Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of Amino-Diamondoid Pharmacophores via Photocatalytic C–H Aminoalkylation

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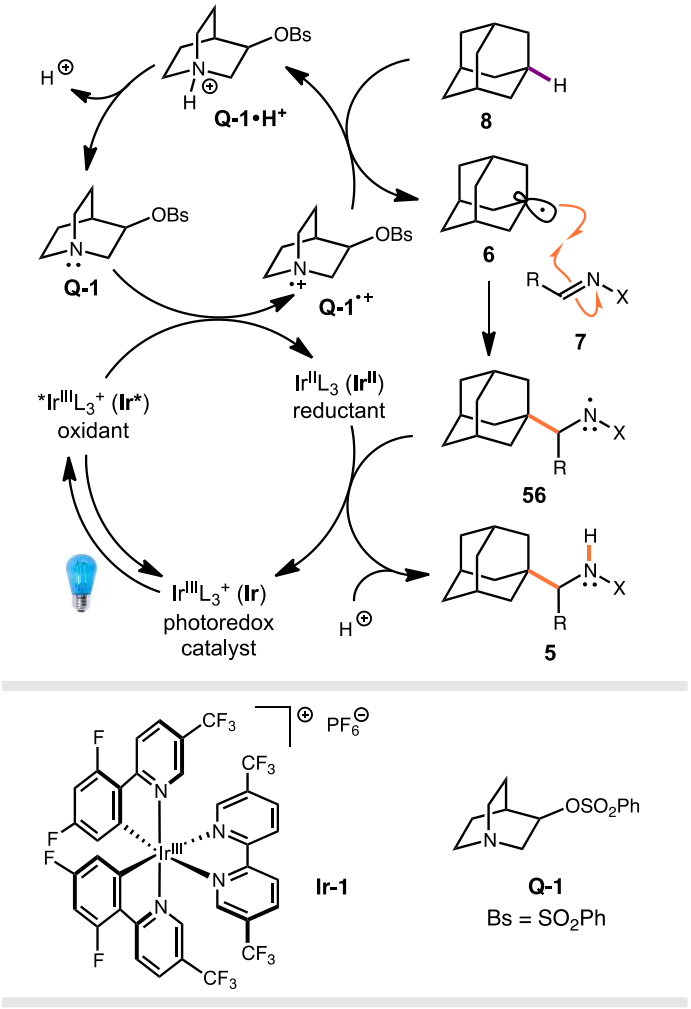
General Methods:

All reactions were carried using oven dried or flame dried glassware charged with a magnetic stir bar and conducted under an inert nitrogen atmosphere using typical Schlenk techniques. Solvents were dried by passage through columns of activated alumina or distilled and stored under nitrogen over 5 Å sieves or otherwise freshly distilled. All starting materials were prepared according to known literature procedures or used as obtained from commercial sources, unless otherwise indicated. Reactions were monitored by thin-layer chromatography (TLC) and carried out on 0.25 mm coated commercial silica gel plates (Analtech TLC Uniplates, F254 precoated glass plates) using UV light as visualizing agent. Unless otherwise indicated, silica gel chromatography was performed using flash chromatography on P60 silica. Alternatively, a Yamazen Smart Flash AI-580S system in conjunction with Yamazen Universal Premium 40g columns with the specified gradient elution mode was used when indicated.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance NEO 400, Bruker Avance III 500, or Bruker Avance III 700 MHz spectrometer and were internally referenced to residual protio solvent signal (note: CDCl3 referenced at δ 7.27 ppm for ^{1}H NMR and δ 77.16 ppm for ^{13}C NMR, respectively. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, app=apparent), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. High-resolution mass spectrometry data were recorded on an Agilent LCTOF instrument using direct injection of samples in dichloromethane into the electrospray source (ESI) with positive ionization. Gas Chromatography was carried out using a Shimadzu GC-2010 Plus instrument equipped with a Shimadzu SH-Rxi-5ms column. Column Specifications: 15 m (L), 0.25 mm (ID), 0. 25 µm (d_f), (diphenyl/dimethyl polysiloxane) stationary phase.

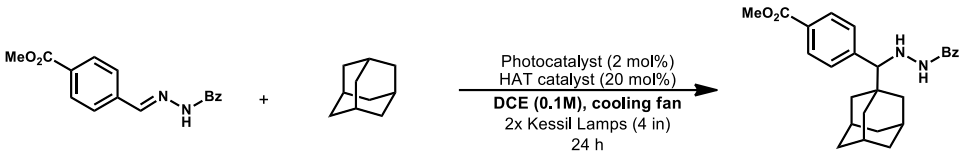
Dual Photocatalytic Cycle for Ir-1/Q-1



Scheme S1: Proposed Photocatalytic Cycle for Indirect HAT with Ir-1/Q-1

Catalyst Optimizations

Table S1: Variation of Catalytic Systems with Bz-Hydrazone **S1**

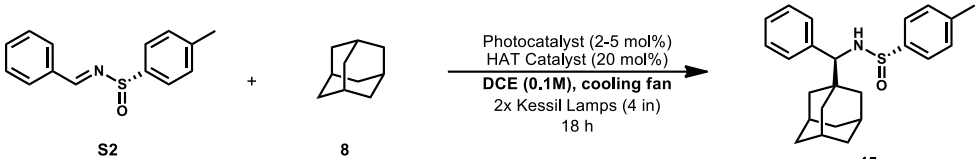


S1 1 equiv, 0.15 mmol + **8** 3 equiv, 0.45 mmol → **28**

Entry	Catalyst System	Light Source	Yield (NMR)*
1	Ir-1, Q-1	456 nm	85 %
2	Ir-2, Q-2	456 nm	24 %
3	Ir-2, Q-2	427 nm	14 %
4	Ir-1, no HAT	456 nm	0 %
5	Q1, No photocat.	456 nm	0 %
6	Ir-1, Q-1	no light	0 %

*NMR ananlysis done using Bn_2O as internal standard.

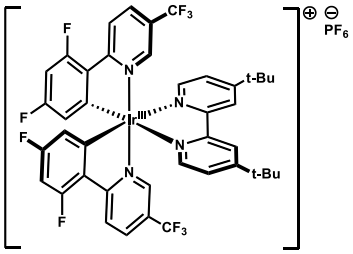
Table S2: Variation of Catalytic Systems with Chiral Sulfinyl Imine **S2**



S2 1 equiv, 0.15 mmol + **8** 3 equiv, 0.45 mmol → **45**

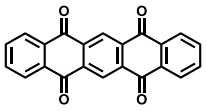
Entry	Catalyst System	Light Source	Yield (NMR)[b]
1	Ir-1, Q-1	456 nm	44 % (9:1 d.r.)
2	Ir-2, Q-2	456 nm	18 %[c]
3	ClAQ[a]	427 nm	<5 %[c]
4	PT[a]	427 nm	53 % (9:1 d.r.)
5	PT[a]	390 nm	77 % (9:1 d.r.)
6	PT[a]	no light	0 %

[a] No dedicated HAT catalyst added.
[b] NMR ananlysis done using Bn_2O as internal standard.
[c] d.r. not determined.

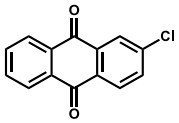


$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$
(Ir-2)

Q-2

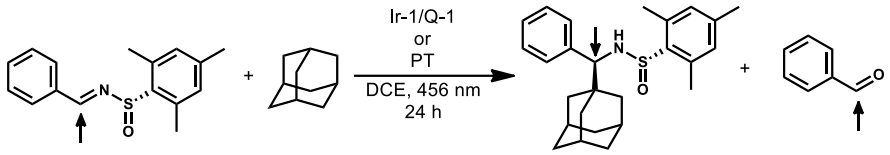


Pentacenetetraone
(PT)



Chloroanthraquinone
(ClAQ

Table S3: Aldehyde Side Product Formation Under Different Catalyst Systems



Cat. Sys.	SM:Prod:Ald
Ir-1/Q-1	28:52:20
PT	45:44:1

*Based on integral ratio of indicated protons

UV-Vis Spectra of Ir-1, Q-1 and PT

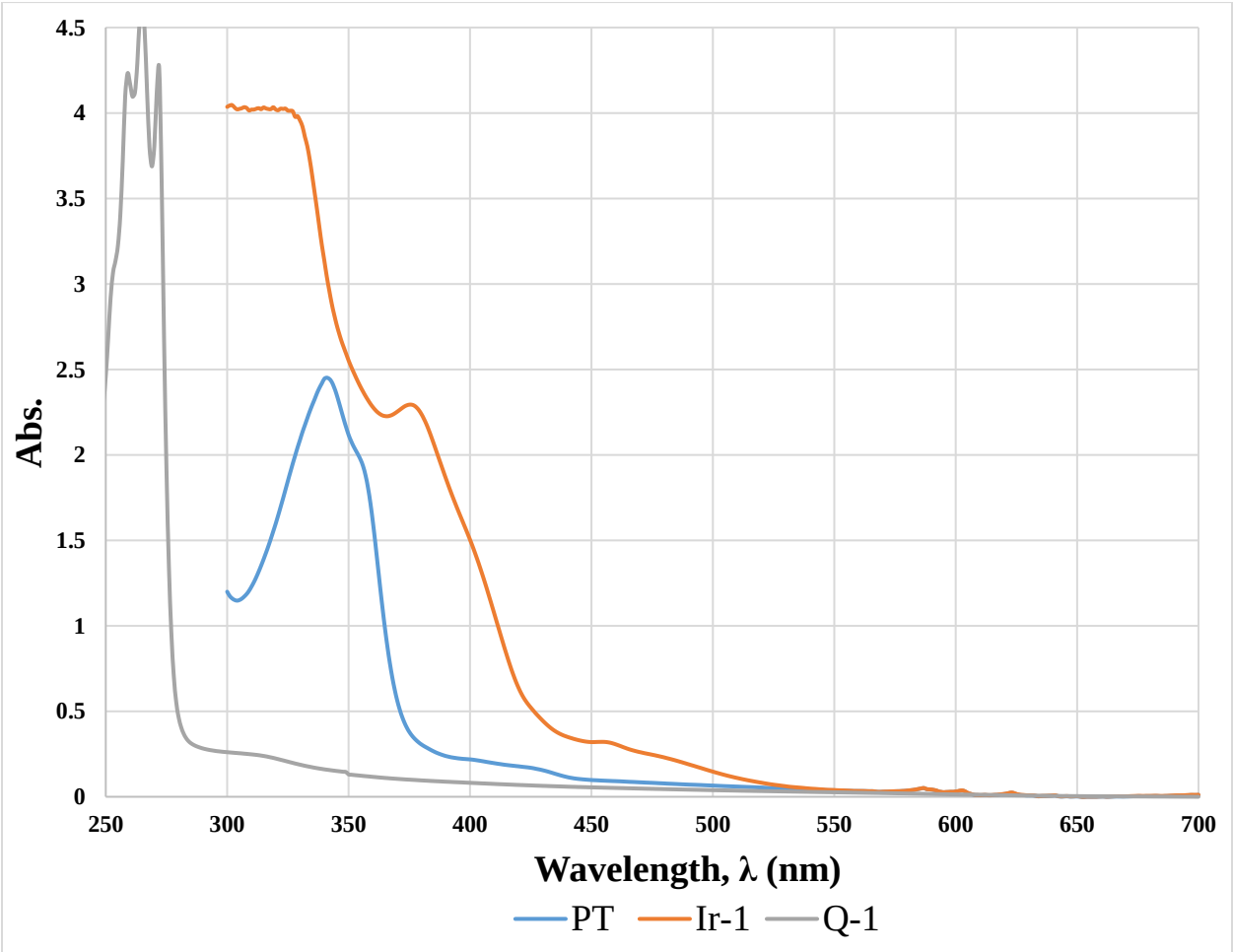


Figure S1: UV-Vis Spectra of the Photocatalysts and HAT Catalyst Used

Solvent Optimizations

Table S4: Effect of Reaction Concentration for Bz-Hydrazone **S1**

S1 1 equiv, 0.15 mmol

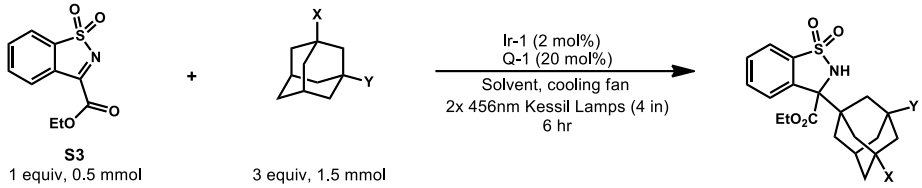
8 3 equiv, 0.45 mmol

28

Entry	DCE (mL)	DCE (M)	% Yield (NMR)*
1	1.0	0.15	47%
2	1.5	0.10	63%
3	3.0	0.05	56%

*NMR ananlysis done using Bn_2O as internal standard.

Table S5: Solvent Studies with Substituted Adamantanes and Cyclic Sulfonimine **S3**



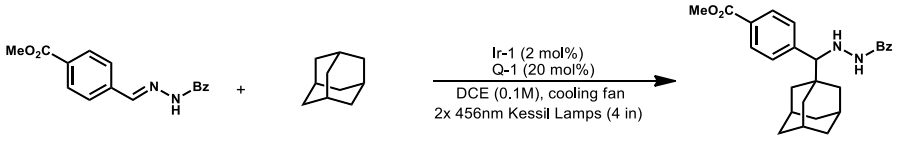
S3 1 equiv, 0.5 mmol

3 equiv, 1.5 mmol

Entry	X	Y	Solvent	Yield (Isolated)
1	H	H	DCE	83%
2	Cl	H	DCE	66%
3	Cl	H	MeCN	74%
4	CN	H	DCE	27%
5	CN	H	MeCN	40%
6	Ac	H	DCE	66%
7	Ac	H	MeCN	62%
8	Me	Me	DCE	80%
9	OH	H	DCE	77%

NMR Time Study

Table S6: Effect of Reaction Duration with Bz-Hydrazone **S1**



S1 1 equiv, 0.15 mmol

8 3 equiv, 0.45 mmol

28

Entry	Reaction Time	SM:Prod (NMR)*
1	20 min	87:13
2	3 hours	67:33
3	8 hours	42:58
4	22 hours	15:85
5	48 hours	9:83**

*SM:Prod ratio calculated via crude NMR analysis of the aryl methyl ester CH_3 signals.
**~ 5% of imine SM underwent hydrolysis back to the benzaldehyde after 48 h.

Effect of Water on Ir-1/Q-1 Catalyst System

Table S7: Water Additive with Bz-Hydrazone **S1**

S1 1 equiv, 0.15 mmol

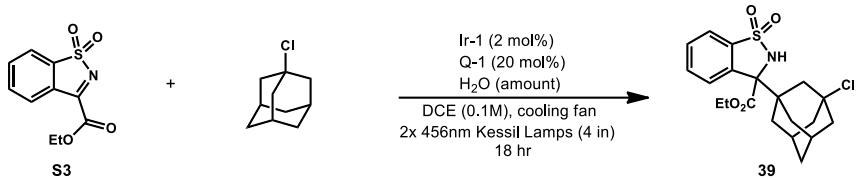
8 3 equiv, 0.45 mmol

28

Entry	H_2O (equiv.)	% Yield (NMR)*	% Yield (GC)*
1	none	77%	76%
2	2.7 uL (1 equiv.)	76%	76%
3	5.4 uL (2 equiv.)	73%	74%

*NMR and GC ananlysis done using Bn_2O as internal standard.

Table S8: Water Additive with Cyclic Sulfonimine **S3**



S3 1 equiv, 0.15 mmol

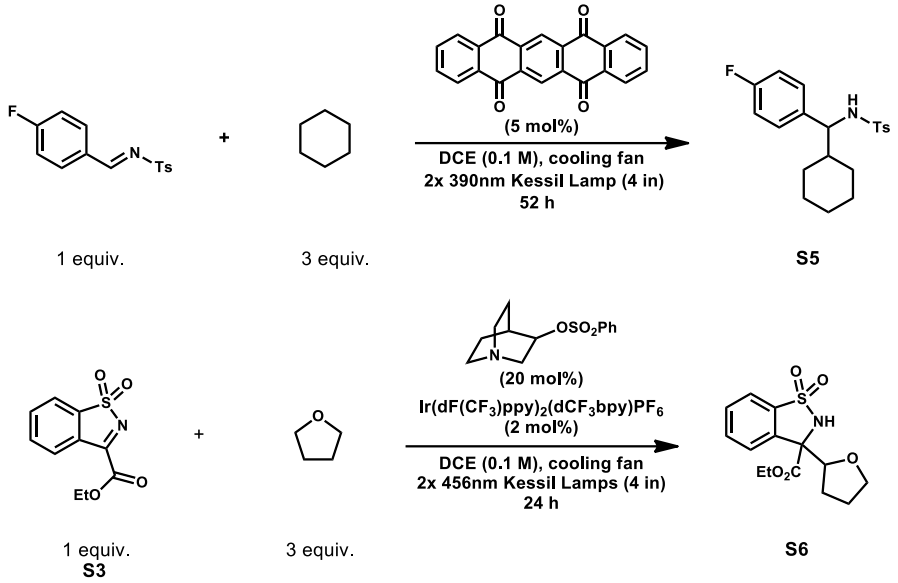
3 equiv, 0.45 mmol

39

Entry	H_2O (equiv.)	% Yield (NMR)*	% Yield (GC)*
1	none	24%	25%
2	2.7 uL (1 equiv.)	26%	27%
3	5.4 uL (2 equiv.)	24%	25%

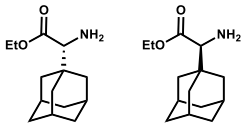
*NMR and GC ananlysis done using Bn_2O as internal standard.

Photocatalytic reactions with non-adamantyl substrates



Scheme S2: Aminoalkylation of cyclohexane and tetrahydrofuran

Optical Rotation Studies



R-52 S-52

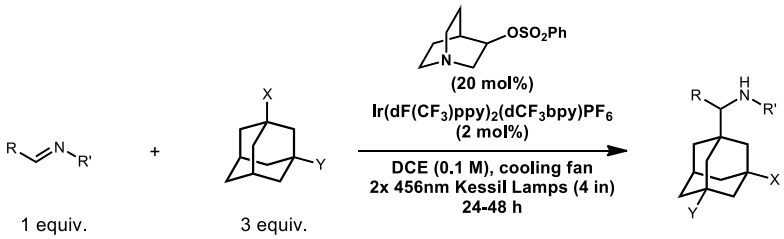
Measurements taken using a Jasco DIP-1000 polarimeter using a sodium lamp and a 100 mm cell.

Table S9: Determination of $[\alpha]_D$ for R-52 and S-52

	Blank	R-52	S-52
run 1	0.0231	-0.0848	0.0566
run 2	0.0220	-0.0890	0.0536
run 3	0.0218	-0.0870	0.0576
run 4	0.0234	-0.0806	0.0540
run 5	0.0228	-0.0840	0.0570
run 6	0.0220	-0.0830	0.0548
run 7	0.0230	-0.0860	0.0590
Average	0.0226	-0.0849	0.0561

length	1	dm
conc R-52	0.0032	g/mL
conc S-52	0.0010	g/mL
α R-52	-0.1075	
α S-52	0.0335	
$[\alpha]_D$ S-52	-33.5938	
$[\alpha]_D$ R-52	33.5000	

General Procedures:



General Procedure A: Photochemical Reactions with Ir-1/Q-1

To an 8-mL glass vial equipped with a magnetic stir bar were sequentially added imine (0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (2 mol%), hydrogen atom transfer catalyst (20 mol%), adamantane (1.50 mmol, 3.0 equiv.), and 1,2-dichloroethane (5.0 mL, 0.1M). The vial was sealed with a Teflon septum and screw-top cap. The resulting mixture was degassed by freezing the vial contents in a dry ice/acetone bath, placing the vial under a static vacuum, then allowing the frozen mixture to thaw (this cycle was repeated 3 times) then backfilled with N_2. The vials were then placed on a stir plate and irradiated between two 456nm Kessil® PR160 LED lamps (http://www.kessil.com/photoredox/Products.php) 4 inches away from the diode source on each side. A single small desktop fan was aimed directly at the vial to facilitate heat dissipation (experiments set up in this manner operate at just over room temperature at approx. 27 °C).

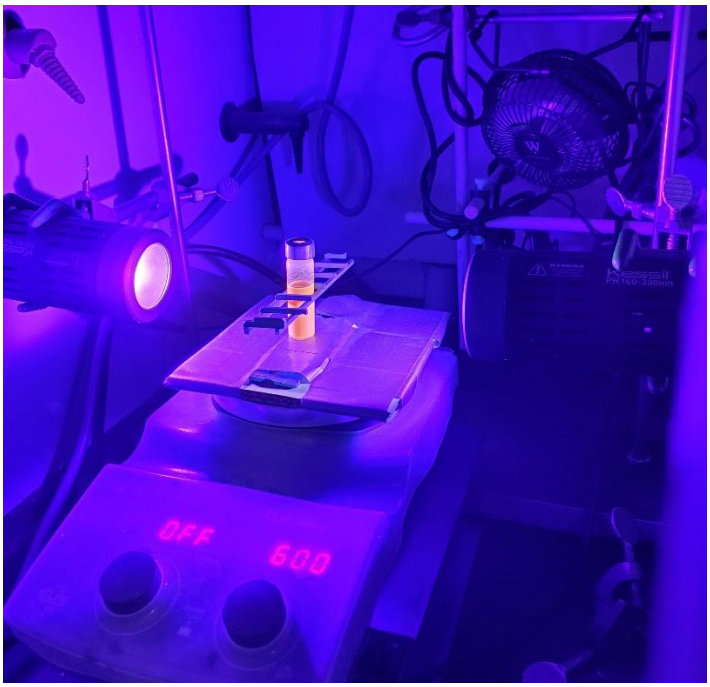
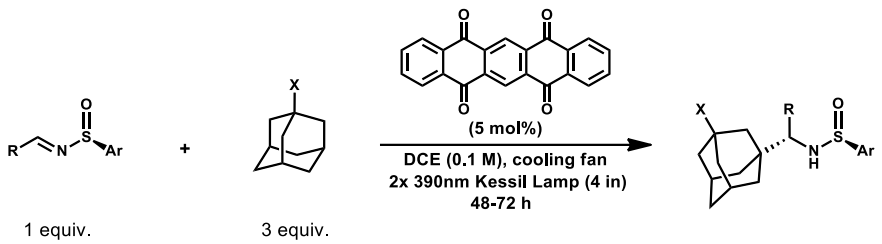
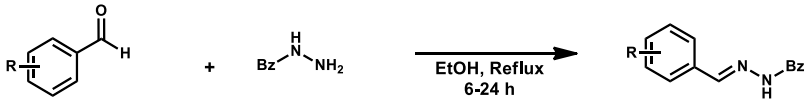


Figure S2: Photochemical Reaction Setup



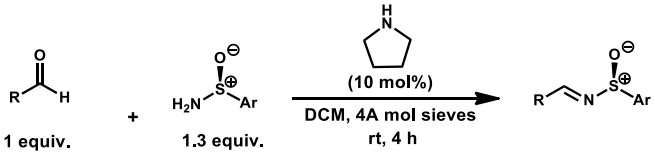
General Procedure B: Photochemical Reactions with PT

To an 8-mL glass vial equipped with a magnetic stir bar were sequentially added chiral sulfinimine (1.0 equiv.), pentacenetetraone photoredox catalyst **PT** (5-10 mol%), adamantane (3.0 equiv.), and 1,2-dichloroethane (0.1 M). The vial was sealed with a Teflon septum and screw-top cap. The resulting mixture was degassed by freezing the vial contents in a dry ice/acetone bath, placing the vial under a static vacuum, then allowing the frozen mixture to thaw (this cycle was repeated 3 times) then backfilled with N_2. The vials were then placed on a stir plate and irradiated between two 390nm Kessil® PR160 LED lamps (http://www.kessil.com/photoredox/Products.php) 4 inches away from the diode source on each side. A single small desktop fan was aimed directly at the vial to facilitate heat dissipation (experiments set up in this manner operate at just over room temperature at approx. 30 °C).



General Procedure C: Hydrazone Condensations

To a round bottom flask equipped with a magnetic stir bar were added *N*-acylhydrazide(7.00 mmol, 1 equiv.) followed by 14 mL ethanol. The aldehyde/ketone (8.40 mmol, 1.2 equiv.) was then added and the flask was fitted with a reflux condenser and sparged with nitrogen for 5 mins. The reaction was then heated to 95 °C and stirred for 4-8 hours at reflux until the reaction was judged complete by TLC. The reaction mixture was allowed to cool to room temperature and was then stored in the freezer (-4 °C) overnight to allow the product to crystallize. The crystals were then collected via vacuum filtration and rinsed with cold ethanol then cold hexanes.

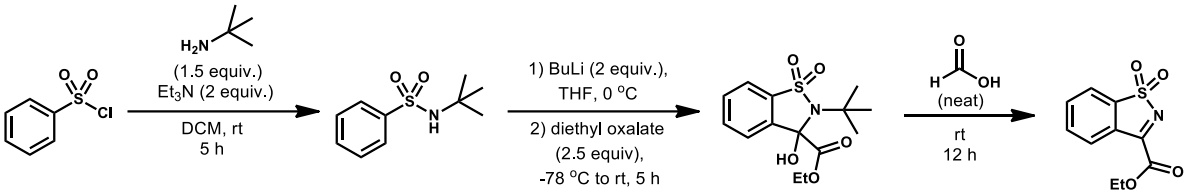


Synthesis of Chiral *N*-Sulfinyl imines

Chiral *N*-Sulfinyl imines were prepared via condensation on to the respective aldehyde according to known literature procedure[1] from the commercially available chiral sulfinamides or synthesized in the case of mesitylsulfinamide according to the following procedure.[2]

[1] S. Morales, F. G. Guijarro, J. L. García Ruano, M. B. Cid, *J. Am. Chem. Soc.* **2014**, *136*, 1082–1089.
[2] Z. Han, D. Krishnamurthy, P. Grover, Q. K. Fang, C. H. Senanayake, *J. Am. Chem. Soc.* **2002**, *124*, 7880–7881*Org. Synth.* **2006**, *83*, 131.

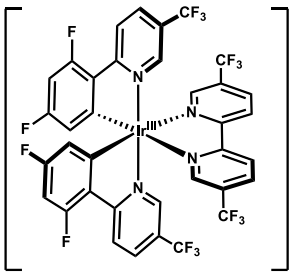
Synthesis of ethyl 5-methylbenzo[d]isothiazole-3-carboxylate 1,1-dioxide (S3):



S3

Cyclic sulfonylimine **S3** was synthesized according to a known literature procedure[3] over 4 steps giving the final product as a white crystalline solid with NMR matching the reported spectra.

Synthesis of Iridium Photocatalysts



$Ir(dF(CF_3)ppy)_2(dCF_3bpy)PF_6$

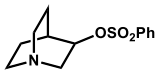
Ir-1

The iridium photocatalyst was synthesized following known literature preparations.[4]

Synthesis of Quinuclidine HAT Catalysts

The quinuclidine sulfonate HAT catalyst was synthesized using the procedure used previously by our group.[5]

(±)-Quinuclidin-3-yl benzenesulfonate (Q-1)



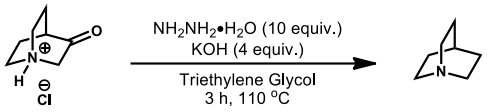
Q-1

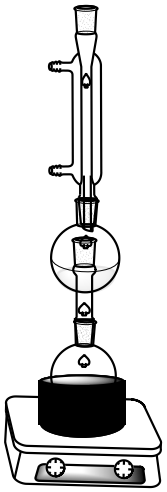
To a solution of quinuclidin-3-ol (1.27 g, 10.0 mmol, 1.0 equiv) and pyridine (1.58 g, 20.0 mmol, 2.0 equiv) in DCM (10.0 mL) were added benzenesulfonyl chloride (1.76 g, 10.0 mmol, 1.0 equiv) via syringe at 0 °C. The mixture was further stirred at 0 °C for 8 h, and then concentrated in vacuo. The residue was diluted with DCM (30.0 mL), and washed with saturated aqueous solution of K_2CO_3 (10.0 mL). The volatiles were removed in vacuo and the crude material was purified using silica gel chromatography (eluent: 20:1 dichloromethane/ethanol to 100:10:1 dichloromethane: ethanol: 30% ammonia solution) to provide Q-1 (white solid, 1.81 g, 68% yield) with HNMR spectra consistent with previously reported data.[5]

[3] Z. Ling, S. Singh, F. Xie, L. Wu, W. Zhang, *Chem. Commun.* **2017**, *53*, 5364–5367.

[4] a)G. J. Choi, Q. Zhu, D. C. Miller, C. J. Gu, R. R. Knowles, *Nature* **2016**, *539*, 268–271M. S. Lowry, W. R. Hudson, R. A. Pascal, S. Bernhard, *J. Am. Chem. Soc.* **2004**, *126*, 14129–14135.

[5] H.-B. Yang, A. Feceu, D. B. C. Martin, *ACS Catal.* **2019**, *9*, 5708–5715.





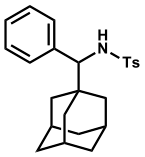
Azabicyclo[2.2.2]octane (Quinuclidine, Q-2):

The following modified procedure[6] was used: To a round bottom flask with a stir bar was added quinuclidinone hydrochloride (1.00 g, 6.76 mmol, 1 equiv.), anhydrous potassium hydroxide pellets (1.52 g, 20.3 mmol, 3 equiv.), 6 mL triethylene glycol, and 6 mL hydrazine hydrate. The round bottom flask was added to a heating mantle and then fitted with a hickman distillation head affixed with a reflux condenser and capped with a septa. The head space was flushed with N_2 for 10 minutes before slowly heating the reaction mixture under N_2 with stirring to 110 °C. This temperature was maintained for 3 hours before raising the temperature to 160 °C. Over a two hour period after reaching this temperature, the distillate collected in the distillation head was repeatedly removed via syringe and set aside. After 2 hours the apparatus was allowed to cool and any solid that formed inside the distillation head was dissolved with ethyl acetate and combined with the collected distillate. The distillates were then washed and extracted using 10 mL portions of ethyl acetate and water then the organic layers were dried using sodium sulfate. The volatiles were then removed via rotary evaporation to give a white solid. This solid was further purified using Kugelrohr vacuum distillation to afford pure quinuclidine matching known NMR spectra[7] as a white solid, 0.327 g, 2.97 mmol, 44%.

[6] Y. Kawamata, M. Yan, Z. Liu, D.-H. Bao, J. Chen, J. T. Starr, P. S. Baran, *J. Am. Chem. Soc.* **2017**, *139*, 7448–7451.
[7] V. K. Aggarwal, I. Emme, S. Y. Fulford, *J. Org. Chem.* **2003**, *68*, 692–700.

Photochemical Reactions

N-adamantan-1-yl(phenyl)methyl)-4-methylbenzenesulfonamide (**9**)



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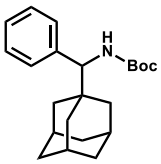
According to *General Procedure A, N*-benzylidene-4-methylbenzenesulfonamide (0.198 g, 0.50 mmol, 1.0 equiv), photoredox catalyst (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv) and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The crude residue was purified by column chromatography on silica gel (EtOAc/Hexanes = 1/5) to afford **1** (149.0 mg, 75% yield) with spectra matching known literature [8] **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.08- 7.01 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.87-6.85 (m, 2H), 5.82 (d, *J* = 9.6 Hz, 1H), 3.85 (d, *J* = 9.6 Hz, 1H), 2.27 (s, 3H), 1.93 (brs, 3H), 1.68-1.60 (m, 6H), 1.51 (d, *J* = 12.1 Hz, 3H), 1.36 (d, *J* = 12.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 142.6, 137.5, 137.4, 129.0, 128.5, 127.4, 127.1, 126.7, 67.9, 38.8, 36.8, 28.4, 21.5.

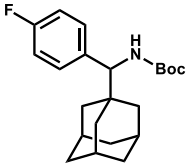
tert-Butyl-(-adamantan-1-yl(phenyl)methyl)carbamate (**10**):



10

According to *General Procedure A, tert*-butyl benzylidenecarbamate (0.103 g, 0.50 mmol, 1.0 equiv), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g,20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv) and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (0-2% ethyl acetate gradient in mixture of 1:6 chloroform : hexanes) to give a tan solid (0.123 g, 72%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 5.23 – 5.06 (m, 1H), 4.39 – 4.07 (m, 1H), 1.97 (s, 3H), 1.72 – 1.60 (m, 6H), 1.57 (d, *J* = 10.9 Hz, 4H), 1.48 – 1.30 (m, 11H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.7, 139.7, 128.4, 127.7, 126.9, 79.3, 64.2, 38.9, 36.9, 36.5, 28.5, 28.4. **IR** (ATR) 3349, 2910, 2848, 1679 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{22}H_{31}NO_2$ $(M+H)^+$ = 364.2254, found 364.2256.

tert-Butyl-(adamantan-1-yl(4-fluorophenyl)methyl)carbamate (**11**):



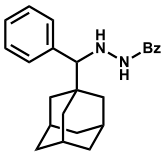
11

According to *General Procedure A, tert*-butyl 4-fluorobenzylidenecarbamate (0.112 g, 0.50 mmol, 1.0 equiv), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv) and 1,2-dichloroethane (5.0 mL) were reacted for 44 hours. The brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (0-2% ethyl acetate gradient in mixture of 1:4 chloroform : hexanes) to give an orange-white solid (0.144 g, 80%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.10 (dd, *J* = 8.4, 5.4 Hz, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 5.15 – 5.04 (m, 1H), 4.26 (d, *J* = 9.2 Hz, 1H), 1.97 (p, *J* = 3.2 Hz, 3H), 1.67 (dt, *J* = 12.5, 2.6 Hz, 3H), 1.64 – 1.52 (m, 7H), 1.45 – 1.35 (m, 11H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.9 (d, *J* = 244.6 Hz), 155.7, 135.5, 129.7 (d, *J* = 7.9 Hz), 114.5 (d, *J* = 21.1 Hz), 79.5, 63.7,

[8] J. Chen, Z. Zhang, B. Li, F. Li, Y. Wang, M. Zhao, I. D. Gridnev, T. Imamoto, W. Zhang, *Nature Communications* **2018**, *9*, 5000.

38.9, 36.9, 36.3, 28.5, 28.4. **IR** (ATR) 3254, 2903, 2848, 1698 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{22}H_{30}FNO_2$ $(M+H)^+$ = 382.2160, found 382.2159.

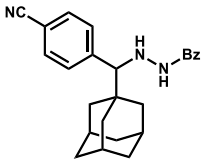
N'-(adamantan-1-yl(phenyl)methyl)benzohydrazide (**12**):



12

According to *General Procedure A, N'*-benzylidenebenzohydrazide (0.112 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate **Q-1** (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv.), and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (4:1 hexanes: ethyl acetate) to give an off-white solid (0.040 g, 22%) with spectra matching known literature [9] . **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.50 – 7.47 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.29 (m, 6H), 7.20 (s, 1H), 5.60 (s, 1H), 3.71 (s, 1H), 1.99 (s, 3H), 1.77 – 1.66 (m, 6H), 1.65 – 1.58 (m, 6H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 166.9, 139.1, 133.1, 131.7, 128.7, 127.9, 127.4, 126.8, 75.1, 39.1, 37.1, 36.3, 28.5. **IR** (ATR) 3244, 3063, 2889, 2845, 1643 cm^{-1} **HRMS** (ESI) m/z calcd. for $C_{24}H_{29}N_2O$ $(M+H)^+$ = 361.2274, found 361.2265.

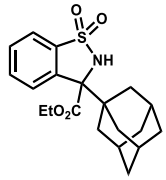
N'-(adamantan-1-yl)((4-(cyanophenyl))methyl)benzohydrazide (**13**):



13

According to *General Procedure A,* N'-(4-cyanobenzylidene)benzohydrazide (0.124 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv.), and 1,2-dichloroethane (5.0 mL) were reacted for 24hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (product dry loaded on silica support followed by elution with 200 mL hexanes then 1:9 ethyl acetate: toluene) to give a light brown solid (0.151 g, 78%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.53 – 7.43 (m, 5H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 5.8 Hz, 1H), 5.51 (d, *J* = 6.0 Hz, 1H), 3.80 (s, 1H), 2.00 (s, 3H), 1.70 (d, *J* = 11.9 Hz, 6H), 1.59 (d, *J* = 11.9 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.4, 145.3, 132.7, 132.0, 131.6, 128.8, 126.8, 119.1, 111.2, 74.8, 39.1, 36.9, 36.5, 28.4. **IR** (ATR) 3307, 3242, 3066, 2917, 2851, 2228, 1622 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{25}H_{28}N_3O$ $(M+H)^+$ = 386.2227, found 386.2221.

ethyl 3-(adamantan-1-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**16**):



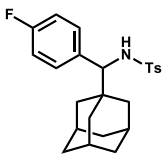
16

According to *General Procedure A,* cyclic sulfonylimine **S3** (0.119 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv.), 1,2-dichloroethane (5.0 mL) and deionized water (18 µL, 0.50 mmol, 1.0 equiv.) were reacted for 18 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (2:1 hexanes:ethyl acetate) to give a tan solid

[9] T. K. Nam, D. O. Jang, *J. Org. Chem.* **2018**, *83*, 7373–7379.

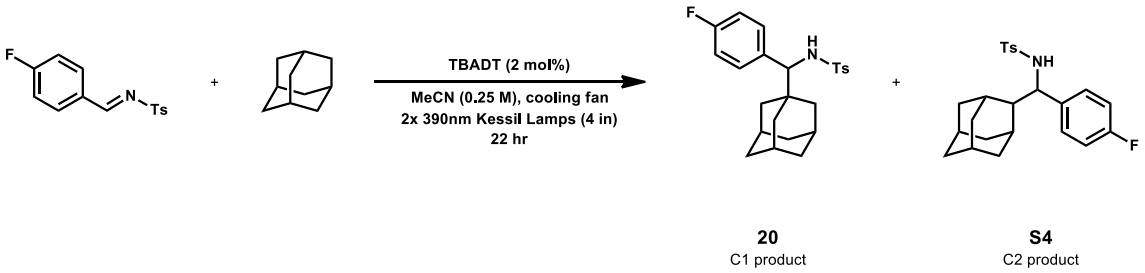
(0.156 g, 83%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.66 – 7.55 (m, 2H), 5.84 (s, 1H), 4.42 – 4.22 (m, 2H), 2.02 – 1.97 (m, 3H), 1.82 – 1.76 (m, 3H), 1.66 – 1.59 (m, 6H), 1.58 – 1.51 (m, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.3, 136.1, 134.9, 132.3, 130.2, 128.2, 121.4, 76.0, 63.3, 42.3, 37.0, 36.4, 28.5, 14.3. **HRMS** (ESI) m/z calcd for $C_{20}H_{26}NO_4S$ $(M+H)^+$ = 376.1577, found 376.1580.

N-(adamantan-1-yl(4-fluorophenyl)methyl)-4'-methylbenzenesulfonamide (**20**):



20

According to *General Procedure A,* *N*-(4-fluorobenzylidene)-4'-methylbenzenesulfonamide (0.139 g, 0.50 mmol, 1.0 equiv), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv) and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (20% ethyl acetate in 2:3 toluene : hexanes) to give a tan solid (0.180 g, 87%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.88 – 6.70 (m, 4H), 5.10 (d, *J* = 8.3 Hz, 1H), 3.87 (d, *J* = 8.8 Hz, 1H), 2.32 (s, 3H), 1.99 – 1.92 (m, 3H), 1.69 – 1.48 (m, 9H), 1.36 – 1.24 (m, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.8 (d, *J* = 245.5 Hz), 143.0, 137.5, 133.3 (d, *J* = 3.1 Hz), 129.9 (d, *J* = 8.0 Hz), 129.2, 127.2, 114.4 (d, *J* = 21.4 Hz), 67.2, 38.8, 36.7, 36.7, 28.3, 21.5. **IR** (ATR) 3272, 2943, 2894, 2838, 1603 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{24}H_{28}FNO_2S$ $(M+H)^+$ = 413.1825, found 413.1824.



