Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Supporting information

Axially chiral dimethylaminobenzimidazoles and their preliminary evaluation as acyl-transfer reagents

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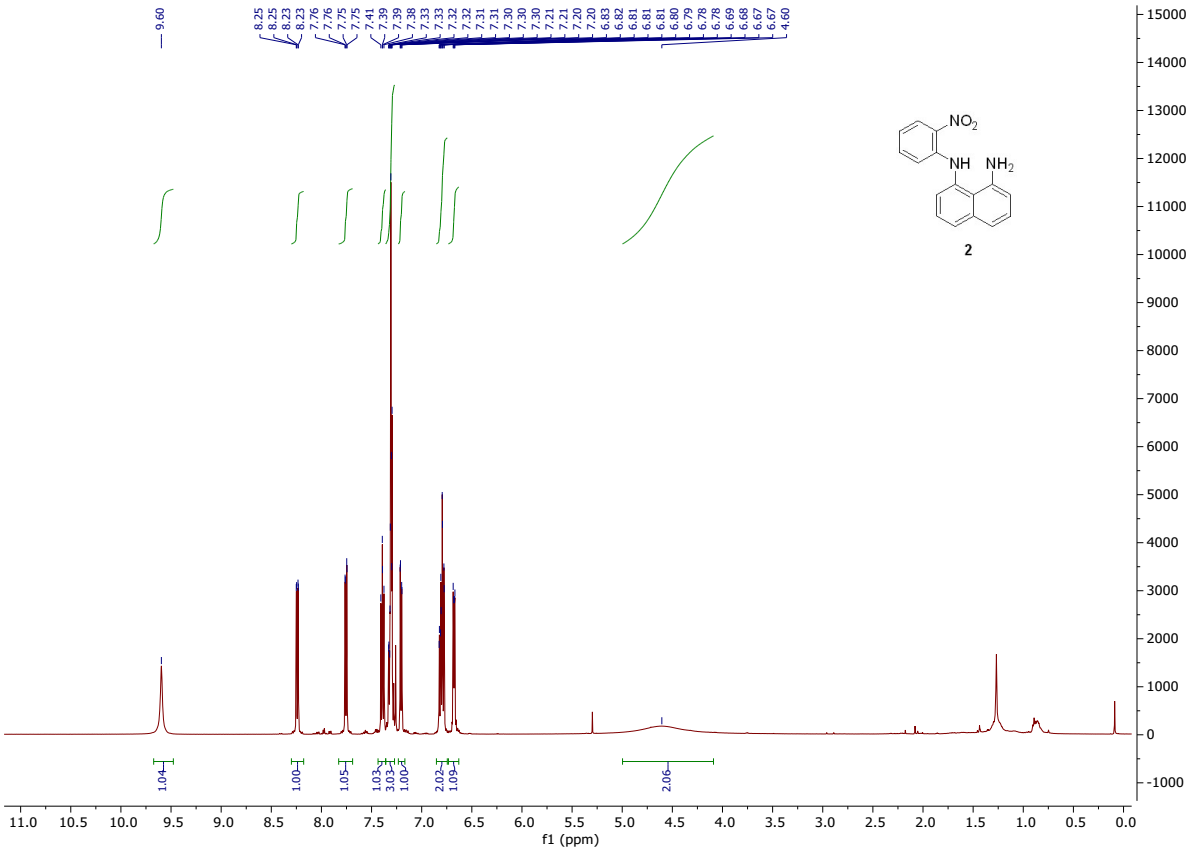
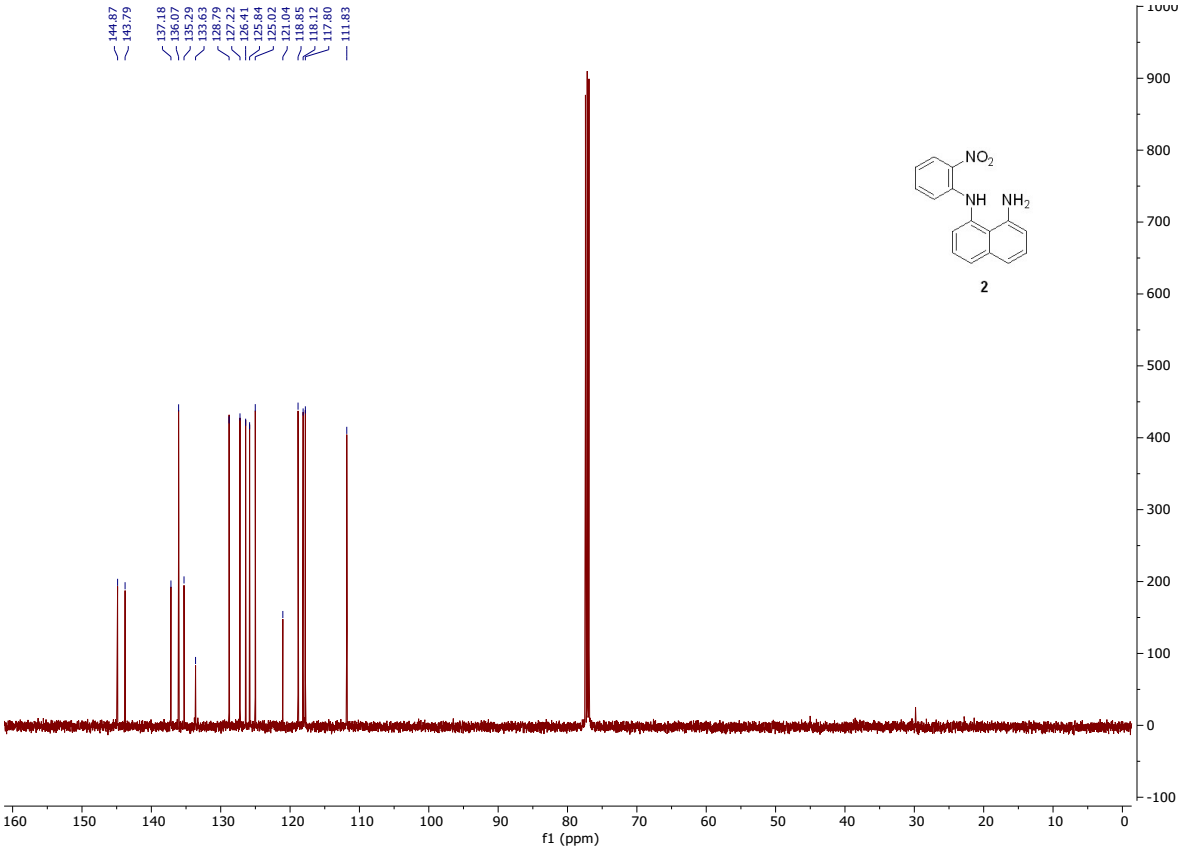
^{1}H NMR

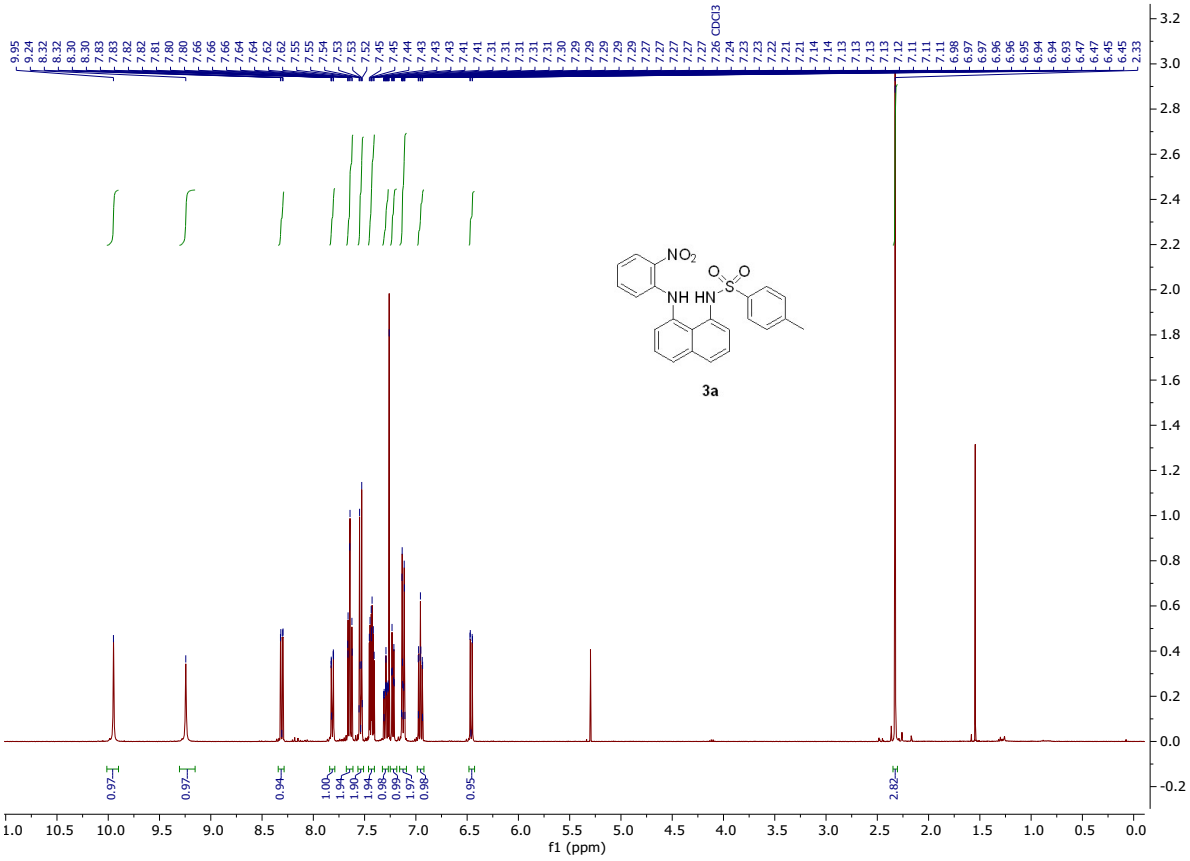


^{13}C NMR



4-Methyl-*N*-(8-[(2-nitrophenyl)amino]naphthalen-1-yl)benzenesulfonamide 3a

^{1}H NMR



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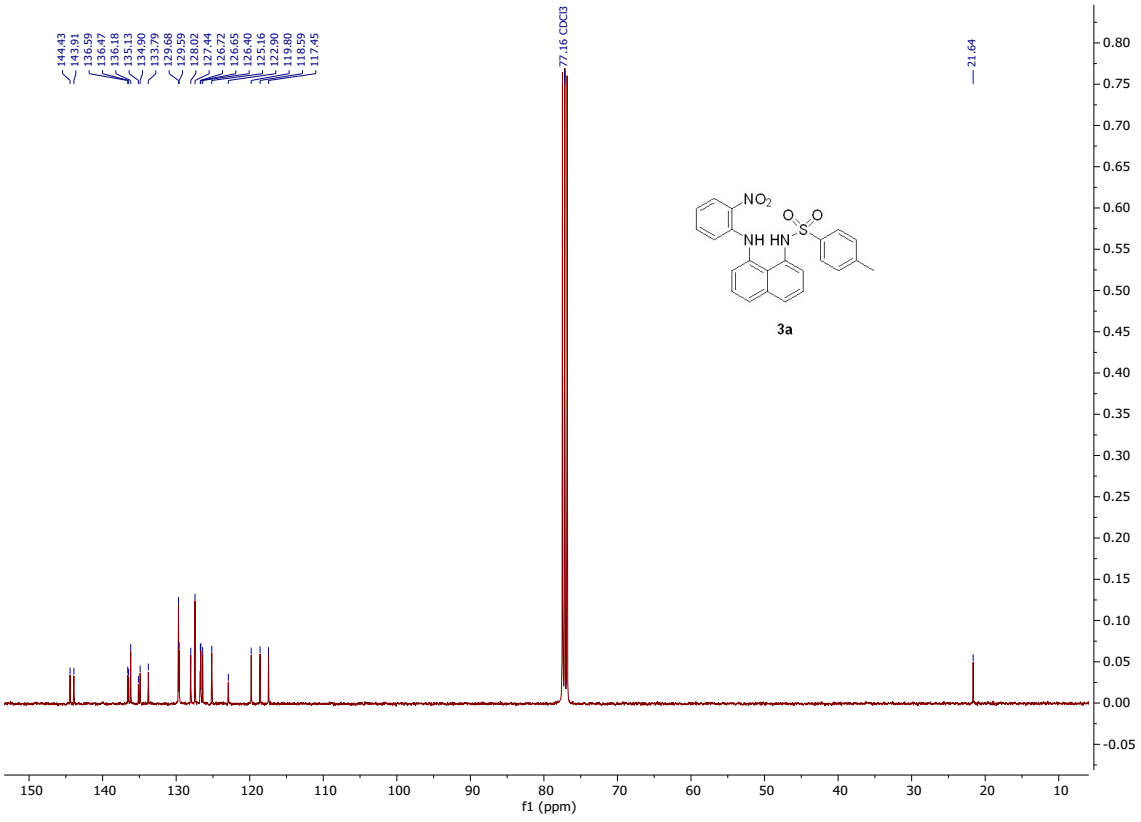

N-(8-[(2-Nitrophenyl)amino]naphthalen-1-yl)naphthalene-2-sulfonamide 3b

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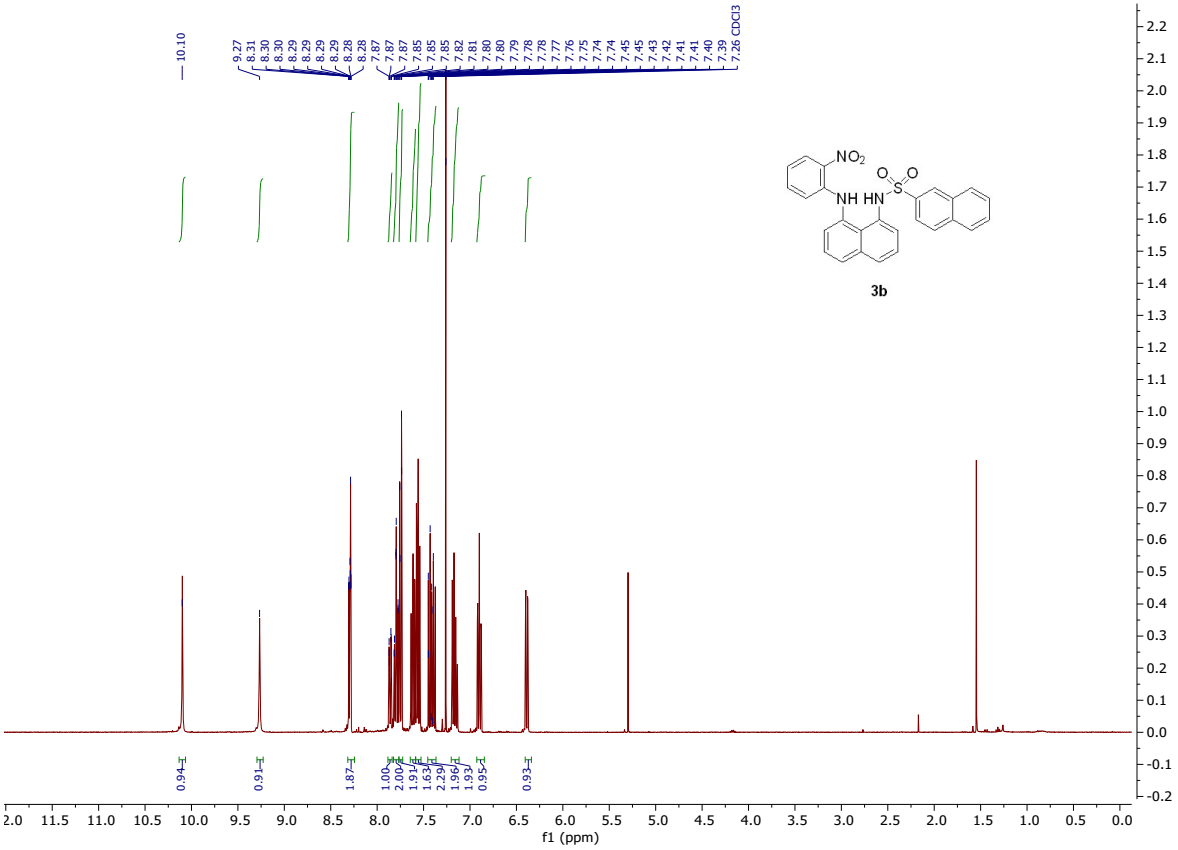

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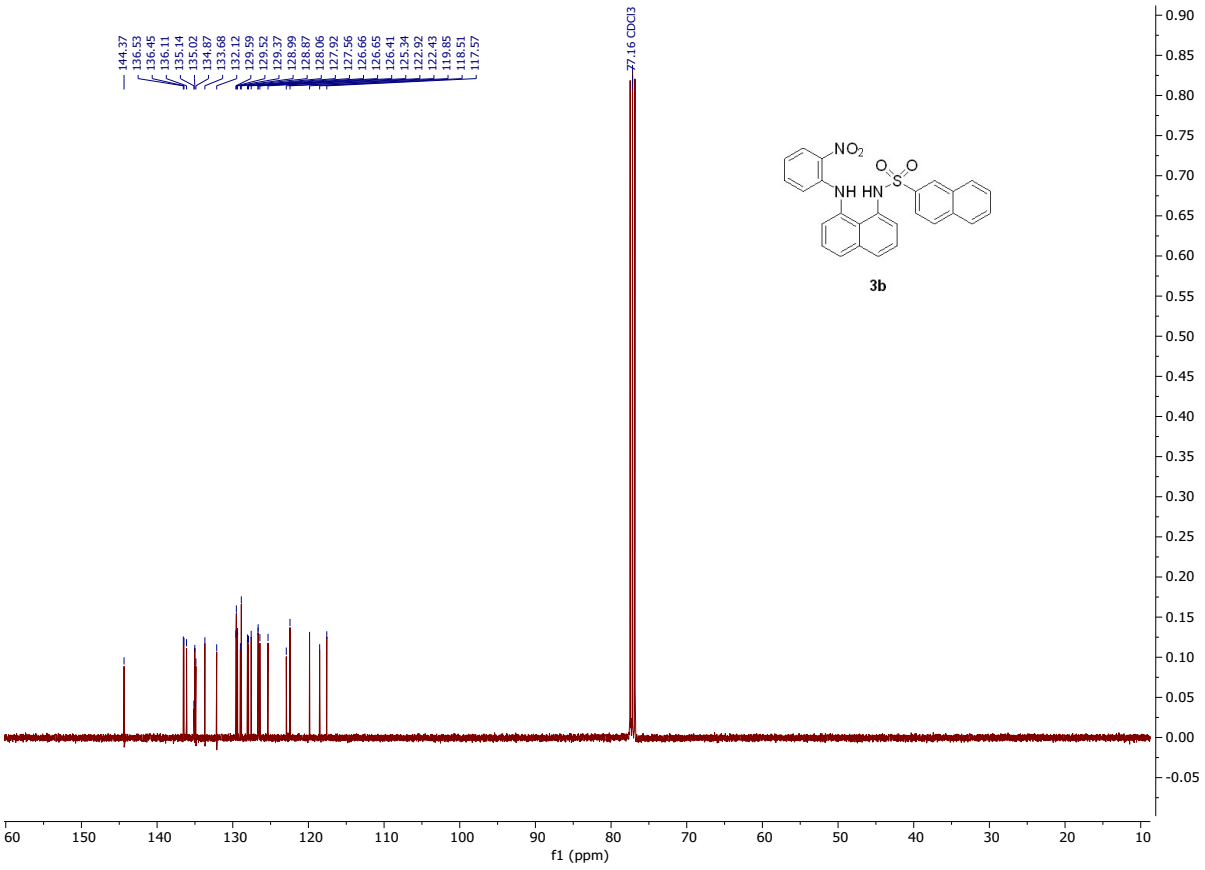
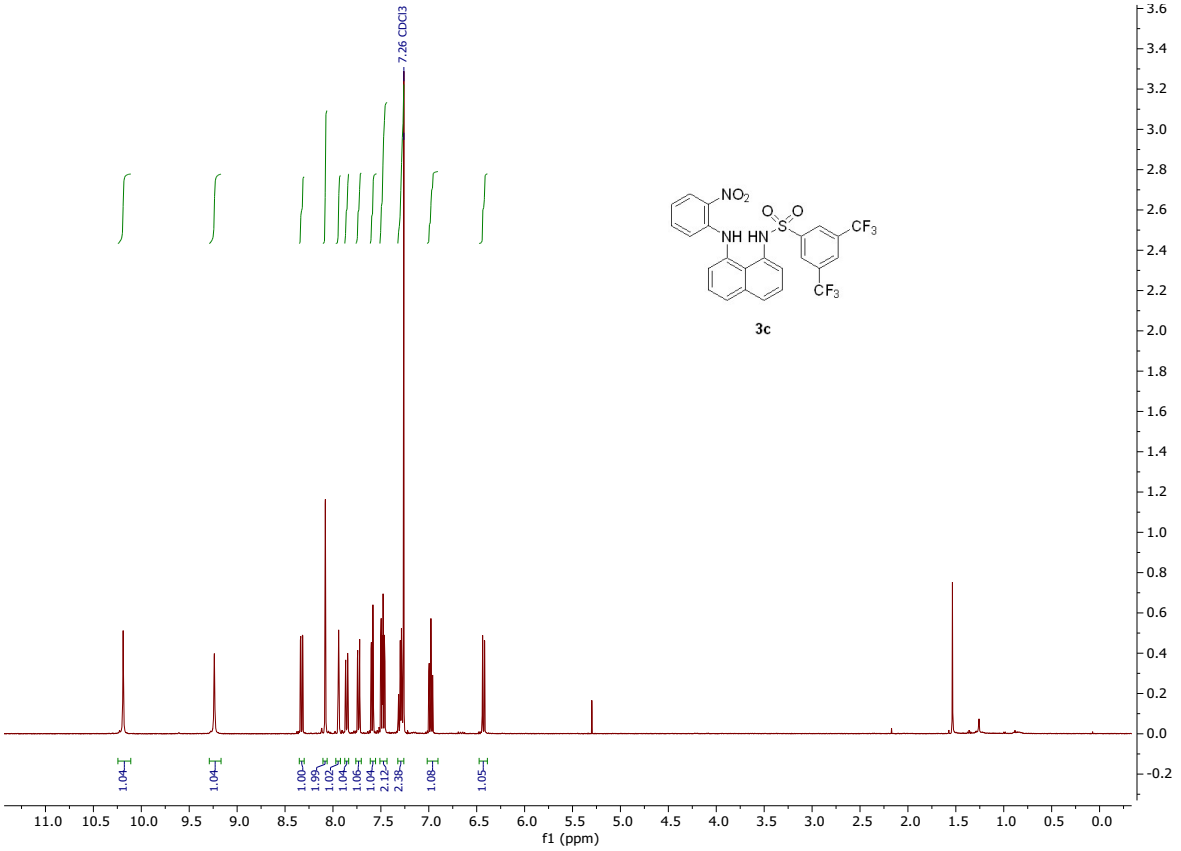


***N*-(8-[(2-Nitrophenyl)amino)naphthalen-1-yl]-3,5-bis(trifluoromethyl)benzenesulfonamide 3c**

^{1}H NMR



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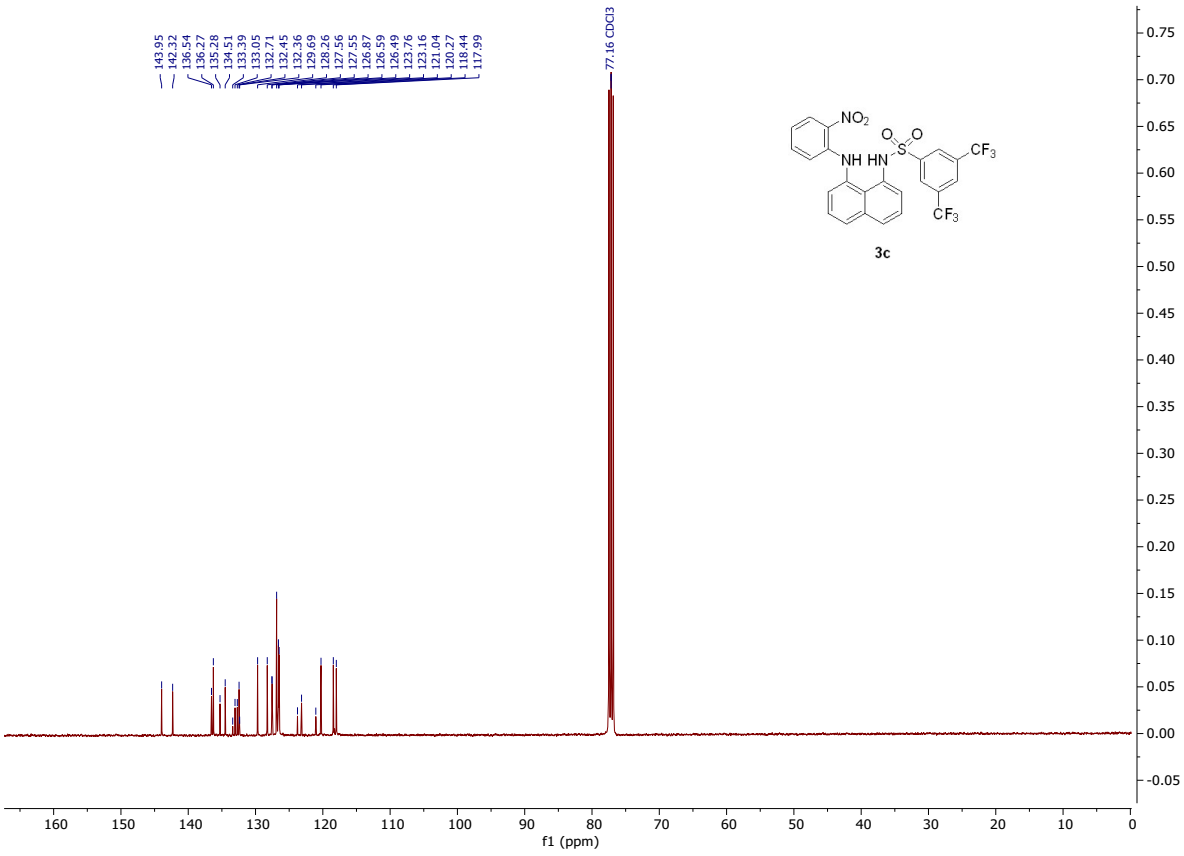
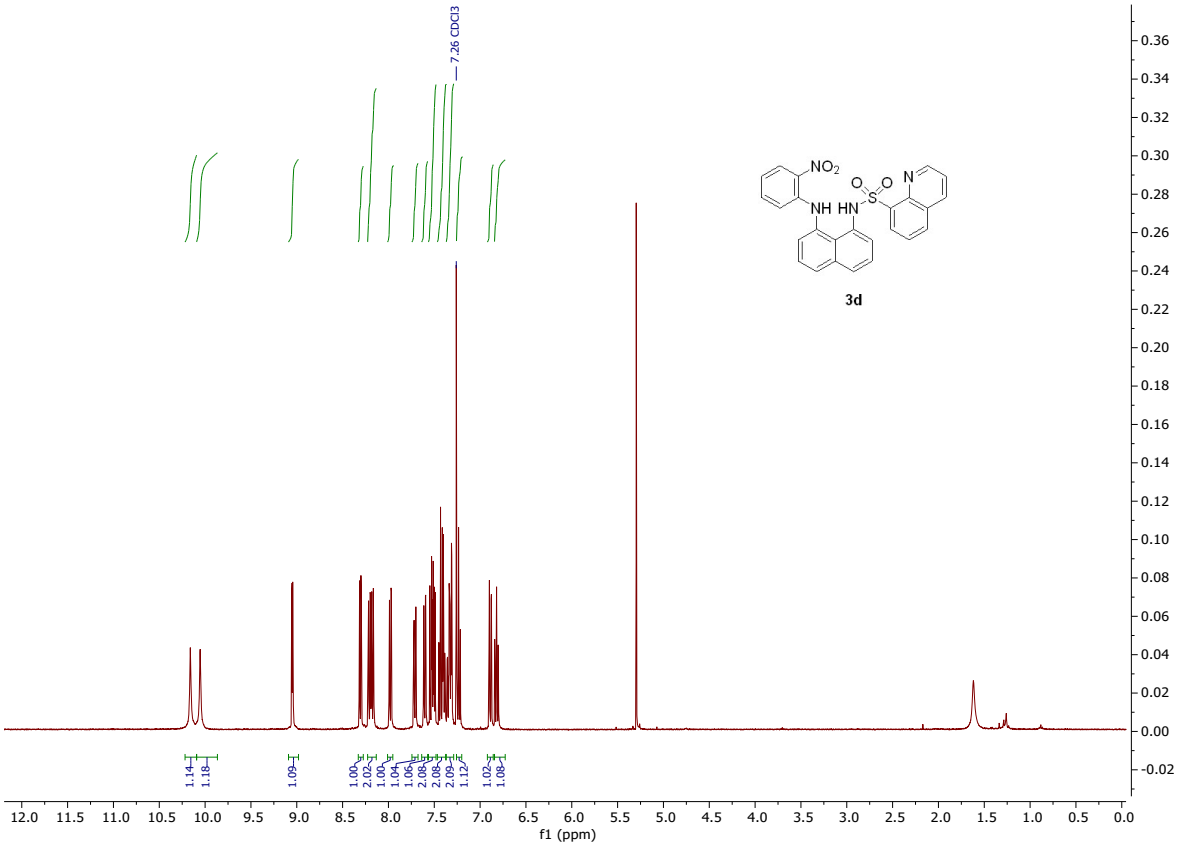


