Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Nickel catalyzed C–S cross coupling of sterically hindered substrates enabled by flexible bidentate phosphines

SUPPORTING INFORMATION

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1. General Information

1.1 Chemicals and General Techniques

All cross-coupling reactions were carried out under an argon atmosphere using standard Schlenk techniques or an argon atmosphere Glovebox (GS MEGA E-Line, Glovebox Systemtechnik) and pre-dried glassware, unless noted otherwise. THF (HPLC-grade) was pre-dried over KOH, subjected to a column of Al_2O_3 (neutral), stored over 3 Å MS for at least 5 days and degassed by bubbling a stream of argon through the solvent for at least 20 min. DCM, *n*-hexane and EtOAc were distilled prior to use. Dry toluene was bought from Acros and degassed by bubbling a stream of argon through the solvent. Column chromatography was carried out either manually using silica gel (0.04–0.063 mm) from Machery&Nagel or by a Puriflash system (Interchim XS420) using pre-packed columns (30 or 50 µm) from Interchim or Büchi. Thin Layer Chromatography was performed on silica gel coated glass plates (0.25 mm) with fluorescence indicator UV254 (Macherey-Nagel, TLC plates SIL G-25 UV254). For detection of spots, irradiation of UV light at 254 nm was used. Chemicals were purchased from abcr, Acros, Alfa Aesar, BLDChem, Carbolution Chemicals, Carl Roth, Fluorochem, Sigma-Aldrich or TCI. $Ni(cod)_2$ was purchased from Sigma Aldrich, Alfa Aesar or abcr without noticeable difference in reactivity and stored at -40 °C in a glovebox. DPEphos was purchased from Sigma Aldrich and used as received. Dppbz was purchased from Alfa Aesar or fluorochem. KOAc was dried prior to use at 110 °C under high vacuum. 1-Adamantane thiol was purchased from Sigma Aldrich or BLDpharm (both 95% purity, used as received), stored and handled in a glovebox at room temperature. Other thiols were stored as received at -15 °C and handled under Argon flow. Pyridine (analytical grade) was used as received.

The aryl bromides **1p** – **1s** were commercially available.

The reaction temperature of experiments performed at “room temperature” varied between 25–32 °C. However, differences in reactivity were small to this variance.

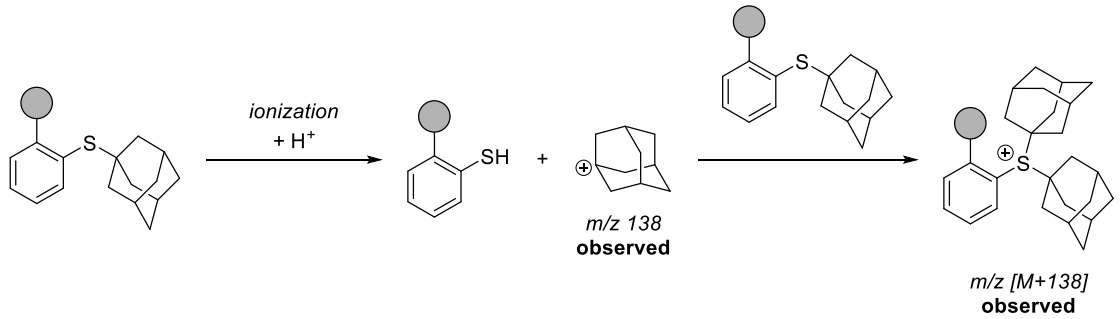
1.2 Analytical Techniques

NMR spectra were recorded using Bruker Avance III HD 400 or Bruker Avance III HDX 600 at room temperature (400 MHz for ^{1}H experiments; 101 MHz for ^{13}C experiments; 162 MHz; 376 MHz for ^{19}F experiments) in commercially available deuterated solvents. ^{13}C-NMR experiments were performed in proton-decoupled mode. Chemical shifts (*δ)* are reported in ppm relative to the residual NMR solvent signals[1] (chloroform: ^{1}H 7.26 ppm and ^{13}C 77.16 ppm). Hetero-NMR chemical shifts are given relative to external standards (^{19}F: $CFCl_3$;

^{31}P: H_3PO_4 (85%)). The coupling constants (*J* values) are given in Hz and spin multiplicity with the usual designations for splitting patterns (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet).

HR-MS (ESI, APCI, EI) measurements were carried out by the mass spectrometry department of the Institute of Organic Chemistry, University of Tübingen. Measurements were carried out using maXis 4G from Bruker (ESI, APCI) or by a MAT95 from Finnegan (EI). The molecular ion $[M]^+$, $[M+H]^+$ and $[M+Na]^+$ respectively are given in m/z units.

Note: When measuring *ortho*-substituted adamantyl-thioethers, we often encountered the issue, that the molecular ion peak was minor. Instead, $[M+138]^+$ was frequently present in the respective mass spectrum, even when using mild ionization methods such as APCI. We ascribe this to the scrambling of the thioether as follows:



Scheme S1: Proposed scrambling of ortho-substituted aryl adamantyl thioethers during measurement of HR-MS spectra.

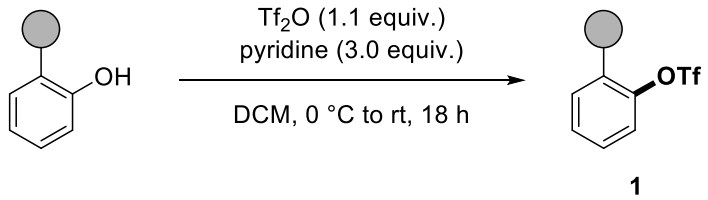
GC-FID (flame ionization detection) analysis was carried out on an Agilent 7820A system using dry hydrogen as carrier gas. An Agilent 19091J-431 column (30 m × 320 µm × 0.25 µm) was used. Program 50-280M15: heating from 50 °C to 280 °C within 15 minutes. Conversion and yield were determined *via* calibration against the internal standard pentadecane.

Melting point determination was achieved by using a Büchi B-540 machine with a visual detection (heating rate 5 °C/min).

FT-IR spectra were recorded using a Cary 630 FTIR by applying the sample neat on a diamond ATR sampler.

2. General Procedures

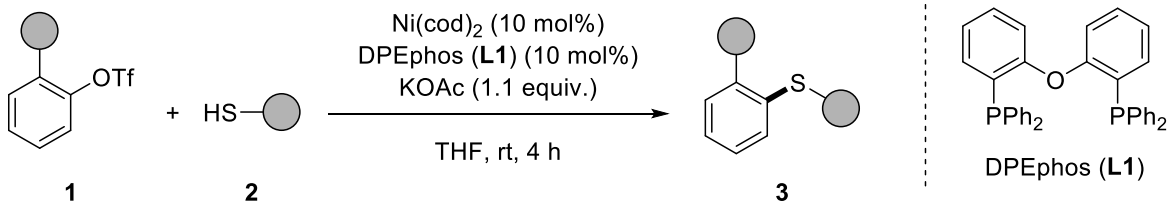
General Procedure A (GP-A): Synthesis of aryl triflates.[2]



1

In a 100 mL Schlenk-flask equipped with a stirring bar, the corresponding phenol (10 mmol, 1 equiv.) was dissolved in DCM (30 mL) and pyridine (3.0 equiv.) was added. After cooling the solution to 0 °C, trifluoromethanesulfonic anhydride (1.1 equiv.) was added dropwise under vigorous stirring, followed by removal of the ice-bath. The resulting mixture was stirred for 18 h at rt, diluted with DCM (10 mL), quenched with aqueous HCl (1 M, 10 mL), or, in the case of basic substrates, water (10 mL) and extracted with DCM (3 × 10 mL). The combined organic phases were washed with water (20 mL), saturated aqueous solution of $NaHCO_3$ (20 mL) and brine (20 mL), dried over anhydrous $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (*n*-hexane/EtOAc).

General Procedure B (GP-B): Nickel-catalyzed C–S cross-coupling of aryl triflates and thiols for product isolation using DPEphos as ligand.



1 **2** **3**

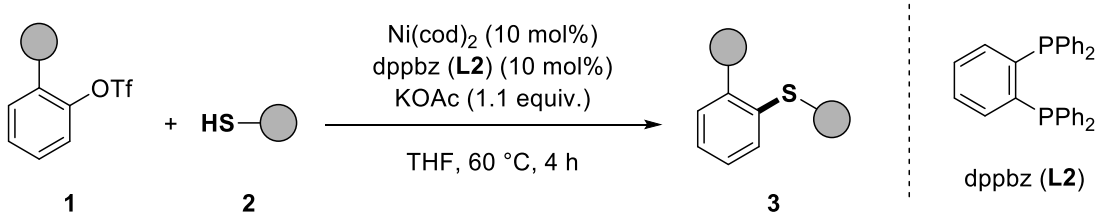
A 25 mL inert, flame-dried and septum-caped Schlenk-tube equipped with a stirring bar was charged with KOAc (108 mg, 1.1 mmol, 1.1 equiv.), DPEphos (53.9 mg, 0.1 mmol, 10 mol%) and $Ni(cod)_2$ (27.5 mg, 0.1 mmol, 10 mol%). After addition of the respective thiol (1.05 mmol, 1.05 equiv.) and the corresponding aryl triflate (1.0 mmol, 1.0 equiv.) the mixture was dissolved in dry THF (2 mL) under stirring. After 4 h at room temperature, the reaction was quenched with EtOAc (10 mL) and the solvent was removed *in vacuo.* The residue was purified by flash column chromatography (*n*-hexane/EtOAc).

Note: In the case of primary or secondary thiols, they were added slowly over the course of two hours *via* syringe, followed by stirring for 2 h. Additionally, 4 ml of THF were used.

Note: In some cases (as indicated), the starting material and product could not be separated by column chromatography. Hence, the mixture was treated with NBu_4OH, effectively

transforming the triflate to the phenol, while leaving the thioether intact. Afterwards, chromatographic separation was possible.

General Procedure C (GP-C): Nickel-catalyzed C–S cross-coupling of aryl triflates and thiols for product isolation using dppbz as ligand.



A 25 mL inert, flame-dried and septum-caped Schlenk-tube equipped with a stirring bar was charged with KOAc (1.1 equiv.), dppbz (10 mol%) and $Ni(cod)_2$ (10 mol%). After addition of the respective thiol (1.05 equiv.) and the corresponding aryl triflate (1 mmol, 1.0 equiv.) the mixture was dissolved in dry THF (2 mL) under stirring. After 4 h at 60 °C, the reaction mixture was diluted with EtOAc (10 mL) and concentrated *in vacuo.* The residue was purified by flash column chromatography (*n*-hexane/EtOAc).

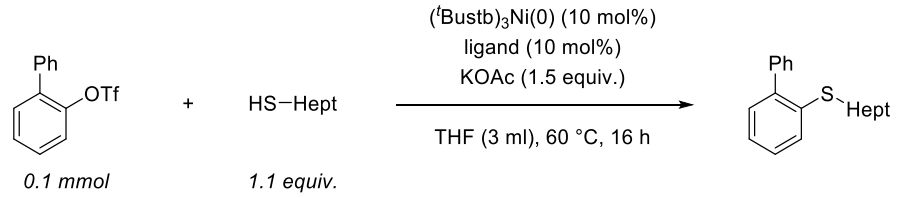
General Procedure D (GP-D): Nickel-catalyzed C–S cross-coupling of aryl and thiols for GC-FID analysis (screening).

A 10 mL inert, flame-dried and septum-caped Schlenk-tube equipped with a stirring bar was charged with KOAc (1.5 equiv.), ligand (10 mol%) and $Ni(cod)_2$ (10 mol%). After addition of the respective thiol (1.1 equiv.) and the corresponding aryl triflate (0.1 mmol, 1.0 equiv.) the mixture was dissolved in dry THF (1 mL) under stirring. After 16 h at 60 °C, the reaction was allowed to cool to rt and the internal standard *n*-pentadecane (50 µL) was added. The reaction mixture was quenched with brine (1 mL) and diluted with EtOAc (3 mL). A sample of the organic phase was filtered (glass pipette filled with cotton, celite, Al_2O_3 and $MgSO_4$) and analyzed *via* GC-FID. Yields and conversion were determined through the internal standard method for quantitative analysis.

3. Detailed Screening Information

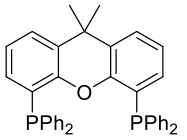
3.1 Ligand screening

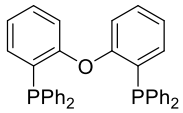
Table S1. Ligand screening. Yields and conversion were determined by quantitative GC-FID.

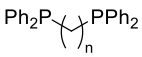


0.1 mmol *1.1 equiv.*

Entry	Ligand	Conv. [%]	Yield [%]
1	Xantphos	16	4
2	DPEPhos	55	45
3	dppm	14	n. d.
4	dtbpx	12	n.d.
5	dppf	53	44
6	L3	21	8
7	L4	12	n. d.
8	Me-Ferrocelan	12	n. d.
9	Josiphos	14	n. d.
10	PPh_3 (20 mol%)	13	n. d.
11	CTC-Q-Phos (20 mol%)	12	n. d.
12	SPhos (20 mol%)	13	n. d.
13	BiPhePhos	3	n. d.
14	IMesCl	13	n. d.
15	L5	17	n. d.


Xantphos


DPEphos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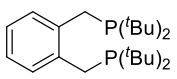
n = 4: dppb
n = 5: dpppent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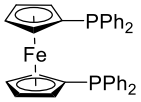
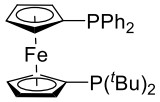

dppf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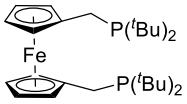
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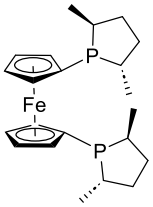
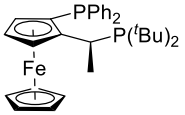
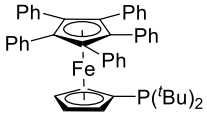
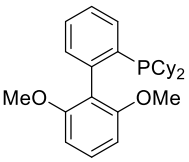
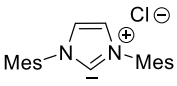
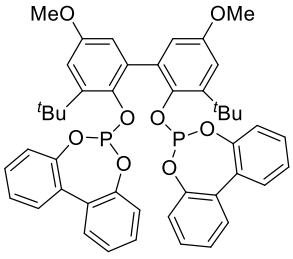

Me-Ferrocelan


Josiphos


CTC-QPhos


SPhos


IMesCl


BiPhePhos

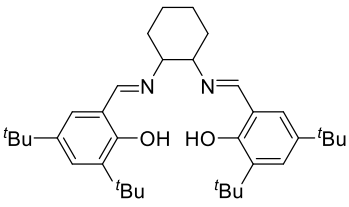
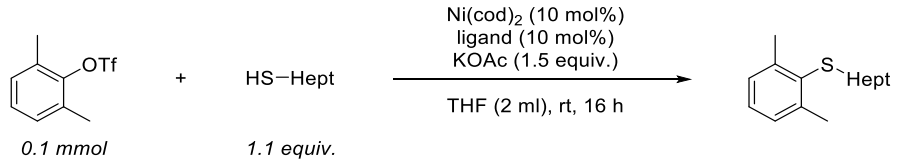
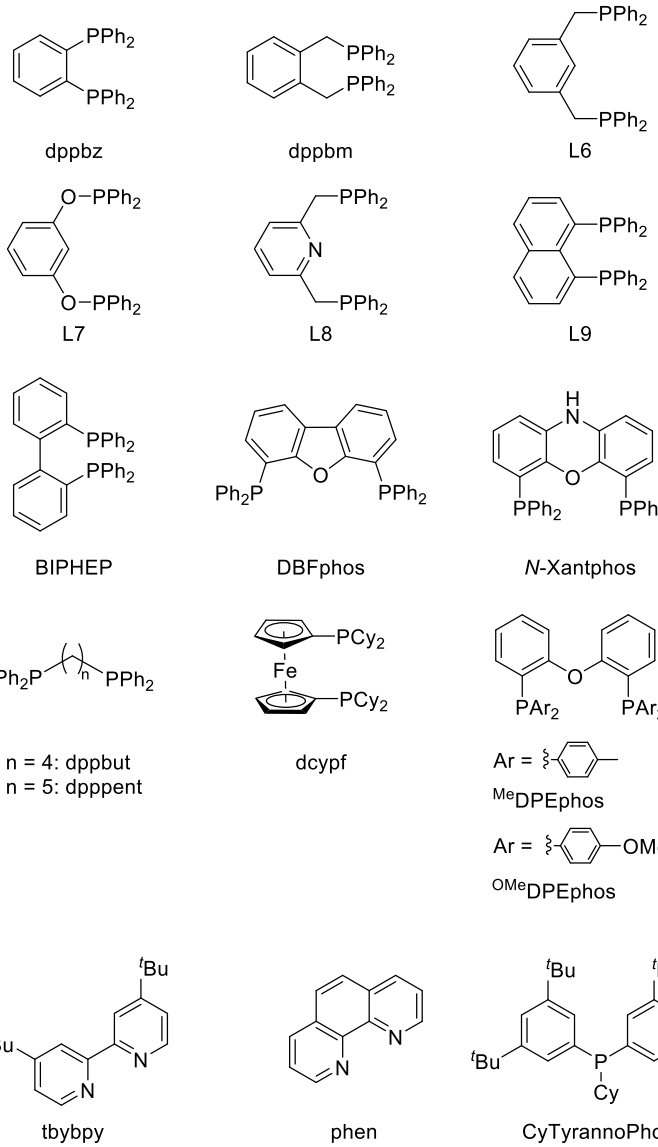

L5

Table S2. Ligand screening for the coupling of 2,6-dimethyl phenyl triflate. Yields were estimated by GC-MS.



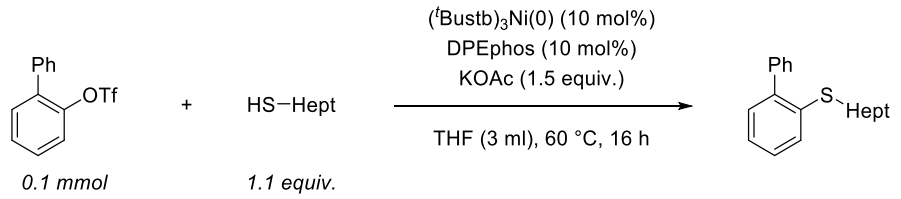
0.1 mmol *1.1 equiv.*

Entry	ligand	Yield [%][a]
1	DPEphos	n. d.
2	dppf	n. d.
3	dppbz	trace
4	dppbz, 60 °C	6
5	dppbz, 100 °C	30
6	dppbm	trace
7	L6	n. d.
8	L7	n. d.
9	L8	n. d.
10	L9	n. d.
11	BIPHEP	trace
12	DBFphos	n. d.
13	*N*-Xantphos	n. d.
14	dppbut	n. d.
15	dpppent	n. d.
16	dcypf	n. d.
17	^{Me}DPEphos	n. d.
18	^{OMe}DPEphos	n. d.
19	CyTyrannophos (20 mol%)	n. d.
20	PCy_3 (20 mol%)	n. d.
21	tbubpy	n. d.
22	phen	n. d.



3.2 Solvent Screening

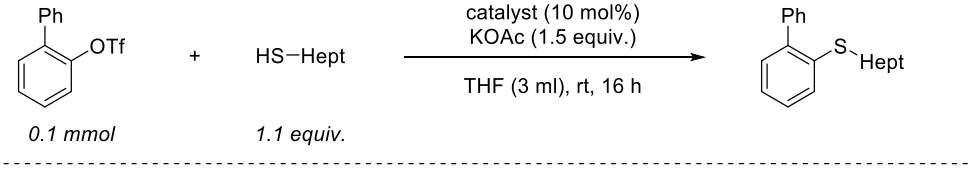
Table S3. Solvent Screening. Yields and conversion were determined by quantitative GC-FID.

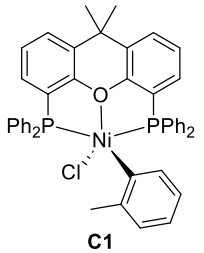


Entry	Solvent	Conv. [%]	Yield [%]
1	THF	55	45
2	NMP instead of THF	52	n. d.
3	THF/NMP (2:1)	29	13
4	2-Me-THF instead of THF	18	4
5	Toluene instead of THF	16	3
6	DMF instead of THF	58	0
7	2-Me-THF, 110 °C	22	9

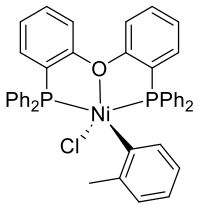
3.3. Catalyst screening

Table S4. (Pre-)Catalyst screening. Yields and conversion were determined by quantitative GC-FID.

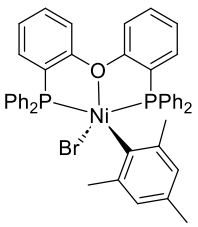




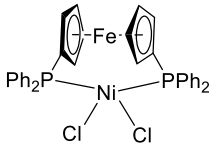
C1



C2



C3



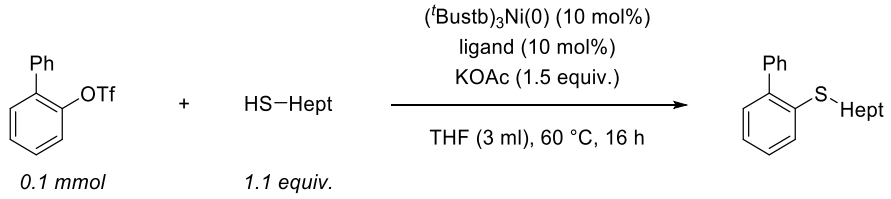
C4

Entry	(Pre-)Catalyst	Conv. [%]	Yield [%]
1	Ni(^{tBu}stilbene)$_3$/DPEphos, 5 mol%	21	8
2	Ni(^{tBu}stilbene)$_3$/DPEphos, 10 mol%	55	45
3	Ni(^{tBu}stilbene)$_3$/DPEphos, 15 mol%	72	69

4	$Ni(cod)_2$/DPEphos, 10 mol%	93	95
5	$Ni(cod)_2$/DPEphos, 5 mol%	21	8
6	**C1**, 1.2 equiv. thiol	N/A	n. d.
7	**C2**, 1.2 equiv. thiol	22	7
8	**C3**, 1.2 equiv. thiol	14	n. d.
9	**C4**, 1.2 equiv. thiol	11	n. d.
10	**C4**, 1.2 equiv. thiol + 1.0 equiv. Zn	13	n. d.
11	$NiOAc_2$/DPEphos (10 mol%), + 1.0 equiv. Zn, 60 °C	quant.	91
11	Pd_2dba_3/DPEphos (10 mol% Pd)	0	n. d.

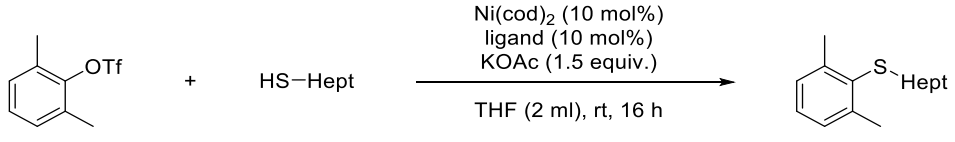
3.4 Other reaction parameters

Table S5. Screening of other reaction parameters. Yields were estimated by GC-MS.



0.1 mmol *1.1 equiv.*

Entry	Variation from standard conditions	Yield [%]
1	none	45
2	Room temperature	70
3	2 days reaction time	50
4	+ LiCl (1.0 equiv.)	trace

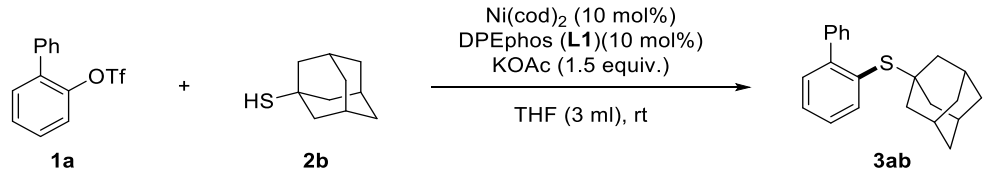


0.1 mmol *1.1 equiv.*

Entry	Variation from standard conditions	Yield [%]
1	none	n. d.
2	CsOAc instead of KOAc	n. d.
3	+ MeCN (1.0 equiv.)	n. d.
4	THF/MeCN (3:1)	n. d.
5	MeCN instead of THF	n. d.
6	+ PhCN (1.0 equiv.)	n. d.
7	Pd_2dba_3 instead of $Ni(cod)_2$	n. d.

3.5 Investigation of the Reaction Progress

A 10 mL inert, flame-dried and septum-caped Schlenk-tube equipped with a stirring bar was charged with KOAc (108 mg, 1.10 mmol, 1.1 equiv.), DPEphos (**L2**) (53.9 mg, 100.0 µmol, 10 mol%) and $Ni(cod)_2$ (27.5 mg, 100.0 µmol, 10 mol%), 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). After addition of 2-biphenyl trifluoromethanesulfonate (**1a**) (302 mg, 1.0 mmol, 1.0 equiv.) and internal standard pentadecane (100 µL), the mixture was dissolved in dry THF (3 mL) under stirring. Samples (ca. 20 µL) were taking from this mixture *via* syringe, quenched with brine and diluted with EtOAc. The organic phase was filtered (glass pipette filled with cotton, celite, Al_2O_3 and $MgSO_4$) and analyzed *via* quantitative GC-FID.



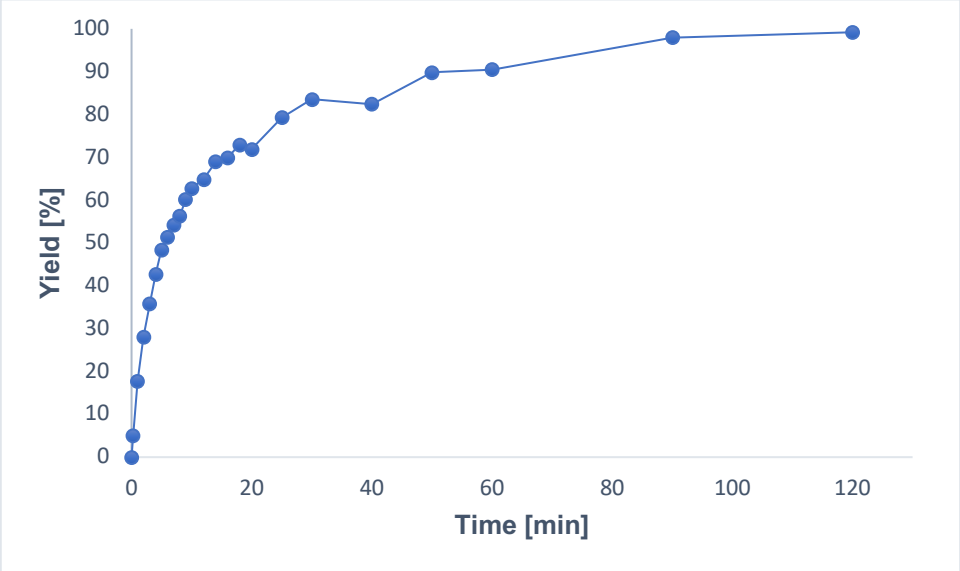
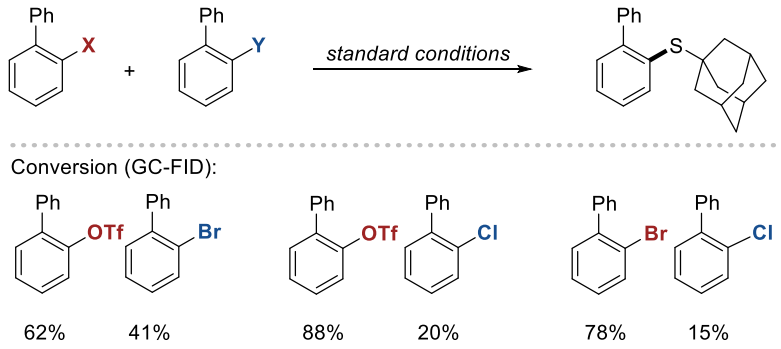


Figure S1. Kinetic investigation of the nickel-catalyzed reaction of **1a** with **2b**. Yields were determined by quantitative GC-FID using pentadecane as internal standard.

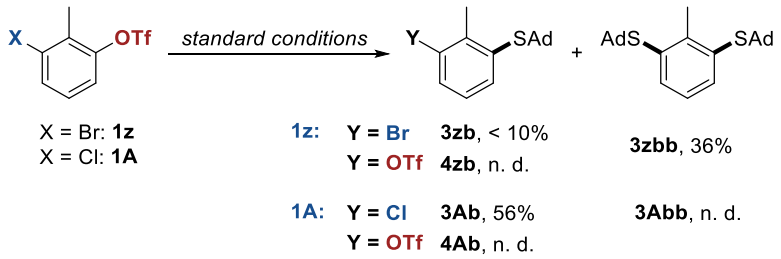
4. Competition Experiments and Mechanistic studies

Intermolecular competition of aryl (pseudo-)halides



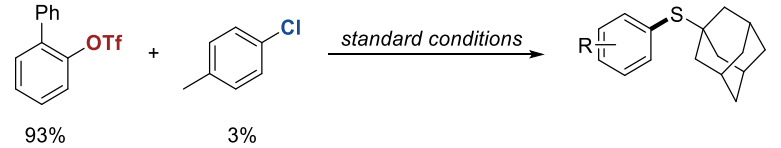
A 25 mL inert, flame-dried and septum-caped Schlenk-tube equipped with a stirring bar was charged with KOAc (21.6 mg, 0.22 mmol, 1.1 equiv.), DPEphos (10.8 mg, 20.0 µmol, 10 mol%) and $Ni(cod)_2$ (5.5 mg, 20 µmol, 10 mol%). After addition 1-admantane thiol (35.3 mg, 210 µmol, 1.05 equiv.) and the corresponding aryl (pseudo-)halides (each 0.2 mmol, 1.0 equiv.) the mixture was dissolved in dry THF (2 mL) under stirring. After 4 h at room temperature, the reaction mixture was quenched with brine and diluted with EtOAc. A sample of the organic phase was filtered (glass pipette filled with cotton, celite, Al_2O_3 and $MgSO_4$) and analyzed *via* quantitative GC-FID.

Intramolecular competition



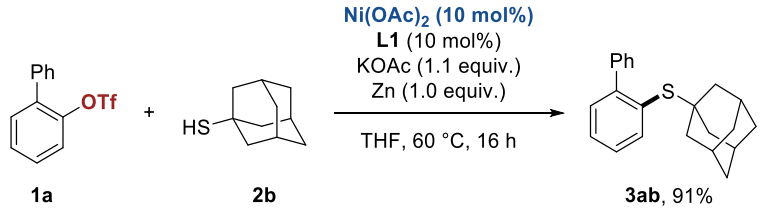
Following GP-B, the corresponding biselectrophile (1 mmol) was subjected to the reaction conditions. Flash chromatography (hexane/EtOAc) gave the corresponding products of the reaction. Side-products were detected by GC-MS.

Steric vs electronic discrimination



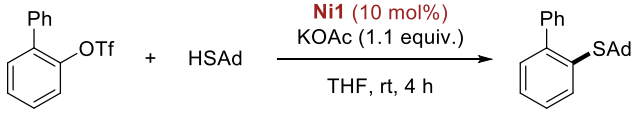
A 25 mL inert, flame-dried and septum-caped Schlenk-tube equipped with a stirring bar was charged with KOAc (21.6 mg, 0.22 mmol, 1.1 equiv.), DPEphos (10.8 mg, 20.0 µmol, 10 mol%) and $Ni(cod)_2$ (5.5 mg, 20 µmol, 10 mol%). After addition 1-admantane thiol (35.3 mg, 210 µmol, 1.05 equiv.) and the corresponding aryl (pseudo-)halides (each 0.2 mmol, 1.0 equiv.) the mixture was dissolved in dry THF (2 mL) under stirring. After 4 h at room temperature, the reaction mixture was quenched with brine and diluted with EtOAc. A sample of the organic phase was filtered (glass pipette filled with cotton, celite, Al_2O_3 and $MgSO_4$) and analyzed *via* quantitative GC-FID.

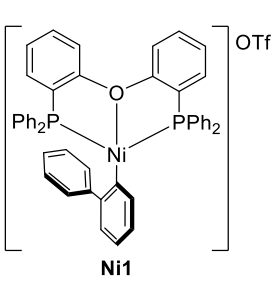
$Ni(OAc)_2$ as precatalyst under reductive conditions



A 25 mL inert, flame-dried and septum-caped Schlenk-tube equipped with a stirring bar was charged with $Ni(OAc)_2(H_2O)_4$ (2.5 mg, 10.0 µmol, 10 mol%) and dried *in vacuo* at 110 °C. After the addition of KOAc (10.8 mg, 0.11 mmol, 1.1 equiv.), DPEphos (5.4 mg, 10.0 µmol, 10 mol%), zinc powder (6.5 mg, 0.1 mmol, 1.0 equiv.), 1-admantane thiol (**2b**) (17.7 mg, 105 µmol, 1.05 equiv.) and 2-biphenyl trifluoromethanesulfonate (**1a**) (30.2 mg, 0.1 mmol, 1.0 equiv.) the mixture was dissolved in dry THF (2 mL) under stirring. After 16 h at 60 °C, the reaction mixture was quenched with brine and diluted with EtOAc. A sample of the organic phase was filtered (glass pipette filled with cotton, celite, Al_2O_3 and $MgSO_4$) and analyzed *via* quantitative GC-FID.

Ni1 as precatalyst



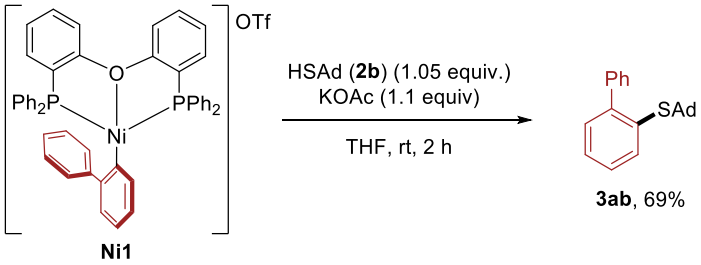


The experiment was performed according to GP-B by using **Ni1** (9.0 mg, 10 µmol, 10 mol%) instead of $Ni(cod)_2$/DPEphos.

A 25 mL inert, flame-dried and septum-caped Schlenk-tube equipped with a stirring bar was charged with KOAc (10.8 mg, 110 µmol, 1.1 equiv.) and **Ni1** (9.0 mg, 10 µmol, 10 mol%). After addition 1-admantane thiol (17.7 mg, 105 µmol, 1.05 equiv.) and 2-biphenyl

trifluoromethanesulfonate (**1a**) (30.2 mg, 0.1 mmol, 1.0 equiv.) the mixture was dissolved in dry THF (2 mL) under stirring. After 4 h at room temperature, the reaction mixture was quenched with brine and diluted with EtOAc. A sample of the organic phase was filtered (glass pipette filled with cotton, celite, Al_2O_3 and $MgSO_4$) and analyzed *via* quantitative GC-FID.

Stochiometric reaction of Ni1 with 1-adamantane thiol (2b)



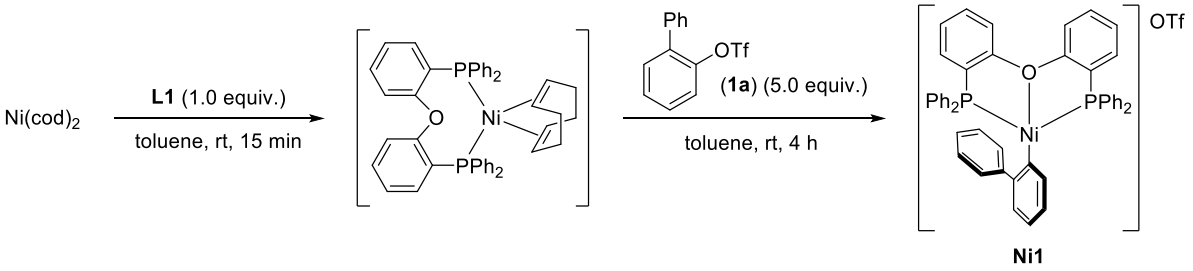
Ni1

3ab, 69%

In a glovebox, a screw-cap glass vial was charged with **Ni1** (90.0 mg, 0.1 mmol, 1.0 equiv.), KOAc (10.8 mg, 110 µmol, 1.1 equiv.) and 1-adamantane thiol (**2b**) (17.7 mg, 105 µmol, 1.05 equiv.). The mixture was dissolved in dry THF and stirred at room temperature for 2 h. Outside the glovebox, the reaction was quenched with brine and diluted with EtOAc. A sample of the organic phase was filtered (glass pipette filled with cotton, celite, Al_2O_3 and $MgSO_4$) and analyzed *via* quantitative GC-FID.

5. Analytical Data

5.1 Synthesis of Ni1.



Ni1

$C_{49}H_{37}F_3NiO_4P_2S$ (899.52 g/mol)

The synthesis of **Ni1** followed a modified literature procedure.[3] In a glovebox, a screw-cap glass vial was charged with $Ni(cod)_2$ (100 mg, 364 µmol, 1.0 equiv.), DPEphos (**L1**) (196 mg, 364 µmol, 2.0 equiv.) and a stirring bar. Toluene (4 ml) was added, and the resulting deep red solution was stirred for 15 minutes. Subsequently, 2-biphenyl trifluoromethanesulfonate (**1a**) (549 mg, 1.82 mmol, 5.0 equiv.) dissolved in toluene (3 ml) was added and the reaction mixture was stirred for 4 h until a red precipitate formed. *n*-Hexane (5 ml) was added, and the resulting suspension was filtered through a P3-frit. The red filter cake was washed with toluene (3 × 4 ml) and *n*-hexane (5 × 2 ml). The resulting solid was dried in dynamic vacuum over night to afford **Ni1** (277 mg, 308 µmol, 85%) as an orange powder. Crystals suitable for X-Ray analysis were obtained from a solution of **Ni1** in THF/toluene by slow evaporation of THF.

^{1}H-NMR (600 MHz, THF-d_8, δ): 8.51 (d, *J* = 7.4 Hz, 2H), 8.06 – 7.92 (m, 2H), 7.85 – 7.79 (m, 2H), 7.71 – 7.41 (m, 15H), 7.37 – 7.32 (m, 2H), 7.25 – 7.21 (m, 4H), 7.09 – 7.06 (m, 1H), 7.04 – 6.99 (m, 2H), 6.87 – 6.82 (m, 5H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.60 – 6.54 (m, 1H).

^{13}C-NMR (101 MHz, THF-d_8, δ): 159.2 (t, *J* = 7.8 Hz), 145.6, 144.1, 138.2, 136.4, 135.9, 135.5, 135.0, 133.9 (t, *J* = 6.2 Hz), 133.1 (t, *J* = 6.4 Hz), 132.3, 132.2, 130.4 (t, *J* = 5.4 Hz), 129.8 (t, *J* = 5.4 Hz), 129.5, 128.7, 128.6, 128.0, 127.8, 126.6, 126.3, 125.8, 125.0, 124.8, 121.6, 121.5, 121.4, 118.1.

Note: Observed triplets due to secondary effects. Additionally, we were unable to detect the characteristic C–F quartet of the OTf group due to low S/N ratio.

^{19}F NMR (565 MHz, THF-d_8, δ): -78.8.

^{31}P NMR (243 MHz, THF-d_8, δ): 7.2.

HR-MS (ESI): m/z calc for $[M–OTf]^+$ 749.16676, found 749.16748.

Elemental Analysis: calc: C: 65.43, H: 4.15, S: 3.56; found: C: 65.50, H: 4.37, S: 3.21.

X-Ray: For crystallographic data, see below.

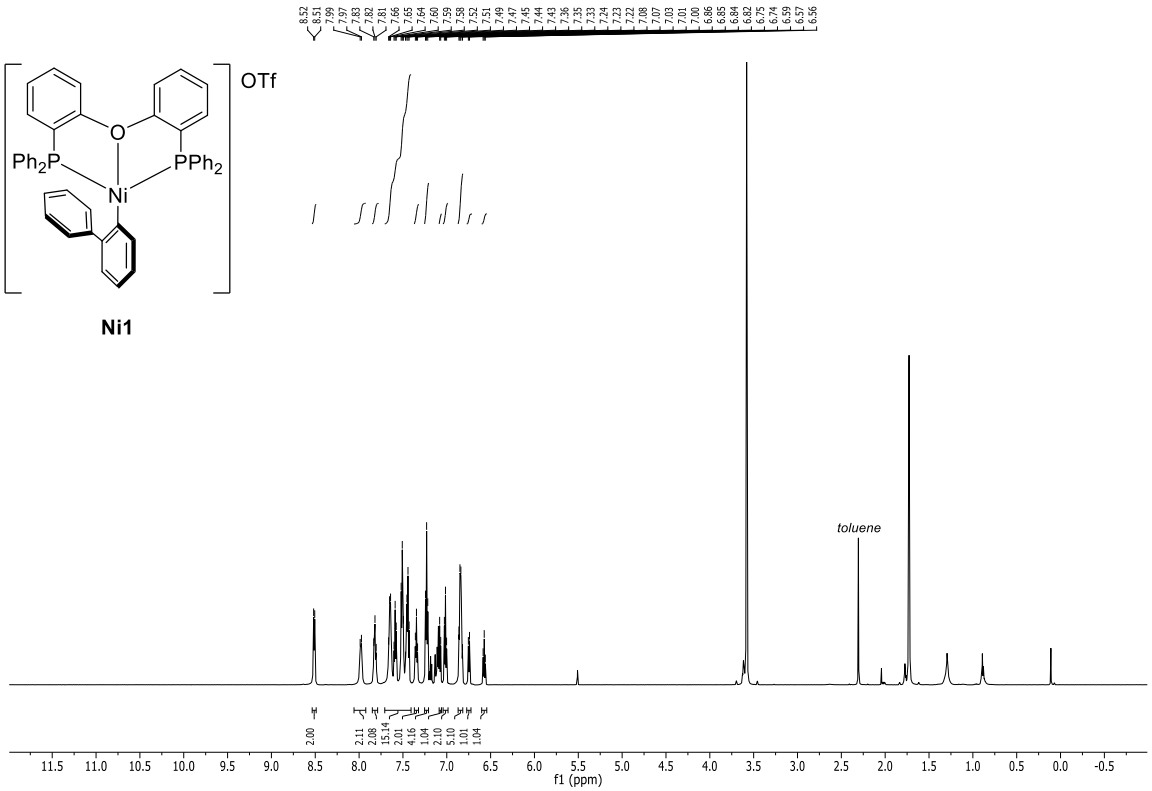


Figure S2. ^{1}H-NMR-spectrum (400 MHz, THF-d_8) of **Ni1**.

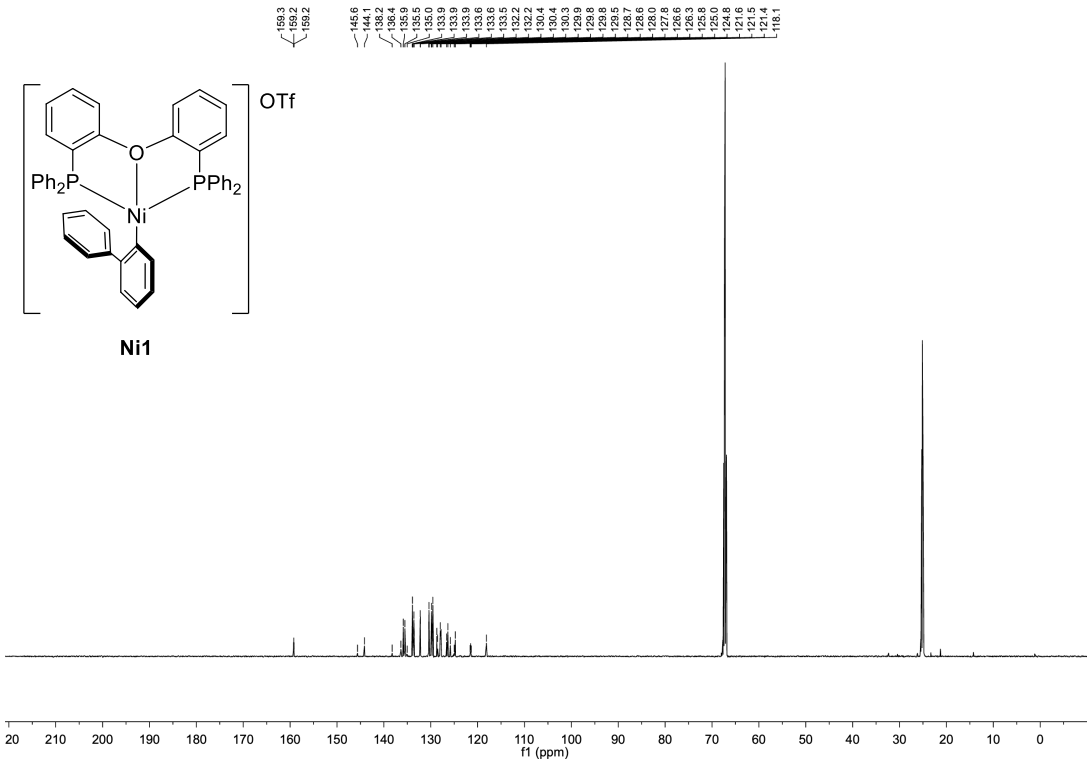


Figure S3. ^{13}C-NMR-spectrum (101 MHz, THF-d_8) of **Ni1**.

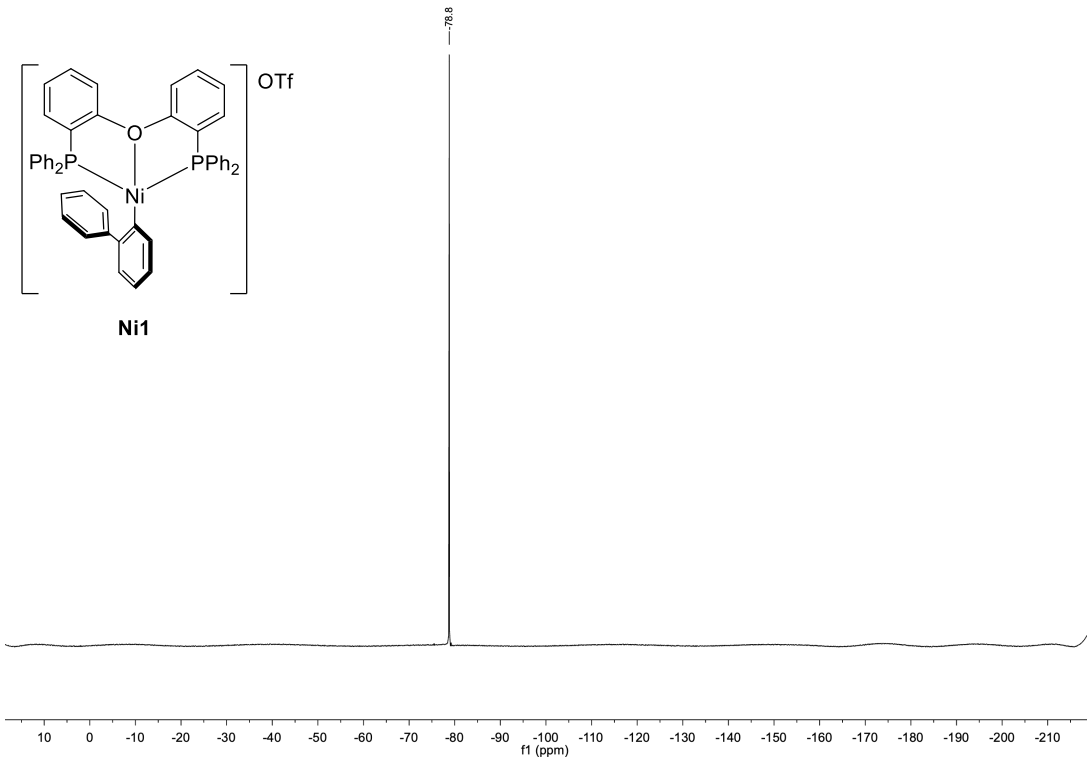


Figure S4. ^{19}F-NMR-spectrum (376 MHz, THF-d_8) of **Ni1**.

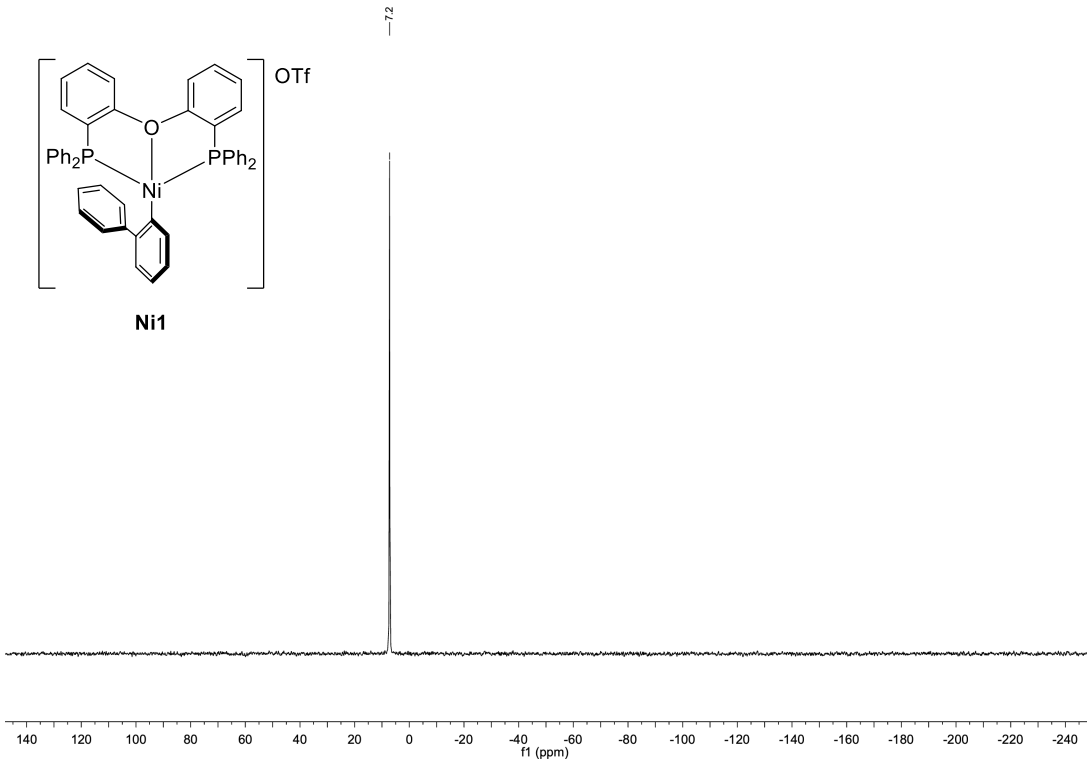
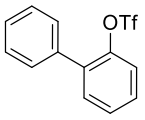


Figure S5. ^{31}P-NMR-spectrum (243 MHz, THF-d_8) of **Ni1**.

5.2 Synthesis of Aryl Triflates

[1,1'-Biphenyl]-2-yl trifluoromethanesulfonate (1a):



1a

$C_{13}H_9F_3O_3S$ (302.27 g/mol)

Following **GP-A**, **1a** was synthesized using [1,1'-biphenyl]-2-ol (5.11 g, 30.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1a** (8.10 g, 26.8 mmol, 89%) as colorless oil. Conforms to reported analytical data.[4]

R_f: 0.66 (*n*-hexane/EtOAc 95:5).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.54 – 7.37 (m, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 147.0, 135.7, 132.1, 129.5, 129.1, 128.7, 128.6, 128.5, 122.2, 118.5 (q, *J* = 320.7 Hz).

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -74.1.

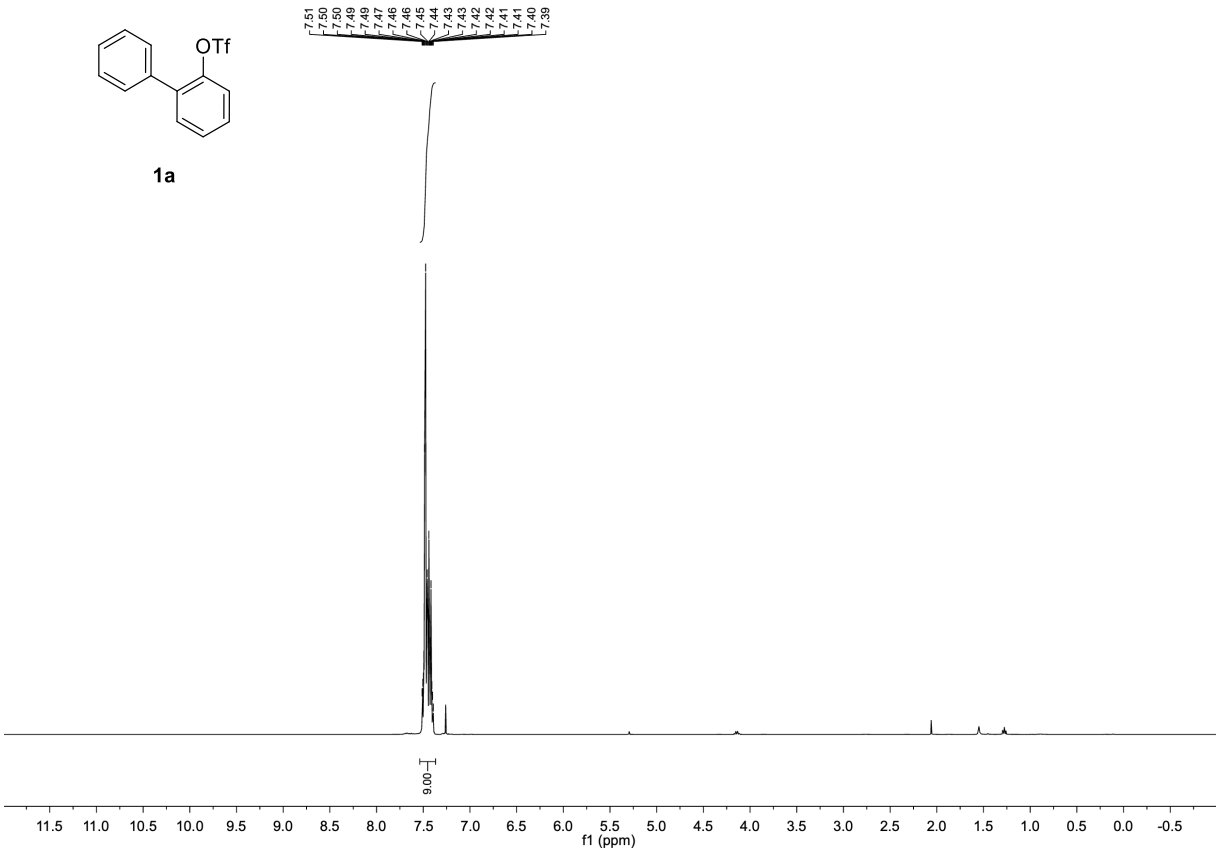


Figure S6. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1a**.

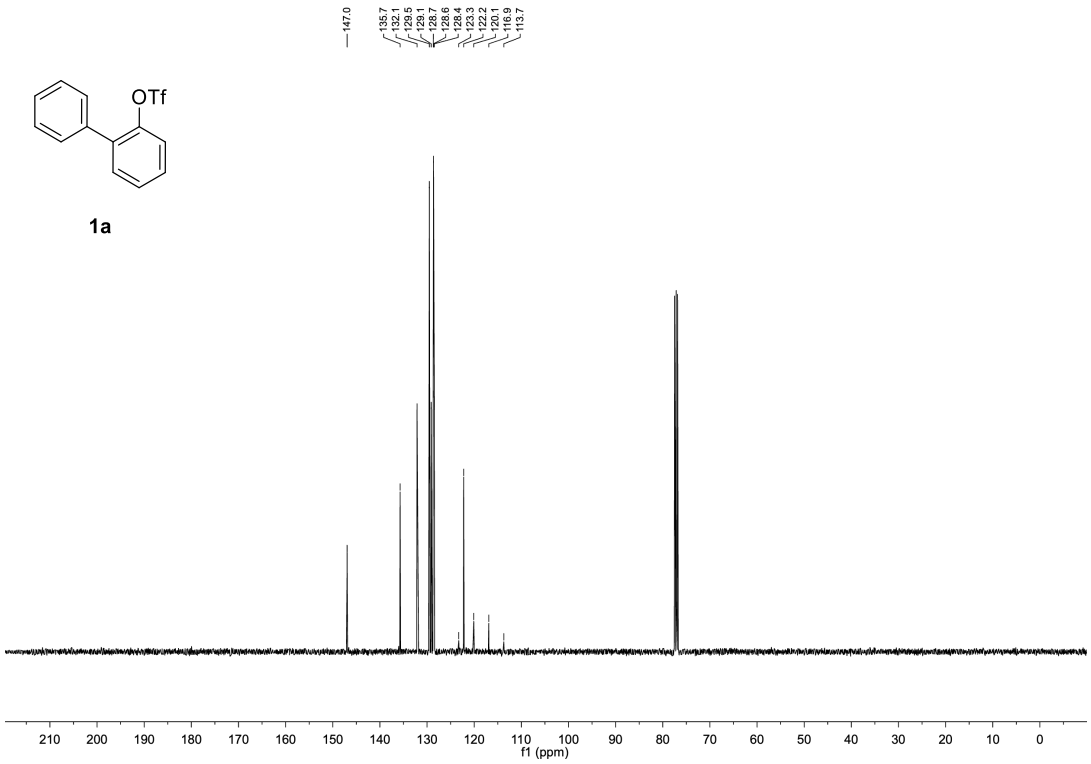


Figure S7. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1a**.

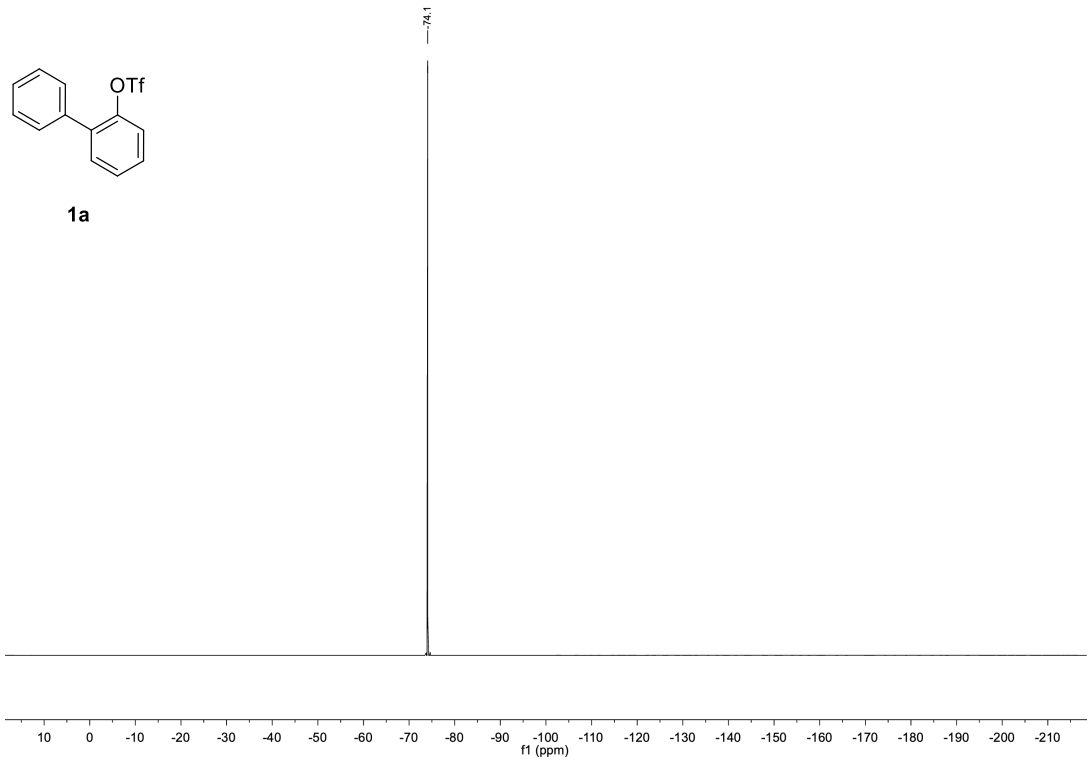
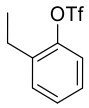


Figure S8. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1a**.

2-Ethylphenyl trifluoromethanesulfonate (1b):



1b

$C_9H_9F_3O_3S$ (254.22 g/mol)

Following **GP-A**, **1b** was synthesized using 2-ethylphenol (1.22 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1b** (2.28 g, 8.97 mmol, 90%) as colorless oil. Conforms to reported analytical data.[5]

R_f: 0.72 (*n*-hexane/EtOAc 95:5).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.39 – 7.21 (m, 4H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 148.1, 136.8, 130.6, 128.6, 127.7, 121.4, 118.8 (q, *J* = 320.1 Hz) 23.1, 14.1.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -74.0.

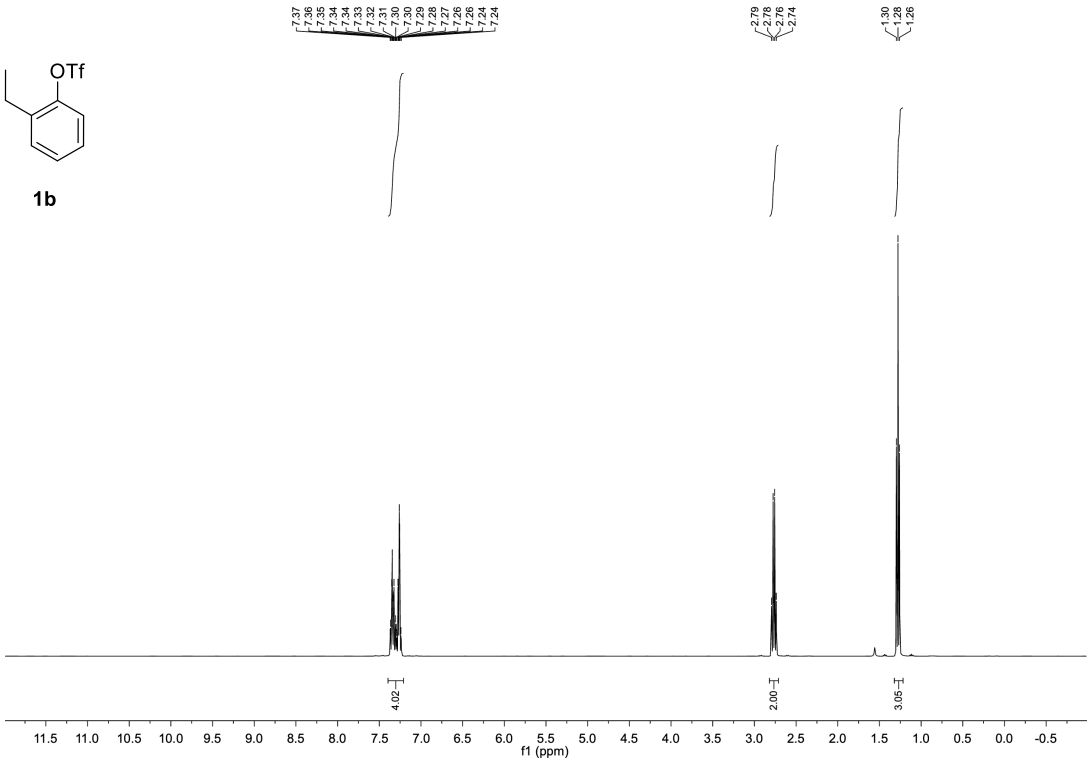


Figure S9. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1b**.

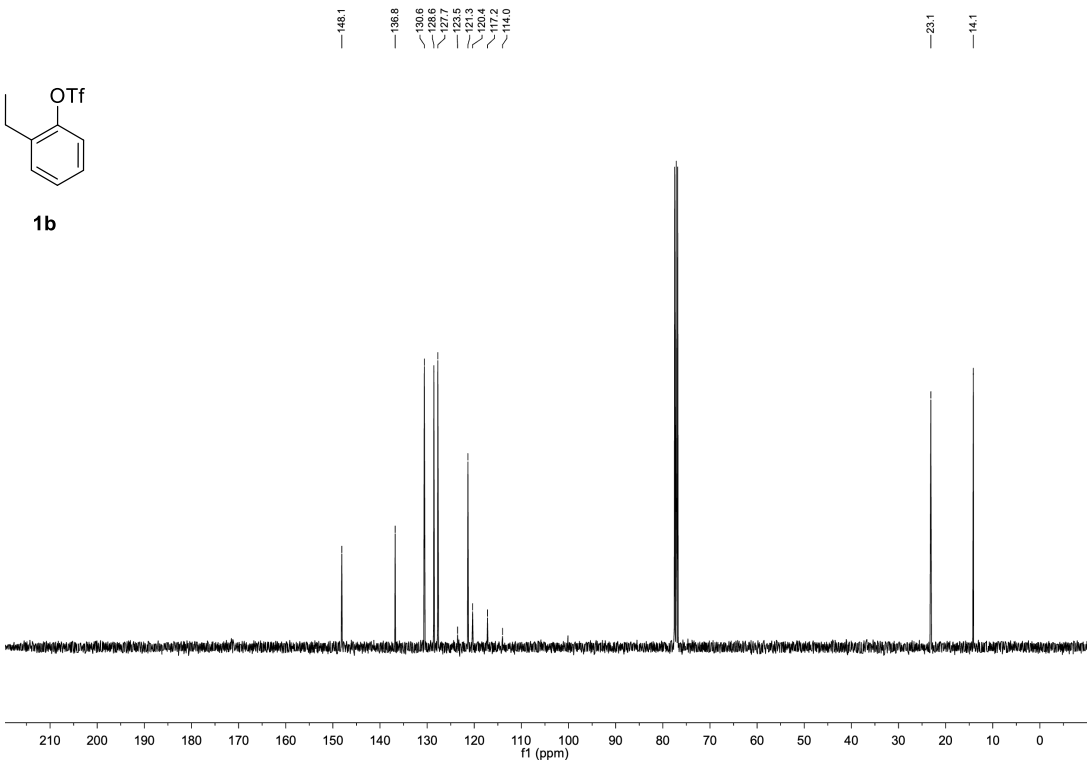


Figure S10. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1b**.

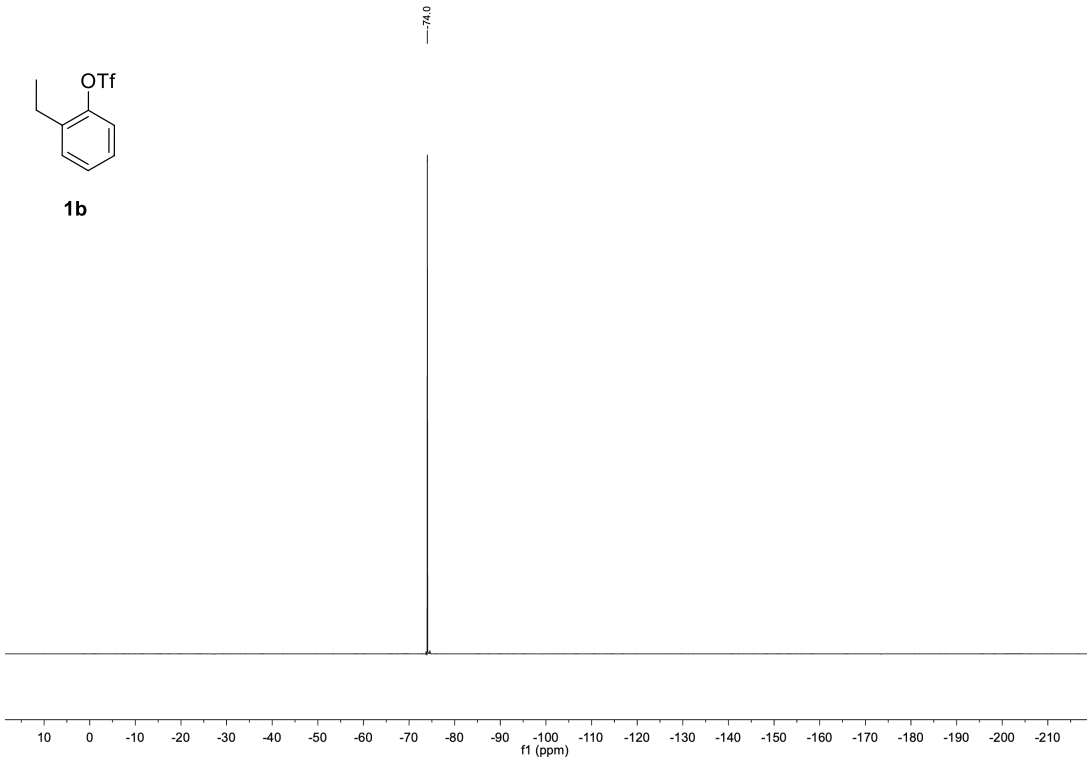
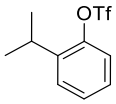


Figure S11. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1b**.

2-Isopropylphenyl trifluoromethanesulfonate (1c):



1c

$C_{10}H_{11}F_3O_3S$ (268.25 g/mol)

Following **GP-A**, **1c** was synthesized using 2-isopropylphenol (1.36 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1c** (2.26 g, 8.42 mmol, 84%) as colorless oil. Conforms to reported analytical data.[4]

R_f: 0.75 (*n*-hexane/EtOAc 95:5).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.45 – 7.41 (m, 1H), 7.37 (m, 1H), 7.30 – 7.24 (m, 2H), 3.32 (sept, *J* = 6.9 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 147.3, 141.4, 128.7, 128.0, 127.6, 121.3, 118.8 (q, *J* = 320.1 Hz) 27.3, 23.3.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -74.0.

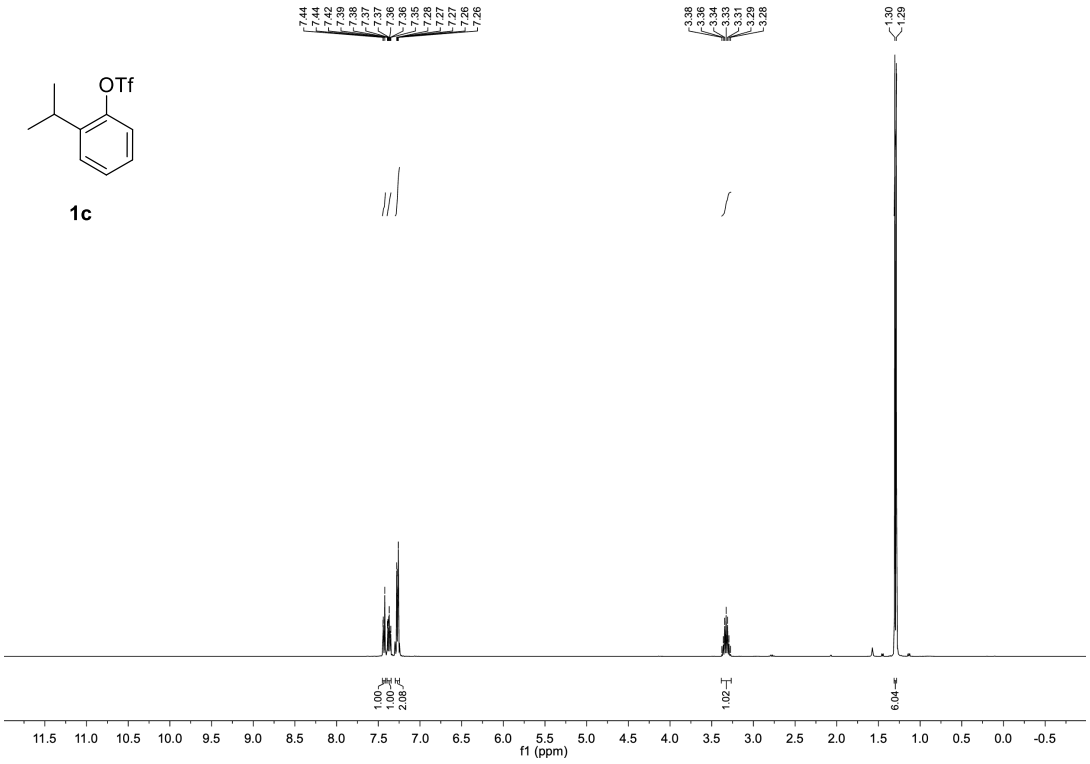


Figure S12. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1c**.

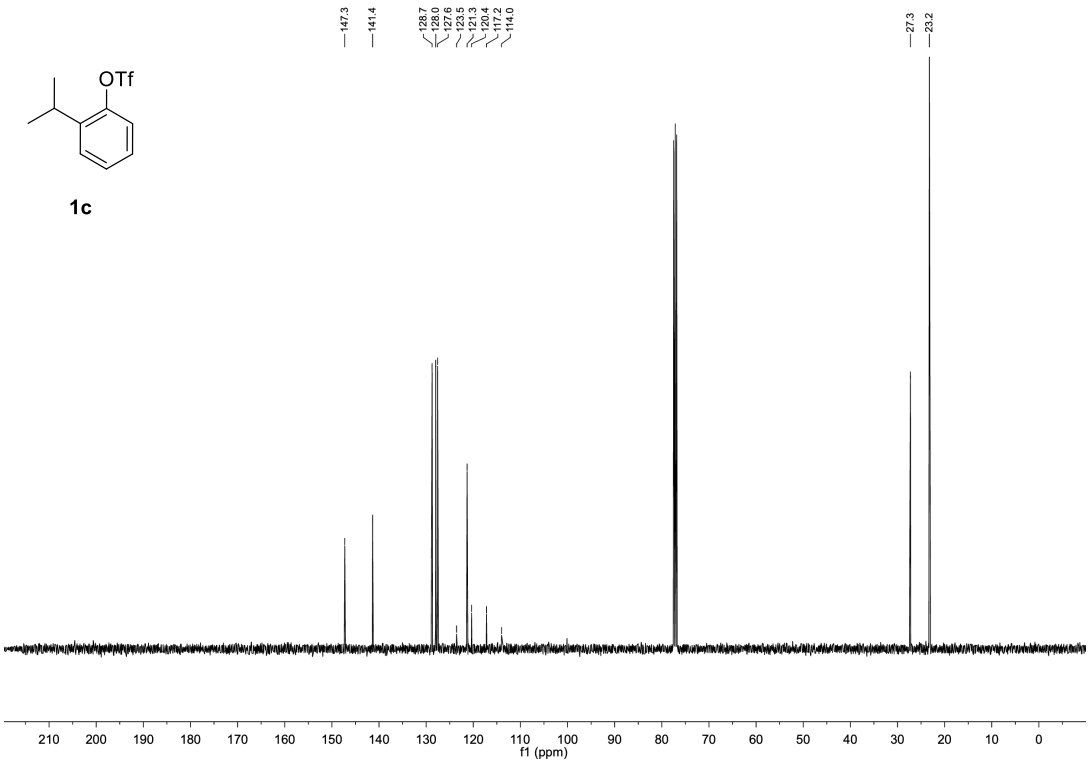


Figure S13. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1c**.

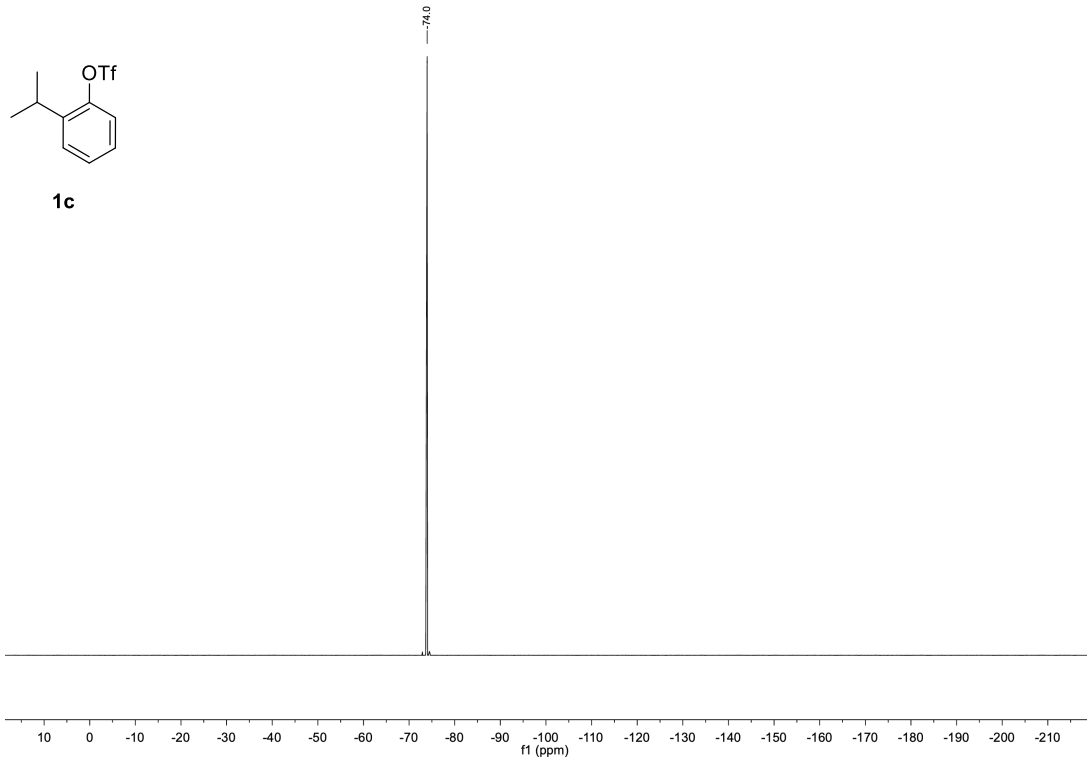
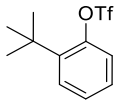


Figure S14. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1c**.

2-(*tert*-Butyl)phenyl trifluoromethanesulfonate (1d):



1d

$C_{11}H_{13}F_3O_3S$ (282.28 g/mol)

Following **GP-A**, **1d** was synthesized using 2-(*tert*-butyl)phenol (1.50 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 95:5) afforded **1d** (2.57 g, 9.10 mmol, 91%) as colorless oil. Conforms to reported analytical data.[6]

R_f: 0.87 (*n*-hexane/EtOAc 95:5).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.51 – 7.46 (m, 1H), 7.39 – 7.34 (m, 1H), 7.31 – 7.26 (m, 2H), 1.44 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 149.3, 141.6, 128.7, 128.0, 127.8, 121.1, 118.5 (q, *J* = 319.9 Hz), 34.9, 30.5.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -74.2.

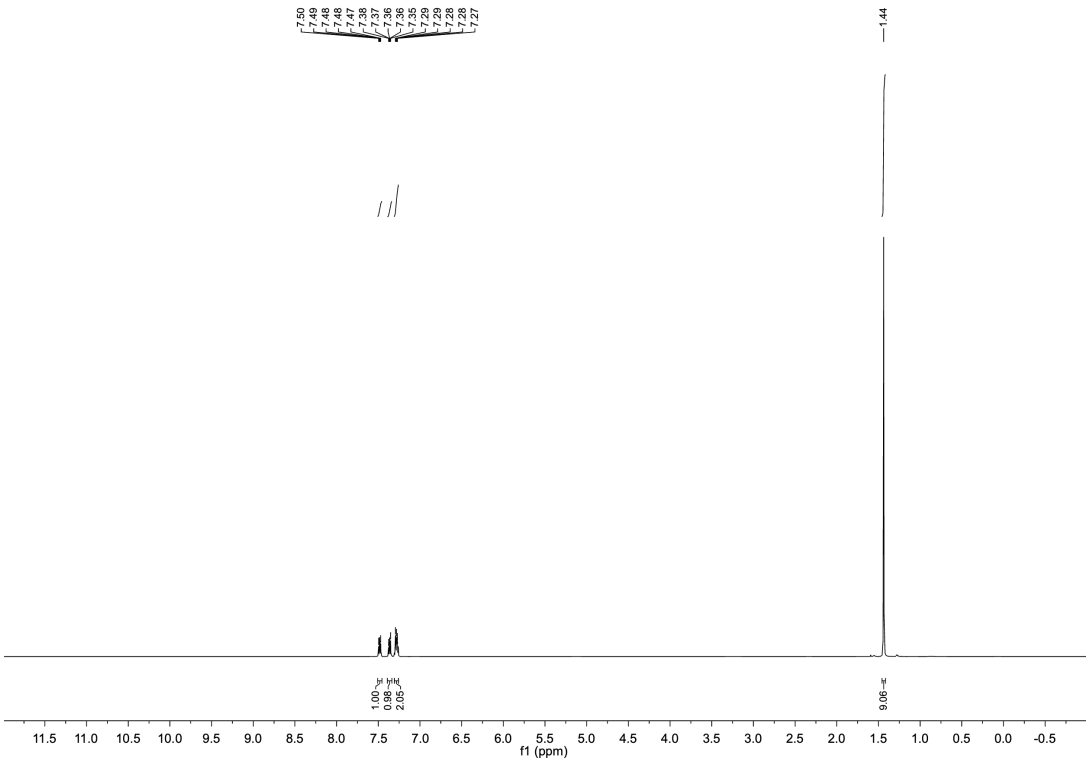


Figure S15. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1d**.

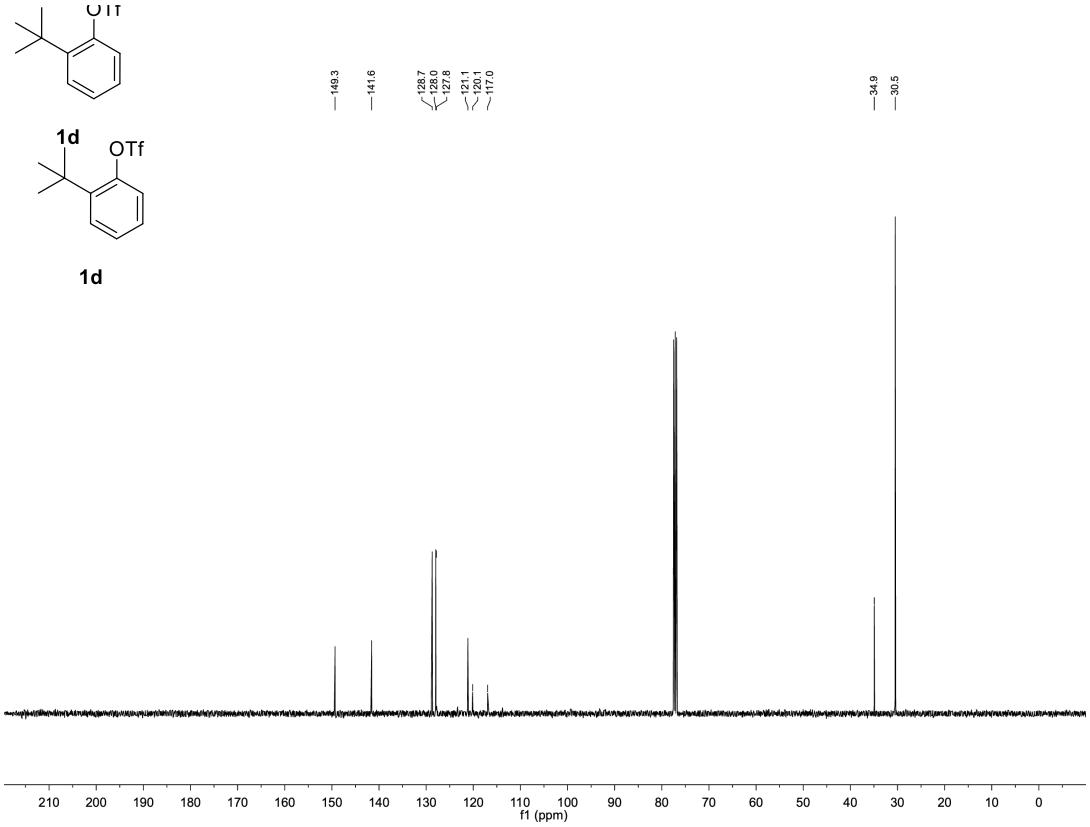


Figure S16. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1d**.