20
C1 product

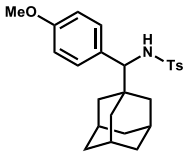
S4
C2 product

A reaction with tetrabutyl ammonium decatungstate (TBADT) photocatalyst was done according to reports by Dilman et. al with slight modifications.[10] To an 8-mL glass vial equipped with a magnetic stir bar were sequentially added *N*-(4-fluorobenzylidene)-4'-methylbenzenesulfonamide (0.111 g, 0.40 mmol, 1.0 equiv), TBADT (0.027 g, 2 mol%), adamantane **8** (0.545 g, 4.0 mmol, 10.0 equiv.), and acetonitrile (1.6 mL). The vial was sealed with a Teflon septum and screw-top cap. The resulting mixture was degassed by freezing the vial contents in a dry ice/acetone bath, placing the vial under a static vacuum, then allowing the frozen mixture to thaw (this cycle was repeated 3 times). The vial was then placed on a stir plate and irradiated between two orthogonally positioned 390nm Kessil® PR160 LED lamps 4 inches away from the diode source and reacted for 22 hours. A single small desktop fan was aimed directly at the vial to facilitate heat dissipation (temperature approx. 30 °C). The dark blue reaction mixture was reduced to dryness under vacuum and the resulting solid was purified using column chromatography (5-10% ethyl acetate gradient in 15% mixture of chloroform in hexanes) to give a white solid which was a mixture of regioisomers (0.165 g, 66%, 6:1 r.r.). Regioisomeric ratio was determined using ^{1}H NMR of purified product.

[10] V. I. Supranovich, V. V. Levin, A. D. Dilman, *Org. Lett.* **2019**, *21*, 4271–4274.

^{1}H NMR (500 MHz, Chloroform-*d*) C1 regioisomer (**20**): δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.84 – 6.71 (m, 4H), 4.93 (d, *J* = 8.7 Hz, 1H), 3.87 (d, *J* = 8.6 Hz, 1H), 2.32 (s, 3H), 1.96 (s, 3H), 1.70 – 1.47 (m, 9H), 1.36 – 1.27 (m, 3H); C2 regioisomer (**S4**): δ 7.26 – 7.20 (m, 4H), 7.07 – 7.04 (m, 2H), 6.95 – 6.89 (m, 2H), 4.62 (d, *J* = 7.9 Hz, 1H), 4.57 – 4.49 (m, 1H), 2.34 (s, 3H), 2.30 – 2.22 (m, 2H), 1.86 (s, 2H), 1.76 (d, *J* = 11.2 Hz, 4H), 1.29 – 1.23 (m, 4H), 1.12 (s, 1H).

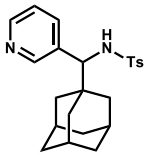
N-(adamantan-1-yl(4-methoxyphenyl)methyl)-4-methylbenzenesulfonamide (**21**):



21

According to *General Procedure A, N*-(4-methoxybenzylidene)-4-methylbenzene sulfonamide (0.145 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv.) and 1,2-dichloroethane (5.0 mL) were reacted for 48 hours. The crude residue was purified by column chromatography on silica gel (EtOAc/Hexanes = 1/4) to afford 3 (130.2 mg, 61% yield), **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 5.77 (d, *J* = 9.4 Hz, 1H), 3.82 (d, *J* = 9.4 Hz, 1H), 3.72 (s, 3H), 2.29 (s, 3H), 1.98 – 1.87 (m, 3H), 1.71 – 1.57 (m, 6H), 1.54 – 1.46 (m, 3H), 1.41 – 1.29 (m, 3H) **^{13}C NMR** (100 MHz, Chloroform-d) δ 158.5, 142.5, 137.7, 129.6, 129.5, 129.0, 127.2, 112.9, 67.4, 55.3, 38.8, 36.8, 28.4, 21.5.

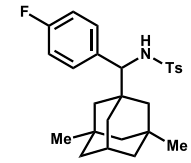
N-(3-adamantan-1-yl(pyridin-3-yl)methyl)-4'-methylbenzenesulfonamide (**22**):



22

According to *General Procedure A,* 4-methyl-*N*-(pyridin-3-ylmethylene)benzenesulfonamide (0.143 g, 0.50 mmol, 1.0 equiv), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv) and acetonitrile (5.0 mL) were reacted for 48 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (10-40% ethyl acetate gradient in mixture of 3:5 toluene : hexanes) to give a tan solid (0.095 g, 48%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 3.9 Hz, 1H), 8.16 (d, *J* = 2.4 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.15 (m, 1H), 7.10 – 6.95 (m, 3H), 5.11 (d, *J* = 8.5 Hz, 1H), 3.91 (d, *J* = 8.5 Hz, 1H), 2.31 (s, 3H), 1.97 (s, 3H), 1.66 (d, *J* = 15.4 Hz, 6H), 1.52 (d, *J* = 12.5 Hz, 3H), 1.32 (d, *J* = 12.2 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 149.4, 147.4, 141.8, 138.2, 135.4, 133.1, 128.8, 126.3, 122.2, 64.8, 38.0, 36.3, 36.1, 27.6, 20.8; peaks at 129.3 and 125.6 do not correspond to product **22**. **IR** (ATR) 3023, 2902, 2852, 2748, 1595 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{23}H_{28}N_2O_2S$ $(M+H)^+$ = 396.1871, found 396.1881.

N-(3,5-dimethyladamantan-1-yl)((4-fluorophenyl)methyl)-4'-methylbenzenesulfonamide (**23**):

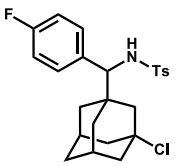


23

According to *General Procedure A, N*-(4-fluorobenzylidene)-4'-methylbenzenesulfonamide (0.139 g, 0.50 mmol, 1.0 equiv), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), 1,3-dimethyl adamantane (0.246 g, 1.50 mmol, 3.0 equiv) and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (3% ethyl acetate in mixture of 2:3 toluene : hexanes) to give a white solid (0.221 g, 79%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.86 – 6.78 (m, 2H), 6.79 – 6.68 (m, 2H), 5.49 (d, *J* = 9.1 Hz, 1H), 3.92 (d, *J* = 9.1 Hz, 1H), 2.31 (s, 3H), 2.09 – 1.93 (m, 1H), 1.44

(d, *J* = 12.7 Hz, 1H), 1.24 (d, *J* = 2.3 Hz, 2H), 1.23 – 1.11 (m, 6H), 1.06 (d, *J* = 12.4 Hz, 1H), 0.99 – 0.85 (m, 2H), 0.74 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.8 (d, *J* = 245.3 Hz), 143.0, 137.5, 133.3 (d, *J* = 2.3 Hz), 129.9 (d, *J* = 8.2 Hz), 129.2, 127.2, 114.4 (d, *J* = 21.4 Hz), 66.7, 50.9, 45.1, 44.9, 43.0, 38.6, 37.5, 31.2, 30.6, 29.8, 29.4, 21.5. **IR** (ATR) 3273, 2942, 2893, 2861, 2838, 1603 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{26}H_{32}FNO_2S$ $(M+H)^+$ = 441.2138, found 441.2137.

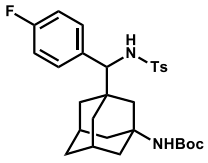
N-(3-chloroadamantan-1-yl(4-fluorophenyl)methyl)-4'-methylbenzenesulfonamide (**24**):



24

According to *General Procedure A,* *N*-(4-fluorobenzylidene)-4'-methylbenzenesulfonamide (0.139 g, 0.50 mmol, 1.0 equiv), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), 1-chloroadamantane (0.256 g, 1.50 mmol, 3.0 equiv) and acetonitrile (5.0 mL) were reacted for 72 hours (cooling fan was omitted for this reaction). The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (7.5% ethyl acetate in mixture of 3:5 toluene : hexanes) to give an off-white solid (0.120 g, 53%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.88 – 6.72 (m, 4H), 5.14 (d, *J* = 9.4 Hz, 1H), 3.95 (d, *J* = 9.5 Hz, 1H), 2.32 (s, 3H), 2.23 – 2.16 (m, 2H), 2.04 (d, *J* = 12.2 Hz, 2H), 1.99 – 1.85 (m, 3H), 1.72 – 1.58 (m, 4H), 1.47 (d, *J* = 13.1 Hz, 1H), 1.32 (d, *J* = 10.1 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.0 (d, *J* = 246.5 Hz), 143.3, 137.2, 132.5 (d, *J* = 3.1 Hz), 129.8 (d, *J* = 7.9 Hz), 129.3, 127.1, 114.8 (d, *J* = 21.5 Hz), 68.2, 66.3, 48.8, 46.9, 46.8, 41.1, 37.1, 36.8, 34.7, 31.2, 21.5. **IR** (ATR) 3272, 2936, 2905, 2856, 1598 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{24}H_{27}ClFNO_2S$ $(M+H)^+$ = 447.1435, found 447.1428.

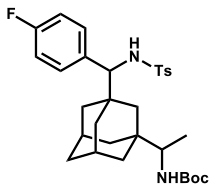
N-(3-(*N'*-tert-butoxycarbonyl-amino)-adamantyl(4-fluorophenyl)methyl)-4'-methyl benzenesulfonamide (**25**):



25

According to *General Procedure A,* *N*-(4-fluorobenzylidene)-4'-methylbenzenesulfonamide (0.139 g, 0.50 mmol, 1.0 equiv), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), *tert*-butyl-adamantan-1-ylcarbamate (0.419 g, 1.50 mmol, 3.0 equiv) and 1,2-dichloroethane (5.0 mL) were reacted for 48 hours. The light brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (15-30% ethyl acetate gradient in mixture of 3:5 toluene : hexanes) to give a brown solid (0.100 g, 35%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.83 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.76 (t, *J* = 8.7 Hz, 2H), 5.39 (d, *J* = 9.5 Hz, 1H), 4.35 (s, 1H), 3.91 (d, *J* = 9.1 Hz, 1H), 2.32 (s, 3H), 2.11 (t, *J* = 3.5 Hz, 2H), 1.85 (d, *J* = 11.7 Hz, 2H), 1.72 (d, *J* = 9.2 Hz, 3H), 1.55 (d, *J* = 12.1 Hz, 3H), 1.41 (s, 11H), 1.34 – 1.21 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.0 (d, *J* = 245.8 Hz), 143.1, 137.4, 133.1 (d, *J* = 3.3 Hz), 129.9 (d, *J* = 7.7 Hz), 129.2, 127.2, 126.6, 114.6 (d, *J* = 21.4 Hz), 66.5, 51.2, 43.2, 41.1, 38.9, 37.8, 29.2, 28.6, 21.5. **IR** (ATR) 3169, 2978, 2935, 2908, 2858, 1671 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{29}H_{37}FN_2O_4S$ $(M+H)^+$ = 528.2458, found 528.2465.

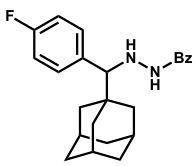
N-(3-(1'-(*N'*-tert-butylcarbonyl)-ethyl)adamantyl(4-fluorophenyl)methyl)-4'-methyl benzenesulfonamide (**26**):



26

According to *General Procedure A, N*-(4-fluorobenzylidene)-4'-methylbenzenesulfonamide (0.139 g, 0.50 mmol, 1.0 equiv), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), *tert*-butyl-((adamantan-1-yl)ethyl)carbamate (0.419 g, 1.50 mmol, 3.0 equiv) and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (5-25% ethyl acetate gradient in mixture of 3:5 toluene : hexanes) to give a tan solid which was an inseparable, complex mixture of diastereomers (0.173 g, 62%). **^{1}H NMR** (400 MHz, Chloroform-*d*) First Diastereomer: δ 5.42 (d, *J* = 8.8 Hz, 1H); Second Diastereomer: δ 5.30 (d, *J* = 8.8 Hz, 1H); Both Diastereomers: δ 7.43 (d, *J* = 6.2 Hz, 2H), 7.02 (dd, *J* = 8.0, 5.4 Hz, 2H), 6.86 – 6.77 (m, 2H), 6.75 (td, *J* = 8.5, 5.6 Hz, 2H), 4.27 (dd, *J* = 19.4, 10.0 Hz, 1H), 3.89 (dd, *J* = 9.2, 5.9 Hz, 1H), 3.31 (q, *J* = 8.6 Hz, 1H), 2.34 – 2.29 (m, 2H), 2.08 – 2.00 (m, 2H), 1.65 (s, 2H), 1.46 (s, 9H), 1.43 – 1.16 (m, 9H), 1.02 (d, *J* = 12.0 Hz, 2H), 0.94 (t, *J* = 6.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.9 (d, *J* = 245.8 Hz), 155.8, 143.1 (d, *J* = 10.0 Hz), 137.5, 133.3 (d, *J* = 3.5 Hz), 129.9 (d, *J* = 8.2 Hz), 129.2 (d, *J* = 5.4 Hz), 128.4, 127.2, 114.5 (d, *J* = 21.4 Hz), 114.5 (d, *J* = 21.3 Hz), 67.0, 54.3, 39.1, 38.9, 38.4, 38.2, 37.4, 36.9, 36.1, 28.6, 28.3, 21.5, 15.1. **IR** (ATR) 3339, 3294, 2976, 2932, 2850, 1678 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{31}H_{41}FN_2O_4S$ $(M+H)^+$ = 556.2771, found 556.2748.

N'-(adamantan-1-yl(4-fluorophenyl)methyl)benzohydrazide (**27**):

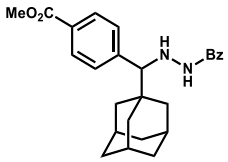


27

According to *General Procedure A, N'*-(4-fluorobenzylidene)benzohydrazide (0.121 g, 0.50 mmol, 1.0 equiv), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv) and acetonitrile (5.0 mL) were reacted for 48 hours (cooling fan was omitted for this reaction). The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (0-7% ethyl acetate gradient in hexanes) to give a white solid (0.100 g, 53%). with spectra matching known literature .[11] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.7 Hz, 2H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.34 (dd, *J* = 16.1, 8.5 Hz, 4H), 7.13 (s, 1H), 7.04 (t, *J* = 8.6 Hz, 2H), 5.55 (s, 1H), 3.71 (s, 1H), 2.15 – 1.94 (m, 3H), 1.70 (t, *J* = 9.3 Hz, 6H), 1.60 (d, *J* = 13.0 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.0, 162.3 (d, *J* = 245.2 Hz), 134.8 (d, *J* = 3.2 Hz), 133.1, 131.8, 130.9 (d, *J* = 7.7 Hz), 128.8, 126.8, 114.8 (d, *J* = 20.9 Hz), 74.4, 39.1, 37.1, 36.3, 28.6. **IR** (ATR) 3304, 3223, 3065, 2902, 2849, 1640 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{24}H_{27}FN_2O$ $(M+H)^+$ = 378.2107, found 378.2102.

[11] T. K. Nam, D. O. Jang, *J. Org. Chem.* **2018**, *83*, 7373–7379.

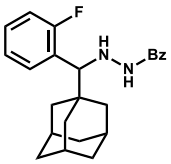
methyl 4-adamantan-1-yl((2-benzoylhydrazinyl)methyl)benzoate (**28**):



28

According to *General Procedure A,* methyl 4-((2-benzoylhydrazono)methyl)benzoate (0.141 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv.), and 1,2-dichloroethane (5.0 mL) reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (gradient from 5-40% ethyl acetate in a 2:1 mixture of hexane : dichloromethane) to give a tan solid (0.161 g, 76%). **^{1}H NMR** (400 MHz,) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.40 (m, 4H), 7.37 – 7.29 (m, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 5.56 (dd, *J* = 7.2, 2.1 Hz, 1H), 3.93 (s, 3H), 3.80 (s, 1H), 1.99 (p, *J* = 3.2 Hz, 3H), 1.77 – 1.65 (m, 6H), 1.65 – 1.58 (m, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.2, 167.2, 144.9, 132.9, 131.8, 129.3, 129.1, 128.7, 126.8, 74.8, 52.2, 39.1, 37.0, 36.4, 28.5. **IR** (ATR) 3366, 2900, 2847, 1708, 1664 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{26}H_{31}N_2O_3$ $(M+H)^+$ = 419.2329, found 419.2327.

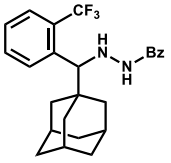
N'-(adamantan-1-yl(2-fluorophenyl)methyl)benzohydrazide (**29**):



29

According to *General Procedure A, N'*-(2-fluorobenzylidene)benzohydrazide (0.121 g, 0.50 mmol, 1.0 equiv), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv) and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours (cooling fan was omitted for this reaction). The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (0-7% ethyl acetate gradient in hexanes) to give a white solid (0.114 g, 60%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 – 7.61 (m, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.23 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.14 (s, 1H), 7.03 (t, *J* = 9.2 Hz, 1H), 5.57 (s, 1H), 4.20 (s, 1H), 2.00 (t, *J* = 3.3 Hz, 3H), 1.82 (d, *J* = 12.4 Hz, 3H), 1.74 – 1.57 (m, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.0, 162.3 (d, *J* = 247.3 Hz), 133.0, 131.8, 129.9, 128.7, 128.6 (d, *J* = 8.4 Hz), 126.9, 123.7 (d, *J* = 3.4 Hz), 115.3 (d, *J* = 23.2 Hz), 66.2, 38.7, 37.1, 37.0, 28.6. **IR** (ATR) 3309, 3281, 2904, 2847, 1634 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{24}H_{27}FN_2O$ $(M+H)^+$ = 378.2107, found 378.2103.

N'-(adamantan-1-yl(2-(trifluoromethyl)phenyl)methyl)benzohydrazide (**30**):

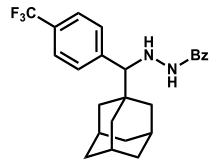


30

According to *General Procedure A, N'*-(2-(trifluoromethyl)benzylidene)benzohydrazide (0.146 g, 0.50 mmol, 1.0 equiv), photoredox catalyst **Ir-1** (0.012 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv) and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours (cooling fan was omitted for this reaction). The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (0-10% ethyl acetate gradient in hexanes) to give a white solid (0.061 g, 29%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.1 Hz, 2H), 7.42 (p, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.00 (s, 1H), 5.63 (s, 1H), 4.24 (s, 1H), 2.00 (s, 3H), 1.93 (d, *J* = 11.7 Hz, 3H), 1.67 (q, *J* = 12.4 Hz, 6H), 1.61 – 1.42 (m, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.3, 139.5, 133.2, 131.7, 131.2, 130.8, 128.7, 127.4, 126.8, 126.1 – 125.9 (m, obscured), 125.9, 124.44 (d, *J* = 275.0

Hz) 68.5, 39.3, 37.2, 37.0, 28.7. **IR** (ATR) 3317, 3214, 3081, 2929, 2904, 2849, 1633 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{25}H_{27}F_3N_2O$ $(M+H)^+$ = 428.2075, found 428.2086.

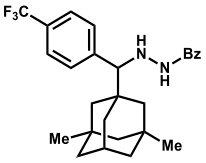
N'-adamantan-1-yl((4-(trifluoromethyl)phenyl)methyl)benzohydrazide (**31**):



31

According to *General Procedure A, N'*-(4-(trifluoromethyl)benzylidene)benzohydrazide (0.146 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), adamantane **8** (0.204 g, 1.50 mmol, 3.0 equiv.), and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (gradient from 1:2 ethyl acetate: hexanes to 3:2 ethyl acetate: hexanes) to give an off white solid (0.060 g, 28%). **^{1}H NMR** (400 MHz,) δ 7.60 (d, *J* = 7.9 Hz, 2H), 7.55 – 7.42 (m, 5H), 7.39 – 7.32 (m, 2H), 7.16 (s, 1H), 3.80 (s, 1H), 2.00 (s, 3H), 1.77 – 1.67 (m, 6H), 1.65 – 1.55 (m, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.3, 132.8, 132.0, 129.9 (m, obscured), 129.6 (q, *J* = 32.5 Hz), 128.8, 126.8, 124.8, 124.8, 124.4 (q, *J* = 272.1 Hz), 74.7, 39.1, 37.0, 36.4, 28.5. **IR** (ATR) 3306, 3242, 2925, 2883, 2850, 1623 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{25}H_{28}F_3N_2O$ $(M+H)^+$ = 429.2148, found 429.2137.

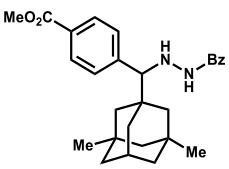
N'-(3,5-dimethyladamantanyl)((4-(trifluoromethyl)phenyl))methyl) benzohydrazide (**32**):



32

According to *General Procedure A, N'*-(4-(trifluoromethyl)benzylidene)benzohydrazide (0.146 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), 3,5-dimethyladamantane (0.278 mL, 1.50 mmol, 3.0 equiv.), and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (product dry loaded on silica support followed by elution with 200 mL hexanes then 1:9 ethyl acetate: toluene) to give a light brown solid (0.101 g, 44%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.44 (m, 5H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.17 (s, 1H), 5.55 (s, 1H), 3.85 (s, 1H), 2.10 – 2.05 (m, 1H), 1.54 (d, *J* = 12.1 Hz, 1H), 1.43 (d, *J* = 12.1 Hz, 1H), 1.37 – 1.19 (m, 8H), 1.14 (d, *J* = 12.3 Hz, 1H), 1.05 (d, *J* = 12.3 Hz, 1H), 0.82 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.3, 143.6, 132.8, 132.0, 129.9 (m, obscured), 129.6 (q, *J* = 32.3 Hz), 128.8, 126.8, 124.9, 124.9, 124.4 (q, *J* = 271.9 Hz), 74.2, 51.1, 45.4, 45.2, 43.2, 38.2, 37.7, 31.3, 30.8, 29.5. **IR** (ATR) 3319, 3261, 2920, 2865, 2839, 1628 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{27}H_{32}F_3N_2O$ $(M+H)^+$ = 457.2461, found 457.2463.

methyl 4-((3,5-dimethyladamantan-1-yl)2-benzoylhydrazinyl)methyl) benzoate (**33**):

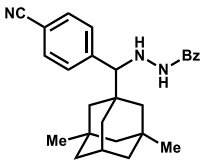


33

According to *General Procedure A,* methyl 4-((2-benzoylhydrazono)methyl)benzoate (0.141 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), 3,5-dimethyladamantane (0.278 mL, 1.50 mmol, 3.0 equiv.), and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (3:2:1 hexanes: dichloromethane: ethyl acetate) to give an off-white solid (0.180 g, 80%). **^{1}H NMR**

(400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.39 (m, 5H), 7.34 – 7.28 (m, 2H), 5.52 (s, 1H), 3.90 (s, 3H), 3.83 (s, 1H), 2.09 – 2.01 (m, 1H), 1.52 (d, *J* = 12.0 Hz, 1H), 1.41 (d, *J* = 12.0 Hz, 1H), 1.36 – 1.16 (m, 8H), 1.11 (d, *J* = 12.3 Hz, 1H), 1.02 (d, *J* = 12.3 Hz, 1H), 0.79 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.2, 167.1, 144.9, 132.8, 131.8, 129.2, 129.1, 128.6, 126.9, 74.2, 52.2, 51.1, 45.3, 45.2, 43.2, 38.2, 37.7, 31.2, 31.2, 30.8, 29.5. **IR** (ATR) 3367, 3306, 3056, 2901, 2846, 1709 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{28}H_{35}N_2O_3$ $(M+H)^+$ = 447.2642, found 447.2632.

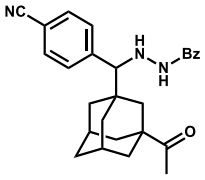
N'-(3,5-dimethyladamantan-1-yl)((4-(cyanophenyl))methyl)benzohydrazide (**34**):



34

According to *General Procedure A, N*'-(4-cyanobenzylidene)benzohydrazide (0.124 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), 3,5-dimethyladamantane (0.278 mL, 1.50 mmol, 3.0 equiv.), and 1,2-dichloroethane (5.0 mL) were reacted for 18 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (product dry loaded on silica support followed by elution with 200 mL hexanes then 1:9 ethyl acetate: toluene) to give a light brown solid (0.150 g, 73%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.43 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 3H), 5.49 (s, 1H), 3.84 (s, 1H), 2.13 – 2.01 (m, 1H), 1.51 (d, *J* = 12.0 Hz, 1H), 1.40 (d, *J* = 12.1 Hz, 1H), 1.35 – 1.00 (m, 11H), 0.81 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.4, 145.3, 132.6, 132.0, 131.6, 128.8, 126.8, 119.1, 111.2, 74.2, 51.0, 45.3, 45.1, 43.1, 38.3, 37.7, 31.2, 30.8, 29.4. **IR** (ATR) 3360, 3306, 3059, 2897, 2842, 2228, 1706 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{27}H_{31}N_3ONa$ $(M+Na)^+$ = 436.2359, found 436.2347.

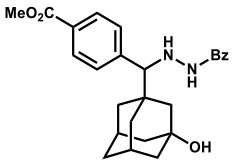
N'-(3-acetyladamantan-1-yl)((4-(cyanophenyl))methyl)benzohydrazide (**35**):



35

According to *General Procedure A, N*'-(4-cyanobenzylidene)benzohydrazide (0.124 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst Ir-1 (0.011 g , 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), 1-acetyladamantane (0.267 g, 1.50 mmol, 3.0 equiv.), 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography dry loaded on silica support, gradient from 35-45% ethyl acetate in toluene to give a white powder (0.070 g, 33%). **^{1}H NMR** (400 MHz,) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.48 (dd, *J* = 17.6, 7.4 Hz, 4H), 7.36 (t, *J* = 7.4 Hz, 3H), 5.47 (d, *J* = 5.3 Hz, 1H), 3.88 (s, 1H), 2.16 (s, 2H), 2.08 (s, 3H), 1.88 – 1.44 (m, 12H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 213.2, 167.6, 144.7, 132.5, 132.1, 131.8, 128.8, 126.8, 118.9, 111.5, 74.2, 47.0, 39.1, 38.5, 38.2, 37.8, 36.9, 35.8, 28.1, 24.6.

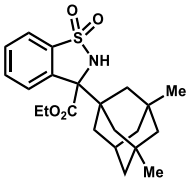
methyl 4-((3-hydroxyadamantan-1-yl)2-benzoylhydrazinyl)methyl)benzoate (**36**):



36

According to *General Procedure A,* methyl 4-((2-benzoylhydrazono)methyl)benzoate (0.141 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), 1-hydroxyadamantane (0.228 g, 0.90 mmol, 3.0 equiv.), and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (3:2:1 hexanes: dichloromethane: ethyl acetate) to give an off-white solid (0.180 g, 31%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.36 – 7.30 (m, 4H), 5.49 (d, *J* = 5.1 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 1H), 2.22 (s, 2H), 1.75 (s, 1H), 1.68 – 1.63 (m, 4H), 1.62 – 1.50 (m, 7H), 1.49 – 1.43 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 167.3, 167.2, 144.4, 132.7, 131.9, 129.5, 129.3, 128.7, 126.9, 73.8, 68.9, 52.3, 46.5, 44.8, 44.7, 40.0, 38.3, 37.6, 35.4, 30.5, 30.4.

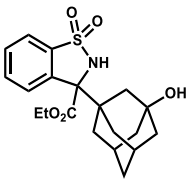
ethyl 3-(3,5-dimethyladamantyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**37**):



37

According to *General Procedure A,* cyclic sulfonylimine **S3** (0.119 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), 2,4-dimethyladamantane (0.278 mL, 1.50 mmol, 3.0 equiv.), 1,2-dichloroethane (5.0 mL) and deionized water (18 µL, 0.50 mmol, 1.0 equiv.) were reacted for 18 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (2:1 hexanes:ethyl acetate) to give an off-white solid (0.163 g, 80%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.57 (m, 2H), 5.81 (s, 1H), 4.38 – 4.25 (m, 2H), 2.11 – 2.07 (m, 1H), 1.66 (d, *J* = 11.7 Hz, 1H), 1.42 (d, *J* = 11.7 Hz, 2H), 1.29 – 1.22 (m, 7H), 1.11 (d, *J* = 12.4 Hz, 1H), 1.02 (d, *J* = 12.3 Hz, 1H), 0.81 (s, 3H), 0.80 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.3, 136.1, 135.0, 132.4, 130.3, 128.2, 121.5, 63.4, 50.6, 44.3, 43.3, 43.2, 42.7, 42.6, 35.6, 31.5, 31.4, 30.8, 30.7, 29.5, 14.3. **HRMS** (ESI) m/z calcd for $C_{22}H_{30}NO_4S$ $(M+H)^+$ = 404.1890, found 404.1892.

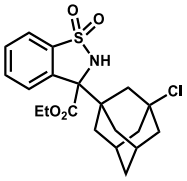
ethyl 3-(3-hydroxyadamantyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**38**):



38

According to *General Procedure A,* cyclic sulfonylimine **S3** (0.119 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), 1-hydroxyadamantane (0.228 g, 1.50 mmol, 3.0 equiv.), 1,2-dichloroethane (5.0 mL) and deionized water (18 µL, 0.50 mmol, 1.0 equiv.) were reacted for 18 hours The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (2:1 hexanes:ethyl acetate) to give a tan solid (0.140 g, 80%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.57 (m, 2H), 5.81 (s, 1H), 4.38 – 4.25 (m, 2H), 2.11 – 2.07 (m, 1H), 1.66 (d, *J* = 11.7 Hz, 1H), 1.42 (d, *J* = 11.7 Hz, 2H), 1.29 – 1.22 (m, 7H), 1.11 (d, *J* = 12.4 Hz, 1H), 1.02 (d, *J* = 12.3 Hz, 1H), 0.81 (s, 3H), 0.80 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.3, 136.1, 135.0, 132.4, 130.3, 128.2, 121.5, 63.4, 50.6, 44.3, 43.3, 43.2, 42.7, 42.6, 35.6, 31.5, 31.4, 30.8, 30.7, 29.5, 14.3. **HRMS** (ESI) m/z calcd for $C_{20}H_{26}NO_4S$ $(M+H)^+$ = 392.1526, found 392.1519.

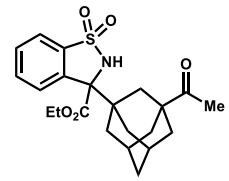
ethyl 3-(3-chloroadamantyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**39**):



39

According to *General Procedure A,* cyclic sulfonylimine **S3** (0.119 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate **Q-1** (0.026 g, 20 mol%), 1-chloroadamantane (0.256 g, 1.50 mmol, 3.0 equiv.), 1,2-dichloroethane (5.0 mL) and deionized water (18 µL, 0.50 mmol, 1.0 equiv.) were reacted for 18 hours The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (2:1 hexanes:ethyl acetate) to give a white solid (0.150 g, 74%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.59 (m, 2H), 5.91 (s, 1H), 4.39 – 4.27 (m, 2H), 2.24 – 2.19 (m, 2H), 2.17 – 2.09 (m, 2H), 2.05 – 1.91 (m, 4H), 1.84 – 1.77 (m, 1H), 1.74 – 1.68 (m, 1H), 1.60 – 1.45 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.8, 136.1, 134.2, 132.7, 130.6, 128.0, 121.6, 75.0, 68.0, 63.7, 47.1, 46.5, 46.5, 46.0, 35.3, 35.1, 34.3, 31.1, 14.2. **HRMS** (ESI) m/z calcd for $C_{20}H_{25}ClNO_4S$ $(M+H)^+$ = 409.1115, found 409.1119.

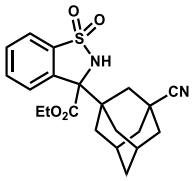
ethyl 3-(3-acetyladamantyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**40**):



40

According to *General Procedure A,* cyclic sulfonylimine **S3** (0.119 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate (0.026 g, 20 mol%), 1-acetyladamantane (0.267 g, 1.50 mmol, 3.0 equiv.), 1,2-dichloroethane (5.0 mL) and deionized water (18 µL, 0.50 mmol, 1.0 equiv.) were reacted for 18 hours The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (2:1 hexanes:ethyl acetate) to give a white solid (0.136 g, 66%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.68 – 7.57 (m, 2H), 5.90 (s, 1H), 4.40 – 4.25 (m, 2H), 2.17 (t, *J* = 3.1 Hz, 2H), 2.08 (s, 3H), 1.85 – 1.78 (m, 2H), 1.76 – 1.69 (m, 4H), 1.64 – 1.54 (m, 6H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 213.0, 169.0, 136.2, 134.5, 132.6, 130.5, 128.2, 121.6, 75.7, 63.6, 47.2, 42.8, 37.7, 37.5, 37.3, 36.1, 35.4, 28.2, 24.7, 14.3. **HRMS** (ESI) m/z calcd for $C_{22}H_{28}NO_5S$ $(M+H)^+$ = 418.1683, found 418.1677.

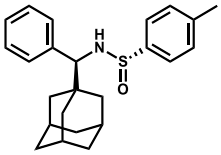
ethyl 3-(3-cyanoadamantyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**41**):



41

According to *General Procedure A,* cyclic sulfonylimine **S3** (0.119 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.011 g, 2 mol%), quinuclidine phenylsulfonate **Q-1** (0.026 g, 20 mol%), 1-adamantanecarbonitrile (0.242 g, 1.50 mmol, 3.0 equiv.), 1,2-dichloroethane (5.0 mL) and deionized water (18 µL, 0.50 mmol, 1.0 equiv.) were reacted for 18 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (2:1 hexanes:ethyl acetate) to give a tan solid (0.080 g, 40%). **^{1}H NMR** (500 MHz,) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.73 – 7.57 (m, 2H), 5.91 (s, 1H), 4.34 (p, *J* = 7.0 Hz, 2H), 2.20 – 1.47 (m, 14H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 168.6, 136.2, 133.9, 132.8, 130.8, 127.9, 124.4, 121.8, 75.1, 63.9, 41.9, 39.5, 38.9, 38.9, 35.6, 35.3, 34.5, 31.2, 27.4, 27.4, 14.3.**HRMS** (ESI) m/z calcd. for $C_{21}H_{25}N_2O_4S$ $(M+H)^+$ = 401.1530, found 401.1525.

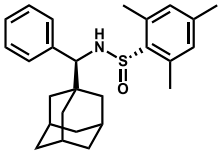
(S)-*N*-((S)-(adamantan-1-yl)(phenyl)methyl)-4-methylbenzenesulfinamide (**45**):



45

According to *General Procedure B,* (S)-*N*-benzylidene-4-methylbenzenesulfinamide (0.036 g, 0.15 mmol, 1.0 equiv.), photoredox catalyst **PT** (0.0025 g, 5 mol%), adamantane (0.061 g, 0.45 mmol, 3.0 equiv.), 1,2-dichloroethane (1.5 mL) were reacted for 24 hours. The reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (1:6 hexane:ethyl acetate) to give a white powder as a 9:1 mixture of diastereomers (0.044 g, 77%). **^{1}H NMR** (major diastereomer, (500 MHz,) δ 7.37 (d, J = 8.2 Hz, 2H), 7.12 (dd, J = 5.0, 1.9 Hz, 3H), 7.03 (d, J = 8.3 Hz, 2H), 6.91 – 6.86 (m, 2H), 4.62 (d, J = 7.2 Hz, 1H), 3.88 (d, J = 7.1 Hz, 1H), 2.30 (s, 3H), 1.98 (s, 3H), 1.69 – 1.62 (m, 7H), 1.55 (d, J = 10.9 Hz, 3H), 1.39 (dd, J = 12.3, 2.7 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 141.2, 140.9, 140.2, 129.0, 128.6, 127.4, 126.6, 125.9, 65.9, 39.2, 36.9, 36.6, 28.5, 21.4. **HRMS** (ESI) m/z calcd for $C_{24}H_{30}NOS$ $(M+H)^+$ = 380.2043, found 380.2047

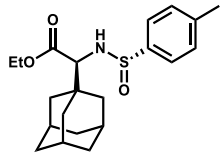
(S)-*N*-((S)-(adamantan-1-yl)(phenyl)methyl)-2,4,6-trimethylbenzene sulfinamide (**46**):



46

According to *General Procedure B,* (S)-*N*-benzylidene-2,4,6-trimethylbenzene sulfinamide (0.081 g, 0.30 mmol, 1.0 equiv.), photoredox catalyst **PT** (0.0051 g, 5 mol%), adamantane **8** (0.122 g, 0.90 mmol, 3.0 equiv.), 1,2-dichloroethane (3.0 mL) were reacted for 48 hours. The reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (3:1 hexane:ethyl acetate) to give a pale yellow oil as a single apparent diastereomer (0.089 g, 73%). **^{1}H NMR** (single diastereomer, 400 MHz,) δ 7.32 – 7.20 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 4.69 (d, J = 7.7 Hz, 1H), 3.88 (d, J = 7.7 Hz, 1H), 2.50 (s, 6H), 2.26 (s, 3H), 1.95 (s, 3H), 1.68 – 1.61 (m, 6H), 1.57 – 1.49 (m, 3H), 1.44 – 1.35 (m, 3H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 140.5, 139.9, 138.5, 136.7, 130.8, 128.2, 127.8, 127.2, 69.6, 39.0, 37.2, 36.9, 28.5, 21.1, 19.6. **HRMS** (ESI) m/z calcd for $C_{26}H_{34}NOS$ $(M+H)^+$ = 408.2356, found 408.2359.

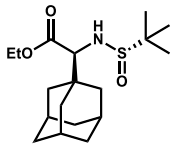
(S)-ethyl 2-(adamantan-1-yl)-2-((S)-4-methylphenylsulfinamido)acetate (**47**):



47

According to *General Procedure B,* (S)-ethyl 2-((*p*-tolylsulfinyl)imino)acetate (0.072 g, 0.30 mmol, 1.0 equiv.), photoredox catalyst **PT** (0.0051 g, 5 mol%), adamantane **8**(0.122 g, 0.90 mmol, 3.0 equiv.), 1,2-dichloroethane (3.0 mL) were reacted for 24 hours. The reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using Yamazen Smart-Flash chromatography using gradient elution (100% hexanes to 4:1 hexane:ethyl acetate) to give a clear oil as a 9:1 mixture of diastereomers (0.046 g, 41%). **^{1}H NMR** (Major diastereomer, 500 MHz, Chloroform-*d*) δ 7.60 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.62 (d, J = 9.8 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.48 (d, J = 9.8 Hz, 1H), 2.42 (s, 3H), 2.06 – 1.99 (m, 3H), 1.77 – 1.61 (m, 9H), 1.53 – 1.45 (m, 3H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 172.0, 142.2, 141.6, 129.7, 125.6, 65.7, 61.1, 38.8, 36.8, 36.5, 28.4, 28.3, 21.5, 14.3. **HRMS** (ESI) m/z calcd for $C_{21}H_{30}NO_3S$ $(M+H)^+$ = 376.1941, found 376.1943.

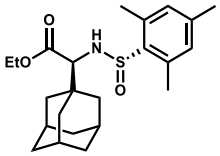
S)-ethyl 2-(adamantan-1-yl)-2-((S)-1,1-dimethylethylsulfinamido)acetate (**48**):



48

According to *General Procedure B,* (S)-ethyl 2-((tert-butylsulfinyl)imino)acetate (0.061 g, 0.30 mmol, 1.0 equiv.), photoredox catalyst **PT** (0.0051 g, 5 mol%), adamantane **8**(0.122 g, 0.90 mmol, 3.0 equiv.), 1,2-dichloroethane (3.0 mL) were reacted for 24 hours. The reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using Yamazen Smart-Flash chromatography using gradient elution (100% hexanes to 4:1 hexane:ethyl acetate) to give a clear oil as a 1.3:1 mixture of diastereomers (0.065 g, 63%).

