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Supporting Information

Photosensitized Intermolecular Carboimination of Alkenes through the Persistent Radical Effect

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1. Contents

1. General Information

1.1. Reagents, solvents and experimental conditions

All reagents were purchased from Alfa Aesar, Sigma-Aldrich, Merck, TCI, Fluorochem, Combi-blocks, VWR and used without further purification, except otherwise stated. THF and diethyl ether were purified by distillation over sodium-ketyl benzophenone under argon atmosphere. CH_2Cl_2, toluene and *n*-hexane were purified by distillation over CaH_2 under argon. All other solvents were bought from Acros in AcroSeal® bottles and were directly stored under 3 or 4 Å molecular sieves, replacing the collected volume with argon. All reactions were carried out in an oven-dried glassware under an atmosphere of argon using standard Schlenk technique, unless otherwise noted. Solvents for chromatographic purification (*n*-pentane, CH_2Cl_2 and EtOAc) were purchased as technical grade and purified by atmospheric pressure distillation. Reaction temperatures are referred to the temperature of the heating medium, unless otherwise stated.

Photocatalyst $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ (**[Ir-F]**, $dF(CF_3)ppy$ = 2-(2,4-difluorophenyl)-3-trifluoromethylpyridine, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine)[1] was prepared according to reported literature procedures.

1.2. Analytical techniques

NMR-spectra were recorded on a Bruker Avance II 300, Avance II 400, Agilent DD2 500 or DD2 600 spectrometers. All spectral data was acquired at 295 K. Deuterated solvents were purchased from Eurisotop ($CDCl_3$, deuteration > 99.8%) or Aldrich (DMSO-d_6, deuteration > 99.9 %). ^1H and ^{13}C chemicals shifts (δ) are quoted in parts per million (ppm) against tetramethylsilane (TMS, δ = 0.00 ppm) and were internally referenced to residual $CHCl_3$ (7.26 ppm for ^1H, 77.16 ppm for ^{13}C) or DMSO (2.50 ppm for ^1H, 39.52 ppm for ^{13}C). ^{19}F chemicals shifts (δ) are quoted in parts per million (ppm) and were calibrated using absolute referencing to the ^1H NMR spectrum, as suggested by IUPAC.[2] Coupling constants (*J*) are reported in Hertz (Hz) to the nearest 0.1 Hz. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quintet, p = pentet, m = multiplet.

High-resolution mass spectra (HRMS) were obtained by the MS service of the Organisch-Chemisches Institut, Westfälische Wilhelms Universität Münster, using electrospray ionisation (ESI) on a Bruker Daltonics, MicroToF spectrometer and calibrated using formate ion clusters.

GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm × 30 m, film: 0.25 μm). The major signals are quoted in *m*/*z* with the relative intensity in parentheses.

Thin layer chromatography was carried out on Merck silica gel 60 F_{254} pre-coated aluminium sheets and were visualized using UV light (254 nm) and stained with basic aqueous potassium permanganate or ethanolic phosphomolybdic acid solution.

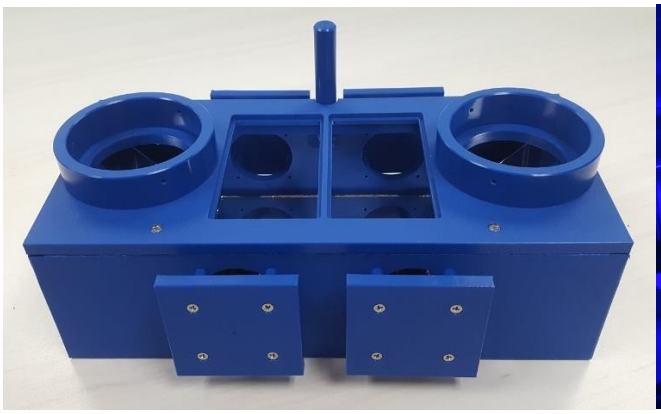
1.3. Compound purification

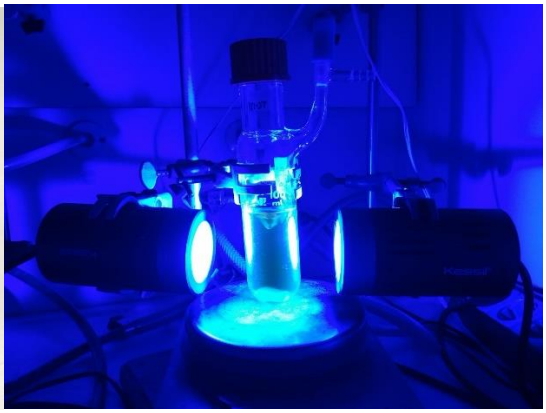
Flash chromatography was carried out according to the report of Still and co-workers[3] using silica gel (Acros Organics, 0.035-0.070 mm, 60 Å) under a light positive pressure of argon, eluting with the specified solvent system.

1.4. Photochemical set-up

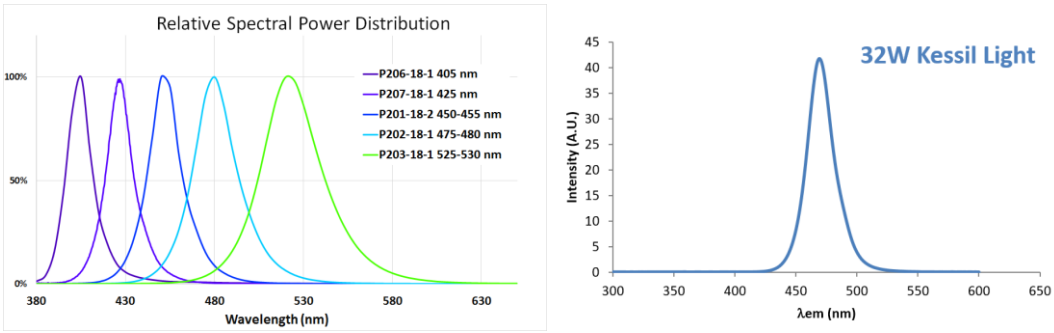
The following set-up was used for the reaction optimization (0.1 mmol scale) and substrate scope (0.3 mmol scale): the EvoluChem™ PhotoRedOx Duo (HCK1006-01-023) parallel reactor (Supplementary Fig. 1 – *(left)*) was equipped with EvoluChem™ Blue LEDs array (30 W, λ_{max} = 450 - 455 nm, HCK1012-01-008) (Supplementary Fig. 2 – *(left)*). Stirring was ensured by magnetic stirring plates (800 rpm). A 10 mL Schlenk tube equipped with a PTFE-screw cap and a PTFE-coated rare-earth "extra power" oval stirring bar (10 x 5 mm) was used for small scale reactions.

For the large scale reactions (> 0.3 mmol), the set-up shown in Supplementary Fig. 1 – *(right)* was used: two 32W H150 blue Kessil® lights (Supplementary Fig. 2 – *(right)*) were placed at ~4 cm from the reaction vessel, while stirring was ensured by a magnetic stirring plate (800 rpm). A 100 mL Schlenk tube, equipped with a PTFE-screw cap and a PTFE-coated stirring bar was used.



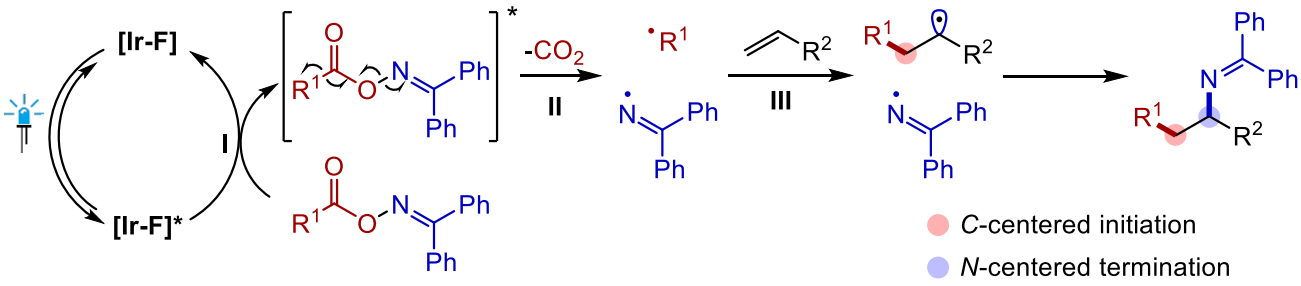


Supplementary Fig. 1 Experimental set-ups: *(left)* EvoluChem™ PhotoRedOx Duo (courtesy of EvoluChem™); *(right)* Scale-up set-up featuring two 34W H150 blue Kessil® lights; *(center-bottom)* EvoluChem™ 30W blue LEDs array - HCK1012-01-008 (courtesy of EvoluChem™).



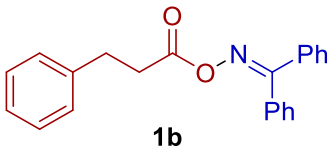
Supplementary Fig. 2 Emission spectra of the used light sources: *(left)* EvoluChem™ Blue LEDs array (courtesy of EvoluChem™); *(right)* 34W H150 blue Kessil® lights.

2. Mechanistic studies



Step		Evidence
I	EnT	▪ Feasibility of TTEnT (section 2.1) ▪ Feasibility of SET (section 2.2) ▪ Direct sensitization (section 2.3) ▪ Yield vs triplet energy correlation (section 2.4)
II	*N*- and *C*- centered radicals formation	▪ Direct C-N coupling (section 3.3.4) ▪ Radical clock (section 2.5)
III	Radicals excaping solvent cage	▪ Crossover experiment (section 2.6)

2.1. Feasibility of TTEnT



1b

The reported triplet energy for **[Ir-F]** is 60.8 kcal mol^{-1}. The triplet energy of **1b** was calculated to be 45.4 kcal mol^{-1}. So, a triplet-triplet energy transfer (TTEnT) from excited photocatalyst to the benzophenone imine ester (**1b**) is **thermodynamically facile**.

Triplet energy calculation

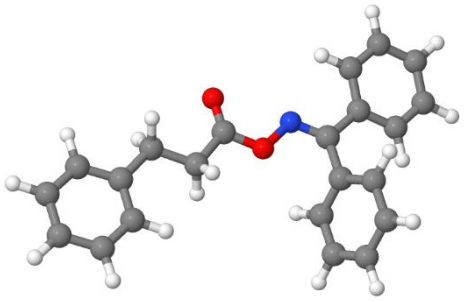
The triplet energy of benzophenone *O*-(3-phenylpropanoyl) oxime (**1b**) was computed using the ORCA 4.1.1 software package.[4] The geometry of the singlet and triplet state, respectively, were optimized using Handy's range-separated CAM-B3LYP functional[5] and Grimme's D3 dispersion correction[6] in the def2-SVP basis set, as developed by Ahlrichs and co-workers.[7] No internal coordinate or symmetry constraints were applied. Optimized geometries were verified to be local minima on the respective potential energy landscape by the absence of negative eigenvalues of the Hessian, as obtained from a harmonic frequency calculation at the same level. More accurate electronic energies were then obtained from a single-point calculation, using the def2-TZVPP triple-zeta basis set.

Free enthalpies were calculated from the single point electronic energies, corrected by zero-point vibrational energy, thermal, enthalpy and entropy corrections, as obtained from the harmonic frequency calculations. All geometries were visualized using Jmol.[8]

	Electronic Energy [E_h]	**ZPVE** [E_h]	**Thermal Correct.** [E_h]	**Enthalpy Corr.** [E_h]	**Entropy Corr.** [E_h]	**Free Enthalpy** [E_h]
Singlet State	-1054.825721	0.3594083	0.02098487	0.00094421	-0.07017112	-1054.514554
Triplet State	-1054.748843	0.35651383	0.02125805	0.00094421	-0.07204305	-1054.4421700

$$E_T = \Delta G = G_{Triplet} - G_{Singlet} = 0.072384\ E_h \approx \mathbf{45.4\ kcal\ mol^{-1}}$$

Singlet State



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C	-1.40870608894533	1.68747635853470	0.09950164117482
C	-1.37627783579394	0.29218074509912	0.07415120565579
C	-2.55538849316504	-0.45307424155061	0.09990780773255
H	-4.79848404942285	2.09258603643453	0.21743506859357
H	-4.71132338227557	-0.39867982886629	0.17147824762110
H	-2.70500648804656	3.40818905733859	0.17133791398930
H	-0.42254609518933	-0.23551880726359	0.03437734869405
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C	-0.16583597320389	2.54703137422282	0.07569670556363
C	1.15262571246805	1.80074026527086	-0.01162235100396
H	-0.15197257281450	3.18640033546711	0.97258376245670
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H	1.20832434634142	1.17026703770988	-0.91347141904338
H	1.29521750579681	1.11297036519410	0.83677843412821
O	2.29964210785844	3.92763097770515	-0.00899419242588
O	3.47618147758350	1.99353361519159	-0.09734463234377
N	4.63850839249864	2.74074592738761	-0.15015406924098
C	5.68810409091527	2.01113444270151	-0.11031651168296
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C	5.05661222485901	-0.23529832628660	-1.04289341464064
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C	5.68033048430411	-2.26968404492611	0.09443683930268
C	5.06413098591319	-1.62396518189810	-0.97537051603950
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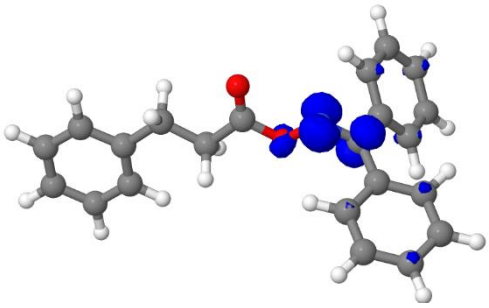
H	10.35484991732960	4.68234141265853	-0.17751124354244
H	6.09098001638535	4.60770642653315	0.45766488647504

Triplet State



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C	-1.14662181127304	1.62675795606445	1.51596218515596
C	-2.26103183859108	1.54331187610787	2.35109952628148
H	-4.69292122305821	2.17713465157348	0.06838099502682

H	-4.40990019650921	1.67404891167992	2.49371623436722
H	-2.71402255571597	2.32468803643877	-1.40710542101161
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H	1.43280316451631	2.60164370403946	0.61239099989681
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O	3.56579468459662	1.73609066915346	-0.57158711765212
N	4.66217145413124	1.93598750923971	-1.36739047759426
C	5.79879737285659	1.44403310850208	-0.70412632713626
C	6.13775063767417	0.06425443327586	-0.99752789545120
C	5.61917575572076	-0.55047063783368	-2.15918105841992
C	6.92194573164004	-0.72342924750618	-0.12833923999776
C	7.19333563105619	-2.05209027569950	-0.42392782448303
C	6.69066928045239	-2.63692013781200	-1.58567136256725
C	5.89789693391338	-1.87801365336456	-2.44684428071353
H	5.00651762778124	0.04177495212528	-2.84037031193655
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C	5.90120034876978	3.51410686644806	0.65249173798579
C	7.92114093787232	2.21451161626467	0.37893596401169
C	6.59786901984372	4.42798708404011	1.42844565128221
C	7.95495041990618	4.24231629386897	1.69209048394891
C	8.61056118066732	3.13431799766521	1.15561997545982
H	9.67878140180628	2.99304803185342	1.33332812373761
H	8.46056119235889	1.38018727734071	-0.06792370880111
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H	8.50156160068198	4.96366082376888	2.30254161695077
H	4.83979139794350	3.66855830380868	0.46053186403855

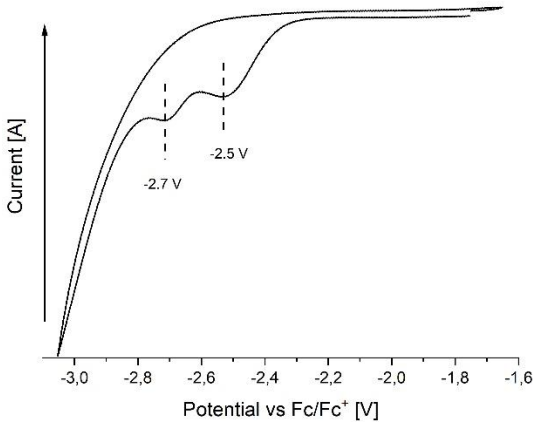
2.2. Feasibility of SET

The possibility of SET reduction of the benzophenone imine ester (**1b**) by **[Ir-F]*** in oxidative quenching (in Ir(III)*/Ir(IV) step) or by the reduced photocatalyst in a reductive quenching cycle (in Ir(II)/Ir(III) step) to generate the iminyl radical **can be completely ruled-out** by comparing the corresponding reduction potential values.

[Ir-F]	1b
$E_{1/2}^{III*/IV}$ = -0.89 V vs SCE	E_{irr}^{red} = -2.05 V vs SCE
$E_{1/2}^{III/II}$ = -1.37 V vs SCE	

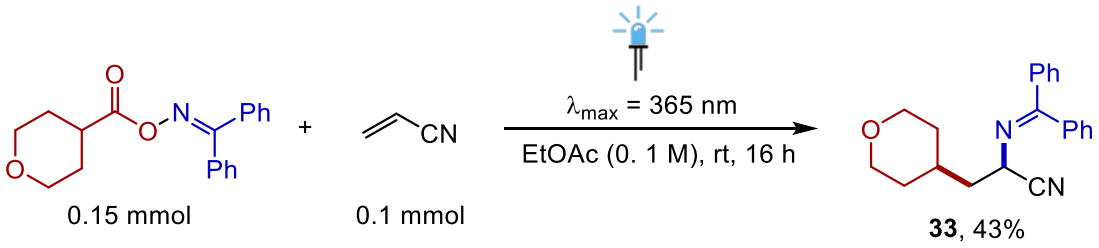
Electrochemical data

Experiments were conducted in a *TSC 1600* closed measuring cell that was connected to a *Metrohm Autolab PGSTAT204* potentiostat. The cell consists of the front-end of a platinum wire as the working electrode, a platinum crucible counter electrode and a silver wire pseudo-reference electrode. **1b** was dissolved in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in DMF. The applied voltage was referenced to the redox potential of the ferrocene/ferrocenium ion pair. A scan rate of 400 mV/s was applied. The CV experiment in MeCN was not conclusive due to the decomposition of the electrolyte (inset about -2.2 V vs Fc/Fc^+). The reduction of **1b** in MeCN is, thus, assumed to occur at potentials below -2.2 V vs Fc/Fc^+. As a result, reduction potential of **1b** was measured in DMF with respect to Fc/Fc^+ ion pair and then converted against SCE using the conversion $E^0_{1/2}$ (Fc/Fc^+) = +0.45 V vs. SCE. In DMF, **1b** is irreversibly reduced at a peak potential of -2.50 V vs Fc/Fc^+. This gives the irreversible reduction peak potential value of -2.05 V vs SCE for **1b** in DMF.



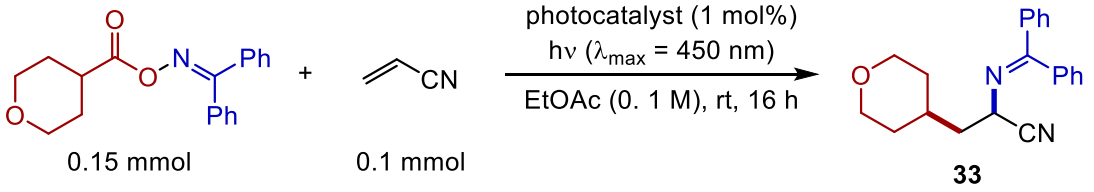
Supplementary Fig. 3 Cyclic voltammogram for **1b**

2.3. Direct sensitization



In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, substrate **S33** (46.4 mg, 0.15 mmol, 1.5 equiv) was charged, then the vessel was evacuated and back-filled with argon for four times. EtOAc (1.0 ml) and acrylonitrile (6.5 μL, 0.10 mmol, 1.0 equiv.) were added under an argon counter flow and the cap was sealed. The reaction was irradiated at 365 nm for 16 hours, then the solvent was removed under reduced pressure. The yield of the final product (**33**, 43%) was determined by ^{1}H NMR, using dibromomethane as internal standard.

2.4. Yield vs triplet energy correlation

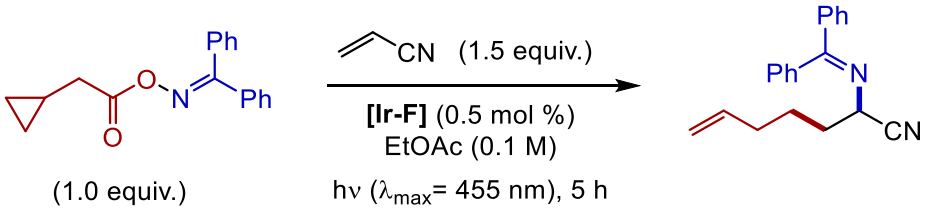


In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, substrate **S33** (46.4 mg, 0.15 mmol, 1.5 equiv) and the corresponding photocatalyst (1.0 μmol, 1.0 mol%) were charged, then the vessel was evacuated and back-filled with argon for four times. EtOAc (1.0 ml) and acrylonitrile (6.5 μL, 0.10 mmol, 1.0 equiv.) were added under an argon counter flow and the cap was sealed. The reaction was irradiated at 455 nm for 5 hours, then the solvent was removed under reduced pressure. For each cases, the yield of the final product (**33**) was determined by ^{1}H NMR, using dibromomethane as internal standard.

Photocatalyst	E_T (kcal·mol^{-1})	$E_{1/2}^{M^*/M^+}$ (V)	$E_{1/2}^{M^-/M}$ (V)	Yield of **33** (%)
[Mes-Acr$^+$]ClO$_4$	44.7	-	+0.57	0
[Ru(bpy)$_3$](PF$_6$)$_2$	46.5	-0.81	+1.33	0
[Ir(ppy)$_2$(dtbbpy)]PF$_6$	49.2	-0.96	+1.51	9
fac-[Ir(ppy)$_3$]	57.8	-1.73	+2.19	29
fac-[Ir(dF(ppy))$_3$]	59.1	-1.44	+2.11	59
[Ir-F]	60.8	-0.89	+1.37	83

Benzophenone imine esters of alkyl carboxylic acids are known to generate *N*-centered iminyl radical through reductive single electron transfer (SET). However, this pathway is only possible either by the excited photocatalyst in oxidative quenching cycle (in M*/M$^+$ step) or by the reduced photocatalyst in reductive quenching cycle (in M$^-$/M step). However, in presence of highly reducing photocatalyst such as *fac*-[Ir(ppy)$_3$] maximum yield was not observed. Similarly, highly oxidizing photocatalyst like [Mes-Acr$^+$]ClO$_4$ ($E_{1/2}^{M^*/M^-}$ = 2.06 V) also did not provide the desired product. Alternatively the yield of **33** was found directly correlated with the increasing triplet energy of the photocatalyst used. This further validates that an energy transfer pathway is operative in this case.

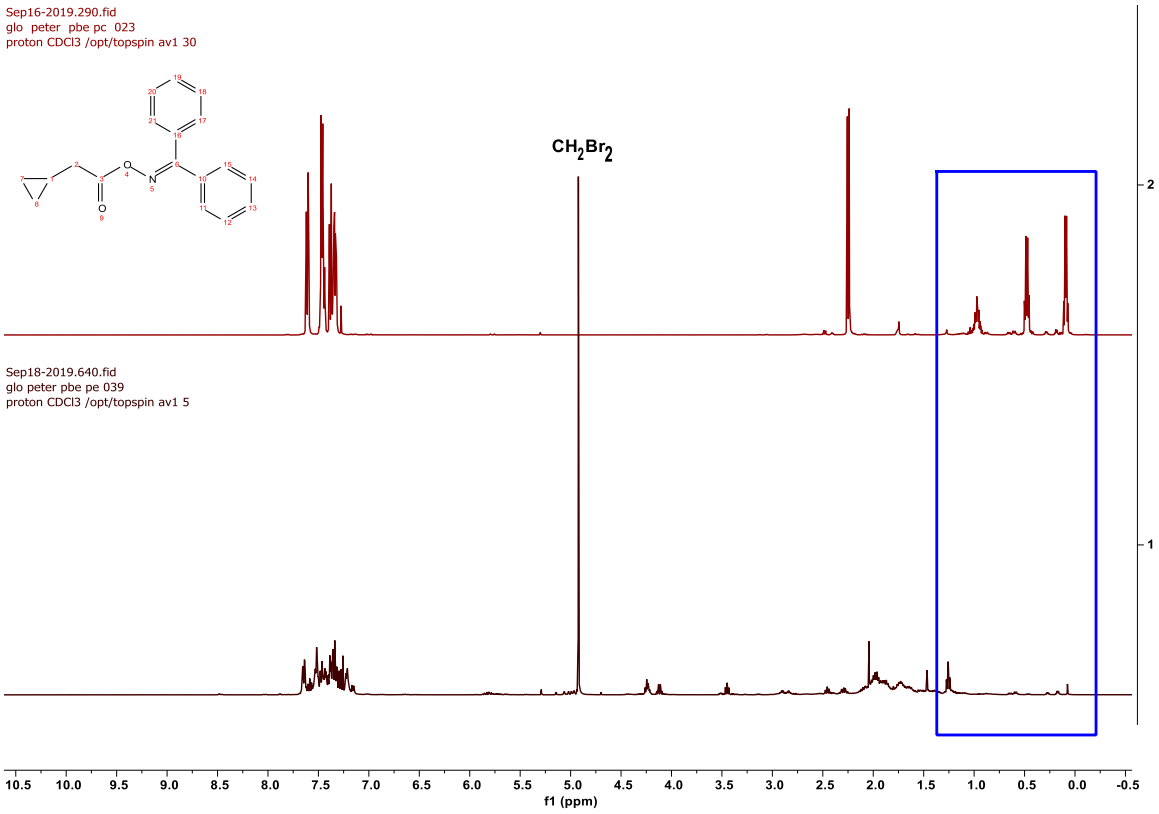
2.5. Radical clock experiment



In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, substrate diphenylmethanone *O*-(2-cyclopropylacetyl) oxime (27.9 mg, 0.1 mmol, 1.0 equiv) and **[Ir-F]** (0.6 mg, 0.5 μmol, 0.5 mol%) were charged, then the vessel was evacuated and back-filled with argon four times. EtOAc (1.0 ml) and acrylonitrile (9.8 μL, 0.15 mmol, 1.5 equiv.) were added under an argon counter flow and the cap was sealed. The reaction was irradiated at 455 nm for 5 hours, then the solvent was removed under reduced pressure. The analysis was performed by ^{1}H NMR, using dibromomethane as internal standard.

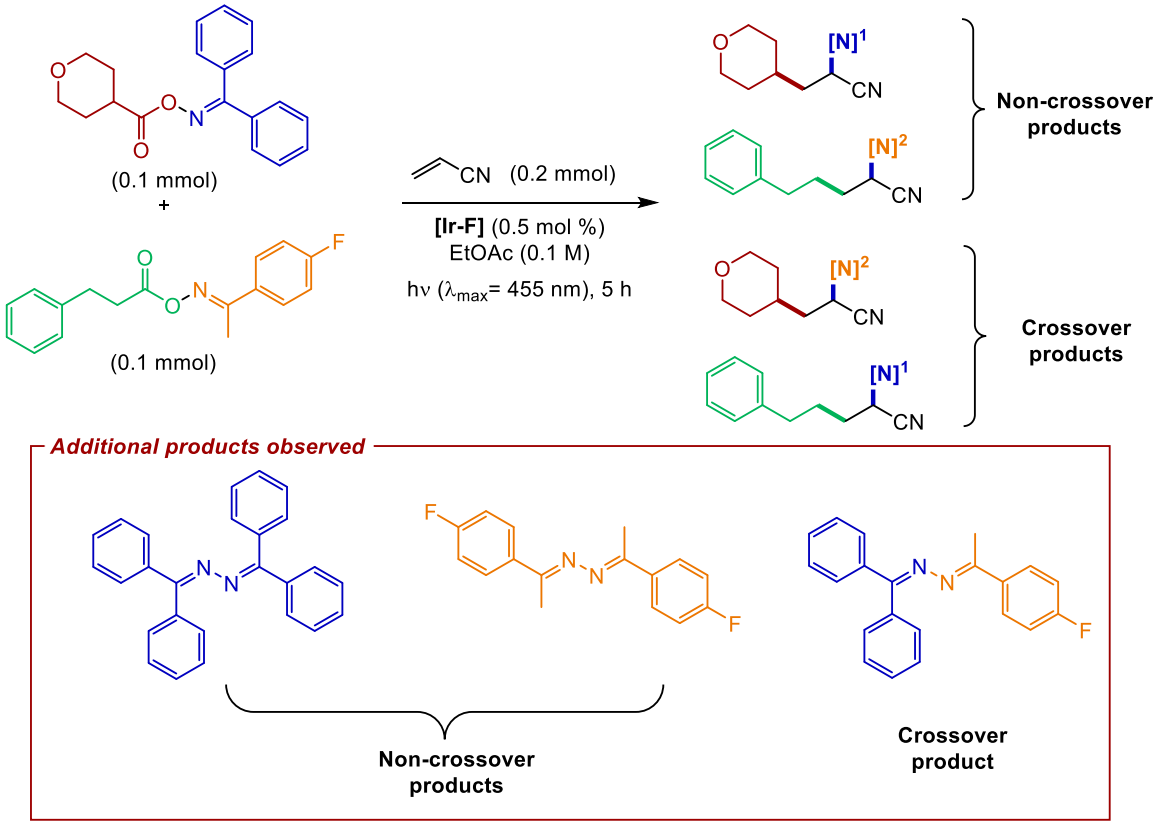
By comparison of the ^{1}H NMR spectrum of the crude mixture with the starting material, the absence of the typical signals that indicate the presence of the cyclopropyl moiety could be observed (**Supplementary Fig. 3**).

Therefore, while a quantification of the product is hampered by the presence of multiple byproduct, we can conclude that the ring-opening process due to the formation of the methylcyclopropyl radical takes place in the reaction.

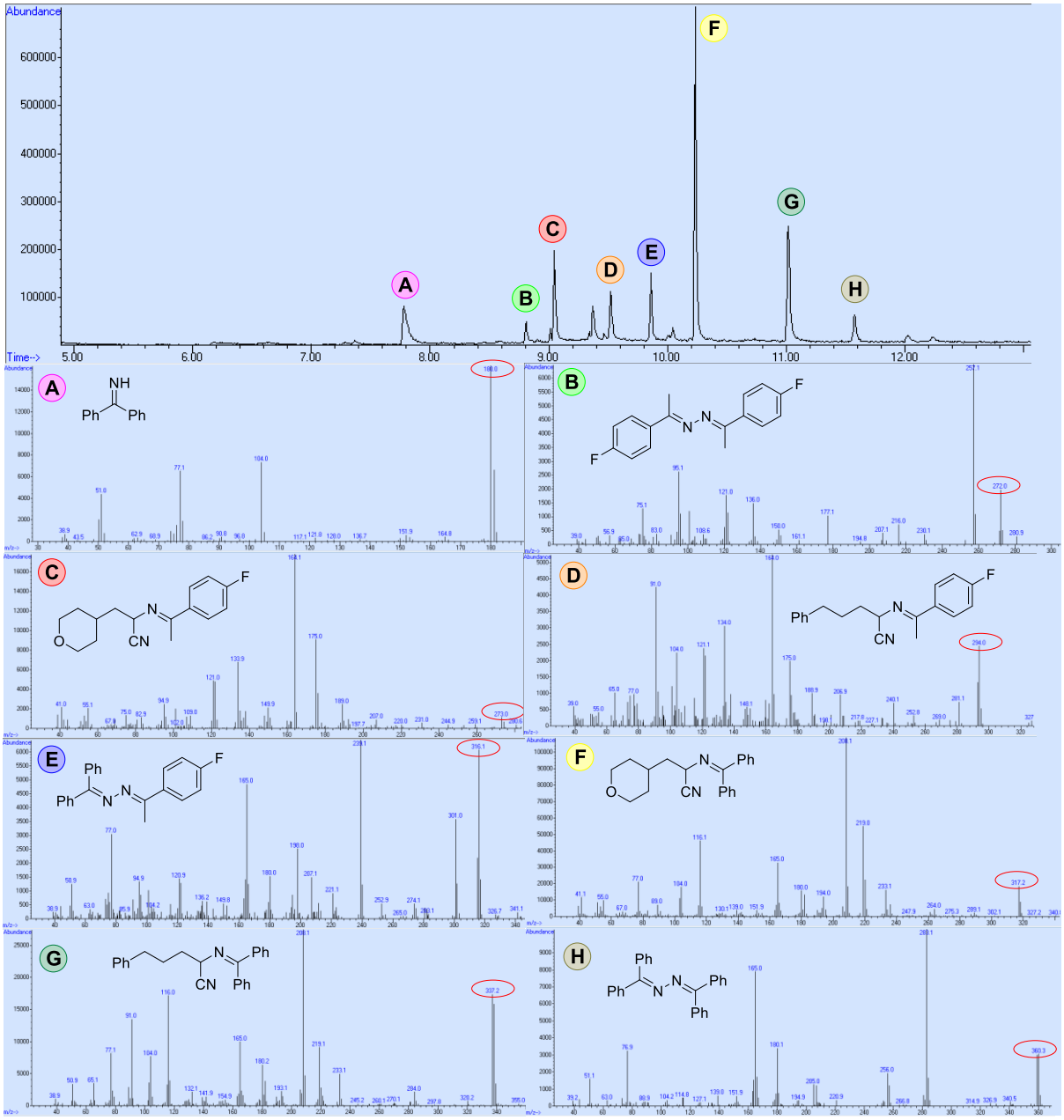


Supplementary Fig. 3 ^{1}H NMR spectra comparison between the starting material (*upper in red)* and the crude reaction mixture (*lower in black*).

2.6. Radical crossover experiment



In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, 1-(4-fluorophenyl)ethan-1-one *O*-(3-phenylpropanoyl) oxime (28.5 mg, 0.1 mmol, 1.0 equiv), diphenylmethanone *O*-tetrahydro-2*H*-pyran-4-carbonyl oxime (30.9 mg, 0.1 mmol, 1.0 equiv) and **[Ir-F]** (1.2 mg, 1.0 µmol, 0.5 mol%) were charged, then the vessel was evacuated and back-filled with argon four times. EtOAc (1.0 ml) and acrylonitrile (13.0 µL, 0.2 mmol, 2.0 equiv) were added under an argon counter flow and the cap was sealed. The reaction was irradiated at 455 nm for 5 hours, then the analysis was performed by GCMS.



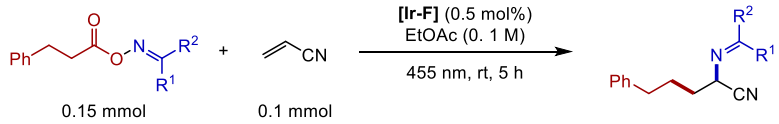
Supplementary Fig. 4 GC-MS trace and MS spectra of the radical crossover experiment mixture.

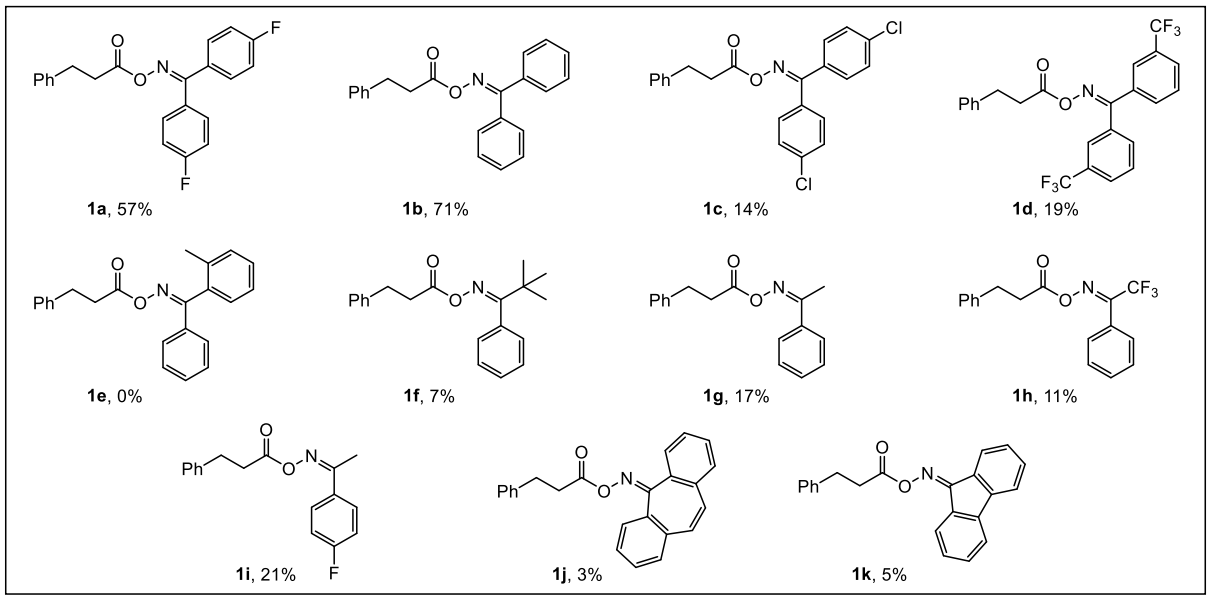
Results: As visible in **Supplementary Fig. 4**, both non-crossover and crossover products could be detected. This confirms that the radical trapping occurs outside the solvent cages. Beside iminyl radical homo-coupling as well as cross-coupling products indicates relatively long lifetimes of the iminyl radical.

3. Experimental Procedures and Characterization Data

3.1. Optimization data

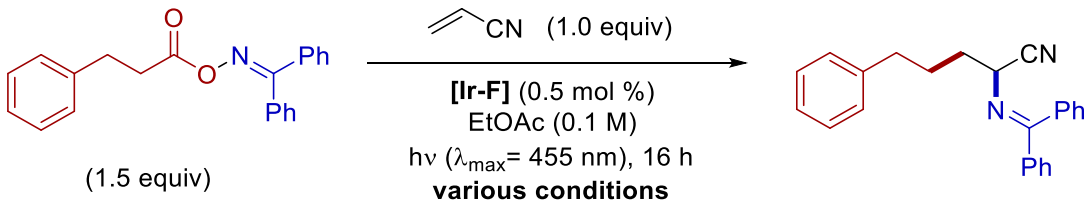
Reaction condition optimization was based on our previous work with oxime esters.[9] Optimization with respect to different iminyl groups were performed.





3.2. Sensitivity screening

The sensitivity assessment of the reaction towards several reaction parameters was performed according to the previous publication by Glorius *et al.*[10] Herein, we describe the protocol that was followed for the screening procedure and we report the results.



Preparation of stock solution 1 (substrate): In an oven-dried Schlenk tube equipped with a PFTE-coated stirring bar, oxime ester **S4** (445 mg, 1.35 mmol, 1.5 equiv) was charged, then the vessel was purged and back-filled with argon four times. Dry ethyl acetate (3.6 ml) was added under argon, then the solution was vigorously stirred for 10 minutes.

Preparation of stock solution 2 (catalyst and acceptor): In an oven-dried Schlenk tube equipped with a PFTE-coated stirring bar, **[Ir-F]** (5.1 mg, 4.5 μmol, 0.5 mol%) was charged, then the vessel was purged and back-filled with argon four times. Dry ethyl acetate (1.8 ml)

was added under argon, then acrylonitrile (59.0 μL, 0.9 mmol, 1.0 equiv) was added and the solution was vigorously stirred for 10 minutes.

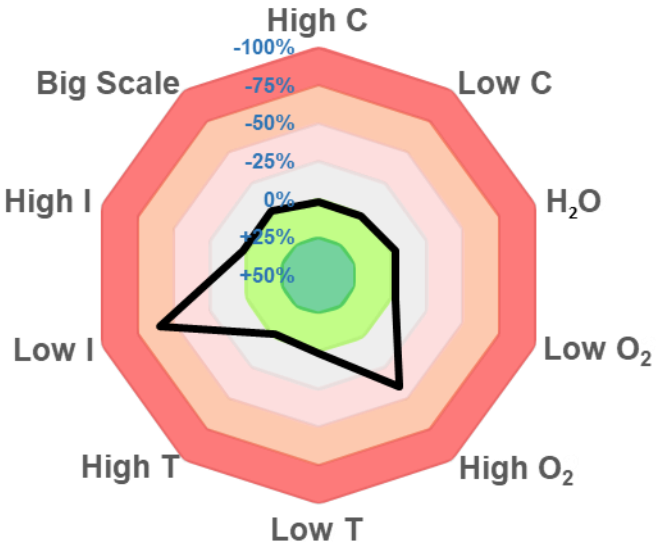
Reaction set-up: An oven-dried Schlenk tube equipped with a PTFE-coated rare-earth "extra power" oval stirring bar (10 x 5 mm) was purged and re-filled four times with argon, then **stock solution 1** (400 μL), followed by **stock solution 2** (200 μL) and the appropriate amount of ethyl acetate (see table) were added under argon counterflow. If required, the addition of substances or protocols were performed at this point. The vessel was sealed, and the reactions were irradiated at 455 nm using the described set-up for 16 hours. The solvent was removed under reduced pressure, then the residue was dissolved in $CDCl_3$ (approx. 0.7 ml) and the standard CH_2Br_2 (0.1 mmol) was added. The yield was obtained by ^1H NMR analysis. In the case of the large-scale reaction, the procedure reported for **33** was used and isolation by flash column chromatography was performed. The yield was compared to the isolated one on 0.3 mmol scale.

Table 1. Set-up of the sensitivity screen experiments.

Entry #		Add solvent / μL	Additive	Notes
1	Standard	400	--	--
2	Low concentration (-10%)	500	--	--
3	High concentration (+10%)	300	--	--
4	Low intensity (1/16x)	400	--	Distance: 0.5 cm
5	High intensity (16x)	400	--	Distance: 8.8 cm
6	High H_2O (10^4 ppm)	400	10 μL H_2O	--
7	Low O_2	400	--	Freeze-pump-thaw 3x
8	High O_2	400	10 ml air	--
9	Low temperature	400	--	Cooling fan
10	High temperature	400	--	Closed box
11	Large scale (5 mmol)	--	--	Isolated yields

Table 2. Deviation of the yield upon different conditions.

Entry #		Difference %
1	Standard	0
2	Low concentration (-10%)	+ 1.8
3	High concentration (+10%)	+ 1.8
4	Low intensity (1/16x)	- 59.6
5	High intensity (16x)	-1.8
6	High H_2O (10000 ppm)	-3.5
7	Low O_2	-3.5
8	High O_2	-40.4
9	Low Temperature	-1.8
10	High temperature	+1.8
11	Large scale (5 mmol)	-2.4

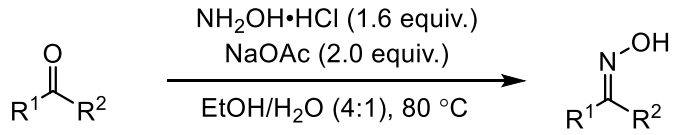


Supplementary Fig. 6 Radar diagram representation of the sensitivity screening.

As graphically reported in **Supplementary Fig.** , the reaction proved to be sensitive towards high oxygen concentration, as well as the reduced light intensity. Conversely, small variations of concentration, temperature and water content had a negligible effect on the outcome of the process. Moreover, the reaction proved to be robust towards scaling-up from 0.3 mmol to 5.0 mmol, with minimal effect on the yield.

3.3. Synthesis of substrate

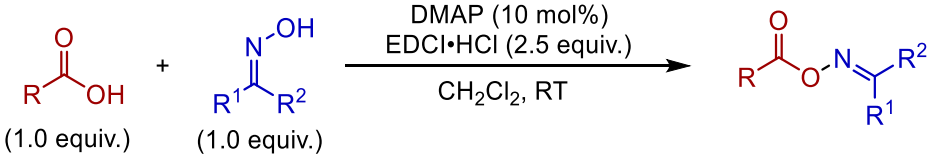
3.3.1. General procedure for the synthesis of ketoximes



All ketoximes were prepared according to the reported literature procedure.[11] In a 50 mL round-bottom flask fitted with a condenser, ketones (10 mmol, 1.0 equiv.) were first dissolved in the 25 mL (4:1, v/v) mixture of EtOH/H_2O. Then, hydroxylamine hydrochloride (16 mmol, 1.6 equiv.) and NaOAc (20 mmol, 2.0 equiv.) were added in one portion. The reaction mixture was stirred at 80 °C until the consumption of the starting material was observed by TLC. The reaction was cooled to room temperature, diluted with water (55 mL) and extracted three times with ethyl acetate (80 mL each time). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was used directly for the ketoxime ester preparation.

***Note**: The oxime esters did not show appreciable decomposition when stored at room temperature under atmosphere. Nevertheless, the starting material were stored in the fridge at 4°C.*

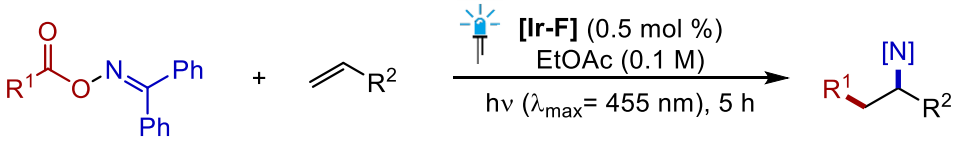
3.3.2. General procedure for the synthesis of oxime esters (General Procedure 1)



Ketoxime esters were prepared following a reported literature procedure.[12] To a solution of ketoxime from previous step (2.0 mmol) and aliphatic carboxylic acid (2.0 mmol) in CH_2Cl_2 (20 mL), DMAP (10 mol%, 0.2 mmol) and EDCI•HCl (5 mmol) was added. The mixture was stirred at room temperature under inert atmosphere until the reaction was complete as observed from TLC monitoring. The mixture was diluted with distilled water (25 mL) and the CH_2Cl_2 layer was separated, dried over anhydrous Na_2SO_4 and concentrated. The crude mass was treated with pentane (3 mL) and sonicated for 15 minutes. The resultant solid was filtered and dried under vacuum to obtain the pure oxime esters. In some cases, final compound was purified by flash column chromatography using pentane/dichloromethane (CH_2Cl_2) or pentane/ethylacetate (EtOAc) as eluent.

***Note:** In the case of highly polar compounds, the extractive work-up could be bypassed to avoid overcomplicated extraction and the crude reaction mixture could be directly loaded on silica for the chromatographic purification.*

3.3.3. General procedure for the carboimination of alkenes (General procedure 2)

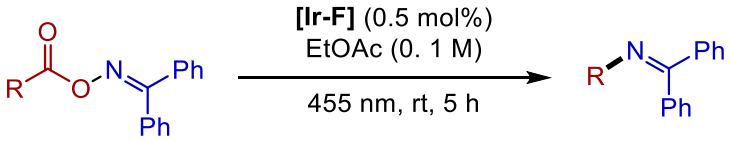


In an-oven dried 10 ml Schlenk tube equipped with a PTFE-coated rare-earth "extra power" oval stirring bar (10 x 5 mm), the appropriate oxime ester (1.5 equiv, unless otherwise stated) and **[Ir-F]** (0.5 mol%) were charged under air, then the vessel was evacuated and re-filled with argon four times. Dry EtOAc (0.1 M) was added under argon counterflow, followed by the appropriate alkene (1.0 equiv). The vessel was sealed with the screw cap, then irradiated at 455 nm using the described set-up for 5 hours, unless otherwise stated. After irradiation, the resulting homogenous solution was mixed with SiO_2 and Et_3N (approx. 1 mL) and the volatiles were removed under reduced pressure, affording a powder which was loaded on column. Purification by flash column chromatography on SiO_2, prebasified with Et_3N using pentane:EtOAc mixtures afforded the corresponding carboiminated product.

Note 1**: Further degassing by "freeze-pump-thaw" was tested (see* **Sensitivity screening), but comparable results to the use of ACROS "extra-dry" solvent under argon atmosphere were obtained.*

***Note 2**: Et_3N was used as the product can be partially hydrolyzed by silica, causing a slight decrease in the yield (approx. 5-10%). The amount of Et_3N added to the eluant was approximately 1 ml for 300 ml of solvent. When Et_3N was used for TLC analysis, one Pasteur pipette drop was used for 10 ml of eluant. "Prebasified" silica refers to silica gel which have been soaked with 2-5% triethylamine in hexanes prior to use.*

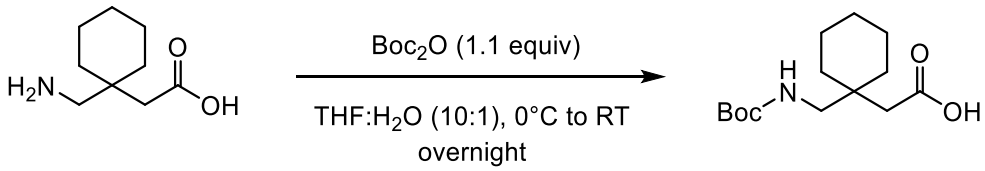
3.3.4. Direct C–N coupling (General procedure 3)



In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, oxime ester substrate (0.3 mmol, 1.0 equiv) and **[Ir-F]** (1.8 mg, 1.5 μmol, 0.5 mol%) were charged, then the vessel was evacuated and back-filled with argon four times. EtOAc (3.0 ml) was added under an argon counter flow and the cap was sealed. The reaction was irradiated at 455 nm for 5 hours, then the solvent was removed under reduced pressure. Purification by flash column chromatography on SiO_2, prebasified with Et_3N using pentane:EtOAc mixtures afforded the corresponding C–N coupling product.

3.4. Characterization data of substrates

2-(1-(((*tert*-butoxycarbonyl)amino)methyl)cyclohexyl)acetic acid (S1)

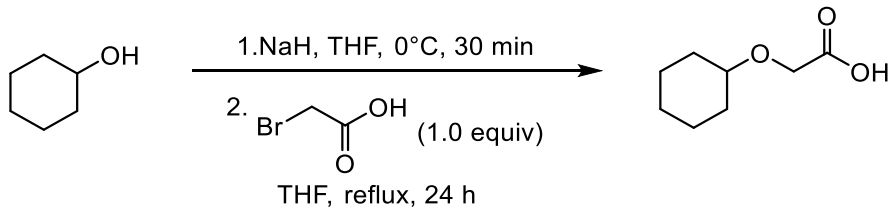


The compound was synthesized from gabapentin (685 mg, 4.00 mmol, 1.0 equiv.) according to the literature procedure[7] and obtained as a white solid (1.085 g, 4.0 mmol, quantitative yield).

^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 12.00 (s, 1H), 6.60 (t, *J* = 6.3 Hz, 1H), 3.02 (d, *J* = 6.4 Hz, 2H), 2.15 (s, 2H), 1.46 – 1.21 (m, 19H).

The experimental data are in accordance to the literature reports.[13]

2-(cyclohexyloxy)acetic acid (S2)

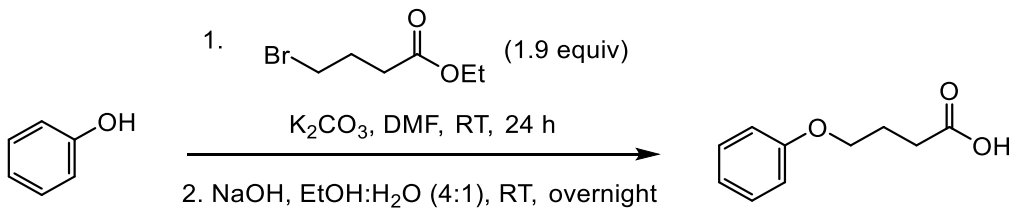


The compound was synthesized from cyclohexanol (541 µL, 5.00 mmol, 1.0 equiv) according to the literature procedure[13] and obtained as a light-yellow oil (645 mg, 4.08 mmol, 82%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 4.12 (s, 2H), 3.48 – 3.34 (m, 1H), 2.01 – 1.84 (m, 2H), 1.85 – 1.72 (m, 2H), 1.67 – 1.47 (m, 1H), 1.47 – 1.09 (m, 5H).

The experimental data are in accordance to the literature reports.[14]

4-phenoxybutanoic acid (S3)



In a round-bottom flask equipped with a PTFE-coated stirring bar, phenol (941 mg, 10.0 mmol, 1.0 equiv) and K_2CO_3 (2.63 g, 19.0 mmol, 1.9 equiv) were charged, then *N*,*N*-DMF (13 ml, ACROS reagent grade) was added, followed by ethyl 4-bromobutyrate (1.57 ml, 11.0 mmol, 1.1 equiv), then the reaction was vigorously stirred at room temperature for 24 hours. The solvent was removed under high vacuum (1.5 mbar @ 50°C), then the residue was taken-up

with EtOAc (50 ml) and water (30 ml), then the layers separated. The organic layer was dried over $MgSO_4$, then the solvent was removed under reduced pressure.

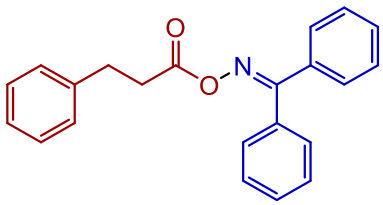
Note: Small amount of DMF might be still present, but the next step outcome is not substantially effected.

The residue was dissolved in EtOH:H_2O (4:1), then NaOH (1.56 g, 39.0 mmol, 3.9 equiv) was added and the reaction was stirred at room temperature overnight, then the solvent was removed under reduced pressure. The system was acidified up to pH 1 with HCl 37%, then extracted three times with EtOAc (30 ml each time). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure, to afford the crude product, which was triturated once with pentane:CH_2Cl_2 10:1, then with pentane, affording a light pink crystalline solid (767 mg, 4.26 mmol, 43% over two steps).

^{1}H NMR (300 MHz, $CDCl_3$): δ 11.02 (s, 1H), 7.34 – 7.21 (m, 2H), 7.01 – 6.92 (m, 1H), 6.92 – 6.84 (m, 2H), 4.02 (t, *J* = 6.0 Hz, 2H), 2.60 (t, *J* = 7.3 Hz, 2H), 2.21 – 2.04 (m, 2H).

The experimental data are in accordance to the literature reports.[15]

Diphenylmethanone *O*-(3-phenylpropanoyl) oxime (S4 or 1b)



Synthesized by **General Procedure 1** from hydrocinnamic acid (1.50 g, 10 mmol) and benzophenone oxime (1.97 g, 10.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 10:1) and obtained as white solid (3.10 g, 94% yield).

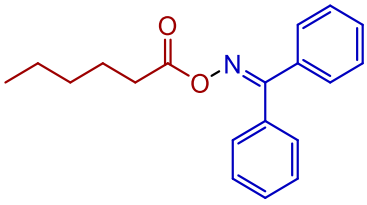
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 – 7.53 (m, 2H), 7.48 – 7.38 (m, 4H), 7.37 – 7.31 (m, 2H), 7.29 – 7.17 (m, 5H), 7.16 – 7.11 (m, 2H), 2.91 (t, *J* = 7.8 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 165.1, 140.3, 134.8, 132.6, 131.0, 129.7, 129.2, 128.9, 128.6, 128.5, 128.4, 128.3, 126.5, 34.8, 30.8.

R_f (pentane:EtOAc 10:1) = 0.30.

HRMS (ESI): m/z calculated for [$C_{22}H_{19}NNaO_2^+$] [M+Na^+]: 352.1308, measured: 352.1314.

Diphenylmethanone *O*-hexanoyl oxime (S19)



Synthesized by **General Procedure 1** from adipic acid (279 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 10:1) and obtained as a colourless oil (591 mg, 2.00 mmol, quantitative yield).

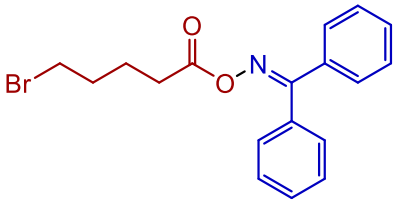
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 – 7.55 (m, 2H), 7.52 – 7.41 (m, 4H), 7.41 – 7.25 (m, 4H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.59 (ddd, *J* = 12.1, 8.5, 6.0 Hz, 2H), 1.38 – 1.16 (m, 4H), 0.98 – 0.76 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.4, 165.0, 134.9, 132.8, 131.0, 129.7, 129.2, 128.9, 128.5, 128.3, 33.1, 31.3, 24.5, 22.4, 14.0.

R_f (pentane:EtOAc 10:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{19}H_{21}O_2NNa$] [M+Na$^+$]: 318.1465, measured: 318.1474.

Diphenylmethanone *O*-(5-bromopentanoyl) oxime (S20)



Synthesized by **General Procedure 1** from 5-bromovaleric acid (434 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 10:1) and obtained as a white waxy solid (708 mg, 1.96 mmol, 98%).

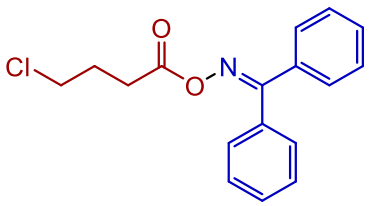
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.56 (m, 2H), 7.53 – 7.42 (m, 4H), 7.38 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.35 – 7.23 (m, 2H), 3.34 (t, *J* = 6.5 Hz, 2H), 2.39 (t, *J* = 7.1 Hz, 2H), 1.85 (tdd, *J* = 8.0, 6.3, 3.5 Hz, 2H), 1.75 (dqd, *J* = 8.7, 7.0, 6.3, 1.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 165.3, 134.7, 132.7, 131.1, 129.7, 129.1, 128.7, 128.5, 128.3, 33.0, 32.1, 31.8, 23.3.

R_f (pentane:EtOAc 10:1) = 0.18.

HRMS (ESI): m/z calculated for [$C_{18}H_{18}O_2N^{79}BrNa$] [M+Na$^+$]: 382.0413, measured: 382.0412; calculated for [$C_{18}H_{18}O_2N^{81}BrNa$] [M+Na$^+$]: 384.0393, measured: 384.0390.

Diphenylmethanone *O*-(4-chlorobutanoyl) oxime (S21)



Synthesized by **General Procedure 1** from 4-chlorobutanoic acid (294 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 10:1) and obtained as a colourless low melting crystalline solid (603 mg, 2.00 mmol, quantitative yield).

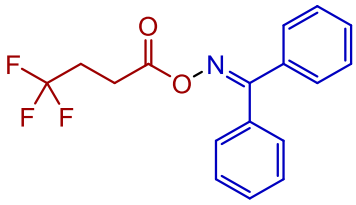
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.53 (m, 2H), 7.51 – 7.39 (m, 4H), 7.35 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.33 – 7.26 (m, 2H), 3.52 (t, *J* = 6.3 Hz, 2H), 2.53 (t, *J* = 7.1 Hz, 2H), 2.05 (p, *J* = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 165.2, 134.6, 132.6, 131.0, 129.7, 129.1, 128.7, 128.5, 128.3, 43.9, 30.0, 27.4.

R_f (pentane:EtOAc 10:1) = 0.25.

HRMS (ESI): m/z calculated for [$C_{17}H_{16}O_2N^{35}ClNa$] [M+$Na^+$]: 324.0762, measured: 324.0765.

Diphenylmethanone *O*-(4,4,4-trifluorobutanoyl) oxime (S22)



Synthesized by **General Procedure 1** from 4,4,4-trifluorobutanoic acid (341 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 10:1) and obtained as a white solid (615 mg, 1.91 mmol, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.53 (m, 2H), 7.52 – 7.42 (m, 4H), 7.41 – 7.33 (m, 2H), 7.33 – 7.23 (m, 2H), 2.62 (dd, *J* = 9.1, 6.7 Hz, 2H), 2.51 – 2.36 (m, 2H).

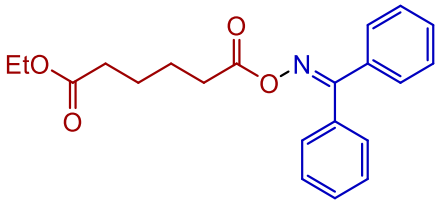
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.8, 165.7, 134.5, 132.5, 131.3, 129.9, 129.2, 128.8, 128.6, 128.4, 124.5 (q, $^1J_{C\text{-}F}$ = 276.3 Hz), 29.2 (q, $^2J_{C\text{-}F}$ = 30.2 Hz), 26.1 (q, $^3J_{C\text{-}F}$ = 3.2 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -67.96.

R_f (pentane:EtOAc 10:1) = 0.30.

HRMS (ESI): m/z calculated for [$C_{17}H_{14}O_2NF_3Na$] [M+Na^+]: 344.0869, measured: 344.0871.

Ethyl 6-(((diphenylmethylene)amino)oxy)-6-oxohexanoate (S23)



Synthesized by **General Procedure 1** from adipic acid monoethyl ester (418 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 4:1) and obtained as a colourless viscous oil (693 mg, 1.96 mmol, 98%).

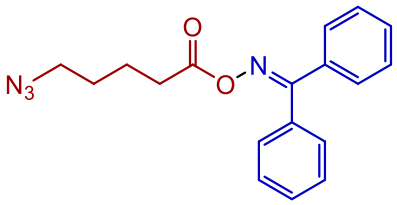
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.47 (m, 2H), 7.42 – 7.33 (m, 4H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.17 (m, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.33 – 2.24 (m, 2H), 2.22 – 2.11 (m, 2H), 1.82 – 1.48 (m, 4H), 1.17 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.3, 170.8, 165.1, 134.8, 132.8, 131.0, 129.7, 129.1, 128.8, 128.5, 128.3, 60.4, 34.0, 32.7, 24.4, 24.2, 14.3.

R_f (pentane:EtOAc 4:1) = 0.24.

HRMS (ESI): m/z calculated for [$C_{21}H_{23}O_4NNa$] [M+Na^+]: 376.1525, measured: 376.1524.

Diphenylmethanone *O*-(5-azidopentanoyl) oxime (S24)



Synthesized by the following two steps procedure:

In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, 5-bromovaleric acid (1.81 g, 10.0 mmol, 1.0 equiv) and dry DMF (12 ml) were charged under argon atmosphere, then NaN_3 (975 mg, 15.0 mmol, 1.5 equiv) was added and the reaction was vigorously stirred at 70°C for 20 hours. The solvent was distilled-off under reduced pressure (approx. 1 mbar @ 50°C), then the residue was taken-up with CH_2Cl_2 (40 ml) and washed with water (30 ml). The water layer was back-extracted twice with CH_2Cl_2 (30 ml each time). The combined organic layers were washed with brine (50 ml), dried over $MgSO_4$ and the solvent was removed under reduced pressure, affording the product as colourless oil.

Note: A small amount of DMF cannot be removed from the intermediate, but no influence on the following step was observed.

The crude intermediate (approx. 5.0 mmol) was converted into the product according to **General Procedure 1**, using benzophenone oxime (596 mg, 3.0 mmol). Final compound was purified by flash column chromatography (SiO_2, pentane:CH_2Cl_2 1:4) and obtained as a colourless gum (155 mg, 0.48 mmol, 16%).

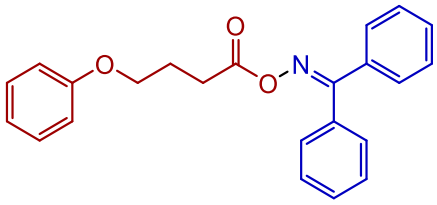
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 – 7.56 (m, 2H), 7.55 – 7.43 (m, 4H), 7.43 – 7.29 (m, 4H), 3.24 (t, *J* = 6.6 Hz, 2H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.79 – 1.50 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 165.1, 134.6, 132.6, 131.0, 129.6, 129.0, 128.6, 128.4, 128.2, 50.9, 32.3, 28.1, 21.8.

R_f (pentane:CH_2Cl_2 1:4) = 0.26.

HRMS (ESI): m/z calculated for [$C_{18}H_{18}O_2N_4Na$] [M+Na^+]: 345.1322, measured: 345.1327.

Diphenylmethanone *O*-(4-phenoxybutanoyl) oxime (S25)



Synthesized by **General Procedure 1** from 4-phenoxybutanoic acid **S6** (399 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.00 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 10:1) and obtained as a colourless gum (661 mg, 1.84 mmol, 92%).

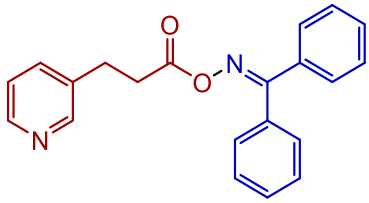
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 – 7.57 (m, 2H), 7.51 – 7.42 (m, 4H), 7.42 – 7.34 (m, 2H), 7.34 – 7.23 (m, 4H), 6.95 (tt, *J* = 7.4, 1.0 Hz, 1H), 6.91 – 6.83 (m, 2H), 3.97 (t, *J* = 6.0 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.11 (tt, *J* = 7.2, 6.0 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 165.1, 158.8, 134.8, 132.6, 131.0, 129.7, 129.5, 129.1, 128.8, 128.5, 128.3, 120.83, 114.5, 66.4, 29.6, 24.5.

R_f (pentane:EtOAc 10:1) = 0.21.

HRMS (ESI): m/z calculated for [$C_{23}H_{21}O_3NNa$] [M+Na^+]: 382.1414, measured: 382.1418.

Diphenylmethanone *O*-(3-(pyridin-3-yl)propanoyl) oxime (S26)



Synthesized by **General Procedure 1** from 3-pyridinpropionic acid (364 mg, 2.4 mmol, 1.2 equiv) and benzophenone oxime (394 mg, 2.00 mmol), but instead of the extractive work-up the crude mixture was loaded on silica for purification. The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 1:4 → 0:1) and obtained as a white crystalline solid (692 mg, 1.79 mmol, 90%).

Note: the extractive work-up was avoided due to the polarity of the product, which could cause a troublesome extraction from the organic layer.

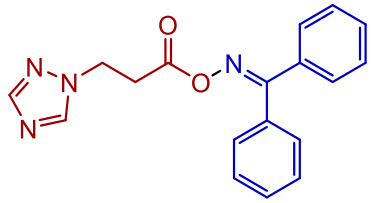
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.46 – 8.41 (m, 1H), 7.62 – 7.55 (m, 2H), 7.54 – 7.41 (m, 5H), 7.41 – 7.33 (m, 2H), 7.30 – 7.24 (m, 2H), 7.21 (ddd, *J* = 7.8, 4.8, 0.9 Hz, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.0, 165.2, 149.9, 148.0, 136.0, 135.6, 134.6, 132.5, 131.1, 129.7, 129.1, 128.7, 128.5, 128.3, 123.4, 34.2, 27.8.

R_f (EtOAc 100%) = 0.30.

HRMS (ESI): m/z calculated for [$C_{21}H_{18}O_2N_2Na$] [M+Na^+]: 353.1260, measured: 353.1266.

Diphenylmethanone *O*-(3-(1H-1,2,4-triazol-1-yl)propanoyl) oxime (S27)



Synthesized by **General Procedure 1** from 1*H*-1,2,4-triazole-1-propanoic acid (423 mg, 3.0 mmol) and benzophenone oxime (592 mg, 3.0 mmol). The compound was purified by flash column chromatography (SiO_2, EtOAc 100%) and obtained as colourless oil (890 mg, 93%).

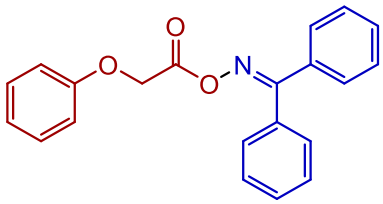
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.90 (s, 1H), 7.58 – 7.50 (m, 2H), 7.45 (qd, *J* = 4.5, 1.4 Hz, 4H), 7.38 – 7.31 (m, 2H), 7.26 – 7.20 (m, 2H), 4.44 (t, *J* = 6.3 Hz, 2H), 2.96 (t, *J* = 6.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 165.6, 152.2, 143.9, 134.3, 132.2, 131.2, 129.9, 129.1, 128.7, 128.5, 128.3, 44.5, 33.0.

R_f (EtOAc 100%) = 0.30.

HRMS (ESI): m/z calculated for [$C_{18}H_{16}O_2N_4Na$] [M+Na^+]: 343.1165, measured: 353.1163.

diphenylmethanone *O*-(2-phenoxyacetyl) oxime (S28)



Synthesized by **General Procedure 1** from phenoxyacetic acid (456 mg, 3.0 mmol, 1.0 equiv) and benzophenone oxime (592 mg, 3.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 10:1) and obtained as a white crystalline solid (910 mg, 2.75 mmol, 91%).

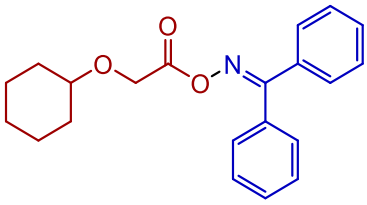
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 – 7.53 (m, 2H), 7.46 – 7.32 (m, 6H), 7.28 – 7.21 (m, 4H), 7.01 – 6.92 (m, 1H), 6.88 – 6.77 (m, 2H), 4.72 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 166.1, 157.8, 134.5, 132.1, 131.3, 130.0, 129.7, 129.3, 129.0, 128.6, 128.4, 121.9, 114.8, 65.0.

R_f (pentane:EtOAc 10:1) = 0.20.

HRMS (ESI): m/z calculated for [$C_{21}H_{17}O_3NNa$] [M+Na^+]: 354.1101, measured: 354.1095.

diphenylmethanone *O*-(2-(cyclohexyloxy)acetyl) oxime (S29)



Synthesized by **General Procedure 1** from 2-(cyclohexyloxy)acetic acid **S5** (635 mg, 4.00 mmol) and benzophenone oxime (656 mg, 3.33 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 7:1) and obtained as a white waxy solid (1.12 g, 3.31 mmol, 99%).

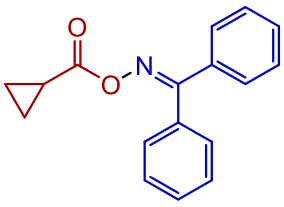
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.55 (m, 2H), 7.51 – 7.43 (m, 4H), 7.42 – 7.35 (m, 2H), 7.35 – 7.27 (m, 2H), 4.22 (s, 2H), 3.38 – 3.19 (m, 1H), 1.94 – 1.77 (m, 2H), 1.77 – 1.62 (m, 2H), 1.62 – 1.43 (m, 1H), 1.35 – 1.08 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.3, 165.5, 134.7, 132.4, 131.1, 129.8, 129.1, 128.9, 128.5, 128.3, 78.6, 64.9, 31.8, 25.7, 24.1.

R_f (pentane:EtOAc 7:1) = 0.35.

HRMS (ESI): m/z calculated for [$C_{21}H_{23}O_3NNa$] [M+Na^+]: 360.1570, measured: 360.1574.

Diphenylmethanone *O*-cyclopropanecarbonyl oxime (S30)



Synthesized by **General Procedure 1** from cyclopropylacetic acid (207 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.00 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 10:1) and obtained as a white waxy solid (469 mg, 1.77 mmol, 89%).

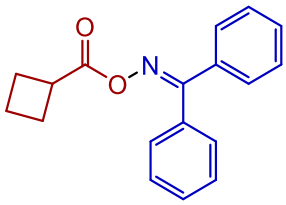
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.55 (m, 2H), 7.54 – 7.41 (m, 4H), 7.41 – 7.24 (m, 4H), 1.59 (tt, *J* = 8.0, 4.6 Hz, 1H), 1.04 (dt, *J* = 4.5, 3.3 Hz, 2H), 0.88 (dt, *J* = 8.2, 3.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.5, 164.6, 134.9, 132.8, 130.9, 129.6, 129.1, 128.9, 128.4, 128.3, 11.7, 9.0.

R_f (pentane:EtOAc 10:1) = 0.25.

HRMS (ESI): m/z calculated for [$C_{17}H_{15}O_2NNa$] [M+Na^+]: 288.0995, measured: 288.1004.

Diphenylmethanone *O*-cyclobutanecarbonyl oxime (S31)



Synthesized by **General Procedure 1** from cyclobutanoic acid (300 mg, 3.0 mmol, 1.0 equiv) and benzophenone oxime (592 mg, 3.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 20:1) and obtained as a white solid (735 mg, 2.64 mmol, 88%).

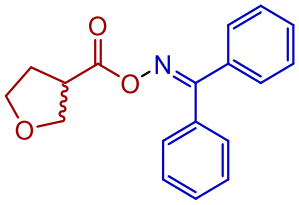
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 – 7.55 (m, 2H), 7.46 – 7.39 (m, 4H), 7.38 – 7.32 (m, 2H), 7.31 – 7.24 (m, 2H), 3.13 (qd, *J* = 8.5, 0.8 Hz, 1H), 2.34 – 2.19 (m, 2H), 2.18 – 2.07 (m, 2H), 1.97 – 1.77 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 173.1, 165.2, 134.9, 132.7, 131.0, 129.7, 129.1, 128.9, 128.5, 128.2, 37.0, 25.3, 18.7.

R_f (pentane:EtOAc 20:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{18}H_{17}NO_2Na$] [M+Na^+]: 302.1151, measured: 302.1167.

(±)-diphenylmethanone *O*-tetrahydrofuran-3-carbonyl oxime (S32)



Synthesized by **General Procedure 1** from (±)-tetrahydrofuran-3-carboxylic acid (288 µL, 3.0 mmol, 1.0 equiv) and benzophenone oxime (592 mg, 3.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 5:1) and obtained as light yellow liquid (753 mg, 2.55 mmol, 85%).

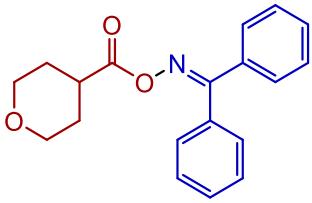
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.55 (m, 2H), 7.51 – 7.41 (m, 4H), 7.40 – 7.32 (m, 2H), 7.31 – 7.25 (m, 2H), 3.90 (t, *J* = 8.4 Hz, 1H), 3.85 – 3.71 (m, 3H), 3.15 – 3.00 (m, 1H), 2.20 – 1.98 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2, 165.9, 134.5, 132.6, 131.2, 129.8, 129.1, 128.7, 128.6, 128.4, 70.1, 68.3, 42.8, 29.4.

R_f (pentane:EtOAc 5:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{18}H_{17}NO_3Na$] [M+Na^+]: 318.1101, measured: 318.1106.

diphenylmethanone *O*-tetrahydro-2*H*-pyran-4-carbonyl oxime (S33)



Synthesized by **General Procedure 1** from tetrahydropyran-4-carboxylic acid (1.3 g, 10.0 mmol, 1.0 equiv) and benzophenone oxime (1.97 g, 10.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 5:1) and obtained as white crystalline solid (2.97 g, 9.60 mmol, 96%).

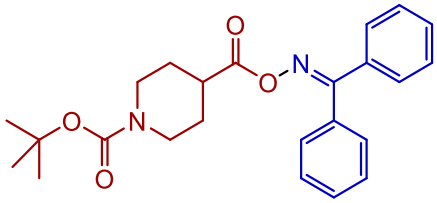
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 – 7.55 (m, 2H), 7.47 – 7.41 (m, 4H), 7.40 – 7.31 (m, 2H), 7.30 – 7.23 (m, 2H), 3.86 (dt, *J* = 10.9, 3.1 Hz, 2H), 3.40 – 3.30 (m, 2H), 2.54 (p, *J* = 8.2, 7.6 Hz, 1H), 1.70 (q, *J* = 6.2, 4.7 Hz, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 165.9, 134.6, 132.7, 131.1, 129.7, 129.1, 128.6, 128.5, 128.3, 67.0, 39.2, 28.4.

R_f (pentane:EtOAc 5:1) = 0.30.

HRMS (ESI): m/z calculated for [$C_{19}H_{19}NO_3Na$] [M+Na^+]: 332.1257, measured: 332.1274.

***tert*-butyl 4-((((diphenylmethylene)amino)oxy)carbonyl)piperidine-1-carboxylate (S34)**



Synthesized by **General Procedure 1** from 1-(*tert*-butoxycarbonyl)piperidine-4-carboxylic acid (348 mg, 3.0 mmol, 1.0 equiv) and benzophenone oxime (592 mg, 3.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 7:1) and obtained as white solid (1.13 g, 2.77 mmol, 92%).

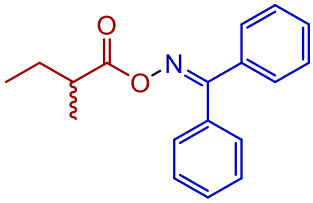
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 – 7.57 (m, 2H), 7.50 – 7.42 (m, 4H), 7.40 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 3.91 (d, *J* = 13.5 Hz, 2H), 2.85 – 2.72 (m, 2H), 2.46 (tt, *J* = 10.7, 4.0 Hz, 1H), 1.80 – 1.71 (m, 2H), 1.66 – 1.54 (m, 2H), 1.44 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 165.9, 154.7, 134.6, 132.7, 131.2, 129.8, 129.1, 128.7, 128.5, 128.4, 79.7, 43.0, 40.2, 28.5, 27.7.

R_f (pentane:EtOAc 7:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{24}H_{28}N_2O_4Na$] [M+Na^+]: 431.1941, measured: 431.1955.

(±)-diphenylmethanone *O*-(2-methylbutanoyl) oxime (S35)



Synthesized by **General Procedure 1** from (±)-2-methylpropionic acid (245 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 15:1) and obtained as a white waxy solid (562 mg, 2.00 mmol, quantitative yield).

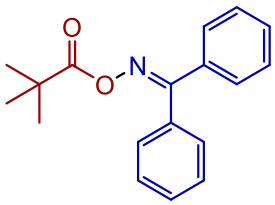
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 – 7.57 (m, 2H), 7.51 – 7.41 (m, 4H), 7.41 – 7.23 (m, 4H), 2.44 – 2.28 (m, 1H), 1.62 (dp, *J* = 13.6, 7.5 Hz, 1H), 1.42 (dqd, *J* = 13.5, 7.4, 6.3 Hz, 1H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 173.9, 165.5, 134.8, 132.9, 131.0, 129.6, 129.1, 128.8, 128.5, 128.2, 40.2, 26.7, 16.6, 11.6.

R_f (pentane:EtOAc 15:1) = 0.26.

HRMS (ESI): m/z calculated for [$C_{18}H_{19}O_2NNa$] [M+Na^+]: 304.1308, measured: 304.1318.

diphenylmethanone *O*-pivaloyl oxime (S36)



Synthesized by **General Procedure 1** from pivalic acid (245 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 13:1) and obtained as a white solid (559 mg, 1.99 mmol, 99%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 – 7.60 (m, 2H), 7.51 – 7.41 (m, 4H), 7.41 – 7.34 (m, 2H), 7.34 – 7.26 (m, 2H), 1.11 (s, 9H).

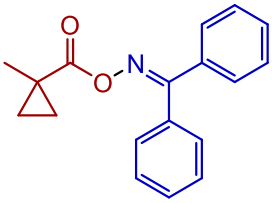
^{13}C NMR (75 MHz, $CDCl_3$): δ 175.3, 165.7, 134.7, 132.9, 131.0, 129.5, 129.1, 128.6, 128.5, 128.2, 38.6, 27.1.

R_f (pentane:EtOAc 13:1) = 0.35.

HRMS (ESI): m/z calculated for [$(C_{18}H_{19}O_2N)_2Na$] [2M+Na^+]: 585.2724, measured: 585.2726.

The experimental data are in accordance to the literature reports.[16]

diphenylmethanone *O*-(1-methylcyclopropane-1-carbonyl) oxime (S37)



Synthesized by **General Procedure 1** from 2-methylcyclopylacetic acid (240 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.00 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 15:1) and obtained as a white solid (498 mg, 1.78 mmol, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 2H), 7.52 – 7.41 (m, 4H), 7.40 – 7.33 (m, 2H), 7.33 – 7.22 (m, 2H), 1.17 – 1.08 (m, 5H)*, 0.66 – 0.61 (m, 2H).

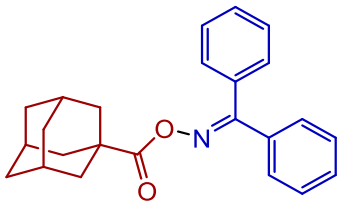
** Overlap between the terminal CH_3 and two protons of the cyclopropyl ring.*

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 165.0, 134.7, 132.9, 131.0, 129.5, 129.1, 128.7, 128.5, 128.2, 19.1, 18.0, 17.2.

R_f (pentane:EtOAc 20:1) = 0.20.

HRMS (ESI): m/z calculated for [$C_{18}H_{18}O_2N$] [M+H^+]: 380.1332, measured: 380.1333.

diphenylmethanone *O*-(adamantane-1-carbonyl) oxime (S38)



Synthesized by **General Procedure 1** from 1-adamantanecarboxylic acid (432 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 10:1) and obtained as a white solid (691 mg, 1.94 mmol, 97%).

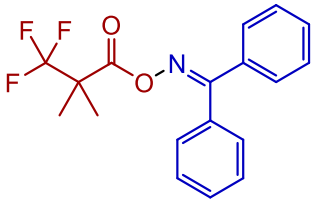
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 – 7.56 (m, 2H), 7.53 – 7.41 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.25 (m, 2H), 2.00 – 1.87 (m, 3H), 1.79 (d, *J* = 2.9 Hz, 6H), 1.73 – 1.53 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.5, 165.7, 134.8, 132.9, 131.0, 129.5, 129.1, 128.8, 128.6, 128.2, 40.6, 38.7, 36.5, 27.9.

R_f (pentane:EtOAc 10:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{24}H_{25}O_2NNa$] [M+Na^+]: 382.1178, measured: 382.1184.

diphenylmethanone *O*-(3,3,3-trifluoro-2,2-dimethylpropanoyl) oxime (S39)



Synthesized by **General Procedure 1** from 3,3,3-trifluoro-2,2-dimethylpropionic acid (375 mg, 2.40 mmol) and benzophenone oxime (394 mg, 2.00 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 20:1) and obtained as a white solid (551 mg, 1.64 mmol, 82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.58 (m, 2H), 7.53 – 7.43 (m, 4H), 7.43 – 7.34 (m, 2H), 7.34 – 7.24 (m, 2H), 1.30 (d, $^4J_{H\text{-}F}$ = 0.8 Hz, 6H).

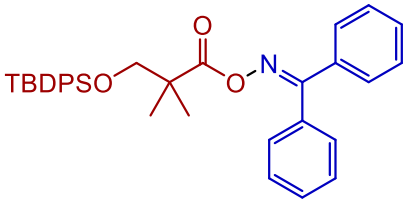
^{13}C NMR (101 MHz, $CDCl_3$): δ 167.5 – 167.3 (m), 167.0, 134.2, 132.5, 131.4, 129.8, 129.2, 128.6, 128.5, 128.3, 126.1 (q, $^1J_{C\text{-}F}$ =283.0 Hz), 48.3 (q, $^2J_{C\text{-}F}$ = 26.9 Hz), 19.6 (q, $^3J_{C\text{-}F}$ = 2.4 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -74.75.

R_f (pentane:EtOAc 10:1) = 0.50.

HRMS (ESI): m/z calculated for [$C_{18}H_{16}O_2NF_3Na$] [M+Na^+]: 358.1025, measured: 358.1043.

diphenylmethanone *O*-(3-((*tert*-butyldiphenylsilyl)oxy)-2,2-dimethylpropanoyl) oxime (S40)



Synthesized by the following two steps procedure:

In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, hydroxypivalic acid (1.18 g, 10.0 mmol, 1.0 equiv), 1H-imidazole (750 mg, 11.0 mmol, 1.1 equiv) and dry CH_2Cl_2 (25 ml) were charged under argon atmosphere, then the solution was cooled to 0°C. *tert*-butyldiphenylsilyl chloride (2.86 ml, 11.0 mmol, 1.1 equiv) was added dropwise, then the reaction was warmed at room temperature and stirred for 60 minutes (*TLC check: EtOAc 100%, R_f starting material: 0.50*). The reaction was quenched by the addition of HCl 2M (30 ml), then the layers were separated. The water layer was extracted once with CH_2Cl_2 (30 ml), then the combined organic layers were washed three times with NaOH 1M (50 ml each time). *Note: upon formation of emulsions, filtration over a short pad of Celite® allows to obtain two layers.* The combined water layers acidified up to pH 2 with HCl 37%. The water phase was extracted three times with CH_2Cl_2 (50 ml each time), then the combined organic layers were dried over

$MgSO_4$ and the solvent was removed under reduced pressure to afford the title product as a colourless gum (1.45 g, 4.07 mmol, 41%).

The crude intermediate (1.03 g, 2.9 mmol) was converted into the product according to **General Procedure 1**, using benzophenone oxime (473 mg, 2.4 mmol). Final compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 17:1 → 15:1) and obtained as a white low-melting solid (934 mg, 1.74 mmol, 73%).

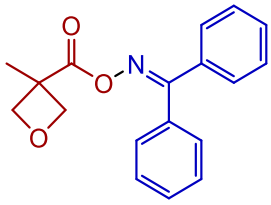
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 – 7.60 (m, 6H), 7.50 – 7.33 (m, 12H), 7.25 – 7.20 (m, 2H), 3.55 (s, 2H), 1.11 (s, 6H), 1.04 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.3, 165.3, 135.8, 134.9, 134.8, 133.5, 132.9, 131.0, 129.7, 129.4, 129.1, 128.7, 128.5, 128.1, 127.82, 127.75, 70.5, 45.0, 26.9, 26.7, 21.9, 19.5.

R_f (pentane:EtOAc 20:1) = 0.15.

HRMS (ESI): m/z calculated for [$C_{34}H_{38}O_3NSi$] [M+H^+]: 536.2615, measured: 536.2612.

diphenylmethanone *O*-(3-methyloxetane-3-carbonyl) oxime (S41)



Synthesized by **General Procedure 1** from 3-methyloxetane-3-carboxylic acid (140 mg, 1.2 mmol, 1.0 equiv) and benzophenone oxime (237 mg, 1.2 mmol, 1.0 equiv.). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 5:1) and obtained as white solid (340 mg, 1.15 mmol, 96%).

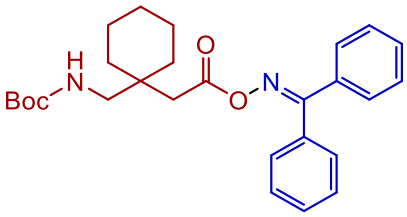
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.59 (m, 2H), 7.50 – 7.43 (m, 4H), 7.38 (td, *J* = 7.1, 6.6, 1.5 Hz, 2H), 7.33 – 7.27 (m, 2H), 4.83 (d, *J* = 6.1 Hz, 2H), 4.29 (d, *J* = 6.1 Hz, 2H), 1.53 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.7, 166.7, 134.3, 132.5, 131.4, 129.9, 129.2, 128.6, 128.6, 128.4, 79.3, 44.2, 21.9.

R_f (pentane:EtOAc 5:1) = 0.30.

HRMS (ESI): m/z calculated for [$C_{18}H_{17}NO_3Na$] [M+Na^+]: 318.1101, measured: 318.1106.

***tert*-butyl ((1-(2-(((diphenylmethylene)amino)oxy)-2-oxoethyl)cyclohexyl)methyl)carbamate (S42)**



Synthesized by **General Procedure 1** from **S4** (905 mg, 3.33 mmol) and benzophenone oxime (657 mg, 3.33 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 20:1 → 9:1) and obtained as a colourless gum (903 mg, 2.00 mmol, 60%).

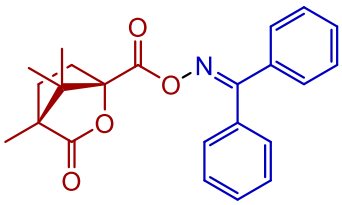
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.55 (m, 2H), 7.50 – 7.41 (m, 4H), 7.40 – 7.32 (m, 2H), 7.32 – 7.25 (m, 2H), 4.40 – 4.47 (m, 1H, *rotamers*), 3.05 (d, *J* = 6.8 Hz, 2H), 2.27 (s, 2H), 1.51 – 1.21 (m, 19H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 165.4, 156.5, 134.5, 133.0, 131.2, 129.7, 129.0, 128.54, 128.53, 128.4, 79.0, 47.3, 39.8, 38.4, 34.0, 28.6, 26.0, 21.5.

R_f (pentane:EtOAc 93:7) = 0.29.

HRMS (ESI): m/z calculated for [$C_{27}H_{34}O_4N_2Na$] [M+Na$^+$]: 473.2411, measured: 473.2407.

(1*S*,4*R*)-1-((((diphenylmethylene)amino)oxy)carbonyl)-4,7,7-trimethyl-2-oxabicyclo[2.2.1]heptan-3-one (S43)



Synthesized by **General Procedure 1** from (-)-camphanic acid (476 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.00 mmol), but instead of the extractive work-up the crude mixture was loaded on silica for purification. The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 6:1) and obtained as a white solid (592 mg, 1.57 mmol, 79%).

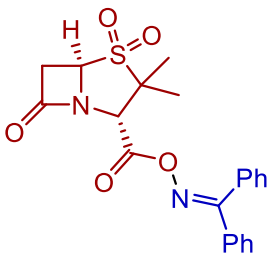
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 – 7.58 (m, 2H), 7.52 – 7.43 (m, 4H), 7.41 – 7.36 (m, 2H), 7.36 – 7.28 (m, 2H), 2.23 (ddd, *J* = 13.5, 10.7, 4.3 Hz, 1H), 1.95 (ddd, *J* = 13.6, 9.3, 4.6 Hz, 1H), 1.88 – 1.74 (m, 1H), 1.61 (ddd, *J* = 13.4, 9.3, 4.3 Hz, 1H), 1.05 (s, 3H), 0.81 (s, 3H), 0.80 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 178.0, 167.2, 164.7, 134.0, 132.4, 131.5, 130.0, 129.2, 128.6, 128.4, 90.7, 54.7, 54.3, 30.6, 28.9, 16.6, 16.5, 9.8.

R_f (pentane:EtOAc 6:1) = 0.27.

HRMS (ESI): m/z calculated for [$C_{23}H_{23}O_4NNa$] [M+Na^+]: 400.1519, measured: 400.1524.

(2S,5R)-2-((((diphenylmethylene)amino)oxy)carbonyl)-3,3-dimethyl-4-thia-1-azabicyclo[3.2.0]heptan-7-one 4,4-dioxide (S44)



Synthesized by **General Procedure 1** from sulbactam (700 mg, 3.0 mmol, 1.0 equiv) and benzophenone oxime (592 mg, 3.0 mmol, 1.0 equiv.). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 5:1) and obtained as colourless gum (829 mg, 2.01 mmol, 67%).

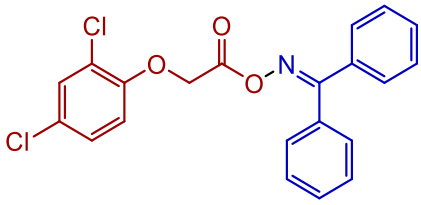
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 – 7.59 (m, 2H), 7.50 (qd, *J* = 5.1, 4.5, 2.1 Hz, 4H), 7.43 – 7.36 (m, 2H), 7.29 (ddd, *J* = 5.2, 2.4, 1.5 Hz, 2H), 4.46 (dd, *J* = 3.9, 2.5 Hz, 1H), 4.33 (s, 1H), 3.41 (t, *J* = 3.1 Hz, 2H), 1.34 (s, 3H), 1.17 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 167.3, 164.2, 133.5, 132.5, 131.8, 130.1, 129.2, 128.8, 128.7, 128.2, 62.7, 62.6, 61.1, 38.5, 20.5, 18.0.

R_f (pentane:EtOAc 5:1) = 0.20.

HRMS (ESI): m/z calculated for [$C_{21}H_{20}N_2O_5SNa$] [M+Na^+]: 435.0985, measured: 435.0991.

diphenylmethanone *O*-(2-(2,4-dichlorophenoxy)acetyl) oxime (S45)



Synthesized by **General Procedure 1** from 2,4-dichlorophenoxy acetic acid (528 mg, 2.4 mmol) and benzophenone oxime (394 mg, 2.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 8:1) and obtained as a white waxy solid (791 mg, 1.98 mmol, 99%).

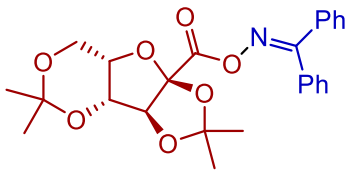
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.54 (m, 2H), 7.50 – 7.33 (m, 7H), 7.26 – 7.20 (m, 2H), 7.10 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 1H), 4.81 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.42, 166.38, 152.4, 134.3, 132.0, 131.4, 130.4, 130.0, 129.2, 128.69, 128.6, 128.4, 127.6, 127.2, 124.3, 66.1.

R_f (pentane:EtOAc 8:1) = 0.19.

HRMS (ESI): m/z calculated for [$C_{21}H_{15}O_3N^{35}Cl_2Na$] [M+Na$^+$]: 422.0321, measured: 422.0317; calculated for [$C_{21}H_{15}O_3N^{35}Cl^{37}ClNa$] [M+Na$^+$]: 424.0293, measured: 424.0299.

diphenylmethanone *O*-((3a*S*,3b*R*,7a*S*,8a*R*)-2,2,5,5-tetramethyltetrahydro-7*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxine-8a-carbonyl) oxime (S46)



Synthesized by **General Procedure 1** from (−)-2,3:4,6-Di-*O*-isopropylidene-2-keto-L-gulonic acid monohydrate (876 mg, 3.0 mmol, 1.0 equiv) and benzophenone oxime (592 mg, 3.0 mmol, 1.0 equiv.). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 5:1) and obtained as colourless gum (762 mg, 1.68 mmol, 56%).

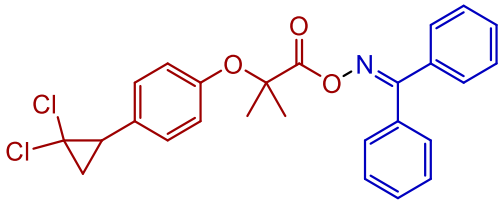
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.57 (m, 2H), 7.49 – 7.41 (m, 6H), 7.37 (td, *J* = 7.1, 6.6, 1.4 Hz, 2H), 4.77 (s, 1H), 4.29 (d, *J* = 2.2 Hz, 1H), 4.14 (q, *J* = 2.1 Hz, 1H), 4.03 (d, *J* = 1.9 Hz, 2H), 1.47 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8, 164.3, 134.8, 132.2, 131.1, 130.1, 129.8, 129.6, 128.5, 128.2, 114.5, 110.2, 97.6, 88.0, 74.2, 72.6, 59.9, 28.8, 27.1, 25.6, 19.0.

R_f (pentane:EtOAc 5:1) = 0.20.

HRMS (ESI): m/z calculated for [$C_{25}H_{27}NO_7Na$] [M+Na$^+$]: 476.1680, measured: 476.1686.

diphenylmethanone *O*-(2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoyl) oxime (S47)



Synthesized by **General Procedure 1** from 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoic acid (553 mg, 1.91 mmol) and benzophenone oxime (359 mg, 1.82 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 10:1) and obtained as a colourless gum (727 mg, 1.55 mmol, 78%).

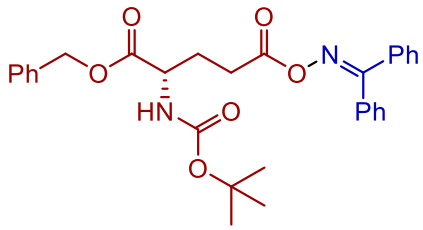
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.56 (m, 2H), 7.49 – 7.41 (m, 1H), 7.41 – 7.28 (m, 5H), 7.16 – 7.04 (m, 4H), 6.83 – 6.74 (m, 2H), 2.84 (dd, *J* = 10.7, 8.3 Hz, 1H), 1.94 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.78 (dd, *J* = 8.3, 7.4 Hz, 1H), 1.50 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.3, 166.6, 154.9, 134.5, 132.3, 131.3, 129.8, 129.7, 129.2, 128.7, 128.5, 128.4, 128.2, 119.0, 79.0, 61.0, 35.0, 26.0, 25.5, 25.4.

R_f (pentane:EtOAc 10:1) = 0.16.

HRMS (ESI): m/z calculated for [$C_{26}H_{23}O_3N^{35}Cl_2Na$] [M+Na$^+$]: 490.0947, measured: 490.0948; calculated for [$C_{26}H_{23}O_3N^{35}Cl^{37}ClNa$] [M+Na$^+$]: 492.0919, measured: 492.0926.

benzyl (*S*)-2-((tert-butoxycarbonyl)amino)-5-(((diphenylmethylene)amino)oxy)-5-oxopentanoate (S48)



Synthesized by **General Procedure 1** from (*S*)-5-(benzyloxy)-4-((*tert*-butoxycarbonyl)amino)-5-oxopentanoic acid (1.01 g, 3.0 mmol, 1.0 equiv) and benzophenone oxime (592 mg, 3.0 mmol, 1.0 equiv.). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 5:1) and obtained as colourless oil (1.13 g, 2.19 mmol, 73%).

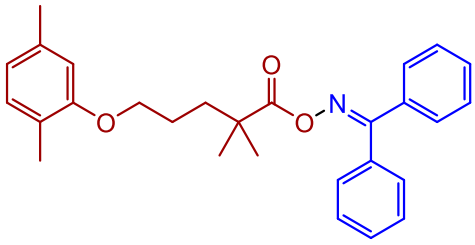
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 – 7.55 (m, 2H), 7.48 – 7.41 (m, 4H), 7.39 – 7.35 (m, 2H), 7.34 (d, *J* = 4.1 Hz, 5H), 7.31 – 7.27 (m, 2H), 5.15 (s, 2H), 5.15 – 5.01 (m, 1H), 4.46 – 4.16 (m, 1H), 2.50 – 2.31 (m, 2H), 2.19 (dt, *J* = 13.4, 7.1 Hz, 1H), 1.97 (dp, *J* = 14.6, 8.4, 7.6 Hz, 1H), 1.42 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9, 170.4, 165.1, 155.4, 135.3, 134.8, 132.6, 131.0, 129.7, 129.1, 128.8, 128.7, 128.5, 128.5, 128.4, 128.3, 80.2, 67.3, 53.1, 29.2, 28.4, 27.6.

R_f (pentane:EtOAc 5:1) = 0.30.

HRMS (ESI): m/z calculated for [$C_{30}H_{32}N_2O_6Na$] [M+Na$^+$]: 539.2153, measured: 539.2160.

diphenylmethanone *O*-(5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl) oxime (S49)



Synthesized by **General Procedure 1** from gemfibrozil (501 mg, 2.0 mmol) and benzophenone oxime (394 mg, 2.0 mmol). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 20:1 → 10:1) and obtained as a white waxy solid (451 mg, 1.02 mmol, 51%).