N-(8-((2-Nitrophenyl)amino)naphthalen-1-yl)quinoline-8-sulfonamide 3d

^{1}H NMR



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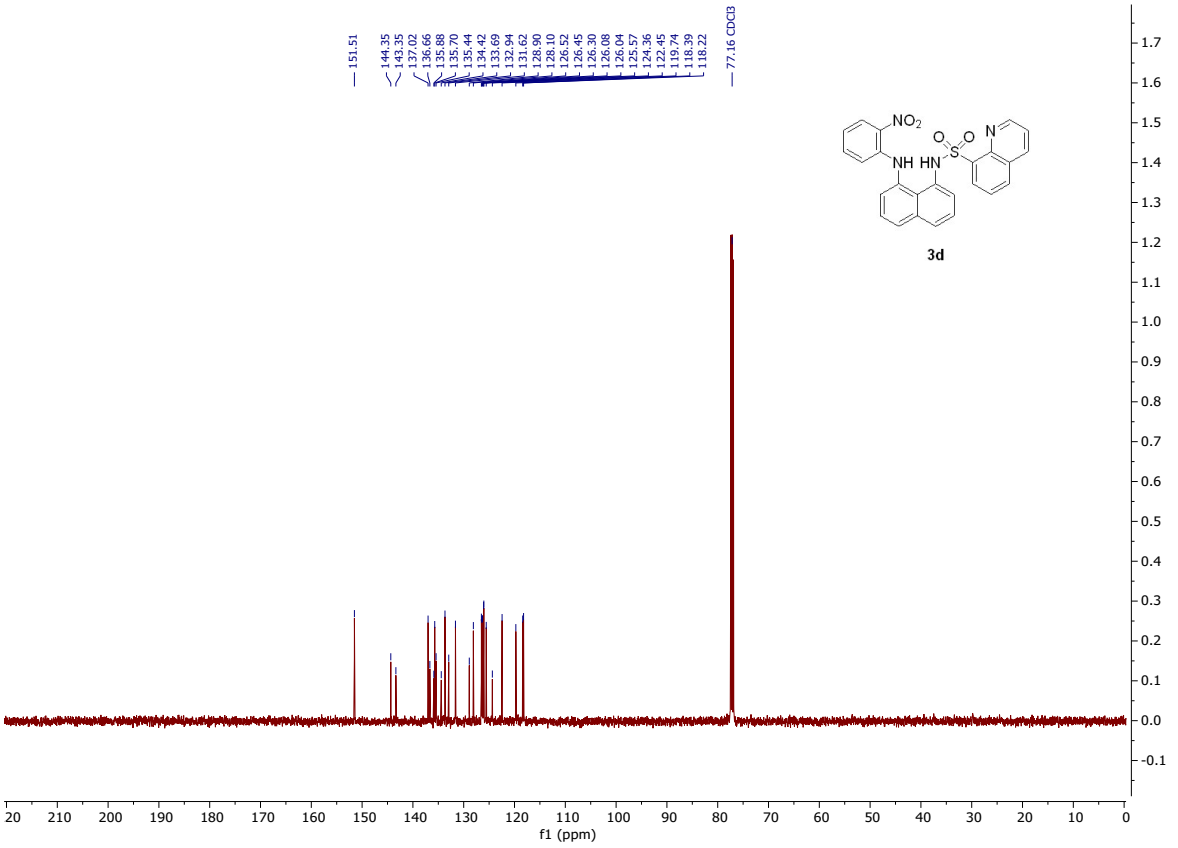

N-(8-[(2-Nitrophenyl)amino)naphthalen-1-yl]methanesulfonamide 3e

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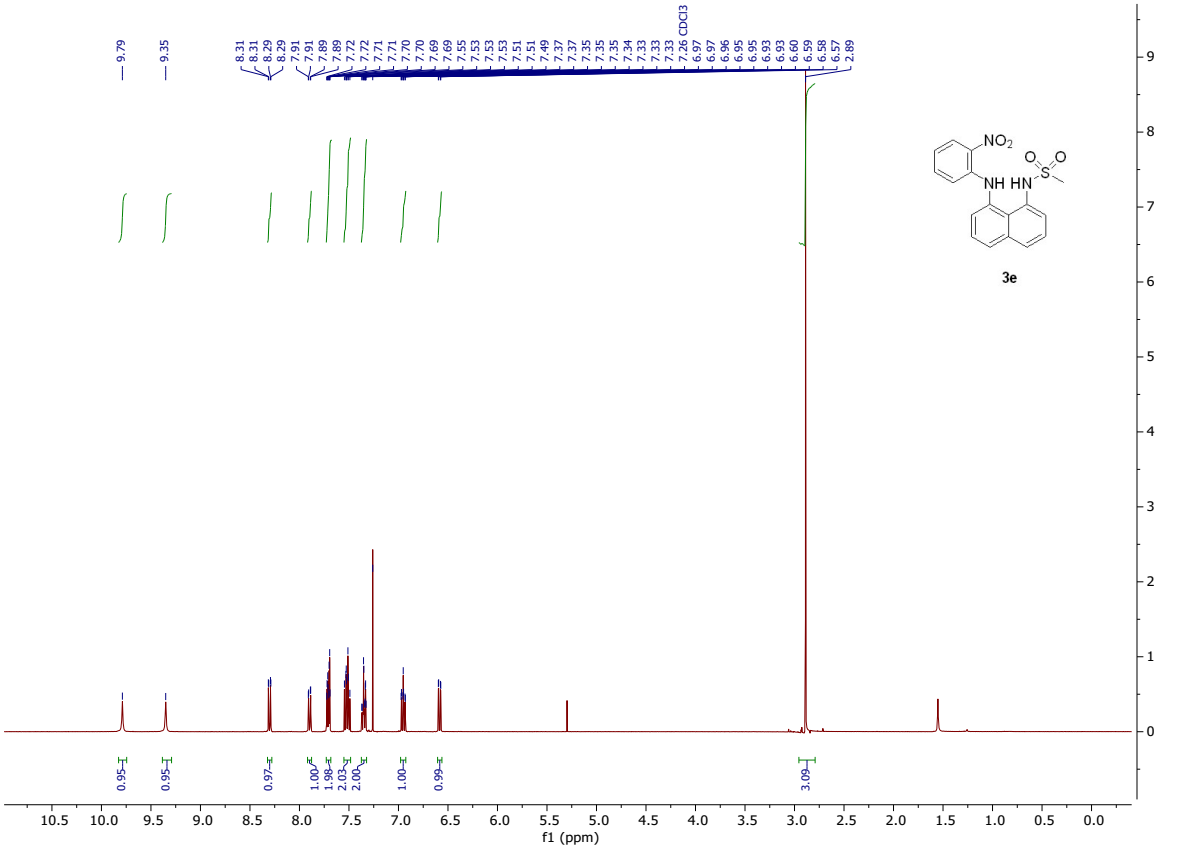

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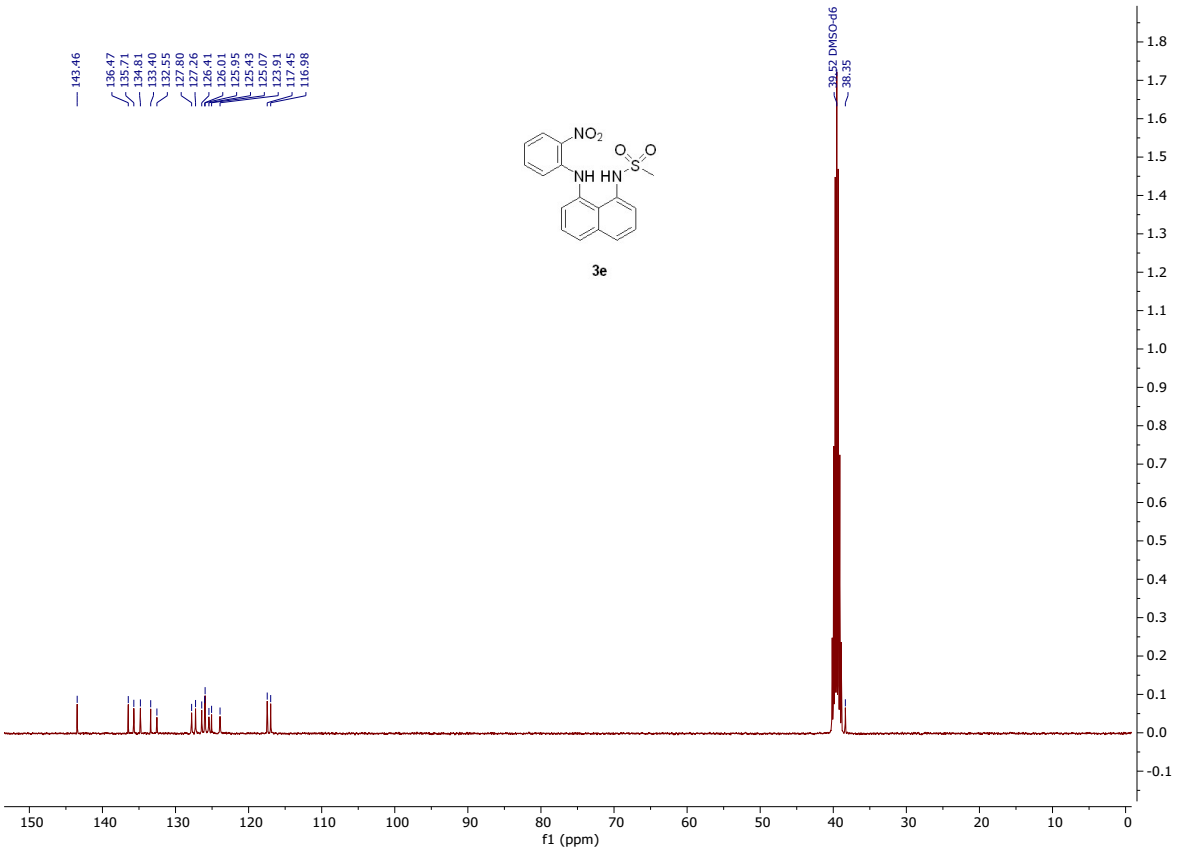

N-(2-Nitrophenyl)-8-(pyrrolidin-1-yl)naphthalen-1-amine 3f

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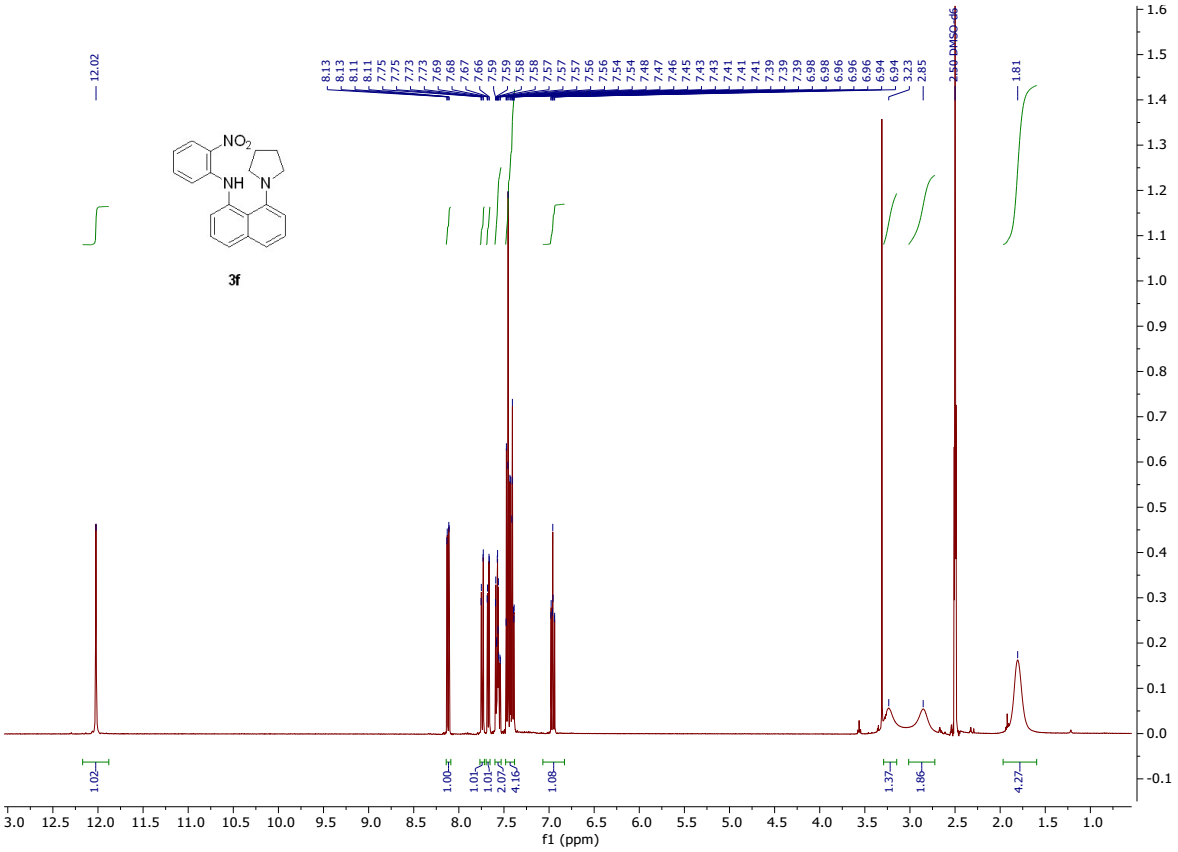

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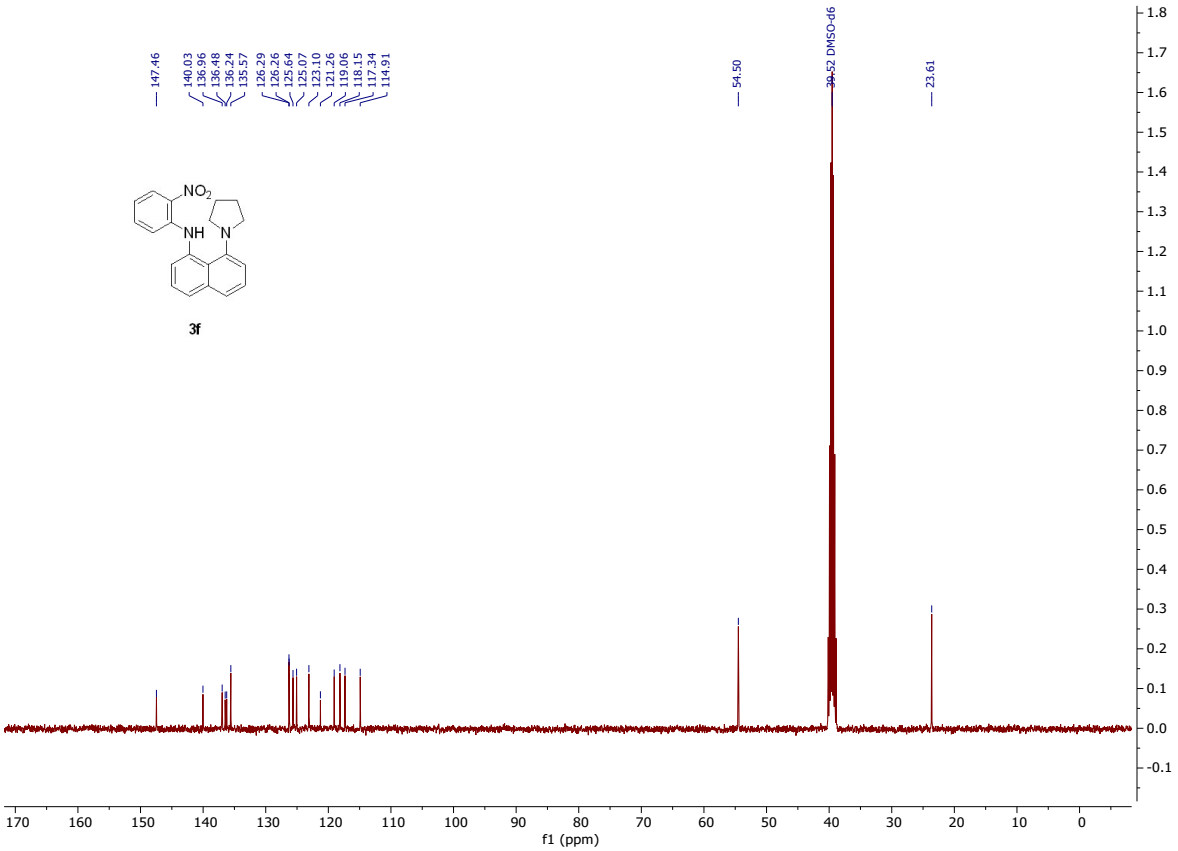
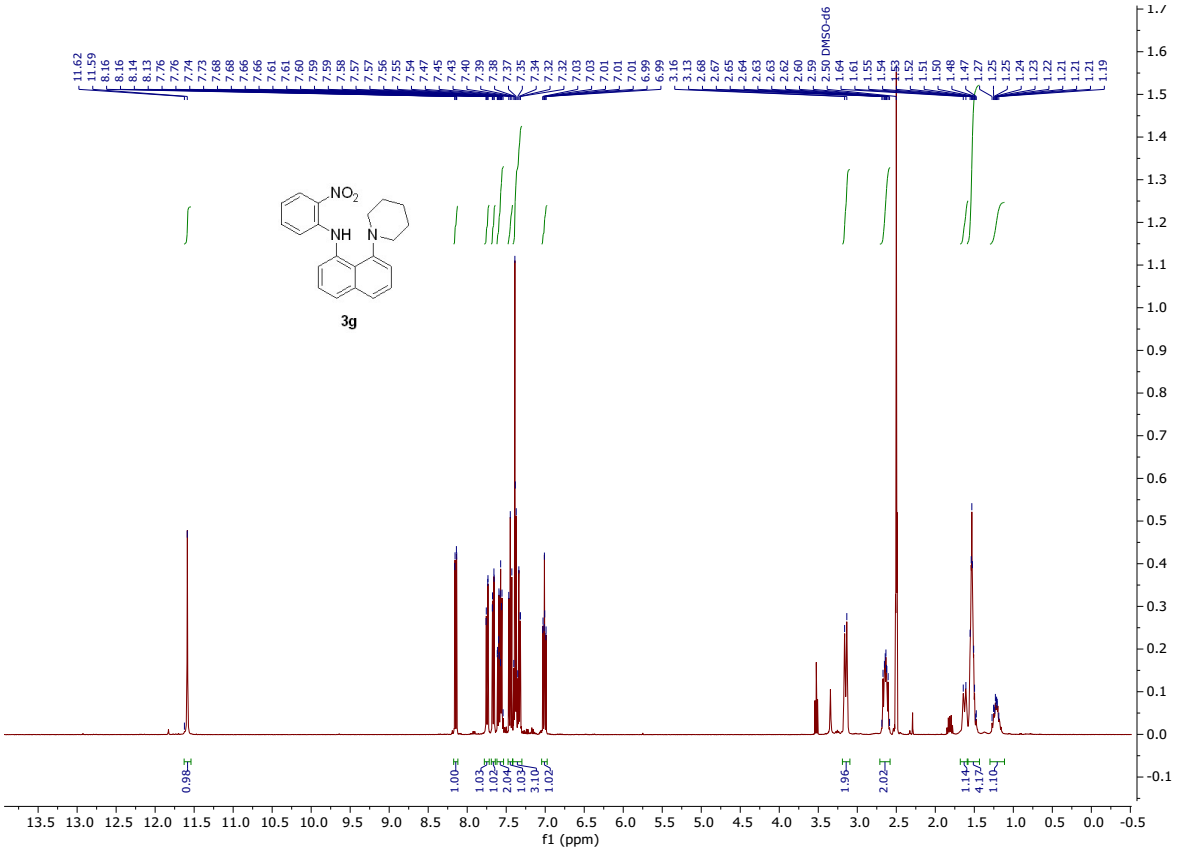


N-(2-Nitrophenyl)-8-(piperidin-1-yl)naphthalen-1-amine 3g

^{1}H NMR



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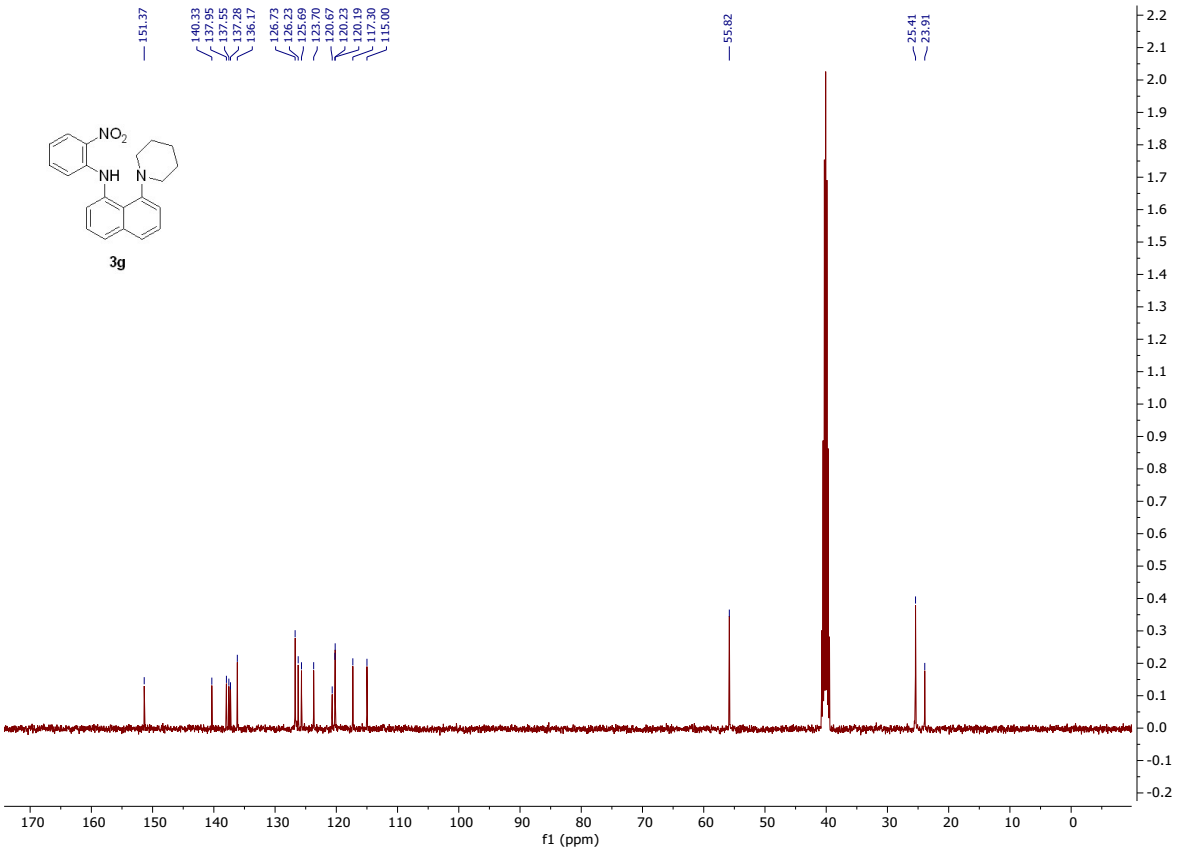
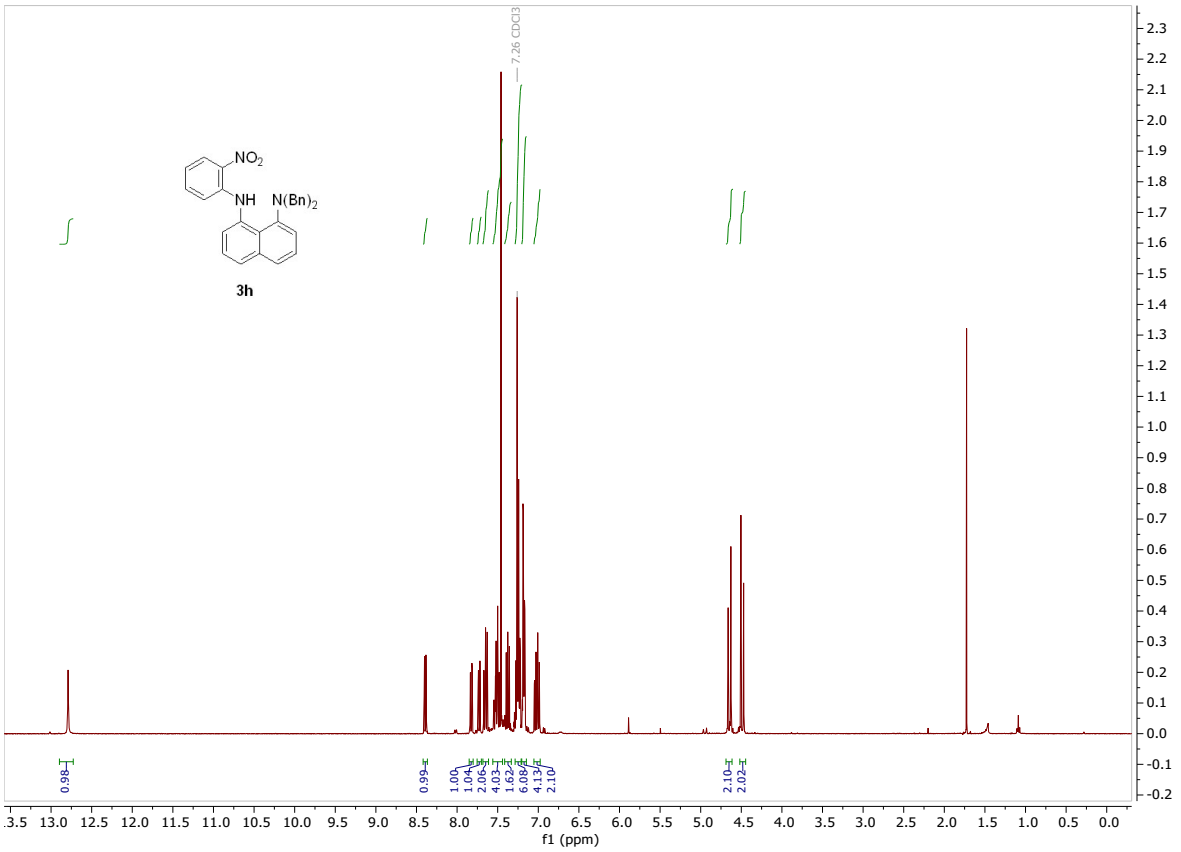