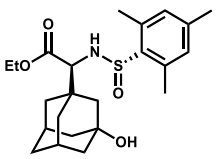
(S)-ethyl 2-(adamantan-1-yl)-2-((S)-2,4,6-trimethylphenylsulfinamido)acetate (**49**):



49

According to *General Procedure B,* (S)-ethyl 2-((mesitylsulfinyl)imino)acetate (0.080 g, 0.30 mmol, 1.0 equiv.), photoredox catalyst **PT** (0.0051 g, 5 mol%), adamantane **8** (0.122 g, 0.90 mmol, 3.0 equiv.), 1,2-dichloroethane (3.0 mL) were reacted for 48 hours. The reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using Yamazen Smart-Flash chromatography using gradient elution (100% hexanes to 9:1 hexane:ethyl acetate) to give a clear oil as a single apparent diastereomer (0.077 g, 63%). **^{1}H NMR** (single diastereomer, 400 MHz, Chloroform-d) δ 6.88 (s, 2H), 4.98 (d, J = 10.3 Hz, 1H), 4.33 – 4.18 (m, 2H), 3.46 (d, J = 10.3 Hz, 1H), 2.58 (s, 6H), 2.30 (s, 3H), 1.98 (s, 3H), 1.72 – 1.65 (m, 6H), 1.64 – 1.57 (m, 3H), 1.52 – 1.46 (m, 3H), 1.32 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 172.3, 141.0, 138.2, 136.9, 130.9, 67.5, 61.3, 38.8, 36.8, 36.7, 28.4, 21.2, 19.5, 14.4. **HRMS** (ESI) m/z calcd for $C_{23}H_{34}NO_3S$ $(M+H)^+$ = 404.2254, found 404.2250.

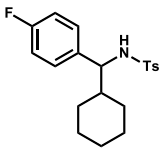
(S)-ethyl 2-(3-hydroxyadamantan-1-yl)-2-((S)-2,4,6-trimethylphenylsulfin-amido)acetate (**50**):



50

According to *General Procedure B,* (S)-ethyl 2-((mesitylsulfinyl)imino)acetate (0.119 g, 0.50 mmol, 1.0 equiv.), photoredox catalyst **PT** (0.0085 g, 5 mol%), 1-hydroxyadamantane (0.228 g, 0.90 mmol, 3.0 equiv.), 1,2-dichloroethane (5.0 mL) were reacted for 48 hours. The reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using Yamazen Smart-Flash chromatography using gradient elution (95:5 hexanes:ethyl acetate to 4:1 hexane:ethyl acetate) to give a clear oil as a single apparent diastereomer (0.0885 g, 42%). **^{1}H NMR** (single diastereomer, 400 MHz, Chloroform-d) δ 6.88 (s, 2H), 5.00 (d, J = 10.2 Hz, 1H), 4.29 – 4.19 (m, 2H), 3.54 (d, J = 10.2 Hz, 1H), 2.57 (s, 6H), 2.30 (s, 3H), 2.25 – 2.18 (m, 3H), 1.68 – 1.38 (m, 12H), 1.31 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 171.9, 141.0, 137.9, 136.8, 130.8, 68.7, 66.4, 61.4, 46.2, 44.5, 44.4, 40.1, 37.4, 35.2, 30.2, 21.1, 19.4, 14.2. **HRMS** (ESI) m/z calcd for $C_{23}H_{34}NO_4S$ $(M+H)^+$ = 420.2204, found 420.2201.

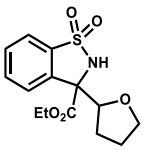
N-(cyclohexyl(4-fluorophenyl)methyl)-4'-methylbenzenesulfonamide (**S5**):



S5

According to *General Procedure B,* *N*-(4-fluorobenzylidene)-4'-methylbenzenesulfonamide (0.50 mmol, 1.0 equiv), photoredox catalyst **PT** (0.017 g, 5 mol%), cyclohexane (0.162 mL, 1.50 mmol, 3.0 equiv.), 1,2-dichloroethane (5.0 mL) were reacted for 52 hours. The reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (0-5% ethyl acetate gradient in 1:1 chloroform : hexanes) to give a brown solid. **^{1}H NMR** (500 MHz,) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.92 – 6.85 (m, 2H), 6.80 (t, *J* = 8.7 Hz, 2H), 4.74 (d, *J* = 7.8 Hz, 1H), 4.05 (t, *J* = 7.8 Hz, 1H), 2.35 (s, 3H), 1.91 (d, *J* = 14.0 Hz, 1H), 1.81 – 1.71 (m, 1H), 1.66 – 1.60 (m, 2H), 1.54 – 1.46 (m, 1H), 1.28 (d, *J* = 13.4 Hz, 1H), 1.18 – 1.04 (m, 3H), 0.98 – 0.76 (m, 2H).

ethyl 3-(tetrahydrofuran-2-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**S6**):

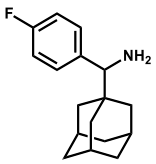


S6

According to *General Procedure A,* cyclic sulfonylimine **S3** (0.035 g, 0.15 mmol, 1.0 equiv.), photoredox catalyst **Ir-1** (0.003 g, 2 mol%), quinuclidine phenylsulfonate (0.008 g, 20 mol%), tetrahydrofuran (0.036 mL, 0.45 mmol, 3.0 equiv.), and 1,2-dichloroethane (1.5 mL) were reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (2:1 hexanes:ethyl acetate) to give a tan solid (0.023 g, 50%). **^{1}H NMR** (500 MHz, Chloroform-*d*) First Diastereomer: δ 5.63 – 5.60 (m, 1H), 4.43 – 4.19 (m, 2H), 2.82 – 2.73 (m, 1H), 1.39 (td, *J* = 7.1, 2.7 Hz, 1H); Second Diastereomer: δ 5.54 – 5.51 (m, 1H), 4.06 – 3.83 (m, 2H), 2.54 – 2.46 (m, 1H), 1.27 (td, *J* = 8.7, 2.7 Hz, 1H); Both Diastereomers: δ 7.80 (d, *J*=7.0 Hz, 1H), 7.66 – 7.56 (m, 3H), 5.26 (d, *J* = 11.5 Hz, 1H), 2.30 – 2.14 (m, 2H), 2.05 – 1.96 (m, 1H), 1.35 – 1.23 (m, 3H). **HRMS** (ESI) m/z calcd for $C_{14}H_{18}NO_5S$ $(M+H)^+$ = 312.0900, found 312.0908.

adamantan-1-yl(4-fluorophenyl)methanamine (**51**):

From *N,N*-benzoyl and *N*-tosyl adamantyl amines, deprotected amine (**51**) was prepared according to previously reported procedures[12], with some modifications.

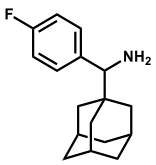


51

A flame-dried flask containing 0.050 g adamantane product **20** (0.121 mmol, 1.0 equiv) was degassed and loaded with 0.50 mL tetrahydrofuran, samarium diiodide (9.30 mL of 1.0 M solution in THF, 10.0 equiv) and water (0.058 mL, 30.0 equiv) under nitrogen. To the dark blue mixture was added pyrrolidine (0.198 mL, 20.0 equiv), causing an amalgamation and rapid discoloration from dark blue to white. After stirring for 10 minutes at room temperature, the mixture was diluted with methylene chloride and washed with 5 mL of potassium sodium tartrate and 5 mL potassium carbonate (10% w/v each). The organic layer was washed with 5 mL brine, dried over sodium sulfate, and concentrated under vacuum. The residue was purified on preparatory TLC (1:2:4 chloroform : ethyl acetate : hexanes), and the resulting product was further flushed through a short plug of silica (hexanes wash then slow increase to 100% ethyl acetate) to afford an off-white solid. (0.034 g, 92%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.25 – 7.14 (m, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 3.51 (s, 1H), 1.97 (s, 3H), 1.67 (d, *J* = 11.1 Hz, 3H), 1.61 – 1.53 (m, 6H), 1.53 – 1.37 (m, 3H). **^{13}C NMR** (125

[12] S. Kobayashi, R. Hirabayashi, *J. Am. Chem. Soc.* **1999**, *121*, 6942–6943T. Ankner, G. Hilmersson, *Org. Lett.* **2009**, *11*, 503–506.

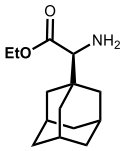
MHz, Chloroform-*d*) δ 161.9 (d, *J* = 244.4 Hz), 130.6, 129.9, 114.2, 114.2, 65.5, 38.8, 37.2, 28.6. **IR** (ATR) 2900, 2848, 1665, 1603 cm^{-1} **HRMS** (ESI) m/z calcd for $C_{17}H_{22}FN$ $(M+H)^+$ = 260.1815, found 260.1807.



51

A flame-dried flask containing 0.050 g adamantane product **27** (0.132 mmol, 1.0 equiv) was degassed and loaded with 0.50 mL methanol, samarium diiodide (4.0 mL of 1.0 M solution in THF, 3.0 equiv) under nitrogen. After stirring for 10 minutes at room temperature, the mixture was diluted with methylene chloride and washed with 5 mL of potassium sodium tartrate and 5 mL potassium carbonate (10% w/v each). The organic layer was washed with 5 mL brine, dried over sodium sulfate, and concentrated under vacuum. The residue was purified on preparatory TLC (1:1:5 chloroform : ethyl acetate : hexanes), and the resulting product was further flushed through a short plug of silica (hexanes wash then slow increase to 100% ethyl acetate) to afford an off-white solid. (0.020 g, 79%). **HRMS** (ESI) m/z calcd for $C_{17}H_{22}FN$ $(M+H)^+$ = 260.1815, found 260.1808.

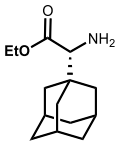
(S)-ethyl 2-(adamantanyl)-2-aminoacetate (**52**):



52

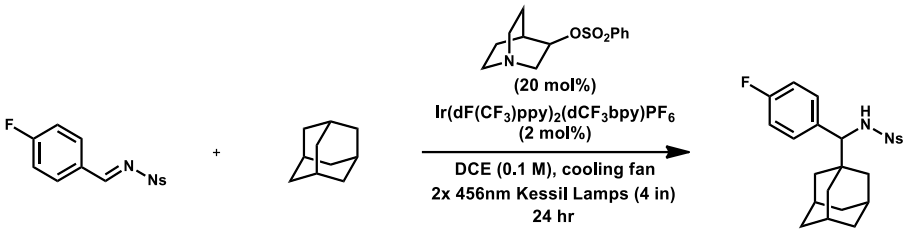
To a round bottom flask containing a stir bar was added mesitylsulfinamine product **49** (0.075 g, 0.185 mmol), 1 mL dichloromethane, and 1 mL trifluoroacetic acid. The head space was flushed with N_2 and then the flask was sealed and stirred at room temperature for 24 h. The volatiles were removed under vacuum and the resulting residue was dissolved in 3 mL of ethyl acetate and extracted with 3 mL saturated aqueous sodium bicarbonate. The organic layer was then washed with 3 mL water, followed by 3 mL brine, then dried over sodium sulfate. The organic layer was reduced under vacuum and the residue was purified using column chromatography. Fractions were collected using 7:3 ethyl acetate: hexanes until a UV active spot was observed by TLC. Then a 3% methanol in ethyl acetate mixture was used until product fractions were detected on TLC using $KMnO_4$ stain. These fractions were rotovapped down to give a white foam (0.031 g, 70%). **^{1}H NMR** (400 MHz,) δ 4.18 (q, J = 7.1 Hz, 2H), 3.00 (s, 1H), 2.06 – 1.93 (m, 3H), 1.76 – 1.60 (m, 10H), 1.54 – 1.47 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 174.5, 64.4, 60.4, 38.6, 37.1, 36.2, 28.5, 14.5. **HRMS** (ESI) m/z calcd for $C_{14}H_{24}NO_2$ $(M+H)^+$ = 238.1802, found 238.1803. **$[\alpha]_D$ =** -33.6 (l=1 dm, c= 0.0032 g/mL, α= -0.1075).

(R)-ethyl 2-(adamantanyl)-2-aminoacetate (**R-52**):



R-52

Prepared according to the same procedure used with S-52 from the corresponding R-mesitylsulfinamine (0.068 g, 0.167 mmol) to afford the product as a clear oil (0.024 g, 62%). **^{1}H NMR** (400 MHz,) δ 4.18 (q, J = 7.2 Hz, 2H), 3.00 (s, 1H), 2.03 – 1.90 (m, 3H), 1.71 – 1.60 (m, 10H), 1.54 – 1.47 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H). **$[\alpha]_D$ =** 33.5 (l=1 dm, c= 0.001 g/mL, α= -0.0335).



8 **S7**

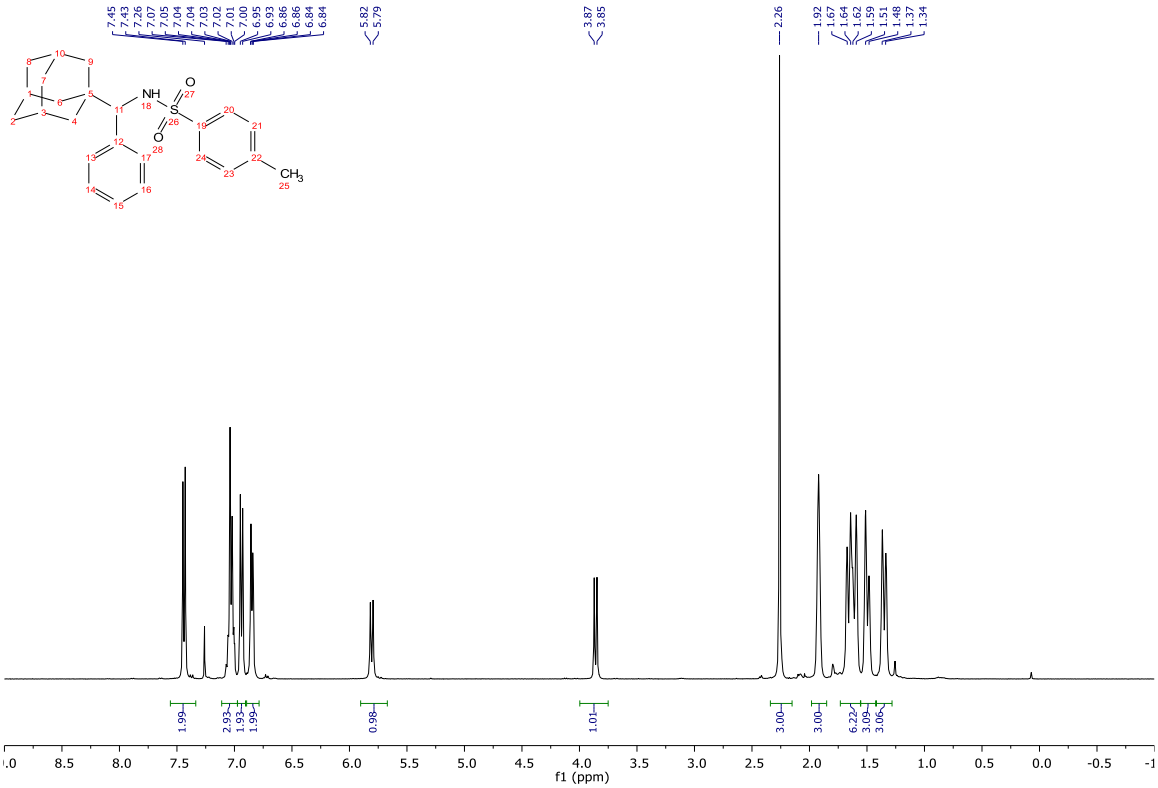
N-(adamantan-1-yl(4-fluorophenyl)methyl)-4'-nitrobenzenesulfonamide (**S7**):

According to *General Procedure A,* 0.139 g *N*-(4-fluorobenzylidene)-4'-nitrobenzenesulfonamide (0.50 mmol, 1.0 equiv), 0.012 g photoredox catalyst (2 mol%), 0.026 g quinuclidine phenylsulfonate (20 mol%), 0.204 g adamantane **8** (1.50 mmol, 3.0 equiv) and 1,2-dichloroethane (5.0 mL) were reacted for 24 hours. The dark brown reaction mixture was then reduced to dryness under vacuum and the resulting solid was purified using column chromatography (2% ethyl acetate in 2:3 chloroform : hexanes) to give an impure tan solid (0.035 g, 16%, >90% pure). Reactions (0.10 mmol scale) were conducted with varying time and solvents. Upon GC analysis (with Bn_2O used as an internal standard), the imine was mostly consumed at 4 hours with a maximum GC product yield of 24%. These results are indicative of notable substrate decomposition under the dual catalytic system, likely due to the highly withdrawn character of the imine. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.13 – 8.00 (m, 2H), 7.81 – 7.62 (m, 2H), 6.95 – 6.64 (m, 4H), 5.10 (d, *J* = 8.7 Hz, 1H), 4.01 (d, *J* = 8.8 Hz, 1H), 1.99 (s, 3H), 1.71 – 1.60 (m, 6H), 1.54 – 1.51 (m, 2H), 1.37 – 1.28 (m, 4H).

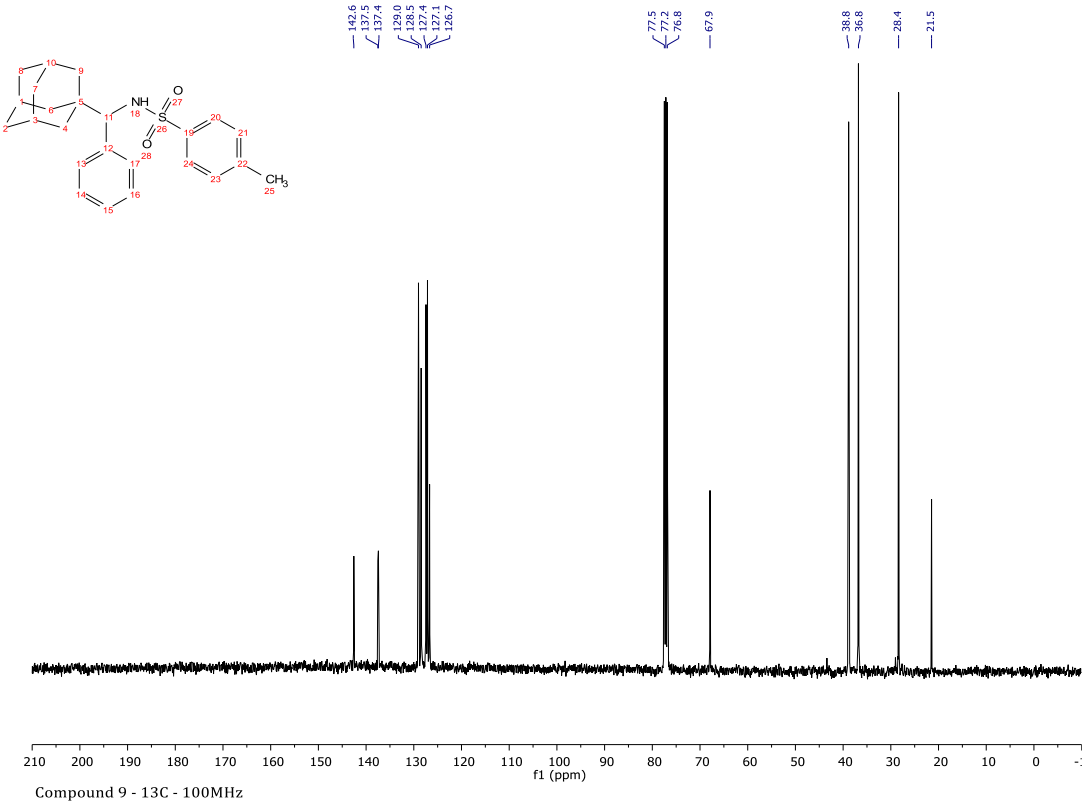
GC conditions: The initial oven temperature was set to 100 °C, and the ramp rate was programmed to 10 °C/min until reaching 300 °C. The temperature is held at 300 °C for 10 minutes before concluding the run. Retention time: t (imine) = 16.0 min, t (Bn_2O) = 7.5 min, t (**S7**) = 23.8 min. Relative response factor: Rf (**S7**) = 1.23.

NMR Spectra

N-adamantan-1-yl(phenyl)methyl)-4-methylbenzenesulfonamide (**9**)

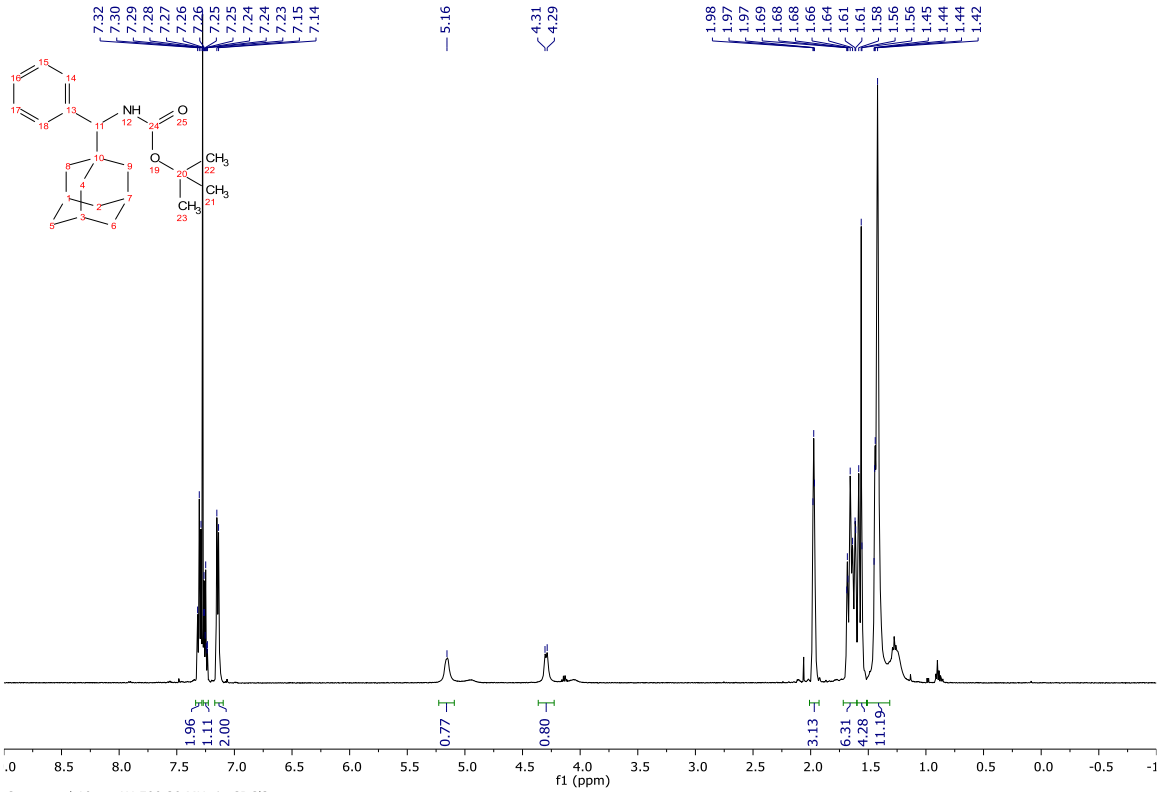


Compound 9 - 1H - 400MHz

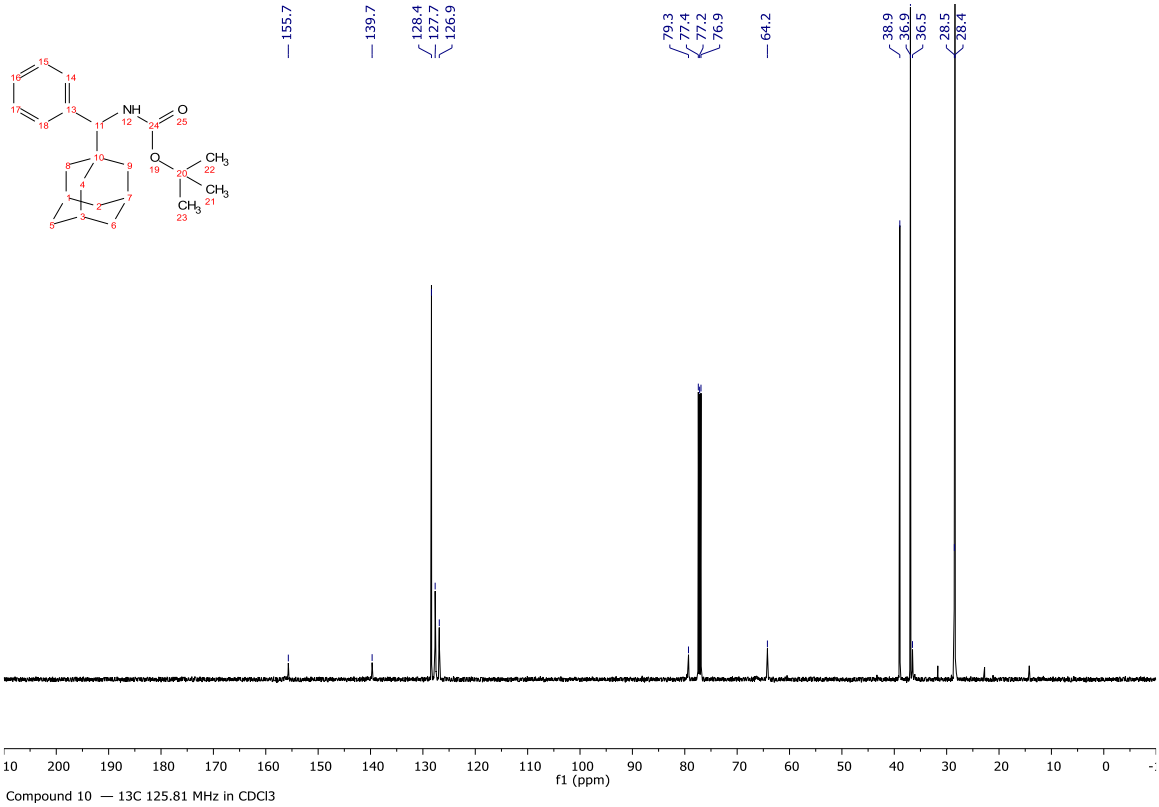


Compound 9 - 13C - 100MHz

tert-Butyl-(-adamantan-1-yl(phenyl)methyl)carbamate (**10**):

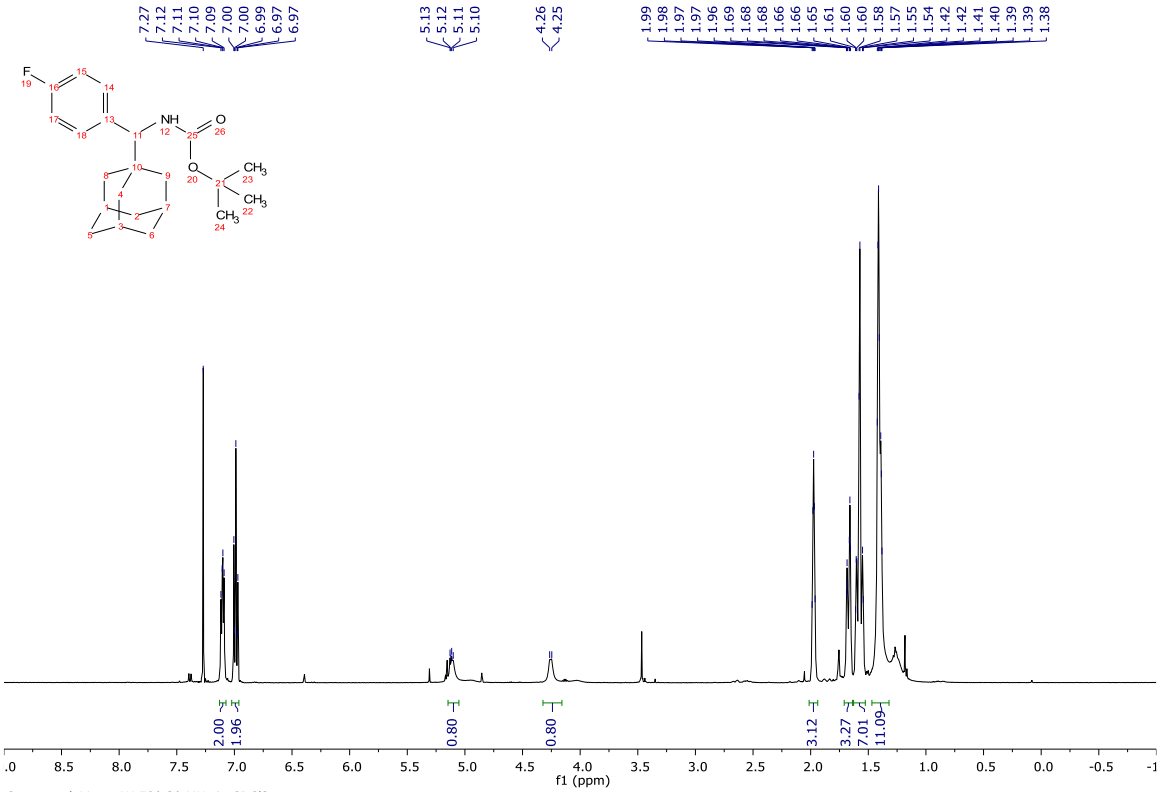


Compound 10 — 1H 500.30 MHz in CDCl3

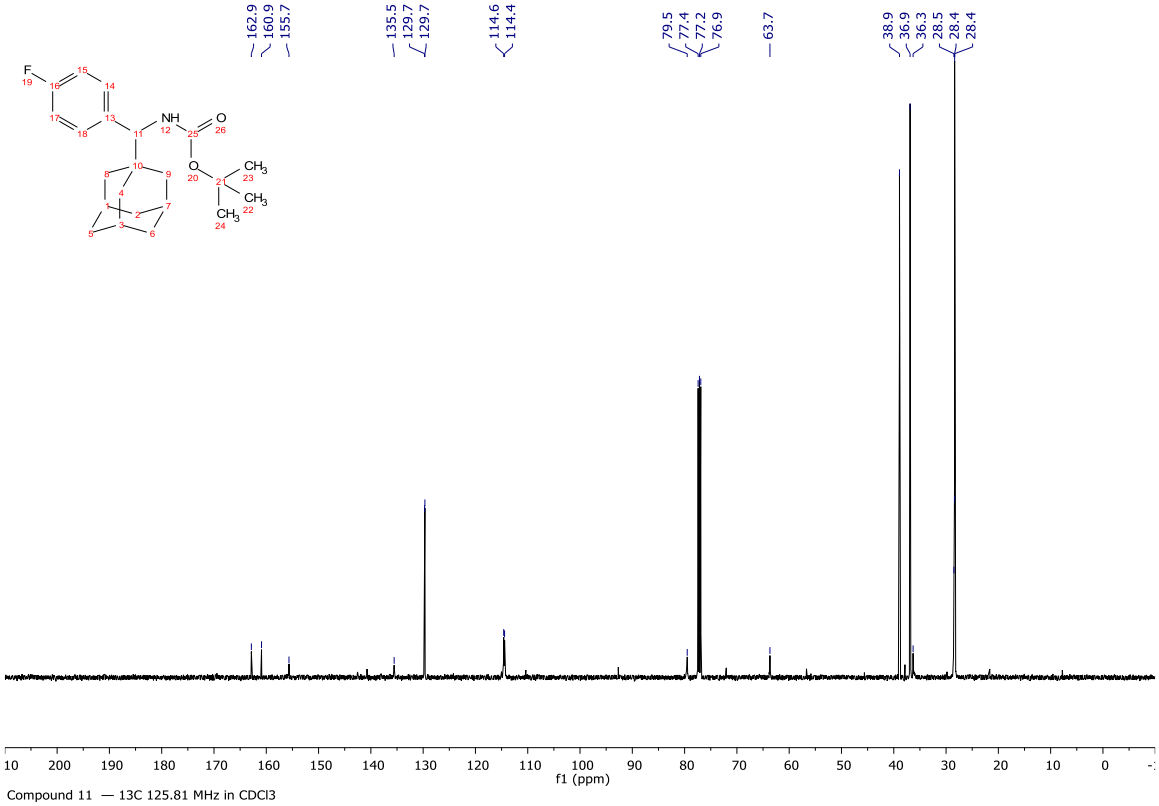


Compound 10 — 13C 125.81 MHz in CDCl3

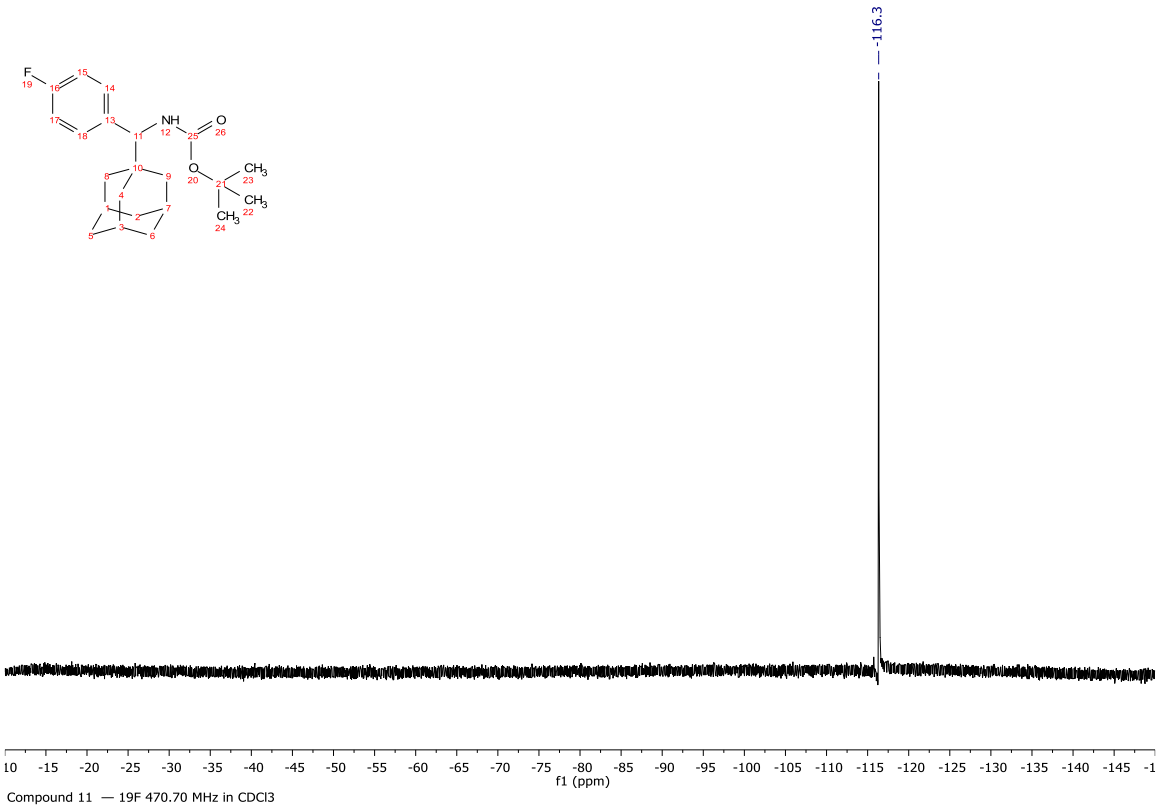
tert-Butyl-(adamantan-1-yl(4-fluorophenyl)methyl)carbamate (**11**):



Compound 11 — 1H 500.30 MHz in CDCl3

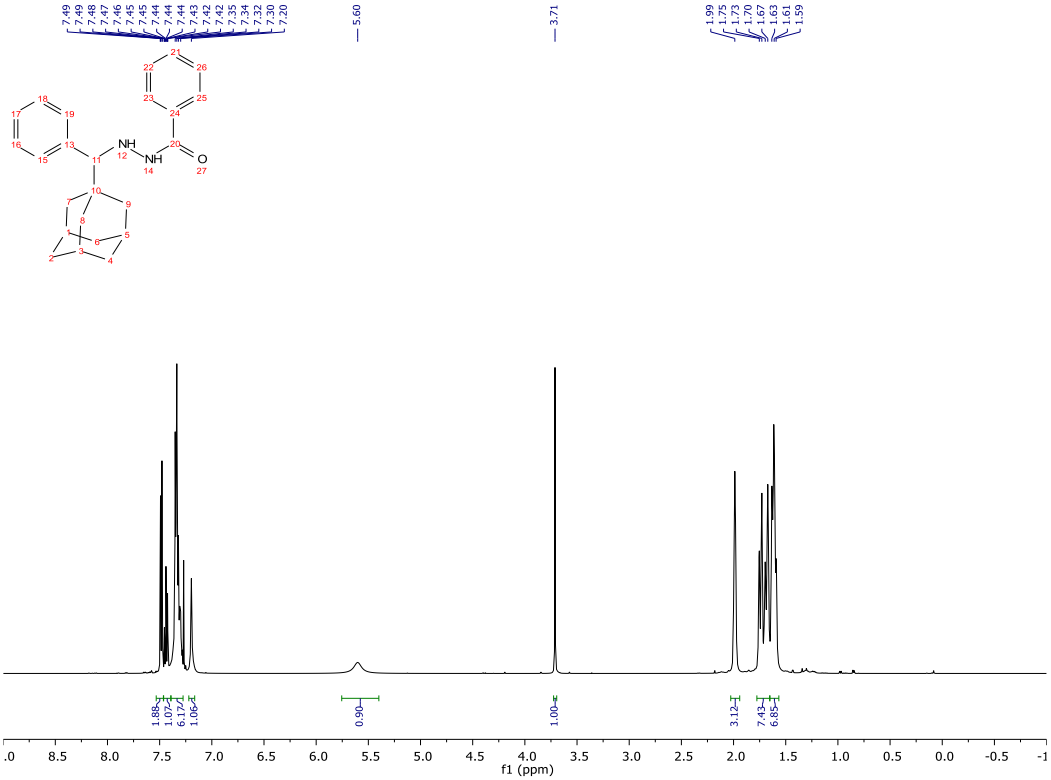


Compound 11 — 13C 125.81 MHz in CDCl3

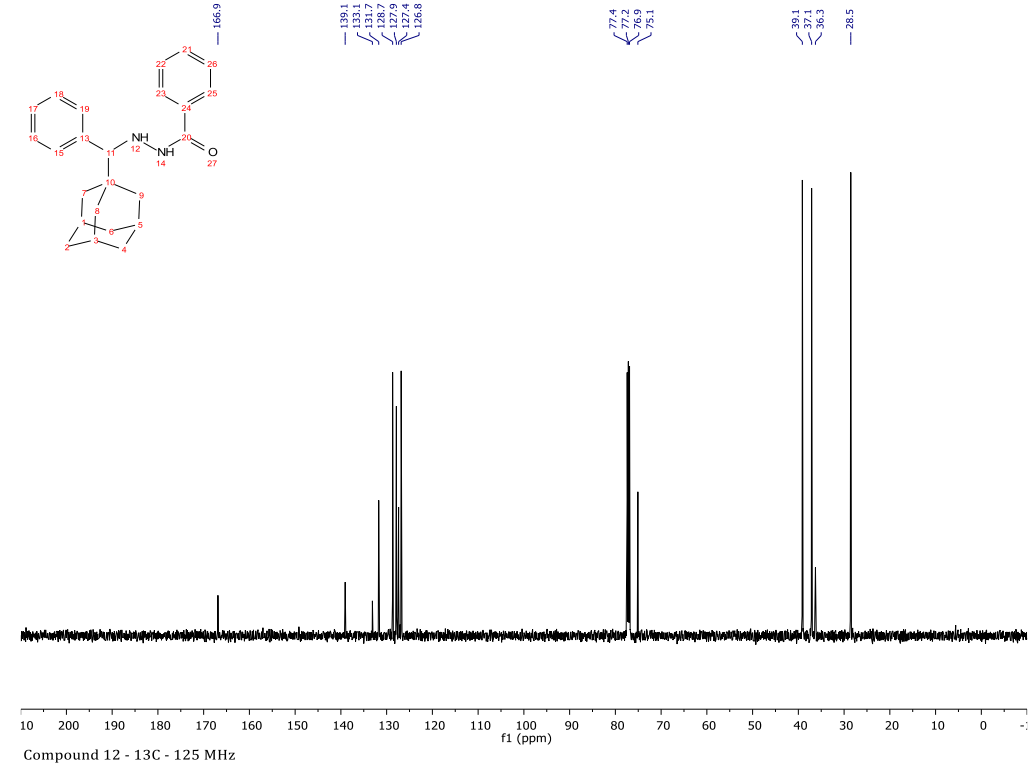


Compound 11 — 19F 470.70 MHz in CDCl3

N'-(adamantan-1-yl(phenyl)methyl)benzohydrazide (**12**):

