Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Hydroalkylation of styrenes enabled by boryl radical mediated halogen atom transfer

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Contents

1. General information

All components as well as reagents and solvents were used as received without further purification, unless stated otherwise. Reagents and solvents were bought from Sigma Aldrich and BLDpharm and if applicable, kept under argon atmosphere. Technical solvents were bought from VWR International and Biosolve, and are used as received. Product isolation was performed using silica (60, F254, Merck™), and TLC analysis was performed using Silica on aluminum foils TLC plates (F254, Supelco Sigma-Aldrich™) with visualization under ultraviolet light (254 nm and 365 nm) or appropriate TLC staining. ^{1}H (400MHz) and ^{13}C (100MHz) NMR spectra were recorded at ambient temperature using a Bruker Avance II+ 600 or a Bruker Avance III HD 400. ^{1}H NMR spectra are reported in parts per million (ppm) downfield relative to $CDCl_3$ (7.26 ppm), ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.2 ppm). NMR spectra uses the following abbreviations to describe the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, hept = heptet, m = multiplet, dd = double doublet, td = triple doublet. Known products were characterized by comparing to the corresponding ^{1}H NMR and ^{13}C NMR from literature. GC analyses were performed on: GC-FID (Varian 430-GC) in combination with an auto sampler (Varian CP-8400), on GC-FID (Shimadzu GC-2014 equipped with CP-Sil 8 CB column and FID-2014 detector), on GC-MS combination (Shimadzu GC-2010 Plus coupled to a Mass Spectrometer; Shimadzu GCMS-QP 2010 Ultra) with an auto sampler unit (AOC-20i, Shimadzu). Melting points were determined with a Buchi B-540 capillary melting point apparatus in open capillaries and are uncorrected.

Chemicals: DMF (99.8%, extra dry), DMA (99.8%, extra dry) and DMSO (99.8%, extra dry) were purchased from Acros Organics and used as purchased. The transition metal photocatalysts $Ru(bpy)_3(PF_6)_2$, $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$, *fac*-Ir, Mes-Acr-Me$^+$ were purchased from commercial sources. The organic photocatalysts 4CzIPN, *t*Bu4CzIPN and 3DPAFIBN were prepared by the procedure outlined in previous publications.[1]
Deuterated solvents were used as purchased ($CDCl_3$).
Photochemical experiments were performed magnetically stirred in 10 mL glass test tubes with screw caps equipped with silicon septa. The tubes were irradiated with a blue Kessil light (456 nm, 40W) or a violet Kessil light (390 nm, 52W) in an EvoluChem™ PhotoRedOx Box. To maintain a constant reaction temperature of 35°C, the setup was cooled by a constant airflow (Figure S1, A, B).

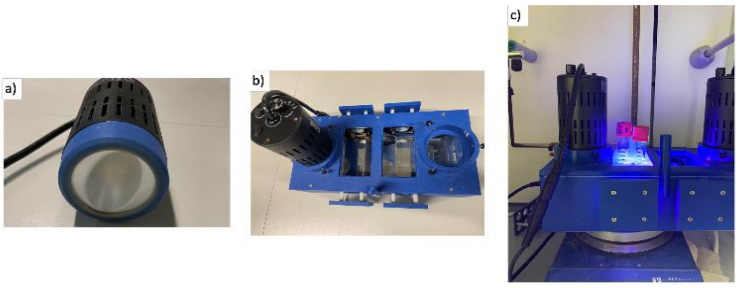
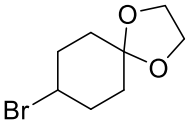


Figure S1: *a) Kessil light; b,c) Setup using EvoluChem™ PhotoRedOx Box.*

2. Synthesis and characterization of starting materials

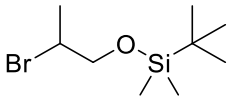
The starting materials described below were prepared according to reported procedures.

2.1 8-bromo-1,4-dioxaspiro[4,5]decane



8-Bromo-1,4-dioxaspiro[4,5]decane was synthesized following a reported procedure.[2] 1,4-Dioxa-spiro[4,5]-decane-8-ol (1 equiv) and CBr_4 (1.2 equiv) were dissolved in dry CH_2Cl_2 (0.1 M). The solution was cooled to 0°C and PPh_3 (1.2 equiv) was added. After 24 h, the solvent was removed and the residue was extracted into diethylether. The crude residue was purified by column chromatography (EtOAc/hexanes 1:3) to afford a colorless liquid.

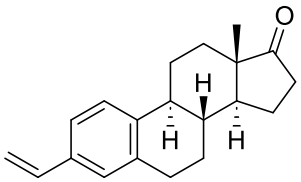
2.2 (2-bromopropoxy)(tert-butyl)dimethylsilane



The compound was synthesized according to a reported procedure.[3] 2-Bromopropan-1-ol (1 equiv) and imidazole (2.5 equiv) were dissolved in DMF (0.6 M). TBDMS-Cl (1.2 equiv) was then added to the reaction mixture. The reaction mixture was stirred for 3 hours until the starting material was consumed. The reaction mixture was then extracted in Et_2O and the combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The crude residue was purified by column chromatography (hexanes) to afford a colourless liquid.

2.3 (8R,9S,13S,14S)-13-methyl-3-vinyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one

The compound was synthesized according to a reported procedure.[4] Estrone (1.0 equiv) was dissolved



in CH_2Cl_2 (0.2 M solution) and the solution was cooled down to 0 °C. Trifluorosulfonic acid anhydride (1.1 equiv) and triethylamine (2.0 equiv) were then slowly added. The mixture was stirred at ambient temperature for 24 h. A saturated aqueous solution of $NaHCO_3$ was then added, the layers were separated and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The crude residue was purified by column chromatography (EtOAc/heptane 1:20).

The compound obtained was then further reacted to form the final desired product (3-[[(Trifluoromethyl)sulfonyl]oxy]estra-1,3,5(10)-trien-17-one).

3-[[(Trifluoromethyl)sulfonyl]oxy]estra-1,3,5(10)-trien-17-one (1 equiv) was dissolved in THF (0.5 M) and potassium vinyltrifluoroborate (1.2 equiv), $PdCl_2$ (2.0 mol%), PPh_3 (6.0 mol%), Cs_2CO_3 (3.0 equiv) and H_2O (0.5 mL) were added sequentially. The suspension was refluxed at 80 °C for 24 h, cooled down to ambient temperature and quenched by the addition of H_2O. The phases were separated, the aqueous layer was extracted with CH_2Cl_2, the combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified via column chromatography (EtOAc/heptane 1:20) to yield (8R,9S,13S,14S)-13-methyl-3-vinyl6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one as a white solid.

3. Optimization studies

To an oven-dried 10 mL glass vial equipped with a magnetic stirring bar, sodium tetraphenylborate (BPh_4Na), photocatalyst (PC), bromocyclohexane and 4-*tert*-butylstyrene were added. The solvent was then added. The vial was closed with a silicon septum and degassed with argon for 20 min. The vial was then irradiated with a Kessil light (456 nm, 40W/ 390 nm, 52W). The progress of the reaction was monitored by TLC and GC/MS. After completion, the solution was diluted with diethylether and transferred in a separatory funnel containing water. The organic layer was separated, and the aqueous layer was extracted with diethylether. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum and the product was isolated through column chromatography (hexane). In some cases, after the extraction, the NMR yield was determined instead using 1,3,5-trimethoxybenzene as internal standard.

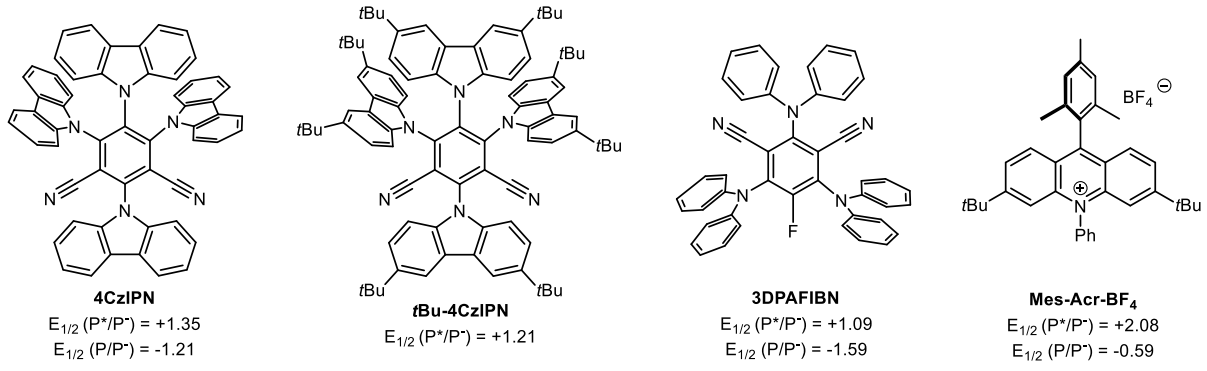


Figure S2: *Photocatalysts employed in the optimization studies.*

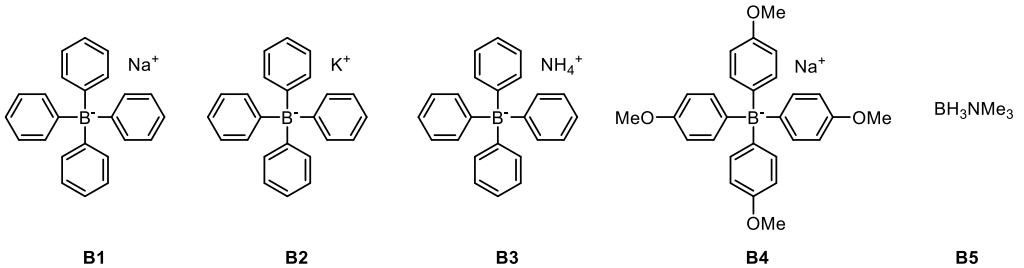
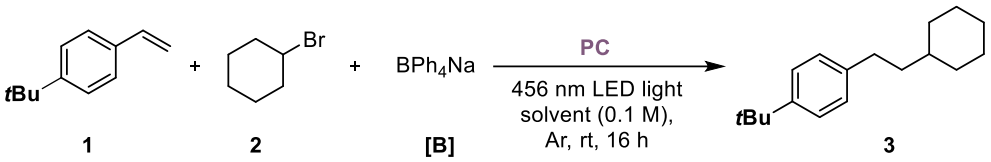


Figure S3: *Boryl radical sources employed in the optimization studies.*

Table S1: *Optimization of the photocatalyst (PC).*

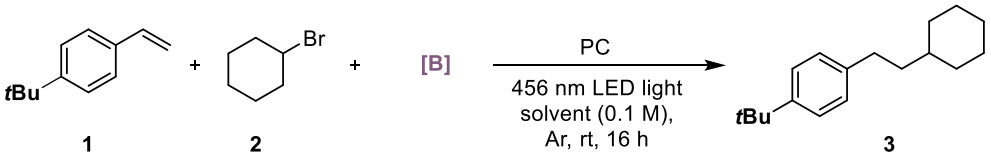


1 2 [B] 3

Entry	PC	Solvent	Equivalent (1/2/[B])	Yield[a]
1	4CzIPN (5 mol%)	DMF	1.5/1/1	65%
2	4CzIPN (5 mol%)	DMF	1/1.5/1.5	50%
3	$(Ir[dF(CF_3)_2ppy]_2(dtbpy))PF_6$ (2 mol%)	DMF	2/1/2	56%
4	$[Ir(dtbbpy)(ppy)_2]PF_6$ (2 mol%)	DMF	2/1/2	30%
5	*fac*-$Ir(ppy)_3$	DMF	2/1/2	-
6	9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (10 mol%)	DMF	2/1/2	-
7	$Ru(bpy)_3(PF_6)_2$ (2 mol%)	DMF	1.5/1/1	-
8	3DPAFIPN (5 mol%)	DMF	1/1.5/1.5	28%
9	*t*Bu-4CzIPN (5 mol%)	DMF	1/1.5/1.5	60%
10	*t*Bu-4CzIPN (5 mol%)	DMF	1.5/1/1	38%

[a]NMR yield, using 1,3,5-trimethoxybenzene as internal standard. Isolated yields in parentheses.

Table S2: *Optimization of the borate.*

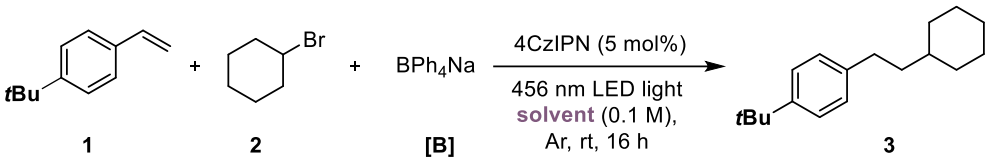


1 2 3

Entry	PC	Solvent	Equivalent (1/2/[B])	Borate	Yield[a]
9	**4CzIPN**	**DMF**	**2/1/2**	**B2**	**75%**
10	4CzIPN	DMF	2/1/2	B3	Traces
11	4CzIPN	DMF	2/1/2	B4	Traces
12	4CzIPN	DMF	2/1/2	B5	-

[a]NMR yield, using 1,3,5-trimethoxybenzene as internal standard. Isolated yields in parentheses.

Table S3: *Optimization of the solvent.*

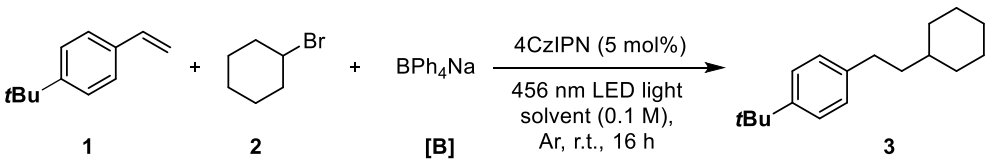


Entry	PC (5 mol%)	Solvent	Equivalents (1/2/[B])	Yield[a]
13	4CzIPN	DMA	1/1.5/1.5	35%
14	4CzIPN	DMA, H_2O (5 equiv)	2/1/2	88%
15	4CzIPN	MeOH	1/1.5/1.5	-
16	4CzIPN	1,4-Dioxane	1/1.5/1.5	< 10%
17	4CzIPN	Acetone	1/1.5/1.5	Traces
18	4CzIPN	*i*PrOAc	1/1.5/1.5	< 10%
19	4CzIPN	Toluene	1/1.5/1.5	-
20	4CzIPN	DCE	1/1.5/1.5	-
21	4CzIPN	ACN	1/1.5/1.5	-
22	4CzIPN	DMSO	1.5/1/1	- *
23	4CzIPN	DMA	1.5/1/1	38%

[a]NMR yield, using 1,3,5-trimethoxybenzene as internal standard. Isolated yields in parentheses.

*Addition of a phenyl radical to the styrene detected in GC-MS.

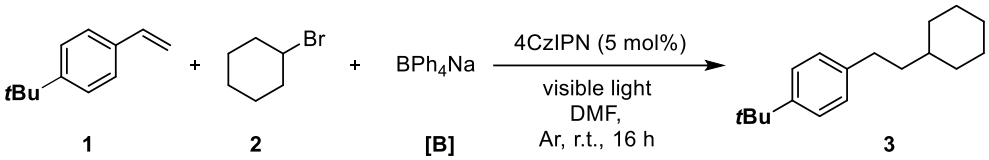
Table S4: *Optimization of the equivalents of the reactants.*



Entry	PC (5 mol%)	Solvent	Equivalent (1/2/[B])	Yield[a]
24	4CzIPN	DMF	1/1.5/1	50%
25	4CzIPN	DMF	2/1/1	53%
26	4CzIPN	DMF	2/1/2	68%
27	4CzIPN	DMF	2/1/3	51%

[a]NMR yield, using 1,3,5-trimethoxybenzene as internal standard. Isolated yields in parentheses.

Table S5: *Optimization of different reaction parameters and additives.*



1 2 [B] 3

Entry	PC (5 mol%)	Equivalent (1/2/[B])	Additive/ light/ concentration	Yield[a]
28	4CzIPN	1/1.5/1.5	4-picoline	42%
29	4CzIPN	1.5/1/1	dtbbpy (50 mol%)	30%
30	4CzIPN	2/1/2	DMAP	61%
31	4CzIPN	2/1/2	4-methoxypyridine	64%
32	4CzIPN	2/1/2	Kessil light (390 nm)	83%
33	*t*Bu4CzIPN	2/1/2	Kessil light (390 nm)	68%
34	4CzIPN	1/2/2.5	Kessil light (390 nm)	70%
35	4CzIPN (2 mol%)	2/1/2	Kessil light (390 nm)	84%
36	4CzIPN	2/1/2	Kessil light (390 nm), 0.2 M	88%
37	4CzIPN	2/1/2	Kessil light (390 nm), 0.05 M	92%
38	4CzIPN	2/1/2	Kessil light (390 nm), H_2O (5 equiv)	95% (85%)

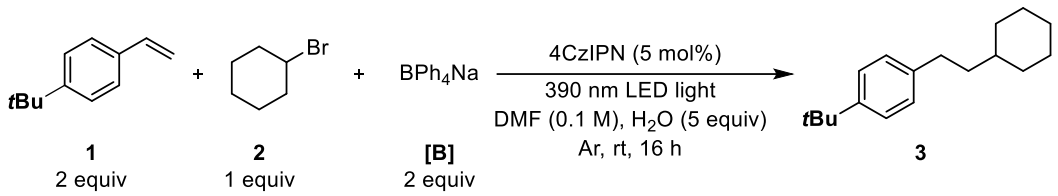
[a]NMR yield, using 1,3,5-trimethoxybenzene as internal standard. Isolated yields in parentheses.

4. Mechanistic investigations

4.1 Control experiments

To elucidate the mechanistic scenario, control experiments were performed. The results can be found in the table reported below.

Table S6: *Control experiments.*



Entry	Variation from standard conditions	Yield[a]
1	None	95%
2	No photocatalyst	-
3	No light	-
4	No BPh_4Na	-
5	No inert atmosphere	30%
6	DMF/H_2O (4:1)	55%
7	Addition of DIPEA (2 equiv) instead of BPh_4Na	-*
8	Addition of tetrabutylammonium bromide instead of BPh_4Na	-*
9	Addition of PPh_3 instead of BPh_4Na	-*
10	Addition of Na-ascorbate instead of BPh_4Na	-*
11	456 nm instead of 390 nm	87%

[a]NMR yield, using 1,3,5-trimethoxybenzene as internal standard. Isolated yields in parentheses. *No product formation was detected, nor the product of a reductive dehalogenation.

The need for PC and light confirms the photocatalytic nature of the reaction under study (**Entry 2**,**3, Table S6**). Inert atmosphere also plays a relevant role in the reaction (**Entry 5**). Oxygen can act as a catalyst quencher, but it can also interfere with boryl radical generation and thus in the halogen atom transfer (XAT) step.[5] In the absence of a boryl radical source (**Entry 4**), the product formation was not detected. Considering the PC redox window, bromocyclohexane cannot undergo direct single electron reduction, thus the need for a halogen atom abstractor.

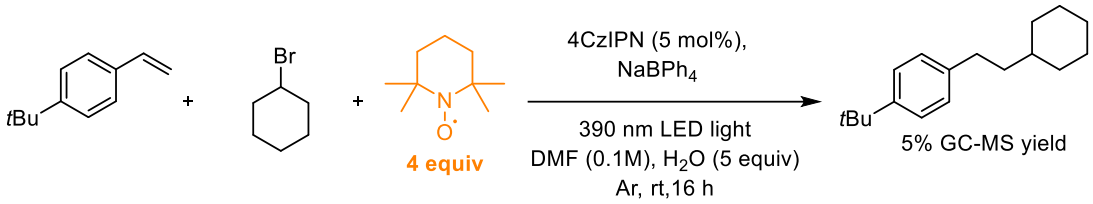
To further exclude the involvement of a multi photon process,[6,7] we evaluated the role of BPh_4Na as an electron shuttle rather than a boryl radical source for XAT. According to previous reports, a photocatalyst, often first quenched by an electron donor, can be further excited in its radical anionic form in a multi photon process, that generates as a result a super reductant species able to reduce highly challenging scaffolds, mostly aryl halides.[7] This process is dependent on the photocatalyst, on the electron shuttle and on the wavelength under use. Under our conditions, the exclusion of $NaBPh_4$ and the addition of different reductants (**Entry 7,8,9,10**), did not lead to product formation. Furthermore, blue irradiation (456 nm, **Entry 11**) is also an alternative efficient irradiation wavelength,

and the reactivity is not limited to a single wavelength (a crucial parameter for multi photon processes).
An increase in the amount of water was found to be detrimental to the reaction, mainly due to PC insolubility (**Entry 6**).
In addition, we also wondered if the change in the wavelength was needed because of the higher energy of the 390 nm light that could lead to a higher temperature in the system. To cross check this, a reaction was run using a 456 nm light without turning on the cooling fan, reaching a temperature of 45 °C. This experiment did not lead to yield improvement.

4.2 Radical inhibition experiments

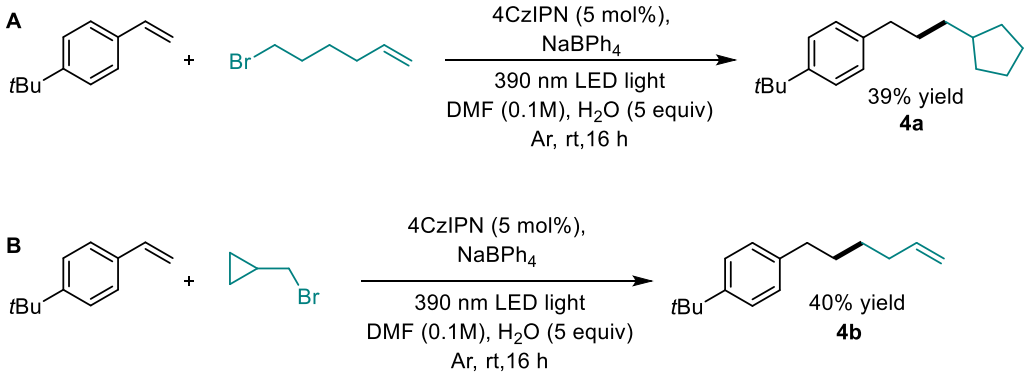
To prove radical involvement in the reaction mechanism, a radical quencher (TEMPO) was added to the reaction.
To an oven-dried 10 mL glass vial equipped with a magnetic stirring bar, sodium tetraphenylborate (BPh_4Na, 2 equiv), photocatalyst (4CzIPN, 5 mol%), bromocyclohexane (1 equiv, 0.2 mmol), 4-*tert*-butylstyrene (2 equiv) and TEMPO (4 equiv) were added. DMF (0.1 M) and H_2O (5 equiv) were then added. The vial was closed with a silicon septum and degassed with argon for 20 min. The vial was then irradiated with a Kessil light (390 nm) for 16h. The result of the reaction was monitored through GC/MS.

Though not possible to isolate a radical adduct, product formation was suppressed (5% GC-MS yield, **Scheme S1**).



***Scheme S1**: Experiment with TEMPO.*

To further prove the involvement of radicals in the devised transformation, two radical clock experiments were also performed (**Scheme S2A and S2B**).



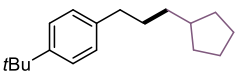
***Scheme S2:** Radical clock experiments.*

2A/2B) To an oven-dried 10 mL glass vial equipped with a magnetic stirring bar, sodium tetraphenylborate (BPh_4Na, 2 equiv), 4CzIPN (5 mol%), 6-bromohex-1-ene (1A, 1 equiv, 0.2 mmol) or (bromomethyl)cyclopropane (1B, 1 equiv, 0.2 mmol) and 4-*tert*-butylstyrene (2 equiv) were added. DMF (0.1 M) and H_2O (5 equiv) were then added. The vial was closed with a silicon septum and degassed with argon for 20 min. The vial was then irradiated with a Kessil light (390 nm) for 16h. After completion, the solution was diluted with diethylether and transferred in a separatory funnel containing water. The organic layer was separated, and the aqueous layer was extracted with diethylether. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum and the product was isolated through column chromatography (hexane).

1-(tert-butyl)-4-(3-cyclopentylpropyl)

Compound 4a was prepared according to the above procedure and isolated as a pale yellow oil.

Column Chromatography: Silica, heptane

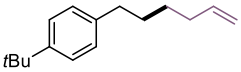


^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 (d, J = 6.9 Hz, 2H), 7.13 (d, J = 7.3 Hz, 2H), 2.58 (t, J = 7.8 Hz, 2H), 1.78 – 1.72 (m, 3H), 1.65 – 1.58 (m, 4H), 1.52 – 1.47 (m, 2H), 1.40 – 1.34 (m, 2H), 1.32 (s, 9H), 1.28 – 1.22 (m, 2H).
^{13}C NMR (101 MHz, CDCl3) δ 148.43, 140.07, 128.14, 125.24, 40.24, 36.20, 35.87, 34.47, 32.85, 31.58, 30.85, 25.35.
HRMS (EI): [M] cal'd for $C_{18}H_{28}$: 244.2191, found: 244.2187

1-(tert-butyl)-4-(hex-5-en-1-yl)benzene

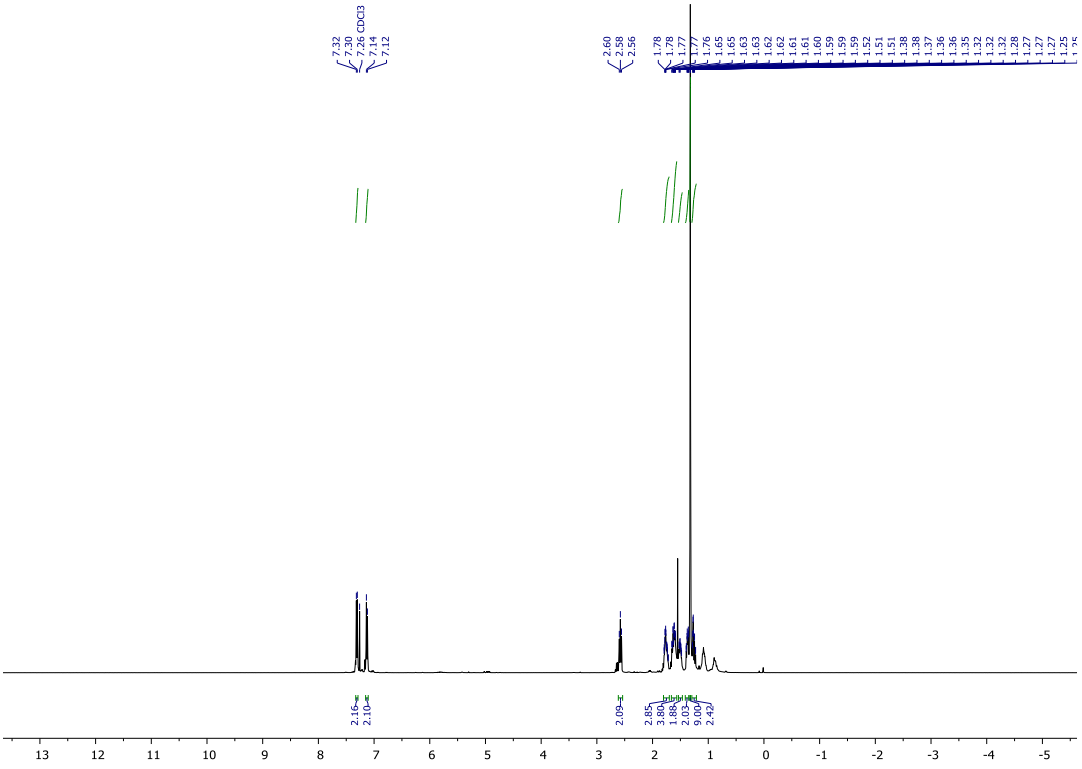
Compound 4b was prepared according to the above procedure and isolated as a pale yellow oil.

Column Chromatography: Silica, heptane

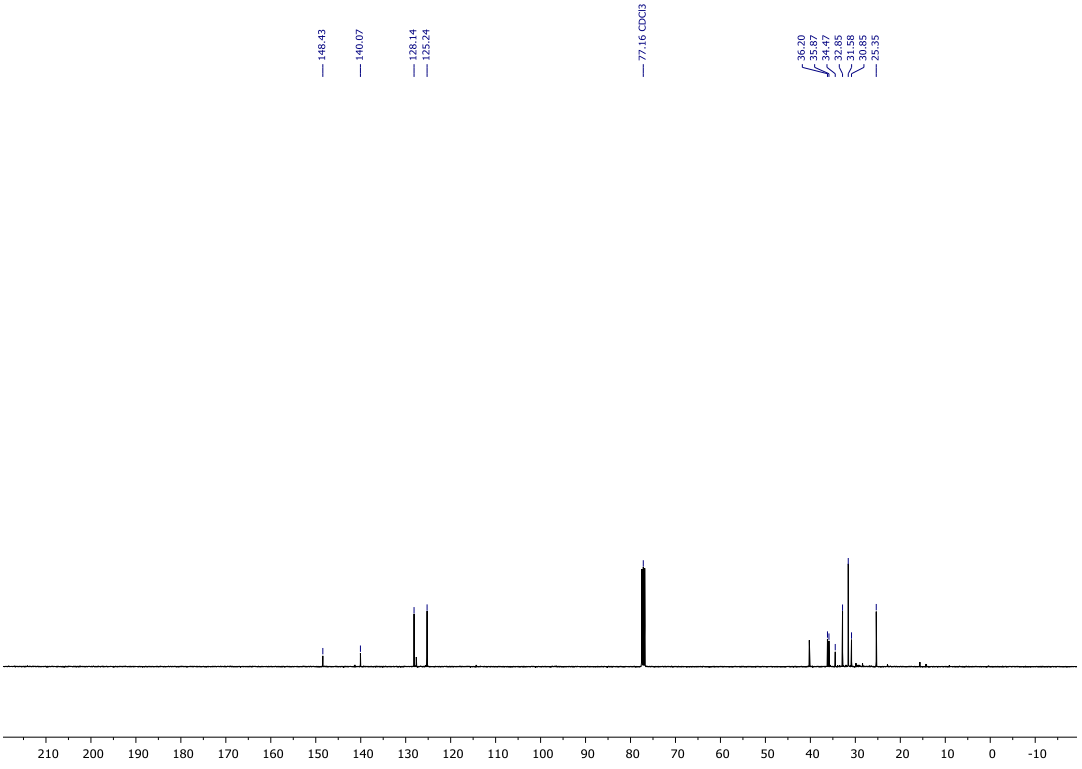


^{1}H NMR (400 MHz, Chloroform-d) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.86 – 5.76 (m, 1H), 5.00 (d, *J* = 17.1 Hz, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 2.59 (t, *J* = 8 Hz, 2H), 2.13 – 2.05 (m, 2H), 1.67 – 1.59 (m, 2H), 1.49 – 1.41 (m, 2H), 1.31 (s, 9H).
13C NMR (101 MHz, $CDCl_3$) δ 148.43, 140.07, 128.14, 125.24, 36.20, 35.87, 34.47, 32.85, 31.58, 30.85, 25.35.
HRMS (EI): [M] cal'd for $C_{16}H_{24}$: 216.1878, found: 216.1870

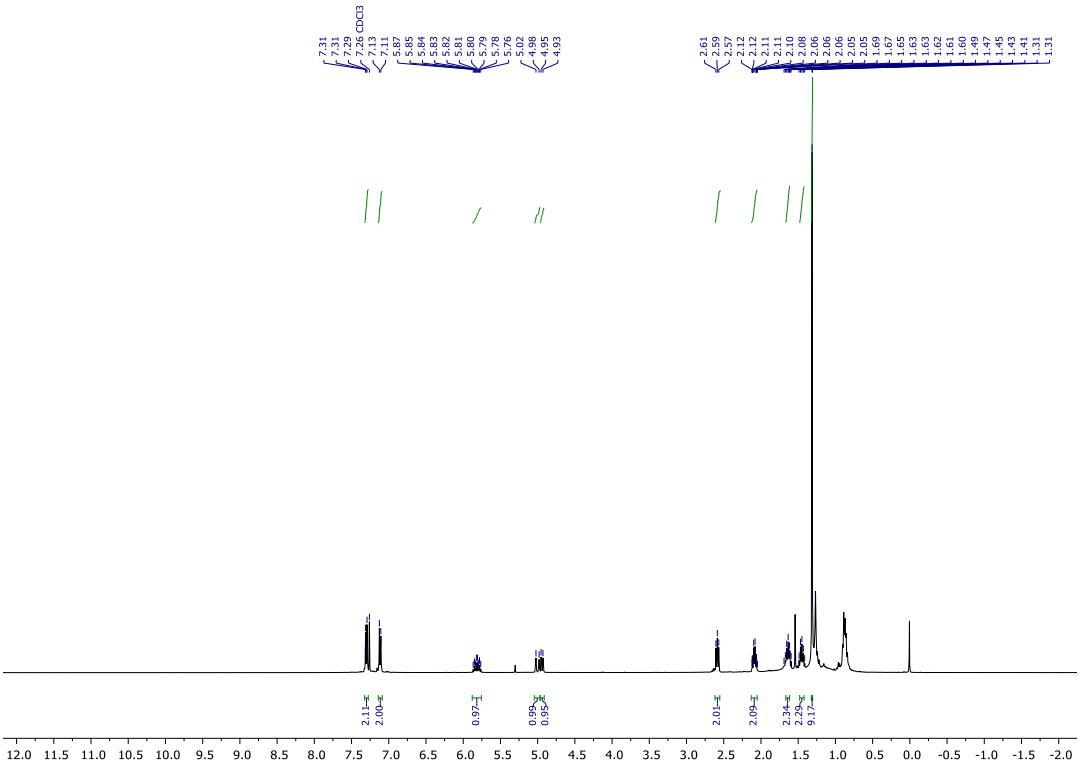
^{1}H spectrum of 4a



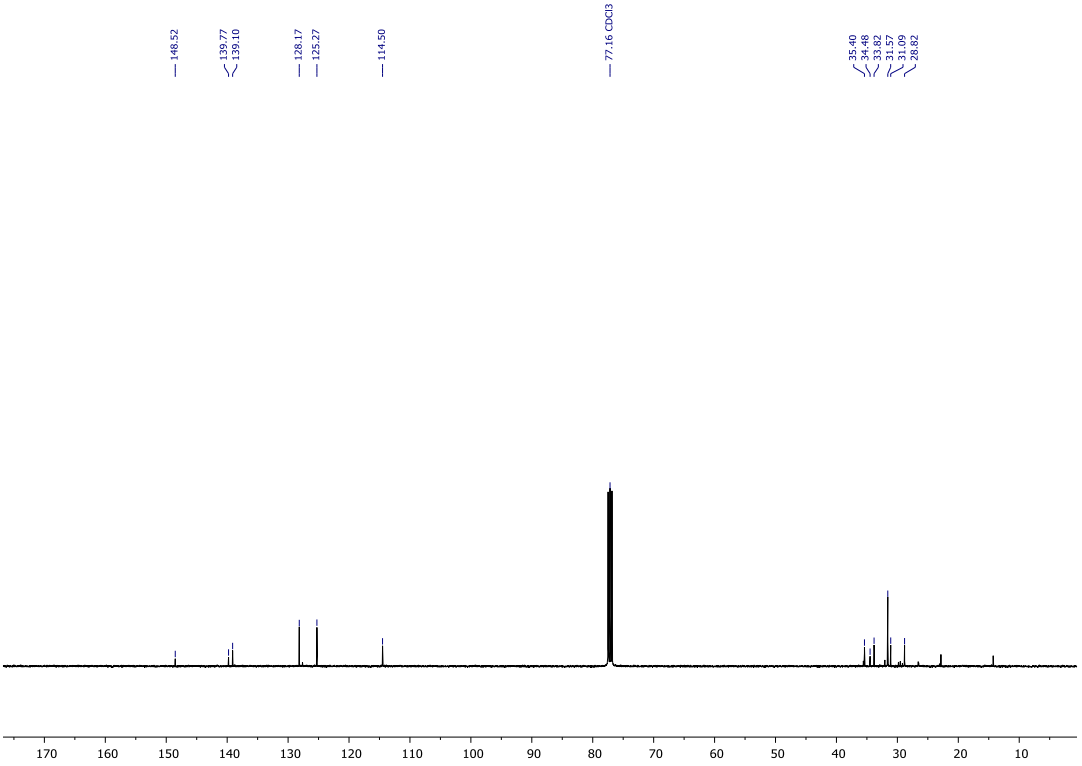
^{13}C spectrum of 4a



^{1}H spectrum of 4b



^{13}C spectrum of 4b



4.3 Light-dark experiment

The light-dark experiment was performed according to the general procedure.
To an oven-dried 10 mL glass vial equipped with a magnetic stirring bar, sodium tetraphenylborate (BPh_4Na, 2 equiv), photocatalyst (4CzIPN, 5 mol%), bromocyclohexane (1 equiv, 0.2 mmol), and 4-*tert*-butylstyrene (2 equiv) were added. DMF (0.1 M) and H_2O (5 equiv) were then added. The vial was closed with a silicon septum and degassed with argon for 20 min. The vial was then irradiated with a Kessil light (390 nm).
Product formation over time was determined through GC-MS. A calibration curve with the pure desired product was used for yield calculation.
As visible from **Figure S4**, in the absence of light irradiation, product formation is suppressed.