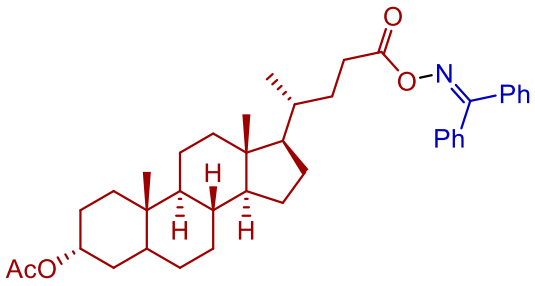
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.50 (m, 2H), 7.40 – 7.33 (m, 4H), 7.32 – 7.26 (m, 2H), 7.25 – 7.19 (m, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 7.4 Hz, 1H), 6.49 (s, 1H), 3.70 (t, *J* = 6.1 Hz, 2H), 2.23 (s, 3H), 2.07 (s, 3H), 1.64 – 1.45 (m, 4H), 1.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.6, 165.8, 157.1, 136.6, 134.6, 133.0, 131.1, 130.4, 129.5, 129.2, 128.53, 128.51, 128.3, 123.7, 120.8, 112.1, 68.0, 42.0, 37.1, 25.17, 25.16, 21.5, 15.9.

R_f (pentane:EtOAc 10:1) = 0.35.

HRMS (ESI): m/z calculated for [$C_{28}H_{32}O_3N$] [M+H^+]: 430.2377, measured: 430.2377.

(3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-5-(((diphenylmethylene)amino)oxy)-5-oxopentan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (S50)



Synthesized by **General Procedure 1** from acetyl protected lithocholic acid (419 mg, 1.0 mmol, 1.0 equiv) and benzophenone oxime (197 mg, 1.0 mmol, 1.0 equiv.). The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 8:1) and obtained as colourless oil (460.3 mg, 0.77 mmol, 77%).

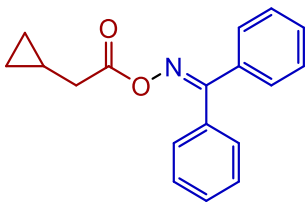
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.48 – 7.43 (m, 4H), 7.39 – 7.34 (m, 2H), 7.33 – 7.30 (m, 2H), 4.71 (td, *J* = 11.2, 5.6 Hz, 1H), 2.35 (td, *J* = 10.0, 4.9 Hz, 1H), 2.23 (ddd, *J* = 15.4, 9.5, 6.7 Hz, 1H), 2.03 (s, 3H), 1.93 (d, *J* = 12.0 Hz, 1H), 1.77 (dddt, *J* = 29.7, 23.3, 19.9, 9.3 Hz, 6H), 1.54 (dd, *J* = 8.7, 4.3 Hz, 2H), 1.46 – 1.33 (m, 7H), 1.28 – 1.22 (m, 3H), 1.19 – 1.09 (m, 2H), 1.08 – 0.98 (m, 5H), 0.92 (s, 3H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.61 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.8, 170.8, 164.9, 134.9, 132.8, 131.0, 129.7, 129.2, 128.9, 128.5, 128.3, 74.5, 56.6, 56.1, 42.9, 42.0, 40.6, 40.3, 35.9, 35.4, 35.2, 34.7, 32.4, 31.0, 30.2, 28.2, 27.2, 26.8, 26.5, 24.3, 23.5, 21.6, 21.0, 18.3, 12.2.

R_f (pentane:EtOAc 8:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{39}H_{52}NO_4$] [M+H^+]: 598.3891, measured: 598.3902.

diphenylmethanone *O*-(2-cyclopropylacetyl) oxime (S51)



Synthesized by **General Procedure 1** from 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoic acid (553 mg, 1.91 mmol) and benzophenone oxime (359 mg, 1.82 mmol).

The compound was purified by flash column chromatography (SiO_2, pentane:EtOAc 10:1) and obtained as a colourless gum (727 mg, 1.55 mmol, 78%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.55 (m, 2H), 7.49 – 7.40 (m, 4H), 7.39 – 7.35 (m, 2H), 7.35 – 7.27 (m, 2H), 2.23 (d, *J* = 7.2 Hz, 2H), 1.02 – 0.90 (m, 1H), 0.51 – 0.42 (m, 2H), 0.08 (dt, *J* = 6.1, 4.7 Hz, 2H).

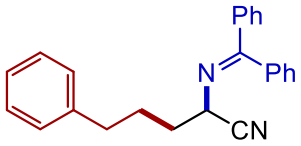
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 165.2, 134.8, 132.8, 131.0, 129.6, 129.1, 128.8, 128.46, 128.3, 38.4, 6.9, 4.6.

R_f (pentane:EtOAc 10:1) = 0.16.

HRMS (ESI): m/z calculated for [$C_{18}H_{17}O_2NNa$] [M+Na^+]: 302.1151, measured: 302.1159.

3.5. Characterization data of products

2-((diphenylmethylene)amino)-5-phenylpentanenitrile (4)



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and acrylonitrile (19.7 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (20:1) as eluent afforded **4** as a colourless oil (71 mg, 0.21 mmol, 70%).

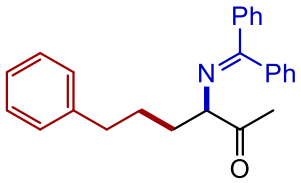
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.59 (m, 2H), 7.48 (dd, *J* = 4.9, 1.8 Hz, 3H), 7.44 – 7.39 (m, 1H), 7.35 – 7.30 (m, 2H), 7.27 – 7.22 (m, 2H), 7.16 (ddd, *J* = 8.2, 5.9, 1.7 Hz, 3H), 7.12 – 7.08 (m, 2H), 4.21 (t, *J* = 6.7 Hz, 1H), 2.58 (t, *J* = 7.4 Hz, 2H), 1.98 – 1.91 (m, 1H), 1.90 – 1.83 (m, 1H), 1.76 (dddd, *J* = 11.8, 7.7, 6.1, 3.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.0, 141.4, 138.6, 135.3, 131.3, 129.4, 129.1, 129.1, 128.5, 128.5, 128.3, 127.5, 126.1, 119.7, 53.0, 35.2, 34.4, 27.2.

R_f (pentane:EtOAc 20:1) = 0.30.

HRMS (ESI): m/z calculated for [$C_{24}H_{22}N_2Na$] [M+Na^+]: 361.1675, measured: 361.1677.

3-((diphenylmethylene)amino)-6-phenylhexan-2-one (5)



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and methyl vinyl ketone (25 μL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (20:1) as eluent afforded **5** as a colourless oil (59.7 mg, 0.168 mmol, 56%).

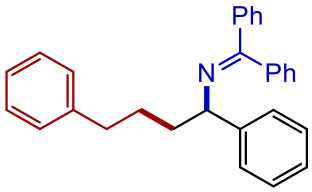
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.63 (m, 2H), 7.46 – 7.38 (m, 4H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 7.06 (dd, *J* = 6.5, 3.0 Hz, 2H), 3.93 (dd, *J* = 7.4, 5.9 Hz, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.23 (s, 3H), 1.87 – 1.78 (m, 2H), 1.62 – 1.52 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 209.8, 169.5, 142.1, 139.6, 136.4, 130.5, 128.8, 128.5, 128.4, 128.3, 127.8, 125.9, 73.2, 35.7, 33.7, 27.7, 27.3.

R_f (pentane:EtOAc 20:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{25}H_{26}NO$] [M+H$^+$]: 356.2009, measured: 356.2031.

***N*-(1,4-diphenylbutyl)-1,1-diphenylmethanimine (6)**



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and styrene (34.5 μL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1) as eluent afforded **6** as a colourless oil (85.3 mg, 0.219 mmol, 73%).

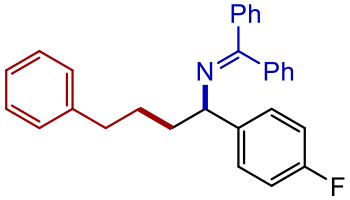
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 – 7.62 (m, 2H), 7.41 – 7.36 (m, 3H), 7.35 – 7.24 (m, 7H), 7.24 – 7.18 (m, 3H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.1 Hz, 2H), 7.04 – 6.99 (m, 2H), 4.35 (dd, *J* = 8.0, 5.4 Hz, 1H), 2.51 (t, *J* = 7.6 Hz, 2H), 2.02 – 1.91 (m, 1H), 1.89 – 1.79 (m, 1H), 1.63 – 1.56 (m, 1H), 1.50 – 1.41 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.7, 145.3, 142.6, 140.2, 137.3, 130.0, 128.7, 128.5, 128.4, 128.4, 128.4, 128.3, 128.1, 128.0, 127.2, 126.7, 125.7, 66.6, 39.3, 35.9, 28.3.

R_f (pentane:EtOAc 40:1) = 0.30.

HRMS (ESI): m/z calculated for [$C_{29}H_{28}N$] [M+H$^+$]: 390.2216, measured: 390.2236.

***N*-(1-(4-fluorophenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (7)**



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and 4-fluorostyrene (36 μL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1) as eluent afforded **7** as a colourless liquid (89.2 mg, 0.219 mmol, 73%).

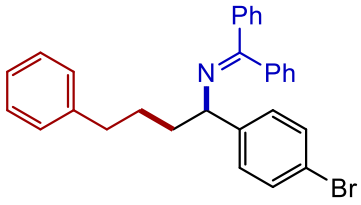
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 – 7.62 (m, 2H), 7.44 – 7.39 (m, 3H), 7.37 – 7.28 (m, 3H), 7.26 – 7.20 (m, 4H), 7.17 – 7.12 (m, 1H), 7.10 – 7.05 (m, 2H), 7.03 – 6.92 (m, 4H), 4.33 (dd, *J* = 7.8, 5.5 Hz, 1H), 2.52 (t, *J* = 7.7 Hz, 2H), 2.00 – 1.87 (m, 1H), 1.86 – 1.75 (m, 1H), 1.63 – 1.54 (m, 1H), 1.50 – 1.38 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8, 163.3, 160.1 (d, *J* = 244.1 Hz), 142.5, 141.0, 141.0 (d, *J* = 3.1 Hz), 140.0, 137.2, 130.2, 130.1, 128.7, 128.6, 128.5 (d, *J* = 6.8 Hz), 128.5, 128.4, 128.4, 128.2, 127.9, 125.8, 115.3, 115.0 (d, *J* = 21.0 Hz), 65.9, 39.3, 35.8, 28.2.

R_f (pentane:EtOAc 40:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{29}H_{27}NF$] [M+H$^+$]: 408.2122, measured: 408.2129.

***N*-(1-(4-bromophenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (8)**



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and 4-bromostyrene (39.9 μL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (39:1) as eluent afforded **8** as a colourless oil (85.7 mg, 0.183 mmol, 61%).

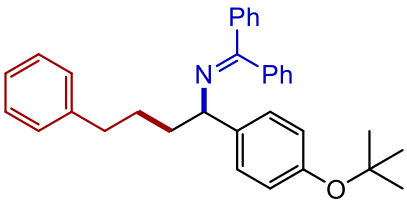
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.61 (m, 2H), 7.42 – 7.37 (m, 5H), 7.35 – 7.28 (m, 3H), 7.24 – 7.21 (m, 2H), 7.16 – 7.12 (m, 3H), 7.07 (d, *J* = 7.1 Hz, 2H), 6.99 (dd, *J* = 6.4, 2.9 Hz, 2H), 4.30 (dd, *J* = 7.8, 5.5 Hz, 1H), 2.51 (t, *J* = 7.7 Hz, 2H), 1.96 – 1.87 (m, 1H), 1.83 – 1.74 (m, 1H), 1.63 – 1.55 (m, 1H), 1.48 – 1.40 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.1, 144.3, 142.4, 139.9, 137.1, 131.5, 130.1, 129.0, 128.7, 128.5, 128.5, 128.4, 128.4, 128.2, 127.8, 125.8, 120.4, 66.0, 39.2, 35.8, 28.2.

R_f (pentane:EtOAc 39:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{29}H_{27}NBr$] [M+H$^+$]: 468.1321, measured: 468.1335.

N-(1-(4-(tert-butoxy)phenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (9)



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and 4-*tert*-butoxystyrene (56.5 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (39:1) as eluent afforded **9** as a colourless oil (78.9 mg, 0.171 mmol, 57%).

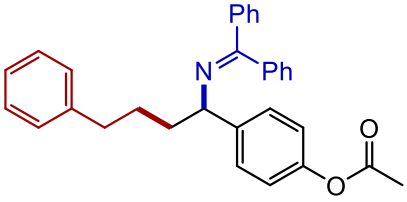
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.39 – 7.35 (m, 3H), 7.32 – 7.27 (m, 3H), 7.23 – 7.17 (m, 2H), 7.16 – 7.09 (m, 3H), 7.08 – 7.04 (m, 2H), 7.03 – 6.97 (m, 2H), 6.90 – 6.84 (m, 2H), 4.30 (dd, *J* = 7.8, 5.5 Hz, 1H), 2.49 (t, *J* = 7.7 Hz, 2H), 2.00 – 1.76 (m, 2H), 1.62 – 1.40 (m, 2H), 1.30 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 154.0, 142.6, 140.2, 140.1, 137.3, 129.9, 129.4, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.5, 125.7, 124.1, 78.3, 66.0, 39.2, 35.8, 29.0, 28.3.

R_f (pentane:EtOAc 39:1) = 0.20.

HRMS (ESI): m/z calculated for [$C_{33}H_{36}NO$] [M+H$^+$]: 462.2791, measured: 462.2808.

4-(1-((diphenylmethylene)amino)-4-phenylbutyl)phenyl acetate (10)



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and 4-acetoxystyrene (46.0 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (19:1) as eluent afforded **10** as a colourless oil (92.6 mg, 0.207 mmol, 69%).

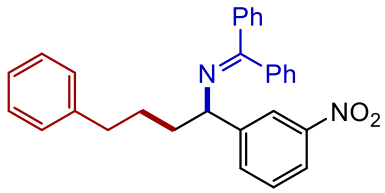
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 – 7.59 (m, 2H), 7.41 – 7.35 (m, 3H), 7.33 – 7.23 (m, 5H), 7.22 – 7.16 (m, 2H), 7.15 – 7.09 (m, 1H), 7.08 – 7.03 (m, 2H), 7.02 – 6.95 (m, 4H), 4.33 (dd, *J* = 7.9, 5.3 Hz, 1H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.24 (s, 3H), 1.99 – 1.85 (m, 1H), 1.85 – 1.73 (m, 1H), 1.63 – 1.53 (m, 1H), 1.50 – 1.36 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 166.8, 149.3, 142.8, 142.4, 140.0, 137.1, 130.0, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1, 127.9, 125.7, 121.3, 66.0, 39.3, 35.8, 28.2, 21.3.

R_f (pentane:EtOAc 19:1) = 0.20.

HRMS (ESI): m/z calculated for [$C_{31}H_{30}NO_2$] [M+H$^+$]: 448.2271, measured: 448.2286.

***N*-(1-(3-nitrophenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (11)**



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and 3-nitrostyrene (42.0 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (19:1) as eluent afforded **11** as a colourless oil (87.3 mg, 0.201 mmol, 67%).

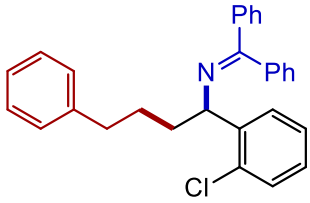
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.13 (m, 1H), 8.08 (ddd, *J* = 8.1, 2.2, 1.0 Hz, 1H), 7.69 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.42 (m, 4H), 7.40 – 7.32 (m, 3H), 7.27 – 7.23 (m, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.0 Hz, 2H), 7.02 (dd, *J* = 6.3, 3.0 Hz, 2H), 4.47 (dd, *J* = 7.8, 5.5 Hz, 1H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.06 – 1.94 (m, 1H), 1.90 – 1.81 (m, 1H), 1.67 – 1.58 (m, 1H), 1.54 – 1.44 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9, 148.5, 147.4, 142.1, 139.6, 136.9, 133.5, 130.4, 129.3, 128.7, 128.7, 128.7, 128.5, 128.4, 128.3, 127.7, 125.9, 122.3, 121.9, 65.9, 39.2, 35.7, 28.0.

R_f (pentane:EtOAc 19:1) = 0.60.

HRMS (ESI): m/z calculated for [$C_{29}H_{27}N_2O_2$] [M+H$^+$]: 435.2067, measured: 435.2072.

***N*-(1-(2-chlorophenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (12)**



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and 2-chlorostyrene (38.0 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (39:1) as eluent afforded **12** as a colourless oil (62.3 mg, 0.147 mmol, 49%).

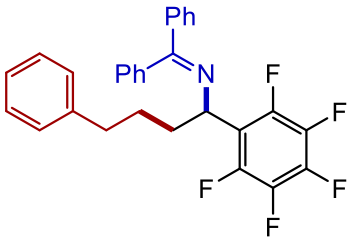
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.38 – 7.35 (m, 3H), 7.34 – 7.28 (m, 3H), 7.23 – 7.19 (m, 4H), 7.13 – 7.07 (m, 4H), 6.95 (dd, *J* = 6.4, 3.0 Hz, 2H), 4.87 (dd, *J* = 7.9, 5.0 Hz, 1H), 2.49 (t, *J* = 7.8 Hz, 2H), 1.93 – 1.78 (m, 2H), 1.66 – 1.58 (m, 1H), 1.52 – 1.46 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 143.2, 142.6, 140.1, 137.2, 132.1, 130.1, 129.5, 129.3, 128.8, 128.5, 128.5, 128.5, 128.3, 128.2, 127.8, 127.6, 127.1, 125.7, 62.1, 38.4, 35.7, 28.1.

R_f (pentane:EtOAc 39:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{29}H_{27}NCl$] [M+H$^+$]: 424.1838, measured: 424.1831.

N-(1-(perfluorophenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (13)



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and 2,3,4,5,6-pentafluorostyrene (58.2 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (39:1) as eluent afforded **13** as a colourless oil (116.5 mg, 0.243 mmol, 81%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.36 – 7.32 (m, 1H), 7.30 – 7.28 (m, 1H), 7.24 (dt, *J* = 5.9, 1.7 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.15 – 7.12 (m, 1H), 7.07 – 7.03 (m, 2H), 7.02 – 6.96 (m, 2H), 4.84 (t, *J* = 7.4 Hz, 1H), 2.54 – 2.47 (m, 2H), 2.02 (q, *J* = 7.7 Hz, 2H), 1.59 – 1.49 (m, 1H), 1.40 (dd, *J* = 14.2, 6.9 Hz, 1H).

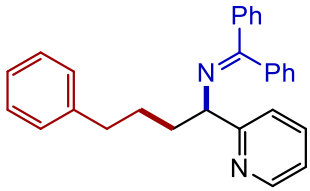
^{13}C NMR (75 MHz, $CDCl_3$): 169.7, 142.0, 139.4, 136.4, 130.6, 130.2, 128.8, 128.5, 128.5, 128.4, 128.2, 127.4, 125.9, 57.5, 35.5, 35.2, 28.4. *(The aromatic carbon signals arising from the pentafluorobenzene moiety are not prominent due to extensive ^{19}F coupling and splitting.)*

^{19}F NMR (282 MHz, $CDCl_3$): δ -140.46 – -140.60 (m), -156.67 (t, $^3J_{F\text{-}F}$ = 21.0 Hz), -162.40 (td, $^3J_{F\text{-}F}$ = 22.2 Hz, $^4J_{F\text{-}F}$ = 7.4 Hz).

R_f (pentane:EtOAc 39:1) = 0.60.

HRMS (ESI): m/z calculated for [$C_{29}H_{23}NF_5$] [M+H$^+$]: 480.1756, measured: 480.1748.

1,1-diphenyl-*N*-(4-phenyl-1-(pyridin-2-yl)butyl)methanimine (14)



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and 2-vinylpyridine (31.5 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (9:1) as eluent afforded **14** as a colourless oil (89.0 mg, 0.228 mmol, 76%).

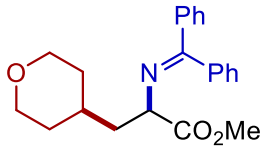
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.62 (td, *J* = 7.7, 1.8 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.30 (m, 6H), 7.22 (ddd, *J* = 7.4, 5.5, 2.0 Hz, 2H), 7.15 – 7.06 (m, 4H), 7.05 – 6.98 (m, 2H), 4.60 (t, *J* = 6.5 Hz, 1H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.05 – 1.95 (m, 2H), 1.68 – 1.48 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 168.0, 164.2, 149.0, 142.6, 140.1, 136.8, 136.6, 130.1, 128.8, 128.6, 128.5, 128.5, 128.3, 128.1, 127.9, 125.7, 121.9, 121.8, 68.1, 38.2, 35.9, 28.1.

R_f (pentane:EtOAc 9:1) = 0.20.

HRMS (ESI): m/z calculated for [$C_{28}H_{27}N_2$] [M+H^+]: 391.2169, measured: 391.2181.

methyl 2-((diphenylmethylene)amino)-3-(tetrahydro-2*H*-pyran-4-yl)propanoate (15)



Synthesized by **General Procedure 2** using oxime ester **S33** (139 mg, 0.45 mmol) and methyl acrylate (27 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (7:1) as eluent afforded **5** as a colourless oil (69.6 mg, 0.198 mmol, 66%).

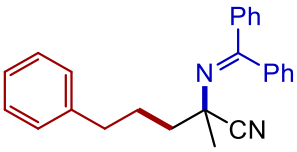
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 – 7.62 (m, 2H), 7.45 (dd, *J* = 4.9, 1.8 Hz, 3H), 7.40 – 7.30 (m, 3H), 7.20 – 7.15 (m, 2H), 4.19 (t, *J* = 6.8 Hz, 1H), 3.90 – 3.79 (m, 2H), 3.73 (s, 3H), 3.34 – 3.18 (m, 2H), 1.86 (t, *J* = 6.7 Hz, 2H), 1.53 – 1.41 (m, 2H), 1.27 – 1.06 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.2, 170.6, 139.5, 136.3, 130.6, 129.0, 129.0, 128.7, 128.2, 127.9, 68.1, 67.9, 62.7, 52.3, 40.9, 33.4, 32.5, 31.6.

R_f (pentane:EtOAc 7:1) = 0.30.

HRMS (ESI): m/z calculated for [$C_{22}H_{26}NO_3$] [M+H^+]: 352.1907, measured: 352.1920.

2-((diphenylmethylene)amino)-2-methyl-5-phenylpentanenitrile (16)



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and methacrylonitrile (25.0 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (19:1) as eluent afforded **16** as a colourless oil (78.3 mg, 0.222 mmol, 74%).

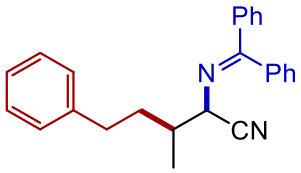
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 – 7.53 (m, 2H), 7.50 – 7.42 (m, 3H), 7.40 – 7.36 (m, 1H), 7.35 – 7.30 (m, 2H), 7.30 – 7.26 (m, 2H), 7.22 – 7.17 (m, 5H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.06 (dd, *J* = 6.1, 3.2 Hz, 1H), 1.97 – 1.82 (m, 3H), 1.63 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): 168.3, 141.8, 140.1, 135.4, 130.7, 130.2, 129.6, 128.7, 128.6, 128.5, 128.3, 128.2, 126.1, 120.6, 57.6, 44.0, 35.6, 29.1, 26.5.

R_f (pentane:EtOAc 19:1) = 0.20.

HRMS (ESI): m/z calculated for [$C_{25}H_{24}N_2Na$] [M+Na^+]: 375.1832, measured: 375.1830.

2-((diphenylmethylene)amino)-3-methyl-5-phenylpentanenitrile (17)



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and 2-butenenitrile (24.4 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (10:1) as eluent afforded **17** as a colourless oil (43.4 mg, 0.123 mmol, 41%) as an inseparable 1:1 mixture of diastereoisomers.

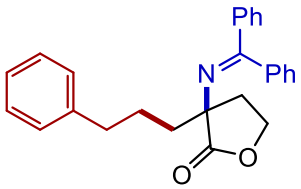
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 4H), 7.53 – 7.48 (m, 7H), 7.36 (dt, *J* = 7.4, 3.7 Hz, 4H), 7.26 (t, *J* = 3.7 Hz, 4H), 7.20 – 7.10 (m, 10H), 4.14 (d, *J* = 5.7 Hz, 1H), 4.11 (d, *J* = 5.2 Hz, 1H), 2.74 – 2.66 (m, 1H), 2.63 – 2.58 (m, 1H), 2.57 – 2.47 (m, 2H), 2.10 – 1.93 (m, 3H), 1.87 – 1.79 (m, 1H), 1.61 – 1.56 (m, 2H), 1.23 (d, *J* = 6.7 Hz, 3H), 1.15 (d, *J* = 6.7 Hz, 3H). *(Mixture of two diastereoisomers in 1:1 ratio).*

^{13}C NMR (101 MHz, $CDCl_3$): 173.3, 173.0, 141.7, 141.7, 138.8, 138.7, 135.5, 135.4, 132.5, 131.3, 130.2, 129.5, 129.4, 129.1, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 127.6, 127.6, 126.1, 126.1, 119.2, 118.9, 58.6, 58.3, 38.0, 37.8, 34.9, 34.2, 33.2, 33.0, 16.3, 15.9. *(Mixture of two diastereoisomers in 1:1 ratio).*

R_f (pentane:EtOAc 10:1) = 0.30.

HRMS (ESI): m/z calculated for [$C_{25}H_{24}N_2Na$] [M+Na^+]: 375.1832, measured: 375.1832.

3-((diphenylmethylene)amino)-3-(3-phenylpropyl)dihydrofuran-2(3*H*)-one (18)



Synthesized by **General Procedure 2** using oxime ester **S4** (140 mg, 0.45 mmol) and 2-butenenitrile (29.4 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (10:1) as eluent afforded **18** as a colourless oil (52.9 mg, 0.138 mmol, 46%).

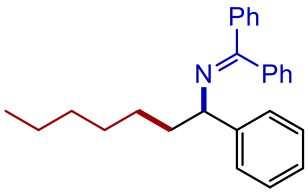
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.44 – 7.33 (m, 4H), 7.36 – 7.27 (m, 4H), 7.27 (d, *J* = 4.1 Hz, 4H), 7.24 – 7.12 (m, 5H), 7.14 – 7.04 (m, 2H), 4.11 – 3.93 (m, 2H), 2.63 (dq, *J* = 15.5, 7.3 Hz, 3H), 2.44 – 2.31 (m, 1H), 2.02 – 1.90 (m, 3H), 1.88 – 1.76 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): 177.9, 168.7, 141.9, 140.5, 137.4, 130.5, 128.9, 128.7, 128.7, 128.5, 128.3, 128.2, 128.1, 126.0, 66.2, 64.7, 38.6, 36.5, 36.0, 25.6.

R_f (pentane:EtOAc 10:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{26}H_{26}NO_2$] [M+Na^+]: 384.1958, measured: 384.1966.

1,1-diphenyl-*N*-(1-phenylheptyl)methanimine (19)



Synthesized by **General Procedure 2** using oxime ester **S19** (131.9 mg, 0.45 mmol) and styrene (34.4 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1) as eluent afforded **19** as a colourless gum (56.5 mg, 0.159 mmol, 53%).

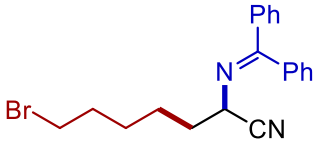
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 – 7.65 (m, 2H), 7.51 – 7.41 (m, 3H), 7.41 – 7.17 (m, 8H), 7.15 – 7.02 (m, 2H), 4.37 (dd, *J* = 8.0, 5.4 Hz, 1H), 2.05 – 1.75 (m, 2H), 1.39 – 1.02 (m, 8H), 0.97 – 0.78 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 145.6, 140.2, 137.4, 129.9, 128.7, 128.40, 128.36, 128.33, 128.1, 128.0, 127.2, 126.6, 66.8, 39.8, 31.9, 29.3, 26.6, 22.8, 14.2.

R_f (pentane 100% + Et_3N) = 0.32.

HRMS (ESI): m/z calculated for [$C_{26}H_{30}O_2N$] [M+H^+]: 356.2373, measured: 356.2382.

7-bromo-2-((diphenylmethylene)amino)heptanenitrile (20)



Synthesized by **General Procedure 2** using oxime ester **S20** (162.1 mg, 0.45 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1 → 35:1 → 30:1) as eluent afforded **20** as a colourless gum (70.3 mg, 0.190 mmol, 63%).

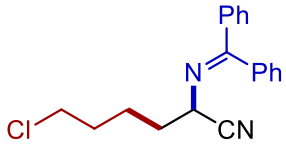
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.61 (m, 2H), 7.57 – 7.48 (m, 3H), 7.48 – 7.41 (m, 1H), 7.36 (tt, *J* = 6.7, 1.4 Hz, 2H), 7.25 – 7.17 (m, 2H), 4.23 (t, *J* = 6.7 Hz, 1H), 3.38 (t, *J* = 6.7 Hz, 1H), 2.03 – 1.78 (m, 4H), 1.57 – 1.34 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.0, 138.5, 135.3, 131.3, 129.5, 129.1, 129.1, 128.3, 127.5, 119.7, 53.0, 34.7, 33.6, 32.5, 27.6, 24.8.

$\mathbf{R_f}$ (pentane:EtOAc 20:1 + Et_3N) = 0.31.

HRMS (ESI): m/z calculated for [$C_{20}H_{21}{}^{79}BrN_2Na$] [M+$Na^+$]: 391.0780, measured: 391.0786; calculated for [$C_{20}H_{21}{}^{81}BrN_2Na$] [M+$Na^+$]: 393.0761, measured: 393.0765.

6-chloro-2-((diphenylmethylene)amino)hexanenitrile (21)



Synthesized by **General Procedure 2** using oxime ester **S21** (135.8 mg, 0.45 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1 → 20:1) as eluent afforded **21** as a light-yellow gum (67.3 mg, 0.217 mmol, 72%).

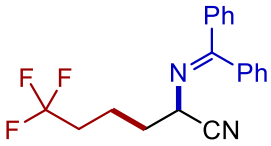
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.58 – 7.49 (m, 3H), 7.49 – 7.43 (m, 1H), 7.37 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.28 – 7.19 (m, 2H), 4.25 (t, *J* = 6.7 Hz, 1H), 3.52 (t, *J* = 6.5 Hz, 2H), 2.05 – 1.86 (m, 2H), 1.78 (dq, *J* = 13.9, 6.7 Hz, 2H), 1.69 – 1.54 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.2, 138.5, 135.3, 131.3, 129.5, 129.2, 129.1, 128.3, 127.5, 119.6, 52.9, 44.5, 34.2, 31.9, 23.1.

$\mathbf{R_f}$ (pentane:EtOAc 10:1 + Et_3N) = 0.36.

HRMS (ESI): m/z calculated for [$C_{19}H_{19}N_2{}^{35}ClNa$] [M+$Na^+$]: 333.1129, measured: 333.1124; calculated for [$C_{19}H_{19}N_2{}^{35}Cl{}^{37}ClNa$] [M+$Na^+$]: 335.1101, measured: 335.1098.

2-((diphenylmethylene)amino)-6,6,6-trifluorohexanenitrile (22)



Synthesized by **General Procedure 2** using oxime ester **S22** (144.6 mg, 0.45 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1 → 30:1) as eluent afforded **22** as a colourless gum 73.4 mg, 0.222 mmol, 74%).

^{1}H NMR (599 MHz, $CDCl_3$): δ 7.68 – 7.64 (m, 2H), 7.57 – 7.51 (m, 3H), 7.46 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.25 – 7.20 (m, 2H), 4.26 (t, *J* = 6.4 Hz, 1H), 2.19 – 2.04 (m, 2H), 2.00 (d, *J* = 7.9 Hz, 1H), 1.97 (d, *J* = 7.9 Hz, 1H), 1.84 – 1.69 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 173.7, 138.3, 135.2, 131.5, 129.6, 129.3, 129.1, 128.4, 127.4, 126.9 (q, $^1J_{F\text{-}C}$ = 276.0 Hz), 119.2, 52.6, 33.9, 33.3 (q, $^2J_{F\text{-}C}$ = 28.9 Hz), 18.4 (q, $^3J_{F\text{-}C}$ = 3.1 Hz).

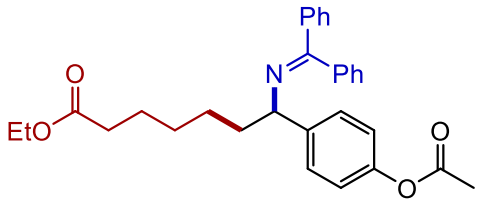
$^{13}C\{^{1}H, ^{19}F\}$ NMR (151 MHz, $CDCl_3$): δ 173.7, 138.3, 135.2, 131.5, 129.6, 129.3, 129.1, 128.4, 127.4, 126.9, 119.2, 52.6, 33.9, 33.3, 18.4.

^{19}F NMR (564 MHz, $CDCl_3$): δ -66.25 (t, $^{3}J_{H\text{-}F}$ = 10.7 Hz).

R_f (pentane:EtOAc 40:1 + Et_3N) = 0.20.

HRMS (ESI): m/z calculated for [$C_{19}H_{17}F_3N_2Na$] [M+Na^+]: 353.1236, measured: 353.1242.

ethyl 7-(4-acetoxyphenyl)-7-((diphenylmethylene)amino)heptanoate (23)



Synthesized by **General Procedure 2** using oxime ester **S23** (159.0 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (25:1 → 20:1 → 17:1 → 12:1) as eluent afforded **23** as a colourless gum (81.2 mg, 0.172 mmol, 57%).

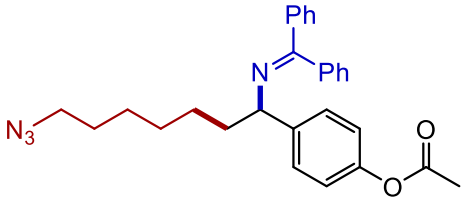
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.54 (m, 2H), 7.39 – 7.18 (m, 8H), 7.00 – 6.94 (m, 2H), 6.94 – 6.88 (m, 2H), 4.24 (dd, *J* = 8.0, 5.3 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.19 (s, 3H), 2.13 (t, *J* = 7.6 Hz, 2H), 1.81 (dddd, *J* = 13.0, 10.2, 8.0, 4.6 Hz, 1H), 1.74 – 1.57 (m, 1H), 1.47 (p, *J* = 7.5 Hz, 2H), 1.19 – 1.10 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.8, 169.6, 166.7, 149.3, 142.8, 140.0, 137.1, 130.4, 130.0 128.6, 128.5, 128.43, 128.38, 128.1, 127.9, 66.0, 60.2, 39.5, 34.4, 29.1, 26.2, 25.0, 21.2, 14.3.

R_f (pentane:EtOAc 10:1 + Et_3N) = 0.28.

HRMS (ESI): m/z calculated for [$C_{30}H_{34}NO_4$] [M+H^+]: 472.2482, measured: 472.2498.

4-(7-azido-1-((diphenylmethylene)amino)heptyl)phenyl acetate (24)



Synthesized by **General Procedure 2** using oxime ester **S24** (145.1 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (30:1 → 25:1 → 20:1) as eluent afforded **24** as a colourless gum (50.5 mg, 0.111 mmol, 37%).

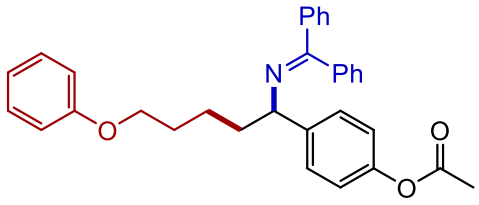
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 – 7.62 (m, 2H), 7.48 – 7.41 (m, 3H), 7.40 – 7.28 (m, 5H), 7.10 – 6.96 (m, 4H), 4.34 (dd, *J* = 7.9, 5.4 Hz, 1H), 3.19 (t, *J* = 6.9 Hz, 2H), 2.29 (s, 3H), 2.00 – 1.85 (m, 1H), 1.84 – 1.70 (m, 1H), 1.61 – 1.46 (m, 2H), 1.38 – 1.07 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 166.8, 149.3, 142.8, 140.0, 137.1, 130.1, 128.6, 128.49, 128.46, 128.14, 128.11, 127.9, 121.4, 66.0, 51.5, 39.5, 28.8, 26.7, 26.0, 21.3.

R_f (pentane:EtOAc 10:1 + Et_3N) = 0.25.

HRMS (ESI): m/z calculated for [$C_{27}H_{29}N_4O_2$] [M+H$^+$]: 441.2285, measured: 441.2270.

4-(1-((diphenylmethylene)amino)-5-phenoxyhexyl)phenyl acetate (25)



Synthesized by **General Procedure 2** oxime ester **S25** (161.7 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (20:1) as eluent afforded **25** as a colourless gum (83.9 mg, 0.176 mmol, 59%).

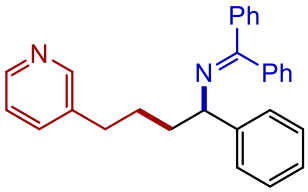
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.64 (m, 2H), 7.48 – 7.42 (m, 3H), 7.42 – 7.33 (m, 5H), 7.32 – 7.26 (m, 2H), 7.12 – 7.07 (m, 2H), 7.08 – 7.02 (m, 2H), 6.95 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.92 – 6.82 (m, 2H), 4.41 (dd, *J* = 8.0, 5.3 Hz, 1H), 3.92 (t, *J* = 6.5 Hz, 2H), 2.32 (s, 3H), 2.02 (dddd, *J* = 13.3, 10.5, 8.1, 5.3 Hz, 1H), 1.88 (ddt, *J* = 13.3, 10.7, 5.5 Hz, 1H), 1.80 – 1.66 (m, 2H), 1.55 – 1.41 (m, 1H), 1.41 – 1.27 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 166.9, 159.2, 149.4, 142.8, 140.0, 137.1, 130.0, 129.5, 128.7, 128.5, 128.4, 128.1, 127.9, 121.4, 120.6, 67.7, 66.0, 39.5, 29.3, 23.1, 21.3.

R_f (pentane:EtOAc 20:1 + Et_3N) = 0.20.

HRMS (ESI): m/z calculated for [$C_{32}H_{32}NO_3$] [M+H$^+$]: 478.2377, measured: 478.2386.

1,1-diphenyl-*N*-(1-phenyl-4-(pyridin-3-yl)butyl)methanimine (26)



Synthesized by **General Procedure 2** using oxime ester **S26** (148.7 mg, 0.45 mmol) and styrene (34.4 µL, 0.30 mmol). Purification by column chromatography using silica prebasified

with Et_3N and pentane/EtOAc (4:1 → 10:3) as eluent afforded **26** as a light-yellow gum (82.8 mg, 0.212 mmol, 71%).

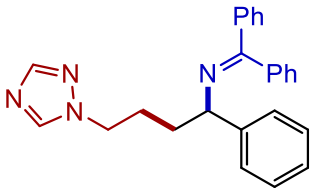
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.41 (d, *J* = 2.3 Hz, 1H), 7.72 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.52 – 7.30 (m, 11H), 7.30 – 7.15 (m, 2H), 7.13 – 6.99 (m, 2H), 4.41 (dd, *J* = 8.0, 5.3 Hz, 1H), 2.56 (t, *J* = 7.7 Hz, 2H), 2.12 – 1.96 (m, 1H), 1.96 – 1.81 (m, 1H), 1.76 – 1.60 (m, 1H), 1.60 – 1.43 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8, 150.0, 147.3, 145.0, 140.0, 137.6, 137.1, 135.8, 130.0, 128.6, 128.43, 128.41, 128.1, 127.8, 127.1, 126.8, 123.3, 66.4, 39.0, 32.9, 27.9.

R_f (pentane:EtOAc 4:1 + Et_3N) = 0.15.

HRMS (ESI): m/z calculated for [$C_{28}H_{27}N_2$] [M+H$^+$]: 391.2169, measured: 391.2211.

1,1-diphenyl-*N*-(1-phenyl-4-(1*H*-1,2,4-triazol-1-yl)butyl)methanimine (27)



Synthesized by **General Procedure 2** using **S27** (128.0 mg, 0.4 mmol) and styrene (34.4 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (1:1 → 1:2) as eluent afforded **27** as a light-yellow oil (70.8 mg, 0.186 mmol, 62%).

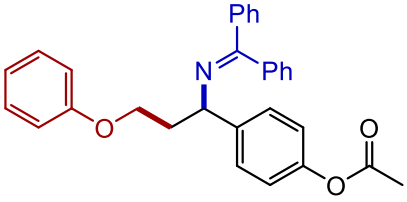
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.0 Hz, 2H), 7.65 (dt, *J* = 6.8, 1.5 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.35 – 7.26 (m, 4H), 7.23 (dd, *J* = 6.6, 1.9 Hz, 4H), 7.02 – 6.96 (m, 2H), 4.35 (dd, *J* = 7.4, 4.8 Hz, 1H), 4.04 (td, *J* = 6.8, 2.5 Hz, 2H), 1.95 – 1.81 (m, 2H), 1.80 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.3, 152.0, 144.4, 142.9, 139.7, 136.9, 130.2, 128.6, 128.5, 128.5, 128.1, 127.7, 127.0, 127.0, 65.8, 49.6, 36.2, 26.8.

R_f (pentane:EtOAc 1:2) = 0.3.

HRMS (ESI): m/z calculated for [$C_{25}H_{25}N_4$] [M+H$^+$]: 381.2074, measured: 381.2090.

4-(1-((diphenylmethylene)amino)-3-phenoxypropyl)phenyl acetate (28)



Synthesized by **General Procedure 2** using **S28** (149.0 mg, 0.45 mmol) and 4-acetoxystyrene (46.0 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with

Et_3N and pentane/EtOAc (10:1) as eluent afforded **28** as a white solid (90.3 mg, 0.201 mmol, 67%).

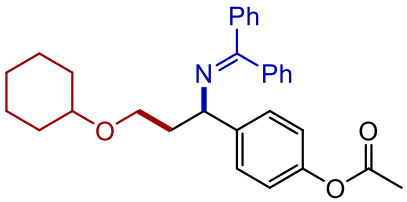
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (dq, *J* = 6.6, 2.2 Hz, 2H), 7.37 – 7.26 (m, 8H), 7.24 – 7.19 (m, 2H), 7.02 – 6.97 (m, 2H), 6.94 – 6.85 (m, 3H), 6.78 – 6.69 (m, 2H), 4.67 (dd, *J* = 8.5, 4.8 Hz, 1H), 3.89 (dd, *J* = 6.8, 5.3 Hz, 2H), 2.44 – 2.30 (m, 1H), 2.27 – 2.20 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 168.0, 158.8, 149.5, 142.2, 139.8, 136.8, 130.2, 129.4, 128.6, 128.4, 128.4, 128.2, 128.1, 127.8, 121.5, 120.6, 114.5, 64.4, 62.3, 38.9, 21.3.

R_f (pentane:EtOAc 9:1) = 0.4.

HRMS (ESI): m/z calculated for [$C_{30}H_{28}NO_3$] [M+H$^+$]: 450.2064, measured: 450.2073.

4-(3-(cyclohexyloxy)-1-((diphenylmethylene)amino)propyl)phenyl acetate (29)



Synthesized by **General Procedure 2** using oxime ester **S29** (151.8 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1 → 25:1 → 15:1) as eluent afforded **29** as a colourless low-melting crystalline solid (89.3 mg, 0.196 mmol, 65%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 – 7.64 (m, 2H), 7.53 – 7.24 (m, 8H), 7.16 – 7.06 (m, 2H), 7.06 – 6.96 (m, 2H), 4.59 (dd, *J* = 8.0, 5.4 Hz, 1H), 3.40 (td, *J* = 6.6, 1.5 Hz, 2H), 3.11 (dt, *J* = 9.4, 4.6 Hz, 1H), 2.30 (s, 3H), 2.26 – 2.15 (m, 1H), 2.15 – 2.01 (m, 1H), 1.94 – 1.43 (m, 5H), 1.37 – 1.07 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 167.2, 149.3, 142.6, 140.1, 136.9, 130.0, 128.7, 128.4, 128.4, 128.2, 128.1, 127.9, 121.3, 77.4, 64.7, 62.8, 39.9, 32.5, 32.2, 25.9, 24.3, 24.2, 21.3.

R_f (pentane:EtOAc 10:1 + Et_3N) = 0.31.

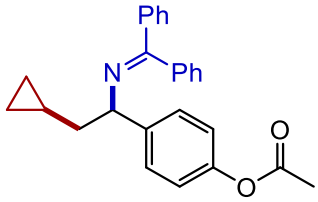
HRMS (ESI): m/z calculated for [$C_{30}H_{34}O_3N$] [M+H$^+$]: 456.2533, measured: 456.2553.

Large scale reaction: In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, substrate **S29** (858 mg, 2.54 mmol, 1.25 equiv) and **[Ir-F]** (11.2 mg, 0.010 mmol, 0.5 mol%) were charged, then the vessel was purged and filled-back with argon four times. Dry EtOAc (20 ml) was added under argon counterflow, followed by 4-acetoxystyrene (311 µL, 2.03 mmol, 1.0 equiv). The vessel was sealed with the screw cap and irradiated under vigorous stirring (1200 rpm) with two 34W blue Kessil® lights (455 nm) for 19 hours. The solvent was evaporated under reduced pressure and the crude was loaded on silica (prebasified with Et_3N). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc

(25:1 → 20:1) as eluent afforded **29** as an off-white waxy solid (526.1 mg, 1.115 mmol, 55% yield).

The experimental data were in accordance with the 0.3 mmol results.

4-(2-cyclopropyl-1-((diphenylmethylene)amino)ethyl)phenyl acetate (30)



Synthesized by **General Procedure 2** using oxime ester **S30** (119.4 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (30:1 → 25:1) as eluent afforded **30** as a colourless gum (52.8 mg, 0.138 mmol, 46%).

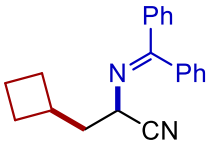
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.50 – 7.41 (m, 3H), 7.41 – 7.30 (m, 5H), 7.17 – 7.07 (m, 2H), 7.07 – 6.97 (m, 2H), 4.50 (dd, *J* = 8.0, 5.4 Hz, 1H), 2.29 (s, 3H), 1.84 (dt, *J* = 13.7, 7.5 Hz, 1H), 1.67 (ddd, *J* = 13.6, 7.0, 5.4 Hz, 1H), 0.72 – 0.47 (m, 1H), 0.48 – 0.22 (m, 2H), 0.07 – -0.04 (m, 1H), -0.04 – -0.15 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 166.5, 149.3, 142.8, 140.1, 137.3, 130.0, 128.6, 128.41, 128.36, 128.2, 128.1, 127.9, 121.3, 66.7, 44.9, 21.3, 8.6, 5.0, 4.5.

R_f (pentane:EtOAc 20:1 + Et_3N) = 0.19.

HRMS (ESI): m/z calculated for [$C_{26}H_{26}O_2N$] [M+H$^+$]: 384.1958, measured: 384.1979.

3-cyclobutyl-2-((diphenylmethylene)amino)propanenitrile (31)



Synthesized by **General Procedure 2** using **S31** (125.6 mg, 0.45 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (39:1) as eluent afforded **31** as a colourless oil (62.3 mg, 0.216 mmol, 72%).

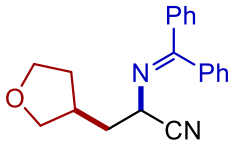
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 – 7.62 (m, 2H), 7.54 – 7.48 (m, 3H), 7.46 – 7.40 (m, 1H), 7.38 – 7.33 (m, 2H), 7.24 – 7.17 (m, 2H), 4.15 (t, *J* = 6.9 Hz, 1H), 2.42 (dt, *J* = 15.7, 7.8 Hz, 1H), 2.11 – 1.92 (m, 4H), 1.89 – 1.72 (m, 2H), 1.64 – 1.48 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 138.6, 135.3, 131.2, 129.4, 129.1, 129.1, 128.3, 127.5, 120.0, 51.8, 41.8, 32.6, 28.2, 18.7.

R_f (pentane:EtOAc 39:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{20}H_{21}N_2$] [M+H^+]: 289.1699, measured: 289.1704.

2-((diphenylmethylene)amino)-3-(tetrahydrofuran-3-yl)propanenitrile (32)



Synthesized by **General Procedure 2** using **S32** (132.0 mg, 0.45 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (17:3) as eluent afforded **32** as a colourless oil (78.5 mg, 0.258 mmol, 86%) as an inseparable 1:1 mixture of diastereoisomers.

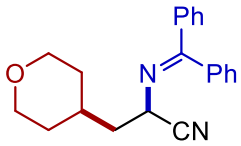
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 – 7.62 (m, 4H), 7.57 – 7.50 (m, 6H), 7.48 – 7.42 (m, 2H), 7.39 – 7.33 (m, 4H), 7.21 (dq, *J* = 6.4, 2.4 Hz, 4H), 4.30 – 4.19 (m, 2H), 3.93 – 3.77 (m, 4H), 3.75 – 3.65 (m, 2H), 3.33 – 3.20 (m, 2H), 2.37 (dp, *J* = 30.0, 7.4 Hz, 2H), 2.09 – 1.93 (m, 6H), 1.54 – 1.34 (m, 2H). *(Mixture of two diastereoisomers in 1:1 ratio).*

^{13}C NMR (75 MHz, $CDCl_3$): δ 173.4, 173.2, 138.3, 138.2, 135.1, 135.1, 131.4, 129.6, 129.6, 129.2, 129.1, 129.1, 128.4, 127.4, 127.3, 119.5, 119.5, 73.0, 72.9, 67.8, 67.7, 52.4, 52.4, 38.5, 38.3, 36.2, 36.0, 32.3, 32.3. *(Mixture of two diastereoisomers in 1:1 ratio).*

R_f (pentane:EtOAc 17:3) = 0.20.

HRMS (ESI): m/z calculated for [$C_{20}H_{20}N_2ONa$] [M+Na^+]: 327.1468, measured: 327.1486.

2-((diphenylmethylene)amino)-3-(tetrahydro-2H-pyran-4-yl)propanenitrile (33)



Synthesized by **General Procedure 2** using **S33** (139.2 mg, 0.45 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (9:1) as eluent afforded **33** as a colourless oil (79.3 mg, 0.249 mmol, 83%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 – 7.62 (m, 2H), 7.56 – 7.49 (m, 3H), 7.48 – 7.42 (m, 1H), 7.39 – 7.33 (m, 2H), 7.24 – 7.17 (m, 2H), 4.32 (t, *J* = 7.1 Hz, 1H), 3.93 – 3.84 (m, 2H), 3.32 (tt, *J* = 11.7, 2.9 Hz, 2H), 2.07 – 1.91 (m, 1H), 1.83 – 1.66 (m, 2H), 1.50 – 1.38 (m, 2H), 1.28 – 1.12 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 173.0, 138.4, 135.1, 131.3, 129.6, 129.1, 129.0, 128.4, 127.4, 119.8, 67.7, 50.6, 41.7, 32.7, 32.6, 31.7.

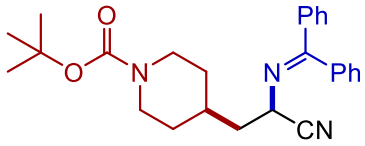
R_f (pentane:EtOAc 9:1) = 0.30.

HRMS (ESI): m/z calculated for [$C_{21}H_{22}N_2ONa$] [M+Na^+]: 341.1624, measured: 341.1643.

Large scale reaction: In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, substrate **S33** (1.7 g, 5.5 mmol, 1.1 equiv.) and **[Ir-F]** (28 mg, 0.025 mmol, 0.5 mol%) were charged, then the vessel was purged and back-filled with argon for four times. Dry EtOAc (50 ml) was added under argon counterflow, followed by acrylonitrile (327 µL, 5.0 mmol, 1.0 equiv). The vessel was sealed with the screw cap and irradiated under vigorous stirring (1000 rpm) with two 34W blue Kessil® lights (455 nm) for 12 hours. The solvent was evaporated under reduced pressure and the crude was loaded on silica (prebasified with Et_3N). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (8:1 → 6:1) as eluent afforded **33** as colorless oil (1.29 g, 4.05 mmol, 81% yield).

The experimental data were in accordance with the 0.3 mmol results.

***tert*-butyl 4-(2-cyano-2-((diphenylmethylene)amino)ethyl)piperidine-1-carboxylate (34)**



Synthesized by **General Procedure 2** using **S34** (183.0 mg, 0.45 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (9:1) as eluent afforded **34** as a colourless oil (78.9 mg, 0.189 mmol, 63%).

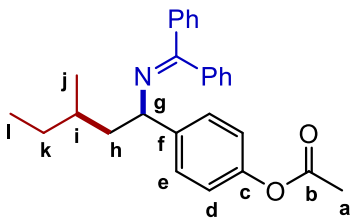
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 – 7.61 (m, 2H), 7.52 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.46 – 7.41 (m, 1H), 7.38 – 7.32 (m, 2H), 7.22 – 7.15 (m, 2H), 4.31 (t, *J* = 7.2 Hz, 1H), 4.01 (d, *J* = 9.9 Hz, 2H), 2.63 (t, *J* = 12.1 Hz, 2H), 2.00 – 1.88 (m, 1H), 1.75 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.60 (ddd, *J* = 10.9, 7.4, 3.9 Hz, 1H), 1.56 – 1.46 (m, 2H), 1.43 (s, 9H), 1.01 (pd, *J* = 12.2, 4.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 173.0, 154.8, 138.3, 135.1, 131.3, 129.6, 129.2, 129.1, 128.4, 127.3, 119.8, 79.5, 50.9, 43.6, 41.4, 32.7, 31.8, 28.5.

R_f (pentane:EtOAc 9:1) = 0.20.

HRMS (ESI): m/z calculated for [$C_{26}H_{31}N_2O_3Na$] [M+Na^+]: 440.2308, measured: 440.2313.

4-(1-((diphenylmethylene)amino)-3-methylpentyl)phenyl acetate (35)



Synthesized by **General Procedure 2** using oxime ester **S35** (126.6 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica

prebasified with Et_3N and pentane/EtOAc (40:1 → 30:1) as eluent afforded **35** an inseparable 1:1 mixture of diastereoisomers as a colourless gum (81.5 mg, 0.204 mmol, 68%).

***Note**: Aromatic protons cannot be assigned to a single diastereoisomer due to overlap, therefore are reported for both diastereoisomers. Carbons (b, c, d, e, f, and belonging to diphenyl moiety) cannot be assigned to the specific diastereoisomer using HSQC and HMBC sequences, due to the insufficient resolution and overlap of the ^1H spectrum, therefore are quoted without distinction:*

^{13}C NMR (151 MHz, $CDCl_3$): δ 169.64 (C_b), 169.63 (C_b), 149.34, 149.25, 143.6, 143.0, 140.2, 140.1, 137.2, 137.1, 129.9, 128.7, 128.6, 128.5, 128.4, 128.34, 128.27, 128.09, 128.05, 128.0, 127.9, 121.34, 121.33, 21.3 (C_a).

R_f (pentane:EtOAc 10:1 + Et_3N) = 0.50.

HRMS (ESI): m/z calculated for [$C_{27}H_{30}O_2N$] [M+H^+]: 400.2271, measured: 400.2284.

Diastereoisomer 1:

^1H NMR (599 MHz, $CDCl_3$): δ 7.69 (ddd, *J* = 8.7, 7.1, 1.5 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.41 – 7.30 (m, 5H), 7.12 – 7.05 (m, 2H), 7.05 – 7.00 (m, 2H), 4.46 (dd, *J* = 9.1, 4.5 Hz, 1H, H_g), 2.30 (s, 3H, H_a), 2.04 (ddd, *J* = 13.4, 8.7, 4.5 Hz, 1H, H_h'), 1.51 (ddd, *J* = 13.4, 8.7, 4.5 Hz, 1H, H_h''), 1.36 – 1.31 (m, 1H, H_i), 1.30 – 1.25 (m, 1H, H_k'), 1.14 (dq, *J* = 13.2, 7.7, 7.1 Hz, 1H, H_k''), 0.84 (t, *J* = 7.3 Hz, 3H, H_l), 0.67 (d, *J* = 6.4 Hz, 3H, H_j).

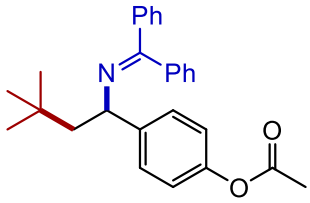
^{13}C NMR (151 MHz, $CDCl_3$): δ 166.3 (C_{imine}), 63.9 (C_g), 46.9 (C_h), 31.3 (C_i), 30.0 (C_k), 19.0 (C_j), 11.3 (C_l).

Diastereoisomer 2:

^1H NMR (599 MHz, $CDCl_3$): δ 7.69 (ddd, *J* = 8.7, 7.1, 1.5 Hz, 2H), 7.47 – 7.41 (m, 3H), 7.41 – 7.30 (m, 5H), 7.12 – 7.05 (m, 2H), 7.05 – 7.00 (m, 2H), 4.47 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.30 (s, 3H), 1.84 (dt, *J* = 13.1, 6.3 Hz, 1H), 1.72 (dt, *J* = 13.9, 7.1 Hz, 1H), 1.29 – 1.18 (m, 2H), 0.97 (qd, *J* = 7.3, 5.6 Hz, 1H), 0.80 – 0.74 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.7 (C_{imine}), 64.4 (C_g), 47.2 (C_h), 31.2 (C_i), 29.2 (C_k), 19.5 (C_j), 11.2 (C_l).

4-(1-((diphenylmethylene)amino)-3,3-dimethylbutyl)phenyl acetate (36)



Synthesized by **General Procedure 2** using oxime ester **S36** (126.6 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1 → 25:1) as eluent afforded **36** as a colourless semi-solid (72.5 mg, 0.182 mmol, 61%).

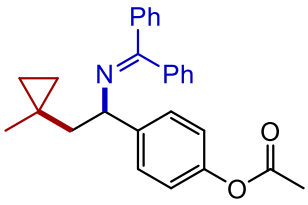
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.64 (m, 2H), 7.49 – 7.40 (m, 3H), 7.40 – 7.31 (m, 3H), 7.31 – 7.23 (m, 2H), 7.09 – 6.98 (m, 4H), 4.53 (dd, *J* = 8.1, 4.0 Hz, 1H), 2.30 (s, 3H), 2.11 (dd, *J* = 14.1, 8.1 Hz, 1H), 1.77 (dd, *J* = 14.1, 4.1 Hz, 1H), 0.83 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.6, 165.7, 149.1, 144.6, 140.2, 137.3, 129.9, 128.7, 128.5, 128.3, 128.1, 128.1, 127.9, 121.3, 64.0, 53.9, 31.1, 30.3, 21.3.

R_f (pentane:EtOAc 10:1 + Et_3N) = 0.50.

HRMS (ESI): m/z calculated for [$C_{27}H_{30}O_2N$] [M+H$^+$]: 400.2271, measured: 400.2281.

4-(1-((diphenylmethylene)amino)-2-(1-methylcyclopropyl)ethyl)phenyl acetate (37)



Synthesized by **General Procedure 2** using oxime ester **S37** (125.7 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (30:1 → 25:1) as eluent afforded **37** as a colourless low-melting crystalline solid (65.7 mg, 0.165 mmol, 55%).

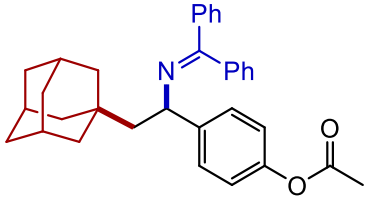
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 – 7.65 (m, 2H), 7.50 – 7.41 (m, 3H), 7.41 – 7.30 (m, 5H), 7.18 – 7.08 (m, 2H), 7.07 – 6.97 (m, 2H), 4.62 (t, *J* = 6.5 Hz, 1H), 2.30 (s, 3H), 1.94 – 1.73 (m, 2H), 0.82 (s, 3H), 0.43 (ddd, *J* = 9.5, 5.8, 3.9 Hz, 1H), 0.21 – 0.11 (m, 1H), 0.10 – -0.01 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 166.0, 149.3, 143.4, 140.1, 137.2, 129.9, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 121.3, 64.8, 49.7, 23.4, 21.3, 13.5, 13.3, 12.7.

R_f (pentane:EtOAc 20:1 + Et_3N) = 0.30.

HRMS (ESI): m/z calculated for [$C_{27}H_{28}O_2N$] [M+H$^+$]: 398.2115, measured: 398.2128.

4-(2-(adamantan-1-yl)-1-((diphenylmethylene)amino)ethyl)phenyl acetate (38)



Synthesized by **General Procedure 2** oxime ester **S38** (161.8 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 μL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1 → 30:1) as eluent afforded **38** as a white foam (91.9 mg, 0.192 mmol, 64%).

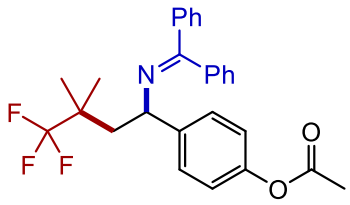
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.45 – 7.37 (m, 3H), 7.37 – 7.28 (m, 3H), 7.27 – 7.20 (m, 2H), 7.07 – 7.01 (m, 2H), 7.01 – 6.95 (m, 2H), 4.56 (dd, *J* = 8.1, 3.8 Hz, 1H), 2.27 (s, 3H), 1.97 (dd, *J* = 14.2, 8.1 Hz, 1H), 1.89 – 1.80 (m, 3H), 1.67 – 1.57 (m, 3H), 1.56 – 1.48 (m, 3H), 1.46 – 1.30 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.6, 165.4, 149.1, 144.9, 140.3, 137.4, 129.8, 128.7, 128.5, 128.3, 128.09, 128.08, 127.9, 62.3, 55.0, 43.1, 37.2, 33.3, 28.8, 21.3.

R_f (pentane:EtOAc 30:1 + Et_3N) = 0.26.

HRMS (ESI): m/z calculated for [$C_{33}H_{36}O_2N$] [M+H$^+$]: 478.2741, measured: 478.2757.

4-(1-((diphenylmethylene)amino)-4,4,4-trifluoro-3,3-dimethylbutyl)phenyl acetate (39)



Synthesized by **General Procedure 2** using oxime ester **S39** (150.9 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 μL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (30:1 → 25:1 → 22:1) as eluent afforded **39** as a colourless gum (92.8 mg, 0.205 mmol, 68%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 – 7.65 (m, 2H), 7.48 – 7.39 (m, 4H), 7.39 – 7.31 (m, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.07 – 7.02 (m, 2H), 7.02 – 6.96 (m, 2H), 4.58 (dd, *J* = 8.6, 3.8 Hz, 1H), 2.38 (dd, *J* = 14.4, 8.6 Hz, 1H), 2.31 (s, 3H), 2.06 (dd, *J* = 14.4, 3.9 Hz, 1H), 1.11 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 169.5, 166.8, 149.5, 143.6, 139.8, 136.9, 130.2, 129.5 (q, $^1J_{F\text{-}C}$ = 282.6 Hz), 128.71, 128.68, 128.4, 128.2, 128.1, 127.7, 121.6, 62.6, 45.2, 40.7 (q, $^2J_{F\text{-}C}$ = 24.1 Hz), 21.7 – 21.5 (m), 21.22, 20.7 – 20.6 (m).

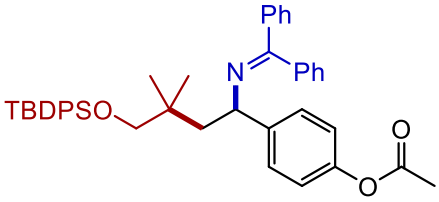
^{13}C{^{1}H, ^{19}F} NMR (126 MHz, $CDCl_3$): δ 169.5, 166.8, 149.5, 143.6, 139.8, 136.9, 130.2, 129.5, 128.71, 128.68, 128.4, 128.2, 128.1, 127.7, 121.6, 62.6, 45.2, 40.7, 21.6, 21.2, 20.7.

^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ -78.91.

R_f (pentane:EtOAc 20:1 + Et_3N) = 0.20.

HRMS (ESI): m/z calculated for [$C_{27}H_{27}O_2NF_3$] [M+H$^+$]: 454.1988, measured: 454.2003.

4-(4-((*tert*-butyldiphenylsilyl)oxy)-1-((diphenylmethylene)amino)-3,3-dimethylbutyl)phenyl acetate (40)



Synthesized by **General Procedure 2** using oxime ester **S40** (241.1 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (30:1 → 25:1) as eluent afforded **40** as a white foam (139.1 mg, 0.213 mmol, 71%).

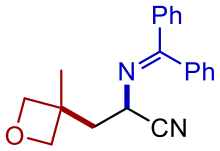
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 – 7.57 (m, 6H), 7.51 – 7.32 (m, 12H), 7.31 – 7.22 (m, 2H), 7.11 – 6.99 (m, 2H), 6.93 (dt, *J* = 6.6, 1.6 Hz, 2H), 4.54 (dd, *J* = 8.5, 3.7 Hz, 1H), 3.33 (d, *J* = 1.4 Hz, 2H), 2.33 (s, 3H), 2.17 (dd, *J* = 14.2, 8.5 Hz, 1H), 1.93 (dd, *J* = 14.1, 3.8 Hz, 1H), 1.09 (s, 9H), 0.91 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 165.9, 149.1, 144.6, 140.0, 137.1, 135.82, 135.77, 134.02, 133.99, 129.9, 129.55, 129.53, 128.7, 128.5, 128.26, 128.04, 128.03, 127.7, 127.6, 121.3, 72.8, 63.4, 49.3, 36.5, 27.07, 25.1, 24.8, 21.3, 19.5.

R_f (pentane:EtOAc 10:1 + Et_3N) = 0.37.

HRMS (ESI): m/z calculated for [$C_{43}H_{48}NO_3Si$] [M+H$^+$]: 654.3398, measured: 654.3408.

2-((diphenylmethylene)amino)-3-(3-methyloxetan-3-yl)propanenitrile (41)



Synthesized by **General Procedure 2** using **S41** (118.0 mg, 0.40 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (7:1) as eluent afforded **41** as a colourless oil (66.6 mg, 0.219 mmol, 73%).

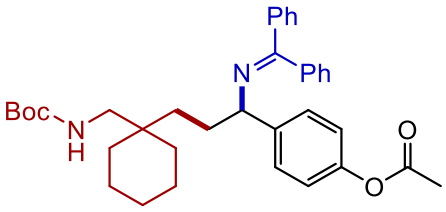
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 – 7.60 (m, 2H), 7.54 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.49 – 7.42 (m, 1H), 7.40 – 7.32 (m, 2H), 7.26 – 7.17 (m, 2H), 4.60 (dd, *J* = 5.8, 3.9 Hz, 2H), 4.35 – 4.25 (m, 2H), 4.21 (d, *J* = 5.9 Hz, 1H), 2.38 (d, *J* = 7.8 Hz, 1H), 2.26 (dd, *J* = 13.9, 6.2 Hz, 1H), 1.24 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 173.5, 138.1, 135.0, 131.5, 129.7, 129.2, 129.0, 128.4, 127.3, 119.5, 82.9, 82.8, 50.0, 42.9, 38.1, 22.9.

R_f (pentane:EtOAc 7:1) = 0.2.

HRMS (ESI): m/z calculated for [$C_{20}H_{20}N_2ONa$] [M+Na^+]: 327.1468, measured: 327.1474.

4-(3-(1-(((tert-butoxycarbonyl)amino)methyl)cyclohexyl)-1-((diphenylmethylene)amino)propyl)phenyl acetate (42)



Synthesized by **General Procedure 2** using oxime ester **S42** (202.8 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (7:1) as eluent afforded **42** as a white foam (114.6 mg, 0.201 mmol, 67%).

***Note**: Due to the presence of rotamers, the ^1H NMR spectrum suffered from signal broadening, while the ^{13}C NMR spectrum showed multiple sets of signals, which were all quoted.*

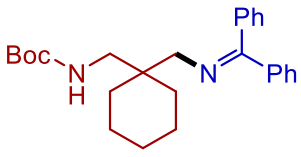
^1H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.73 (m, 2H), 7.57 – 7.49 (m, 3H), 7.49 – 7.37 (m, 5H), 7.20 – 7.05 (m, 4H), 4.59 – 4.44 (m, 1H), 4.36 (dd, *J* = 7.8, 5.2 Hz, 1H), 3.22 – 2.96 (m, 2H), 2.38 (s, 3H), 1.98 – 1.74 (m, 2H), 1.61 – 1.15 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.4, 169.6, 167.5, 167.0, 156.3, 149.5, 149.4, 142.7, 142.0, 139.9, 139.7, 137.2, 136.8, 130.0, 128.7, 128.6, 128.5, 128.4, 128.12, 128.09, 128.07, 127.9, 127.8, 127.7, 121.43, 121.35, 78.9, 66.5, 65.0, 60.3, 46.6, 36.2, 34.5, 33.6, 33.5, 33.1, 32.0, 31.2, 28.5, 26.3, 21.5, 21.3.

R_f (pentane:EtOAc 5:1 + Et_3N) = 0.30.

HRMS (ESI): m/z calculated for [$C_{36}H_{45}N_2O_4$] [M+H^+]: 569.3374, measured: 569.3381.

***tert*-butyl ((1-(((diphenylmethylene)amino)methyl)cyclohexyl)methyl)carbamate (42-SP)**



The reaction byproduct was isolated using an independent reaction, set-up according to **General Procedure 2** using oxime ester **S42** (202.8 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (30:1) as eluent afforded the title compound as a white waxy solid (48.3 mg, 0.119 mmol, 26% from 0.45 mmol).

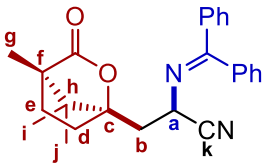
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.55 (m, 2H), 7.51 – 7.42 (m, 3H), 7.40 – 7.36 (m, 1H), 7.36 – 7.30 (m, 2H), 7.14 (dd, *J* = 7.7, 1.7 Hz, 2H), 6.55 (br t, *J* = 5.6 Hz, 1H), 3.32 (d, *J* = 5.6 Hz, 2H), 3.25 (s, 2H), 1.48 (s, 9H), 1.43 – 1.13 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.5, 156.7, 139.7, 136.5, 130.2, 128.7, 128.6, 128.4, 128.3, 127.9, 78.4, 63.1, 48.4, 38.0, 32.6, 28.7, 26.3, 21.6.

R_f (pentane:EtOAc 30:1 + Et_3N) = 0.18.

HRMS (ESI): m/z calculated for [$C_{26}H_{35}N_2O_2$] [M+H^+]: 407.2699, measured: 407.2706.

2-((diphenylmethylene)amino)-3-((1*R*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)propanenitrile (43)



Synthesized by **General Procedure 2** using oxime ester **S43** (169.8 mg, 0.45 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (12:1 → 9:1 → 8:1) as eluent afforded **43** as an inseparable mixture of diastereoisomers (1:1), as an off-white foam (77.7 mg, 0.201 mmol, 67%).

***Note**: Due to the extensive signal overlap for both diastereoisomers, only the signals that can be deconvolved using COSY, HSQC and HMBC are reported to a single diastereoisomers. The other signals are quoted below (integrals consider both diastereoisomers as a single species):*

^{1}H NMR (599 MHz, $CDCl_3$): δ 7.51 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.35 – 7.28 (m, 1H), 7.26 – 7.19 (m, 2H), 7.15 – 7.07 (m, 2H), 4.41 – 4.36 (m, 1H), 2.39 – 2.32 (m, 1H) 0.93 (d, *J* = 4.1 Hz, 3H), 0.74 (d, *J* = 4.5 Hz, 3H), 0.73 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 179.44, 179.36, 174.3, 173.7, 138.6, 138.3, 135.1, 134.8, 131.5, 131.4, 129.8, 129.7, 129.24, 129.18, 129.17, 129.1, 128.4, 128.3, 127.5, 127.2, 52.34, 52.32, 16.6, 16.5, 16.3, 16.2, 10.02, 9.97.

R_f (*pentane*:EtOAc 10:1 + Et_3N) = 0.18.

HRMS (ESI): m/z calculated for [$C_{25}H_{26}N_2O_2Na$] [M+Na^+]: 409.1886, measured: 409.1890.

Diastereoisomer 1

^{1}H NMR (599 MHz, $CDCl_3$): δ 2.08 (dd, *J* = 14.8, 4.3 Hz, 1H), 1.91 (ddd, *J* = 13.7, 10.7, 4.1 Hz, 1H), 1.79 – 1.74 (m, 1H), 1.54 (ddd, *J* = 13.7, 9.2, 4.5 Hz, 1H), 1.44 (ddd, *J* = 13.5, 9.5, 4.2 Hz, 1H).

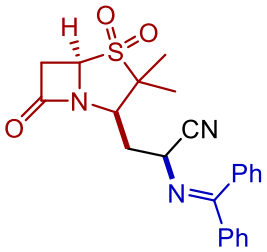
^{13}C NMR (151 MHz, $CDCl_3$) δ 120.0, 91.4, 53.5, 49.2, 35.4, 30.2, 29.0.

Diastereoisomer 2

^{1}H NMR (599 MHz, $CDCl_3$): δ 2.28 (dd, *J* = 14.5, 3.4 Hz, 1H), 1.68 – 1.57 (m, 2H), 1.39 (ddd, *J* = 12.9, 9.2, 4.1 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 119.3, 91.6, 53.7, 49.1, 34.7, 31.0, 29.1.

3-((5*R*)-3,3-dimethyl-4,4-dioxido-7-oxo-4-thia-1-azabicyclo[3.2.0]heptan-2-yl)-2-((diphenylmethylene)amino)propanenitrile (44)



Synthesized by **General Procedure 2** using **S44** (124.0 mg, 0.3 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (4:1→ 2:1) as eluent afforded **44** as a light-yellow oil (45.5 mg, 0.108 mmol, 36%) as an inseparable 1:1 mixture of diastereoisomers.

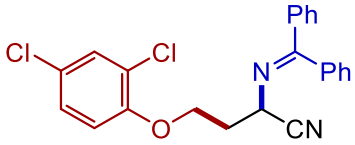
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (ddd, *J* = 6.2, 4.7, 1.4 Hz, 4H), 7.57 – 7.51 (m, 6H), 7.47 (td, *J* = 6.0, 5.2, 2.8 Hz, 2H), 7.37 (td, *J* = 7.4, 1.5 Hz, 4H), 7.24 – 7.16 (m, 4H), 5.57 (s, 2H), 4.40 (t, *J* = 6.5 Hz, 1H), 4.32 (t, *J* = 6.5 Hz, 1H), 4.11 – 4.02 (m, 1H), 4.01 – 3.92 (m, 1H), 3.11 (ddd, *J* = 20.1, 15.1, 5.1 Hz, 2H), 2.68 (dd, *J* = 15.1, 2.1 Hz, 1H), 2.59 (dd, *J* = 15.1, 2.1 Hz, 1H), 2.46 (ddd, *J* = 13.8, 6.1, 3.9 Hz, 1H), 2.34 (ddd, *J* = 13.8, 6.4, 5.0 Hz, 1H), 2.16 – 2.00 (m, 2H), 1.72 (s, 3H), 1.66 (s, 6H), 1.63 (s, 3H). *(Mixture of two diastereoisomers in 1:1 ratio).*

^{13}C NMR (75 MHz, $CDCl_3$): δ 174.0, 173.9, 164.5, 164.3, 138.0, 138.0, 134.9, 134.9, 131.7, 129.9, 129.7, 129.5, 129.4, 129.3, 129.3, 129.2, 129.1, 128.5, 127.3, 127.3, 118.8, 118.8, 116.0, 115.8, 50.7, 50.7, 50.4, 50.3, 43.0, 42.8, 38.5, 22.8, 22.7, 18.8, 18.8. *(Mixture of two diastereoisomers in 1:1 ratio).*

R_f (pentane:EtOAc 2:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{23}H_{23}N_3O_3SNa$] [$M+Na^+$]: 444.1352, measured: 444.1367.

4-(2,4-dichlorophenoxy)-2-((diphenylmethylene)amino)butanenitrile (45)



Synthesized by **General Procedure 2** using oxime ester **S45** (180.1 mg, 0.45 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (30:1 → 20:1) as eluent afforded **45** as a light yellow waxy solid (79.0 mg, 0.193 mmol, 64%).

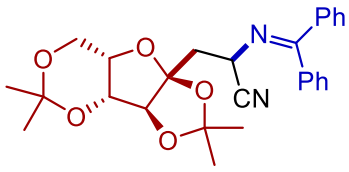
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 – 7.63 (m, 2H), 7.53 – 7.43 (m, 4H), 7.41 – 7.30 (m, 3H), 7.20 – 7.11 (m, 3H), 6.78 (d, *J* = 8.8 Hz, 1H), 4.71 (dd, *J* = 7.7, 6.3 Hz, 1H), 4.24 – 4.02 (m, 2H), 2.62 – 2.37 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 174.6, 152.7, 138.4, 134.9, 131.4, 130.0, 129.5, 129.2, 129.1, 128.4, 127.6, 1273, 126.1, 123.7, 119.3, 113.7, 64.5, 49.5, 34.5.

R_f (pentane:EtOAc 10:1 + Et_3N) = 0.21.

HRMS (ESI): m/z calculated for [$C_{23}H_{18}ON^{35}Cl_2Na$] [M+$Na^+$]: 431.0694, measured: 431.0677.

2-((diphenylmethylene)amino)-3-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)propanenitrile (46)



Synthesized by **General Procedure 2** using **S46** (136.0 mg, 0.3 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (10:1 →7:1) as eluent afforded **46** as a colourless oil (87.4 mg, 0.189 mmol, 63%) as an inseparable 1:1 mixture of diastereoisomers.

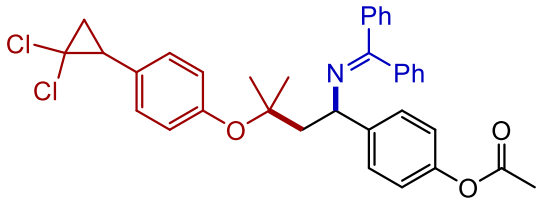
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (ddd, *J* = 7.0, 3.0, 1.6 Hz, 4H), 7.50 – 7.46 (m, 6H), 7.44 – 7.41 (m, 2H), 7.37 – 7.32 (m, 4H), 7.26 – 7.22 (m, 4H), 4.78 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.68 (dd, *J* = 7.8, 5.2 Hz, 1H), 4.40 (s, 1H), 4.30 (s, 1H), 4.26 – 4.21 (m, 2H), 4.04 – 3.89 (m, 5H), 3.84 – 3.78 (m, 1H), 2.88 – 2.79 (m, 2H), 2.50 (dd, *J* = 14.4, 5.3 Hz, 1H), 2.33 (dd, *J* = 14.1, 3.3 Hz, 1H), 1.45 (s, 3H), 1.41 (s, 6H), 1.37 (s, 6H), 1.35 (s, 3H), 1.27 (s, 3H), 1.22 (s, 3H). *(Mixture of two diastereoisomers in 1:1 ratio)*

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.8, 139.0, 138.8, 135.3, 135.1, 132.5, 131.1, 131.1, 130.1, 129.3, 129.2, 129.1, 129.0, 128.9, 128.5, 128.4, 128.4, 128.3, 128.2, 127.7, 127.7, 120.2, 120.0, 113.1, 112.8, 112.2, 111.5, 97.4, 87.0, 85.9, 77.4, 73.5, 73.4, 72.3, 72.3, 60.2, 49.7, 49.6, 42.9, 42.8, 29.1, 28.8, 27.3, 27.3, 26.7, 26.5, 18.8, 18.8. *(Mixture of two diastereoisomers in 1:1 ratio)*

R_f (pentane:EtOAc 7:1) = 0.30.

HRMS (ESI): m/z calculated for [$C_{27}H_{31}N_2O_5$] [M+H^+]: 463.2227, measured: 463.2239.

4-((3-(4-(2,2-dichlorocyclopropyl)phenoxy)-1-((diphenylmethylene)amino)-3-methylbutyl)phenyl acetate (47)



Synthesized by **General Procedure 2** using oxime ester **S47** (210.8 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (20:1 → 15:1 → 10:1) as eluent afforded **47** as a white foam (111.9 mg, 0.191 mmol, 64%).

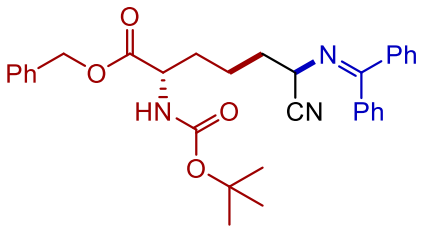
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.63 (m, 2H), 7.47 – 7.31 (m, 6H), 7.30 – 7.21 (m, 2H), 7.12 – 7.06 (m, 2H), 7.06 – 6.98 (m, 4H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.80 (dd, *J* = 8.2, 3.5 Hz, 1H), 2.86 (dd, *J* = 10.7, 8.3 Hz, 1H), 2.55 (dd, *J* = 14.3, 8.2 Hz, 1H), 2.32 – 2.25 (m, 4H), 1.96 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.80 (dd, *J* = 8.4, 7.3 Hz, 1H), 1.27 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.6, 166.5, 155.0, 149.3, 144.0, 140.1, 137.1, 130.0, 129.4, 128.9, 128.9, 128.7, 128.6, 128.3, 128.1, 127.9, 80.4, 62.8, 61.1, 51.9, 35.1, 28.3 (d, *J* = 1.7 Hz), 27.1, 25.9, 21.3.

R_f (pentane:EtOAc 10:1 + Et_3N) = 0.20.

HRMS (ESI): m/z calculated for $[C_{35}H_{34}NO_3{}^{35}Cl_2]$ $[M+H^+]$: 586.1910, measured: 586.1930; calculated for $[C_{35}H_{34}NO_3{}^{35}Cl^{37}Cl]$ $[M+H^+]$: 588.1884, measured: 588.1906.

benzyl (2*S*)-2-((*tert*-butoxycarbonyl)amino)-6-cyano-6-((diphenylmethylene)amino)hexanoate (48)



Synthesized by **General Procedure 2** using **S48** (155 mg, 0.3 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (18:1 → 9:1) as eluent afforded **48** as a colourless gum as an inseparable mixture of two diastereomers in 1:1 ratio (110.4 mg, 0.210 mmol, 70%).

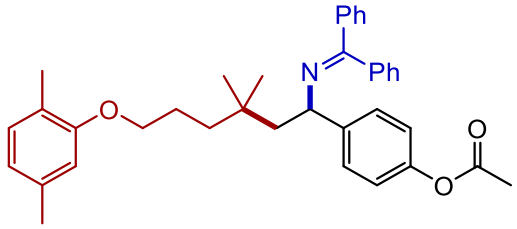
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.61 (m, 2H), 7.53 – 7.47 (m, 3H), 7.46 – 7.42 (m, 1H), 7.37 – 7.29 (m, 7H), 7.18 (ddd, *J* = 7.0, 5.4, 2.4 Hz, 2H), 5.15 (d, *J* = 4.7 Hz, 2H), 5.06 (d, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 5.1 Hz, 1H), 4.18 (q, *J* = 6.5 Hz, 1H), 2.02 – 1.85 (m, 2H), 1.80 (d, *J* = 5.5 Hz, 1H), 1.67 – 1.58 (m, 1H), 1.53 – 1.45 (m, 2H), 1.41 (d, *J* = 14.9 Hz, 9H). *(Mixture of two diastereoisomers in 1:1 ratio)*

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.2, 172.4, 155.4, 138.4, 138.4, 135.3, 135.3, 135.2, 131.3, 129.4, 129.1, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 127.4, 119.4, 80.0, 77.4, 67.2, 53.2, 52.9, 52.7, 34.5, 34.3, 32.3, 32.2, 28.4, 28.3, 21.6, 21.5. (*Mixture of two diastereoisomers in 1:1 ratio. Some of the peaks from two isomers could not be distinguished.)*

R_f (pentane:EtOAc 9:1) = 0.20.

HRMS (ESI): m/z calculated for [$C_{32}H_{35}O_4N_3Na$] [M+Na^+]: 548.2520, measured: 548.2524.

4-(6-(2,5-dimethylphenoxy)-1-((diphenylmethylene)amino)-3,3-dimethylhexyl)phenyl acetate (49)



Synthesized by **General Procedure 2** using oxime ester **S49** (193.3 mg, 0.45 mmol) and 4-acetoxystyrene (45.9 μL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1 → 30:1 → 20:1) as eluent afforded **49** as a colourless gum (107.6 mg, 0.196 mmol, 65%).

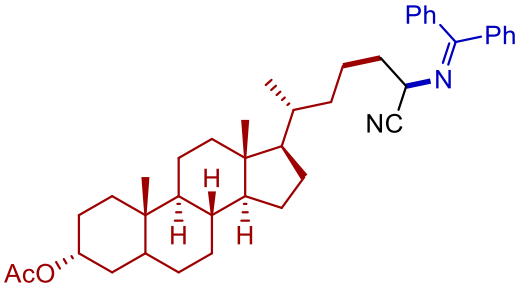
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.65 (m, 2H), 7.48 – 7.24 (m, 8H), 7.11 – 6.96 (m, 5H), 6.70 (d, *J* = 7.4 Hz, 1H), 6.58 (s, 1H), 4.56 (dd, *J* = 8.2, 3.9 Hz, 1H), 3.78 (td, *J* = 6.6, 2.4 Hz, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 2.24 – 2.14 (m, 4H), 1.87 – 1.77 (m, 2H), 1.77 – 1.65 (m, 1H), 1.38 – 1.20 (m, 2H), 0.87 (s, 3H), 0.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.6, 165.8, 157.2, 149.2, 144.6, 140.0, 137.2, 136.4, 130.3, 129.9, 128.6, 128.5, 128.3, 128.1, 127.8, 123.7, 121.4, 120.6, 112.1, 68.7, 63.6, 51.4, 38.8, 33.4, 28.24, 28.17, 24.3, 21.5, 21.3, 15.9.

R_f (pentane:EtOAc 20:1 + Et_3N) = 0.24.

HRMS (ESI): m/z calculated for [$C_{37}H_{42}O_3N$] [M+H^+]: 548.3159, measured: 548.3170.

(3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((2*R*)-6-cyano-6-((diphenylmethylene)amino)hexan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (50)



Synthesized by **General Procedure 2** using **S50** (179 mg, 0.3 mmol) and acrylonitrile (19.6 µL, 0.30 mmol). Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (10:1) as eluent afforded **50** as a colourless oil (120.1 mg, 0.198 mmol, 66%).

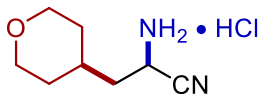
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 – 7.61 (m, 2H), 7.51 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.46 – 7.41 (m, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.21 (dd, *J* = 6.5, 2.8 Hz, 2H), 4.72 (dt, *J* = 11.3, 6.4 Hz, 1H), 4.21 (td, *J* = 6.8, 4.1 Hz, 1H), 2.02 (s, 3H), 1.97 – 1.67 (m, 8H), 1.40 (ddd, *J* = 38.9, 29.3, 22.8 Hz, 15H), 1.17 – 0.99 (m, 7H), 0.92 (s, 3H), 0.87 (d, *J* = 6.3 Hz, 3H), 0.62 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.8, 172.7, 170.7, 138.6, 135.4, 131.2, 129.4, 129.1, 128.3, 127.5, 127.5, 119.9, 119.9, 74.5, 56.6, 56.4, 56.3, 53.2, 53.2, 42.8, 42.0, 40.5, 40.2, 35.9, 35.6, 35.6, 35.4, 35.3, 35.2, 35.2, 35.1, 34.7, 32.3, 28.4, 27.1, 26.7, 26.4, 24.3, 23.4, 22.3, 22.3, 21.6, 20.9, 18.6, 18.6, 12.1.

R_f (pentane:EtOAc 10:1) = 0.40.

HRMS (ESI): m/z calculated for [$C_{41}H_{55}O_2N_2$] [M+H$^+$]: 607.4258, measured: 607.4255.

2-amino-3-(tetrahydro-2*H*-pyran-4-yl)propanenitrile hydrochloride (51)



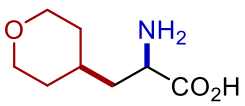
In a vial containing magnetic stir-bar, 2-((diphenylmethylene)amino)-3-(tetrahydro-2*H*-pyran-4-yl)propanenitrile (**33**, 159.2 mg, 0.5 mmol) was dissolved in 5 mL MeOH and at room temperature. 0.75 mL of 1.0 M aq. HCl solution (1.5 equiv., 0.75 mmol) was added dropwise under air. This solution was stirred at room temperature for 1 hour. Next, 5 mL diethyl ether and 5 mL water were added for extraction. The aqueous layer was again extracted twice with 2 mL of diethyl ether each time. Combined organic layers were extracted with additional 2 mL of water. Subsequently, both aqueous layers were combined, and water was removed at reduced pressure. Further drying under vacuum provided pure ammonium chloride salt **51** as white powder (84.8 mg, 0.445 mmol, 89%).

^{1}H NMR (300 MHz, D_2O): δ 4.68 – 4.62 (m, 1H), 4.03 (dd, *J* = 11.5, 3.6 Hz, 2H), 3.54 (tdd, *J* = 11.9, 4.0, 2.1 Hz, 2H), 2.19 – 2.05 (m, 1H), 2.02 – 1.88 (m, 2H), 1.79 (d, *J* = 13.3 Hz, 2H), 1.42 (dtt, *J* = 18.5, 13.1, 6.7 Hz, 2H). *(peak for NH_2 proton is buried inside residual H_2O peak in D_2O).*

^{13}C NMR (75 MHz, D_2O): δ 116.1, 67.4, 67.3, 39.5, 36.8, 31.8, 31.1, 30.8.

HRMS (ESI): m/z calculated for [$C_8H_{15}ON_2$] [M+H$^+$]: 155.1179, measured: 155.1174.

2-amino-3-(tetrahydro-2*H*-pyran-4-yl)propanoic acid (52)



A Schlenk tube containing magnetic stir-bar was charged with 2-((diphenylmethylene)amino)-3-(tetrahydro-2*H*-pyran-4-yl)propanenitrile (**33**, 95.5 mg, 0.3 mmol). 2 mL of 6 (N) aq. HCl solution was added dropwise under air. This solution was stirred at 100 °C for 12 hour. Next, 5 mL diethyl ether and 5 mL water were added for extraction. The aqueous layer was again extracted twice with 3 mL of diethyl ether each time. Combined organic layers were extracted with additional 2 mL of water. Subsequently, both aqueous layers were combined and the pH was maintained at 7-8 using 10% aq. NH_4OH solution. The water was removed at reduced pressure. Finally the crude white solid was purified by column chromatography using silica with CH_2Cl_2/MeOH (1:2) as eluent affording **52** as white powder (42.0 mg, 0.243 mmol, 81%).

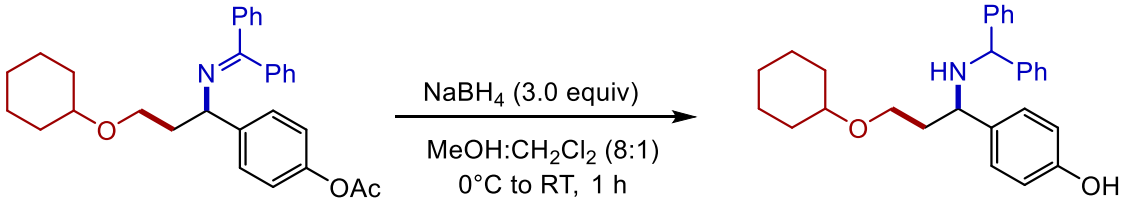
^{1}H NMR (300 MHz, D_2O): δ 4.02 (dt, *J* = 9.7, 4.1 Hz, 2H), 3.81 (t, *J* = 6.6 Hz, 1H), 3.60 – 3.47 (m, 2H), 1.82 (dt, *J* = 25.5, 10.7 Hz, 5H), 1.44 – 1.31 (m, 2H). *(Peaks for NH_2 and CO_2H protons were not visible due to exchange in D_2O).*

^{13}C NMR (75 MHz, D_2O): δ 175.2, 67.5, 67.5, 52.4, 37.7, 32.1, 31.6, 30.5.

R_f (CH_2Cl_2:MeOH 1:1) = 0.35.

HRMS (ESI): m/z calculated for [$C_8H_{16}NO_3$] [M+H$^+$]: 174.1125, measured: 174.1123.

4-(1-(benzhydrylamino)-3-(cyclohexyloxy)propyl)phenol (53)



In a Schlenk tube equipped with a PTFE-coated stirring bar, **29** (110 mg, 0.24 mmol, 1.0 equiv) was dissolved in MeOH:CH_2Cl_2 8:1 (1.3 ml), then the solution was cooled to 0°C. $NaBH_4$ (27.4 mg, 0.72 mmol, 3.0 equiv) was added portionwise, then the reaction was warmed to room temperature and stirred for 1 hour. The solvent was removed under reduced pressure, then the crude was absorbed on silica prebasified with Et_3N and purified by flash column chromatography (SiO_2 prebasified with Et_3N, pentane:EtOAc 7:3), affording the **53** as a white foam (65.2 mg, 0.142 mmol, 59%).

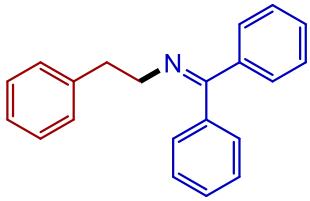
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.26 (m, 4H), 7.26 – 7.17 (m, 5H), 7.15 – 7.09 (m, 1H), 7.03 – 6.96 (m, 2H), 6.74 – 6.64 (m, 2H), 4.57 (s, 1H), 4.40 – 3.80 (br, 1H), 3.58 (dd, *J* = 7.6, 6.0 Hz, 1H), 3.46 (qt, *J* = 9.5, 6.3 Hz, 2H), 3.24 – 3.10 (m, 1H), 2.05 – 1.95 (m, 1H), 1.91 – 1.75 (m, 3H), 1.75 – 1.61 (m, 2H), 1.57 – 1.44 (m, 1H), 1.29 – 1.08 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.0, 144.9, 143.5, 135.7, 128.5, 128.5, 128.4, 127.9, 127.4, 127.0, 126.9, 115.5, 78.0, 65.9, 63.5, 57.5, 38.5, 32.5, 32.3, 25.9, 24.38, 24.36.

R_f (pentane:EtOAc 1:1 + Et_3N) = 0.32.

HRMS (ESI): m/z calculated for [$C_{28}H_{34}NO_2$] [M+H$^+$]: 416.2590, measured: 416.2597.

***N*-phenethyl-1,1-diphenylmethanimine (54):**



Synthesized by **General Procedure 3** using oxime ester **S4** (98.8 mg, 0.3 mmol) and **[Ir-F]** (1.8 mg, 0.5 mol%) in absence of any alkenes. Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1 → 20:1) as eluent afforded **54** as a colourless oil (45.4 mg, 0.159 mmol, 53%).

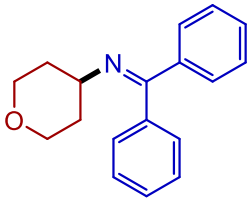
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.55 (m, 2H), 7.38 – 7.33 (m, 4H), 7.32 – 7.29 (m, 2H), 7.21 (ddd, *J* = 7.5, 5.8, 1.2 Hz, 2H), 7.16 – 7.10 (m, 3H), 6.98 – 6.90 (m, 2H), 3.63 (t, *J* = 7.4 Hz, 2H), 2.99 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 140.5, 140.0, 136.9, 130.0, 129.2, 128.5, 128.5, 128.4, 128.3, 128.2, 127.8, 126.0, 55.7, 37.8.

R_f (pentane:EtOAc 20:1) = 0.3.

HRMS (ESI): m/z calculated for [$C_{21}H_{20}N$] [M+H$^+$]: 286.1590, measured: 286.1627.

1,1-diphenyl-*N*-(tetrahydro-2*H*-pyran-4-yl)methanimine (55):



Synthesized by **General Procedure 3** using oxime ester **S33** (92.8 mg, 0.3 mmol) and **[Ir-F]** (1.8 mg, 0.5 mol%) in absence of any alkenes. Purification by column chromatography using silica prebasified with Et_3N and pentane/EtOAc (40:1 → 20:1) as eluent afforded **55** as a white solid (52.5 mg, 0.198 mmol, 66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dq, *J* = 6.5, 2.3 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.38 – 7.28 (m, 3H), 7.20 – 7.11 (m, 2H), 4.01 (dt, *J* = 11.5, 3.9 Hz, 2H), 3.49 (tt, *J* = 9.3, 4.3 Hz, 1H), 3.37 (td, *J* = 11.3, 2.5 Hz, 2H), 1.98 – 1.84 (m, 2H), 1.63 – 1.53 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 140.1, 137.2, 130.0, 128.7, 128.5, 128.4, 128.2, 127.7, 66.1, 58.0, 33.9.

R_f (pentane:EtOAc 20:1) = 0.3.

HRMS (ESI): m/z calculated for [$C_{28}H_{20}NO$] [M+H$^+$]: 266.1539, measured: 266.1551.