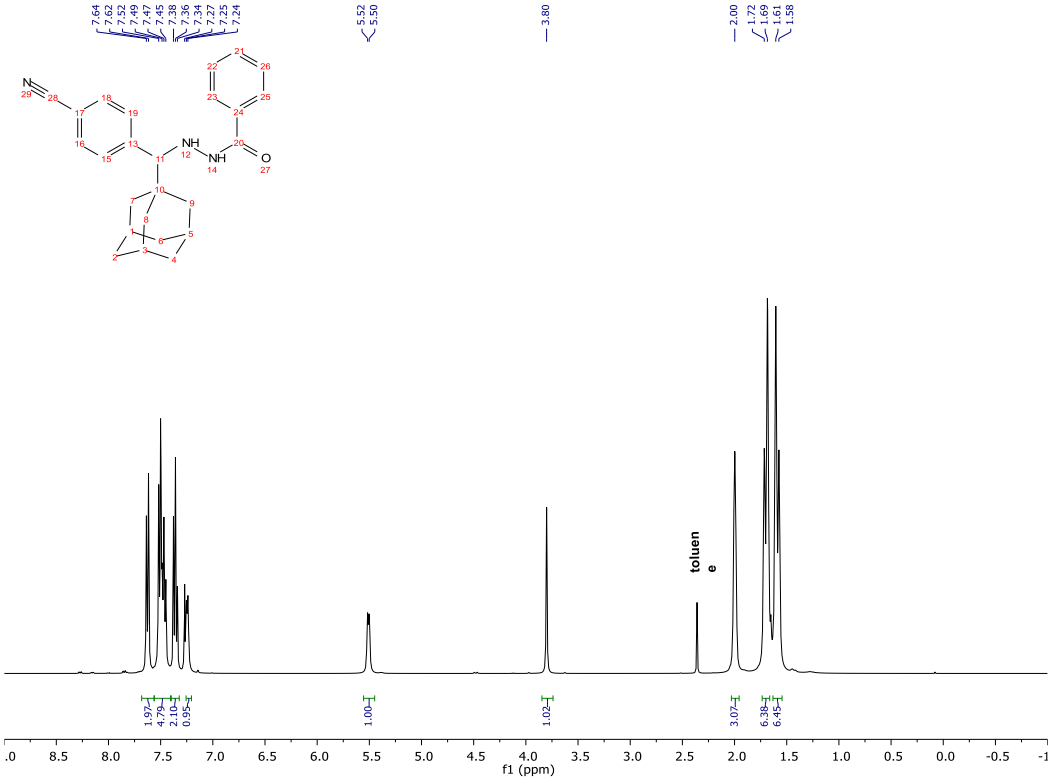


Compound 12 - 1H - 500 MHz

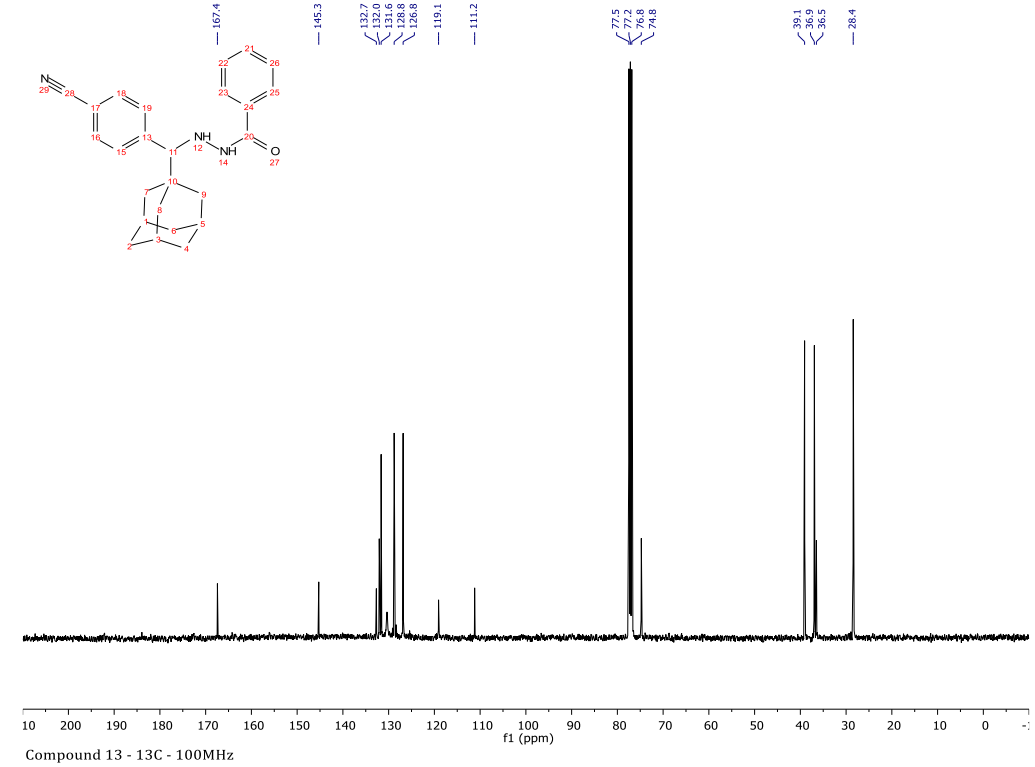


Compound 12 - 13C - 125 MHz

N'-adamantan-1-yl((4-(cyanophenyl))methyl)benzohydrazide (**13**):

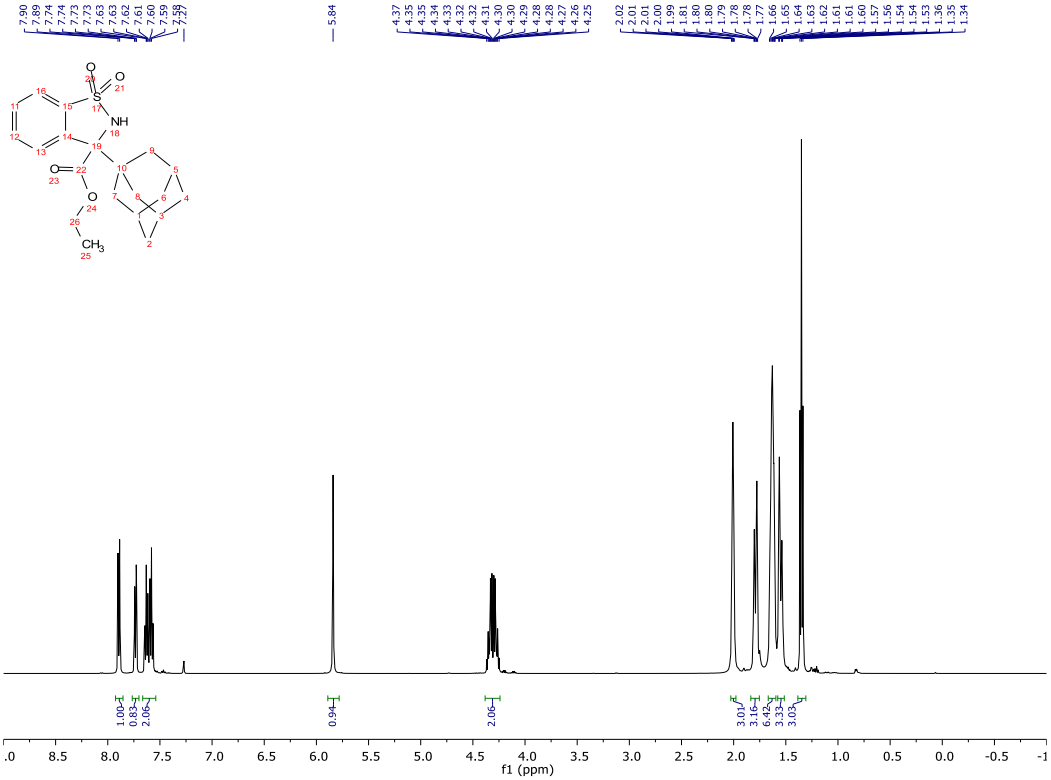


Compound 13 - 1H - 400MHz

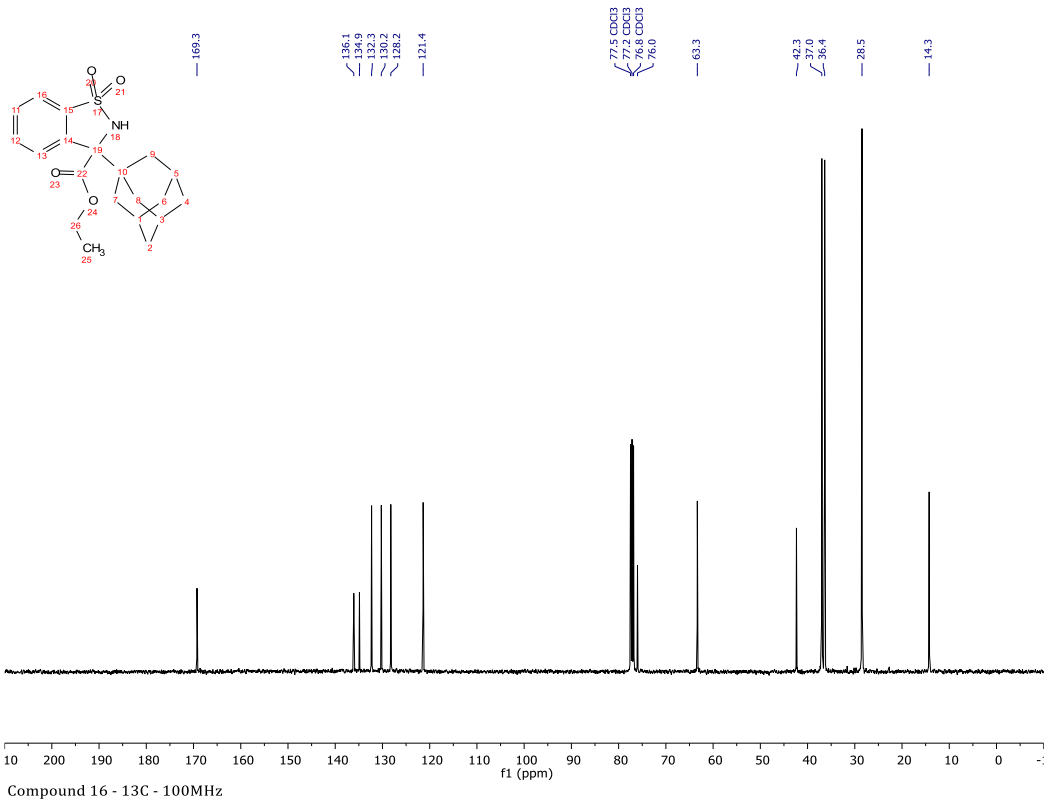


Compound 13 - 13C - 100MHz

ethyl 3-(adamantyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**16**):

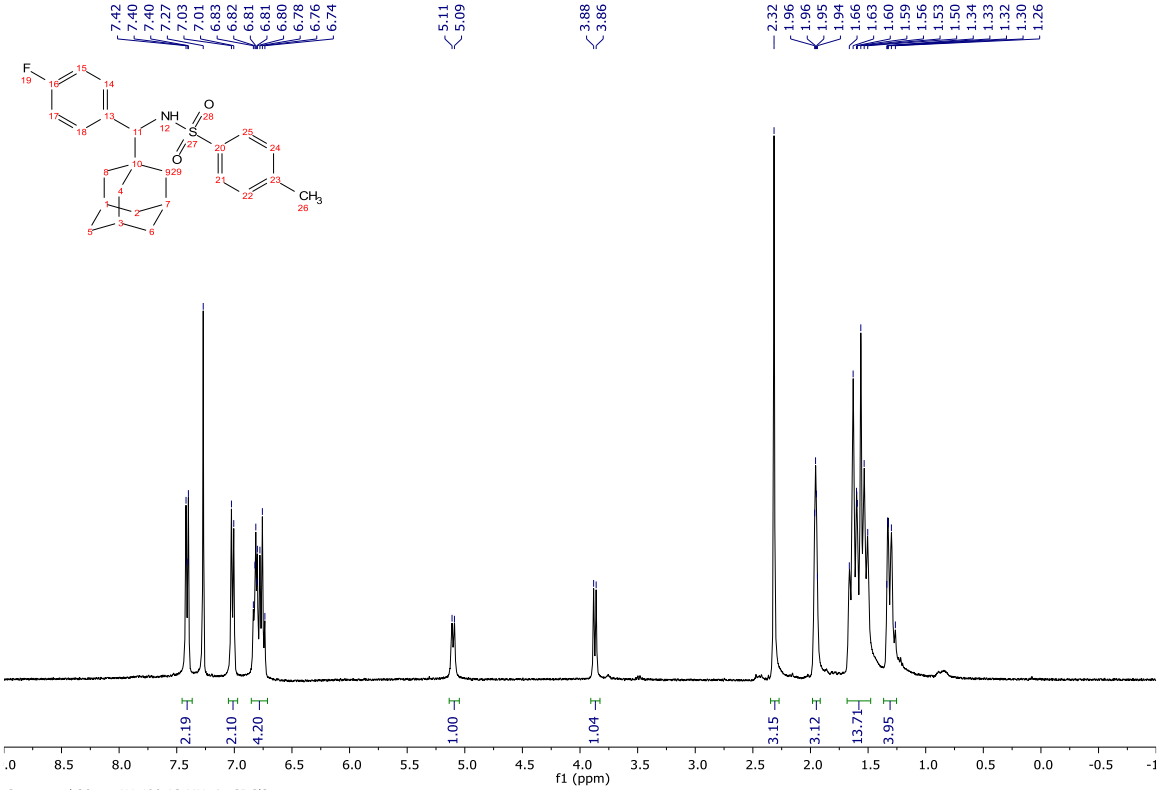


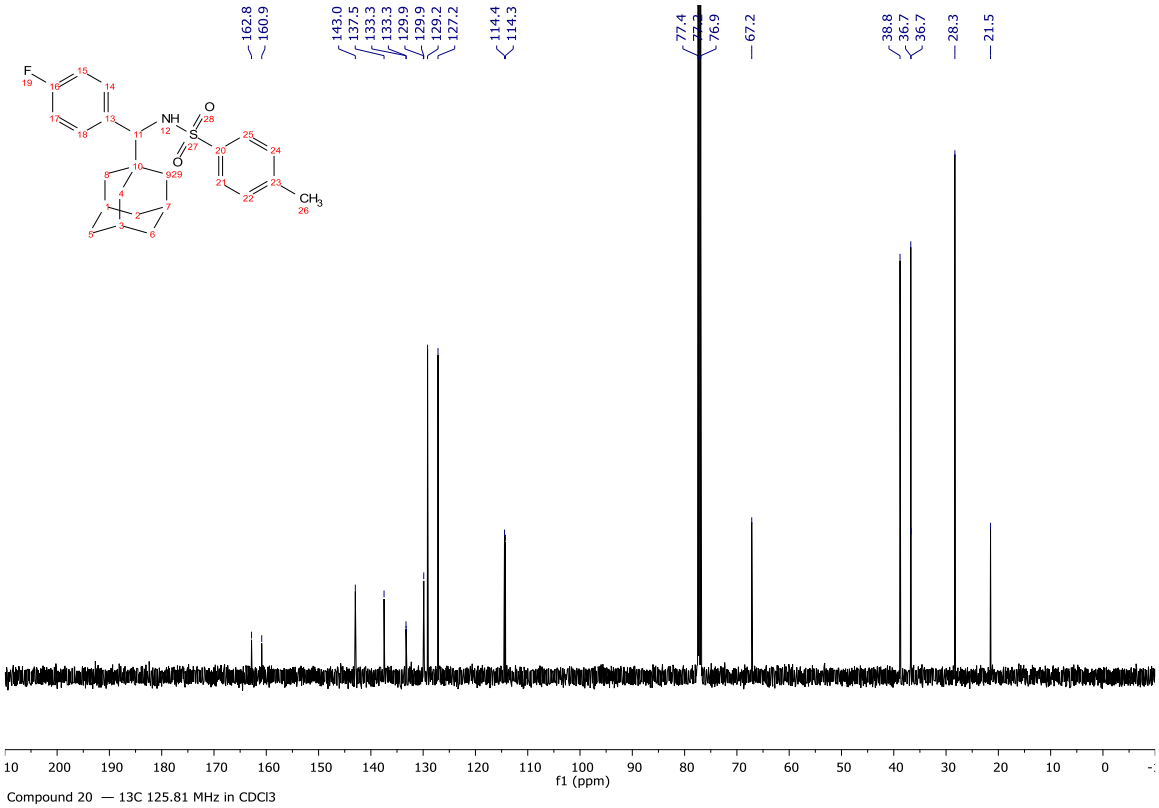
Compound 16 - 1H - 500MHz

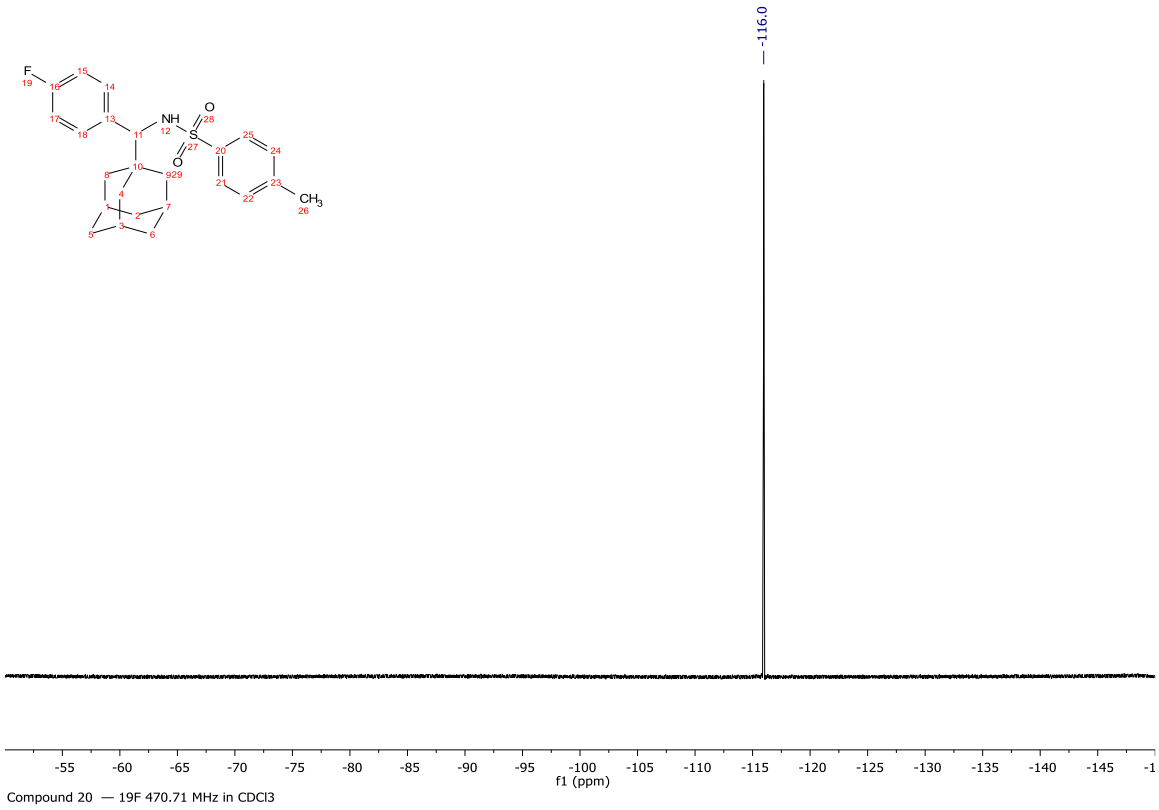


Compound 16 - 13C - 100MHz

N-(adamantan-1-yl(4-fluorophenyl)methyl)-4'-methylbenzenesulfonamide (**20**):

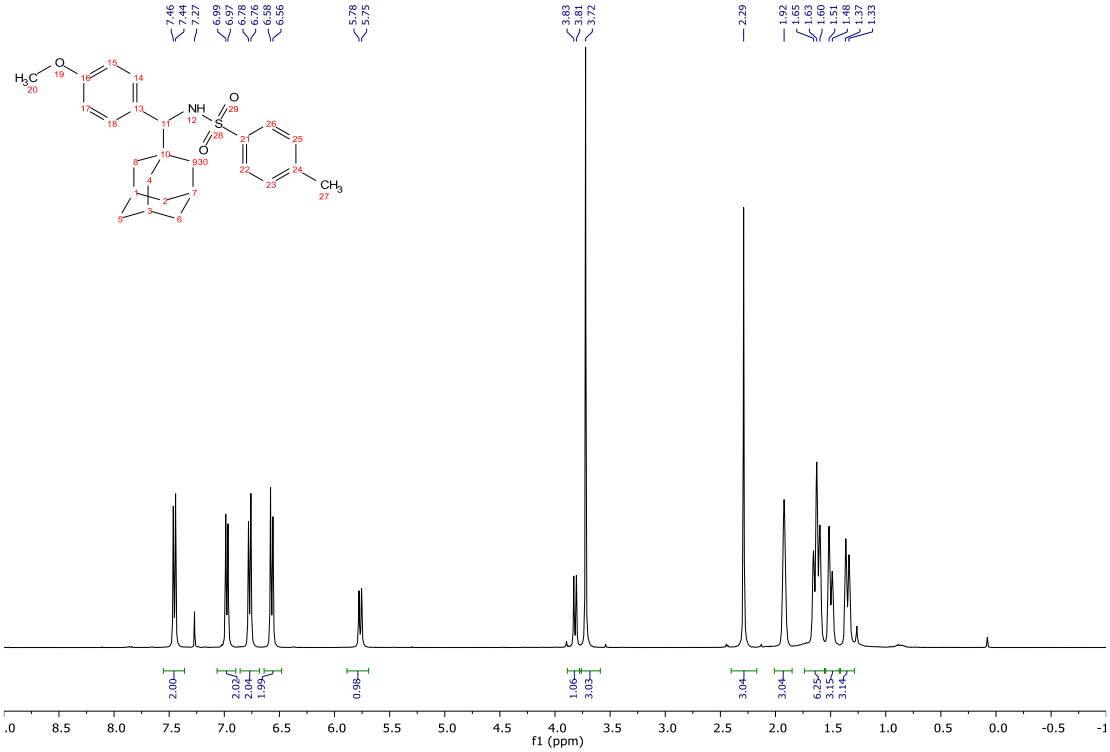




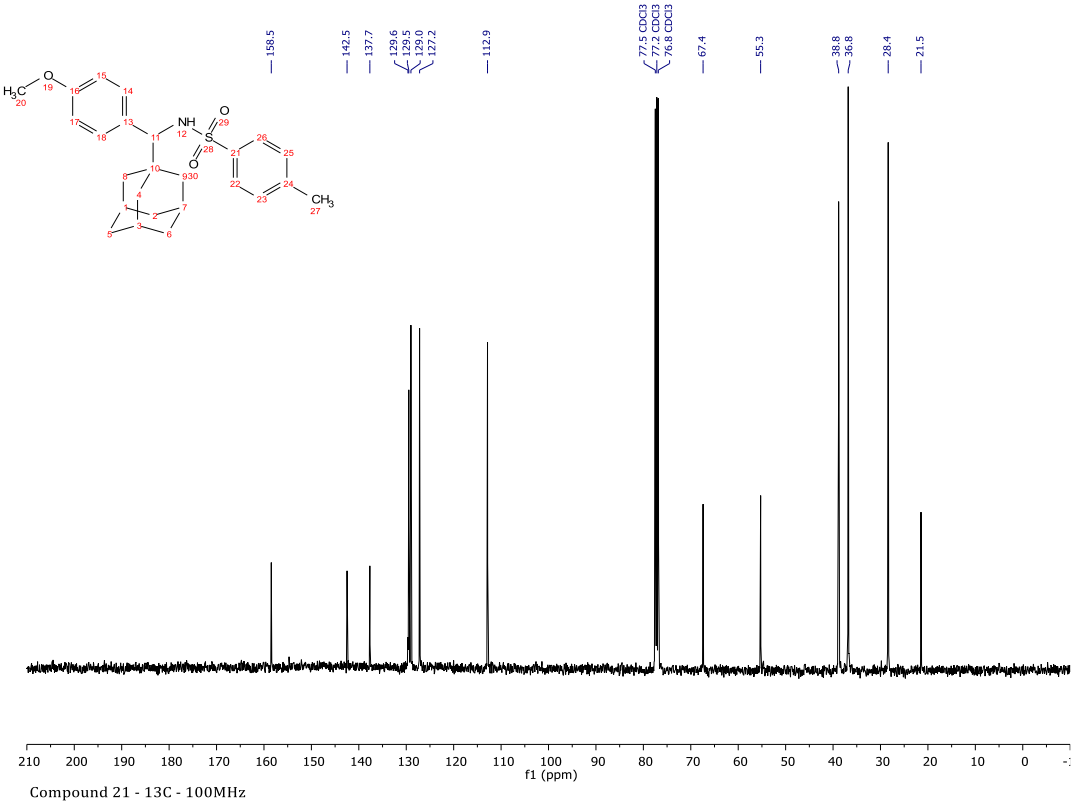


Compound 20 — 19F 470.71 MHz in CDCl3

N-(adamantan-1-yl(4-methoxyphenyl)methyl)-4-methylbenzenesulfonamide (**21**):

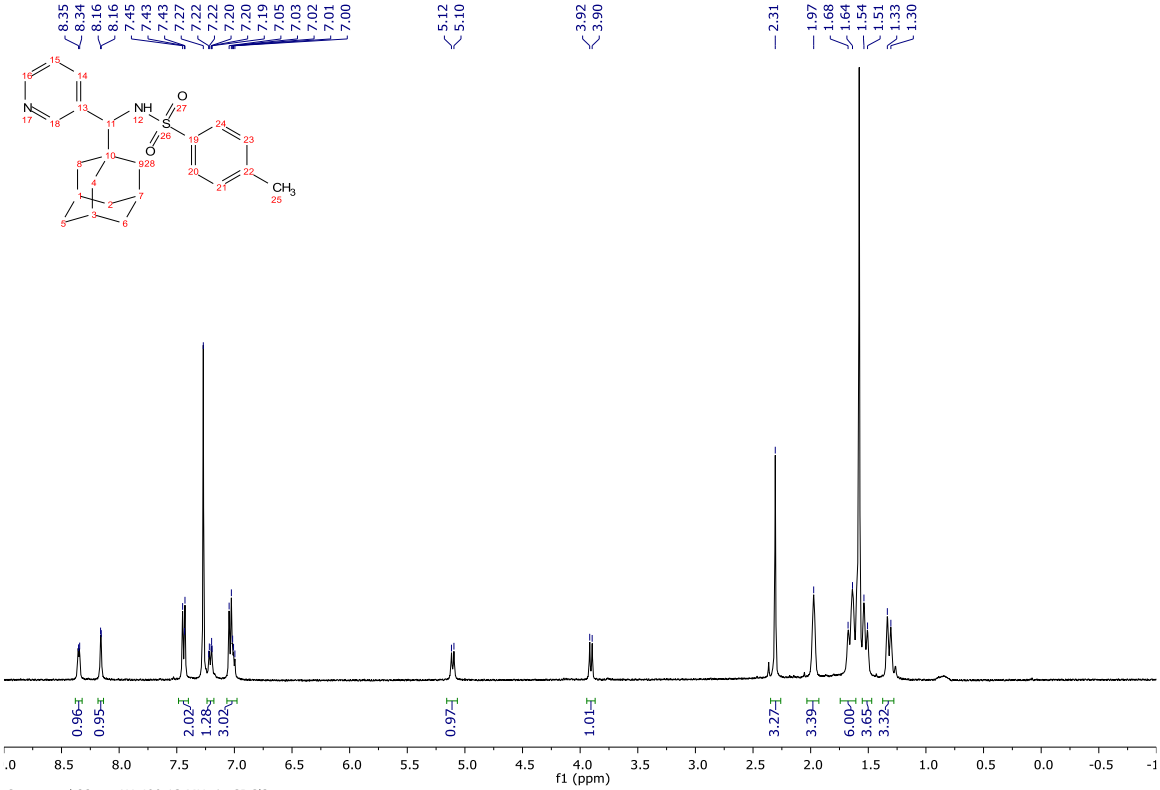


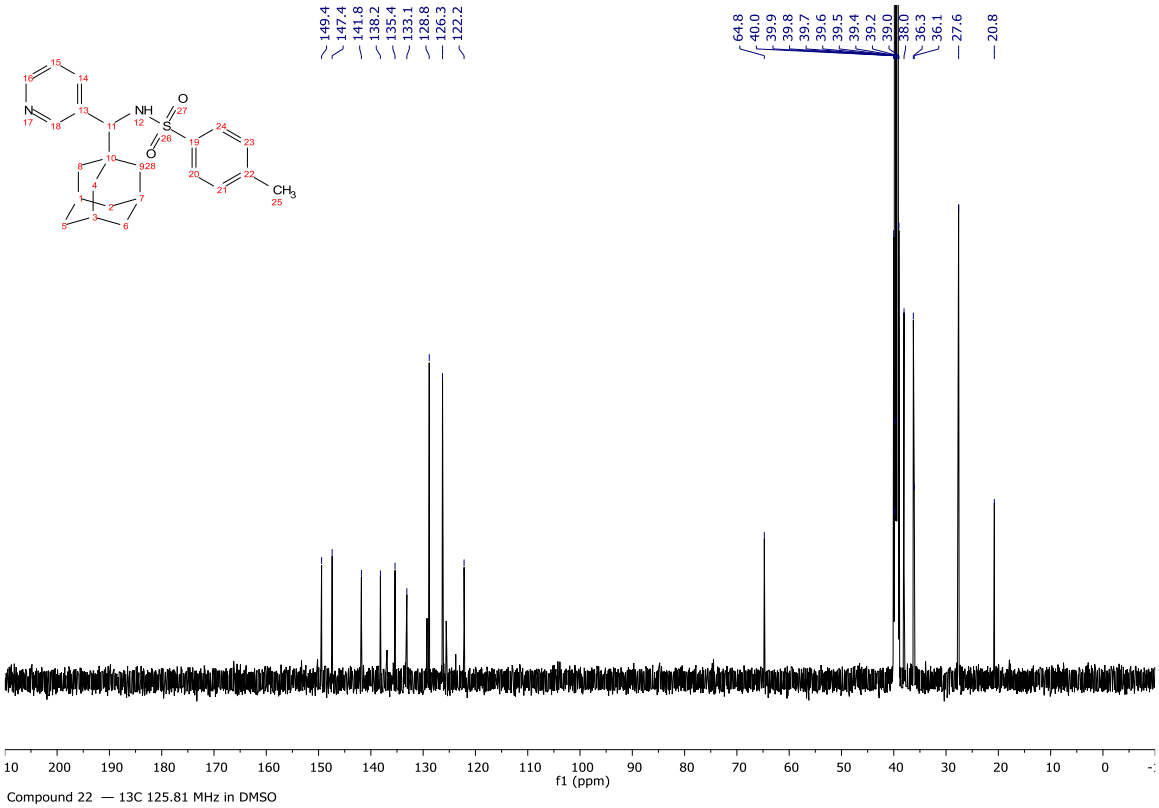
Compound 21 - 1H - 400 MHz



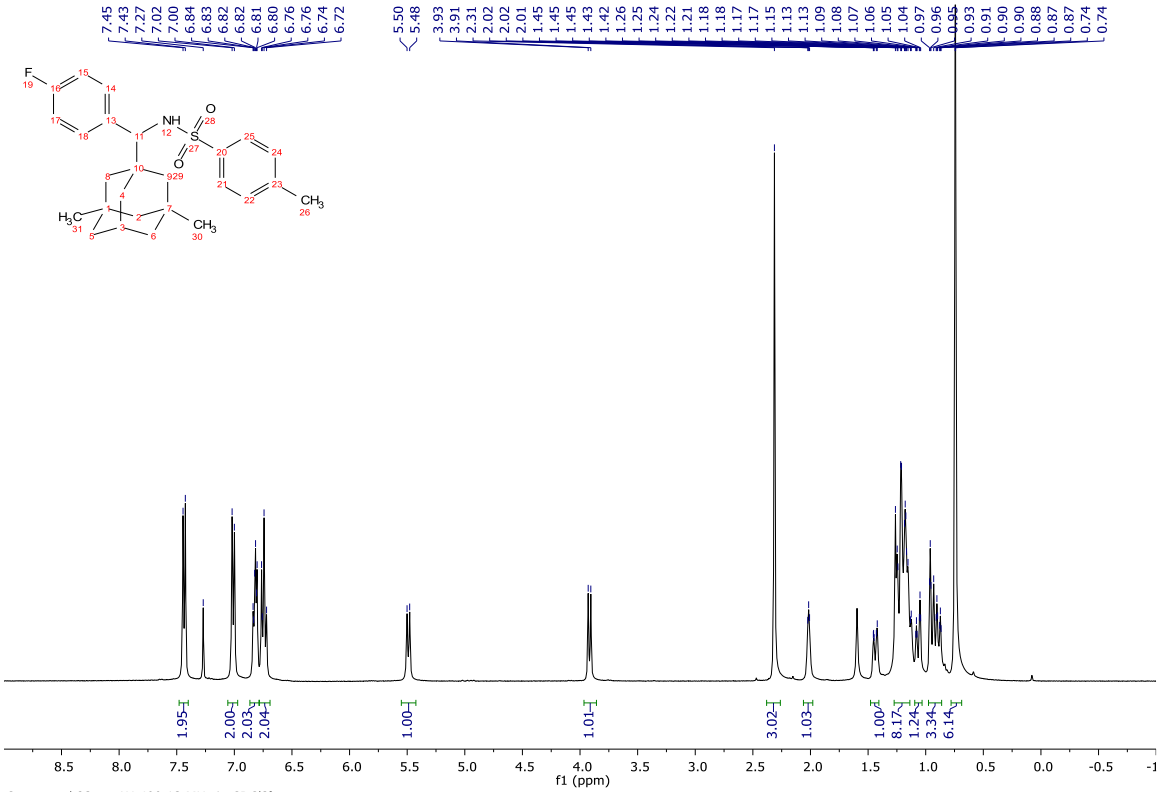
Compound 21 - 13C - 100MHz

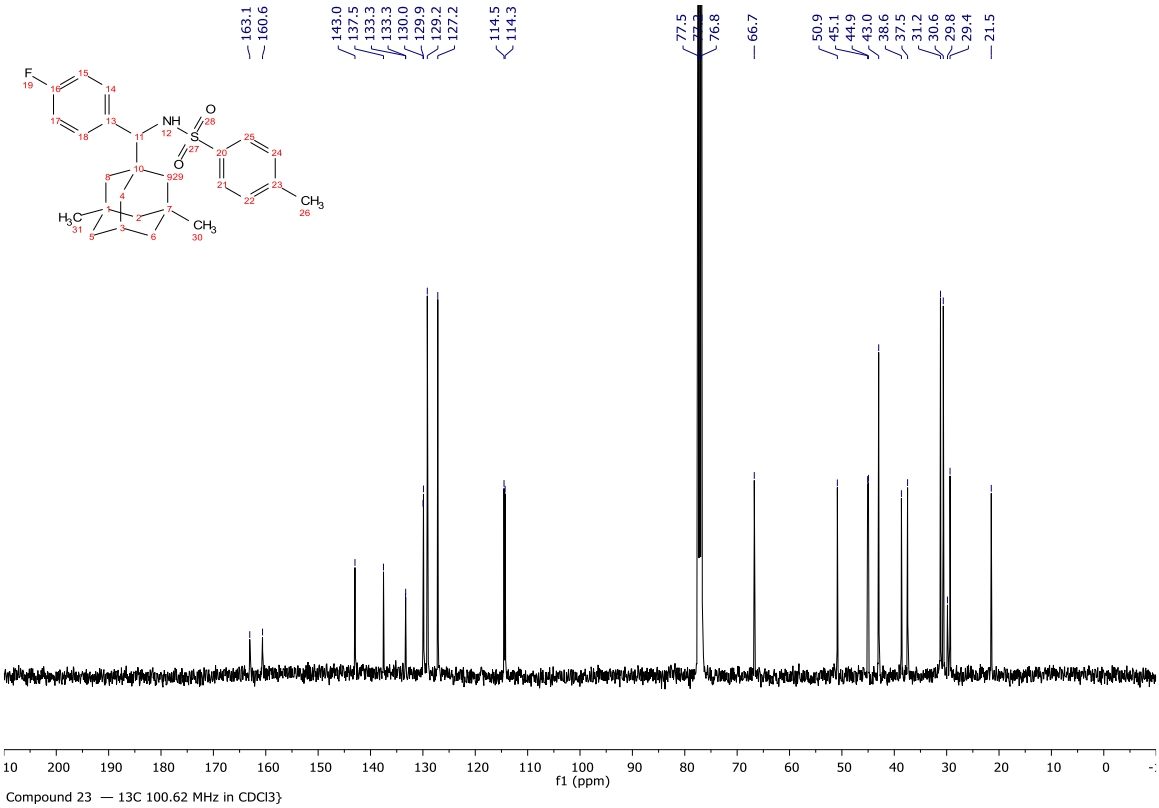
N-(3-adamantan-1-yl(pyridin-3-yl)methyl)-4'-methylbenzenesulfonamide (**22**):

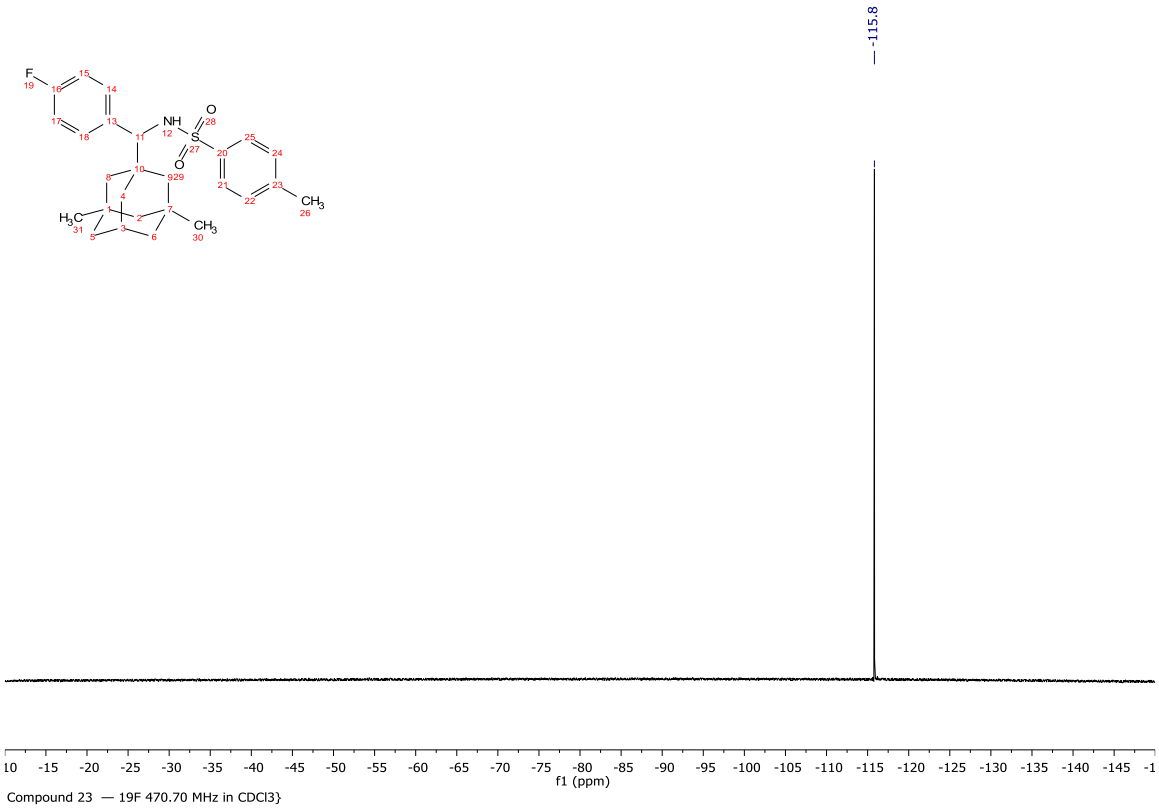




N-(3,5-dimethyladamantan-1-yl)((4-fluorophenyl)methyl)-4'-methylbenzenesulfonamide (**23**):