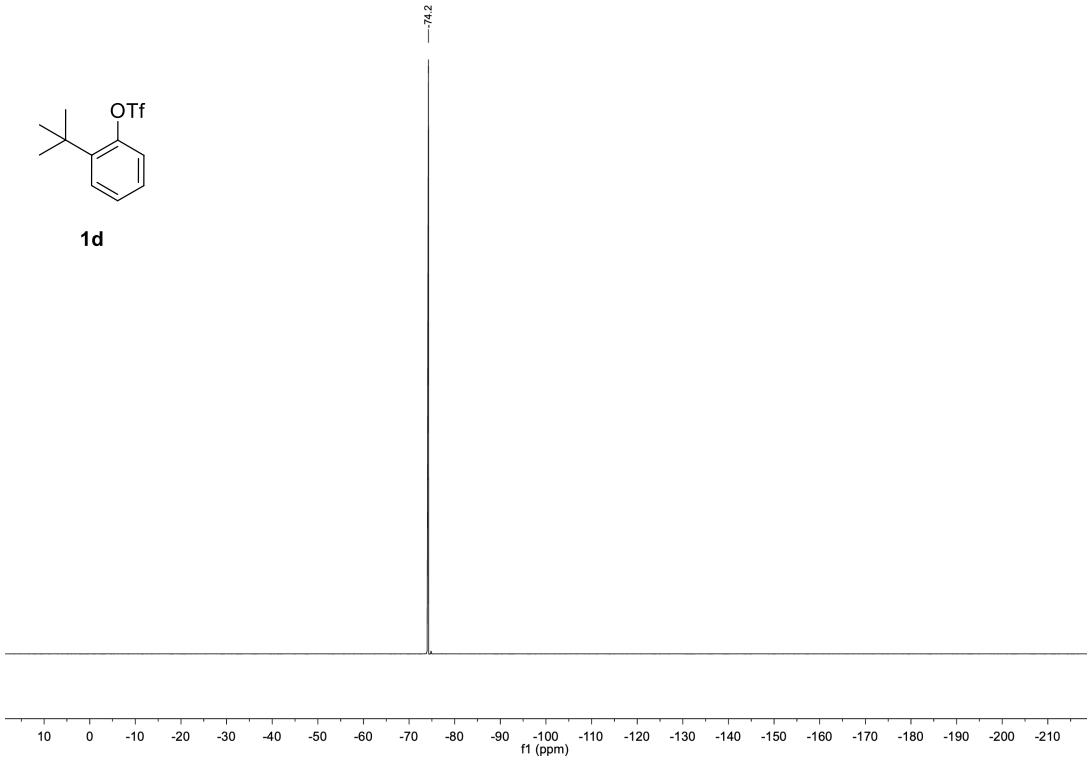
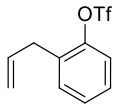


Figure S17. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1d**.

2-Allylphenyl trifluoromethanesulfonate (1e):



1e

$C_{10}H_9F_3O_3S$ (266.23 g/mol)

Following **GP-A**, **1e** was synthesized using 2-allylphenol (1.34 g, 10.0 mmol, 1.0 equiv.). Aqueous work-up afforded **1e** (2.18 g, 8.19 mmol, 82%) as yellow oil, which was used without further purification. Conforms to reported analytical data.[7]

R_f: 0.32 (*n*-hexane).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.41 – 7.27 (m, 4H), 6.02 – 5.88 (m, 1H), 5.22 – 5.11 (m, 2H), 3.52 (d, *J* = 6.6 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 148.1, 134.7, 133.0, 131.5, 128.5, 128.3, 121.5, 118.8 (q, *J* = 319.8 Hz), 117.5, 34.1.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -74.0.

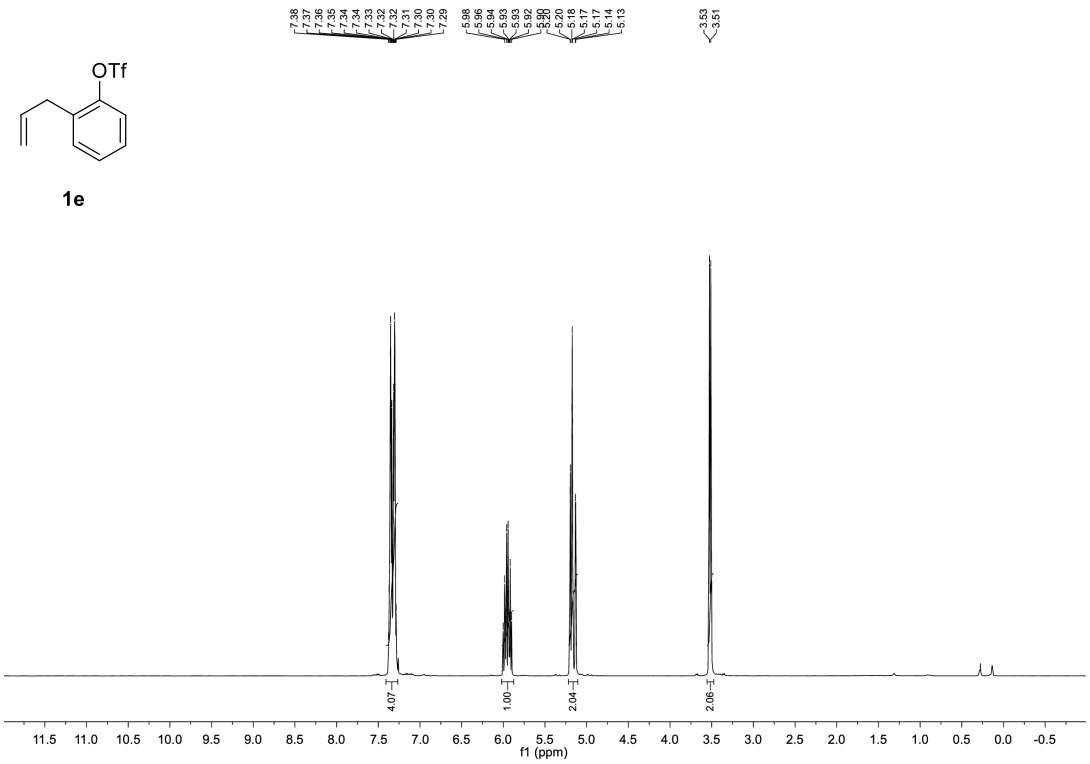


Figure S18. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1e**.

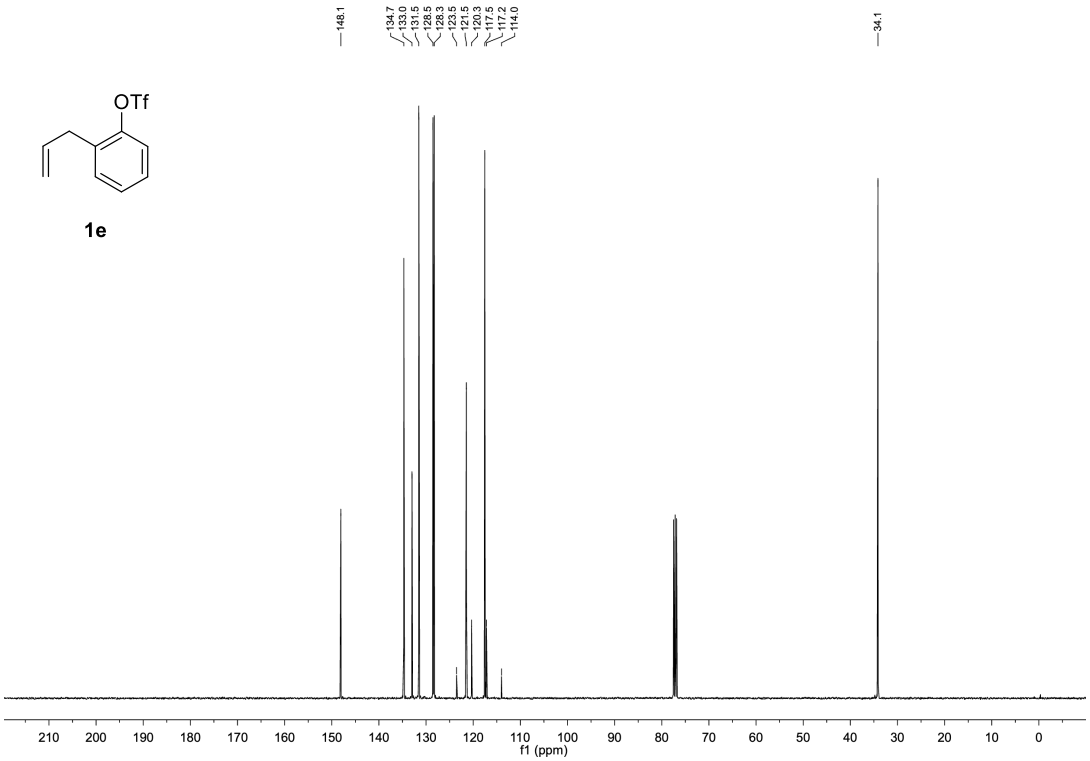


Figure S19. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1e**.

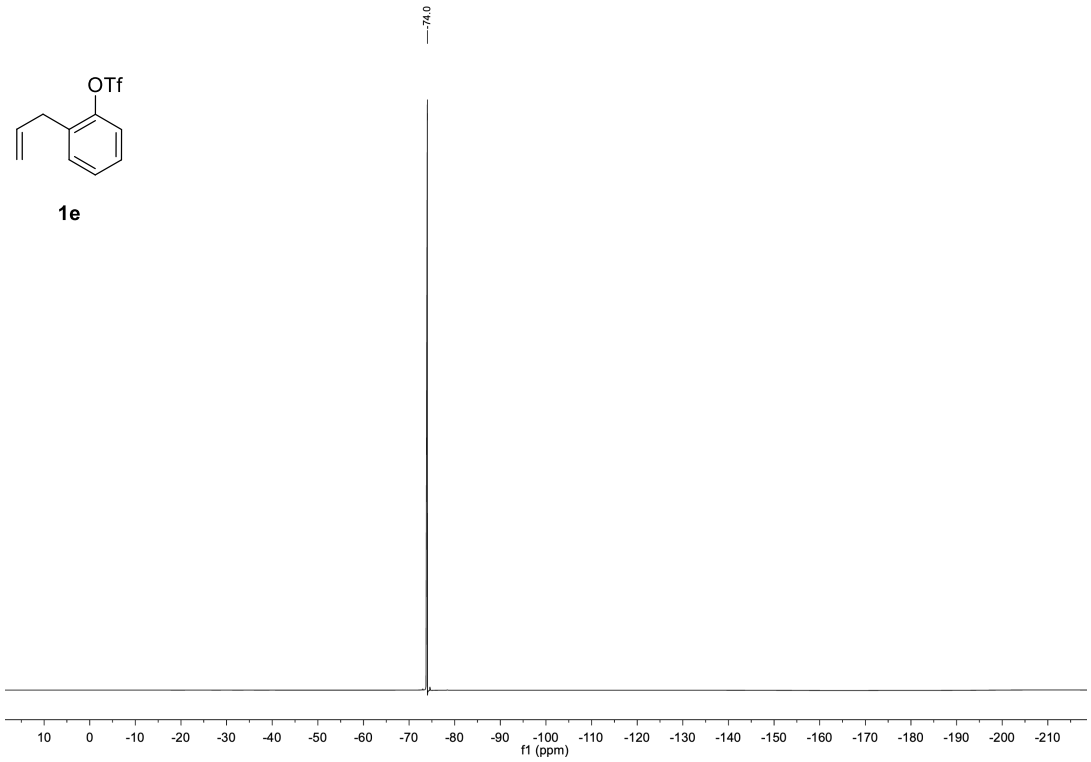
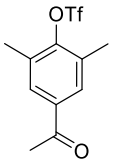


Figure S20. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1e**.

4-Acetyl-2,6-dimethylphenyl trifluoromethanesulfonate (1f):



1f

$C_{11}H_{11}F_3O_4S$ (296.26 g/mol)

Following **GP-A**, **1f** was synthesized using 3,5-dimethyl-4-hydroxyacetophenone (1.64 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1f** (2.66 g, 8.99 mmol, 90%) as a pale yellow solid. Conforms to reported analytical data.[8]

R_f: 0.33 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.71 (s, 2H), 2.58 (s, 3H), 2.44 (s, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 196.9, 149.9, 136.4, 132.3, 130.1, 118.7 (q, *J* = 320.0 Hz), 26.8, 17.4.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.3.

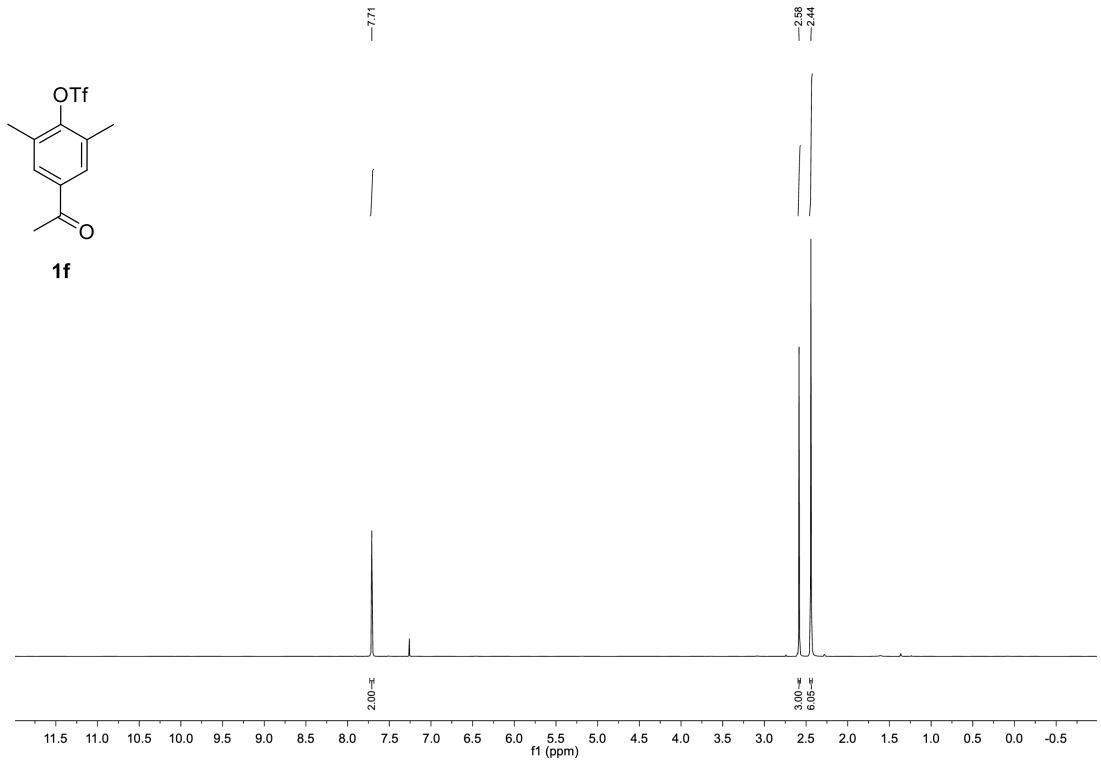


Figure S21. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1f**.

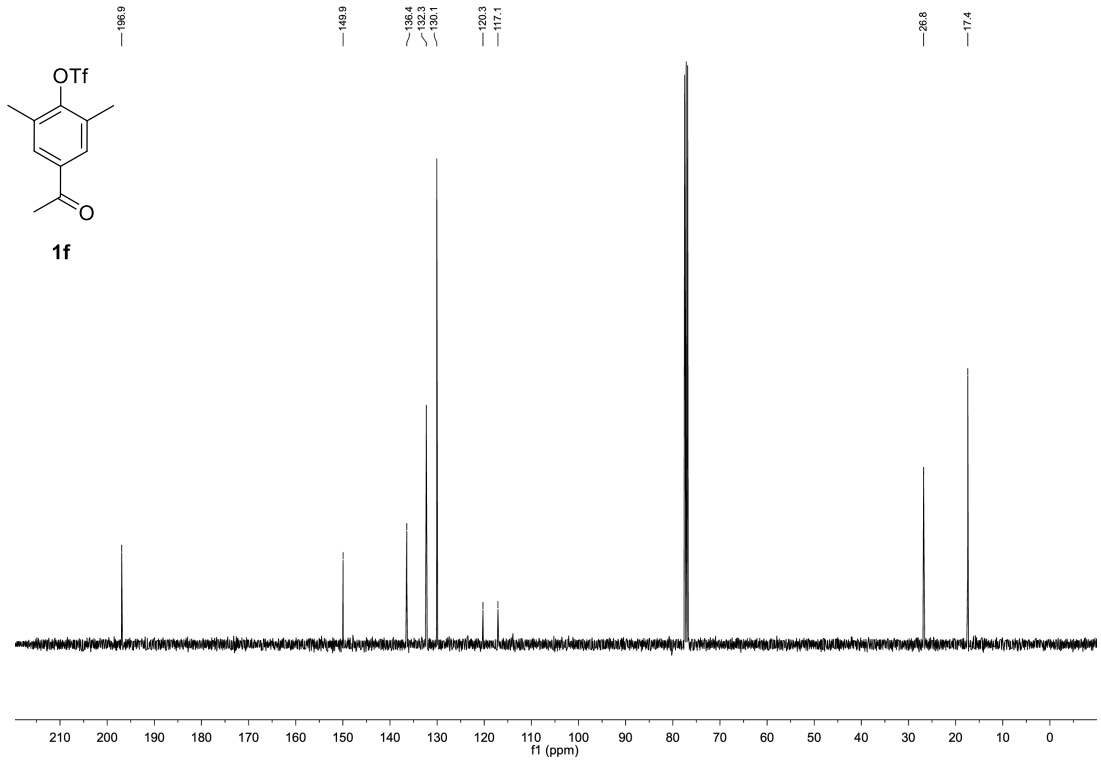


Figure S22. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1f**.

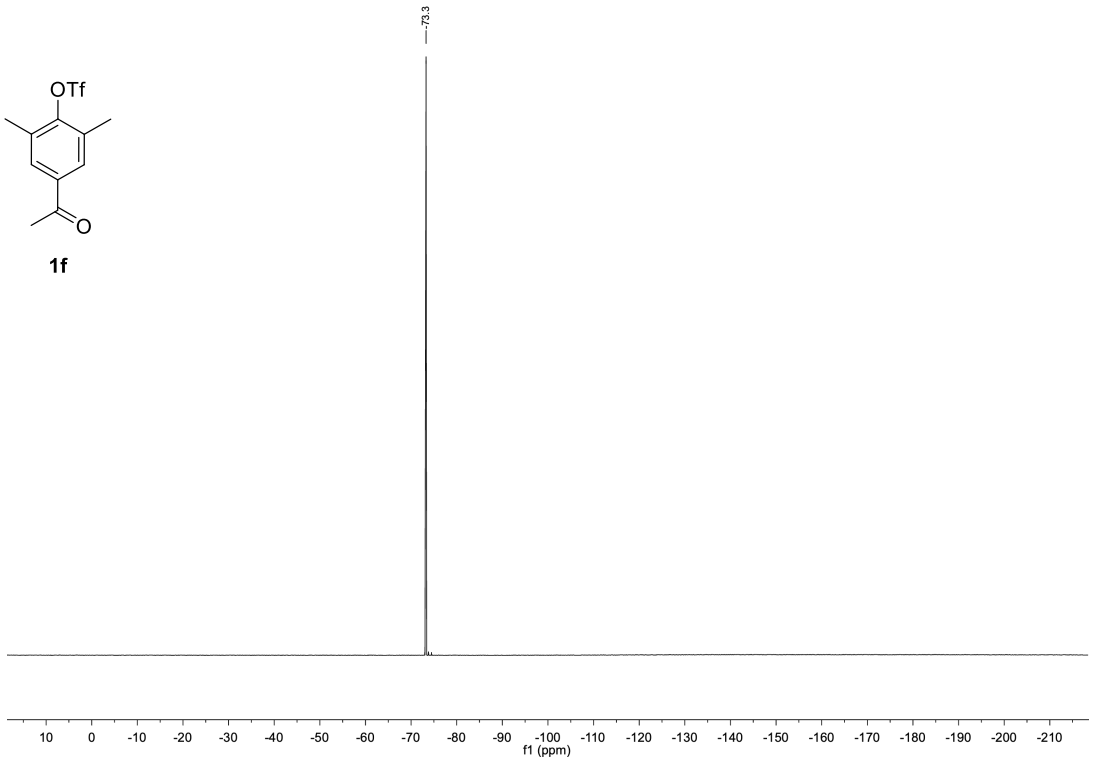
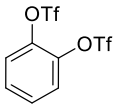


Figure S23. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1f**.

1,2-Phenylene bis(trifluoromethanesulfonate) (1g):



1g

$C_8H_4F_6O_6S_2$ (374.22 g/mol)

Following **GP-A**, **1g** was synthesized using catechol (1.10 g, 10.0 mmol, 1.0 equiv.), pyridine (4.75 g, 60.0 mmol, 6.0 equiv.) and trifluoromethanesulfonic anhydride (6.21g, 22.0 mmol, 2.2 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1g** (1.75 g, 4.68 mmol, 47%) as colorless oil. Conforms to reported analytical data.[9]

R_f: 0.43 (*n*-hexane/EtOAc 95:5).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.49 (s, 4H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 140.7, 129.8, 123.9, 118.7 (q, *J* = 320.7 Hz).

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.2.

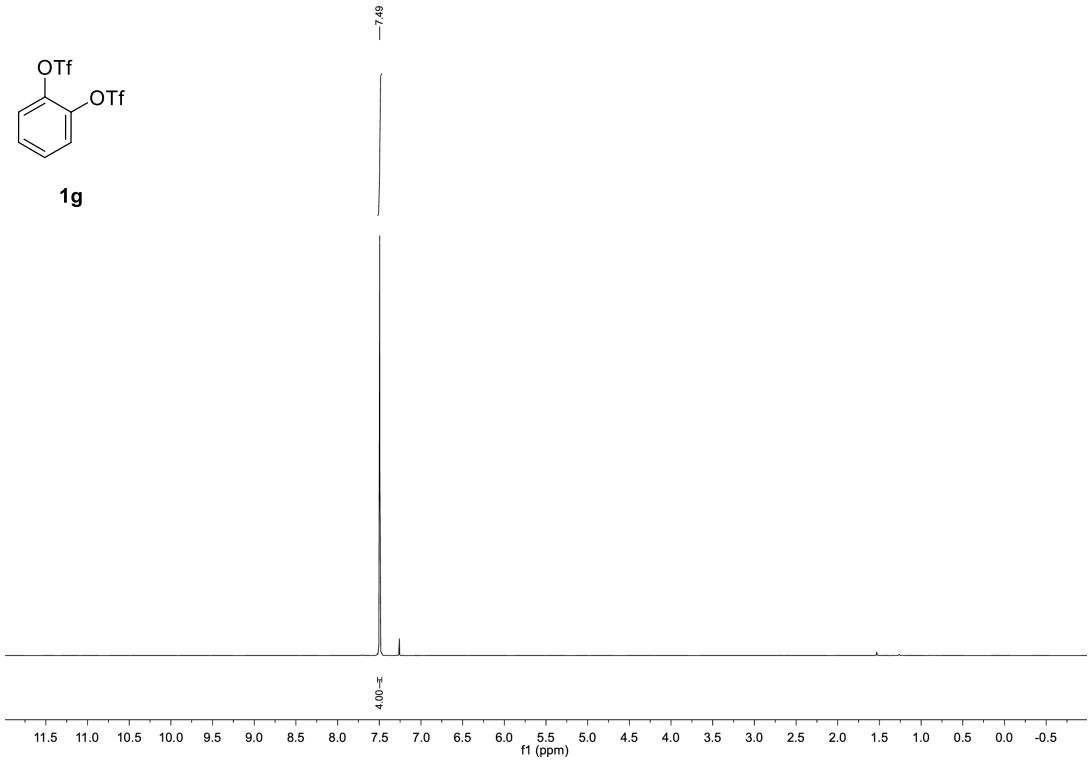


Figure S24. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1g**.

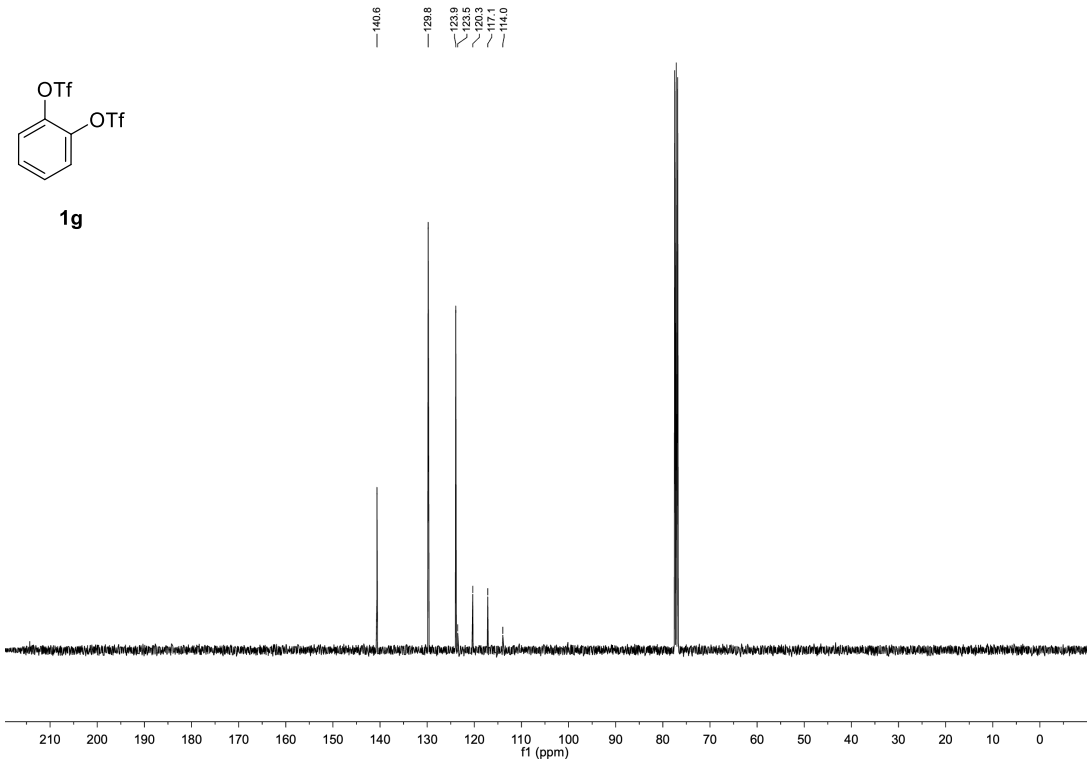


Figure S25. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1g**.

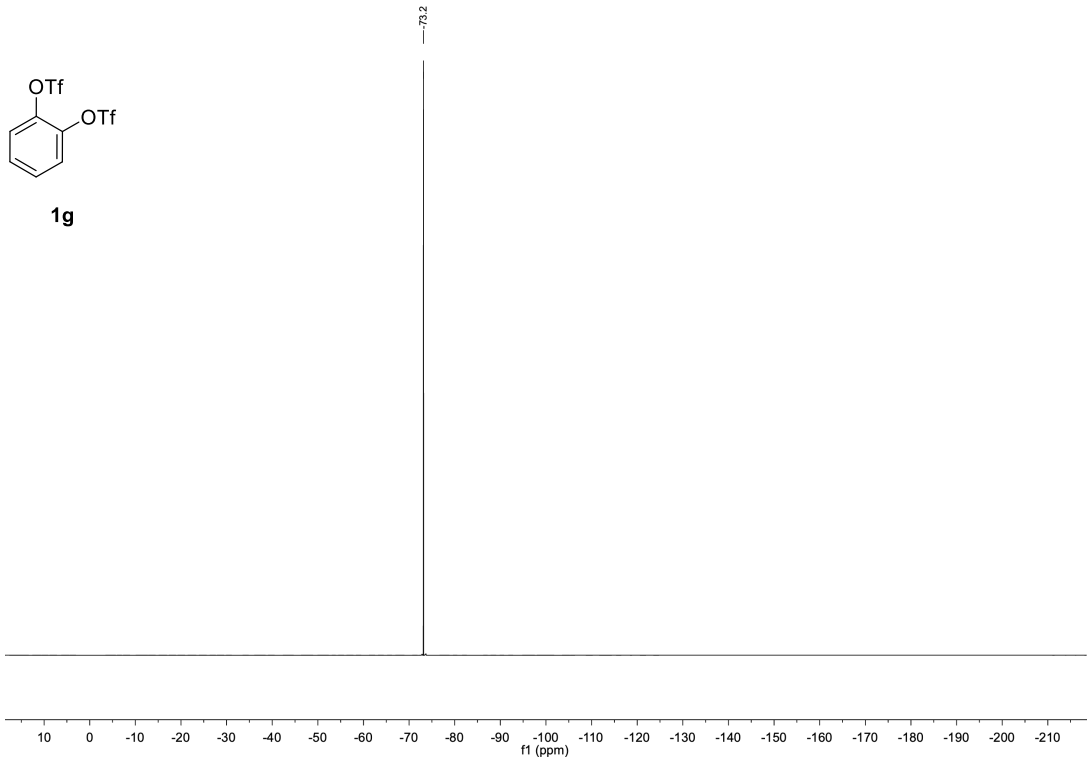
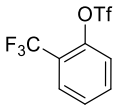


Figure S26. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1g**.

2-(Trifluoromethyl)phenyl trifluoromethanesulfonate (1h):



1h

$C_8H_4F_6O_3S$ (294.17 g/mol)

Following **GP-A**, **1h** was synthesized using 2-(trifluoromethyl)phenol (1.62 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1h** (1.71 g, 5.81 mmol, 58%) as a colorless oil. Conforms to reported analytical data.[10]

R_f: 0.58 (*n*-hexane/EtOAc 95:5).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.80 – 7.74 (m, 1H), 7.71 – 7.63 (m, 1H), 7.56 – 7.46 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 146.3 (q, *J* = 1.9 Hz), 134.1, 128.2 (q, *J* = 4.8 Hz), 123.2, 122.5, 122.2 (q, *J* = 273.1 Hz), 118.6 (q, *J* = 320.2 Hz).

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -60.9, -73.7.

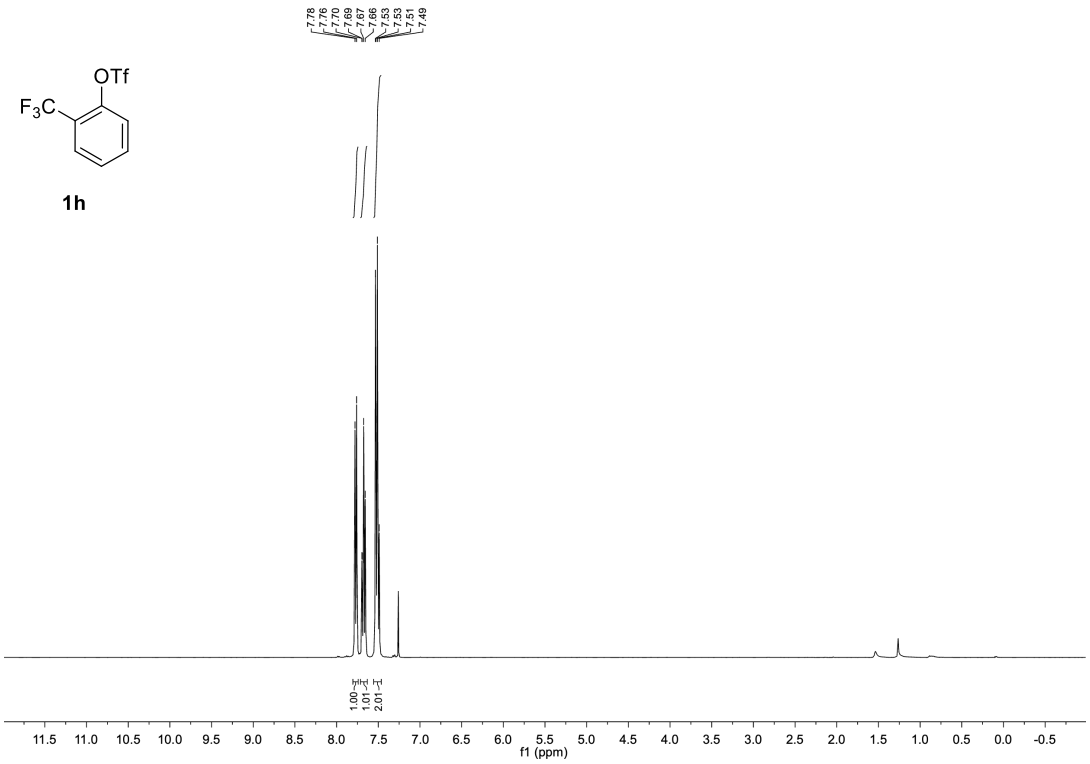


Figure S27. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1h**.

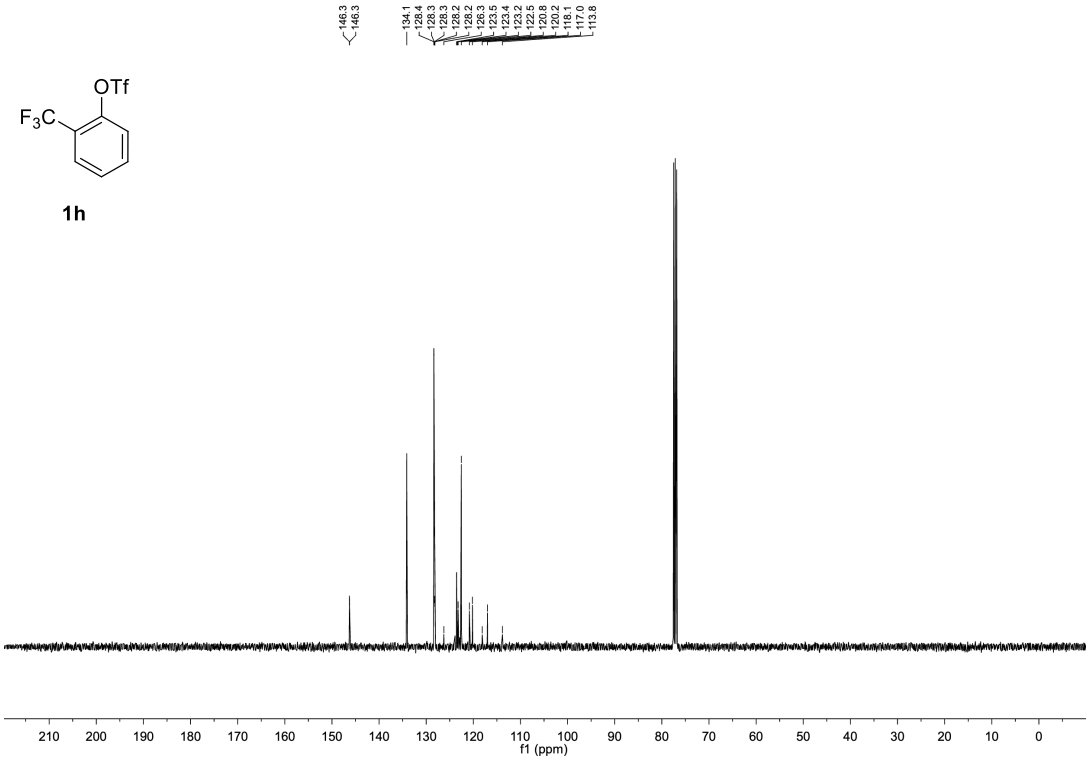


Figure S28. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1h**.

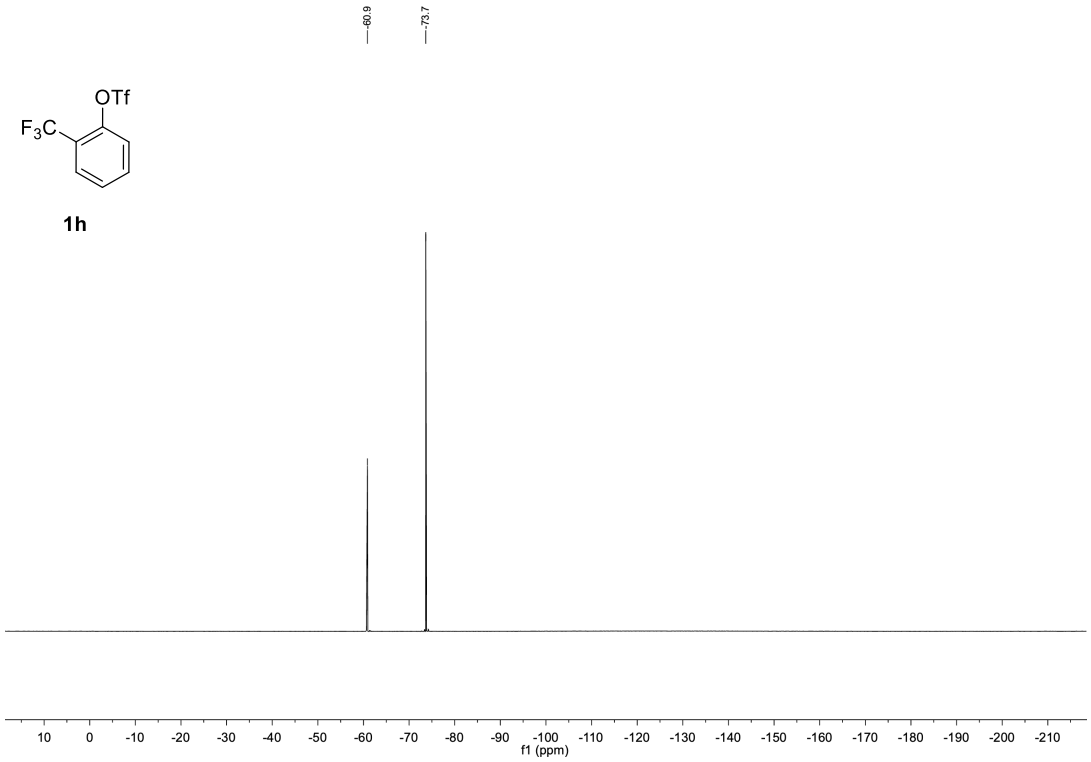
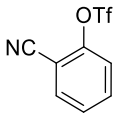


Figure S29. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1h**.

2-Cyanophenyl trifluoromethanesulfonate (1i):



1i

$C_8H_4F_3NO_3S$ (251.18 g/mol)

Following **GP-A**, **1i** was synthesized using 2-hydroxybenzonitrile (1.19 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 80:20) afforded **1i** (2.22 g, 8.84 mmol, 88%) as colorless oil. Conforms to reported analytical data.[11]

R_f: 0.91 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.82 – 7.68 (m, 2H), 7.58 – 7.46 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 149.8, 134.9, 134.6, 128.9, 122.8, 118.7 (q, *J* = 320.8 Hz), 113.6, 107.5.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -72.7.

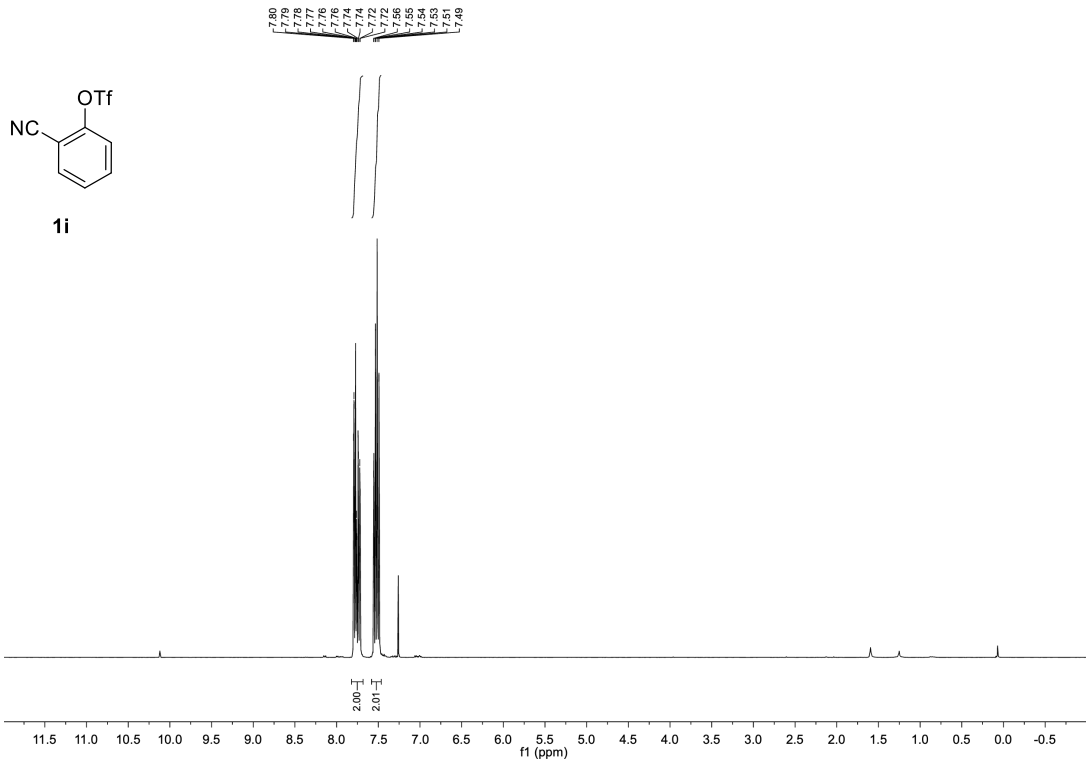


Figure S30. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1i**.

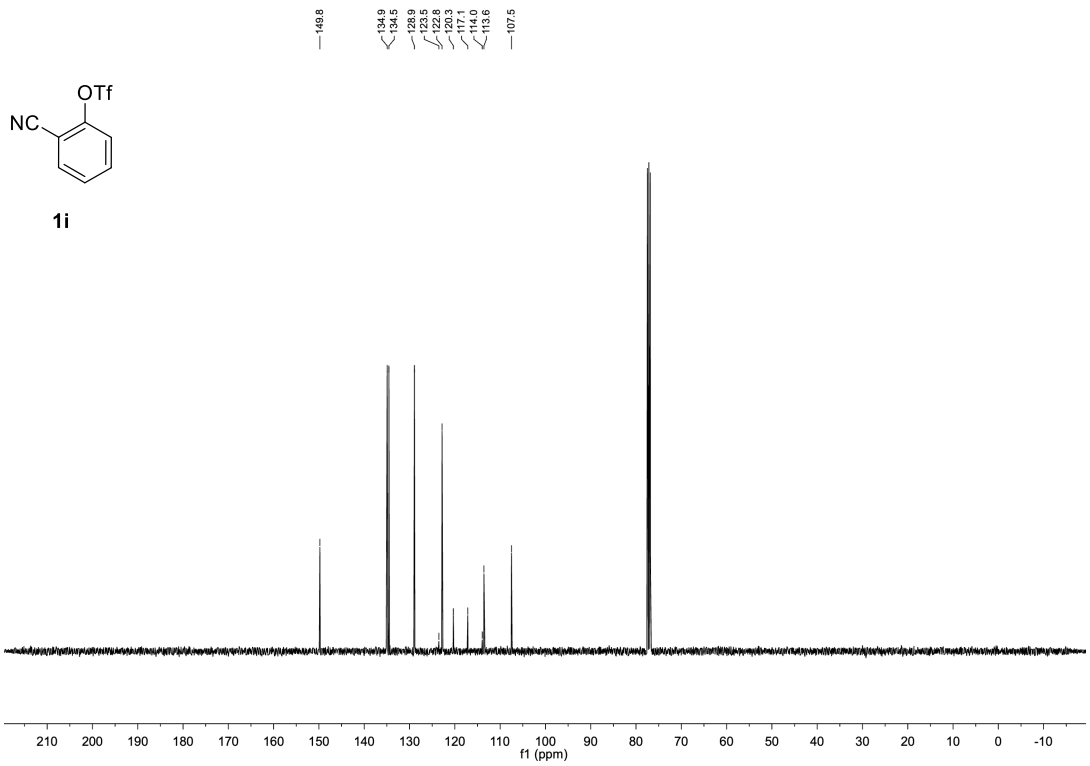


Figure S31. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1i**.

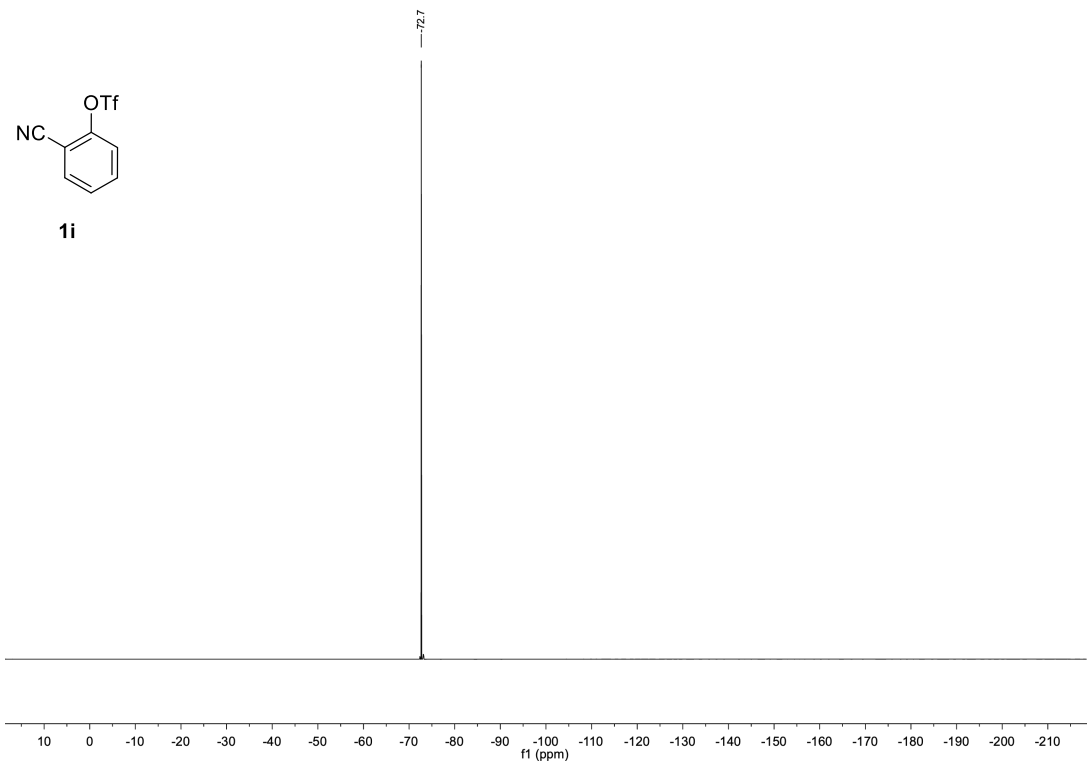
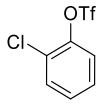


Figure S32. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1i**.

2-Chlorophenyl trifluoromethanesulfonate (1j):



1j

$C_7H_4ClF_3O_3S$ (260.61 g/mol)

Following **GP-A**, **1j** was synthesized using 2-chlorophenol (1.29 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1j** (2.23 g, 8.56 mmol, 86%) as colorless oil. Conforms to reported analytical data.[12]

R_f: 0.68 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.56 – 7.50 (m, 1H), 7.38 – 7.31 (m, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 145.9, 131.5, 129.4, 128.5, 127.4, 123.2, 118.8 (q, *J* = 320.5 Hz).

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.5.

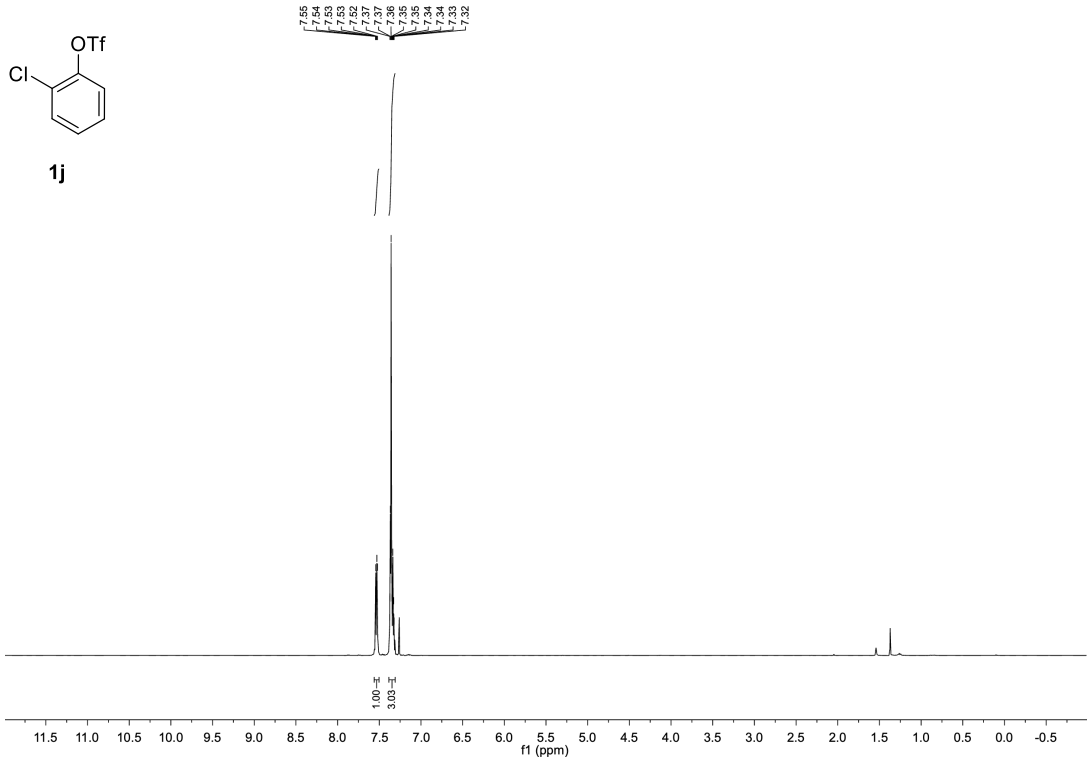


Figure S33. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1j**.

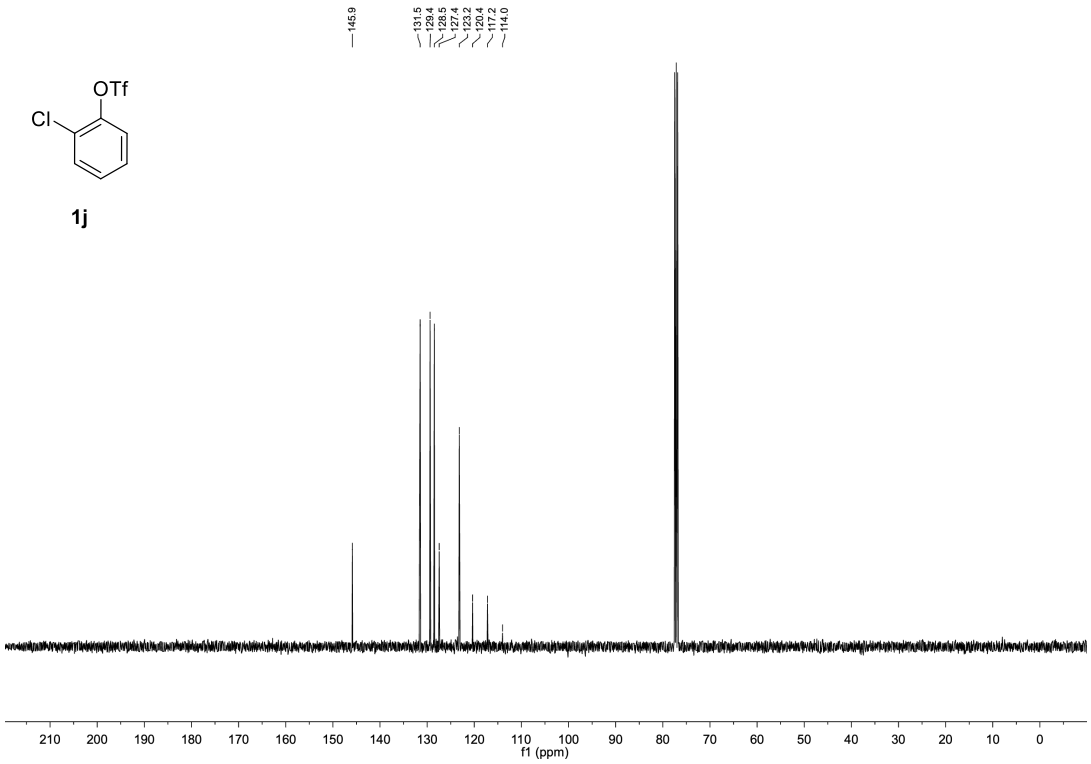


Figure S34. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1j**.

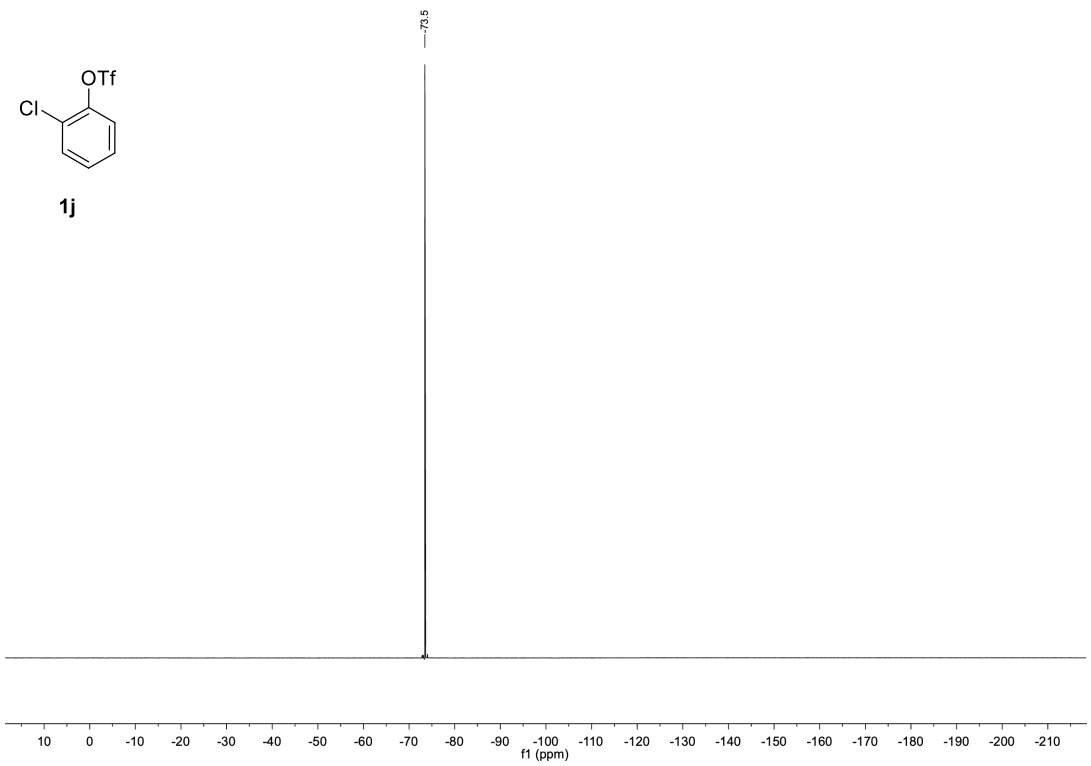
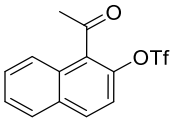


Figure S35. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1j**.

1-Acetylnaphthalen-2-yl trifluoromethanesulfonate (1k):



1k

$C_{13}H_9F_3O_4S$ (318.27 g/mol)

Following **GP-A**, **1k** was synthesized using 1-(2-hydroxynaphthalen-1-yl)ethan-1-one (1.86 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 80:20) afforded **1k** (2.66 g, 8.36 mmol, 84%) as a pale-yellow oil. Conforms to reported analytical data.[5]

R_f: 0.15 (*n*-hexane/EtOAc 99:1).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.01 – 7.89 (m, 2H), 7.85 – 7.78 (m, 1H), 7.67 – 7.56 (m, 2H), 7.49 – 7.42 (m, 1H), 2.73 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 200.8, 142.5, 132.6, 132.1, 131.8, 129.8, 128.8, 128.7, 127.7, 125.1, 119.2, 118.6 (q, *J* = 320.5 Hz), 32.9.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.3.

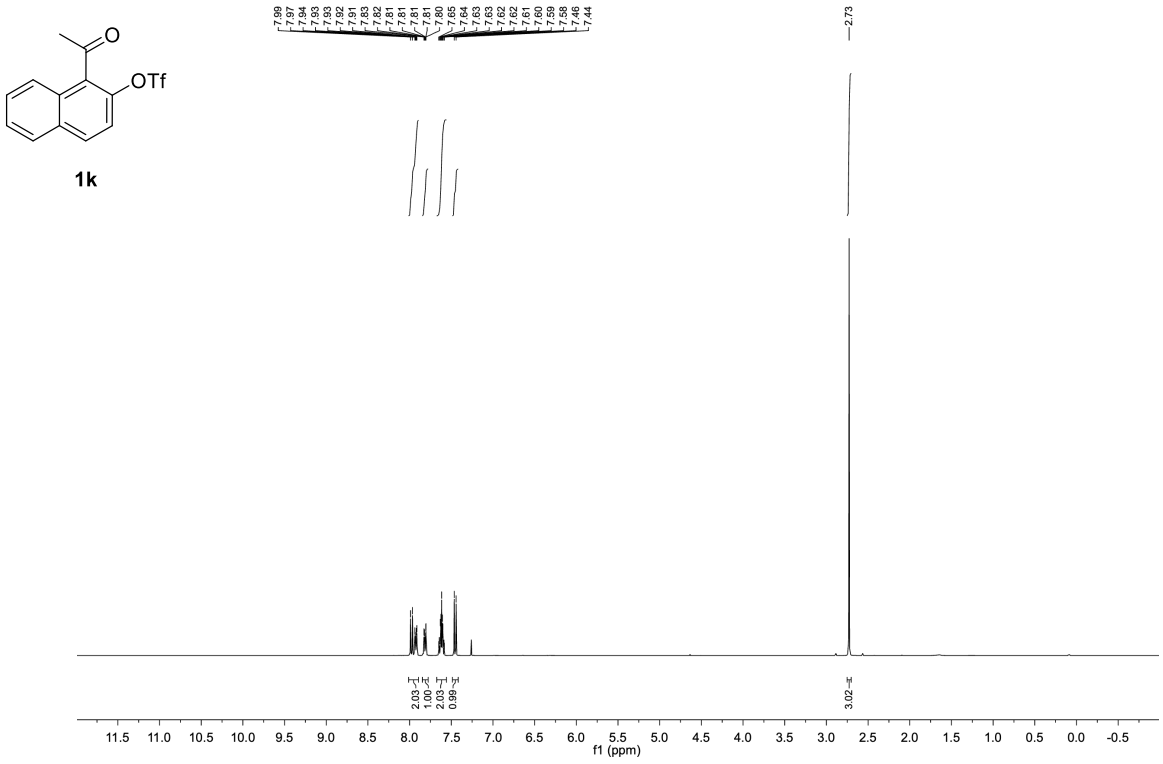


Figure S36. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1k**.

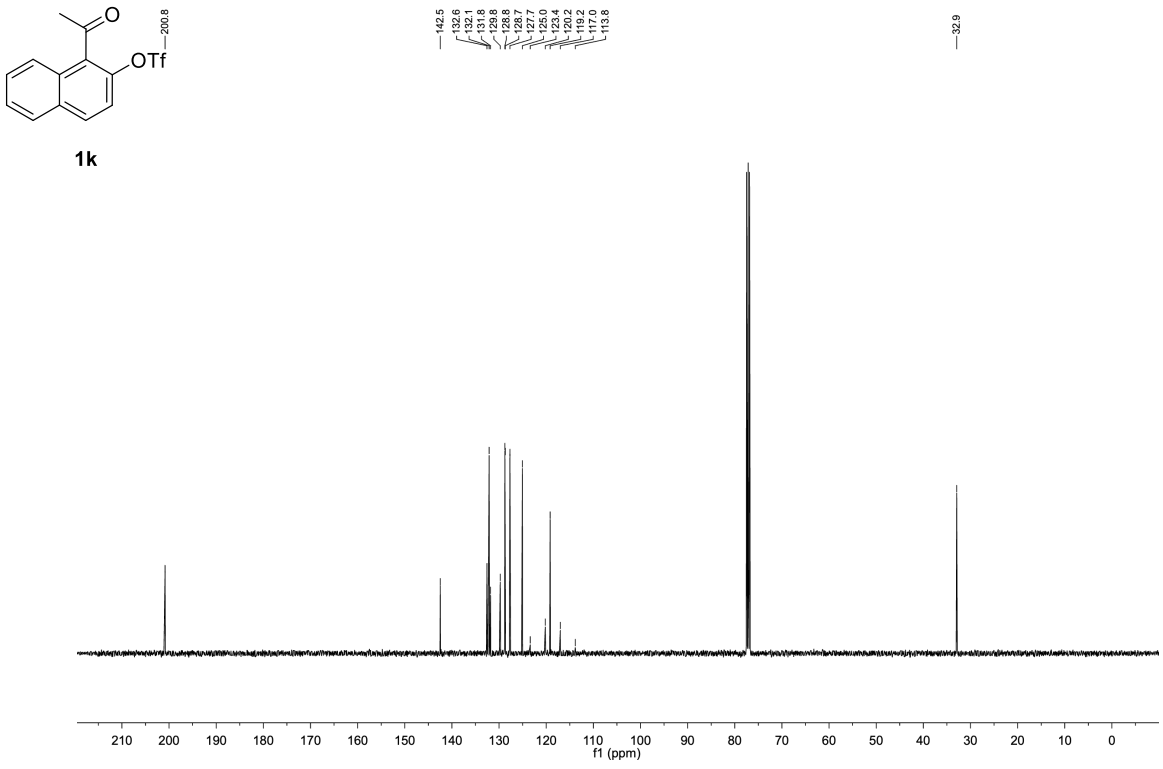


Figure S37. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1k**.

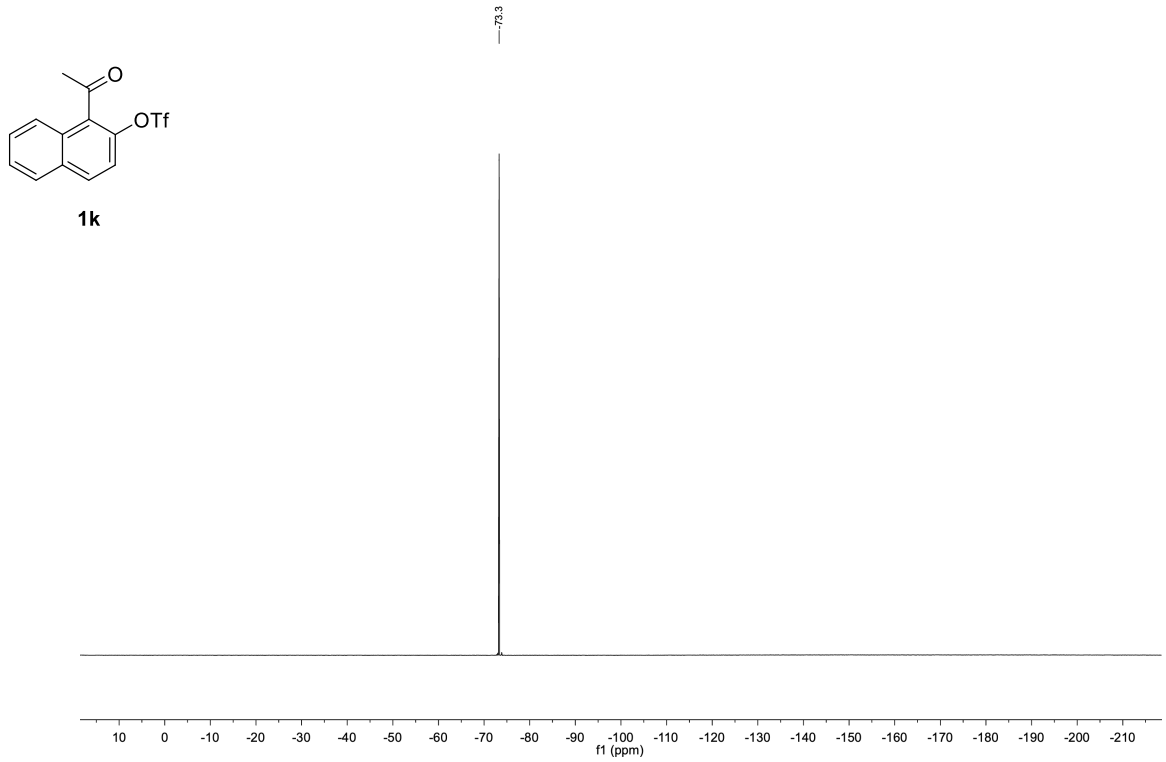
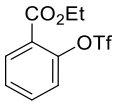


Figure S38. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1k**.

Ethyl 2-(((trifluoromethyl)sulfonyl)oxy)benzoate (1l):



1l

$C_{10}H_9F_3O_5S$ (298.23 g/mol)

Following **GP-A**, **1l** was synthesized using ethyl 2-hydroxybenzoate (1.66 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1l** (2.71 g, 9.10 mmol, 91%) as a colorless oil. Conforms to reported analytical data.[13]

R_f: 0.32 (*n*-hexane/EtOAc 10:1).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.09 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.52 – 7.43 (m, 1H), 7.33 – 7.27 (m, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 163.9, 148.4, 134.2, 132.9, 128.5, 125.0, 122.8, 118.8 (q, *J* = 320.7 Hz), 62.3, 14.2.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.4.

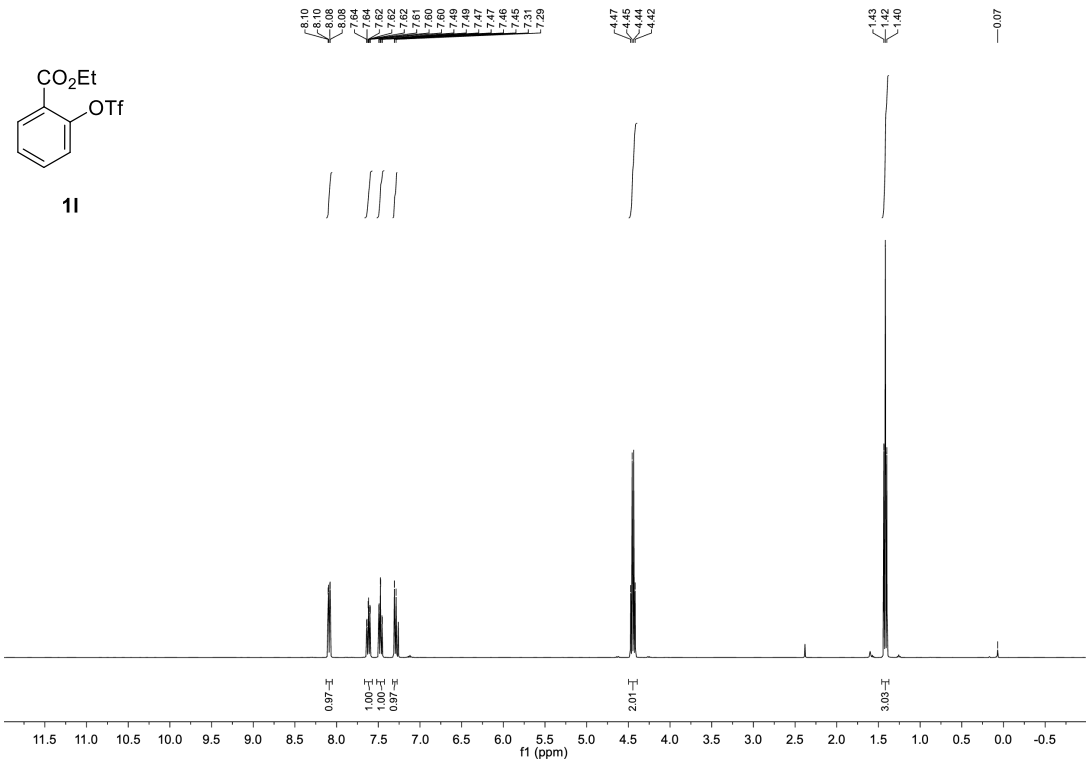


Figure S39. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1l**.

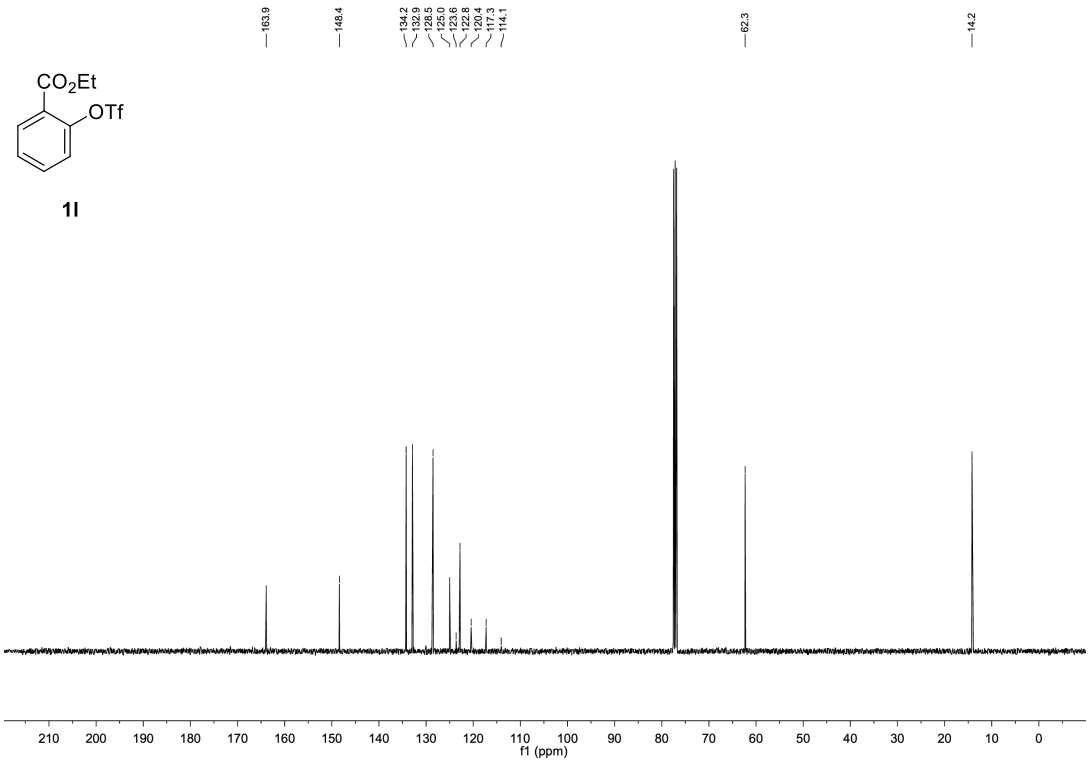


Figure S40. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1l**.

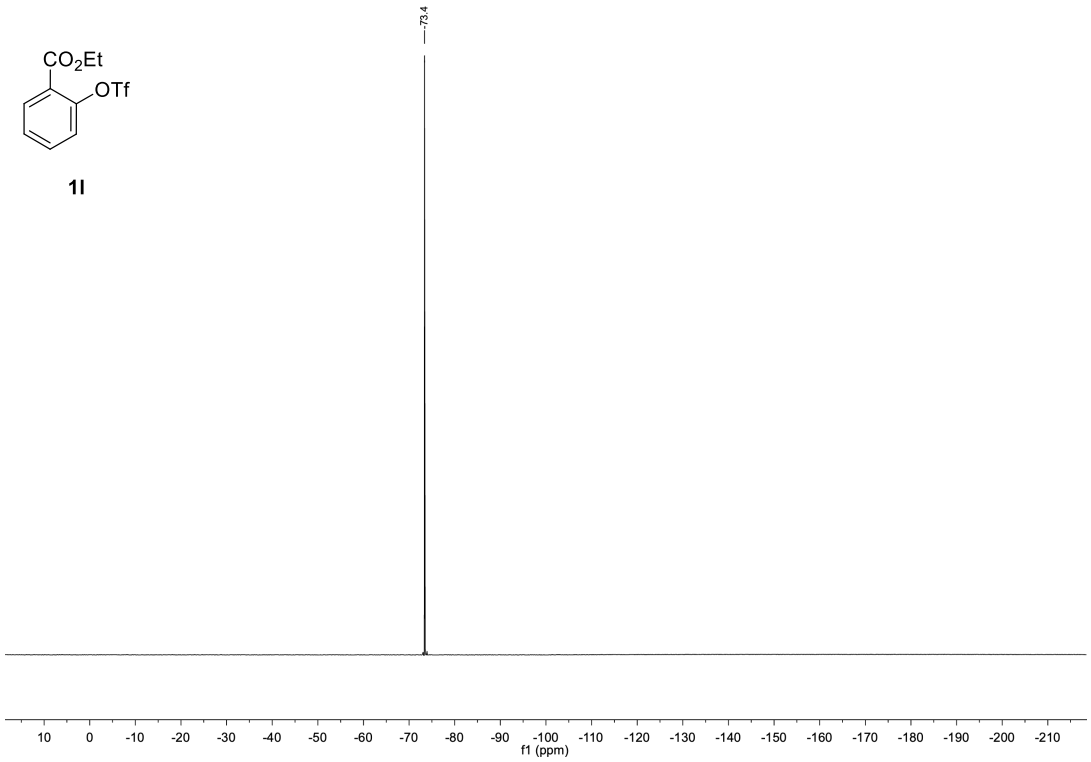
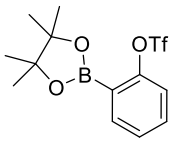


Figure S41. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1l**.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate (1m):



1m

$C_{13}H_{16}BF_3O_5S$ (352.13 g/mol)

Following **GP-A**, **1m** was synthesized using 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (2.20 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1m** (3.25 g, 9.23 mmol, 92%) as colorless oil. Conforms to reported analytical data.[11]

R_f: 0.66 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.89 – 7.84 (m, 1H), 7.55 – 7.49 (m, 1H), 7.40 – 7.35 (m, 1H), 7.24 – 7.20 (m, 1H), 1.37 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 154.4, 137.3, 133.0, 127.9, 121.2, 119.0 (q, *J* = 320.8 Hz), 100.1, 84.7, 24.9.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.1.

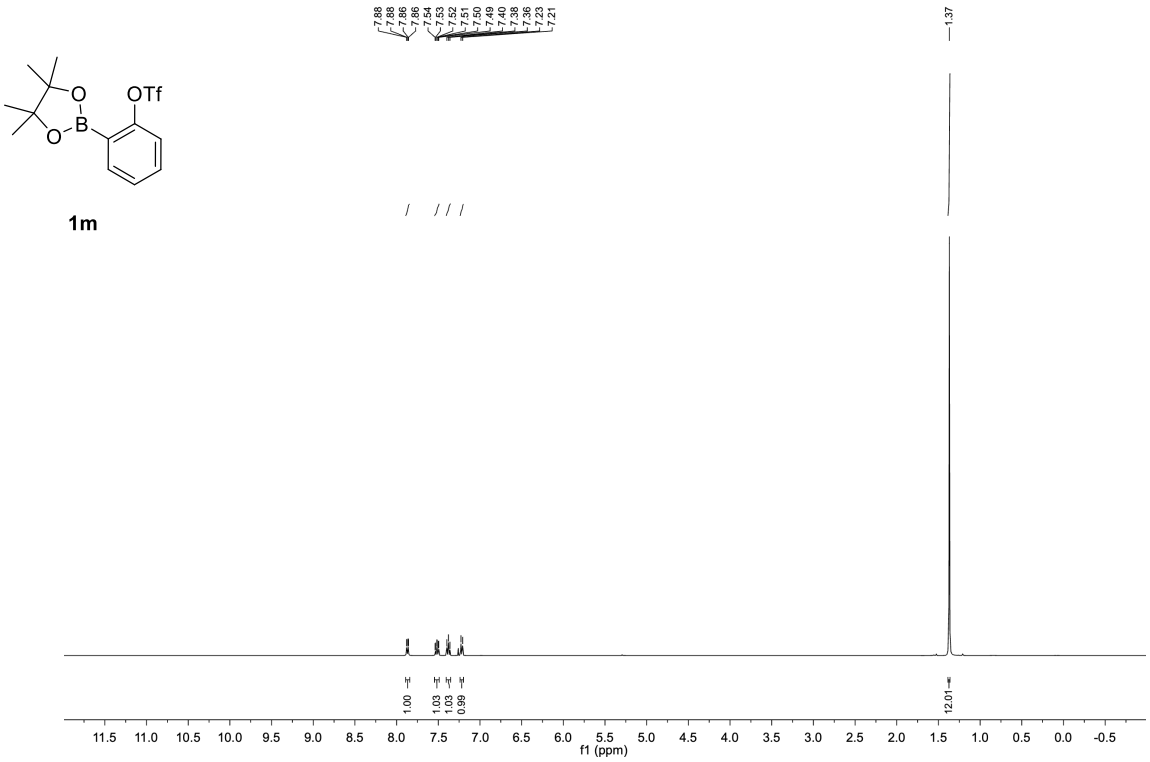


Figure S42. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1m**.

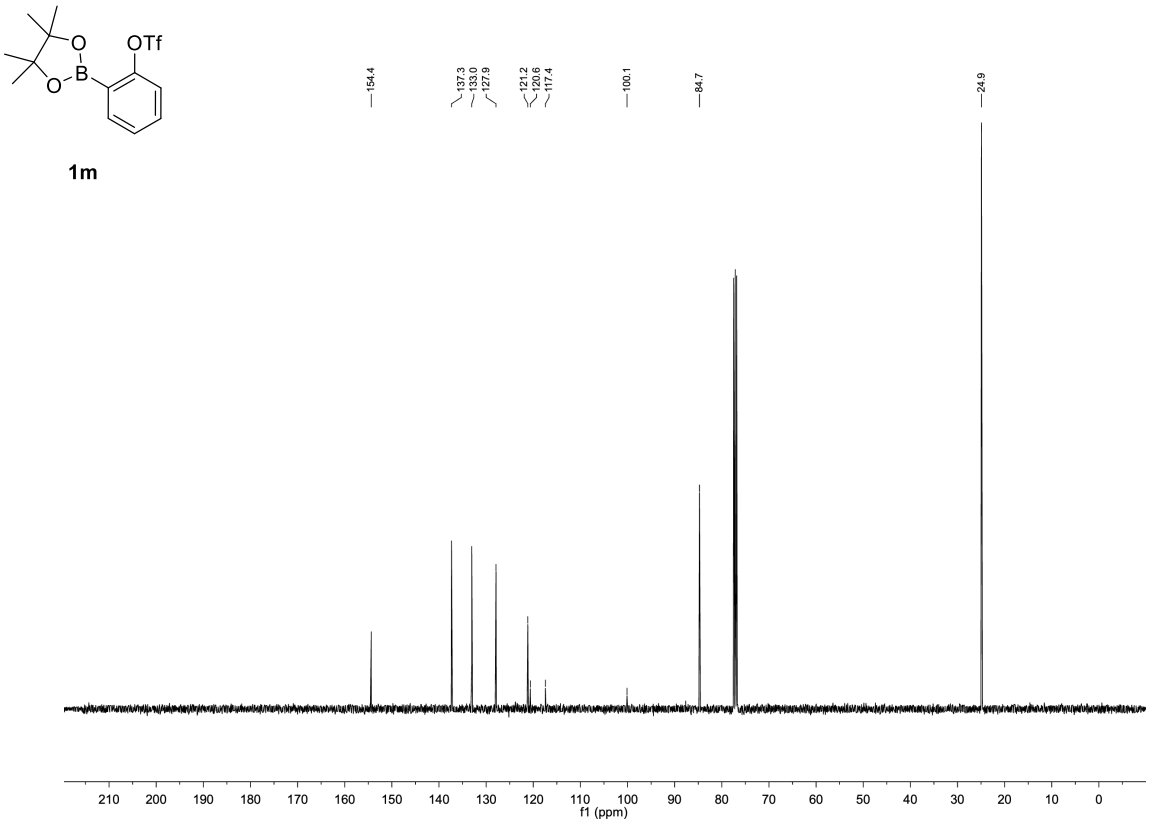


Figure S43. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1m**.

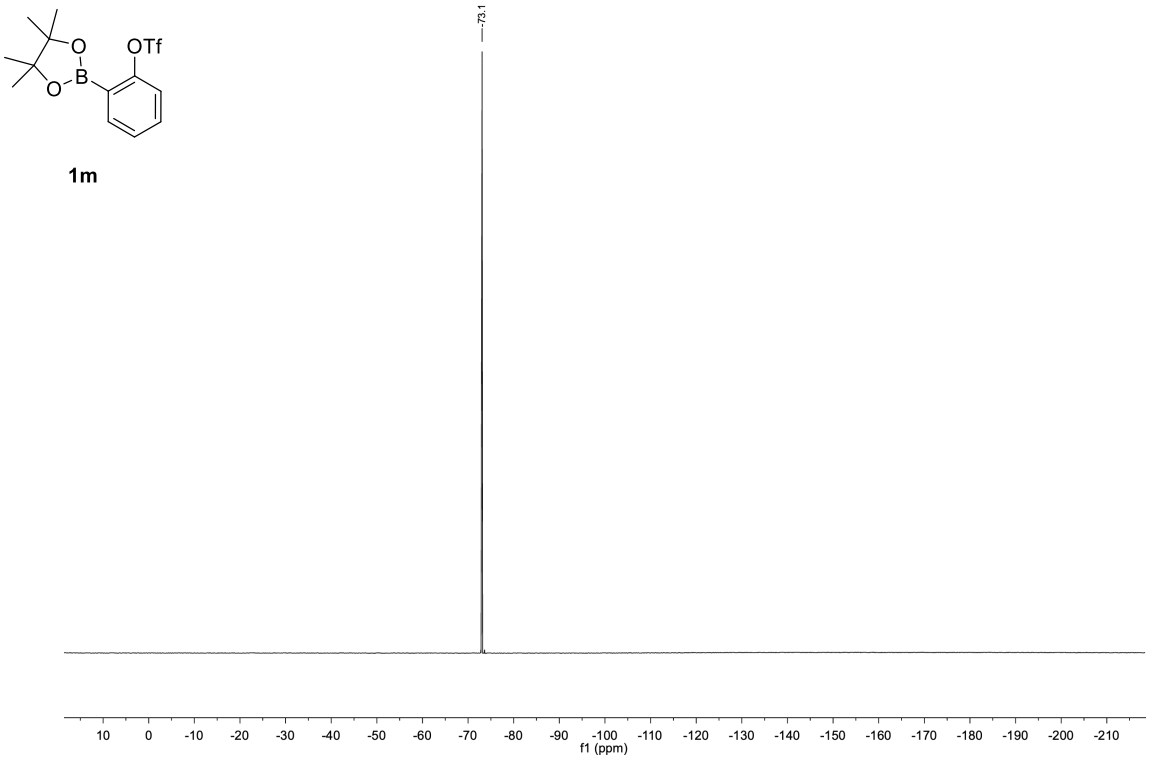
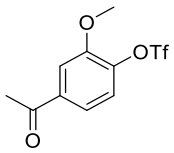


Figure S44. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1m**.

4-Acetyl-2-methoxyphenyl trifluoromethanesulfonate (1n):



1n

$C_{10}H_9F_3O_5S$ (298.23 g/mol)

Following **GP-A**, **1n** was synthesized using acetovanillon (1.66 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 80:20) afforded **1n** (1.44 g, 4.83 mmol, 48%) as a colorless solid. Conforms to reported analytical data.[14]

R_f: 0.40 (*n*-hexane/EtOAc 80:20).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.66 (d, *J* = 2.0 Hz, 1H), 7.57 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 3.98 (s, 3H), 2.62 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 196.5, 151.8, 142.0, 137.9, 122.7, 121.8, 118.6 (q, *J* = 321.1 Hz), 112.4, 56.6, 26.8.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.7.

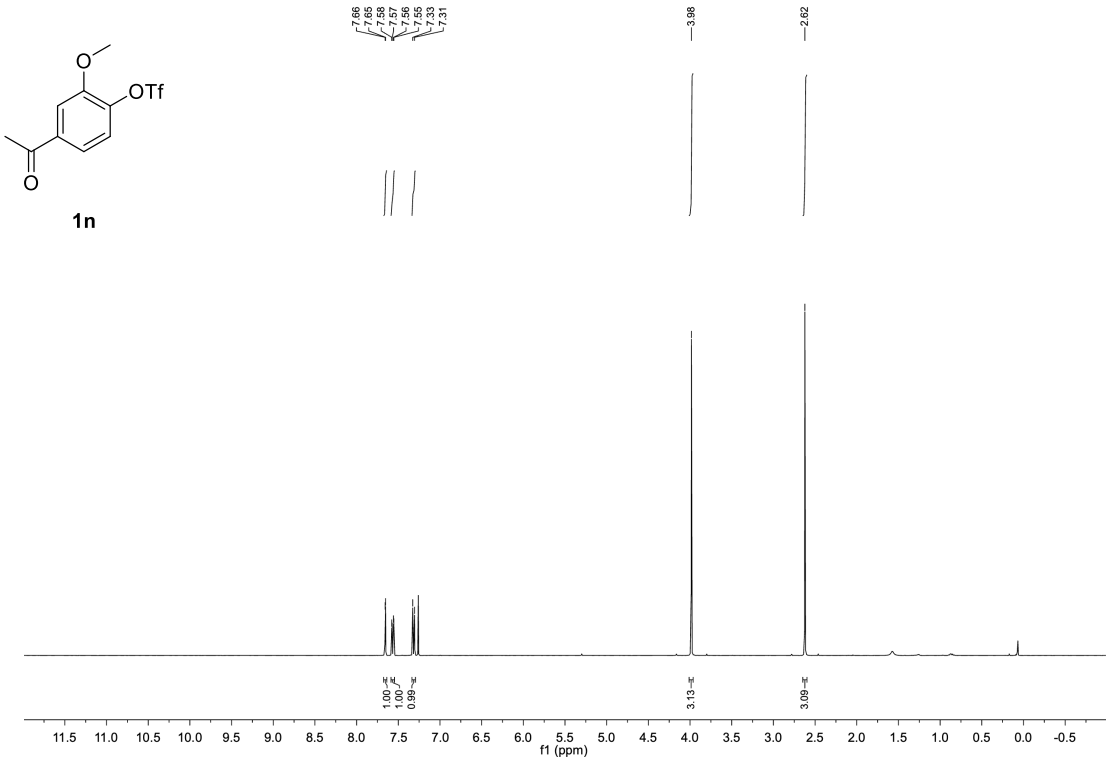


Figure S45. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1n**.