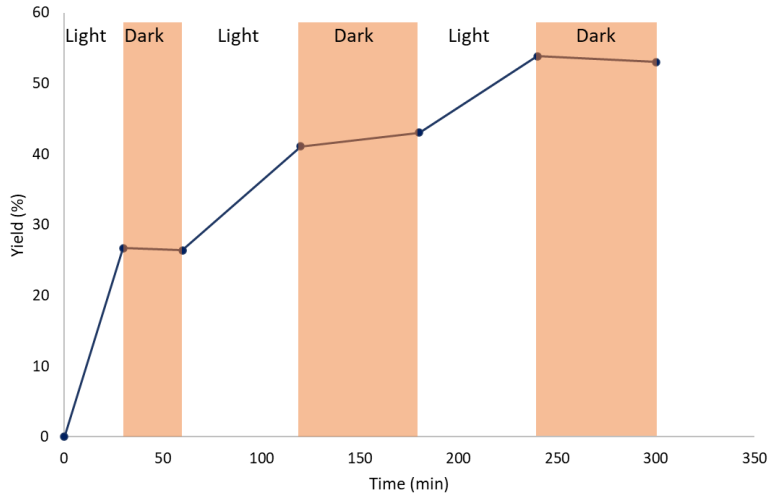


Figure S4: *Light-dark experiment.*

4.4 Fluorescence quenching experiment

The experiment was performed on a fluorescence spectrophotometer (FLS 920, Edinburgh Instruments). In a typical experiment, to a 0.1 mM solution of 4CzIPN in dry acetonitrile (ACN), an appropriate amount of quencher was added in a 1.0 cm quartz cuvette. The solutions were irradiated at 400 nm and emission was measured at 540 nm. The relative intensity I0/I was calculated as a function of quencher concentration, where I0 is the luminescence intensity in the absence of a quencher, while I is the intensity in the presence of the quencher. Before each measurement, the solutions were degassed and kept under nitrogen atmosphere.

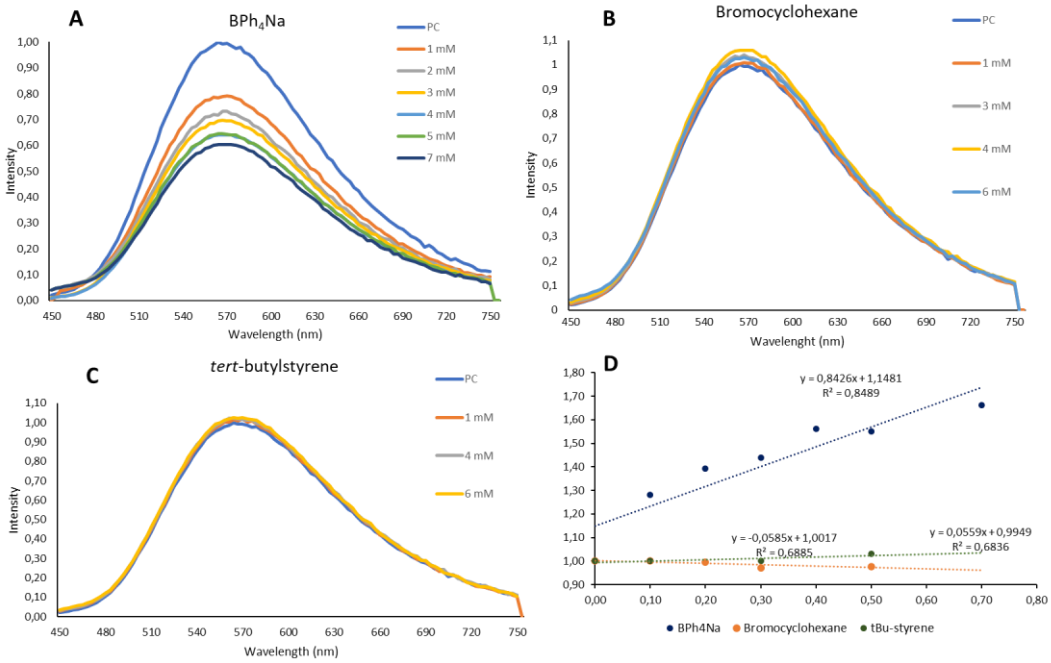


Figure S5: *Fluorescence quenching experiment. A) Quenching of sodium tetraphenylborate; B) Quenching of bromocyclohexane; C) Quenching of 4-tert-butylstyrene; D) Stern-Volmer quenching plot.*

The analysis revealed that BPh_4Na acts as a quencher in the reaction, while bromocyclohexane and *4-tert-butylstyrene* cannot quench the excited photocatalyst (**Figure S5**).

4.5 Cyclic voltammetry

The experiments were conducted using a cyclic potentiometer (Metrohm PGSTAT20 potentiostat/ galvanostat) with a glassy carbon working electrode, a Pt counter electrode and an Ag/AgCl reference electrode. In the standard procedure, 0.02 mmol of substrate were dissolved in 10 mL of a 0.1 M $[N(Bu)_4]PF_6$ electrolyte solution in degassed ACN. The reactor was sealed with a rubber septum and purged with nitrogen. Each measurement was conducted at 100 mV/s at room temperature under nitrogen atmosphere without stirring, using ferrocene as internal standard.[8]

As evident from the graphs here reported, bromocyclohexane and 4-*tert*-butylstyrene have redox potentials that lie outside the redox window of 4CzIPN ($E_{1/2}$ (P^*/P^-) = +1.35, $E_{1/2}$ (P/P^-) = -1.21 *vs* SCE). BPh_4Na, on the other hand, shows an oxidation peak at +1.2 V *vs* SCE and can therefore be oxidized by the PC employed.

To correctly define the oxidation potential of the species, in our case the Nernst equation could not be employed, since an irreversible cyclic voltammogram was obtained. This result can be accounted for the reactivity of the oxidized species, which undergoes degradation. To estimate the value of $E^0_{1/2}$,

the half peak potential Ep/2 (which corresponds to the potential at half the maximum of the local maximum current in the cyclic voltammogram) was calculated with the following equation:[8]

$$f\left(\frac{Ep}{2}\right) = \frac{Cmax}{2}$$

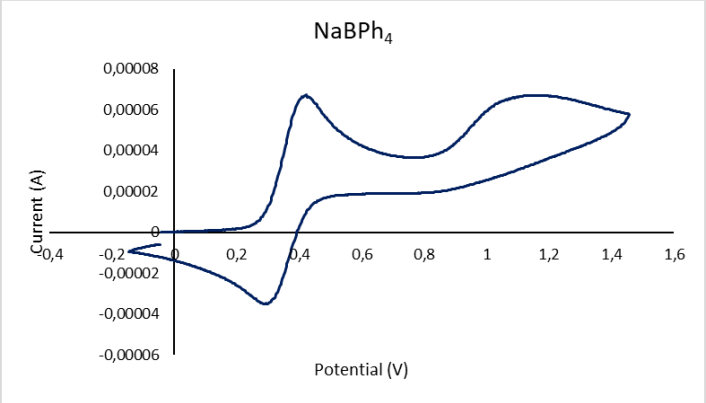


Figure S6: *Cyclic voltammogram of BPh_4Na, using ferrocene as internal standard.*

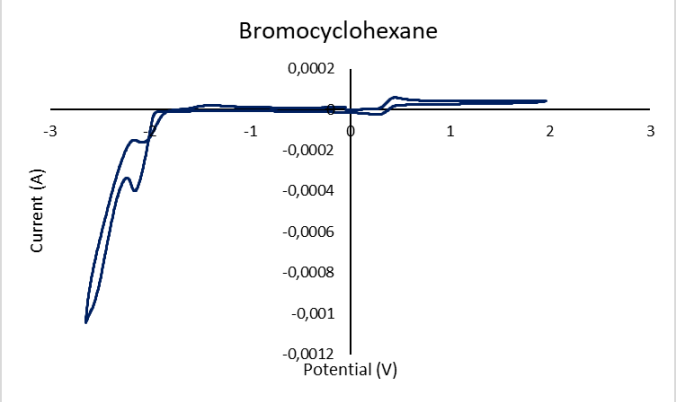


Figure S7: *Cyclic voltammogram of bromocyclohexane, using ferrocene as internal standard.*

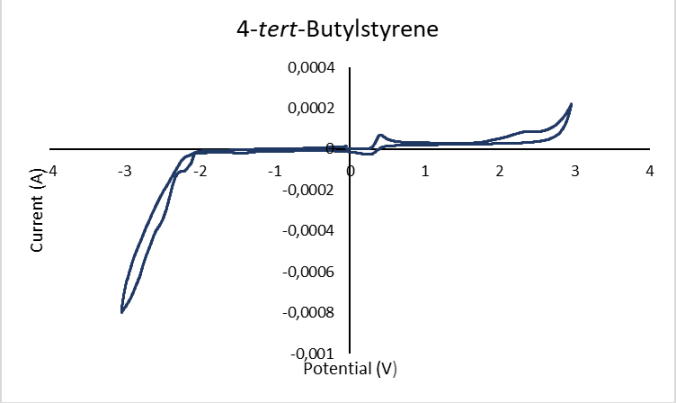
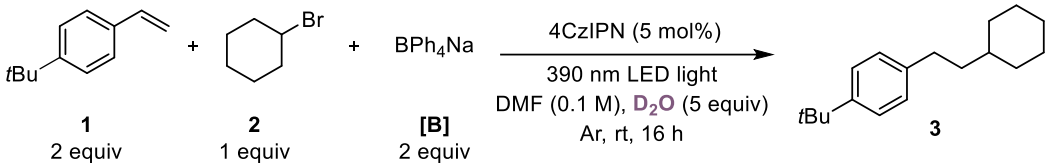


Figure S8: *Cyclic voltammogram of tert-butylstyrene, using ferrocene as internal standard.*

4.6 Deuteration experiments

In order to find evidence of a final protonation or HAT step in the reaction mechanism, isotope labelling experiments were performed.



To an oven-dried 10 mL glass vial equipped with a magnetic stirring bar, sodium tetraphenylborate (BPh_4Na, 2 equiv), photocatalyst (4CzIPN, 5 mol%), bromocyclohexane (1 equiv, 0.2 mmol) and 4-*tert*-butylstyrene (2 equiv) were added. DMF (0.1 M) and D_2O (5 equiv) were then added. The vial was closed with a silicon septum and degassed with argon for 20 min. The vial was then irradiated with a Kessil light (390 nm) for 16h. After completion, the solution was diluted with diethylether and transferred in a separatory funnel containing water. The organic layer was separated, and the aqueous layer was extracted with diethylether. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum and the product was isolated through column chromatography (hexane, 90% yield, 80% deuterium incorporation).

In the attempt to increase deuterium incorporation, we added 20 equiv of D_2O, with no improvement. Though this result could suggest that a protonation might be undergoing,[9] several precedent literature works highlight how the generation of an anion from the intermediate benzylic radical (generated upon radical addition) is not favoured because of the high reduction potential of this reaction intermediate.[9,10]

Nevertheless, taking into account that the O-H and O-D bond dissociation energy in H_2O and D_2O is high, an HAT step seemed at first not probable.

To gain further insight in this step, we performed further reactions using DMF-*d7*, which is also known to undergo HAT.

Table S7: Deuterium labelling studies.

Variation	**Result**
20 equiv D_2O (in DMF)	80% D incorporation
20 equiv ACN-*d3* (in DMF)	No D incorporation
20 equiv acetone-*d6* (in DMF)	No D incorporation
DMF-*d7* and 5 equiv H_2O	10% D incorporation
DMF-*d7* and 5 equiv D_2O	84% D incorporation

Adding DMF and different co-solvents instead of D_2O, such as ACN-*d3* (also able to undergo HAT) or acetone-*d6*, no deuterium incorporation was observed.

The results obtained led us to understand that a solvent mediated HAT step leads to at least 10% of product formation, but it is not the main hydrogen source. Similar deuterium incorporation values were obtained when varying the alkyl bromide or styrene in the reaction (see below).

Considering HAT a more probable step than anion generation, we started investigating what in our system could promote HAT from H_2O or D_2O, with the aid of computational calculations as well.

We performed a control experiment where bromocyclohexane was not added. The reaction mixture was treated according to the general procedure and the reaction outcome was monitored through GC-MS. The hydrogenation of 4-*tert*-butylstyrene was observed. Similarly, if instead of H_2O, D_2O was

added, deuterium incorporation could be detected. Similar results were obtained with p-methoxystyrene as well.

In the case of p-CF_3-styrene or p-Cl-styrene, decomposition of the initial styrene was observed. This might explain the reluctance of these substrates to undergo radical addition, as a result of a faster decomposition rate.

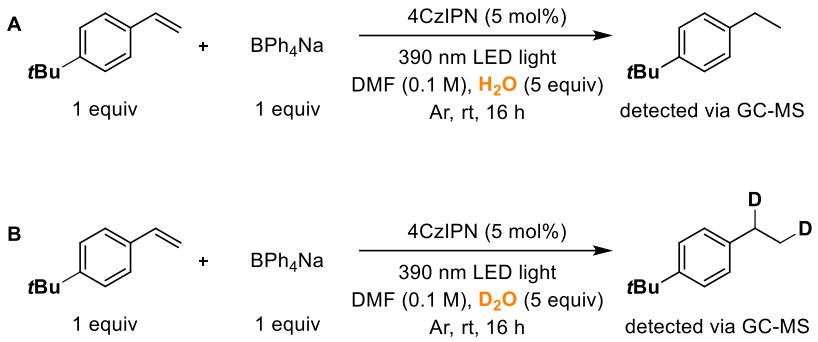


***Figure S9**: Reduction of styrenes obtained omitting the addition of alkyl bromides suggests a HAT mediated mechanism.*

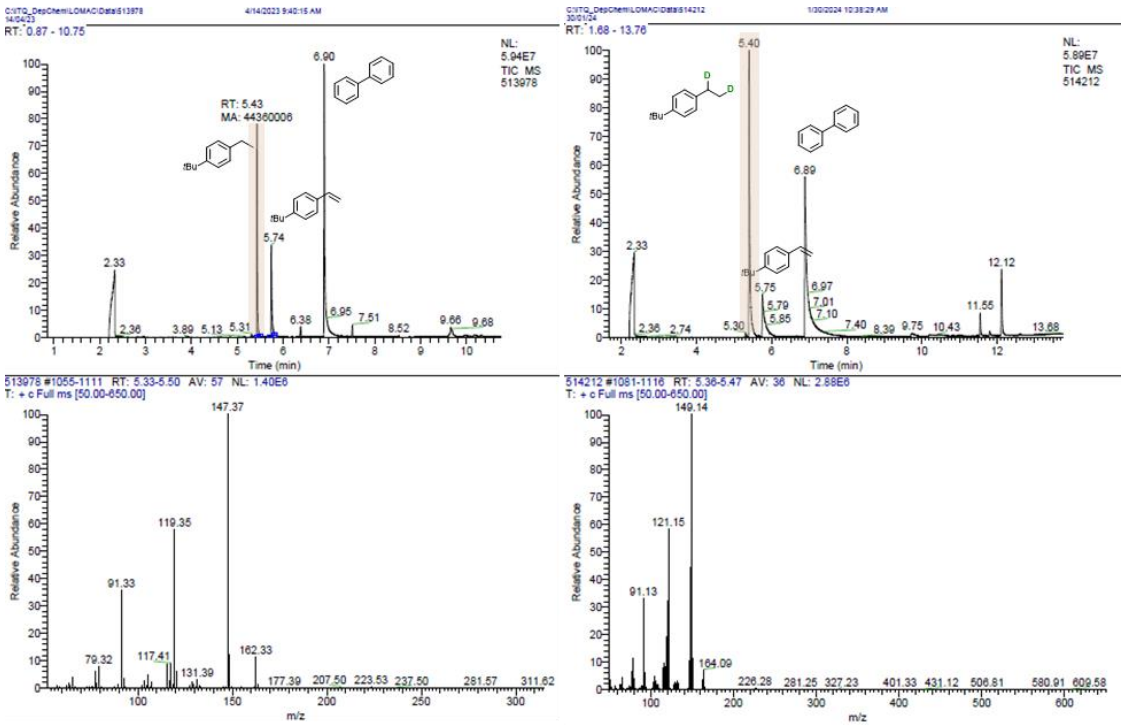
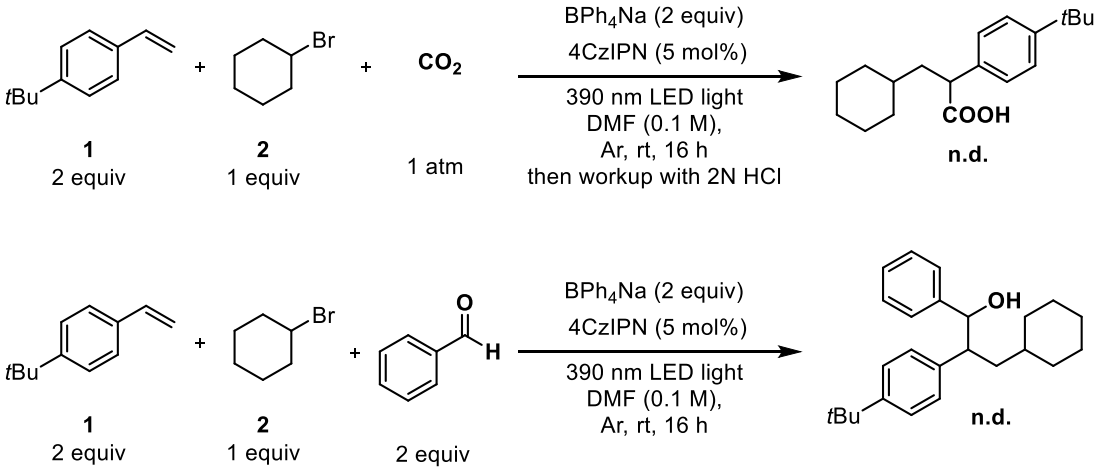


Figure S10: GC-MS chromatograms of reactions A and B described in Figure S9.

We took into consideration different reaction pathways. It has been demonstrated that a complex between borane and water can act as a HAT mediator, activating water toward a homolytic O-H bond cleavage.[11,12] Similarly, water activation toward HAT was presented in a recent work by Studer and co-workers.[13] Nonetheless, the involvement of borinic acid or HBr (side products of the reaction) as HAT mediators could not be excluded.

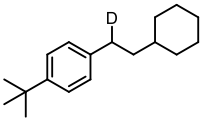
Though not possible to determine the exact pathway of the last HAT step, these results led us to consider a HAT step as final step of the transformation, involving water as hydrogen source. Further proves of this hypothesis were studied through DFT calculations.

Aware that an anion formation could not be excluded, we attempted trapping the anion through the addition of different electrophiles to the reaction mixture. The electrophiles were not trapped. Therefore we tend to consider HAT a more probable step (Scheme S3).



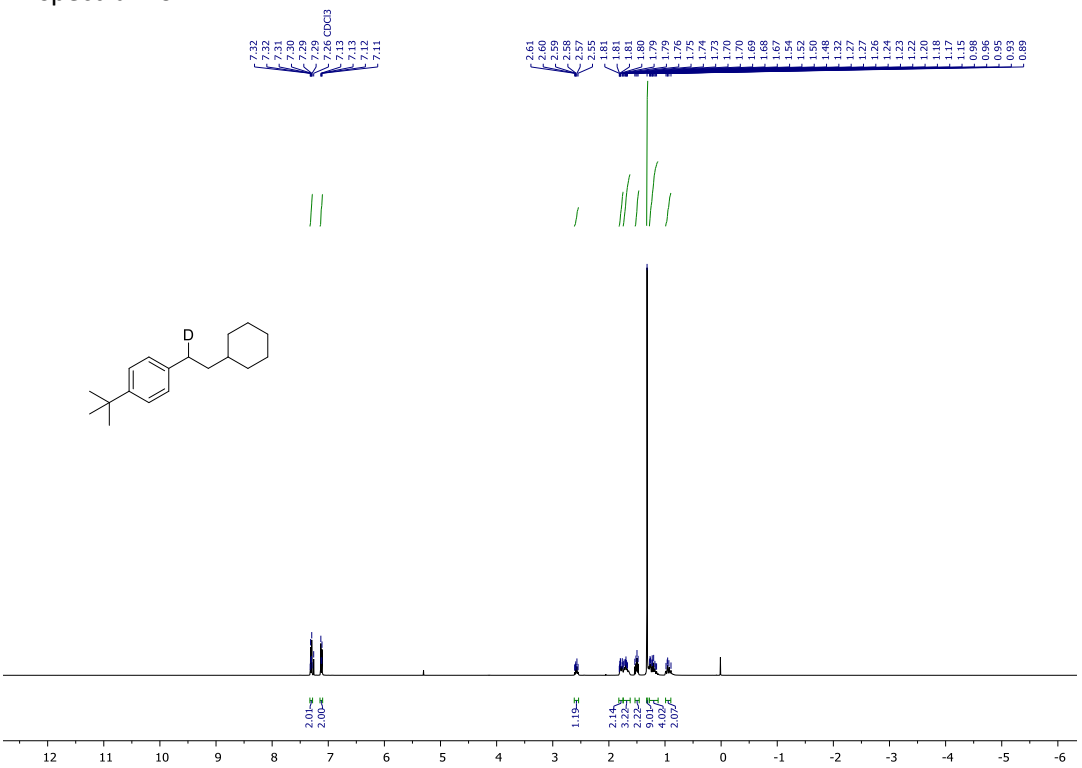
Scheme S3: Anion trapping experiments.

1-(tert-butyl)-4-(2-cyclohexylethyl)benzene-*d*

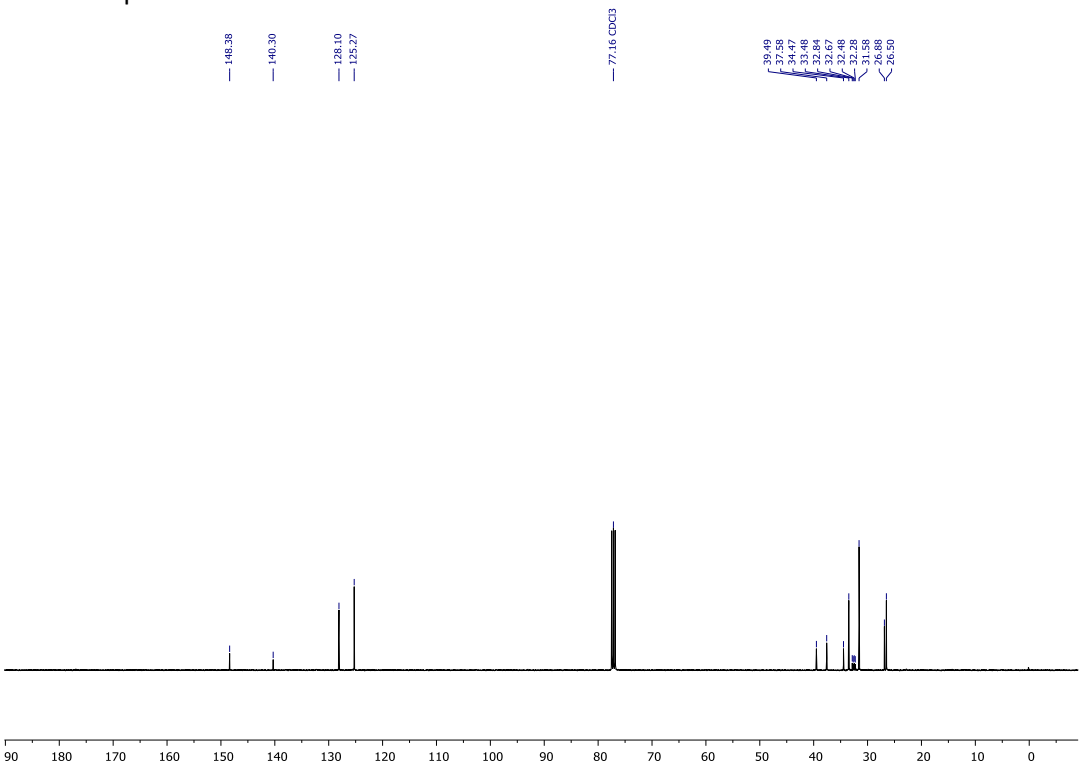


Compound D1 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.27 (m, 2H), 7.15 – 7.09 (m, 2H), 2.61 – 2.55 (m, 1.19 H), 1.82 – 1.75 (m, 2H), 1.74 – 1.63 (m, 3H), 1.54 – 1.47 (m, 2H), 1.32 (s, 9H), 1.28 – 1.14 (m, 4H), 0.99 – 0.89 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.38, 140.30, 128.10, 125.27, 39.49, 37.58, 34.47, 33.48, 32.84, 32.48 (t, *J* = 19 Hz), 31.58, 26.88, 26.50.
HRMS (EI): [M] cal'd for $C_{15}H_{22}$: 245.2254, found: 245.2249

^{1}H NMR spectrum of **D1**



^{13}C NMR spectrum of **D1**



4.7 UV-Vis spectroscopic analyses

Fate of the photocatalyst

A discoloration of the reaction mixture was observed at the end of the irradiation time. We hypothesized that the need of 390 nm as irradiation wavelength could be justified by a change in the catalyst structure, that could lead to the formation of an active species with a different absorption profile.[14] The fate of the photocatalyst was therefore analysed.

To an oven-dried 10 mL glass vial equipped with a magnetic stirring bar sodium a $1x10^{-5}$ M solution of BPh_4Na and 4CzIPN in DMF was prepared (Figure S11-A). The vial was closed with a silicon septum and degassed with argon for 20 min. The vial was then irradiated at 2 cm away from a Kessil light (390 nm, 40W) and samples were taken at different time frames. The sample was further diluted (10x) and analyzed with a Carey 5000, Varian, United States UV/Vis spectrometer. The same procedure was repeated mixing 4CzIPN with bromocyclohexane (Figure S11-B) and *4-tert*-butylstyrene (Figure S11-C) respectively. The results obtained are shown in Figure S11-B and C.

In the case of Figure S11-D, the reaction was prepared according to the General Procedure. Aliquots of 20 µL were then diluted and the absorbance profile of the reaction mixture was analyzed before and after irradiation. In the last case, we observed a decrease in the absorbance at 456 nm, wavelength usually employed in the presence of 4CzIPN, and observed an increase in the absorbance before 400 nm. This could explain the need of a different wavelength to increase the reaction outcome. Considering the overall analysis, the decomposition product of the photocatalyst was not further studied, but it was possible to understand that the decomposition might be promoted by BPh_4Na and lead to the formation of a different photocatalytic species.

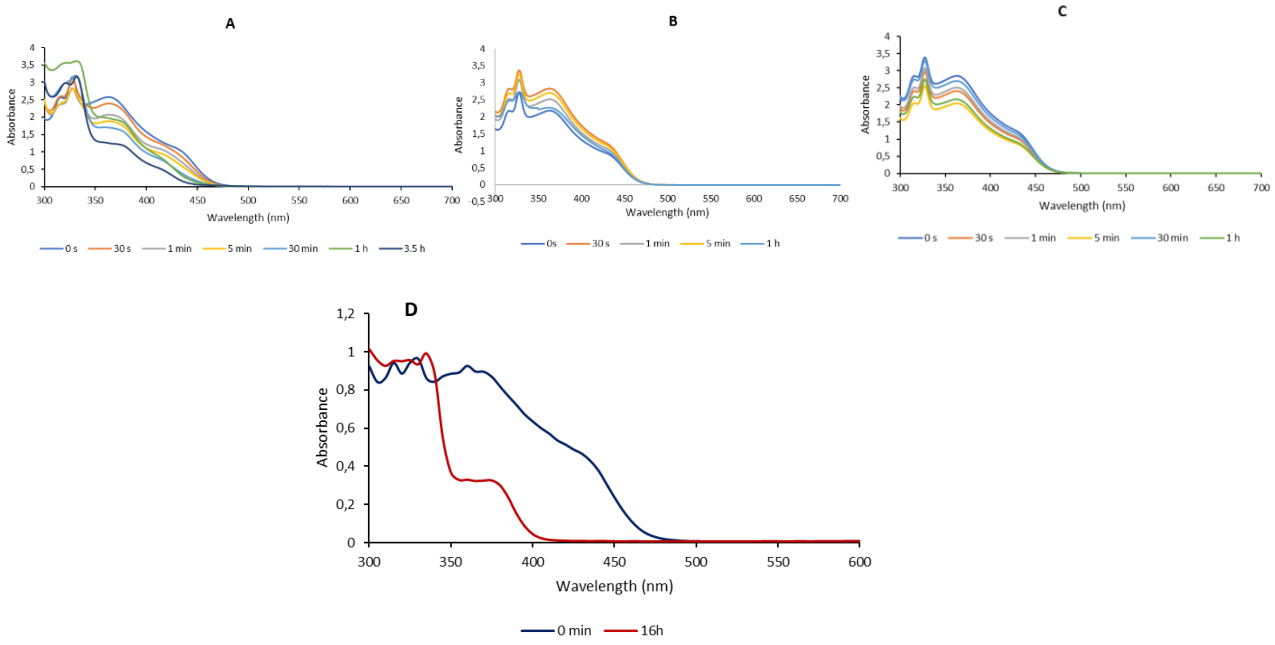


Figure S11: *UV-Vis absorption spectra of A) $1x10^{-5}$ M solution of 4CzIPN and BPh_4Na B) $1x10^{-5}$ M solution of 4CzIPN and bromocyclohexane C) $1x10^{-5}$ M solution of 4CzIPN and tert-butylstyrene. D) $1x10^{-5}$ M solution of the reaction mixture.*

Electron-donor acceptor complex?

To further study the possible interaction between the reactants, the absorption of single components and combinations of them were evaluated. No changes in the absorption spectra were observed. We could therefore exclude the involvement of EDA complexes in the observed reactivity. The only absorbing species in the visible range was confirmed to be 4CzIPN (Figure S12).

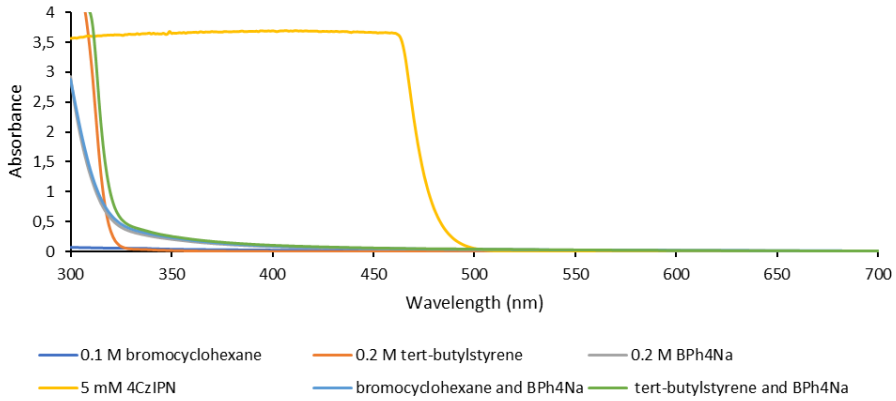


Figure S12: *Absorption spectra of reaction components and their combinations.*

4.8 Hammett plot

The effect of substituents on the styrene was investigated through an Hammett plot.

To an oven-dried 10 mL glass vial equipped with a magnetic stirring bar, sodium tetraphenylborate (BPh_4Na, 2 equiv), photocatalyst (4CzIPN, 5 mol%), bromocyclohexane (1 equiv, 0.2 mmol), and the appropriate styrene (2 equiv) were added. DMF (0.1 M) and H_2O (5 equiv) were then added. The vial was closed with a silicon septum and degassed with argon for 20 min. The vial was then irradiated with a Kessil light (390 nm). Aliquots of 50 µL of the reaction were taken every 30 min for 2.5 h. 50 µL of a 0.05 M solution of dodecane as internal standard was added and the sample was analyzed by GC-FID.

The result of the Hammett analysis is reported below. While electron donating groups show similar rates, electron withdrawing groups slow down the reaction (Figure S13). This could be due to polarity match for the final HAT step, that is favoured by more nucleophilic radicals.