4. References

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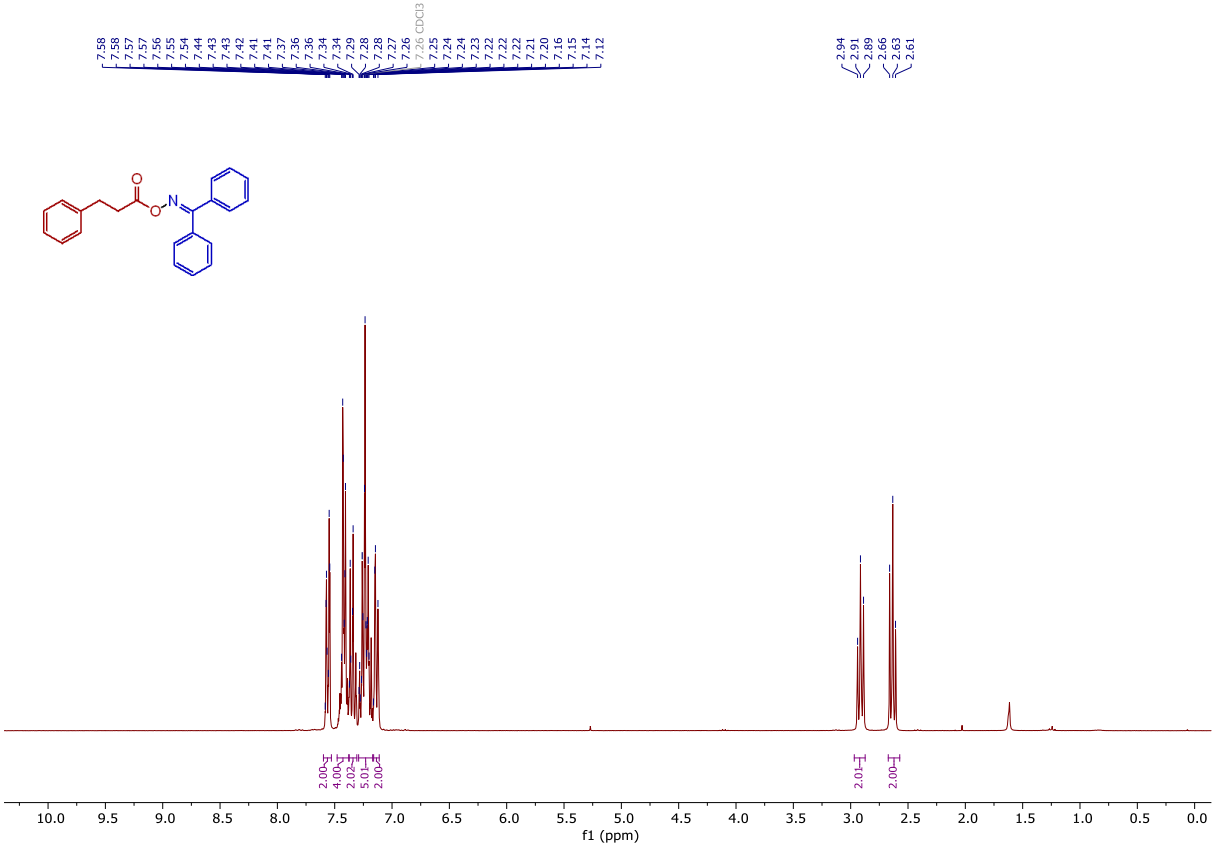
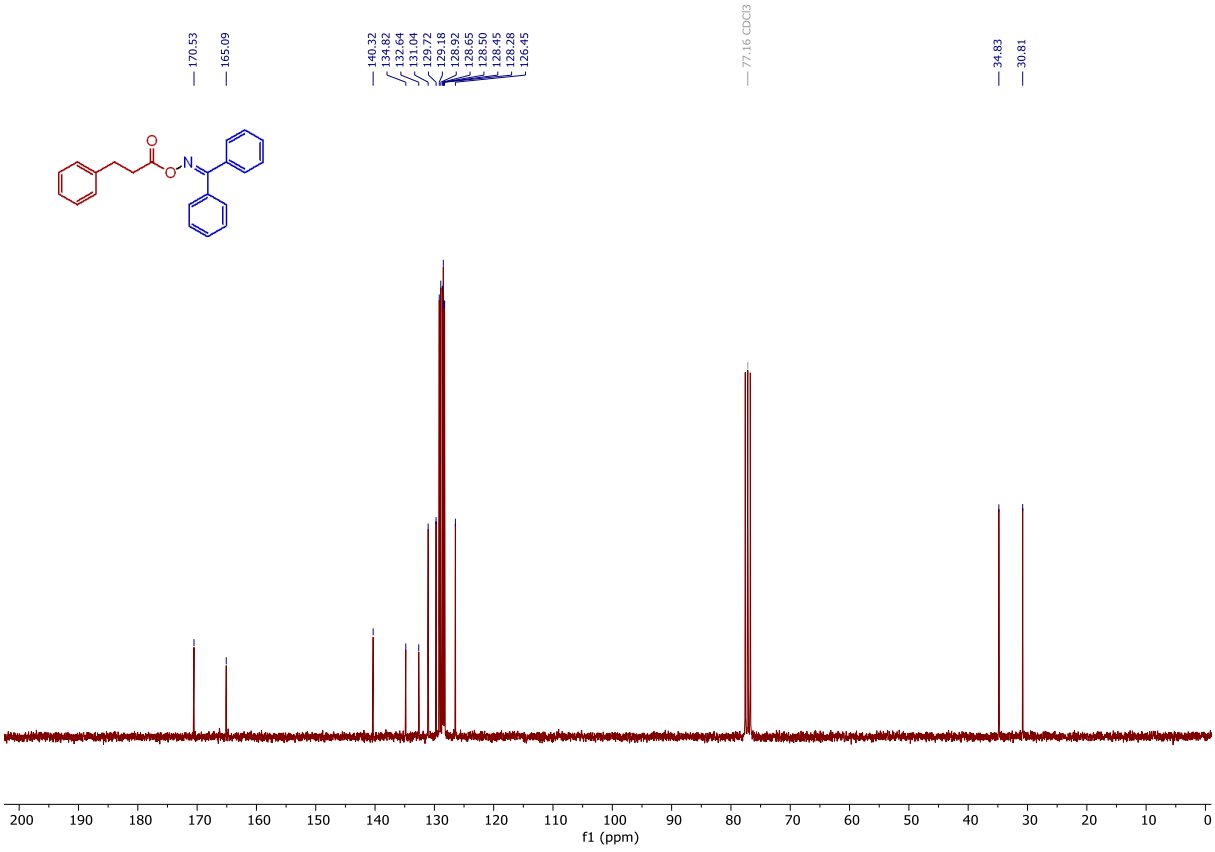
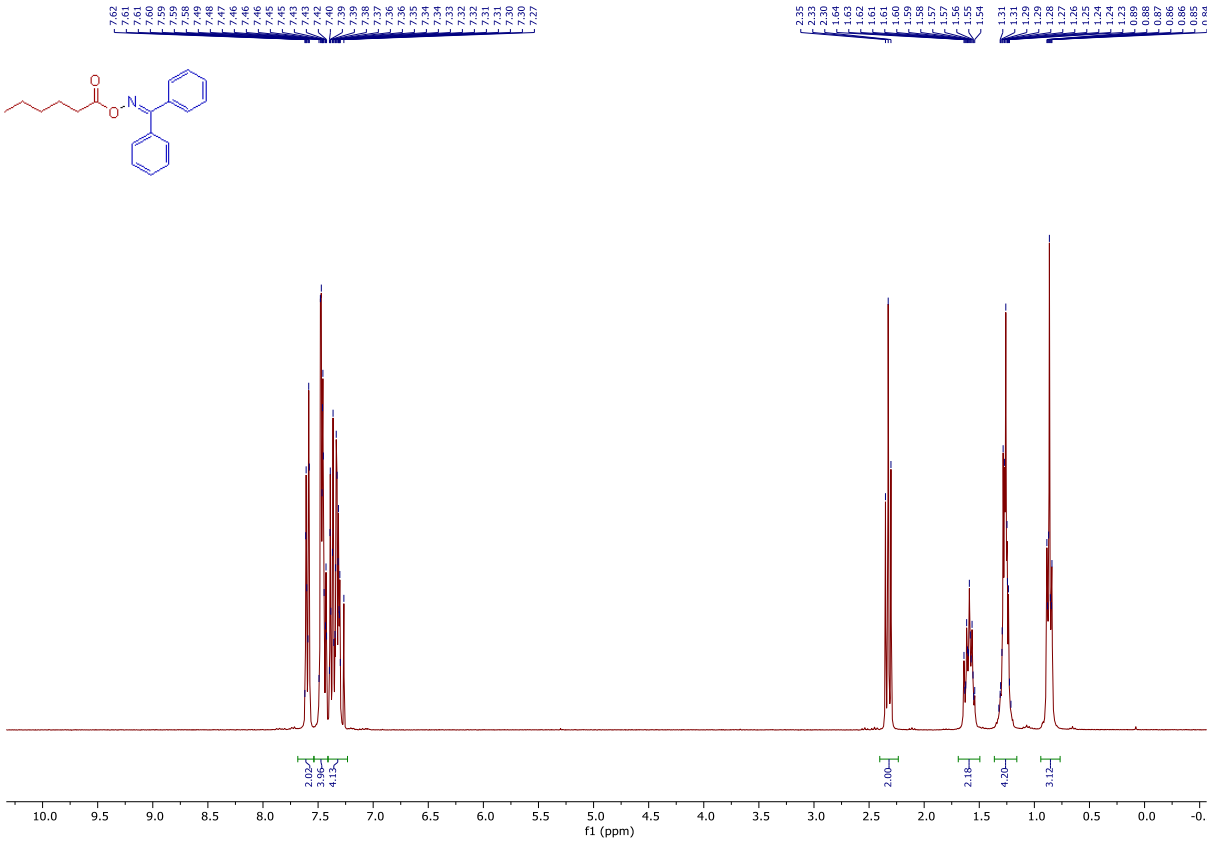
5. NMR spectra

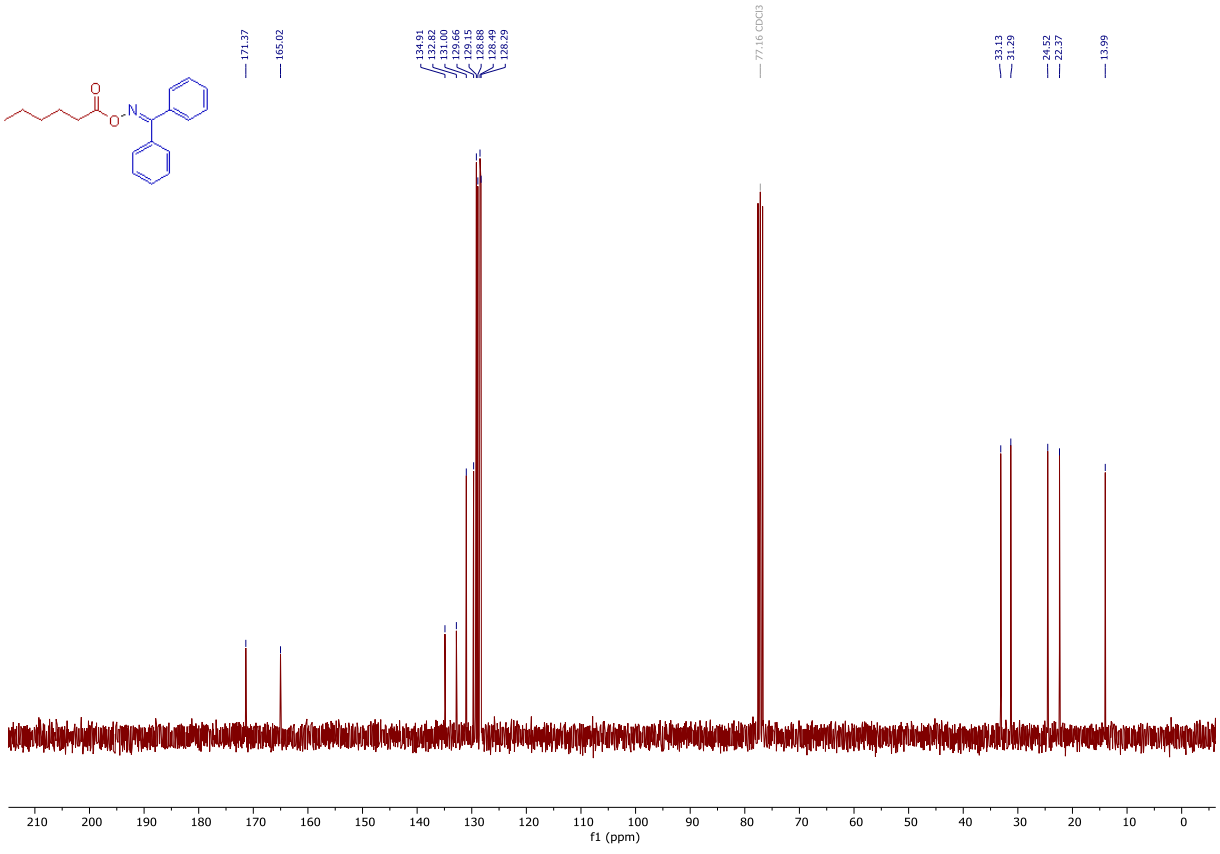
Diphenylmethanone *O*-(3-phenylpropanoyl) oxime (S4 or 1b)



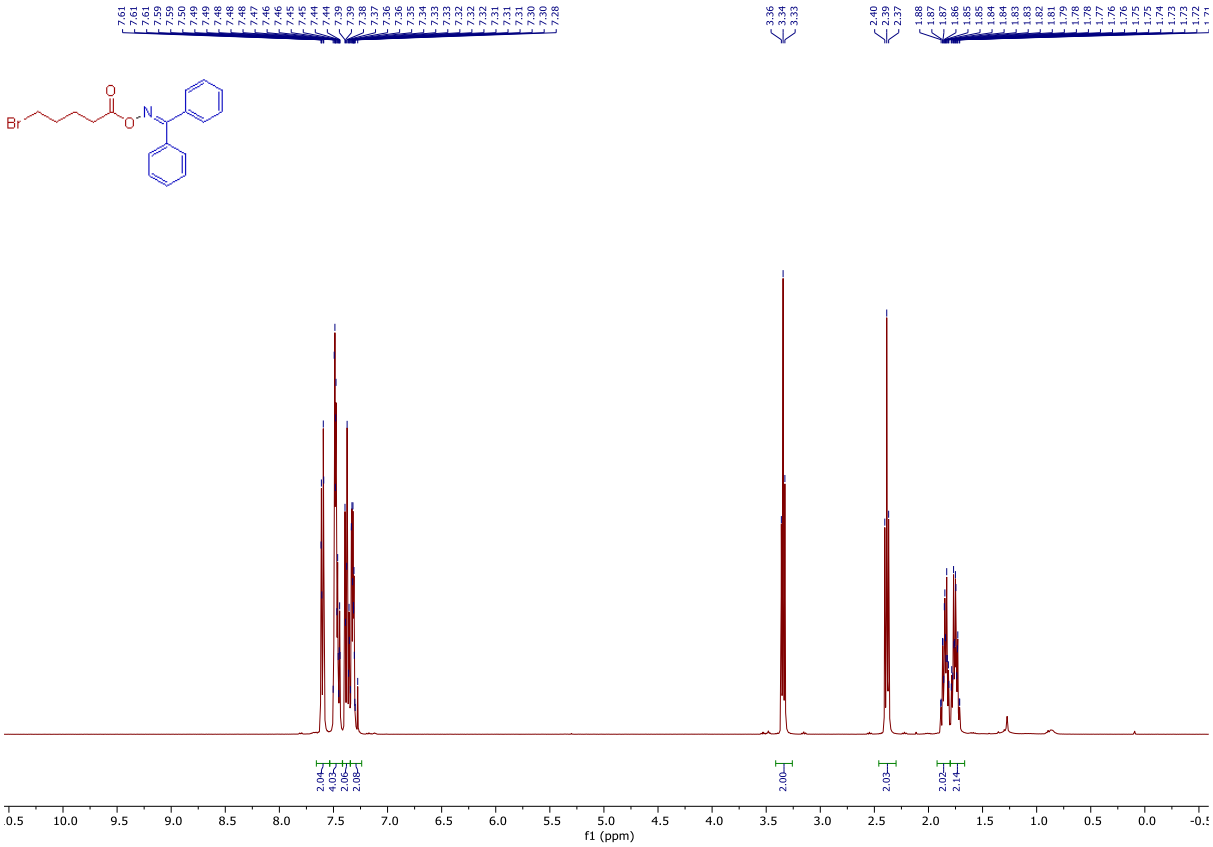


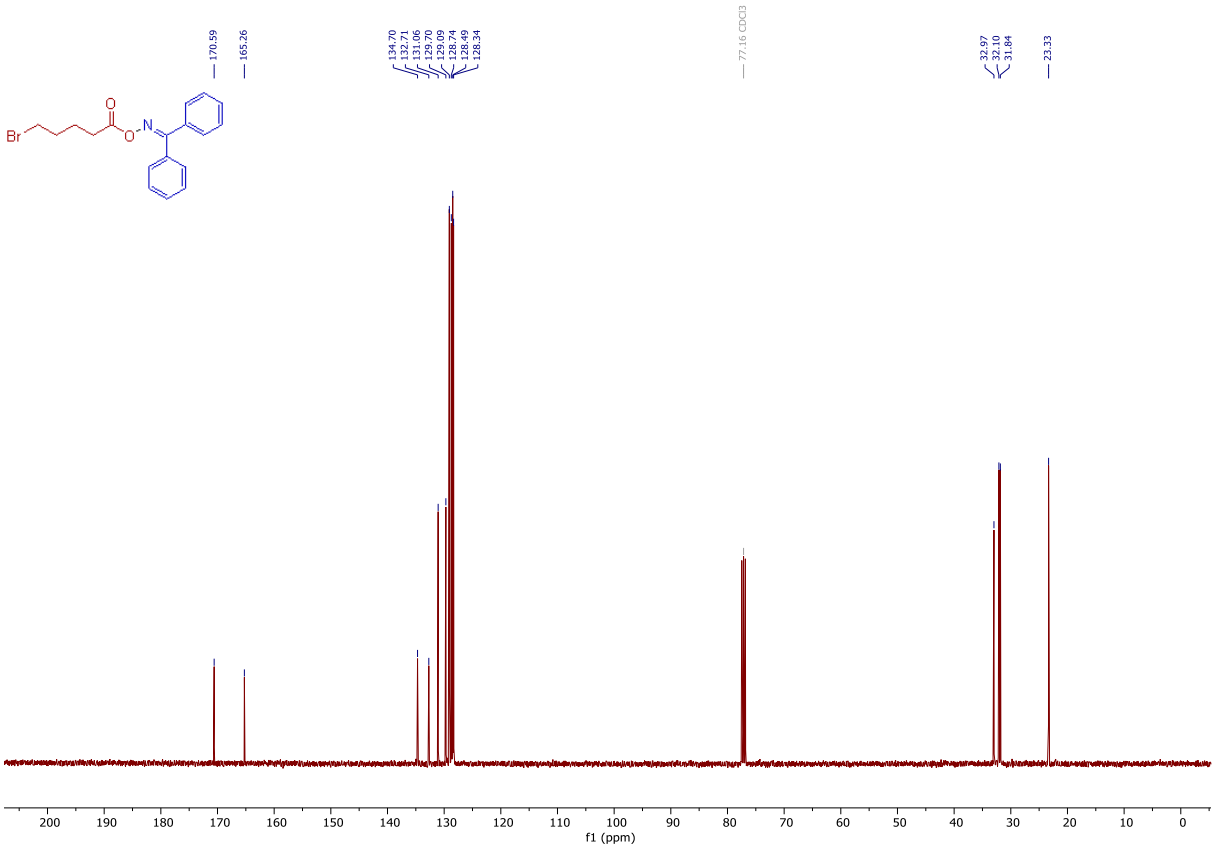
diphenylmethanone *O*-hexanoyl oxime (S19)



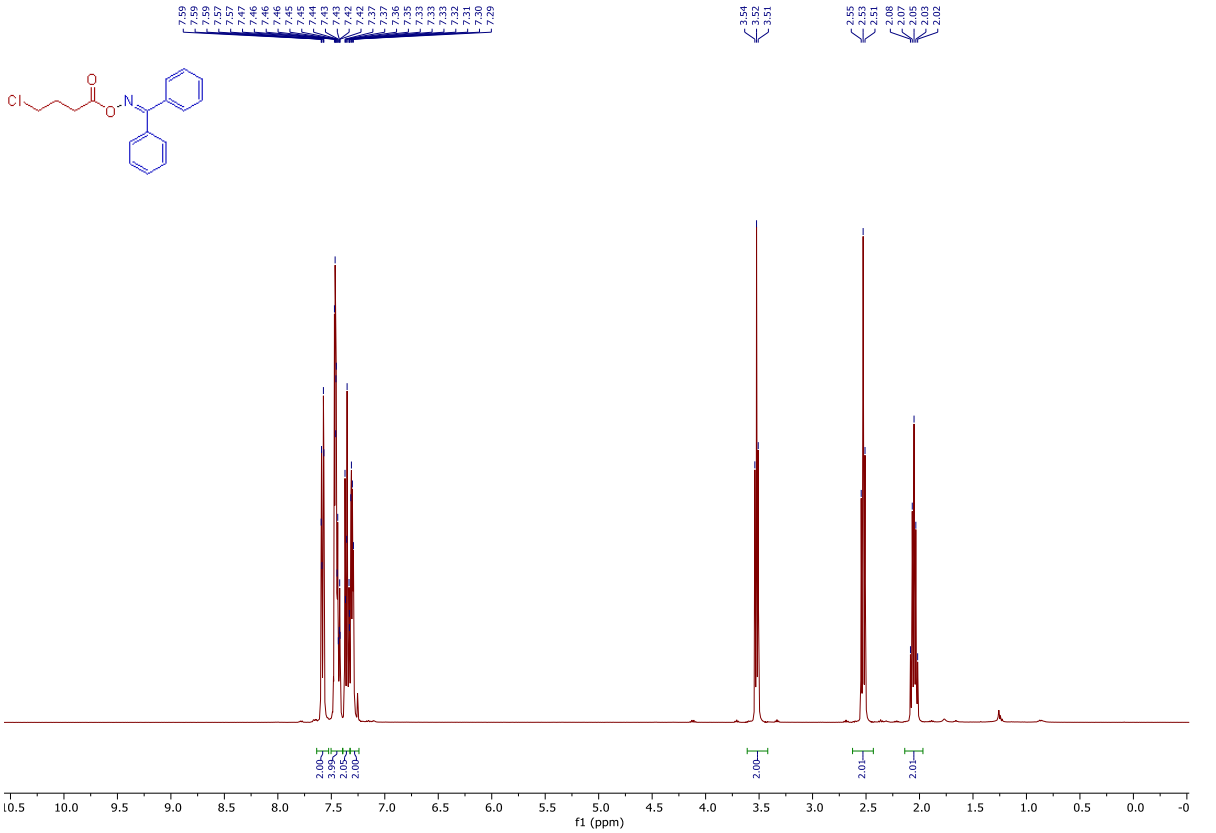


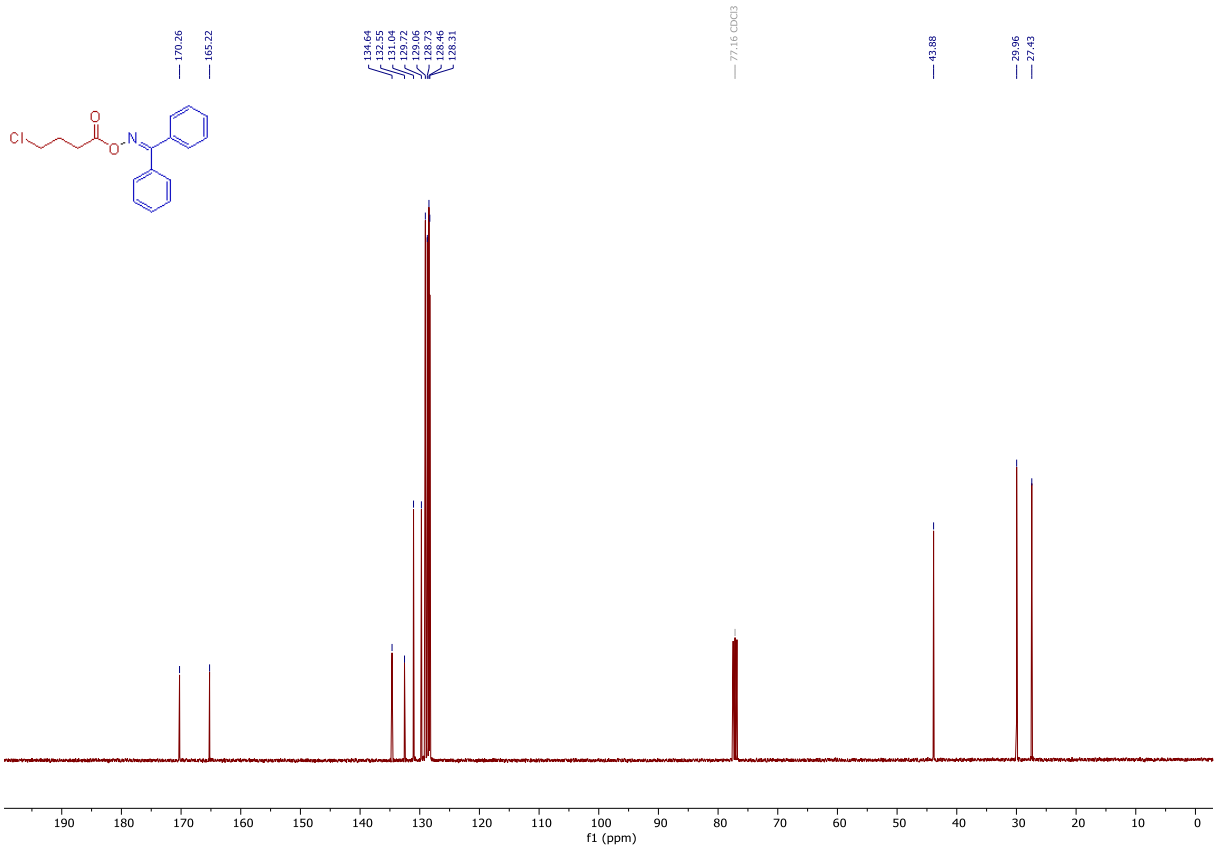
diphenylmethanone *O*-(5-bromopentanoyl) oxime (S20)



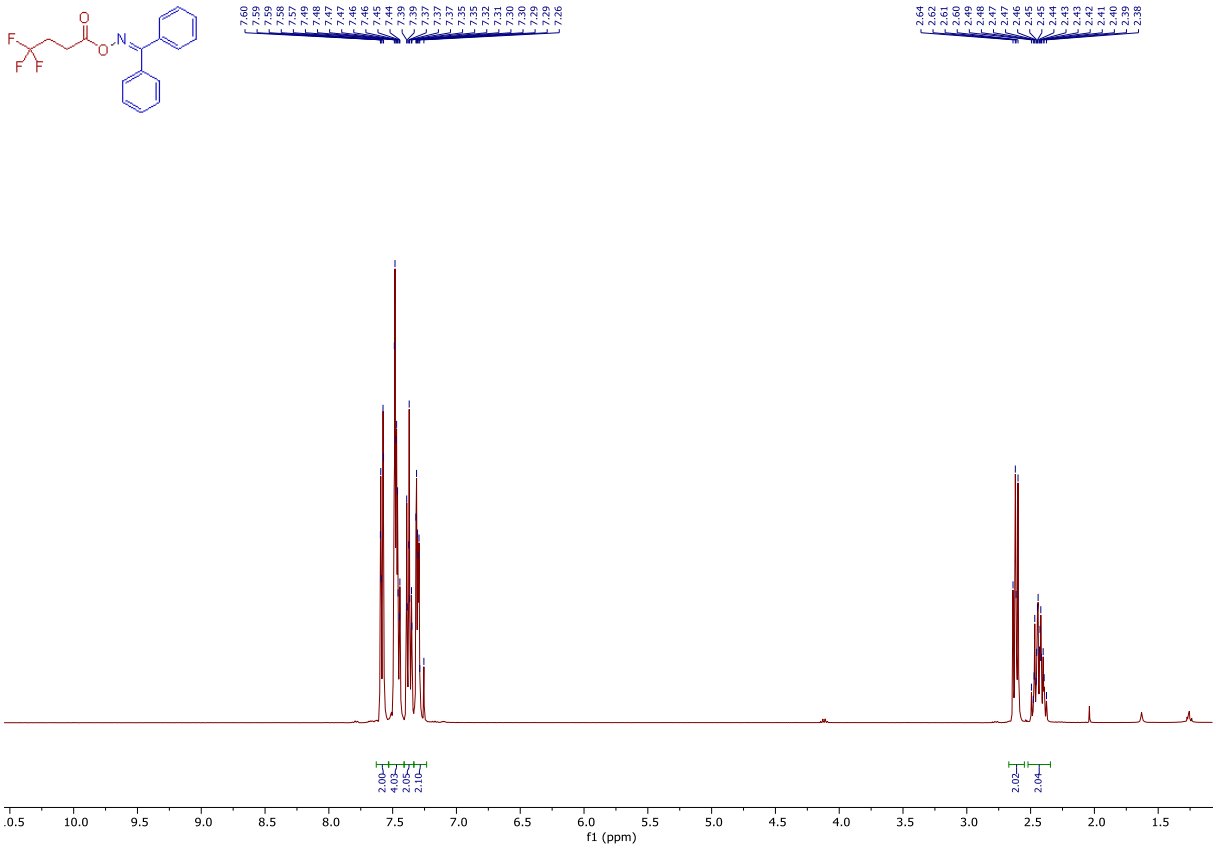


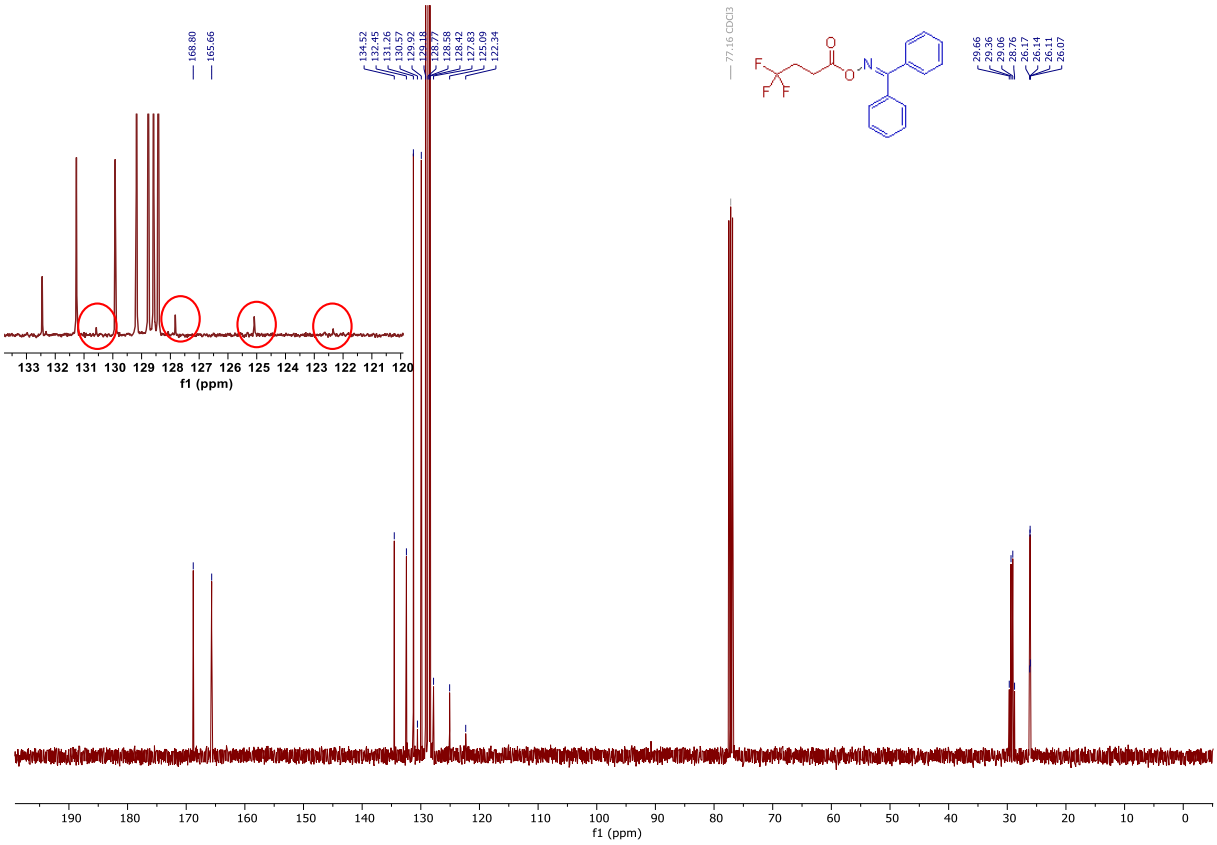
diphenylmethanone *O*-(4-chlorobutanoyl) oxime (S21)

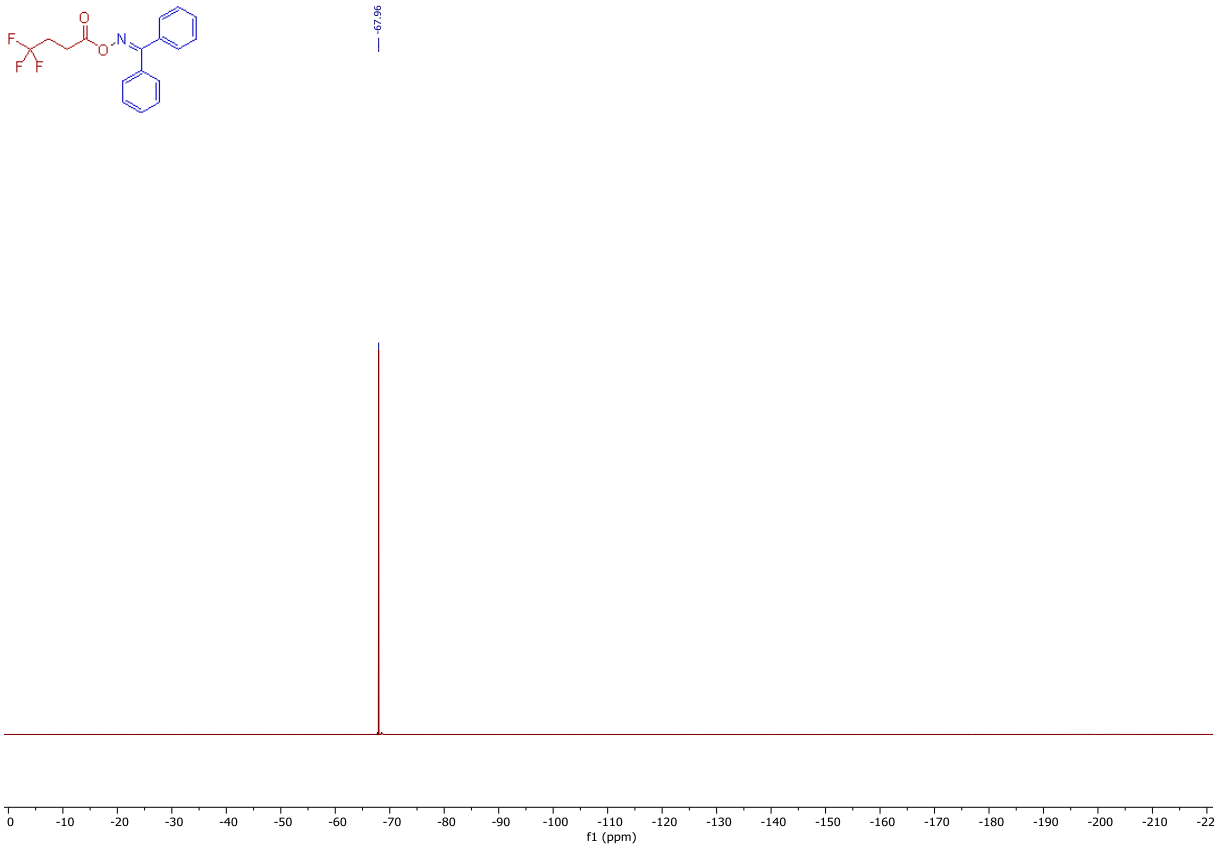




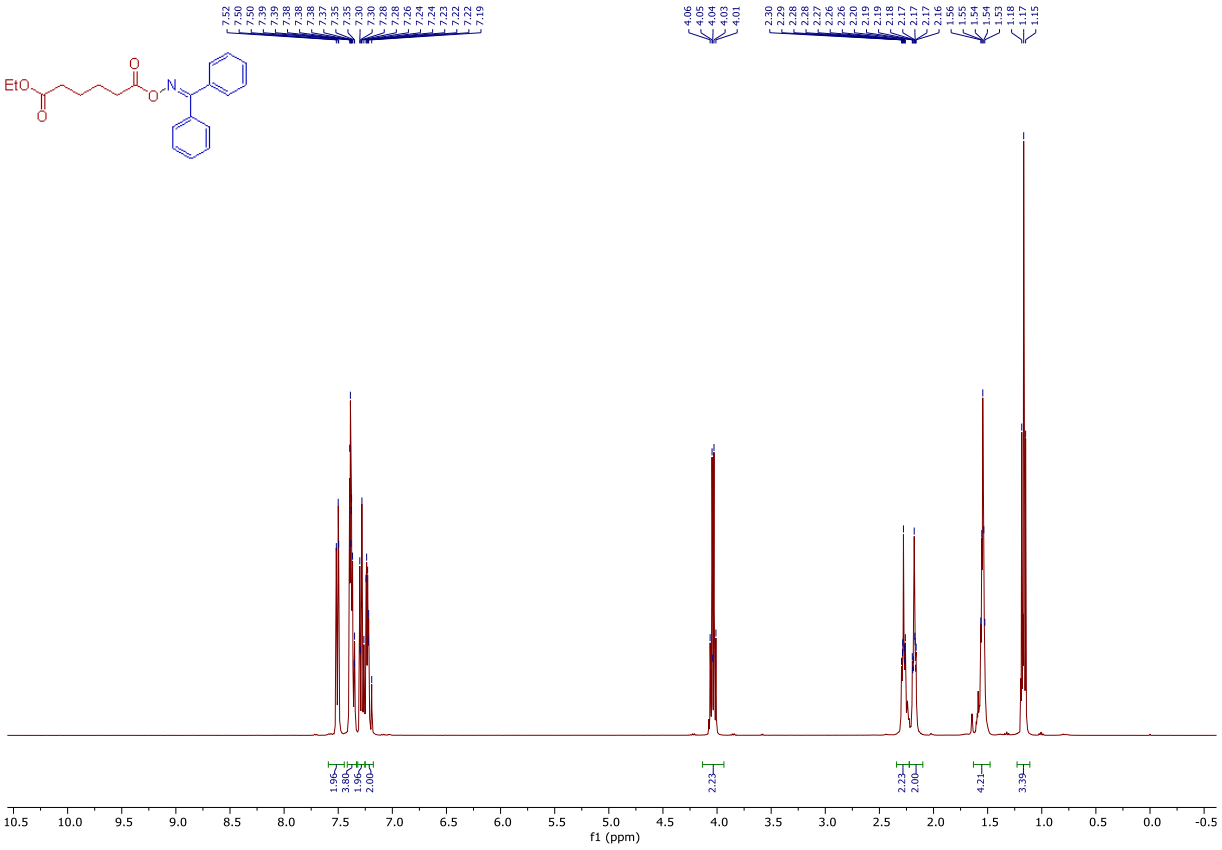
diphenylmethanone *O*-(4,4,4-trifluorobutanoyl) oxime (S22)

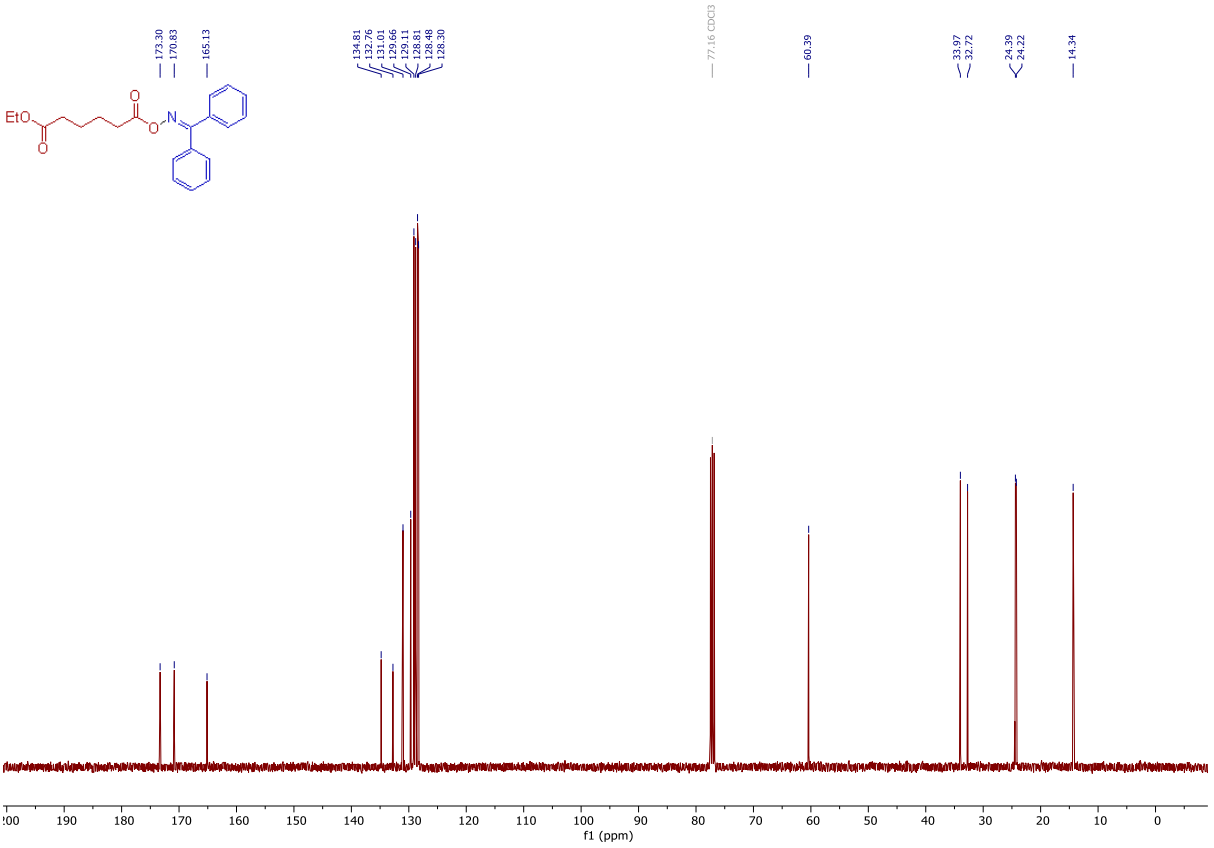




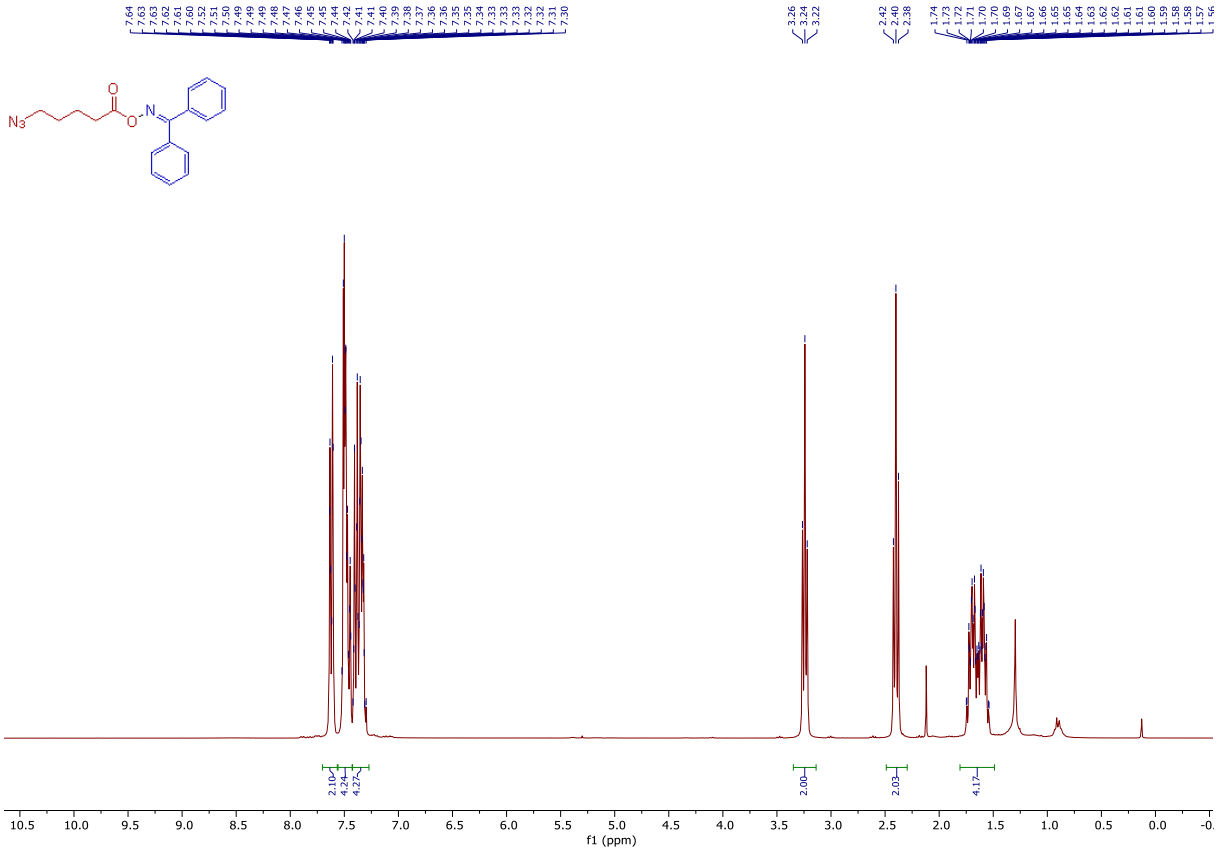

F
F
F
O
O
N
-67.96
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)

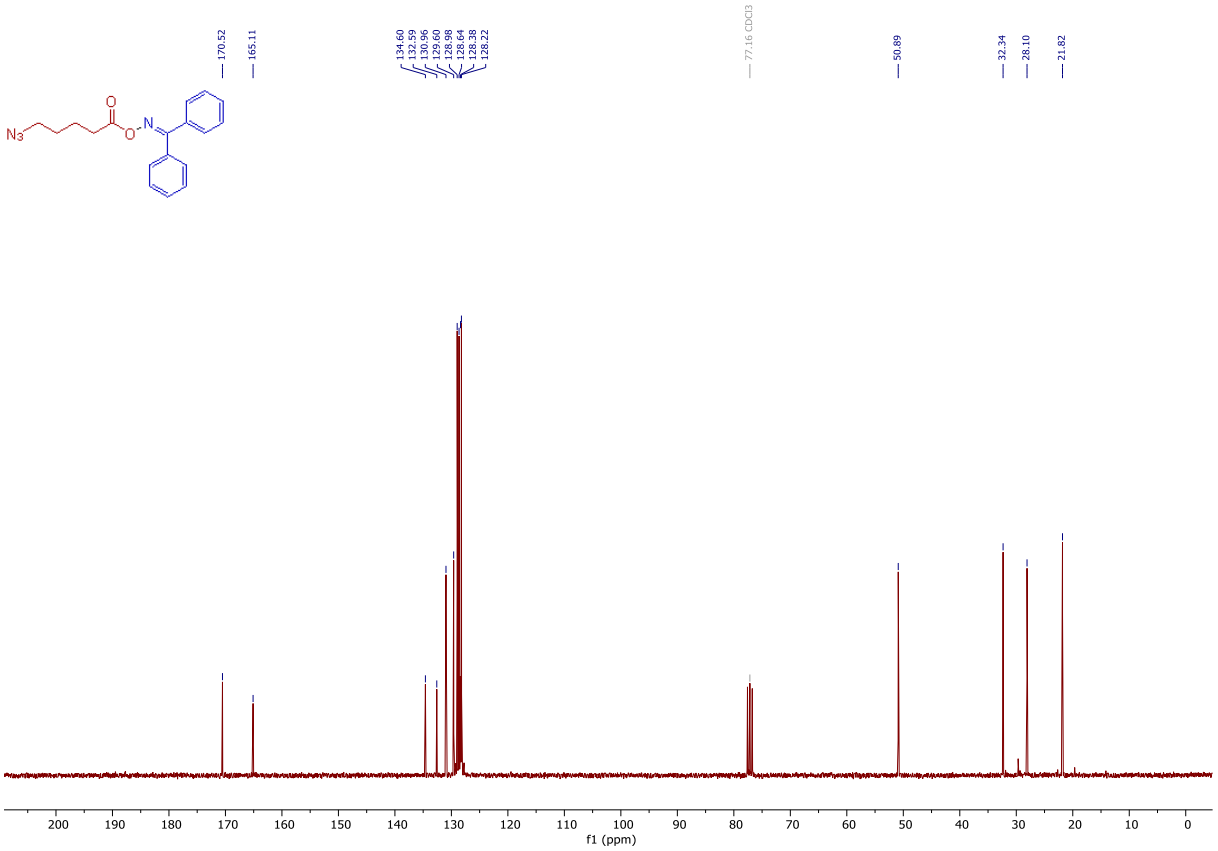
ethyl 6-(((diphenylmethylene)amino)oxy)-6-oxohexanoate (S23)



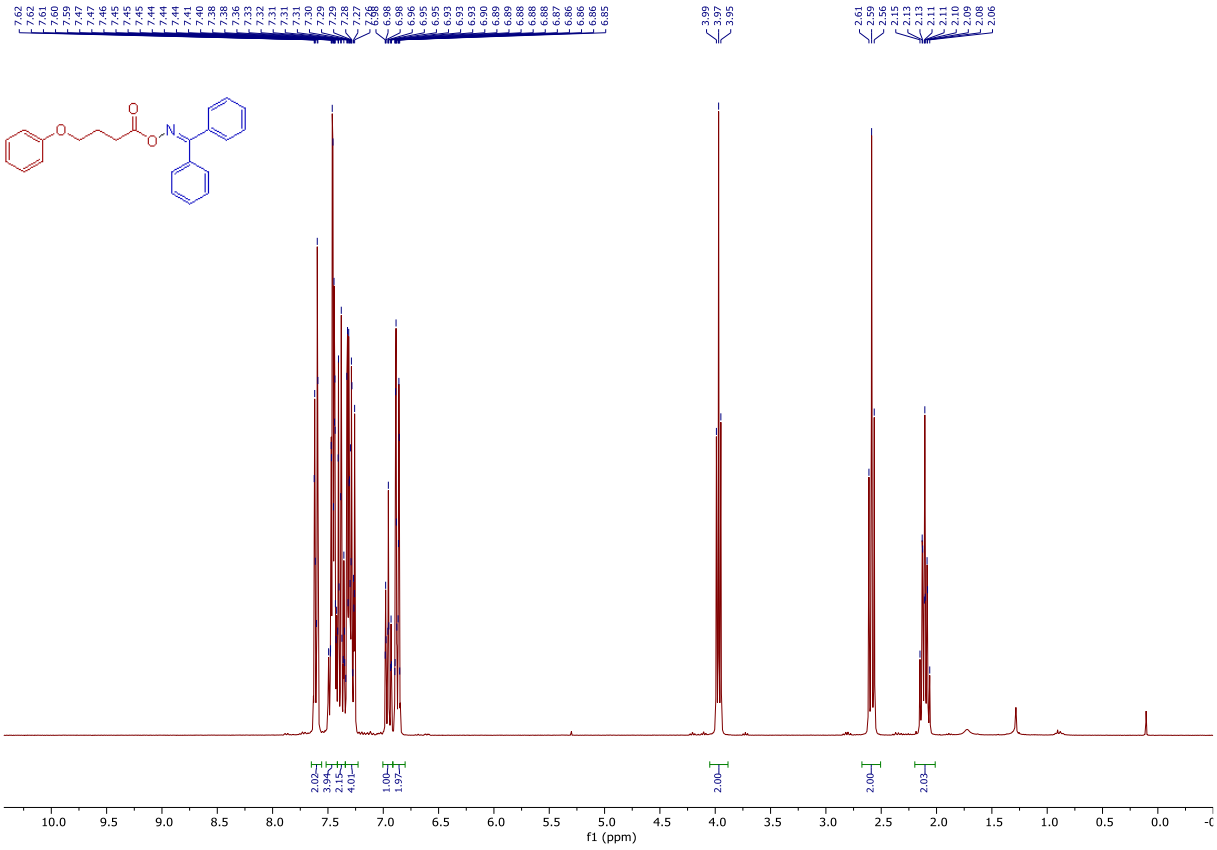


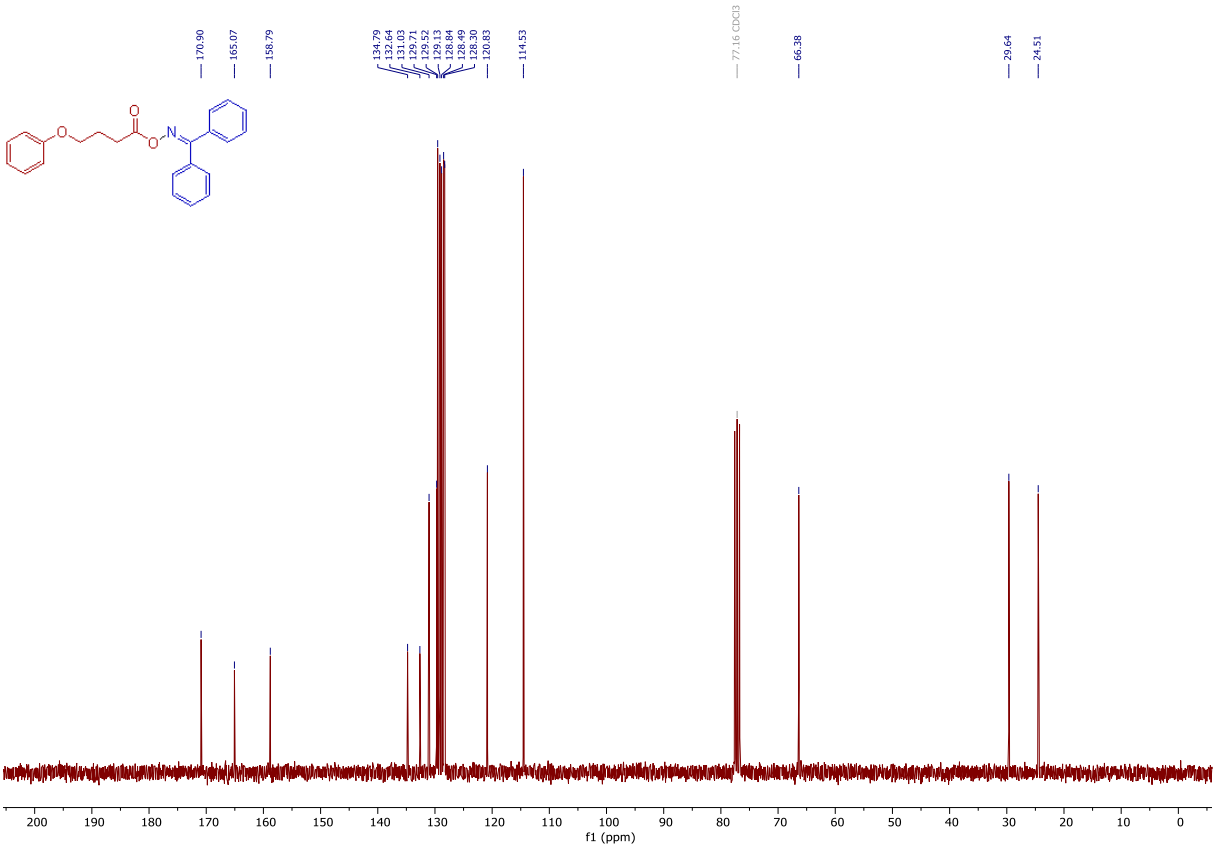
diphenylmethanone *O*-(5-azidopentanoyl) oxime (S24)



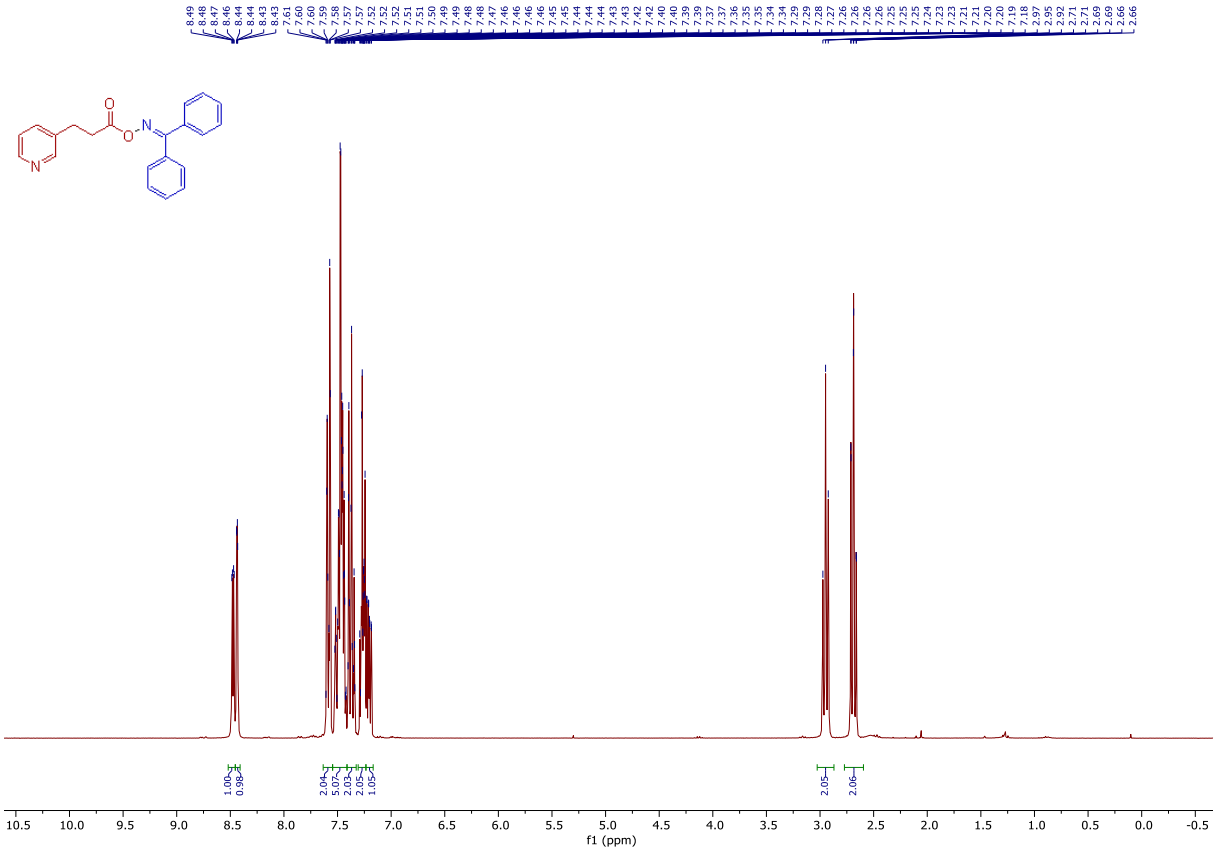


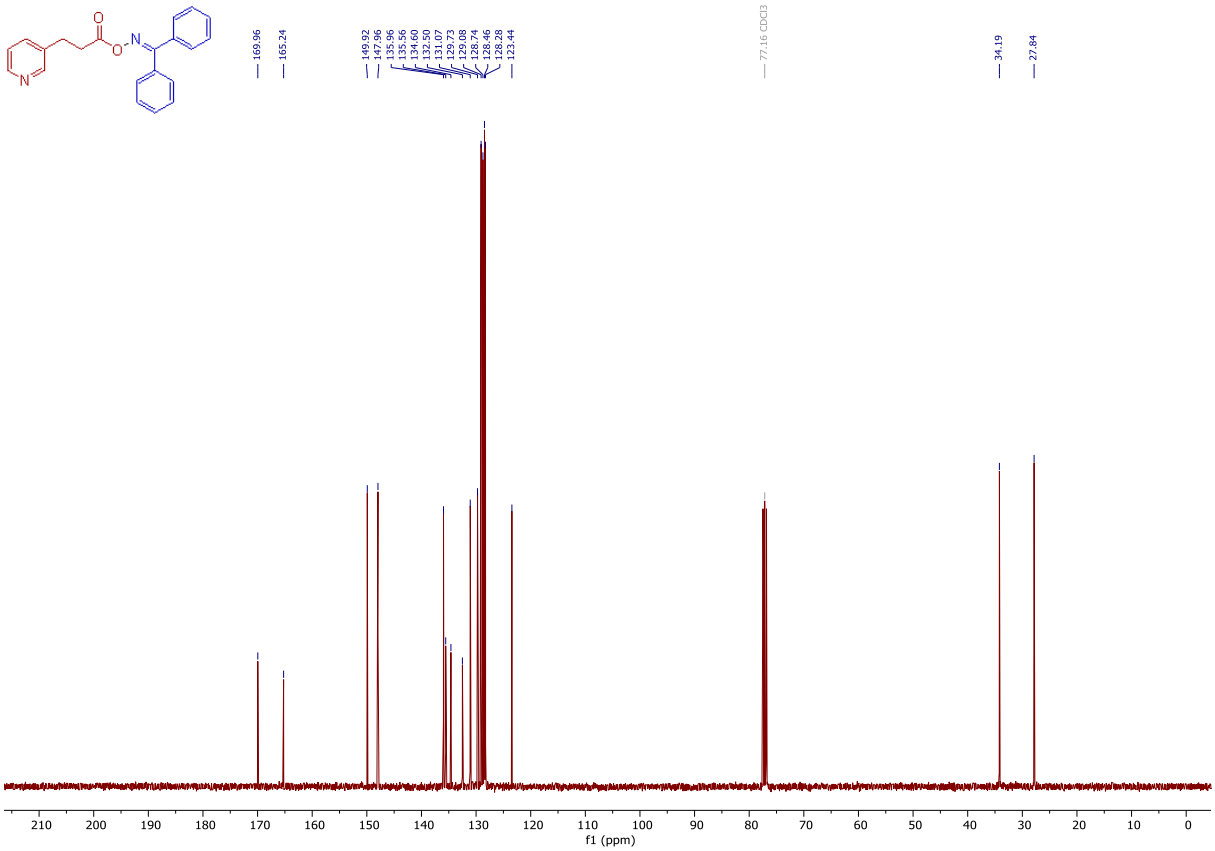
diphenylmethanone *O*-(4-phenoxybutanoyl) oxime (S25)



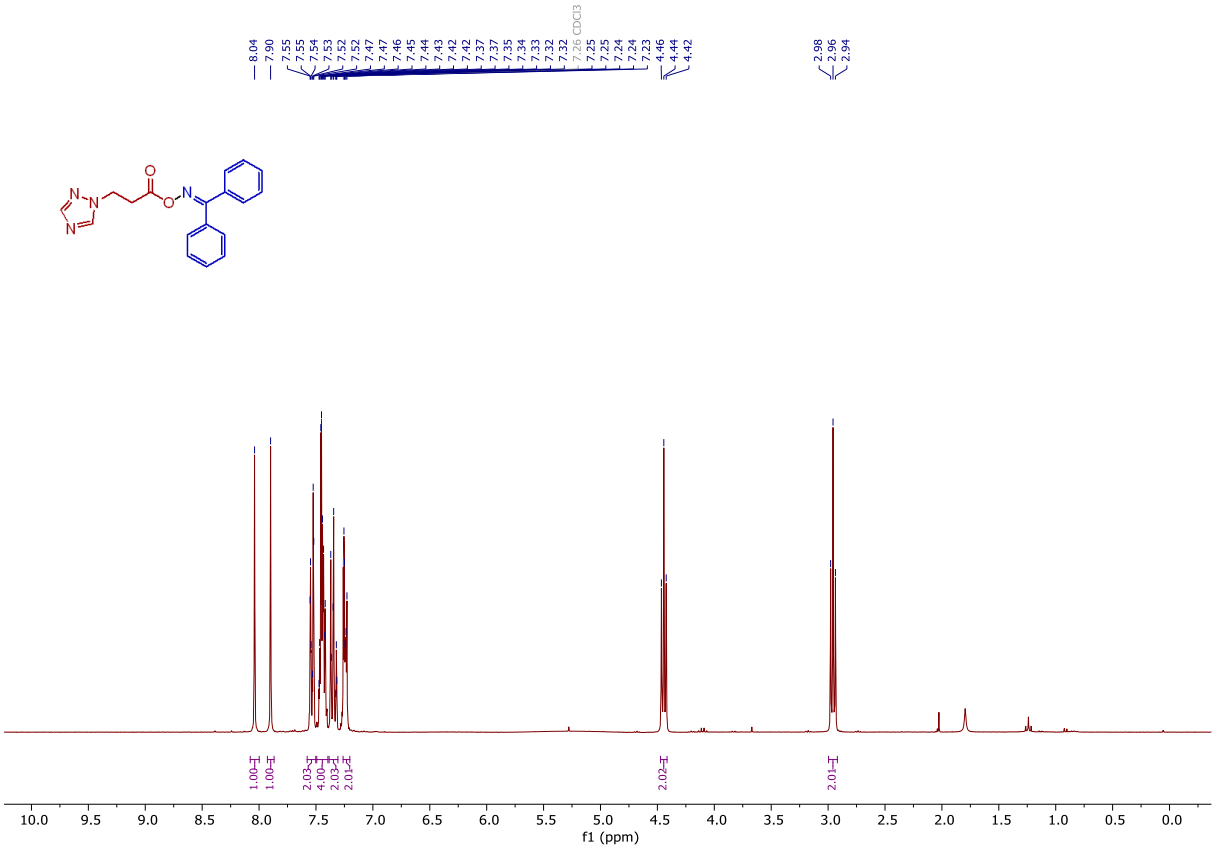


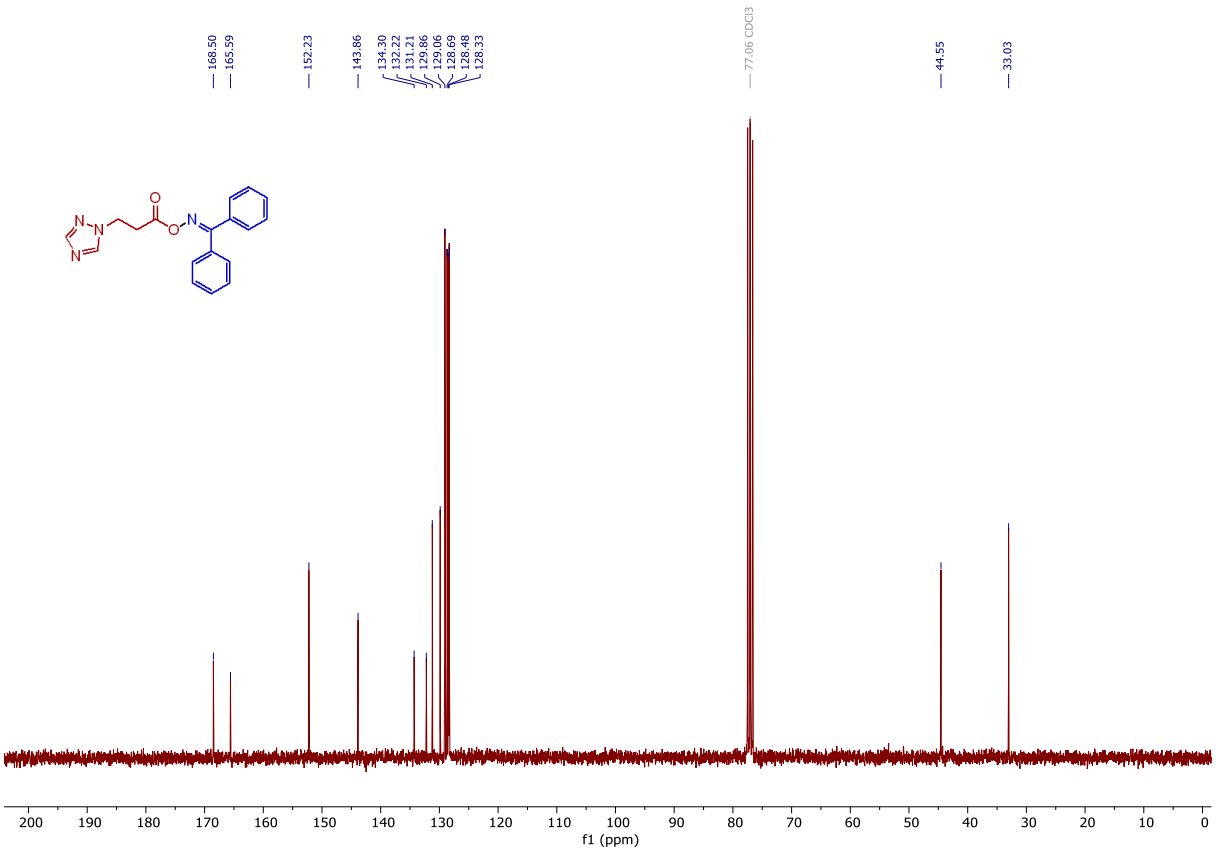
diphenylmethanone *O*-(3-(pyridin-3-yl)propanoyl) oxime (S26)



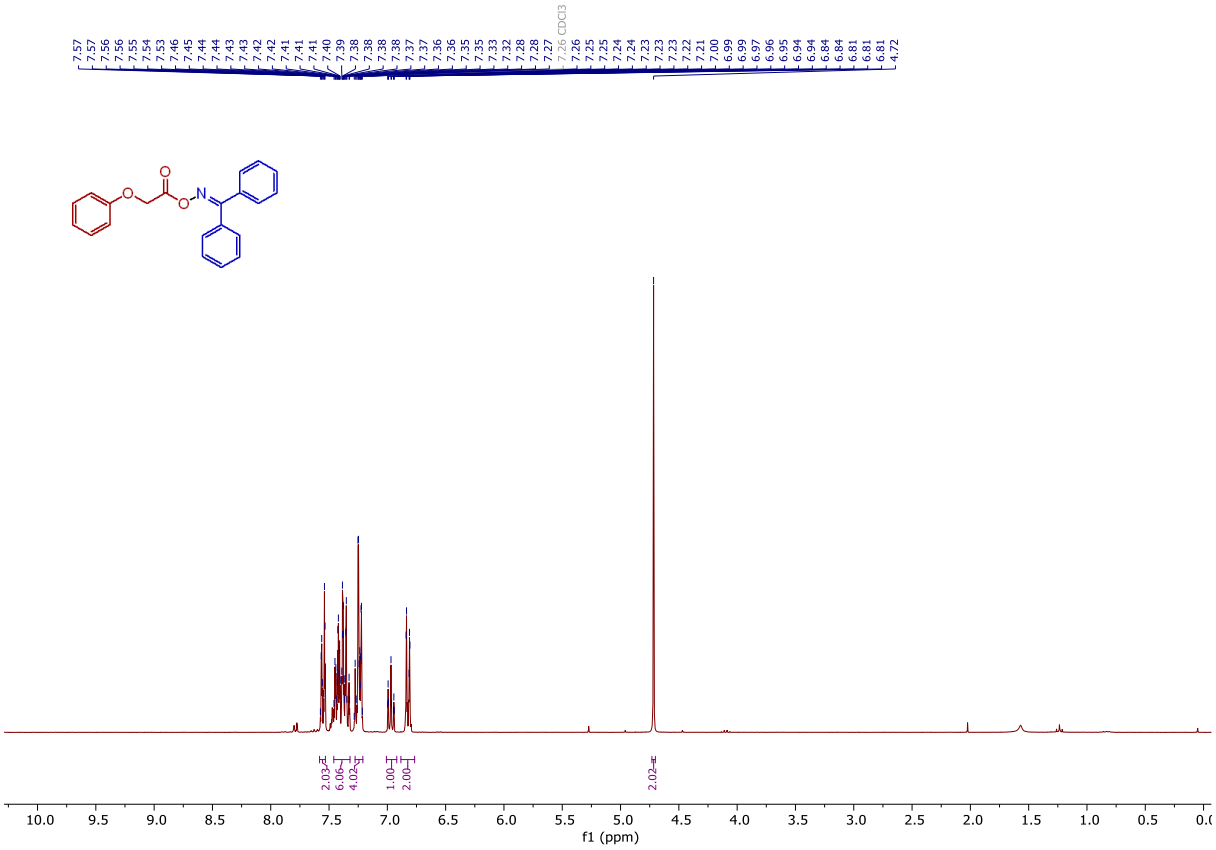


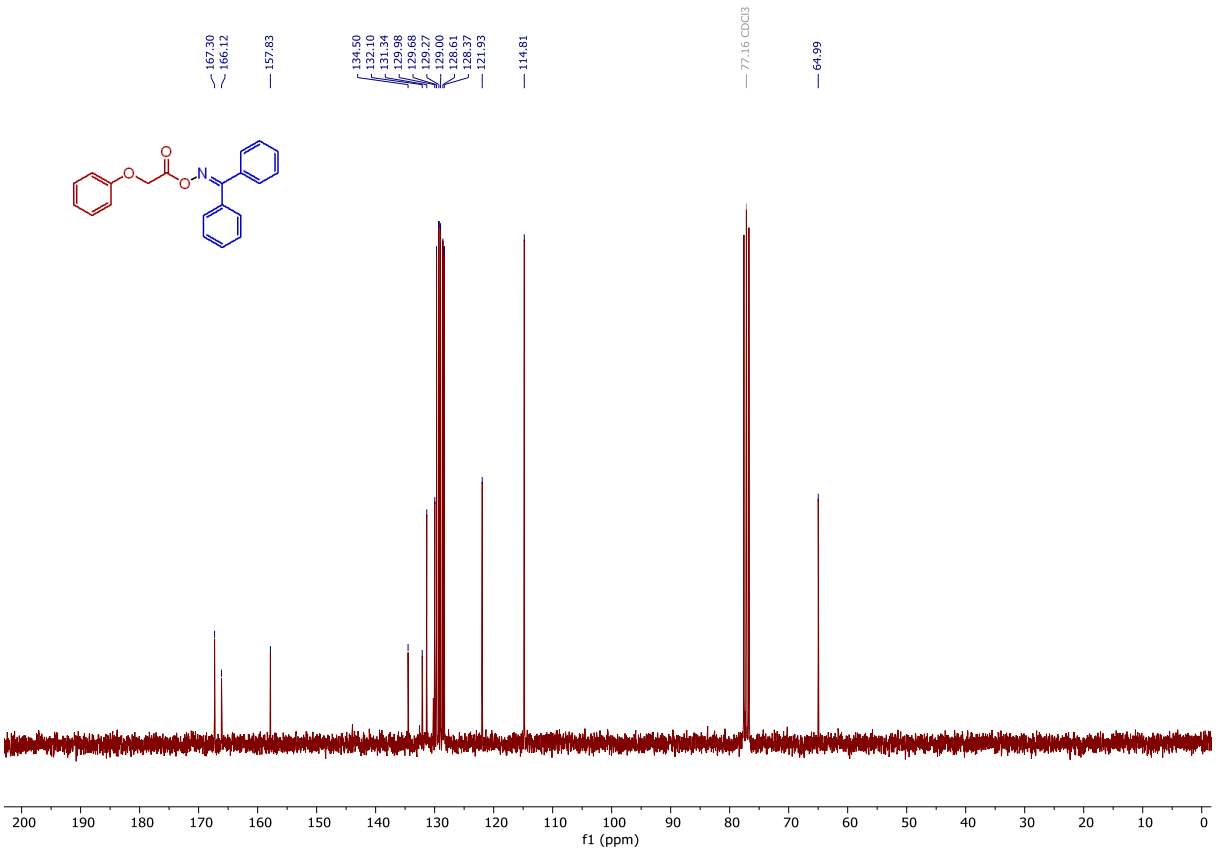
Diphenylmethanone *O*-(3-(1H-1,2,4-triazol-1-yl)propanoyl) oxime (S27)



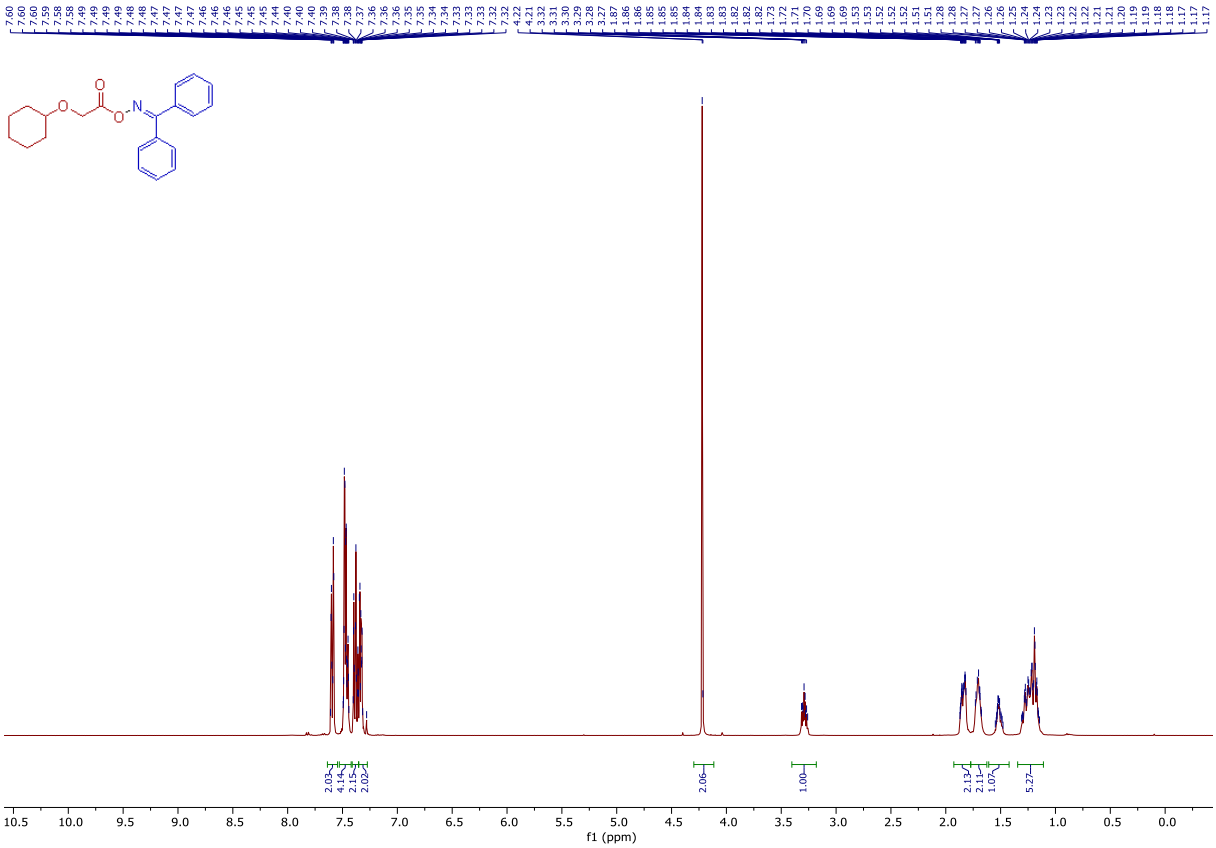


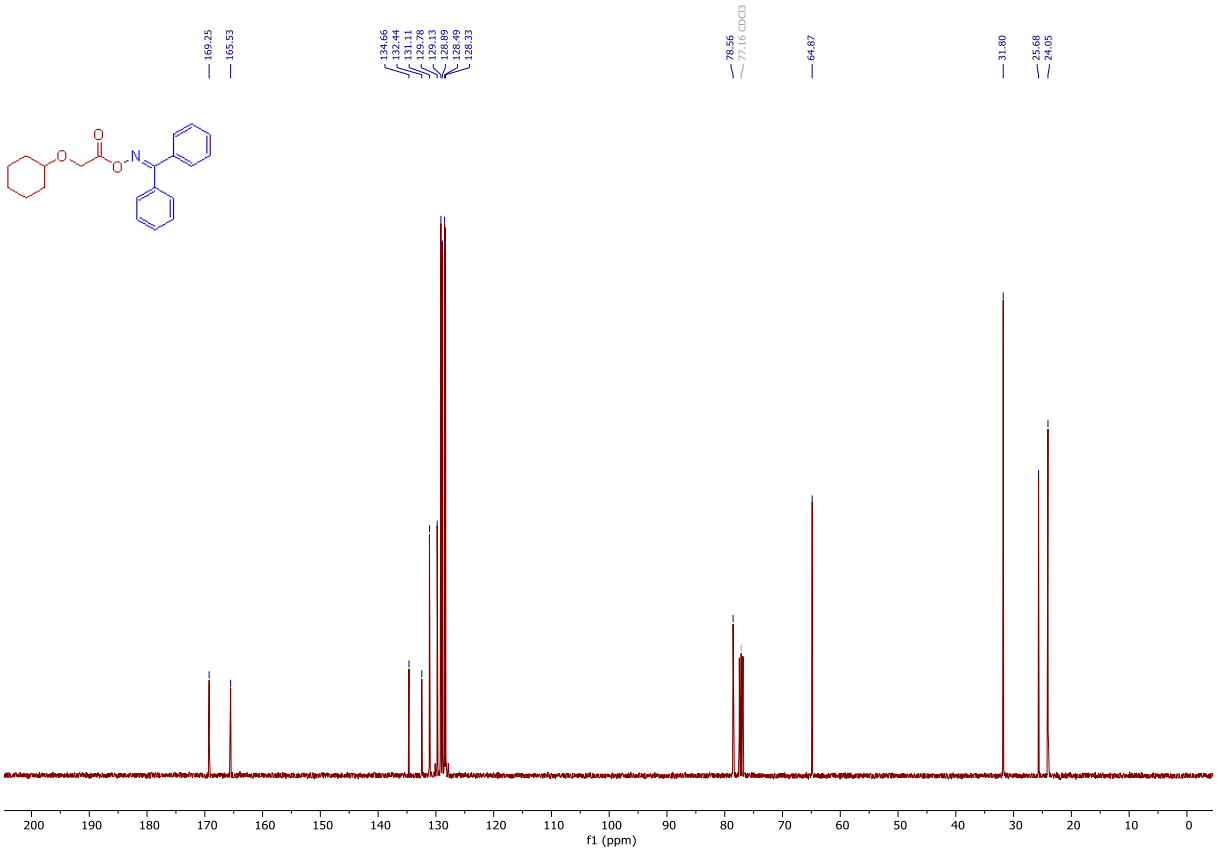
diphenylmethanone *O*-(2-phenoxyacetyl) oxime (S28)



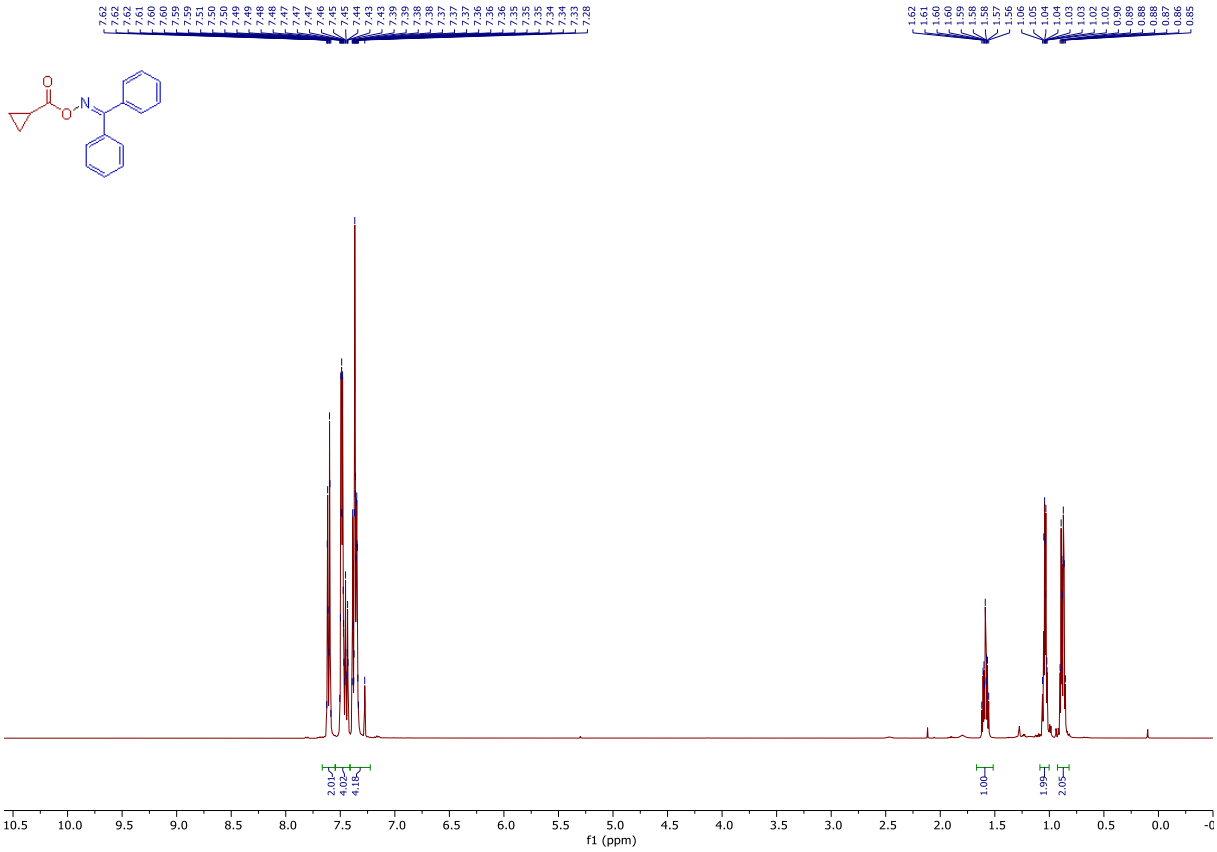


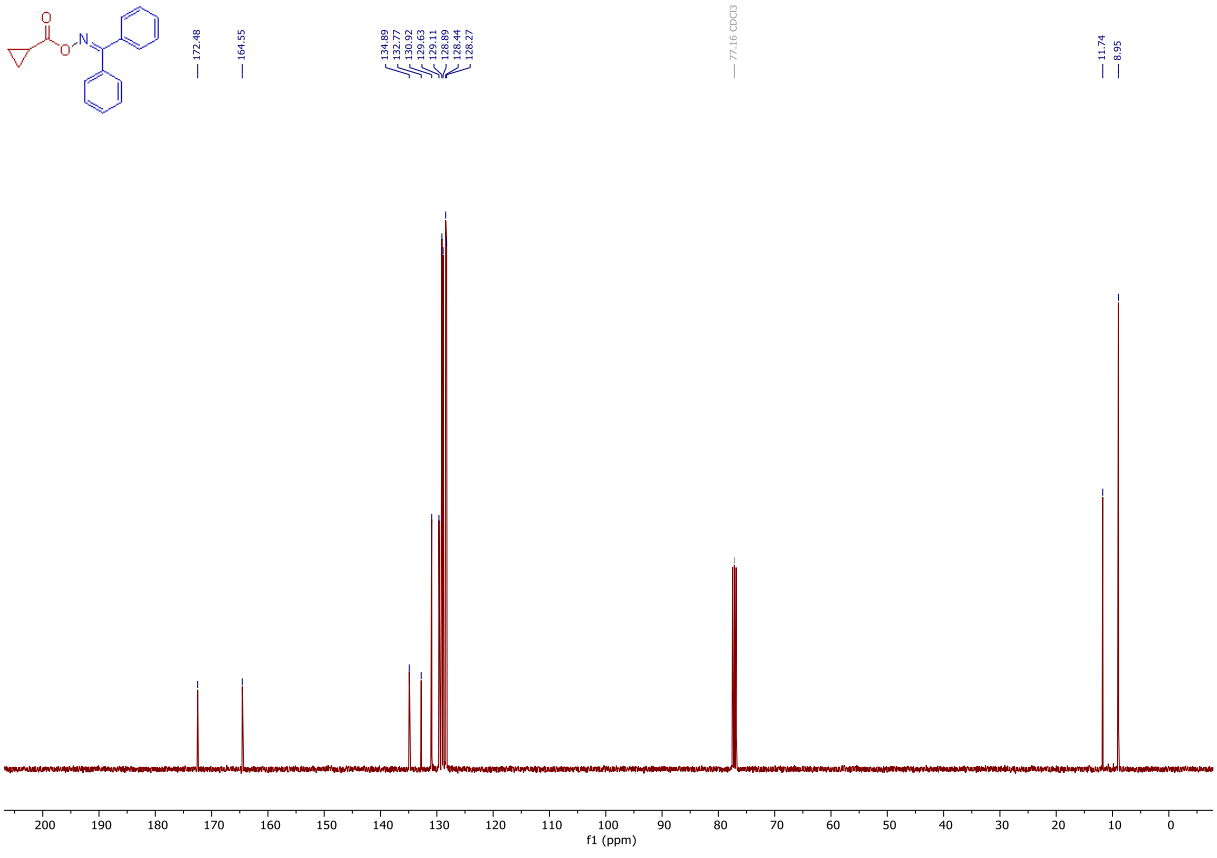
diphenylmethanone *O*-(2-(cyclohexyloxy)acetyl) oxime (S29)



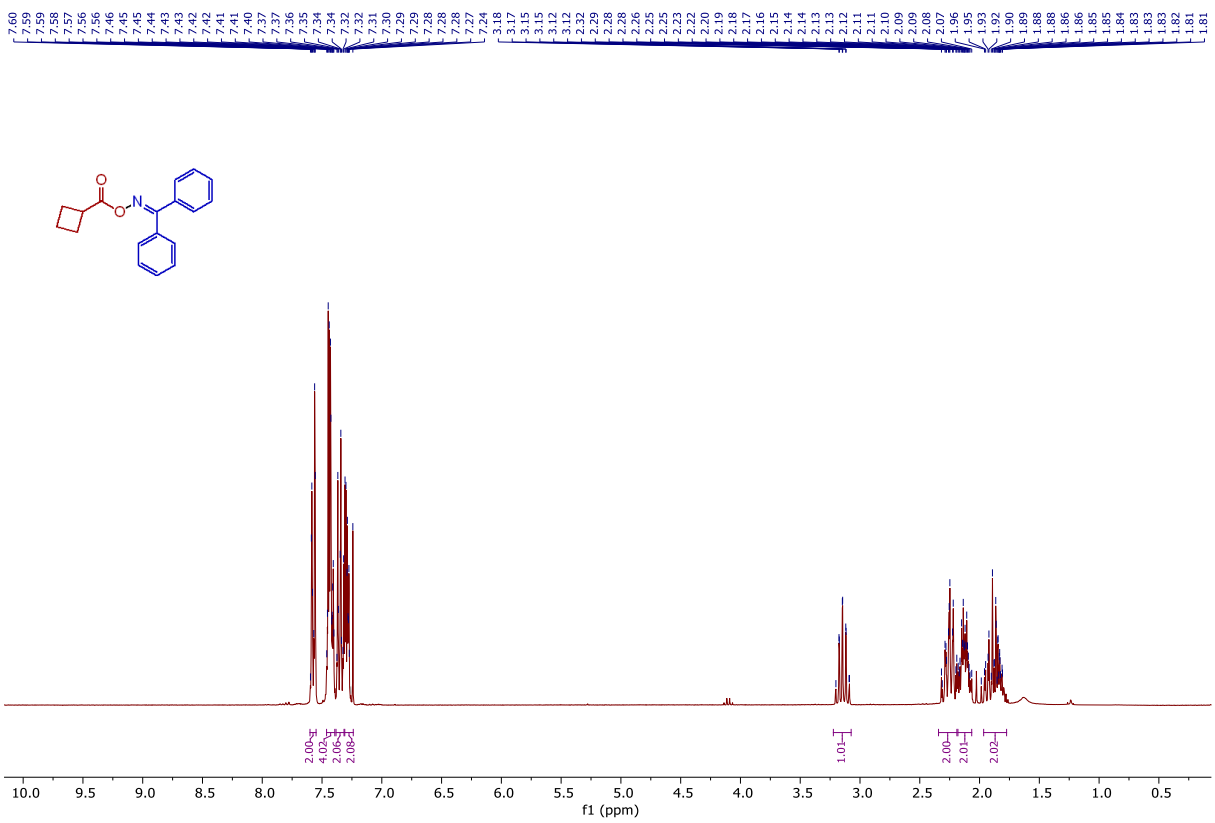


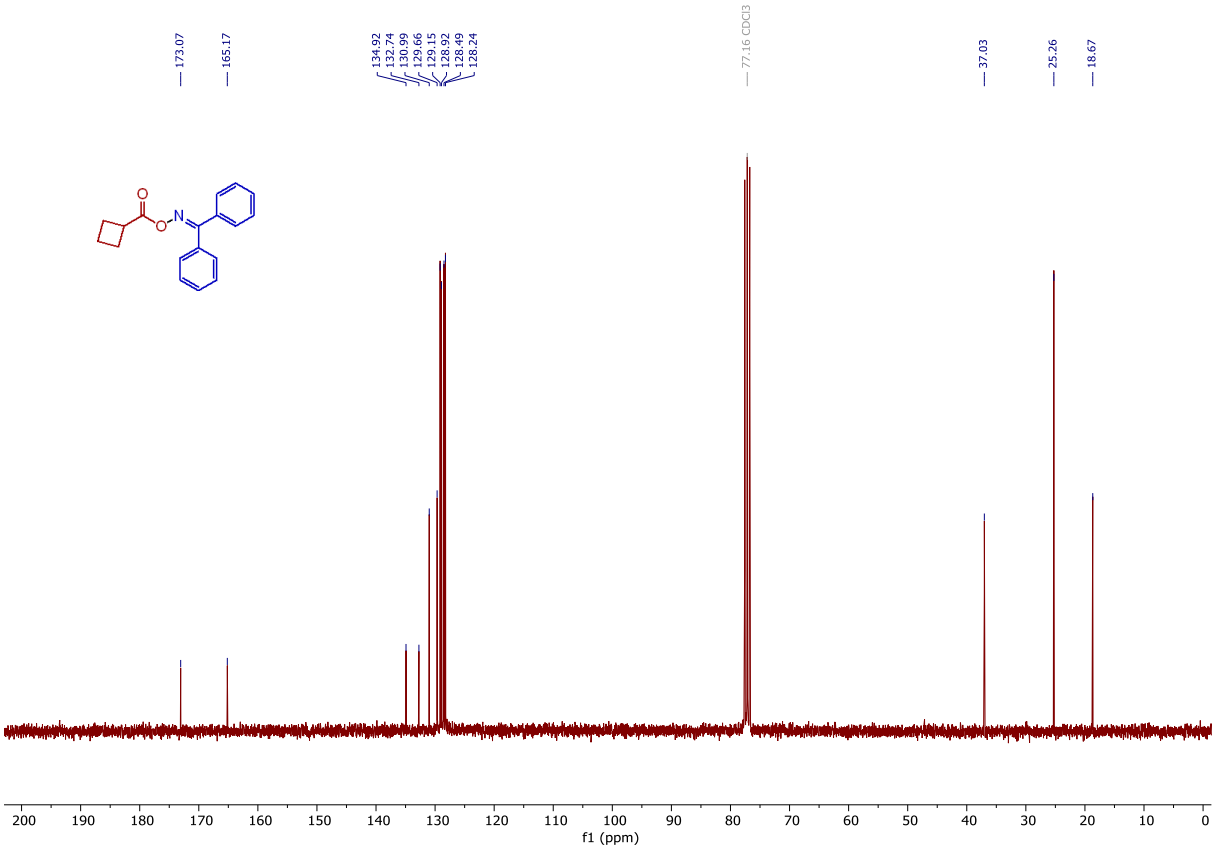
diphenylmethanone *O*-cyclopropanecarbonyl oxime (S30)