N^1,N^1-Dibenzyl-N^8-(2-nitrophenyl)naphthalene-1,8-diamine 3h

^{1}H NMR



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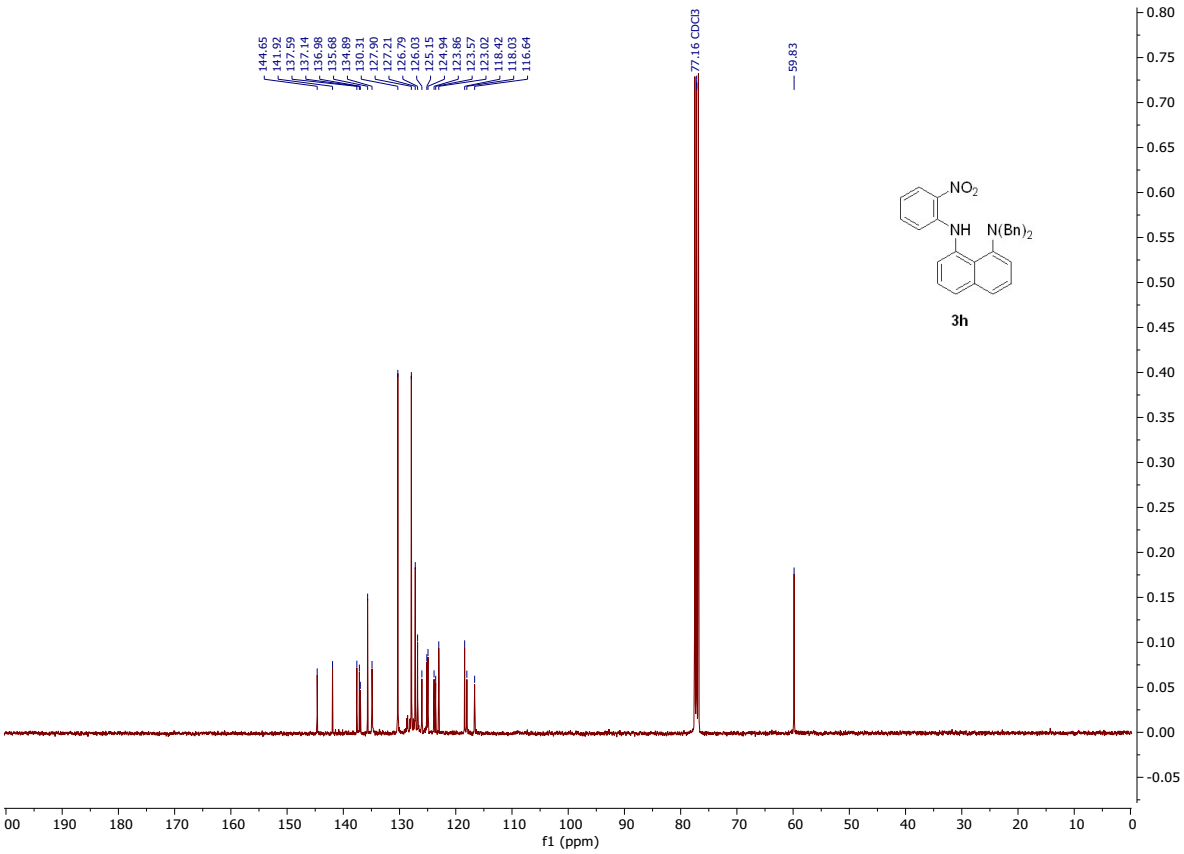
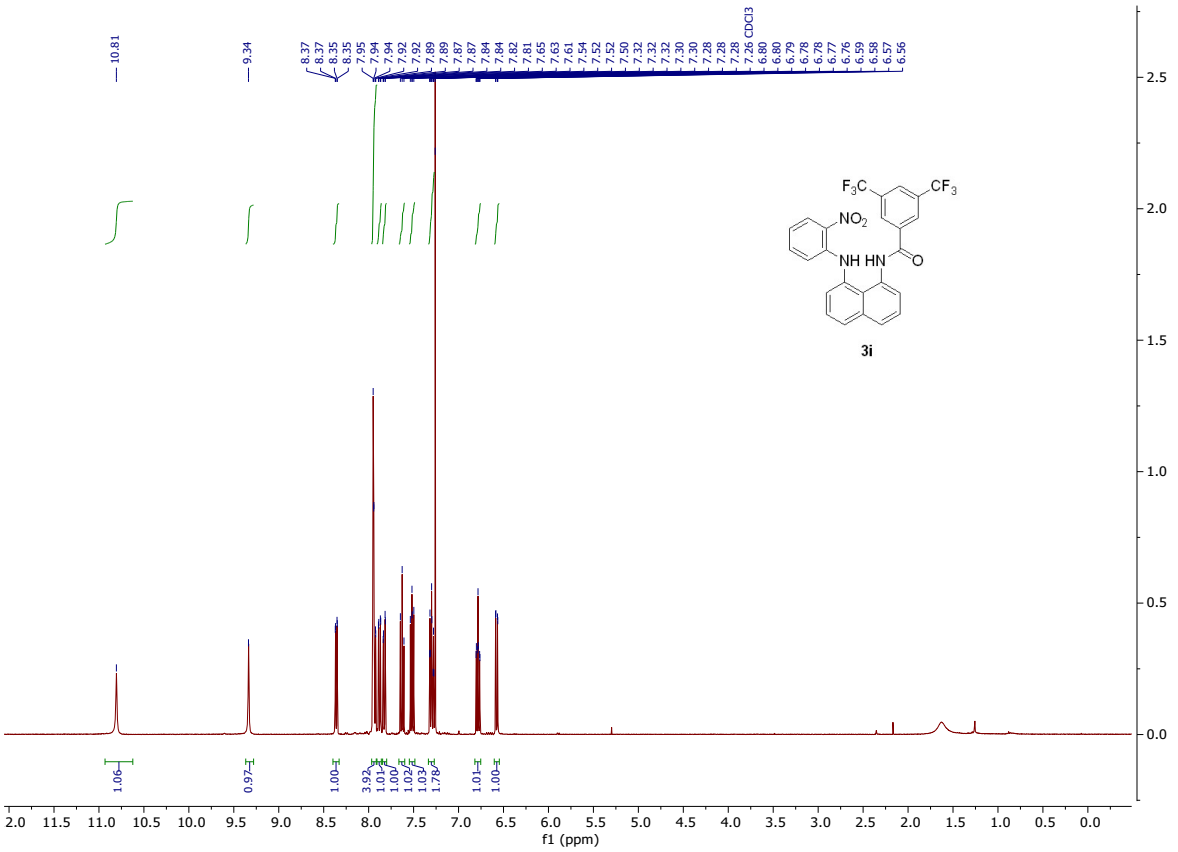


N-(8-((2-Nitrophenyl)amino)naphthalen-1-yl)-3,5-bis(trifluoromethyl)benzamide 3i

^{1}H NMR



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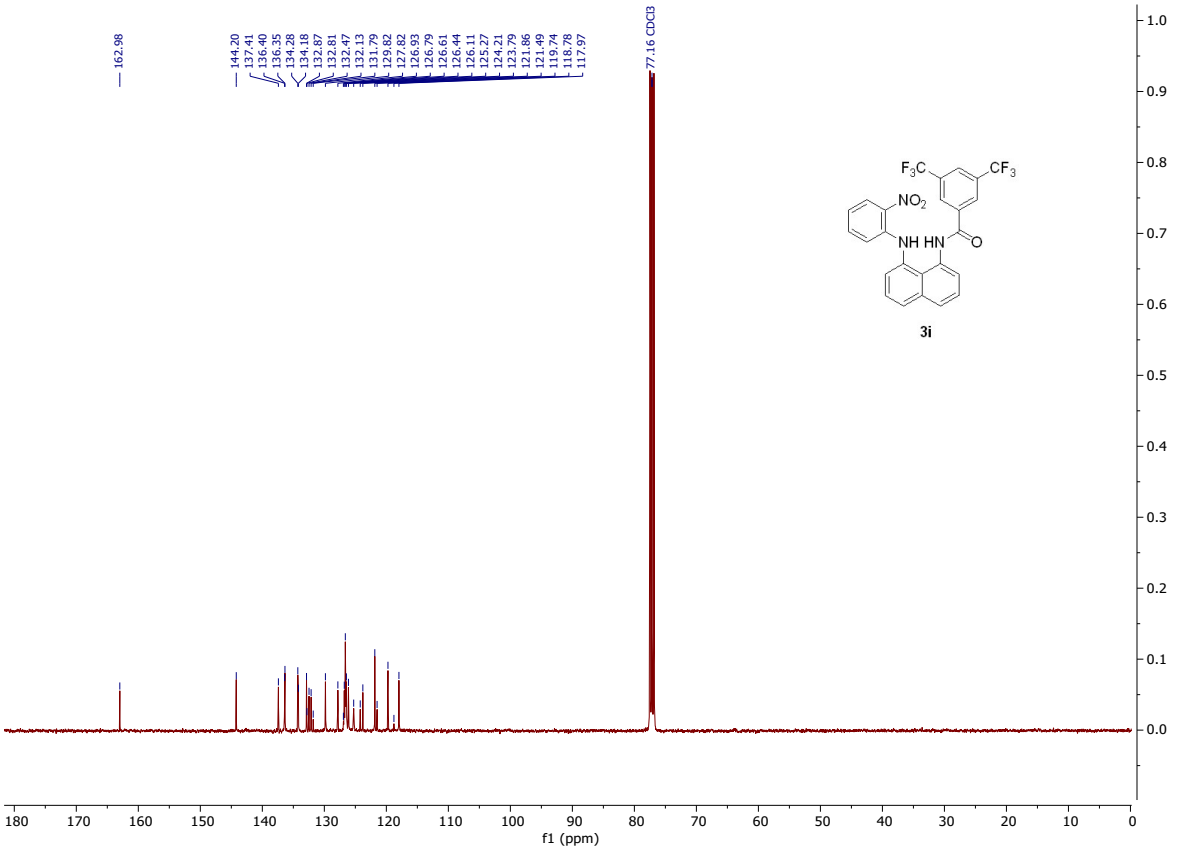
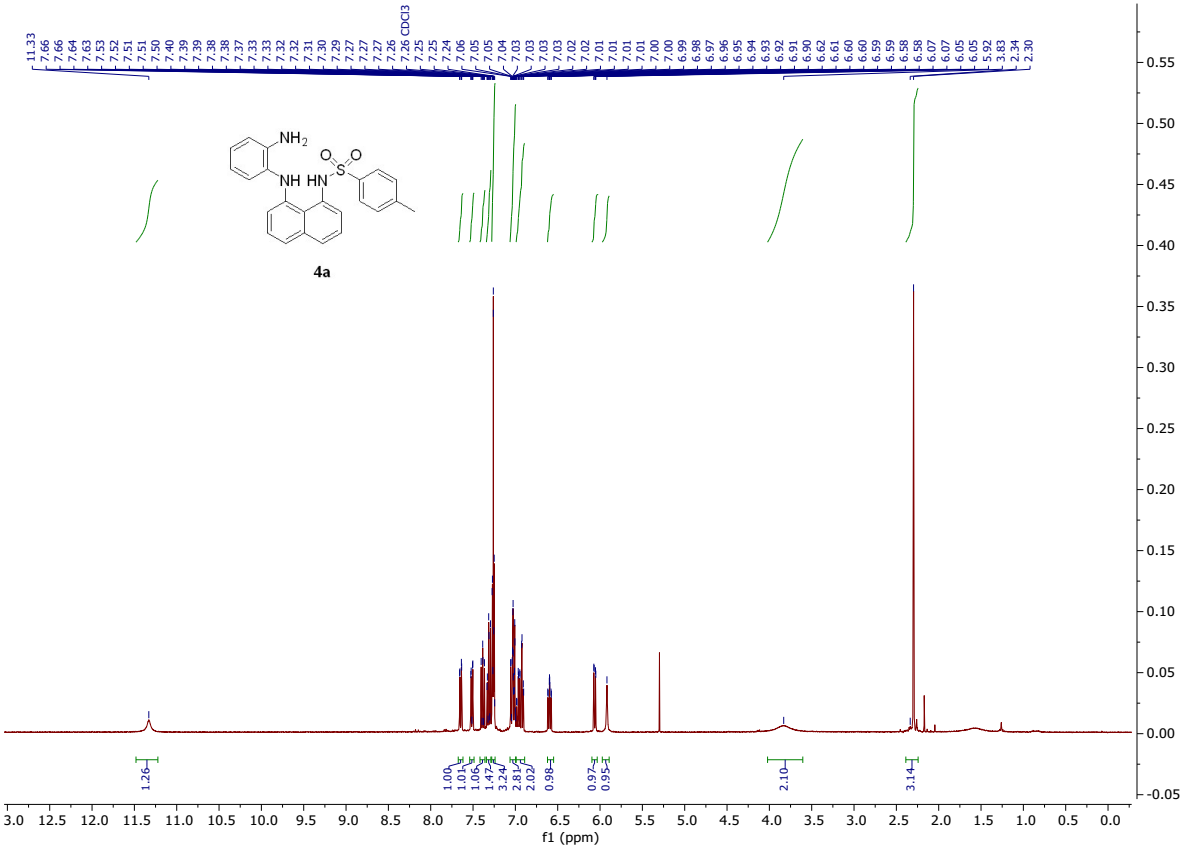


N-(8-((2-Aminophenyl)amino)naphthalen-1-yl)-4-methylbenzenesulfonamide 4a

^{1}H NMR



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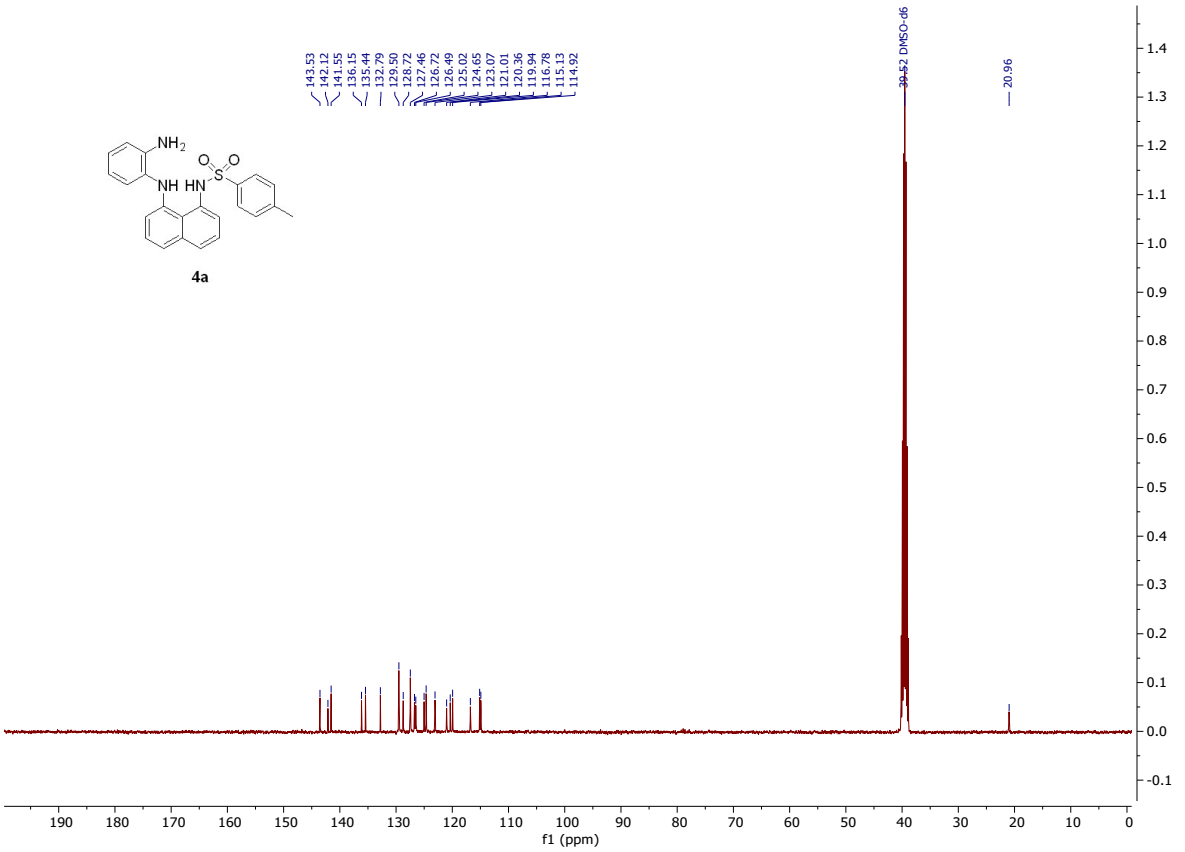
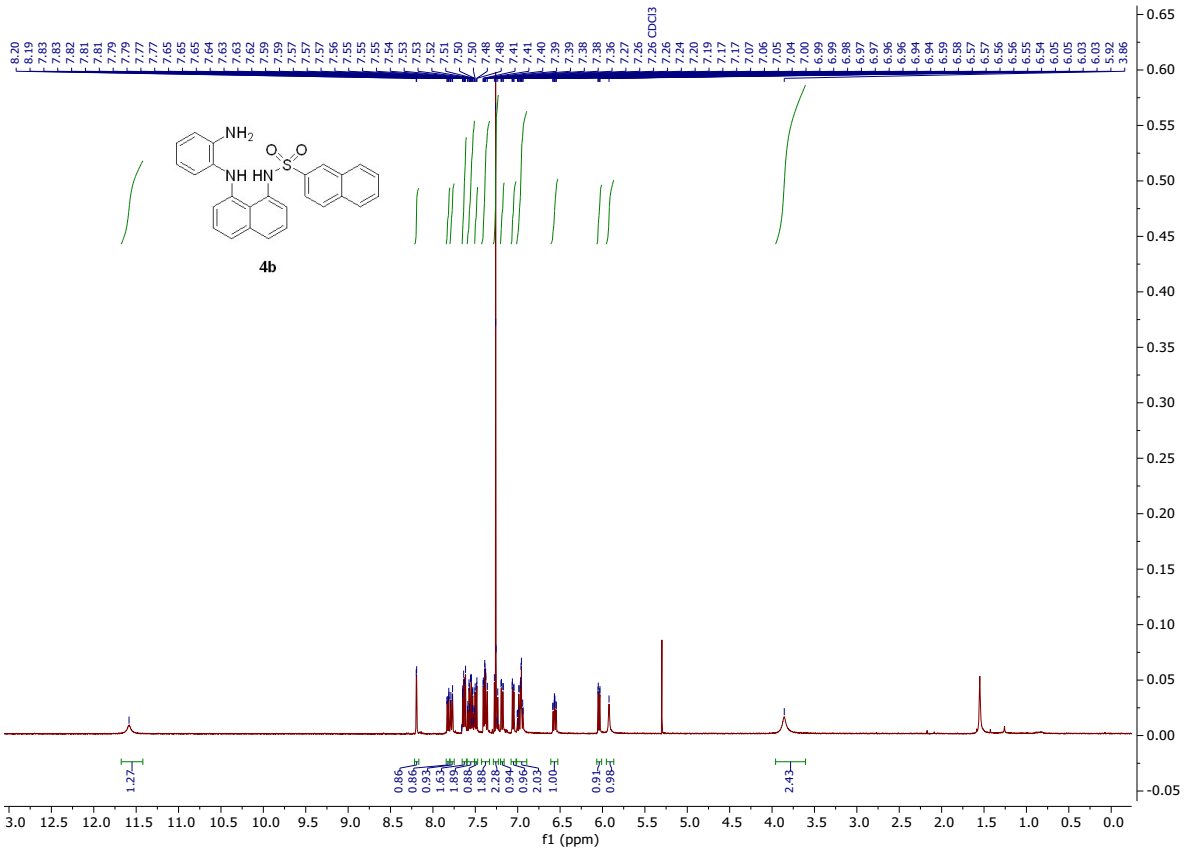


N-(8-((2-aminophenyl)amino)naphthalen-1-yl)naphthalene-2-sulfonamide 4b

^{1}H NMR



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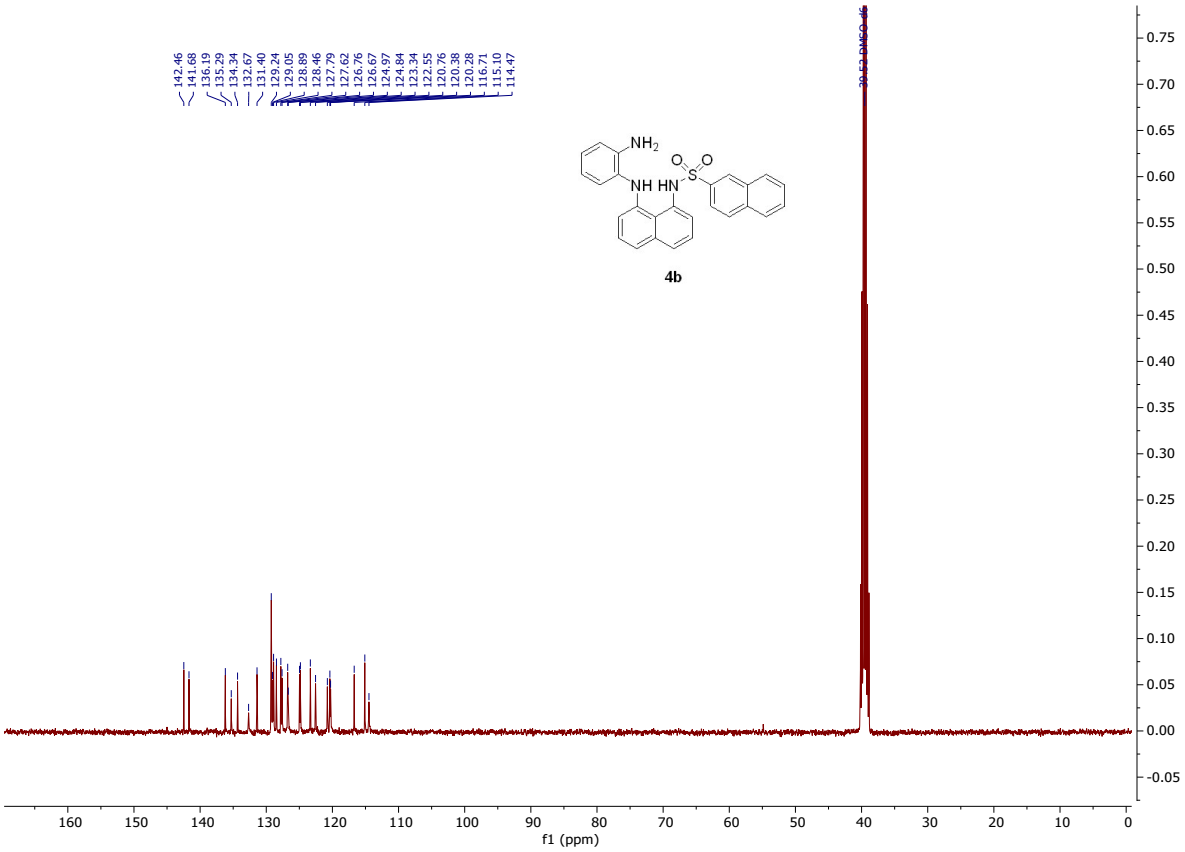
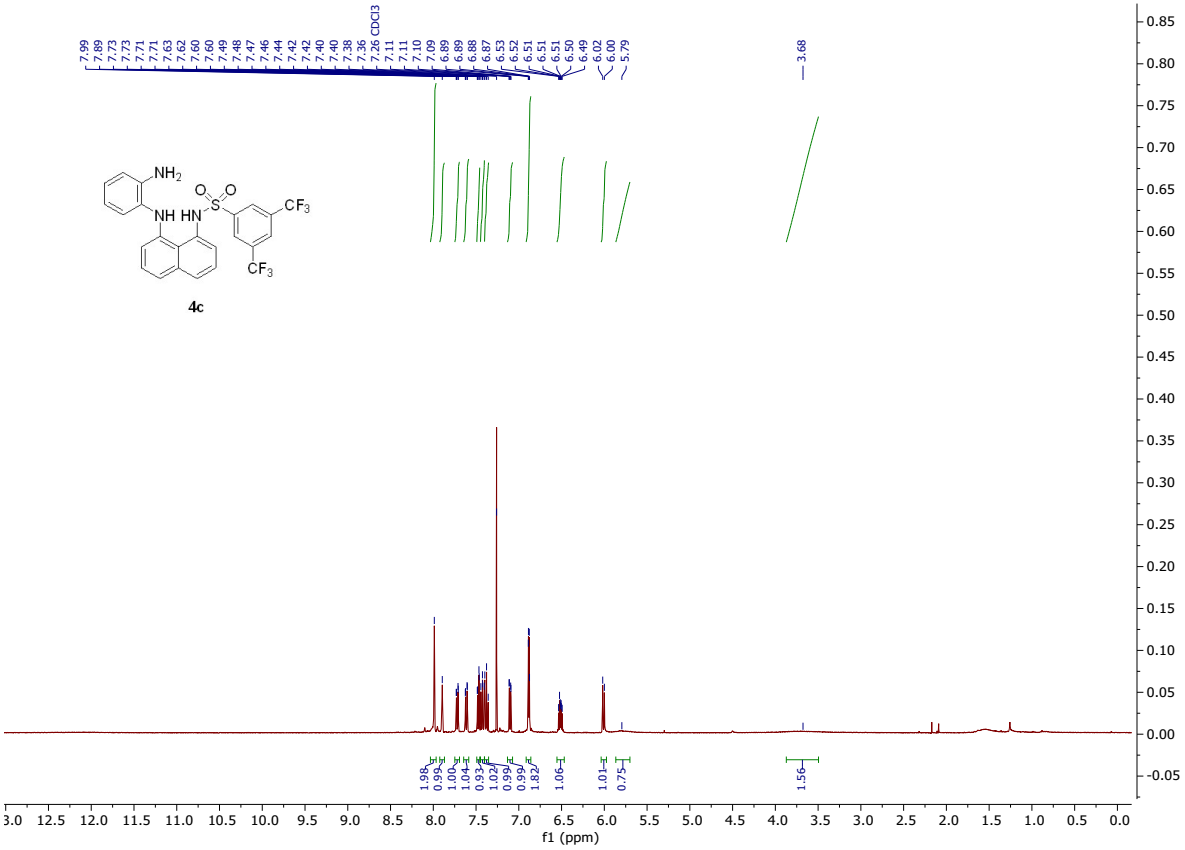


N-(8-((2-aminophenyl)amino)naphthalen-1-yl)-3,5-bis(trifluoromethyl)benzenesulfonamide 4c

^{1}H NMR



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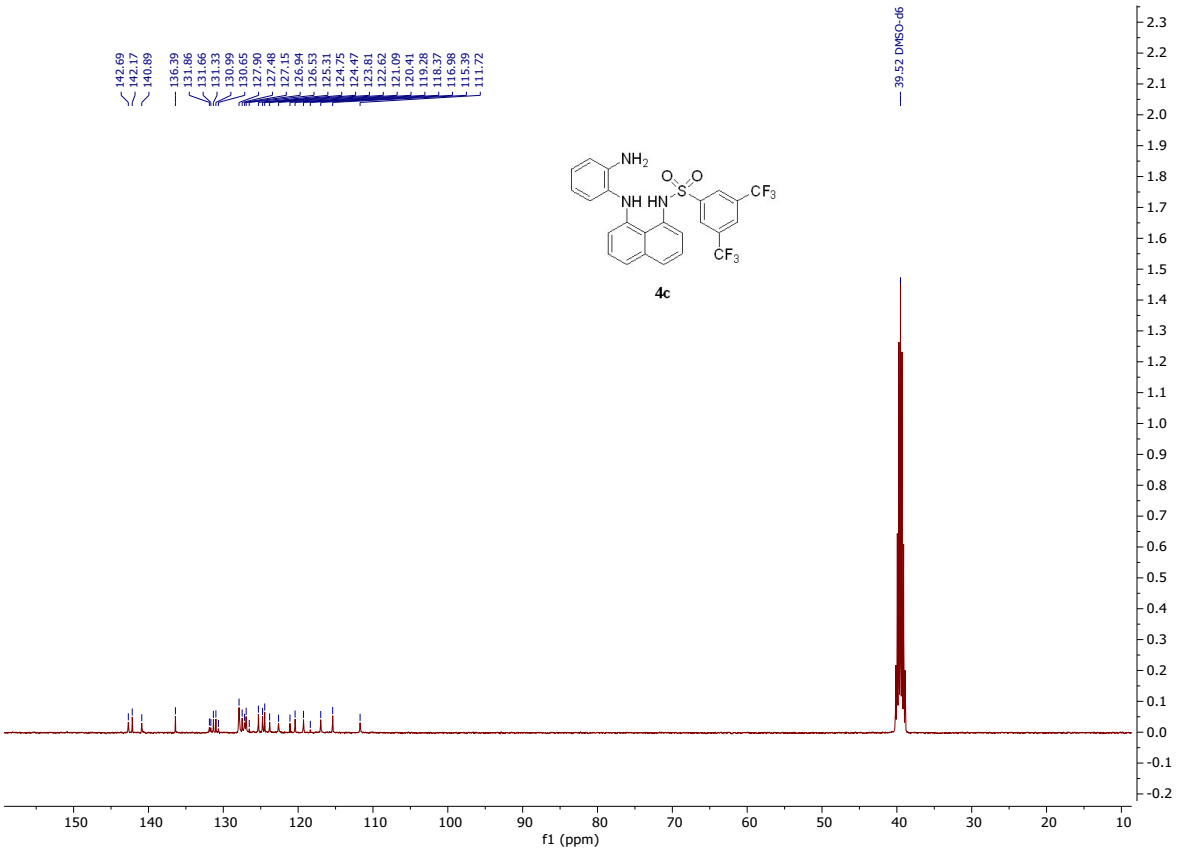
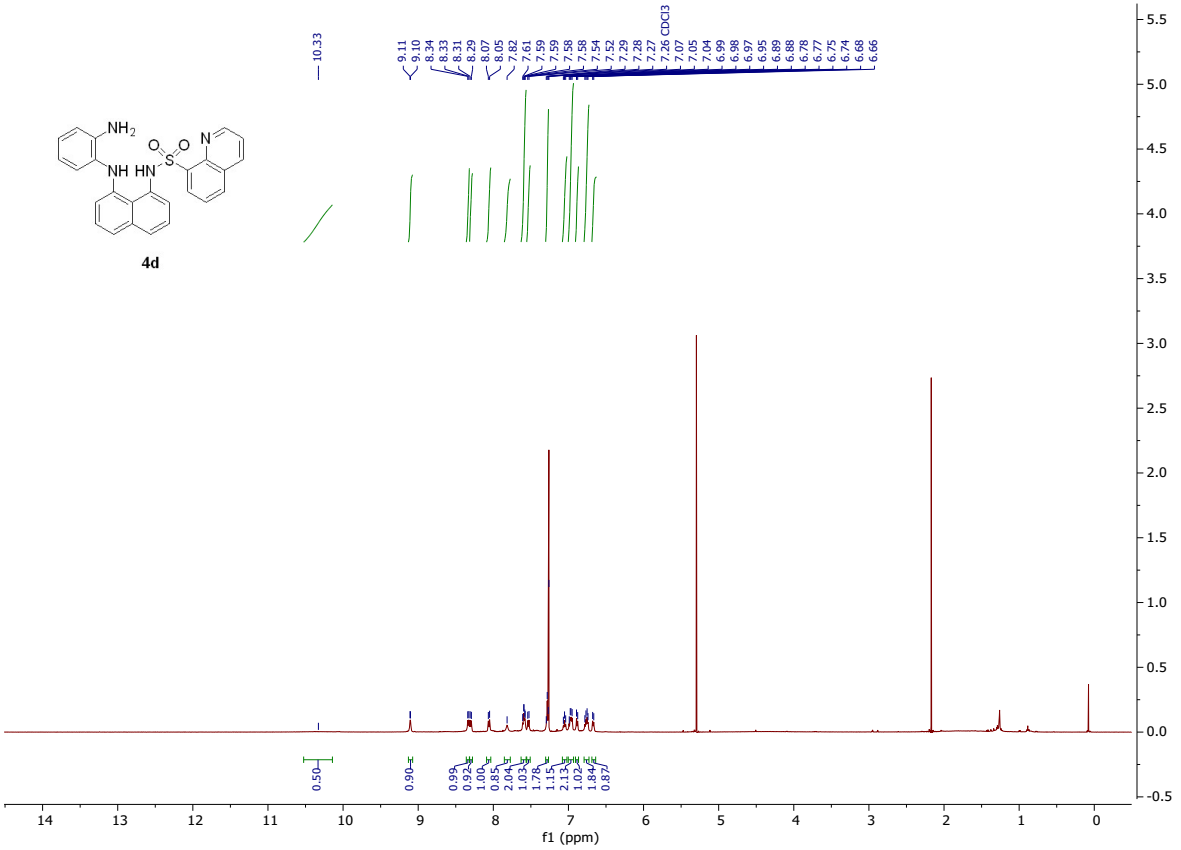