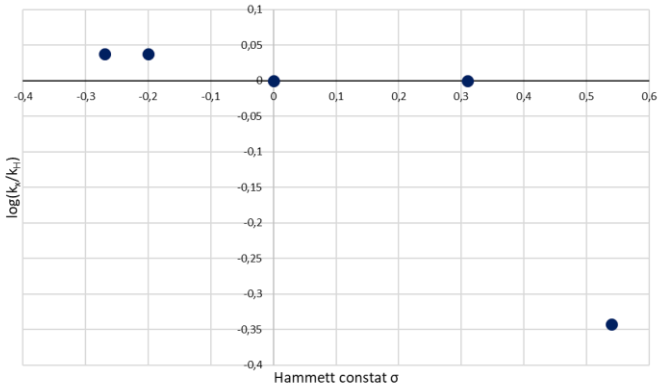
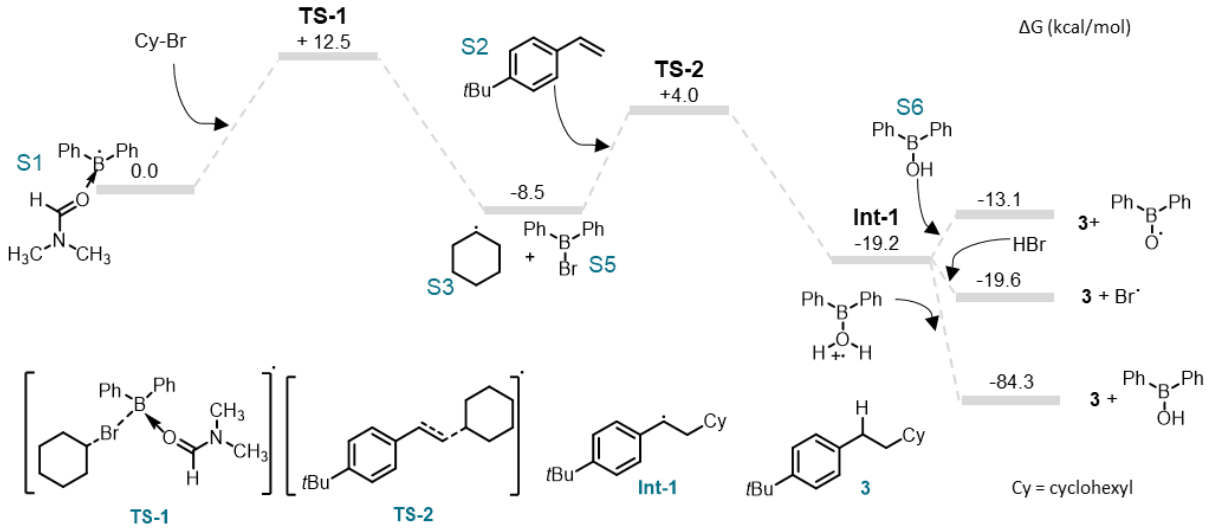


Figure S13: *Hammett plot analysis of the reaction.*

5. DFT calculations

Density functional theory (DFT) calculations were employed using Gaussian 16 package[15] to obtain the equilibrium structures of all molecules using the B3LYP[16] functional with a flexible triple zeta basis set (def2-TZVP).[17] To modulate the solvation effects, the calculations were carried out in *N,N*-Dimethylformamide (DMF) with the SMD solvation model of Truhlar and coworkers[18] and an atom-pairwise dispersion correction (D3) was added in all calculations.[19] The transition states were identified at the same level of theory and confirmed by the presence of an imaginary frequency.



*Ground state optimized geometry (Å)of **S1**:*

C	2.90750100	1.24038200	-0.76219600
C	3.97150900	0.60687300	-0.12381600
C	1.63425800	0.69055700	-0.69938200
C	3.76187200	-0.58804300	0.56263200
C	1.39804700	-0.52622000	-0.02342100
C	2.49667800	-1.15713500	0.59382500
H	3.07132000	2.16917000	-1.29544400
H	4.96300900	1.04150500	-0.16334000
H	4.59018900	-1.07995800	1.05792300
H	2.34641300	-2.10072800	1.10537400
H	0.80792900	1.20080600	-1.17974500
B	-0.00000300	-1.13178600	-0.00004300
C	-1.39805000	-0.52621500	0.02338500
C	-1.63423300	0.69057300	0.69933500
C	-2.90747200	1.24040400	0.76218700
H	-0.80788400	1.20082600	1.17965900
C	-3.97150500	0.60688600	0.12385800
H	-3.07126900	2.16920100	1.29542500
C	-3.76189900	-0.58804300	-0.56257600
H	-4.96300200	1.04152000	0.16341300
C	-2.49670600	-1.15713700	-0.59381000
H	-4.59023600	-1.07996500	-1.05782700
H	-2.34646100	-2.10073700	-1.10535100

*Ground state optimized geometry (Å)of **S2**:*

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C -0.07235500  1.30020400 -0.00000400
C  2.11848600  0.23805400  0.00001000
C -0.72708500  0.06864100  0.00000000
C  1.46295300 -1.00286700  0.00001700
C  0.08156700 -1.07966800  0.00001200
H -0.63728300  2.22143600 -0.00001100
C -2.25359300 -0.07016000 -0.00000300
H  1.78951700  2.35891100 -0.00000100
C  3.57969700  0.38295200  0.00001100
H -0.37899100 -2.05936900  0.00002000
H  2.03800800 -1.92045500  0.00002800
C  4.49050500 -0.59288900 -0.00002600
H  3.93020200  1.41193400  0.00004200
H  4.22535500 -1.64382600 -0.00006200
H  5.54844500 -0.36063200 -0.00002200
C -2.96455900  1.28960400 -0.00001800
C -2.69608600 -0.84655100  1.25647100
C -2.69608100 -0.84657500 -1.25646500
H -2.71444900  1.87846500  0.88512900
H -4.04550100  1.13440400 -0.00002800
H -2.71443100  1.87845400 -0.88516700
H -2.39439500 -0.32050400  2.16545900
H -2.26486400 -1.84842500  1.28590900
H -3.78404600 -0.95066800  1.26961000
H -2.39437900 -0.32055000 -2.16546200
H -3.78404200 -0.95068400 -1.26961000
H -2.26486700 -1.84845300 -1.28587900
```

*Ground state optimized geometry (Å)of **S3**:*

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C -0.40659400  1.36498000 -0.27470600
C -1.48544100  0.34566700 -0.11495200
C  0.93329600  1.09156200  0.31202900
H -0.64616600  2.34093100 -0.68065400
C -0.92663000 -0.97946100  0.42239500
H -1.97944000  0.16684400 -1.08103500
H -2.28274900  0.71815400  0.54701200
C  1.48006300 -0.30836600 -0.07777100
H  0.85850600  1.12800400  1.41163900
H  1.65057800  1.86798300  0.03866000
C  0.35888300 -1.34142700 -0.32496200
H -1.67208400 -1.77100300  0.31525200
H -0.71523000 -0.88864600  1.49307500
H  0.12744900 -1.38347500 -1.39458500
H  0.70200800 -2.33959400 -0.04237700
H  2.14232900 -0.65847300  0.71836900
H  2.09333700 -0.21844900 -0.97755100
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*Ground state optimized geometry (Å)of **3**:*

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C  1.27987600  0.71268400 -1.25216700
C  2.63324500  0.85244000 -0.94843000
C  0.51092000 -0.30470400 -0.69232400
C  3.27649800 -0.01938200 -0.06799700
C  1.15066700 -1.18120300  0.18835000
C  2.49791700 -1.04133800  0.49192000
H  3.17959300  1.65905500 -1.41700500
C  4.76226300  0.09966700  0.29642000
H  0.81815700  1.41114300 -1.94202600
```

```
H  2.94950600 -1.74662700  1.17841500
H  0.58399400 -1.98744700  0.64197500
C -1.82001900  0.33263400  0.04591100
C  5.44848500  1.27071600 -0.41931200
C  5.49379000 -1.19935400 -0.09574600
C  4.89892800  0.31734600  1.81647100
H  5.41245900  1.15992100 -1.50530900
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H  4.99401400  2.22886900 -0.15804000
H  5.41371600 -1.38182800 -1.17021800
H  5.08557400 -2.06664900  0.42568500
H  6.55457500 -1.12610300  0.15785800
H  4.39203000  1.23497200  2.12503400
H  5.95320800  0.40237400  2.09253800
H  4.47113900 -0.51155200  2.38275700
C -3.32779300  0.30262600 -0.22636300
H -1.48528400  1.37530700  0.06629200
C -4.06841300  1.25759200  0.72127400
H -1.62620100 -0.07346400  1.04540600
H -3.86202700  0.95522600  1.75574400
C -5.58138600  1.25539000  0.48987100
H -3.67155400  2.27097900  0.60599900
C -6.15994700 -0.15729600  0.59433500
H -5.79249000  1.65638800 -0.50856600
H -6.07185200  1.92118200  1.20606100
C -5.43810700 -1.11721300 -0.35334900
H -7.23261300 -0.14605100  0.37994600
H -6.04688000 -0.51655500  1.62422300
H -5.64303100 -0.82006000 -1.38874600
H -5.82853500 -2.13233100 -0.23561200
C -3.92431300 -1.10861100 -0.12118000
H -3.44087000 -1.78059100 -0.83415000
H -3.70927200 -1.50395900  0.87984400
H -3.49248100  0.65918200 -1.25263900
C -0.96331000 -0.42758200 -0.97930600
H -1.17770600 -0.03621900 -1.97816900
H -1.24249000 -1.48331200 -0.98229300
```

*Ground state optimized geometry (Å)of **S5**:*

```
C -2.70987700 -2.23879900 -0.72737900
C -3.84009200 -1.67672100 -0.14199500
C -1.49100200 -1.57557900 -0.66020900
C -3.74915500 -0.44137000  0.49549200
C -2.53610200  0.23103800  0.53564700
C -1.37365100 -0.32227900 -0.03023700
H -2.77783100 -3.19475700 -1.23205800
H -4.78925600 -2.19711900 -0.18402300
H -4.62664800 -0.00157200  0.95350100
H -2.48565500  1.19643800  1.02312000
B -0.00000100  0.39401800  0.00001600
H -0.62054800 -2.02710300 -1.11854900
Br 0.00000100  2.36464600 -0.00000100
C  1.37364900 -0.32227900  0.03025200
C  1.49100900 -1.57557900  0.66022100
C  2.70988500 -2.23879800  0.72737700
H  0.62056000 -2.02710500  1.11857100
C  2.53609300  0.23103900 -0.53564500
H  2.48563900  1.19644000 -1.02311700
C  3.74914800 -0.44136700 -0.49550500
```

```
C  3.84009300 -1.67671800  0.14198100
H  2.77784600 -3.19475600  1.23205500
H  4.62663400 -0.00156900 -0.95352400
H  4.78925800 -2.19711500  0.18399800
```

*Ground state optimized geometry (Å)of **S6**:*

```
C  2.80340700 -1.51419800  0.73312700
C  3.89331800 -0.93228800  0.09201300
C  1.56094600 -0.89059500  0.69687000
C  3.73640600  0.27974200 -0.57471300
C  1.37817200  0.33584500  0.03990100
C  2.49578400  0.90712900 -0.58990400
H  2.92190100 -2.45491800  1.25739300
H  4.86003300 -1.42092200  0.11104500
H  4.58008500  0.73468100 -1.07968000
H  2.39723800  1.85008300 -1.11816700
H  0.72142800 -1.35775800  1.19732100
B -0.01042000  1.06949800  0.03751800
C -1.39016400  0.32923100 -0.02690500
C -1.51776300 -0.96173400 -0.56164900
C -2.75284600 -1.59775700 -0.63171500
H -0.64067700 -1.47318100 -0.93884600
C -3.89226800 -0.95758800 -0.15350700
H -2.82735700 -2.59183700 -1.05613000
C -3.79212300  0.32385900  0.38363500
H -4.85440700 -1.45359100 -0.20017200
C -2.55714200  0.95847900  0.43684100
H -4.67720500  0.82542500  0.75666200
H -2.49113300  1.95798100  0.84985500
O -0.06628900  2.43712300  0.09736800
H  0.79814400  2.85881400  0.19022200
```

*Ground state optimized geometry (Å)of **Int-1**:*

```
C -1.33796200  1.28397300 -0.85664100
C -2.69737900  1.19526400 -0.61941600
C -0.44681400  0.23235300 -0.51489900
C -3.27200200  0.05919000 -0.02956700
C -1.03674000 -0.91678400  0.08141900
C -2.39567300 -0.98834200  0.30954600
H -3.31836400  2.03360100 -0.90290300
C -4.77220800 -0.07695700  0.24680500
H -0.93469400  2.18015700 -1.31535500
C  0.93369400  0.34964700 -0.76848800
H -2.79218600 -1.88721200  0.76542100
H -0.41198800 -1.75583700  0.35973300
C  1.96355100 -0.68910500 -0.47369000
C -5.56331600  1.16330700 -0.18982300
C -4.99861200 -0.28550400  1.75807700
C -5.32617000 -1.29568300 -0.51914300
H -5.23787500  2.06017800  0.34177400
H -6.62295000  1.01458400  0.02876300
H -5.46894900  1.34832600 -1.26210500
H -4.61969100  0.56564000  2.32907300
H -4.49964500 -1.18547200  2.12112600
H -6.06650600 -0.38729500  1.96847000
H -5.18310100 -1.17597700 -1.59584200
H -6.39706200 -1.40521800 -0.32886500
```

```
H -4.83663300 -2.22184100 -0.21380400
H  1.27012000  1.25812800 -1.25870800
C  3.40074700 -0.15368200 -0.45404200
H  1.89673700 -1.49096000 -1.22545500
C  4.41929300 -1.29682100 -0.36587900
H  1.75404100 -1.17882500  0.48500000
H  4.21839900 -1.87799000  0.54292400
C  5.86133500 -0.78437600 -0.32787500
H  4.28357800 -1.97874100 -1.21107500
C  6.07114600  0.21564300  0.81181500
H  6.09272200 -0.29481000 -1.28126300
H  6.55588000 -1.62363800 -0.22893800
C  5.06233600  1.36390100  0.73158600
H  7.09306400  0.60533400  0.79120000
H  5.94916700 -0.30220600  1.77064500
H  5.25684500  1.95000000 -0.17443100
H  5.19235000  2.04323400  1.57904300
C  3.62367000  0.84275200  0.69198200
H  2.92301700  1.67797500  0.60486900
H  3.39455400  0.33900800  1.63967700
H  3.57579100  0.37721100 -1.39958200
```

*Ground state optimized geometry (Å)of **TS-1**:*

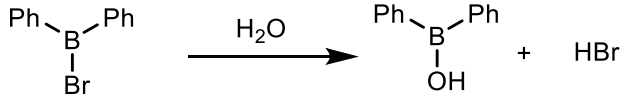
```
C  0.87776800  3.02388500 -1.53106200
C  1.65362600  3.75508600 -0.63676200
C -0.07440900  2.13042500 -1.05429400
C  1.46677000  3.59579900  0.73564200
C  0.50978700  2.70885900  1.20696100
C -0.28114000  1.94890500  0.32643100
H  1.02416900  3.14093800 -2.59819700
H -0.66026000  1.55350600 -1.75944800
H  2.40230300  4.44562800 -1.00589300
H  2.06947200  4.16452700  1.43343800
B -1.33635000  0.94295200  0.82037100
H  0.37646000  2.58589700  2.27515300
C -2.45008700  0.16384200  0.14685300
Br 0.38242000 -0.88538700  1.84930200
C -3.33358300  0.92507500 -0.66635000
C -2.75148300 -1.20955700  0.29023500
C -3.84801500 -1.78225400 -0.33722300
H -2.11270700 -1.83399800  0.89953400
C -4.70152700 -1.01120900 -1.12530400
H -4.04078600 -2.84131400 -0.20983600
C -4.43406800  0.34895300 -1.28143400
H -5.55833600 -1.46181300 -1.61061200
H -3.14612800  1.98300000 -0.80937200
H -5.08398900  0.96221000 -1.89506700
C  1.27457600 -1.15402500  0.03929200
C  2.53007500 -0.30976900 -0.03386700
C  1.52526200 -2.62994700 -0.19188700
H  0.50769500 -0.77478700 -0.63346200
C  2.18075900 -2.81309300 -1.57182600
H  0.59104300 -3.19042700 -0.13688900
H  2.19298200 -3.01440300  0.58411400
C  3.45468500 -1.97653500 -1.70411500
H  1.46812400 -2.51666100 -2.34878100
H  2.39581700 -3.87341700 -1.72446200
C  3.17745700 -0.50036000 -1.41525600
H  3.87618900 -2.09165100 -2.70606900
H  4.20512500 -2.34776400 -0.99729000
```

```
H  3.22848000 -0.62787900  0.74535400
H  2.29446600  0.74026600  0.13479800
H  2.50837700 -0.09632100 -2.18230300
H  4.09983100  0.08376600 -1.45833000
```

*Ground state optimized geometry (Å)of **TS-2**:*

```
C -1.37352000 -1.82024900 -0.97014700
C -2.55091500 -1.08050400 -0.93732100
C -0.33997400 -1.60582500 -0.04736700
C -2.76176600 -0.08553200  0.01934200
C -0.55412400 -0.60406700  0.91853600
C -1.72746700  0.12749700  0.94564100
H -3.30709100 -1.29522800 -1.67942000
C -4.04159100  0.75445800  0.09254000
H -1.24980700 -2.58230500 -1.73200300
C  0.87653400 -2.40072000 -0.12598700
H -1.84119400  0.88747100  1.70868200
H  0.20947900 -0.39305900  1.65620200
C  1.98493200 -2.26743000  0.64576200
C -5.04937800  0.38103600 -1.00254600
C -3.68583200  2.24617800 -0.06813300
C -4.71696400  0.54063900  1.46216300
H -4.63887600  0.53779100 -2.00248200
H -5.93911200  1.00717400 -0.90767800
H -5.36746200 -0.66077900 -0.92313800
H -3.20527000  2.42967700 -1.03224200
H -3.00936600  2.58741200  0.71719500
H -4.59102000  2.85695400 -0.01811500
H -4.98265000 -0.50964500  1.60495300
H -5.63240600  1.13447900  1.52762000
H -4.06591900  0.83946600  2.28531900
H  0.89789200 -3.13147200 -0.92988100
C  3.48060000 -0.62736100 -0.30920900
H  2.79080100 -2.98409300  0.56337700
C  4.39745400 -0.28502100  0.82034800
H  1.99622800 -1.64018900  1.52717300
H  3.80917600 -0.02341700  1.70920300
C  5.26135600  0.94221200  0.44429100
H  5.03554200 -1.13011100  1.08961300
C  4.38441400  2.11088000 -0.01498700
H  5.94682500  0.66335900 -0.36330900
H  5.87667500  1.23748800  1.29961500
C  3.45824100  1.70885600 -1.16688600
H  5.01231800  2.95476200 -0.31506300
H  3.77548400  2.45460400  0.82958300
H  4.06026600  1.46352100 -2.04862800
H  2.80801700  2.54389400 -1.44479900
C  2.59927000  0.48232600 -0.78185300
H  1.97951800  0.16892800 -1.62466800
H  1.91968800  0.78352300  0.02393500
H  3.86463900 -1.30444300 -1.06616400
```

Bromodiphenylborane **Borinic acid**



*Ground state optimized geometry (Å)of **diphenylborane**:*

```
C -2.70987700 -2.23879900 -0.72737900
C -3.84009200 -1.67672100 -0.14199500
C -1.49100200 -1.57557900 -0.66020900
C -3.74915500 -0.44137000  0.49549200
C -2.53610200  0.23103800  0.53564700
C -1.37365100 -0.32227900 -0.03023700
H -2.77783100 -3.19475700 -1.23205800
H -4.78925600 -2.19711900 -0.18402300
H -4.62664800 -0.00157200  0.95350100
H -2.48565500  1.19643800  1.02312000
B -0.00000100  0.39401800  0.00001600
H -0.62054800 -2.02710300 -1.11854900
Br 0.00000100  2.36464600 -0.00000100
C  1.37364900 -0.32227900  0.03025200
C  1.49100900 -1.57557900  0.66022100
C  2.70988500 -2.23879800  0.72737700
H  0.62056000 -2.02710500  1.11857100
C  2.53609300  0.23103900 -0.53564500
H  2.48563900  1.19644000 -1.02311700
C  3.74914800 -0.44136700 -0.49550500
C  3.84009300 -1.67671800  0.14198100
H  2.77784600 -3.19475600  1.23205500
H  4.62663400 -0.00156900 -0.95352400
H  4.78925800 -2.19711500  0.18399800
```

*Ground state optimized geometry (Å)of **borinic acid = S6***

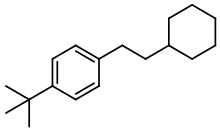
6. General procedure

To an oven-dried 10 mL glass vial equipped with a magnetic stirring bar, sodium tetraphenylborate (BPh_4Na, 2 equiv), 4CzIPN (5 mol%), organohalide (1 equiv, 0.3 mmol), styrene (2 equiv) and water (5 equiv) were added. DMF was then added. The vial was closed with a silicon septum and degassed with argon for 20 min. The vial was then irradiated with a Kessil light (390 nm, 52W) for 16h. After completion, the solution was diluted with diethylether and transferred in a separatory funnel containing water. The organic layer was separated, and the aqueous layer was extracted with diethylether. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum and the product was isolated through column chromatography.
Note: all the reactions can also be performed at 456 nm (difference in yield 10-15%).

Limitations of the method: Electron-poor styrenes (e.g. p-CF_3 or p-NO_2, p-Cl styrenes) showed very limited or no reactivity. Side products deriving from their polymerization and decomposition could be detected. Concerning the alkyl bromides, *tert*-butyl bromide was not a competent reaction partner, probably due to steric factors.

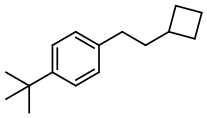
7. NMR spectra

1-(tert-butyl)-4-(2-cyclohexylethyl)benzene[20]



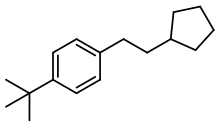
Compound 3 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.63 – 2.57 (m, 2H), 1.83 – 1.76 (m, 2H), 1.75 – 1.64 (m, 3H), 1.56 – 1.50 (m, 2H), 1.33 (s, 9H), 1.29 – 1.15 (m, 4H), 1.00-0.90 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.38, 140.33, 128.10, 125.27, 39.57, 37.61, 34.47, 33.48, 32.85, 31.58, 26.88, 26.51
Spectroscopic data were consistent with literature values.

1-(tert-butyl)-4-(2-cyclobutylethyl)benzene



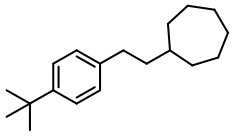
Compound 4 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.55 – 2.49 (t, *J* = 7.9 Hz, 2H), 2.33 (p, *J* = 7.8 Hz, 1H), 2.13 – 2.05 (m, 2H), 1.94 – 1.81 (m, 2H), 1.77 – 1.70 (m, 2H), 1.70 – 1.63 (m, 2H), 1.35 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.43, 139.88, 128.15, 125.23, 38.97, 35.82, 34.47, 33.01, 31.58, 28.36, 18.58.
HRMS (EI): [M] cal'd for $C_{16}H_{24}$: 216.1878, found: 216.1878

1-(tert-butyl)-4-(2-cyclopentylethyl)benzene[21]



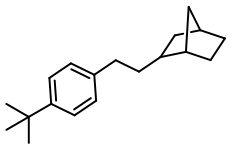
Compound 5 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.30 (m, 2H), 7.17 – 7.12 (m, 2H), 2.64 – 2.59 (m, 2H), 1.85-1.77 (m, 3H), 1.69 – 1.60 (m, 4H), 1.58-1.49 (m, 2H), 1.34 (s, 9H), 1.21-1.11 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.40, 140.15, 128.11, 125.25, 39.89, 38.29, 34.71, 34.47, 32.81, 31.58, 25.39.
Spectroscopic data were consistent with literature values.

(4-(tert-butyl)phenethyl)cycloheptane



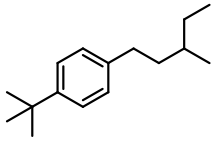
Compound 6 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.31 (m, 2H), 7.18 – 7.13 (m, 2H), 2.65 – 2.60 (m, 2H), 1.84 – 1.77 (m, 2H), 1.75 – 1.64 (m, 2H), 1.66 – 1.46 (m, 8H), 1.36 (s, 9H), 1.35 – 1.24 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.37, 140.30, 128.13, 125.27, 40.27, 39.15, 34.70, 34.46, 33.43, 31.59, 28.75, 26.65.
HRMS (EI): [M] cal'd for $C_{19}H_{30}$: 258.2342, found: 258.2336

(1S,4R)-2-(4-(tert-butyl)phenethyl)bicyclo[2.2.1]heptane



Compound 7 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 2.62 – 2.57 (m, 2H), 2.26 – 2.22 (m, 1H), 2.06 – 2.03 (m, 1H), 1.69 – 1.60 (m, 1H), 1.56 – 1.42 (m, 6H), 1.36 (s, 9H), 1.23 – 1.15 (m, 2H), 1.16 – 1.09 (m, 2H).
^{13}C NMR (101 MHz, CDCl3) δ 148.39, 140.09, 128.18, 125.25, 42.10, 41.27, 39.04, 38.40, 36.75, 35.53, 34.47, 33.84, 31.59, 30.26, 28.99.
HRMS (EI): [M] cal'd for $C_{19}H_{28}$: 256.2191, found: 256.2185

1-(tert-butyl)-4-(3-methylpentyl)benzene

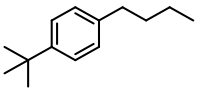


Compound 8 was prepared according to the general procedure (GP) and isolated as pale yellow oil.

Column Chromatography: Silica, heptane

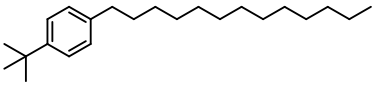
^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.33 (m, 2H), 7.18 – 7.15 (m, 2H), 2.72 – 2.53 (m, 2H), 1.74 – 1.62 (m, 1H), 1.51 – 1.40 (m, 2H), 1.36 (s, 9H), 1.31 – 1.19 (m, 2H), 0.97 (d, *J* = 6.2 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.41, 140.28, 128.11, 125.28, 38.67, 34.47, 34.35, 33.09, 31.58, 29.52, 19.27, 11.45.
HRMS (EI): [M] cal'd for $C_{16}H_{26}$: 218.2034, found: 218.2033

1-(tert-butyl)-4-butylbenzene[22]



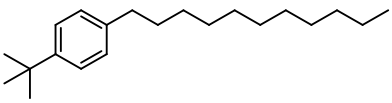
Compound 9 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.32 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.66 – 2.56 (m, 2H), 1.65 – 1.58 (m, 2H), 1.43 – 1.35 (m, 2H), 1.34 (s, 9H), 0.95 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.43, 139.98, 128.18, 125.23, 35.26, 34.47, 33.80, 31.44, 22.63, 14.13.
Spectroscopic data were consistent with literature values.

1-(tert-butyl)-4-tridecylbenzene



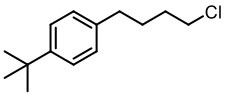
Compound 10 (X = Br) was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 1.63 (p, *J* = 7.3 Hz, 2H), 1.33-1.32 (m, 12H), 1.29 – 1.27 (m, 17H), 0.91 (t, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.42, 140.05, 128.16, 125.23, 35.60, 34.47, 32.10, 31.67, 31.58, 29.85, 29.82, 29.78, 29.71, 29.64, 29.53, 22.86, 14.28..
HRMS (EI): [M] cal'd for $C_{23}H_{40}$: 316.3130, found: 316.3120

1-(tert-butyl)-4-undecylbenzene[23]



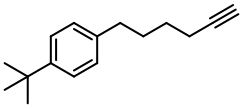
Compound 10 (X = I) was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 2.64 – 2.54 (m, 2H), 1.66 – 1.56 (m, 2H), 1.32 (s, 16H), 1.27 (s, 9H), 0.89 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.41, 140.04, 128.15, 125.22, 35.59, 34.46, 32.08, 31.66, 31.57, 29.83, 29.80, 29.76, 29.69, 29.62, 29.51, 22.84, 14.27.
Spectroscopic data were consistent with literature values.

1-(tert-butyl)-4-(4-chlorobutyl)benzene[24]



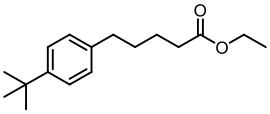
Compound 11 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 3.56 (t, *J* = 6.4 Hz, 2H), 2.62 (t, *J* = 7.3 Hz, 2H), 1.88 – 1.71 (m, 4H), 1.32 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.83, 138.90, 128.16, 125.39, 45.11, 34.67, 34.50, 32.32, 31.55, 28.70.
Spectroscopic data were consistent with literature values.

1-(tert-butyl)-4-(hex-5-yn-1-yl)benzene



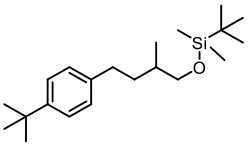
Compound 12 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.24 (td, *J* = 7.1, 2.7 Hz, 2H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.80 – 1.70 (m, 2H), 1.64 – 1.56 (m, 2H), 1.33 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.65, 139.28, 128.17, 125.32, 84.62, 68.43, 34.94, 34.48, 31.56, 30.56, 28.23, 18.45.
HRMS (EI): [M] cal'd for $C_{16}H_{22}$: 214.1721, found: 214.1716

Ethyl 5-(4-(tert-butyl)phenyl)pentanoate[25]



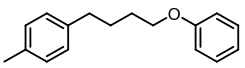
Compound 13 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:50)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 2.59 (t, *J* = 6.0 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.71 – 1.61 (m, 4H), 1.33 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.94, 148.54, 139.57, 128.13, 125.26, 60.30, 35.29, 34.43, 31.55, 31.19, 28.97, 24.99, 14.38.
Spectroscopic data were consistent with literature values.

Tert-butyl(4-(4-(tert-butyl)phenyl)-2-methylbutoxy)dimethylsilane



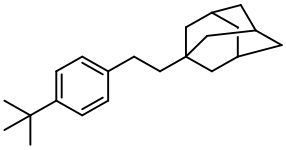
Compound 14 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:50)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.30 (m, 2H), 7.16 – 7.12 (m, 2H), 3.49 – 3.45 (m, 1H), 3.42 – 3.37 (m, 1H), 2.59 (t, *J* = 7.7 Hz, 2H), 1.72 – 1.57 (m, 2H), 1.54-1.46 (m, 1H), 1.34 (s, 9H), 0.92 (s, 9H), 0.91-0.89 (m, 3H), 0.06 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.46, 139.89, 128.17, 125.26, 68.47, 35.91, 35.84, 34.47, 33.11, 31.58, 26.12, 18.51, 16.85, -5.19.
GC-MS: [M] cal'd for $C_{21}H_{38}OSi$: 334.27, found: 333.00 (290.93, -*t*Bu)

1-methyl-4-(4-phenoxybutyl)benzene[26]



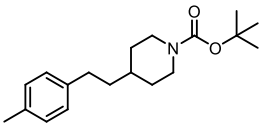
Compound 15 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:50)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.29 (m, 2H), 7.15 (singlet like multiplet, 4H), 7.00 – 6.97 (m, 1H), 6.96 – 6.93 (m, 2H), 4.01 (t, *J* = 6.1 Hz, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.93 – 1.78 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.21, 139.26, 135.31, 129.53, 129.14, 128.44, 120.63, 114.62, 67.77, 35.27, 29.02, 28.10, 21.12.
Spectroscopic data were consistent with literature values.

(3r,5r,7r)-1-(4-(tert-butyl)phenethyl)adamantane[20]



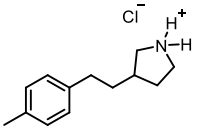
Compound 16 was prepared according to the general procedure (GP) and isolated as pale yellow viscous liquid.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.61 – 2.55 (m, 2H), 2.07 – 1.99 (m, 3H), 1.79 - 1.76 (m, 3 H), 1.74 – 1.68 (m, 3H), 1.61 (d, *J* = 3.1 Hz, 6H), 1.46 – 1.39 (m, 2H), 1.36 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.31, 140.84, 128.10, 125.30, 47.02, 42.59, 37.44, 34.45, 32.61, 31.59, 28.95, 28.64.
Spectroscopic data were consistent with literature values.

tert-butyl 4-(4-methylphenethyl)piperidine-1-carboxylate[27]



Compound 17 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:20)
^{1}H NMR (600 MHz, Chloroform-d) δ 7.10 – 7.05 (m, 4H), 4.07 (bs, 2H), 2.63 – 2.70 (m, 2H), 2.61 – 2.57 (m, 2H), 2.32 (s, 3H), 1.67 – 1.72 (m, 2H), 1.57 – 1.52 (m, 2H), 1.46 (s, 9H), 1.42 – 1.37 (m, 1H), 1.17 – 1.08 (m, 2H).
Spectroscopic data were consistent with literature values.

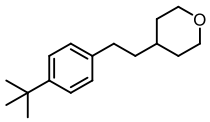
3-(4-methylphenethyl)pyrrolidin-1-ium chloride



Compound 18 was prepared according to the general procedure (GP) and isolated as pale yellow oil. Due to unknown impurities that could not be separated during the purification, the compound was then Boc-deprotected. Compound 18 was dissolved in a cooled (0 °C) 0.1 M solution of HCl (4N in dioxane) and stirred at room temperature for 4h. The solvent was removed in vacuo and compound 18' was washed with Et_2O.

Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:20)
^{1}H NMR (600 MHz, Chloroform-d) δ 9.71 (s, 1H), 9.65 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 3.47 – 3.39 (m, 2H), 3.26 – 3.21 (m, 1H), 2.87 – 2.81 (m, 1H), 2.66 – 2.55 (m, 2H), 2.31 (s, 3H), 2.19 – 2.11 (m, 1H), 1.81 – 1.70 (m, 3H), 1.66 – 1.60 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 137.91, 135.87, 129.39, 128.26, 49.90, 44.86, 38.05, 34.44, 34.04, 30.69, 21.12.
HRMS (ESI+): $[M+H]^+$ cal'd for $C_{13}H_{19}N$: 190.1590, found: 190.1589

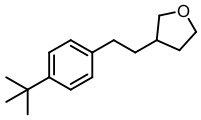
4-(4-(tert-butyl)phenethyl)tetrahydro-2H-pyran



Compound 19 was prepared according to the general procedure (GP) and isolated as pale yellow oil.

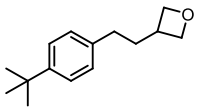
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:20)
^{1}H NMR (600 MHz, Chloroform-d) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 3.99 (dd, *J* = 11.42, 4.41, 2H), 3.40 (td, *J* = 11.72, 2.11, 2H), 2.65 – 2.61 (m, 2H), 1.71-1.66 (m, 2H), 1.62-1.58 (m, 3H), 1.40-1.35 (m, 2H), 1.34 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.59, 139.56, 128.05, 125.33, 68.19, 38.85, 34.71, 34.45, 33.23, 32.21, 31.54.
HRMS (EI): [M] cal'd for $C_{17}H_{26}O$: 246.1983, found: 246.1978

3-(4-(tert-butyl)phenethyl)tetrahydrofuran



Compound 20 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:20)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 3.96 – 3.91 (t, *J* = 7.8 Hz, 1H), 3.88 (td, *J* = 8.3, 4.7 Hz, 1H), 3.76 (q, *J* = 7.9 Hz, 1H), 3.41-3.37 (m, 1H), 2.68 – 2.56 (m, 2H), 2.28 – 2.17 (m, 1H), 2.12-2.04 (m, 1H), 1.76 – 1.70 (m, 2H), 1.61-1.52 (m, 1H), 1.33 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.78, 139.07, 128.08, 125.38, 73.46, 68.08, 39.03, 35.27, 34.48, 34.38, 32.61, 31.54.
HRMS (EI): [M] cal'd for $C_{16}H_{24}O$: 232.1827, found: 232.1821

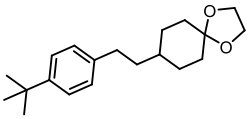
3-(4-(tert-butyl)phenethyl)oxetane



Compound 21 was prepared according to the general procedure (GP) and isolated as pale yellow oil.