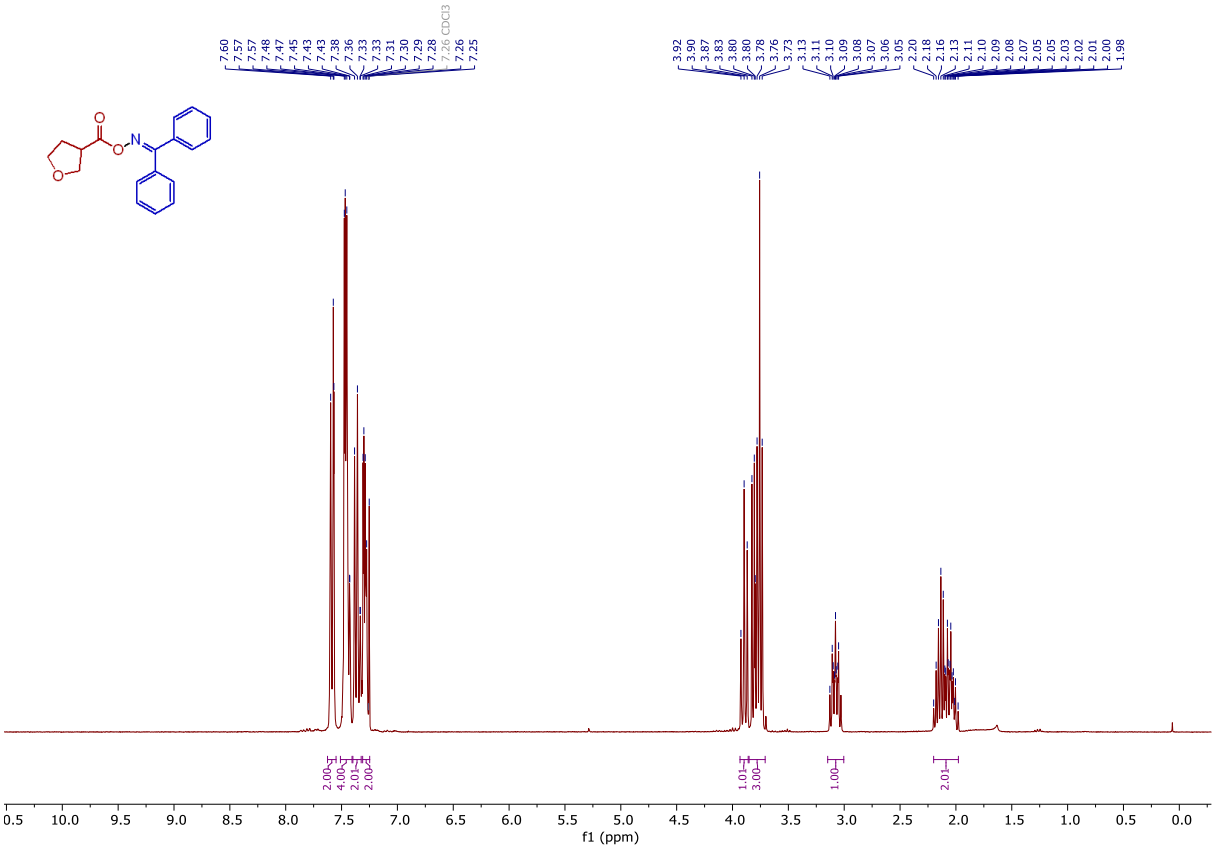


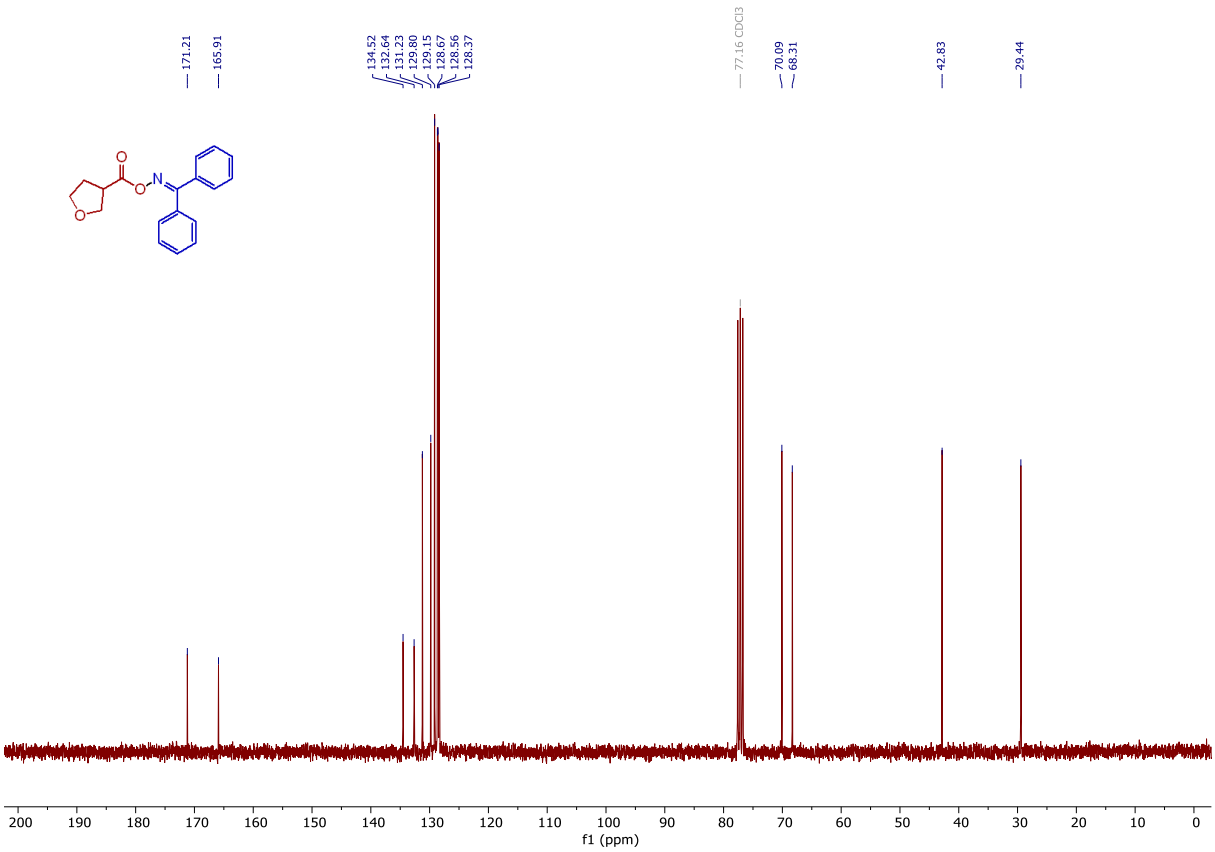
Diphenylmethanone *O*-cyclobutanecarbonyl oxime (S31)



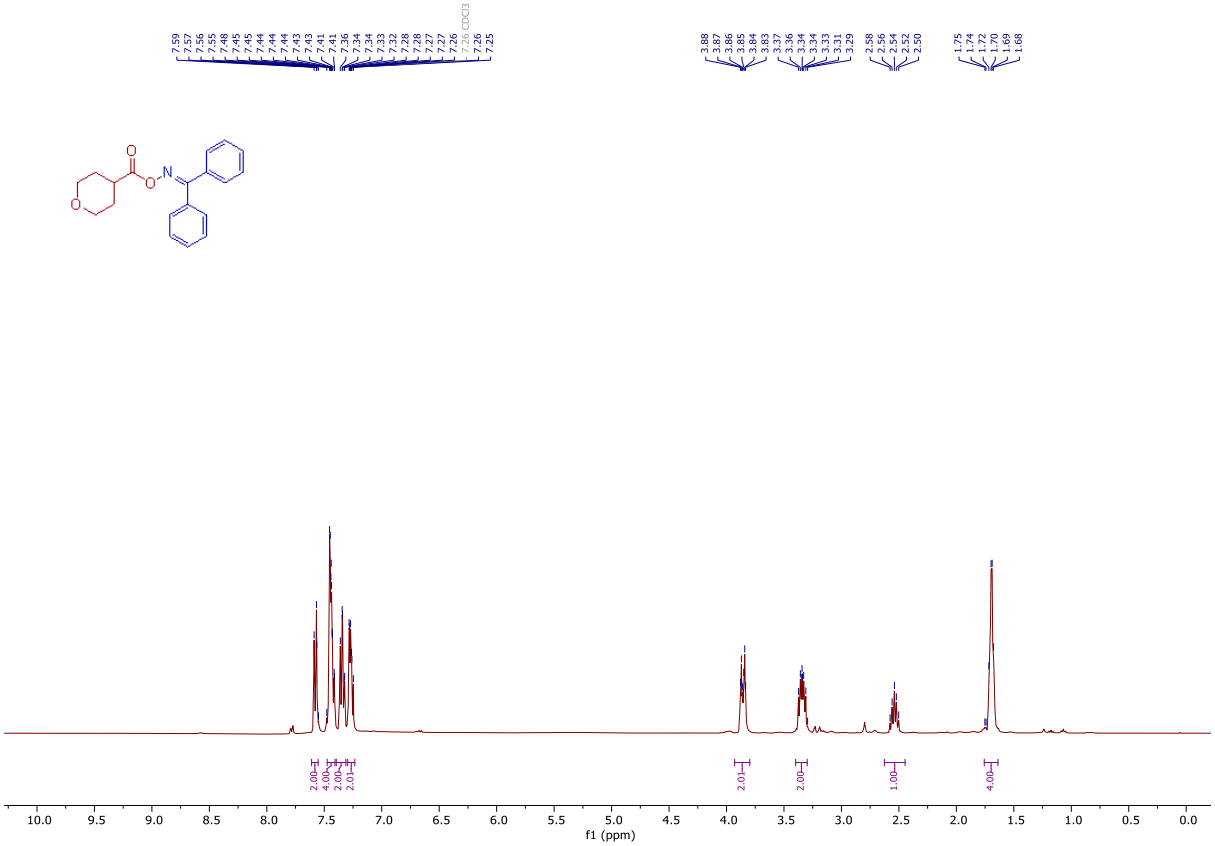


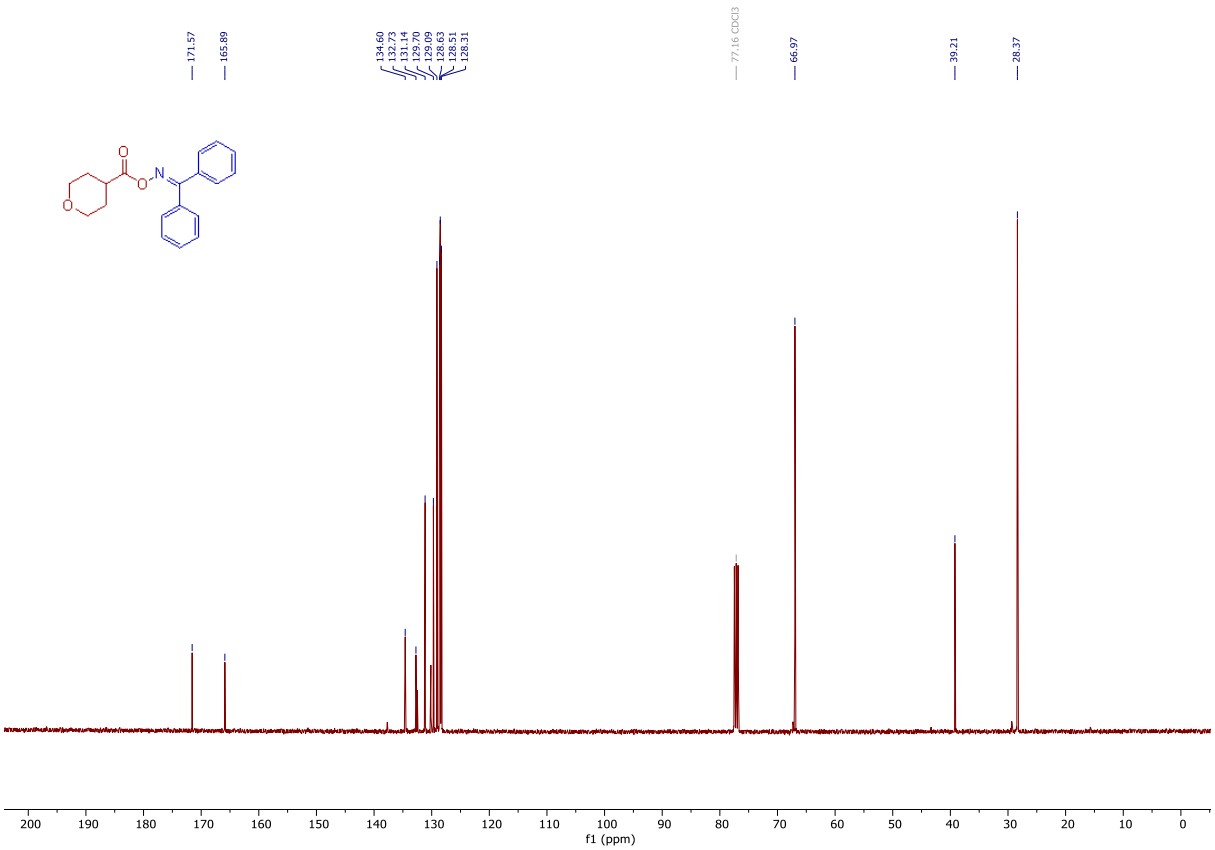
(±)-diphenylmethanone *O*-tetrahydrofuran-3-carbonyl oxime (S32)



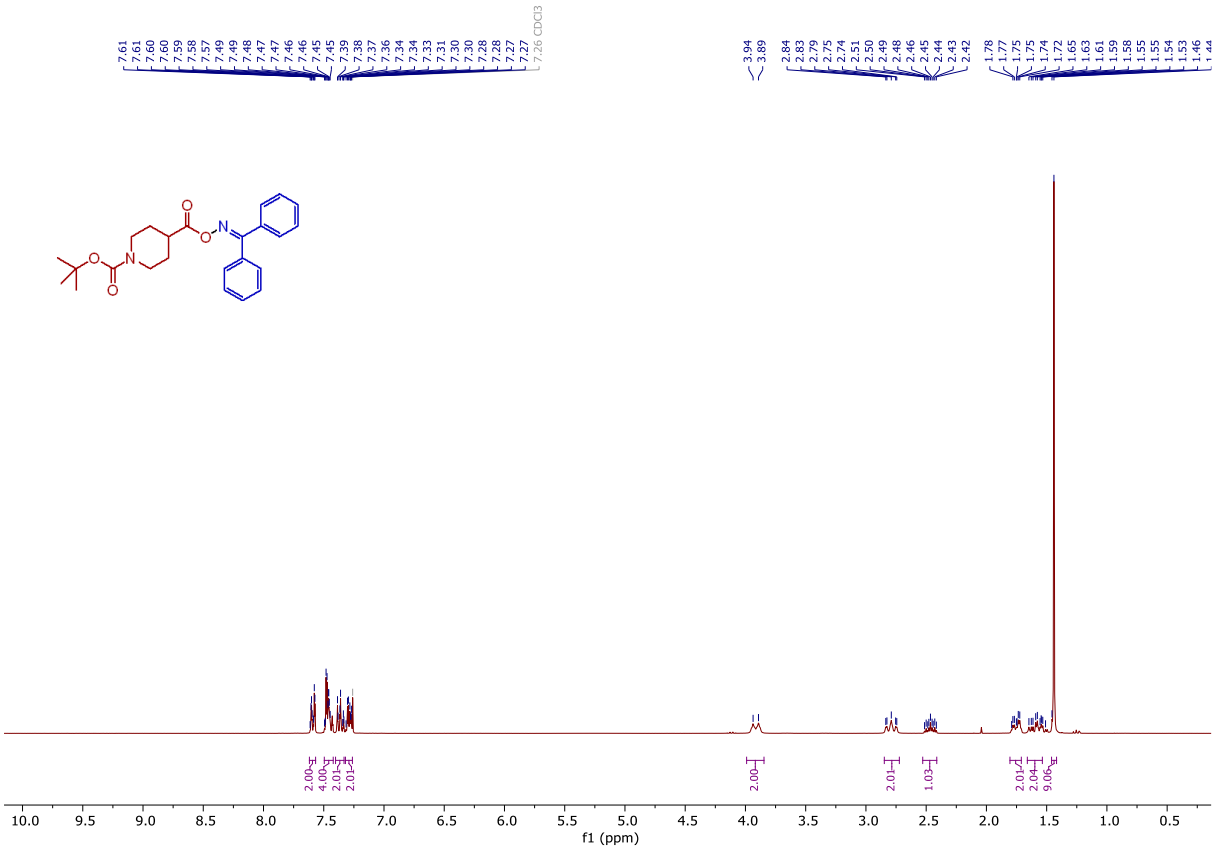


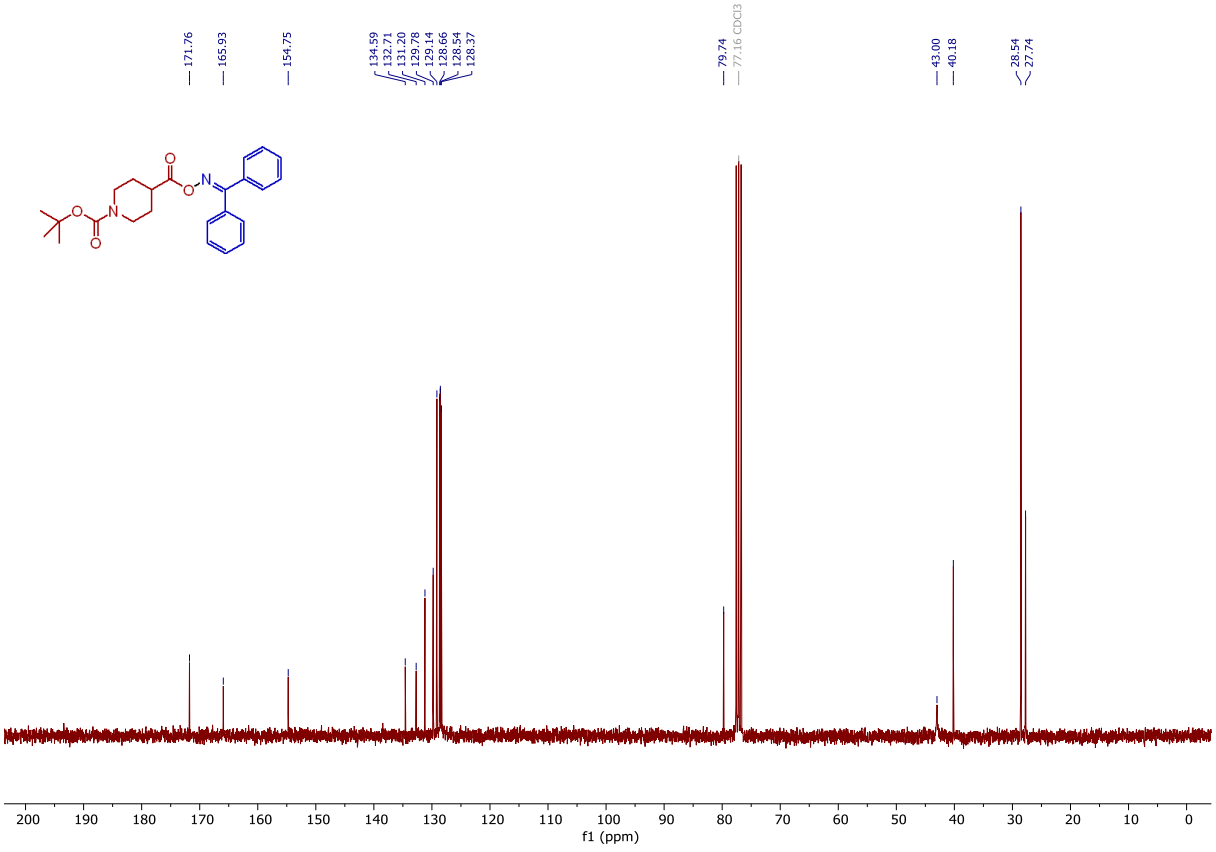
diphenylmethanone *O*-tetrahydro-2H-pyran-4-carbonyl oxime (S33)



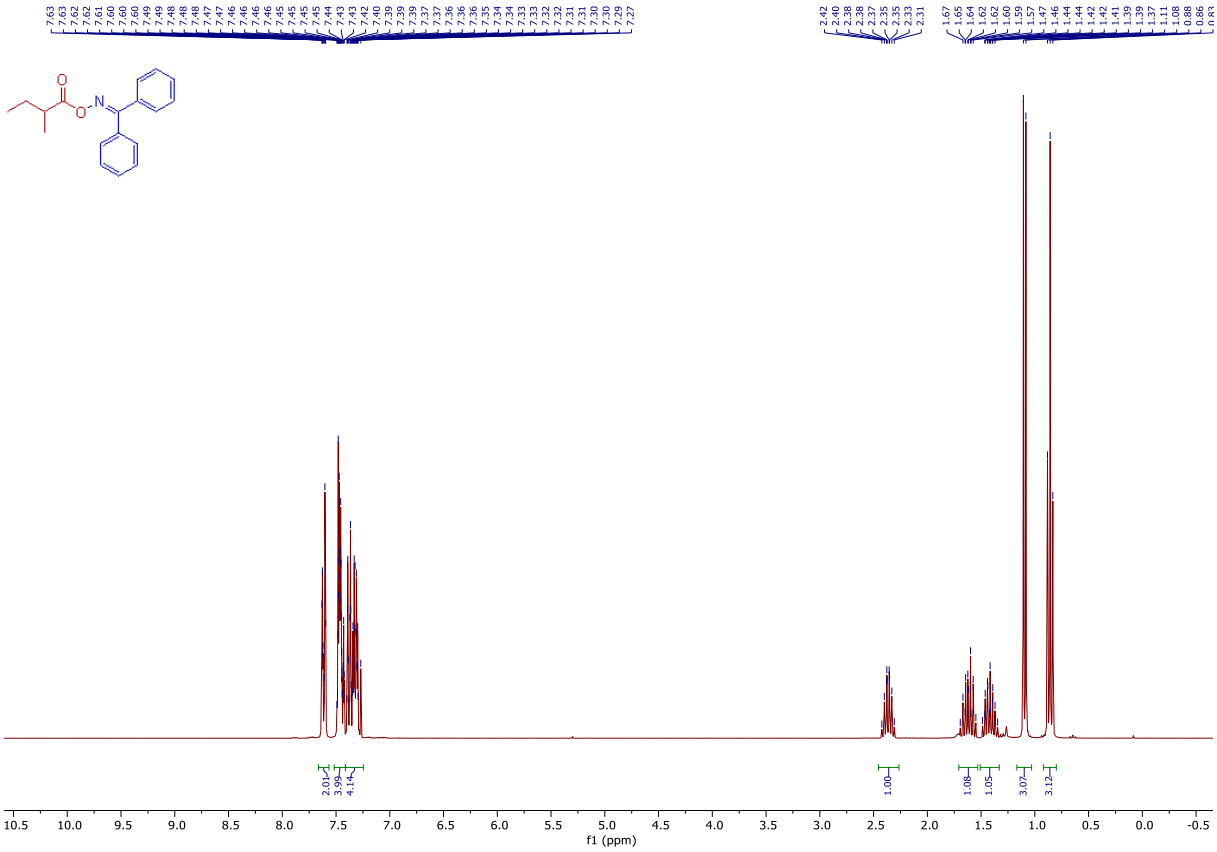


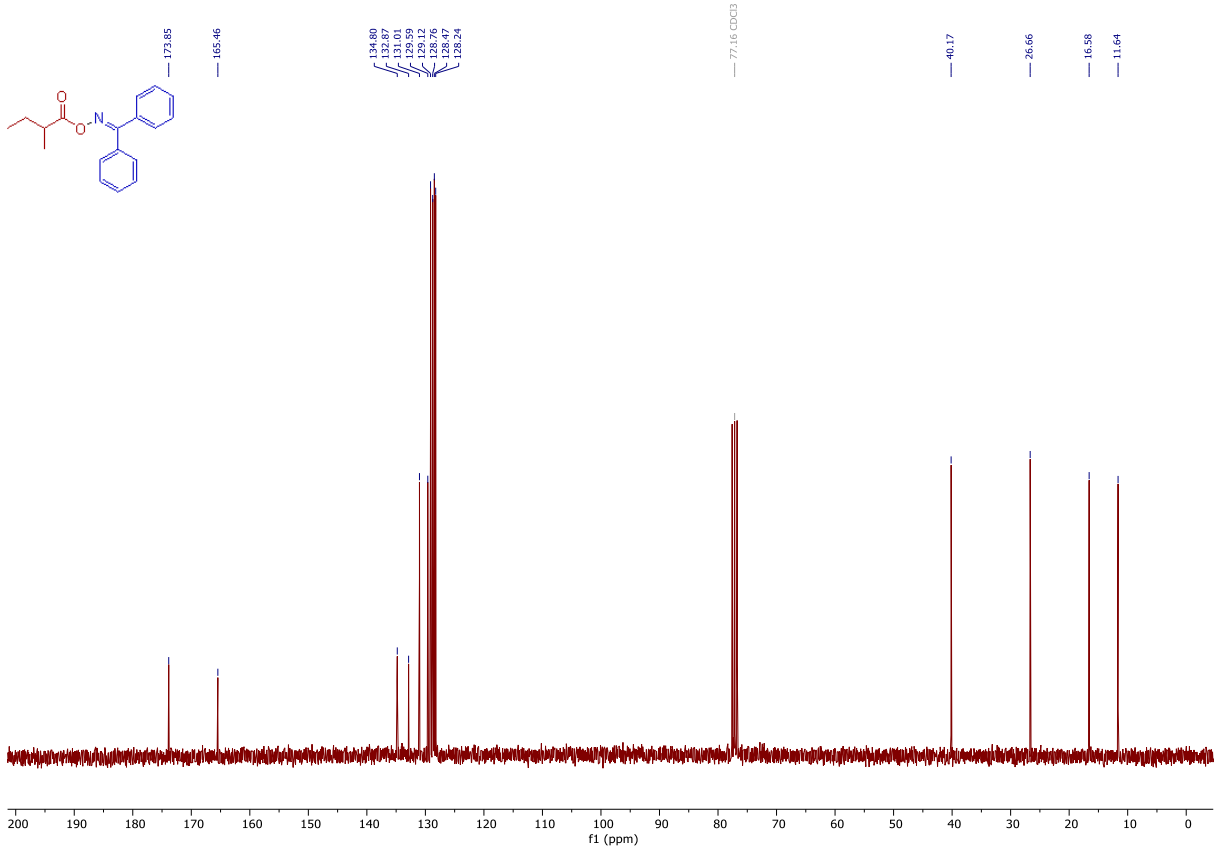
tert-butyl 4-((((diphenylmethylene)amino)oxy)carbonyl)piperidine-1-carboxylate (S34)



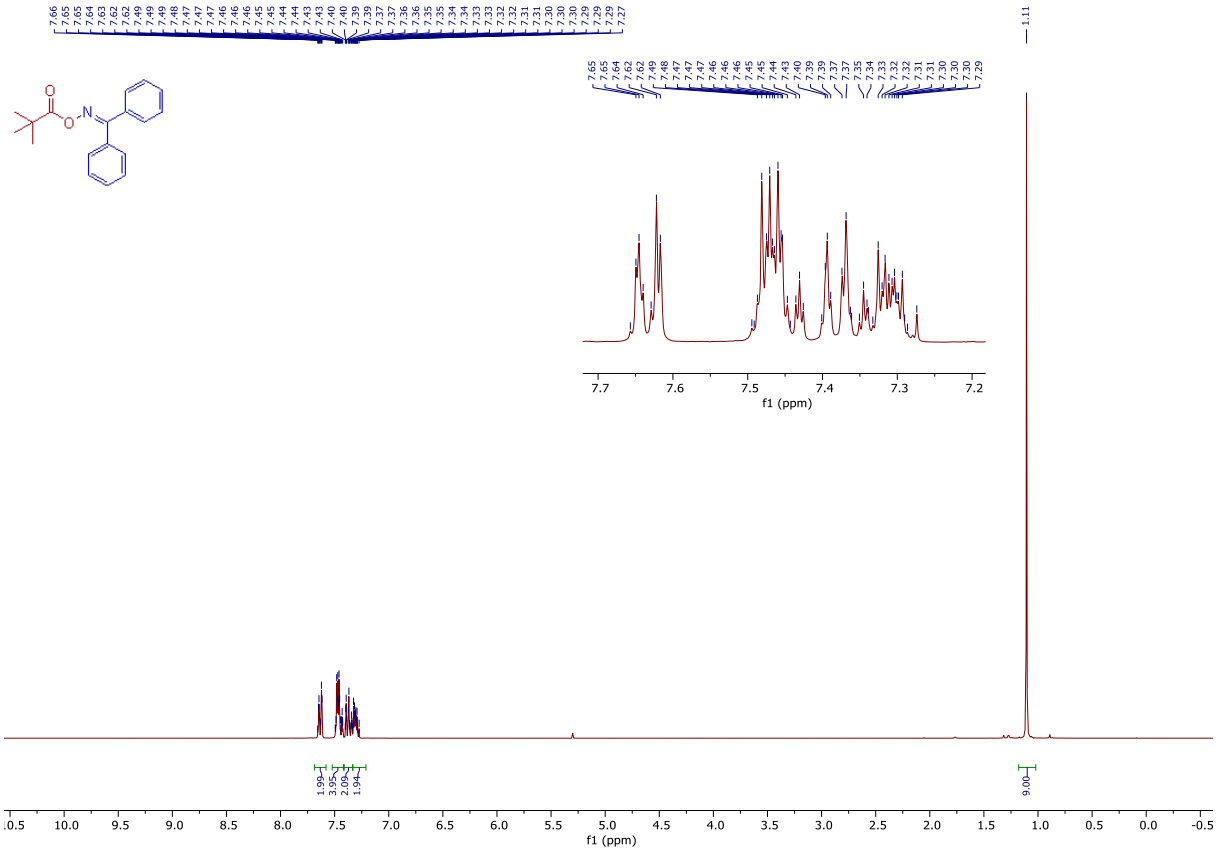


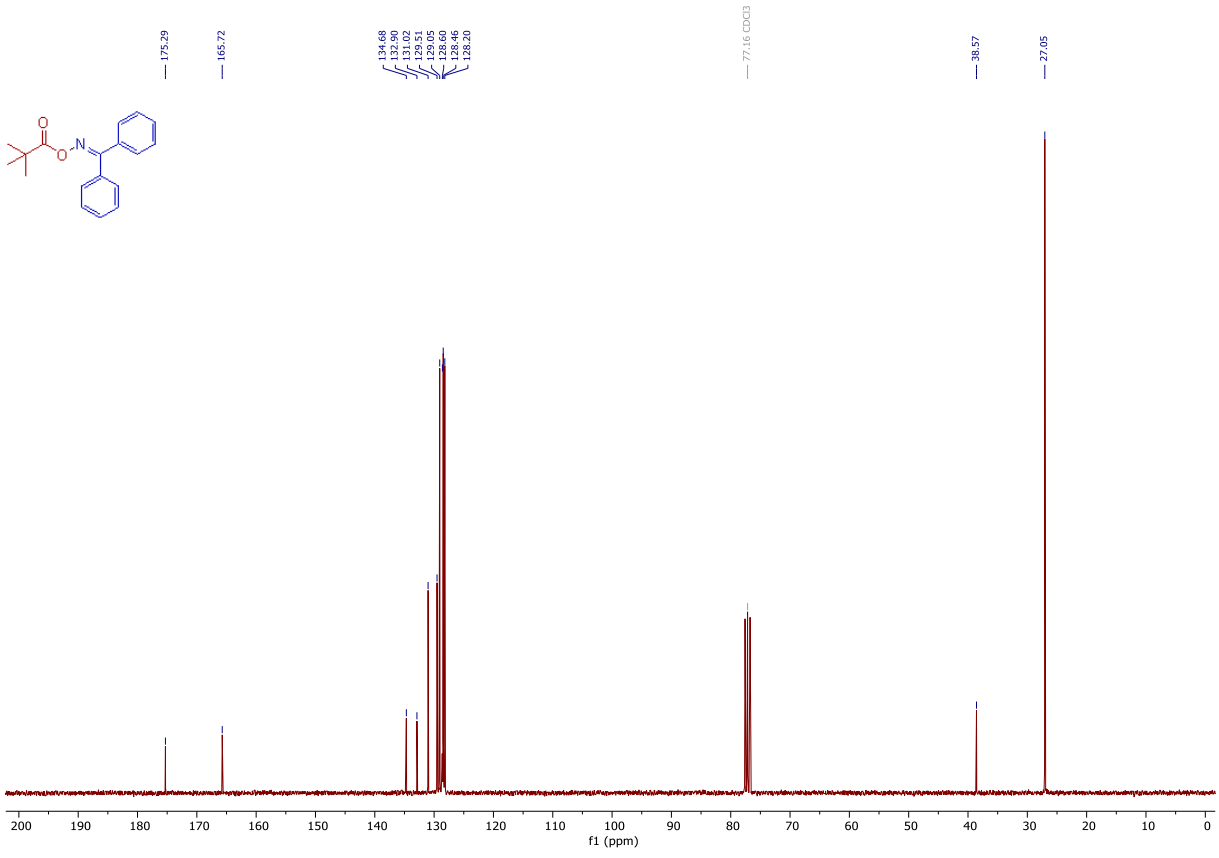
(±)-diphenylmethanone *O*-(2-methylbutanoyl) oxime (S35)



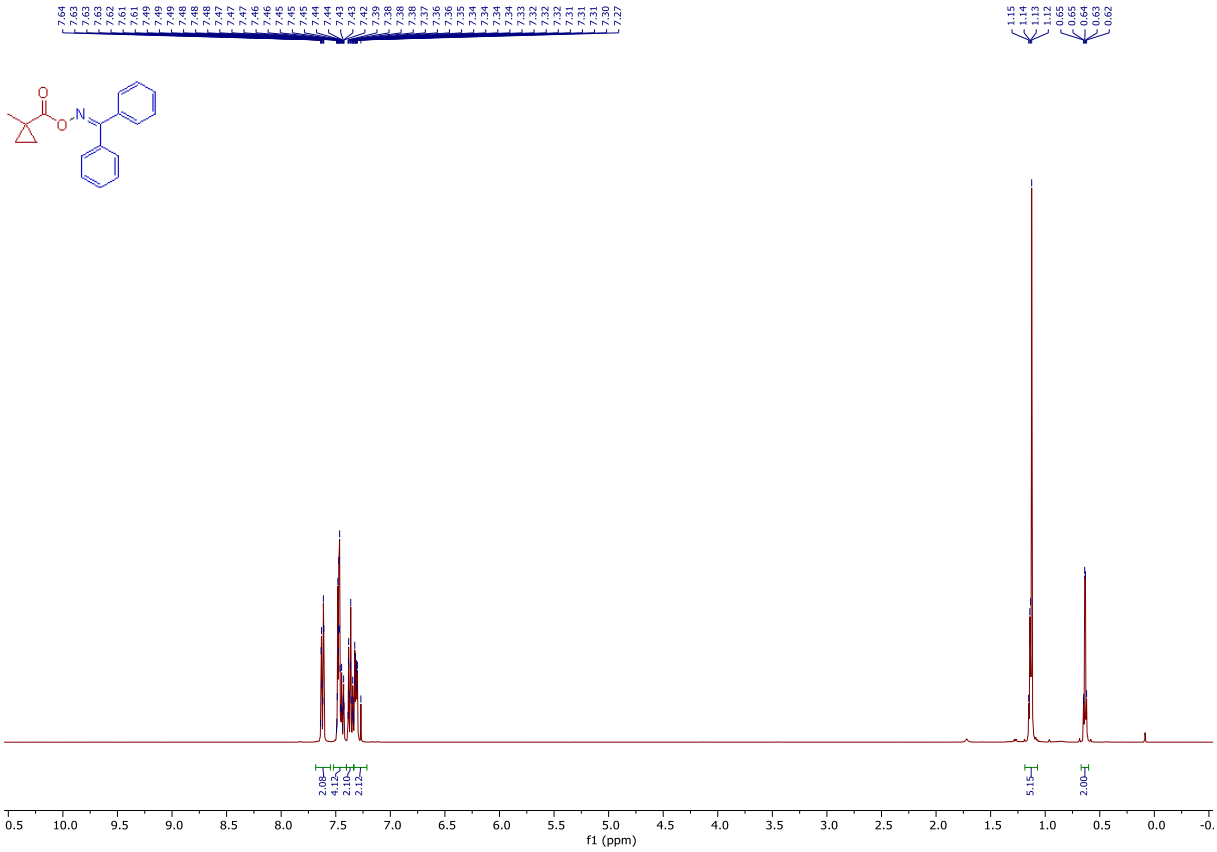


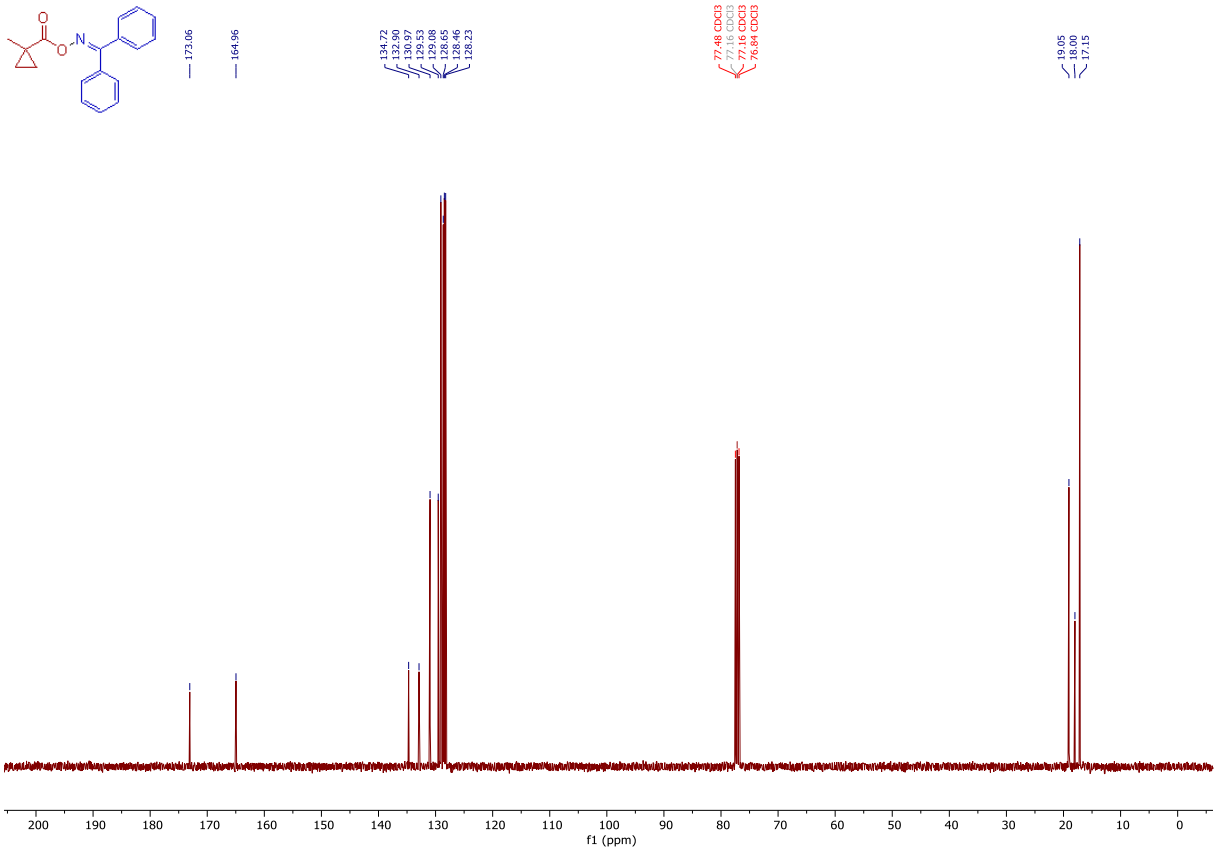
diphenylmethanone *O*-pivaloyl oxime (S36)



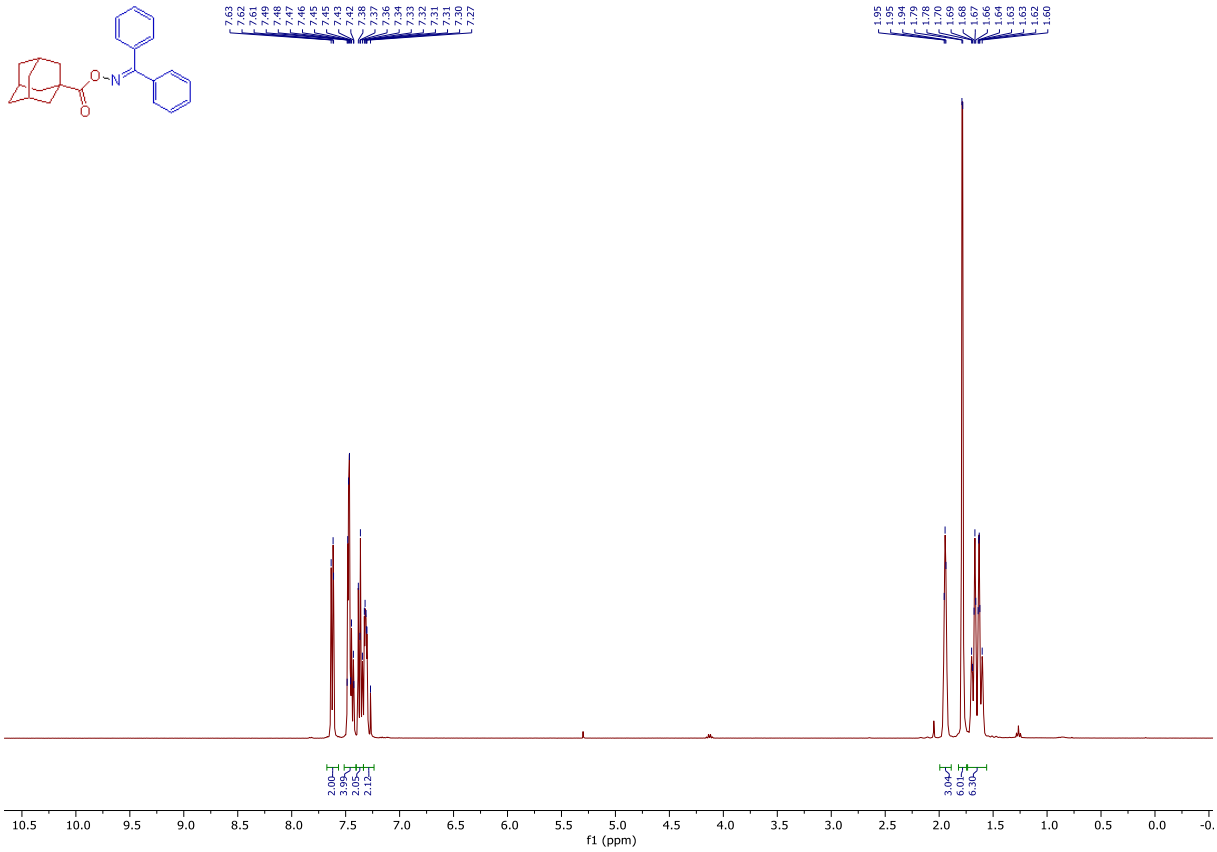


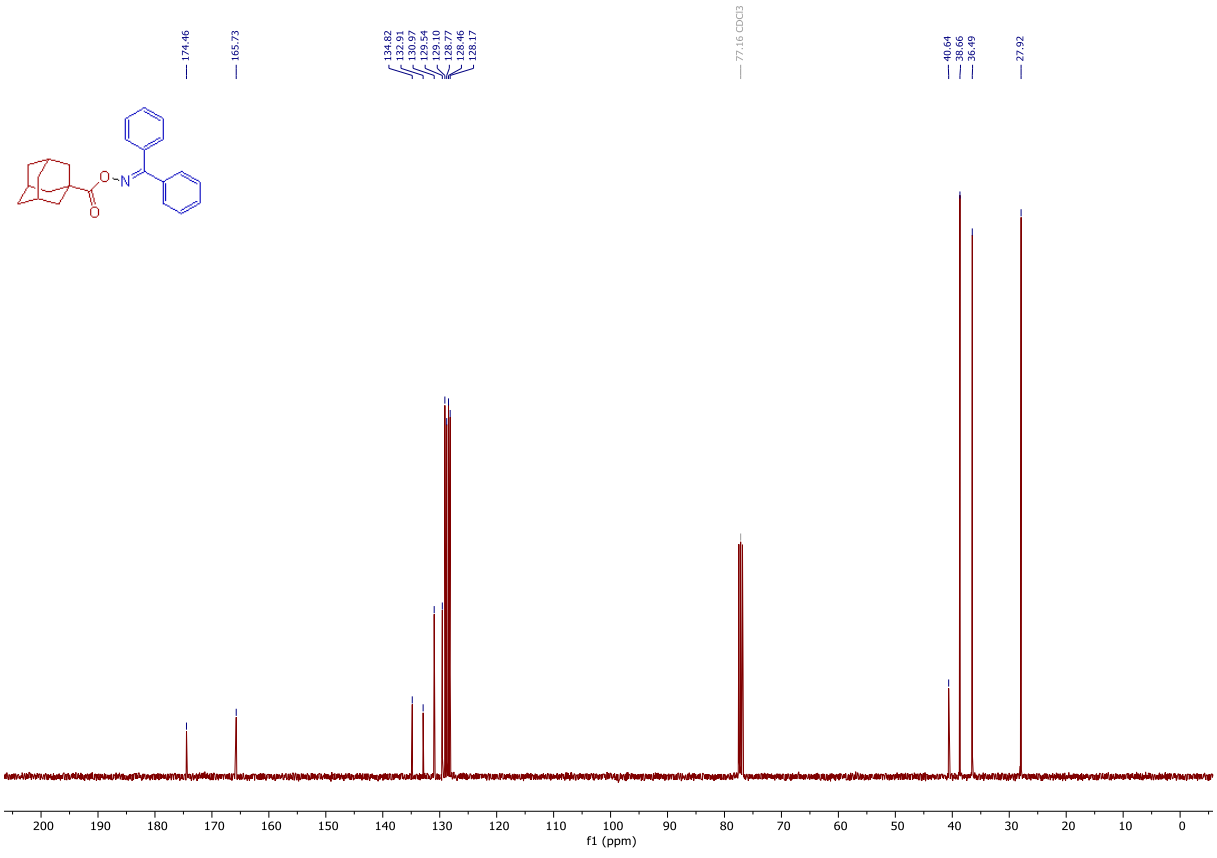
diphenylmethanone *O*-(1-methylcyclopropane-1-carbonyl) oxime (S37)



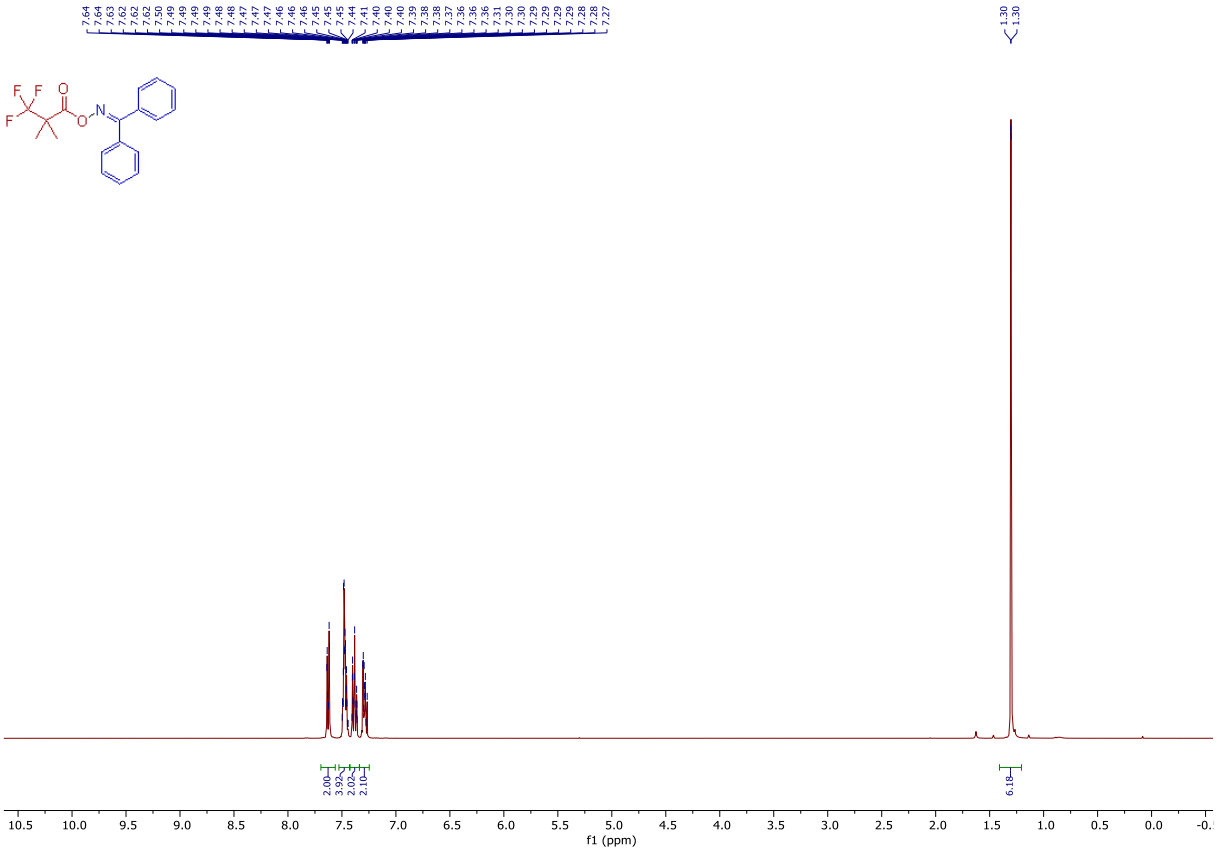


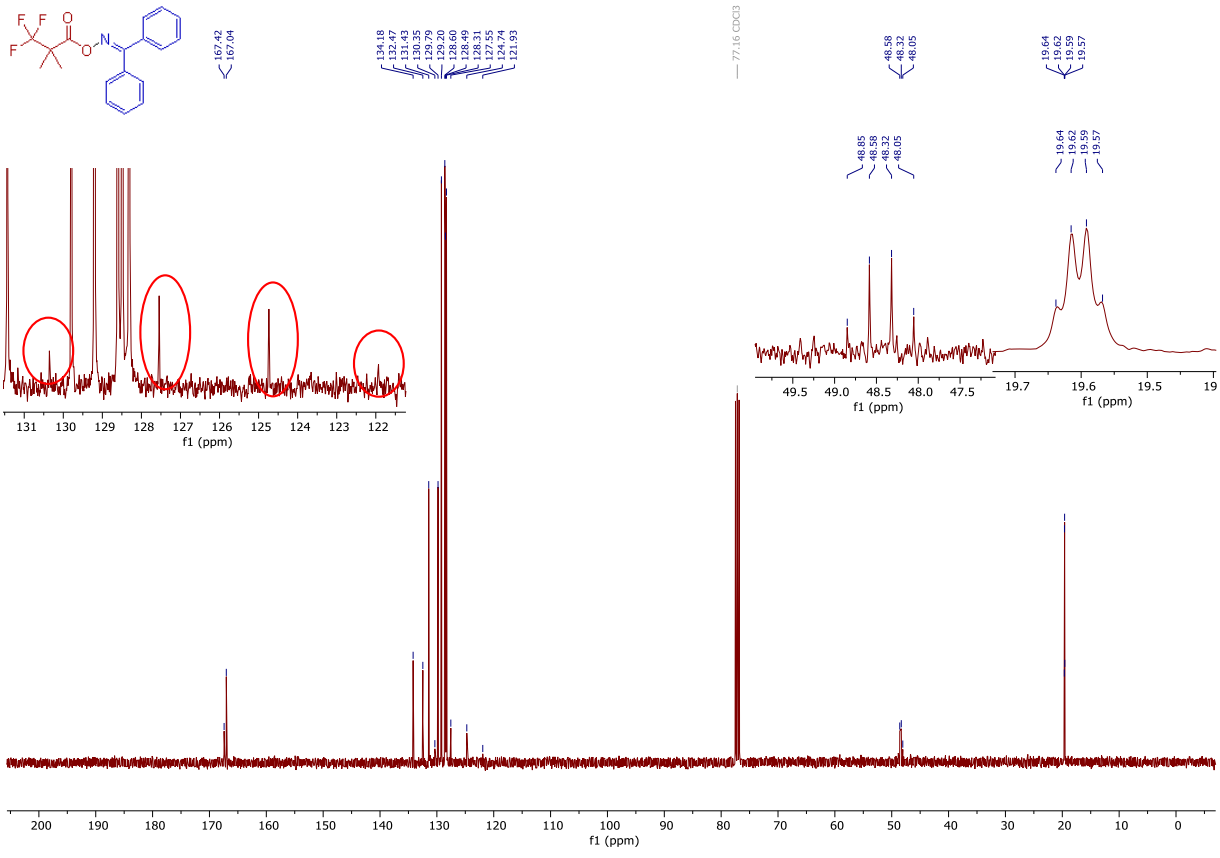
diphenylmethanone *O*-(adamantane-1-carbonyl) oxime (S38)

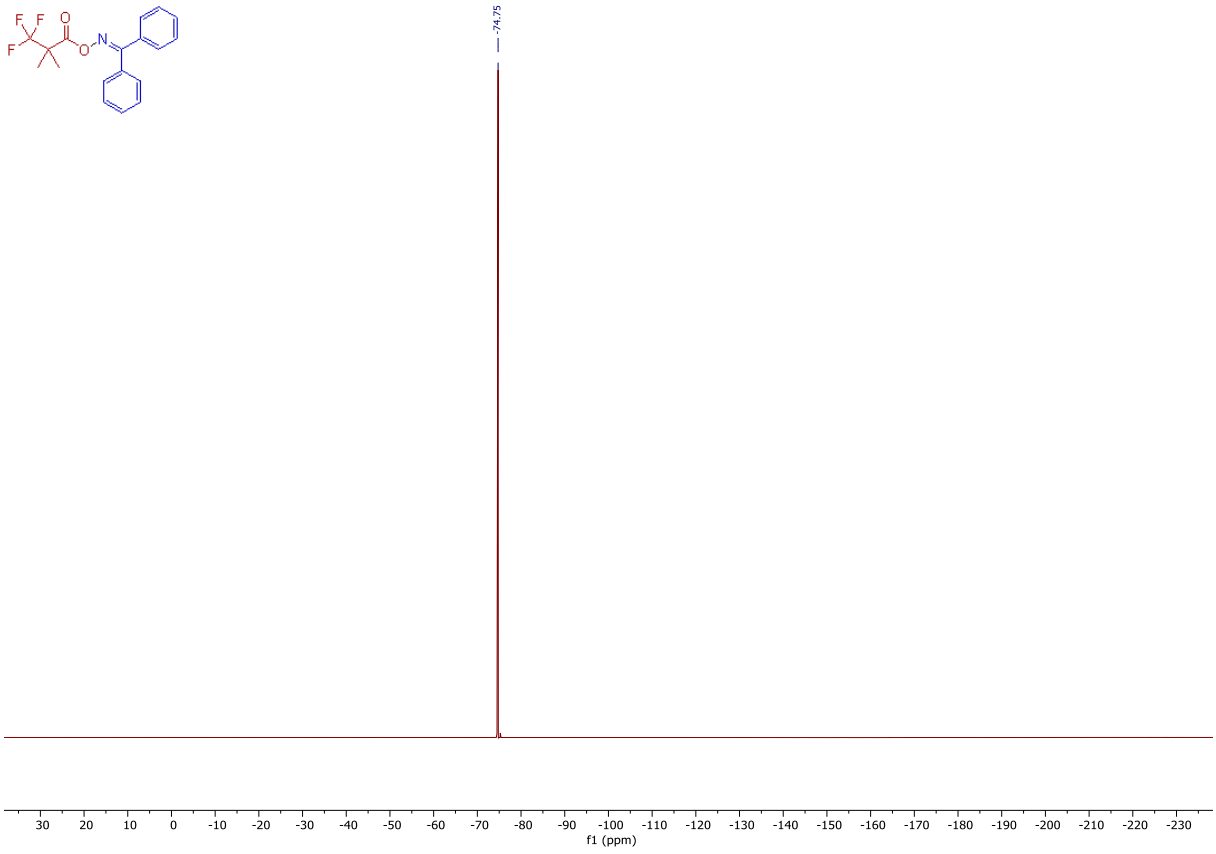




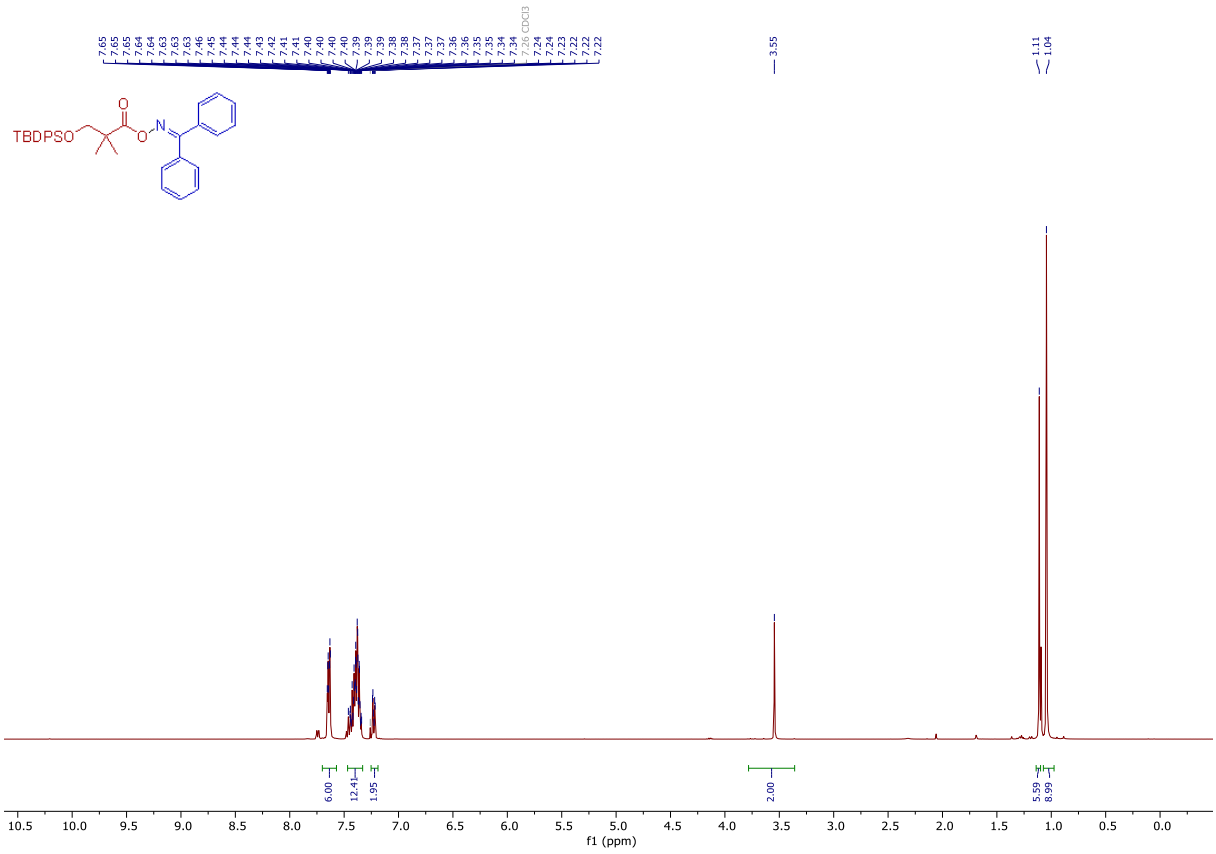
diphenylmethanone *O*-(3,3,3-trifluoro-2,2-dimethylpropanoyl) oxime (S39)

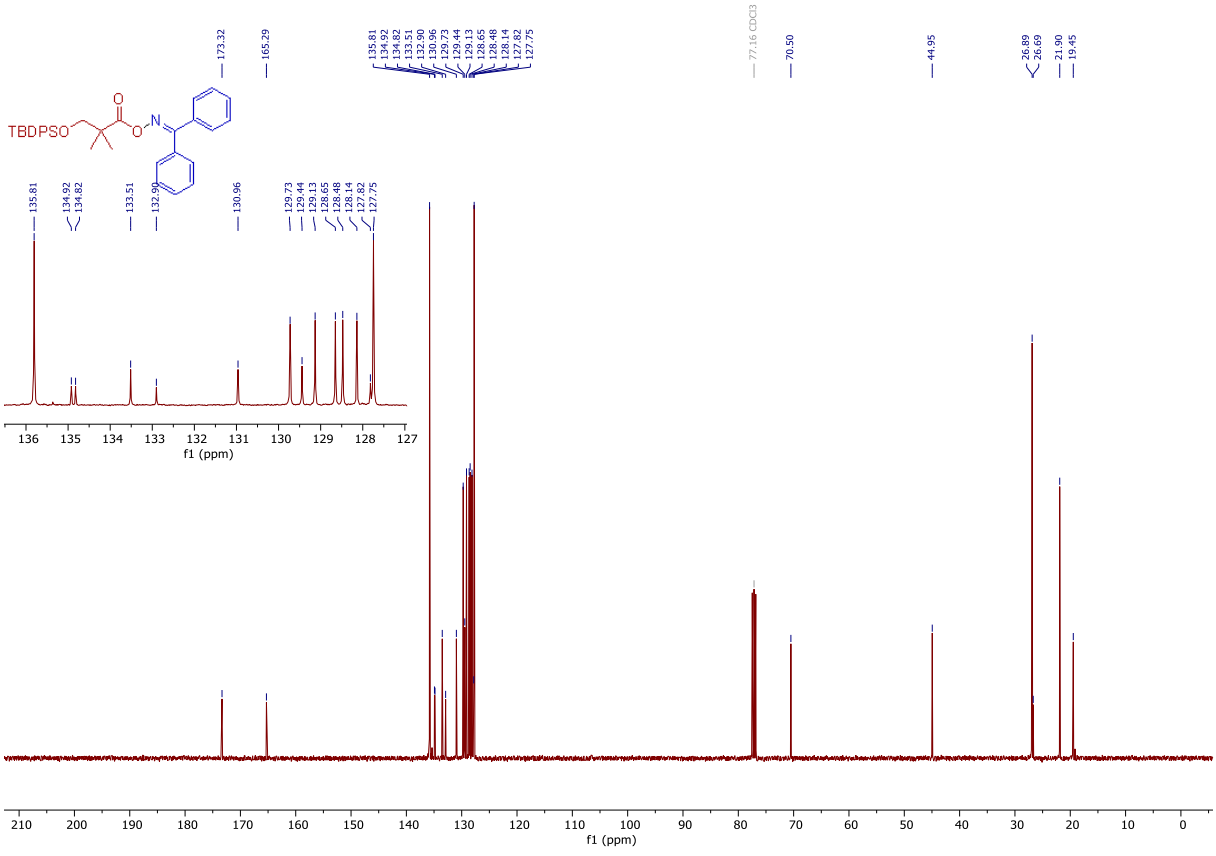




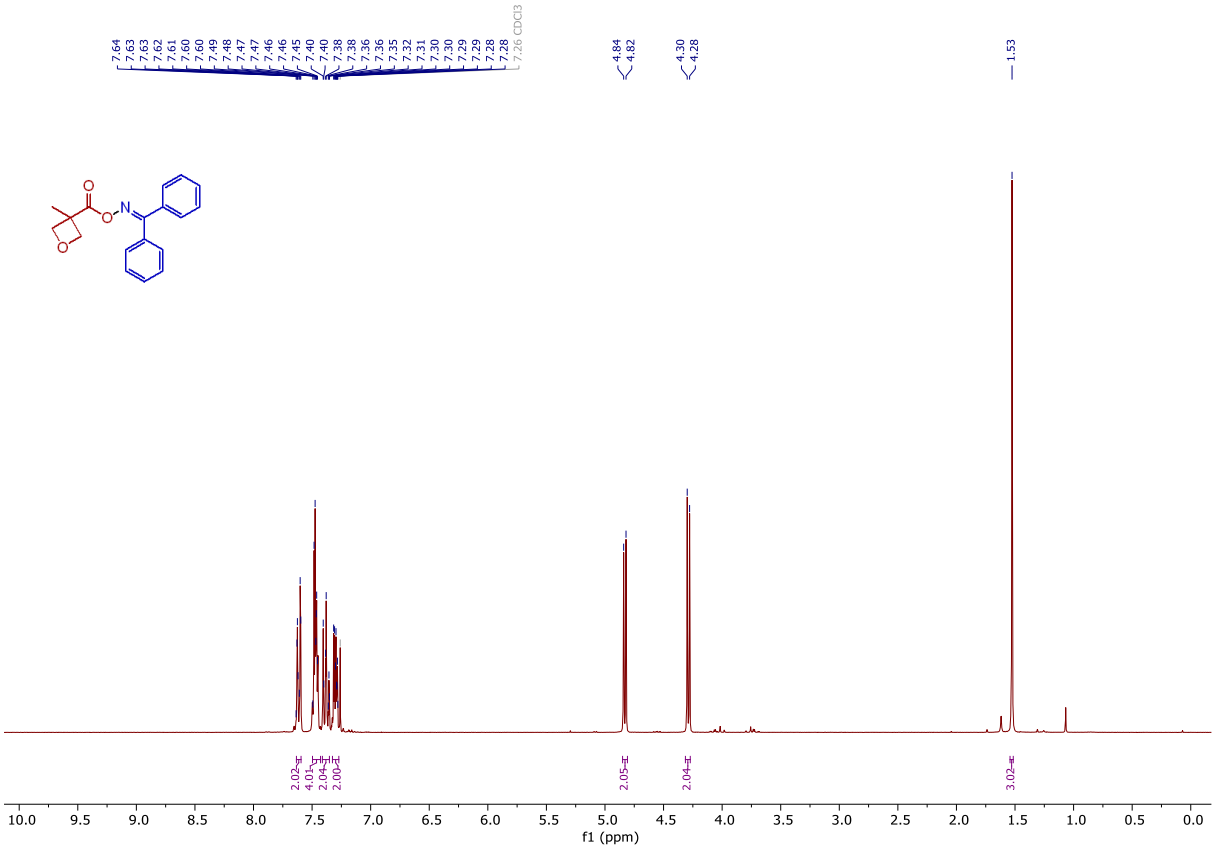

-74.75
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

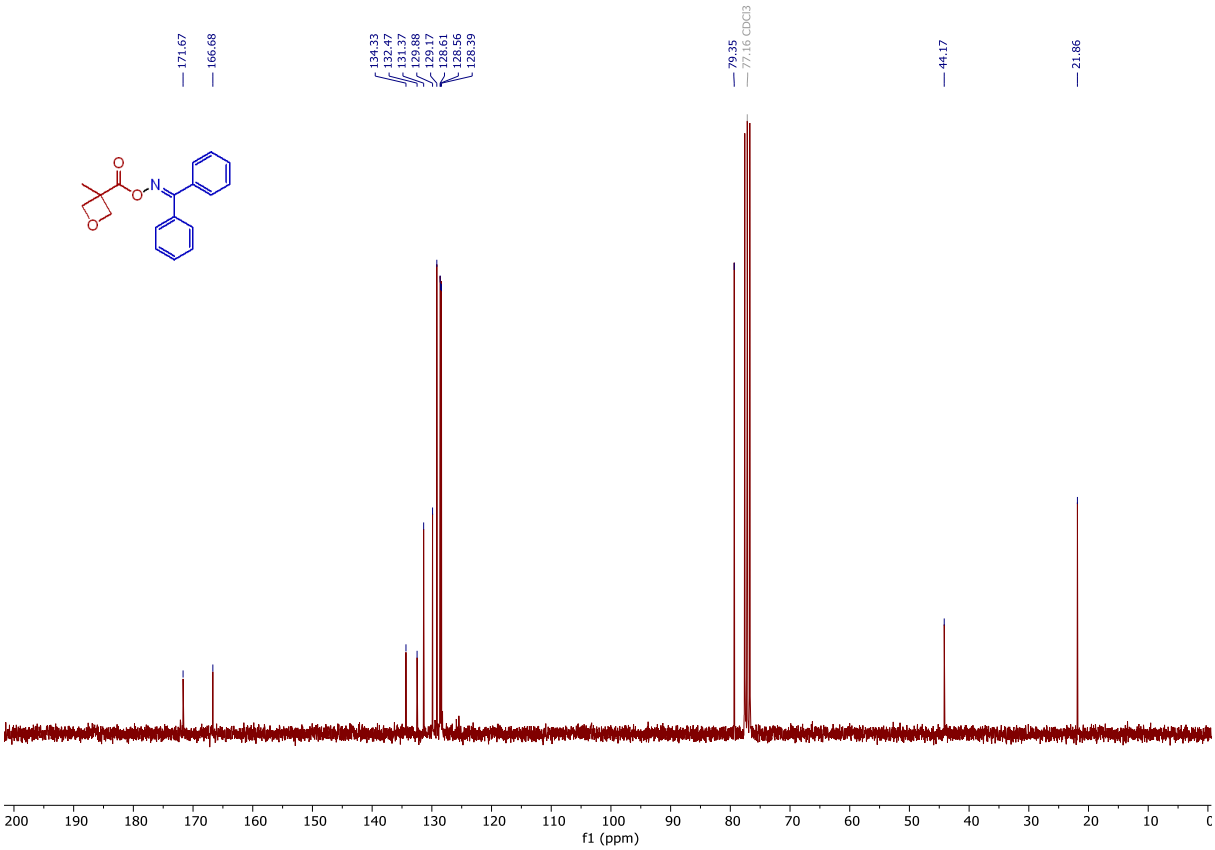
diphenylmethanone oxime (S40) ***O*-(3-((*tert*-butyldiphenylsilyl)oxy)-2,2-dimethylpropanoyl)**



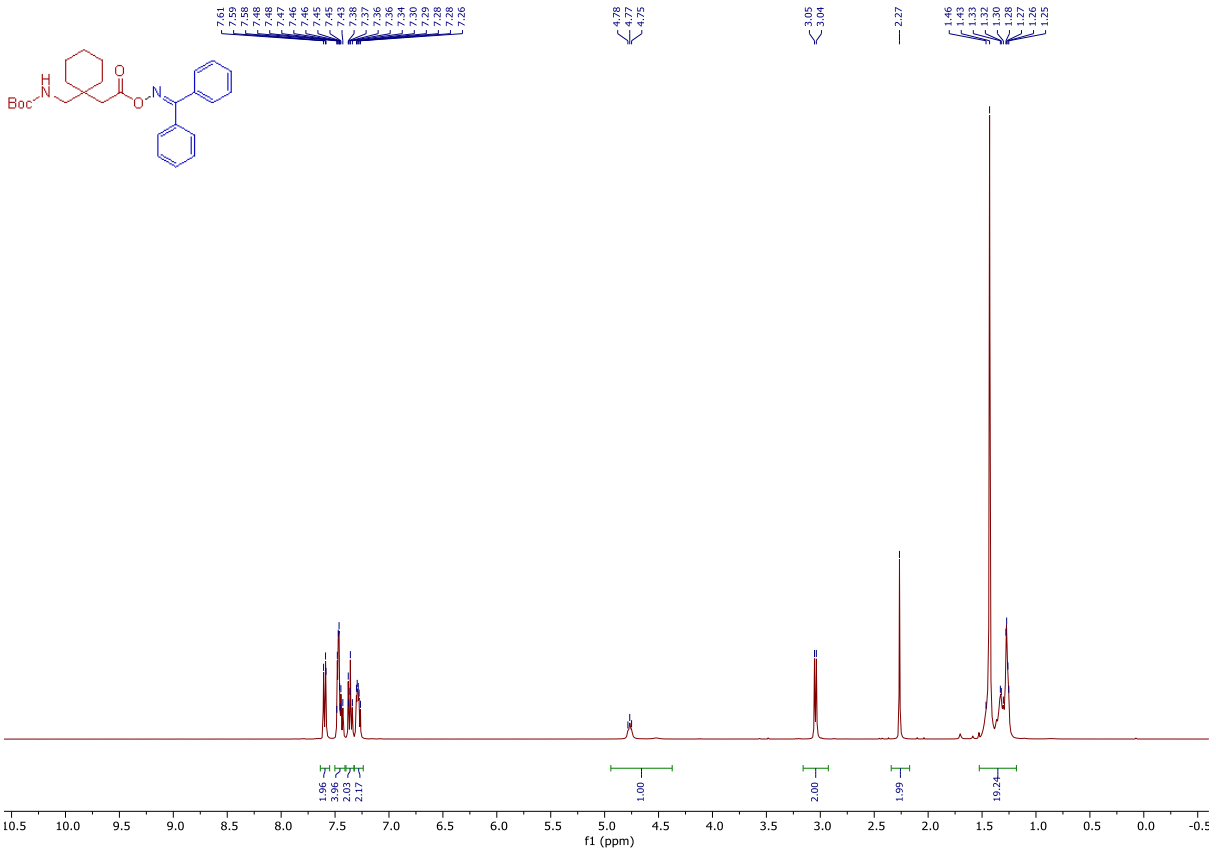


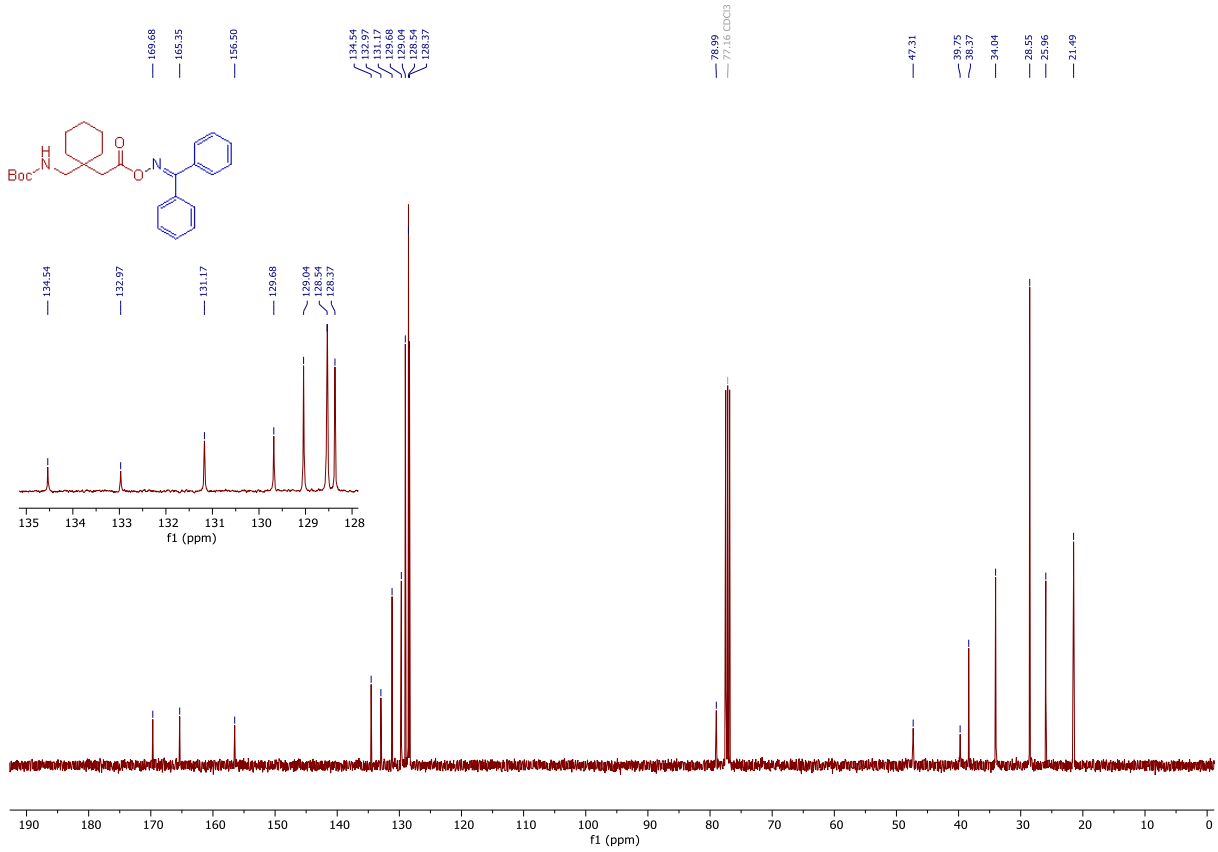
diphenylmethanone *O*-(3-methyloxetane-3-carbonyl) oxime (S41)



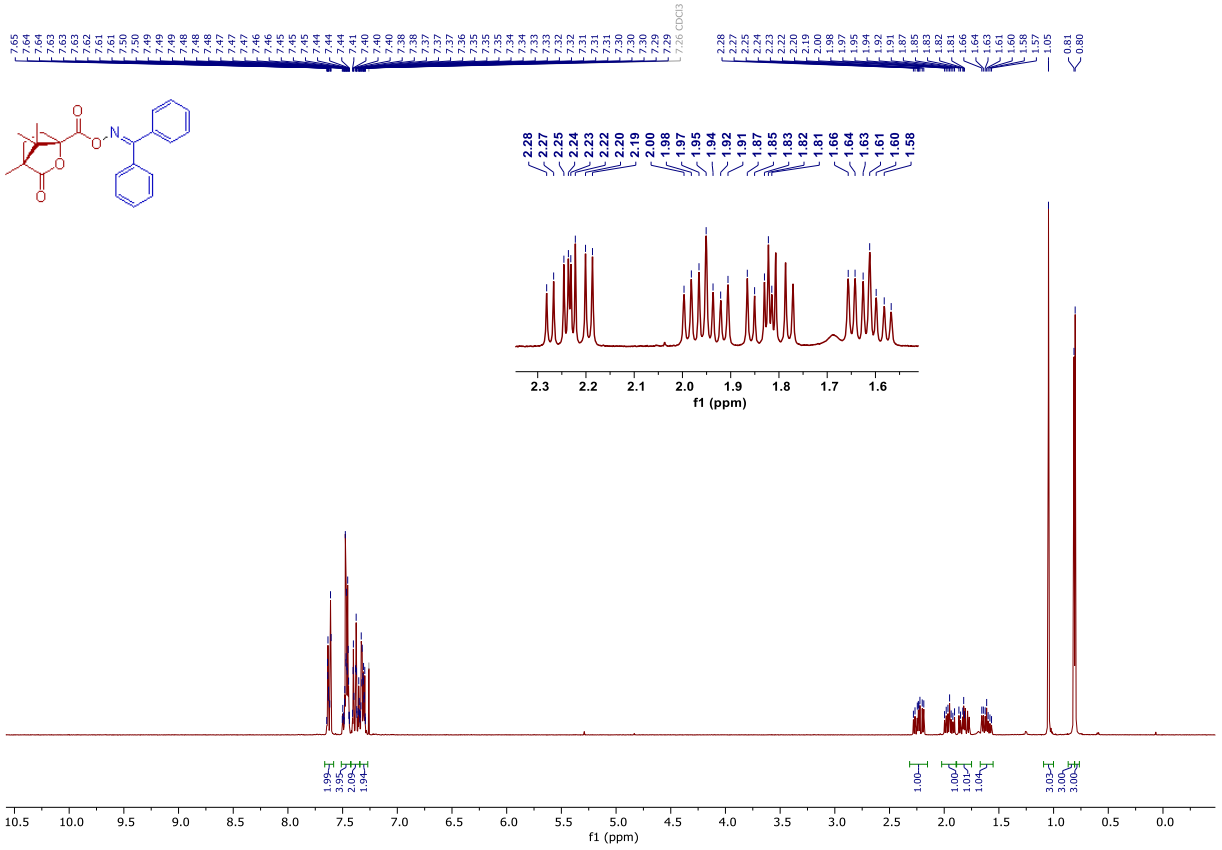


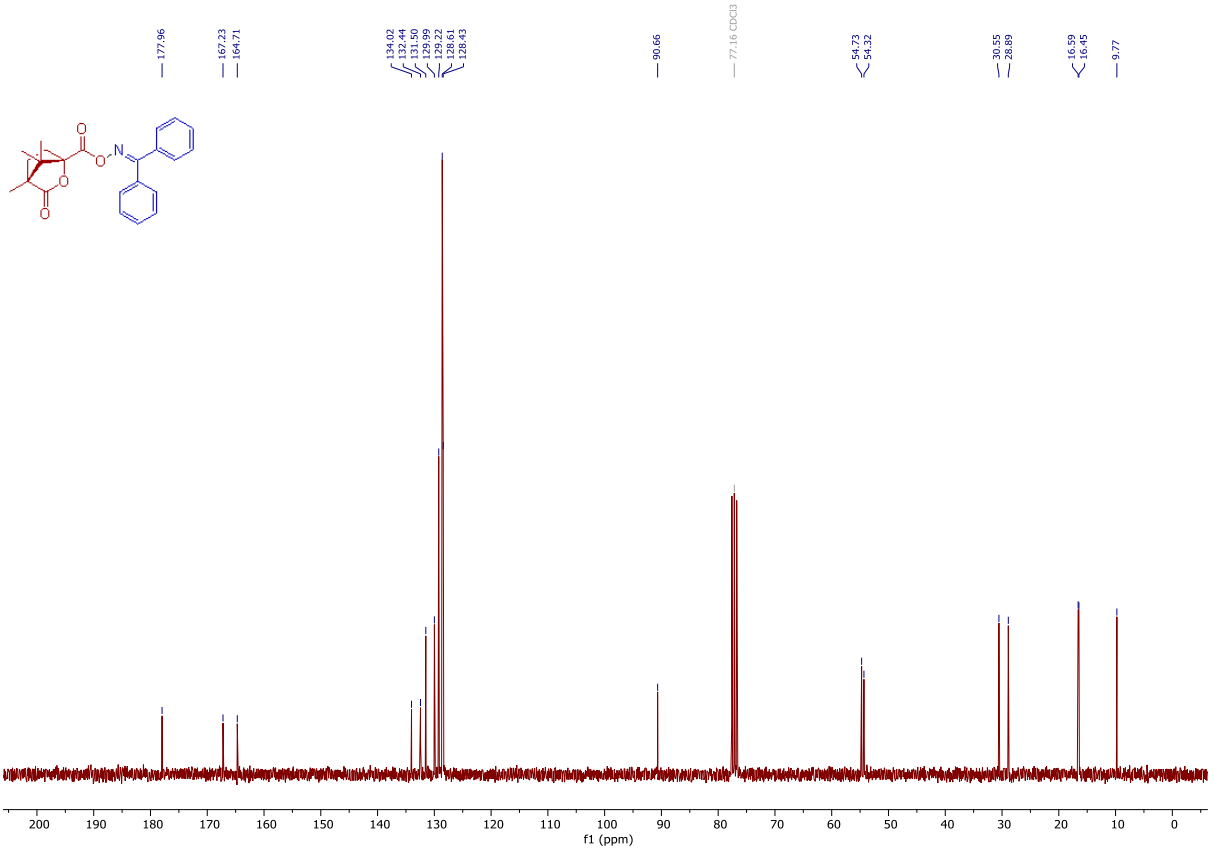
***tert*-butyl ((1-(2-(((diphenylmethylene)amino)oxy)-2-oxoethyl)cyclohexyl)methyl)carbamate (S42)**



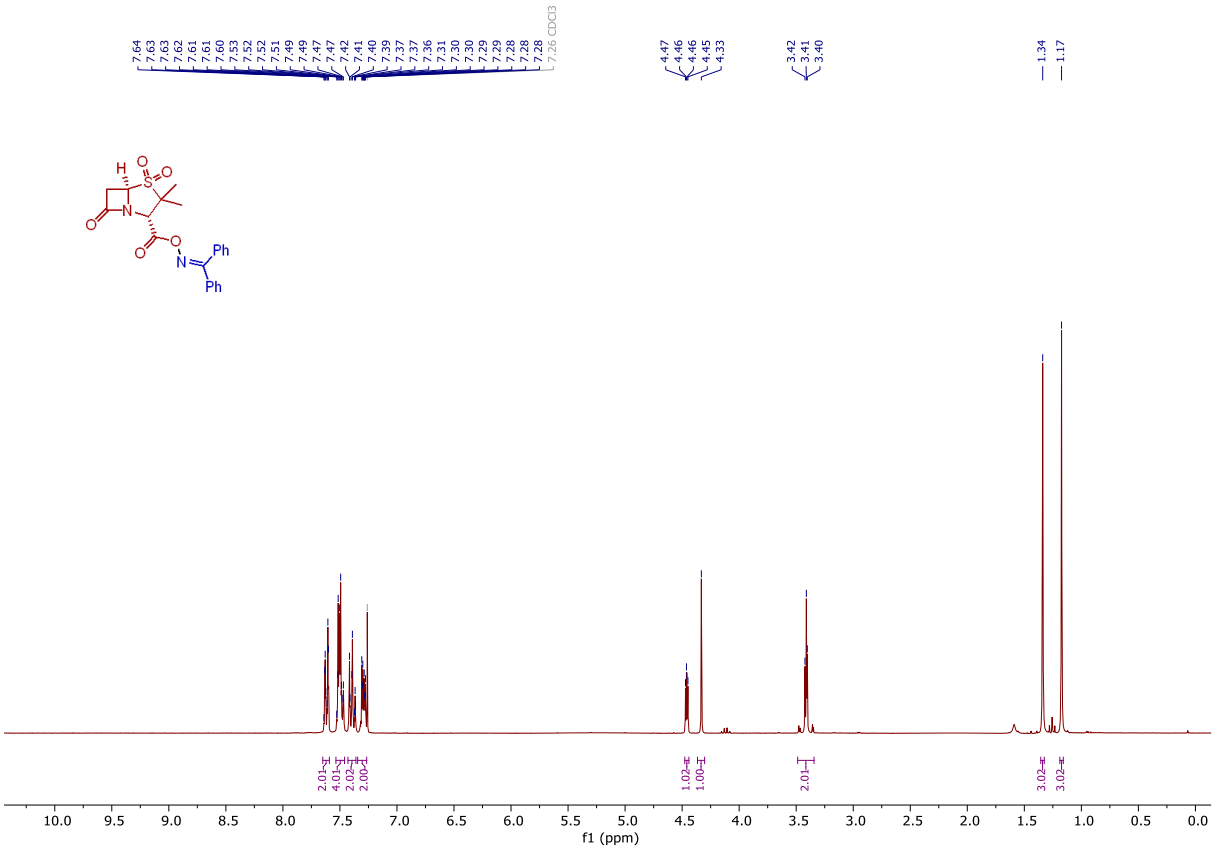


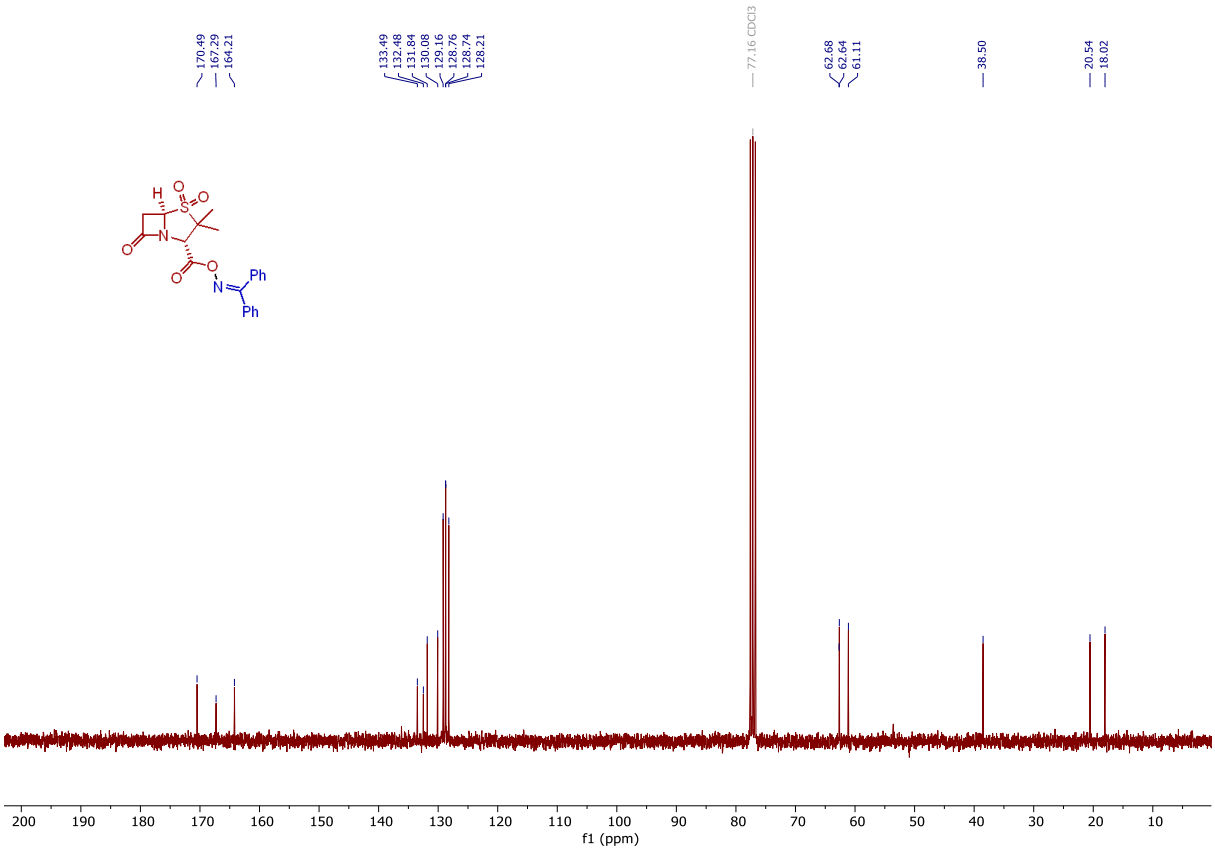
(1*S*,4*R*)-1-((((diphenylmethylene)amino)oxy)carbonyl)-4,7,7-trimethyl-2-oxabicyclo[2.2.1]heptan-3-one (S43)



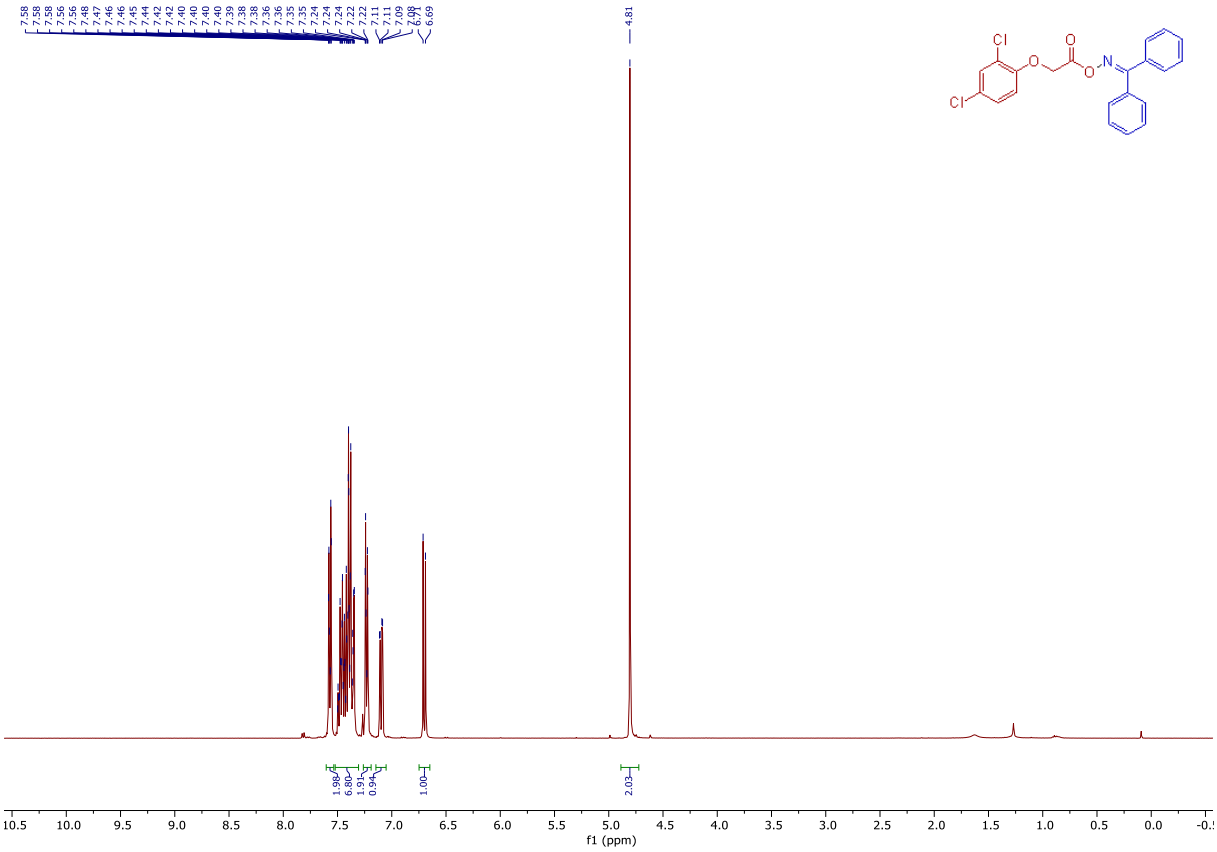


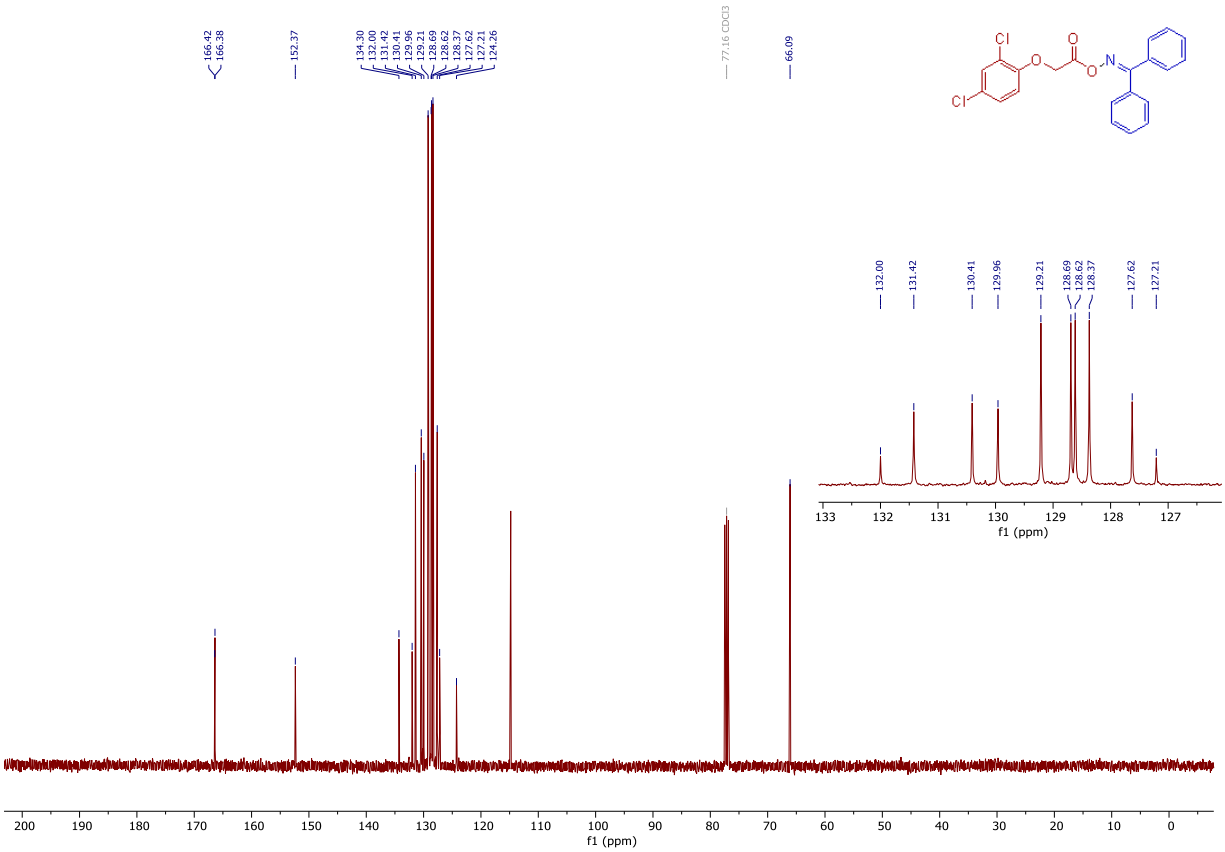
(2S,5R)-2-((((diphenylmethylene)amino)oxy)carbonyl)-3,3-dimethyl-4-thia-1-azabicyclo[3.2.0]heptan-7-one 4,4-dioxide (S44)



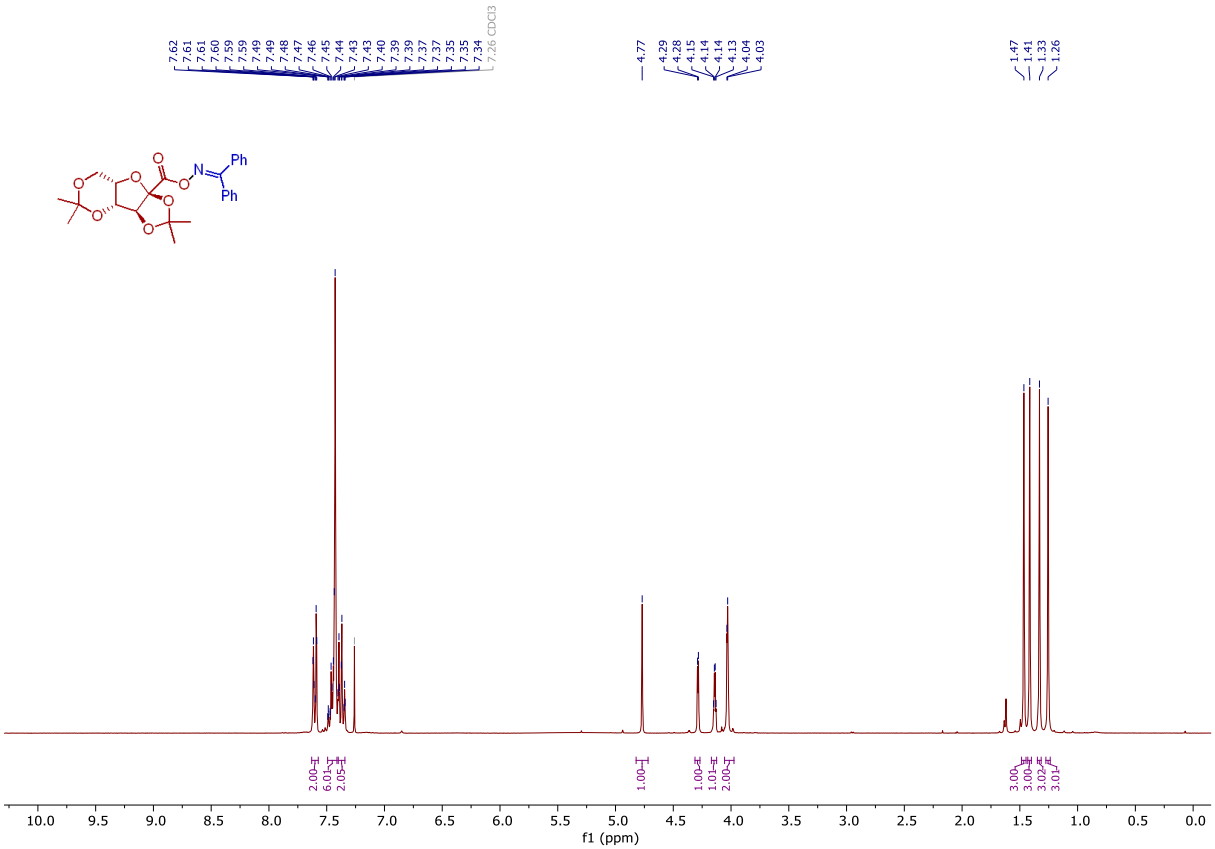


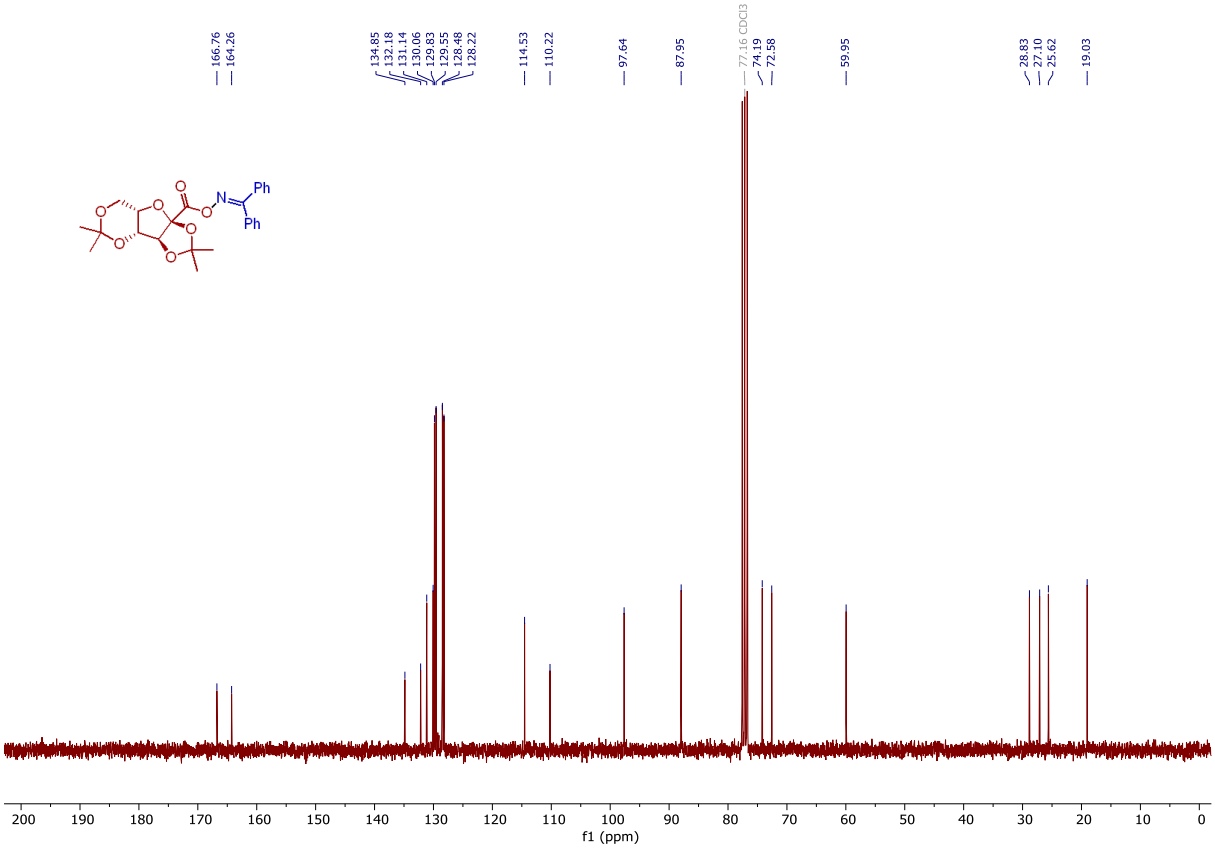
diphenylmethanone *O*-(2-(2,4-dichlorophenoxy)acetyl) oxime (S45)