N-(8-((2-nitrophenyl)amino)naphthalen-1-yl)quinoline-8-sulfonamide 4d

^{1}H NMR



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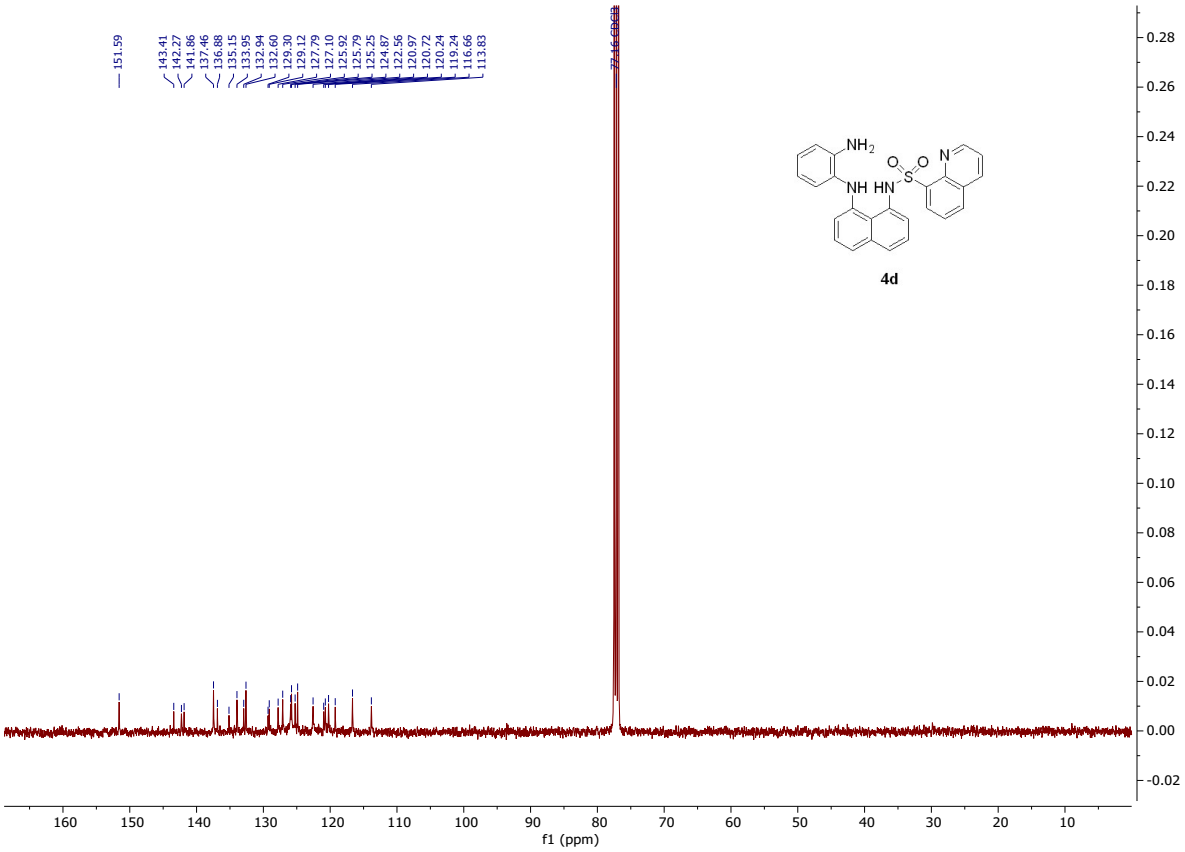
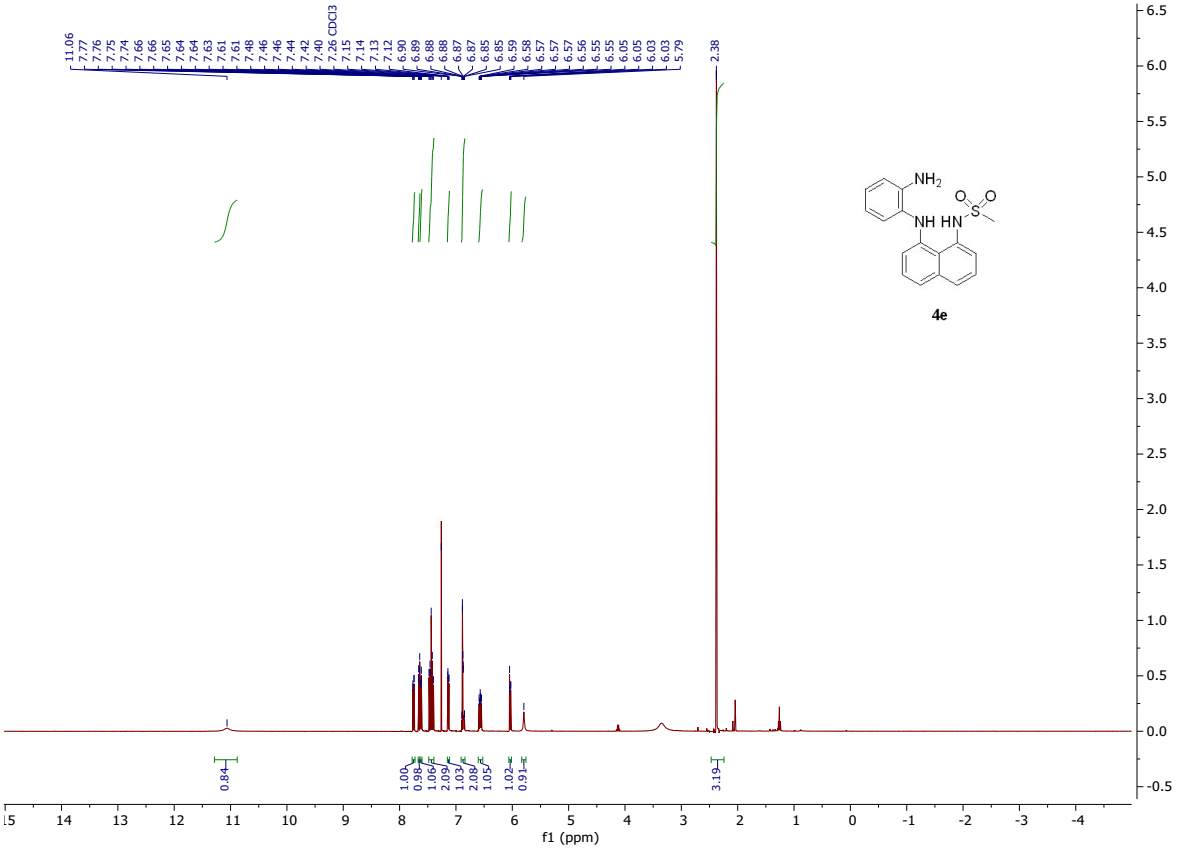
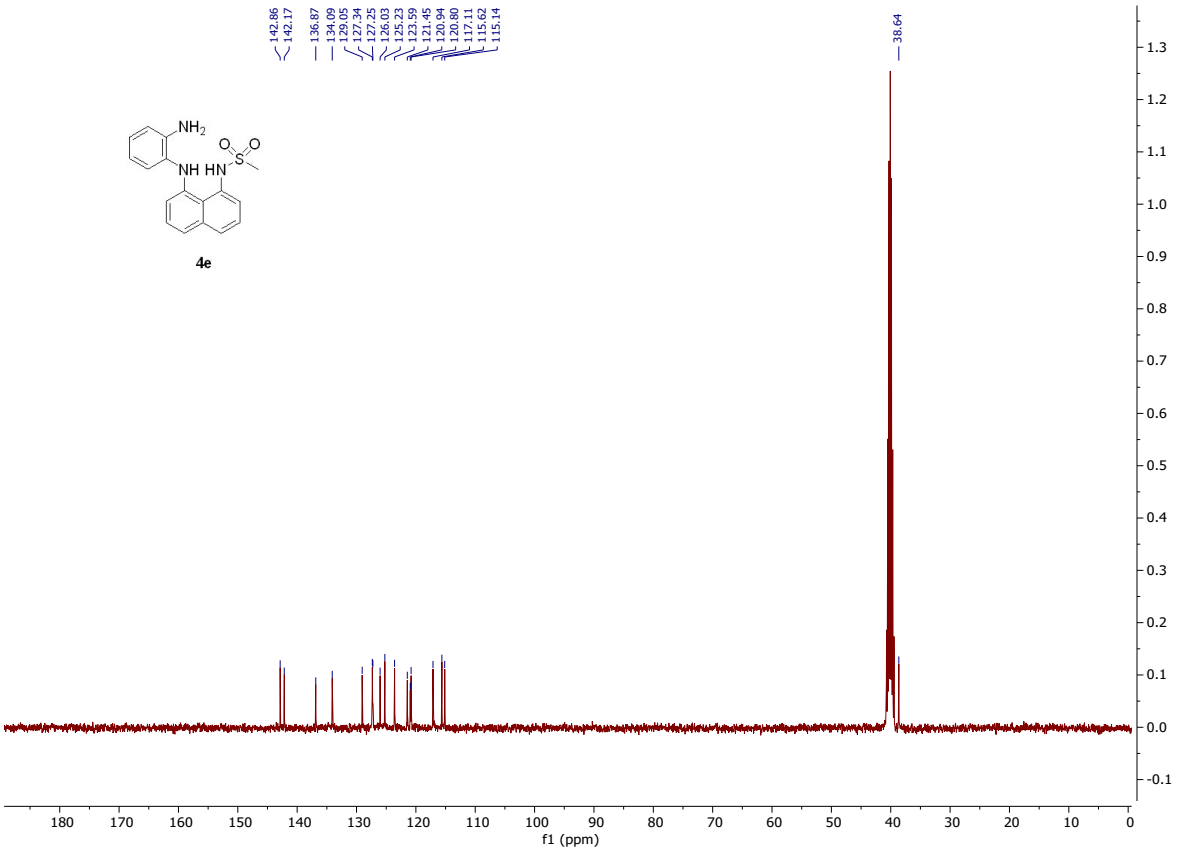


N-(8-((2-Aminophenyl)amino)naphthalen-1-yl)methanesulfonamide 4e

^{1}H NMR

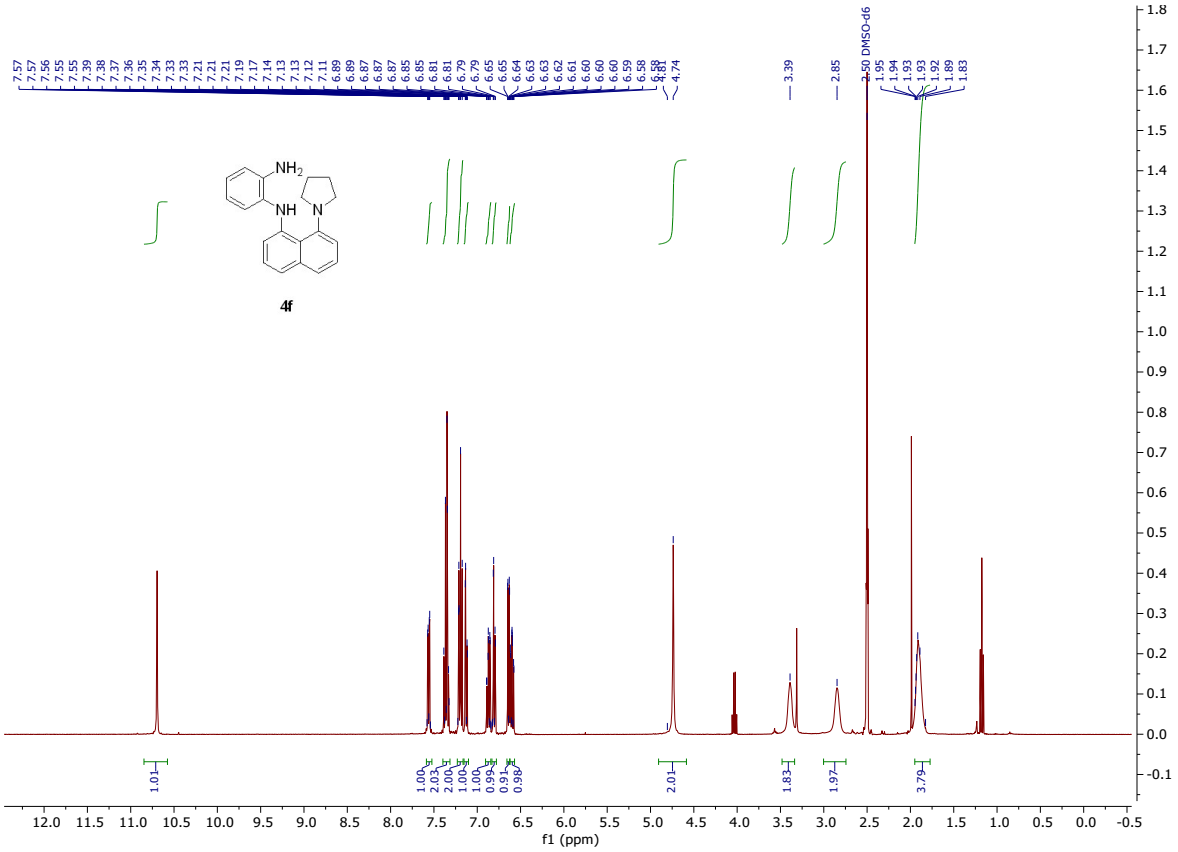


^{13}C NMR



N[1]-(8-(Pyrrolidin-1-yl)naphthalen-1-yl)benzene-1,2-diamine 4f

^{1}H NMR



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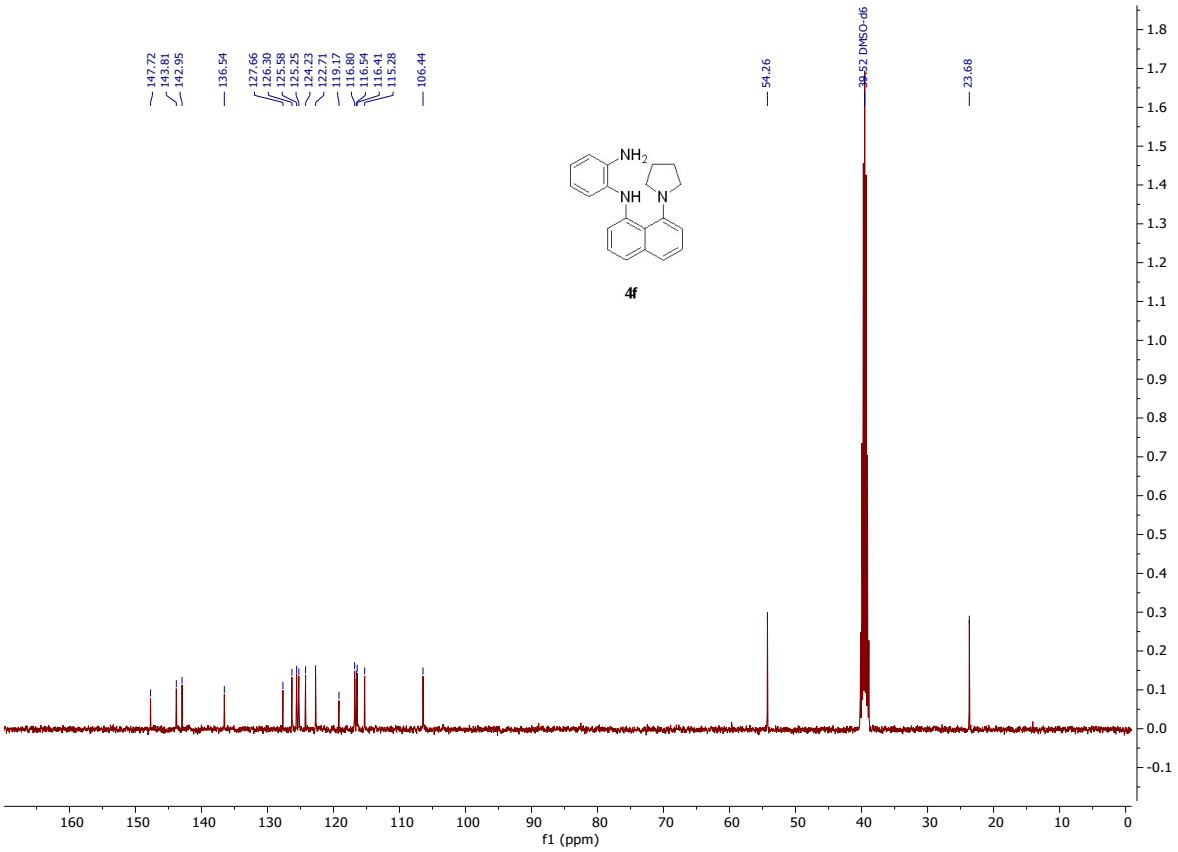
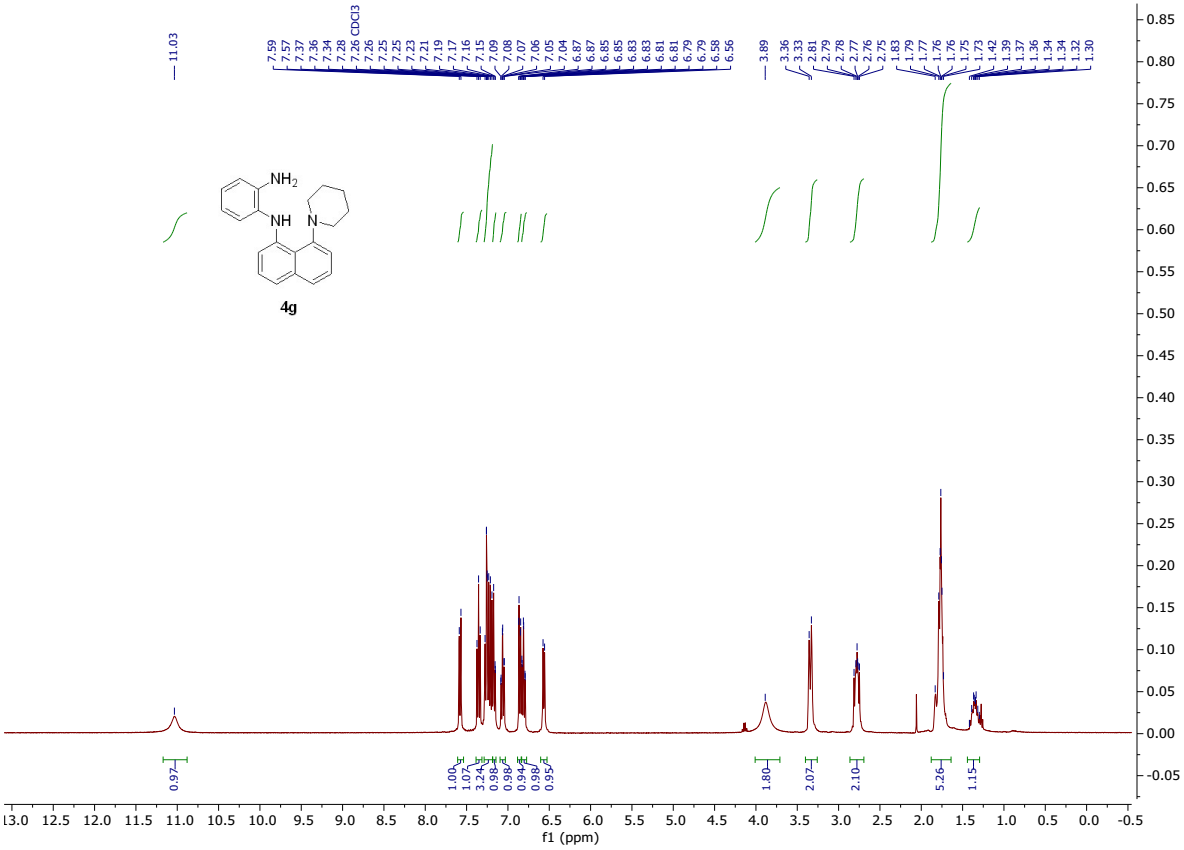


N[1]-(8-(Piperidin-1-yl)naphthalen-1-yl)benzene-1,2-diamine 4g

^{1}H NMR



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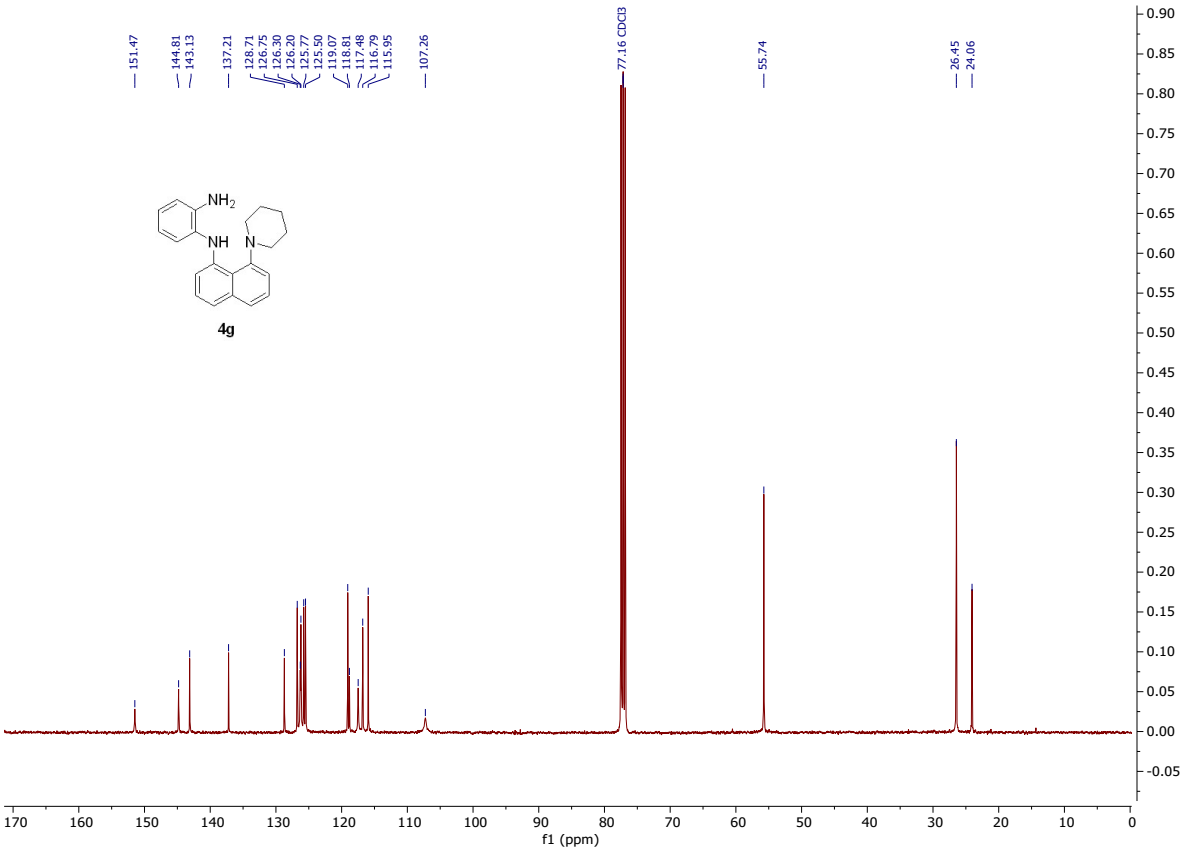
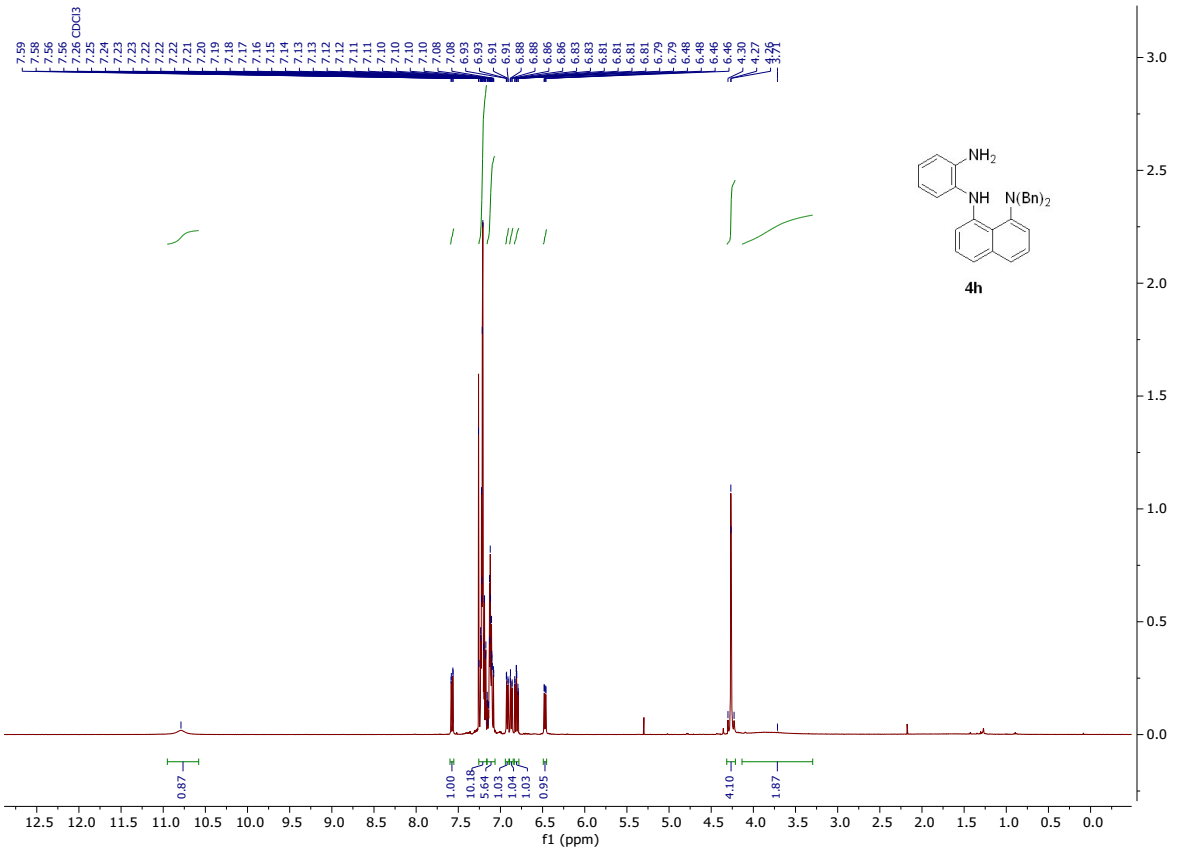