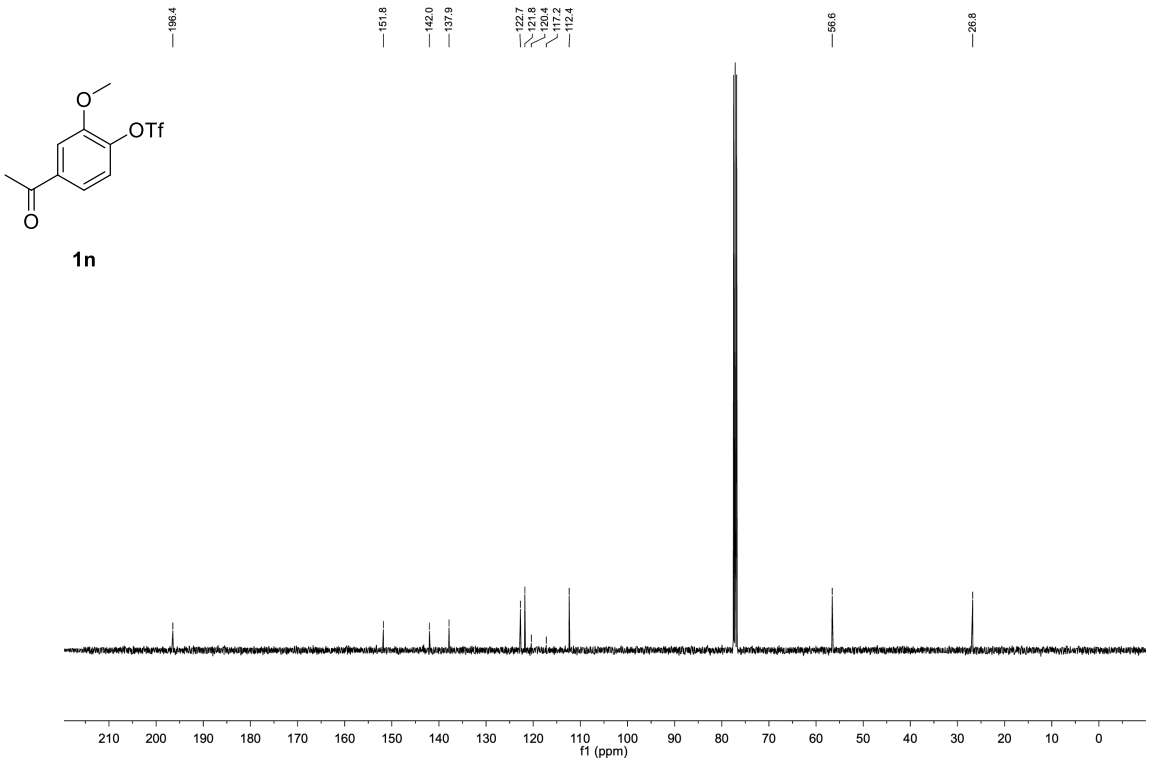


Figure S46. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1n**.

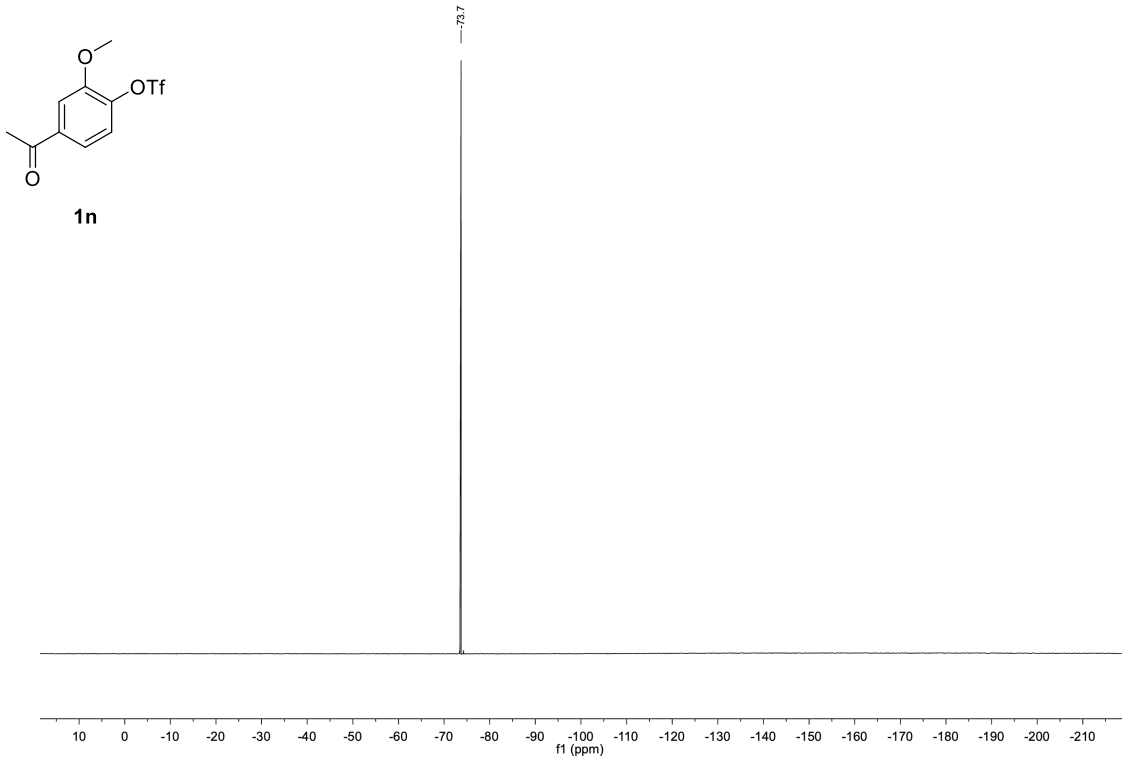
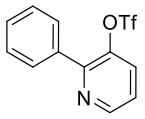


Figure S47. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1n**.

2-Phenylpyridin-3-yl trifluoromethanesulfonate (1o):



1o

$C_{12}H_8F_3NO_3S$ (303.26 g/mol)

Following **GP-A**, **1o** was synthesized using 2-phenylpyridin-3-ol (270 mg, 1.58 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1o** (390 mg, 1.29 mmol, 82%) as a colorless oil.

R_f: 0.24 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.73 (m, 1H), 7.81 – 7.71 (m, 3H), 7.55 – 7.43 (m, 3H), 7.42 – 7.35 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 152.4, 149.3, 144.7, 135.2, 130.5, 129.9, 129.4, 128.7, 123.4, 118.4 (q, *J* = 321.0 Hz).

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.6.

HR-MS (ESI): m/z calc for $[M+H]^+$ 304.02498, found 304.02537.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w), 1590 (w), 1419 (vs), 1206 (vs), 1135 (vs), 1101 (s), 1050 (m), 1019 (w), 875 (vs), 807 (s), 788 (s), 740 (s), 698 (s).

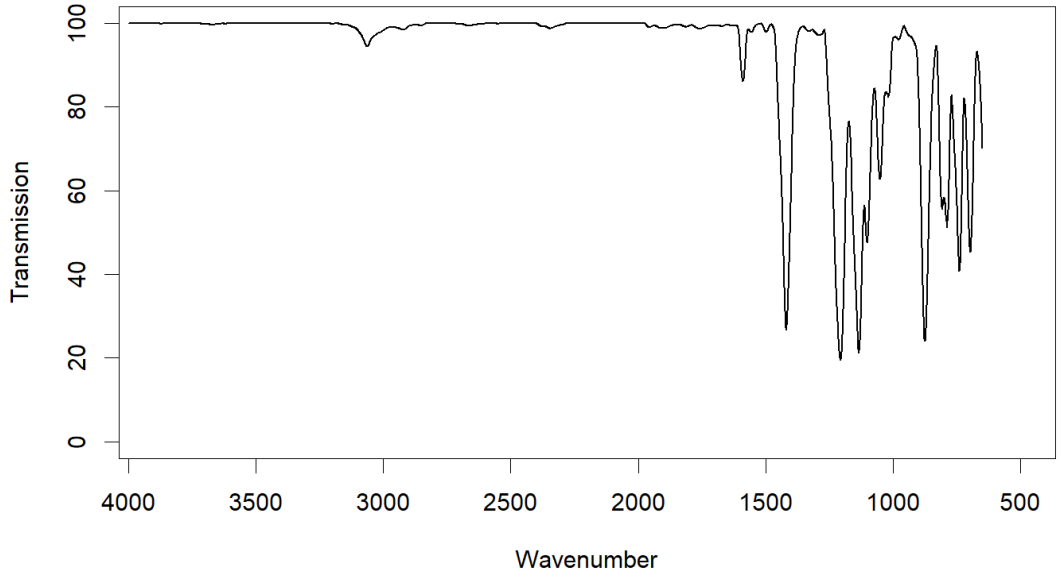


Figure S48. IR-spectrum (ATR, neat) of **1o**.

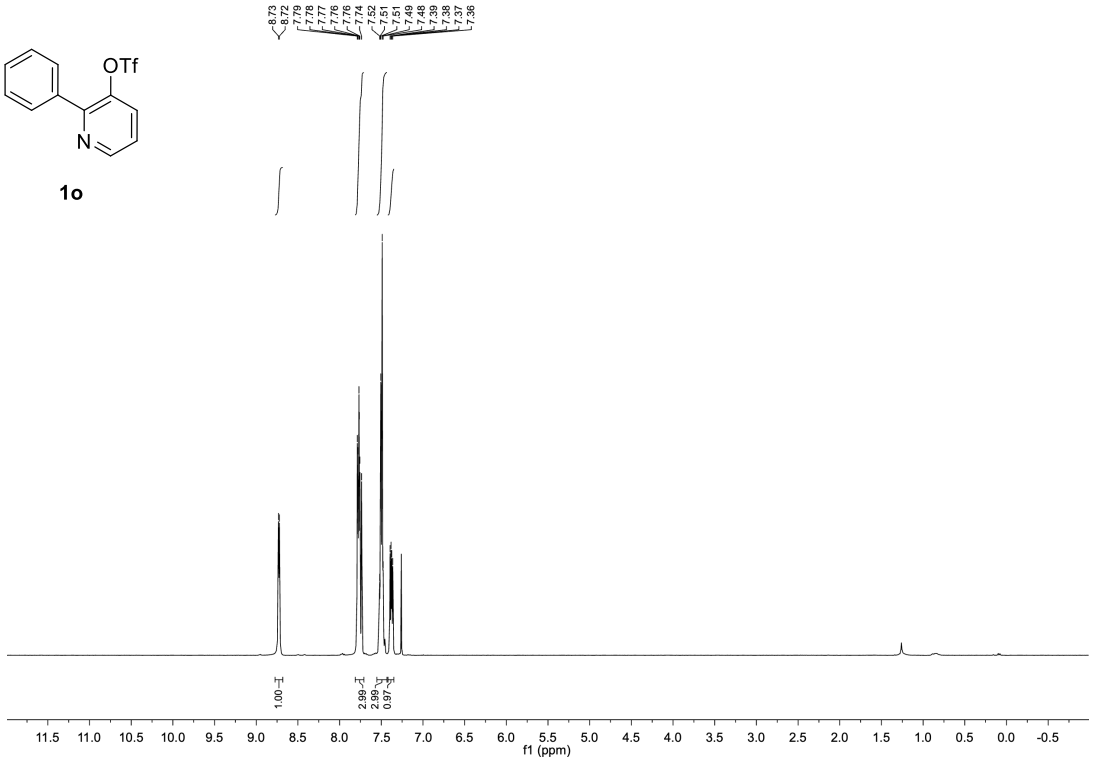


Figure S49. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1o**.

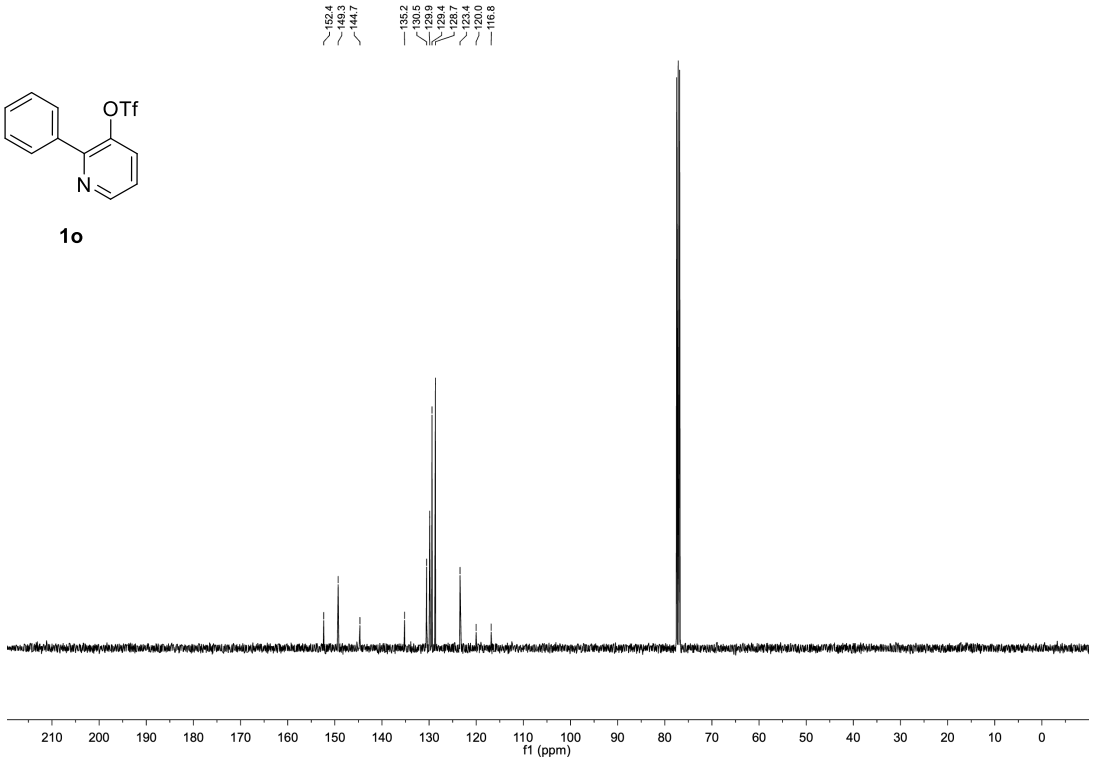


Figure S50. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1o**.

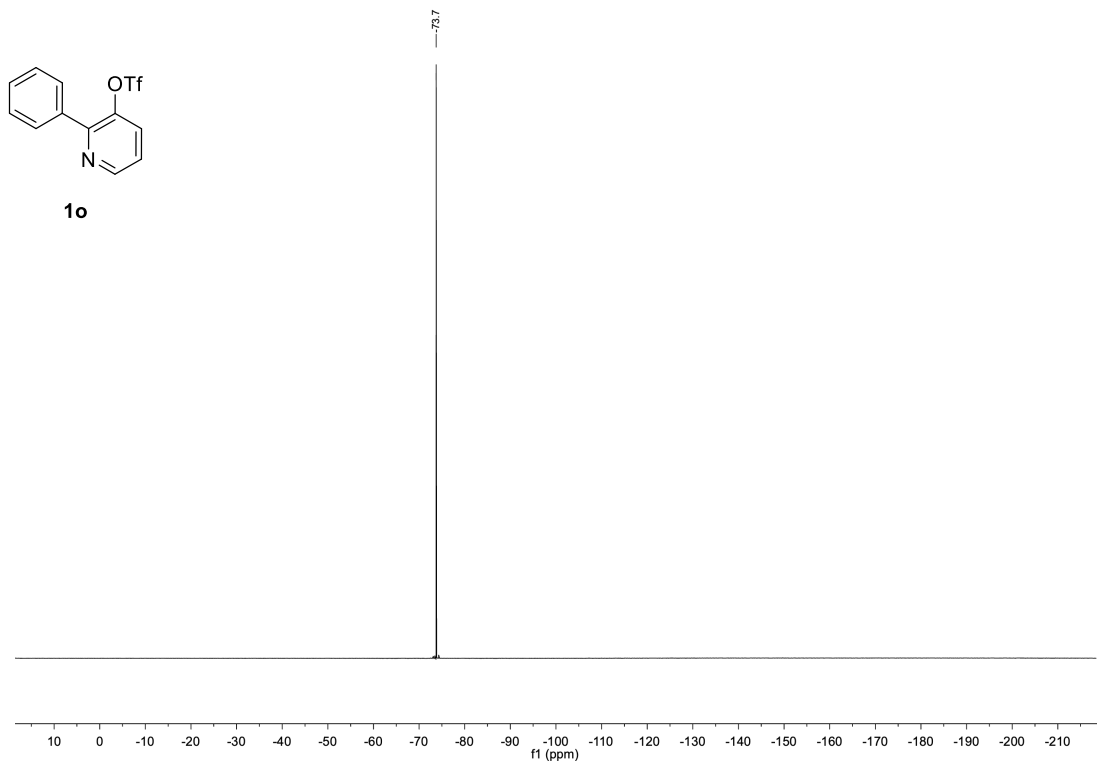
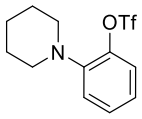


Figure S51. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1o**.

2-(Piperidin-1-yl)phenyl trifluoromethanesulfonate (1t):



1t

$C_{12}H_{14}F_3NO_3S$ (309.30 g/mol)

Following **GP-A**, **1t** was synthesized using 2-(piperidin-1-yl)phenol (0.787 g, 4.44 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1t** (1.27 g, 4.11 mmol, 93%) as a colorless oil.

R_f: 0.88 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.33 – 7.27 (m, 1H), 7.19 – 7.12 (m, 2H), 7.08 – 7.02 (m, 1H), 2.98 – 2.90 (m, 4H), 1.80 – 1.73 (m, 4H), 1.61 – 1.53 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 147.4, 144.6, 129.1, 123.5, 121.8, 121.6, 118.9 (q, *J* = 320.2 Hz), 53.0, 25.9, 24.2.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -74.6.

HR-MS (ESI): m/z calc for $[M+H]^+$ 310.07193, found 310.07232.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2939 (w), 2857 (w), 2809 (w), 1605 (w), 1492 (m), 1452 (w), 1418 (vs), 1385 (w), 1336 (w), 1277 (w), 1240 (s), 1199 (vs), 1139 (vs), 1087 (s), 1038 (m), 926 (m), 874 (vs), 837 (m), 758 (s), 717 (w).

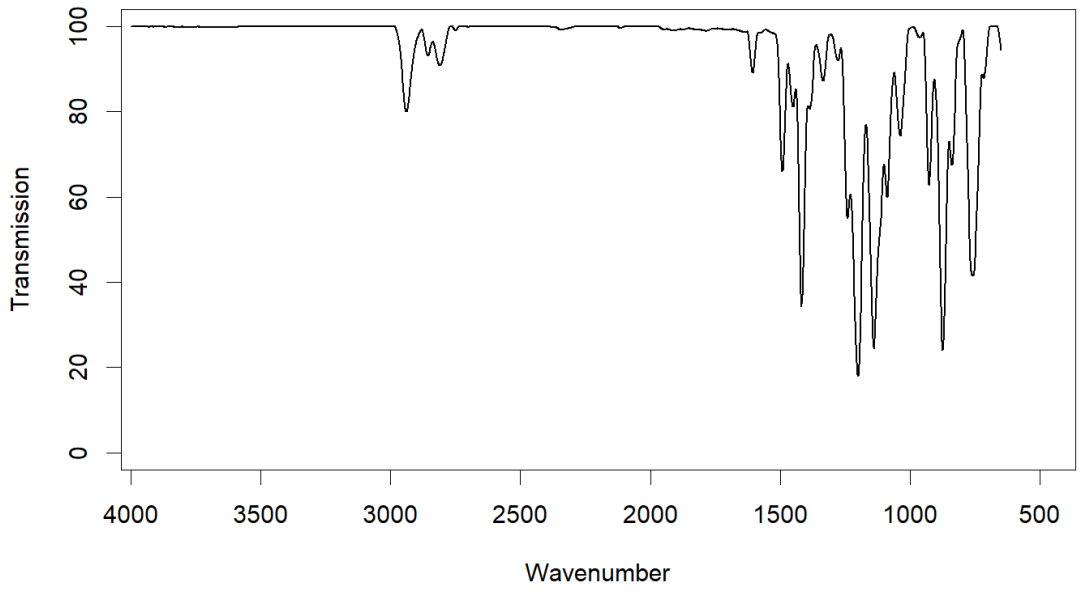


Figure S52. IR-spectrum (ATR, neat) of **1t**.

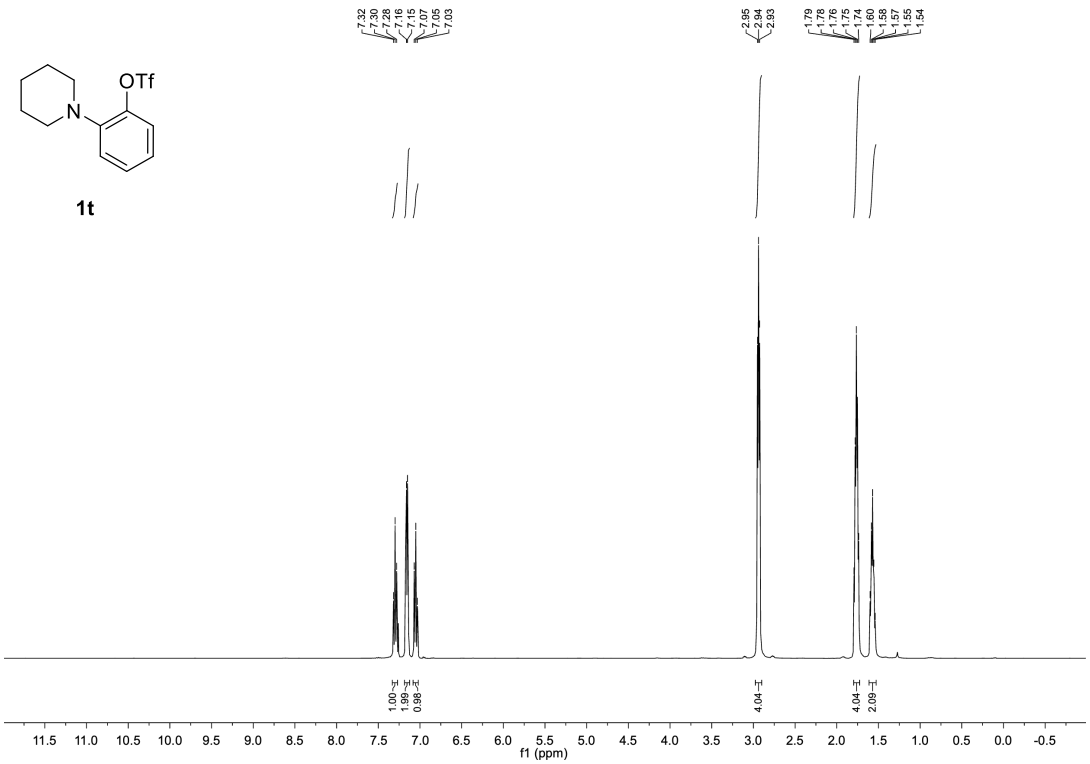


Figure S53. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1t**.

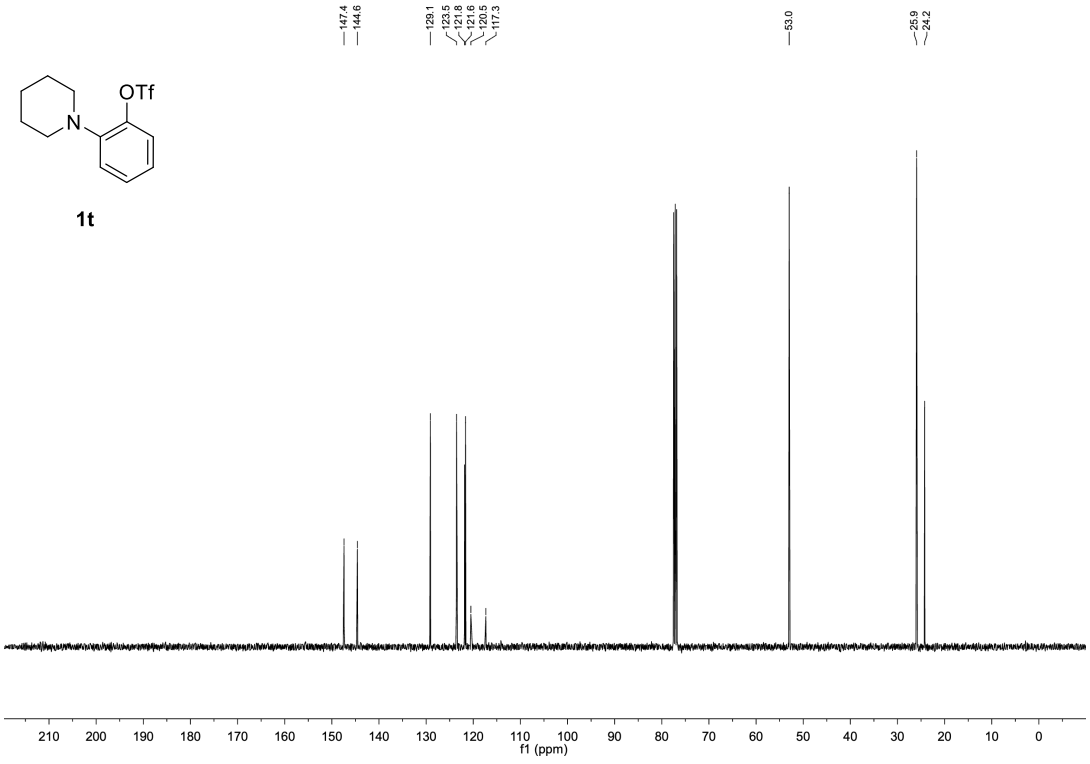


Figure S54. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1t**.

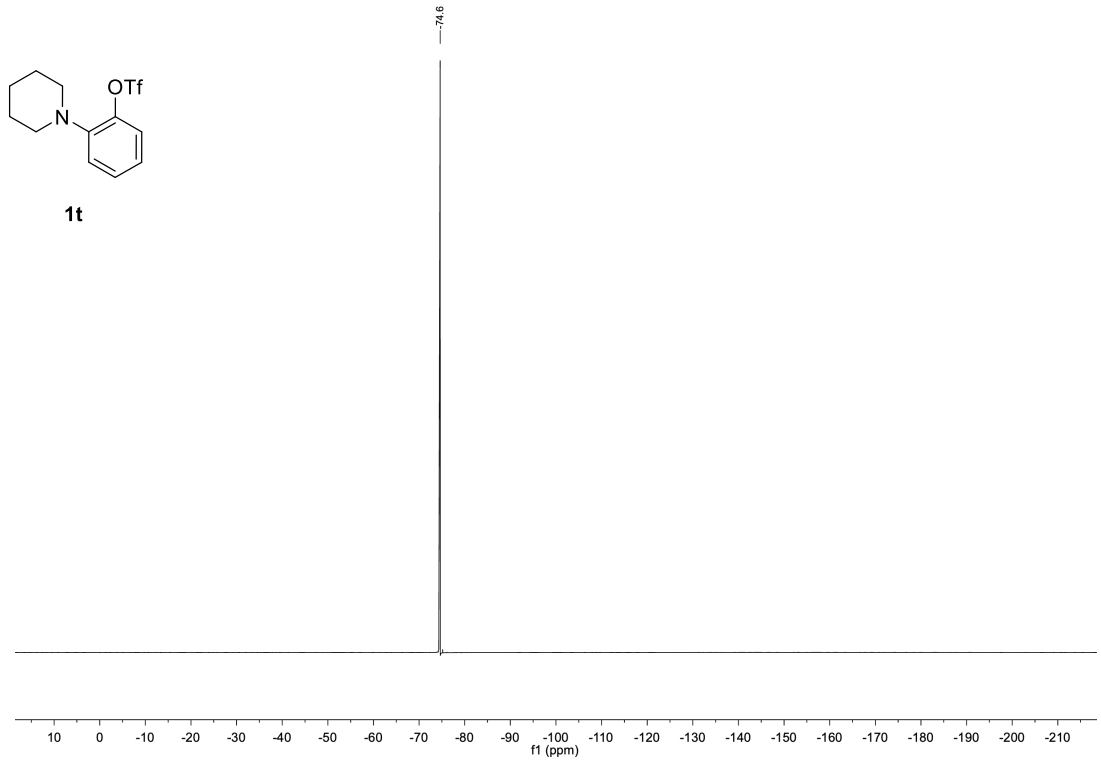
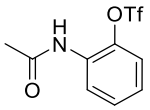


Figure S55. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1t**.

2-Acetamidophenyl trifluoromethanesulfonate (1u):



1u

$C_9H_8F_3NO_4S$ (283.22 g/mol)

Following **GP-A**, **1u** was synthesized using *N*-(2-hydroxyphenyl)acetamide (1.51 g, 10.0 mmol, 1.0 equiv.). Purification by DC-VC (SiO_2, gradient from *n*-hexane to EtOAc 100:0 to 0:100) afforded **1u** (1.65 g, 5.83 mmol, 58%) as yellow solid. Conforms to reported analytical data.[15]

R_f: 0.17 (*n*-hexane/EtOAc 80:20).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.19 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.26 (m, 3H), 7.22 – 7.14 (m, 1H), 2.22 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 168.7, 139.9, 130.4, 129.1, 125.6, 124.6, 121.6, 118.7 (q, *J* = 320.4 Hz), 24.3.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.4.

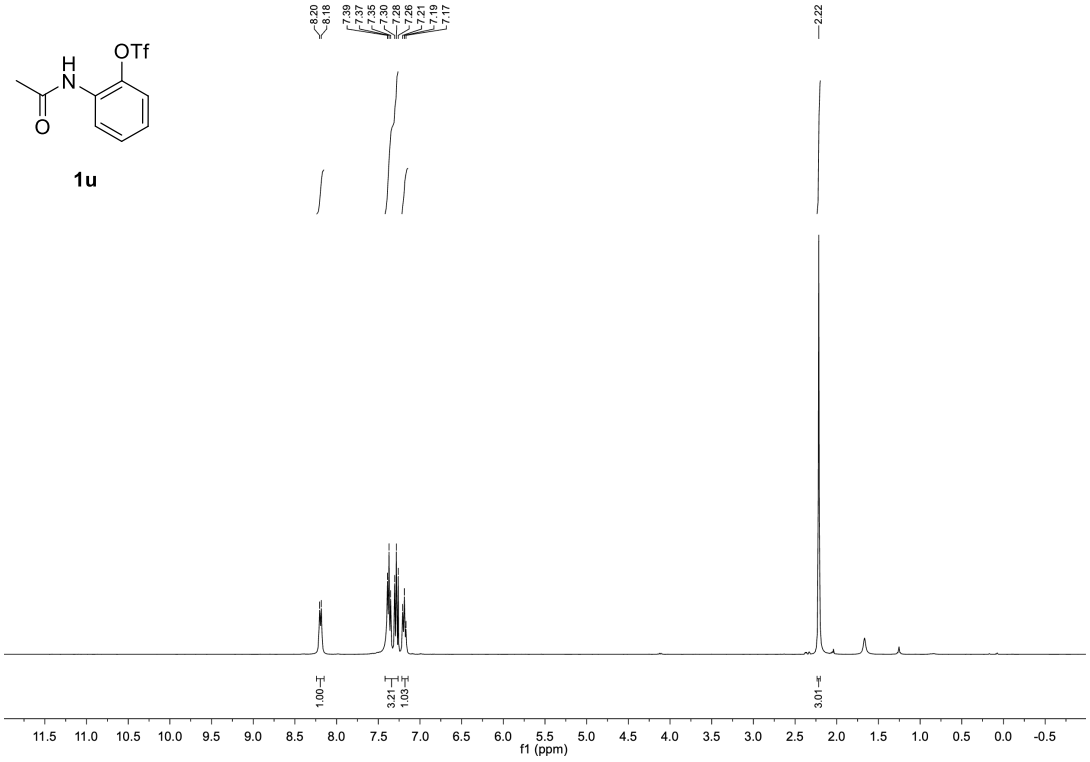


Figure S56. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1u**.

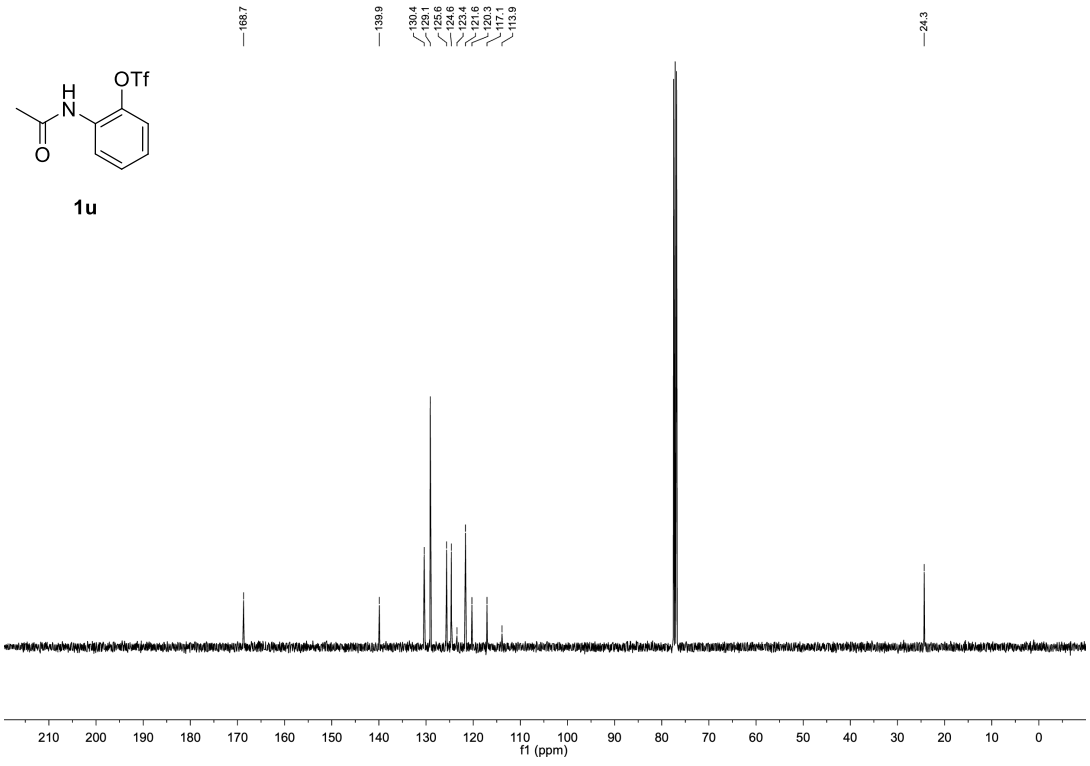


Figure S57. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1u**.

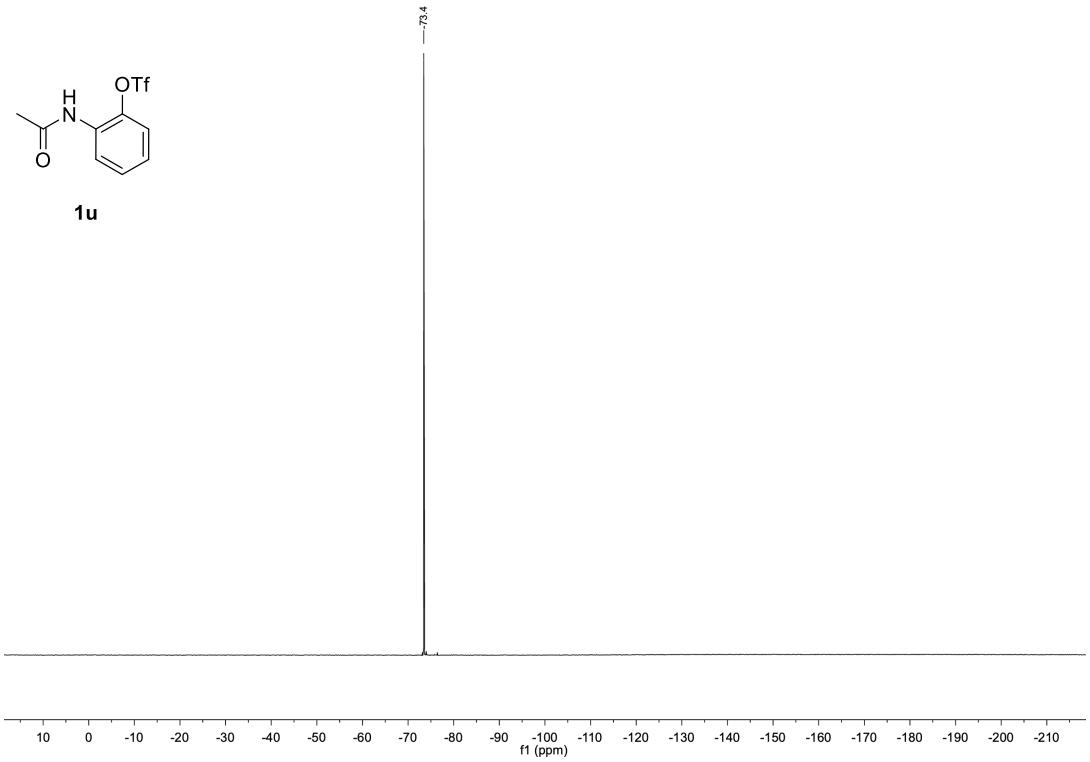
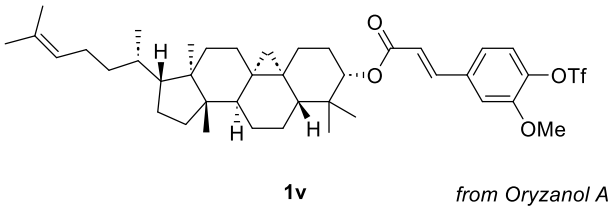


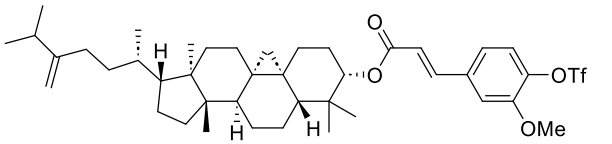
Figure S58. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1u**.

(2a*R*,3*R*,5a*S*,5b*S*,7a*R*,9*S*,11a*R*,12a*R*)-2a,5a,8,8-tetramethyl-3-((*S*)-6-methylhept-5-en-2-yl)tetradecahydro-1*H*,12*H*-cyclopenta[*a*]cyclopropa[*e*]phenanthren-9-yl (*E*)-3-(3-methoxy-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)acrylate (1v):

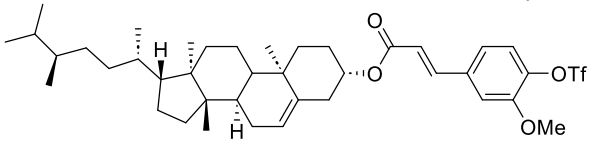


1v *from Oryzanol A*

side components:



from Oryzanol C



from Campesteryl ferulate

$C_{41}H_{57}F_3O_6S$ (734.96 g/mol)

Following **GP-A**, **1v** was synthesized using *γ*-Oryzanol (purchased from TCI; a mixture containing Oryzanol A, Oryzanol C and Campesteryl ferulate as main components)[16] (2.94 g, 5.00 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1v** (2.56 g, 3.48 mmol, 70%, mixture according to starting material) as colorless solid. Conforms to reported analytical data.[17]

R_f: 0.32 (*n*-hexane/EtOAc 95:5).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.61 (d, *J* = 15.9 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.18 – 7.11 (m, 2H), 6.42 (d, *J* = 15.9 Hz, 1H), 4.78 – 4.62 (m, 2H), 3.95 (s, 3H), 2.43 –1.81 (m, 6H), 1.68 – 1.51 (m, 8H), 1.48 – 1.28 (m, 7H), 1.20 – 1.07 (m, 3H), 1.07 – 0.75 (m, 21H), 0.70 – 0.36 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 166.3, 165.9, 157.0, 151.8, 142.7, 142.5, 139.7, 136.0, 131.0, 125.4, 122.0, 121.1, 121.0, 120.9, 118.6 (q, *J* = 320.7 Hz), 112.0, 106.1, 81.3, 74.6, 56.8, 56.4, 56.4, 52.4, 50.2, 49.0, 48.0, 47.4, 45.44, 45.42, 42.5, 39.8, 38.3, 37.1, 36.8, 36.5, 36.3, 36.0, 35.7, 35.1, 33.9, 33.0, 32.0, 31.8, 31.5, 29.9, 28.3, 28.0, 27.1, 26.7, 26.1, 26.0, 25.9, 25.6, 25.1, 22.1, 22.0, 21.2, 21.1, 20.3, 19.5, 19.5, 19.4, 18.5, 18.4, 18.1, 17.8, 15.4, 12.0.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.8.

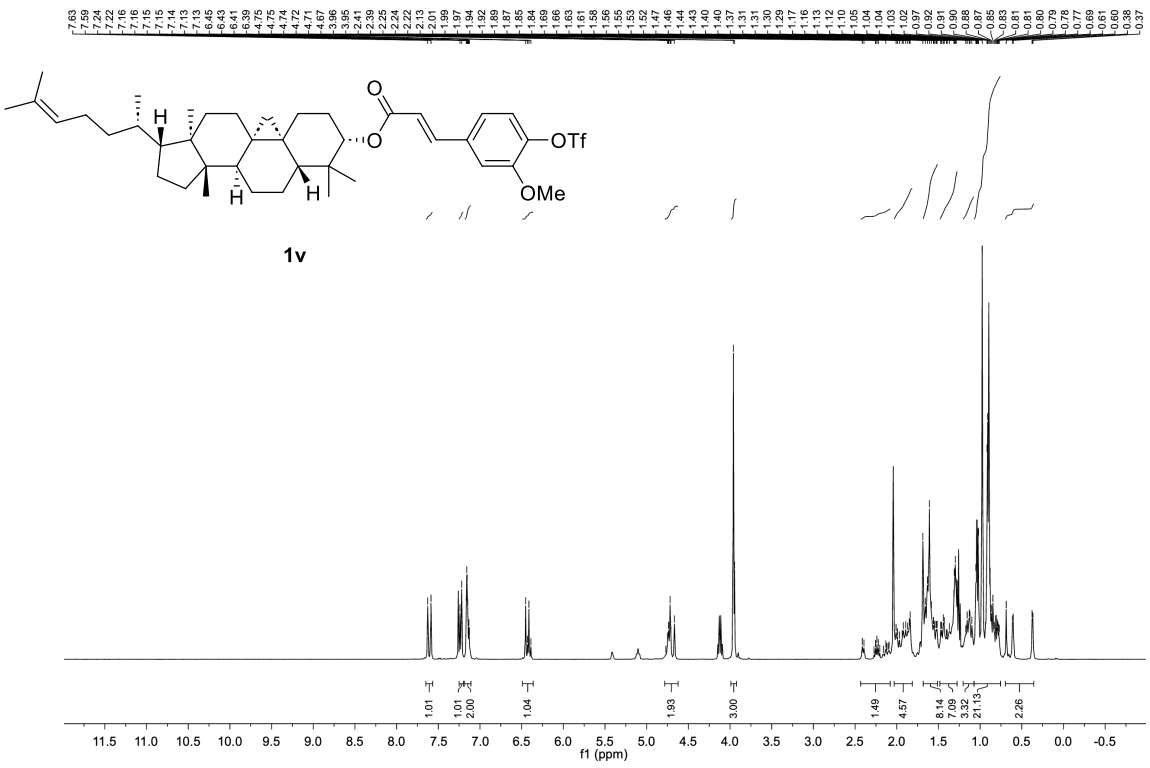


Figure S59. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1v**.

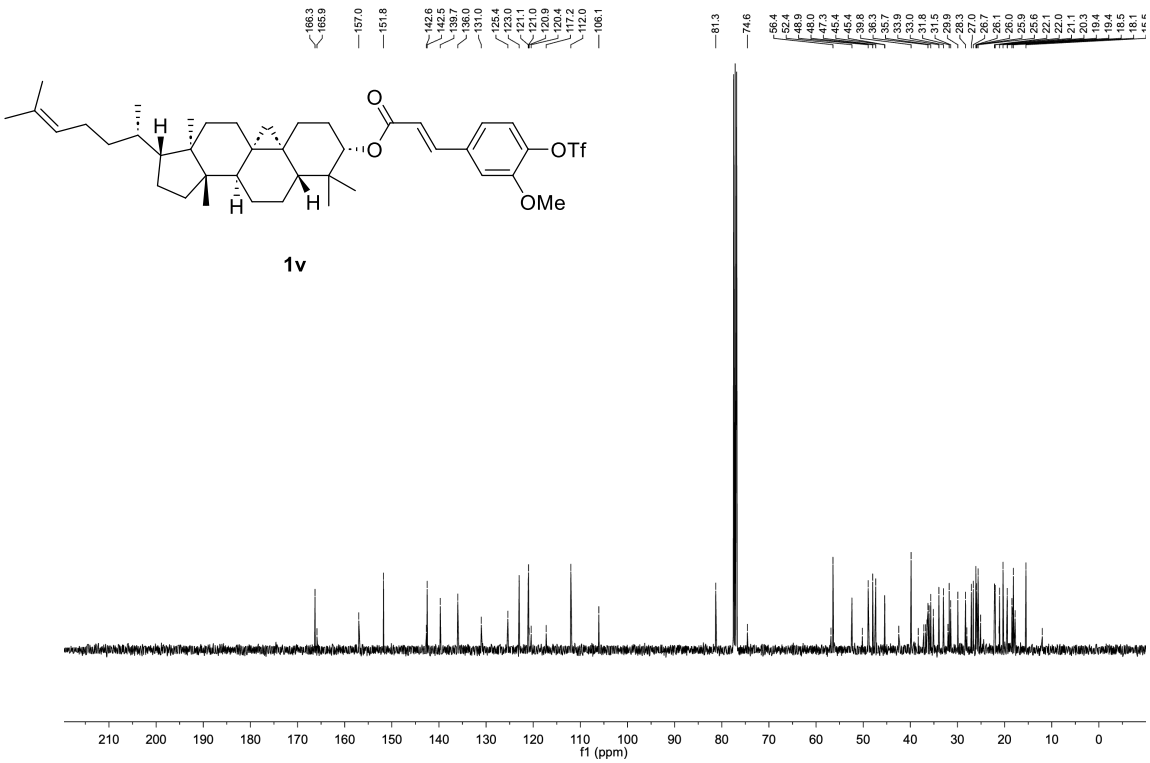


Figure S60. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1v**.

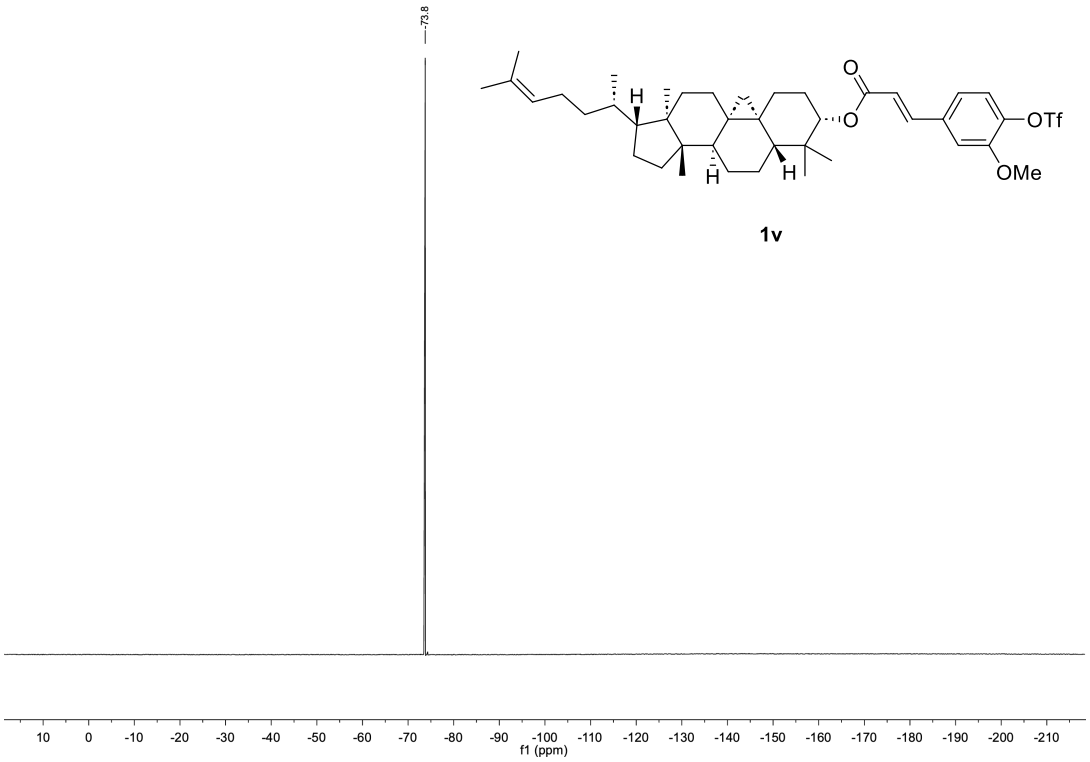
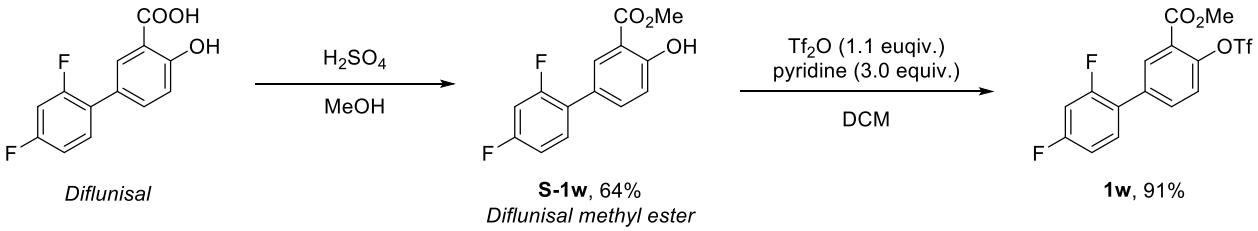


Figure S61. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1v**.

Methyl 2',4'-difluoro-4-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-3-carboxylate (1w):



Diflunisal

S-1w, 64%
Diflunisal methyl ester

1w, 91%

Step 1: **S-1w** (Diflunisal methyl ester) ($C_{14}H_{10}O_3$, 264.23 g/mol)

The synthesis of **S-1w** followed a literature procedure and was conducted under air.[18] In a 250 mL round-bottom flask, Diflunisal (5.00 g, 20.0 mmol, 1.0 equiv.) was dissolved in MeOH (100 mL) and aq. H_2SO_4 (96%, 4 mL) was added. The mixture was heated to reflux under stirring for 16 h. After cooling to rt, the precipitate was collected by filtration, washed with MeOH (3 × 25 mL) and dried *in vacuo*. **S-1w** (3.39 g, 12.8 mmol, 64%) was obtained as colorless solid. Conforms to reported analytical data.[18]

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 10.82 (s, 1H), 7.98 (s, 1H), 7.64 – 7.56 (m, 1H), 7.42 – 7.31 (m, 1H), 7.06 (d, *J* = 8.7 Hz, 1H), 6.99 – 6.85 (m, 2H), 3.97 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 170.5, 161.3, 161.1 (d, *J* = 13.0 Hz), 136.3 (d, *J* = 3.0 Hz), 131.2 (m), 130.3 (d, *J* = 2.9 Hz) 126.2, 118.0, 112.6, 111.9 (d, *J* = 4.0 Hz), 111.7 (d, *J* = 4.1 Hz), 104.7 (d, *J* = 25.2 Hz), 104.5 (d, *J* = 25.7 Hz), 52.6.

Note: Observed complexity due to C–F coupling.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -111.4 (m), -113.8 (m).

Note: Observed complexity due to F–F/F–H coupling.

Step 2: **1w** ($C_{15}H_9F_5O_5S$, 396.28 g/mol)

Following **GP-A**, **1w** was synthesized using Diflunisal methyl ester (**S-1w**) (1.32 g, 5.00 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1w** (1.81 g, 4.57 mmol, 91%) as a colorless oil.

R_f: 0.53 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.23 – 8.17 (m, 1H), 7.80 – 7.71 (m, 1H), 7.48 – 7.34 (m, 2H), 7.06 – 6.90 (m, 2H), 3.99 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 164.3, 163.1 (dd, *J* = 251.1, 11.9 Hz), 159.8 (dd, *J* = 251.1, 11.9 Hz), 147.6, 135.6, 134.5 (d, *J* = 3.6 Hz), 133.0 (d, *J* = 2.8 Hz), 131.4 (dd, *J* = 9.8, 4.1 Hz), 124.6, 123.0, 122.5

(dd, *J* = 13.1, 3.8 Hz), 118.8 (q, *J* = 320.8 Hz), 112.1 (dd, *J* = 21.5, 3.7 Hz), 104.7 (dd, *J* = 25.9, 25.9 Hz), 52.7.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.7, -109.0 (m), -113.3 (m).

Note: Observed complexity due to F–F/F–H splitting.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 418.99831, found 418.99866.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2957 (w), 1730 (s), 1612 (w), 1511 (w), 1482 (m), 1425 (s), 1314 (m), 1254 (s), 1205 (vs), 1135 (vs), 1105 (s), 1075 (s), 1038 (w), 967 (m), 889 (vs), 843 (vs), 818 (s), 784 (m), 733 (w), 684 (w).

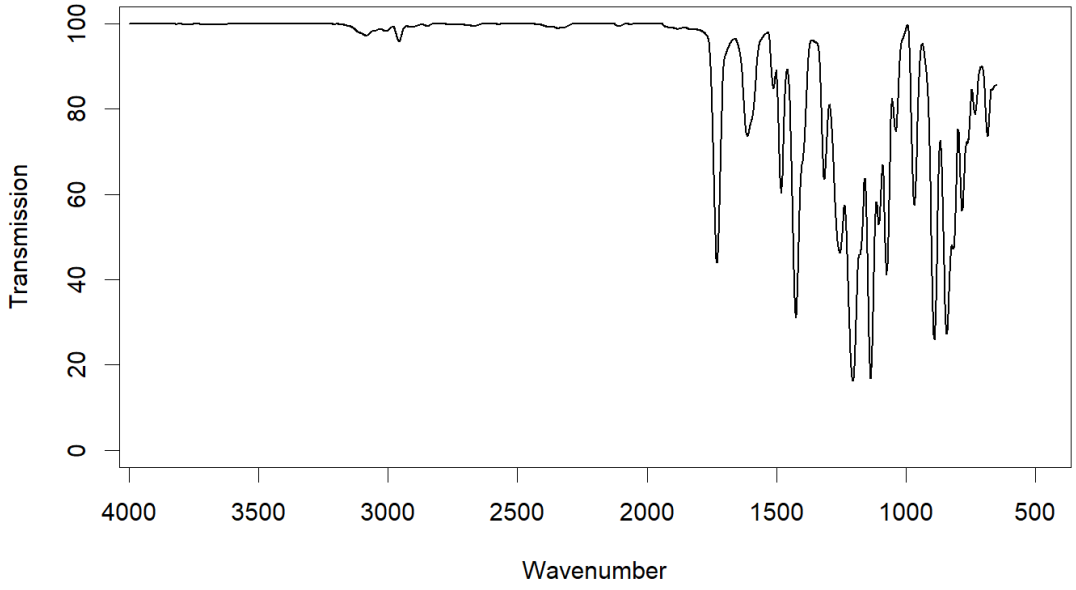


Figure S62. IR-spectrum (ATR, neat) of **1w**.

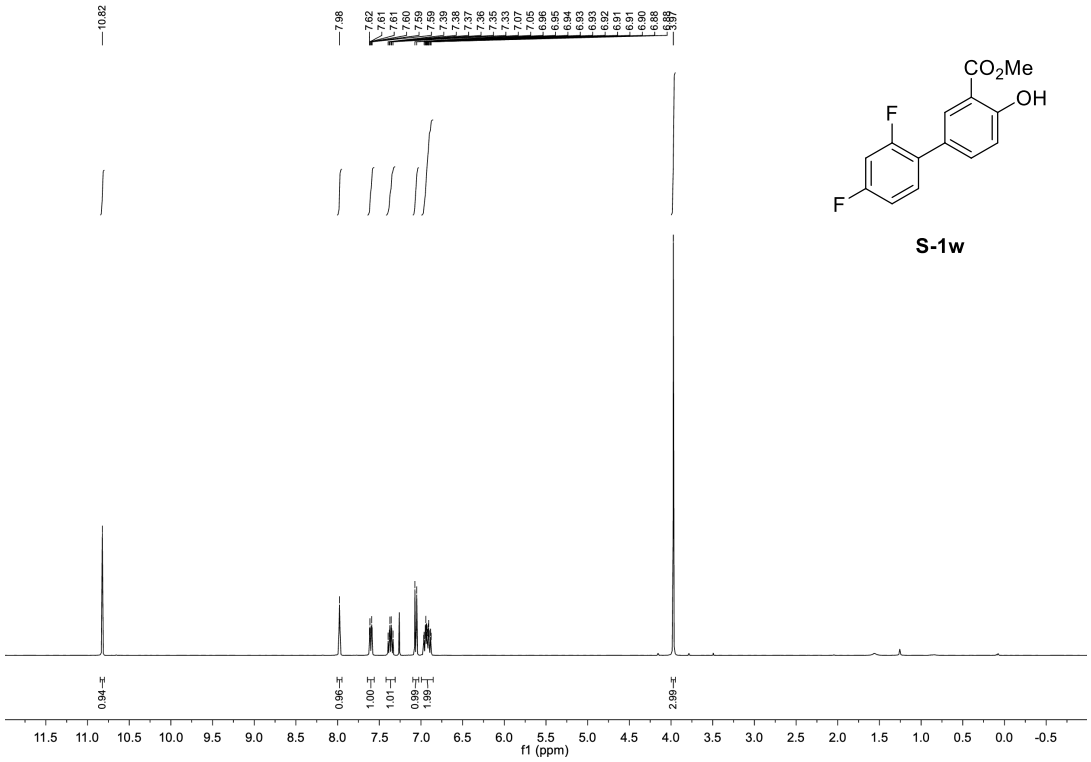


Figure S63. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **S-1w**.

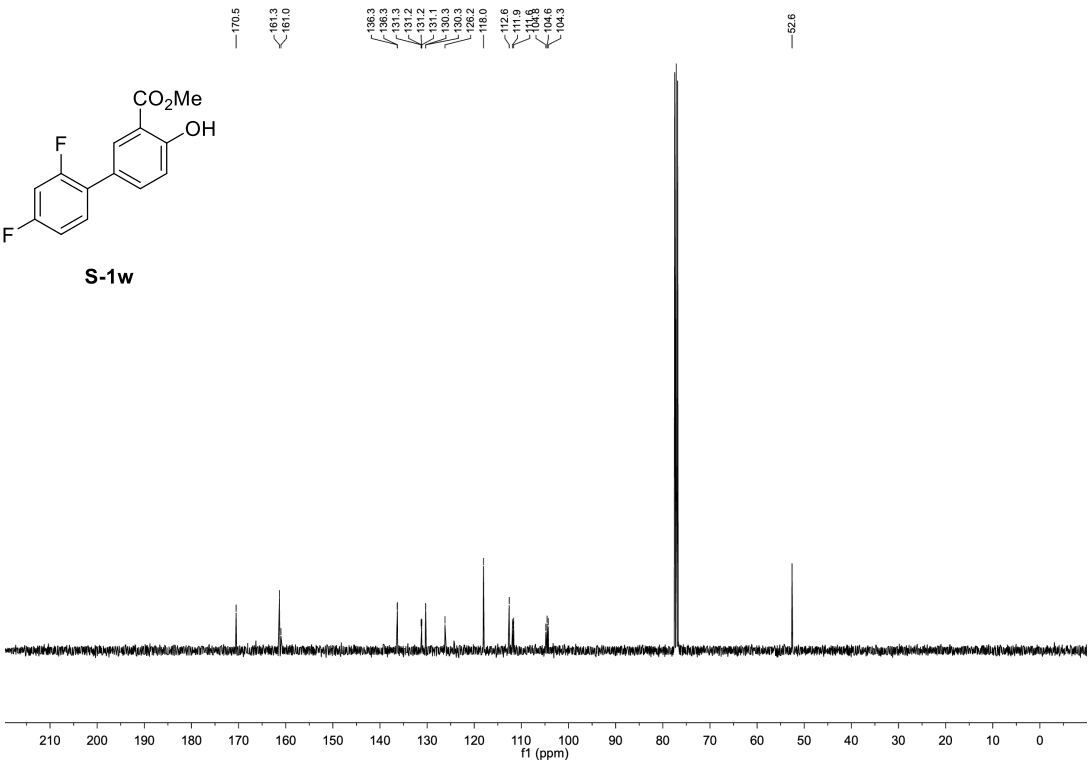


Figure S64. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **S-1w**.

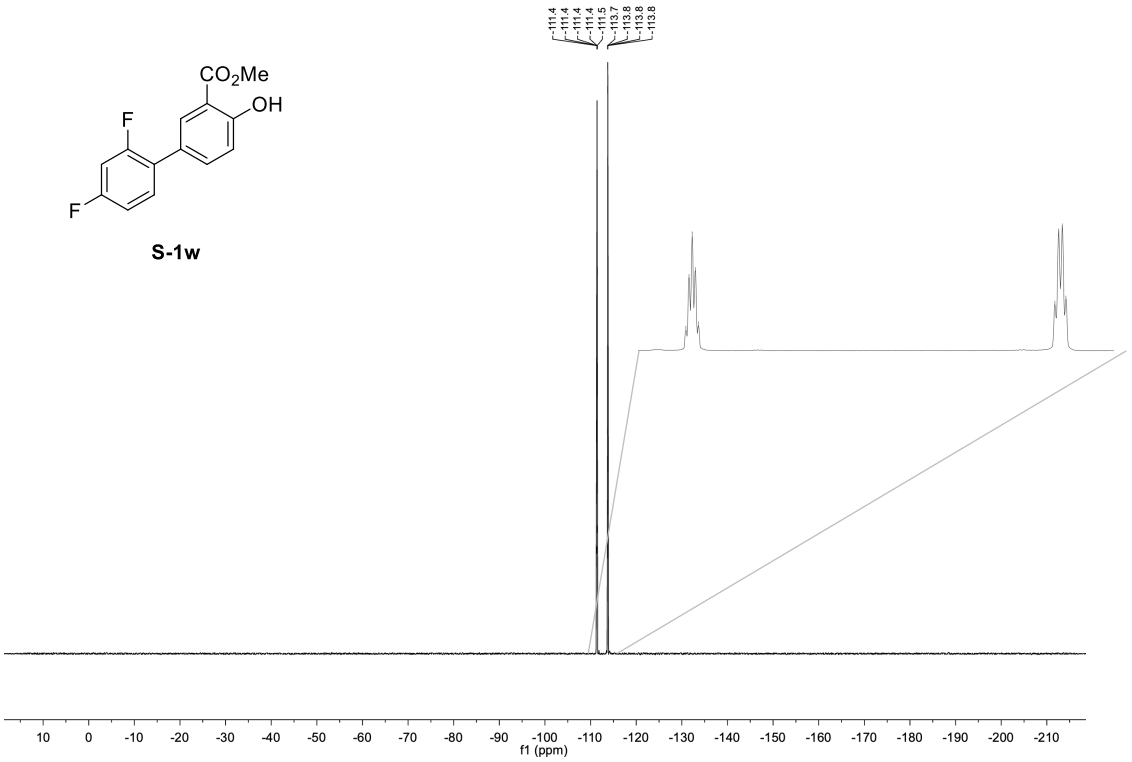


Figure S65. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **S-1w**.

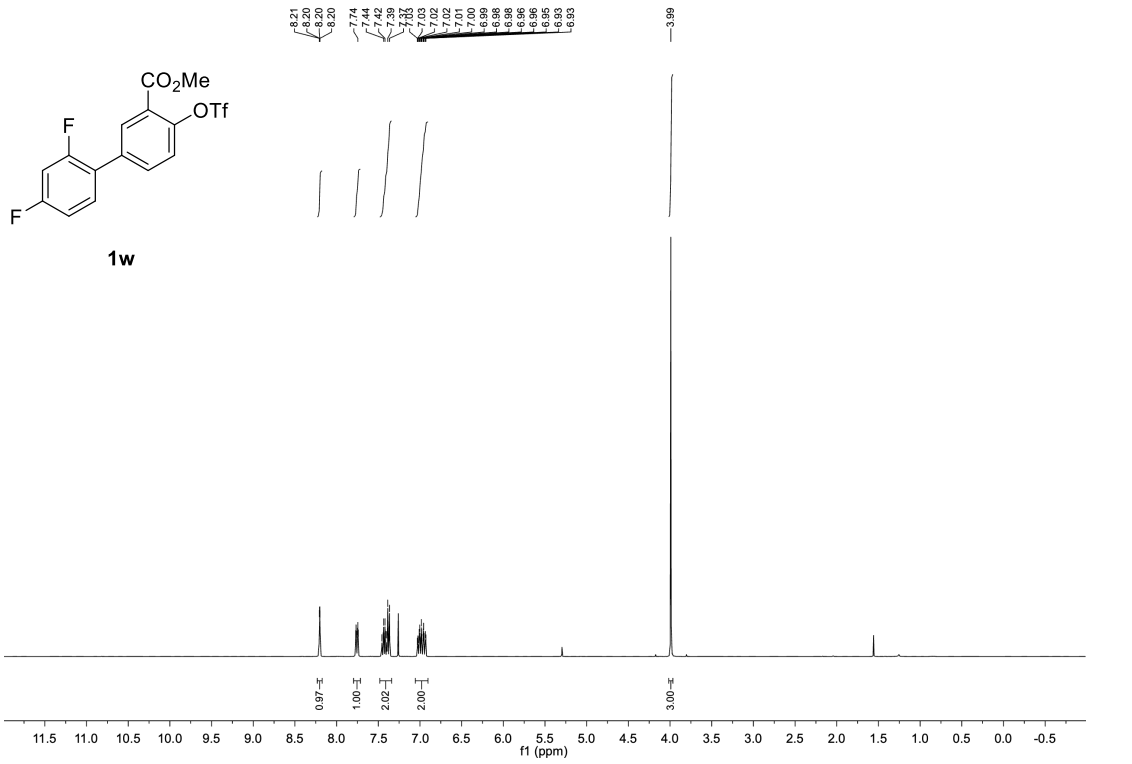


Figure S66. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1w**.

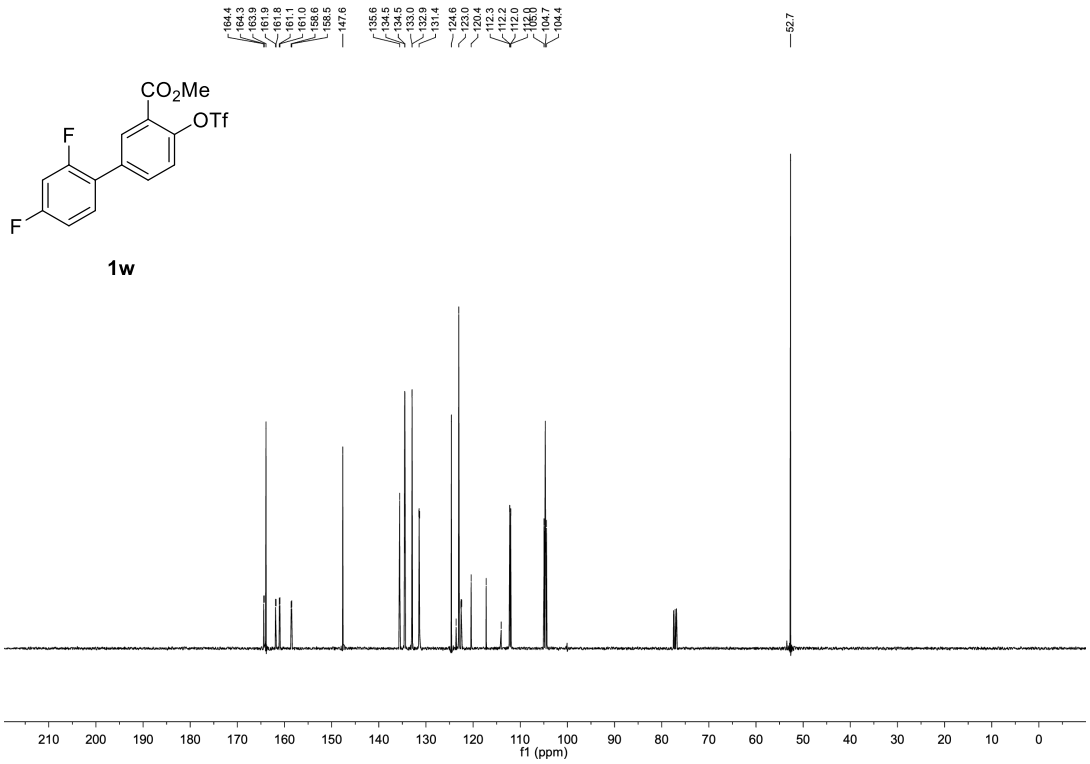


Figure S67. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1w**.

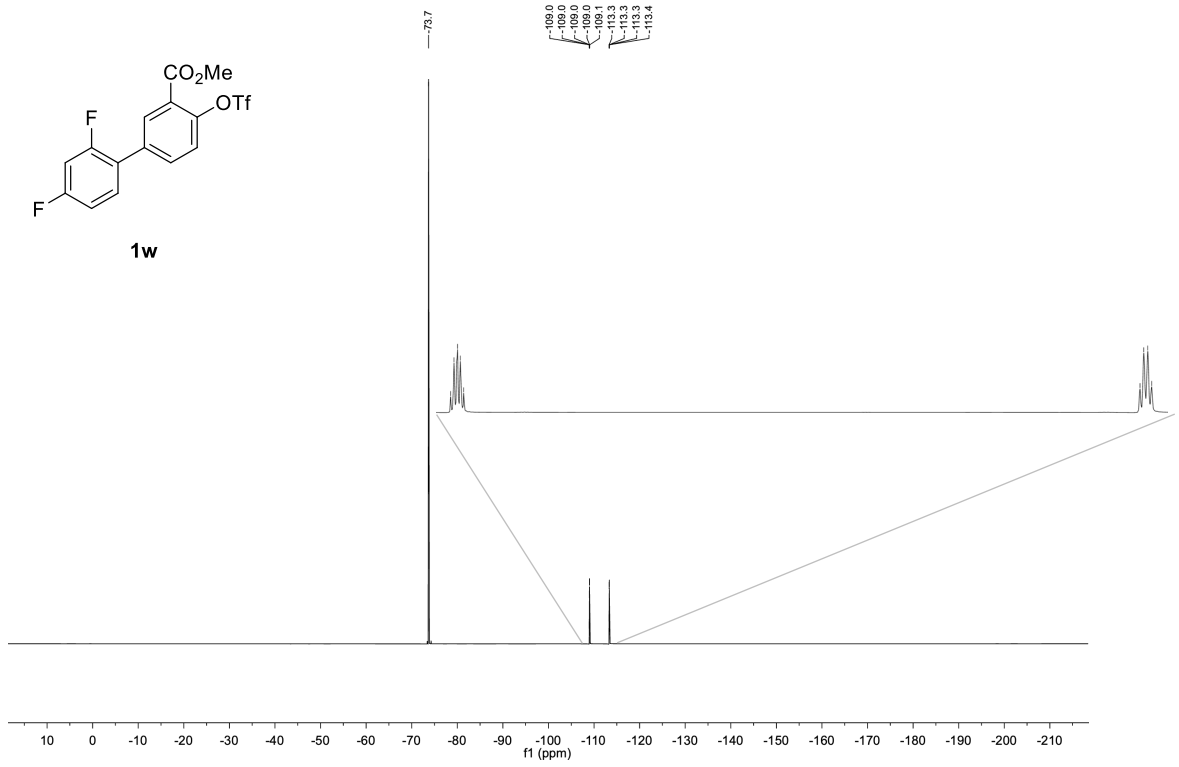
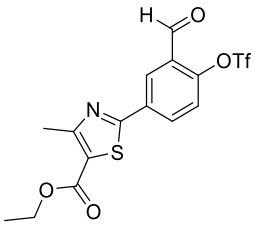


Figure S68. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1w**.

Ethyl 2-(3-formyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-4-methylthiazole-5-carboxylate (1x):



1x

$C_{15}H_{12}F_3NO_6S_2$ (423.38 g/mol)

Following **GP-A**, **1x** was synthesized using methyl 2-(3-formyl-4-hydroxyphenyl)-4-methylthiazole-5-carboxylate (2.91 g, 10.0 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 80:20) afforded **1x** (2.44 g, 5.76 mmol, 58%) as a colorless solid.

R_f: 0.54 (*n*-hexane/EtOAc 80:20).

m. p.: 91.2 – 92.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 10.30 (s, 1H), 8.52 (d, *J* = 2.4 Hz, 1H), 8.32 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.79 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 185.8, 165.8, 161.9, 161.5, 150.8, 134.0, 133.5, 129.1, 129.0, 123.8, 123.5, 118.8 (q, *J* = 320.7 Hz), 61.7, 17.6, 14.4.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -72.6.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 445.99503, found 445.99550.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2980 (w), 1698 (s), 1604 (w), 1582 (w), 1515 (w), 1482 (w), 1419 (s), 1366 (m), 1321 (w), 1269 (s), 1250 (s), 1206 (vs), 1135 (s), 1094 (vs), 1012 (m), 907 (s), 863 (s), 826 (vs), 755 (s), 710 (m).

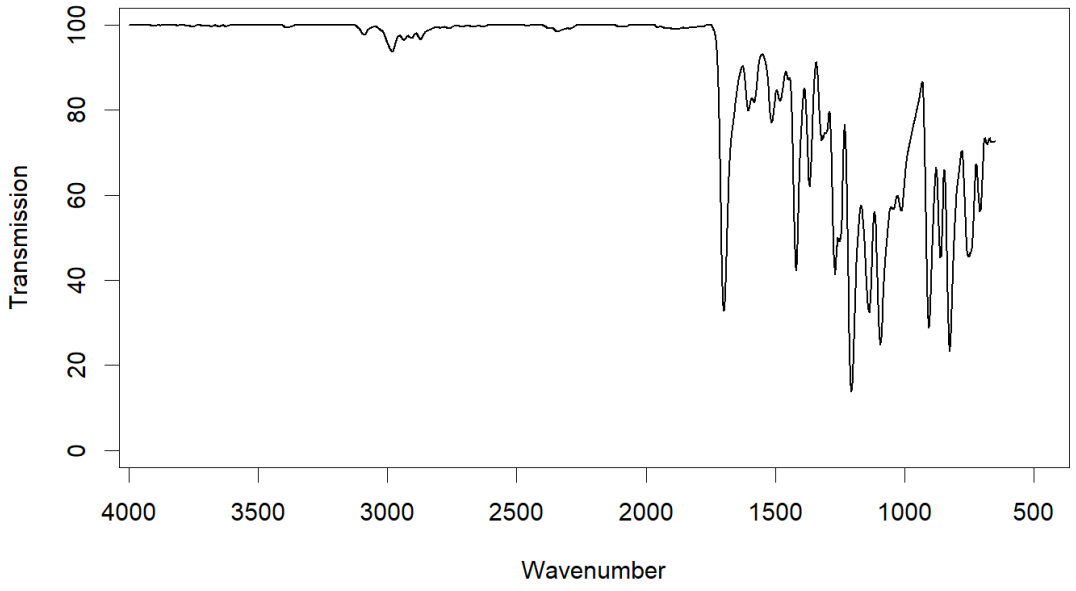


Figure S69. IR-spectrum (ATR, neat) of **1x**.

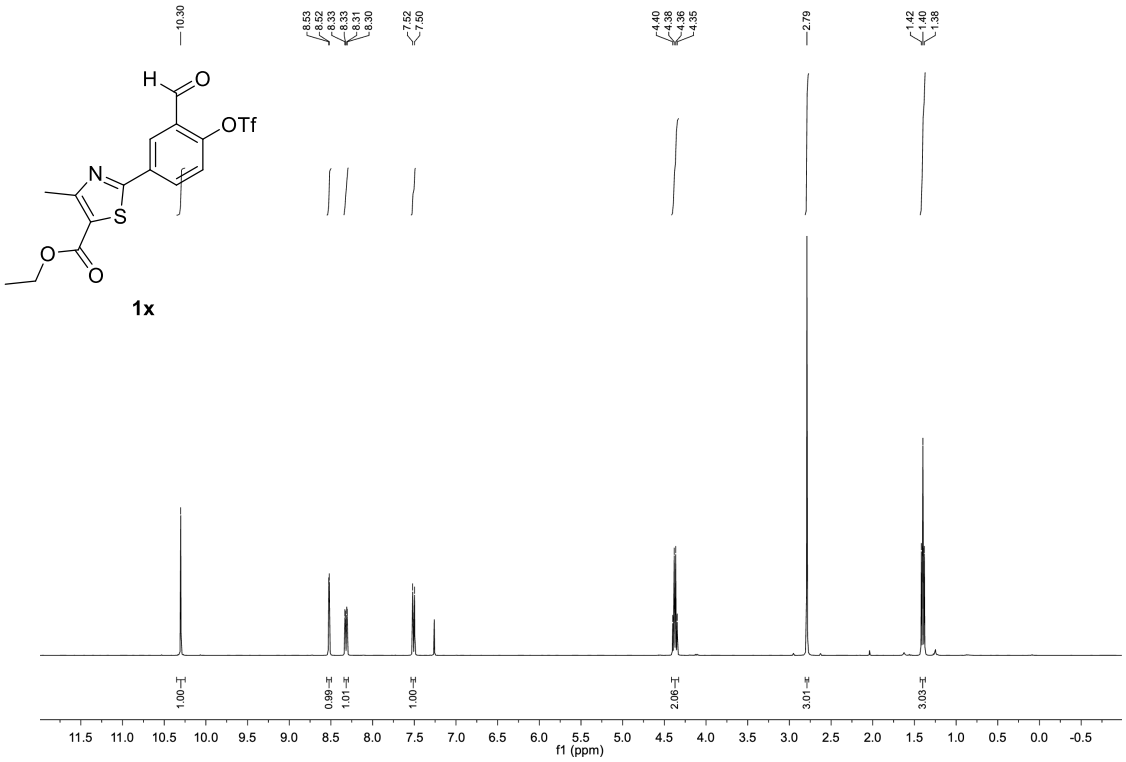


Figure S70. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1x**.

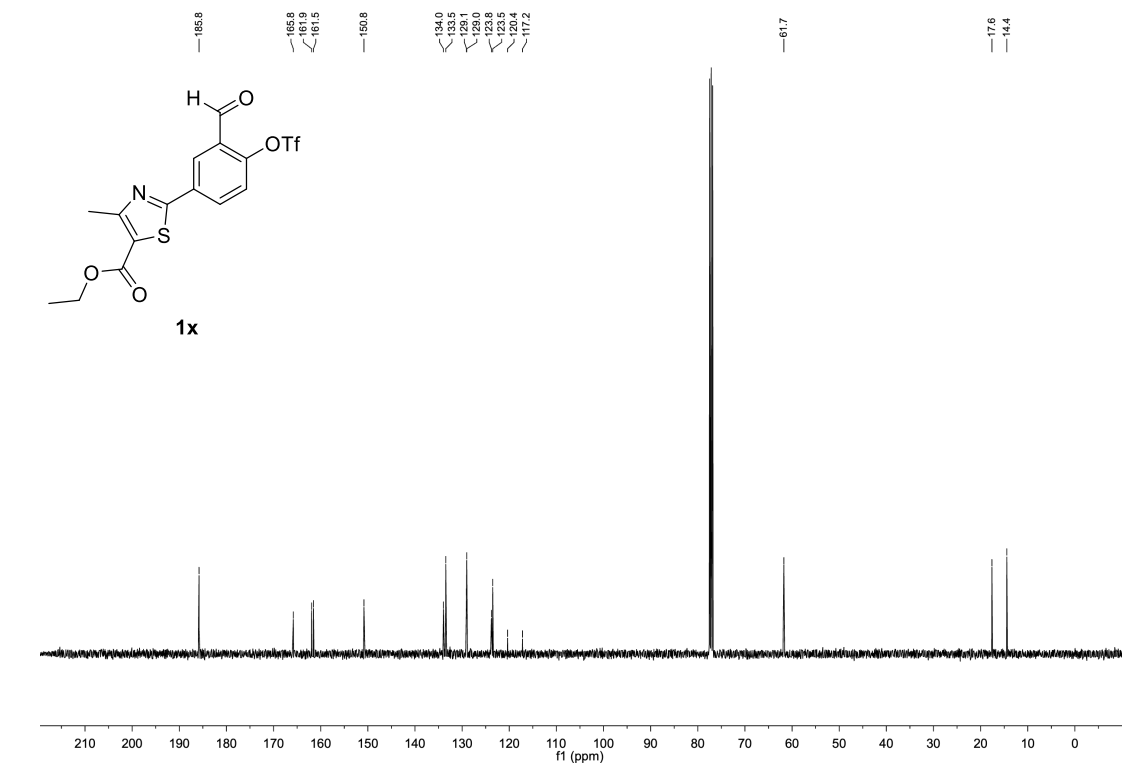


Figure S71. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1x**.

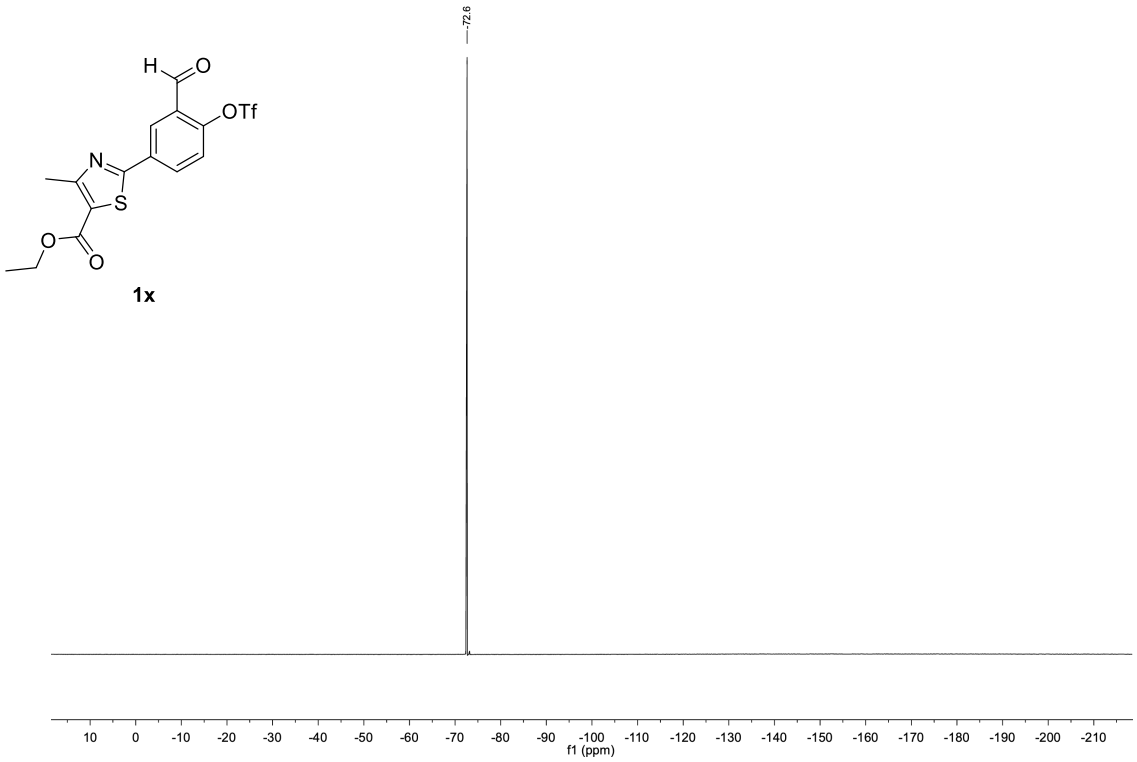
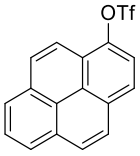


Figure S72. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1x**.