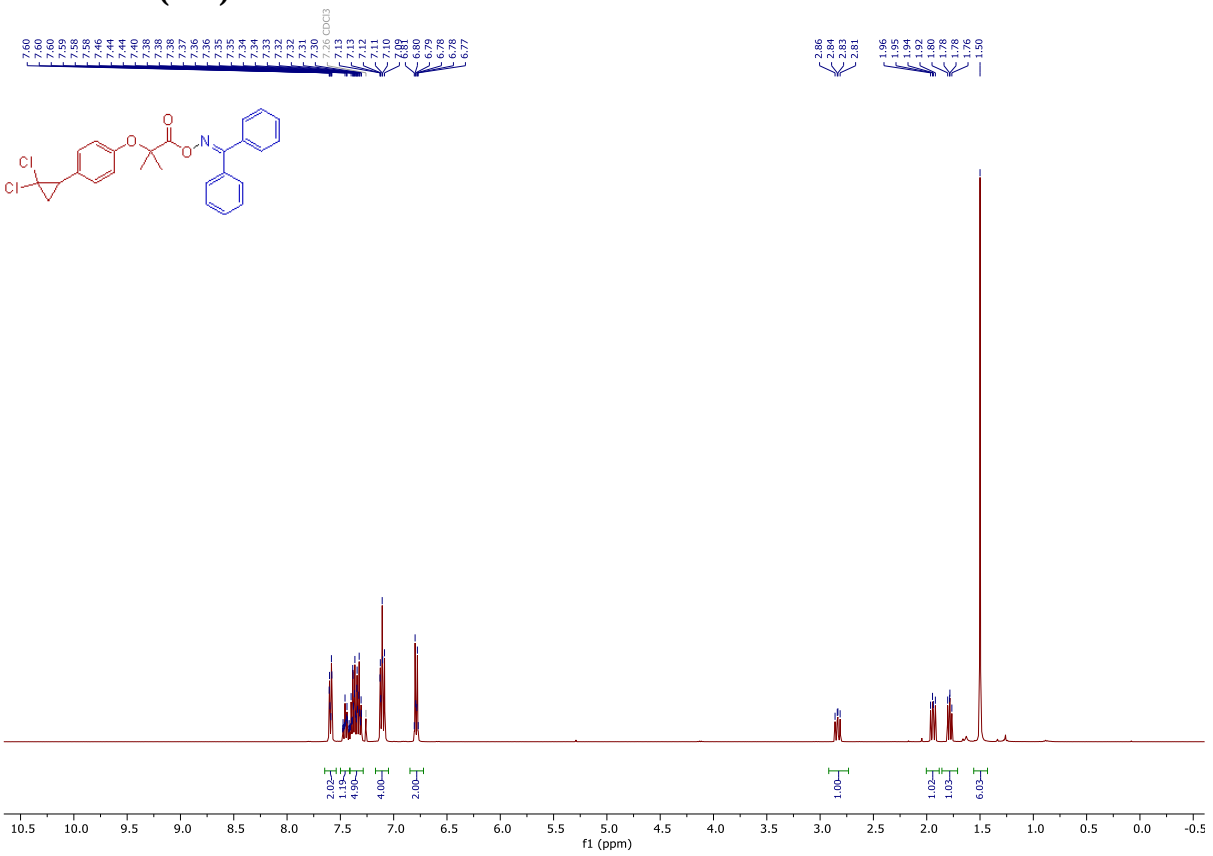


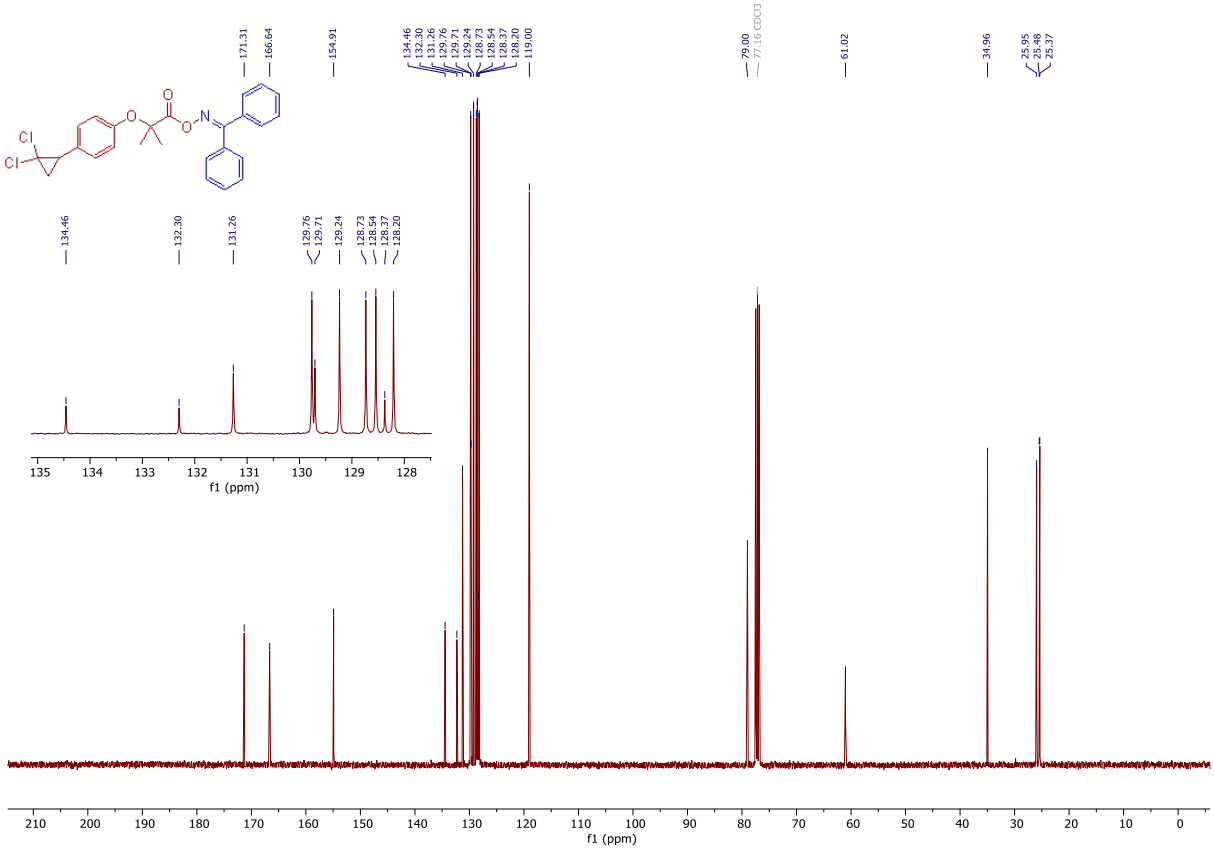
diphenylmethanone *O*-((3a*S*,3b*R*,7a*S*,8a*R*)-2,2,5,5-tetramethyltetrahydro-7*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxine-8a-carbonyl) oxime (S46)



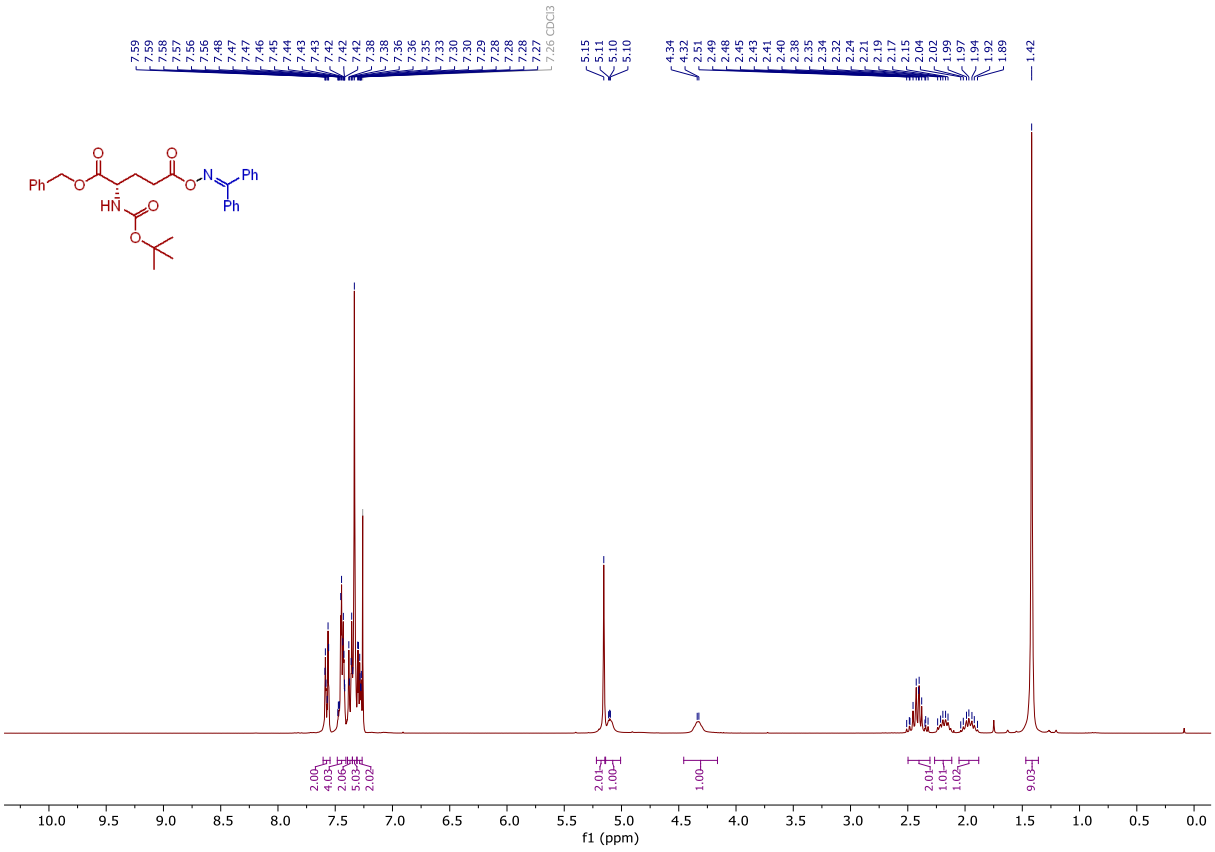


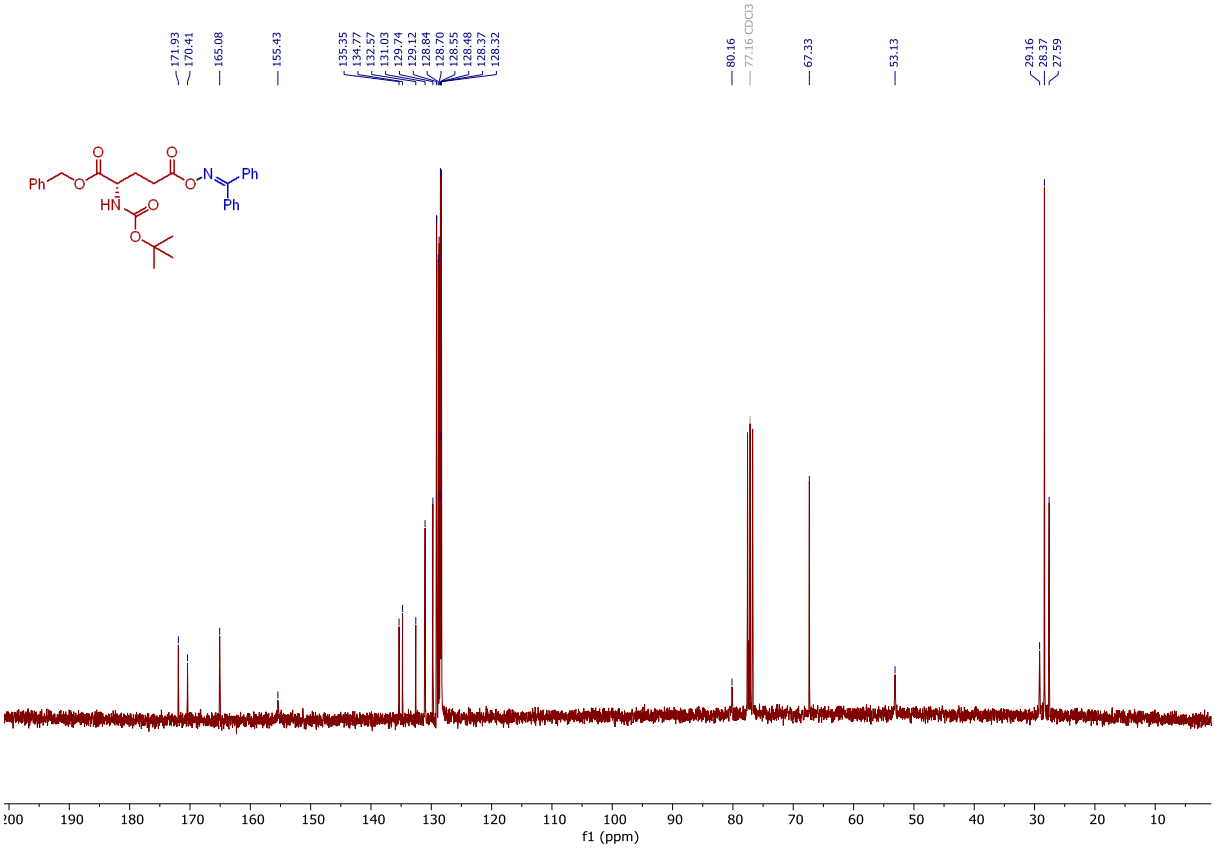
diphenylmethanone *O*-(2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoyl) oxime (S47):



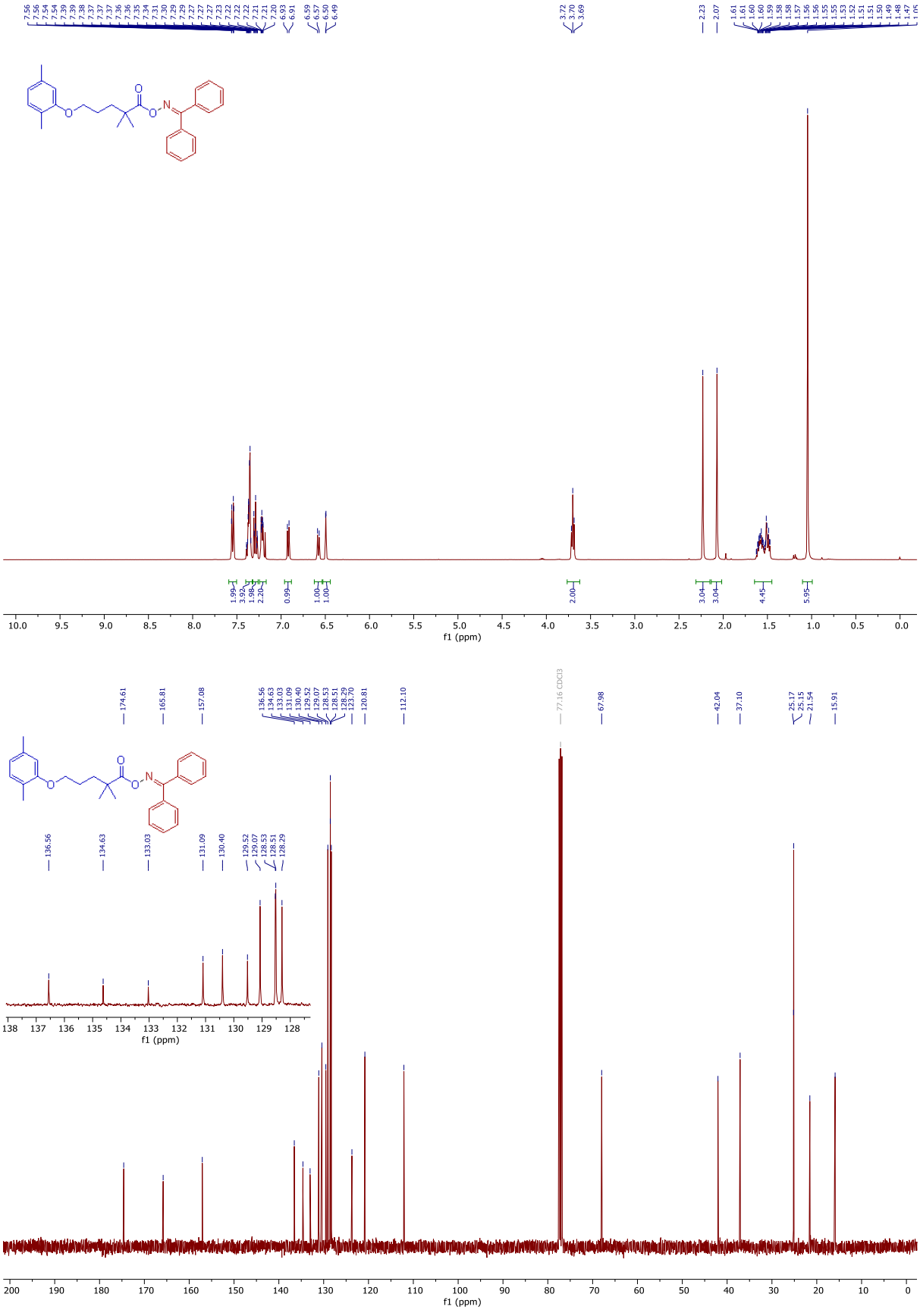


benzyl (*S*)-2-((tert-butoxycarbonyl)amino)-5-((((diphenylmethylene)amino)oxy)-5-oxopentanoate (S48)

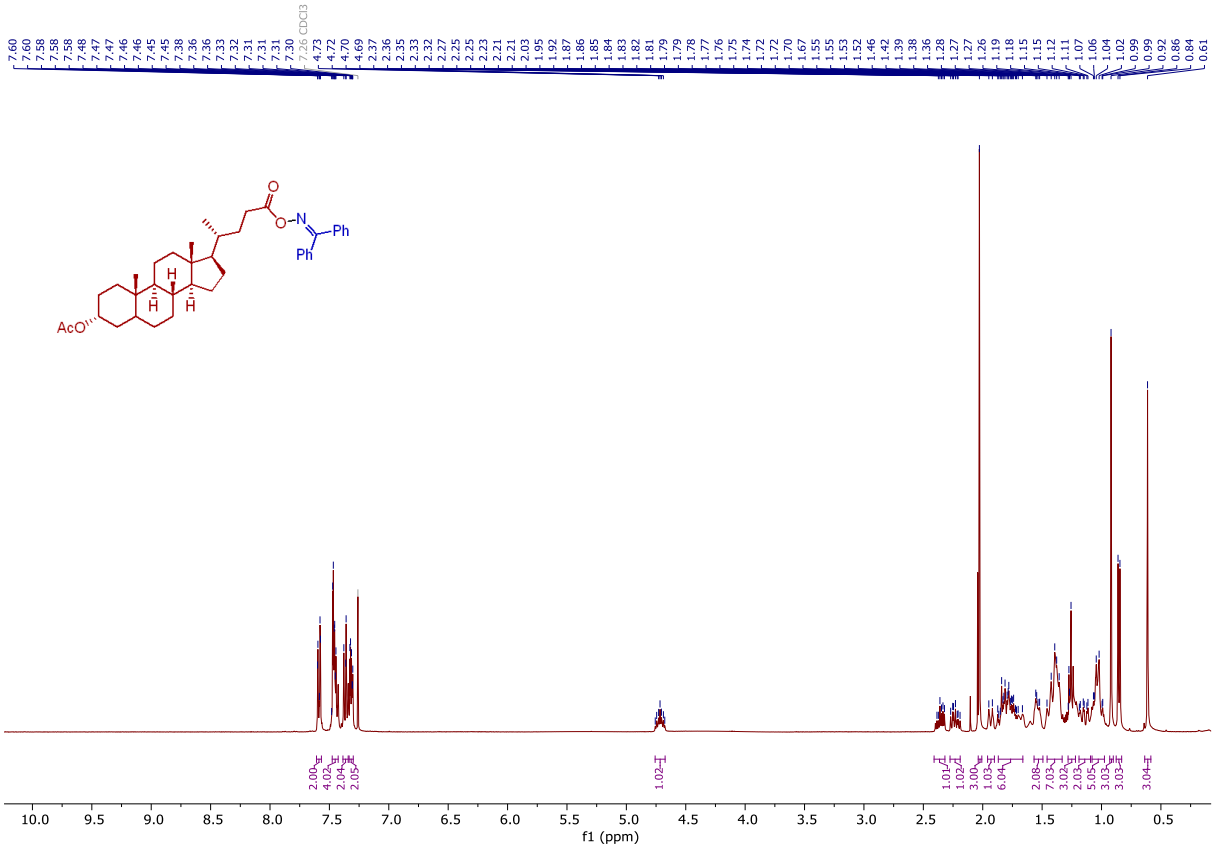


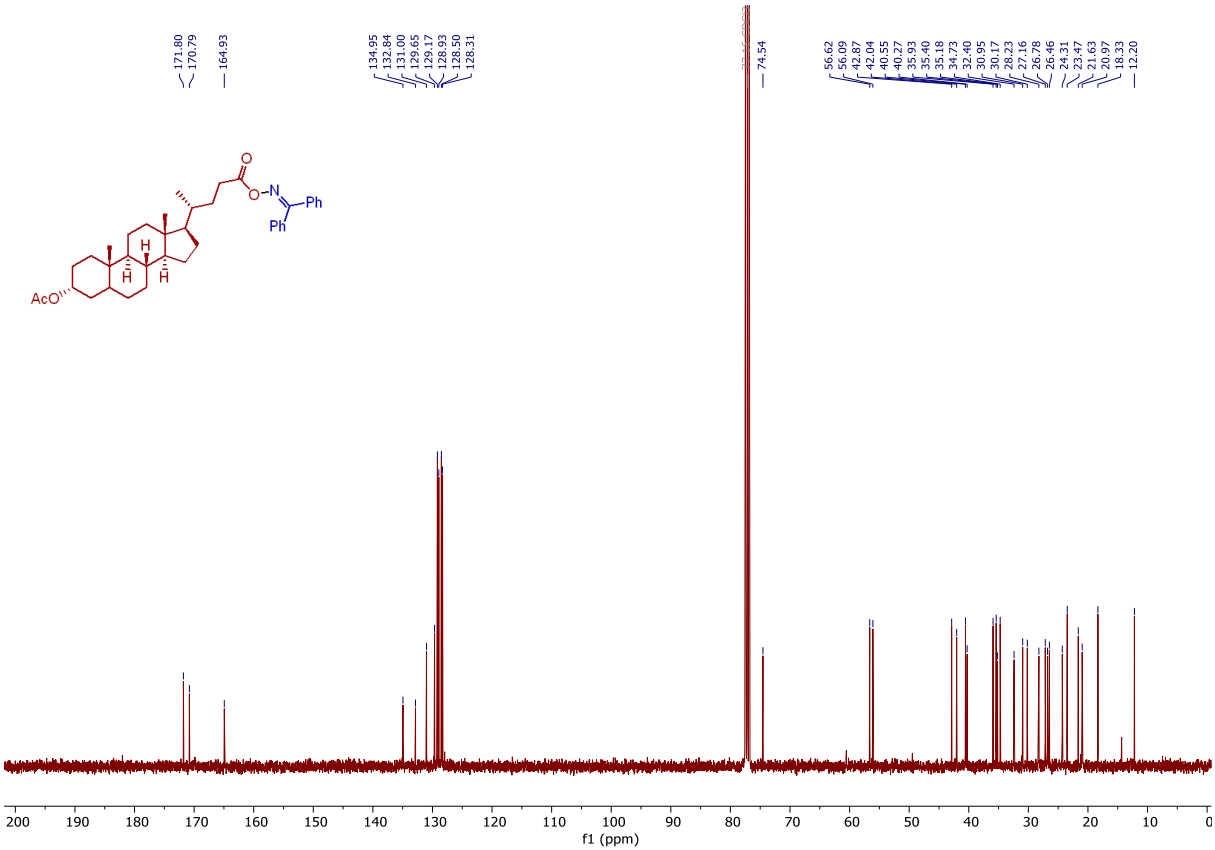


diphenylmethanone *O*-(5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl) oxime (S49)

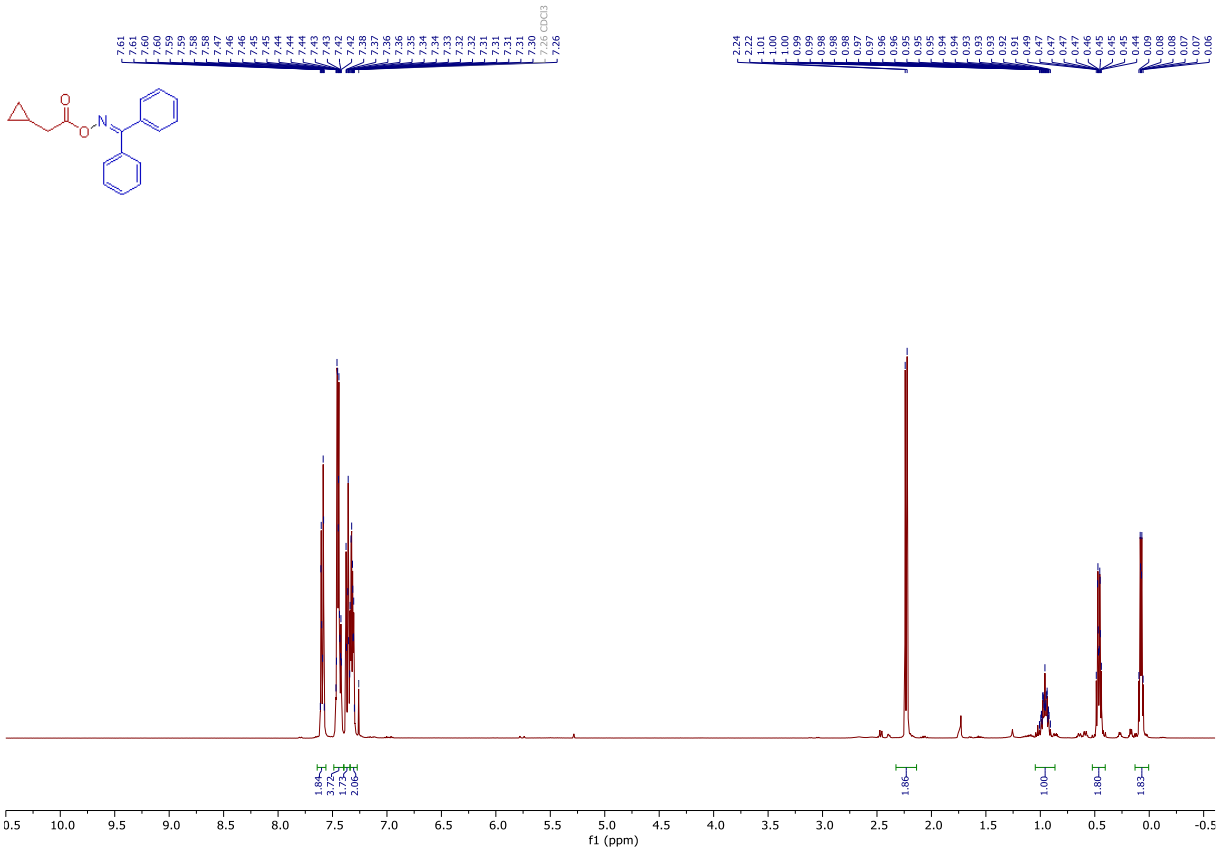


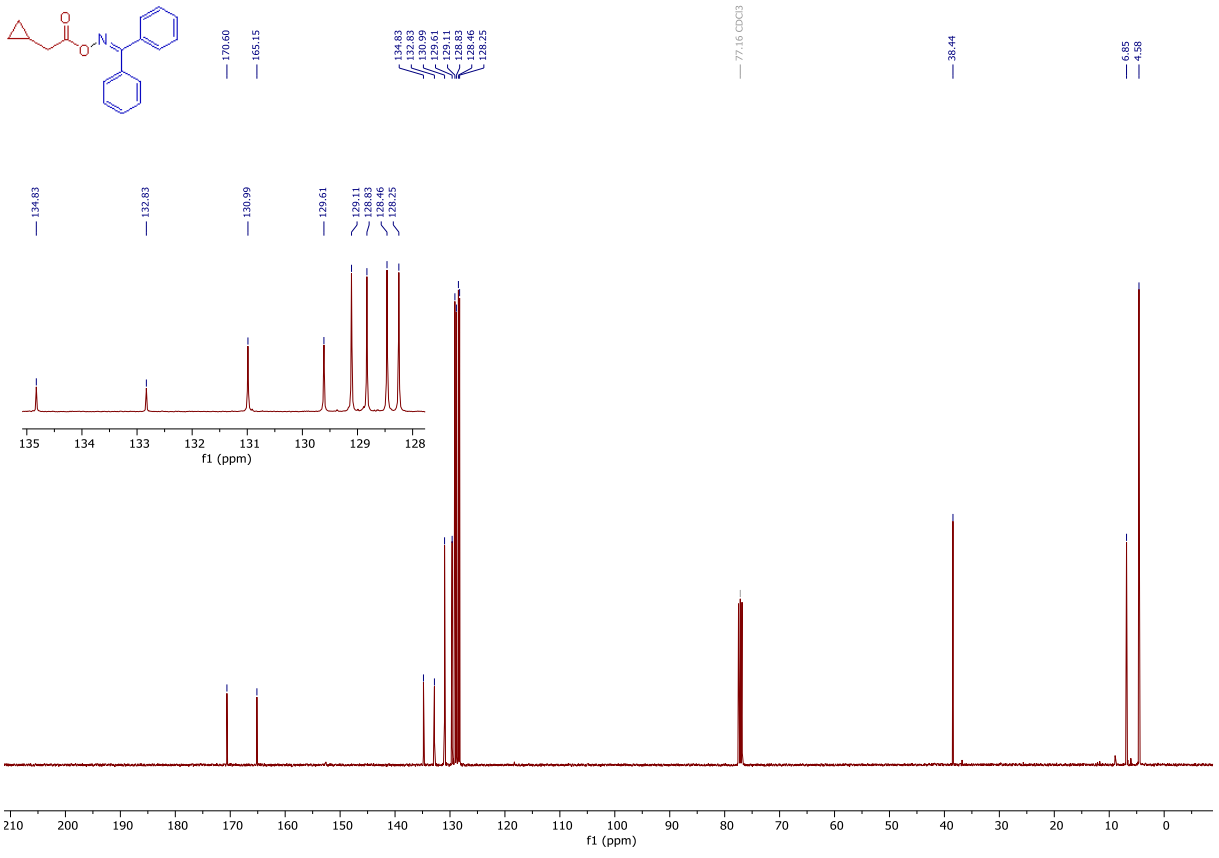
(3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-5-(((diphenylmethylene)amino)oxy)-5-oxopentan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (S50)



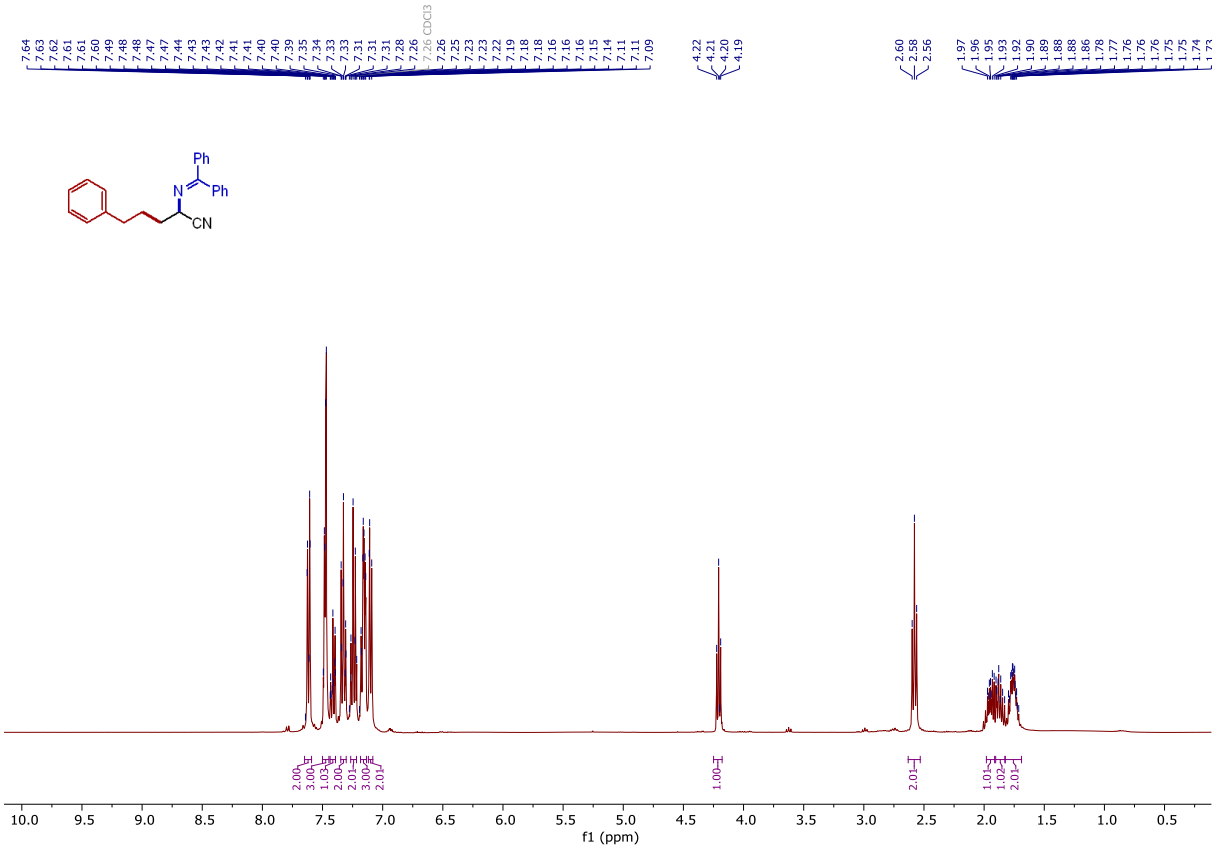


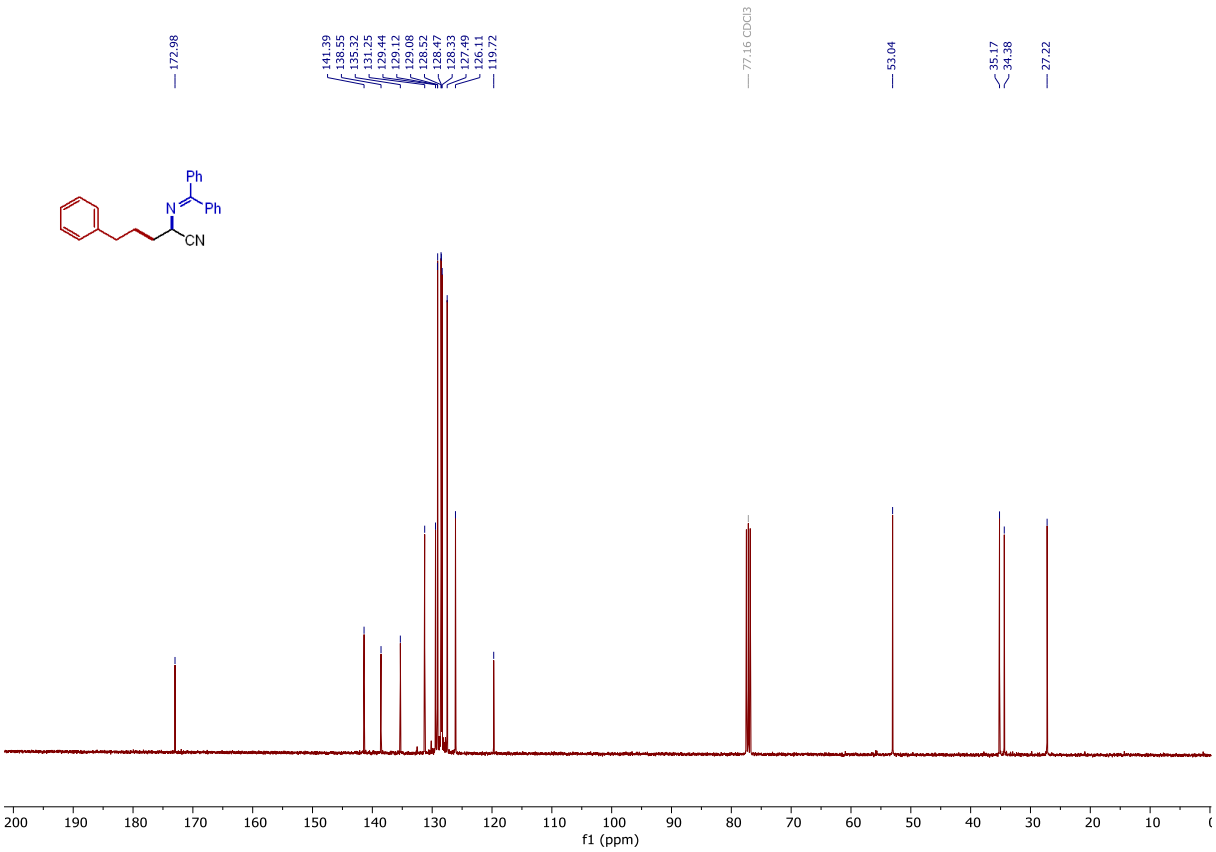
diphenylmethanone *O*-(2-cyclopropylacetyl) oxime (S51)



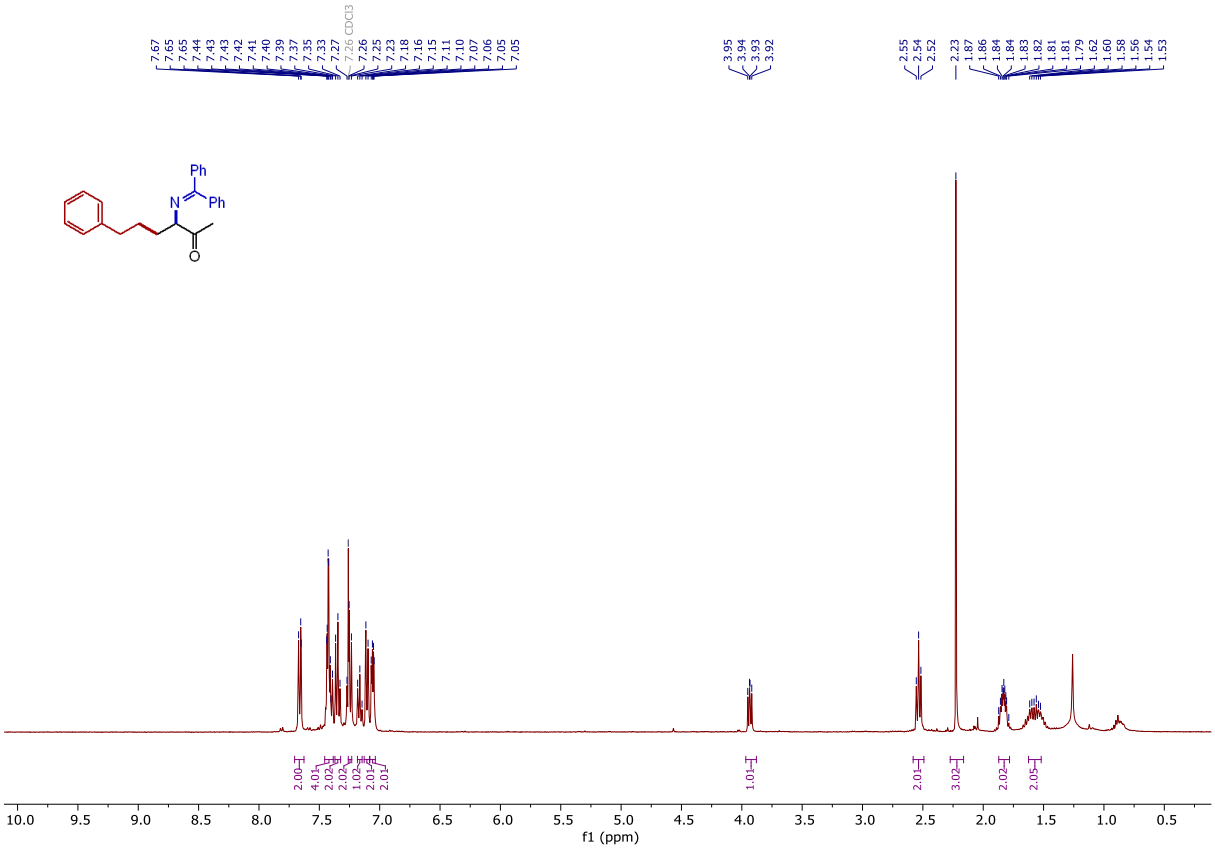


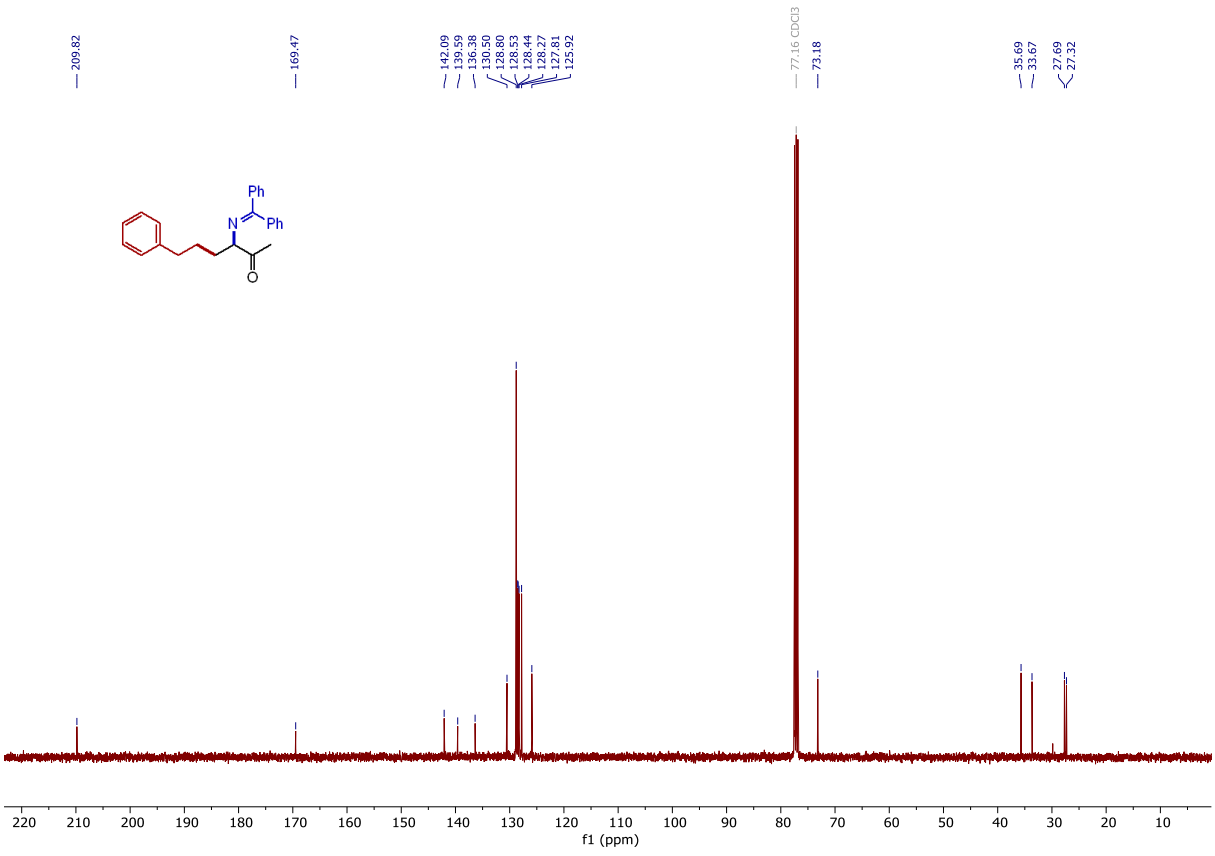
2-((diphenylmethylene)amino)-5-phenylpentanenitrile (4)



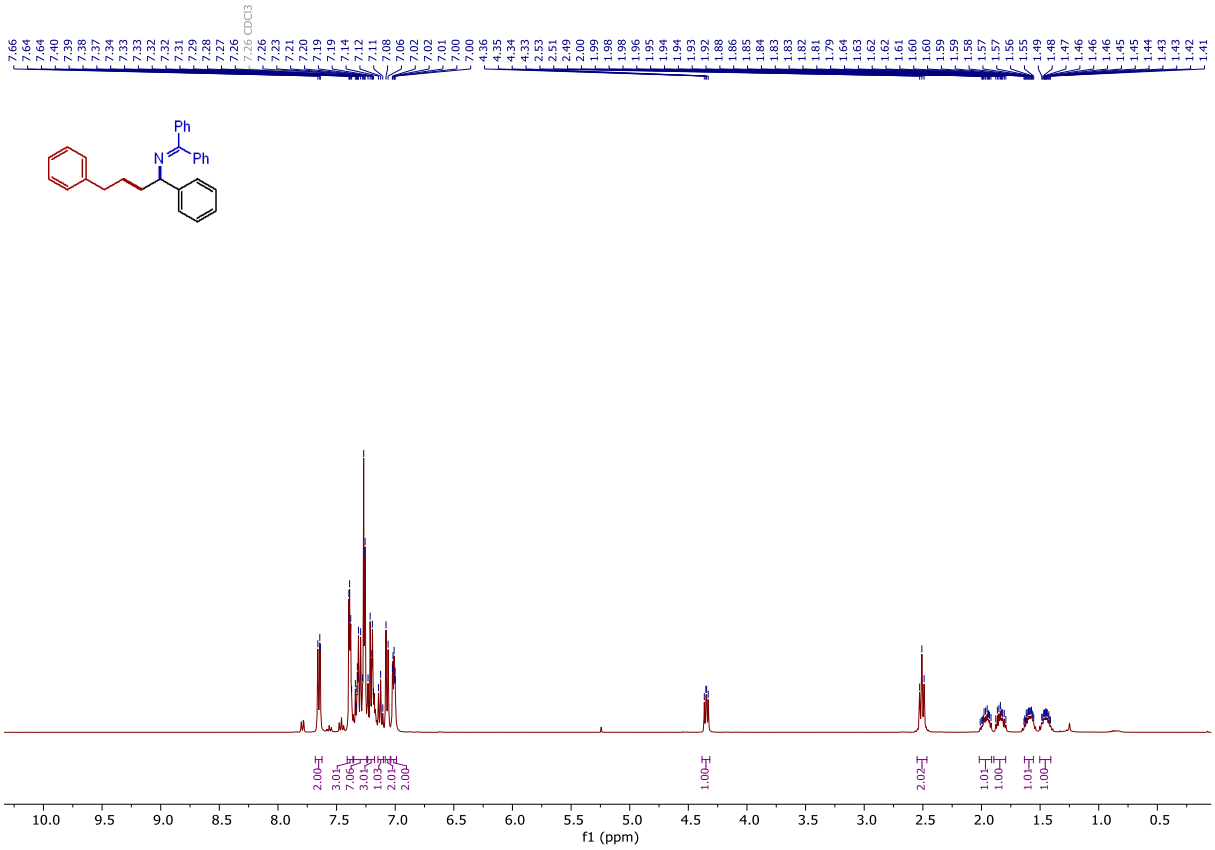


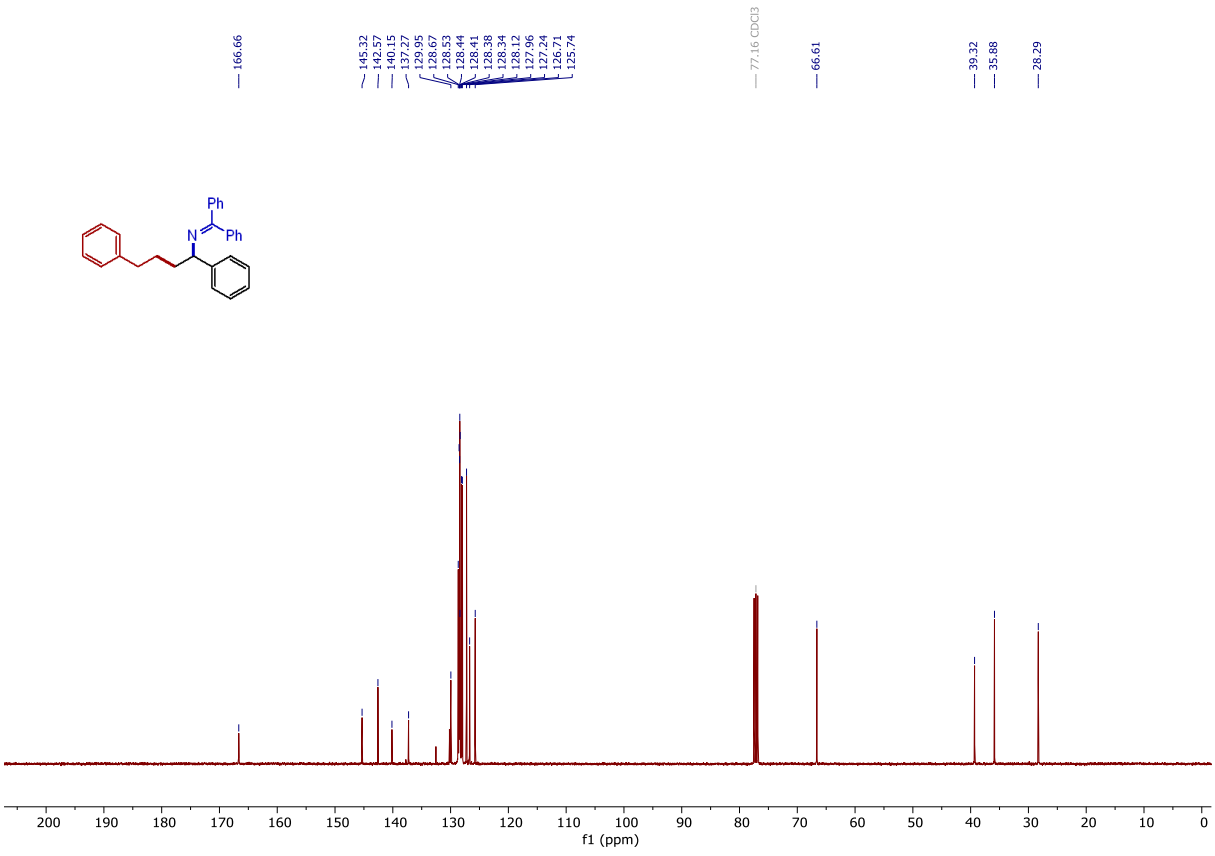
3-((diphenylmethylene)amino)-6-phenylhexan-2-one (5)



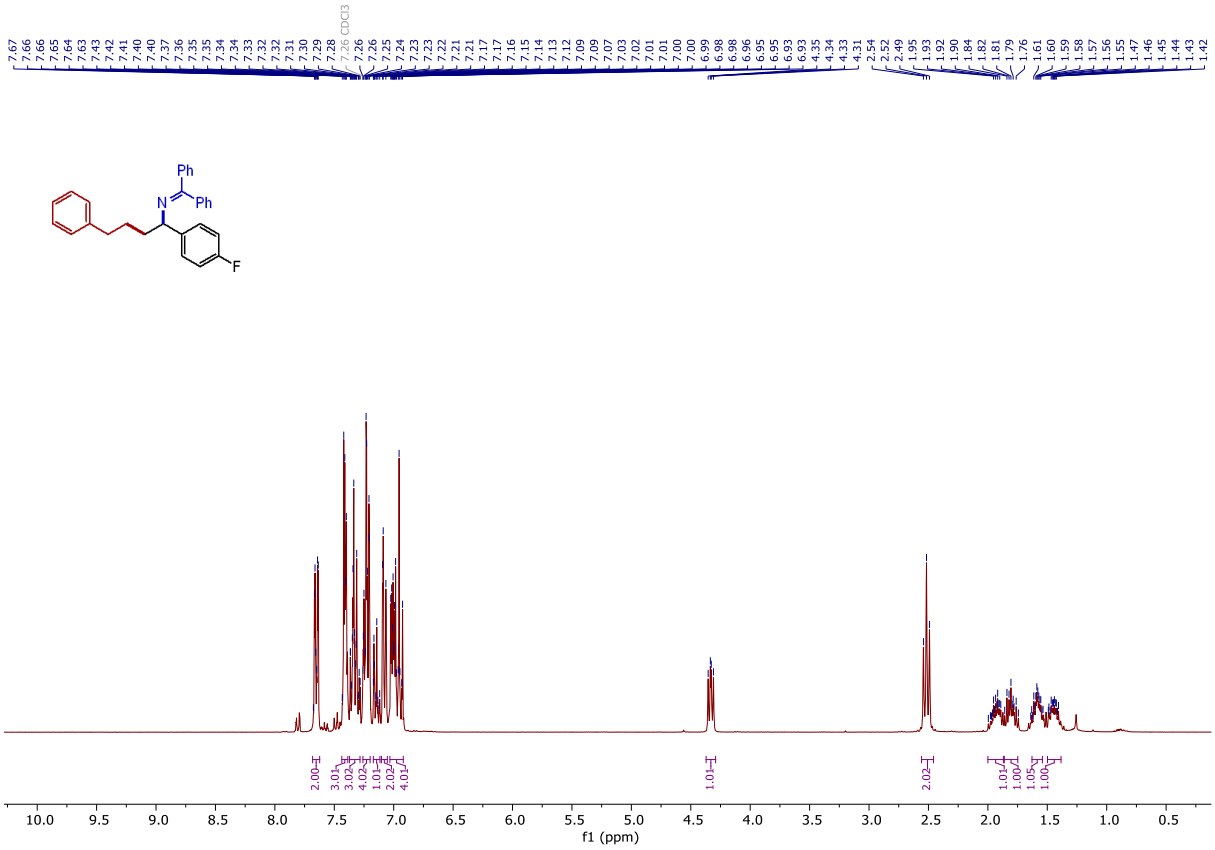


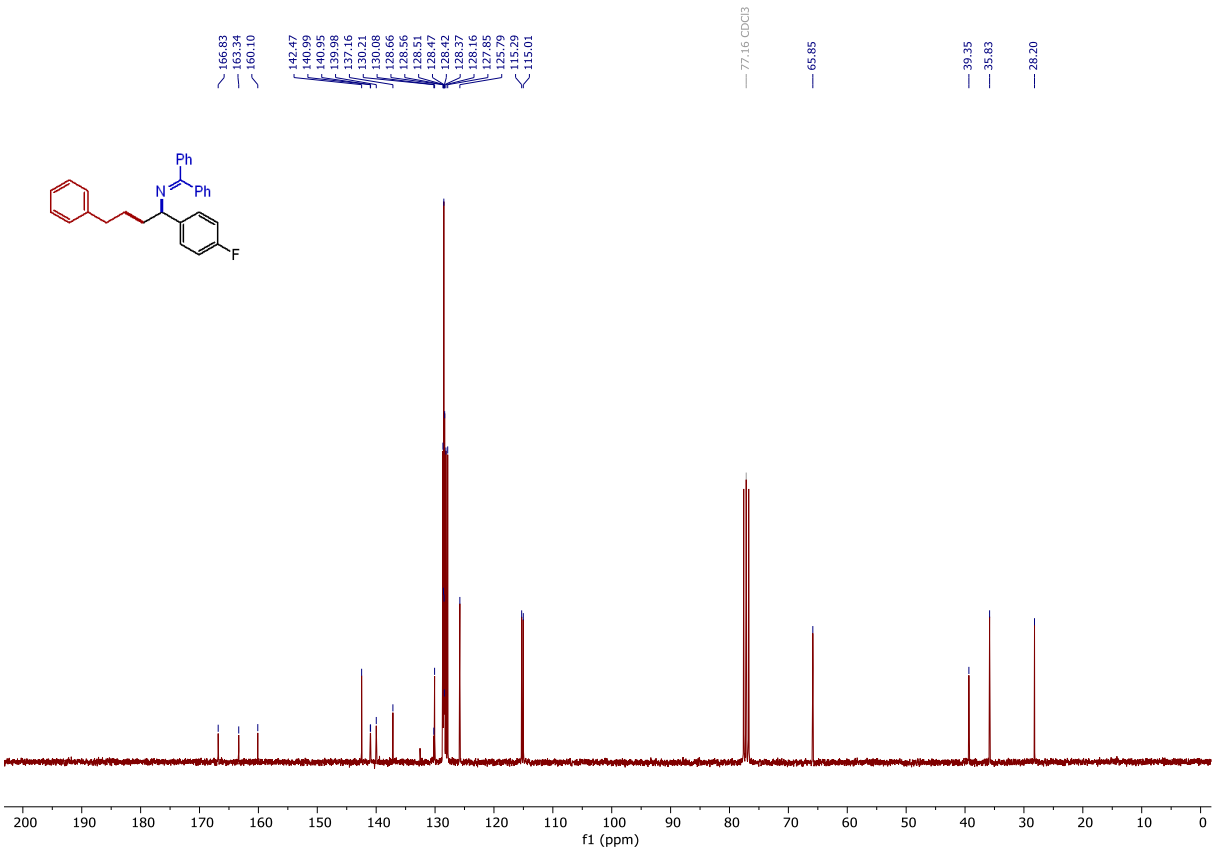
N-(1,4-diphenylbutyl)-1,1-diphenylmethanimine (6)



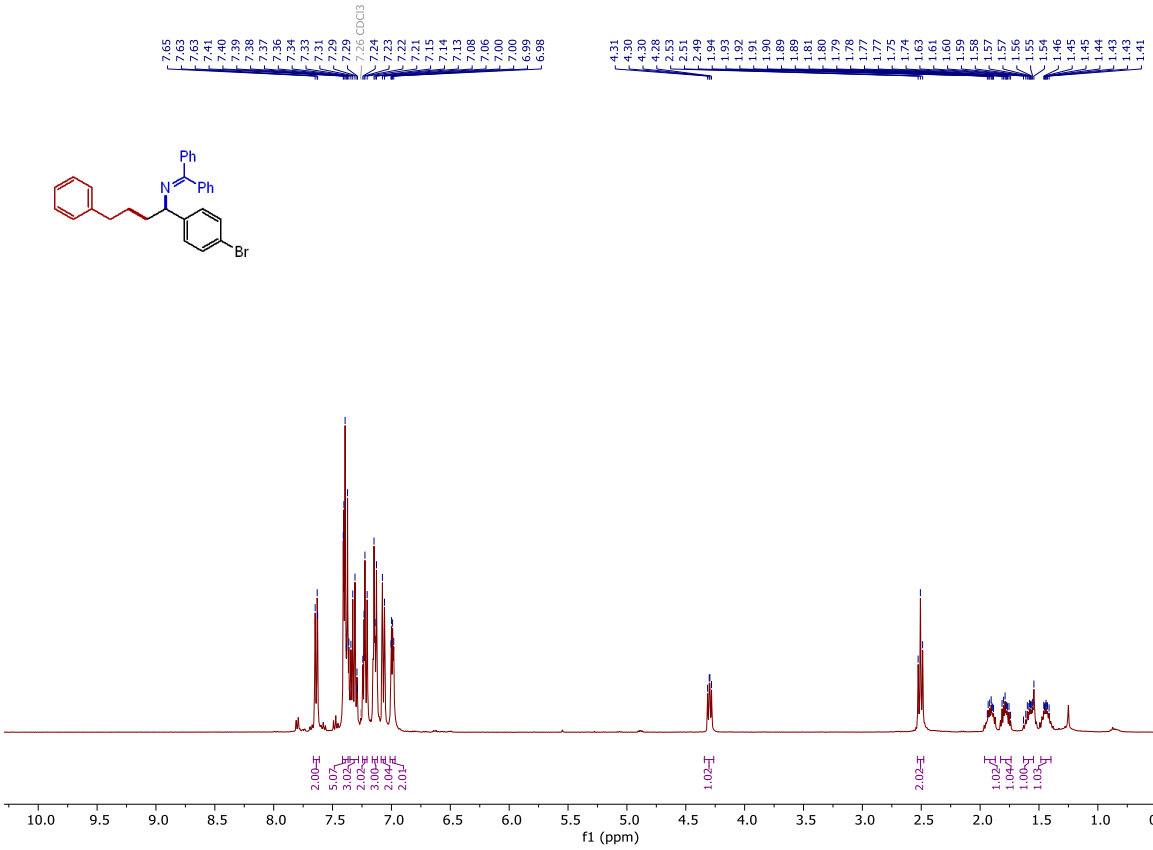


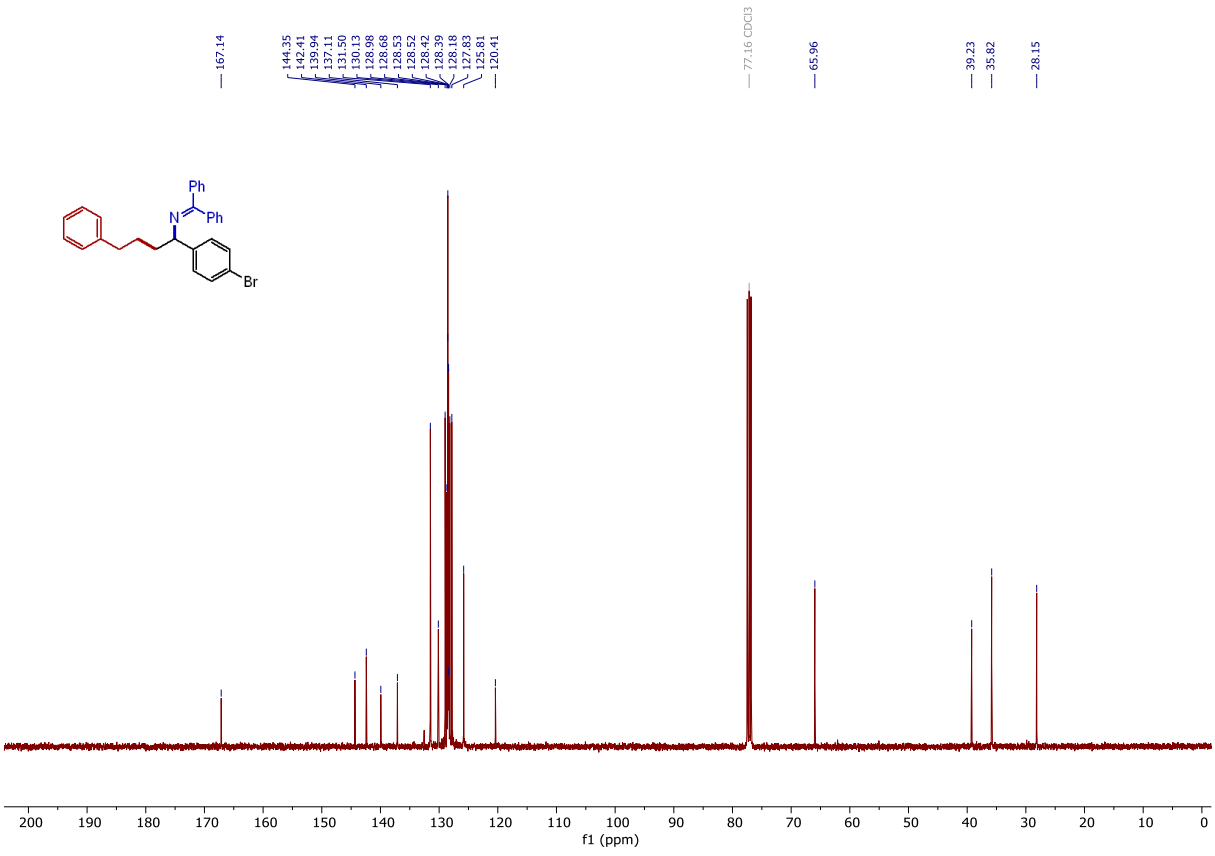
N-(1-(4-fluorophenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (7)



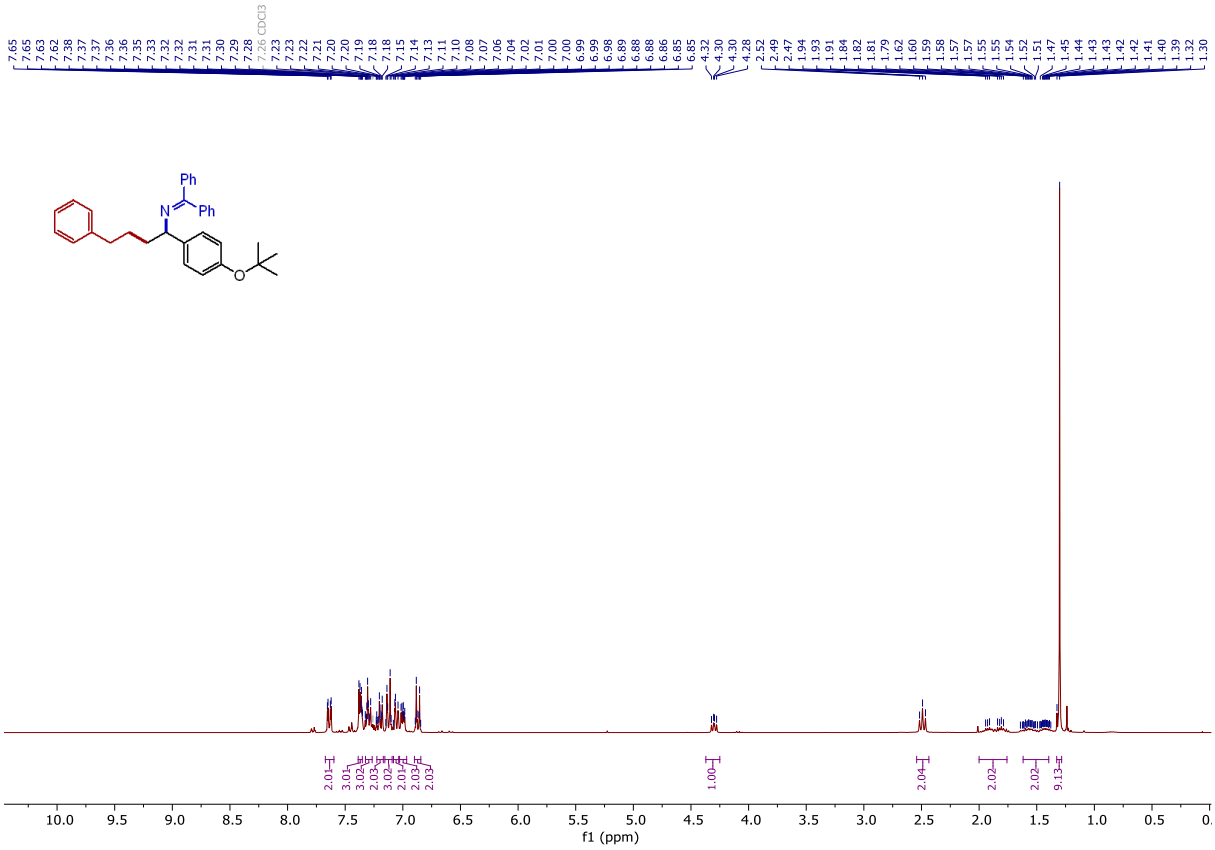


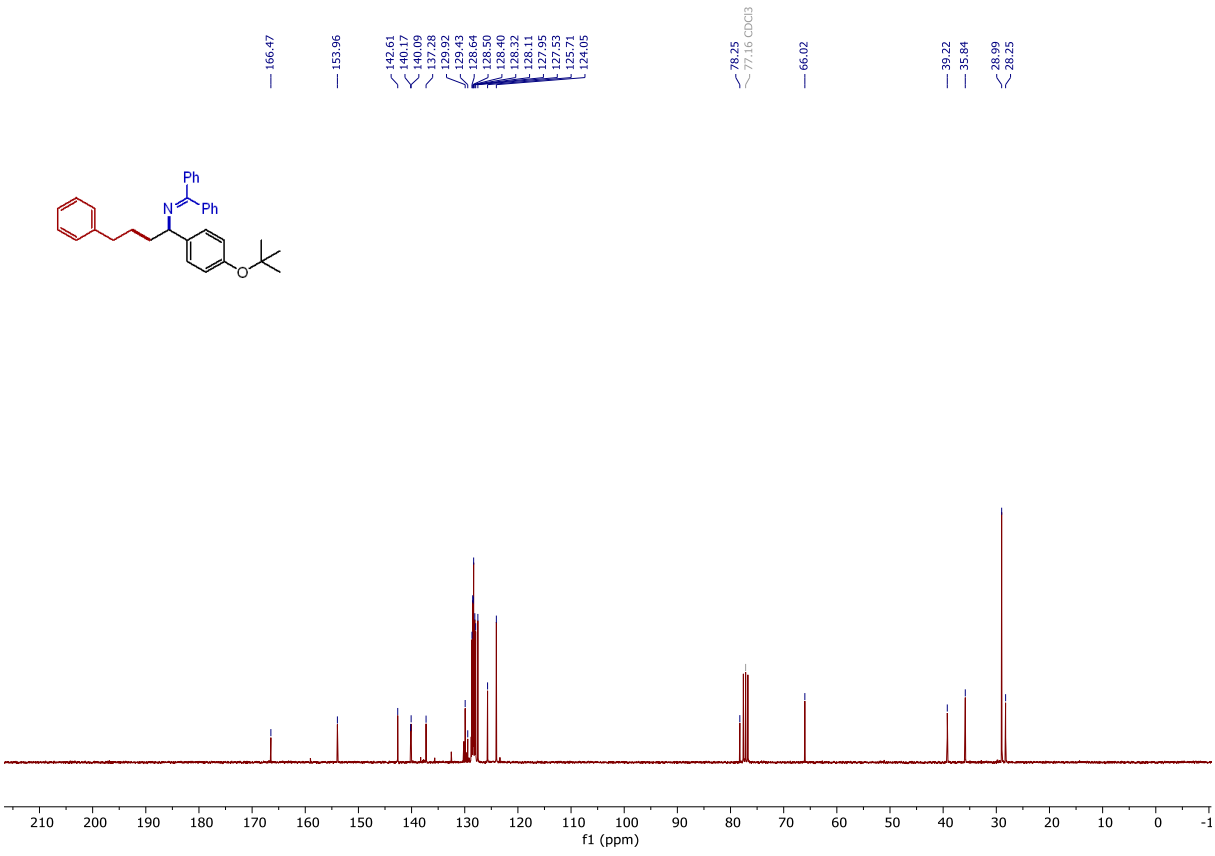
N-(1-(4-bromophenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (8)



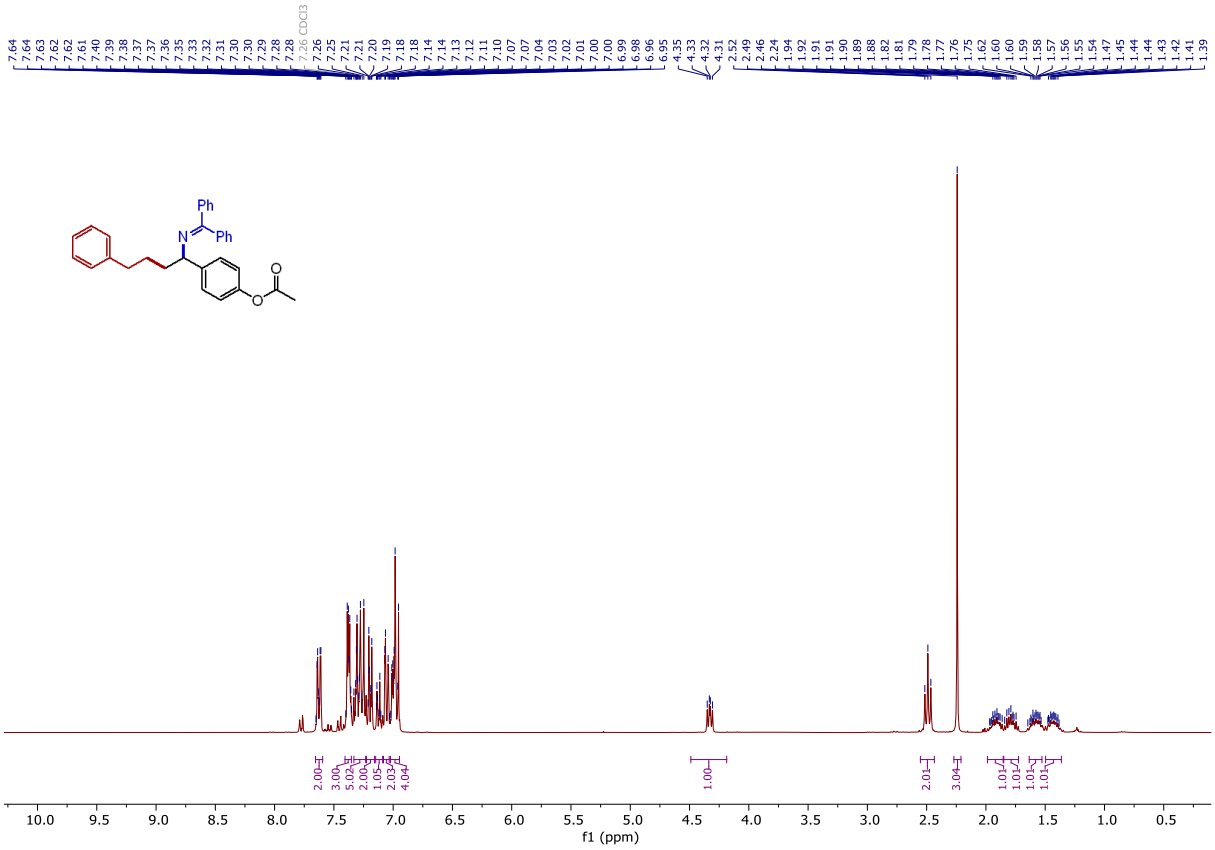


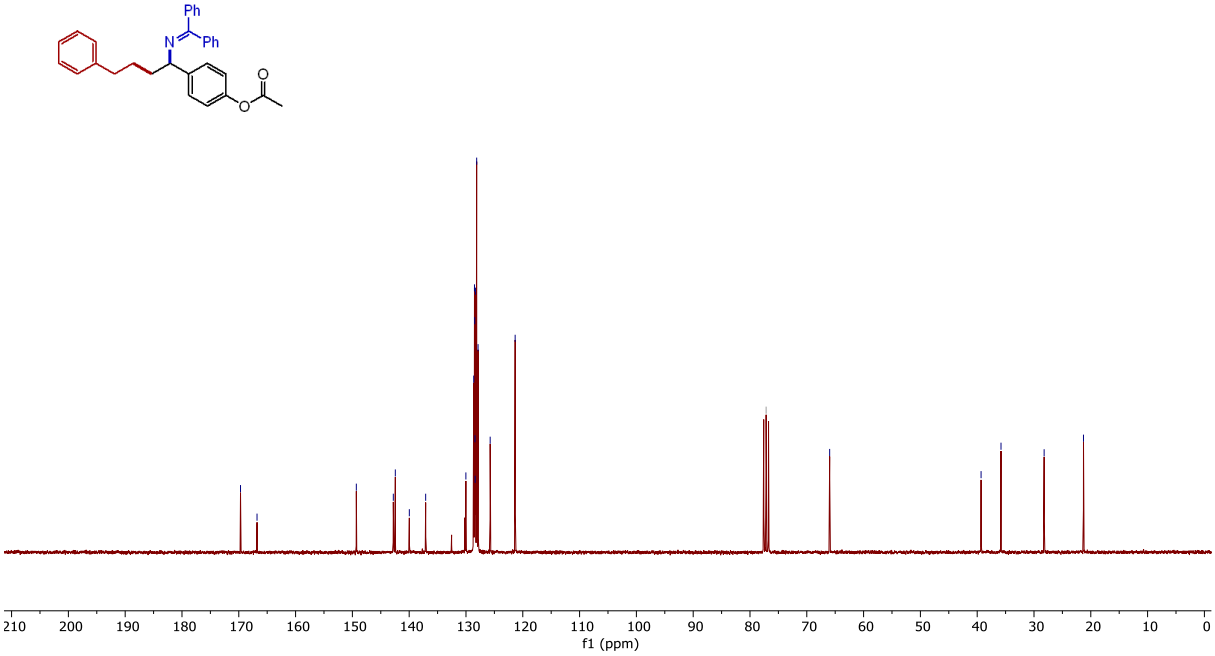
N-(1-(4-(tert-butoxy)phenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (9)



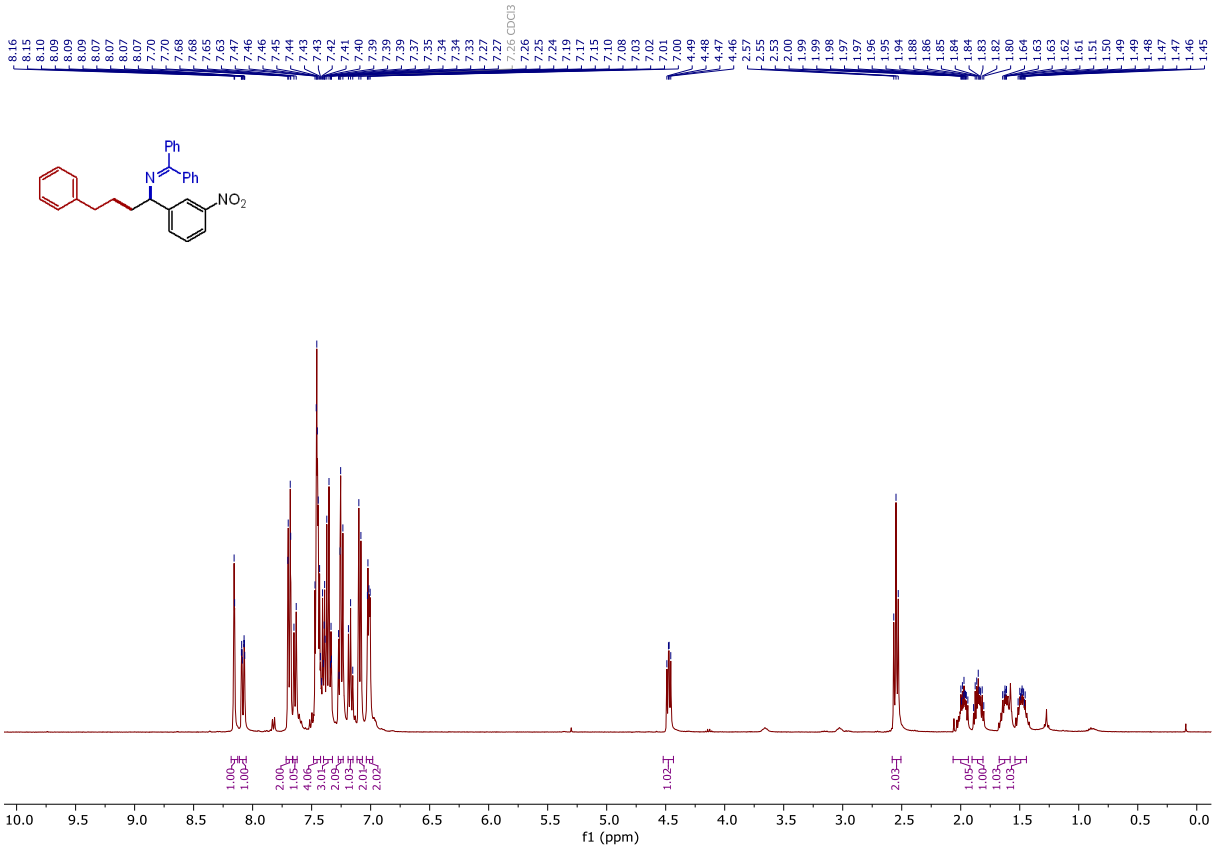


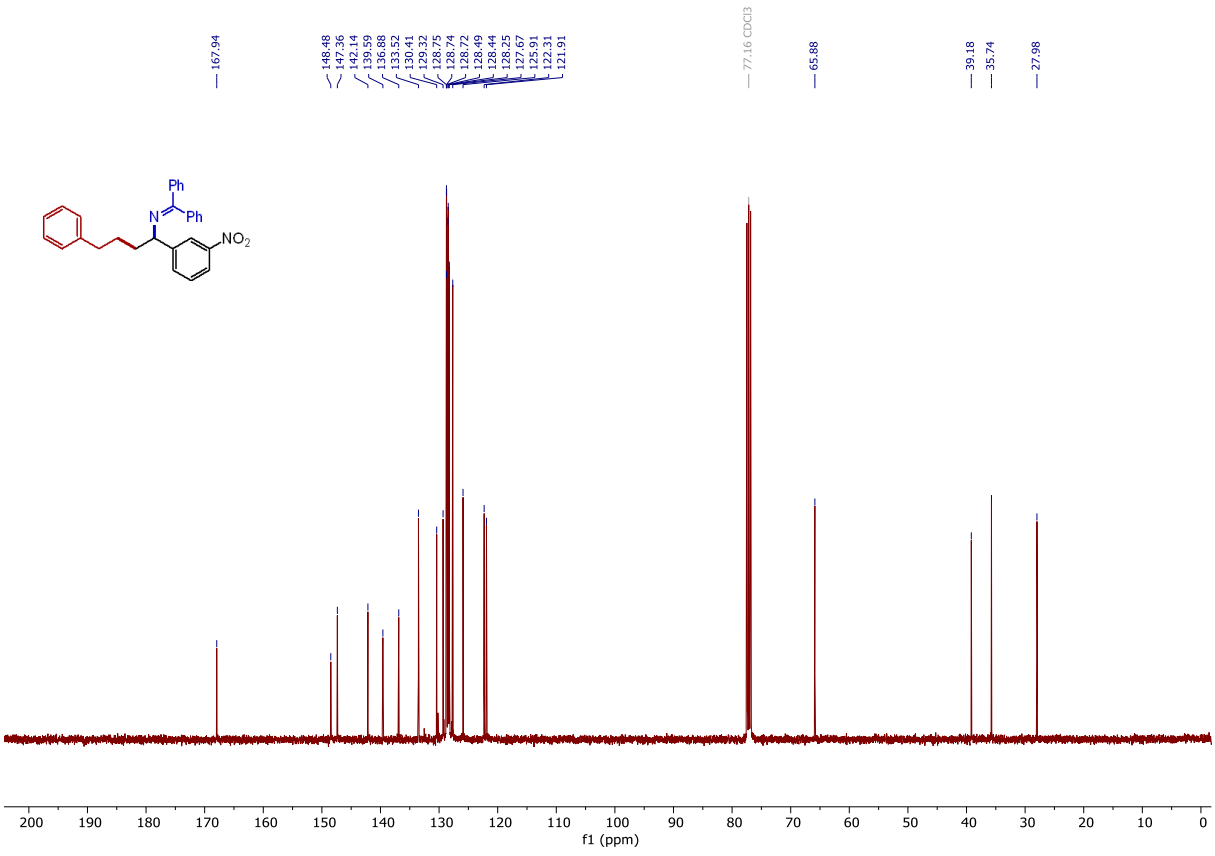
4-(1-((diphenylmethylene)amino)-4-phenylbutyl)phenyl acetate (10)



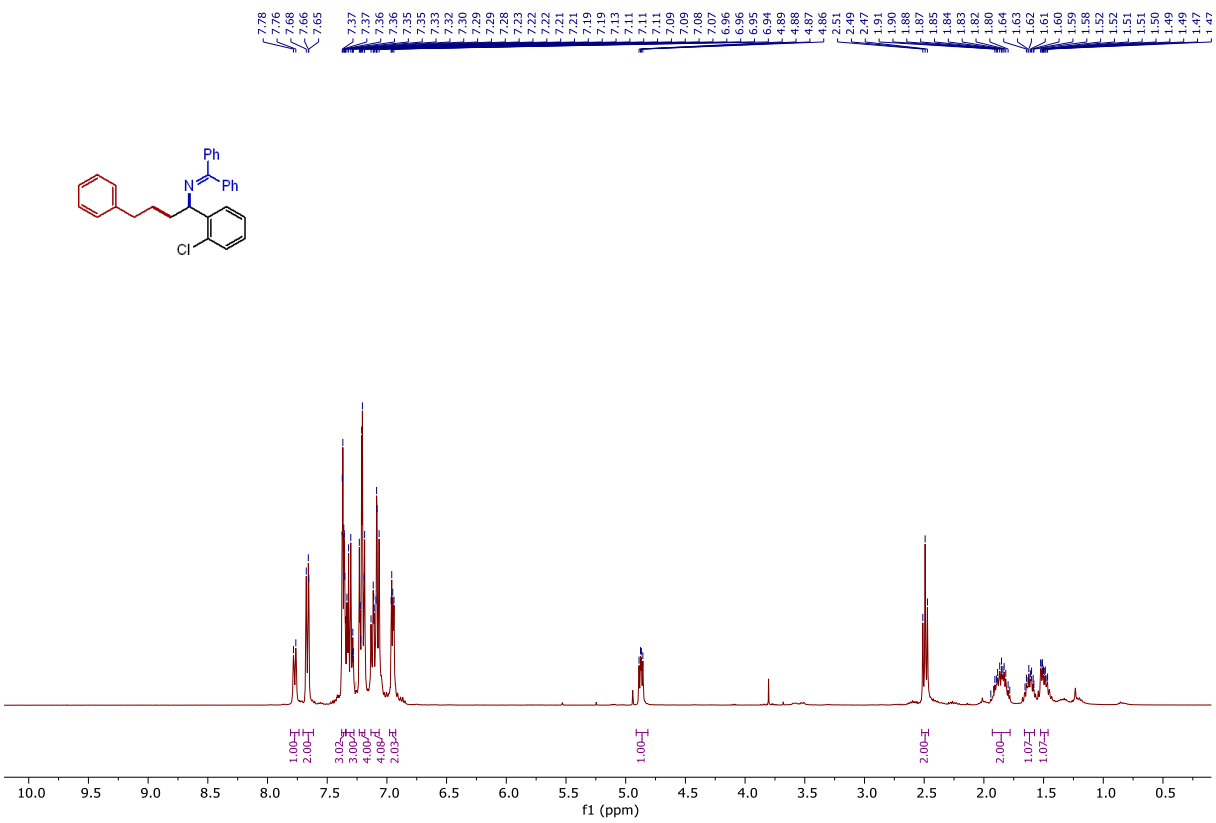


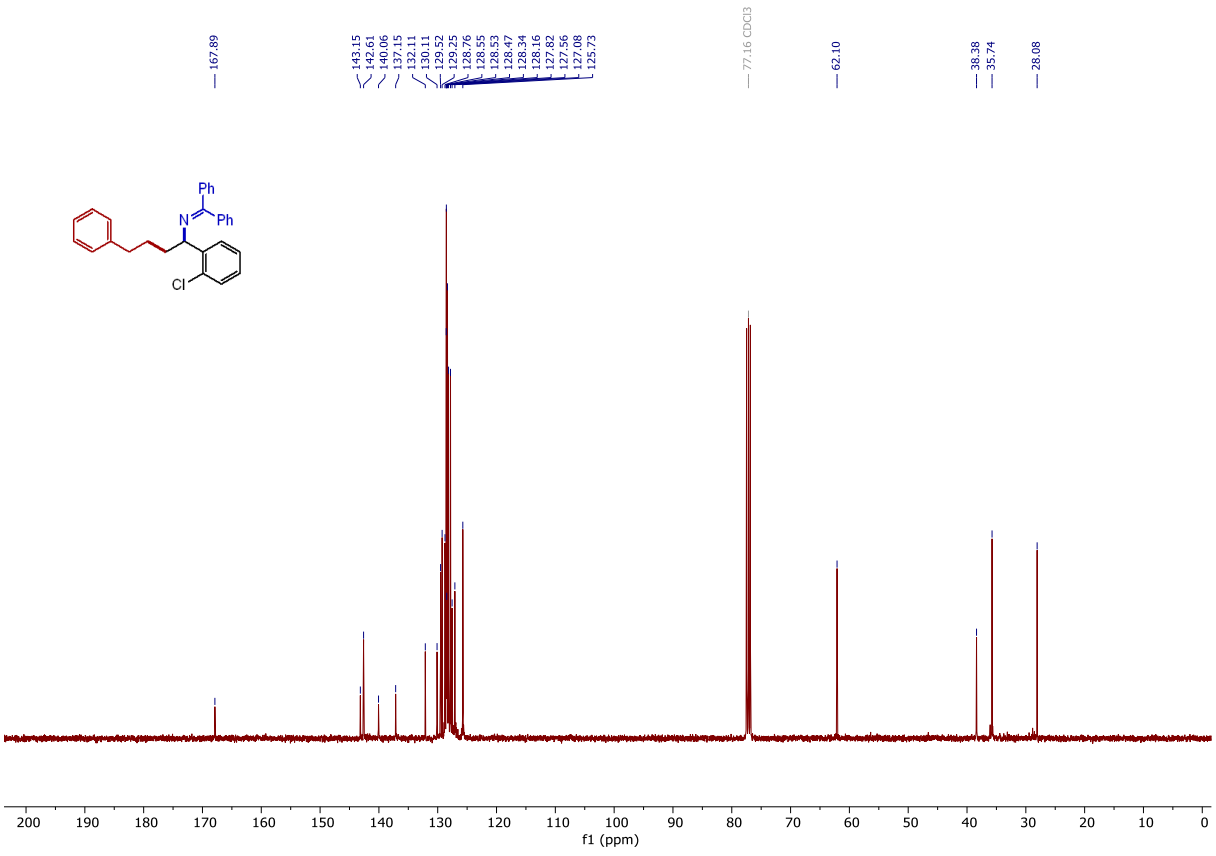
N-(1-(3-nitrophenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (11)



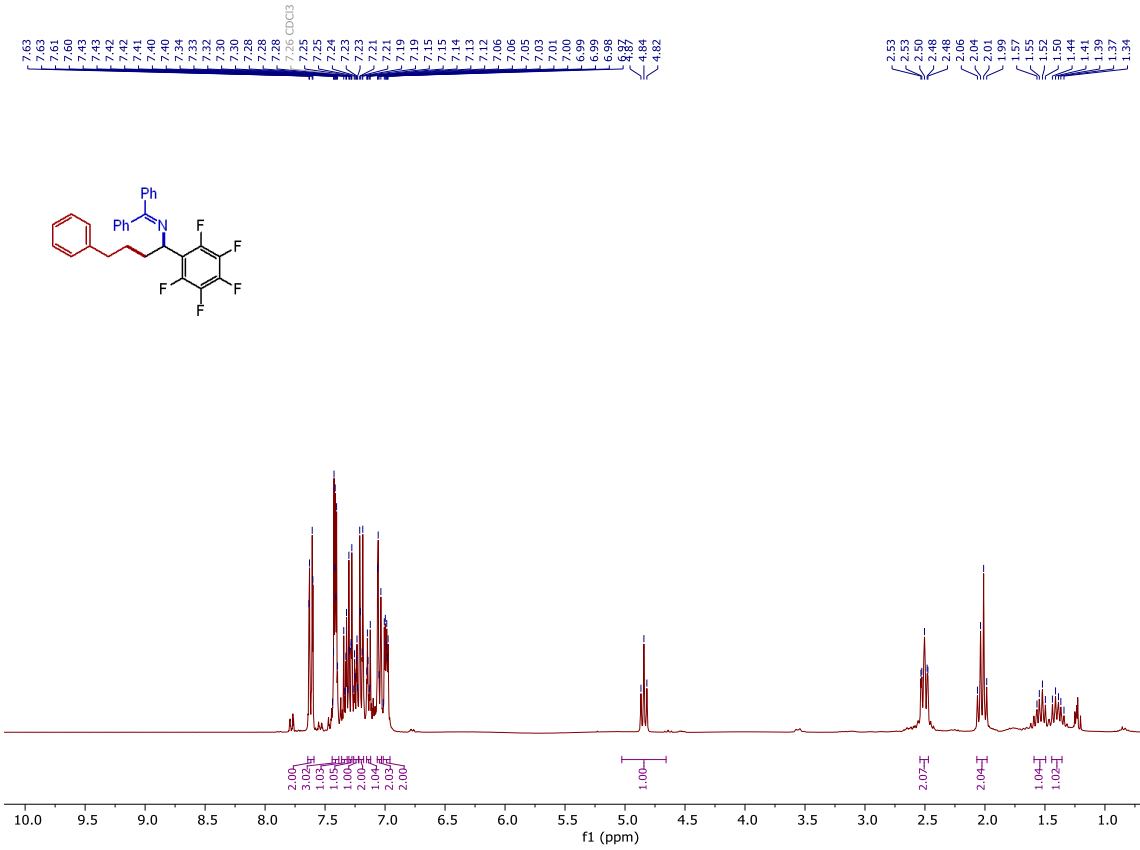


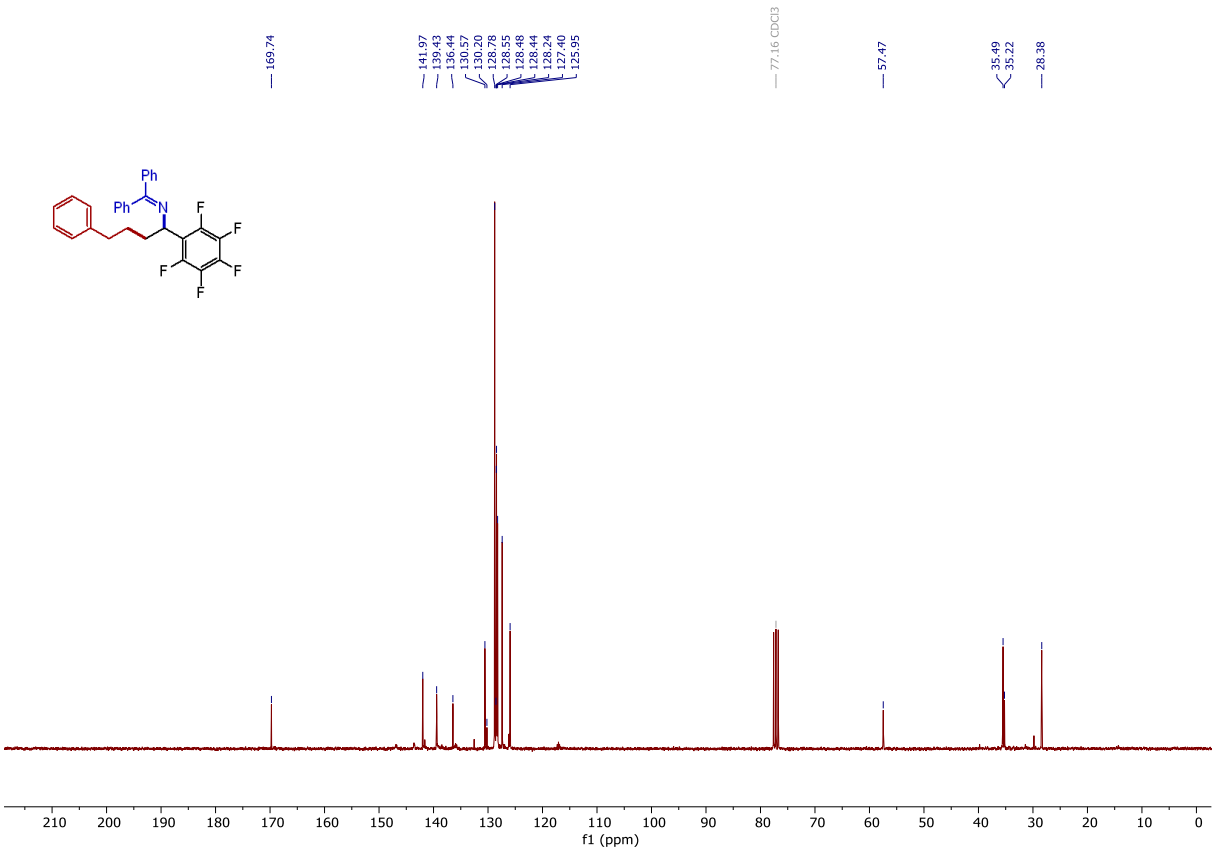
N-(1-(2-chlorophenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (12)