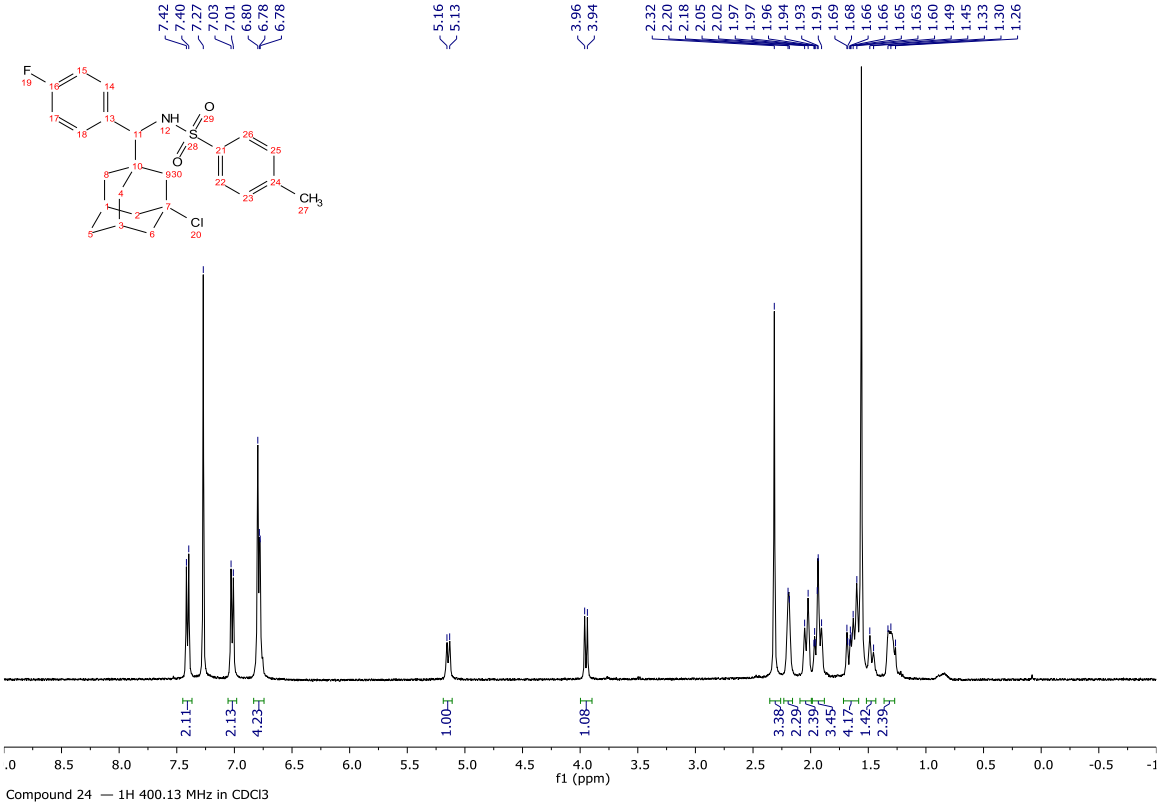


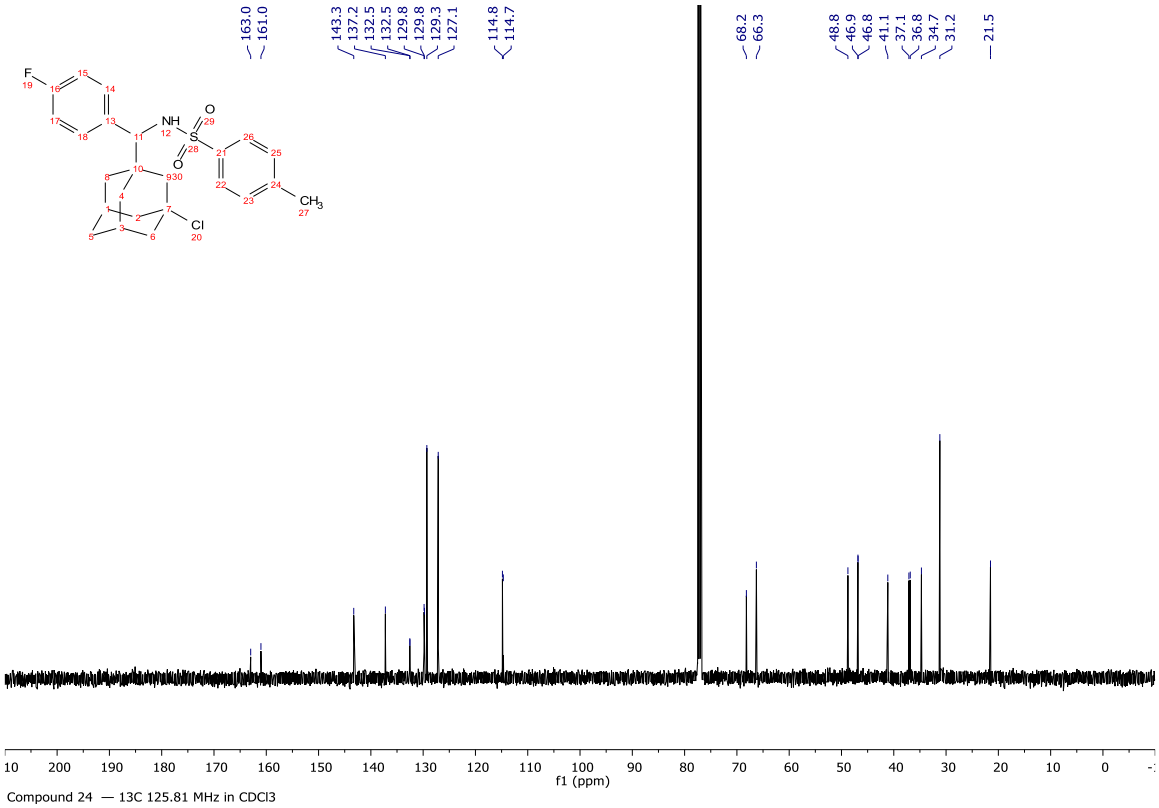


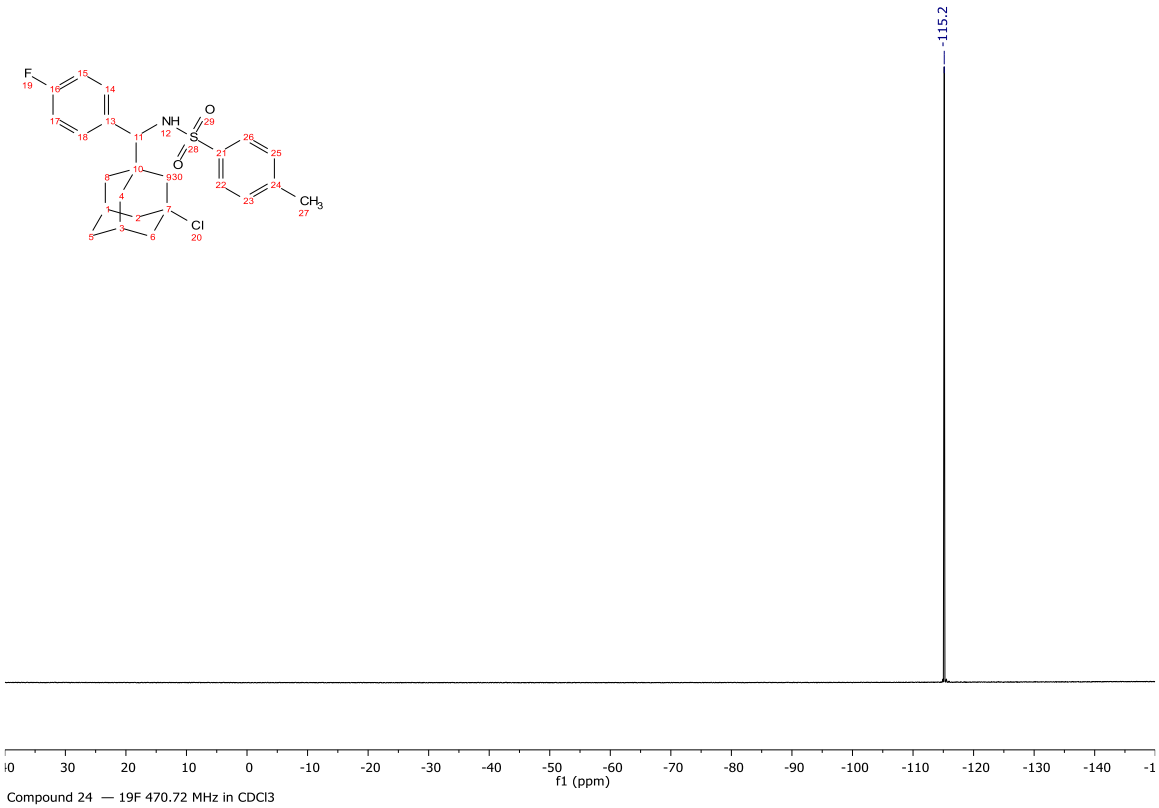


Compound 23 — 19F 470.70 MHz in CDCl3}

N-(3-chloroadamantan-1-yl(4-fluorophenyl)methyl)-4'-methylbenzenesulfonamide (**24**):

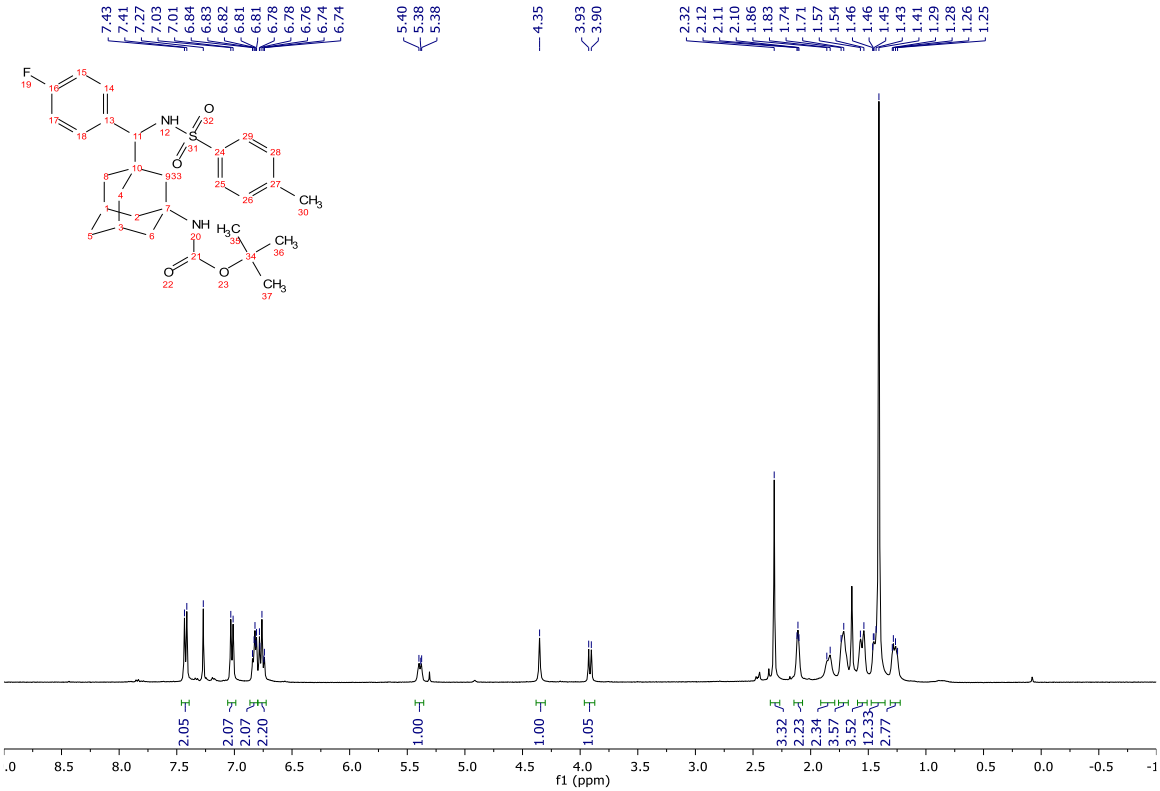


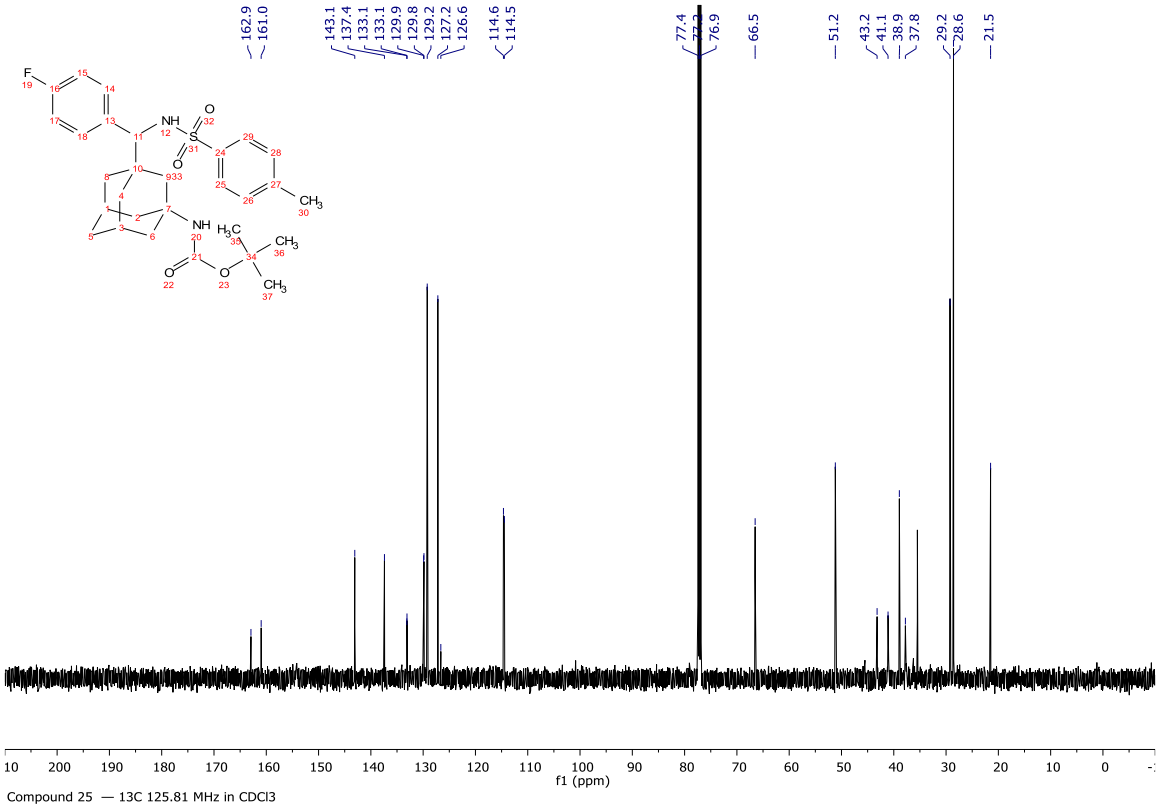


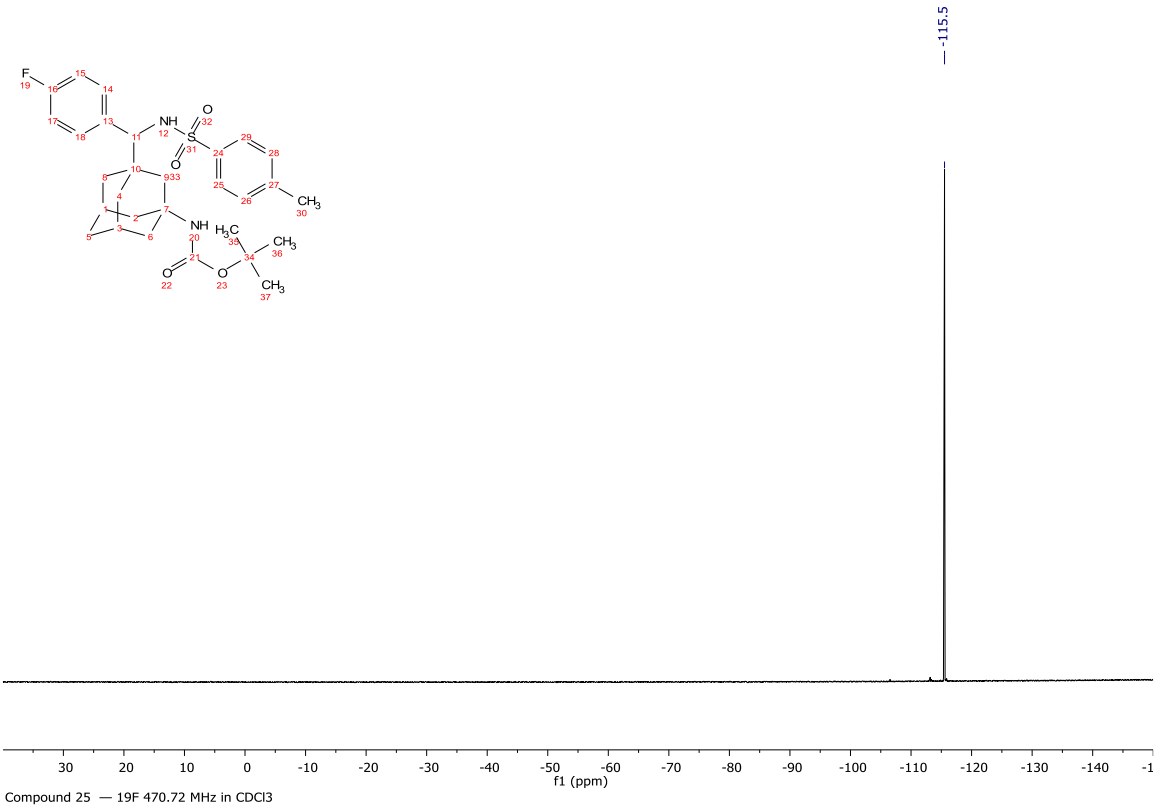


Compound 24 — 19F 470.72 MHz in CDCl3

N-(3-(*N'*-tert-butoxycarbonyl-amino)-adamantyl(4-fluorophenyl)methyl)-4'-methylbenzenesulfonamide (**25**):

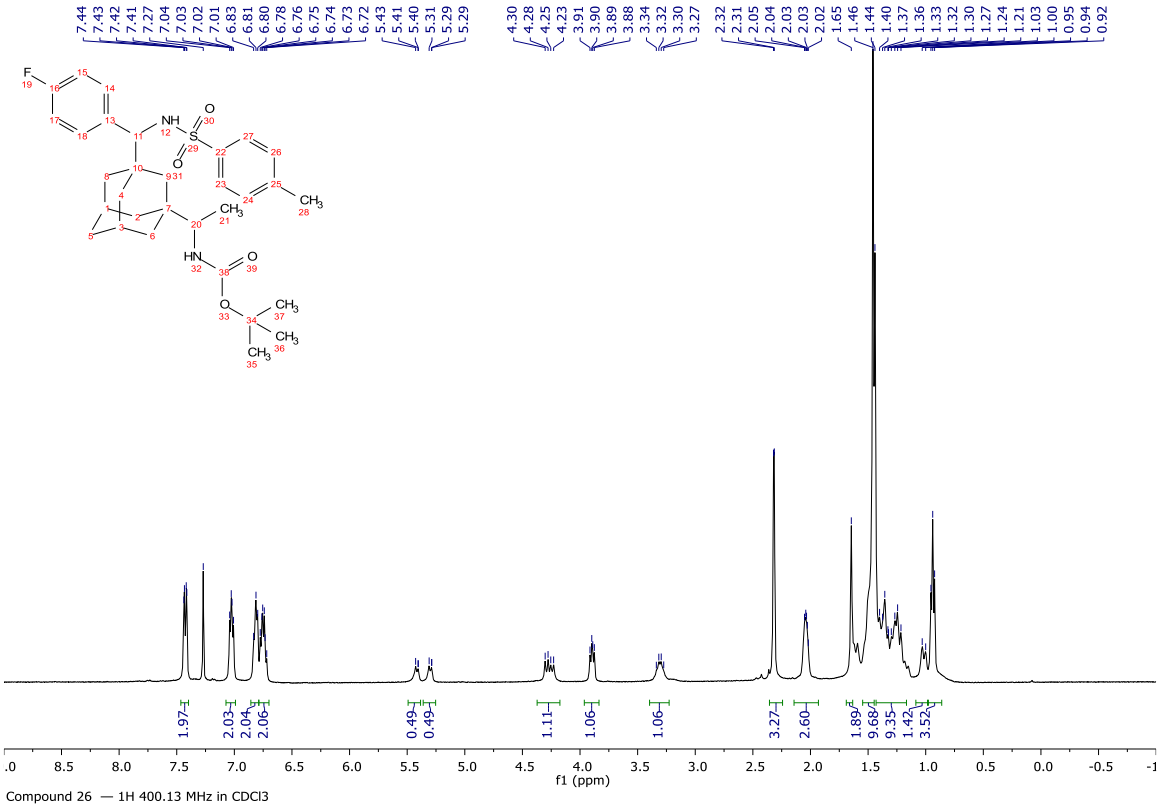


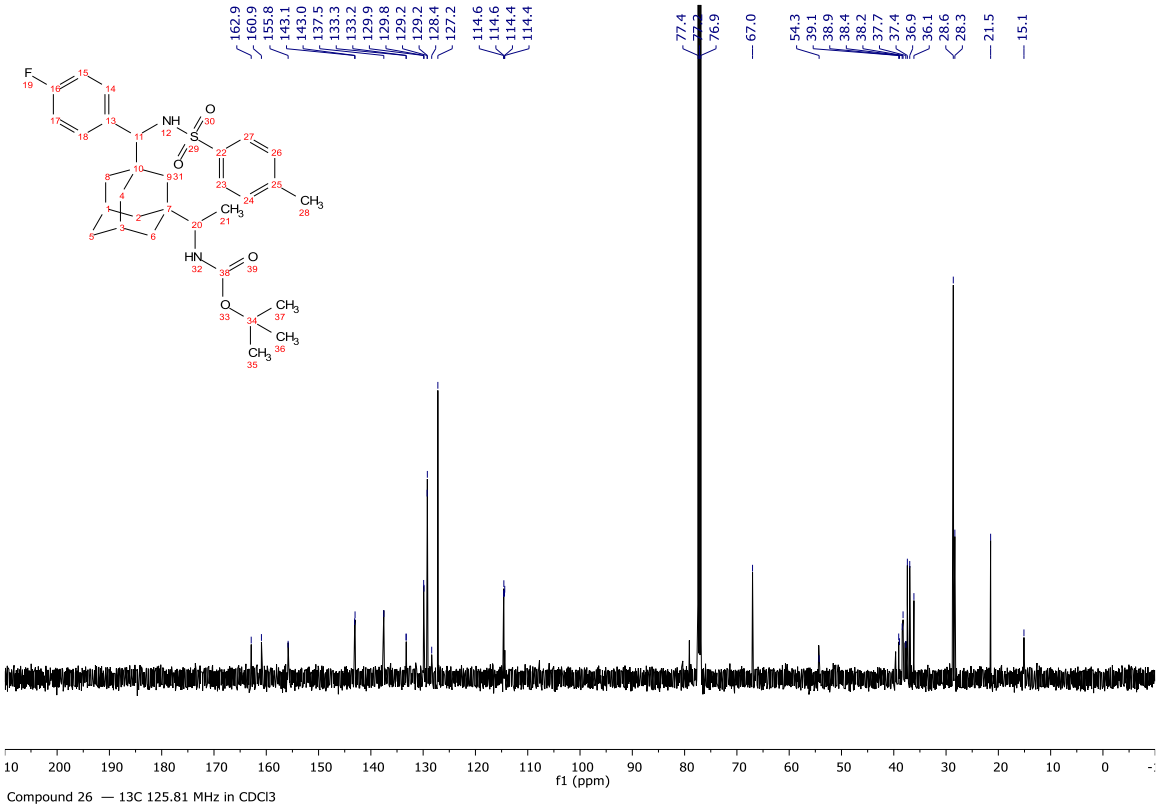


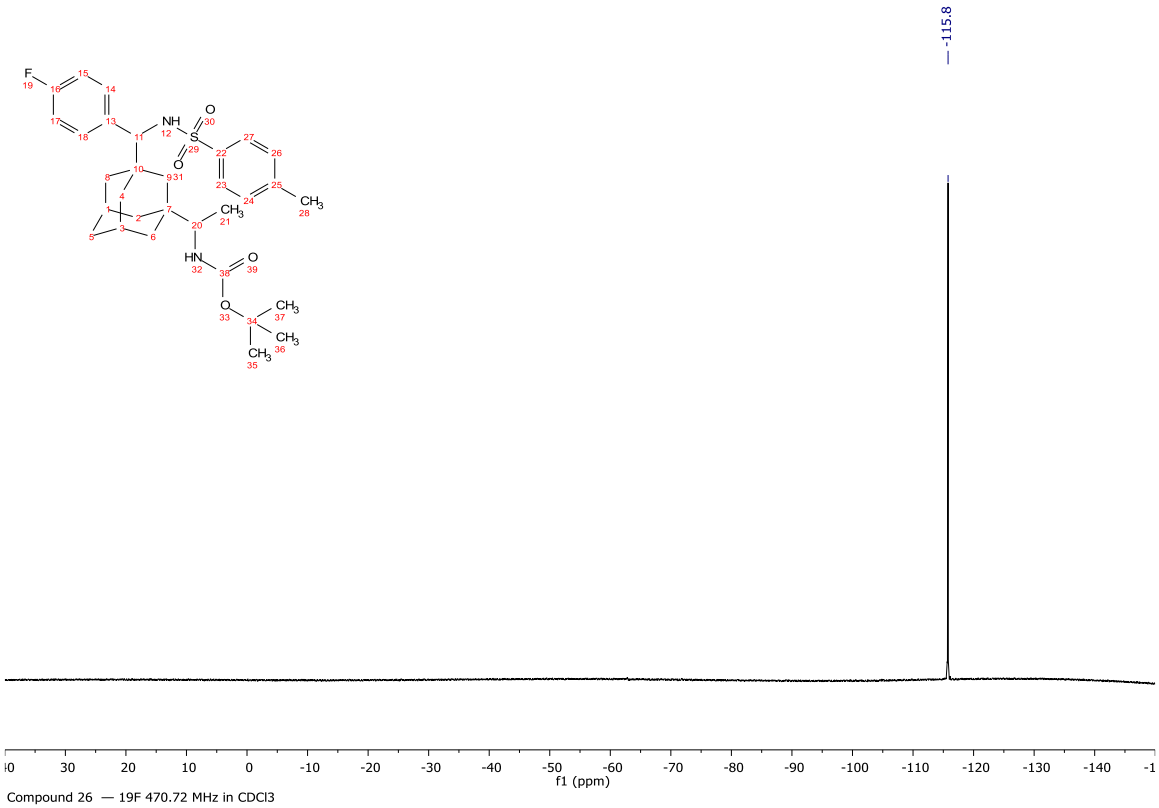


Compound 25 — 19F 470.72 MHz in CDCl3

N-(3-(1’-(*N’*-tert-butylcarbonyl)-ethyl)adamantyl(4-fluorophenyl)methyl)-4’-methylbenzenesulfonamide (**26**):

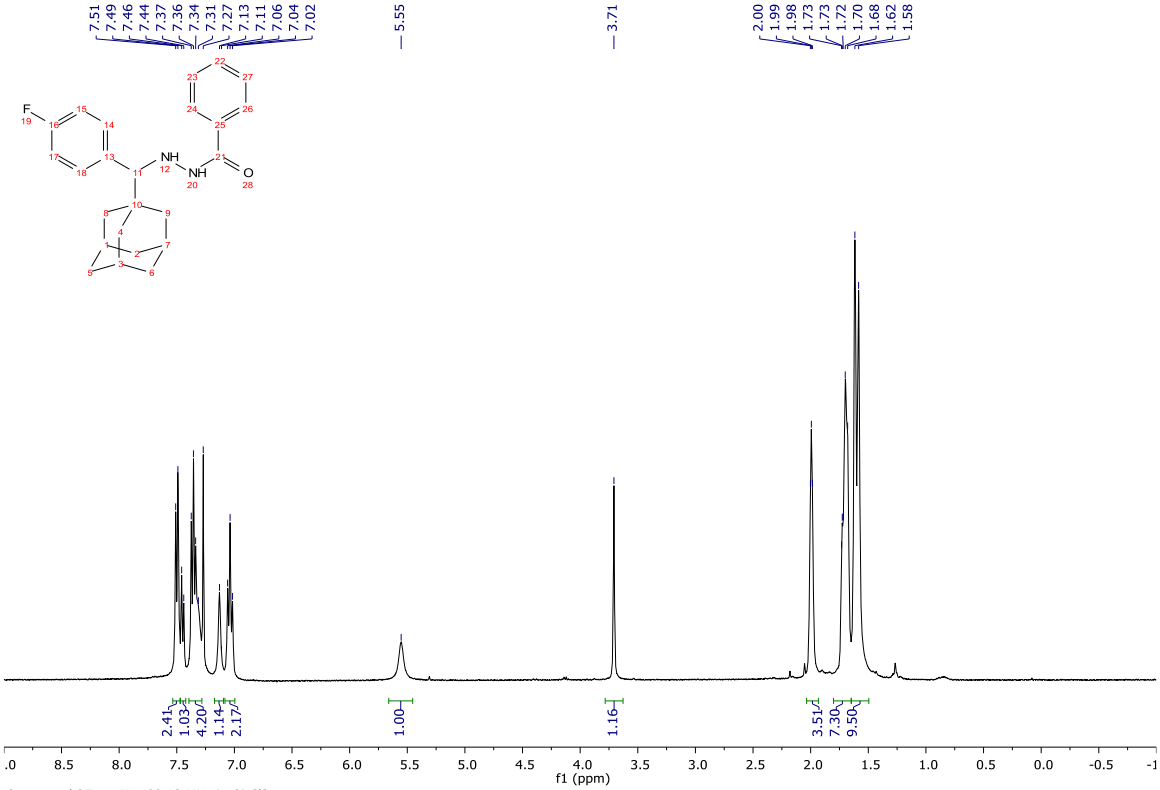


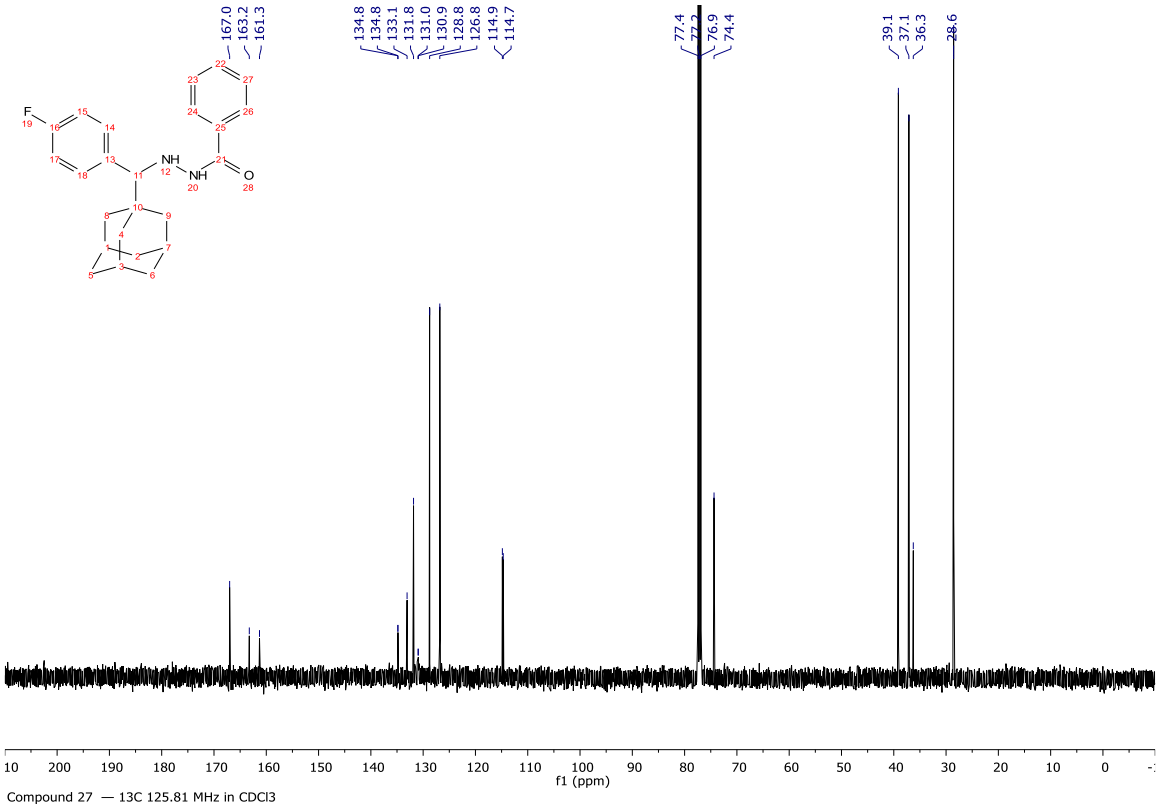


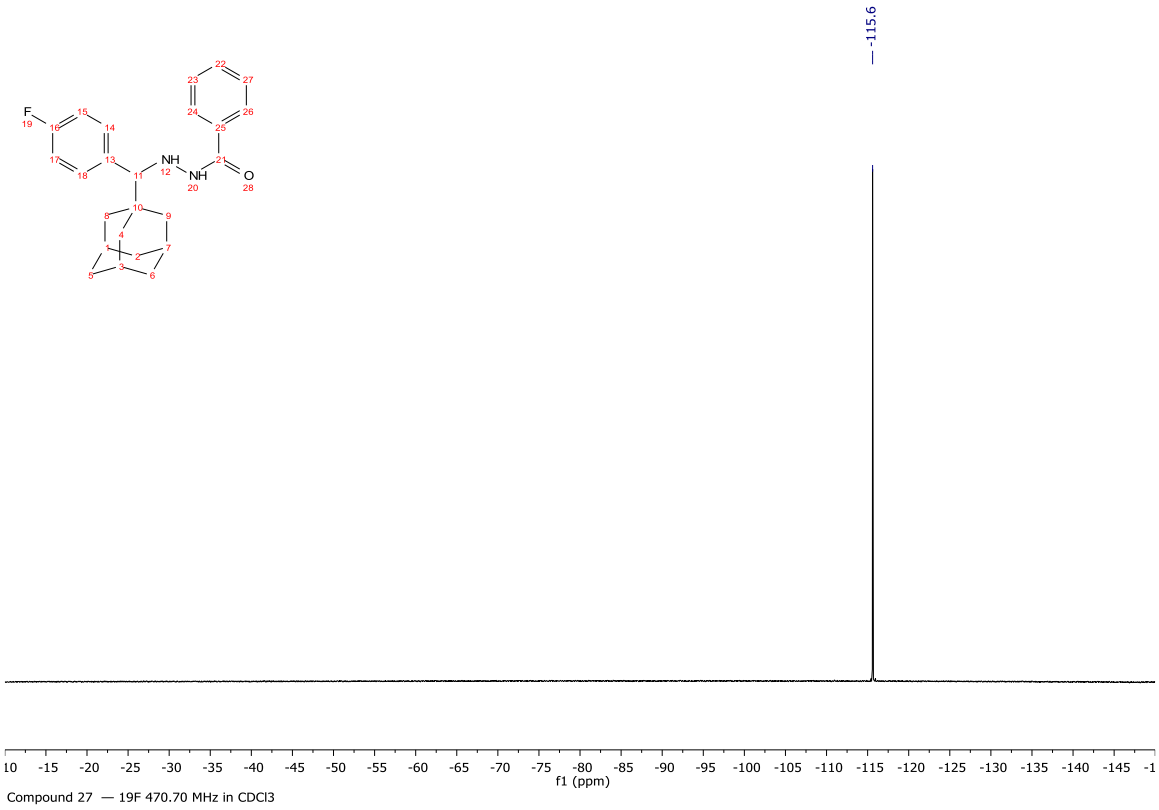


Compound 26 — 19F 470.72 MHz in CDCl3

N'-(adamantan-1-yl(4-fluorophenyl)methyl)benzohydrazide (**27**):

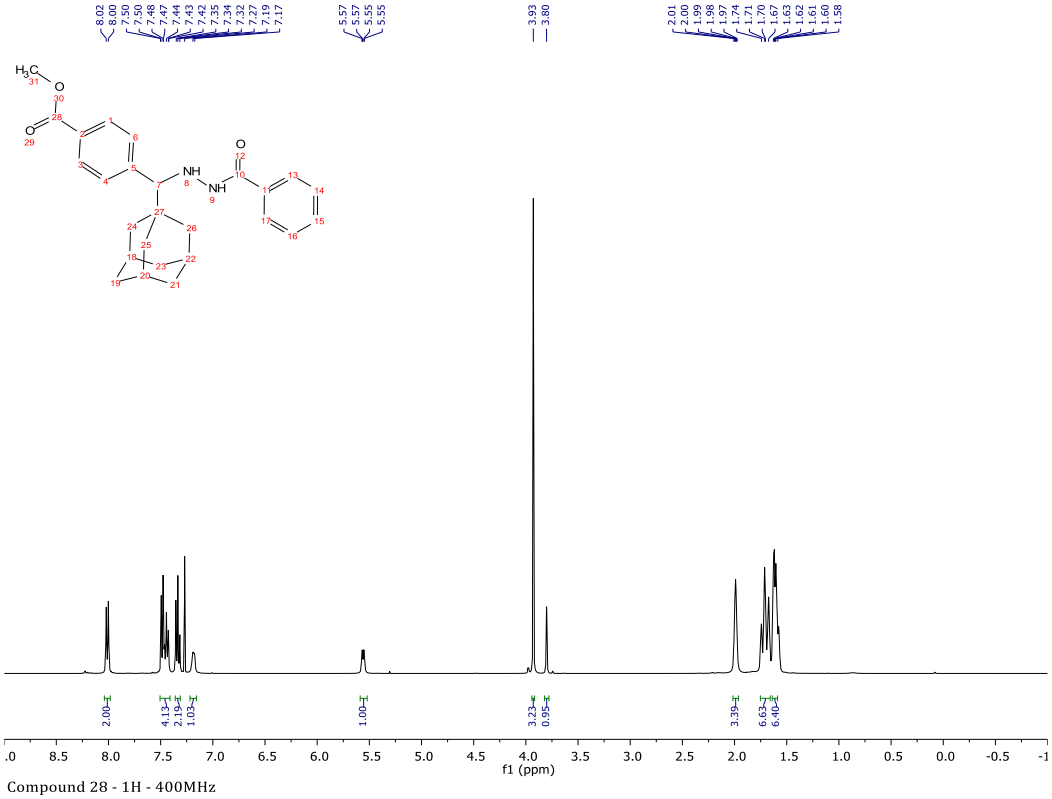




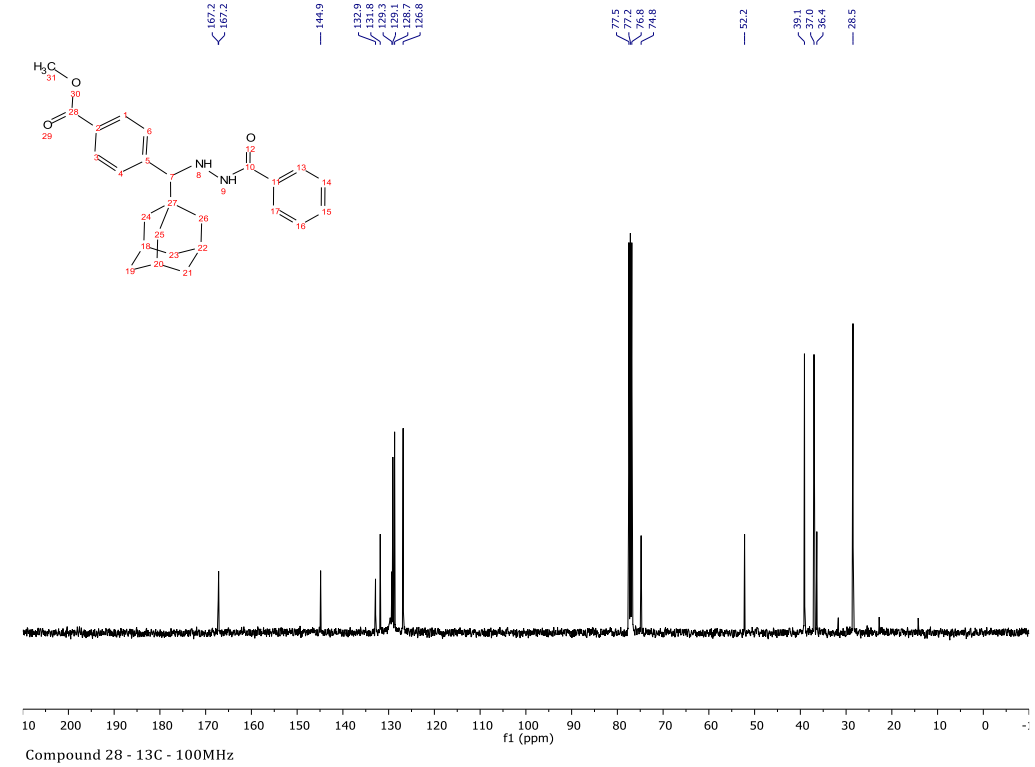


Compound 27 — 19F 470.70 MHz in CDCl3

methyl 4-adamantan-1-yl((2-benzoylhydrazinyl)methyl)benzoate (**28**):