Pyren-1-yl trifluoromethanesulfonate (1y):



1y

$C_{17}H_9F_3O_3S$ (350.31 g/mol)

Following **GP-A**, **1y** was synthesized using pyren-1-ol (1.04 g, 4.77 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 90:10) afforded **1y** (984 mg, 2.81 mmol, 59%) as a pale yellow solid.

R_f: 0.66 (*n*-hexane/EtOAc 90:10).

Note: The compound showed fluorescence on the TLC plate under 356 nm irradiation.

m. p.: 83 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.28 – 8.16 (m, 4H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.09 – 7.98 (m, 3H), 7.94 (d, *J* = 8.5 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 142.7, 131.0, 131.0, 130.7, 129.8, 128.6, 127.0, 126.8, 126.5, 126.2, 125.7, 125.1, 124.0, 123.7, 119.4, 119.0 (q, *J* = 320.4 Hz), 118.7.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.1.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 373.01167, found 373.01219.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3058 (w), 1594 (w), 1488 (w), 1458 (w), 1415 (s), 1243 (w), 1202 (vs), 1131 (s), 1083 (s), 1038 (s), 968 (w), 900 (s), 836 (s), 818 (s), 756 (s), 714 (s), 676 (m).

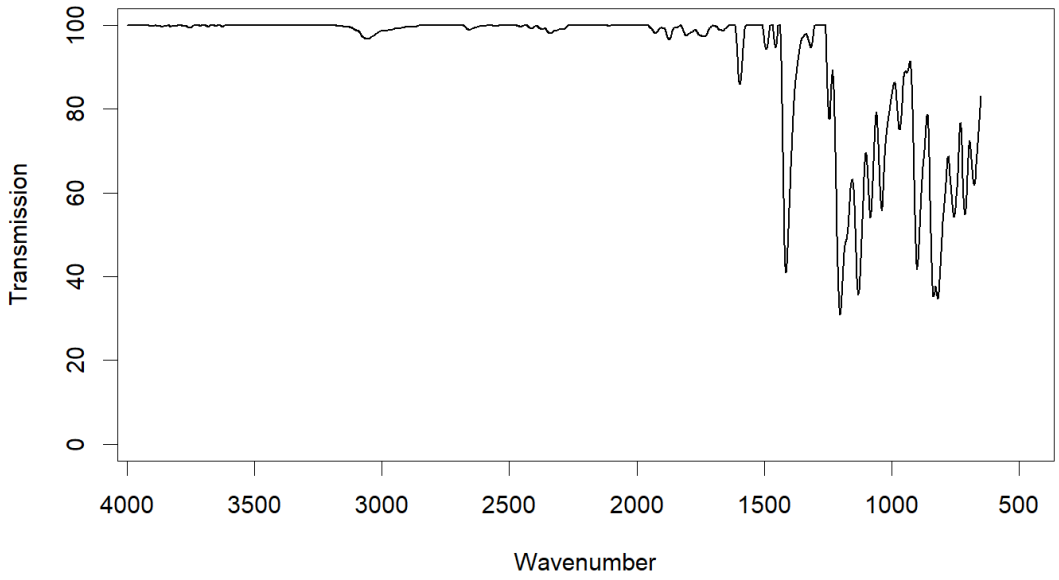


Figure S73. IR-spectrum (ATR, neat) of **1o**.

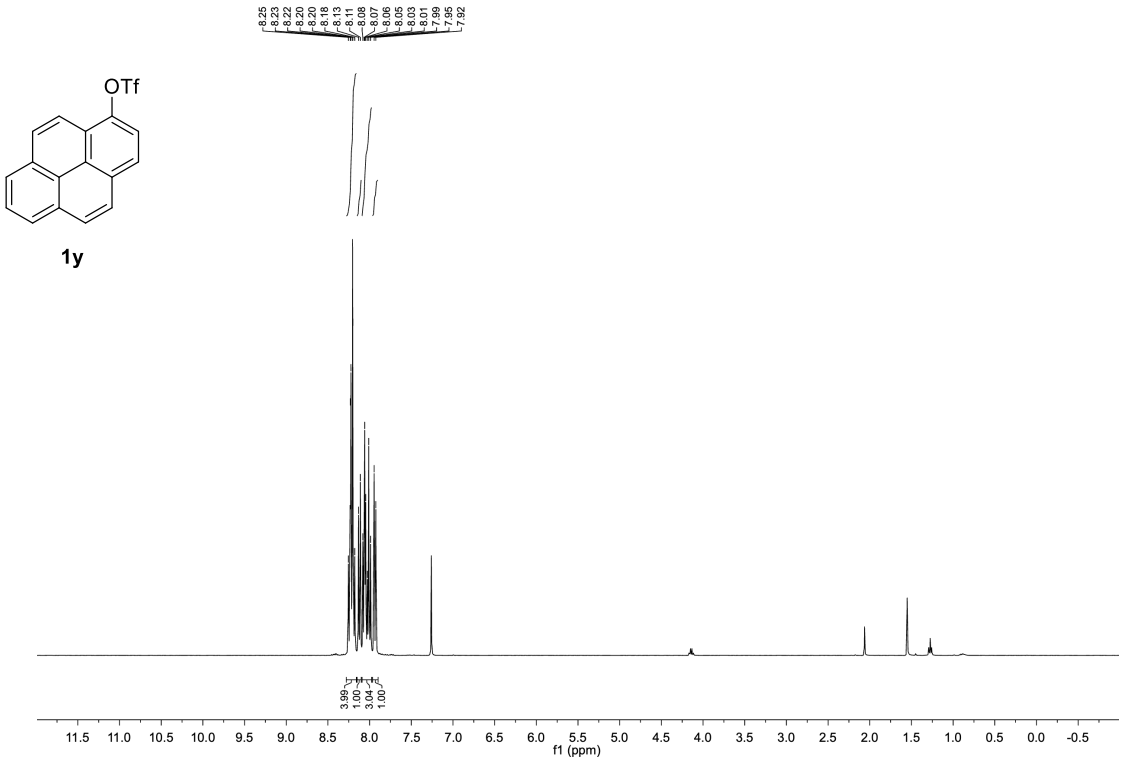
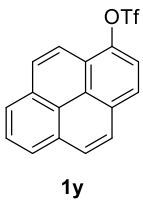


Figure S74. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1y**.



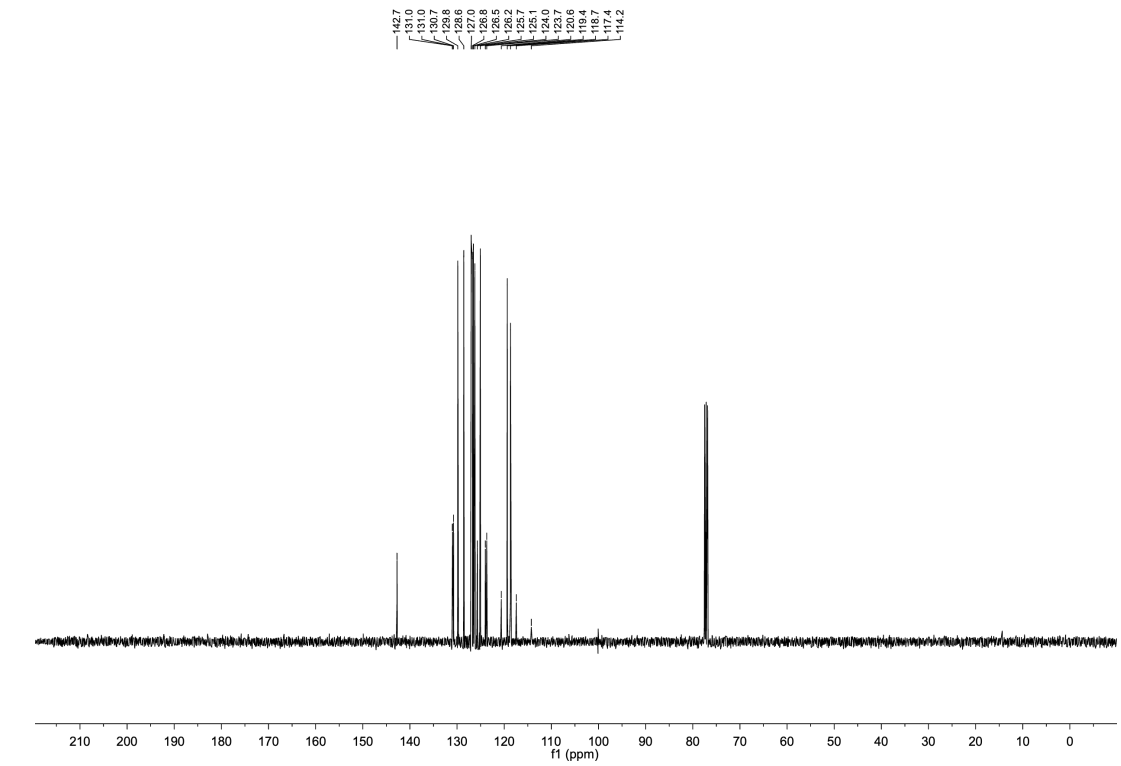


Figure S75. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1y**.

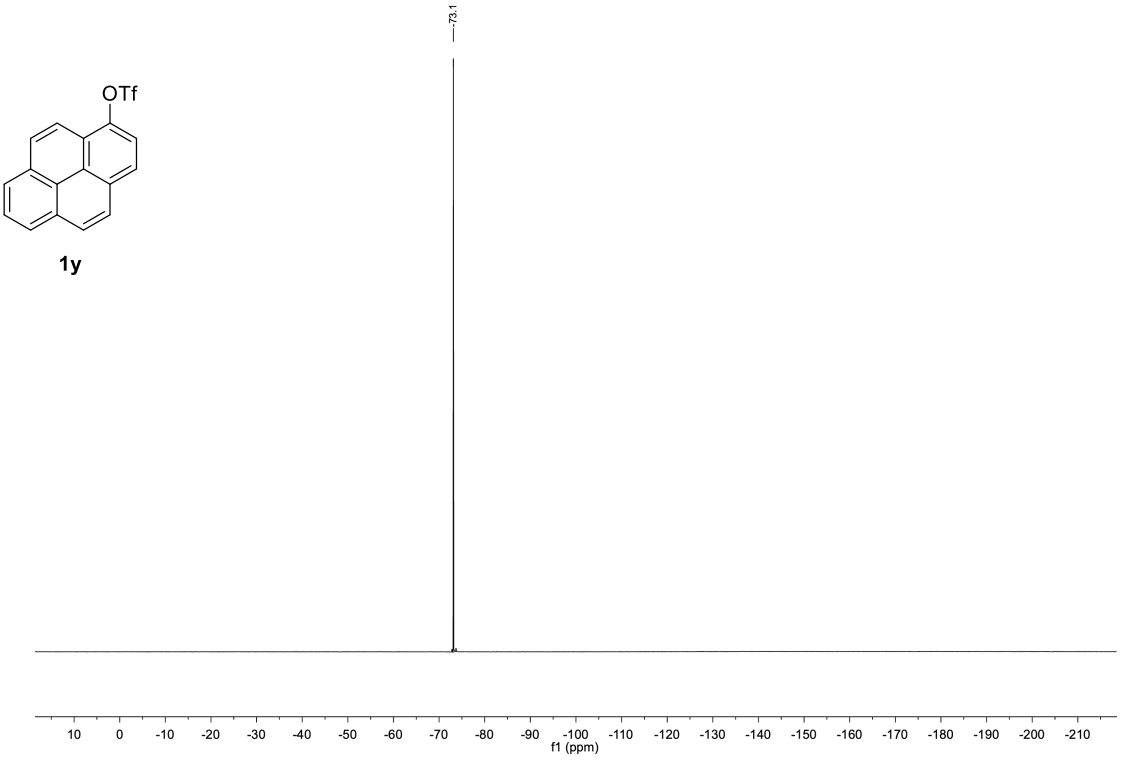
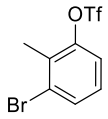


Figure S76. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1y**.

3-Bromo-2-methylphenyl trifluoromethanesulfonate (1z):



1z

$C_8H_6BrF_3O_3S$ (319.09 g/mol)

Following **GP-A**, **1z** was synthesized using 3-bromo-2-methylphenol (1.00 g, 5.35 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 95:5) afforded **1z** (1.49 g, 4.67 mmol, 87%) as a colorless oil.

R_f: 0.89 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.59 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.15 (dd, *J* = 8.2, 8.0 Hz, 1H), 2.45 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 148.4, 132.7, 131.9, 128.1, 126.8, 120.7, 118.7 (q, *J* = 320.4 Hz), 17.1.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.6.

HR-MS (APCI): m/z calc for $[M+H]^+$ 317.91676, found 317.91731.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 1567 (w), 1418 (vs), 1206 (vs), 1135 (vs), 1109 (s), 1001 (s), 885 (vs), 787 (vs), 751 (m), 699 (m).

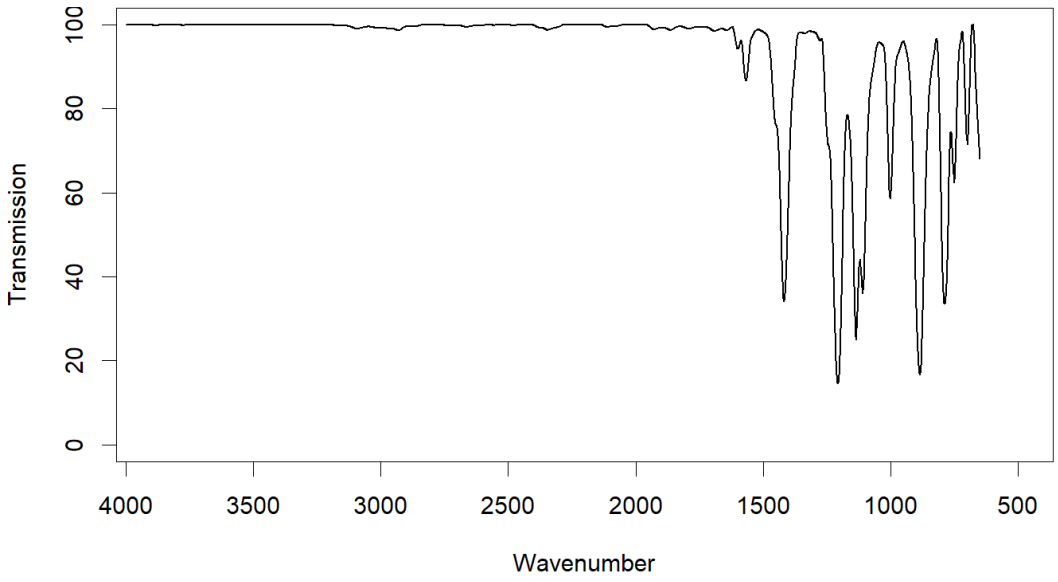


Figure S77. IR-spectrum (ATR, neat) of **1z**.

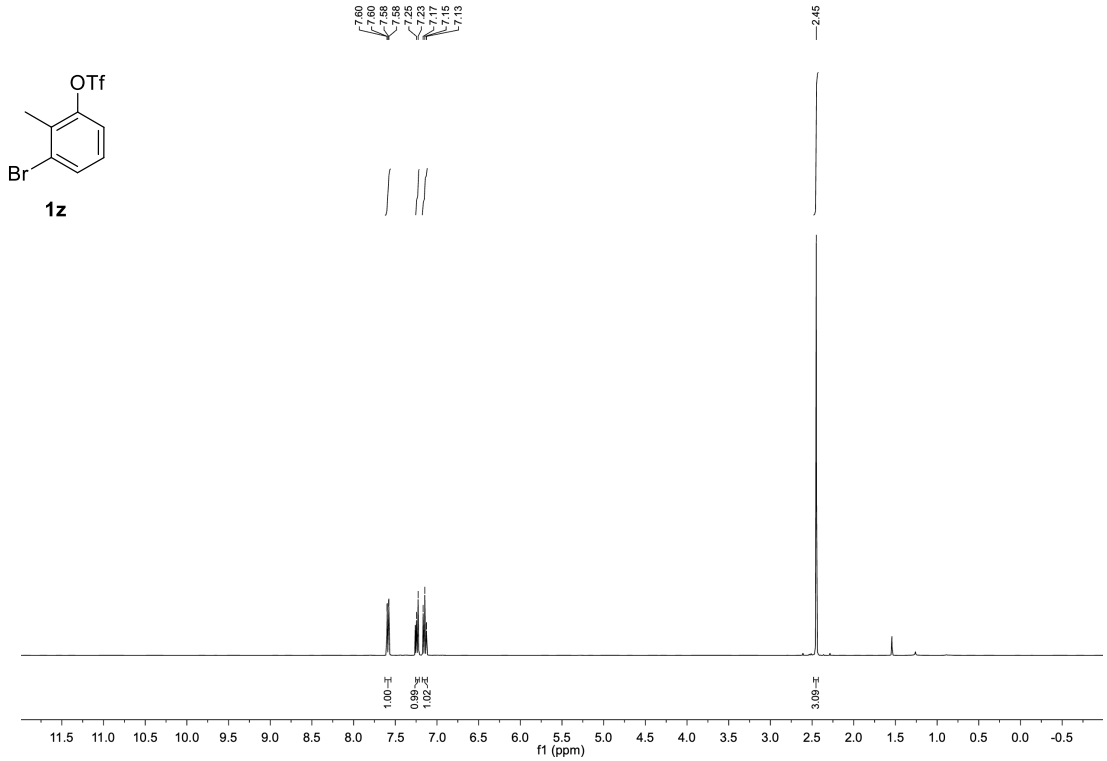


Figure S78. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1z**.

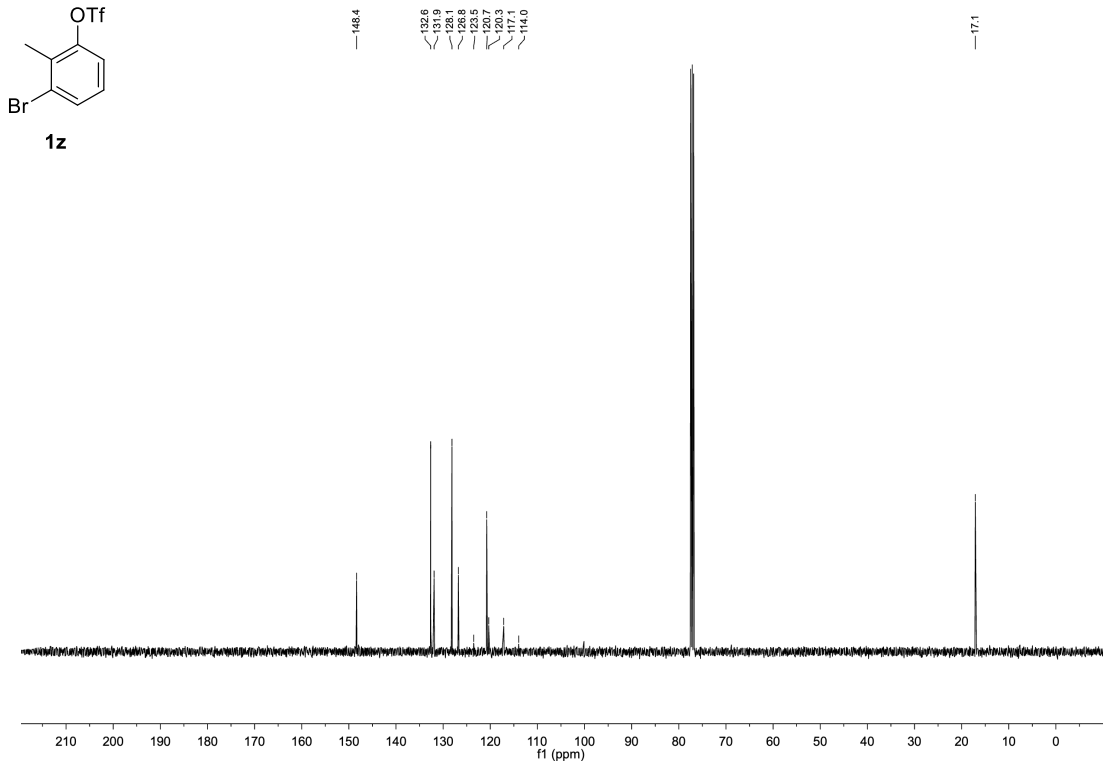


Figure S79. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1z**.

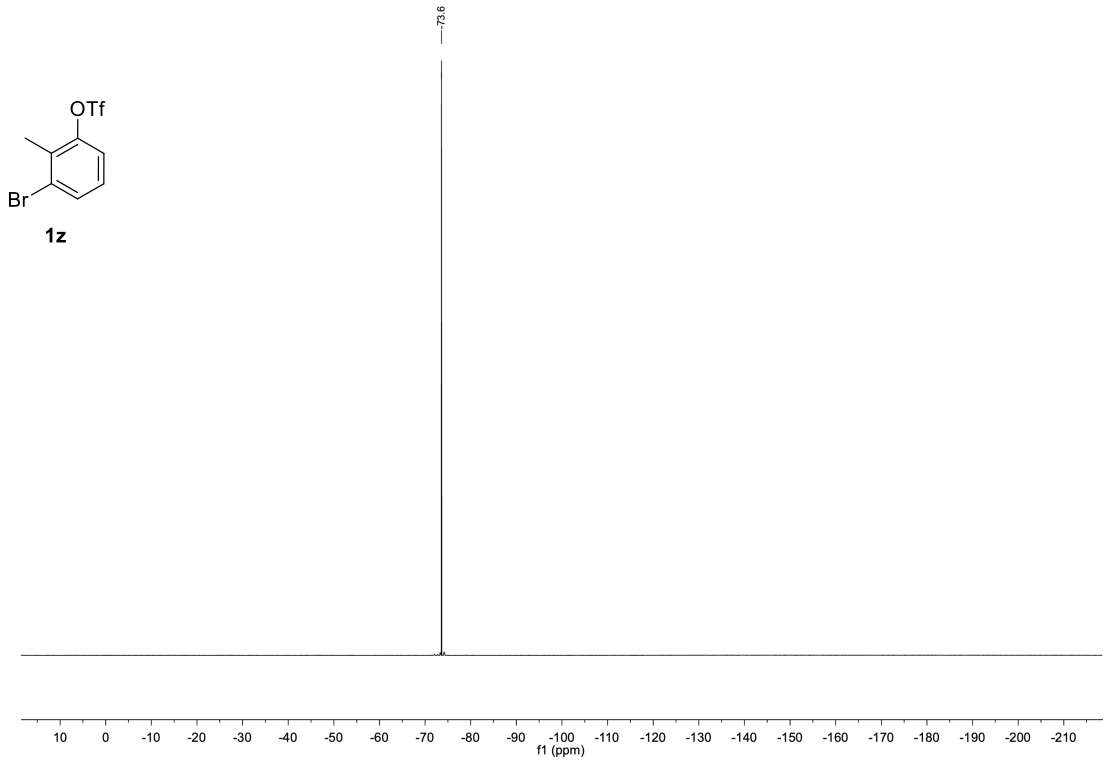
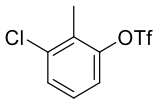


Figure S80. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1z**.

3-Chloro-2-methylphenyl trifluoromethanesulfonate (1A):



1A

$C_8H_6ClF_3O_3S$ (274.64 g/mol)

Following **GP-A**, **1A** was synthesized using 3-chloro-2-methylphenol (1.31 g, 9.19 mmol, 1.0 equiv.). Purification by column chromatography (SiO_2, *n*-hexane/EtOAc 95:5) afforded **1A** (2.17 g, 7.90 mmol, 79%) as a colorless oil.

R_f: 0.82 (*n*-hexane/EtOAc 95:5).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.41 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.25 – 7.16 (m, 2H), 2.46 – 2.37 (m, 7H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 148.7, 136.6, 130.3, 129.4, 127.6, 120.1, 118.7 (q, *J* = 320.1 Hz), 14.1.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -73.6.

HR-MS (APCI): m/z calc for $[M]^{\bullet+}$ 273.96728, found 273.96760.

IR (ATR, $\tilde{\upsilon}$ [cm^{-1}]): 1571 (w), 1452 (m), 1419 (s), 1209 (vs), 1132 (vs), 1012 (s), 894 (vs), 792 (s), 755 (m), 703 (w), 660 (w).

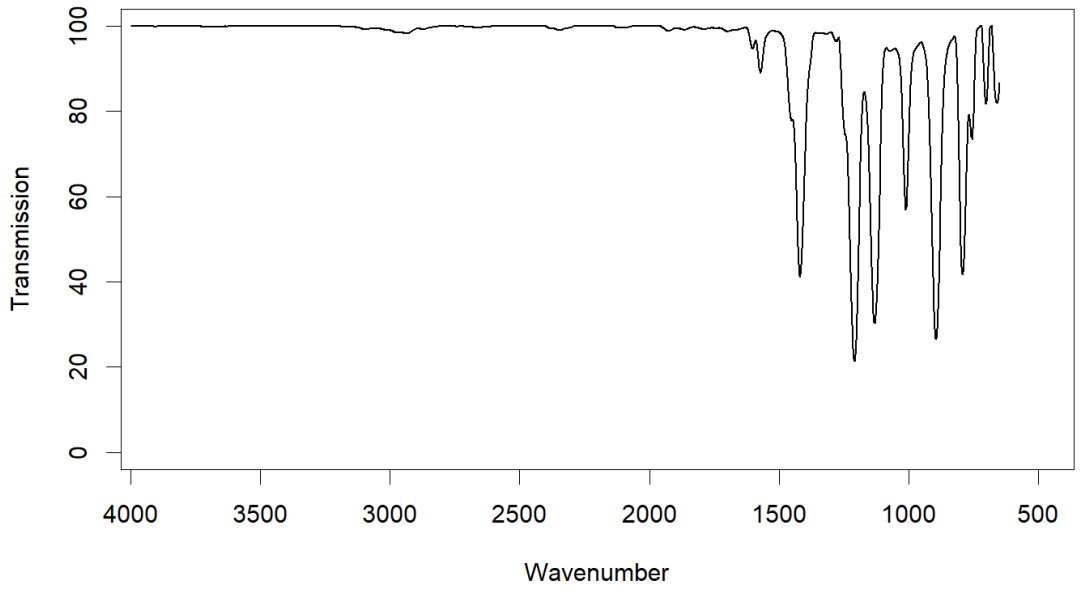


Figure S81. IR-spectrum (ATR, neat) of **1A**.

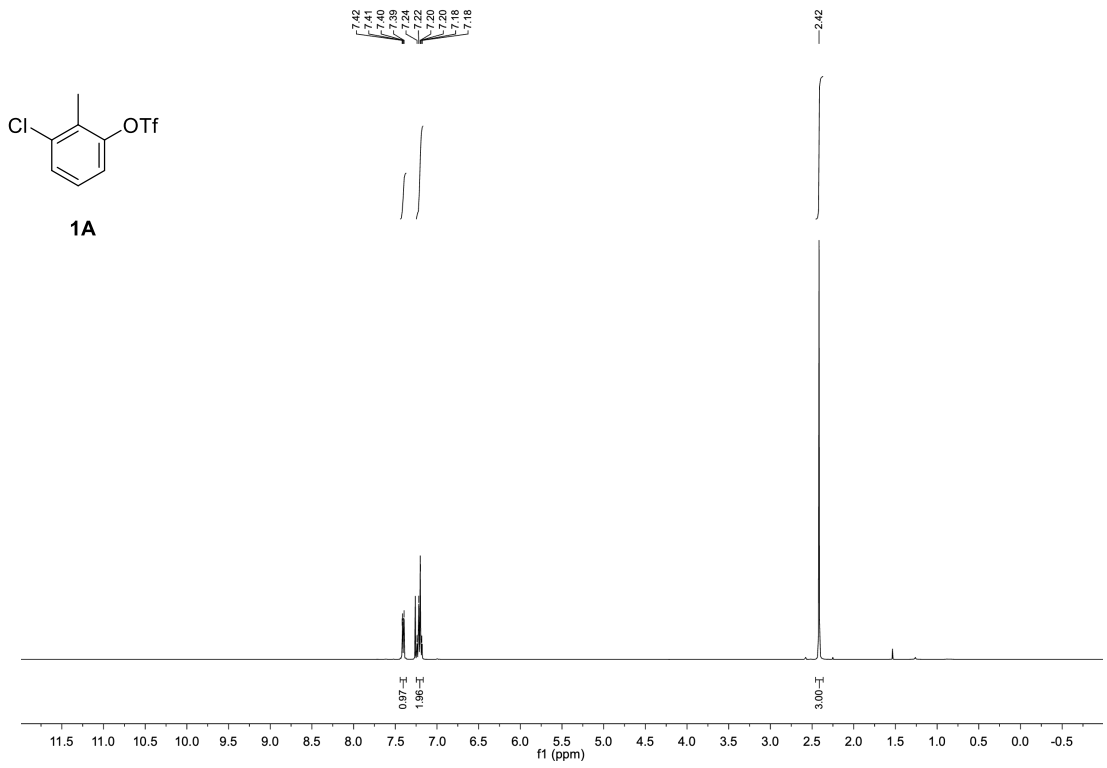


Figure S82. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **1A**.

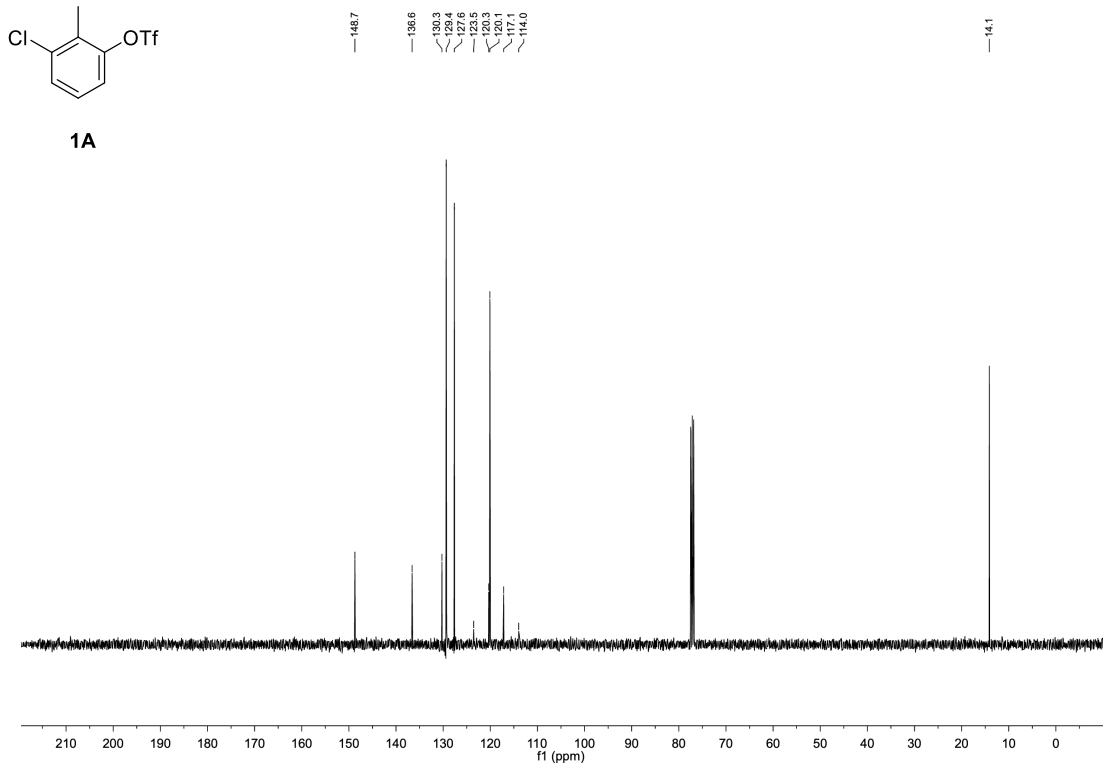


Figure S83. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **1A**.

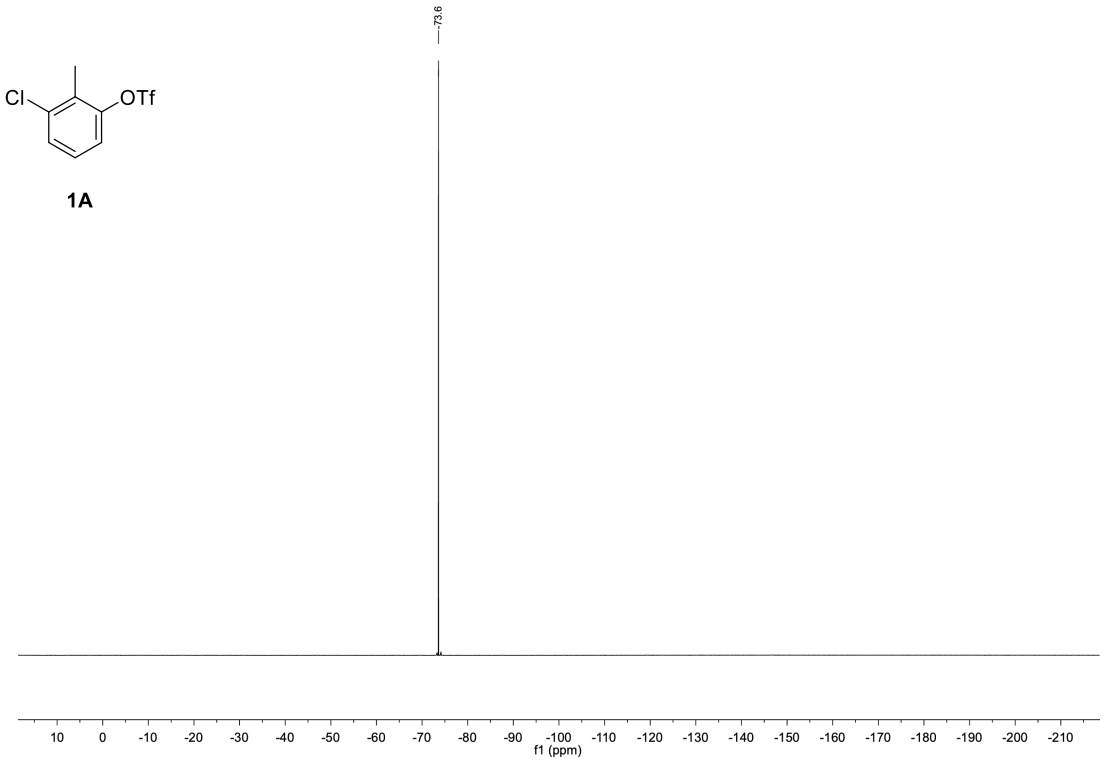
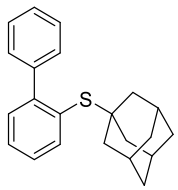


Figure S84. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **1A**.

5.3 Synthesis of *ortho*-substituted aryl alkyl thioethers

[1,1'-biphenyl]-2-yl((1s,3s)-adamantan-1-yl)sulfane (3ab):



3ab

$C_{22}H_{24}S$ (320.49 g/mol)

Following **GP-B**, **3ab** was synthesized using [1,1'-biphenyl]-2-yl trifluoromethanesulfonate (**1a**) (302 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (2b) (177 mg, 1.05 mmol, 1.05 equiv.). The reaction time was shortened to 2 h. Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 95:5 over 10 CV) afforded **3ab** (297 mg, 927 µmol, 93%) as colorless oil.

R_f: 0.3 (*n*-hexane).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.73 (m, 1H), 7.45 – 7.30 (m, 8H), 1.94 – 1.87 (m, 3H), 1.62 – 1.48 (m, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 148.7, 142.2, 139.8, 130.8, 130.8, 129.2, 128.8, 127.4, 126.9, 126.9, 49.7, 43.7, 36.2, 30.1.

HR-MS (APCI): m/z calc for $[M+H]^+$ 321.16715, found 321.16727.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3054 (w), 2901 (s), 2846 (m), 1452 (m), 1422 (m), 1343 (w), 1295 (w), 1247 (w), 1210 (m), 1139 (m), 1101 (w), 1072 (w), 1034 (m), 1005 (w), 974 (w), 885 (m), 822 (w), 742 (s), 695 (s).

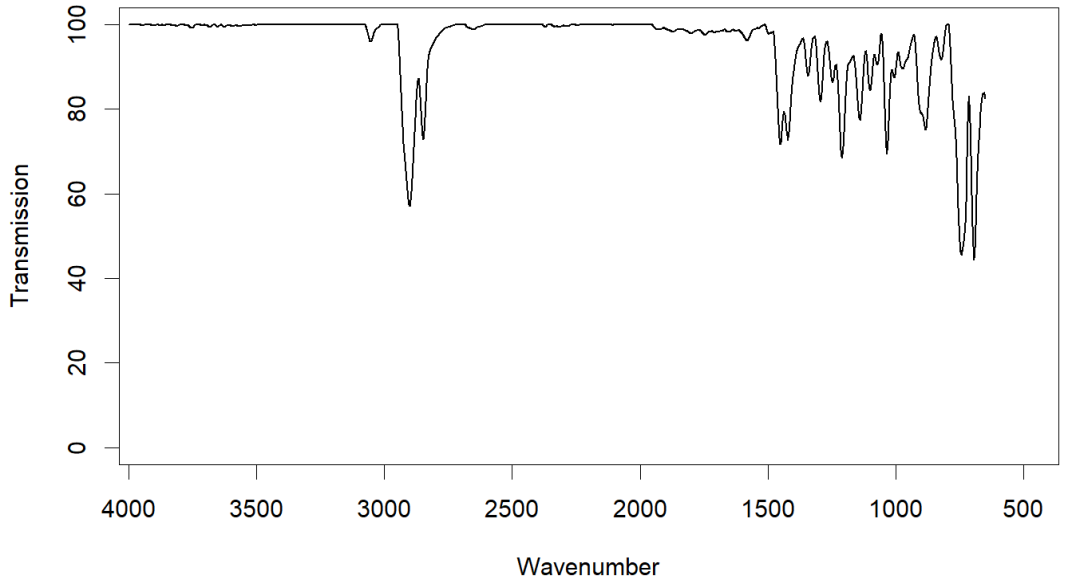


Figure S85. IR-spectrum (ATR, neat) of **3ab**.

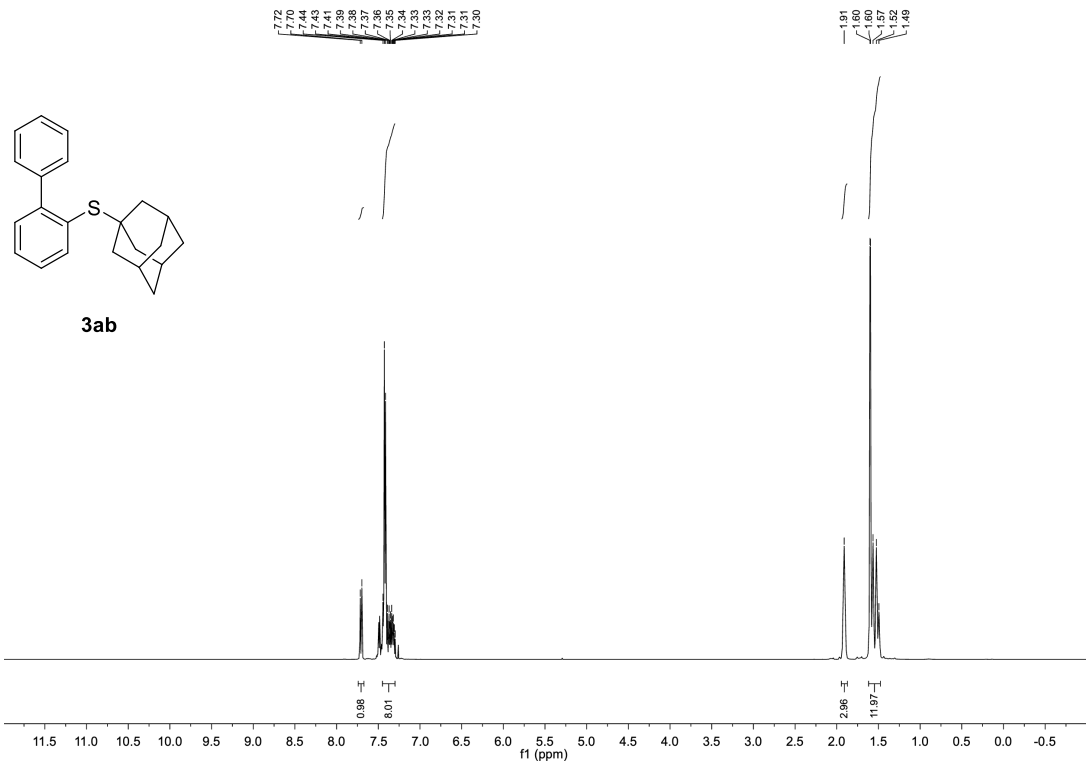


Figure S86. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3ab**.

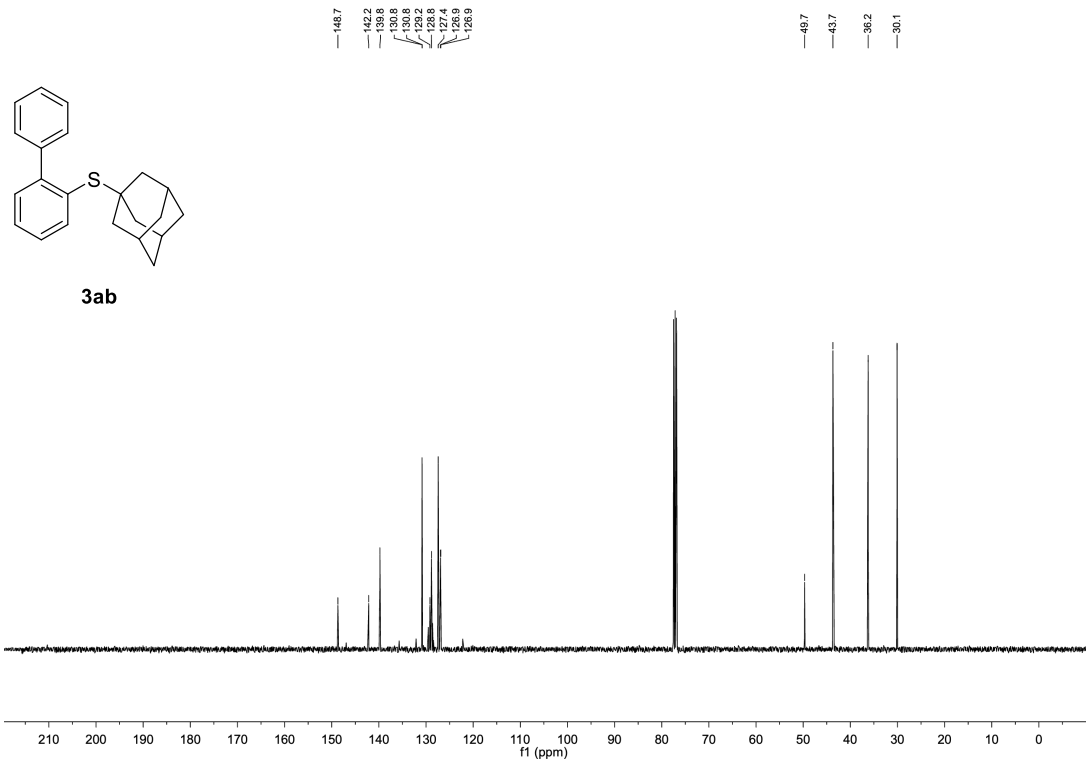
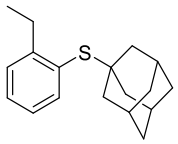


Figure S87. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3ab**.

((1*s*,3*s*)-Adamantan-1-yl)(2-ethylphenyl)sulfane (3bb):



3bb

$C_{18}H_{24}S$ (272.45 g/mol)

Following **GP-B**, **3bb** was synthesized using 2-ethylphenyl trifluoromethanesulfonate (**1b**) (254 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). The reaction time was shortened to 2 h. Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 95:5 over 10 CV) afforded **3bb** (236 mg, 866 µmol, 87%) as colorless solid.

R_f: 0.46 (*n*-hexane/EtOAc 95:5).

m. p.: 46.2 – 48.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.54 – 7.50 (m, 1H), 7.33 – 7.27 (m, 2H), 7.18 – 7.11 (m, 1H), 2.99 (q, *J* = 7.5 Hz, 2H), 2.04 – 2.00 (m, 3H), 1.89 – 1.84 (m, 6H), 1.68 – 1.60 (m, 6H), 1.21 (t, *J* = 7.5 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 150.0, 139.4, 129.6, 129.1, 128.8, 125.5, 49.1, 43.9, 36.3, 30.2, 27.9, 15.9.

HR-MS (APCI): m/z calc for $[M+H]^+$ 273.16715, found 273.16684.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2965 (w), 2898 (s), 2846 (m), 1445 (m), 1373 (w), 1340 (m), 1295 (m), 1254 (w), 1184 (w), 1131 (w), 1101 (w), 1031 (s), 971 (w), 889 (w), 822 (w), 785 (w), 747 (s), 681 (m).

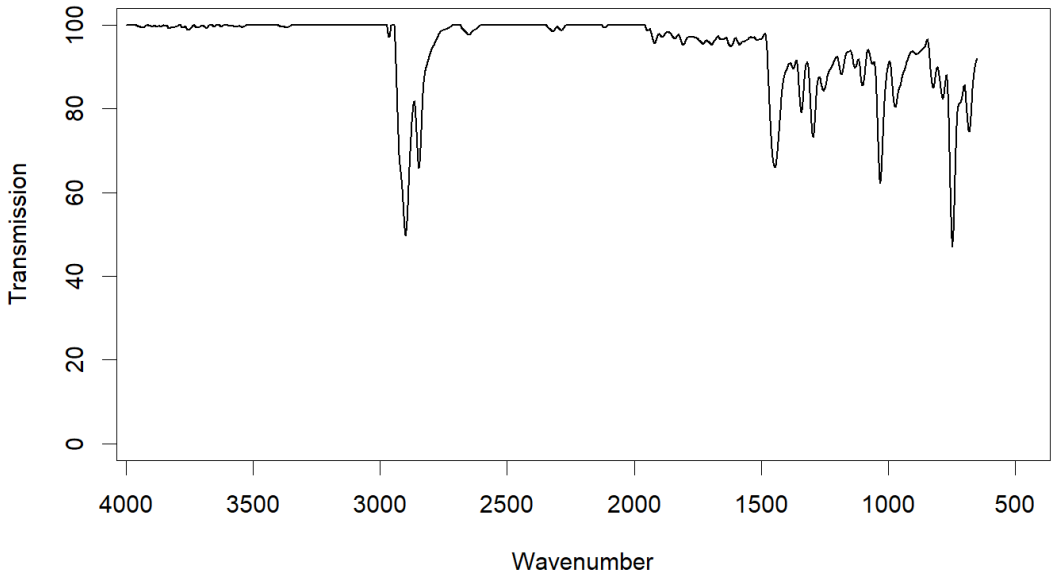


Figure S88. IR-spectrum (ATR, neat) of **3bb**.

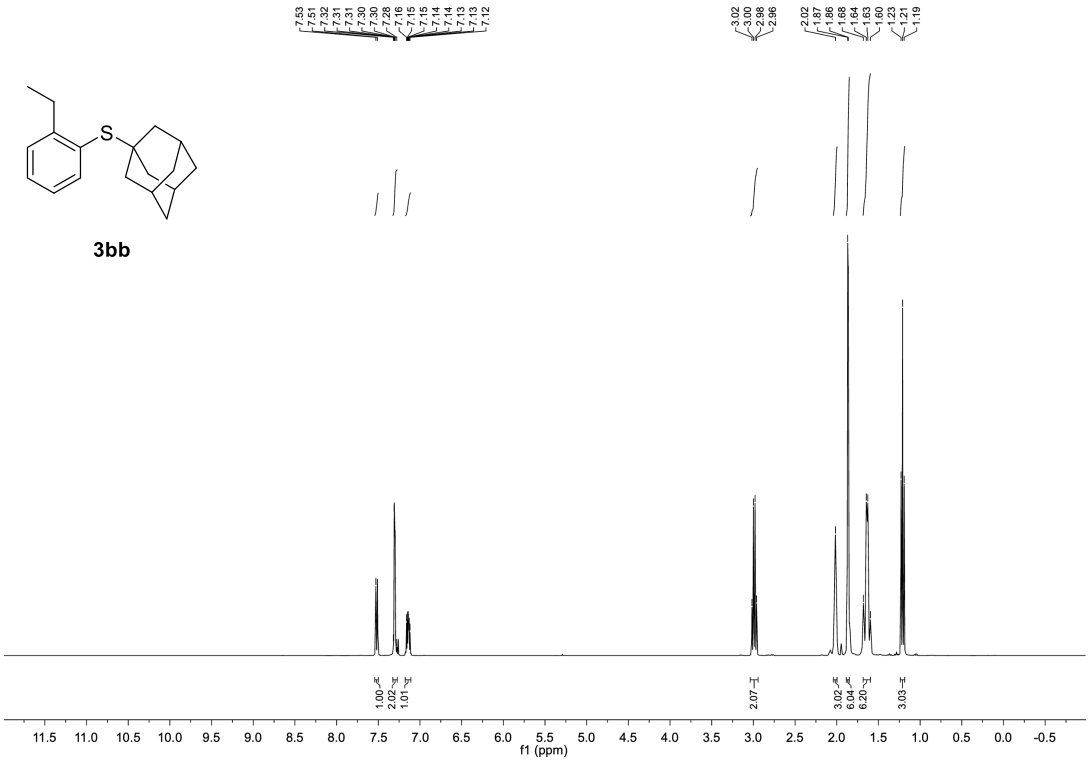


Figure S89. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3bb**.

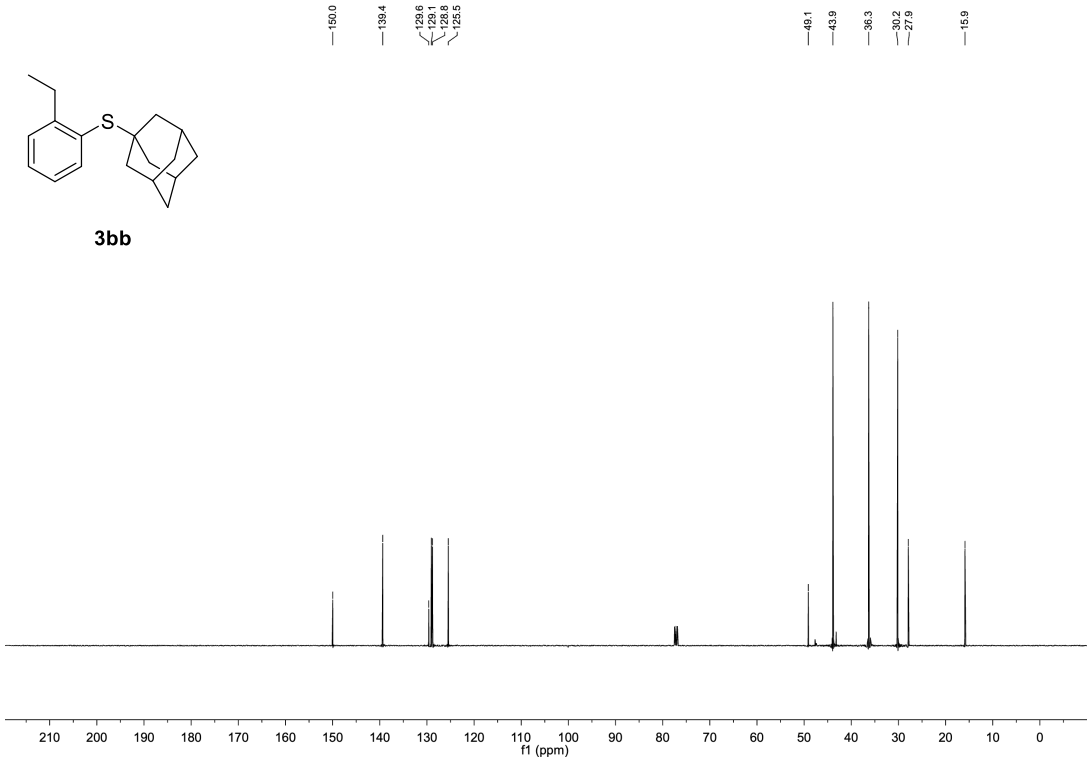
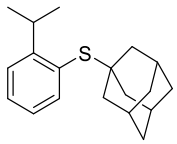


Figure S90. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3bb**.

((1*s*,3*s*)-Adamantan-1-yl)(2-isopropylphenyl)sulfane (3cb):



3cb

$C_{19}H_{26}S$ (286.48 g/mol)

Following **GP-B**, **3cb** was synthesized using 2-isopropylphenyl trifluoromethanesulfonate (**1c**) (268 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 95:5 over 10 CV) afforded **3cb** (268 mg, 918 µmol, 92%) as colorless solid.

R_f: 0.48 (*n*-hexane/EtOAc 95:5).

m. p.: 74.9 – 76.4 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.53 – 7.49 (m, 1H), 7.36 – 7.31 (m, 2H), 7.15 – 7.08 (m, 1H), 3.94 (d, *J* = 6.9 Hz, 1H), 2.04 – 1.99 (m, 3H), 1.86 – 1.83 (m, 6H), 1.68 – 1.59 (m, 6H), 1.20 (d, *J* = 6.9 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 154.4, 139.4, 129.3, 129.0, 125.9, 125.2, 48.9, 43.9, 36.4, 30.7, 30.2, 24.1.

HR-MS (APCI): m/z calc for $[M+H]^+$ 287.18280, found 287.18233.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2958 (w), 2898 (s), 2846 (m), 1444 (m), 1381 (w), 1344 (w), 1295 (m), 1254 (w), 1202 (w), 1150 (w), 1101 (w), 1031 (s), 966 (w), 956 (w), 893 (w), 822 (w), 755 (s), 681 (m).

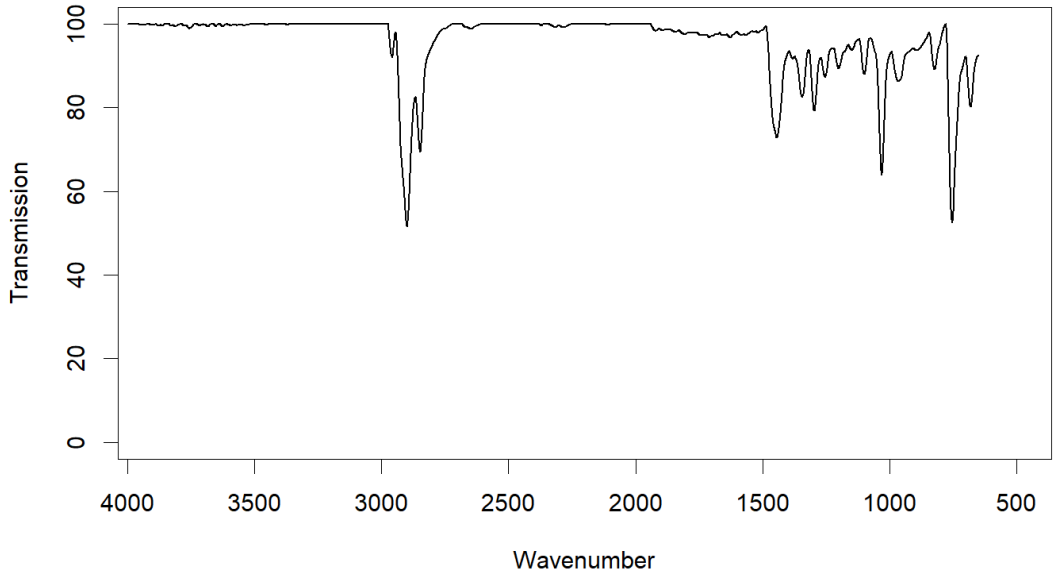


Figure S91. IR-spectrum (ATR, neat) of **3cb**.

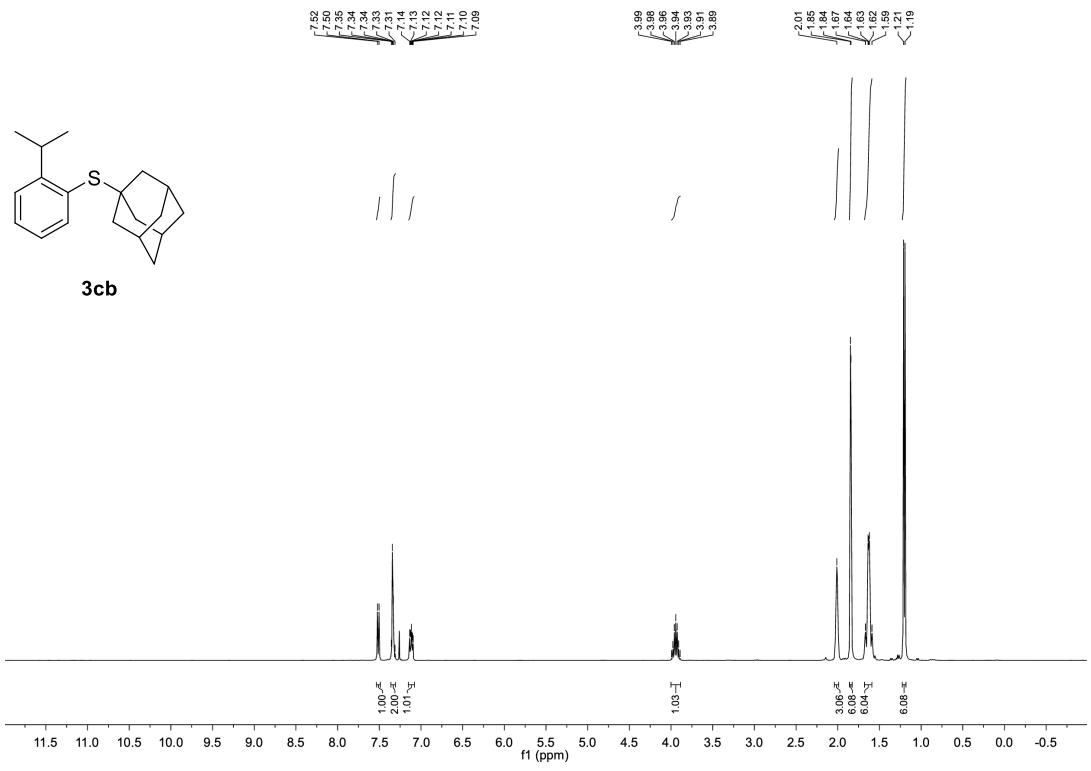


Figure S92. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3cb**.

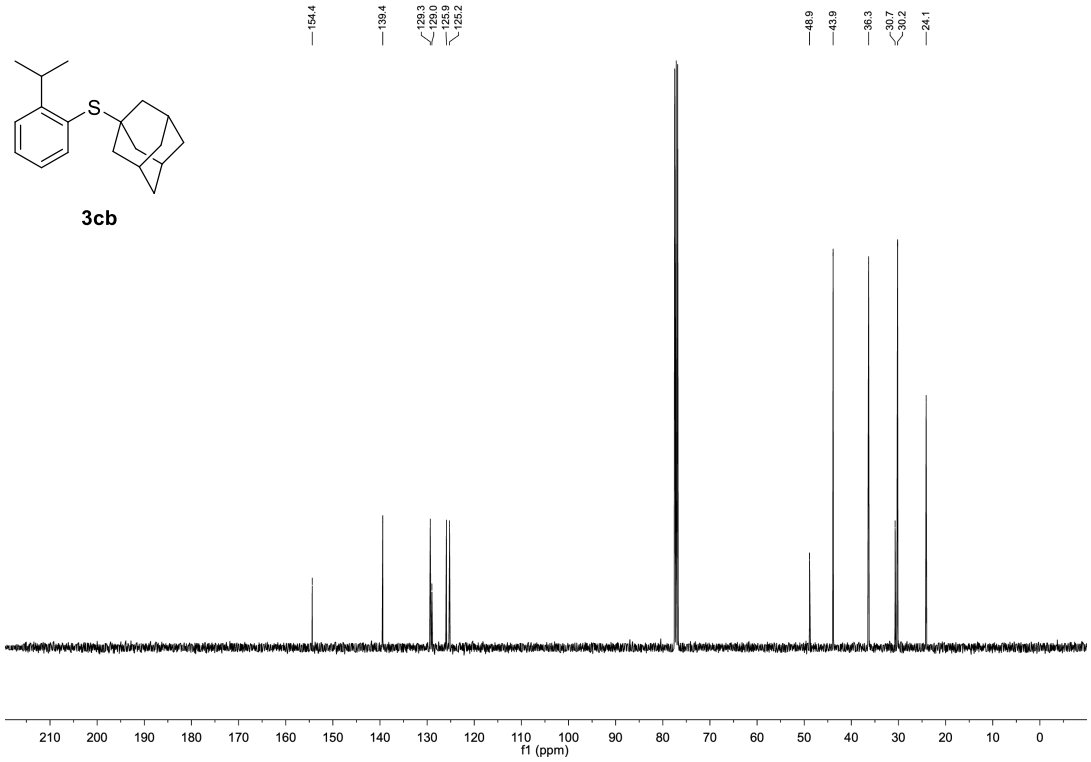
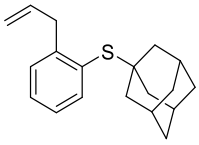


Figure S93. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3cb**.

((1*s*,3*s*)-Adamantan-1-yl)(2-allylphenyl)sulfane (3eb):



3eb

$C_{19}H_{24}S$ (284.46 g/mol)

Following **GP-B**, **3eb** was synthesized using 2-allylphenyl trifluoromethanesulfonate (**1e**) (266 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV) afforded **3eb** (246 mg, 865 µmol, 87%) as yellow oil.

R_f: 0.93 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.55 – 7.51 (m, 1H), 7.32 – 7.28 (m, 2H), 7.19 – 7.13 (m, 1H), 6.03 – 5.88 (m, 1H), 5.12 – 4.96 (m, 2H), 3.76 (d, *J* = 6.6 Hz, 2H), 2.04 – 1.99 (m, 3H), 1.86 – 1.83 (m, 6H), 1.67 – 1.58 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 145.8, 139.4, 137.8, 130.1, 129.8, 129.1, 126.0, 115.9, 49.4, 43.9, 39.0, 36.3, 30.2.

HR-MS (APCI): m/z calc for $[M+H]^+$ 285.16715, found 285.16748.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3055 (w), 2901 (s), 2846 (m), 1634 (w), 1445 (m), 1343 (w), 1295 (m), 1254 (w), 1205 (w), 1186 (w), 1101 (w), 1034 (s), 986 (m), 908 (s), 819 (w), 751 (s), 684 (m).

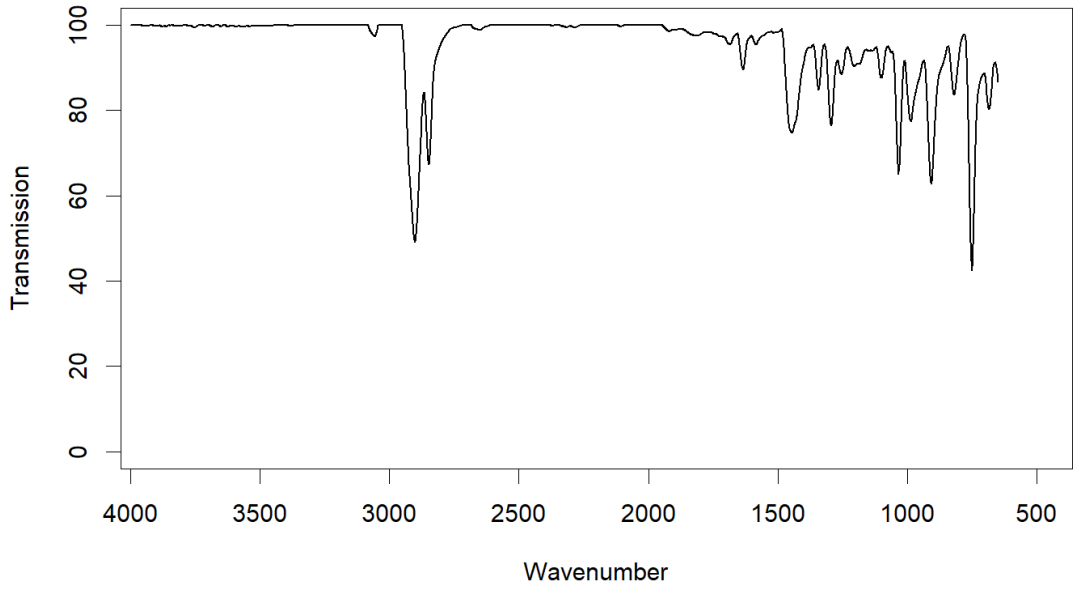


Figure S94. IR-spectrum (ATR, neat) of **3eb**.

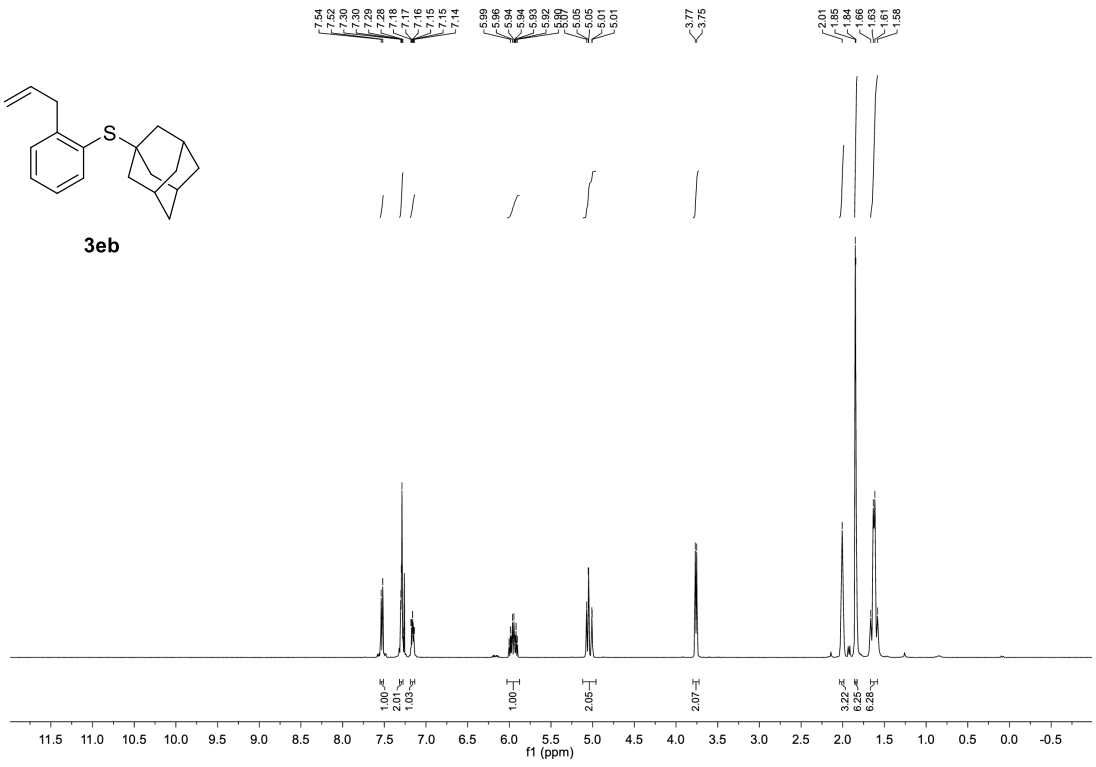


Figure S95. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3eb**.

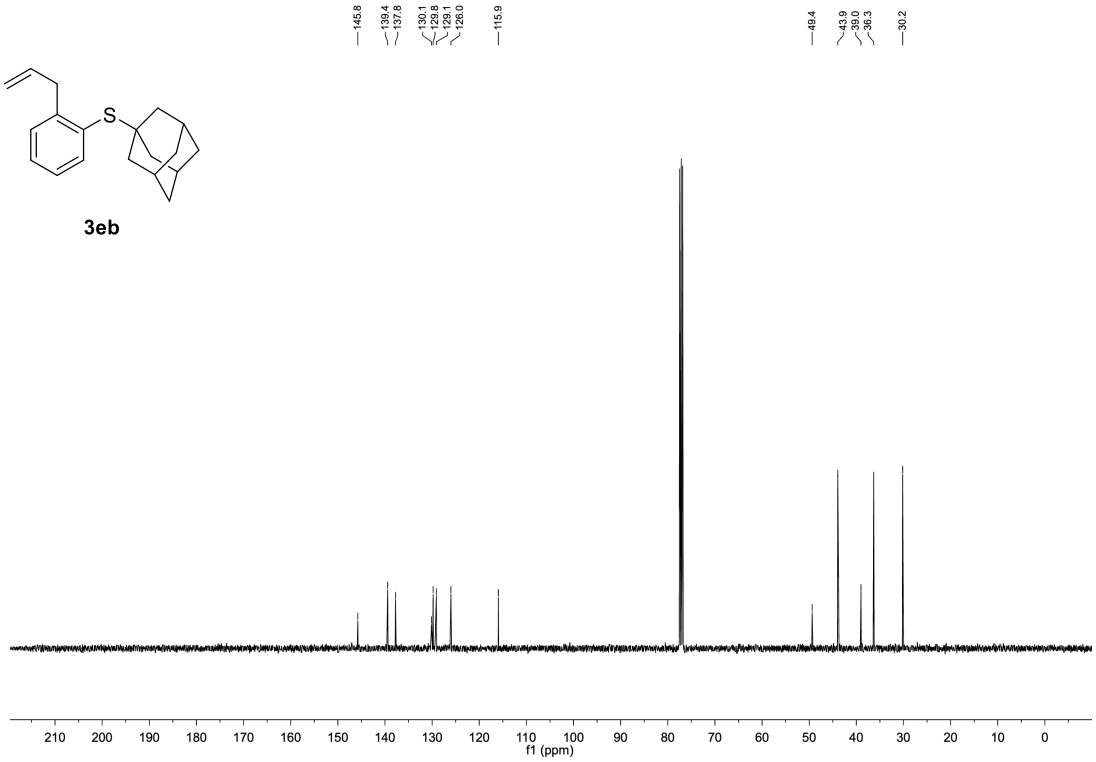
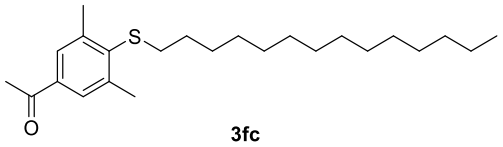


Figure S96. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3eb**.

1-(3,5-Dimethyl-4-(tetradecylthio)phenyl)ethan-1-one (3fc):



3fc

$C_{24}H_{40}OS$ (376.64 g/mol)

Following **GP-C**, **3fc** was synthesized using 4-acetyl-2,6-dimethylphenyl trifluoromethanesulfonate (**1f**) (296 mg, 1.00 mmol, 1.0 equiv.) and *n*-tetradecane thiol (**2c**) (242 mg, 1.05 mmol, 1.05 equiv.). The reaction temperature was set to 100 °C and the reaction time was prolonged to 16 h. Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV, then to 60:40 over 5 CV) afforded **3fc** (153 mg, 406 µmol, 41%) as colorless solid.

R_f: 0.24 (*n*-hexane/EtOAc 95:5).

m. p.: 48.7 – 50.6 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.65 (s, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.58 (s, 6H), 2.57 (s, 3H), 1.57 – 1.47 (m, 2H), 1.41 – 1.21 (m, 23H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 198.4, 143.4, 140.6, 136.2, 127.6, 35.5, 32.1, 30.1, 29.83, 29.80, 29.77, 29.71, 29.65, 29.5, 29.3, 29.0, 26.8, 22.8, 22.4, 14.3.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 399.26921, found 399.26934.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2950 (w), 2913 (m), 2846 (m), 1679 (m), 1586 (w), 1556 (w), 1459 (m), 1412 (w), 1377 (w), 1351 (w), 1299 (m), 1206 (m), 1120 (w), 1079 (w), 1042 (w), 1023 (w), 978 (w), 929 (w), 866 (w), 784 (w), 721 (m).

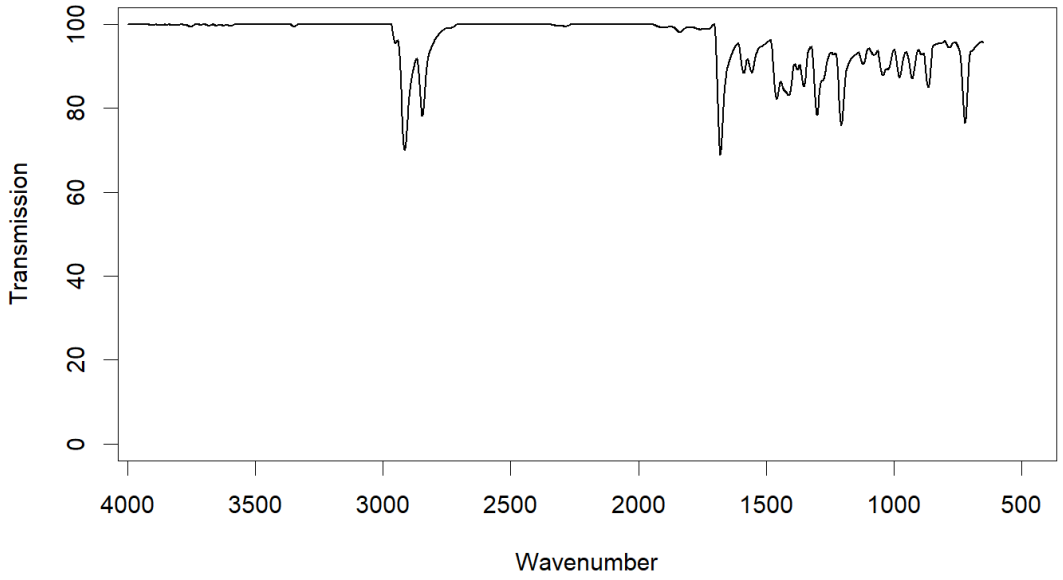


Figure S97. IR-spectrum (ATR, neat) of **3fc**.

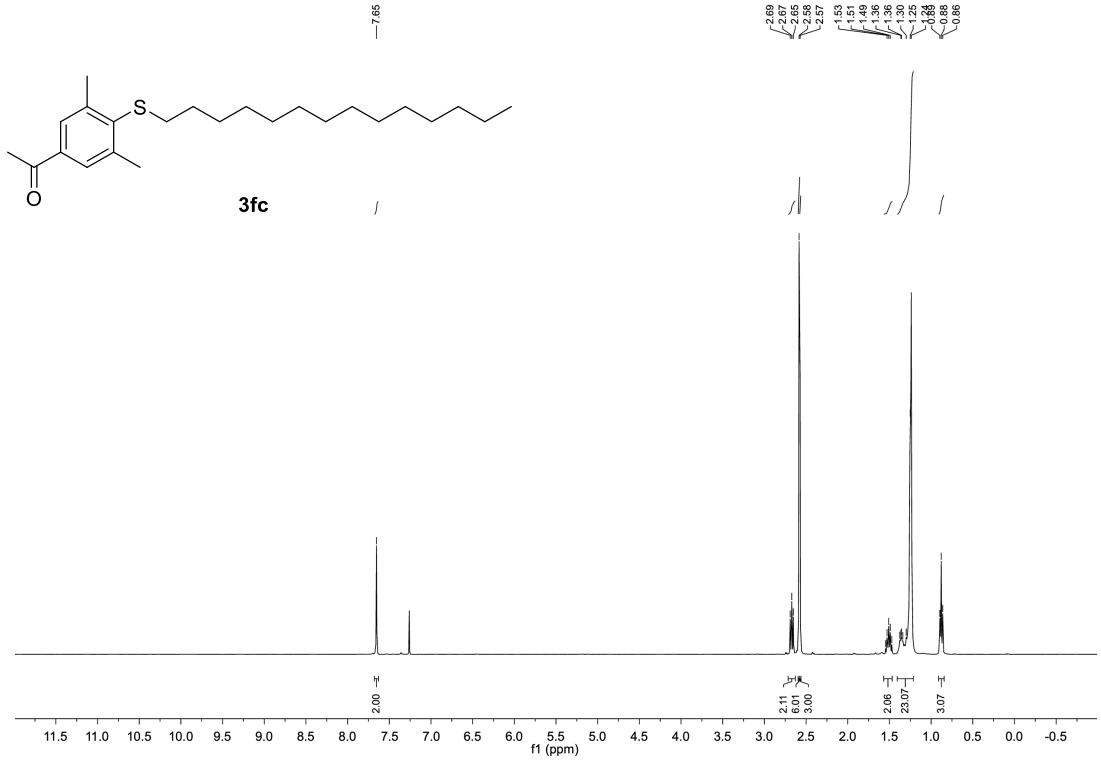


Figure S98. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3fc**.

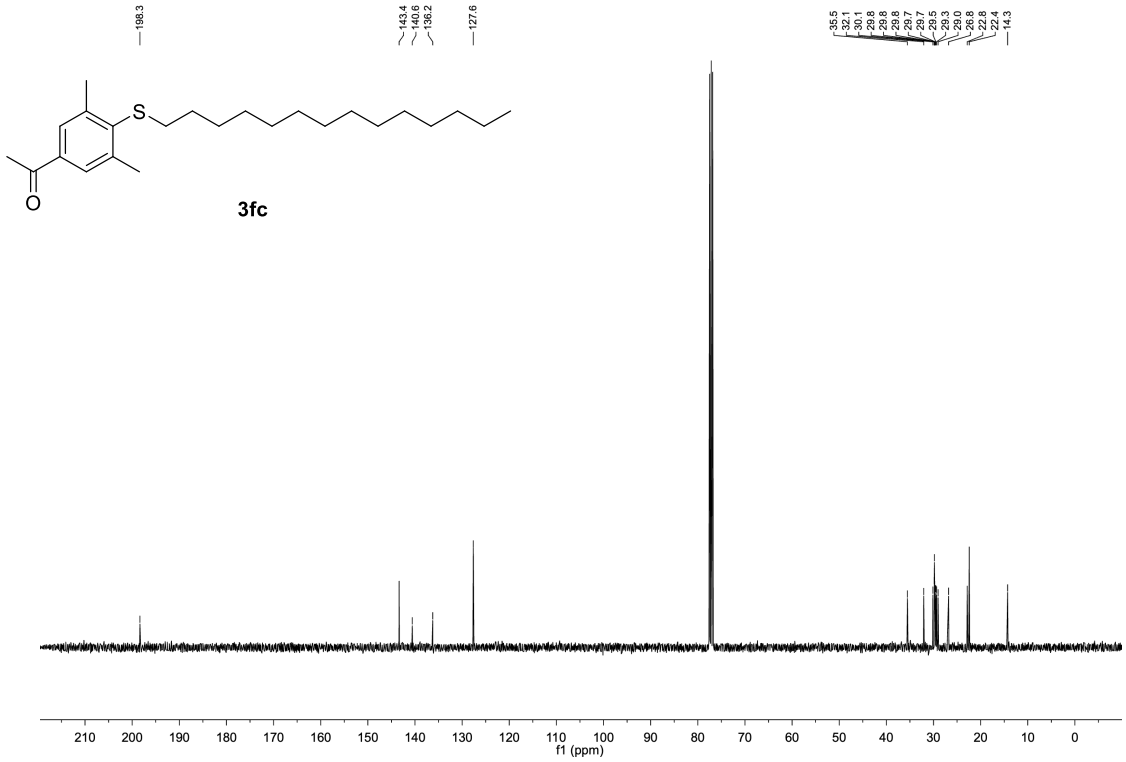
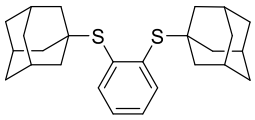


Figure S99. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3fc**.

1,2-Bis(((1*s*,3*S*)-adamantan-1-yl)thio)benzene (3gb):



3gb

$C_{26}H_{34}S_2$ (410.68 g/mol)

Following **GP-B**, **3gb** was synthesized using 1,2-phenylene bis(trifluoromethanesulfonate) (**1g**) (374 mg, 1.00 mmol, 1.0 equiv.), 1-adamantane thiol (**2b**) (353 mg, 2.10 mmol, 2.10 equiv.), potassium acetate (216 mg, 2.20 mmol, 2.2 equiv.), $Ni(cod)_2$ (27.5 mg, 100 µmol, 10 mol%) and **L2** (44.7 mg, 100 µmol, 10 mol%). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 95:5 over 10 CV) afforded **3gb** (363 mg, 885 µmol, 89%) as colorless solid.

R_f: 0.10 (*n*-hexane).

m. p.: 106.5 – 111.1 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.73 – 7.63 (m, 2H), 7.29 – 7.24 (m, 2H), 2.04 – 1.97 (m, 6H), 1.91 – 1.81 (m, 12H), 1.68 – 1.58 (m, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 139.0, 138.6, 128.0, 50.1, 43.9, 36.4, 30.2.

HR-MS (APCI): m/z calc for $[M+H]^+$ 411.21747, found 411.21794.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2894 (s), 2846 (m), 1567 (w), 1441 (m), 1340 (m), 1292 (m), 1250 (w), 1209 (w), 1142 (w), 1101 (w), 1030 (m), 971 (w), 885 (w), 817 (w), 747 (s), 684 (m).

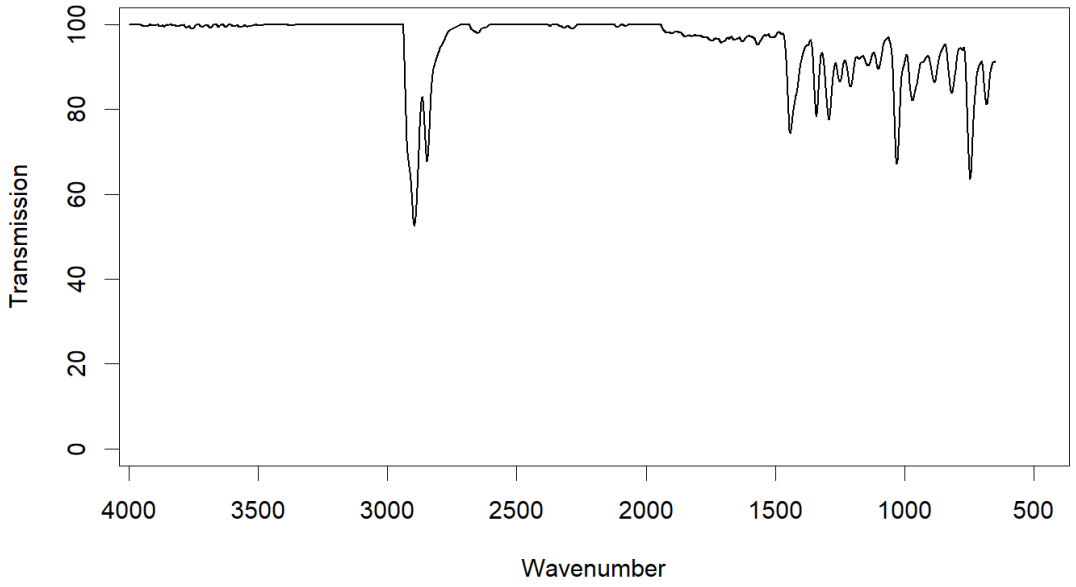


Figure S100. IR-spectrum (ATR, neat) of **3gb**.

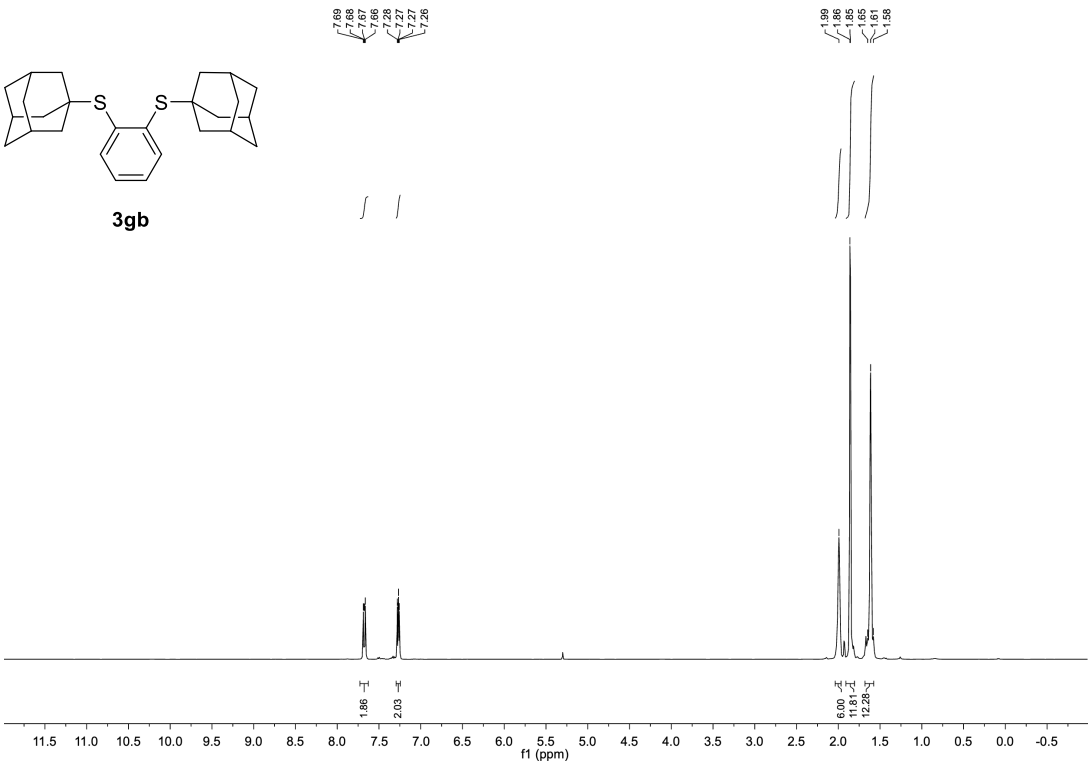


Figure S101. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3gb**.