N^{1}-(2-Aminophenyl)-*N*^{8},*N*^{8}-dibenzylnaphthalene-1,8-diamine 4h

^{1}H NMR



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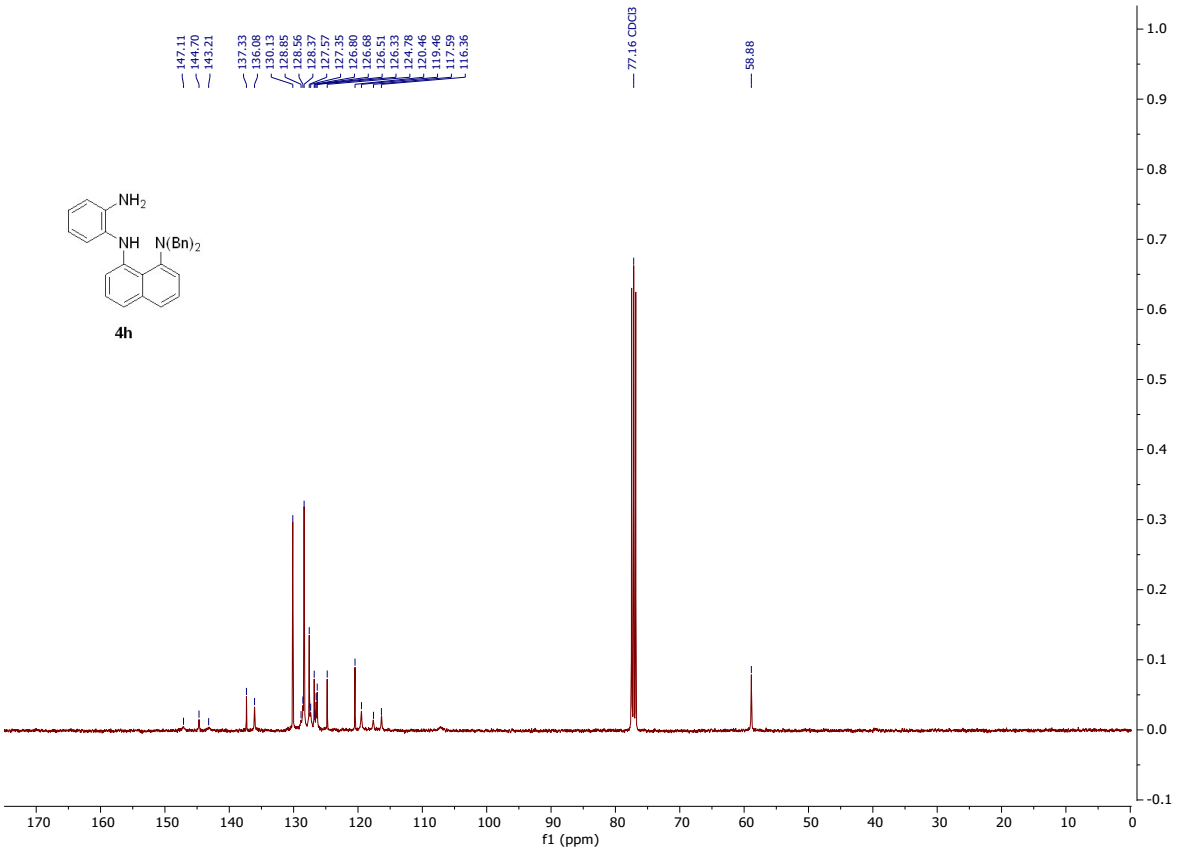
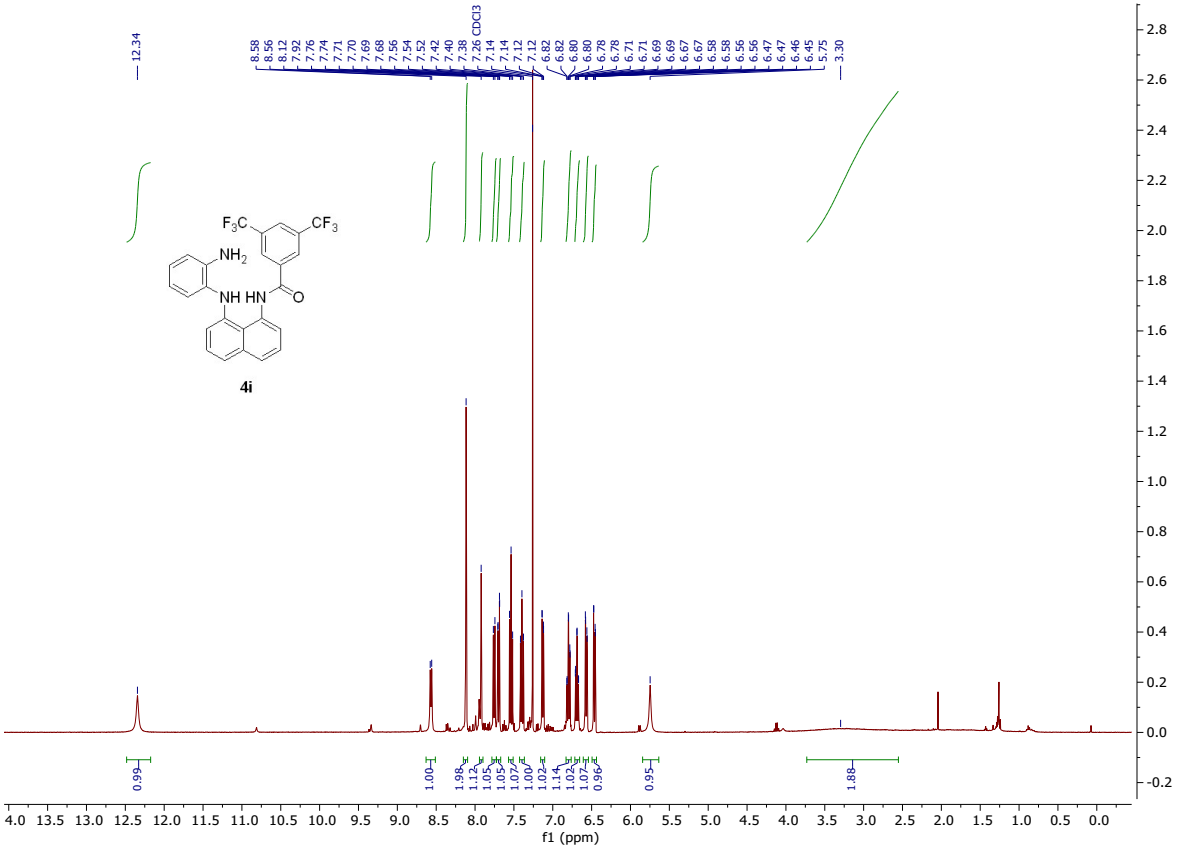


N-(8-((2-Aminophenyl)amino)naphthalen-1-yl)-3,5-bis(trifluoromethyl)benzamide 4i

^{1}H NMR



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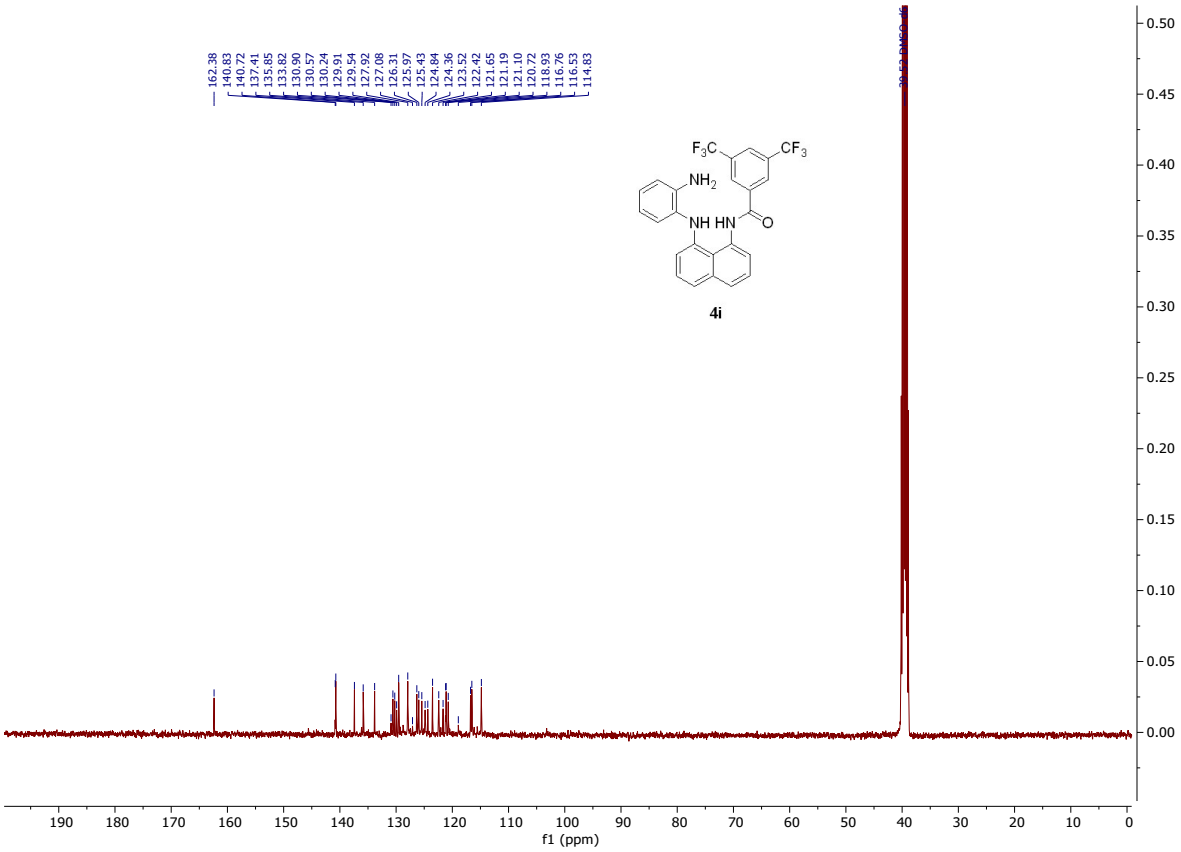
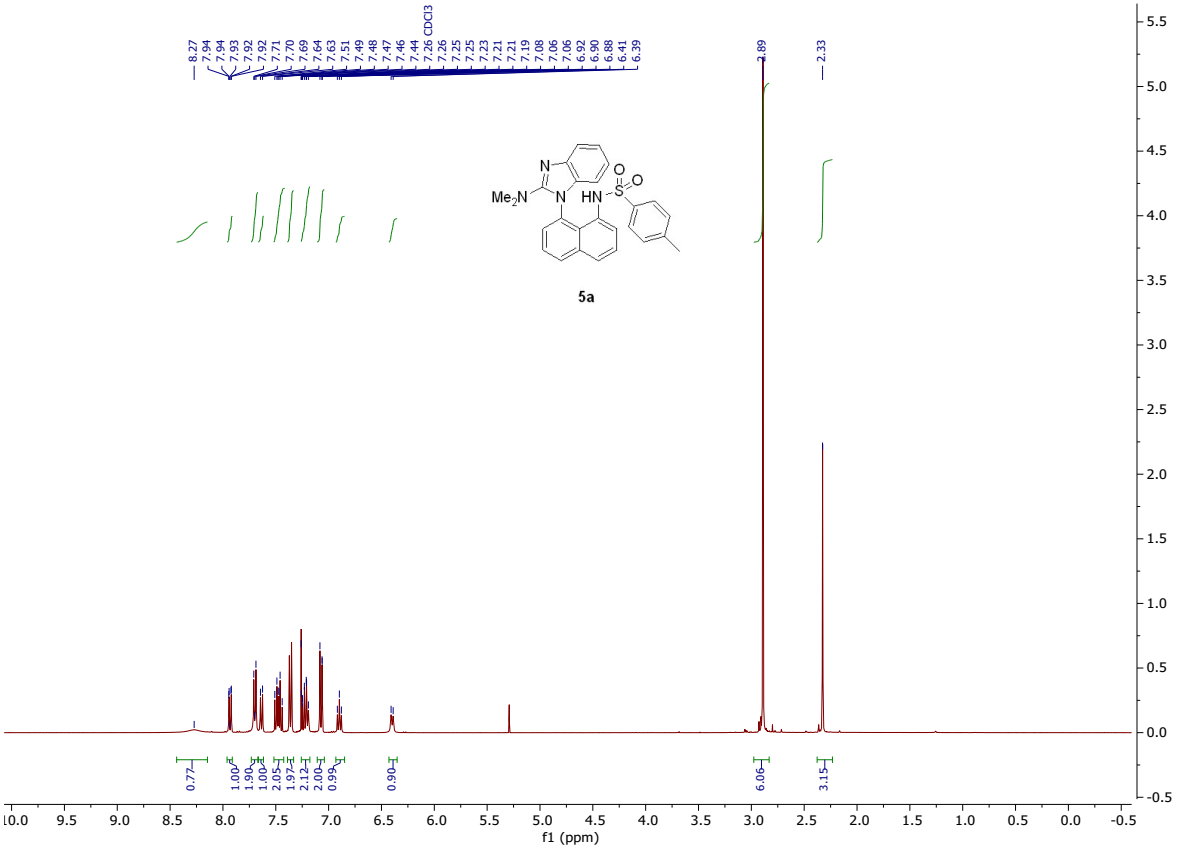


N-(8-(2-(dimethylamino)-*1H*-benzimidazol-1-yl)naphthalen-1-yl)-4-methylbenzenesulfonamide 5a

^{1}H NMR



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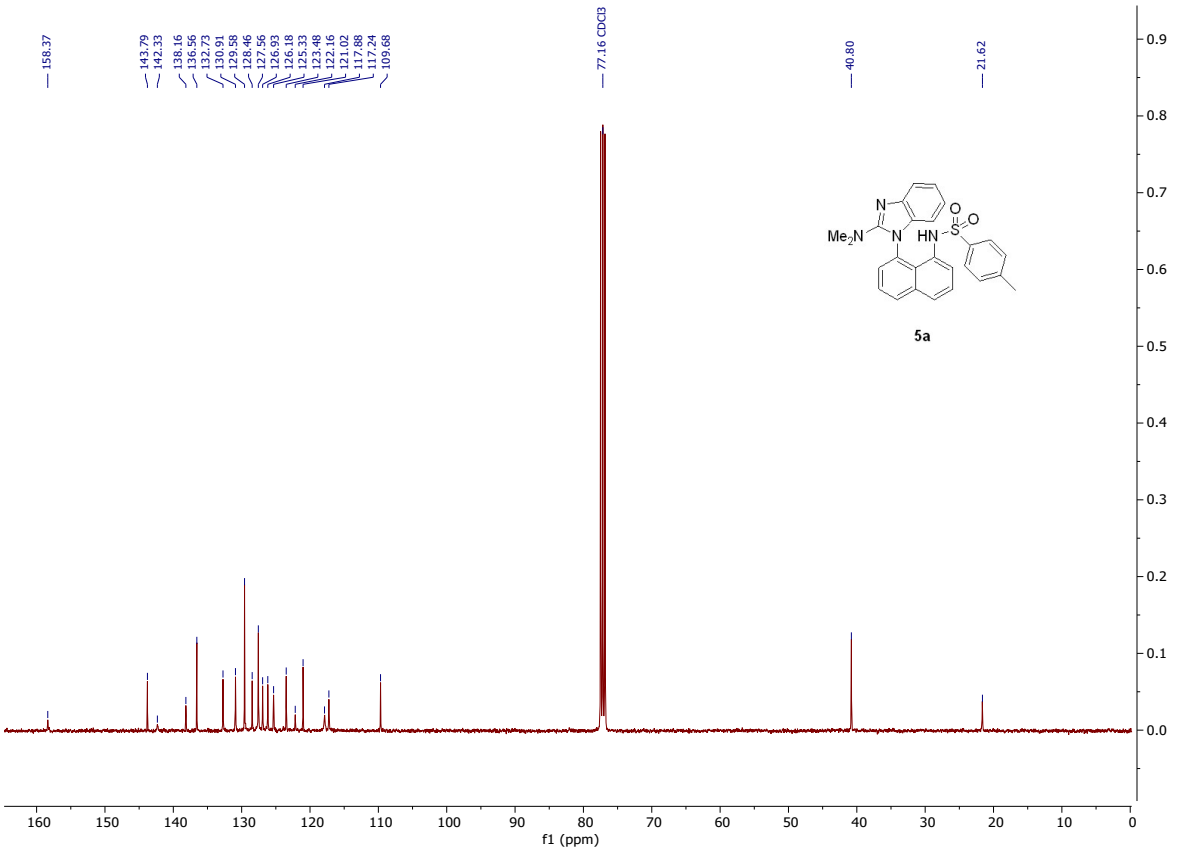
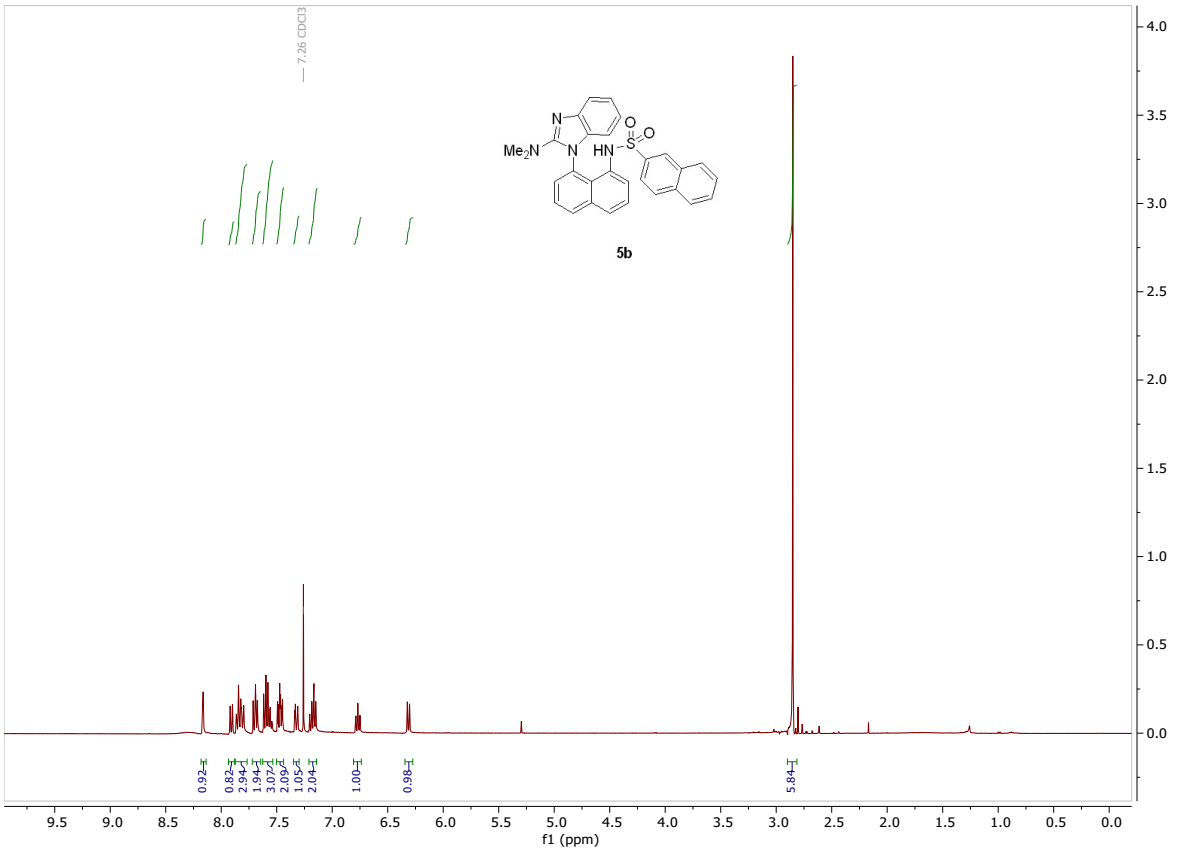


N-(8-(2-(dimethylamino)-*1H*-benzimidazol-1-yl)naphthalen-1-yl)naphthalene-2-sulfonamide 5b

^{1}H NMR



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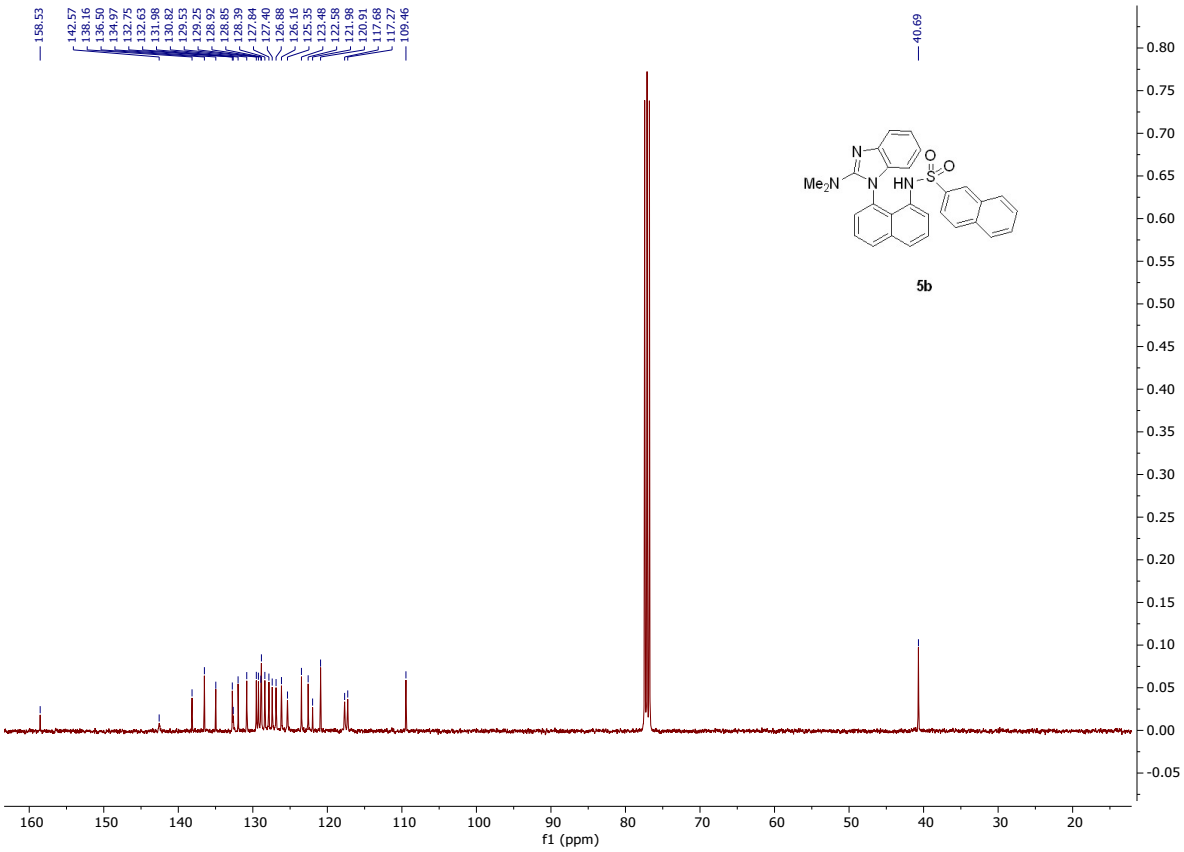
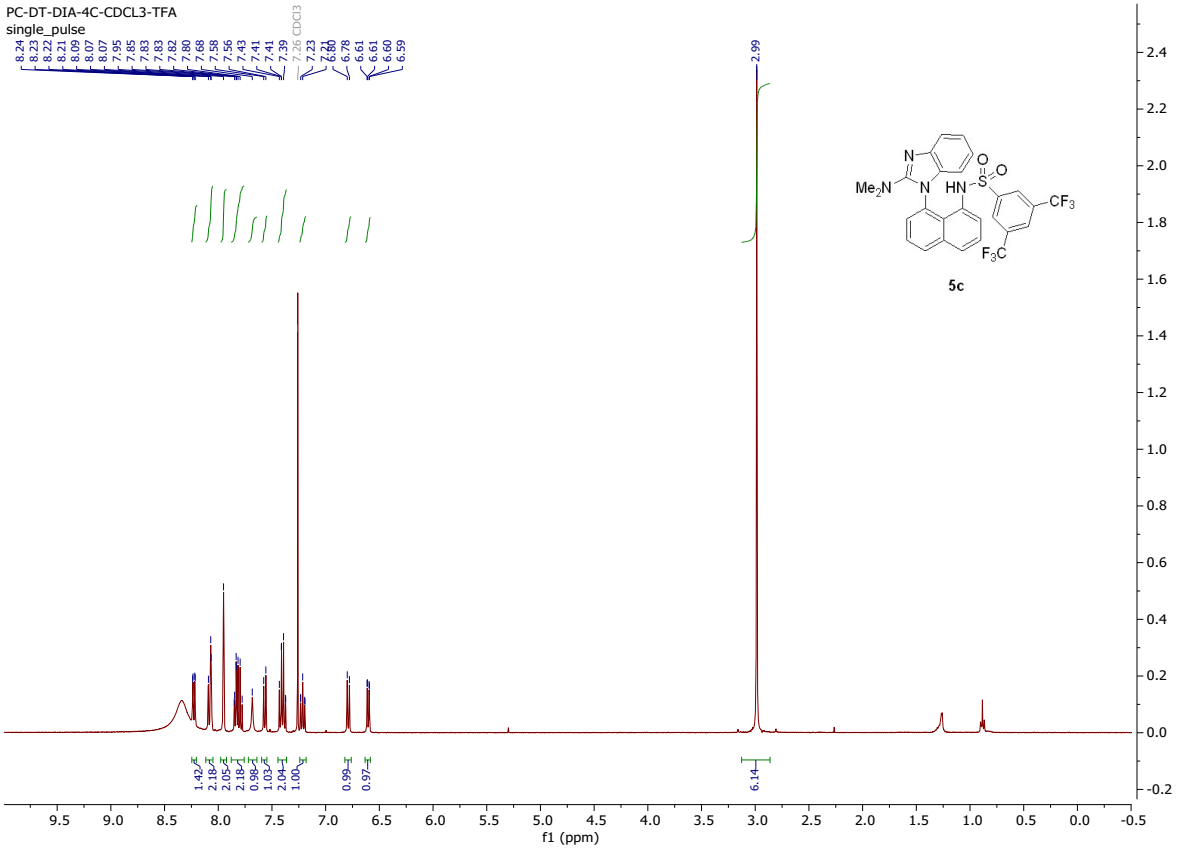


N-(8-(2-(dimethylamino)-*1H*-benzimidazol-1-yl)naphthalen-1-yl)-3,5-bis(trifluoromethyl)benzenesulfonamide 5c

^{1}H NMR ($CDCl_3$ + TFA):



