni, Cl, and S-LANL2DZ) for reductive elimination leading to sulfone and radical addition leading to sulfide, with respect to Ni(III)-aryl-bromo-SO_2Ph, and Hammett σ_p.[47]

[47] Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165-195.

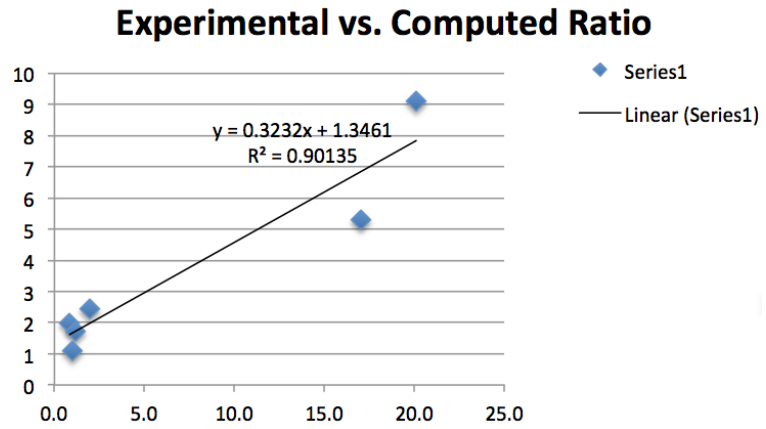
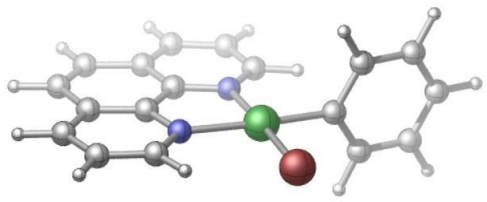


Figure S7. Experimental vs. calculated product selectivity.[47] Calculated product selectivity was determine from free energy difference between "complex disproportionation" threshold (15.2 kcal/mol; UM06/6-311+G(d,p)-(Br,Ni, Cl, and S-SDD-TMH(SMD)//UB3LYP/6-31G(d)-(Br, Ni, Cl, and S-LANL2DZ)) and overall barrier for sulfone reductive elimination.

Coordinates and Energies:

Figure S1; E



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.265679 (Hartree/Particle)

Thermal correction to Energy= 0.283659

Thermal correction to Enthalpy= 0.284603

Thermal correction to Gibbs Free Energy= 0.217389

Sum of electronic and zero-point Energies= -985.543483

Sum of electronic and thermal Energies= -985.525503

Sum of electronic and thermal Enthalpies= -985.524559

Sum of electronic and thermal Free Energies= -985.591774

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

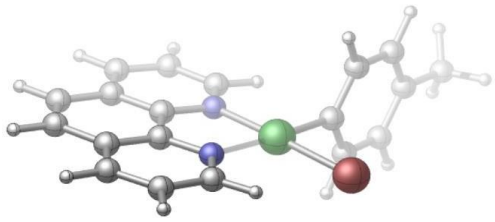
HF=-987.2725757

C	-0.4332	1.90515	0.86978
C	1.42778	2.28609	2.18064
C	0.9153	3.53141	2.59586
C	-0.31036	3.95866	2.12322
C	-1.03054	3.13578	1.2278
C	-1.09906	1.01641	-0.03387
C	-1.05463	-0.99723	-1.16927
C	-2.309	-0.73054	-1.74834
C	-2.96526	0.4482	-1.45338
C	-2.35982	1.36848	-0.56907
H	2.38634	1.90822	2.52492
H	1.49381	4.13896	3.28396
H	-0.7262	4.91511	2.42947

H	-0.51697	-1.91266	-1.38257
H	-2.74249	-1.46176	-2.4225
H	-3.93454	0.67522	-1.88931
N	0.77194	1.4924	1.34006
N	-0.4563	-0.14991	-0.33137
Ni	1.28826	-0.33935	0.57899
C	1.19353	-3.20707	0.37805
C	2.42895	-3.32197	-2.11817
C	1.34795	-4.43671	-0.27306
H	0.72662	-3.18461	1.36065
C	1.96306	-4.49779	-1.52557
H	2.9213	-3.35933	-3.08799
H	0.99306	-5.34821	0.20397
H	2.08712	-5.45304	-2.02996
Br	3.3548	-0.47471	1.73041
C	2.27333	-2.09355	-1.46542
H	2.65785	-1.19201	-1.93809
C	1.64562	-2.01817	-0.21316

C	-2.94612	2.62376	-0.18962
H	-3.91488	2.88688	-0.60533
C	-2.3104	3.47076	0.67057
H	-2.76683	4.41714	0.9477

Figure S2; E



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.293184 (Hartree/Particle)

Thermal correction to Energy= 0.313069

Thermal correction to Enthalpy= 0.314013

Thermal correction to Gibbs Free Energy= 0.241789

Sum of electronic and zero-point Energies= -1024.832773

Sum of electronic and thermal Energies= -1024.812888

Sum of electronic and thermal Enthalpies= -1024.811943

Sum of electronic and thermal Free Energies= -1024.884167

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

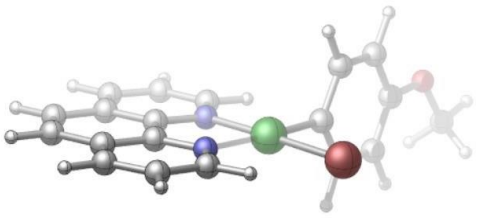
HF=-1026.5665331

C	-0.61609	2.40781	1.06305
C	1.24142	2.79108	2.37806

C	0.72636	4.03561	2.79232
C	-0.49887	4.46142	2.31691
C	-1.21577	3.63765	1.41982
C	-1.27905	1.51793	0.15772
C	-1.22926	-0.49601	-0.9771
C	-2.4826	-0.23106	-1.55911
C	-3.14118	0.94696	-1.26591
C	-2.53904	1.86815	-0.38041
H	2.19973	2.41443	2.72437
H	1.30252	4.64378	3.48185
H	-0.91664	5.41729	2.62232
H	-0.68929	-1.41052	-1.18857
H	-2.91365	-0.96292	-2.23414
H	-4.10975	1.17258	-1.70415
N	0.5885	1.99652	1.53584
N	-0.63405	0.3525	-0.13803
Ni	1.10887	0.1646	0.77537
C	1.02206	-2.70594	0.57313
C	2.2497	-2.82666	-1.91585
C	1.1805	-3.93444	-0.07785
H	0.55063	-2.68885	1.55376
C	1.79792	-4.01767	-1.33236
H	2.73778	-2.86055	-2.88919
H	0.82357	-4.84457	0.40262
Br	3.17421	0.03368	1.9302
C	2.09298	-1.59688	-1.26806

H	2.47138	-0.69791	-1.75068
C	1.46885	-1.51476	-0.01508
C	-3.12824	3.12278	-0.00238
H	-4.09641	3.38498	-0.42011
C	-2.49506	3.97076	0.85931
H	-2.95287	4.91652	1.13611
C	2.00539	-5.35069	-2.01598
H	1.95996	-5.2561	-3.10723
H	2.98682	-5.77955	-1.77082
H	1.24866	-6.08193	-1.7097

Figure S3; E



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.298433 (Hartree/Particle)

Thermal correction to Energy= 0.319041

Thermal correction to Enthalpy= 0.319985

Thermal correction to Gibbs Free Energy= 0.246420

Sum of electronic and zero-point Energies= -1100.030457

Sum of electronic and thermal Energies= -1100.009849

Sum of electronic and thermal Enthalpies= -1100.008905

Sum of electronic and thermal Free Energies= -1100.082470

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

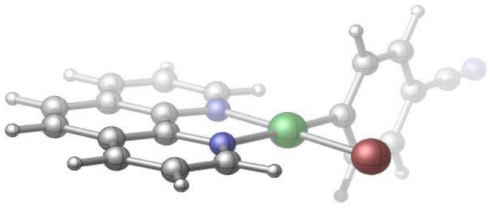
HF=- 1101.7649963

C	-0.60225	2.6667	0.99179
C	1.2541	3.04418	2.30994
C	0.7551	4.30249	2.70162
C	-0.46152	4.73825	2.21331
C	-1.1859	3.91054	1.32596
C	-1.27373	1.77216	0.09747
C	-1.24742	-0.26041	-1.00425
C	-2.49477	0.01225	-1.59558
C	-3.13795	1.20401	-1.32443
C	-2.52653	2.13112	-0.45152
H	2.20518	2.65945	2.6671
H	1.33674	4.9133	3.38419
H	-0.86684	5.70483	2.50129

H	-0.71786	-1.18457	-1.19946
H	-2.93319	-0.72431	-2.26069
H	-4.10141	1.43599	-1.77055
N	0.59393	2.24558	1.47717
N	-0.64358	0.59362	-0.17716
Ni	1.0937	0.3956	0.74581
C	1.02692	-2.48272	0.59141
C	2.19626	-2.62853	-1.92704
C	1.18067	-3.73148	-0.03079
H	0.58693	-2.45687	1.58613
C	1.76802	-3.8052	-1.29757
H	2.66231	-2.70417	-2.90581
H	0.85088	-4.62685	0.48601
Br	3.15013	0.2566	1.91585
C	2.03535	-1.39657	-1.29392
H	2.39409	-0.50294	-1.80066
C	1.43819	-1.29768	-0.02549
C	-3.09937	3.4	-0.09655

H	-4.0619	3.66914	-0.52278
C	-2.45775	4.25272	0.75415
H	-2.90311	5.20933	1.01342
O	1.96858	-4.96695	-2.00208
C	1.61876	-6.18743	-1.37952
H	0.54168	-6.24453	-1.16584
H	1.88414	-6.97587	-2.08753
H	2.17345	-6.3408	-0.44342

Figure S4; E



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.264442 (Hartree/Particle)

Thermal correction to Energy= 0.284218

Thermal correction to Enthalpy= 0.285162

Thermal correction to Gibbs Free Energy= 0.213531

Sum of electronic and zero-point Energies= -1077.790561

Sum of electronic and thermal Energies= -1077.770786

Sum of electronic and thermal Enthalpies= -1077.769841

Sum of electronic and thermal Free Energies= -1077.841472

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

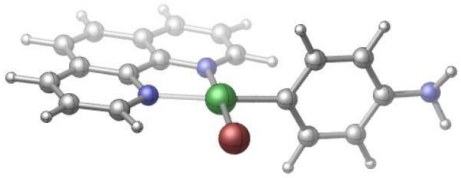
HF=-1079.4909238

C	-0.50445	2.10063	0.94495
C	1.36033	2.47396	2.25369
C	0.85133	3.71948	2.67233
C	-0.37407	4.15078	2.20274
C	-1.09777	3.3316	1.30669
C	-1.17426	1.21576	0.04036
C	-1.13643	-0.79538	-1.09958
C	-2.3908	-0.52551	-1.67671
C	-3.04347	0.6543	-1.37778
C	-2.43482	1.57145	-0.49234
H	2.31854	2.09451	2.5963
H	1.43263	4.32385	3.36072

H	-0.78677	5.10753	2.51191
H	-0.60391	-1.71238	-1.31786
H	-2.82661	-1.25434	-2.35177
H	-4.01276	0.88417	-1.81194
N	0.70077	1.68363	1.4123
N	-0.53478	0.04852	-0.26075
Ni	1.20867	-0.1393	0.6504
C	1.13974	-3.01088	0.46466
C	2.39298	-3.12062	-2.02833
C	1.30776	-4.24166	-0.16825
H	0.66824	-2.98825	1.44416
C	1.9322	-4.305	-1.42657
H	2.88705	-3.1691	-2.99461
H	0.96288	-5.15714	0.30408
Br	3.27618	-0.2889	1.79405
C	2.21732	-1.89777	-1.38255
H	2.59482	-0.99697	-1.86038
C	1.57951	-1.81753	-0.13285

C	-3.0181	2.82727	-0.10935
H	-3.98678	3.094	-0.52263
C	-2.37813	3.67074	0.75184
H	-2.83109	4.61755	1.03258
C	2.09211	-5.56376	-2.09186
N	2.21194	-6.58525	-2.63762

4-NH_2-Ph-(Byp)Ni(II)-Br



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.282352 (Hartree/Particle)

Thermal correction to Energy= 0.301836

Thermal correction to Enthalpy= 0.302780

Thermal correction to Gibbs Free Energy= 0.232308

Sum of electronic and zero-point Energies= -1040.877404

Sum of electronic and thermal Energies= -1040.857920

Sum of electronic and thermal Enthalpies= -1040.856976

Sum of electronic and thermal Free Energies= -1040.927448

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

HF=-1042.6175588

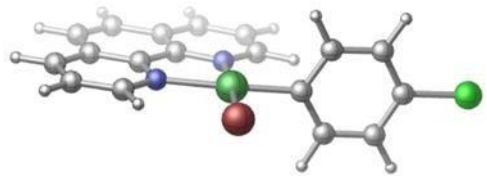
C	-0.43359	1.90682	0.87098
C	1.43292	2.27383	2.17774
C	0.92915	3.52132	2.5969
C	-0.29528	3.95701	2.12833
C	-1.02253	3.14032	1.23319
C	-1.10728	1.02391	-0.03336
C	-1.07647	-0.98753	-1.17327
C	-2.33089	-0.71239	-1.7485
C	-2.98	0.46942	-1.44942
C	-2.36727	1.38438	-0.56462
H	2.39009	1.88916	2.51854
H	1.51313	4.12398	3.28473
H	-0.70453	4.91533	2.43762
H	-0.54287	-1.90483	-1.38912
H	-2.77001	-1.43978	-2.4232
H	-3.94908	0.70281	-1.88252
N	0.77016	1.48564	1.33722

N	-0.47175	-0.145	-0.335
Ni	1.2752	-0.34958	0.56951
C	1.16883	-3.22268	0.3479
C	2.38829	-3.33515	-2.14727
C	1.31462	-4.45113	-0.30359
H	0.70766	-3.2118	1.3335
C	1.92732	-4.52469	-1.56356
H	2.87417	-3.37009	-3.12162
H	0.95656	-5.36356	0.17168
N	2.02432	-5.75294	-2.25068
Br	3.34361	-0.49715	1.71896
C	2.237	-2.11205	-1.48741
H	2.6264	-1.2154	-1.96558
C	1.61558	-2.02836	-0.23375
C	-2.94553	2.64235	-0.18093
H	-3.9138	2.91244	-0.59339
C	-2.30209	3.48387	0.67952
H	-2.75171	4.43237	0.96045

H 2.80196 -5.78466 -2.90125

H 2.06622 -6.55424 -1.63011

4-Cl-Ph-(Byp)Ni(II)-Br



UB3LYP/6-31g(d)-(Br, Ni, Cl-LANL2DZ)-gas

Zero-point correction= 0.255986 (Hartree/Particle)

Thermal correction to Energy= 0.275243

Thermal correction to Enthalpy= 0.276187

Thermal correction to Gibbs Free Energy= 0.205470

Sum of electronic and zero-point Energies= -999.898666

Sum of electronic and thermal Energies= -999.879409

Sum of electronic and thermal Enthalpies= -999.878465

Sum of electronic and thermal Free Energies= -999.949182

UM06/6-311+g(d,p)-(Br, Ni, Cl -SDD)-SMD(THF)

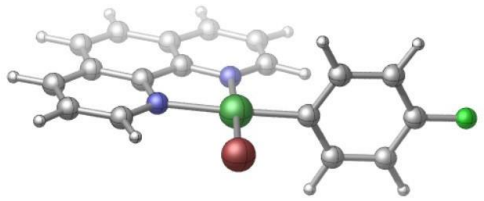
HF=-1446.8285917

C -0.43665 1.90643 0.86835

C	1.42806	2.28237	2.1759
C	0.91827	3.52777	2.59397
C	-0.30776	3.95769	2.1247
C	-1.03106	3.13723	1.22959
C	-1.106	1.02037	-0.03555
C	-1.06642	-0.99113	-1.17464
C	-2.32134	-0.72233	-1.75131
C	-2.97531	0.45685	-1.45272
C	-2.36713	1.37485	-0.56788
H	2.38674	1.90333	2.51803
H	1.49937	4.13319	3.28168
H	-0.72129	4.91429	2.43337
H	-0.53174	-1.90726	-1.39156
H	-2.75671	-1.45183	-2.426
H	-3.94503	0.68573	-1.88654
N	0.76901	1.4908	1.3354
N	-0.46549	-0.14631	-0.33622
Ni	1.27967	-0.33605	0.57341

C	1.19536	-3.20736	0.37567
C	2.45112	-3.32376	-2.11672
C	1.3559	-4.44415	-0.26106
H	0.72223	-3.18931	1.35488
C	1.97869	-4.47778	-1.50304
H	2.94665	-3.37929	-3.08065
H	1.00859	-5.3617	0.20293
Cl	2.18182	-6.0686	-2.34395
Br	3.34684	-0.47746	1.72029
C	2.27975	-2.09794	-1.46228
H	2.66557	-1.20029	-1.94013
C	1.64235	-2.01636	-0.2153
C	-2.95133	2.63033	-0.1852
H	-3.92049	2.89593	-0.59823
C	-2.31188	3.47489	0.67522
H	-2.76571	4.42145	0.95556

4-F-Ph-(Byp)Ni(II)-Br



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.257561 (Hartree/Particle)

Thermal correction to Energy= 0.276373

Thermal correction to Enthalpy= 0.277318

Thermal correction to Gibbs Free Energy= 0.207968

Sum of electronic and zero-point Energies= -1084.785016

Sum of electronic and thermal Energies= -1084.766203

Sum of electronic and thermal Enthalpies= -1084.765259

Sum of electronic and thermal Free Energies= -1084.834609

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

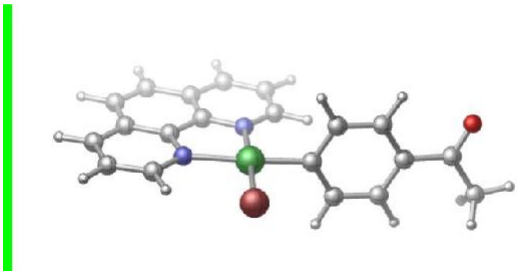
HF=-1086.5146061

C	-0.43621	1.90657	0.86885
C	1.42726	2.28226	2.17784
C	0.91742	3.5278	2.59548
C	-0.30813	3.95799	2.12511

C	-1.03076	3.13762	1.22946
C	-1.10505	1.0204	-0.03549
C	-1.065	-0.99144	-1.17386
C	-2.3195	-0.72236	-1.75136
C	-2.97355	0.45706	-1.45377
C	-2.36578	1.37512	-0.56879
H	2.3856	1.90266	2.52056
H	1.49801	4.13317	3.2837
H	-0.72179	4.91471	2.43333
H	-0.52899	-1.90723	-1.38918
H	-2.75478	-1.45188	-2.42614
H	-3.94293	0.68609	-1.88836
N	0.76888	1.49073	1.33684
N	-0.46449	-0.14637	-0.33537
Ni	1.28083	-0.33891	0.57386
C	1.19566	-3.21111	0.37514
C	2.44479	-3.32598	-2.12071
C	1.35779	-4.44712	-0.26233

H	0.72535	-3.19131	1.35566
C	1.97999	-4.48118	-1.50421
H	2.93763	-3.39455	-3.08617
H	1.01965	-5.37315	0.19356
F	2.1378	-5.67347	-2.13131
Br	3.34756	-0.47717	1.72365
C	2.27313	-2.09967	-1.46755
H	2.65452	-1.20018	-1.9455
C	1.63946	-2.01979	-0.21821
C	-2.94995	2.63084	-0.18681
H	-3.91875	2.8966	-0.60067
C	-2.31104	3.47545	0.67397
H	-2.76492	4.42218	0.95378

4-COMe-Ph-(Byp)Ni(II)-Br



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.303391 (Hartree/Particle)

Thermal correction to Energy= 0.324917

Thermal correction to Enthalpy= 0.325861

Thermal correction to Gibbs Free Energy= 0.250082

Sum of electronic and zero-point Energies= -1138.153382

Sum of electronic and thermal Energies= -1138.131857

Sum of electronic and thermal Enthalpies= -1138.130912

Sum of electronic and thermal Free Energies= -1138.206691

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

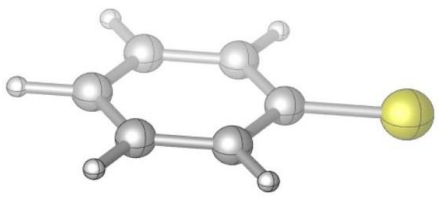
HF=-1139.8803023

C	-0.43736	1.90202	0.86997
C	1.41688	2.25473	2.19884
C	0.91168	3.50045	2.62154
C	-0.30677	3.94238	2.1437
C	-1.02681	3.13406	1.23501
C	-1.10317	1.02809	-0.04829
C	-1.06472	-0.97308	-1.20574
C	-2.3114	-0.6903	-1.79344

C	-2.96086	0.49023	-1.49055
C	-2.35613	1.39589	-0.59077
H	2.36939	1.86631	2.54758
H	1.49017	4.09662	3.31944
H	-0.71671	4.89942	2.45575
H	-0.53234	-1.88895	-1.42939
H	-2.74366	-1.40988	-2.48065
H	-3.9241	0.72987	-1.9329
N	0.76051	1.47434	1.34595
N	-0.46724	-0.14017	-0.35293
Ni	1.26351	-0.35124	0.57678
C	1.23195	-3.22425	0.40477
C	2.3608	-3.32486	-2.14058
C	1.39553	-4.45291	-0.23775
H	0.80874	-3.2065	1.40635
C	1.95728	-4.52123	-1.5233
H	2.80362	-3.38372	-3.13051
H	1.08378	-5.36051	0.27238

C	2.14652	-5.80376	-2.26153
Br	3.3145	-0.52519	1.74886
C	2.20112	-2.10109	-1.49507
H	2.53846	-1.19465	-1.99344
C	1.62332	-2.02697	-0.2146
C	-2.93579	2.65205	-0.20344
H	-3.8987	2.92775	-0.62437
C	-2.2996	3.48505	0.67055
H	-2.74985	4.4324	0.954
O	2.58652	-5.81942	-3.40415
C	1.78355	-7.11107	-1.5682
H	0.72353	-7.13141	-1.2873
H	2.36608	-7.24413	-0.64875
H	1.99113	-7.93692	-2.25115

PhS•



UB3LYP-(S-LANL2DZ)/6-31g(d)-gas

Zero-point correction= 0.090799 (Hartree/Particle)

Thermal correction to Energy= 0.096381

Thermal correction to Enthalpy= 0.097325

Thermal correction to Gibbs Free Energy= 0.060292

Sum of electronic and zero-point Energies= -241.631247

Sum of electronic and thermal Energies= -241.625665

Sum of electronic and thermal Enthalpies= -241.624721

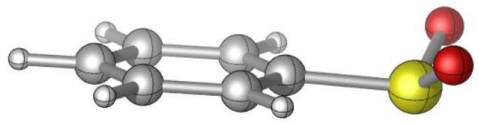
Sum of electronic and thermal Free Energies= -241.66175

UM06/6-311+g(d,p)-(S-SDD)-SMD(THF)

HF=-629.6371416

C	0.37694	-0.33749	-1.27684
C	1.37058	-0.27635	-0.30737
C	1.04345	0.06272	1.01212
C	-0.28462	0.34158	1.36075
C	-1.28395	0.28286	0.39706
C	-0.96987	-0.05834	-0.94077
H	0.61524	-0.59853	-2.30281
H	2.40189	-0.49155	-0.57286
H	1.82269	0.10964	1.76795
H	-0.53334	0.60385	2.38533
H	-2.31685	0.49634	0.65223
S	-2.24215	-0.13474	-2.17479

$PhSO_2$•



UB3LYP-(S-LANL2DZ)/6-31g(d)-gas

Zero-point correction= 0.097095 (Hartree/Particle)

Thermal correction to Energy= 0.105000

Thermal correction to Enthalpy= 0.105944

Thermal correction to Gibbs Free Energy= 0.063082

Sum of electronic and zero-point Energies= -391.918574

Sum of electronic and thermal Energies= -391.910670

Sum of electronic and thermal Enthalpies= -391.909726

Sum of electronic and thermal Free Energies= -391.952587

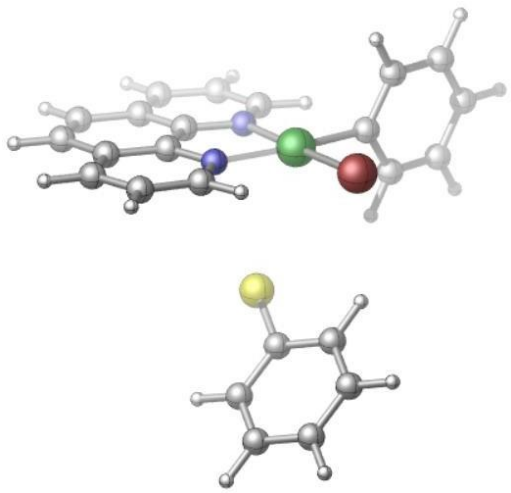
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

HF=-779.9046333

C	-1.11814	0.00012	-0.51761
C	-0.41916	0.33519	-1.67943
C	0.95981	0.55687	-1.63009
C	1.65454	0.44197	-0.42287
C	0.97367	0.10763	0.7499
C	-0.395	-0.10875	0.66259
H	-2.18578	-0.19144	-0.52573
H	-0.95313	0.41785	-2.62159
H	1.49611	0.8194	-2.5375
H	2.72751	0.6074	-0.39149

H	1.48733	-0.00254	1.69897
S	-1.33082	-0.50722	2.23872
O	-0.27604	-1.18484	3.19781
O	-2.62091	-1.29165	1.77833

Figure S1; E'-TS_{RA}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -37.72 cm^{-1}

Zero-point correction= 0.356856 (Hartree/Particle)

Thermal correction to Energy= 0.381983

Thermal correction to Enthalpy= 0.382928

Thermal correction to Gibbs Free Energy= 0.294710

Sum of electronic and zero-point Energies= -1227.178275

Sum of electronic and thermal Energies= -1227.153148

Sum of electronic and thermal Enthalpies= -1227.152204

Sum of electronic and thermal Free Energies= -1227.240422

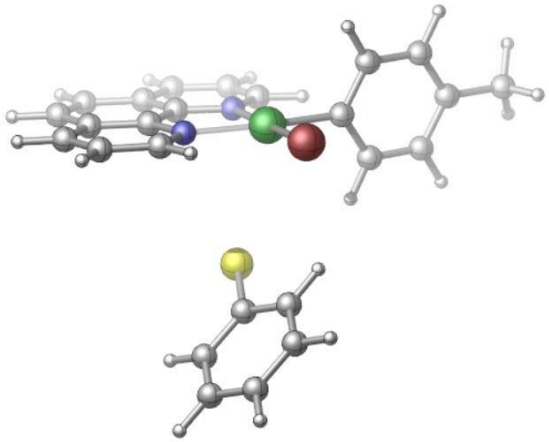
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

HF=-1616.9185565

C	-1.05231	2.13083	-0.24943
C	1.00271	2.71756	0.62181
C	0.44387	3.84408	1.25769
C	-0.90593	4.10499	1.12324
C	-1.70429	3.23391	0.34828
C	-1.79333	1.20213	-1.04926
C	-1.75835	-0.71683	-2.33862
C	-3.14022	-0.61208	-2.58293
C	-3.85569	0.4361	-2.03893
C	-3.18189	1.38754	-1.24162
H	2.05838	2.47316	0.69605
H	1.0848	4.49251	1.84596
H	-1.36011	4.96757	1.60409
H	-1.17167	-1.52958	-2.74851
H	-3.62346	-1.36311	-3.19892
H	-4.92348	0.53729	-2.21417
N	0.27529	1.8825	-0.1125
N	-1.09397	0.16478	-1.59195
Ni	0.83132	0.19056	-1.13264
C	1.00914	-2.63735	-1.63069
C	1.77438	-2.37138	-4.29962
C	1.1821	-3.77448	-2.42984
H	0.71101	-2.75569	-0.5913
C	1.56125	-3.64536	-3.76768
H	2.0813	-2.25925	-5.33771

H	1.02216	-4.76267	-2.00249
C	1.60616	-1.2355	-3.49941
H	1.80003	-0.25424	-3.92721
C	1.21218	-1.35394	-2.15854
C	2.08483	-1.44018	2.7469
C	3.07724	-1.37431	3.71847
C	2.75044	-1.03936	5.03828
C	1.42256	-0.75582	5.38705
C	0.42534	-0.80449	4.42116
C	0.73991	-1.15734	3.08641
H	2.33182	-1.67888	1.71813
H	4.1086	-1.58126	3.44782
H	3.52938	-0.99466	5.79485
H	1.17379	-0.49384	6.41196
H	-0.60651	-0.58251	4.6749
S	-0.53649	-1.25091	1.85701
C	-3.82145	2.5161	-0.62442
H	-4.88873	2.65151	-0.77669
C	-3.11456	3.40089	0.1368
H	-3.61203	4.2497	0.59806
Br	3.14702	0.36966	-0.60232
H	1.69746	-4.52839	-4.38754

Figure S2; E'-TS_{RA}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -37.97 cm^{-1}

Zero-point correction= 0.384385 (Hartree/Particle)

Thermal correction to Energy= 0.411411

Thermal correction to Enthalpy= 0.412356

Thermal correction to Gibbs Free Energy= 0.319240

Sum of electronic and zero-point Energies= -1266.467511

Sum of electronic and thermal Energies= -1266.440485

Sum of electronic and thermal Enthalpies= -1266.439541

Sum of electronic and thermal Free Energies= -1266.532656

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

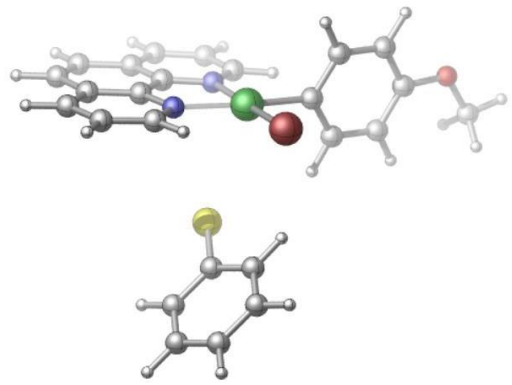
HF=-1656.212499

C	-1.15934	2.46207	0.0458
C	0.89382	3.04235	0.92558
C	0.33566	4.17002	1.56002
C	-1.01286	4.43489	1.42039
C	-1.81057	3.56662	0.64163
C	-1.89977	1.53603	-0.75764
C	-1.86477	-0.38209	-2.04823

C	-3.24529	-0.27311	-2.29826
C	-3.96011	0.77669	-1.7565
C	-3.28698	1.72561	-0.95565
H	1.94849	2.79485	1.0038
H	0.97608	4.81622	2.15129
H	-1.46649	5.29844	1.90002
H	-1.27818	-1.19604	-2.45589
H	-3.72817	-1.02226	-2.91685
H	-5.02687	0.88105	-1.93617
N	0.167	2.20985	0.18776
N	-1.20113	0.49705	-1.29802
Ni	0.72227	0.51639	-0.83113
C	0.8892	-2.31399	-1.33429
C	1.67129	-2.05809	-3.989
C	1.0619	-3.4497	-2.13414
H	0.57795	-2.43684	-0.29919
C	1.45626	-3.34316	-3.47383
H	1.98213	-1.94404	-5.02684
H	0.88831	-4.43629	-1.70573
C	1.50482	-0.92015	-3.19295
H	1.70328	0.05761	-3.62675
C	1.10228	-1.03008	-1.85473
C	1.95403	-1.13691	3.04028
C	2.94768	-1.08364	4.01138
C	2.6244	-0.75381	5.33333
C	1.29889	-0.46262	5.68481

C	0.30058	-0.49861	4.7195
C	0.61148	-0.8463	3.38255
H	2.19848	-1.37142	2.00995
H	3.97732	-1.29635	3.73864
H	3.40427	-0.71893	6.08946
H	1.05286	-0.20451	6.71137
H	-0.72941	-0.27043	4.97533
S	-0.66653	-0.92363	2.15365
C	-3.9258	2.85558	-0.34025
H	-4.99205	2.99421	-0.49682
C	-3.21949	3.73776	0.42452
H	-3.71641	4.58767	0.88437
Br	3.03662	0.69028	-0.29192
C	1.67799	-4.57371	-4.32476
H	2.71664	-4.92649	-4.2597
H	1.03608	-5.4036	-4.00739
H	1.47214	-4.37445	-5.38281

Figure S3; E'-TS_{RA}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -37.49 cm^{-1}

Zero-point correction= 0.389646 (Hartree/Particle)

Thermal correction to Energy= 0.417398

Thermal correction to Enthalpy= 0.418342

Thermal correction to Gibbs Free Energy= 0.323738

Sum of electronic and zero-point Energies= -1341.665220

Sum of electronic and thermal Energies= -1341.637468

Sum of electronic and thermal Enthalpies= -1341.636524

Sum of electronic and thermal Free Energies= -1341.731128

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

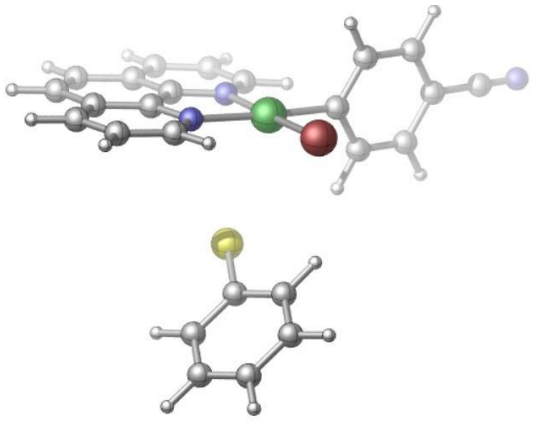
HF=-1731.4110566

C	-1.14936	2.62952	0.05015
C	0.9139	3.20555	0.90867
C	0.36721	4.34199	1.53741
C	-0.98079	4.61354	1.40593
C	-1.78953	3.74319	0.64103
C	-1.90132	1.70123	-0.73976
C	-1.88661	-0.22729	-2.01499

C	-3.26811	-0.11182	-2.25671
C	-3.97294	0.9465	-1.71835
C	-3.28867	1.89769	-0.92973
H	1.96781	2.9529	0.98054
H	1.016	4.98969	2.1178
H	-1.42557	5.48404	1.88127
H	-1.30668	-1.04723	-2.4202
H	-3.75964	-0.86248	-2.86659
H	-5.04021	1.05601	-1.89181
N	0.17657	2.3706	0.18409
N	-1.21276	0.65365	-1.27623
Ni	0.71462	0.66482	-0.82443
C	0.87201	-2.17055	-1.30375
C	1.63287	-1.94066	-3.96963
C	1.03636	-3.32805	-2.08184
H	0.57535	-2.28414	-0.2634
C	1.41658	-3.21279	-3.42215
H	1.93987	-1.86922	-5.00963
H	0.8703	-4.29995	-1.62834
C	1.47125	-0.80165	-3.18221
H	1.67144	0.17025	-3.62774
C	1.07641	-0.89477	-1.83693
C	1.94785	-0.89029	3.08338
C	2.93597	-0.79216	4.05664
C	2.59844	-0.44988	5.37187
C	1.26379	-0.19124	5.71418

C	0.27051	-0.27189	4.74639
C	0.59625	-0.6326	3.4164
H	2.20294	-1.13471	2.05788
H	3.97228	-0.9796	3.79069
H	3.37416	-0.38002	6.12985
H	1.00665	0.07655	6.73553
H	-0.76655	-0.06926	4.99501
S	-0.67449	-0.76678	2.18483
C	-3.9162	3.03667	-0.3193
H	-4.98267	3.18063	-0.46946
C	-3.19898	3.92098	0.43277
H	-3.68735	4.77787	0.88881
Br	3.03374	0.83236	-0.30402
O	1.60194	-4.2713	-4.27817
C	1.4483	-5.57667	-3.75785
H	1.66054	-6.25948	-4.58382
H	2.15151	-5.77372	-2.93664
H	0.42506	-5.75606	-3.39745

Figure S4; E'-TS_{RA}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -33.24 cm^{-1}

Zero-point correction= 0.355624 (Hartree/Particle)

Thermal correction to Energy= 0.382553

Thermal correction to Enthalpy= 0.383498

Thermal correction to Gibbs Free Energy= 0.290868

Sum of electronic and zero-point Energies= -1319.425817

Sum of electronic and thermal Energies= -1319.398888

Sum of electronic and thermal Enthalpies= -1319.397944

Sum of electronic and thermal Free Energies= -1319.490574

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

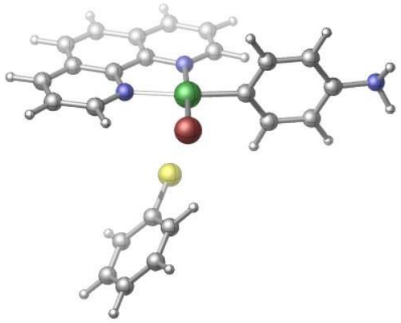
HF =-1709.1373936

C	-1.08381	2.24208	-0.12963
C	0.98293	2.81602	0.72383
C	0.43619	3.94565	1.36453
C	-0.91306	4.21469	1.24211
C	-1.72364	3.34854	0.47415
C	-1.83742	1.31847	-0.9226
C	-1.82554	-0.60099	-2.21149

C	-3.209	-0.49006	-2.44249
C	-3.91305	0.56243	-1.89189
C	-3.22666	1.51078	-1.10159
H	2.03772	2.56656	0.78958
H	1.08632	4.59004	1.94695
H	-1.35746	5.07994	1.72708
H	-1.2501	-1.41784	-2.62861
H	-3.70194	-1.23895	-3.05321
H	-4.98186	0.6689	-2.0569
N	0.24379	1.9855	-0.0043
N	-1.14883	0.27752	-1.47248
Ni	0.77898	0.30021	-1.02684
C	0.98565	-2.52674	-1.53883
C	1.73037	-2.22893	-4.21546
C	1.16744	-3.65745	-2.33484
H	0.6987	-2.65374	-0.49806
C	1.5364	-3.51654	-3.68418
H	2.02654	-2.11831	-5.2548
H	1.02585	-4.65188	-1.92066
C	1.54942	-1.10799	-3.40718
H	1.72596	-0.1236	-3.83339
C	1.16432	-1.23509	-2.06176
C	2.08485	-1.31573	2.88881
C	3.03797	-1.22577	3.89676
C	2.65819	-0.86368	5.19527
C	1.31678	-0.57782	5.48542

C	0.35844	-0.65081	4.48251
C	0.72664	-1.03049	3.1689
H	2.37193	-1.5772	1.87612
H	4.07968	-1.4362	3.67248
H	3.40645	-0.8006	5.98081
H	1.02707	-0.29582	6.49404
H	-0.68338	-0.42865	4.6911
S	-0.50064	-1.15599	1.89391
C	-3.85419	2.64283	-0.47846
H	-4.92199	2.78423	-0.6205
C	-3.13488	3.52358	0.27579
H	-3.62305	4.37521	0.74155
Br	3.10001	0.46075	-0.5241
C	1.70789	-4.67343	-4.51148
N	1.83801	-5.61363	-5.18596

TS_{RA}-4-NH_2-Ph-(Byp)Ni(II)-Br



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Imaginary frequency = -38.25 cm^{-1}

Zero-point correction= 0.373539 (Hartree/Particle)

Thermal correction to Energy= 0.400179

Thermal correction to Enthalpy= 0.401123

Thermal correction to Gibbs Free Energy= 0.309574

Sum of electronic and zero-point Energies= -1282.512082

Sum of electronic and thermal Energies= -1282.485441

Sum of electronic and thermal Enthalpies= -1282.484497

Sum of electronic and thermal Free Energies= -1282.576047

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

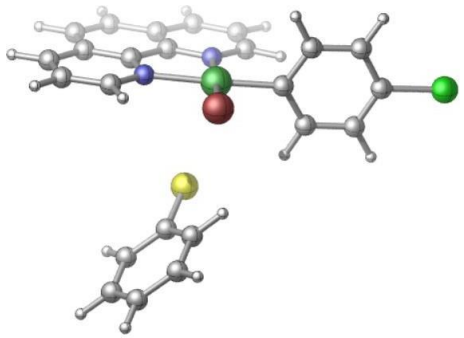
HF=-1672.2635138

C	-1.06063	2.34021	-0.10177
C	1.02963	2.90969	0.69349
C	0.51284	4.06875	1.30589
C	-0.83435	4.35491	1.19944
C	-1.6722	3.47679	0.47595
C	-1.84322	1.40311	-0.85065
C	-1.88411	-0.55631	-2.07757
C	-3.26987	-0.42893	-2.2875
C	-3.94772	0.65182	-1.75926
C	-3.23215	1.61334	-1.01201
H	2.0817	2.64491	0.74687
H	1.18353	4.72205	1.85427
H	-1.25645	5.24289	1.66305
H	-1.32458	-1.39355	-2.47635
H	-3.78563	-1.18857	-2.86542
H	-5.01756	0.77103	-1.90904
N	0.26461	2.06666	0.00797
N	-1.18131	0.33394	-1.37786

Ni	0.75735	0.32941	-0.97333
C	0.84966	-2.51968	-1.41332
C	1.57212	-2.34186	-4.09319
C	0.97769	-3.68108	-2.18241
H	0.57074	-2.61461	-0.36611
C	1.33957	-3.60828	-3.53564
H	1.86149	-2.26274	-5.14042
H	0.79705	-4.65475	-1.72816
C	1.44656	-1.18699	-3.3162
H	1.66257	-0.22613	-3.77843
C	1.07157	-1.25184	-1.96739
C	2.01052	-1.06542	2.97549
C	3.00399	-0.9204	3.9375
C	2.66918	-0.55618	5.2475
C	1.33143	-0.32255	5.59565
C	0.33243	-0.44981	4.63876
C	0.65587	-0.83296	3.31451
H	2.2632	-1.32735	1.95364
H	4.0423	-1.08867	3.66648
H	3.4492	-0.44989	5.99682
H	1.0762	-0.03775	6.61288
H	-0.70724	-0.26692	4.8918
S	-0.62131	-1.02623	2.09745
C	-3.83015	2.77541	-0.41562
H	-4.89804	2.92981	-0.54382
C	-3.08377	3.6685	0.29663

H	-3.54991	4.543	0.74241
Br	3.09002	0.4708	-0.50078
N	1.40979	-4.77203	-4.33054
H	2.04834	-4.68101	-5.11343
H	1.63897	-5.60452	-3.79823

TS_{RA}-4-Cl-Ph-(Byp)Ni(II)-Br



UB3LYP/6-31g(d)-(Br, Ni,Cl-LANL2DZ)-gas

Imaginary frequency = -35.23 cm^{-1}

Zero-point correction= 0.347174 (Hartree/Particle)

Thermal correction to Energy= 0.373585

Thermal correction to Enthalpy= 0.374529

Thermal correction to Gibbs Free Energy= 0.282812

Sum of electronic and zero-point Energies= -1241.533770

Sum of electronic and thermal Energies= -1241.507360

Sum of electronic and thermal Enthalpies= -1241.506416

Sum of electronic and thermal Free Energies= -1241.598133

UM06/6-311+g(d,p)-(Br, Ni ,Cl-SDD)-SMD(THF)

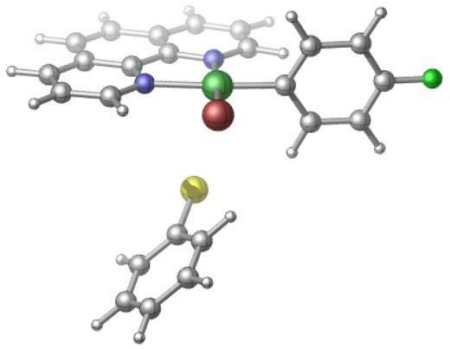
HF=-2076.4751655

C	-1.11774	2.12229	-0.18262

C	0.89232	2.70942	0.78817
C	0.28431	3.78634	1.46357
C	-1.06644	4.02233	1.29713
C	-1.81658	3.17572	0.45005
C	-1.80863	1.2202	-1.05404
C	-1.68338	-0.62722	-2.43839
C	-3.05788	-0.54074	-2.72682
C	-3.81667	0.46072	-2.15428
C	-3.19395	1.38368	-1.28515
H	1.95067	2.48666	0.88616
H	0.88912	4.41684	2.10689
H	-1.55782	4.84675	1.80733
H	-1.0653	-1.40482	-2.86929
H	-3.50095	-1.26866	-3.39818
H	-4.87996	0.54671	-2.36169
N	0.21087	1.89851	-0.01436
N	-1.06637	0.22799	-1.62366
Ni	0.84009	0.27614	-1.09129
C	1.09691	-2.52616	-1.68322
C	1.98904	-2.15651	-4.30598
C	1.32827	-3.6403	-2.50029
H	0.7517	-2.68871	-0.66491
C	1.7661	-3.4328	-3.80252
H	2.34359	-2.02235	-5.32292
H	1.17114	-4.64799	-2.1288
C	1.75656	-1.05654	-3.47178

H	1.95505	-0.06154	-3.8629
C	1.29778	-1.2212	-2.15654
C	2.06179	-1.5201	2.74654
C	3.02142	-1.47846	3.75154
C	2.65176	-1.16861	5.06626
C	1.314	-0.88653	5.37637
C	0.34931	-0.91171	4.37721
C	0.70718	-1.23858	3.04667
H	2.34172	-1.73919	1.72196
H	4.06051	-1.68463	3.51174
H	3.40517	-1.14256	5.84902
H	1.03221	-0.6444	6.39756
H	-0.6897	-0.69128	4.60115
S	-0.52796	-1.30109	1.7743
C	-3.88177	2.46244	-0.63194
H	-4.94632	2.58123	-0.81384
C	-3.22288	3.32078	0.19942
H	-3.7564	4.13173	0.68761
Br	3.13325	0.49141	-0.48753
Cl	2.0548	-4.86521	-4.87372

TS_{RA}-4-F-Ph-(Byp)Ni(II)-Br



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Imaginary frequency = -37.00 cm^{-1}

Zero-point correction= 0.348740 (Hartree/Particle)

Thermal correction to Energy= 0.374711

Thermal correction to Enthalpy= 0.375655

Thermal correction to Gibbs Free Energy= 0.285071

Sum of electronic and zero-point Energies= -1326.419990

Sum of electronic and thermal Energies= -1326.394019

Sum of electronic and thermal Enthalpies= -1326.393075

Sum of electronic and thermal Free Energies= -1326.483659

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

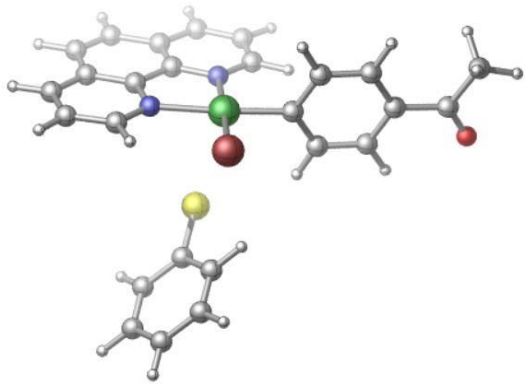
HF=-1716.161073

C	-1.11122	2.11174	-0.18556
C	0.89911	2.69744	0.78505
C	0.2915	3.77334	1.46246
C	-1.05937	4.00959	1.29706
C	-1.80985	3.16428	0.44906
C	-1.80258	1.21082	-1.05803
C	-1.67794	-0.63471	-2.44485

C	-3.05264	-0.54768	-2.73231
C	-3.81126	0.45304	-2.1582
C	-3.18806	1.37477	-1.28817
H	1.95754	2.47421	0.88194
H	0.89657	4.40287	2.10654
H	-1.55057	4.83321	1.80878
H	-1.05872	-1.41128	-2.87612
H	-3.49632	-1.2747	-3.4043
H	-4.87469	0.53937	-2.36493
N	0.21737	1.88772	-0.01837
N	-1.06061	0.21946	-1.62931
Ni	0.84695	0.26464	-1.10002
C	1.09609	-2.53818	-1.69638
C	1.98934	-2.16632	-4.31831
C	1.32731	-3.65068	-2.51549
H	0.75019	-2.69961	-0.67816
C	1.76847	-3.44316	-3.81625
H	2.34585	-2.04493	-5.3371
H	1.1742	-4.66445	-2.15646
C	1.75806	-1.06628	-3.48426
H	1.95666	-0.07013	-3.87236
C	1.29908	-1.233	-2.16904
C	2.05005	-1.51153	2.74046
C	3.01474	-1.46212	3.74037
C	2.64919	-1.15936	5.05785
C	1.31029	-0.89198	5.37597

C	0.34046	-0.9248	4.38198
C	0.69431	-1.24488	3.04876
H	2.32681	-1.72479	1.71376
H	4.05461	-1.65648	3.49412
H	3.40661	-1.1272	5.83653
H	1.03162	-0.65508	6.39926
H	-0.69951	-0.71539	4.61204
S	-0.54698	-1.31704	1.78267
C	-3.87551	2.45263	-0.63308
H	-4.94017	2.57171	-0.81429
C	-3.21626	3.30973	0.19927
H	-3.74957	4.11997	0.68894
Br	3.14018	0.48026	-0.49311
F	1.98866	-4.51507	-4.6184

TS_{RA}-4-COMe-Ph-(Byp)Ni(II)-Br



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Imaginary frequency = -35.02 cm^{-1}

Zero-point correction= 0.394595 (Hartree/Particle)

Thermal correction to Energy= 0.423263

Thermal correction to Enthalpy= 0.424207

Thermal correction to Gibbs Free Energy= 0.327833

Sum of electronic and zero-point Energies= -1379.788330

Sum of electronic and thermal Energies= -1379.759662

Sum of electronic and thermal Enthalpies= -1379.758718

Sum of electronic and thermal Free Energies= -1379.855092

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

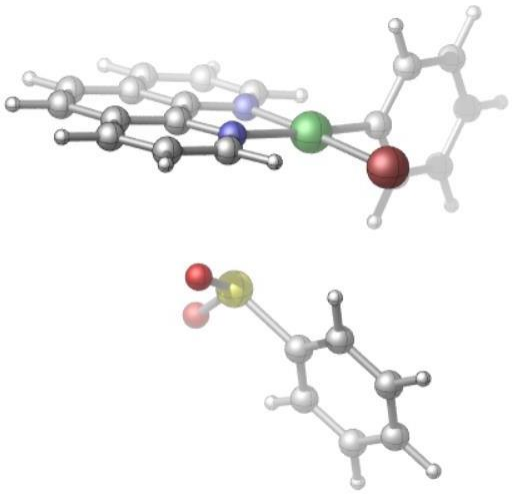
HF=-1769.5267553

C	-1.12409	2.14927	-0.20919
C	0.89094	2.73745	0.75076
C	0.29313	3.83484	1.4019
C	-1.05508	4.08052	1.22883
C	-1.81297	3.223	0.39981
C	-1.82331	1.23461	-1.06072
C	-1.71648	-0.64611	-2.40129
C	-3.0907	-0.5547	-2.68939
C	-3.8395	0.46732	-2.1406
C	-3.20738	1.40501	-1.29432
H	1.94693	2.50643	0.85477
H	0.90352	4.47305	2.03221
H	-1.53873	4.9206	1.72052
H	-1.10703	-1.4409	-2.81282
H	-3.54153	-1.29545	-3.34125
H	-4.90233	0.55773	-2.34853
N	0.20206	1.91629	-0.03474
N	-1.09051	0.22326	-1.60864

Ni	0.81685	0.26875	-1.08106
C	1.03746	-2.54272	-1.65458
C	1.979	-2.19197	-4.25532
C	1.26359	-3.6498	-2.46995
H	0.67236	-2.69226	-0.64113
C	1.73428	-3.49285	-3.78467
H	2.35402	-2.03573	-5.26341
H	1.08284	-4.65792	-2.10829
C	1.75149	-1.0836	-3.43787
H	1.97054	-0.09114	-3.82425
C	1.26872	-1.23895	-2.12874
C	2.04762	-1.60263	2.71118
C	3.02366	-1.62207	3.70087
C	2.69345	-1.29772	5.02255
C	1.37952	-0.93967	5.35502
C	0.39955	-0.90336	4.37115
C	0.71678	-1.24394	3.03389
H	2.29761	-1.83373	1.68158
H	4.045	-1.88768	3.44389
H	3.45927	-1.31968	5.79329
H	1.1283	-0.68662	6.38153
H	-0.62115	-0.6236	4.61247
S	-0.53959	-1.22838	1.78098
C	-3.88486	2.50484	-0.6659
H	-4.94838	2.62912	-0.85013
C	-3.21778	3.37582	0.14553

H	-3.74366	4.20249	0.6153
Br	3.11368	0.47549	-0.48731
C	1.95278	-4.71261	-4.61486
O	1.6881	-5.82901	-4.18653
C	2.51736	-4.55284	-6.02113
H	1.85932	-3.93607	-6.64526
H	2.61685	-5.54242	-6.47103
H	3.49798	-4.06256	-5.99946

Figure S1; E-TS_{RA}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -27.27 cm^{-1}

Zero-point correction= 0.363064 (Hartree/Particle)

Thermal correction to Energy= 0.390587

Thermal correction to Enthalpy= 0.391531

Thermal correction to Gibbs Free Energy= 0.297814

Sum of electronic and zero-point Energies= -1377.470391

Sum of electronic and thermal Energies= -1377.442869

Sum of electronic and thermal Enthalpies= -1377.441924

Sum of electronic and thermal Free Energies= -1377.535641

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

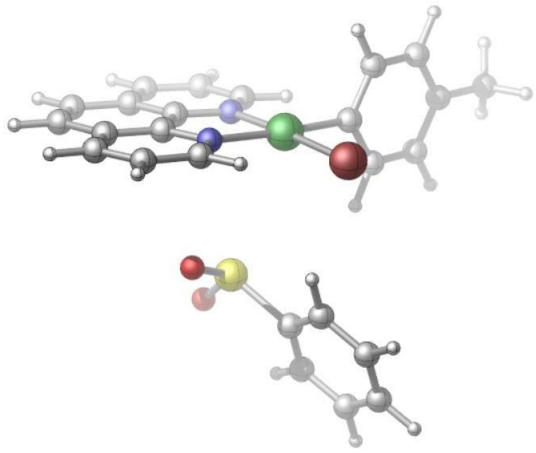
HF=-1767.1899119

C	-1.47433	2.3488	-0.41401
C	0.44542	3.46607	0.20281
C	-0.30987	4.52092	0.75184
C	-1.6888	4.46829	0.70816
C	-2.31792	3.35427	0.10912
C	-2.038	1.18846	-1.03426
C	-1.65522	-0.83285	-2.09381
C	-3.03731	-1.05388	-2.23384
C	-3.9333	-0.11996	-1.75213
C	-3.44193	1.04767	-1.128
H	1.53089	3.46404	0.22096
H	0.20562	5.36066	1.20595
H	-2.29351	5.26767	1.12844
H	-0.92892	-1.54915	-2.45683
H	-3.37803	-1.96309	-2.71769
H	-5.00533	-0.2721	-1.84461
N	-0.11961	2.40762	-0.36632
N	-1.15949	0.25807	-1.50862
Ni	0.72963	0.73526	-1.1859
C	1.56781	-2.03277	-1.336
C	1.97935	-1.98657	-4.09146
C	1.942	-3.20167	-2.0094

H	1.43481	-2.0699	-0.25678
C	2.14553	-3.18339	-3.39078
H	2.14763	-1.95695	-5.16618
H	2.08026	-4.12524	-1.45071
C	1.60393	-0.81992	-3.41548
H	1.4944	0.10407	-3.97999
C	1.38388	-0.82788	-2.02964
C	1.06847	-2.36361	3.76568
C	2.26244	-2.79893	4.34411
C	3.45434	-2.11203	4.0962
C	3.46621	-0.98589	3.26949
C	2.2827	-0.527	2.68572
C	1.1182	-1.23115	2.9625
H	0.126	-2.87334	3.93237
H	2.25831	-3.67408	4.98765
H	4.38062	-2.46216	4.54308
H	4.39526	-0.46284	3.06417
H	2.28634	0.33154	2.02084
C	-4.2783	2.08359	-0.58931
H	-5.35604	1.96693	-0.66117
C	-3.73982	3.18808	0.00384
H	-4.38423	3.96254	0.41066
Br	2.97103	1.36397	-0.68181
H	2.43968	-4.08976	-3.91435
S	-0.47693	-0.64936	2.15988
O	-0.56777	0.91111	2.39861

O -1.61612 -1.57416 2.73693

Figure S2; E-TS_{RA}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -27.49 cm^{-1}

Zero-point correction= 0.390574 (Hartree/Particle)

Thermal correction to Energy= 0.420015

Thermal correction to Enthalpy= 0.420959

Thermal correction to Gibbs Free Energy= 0.322044

Sum of electronic and zero-point Energies= -1416.759706

Sum of electronic and thermal Energies= -1416.730265

Sum of electronic and thermal Enthalpies= -1416.729320

Sum of electronic and thermal Free Energies= -1416.828236

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

HF=-1806.4839776

C -1.63867 2.63205 -0.15661

C 0.28286 3.7545 0.44485

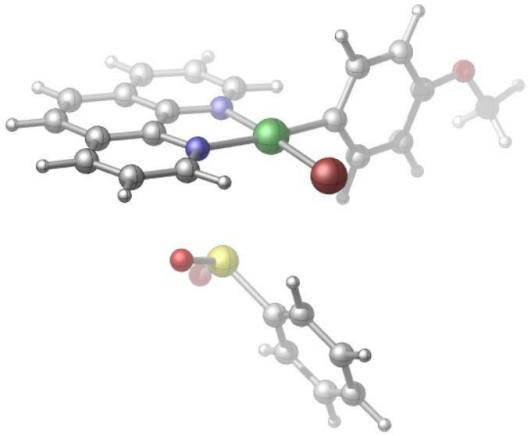
C -0.47085 4.80955 0.99567

C -1.84995 4.75431 0.96092

C	-2.48079	3.63747	0.369
C	-2.20415	1.46912	-0.77034
C	-1.82415	-0.554	-1.82742
C	-3.20669	-0.77777	-1.95843
C	-4.10144	0.15566	-1.4734
C	-3.60836	1.32565	-0.8551
H	1.36844	3.75445	0.45603
H	0.04598	5.65155	1.44406
H	-2.45344	5.55379	1.38275
H	-1.0983	-1.2695	-2.19292
H	-3.54883	-1.6887	-2.43802
H	-5.17375	0.00136	-1.55892
N	-0.28381	2.69335	-0.1176
N	-1.32693	0.53921	-1.24781
Ni	0.56336	1.01944	-0.93773
C	1.40392	-1.75085	-1.09161
C	1.80058	-1.71531	-3.83935
C	1.7754	-2.91867	-1.76652
H	1.27259	-1.79336	-0.01229
C	1.98164	-2.92236	-3.15188
H	1.9582	-1.68568	-4.91675
H	1.91234	-3.84106	-1.20345
C	1.42793	-0.54653	-3.16715
H	1.31074	0.3717	-3.7396
C	1.21485	-0.54528	-1.7811
C	0.93663	-2.07203	4.01868

C	2.13462	-2.49844	4.59543
C	3.32239	-1.80734	4.33949
C	3.32606	-0.68593	3.50631
C	2.13839	-0.23592	2.92408
C	0.97821	-0.94396	3.20891
H	-0.00284	-2.58529	4.19138
H	2.13686	-3.36993	5.24394
H	4.25185	-2.15052	4.78518
H	4.25191	-0.15969	3.29473
H	2.13587	0.61879	2.25424
C	-4.44321	2.36147	-0.31385
H	-5.52118	2.24274	-0.37871
C	-3.90303	3.46847	0.27304
H	-4.54628	4.24287	0.68181
Br	2.80661	1.65383	-0.44781
S	-0.62272	-0.37387	2.40921
O	-0.72244	1.18662	2.64438
O	-1.75455	-1.30383	2.99246
C	2.42092	-4.17621	-3.87437
H	2.08096	-4.17991	-4.9163
H	3.51574	-4.26762	-3.89201
H	2.0305	-5.0784	-3.38952

Figure S3; E-TS_{RA}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -28.47 cm^{-1}

Zero-point correction= 0.395930 (Hartree/Particle)

Thermal correction to Energy= 0.426048

Thermal correction to Enthalpy= 0.426993

Thermal correction to Gibbs Free Energy= 0.327190

Sum of electronic and zero-point Energies= -1491.957274

Sum of electronic and thermal Energies= -1491.927156

Sum of electronic and thermal Enthalpies= -1491.926212

Sum of electronic and thermal Free Energies= -1492.026014

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

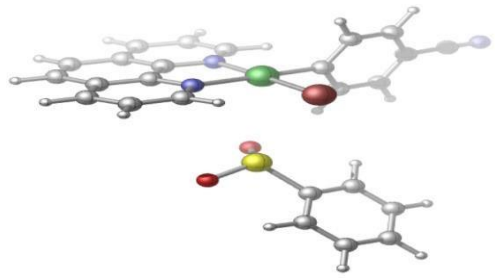
HF=-1881.6826728

C	-1.66742	2.79629	-0.19398
C	0.26156	3.90184	0.41493
C	-0.48444	4.97486	0.94103
C	-1.86369	4.93736	0.89008
C	-2.50219	3.82031	0.30689
C	-2.24113	1.63248	-0.79814

C	-1.87561	-0.41032	-1.82159
C	-3.25938	-0.61949	-1.96298
C	-4.14728	0.33229	-1.50164
C	-3.646	1.50528	-0.89576
H	1.34684	3.88741	0.43924
H	0.03823	5.81665	1.38305
H	-2.4615	5.75095	1.29263
H	-1.1543	-1.13895	-2.16971
H	-3.60792	-1.53344	-2.4321
H	-5.2205	0.18999	-1.59612
N	-0.31246	2.84	-0.13879
N	-1.37092	0.68578	-1.25422
Ni	0.52302	1.14593	-0.93093
C	1.38444	-1.62419	-1.07656
C	1.72139	-1.60207	-3.83524
C	1.75755	-2.80428	-1.73882
H	1.2853	-1.65966	0.00623
C	1.92546	-2.79413	-3.12664
H	1.86853	-1.6071	-4.91187
H	1.92038	-3.70855	-1.16162
C	1.34973	-0.44039	-3.16018
H	1.21363	0.47205	-3.73748
C	1.1632	-0.42917	-1.7667
C	0.83938	-1.90418	4.06598
C	2.01733	-2.28225	4.71345
C	3.19811	-1.56578	4.49824

C	3.21477	-0.46728	3.63519
C	2.04673	-0.06564	2.98212
C	0.89231	-0.79724	3.22817
H	-0.09392	-2.43839	4.20541
H	2.0094	-3.13585	5.38533
H	4.11231	-1.87108	4.99963
H	4.13621	0.07838	3.45594
H	2.05562	0.77005	2.28859
C	-4.47331	2.55964	-0.37926
H	-5.55196	2.45378	-0.45452
C	-3.92539	3.6684	0.19692
H	-4.56301	4.45722	0.58654
Br	2.76678	1.75721	-0.41361
S	-0.68233	-0.28643	2.34025
O	-0.85144	1.26933	2.56778
O	-1.80925	-1.25582	2.86575
O	2.28429	-3.88336	-3.88109
C	2.55195	-5.09731	-3.20688
H	1.66749	-5.47177	-2.67189
H	2.83344	-5.81694	-3.97897
H	3.37999	-4.99248	-2.49205

Figure S4; E-TS_{RA}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -11.24 cm^{-1}

Zero-point correction= 0.362175 (Hartree/Particle)

Thermal correction to Energy= 0.391328

Thermal correction to Enthalpy= 0.392272

Thermal correction to Gibbs Free Energy= 0.295746

Sum of electronic and zero-point Energies= -1469.719185

Sum of electronic and thermal Energies= -1469.690032

Sum of electronic and thermal Enthalpies= -1469.689088

Sum of electronic and thermal Free Energies= -1469.785614

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

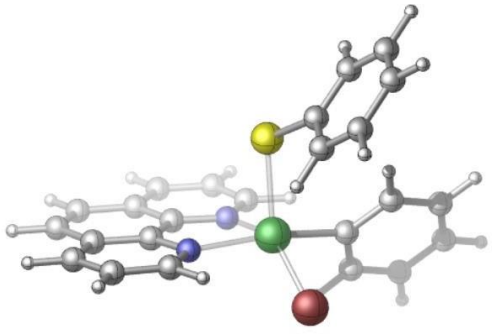
HF=-1859.4109009

C	-1.92674	2.34475	-0.33148
C	-0.09504	3.35927	0.63878
C	-0.91953	4.30792	1.27493
C	-2.28631	4.25636	1.09053
C	-2.83421	3.2513	0.26155
C	-2.40627	1.30366	-1.18866
C	-1.88797	-0.49869	-2.54098
C	-3.24521	-0.69048	-2.85773
C	-4.19974	0.14409	-2.3115

C	-3.79137	1.18347	-1.44689
H	0.98342	3.36382	0.76082
H	-0.46558	5.06259	1.90803
H	-2.94378	4.97427	1.57366
H	-1.1213	-1.14497	-2.94843
H	-3.51983	-1.49819	-3.52777
H	-5.25448	0.01314	-2.53794
N	-0.58244	2.40111	-0.14336
N	-1.47038	0.46908	-1.72561
Ni	0.36107	0.86793	-1.11011
C	1.02781	-1.89095	-1.45704
C	2.17086	-1.58536	-3.98824
C	1.49673	-3.01145	-2.14193
H	0.58232	-2.01653	-0.4731
C	2.06933	-2.86691	-3.41829
H	2.62054	-1.4714	-4.97056
H	1.42123	-4.00138	-1.70012
C	1.70217	-0.47318	-3.29003
H	1.80968	0.51014	-3.741
C	1.11719	-0.6055	-2.02014
C	2.29033	-0.56358	4.65899
C	3.19466	-1.39346	5.32565
C	3.71466	-2.52202	4.68671
C	3.33645	-2.83346	3.37775
C	2.43081	-2.01843	2.69577
C	1.92743	-0.90994	3.3644

