Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Formation of quaternary centres by copper catalysed asymmetric conjugate addition to β-substituted cyclopentenones with the aid of a quantitative structure-selectivity relationship

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Ligand Screening

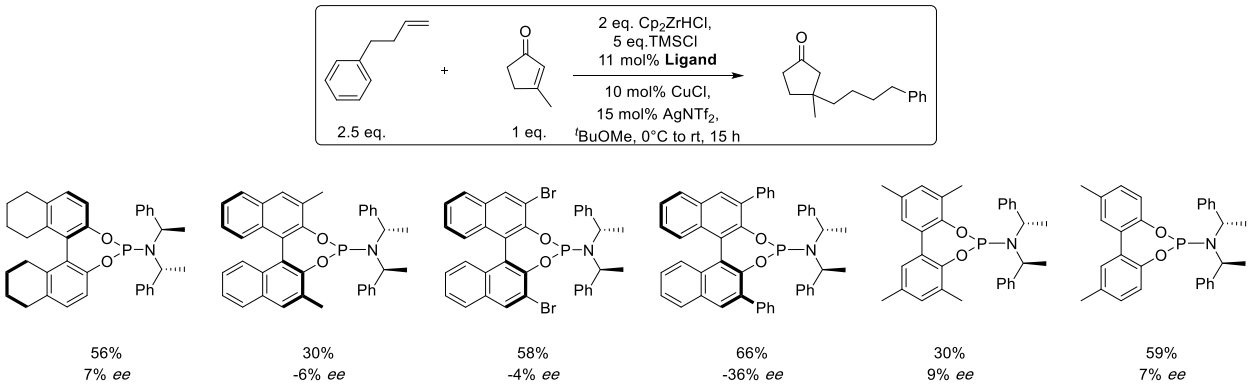


Figure S1. Ligand screening on different backbones with Feringa's amine. Yield based on ^{1}H NMR with $MeNO_2$ as internal standard. *Ee* were determined by chiral HPLC.

The yields and enantiomeric excess (%) of conjugate addition products obtained from different ligand backbones with the amido part unaltered as Feringa's amine are shown in Figure S1. Partly reduced BINOL resulted in very poor *ee* (7%). *Ortho*-substituted BINOL performed equally well or worse than BINOL (4% - 36% *ee* compared to 35% *ee* for BINOL, see **L4rrr**, manuscript). Other disubstituted aryls also gave very poor *ee* (upto 9% *ee*).

For BINOL based backbones, both amido and the BINOL parts are or can be chiral. In every case, the major enantiomer of the product is determined by the chirality of the BINOL while the chirality of the amines resulted in an enhanced or reduced level of selectivity rather than influencing the absolute stereochemistry of the product (35% *ee* for **L4rrr** vs. –20% *ee* **L4srr**, manuscript). The switching of the major enantiomer is reported as the change in sign of the *ee*: (*R*)-BINOL and its derivatives give positive % *ee* whereas (*S*)-BINOL and its derivatives give negative % *ee*. Therefore when BINOL is unaltered and only the amido part is modified, we omitted the sign of the % *ee* for simplicity (see manuscript).

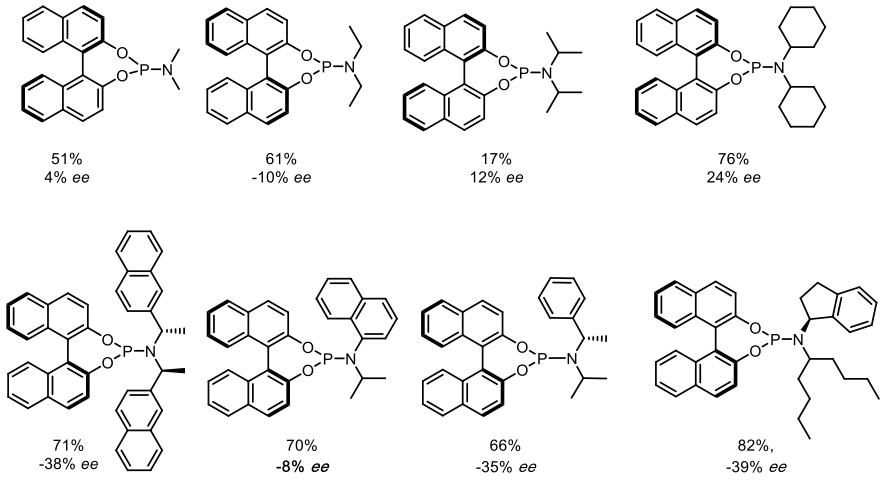
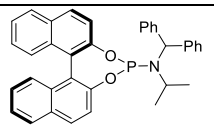
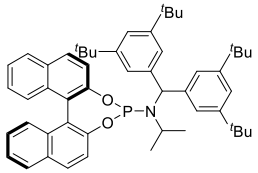
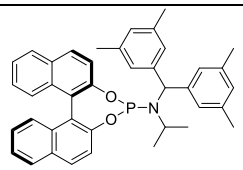
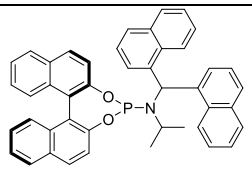
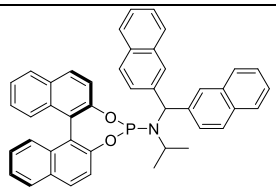


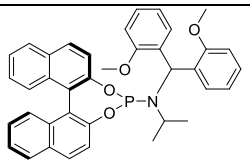
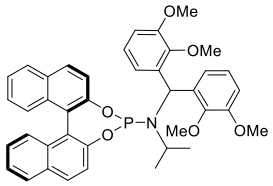
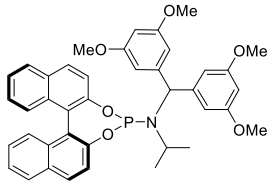
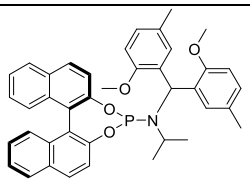
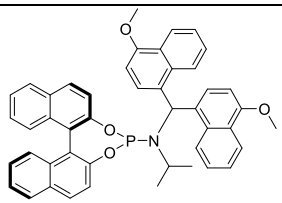
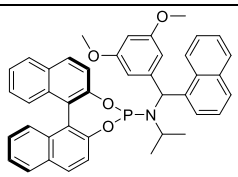
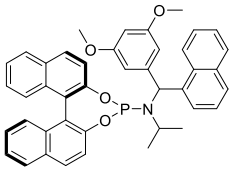
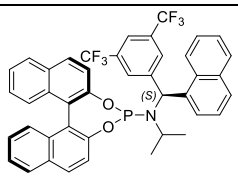
Figure S2. Ligand screening on different amido substituents with BINOL backbone. Yield based on ^{1}H NMR with $MeNO_2$ as internal standard. *Ee* were determined by chiral HPLC.

The observed enantiomeric excesses (%) of conjugate addition products are poor for simple alkyl amido substituents (4-24% *ee*). A naphthyl analogue of Feringa's ligand did not significantly improve the *ee* compared to Feringa's ligand (38% *ee* compared to 35% *ee* for **L4rrr,** manuscript). A ligand bearing an amido naphthyl group also gave poor *ee* (8%). Interestingly, the ligand that resembles Feringa's ligand where one chiral substituent was replaced with an isopropyl group resulted in the same level of *ee* (35% *ee*). Finally, we tested a chiral amido ligand shown to induce excellent enantiocontrol in copper catalysed conjugate addition to acyclic enones.[1] Unfortunately it did not significantly improve *ee* (39% *ee*)

Reproducibility

Multiple repeats (2-6) are carried out using the screening reaction condition (Figure S1) with different ligands. Average yield and *ee* of these repeats are tabulated in Table S1. The yield and *ee* are dependent on the quality of Schwartz reagent ($ZrHClCp_2$), the quality of silver salt ($AgNTf_2$). The inert atmosphere and TMSCl are required for reactivity. The Schwartz reagent is synthesised in a large batch. The use of slightly older Schwartz reagent at the end of the batch resulted in slightly decreased in *ee* and noticeable reduction in yield. To test the quality of reagents, test reactions with ligand **L8** are carried out to give *ee* of 85% (±3%).