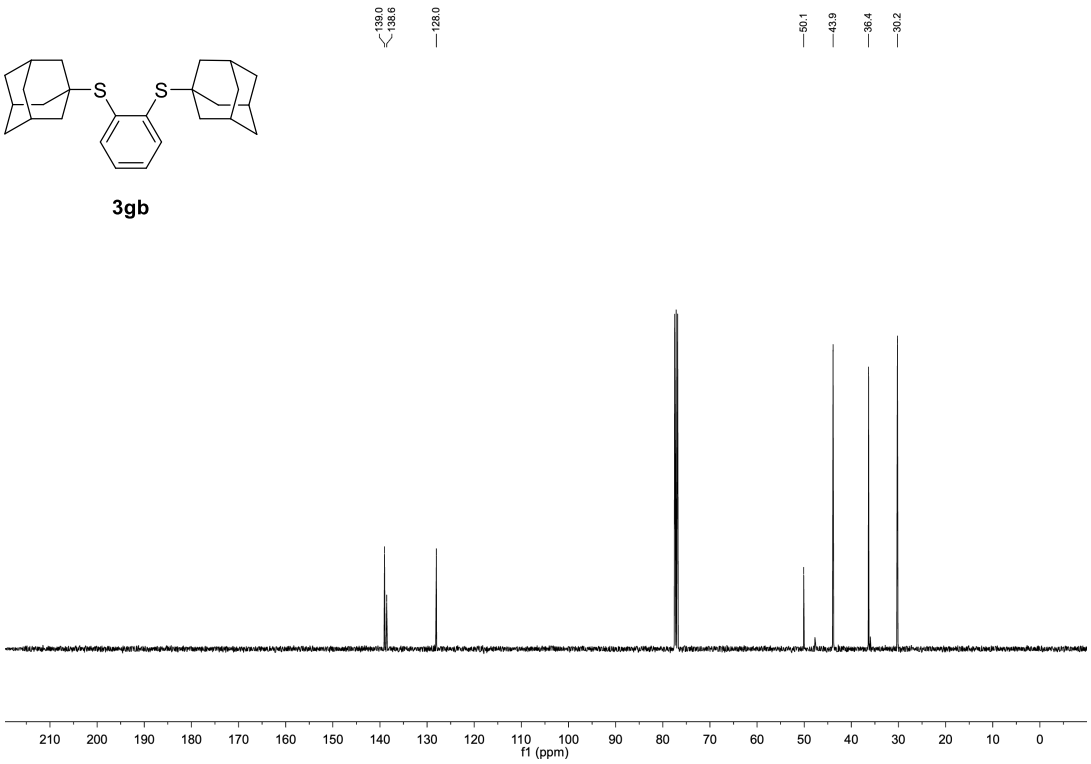
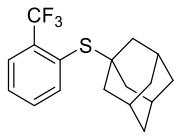


Figure S102. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3gb**.

((1*s*,3*s*)-Adamantan-1-yl)(2-(trifluoromethyl)phenyl)sulfane (3hb):



3hb

$C_{17}H_{19}F_3S$ (312.39 g/mol)

Following **GP-A**, **3hb** was synthesized using 2-(trifluoromethyl)phenyl trifluoromethanesulfonate (**1h**) (294 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 95:5 over 10 CV) afforded **3hb** (220 mg, 657 µmol, 66%) as colorless oil.

R_f: 0.47 (*n*-hexane).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.76 – 7.65 (m, 2H), 7.52 – 7.38 (m, 2H), 2.06 – 2.00 (m, 3H), 1.90 – 1.86 (m, 6H), 1.68 – 1.59 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 140.2, 134.8 (q, *J* = 28.7 Hz), 130.9, 128.3, 126.9 (q, *J* = 5.9 Hz), 123.6 (q, *J* = 274.0 Hz), 50.3, 44.0, 36.1, 30.2.

Note: We were unable to observe the expected signal of the C(Ar)–S carbon.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -57.9.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 335.10518, found 335.10579.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2902 (s), 2850 (m), 1590 (w), 1441 (m), 1344 (w), 1303 (vs), 1255 (m), 1164 (s), 1135 (vs), 1103 (vs), 1030 (vs), 966 (w), 881 (w), 818 (w), 766 (s), 740 (m), 706 (w), 680 (w).

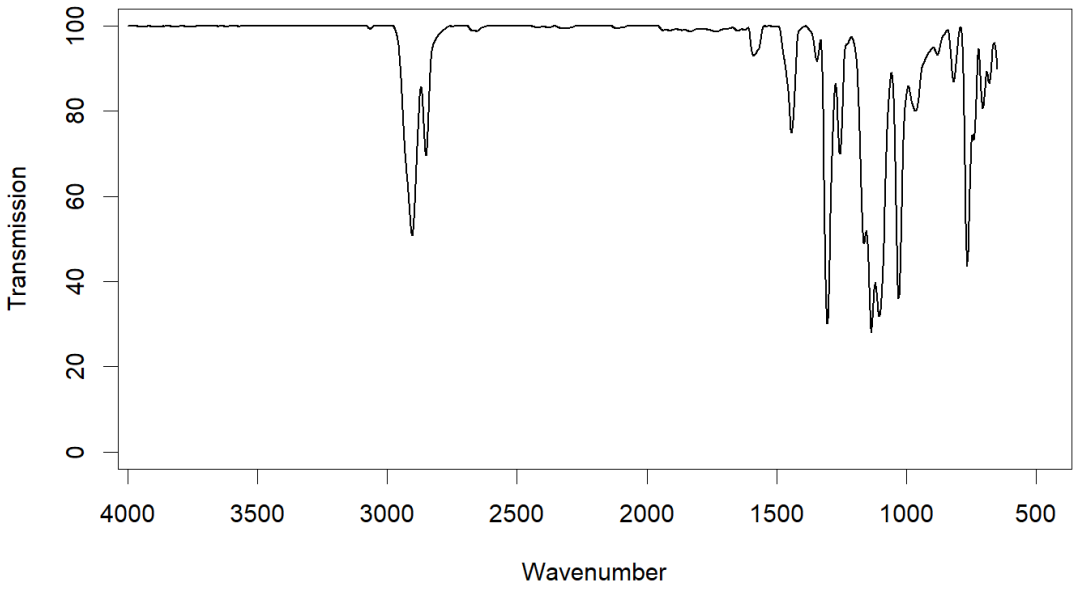


Figure S103. IR-spectrum (ATR, neat) of **3hb**.

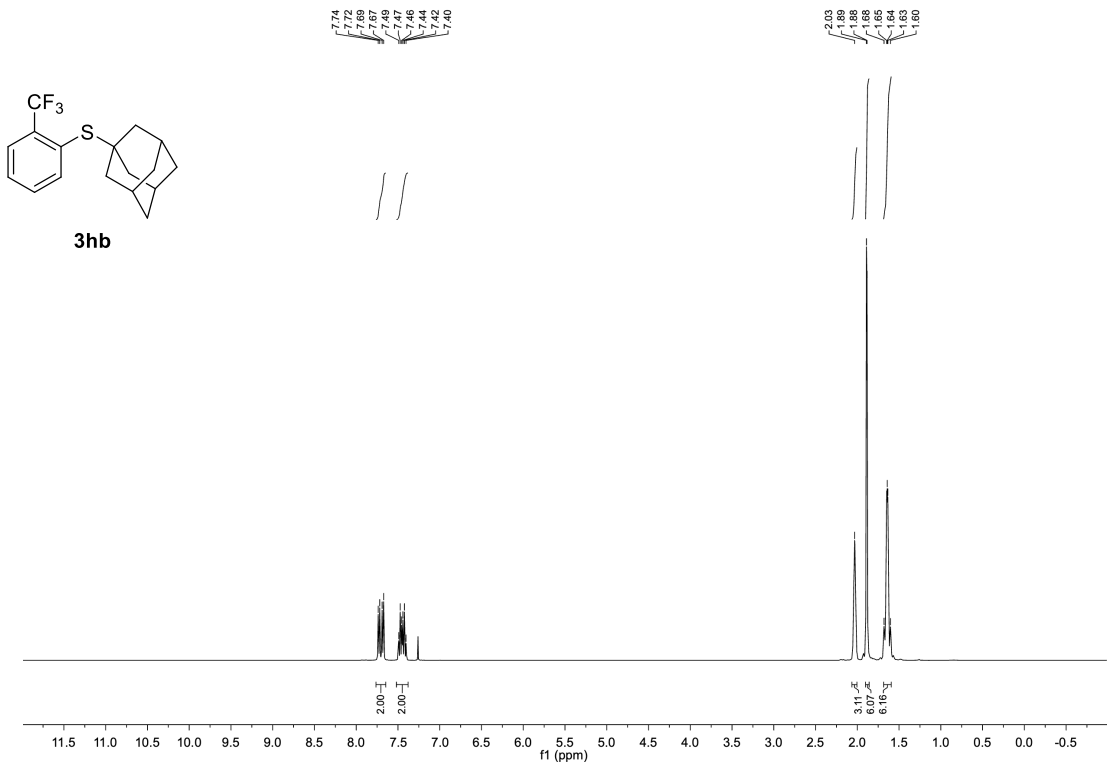


Figure S104. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3hb**.

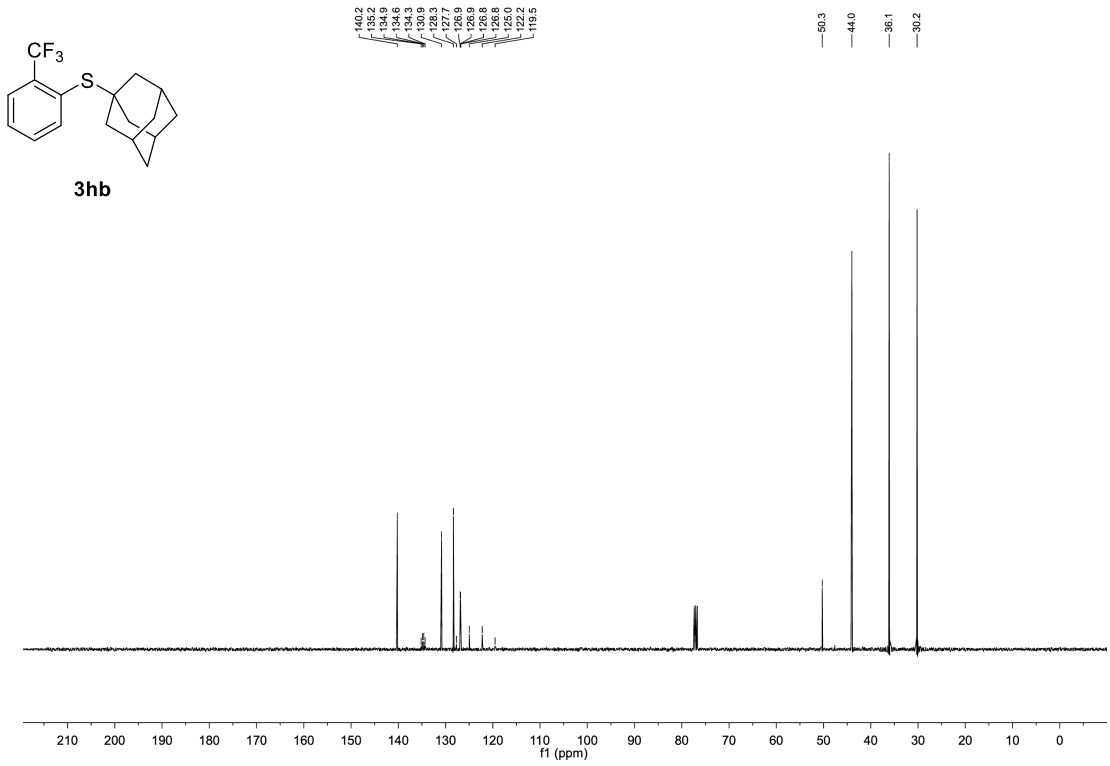


Figure S105. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3hb**.

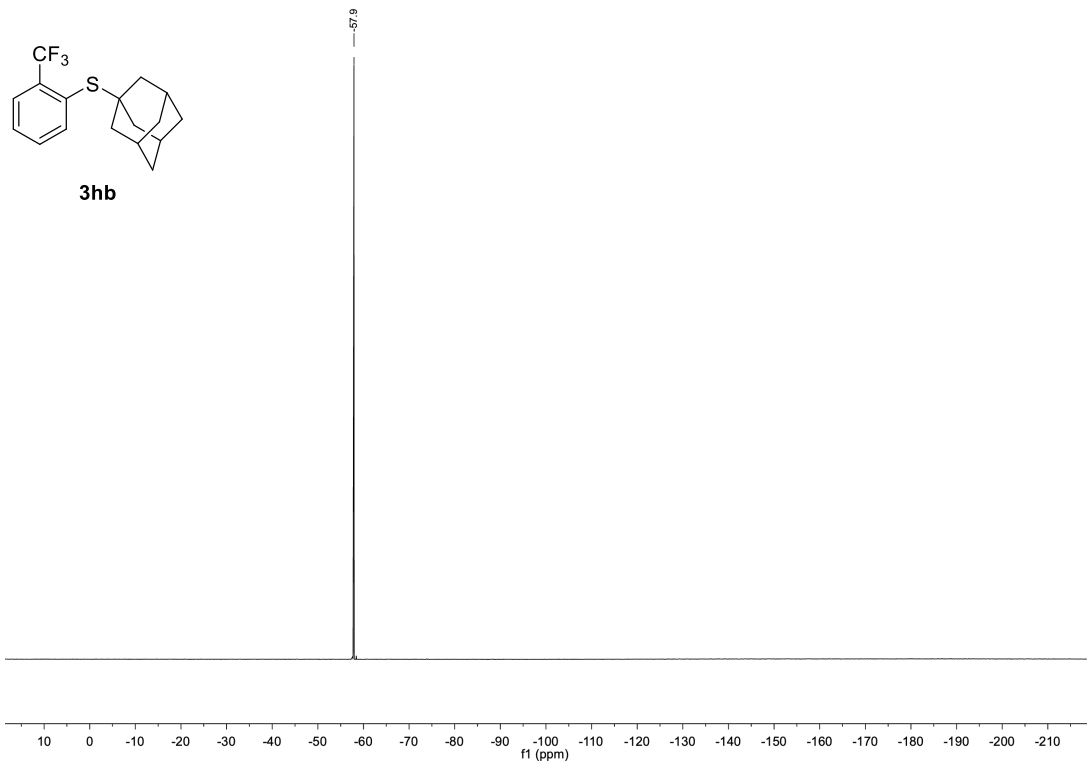
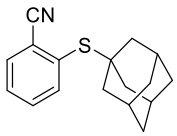


Figure S106. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **3hb**.

2-(((1*s*,3*s*)-Adamantan-1-yl)thio)benzonitrile (3ib):



3ib

$C_{17}H_{19}NS$ (269.41 g/mol)

Following **GP-B**, **3ib** was synthesized using 2-cyanophenyl trifluoromethanesulfonate (**1i**) (251 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). The reaction time was shortened to 2 h. Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV) afforded **3ib** (244 mg, 906 µmol, 91%) as colorless solid.

R_f: 0.43(*n*-hexane/EtOAc 95:5).

m. p.: 76.6 – 78.3 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.81 – 7.60 (m, 2H), 7.57 – 7.39 (m, 2H), 2.09 – 1.98 (m, 3H), 1.95 – 1.83 (m, 6H), 1.70 – 1.57 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 139.4, 134.8, 133.7, 132.1, 129.2, 121.6, 118.5, 51.3, 43.7, 36.1, 30.2.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 292.11304, found 292.11314.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2898 (s), 2849 (m), 2227 (w), 1724 (w), 1650 (w), 1579 (w), 1448 (m), 1344 (w), 1291 (m), 1254 (w), 1191 (w), 1124 (w), 1101 (w), 1064 (w), 1031 (m), 968 (w), 882 (w), 818 (w), 763 (s), 680 (m).

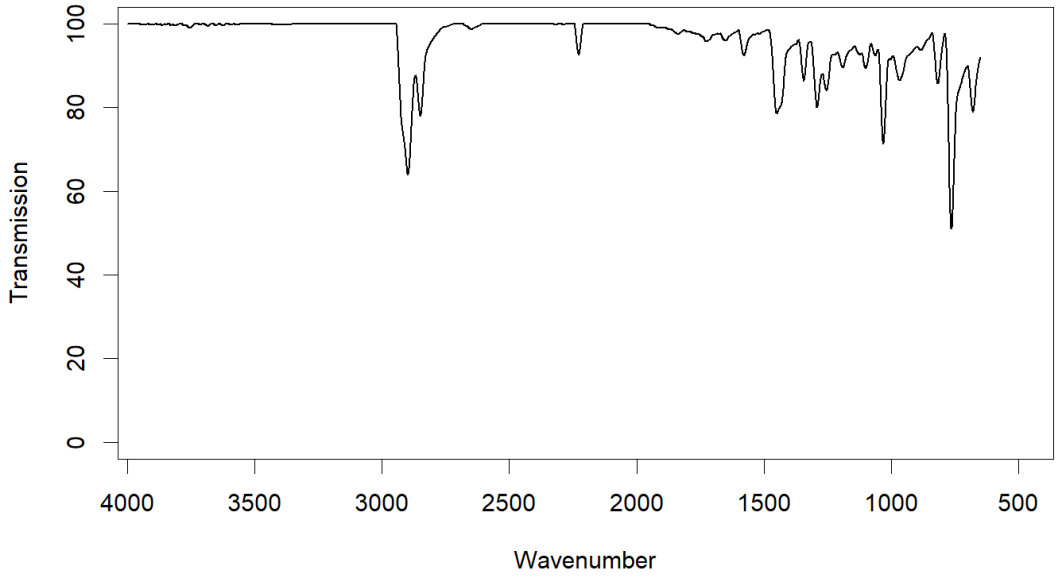


Figure S107. IR-spectrum (ATR, neat) of **3ib**.

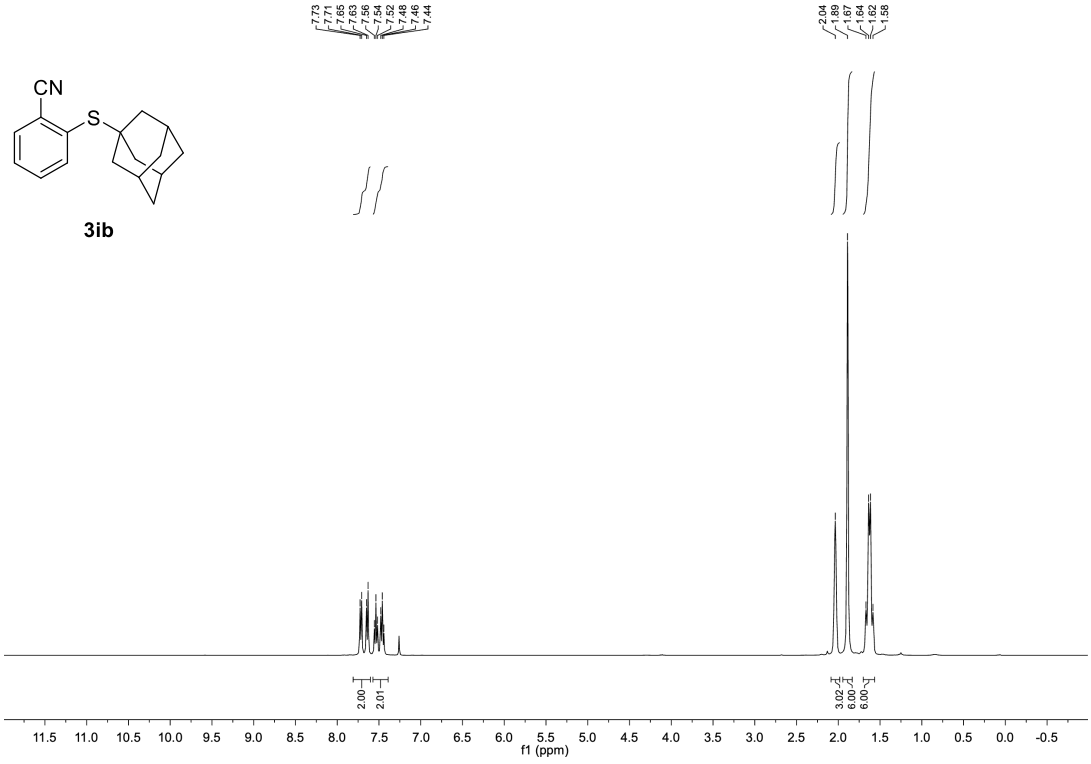


Figure S108. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3ib**.

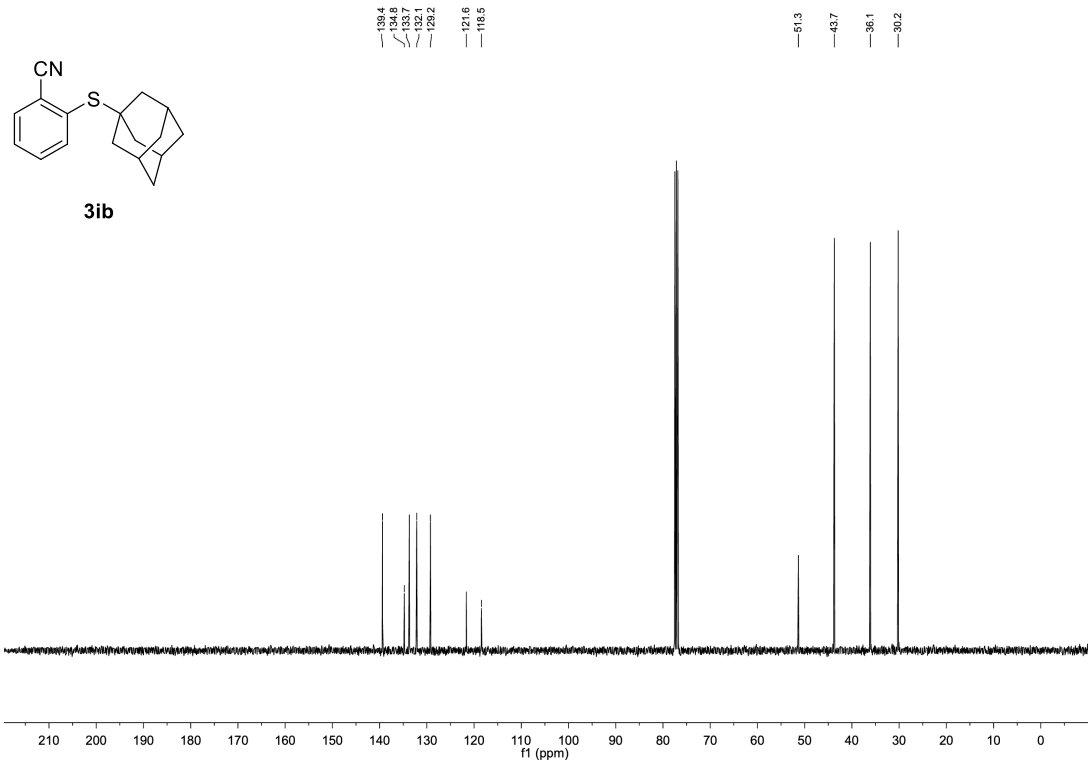
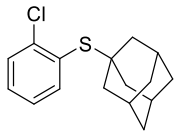


Figure S109. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3ib**.

((1*s*,3*s*)-Adamantan-1-yl)(2-chlorophenyl)sulfane (3jb):



3jb

$C_{16}H_{19}ClS$ (278.84 g/mol)

Following **GP-B**, **3jb** was synthesized using 2-chlorophenyl trifluoromethanesulfonate (**1j**) (261 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV) afforded **3jb** (190 mg, 683 µmol, 68%) as colorless solid.

R_f: 0.80 (*n*-hexane/EtOAc 95:5).

m. p.: 79.5 – 81.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.63 – 7.57 (m, 1H), 7.51 – 7.45 (m, 1H), 7.32 – 7.26 (m, 1H), 7.24 – 7.18 (m, 1H), 2.04 – 2.00 (m, 3H), 1.91 – 1.87 (m, 6H), 1.67 – 1.59 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 141.5, 140.5, 130.22, 130.16, 126.5, 50.7, 43.8, 36.3, 30.2.

HR-MS (APCI): m/z calc for $[M]^{\bullet+}$ 278.08905, found 278.08915.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2894 (s), 2842 (m), 1803 (w), 1694 (w), 1567 (w), 1444 (m), 1422 (m), 1340 (w), 1292 (m), 1254 (w), 1214 (w), 1180 (w), 1108 (w), 1031 (s), 971 (m), 949 (w), 885 (w), 820 (w), 743 (s), 681 (m).

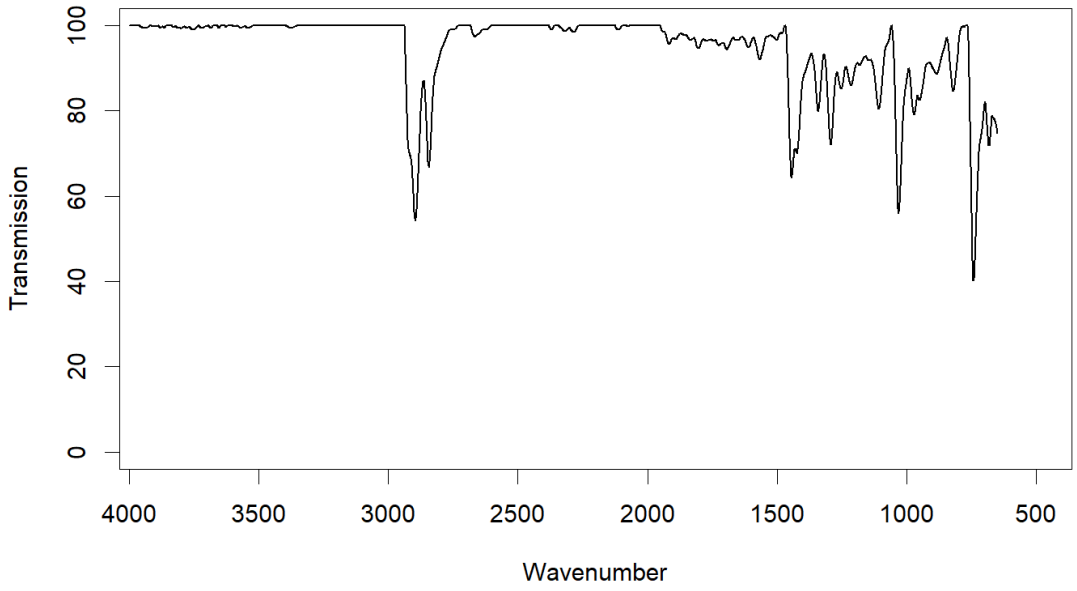


Figure S110. IR-spectrum (ATR, neat) of **3jb**.

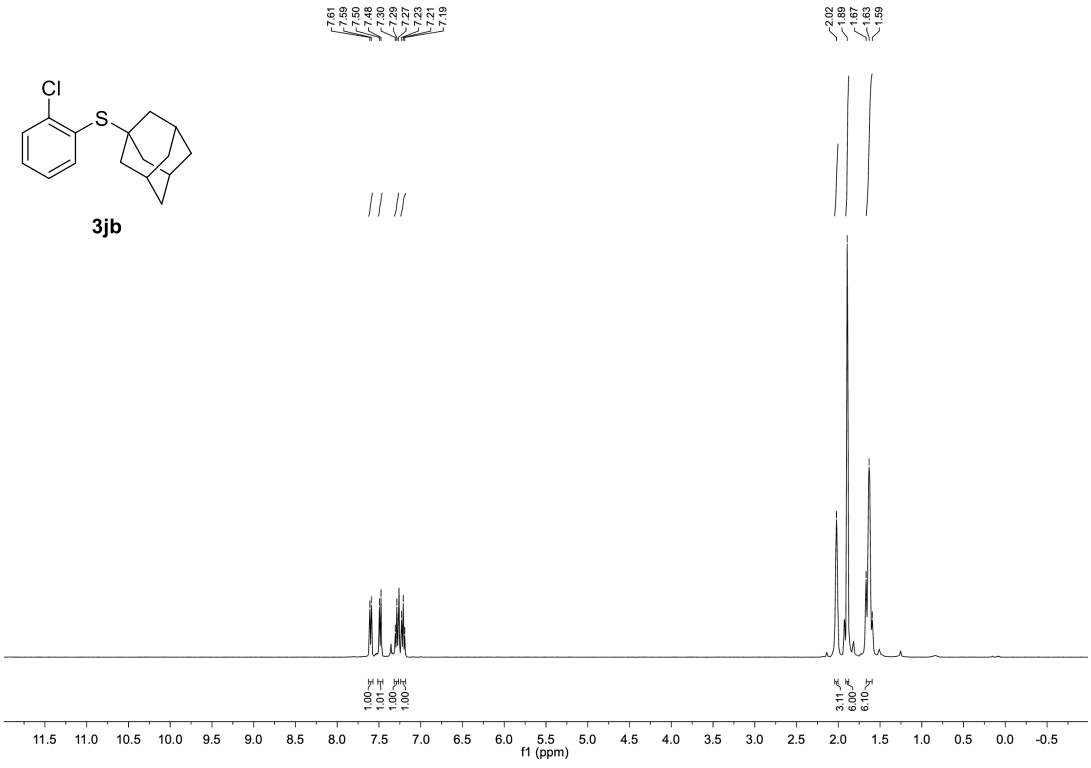


Figure S111. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3jb**.

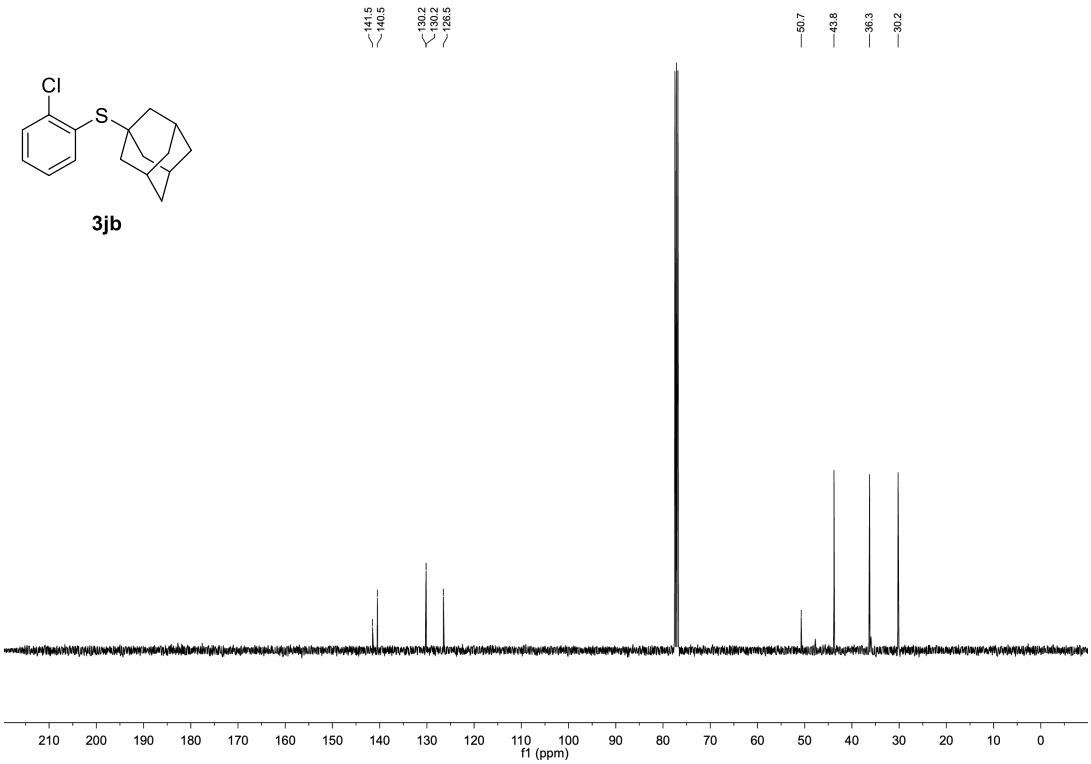
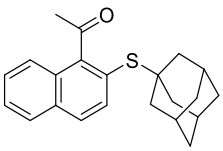


Figure S112. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3jb**.

1-(2-(((1*s*,3*s*)-Adamantan-1-yl)thio)naphthalen-1-yl)ethan-1-one (3kb):



3kb

$C_{22}H_{24}OS$ (336.49 g/mol)

Following **GP-C**, **3kb** was synthesized using 1-acetylnaphthalen-2-yl trifluoromethanesulfonate (**1k**) (318 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV) afforded **3kb** (308 mg, 915 µmol, 92%) as colorless solid.

R_f: 0.53 (*n*-hexane/EtOAc 90:10).

m. p.: 122.2 – 124.0 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.90 – 7.84 (m, 1H), 7.82 – 7.75 (m, 1H), 7.69 – 7.63 (m, 1H), 7.59 – 7.48 (m, 3H), 2.68 (s, 3H), 2.05 – 1.97 (m, 3H), 1.91 – 1.79 (m, 6H), 1.65 – 1.56 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 206.3, 147.3, 134.9, 133.3, 129.2, 128.3, 128.2, 127.4, 127.1, 124.9, 123.6, 50.6, 44.0, 36.2, 34.3, 30.3.

HR-MS (APCI): m/z calc for $[M+H]^+$ 337.16206, found 337.16259.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2901 (m), 2842 (w), 1701 (m), 1578 (w), 1496 (w), 1445 (w), 1414 (w), 1373 (w), 1343 (m), 1291 (w), 1258 (w), 1209 (m), 1172 (w), 1124 (w), 1105 (w), 1031 (m), 952 (m), 860 (w), 815 (m), 785 (w), 748 (m), 677 (m).

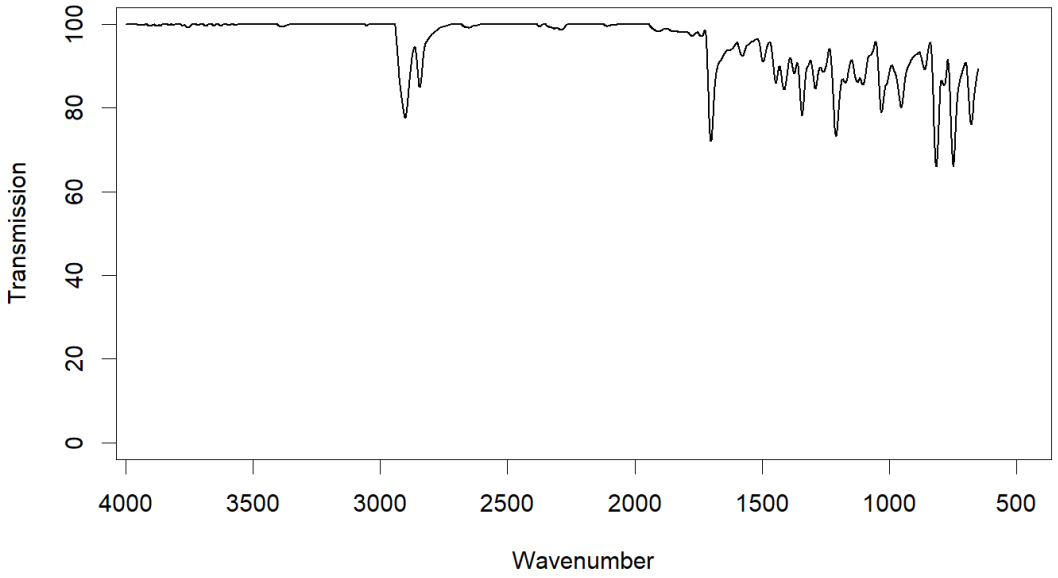


Figure S113. IR-spectrum (ATR, neat) of **3kb**.

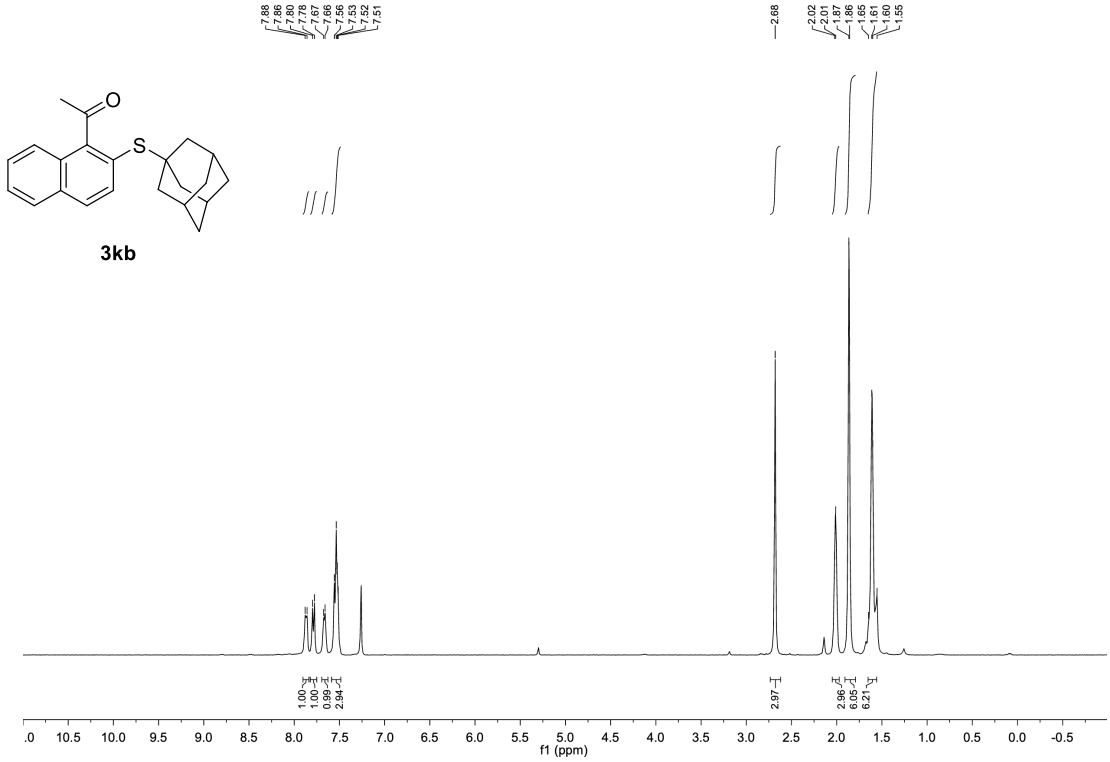


Figure S114. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3kb**.

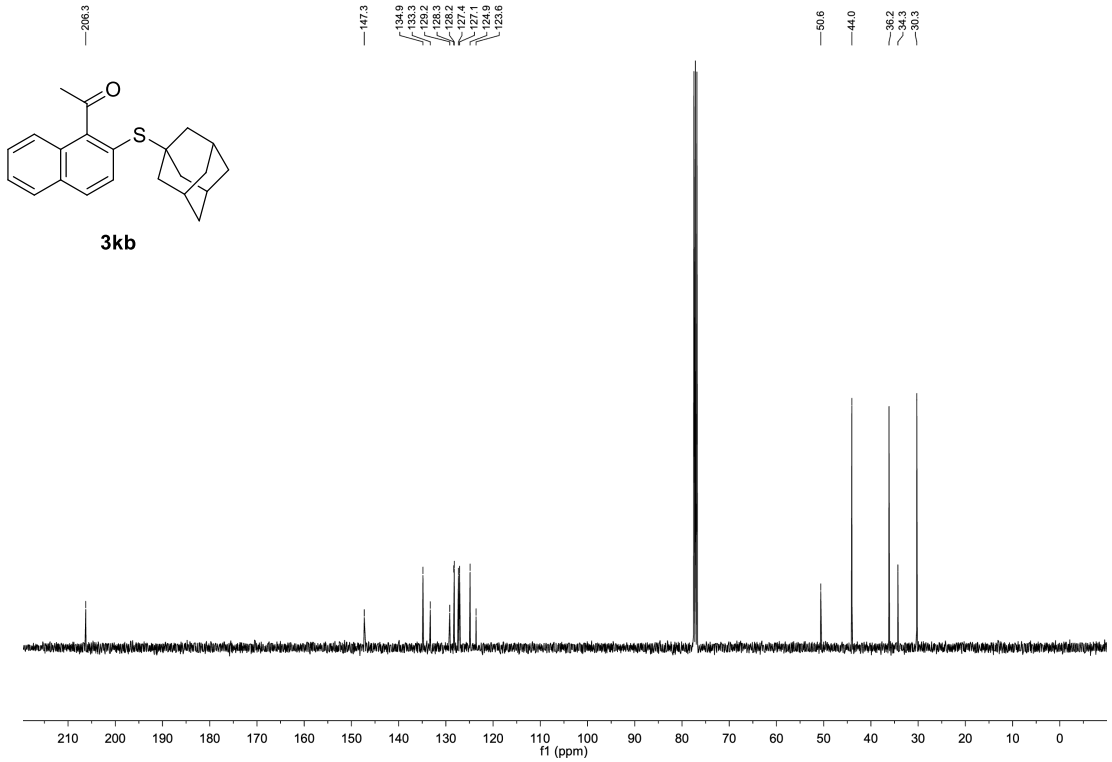
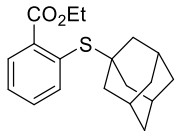


Figure S115. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3kb**.

Ethyl 2-(((1*s*,3*s*)-adamantan-1-yl)thio)benzoate (3lb):



3lb

$C_{19}H_{24}O_2S$ (316.46 g/mol)

Following **GP-C**, **3lb** was synthesized using ethyl 2-(((trifluoromethyl)sulfonyl)oxy)benzoate (**1l**) (298 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). The reaction time was prolonged to 6 h. Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV) afforded **3lb** (245 mg, 775 µmol, 78%) as colorless oil.

R_f: 0.56 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.60 – 7.51 (m, 2H), 7.41 – 7.34 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.03 – 1.96 (m, 3H), 1.82 – 1.77 (m, 6H), 1.65 – 1.55 (m, 6H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 168.8, 140.3, 139.3, 129.8, 129.4, 128.5, 128.4, 61.4, 49.5, 43.9, 36.2, 30.2, 14.4.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 339.13892, found 339.13908.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2980 (w), 2902 (s), 2849 (m), 1723 (s), 1443 (w), 1363 (w), 1285 (s), 1243 (s), 1213 (m), 1169 (w), 1109 (s), 1053 (m), 1031 (m), 975 (w), 897 (w), 852 (w), 822 (w), 736 (s), 710 (s).

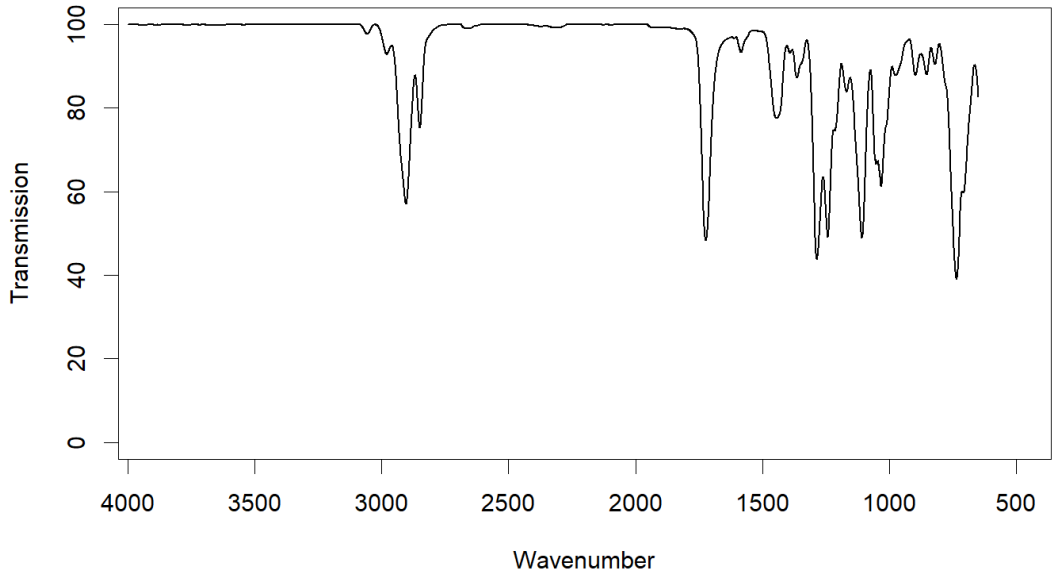


Figure S116. IR-spectrum (ATR, neat) of **3lb**.

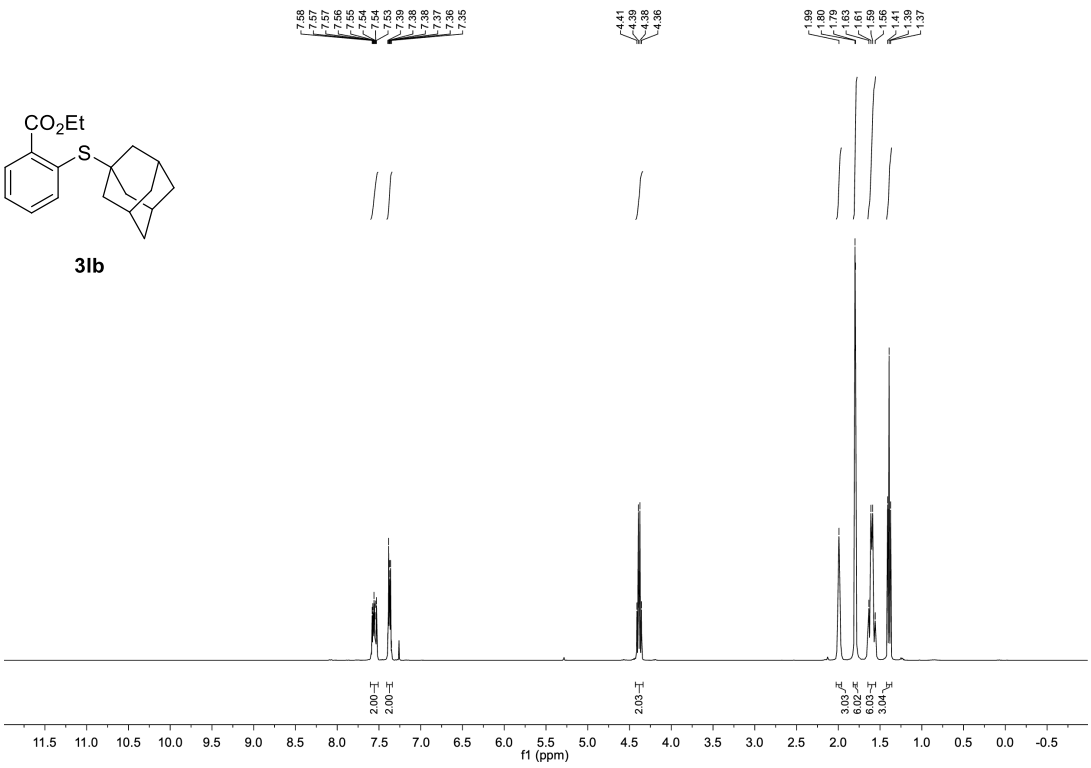


Figure S117. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3lb**.

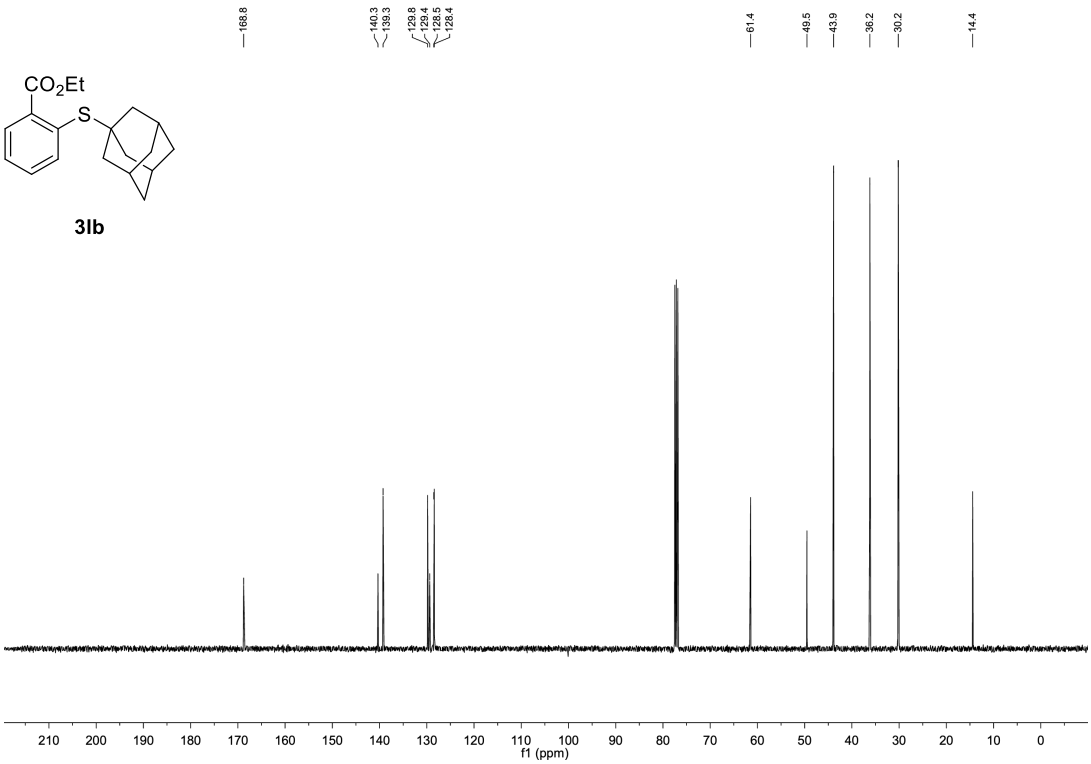
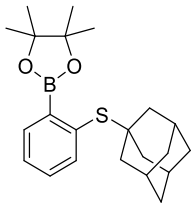


Figure S118. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3lb**.

2-(2-(((1*s*,3*s*)-Adamantan-1-yl)thio)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3mb):



3mb

$C_{22}H_{31}BO_2S$ (370.36 g/mol)

Following **GP-C**, **3mb** was synthesized using 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate (**1m**) (352 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 95:5 over 10 CV) afforded **3mb** (288 mg, 778 µmol, 78%) as colorless solid.

R_f: 0.66 (*n*-hexane/EtOAc 95:5).

m. p.: 88.8 – 89.3 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.54 – 7.47 (m, 2H), 7.35 – 7.29 (m, 2H), 2.04 – 1.97 (m, 3H), 1.86 – 1.80 (m, 6H), 1.66 – 1.56 (m, 6H), 1.40 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 138.2, 134.6, 133.4, 129.4, 127.8, 84.2, 48.5, 44.0, 36.4, 30.2, 25.1.

HR-MS (ESI): m/z calc for $[M+H]^+$ 371.22145, found 371.22178.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2980 (w), 2898 (m), 2846 (w), 1586 (w), 1474 (w), 1448 (w), 1426 (w), 1377 (w), 1343 (s), 1302 (s), 1250 (w), 1217 (w), 1146 (m), 1098 (m), 1034 (m), 963 (w), 855 (m), 822 (w), 755 (m), 670 (m).

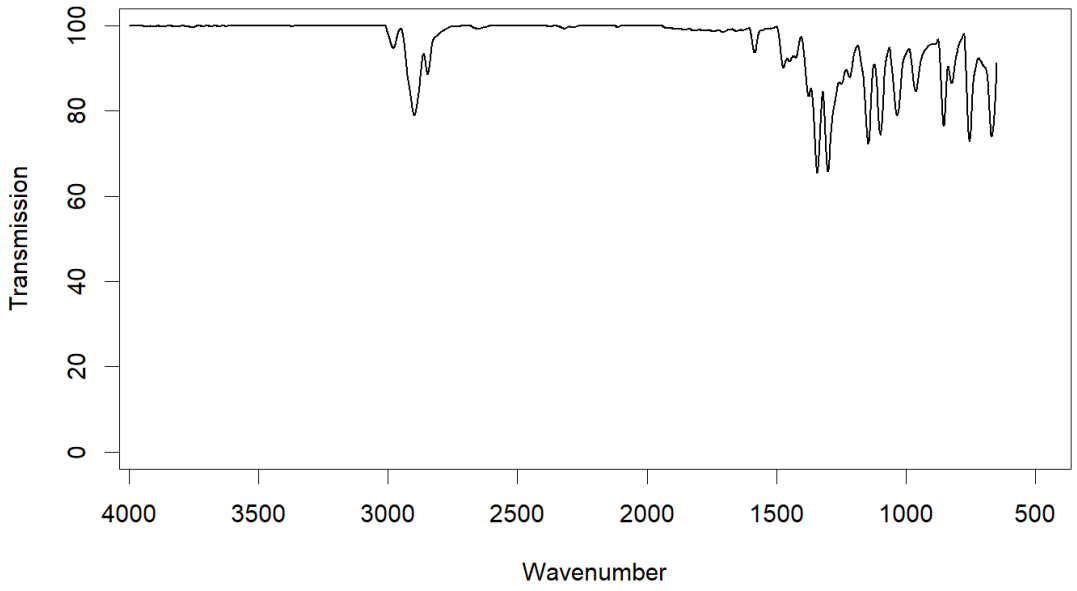


Figure S119. IR-spectrum (ATR, neat) of **3mb**.

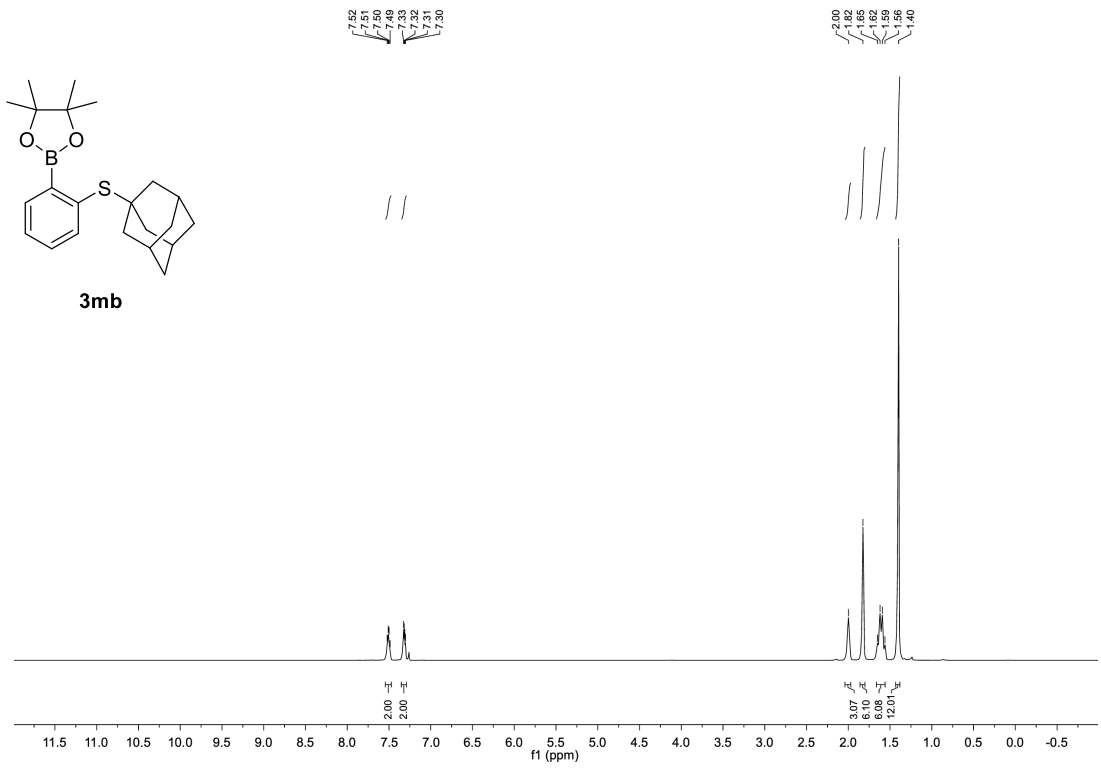


Figure S120. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3mb**.

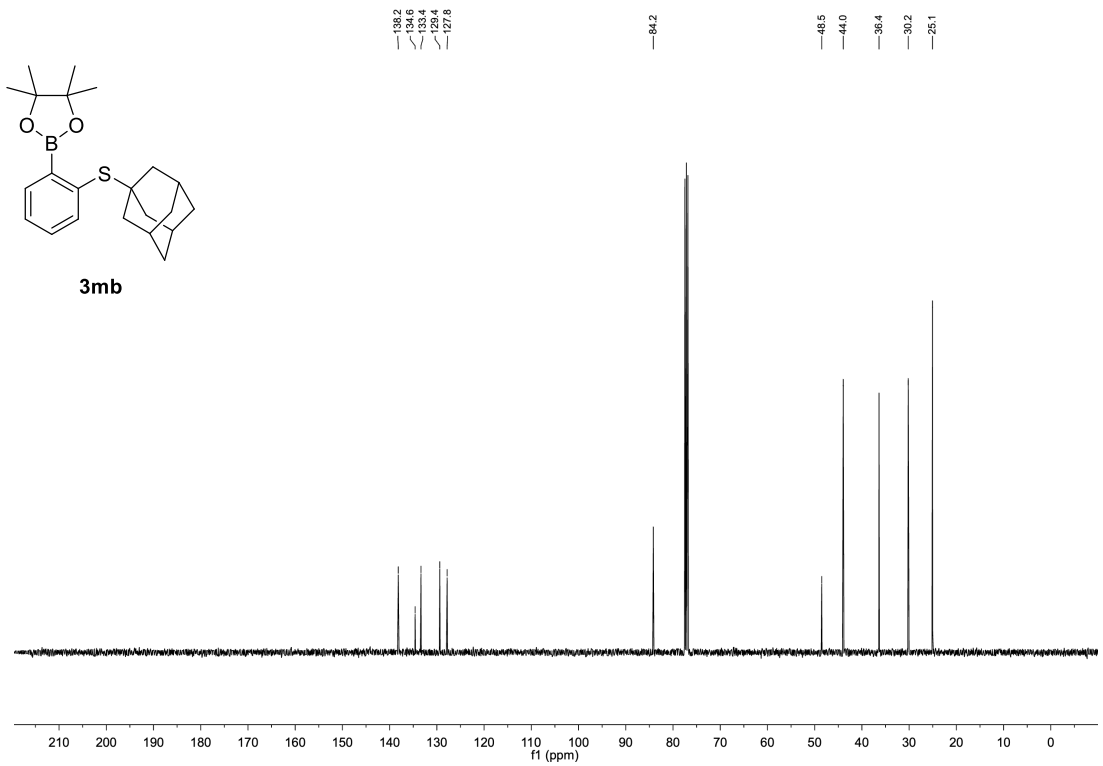
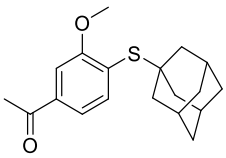


Figure S121. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3mb**.

1-(4-(((1*s*,3*s*)-Adamantan-1-yl)thio)-3-methoxyphenyl)ethan-1-one (3nb):



3nb

$C_{19}H_{24}O_2S$ (316.46 g/mol)

Following **GP-B**, **3nb** was synthesized using 4-acetyl-2-methoxyphenyl trifluoromethanesulfonate (**1n**) (298 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 80:20 over 10 CV) afforded **3nb** (310 mg, 979 µmol, 98%) as colorless solid.

R_f: 0.42 (*n*-hexane/EtOAc 90:10).

m. p.: 104.2 – 107.3 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.57 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 7.46 (dd, *J* = 7.8, 1.7 Hz, 1H), 3.92 (s, 3H), 2.61 (s, 3H), 2.03 – 1.97 (m, 3H), 1.88 – 1.83 (m, 6H), 1.67 – 1.57 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 197.8, 161.5, 139.9, 138.9, 125.8, 120.7, 109.5, 56.1, 50.2, 43.8, 36.3, 30.3, 26.8.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 339.13892, found 339.13942.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2902 (m), 2846 (w), 1679 (m), 1582 (w), 1556 (w), 1456 (m), 1392 (m), 1344 (w), 1273 (s), 1251 (m), 1217 (s), 1180 (m), 1146 (w), 1097 (w), 1057 (w), 1027 (s), 971 (m), 870 (m), 810 (m), 770 (w), 710 (m), 684 (m).

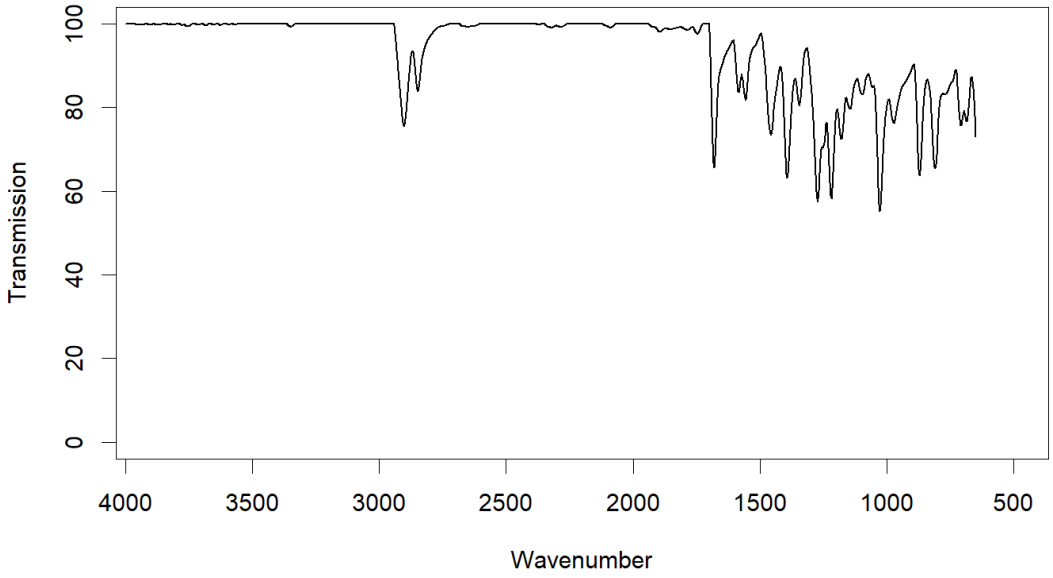


Figure S122. IR-spectrum (ATR, neat) of **3nb**.

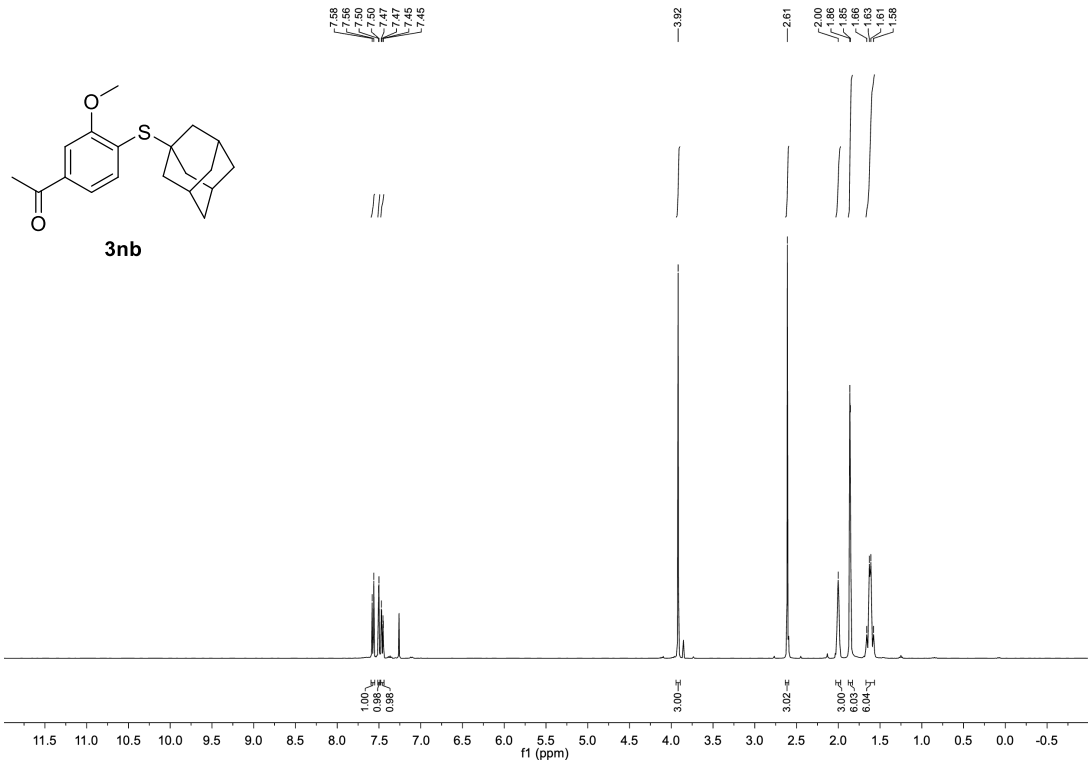


Figure S123. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3nb**.

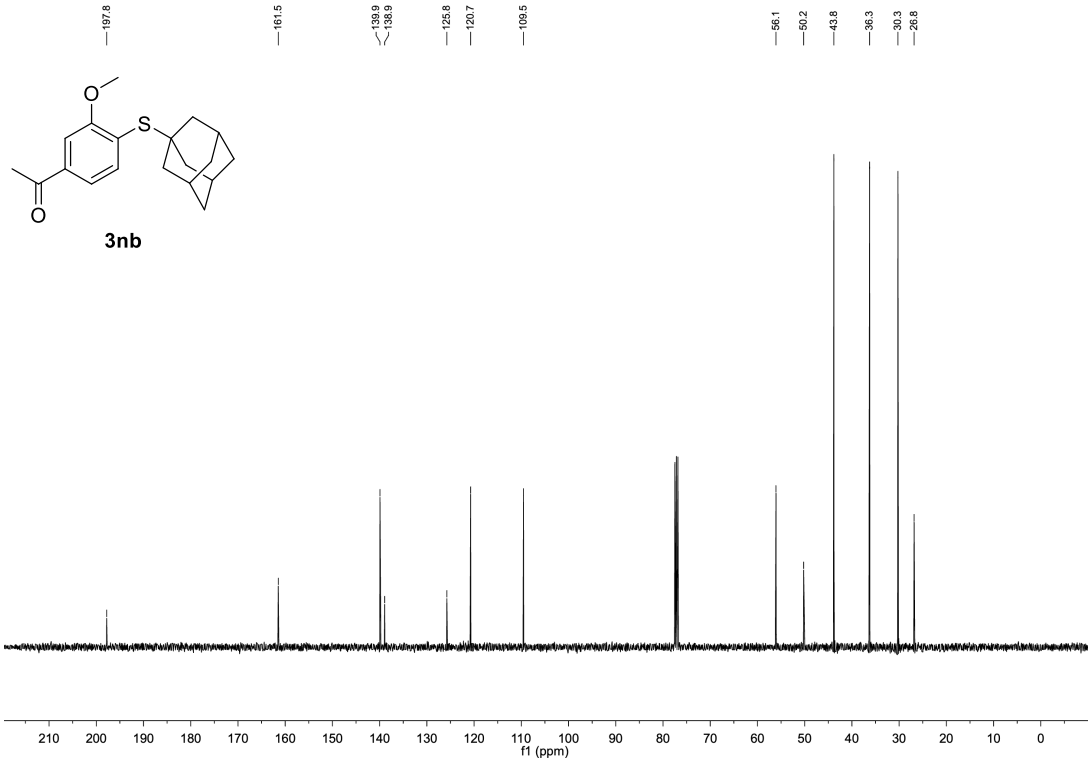
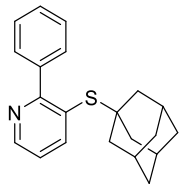


Figure S124. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3nb**.

3-(((1*s*,3*s*)-Adamantan-1-yl)thio)-2-phenylpyridine (3ob):



3ob

$C_{21}H_{23}NS$ (321.48 g/mol)

Following **GP-B**, **3ob** was synthesized using 2-phenylpyridin-3-yl trifluoromethanesulfonate (**1o**) (303 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). The reaction time was prolonged to 6 h. Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 70:30 over 10 CV) afforded a mixture of starting material and product. This mixture was dissolved in THF (10 ml) and an aqueous solution of NBu_4OH (649 mg, 40% w/w, 1 equiv.) was added and stirred for 16 h. The solution was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting yellow oil was purified by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 70:30 over 10 CV) to give **3ob** (231 mg, 720 µmol, 72%) as colorless sticky honey.

R_f: 0.36 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.65 (dd, *J* = 4.7, 1.7 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.44 – 7.34 (m, 3H), 7.21 (dd, *J* = 7.8, 4.7 Hz, 1H), 1.92 – 1.86 (m, 3H), 1.57 – 1.45 (m, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 164.7, 149.3, 147.5, 140.8, 130.7, 128.1, 127.5, 126.1, 121.6, 50.6, 43.6, 36.1, 30.0.

HR-MS (ESI): m/z calc for $[M+H]^+$ 322.16240, found 322.16298.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3032 (w), 2901 (s), 2846 (m), 1549 (w), 1448 (m), 1407 (s), 1343 (w), 1292 (m), 1258 (w), 1180 (w), 1124 (w), 1097 (w), 1028 (s), 971 (w), 915 (w), 795 (m), 740 (s), 691 (s).

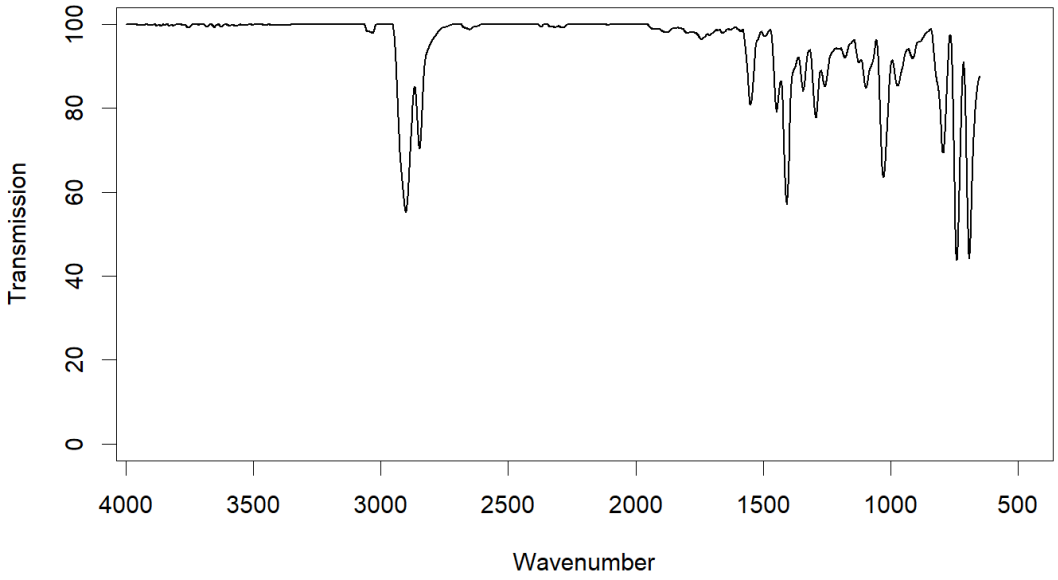


Figure S125. IR-spectrum (ATR, neat) of **3ob**.

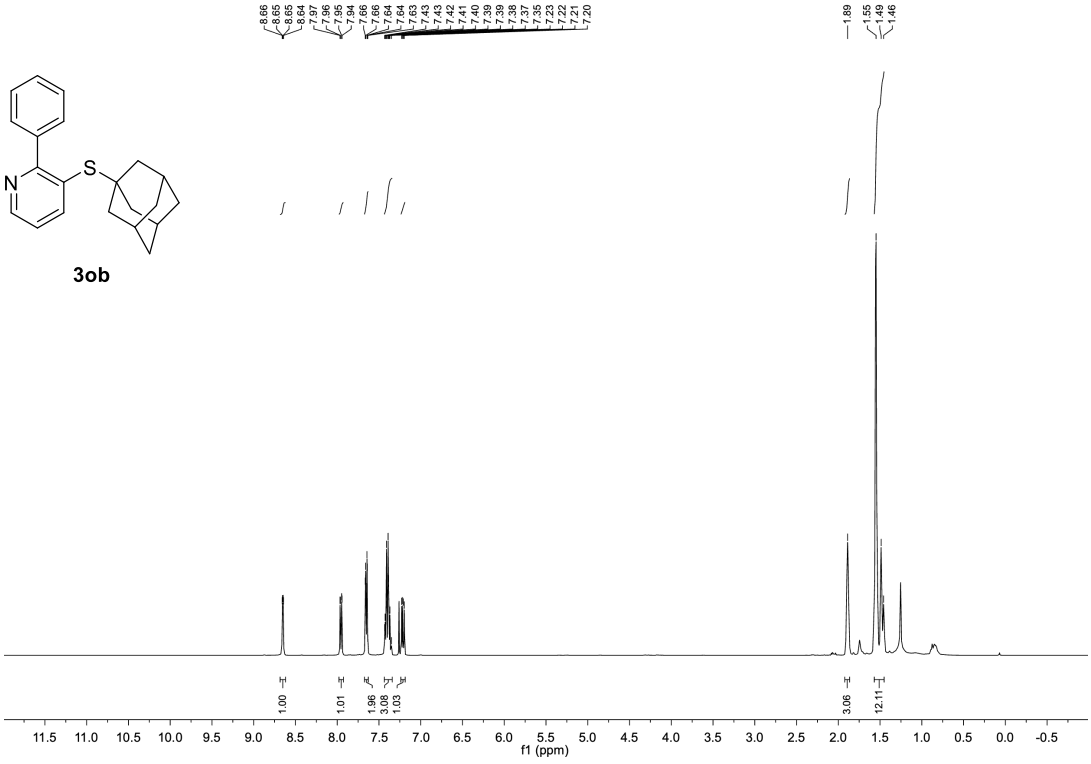


Figure S126. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3ob**.

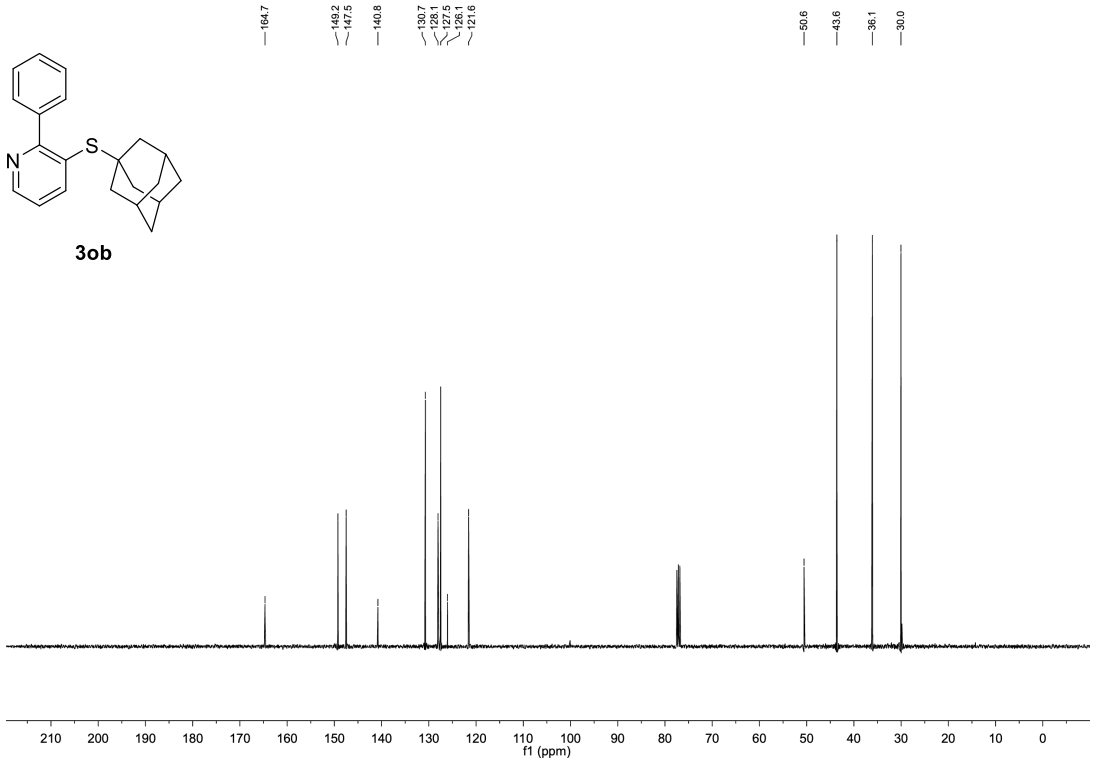
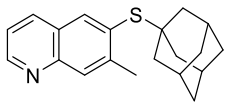


Figure S127. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3ob**.

6-(((1*s*,3*s*)-Adamantan-1-yl)thio)-7-methylquinoline (3pb):



3pb

$C_{20}H_{23}NS$ (309.47 g/mol)

Following **GP-B**, **3pb** was synthesized using 6-bromo-7-methylquinoline (**1p**) (222 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV, then to 30:70 over 8 CV) afforded **3pb** (263 mg, 850 µmol, 85%) as colorless solid.

R_f: 0.16 (*n*-hexane/EtOAc 95:5).

m. p.: 142.0 – 143.7 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.92 – 8.85 (m, 1H), 8.14 – 8.06 (m, 1H), 8.03 – 7.95 (m, 2H), 7.35 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.70 (s, 3H), 2.04 – 1.98 (m, 3H), 1.92 – 1.85 (m, 6H), 1.67 – 1.55 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 151.2, 151.2, 148.5, 145.0, 138.5, 135.7, 130.4, 129.6, 126.6, 120.7, 50.1, 43.9, 36.3, 30.2, 22.9.

HR-MS (ESI): m/z calc for $[M+H]^+$ 310.16240, found 310.16289.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2917 (m), 2887 (m), 2846 (m), 1612 (w), 1582 (w), 1556 (w), 1467 (m), 1445 (m), 1373 (w), 1337 (w), 1295 (m), 1254 (w), 1187 (w), 1105 (w), 1035 (m), 1001 (w), 971 (w), 915 (w), 878 (m), 818 (w), 796 (w), 766 (m), 681 (w).

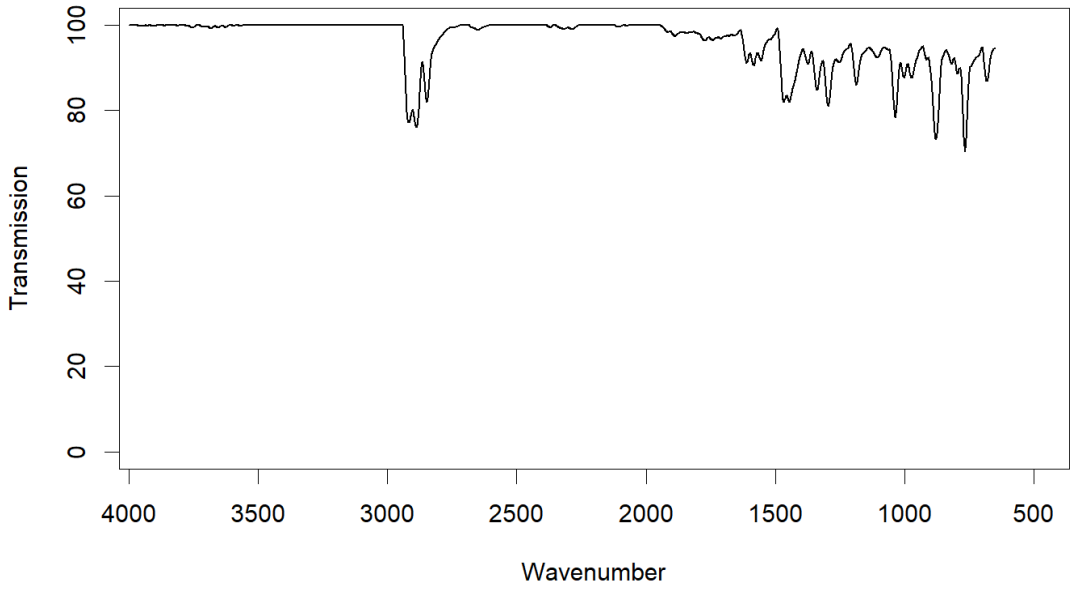


Figure S128. IR-spectrum (ATR, neat) of **3pb**.

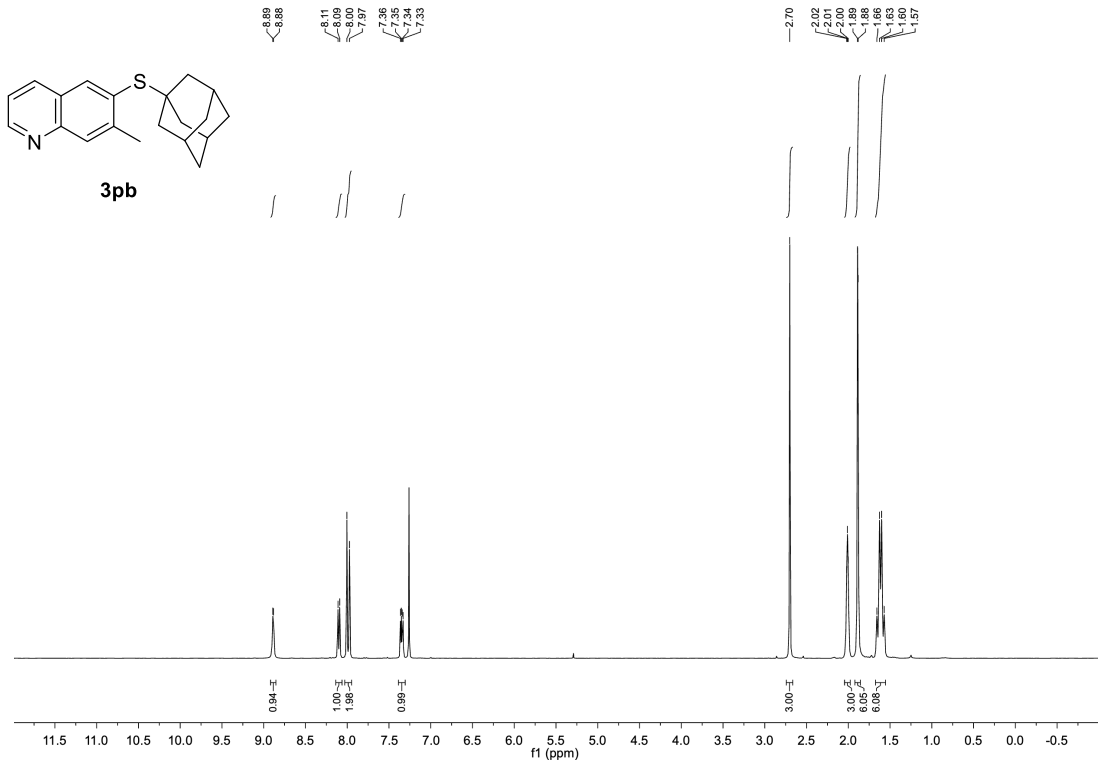


Figure S129. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3pb**.