H	1.86618	0.31883	5.12562
H	3.49013	-1.15657	6.34376
H	4.4221	-3.15966	5.20925
H	3.74652	-3.70912	2.88324
H	2.12839	-2.23746	1.67743
C	-4.69448	2.1129	-0.82784
H	-5.75757	2.01068	-1.027
C	-4.23632	3.10328	-0.0088
H	-4.93017	3.79988	0.45348
Br	2.54676	1.41662	-0.30542
S	0.75148	0.21838	2.43852
O	0.11041	1.16558	3.52764
O	-0.20468	-0.73085	1.60886
C	2.53983	-4.01634	-4.13222
N	2.9149	-4.95314	-4.71318

Figure S1; C’



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Zero-point correction= 0.357041 (Hartree/Particle)

Thermal correction to Energy= 0.382809

Thermal correction to Enthalpy= 0.383753

Thermal correction to Gibbs Free Energy= 0.296382

Sum of electronic and zero-point Energies= -1227.189545

Sum of electronic and thermal Energies= -1227.163777

Sum of electronic and thermal Enthalpies= -1227.162833

Sum of electronic and thermal Free Energies= -1227.250204

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

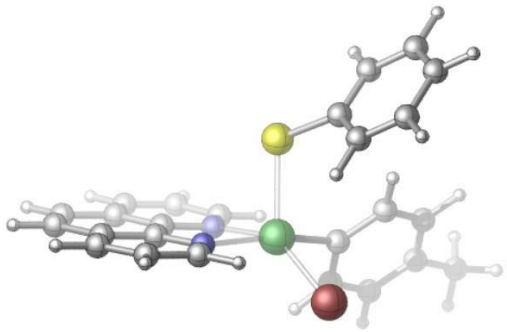
HF=-1616.936638

C	-1.78678	1.21254	1.8777
C	-0.06494	0.64205	3.3064
C	-0.51551	1.55798	4.27678
C	-1.63986	2.31642	4.01931
C	-2.31658	2.15817	2.78931
C	-2.42674	1.01283	0.60404
C	-2.42254	-0.07072	-1.43805
C	-3.5534	0.64882	-1.8672
C	-4.1318	1.56747	-1.01407
C	-3.56869	1.77967	0.2637
H	0.80105	0.01032	3.47641
H	0.02676	1.65354	5.21158
H	-2.01053	3.03277	4.74792
H	-1.94267	-0.80241	-2.07839
H	-3.95286	0.47124	-2.86007
H	-5.00827	2.13529	-1.31542
N	-0.67786	0.47919	2.14084
N	-1.88566	0.09213	-0.23434

Ni	-0.05015	-0.75929	0.5112
C	1.34106	-2.2198	-1.72598
C	-0.86056	-3.92184	-2.0328
C	1.34702	-3.22062	-2.70467
H	2.20772	-1.57992	-1.6098
C	0.24879	-4.06772	-2.8651
H	-1.71318	-4.59036	-2.12787
H	2.22085	-3.33265	-3.34221
H	0.26273	-4.84444	-3.62528
Br	1.00678	-2.38604	2.03559
C	-0.87516	-2.92451	-1.04788
H	-1.73355	-2.84646	-0.38513
C	0.21998	-2.06774	-0.91849
C	3.56751	0.25566	0.39327
C	4.94418	0.0625	0.28417
C	5.60426	0.32912	-0.91862
C	4.87233	0.7781	-2.02039
C	3.49128	0.95192	-1.92416
C	2.82452	0.70298	-0.71177
H	3.06004	0.04378	1.32826
H	5.50361	-0.29478	1.14505
H	6.67836	0.18354	-0.99736
H	5.37504	0.98357	-2.96237
H	2.91831	1.28654	-2.78376
C	-3.4877	2.90385	2.4243
H	-3.88553	3.62392	3.13418

C	-4.08593	2.72518	1.21223
H	-4.96614	3.30167	0.94116
S	1.04041	1.02652	-0.61223

Figure S2; C'



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Zero-point correction= 0.384560 (Hartree/Particle)

Thermal correction to Energy= 0.412248

Thermal correction to Enthalpy= 0.413192

Thermal correction to Gibbs Free Energy= 0.320809

Sum of electronic and zero-point Energies= -1266.479091

Sum of electronic and thermal Energies= -1266.451403

Sum of electronic and thermal Enthalpies= -1266.450459

Sum of electronic and thermal Free Energies= -1266.542842

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

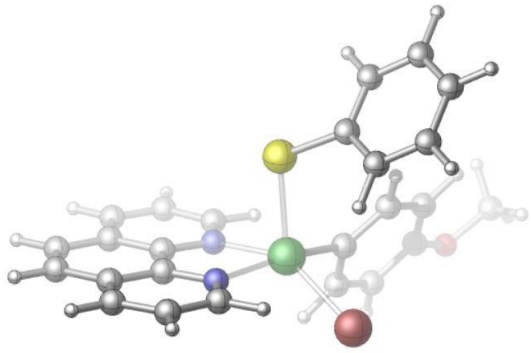
HF=-1656.2310687

H	5.34099	1.33485	-2.72765
C	4.84296	1.12555	-1.78401
H	2.88413	1.62929	-2.53801
H	6.6553	0.53445	-0.77003

C	3.4618	1.29469	-1.68156
C	5.58106	0.67632	-0.68644
H	2.21115	-3.01022	-3.06386
C	2.80088	1.0409	-0.46702
C	4.9268	0.40463	0.51836
C	1.33149	-2.89737	-2.43252
H	2.19377	-1.25712	-1.346
S	1.01623	1.35929	-0.35959
C	3.54994	0.59318	0.63372
H	5.49091	0.04704	1.37607
C	1.32439	-1.89372	-1.46039
C	0.26119	-4.82774	-3.67905
C	0.23947	-3.75862	-2.61023
H	-3.98848	0.78413	-2.5805
H	-1.97028	-0.48137	-1.80423
C	-3.58449	0.96615	-1.59025
H	3.04715	0.37723	1.57032
C	-2.44943	0.25125	-1.16439
C	0.20269	-1.73406	-0.65418
C	-0.86498	-3.59451	-1.76952
C	-4.16124	1.88604	-0.73735
H	-5.04082	2.45039	-1.0362
N	-1.90717	0.4196	0.03608
C	-0.88631	-2.59482	-0.78671
Ni	-0.06545	-0.42528	0.77462
H	-1.71805	-4.26442	-1.86096

C	-3.59238	2.1041	0.53688
C	-2.44665	1.34151	0.87407
H	-1.74802	-2.52279	-0.12752
C	-4.10745	3.0514	1.48481
H	-4.99056	3.6246	1.21622
C	-1.80095	1.54712	2.14392
N	-0.68895	0.81745	2.40401
Br	1.00041	-2.04519	2.30042
C	-3.50363	3.2358	2.69326
C	-2.32873	2.49446	3.05495
C	-0.0707	0.98584	3.56593
H	0.79766	0.3568	3.73377
H	-3.89985	3.95722	3.40267
C	-1.6463	2.65866	4.281
C	-0.51874	1.90397	4.53542
H	-2.01519	3.37656	5.00901
H	0.02795	2.00414	5.46717
H	1.20043	-5.39312	-3.66136
H	0.16645	-4.39437	-4.68383
H	-0.56043	-5.53993	-3.54937

Figure S3; C'



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Zero-point correction= 0.389837 (Hartree/Particle)

Thermal correction to Energy= 0.418257

Thermal correction to Enthalpy= 0.419201

Thermal correction to Gibbs Free Energy= 0.325372

Sum of electronic and zero-point Energies= -1341.676947

Sum of electronic and thermal Energies= -1341.648527

Sum of electronic and thermal Enthalpies= -1341.647583

Sum of electronic and thermal Free Energies= -1341.741413

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

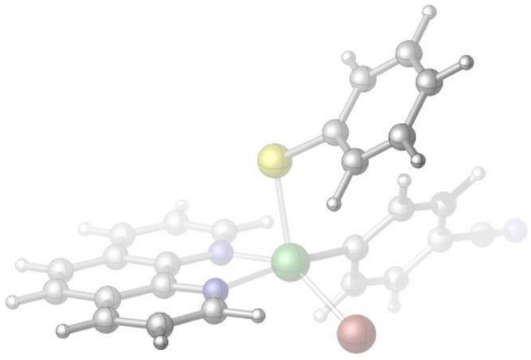
HF=-1731.4299491

H	5.3252	1.50665	-2.4422
C	4.80906	1.25059	-1.52
H	2.87099	1.83183	-2.2719
H	6.59556	0.57118	-0.51539
C	3.42922	1.4369	-1.42823
C	5.52248	0.72594	-0.43981
H	2.09215	-2.77716	-3.04642
C	2.74501	1.12428	-0.24047

C	4.84458	0.39574	0.73708
C	1.23022	-2.71606	-2.39116
H	2.06423	-1.0729	-1.29468
S	0.96411	1.46764	-0.14291
C	3.46931	0.60049	0.84318
H	5.38901	-0.02093	1.58076
C	1.21173	-1.73506	-1.38944
C	0.15128	-3.59488	-2.533
H	-4.00838	0.88912	-2.53095
H	-2.00335	-0.37699	-1.72106
C	-3.62739	1.06332	-1.53024
H	2.94814	0.33672	1.75718
C	-2.49972	0.34796	-1.08564
C	0.11715	-1.62453	-0.545
C	-0.94068	-3.49506	-1.66086
C	-4.22642	1.97363	-0.6823
H	-5.10043	2.53839	-0.99632
N	-1.98582	0.50755	0.12837
C	-0.95088	-2.52152	-0.66201
Ni	-0.16711	-0.34175	0.90188
H	-1.76015	-4.20049	-1.76329
C	-3.6887	2.18044	0.60734
C	-2.54929	1.41744	0.96362
H	-1.79323	-2.48714	0.02441
C	-4.22855	3.11593	1.55329
H	-5.10609	3.69057	1.26994

C	-1.93656	1.60781	2.25185
N	-0.83128	0.87489	2.53113
Br	0.86839	-1.98394	2.42298
C	-3.65478	3.28741	2.77829
C	-2.48816	2.54331	3.16076
C	-0.24227	1.02915	3.71001
H	0.62274	0.39914	3.89127
H	-4.06972	4.00008	3.48586
C	-1.83692	2.69248	4.40561
C	-0.71546	1.93518	4.67898
H	-2.22454	3.40102	5.13305
H	-0.19251	2.02427	5.62536
O	0.06541	-4.58014	-3.47894
C	1.16498	-4.76183	-4.35345
H	0.8937	-5.59108	-5.01012
H	2.08094	-5.01903	-3.80439
H	1.35278	-3.86653	-4.962

Figure S4; C’



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Zero-point correction= 0.355925 (Hartree/Particle)

Thermal correction to Energy= 0.383413

Thermal correction to Enthalpy= 0.384358

Thermal correction to Gibbs Free Energy= 0.293257

Sum of electronic and zero-point Energies= -1319.433770

Sum of electronic and thermal Energies= -1319.406281

Sum of electronic and thermal Enthalpies= -1319.405337

Sum of electronic and thermal Free Energies= -1319.496438

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

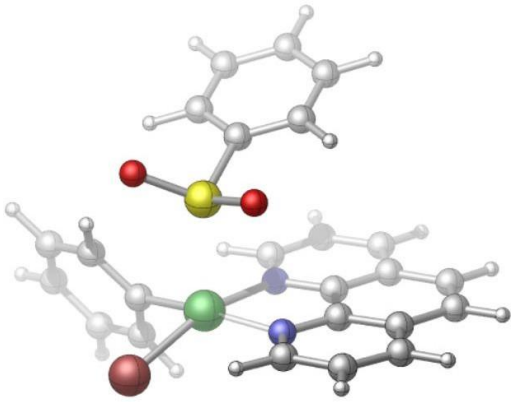
HF=-1709.1520757

H	6.64312	0.33293	-0.80341
C	5.5668	0.47397	-0.75469
H	5.44334	0.06107	1.36012
C	4.89246	0.3225	0.46037
H	5.36396	0.9197	-2.85643
C	4.84837	0.80337	-1.9065
C	3.51279	0.51027	0.52951
C	3.46446	0.9706	-1.84807
H	2.99337	0.39401	1.47482
C	2.78261	0.8349	-0.626
H	2.90107	1.21148	-2.74445
H	0.08217	1.7994	5.26521
C	-0.47552	1.6996	4.34006
H	0.83533	0.15872	3.52119
S	0.99409	1.1413	-0.57956
C	-0.03604	0.78576	3.36318

H	-1.97235	3.16411	4.83609
C	-1.60957	2.44984	4.10159
H	2.25342	-1.49829	-1.41734
N	-0.66787	0.61803	2.20802
Br	0.91831	-2.28586	2.12267
C	-2.30704	2.28525	2.88415
Ni	-0.07174	-0.62565	0.59247
C	-1.78717	1.34275	1.96374
H	-3.8804	3.73934	3.25652
C	1.38055	-2.12051	-1.57503
C	-3.48992	3.02216	2.53981
H	2.32353	-3.25469	-3.14399
C	0.22237	-1.93749	-0.82287
C	-2.44849	1.13715	0.70256
C	1.42602	-3.11745	-2.54841
C	-4.10798	2.83896	1.33846
N	-1.9159	0.21913	-0.14462
C	-3.60054	1.89689	0.38126
H	-4.99672	3.40912	1.08271
C	-2.4699	0.0569	-1.34086
C	-0.87899	-2.77986	-1.0114
H	-1.99544	-0.66749	-1.9933
C	0.31365	-3.94846	-2.76697
C	-4.18291	1.68239	-0.8875
C	-3.61152	0.76967	-1.7517
H	-1.76876	-2.68661	-0.39472

C	-0.8398	-3.77897	-1.9854
H	-5.06796	2.24435	-1.17404
H	-4.02454	0.59149	-2.73882
H	-1.69269	-4.43524	-2.13082
C	0.35507	-4.96475	-3.77657
N	0.38291	-5.78576	-4.60104

Figure S1; C



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Zero-point correction= 0.364218 (Hartree/Particle)

Thermal correction to Energy= 0.391961

Thermal correction to Enthalpy= 0.392905

Thermal correction to Gibbs Free Energy= 0.301387

Sum of electronic and zero-point Energies= -1377.470110

Sum of electronic and thermal Energies= -1377.442367

Sum of electronic and thermal Enthalpies= -1377.441423

Sum of electronic and thermal Free Energies= -1377.532941

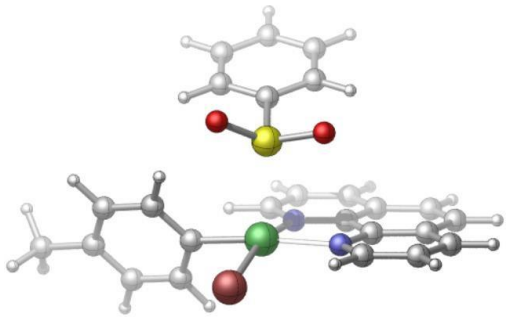
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

HF=-1767.2133162

C	0.53639	2.51904	-0.18184
C	2.81488	2.63674	-0.52946
C	2.86167	3.93543	0.01531
C	1.69813	4.52899	0.46059
C	0.47972	3.81736	0.37345
C	-0.65358	1.72277	-0.26805
C	-1.60568	-0.30808	-0.8426
C	-2.87237	0.12604	-0.41117
C	-3.01604	1.39996	0.10134
C	-1.88651	2.24331	0.19146
H	3.70442	2.13636	-0.89783
H	3.81495	4.44891	0.07932
H	1.7074	5.53044	0.88281
H	-1.45789	-1.29929	-1.25395
H	-3.71659	-0.55098	-0.48405
H	-3.98352	1.75875	0.44258
N	1.68208	1.95606	-0.63529
N	-0.52697	0.46787	-0.78263
Ni	1.38828	0.02915	-1.3301
C	1.40947	-2.88836	-1.62613
C	-0.27873	-2.80527	-3.86012
C	0.96866	-4.07376	-2.22867
H	2.09901	-2.92846	-0.78629
C	0.12321	-4.0365	-3.33939
H	-0.91729	-2.7629	-4.73966
H	1.30602	-5.02886	-1.83255

C	0.15214	-1.6149	-3.26061
H	-0.15178	-0.66284	-3.69069
C	0.97265	-1.66281	-2.12857
C	-0.24958	-0.33173	2.86112
C	-1.41046	-0.70208	3.54575
C	-1.94592	-1.98156	3.37551
C	-1.32063	-2.9	2.52712
C	-0.15738	-2.54198	1.84077
C	0.34782	-1.25934	2.01803
H	0.21067	0.643	2.9881
H	-1.88754	0.00304	4.2217
H	-2.84642	-2.26774	3.91259
H	-1.73004	-3.89969	2.40841
H	0.35512	-3.24496	1.19266
S	1.91943	-0.75964	1.09681
O	2.80861	-2.0646	1.15006
O	2.40508	0.52844	1.87701
C	-1.92072	3.57396	0.72983
H	-2.87244	3.96789	1.07529
C	-0.78605	4.32678	0.8194
H	-0.82326	5.32851	1.23859
Br	3.45736	-0.09196	-2.50791
H	-0.20582	-4.96051	-3.808

Figure S2; C



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Zero-point correction= 0.391743 (Hartree/Particle)

Thermal correction to Energy= 0.421389

Thermal correction to Enthalpy= 0.422333

Thermal correction to Gibbs Free Energy= 0.326189

Sum of electronic and zero-point Energies= -1416.759663

Sum of electronic and thermal Energies= -1416.730016

Sum of electronic and thermal Enthalpies= -1416.729072

Sum of electronic and thermal Free Energies= -1416.825216

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

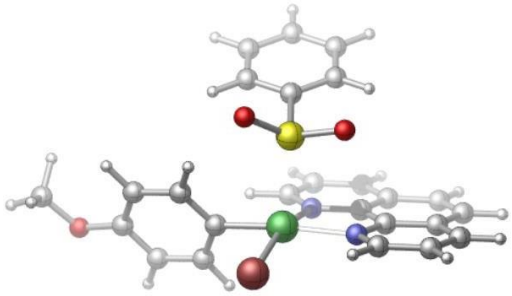
HF=-1806.5080694

C	0.5796	2.87183	0.21022
C	2.86317	2.99464	-0.09991
C	2.90779	4.26654	0.50472
C	1.74063	4.84446	0.96079
C	0.52065	4.14379	0.82341
C	-0.61318	2.08754	0.06933
C	-1.56827	0.09252	-0.61572
C	-2.83915	0.51424	-0.18436

C	-2.98322	1.76334	0.38588
C	-1.85037	2.59404	0.53327
H	3.75576	2.50793	-0.47929
H	3.86215	4.77213	0.60527
H	1.74815	5.82529	1.42894
H	-1.41921	-0.87889	-1.07161
H	-3.68618	-0.15281	-0.30248
H	-3.95378	2.11215	0.72875
N	1.72942	2.32429	-0.25171
N	-0.48608	0.85735	-0.50142
Ni	1.43858	0.42886	-1.03331
C	1.4695	-2.4748	-1.46193
C	-0.19369	-2.3069	-3.69702
C	1.03982	-3.63118	-2.12113
H	2.14888	-2.5547	-0.61676
C	0.2039	-3.57011	-3.24479
H	-0.82835	-2.22547	-4.57777
H	1.37884	-4.60053	-1.75933
C	0.22436	-1.14004	-3.04461
H	-0.0873	-0.17484	-3.43855
C	1.03354	-1.22721	-1.90889
C	-0.34638	-0.18981	3.06692
C	-1.51866	-0.62358	3.69212
C	-2.01079	-1.90779	3.44418
C	-1.33031	-2.76774	2.57728
C	-0.15524	-2.3459	1.94969

C	0.30597	-1.05954	2.20302
H	0.08111	0.78977	3.25567
H	-2.03858	0.03552	4.38277
H	-2.92031	-2.2435	3.93543
H	-1.70599	-3.77168	2.39826
H	0.39942	-3.00329	1.28881
S	1.89439	-0.47333	1.3645
O	2.81739	-1.75523	1.38297
O	2.31603	0.78394	2.22806
C	-1.88606	3.89849	1.13234
H	-2.84092	4.28168	1.48124
C	-0.749	4.63951	1.27365
H	-0.78722	5.62097	1.73823
Br	3.52758	0.34933	-2.18081
C	-0.21726	-4.82917	-3.96865
H	0.5905	-5.2108	-4.60727
H	-0.47613	-5.63	-3.26621
H	-1.08549	-4.6513	-4.6122

Figure S3; C



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Zero-point correction= 0.396987 (Hartree/Particle)

Thermal correction to Energy= 0.427359

Thermal correction to Enthalpy= 0.428303

Thermal correction to Gibbs Free Energy= 0.331050

Sum of electronic and zero-point Energies= -1491.957903

Sum of electronic and thermal Energies= -1491.927531

Sum of electronic and thermal Enthalpies= -1491.926587

Sum of electronic and thermal Free Energies= -1492.023840

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

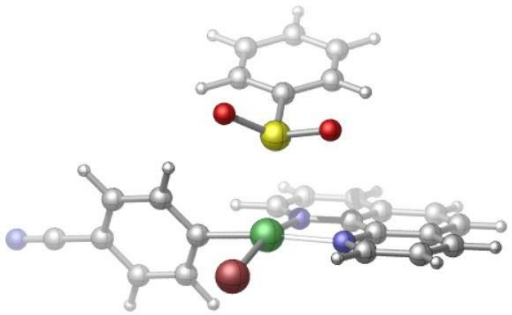
HF=-1881.7072537

C	0.55075	3.03865	0.25445
C	2.83126	3.15029	-0.08156
C	2.89053	4.41757	0.53142
C	1.73215	4.99928	1.00481
C	0.50649	4.30677	0.8769
C	-0.64816	2.26188	0.12353
C	-1.62166	0.27521	-0.559
C	-2.88508	0.70111	-0.11001
C	-3.01559	1.94804	0.4682
C	-1.87665	2.77209	0.60604
H	3.71645	2.66124	-0.47487
H	3.84903	4.9167	0.62457
H	1.75095	5.97682	1.47951
H	-1.48262	-0.69522	-1.02012
H	-3.73694	0.03902	-0.22114

H	-3.98005	2.30006	0.82477
N	1.69178	2.48788	-0.22511
N	-0.53469	1.03442	-0.45534
Ni	1.38351	0.59928	-1.01888
C	1.41646	-2.29843	-1.48118
C	-0.30701	-2.11556	-3.67222
C	0.98692	-3.46352	-2.13328
H	2.11982	-2.38226	-0.65617
C	0.11983	-3.37527	-3.22809
H	-0.95875	-2.06116	-4.5395
H	1.35373	-4.42341	-1.786
C	0.12096	-0.96127	-3.01725
H	-0.20331	0.00524	-3.39708
C	0.95723	-1.0521	-1.89624
C	-0.32035	-0.03695	3.10611
C	-1.48758	-0.46209	3.74661
C	-2.00637	-1.73316	3.48576
C	-1.35768	-2.58869	2.59052
C	-0.18795	-2.17536	1.94755
C	0.30019	-0.90169	2.21433
H	0.12741	0.93204	3.30261
H	-1.98293	0.19326	4.45855
H	-2.91198	-2.06227	3.98859
H	-1.75435	-3.58262	2.40104
H	0.34219	-2.82962	1.26374
S	1.88033	-0.32626	1.35345

O	2.78756	-1.61985	1.34185
O	2.33462	0.91495	2.22371
C	-1.89777	4.07307	1.21328
H	-2.84614	4.45943	1.5761
C	-0.75486	4.80677	1.34546
H	-0.78184	5.78545	1.81665
Br	3.44739	0.53125	-2.21234
O	-0.35853	-4.44577	-3.93331
C	0.09536	-5.73871	-3.57202
H	-0.38657	-6.43117	-4.26523
H	1.18545	-5.82732	-3.6702
H	-0.19293	-5.99805	-2.54398

Figure S4; C



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Zero-point correction= 0.362896 (Hartree/Particle)

Thermal correction to Energy= 0.392468

Thermal correction to Enthalpy= 0.393412

Thermal correction to Gibbs Free Energy= 0.297797

Sum of electronic and zero-point Energies= -1469.714607

Sum of electronic and thermal Energies= -1469.685035

Sum of electronic and thermal Enthalpies= -1469.684090

Sum of electronic and thermal Free Energies= -1469.779705

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

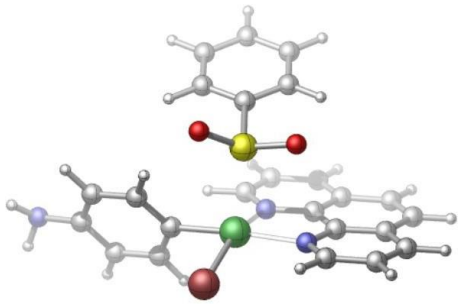
HF=-1859.4266451

C	0.53876	2.62112	-0.02656
C	2.82251	2.75519	-0.33663
C	2.85454	4.0405	0.23999
C	1.68206	4.61898	0.68183
C	0.46799	3.90489	0.55938
C	-0.64459	1.82212	-0.15082
C	-1.57504	-0.19876	-0.79189
C	-2.85043	0.21696	-0.36857
C	-3.0101	1.4766	0.17394
C	-1.88718	2.32383	0.30243
H	3.71994	2.26753	-0.70251
H	3.80451	4.55601	0.33042
H	1.68122	5.61013	1.12759
H	-1.41866	-1.17866	-1.22573
H	-3.68916	-0.46273	-0.47275
H	-3.98507	1.82076	0.50853
N	1.69385	2.07241	-0.47636
N	-0.50083	0.58094	-0.69572
Ni	1.40501	0.18859	-1.2421
C	1.39699	-2.71792	-1.6171
C	-0.19108	-2.5451	-3.92096

C	0.97205	-3.88136	-2.25987
H	2.04847	-2.79555	-0.75013
C	0.16898	-3.80398	-3.41088
H	-0.792	-2.48153	-4.82338
H	1.27034	-4.85412	-1.87997
Br	3.51374	0.06622	-2.32863
C	0.23173	-1.38653	-3.26979
H	-0.04384	-0.42126	-3.68802
C	1.00558	-1.46568	-2.10256
C	-0.21353	-0.2164	2.9888
C	-1.38125	-0.56943	3.6708
C	-1.93668	-1.84013	3.49863
C	-1.3257	-2.76838	2.65063
C	-0.15611	-2.429	1.96578
C	0.36883	-1.15522	2.14757
H	0.26059	0.75098	3.11934
H	-1.84758	0.14258	4.34671
H	-2.84218	-2.1121	4.03431
H	-1.75055	-3.76126	2.53098
H	0.34816	-3.14039	1.32048
S	1.9455	-0.68352	1.2244
O	2.78881	-2.0191	1.22302
O	2.48473	0.5699	2.0214
C	-1.93645	3.64062	0.87297
H	-2.89531	4.02149	1.21302
C	-0.80724	4.39683	0.99824

H	-0.85644	5.38788	1.44073
C	-0.28036	-4.99847	-4.0631
N	-0.65756	-5.96649	-4.58789

4-NH_2-Ph-(Byp)Ni(II)-Br-SO_2-Ph



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.380904 (Hartree/Particle)

Thermal correction to Energy= 0.410133

Thermal correction to Enthalpy= 0.411077

Thermal correction to Gibbs Free Energy= 0.316749

Sum of electronic and zero-point Energies= -1432.805356

Sum of electronic and thermal Energies= -1432.776127

Sum of electronic and thermal Enthalpies= -1432.775182

Sum of electronic and thermal Free Energies= -1432.869511

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

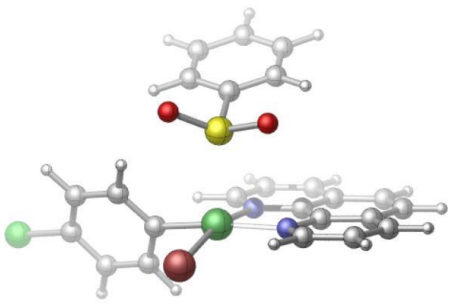
HF=-1822.5608658

C	-0.11044	2.73466	1.11939
C	2.16433	2.82641	0.74325
C	2.23277	4.12616	1.28299
C	1.08137	4.73409	1.74019
C	-0.14571	4.03594	1.6697

C	-1.31131	1.95254	1.05047
C	-2.29437	-0.06911	0.49646
C	-3.5513	0.38249	0.93875
C	-3.67343	1.66041	1.44693
C	-2.53263	2.49015	1.52155
H	3.04376	2.31589	0.36445
H	3.19248	4.6291	1.33361
H	1.10668	5.73667	2.15908
H	-2.16034	-1.06507	0.09119
H	-4.40449	-0.28448	0.87861
H	-4.6326	2.03274	1.79718
N	1.02338	2.15727	0.65466
N	-1.2067	0.69453	0.54045
Ni	0.70896	0.22044	-0.01884
C	0.77575	-2.70271	-0.30592
C	-1.00023	-2.68329	-2.46243
C	0.34981	-3.90295	-0.87848
H	1.50051	-2.72357	0.50441
C	-0.54579	-3.91322	-1.96079
H	-1.67874	-2.66468	-3.31347
H	0.73113	-4.84584	-0.4901
C	-0.57793	-1.48175	-1.8857
H	-0.92644	-0.54623	-2.31842
C	0.27948	-1.48882	-0.78197
C	-0.98316	-0.22797	4.12863
C	-2.14197	-0.6426	4.79084

C	-2.63707	-1.93439	4.59337
C	-1.97275	-2.8205	3.74031
C	-0.81092	-2.41777	3.07651
C	-0.34644	-1.12355	3.27962
H	-0.55379	0.75806	4.27528
H	-2.64945	0.03779	5.47009
H	-3.53661	-2.2551	5.11233
H	-2.35132	-3.82939	3.59908
H	-0.27137	-3.09527	2.42341
S	1.2209	-0.5581	2.38872
O	2.16275	-1.8254	2.45004
O	1.64151	0.74244	3.18755
C	-2.54468	3.82327	2.05475
H	-3.48751	4.23014	2.40959
C	-1.40002	4.56242	2.12814
H	-1.42003	5.56612	2.54385
Br	2.74408	0.0988	-1.26407
N	-1.01171	-5.12361	-2.4969
H	-1.28888	-5.06519	-3.47012
H	-0.38202	-5.90497	-2.35393

4-Cl-Ph-(Byp)Ni(II)-Br-SO_2-Ph



UB3LYP/6-31g(d)-(Br, Ni,Cl-LANL2DZ)-gas

Zero-point correction= 0.373539 (Hartree/Particle)

Thermal correction to Energy= 0.400179

Thermal correction to Enthalpy= 0.401123

Thermal correction to Gibbs Free Energy= 0.309574

Sum of electronic and zero-point Energies= -1282.512082

Sum of electronic and thermal Energies= -1282.485441

Sum of electronic and thermal Enthalpies= -1282.484497

Sum of electronic and thermal Free Energies= -1282.576047

UM06/6-311+g(d,p)-(Br, Ni,Cl -SDD)-SMD(THF)

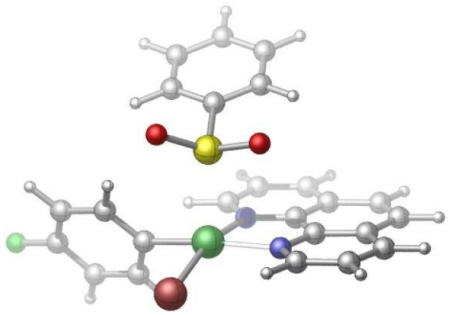
HF=-1672.2635138

C	-1.06063	2.34021	-0.10177
C	1.02963	2.90969	0.69349
C	0.51284	4.06875	1.30589
C	-0.83435	4.35491	1.19944
C	-1.6722	3.47679	0.47595
C	-1.84322	1.40311	-0.85065
C	-1.88411	-0.55631	-2.07757
C	-3.26987	-0.42893	-2.2875
C	-3.94772	0.65182	-1.75926
C	-3.23215	1.61334	-1.01201
H	2.0817	2.64491	0.74687
H	1.18353	4.72205	1.85427
H	-1.25645	5.24289	1.66305
H	-1.32458	-1.39355	-2.47635
H	-3.78563	-1.18857	-2.86542

H	-5.01756	0.77103	-1.90904
N	0.26461	2.06666	0.00797
N	-1.18131	0.33394	-1.37786
Ni	0.75735	0.32941	-0.97333
C	0.84966	-2.51968	-1.41332
C	1.57212	-2.34186	-4.09319
C	0.97769	-3.68108	-2.18241
H	0.57074	-2.61461	-0.36611
C	1.33957	-3.60828	-3.53564
H	1.86149	-2.26274	-5.14042
H	0.79705	-4.65475	-1.72816
C	1.44656	-1.18699	-3.3162
H	1.66257	-0.22613	-3.77843
C	1.07157	-1.25184	-1.96739
C	2.01052	-1.06542	2.97549
C	3.00399	-0.9204	3.9375
C	2.66918	-0.55618	5.2475
C	1.33143	-0.32255	5.59565
C	0.33243	-0.44981	4.63876
C	0.65587	-0.83296	3.31451
H	2.2632	-1.32735	1.95364
H	4.0423	-1.08867	3.66648
H	3.4492	-0.44989	5.99682
H	1.0762	-0.03775	6.61288
H	-0.70724	-0.26692	4.8918
S	-0.62131	-1.02623	2.09745

C	-3.83015	2.77541	-0.41562
H	-4.89804	2.92981	-0.54382
C	-3.08377	3.6685	0.29663
H	-3.54991	4.543	0.74241
Br	3.09002	0.4708	-0.50078
N	1.40979	-4.77203	-4.33054
H	2.04834	-4.68101	-5.11343
H	1.63897	-5.60452	-3.79823

4-F-Ph-(Byp)Ni(II)-Br-SO_2-Ph



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.356106 (Hartree/Particle)

Thermal correction to Energy= 0.384690

Thermal correction to Enthalpy= 0.385634

Thermal correction to Gibbs Free Energy= 0.292001

Sum of electronic and zero-point Energies= -1476.710885

Sum of electronic and thermal Energies= -1476.682301

Sum of electronic and thermal Enthalpies= -1476.681357

Sum of electronic and thermal Free Energies= -1476.774991

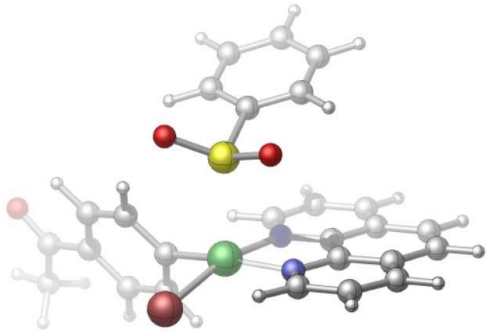
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

HF=-1866.4536196

C	-0.11441	2.70688	1.10865
C	2.16251	2.80899	0.74691
C	2.22039	4.10974	1.28557
C	1.06325	4.71284	1.73454
C	-0.15988	4.0083	1.65733
C	-1.30934	1.91789	1.03311
C	-2.27625	-0.11051	0.47568
C	-3.53822	0.33365	0.91036
C	-3.67198	1.61149	1.4158
C	-2.5368	2.44825	1.49603
H	3.04696	2.30243	0.37482
H	3.17729	4.61739	1.34143
H	1.08111	5.71617	2.15189
H	-2.13638	-1.10567	0.07146
H	-4.38664	-0.33888	0.84546
H	-4.63574	1.97814	1.75914
N	1.02521	2.13384	0.65142
N	-1.19249	0.65935	0.52464
Ni	0.71337	0.21177	-0.03515
C	0.76692	-2.70552	-0.32213
C	-0.96763	-2.66293	-2.5268
C	0.34972	-3.90624	-0.90746
H	1.47271	-2.73154	0.50437
C	-0.51323	-3.86416	-1.99636
H	-1.62111	-2.66858	-3.39385
H	0.70257	-4.86503	-0.53968

C	-0.54966	-1.46678	-1.93072
H	-0.88652	-0.52557	-2.3594
C	0.29253	-1.48655	-0.81288
C	-0.97634	-0.21035	4.13271
C	-2.13687	-0.61446	4.79832
C	-2.62634	-1.91228	4.62805
C	-1.955	-2.81565	3.79901
C	-0.7916	-2.42418	3.13137
C	-0.33311	-1.1242	3.30841
H	-0.55213	0.78032	4.26097
H	-2.64962	0.07924	5.45971
H	-3.52695	-2.22424	5.15025
H	-2.32861	-3.82917	3.68038
H	-0.24376	-3.11471	2.49915
S	1.23462	-0.57767	2.40911
O	2.1592	-1.85746	2.46118
O	1.67656	0.72058	3.19741
C	-2.55997	3.78197	2.02737
H	-3.5074	4.1838	2.37541
C	-1.42011	4.528	2.10714
H	-1.4488	5.53212	2.52117
Br	2.77955	0.07656	-1.21242
F	-0.91612	-5.02454	-2.5634

4-COMe-Ph-(Byp)Ni(II)-Br-SO_2-Ph



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.401750 (Hartree/Particle)

Thermal correction to Energy= 0.433130

Thermal correction to Enthalpy= 0.434074

Thermal correction to Gibbs Free Energy= 0.333389

Sum of electronic and zero-point Energies= -1530.077853

Sum of electronic and thermal Energies= -1530.046473

Sum of electronic and thermal Enthalpies= -1530.045529

Sum of electronic and thermal Free Energies= -1530.146214

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

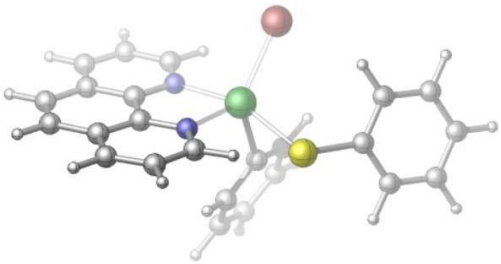
HF=-1919.8172184

C	-0.10716	2.66626	1.10786
C	2.17057	2.76321	0.74903
C	2.22944	4.06547	1.2841
C	1.07268	4.67167	1.73014
C	-0.15157	3.96884	1.65339
C	-1.30263	1.87867	1.03156
C	-2.27013	-0.14982	0.47417
C	-3.5321	0.29597	0.907
C	-3.66592	1.57461	1.41061

C	-2.53033	2.41077	1.49129
H	3.05472	2.25363	0.3803
H	3.18699	4.5719	1.33977
H	1.09179	5.67608	2.14478
H	-2.13186	-1.14542	0.07071
H	-4.38084	-0.37615	0.84205
H	-4.63001	1.94213	1.75201
N	1.03216	2.08971	0.6538
N	-1.18538	0.61916	0.52467
Ni	0.70983	0.17586	-0.0357
C	0.67695	-2.74315	-0.30357
C	-0.9644	-2.64868	-2.56831
C	0.22093	-3.92139	-0.89377
H	1.35503	-2.79125	0.54483
C	-0.60738	-3.89351	-2.02785
H	-1.58447	-2.59087	-3.45869
H	0.51142	-4.88868	-0.49497
C	-0.52353	-1.46407	-1.97272
H	-0.8047	-0.51253	-2.41855
C	0.279	-1.50731	-0.82517
C	-0.97053	-0.19348	4.15833
C	-2.13386	-0.57493	4.83231
C	-2.63464	-1.87152	4.68719
C	-1.9722	-2.7966	3.87521
C	-0.80601	-2.42855	3.19914
C	-0.33642	-1.12948	3.35189

H	-0.53801	0.79571	4.2684
H	-2.63964	0.13567	5.48093
H	-3.53728	-2.16559	5.21616
H	-2.35417	-3.80902	3.77637
H	-0.26452	-3.13655	2.58102
S	1.23457	-0.61534	2.44016
O	2.13702	-1.91009	2.49348
O	1.70253	0.68339	3.21155
C	-2.55265	3.74561	2.02005
H	-3.50014	4.14925	2.36578
C	-1.41209	4.49072	2.10008
H	-1.44061	5.49576	2.51186
Br	2.78966	0.00305	-1.17568
C	-1.06192	-5.19291	-2.61215
O	-0.78248	-6.25611	-2.07629
C	-1.88408	-5.1744	-3.89367
H	-2.82085	-4.62073	-3.75586
H	-2.11313	-6.20361	-4.17563
H	-1.33426	-4.6877	-4.70809

Figure S1; C'-TS_{RE}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -111.61 cm^{-1}

Zero-point correction= 0.356495 (Hartree/Particle)

Thermal correction to Energy= 0.381654

Thermal correction to Enthalpy= 0.382599

Thermal correction to Gibbs Free Energy= 0.297510

Sum of electronic and zero-point Energies= -1227.193206

Sum of electronic and thermal Energies= -1227.168046

Sum of electronic and thermal Enthalpies= -1227.167102

Sum of electronic and thermal Free Energies= -1227.252191

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

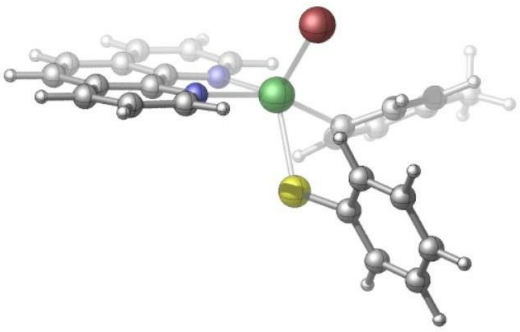
HF=-1616.9378483

C	-1.41706	2.1822	1.22094
C	-0.16181	1.2981	2.9494
C	-0.98385	1.91109	3.91396
C	-2.05822	2.67257	3.4971
C	-2.30397	2.83196	2.11511
C	-1.59863	2.33592	-0.20076
C	-0.82033	1.87433	-2.3279
C	-1.8618	2.62162	-2.9114
C	-2.78664	3.24342	-2.09542
C	-2.67081	3.11999	-0.69268
H	0.68872	0.68865	3.23877
H	-0.76344	1.77597	4.96762
H	-2.71326	3.15543	4.21774
H	-0.05015	1.39891	-2.92654

H	-1.91818	2.70545	-3.99159
H	-3.59685	3.8327	-2.51711
N	-0.37498	1.42059	1.64297
N	-0.70185	1.72989	-1.01414
Ni	0.77818	0.60508	-0.01607
C	0.49078	-1.81609	-1.53565
C	-2.05909	-2.42308	-0.54968
C	-0.35948	-2.66674	-2.25122
H	1.48653	-1.59383	-1.90674
C	-1.63294	-2.96966	-1.76462
H	-3.04202	-2.67018	-0.15468
H	-0.01529	-3.09887	-3.18791
H	-2.28324	-3.64215	-2.31772
Br	2.58855	1.5226	-1.51479
C	-1.22121	-1.57071	0.17265
H	-1.54501	-1.17136	1.12924
C	0.0348	-1.23768	-0.34732
C	2.98121	-3.45718	0.71267
C	4.00967	-4.24592	0.19795
C	5.09612	-3.64804	-0.44675
C	5.14999	-2.25838	-0.57426
C	4.12863	-1.45842	-0.05734
C	3.04313	-2.06157	0.58996
H	2.13204	-3.91336	1.21208
H	3.96043	-5.32725	0.2977
H	5.8961	-4.26402	-0.84939

H	5.98949	-1.78854	-1.07982
H	4.15542	-0.38091	-0.17233
C	-3.38664	3.61271	1.58532
H	-4.06296	4.10012	2.28226
C	-3.5636	3.74817	0.23996
H	-4.38431	4.34448	-0.1496
S	1.72785	-1.06797	1.37005

Figure S2; C'-TS_{RE}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -189.48 cm^{-1}

Zero-point correction= 0.383786 (Hartree/Particle)

Thermal correction to Energy= 0.411000

Thermal correction to Enthalpy= 0.411944

Thermal correction to Gibbs Free Energy= 0.320467

Sum of electronic and zero-point Energies= -1266.471751

Sum of electronic and thermal Energies= -1266.444538

Sum of electronic and thermal Enthalpies= -1266.443593

Sum of electronic and thermal Free Energies= -1266.535070

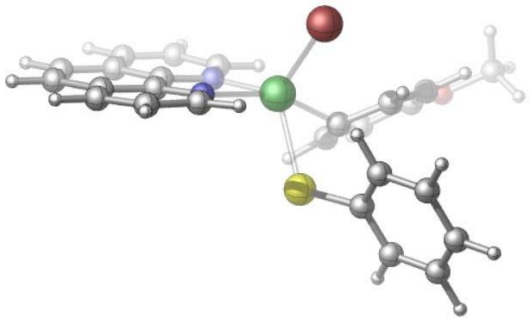
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

HF=-1656.2199237

C	-0.99538	2.77434	1.45767
C	1.21303	2.63211	2.10277
C	1.02876	3.61055	3.09961
C	-0.21848	4.18293	3.25728
C	-1.27963	3.77914	2.41657
C	-2.02777	2.33363	0.55179
C	-2.63	1.01834	-1.24993
C	-3.91523	1.58889	-1.29391
C	-4.25967	2.54131	-0.35585
C	-3.30525	2.94778	0.60205
H	2.18382	2.1804	1.92537
H	1.86672	3.90745	3.72177
H	-0.39189	4.94711	4.01064
H	-2.33469	0.25304	-1.95975
H	-4.61634	1.26778	-2.05711
H	-5.24927	2.99106	-0.35196
N	0.22936	2.22252	1.31522
N	-1.71733	1.35806	-0.34417
Ni	0.31975	0.64792	-0.22457
C	1.22146	-1.59997	-1.89469
C	-1.32721	-2.59108	-2.45289
C	0.99044	-2.3664	-3.03732
H	2.21703	-1.22351	-1.69252
C	-0.28287	-2.8659	-3.34669
H	-2.31727	-3.00305	-2.64104

H	1.82397	-2.57498	-3.70517
Br	2.31129	1.72986	-1.32006
C	-1.1119	-1.83019	-1.30258
H	-1.92109	-1.69238	-0.59123
C	0.15245	-1.27854	-1.04819
C	2.25275	-3.29908	1.67949
C	3.51228	-3.88357	1.8149
C	4.66442	-3.14362	1.53857
C	4.55011	-1.81302	1.13073
C	3.29488	-1.21284	1.01057
C	2.14268	-1.95881	1.28515
H	1.35459	-3.8753	1.87973
H	3.59096	-4.92207	2.12618
H	5.64449	-3.60296	1.63604
H	5.44041	-1.23209	0.90454
H	3.21253	-0.18328	0.67626
C	-2.59781	4.3442	2.47133
H	-2.80517	5.10842	3.21567
C	-3.56641	3.95053	1.59657
H	-4.55632	4.39736	1.6314
S	0.46168	-1.23596	1.22443
C	-0.51736	-3.67406	-4.601
H	0.32456	-4.34337	-4.81118
H	-1.42305	-4.28505	-4.52202
H	-0.63704	-3.02365	-5.47844

Figure S3; C'-TS_{RE}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -196.68 cm^{-1}

Zero-point correction= 0.389137 (Hartree/Particle)

Thermal correction to Energy= 0.417072

Thermal correction to Enthalpy= 0.418017

Thermal correction to Gibbs Free Energy= 0.325643

Sum of electronic and zero-point Energies= -1341.670456

Sum of electronic and thermal Energies= -1341.642521

Sum of electronic and thermal Enthalpies= -1341.641576

Sum of electronic and thermal Free Energies= -1341.733950

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

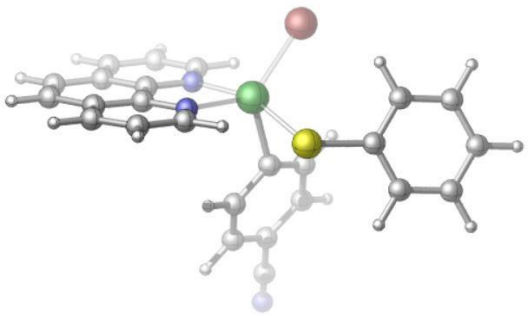
HF=-1731.4191365

C	-1.0918	2.88342	1.59067
C	1.08721	2.70574	2.3225
C	0.87654	3.68177	3.3165
C	-0.36768	4.27164	3.42734
C	-1.4001	3.88727	2.54287
C	-2.09311	2.46084	0.64257

C	-2.64036	1.15827	-1.18524
C	-3.91671	1.74336	-1.27586
C	-4.28576	2.69746	-0.3488
C	-3.36414	3.08999	0.64642
H	2.05751	2.24141	2.17858
H	1.69305	3.96357	3.97324
H	-0.56009	5.03461	4.17733
H	-2.32782	0.39167	-1.88624
H	-4.5921	1.43183	-2.06577
H	-5.26965	3.15847	-0.38134
N	0.1298	2.31471	1.4939
N	-1.75879	1.48552	-0.24471
Ni	0.26944	0.75001	-0.03904
C	1.17688	-1.46876	-1.72129
C	-1.36511	-2.45485	-2.32951
C	0.98135	-2.21992	-2.88476
H	2.16894	-1.094	-1.49858
C	-0.29243	-2.707	-3.2013
H	-2.33757	-2.87777	-2.56527
H	1.83005	-2.40714	-3.53312
Br	2.38355	1.77789	-0.9728
C	-1.16336	-1.71151	-1.1732
H	-1.9868	-1.57788	-0.47767
C	0.09737	-1.15453	-0.8893
C	2.03343	-3.32064	1.79479
C	3.26087	-3.96833	1.93824

C	4.45278	-3.26871	1.73479
C	4.41088	-1.9156	1.39198
C	3.18797	-1.2536	1.26394
C	1.99603	-1.95908	1.46554
H	1.10424	-3.86348	1.93855
H	3.28379	-5.02333	2.19919
H	5.40801	-3.77648	1.83906
H	5.33311	-1.36563	1.22363
H	3.15959	-0.20627	0.97998
C	-2.71189	4.4697	2.54814
H	-2.93838	5.23347	3.28736
C	-3.65077	4.09225	1.6345
H	-4.63544	4.55186	1.63296
S	0.35466	-1.15143	1.39538
O	-0.59159	-3.44726	-4.30809
C	0.45696	-3.75308	-5.21342
H	0.00075	-4.34018	-6.01284
H	0.90098	-2.8436	-5.63925
H	1.2457	-4.34666	-4.73256

Figure S4; C'-TS_{RE}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -83.81 cm^{-1}

Zero-point correction= 0.355230 (Hartree/Particle)

Thermal correction to Energy= 0.382163

Thermal correction to Enthalpy= 0.383107

Thermal correction to Gibbs Free Energy= 0.293748

Sum of electronic and zero-point Energies= -1319.437987

Sum of electronic and thermal Energies= -1319.411054

Sum of electronic and thermal Enthalpies= -1319.410110

Sum of electronic and thermal Free Energies= -1319.499469

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

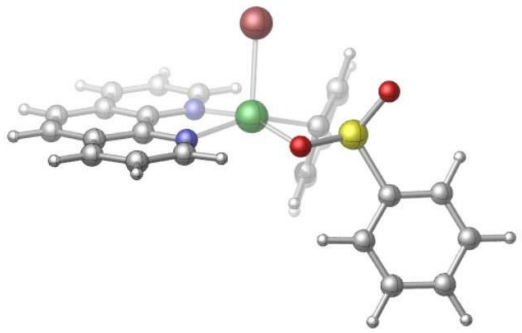
HF=-1709.1532681

C	-1.44089	2.22654	1.28529
C	-0.25189	1.31448	3.04677
C	-1.1327	1.88126	3.98732
C	-2.20161	2.63351	3.54076
C	-2.38372	2.83049	2.15362
C	-1.5564	2.41992	-0.13801
C	-0.66544	2.04	-2.23823
C	-1.69346	2.78341	-2.84944
C	-2.67028	3.36028	-2.06164
C	-2.61985	3.19664	-0.65893
H	0.59606	0.71364	3.36051
H	-0.96087	1.71828	5.04598
H	-2.90107	3.08047	4.24244
H	0.14346	1.59989	-2.81212

H	-1.69955	2.89842	-3.92809
H	-3.47231	3.94439	-2.50526
N	-0.40413	1.47324	1.73551
N	-0.60836	1.85714	-0.92482
Ni	0.83893	0.73491	0.10914
C	0.64163	-1.65742	-1.4873
C	-1.91787	-2.35378	-0.57925
C	-0.14124	-2.53917	-2.23036
H	1.63939	-1.39861	-1.82779
C	-1.42832	-2.89037	-1.78566
H	-2.90443	-2.64017	-0.2267
H	0.24164	-2.96283	-3.15405
Br	2.69554	1.67608	-1.29654
C	-1.13614	-1.47147	0.15886
H	-1.51288	-1.08198	1.09957
C	0.12749	-1.09022	-0.31398
C	3.05235	-3.30825	0.77924
C	4.10352	-4.07462	0.27737
C	5.22161	-3.44957	-0.28211
C	5.28537	-2.05551	-0.33754
C	4.24092	-1.27777	0.16613
C	3.12315	-1.90817	0.72776
H	2.17998	-3.78529	1.21495
H	4.04784	-5.15914	0.32095
H	6.03928	-4.04832	-0.67473
H	6.15029	-1.56545	-0.77631

H	4.27584	-0.19635	0.10639
C	-3.45609	3.60497	1.59464
H	-4.17609	4.05677	2.27136
C	-3.57036	3.77778	0.24674
H	-4.38415	4.36842	-0.16502
S	1.77536	-0.9488	1.49182
C	-2.23435	-3.79714	-2.54602
N	-2.89516	-4.53052	-3.16321

Figure S1; C-TS_{RE}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -196.30 cm^{-1}

Zero-point correction= 0.362262 (Hartree/Particle)

Thermal correction to Energy= 0.389632

Thermal correction to Enthalpy= 0.390576

Thermal correction to Gibbs Free Energy= 0.300525

Sum of electronic and zero-point Energies= -1377.459815

Sum of electronic and thermal Energies= -1377.432445

Sum of electronic and thermal Enthalpies= -1377.431501

Sum of electronic and thermal Free Energies= -1377.521552

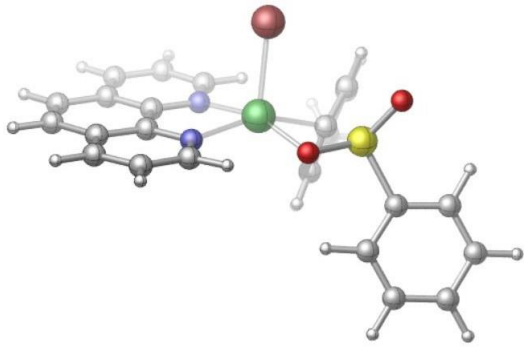
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

HF=-1767.1879182

C	-1.23922	2.61631	1.21607
C	-0.06404	1.63454	2.9508
C	-0.69077	2.46834	3.8965
C	-1.62271	3.39481	3.46647
C	-1.92226	3.49701	2.08928
C	-1.47252	2.68527	-0.20491
C	-0.93606	1.9113	-2.31458
C	-1.83513	2.81228	-2.91593
C	-2.56541	3.67158	-2.11767
C	-2.39367	3.632	-0.71624
H	0.68075	0.89712	3.23508
H	-0.43438	2.37555	4.94671
H	-2.12248	4.05165	4.1739
H	-0.33425	1.23426	-2.91098
H	-1.93644	2.8253	-3.9961
H	-3.26246	4.38265	-2.5537
N	-0.34012	1.70358	1.65375
N	-0.76491	1.84326	-0.99969
Ni	0.71587	0.73382	0.08228
C	1.88646	-0.69809	-2.49396
C	-0.69614	-1.81552	-2.45585
C	1.2306	-0.99605	-3.68039
H	2.88132	-0.26478	-2.49148
C	-0.06507	-1.54905	-3.67132

H	-1.68614	-2.26517	-2.4398
H	1.72688	-0.79707	-4.62729
C	-0.04817	-1.53774	-1.24676
H	-0.52166	-1.79716	-0.30288
C	1.21328	-0.8995	-1.26835
C	0.97059	-3.49667	1.7266
C	0.7299	-4.8155	2.11901
C	1.58275	-5.83937	1.69826
C	2.6867	-5.55375	0.88963
C	2.94014	-4.24059	0.48959
C	2.07159	-3.24298	0.91716
H	0.34415	-2.67687	2.06181
H	-0.1181	-5.04047	2.76002
H	1.39016	-6.86318	2.0068
H	3.35488	-6.35076	0.57591
H	3.80234	-3.98547	-0.11848
C	-2.85972	4.43615	1.53992
H	-3.38269	5.10503	2.21822
C	-3.08631	4.49869	0.19642
H	-3.79256	5.21801	-0.2095
S	2.41327	-1.49407	0.33532
O	1.61989	-0.58017	1.41335
O	3.95557	-1.37046	0.18033
Br	2.55468	2.33598	-0.49574
H	-0.5584	-1.79404	-4.60761

Figure S2; C-TS_{RE}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -195.67 cm^{-1}

Zero-point correction= 0.389773 (Hartree/Particle)

Thermal correction to Energy= 0.419035

Thermal correction to Enthalpy= 0.419979

Thermal correction to Gibbs Free Energy= 0.325259

Sum of electronic and zero-point Energies= -1416.749596

Sum of electronic and thermal Energies= -1416.720334

Sum of electronic and thermal Enthalpies= -1416.719390

Sum of electronic and thermal Free Energies= -1416.814110

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

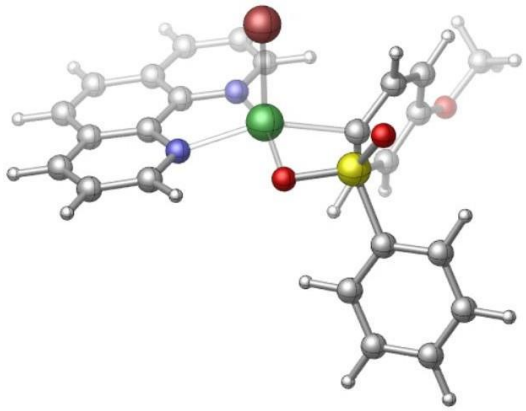
HF=-1806.4830318

C	-1.18475	2.73587	1.52368
C	-0.02029	1.75116	3.26388
C	-0.6544	2.58198	4.20724
C	-1.58449	3.50855	3.77323
C	-1.8747	3.61375	2.3943
C	-1.40857	2.80803	0.10139

C	-0.85567	2.04003	-2.00603
C	-1.75094	2.94173	-2.61182
C	-2.48825	3.79816	-1.81673
C	-2.32689	3.75524	-0.41422
H	0.72318	1.01365	3.55136
H	-0.40513	2.48682	5.25896
H	-2.08983	4.16304	4.47888
H	-0.24726	1.36536	-2.59867
H	-1.84401	2.95815	-3.69271
H	-3.18269	4.5097	-2.25619
N	-0.2875	1.82301	1.96503
N	-0.69465	1.96857	-0.69019
Ni	0.77896	0.85509	0.39977
C	1.948	-0.58487	-2.17165
C	-0.62442	-1.70082	-2.14585
C	1.29809	-0.89055	-3.35644
H	2.94169	-0.14865	-2.17215
C	-0.0016	-1.45084	-3.37221
H	-1.61571	-2.14957	-2.12892
H	1.80178	-0.6927	-4.301
C	0.01511	-1.41741	-0.93306
H	-0.4693	-1.67331	0.00632
C	1.27352	-0.77768	-0.94473
C	1.00801	-3.37073	2.04944
C	0.75832	-4.68792	2.44178
C	1.60977	-5.71623	2.02906

C	2.7212	-5.43654	1.22866
C	2.98347	-4.12502	0.82885
C	2.11623	-3.12279	1.24813
H	0.38271	-2.54765	2.37876
H	-0.09561	-4.90821	3.07654
H	1.41026	-6.73875	2.33754
H	3.38837	-6.23691	0.92135
H	3.85158	-3.87441	0.2273
C	-2.80939	4.55321	1.84065
H	-3.33776	5.21987	2.51697
C	-3.02677	4.61896	0.49577
H	-3.73091	5.33864	0.08681
S	2.46988	-1.37598	0.66568
O	1.67606	-0.45749	1.7395
O	4.01445	-1.2614	0.5218
Br	2.62341	2.455	-0.17327
C	-0.66628	-1.80723	-4.6804
H	-0.66556	-0.96038	-5.37841
H	-1.70552	-2.11705	-4.52993
H	-0.14519	-2.63248	-5.18407

Figure S3; C-TS_{RE}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -226.45 cm^{-1}

Zero-point correction= 0.394855 (Hartree/Particle)

Thermal correction to Energy= 0.424989

Thermal correction to Enthalpy= 0.425934

Thermal correction to Gibbs Free Energy= 0.328917

Sum of electronic and zero-point Energies= -1491.947544

Sum of electronic and thermal Energies= -1491.917409

Sum of electronic and thermal Enthalpies= -1491.916465

Sum of electronic and thermal Free Energies= -1492.013482

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

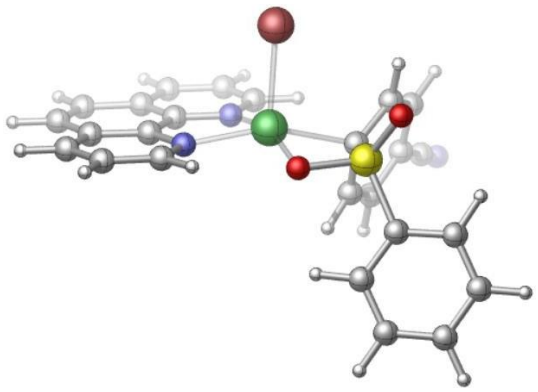
HF=-1881.6809623

C	-1.1961	2.73176	1.72954
C	0.05829	1.78731	3.42882
C	-0.5568	2.61047	4.39096
C	-1.52556	3.51154	3.98826
C	-1.87239	3.59913	2.6214
C	-1.47807	2.78773	0.31708

C	-0.99388	2.01668	-1.80581
C	-1.93857	2.88734	-2.3804
C	-2.66377	3.73198	-1.56169
C	-2.44197	3.70609	-0.16725
H	0.82826	1.06816	3.69208
H	-0.26417	2.52884	5.43263
H	-2.01856	4.15885	4.7091
H	-0.39398	1.35342	-2.41945
H	-2.07921	2.88941	-3.45624
H	-3.3952	4.42064	-1.97689
N	-0.26106	1.84259	2.14063
N	-0.7742	1.96124	-0.49745
Ni	0.77334	0.89778	0.53218
C	1.9061	-0.55777	-2.04293
C	-0.65038	-1.71217	-2.05052
C	1.28443	-0.85406	-3.24968
H	2.89588	-0.11324	-2.02886
C	-0.00403	-1.42848	-3.26264
H	-1.63102	-2.17794	-2.08041
H	1.80494	-0.63603	-4.17588
C	-0.0257	-1.43011	-0.83878
H	-0.51863	-1.70049	0.09188
C	1.22403	-0.76519	-0.82622
C	0.94404	-3.28273	2.22017
C	0.65958	-4.58376	2.64145
C	1.46764	-5.64697	2.22959

C	2.56965	-5.41857	1.40045
C	2.86599	-4.12379	0.97083
C	2.04215	-3.0861	1.39097
H	0.35273	-2.43387	2.54728
H	-0.18724	-4.76434	3.29789
H	1.24128	-6.65669	2.56079
H	3.20303	-6.24611	1.09354
H	3.72765	-3.91218	0.34549
C	-2.85219	4.51046	2.09957
H	-3.36955	5.16912	2.79208
C	-3.12609	4.55927	0.76437
H	-3.8649	5.25709	0.37935
S	2.4363	-1.36282	0.76697
O	1.72677	-0.39805	1.85416
O	3.97652	-1.30843	0.5539
Br	2.57411	2.50773	-0.15641
O	-0.68965	-1.76233	-4.39484
C	-0.0575	-1.56547	-5.65005
H	-0.76729	-1.91807	-6.40063
H	0.87205	-2.144	-5.72949
H	0.16289	-0.50485	-5.83086

Figure S4; C-TS_{RE}



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas

Imaginary frequency = -122.19 cm^{-1}

Zero-point correction= 0.361111 (Hartree/Particle)

Thermal correction to Energy= 0.390184

Thermal correction to Enthalpy= 0.391128

Thermal correction to Gibbs Free Energy= 0.297094

Sum of electronic and zero-point Energies= -1469.705045

Sum of electronic and thermal Energies= -1469.675973

Sum of electronic and thermal Enthalpies= -1469.675028

Sum of electronic and thermal Free Energies= -1469.769062

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

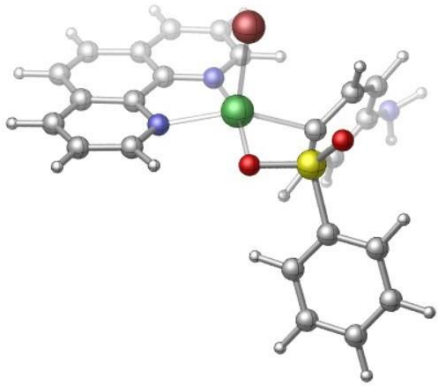
HF=-1859.4045318

C	-1.19302	2.69803	1.37443
C	0.04787	1.79097	3.10494
C	-0.5545	2.65552	4.03913
C	-1.50644	3.55898	3.6051
C	-1.85316	3.60691	2.23567
C	-1.47586	2.7092	-0.03906

C	-1.01074	1.85474	-2.13533
C	-1.9344	2.72784	-2.74012
C	-2.64078	3.61381	-1.95021
C	-2.41971	3.63014	-0.55482
H	0.8074	1.07025	3.39281
H	-0.26308	2.60436	5.08293
H	-1.98704	4.23936	4.3034
H	-0.42801	1.15869	-2.72813
H	-2.07388	2.69568	-3.81543
H	-3.35753	4.30325	-2.38874
N	-0.27146	1.81059	1.81674
N	-0.79316	1.83831	-0.82546
Ni	0.71643	0.77719	0.24322
C	1.96552	-0.61669	-2.31781
C	-0.57614	-1.82926	-2.4117
C	1.38603	-0.90685	-3.53658
H	2.94489	-0.15335	-2.26154
C	0.09944	-1.50597	-3.60609
H	-1.54889	-2.30978	-2.46036
H	1.91198	-0.67222	-4.45726
C	0.00396	-1.55421	-1.18089
H	-0.50977	-1.84731	-0.26877
C	1.24214	-0.85504	-1.1183
C	0.94518	-3.46855	1.83957
C	0.69975	-4.79072	2.21707
C	1.54211	-5.81442	1.77518