Ligand	Ligand Structure	Number of Repeats	Averaged Yield	Averaged *ee* (%)	Averaged $\Delta\Delta G^{\ddagger}$ (kJ/mol)	RMSE $\Delta\Delta G^{\ddagger}$ (kJ/mol)
L6		2	76%	64%	3.45	0.21
L9		2	10%	22%	1.02	0.14
L8		6	45%	85%	5.71	0.09
L10		2	66%	84%	5.56	0.44
L11		2	78%	72%	4.13	0.27

L14		2	69%	77%	4.67	0.64
L15		3	39%	71%	4.02	0.46
L16		2	54%	72%	4.07	0.07
L18		2	28%	84%	5.47	0.11
L17		2	32%	85%	5.63	0.34
L27a		2	90%	80%	4.93	0.09
L27b		2	89%	71%	3.98	0.06
L28S		3	55%	47%	2.30	0.30

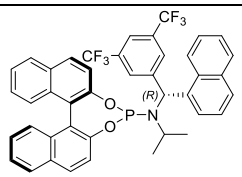
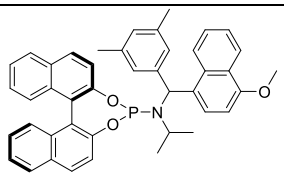
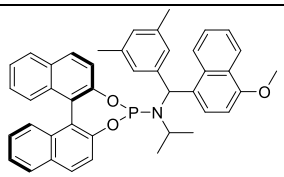
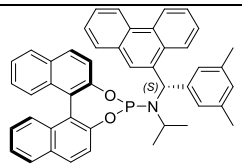
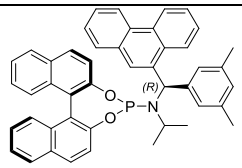
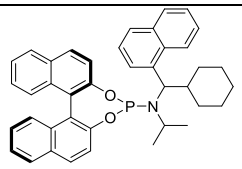
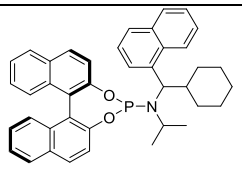
L28R		2	19%	78%	4.75	0.16
L29a		2	59%	81%	5.06	0.27
L29b		2	13%	89%	6.35	0.15
L30S		2	17%	91%	6.83	0.54
L30R		2	17%	90%	6.68	0.00
L31a		2	70%	35%	1.66	0.15
L31b		2	33%	19%	0.85	0.03

Table S1. Number of repeats, averaged yield (based on ^{1}H NMR with $MeNO_2$ as internal standard, averaged *ee* (% and kJ/mol) and standard deviation of the *ee* (kJ/mol).

Experimental section

General experimental information

All reactions were performed under $Ar_{(g)}$ atmosphere. Anhydrous Et_2O, DCM and THF were obtained from mBraun SPS-800 solvent purification system equipped with anhydrous alumina columns. Anhydrous *t*-BuOMe was dried in 4 Å molecular sieves. Anhydrous MeOH and other solvents were used as purchased. Preformed ligand-copper complexes were filtered under $Ar_{(g)}$ atmosphere through polytetrafluorethane syringe filter (13 mm, 0.2 µm). Freshly distilled PCl_3 and distilled TMSCl in $CaH_{2(s)}$ were used. Thin layer chromatography (TLC) plates were examined under UV light (λ_{max} = 254 nm) and stained using ceric ammonium molybdate (CAM) or Potassiumpermanganate ($KMnO_4$) solutions.

^1H, ^{13}C and ^{31}P NMR spectra were measured by Bruker AVIII400, AVII400, and Ascend^{TM} 400 MHz machines in $CDCl_3$ solvent. Chemical shifts were reported in part per million, referenced to solvent residue peaks. Scalar coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m). Broad peaks are indicated as (br). Coupling constants (*J*) were quoted to one decimal place. Chemical shifts were quoted to two decimal places in ^1H NMR and one decimal place in ^{13}C NMR and ^{31}P NMR. HSQC, COSY, DEPTQ and HMBC based experiments were performed to aid the assignment of spectra.

Chiral HPLC separations were achieved using an Agilent 1260 Infinity series normal phase HPLC unit and HP Chemstation software. Preparative chiral SFC separations were carried out by the analytical group at Vertex Pharmaceuticals, Milton Park, Abingdon using a Waters SFC 100 or a Berger Minigram. Chiral columns (250x20 mm (SFC 100) or 250x10 mm (Minigram)) were used as specified in the text. Chiral GC measurements were conducted on a HP6890 (H2 as vector gas) or HP6850 (H2 as vector gas) with the stated column in the characterization. Temperature programs are described as follows: initial temperature (°C) - initial time (min) - temperature gradient (°C/min) –[certain temperature – holding time - temperature gradient (°C/min)]- final temperature (°C) – holding time. Retention times (t_R) are given in min. Chiralpak® columns (250×4.6 mm), fitted with matching Chiralpak® Guard Cartridges (10×4 mm), were used as specified in the text. Chiral SFC (supercritical fluid chromatography) separations were conducted on a Waters Acquity UPC^2 system using Waters Empower software. Chiralpak® columns (150 × 3 mm, particle size 3 µm) were used. Solvents used were of HPLC grade (Fisher Scientific, Sigma Aldrich or Rathburn). Solvents used were of HPLC grade (Fisher Scientific, Sigma Aldrich or Rathburn); all eluent systems were isocratic.

Infra-red spectra were recorded on a Bruker Tensor 27 FTIR spectrometer equipped with a PIKE Miracle Attenuated Total Reflectance sampling accessory using a solid sample or thin film for liquid compounds. IR data was reported in wavenumbers (cm^{-1}).

High Resolution Mass spectra were carried out by internal service at the university of Oxford. (1) Electron spray ionisation (ESI+) were recorded on a Fisons Platform II. (2) Electron ionisation (EI)/Chemical ionisation (CI): Analyses were performed on an Agilent 7200 quadrupole time of flight (Q-ToF) instrument equipped with a direct insertion probe supplied by Scientific instrument Manufacturer (SIM) GmbH. Instrument control and data processing were performed using Agilent MassHunter software. The system was calibrated on the day of the analysis and its mass accuracy with external calibration (as used for these experiments) is better than 5ppm for 24 hours following calibration. Source conditions for both EI and CI were adjusted to maximise sensitivity, the reagent gas used in CI was either methane or ammonia (and should be apparent in the metadata associated with the data). (3) Atmospheric pressure chemical ionisation (APCI+): Analyses were performed using a Thermo Exactive mass spectrometer equipped with Waters Acquity liquid chromatography system. Instrument control and data processing were performed using Thermo Xcalibur Software. The system was calibrated on the day of the analysis and its mass accuracy with external calibration (as used for these experiments) is better than 5ppm for 24 hours following calibration. The mass spec was operated using the APCI probe and resolution was set to 50,000. APCI source conditions were adjusted to maximise sensitivity. A mixture of 10% water, 89.9% methanol and 0.1% formic acid was used to transport samples to the mass spectrometer at a flow rate of 0.2 mL/min.

Chemical names were generated from CambridgeSoft ChemBioDraw Ultra 14.0 programme. Optical rotations ($[\alpha]_D^T$) were recorded from a Perkin Elmer 241 Polarimeter and are reported in degree·ml(·g·dm)$^{-1}$. Samples were prepared at concentration (*c*) measured in mg·ml^{-1}.

General procedures

Schwartz reagent ($ZrHClCp_2$) was prepared according to procedure developed by Widf[2]. $AgNTf_2$ was prepared according to procedure developed by Huber and Rolling[3].

General procedure A – conjugate addition

In a foil wrapped, flame dried round bottom flask with a stirrer bar, $CuCl_{(s)}$ (0.10 eq.), $ligand_{(s)}$ (0.11 eq.), and solvent (1.0 ml) were added and stirred at rt for 1 h. $AgNTf_{2(s)}$ (0.15 eq.) was added and the mixture was stirred for further 30 mins. In the meantime, in a separate, dried, foil wrapped round bottom flask, dried DCM (0.20 ml) $alkene_{(l)}$ and Schwartz $reagent_{(s)}$ ($ZrHClCp_2$, 0.20 eq.) was stirred at rt in the dark. Once a clear yellow/orange solution of organozirconium was obtained, the ligand mixture was filtered into the organozirconium flask and the combined solution was stirred at 0 ˚C for 25 mins. Enone (1 eq.) and $TMSCl_{(l)}$ (5 eq.) was added and the reaction mixture was stirred while left to slowly warm up to rt over 15 h. Et_2O (ca.3 ml) and 1 M $NH_4Cl_{(aq)}$ (ca.2 ml) were added to the reaction and stirred for 30 mins before

the mixture was partitioned into aqueous and organic phases. The aqueous layer was then extracted with Et_2O three times. The combined organic layer was washed with sat.$NaHCO_{3(aq)}$ and dried with anhydrous $Na_2SO_{4(s)}$. The solvent was evaporated under reduced pressure. The crude mixture was purified by flash column chromatography.

The stereochemistry of the conjugate addition products were assigned compared to literature known compounds or based on BINOL chirality in the ligand.

Ligand screening:

Screening of ligands was carried out according to **procedure A** with 4-phenyl-1-butene (2.5 eq.).

Yields were calculated based on ^1H NMR of the crude mixture with $MeNO_2$ as an internal standard. The crude mixture was filtered through silica gel (petrol/EtOAc = 95:5) and solvent was removed *in vacuo* prior to *ee* analysis by chiral HPLC.