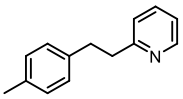
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:20)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 4.77 (dd, *J* = 7.8, 5.9 Hz, 2H), 4.37 (t, *J* = 6.1 Hz, 2H), 3.01 (tt, *J* = 7.8, 6.3 Hz, 1H), 2.55 – 2.50 (t, *J* = 98 Hz, 2H), 2.02 (q, *J* = 7.7 Hz, 2H), 1.32 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.97, 138.47, 128.09, 125.42, 77.71, 35.55, 34.92, 34.49, 32.85, 31.52.
HRMS (EI): [M] cal'd for $C_{15}H_{22}O$: 218.1670, found: 218.1665

8-(4-(tert-butyl)phenethyl)-1,4-dioxaspiro[4.5]decane



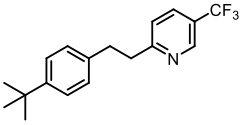
Compound 22 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:20)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 – 7.30 (m, 2H), 7.14 – 7.11 (m, 2H), 3.95 (s, 4H), 2.64 – 2.58 (m, 2H), 1.83 – 1.73 (m, 4H), 1.62 – 1.51 (m, 4H), 1.34-1.31 (m, 2H), 1.32 (s, 9H), 0.96 – 0.86 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.48, 139.91, 128.05, 125.29, 109.32, 64.30, 38.22, 36.14, 34.61, 34.45, 33.10, 31.55, 30.25.
GC-MS: [M] cal'd for $C_{20}H_{30}O_2$: 302.22, found: 301.74

2-(4-methylphenethyl)pyridine[28]



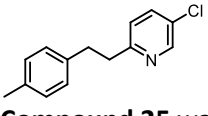
Compound 23 was prepared according to the general procedure (GP) and isolated as a white solid.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:10)
^{1}H NMR (400 MHz, Chloroform-d**)** δ 8.58 – 8.55 (m, 1H), 7.57 (td, *J* = 7.6, 1.9 Hz, 1H), 7.14 – 7.07 (m, 6H), 3.12 – 2.99 (m, 4H), 2.32 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.42, 149.25, 138.52, 136.57, 135.48, 129.15, 128.46, 123.19, 121.31, 40.35, 35.75, 21.12.
Spectroscopic data were consistent with literature values.

2-(4-(tert-butyl)phenethyl)-5-(trifluoromethyl)pyridine



Compound 24 was prepared according to the general procedure (GP) and isolated as white solid.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:10)
^{1}H NMR (400 MHz, Chloroform-d) δ 8.84 – 8.83 (m, 1H), 7.81 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.17 – 7.13 (m, 2H), 3.20 – 3.16 (m, 2H), 3.07 – 3.03 (m, 2H), 1.32 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.64 (d, *J* = 1.35), 149.18, 146.41 (q, *J* = 4.05), 138.01, 133.47 (q, *J* = 3.46), 128.19, 125.52, 124.41 (q, *J* = 32.91), 123.39 (q, *J* = 272.01), 122.80, 40.25, 35.19, 34.53, 31.53.
^{19}F NMR (376 MHz, CDCl3) δ -62.20.
HRMS (ESI+): $[M+H]^+$ cal'd for $C_{18}H_{20}F_3N$: 308.1620, found: 308.1628
M.p.: 58-62 °C

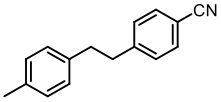
5-chloro-2-(4-methylphenethyl)pyridine



Compound 25 was prepared according to the general procedure (GP) and isolated as a white solid.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:10)
^{1}H NMR (600 MHz, Chloroform-d) δ 8.51 (d, *J* = 2.5 Hz, 1H), 7.53 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.10 – 7.05 (m, 4H), 7.01 (d, *J* = 8.3 Hz, 1H), 3.08 – 3.03 (m, 2H), 3.02 – 2.98 (m, 2H), 2.32 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.67, 148.27, 138.19, 136.06, 135.66, 129.59, 129.23, 128.45, 123.89, 39.71, 35.54, 21.15.

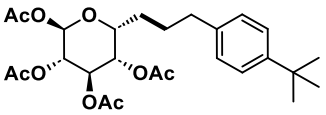
HRMS (ESI+): $[M+H]^+$ cal'd for $C_{14}H_{14}ClN$: 232.0887 , found: 232.0889
M.p.: 69-71 °C

4-(4-methylphenethyl)benzonitrile[29]



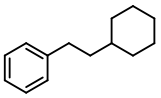
Compound 26 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:10)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 2.98 – 2.94 (m, 2H), 2.90 – 2.85 (m, 2H), 2.32 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.50, 137.66, 135.88, 132.26, 129.46, 129.27, 128.41, 119.25, 109.92, 38.17, 36.92, 21.15.
Spectroscopic data were consistent with literature values.

(2R,3S,4R,5S,6R)-6-(3-(4-(tert-butyl)phenyl)propyl)tetrahydro-2H-pyran-2,3,4,5-tetrayl tetraacetate



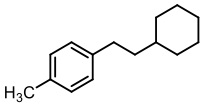
Compound 27 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:4)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.31 (m, 2H), 7.16 – 7.12 (m, 2H), 5.36 – 5.29 (m, 1H), 5.10 (dd, *J* = 9.5, 5.8 Hz, 1H), 4.99 (t, *J* = 9.2 Hz, 1H), 4.26 – 4.17 (m, 2H), 4.07 (dd, *J* = 12.2, 2.6 Hz, 1H), 3.87 (ddd, *J* = 9.6, 5.6, 2.6 Hz, 1H), 2.74 (ddd, *J* = 14.7, 10.1, 4.9 Hz, 1H), 2.59 (ddd, *J* = 14.0, 9.6, 6.9 Hz, 1H), 2.10 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.87 – 1.76 (m, 2H), 1.32 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.79, 170.26, 169.74, 169.67, 149.21, 137.98, 128.16, 125.56, 72.28, 70.66, 70.46, 69.07, 68.80, 62.57, 34.50, 31.49, 30.71, 27.39, 20.88, 20.83, 20.80, 20.76.
HRMS (ESI+): $[M+H]^+$ cal'd for $C_{26}H_{36}O_9$: 493.24831, found: 493.2436

(2-cyclohexylethyl)benzene[30]



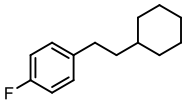
Compound 28 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.24 (m, 2H), 7.19 – 7.15 (m, 3H), 2.64 – 2.58 (m, 2H), 1.80 – 1.73 (m, 2H), 1.73 – 1.63 (m, 3H), 1.54 – 1.46 (m, 2H), 1.33 – 1.16 (m, 4H), 0.93 (qd, *J* = 11.7, 3.2 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.41, 128.49, 128.38, 125.63, 39.57, 37.48, 33.47, 33.41, 26.86, 26.49.
Spectroscopic data were consistent with literature values.

1-(2-cyclohexylethyl)-4-methylbenzene[31]



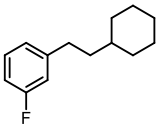
Compound 29 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.11 (br. s, 4H), 2.63 – 2.59 (t, *J* = 6 Hz, 2H), 2.35 (s, 3H), 1.84 – 1.77 (m, 2H), 1.77 – 1.65 (m, 3H), 1.56 – 1.48 (m, 2H), 1.33 – 1.19 (m, 4H), 1.00-0.88 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.30, 135.00, 129.07, 128.36, 39.72, 37.44, 33.47, 32.92, 26.87, 26.49, 21.13.
Spectroscopic data were consistent with literature values.

1-(2-cyclohexylethyl)-4-fluorobenzene[32]



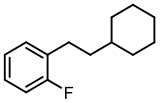
Compound 30 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.15 – 7.10 (m, 2H), 6.99 – 6.93 (m, 2H), 2.62 – 2.56 (m, 2H), 1.81 – 1.66 (m, 5H), 1.53 – 1.45 (m, 2H), 1.27 – 1.16 (m, 4H), 1.00 – 0.85 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.23 (d, *J* = 242.8 Hz), 138.91 (d, *J* = 3.2 Hz), 129.71 (d, *J* = 7.7 Hz), 115.06 (d, *J* = 21.0 Hz), 39.66, 37.37, 33.44, 32.56, 26.82, 26.47.
Spectroscopic data were consistent with literature values.

1-(2-cyclohexylethyl)-3-fluorobenzene



Compound 31 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.22 (td, *J* = 7.8, 6.0 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.91 – 6.83 (m, 2H), 2.65 – 2.59 (m, 2H), 1.82 – 1.61 (m, 5H), 1.54 – 1.46 (m, 2H), 1.33 – 1.15 (m, 4H), 0.97 – 0.89 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.06 (d, *J* = 244.8 Hz), 146.00 (d, *J* = 7.1 Hz), 129.71 (d, *J* = 8.3 Hz), 124.12 (d, *J* = 2.7 Hz), 115.25 (d, *J* = 20.6 Hz), 112.48 (d, *J* = 21.1 Hz), 39.19, 37.39, 33.42, 33.15, 26.81, 26.46.
^{19}F NMR (376 MHz, CDCl3) δ -114.13.
HRMS (EI): [M] cal'd for $C_{14}H_{19}F$: 206.1471, found: 206.1468

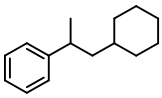
1-(2-cyclohexylethyl)-2-fluorobenzene



Compound 32 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.21 – 7.12 (m, 2H), 7.06 – 7.04 (m, 1H), 7.02 – 6.97 (m, 1H), 2.68 – 2.62 (t, *J* = 8.0 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.74 – 1.65 (m, 3H), 1.55 – 1.45 (m, 2H), 1.24 – 1.15 (m, 4H), 1.00 – 0.89 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.28 (d, *J* = 244.3 Hz), 130.61 (d, *J* = 5.3 Hz), 130.11 (d, *J* = 16.0 Hz), 127.30 (d, *J* = 8.1 Hz), 123.96 (d, *J* = 3.5 Hz), 115.25 (d, *J* = 22.3 Hz), , 38.09, 37.59, 33.38, 26.84, 26.51, 26.48.

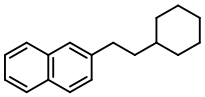
^{19}F NMR (376 MHz, CDCl3) δ -119.16.
HRMS (EI): [M] cal'd for $C_{14}H_{19}F$: 206.1471, found: 206.1468

(1-cyclohexylpropan-2-yl)benzene



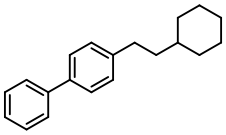
Compound 33 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.29 (m, 2H), 7.23 – 7.18 (m, 3H), 2.85 (m, 1H), 1.82-1.77 (m, 1H), 1.73 – 1.61 (m, 4H), 1.57 – 1.49 (m, 1H), 1.45 – 1.35 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 3H), 1.22 – 1.11 (m, 4H), 0.99 – 0.81 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.32, 128.42, 127.11, 125.83, 46.51, 36.78, 35.20, 33.80, 33.50, 26.86, 26.40, 22.93.
HRMS (EI): [M] cal'd for $C_{15}H_{22}$: 202.1721, found: 202.1720

2-(2-cyclohexylethyl)naphthalene[33]



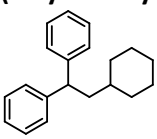
Compound 34 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.78 (m, 3H), 7.64 (s, 1H), 7.51 – 7.42 (m, 2H), 7.38 (td, *J* = 8.2, 1.8 Hz, 1H), 2.82 (t, *J* = 8Hz, 2H), 1.86 – 1.82 (m, 2H), 1.81 – 1.59 (m, 5H), 1.34 – 1.18 (m, 4H), 1.08 – 0.98 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.89, 133.82, 132.04, 127.93, 127.87, 127.73, 127.59, 126.30, 125.96, 125.14, 39.40, 37.47, 33.55, 33.50, 26.86, 26.50.
Spectroscopic data were consistent with literature values.

4-(2-cyclohexylethyl)-1,1'-biphenyl



Compound 35 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.59-7.56 (m, 2H), 7.53 – 7.48 (m, 2H), 7.45 – 7.38 (m, 2H), 7.34 – 7.28 (m, 1H), 7.27 – 7.23 (m, 2H), 2.69 – 2.61 (m, 2H), 1.83 – 1.75 (m, 2H), 1.75 – 1.62 (m, 3H), 1.56-1.50 (m, 2H), 1.23-1.14 (m, 2H), 1.01 – 0.91 (m, 2H), 0.91 – 0.81 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.57, 141.34, 138.63, 128.90, 128.83, 127.15, 127.13, 127.08, 39.55, 37.51, 33.48, 33.04, 26.86, 26.50.
HRMS (EI): [M] cal'd for $C_{20}H_{24}$: 264.1878, found: 264.1867

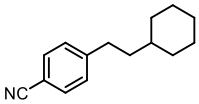
(2-cyclohexylethane-1,1-diyl)dibenzene[34]



Compound 36 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane

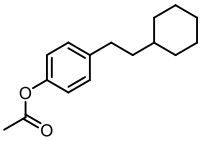
^{1}H NMR (400 MHz, Chloroform-d) δ 7.27 – 7.21 (m, 8H), 7.16 – 7.13 (m, 2H), 4.06 (t, *J* = 8.0 Hz, 1H), 1.91 (t, *J* = 8 Hz, 2H), 1.80 – 1.72 (m, 2H), 1.65 – 1.60 (m, 3H), 1.21 – 1.07 (m, 4H), 0.99 – 0.82 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.59, 128.89, 128.03, 126.08, 48.11, 43.76, 35.00, 33.56, 26.78, 26.28.
Spectroscopic data were consistent with literature values.

4-(2-cyclohexylethyl)benzonitrile



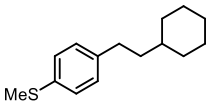
Compound 37 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.21 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 2.64 – 2.60 (m, 2H), 1.73 – 1.60 (m, 5H), 1.48 – 1.43 (m, 2H), 1.25 – 1.11 (m, 4H), 0.94 – 0.84 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.59, 134.95, 129.04, 127.35, 39.48, 37.36, 33.43, 32.81, 26.82, 26.46, 16.58.
HRMS (EI): [M] cal'd for $C_{15}H_{19}N$ 213.1517, found: 213.1518

4-(2-cyclohexylethyl)phenyl acetate



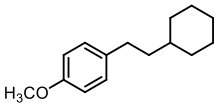
Compound 38 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:20)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.17 (d, *J* = 8.5 Hz, 2H), 7.00 – 6.96 (m, 2H), 2.63 – 2.58 (m, 2H), 2.29 (s, 3H), 1.80 – 1.67 (m, 4H), 1.54 – 1.46 (m, 2H), 1.24 – 1.16 (m, 4H), 0.99 – 0.88 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.57, 129.71, 128.90, 127.39, 127.31, 126.80, 120.48, 110.36, 37.80, 37.78, 33.51, 32.08, 27.55, 26.93, 26.55.
HRMS (EI): [M] cal'd for $C_{16}H_{22}O_2$: 246.1620, found: 246.1620

(4-(2-cyclohexylethyl)phenyl)(methyl)sulfane[35]



Compound 39 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane
^{1}H NMR (400 MHz, Chloroform-d) δ 7.21 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 2.61 – 2.56 (m, 2H), 2.48 (s, 3H), 1.80 – 1.64 (m, 5H), 1.53 – 1.44 (m, 2H), 1.26 – 1.16 (m, 4H), 1.00 – 0.85 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.59, 134.95, 129.04, 127.35, 39.48, 37.36, 33.43, 32.81, 26.82, 26.46, 16.58.
Spectroscopic data were consistent with literature values.

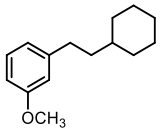
1-(2-cyclohexylethyl)-4-methoxybenzene[35]



Compound 40 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:20)

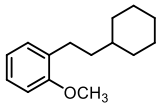
^{1}H NMR (400 MHz, Chloroform-d) δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 2.65 – 2.58 (m, 2H), 1.86 – 1.67 (m, 5H), 1.57 – 1.48 (m, 2H), 1.36 – 1.21 (m, 4H), 1.03 – 0.93 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.68, 135.42, 129.29, 113.79, 55.32, 39.78, 37.36, 33.45, 32.42, 26.85, 26.48.
Spectroscopic data were consistent with literature values.

1-(2-cyclohexylethyl)-3-methoxybenzene



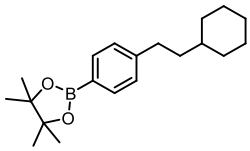
Compound 41 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:20)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.24 – 7.18 (m, 1H), 6.83 – 6.71 (m, 3H), 3.81 (s, 3H), 2.61 (t, *J* = 8 Hz, 2H), 1.83 – 1.63 (m, 5H), 1.59 – 1.47 (m, 2H), 1.33 – 1.18 (m, 4H), 0.99 – 0.91 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.72, 145.07, 129.30, 120.94, 114.27, 110.89, 55.24, 39.41, 37.46, 33.45, 26.84, 26.48.
HRMS (EI): [M] cal'd for $C_{15}H_{22}O$: 218.1671, found: 218.1670

1-(2-cyclohexylethyl)-2-methoxybenzene



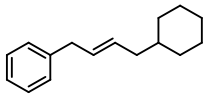
Compound 42 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:20)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.18 – 7.16 (m, 1H), 7.14-7.12 (m, 1H), 6.90 – 6.88 (m, 1H), 6.86-6.83 (m, 1H), 3.82 (s, 3H), 2.64 – 2.59 (m, 2H), 1.84 – 1.76 (m, 2H), 1.73 – 1.62 (m, 4H), 1.50 – 1.43 (m, 2H), 1.23 – 1.13 (m, 3H), 0.98 – 0.92 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.57, 131.85, 129.71, 126.80, 120.48, 110.36, 55.41, 37.80, 37.78, 33.50, 27.55, 26.93, 26.55.
HRMS (EI): [M] cal'd for $C_{15}H_{22}O$: 218.1671, found: 218.1670

2-(4-(2-cyclohexylethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



Compound 43 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 1:20)
The yield was determined using CH_2Br_2 as internal standard.
Spectroscopic data were consistent with literature values.

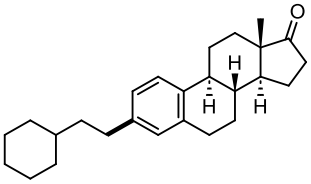
(E)-(4-cyclohexylbut-2-en-1-yl)benzene[36]



Compound 44 was prepared according to the general procedure (GP) and isolated as pale yellow oil.
Column Chromatography: Silica, heptane

^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.31 (m, 2H), 7.25 – 7.22 (m, 3H), 5.65 – 5.49 (m, 2H), 3.39 (d, *J* = 5.8 Hz, 1.88 H), 3.36 (s, 0.16 H), 1.98 (t, *J* = 6.3 Hz, 2H), 1.78 – 1.60 (m, 5H), 1.34 – 1.15 (m, 4H), 0.98 – 0.89 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.29, 129.82, 128.89, 128.61, 128.46, 125.97, 40.72, 39.27, 38.19, 33.30, 26.77, 26.52.
E/Z ratio: 12:1
Spectroscopic data were consistent with literature values.

(8R,9S,13S,14S)-3-(2-cyclohexylethyl)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one



Compound 45 was prepared according to the general procedure (GP) and isolated as a white solid.
Column Chromatography: Silica, EtOAc/heptane (0:100 to 2:98)
^{1}H NMR (400 MHz, Chloroform-d) δ 7.20 (*d*, J = 8.0 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.92 (s, 1H), 2.92 – 2.88 (m, 2H), 2.58 – 2.50 (m, 2H), 2.50 – 2.38 (m, 2H), 2.32 – 2.26 (m, 1H), 2.19 – 1.93 (m, 5H), 1.81 – 1.58 (m, 9H), 1.58 – 1.38 (m, 9H), 0.91 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.92, 137.02, 136.40, 129.10, 125.96, 125.40, 50.67, 48.18, 44.46, 39.66, 38.41, 37.62, 36.03, 33.47, 32.87, 31.77, 29.56, 26.86, 26.75, 26.49, 25.89, 21.74, 14.01. N.B. C-carbonyl is not visible.
HRMS (ESI+): $[M+H]^+$ cal'd for $C_{26}H_{36}O$: 365.2839, found: 365.2835
M.p.: 71-73 °C

9. References

(1) Speckmeier, E.; Fischer, T. G.; Zeitler, K. A Toolbox Approach To Construct Broadly Applicable Metal-Free Catalysts for Photoredox Chemistry: Deliberate Tuning of Redox Potentials and Importance of Halogens in Donor–Acceptor Cyanoarenes. *J. Am. Chem. Soc.* **2018**, *140* (45), 15353–15365. https://doi.org/10.1021/jacs.8b08933.

(2) Kabalka, G. .; Wu, Z. .; Yao, M.-L.; Natarajan, N. The Syntheses and in Vivo Biodistribution of Novel Boronated Unnatural Amino Acids. *Appl. Radiat. Isot.* **2004**, *61* (5), 1111–1115. https://doi.org/10.1016/j.apradiso.2004.05.012.

(3) Urbanczyk-Pearson, L. M.; Femia, F. J.; Smith, J.; Parigi, G.; Duimstra, J. A.; Eckermann, A. L.; Luchinat, C.; Meade, T. J. Mechanistic Investigation of β-Galactosidase-Activated MR Contrast Agents. *Inorg. Chem.* **2008**, *47* (1), 56–68. https://doi.org/10.1021/ic700888w.

(4) Drennhaus, T.; Leifert, D.; Lammert, J.; Drennhaus, J. P.; Bergander, K.; Daniliuc, C. G.; Studer, A. Enantioselective Copper-Catalyzed Fukuyama Indole Synthesis from 2-Vinylphenyl Isocyanides. *J. Am. Chem. Soc.* **2023**, *145* (15), 8665–8676. https://doi.org/10.1021/jacs.3c01667.

(5) Music, A.; Baumann, A. N.; Boser, F.; Müller, N.; Matz, F.; Jagau, T. C.; Didier, D. Photocatalyzed Transition-Metal-Free Oxidative Cross-Coupling Reactions of Tetraorganoborates**. *Chem. – A Eur. J.* **2021**, *27* (13), 4322–4326. https://doi.org/10.1002/chem.202005282.

(6) Forni, J. A.; Gandhi, V. H.; Polyzos, A. Carbonylative Hydroacylation of Styrenes with Alkyl Halides by Multiphoton Tandem Photoredox Catalysis in Flow. *ACS Catal.* **2022**, *12* (16), 10018–10027. https://doi.org/10.1021/acscatal.2c02531.

(7) Lepori, M.; Schmid, S.; Barham, J. P. Photoredox Catalysis Harvesting Multiple Photon or Electrochemical Energies. *Beilstein J. Org. Chem.* **2023**, *19*, 1055–1145. https://doi.org/10.3762/bjoc.19.81.

(8) Lima, F.; Sharma, U. K.; Grunenberg, L.; Saha, D.; Johannsen, S.; Sedelmeier, J.; Van der Eycken, E. V.; Ley, S. V. A Lewis Base Catalysis Approach for the Photoredox Activation of Boronic Acids and Esters. *Angew. Chem. Int. Ed.* **2017**, *56* (47), 15136–15140. https://doi.org/10.1002/anie.201709690.

(9) Wu, Z.; Gockel, S. N.; Hull, K. L. Anti-Markovnikov Hydro(Amino)Alkylation of Vinylarenes via Photoredox Catalysis. *Nat. Commun.* **2021**, *12* (1), 5956. https://doi.org/10.1038/s41467-021-26170-6.

(10) Giese, B. Formation of CC Bonds by Addition of Free Radicals to Alkenes. *Angew. Chem. Int. Ed. English* **1983**, *22* (10), 753–764. https://doi.org/10.1002/anie.198307531.

(11) Spiegel, D. A.; Wiberg, K. B.; Schacherer, L. N.; Medeiros, M. R.; Wood, J. L. Deoxygenation of Alcohols Employing Water as the Hydrogen Atom Source. *J. Am. Chem. Soc.* **2005**, *127* (36), 12513–12515. https://doi.org/10.1021/ja052185l.

(12) Tantawy, W.; Zipse, H. Hydroxylic Solvents as Hydrogen Atom Donors in Radical Reactions. *European J. Org. Chem.* **2007**, *2007* (35), 5817–5820. https://doi.org/10.1002/ejoc.200700948.

(13) Zhang, J.; Mück-Lichtenfeld, C.; Studer, A. Photocatalytic Phosphine-Mediated Water Activation for Radical Hydrogenation. *Nature* **2023**, *619* (7970), 506–513. https://doi.org/10.1038/s41586-023-06141-1.

(14) Grotjahn, S.; König, B. Photosubstitution in Dicyanobenzene-Based Photocatalysts. *Org. Lett.* **2021**, *23* (8), 3146–3150. https://doi.org/10.1021/acs.orglett.1c00836.

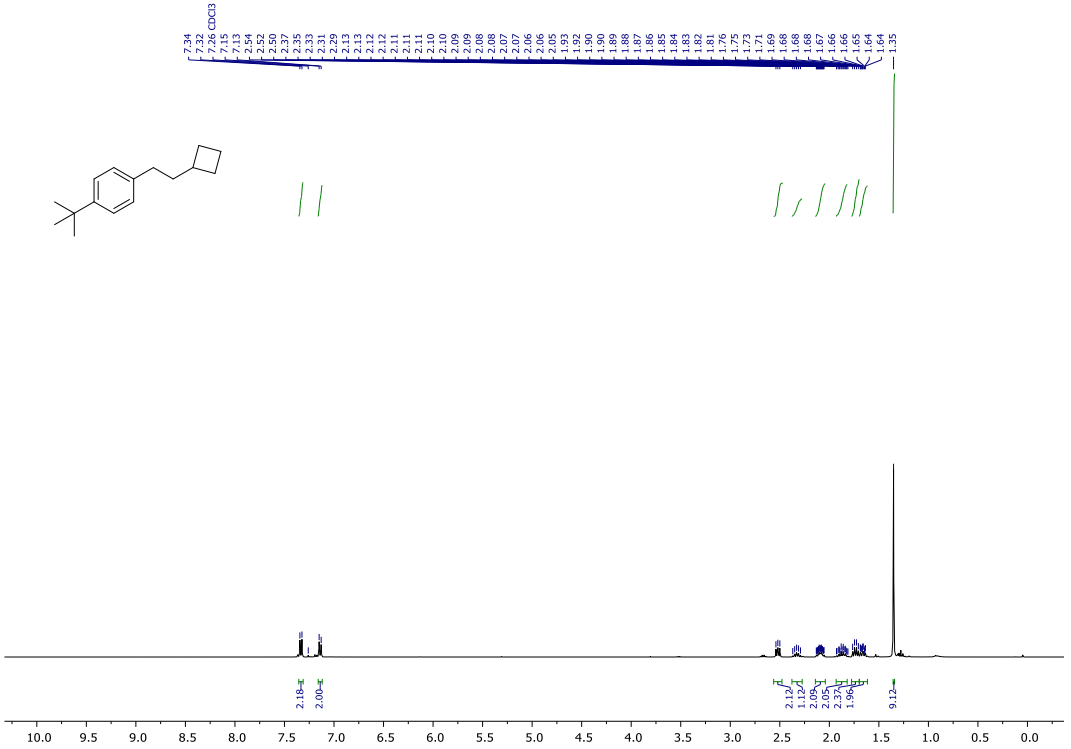
(15) Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.V.; Bloino, J., Janesko, B.G., Gomperts, R., Mennucci, B., Hratchian, H.P., D. J. G. Inc., Wallingford CT, GaussView 5.0. Wallingford, E.U.A. 2016.

(16) Becke, A. D. A New Mixing of Hartree–Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1993**, *98* (2), 1372–1377. https://doi.org/10.1063/1.464304.

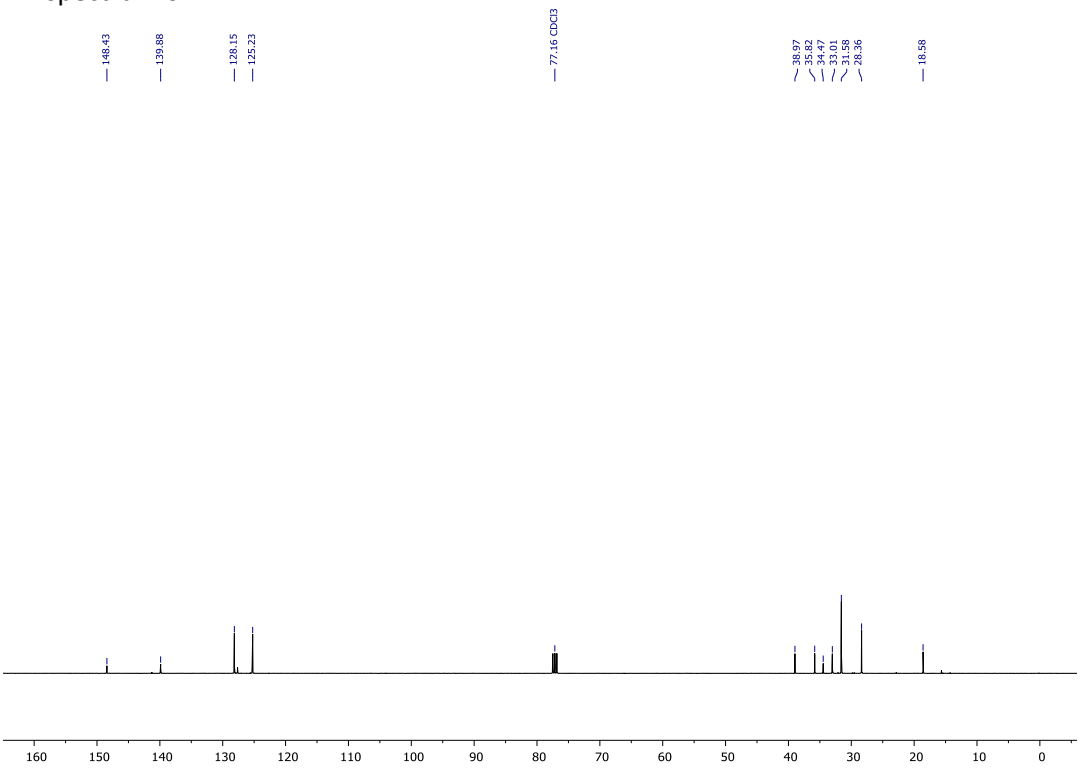
(17) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297. https://doi.org/10.1039/b508541a.
(18) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113* (18), 6378–6396. https://doi.org/10.1021/jp810292n.
(19) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32* (7), 1456–1465. https://doi.org/10.1002/jcc.21759.
(20) Scamp, R. J.; Scheffer, B.; Schomaker, J. M. Regioselective Differentiation of Vicinal Methylene C–H Bonds Enabled by Silver-Catalysed Nitrene Transfer. *Chem. Commun.* **2019**, *55* (51), 7362–7365. https://doi.org/10.1039/C9CC04006D.
(21) Yus, M.; Ortiz, R. Tandem Intramolecular Carbolithiation-Lithium/Zinc Transmetallation and Applications to Carbon−Carbon Bond-Forming Reactions. *Eur. J. Org. Chem.* **2004**, *2004* (18), 3833–3841. https://doi.org/10.1002/ejoc.200400349.
(22) Hamby, T. B.; LaLama, M. J.; Sevov, C. S. Controlling Ni Redox States by Dynamic Ligand Exchange for Electroreductive Csp^3–Csp^2 Coupling. *Science.* **2022**, *376* (6591), 410–416. https://doi.org/10.1126/science.abo0039.
(23) Chen, H.; Hu, L.; Ji, W.; Yao, L.; Liao, X. Nickel-Catalyzed Decarboxylative Alkylation of Aryl Iodides with Anhydrides. *ACS Catal.* **2018**, *8* (11), 10479–10485. https://doi.org/10.1021/acscatal.8b03396.
(24) Perlmutter, J. I.; Forbes, L. T.; Krysan, D. J.; Ebsworth-Mojica, K.; Colquhoun, J. M.; Wang, J. L.; Dunman, P. M.; Flaherty, D. P. Repurposing the Antihistamine Terfenadine for Antimicrobial Activity against Staphylococcus Aureus. *J. Med. Chem.* **2014**, *57* (20), 8540–8562. https://doi.org/10.1021/jm5010682.
(25) Pang, H.; Wang, Y.; Gallou, F.; Lipshutz, B. H. Fe-Catalyzed Reductive Couplings of Terminal (Hetero)Aryl Alkenes and Alkyl Halides under Aqueous Micellar Conditions. *J. Am. Chem. Soc.* **2019**, *141* (43), 17117–17124. https://doi.org/10.1021/jacs.9b04510.
(26) Nagano, T.; Hayashi, T. Iron-Catalyzed Grignard Cross-Coupling with Alkyl Halides Possessing β-Hydrogens. *Org. Lett.* **2004**, *6* (8), 1297–1299. https://doi.org/10.1021/ol049779y.
(27) Knez, D.; Colettis, N.; Iacovino, L. G.; Sova, M.; Pišlar, A.; Konc, J.; Lešnik, S.; Higgs, J.; Kamecki, F.; Mangialavori, I.; Dolšak, A.; Žakelj, S.; Trontelj, J.; Kos, J.; Binda, C.; Marder, M.; Gobec, S. Stereoselective Activity of 1-Propargyl-4-Styrylpiperidine-like Analogues That Can Discriminate between Monoamine Oxidase Isoforms A and B. *J. Med. Chem.* **2020**, *63* (3), 1361–1387. https://doi.org/10.1021/acs.jmedchem.9b01886.
(28) Yang, X.-W.; Li, D.-H.; Song, A.-X.; Liu, F.-S. "Bulky-Yet-Flexible" α-Diimine Palladium-Catalyzed Reductive Heck Cross-Coupling: Highly Anti-Markovnikov-Selective Hydroarylation of Alkene in Air. *J. Org. Chem.* **2020**, *85* (18), 11750–11765. https://doi.org/10.1021/acs.joc.0c01509.
(29) Li, H.; Li, S.; Hu, H.; Sun, R.; Liu, M.; Ding, A.; Liu, X.; Luo, W.; Fu, Z.; Guo, S.; Cai, H. Visible-light-induced $C(sp^3)$–$C(sp^3)$ bond formation *via* radical/radical cross-coupling, **2023**, 59, 1205–1208. https://doi.org/10.1039/d2cc05840e.
(30) Aragón, J.; Sun, S.; Pascual, D.; Jaworski, S.; Lloret-Fillol, J. Photoredox Activation of Inert Alkyl Chlorides for the Reductive Cross-Coupling with Aromatic Alkenes. *Angew. Chem. Int. Ed.* **2022**, *61* (21). https://doi.org/10.1002/anie.202114365.
(31) Bedford, R. B.; Betham, M.; Bruce, D. W.; Danopoulos, A. A.; Frost, R. M.; Hird, M. Iron - Phosphine , - Phosphite , - Arsine , and - Carbene Catalysts for the Coupling of Primary and Secondary Alkyl Halides with Aryl Grignard Reagents. *J. Org. Chem.* **2006**, 71, 3, 1104–1110. https://doi.org/10.1021/jo052250+
(32) Liu, J.; Yang, C.; Lu, X.; Zhang, Z.; Xu, L.; Cui, M.; Lu, X.; Xiao, B.; Fu, Y.; Liu, L. Copper-Catalyzed Reductive Cross-Coupling of Nonactivated Alkyl Tosylates and Mesylates with Alkyl and Aryl

Bromides. *Chem. – A Eur. J.* **2014**, *20* (47), 15334–15338. https://doi.org/10.1002/chem.201405223.
(33) Tobisu, M.; Takahira, T.; Morioka, T.; Chatani, N. Nickel-Catalyzed Alkylative Cross-Coupling of Anisoles with Grignard Reagents via C–O Bond Activation. *J. Am. Chem. Soc.* **2016**, *138* (21), 6711–6714. https://doi.org/10.1021/jacs.6b03253.
(34) Nozawa-Kumada, K.; Onuma, S.; Ono, K.; Kumagai, T.; Iwakawa, Y.; Sato, K.; Shigeno, M.; Kondo, Y. Transition-Metal-Free Intermolecular Hydrocarbonation of Styrenes Mediated by NaH/1,10-Phenanthroline. *Chem. – A Eur. J.* **2023**, *29* (18), e202203143. https://doi.org/10.1002/chem.202203143
(35) Zhang, W.; Lin, S. Electroreductive Carbofunctionalization of Alkenes with Alkyl Bromides via a Radical-Polar Crossover Mechanism. *J. Am. Chem. Soc.* **2020**, *142* (49), 20661–20670. https://doi.org/10.1021/jacs.0c08532.
(36) Wiskur, S. L.; Korte, A.; Fu, G. C. Cross-Couplings of Alkyl Electrophiles under “Ligandless” Conditions: Negishi Reactions of Organozirconium Reagents. *J. Am. Chem. Soc.* **2004**, *126* (1), 82–83. https://doi.org/10.1021/ja0393729.