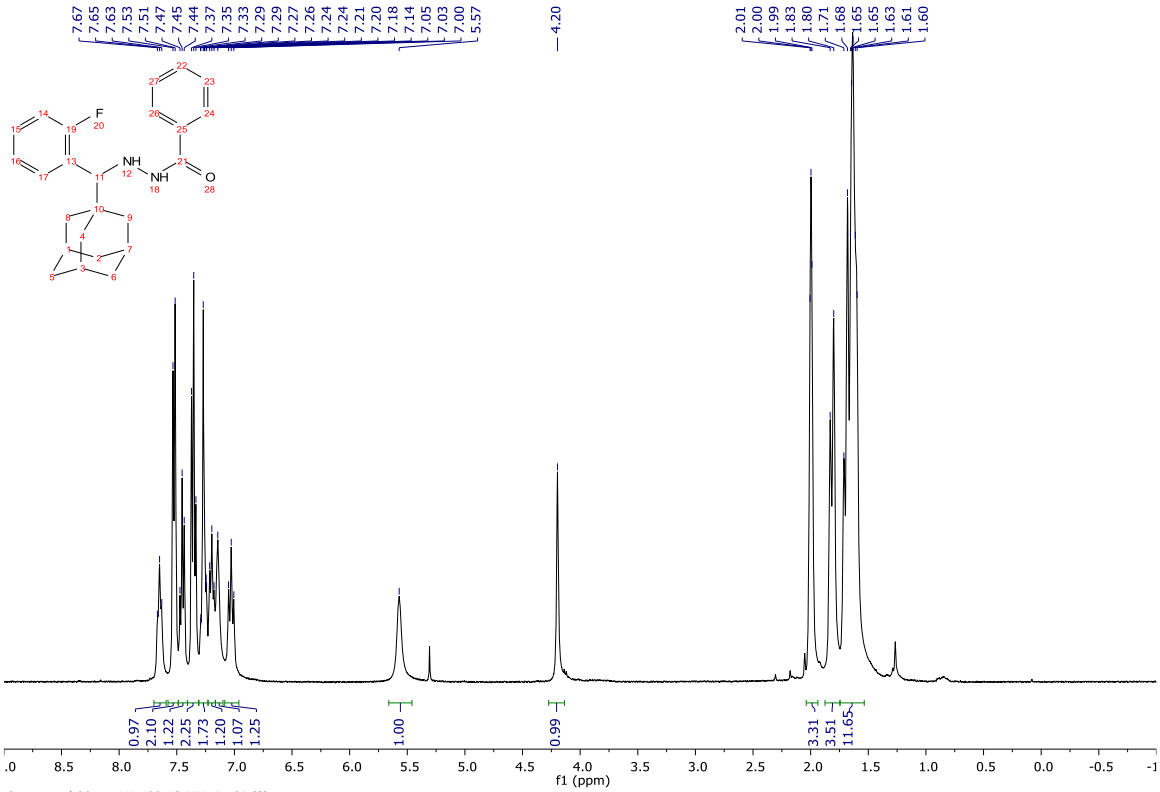


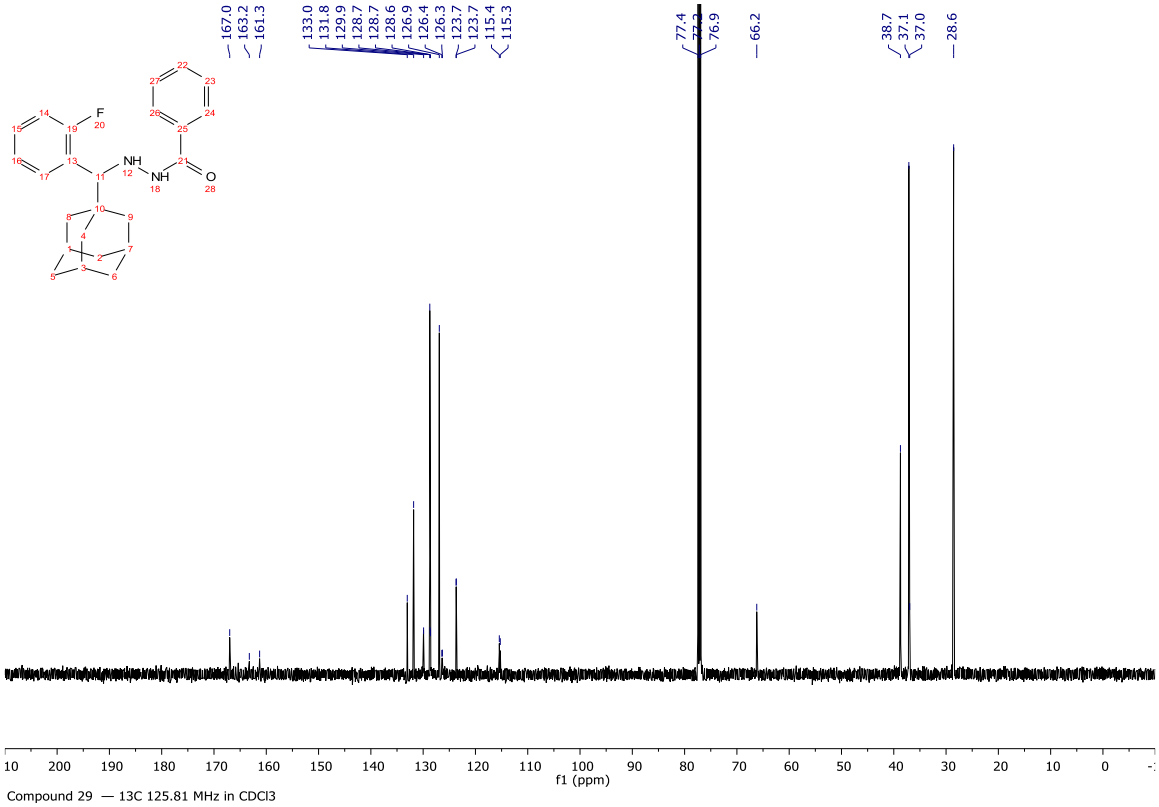
Compound 28 - 1H - 400MHz

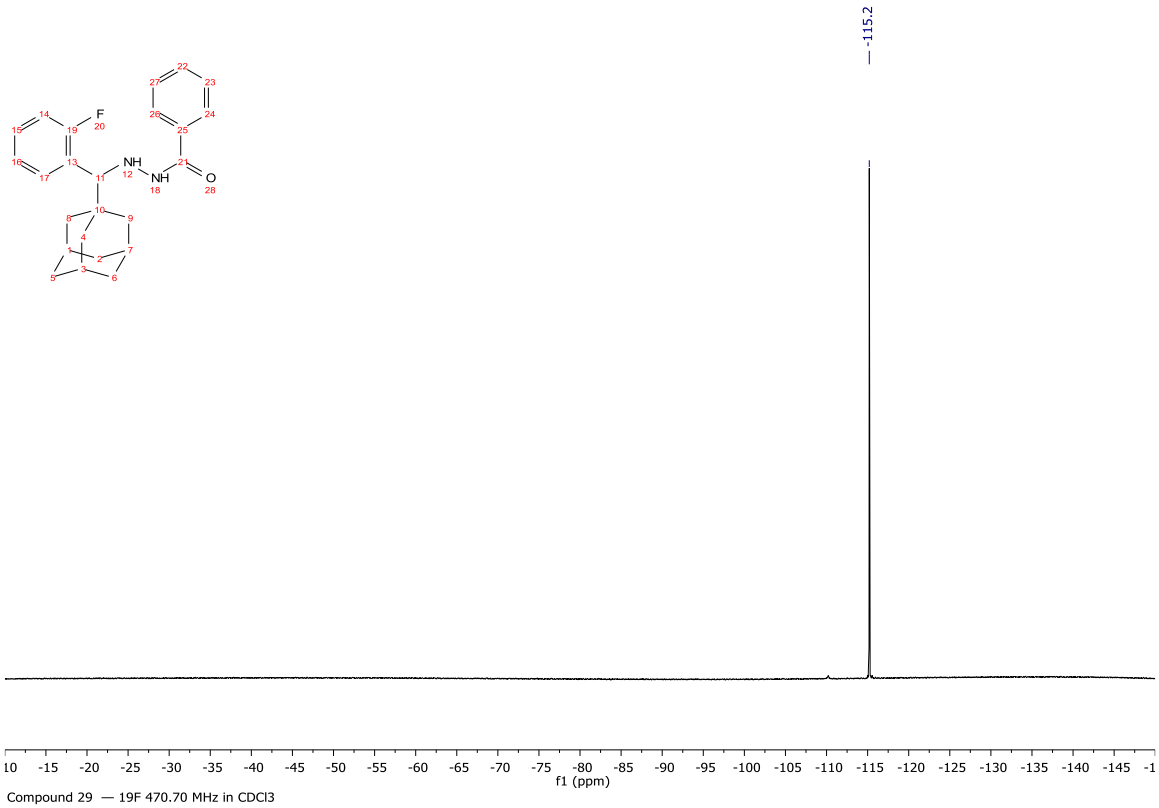


Compound 28 - 13C - 100MHz

N'-(adamantan-1-yl(2-fluorophenyl)methyl)benzohydrazide (**29**):

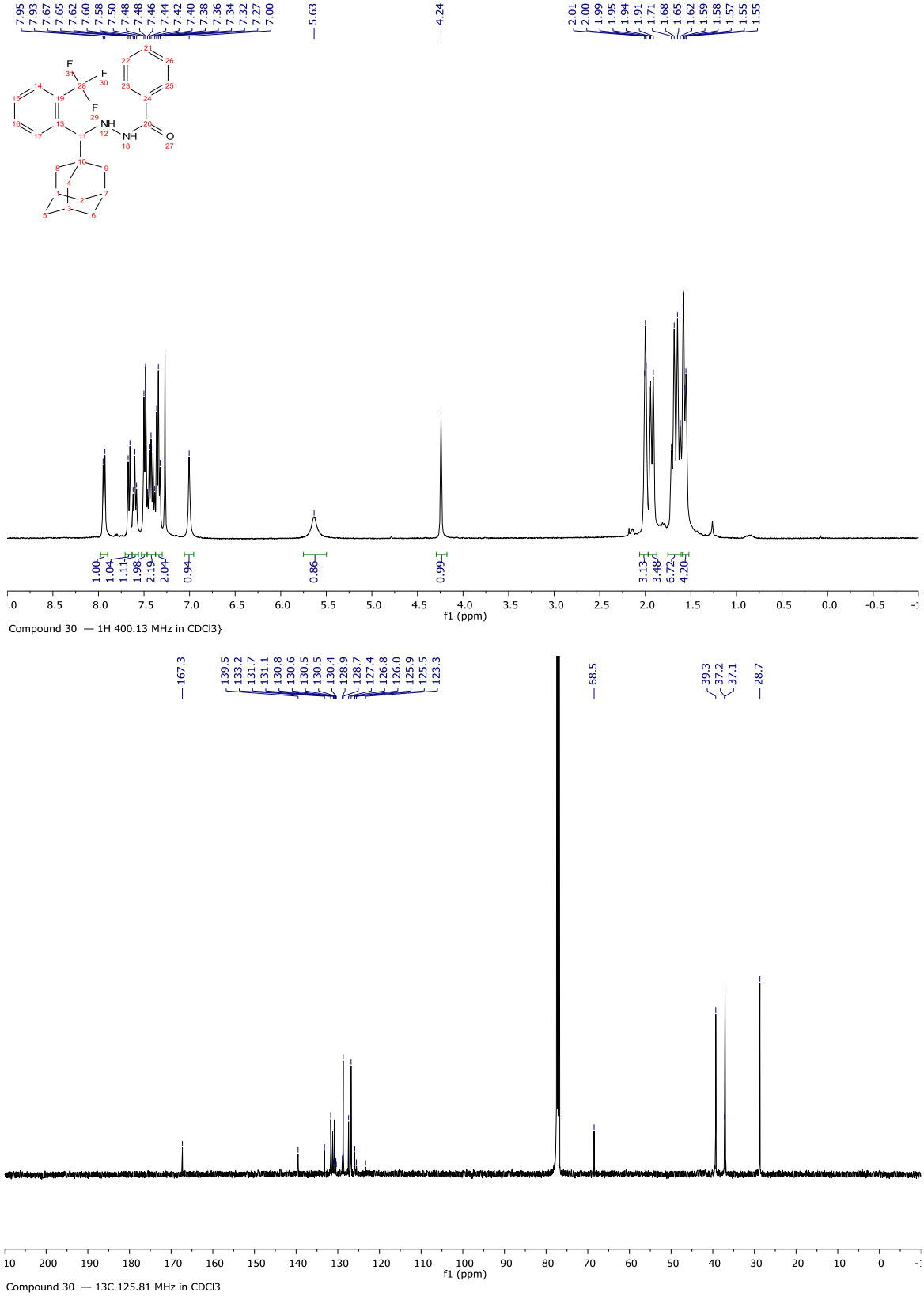


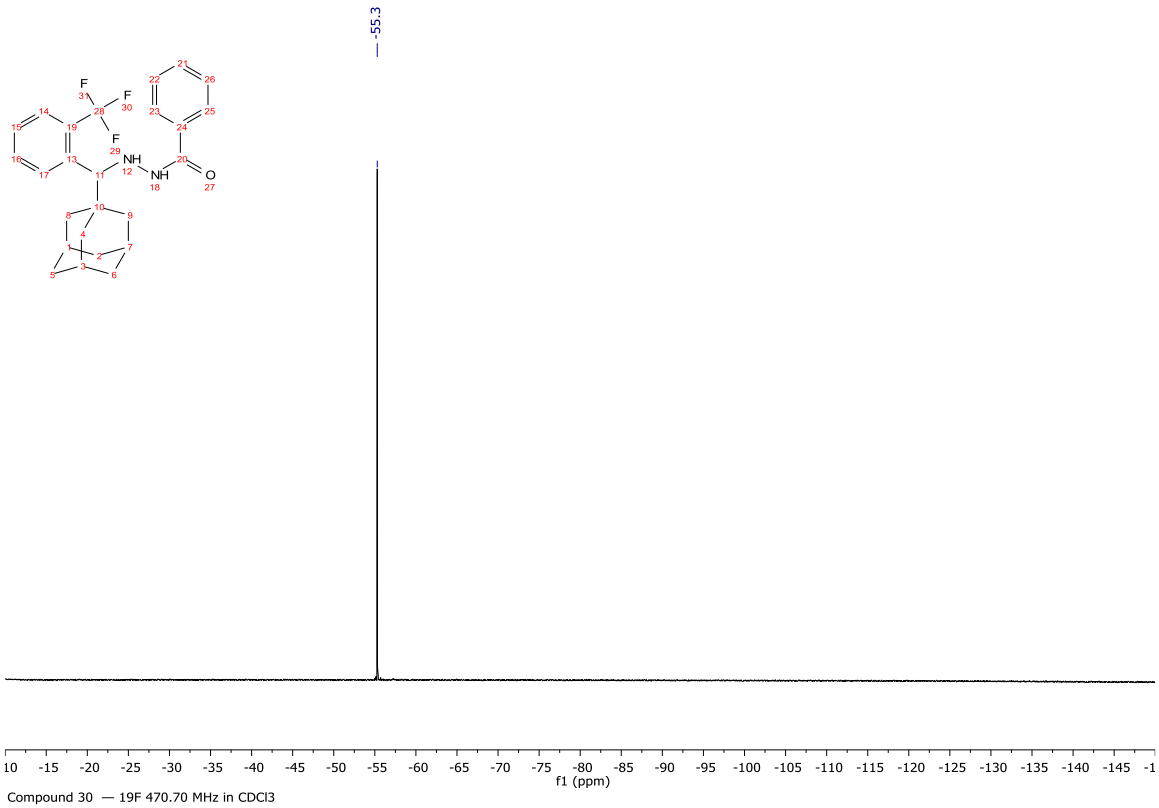




Compound 29 — 19F 470.70 MHz in CDCl3

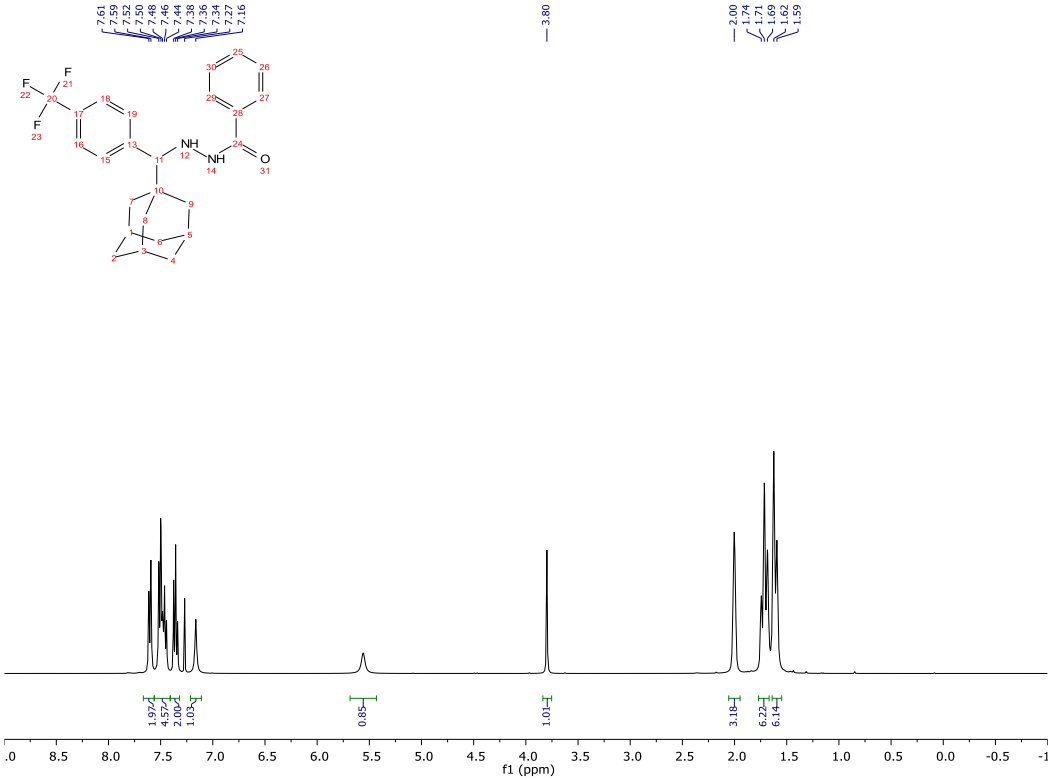
N'-(adamantan-1-yl(2-(trifluoromethyl)phenyl)methyl)benzohydrazide (**30**):



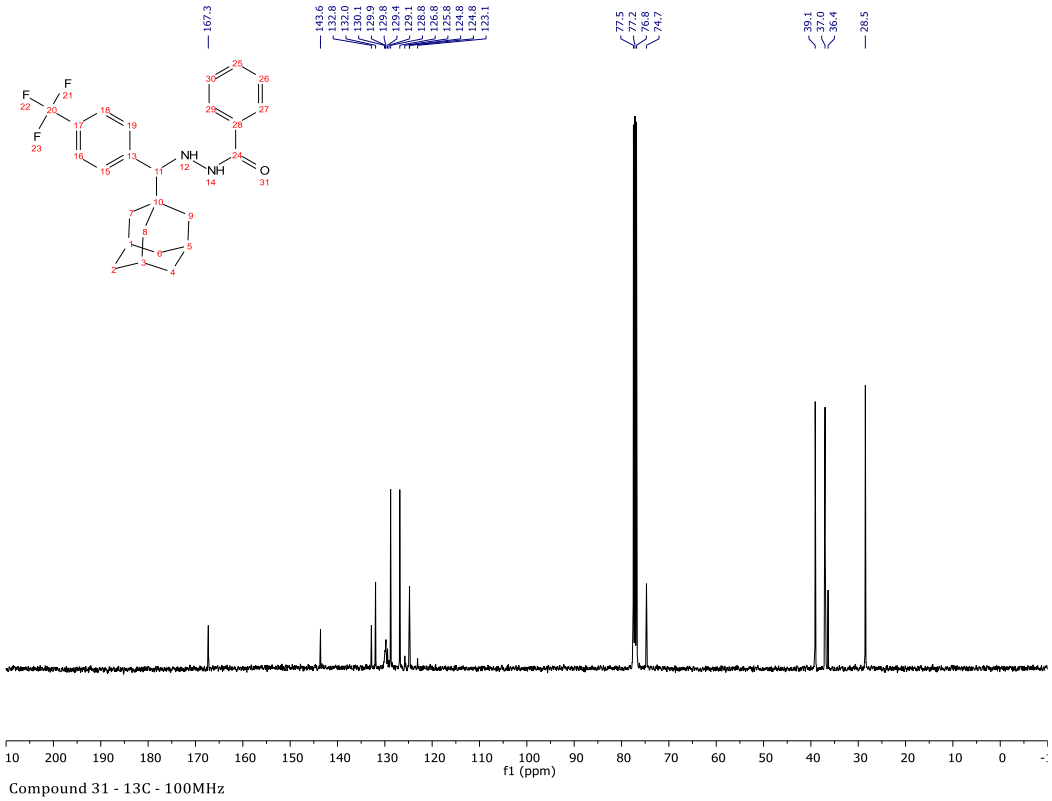


Compound 30 — 19F 470.70 MHz in CDCl3

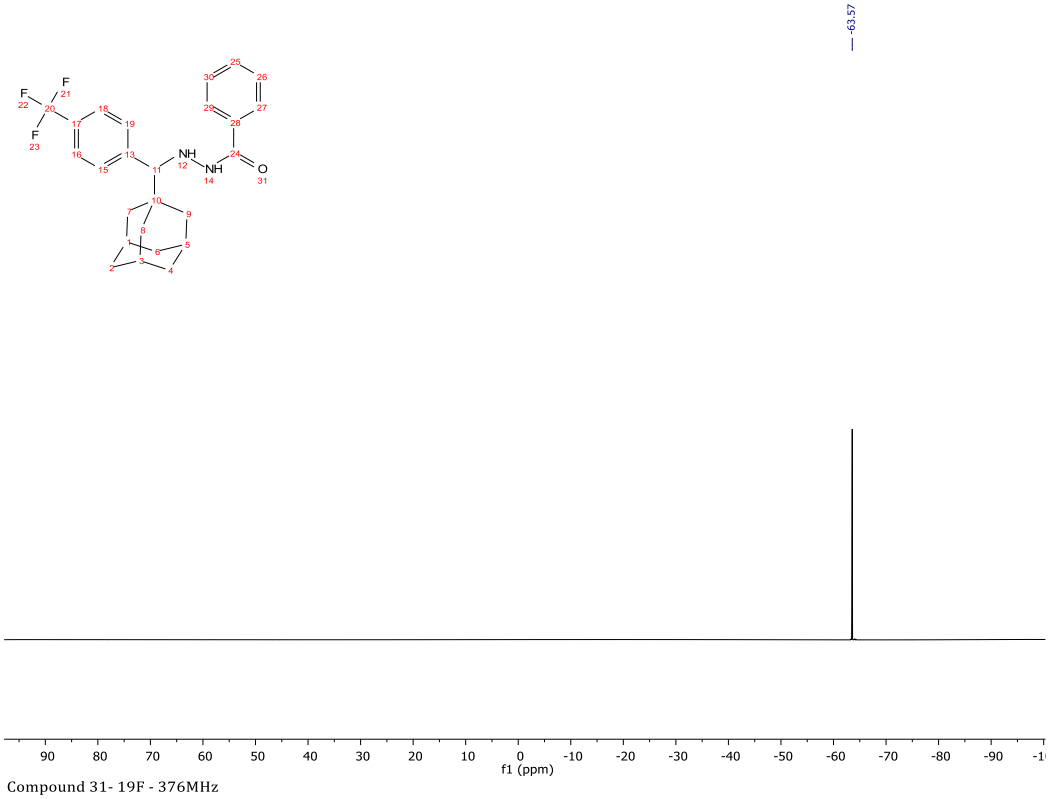
N'-adamantan-1-yl((4-(trifluoromethyl)phenyl)methyl)benzohydrazide (**31**):



Compound 31- 1H - 400MHz

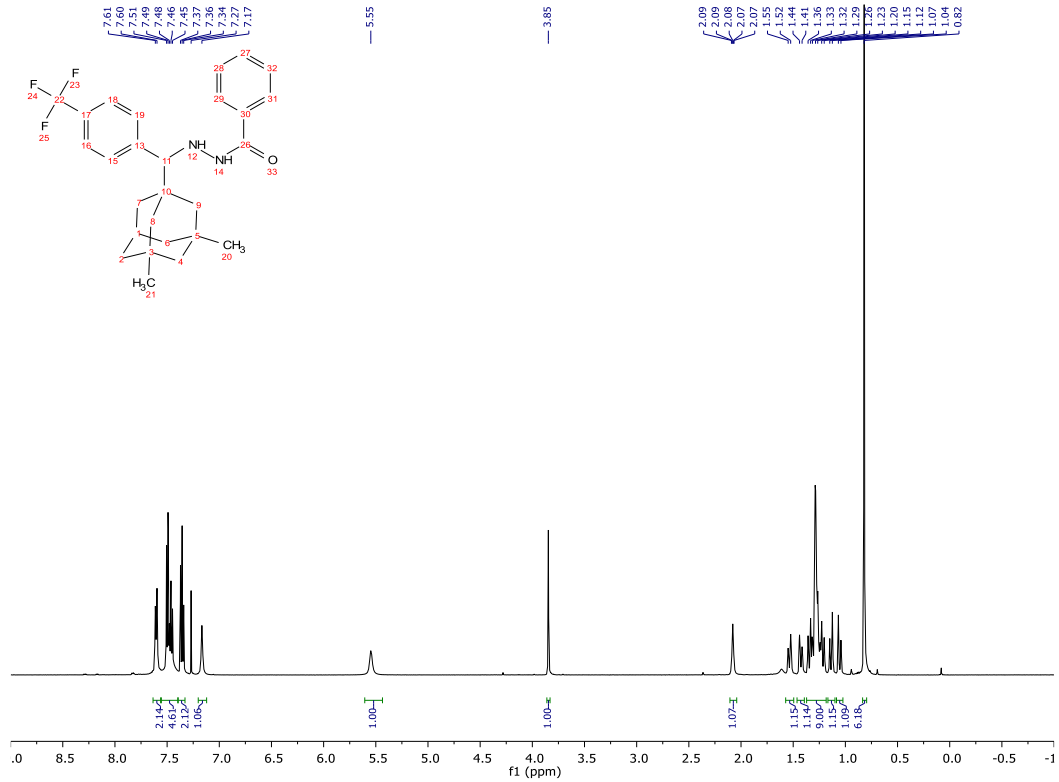


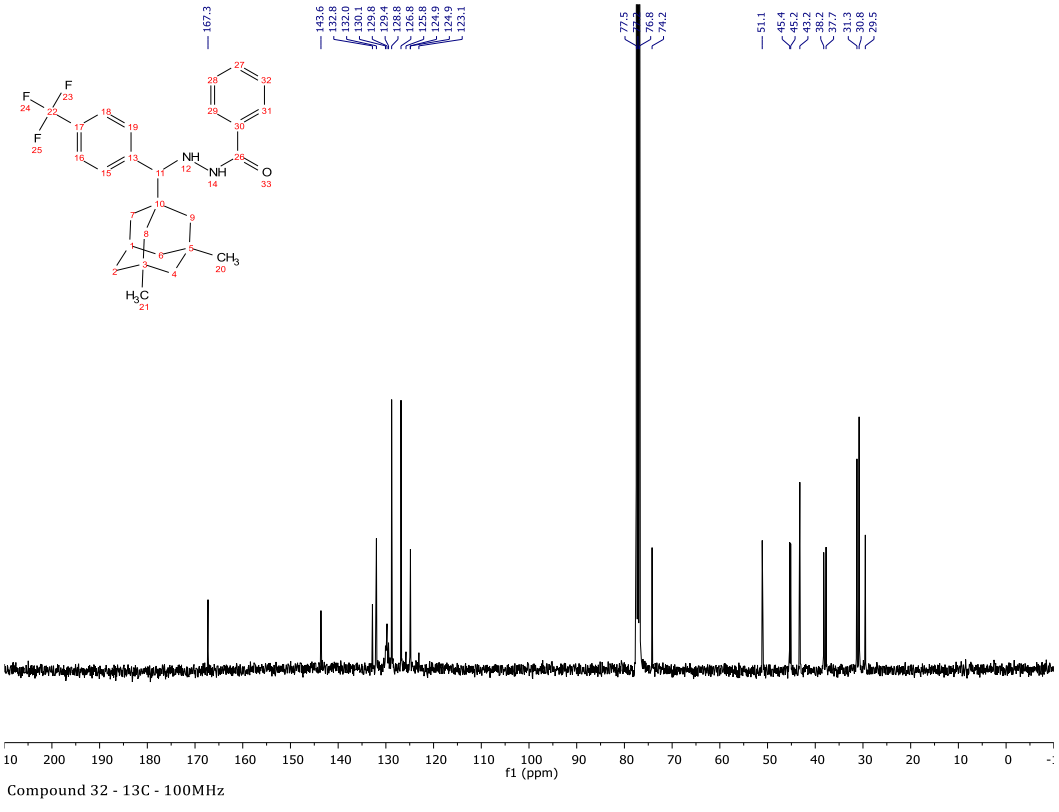
Compound 31 - 13C - 100MHz

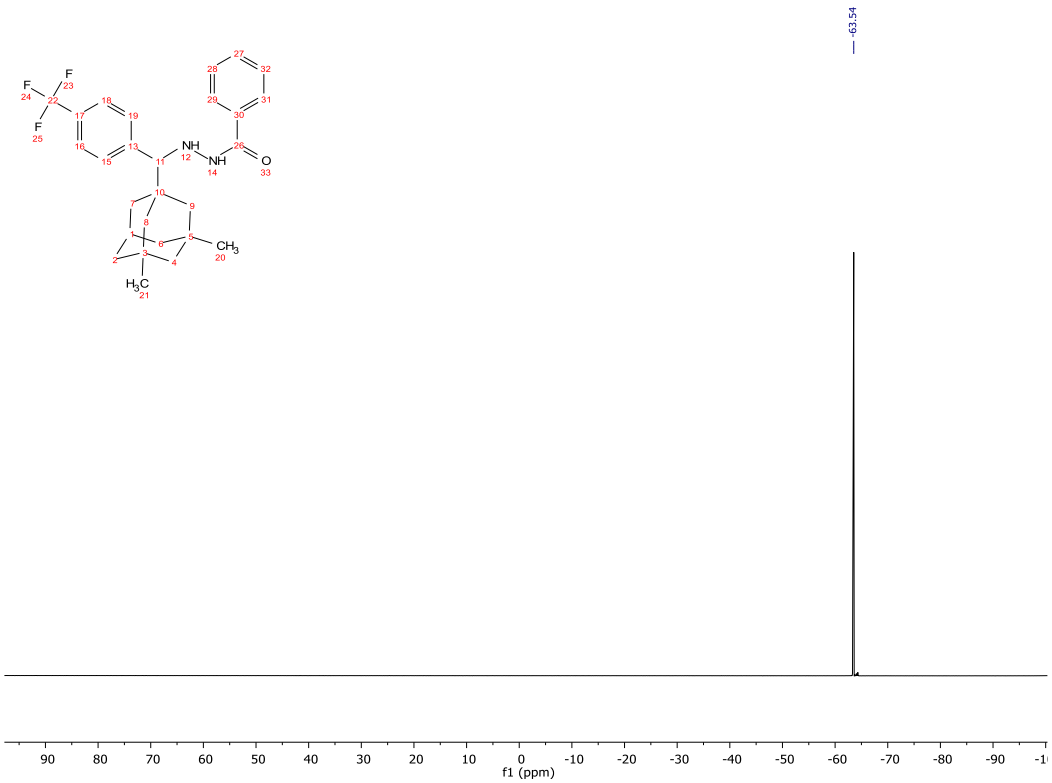


Compound 31- 19F - 376MHz

N'-(3,5-dimethyladamantan-1-yl)((4-(trifluoromethyl)phenyl))methyl)benzohydrazide (**32**):

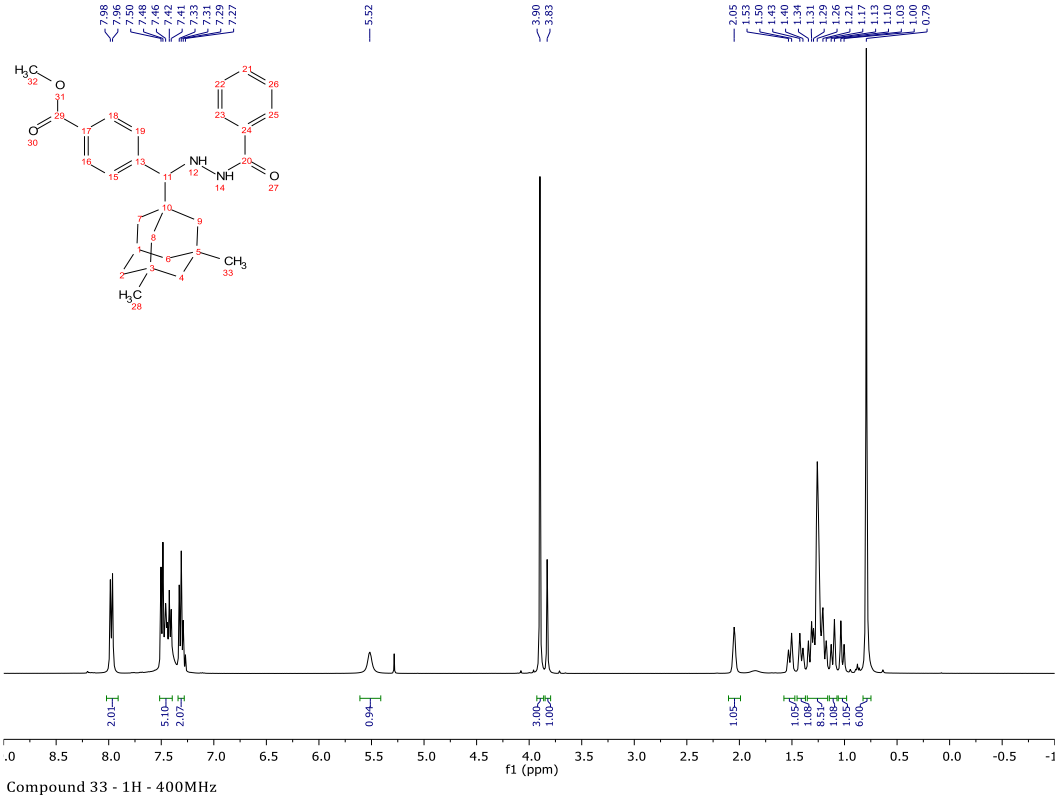




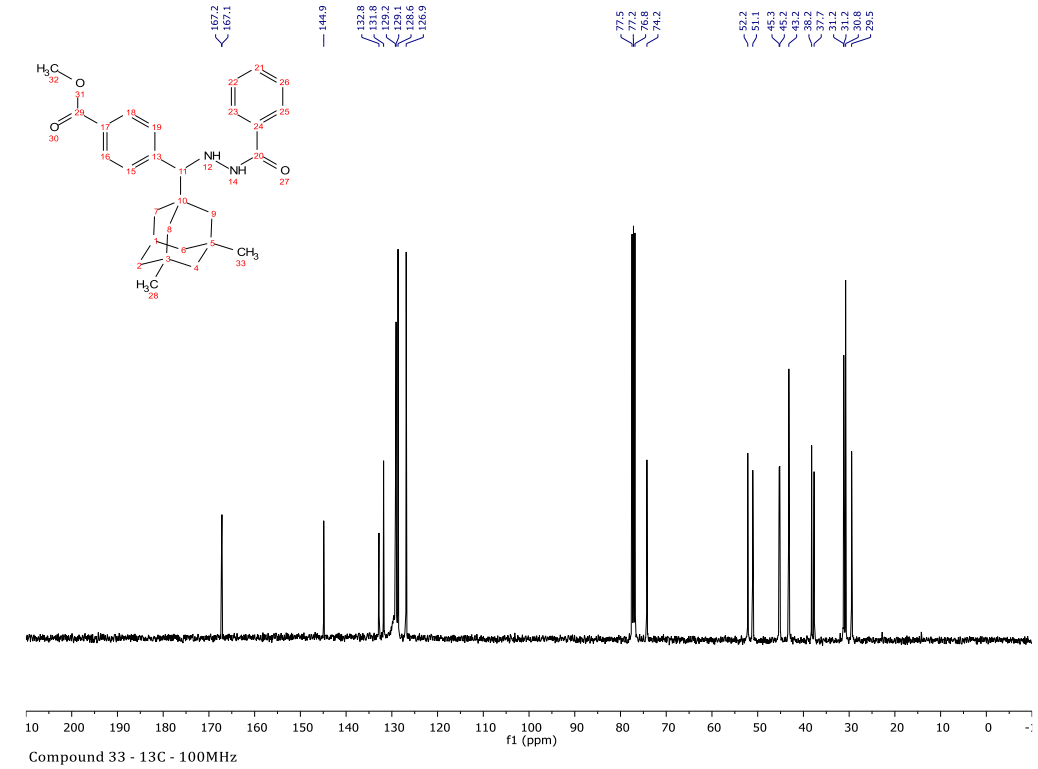


Cpompound 32 - 19F - 376 MHz

methyl 4-((3,5-dimethyladamantan-1-yl)2-benzoylhydrazinyl)methyl)benzoate (**33**):