General Procedure B – Amine synthesis[4]

Ketone (1.0 eq.) was dissolved in DCM and cooled in an ice bath. After 10 mins, $TiCl_4$ solution in DCM (1.0 M, 1.1 eq.) was added dropwise to the solution of the ketone at 0 ˚C. The ice bath was removed and the stirring solution was slowly warmed up to rt. After 10 mins, a solution of amine (2.2-3.0 eq.) was diluted in THF and was added dropwise to the stirring ketone solution. The mixture was stirred at rt for 3 h. Solution of $NaB(CN)H_3$ dried under high vacuum before used, 1.2-5.0 eq.) in THF was slowly added to the stirring reaction mixture followed by the addition of anhydrous MeOH and the suspension was stirred at rt for a specified length of time. $NaOH_{(aq)}$ (2 M) was then added while stirring. The mixture was filtered through celite/EtOAc. $NaHCO_{3(sat.)}$ was added and the mixture was partitioned between organic and aqueous phase. The aqueous layer was extracted by Et_2O three times. The combined organic layer was concentrated *in vacuo* and acidified with concentrated HCl. The acidic mixture was partitioned and the ethereal layer was extracted with 1 M HCl three times. The conbined acidic aqueous layer was basified with 25% NaOH until pH≈14. The basic layer was extracted with DCM three times. The combined DCM fractions was dried with $MgSO_{4(s)}$. The mixture was filtered before the solvent was remove *in vacuo* and dried or freeze-dried under high vacuum.

Alternative purification techniques:

$NaHCO_{3(sat)}$ was then added while stirring. The mixture was filtered through celite/EtOAc. The biphasic solution was concentrated *in vacuo* and the aqueous layer was extracted by EtOAc three times. The combined organic layer was dried with $MgSO_{4(s)}$ and was concentrated *in vacuo* and filtered through a strong cation exchange column ISOLUTE® SCX-2 (propylsulfonic

acid) with MeOH to wash off non-basic component followed by ammonia solution in MeOH (2 M). The ammonium solution was concentrated and dry under high vacuum.

General procedure C - Ligand Synthesis[5]

Freshly distilled $PCl_{3(l)}$ (1.1 eq.) was diluted in DCM and cooled in an ice bath. Et_3N (5 eq.) was added dropwise to the cooled, stirring solution of PCl_3. The ice bath was removed and the solution was left to slowly warm up to rt over 10 mins. The amine (1.0 eq.) in DCM was added dropwise to the stirred solution of Et_3N. The reaction mixture was stirred at rt for 5 h before enaniopure binol (1.3 eq.) was added and the mixture was continued to stir overnight at rt. The mixture was filtered through celite/DCM and solvent was evaporated under reduced pressure. The crude mixture was purified by flash column chromatography.

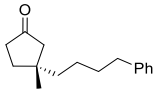
Procedures for ligands that were not synthesised by the author but were used in this work can be found in previously reported procedures.[6]

General procedure D – Derivatisation of ketone[7]

To a flamed dried round bottom flask with a stirrer bar, ketone (1.0 eq.), DCM (0.5 M) and mCPBA (2.6 eq.) were added and stirred under $Ar_{(g)}$. The flask was placed in ice bath and wrapped in foil before trifluoroacetic $acid_{(l)}$ (1.0 eq.) was added dropwise over 10 mins. The reaction mixture was stirred overnight and slowly warm up to rt. The conversion of the ketone starting material was monitored by TLC with $KMnO_4$ stain. Once the starting material is consumed, the reaction mixture was washed with $Na_2SO_{3\ (aq)}$ (5% solution, ca 2 ml), $NaHCO_{3(sat)}$ and $H_2O_{(l)}$. The organic layer was dried with $MgSO_{4(s)}$. The crude reaction mixture was used in the subsequent step without further purification.

To a flamed dried round bottom flask with a stirrer bar, the crude reaction mixture (1.0 eq.), DCM (0.1 M) and $AlMe_3$ (1.6 eq.) were added and stirred under $Ar_{(g)}$. The flask was placed in ice bath before $benzylamine_{(l)}$ (2.0 eq.) was added dropwise. The reaction mixture was stirred overnight and slowly warm up to rt. The conversion of the ketone starting material was monitored by TLC with $KMnO_4$ stain. Once the starting material is consumed, $HCl_{(aq)}$ (1 M, ca 3 ml) was added and the aqueous layer was extracted by DCM (ca 5 ml) three times. The combined organic layer was dried with $MgSO_{4(s)}$ and dried *in vacuo*. The crude reaction mixture was filtered through silica gel with ETOAc:Et_3N eluent and the solvent was removed *in vacuo*.

Experimental details



(+)-*(R)*-3-methyl-3-(4-phenylbutyl)cyclopentan-1-one **3**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.04 mmol, 0.10 eq.), (R_a)-*N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (28.2 mg, 0.22 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.4 ml) 4-phenyl--1-butene$_{(l)}$ (150 µl, 1.0 mmol, 2.5 eq.), $ZrHClCp_2$ (206.2 mg, 0.80 mmol, 2.0 eq.), 3-methyl-2-cyclopentenone (40 µl, 0.40 mmol, 1 eq.) and $TMSCl_{(l)}$ (0.25 ml, 1.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/EtOAc = 95:5] to afford colourless oil of (+)-*(R)*-3-methyl-3-(4-phenylbutyl)cyclopentan-1-one (82.3 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.38 – 7.26 (m, 2H, $C_{Ar}H$), 7.25 – 7.17 (m, 3H, $C_{Ar}H$), 2.70 – 2.61 (m, 2H, $CH_2CH_2CH_2Ph$), 2.39 – 2.21 (m, 2H, CH_2CH_2CO), 2.18 – 1.98 (m, 2H, $MeCCH_2CO$), 1.89 – 1.71 (m, 2H, CH_2CH_2CO), 1.73 – 1.54 (m, 2H, CH_2CH_2Ph), 1.52 – 1.21 (m, 4H, CH_2Ph and $MeCCH_2$), 1.06 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 220.2, 142.6, 128.5 (2C), 128.4 (2C), 125.8, 52.4, 41.7, 39.7, 36.9, 36.0, 35.4, 32.2, 25.2, 24.5.

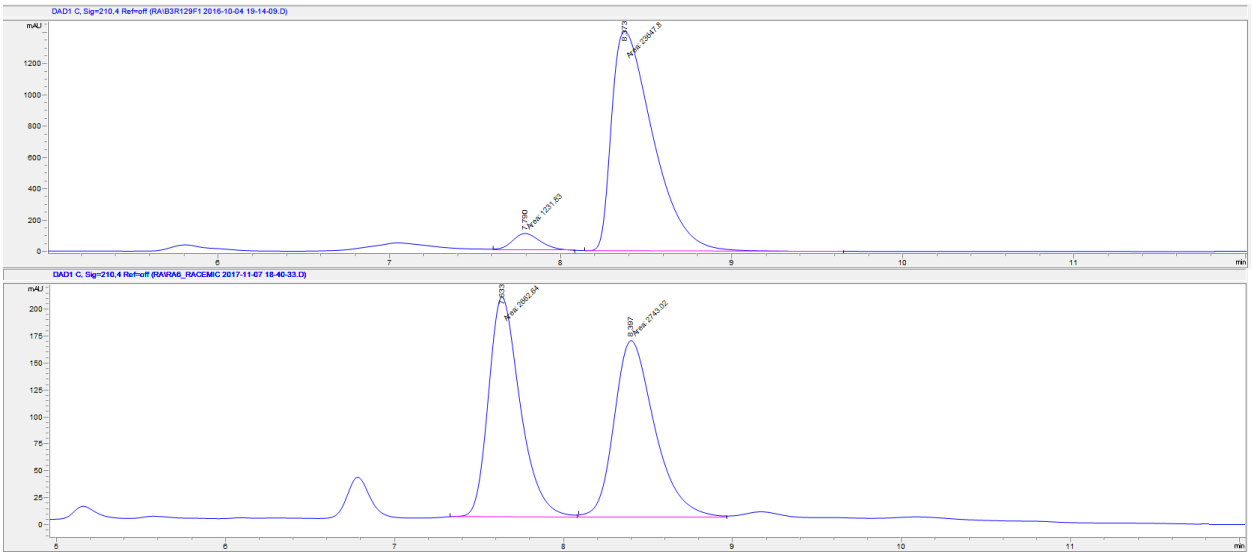
IR υ_{max} (liq): 2930, 1738, 1496, 1153, 698.

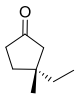
HRMS (ESI^+) $[C_{16}H_{22}ONa]^+$ predicted 253.1568, found 253.1563 (Δ –0.1 ppm).

HPLC analysis indicated an enantiomeric excess of 90% [Chiralpak® AY-H; flow: 1 mL/min; hexane/i-PrOH = 95:5; λ = 210 nm; minor enantiomer (–)-(*S*)-3-methyl-3-(4-phenylhexyl)cyclopentanone, t_R = 7.77 min; major enantiomer (+)-(*R*)-3-methyl-3-(4-phenylhexyl)cyclopentanone, t_R = 8.30 min].