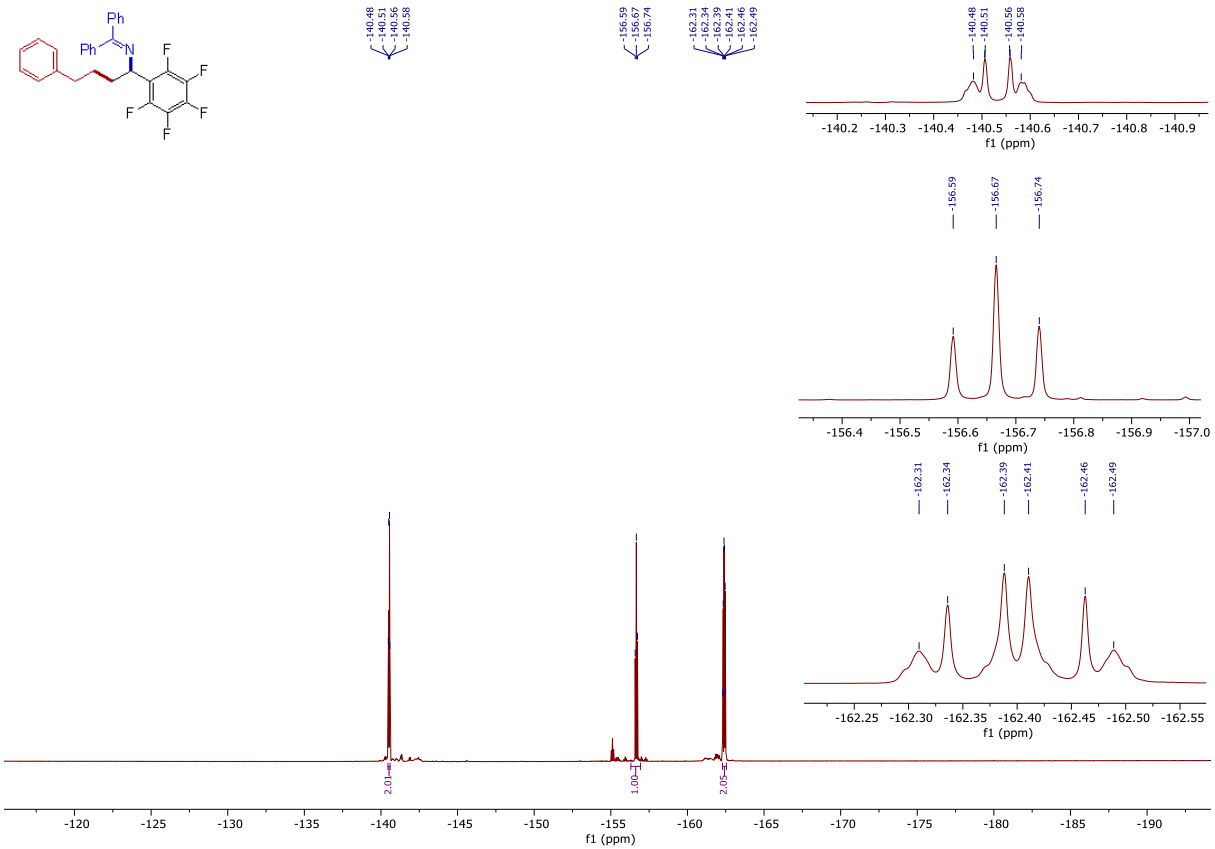




N-(1-(perfluorophenyl)-4-phenylbutyl)-1,1-diphenylmethanimine (13)






Ph
Ph
N
F
F
F
F
F
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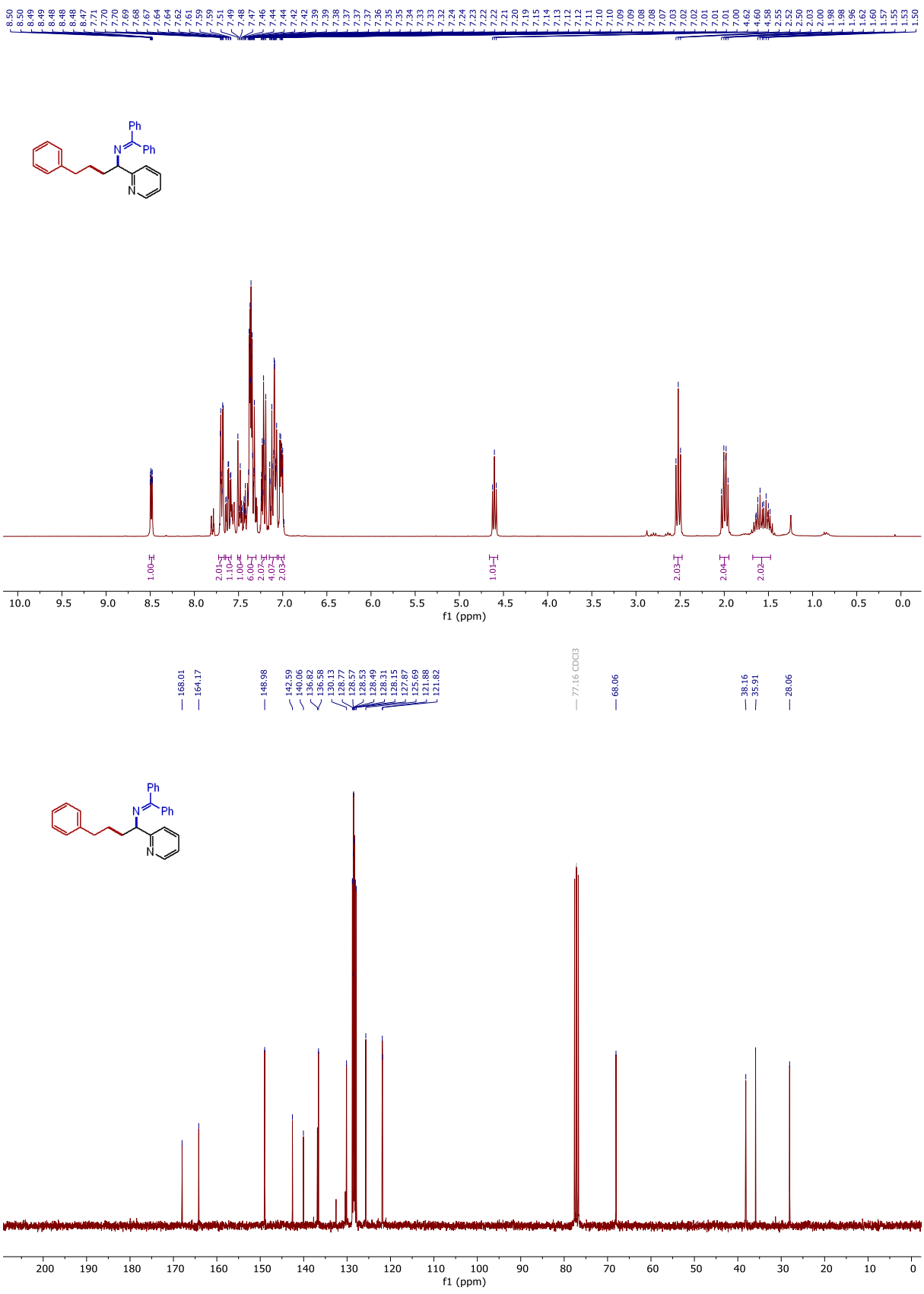
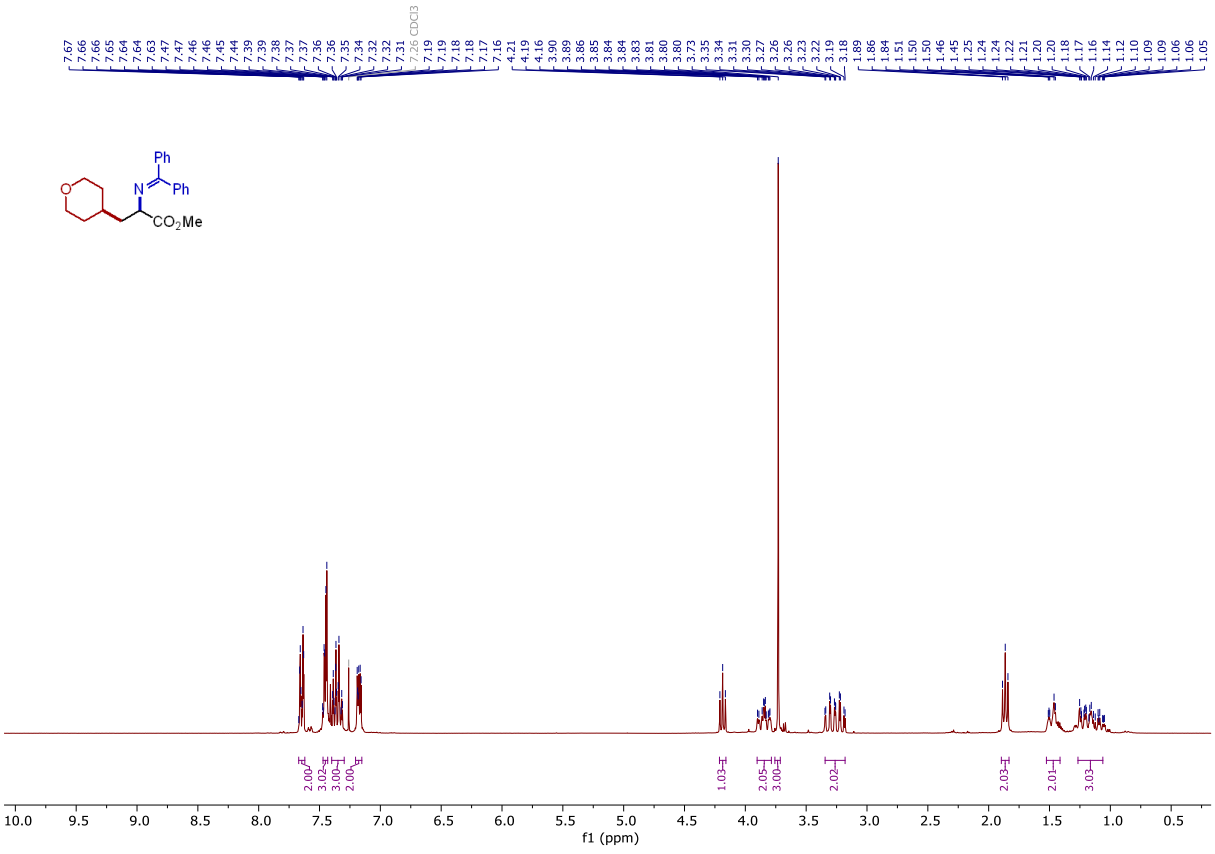
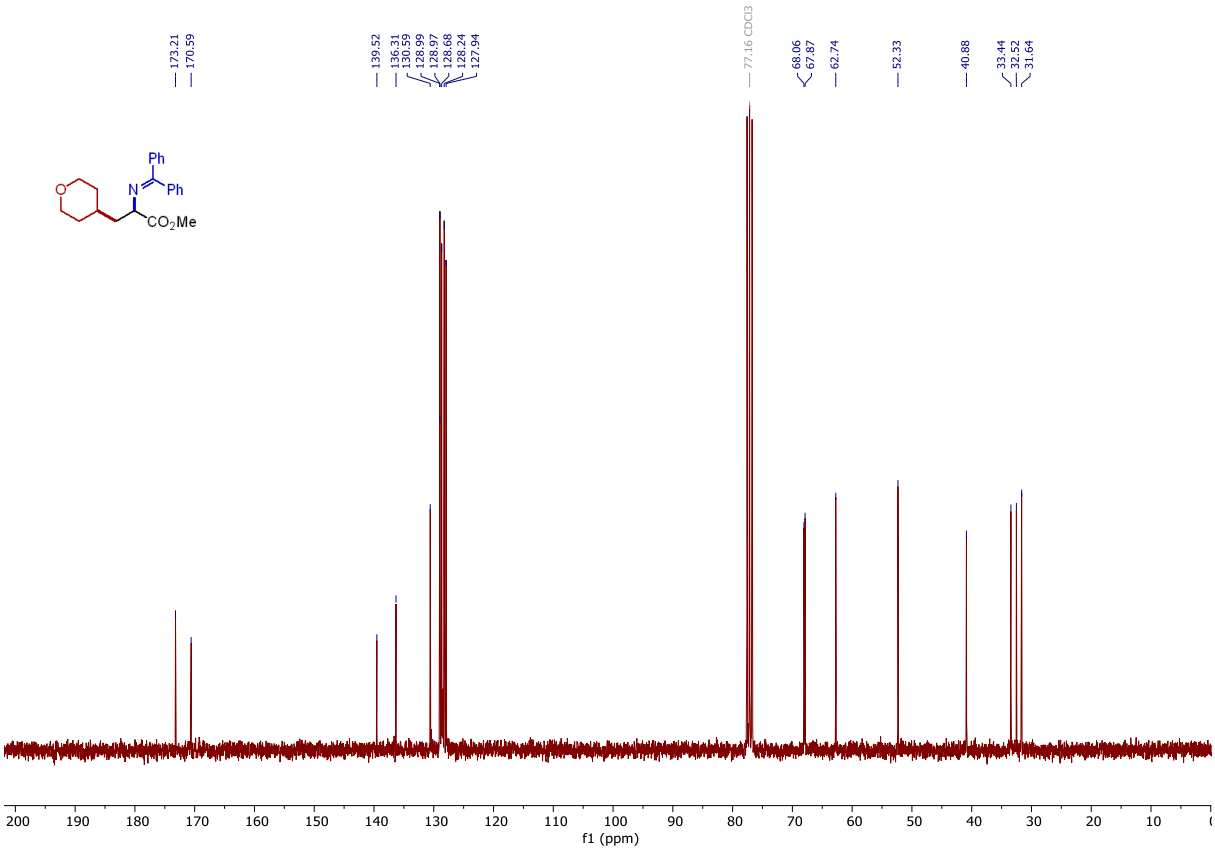
-140.51
-140.56
-140.58
-156.59
-156.67
-156.74
-162.31
-162.34
-162.39
-162.41
-162.46
-162.49
-140.2 -140.3 -140.4 -140.5 -140.6 -140.7 -140.8 -140.9
f1 (ppm)
-156.4 -156.5 -156.6 -156.7 -156.8 -156.9 -157.0
f1 (ppm)
-162.25 -162.30 -162.35 -162.40 -162.45 -162.50 -162.55
f1 (ppm)
2.01
1.00
2.05
-120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190
f1 (ppm)

1,1-diphenyl-*N*-(4-phenyl-1-(pyridin-2-yl)butyl)methanimine (14)

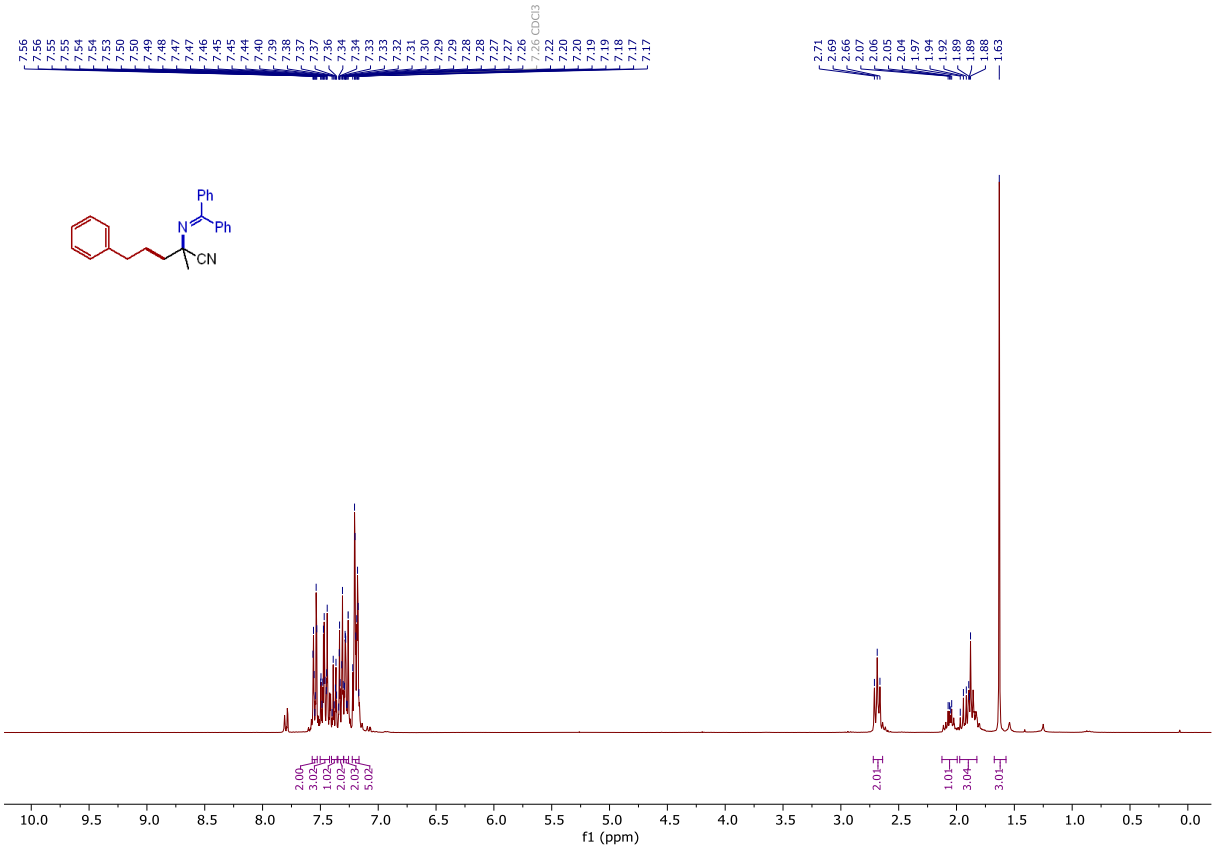


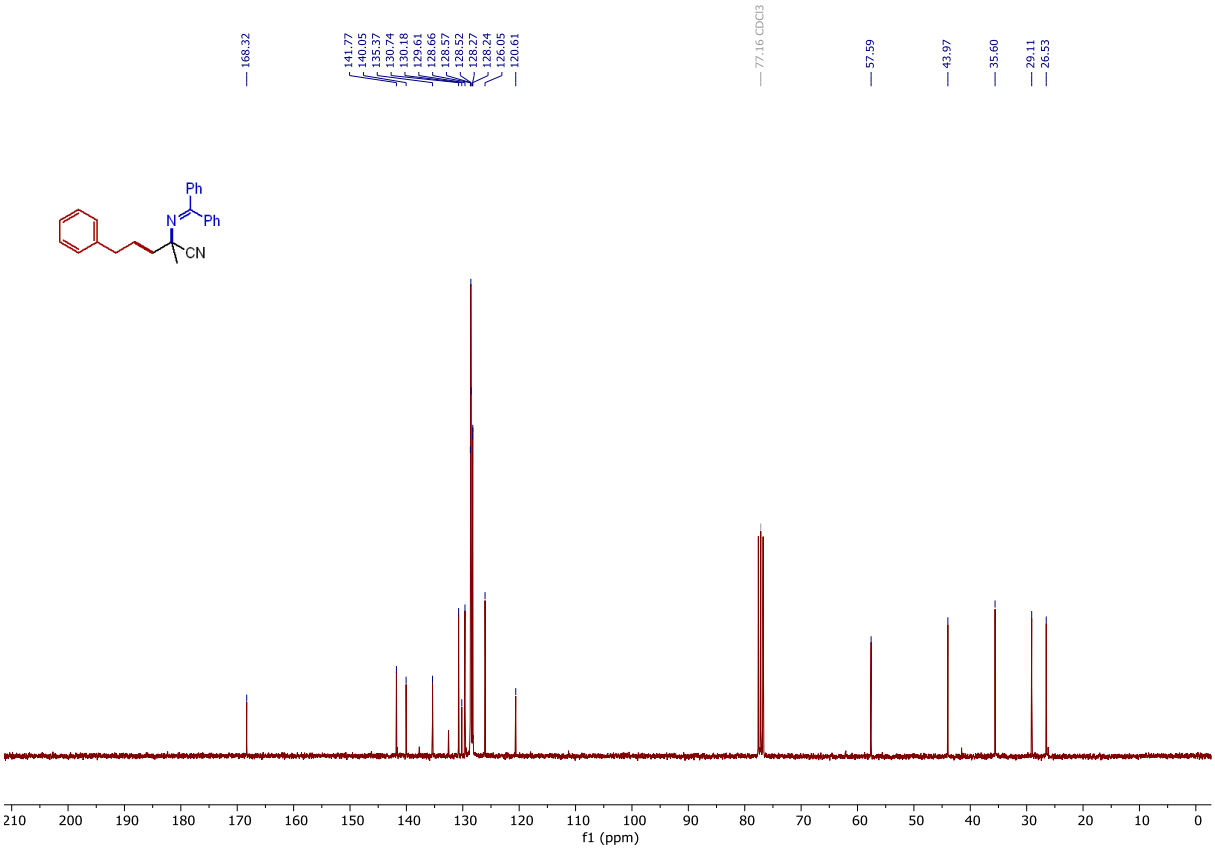
methyl 2-((diphenylmethylene)amino)-3-(tetrahydro-2*H*-pyran-4-yl)propanoate (15)



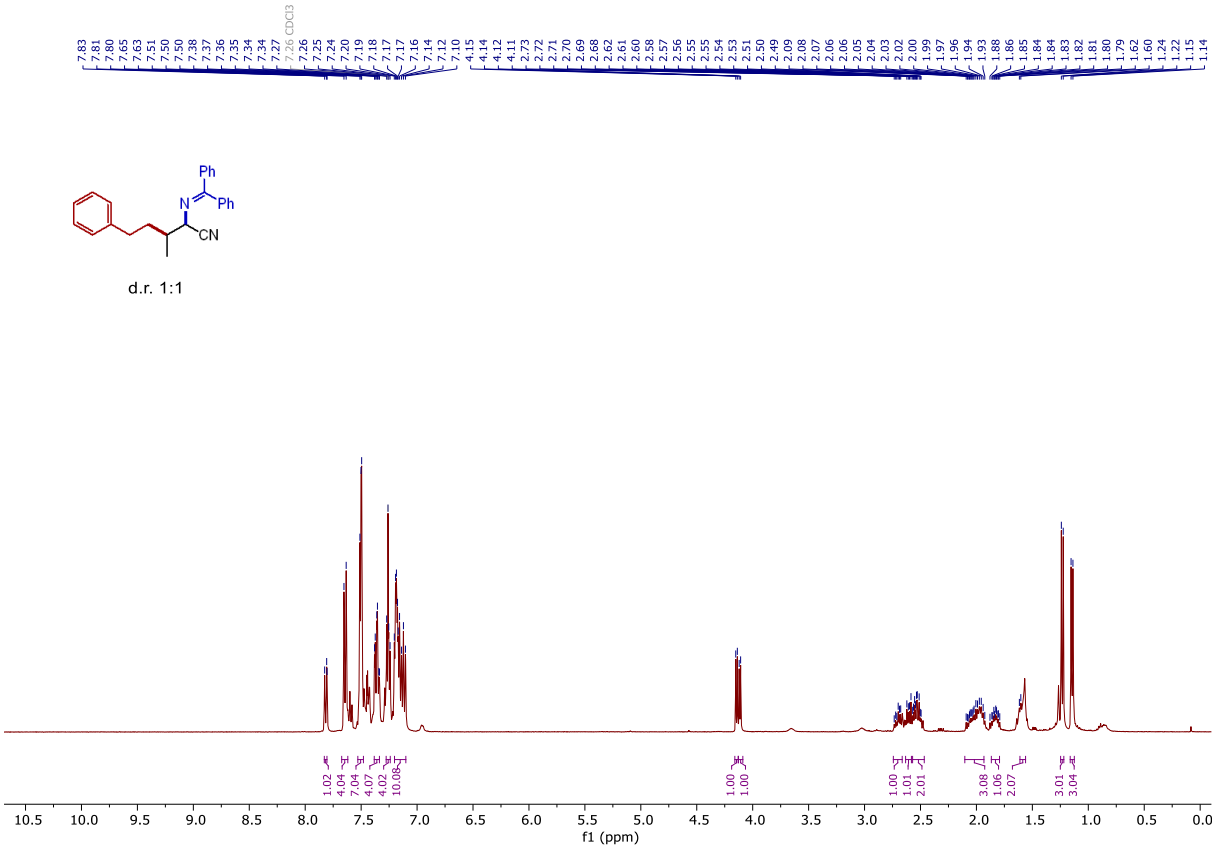


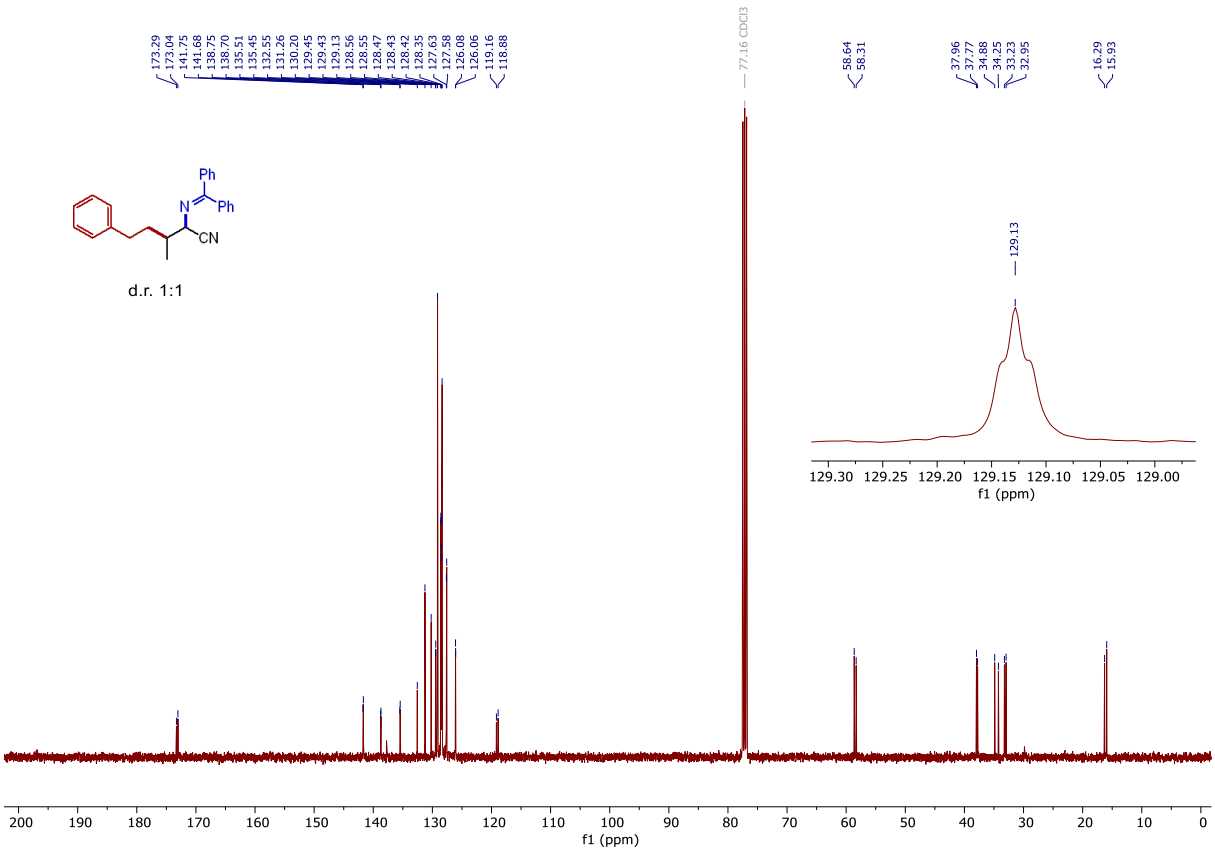
2-((diphenylmethylene)amino)-2-methyl-5-phenylpentanenitrile (16)



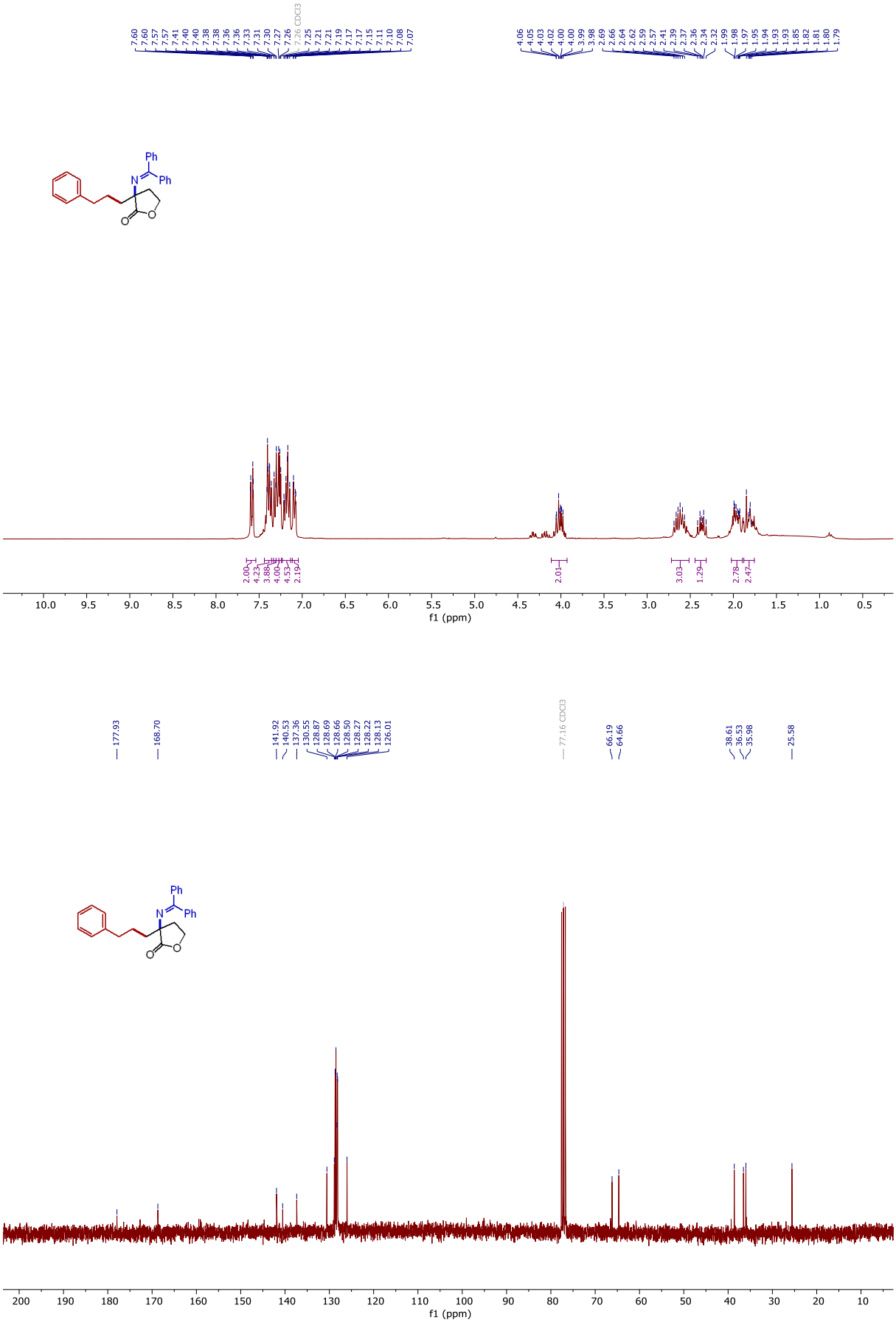


2-((diphenylmethylene)amino)-3-methyl-5-phenylpentanenitrile (17)

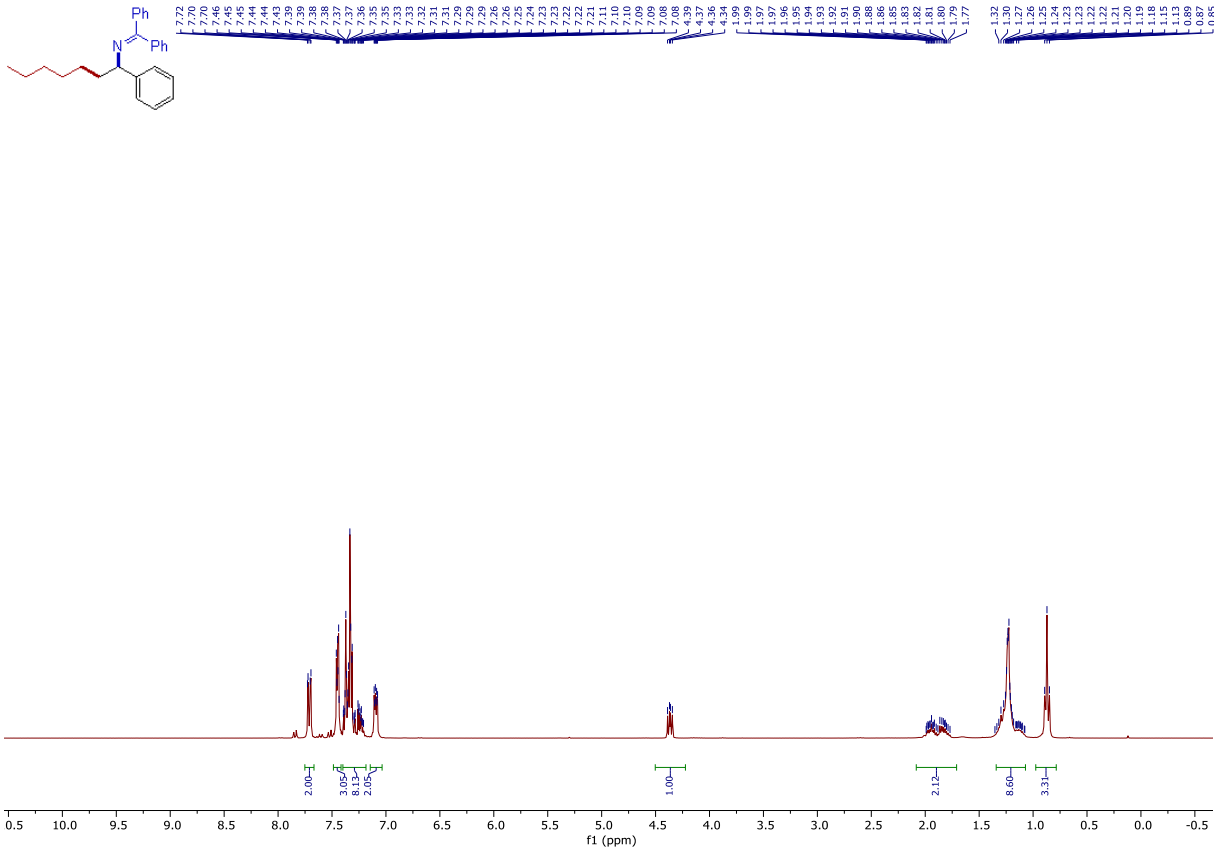




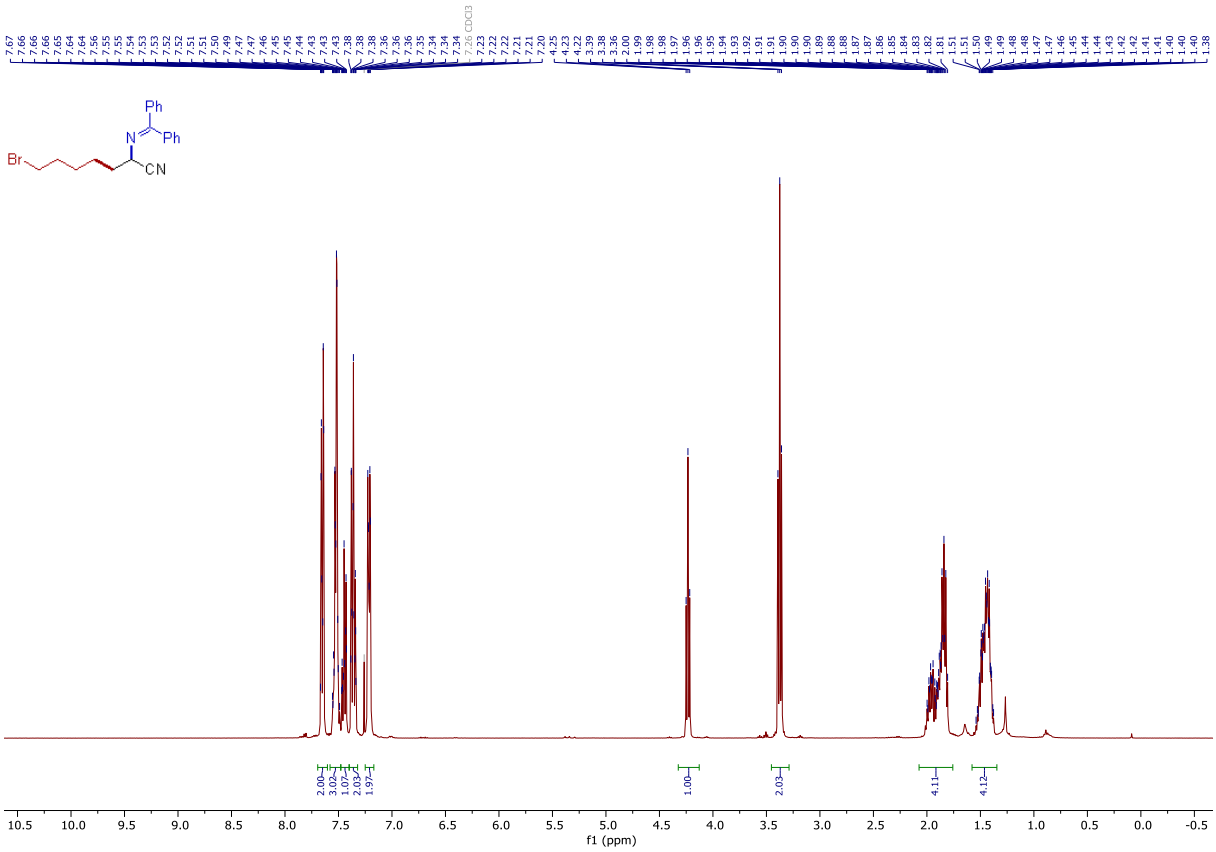
3-((diphenylmethylene)amino)-3-(3-phenylpropyl)dihydrofuran-2(3*H*)-one (18)

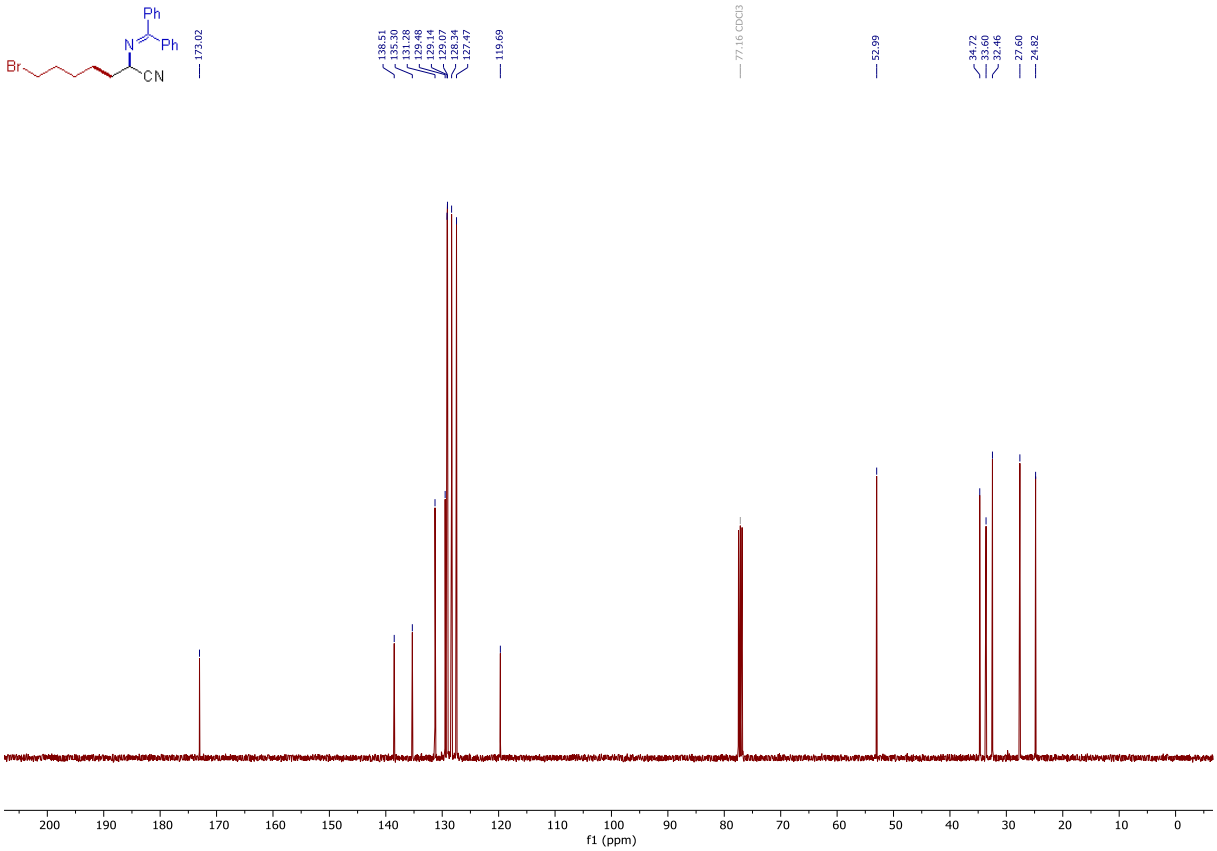


1,1-diphenyl-*N*-(1-phenylheptyl)methanimine (19)

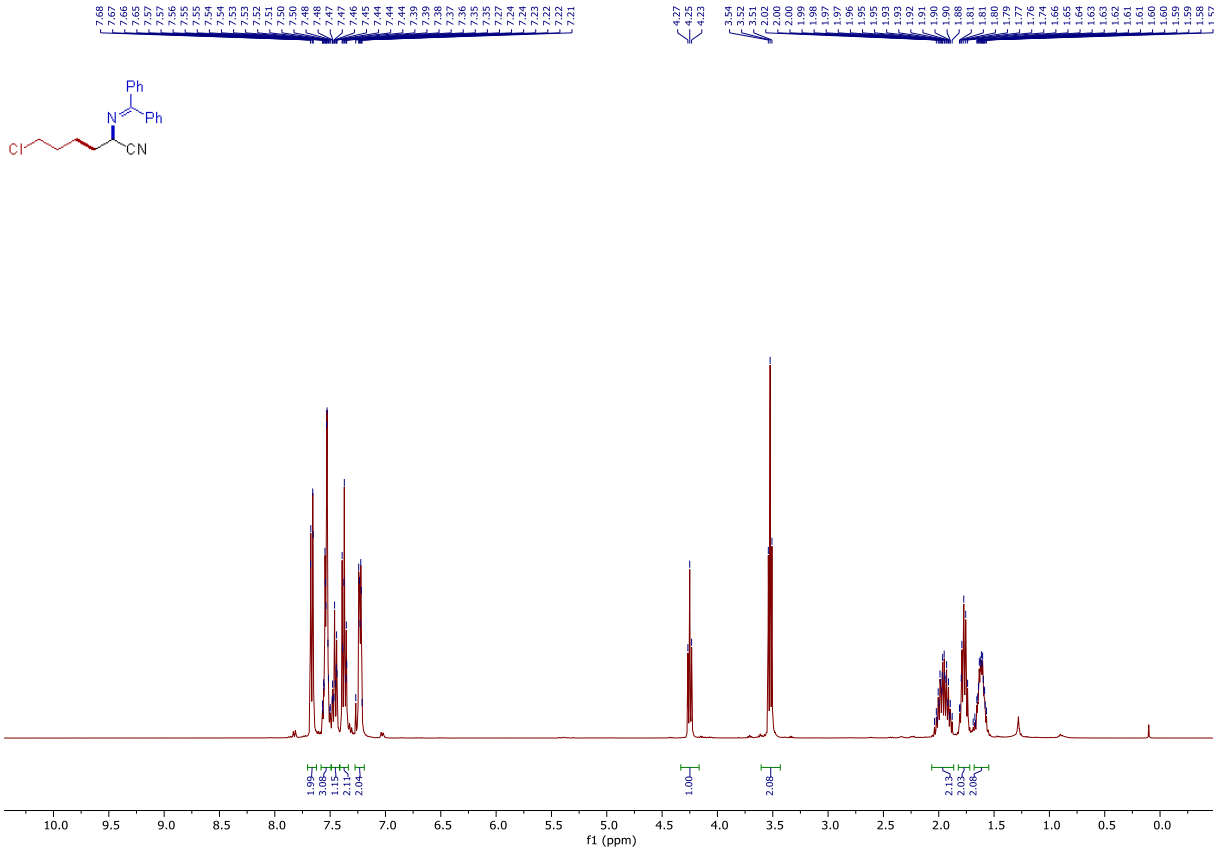


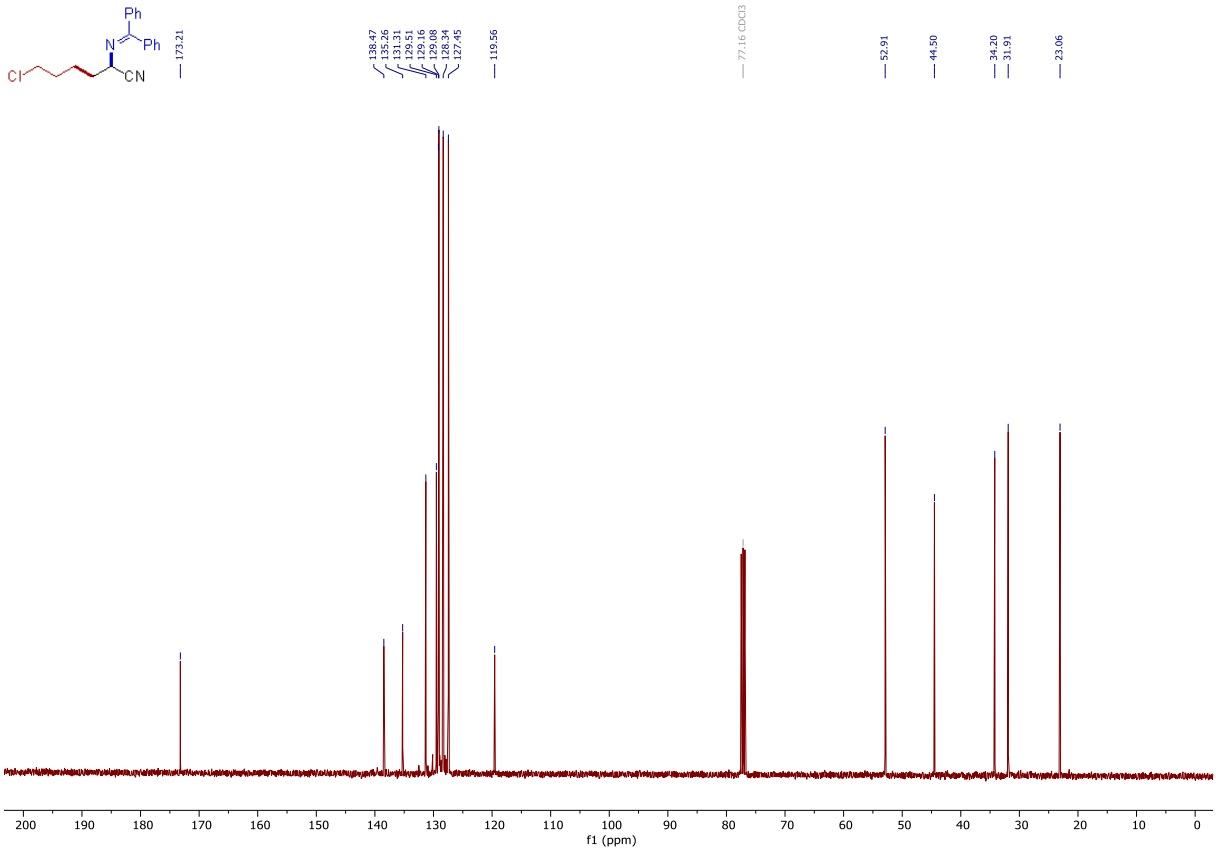
7-bromo-2-((diphenylmethylene)amino)heptanenitrile (20)



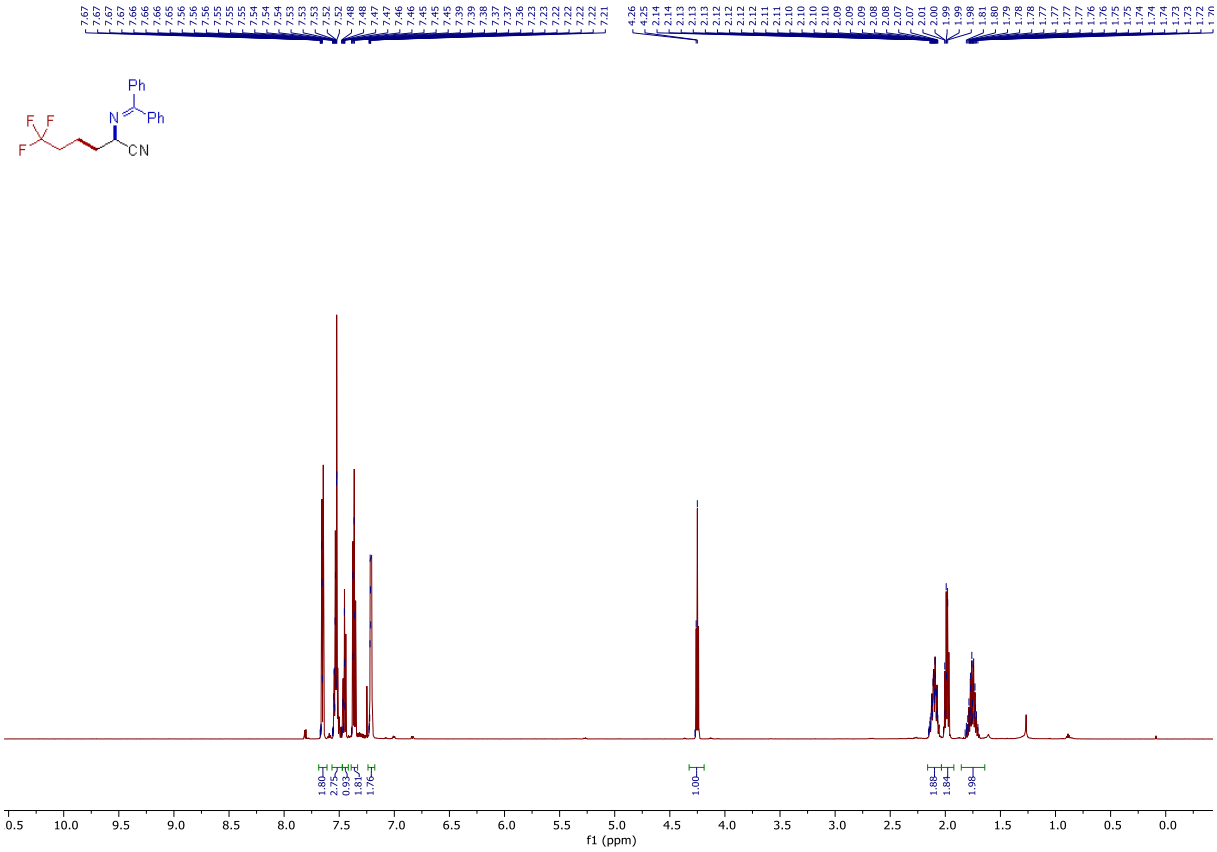


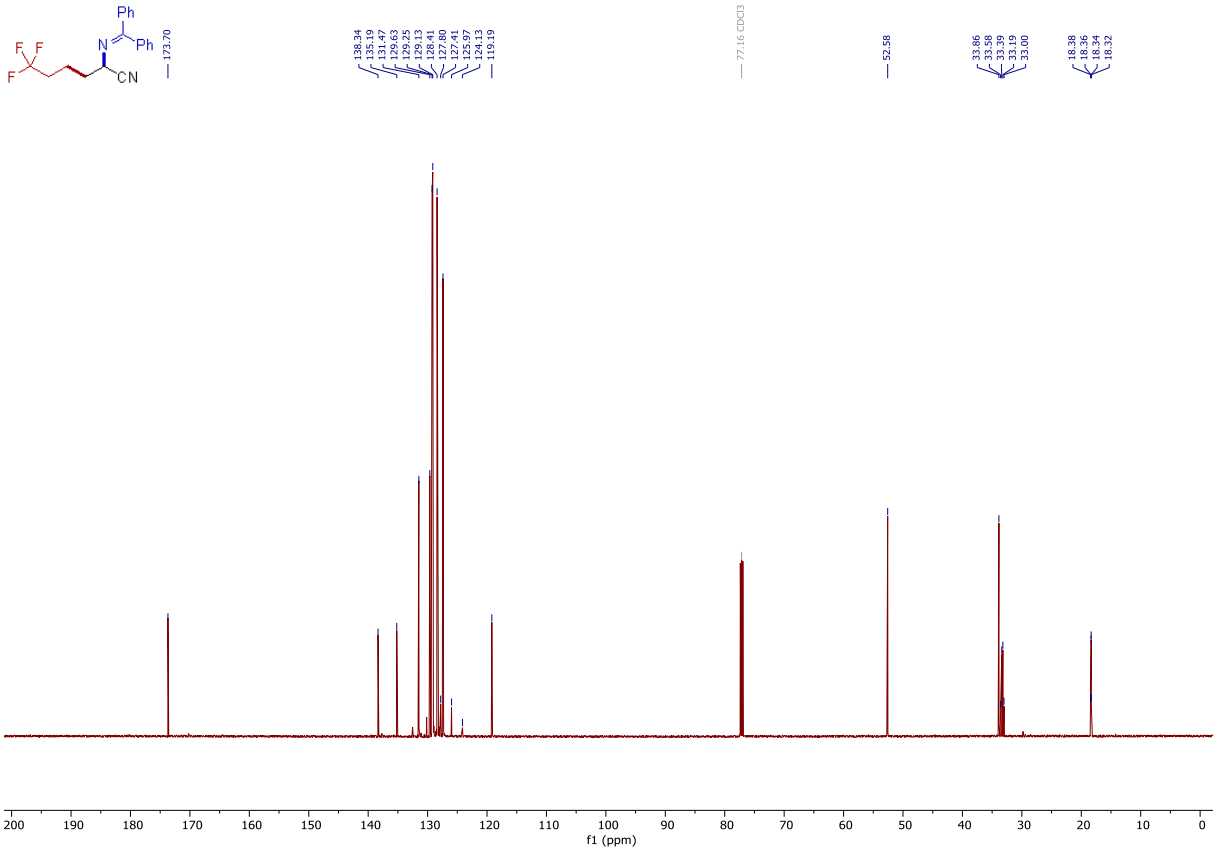
6-chloro-2-((diphenylmethylene)amino)hexanenitrile (21)

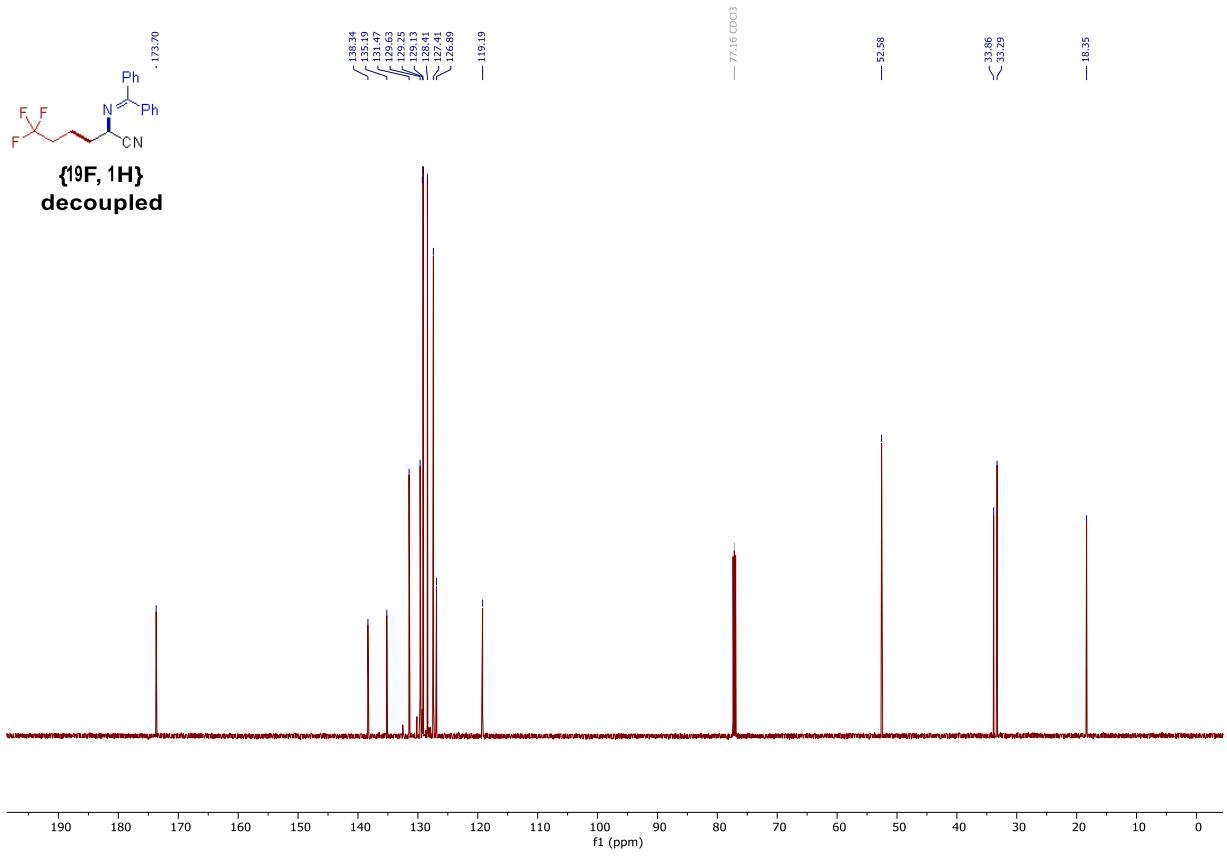


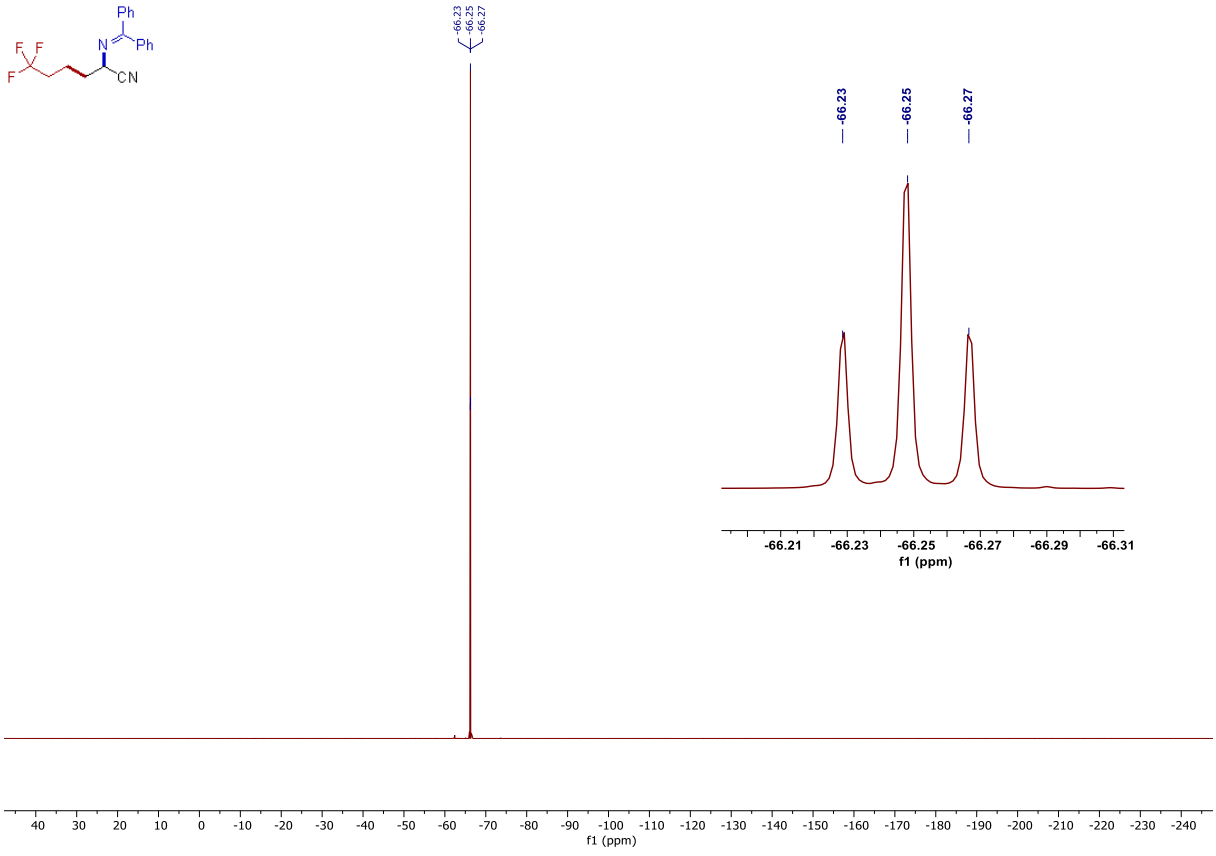


2-((diphenylmethylene)amino)-6,6,6-trifluorohexanenitrile (22)

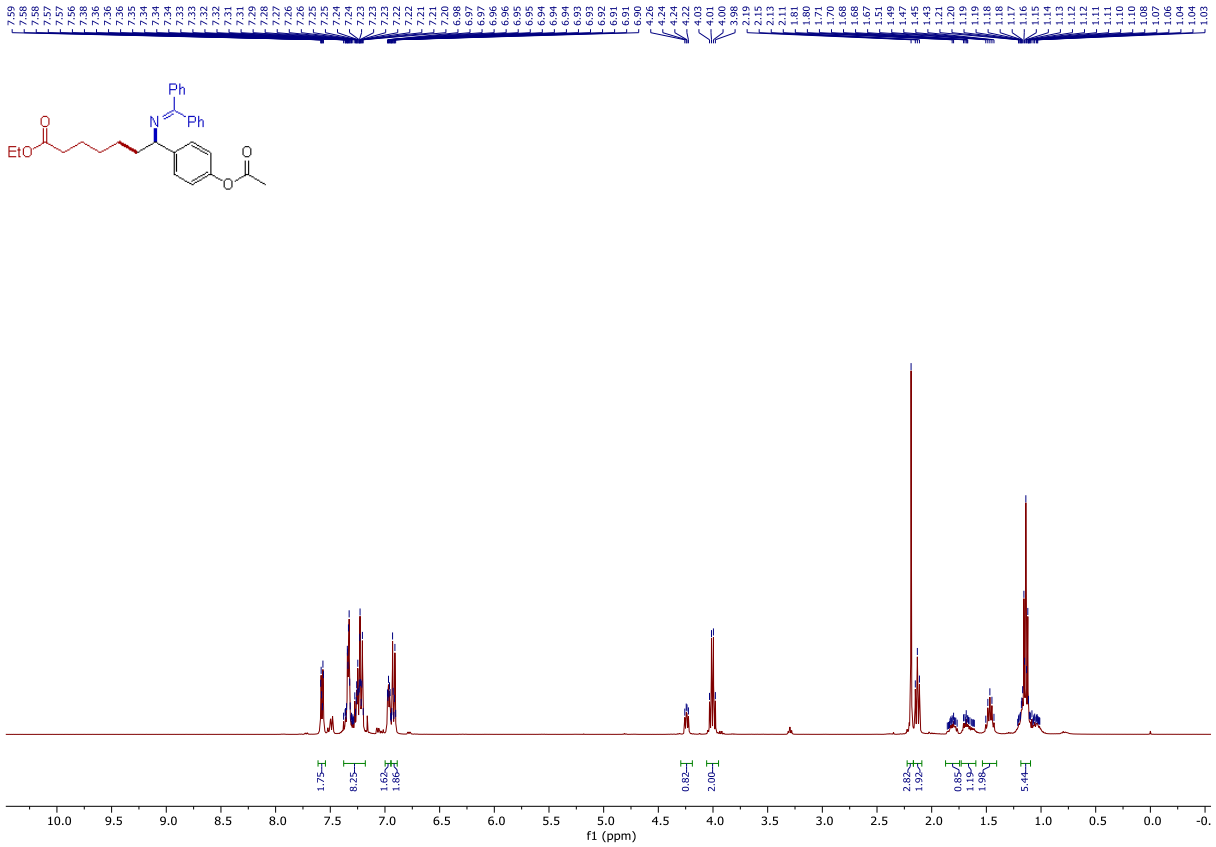


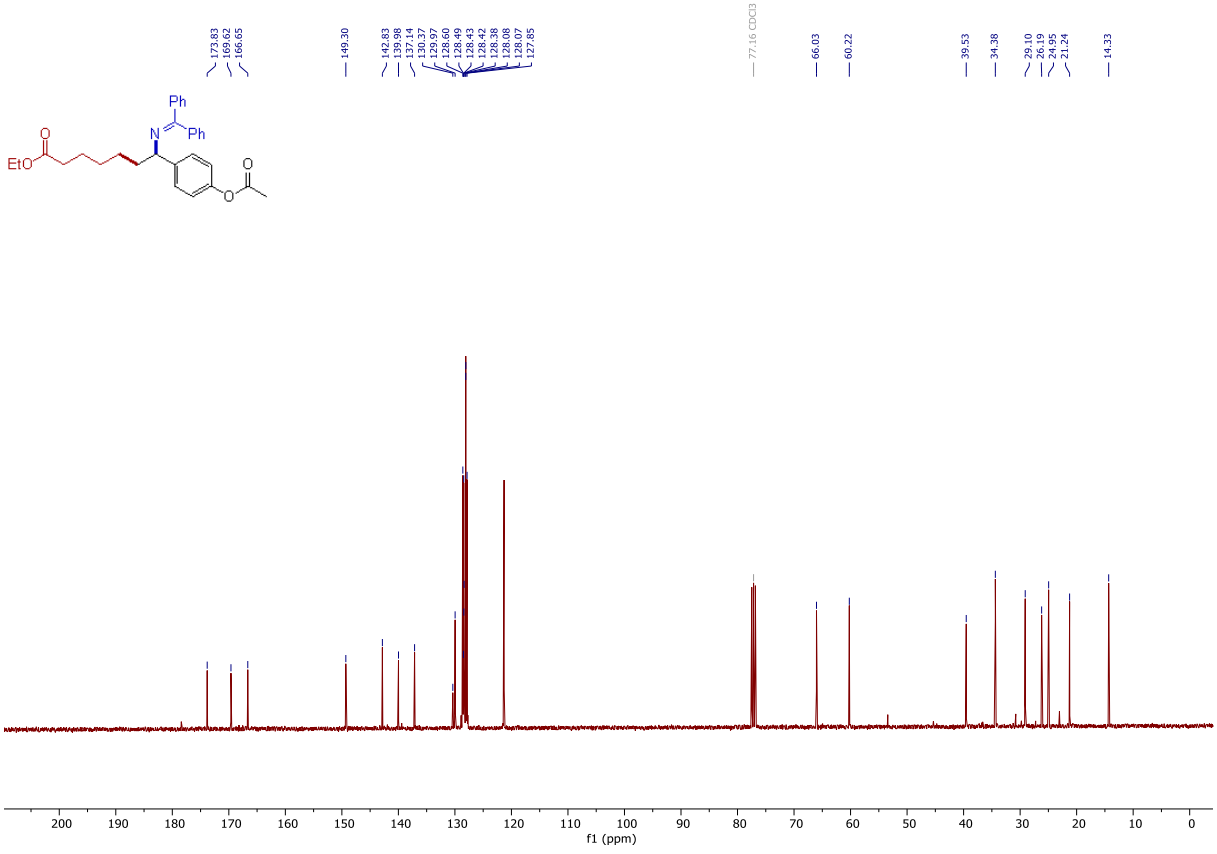



Ph
N
Ph
F
F
F
CN
{19F, 1H}
decoupled
173.70
138.34
135.19
131.47
129.63
129.25
129.13
128.41
127.41
126.89
119.19
77.16 CDCl3
52.58
33.86
33.29
18.35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

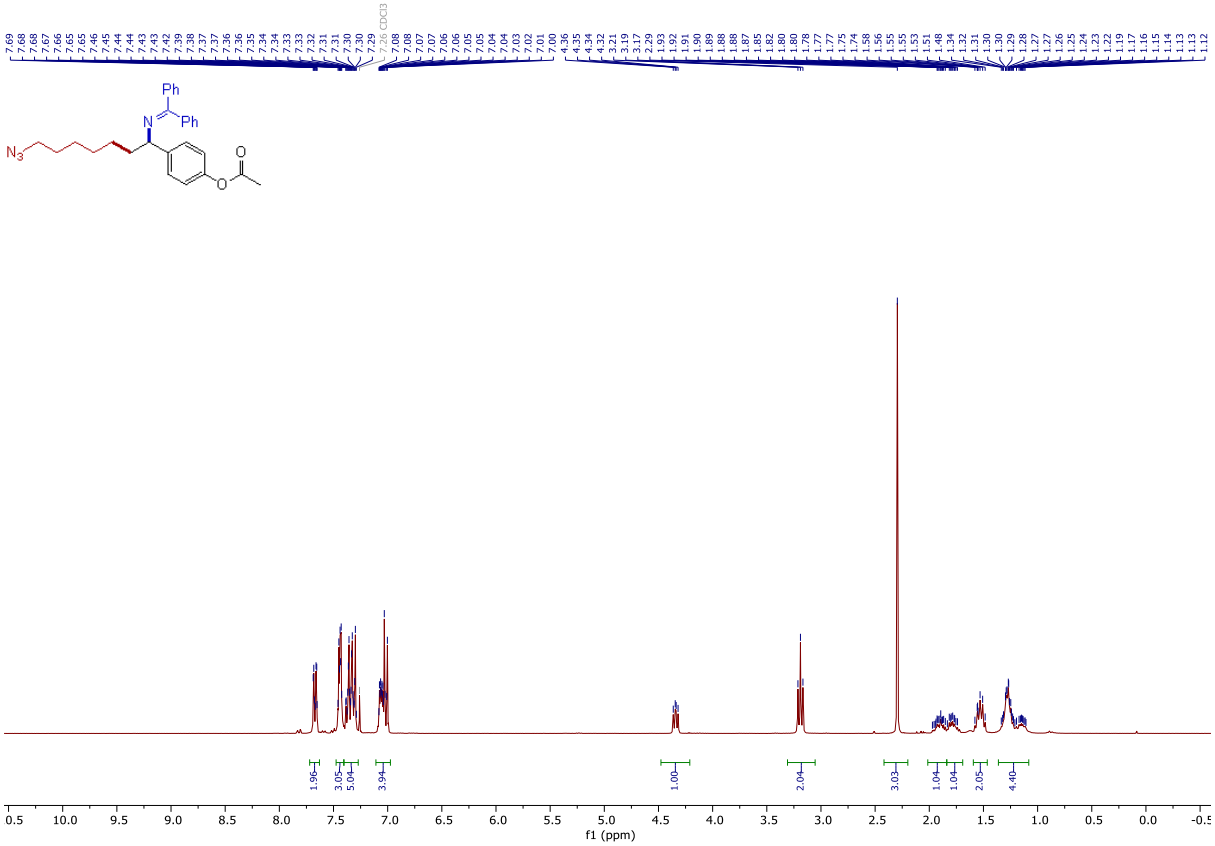

Ph
N
Ph
F
F
F
CN
-66.23
-66.25
-66.27
-66.21 -66.23 -66.25 -66.27 -66.29 -66.31
f1 (ppm)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

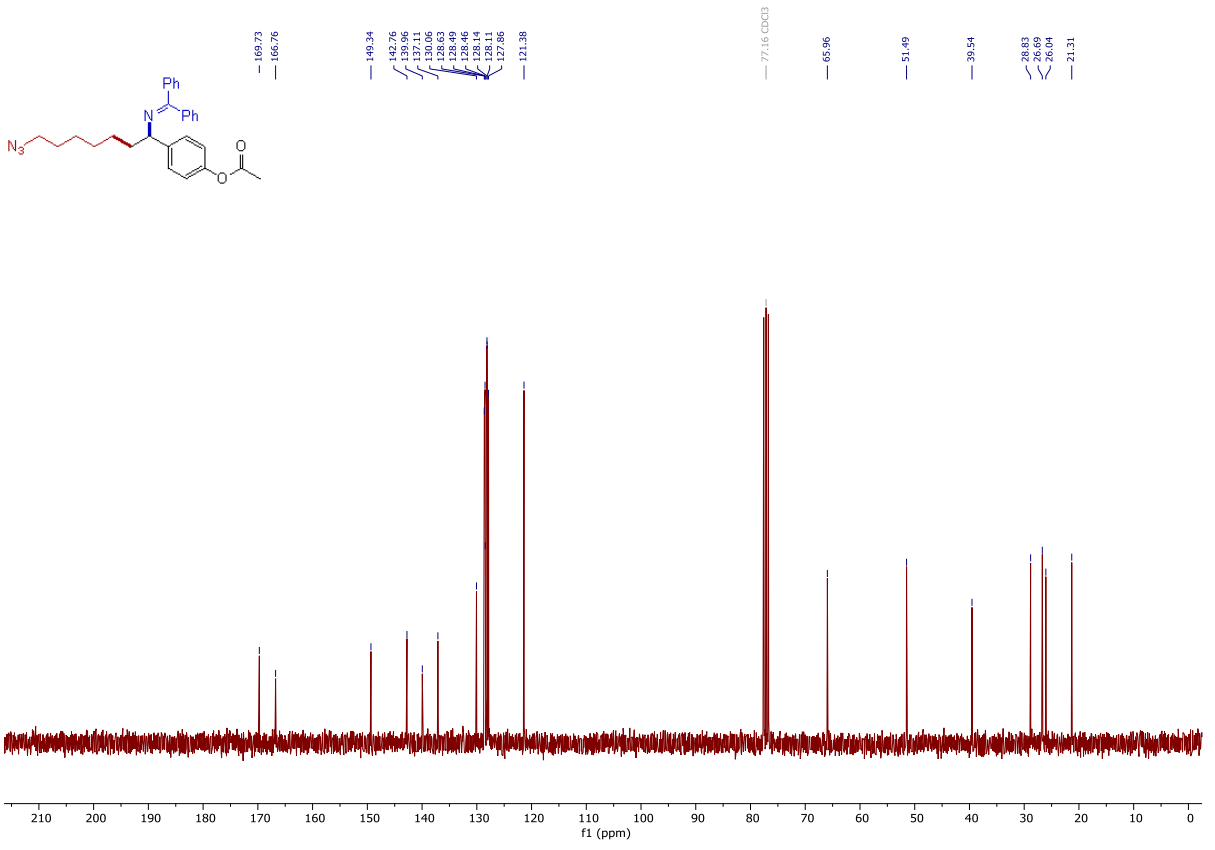
ethyl 7-(4-acetoxyphenyl)-7-((diphenylmethylene)amino)heptanoate (23)



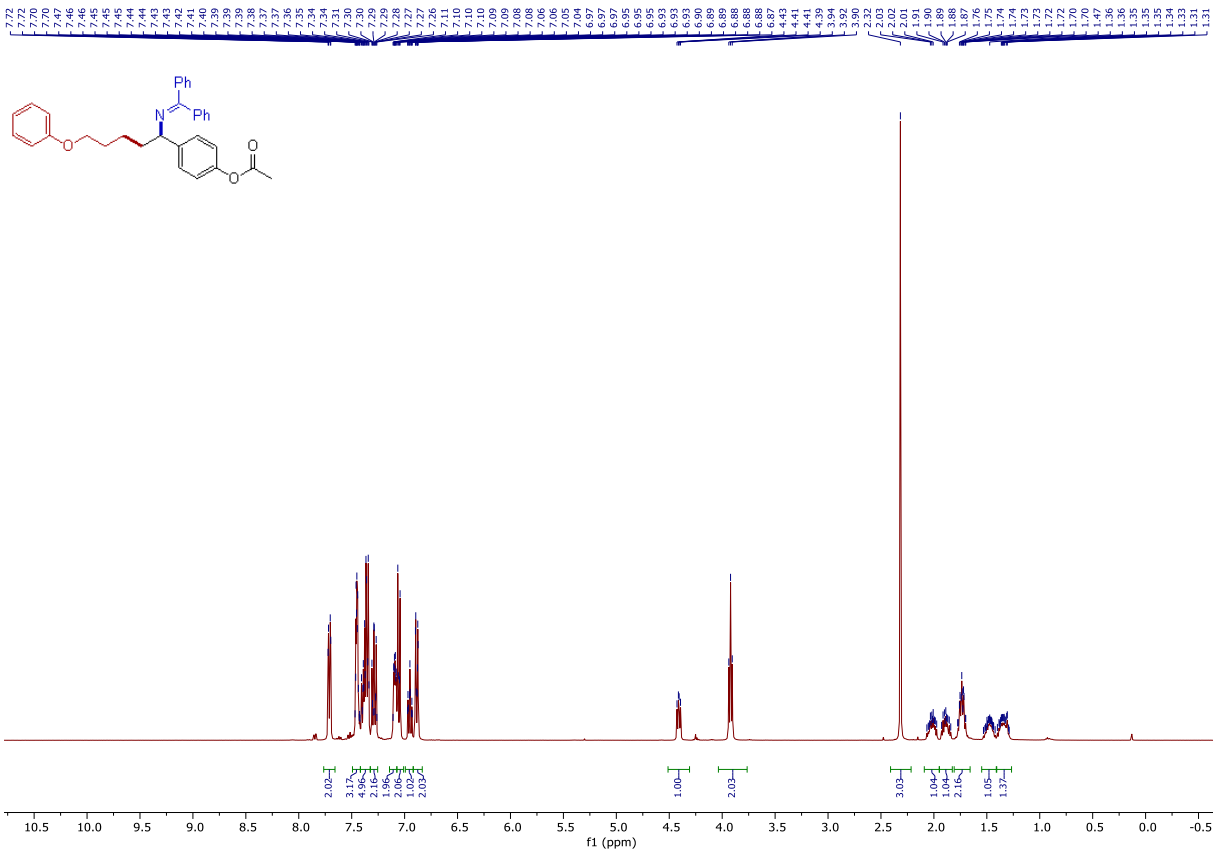


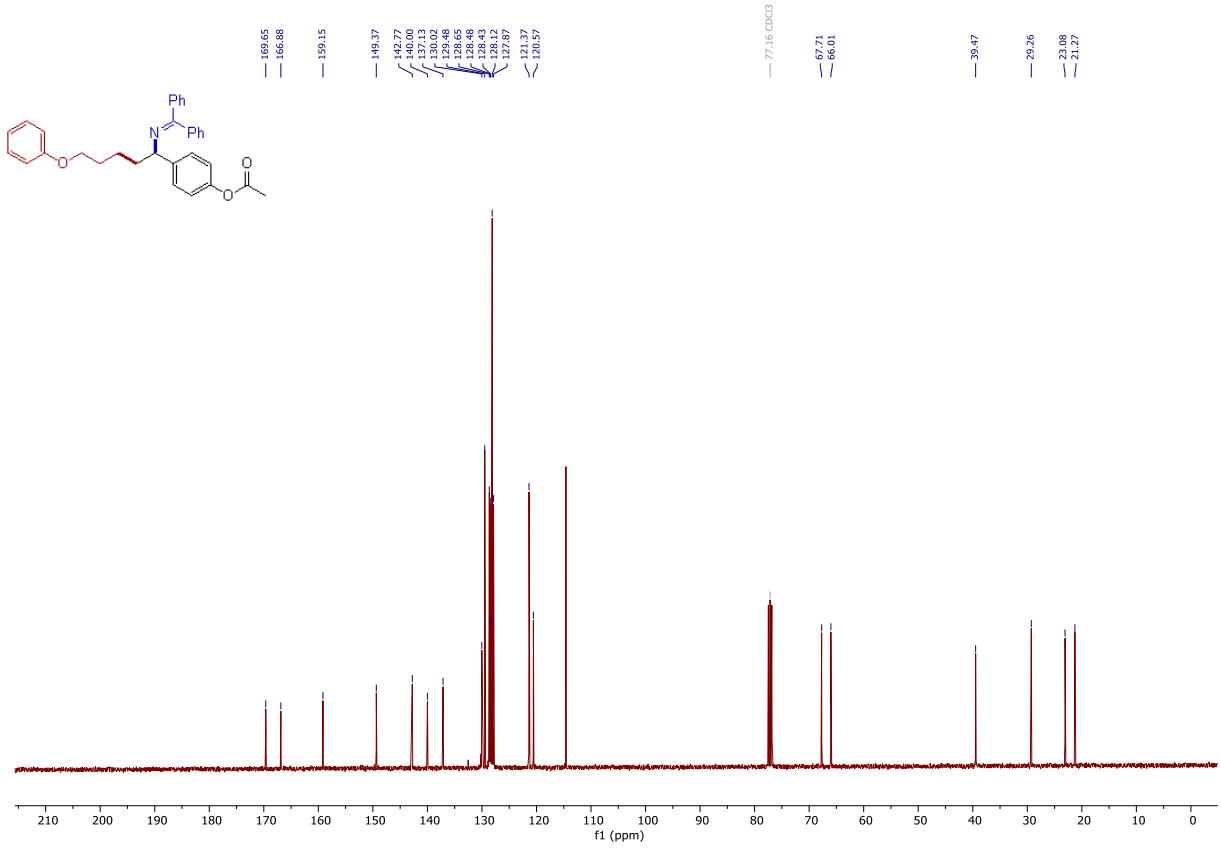
4-(7-azido-1-((diphenylmethylene)amino)heptyl)phenyl acetate (24)



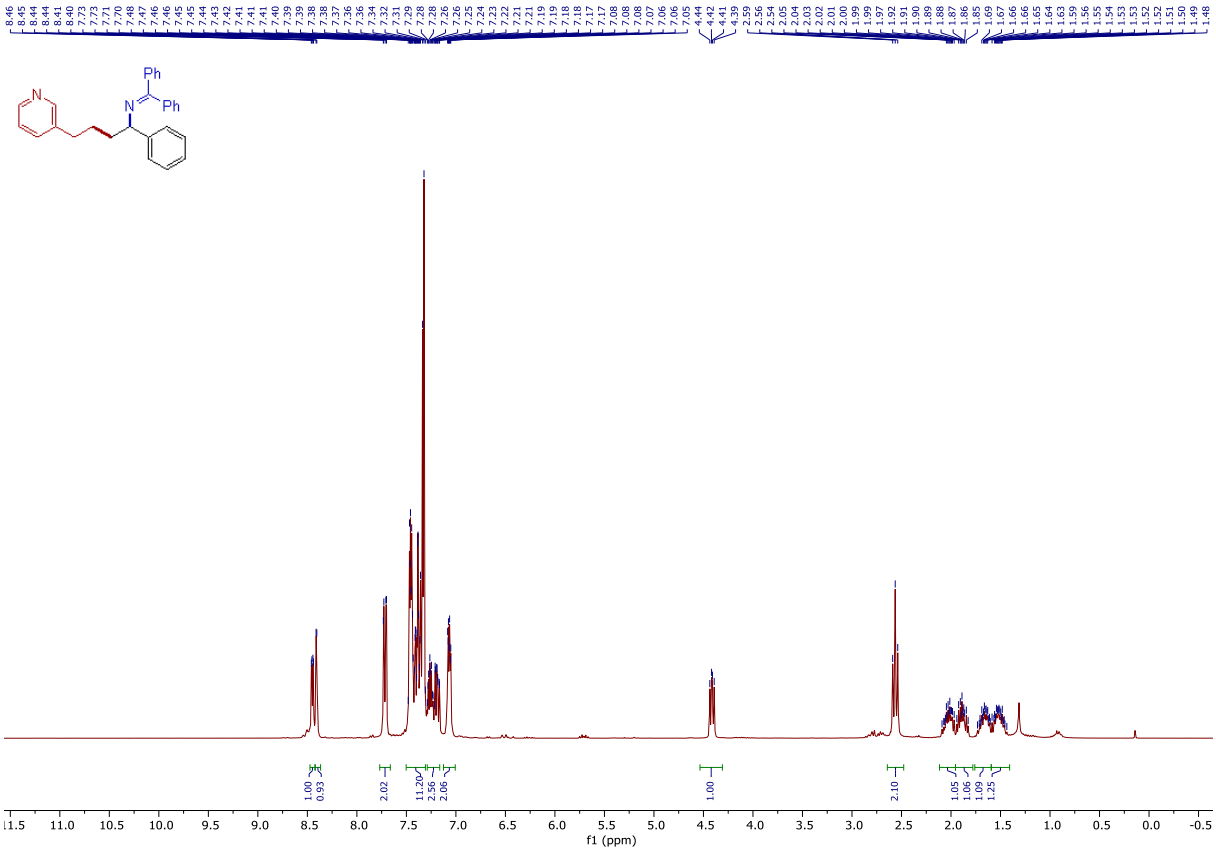


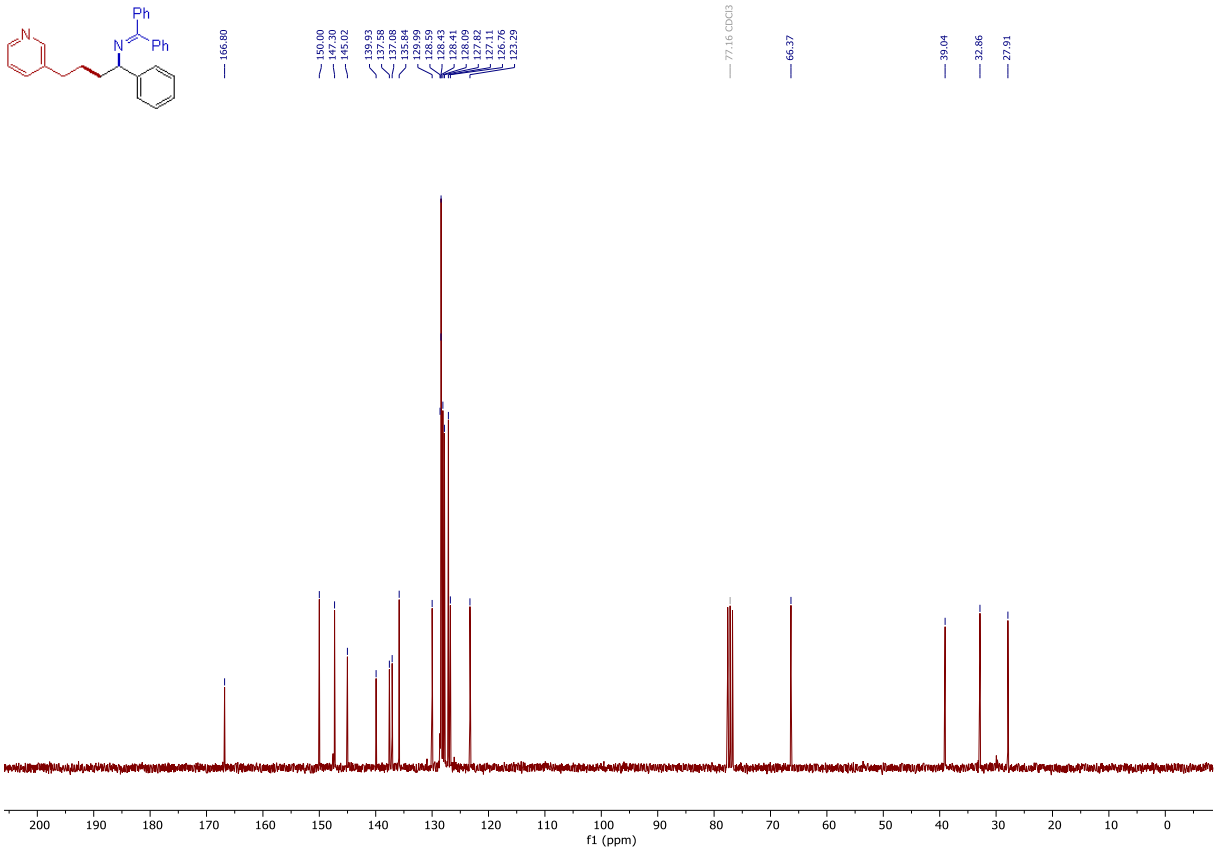
4-(1-((diphenylmethylene)amino)-5-phenoxyhexyl)phenyl acetate (25)



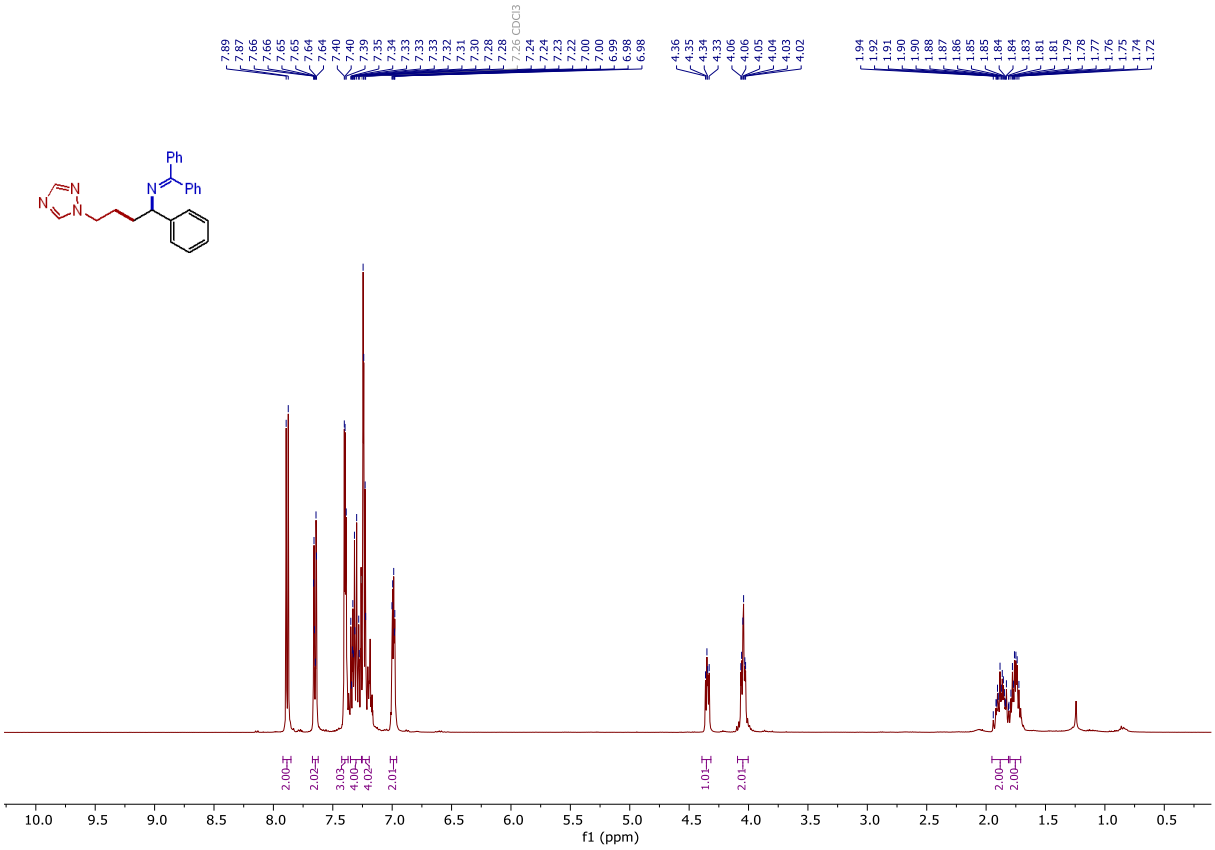


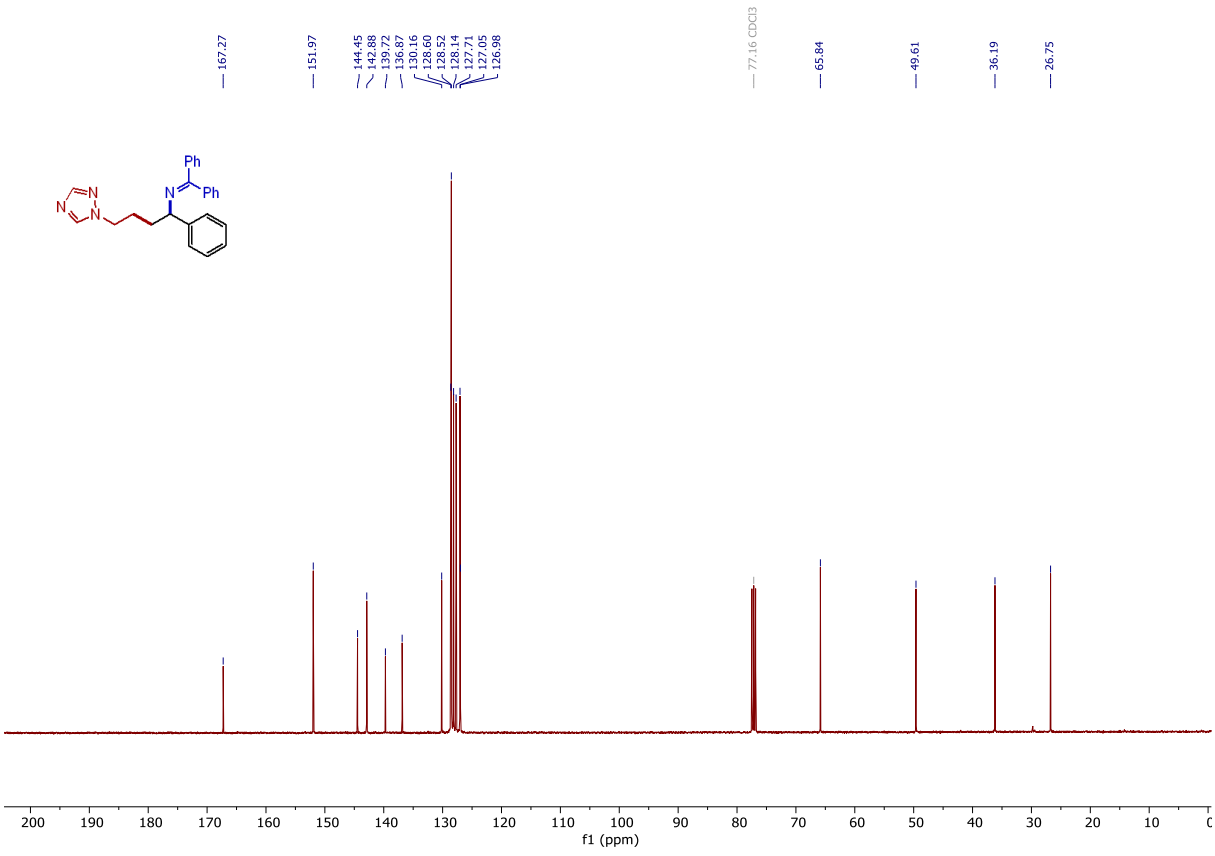
1,1-diphenyl-*N*-(1-phenyl-4-(pyridin-3-yl)butyl)methanimine (26)



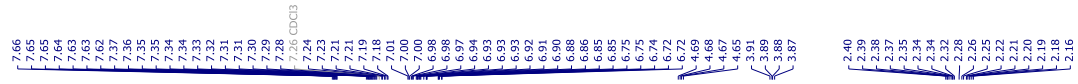


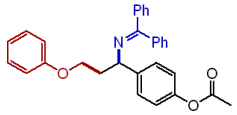
1,1-diphenyl-*N*-(1-phenyl-4-(1*H*-1,2,4-triazol-1-yl)butyl)methanimine (27)

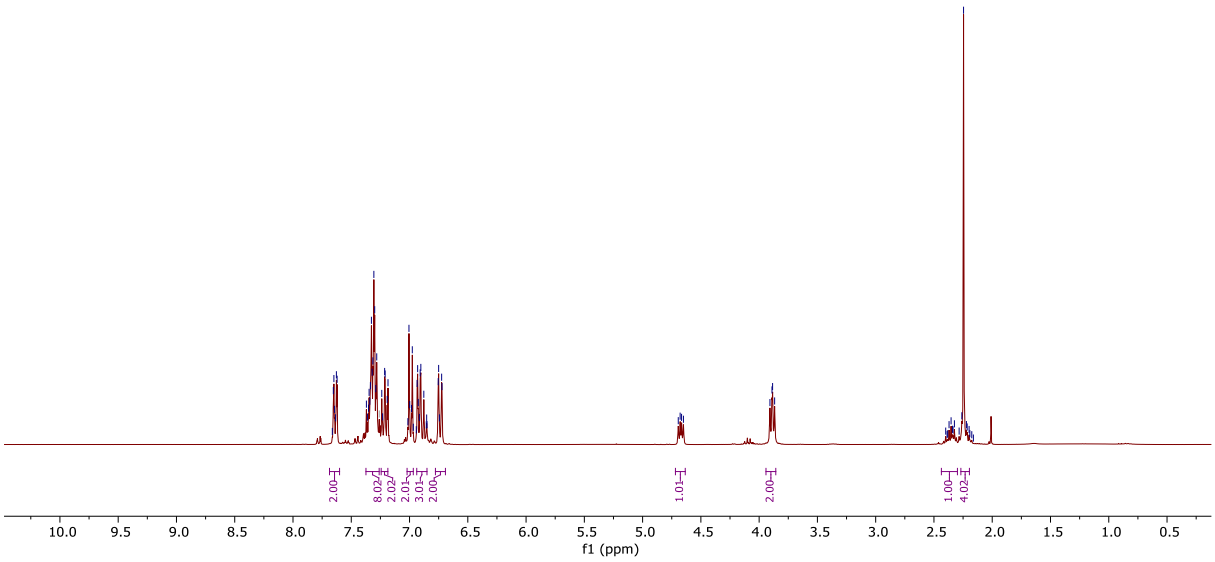


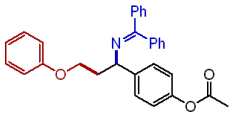


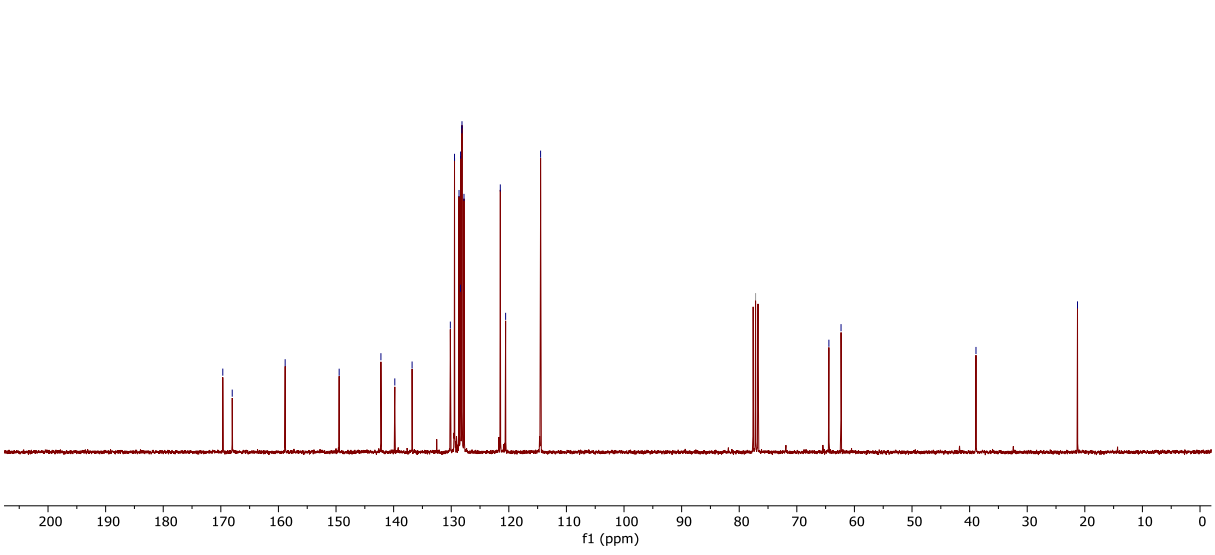
4-(1-((diphenylmethylene)amino)-3-phenoxypropyl)phenyl acetate (28)