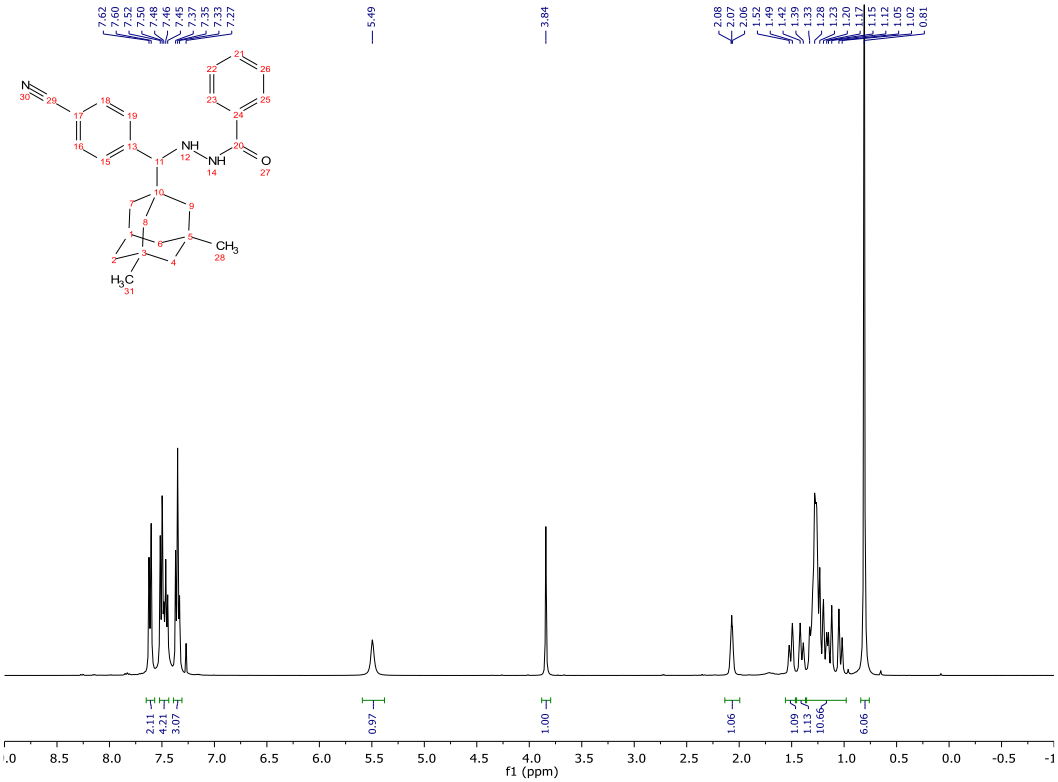


Compound 33 - 1H - 400MHz

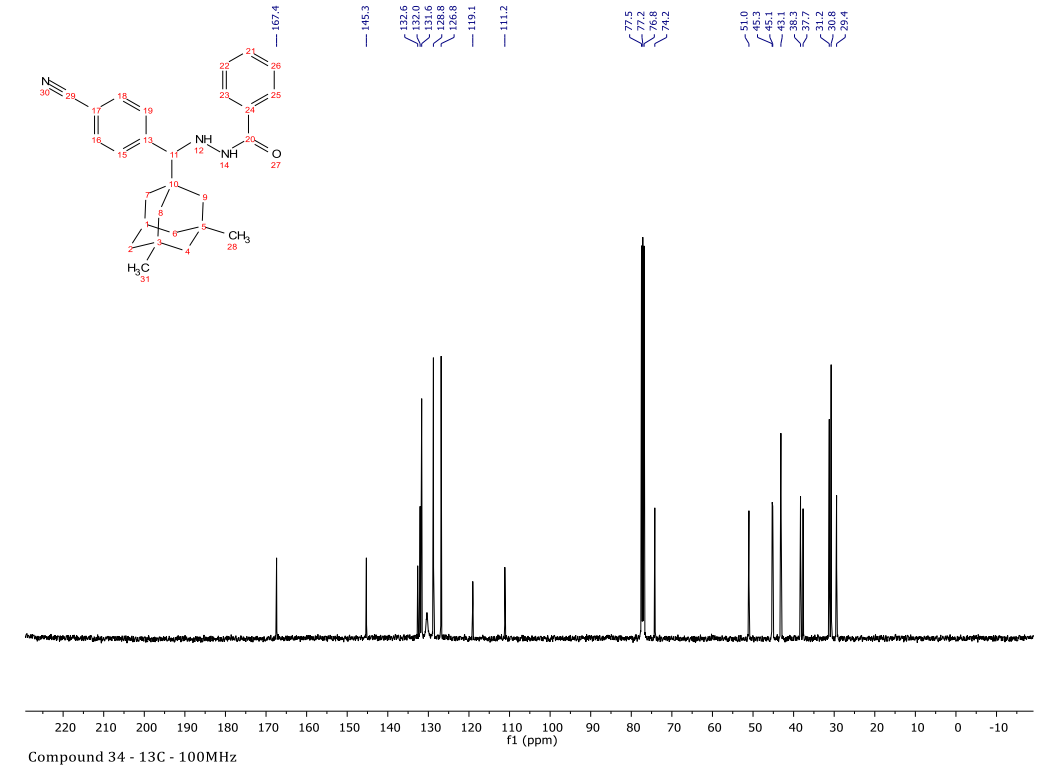


Compound 33 - 13C - 100MHz

N'-(3,5-dimethyladamantan-1-yl)((4-(cyanophenyl))methyl)benzohydrazide (**34**):

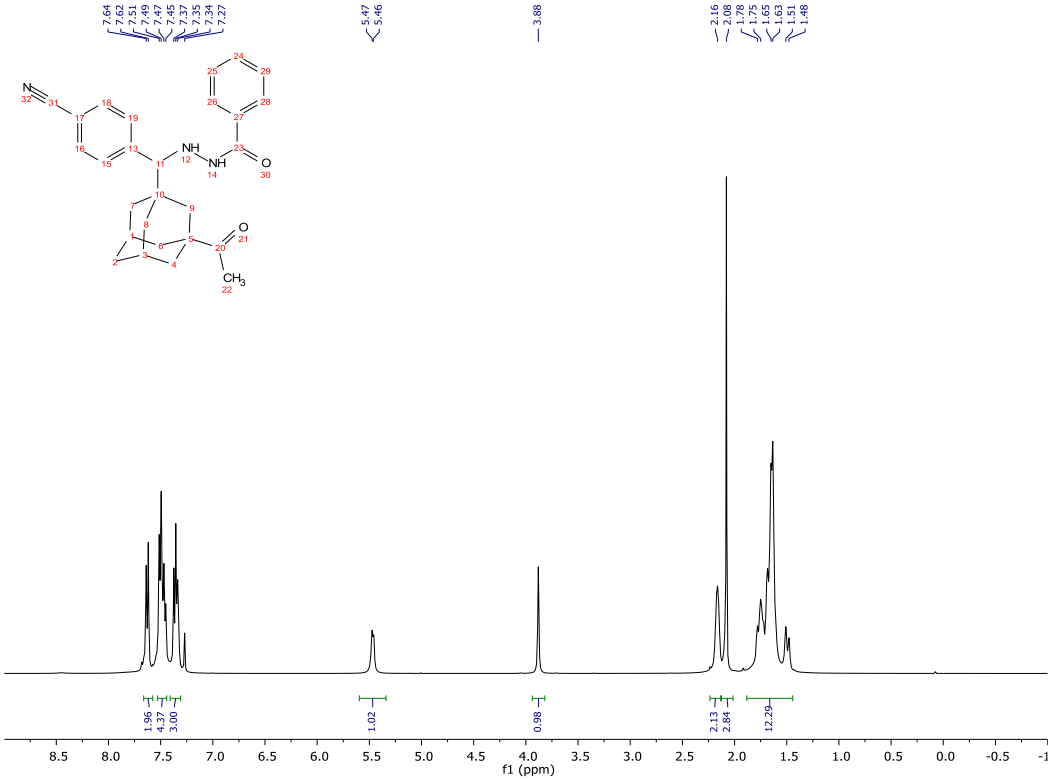


Compound 34 - 1H - 400MHz

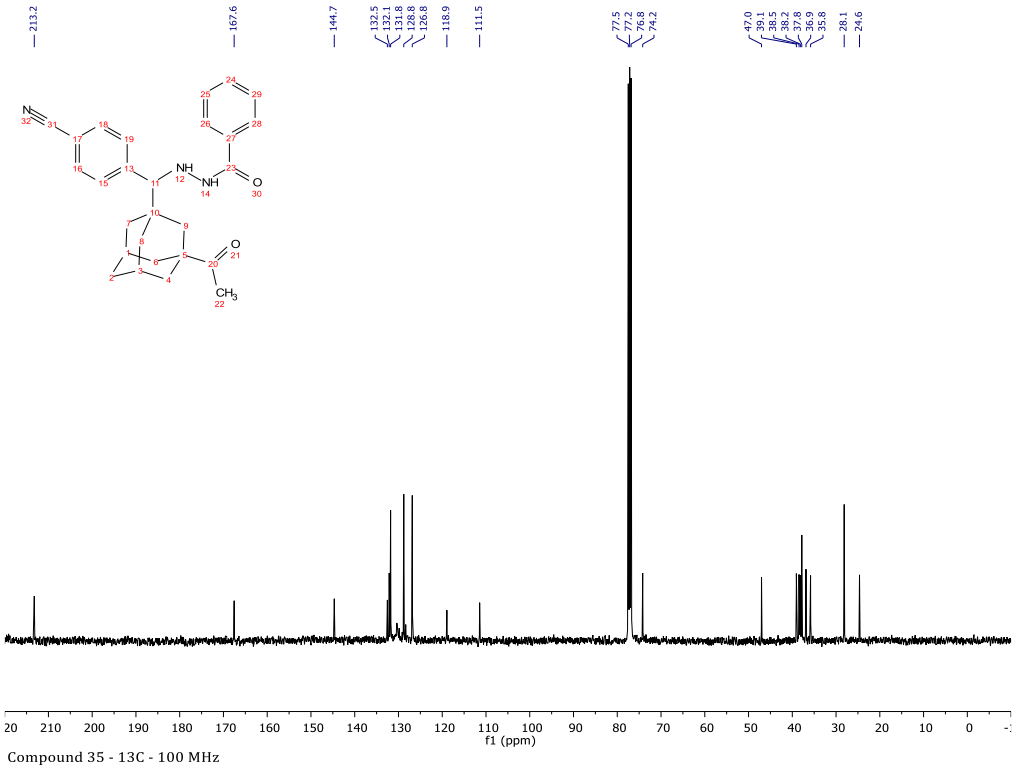


Compound 34 - 13C - 100MHz

N'-(3-acetyladamantan-1-yl)((4-(cyanophenyl))methyl)benzohydrazide (**35**):

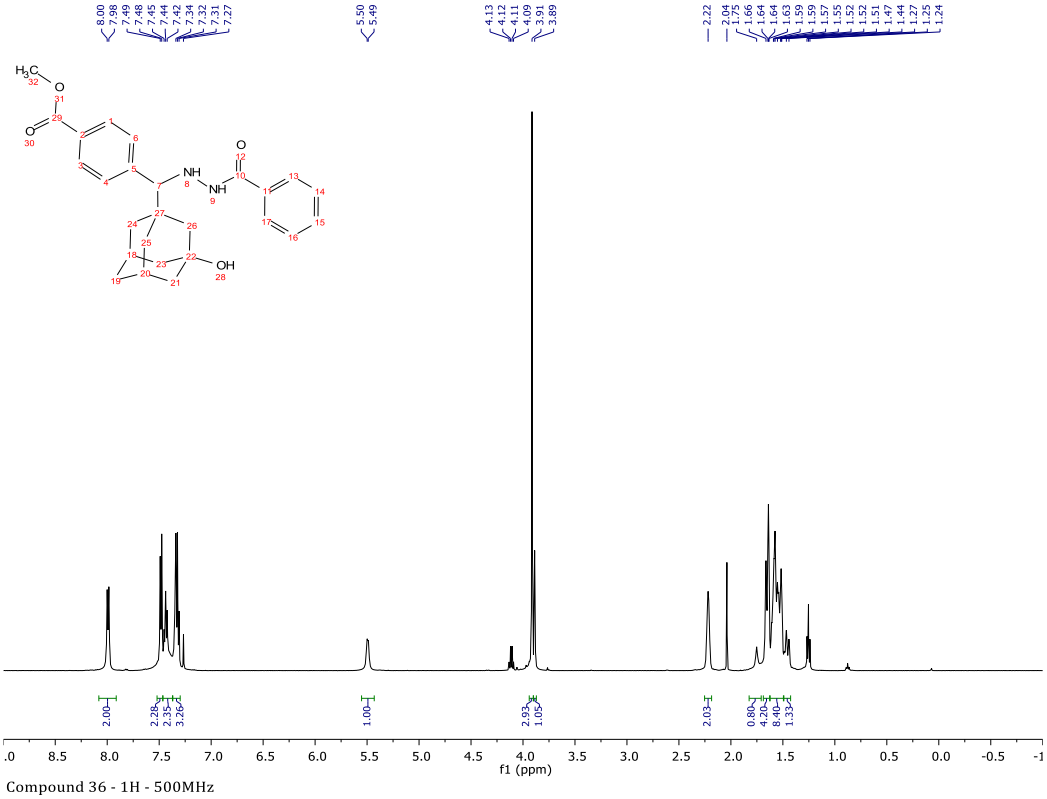


Compound 35 - 1H - 400 MHz

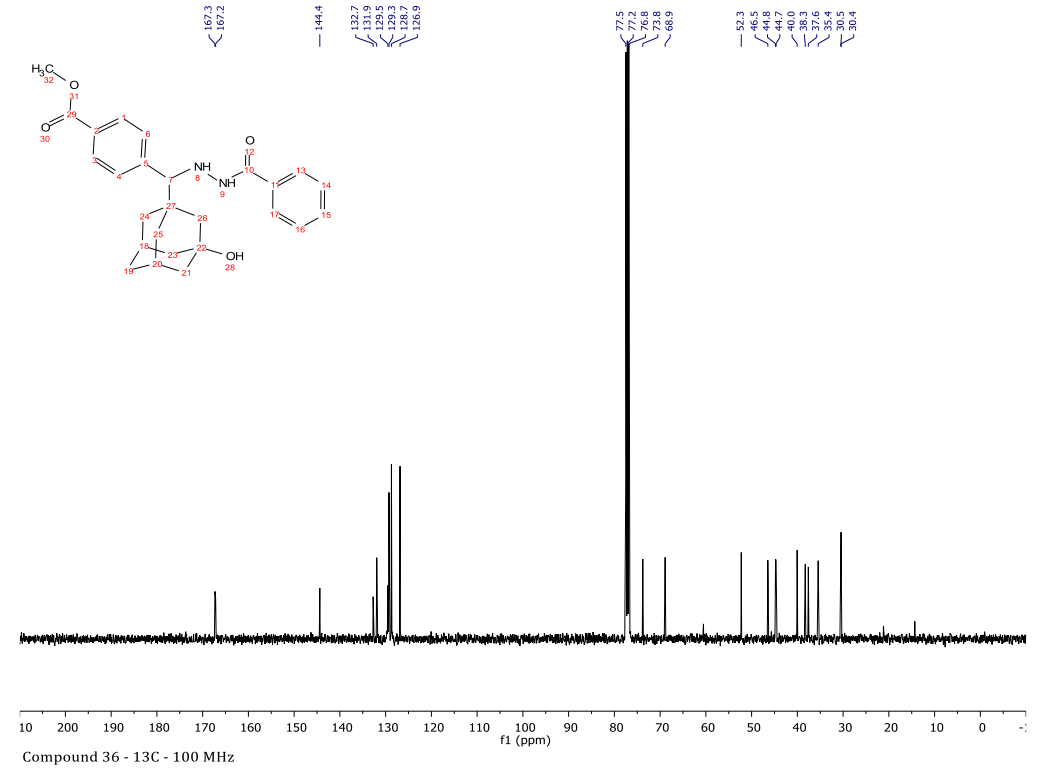


Compound 35 - 13C - 100 MHz

methyl 4-((3-hydroxyadamantan-1-yl)2-benzoylhydrazinyl)methyl)benzoate (**36**):

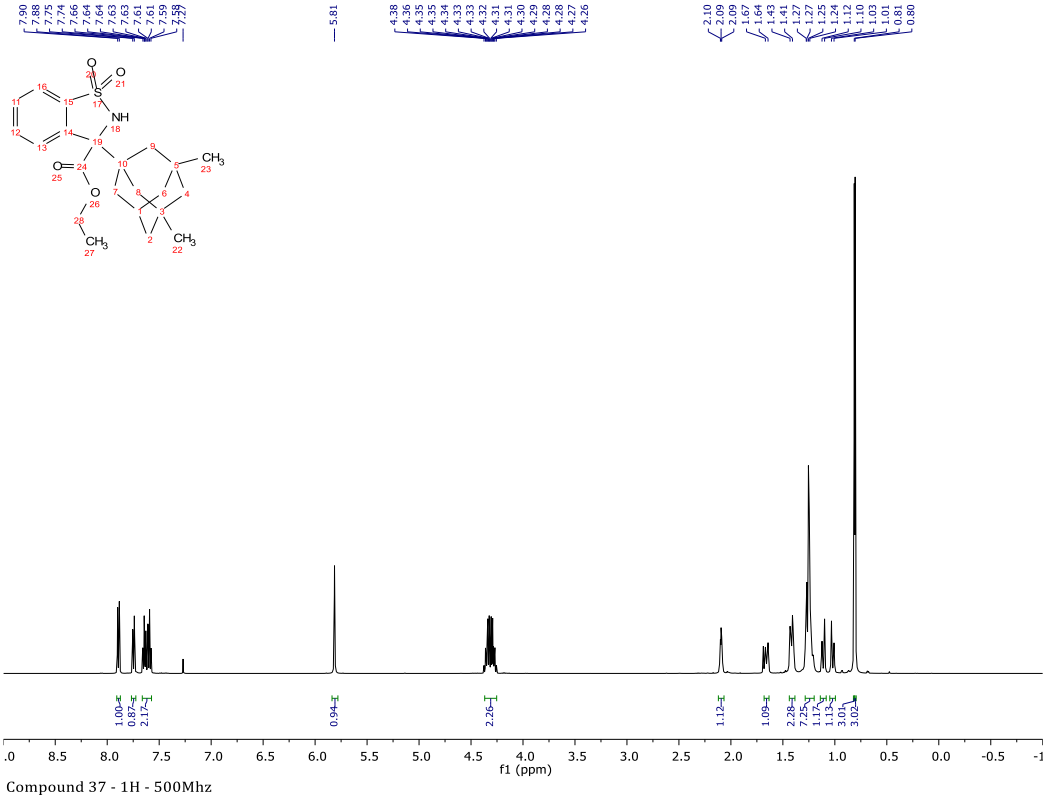


Compound 36 - 1H - 500MHz

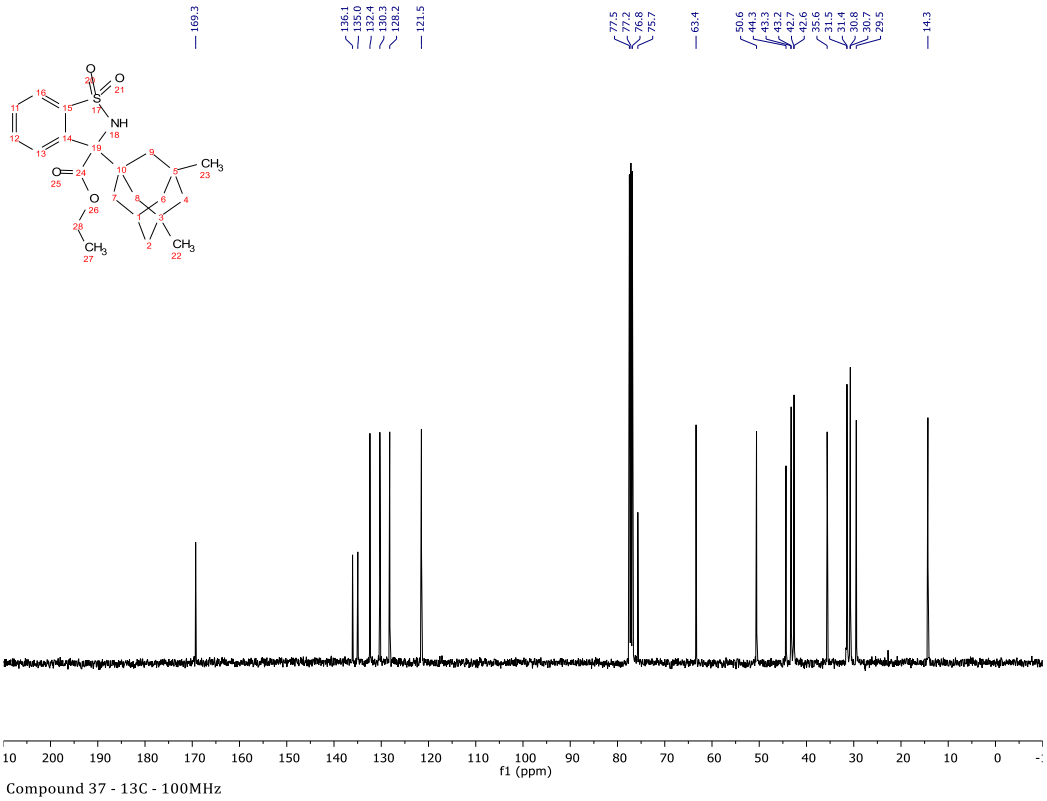


Compound 36 - 13C - 100 MHz

ethyl 3-(3,5-dimethyladamantyl)- 2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**37**):

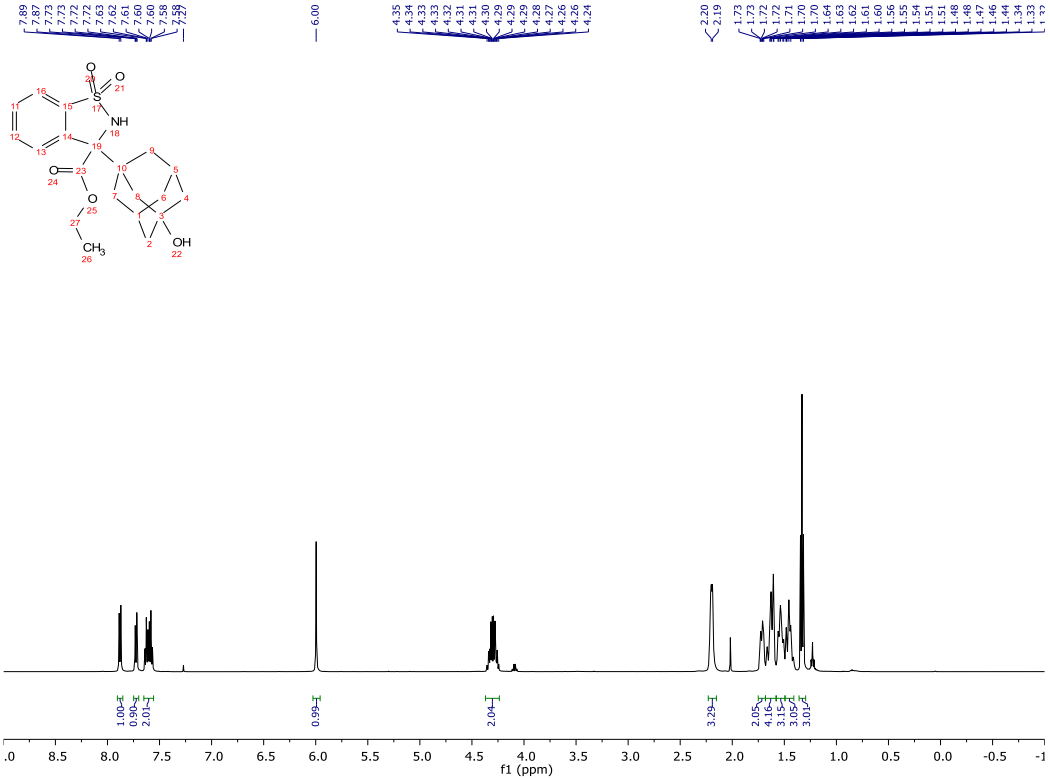


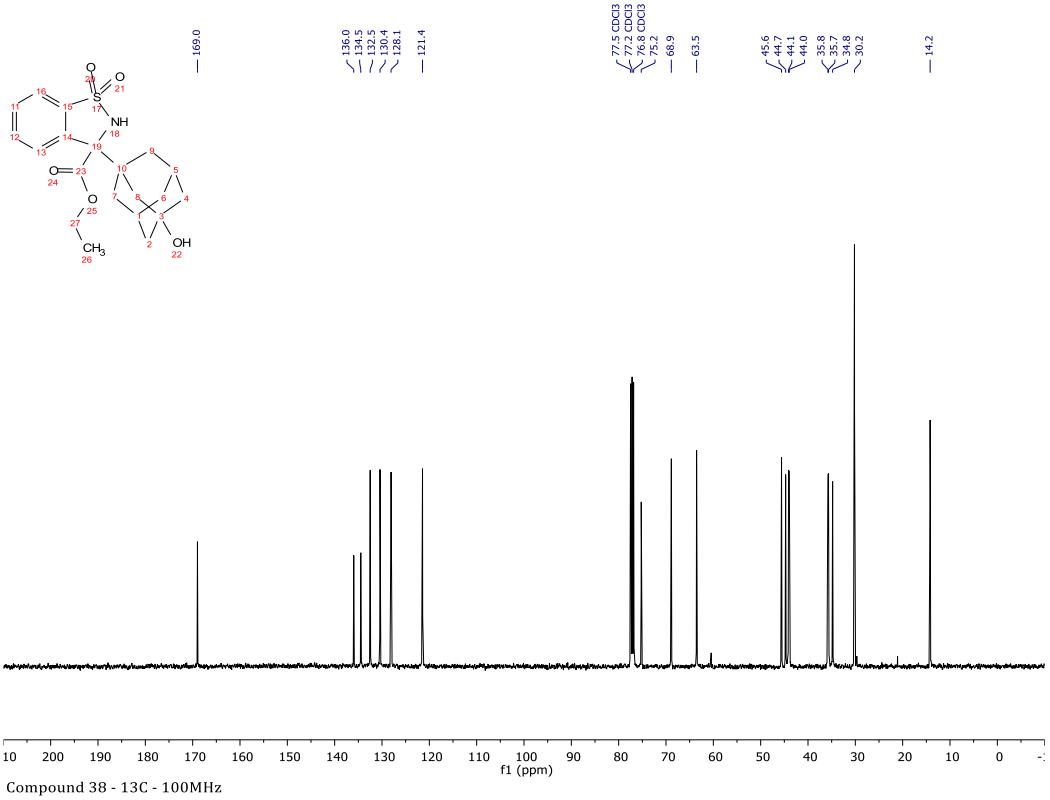
Compound 37 - 1H - 500Mhz



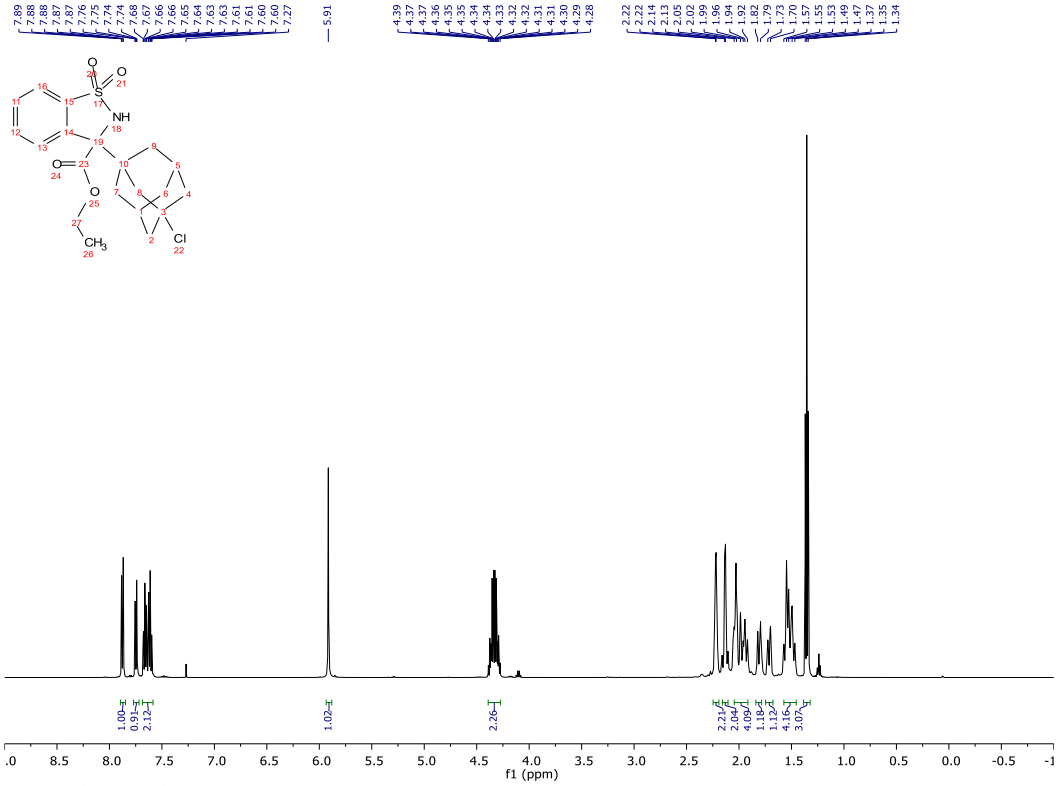
Compound 37 - 13C - 100MHz

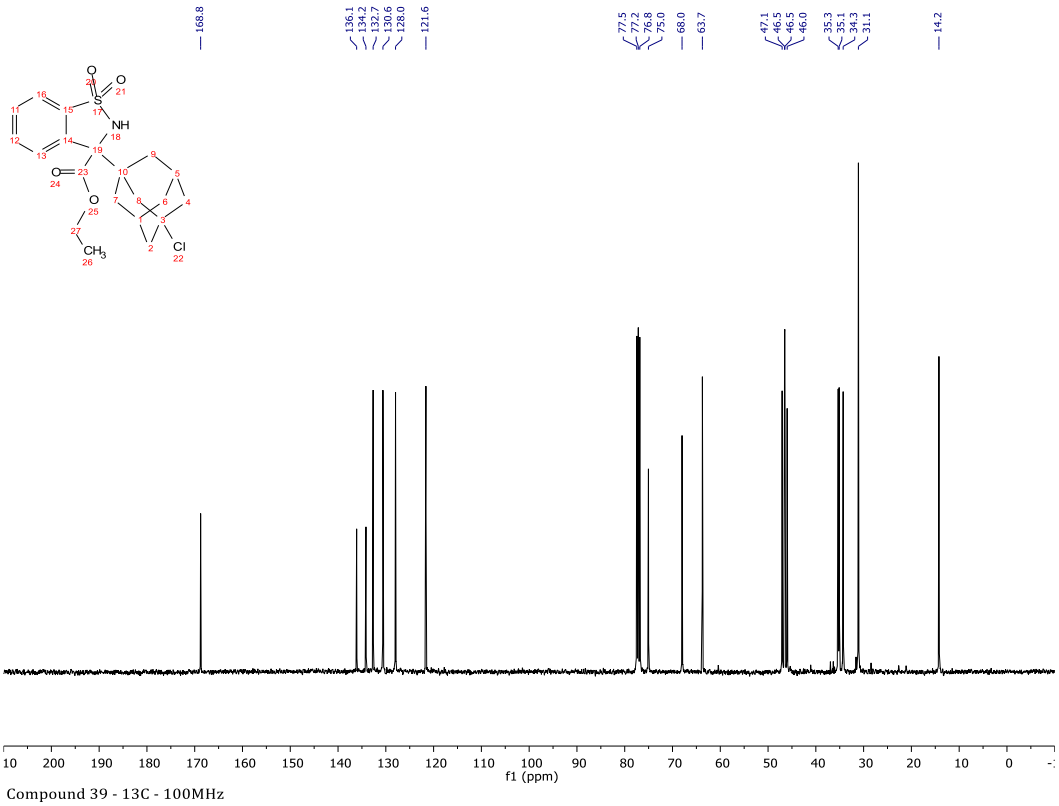
ethyl 3-(3-hydroxyadamantyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**38**):



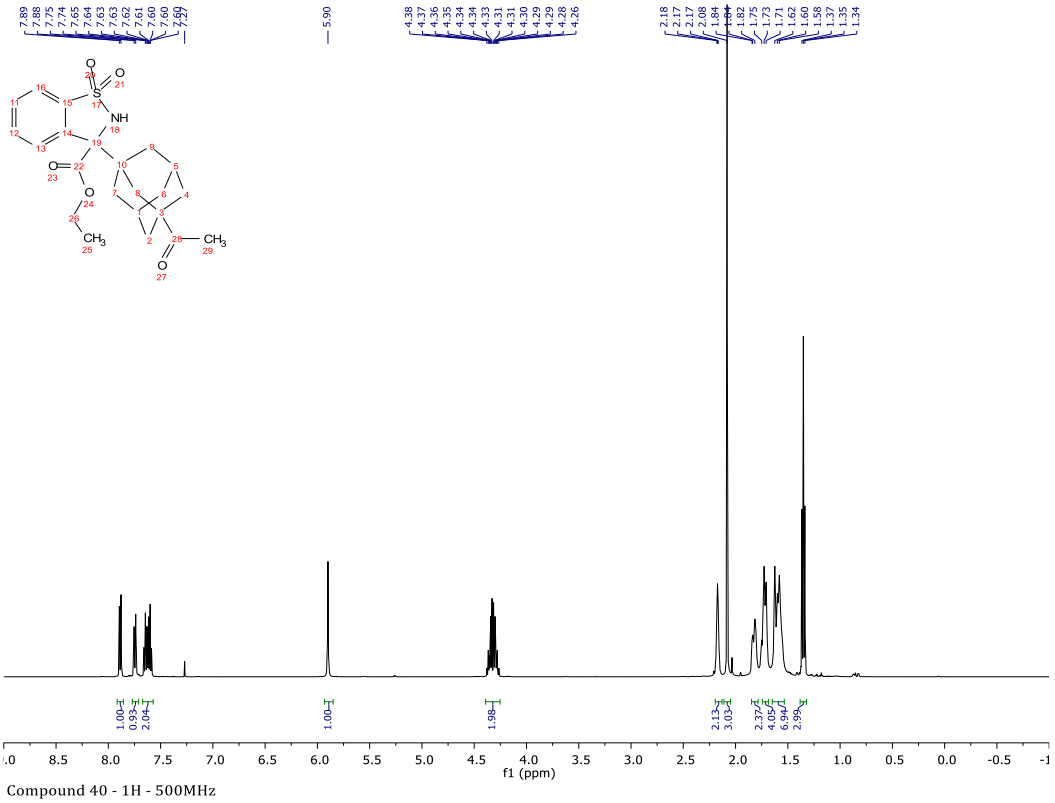


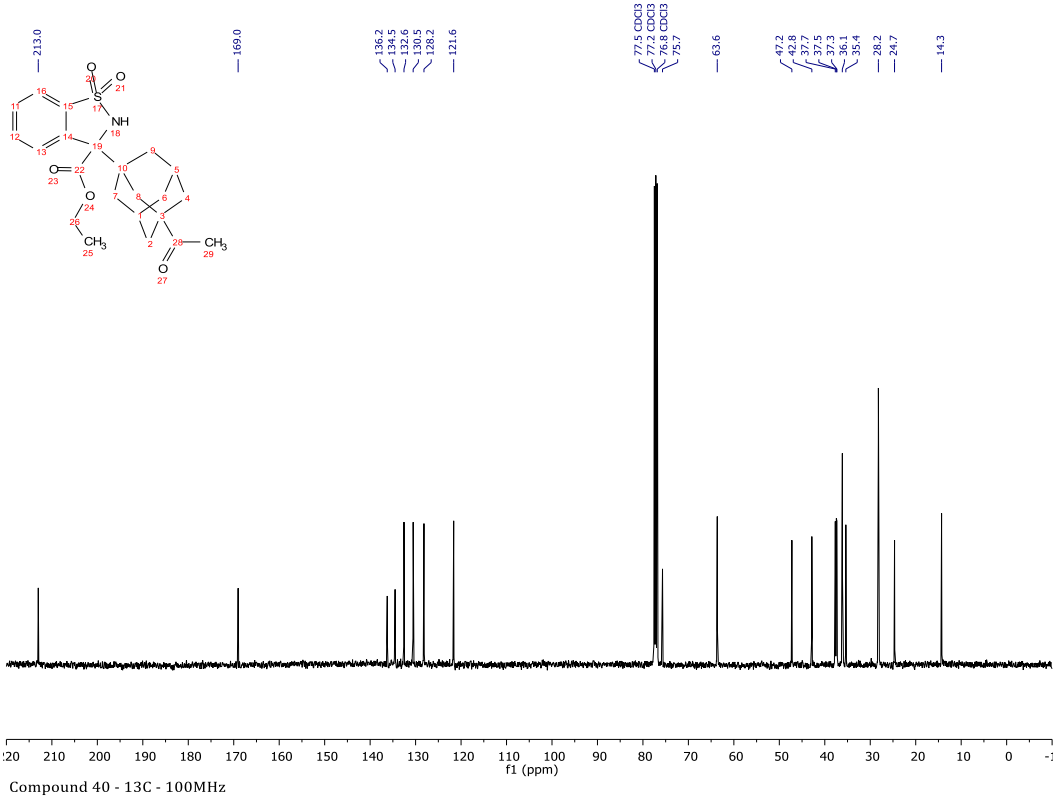
ethyl 3-(3-chlorodamantan-1-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**39**):



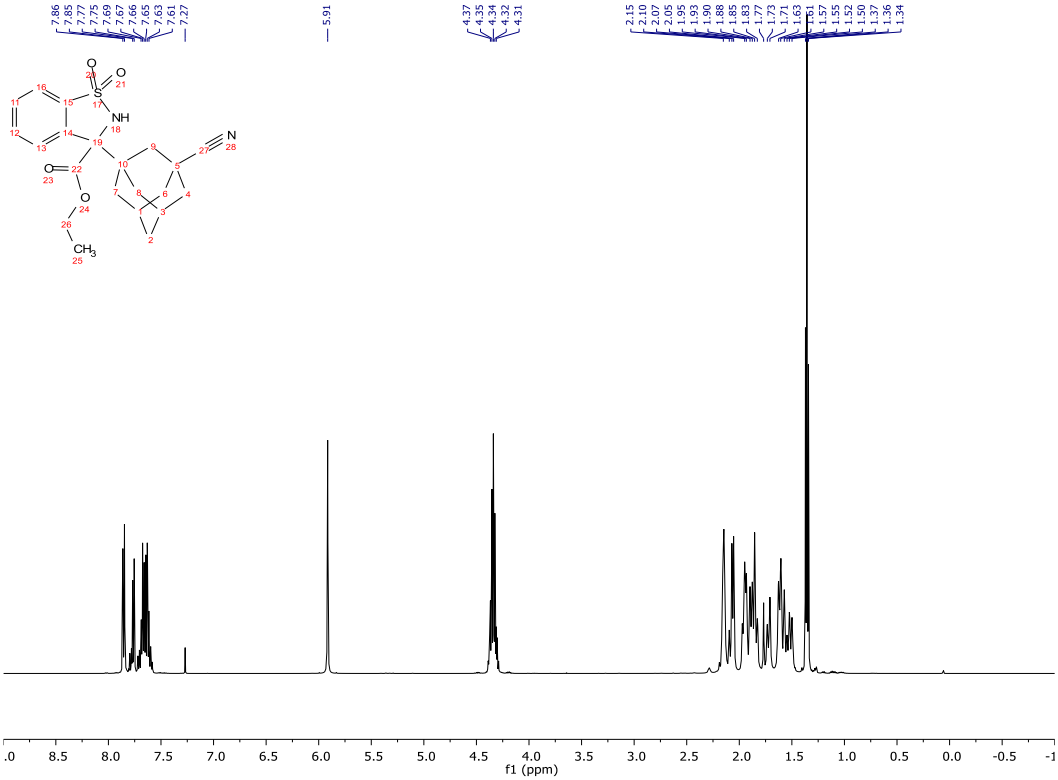


ethyl 3-(3-acetyladamantyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**40**):

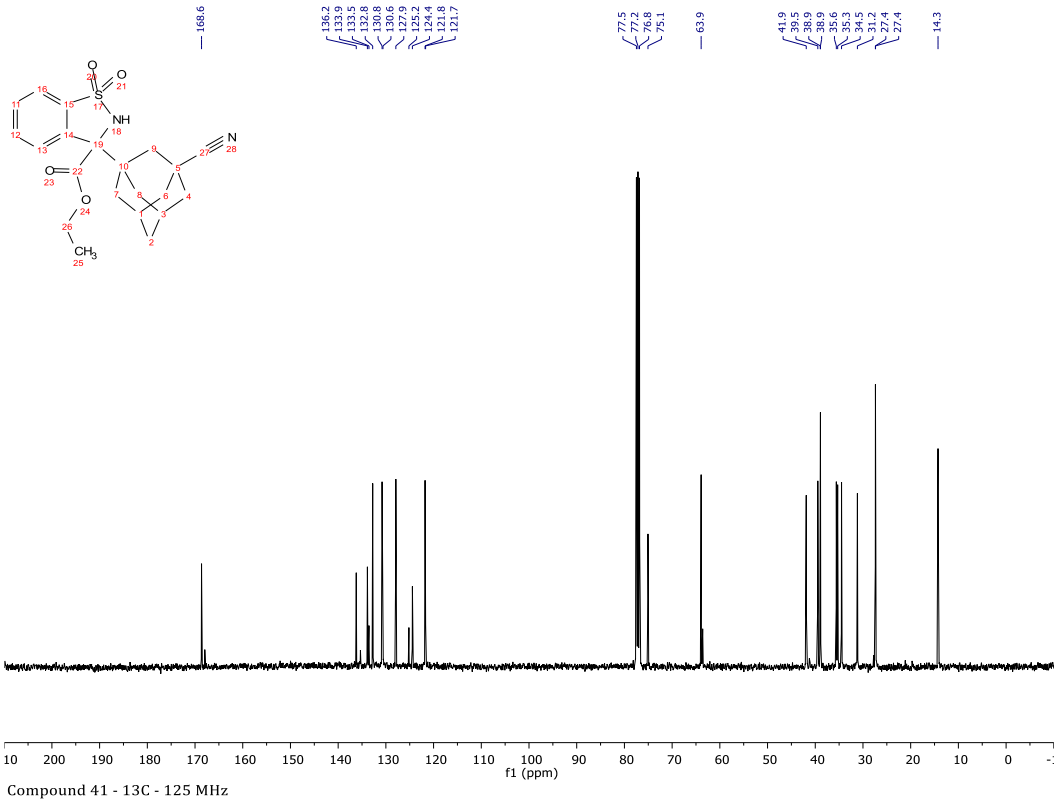




ethyl 3-(3-cyanodamantan-1-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**41**):