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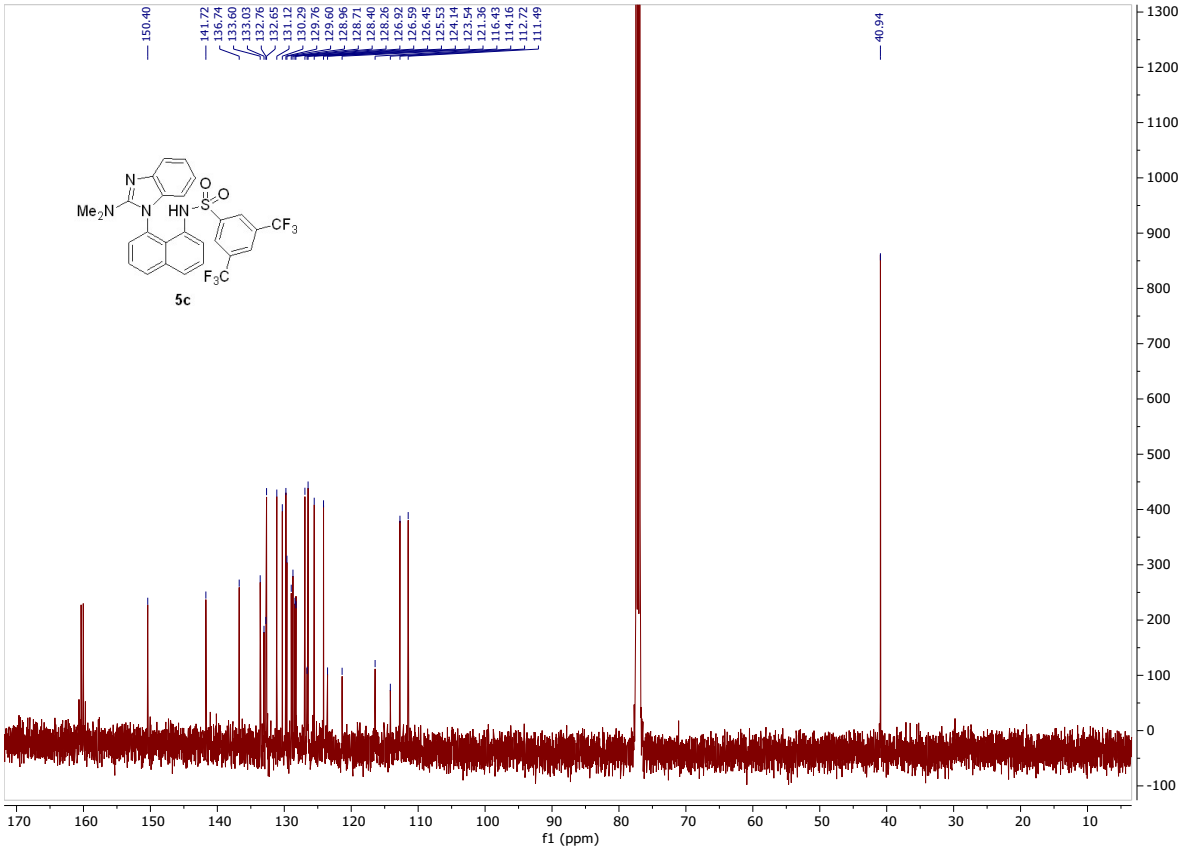
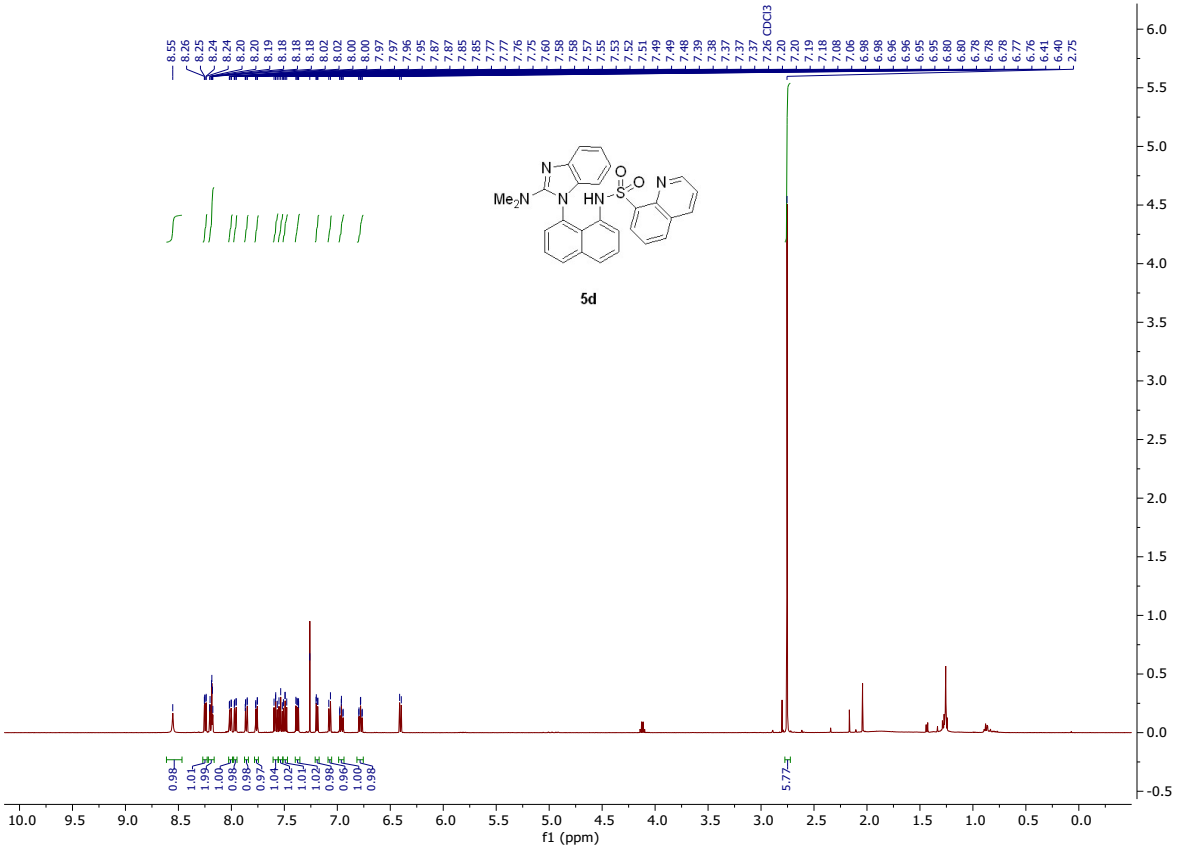


***N*-(8-(2-(dimethylamino)-*1H*-benzimidazol-1-yl)naphthalen-1-yl)quinoline-8-sulfonamide 5d**

^{1}H NMR



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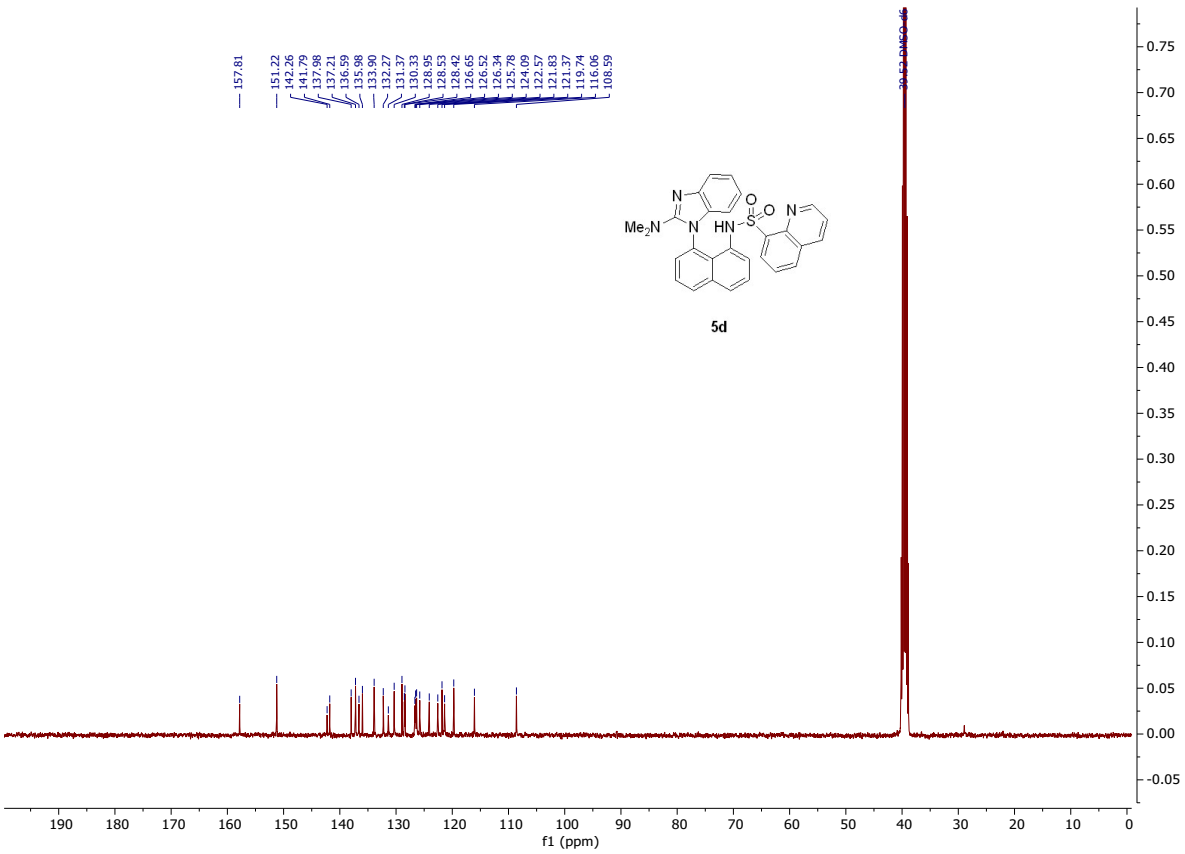
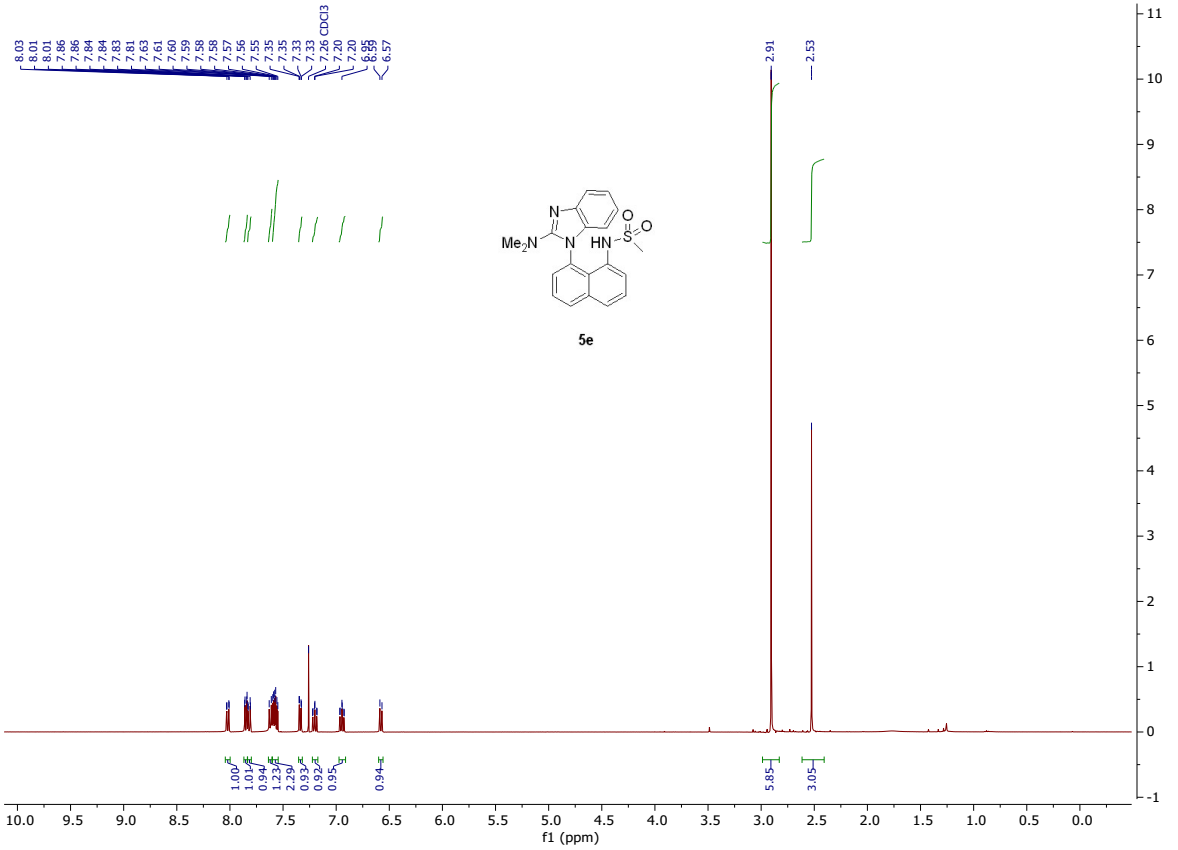


N-(8-(2-(dimethylamino)-*1H*-benzimidazol-1-yl)naphthalen-1-yl)methanesulfonamide 5e

^{1}H NMR



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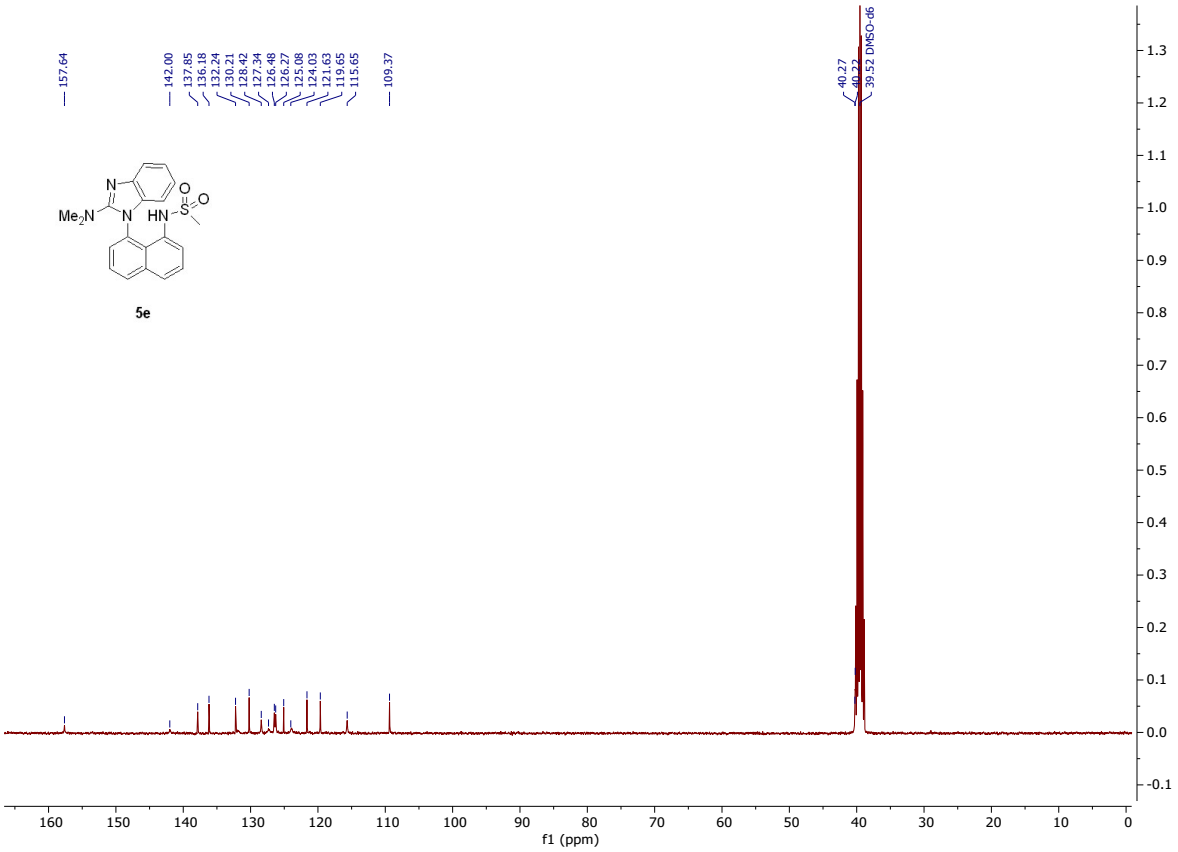
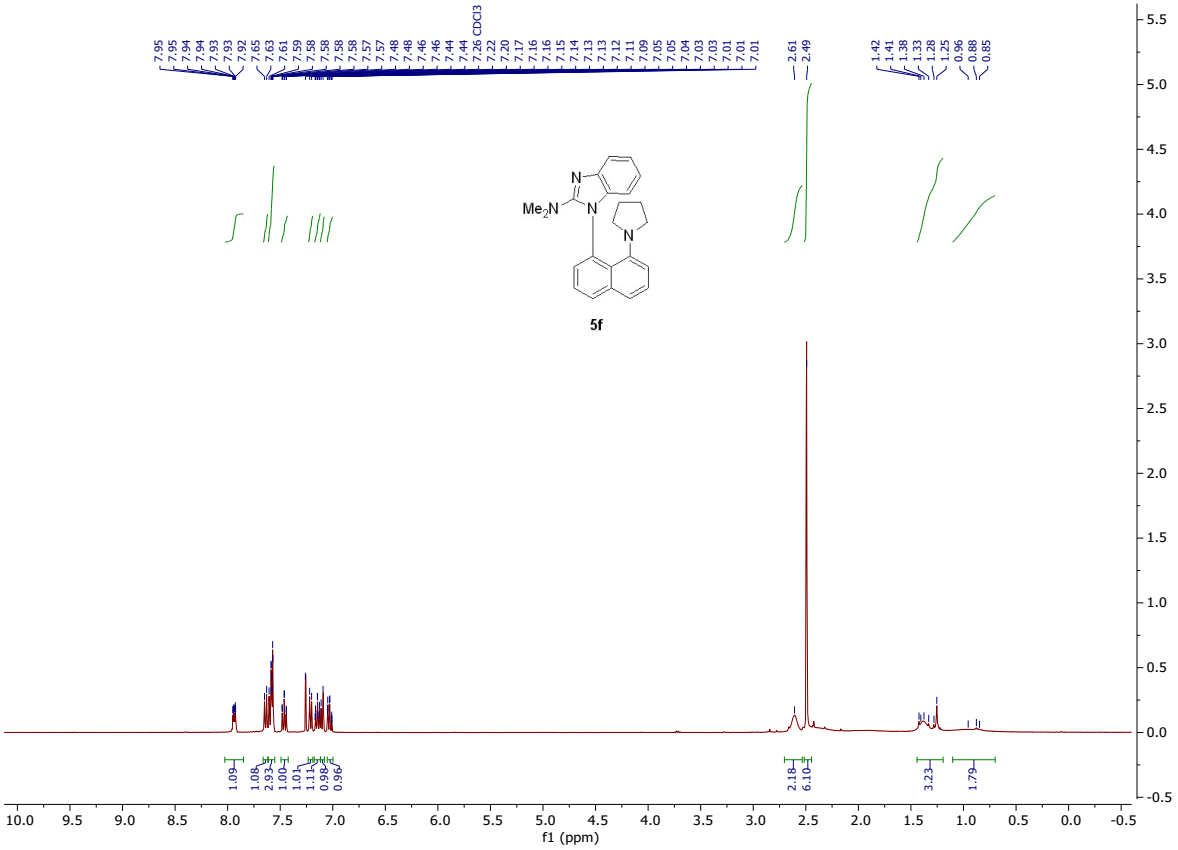
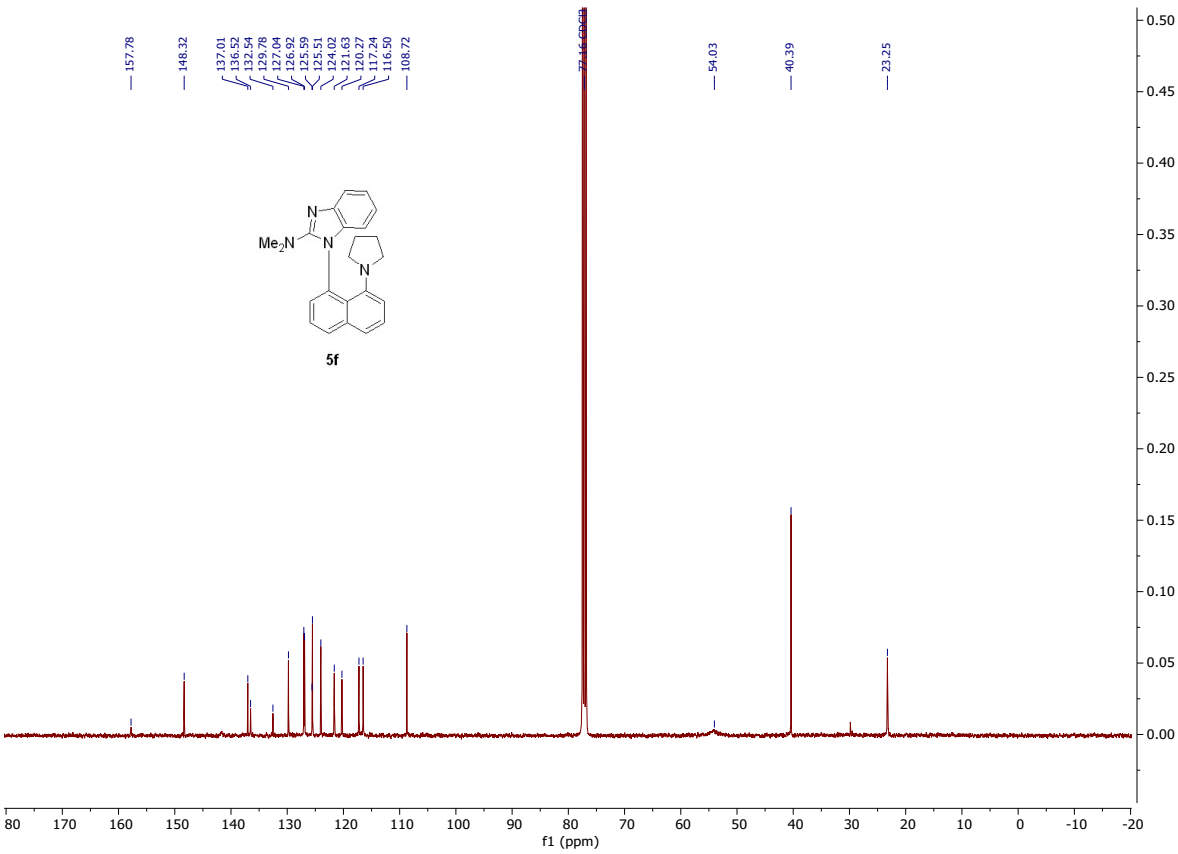


N,*N*-dimethyl-1-(8-(pyrrolidin-1-yl)naphthalen-1-yl)-*1H*-benzimidazol-2-amine 5f