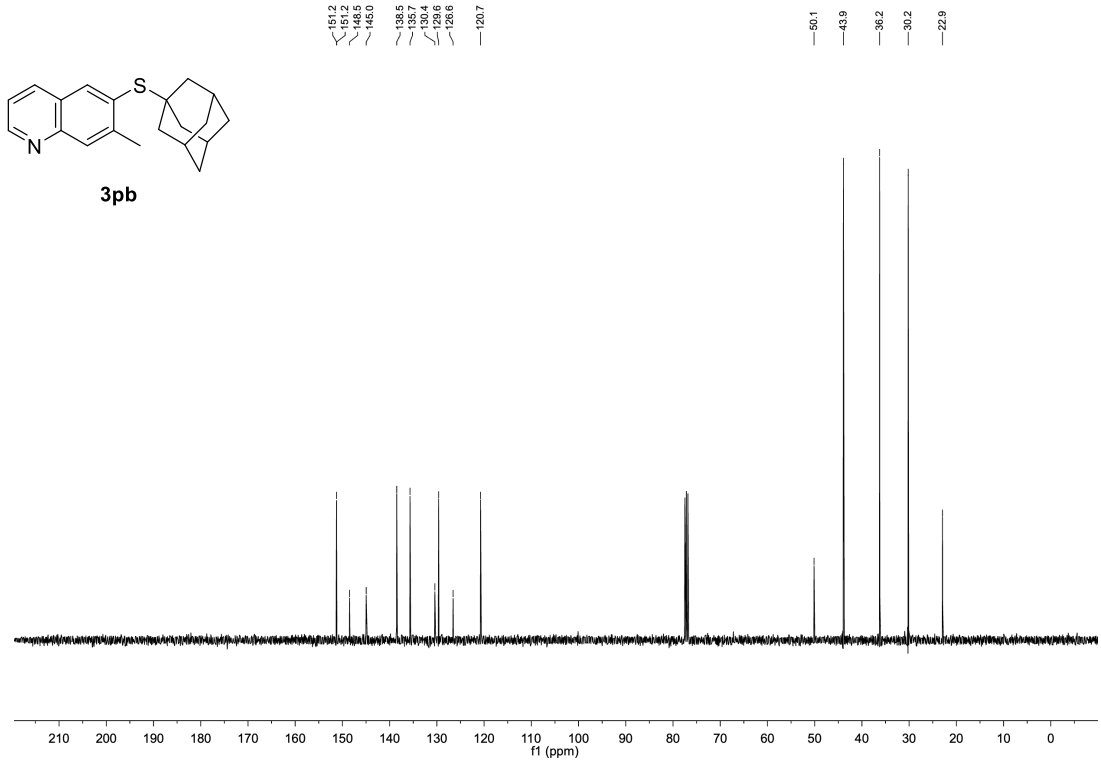
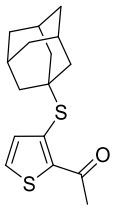


Figure S130. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3pb**.

1-(3-(((1*s*,3*s*)-Adamantan-1-yl)thio)thiophen-2-yl)ethan-1-one (3qb):



3qb

$C_{16}H_{20}OS_2$ (292.45 g/mol)

Following **GP-C**, **3qb** was synthesized using 1-(3-bromothiophen-2-yl)ethan-1-one (**1q**) (205 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). The reaction time was prolonged to 6 h. Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 85:15 over 10 CV) afforded **3qb** (246 mg, 841 µmol, 84%) as colorless solid.

R_f: 0.77 (*n*-hexane/EtOAc 90:10).

m. p.: 51.9 – 54.1 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.51 (d, *J* = 5.1 Hz, 1H), 7.13 (d, *J* = 5.1 Hz, 1H), 2.80 (s, 3H), 2.08 – 2.03 (m, 3H), 1.92 – 1.87 (m, 6H), 1.70 – 1.60 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 192.9, 146.9, 137.3, 132.4, 130.2, 51.1, 44.1, 36.2, 30.5, 30.2.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 315.08478, found 315.08507.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3110 (w), 2893 (m), 2846 (m), 1646 (s), 1522 (w), 1478 (w), 1448 (w), 1418 (w), 1385 (s), 1347 (s), 1291 (m), 1251 (s), 1180 (w), 1154 (w), 1079 (w), 1031 (s), 975 (w), 948 (m), 882 (m), 820 (m), 758 (s), 684 (m).

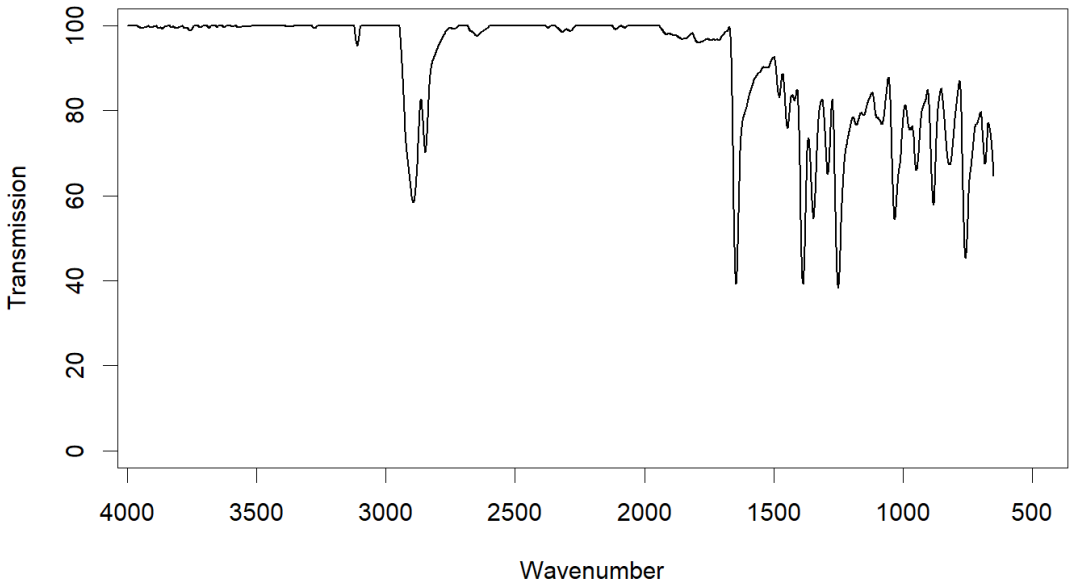


Figure S131. IR-spectrum (ATR, neat) of **3qb**.

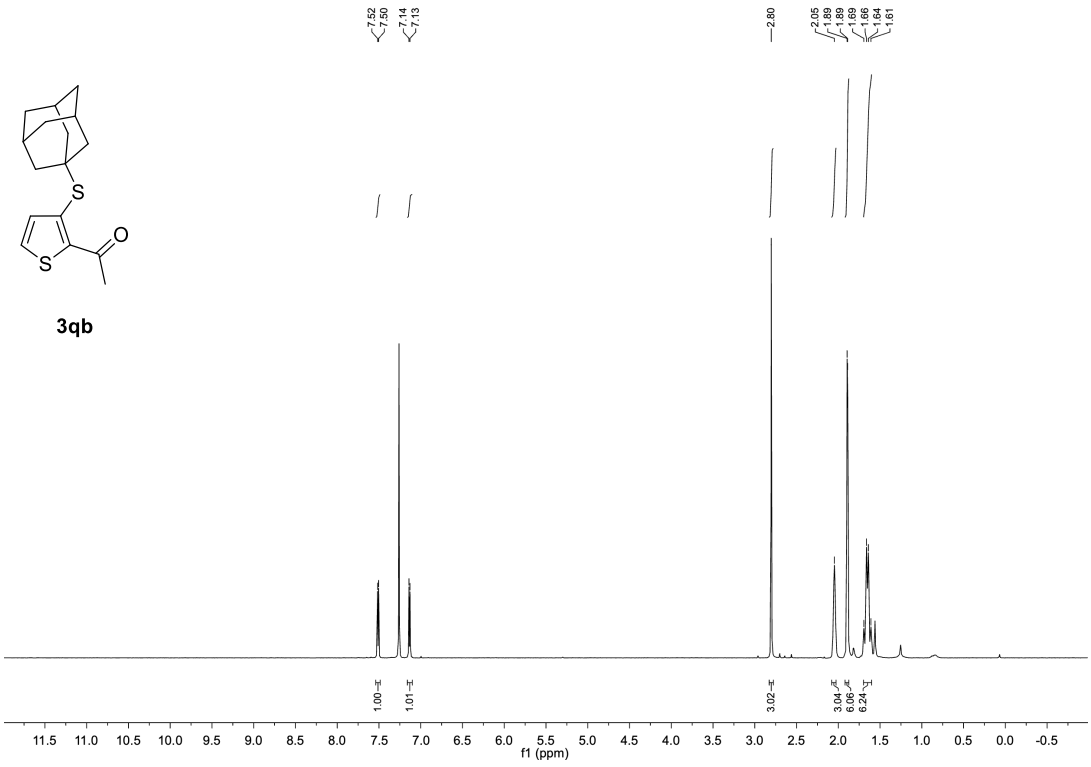


Figure S132. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3qb**.

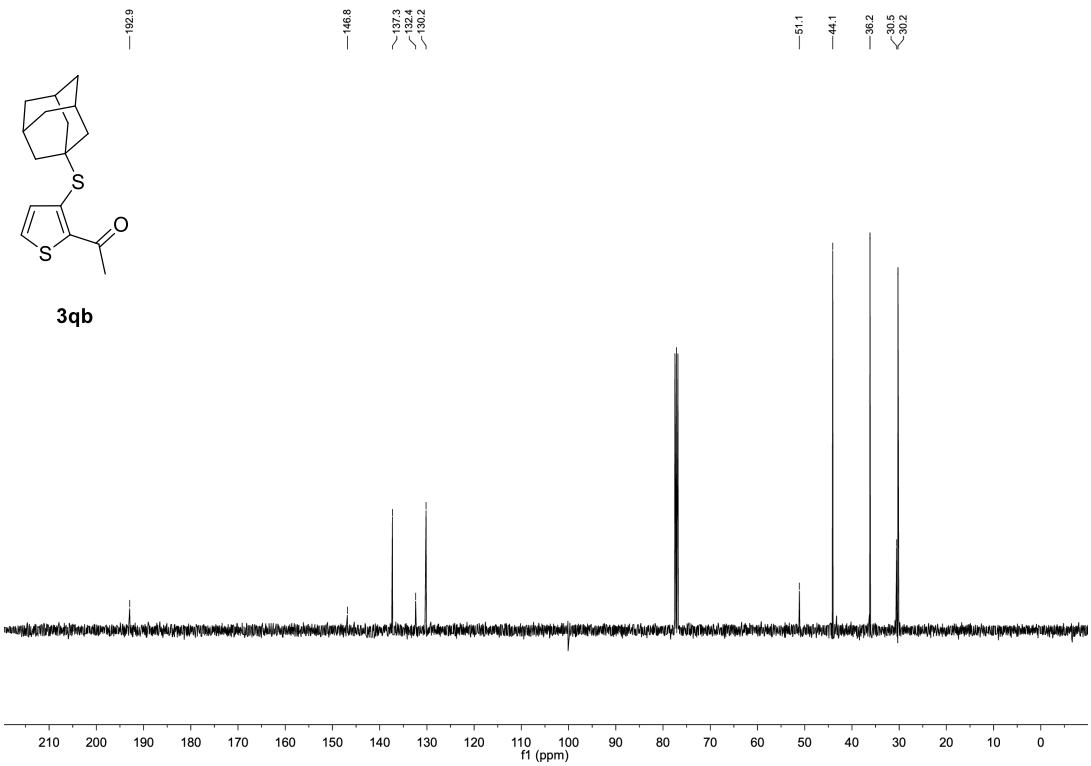
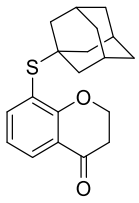


Figure S133. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3qb**.

8-(((3*s*,5*s*,7*s*)-Adamantan-1-yl)thio)chroman-4-one (3rb):



3rb

$C_{19}H_{22}O_2S$ (314.44 g/mol)

Following **GP-B**, **3rb** was synthesized using 8-bromochroman-4-one (**1r**) (227 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). The reaction temperature was set to 60 °C and the time to 6 h. Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 80:20 over 15 CV) afforded **3rb** (291 mg, 925 µmol, 93%) as colorless solid.

R_f: 0.33 (*n*-hexane/EtOAc 90:10).

m. p.: 74.7 – 78.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.92 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.9 Hz, 1H), 6.96 (dd, *J* = 7.6, 7.6 Hz, 1H), 4.57 (t, *J* = 6.5 Hz, 2H), 2.81 (t, *J* = 6.5 Hz, 2H), 2.02 – 1.96 (m, 3H), 1.85 – 1.79 (m, 6H), 1.65 – 1.55 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 191.8, 163.6, 146.6, 128.7, 121.9, 120.8, 119.7, 67.2, 49.4, 43.5, 37.5, 36.1, 30.1.

HR-MS (APCI): m/z calc for $[M+H]^+$ 315.14133, found 315.14126.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2899 (m), 2846 (w), 1686 (s), 1579 (m), 1456 (m), 1426 (m), 1374 (m), 1344 (w), 1277 (s), 1251 (m), 1213 (m), 1180 (w), 1138 (w), 1106 (w), 1068 (m), 1030 (s), 975 (w), 926 (w), 870 (w), 825 (w), 792 (m), 740 (s), 684 (m).

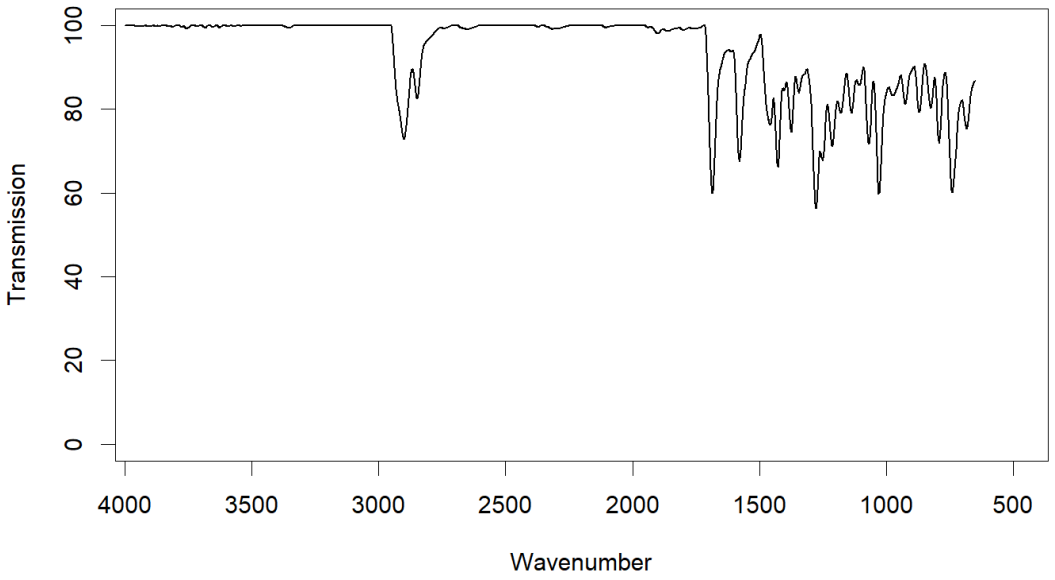


Figure S134. IR-spectrum (ATR, neat) of **3rb**.

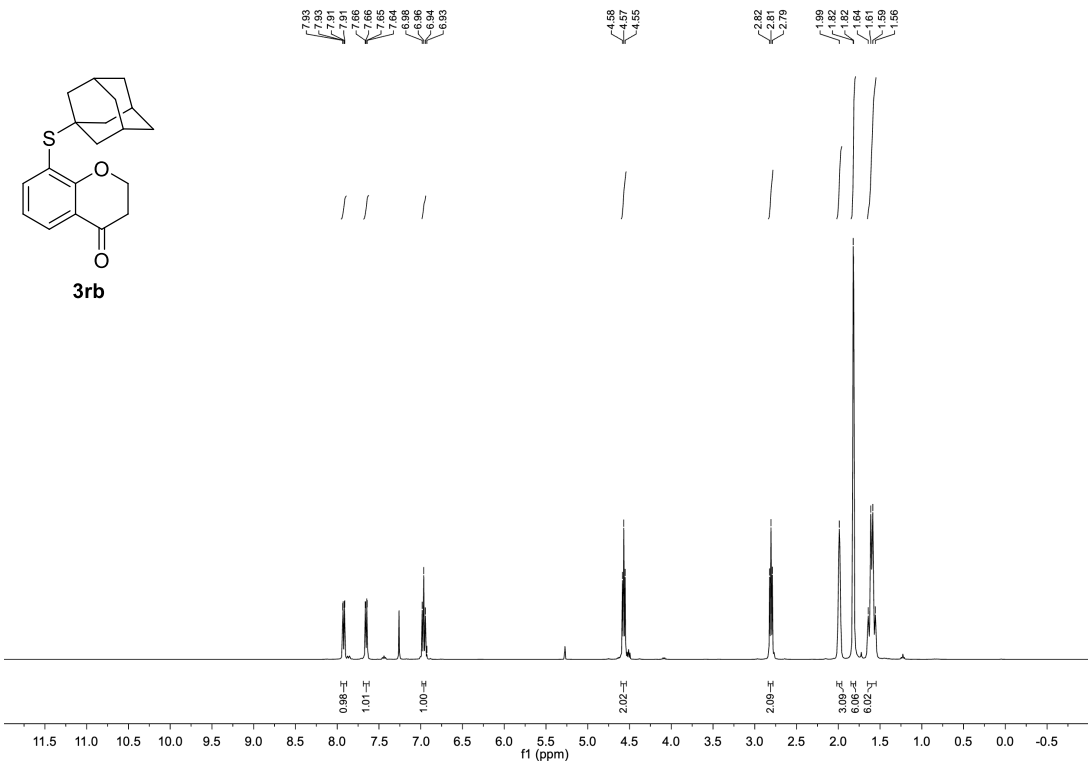


Figure S135. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3rb**.

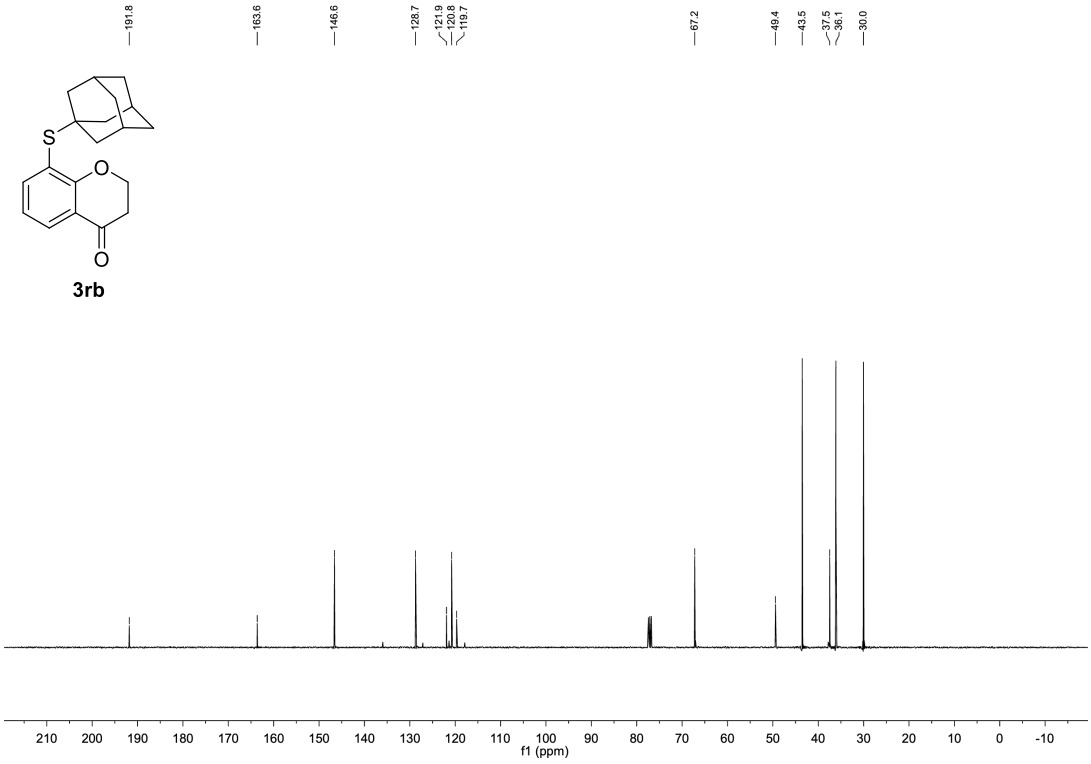
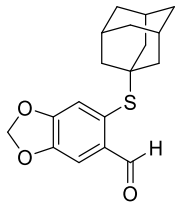


Figure S136. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3rb**.

6-(((3*s*,5*s*,7*s*)-Adamantan-1-yl)thio)benzo[d][1,3]dioxole-5-carbaldehyde (3sb):



3sb

$C_{18}H_{20}O_3S$ (316.41 g/mol)

Following **GP-C**, **3sb** was synthesized using 6-bromobenzo[d][1,3]dioxole-5-carbaldehyde (**1s**) (229 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 80:20 over 10 CV) afforded **3sb** (275 mg, 869 µmol, 87%) as colorless solid.

R_f: 0.54 (*n*-hexane/EtOAc 90:10).

m. p.: 125.8 – 126.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 10.61 (s, 1H), 7.44 (s, 1H), 6.99 (s, 1H), 6.09 (s, 2H), 2.06 – 2.00 (m, 3H), 1.81 – 1.77 (m, 6H), 1.68 – 1.57 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 192.4, 151.8, 149.4, 135.5, 130.7, 118.9, 107.3, 102.4, 49.9, 43.8, 36.2, 30.2.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 339.10254, found 339.10281.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2887 (w), 2850 (w), 1669 (m), 1604 (w), 1501 (w), 1467 (s), 1388 (m), 1337 (m), 1299 (w), 1240 (s), 1109 (m), 1030 (s), 990 (m), 926 (m), 870 (m), 821 (w), 784 (m), 725 (w), 688 (m).

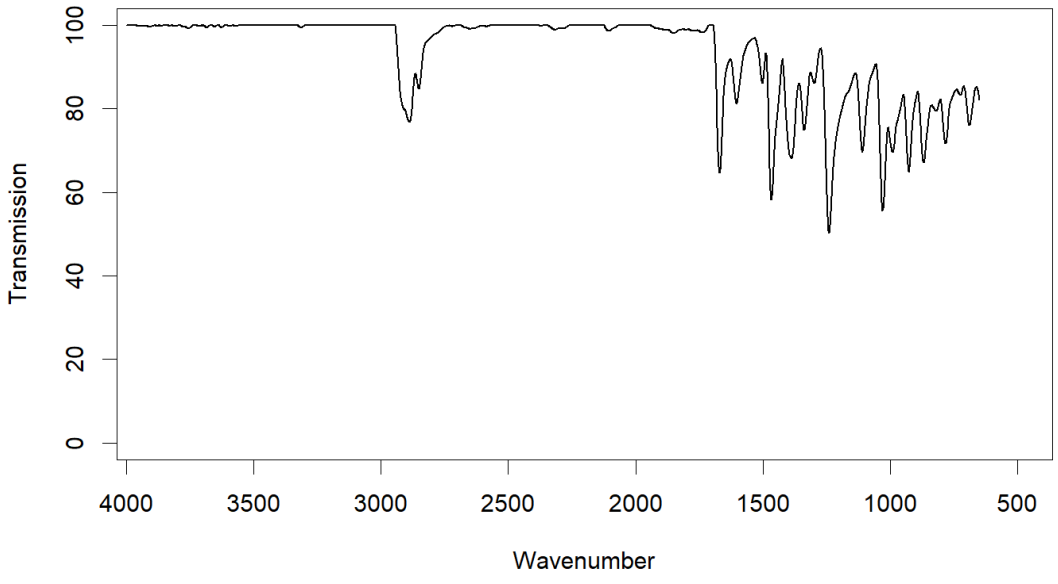


Figure S137. IR-spectrum (ATR, neat) of **3sb**.

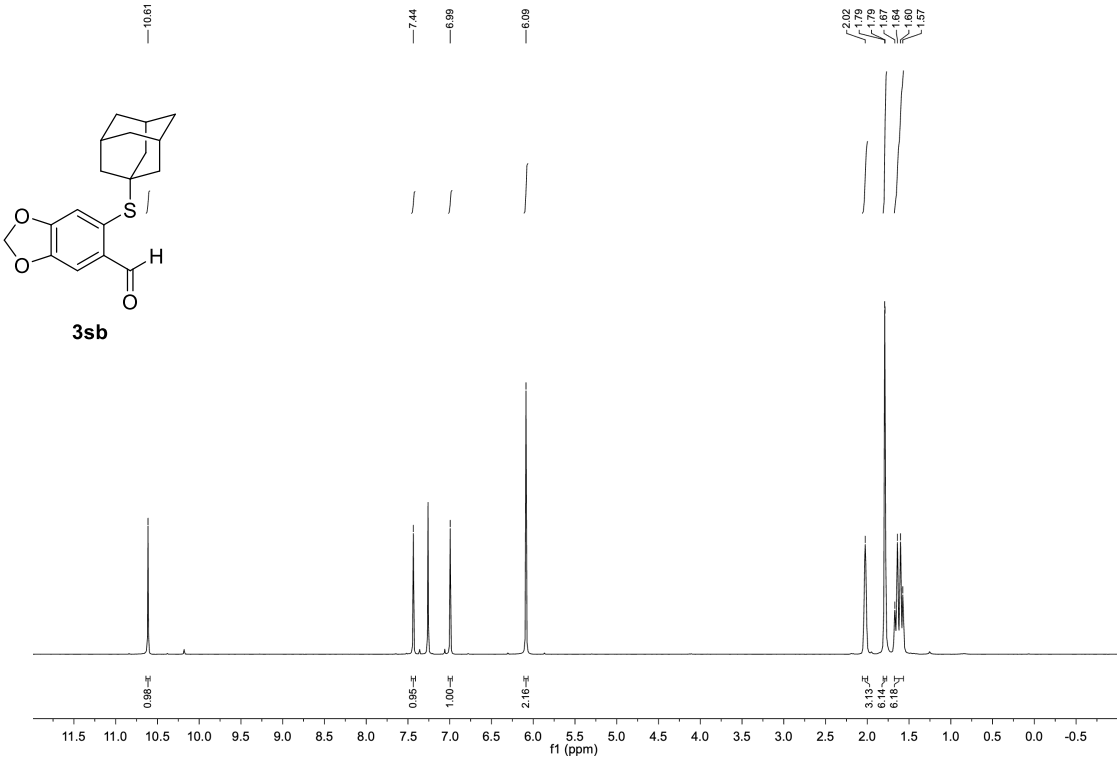


Figure S138. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3sb**.

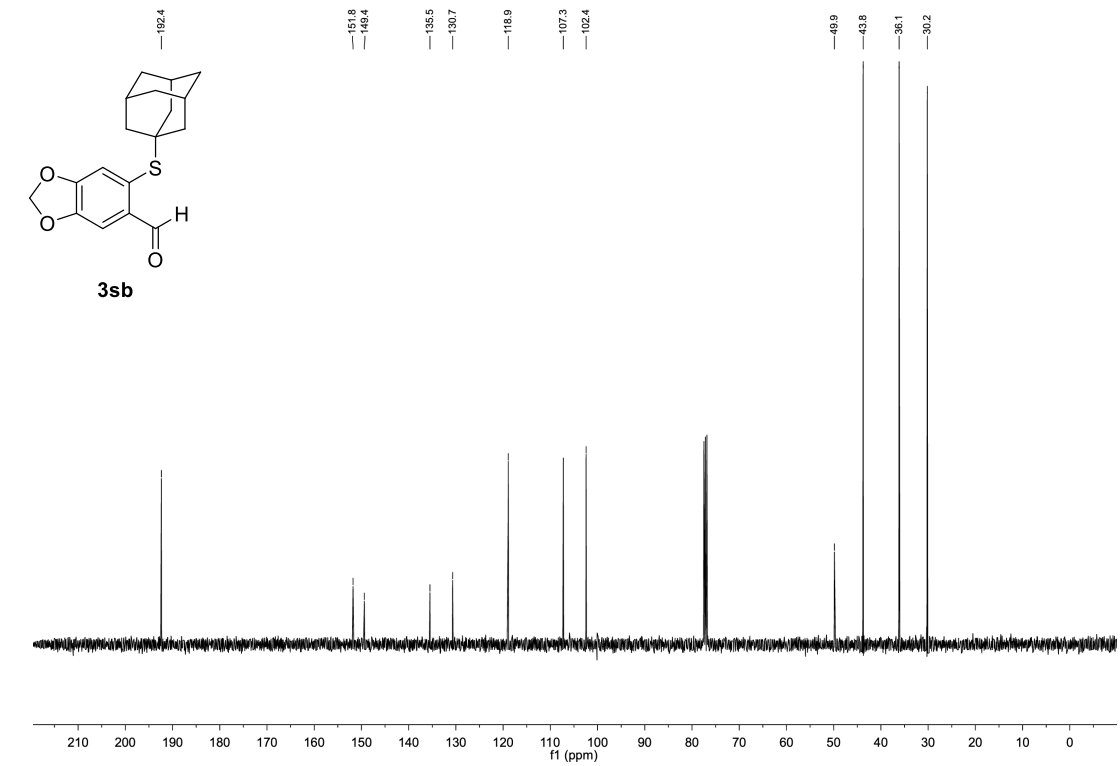
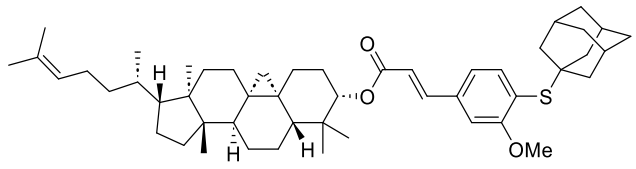


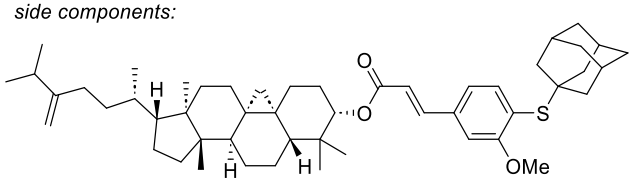
Figure S139. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3sb**.

(2a*R*,3*R*,5a*S*,5b*S*,7a*R*,9*S*,11a*R*,12a*R*)-2a,5a,8,8-Tetramethyl-3-((*S*)-6-methylhept-5-en-2-yl)tetradecahydro-1*H*,12*H*-cyclopenta[*a*]cyclopropa[*e*]phenanthren-9-yl (*E*)-3-(4-(((3*R*,5*R*,7*R*)-adamantan-1-yl)thio)-3-methoxyphenyl)acrylate (3vb):

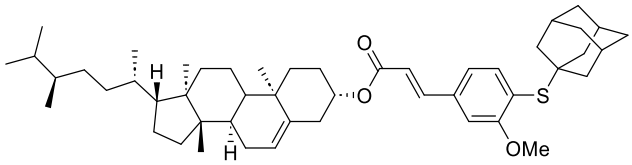


3vb

side components:



from Oryzanol C



from Campesteryl ferulate

$C_{50}H_{72}O_3S$ (753.18 g/mol)

Following **GP-B**, **3vb** was synthesized using *γ*-Oryzanol trifluoromethanesulfonate (**1v**) (360 mg, 500 µmol, 1.0 equiv.; *γ*-Oryzanol was purchased from TCI and the mixture contained Oryzanol A, Oryzanol C and Campesteryl ferulate as main components)[16] and 1-adamantane thiol (**2b**) (88.4 mg, 525 µmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 85:15 over 10 CV) afforded **3vb** (328 mg, 436 µmol, 87%; mixture according to starting material) as colorless solid.

R_f: 0.33 (*n*-hexane/EtOAc 95:5).

m. p.: 157.3 – 159.1 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.64 (d, *J* = 16.0 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.00 (m, 2H), 6.52 – 6.39 (m, 1H), 4.81 – 4.61 (m, 2H), 3.89 (s, 3H), 2.45 – 2.16 (m, 1H), 2.03 – 1.95 (m, 4H), 1.94 – 1.79 (m, 9H), 1.70 – 1.50 (m, 16H), 1.48 – 1.25 (m, 8H), 1.19 – 1.08 (m, 3H), 1.06 – 1.01 (m, 4H), 1.00 – 0.95 (m, 5H), 0.95 – 0.76 (m, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 166.7, 161.7, 157.0, 143.8, 140.7, 137.0, 125.4, 121.7, 120.3, 119.9, 110.0, 106.1, 81.0, 56.0, 52.4, 49.9, 49.0, 48.0, 47.4, 45.4, 43.8, 39.9, 36.3, 35.7, 34.0, 33.0, 31.8, 31.5, 30.3, 29.9, 28.3, 27.1, 26.7, 26.1, 26.0, 25.6, 22.2, 22.0, 21.1, 20.3, 19.5, 18.5, 18.1, 15.5.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 775.50944, found 775.50900.

For the thioether corresponding to Oryzanol C: m/z calc for $[M+Na]^+$ 789.52509, found 789.52471.

For the thioether corresponding to Campesteryl ferulate: m/z calc for $[M+Na]^+$ 749.49379, found 749.49305.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2902 (m), 2859 (w), 1709 (m), 1634 (w), 1589 (w), 1552 (w), 1456 (w), 1400 (w), 1374 (w), 1305 (m), 1239 (m), 1161 (s), 1098 (w), 1068 (w), 1034 (m), 978 (m), 930 (w), 885 (w), 841 (w), 818 (m), 713 (w), 675 (w).

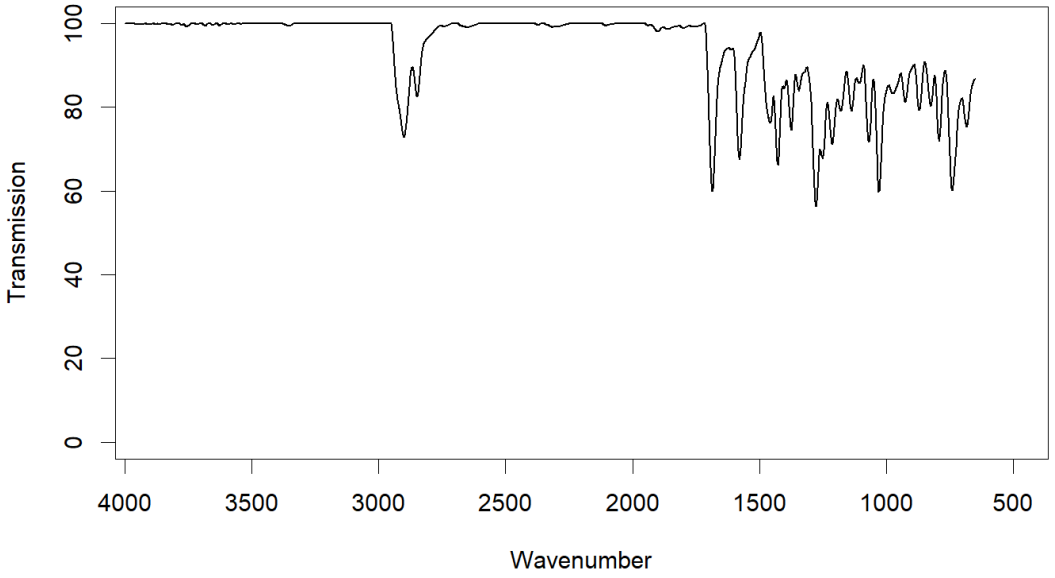


Figure S140. IR-spectrum (ATR, neat) of **3vb**.

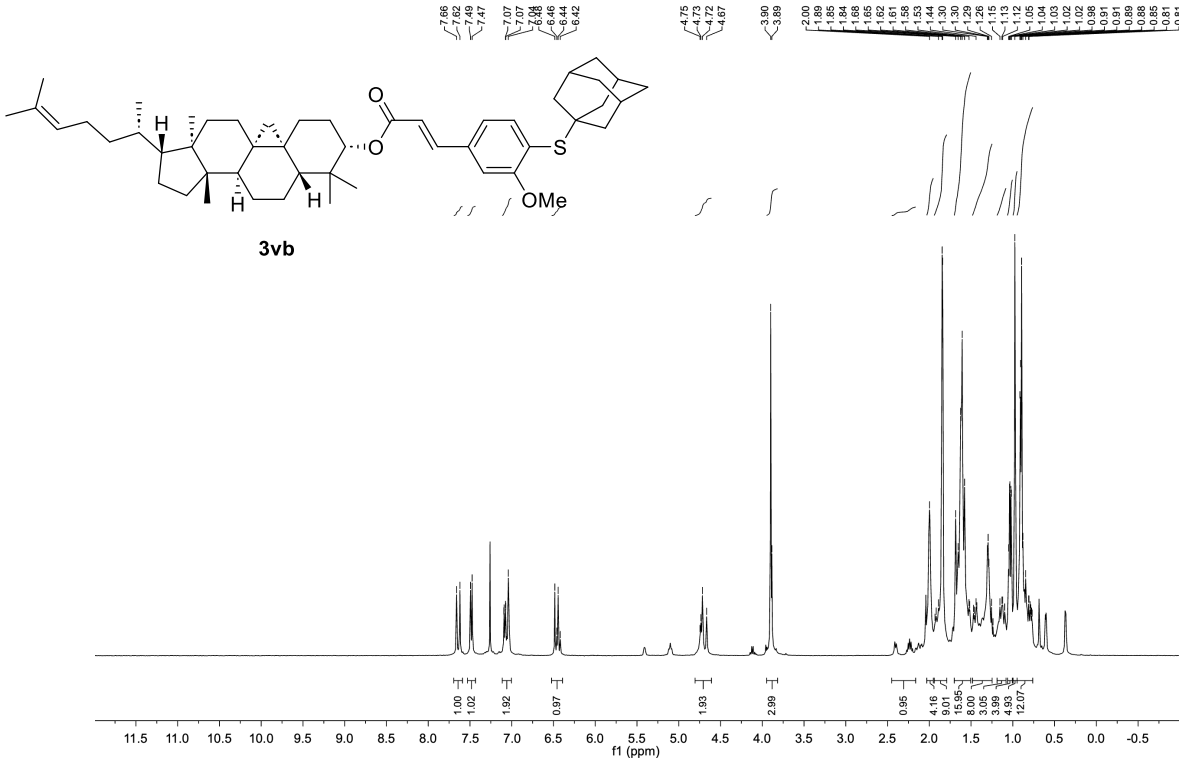


Figure S141. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3vb**.

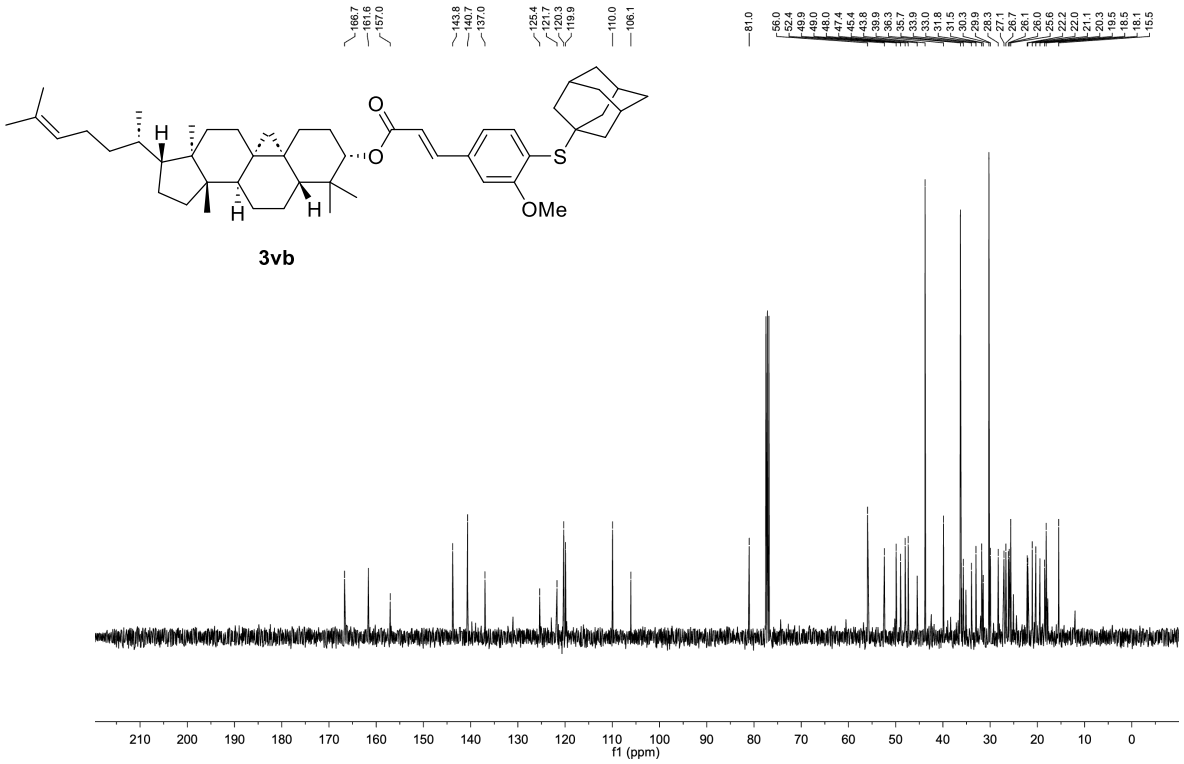
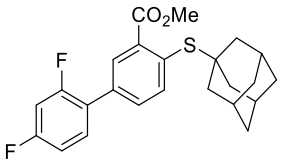


Figure S142. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3vb**.

Methyl 4-(((1*s*,3*s*)-adamantan-1-yl)thio)-2',4'-difluoro-[1,1'-biphenyl]-3-carboxylate (3wb):



3wb

$C_{24}H_{24}F_2O_2S$ (414.51 g/mol)

Following **GP-C**, **3wb** was synthesized using methyl 2',4'-difluoro-4-(((trifluoromethyl)sulfonyl)oxy)-[1,1'-biphenyl]-3-carboxylate (**1w**) (198 mg, 500 µmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (88.4 mg, 525 µmol, 1.05 equiv.). The reaction time was prolonged to 6 h. Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV) afforded a mixture of starting material and product. This mixture was dissolved in THF (10 ml) and an aqueous solution of NBu_4OH (324 mg, 40% w/w, 1 equiv.) was added and stirred for 16 h. The solution was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting oil was purified by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV) to give **3wb** (138 mg, 333 µmol, 67%) as colorless sticky oil.

R_f: 0.58 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.72 – 7.68 (m, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.54 (dt, *J* = 8.1, 1.9 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.00 – 6.89 (m, 2H), 3.93 (s, 3H), 2.07 – 1.97 (m, 3H), 1.90 – 1.78 (m, 6H), 1.68 – 1.56 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 168.9, 162.8 (dd, *J* = 250.3, 11.8 Hz), 159.9 (dd, *J* = 251.8, 11.7 Hz), 140.0, 139.3, 135.3, 131.5 (dd, *J* = 9.6, 4.5 Hz), 130.3 (d, *J* = 3.3 Hz), 129.3, 128.9 (d, *J* = 3.1 Hz), 123.8 (m), 112.0 (dd, *J* = 21.2, 3.9 Hz), 104.7 (dd, *J* = 25.9, 25.9 Hz), 52.5, 50.0, 43.9, 36.2, 30.3.

^{19}F-NMR (376 MHz, $CDCl_3$, δ): -110.0 (m), -112.9 (m).

HR-MS (ESI): m/z calc for $[M+Na]^+$ 437.13573, found 437.13642.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2902 (m), 2849 (w), 1729 (s), 1612 (w), 1597 (w), 1504 (m), 1459 (m), 1433 (m), 1385 (w), 1344 (w), 1307 (m), 1265 (s), 1221 (s), 1133 (m), 1102 (s), 1053 (m), 1034 (m), 967 (s), 904 (w), 848 (s), 811 (s), 774 (m), 732 (m), 675 (w).

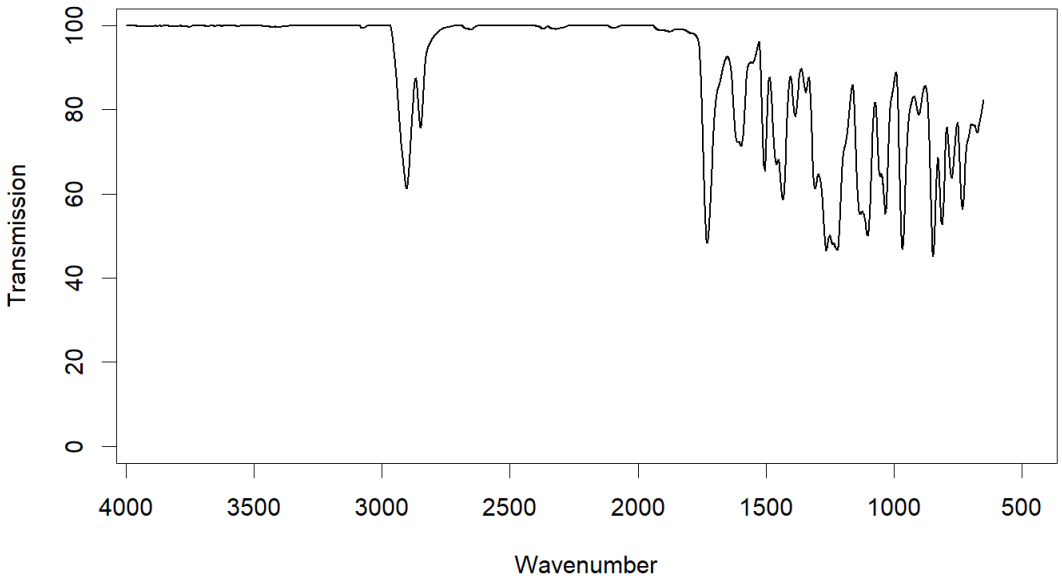


Figure S143. IR-spectrum (ATR, neat) of **3wb**.

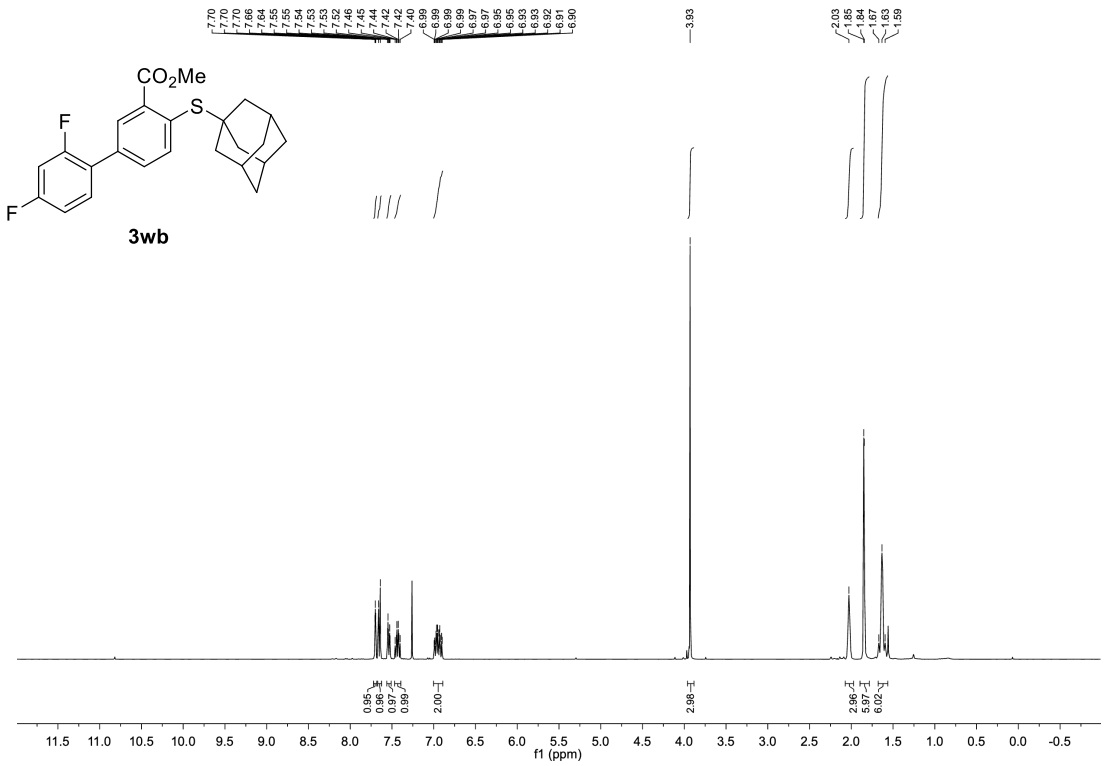


Figure S144. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3wb**.

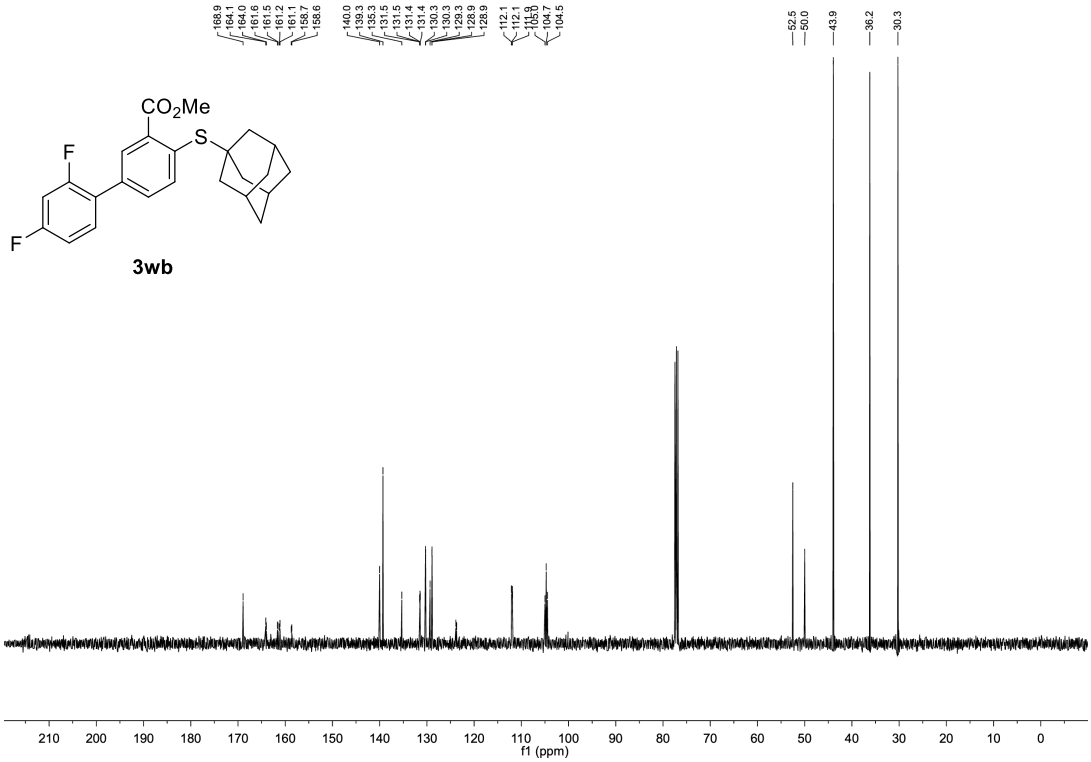


Figure S145. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3wb**.

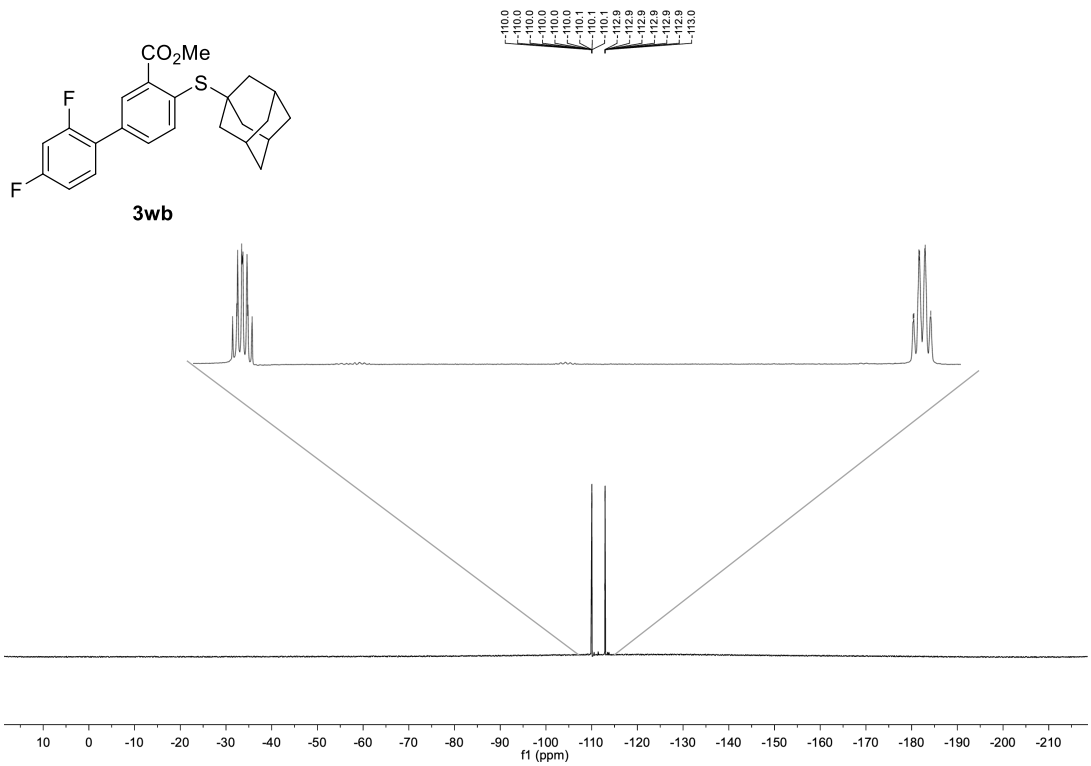
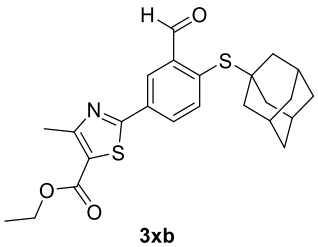


Figure S146. ^{19}F-NMR-spectrum (376 MHz, $CDCl_3$) of **3wb**.

Ethyl 2-(4-(((1*s*,3*s*)-adamantan-1-yl)thio)-3-formylphenyl)-4-methylthiazole-5-carboxylate (3xb):



3xb

$C_{24}H_{27}NO_3S_2$ (441.60 g/mol)

Following **GP-C**, **3xb** was synthesized using ethyl 2-(3-formyl-4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-4-methylthiazole-5-carboxylate (**1x**) (423 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV) afforded **3xb** (250 mg, 566 µmol, 57%) as colorless solid.

R_f: 0.56 (*n*-hexane/EtOAc 90:10).

m.p.: 155.1 – 156.1 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 10.81 (s, 1H), 8.47 (d, *J* = 2.2 Hz, 1H), 8.19 (dd, *J* = 8.0, 2.2 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.79 (s, 3H), 2.06 – 1.99 (m, 3H), 1.86 – 1.78 (m, 6H), 1.68 – 1.54 (m, 6H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 192.9, 167.8, 162.2, 161.4, 141.0, 140.3, 137.6, 134.1, 130.7, 126.3, 123.1, 61.6, 50.9, 43.9, 36.1, 30.2, 17.6, 14.5.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 464.13246, found 464.13258.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2908 (w), 2850 (w), 1705 (m), 1683 (m), 1589 (w), 1515 (w), 1470 (w), 1437 (w), 1363 (m), 1314 (w), 1251 (s), 1169 (w), 1090 (s), 1030 (m), 1012 (m), 982 (w), 969 (w), 889 (w), 856 (m), 818 (w), 758 (m), 729 (m), 684 (w).

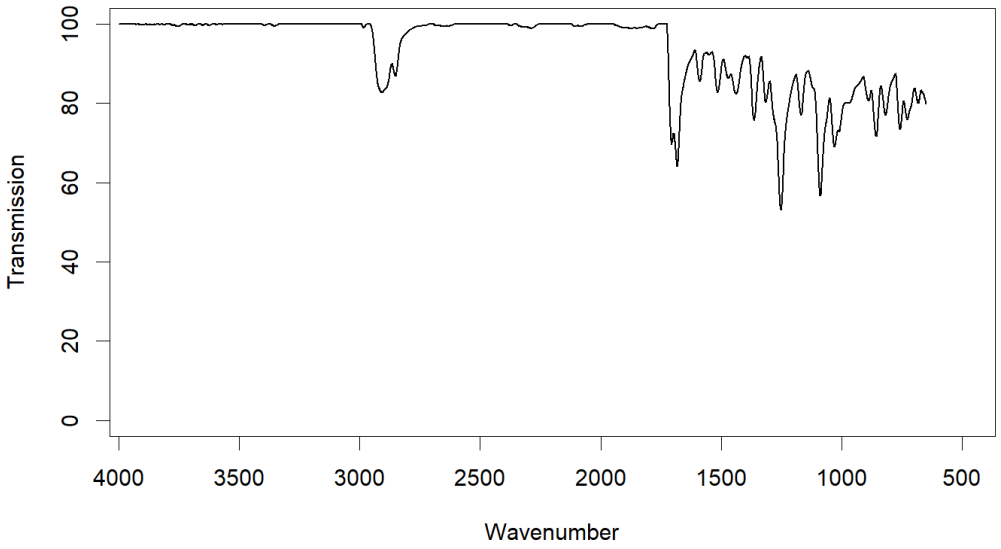


Figure S147. IR-spectrum (ATR, neat) of **3xb**.

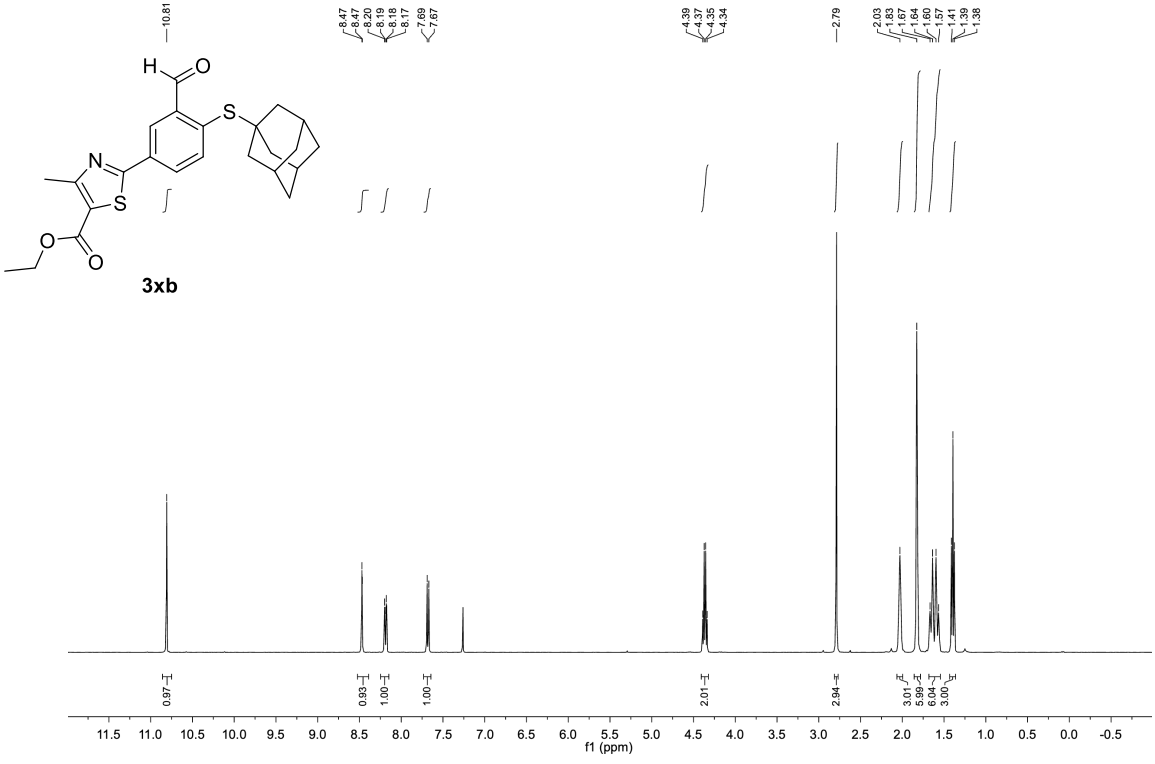


Figure S148. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3xb**.

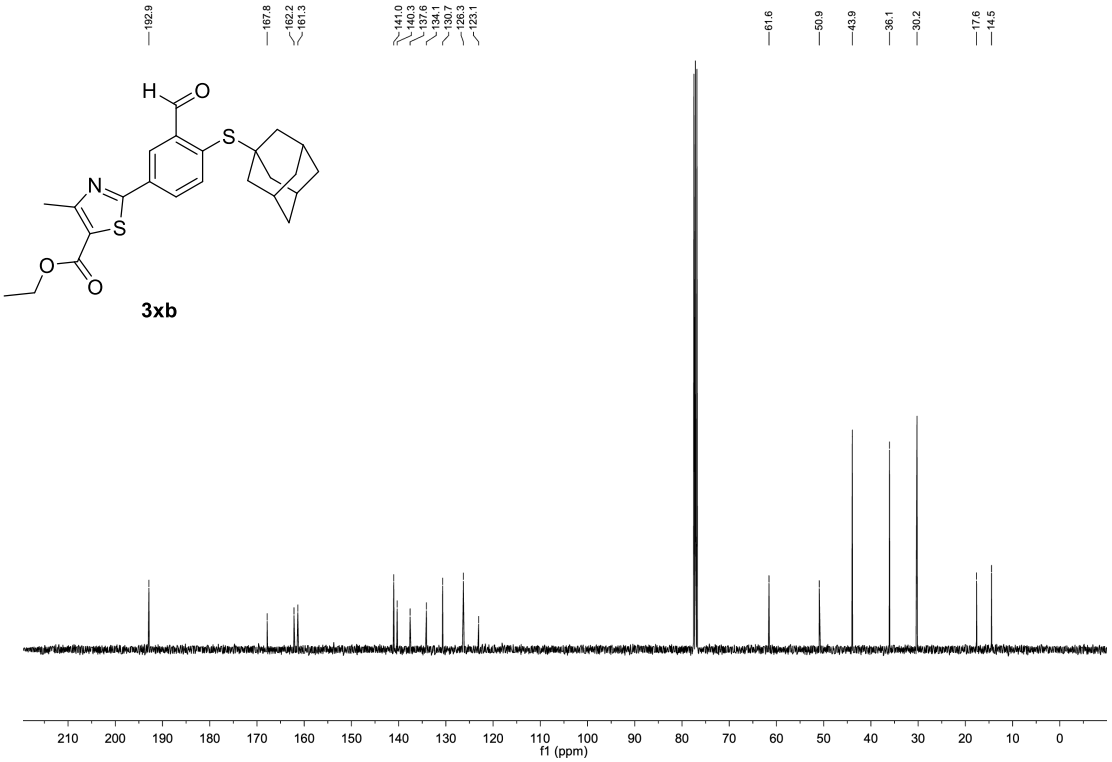
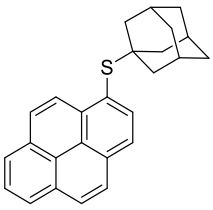


Figure S149. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3xb**.

((3*s*,5*s*,7*s*)-Adamantan-1-yl)(pyren-1-yl)sulfane (3yb):



3yb

$C_{26}H_{24}S$ (368.54 g/mol)

Following **GP-B**, **3yb** was synthesized using pyren-1-yl trifluoromethanesulfonate (**1y**) (350 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV) afforded **3yb** (208 mg, 564 µmol, 56%) as pale yellow solid.

R_f: 0.72 (*n*-hexane/EtOAc 95:5).

m. p.: 140.7 – 143.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 9.06 (d, *J* = 8.9 Hz, 1H), 8.27 – 8.03 (m, 8H), 2.02 – 1.90 (m, 9H), 1.64 – 1.54 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 137.0, 135.8, 132.0, 131.2, 131.0, 128.3, 127.7, 127.3, 127.0, 126.13, 126.08, 125.44, 125.40, 125.2, 124.4, 124.1, 50.4, 44.0, 36.2, 30.1.

HR-MS (APCI): m/z calc for $[M+H]^+$ 369.16715, found 369.16725.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3040 (w), 2898 (m), 2845 (w), 1895 (w), 1773 (w), 1746 (w), 1661 (w), 1630 (w), 1587 (w), 1482 (w), 1448 (w), 1422 (m), 1340 (w), 1292 (w), 1243 (w), 1212 (m), 1183 (w), 1138 (w), 1094 (w), 1035 (w), 967 (w), 907 (w), 833 (s), 743 (w), 707 (m), 677 (m).

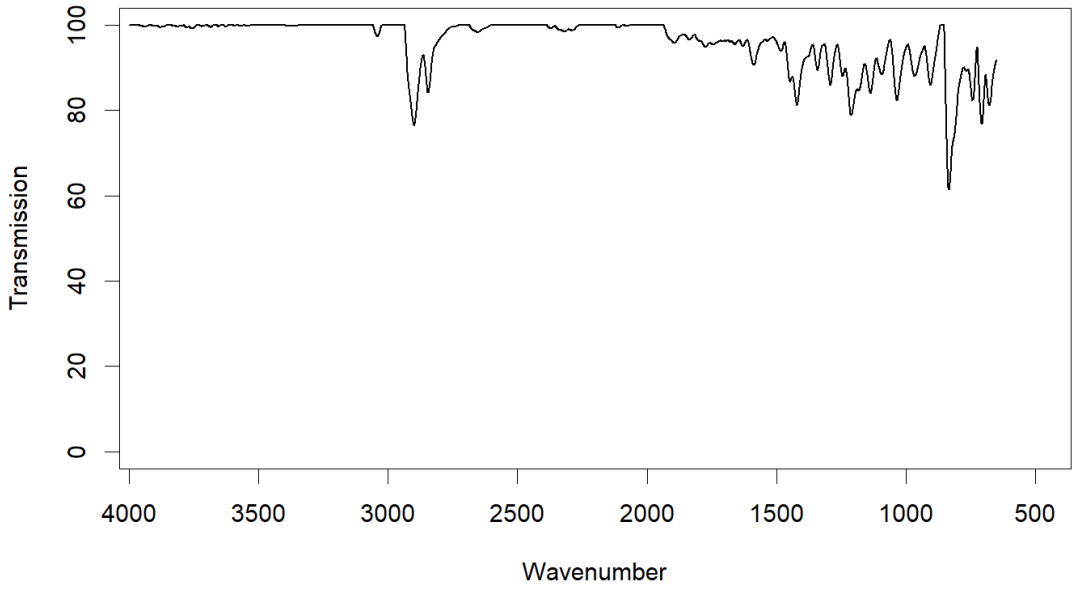


Figure S150. IR-spectrum (ATR, neat) of **3yb**.

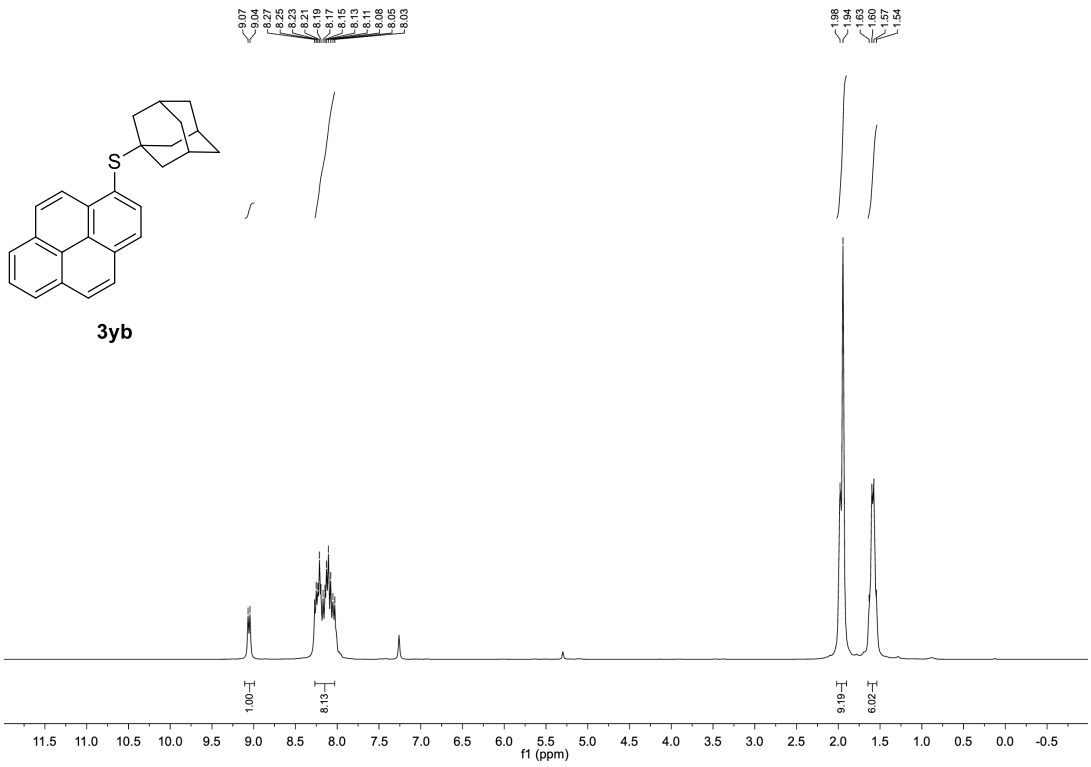


Figure S151. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3yb**.

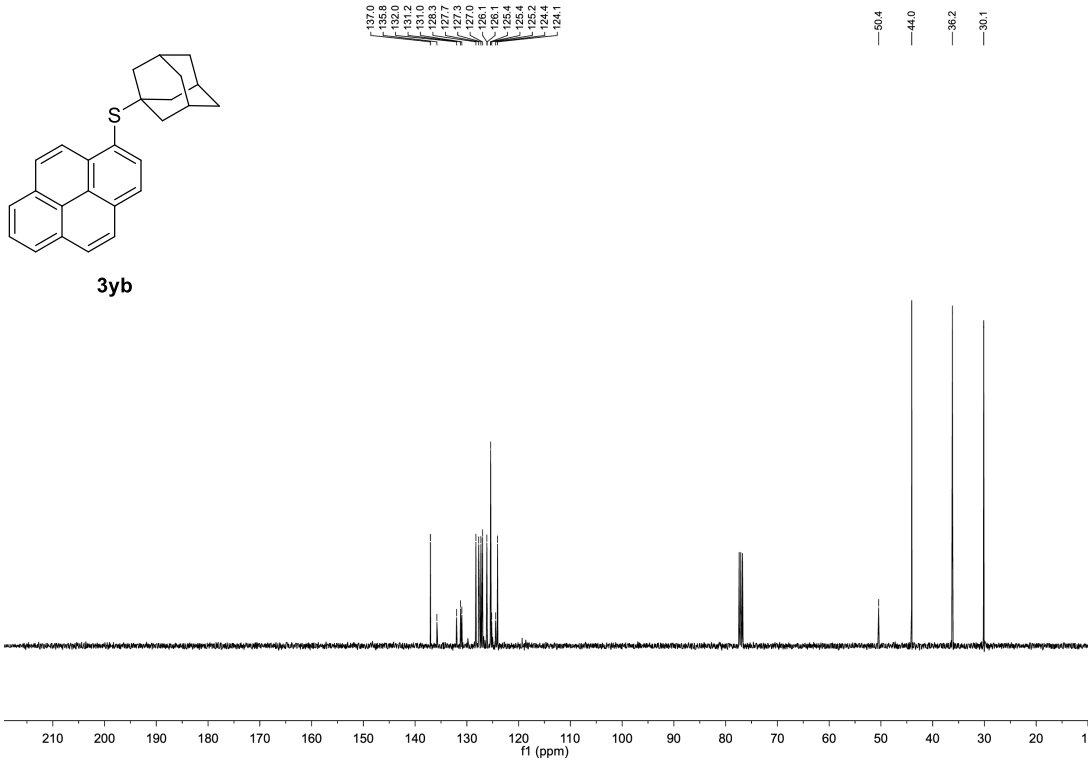
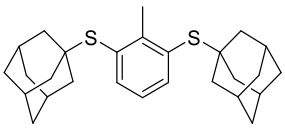


Figure S152. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3yb**.

(2-Methyl-1,3-phenylene)bis(((1*s*,3*S*)-adamantan-1-yl)sulfane) (3zbb):



3zbb

$C_{27}H_{36}S_2$ (424.71 g/mol)

3zbb was isolated from an intramolecular competition experiment (described above), using 3-bromo-2-methylphenyl trifluoromethanesulfonate (**1z**) (319 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 95:5 over 10 CV) afforded **3zbb** (154 mg, 363 µmol, 36%) as colorless solid.

R_f: 0.13 (*n*-hexane).

m. p.: 258.0 – 259.1 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.52 (d, *J* = 7.6 Hz, 2H), 7.06 (dd, *J* = 7.6, 7.6 Hz, 1H), 2.77 (s, 3H), 2.03 – 1.96 (m, 6H), 1.86 – 1.81 (m, 12H), 1.69 – 1.57 (m, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 150.4, 140.2, 131.6, 124.6, 50.0, 43.9, 36.3, 30.2, 22.3.

HR-MS (APCI): m/z calc for $[M+H]^+$ 425.23312, found 425.23351.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2898 (m), 2846 (m), 1444 (m), 1411 (w), 1370 (w), 1340 (w), 1292 (m), 1254 (w), 1098 (w), 1034 (m), 981 (w), 819 (w), 792 (m), 762 (w), 713 (w), 680 (w).

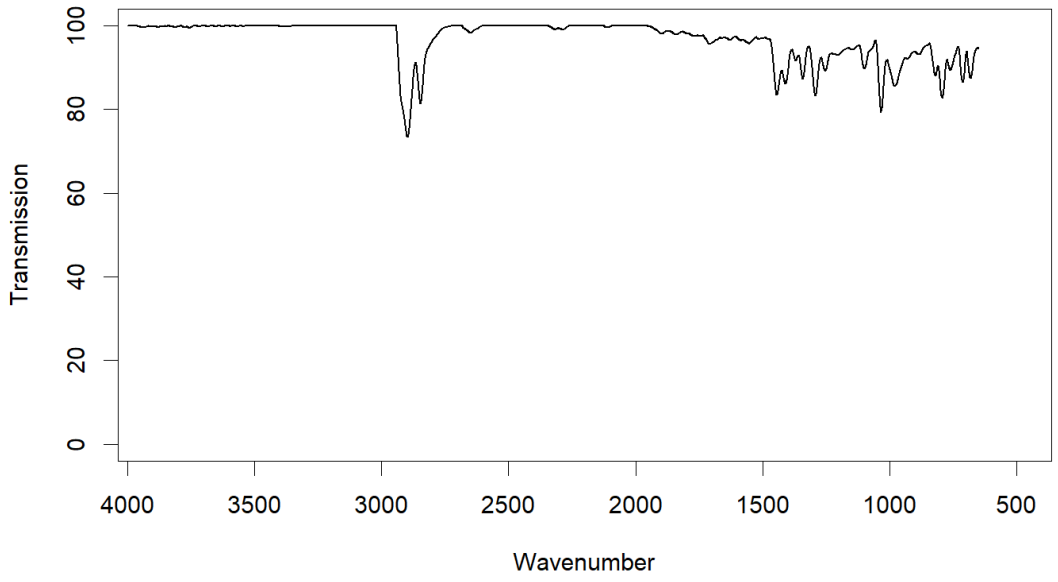


Figure S153. IR-spectrum (ATR, neat) of **3zbb**.

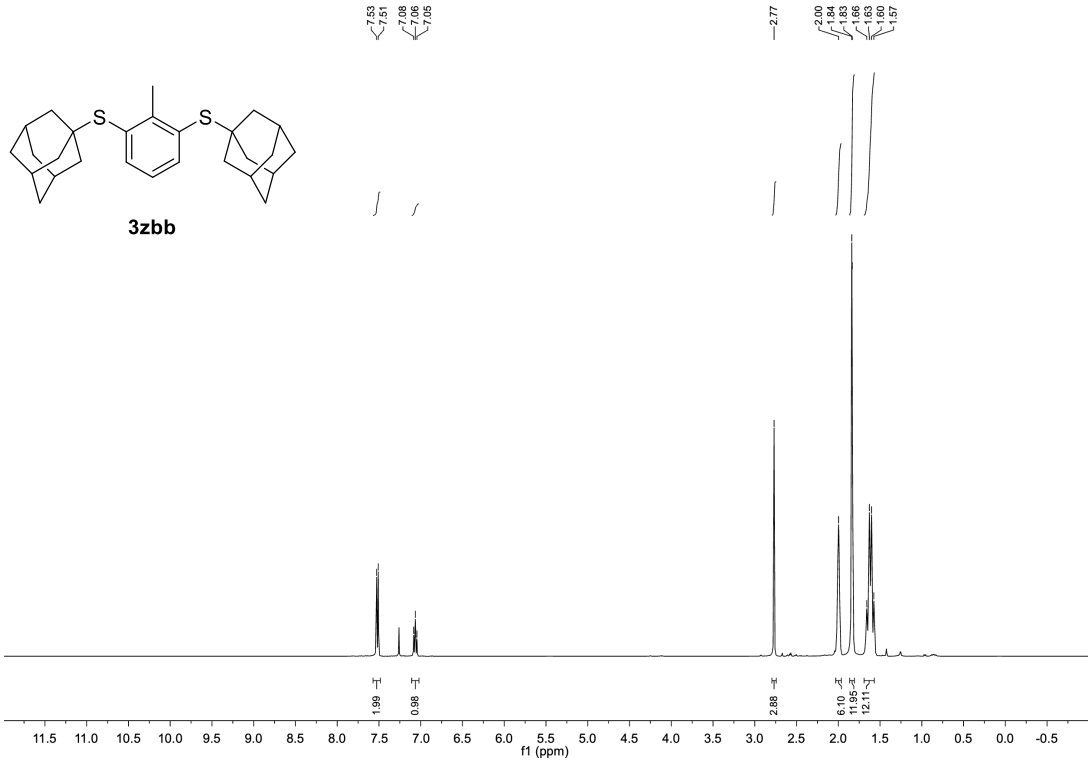


Figure S154. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3zbb**.

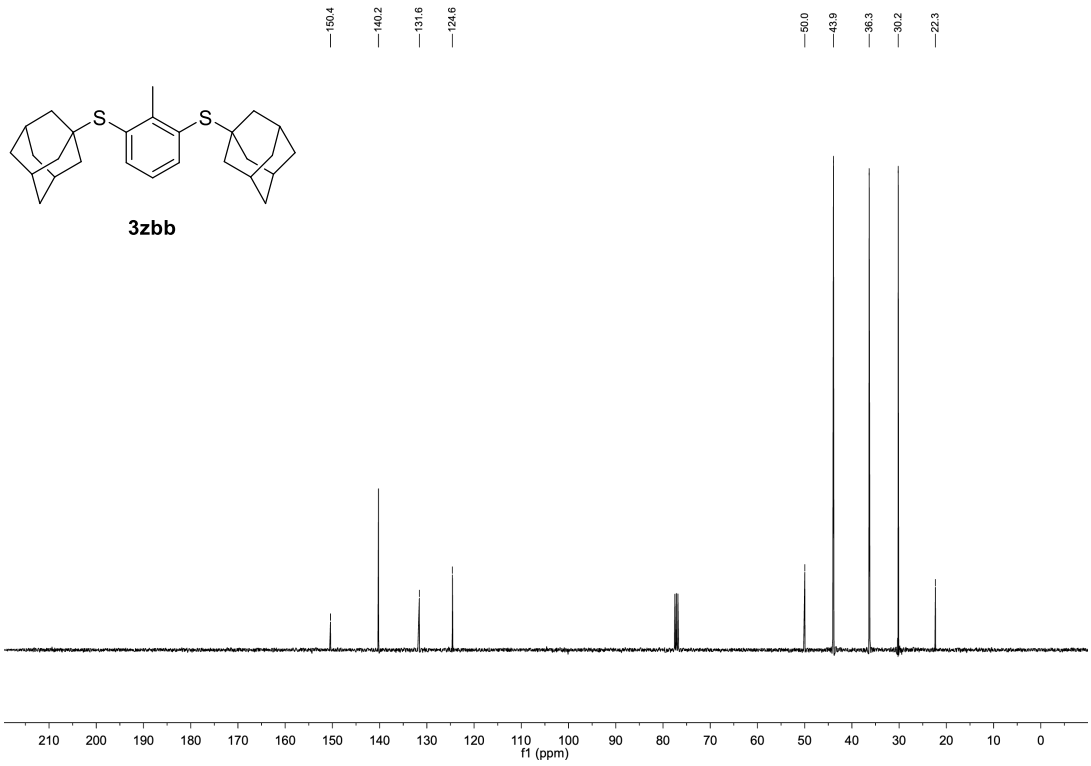
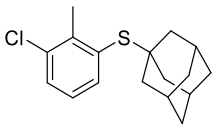


Figure S155. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3zbb**.

(((1*s*,3*s*)-Adamantan-1-yl)(3-chloro-2-methylphenyl)sulfane (3Ab):



3Ab

$C_{17}H_{21}ClS$ (292.87 g/mol)

3Ab was isolated from an intramolecular competition experiment (described above), using 3-chloro-2-methylphenyl trifluoromethanesulfonate (**1A**) (275 mg, 1.00 mmol, 1.0 equiv.) and 1-adamantane thiol (**2b**) (177 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 95:5 over 10 CV) afforded **3Ab** (164 mg, 560 µmol, 56%) as colorless solid.

R_f: 0.50 (*n*-hexane).

m. p.: 110.3 – 111.7 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.44 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.06 (dd, *J* = 7.7, 7.9 Hz, 1H), 2.63 (s, 3H), 2.04 – 1.98 (m, 3H), 1.85 – 1.81 (m, 6H), 1.67 – 1.56 (m, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 142.3, 138.0, 138.0, 135.4, 132.5, 130.1, 130.1, 125.9, 50.1, 43.8, 36.3, 30.2, 20.0.

HR-MS (APCI): m/z calc for $[M]^{\bullet+}$ 292.10470, found 292.10419.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2907 (m), 2846 (m), 1552 (w), 1448 (w), 1422 (m), 1370 (w), 1340 (w), 1296 (w), 1254 (w), 1202 (w), 1176 (w), 1150 (w), 1105 (w), 1079 (w), 1034 (m), 987 (m), 817 (w), 771 (m), 703 (m), 684 (w).

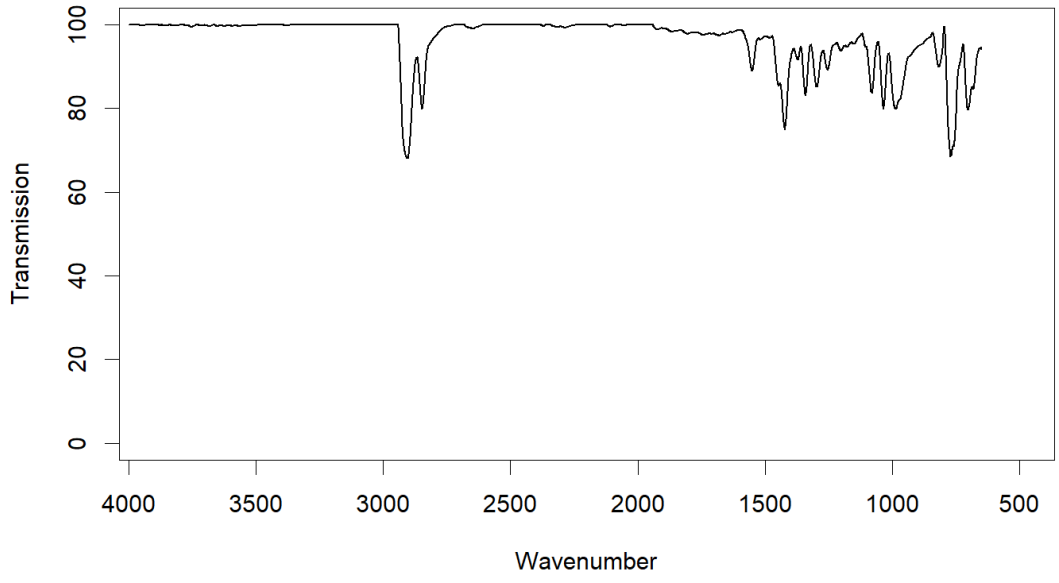


Figure S156. IR-spectrum (ATR, neat) of **3Ab**.