$[\alpha]_{589}^{25}$ = +27.4 (*c* 1.00, $CHCl_3$)

Data was consistent with previously reported values.[8]





(*R*)-3-ethyl-3-methylcyclopentan-1-one **4**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.) in ethene$_{(g)}$ atmosphere (balloon), 3-methyl-2-cyclopentenone (40 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/EtOAc = 96:4] to afford pale yellow oil of (*R*)-3-ethyl-3-methylcyclopentan-1-one (49.1 mg, 97%).

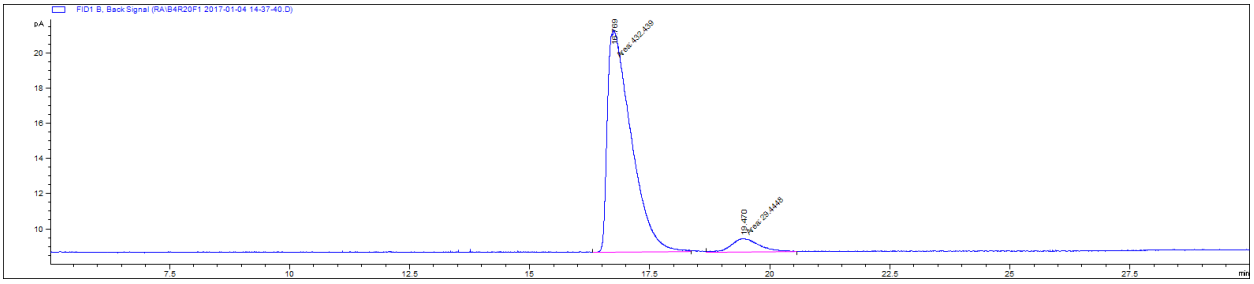
GC analysis indicated an enantiomeric excess of 87% [Macherey & Nagel, Lipodex® E; 60-30 λ = 210 nm; major enantiomer, t_R = 16.8 min; minor enantiomer, t_R = 19.5 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 2.38 – 2.22 (m, 2H, COCH_2), 2.12 – 1.95 (m, 2H, COCH_2), 1.88 – 1.66 (m, 2H, CH_2), 1.44 (q, *J* = 7.6 Hz, 2H, CH_2CH$_3$), 1.03 (s, 3H, CH_3), 0.90 (t, *J* = 7.5 Hz, 3H, CH_2CH_3).

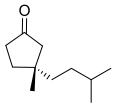
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 220.4, 52.0, 39.9, 37.0, 34.9, 34.1, 24.7, 9.2.

IR υ_{max} (film): 3051, 2980, 1737, 777.

$[\alpha]_{589}^{25}$ = +28.7 (*c* 1.00, $CHCl_3$)



Data was consistent with previously reported values.[9]



(*R*)-3-isopentyl-3-methylcyclopentan-1-one **5**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) 3-methylbut-1-ene$_{(l)}$ (70 mg, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-methyl-2-cyclopentenone (40 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/EtOAc = 97:3] to afford colourless oil of 3-isopentyl-3-methylcyclopentan-1-one (48.5 mg, 72%).

GC analysis indicated an enantiomeric excess of 89% [Macherey & Nagel, Lipodex® E; 60-30-0.1-70-10, λ = 210 nm; major enantiomer, t_R = 61.3 min; minor enantiomer, t_R = 65.0 min].

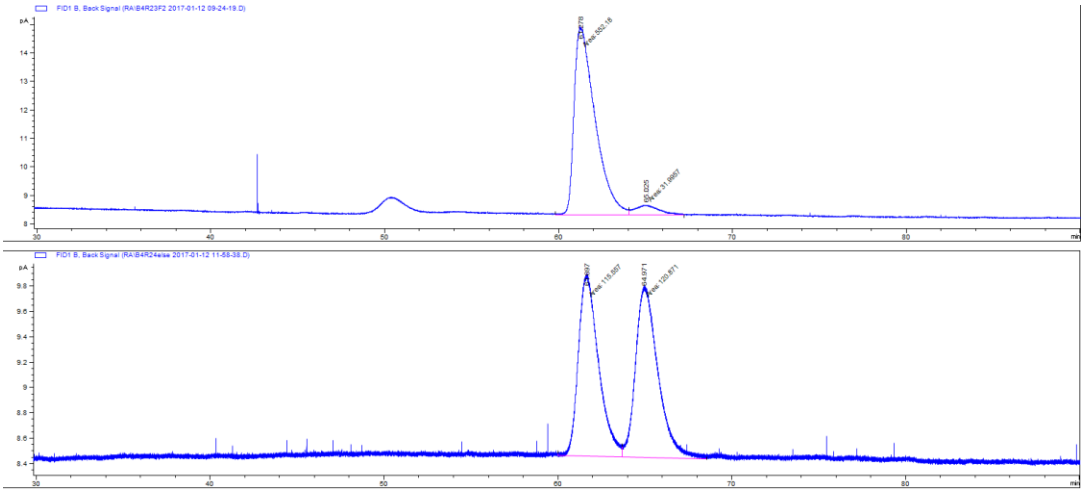
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 2.36 – 2.17 (m, 2H, COCH_2), 2.10 – 1.93 (m, 2H, COCH_2), 1.85 – 1.67 (m, 2H, CH_2), 1.52 – 1.32 (m, 3H, CH_2, CH), 1.25 – 1.06 (m, 2H, CH_2), 1.02 (s, 3H, CH_3), 0.87 (d, J = 6.6 Hz, CH(CH_3)$_2$).

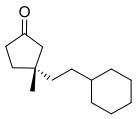
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 220.3, 66.0, 52.4, 39.6, 39.5, 36.9, 35.3, 33.9, 28.7, 25.2, 25.1, 22.8, 22.7, 15.4 (2C).

HRMS (ESI$^+$) $[C_{11}H_{21}O]^+$ predicted 169.15869, found 169.15880 (Δ 0.63 ppm).

IR υ_{max} (film): 1954, 2962, 2870, 1739, 1137.

$[\alpha]_{589}^{25}$ = +28.7 (*c* 1.0, $CHCl_3$)





(*R*)-3-(2-cyclohexylethyl)-3-methylcyclopentan-1-one **6**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) vinylcyclohexane$_{(l)}$ (140 µl, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-methyl-2-cyclopentenone (40 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/EtOAc = 98:2] to afford colourless oil of 3-(2-cyclohexylethyl)-3-methylcyclopentan-1-one (70.5 mg, 42%).

The enantiomeric excess of the product was determined by chiral SFC after two steps derivatisation (**General procedure D**).

SFC analysis indicated an enantiomeric excess of 92% [Chiralpak® IA-3; 1500 psi, 30 °C, flow: 1.5 mL/min; 1% to 30% MeOH in 8 min; λ = 210 nm; major enantiomer, t_R = 4.39 min; minor enantiomer, t_R = 4.57 min].

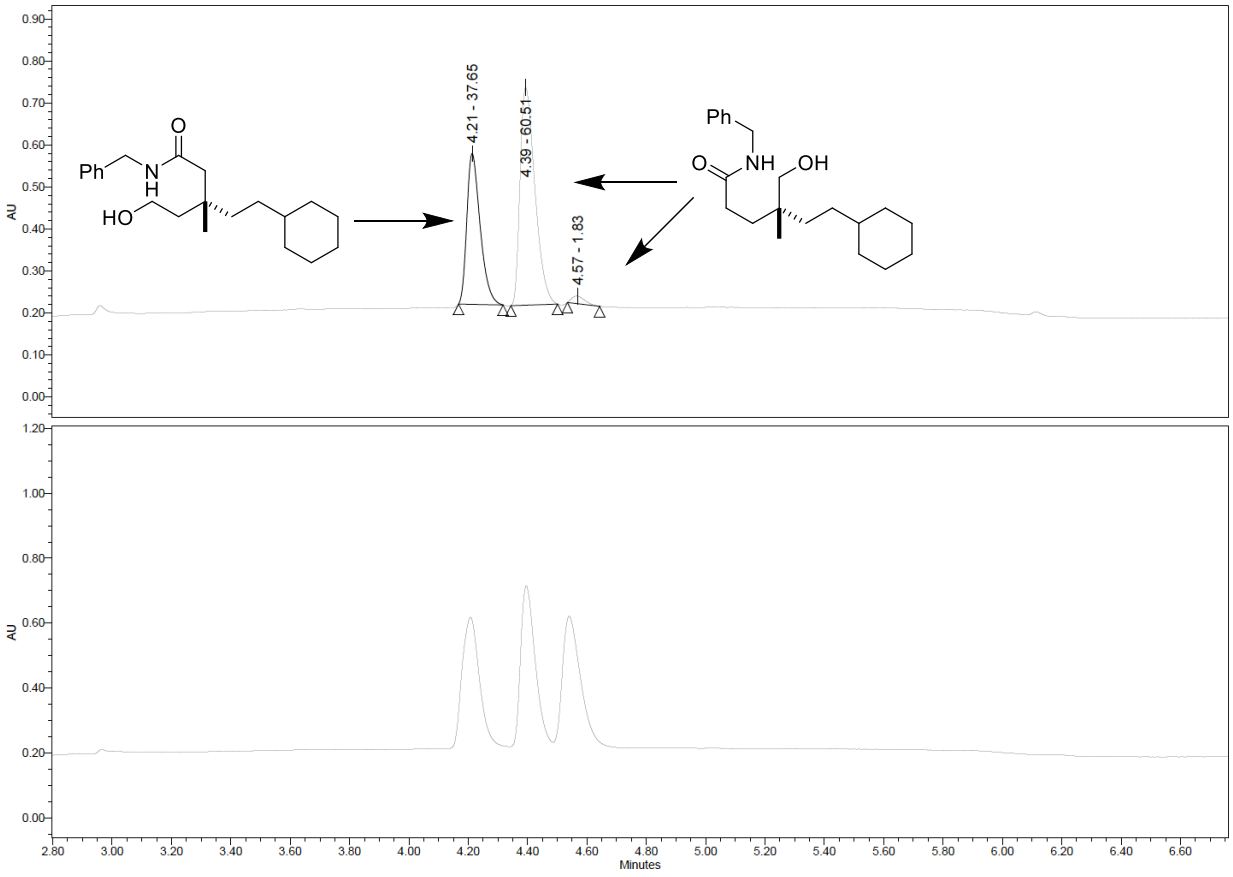
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 2.37 – 2.22 (m, 2H, COCH_2), 2.13 – 1.95 (m, 2H, COCH_2), 1.85 – 1.58 (m, 9H, 3(CH_2), CH_aH$_b$), 1.43 – 1.33 (m, 2H, CH_2), 1.28 – 1.06 (m, 4H, CH, CH_2, CH$_a$$H_b$), 1.02 (s, 3H, C$H_3$), 0.93 – 0.80 (m, 2H, C$H_2$).