^{1}H NMR

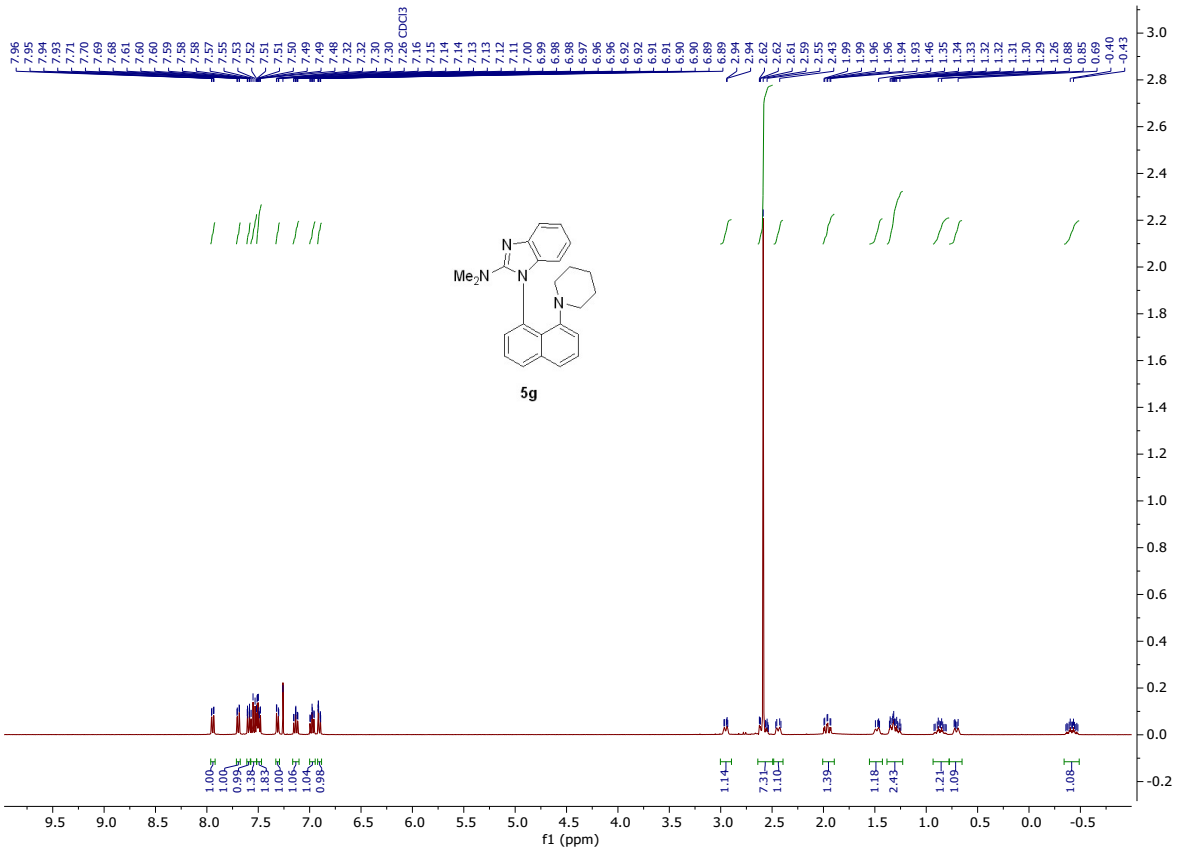


^{13}C NMR

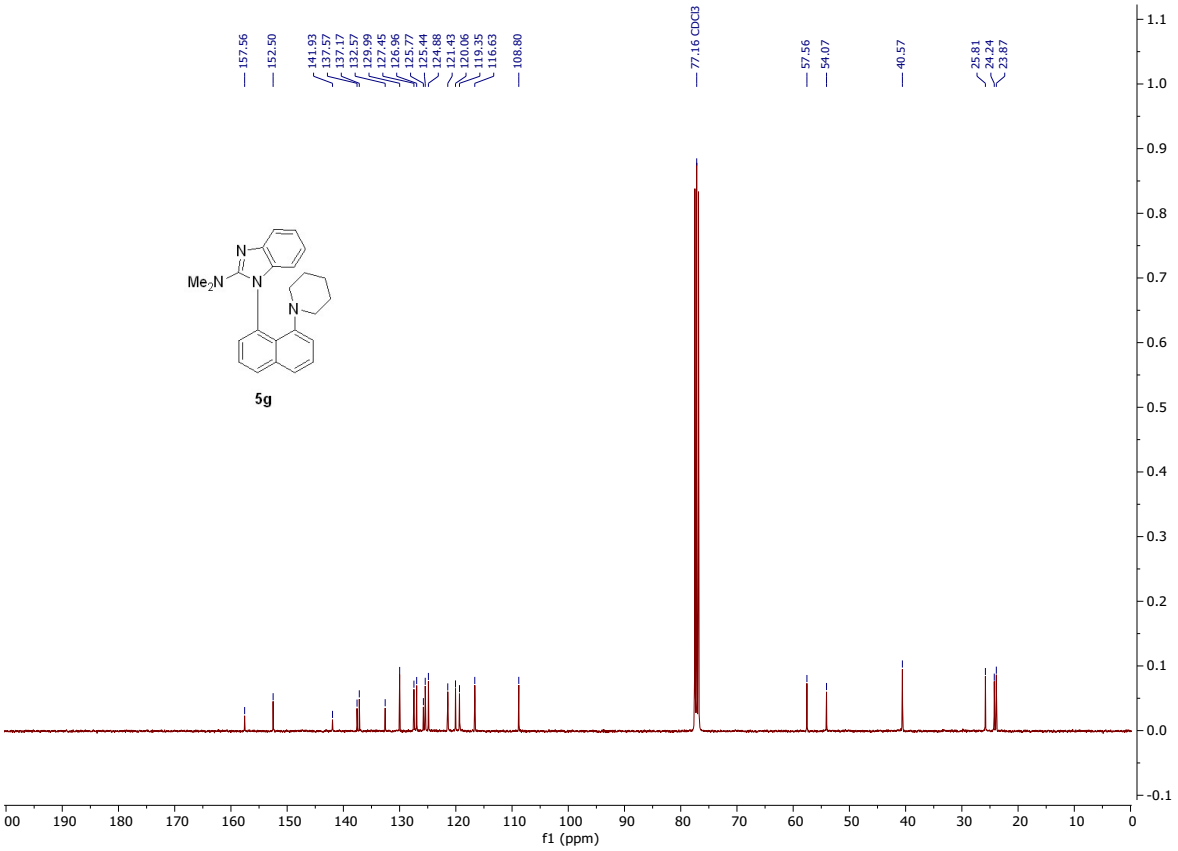


N,*N*-dimethyl-1-(8-(piperidin-1-yl)naphthalen-1-yl)-1H-benzimidazol-2-amine 5g

^{1}H NMR

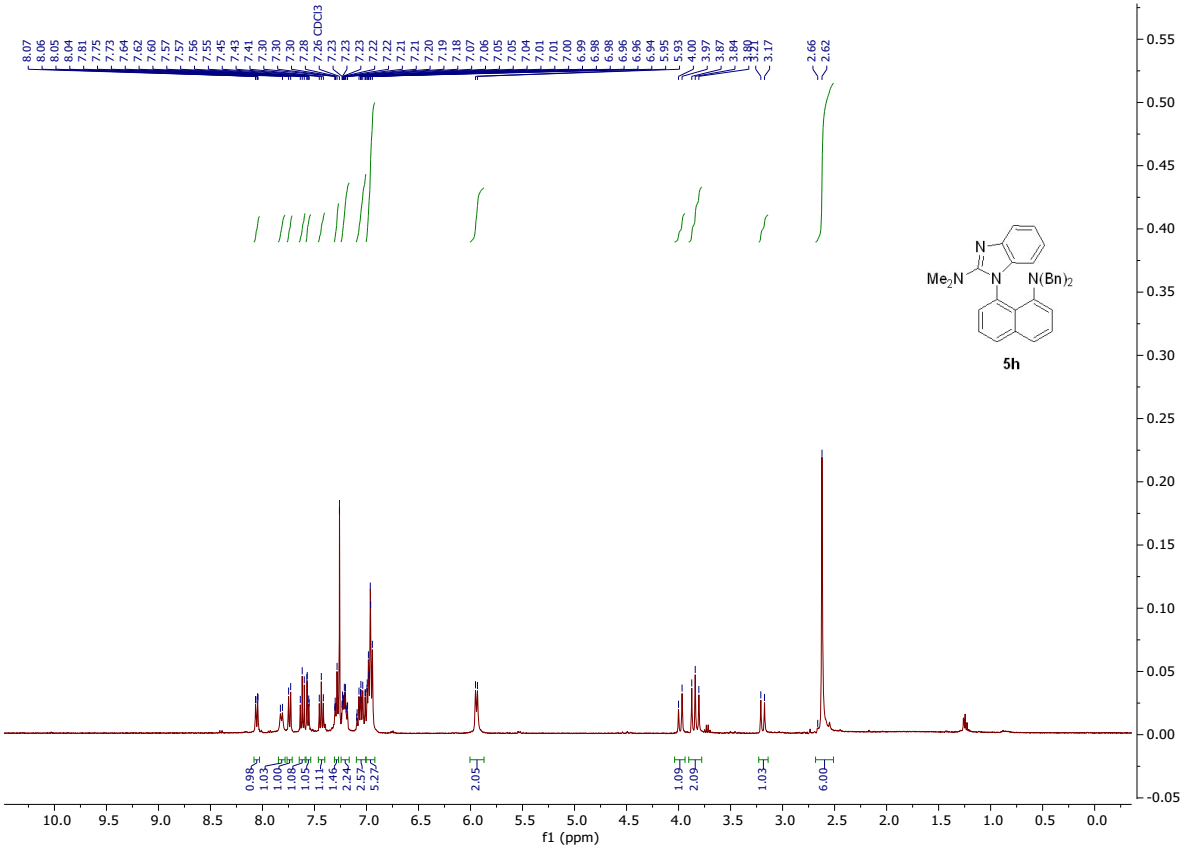


^{13}C NMR

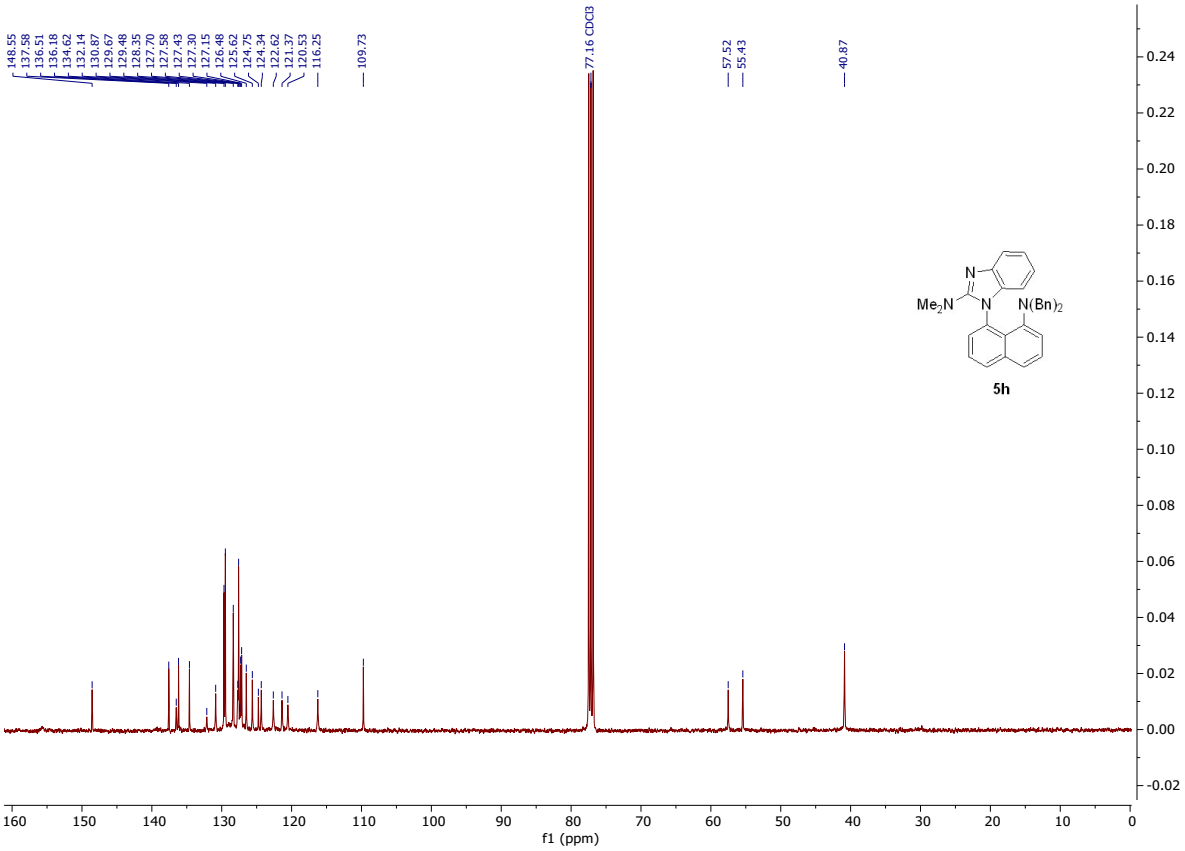


1-[8-(Dibenzylamino)naphthalen-1-yl]-*N*,*N*-dimethyl-*1H*-benzimidazol-2-amine 5h

^{1}H NMR

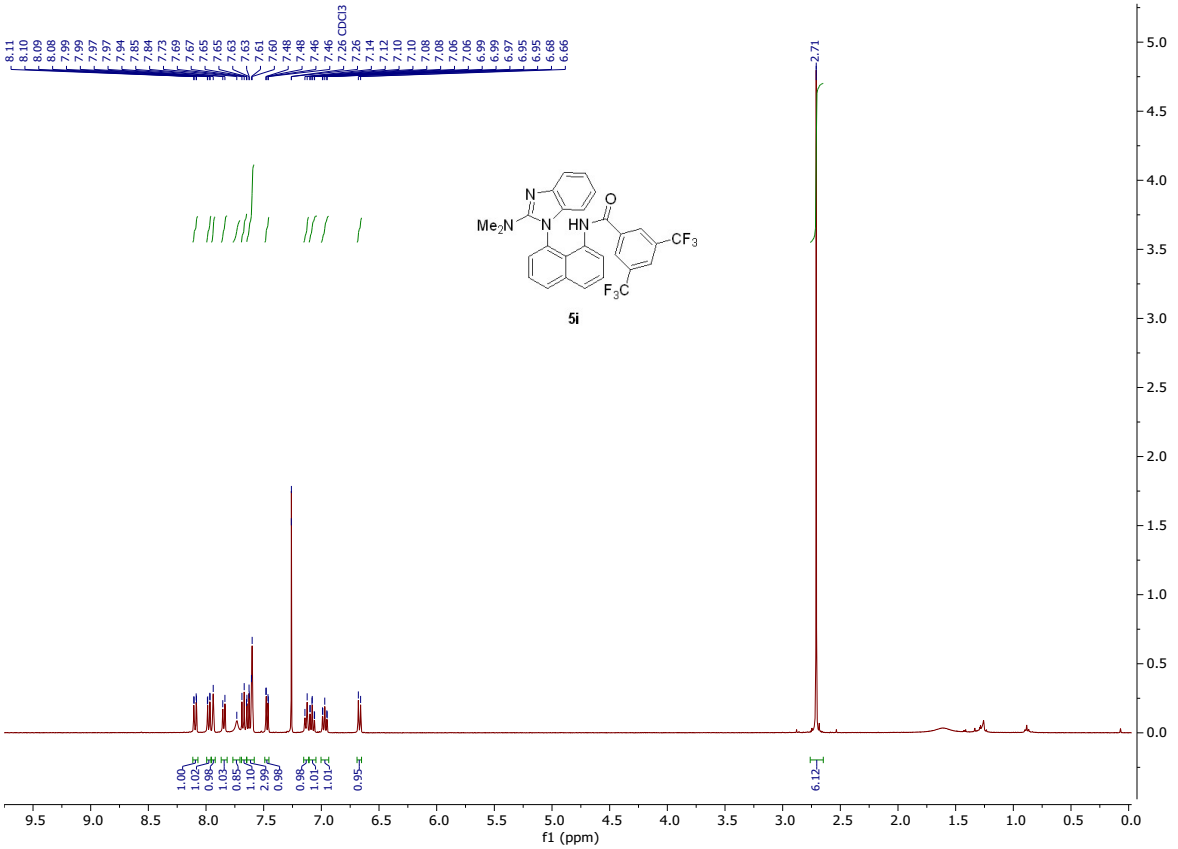


^{13}C NMR



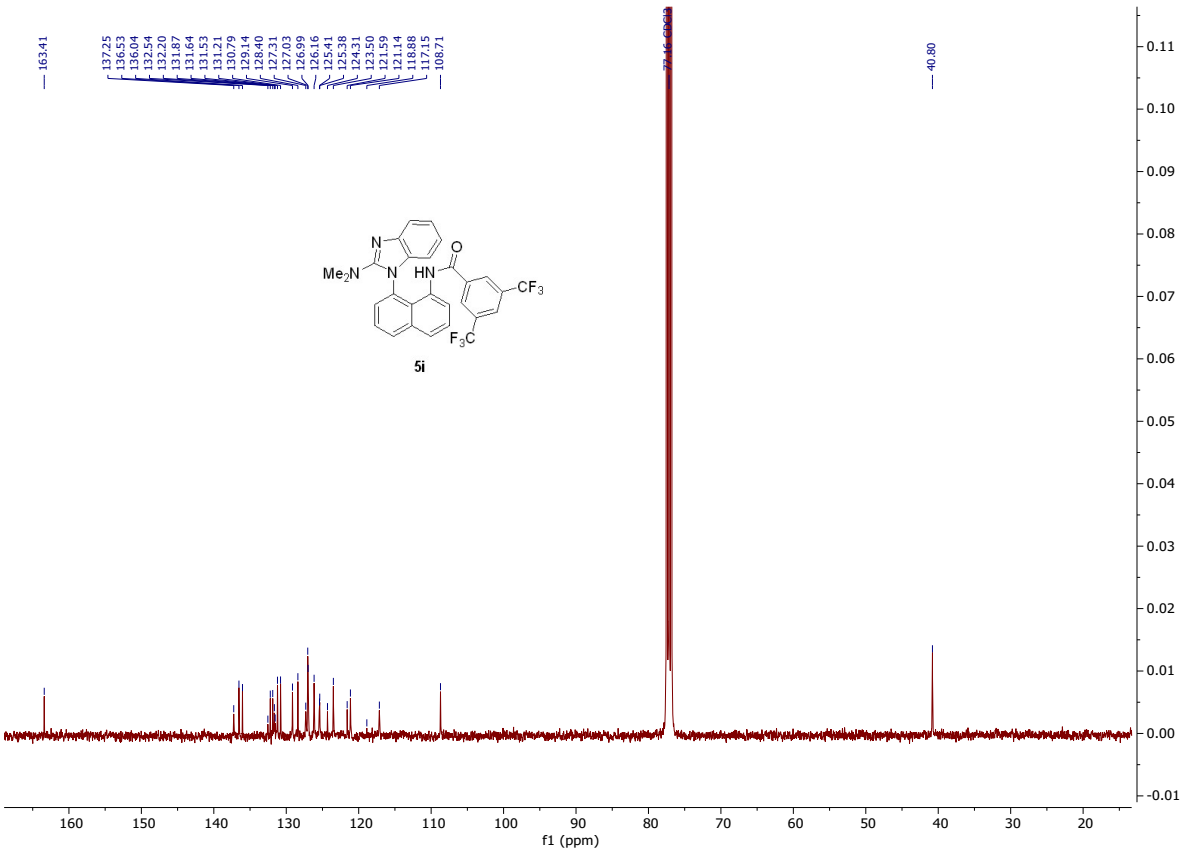
***N*-(8-(2-(Dimethylamino)-*1H*-benzimidazol-1-yl)naphthalen-1-yl)-3,5-bis(trifluoromethyl)benzamide 5i**

^{1}H NMR



5i

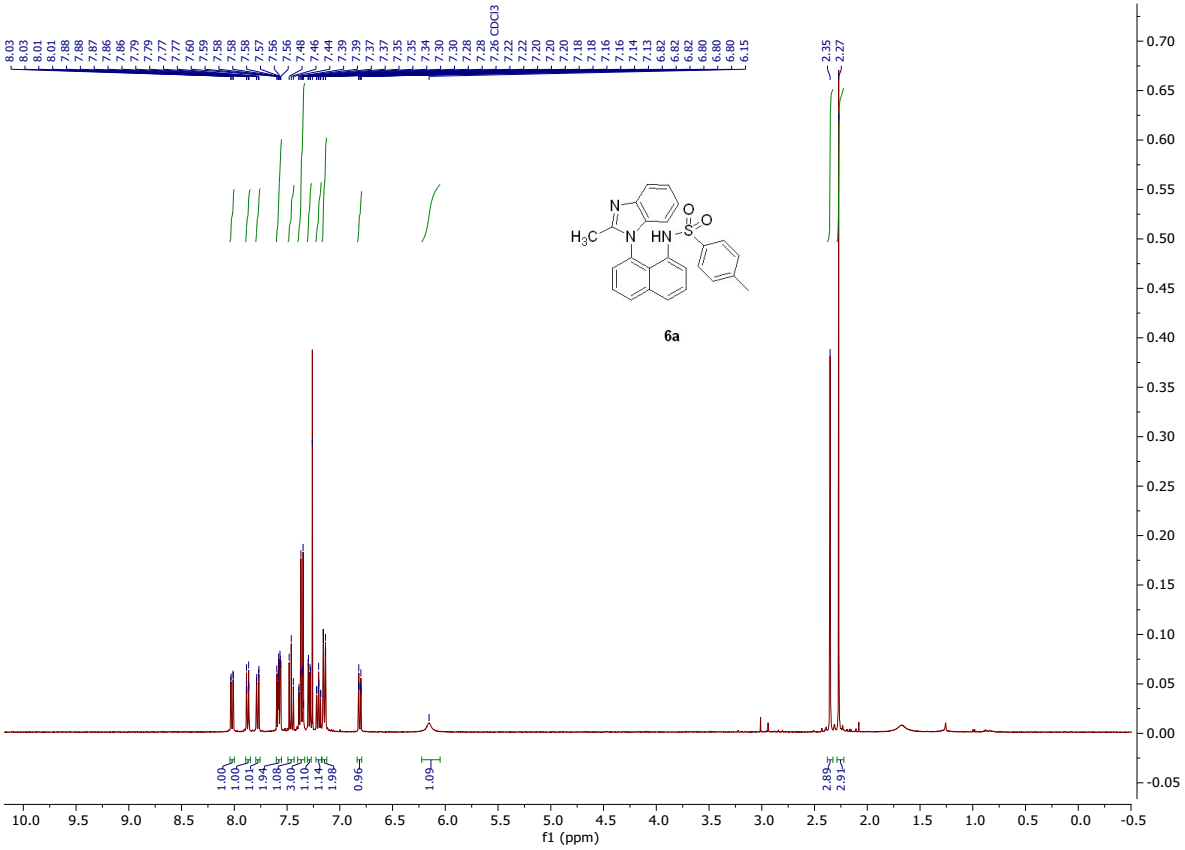
^{13}C NMR



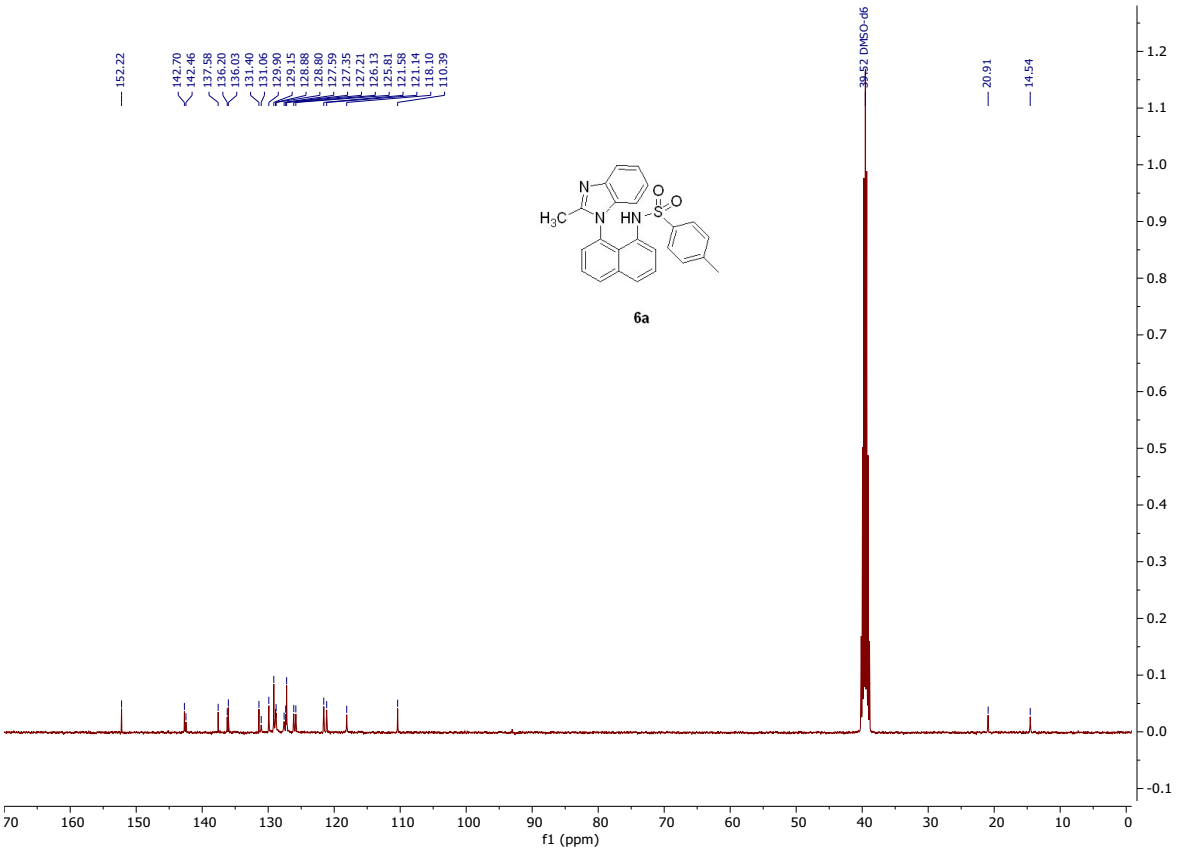
5i

4-Methyl-*N*-(8-(2-methyl-1H-benzimidazol-1-yl)naphthalen-1-yl)benzenesulfonamide 6a

^{1}H NMR

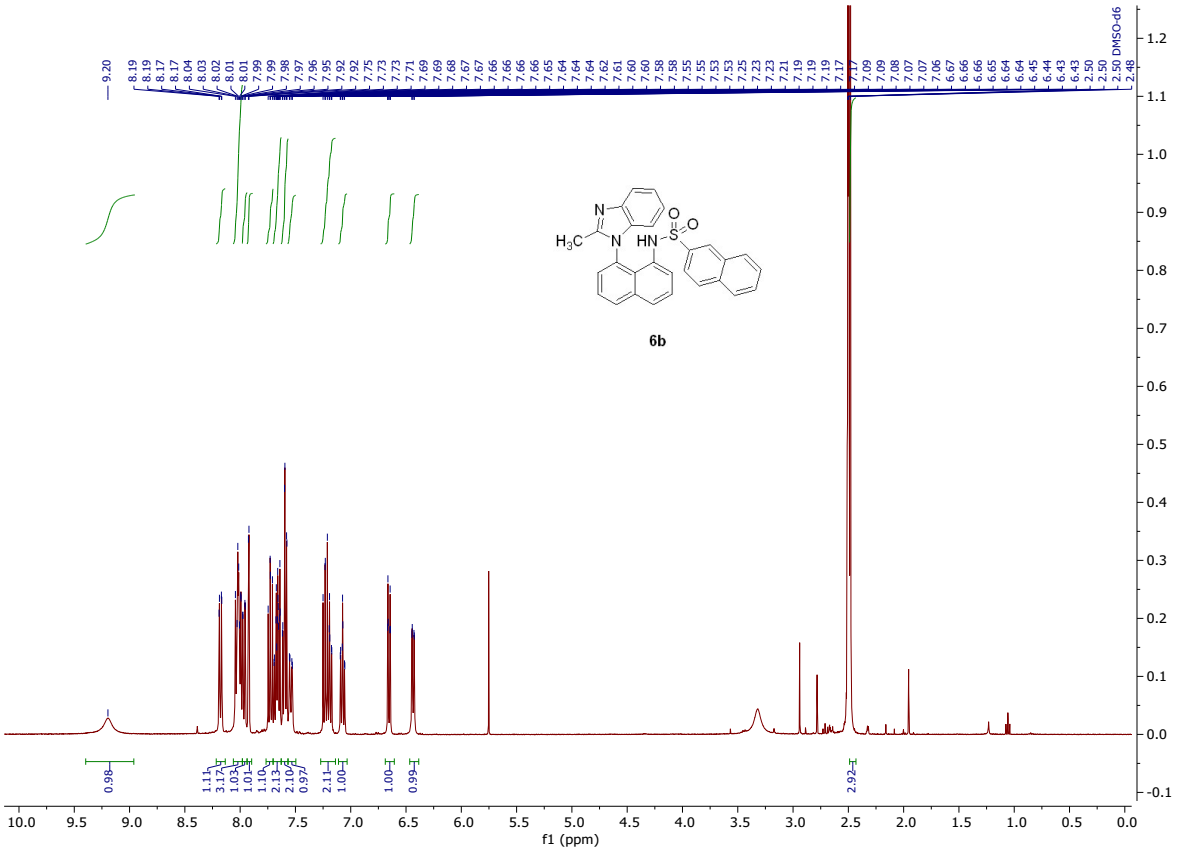


^{13}C NMR

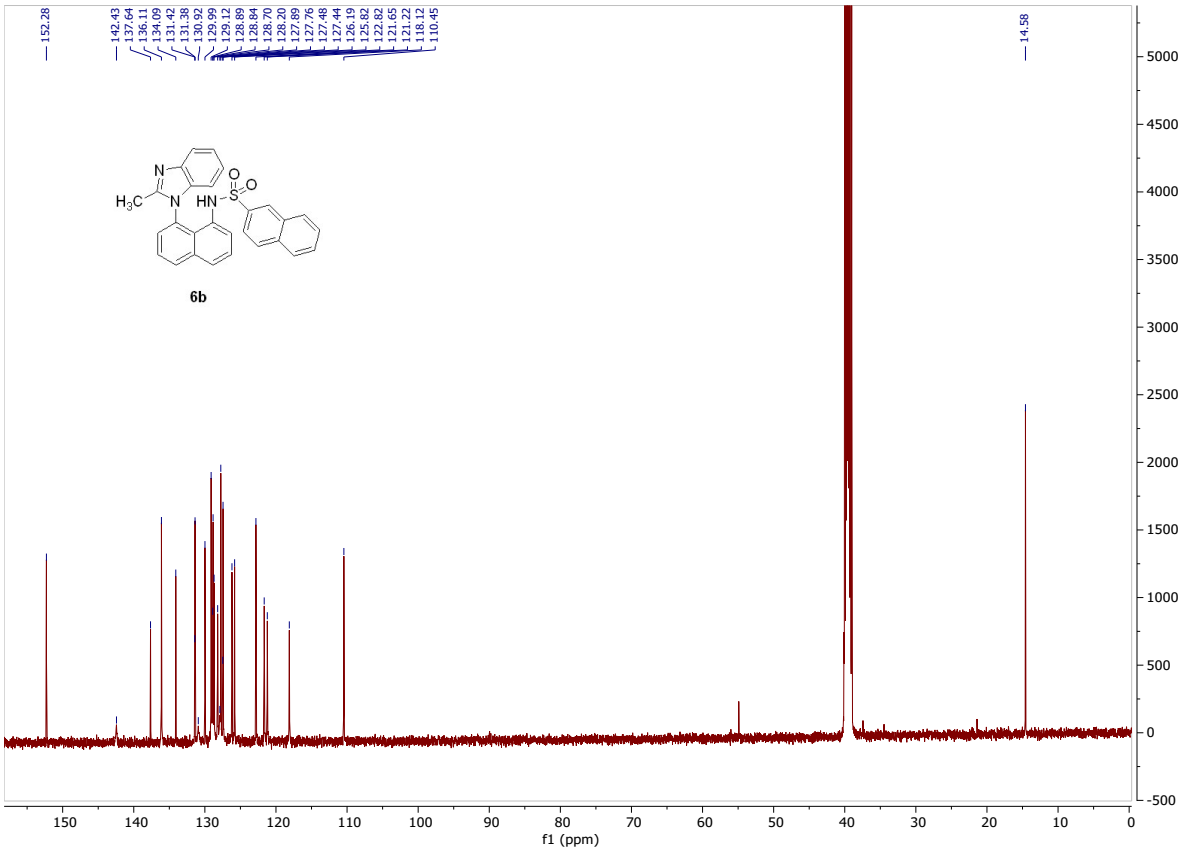


N-(8-(2-Methyl-1H-benzimidazol-1-yl)naphthalen-1-yl)naphthalene-2-sulfonamide 6b

^{1}H NMR



^{13}C NMR

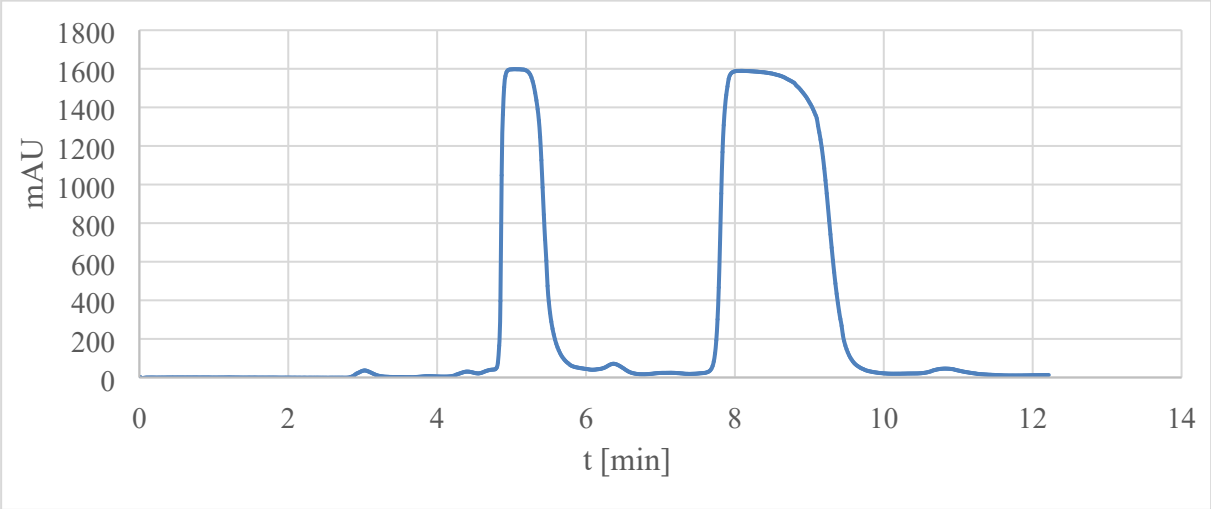


Chiral HPLC

Conditions for chiral resolution of 5f

Both atropisomers of compound **5f** were isolated using semipreparative chiral HPLC. Column: Lux Cellulose-3, (250 × 10 mm; 5 µm), mobile phase: *n*-hexane:MeOH:EtOH 40:1:1 (v/v/v), Flow rate: 5 mL/min), T = 25 °C, loading: 1000 µl, UV detection: λ = 274 nm.