C	2.64072	-5.52663	0.96017
C	2.90028	-4.2105	0.5742
C	2.04125	-3.21413	1.02346
H	0.32584	-2.64975	2.18987
H	-0.14418	-5.01832	2.8622
H	1.34489	-6.84072	2.07177
H	3.29968	-6.32411	0.62935
H	3.7581	-3.95469	-0.03955
C	-2.81513	4.51874	1.68305
H	-3.31988	5.2101	2.35235
C	-3.08676	4.52811	0.34649
H	-3.81112	5.22692	-0.06294
S	2.38919	-1.46341	0.46247
O	1.60276	-0.54903	1.54765
O	3.92631	-1.33186	0.29007
Br	2.52251	2.39731	-0.35537
C	-0.49727	-1.79499	-4.86911
N	-0.99226	-2.02248	-5.89972

TS_{RE}-4-NH_2-(Byp)Ni(II)-Br-SO_2-Ph



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Imaginary frequency = -232.86 cm^{-1}

Zero-point correction= 0.378752 (Hartree/Particle)

Thermal correction to Energy= 0.407721

Thermal correction to Enthalpy= 0.408665

Thermal correction to Gibbs Free Energy= 0.314841

Sum of electronic and zero-point Energies= -1432.796179

Sum of electronic and thermal Energies= -1432.767211

Sum of electronic and thermal Enthalpies= -1432.766266

Sum of electronic and thermal Free Energies= -1432.860090

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

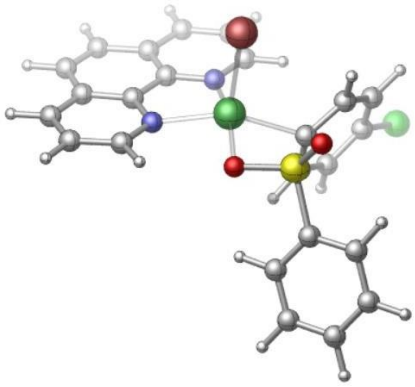
HF=-1822.5360531

C	-1.20591	2.69429	1.42309
C	0.07651	1.79621	3.12673
C	-0.54096	2.6275	4.08012
C	-1.5259	3.50818	3.6712
C	-1.88619	3.56741	2.3064
C	-1.50083	2.72244	0.01262
C	-1.02433	1.92134	-2.10094
C	-1.9876	2.7675	-2.68158
C	-2.71766	3.61594	-1.87104
C	-2.48265	3.61794	-0.47847
H	0.85887	1.09239	3.39477
H	-0.23757	2.56798	5.12024
H	-2.02128	4.161	4.38545
H	-0.42089	1.2568	-2.70958

H	-2.13752	2.74752	-3.75597
H	-3.46287	4.28663	-2.29125
N	-0.25539	1.82459	1.84073
N	-0.79157	1.89261	-0.79376
Ni	0.7775	0.86494	0.24623
C	1.91102	-0.5828	-2.31938
C	-0.61559	-1.80309	-2.27761
C	1.27541	-0.90633	-3.50411
H	2.88998	-0.11453	-2.32582
C	-0.00421	-1.51591	-3.50801
H	-1.58837	-2.29076	-2.25999
H	1.76038	-0.68292	-4.45257
C	0.02238	-1.49002	-1.07626
H	-0.44835	-1.76767	-0.13626
C	1.25001	-0.79002	-1.0862
C	1.06527	-3.29622	1.98472
C	0.81982	-4.59955	2.42329
C	1.65674	-5.6442	2.02164
C	2.7489	-5.39421	1.18564
C	3.00596	-4.09672	0.73905
C	2.15408	-3.07769	1.14883
H	0.45158	-2.46039	2.30423
H	-0.01872	-4.79617	3.08582
H	1.46123	-6.65576	2.36673
H	3.4055	-6.20673	0.88731
H	3.85966	-3.86769	0.10884

C	-2.88362	4.45559	1.77806
H	-3.40394	5.11885	2.46398
C	-3.17053	4.47714	0.44485
H	-3.92285	5.1576	0.05484
S	2.49772	-1.35009	0.5029
O	1.76442	-0.39645	1.58497
O	4.03698	-1.25781	0.28976
Br	2.54891	2.5082	-0.45321
N	-0.65088	-1.78352	-4.71708
H	-0.0348	-1.91572	-5.51027
H	-1.35785	-2.50765	-4.67369

TS_{RE}-4-Cl-Ph-(Byp)Ni(II)-Br-SO_2-Ph



UB3LYP/6-31g(d)-(Br, Ni, Cl-LANL2DZ)-gas

Imaginary frequency = -174.66 cm^{-1}

Zero-point correction= 0.352460 (Hartree/Particle)

Thermal correction to Energy= 0.381145

Thermal correction to Enthalpy= 0.382089

Thermal correction to Gibbs Free Energy= 0.288349

Sum of electronic and zero-point Energies= -1391.812464

Sum of electronic and thermal Energies= -1391.783779

Sum of electronic and thermal Enthalpies= -1391.782835

Sum of electronic and thermal Free Energies= -1391.876575

UM06/6-311+g(d,p)-(Br, Ni, Cl -SDD)-SMD(THF)

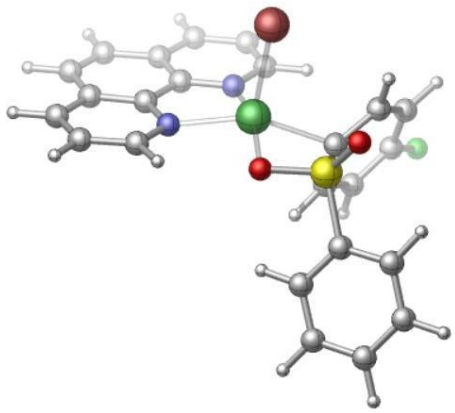
HF=-2226.7415173

C	-1.22223	2.63253	1.2194
C	-0.01614	1.68941	2.95477
C	-0.64521	2.52625	3.89617
C	-1.59418	3.434	3.46369
C	-1.90905	3.51441	2.08838
C	-1.47112	2.67995	-0.19984
C	-0.94549	1.88868	-2.30562
C	-1.86385	2.76823	-2.90907
C	-2.59835	3.62615	-2.11339
C	-2.4108	3.60693	-0.7134
H	0.74107	0.96575	3.24151
H	-0.37727	2.45039	4.94482
H	-2.09616	4.09271	4.16776
H	-0.33848	1.21612	-2.90151
H	-1.9769	2.76439	-3.98802
H	-3.31098	4.32079	-2.55057
N	-0.30563	1.73847	1.65973
N	-0.7602	1.8377	-0.99181
Ni	0.73725	0.75452	0.08871
C	1.89667	-0.71147	-2.47201

C	-0.68351	-1.84655	-2.4295
C	1.25445	-1.01648	-3.66235
H	2.88956	-0.27379	-2.47413
C	-0.03469	-1.57094	-3.62749
H	-1.6688	-2.30094	-2.4303
H	1.73782	-0.82586	-4.61497
C	-0.03432	-1.55417	-1.22622
H	-0.51436	-1.81138	-0.28545
C	1.22342	-0.90363	-1.24165
C	0.98593	-3.46384	1.76863
C	0.73998	-4.77889	2.17013
C	1.57641	-5.81203	1.7391
C	2.66925	-5.54009	0.91094
C	2.92831	-4.23107	0.50115
C	2.07584	-3.22449	0.93991
H	0.37232	-2.63724	2.11082
H	-0.09924	-4.99362	2.82588
H	1.37942	-6.83279	2.05462
H	3.3243	-6.3445	0.58887
H	3.78211	-3.98682	-0.12295
C	-2.86541	4.4331	1.53713
H	-3.39106	5.10291	2.21235
C	-3.10642	4.47529	0.19537
H	-3.82707	5.17905	-0.21237
S	2.42203	-1.48259	0.34533
O	1.6528	-0.55192	1.42334

O	3.95957	-1.36773	0.15361
Br	2.57362	2.33097	-0.54838
Cl	-0.85519	-1.96587	-5.18109

TS_{RE}-4-Cl-Ph-(Byp)Ni(II)-Br-SO_2-Ph



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Imaginary frequency = -200.31 cm^{-1}

Zero-point correction= 0.353989 (Hartree/Particle)

Thermal correction to Energy= 0.382266

Thermal correction to Enthalpy= 0.383210

Thermal correction to Gibbs Free Energy= 0.290700

Sum of electronic and zero-point Energies= -1476.699666

Sum of electronic and thermal Energies= -1476.671389

Sum of electronic and thermal Enthalpies= -1476.670445

Sum of electronic and thermal Free Energies= -1476.762955

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

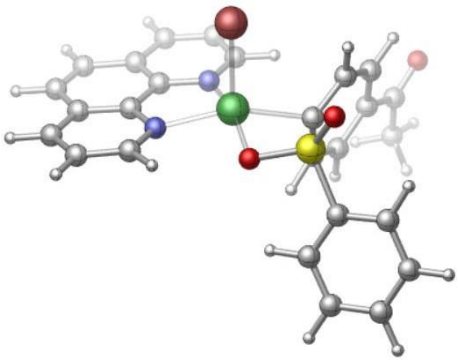
HF=-1866.4279038

C	-1.22519	2.62183	1.20954
C	-0.02115	1.66399	2.938

C	-0.65025	2.49369	3.88552
C	-1.59874	3.40542	3.45995
C	-1.91224	3.49704	2.08516
C	-1.47237	2.68146	-0.20941
C	-0.94337	1.90843	-2.32072
C	-1.8604	2.79331	-2.91815
C	-2.59611	3.64483	-2.11638
C	-2.41101	3.61334	-0.71647
H	0.73542	0.93748	3.21915
H	-0.38302	2.40922	4.93373
H	-2.10101	4.05857	4.16899
H	-0.33497	1.24031	-2.9204
H	-1.97124	2.80017	-3.9974
H	-3.30737	4.34385	-2.54885
N	-0.30965	1.72315	1.64291
N	-0.76013	1.84599	-1.00718
Ni	0.74017	0.75525	0.06665
C	1.88392	-0.71983	-2.49775
C	-0.70141	-1.84515	-2.43796
C	1.2344	-1.02838	-3.68329
H	2.87838	-0.28593	-2.50369
C	-0.05416	-1.57987	-3.63743
H	-1.68779	-2.29847	-2.44669
H	1.7032	-0.85083	-4.64647
C	-0.04494	-1.54956	-1.23829
H	-0.51899	-1.79974	-0.29268

C	1.21461	-0.9064	-1.26532
C	0.98324	-3.4547	1.76136
C	0.73409	-4.76678	2.17063
C	1.5714	-5.80367	1.75043
C	2.66814	-5.53808	0.92534
C	2.92998	-4.23199	0.50794
C	2.07689	-3.22131	0.93588
H	0.36922	-2.62515	2.0957
H	-0.10814	-4.97627	2.82429
H	1.37223	-6.8221	2.07218
H	3.32422	-6.34517	0.61201
H	3.78695	-3.99223	-0.1136
C	-2.86767	4.42068	1.54042
H	-3.39368	5.08517	2.22065
C	-3.10737	4.47426	0.19883
H	-3.82721	5.18187	-0.20369
S	2.42713	-1.48295	0.33018
O	1.66359	-0.54645	1.40632
O	3.96644	-1.37691	0.14008
Br	2.57741	2.33216	-0.57984
F	-0.67144	-1.88357	-4.80014

TS_{RE}-4-COMe-Ph-(Byp)Ni(II)-Br-SO_2-Ph



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Imaginary frequency = -134.03 cm^{-1}

Zero-point correction= 0.400016 (Hartree/Particle)

Thermal correction to Energy= 0.430867

Thermal correction to Enthalpy= 0.431811

Thermal correction to Gibbs Free Energy= 0.333627

Sum of electronic and zero-point Energies= -1530.069383

Sum of electronic and thermal Energies= -1530.038532

Sum of electronic and thermal Enthalpies= -1530.037588

Sum of electronic and thermal Free Energies= -1530.135772

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)

HF=-1919.795899

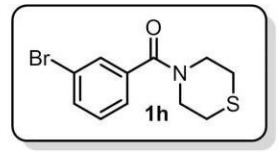
C	-1.22538	2.66058	1.24621
C	-0.01628	1.72234	2.98252
C	-0.61957	2.58543	3.91759
C	-1.55515	3.50461	3.48086
C	-1.88436	3.56987	2.10784
C	-1.48927	2.68968	-0.17071
C	-1.002	1.85165	-2.26904

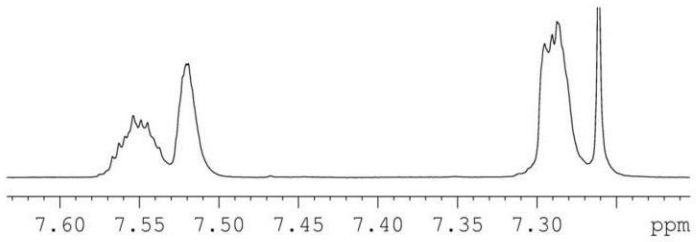
C	-1.90238	2.7465	-2.87786
C	-2.60963	3.63299	-2.08914
C	-2.4118	3.62984	-0.69015
H	0.73198	0.9904	3.27172
H	-0.34114	2.52127	4.96423
H	-2.03548	4.18457	4.17978
H	-0.41742	1.15453	-2.85935
H	-2.02174	2.73211	-3.95605
H	-3.30808	4.33884	-2.53124
N	-0.32025	1.75769	1.69104
N	-0.80744	1.81772	-0.95601
Ni	0.67638	0.72711	0.12178
C	1.86965	-0.65154	-2.46882
C	-0.65912	-1.88307	-2.48914
C	1.25397	-0.96083	-3.66516
H	2.84586	-0.17832	-2.44413
C	-0.02503	-1.57501	-3.70664
H	-1.62904	-2.37243	-2.48398
H	1.73922	-0.73694	-4.61019
C	-0.05305	-1.58896	-1.27181
H	-0.54116	-1.8742	-0.34291
C	1.18055	-0.88478	-1.24967
C	0.95573	-3.52602	1.71548
C	0.73436	-4.85087	2.0987
C	1.59649	-5.86065	1.66297
C	2.69087	-5.55548	0.84856

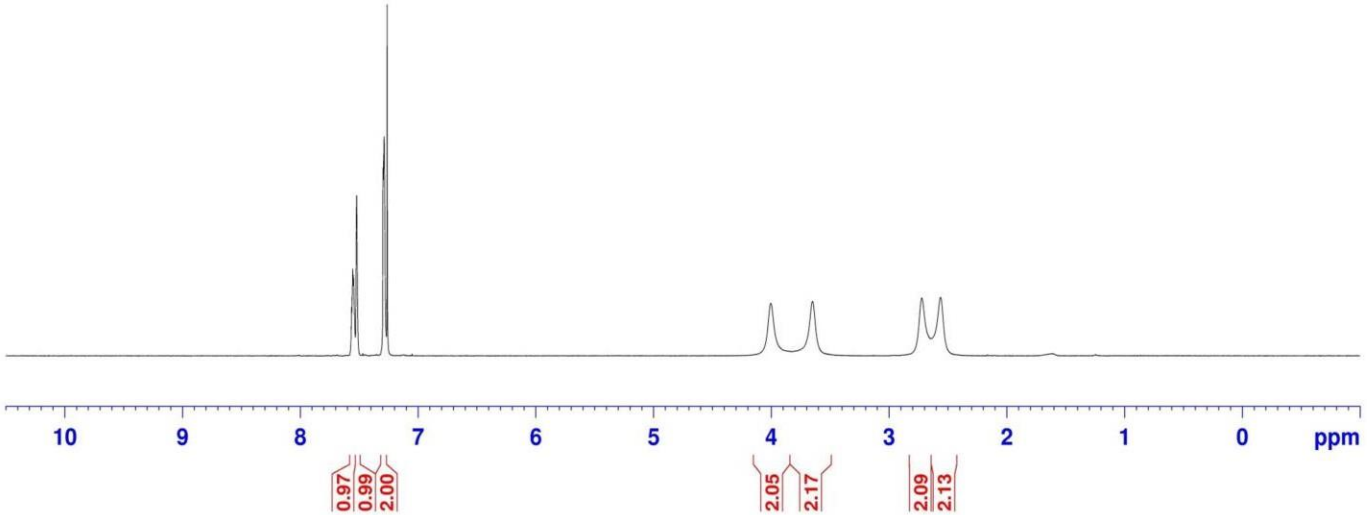
C	2.92604	-4.23621	0.45759
C	2.048	-3.25354	0.90026
H	0.32118	-2.71709	2.06143
H	-0.10594	-5.09141	2.74403
H	1.4185	-6.88915	1.96435
H	3.36584	-6.34173	0.52287
H	3.78055	-3.96665	-0.15499
C	-2.82662	4.49998	1.55158
H	-3.331	5.19149	2.22106
C	-3.07931	4.52722	0.21147
H	-3.7878	5.24082	-0.20034
S	2.36772	-1.49687	0.3334
O	1.55987	-0.59879	1.42186
O	3.90621	-1.34399	0.18247
Br	2.48993	2.35583	-0.43752
C	-0.62124	-1.88341	-5.03212
O	-0.04775	-1.57105	-6.07012
C	-1.96484	-2.60025	-5.08861
H	-2.74823	-2.02531	-4.57965
H	-1.91201	-3.58165	-4.6017
H	-2.24172	-2.7342	-6.13583

^{1}H NMR Spectra of Synthesized Compounds

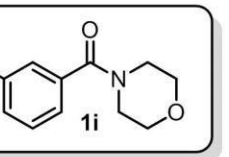
(3–bromophenyl)(thiomorpholino)methanone
500 MHz, CDCl3

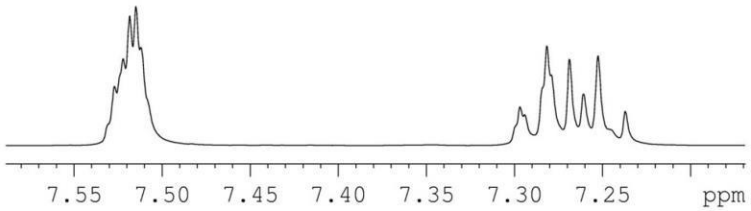


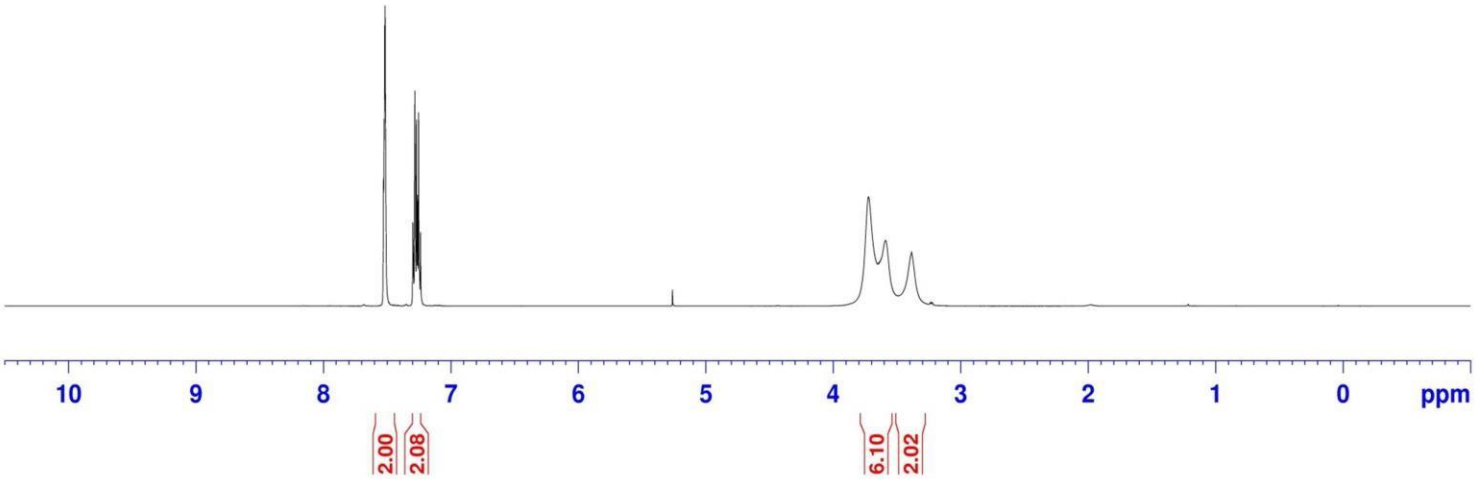




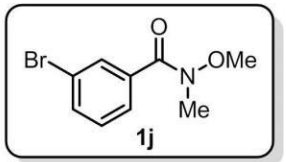
(3–bromophenyl)(morpholino)methanone
500 MHz, CDCl3

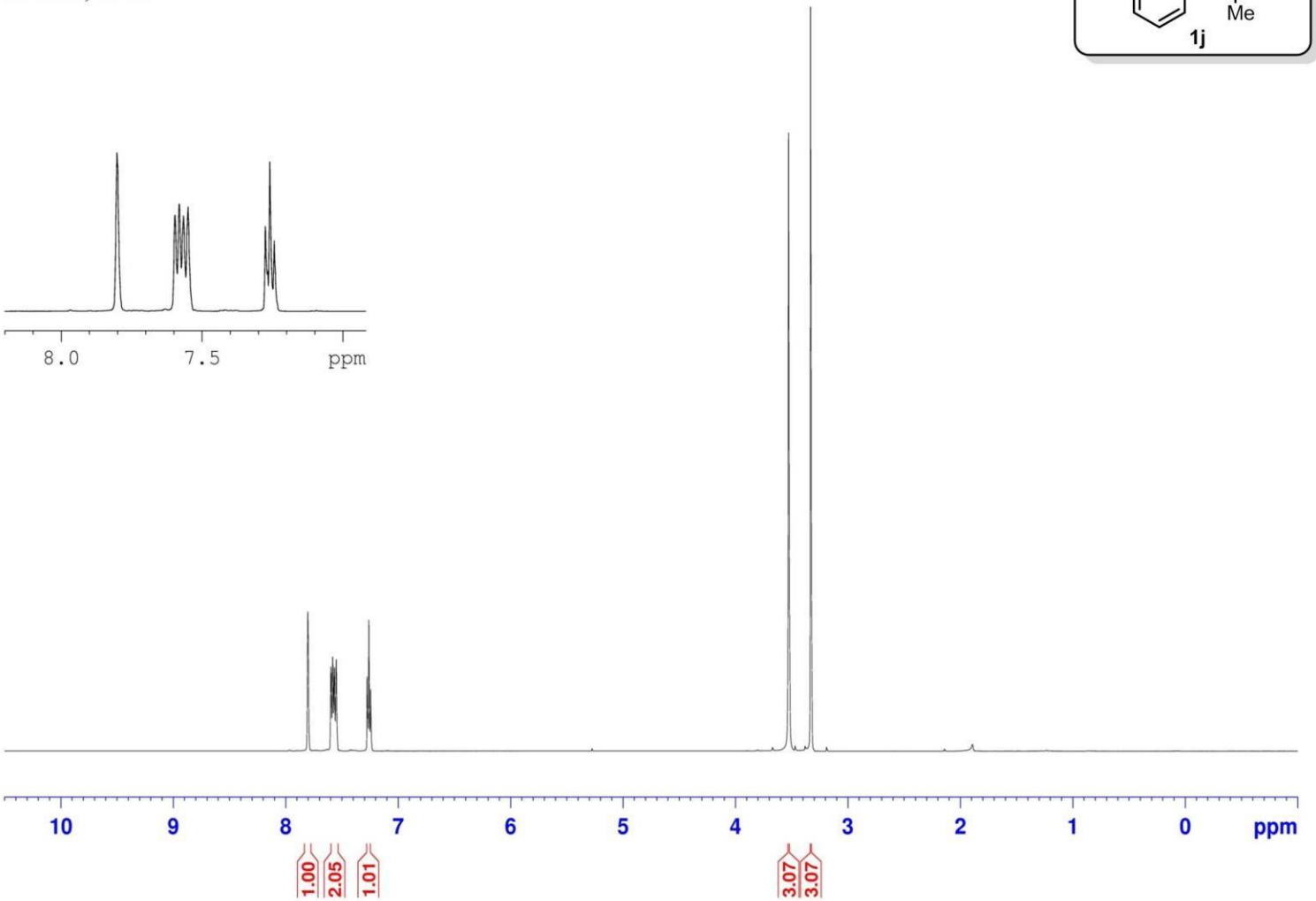




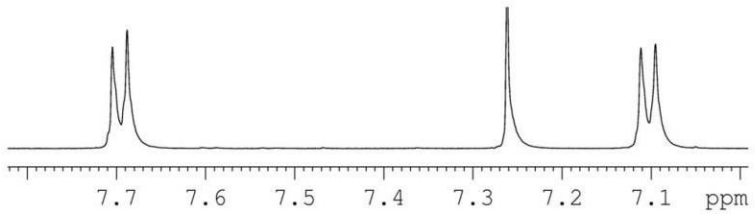


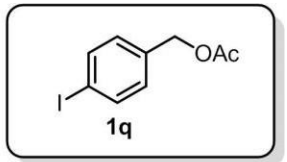
3–bromo–N–methoxy–N–methylbenzamide
500 MHz, CDCl3





4–Iodobenzyl Acetate
500 MHz, CDCl3





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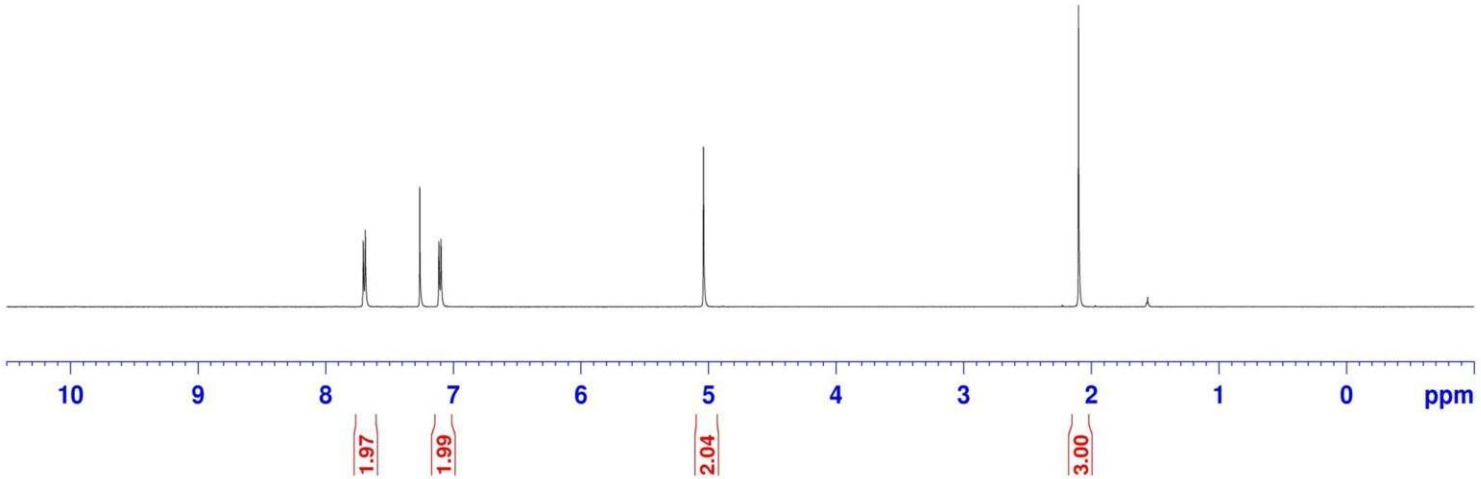
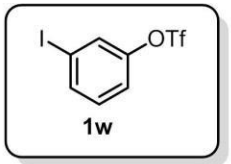
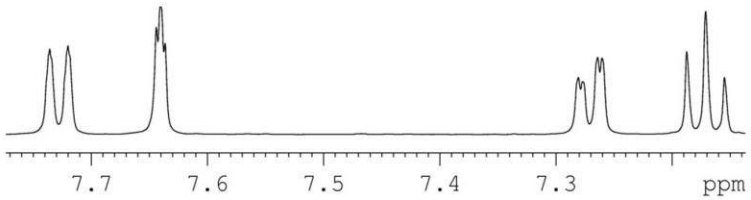
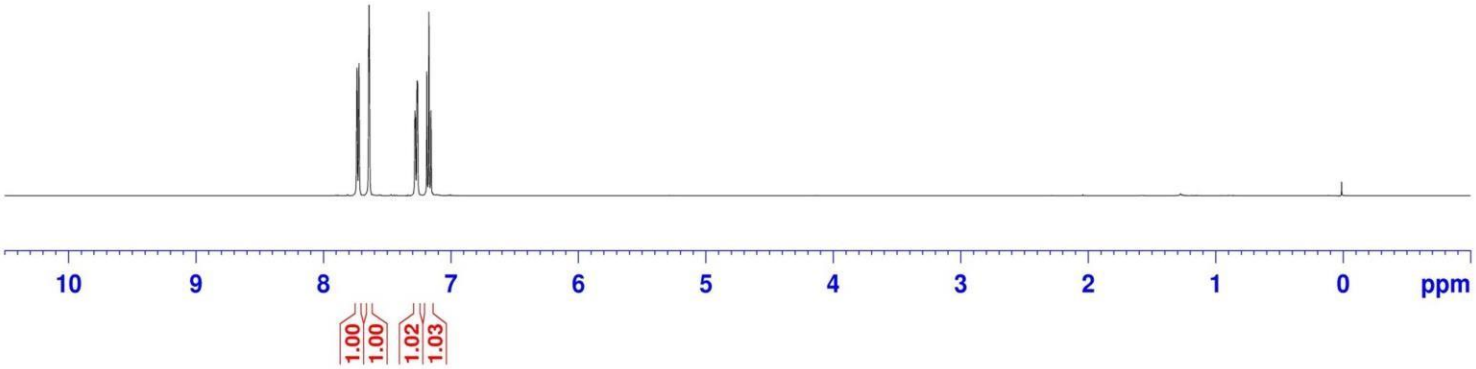


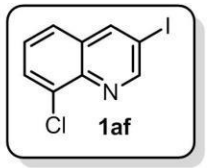
3–iodophenyl trifluoromethanesulfonate
500 MHz, CDCl3

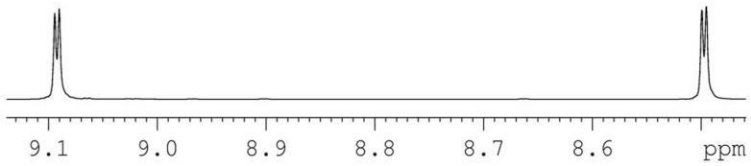


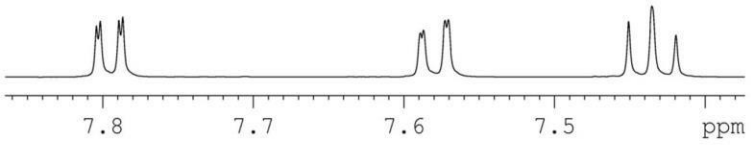


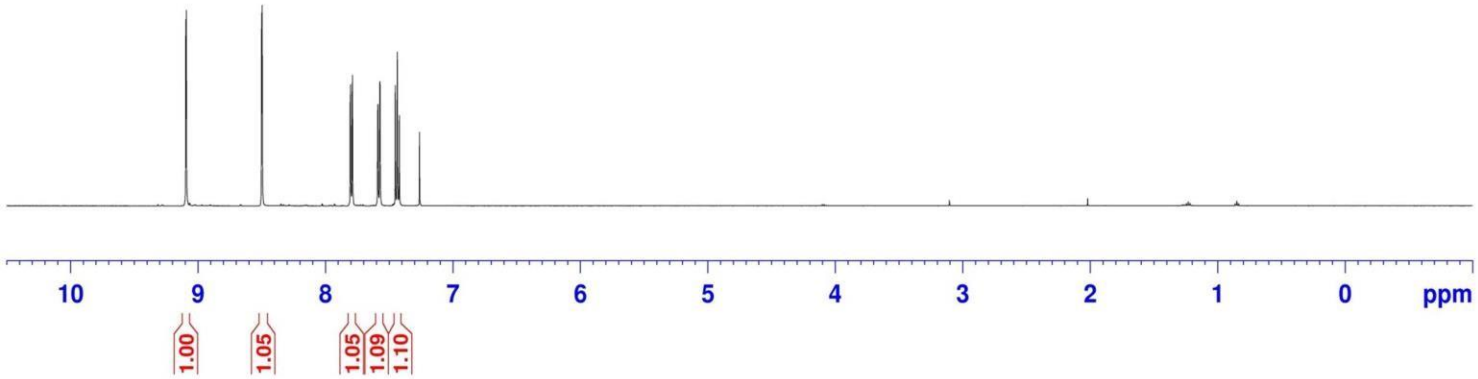


8–Chloro–3–iodoquinoline
500 MHz, CDCl3

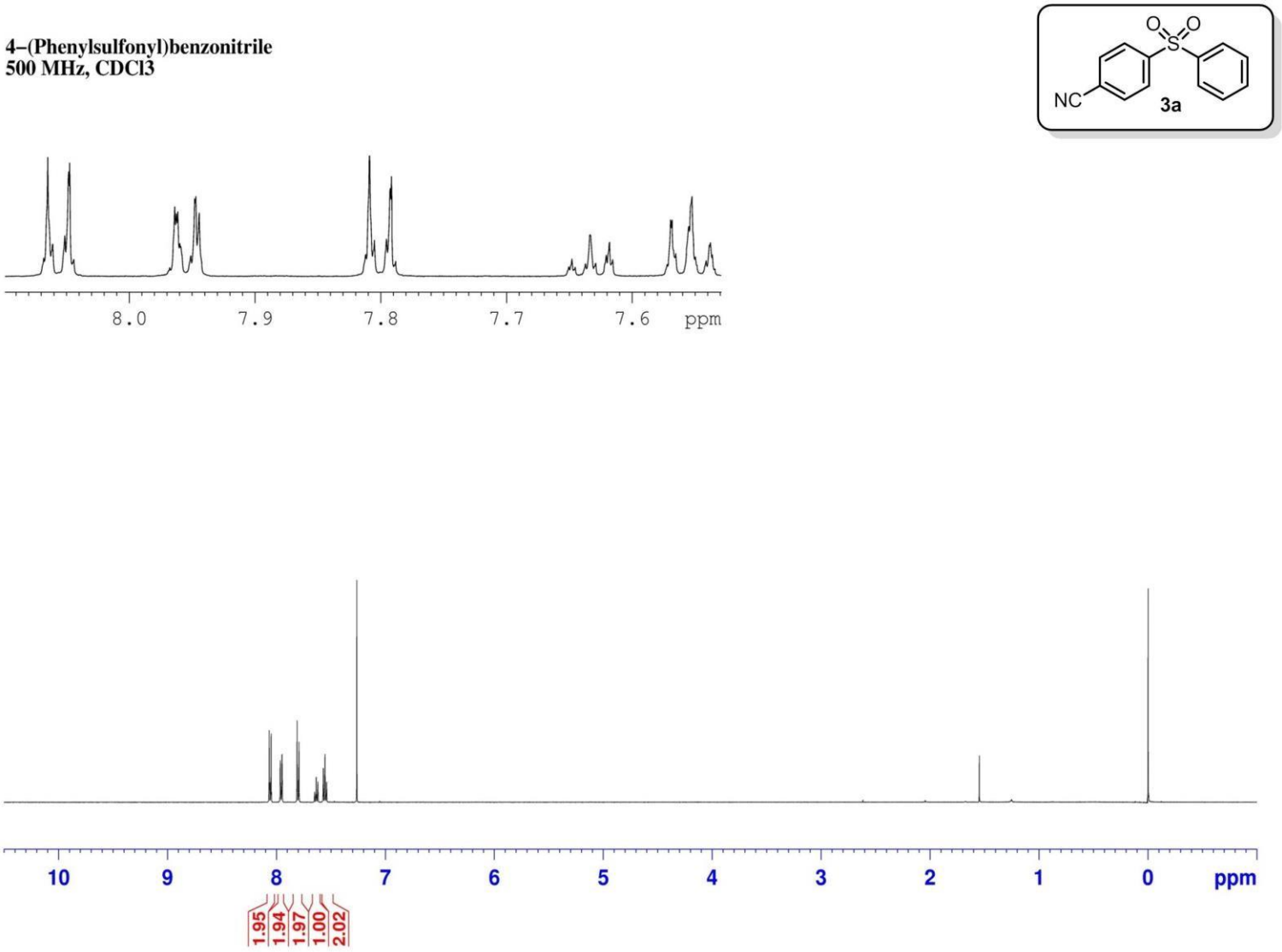




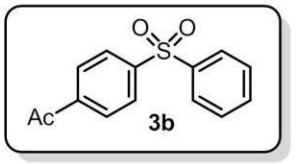


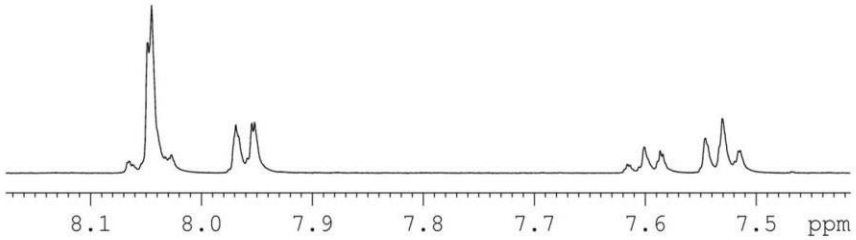


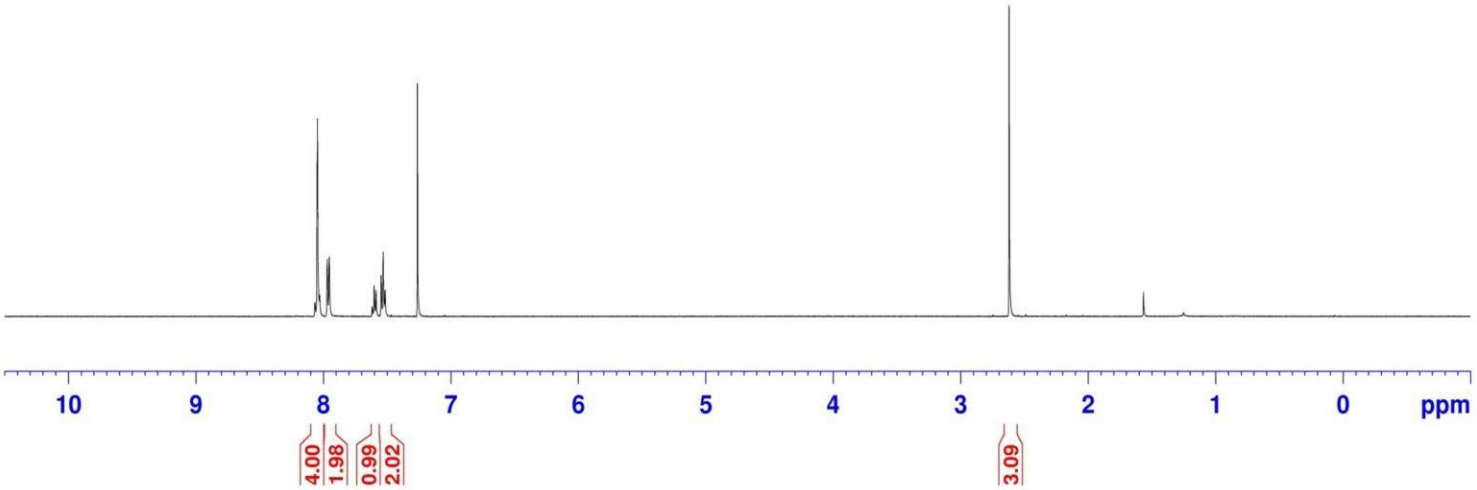
4–(Phenylsulfonyl)benzonitrile
500 MHz, CDCl3



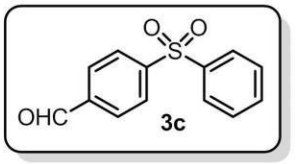
1–(4–(Phenylsulfonyl)phenyl)ethanone
500 MHz, CDCl3

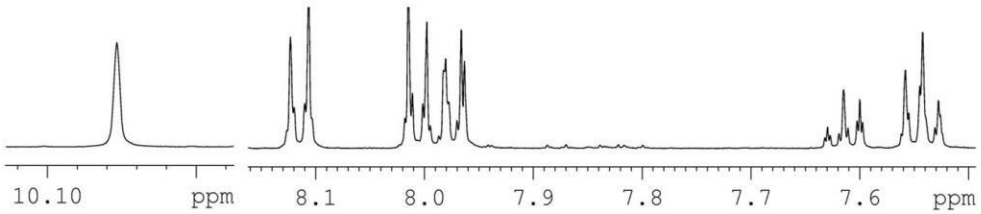


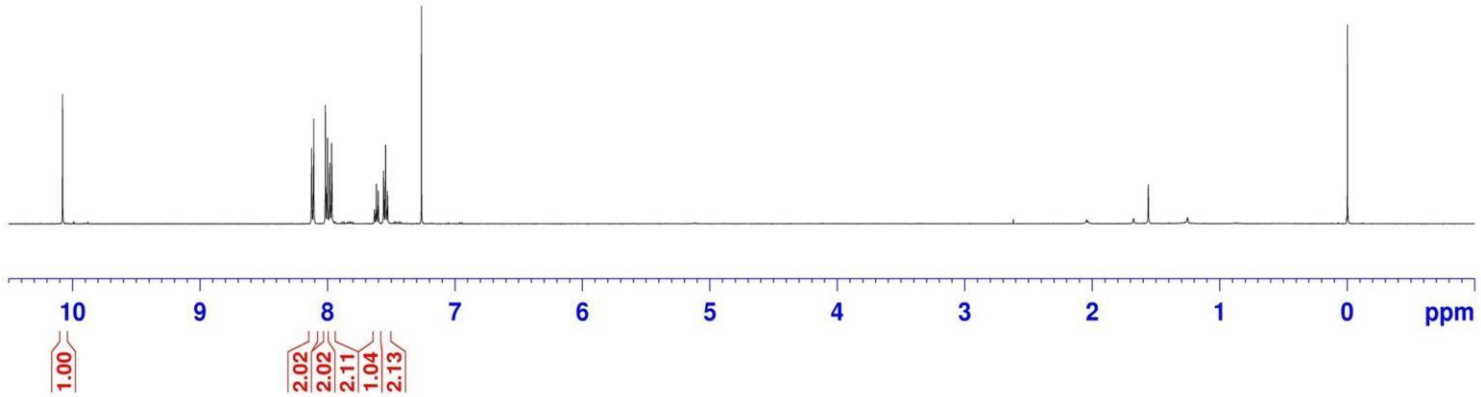




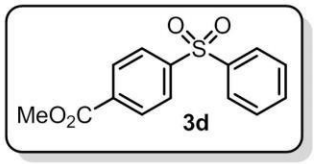
4–(Phenylsulfonyl)benzaldehyde
500 MHz, CDCl3

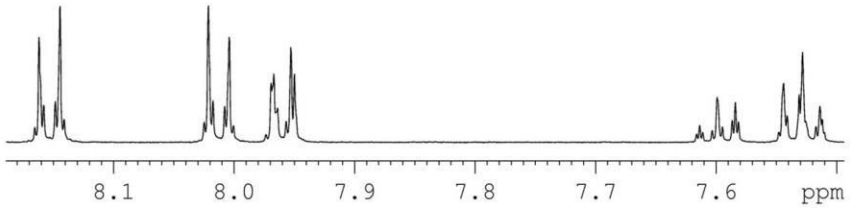


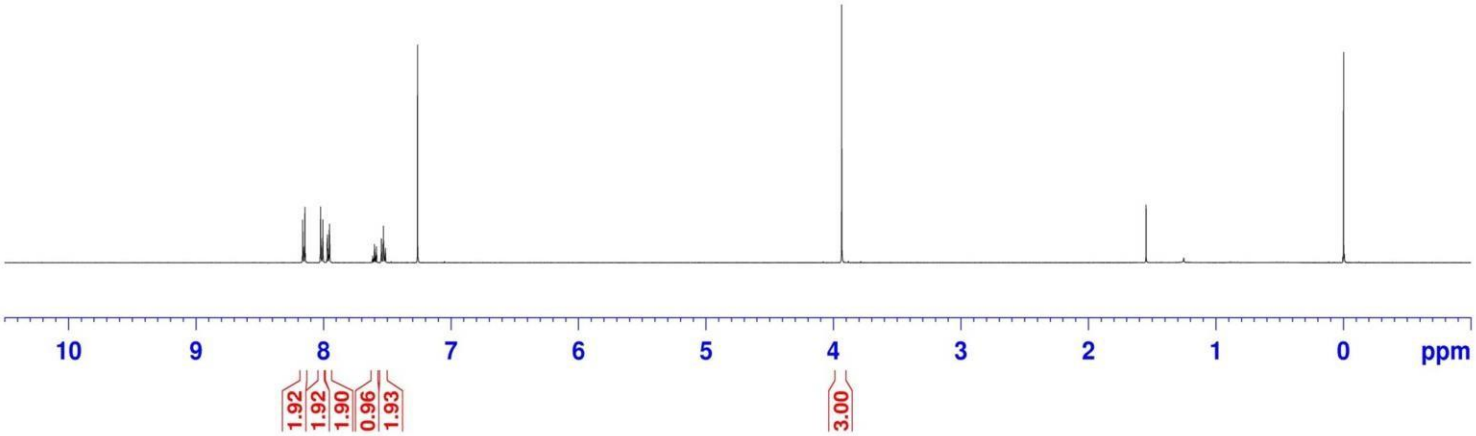




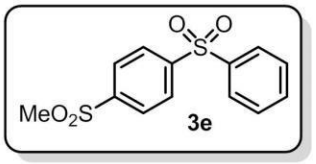
Methyl 4–(Phenylsulfonyl)benzoate
500 MHz, CDCl3

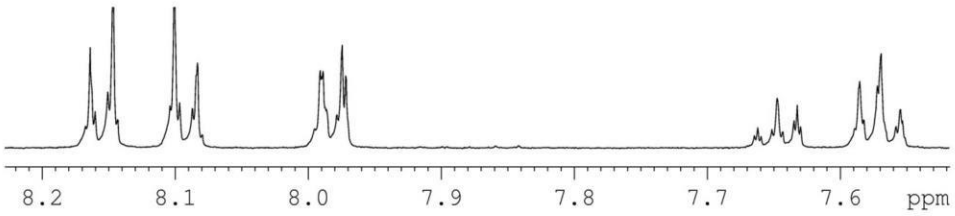


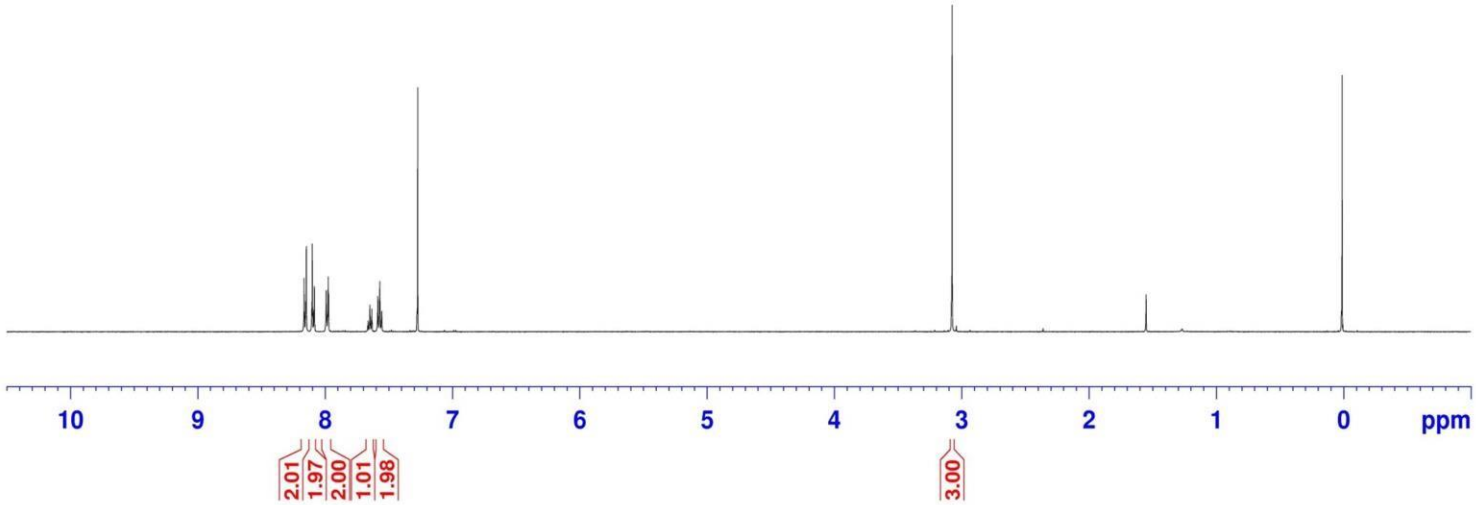




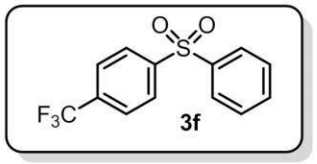
1–(Methylsulfonyl)–4–(phenylsulfonyl)benzene
500 MHz, CDCl3

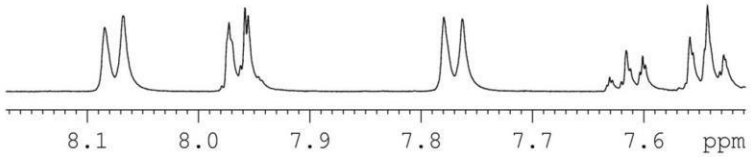


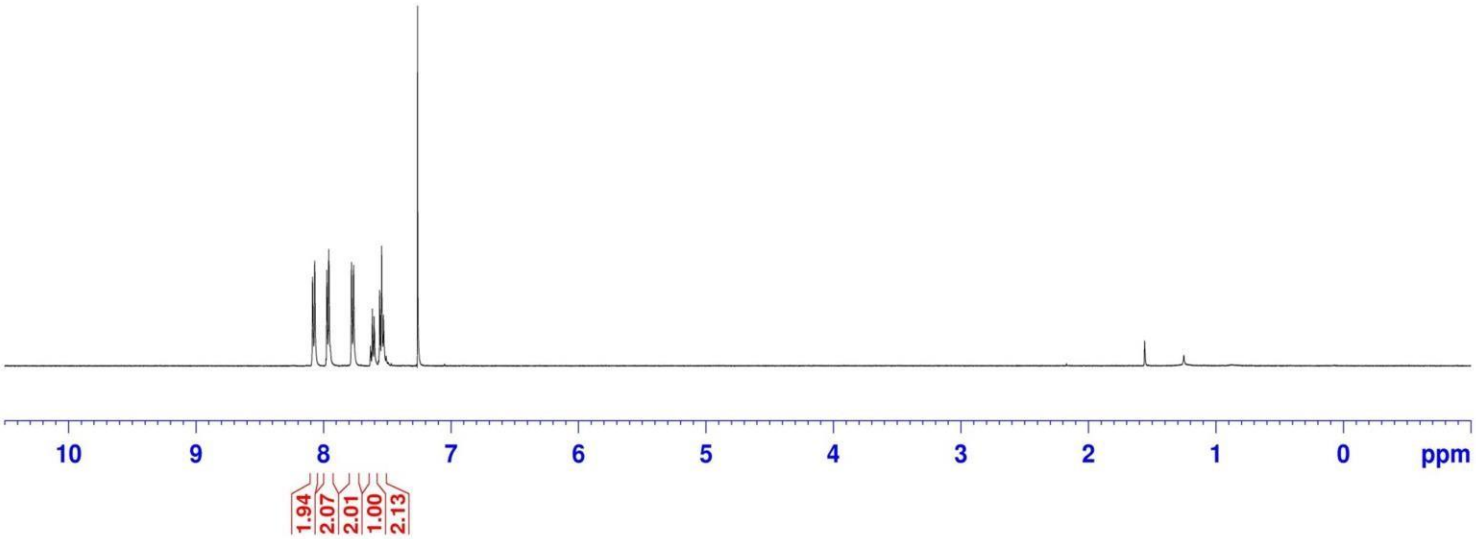




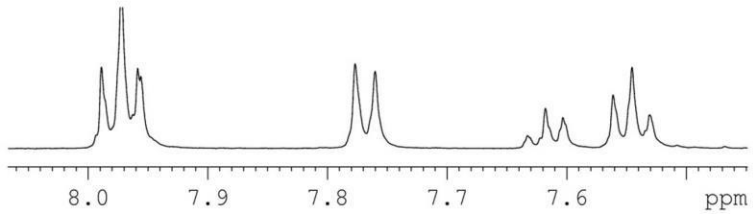
1–(Phenylsulfonyl)–4–(trifluoromethyl)benzene
500 MHz, CDCl3

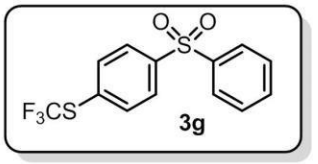


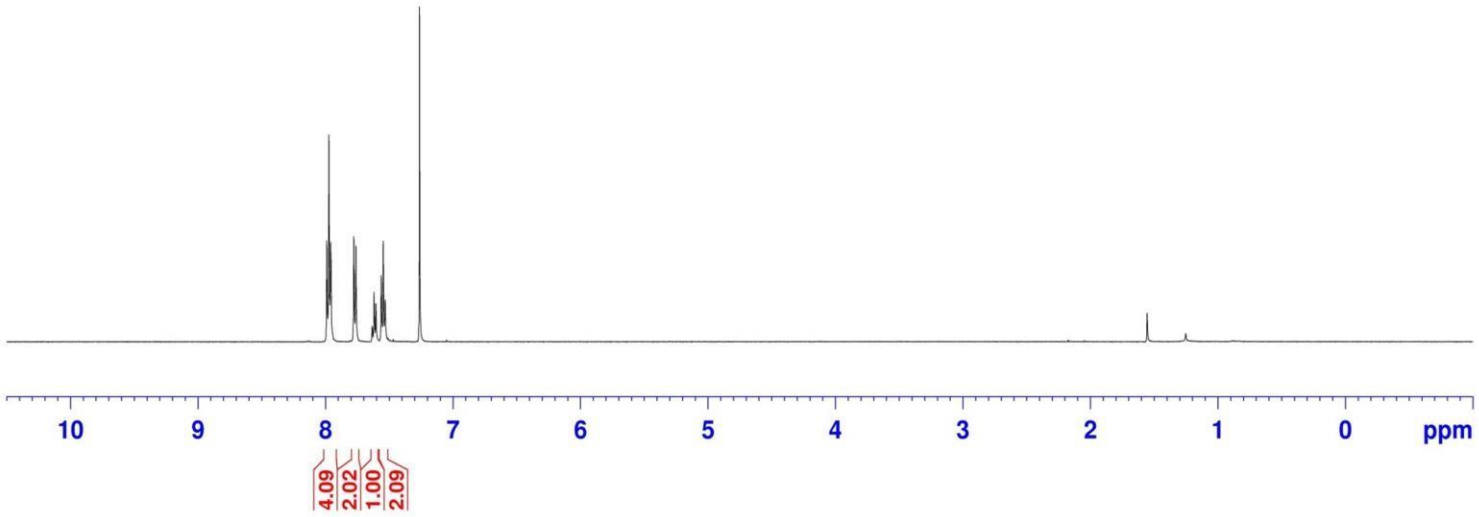




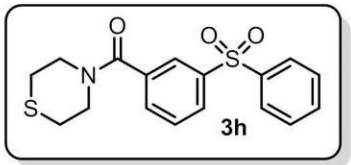
(4–(Phenylsulfonyl)phenyl)(trifluoromethyl)sulfane
500 MHz, CDCl3

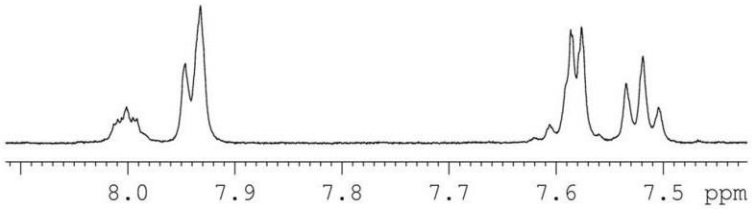


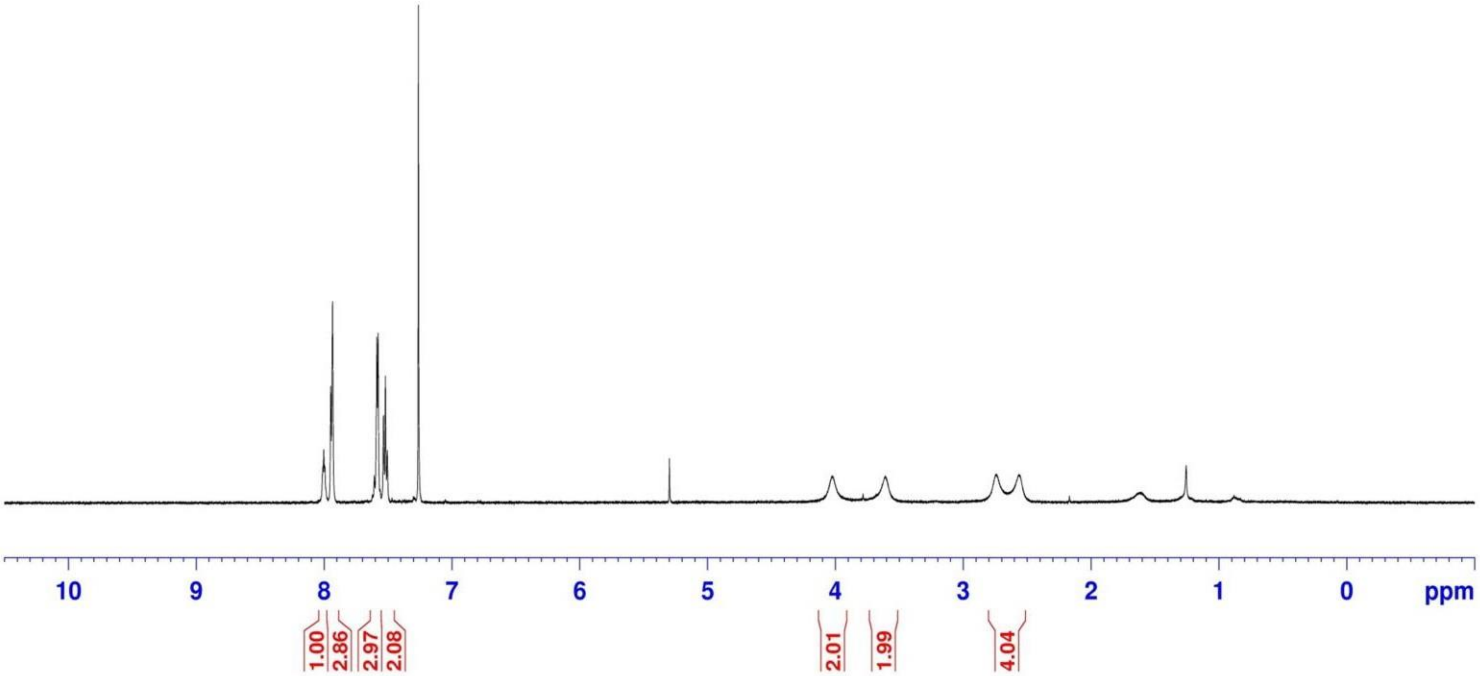




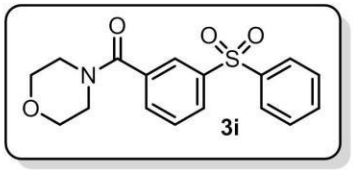
(3–(Phenylsulfonyl)phenyl)(thiomorpholino)methanone
500 MHz, CDCl3

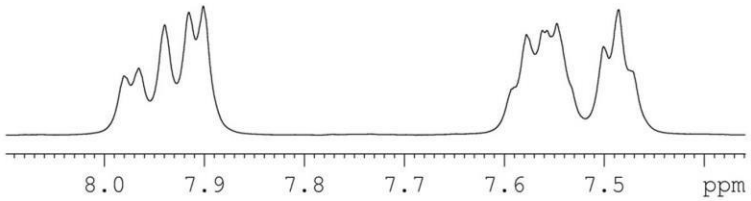


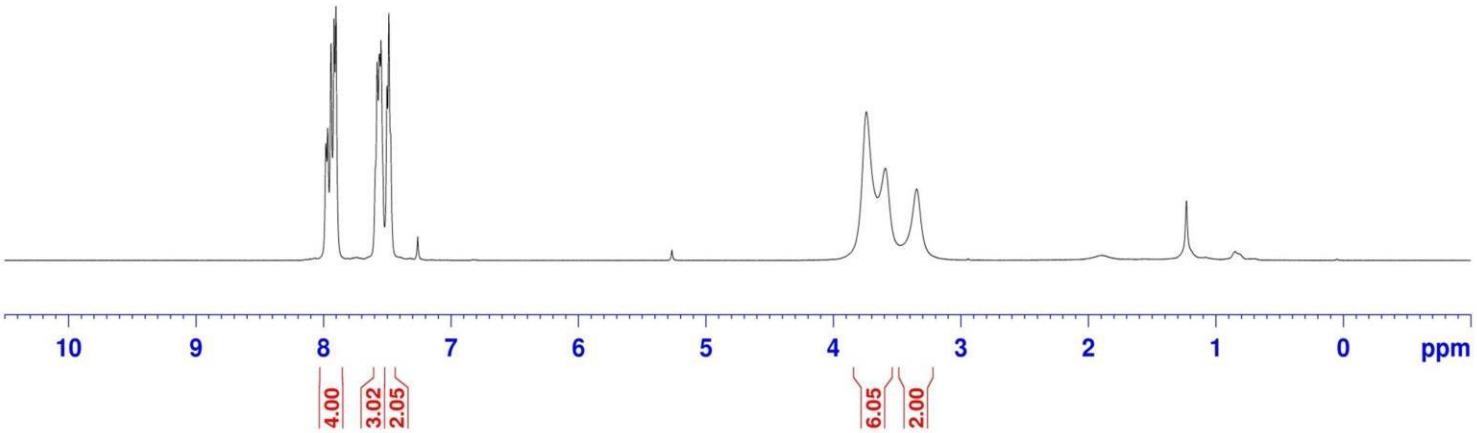




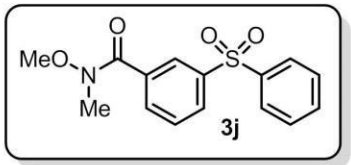
(3–Bromophenyl)(morpholino)methanone
500 MHz, CDCl3

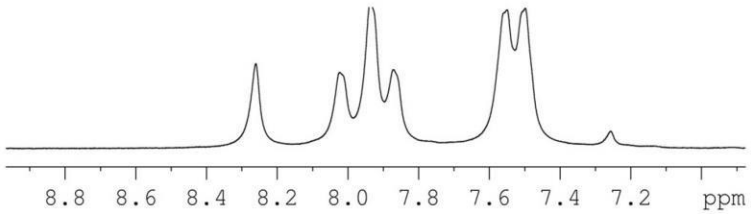


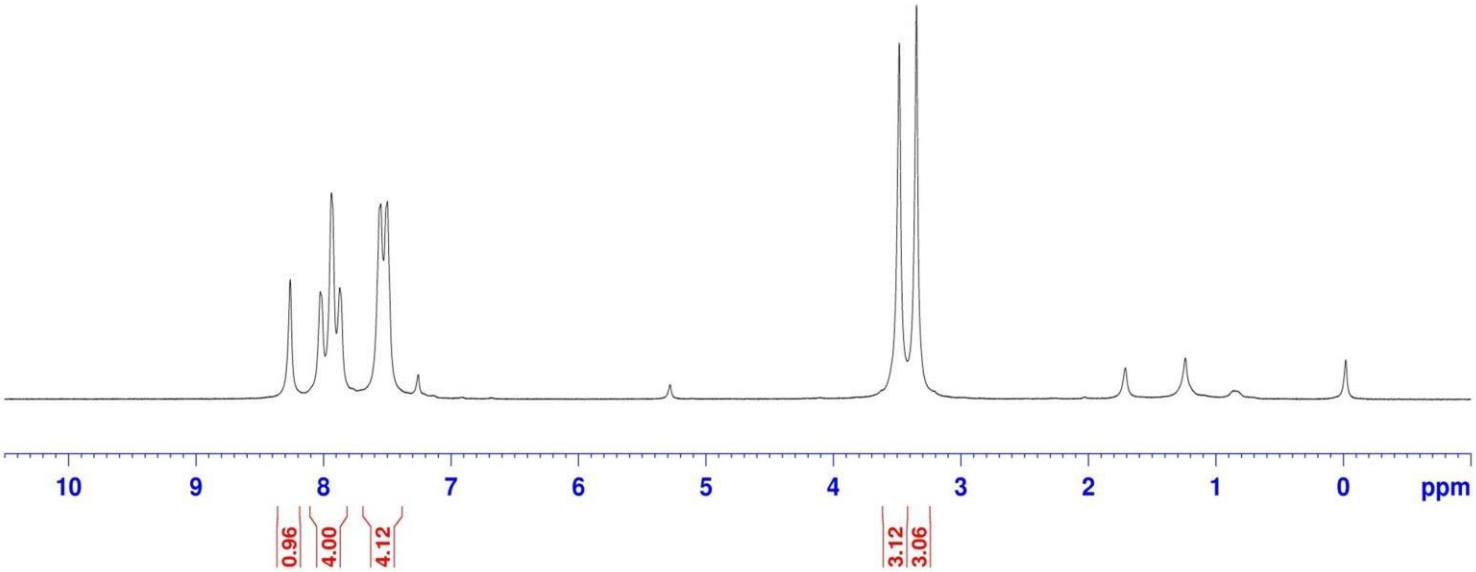




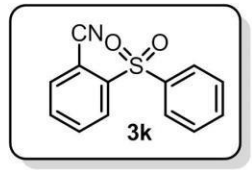
N–Methoxy–N–methyl–3–(phenylsulfonyl)benzamide
500 MHz, CDCl3