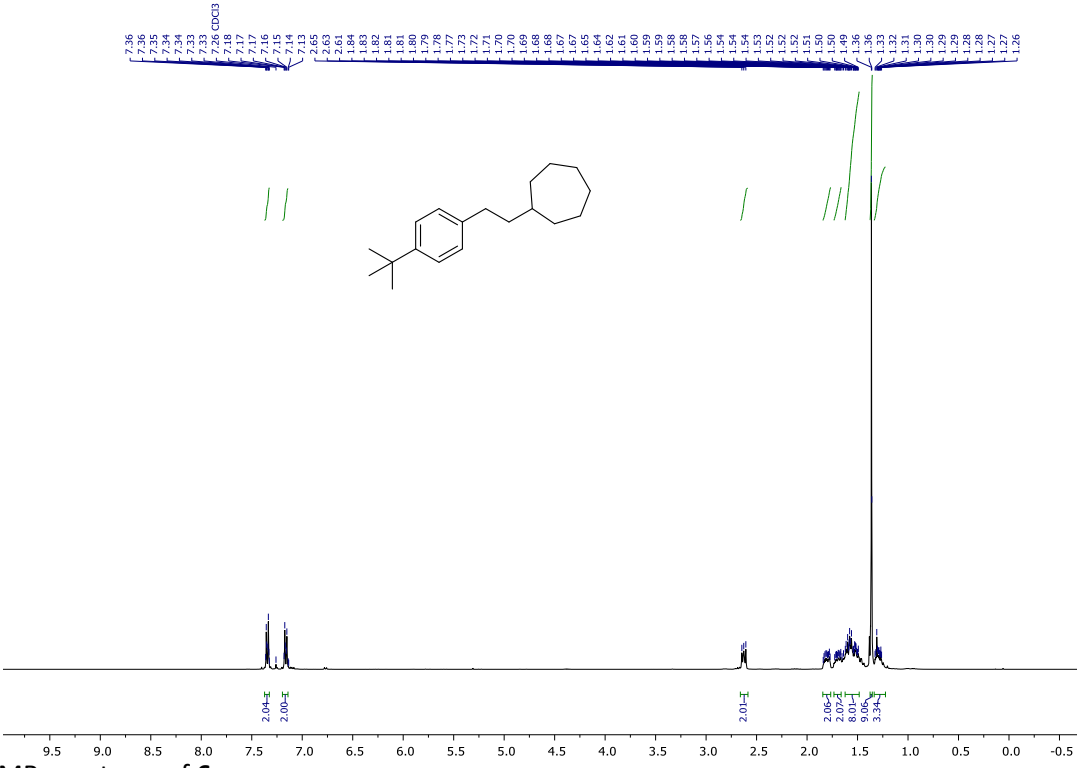
^{1}H NMR spectrum of **4**



^{13}C NMR spectrum of **4**



^{1}H NMR spectrum of **6**



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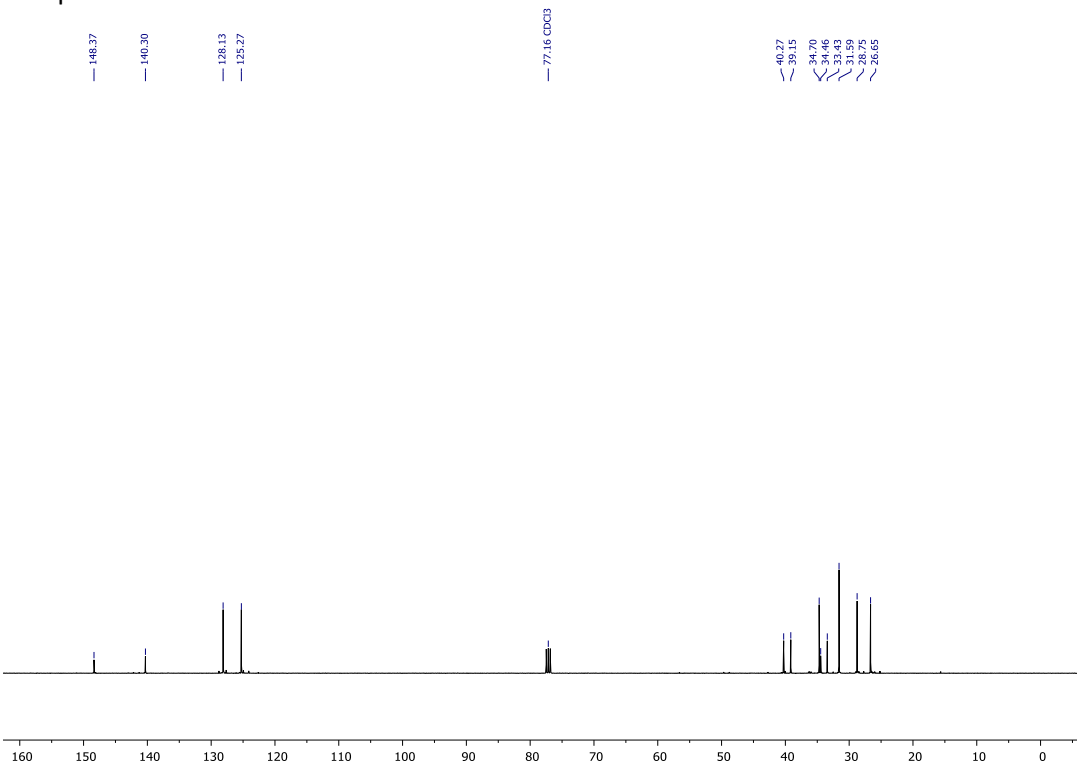

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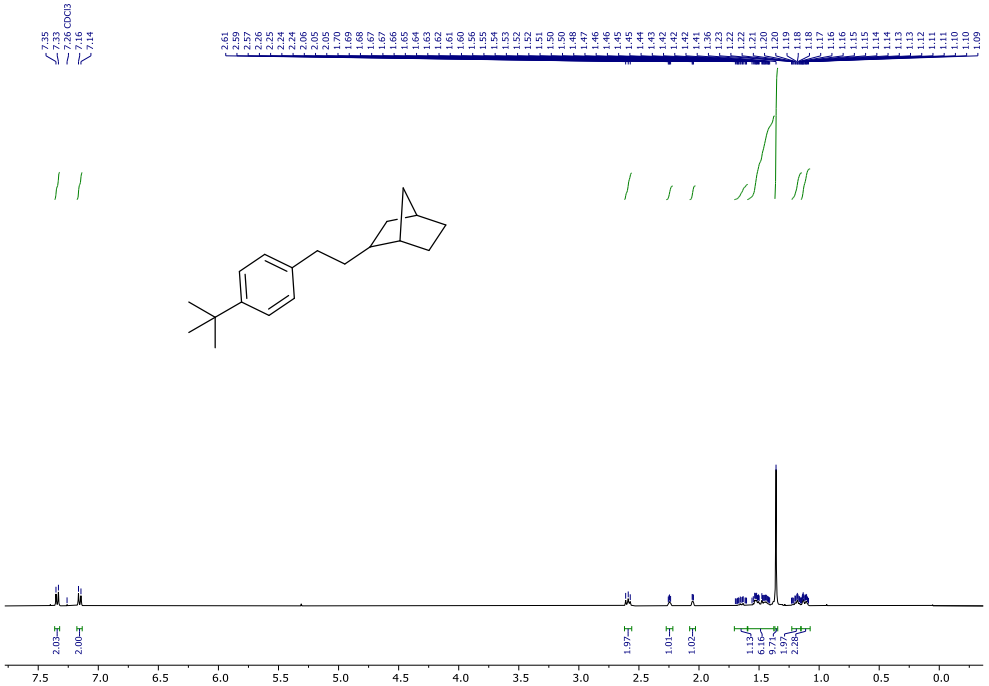
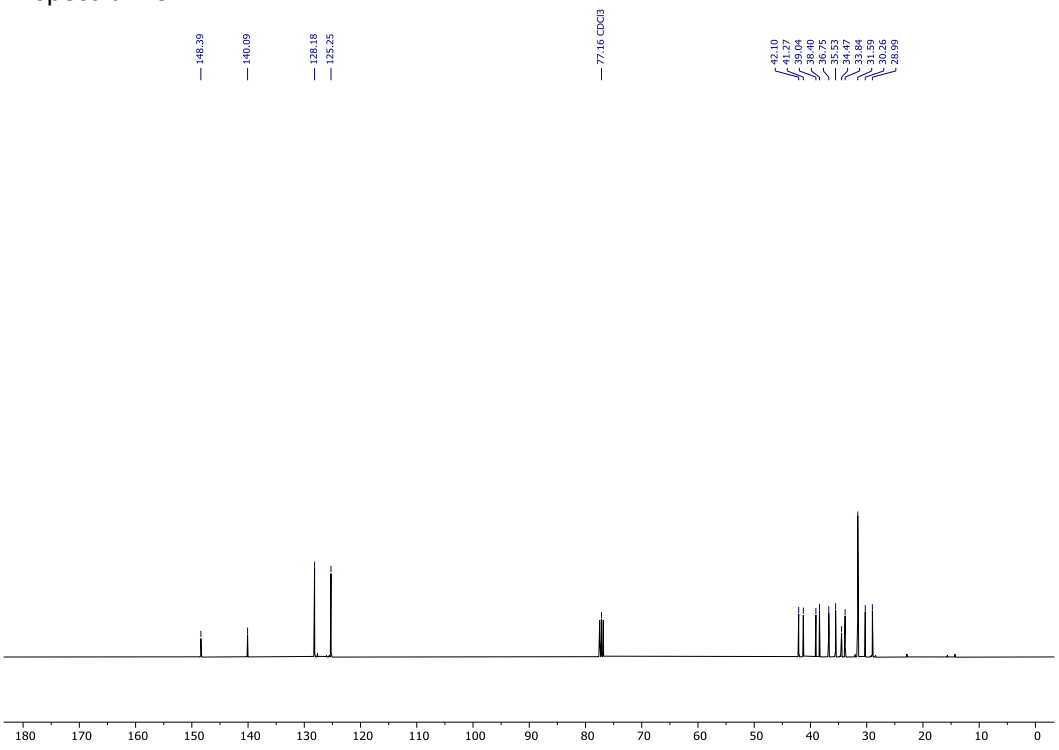
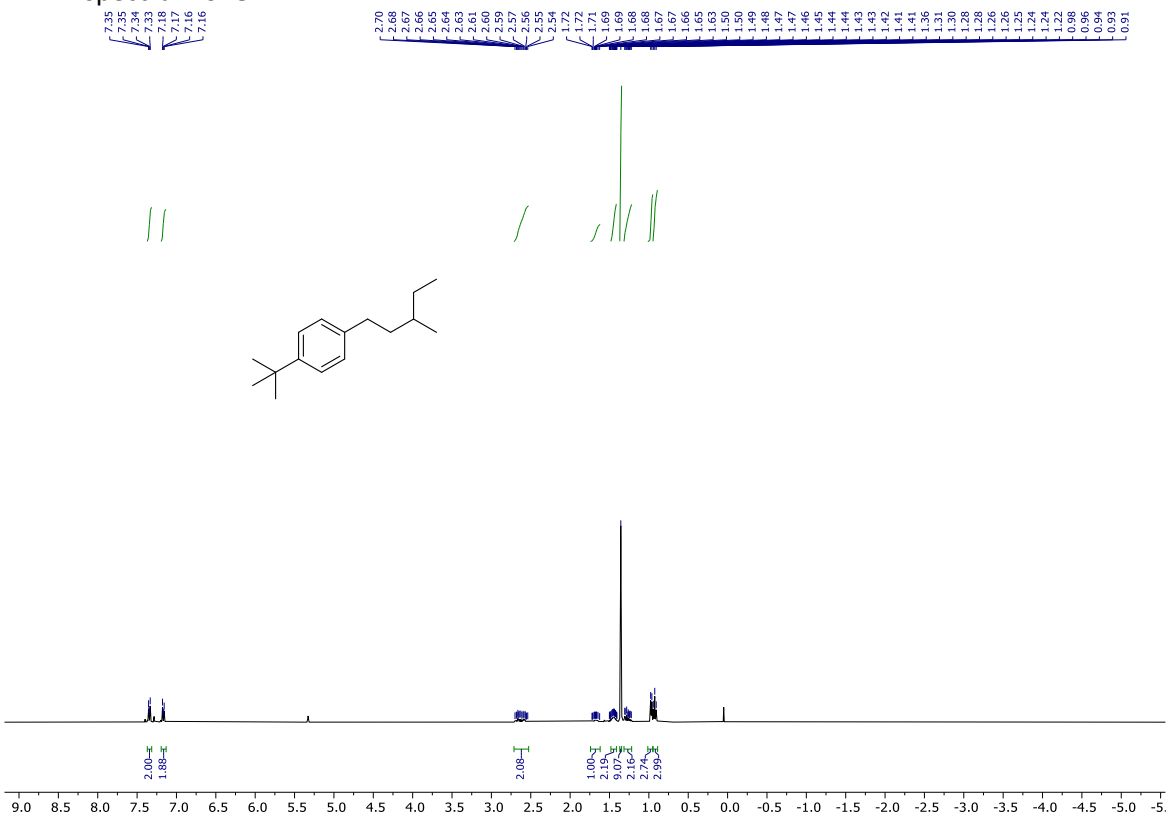


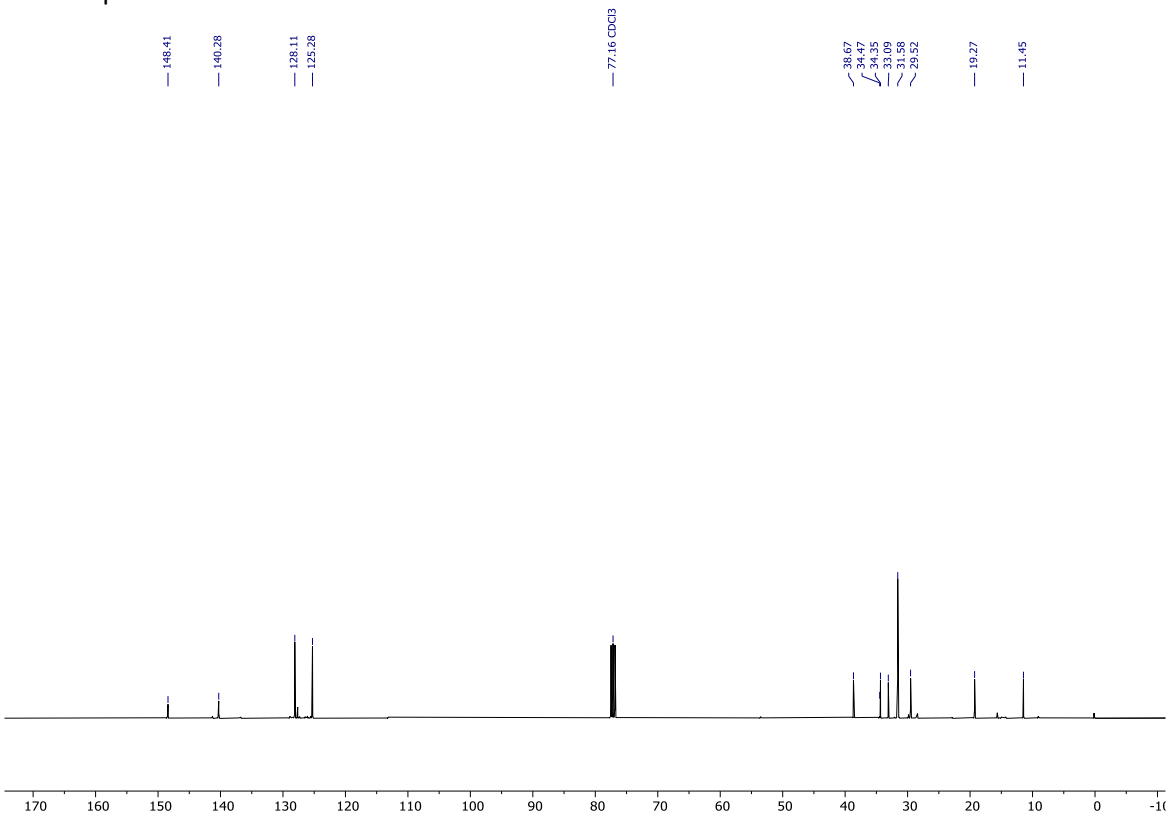
^{13}C NMR spectrum of **7**



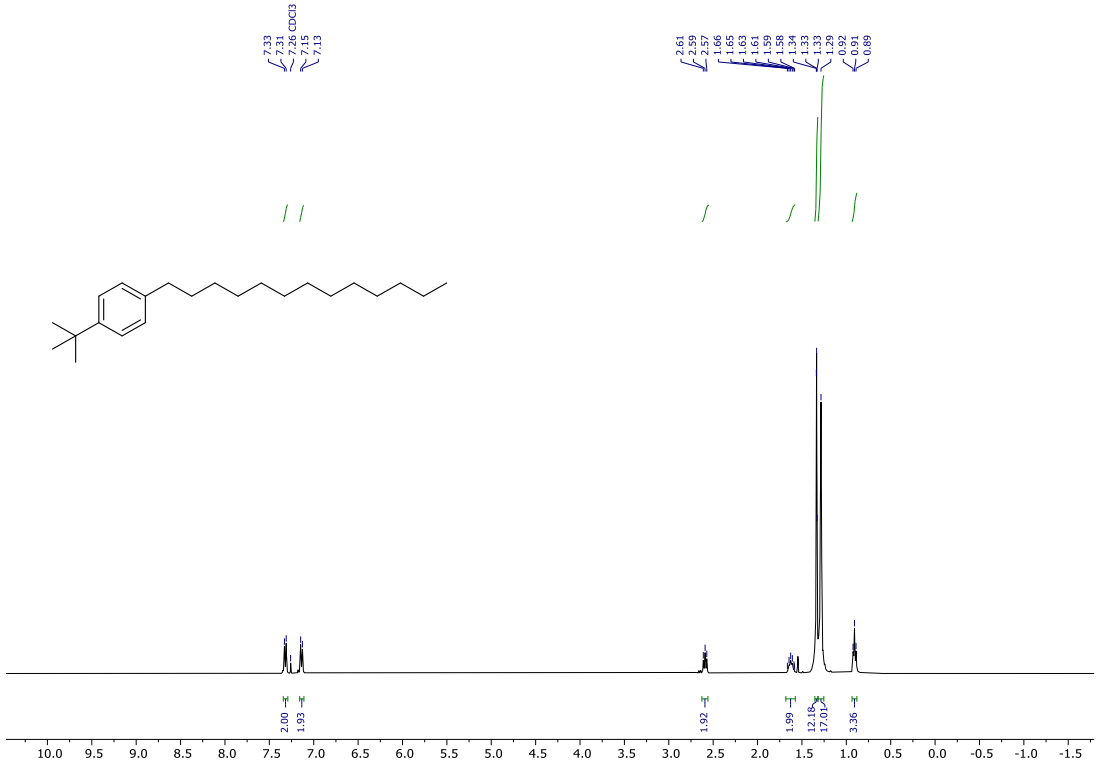
^{1}H NMR spectrum of **8**



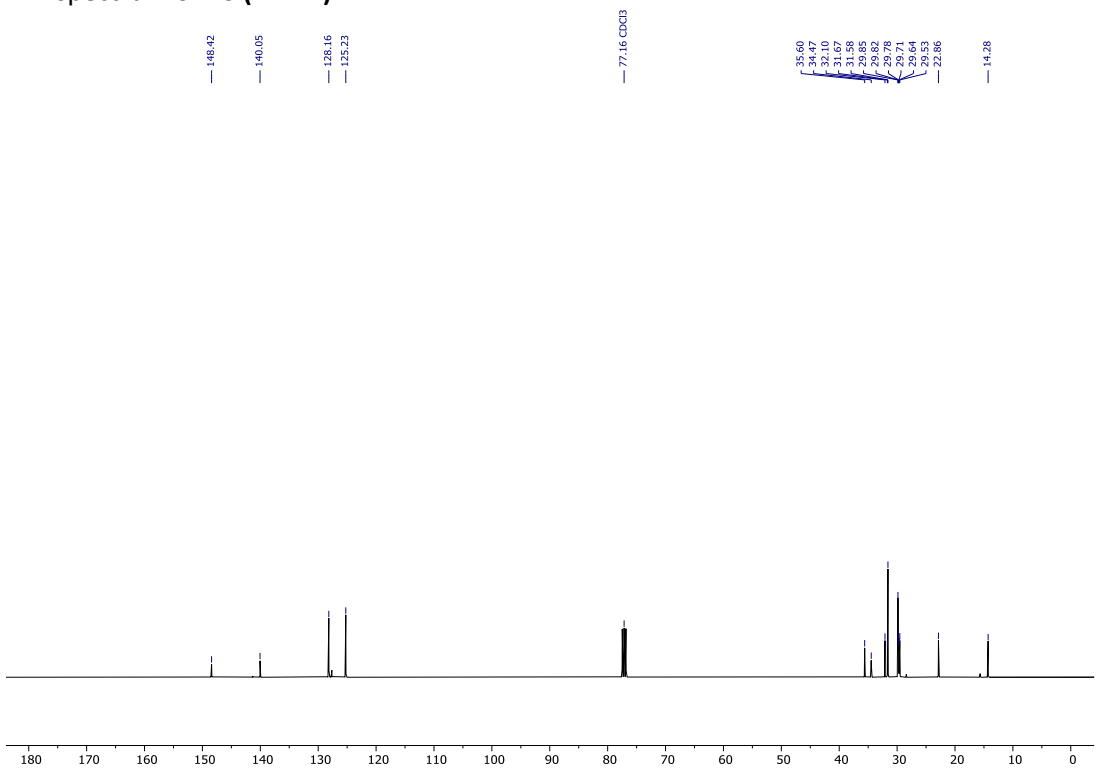
^{13}C NMR spectrum of **8**



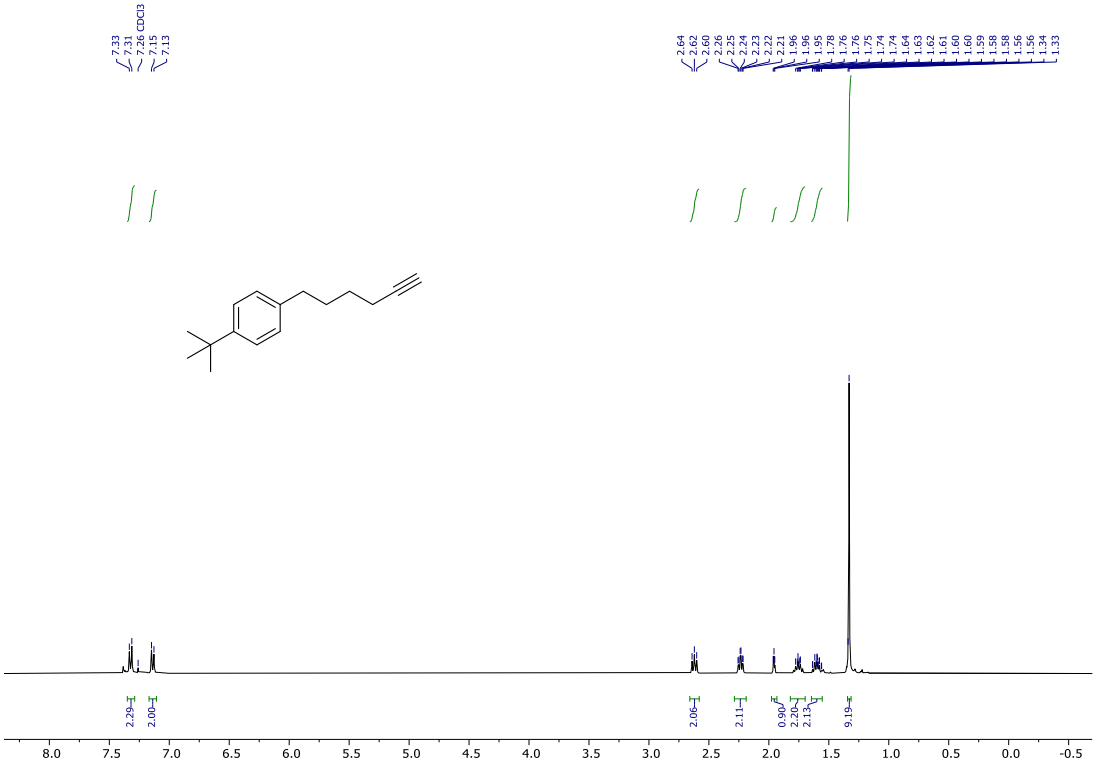
^{1}H NMR spectrum of **10 (X = Br)**



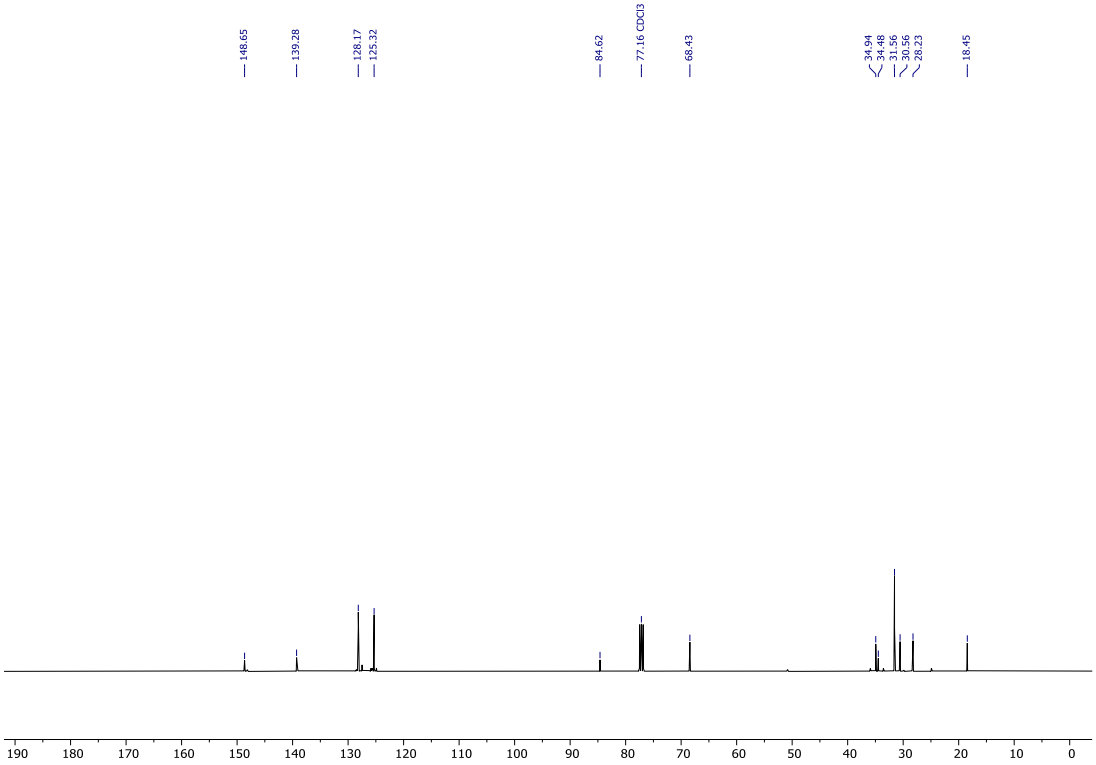
^{13}C NMR spectrum of **10 (X = Br)**



^{1}H NMR spectrum of **12**



^{13}C NMR spectrum of **12**



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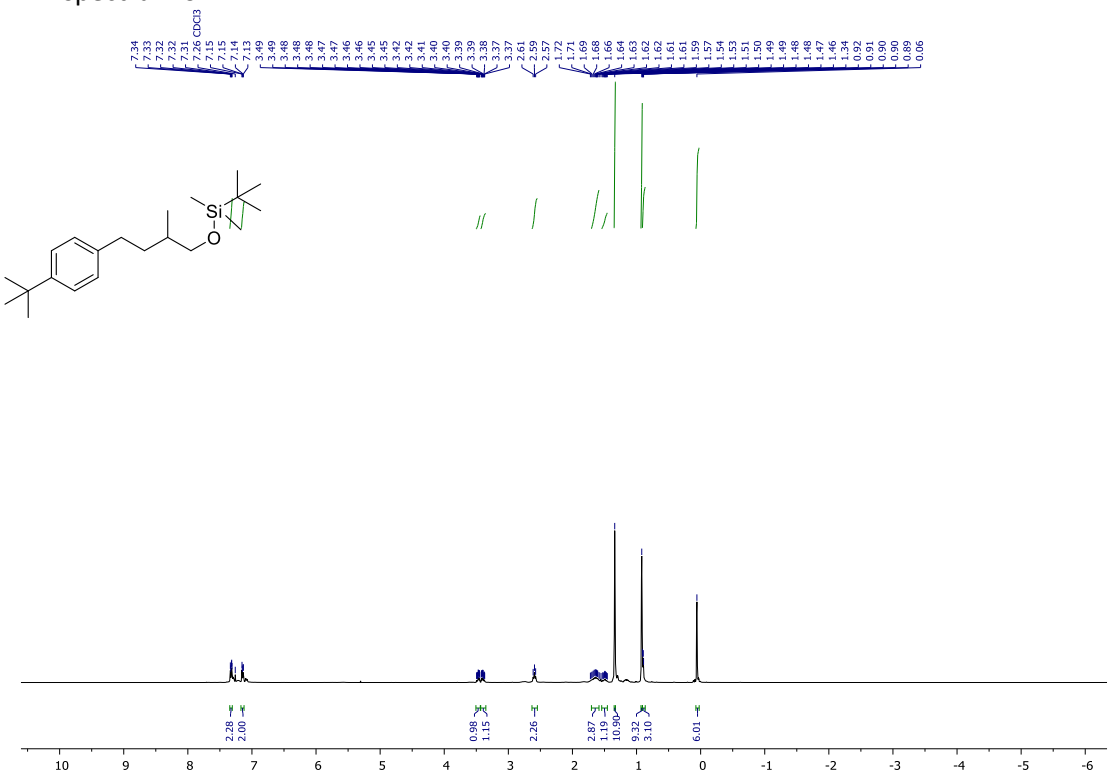

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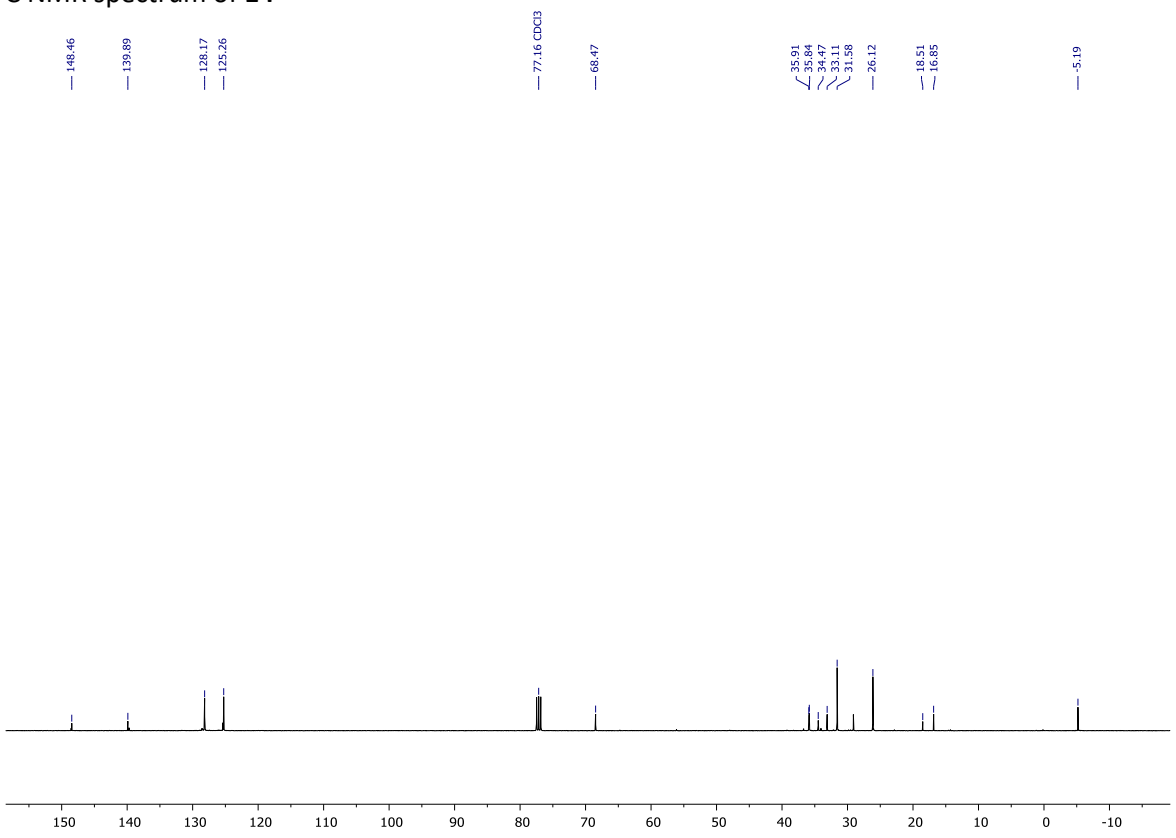