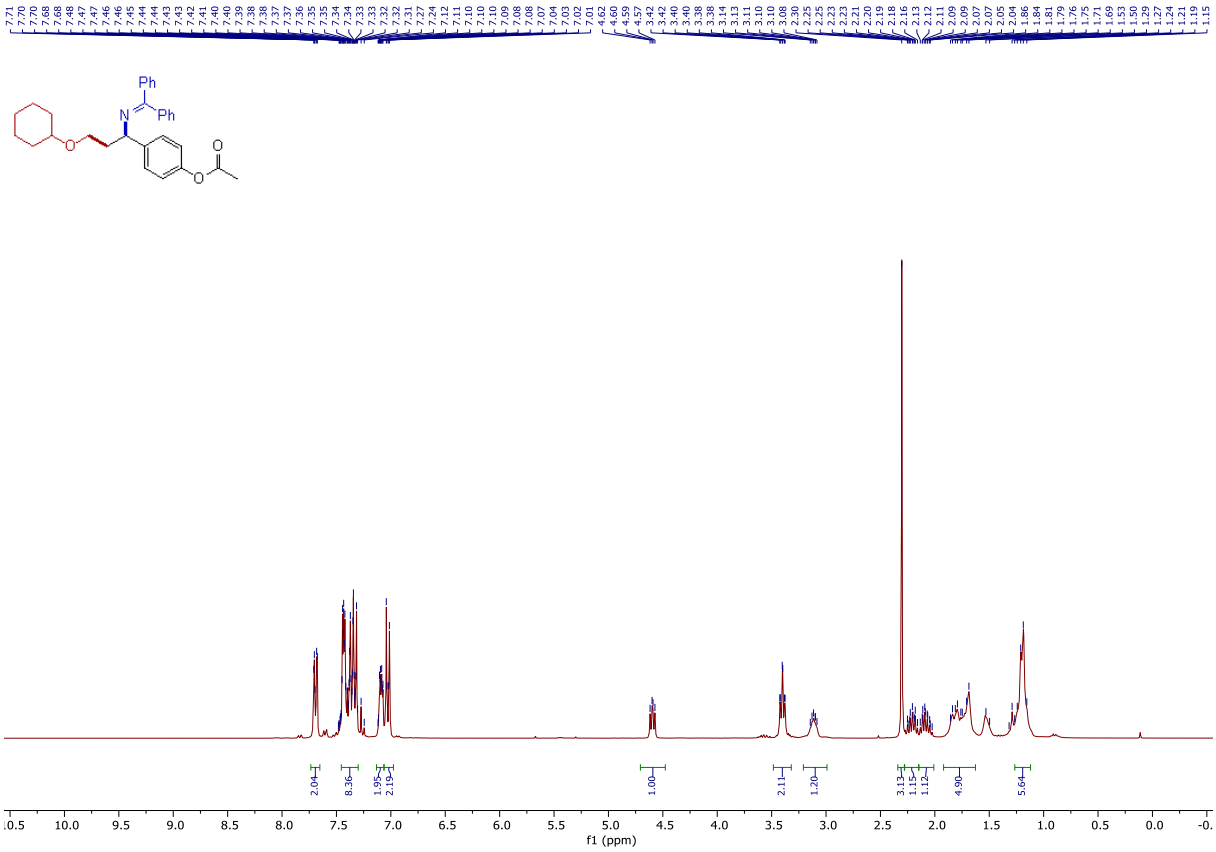


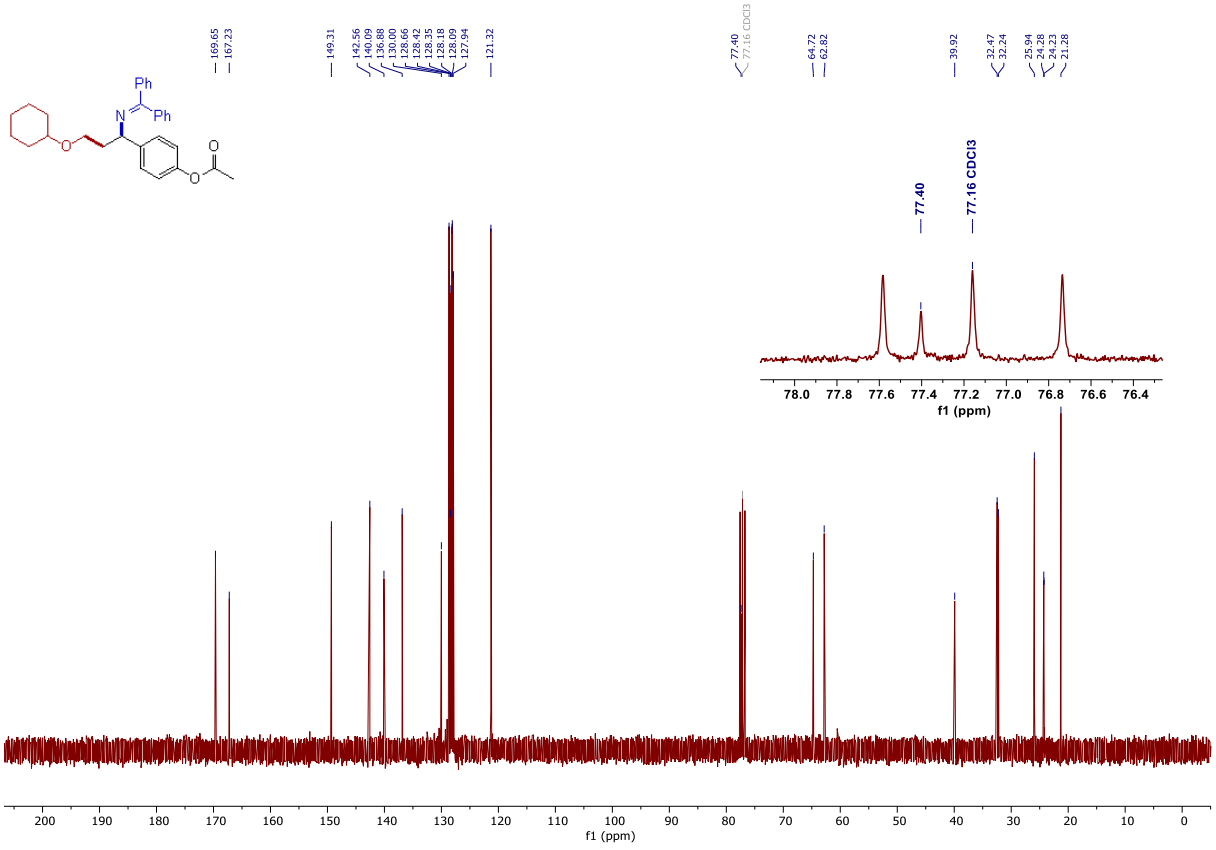




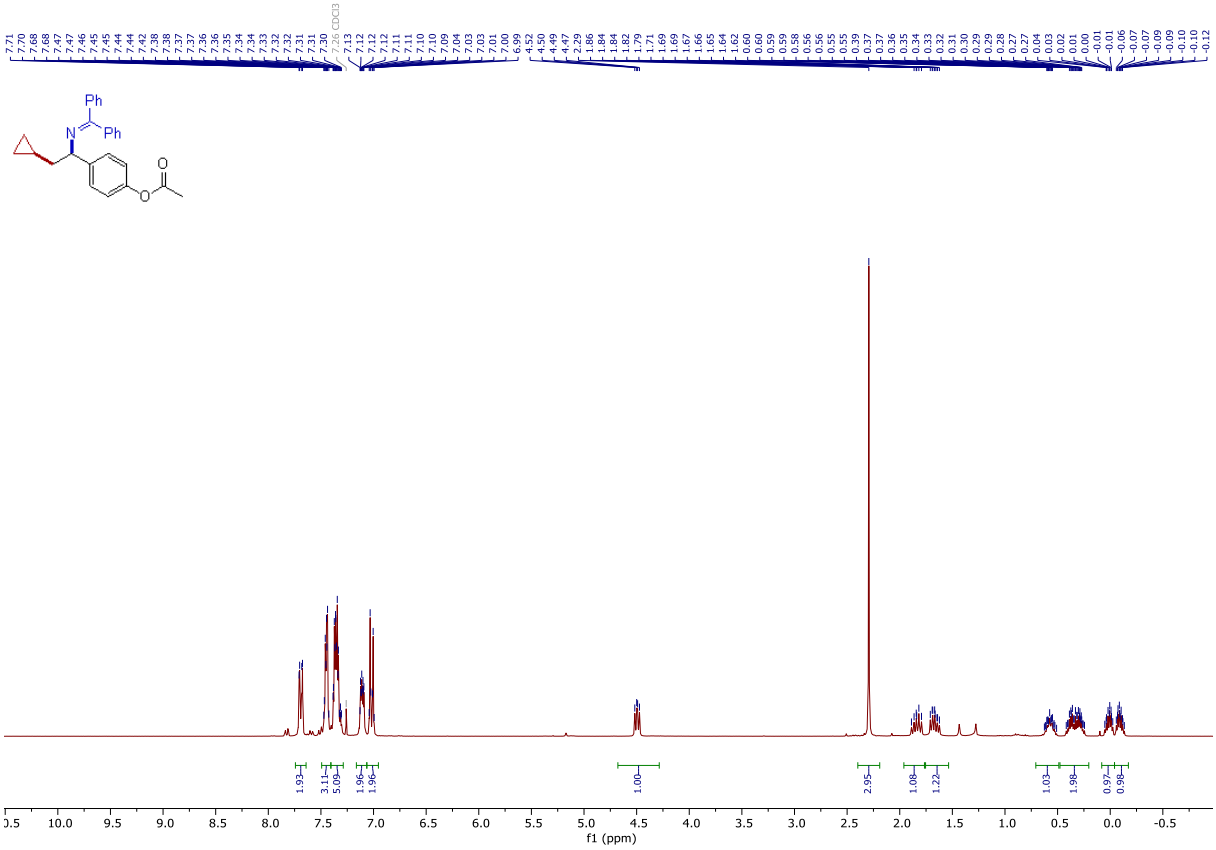


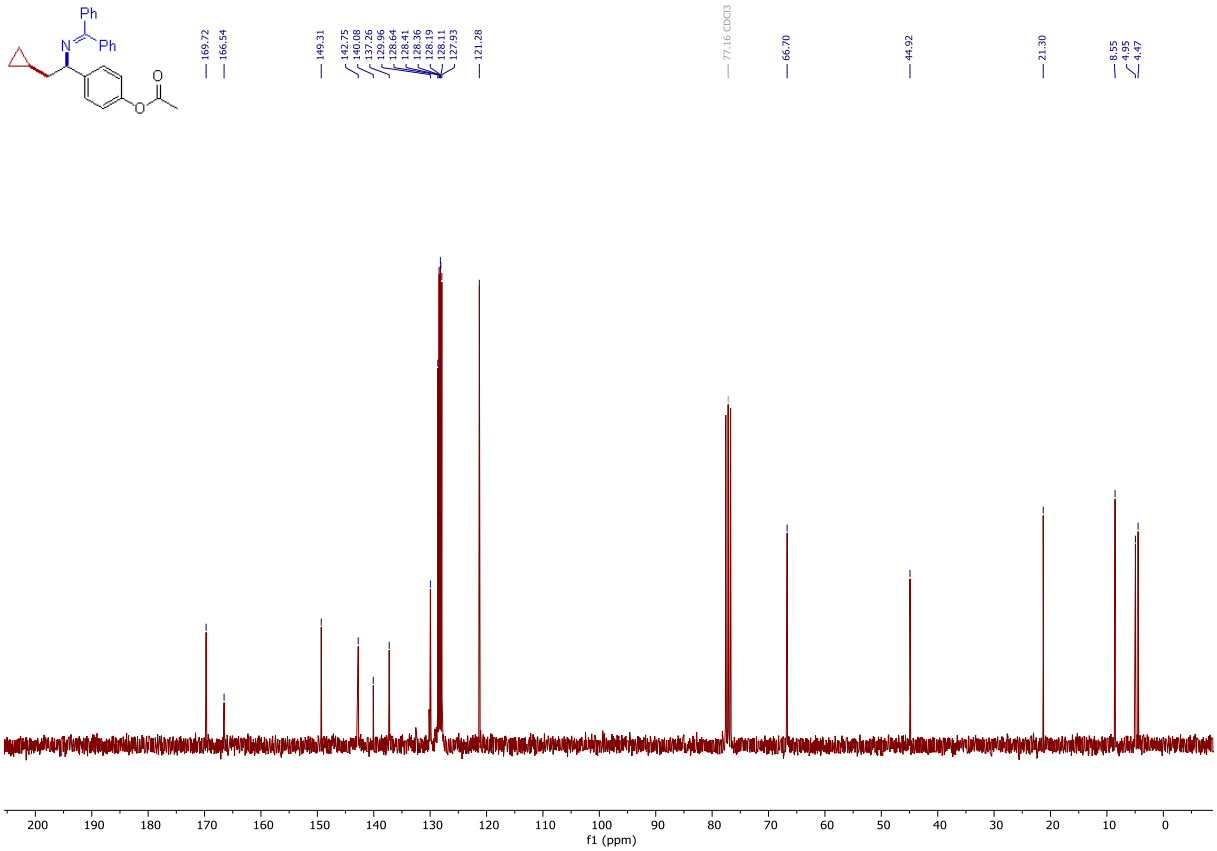
4-(3-(cyclohexyloxy)-1-((diphenylmethylene)amino)propyl)phenyl acetate (29)



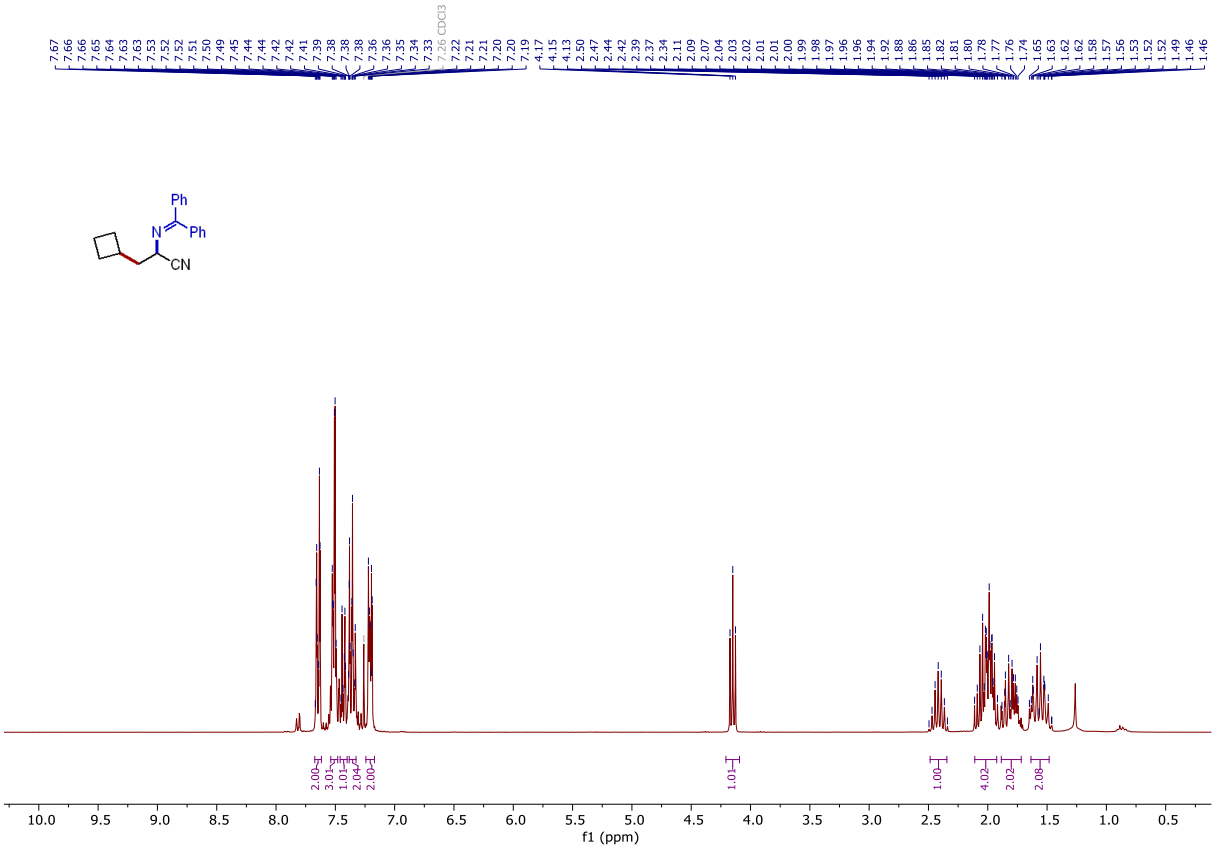


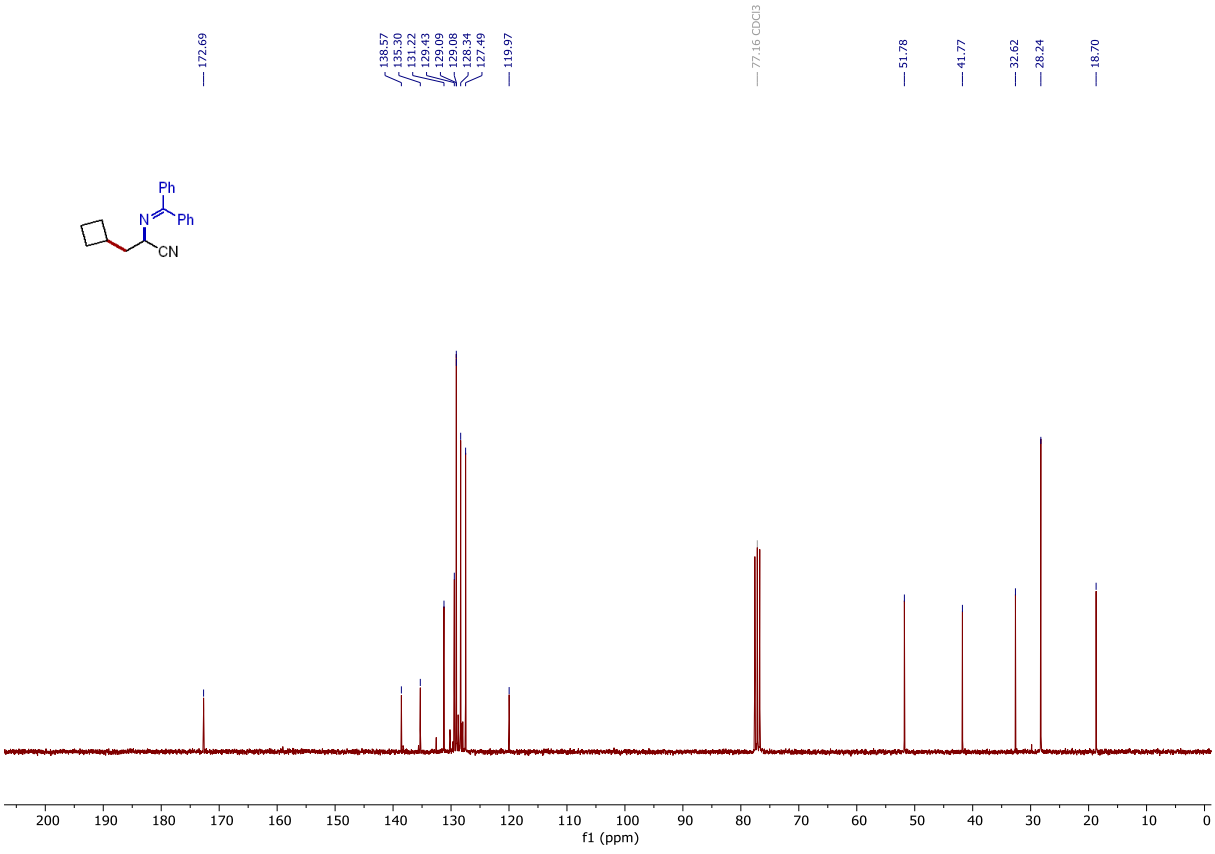
4-(2-cyclopropyl-1-((diphenylmethylene)amino)ethyl)phenyl acetate (30)



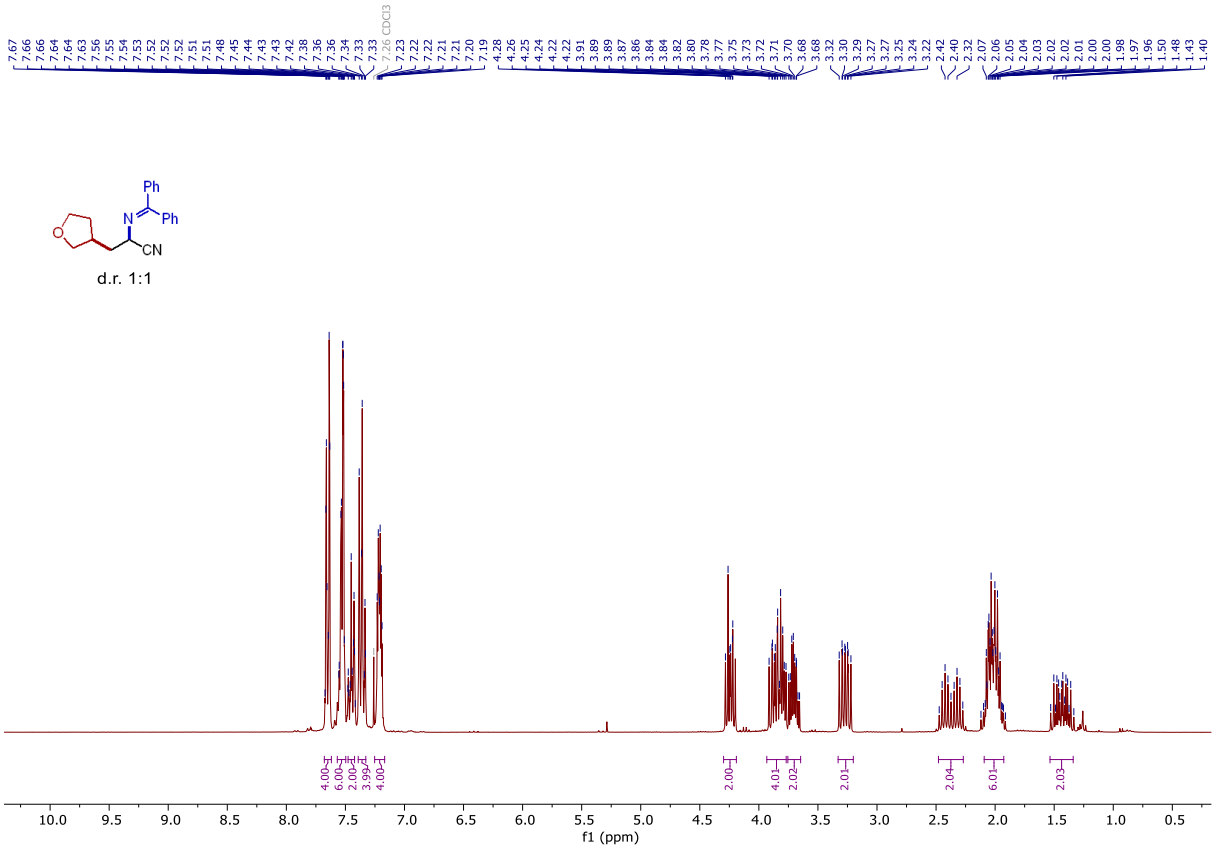


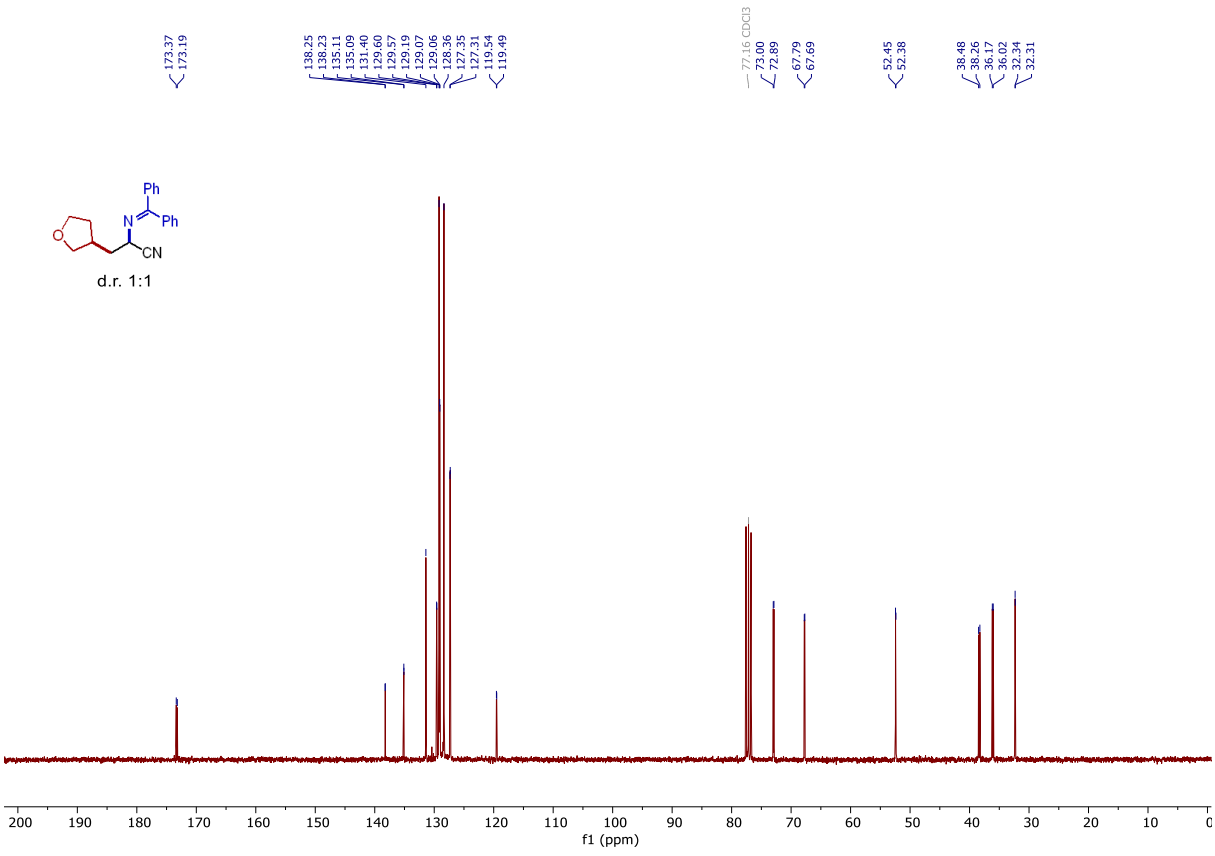
3-cyclobutyl-2-((diphenylmethylene)amino)propanenitrile (31)



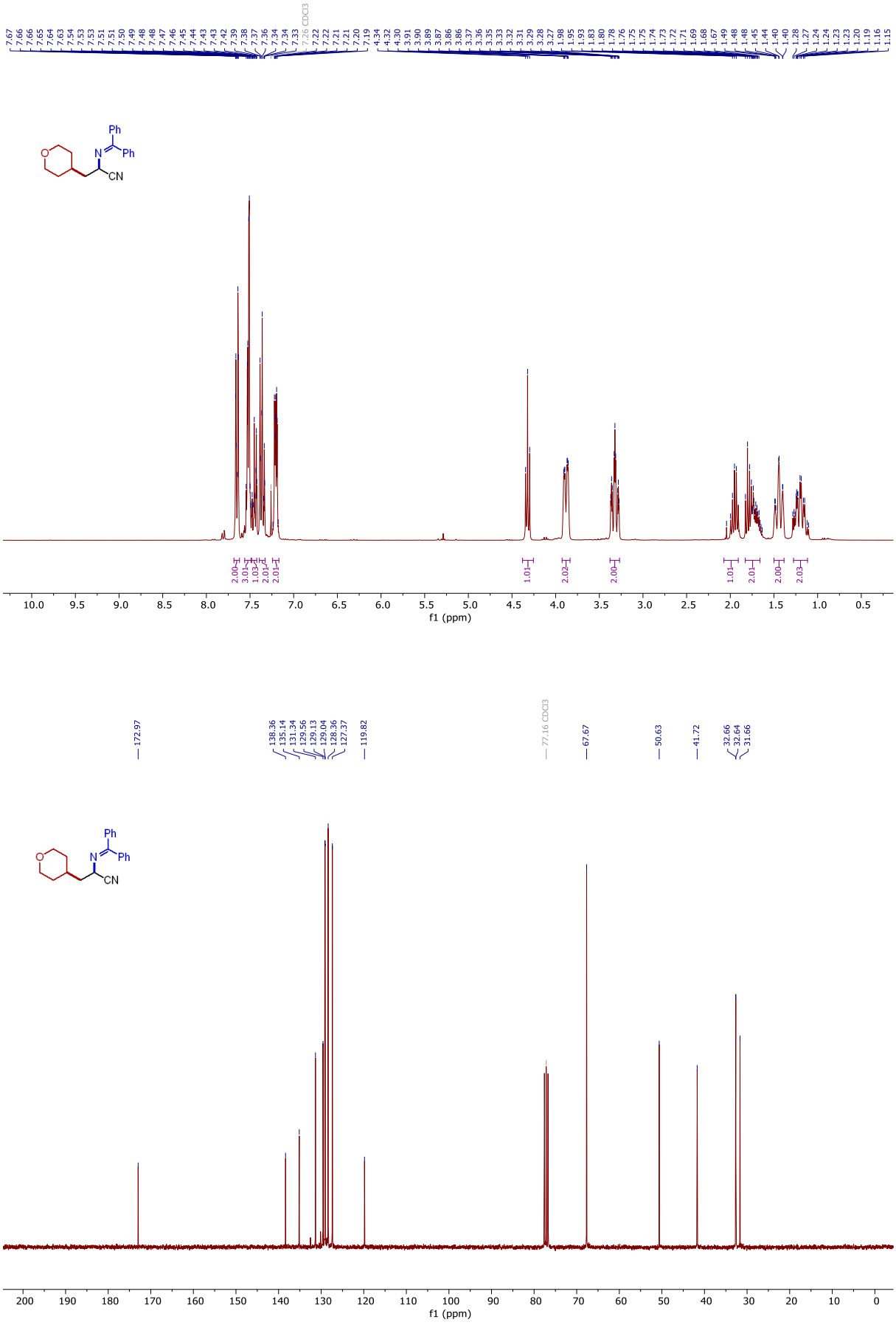


2-((diphenylmethylene)amino)-3-(tetrahydrofuran-3-yl)propanenitrile (32)

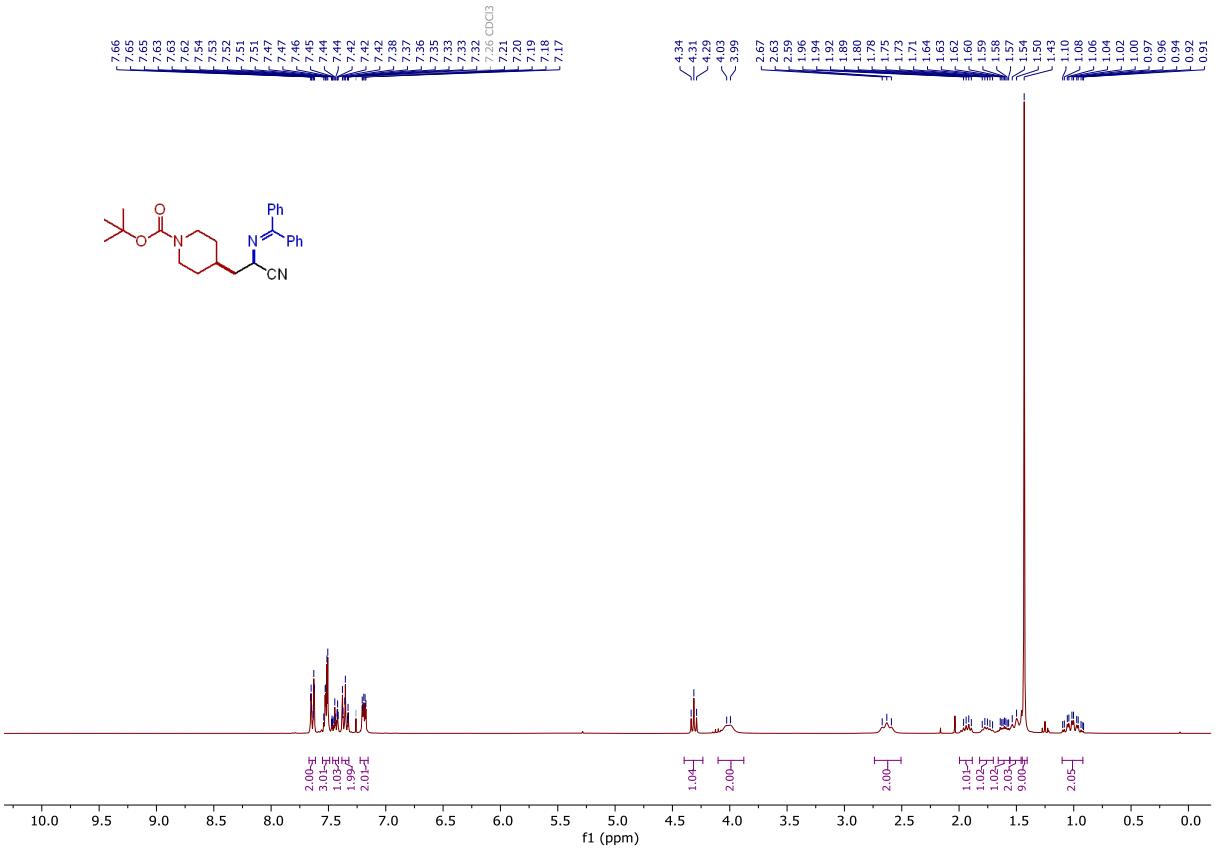


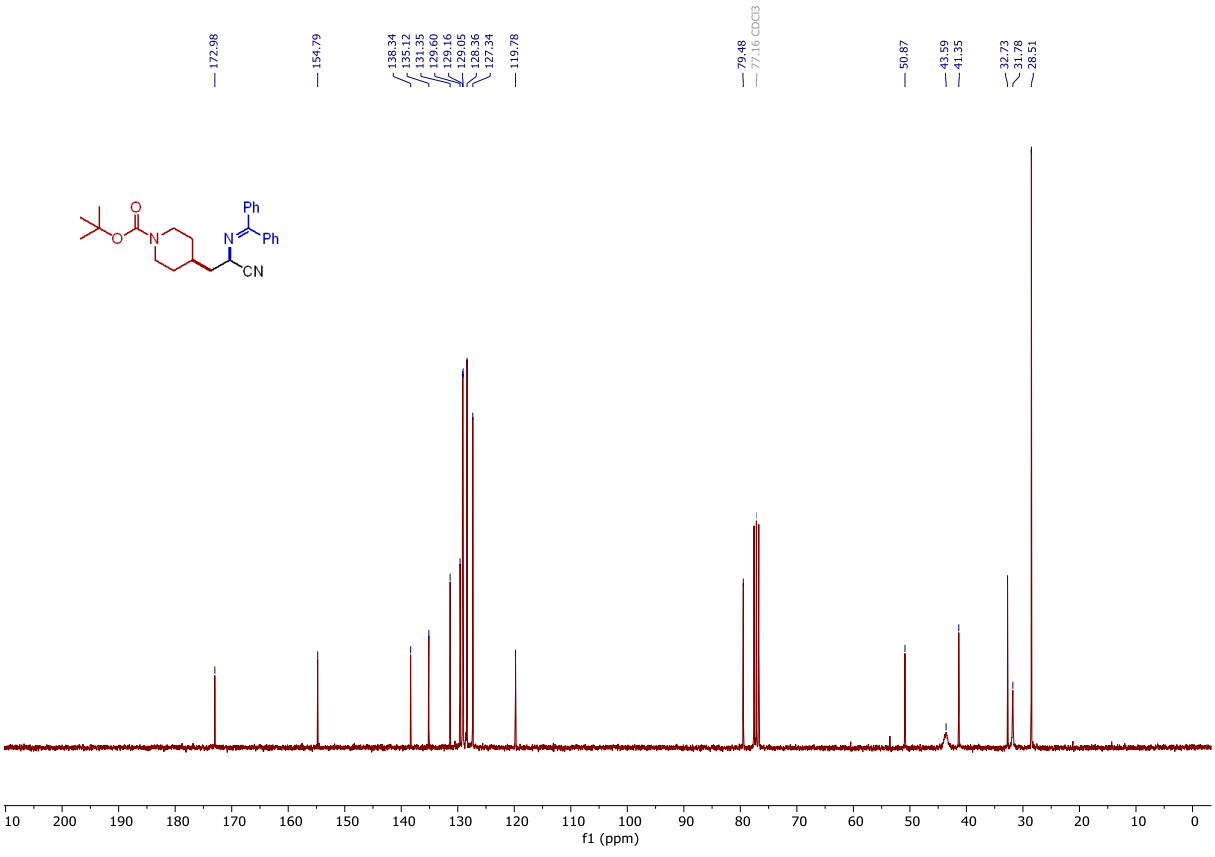


2-((diphenylmethylene)amino)-3-(tetrahydro-2H-pyran-4-yl)propanenitrile (33)

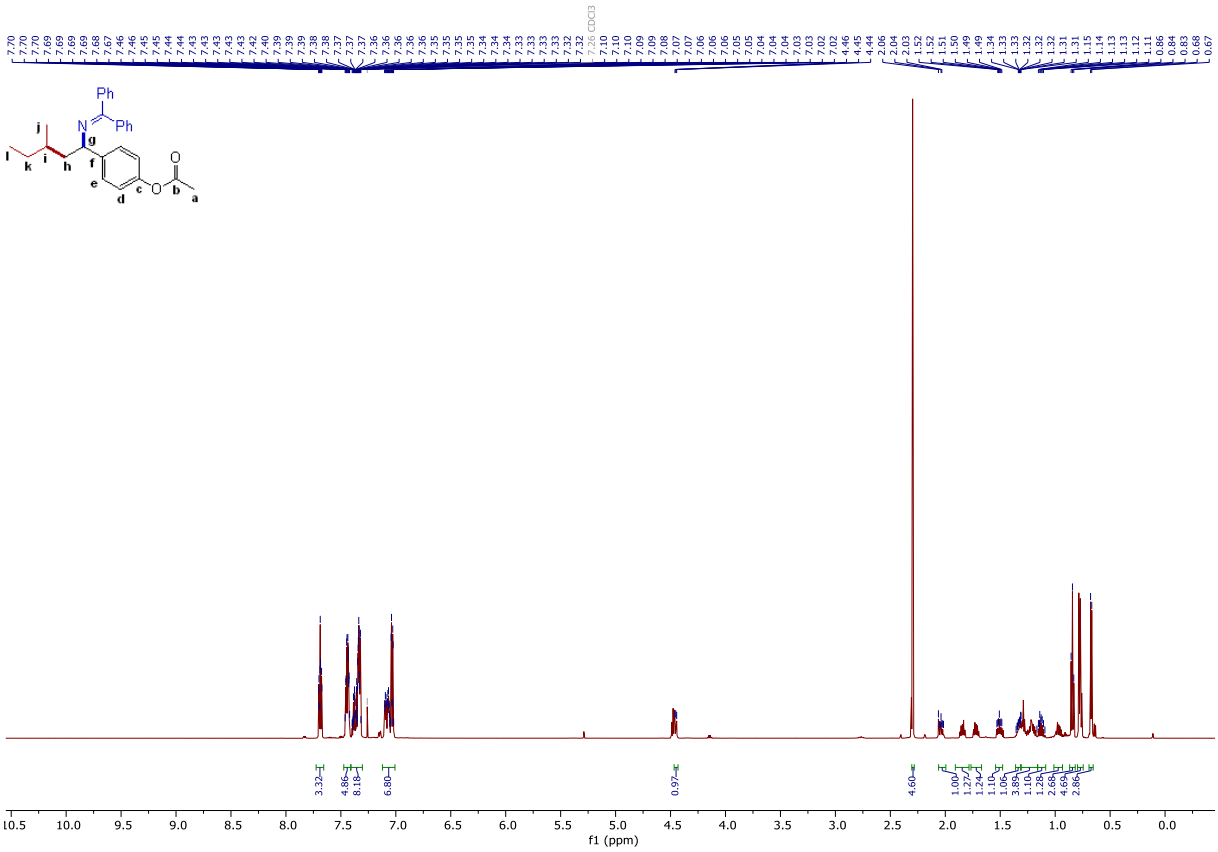


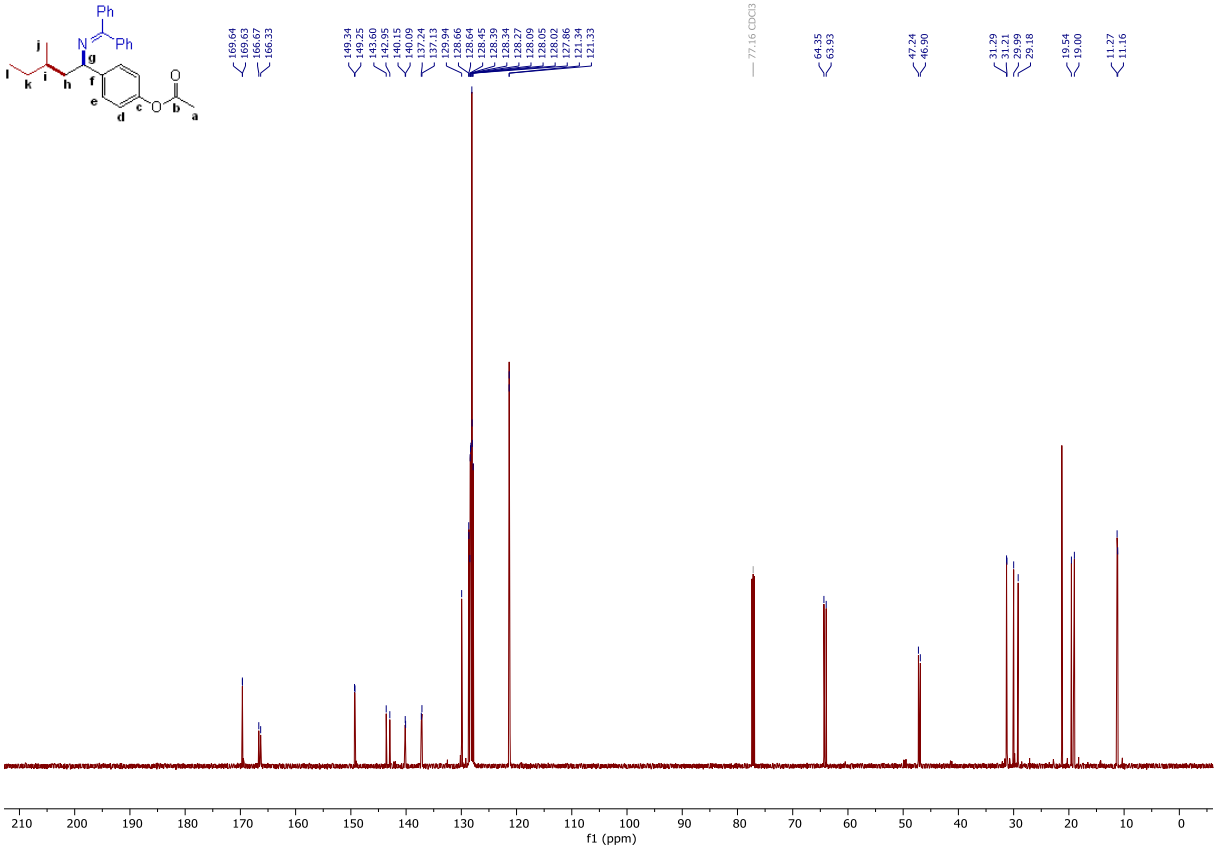
***tert*-butyl 4-(2-cyano-2-((diphenylmethylene)amino)ethyl)piperidine-1-carboxylate (34)**

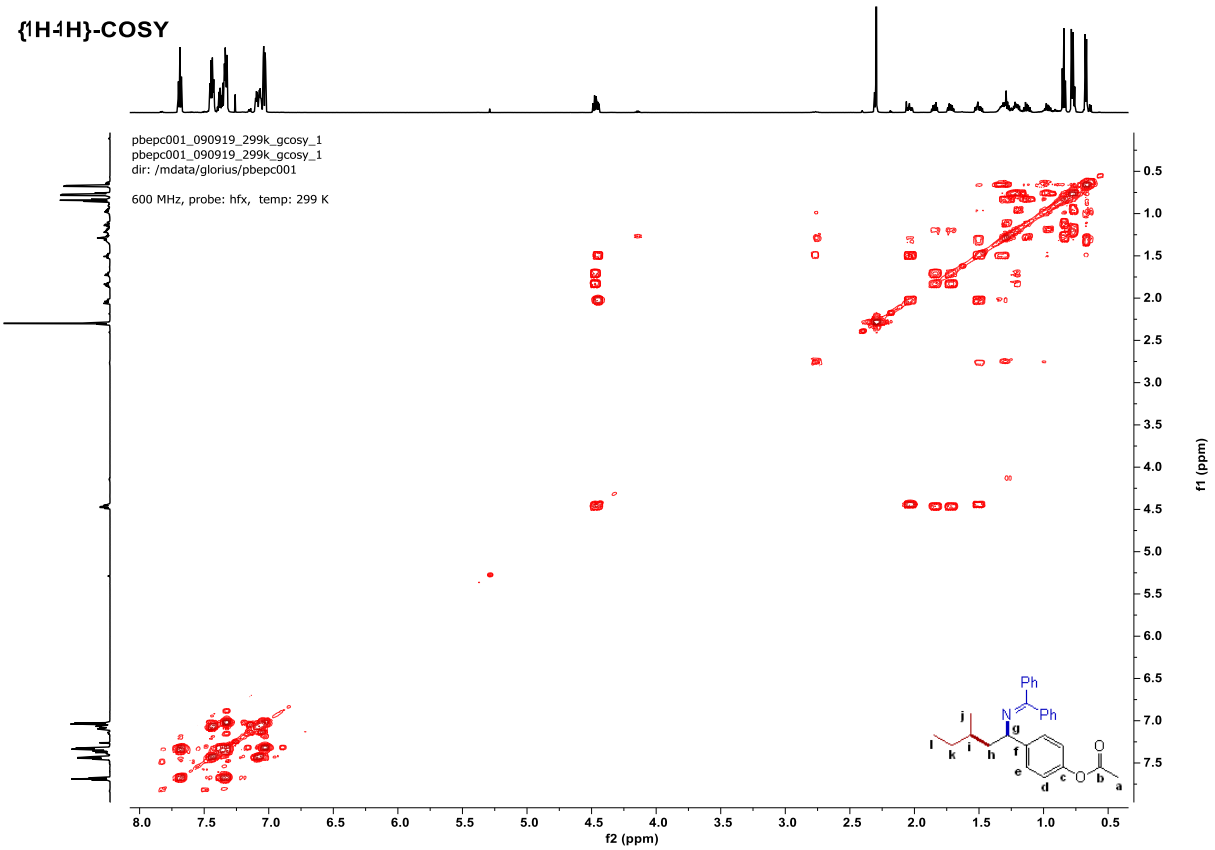


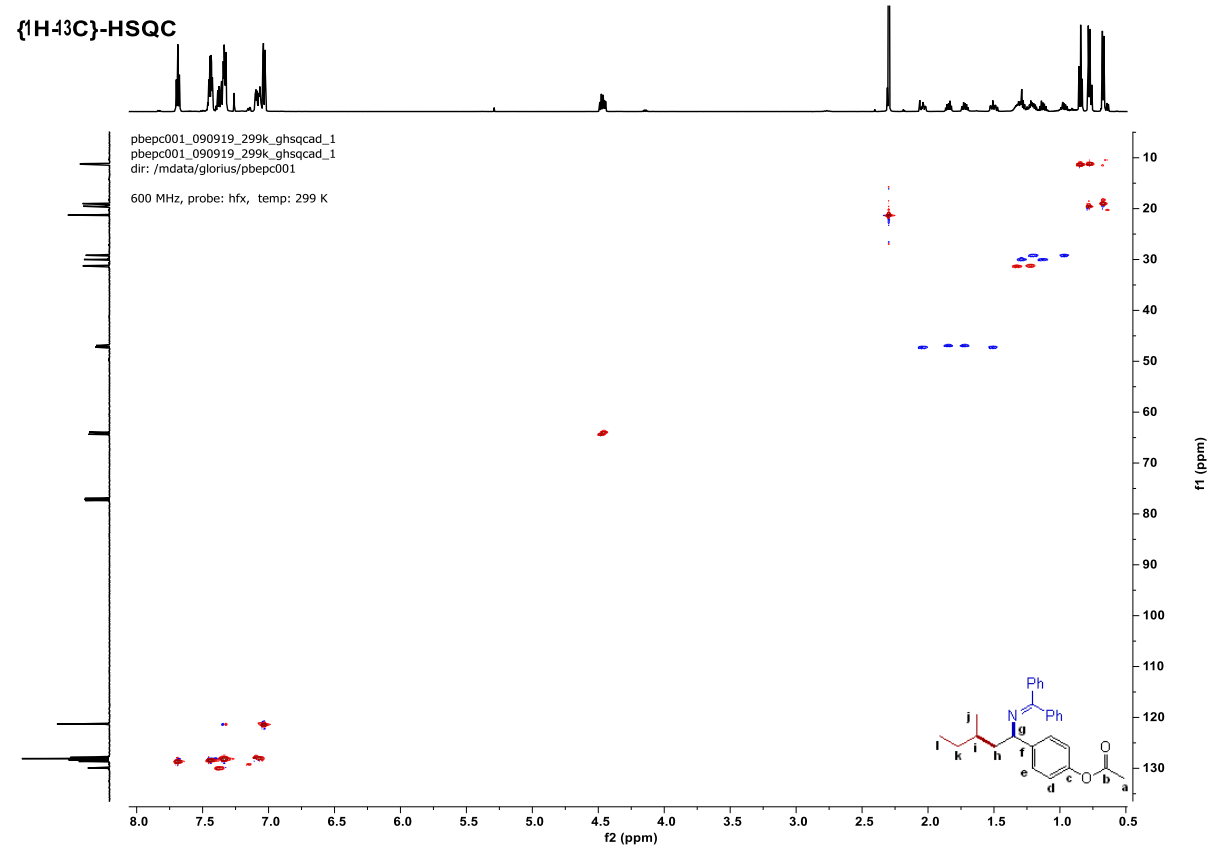


4-(1-((diphenylmethylene)amino)-3-methylpentyl)phenyl acetate (35)






{1H-1H}-COSY
pbepc001_090919_299k_gcosy_1
pbepc001_090919_299k_gcosy_1
dir: /mdata/glorius/pbepc001
600 MHz, probe: hfx, temp: 299 K
f2 (ppm)
f1 (ppm)


{1H-13C}-HSQC
pbepc001_090919_299k_ghsqcad_1
pbepc001_090919_299k_ghsqcad_1
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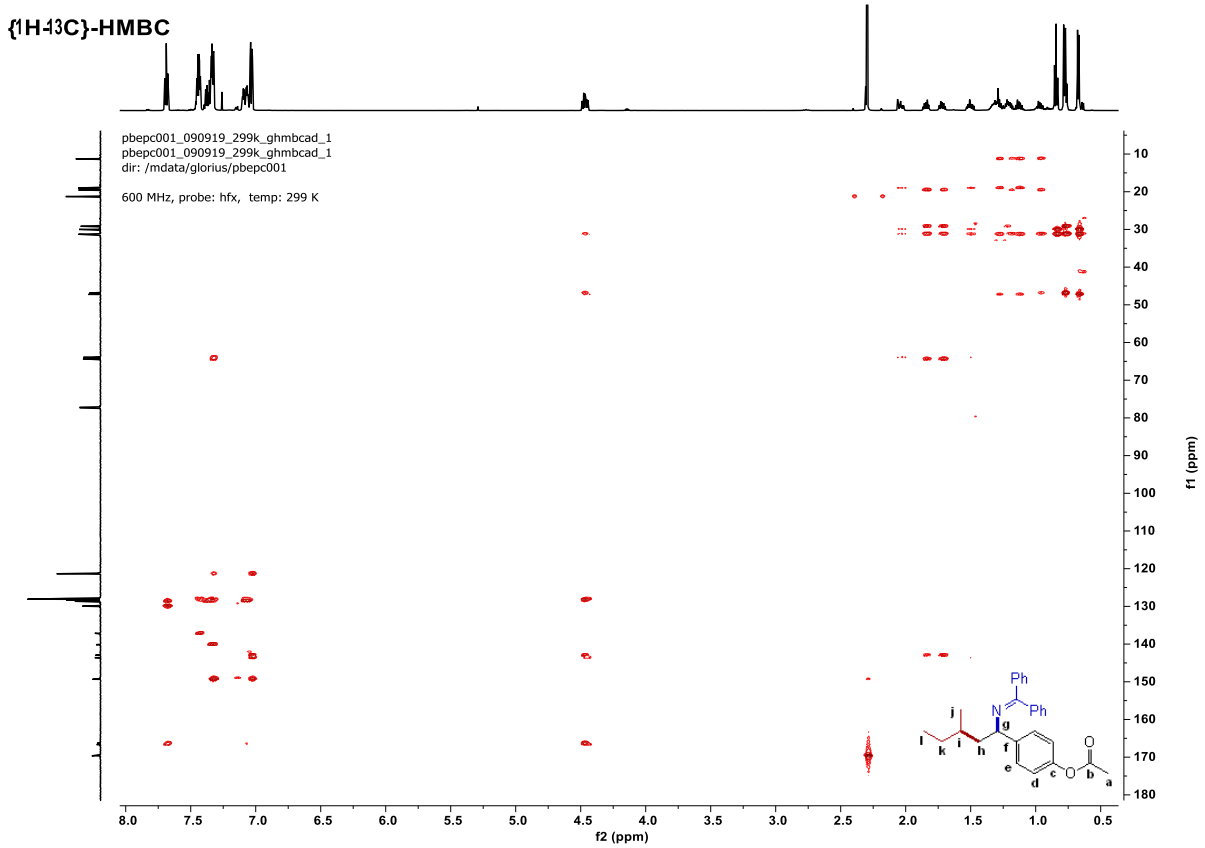
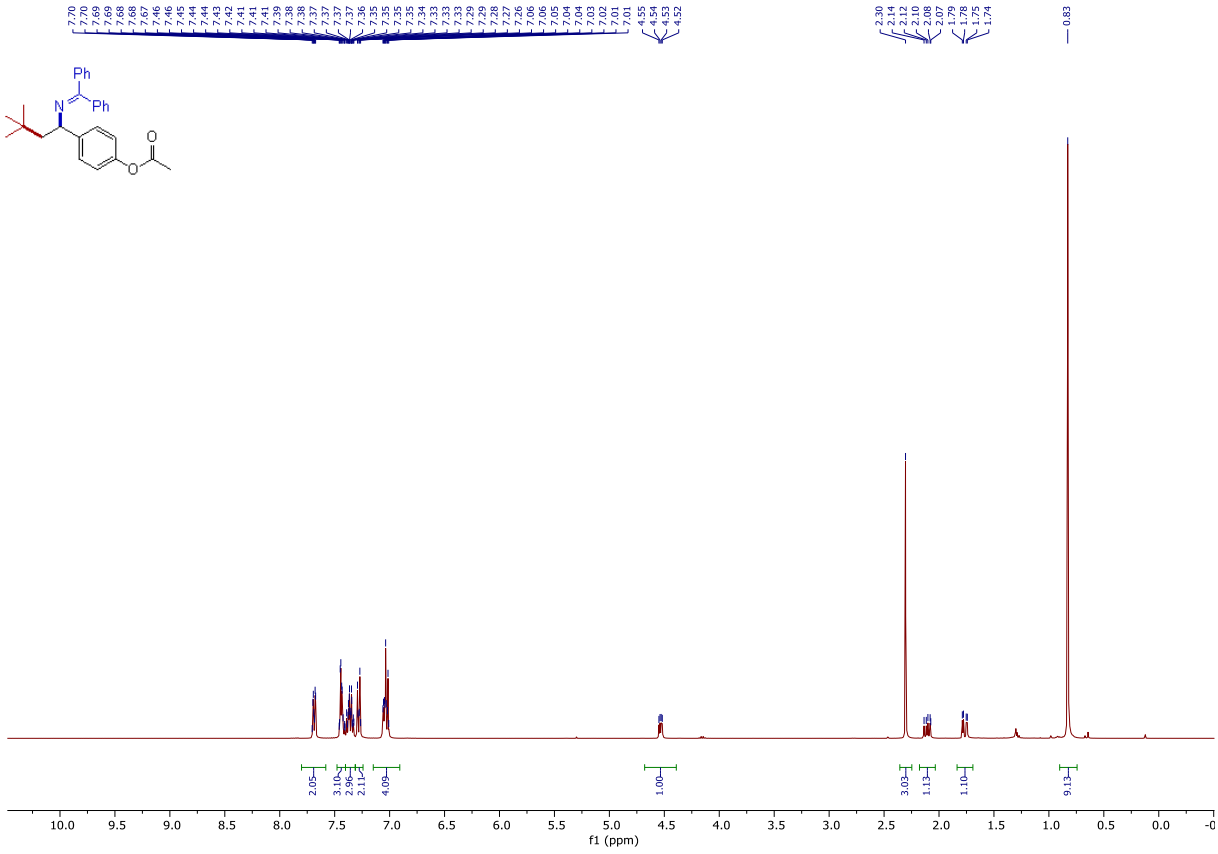
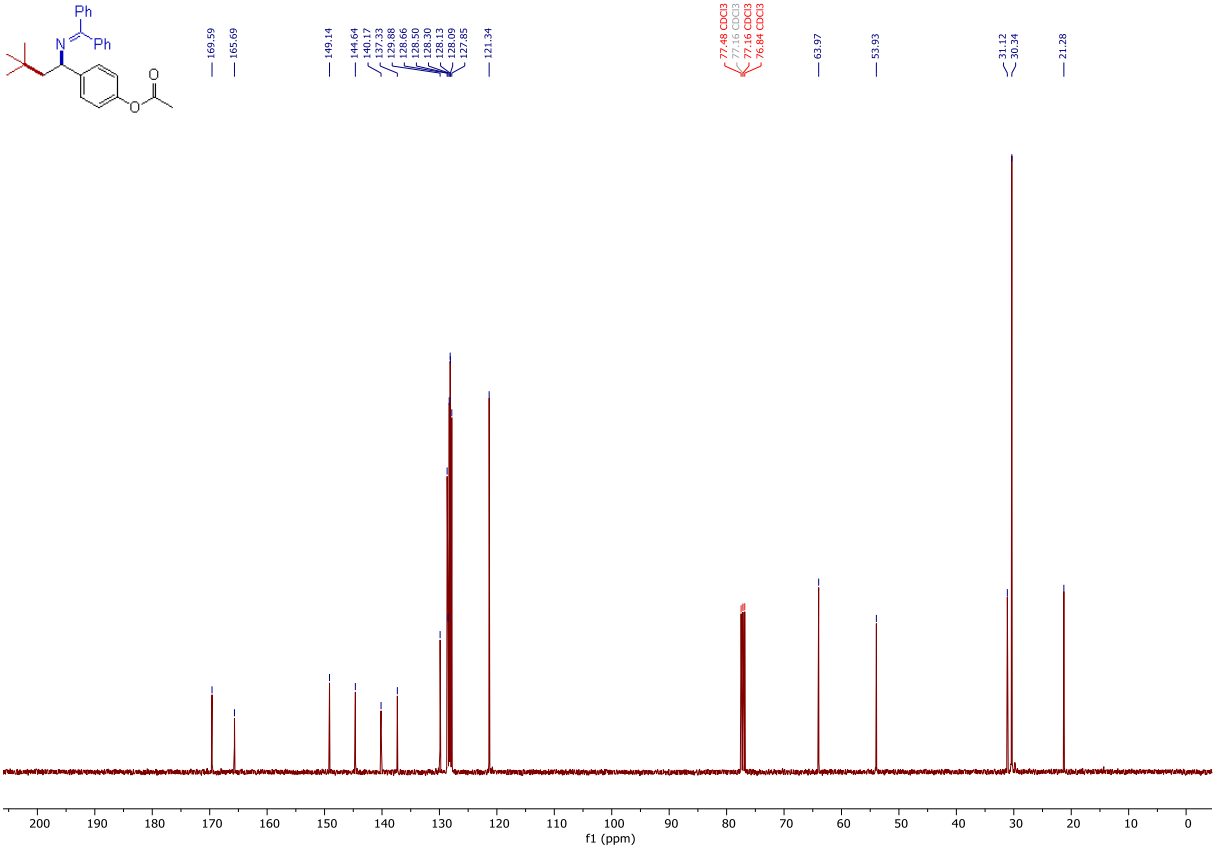
600 MHz, probe: hfx, temp: 299 K
f2 (ppm)
f1 (ppm)

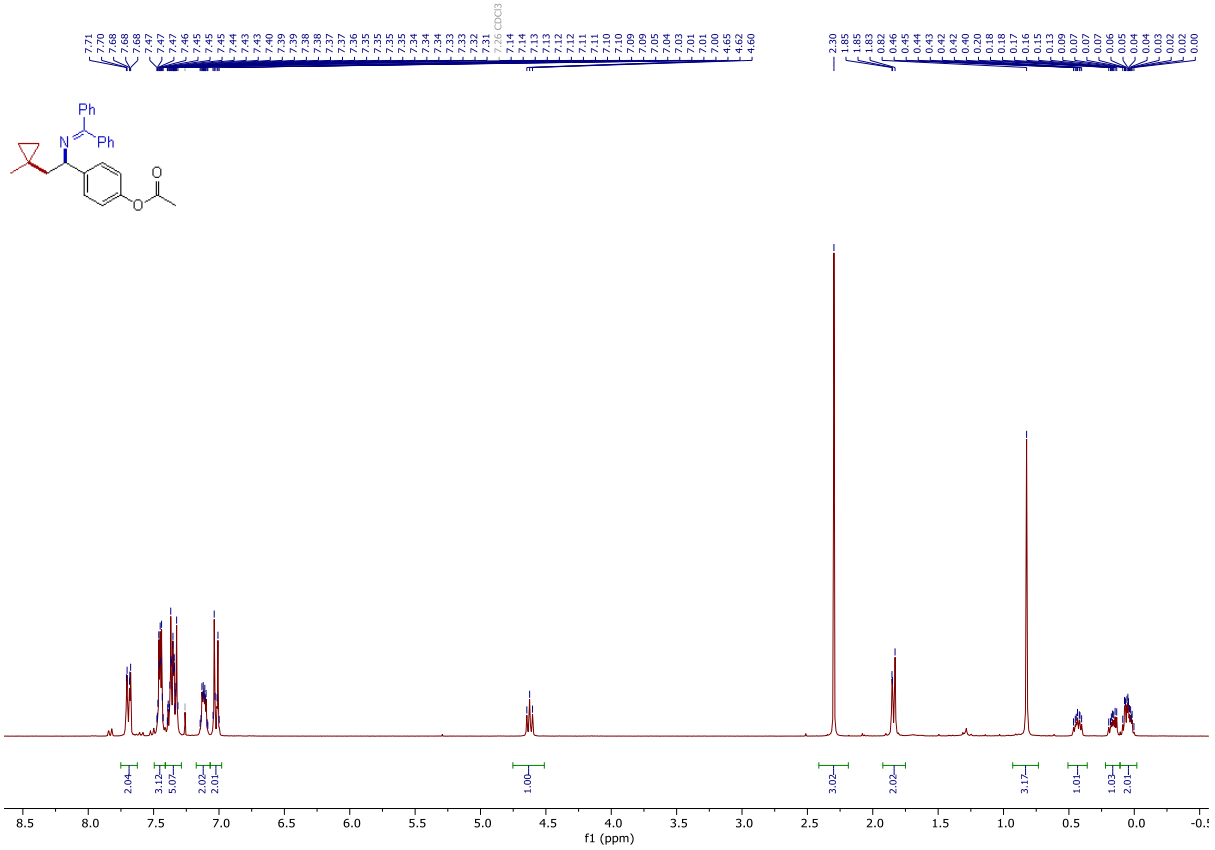

{1H-13C}-HMBC
pbepc001_090919_299k_ghmbcad_1
pbepc001_090919_299k_ghmbcad_1
dir: /mdata/glorius/pbepc001
600 MHz, probe: hfx, temp: 299 K
f2 (ppm)
f1 (ppm)
Ph
Ph
N

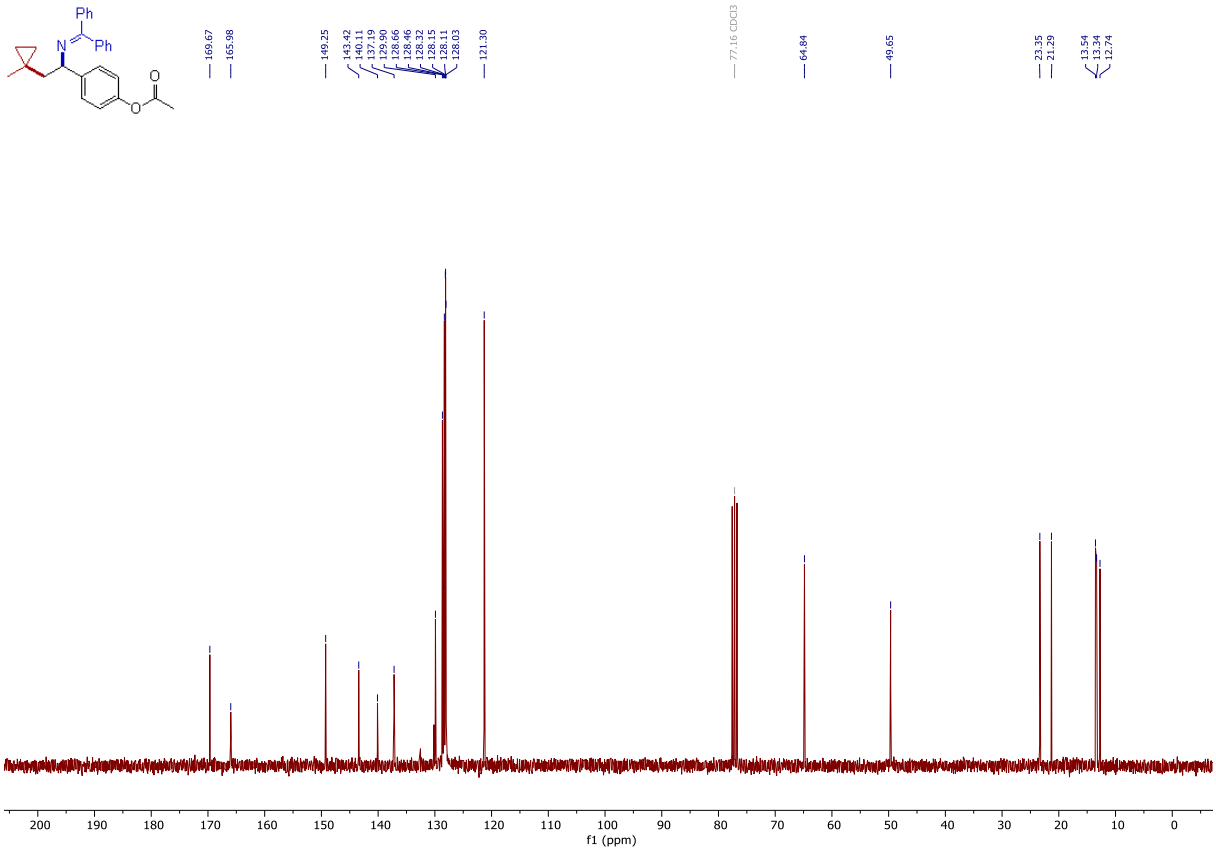
4-(1-((diphenylmethylene)amino)-3,3-dimethylbutyl)phenyl acetate (36)



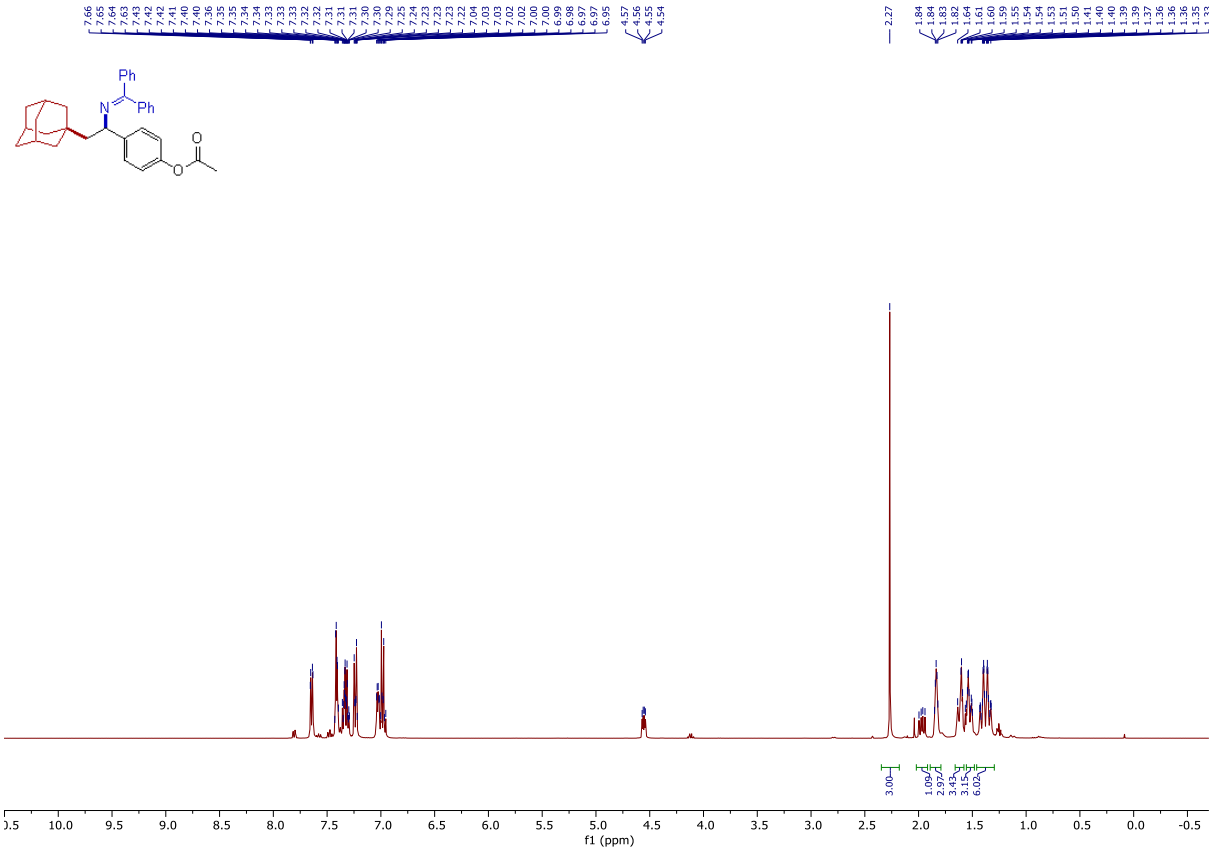


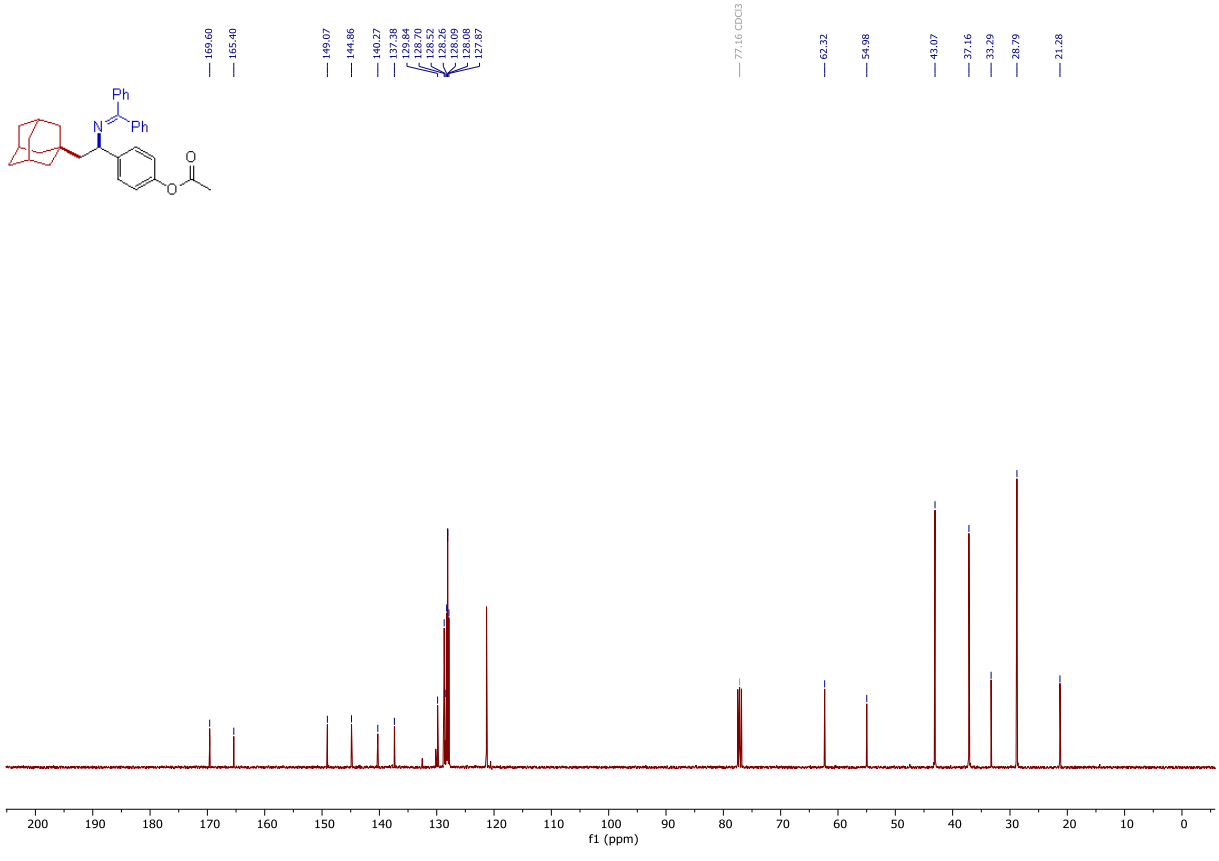
4-(1-((diphenylmethylene)amino)-2-(1-methylcyclopropyl)ethyl)phenyl acetate (37)



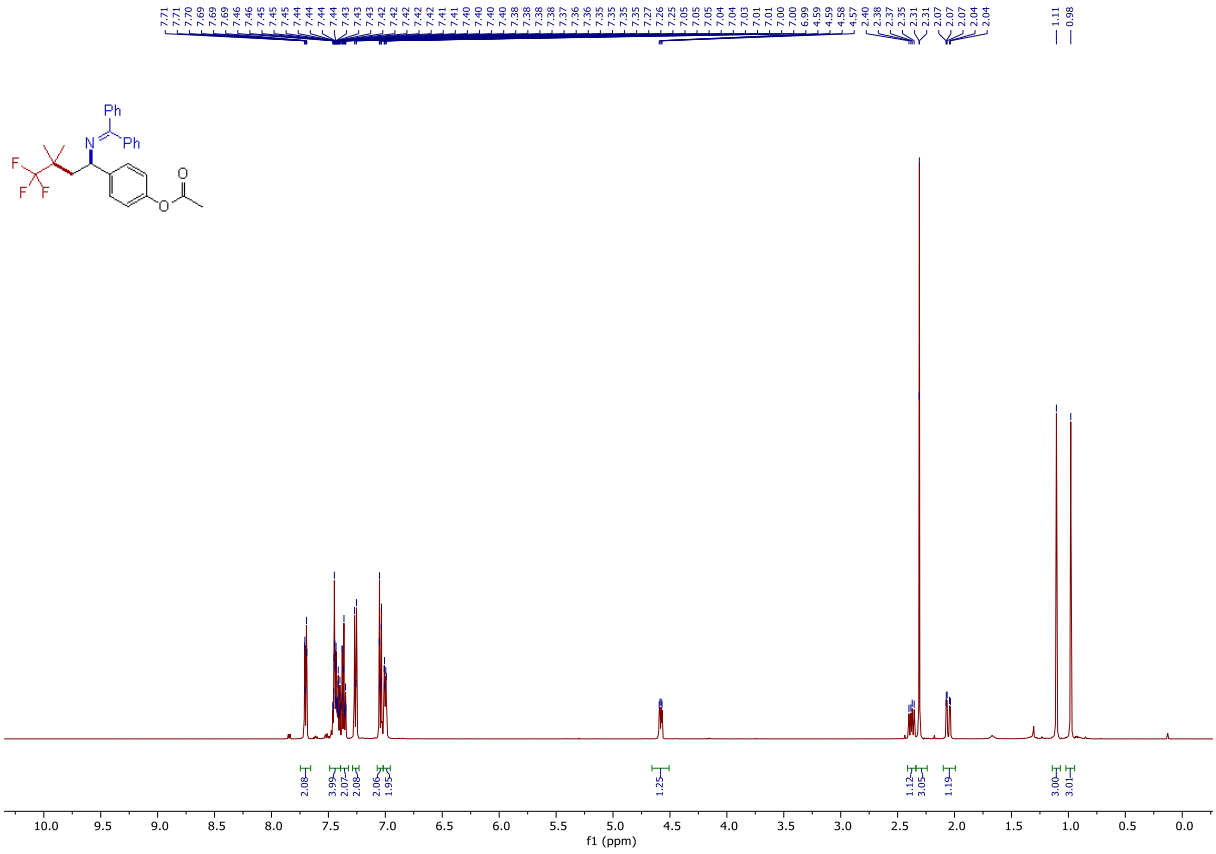


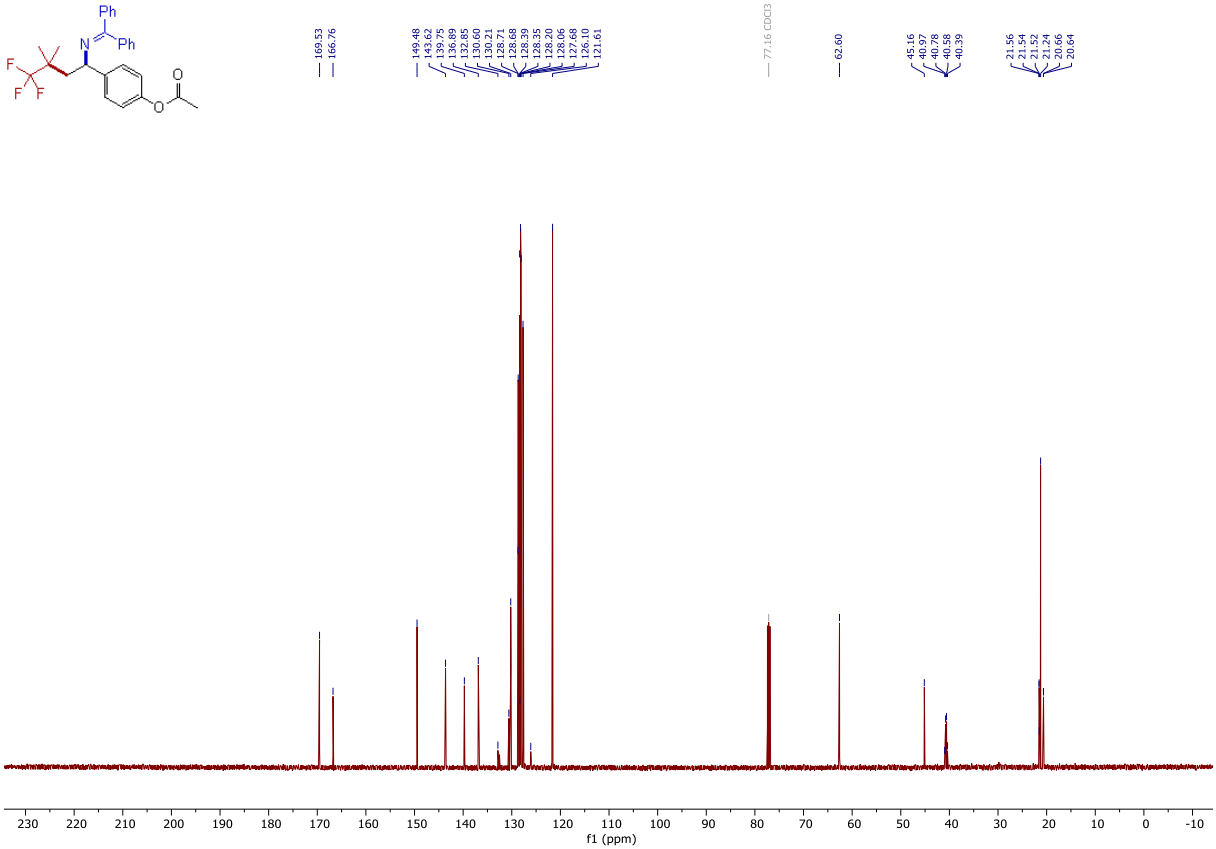
4-(2-(adamantan-1-yl)-1-((diphenylmethylene)amino)ethyl)phenyl acetate (38)

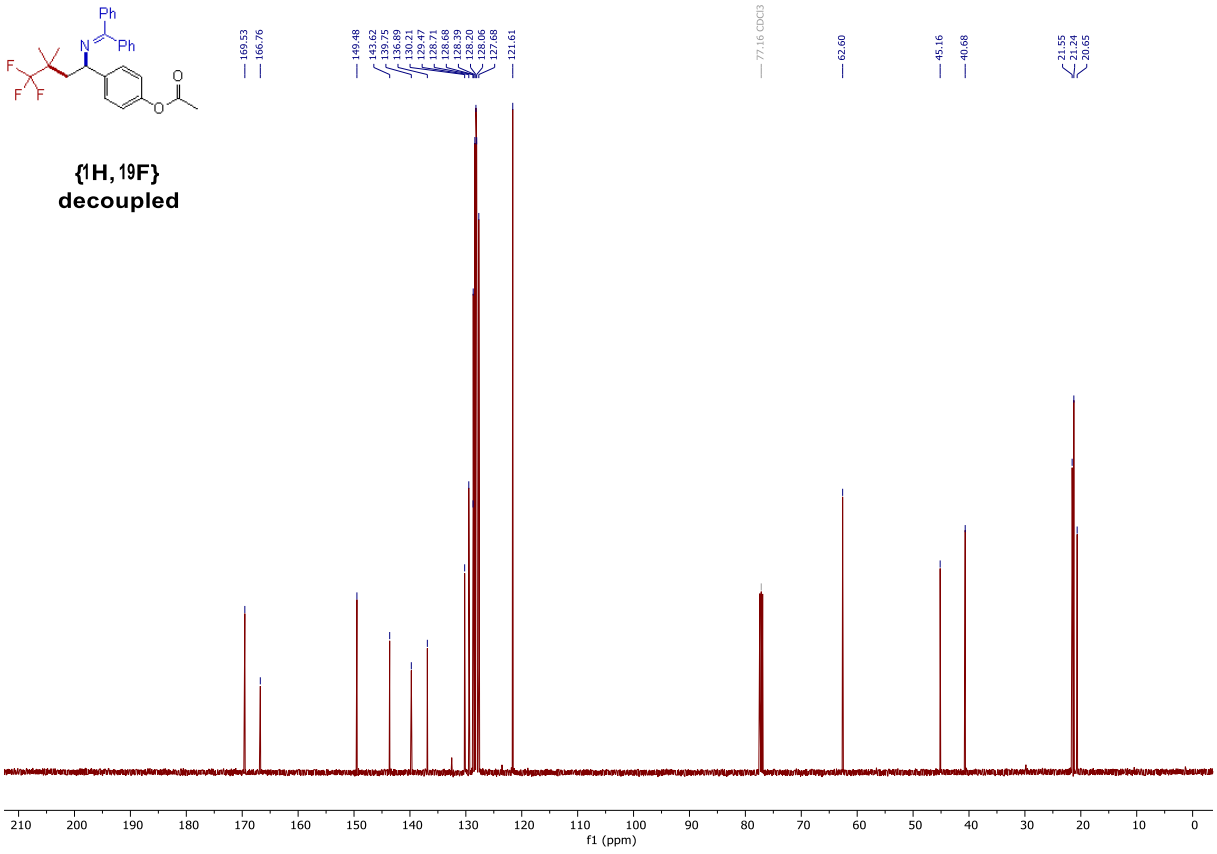


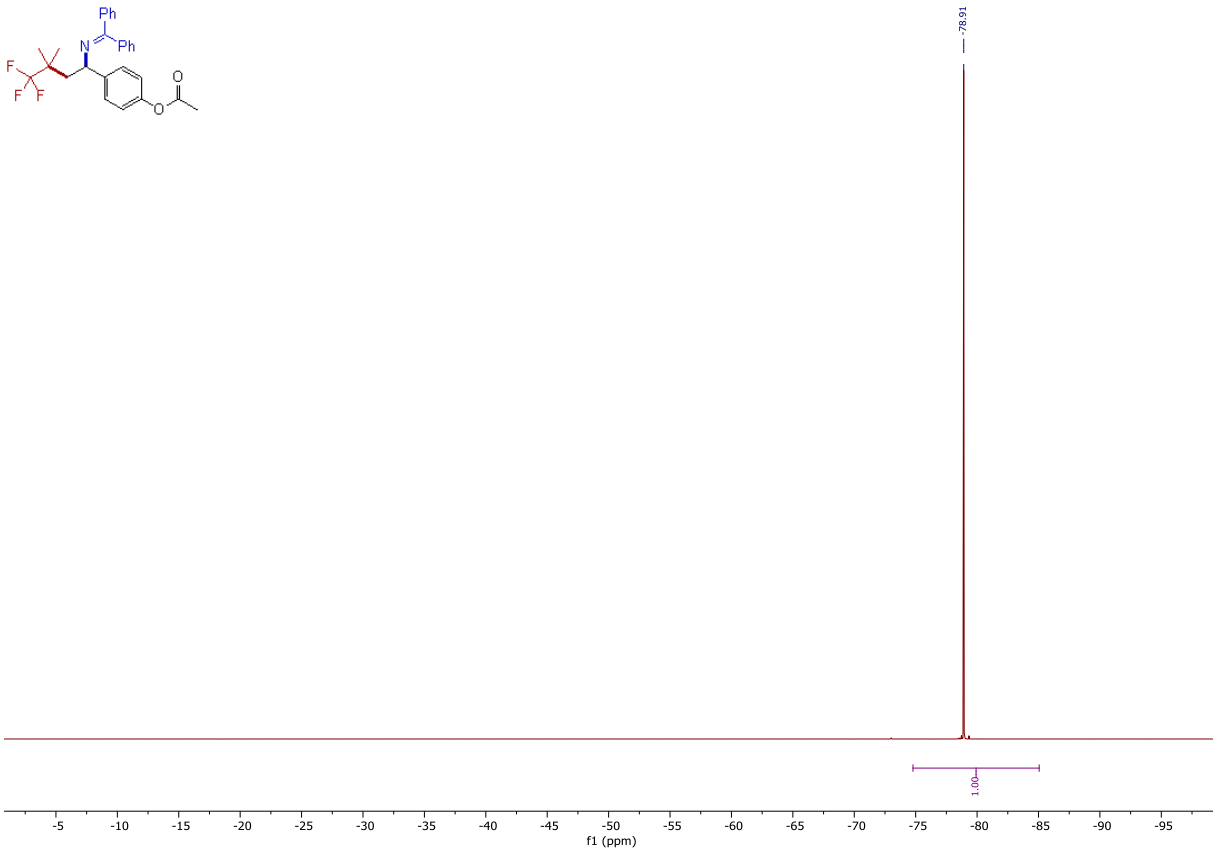


4-(1-((diphenylmethylene)amino)-4,4,4-trifluoro-3,3-dimethylbutyl)phenyl acetate (39)

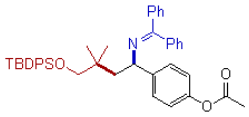


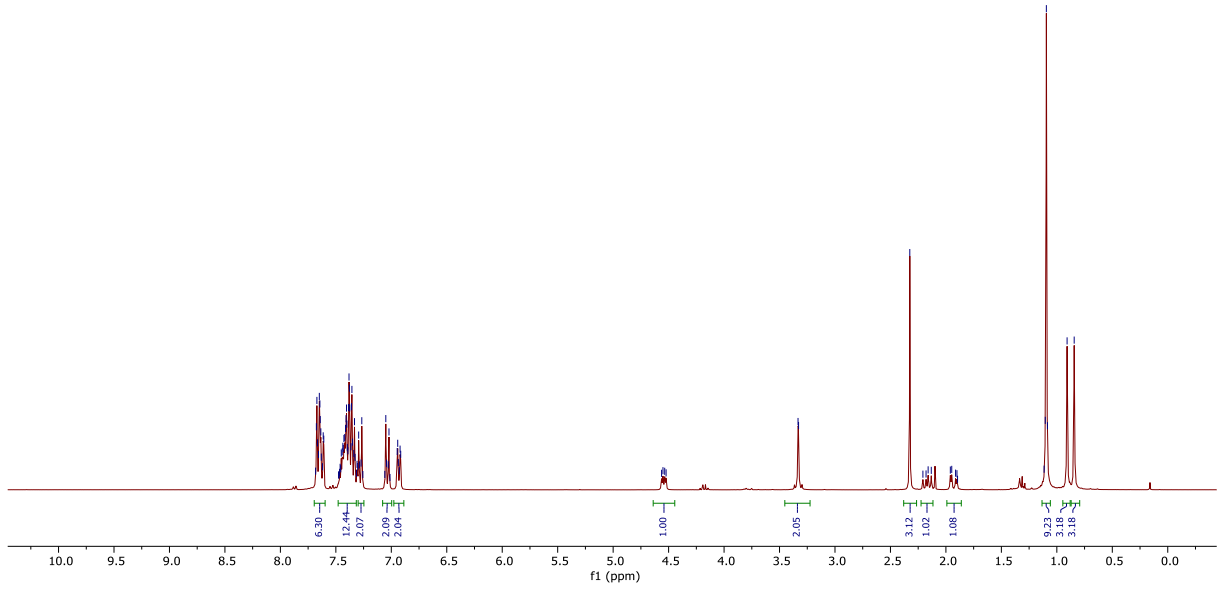


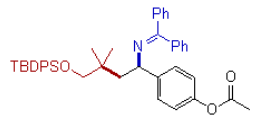

{1H, 19F}
decoupled
169.53
166.76
149.48
143.62
139.75
136.89
130.21
129.47
128.71
128.68
128.39
128.20
128.06
127.68
121.61
77.16 CDCl3
62.60
45.16
40.68
21.55
21.24
20.65
f1 (ppm)

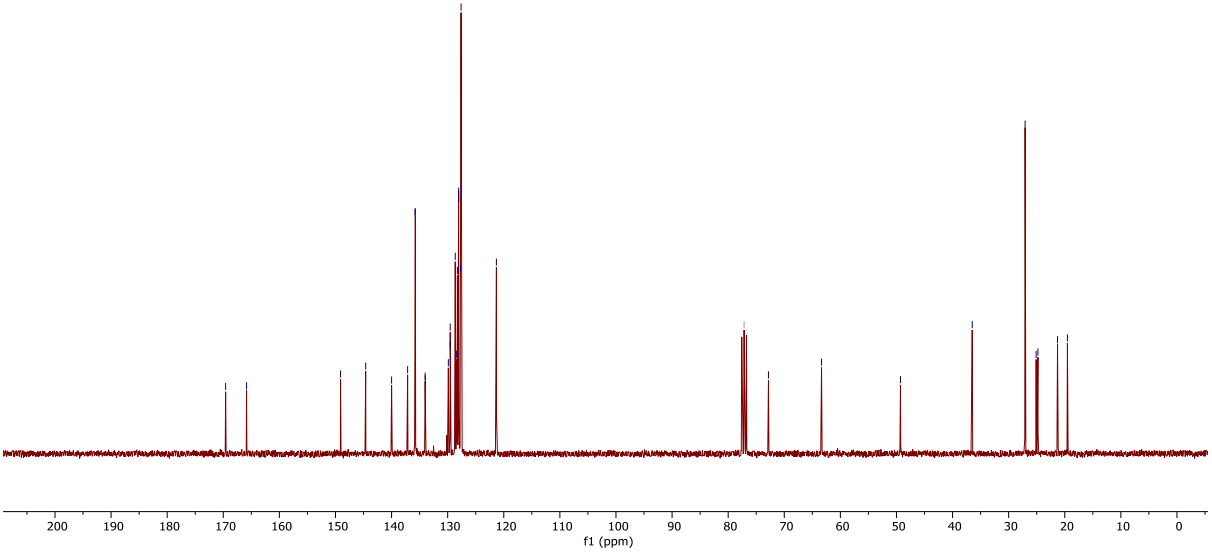

-78.91
1.00
f1 (ppm)

4-(4-((*tert*-butyldiphenylsilyl)oxy)-1-((diphenylmethylene)amino)-3,3-dimethylbutyl)phenyl acetate (40)