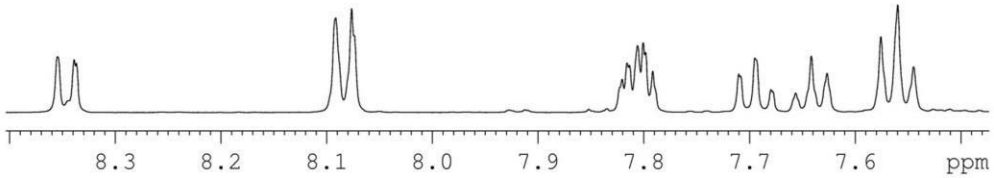


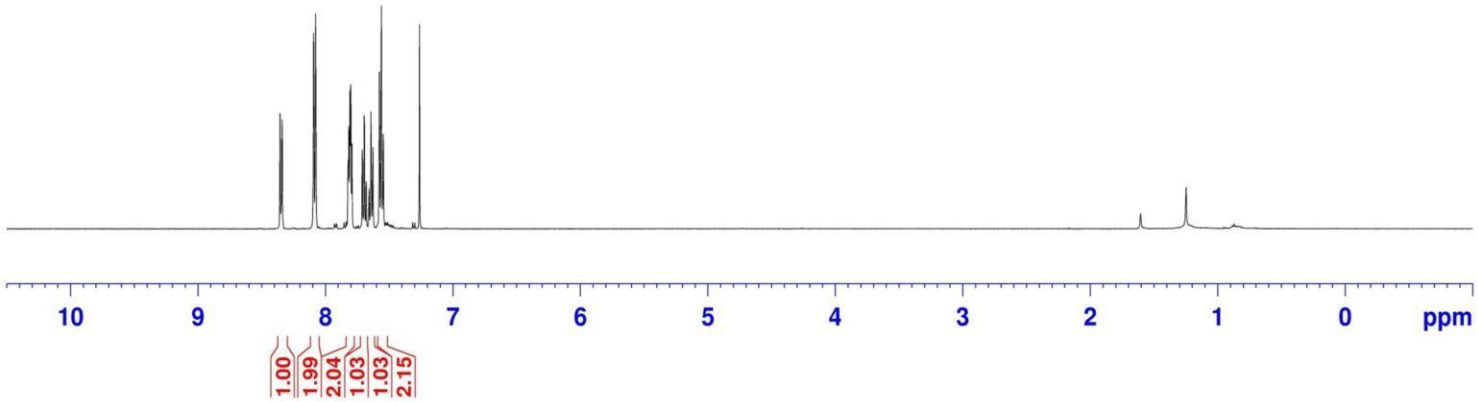




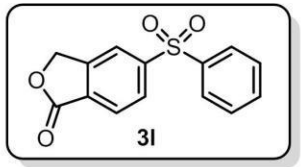
2–(Phenylsulfonyl)benzonitrile
500 MHz, CDCl3

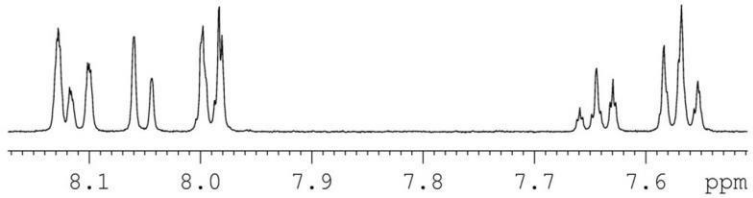


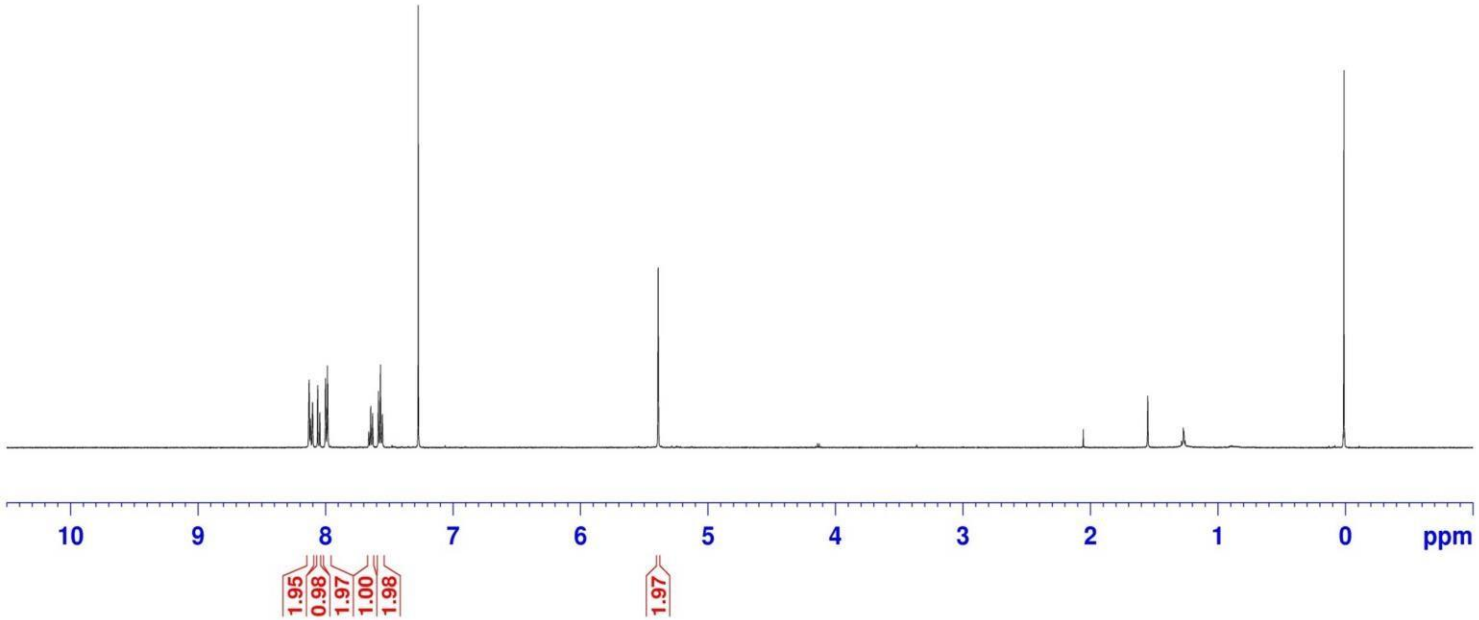




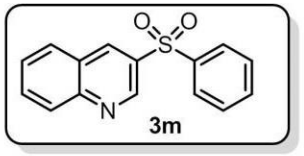
5–(Phenylsulfonyl)isobenzofuran–1(3H)–one
500 MHz, CDC:3

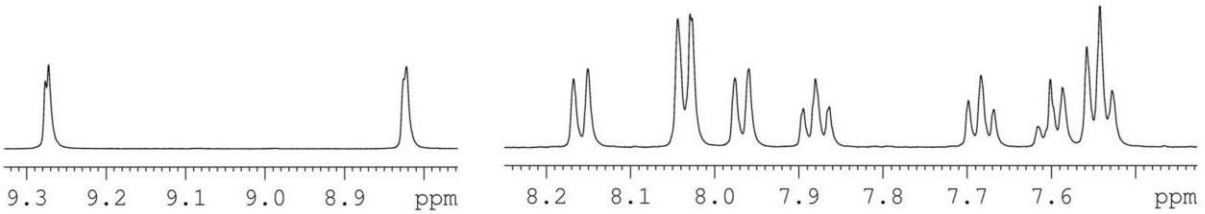


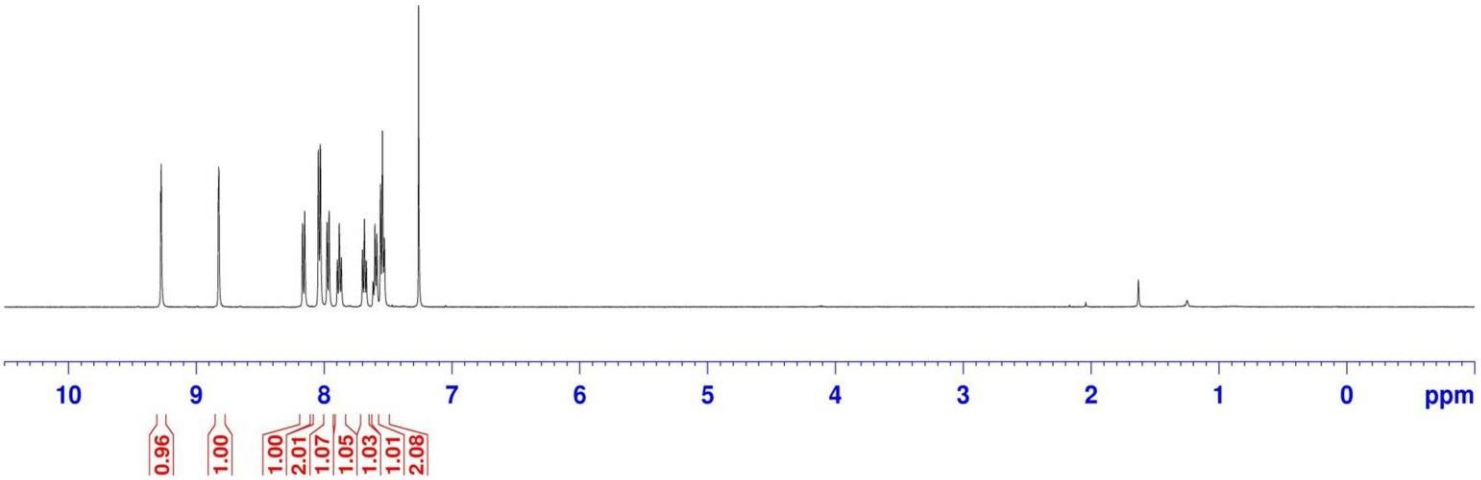




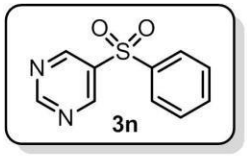
3–(Phenylsulfonyl)quinoline
500 MHz, CDCl3

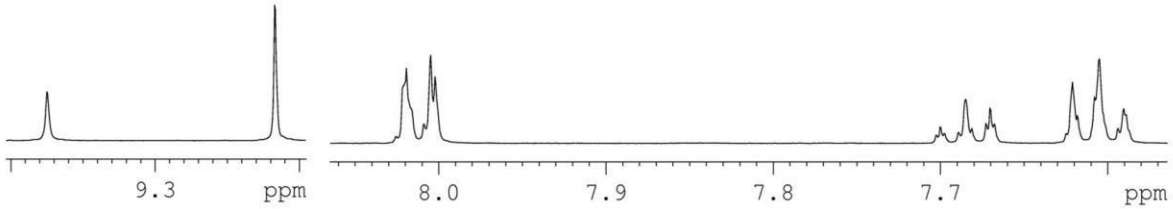


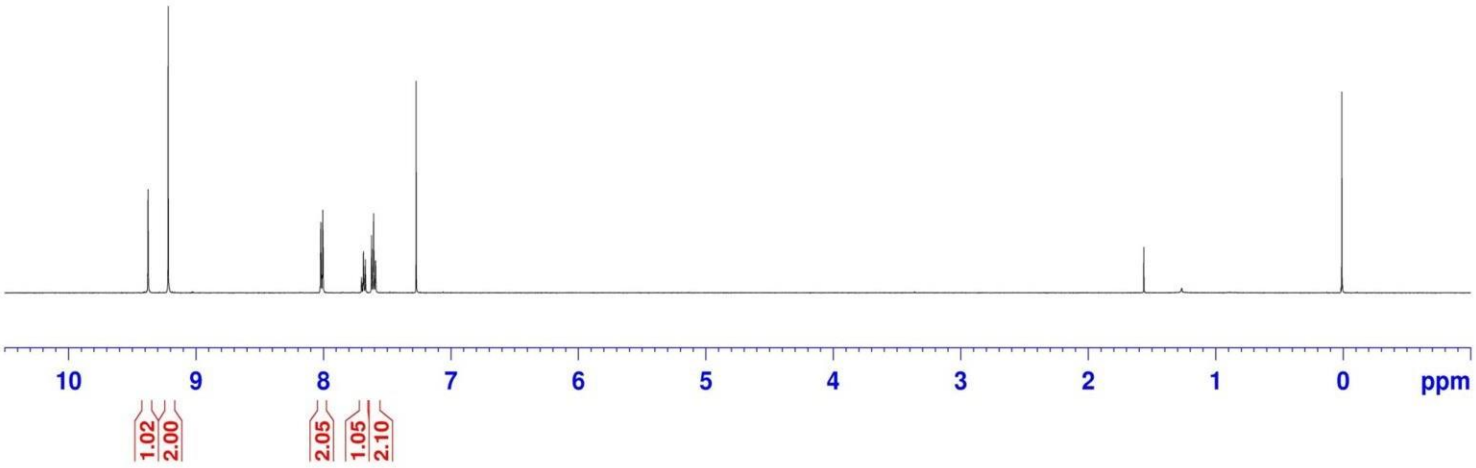




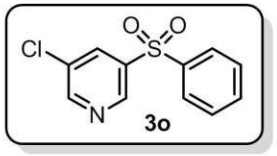
5–(Phenylsulfonyl)pyrimidine
500 MHz, CDCl3

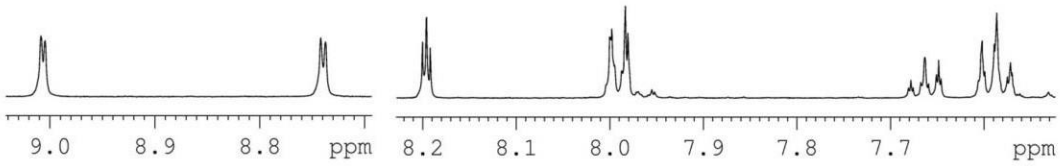


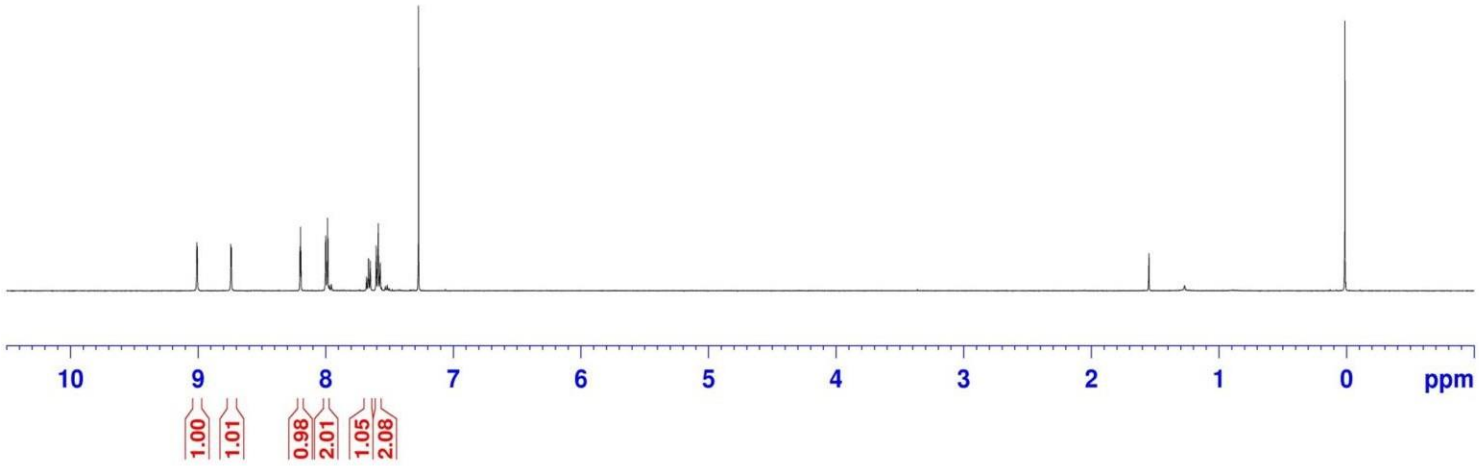




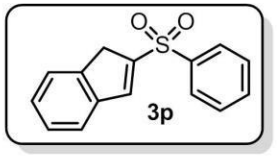
3–Chloro–5–(phenylsulfonyl)pyridine
500 MHz, CDCl3

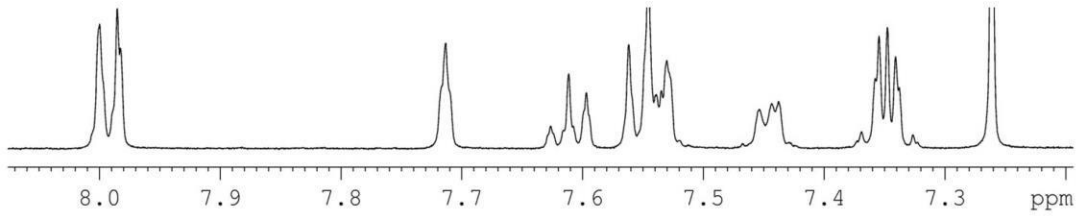


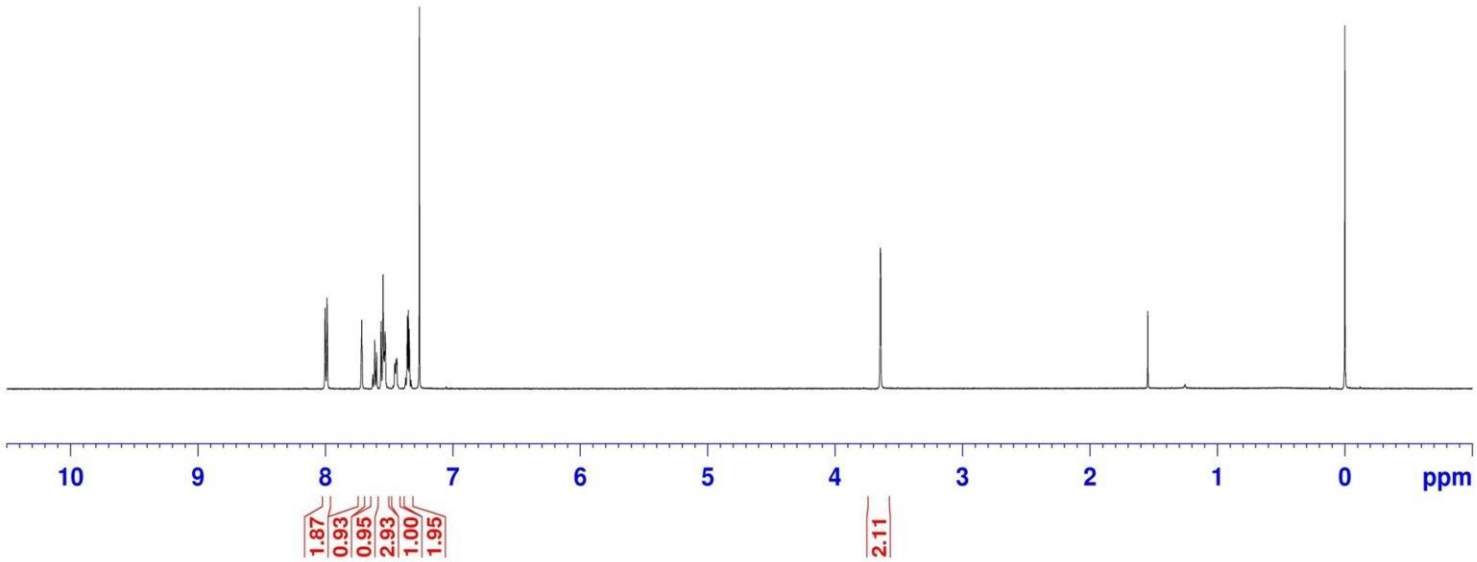




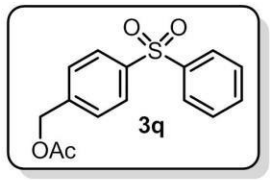
2–(Phenylsulfonyl)–1H–indene
500 MHz, CDCl3

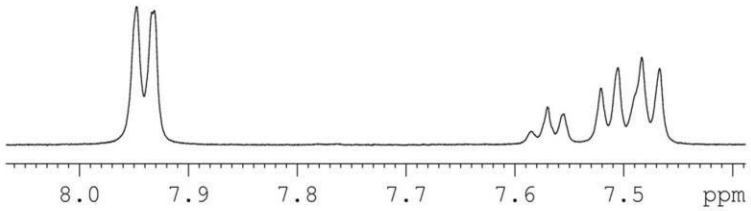


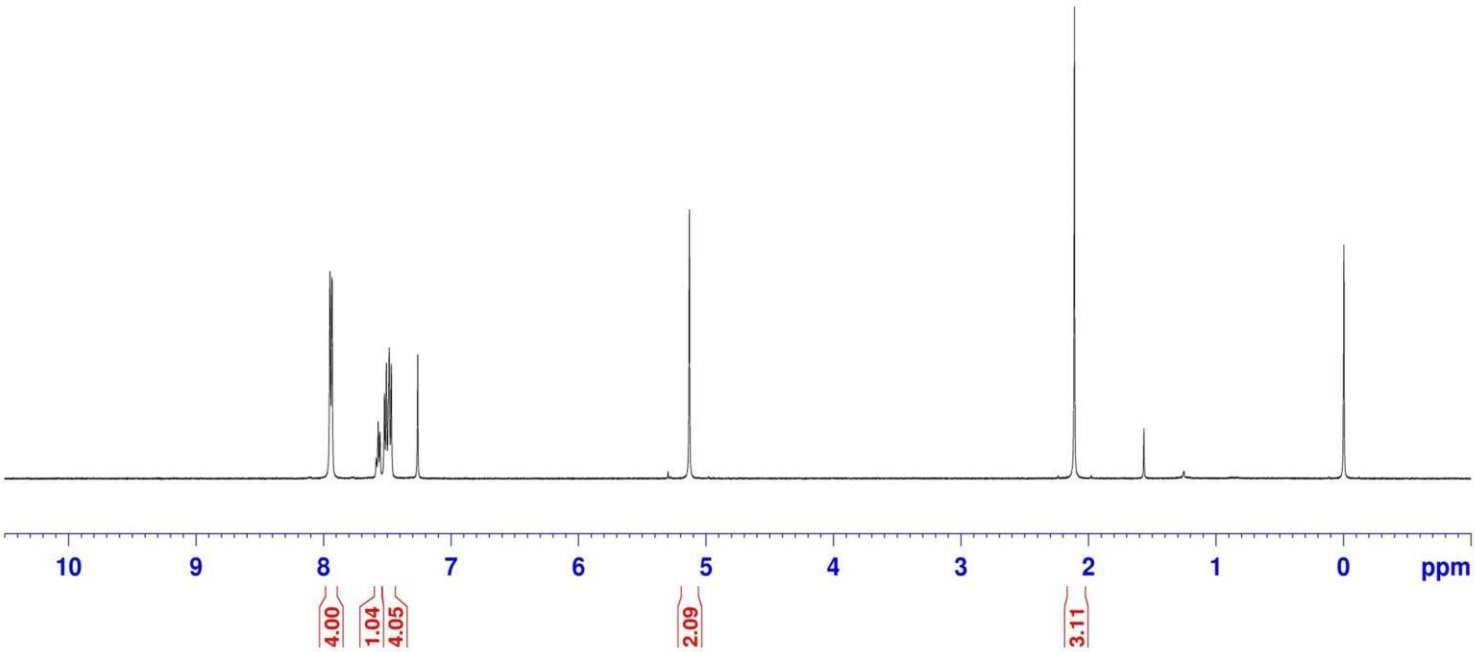




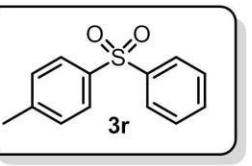
4–(Phenylsulfonyl)benzyl acetate
500 MHz, CDCl3

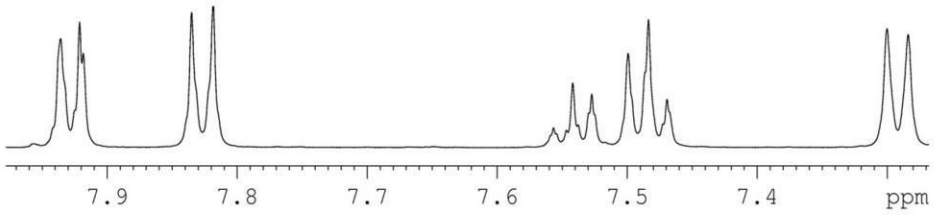


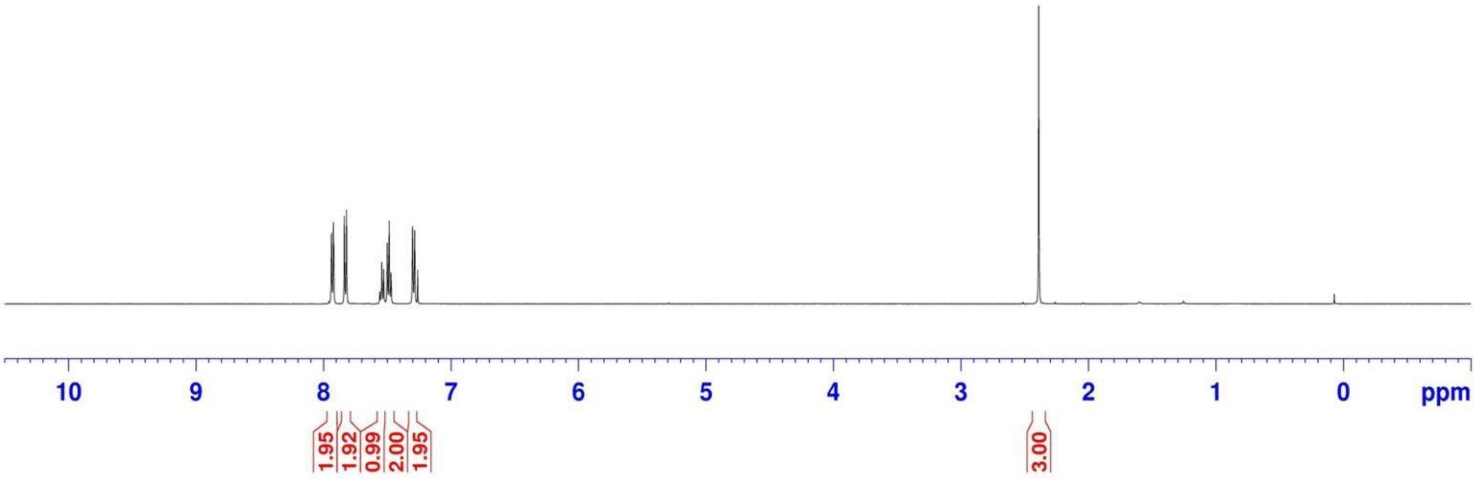




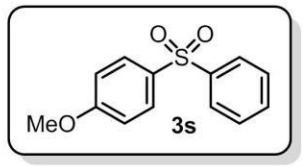
1–Methyl–4–(phenylsulfonyl)benzene
500 MHz, CDCl3

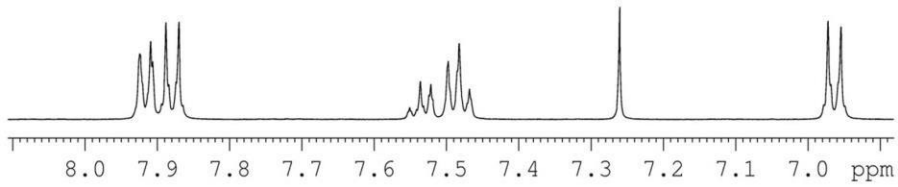


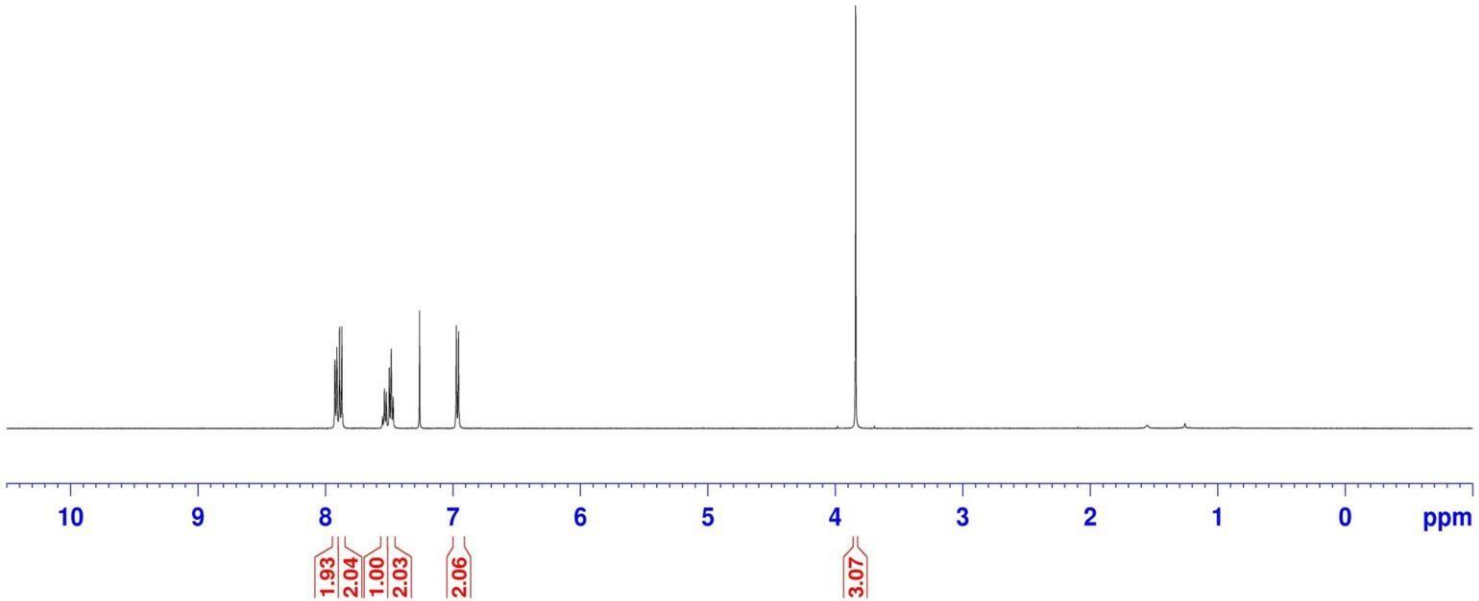




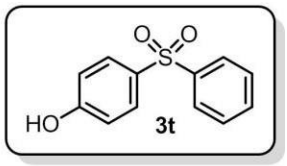
1−Methoxy−4−(phenylsulfonyl)benzene
500 MHz, CDCl3

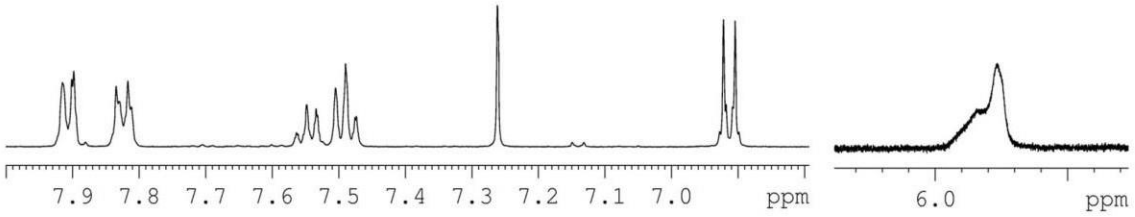


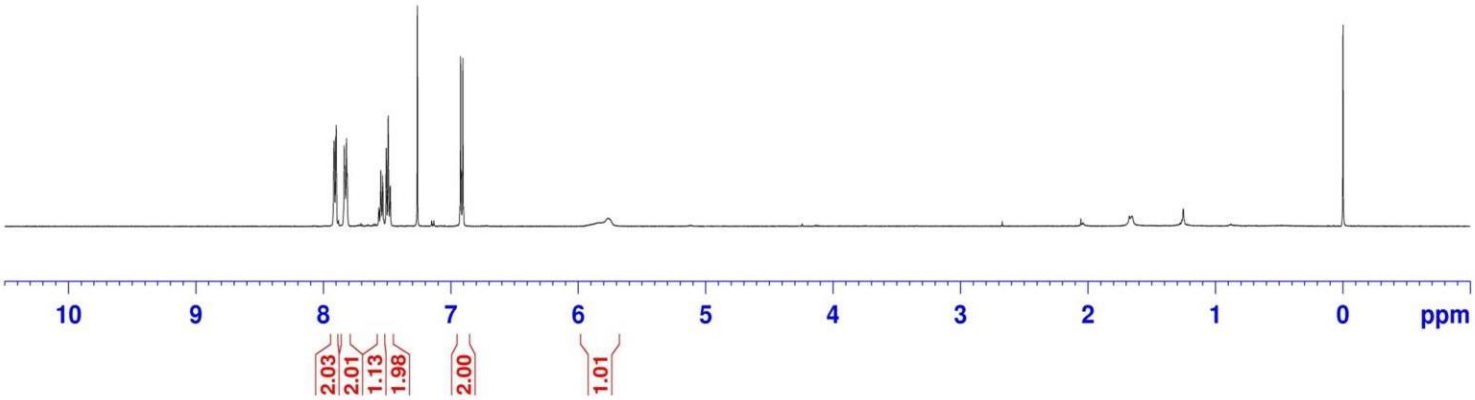




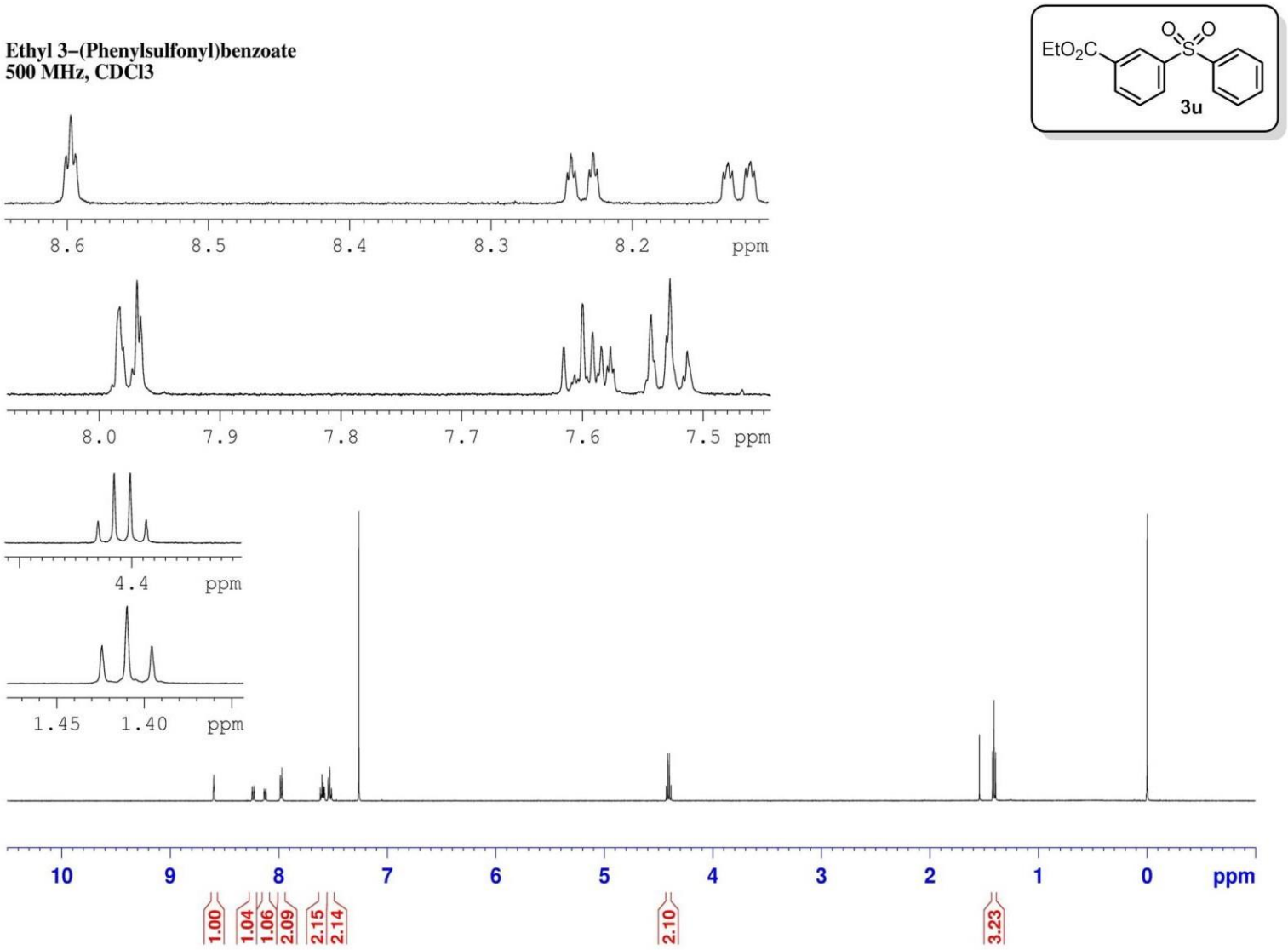
4–(Phenylsulfonyl)phenol
500 MHz, CDCl3



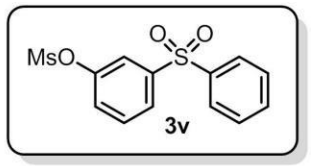


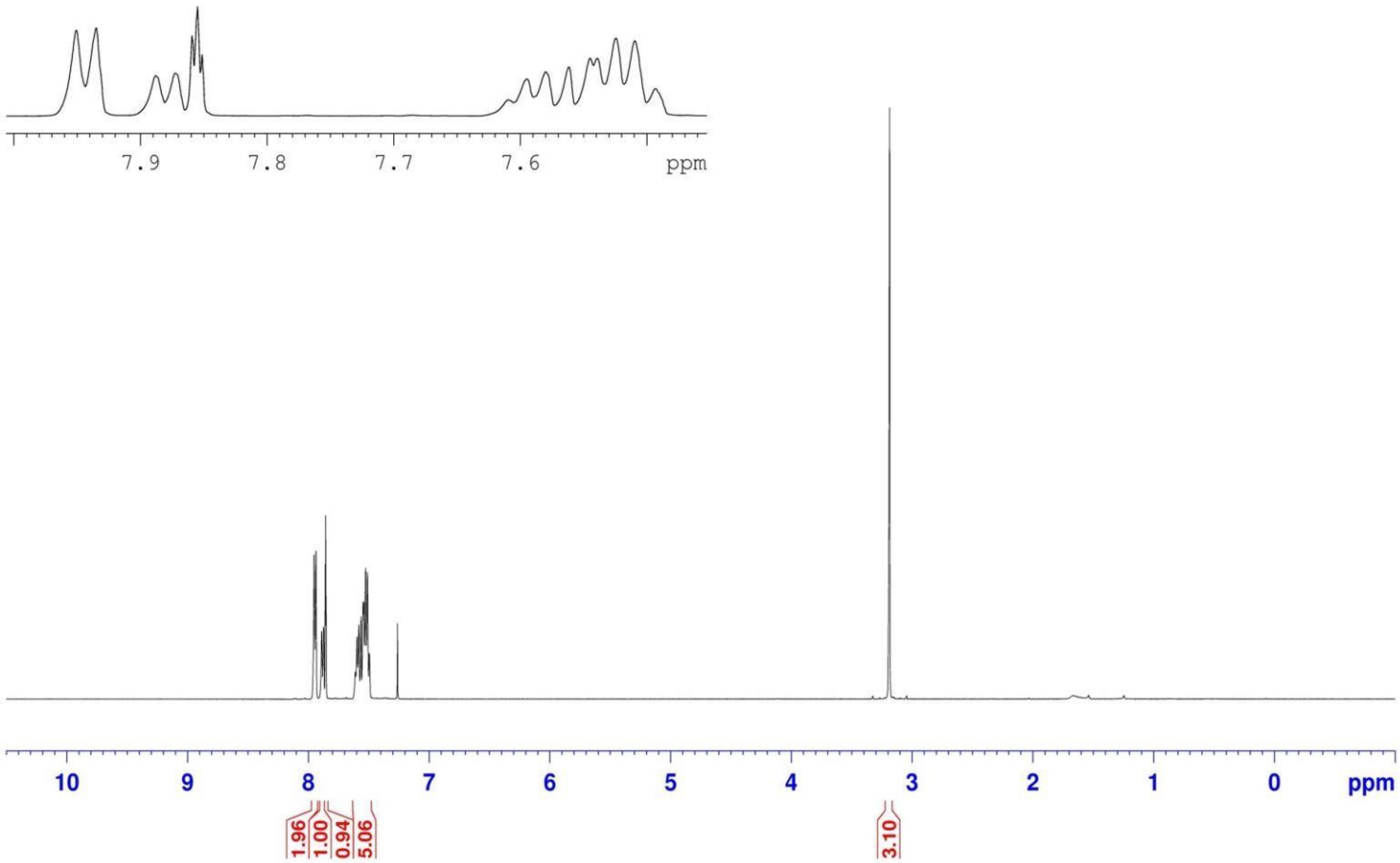


Ethyl 3–(Phenylsulfonyl)benzoate
500 MHz, CDCl3

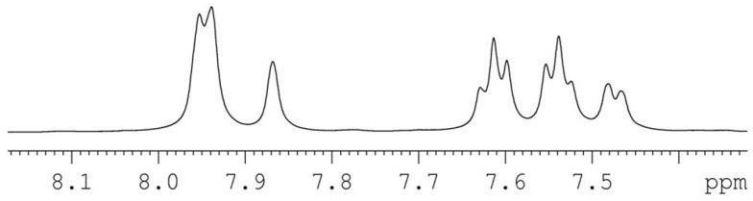


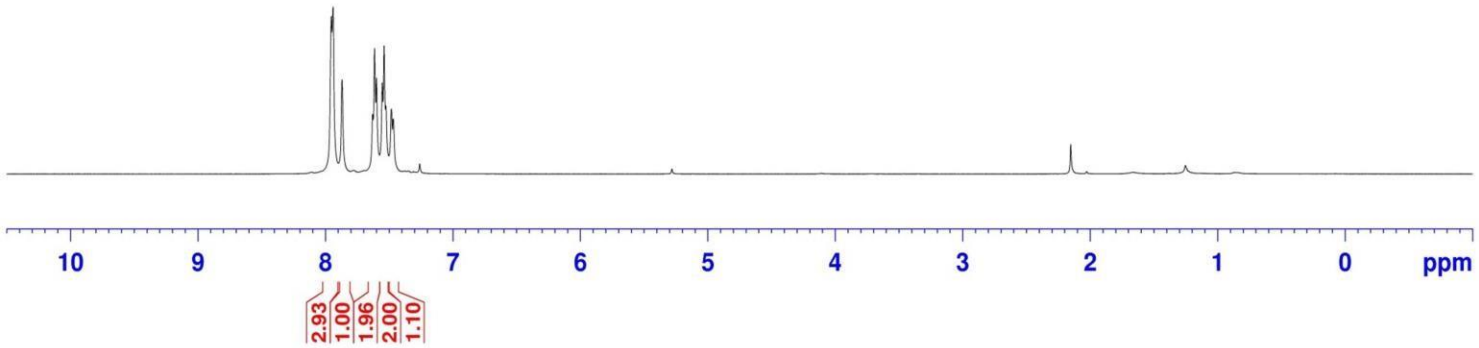
3–(Phenylsulfonyl)phenyl methanesulfonate
500 MHz, CDCl3

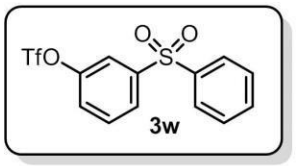




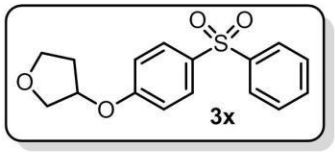
3–(Phenylsulfonyl)phenyl trifluoromethanesulfonate
500 MHz, CDCl3

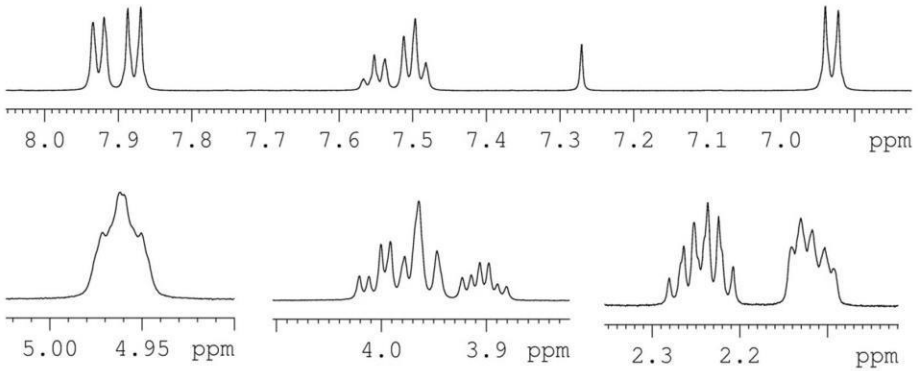


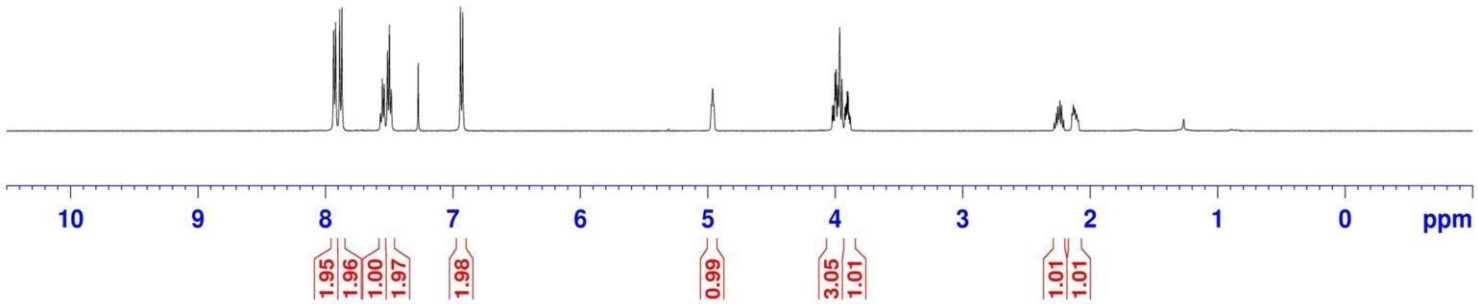




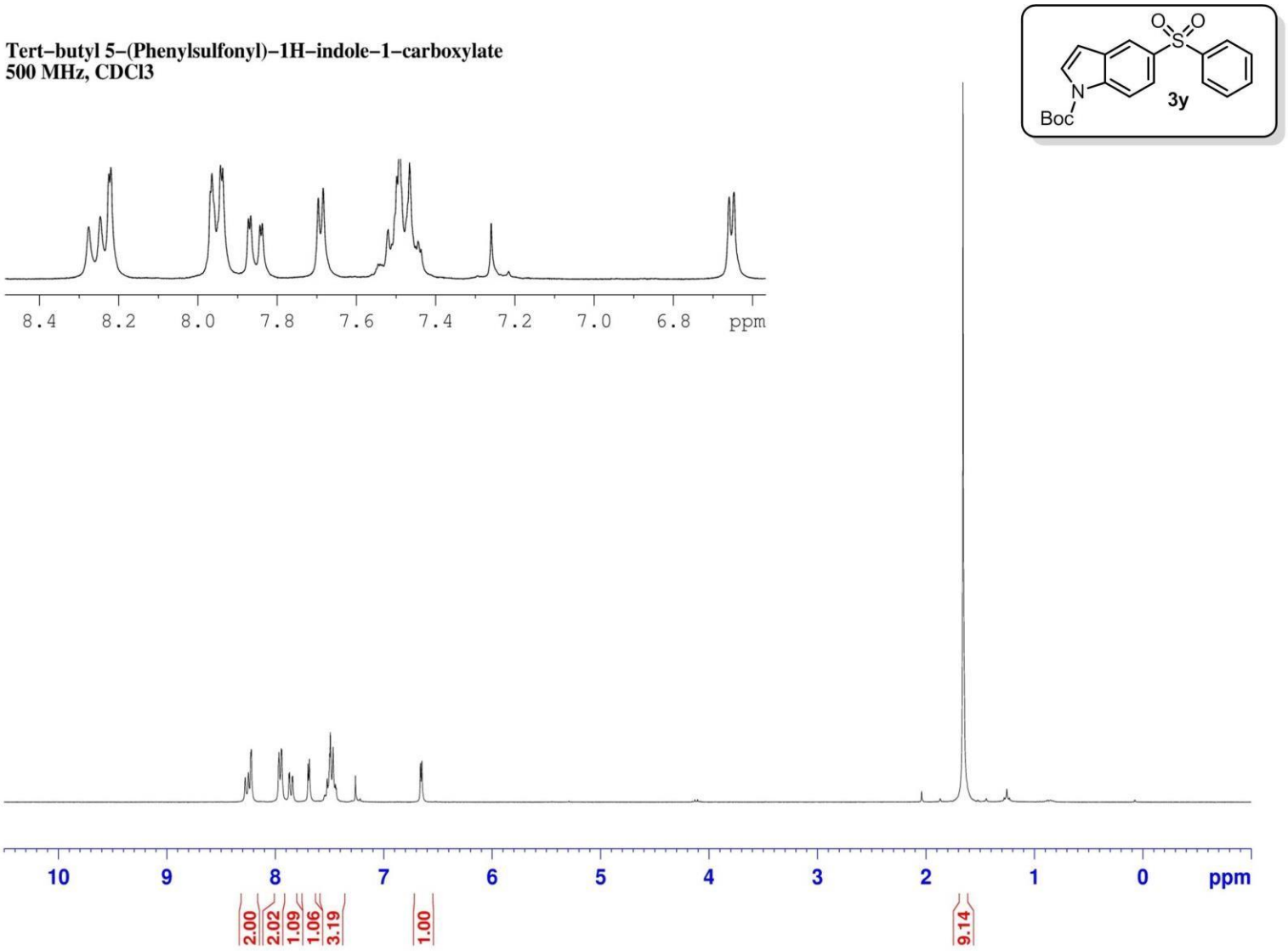
3–(4–(Phenylsulfonyl)phenoxy)tetrahydrofuran
500 MHz, CDCl3



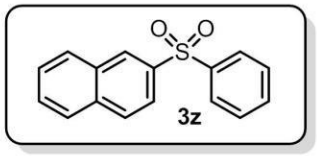


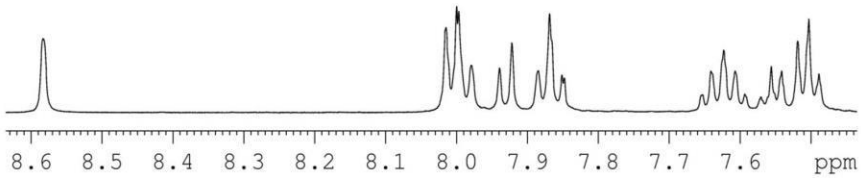


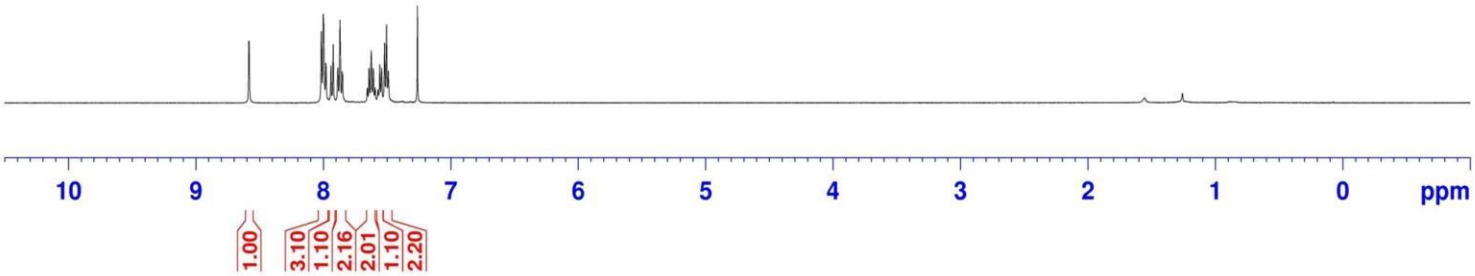
Tert–butyl 5–(Phenylsulfonyl)–1H–indole–1–carboxylate
500 MHz, CDCl3



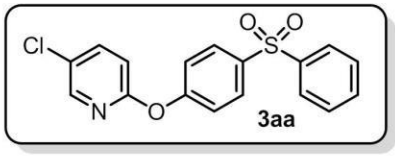
2–(Phenylsulfonyl)naphthalene
500 MHz, CDCl3

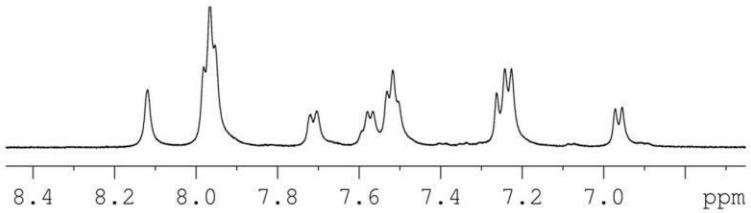


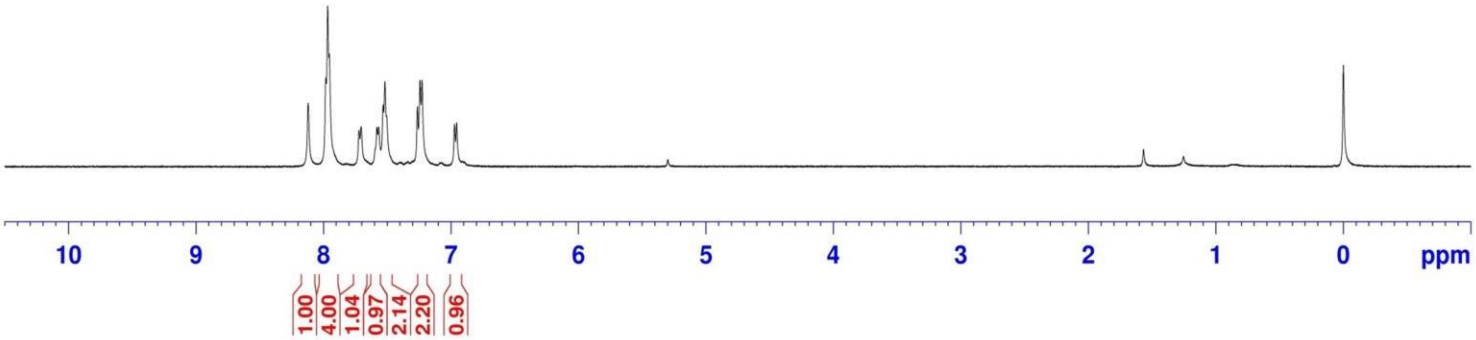




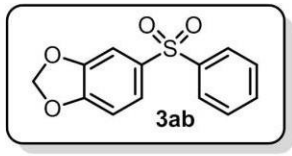
5–Chloro–2–(4–(phenylsulfonyl)phenoxy)pyridine
500 MHz, CDCl3

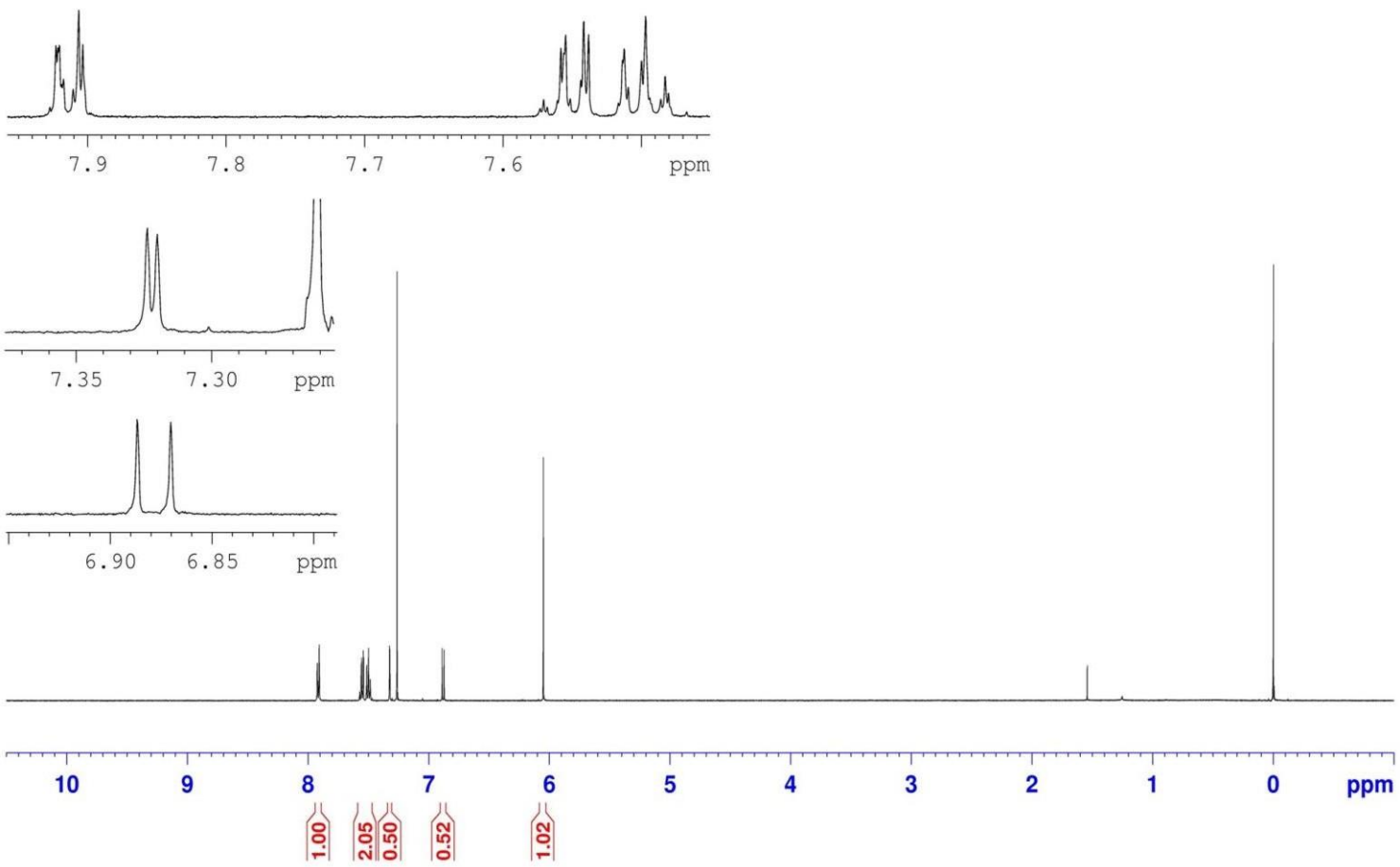




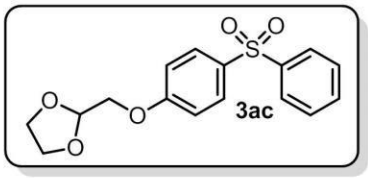


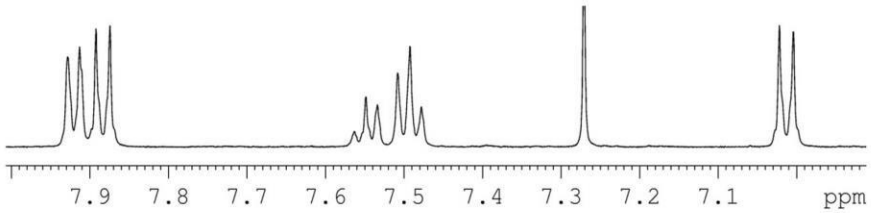
5–(Phenylsulfonyl)benzo[d][1,3]dioxole
500 MHz, CDCl3

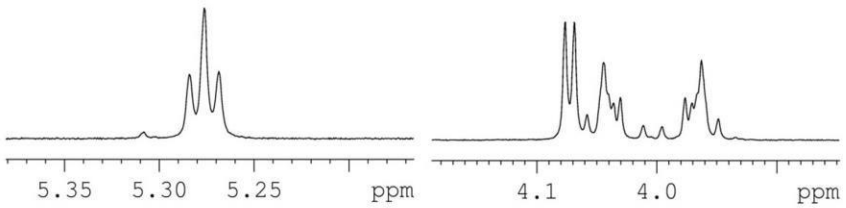


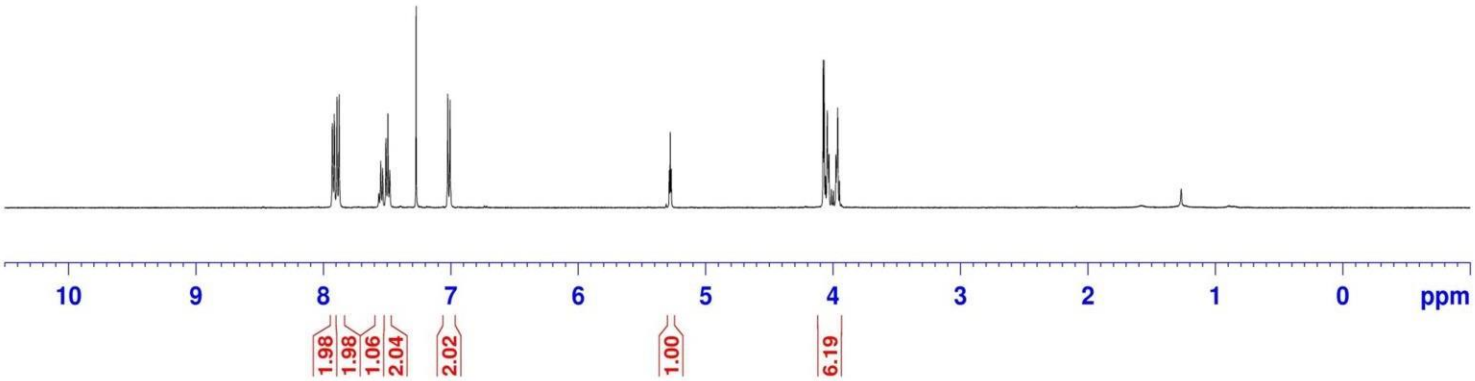


2–((4–(Phenylsulfonyl)phenoxy)methyl)–1,3–dioxolane
500 MHz, CDCl3

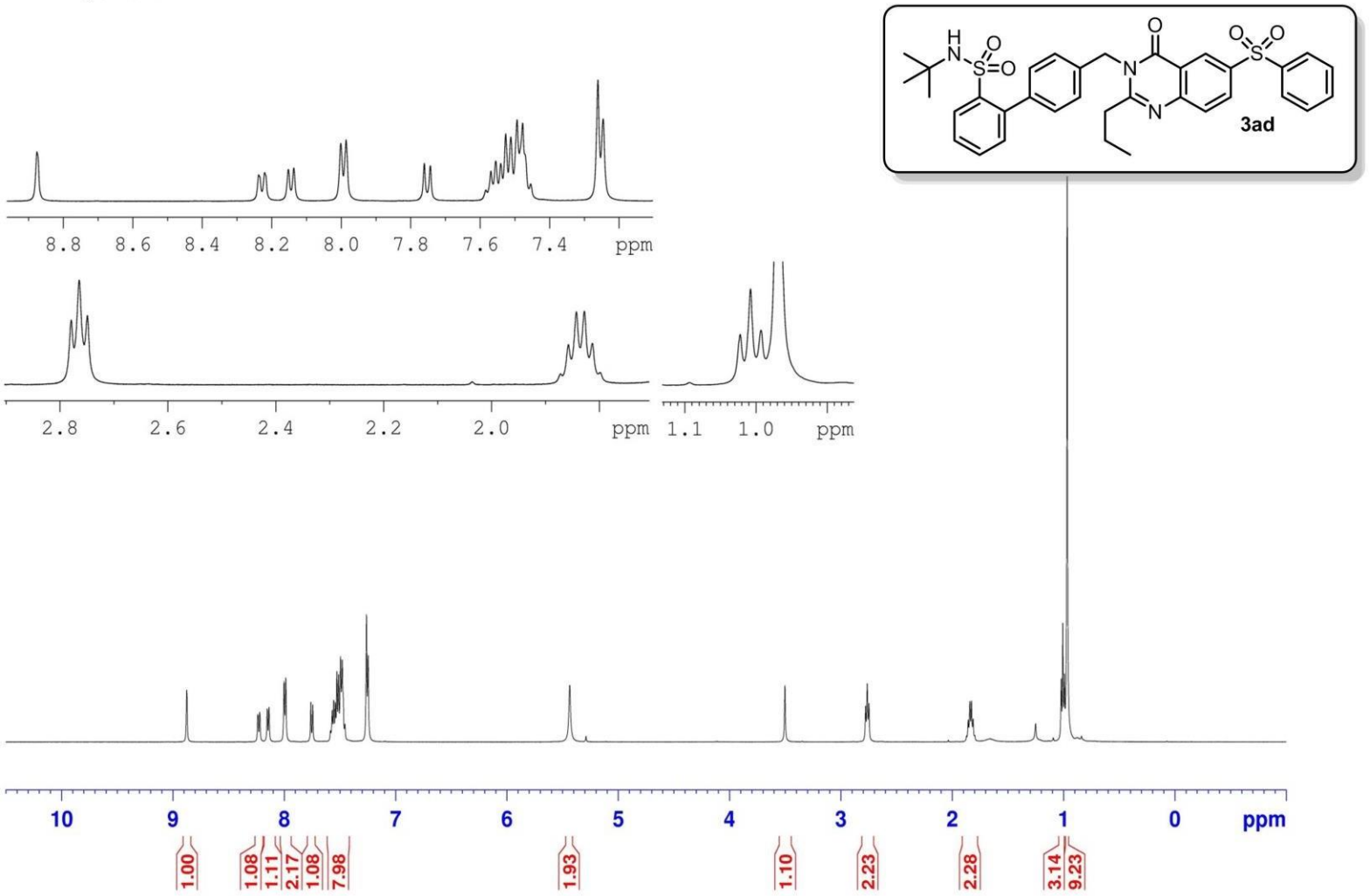




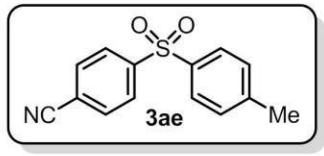


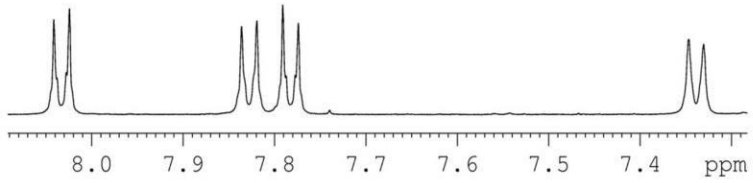


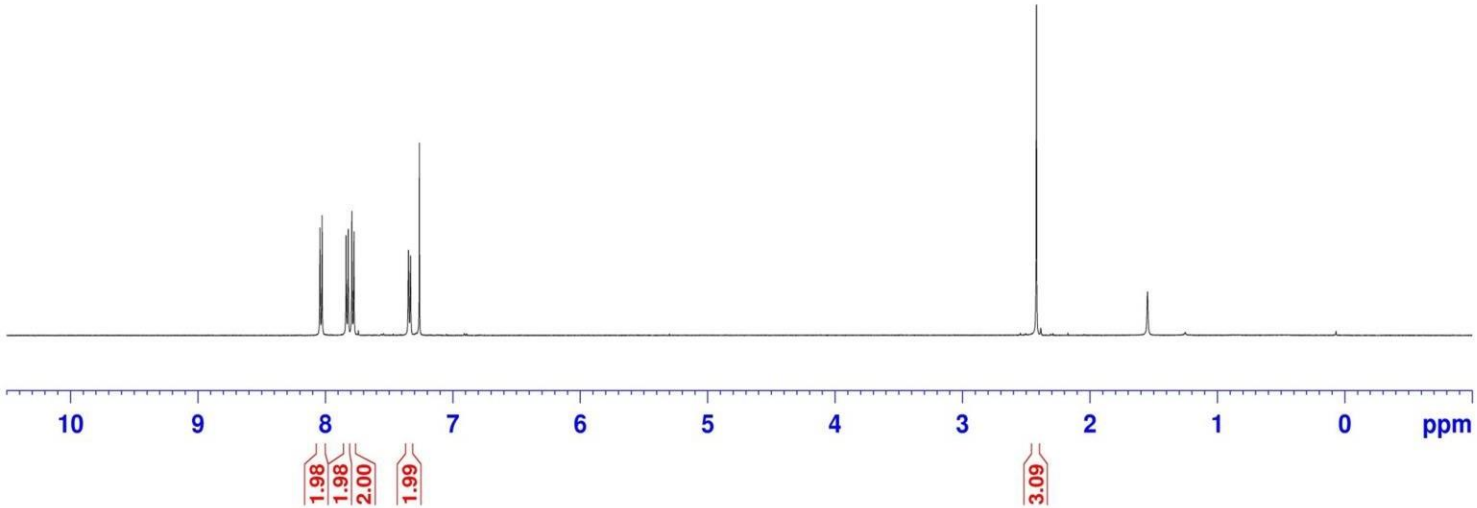
N–(Tert–butyl)–4'–((4–oxo–6–(phenylsulfonyl)–2–propylquinazolin–3(4H)–yl)methyl)–[1,1'–biphenyl]–2–sulfonamide
500 MHz, CDCl3