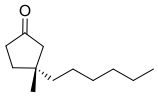
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 220.5, 52.4, 39.6, 39.1, 38.4, 37.0, 35.3, 33.6, 33.5, 32.5, 26.8, 26.5 (2C), 25.2.

HRMS (ESI$^+$) $[C_{14}H_{25}O]^+$ predicted 209.19026, found 209.18999 (Δ 1.29 ppm).

IR υ_{max} (film): 2989, 2920, 2851, 1740, 1449, 1380, 1163, 957.

$[\alpha]_{589}^{25}$ = +29.6 (*c* 1.0, $CHCl_3$)




(*R*)-3-hexyl-3-methylcyclopentan-1-one **7**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) 1-hexene$_{(l)}$ (124 µl, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-methyl-2-cyclopentenone (40 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/EtOAc = 92:8] to afford pale yellow oil of 3-hexyl-3-methylcyclopentan-1-one (55.0 mg, 75%).

GC analysis indicated an enantiomeric excess of 86% [Macherey & Nagel, Lipodex® E; 70-30-0.2-85-10, λ = 210 nm; major enantiomer, t_R = 79.3 min; minor enantiomer, t_R = 82.4 min].

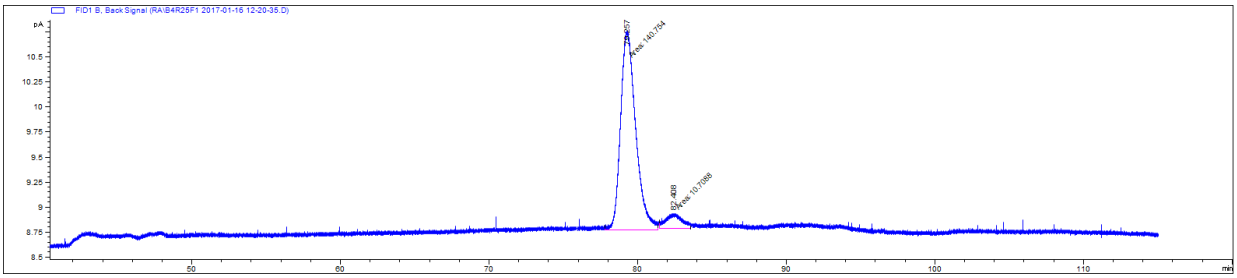
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 2.36 – 2.21 (m, 2H, COCH_2), 2.11 – 1.94 (m, 2H, COCH_2), 1.85 – 1.67 (m, 2H, CH_2), 1.39 – 1.20 (m, 10H, 5CH_2), 1.03 (s, 3H, CCH_3), 0.91 – 0.83 (m, 3H, CH_2CH_3).

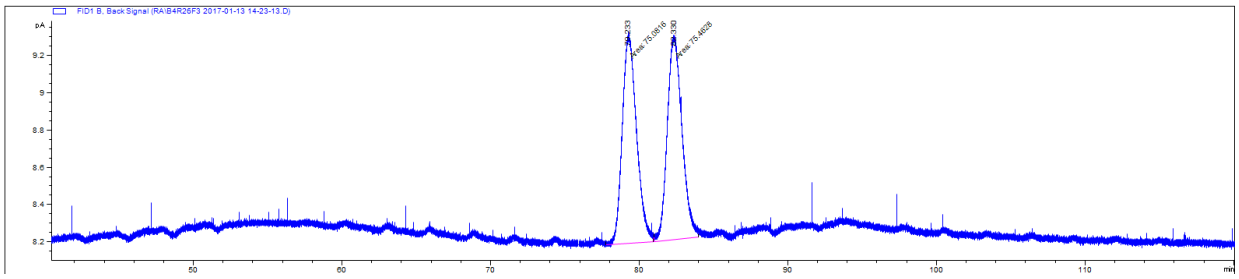
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 220.4, 52.4, 41.9, 39.6, 36.9, 35.4, 31.9, 30.1, 25.2, 24.8, 22.8, 14.2.

HRMS (ESI^+) $[C_{12}H_{22}O^{23}Na]^+$ predicted 205.15633, found 205.15629 (Δ 0.19 ppm).

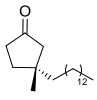
IR υ_{max} (film): 2955, 2927, 1740, 1464, 1405, 1379, 1166, 1134.

$[\alpha]_{589}^{25}$ = +32.8 (*c* 1.0, $CHCl_3$)





^{1}H and IR spectra are consistent with previously reported values.[10]



(*R*)-3-methyl-3-tetradecylcyclopentan-1-one **8**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand **L**(*R_a*)-*N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) 1-tetradecene$_{(l)}$ (253 µl, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-methyl-3-tetradecylcyclopentan-1-one (40 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/Et_2O = 97:3] to afford colourless oil of 3-methyl-3-tetradecylcyclopentan-1-one (92.5 mg, 79%).

The enantiomeric excess of the product was determined by chiral HPLC after two steps derivatisation (**General procedure D**).

SFC analysis indicated an enantiomeric excess of 90% [Chiralpak® IG-3; 1500 psi, 30 °C, flow: 1.5 mL/min; 1% to 30% MeOH in 10 min; λ = 211.9 nm; minor enantiomer, t_R = 9.58 min; major enantiomer, t_R = 94.78 min].