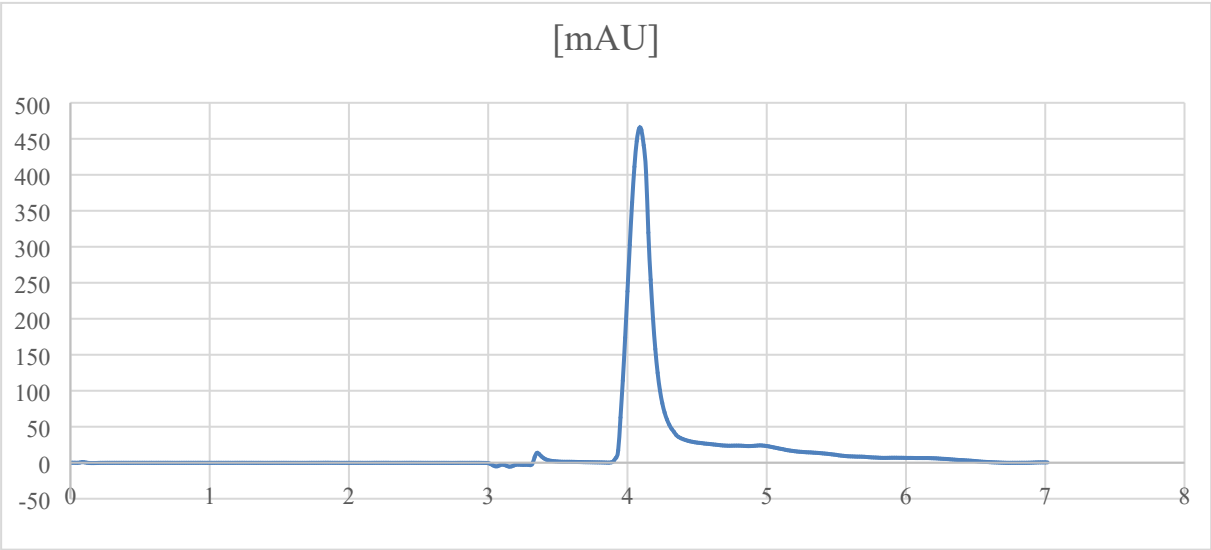
Semipreparative chromatogram (*n*-hexane:MeOH:EtOH 40:1:1)



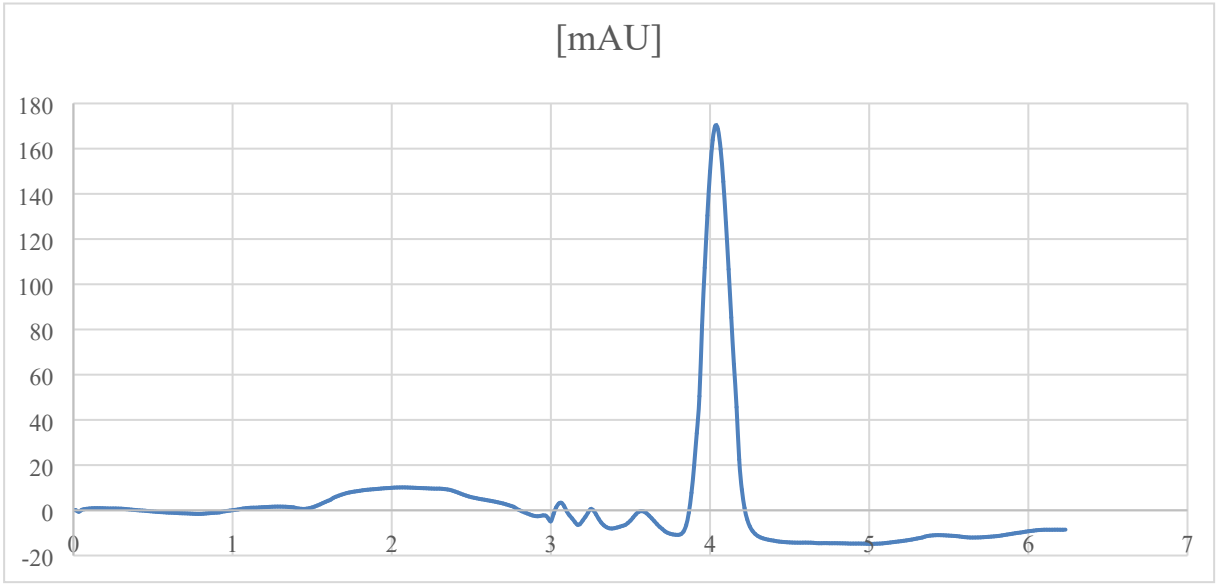
Stability of compound (-)-5f:

Study of optical stability of atropisomers was measured using analytical conditions. Column: Lux Cellulose-3, (250 × 4,6 mm; 5 µm), mobile phase: *n*-hexan:MeOH:EtOH 10:1:1 (v/v/v), flow rate: 1 mL/min, T = 25 °C, loading 20 µl, UV detection, λ = 274 nm.

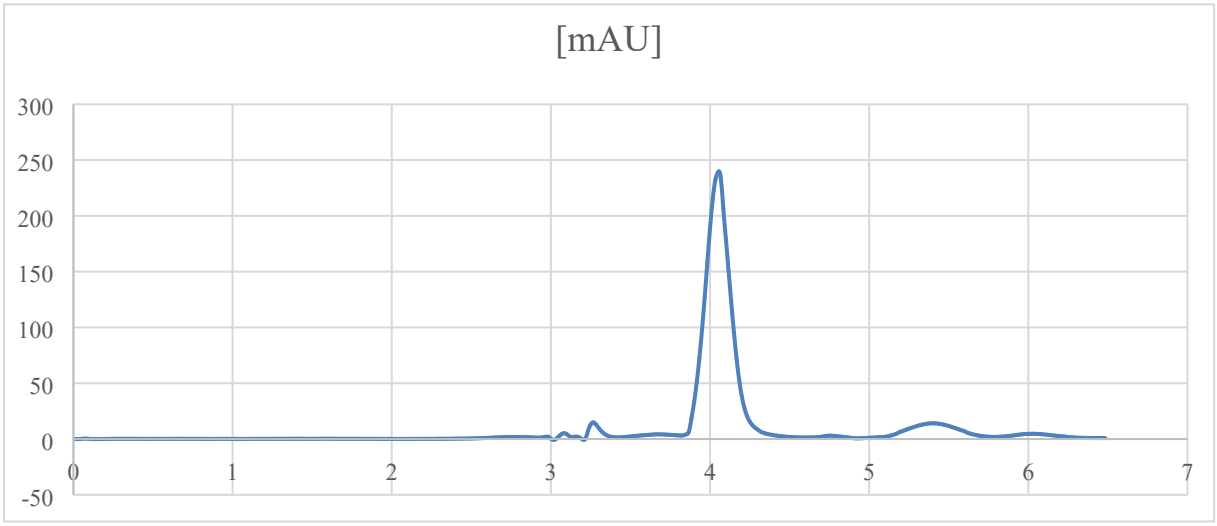
80 °C, 8 h:



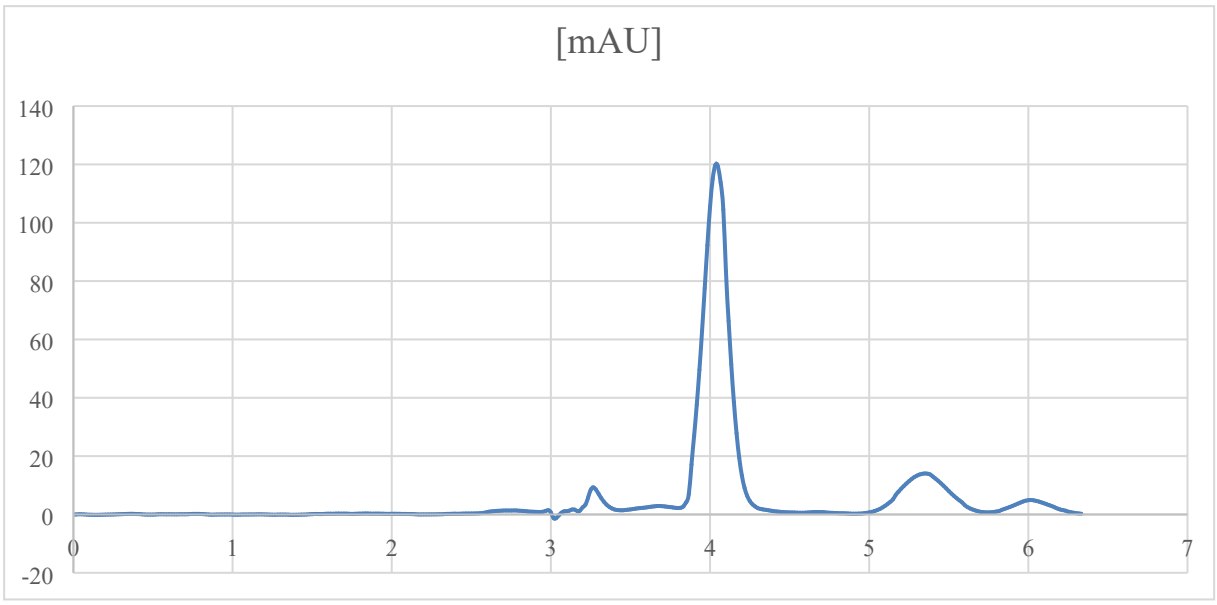
120 °C, 8 h:



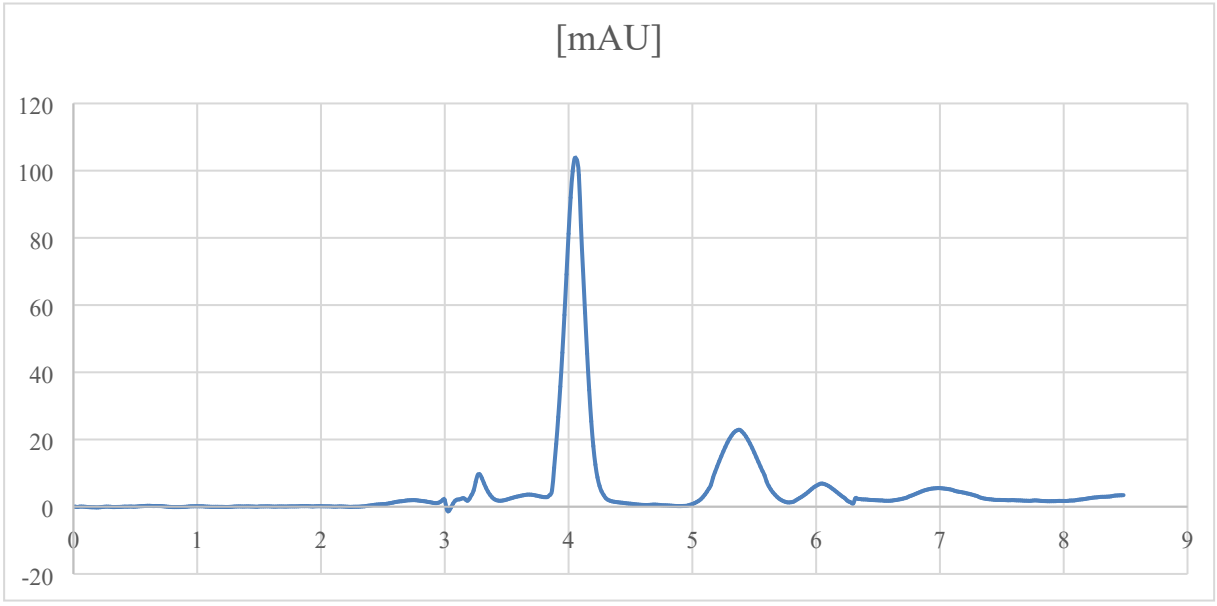
160 °C, 0.5 h:



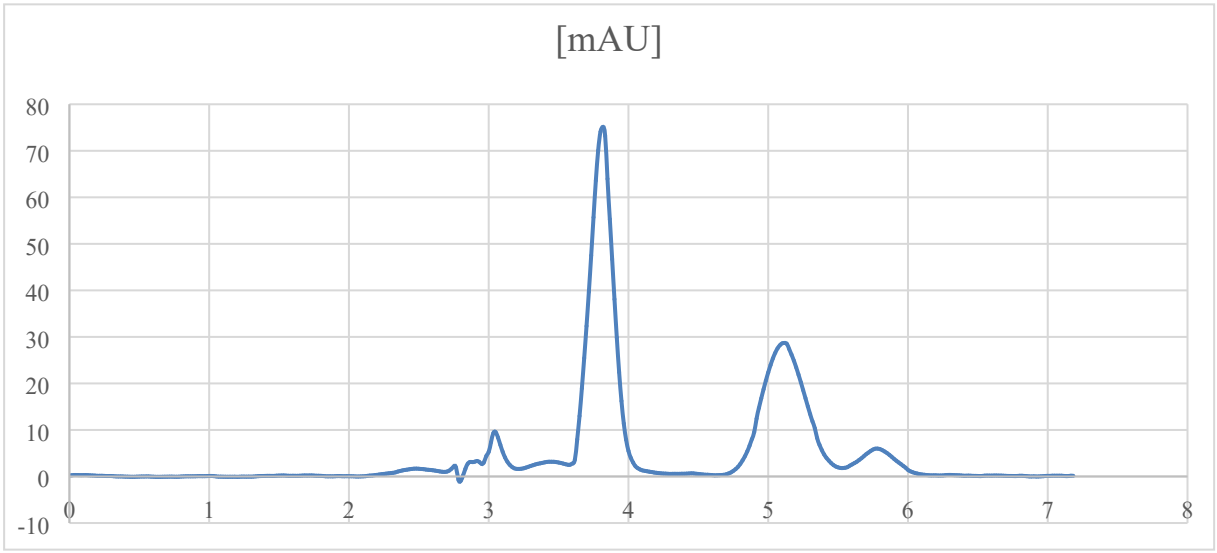
160 °C, 1 h:



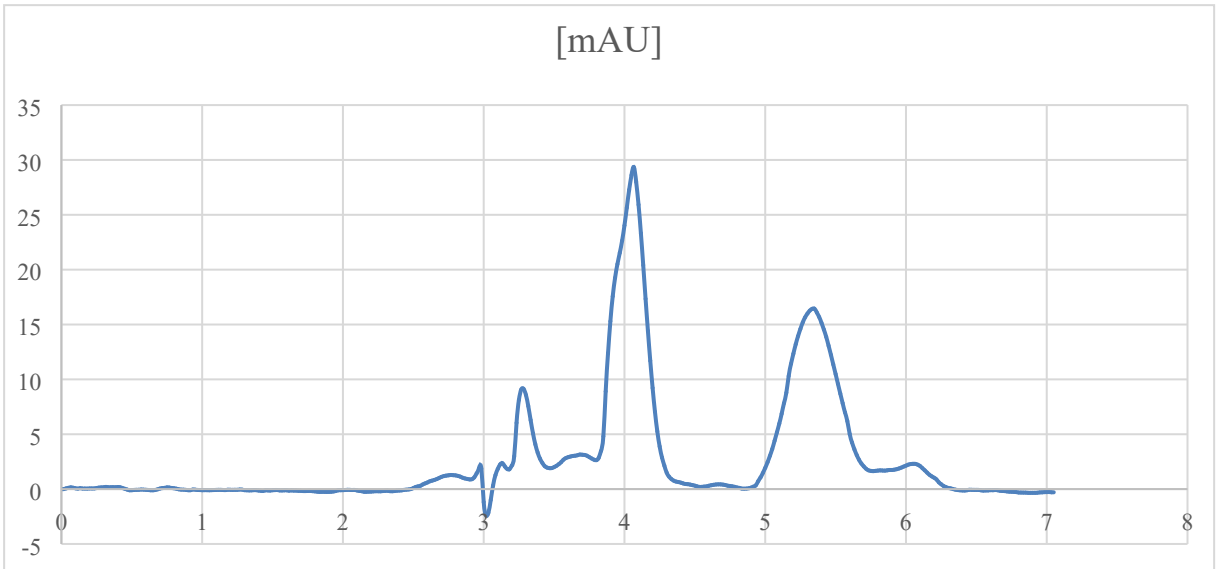
160 °C, 2 h:



160 °C, 4 h:



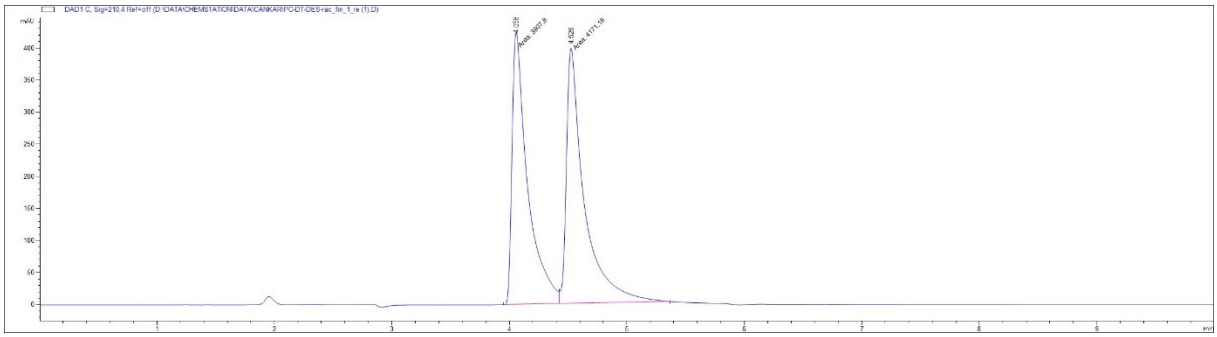
160 °C, 8 h:



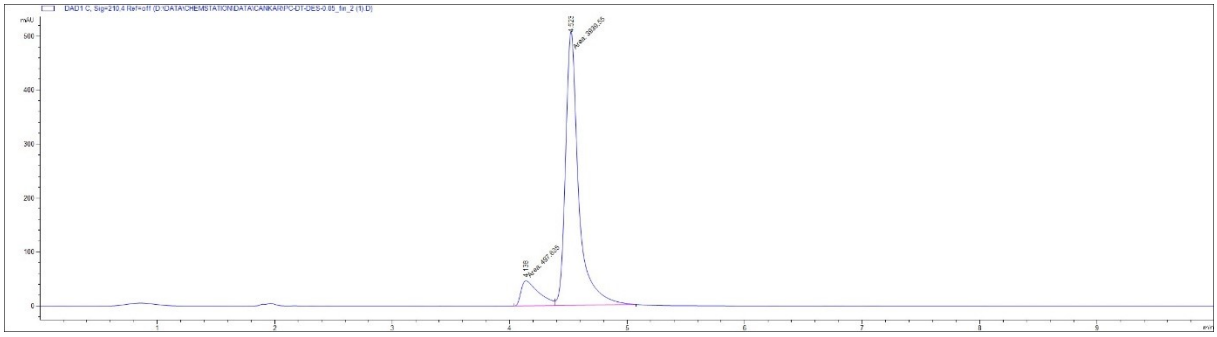
Chiral HPLC chromatograms of compound 7 after desymmetrization experiments with (+)-(S_a)-5f:

HPLC separation conditions: *n*-hexan/isopropanol 90:10, column Chiral Art Cellulose-SB (100x4.6 mm, 3 µm), flow rate: 0.6 mL/min, T = 25 °C, loading 2 µl, UV detection, λ = 210 nm.

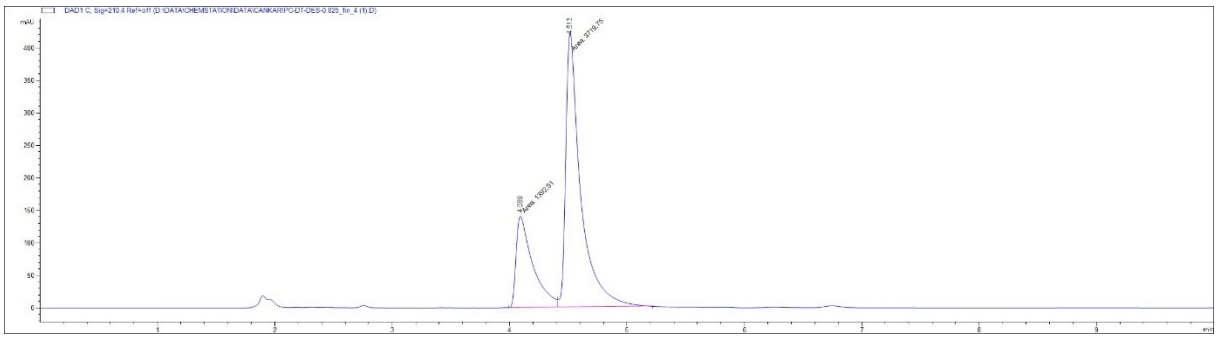
Racemic mixture of **7** (ratio 48:52):



Desymmetrization performed at concentration 0.05M (ratio 11:89):



Desymmetrization performer at concentration 0.025M (ratio 27:73):



Crystallography

All the diffraction data were collected using an XtaLAB Synergy-I diffractometer equipped with a HyPix3000 hybrid pixel array detector and a microfocused PhotonJet-I X-ray source (Cu Kα, 1.54184 Å). Absorption corrections were applied using the program CrysAlisPro 1.171.40.82a [i]. The crystal structures were solved using SHELXT [ii] program and refined using the full matrix least-squares procedure with SHELXL [iii] in OLEX2 (version 1.3) [iv]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located from the Fourier difference map and refined using the "riding" model.

Both compounds, (-)-(R_a)-**5f** and (+)-(S_a)-**5f**, crystallize in the monoclinic $P2_1$ space group as ethanol solvates. This space group belongs to the Sohncke space groups; therefore, the measurement strategy was based on collecting intensities of Friedel pairs. The resulting crystal structures confirmed the expected axial chirality (**Fig.1**). Nevertheless, the elements constituting the molecules of (-)-(R_a)-**5f** and (+)-(S_a)-**5f** are weak anomalous scatterers. As a result, the Flack parameters exhibit inconclusive statistics.

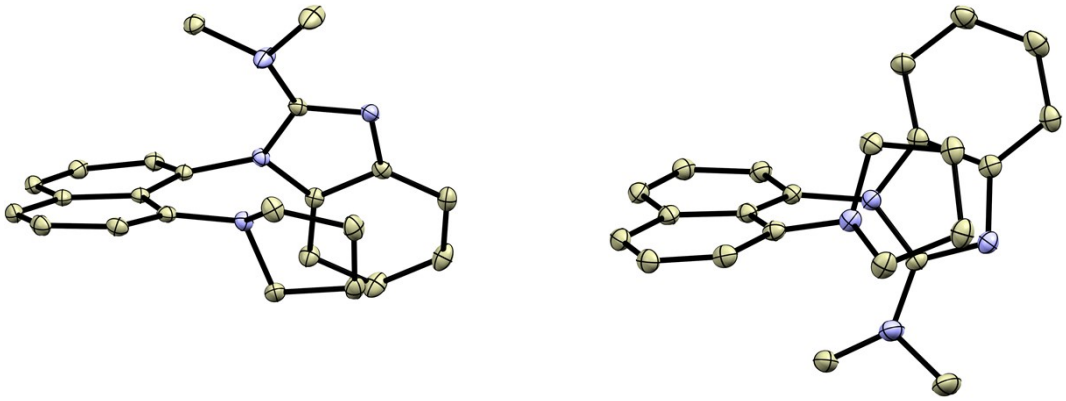


Fig.1 The molecular structures of (-)-(R_a)-**5f** (CCDC 2407034; *left*) and (+)-(S_a)-**5f** (CCDC 2407035; *right*). Colour code: carbon (light brown) and nitrogen (light blue). The thermal ellipsoids were drawn at a 30% probability level. The hydrogen atoms and ethanol molecules were omitted for clarity.

	(-)-(R_a)-**5f**	(+)-(S_a)-**5f**,
Empirical formula	$C_{25}H_{30}N_4O$	$C_{25}H_{30}N_4O$
Formula weight	402.53	402.53
Temperature/K	89.9(4)	89.9(4)
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a/Å	7.46170(10)	7.4550(2)
b/Å	13.90680(10)	13.9094(2)
c/Å	10.46010(10)	10.4634(2)
α/°	90	90
β/°	93.5230(10)	93.455(2)
γ/°	90	90
Volume/Å^3	1083.376(19)	1083.03(4)
Z	2	2
ρ_{calc} g/cm^3	1.234	1.234
μ/mm^{-1}	0.602	0.603
F(000)	432.0	432.0
Reflections collected/indep.	23039/4030. [R_{int} = 0.0362]	23167/3941. [R_{int} = 0.0509]
Data/restraints/parameters	4030/1/275	3941/1/275
Goodness-of-fit on F2	1.065	1.048

Final R indexes [I>=2σ (I)]	R_1 = 0.0286, wR_2 = 0.0711	R_1 = 0.0366, wR_2 = 0.0942
Final R indexes [all data]	R_1 = 0.0297, wR_2 = 0.0717	R_1 = 0.0382, wR_2 = 0.0952
Flack parameter	-0.09(9)	-0.17(13)
CSD number	2407034	2407035

Therefore, to include atoms with larger anomalous scattering, we recrystallized both compounds from ethanol solutions acidified with a few drops of HCl to adjust pH of the resulting solution to 4. The solutions were then left to crystallize isothermally over several days. The resulting colorless crystals consisted of protonated molecules, a chloride anion and co-crystallized water molecule. Both compounds crystallized in the orthorhombic Sohncke space group $P2_12_12_1$. The measurements unequivocally confirmed the expected axial chirality (**Fig.2**).

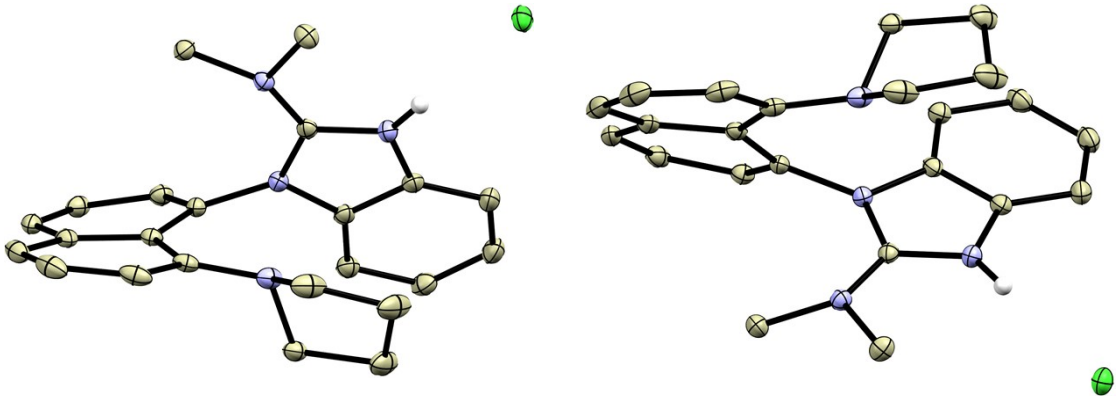


Fig.2 The molecular structures of (-)-(R_a)-**5f**·HCl·H_2O (CCDC 2407033; *left*) and (+)-(S_a)-**5f**·HCl·H_2O (CCDC 2407032; *right*). Colour code: carbon (light brown), chlorine (green) and nitrogen (light blue). The hydrogen atoms (except for the protonated benzimidazole hydrogen atom) and ethanol molecules were omitted for clarity. The thermal ellipsoids were drawn at a 30% probability level.

	(-)-(R_a)-**5f** HCl H_2O	(+)-(S_a)-**5f** HCl H_2O,
Empirical formula	$C_{23}H_{27}ClN_4O$	$C_{23}H_{27}ClN_4O$
Formula weight	410.93	410.93
Temperature/K	99.99(13)	99.99(13)
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	10.13790(5)	10.13520(10)
b/Å	11.24899(6)	11.23990(10)
c/Å	18.30377(9)	18.2950(2)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	2087.382(18)	2084.14(4)
Z	4	4
ρ_{calc} g/cm^3	1.308	1.310
μ/mm^{-1}	1.786	1.789
F(000)	872.0	872.0
Reflections collected/indep.	54502/3931. [R_{int} = 0.0332]	10810/3796. [R_{int} = 0.0242]
Data/restraints/parameters	3931/0/267	3796/0/268
Goodness-of-fit on F2	1.069	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0252, wR_2 = 0.0664	R_1 = 0.0260, wR_2 = 0.0681
Final R indexes [all data]	R_1 = 0.0256, wR_2 = 0.0666	R_1 = 0.0268, wR_2 = 0.0688
Flack parameter	0.016(13)	0.022(13)
CSD number	2407033	2407032

[i] Rigaku Oxford Diffraction (2020) CrysAlisPro 1.171.40.82a.
[ii] G. M. Sheldrick, Acta Crystallogr. Sect. A 71 (2015) 3–8.
[iii] L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, Acta Crystallogr. Sect. A 71 (2015) 59–75, doi:10.1107/S2053273314022207.
[iv] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 42 (2009) 339–341.