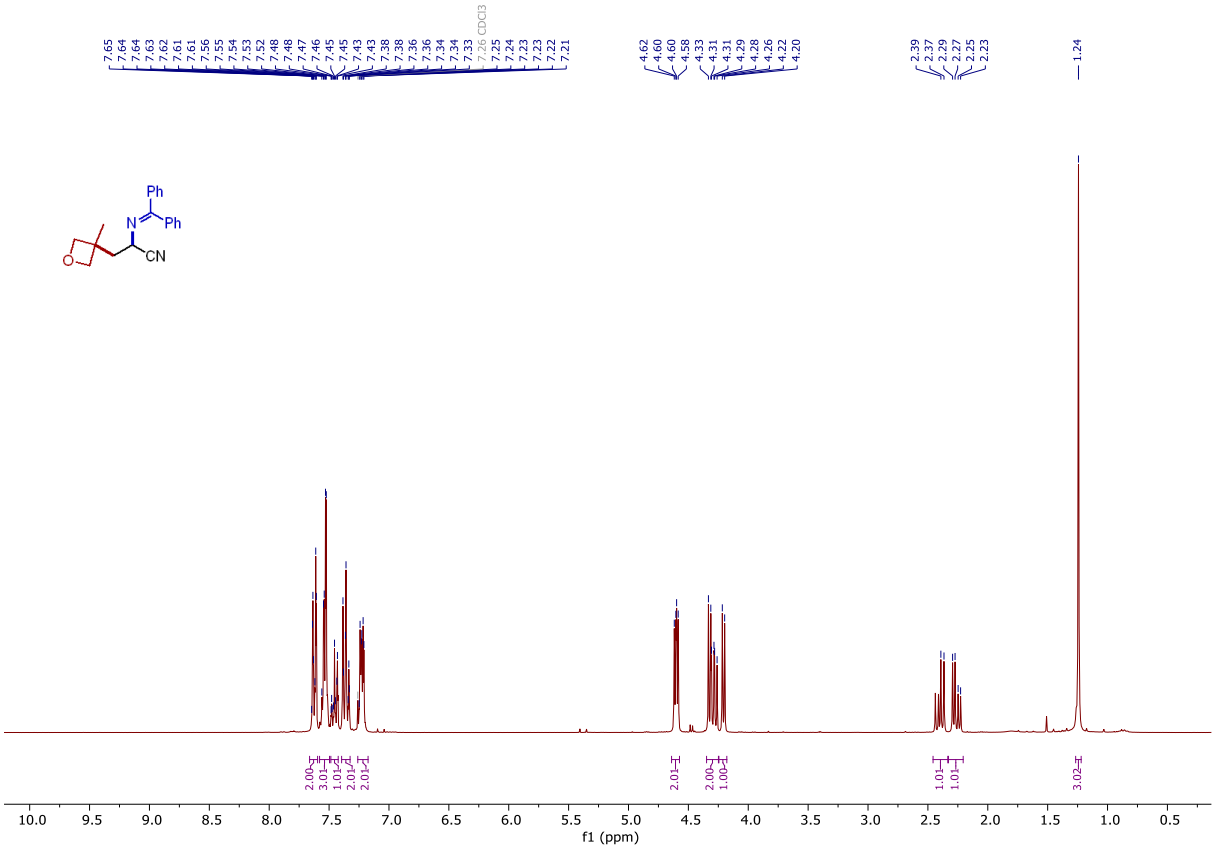


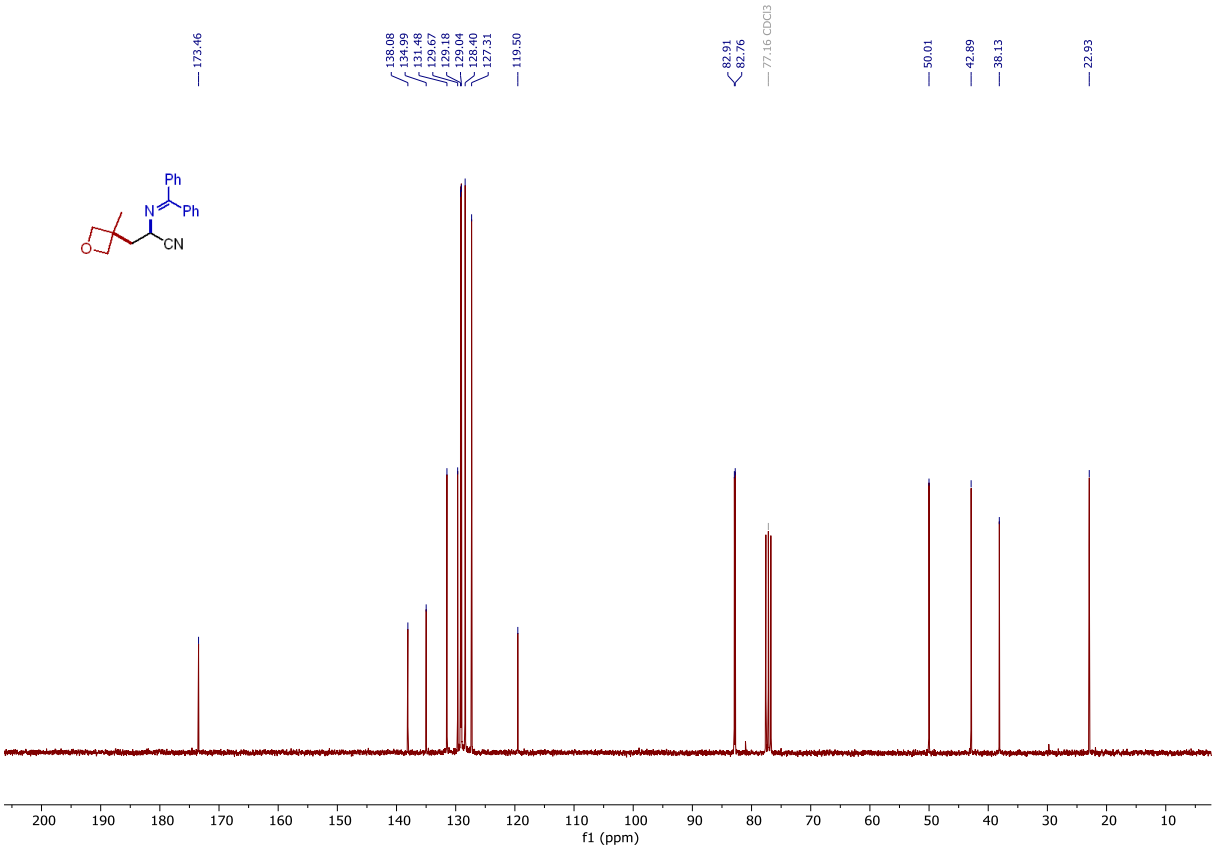




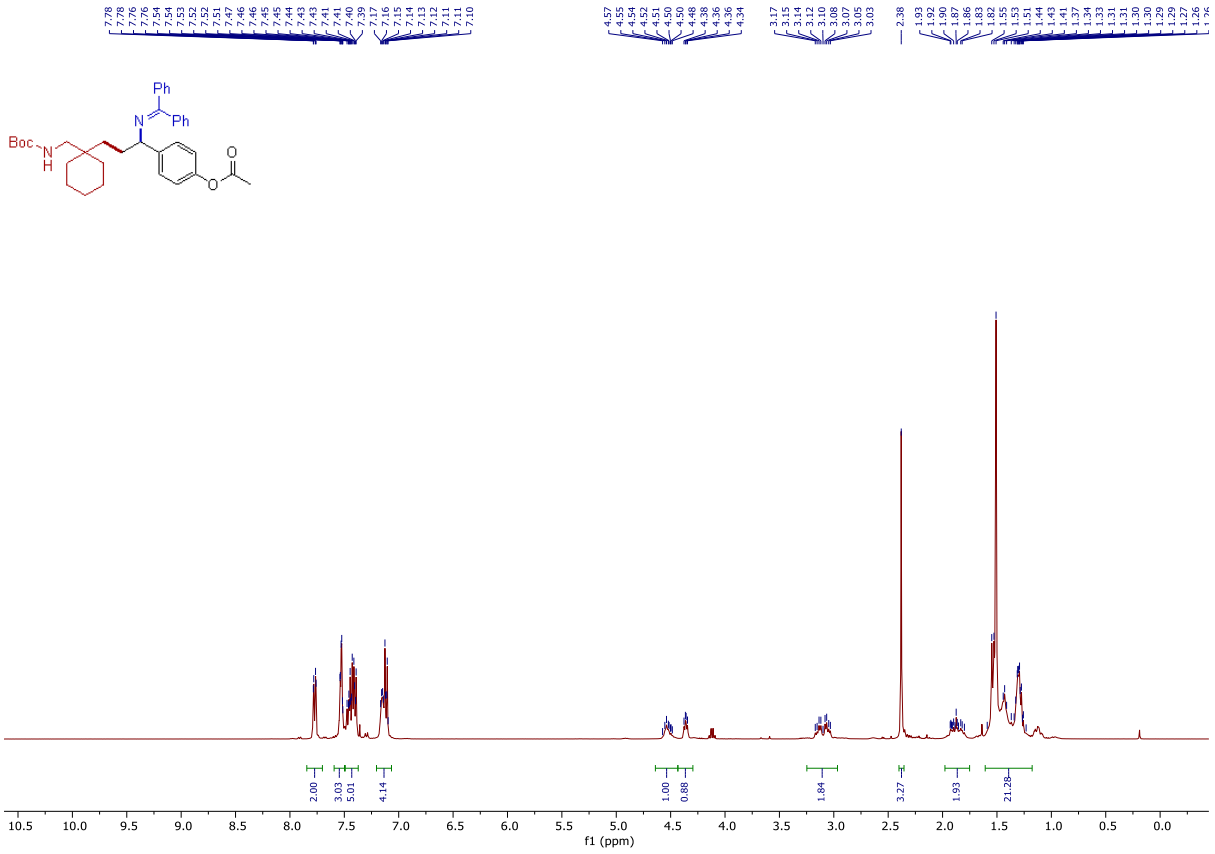


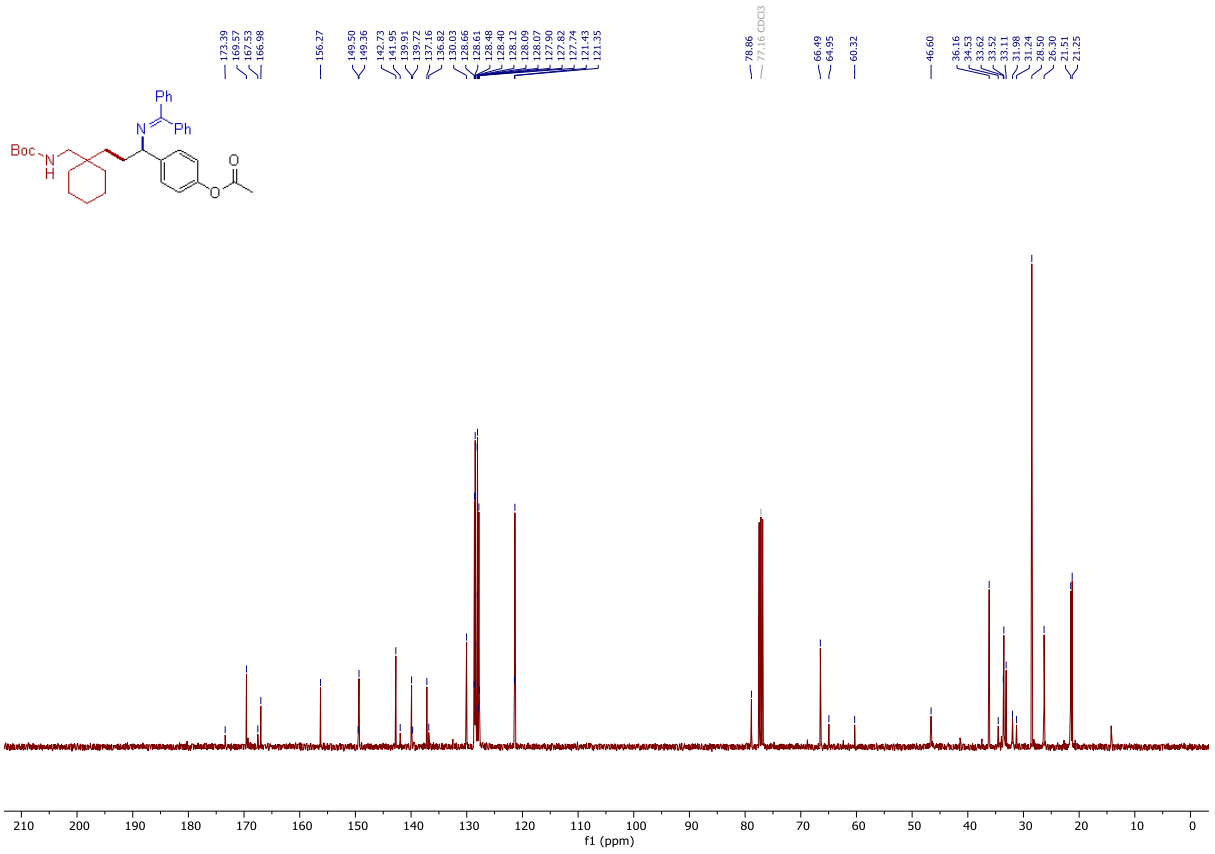
2-((diphenylmethylene)amino)-3-(3-methyloxetan-3-yl)propanenitrile (41)



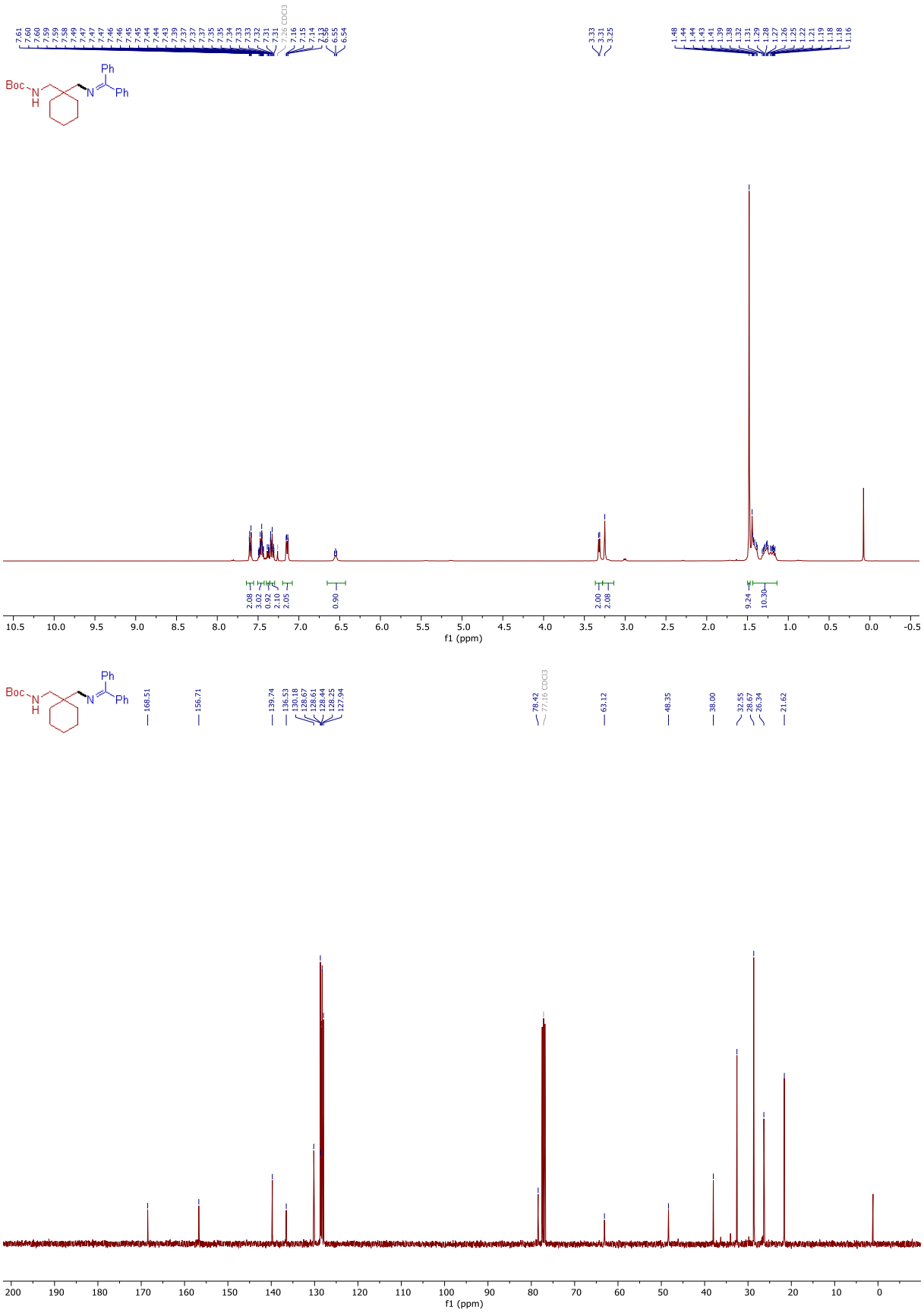


4-(3-(1-(((*tert*-butoxycarbonyl)amino)methyl)cyclohexyl)-1-((diphenylmethylene)amino)propyl)phenyl acetate (42)

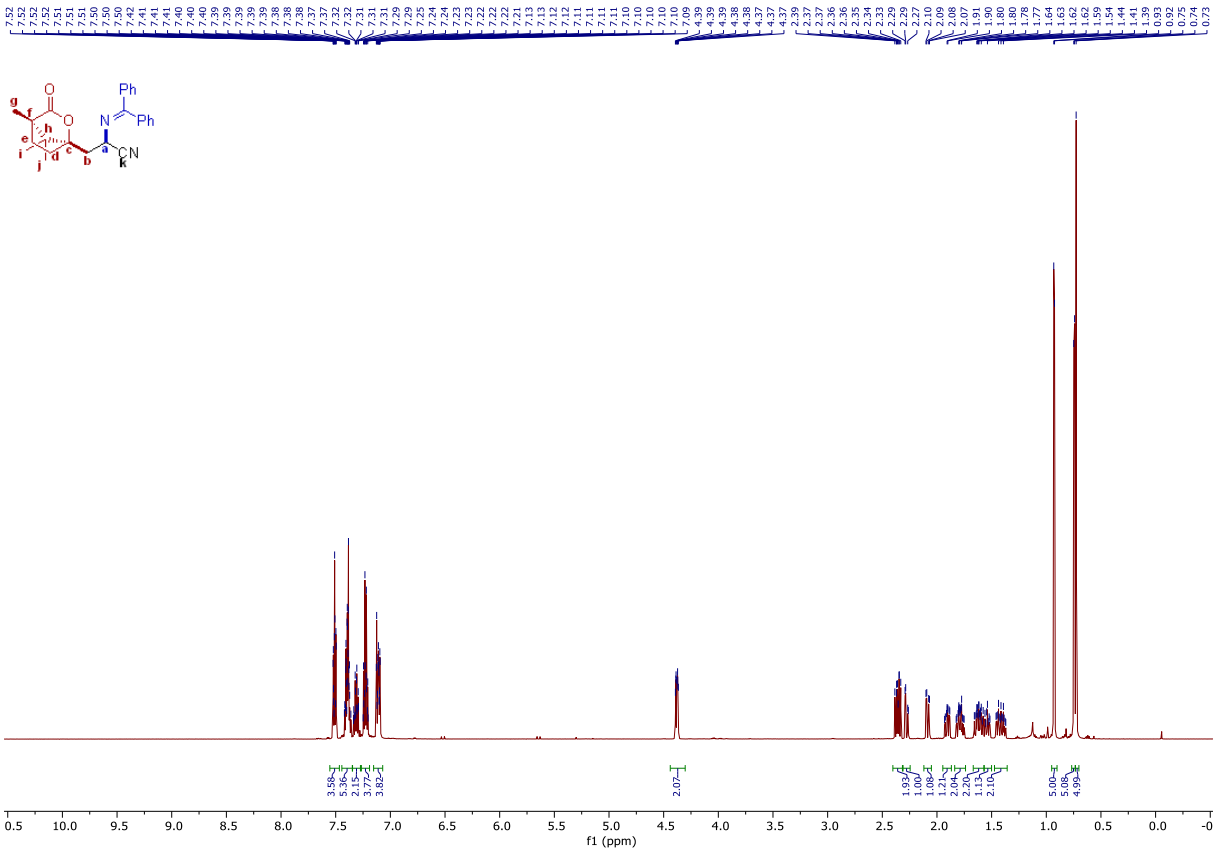


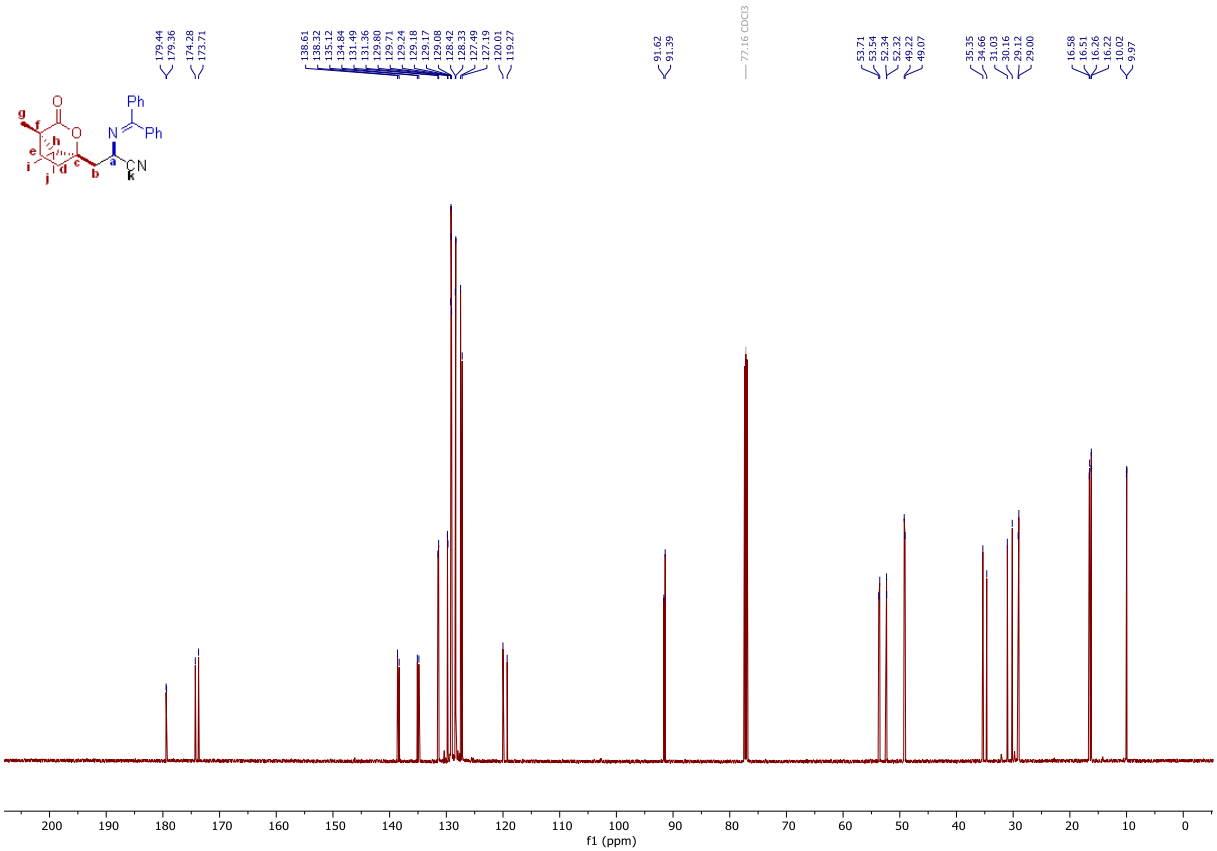


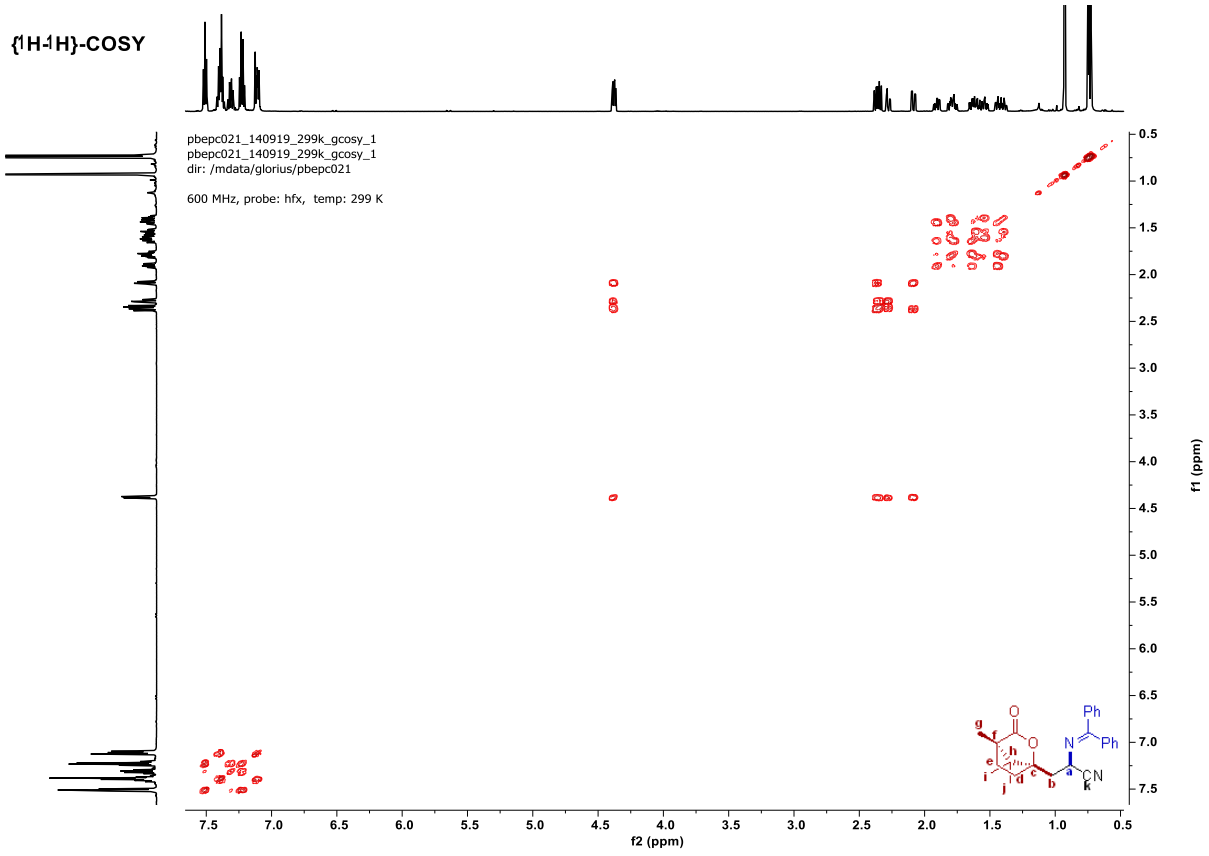
***tert*-butyl ((1-(((diphenylmethylene)amino)methyl)cyclohexyl)methyl)carbamate (42-SP)**

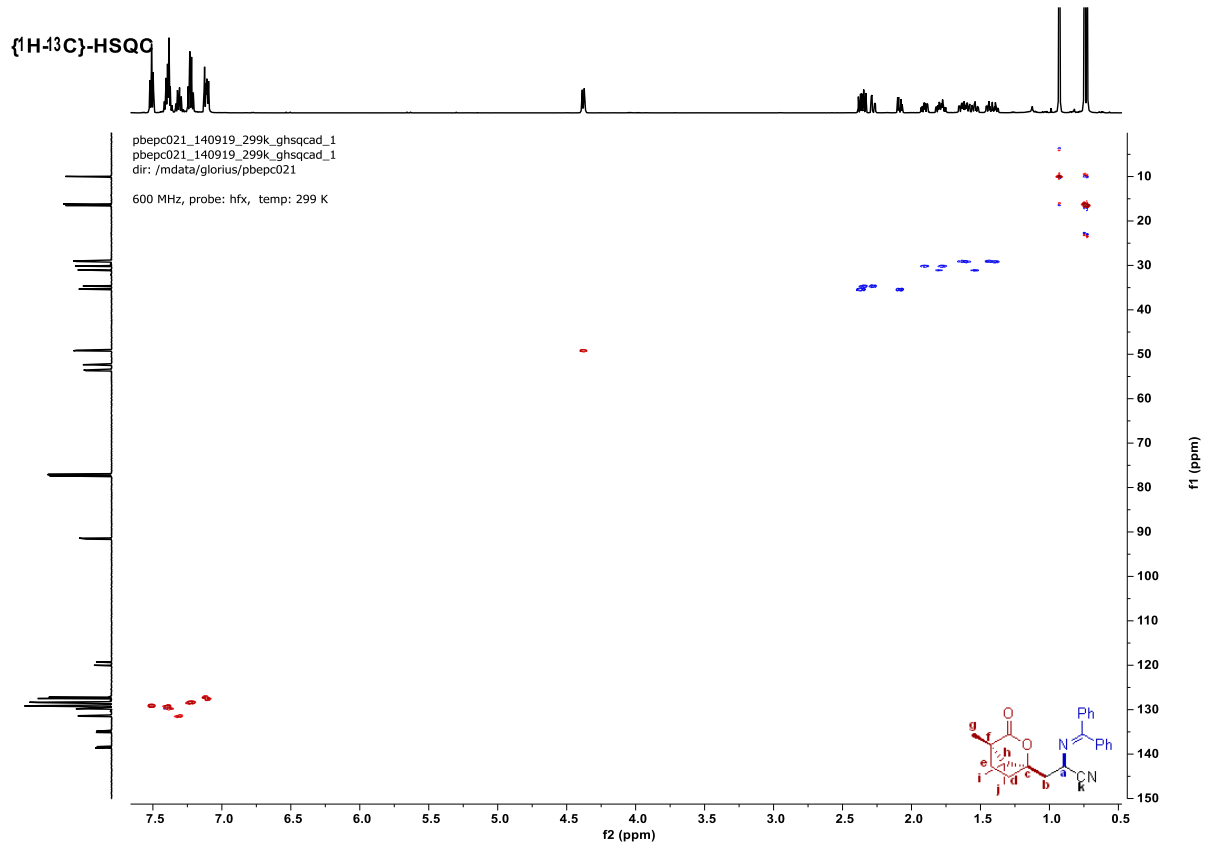


2-((diphenylmethylene)amino)-3-((1*R*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptan-1-yl)propanenitrile (43)






{1H-1H}-COSY
pbepc021_140919_299k_gcosy_1
pbepc021_140919_299k_gcosy_1
dir: /mdata/glorius/pbepc021
600 MHz, probe: hfx, temp: 299 K
f2 (ppm)
f1 (ppm)


{1H-13C}-HSQC
pbepc021_140919_299k_ghsqcad_1
pbepc021_140919_299k_ghsqcad_1
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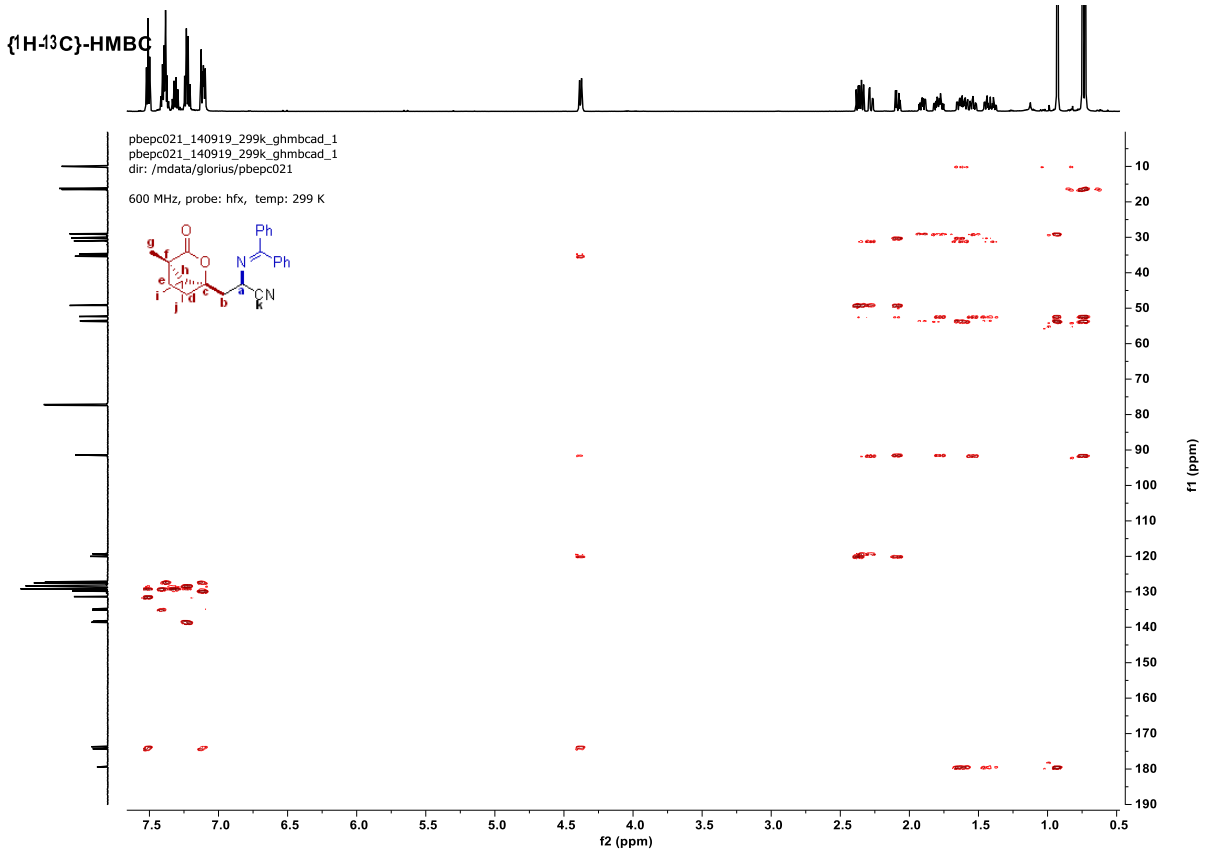
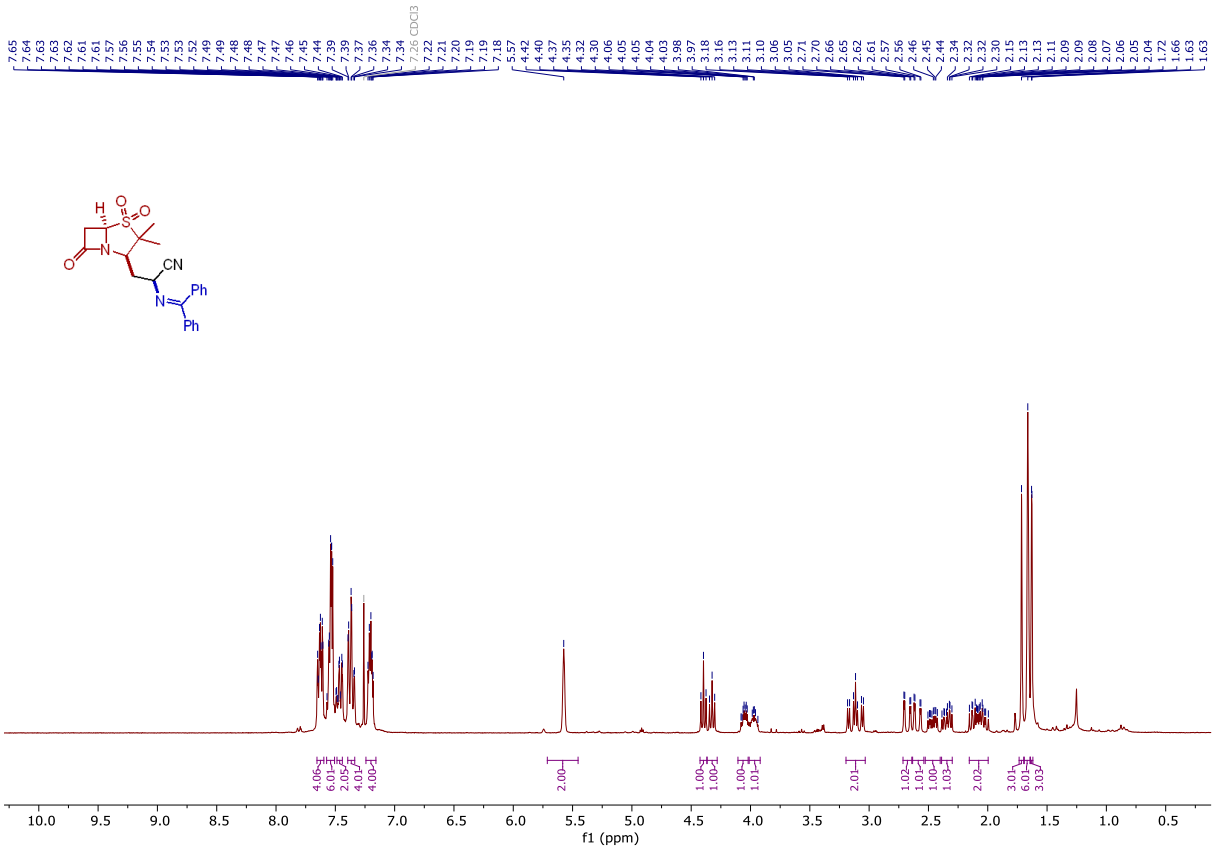
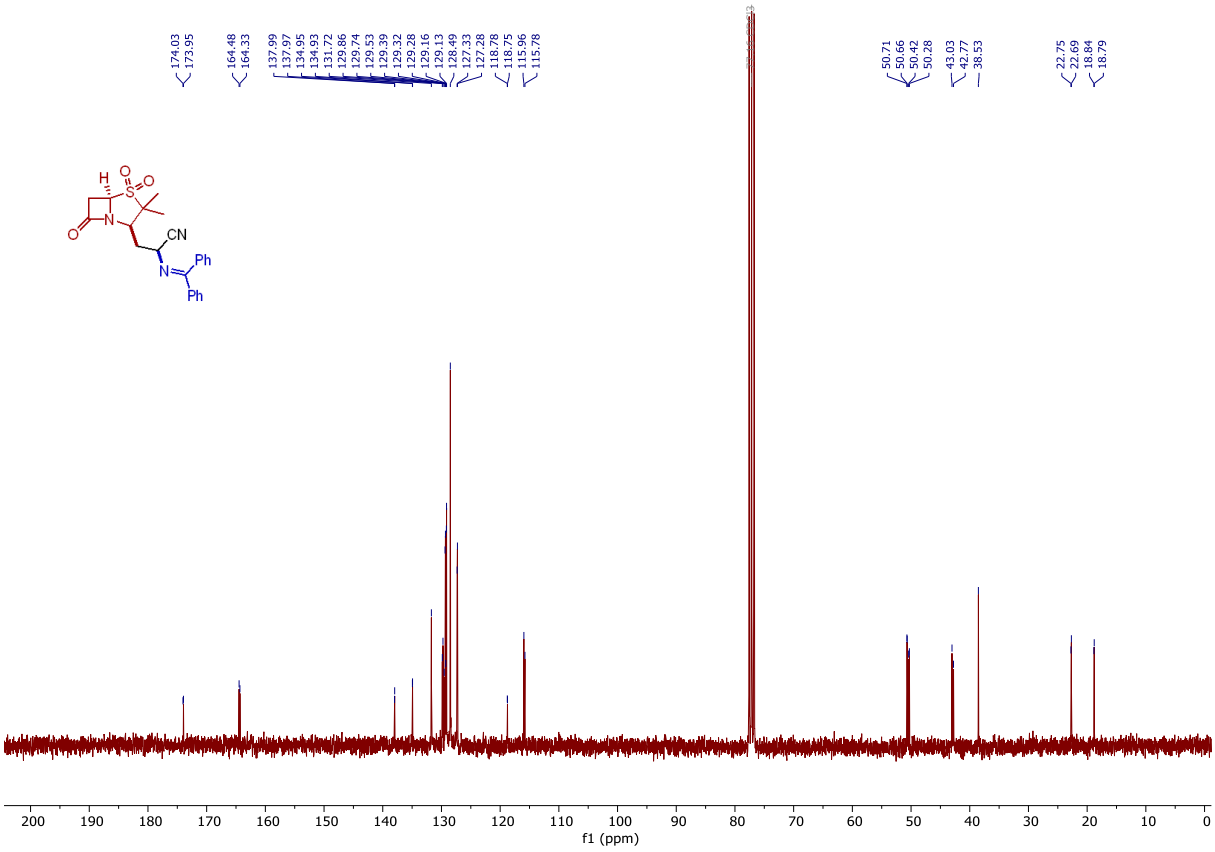
600 MHz, probe: hfx, temp: 299 K
f2 (ppm)
f1 (ppm)

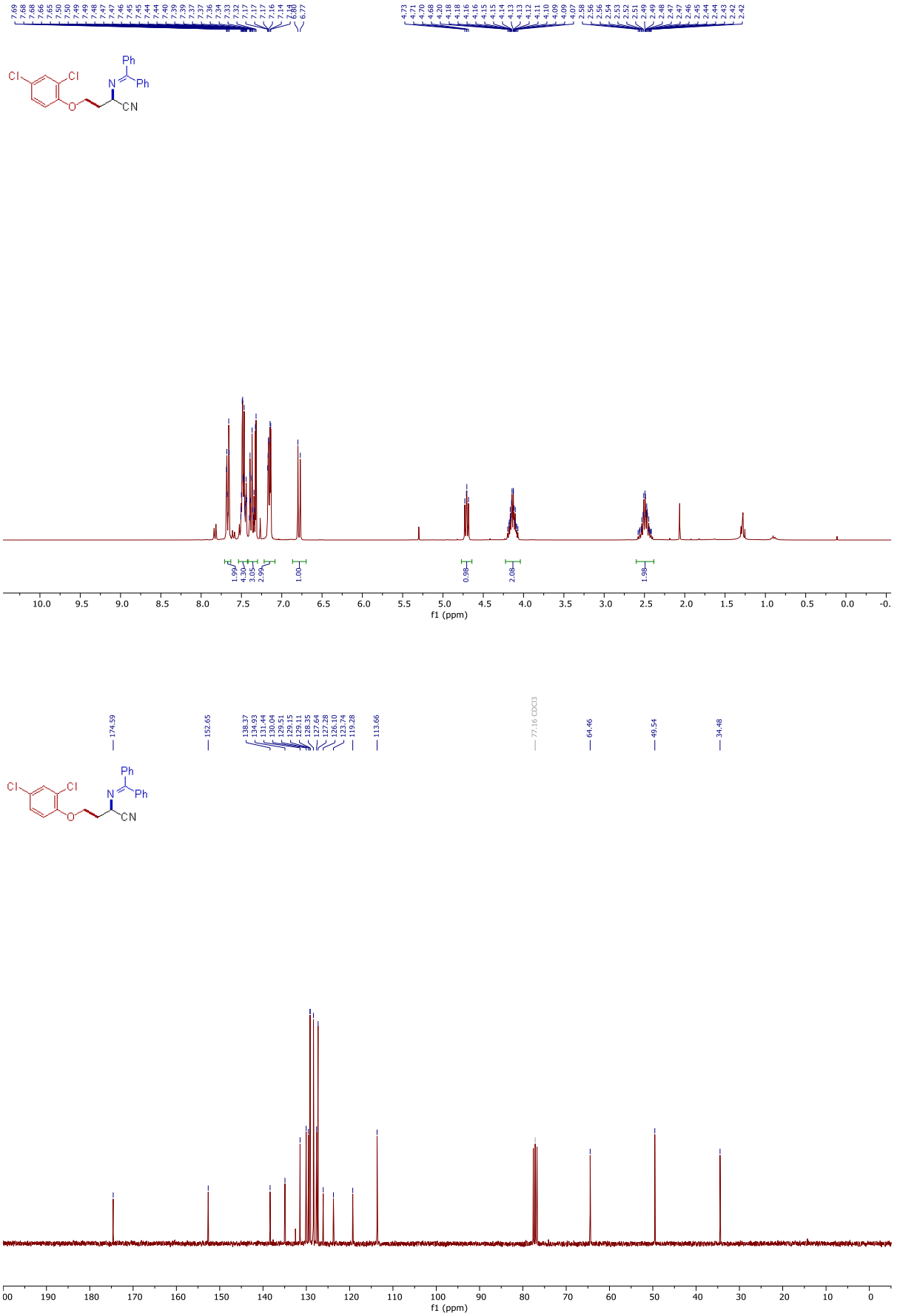

{1H-13C}-HMBC
pbepc021_140919_299k_ghmbcad_1
pbepc021_140919_299k_ghmbcad_1
dir: /mdata/glorius/pbepc021
600 MHz, probe: hfx, temp: 299 K
f2 (ppm)
f1 (ppm)

3-((5*R*)-3,3-dimethyl-4,4-dioxido-7-oxo-4-thia-1-azabicyclo[3.2.0]heptan-2-yl)-2-((diphenylmethylene)amino)propanenitrile (44)

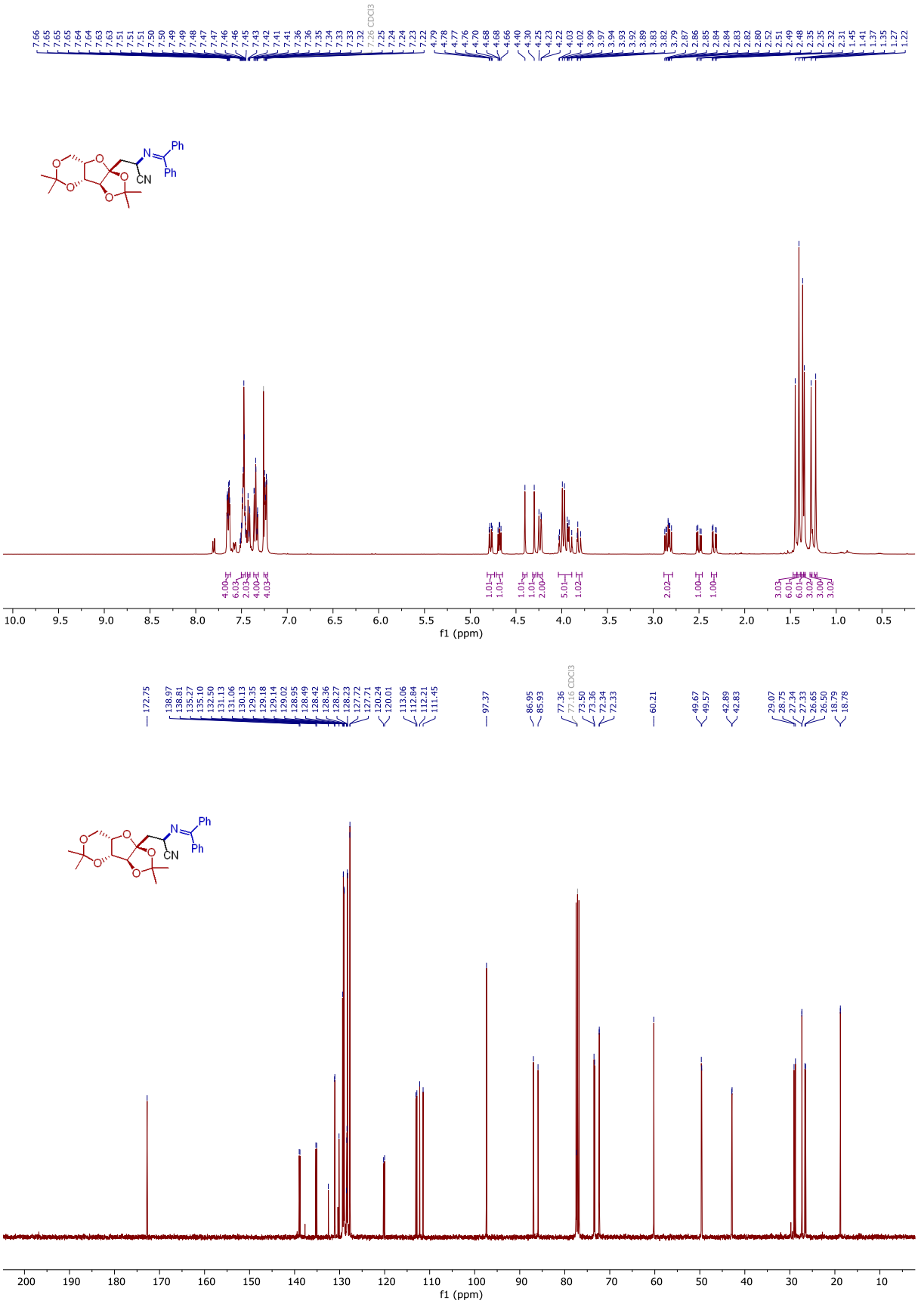




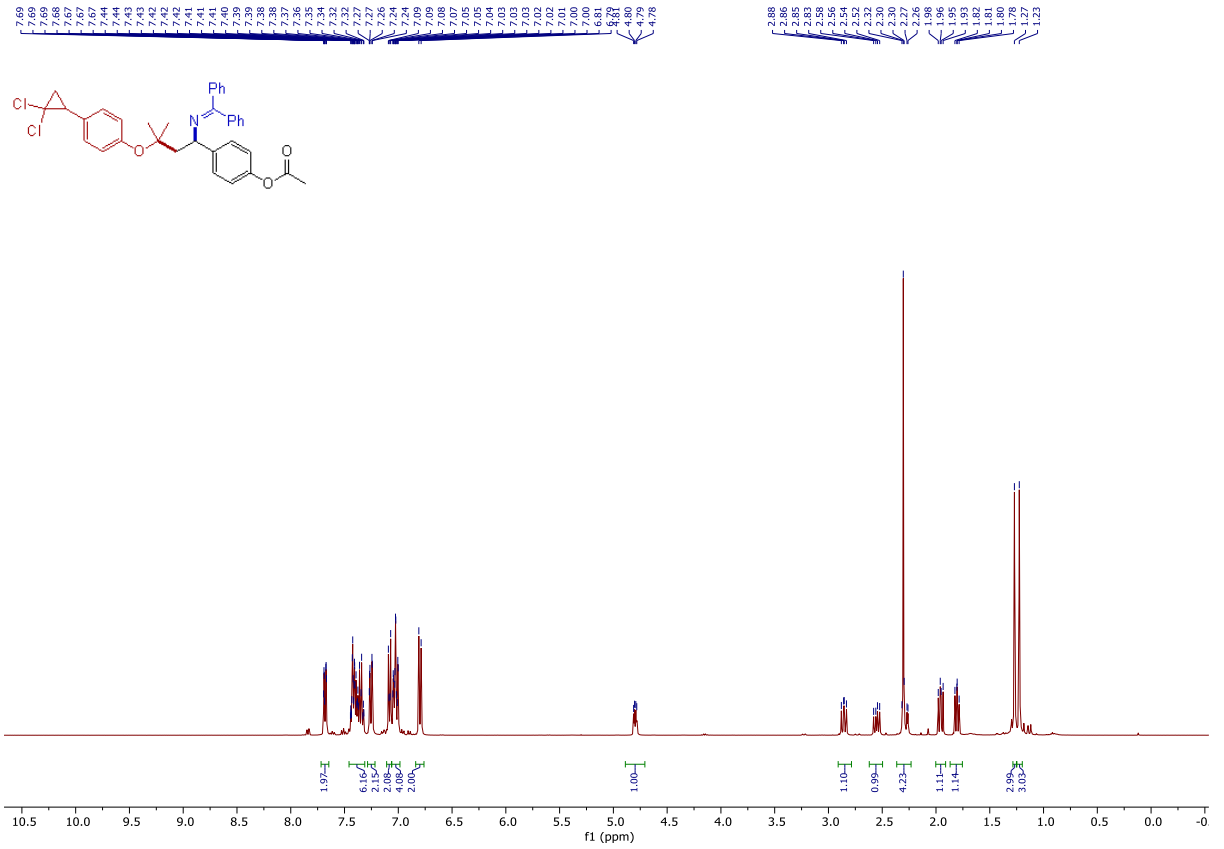
4-(2,4-dichlorophenoxy)-2-((diphenylmethylene)amino)butanenitrile (45)

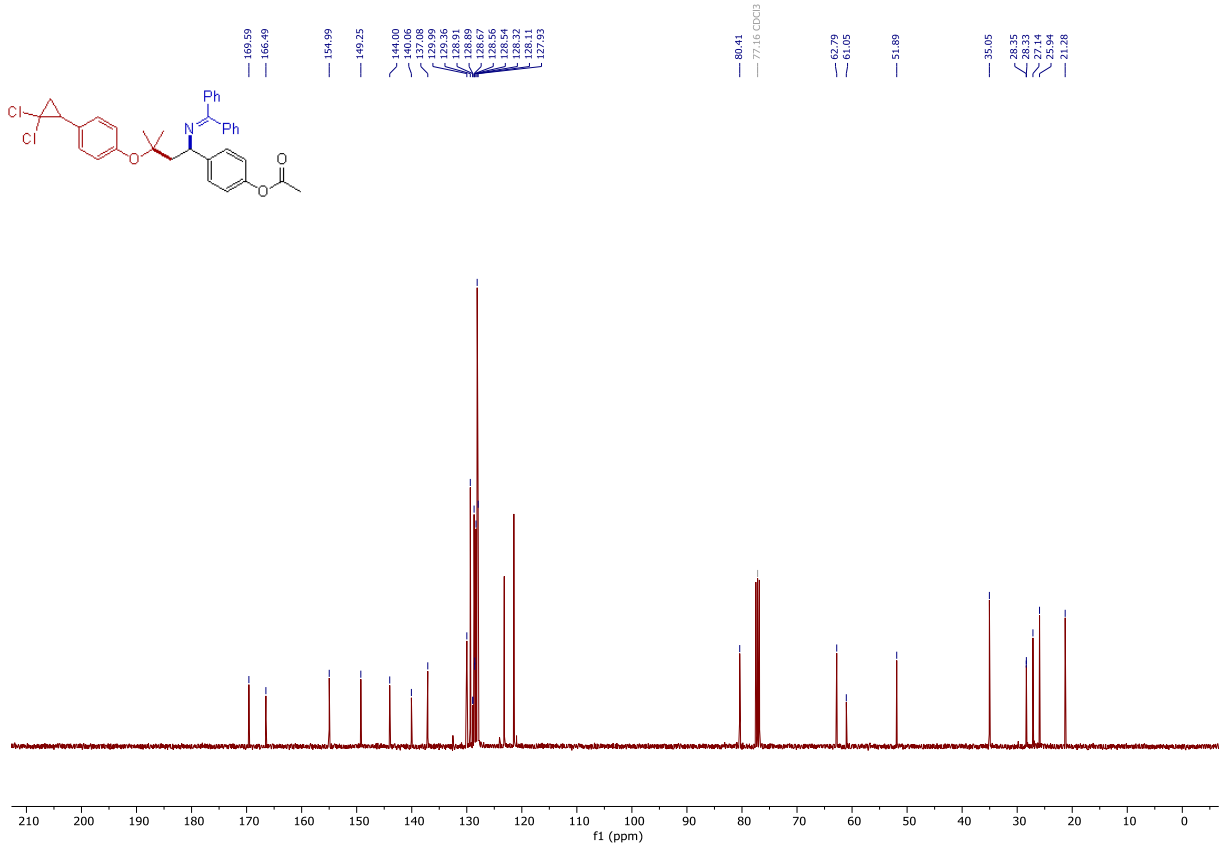


2-((diphenylmethylene)amino)-3-((3a*S*,3b*R*,7a*S*,8a*S*)-2,2,5,5-tetramethyltetrahydro-8a*H*-[1,3]dioxolo[4',5':4,5]furo[3,2-*d*][1,3]dioxin-8a-yl)propanenitrile (46)

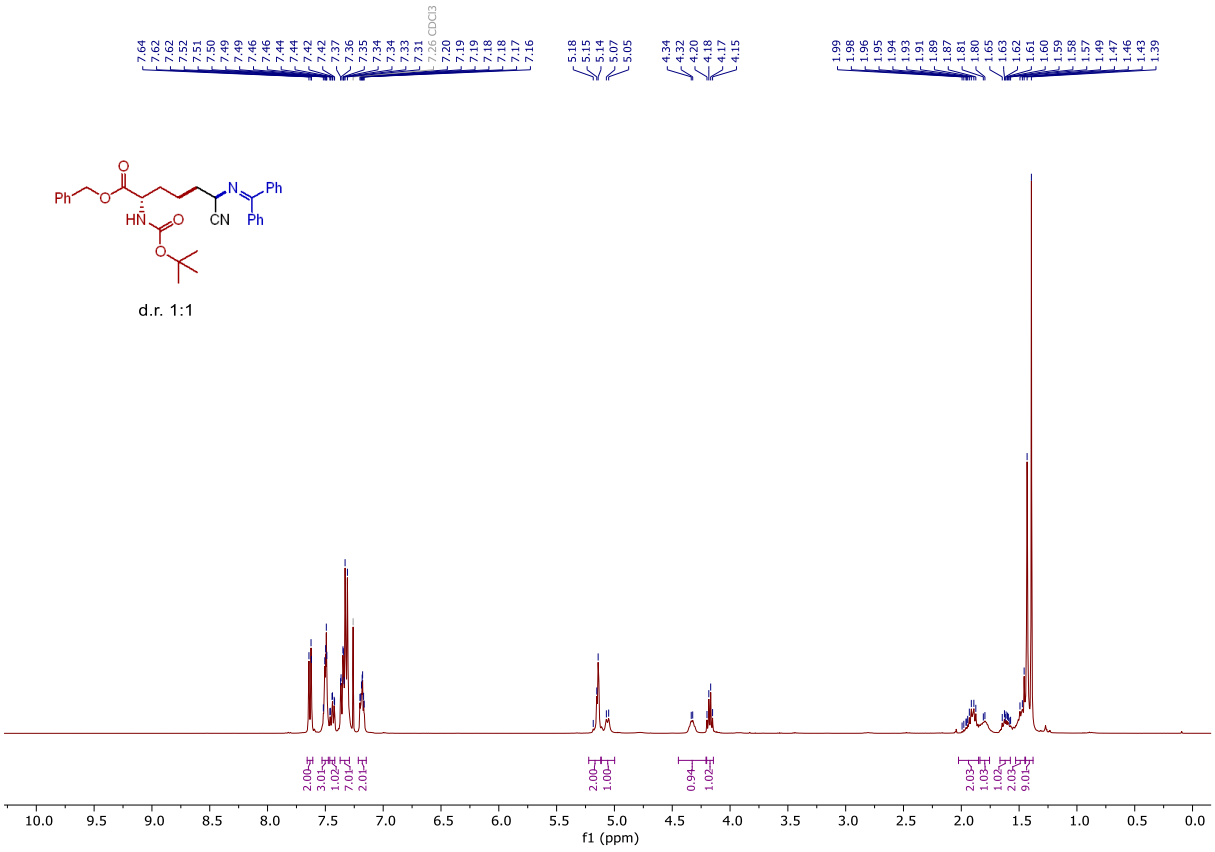


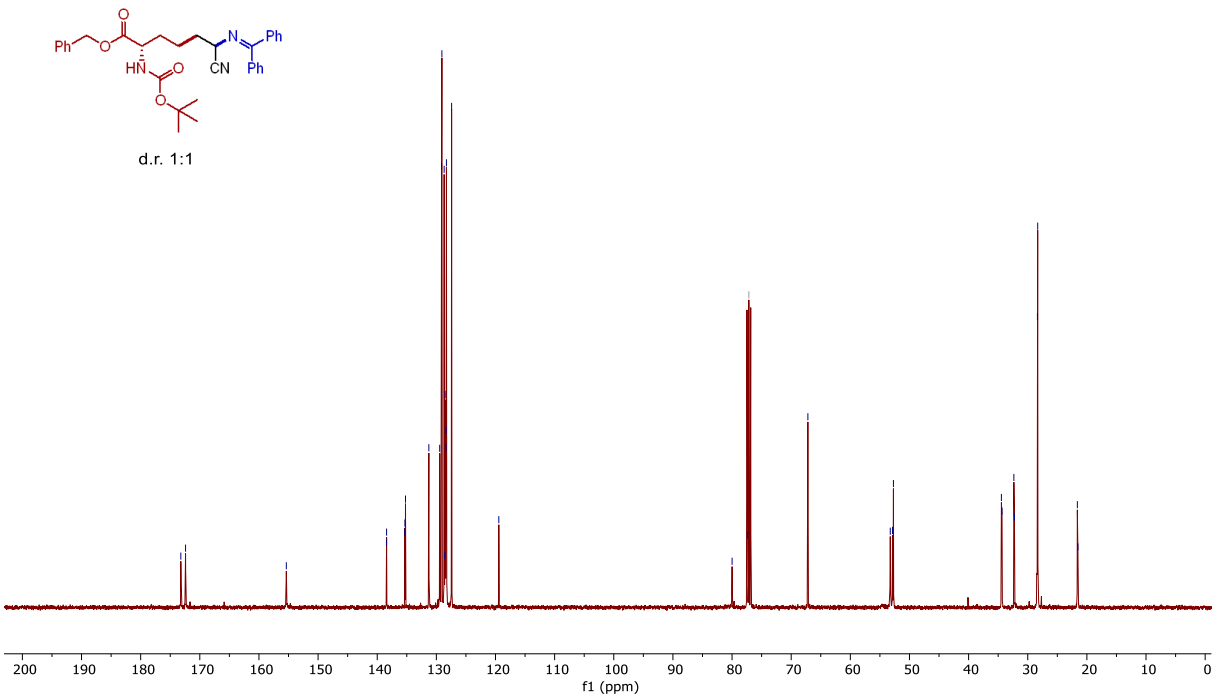
4-((3-(4-(2,2-dichlorocyclopropyl)phenoxy)-1-((diphenylmethylene)amino)-3-methylbutyl)phenyl acetate (47)



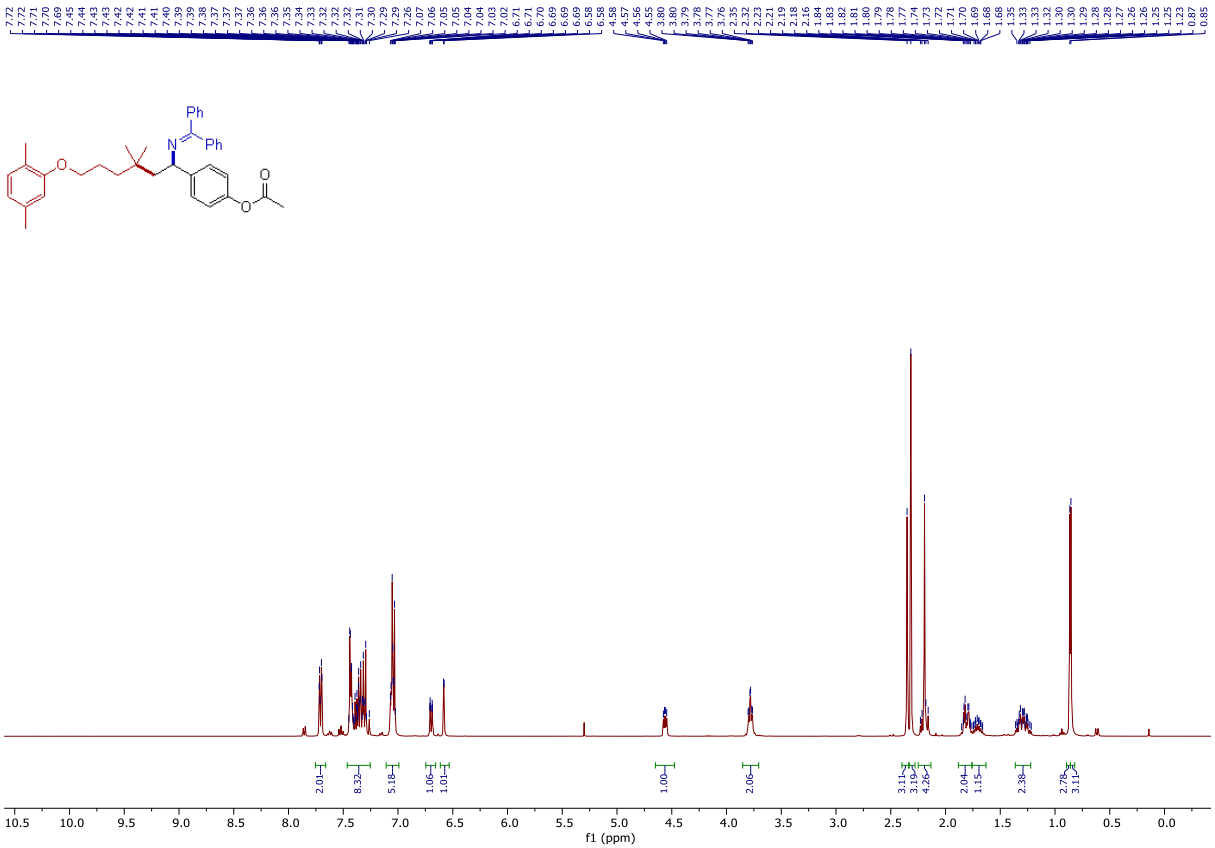


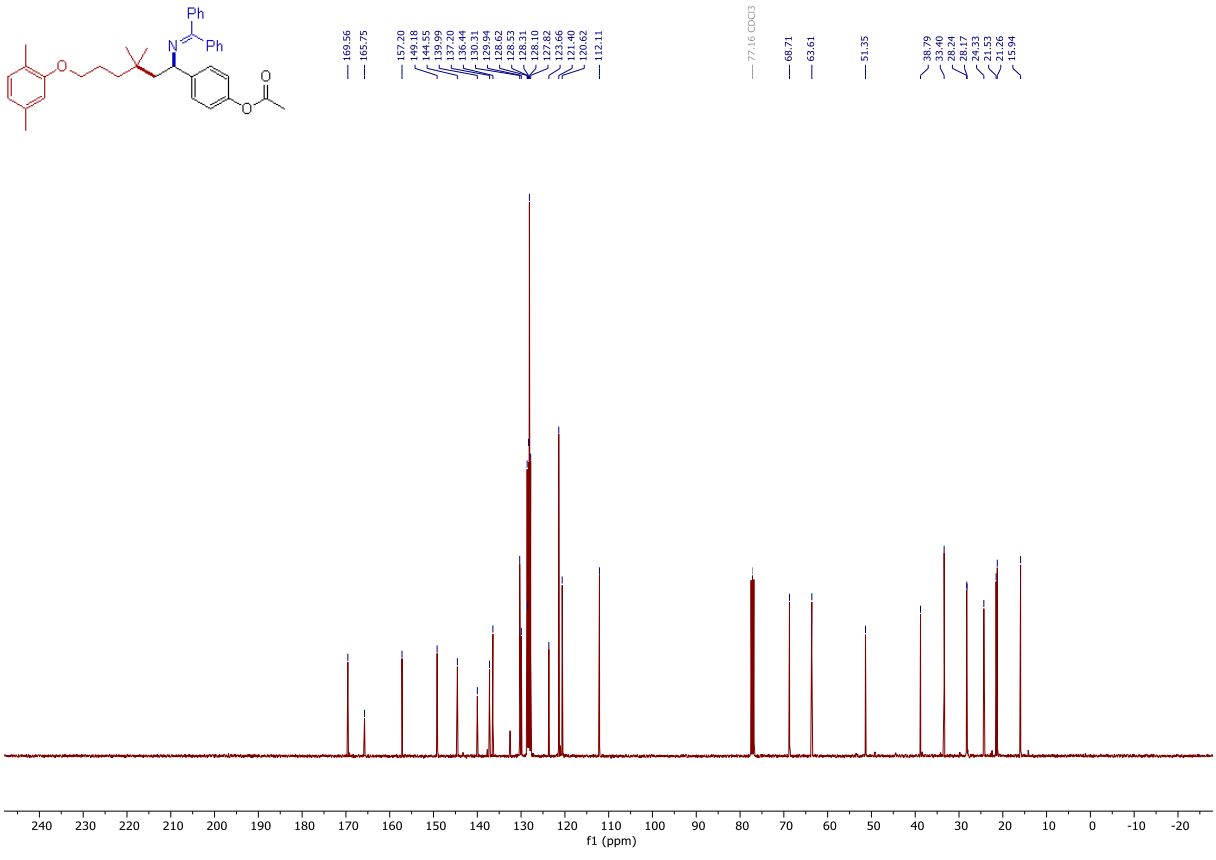
benzyl (2*S*)-2-((*tert*-butoxycarbonyl)amino)-6-cyano-6-((diphenylmethylene)amino)hexanoate (48)



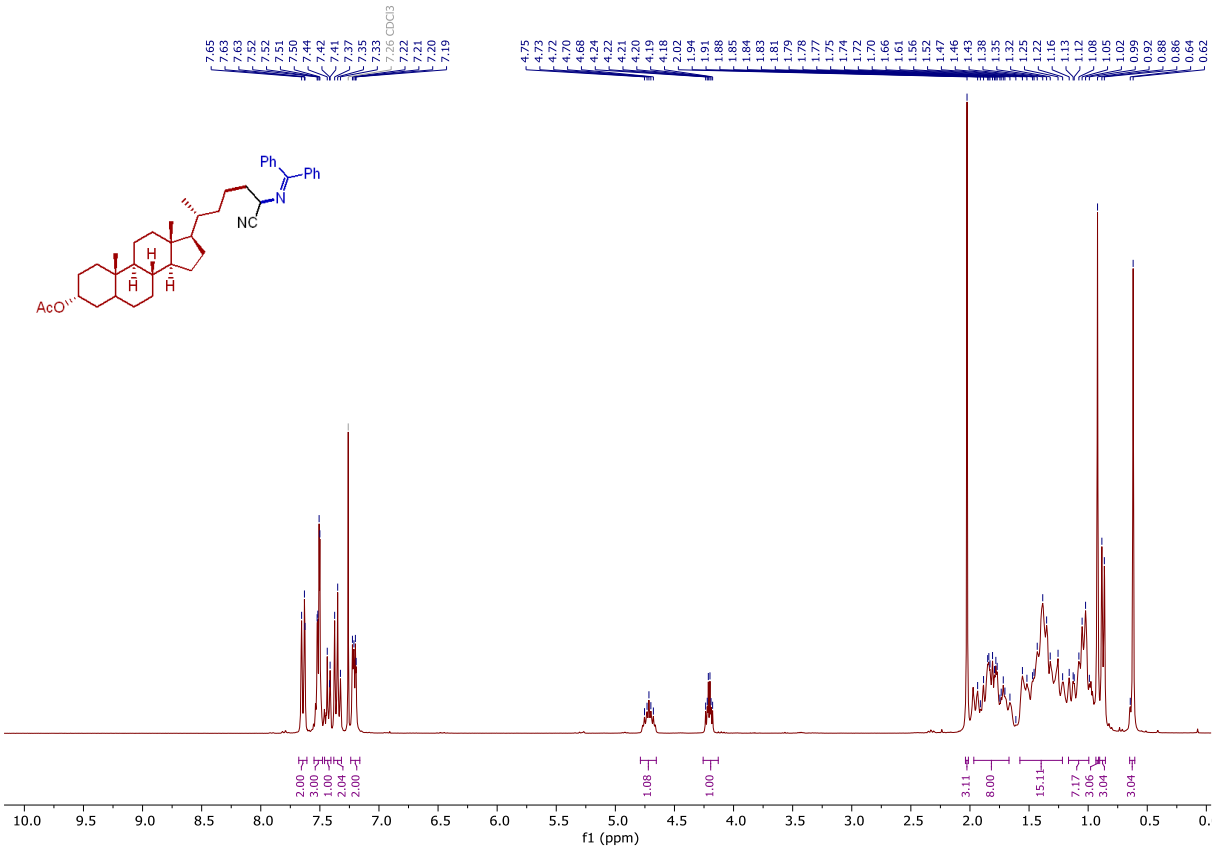


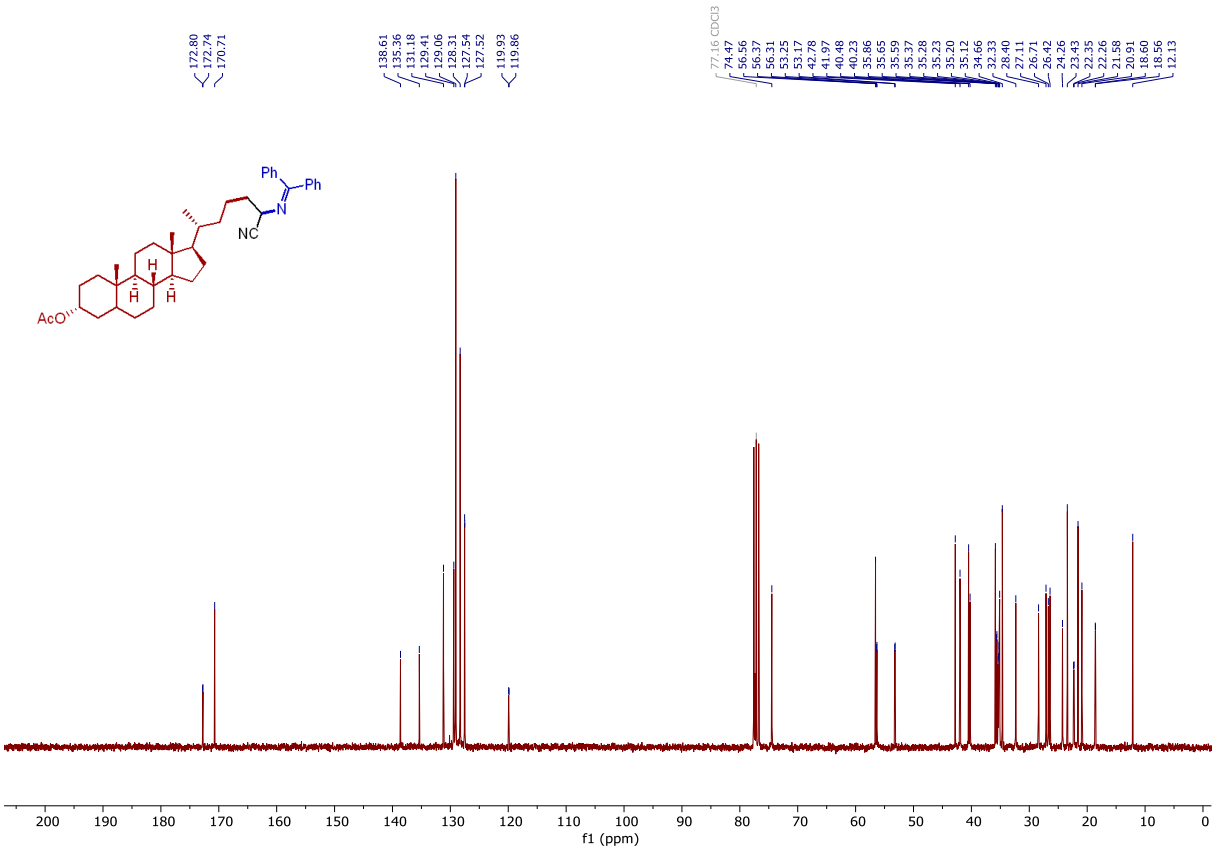
4-(6-(2,5-dimethylphenoxy)-1-((diphenylmethylene)amino)-3,3-dimethylhexyl)phenyl acetate (49)



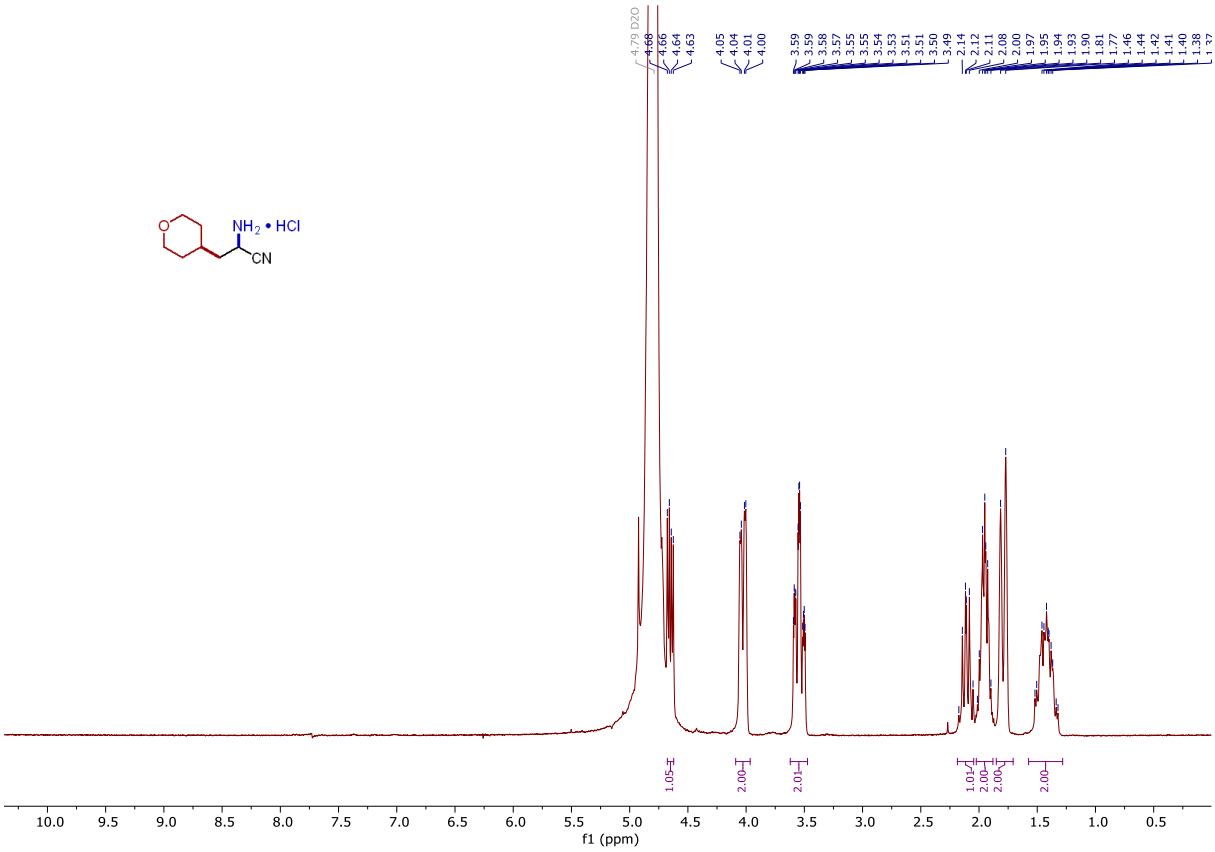


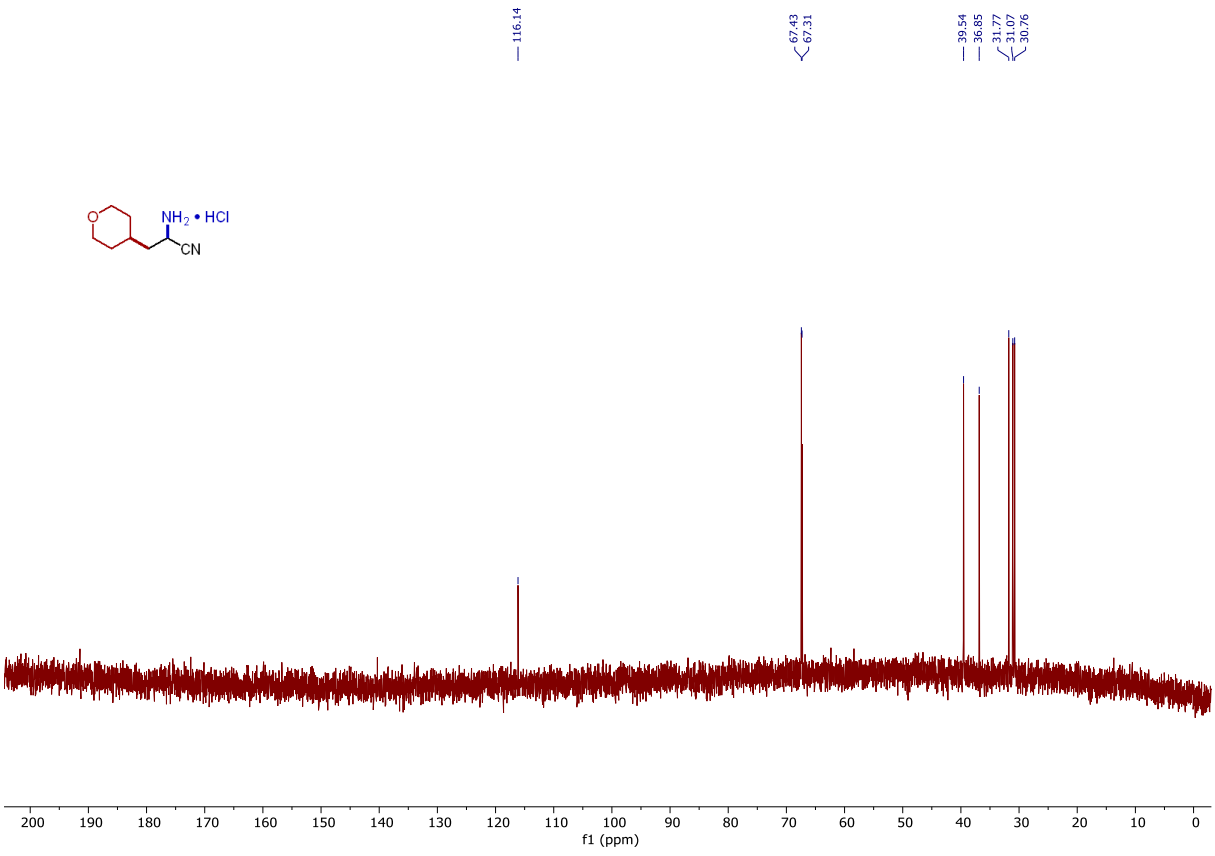
(3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((2*R*)-6-cyano-6-((diphenylmethylene)amino)hexan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (50)



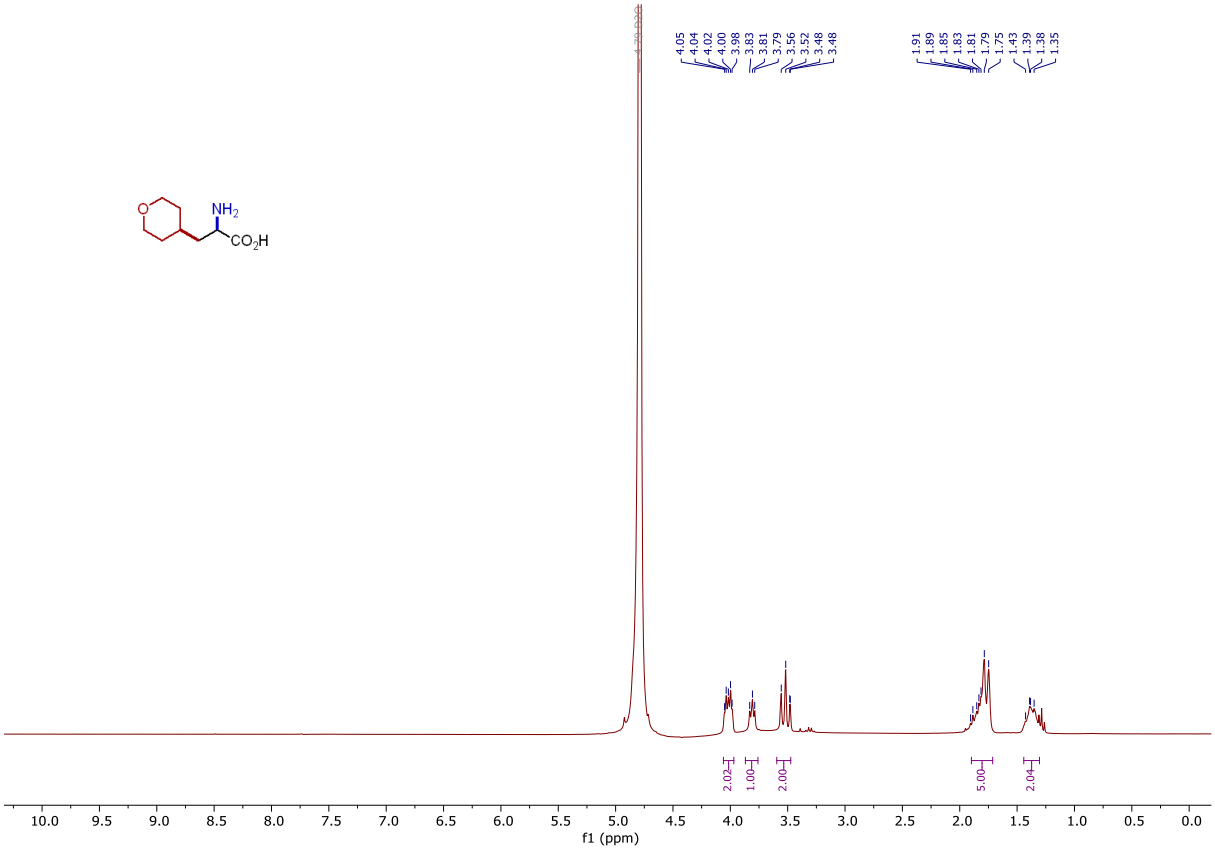


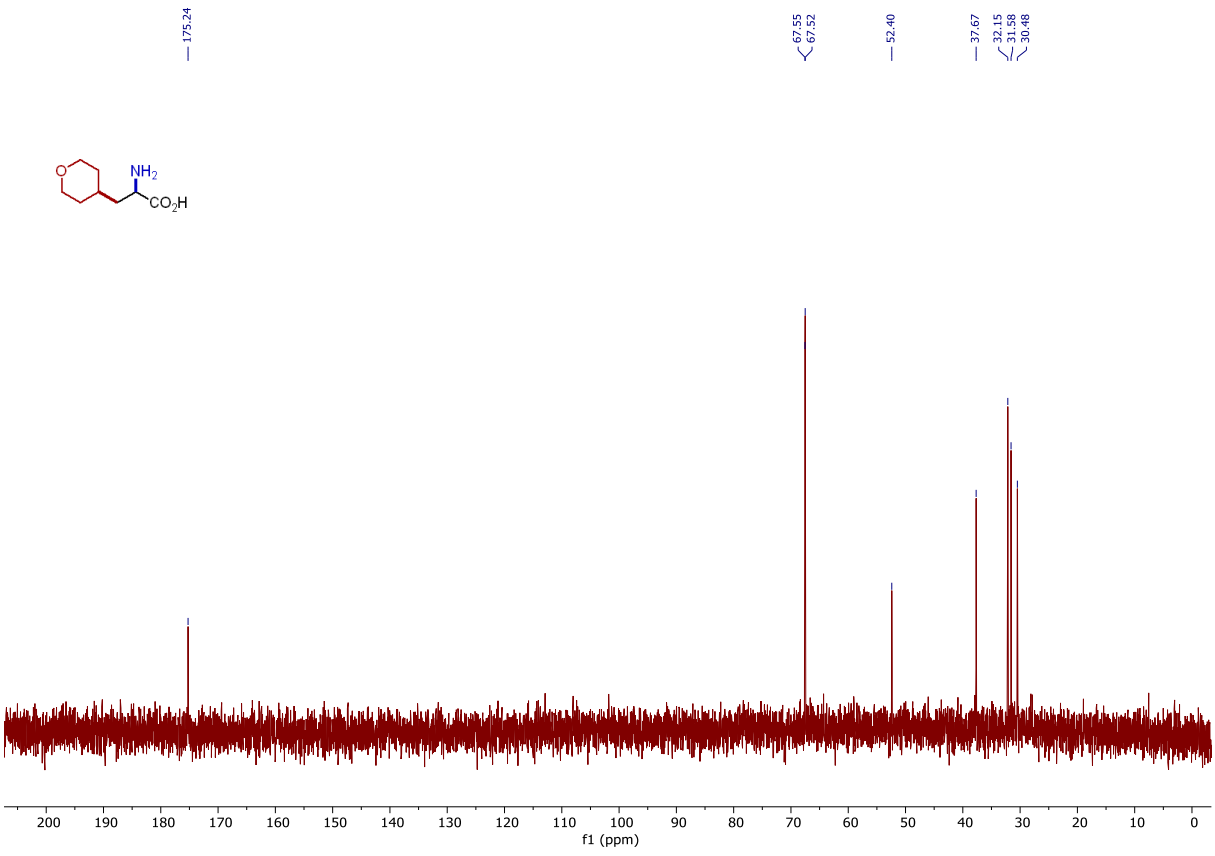
2-amino-3-(tetrahydro-2*H*-pyran-4-yl)propanenitrile hydrochloride (51)



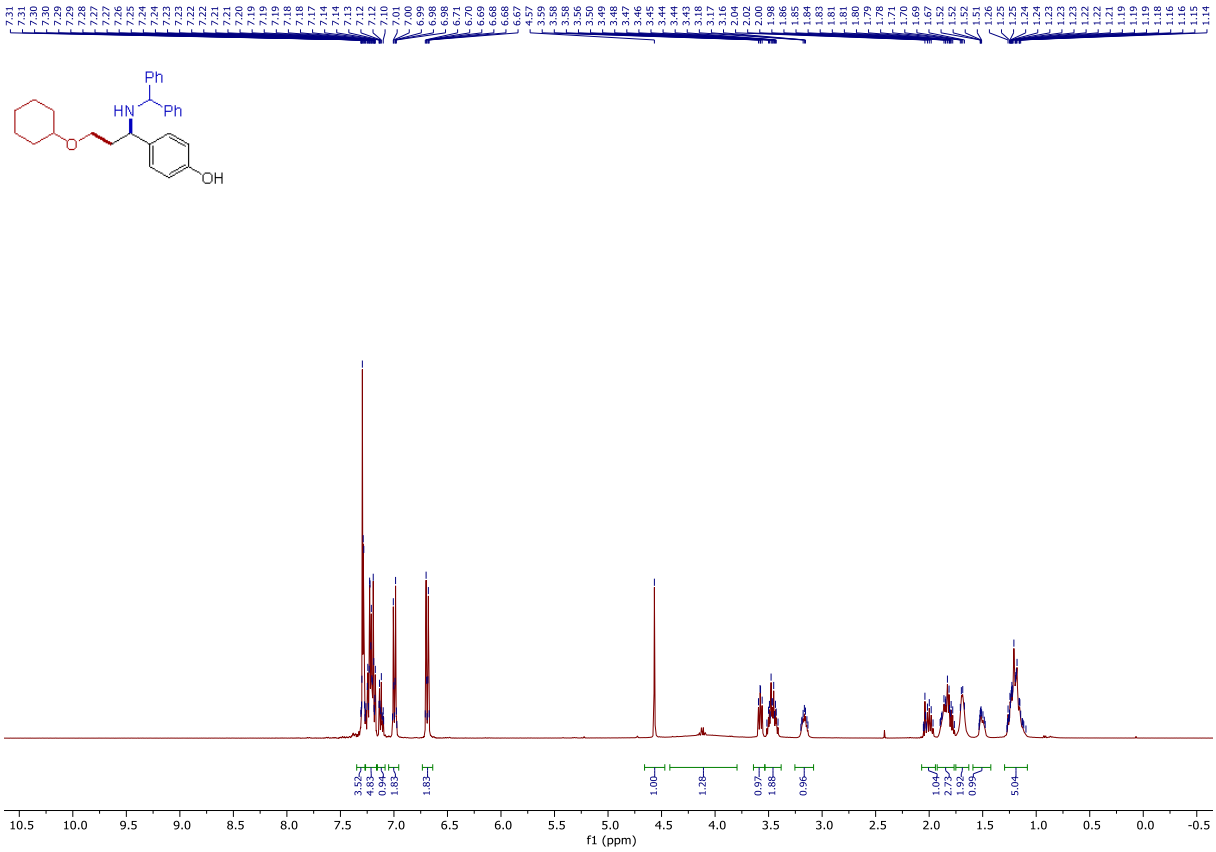


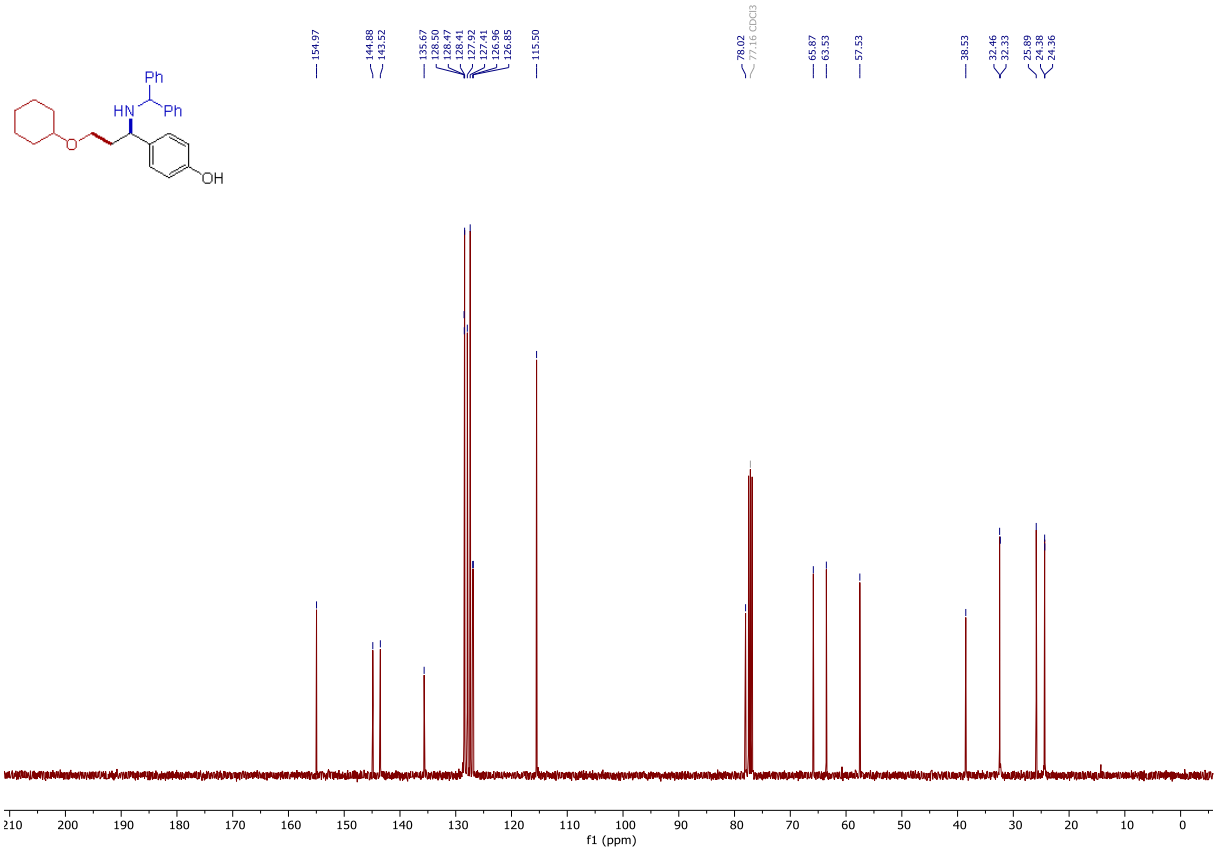
2-amino-3-(tetrahydro-2*H*-pyran-4-yl)propanoic acid (52)



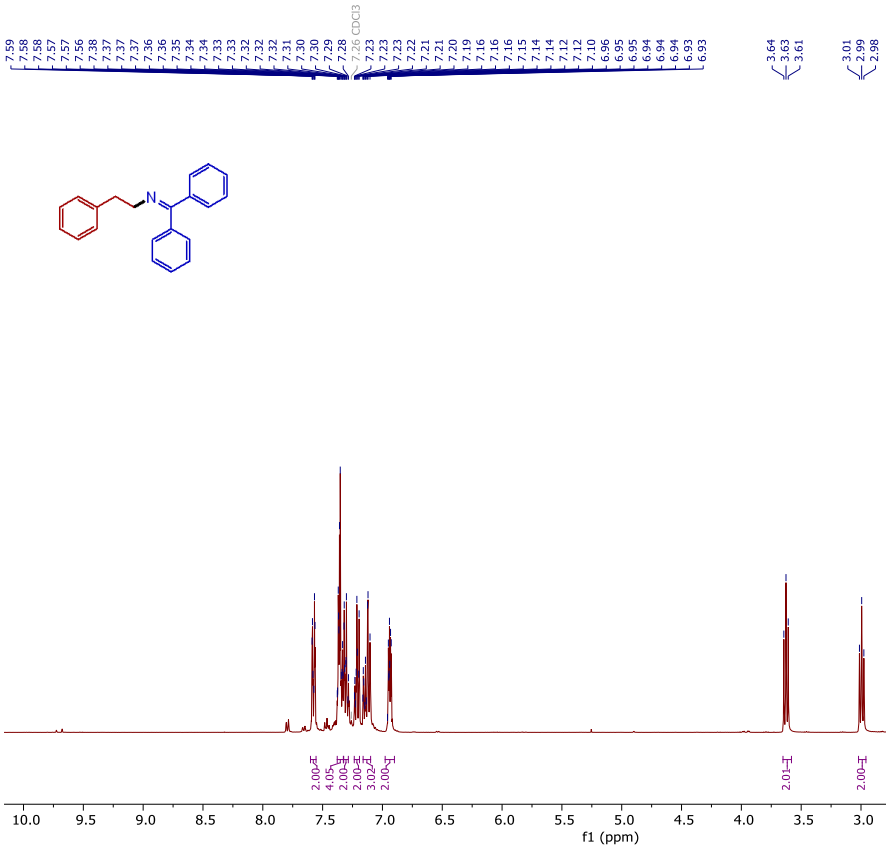


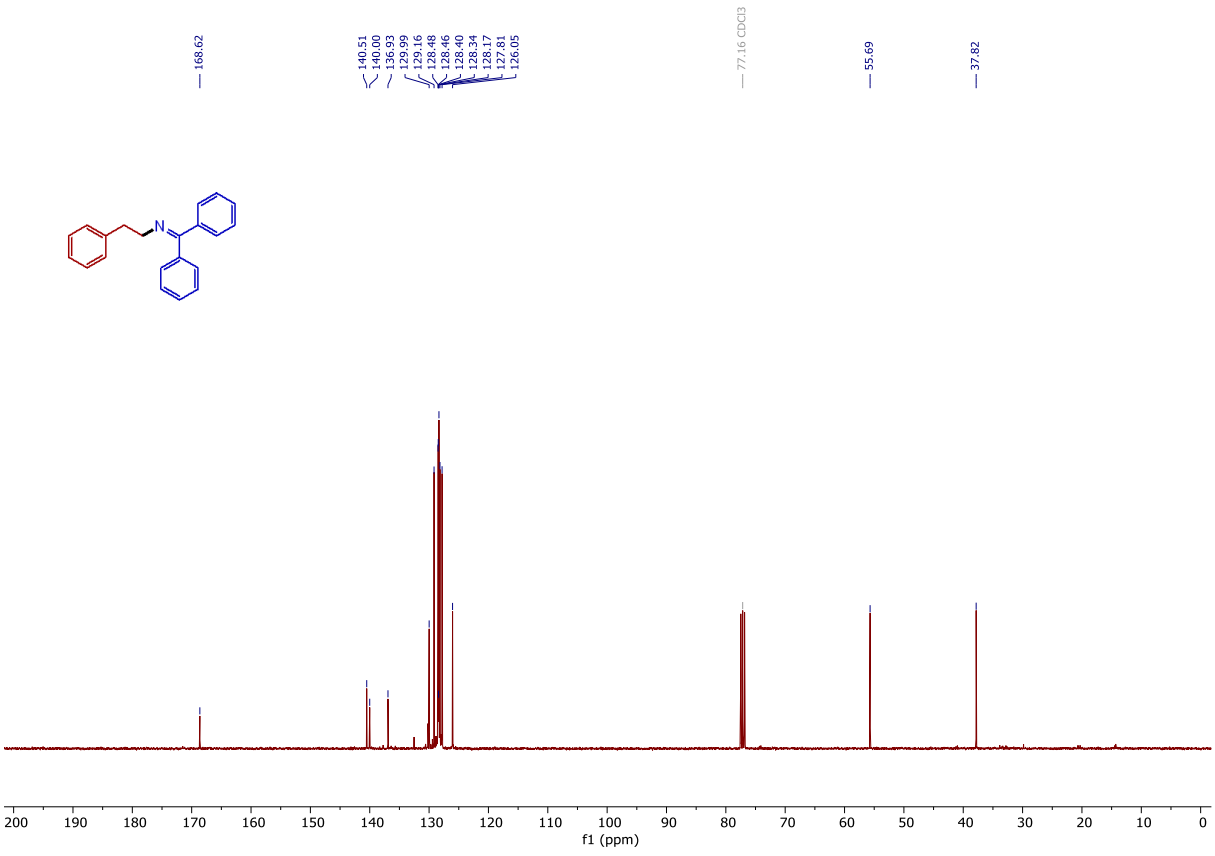
4-(1-(benzhydrylamino)-3-(cyclohexyloxy)propyl)phenol (53)





N-phenethyl-1,1-diphenylmethanimine (54)





1,1-diphenyl-*N*-(tetrahydro-2*H*-pyran-4-yl)methanimine (55):