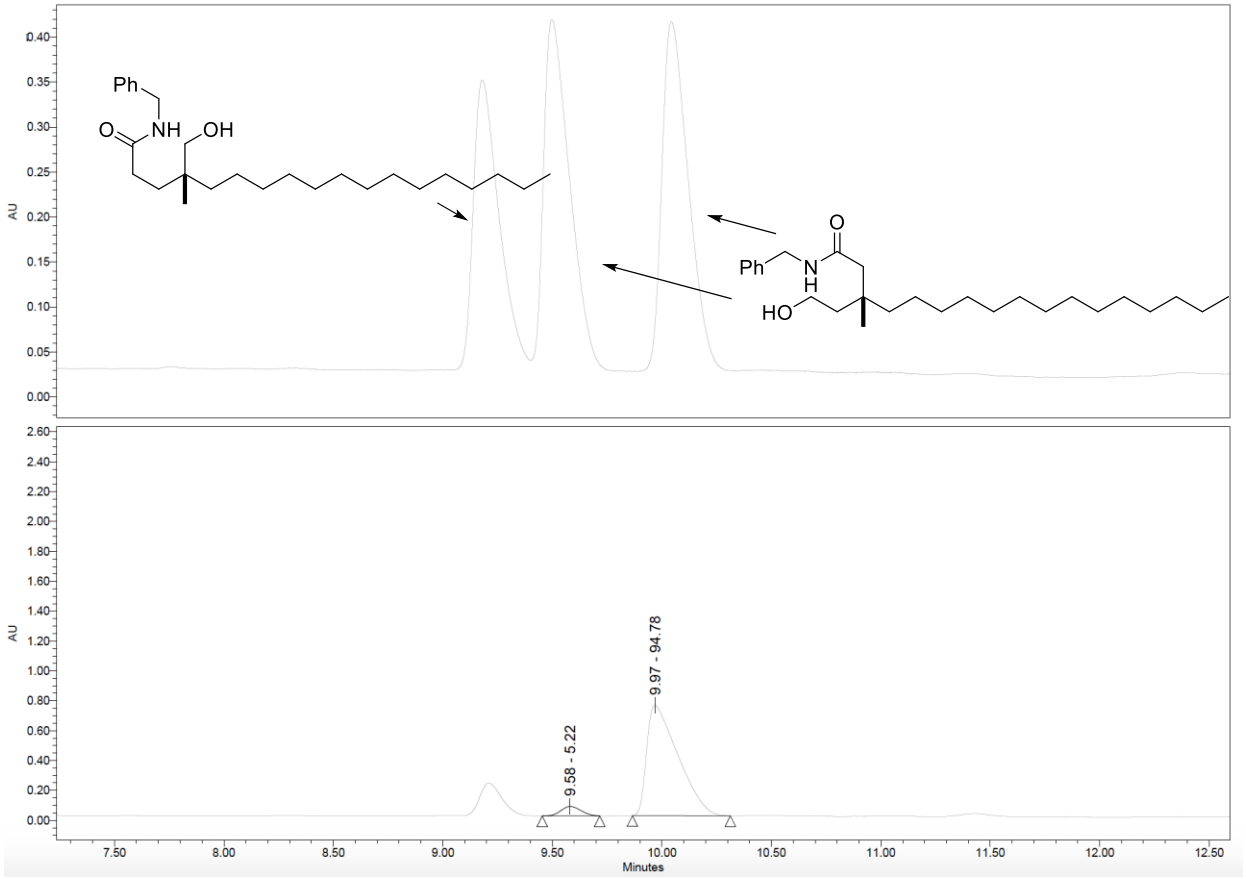
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 2.31 – 2.21 (m, 2H, COC*H*$_2$), 2.07 (d, *J* = 17.9 Hz, 1H, COC*H*$_A$H$_B$), 1.99 (d, *J* = 17.9 Hz, 1H, COCH$_A$*H*$_B$), 1.85 – 1.67 (m, 2H, C*H*$_2$), 1.43 – 1.18 (s, 26H, 13C*H*$_2$), 1.03 (s, 3H, CC*H*$_3$), 0.87 (t, *J* = 6.8 Hz, 2H, CH_2C*H*$_3$).

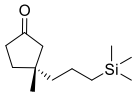
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 220.3, 52.4, 42.0, 39.6, 36.9, 35.4, 32.1, 30.5, 29.8, 29.8 (5C), 29.8, 29.5, 25.2, 24.9, 22.8, 14.3.

HRMS (CI^+) $[C_{20}H_{38}O]^+$ predicted 295.2987, found 295.2987 (Δ 3.32 ppm).

IR υ_{max} (liq): 2980, 2957, 2922, 2853, 1742, 1464, 1152, 721.

$[\alpha]_{589}^{25}$ = +25.5 (*c* 1.09, $CHCl_3$)





(S)-3-methyl-3-(3-(trimethylsilyl)propyl)cyclopentan-1-one **9**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) allyltrimethylsilane$_{(l)}$ (159 µl, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-methyl-2-cyclopentenone (40 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/EtOAc = 92:8] to afford pale yellow oil of 3-methyl-3-(3-(trimethylsilyl)propyl)cyclopentan-1-one (58.5 mg, 69%).

The enantiomeric excess of the product was determined by chiral HPLC after two steps derivatisation (**General procedure D**).

HPLC analysis indicated an enantiomeric excess of 90% [Chiralpak® ID; flow: 1 mL/min; hexane/i-PrOH = 92:8; λ = 210 nm; major enantiomer, t_R = 18.5 min; minor enantiomer, t_R = 20.7 min].

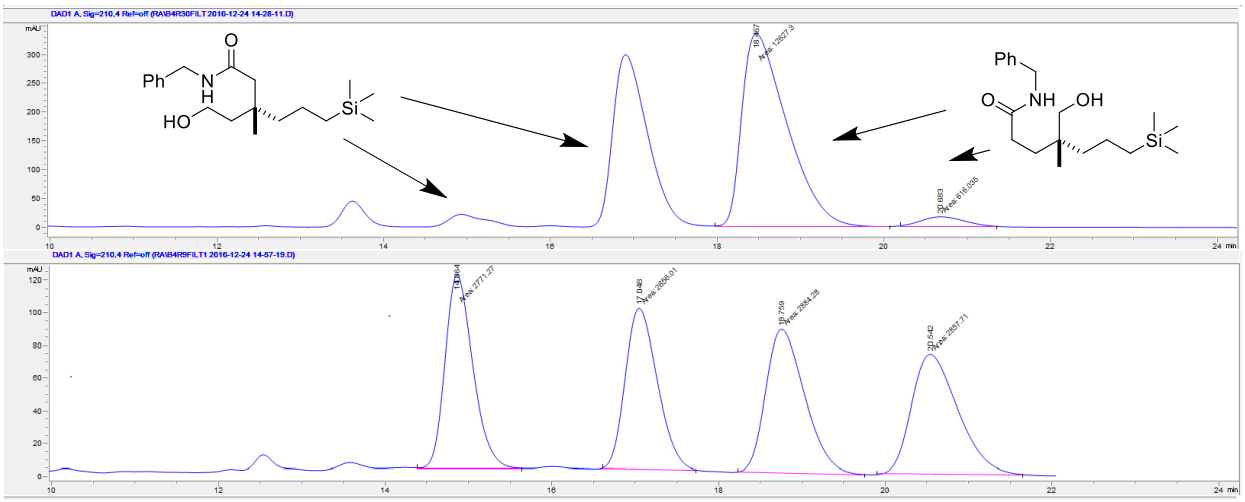
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 2.33 – 2.20 (m, 2H, COCH_2), 2.10 – 1.93 (m, 2H, COCH_2), 1.84 – 1.66 (m, 2H, CH_2), 1.47 – 1.13 (m, 4H,CH_2), 1.02 (s, 3H, CCH_3), 0.50 – 0.41 (m, 2H, CH_2Si), -0.04 (s, 9H,Si(CH_3)$_3$).

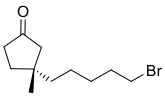
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 220.2, 52.3, 46.1, 39.7, 36.8, 35.4, 25.1, 19.1, 17.5, -1.5 (3C).

HRMS (EI$^+$) $[C_{12}H_{24}OSi]^+$ predicted 212.1596, found 213.1664 (Δ 2.3 ppm).

IR υ_{max} (film): 2953, 2923, 1743, 1247, 861, 837.

$[\alpha]_{589}^{25}$ = +29.2 (*c* 1.0, $CHCl_3$)





(R)-3-(5-bromopentyl)-3-methylcyclopentan-1-one **10**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) 5-bromopentene$_{(l)}$ (118 µl, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-methyl-2-cyclopentenone (40 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/EtOAc = 95:5] to afford colourless oil of 3-(5-bromopentyl)-3-methylcyclopentan-1-one (65.3 mg, 66%).

HPLC analysis indicated an enantiomeric excess of 86% [Chiralpak® AY-H; flow: 1 mL/min; hexane/i-PrOH = 95:5; λ = 210 nm; major enantiomer (+)-(*R*)- 3-(5-bromopentyl)-3-methylcyclopentan-1-one, t_R = 12.1 min; minor enantiomer (–)-(*S*)- 3-(5-bromopentyl)-3-methylcyclopentan-1-one, t_R = 13.7 min].

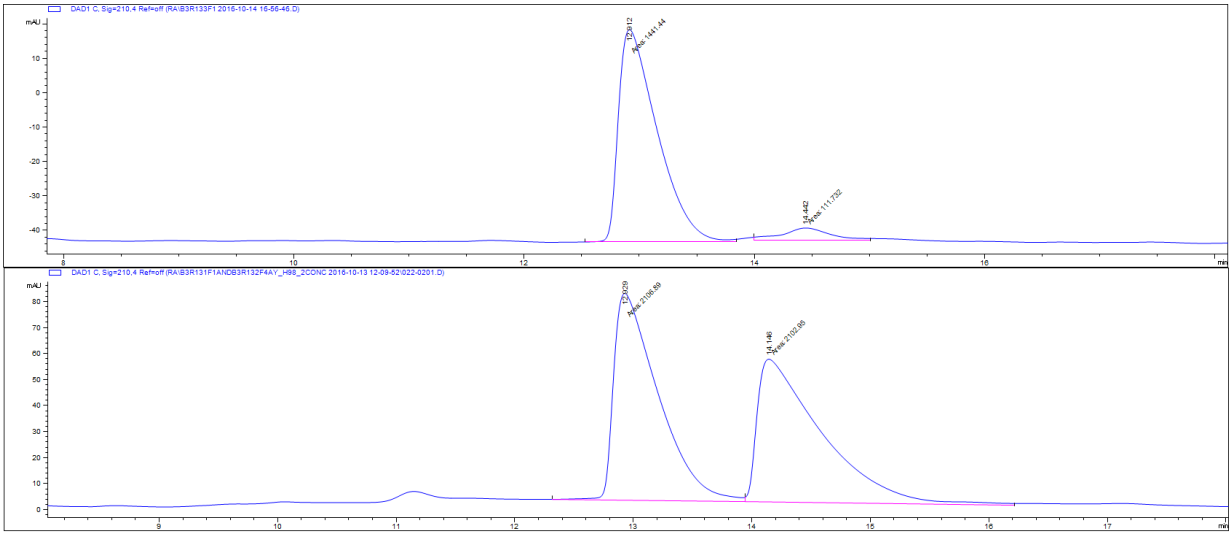
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 3.38 (t, *J* = 6.8 Hz, 2H, C*H*$_2$Br), 2.30 – 2.17 (m, 2H, COC*H*$_2$), 2.09 – 1.98 (m, 2H, COC*H*$_2$), 1.91 – 1.79 (m, 2H, C*H*$_2$), 1.79 – 1.69 (m, 2H, C*H*$_2$), 1.48 – 1.37 (m, 2H, C*H*$_2$), 1.42 – 1.34 (m, 2H, C*H*$_2$), 1.38 – 1.18 (m, 2H, C*H*$_2$), 1.02 (s, 3H, C*H*$_3$).