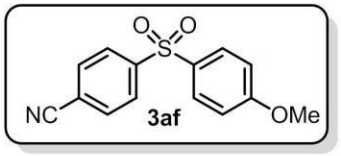
4–Tosylbenzonitrile
500 MHz, CDCl3

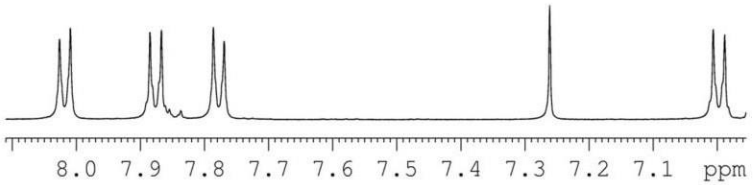


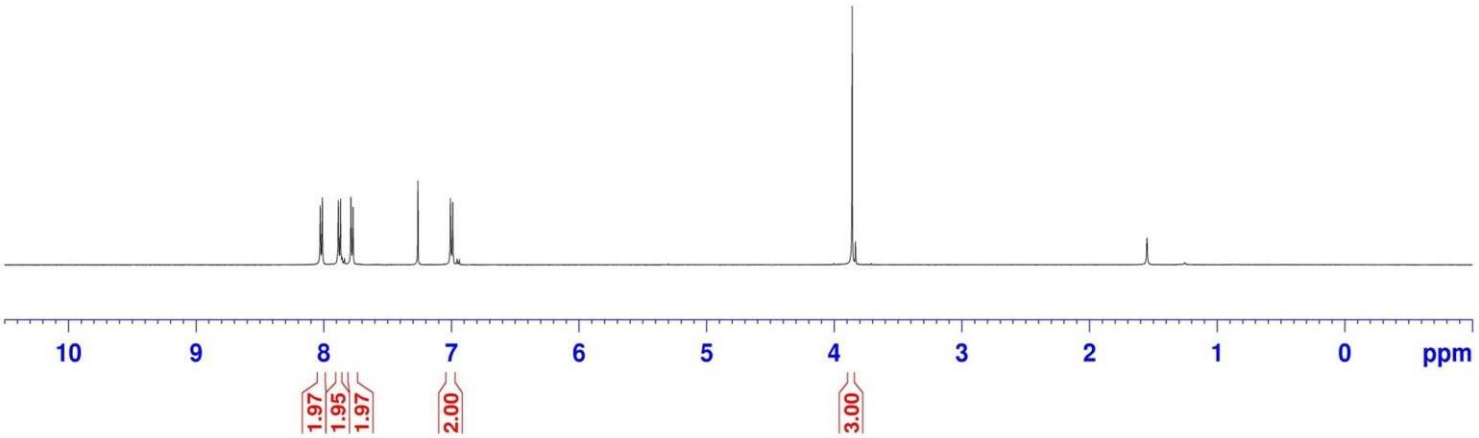




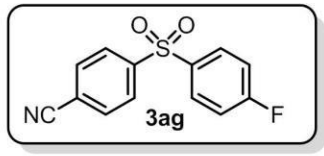
4–((4–Methoxyphenyl)sulfonyl)benzonitrile
500 MHz, CDCl3

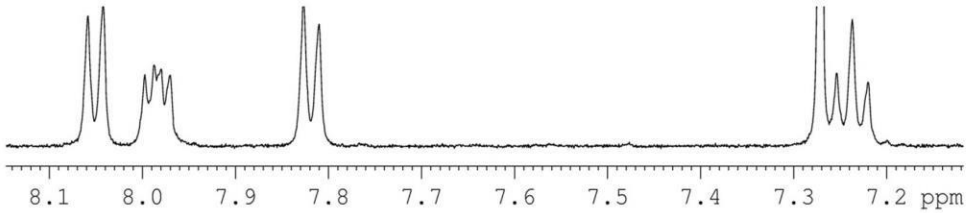


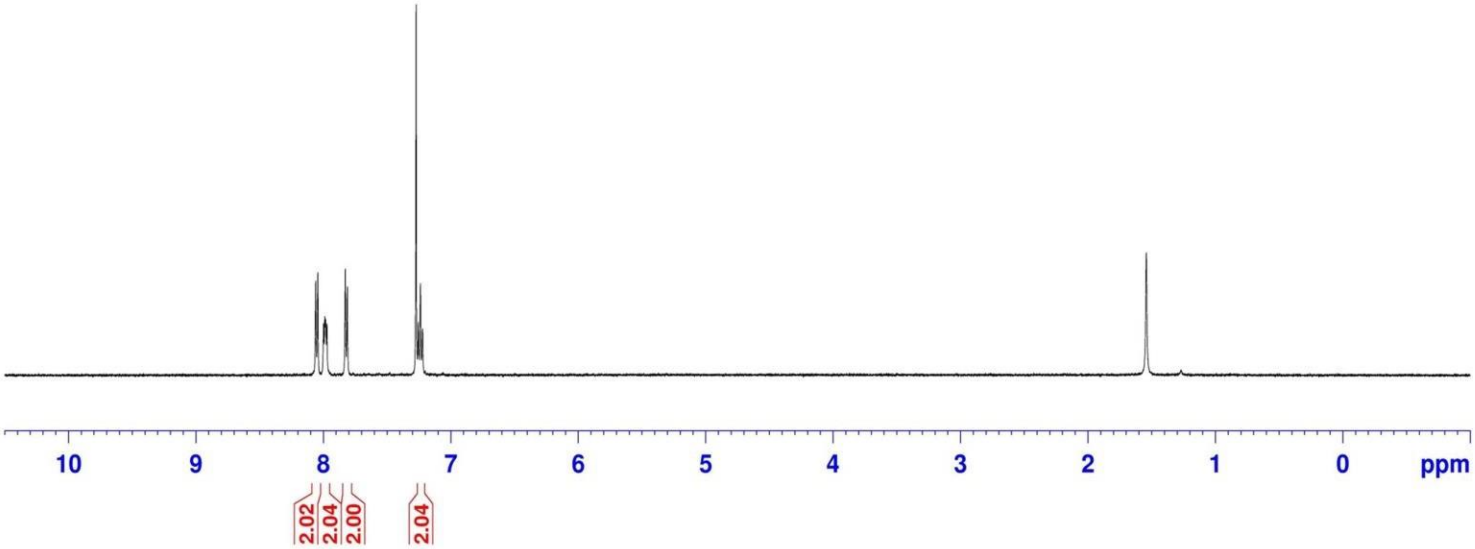




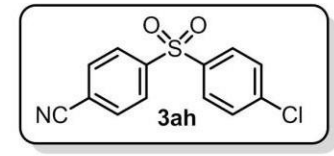
4–((4–Fluorophenyl)sulfonyl)benzonitrile
500 MHz, CDCl3

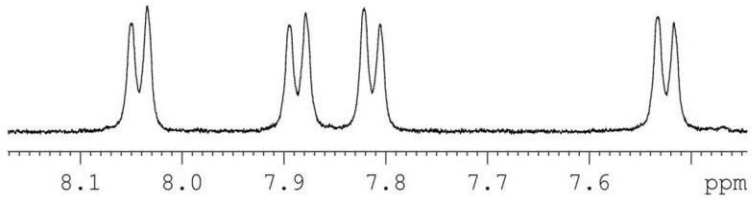


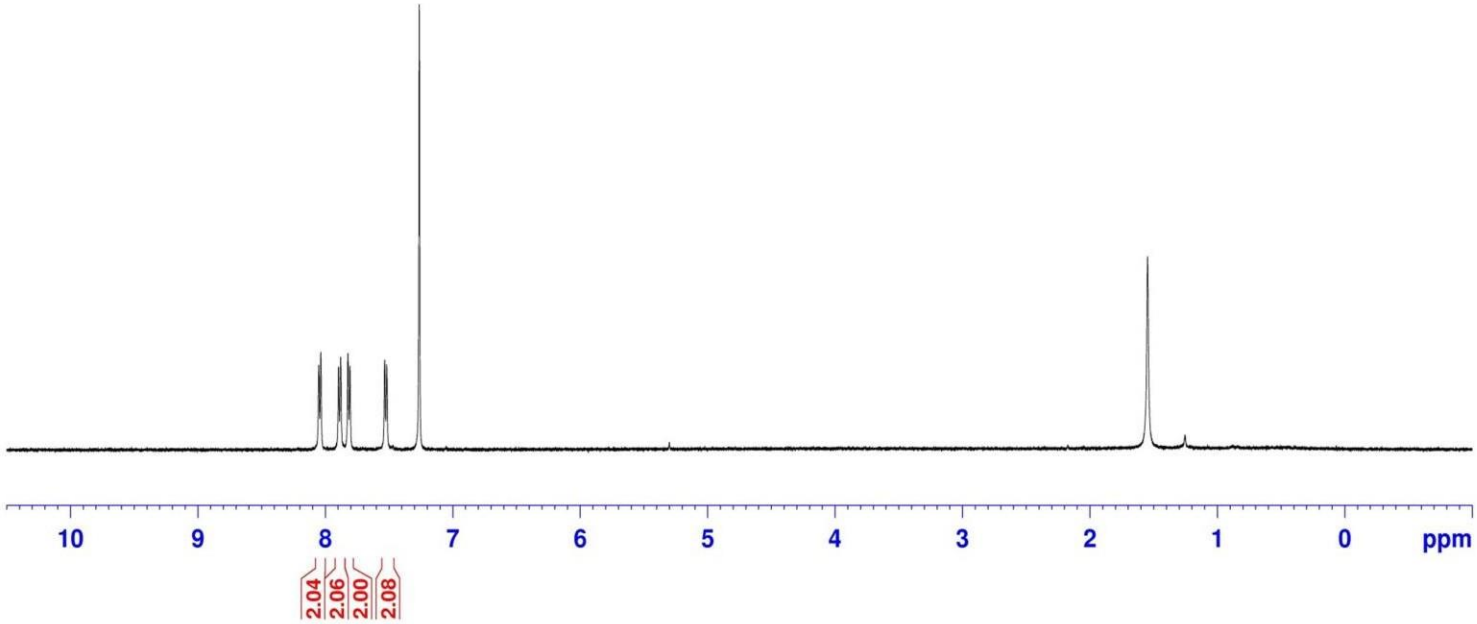




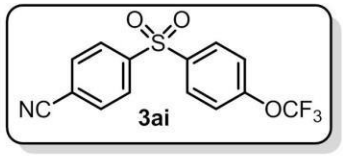
4–((4–Chlorophenyl)sulfonyl)benzonitrile
500 MHz, CDCl3

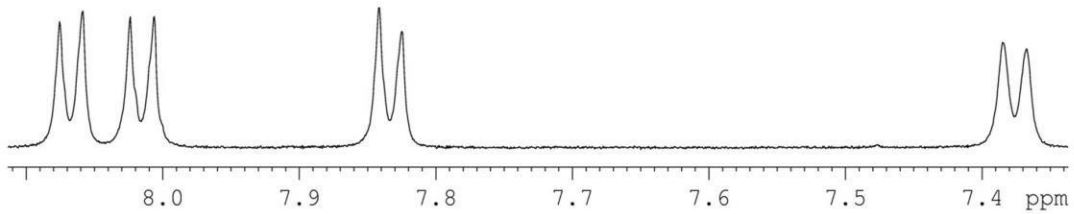


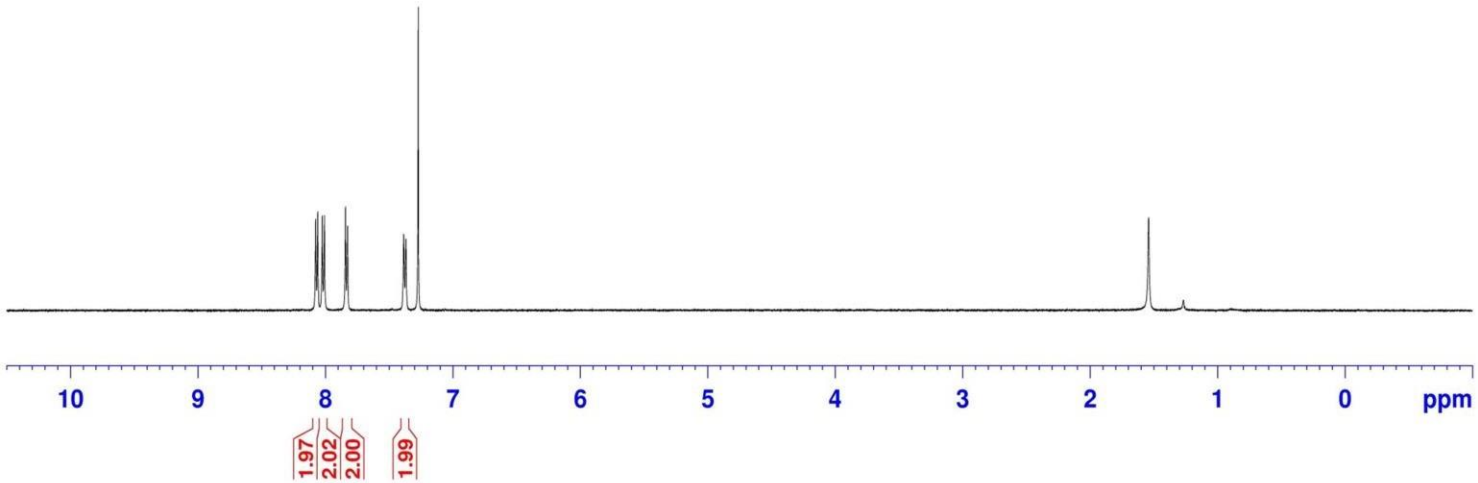




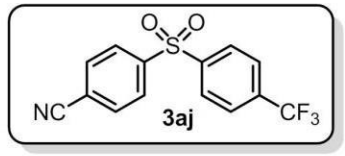
4–((4–(Trifluoromethoxy)phenyl)sulfonyl)benzonitrile
500 MHz, CDCl3

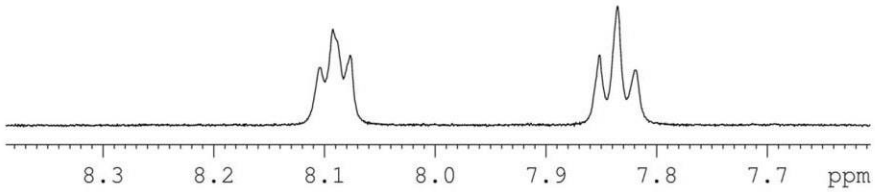


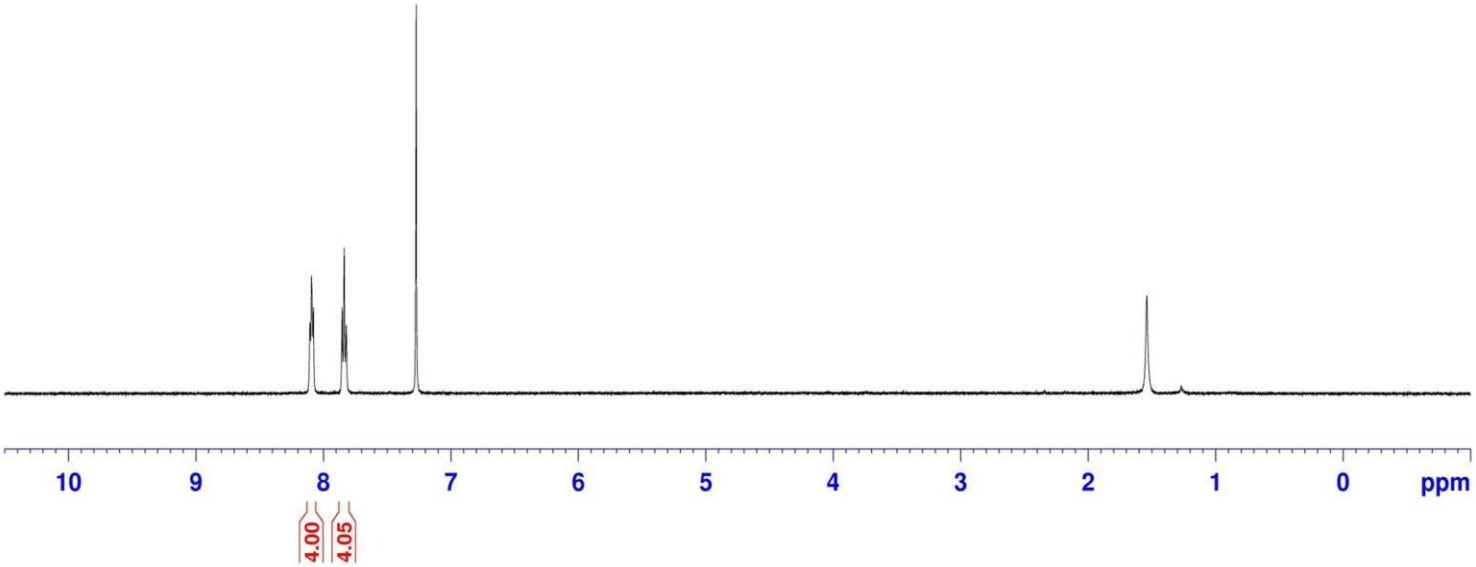




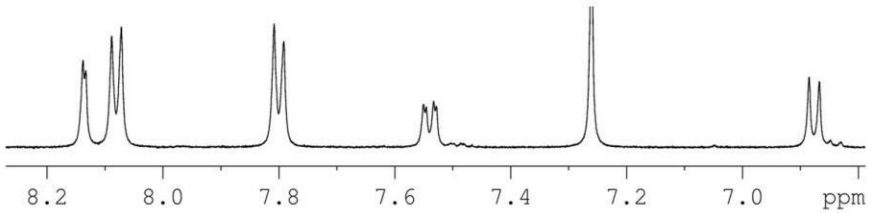
4–((4–(Trifluoromethyl)phenyl)sulfonyl)benzonitrile
500 MHz, CDCl3

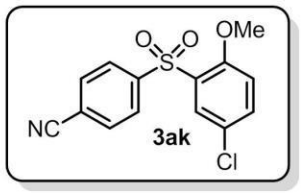


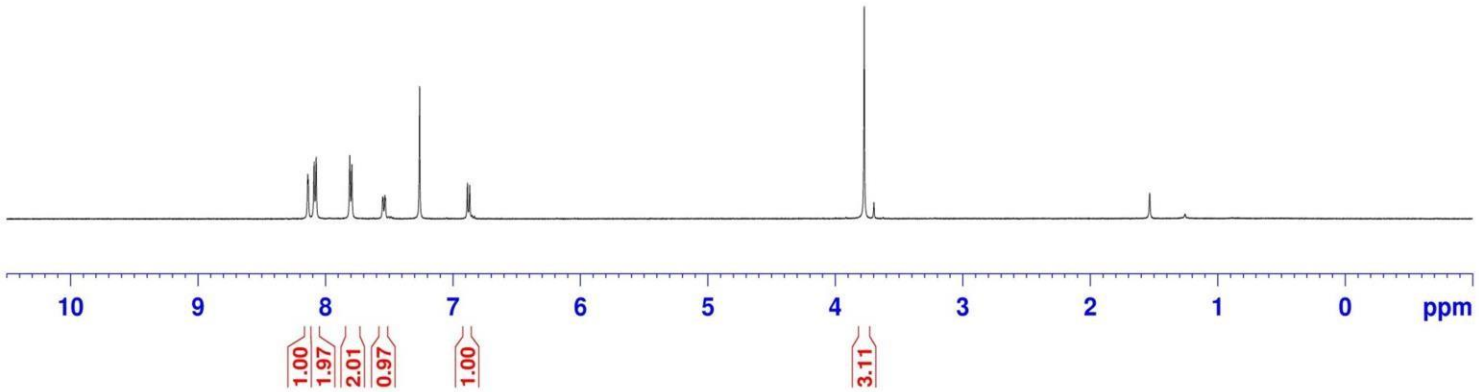




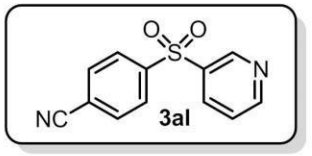
4–((5–Chloro–2–methoxyphenyl)sulfonyl)benzonitrile
500 MHz, CDCl3

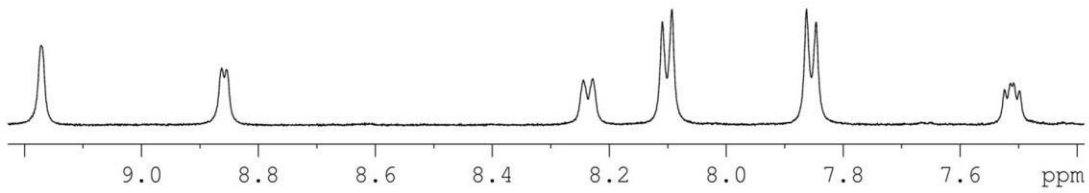


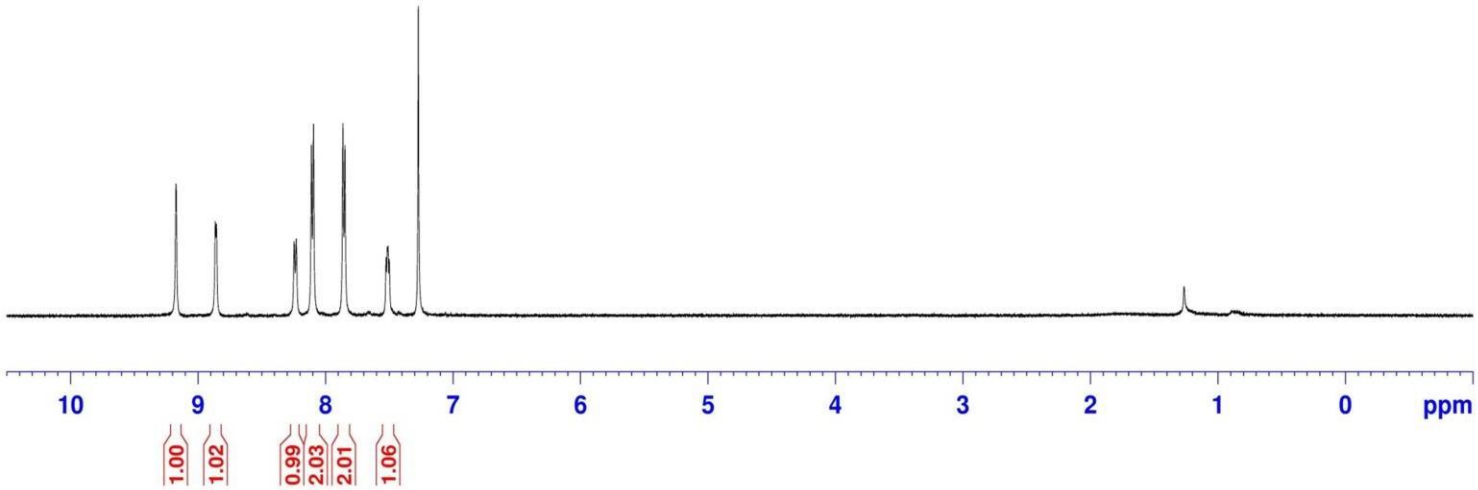




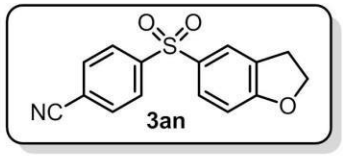
4–(Pyridin–3–ylsulfonyl)benzonitrile
500 MHz, CDCl3

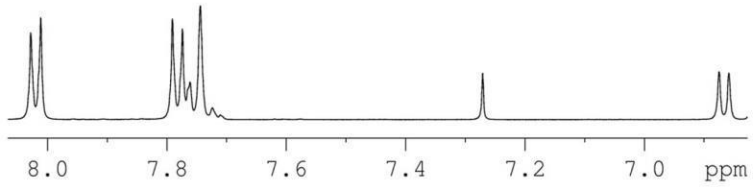


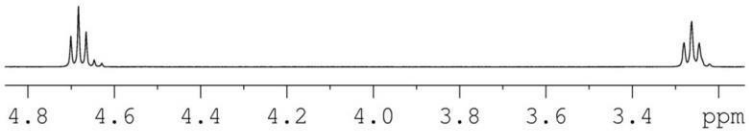


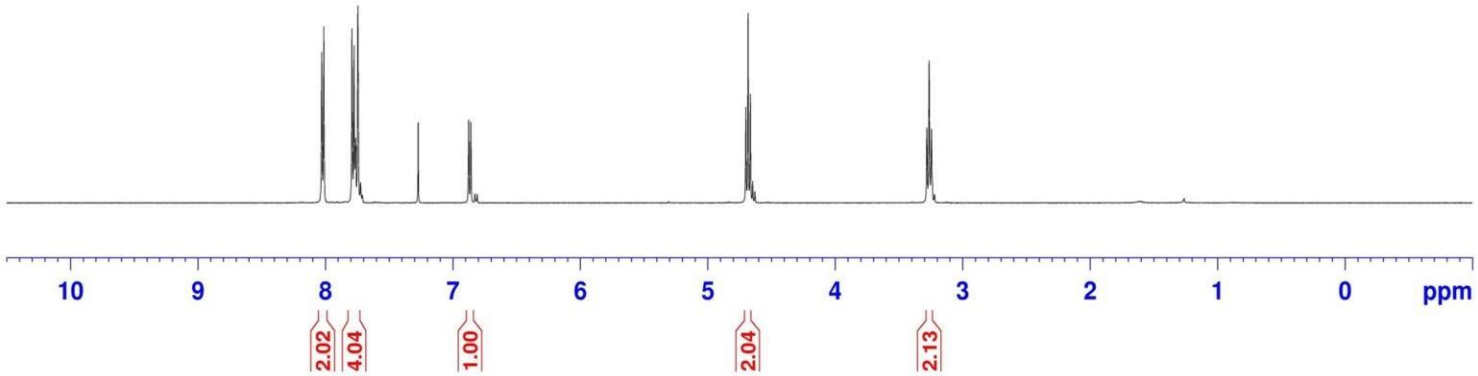


4–((2,3–Dihydrobenzofuran–5–yl)sulfonyl)benzonitrile
500 MHz, CDCl3

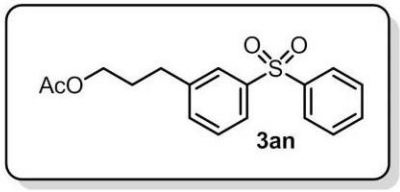


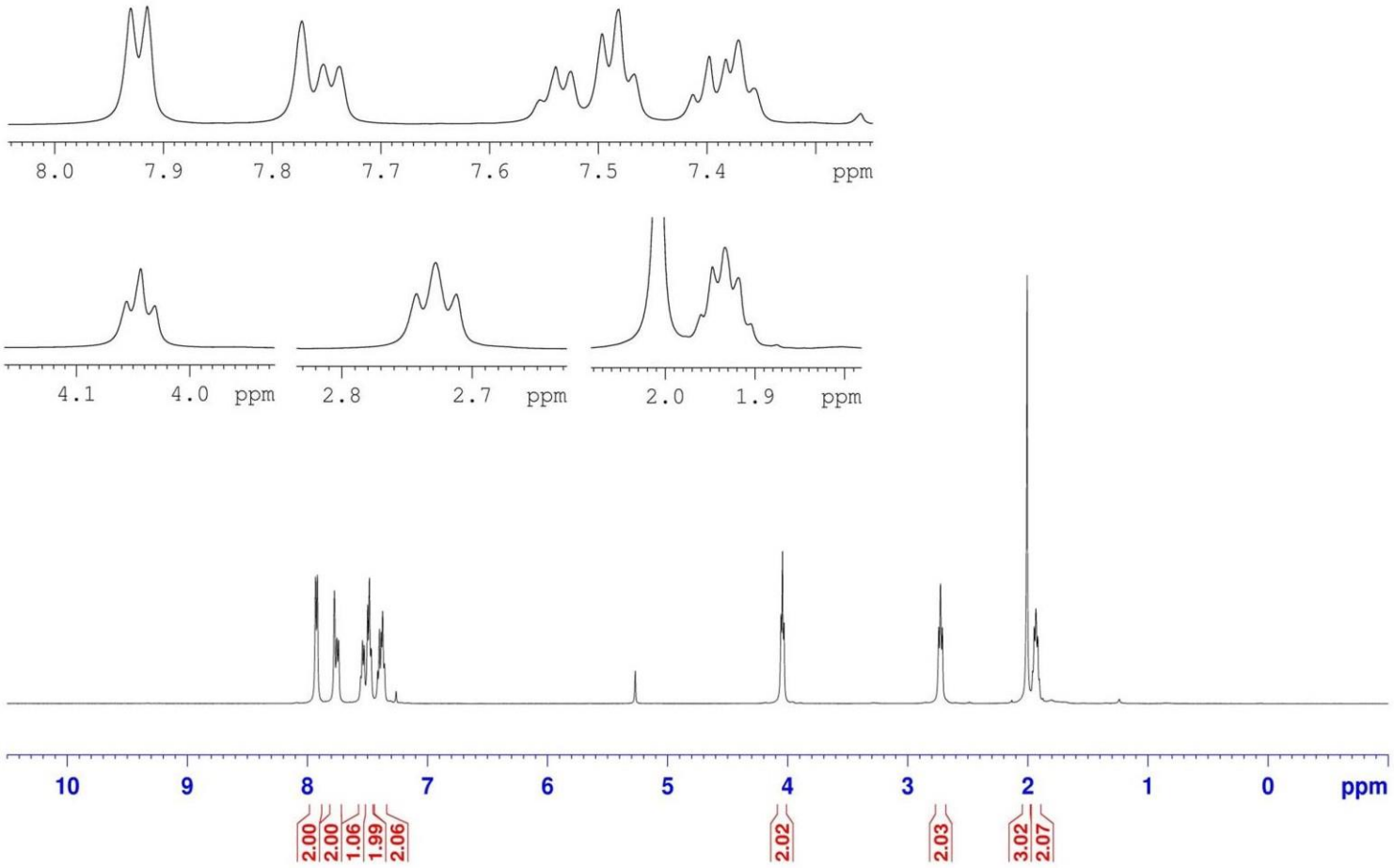




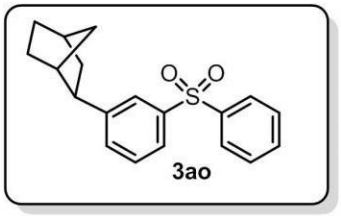


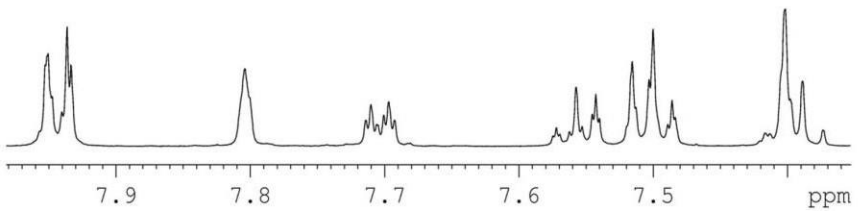
3–(3–(Phenylsulfonyl)phenyl)propyl Acetate
500 MHz, CDCl3

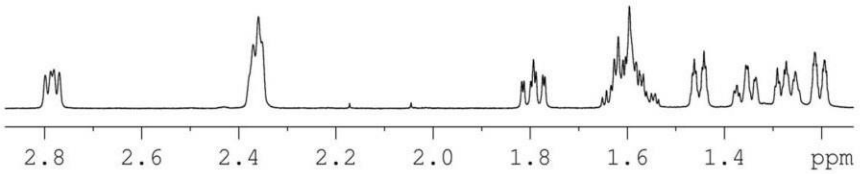


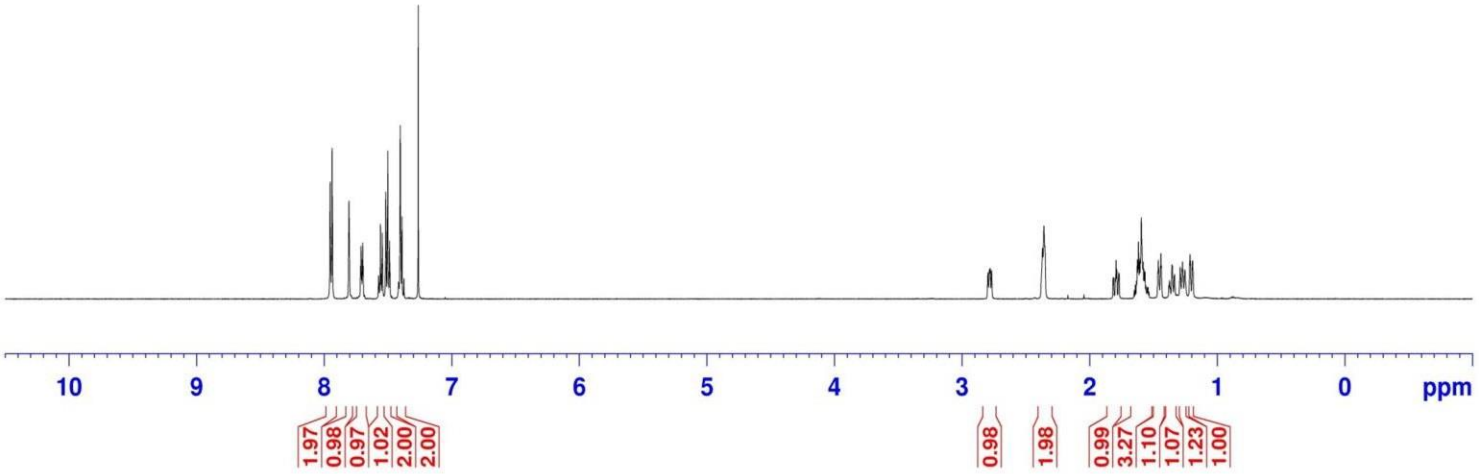


(±)−2−(3−(Phenylsulfonyl)phenyl)bicyclo[2.2.1]heptane
500 MHz, CDCl3

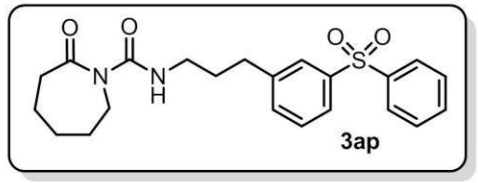


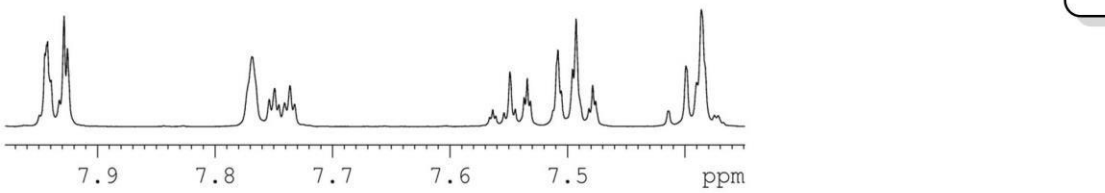


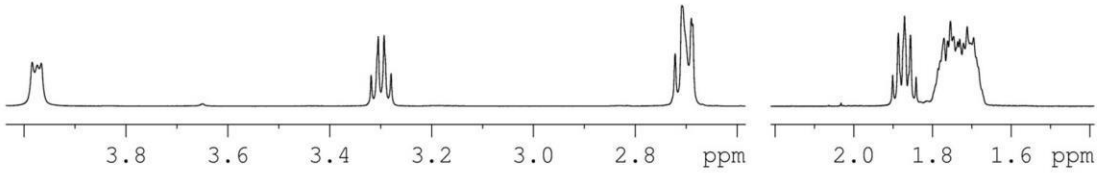


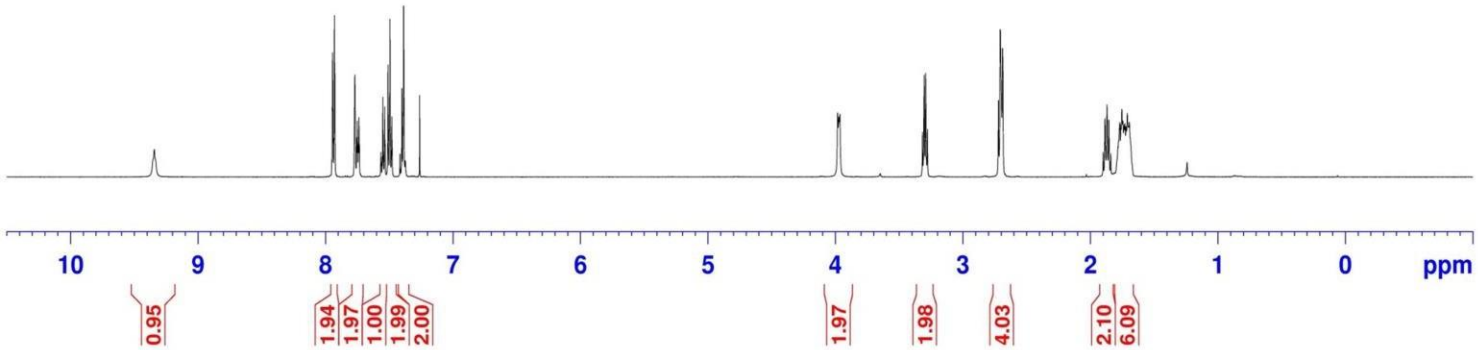


2-Oxo-N-(3-(3-(phenylsulfonyl)phenyl)propyl)azepane-1-carboxamide
500 MHz, CDCl3

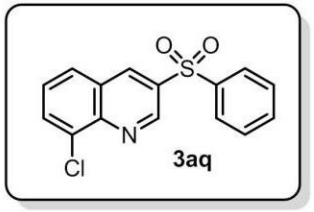


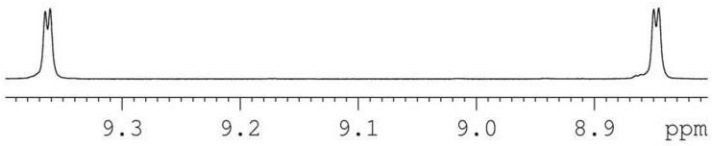


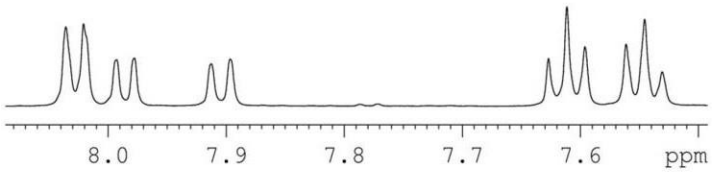


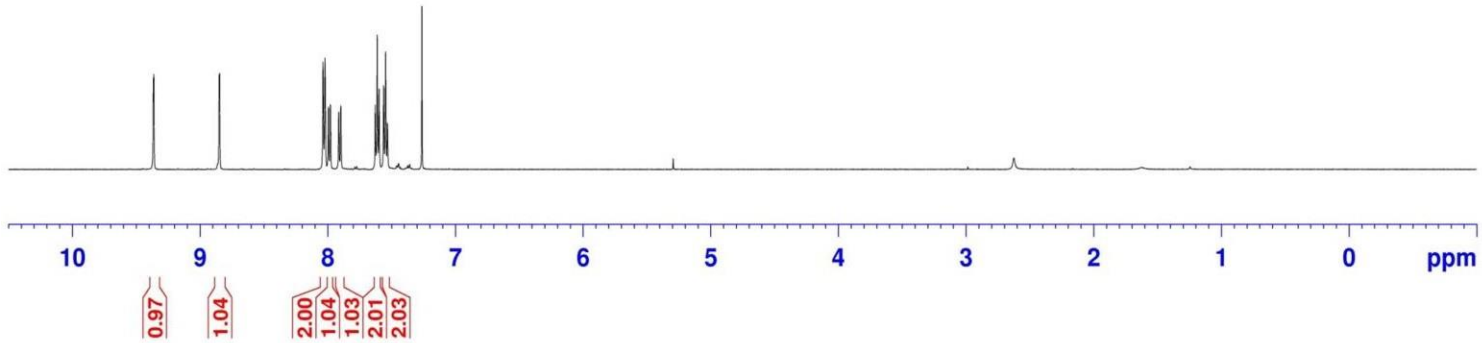


8–Chloro–3–(phenylsulfonyl)quinoline
500 MHz, CDCl3

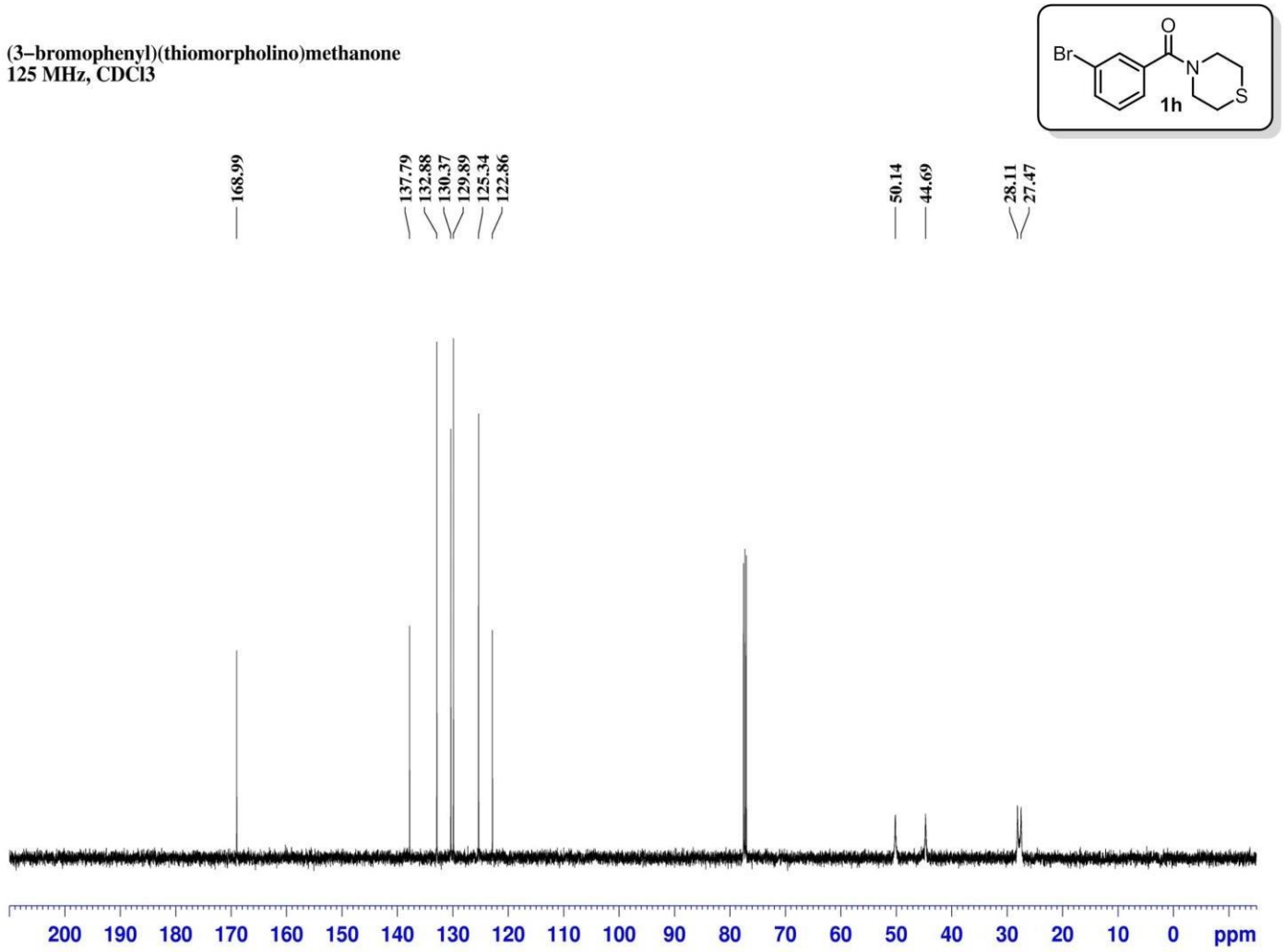




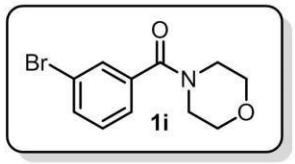


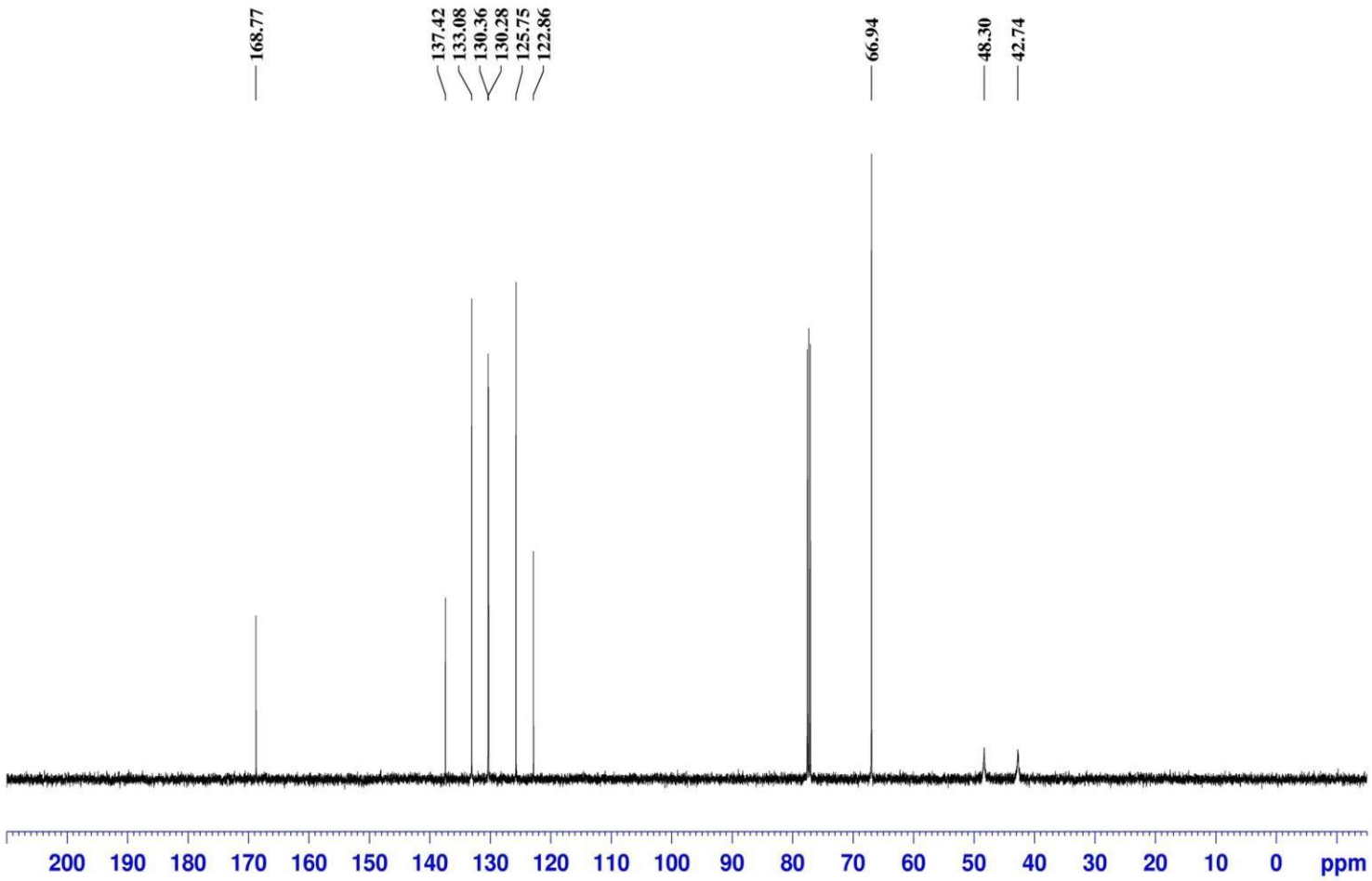


^{13}C NMR Spectra of Synthesized Compounds

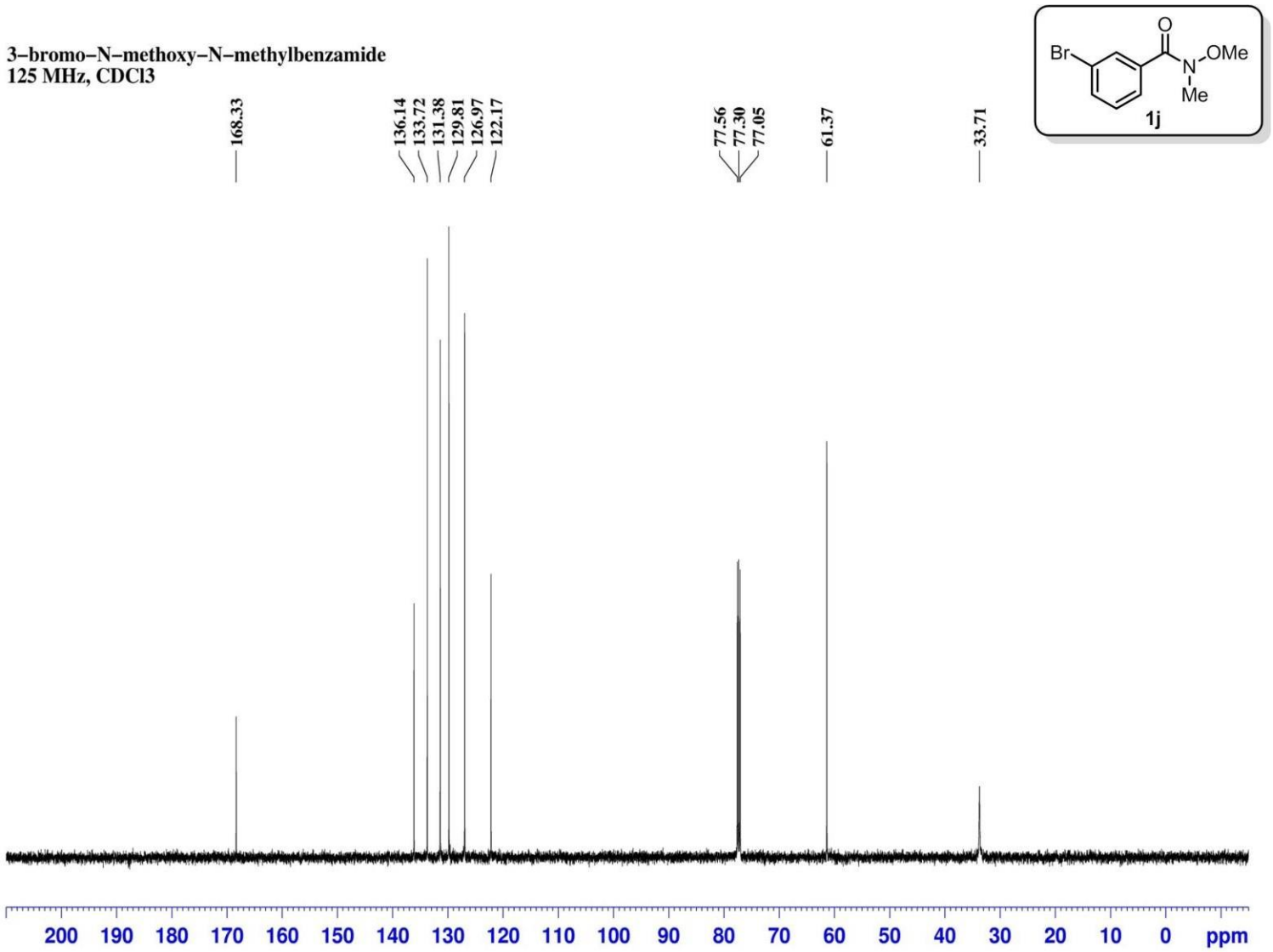


(3–bromophenyl)(morpholino)methanone
125 MHz, CDCl3

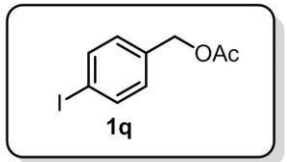




3–bromo–N–methoxy–N–methylbenzamide
125 MHz, CDCl3



4–Iodobenzyl Acetate
125 MHz, CDCl3



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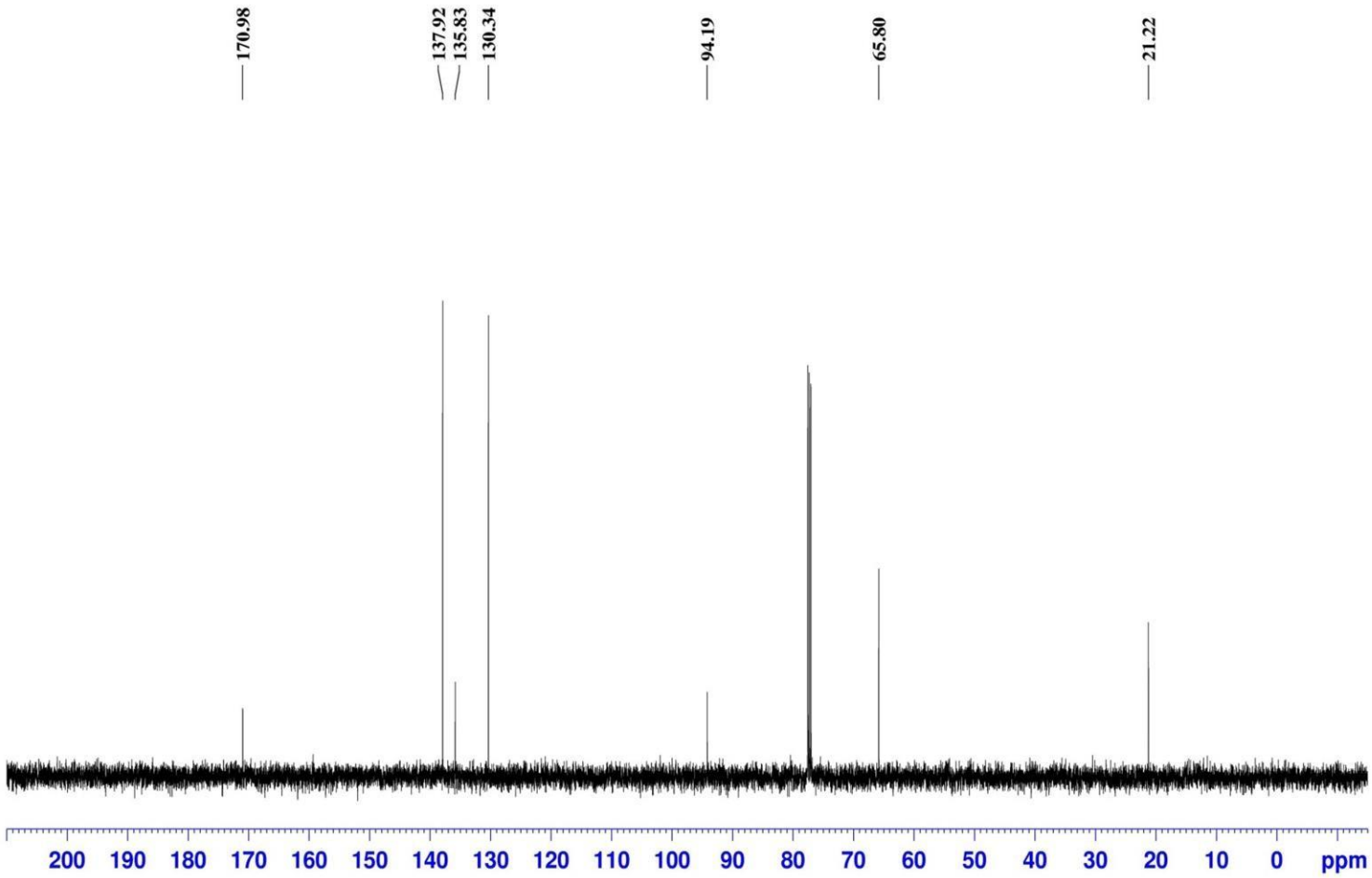
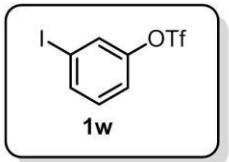
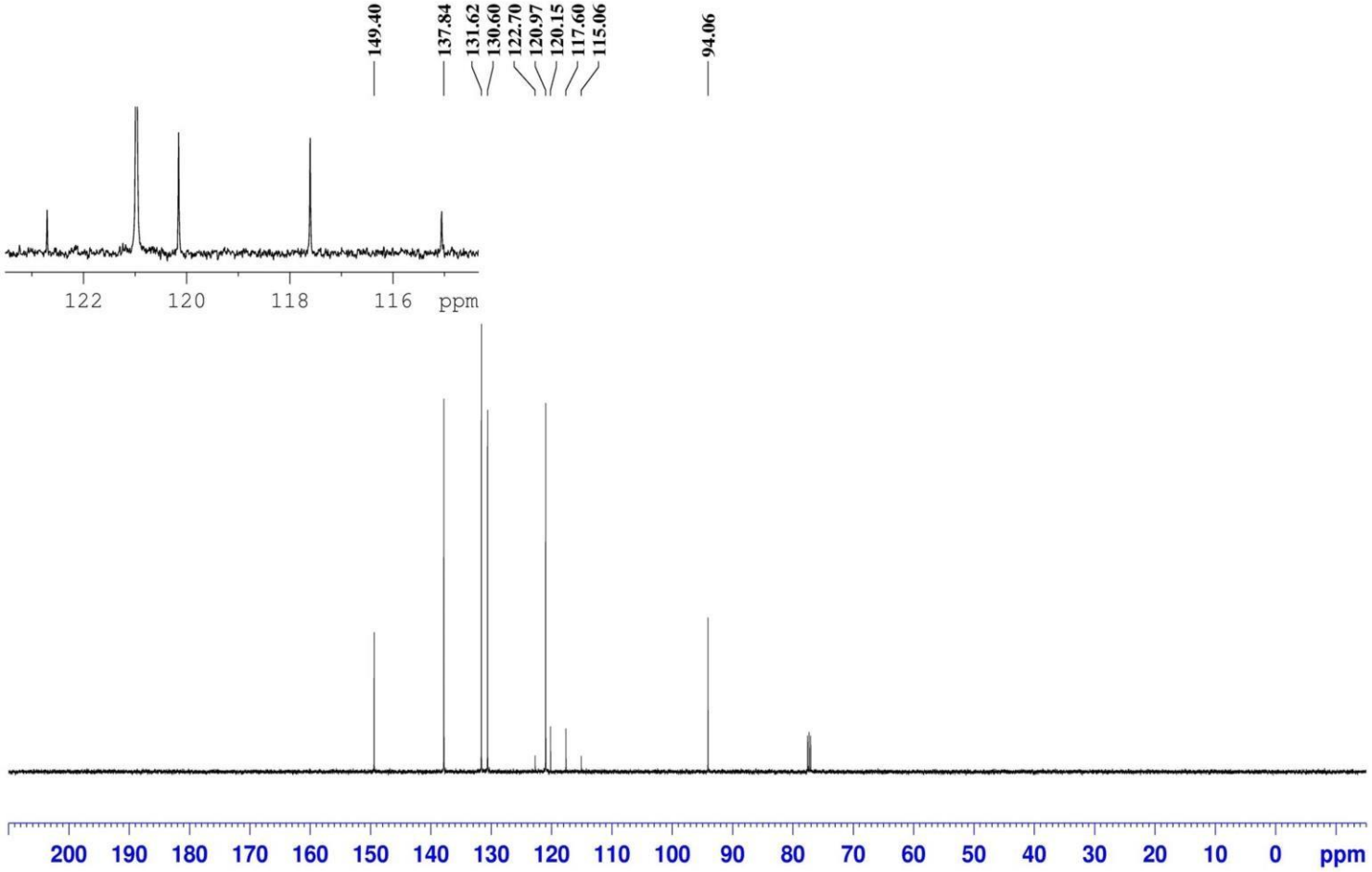
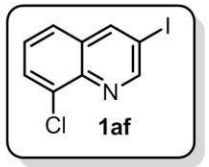


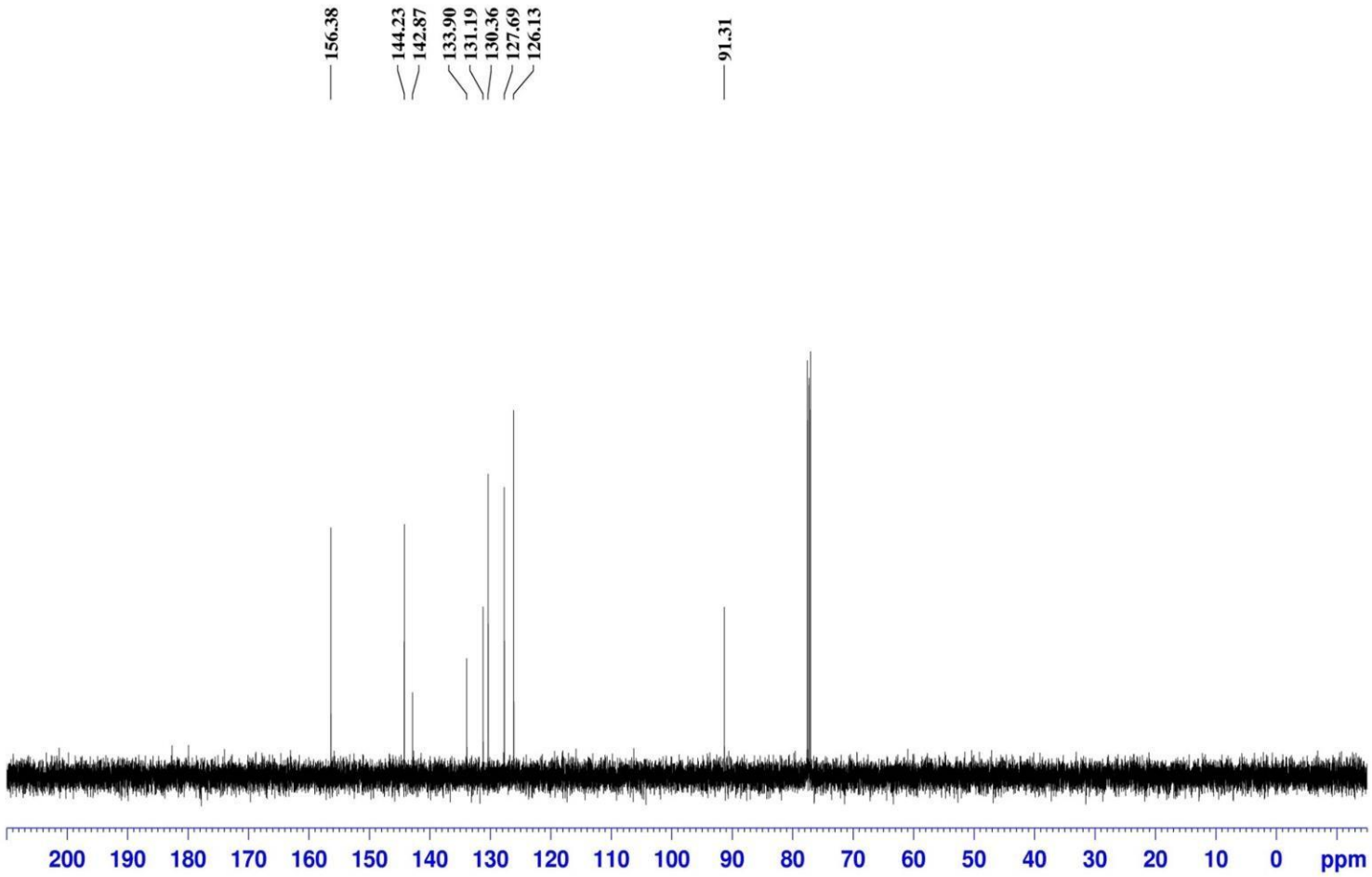
3–iodophenyl trifluoromethanesulfonate
125 MHz, CDCl3