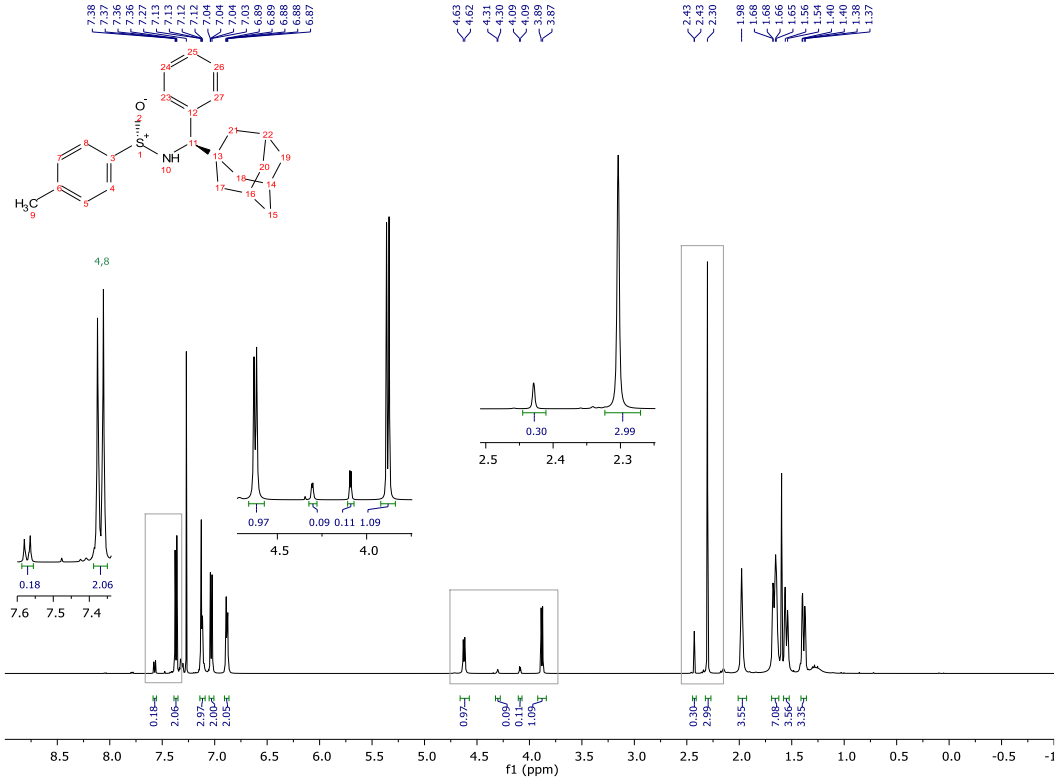


Compound 41 - 1H - 500 MHz

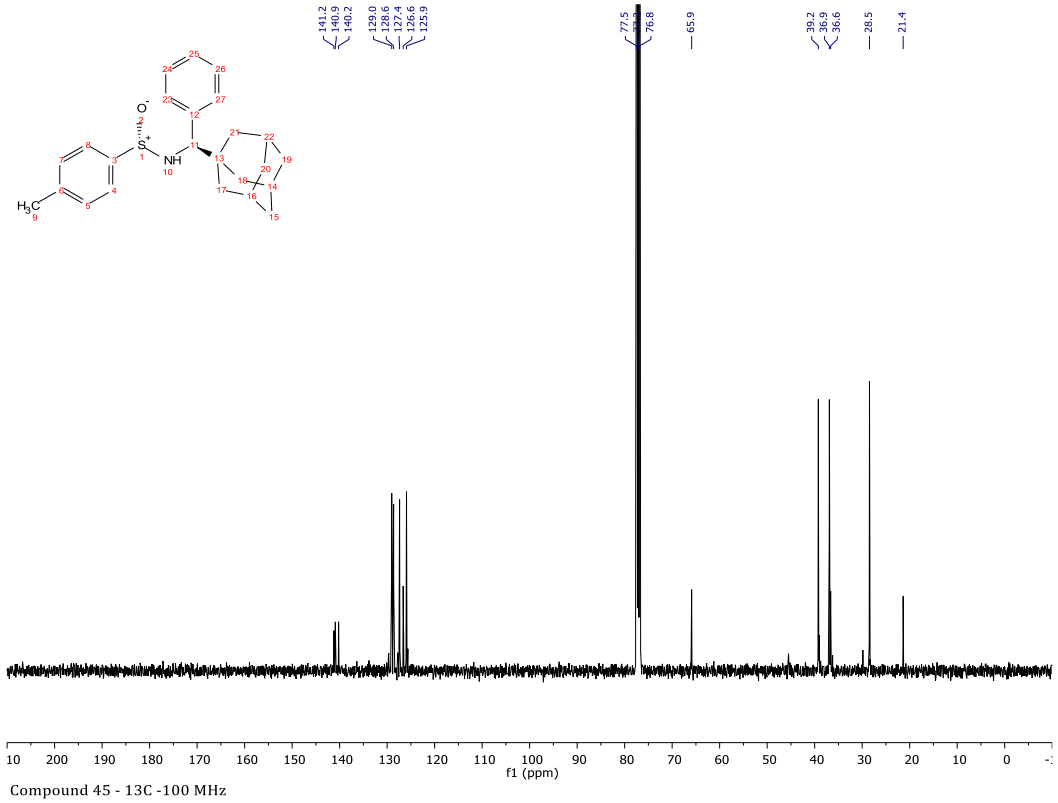


Compound 41 - 13C - 125 MHz

(S)-*N*-((R)-((adamantyl)(phenyl)methyl)-4-methylbenzenesulfinamide (**45**):

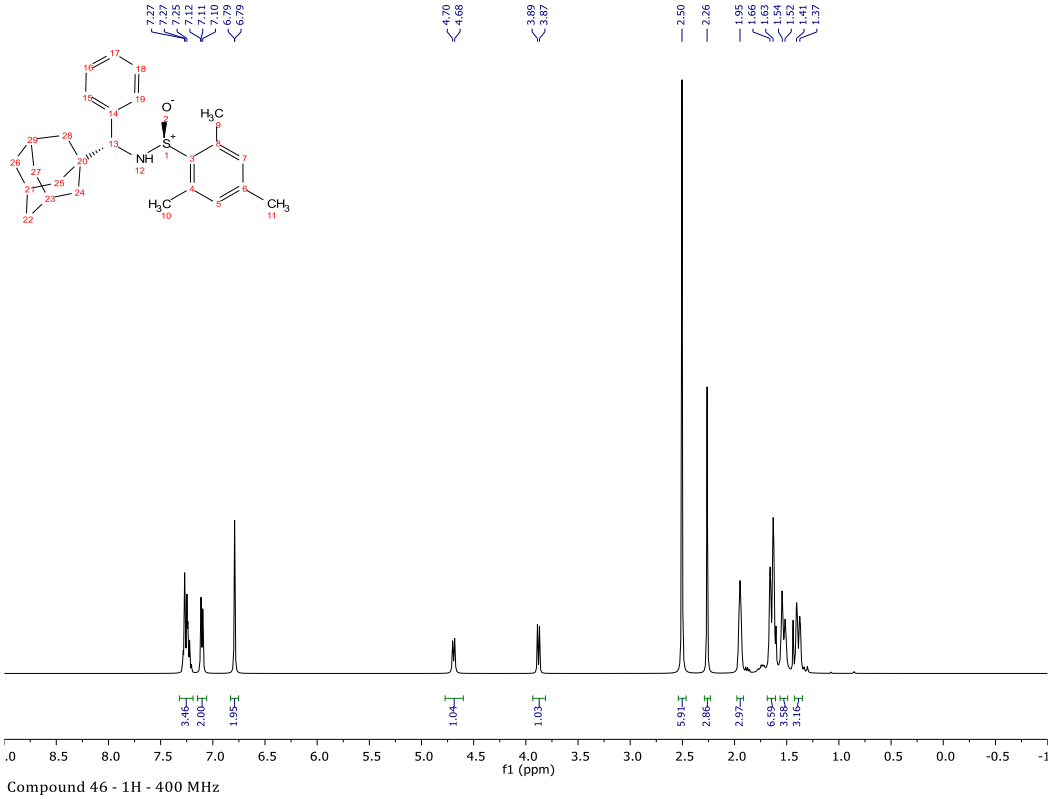


Compound 45 - 1H -500 MHz

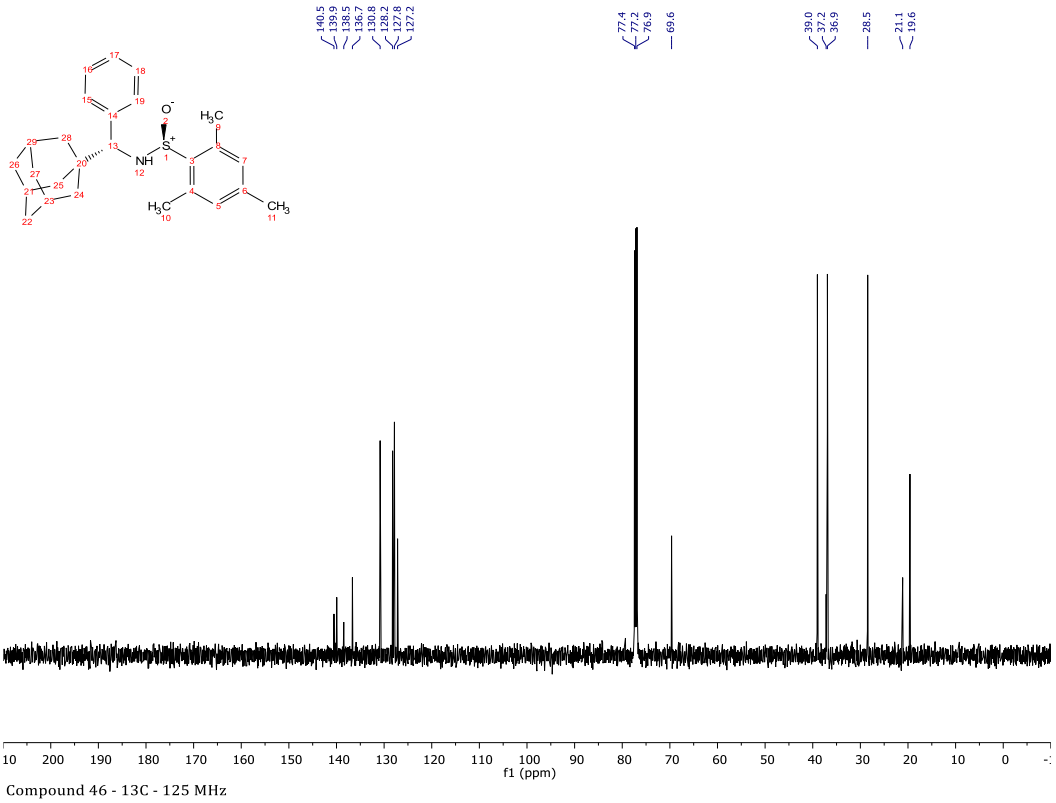


Compound 45 - 13C -100 MHz

(S)-*N*-((R)-((3-adamantanyl)(phenyl)methyl)-2,4,6-trimethylbenzenesulfinamide (**46**):

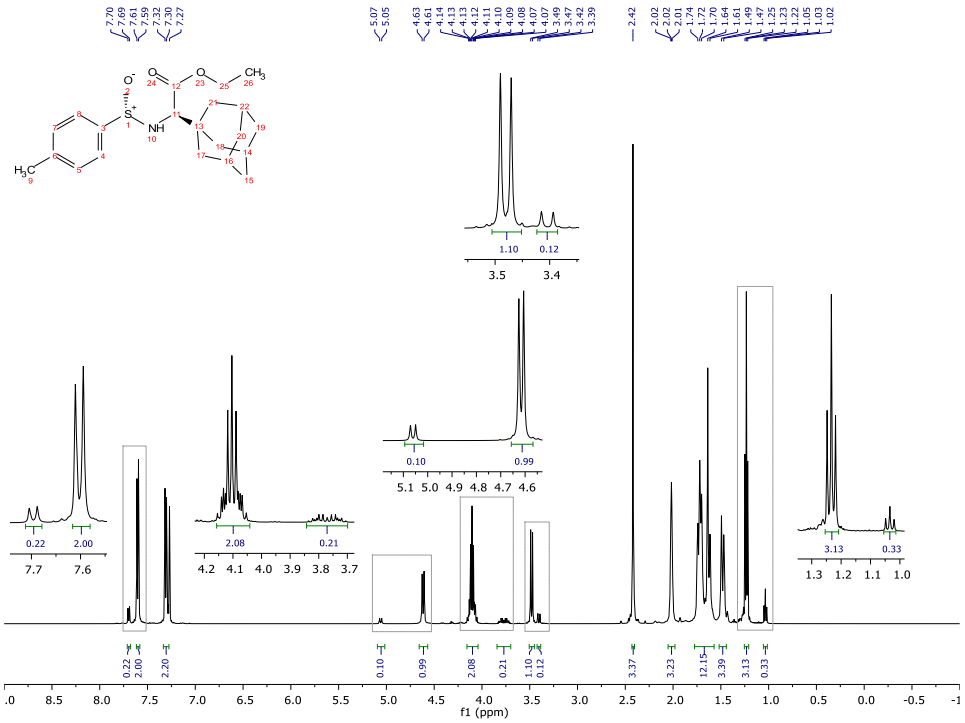


Compound 46 - 1H - 400 MHz

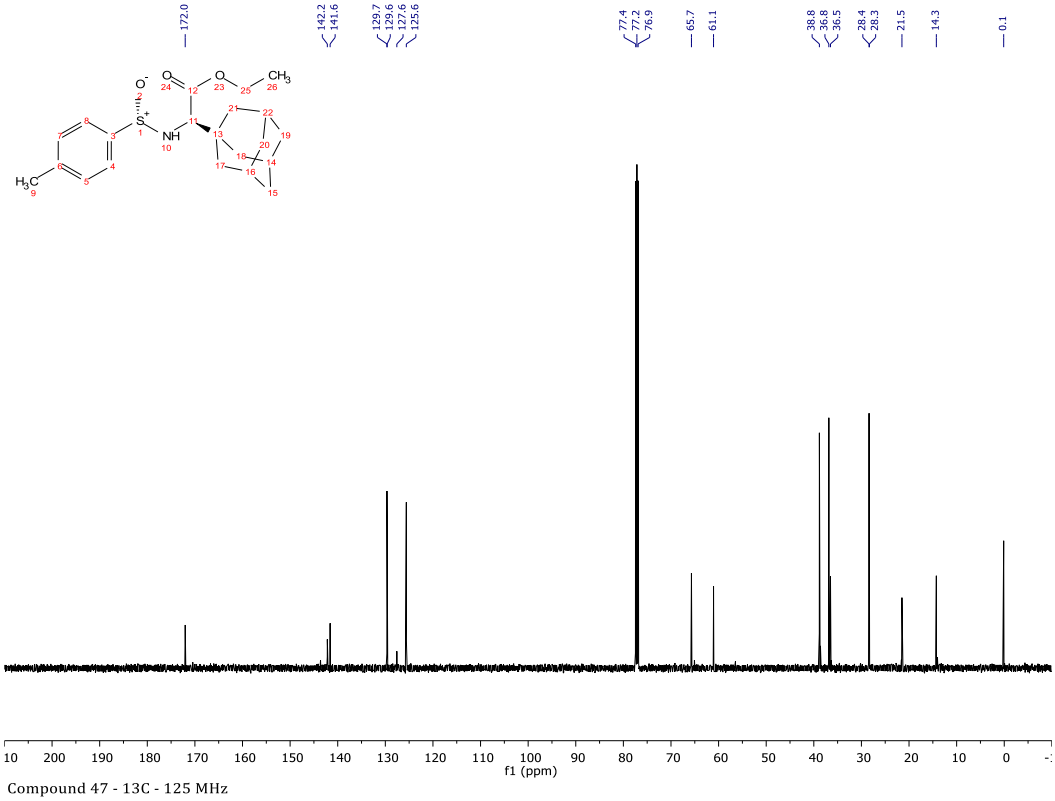


Compound 46 - 13C - 125 MHz

((R)-ethyl 2-(adamantan-1-yl)-2-((S)-4-methylphenylsulfinamido)acetate (**47**):

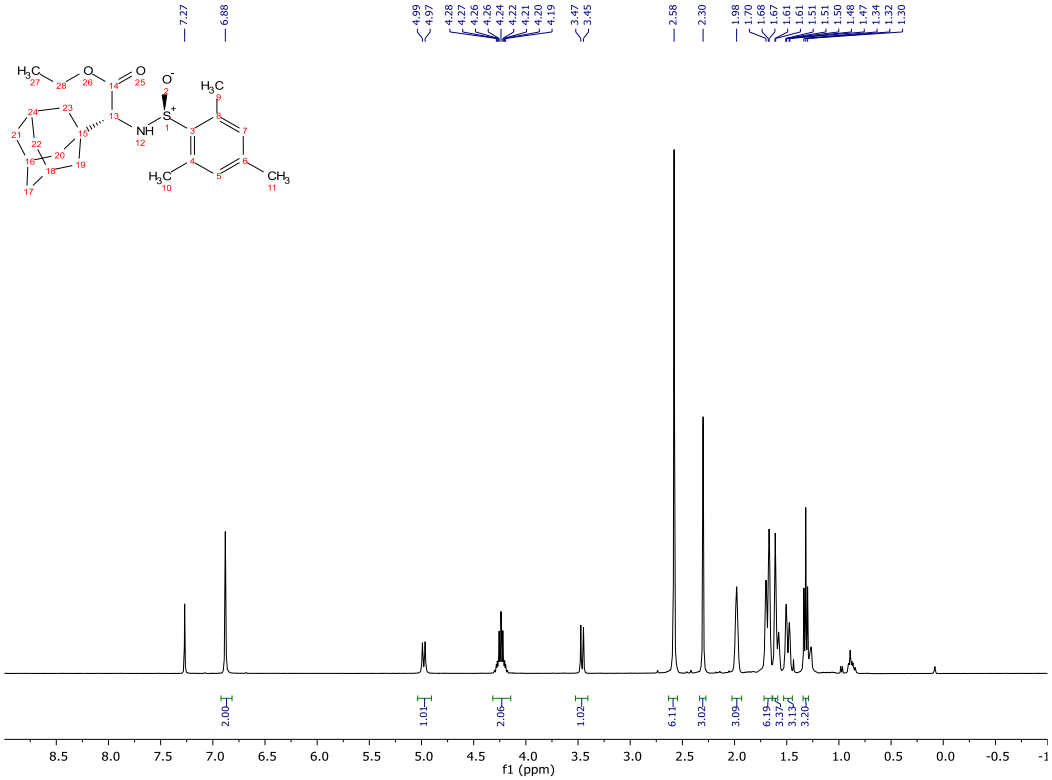


Compound 47 - 1H -500 MHz

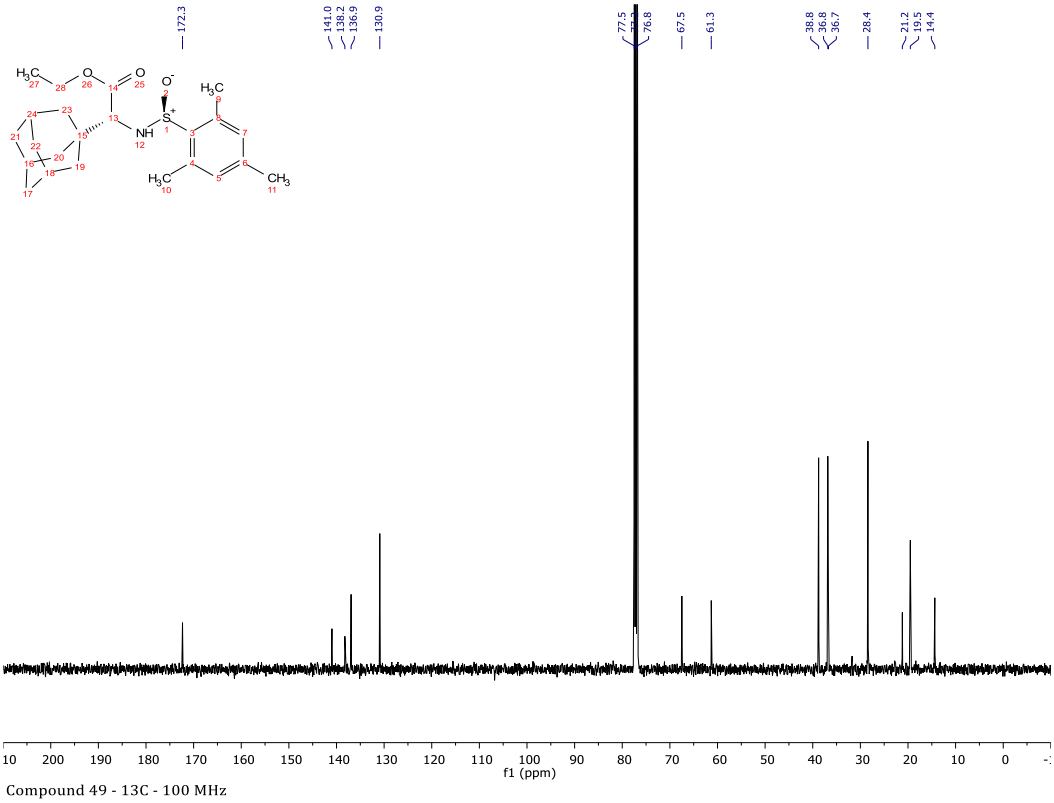


Compound 47 - 13C - 125 MHz

(R)-ethyl 2-(adamantyl)-2-((S)-2,4,6-trimethylphenylsulfinamido)acetate (**49**):

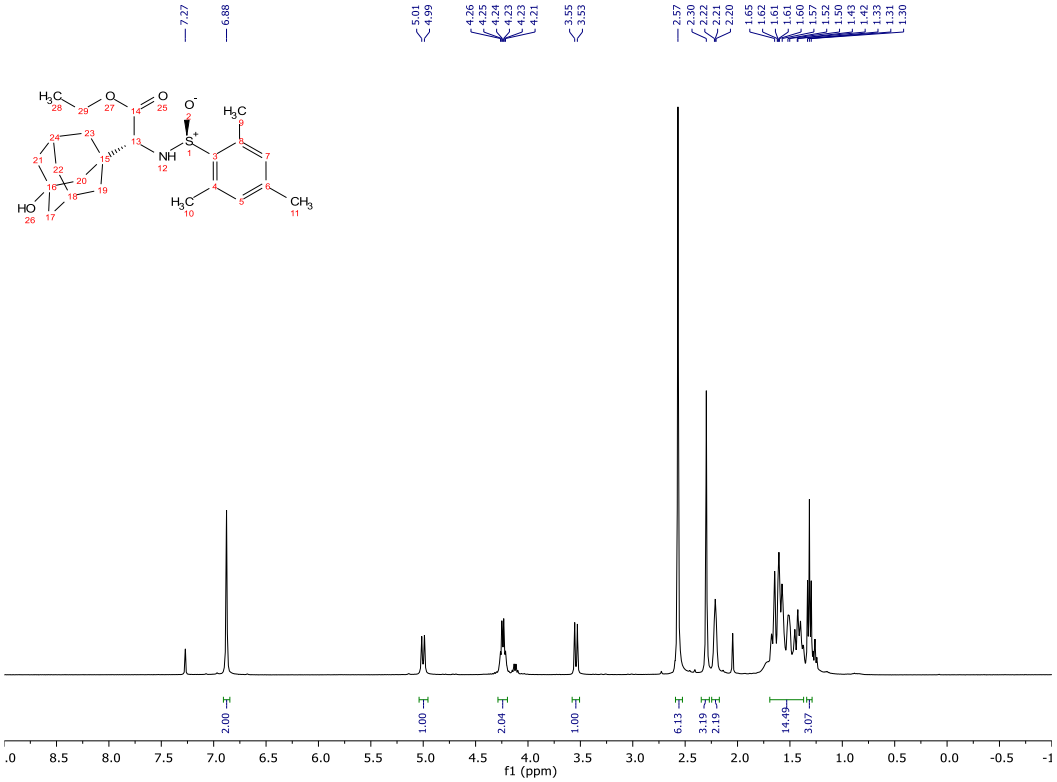


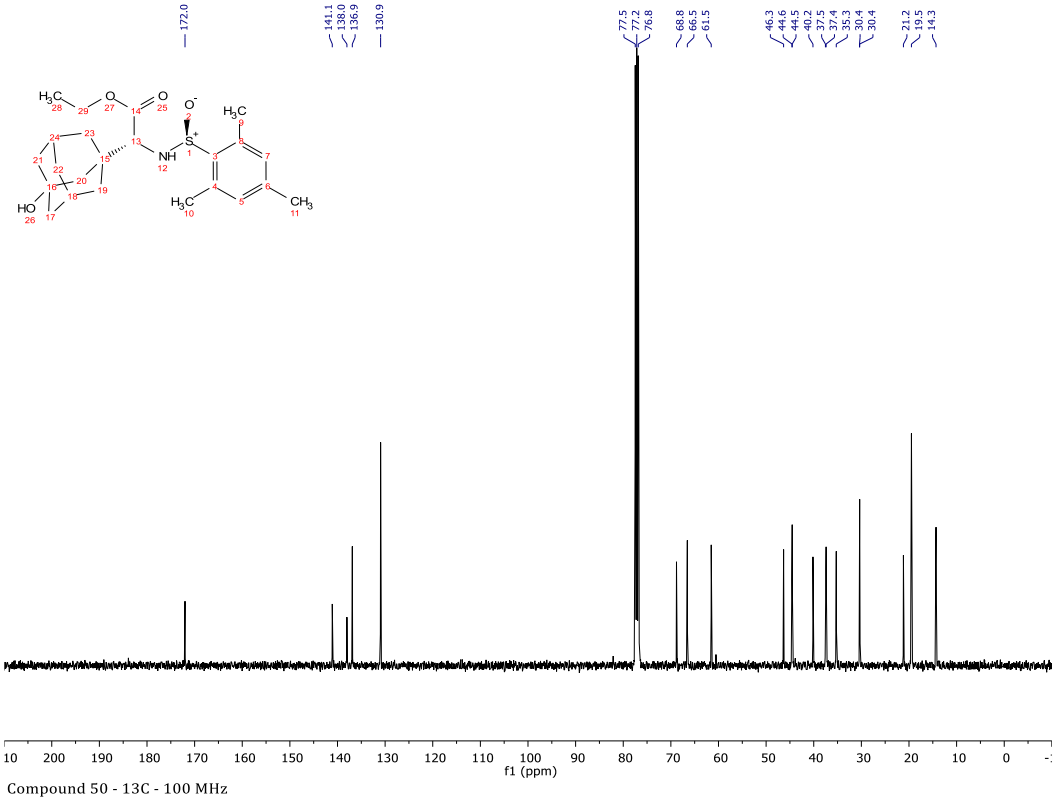
Compound 49 - 1H - 400 MHz



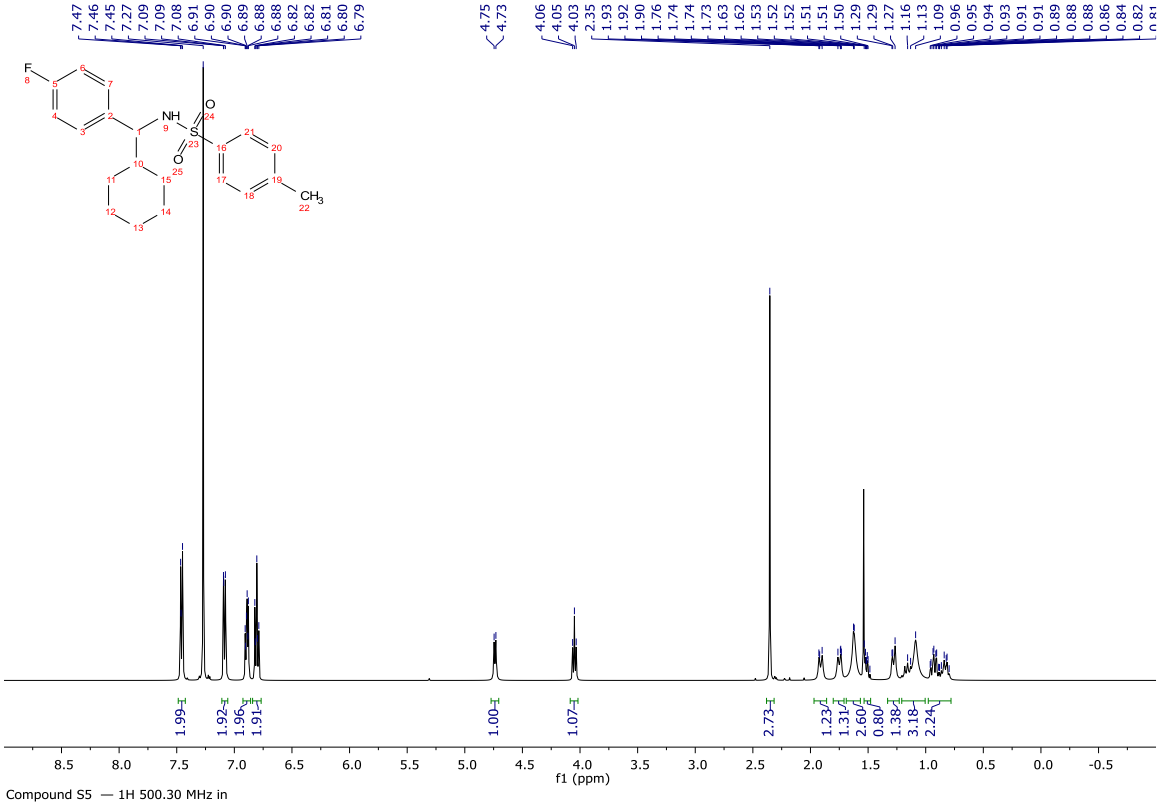
Compound 49 - 13C - 100 MHz

(R)-ethyl 2-(3-hydroxyadamantan-1-yl)-2-((S)-2,4,6-trimethylphenylsulfinamido)acetate (**50**):

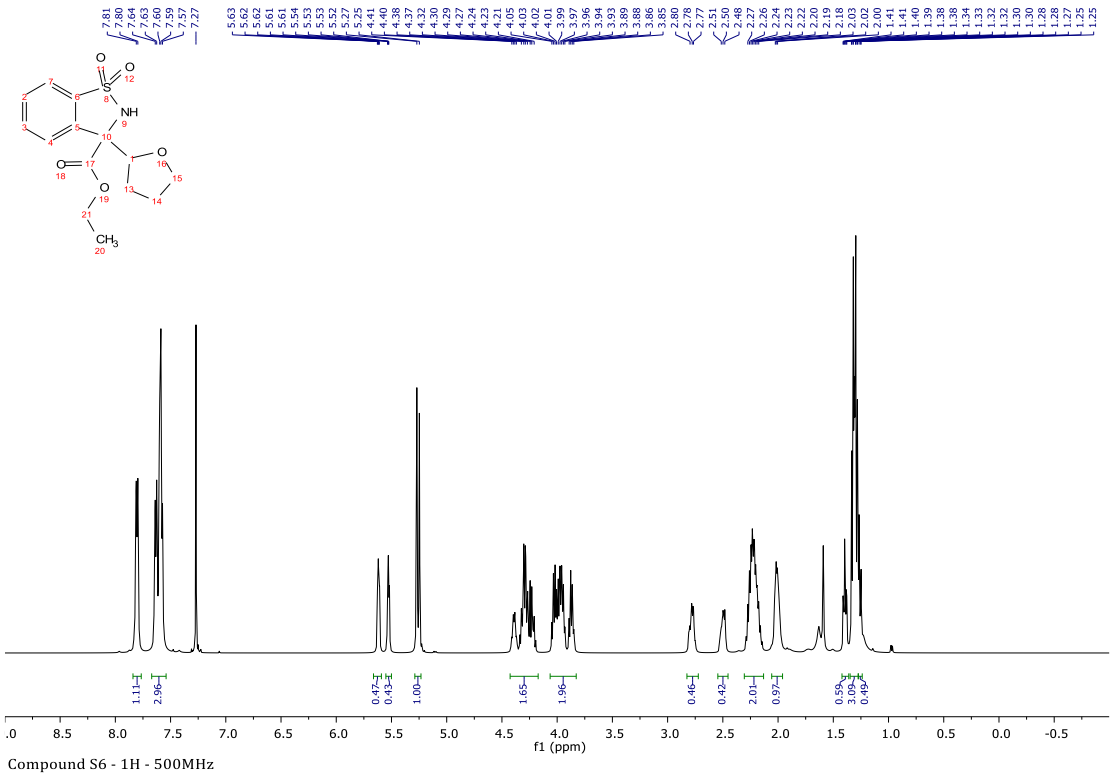




N-(cyclohexyl(4-fluorophenyl)methyl)-4’-methylbenzenesulfonamide (**S5**):

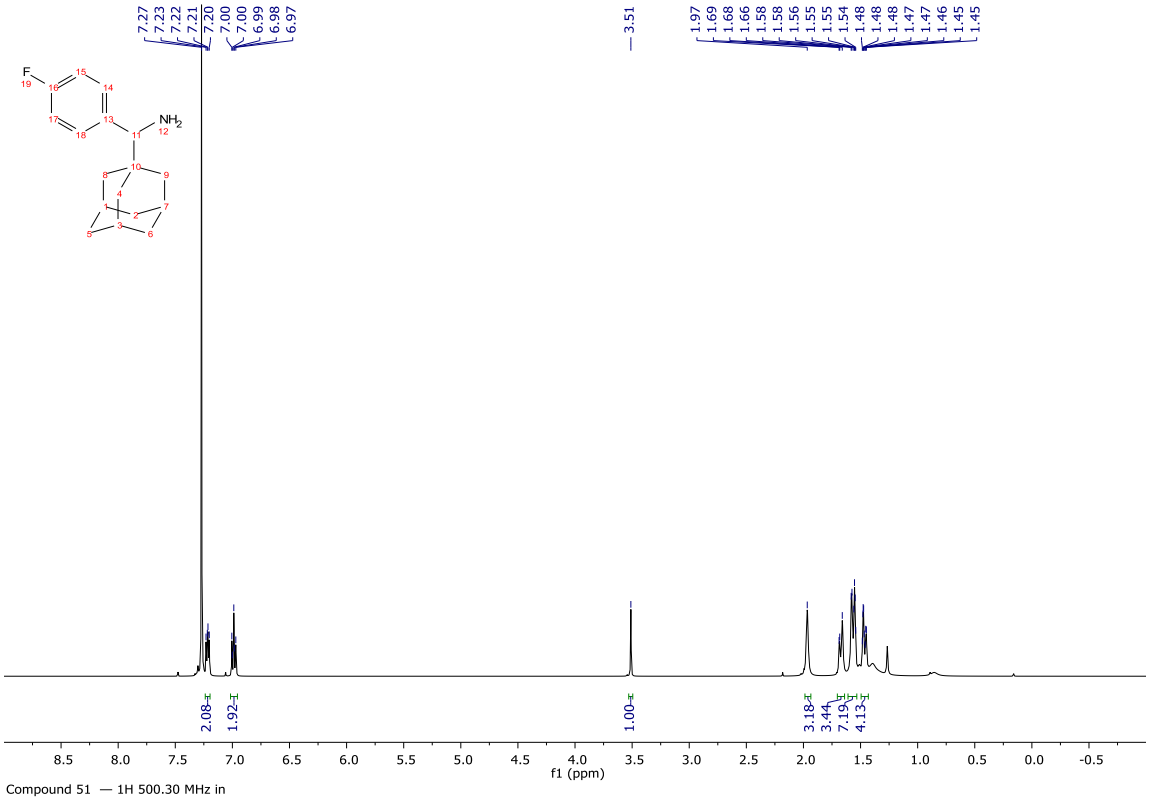


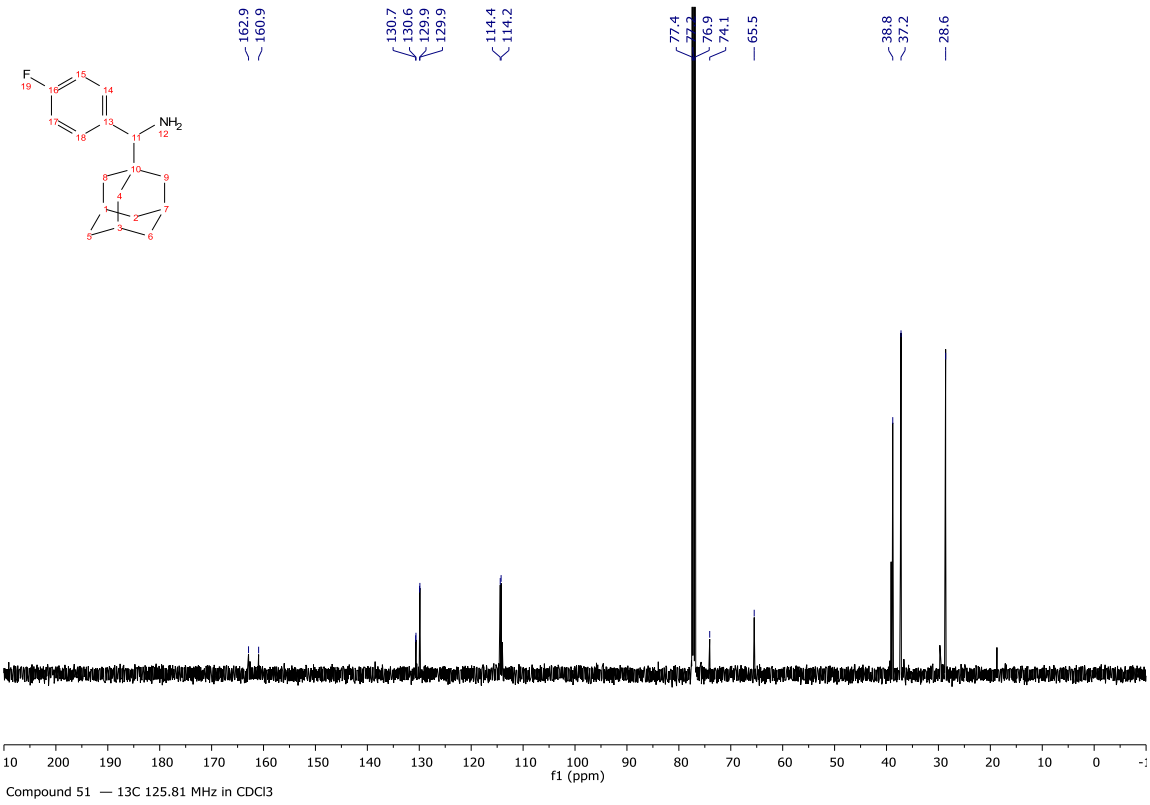
ethyl 3-(tetrahydrofuran-2-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (**S6**):



Compound S6 - 1H - 500MHz

adamantan-1-yl(4-fluorophenyl)methanamine (**51**):





(S)-ethyl-2-(adamantan-1-yl)-2-aminoacetate (**52**):