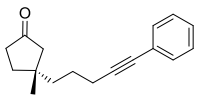
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 219.9, 52.3, 41.7, 39.5, 36.8, 35.3, 33.9, 32.8, 28.9, 25.1, 24.1.

HRMS (ESI^+) $[C_{11}H_{20}O^{79}Br]^+$ predicted 247.0694, found 247.0692 (Δ 0.66 ppm).

IR υ_{max} (liq): 2931, 1738, 1462, 1404, 1255, 1151.

$[\alpha]_{589}^{25}$ = +5.4 (*c* 0.25, $CHCl_3$)





(*R*)-3-methyl-3-(5-phenylpent-4-yn-1-yl)cyclopentan-1-one **11**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) 1-

phenyl-4-penten-1-yne$_{(l)}$ (152 µl, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-methyl-2-cyclopentenone (40 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/EtOAc = 95:5] to afford colourless oil of 3-methyl-3-(5-phenylpent-4-yn-1-yl)cyclopentan-1-one (62.7 mg, 65%).

HPLC analysis indicated an enantiomeric excess of 88% [Chiralpak® IB; flow: 1 mL/min; hexane/i-PrOH = 95:5; λ = 238 nm; minor enantiomer (–)-(*R*)-3-methyl-3-(5-phenylpent-4-yn-1-yl)cyclopentan-1-one, t_R = 15.1 min; major enantiomer (+)-(*S*)-3-methyl-3-(5-phenylpent-4-yn-1-yl)cyclopentan-1-one, t_R = 19.3 min].

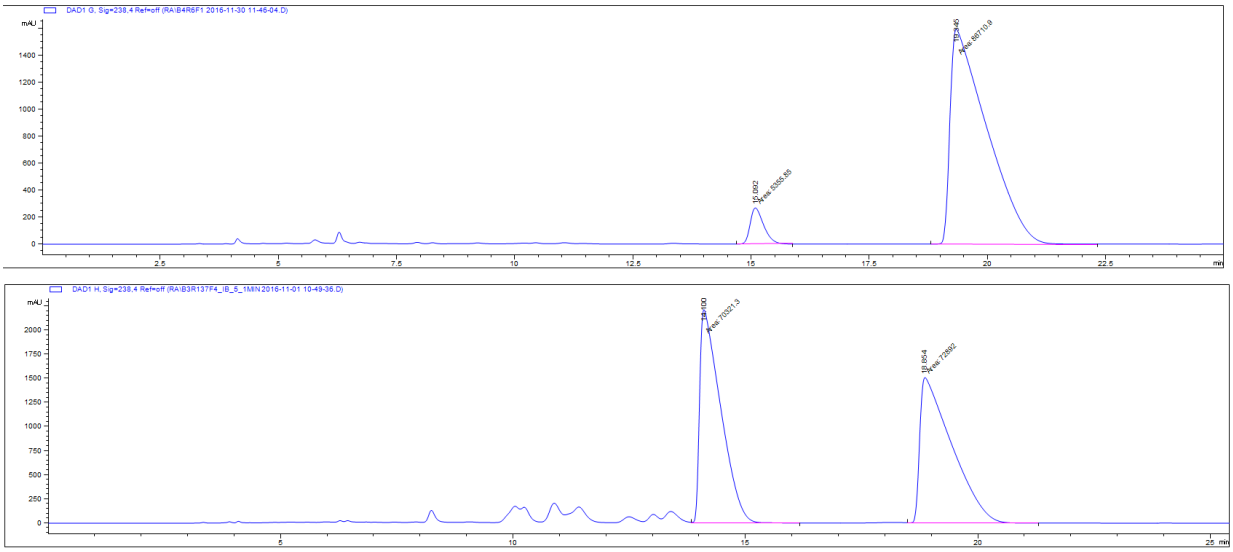
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 – 7.26 (m, 2H, $C_{Ar}H$), 7.20 (dd, *J* = 5.0, 2.0 Hz, 3H, $C_{Ar}H$), 2.41 – 2.29 (m, 2H, C*H*CCPh), 2.26 – 2.15 (m, 2H, C*H*CO), 2.09 – 1.91 (m, 2H, C*H*CO), 1.84 – 1.66 (m, 2H, CH_2), 1.63 – 1.43 (m, 4H, CH_2), 1.00 (s, 3H, CH_3).

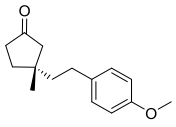
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 219.7, 131.5, 128.2, 127.6, 123.8, 89.8, 81.0, 52.3, 41.1, 39.4, 36.8, 35.2, 25.0, 24.3, 20.0.

HRMS (ESI$^+$) $[C_{17}H_{21}O]^+$ predicted 241.1589, found 241.1587 (Δ 0.88 ppm).

IR υ_{max} (liq): 2953, 1737, 1490, 1156, 756, 692.

$[\alpha]_{589}^{25}$ = +22.8 (*c* 1.00, $CHCl_3$)





(*R*)-3-(4-methoxyphenethyl)-3-methylcyclopentan-1-one **12**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) 1-methoxy-4-vinylbenzene $_{(l)}$ (134 µl, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-methyl-2-cyclopentenone (40 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/EtOAc = 95:5] to afford colourless oil of 3-(4-methoxyphenethyl)-3-methylcyclopentan-1-one (56.6 mg, 61%).

HPLC analysis indicated an enantiomeric excess of 89% [Chiralpak® IB; flow: 1 mL/min; hexane/i-PrOH = 98:2; λ = 210 nm; major enantiomer, t_R = 11.8 min; minor enantiomer, t_R = 13.1 min].

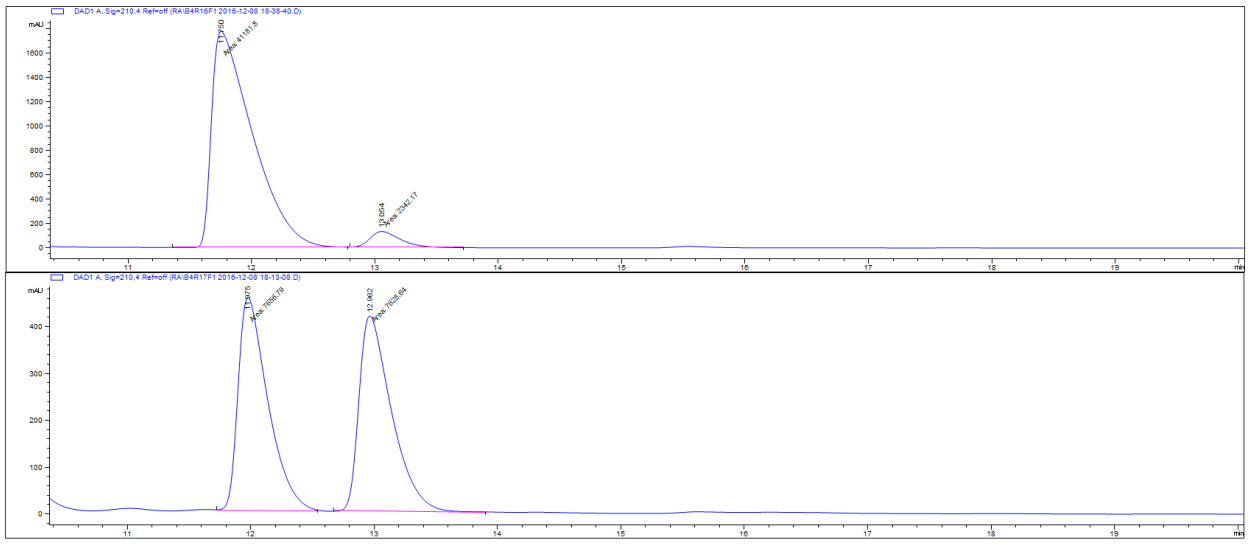
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.16 – 7.08 (m, 2H, $C_{Ar}H$), 6.90 – 6.82 (m, 2H, $C_{Ar}H$), 3.81 (s, 3H, OCH_3), 2.70 – 2.49 (m, 2H, CH_2), 2.39 – 2.24 (m, 2H, CH_2), 2.21 – 2.04 (m, 2H, $COCH_2$), 1.95 – 1.80 (m, 2H, CH_2), 1.77 – 1.68 (m, 2H, CH_2), 1.16 (s, 3H, CCH_3).