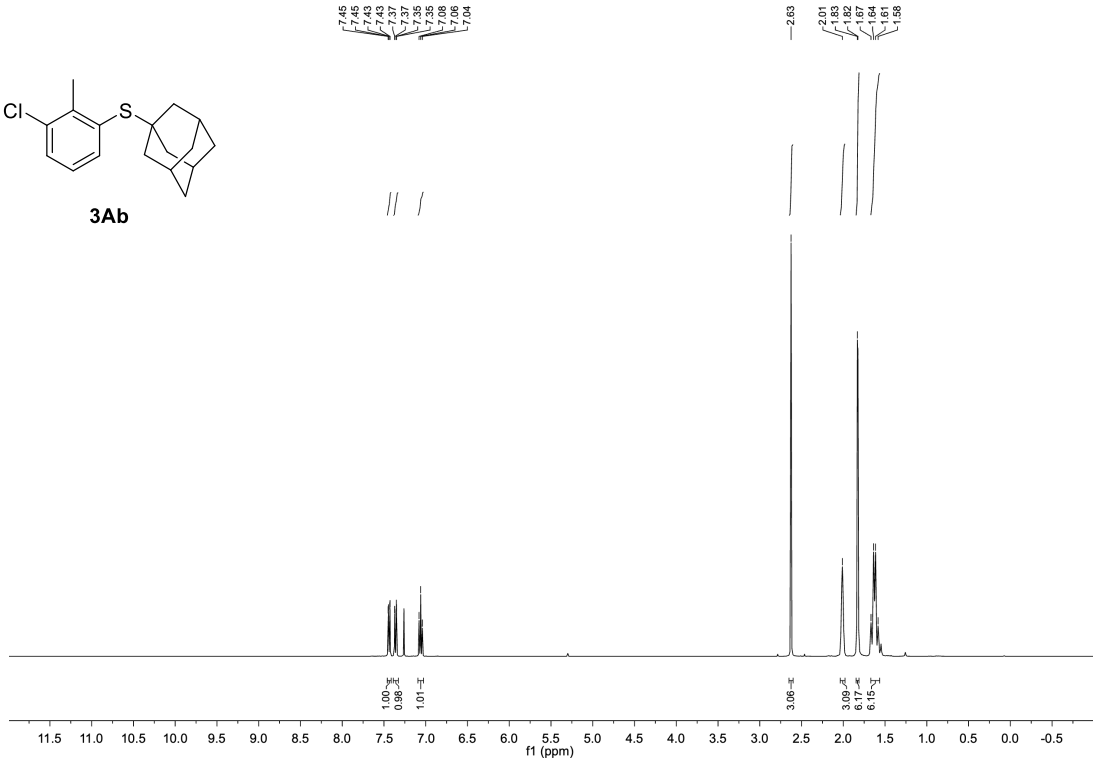


Figure S157. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3Ab**.

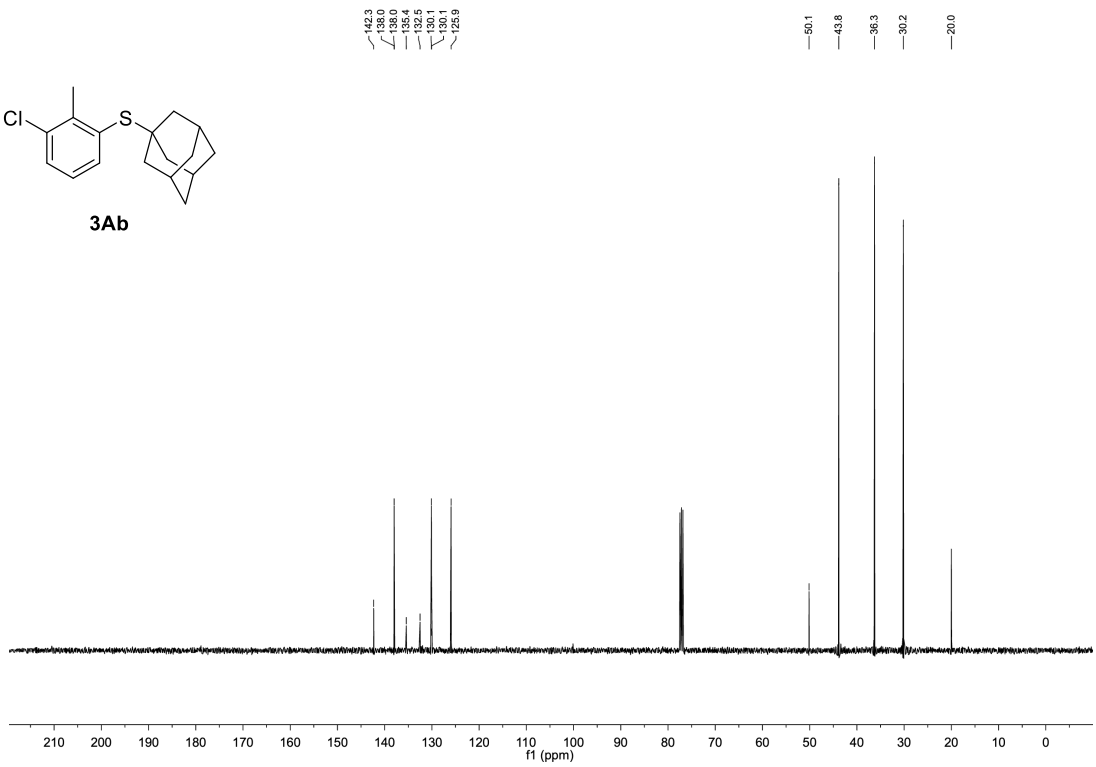
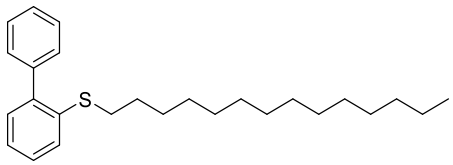


Figure S158. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3Ab**.

[1,1'-Biphenyl]-2-yl(tetradecyl)sulfane (3ac):



3ac

$C_{26}H_{38}S$ (382.65 g/mol)

Following **GP-B**, **3ac** was synthesized using [1,1'-biphenyl]-2-yl trifluoromethanesulfonate (**1a**) (302 mg, 1.00 mmol, 1.0 equiv.) and *n*-tetradecane thiol (**2c**) (242 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 95:5 over 10 CV) afforded **3ac** (298 mg, 779 µmol, 78%) as off-white solid.

R_f: 0.26 (*n*-hexane).

m.p.: 39.2 – 40.1 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.46 – 7.36 (m, 6H), 7.33 – 7.19 (m, 3H), 2.76 (t, *J* = 7.4 Hz, 2H), 1.61 – 1.52 (m, 2H), 1.32 – 1.19 (m, 22H), 0.90 (t, *J* = 6.5 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 142.2, 141.0, 136.0, 130.4, 129.5, 128.1, 127.9, 127.8, 127.5, 125.4, 33.4, 32.1, 29.84, 29.81, 29.7, 29.6, 29.5, 29.3, 29.1, 28.9, 22.9, 14.3.

HR-MS (APCI): m/z calc for $[M+H]^+$ 383.27670, found 383.27708.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3054 (w), 2958 (w), 2913 (s), 2842 (s), 1895 (w), 1582 (w), 1493 (w), 1459 (s), 1373 (w), 1273 (w), 1238 (w), 1180 (w), 1124 (w), 1075 (w), 1038 (w), 1001 (w), 911 (w), 859 (w), 740 (s), 691 (s).

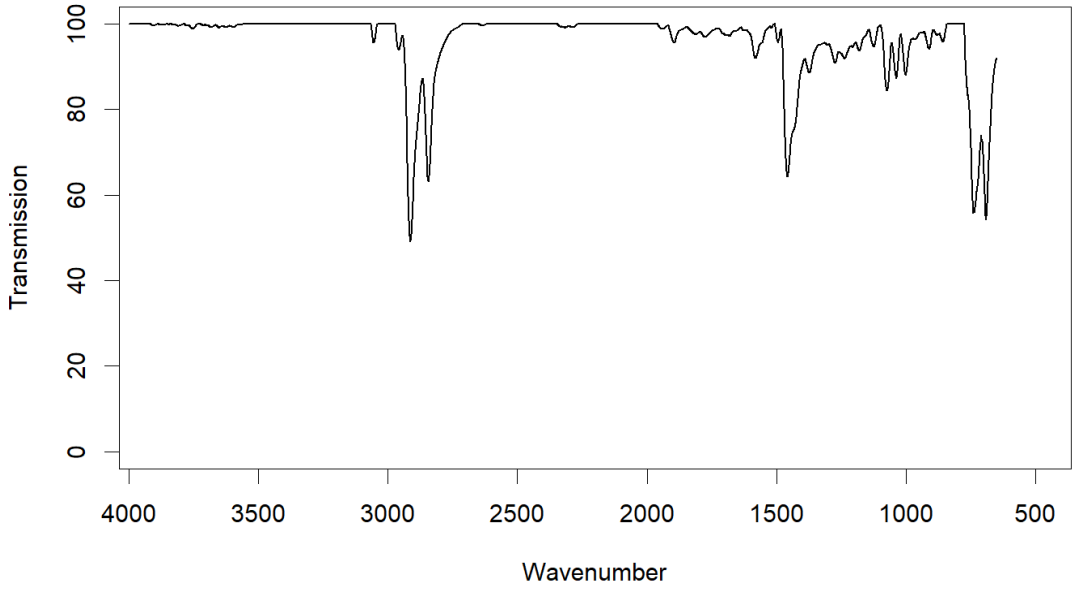


Figure S159. IR-spectrum (ATR, neat) of **3ac**.

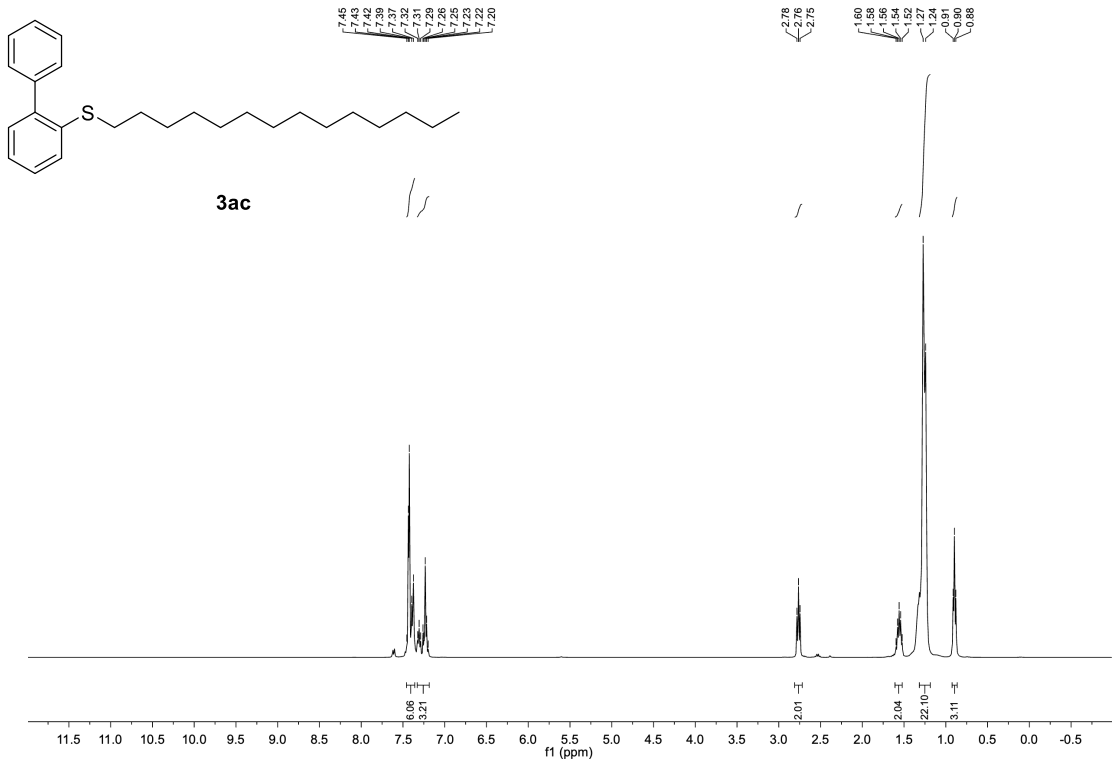


Figure S160. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3ac**.

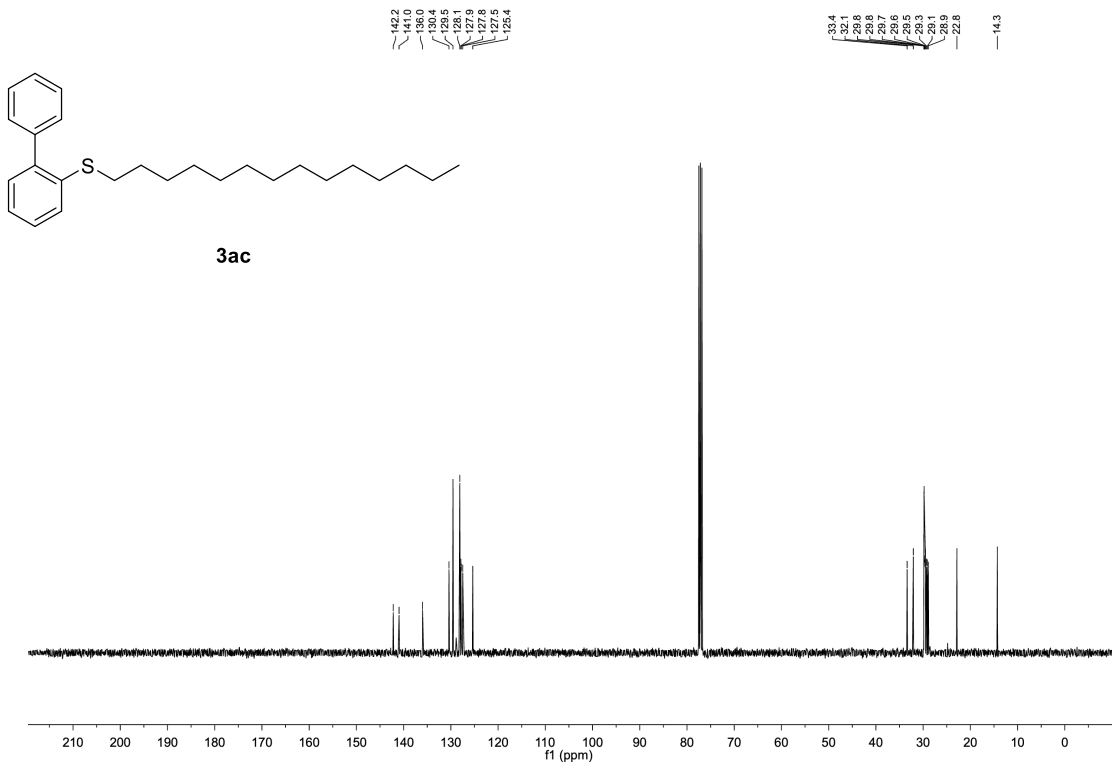
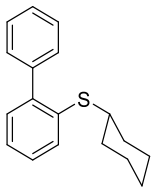


Figure S161. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3ac**.

[1,1'-Biphenyl]-2-yl(cyclohexyl)sulfane (3ad):



3ad

$C_{18}H_{20}S$ (268.42 g/mol)

Following **GP-B**, **3ad** was synthesized using [1,1'-biphenyl]-2-yl trifluoromethanesulfonate (**1a**) (302 mg, 1.00 mmol, 1.0 equiv.) and cyclohexane thiol (**2d**) (122 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 95:5 over 10 CV) afforded **3ad** (223 mg, 831 µmol, 83%) as colorless oil.

R_f: 0.19 (*n*-hexane).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.47 – 7.43 (m, 1H), 7.41 – 7.30 (m, 5H), 7.29 – 7.19 (m, 3H), 2.95 – 2.81 (m, 1H), 1.87 – 1.77 (m, 2H), 1.71 – 1.60 (m, 2H), 1.57 – 1.47 (m, 1H), 1.27 – 1.10 (m, 5H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 143.7, 141.3, 134.4, 130.9, 130.6, 129.7, 128.0, 127.7, 127.3, 126.2, 46.0, 33.2, 26.2, 25.9.

HR-MS (APCI): m/z calc for $[M+H]^+$ 269.13585, found 269.13616.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3051 (w), 3024 (w), 2924 (s), 2849 (m), 1582 (w), 1450 (s), 1336 (w), 1261 (w), 1202 (w), 1072 (w), 1038 (w), 998 (m), 885 (w), 743 (s), 695 (s).

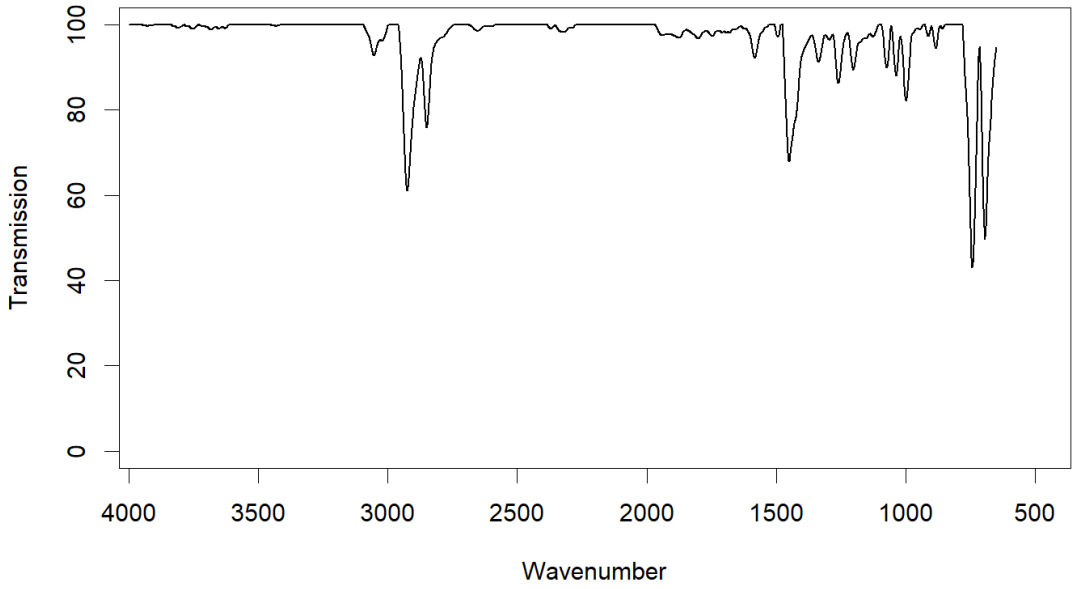


Figure S162. IR-spectrum (ATR, neat) of **3ad**.

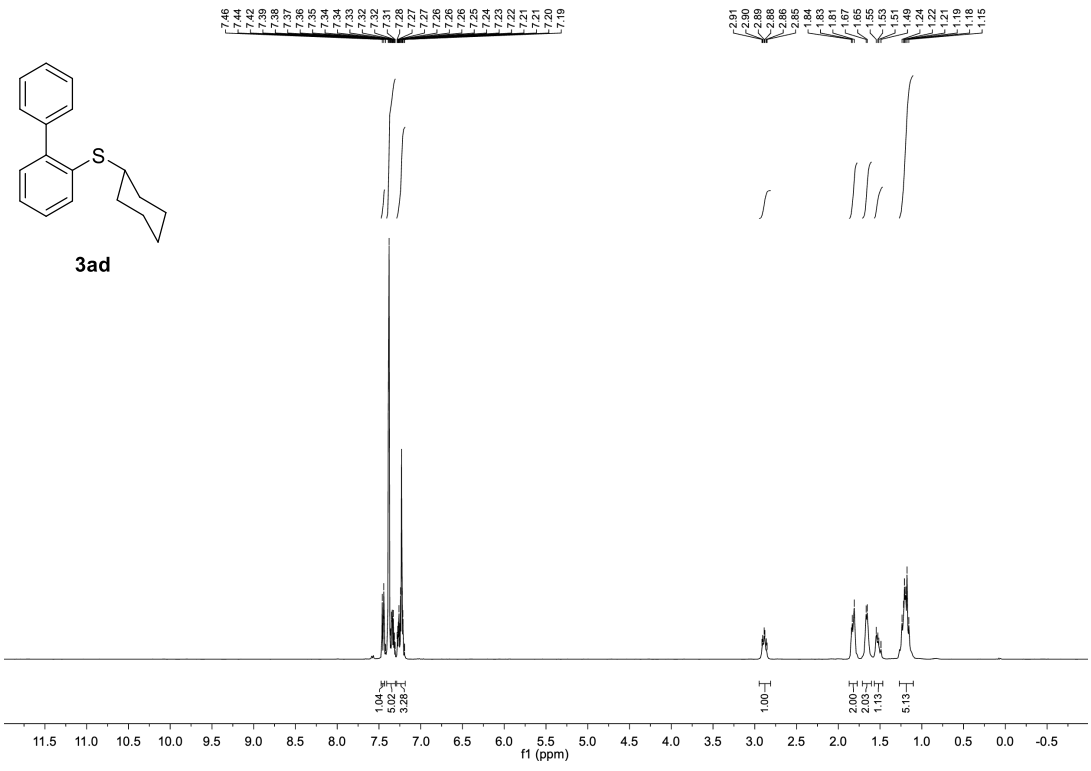


Figure S163. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3ad**.

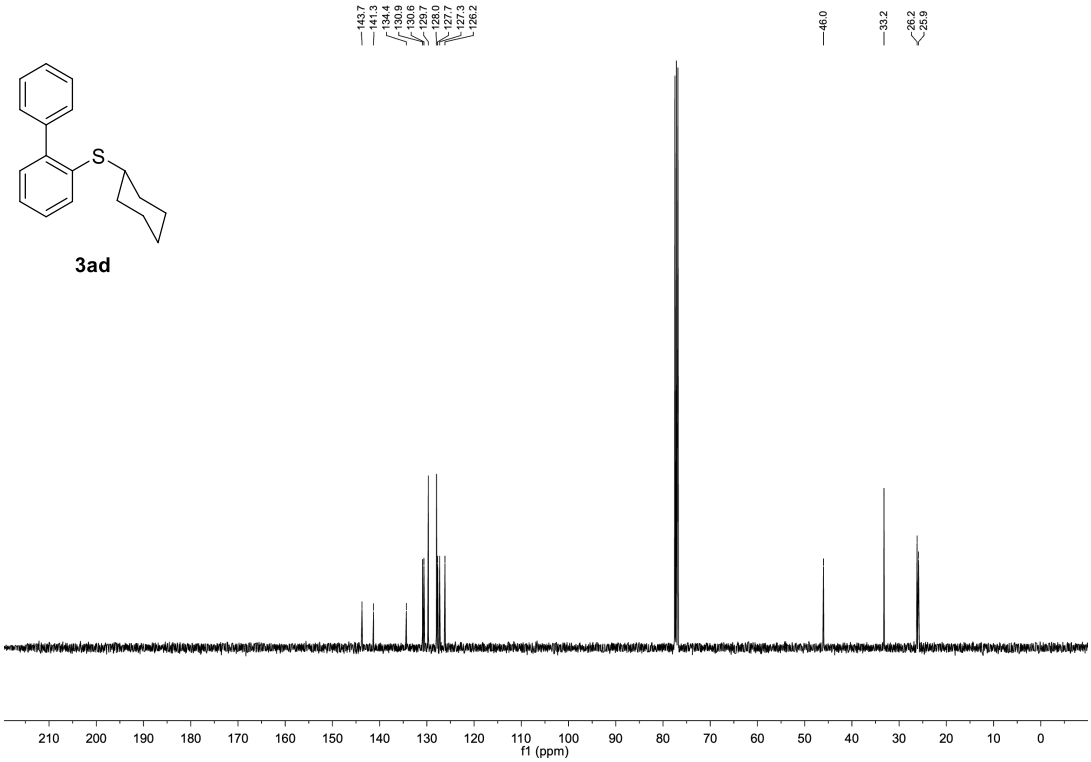
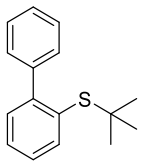


Figure S164. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3ad**.

[1,1'-Biphenyl]-2-yl(*tert*-butyl)sulfane (3ae):



3ae

$C_{16}H_{18}S$ (242.38 g/mol)

Following **GP-B**, **3ae** was synthesized using [1,1'-biphenyl]-2-yl trifluoromethanesulfonate (**1a**) (302 mg, 1.00 mmol, 1.0 equiv.) and *tert*-butane thiol (**2e**) (94.7 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 95:5 over 10 CV) afforded **3ae** (224 mg, 924 µmol, 92%) as colorless solid.

R_f: 0.21 (*n*-hexane).

m. p.: 46.2 – 49.2 °C.

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.74 – 7.67 (m, 1H), 7.42 – 7.29 (m, 8H), 1.04 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 148.5, 142.0, 139.6, 131.2, 130.9, 130.8, 129.0, 127.4, 127.2, 126.9, 47.6, 31.1.

HR-MS (APCI): m/z calc for $[M+H]^+$ 243.12020, found 243.12059.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3051 (w), 2966 (m), 2924 (w), 2894 (w), 2860 (w), 1873 (w), 1839 (w), 1802 (w), 1751 (w), 1711 (w), 1661 (w), 1582 (w), 1453 (m), 1418 (m), 1396 (w), 1358 (m), 1247 (w), 1213 (w), 1161 (m), 1072 (w), 1034 (w), 1008 (w), 960 (w), 911 (w), 777 (w), 742 (s), 695 (s).

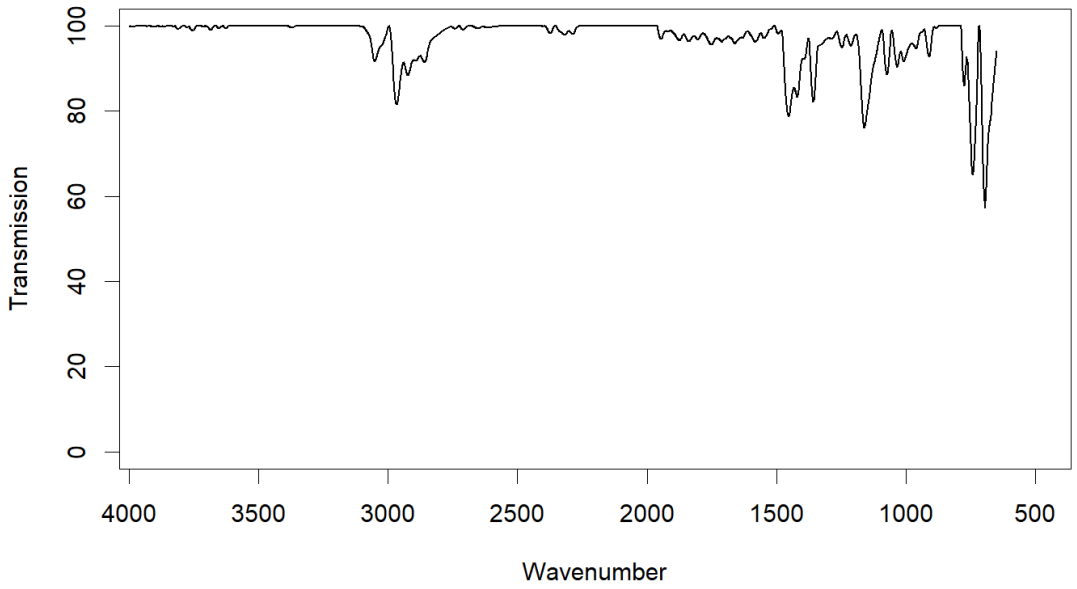


Figure S165. IR-spectrum (ATR, neat) of **3ae**.

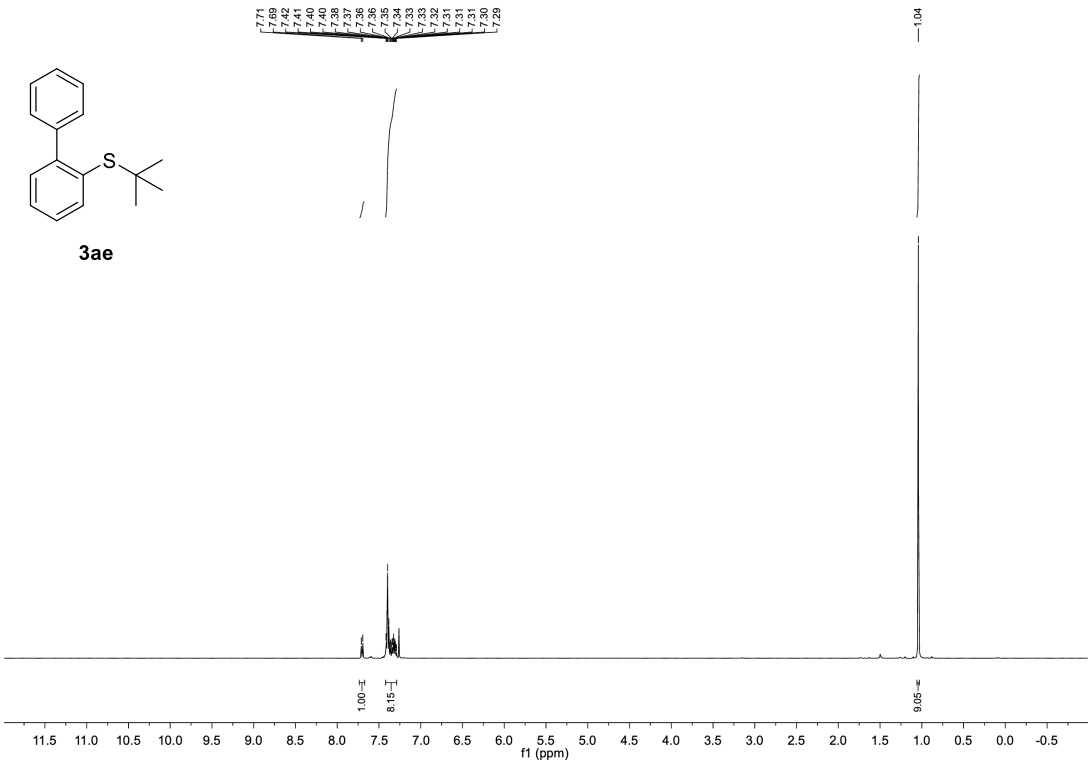


Figure S166. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3ae**.

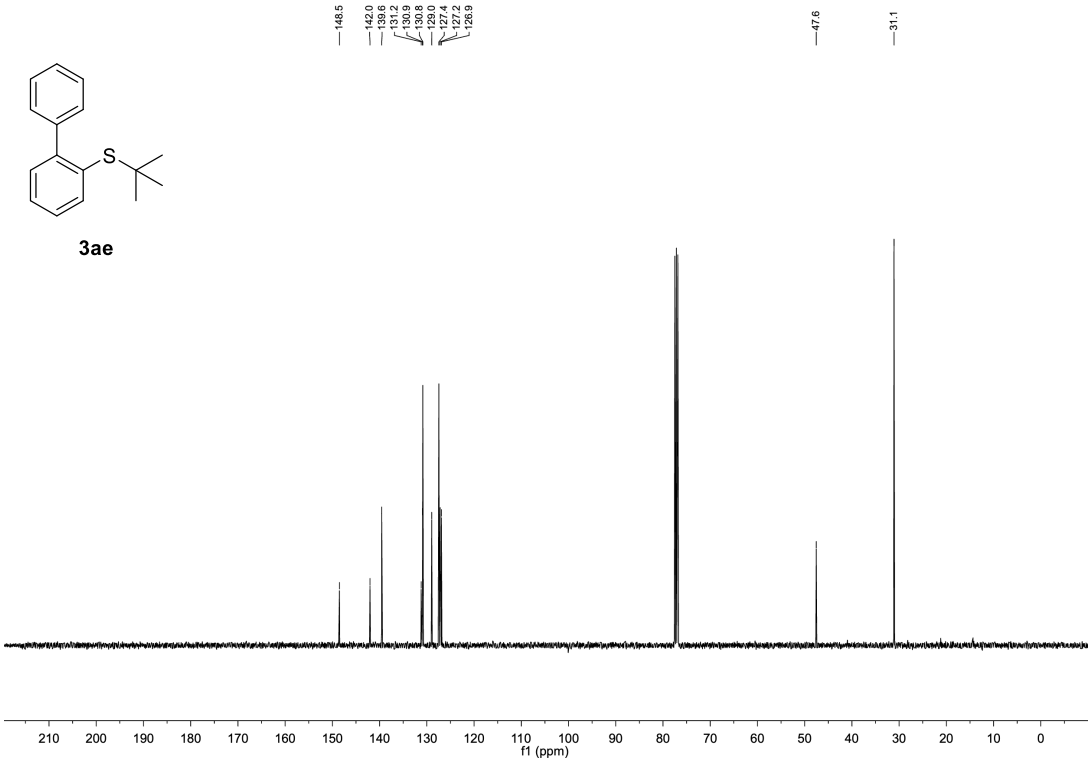
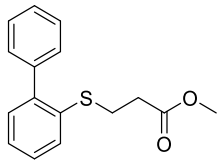


Figure S167. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3ae**.

Methyl 3-([1,1'-biphenyl]-2-ylthio)propanoate (3af):



3af

$C_{16}H_{16}O_2S$ (272.36 g/mol)

Following **GP-B**, **3af** was synthesized using [1,1'-biphenyl]-2-yl trifluoromethanesulfonate (**1a**) (302 mg, 1.00 mmol, 1.0 equiv.) and methyl 3-mercaptopropanoate (**2f**) (126 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 80:20 over 10 CV) afforded **3af** (111 mg, 408 µmol, 41%) as colorless oil.

R_f: 0.40 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.42 – 7.22 (m, 9H), 3.61 (s, 3H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 172.3, 143.1, 140.7, 134.1, 130.7, 129.6, 129.1, 128.1, 128.1, 127.6, 126.3, 51.9, 34.0, 28.6.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 295.07632, found 295.07631.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3051 (w), 3021 (w), 2946 (w), 1732 (vs), 1582 (w), 1456 (m), 1429 (s), 1352 (m), 1288 (w), 1239 (s), 1198 (s), 1168 (s), 1143 (s), 1075 (w), 1038 (m), 1012 (m), 978 (m), 945 (w), 915 (w), 889 (w), 852 (w), 848 (w), 826 (w), 744 (vs), 695 (s).

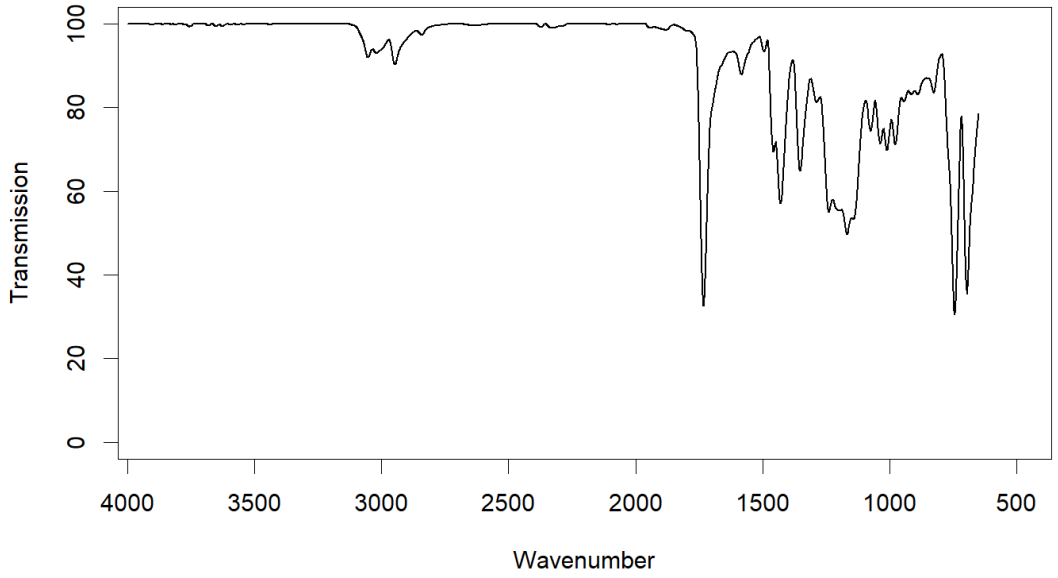


Figure S168. IR-spectrum (ATR, neat) of **3af**.

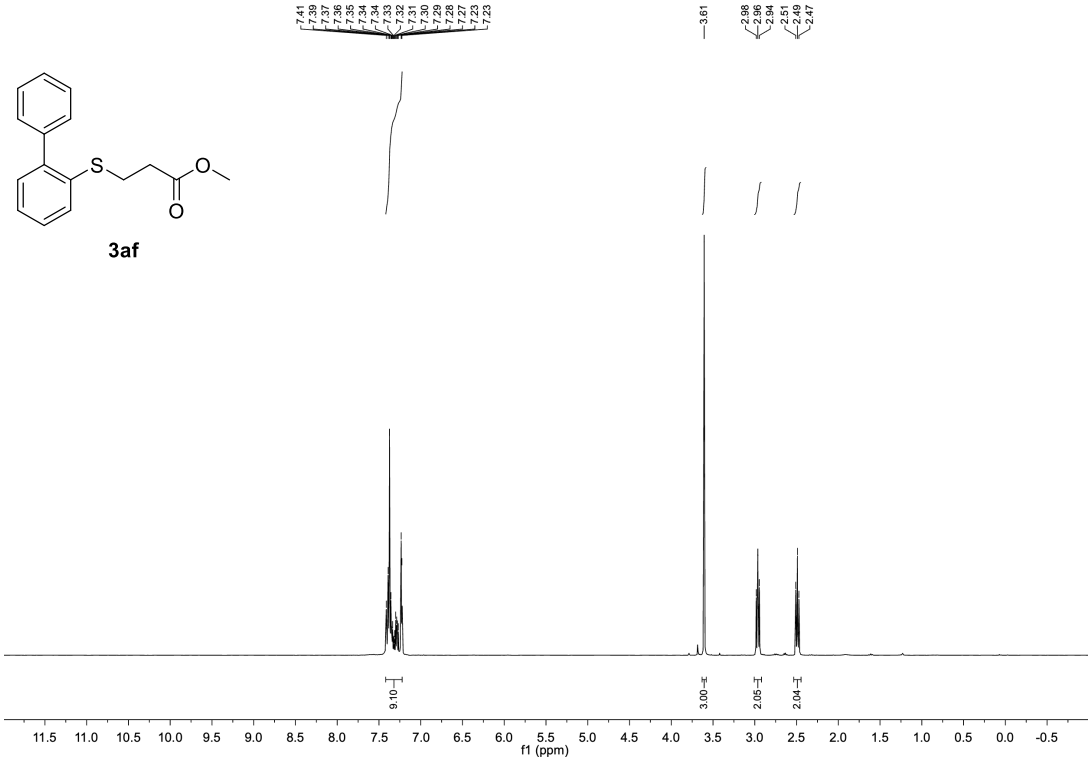


Figure S169. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3af**.

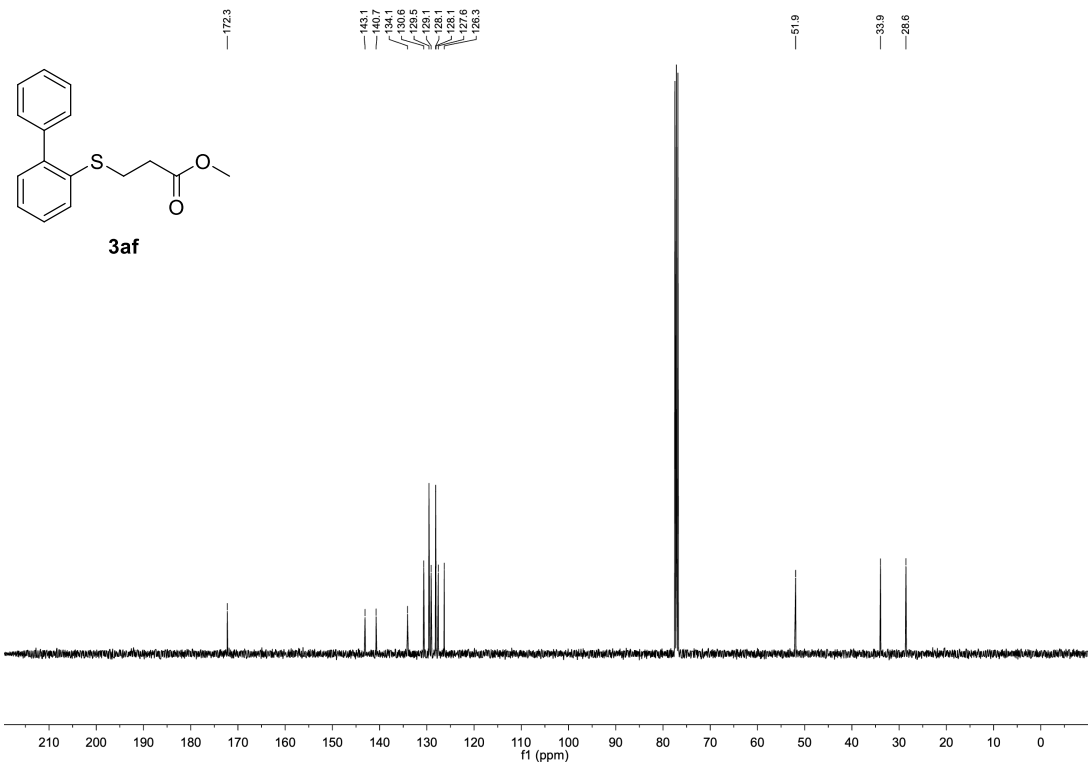
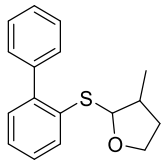


Figure S170. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3af**.

2-([1,1'-Biphenyl]-2-ylthio)-3-methyltetrahydrofuran (3ag):



3ag

$C_{17}H_{18}OS$ (270.39 g/mol)

Following **GP-B**, **3ag** was synthesized using [1,1'-biphenyl]-2-yl trifluoromethanesulfonate (**1a**) (302 mg, 1.00 mmol, 1.0 equiv.) and 3-methyltetrahydrofuran-2-thiol (**2g**) (mixture of diastereomers ca. 6:4) (124 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 80:20 over 10 CV) afforded **3ag** (177 mg, 655 µmol, 66%, diastereomeric mixture according to starting material) as colorless oil.

R_f: 0.40, 0.49 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): Mixture of diastereomers: 7.46 – 7.20 (m, 9H), 4.12 – 2.89 (m, 4H), 2.28 – 2.10 (m, 1H), 1.88 – 1.70 (m, 1H), 1.13 – 0.99 (m, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): Mixture of diastereomers: 143.7, 143.2, 140.9, 134.9, 134.1, 131.2, 130.7, 130.1, 129.7, 129.6, 128.1, 127.9, 127.6, 127.5, 126.8, 126.3, 80.3, 66.7, 65.9, 51.0, 49.3, 34.3, 33.2, 19.7, 17.0.

HR-MS (APCI): m/z calc for $[M+H]^+$ 271.11511, found 271.11563.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3051 (w), 3021 (w), 2969 (w), 2928 (w), 2861 (w), 1582 (w), 1455 (m), 1435 (m), 1377 (w), 1351 (w), 1317 (w), 1287 (w), 1221 (w), 1187 (w), 1105 (m), 1068 (m), 1038 (m), 1012 (m), 945 (w), 915 (w), 854 (m), 744 (vs), 695 (s).

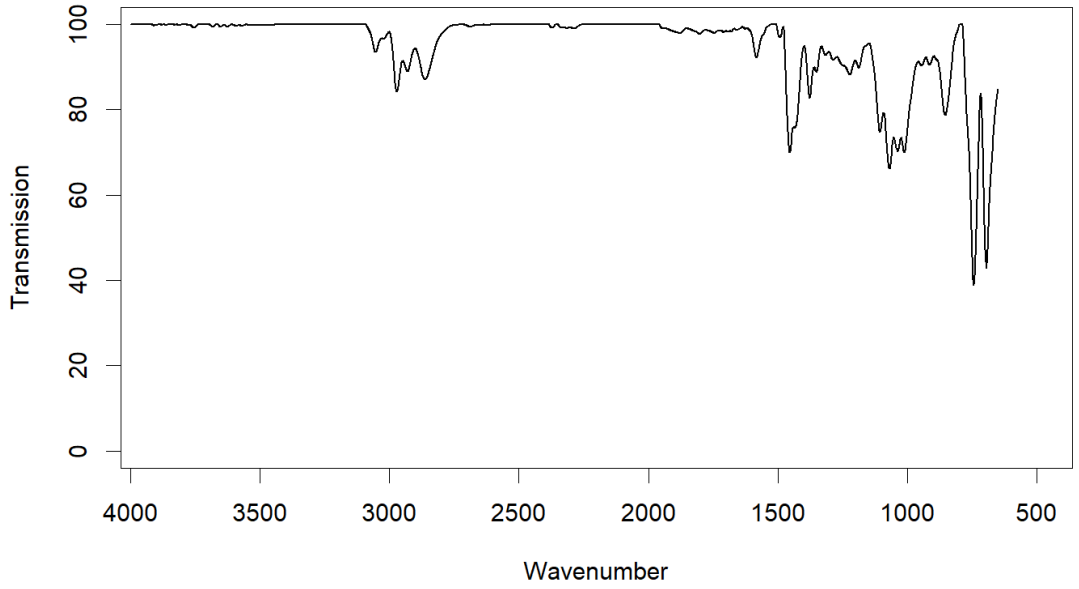


Figure S171. IR-spectrum (ATR, neat) of **3ag**.

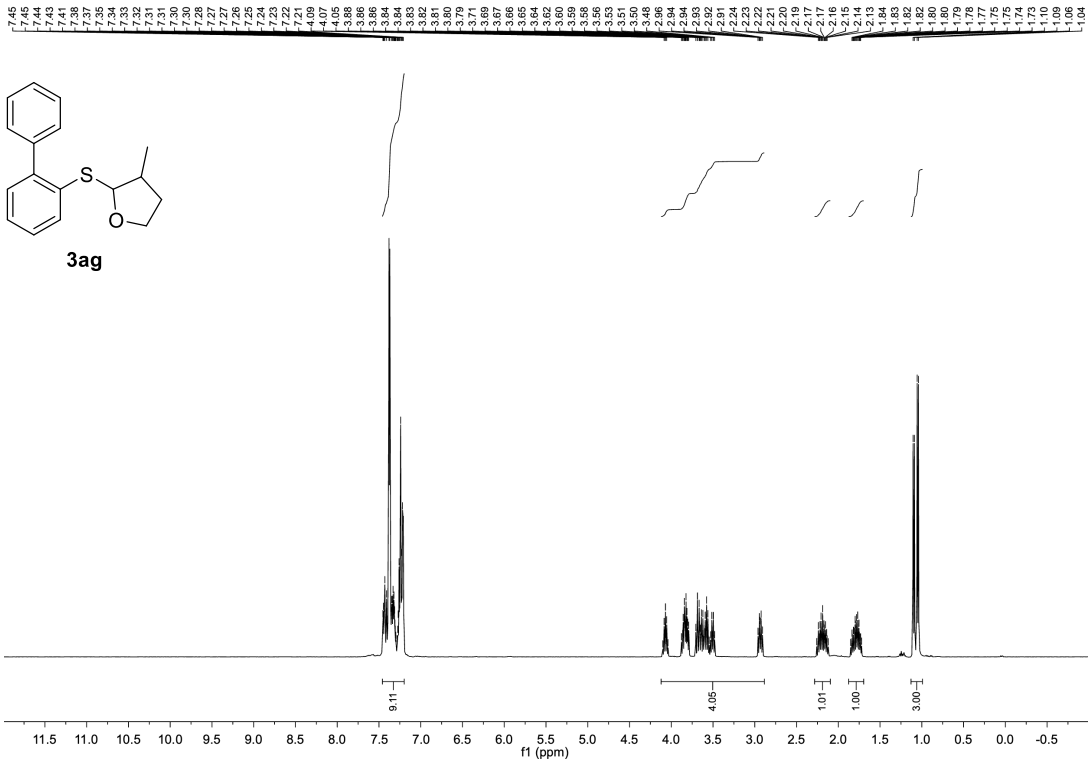


Figure S172. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3ag**.

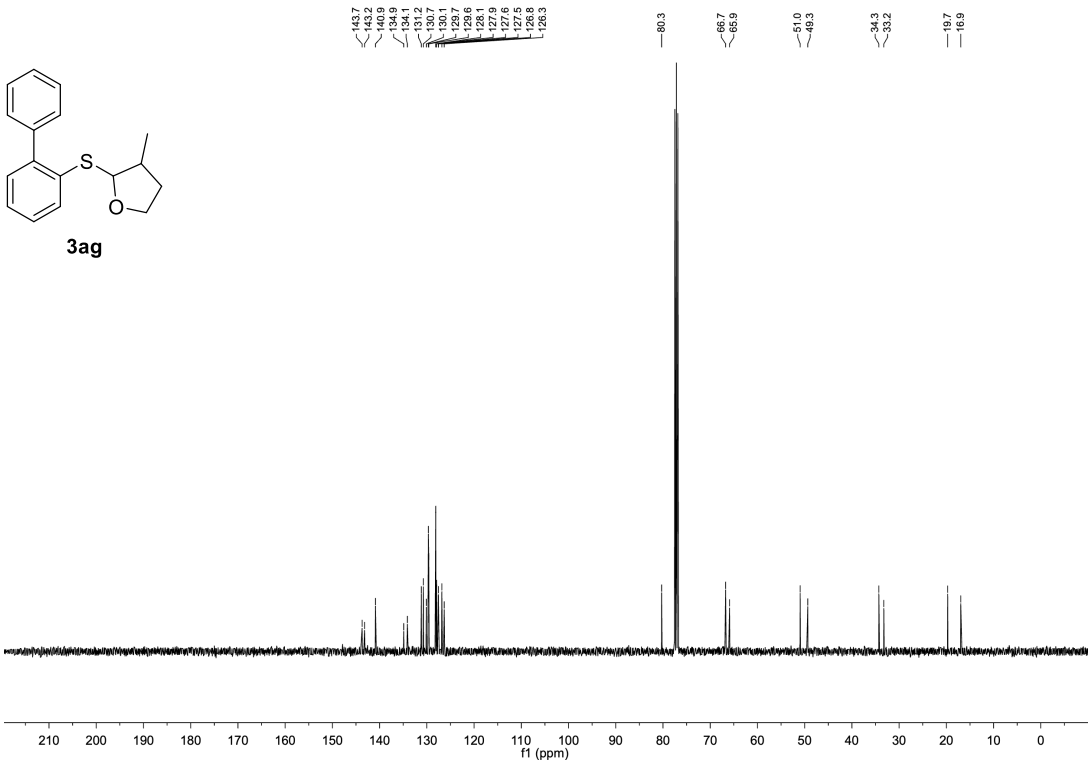
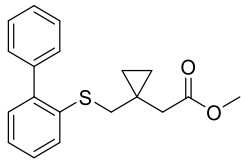


Figure S173. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3ag**.

Methyl 2-(1-(([1,1'-biphenyl]-2-ylthio)methyl)cyclopropyl)acetate (3ah):



3ah

$C_{19}H_{20}O_2S$ (312.43 g/mol)

Following **GP-B**, **3ah** was synthesized using [1,1'-biphenyl]-2-yl trifluoromethanesulfonate (**1a**) (302 mg, 1.00 mmol, 1.0 equiv.) and methyl 2-(1-(mercaptomethyl)cyclopropyl)acetate (**2h**) (168 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 15 CV) afforded **3ah** (162 mg, 519 µmol, 52%) as colorless oil.

R_f: 0.59 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.48 – 7.36 (m, 6H), 7.31 – 7.23 (m, 3H), 3.62 (s, 3H), 2.89 (s, 2H), 2.31 (s, 2H), 0.43 (s, 4H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 172.7, 143.1, 141.0, 135.6, 130.4, 130.0, 129.7, 128.0, 127.9, 127.4, 126.2, 51.5, 42.6, 40.0, 16.8, 12.6.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 335.10762, found 335.10822.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3055 (w), 3002 (w), 2947 (w), 2917 (w), 2842 (w), 1732 (s), 1582 (w), 1459 (m), 1429 (m), 1363 (w), 1306 (w), 1232 (m), 1198 (m), 1159 (s), 1079 (w), 1015 (s), 964 (w), 900 (m), 874 (w), 837 (w), 744 (s), 699 (s).

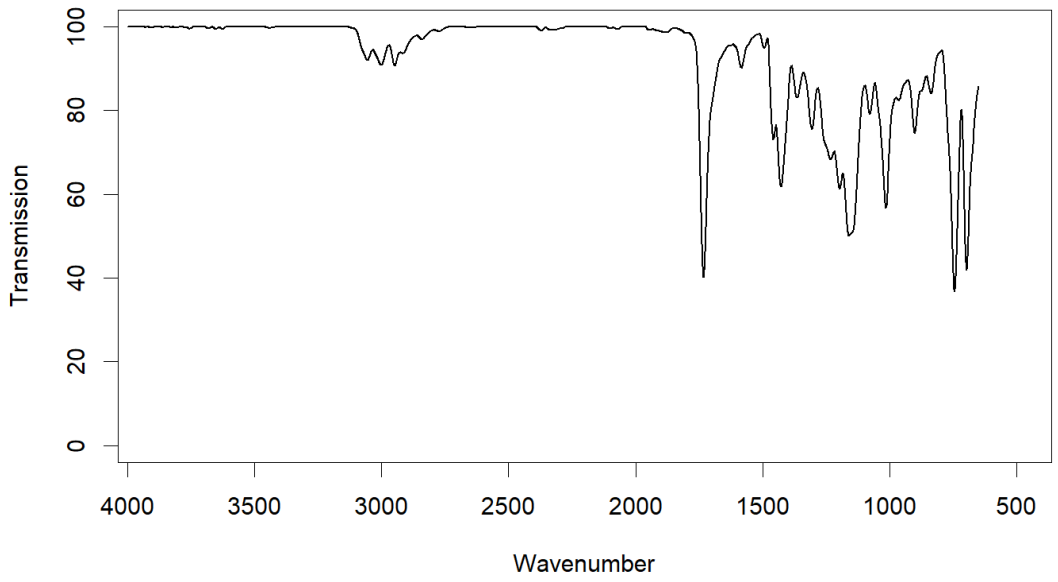


Figure S174. IR-spectrum (ATR, neat) of **3ah**.

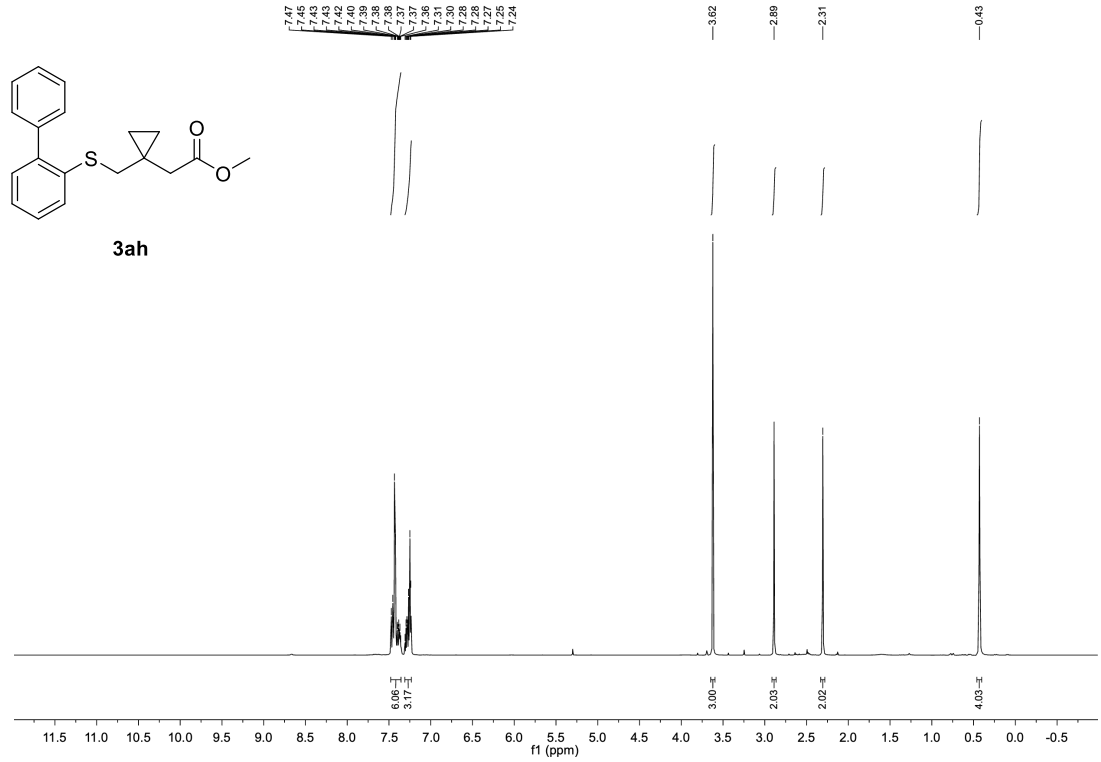


Figure S175. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3ah**.

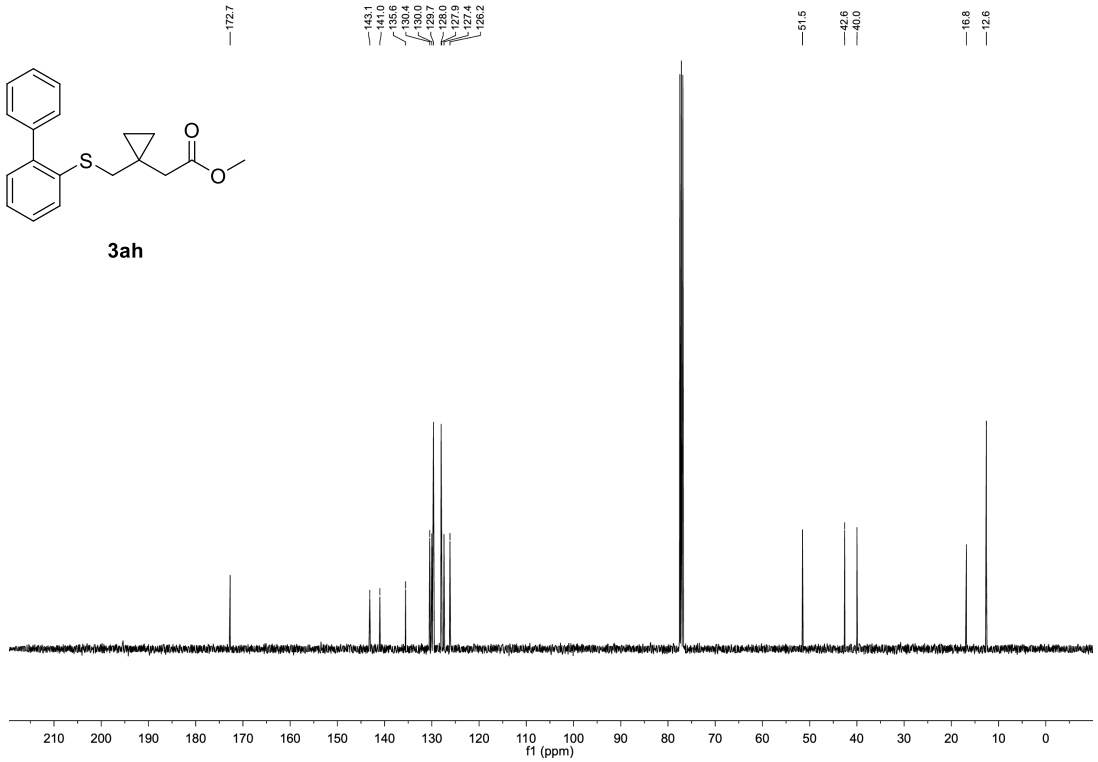
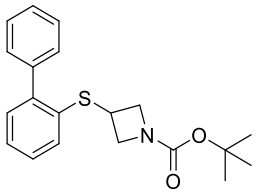


Figure S176. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3ah**.

***tert*-Butyl 3-([1,1'-biphenyl]-2-ylthio)azetidine-1-carboxylate (3ai):**



3ai

$C_{20}H_{23}NO_2S$ (341.47 g/mol)

Following **GP-B**, **3ai** was synthesized using [1,1'-biphenyl]-2-yl trifluoromethanesulfonate (**1a**) (302 mg, 1.00 mmol, 1.0 equiv.) and *tert*-butyl 3-mercaptoazetidine-1-carboxylate (**2i**) (199 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 90:10 over 10 CV) afforded **3ai** (52 mg, 152 µmol, 15%) as colorless oil.

R_f: 0.37 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.50 – 7.38 (m, 5H), 7.34 – 7.24 (m, 3H), 7.11 (d, *J* = 7.5 Hz, 1H), 4.31 – 4.22 (m, 2H), 3.90 – 3.81 (m, 1H), 3.81 – 3.73 (m, 2H), 1.43 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): 155.9, 142.0, 140.4, 134.4, 130.7, 129.4, 128.3, 128.2, 127.8, 127.4, 126.2, 79.8, 56.3, 33.2, 28.5.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 364.13417, found 364.13461.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3058 (w), 2973 (w), 2880 (w), 1690 (s), 1459 (w), 1393 (s), 1303 (w), 1247 (w), 1133 (s), 1038 (w), 975 (w), 907 (s), 856 (w), 725 (s).

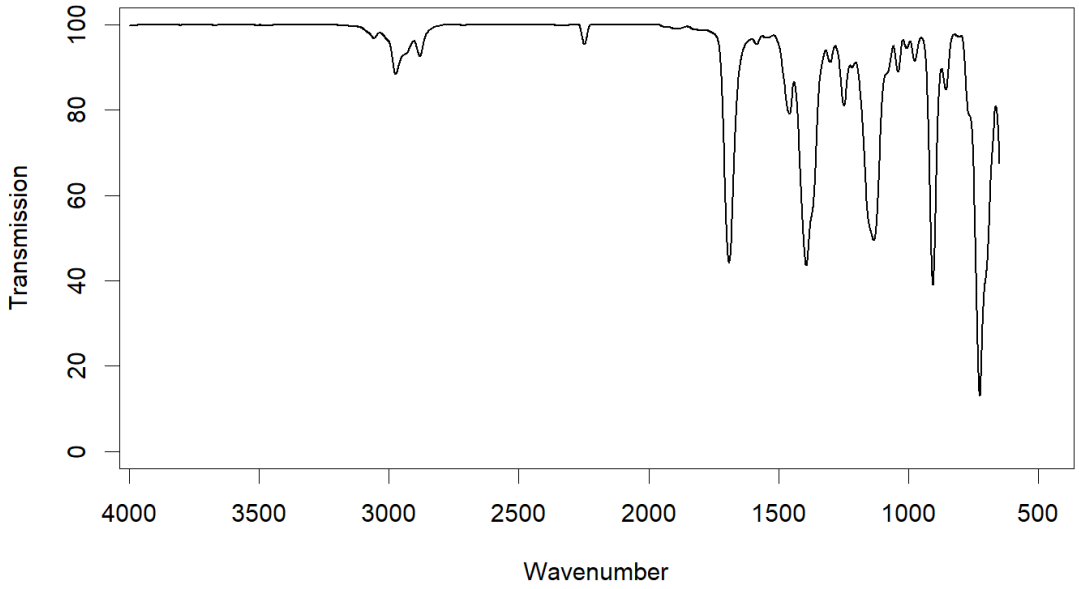


Figure S177. IR-spectrum (ATR, neat) of **3ai**.

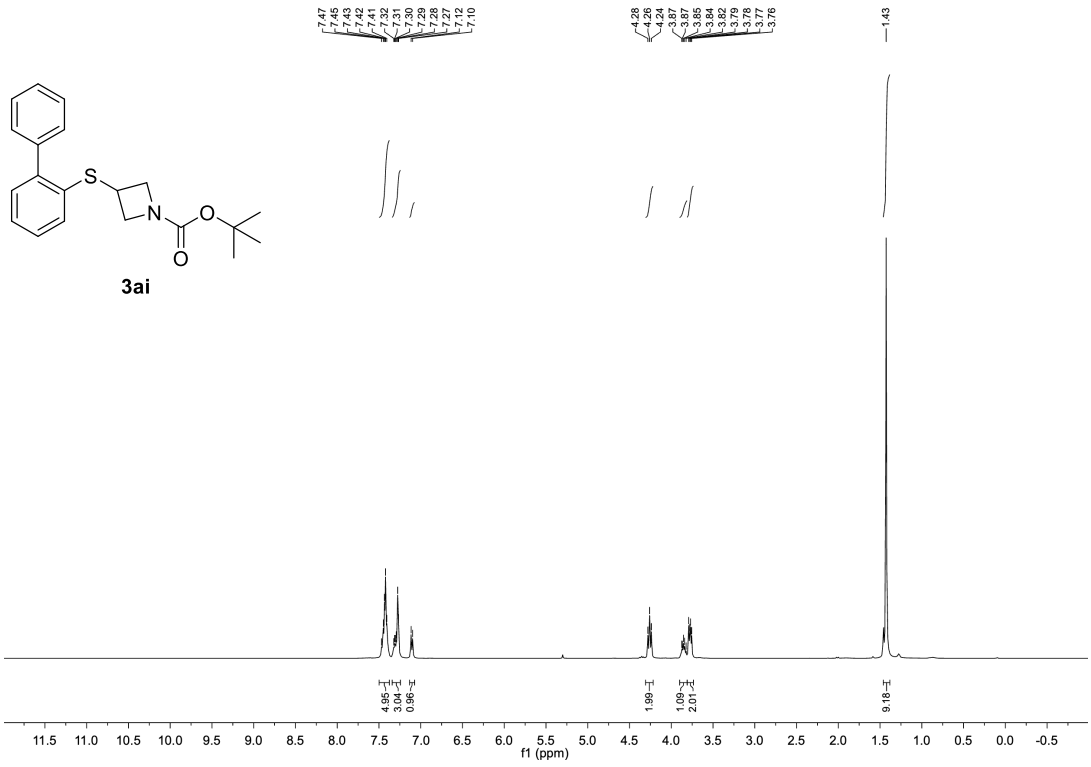


Figure S178. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3ai**.

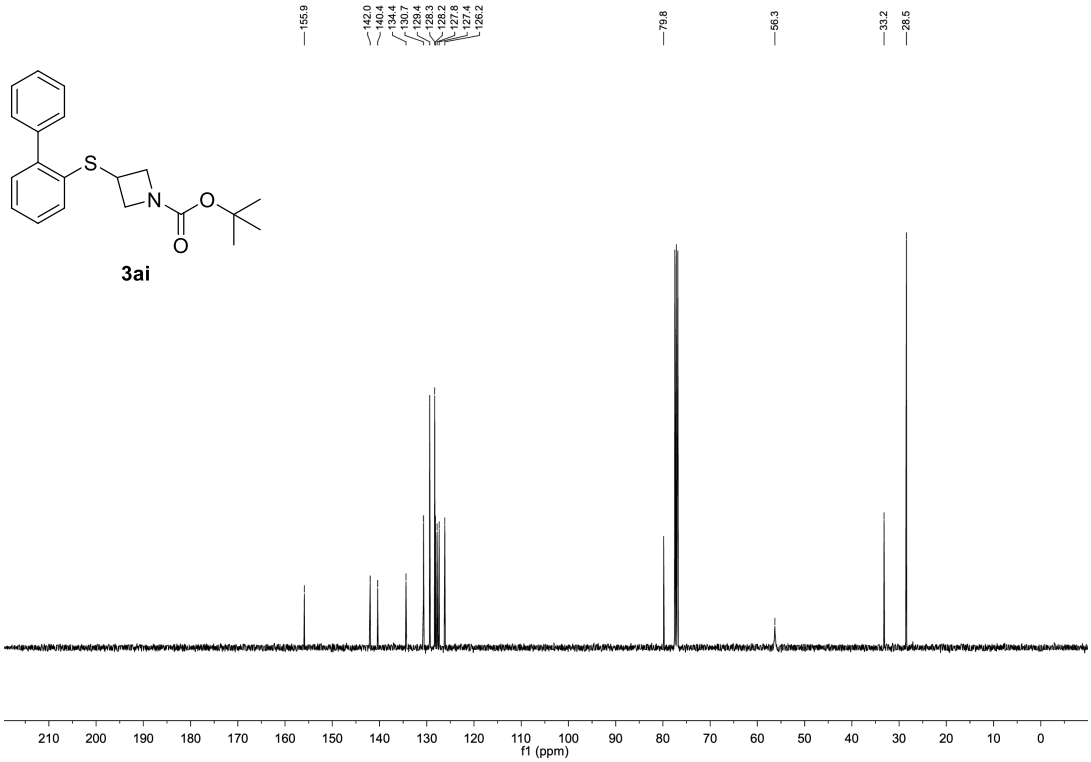
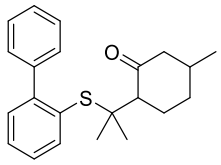


Figure S179. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3ai**.

2-(2-([1,1'-Biphenyl]-2-ylthio)propan-2-yl)-5-methylcyclohexan-1-one (3aj):



3aj

$C_{22}H_{26}OS$ (338.51 g/mol)

Following **GP-B**, **3aj** was synthesized using [1,1'-biphenyl]-2-yl trifluoromethanesulfonate (**1a**) (302 mg, 1.00 mmol, 1.0 equiv.) and 8-mercaptomenthone (**2j**) (mixture of diastereomers ca. 8:2) (196 mg, 1.05 mmol, 1.05 equiv.). Purification by flash chromatography (SiO_2, gradient *n*-hexane/EtOAc 100:0 to 85:15 over 15 CV) afforded **3aj** (240 mg, 709 µmol, 71%, diastereomeric mixture according to starting material) as colorless oil.

R_f: 0.63, 0.70 (*n*-hexane/EtOAc 90:10).

^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.72 – 7.64 (m, 1H), 7.46 – 7.27 (m, 8H), 2.23 – 2.03 (m, 3H), 1.85 – 1.62 (m, 3H), 1.48 – 1.41 (m, 1H), 1.33 – 1.21 (m, 1H), 1.17 – 1.09 (m, 6H), 0.95 – 0.84 (m, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ): Major isomer: 211.1, 148.6, 142.0, 140.0, 131.1, 130.9, 130.7, 129.2, 127.7, 127.2, 127.1, 58.4, 52.6, 52.4, 36.9, 34.6, 29.8, 28.0, 24.7, 22.4.

HR-MS (ESI): m/z calc for $[M+Na]^+$ 361.15966, found 361.16021.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3054 (w), 2954 (m), 2924 (w), 2868 (w), 1705 (s), 1585 (w), 1453 (m), 1359 (w), 1314 (w), 1276 (w), 1202 (w), 1161 (w), 1120 (m), 1087 (w), 1042 (m), 989 (w), 953 (w), 915 (w), 874 (w), 841 (w), 748 (s), 699 (s).

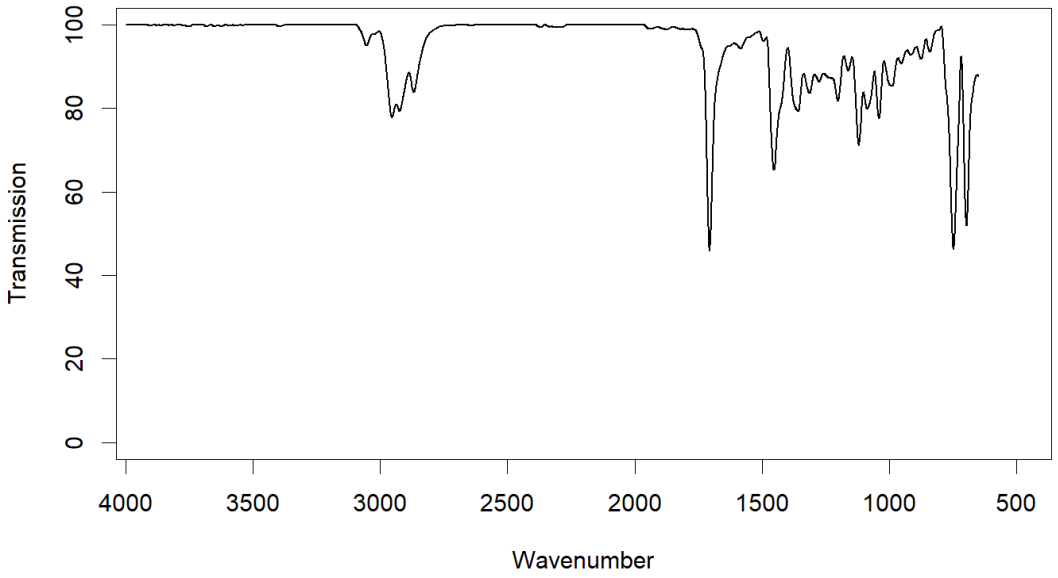


Figure S180. IR-spectrum (ATR, neat) of **3aj**.

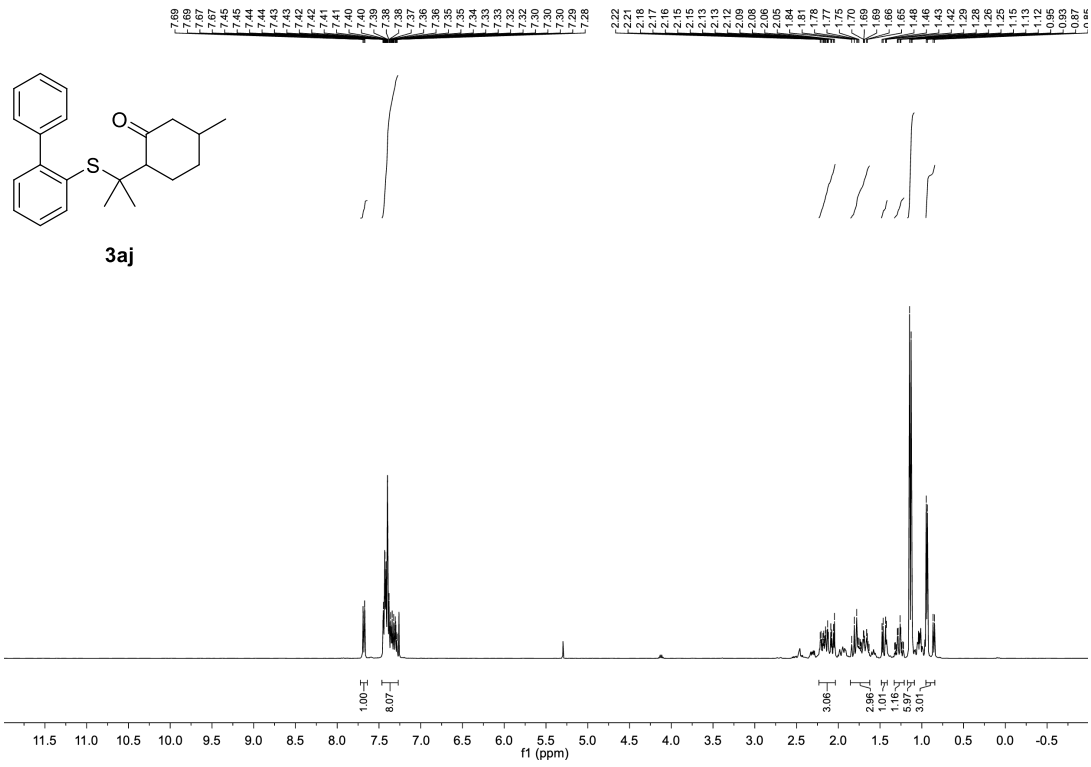
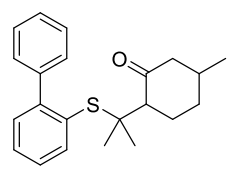


Figure S181. ^{1}H-NMR-spectrum (400 MHz, $CDCl_3$) of **3aj**.



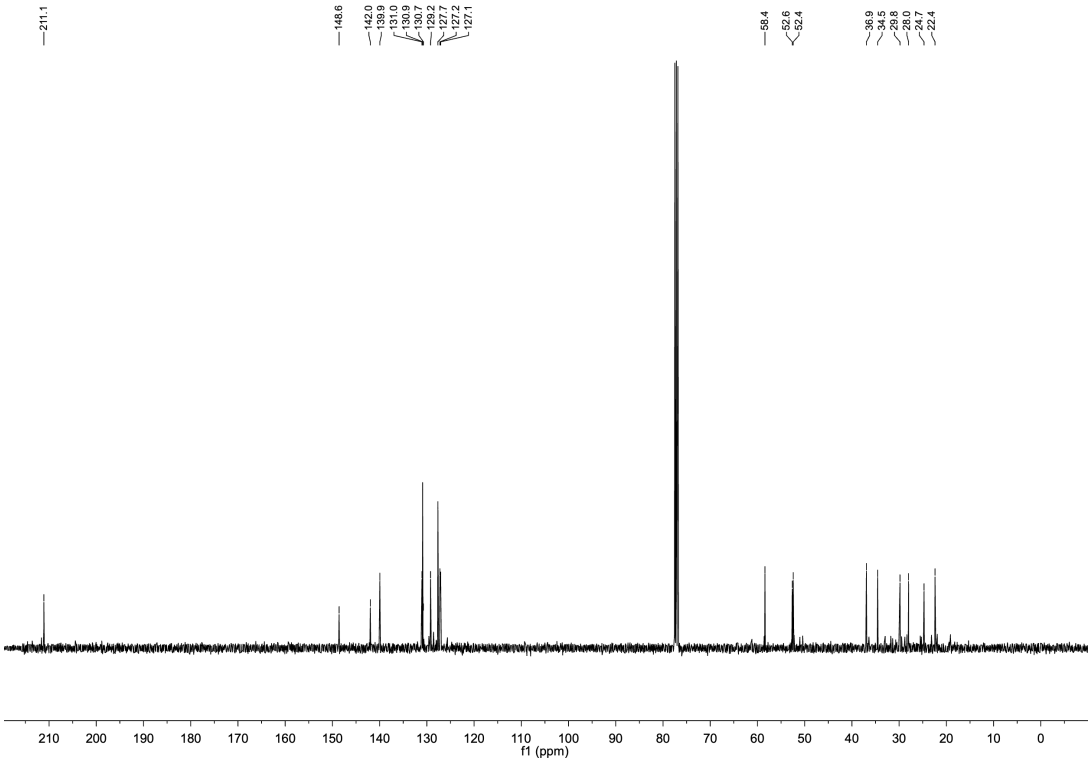


Figure S182. ^{13}C-NMR-spectrum (101 MHz, $CDCl_3$) of **3aj**.

6. Unsuccessful Substrates

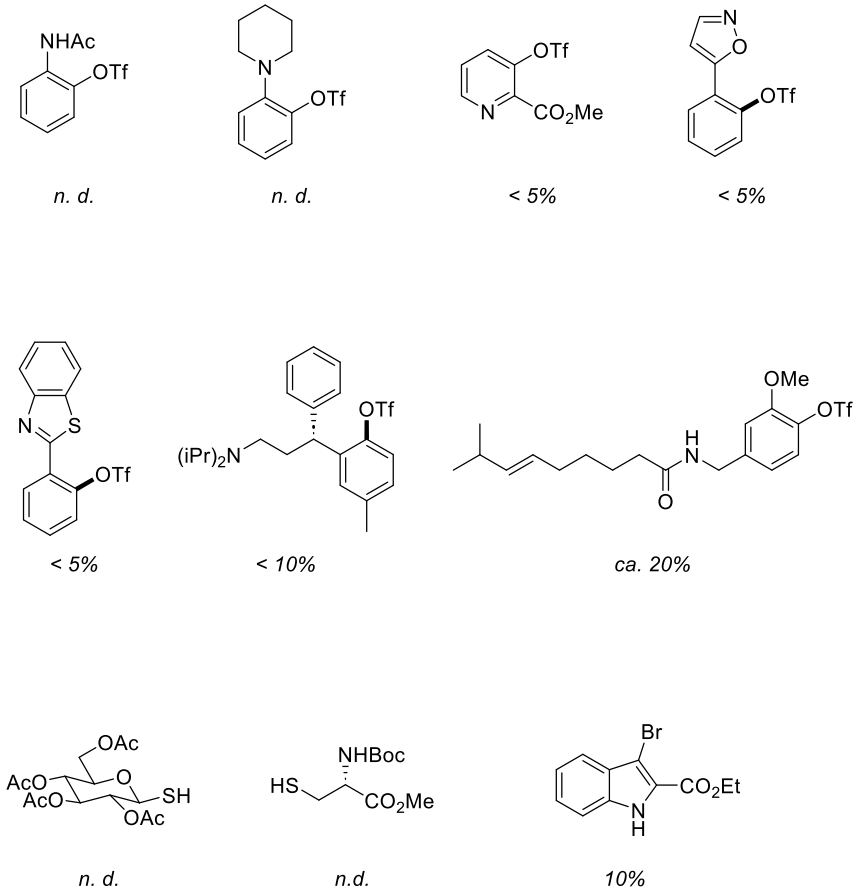


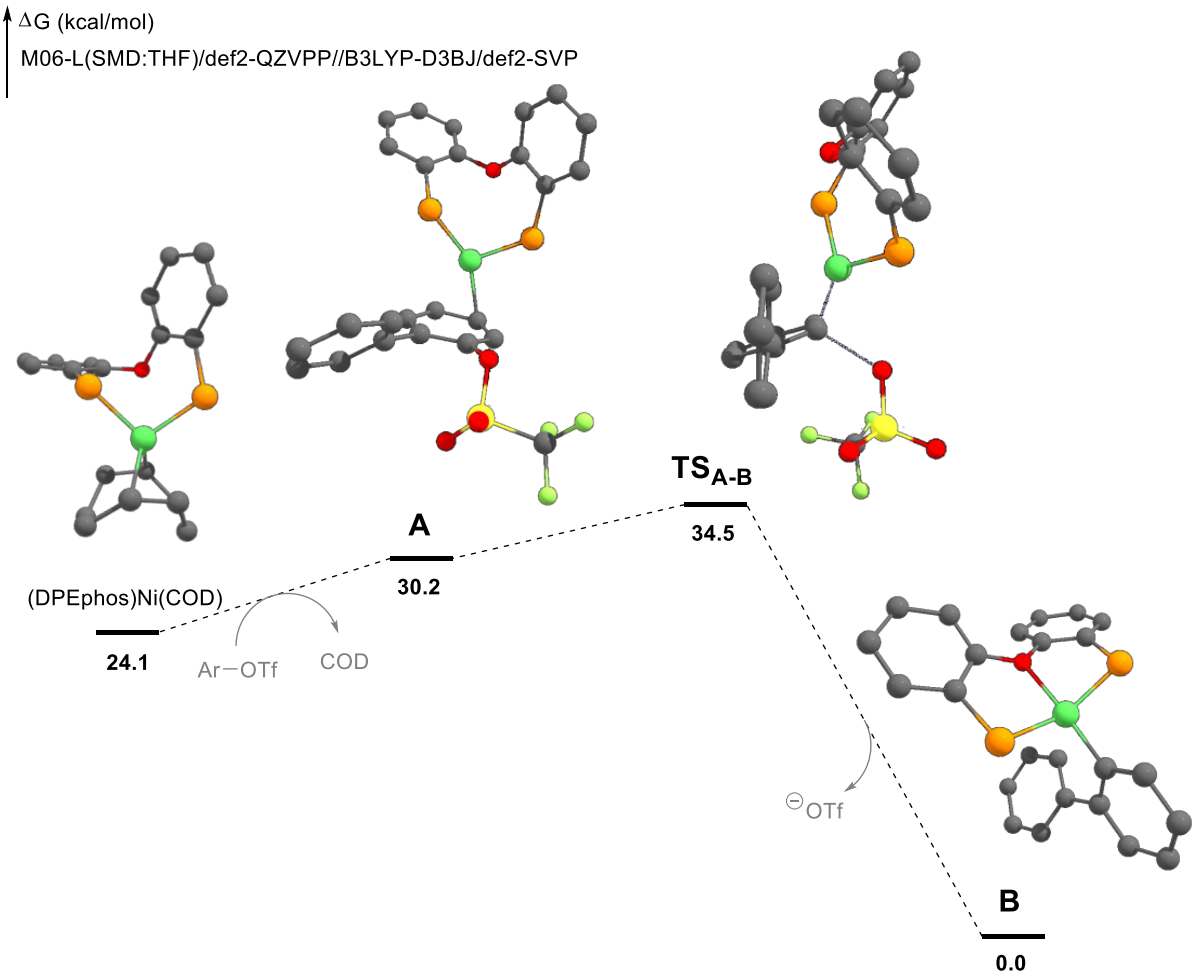
Figure S183. Unsuccessful substrates in the nickel-catalyzed C–S cross-coupling with adamantane thiol (**2b**).

7. Computational Methods and Data

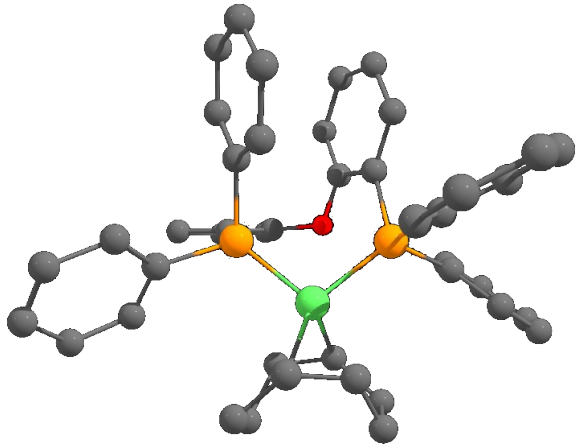
All reported computations were performed with the gaussian16 program.[19] Geometries were fully optimized at the B3LYP-D3BJ/def2-SVP level of theory.[20-22] Analytical frequency computations were undertaken in order to assure the nature of the stationary point with minima exhibiting zero and transition states exactly one imaginary mode. Intrinsic reaction coordinates were computed starting from the transition states by using the local quadratic approximation.[23, 24] Free energies were computed using standard thermochemistry equations implemented in gaussian.[25] Free energies were corrected for the one-molar standard state by adding 1.89 kcal mol^{-1} to each structure's energy.[26] In addition, M06-L/def2-QZVPP single point energies were computed on top of each structure utilizing the SMD solvation model with THF as a solvent.[27]

In the following energy landscapes of the oxidative addition, as well as the base-assisted thiol coordination, the phenyl groups of DPEphos and all hydrogens (except HS–Ad) are omitted for clarity. In the single-point structures, phenyl groups or hydrogens were omitted if necessary.