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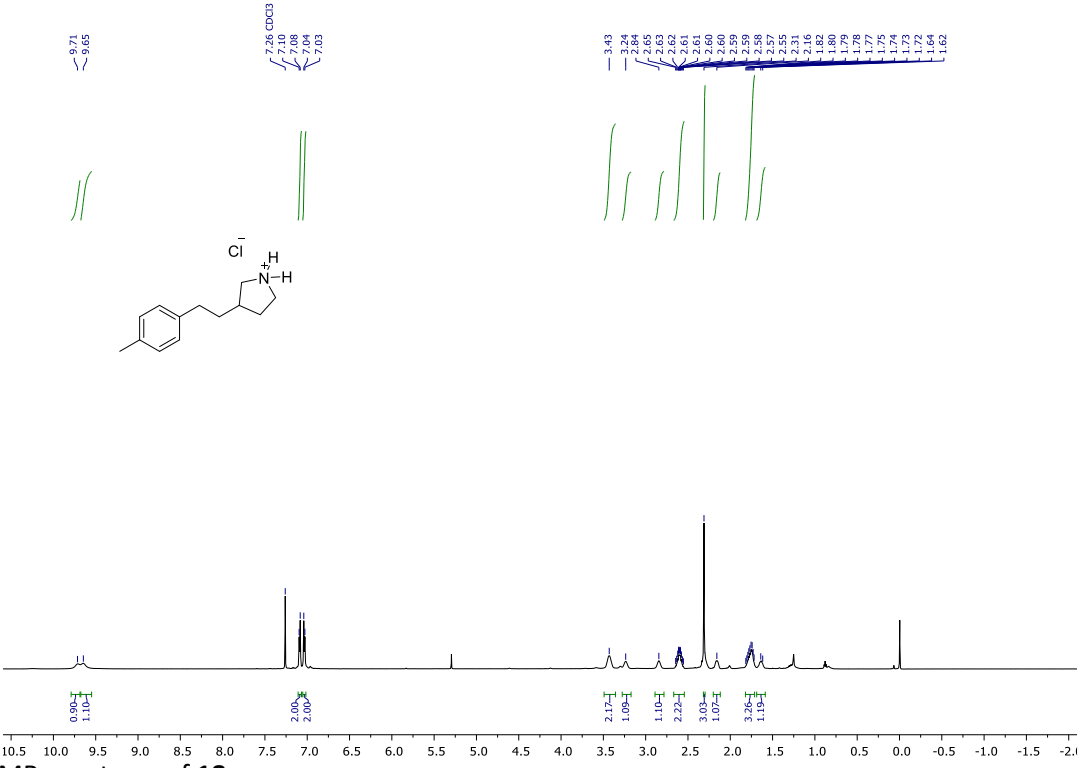

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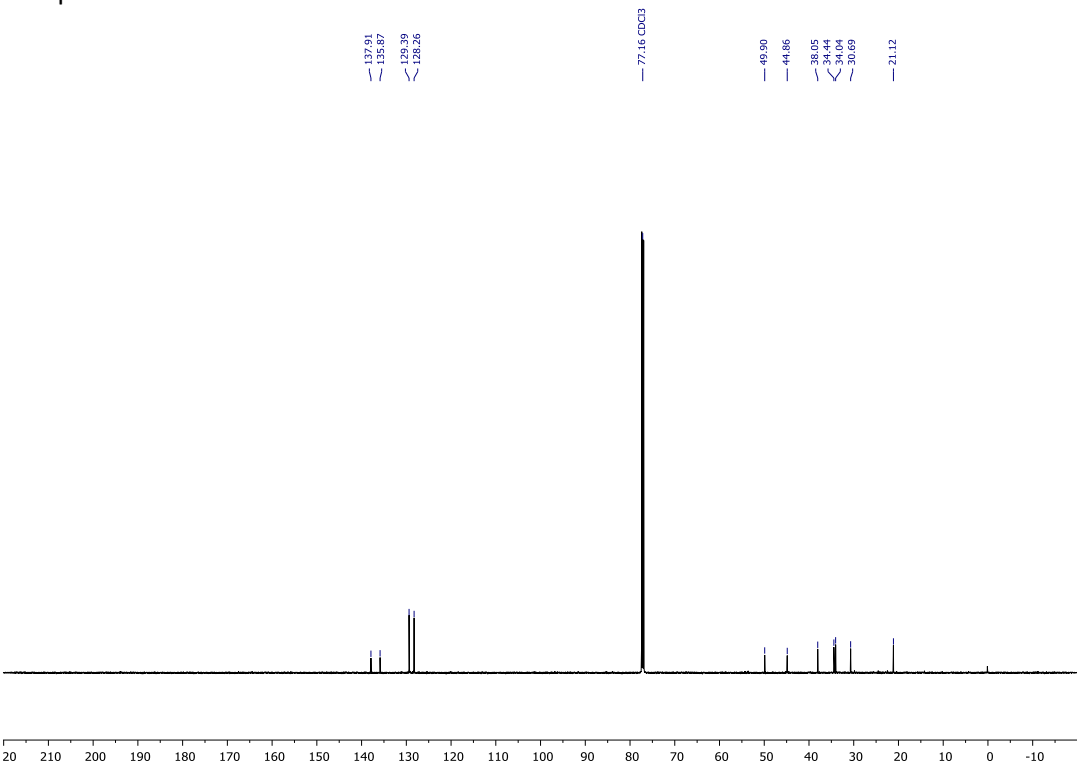

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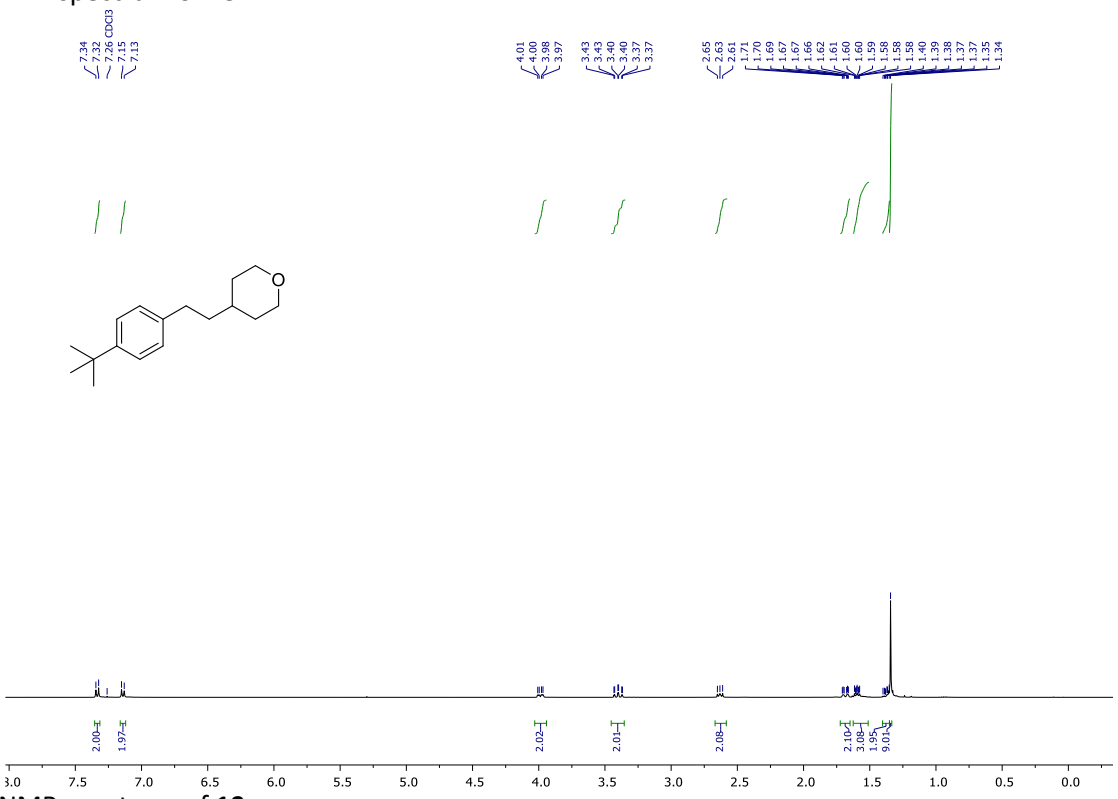

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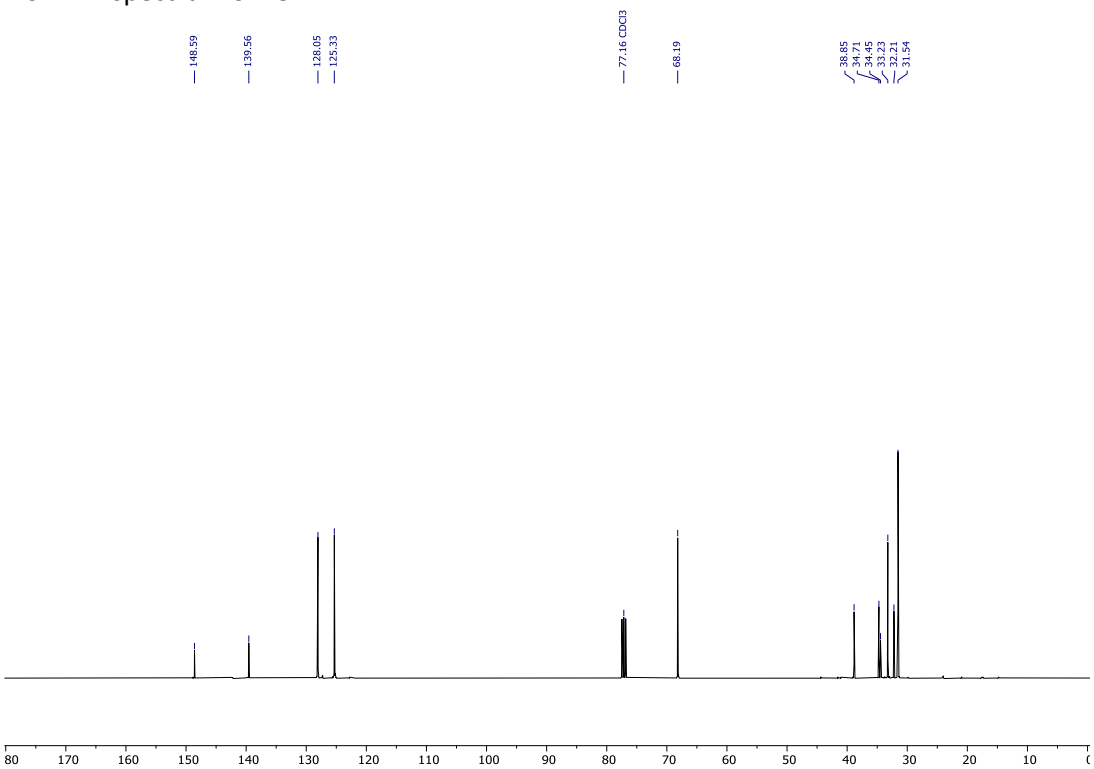

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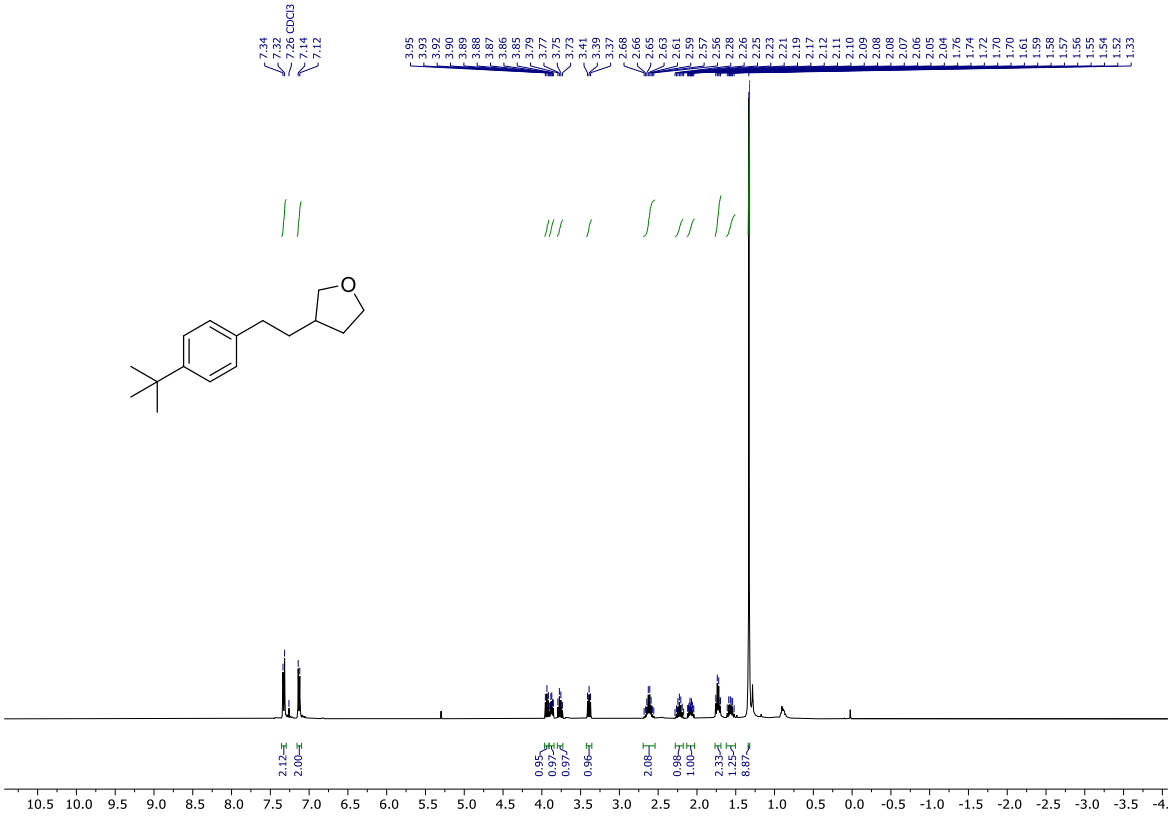
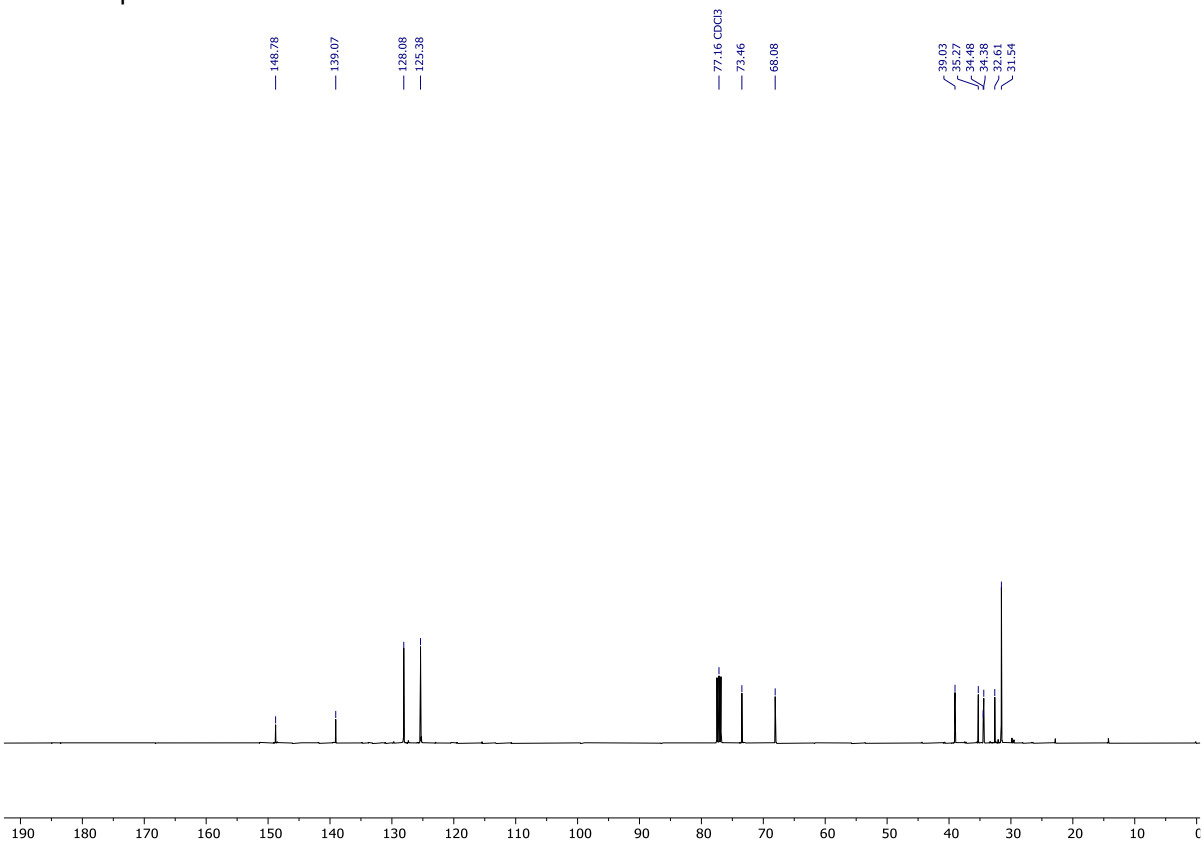
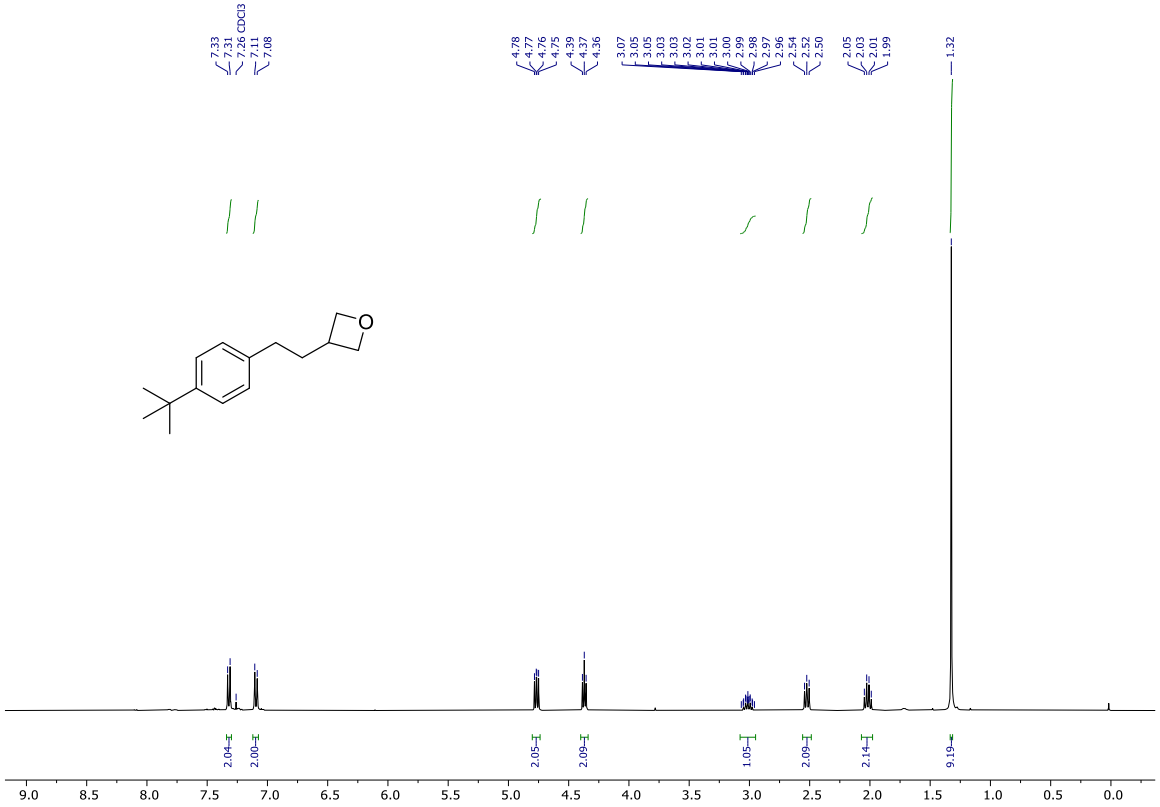