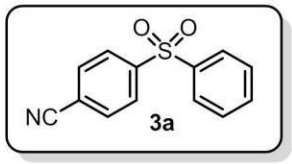


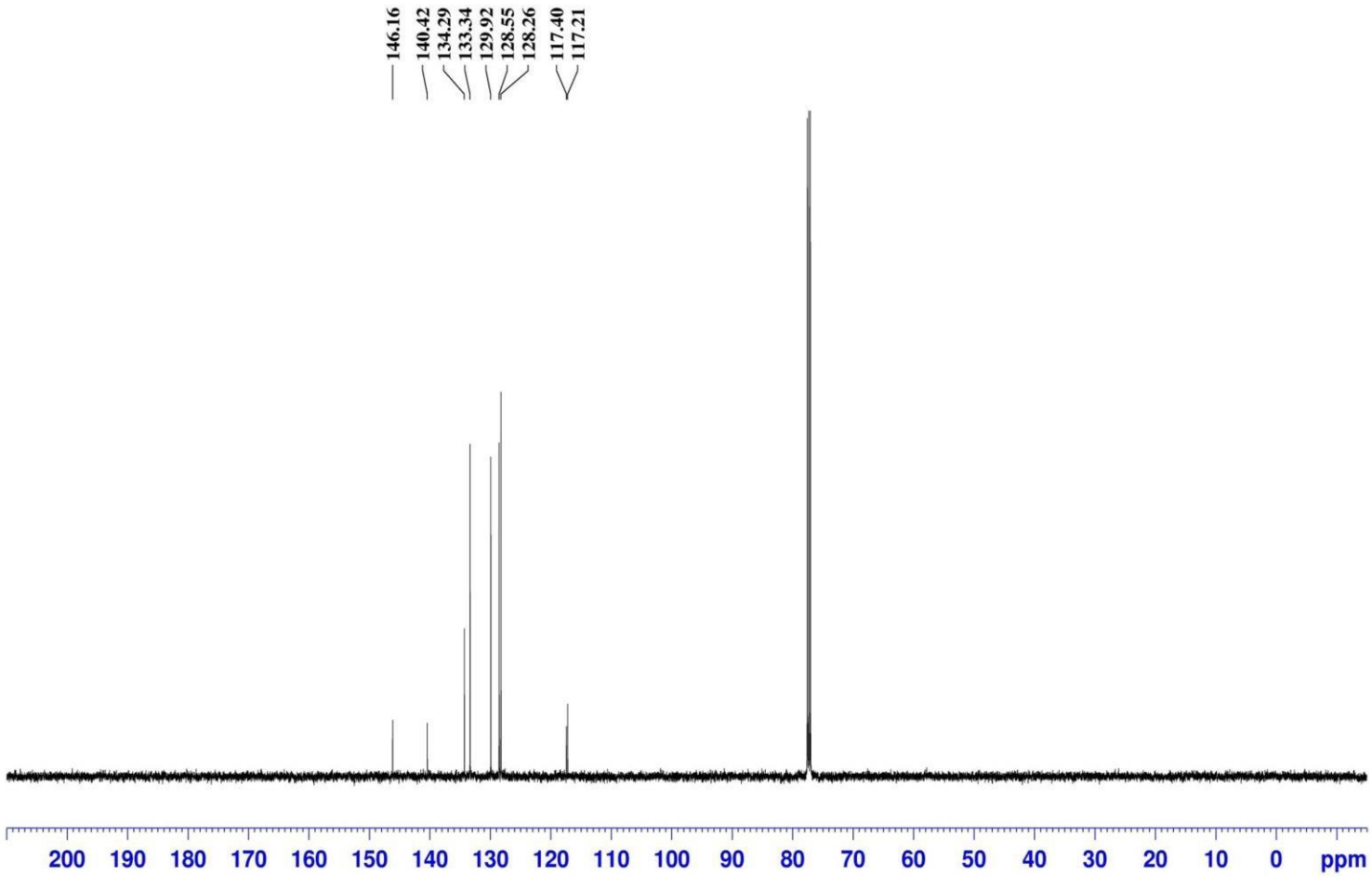
8–Chloro–3–iodoquinoline
125 MHz, CDCl3



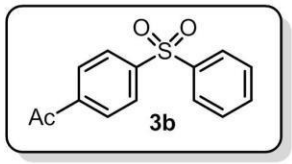


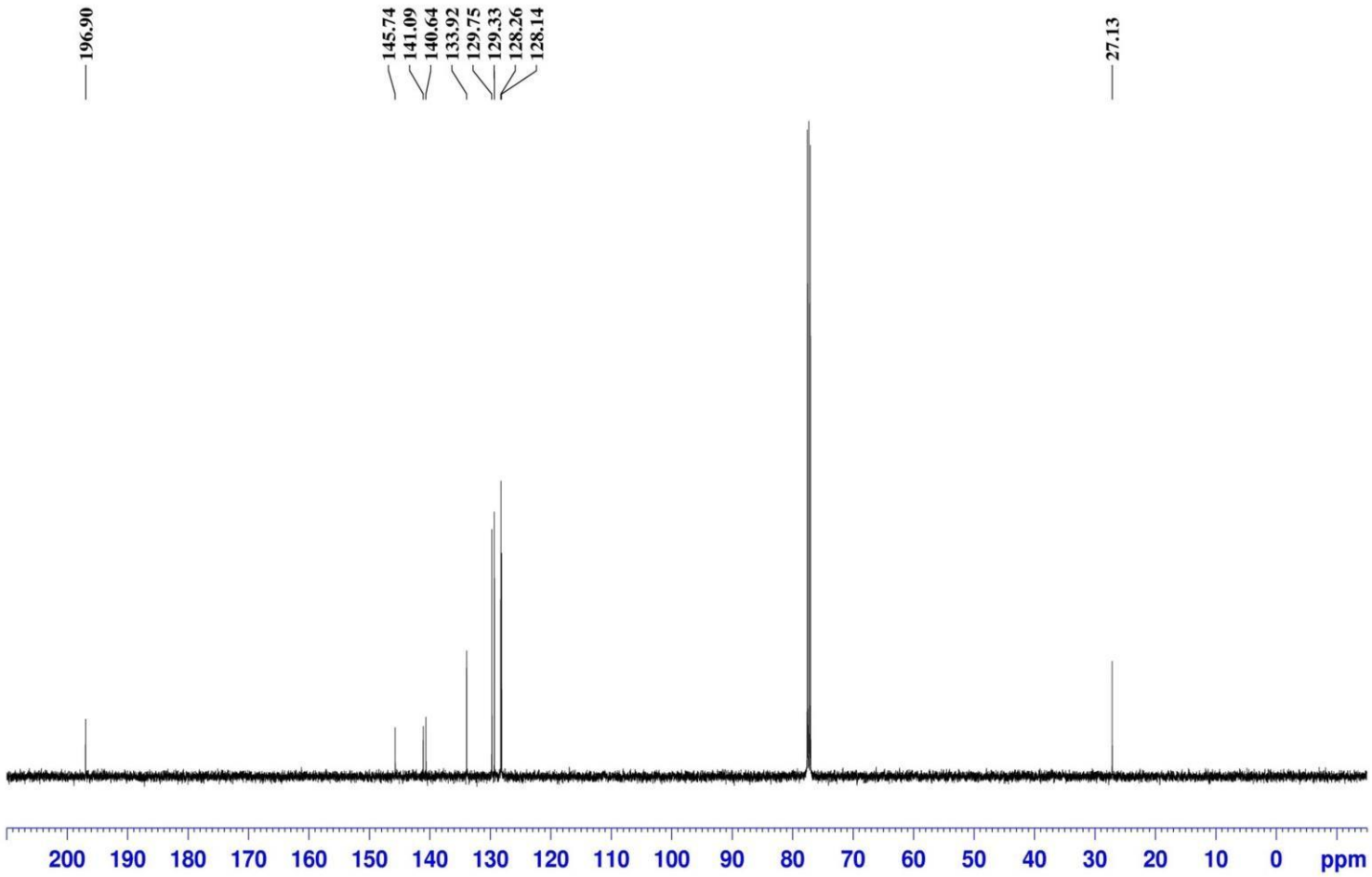
4–(Phenylsulfonyl)benzonitrile
125 MHz, CDCl3



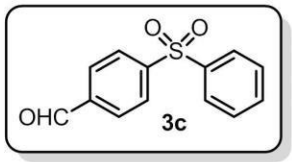


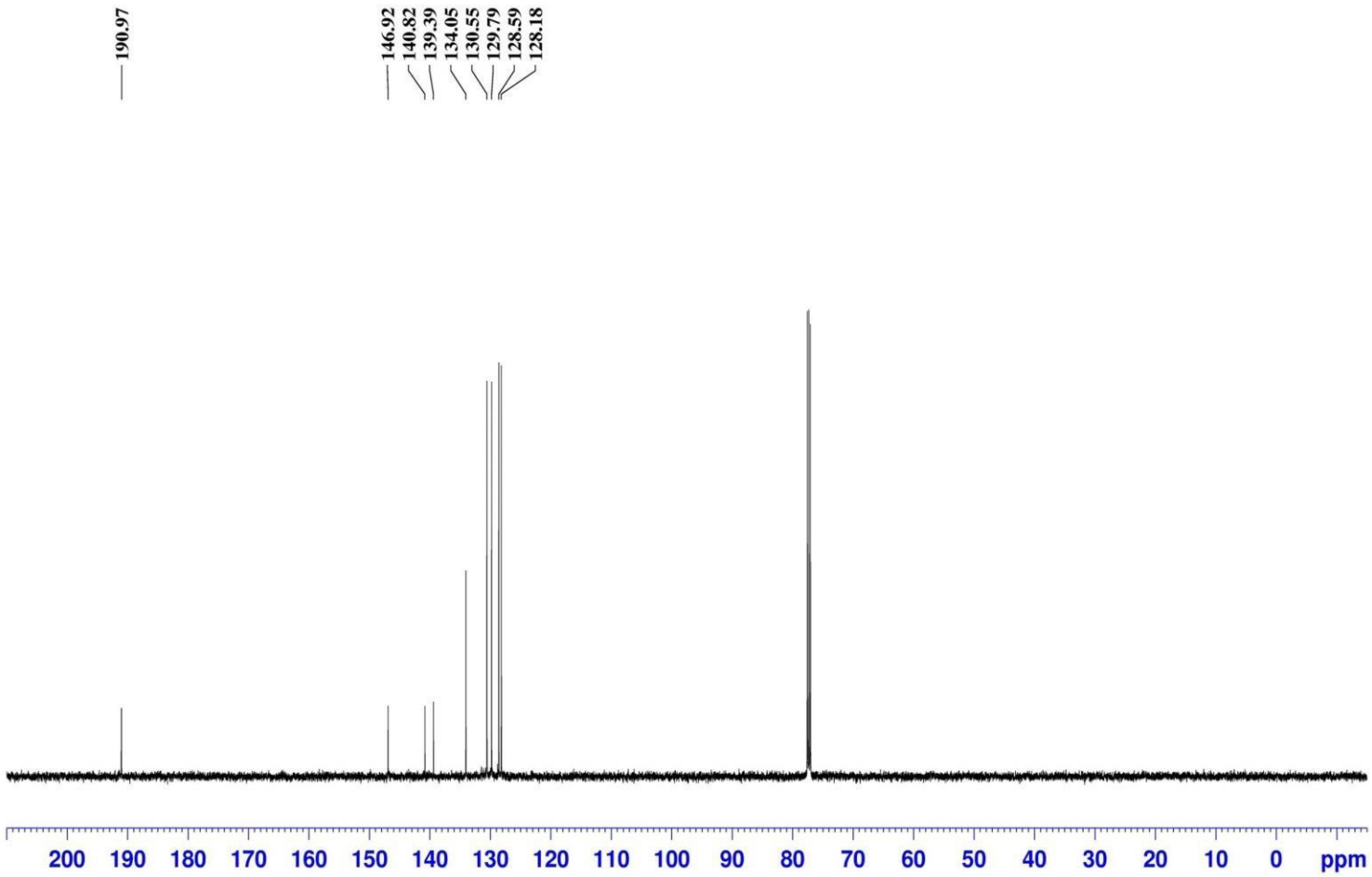
1–(4–(Phenylsulfonyl)phenyl)ethanone
125 MHz, CDCl3



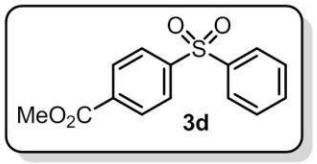


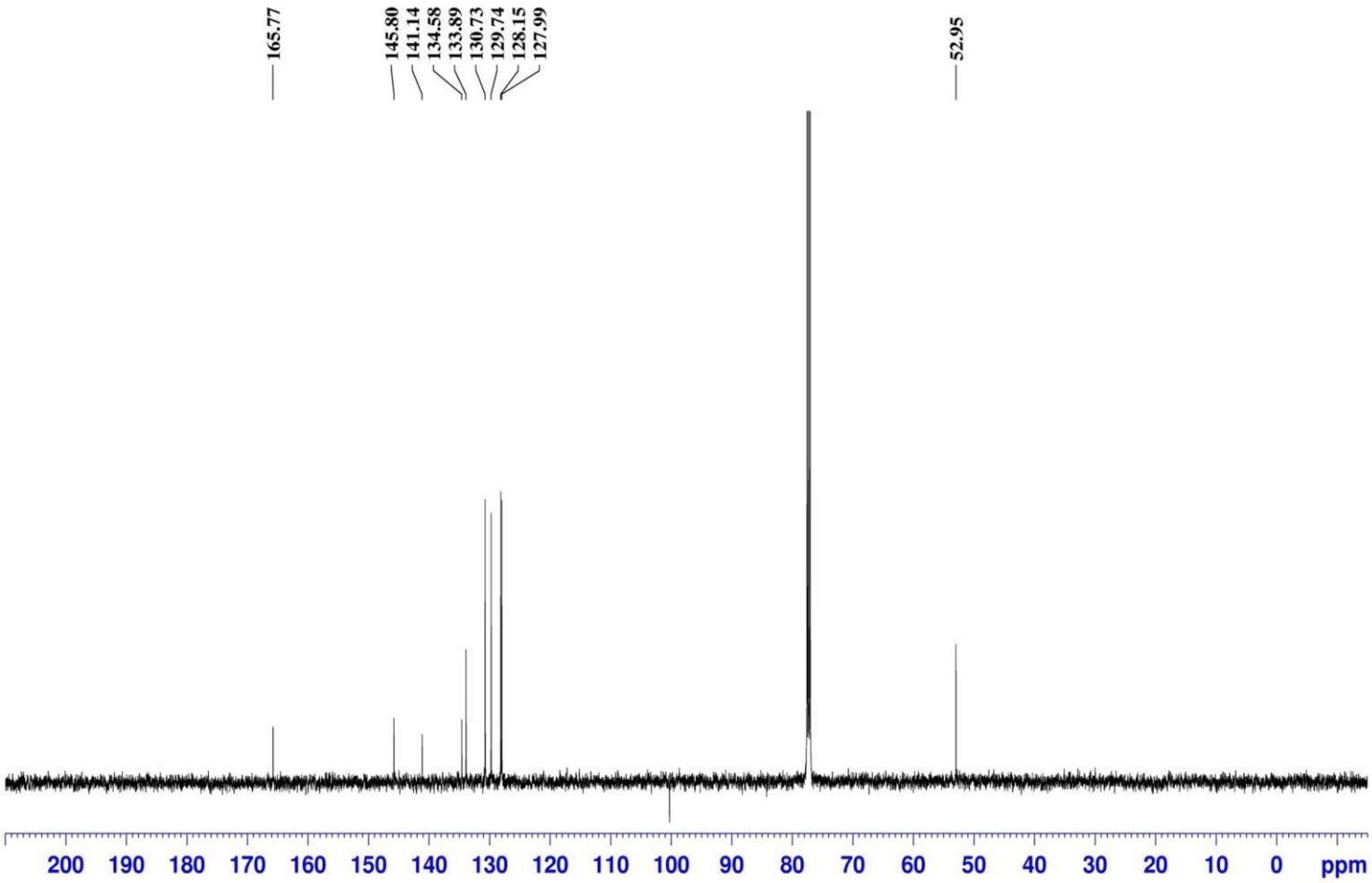
4–(Phenylsulfonyl)benzaldehyde
125 MHz, CDCl3



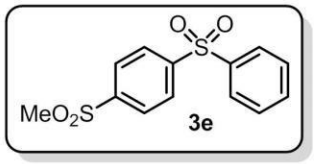


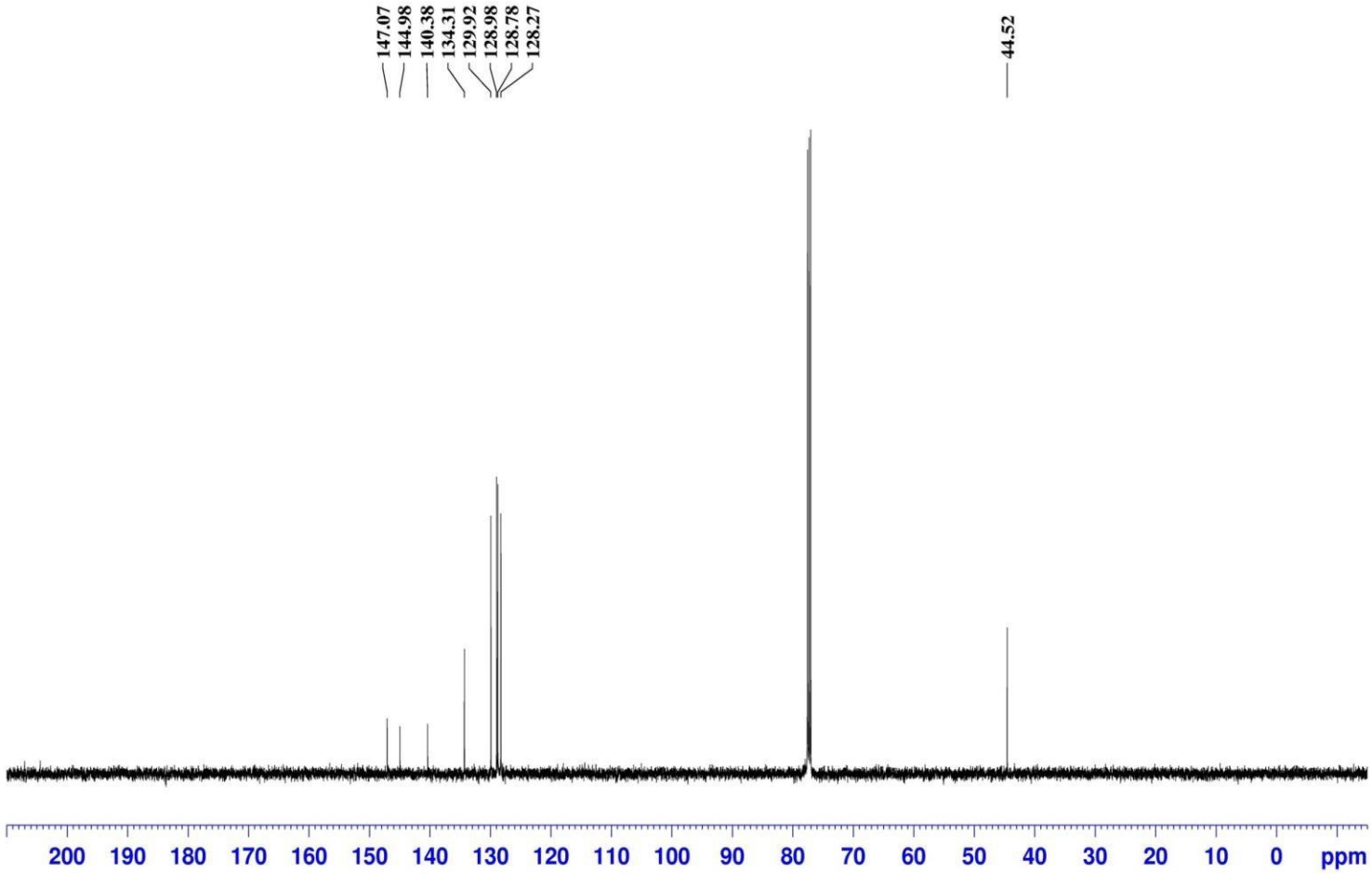
Methyl 4–(Phenylsulfonyl)benzoate
125 MHz, CDCl3



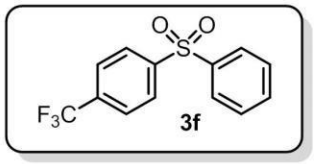


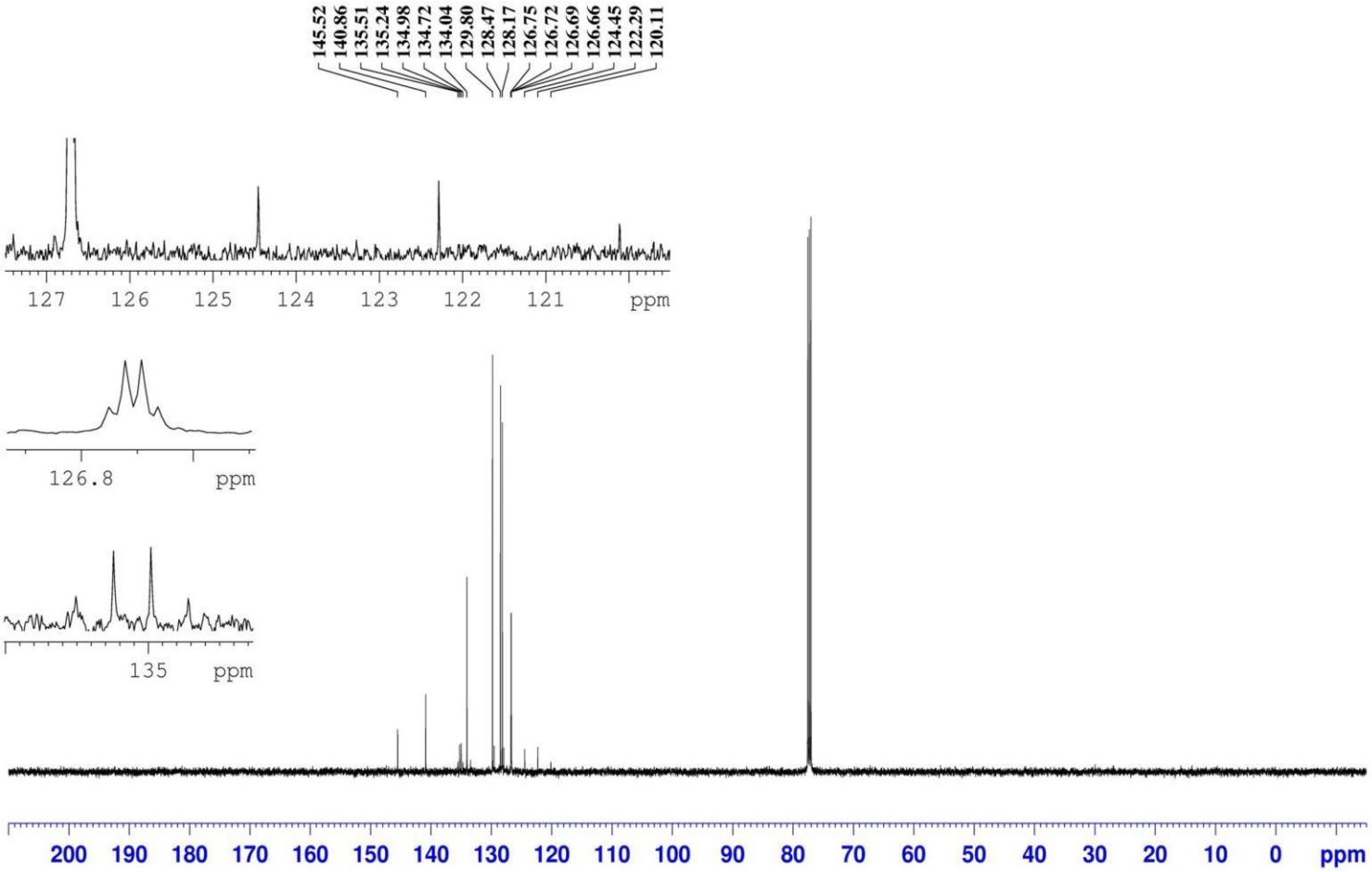
1–(Methylsulfonyl)–4–(phenylsulfonyl)benzene
125 MHz, CDCl3



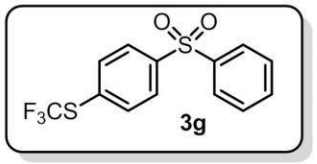


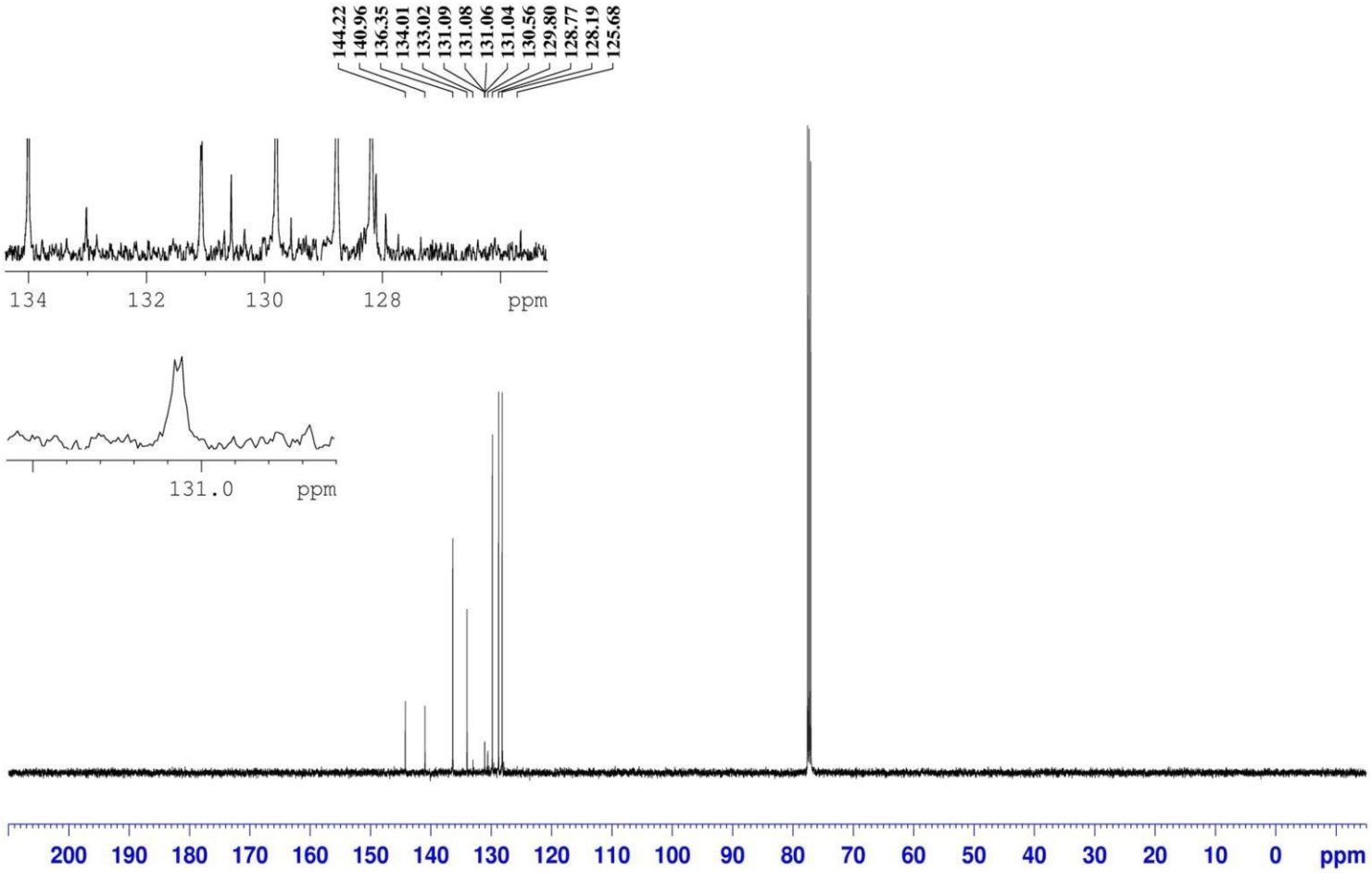
1–(Phenylsulfonyl)–4–(trifluoromethyl)benzene
125 MHz, CDCl3



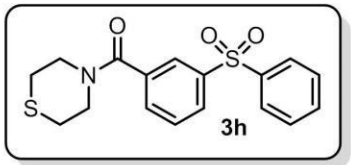


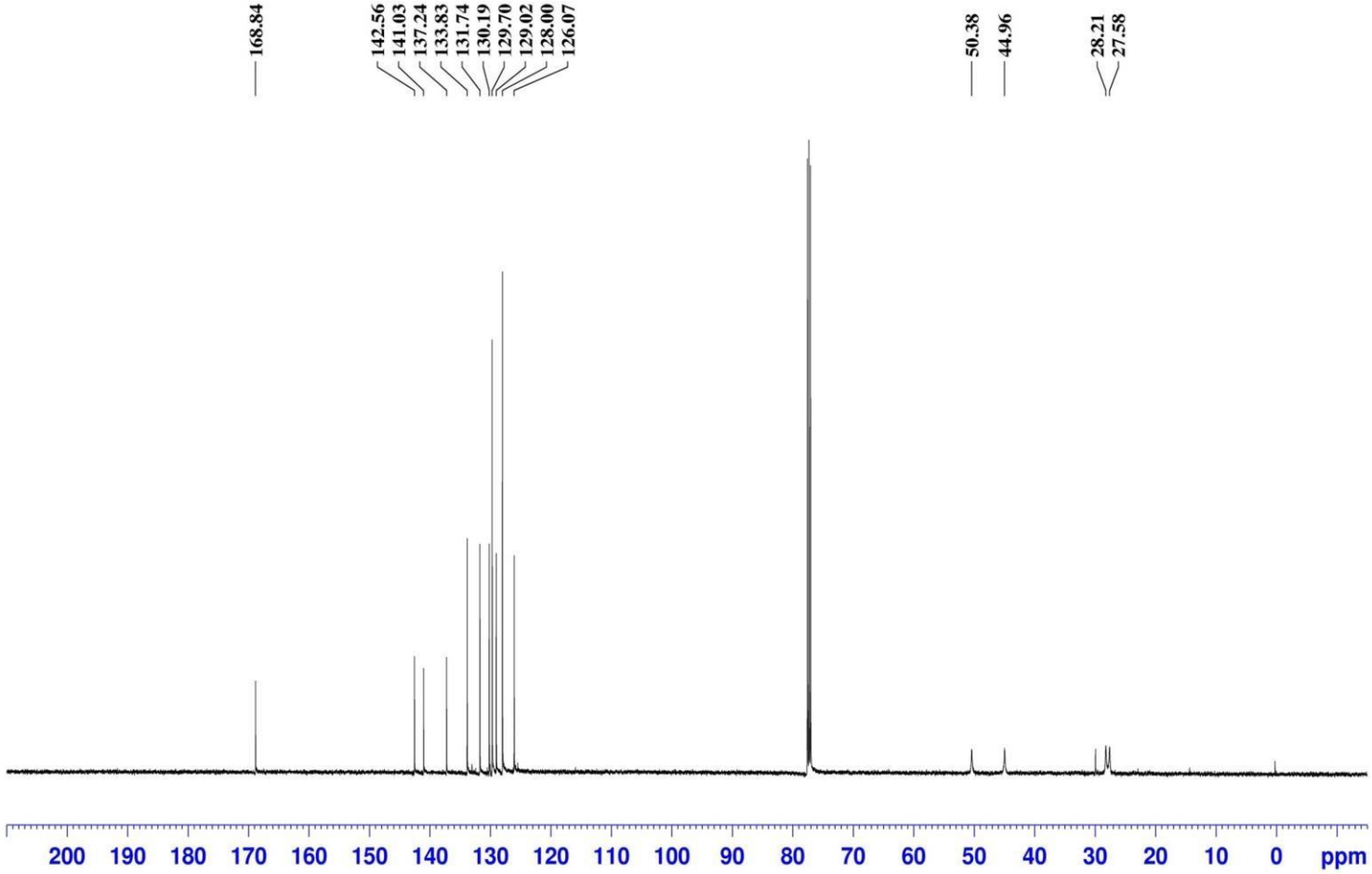
(4–(Phenylsulfonyl)phenyl)(trifluoromethyl)sulfane
125 MHz, CDCl3



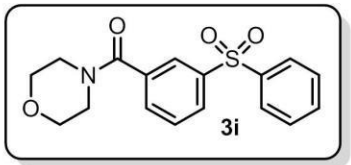


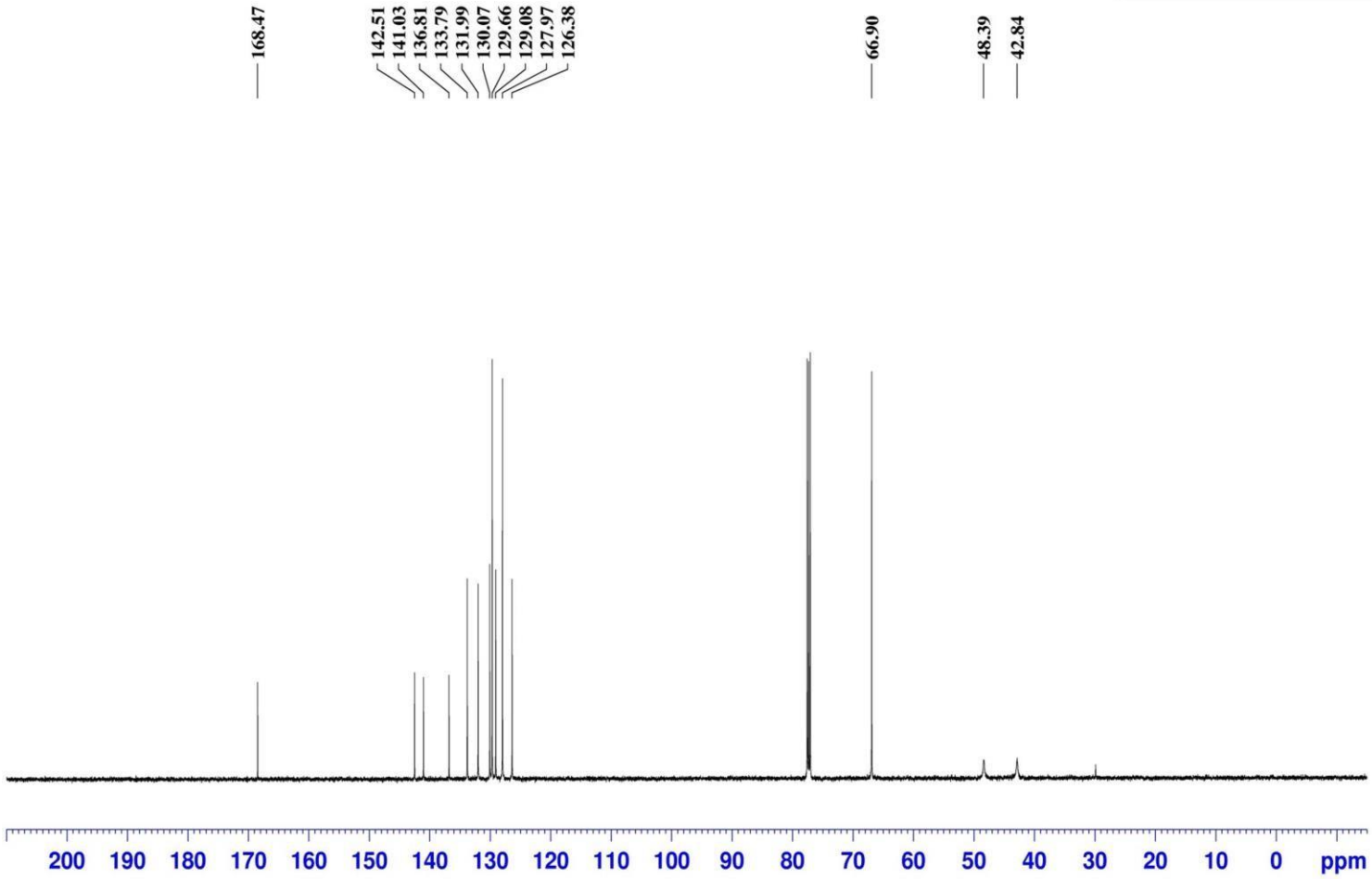
(3–(Phenylsulfonyl)phenyl)(thiomorpholino)methanone
125 MHz, CDCl3



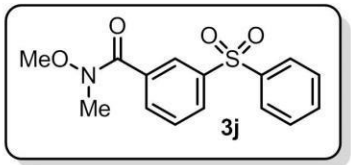


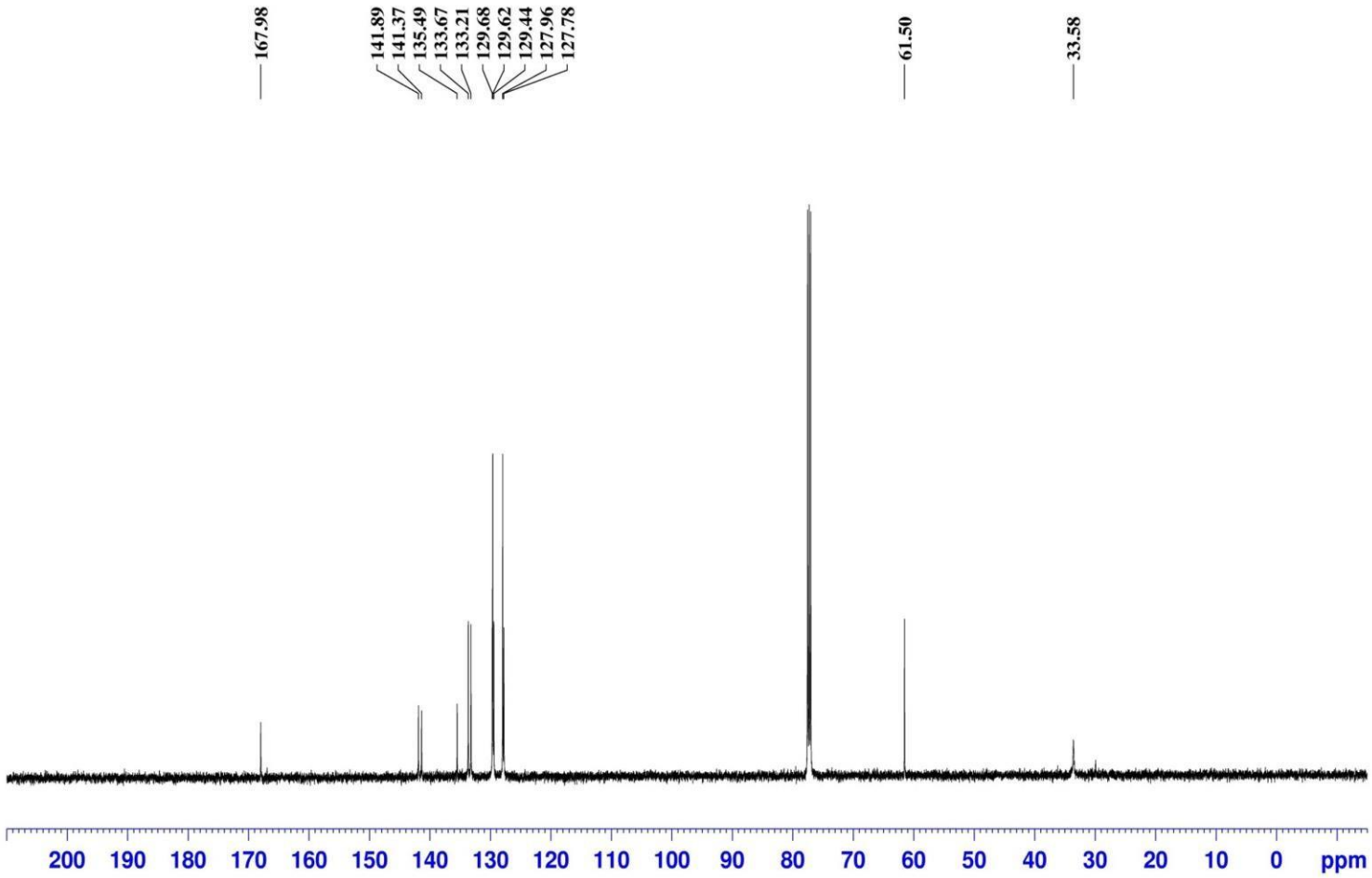
(3–Bromophenyl)(morpholino)methanone
125 MHz, CDCl3



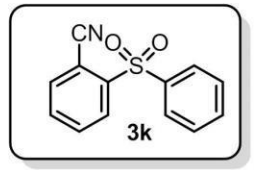


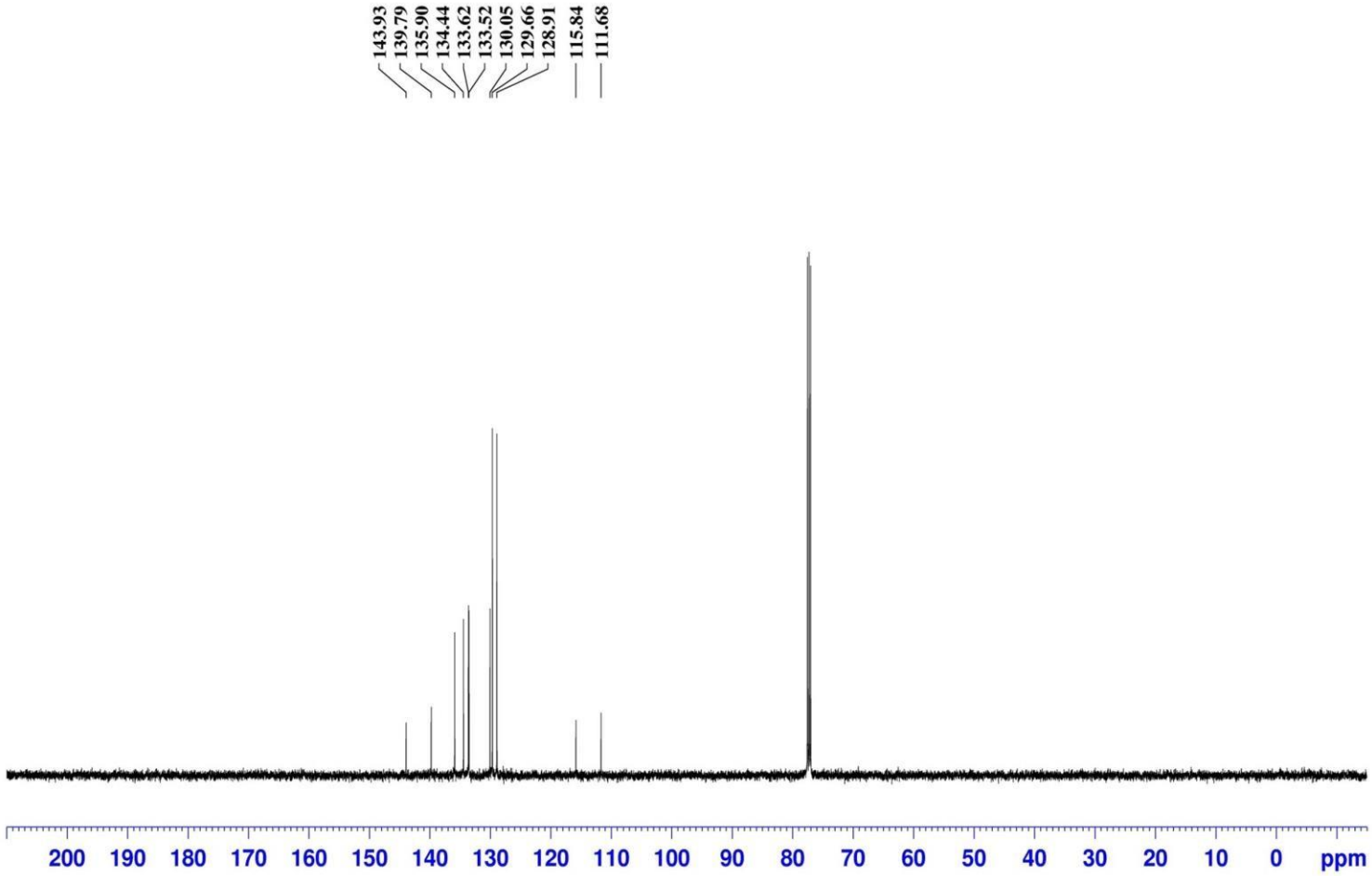
N–Methoxy–N–methyl–3–(phenylsulfonyl)benzamide
125 MHz, CDCl3



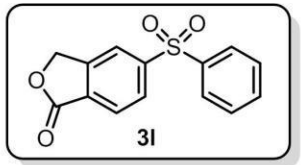


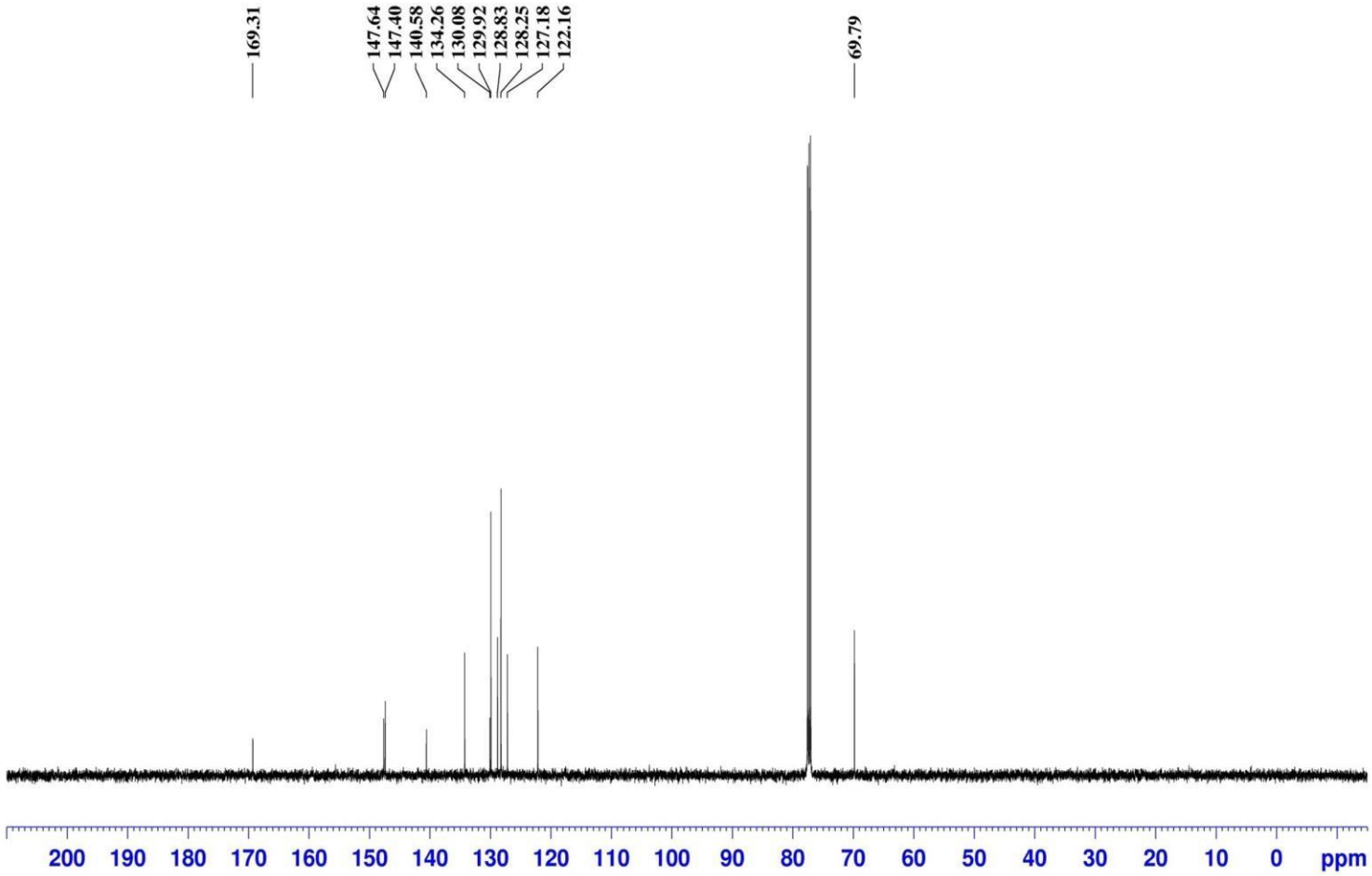
2–(Phenylsulfonyl)benzonitrile
125 MHz, CDCl3



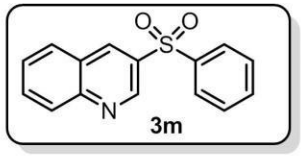


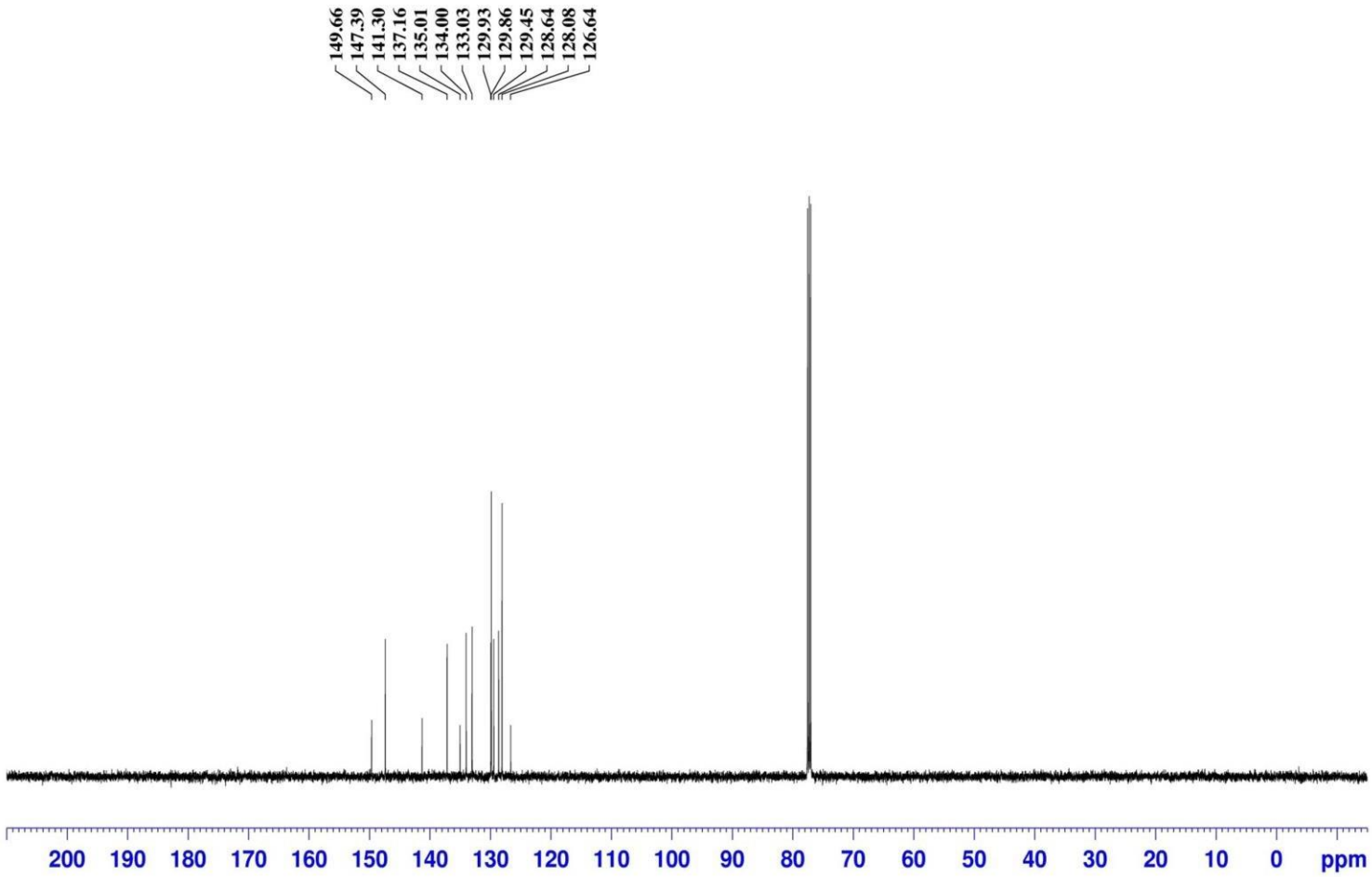
5–(Phenylsulfonyl)isobenzofuran–1(3H)–one
125 MHz, CDCl3



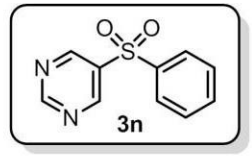


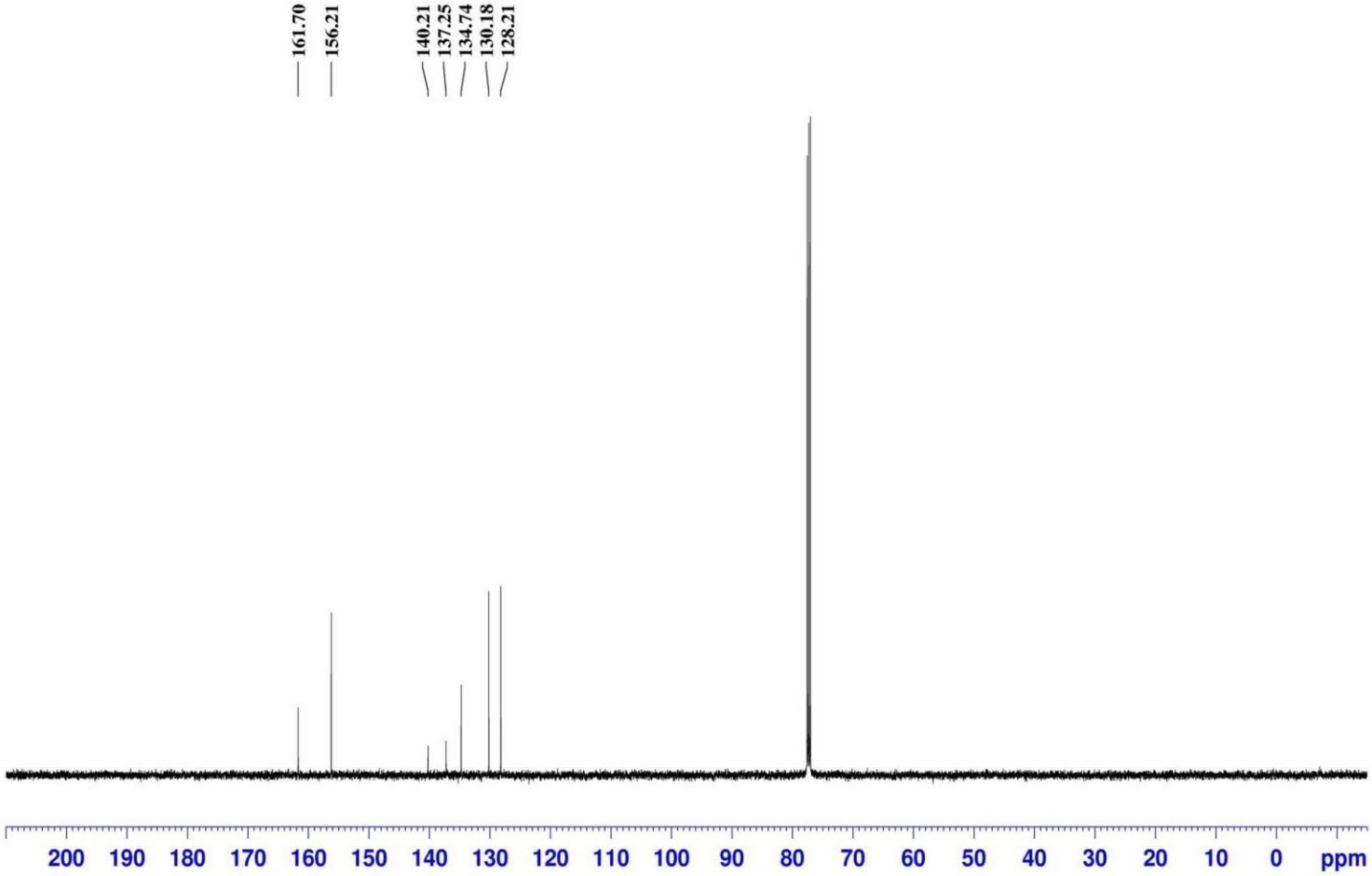
3–(Phenylsulfonyl)quinoline
125 MHz, CDCl3



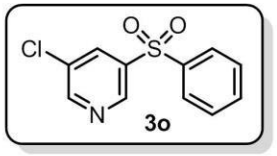


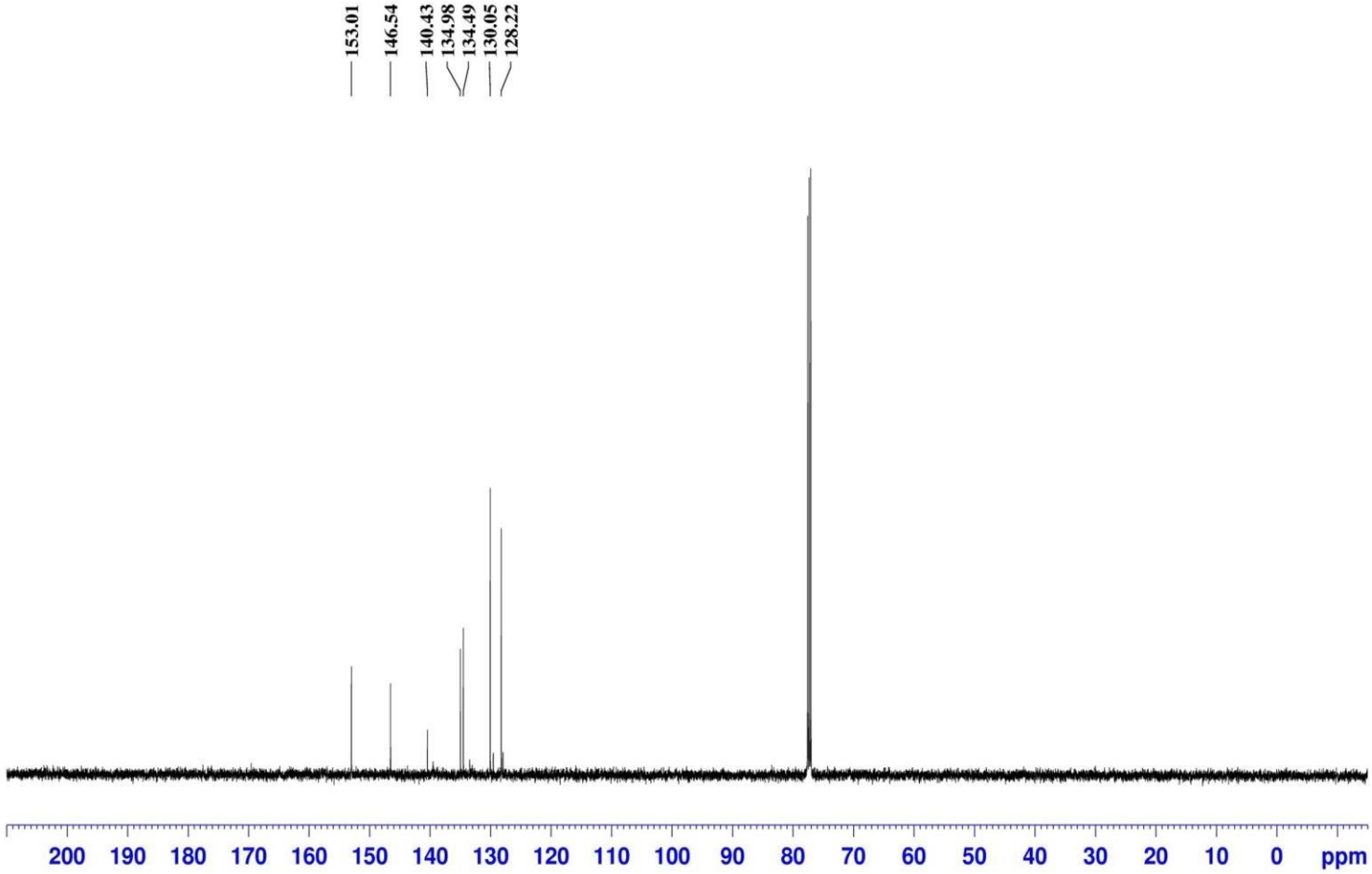
5–(Phenylsulfonyl)pyrimidine
125 MHz, CDCl3



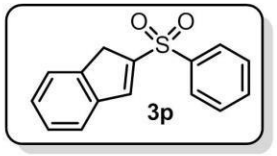


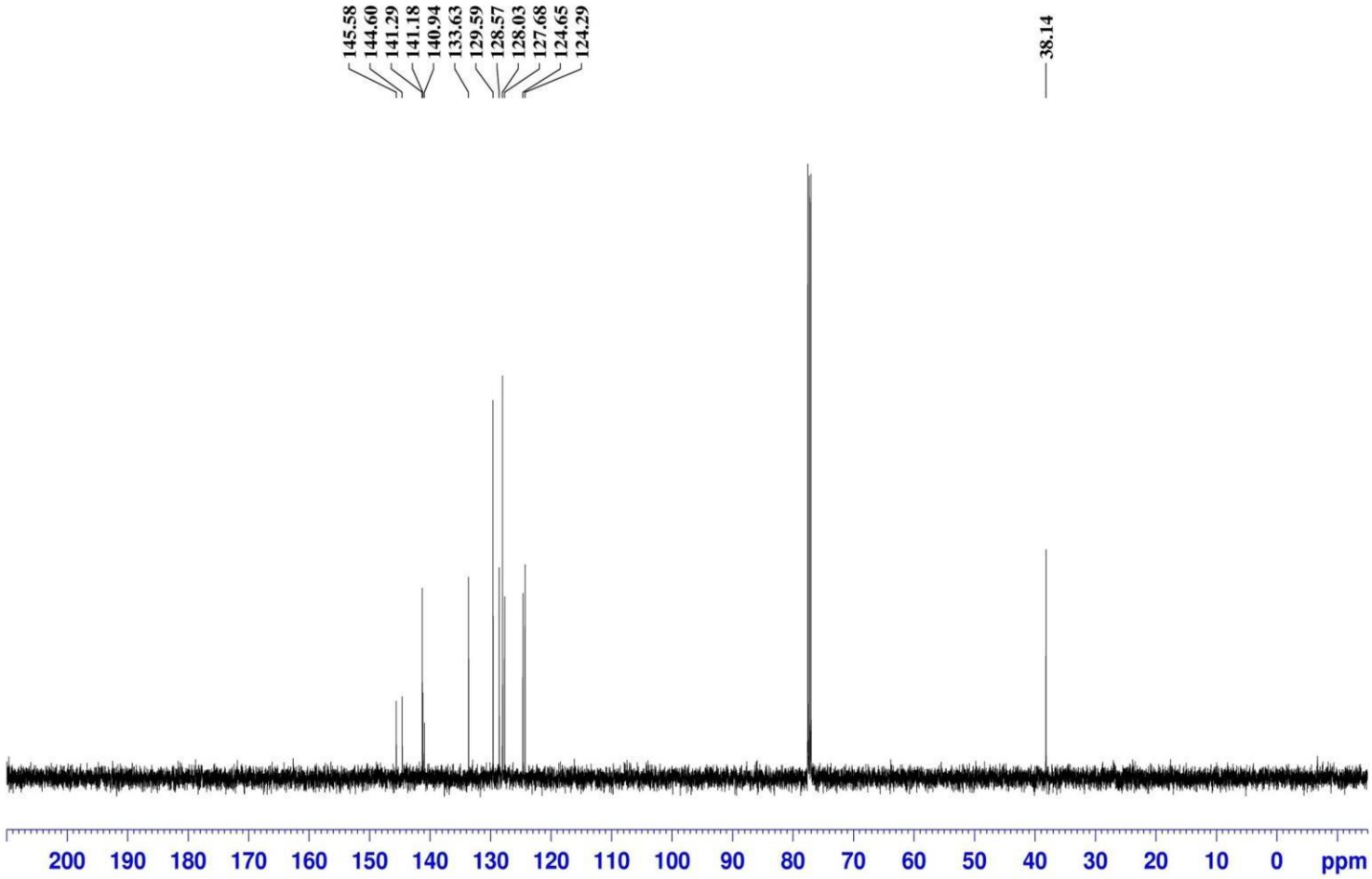
3–Chloro–5–(phenylsulfonyl)pyridine
125 MHz, CDCl3