Oxidative Addition of 2-Ph-PhOTf (1a) to (DPEphos)Ni(COD)


ΔG (kcal/mol)
M06-L(SMD:THF)/def2-QZVPP//B3LYP-D3BJ/def2-SVP
(DPEphos)Ni(COD)
24.1
Ar—OTf
COD
A
30.2
TS A-B
34.5
⊖OTf
B
0.0

(DPEphos)Ni(COD):



Ni	-0.01336200	-1.20338000	-0.42670900
P	1.67854300	0.13217600	-0.11456400
P	-1.71988200	0.08238000	-0.03574500
O	-0.07103500	0.28603500	2.42358800
C	0.93771700	-2.85219000	0.59245000
H	1.67089900	-2.42431000	1.28112800
C	0.38281000	-2.29110100	-2.17784700
H	0.60581000	-1.58872200	-2.98959600
C	-0.51806000	1.54030000	2.04277800
C	-1.36737900	1.62772200	0.92817200
C	1.48034900	-3.29064100	-1.88602900
H	2.44368900	-2.79921400	-2.07703300
H	1.43183500	-4.13886600	-2.59849400
C	-5.09603000	-2.09556600	0.89391900
H	-5.85555500	-2.64625200	0.33328300
C	-3.14074600	-0.68840700	2.30577400
H	-2.37477600	-0.15747000	2.87004600
C	3.25753500	-0.32875900	-0.96279700
C	1.46984700	-3.83669000	-0.43752200
H	0.87595700	-4.76255300	-0.38959200
H	2.49527000	-4.13193800	-0.16306500
C	3.69808200	0.35181700	-2.10854300
H	3.17011400	1.24292900	-2.44956500
C	2.23144700	0.21983400	1.66643700

C	-0.95375900	-2.46354200	-1.81775200
H	-1.69358800	-1.87950900	-2.37008400
C	3.58327300	0.19556700	2.04914800
H	4.35382400	0.26804600	1.28175400
C	-3.11805000	-0.67312000	0.90254200
C	-1.77468400	2.91198100	0.53234100
H	-2.39191600	3.02771800	-0.35693800
C	-1.50069700	-3.71302200	-1.13891800
H	-0.93709100	-4.59220100	-1.48981100
H	-2.53765500	-3.87498400	-1.47400700
C	-4.10520600	-1.39334300	0.20637100
H	-4.09688200	-1.41010200	-0.88490600
C	-1.48548600	-3.65259800	0.40739600
H	-2.44767100	-3.26399800	0.76302200
H	-1.40946800	-4.67936000	0.81726700
C	-3.90214500	1.37266800	-1.37637600
H	-4.38411100	1.43443700	-0.39861600
C	-1.37735900	4.05200600	1.23162100
H	-1.69949600	5.03668100	0.88671600
C	-0.12698500	2.67090400	2.76356600
H	0.53152200	2.55495300	3.62511800
C	-0.38985900	-2.78305300	0.98047900
H	-0.61893300	-2.29200000	1.93068300
C	4.81320400	-0.09643600	-2.82299300
H	5.13622700	0.44947900	-3.71299800
C	-4.54837100	1.89208900	-2.49909700
H	-5.52898300	2.36252600	-2.39188500
C	-5.11293400	-2.10122500	2.29173800
H	-5.88627200	-2.65294100	2.83141100
C	-3.94453100	1.80905400	-3.75886600
H	-4.45216300	2.21396300	-4.63780900
C	3.97101200	-1.47023900	-0.55190900
H	3.65035500	-2.02352700	0.33059600
C	1.54671200	1.91907400	-0.56824300
C	5.51708800	-1.22568300	-2.40019900

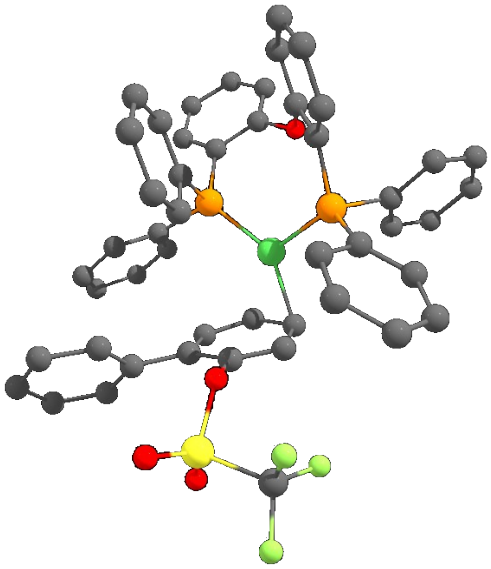
H	6.39142800	-1.57195600	-2.95629200
C	-4.13040700	-1.39669300	2.99231100
H	-4.13242400	-1.39570900	4.08527300
C	-0.56108200	3.93118000	2.35739600
H	-0.24711100	4.81810800	2.91246700
C	1.27555800	0.16815700	2.70229400
C	2.09393800	2.95814200	0.19561000
H	2.62586400	2.73098200	1.12059700
C	1.64689800	0.00168900	4.03697900
H	0.85932400	-0.05844100	4.79026400
C	-2.05281100	0.67733400	-2.76125700
H	-1.08662900	0.18168200	-2.85991100
C	5.09220300	-1.90826100	-1.25602300
H	5.63148700	-2.79462700	-0.91275200
C	3.96788100	0.06135700	3.38558600
H	5.02909200	0.04274200	3.64374200
C	-2.69625300	1.19694000	-3.88847800
H	-2.22300100	1.11456500	-4.86999200
C	0.85606200	2.23797900	-1.74630800
H	0.41588100	1.43447500	-2.33435700
C	0.71965400	3.56268600	-2.16184100
H	0.17257200	3.78841100	-3.08038800
C	1.26484200	4.59323800	-1.39110700
H	1.15013200	5.63391100	-1.70402800
C	-2.63854100	0.76774100	-1.49209400
C	2.99774200	-0.06297900	4.38207600
H	3.28845700	-0.19138400	5.42720100
C	1.94885500	4.28651400	-0.21206400
H	2.36850800	5.08793100	0.40102100

B3LYP (E_h): **-3965.710229**

M06-L (E_h): **-3967.652466**

G-E (E_h): **0.643406**

(DPEphos)Ni(2-Ph-PhOTf) (A):



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C	-1.98557446	2.33337556	0.99501600
C	-3.33753346	2.01933856	0.85208300
C	-3.72929646	0.68534456	0.72376700
C	-2.76435846	-0.32473244	0.74471000
H	-0.66436146	-0.79240944	0.85714500
H	-4.06443346	2.83347956	0.84777500
H	-4.78745146	0.43713956	0.61423000
H	-3.06248646	-1.37208844	0.66001900
O	-1.62498146	3.65654156	1.12843100
C	-1.37794046	4.15794556	2.38936100
C	-0.32476146	5.08264656	2.49566400
C	-2.14285446	3.78967856	3.49605700
C	-0.07727246	5.65486756	3.75070400
C	-1.86184446	4.35766956	4.74045200
H	-2.94441846	3.05916756	3.38280000
C	-0.83415446	5.29373156	4.86847400
H	0.72657354	6.38342156	3.85817400
H	-2.45422146	4.06697756	5.61111500
H	-0.61611946	5.74347256	5.83938100

P	0.69879254	5.34112056	0.98745500
P	0.79331254	1.82802456	0.96088400
C	1.97653154	6.54020756	1.53090200
C	2.20797554	7.73798556	0.83787800
C	2.90480054	6.13502456	2.50786000
C	3.34206854	8.50825156	1.11412800
H	1.50888454	8.06460156	0.06628100
C	4.02907954	6.90937556	2.78929400
H	2.75928254	5.19175256	3.03425200
C	4.25720254	8.09662256	2.08645600
H	3.51282554	9.43432956	0.55954200
H	4.74996254	6.56562756	3.53346900
H	5.15220554	8.68886056	2.28756700
C	-0.42129446	6.34296056	-0.06825000
C	-0.44603346	6.07405056	-1.44307500
C	-1.24485746	7.35219156	0.45161100
C	-1.27315146	6.81251656	-2.29332800
H	0.18771254	5.27493856	-1.83487800
C	-2.07253346	8.08913856	-0.39722300
H	-1.23726846	7.55869156	1.52436100
C	-2.08667946	7.82128656	-1.77080500
H	-1.28632146	6.59596256	-3.36425700
H	-2.71157946	8.87493056	0.01324300
H	-2.73678446	8.39823956	-2.43312900
C	1.62611854	0.26444156	0.46815200
C	2.63198154	-0.32499344	1.24444900
C	1.38779954	-0.22960244	-0.82740500
C	3.39780054	-1.37720344	0.73230700
H	2.84748654	0.05288456	2.24372100
C	2.13461354	-1.29438144	-1.32785000
H	0.62477554	0.24036656	-1.45388800
C	3.15182254	-1.86518144	-0.55108500
H	4.20405054	-1.79687244	1.33692900
H	1.93794254	-1.66988544	-2.33517900
H	3.75636354	-2.68154144	-0.95297900

C	1.22648754	1.98290456	2.74158300
C	0.40418654	1.55509356	3.79012200
C	2.45314754	2.59964856	3.03934600
C	0.79683554	1.75292556	5.11702200
H	-0.55223346	1.07730556	3.57171200
C	2.85533054	2.77422156	4.36333700
H	3.09045254	2.94155856	2.22188500
C	2.02150454	2.35931056	5.40694000
H	0.13939654	1.43227256	5.92860300
H	3.81608054	3.24814756	4.57973300
H	2.32585954	2.51103856	6.44521400
C	4.12680154	4.79333556	-0.13853300
C	3.08670054	4.42916156	-1.05619700
C	2.95246554	3.02837956	-1.38699500
C	3.87966154	2.09168456	-0.83677000
C	4.81161954	2.43761056	0.12436500
C	4.88365054	3.82848256	0.47150200
H	4.30970954	5.83939156	0.09828500
H	2.70898554	5.20670856	-1.72659200
H	2.39467454	2.72603956	-2.27926600
H	3.81570554	1.04935456	-1.14774900
O	5.75795354	4.23462156	1.50221800
S	7.37680254	4.29281956	1.26099900
O	7.73476754	3.77794156	-0.04703900
C	5.65922254	1.40098256	0.75765300
C	6.26557654	0.40798956	-0.03216500
C	5.83310854	1.33739356	2.15182600
C	7.00038054	-0.62415544	0.54957000
H	6.16429254	0.45985956	-1.11761600
C	6.56888954	0.30461656	2.73459400
H	5.38054254	2.09655856	2.78773500
C	7.15293154	-0.68397344	1.93834900
H	7.46577454	-1.38178544	-0.08594200
H	6.68619754	0.27478856	3.82050000
H	7.73348454	-1.48869844	2.39578700

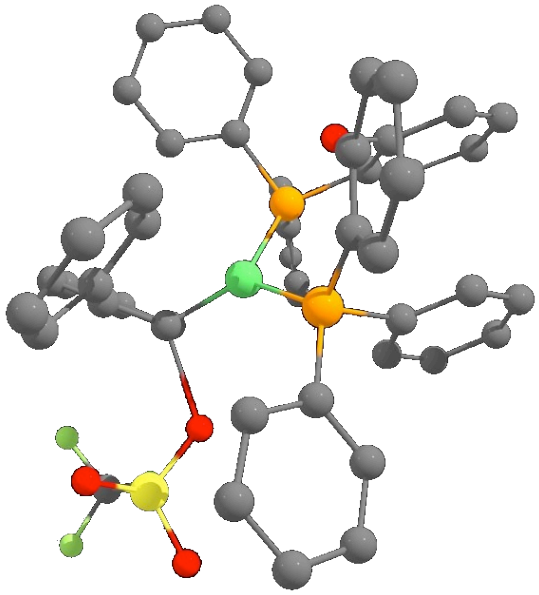
O	8.00655254	3.88592956	2.50033100
C	7.56149954	6.15752856	1.17638400
F	8.82769254	6.44119856	0.89767000
F	7.23716854	6.70100456	2.34518700
F	6.77950954	6.65707056	0.22632500

B3LYP (E_h): **-5077.154888**

M06-L (E_h): **-5080.044143**

G-E (E_h): **0.648249**

(DPEphos)Ni(2-Ph-PhOTf) ($TS_{A–B}$):



Ni	1.53696499	1.69260698	0.00000000
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C	-1.71826501	3.78245998	-0.05005600
C	-2.54298801	4.81533498	-0.49294400
C	-3.52956801	4.53388098	-1.44210100
C	-3.68666401	3.23821198	-1.93925800
H	-2.97475001	1.19759798	-1.87003300
H	-2.40413801	5.82725698	-0.11151500

H	-4.17605701	5.33951598	-1.79767400
H	-4.45140801	3.02607198	-2.68900200
O	-0.72244201	3.96046398	0.88478500
C	0.03455199	5.11397798	0.85721400
C	1.17542899	5.17744198	0.03645100
C	-0.33534201	6.17319998	1.68557900
C	1.90061299	6.38054498	0.03324000
C	0.41270699	7.35233198	1.67633600
H	-1.20961101	6.05359798	2.32770100
C	1.52167699	7.45902798	0.83475600
H	2.78940899	6.46266898	-0.59146900
H	0.12588399	8.18401198	2.32370500
H	2.10948299	8.37892198	0.81206000
P	1.78507399	3.69249698	-0.88610500
P	-0.64831501	1.25341098	0.07950100
C	3.42055099	4.24683898	-1.48718900
C	3.68646299	4.41754198	-2.85180900
C	4.45135299	4.43740798	-0.55437200
C	4.97451699	4.75422898	-3.27498200
H	2.89970099	4.27118598	-3.59194800
C	5.73077499	4.77966598	-0.98065500
H	4.26486499	4.28638098	0.50494700
C	5.99840099	4.92786298	-2.34403900
H	5.18016399	4.86006698	-4.34250300
H	6.52902599	4.87848398	-0.24383700
H	7.01167599	5.15509098	-2.68115400
C	0.76500299	3.61244498	-2.40714700
C	0.89499599	2.45296598	-3.19120100
C	-0.14607601	4.60176498	-2.78968800
C	0.10882999	2.28038498	-4.32936900
H	1.63584599	1.69842098	-2.91233200
C	-0.94528401	4.41957698	-3.92198200
H	-0.24213601	5.51185998	-2.19667400
C	-0.82367901	3.25970398	-4.68951000
H	0.21908299	1.37752598	-4.93446600

H	-1.66921501	5.18831898	-4.20083200
H	-1.45208101	3.11842298	-5.57192800
C	-1.16703201	-0.30682702	-0.72971200
C	-2.22338901	-1.09207002	-0.24426600
C	-0.47298101	-0.72176902	-1.87632400
C	-2.58497701	-2.26831102	-0.90504700
H	-2.75903001	-0.78747402	0.65683200
C	-0.83842101	-1.89522602	-2.53865000
H	0.35785199	-0.12099102	-2.24699500
C	-1.89550301	-2.67042802	-2.05323400
H	-3.40616501	-2.87653402	-0.51841600
H	-0.29019901	-2.20905202	-3.42995900
H	-2.17787701	-3.59299002	-2.56591000
C	-1.09425701	1.02840698	1.84422700
C	-2.35416401	1.36402198	2.35994000
C	-0.10945001	0.51452698	2.70252800
C	-2.62763701	1.17875498	3.71737500
H	-3.12003001	1.77975198	1.70170900
C	-0.38799301	0.32766898	4.05733300
H	0.87673199	0.26099698	2.31281500
C	-1.64627801	0.65991398	4.56755900
H	-3.61067801	1.44466898	4.11363400
H	0.38766799	-0.07116202	4.71497500
H	-1.86141301	0.51990198	5.62960600
C	2.63467199	-0.17917702	0.11108100
C	2.68296999	-1.27589302	1.00244600
C	3.22563099	-1.10598002	2.26656300
C	3.70324299	0.15816998	2.66980200
C	3.67168999	1.26959998	1.82553300
C	3.13229299	1.07444298	0.53509400
H	2.45774299	-0.37022702	-0.95045000
H	2.35072799	-2.26055702	0.66514100
H	3.28406299	-1.94831302	2.95911800
H	4.04880199	0.30154098	3.69723200
O	6.48235099	1.84198098	0.18520200

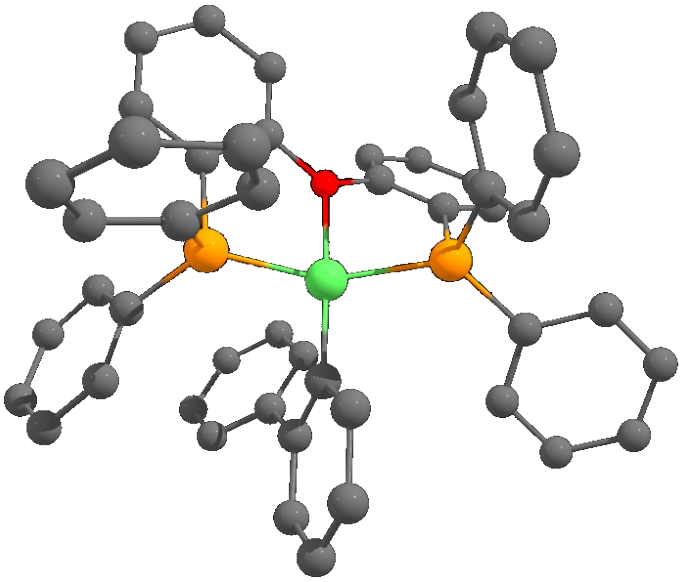
S	5.87940299	1.36486698	-1.06894400
O	4.37077099	1.50297098	-1.11565700
O	6.52054199	1.73331198	-2.33362900
C	3.95527399	2.63299898	2.34809100
C	2.87648199	3.51167798	2.54695000
C	5.25458999	3.06583098	2.64389400
C	3.09170999	4.81030098	3.01034300
H	1.86238199	3.16811098	2.33153100
C	5.46786699	4.36693798	3.10767400
H	6.09184599	2.39994398	2.43920000
C	4.39218699	5.24293398	3.28540600
H	2.24386899	5.48488698	3.14543900
H	6.48653799	4.70415298	3.31436900
H	4.56739699	6.26281598	3.63661100
C	6.08484599	-0.49341002	-0.97046600
F	7.35572199	-0.83892002	-1.17732200
F	5.32603999	-1.10643502	-1.88914600
F	5.71844999	-0.94814902	0.23489600

B3LYP (E_h): **-5077.134578**

M06-L (E_h): **-5080.034164**

G-E (E_h): **0.645091**

[(DPEphos)Ni(2-Ph-Ph)]$^+$ (B):



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C	-2.04013170	1.98400450	-1.39714601
H	-2.18242770	1.08042850	-1.99355501
C	-2.13940070	3.23925550	-1.99983201
H	-2.36488570	3.31044450	-3.06616401
C	-1.95087070	4.40029250	-1.24277401
H	-2.02805170	5.38116050	-1.71680001
C	-1.67209170	4.30375450	0.12384599
H	-1.53181070	5.20836250	0.71940999
C	-1.57483370	3.05173250	0.73403099
H	-1.35792070	2.98664250	1.80177499
C	-2.61216670	-0.91448950	0.04947799
C	-2.19744170	-2.20934250	-0.30149101
H	-1.14482870	-2.48612750	-0.22942001
C	-3.13405370	-3.13452850	-0.76748501
H	-2.80913470	-4.13956750	-1.04418201
C	-4.47762970	-2.77083250	-0.89036701
H	-5.20696270	-3.49557850	-1.25907301
C	-4.89138670	-1.47703150	-0.55252201
H	-5.94049170	-1.19218150	-0.65755501
C	-3.96262370	-0.54666850	-0.08596401
H	-4.28303870	0.46781250	0.16239399
C	-1.59459970	0.36733150	2.50035999
C	-2.73402970	-0.05101750	3.19608399

H	-3.62069870	-0.35708450	2.63820899
C	-2.72982070	-0.10998350	4.59275999
H	-3.62408270	-0.43708150	5.12614399
C	-1.57159570	0.21790950	5.29997699
H	-1.55305870	0.13876450	6.38884099
C	-0.41587370	0.63225950	4.62701299
H	0.49674730	0.85354550	5.17873099
C	-0.45187170	0.72775450	3.23952099
C	1.66602630	1.98367150	2.81538499
C	2.82647630	1.94292850	2.02286499
C	3.86864530	2.83355950	2.31518399
H	4.76803130	2.82130150	1.69576699
C	3.75540130	3.74523650	3.36447399
H	4.57466830	4.43169950	3.58494699
C	2.57263930	3.79732150	4.10716599
H	2.45942230	4.53262850	4.90648299
C	1.51695030	2.92265350	3.83580399
H	0.59239930	2.98798050	4.40659699
C	2.95979030	2.13152950	-0.83521801
C	4.19357530	2.51076750	-1.38336001
H	5.11561230	2.03123450	-1.04960601
C	4.24114030	3.50068050	-2.36831101
H	5.20273330	3.79108150	-2.79719301
C	3.06464030	4.11732950	-2.80397701
H	3.10750530	4.88997050	-3.57485601
C	1.83360530	3.74265050	-2.25596401
H	0.90968130	4.21758550	-2.59191701
C	1.77874130	2.74902650	-1.27903901
H	0.81601830	2.45474050	-0.85718401
C	4.30804330	-0.10634650	0.48962899
C	5.02824530	-0.37578150	1.66170899
H	4.72685030	0.07543250	2.60840599
C	6.13115730	-1.23088350	1.61867999
H	6.69122230	-1.43698350	2.53318899
C	6.51558930	-1.82123550	0.41235699

H	7.38185730	-2.48576850	0.38126199
C	5.78807230	-1.56623850	-0.75501801
H	6.08002830	-2.03483950	-1.69734501
C	4.68195530	-0.71807050	-0.72023101
H	4.10627530	-0.53517750	-1.62978501
C	1.04098830	-0.96167650	-0.90334101
C	0.69291330	-0.53922550	-2.19082001
H	0.29706830	0.46651350	-2.34874001
C	0.86298230	-1.38602450	-3.29128701
H	0.58558430	-1.04152150	-4.29057201
C	1.38742630	-2.66888950	-3.10881201
H	1.51411830	-3.33857450	-3.96218801
C	1.75056130	-3.09321550	-1.83063701
H	2.15505730	-4.09801850	-1.68689501
C	1.58987630	-2.25400350	-0.71252401
C	2.04146230	-2.68591750	0.63555999
C	3.24307030	-3.39453150	0.80479999
H	3.83255330	-3.66511550	-0.07162501
C	3.72312130	-3.70053650	2.07792699
H	4.67054230	-4.23367050	2.18143699
C	3.01414030	-3.30719250	3.21777999
H	3.39826530	-3.54054950	4.21320499
C	1.80238530	-2.62915650	3.06991399
H	1.21692930	-2.34458250	3.94773899
C	1.31841730	-2.33681650	1.79287599
H	0.32745630	-1.88516650	1.69370499
Ni	0.81852230	0.06939150	0.63984399
O	0.66136130	1.07712350	2.46686799
P	-1.37821770	0.24736650	0.67741699
P	2.80788930	0.90442950	0.50482699

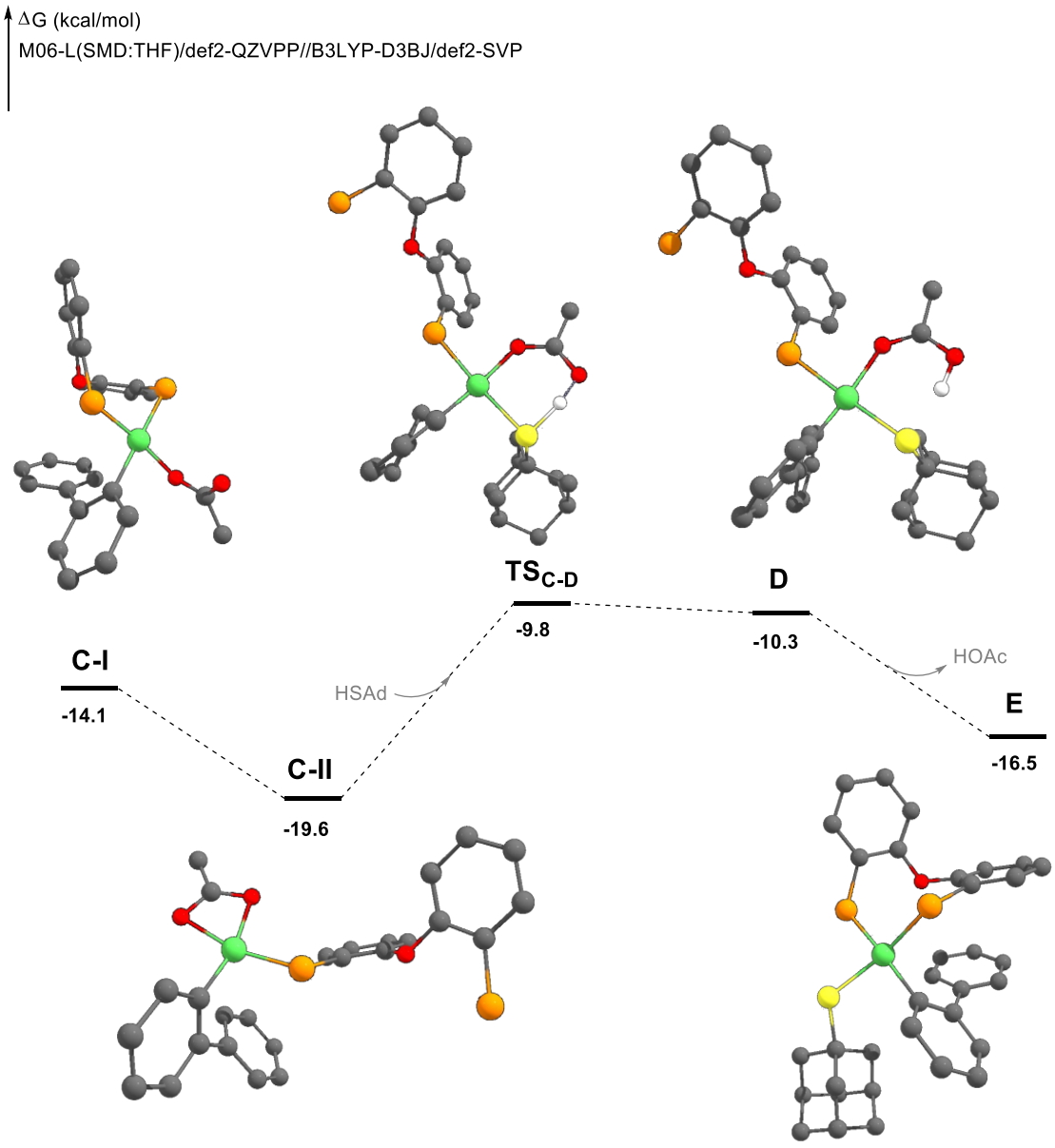
B3LYP (E_h): **-4116.090958**

M06-L (E_h): **-4118.201038**

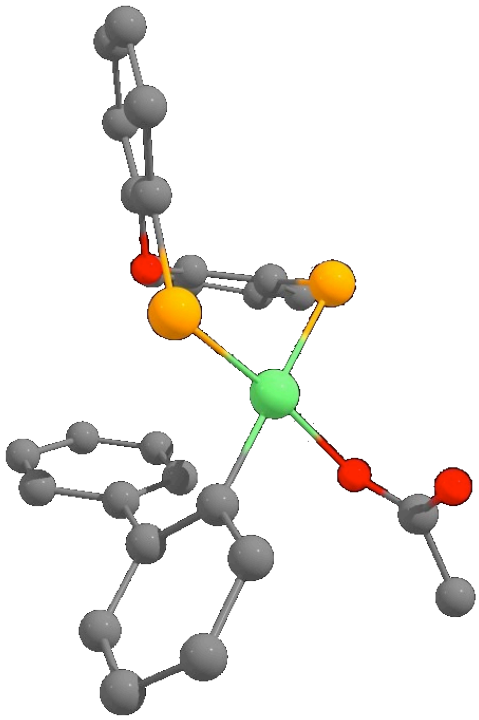
G-E (E_h): **0.629707**

Thiol Coordination of HS–Ad (2b) to (DPEphos)Ni(2-Ph-Ph)(OAc)

Energies are given relative to the oxidative addition.



(DPEphos)Ni(2-Ph-Ph)(η^1-OAc) (C-I):



C	4.37190076	2.04958688	0.00000000
C	3.08249976	1.96843188	0.53822500
C	2.25806776	0.88882288	0.21397800
C	2.74470276	-0.11239012	-0.62619500
C	4.04210976	-0.04418412	-1.16393800
C	4.86790676	1.06434088	-0.86780500
H	5.00280576	2.89299088	0.27702800
H	2.72645676	2.75336888	1.21132600
H	1.24824376	0.81672088	0.62604100
H	2.12001776	-0.97792712	-0.86142600
Ni	6.66219776	1.14552088	-1.59983200
C	4.51227776	-1.15000012	-2.03814500
C	3.70965676	-1.62603112	-3.08765700
C	5.75391376	-1.77090612	-1.80434600
C	4.13337176	-2.69030912	-3.88616900
H	2.75419276	-1.13940312	-3.28894400
C	6.16852576	-2.84277612	-2.59514600
H	6.37016476	-1.42780012	-0.97206500
C	5.36328276	-3.30618012	-3.63919000

H	3.49897976	-3.03885012	-4.70561400
H	7.13272976	-3.31619912	-2.39651100
H	5.69539376	-4.14225812	-4.25992300
O	7.23907076	0.26287488	0.07095000
C	7.22137676	1.02306188	1.11409000
O	7.25573176	2.25959688	1.08193600
C	7.16210676	0.27473088	2.43257200
H	6.15780376	-0.16711112	2.53534600
H	7.88672876	-0.55304112	2.43494800
H	7.34924476	0.95513588	3.27309200
C	6.83198876	3.58356488	-5.55707100
C	6.63093076	2.39725188	-4.84085000
C	7.13824376	1.20901588	-5.38427400
C	7.77458476	1.17717288	-6.62433200
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C	7.48836376	3.57264488	-6.78933800
H	6.49264276	4.53048788	-5.13851500
H	8.14819676	0.22927488	-7.01389800
H	8.45398676	2.35660588	-8.29590000
H	7.64764176	4.51051988	-7.32487000
O	6.94583276	0.06442388	-4.64293200
C	7.98576476	-0.81269612	-4.42056200
C	8.92385976	-0.55750512	-3.39840900
C	8.00585076	-1.99785412	-5.15264700
C	9.81907576	-1.59197512	-3.07883800
C	8.94368076	-2.98583412	-4.85364400
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C	9.83509176	-2.78981812	-3.79776900
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H	10.54641376	-3.57182812	-3.52383300
P	8.82271676	1.01942188	-2.44060800
P	5.73801076	2.27913588	-3.22563800
C	10.28584876	1.02269388	-1.31889100
C	11.56821276	0.69339188	-1.79649300

C	10.15500876	1.54147588	-0.02493400
C	12.68446276	0.81412988	-0.97028300
H	11.70528576	0.36346688	-2.82717100
C	11.27980376	1.67090588	0.79726900
H	9.18855476	1.88906388	0.33536600
C	12.54117776	1.29379388	0.33661600
H	13.67250976	0.54728488	-1.35324000
H	11.15880376	2.07791288	1.80394700
H	13.41666776	1.39149288	0.98329500
C	9.47207276	2.32945288	-3.56654600
C	9.31411476	3.65417788	-3.13151700
C	10.21698276	2.07195388	-4.72193800
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H	8.74093376	3.86444588	-2.22760300
C	10.78818876	3.12706088	-5.43818400
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C	10.62675476	4.44410388	-5.00274000
H	9.75081876	5.73203288	-3.49691800
H	11.35972476	2.91624488	-6.34532100
H	11.07466376	5.26626388	-5.56586100
C	5.59111676	4.01336688	-2.65453700
C	6.27622676	4.38434888	-1.48639300
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C	6.20869976	5.70060588	-1.02283900
H	6.83204276	3.63979788	-0.90764600
C	4.74746376	6.28018688	-2.86345200
H	4.24151176	4.67558588	-4.21489600
C	5.45173176	6.65073188	-1.71275900
H	6.73882176	5.97326288	-0.10755200
H	4.13910776	7.01587388	-3.39504700
H	5.39589676	7.67862588	-1.34600800
C	4.04188376	1.87045988	-3.82059500
C	2.92669776	2.28957088	-3.07740500
C	3.83829176	1.12396888	-4.98982200
C	1.63671776	1.97030088	-3.49921600

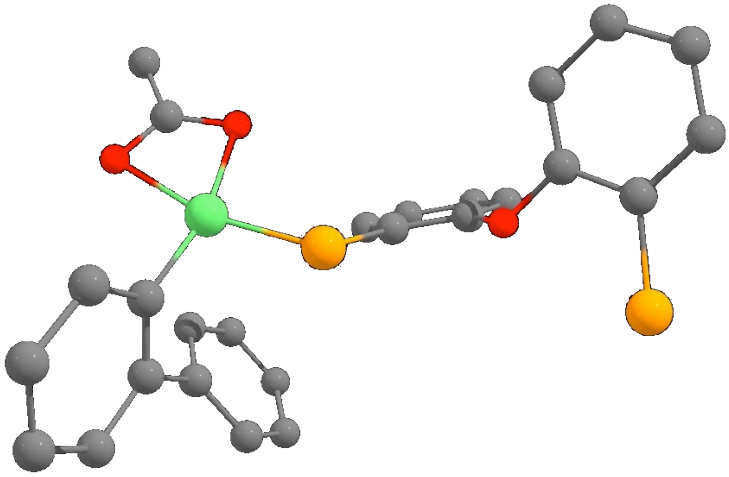
H	3.06435176	2.85163788	-2.15460700
C	2.54450776	0.81004788	-5.41226700
H	4.68464776	0.77049588	-5.57551400
C	1.43988276	1.23055188	-4.66906400
H	0.78294076	2.29453688	-2.90030000
H	2.40432876	0.22480988	-6.32409100
H	0.42825776	0.98053788	-4.99794900

B3LYP (E_h): **-4344.621208**

M06-L (E_h): **-4346.924598**

G-E (E_h): **0.677635**

(DPEphos)Ni(2-Ph-Ph)(η^2-OAc) (C-II):



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C	-4.37033400	3.37767200	-0.34168200
C	-4.14635500	2.03025500	-0.01627100
C	-3.82036700	1.10848500	-1.03410300
H	-3.48940300	0.85436500	-3.15907300
H	-3.92059400	3.23255400	-3.71891300
H	-4.46760300	4.86391600	-1.90735900
H	-4.62185600	4.08555000	0.45270200
Ni	-3.51030300	-0.68746700	-0.62430800
C	-4.18482000	1.55986800	1.39069100

C	-3.48782300	2.23797700	2.40275800
C	-4.87231400	0.37668000	1.72571600
C	-3.45142000	1.73605300	3.70575400
H	-2.93108200	3.14211800	2.15068600
C	-4.84086900	-0.12054200	3.03008800
H	-5.45527500	-0.13547000	0.95746800
C	-4.12204600	0.55173400	4.02366600
H	-2.88168400	2.26584400	4.47332900
H	-5.38461000	-1.03725100	3.27298800
H	-4.08853000	0.15677200	5.04195200
O	-3.61449200	-2.73874200	-0.42835400
C	-4.81561300	-2.67315800	-0.84619500
O	-5.29364000	-1.53964300	-1.14892000
C	-5.66077600	-3.91450700	-0.93870800
H	-5.03033200	-4.79244100	-1.13316600
H	-6.17038000	-4.06652800	0.02702600
H	-6.42797900	-3.79990800	-1.71580900
C	4.75241100	-2.04080300	-0.59109600
C	3.70685600	-1.34176600	0.03335100
C	2.42103100	-1.90255600	-0.02133200
C	2.17022300	-3.11010200	-0.67640100
C	3.22552000	-3.78397700	-1.29030400
C	4.51811200	-3.25172100	-1.24636500
H	5.76313200	-1.63061300	-0.55522000
H	1.15212000	-3.49887500	-0.71305500
H	3.03384300	-4.72472900	-1.81141400
H	5.34580000	-3.77891700	-1.72617200
O	1.39208500	-1.17964200	0.54047600
C	0.46372400	-1.80526100	1.32892500
C	-0.88541400	-1.45224700	1.15922800
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C	-1.83979000	-2.00379300	2.02718900
C	-0.11540600	-3.25023000	3.17157500
H	1.90645000	-2.96306000	2.43155200
C	-1.46014400	-2.89353700	3.03153400

H	-2.88686100	-1.73192500	1.90312500
H	0.18863200	-3.94969500	3.95404800
H	-2.21535300	-3.31289100	3.69905300
P	-1.43512700	-0.30717500	-0.15669900
P	3.88238100	0.27384100	0.92453000
C	-0.83120100	1.33212200	0.38191800
C	-1.00882500	2.45068000	-0.44839800
C	-0.29235100	1.51125700	1.66464000
C	-0.67656500	3.72535600	0.00933100
H	-1.43577000	2.33455700	-1.44383700
C	0.04568500	2.78825700	2.11631600
H	-0.15313000	0.65610900	2.32528900
C	-0.15600400	3.90007600	1.29477500
H	-0.84284000	4.58618200	-0.64161600
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C	-0.49232900	-0.78845200	-1.65170000
C	-0.89108400	-1.98366300	-2.27629700
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C	-0.21491600	-2.43731400	-3.40993300
H	-1.72269000	-2.56040100	-1.86302000
C	1.23664800	-0.50482000	-3.31934700
H	0.90834400	0.86484000	-1.68521400
C	0.84762200	-1.69662700	-3.93544400
H	-0.52319400	-3.37125500	-3.88608800
H	2.06980300	0.07464700	-3.71784400
H	1.37546700	-2.04984600	-4.82450800
C	5.72253500	0.37809400	1.06541600
C	6.34757900	-0.49873800	1.97184700
C	6.51207000	1.32461500	0.39592100
C	7.72580400	-0.45125300	2.17901900
H	5.74505400	-1.23248000	2.51522800
C	7.89274100	1.38206600	0.61546800
H	6.05015300	2.02174000	-0.30452600
C	8.50486400	0.49296200	1.50067600

H	8.19425100	-1.14812700	2.87857900
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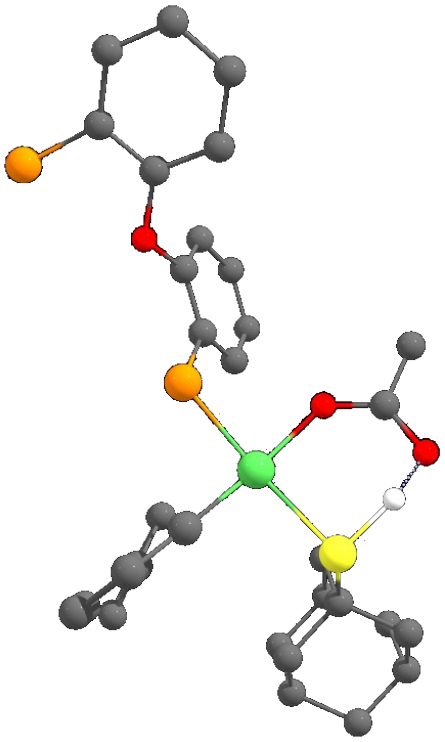
H	4.50368700	0.27663200	-2.02916600
C	2.54005400	3.52634500	-1.21031300
H	2.46939200	2.79244400	0.81952700
C	2.96945000	3.28201700	-2.51600100
H	4.02228400	1.91776800	-3.82542700
H	1.97309200	4.42908500	-0.97750900
H	2.74507400	3.99742900	-3.31083900

B3LYP (E_h): **-4344.609927**

M06-L (E_h): **-4346.925655**

G-E (E_h): **0.669851**

(DPEphos)Ni(2-Ph-Ph)(HSAd)(OAc) ($TS_{C–D}$):



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C	-5.07268164	1.48202272	-2.69637400
C	-7.74193564	2.21632772	-2.33797400
C	-6.04448864	1.04104472	-3.59220800
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C	-7.38172764	1.41794672	-3.42240800
H	-8.78710364	2.48123672	-2.18628900
H	-5.75359764	0.41047972	-4.43572800
H	-8.14416164	1.08241472	-4.12840900

P	-7.31822864	3.69771172	0.00781800
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C	-6.36380164	5.66663972	-1.76556800
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H	-6.54004664	8.51037472	0.86994600
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H	-5.93978664	9.04076172	-1.49862800
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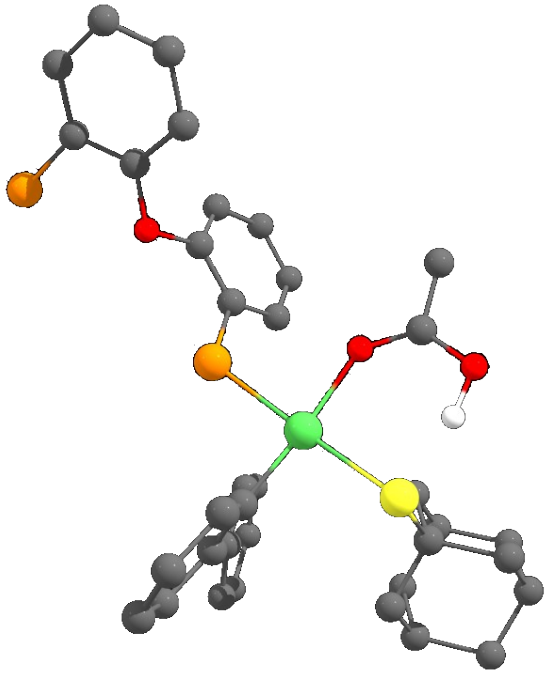
B3LYP (E_h): **-5133.229817**

M06-L (E_h): **-5135.987510**

G-E (E_h): **0.902105**

(DPEphos)Ni(2-Ph-Ph)(SAd)(HOAc) (D):



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H	-1.08694070	1.03459469	-0.14445600
H	-5.78498270	-0.47429931	0.53422300
H	-3.88719070	-1.83574331	1.44775900
H	-1.53686070	-1.06668331	1.09876300
O	-5.50911270	1.79214869	-0.78433300
C	-6.43205470	1.26901969	-1.64634400
C	-7.77320370	1.65110969	-1.48501900
C	-6.03630570	0.43706569	-2.70100500
C	-8.70316670	1.21884269	-2.44594600
C	-6.98156670	0.00744169	-3.63012600
H	-4.98618270	0.15579669	-2.79115400
C	-8.31712870	0.40960169	-3.51345500

H	-9.74833370	1.50516769	-2.33714900
H	-6.67012170	-0.63248631	-4.45915500
H	-9.05779770	0.08633169	-4.24780900
P	-8.35574170	2.69693369	-0.08956800
P	-2.99443370	3.04944569	-1.47003600
C	-7.76470470	4.36630169	-0.54892600
C	-7.82152070	5.41177969	0.38651000
C	-7.39724370	4.65452369	-1.87278600
C	-7.54169370	6.72052369	-0.00438700
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C	-7.11540070	5.96603669	-2.25875000
H	-7.34535070	3.85589269	-2.61305100
C	-7.19799370	7.00461869	-1.32803900
H	-7.61252070	7.52245369	0.73335800
H	-6.84117970	6.17568369	-3.29520200
H	-6.99301070	8.03329569	-1.63465600
C	-7.40118770	2.18886269	1.39226200
C	-7.88157070	1.08265669	2.11213900
C	-6.24829270	2.85139969	1.83585700
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H	-8.78973870	0.57867169	1.77996300
C	-5.58199370	2.40188569	2.97660900
H	-5.85486070	3.70205769	1.28008300
H	-7.58444970	-0.23495231	3.79565400
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C	-0.58168770	2.26425469	-2.61564400
C	-0.32615270	4.02677569	-0.98315300
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C	1.04940930	4.05386969	-1.23673500
H	-0.75097470	4.71229969	-0.24868300
C	1.61371230	3.17890669	-2.16698600
H	1.22295130	1.59627069	-3.59191900
H	1.68293030	4.76345669	-0.69848700

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C	-3.10793370	4.96761369	2.21869400
H	-2.34656170	3.09405869	1.46942100
C	-4.22445970	6.38275369	0.60693800
H	-4.34952370	5.60994669	-1.40559300
C	-3.78841770	6.15139269	1.91276100
H	-2.76565370	4.78164469	3.24001000
H	-4.76582270	7.29711769	0.36240100
H	-3.98251970	6.88951369	2.69464000
Ni	-10.52825370	2.35019969	0.41132000
C	-10.62872170	4.10639769	1.07317100
C	-10.29717670	4.20398669	2.43834900
C	-10.96441970	5.29464169	0.37758900
C	-10.26431970	5.42441369	3.11206700
C	-10.92392970	6.52232869	1.07445300
C	-10.57719170	6.59851169	2.41958400
H	-10.05290070	3.29551469	2.99582800
H	-9.99503370	5.45877669	4.17123700
H	-11.13331970	7.44725269	0.53430300
H	-10.54611870	7.56808769	2.92274500
O	-11.89927370	-0.82559531	0.63154400
C	-10.79894370	-0.65303831	-0.01879000
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C	-10.16445670	-1.88937231	-0.59791700
H	-9.44518970	-2.28571631	0.13789700
H	-9.60811270	-1.63028431	-1.50843800
H	-10.91829270	-2.66263531	-0.79351000
C	-11.33120370	5.32095869	-1.06602500
C	-12.14989870	6.33958469	-1.59534500
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H	-12.56941970	7.09436769	-0.92890400

C	-11.18275070	4.38791069	-3.32534700
H	-10.26895470	3.52802569	-1.58254800
C	-11.97918070	5.41683569	-3.83205300
H	-13.11318070	7.18743969	-3.32559100
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H	-12.22974170	5.45457169	-4.89466700
C	-14.28138170	3.63261869	0.15756900
H	-14.60377370	3.90424469	1.17545200
H	-13.42377570	4.27008869	-0.08839900
C	-15.42120070	3.85648869	-0.85180700
H	-15.71531570	4.91944869	-0.83380800
C	-13.84506070	2.15758069	0.14324500
C	-15.05139970	1.27563369	0.52011400
H	-15.38313070	1.52280569	1.54167900
H	-14.74942170	0.21524069	0.52380700
C	-16.62198570	2.97543069	-0.46836400
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C	-16.19759270	1.49646269	-0.48633500
H	-17.05294970	0.85992369	-0.20305900
C	-15.71636570	1.11881869	-1.89851600
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H	-16.53519070	1.25326969	-2.62604500
C	-14.93390970	3.48081569	-2.26153200
H	-14.08341870	4.11698369	-2.54818200
H	-15.73575070	3.65660969	-2.99964000
C	-13.37715270	1.77707769	-1.27187500
H	-12.50645870	2.39000069	-1.54356900
H	-13.06181670	0.72173269	-1.28633100
C	-14.51617770	2.00073469	-2.28292300
H	-14.16051470	1.73031569	-3.29194800
S	-12.51448270	1.89431069	1.40780200
H	-12.22198070	0.13833669	1.00907400
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H	-5.52245670	0.94098169	4.57033100

B3LYP (E_h): **-5133.229474**

M06-L (E_h): **-5135.988262**

G-E (E_h): **0.901738**

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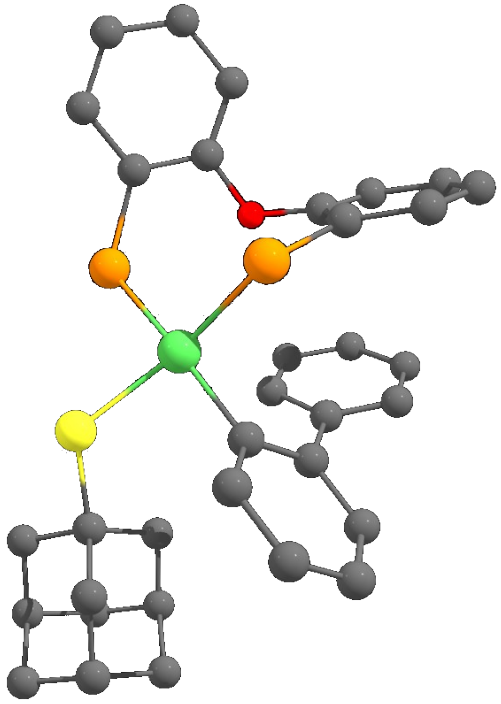

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C	0.44461439	2.13181804	2.32381900
C	-0.22273261	3.37182704	2.39643400
C	-0.40966461	4.13682504	1.21736200
H	-0.12488161	4.15592404	-0.92029100
H	0.97326139	1.94476404	-1.03349100
H	1.39883139	0.65373604	1.07108200
H	0.62746439	1.57204004	3.24466100
Ni	-1.32832061	5.83656904	1.27147100
C	-4.75899761	9.15205604	1.25246900
C	-3.98376961	8.22762004	1.96445800
C	-4.63904961	7.36055204	2.85078300
C	-6.01787161	7.42216504	3.05364300
C	-6.76848361	8.35814304	2.33965600

C	-6.14265361	9.21595204	1.43339700
H	-4.27495661	9.82006304	0.54017600
H	-6.49596961	6.73412104	3.75105400
H	-7.84962461	8.40745904	2.48848500
H	-6.73060061	9.93616004	0.86091600
O	-3.83514661	6.46096004	3.52199100
C	-4.32406061	5.18505604	3.69725200
C	-4.24710161	4.26815404	2.63388000
C	-4.89212561	4.84423904	4.92259600
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C	-5.45084961	3.57801304	5.09571000
H	-4.88847961	5.58598204	5.72183500
C	-5.44944761	2.67135504	4.03362900
H	-4.84397161	2.28824104	2.00688100
H	-5.89602261	3.30565004	6.05519900
H	-5.90738161	1.68671104	4.14987300
P	-3.27364361	4.71417404	1.12621500
P	-2.16883861	8.00508304	1.74703500
C	-3.16465461	3.11157204	0.22407800
C	-3.46162961	3.03204004	-1.14356700
C	-2.65934261	1.97319104	0.87439300
C	-3.24825561	1.84234104	-1.84666200
H	-3.85488661	3.90005204	-1.67250500
C	-2.45301361	0.78784304	0.17324100
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H	-3.48036061	1.79968104	-2.91355100
H	-2.04300161	-0.07880696	0.69572700
H	-2.57112261	-0.20880996	-1.74488600
C	-4.43655961	5.65830904	0.06141900
C	-3.87631661	6.42778804	-0.96942500
C	-5.82668261	5.62709504	0.21752000
C	-4.69240661	7.15781804	-1.83307600
H	-2.79122861	6.45075504	-1.08484200
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H	-6.27111161	5.03598604	1.02006600
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H	-4.24202861	7.75977804	-2.62552000
H	-7.72678661	6.35088804	-0.50281500
H	-6.72293761	7.71198504	-2.33192700
C	-1.77044961	9.38277504	0.59881200
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C	-1.52203561	11.76011704	0.16200300
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H	-1.45944861	8.09195104	-1.10753200
C	-1.27921261	11.49198804	-1.18827300
H	-1.51915061	12.79020004	0.52662100
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H	-1.08590361	12.31233204	-1.88383800
C	-1.51170461	8.62921604	3.36035700
C	-2.34235361	9.05653304	4.40636500
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C	0.42806639	9.10635804	4.74494100
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C	-0.40517161	9.51538104	5.79070500
H	-2.45191861	9.82126504	6.42026500
H	1.51393239	9.12212704	4.86684800
H	0.02329139	9.85215604	6.73780800
C	-0.76671161	3.82350404	3.70537200
C	-1.36077961	2.90665804	4.59410100
C	-0.72922561	5.17558004	4.08982900
C	-1.88385961	3.32467904	5.81826800
H	-1.43033261	1.85387904	4.31131100
C	-1.25086361	5.59815704	5.31222900
H	-0.26127661	5.90148604	3.42646600
C	-1.82645961	4.67254004	6.18523600

H	-2.35244561	2.59477704	6.48306500
H	-1.20342561	6.65517604	5.57713500
H	-2.23752261	5.00031604	7.14333400
S	0.52815139	6.96380504	0.59450300
C	2.24669639	6.43224204	1.07754400
C	4.30802739	5.12773804	0.41362900
C	3.09216439	7.72590904	1.05424100
C	2.32944039	5.82247504	2.48499300
H	4.71121039	4.41237904	-0.32347800
C	5.13743939	6.42170904	0.38863600
C	4.36166439	4.50559104	1.81972600
H	2.67494739	8.45271704	1.77025000
H	3.02624839	8.18948804	0.05638100
C	4.55890739	7.41638704	1.40899100
H	1.73096839	4.90551104	2.52534100
H	1.90908039	6.52327604	3.22266700
C	3.79326639	5.50416004	2.84248300
H	5.11751139	6.86344204	-0.62234300
H	6.19351939	6.20552204	0.62678200
H	3.77345139	3.57273504	1.84000900
H	5.40159039	4.24343304	2.08165800
H	5.14042839	8.35401004	1.38678200
C	4.62224239	6.79886904	2.81632500
H	3.82580239	5.06053204	3.85208700
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C	2.84363139	5.44541504	0.05822700
H	2.25325439	4.52237404	0.05349300
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B3LYP (E_h): **-4904.295099**

M06-L (E_h): **-4906.814977**

G-E (E_h): **0.856292**

Miscellaneous molecules:

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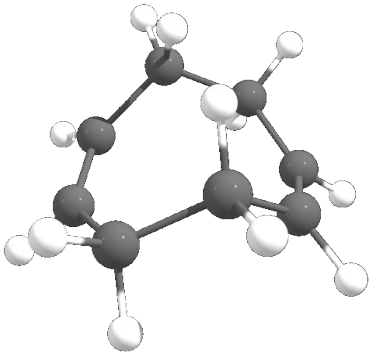

C	-0.47202799	1.80069927	0.00000000
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C	-2.37484399	3.49283127	0.20190900
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C	-1.53600299	2.40013027	0.88941800
H	-1.10658599	2.78851327	1.82226500
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C	-0.43945799	5.19620927	0.00001100
H	-0.14827699	6.12495427	-0.50528400
C	0.62446301	4.59675727	0.88947700
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H	1.31384801	5.39975527	1.19602100
C	1.46333101	3.50412727	0.20189200
H	1.97853901	3.95194827	-0.66752300
H	2.27952101	3.19715027	0.88460500
C	0.75326201	2.26681927	-0.28039500
H	1.35531401	1.66034227	-0.96859300

B3LYP (E_h): **-311.843127**

M06-L (E_h): **-312.127470**

G-E (E_h): **0.148365**

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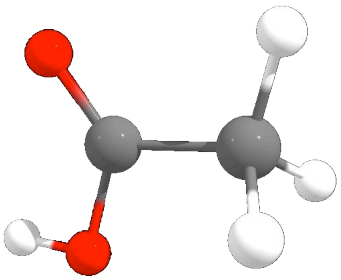

C	-0.47341116	1.84809062	-0.02419283
C	1.01406884	1.60967962	-0.02424783
H	1.29722684	1.01930562	-0.90923683
H	1.54138684	2.57038562	-0.02559583
H	1.29777984	1.02160162	0.86201117
O	-1.01803516	2.92275462	-0.02424383
O	-1.16237716	0.68556262	-0.02423083
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M06-L (E_h): **-229.17542**

G-E (E_h): **0.034649**

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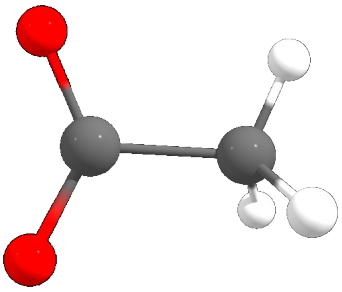

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H	-2.21138929	0.09590341	-0.00004600
H	-2.22333729	1.66699141	0.88418200

H	-2.22332729	1.66704641	-0.88417500
O	0.22194671	2.34415441	-0.00001300
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B3LYP (E_h): **-228.338549**

M06-L (E_h): **-228.676546**

G-E (E_h): **0.020310**

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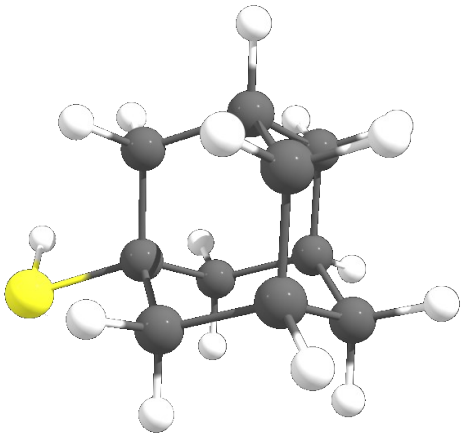

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C	-0.24782504	2.60624850	-1.25590800
C	-2.31228604	1.89054350	0.00099800
H	-2.67426304	1.37154450	0.90407000
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H	-2.46749804	3.86612650	0.90786600
H	-3.91886404	3.36320450	0.02135200
C	-0.76043604	4.06018850	-1.25590000
H	-0.37544504	4.58859750	-2.14373300
H	-0.37544304	4.58858850	-0.36806200
C	-2.30012504	4.06720550	-1.25589900
H	-2.65348504	5.11159450	-1.25589200
C	-2.81610704	3.34438750	-2.51237900
H	-3.91886504	3.36321850	-2.53315600
H	-2.46750004	3.86615250	-3.41966600

C	-0.77172504	1.88717550	-2.51182600
H	-0.39377804	0.85089650	-2.52908600
H	-0.38052804	2.38840750	-3.41128600
C	-2.82719304	1.16772850	-1.25591700
H	-2.48624904	0.11835650	-1.25592300
H	-3.93014104	1.14764250	-1.25591700
C	-2.31228604	1.89055850	-2.51282200
H	-2.67426304	1.37157050	-3.41590000
S	1.59821496	2.69625150	-1.25590700
H	1.80990796	1.35888550	-1.25591600

B3LYP (E_h): **-788.589746**

M06-L (E_h): **-789.057744**

G-E (E_h): **0.209116**

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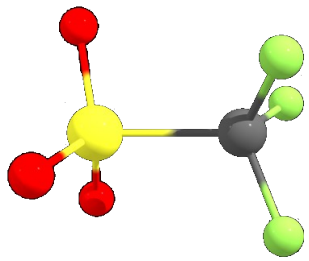

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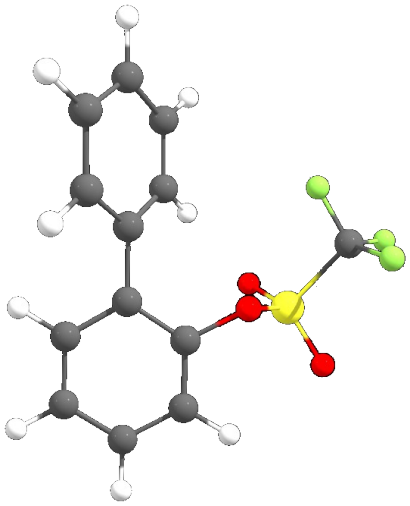
F	2.51225588	-0.86479298	1.23551900
F	2.51228288	-1.65414398	-0.77979300
O	5.20751688	0.45218102	0.90175500
O	5.20752188	-0.46166598	-1.42936100
O	5.20752988	-2.02355498	0.52761100
S	4.89789088	-0.67768298	0.00000300

B3LYP (E_h): **-960.961523**

M06-L (E_h): **-961.870401**

G-E (E_h): **-0.005264**

2-Ph-PhOTf:



C	1.80548200	0.81851200	0.00955100
C	2.89747900	1.67936400	-0.20168800
C	2.75540100	3.06648100	-0.16040200
C	1.50787700	3.63515100	0.10958300
C	0.40875300	2.80976900	0.34834100
C	0.57178600	1.42561000	0.29257700
H	3.86969300	1.23626200	-0.42678900
H	3.62159700	3.70581500	-0.34395300
H	1.38791100	4.71987700	0.14517100
H	-0.57128000	3.22241000	0.59048000
C	1.98639300	-0.65520800	-0.03674700
C	1.17021300	-1.46902000	-0.83965500
C	3.01396700	-1.25486200	0.71074600
C	1.37238500	-2.84900900	-0.88204800
H	0.38333200	-1.01704500	-1.44298800
C	3.21452500	-2.63572600	0.66660400
H	3.64749500	-0.63191700	1.34642200
C	2.39215400	-3.43777300	-0.12900200
H	0.72923400	-3.46763200	-1.51246100
H	4.01257900	-3.08702800	1.26101900
H	2.54651100	-4.51888400	-0.16304800
O	-0.51910400	0.59801800	0.61037700
S	-1.85152400	0.66152700	-0.34536200

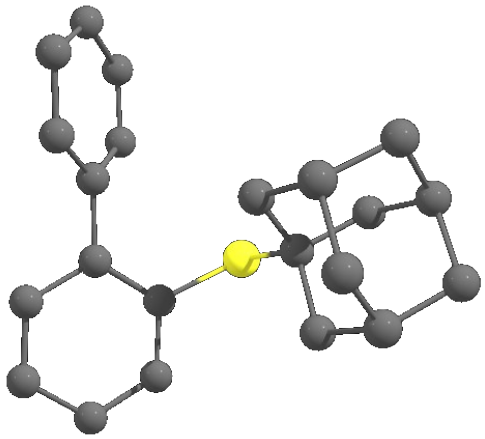
C	-2.59938800	-0.91579900	0.34340200
F	-3.78964400	-1.05750000	-0.22457100
F	-1.83615500	-1.95362600	0.04384700
F	-2.73617400	-0.81586800	1.65405700
O	-2.70718900	1.76475100	0.05282100
O	-1.48959400	0.43619600	-1.73515400

B3LYP (E_h): **-1423,298022**

M06-L (E_h): **-1424,529961**

G-E (E_h): **0.154415**

2-Ph-PhSAd:



C	-2.81468542	1.62587410	0.00000000
C	-2.66502942	0.24366210	-0.10465700
C	-3.48616942	-0.53041890	-0.94577900
C	-4.49699142	0.13306610	-1.68589200
C	-4.63008442	1.52724810	-1.58128800
C	-3.80069042	2.27498310	-0.74560900
H	-2.15261342	2.19629610	0.65586900
H	-1.87774342	-0.25918390	0.46108300
H	-5.40655342	2.01747810	-2.17073000
H	-3.92332842	3.35863810	-0.68057500
C	-3.26044942	-2.00040490	-0.98990800
C	-3.09819442	-2.69076990	-2.20225700
C	-3.18571542	-2.72844890	0.20945600

C	-2.88332942	-4.06954690	-2.21264100
H	-3.13934942	-2.14087790	-3.14218500
C	-2.97869842	-4.10916390	0.20025700
H	-3.32087342	-2.20641390	1.15956600
C	-2.83016742	-4.78581290	-1.01299500
H	-2.75607442	-4.58854090	-3.16578500
H	-2.93878342	-4.65827290	1.14417500
H	-2.66954342	-5.86657190	-1.02426600
S	-5.62841942	-0.72448990	-2.78163000
C	-8.80026942	-3.27597990	-0.56544400
H	-8.32296142	-4.18404190	-0.97088200
H	-9.67223142	-3.60511890	0.02489600
C	-9.25706142	-2.36130690	-1.71507700
H	-9.96197142	-2.90440990	-2.36622700
C	-7.80841842	-2.51536990	0.33117300
H	-7.47003942	-3.17033790	1.15121500
C	-6.58682442	-2.09009090	-0.50508500
H	-6.06874342	-2.97123690	-0.91211600
H	-5.86515442	-1.55799490	0.13221200
C	-8.03346442	-1.93652090	-2.54832900
H	-8.34628742	-1.29333490	-3.38757200
H	-7.53776842	-2.82147790	-2.97991300
C	-7.03835842	-1.17445490	-1.65262700
C	-7.72677442	0.07185810	-1.07542600
H	-7.01692142	0.63434010	-0.44894100
H	-8.03500142	0.73617710	-1.89891100
C	-9.94194342	-1.11136190	-1.13586000
H	-10.83277042	-1.40377690	-0.55453900
H	-10.29039442	-0.45728390	-1.95309600
C	-8.49190342	-1.26554790	0.91115300
H	-9.35700742	-1.55766590	1.53043200
H	-7.79204842	-0.72320590	1.56941900
C	-8.94985042	-0.35149690	-0.23834100
H	-9.43455042	0.54985310	0.17250100

B3LYP (E_h): **-1250.418897**

M06-L (E_h): **-1251.295872**

G-E (E_h): **0.359871**

8. Crystallographic Data

Suitable crystals of **Ni1** for X-ray structure analysis were selected in a glovebox and coated with Parabar 10312. X-ray data were collected on a Bruker APEX III DUO (MoK_α (λ = 0.71073 Å)). The structure was solved by direct methods and refined against all data by full-matrix least-squares methods on F2 using ShelXtl and ShelXle. However, due to bad crystal quality, only a connectivity could be obtained, and structural parameters should not be discussed. The structure of **Ni1** showed disorder in the solvent molecules and part of the ligand.

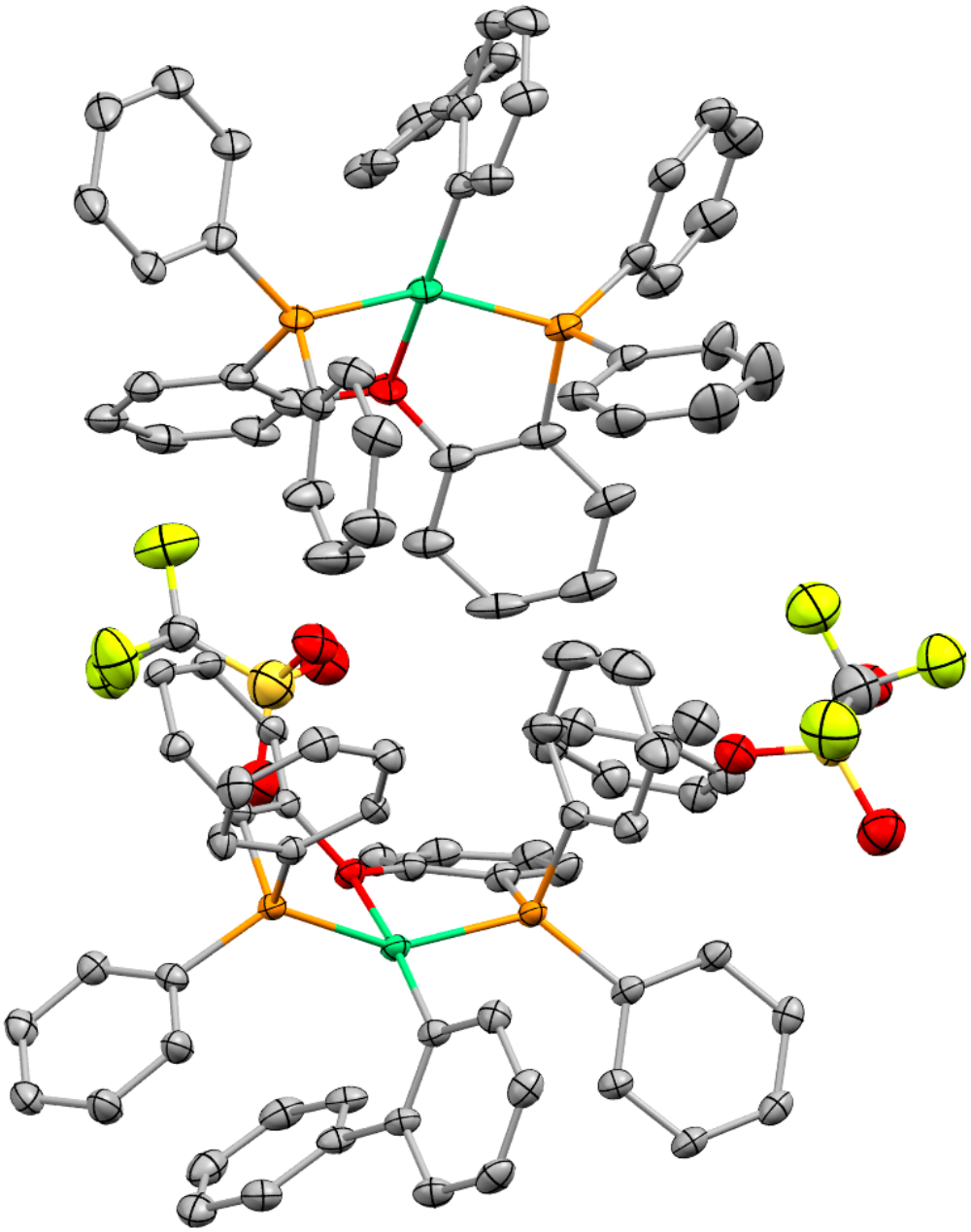


Figure S184. ORTEP of **Ni1**. Hydrogen atoms and the disorder of the whole molecule are omitted for clarity. The unit cell contains two independent molecules and one molecule of co-crystallized toluene. Atomic

displacement ellipsoids were set at 50% probability. The crystal quality does not allow for discussion of bond distances and angles.

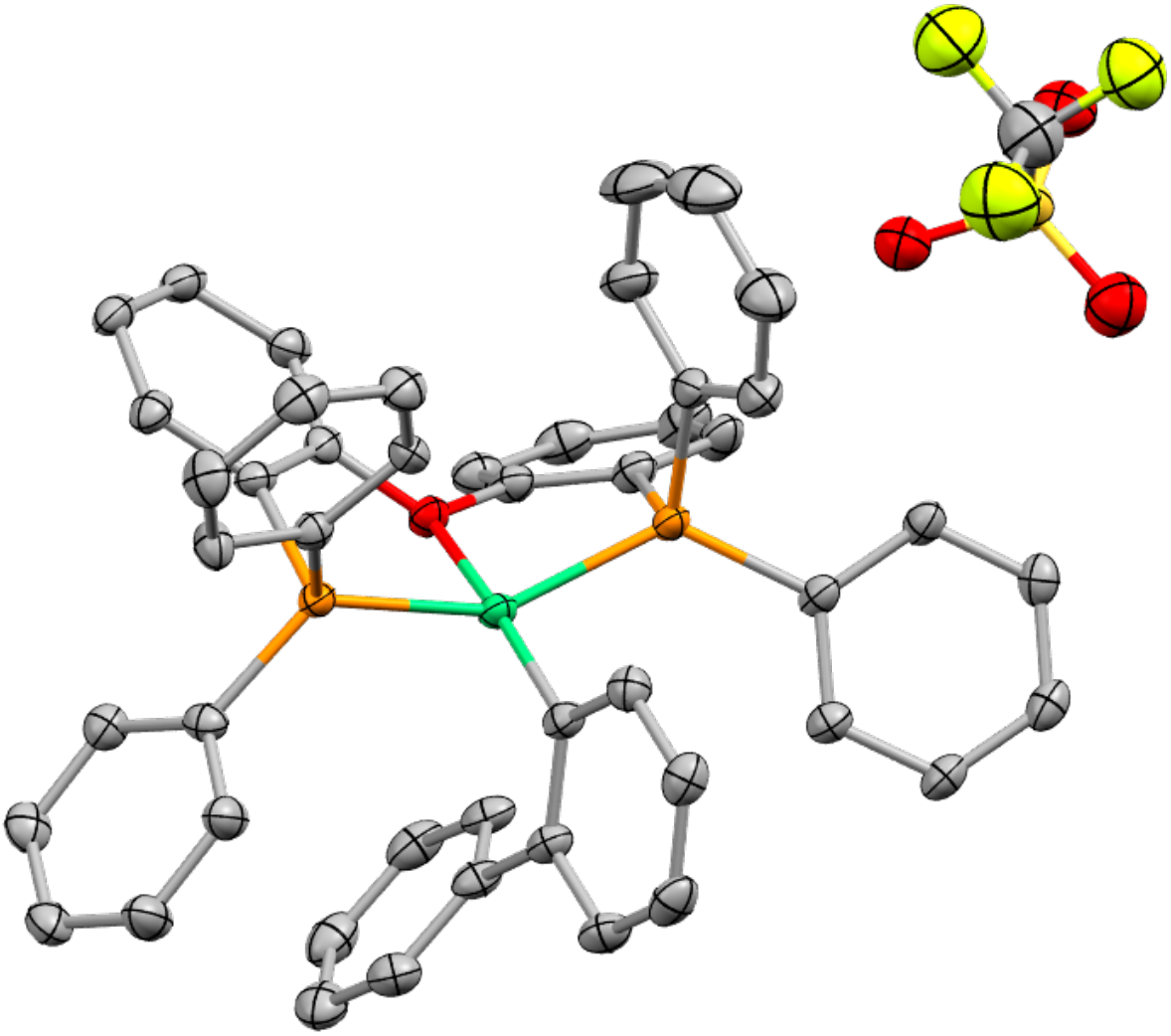


Figure S185. Molecular structure of **Ni1**. Only one molecules of the unit cell is displayed, and hydrogen atoms as well as co-crystallized toluene are omitted for clarity.

Table S6. Crystallographic data of **Ni1**.

Empirical formula	$C_{52.5}H_{41}F_3NiO_4P_2S$
M_r / g mol^{-1}	945.56
***T* / [K]**	100(2)
Λ / [Å]	0.71073
Crystal system	triclinic
Space group	P$\bar{1}$
Z	4
***a* [Å]**	13.2226(6)
***b* [Å]**	13.9605(7)
***c* [Å]**	24.1892(12)
α [°]	90.909(2)
β [°]	91.683(2)
γ [°]	94.416(2)
***V* / [Å^3]**	4449.3(4)
***D_c* / [mg m^{-3}]**	1.412
***μ* / [mm^{-1}]**	0.615
F(000)	1956
Crystal size / mm	0.303x0.247x0.190
***Θ* range / °**	1.545– 27.359
Limiting indices	$-17 \le h \ge 17$ $-18 \le k \ge 18$ $0 \le l \ge 31$
Reflects. Collect.	20063
Independent Reflects	20063
Completeness	99.7%
Absorp. Corr.	empirical
Parameters/ restraints	1405/1775
***R_1*, *ωR_2* [*I* >2σ(*I*)]**	0.0667, 0.1868
***R_1*, *ωR_2* (all data)**	0.0870, 0.2031
GooF on *F*^{2}	1.141
$\Delta\rho_{max,min}$ / e Å^{-3}	3.174, -1.433

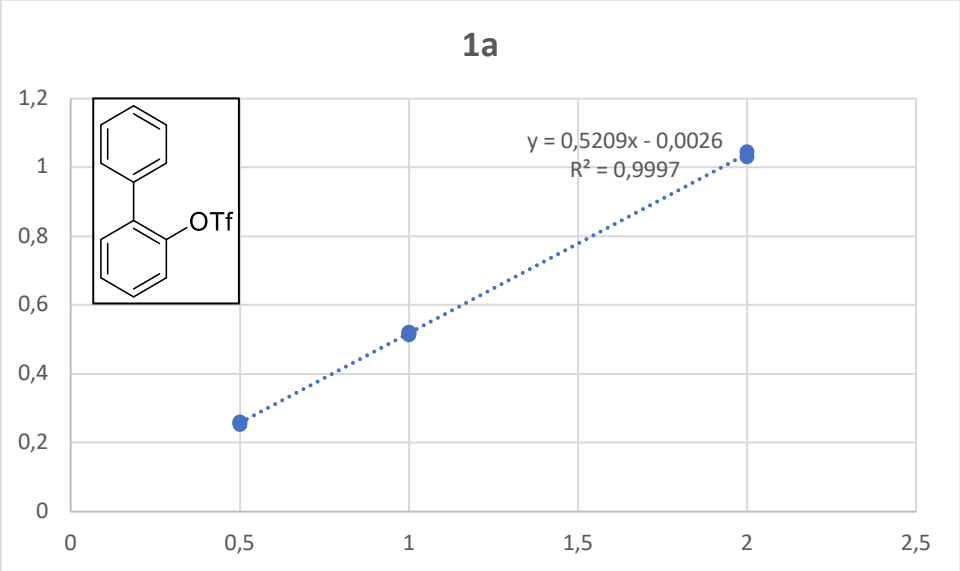
9. GC-FID Calibration Data

The quantification of GC-yields was achieved by adding a standard compound (n-pentadecane) to reaction mixtures before quenching (usually 100 µL) and applying the general formula:

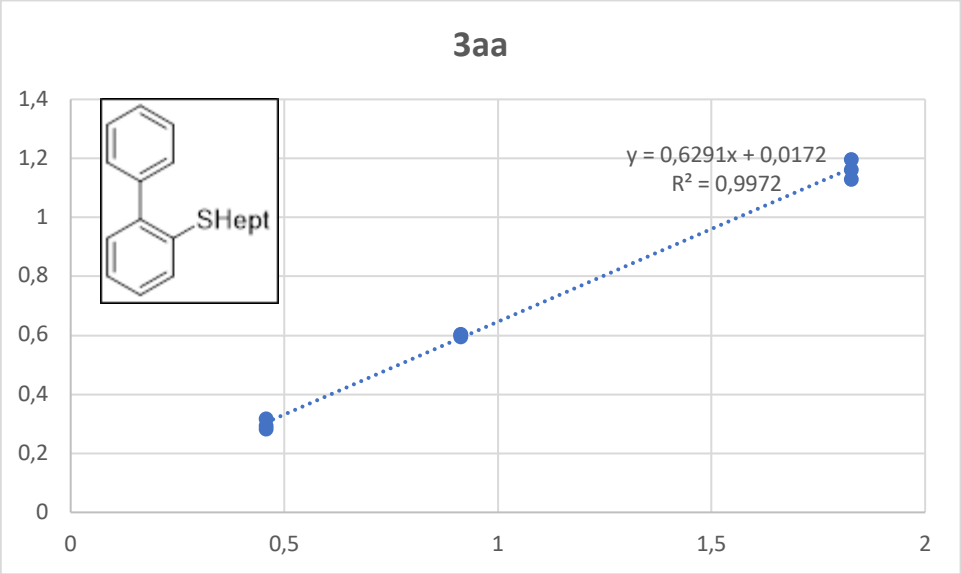
$$\frac{A(\text{compound})}{A(\text{standard})} = R \times \frac{(\text{compound})}{m(\text{standard})}$$

R: Response factor of compound
A: Peak area determined by GC-FID
m: mass of compound

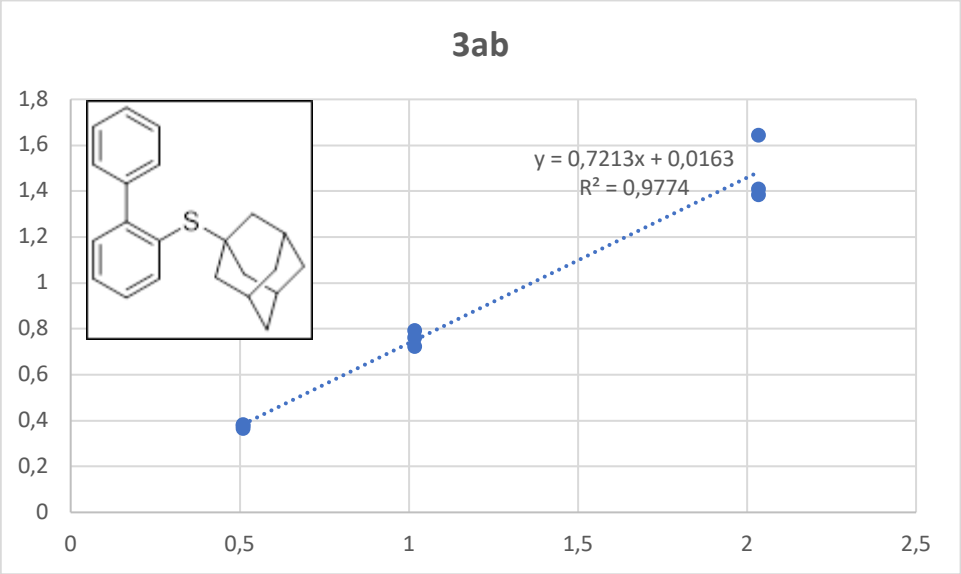
The R values were determined by GC calibrations of respective compounds with pentadecane in ethyl acetate and measuring different mass ratios.



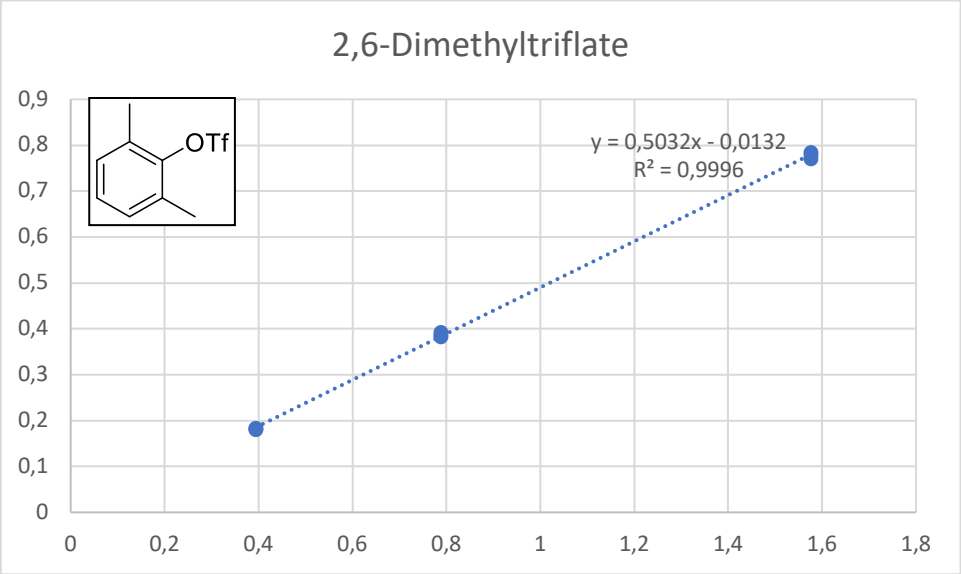
	m(Sub)	**m**(St)	**m**(Sub)/**m**(St)	**A**(Sub)	**A**(St)	**A**(Sub)/**A**(St)
f1	2,47	4,93333333	0,5	3557	14054	0,2530952
f2	2,47	4,93333333	0,5	3853	14900	0,2585906
f3	2,47	4,93333333	0,5	3806	14588	0,26089937
f4	2,47	2,46666667	1	3855	7397	0,52115723
f5	2,47	2,46666667	1	3881	7480	0,51885027
f6	2,47	2,46666667	1	3512	6740	0,52106825
f7	4,93	2,46666667	2	7214	6890	1,04702467
f8	4,93	2,46666667	2	7661	7431	1,03095142
f9	2,47	2,46666667	1	3883	7558	0,51376025



	m(Sub)	**m**(St)	**m**(Sub)/**m**(St)	**A**(Sub)	**A**(St)	**A**(Sub)/**A**(St)
f1	2,54	5,56666667	0,45658683	4468	14040	0,31823362
f2	2,54	5,56666667	0,45658683	4457	15181	0,29359067
f3	2,54	5,56666667	0,45658683	4217	14880	0,28340054
f4	2,54	2,78333333	0,91317365	4772	8007	0,59597852
f5	2,54	2,78333333	0,91317365	4648	7711	0,60277526
f6	2,54	2,78333333	0,91317365	4228	7005	0,60356888
f7	5,08	2,78333333	1,82634731	8449	7063	1,19623389
f8	5,08	2,78333333	1,82634731	9077	8033	1,1299639
f9	5,08	2,78333333	1,82634731	8386	7209	1,16326814



	m(Sub)	**m**(St)	**m**(Sub)/**m**(St)	**A**(Sub)	**A**(St)	**A**(Sub)/**A**(St)
f1	2,95	5,8	0,50862069	6289	16593	0,37901525
f2	2,95	5,8	0,50862069	5675	14764	0,38438093
f3	2,95	5,8	0,50862069	5574	15221	0,36620459
f4	2,95	2,9	1,01724138	5572	7025	0,79316726
f5	2,95	2,9	1,01724138	5723	7918	0,72278353
f6	2,95	2,9	1,01724138	5934	7771	0,76360829
f7	5,90	2,9	2,03448276	9784	7055	1,38681786
f8	5,90	2,9	2,03448276	11193	6809	1,64385372
f9	5,90	2,9	2,03448276	11087	7860	1,4105598



	m(Sub)	**m**(St)	**m**(Sub)/**m**(St)	**A**(Sub)	**A**(St)	**A**(Sub)/**A**(St)
f1	2,69	6,83333333	0,39390244	3292	18195	0,18092883
f2	2,69	6,83333333	0,39390244	3392	18442	0,18392799
f3	2,69	6,83333333	0,39390244	3316	18136	0,18284076
f4	2,69	3,41666667	0,78780488	3191	8283	0,38524689
f5	2,69	3,41666667	0,78780488	3389	8624	0,3929731
f6	2,69	3,41666667	0,78780488	3200	8367	0,38245488
f7	5,38	3,41666667	1,57560976	6970	8884	0,78455651
f8	5,38	3,41666667	1,57560976	6591	8455	0,77953873
f9	5,38	3,41666667	1,57560976	6685	8670	0,7710496

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