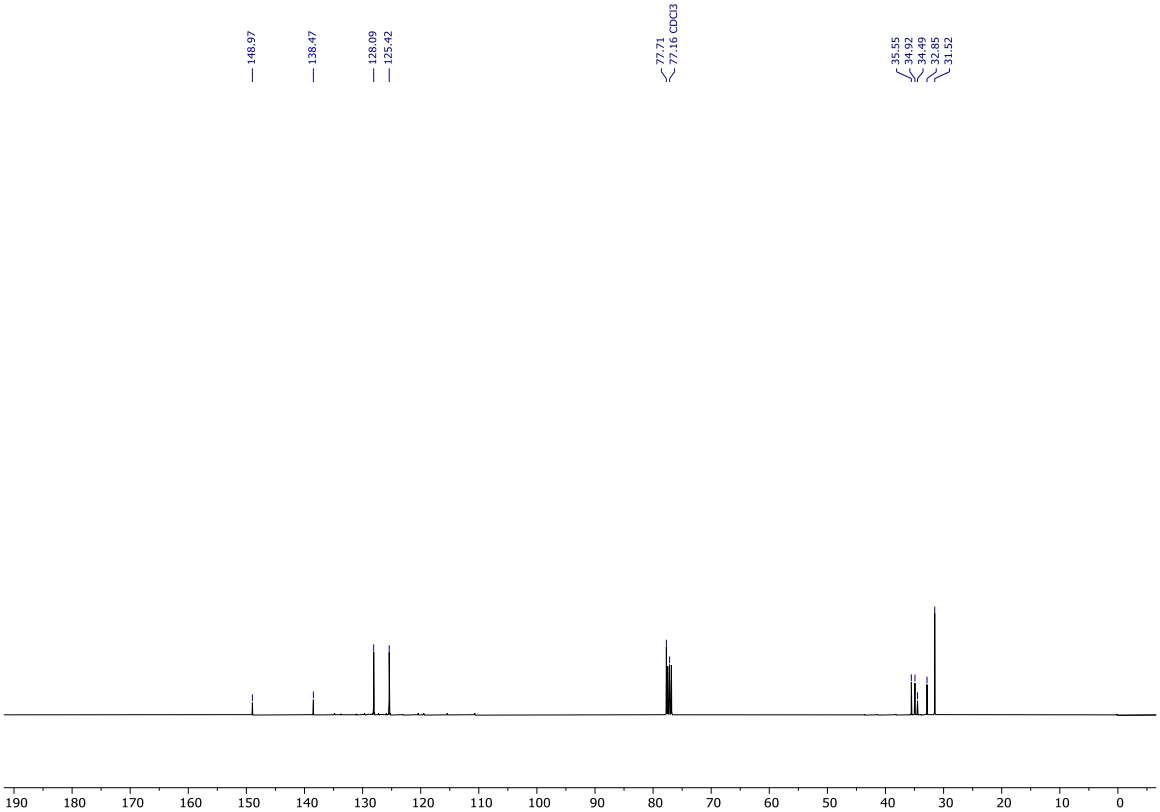
^{13}C NMR spectrum of **20**



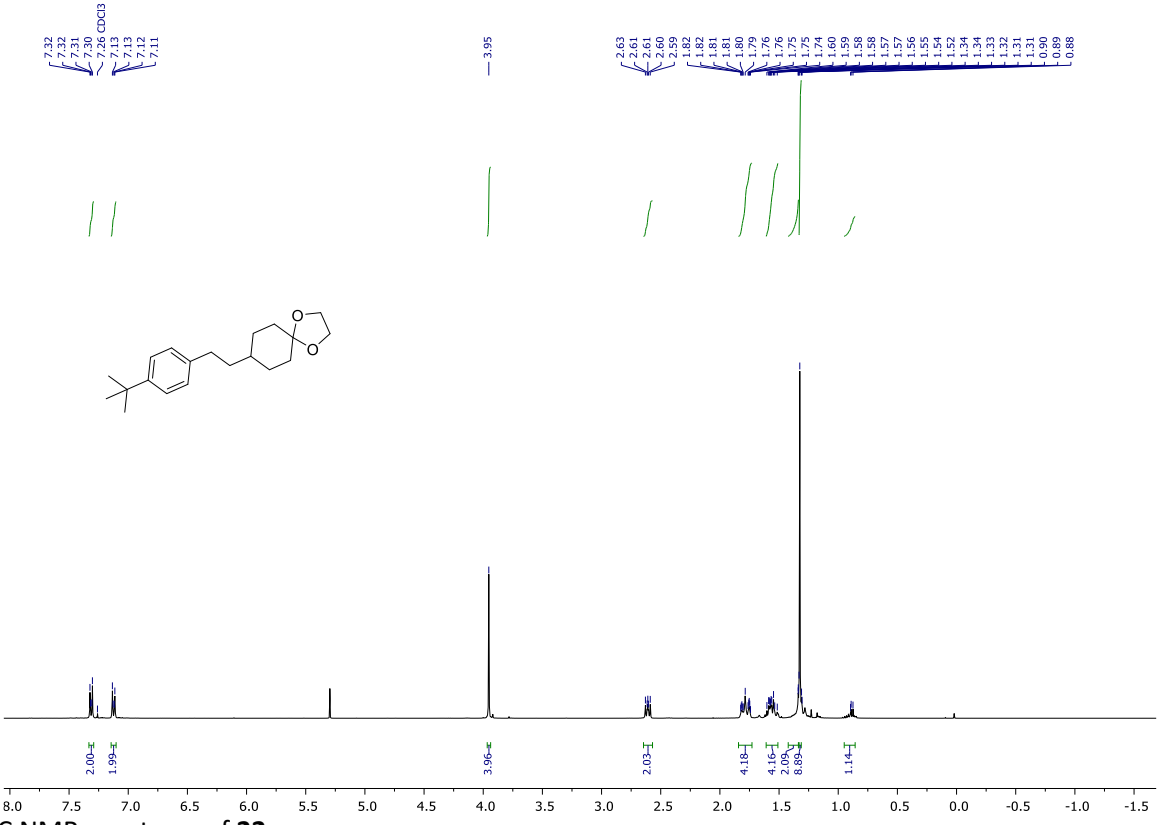
^{1}H NMR spectrum of **21**



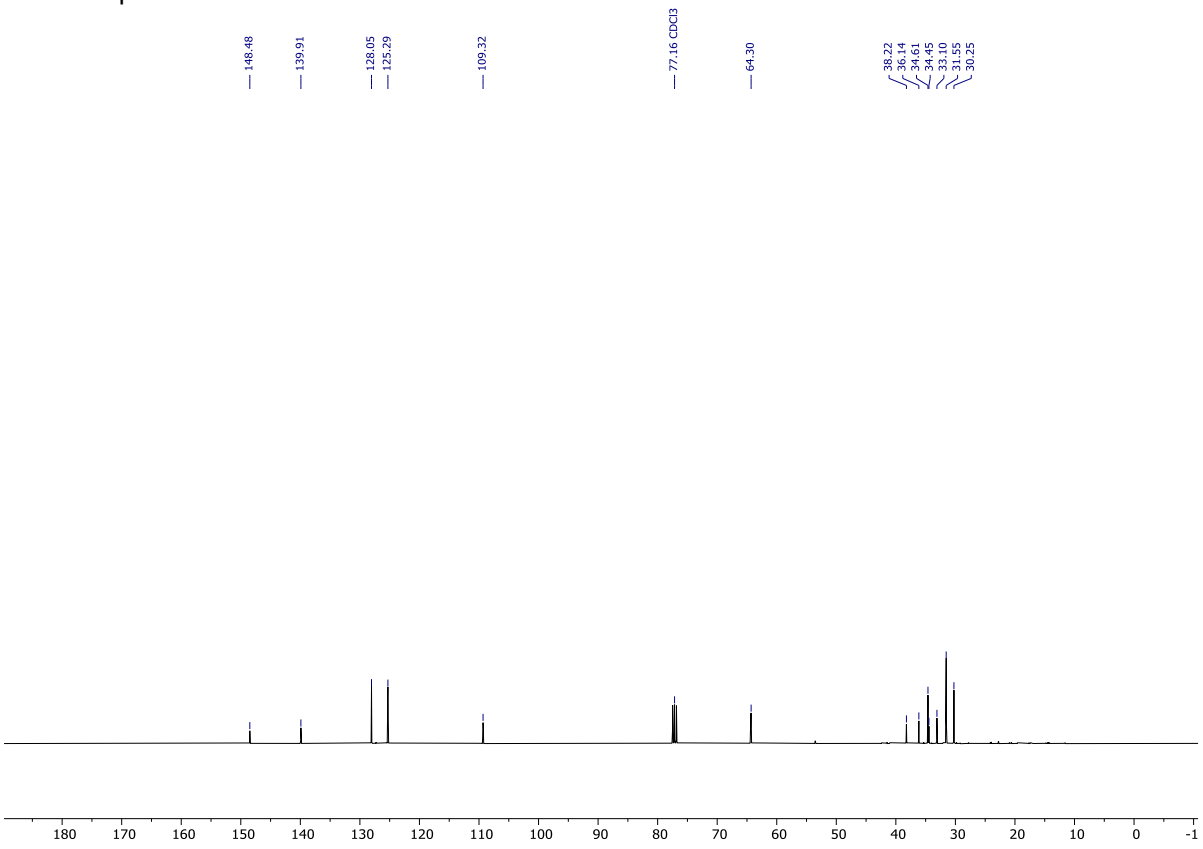
^{13}C NMR spectrum of **21**



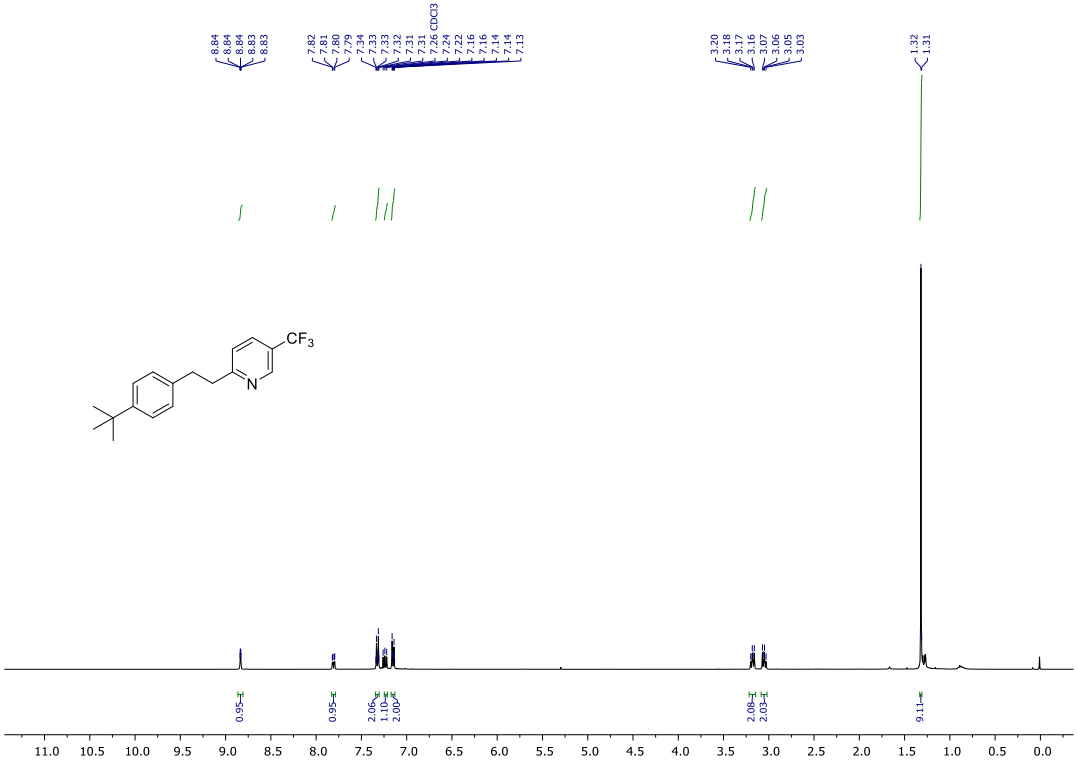
^{1}H NMR spectrum of **22**



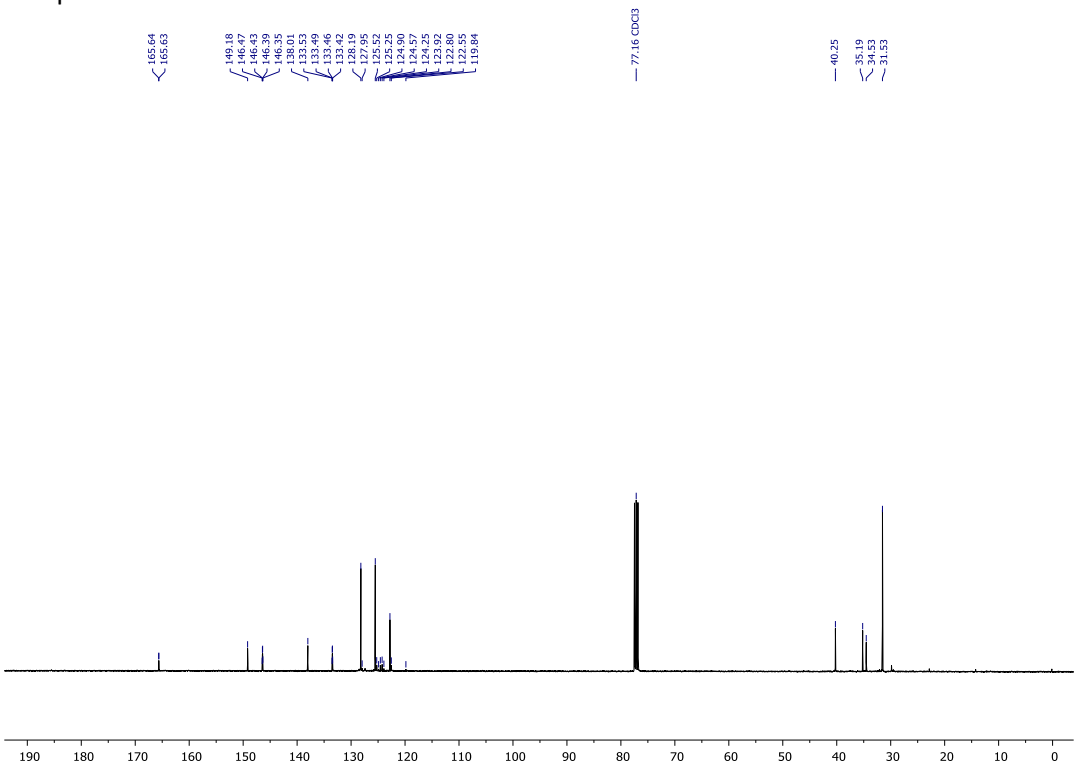
^{13}C NMR spectrum of **22**



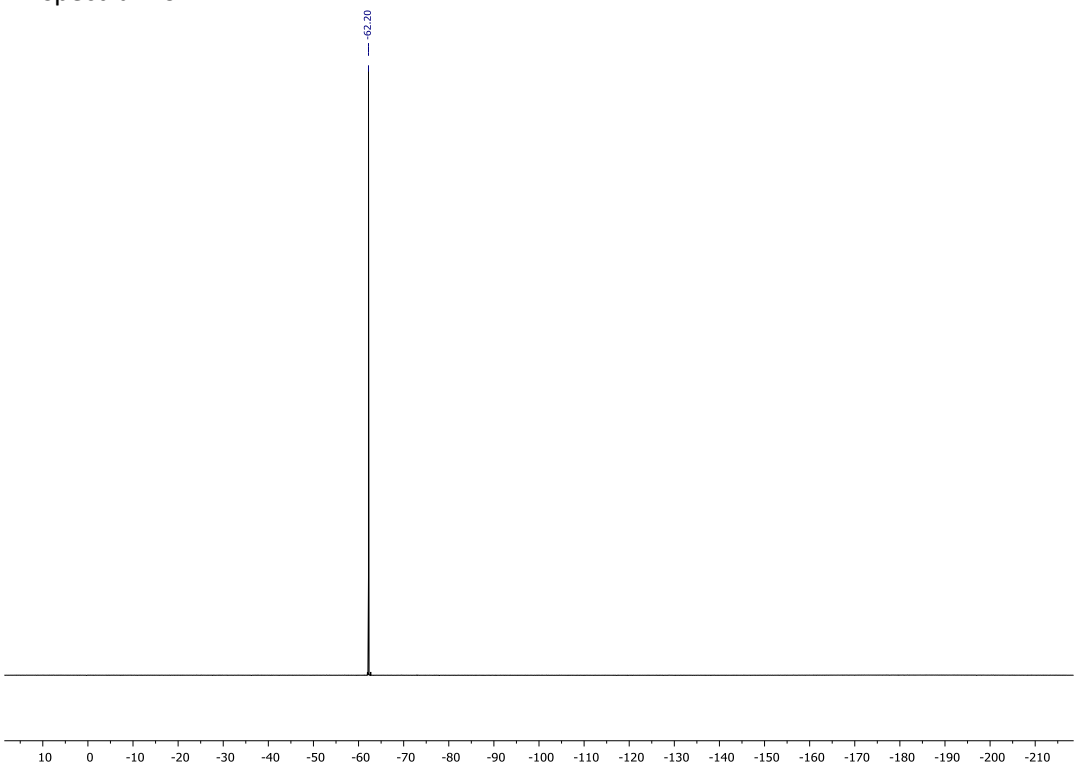
^{1}H NMR spectrum of **24**



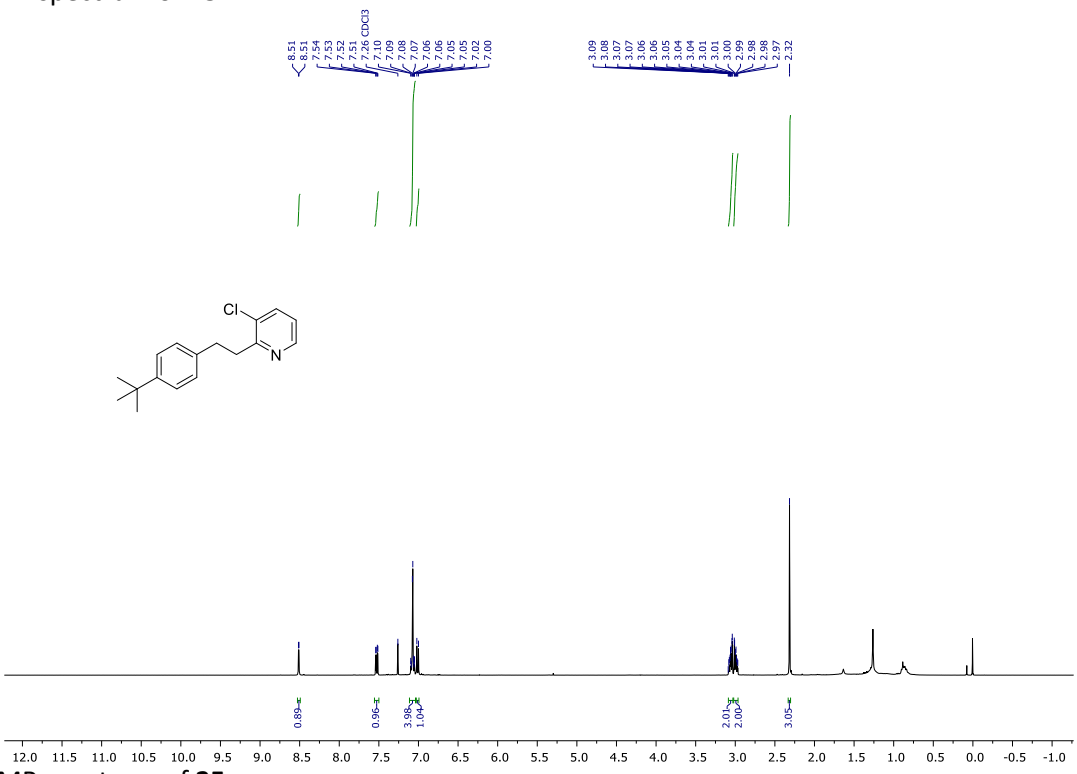
^{13}C NMR spectrum of **24**



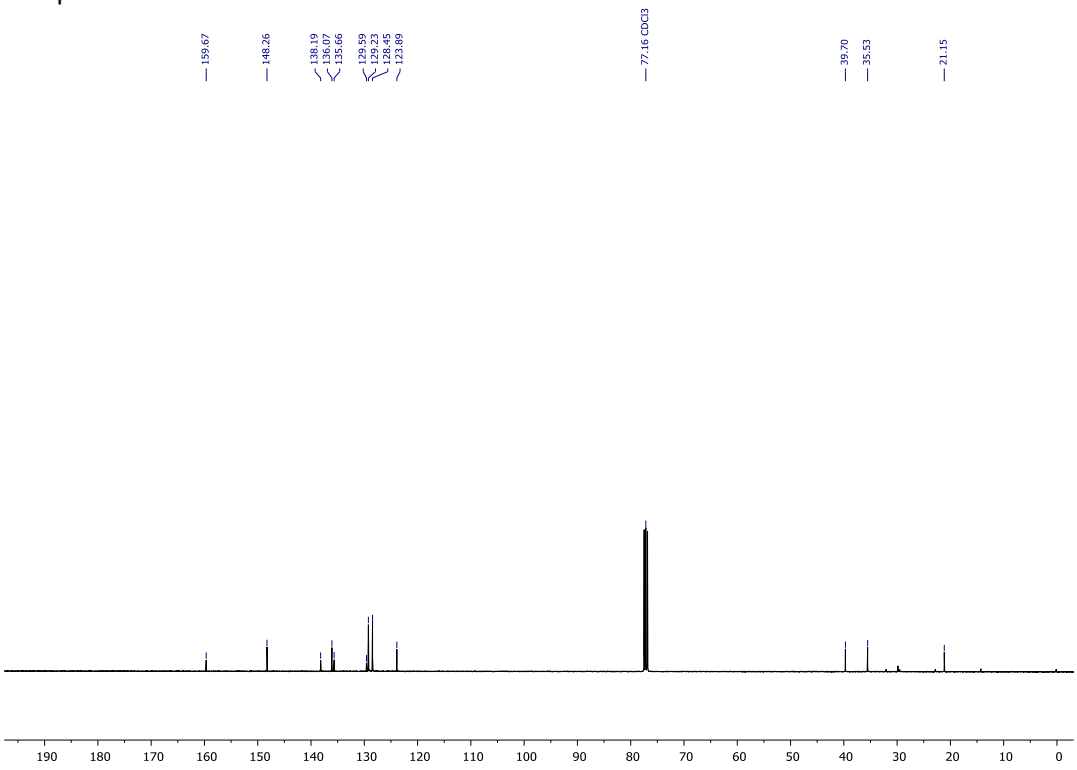
^{19}F NMR spectrum of **24**



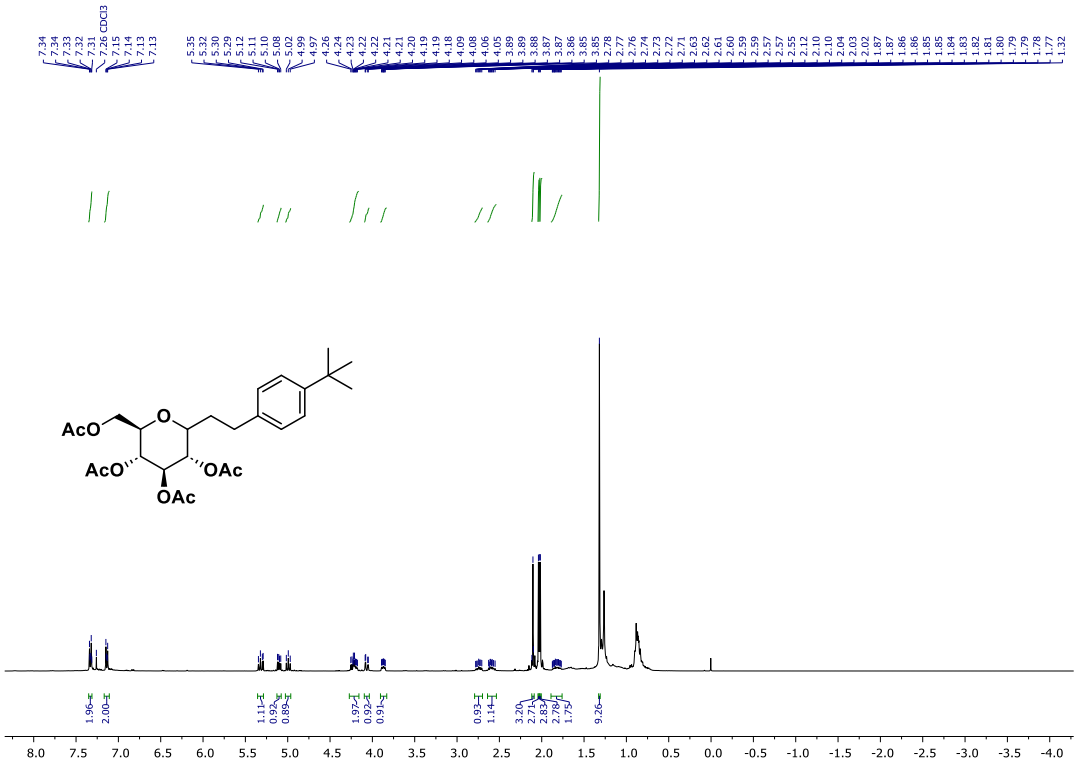
^{1}H NMR spectrum of **25**



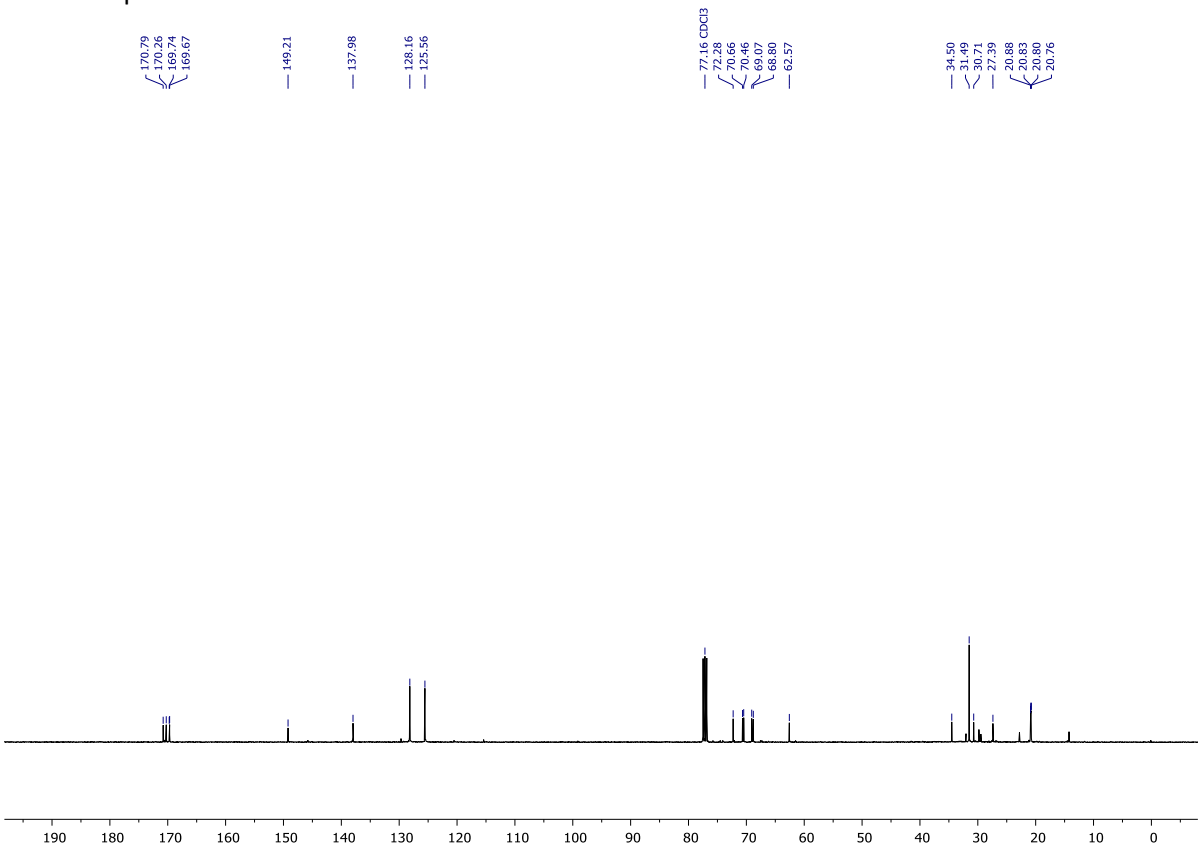
^{13}C NMR spectrum of **25**



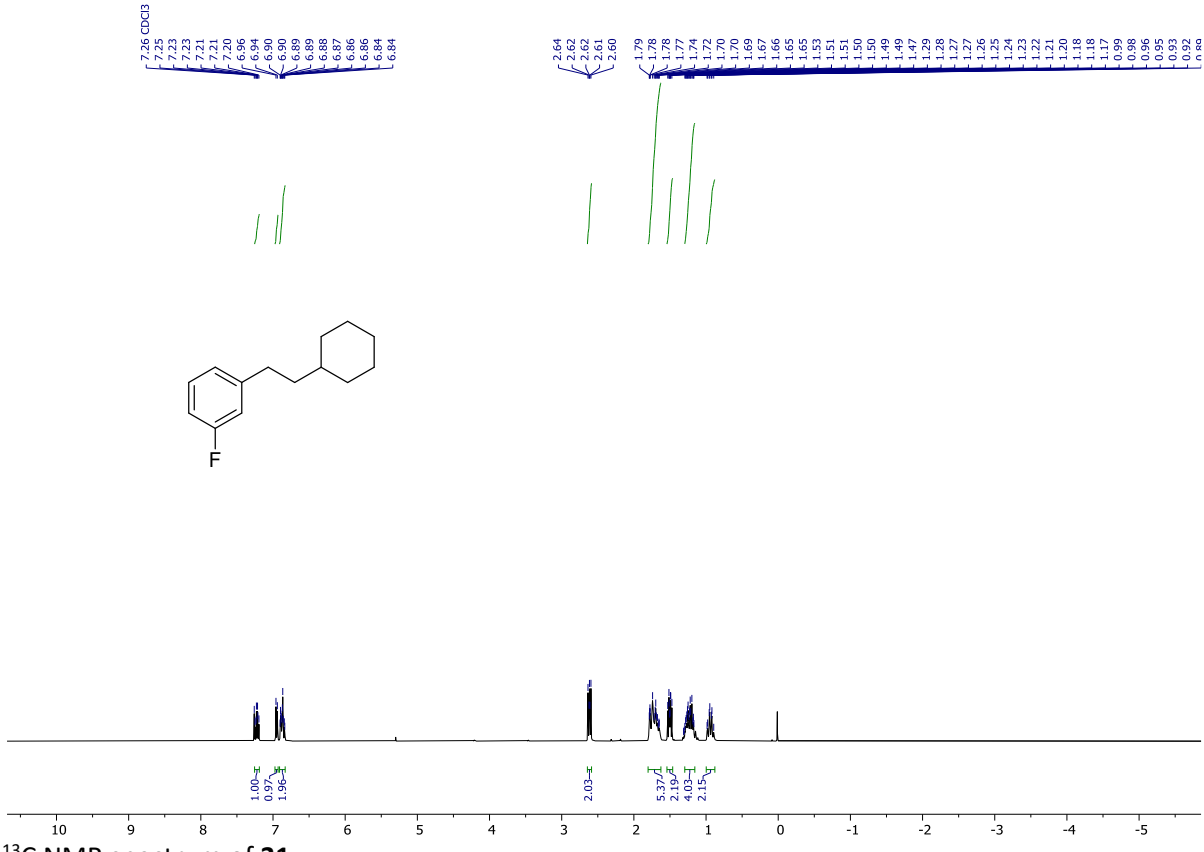
^{1}H NMR spectrum of **27**



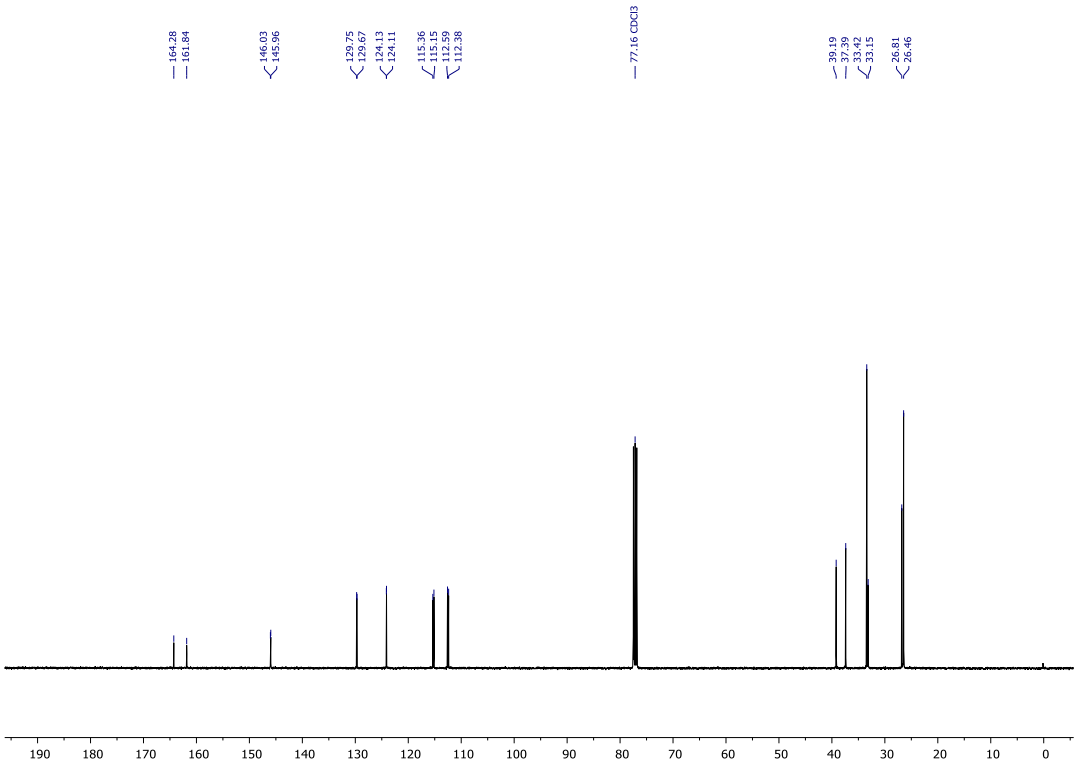
^{13}C NMR spectrum of **27**



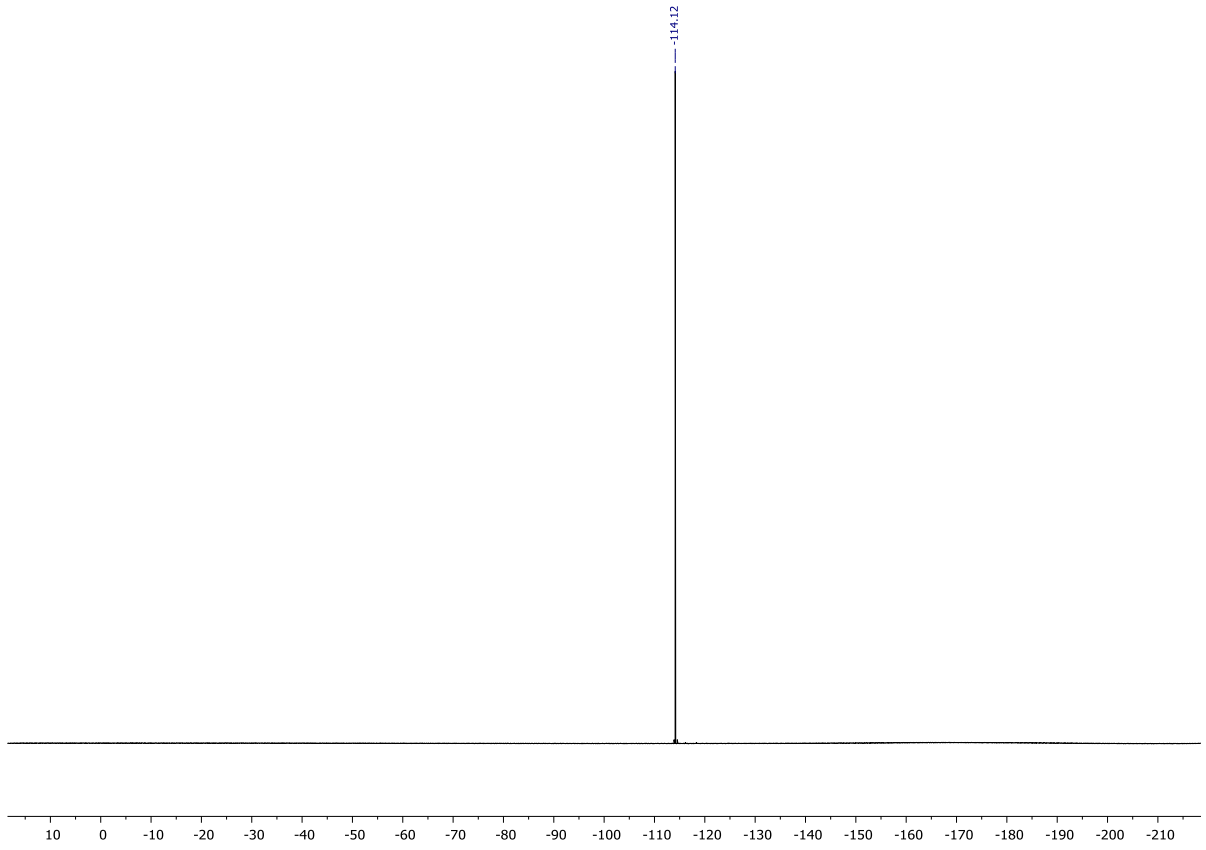
^{1}H NMR spectrum of **31**



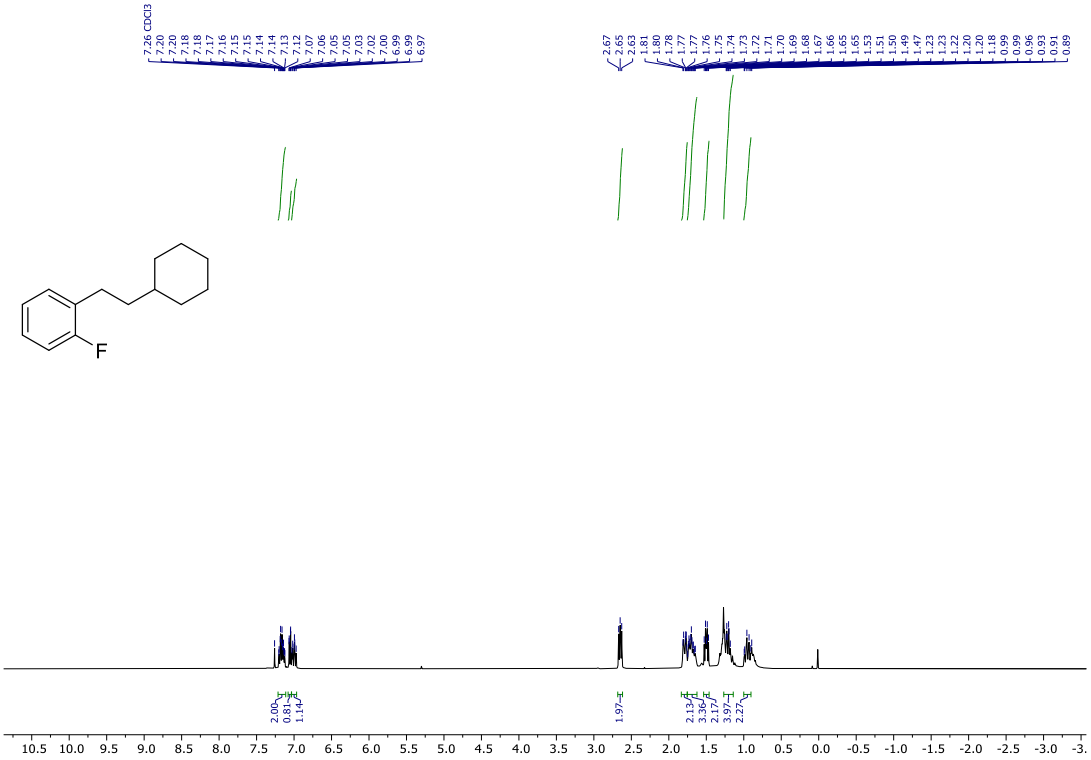
^{13}C NMR spectrum of **31**



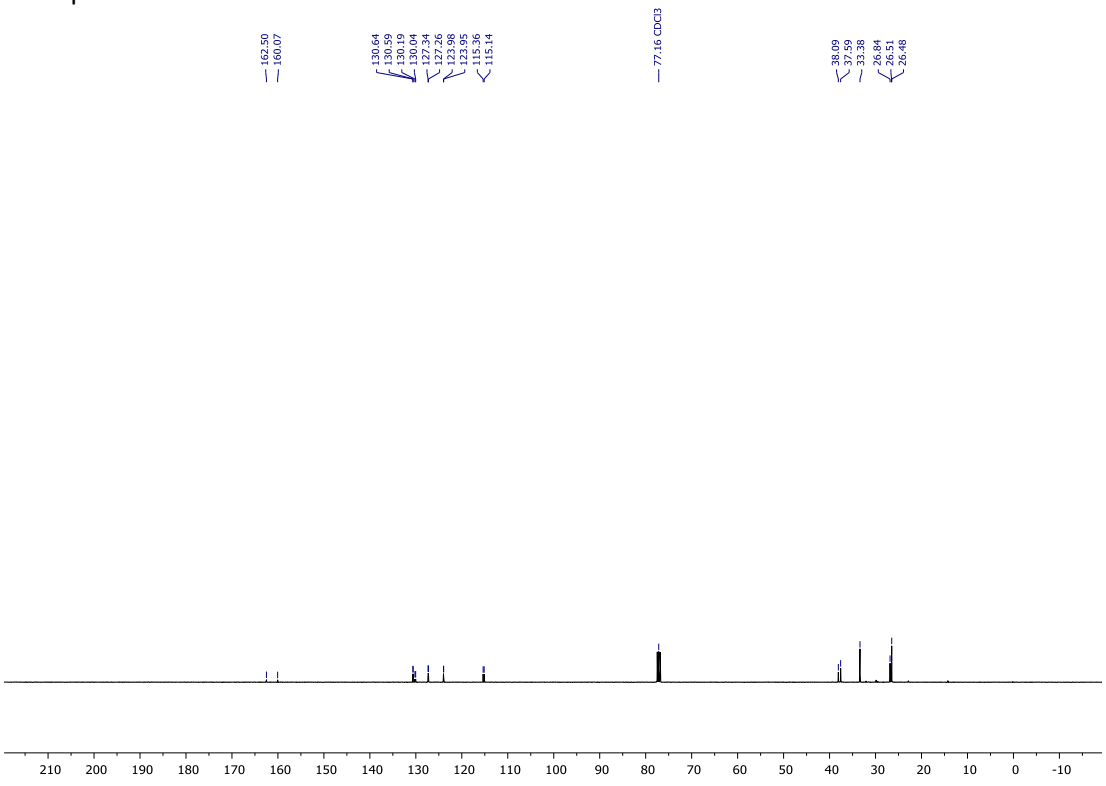
^{19}F NMR spectrum of **31**