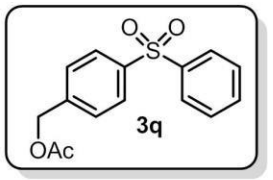


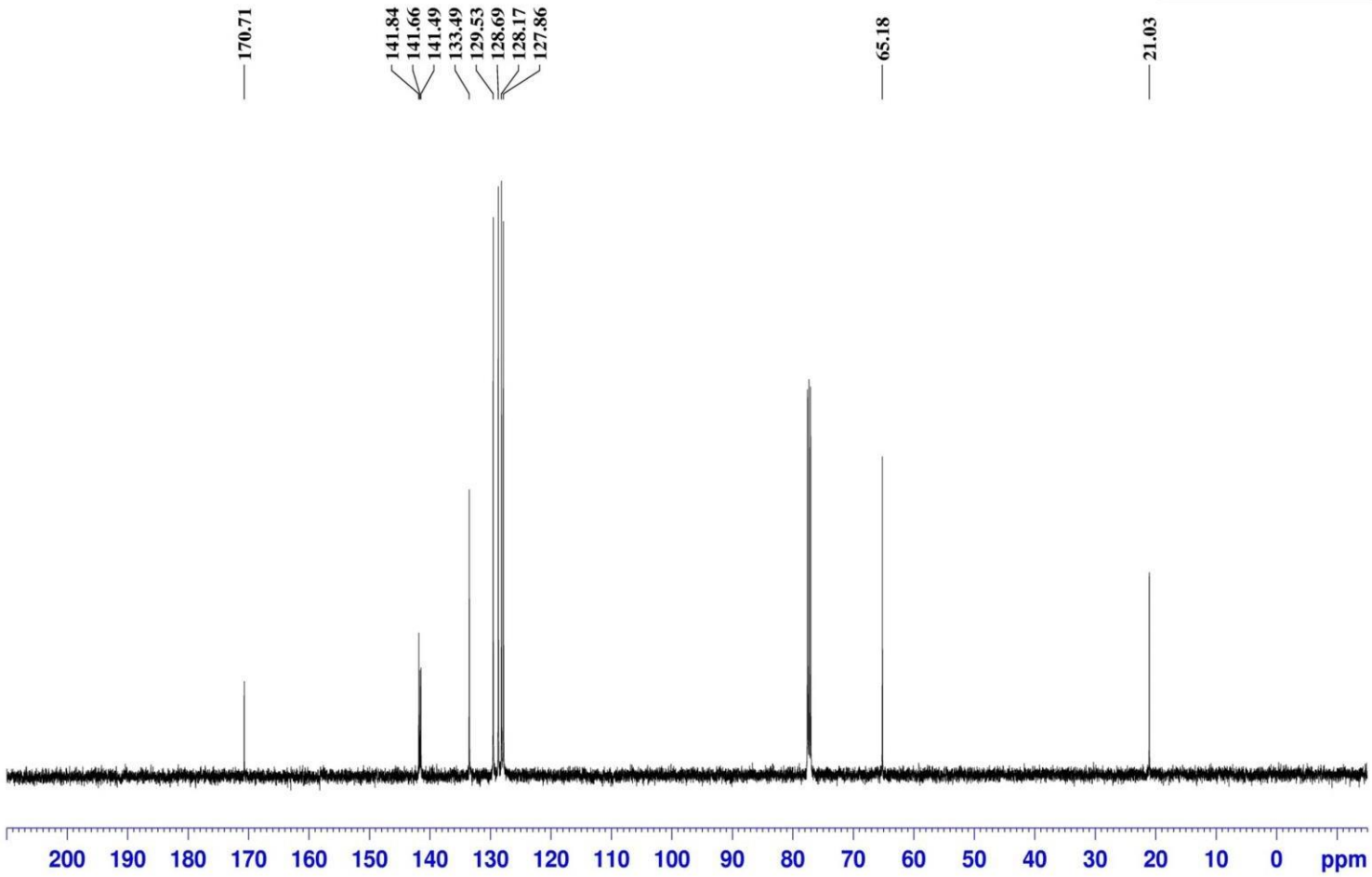
2–(Phenylsulfonyl)–1H–indene
125 MHz, CDCl3



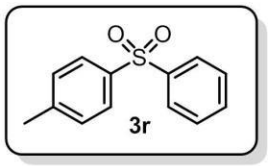


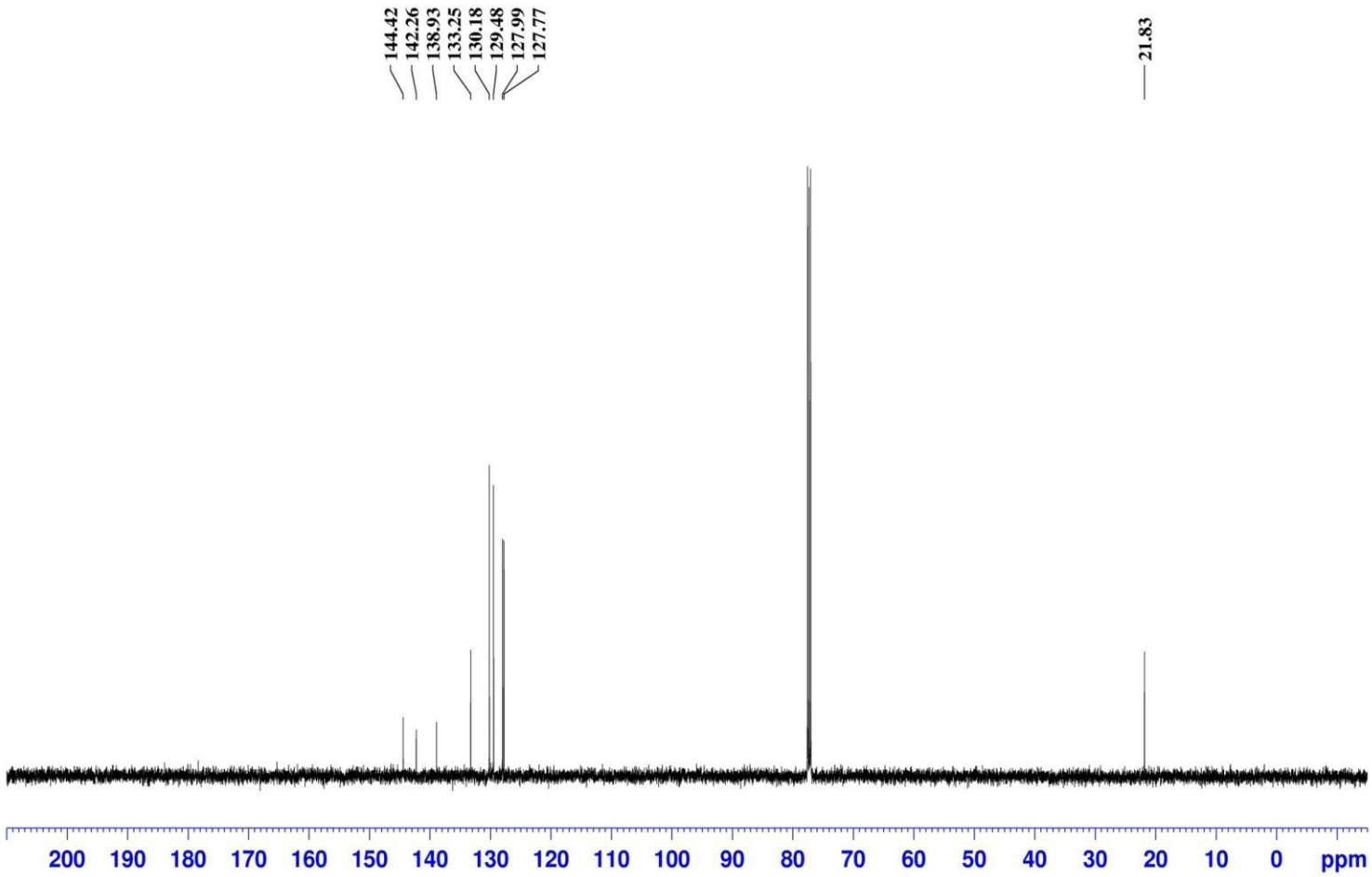
4–(Phenylsulfonyl)benzyl acetate
125 MHz, CDCl3



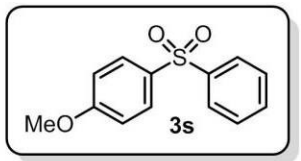


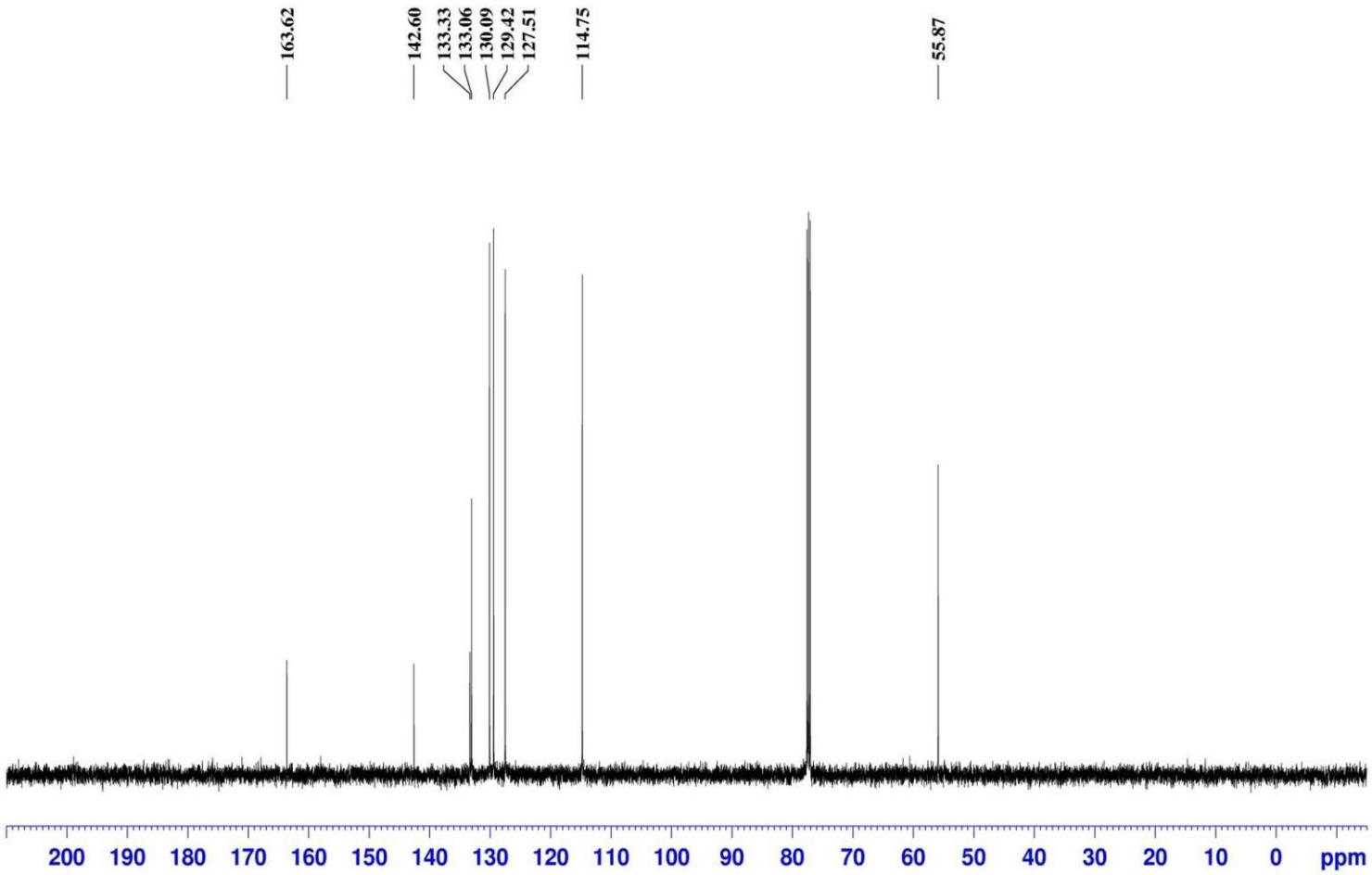
1–Methyl–4–(phenylsulfonyl)benzene
125 MHz, CDCl3



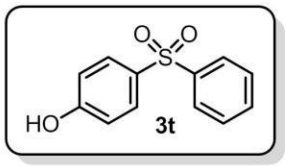


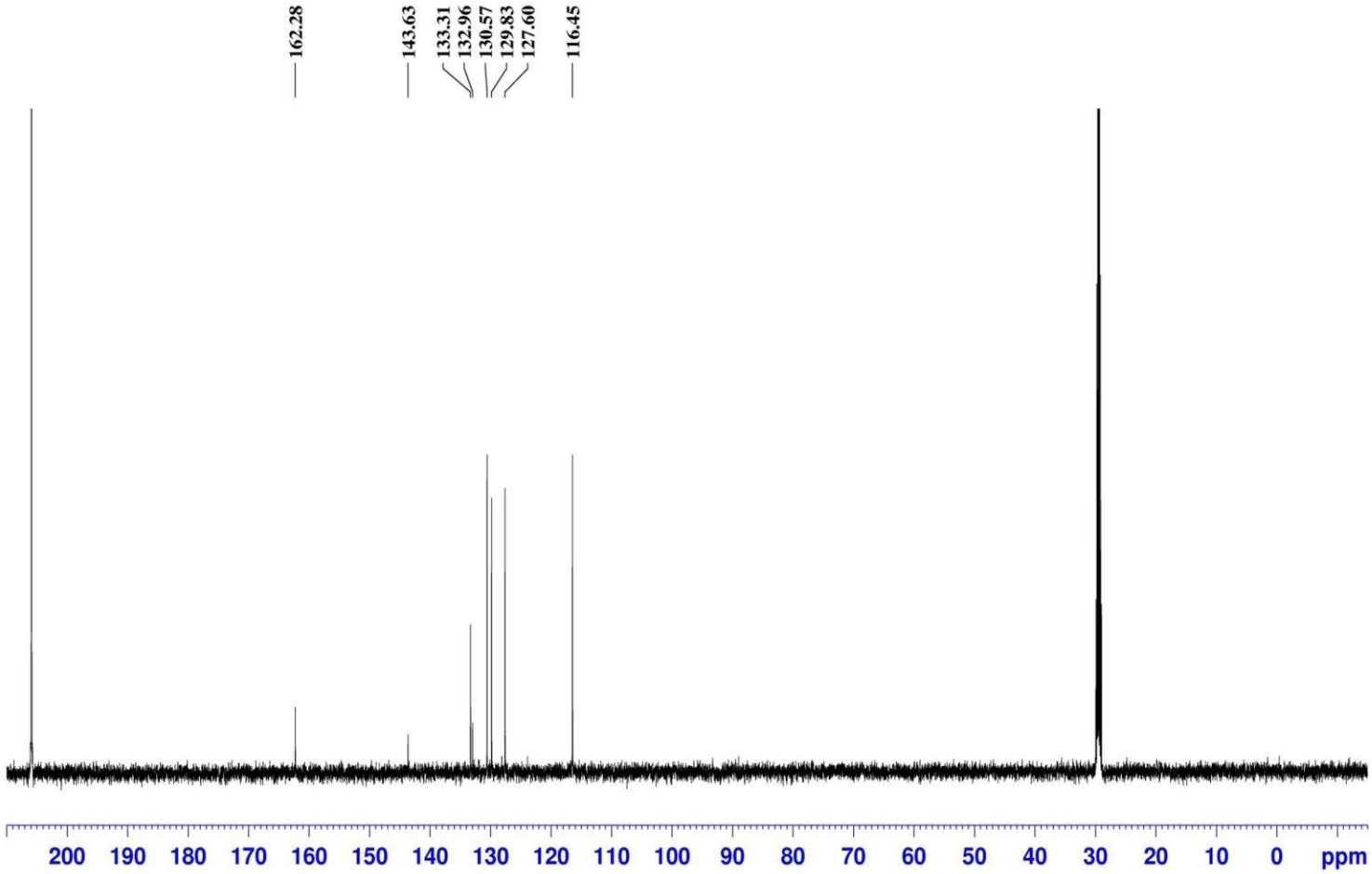
1–Methoxy–4–(phenylsulfonyl)benzene
125 MHz, CDCl3



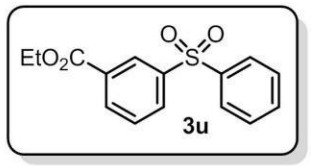


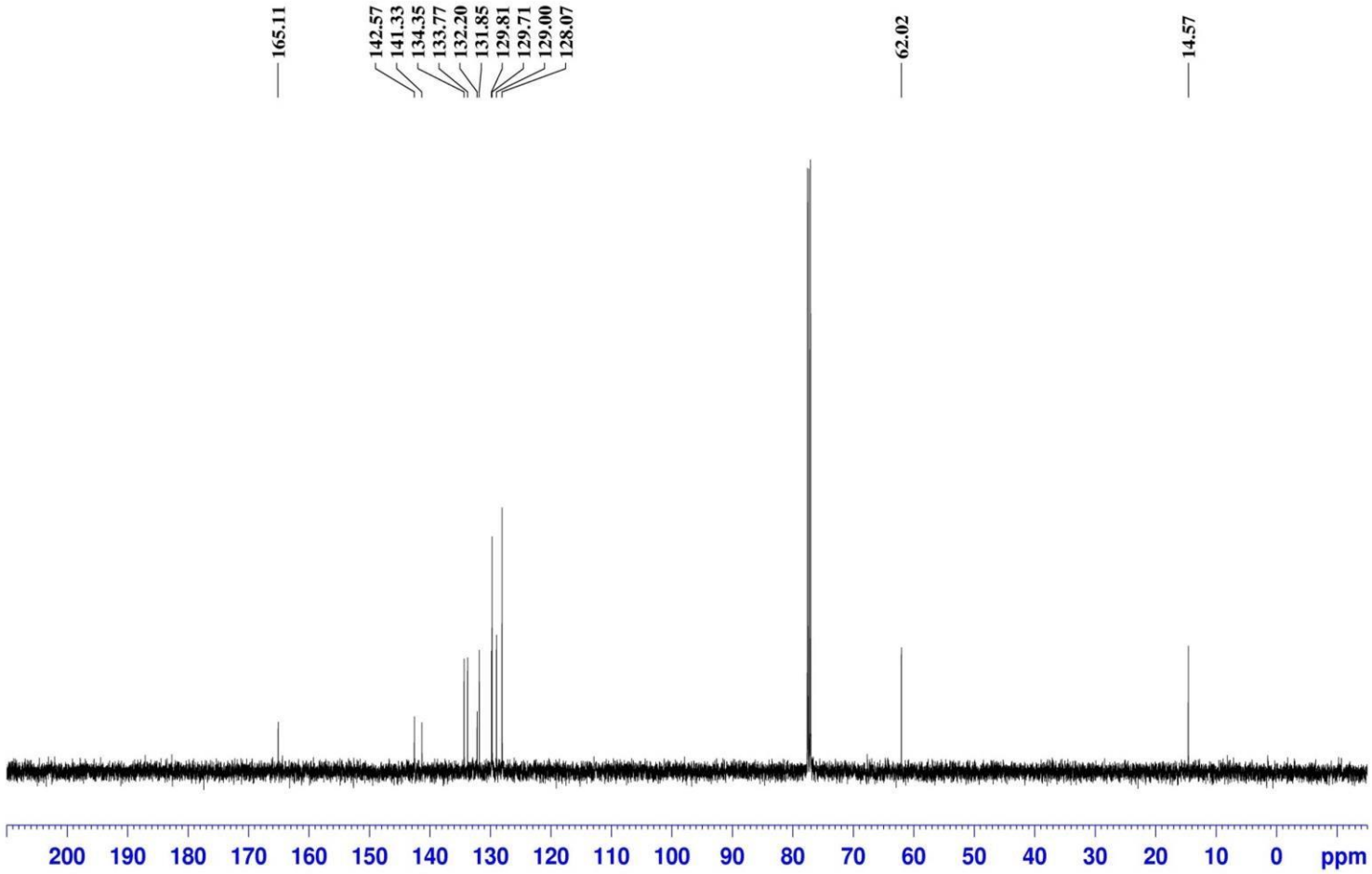
4–(Phenylsulfonyl)phenol
125 MHz, acetone–d6



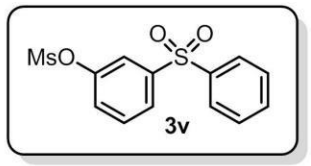


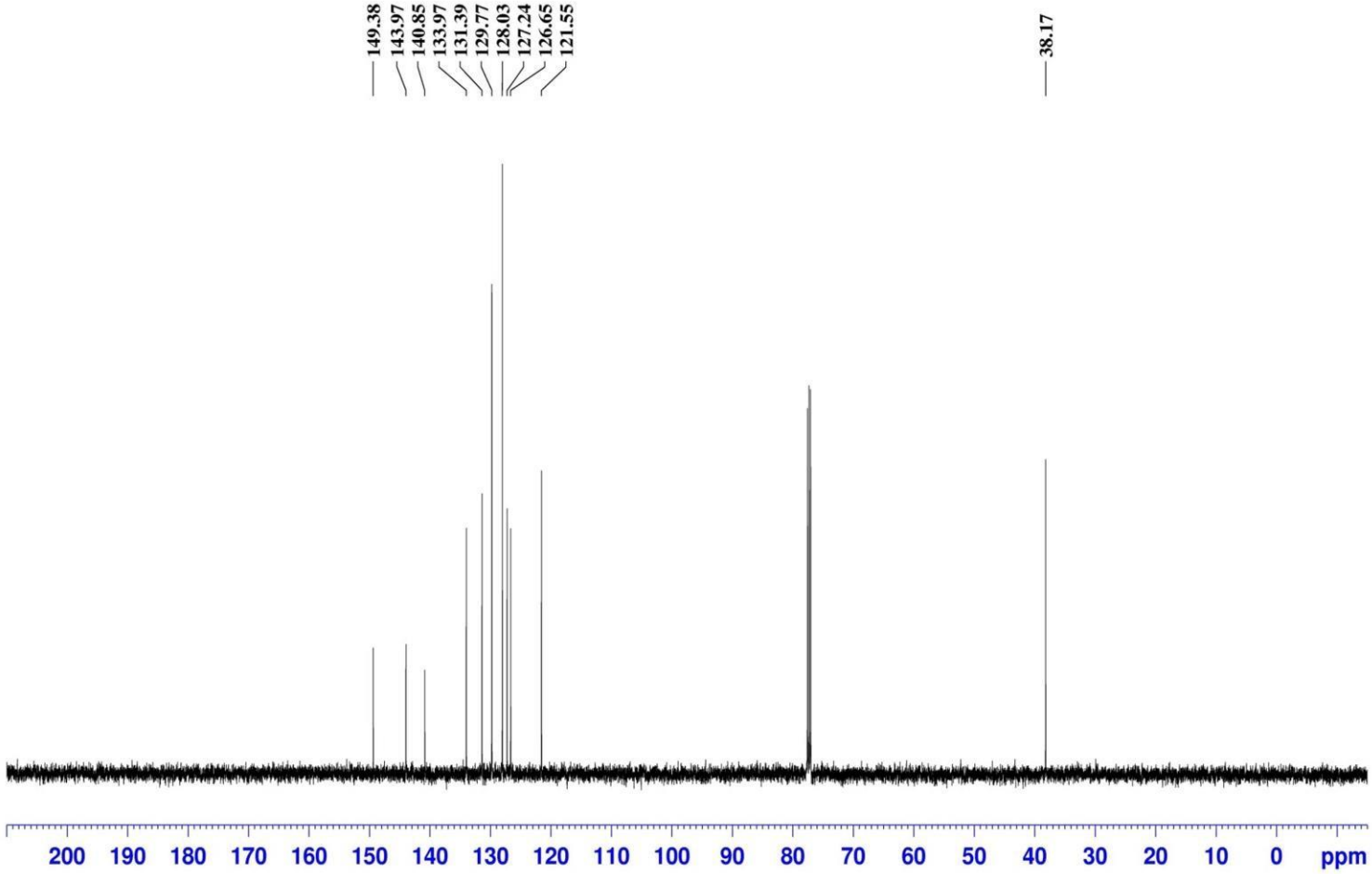
Ethyl 3–(Phenylsulfonyl)benzoate
125 MHz, CDCl3



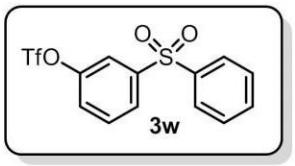


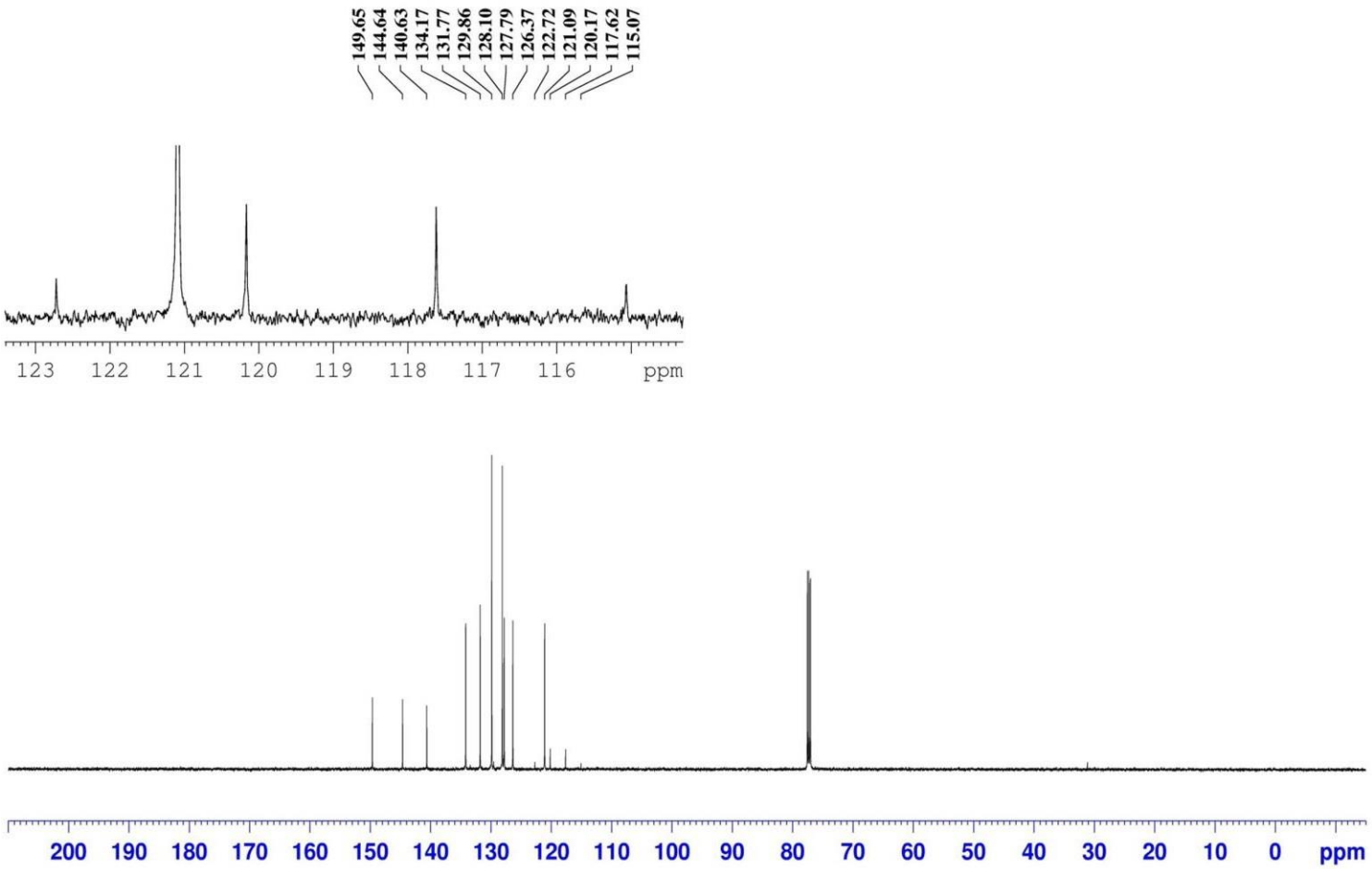
3–(Phenylsulfonyl)phenyl methanesulfonate
125 MHz, CDCl3



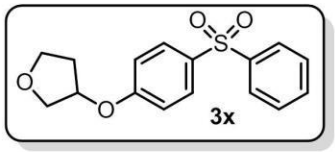


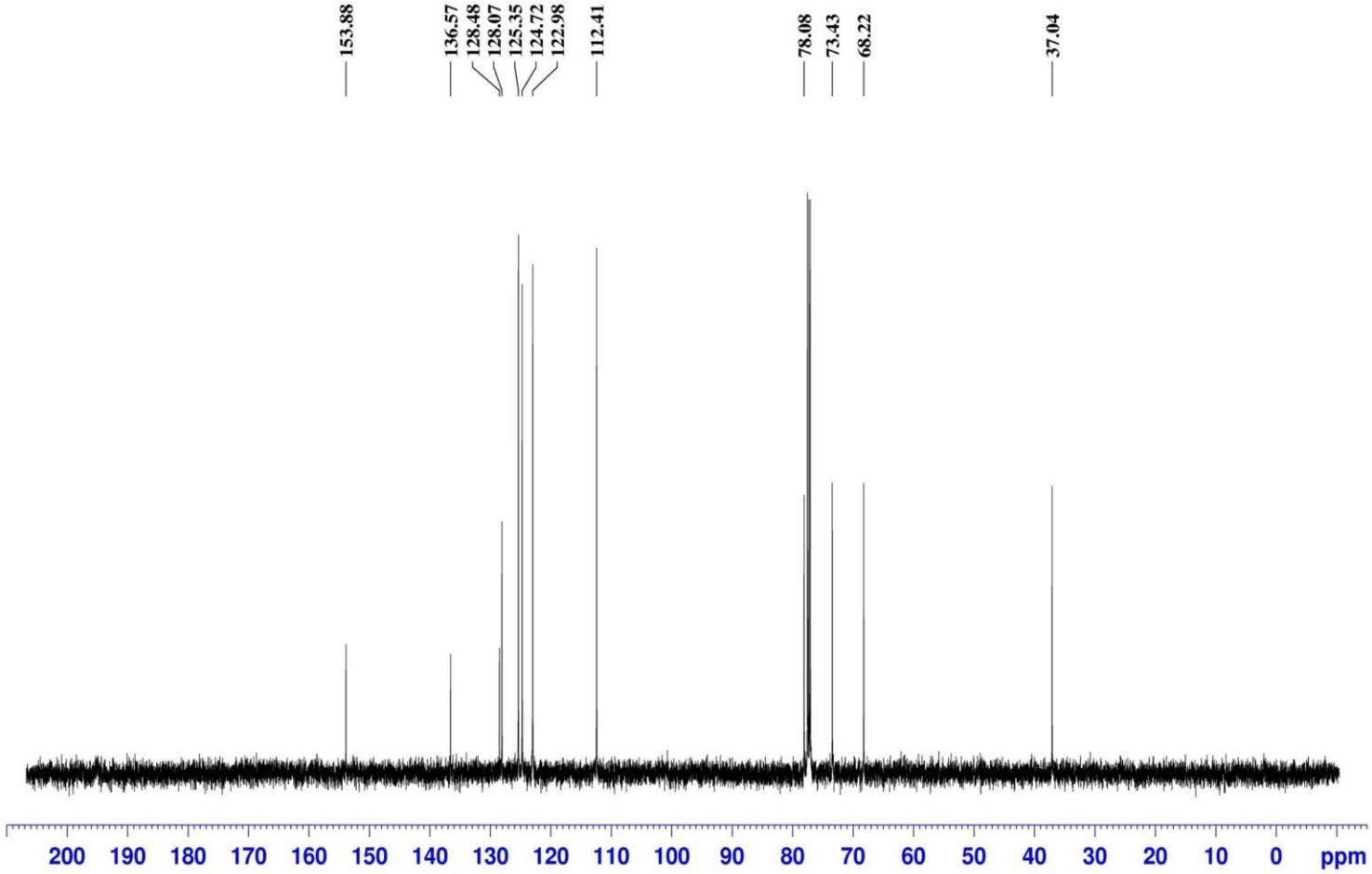
3–(Phenylsulfonyl)phenyl trifluoromethanesulfonate
125 MHz, CDCl3



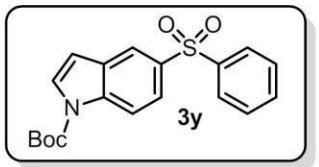


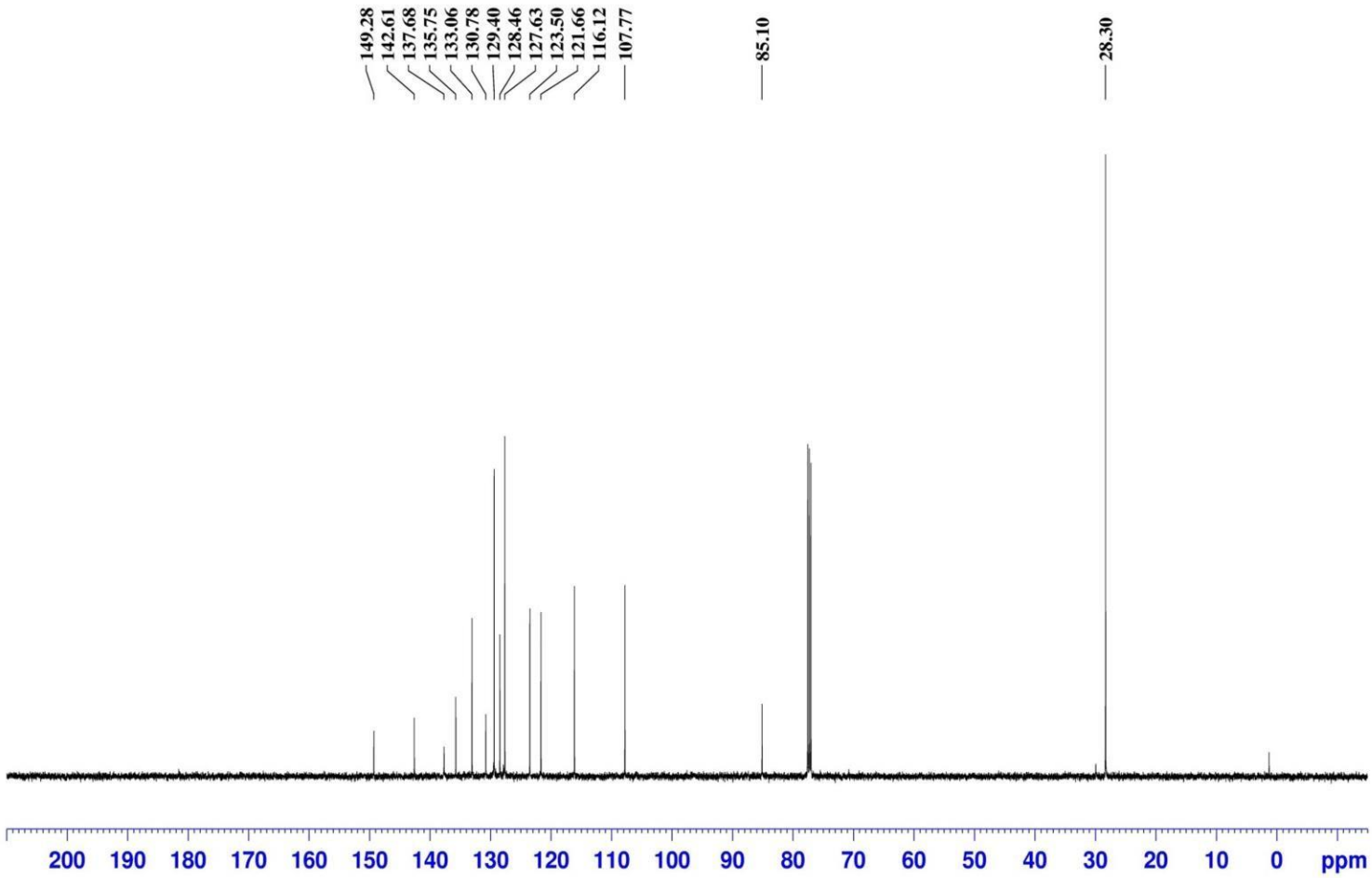
3–(4–(Phenylsulfonyl)phenoxy)tetrahydrofuran
125 MHz, CDCl3



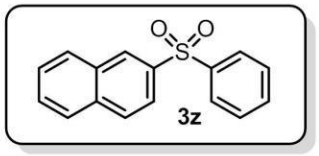


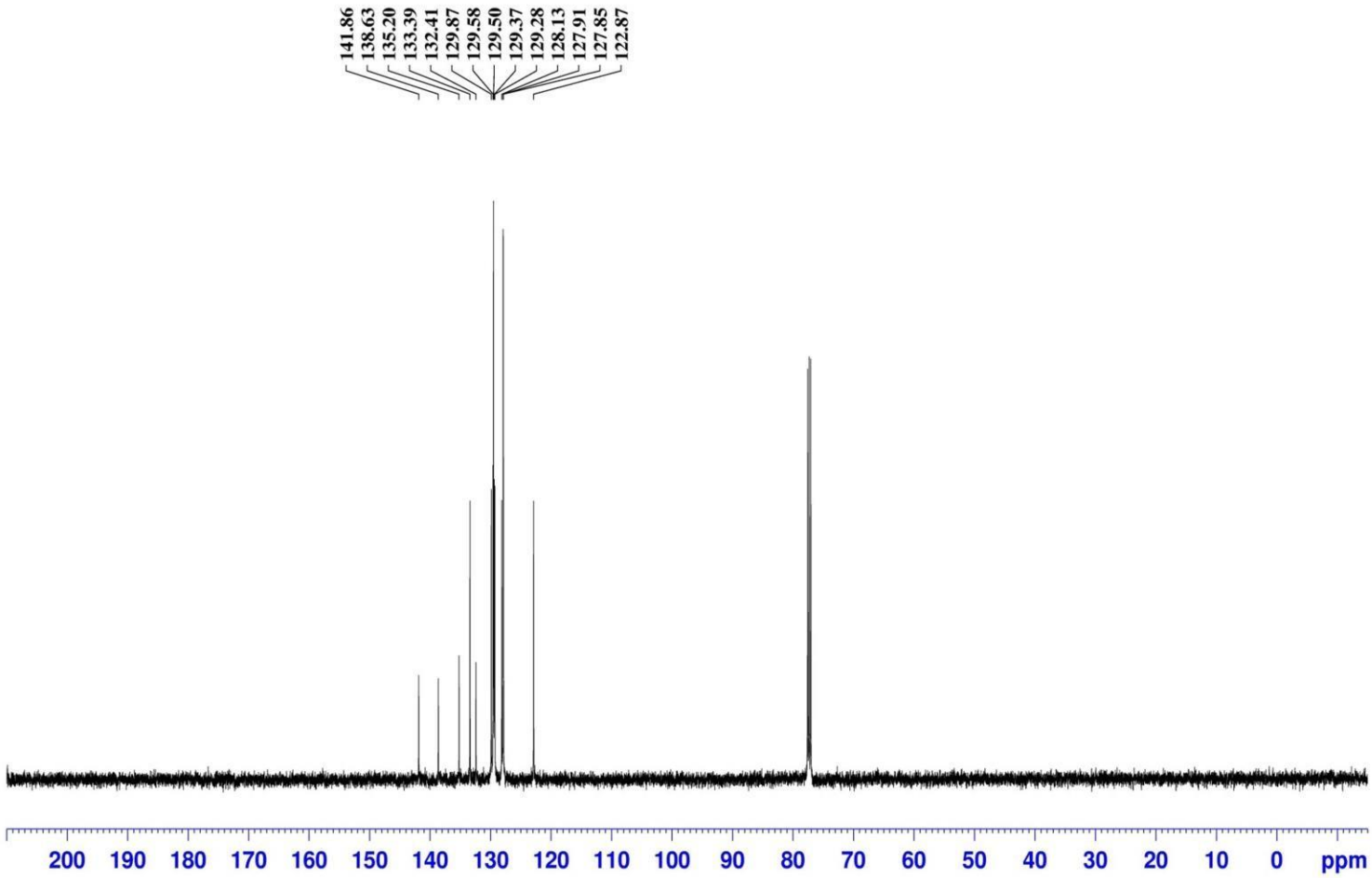
Tert−butyl 5−(Phenylsulfonyl)−1H−indole−1−carboxylate
125 MHz, CDCl3



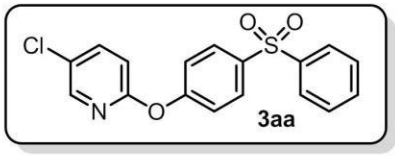


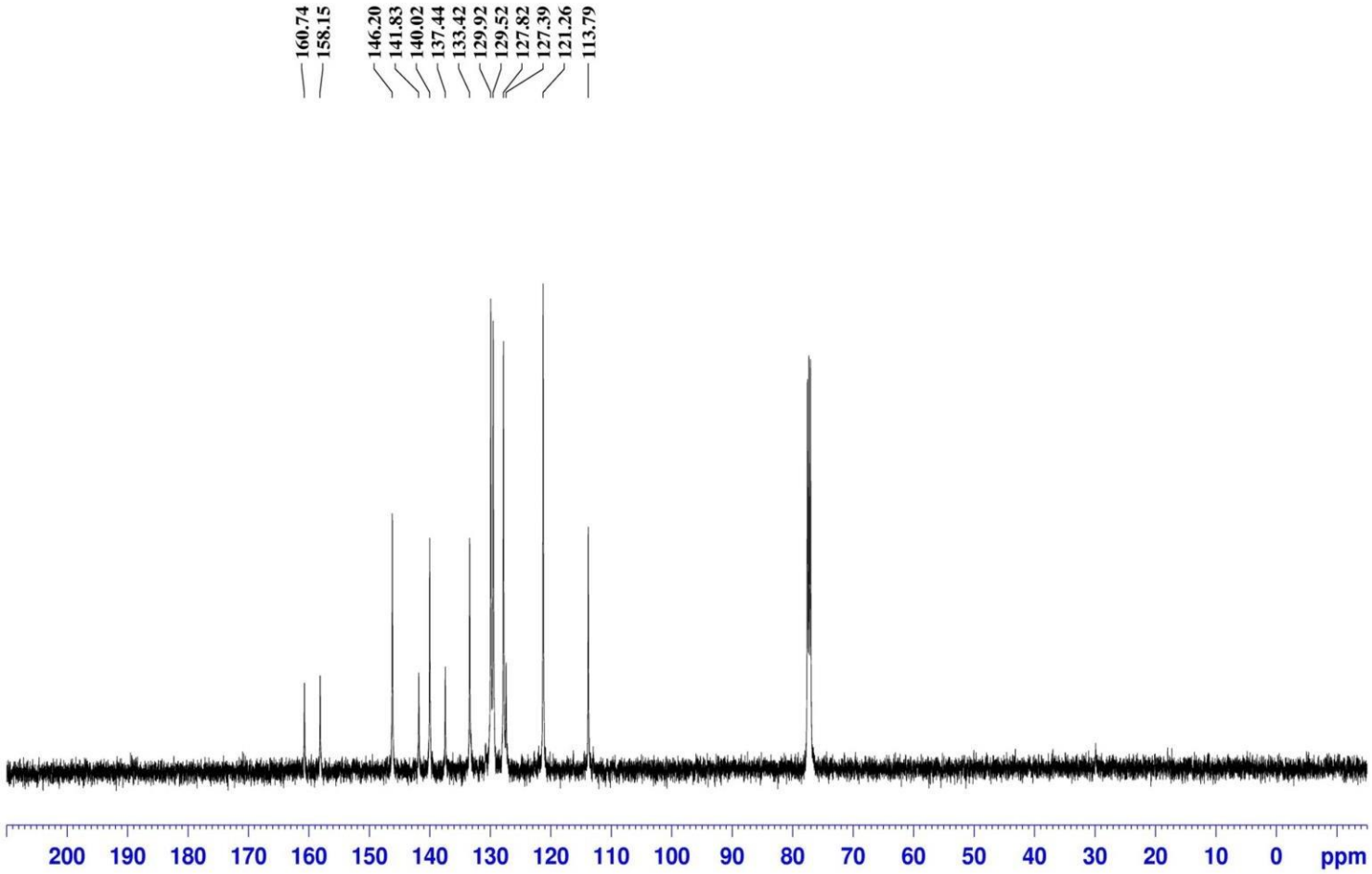
2–(Phenylsulfonyl)naphthalene
125 MHz, CDCl3



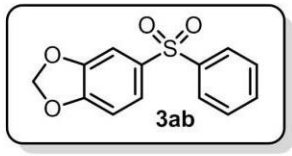


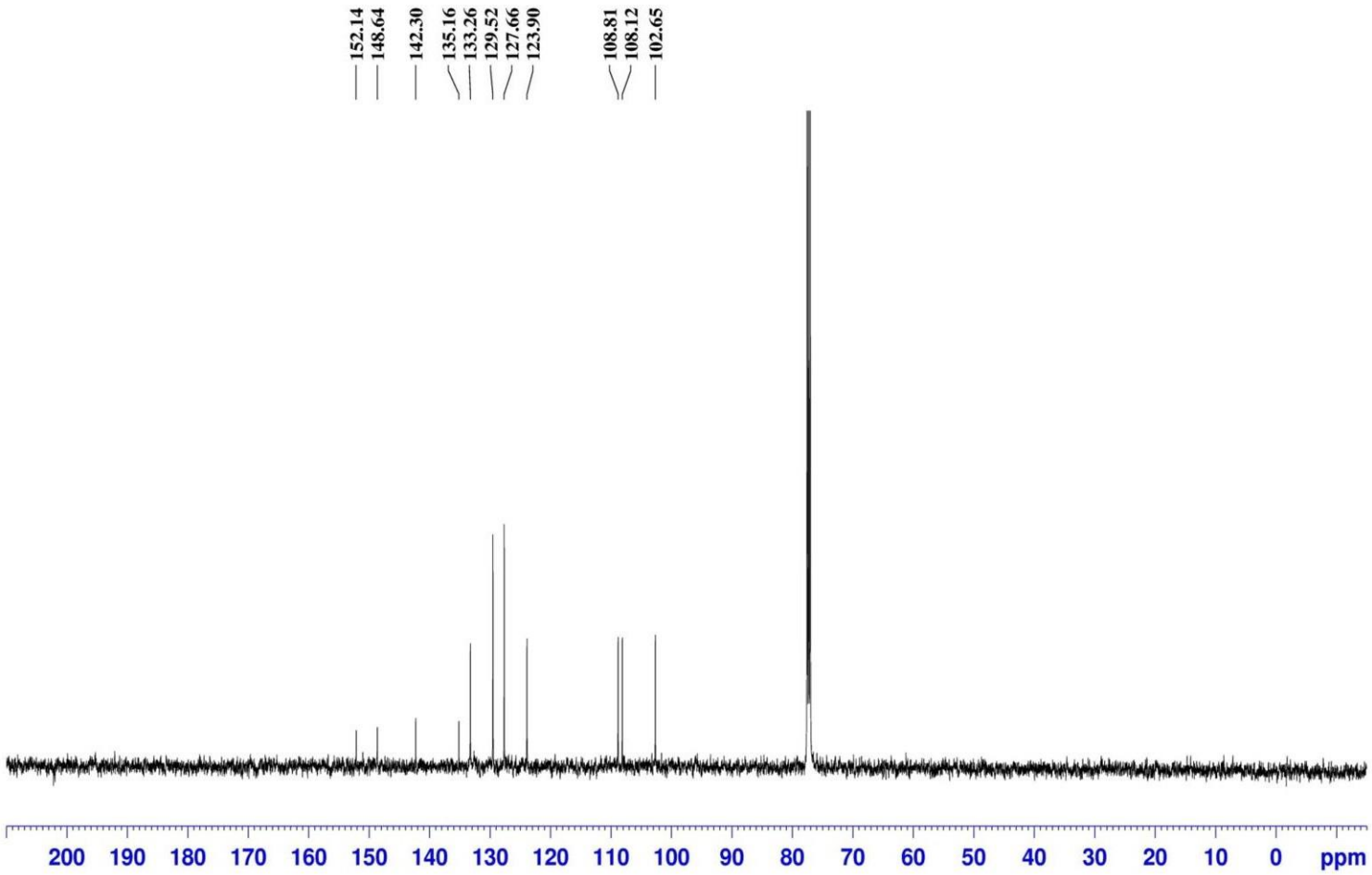
5–Chloro–2–(4–(phenylsulfonyl)phenoxy)pyridine
125 MHz, CDCl3



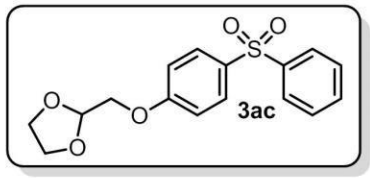


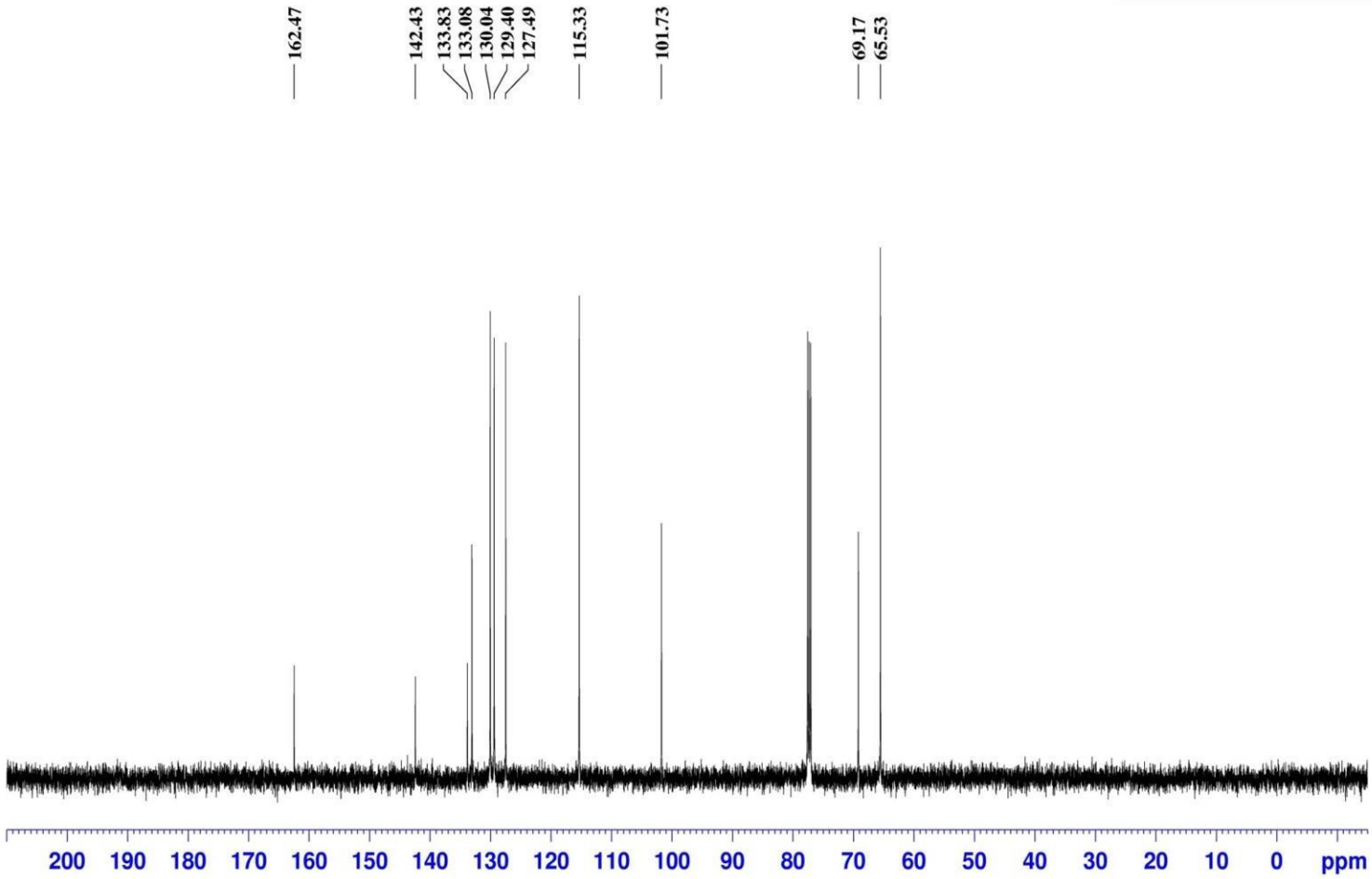
5–(Phenylsulfonyl)benzo[d][1,3]dioxole
125 MHz, CDCl3



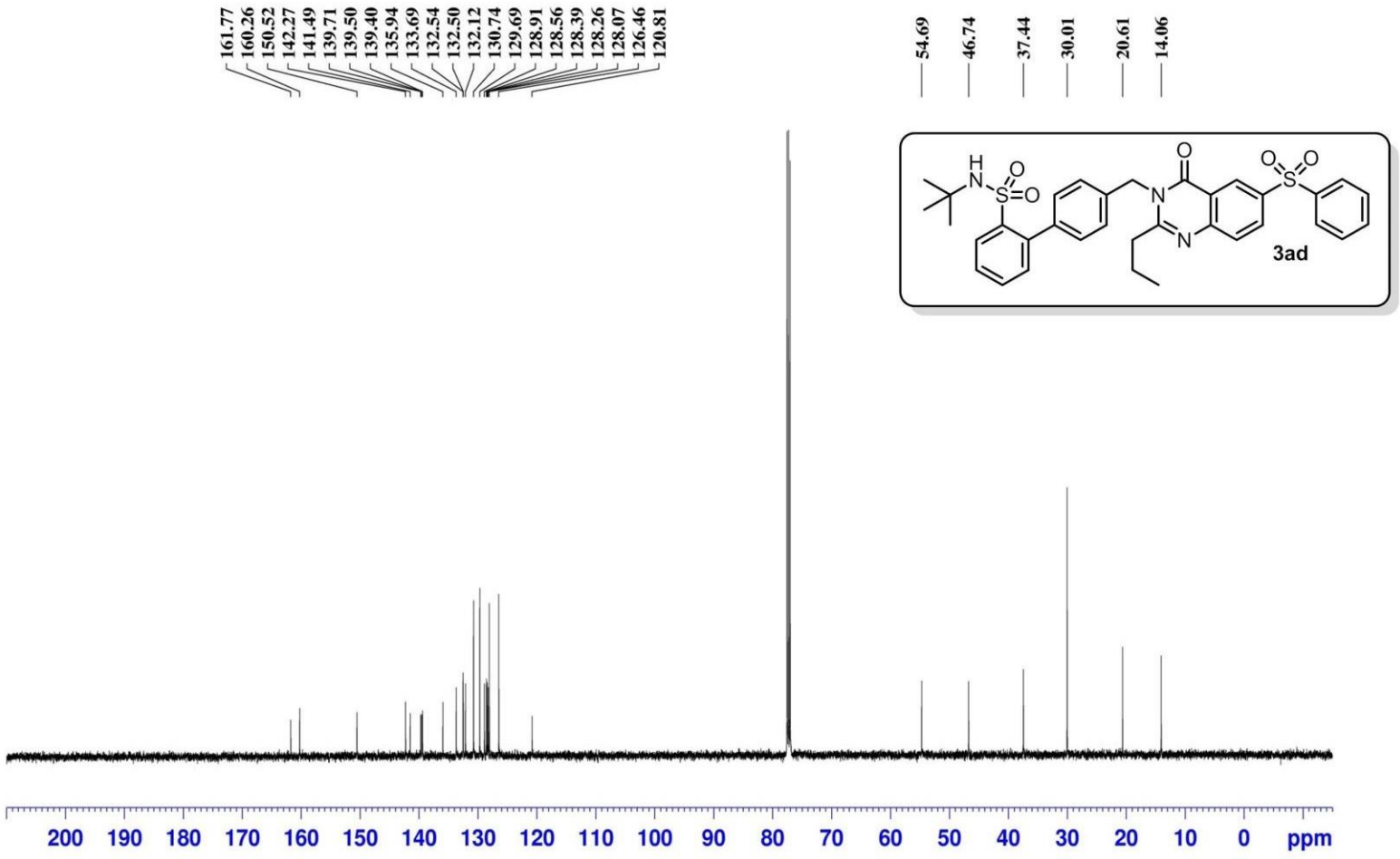


2–((4–(Phenylsulfonyl)phenoxy)methyl)–1,3–dioxolane
125 MHz, CDCl3

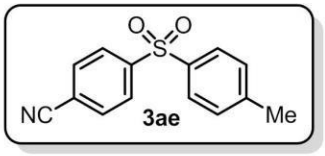


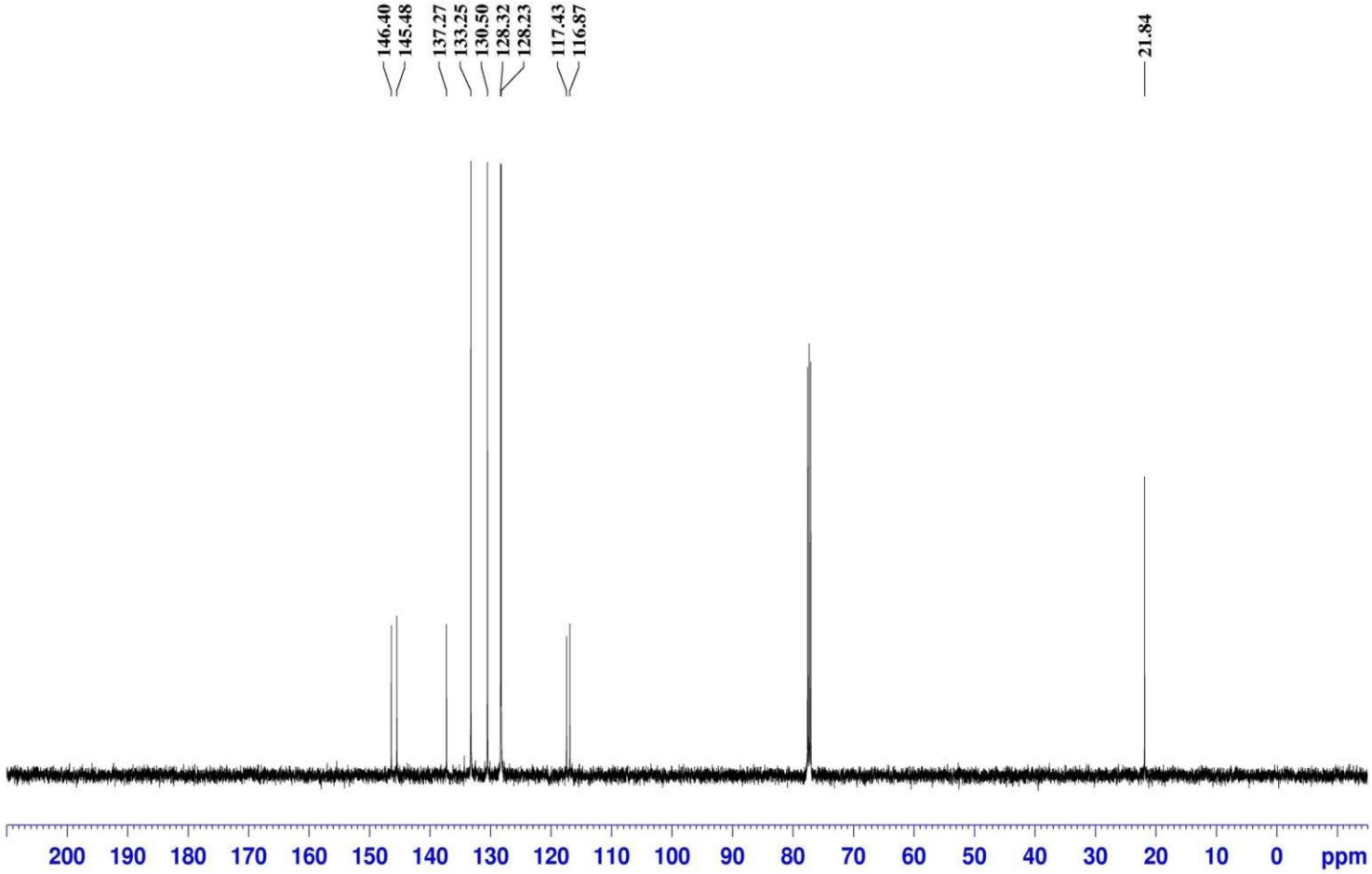


N–(Tert–butyl)–4'–((4–oxo–6–(phenylsulfonyl)–2–propylquinazolin–3(4H)–yl)methyl)–[1,1'–biphenyl]–2–sulfonamide
125 MHz, CDCl3

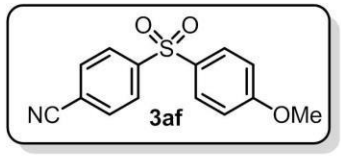


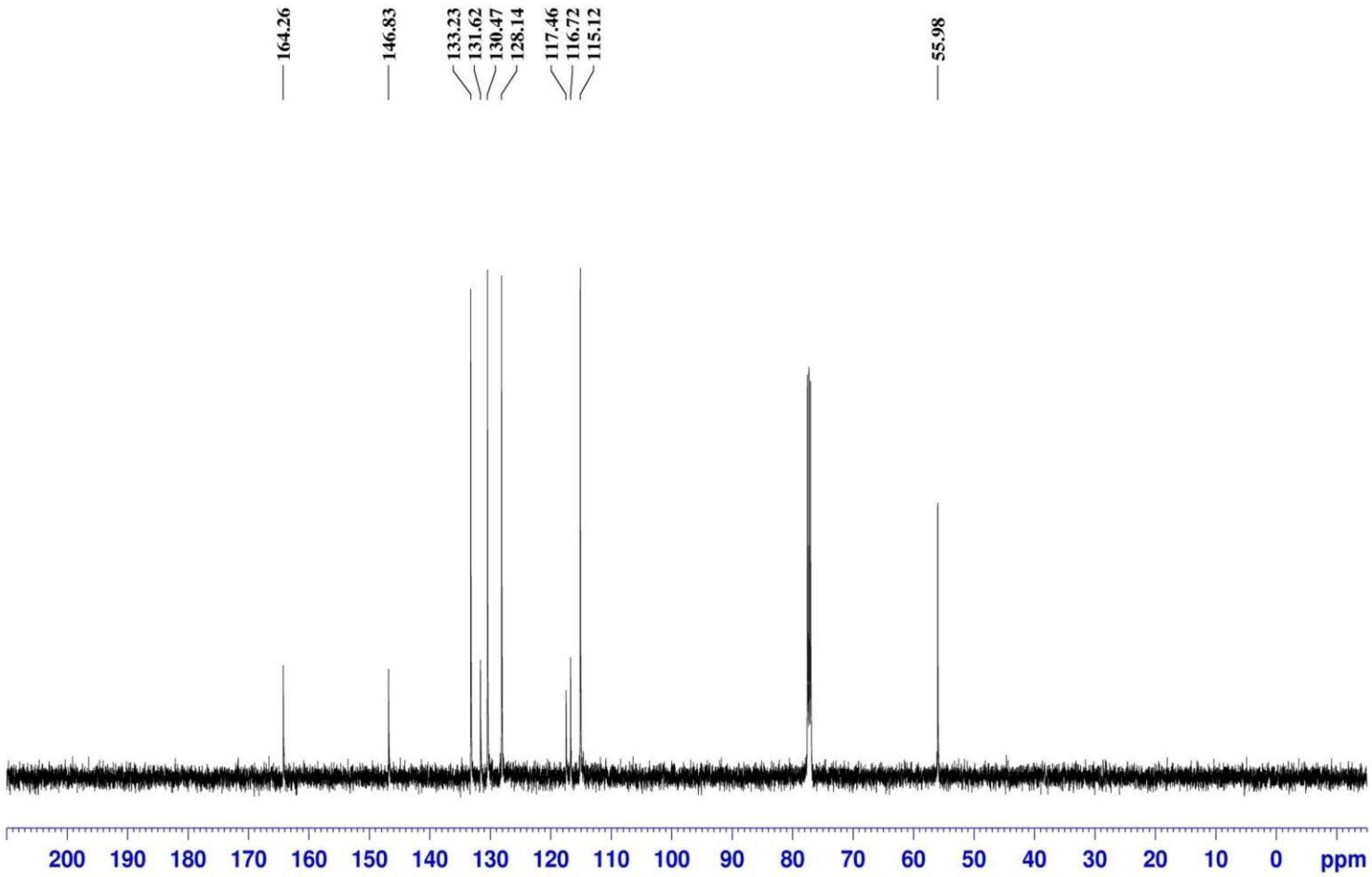
4–Tosylbenzonitrile
125 MHz, CDCl3



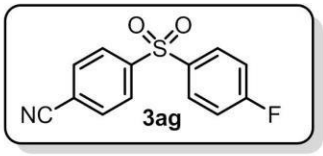


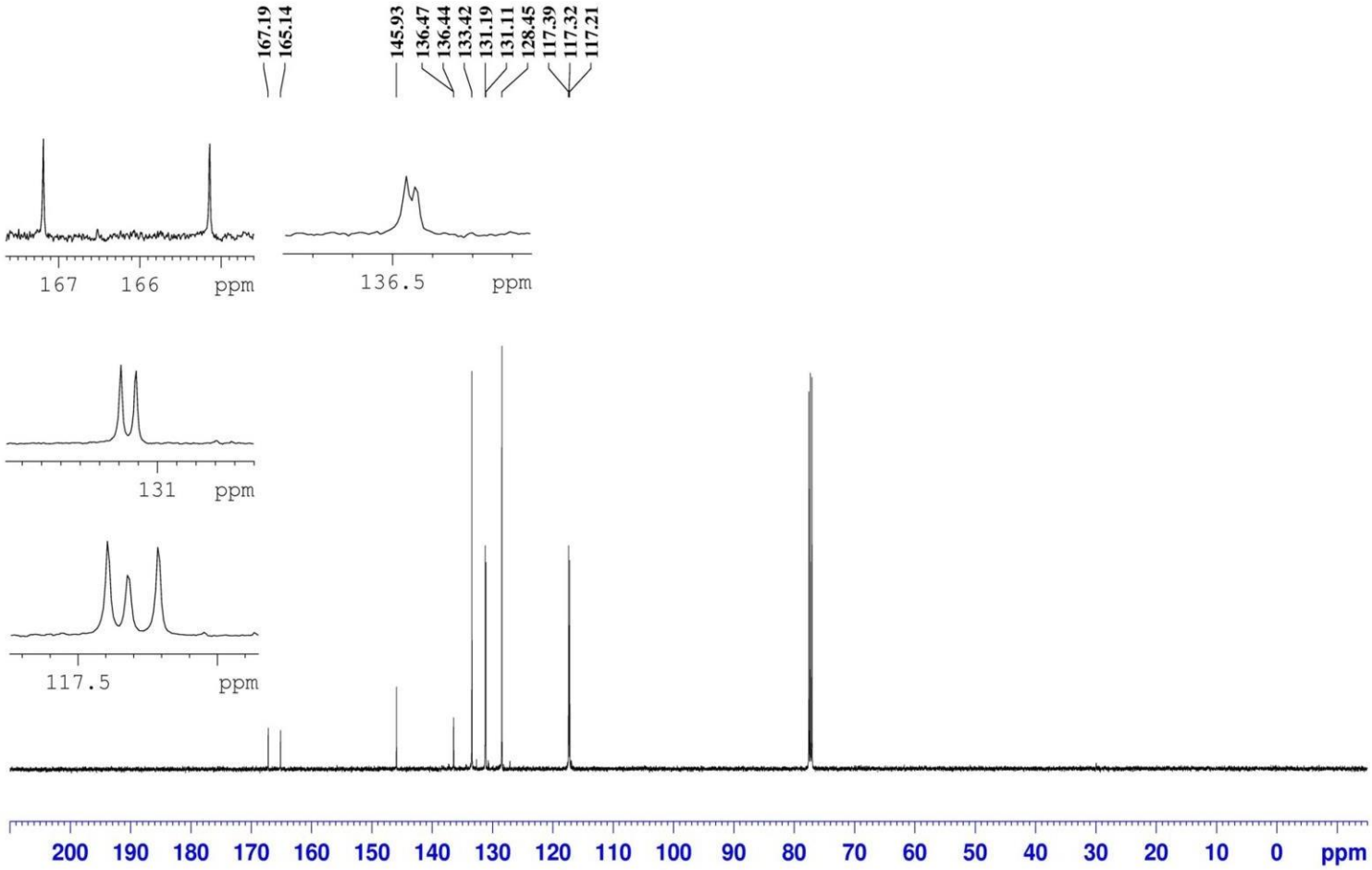
4–((4–Methoxyphenyl)sulfonyl)benzonitrile
125 MHz, CDCl3