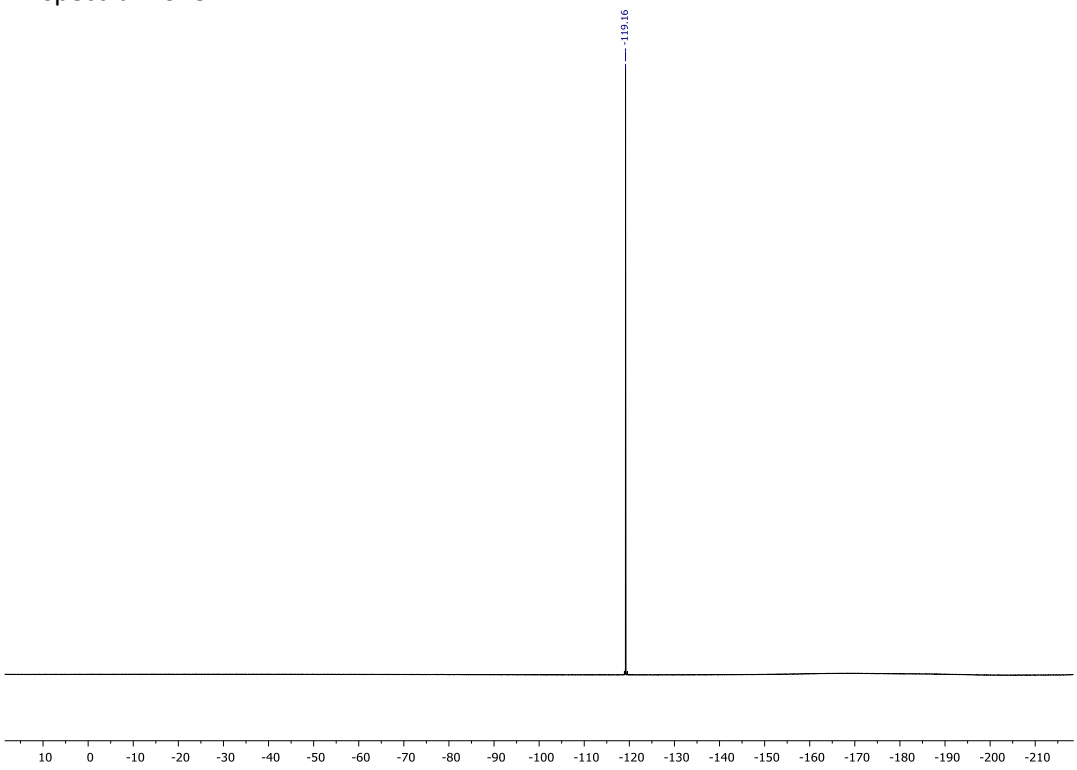
^{1}H NMR spectrum of **32**



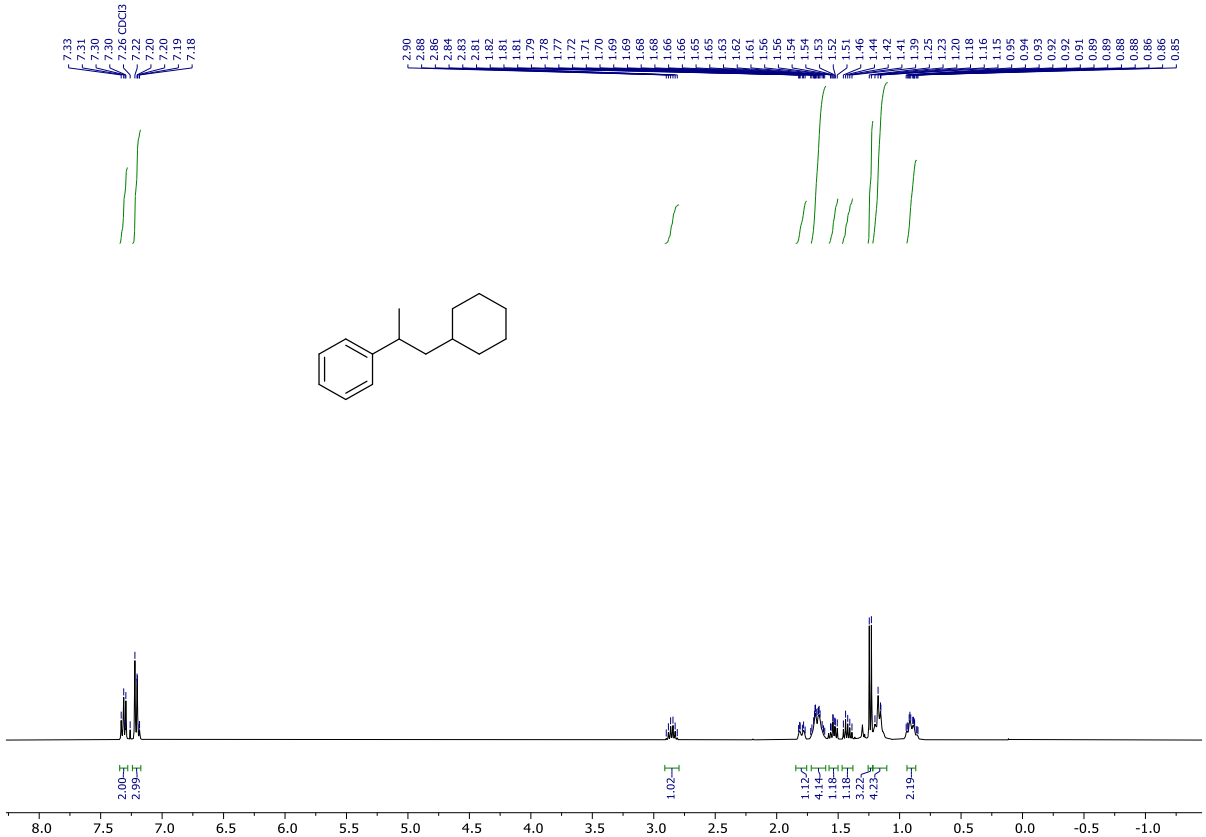
^{13}C NMR spectrum of **32**



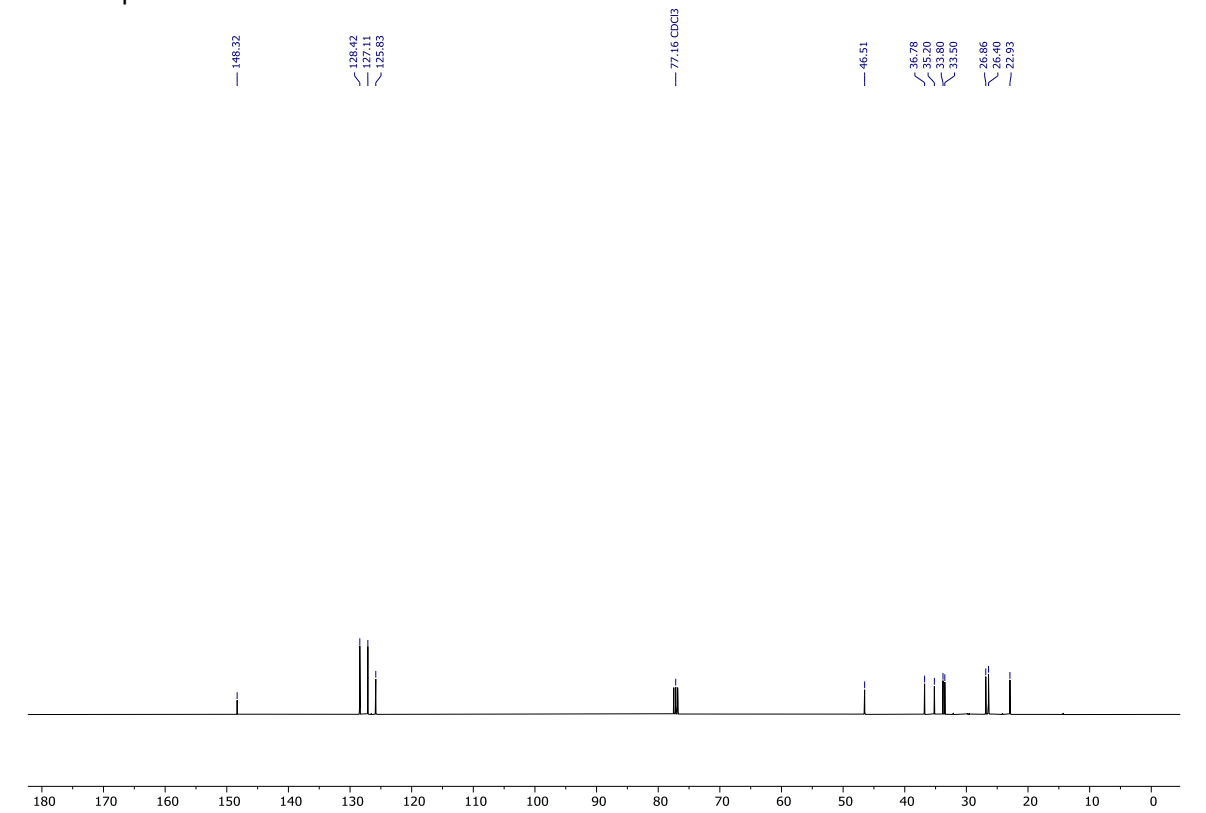
^{19}F NMR spectrum of **32**



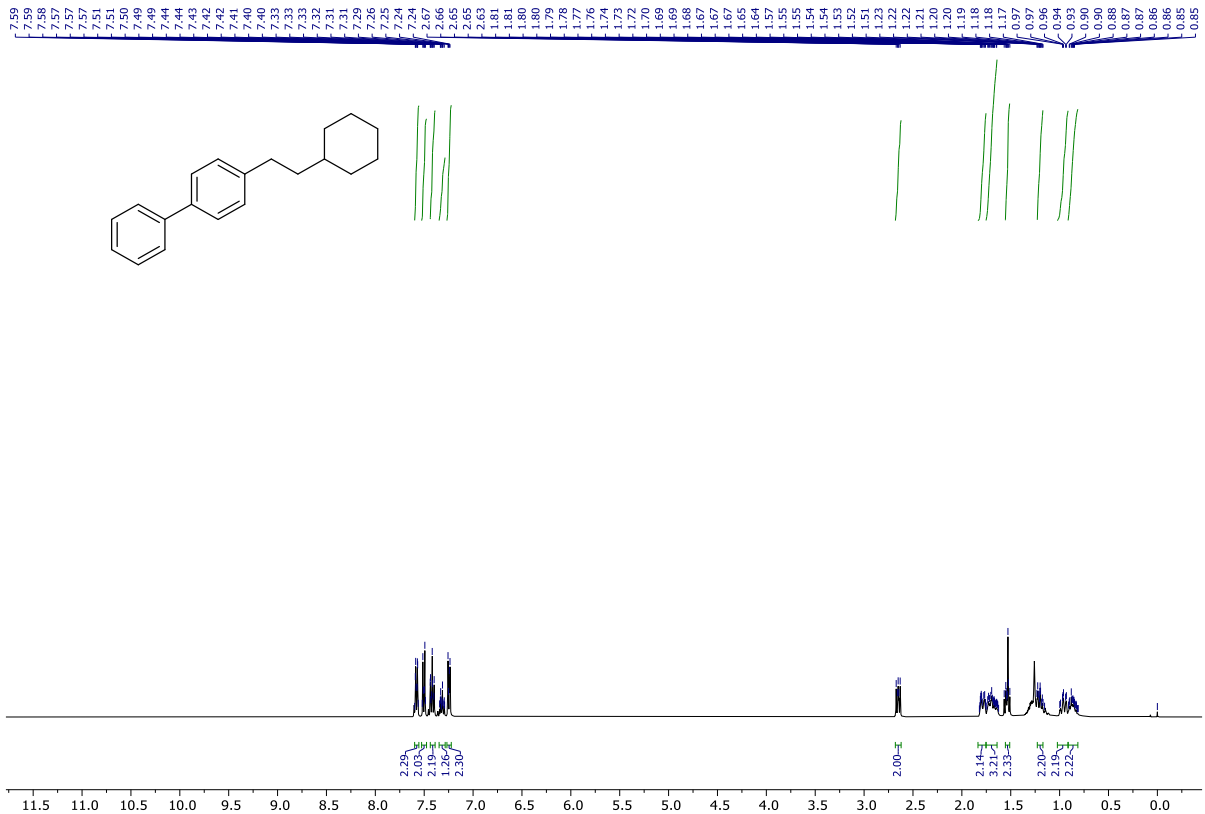
^{1}H NMR spectrum of **33**



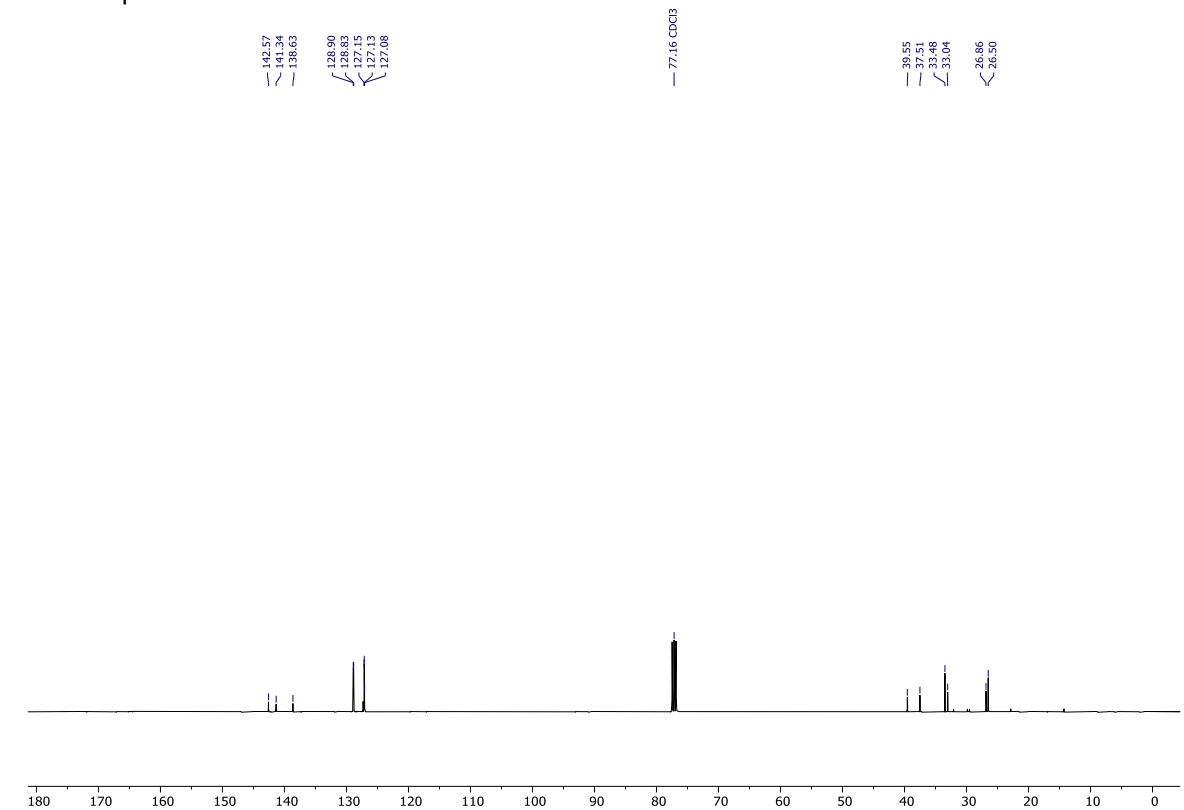
^{13}C NMR spectrum of **33**



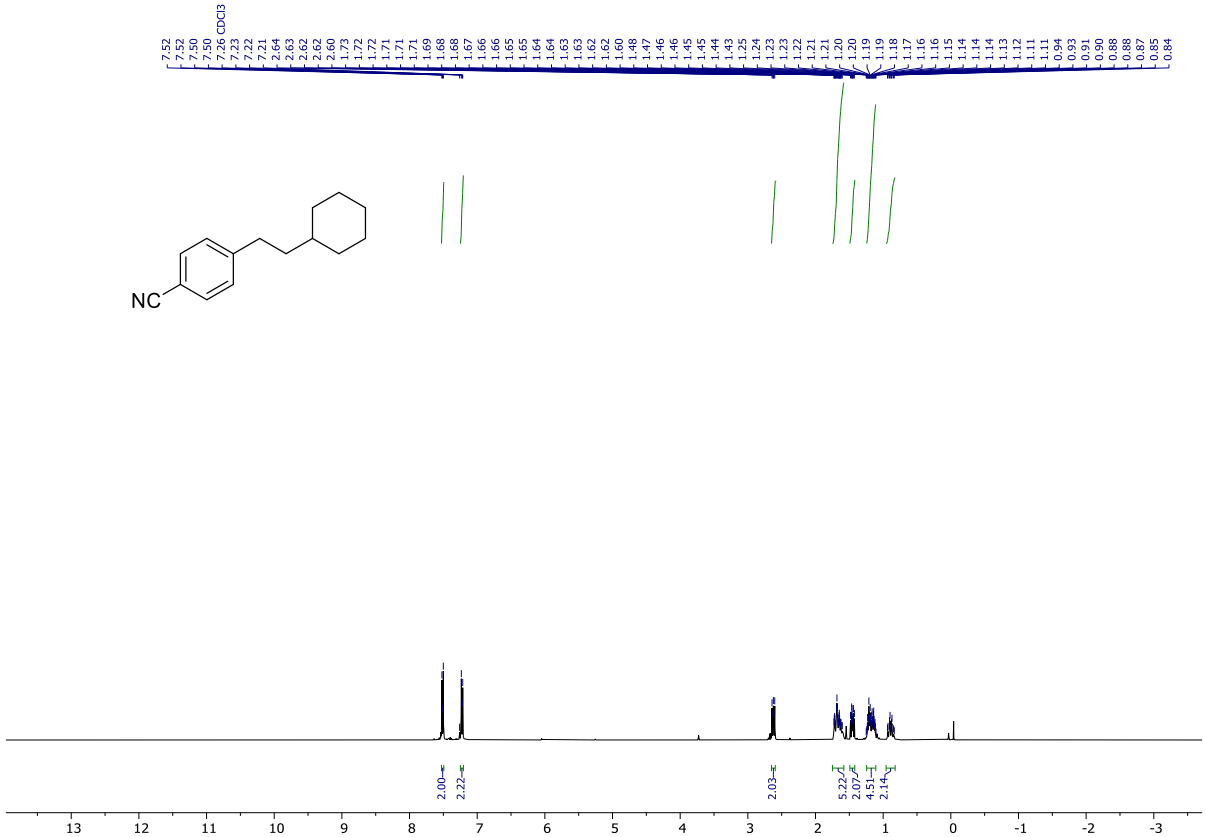
^{1}H NMR spectrum of **35**



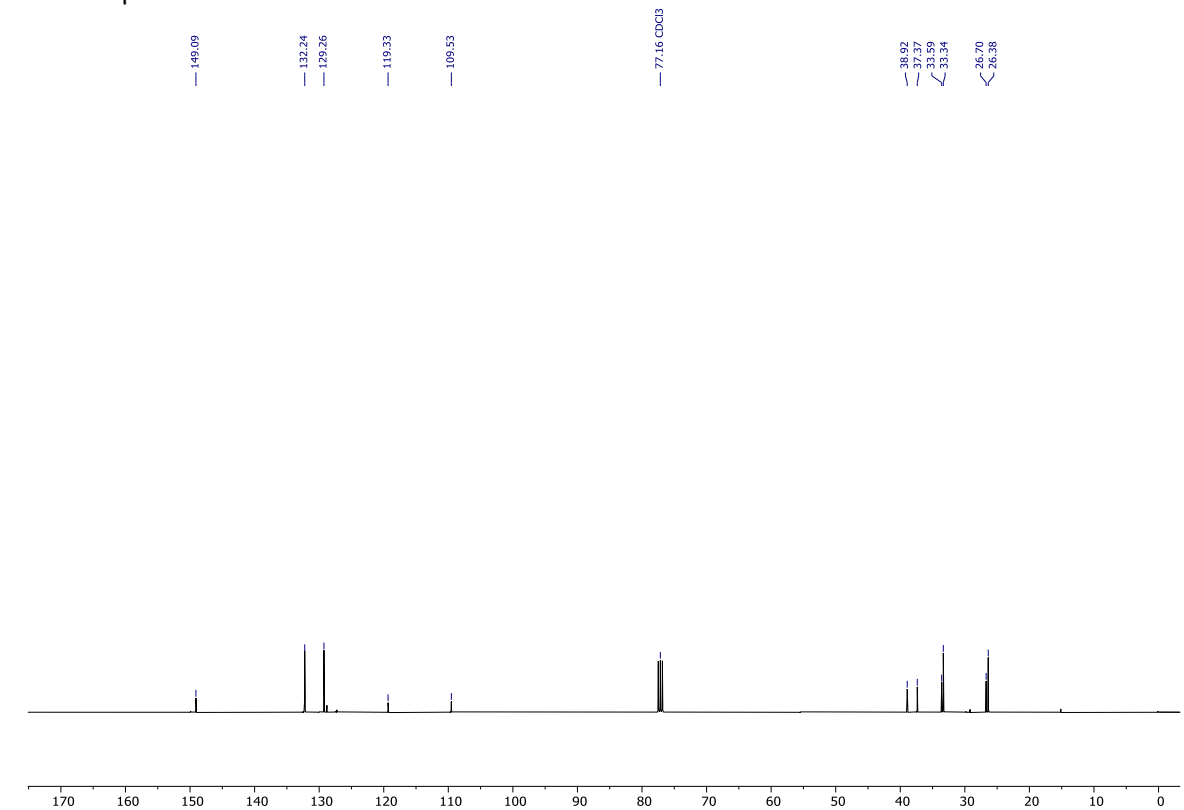
^{13}C NMR spectrum of **35**



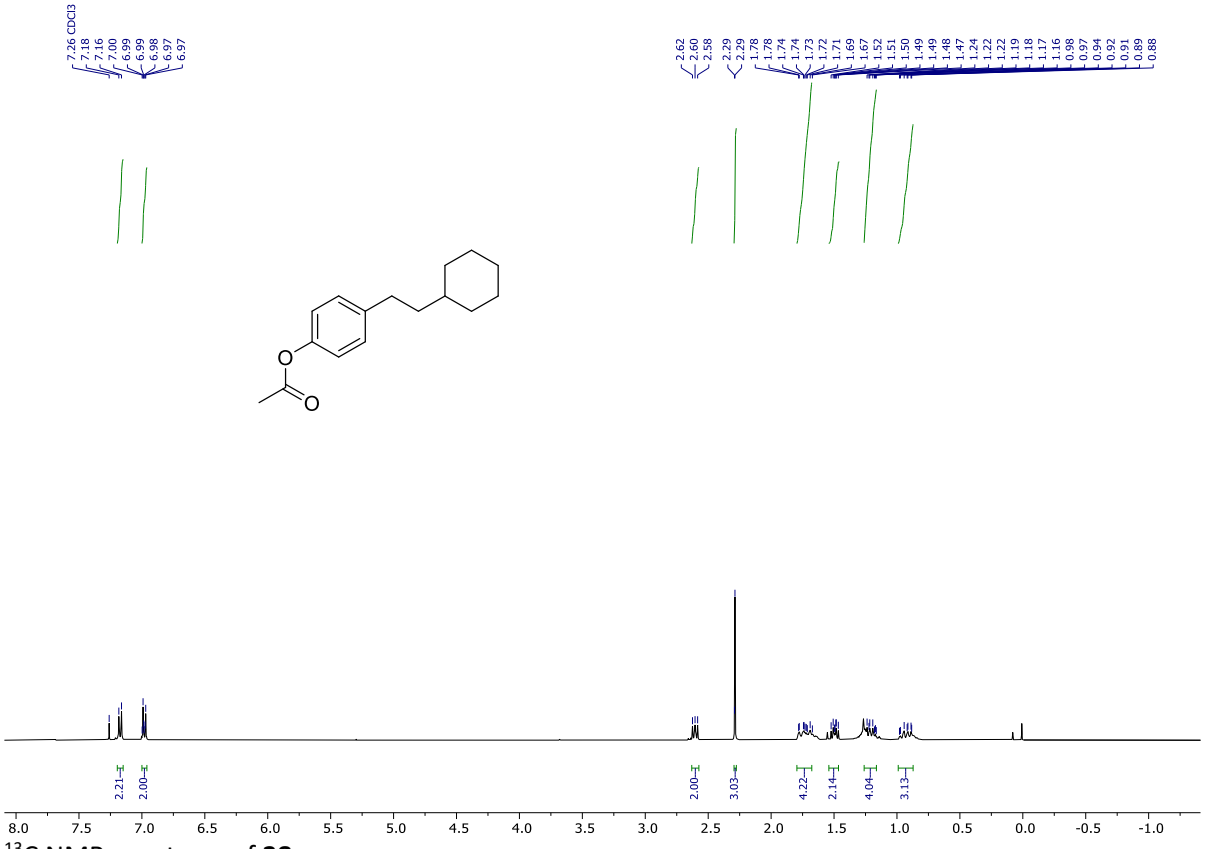
^{1}H NMR spectrum of **37**



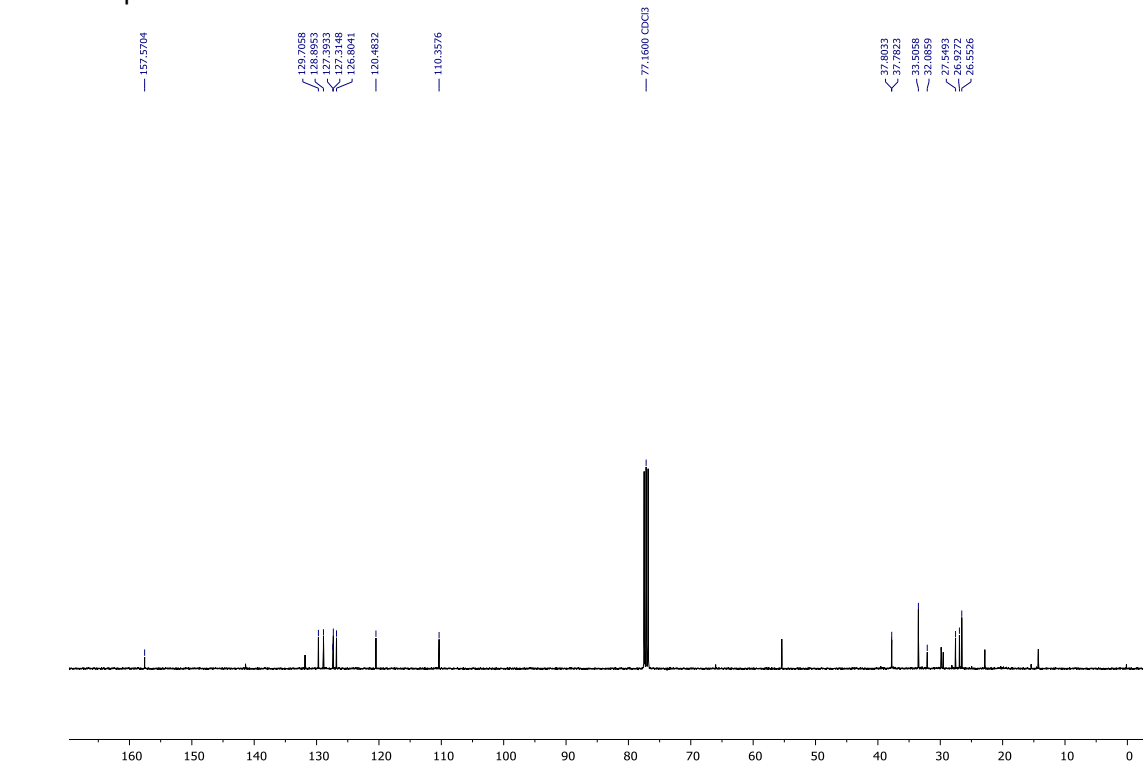
^{13}C NMR spectrum of **37**



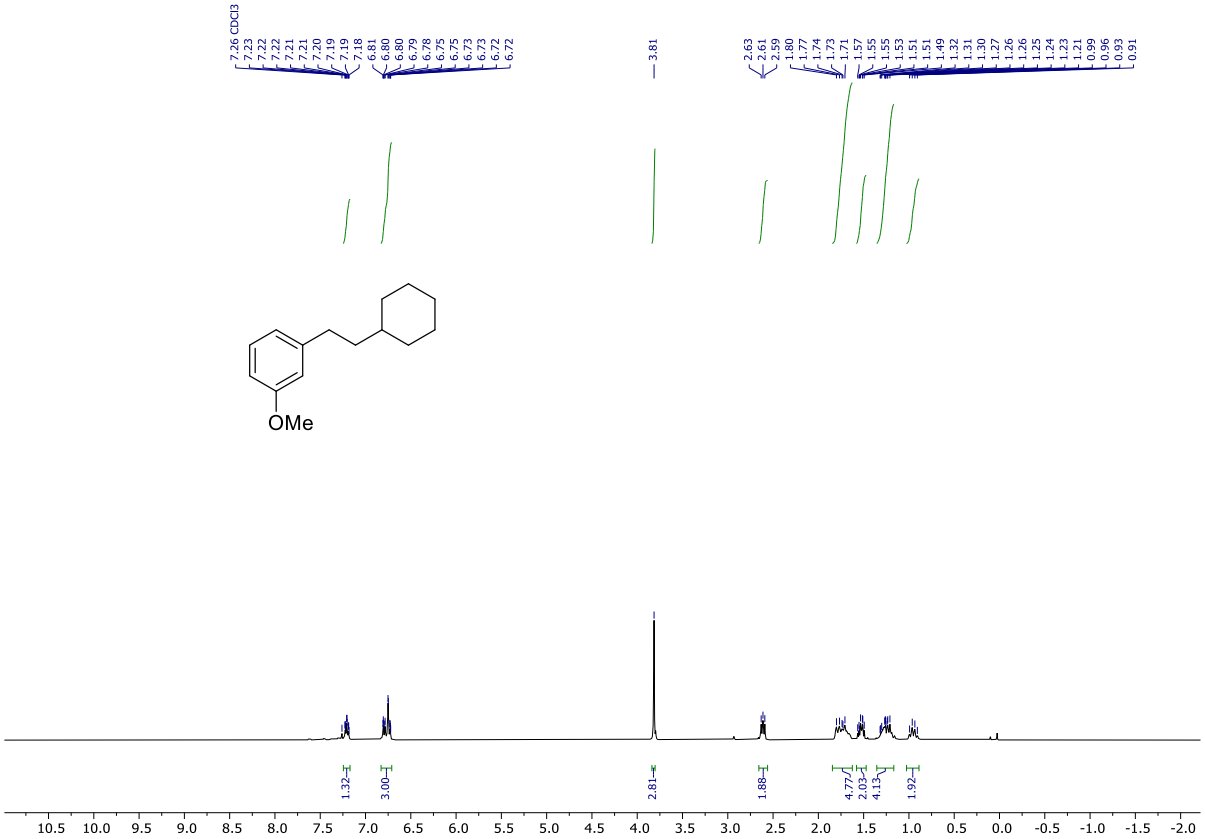
^{1}H NMR spectrum of **38**



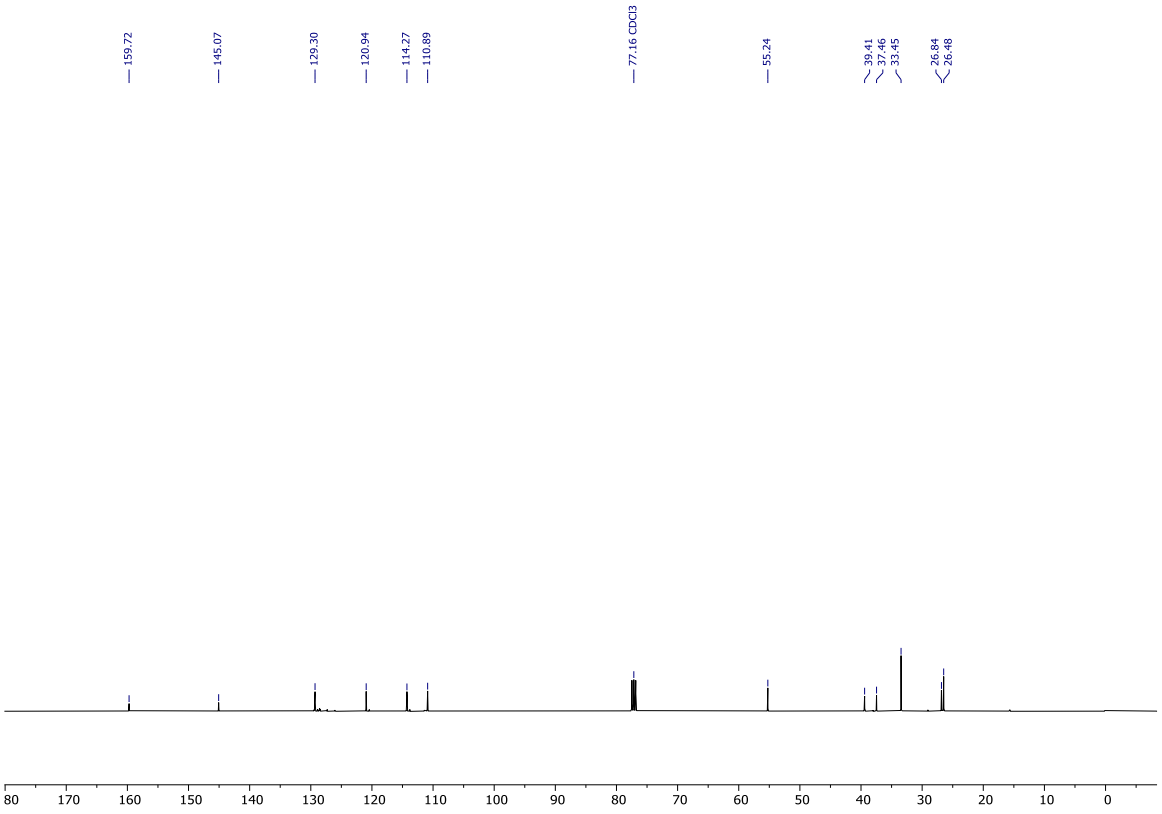
^{13}C NMR spectrum of **38**



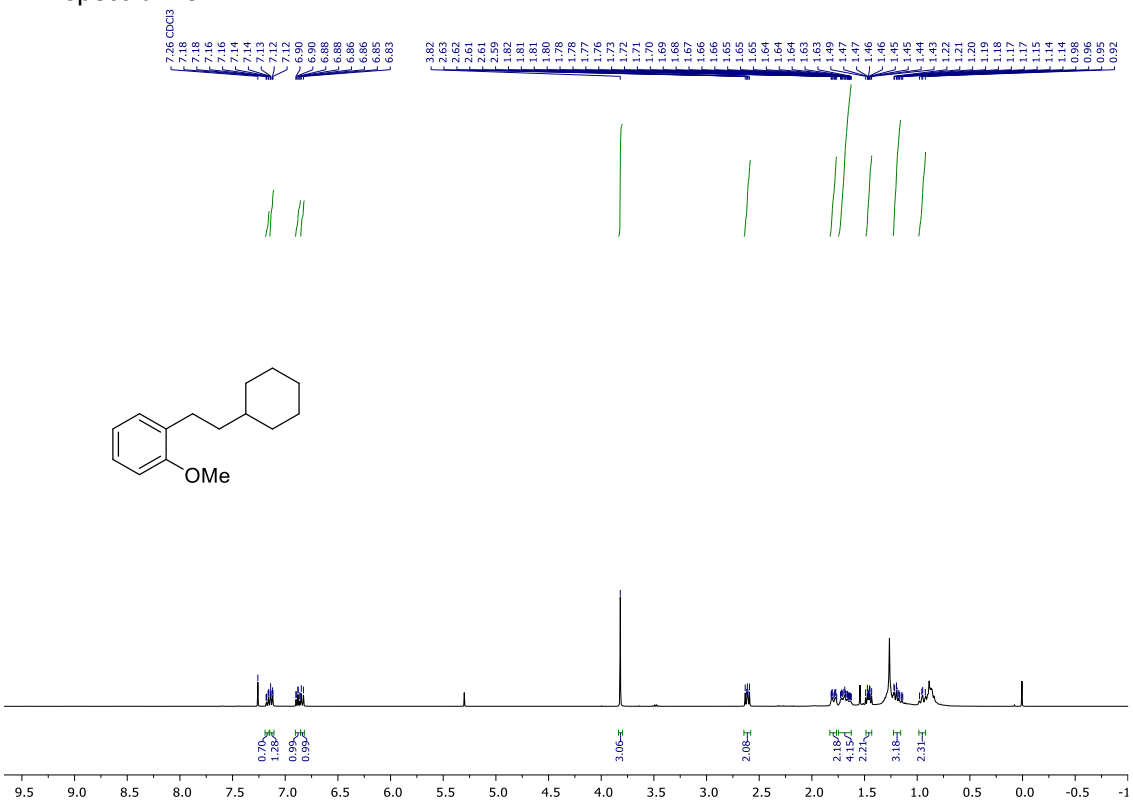
^{1}H NMR spectrum of **41**



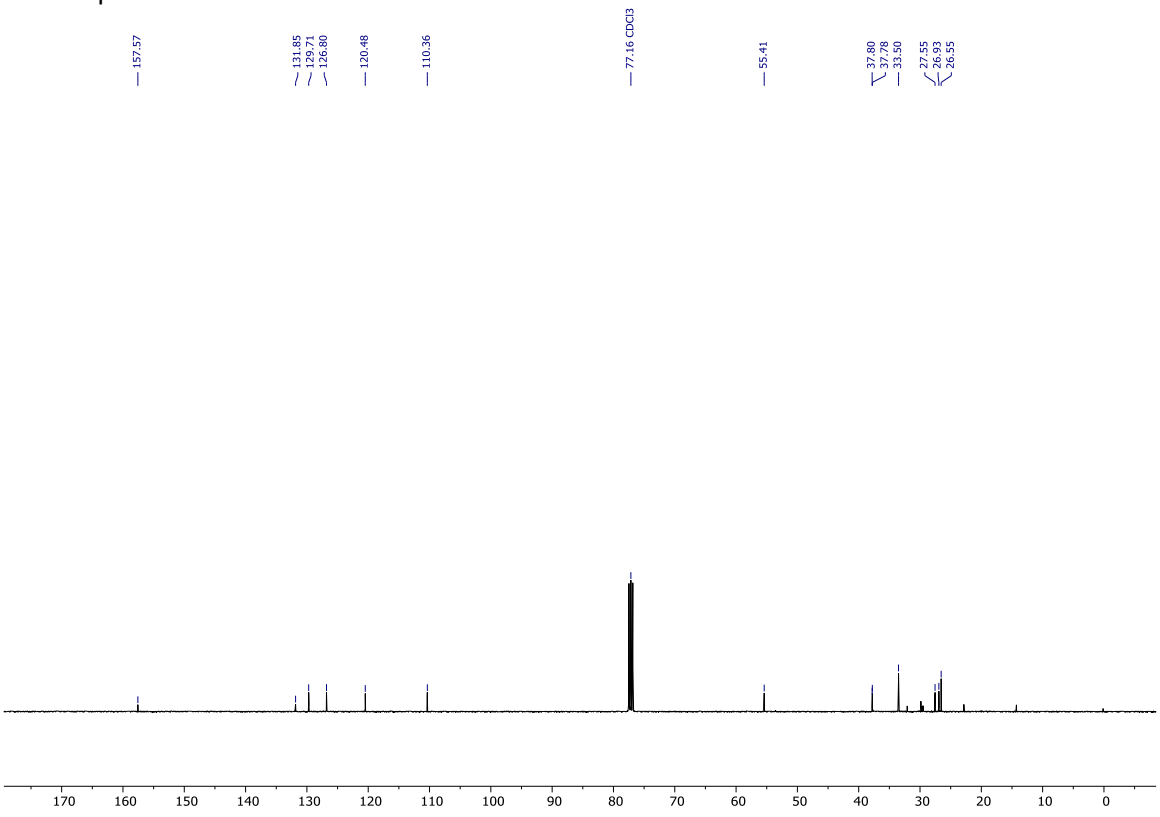
^{13}C NMR spectrum of **41**



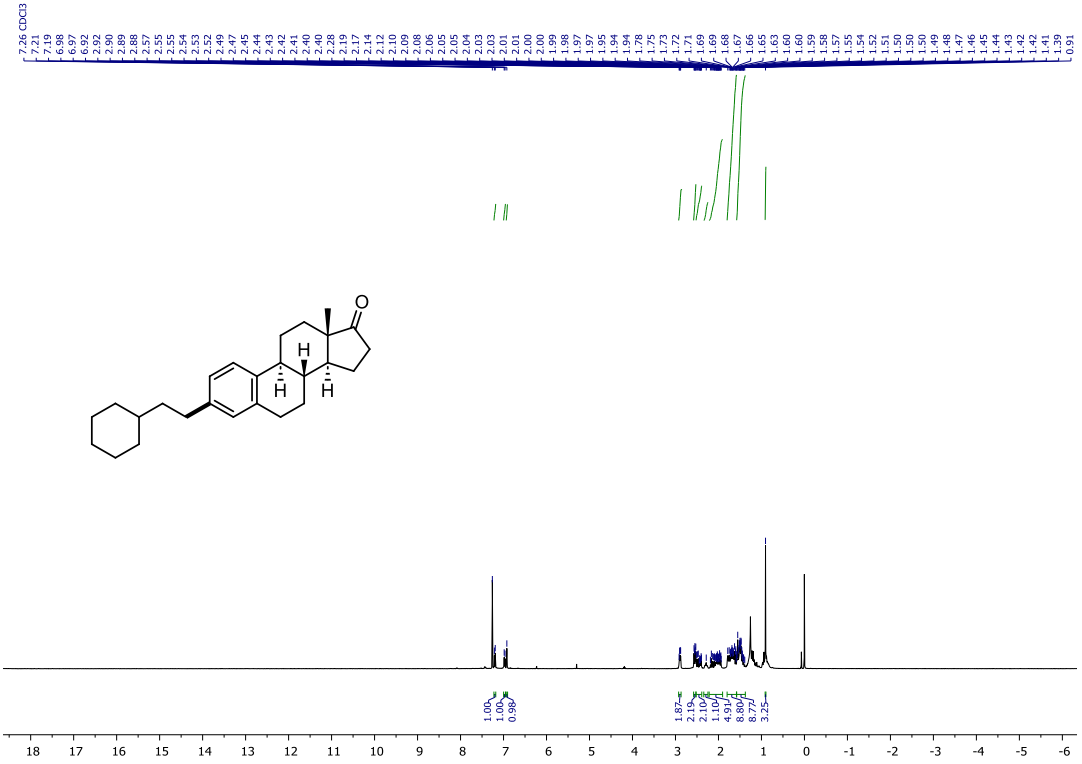
^{1}H NMR spectrum of **42**



^{13}C NMR spectrum of **42**



^{1}H NMR spectrum of **45**



^{13}C NMR spectrum of **45**