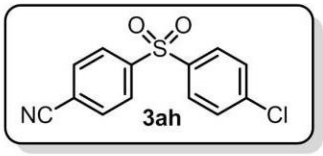


4–((4–Fluorophenyl)sulfonyl)benzonitrile
125 MHz, CDCl3

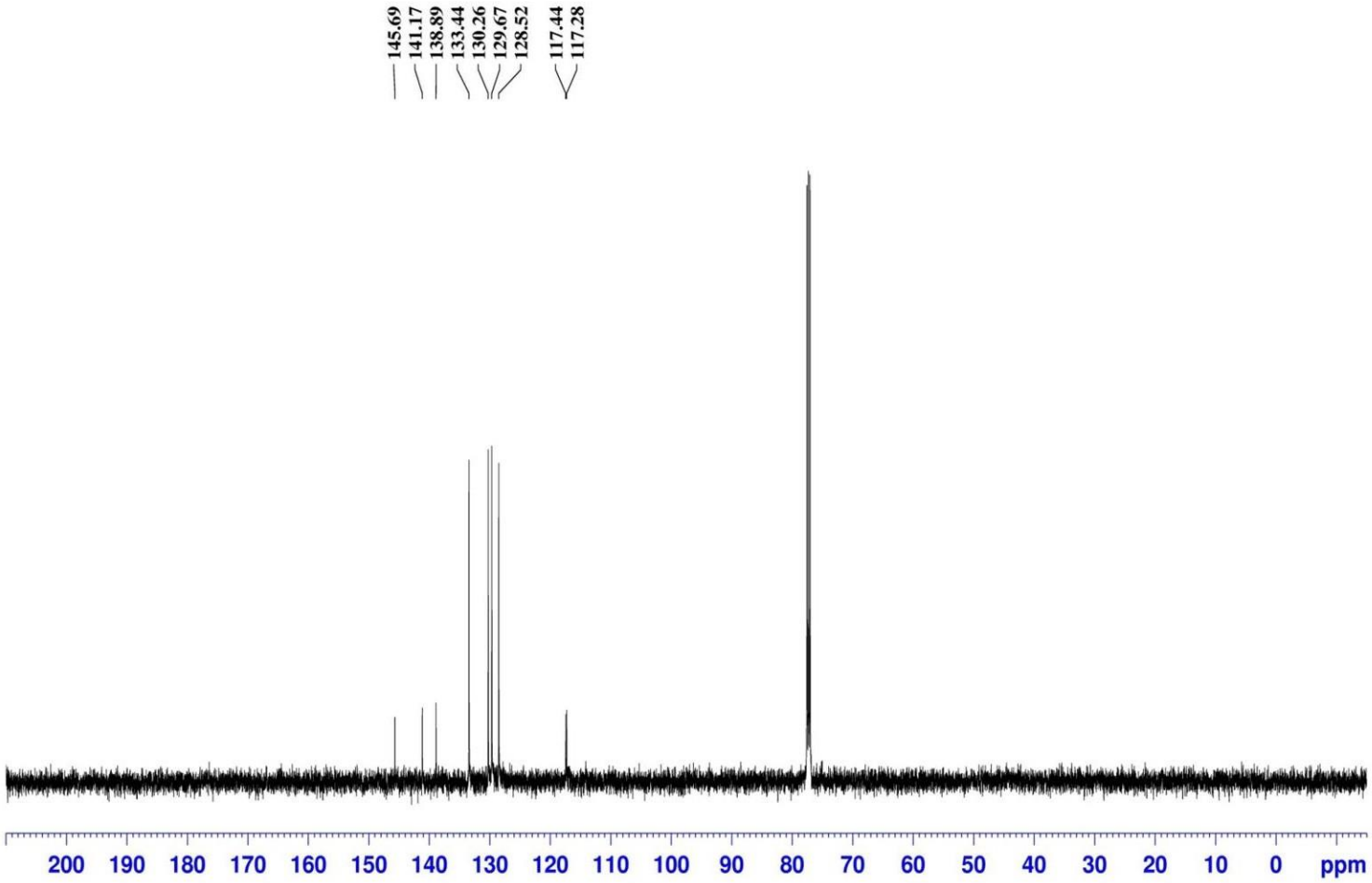




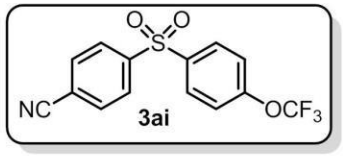
4–((4–Chlorophenyl)sulfonyl)benzonitrile
125 MHz, CDCl3

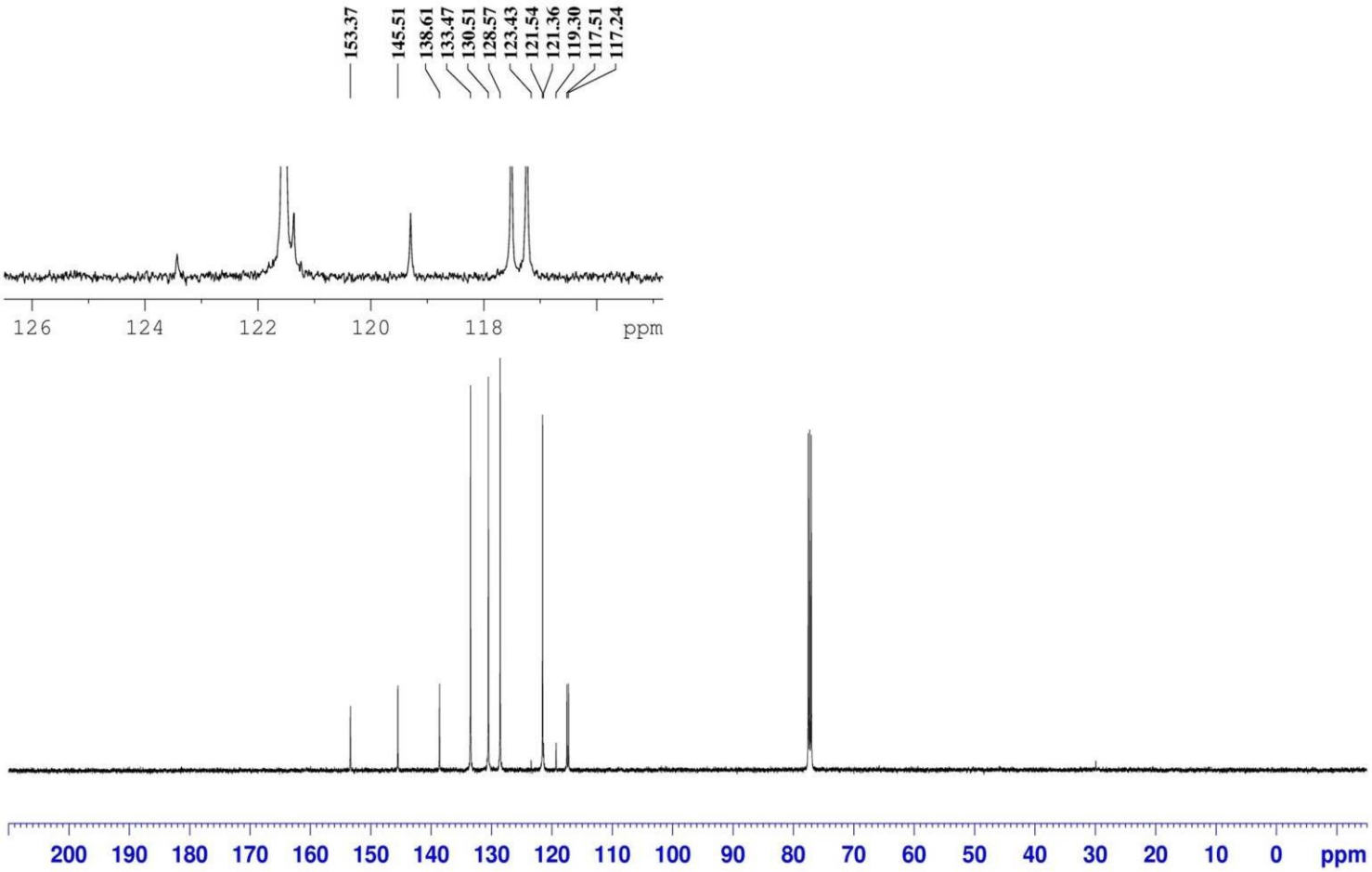


3ah

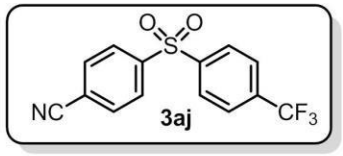


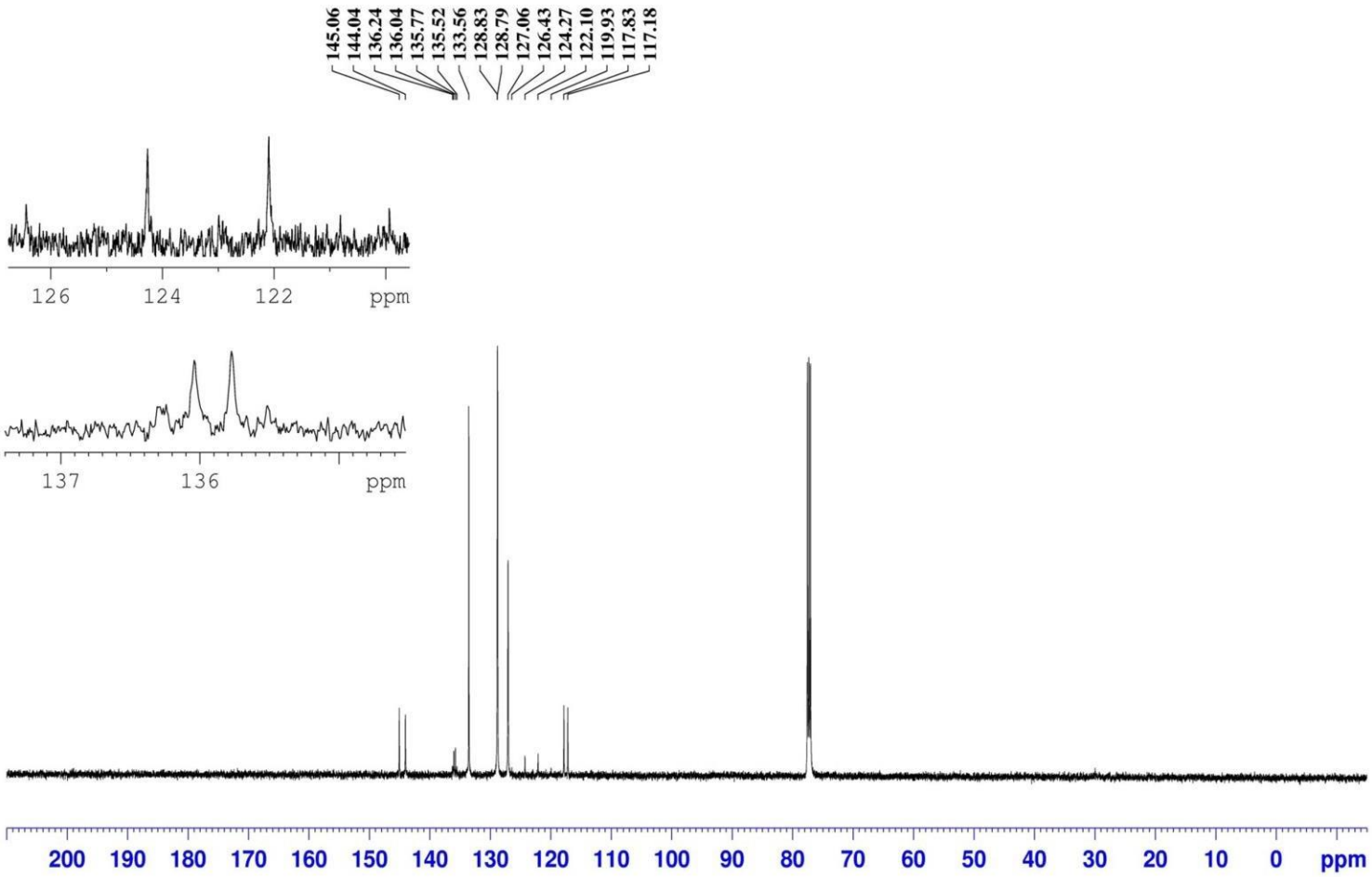
4–((4–(Trifluoromethoxy)phenyl)sulfonyl)benzonitrile
125 MHz, CDCl3



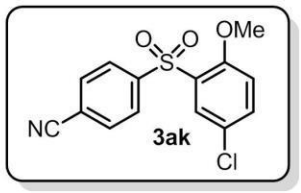


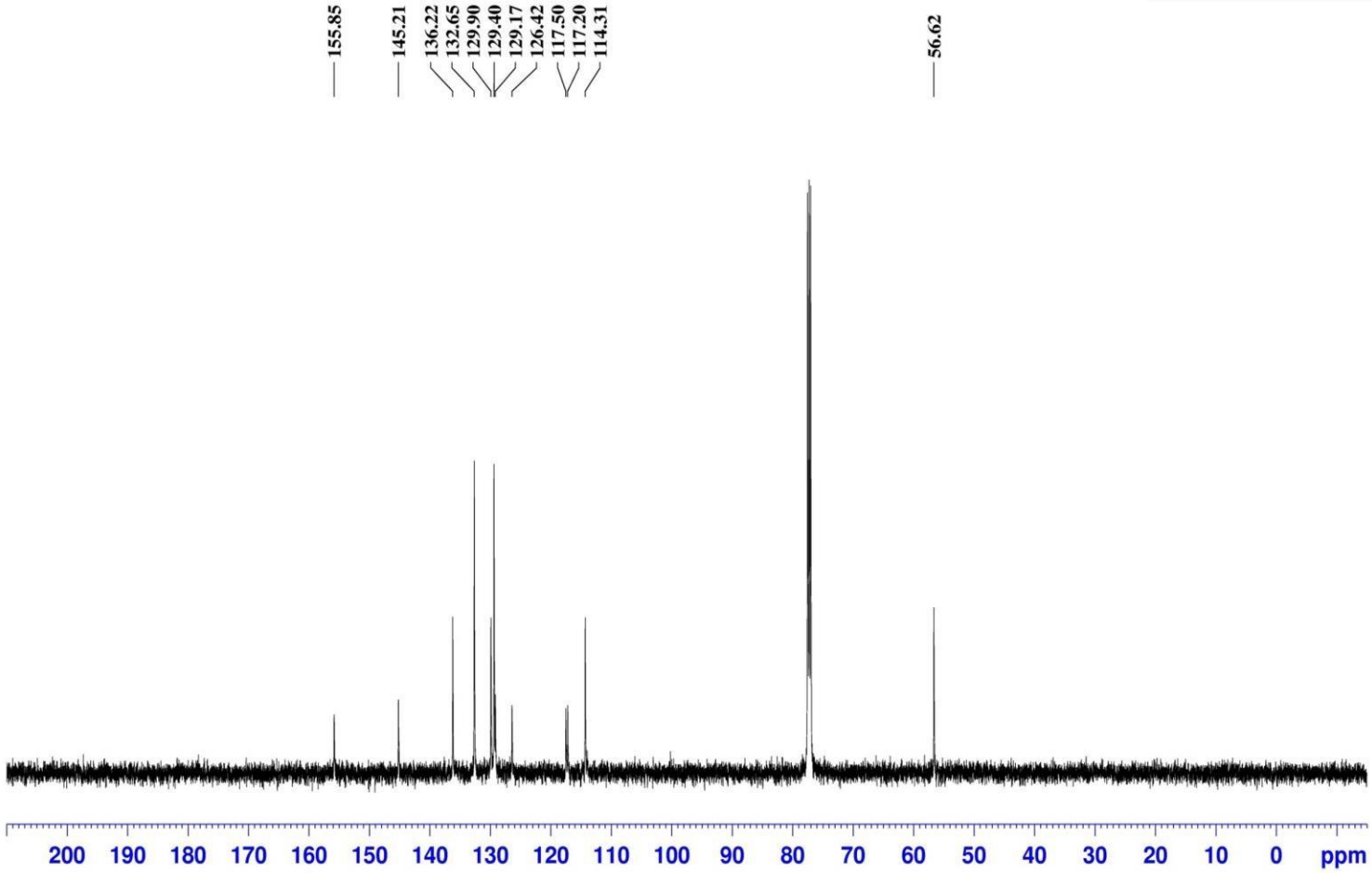
4–((4–(Trifluoromethyl)phenyl)sulfonyl)benzonitrile
125 MHz, CDCl3



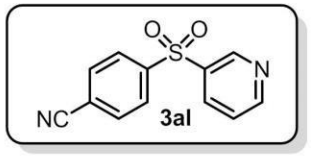


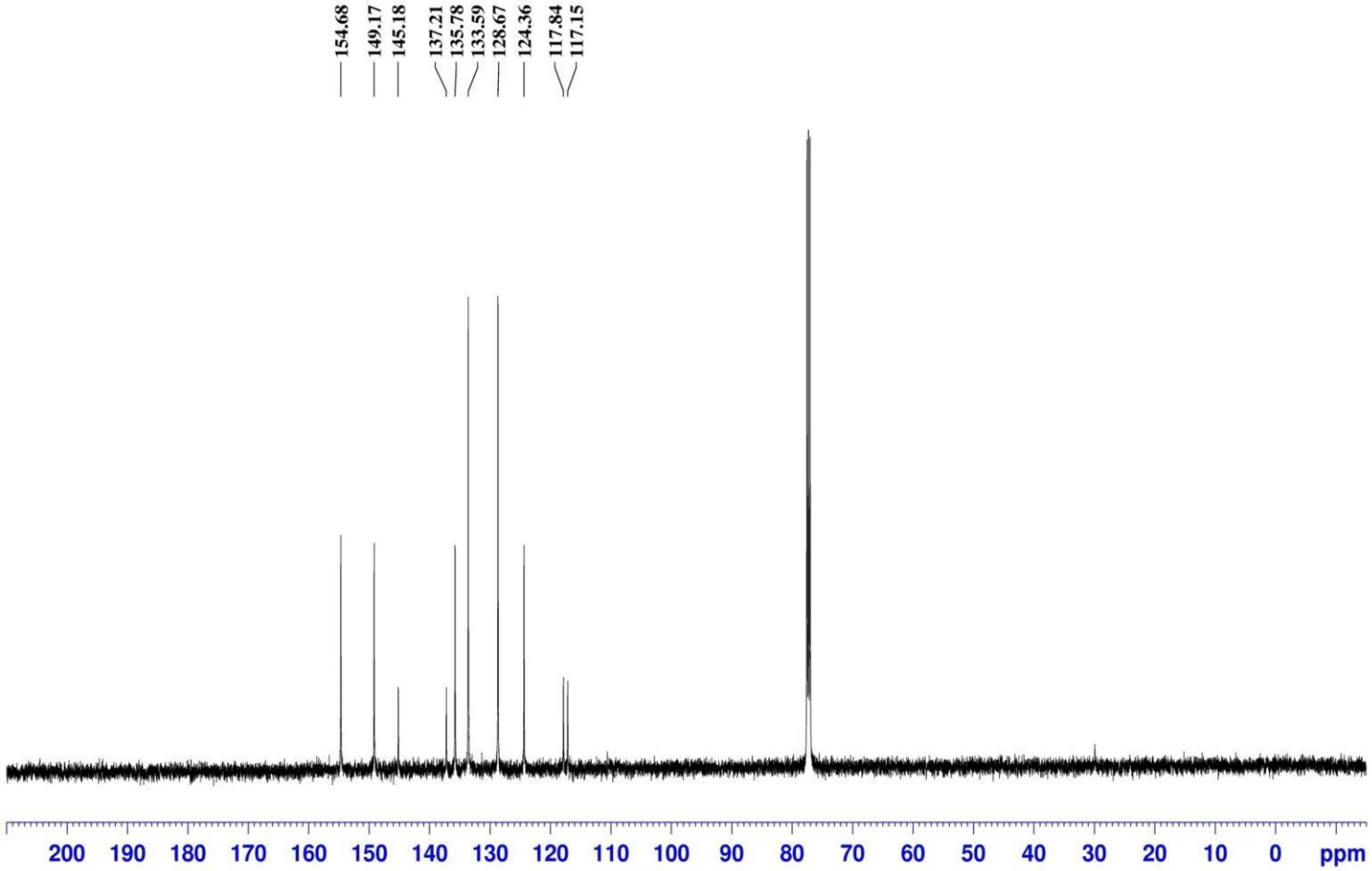
4–((5–Chloro–2–methoxyphenyl)sulfonyl)benzonitrile
125 MHz, CDCl3



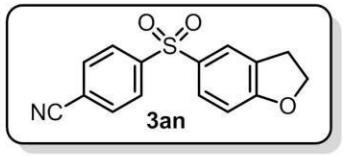


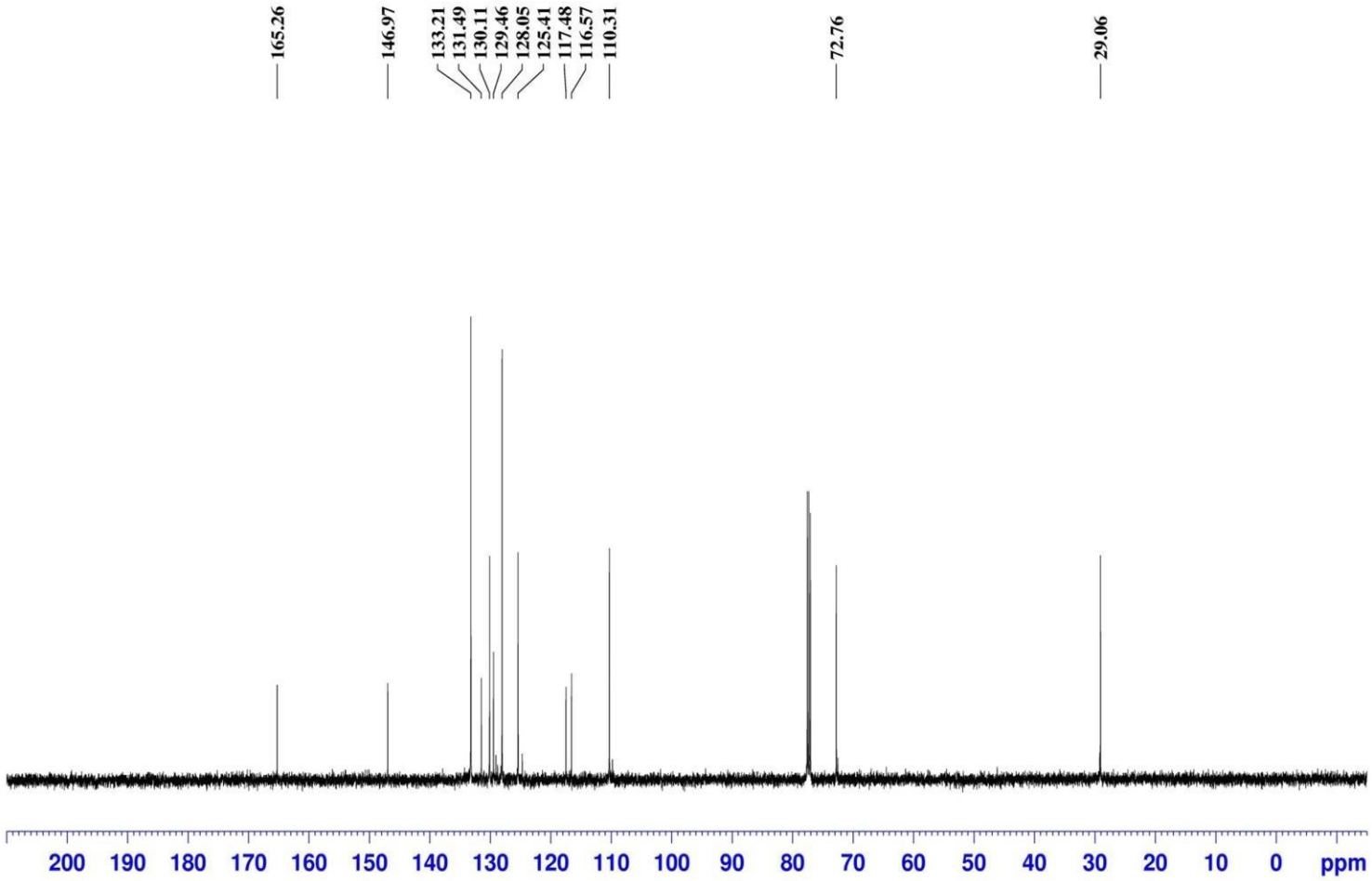
4–(Pyridin–3–ylsulfonyl)benzonitrile
125 MHz, CDCl3



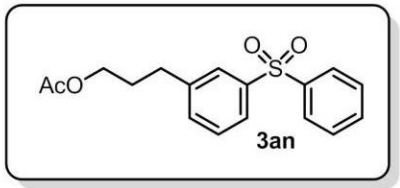


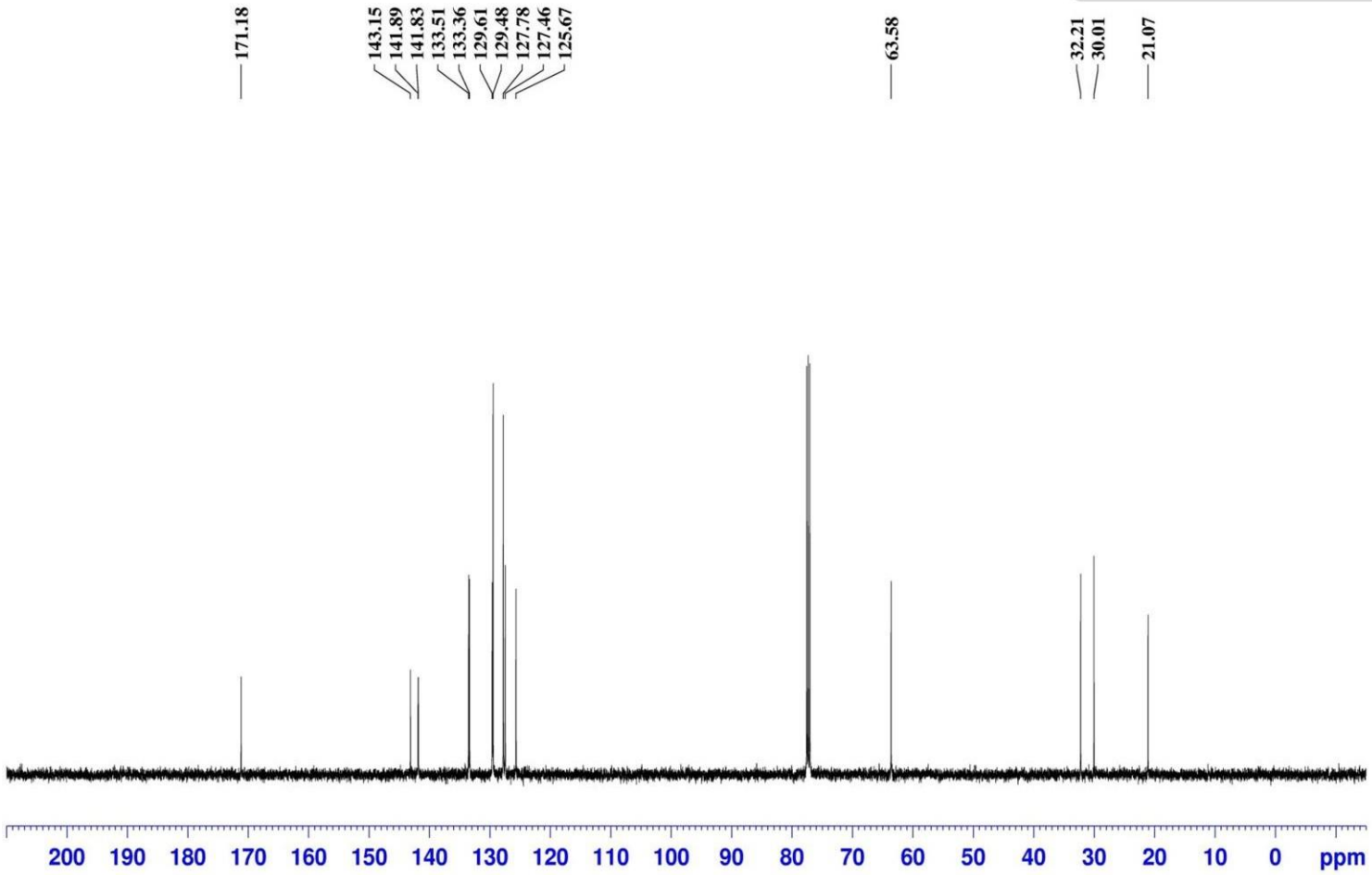
4–((2,3–Dihydrobenzofuran–5–yl)sulfonyl)benzonitrile
125 MHz, CDCl3



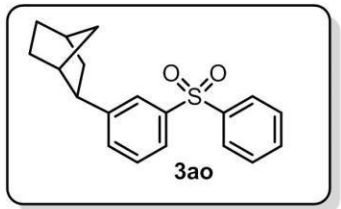


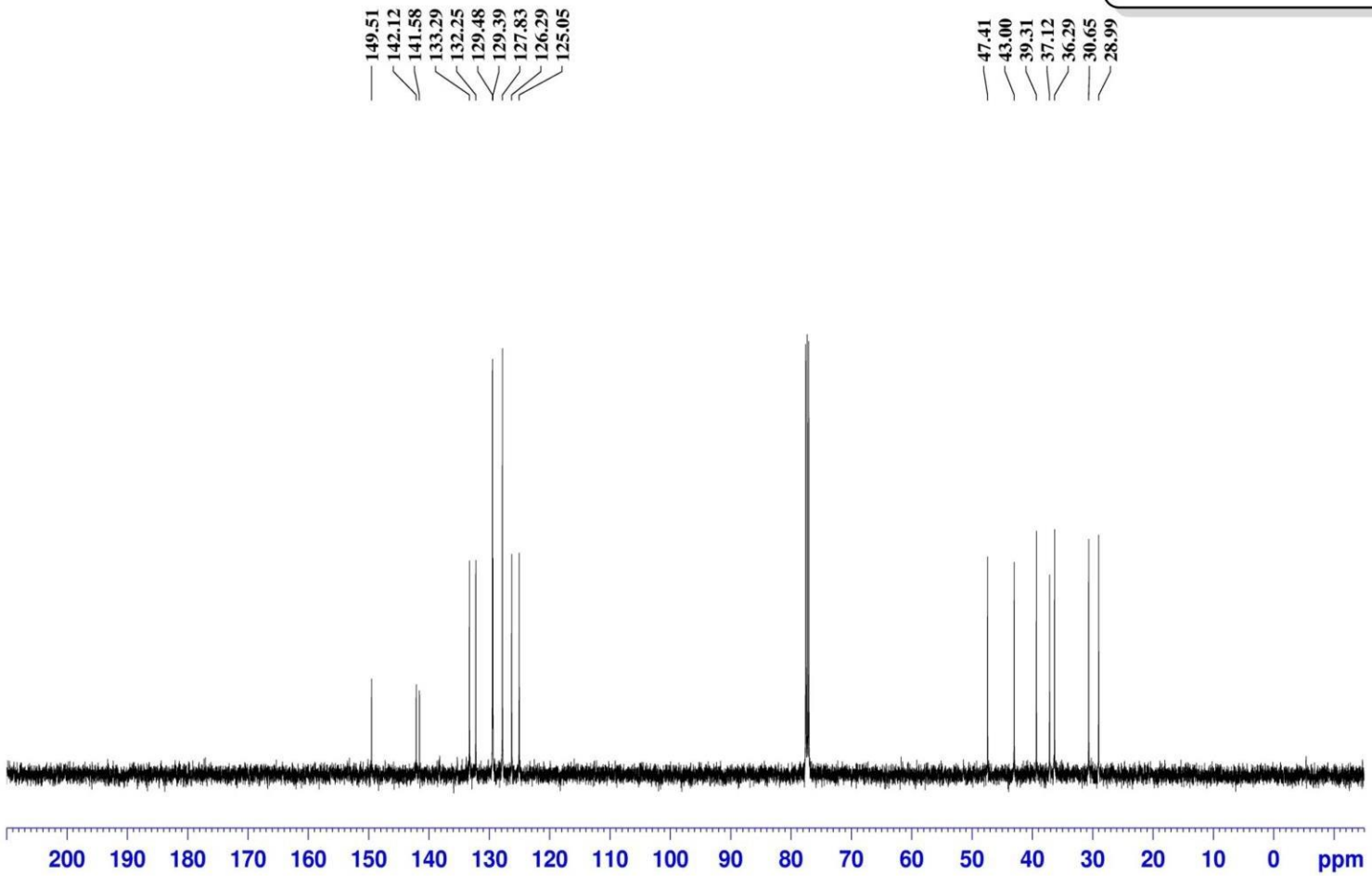
3–(3–(Phenylsulfonyl)phenyl)propyl Acetate
125 MHz, CDCl3



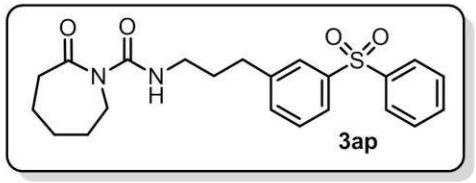


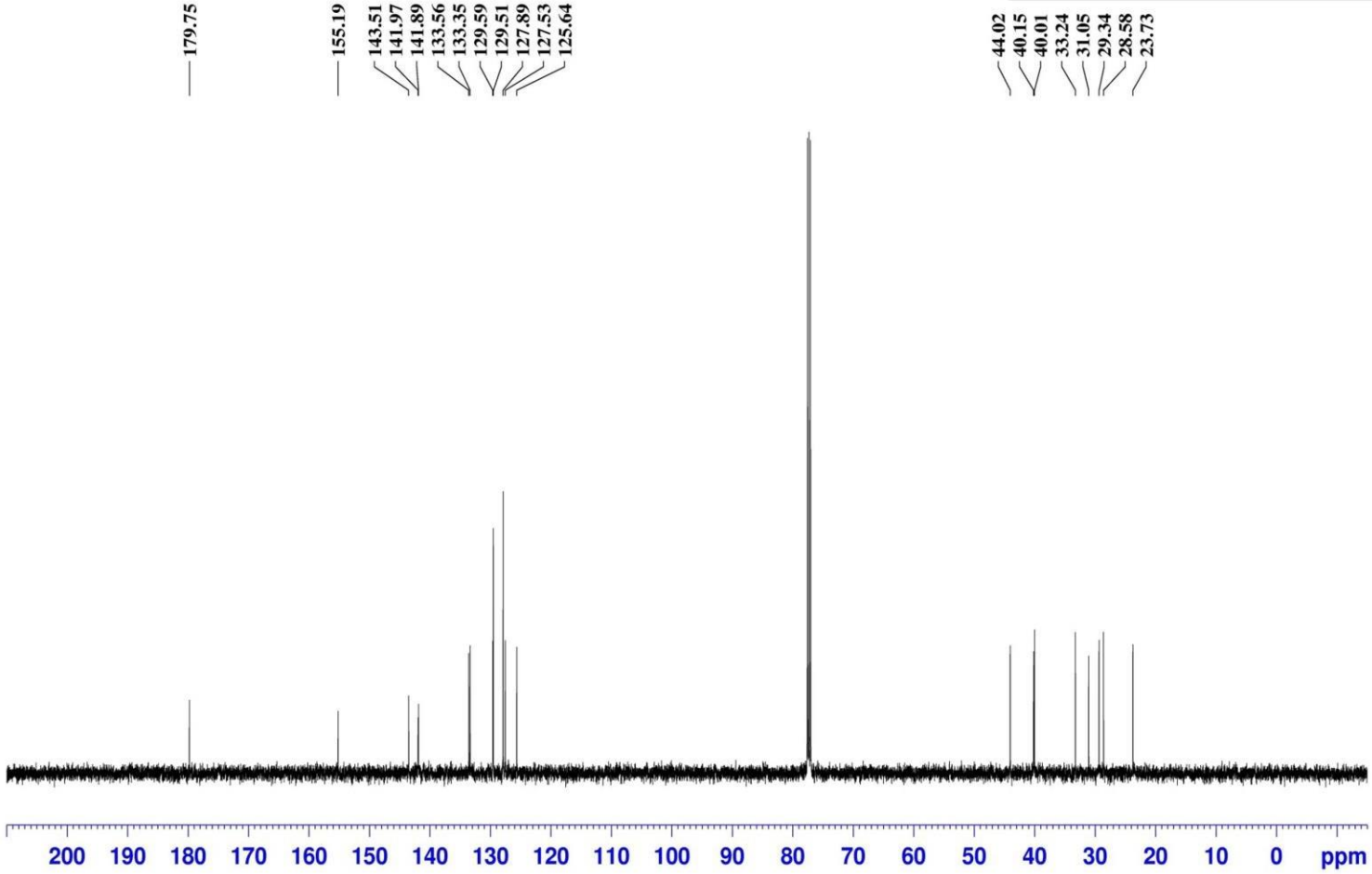
(±)−2−(3−(Phenylsulfonyl)phenyl)bicyclo[2.2.1]heptane
125 MHz, CDCl3



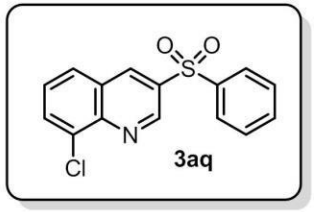


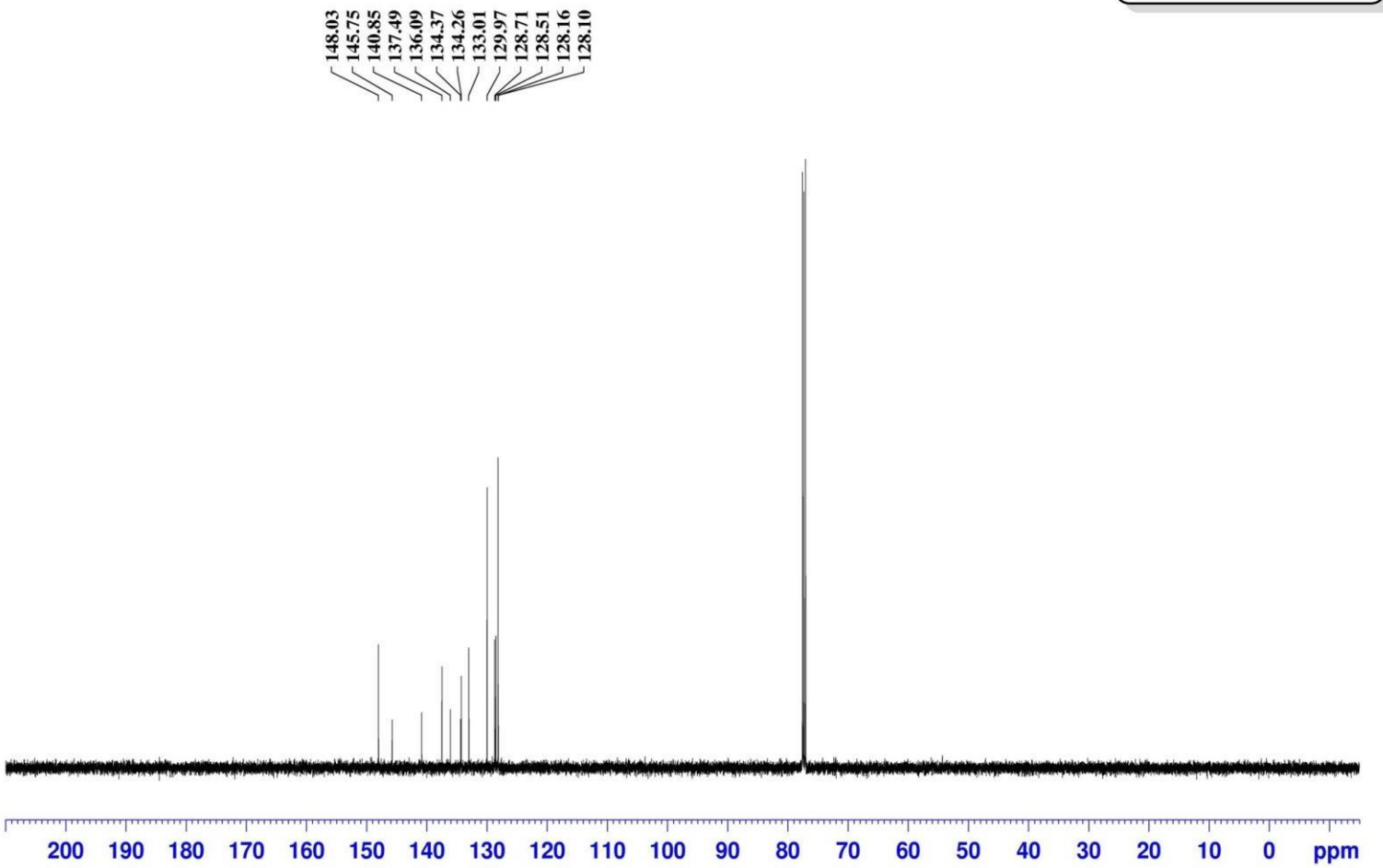
2–Oxo–N–(3–(3–(phenylsulfonyl)phenyl)propyl)azepane–1–carboxamide
125 MHz, CDCl3





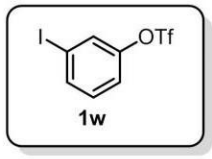
8−Chloro−3−(phenylsulfonyl)quinoline
125 MHz, CDCl3

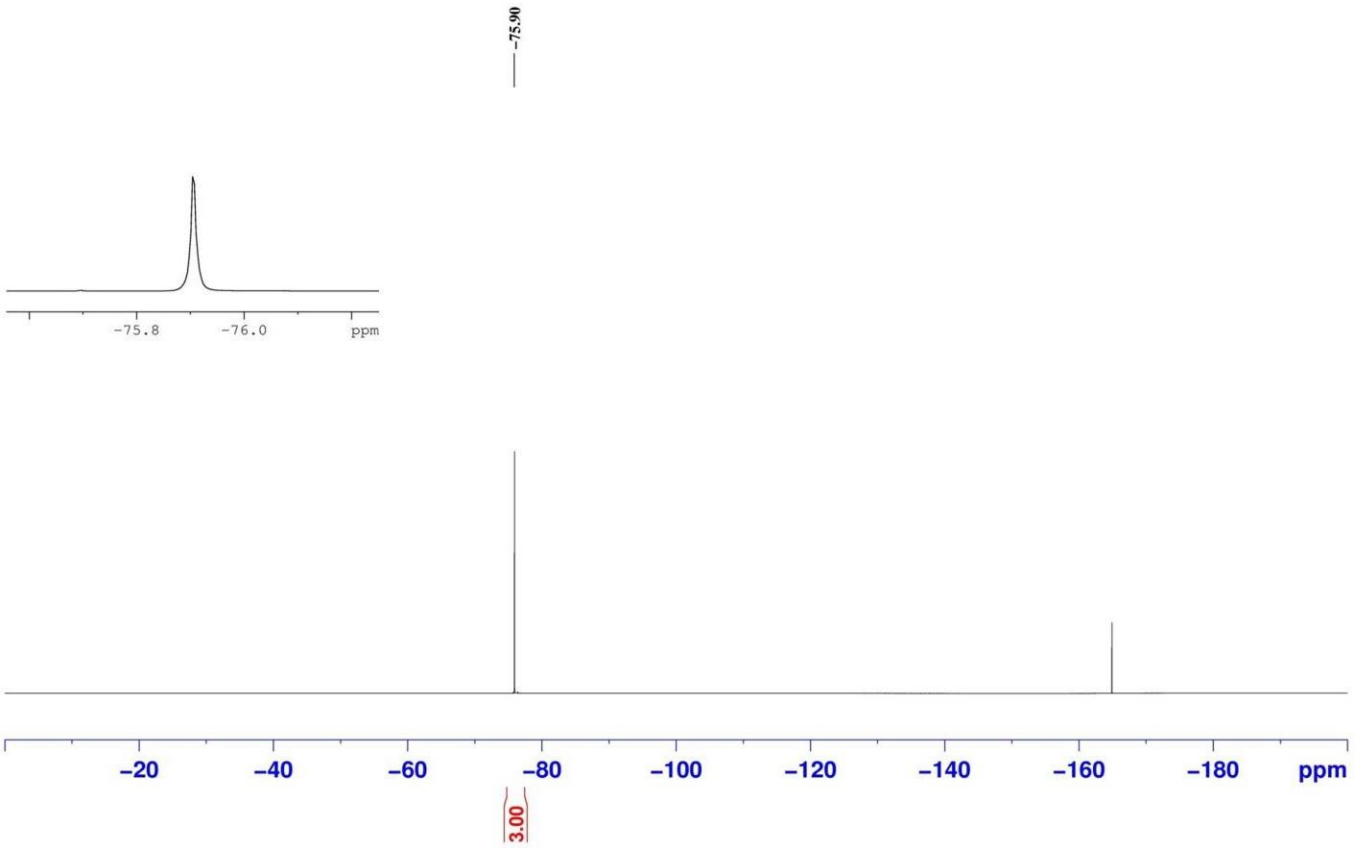




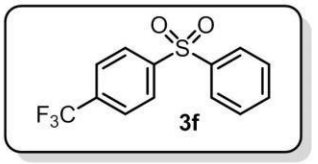
^{19}F NMR Spectra of Synthesized Compounds

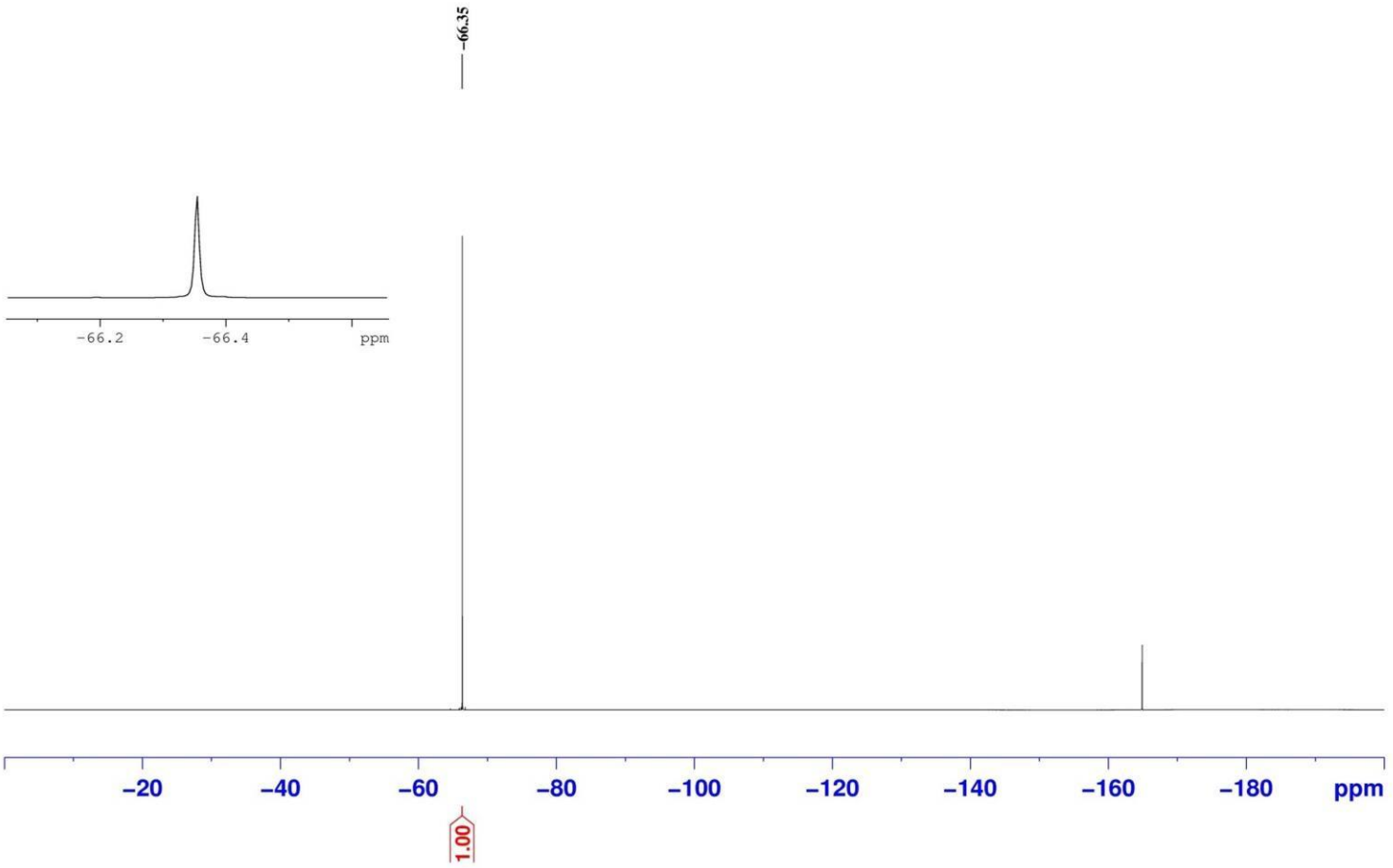
3–iodophenyl trifluoromethanesulfonate
471 MHz, CDCl3



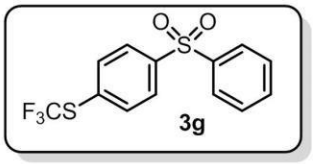


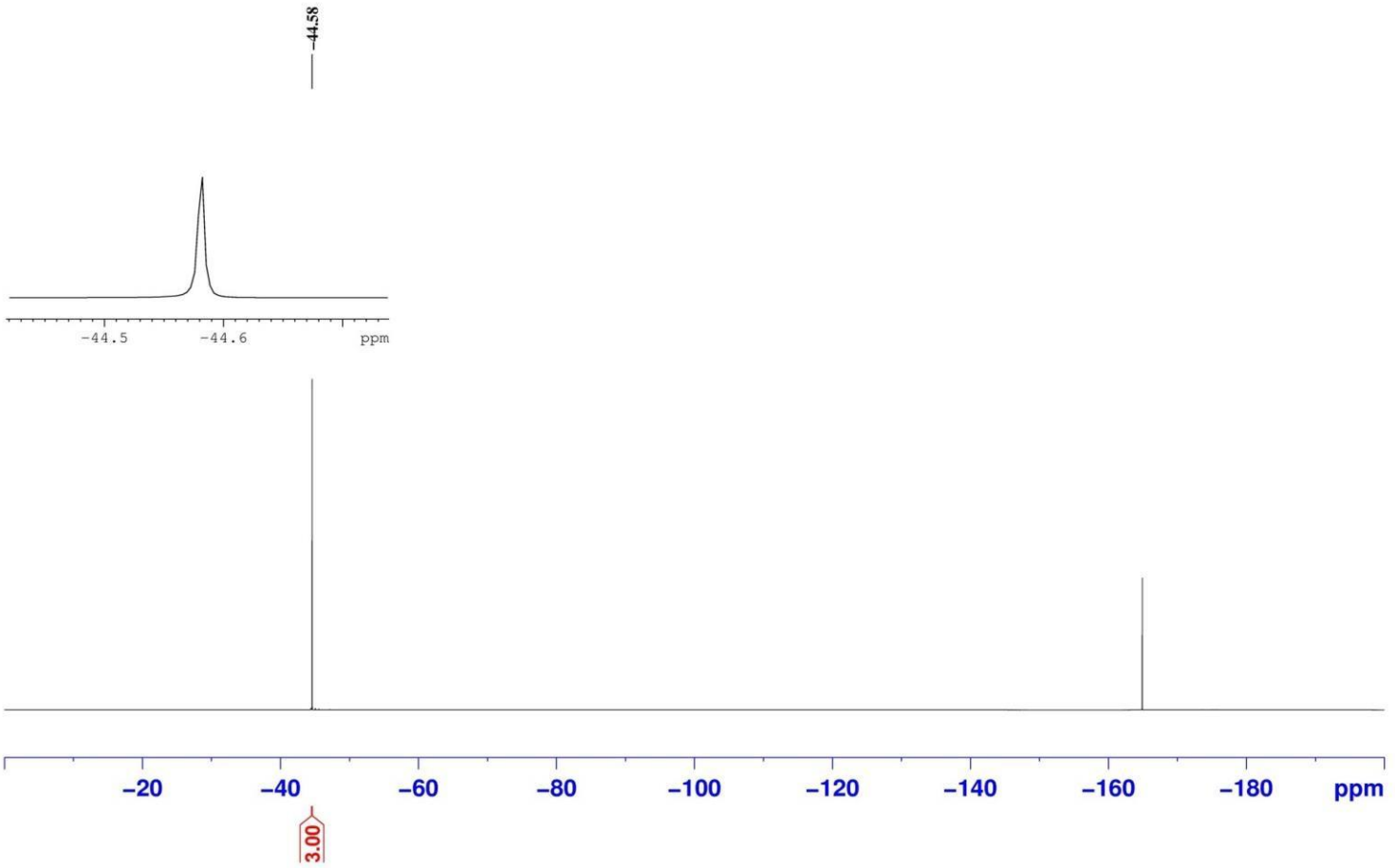
1–(Phenylsulfonyl)–4–(trifluoromethyl)benzene
471 MHz, CDCl3



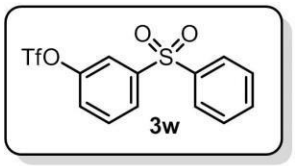


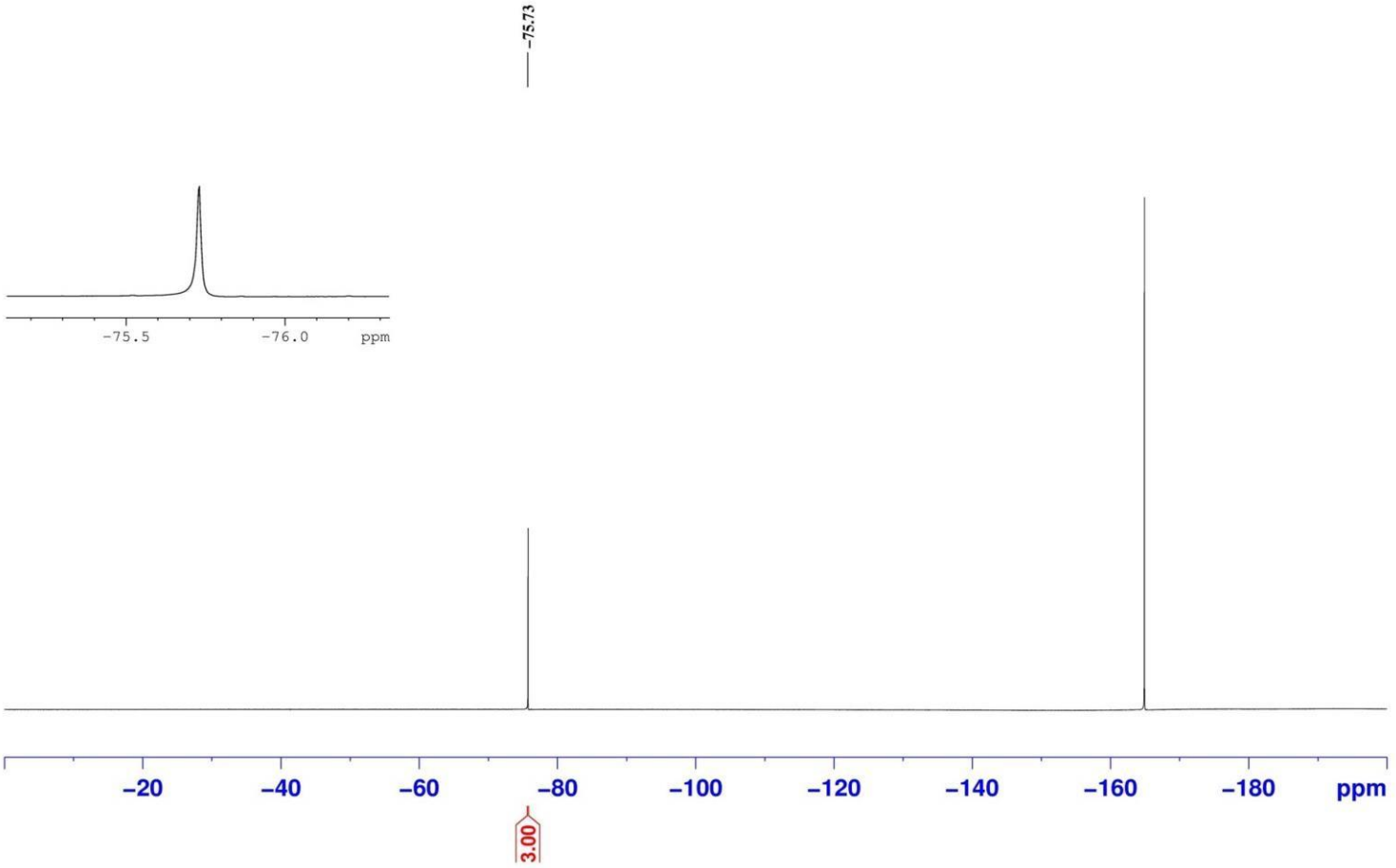
(4–(Phenylsulfonyl)phenyl)(trifluoromethyl)sulfane
471 MHz, CDCl3



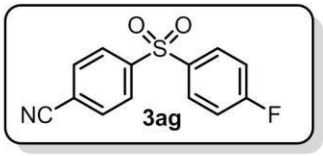


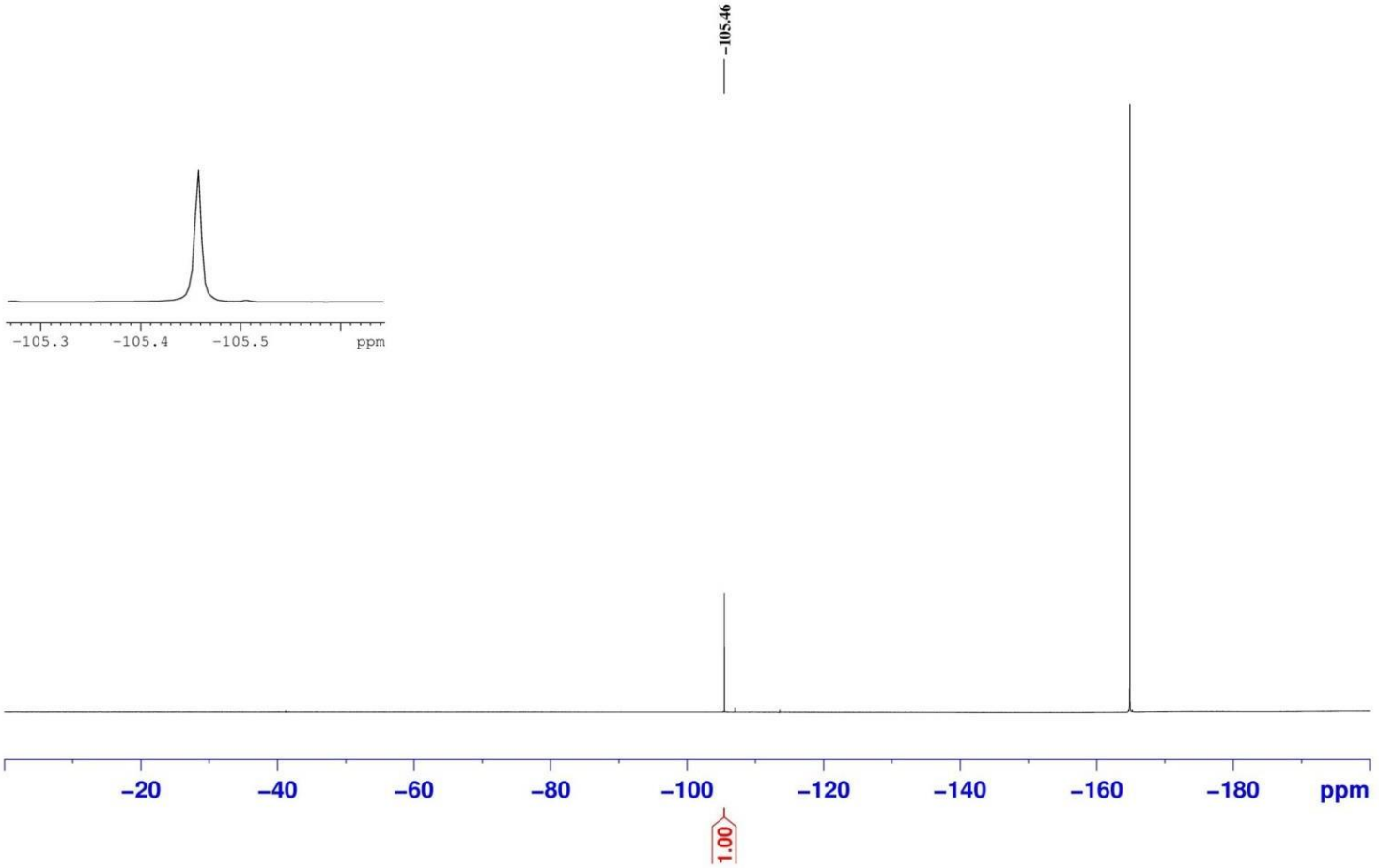
3–(Phenylsulfonyl)phenyl trifluoromethanesulfonate
471 MHz, CDCl3



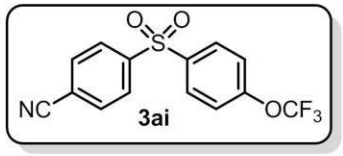


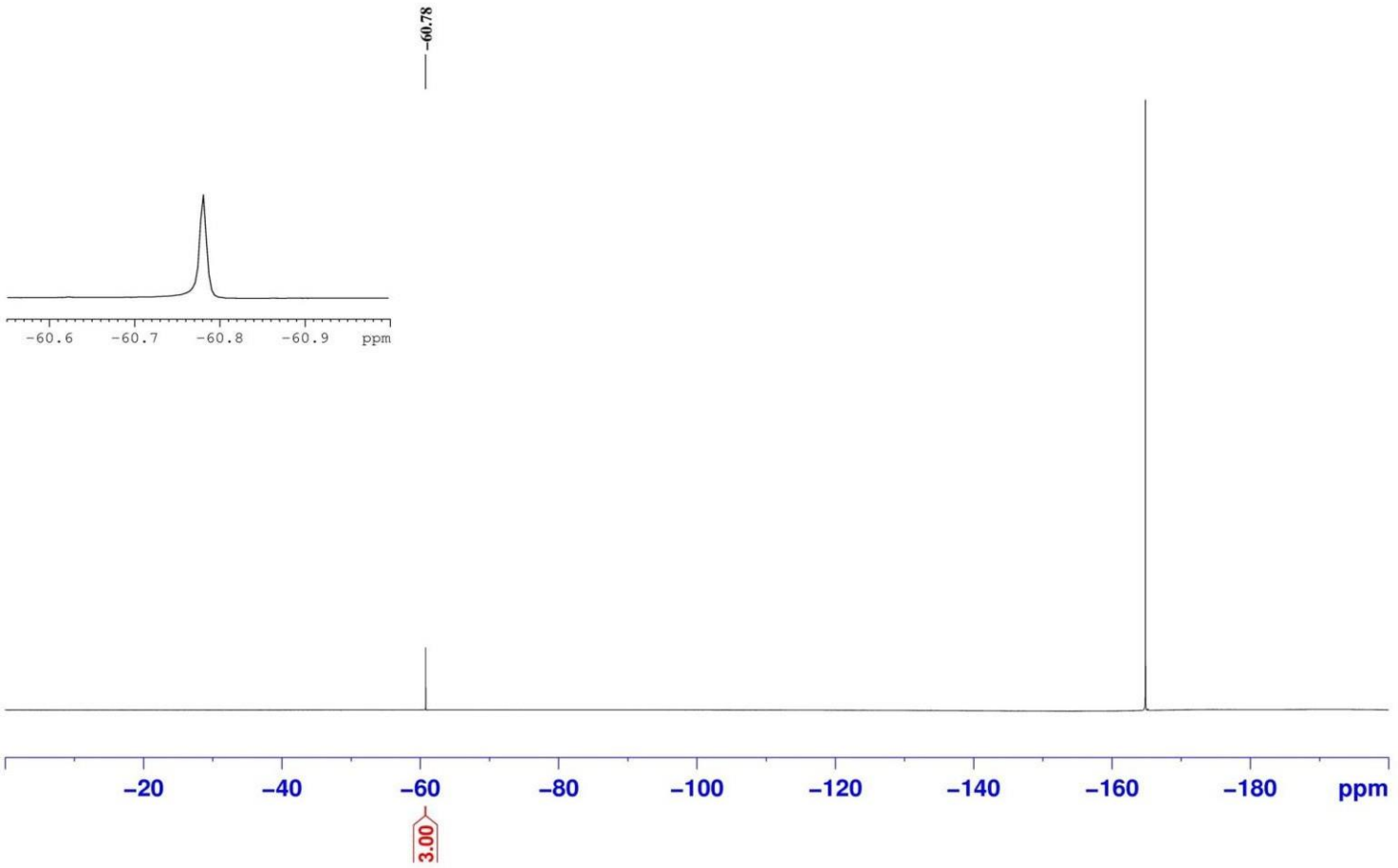
4–((4–Fluorophenyl)sulfonyl)benzonitrile
471 MHz, CDCl3





4–((4–(Trifluoromethoxy)phenyl)sulfonyl)benzonitrile
471 MHz, CDCl3





4–((4–(Trifluoromethyl)phenyl)sulfonyl)benzonitrile
471 MHz, CDCl3