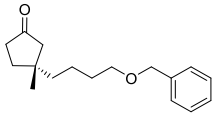
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 219.9, 157.9, 134.5, 129.2 (2C), 114.0 (2C), 55.4, 52.3, 44.3, 39.7, 36.8, 35.4, 30.5, 25.0.

HRMS (EI^+) $[C_{15}H_{20}O_2]^+$ predicted 232.1463, found 232.1463 (Δ -2.6 ppm).

IR υ_{max} (liq): 2954, 1736, 1490, 1511, 1243, 1035, 821.

$[\alpha]_{589}^{25}$ = +21.1 (*c* 1.00, $CHCl_3$)





(*R*)-3-(4-(benzyloxy)butyl)-3-methylcyclopentan-1-one **13**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) ((but-3-en-1-yloxy)methyl)benzene $_{(l)}$ (162 mg, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-methyl-2-cyclopentenone (40 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/EtOAc = 95:5] to afford colourless oil of 3-(4-(benzyloxy)butyl)-3-methylcyclopentan-1-one (85.3 mg, 82%).

HPLC analysis indicated an enantiomeric excess of 89% [Chiralpak® IB; flow: 1 mL/min; hexane/i-PrOH = 95:5; λ = 210 nm; minor enantiomer, t_R = 11.6 min; major enantiomer, t_R = 14.0 min].

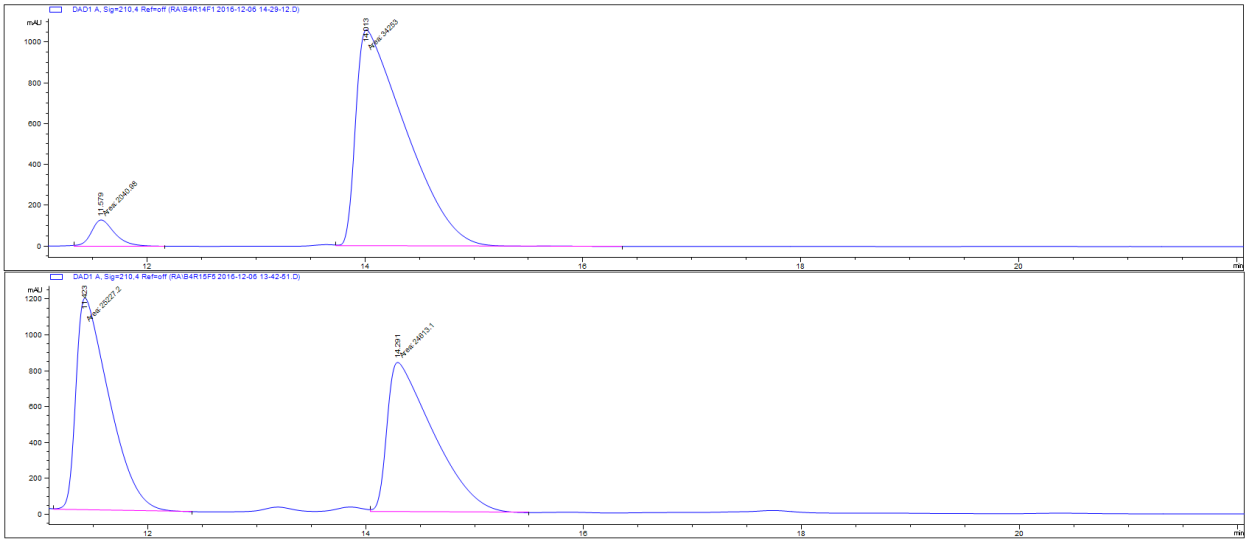
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.31 – 7.14 (m, 5H, $C_{Ar}H$), 4.42 (s, 2H ArCH_2), 3.40 (t, *J* = 6.4 Hz, 2H, OCH_2), 2.29 – 2.11 (m, 2H, COCH_2), 2.03 – 1.87 (m, 2H, COCH_2), 1.76 – 1.62 (m, 2H, CH_2), 1.59 – 1.45 (m, 2H, CH_2), 1.39 – 1.19 (m, 4H, CH_2), 0.96 (s, 3H, CH_3).

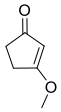
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 220.1, 138.6, 128.4 (2C), 127.7 (2C), 127.6, 73.0, 70.2, 52.3, 41.7, 39.6, 36.8, 35.2, 30.4, 25.0, 21.5.

HRMS (EI$^+$) $[C_{15}H_{20}O_2]^+$ predicted 232.1463, found 232.1463 (Δ -2.6 ppm).

IR υ_{max} (liq): 2934, 2863, 1737, 1163, 735, 697.

$[\alpha]_{589}^{25}$ = +25.3 (*c* 1.0, $CHCl_3$)





3-Methoxycyclopent-2-en-1-one

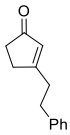
3-methoxycyclopent-2-en-1-one was synthesized based on the procedure reported by Zubaidha.[11]

To a dried round bottom flask with magnetic stirrer, cyclopentane-1,3-dione (25 g, 255 mmol, 1.0 eq.) and MeOH (600 ml, 0.4 M) was added followed by I_2 (1.94 g, 7.6 mmol, 0.03 eq.). The reaction mixture was stirred and heated to 30°C over night. Remove the reaction from the heat. Add $NaSO_4$(s) and leave the reaction to stir for 5 mins. Filter the reaction mixture though small amount of silica gel and wash with EtOAc. Remove the solvent *in vacuo*. Purification by flash column chromatography [SiO_2, EtOAc] and recrystallisation in Et_2O resulted in 3-methoxycyclopent-2-en-1-one as white solid (7.57 g, 26%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 5.30 – 5.21 (m, 1H, C=C*H*), 3.78 (s, 3H, CH_3), 2.60 – 2.52 (m, 2H, CH_2), 2.45 – 2.36 (m, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 206.0, 191.3, 104.5, 58.8, 34.2, 28.3.

Data was consistent with previously reported values.[11]



3-Phenethylcyclopent-2-en-1-one

3-phenethylcyclopent-2-en-1-one was synthesized based on the procedure reported by Buchwald.[12]

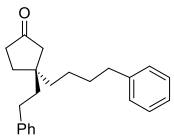
To a dried multi-neck round bottom flask with a condenser attached, $Mg_{(s)}$ (865 mg, 36 mmol, 2.0 eq.), $I_{2(s)}$ (1 crystal) and THF (8 ml) was stirred at 40 ˚C for 30 mins. Then 1-bromo-2-phenylethane (4.9 ml, 35.6 mmol, 2.0 eq.) in THF (10 ml) was added and the stirring mixture was heated to reflux (70 ˚C) for 5 h.

To a separate dried round bottom flask containing 3-methoxycyclopent-2-en-1-one (2.0 g, 17.8 mmol, 1.0 eq.) in THF (18 ml), the reaction of premade Grignard reagent at rt was added dropwise. The suspension was stirred at rt for 16 h. Then distilled H_2O (10 ml), $HCl_{(aq.)}$ (2 M, *ca.* 10 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography [SiO_2, hexane/EtOAc = 10:1 to 5:1] to afford 3-phenethylcyclopent-2-en-1-one as a yellow viscous oil which turned to soft solid upon standing (2.88 g, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.23 – 7.14 (m, 2H, 2$C_{Ar}H$), 7.14 – 7.05 (m, 3H, 3$C_{Ar}H$), 5.91 – 5.76 (m, 1H, C=C*H*), 2.88 – 2.74 (m, 2H, CH_2), 2.71 – 2.56 (m, 2H, CH_2), 2.55 – 2.42 (m, 2H, CH_2), 2.35 – 2.20 (m, 2H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 209.7, 181.7, 140.4, 129.6, 128.4 (2C), 128.0 (2C), 126.2, 35.1, 34.8, 33.1, 31.5.

Data was consistent with previously reported values.[12]



(*S*)-3-phenethyl-3-(4-phenylbutyl)cyclopentan-1-one **14**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) 4-phenyl-1-butene$_{(l)}$ (150 mg, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-

phenethylcyclopent-2-en-1-one (73 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/Et_2O = 95:5] to afford colourless oil of 3-phenethyl-3-(4-phenylbutyl)cyclopentan-1-one (85.1 mg, 66%).

SFC analysis indicated an enantiomeric excess of 87% [Chiralpak® IA-3; 1500 psi, 30 °C, flow: 1.5 mL/min; 1% to 30% MeOH in 8 min; λ = 210 nm; minor enantiomer, t_R = 3.82 min; major enantiomer, t_R = 4.58 min].

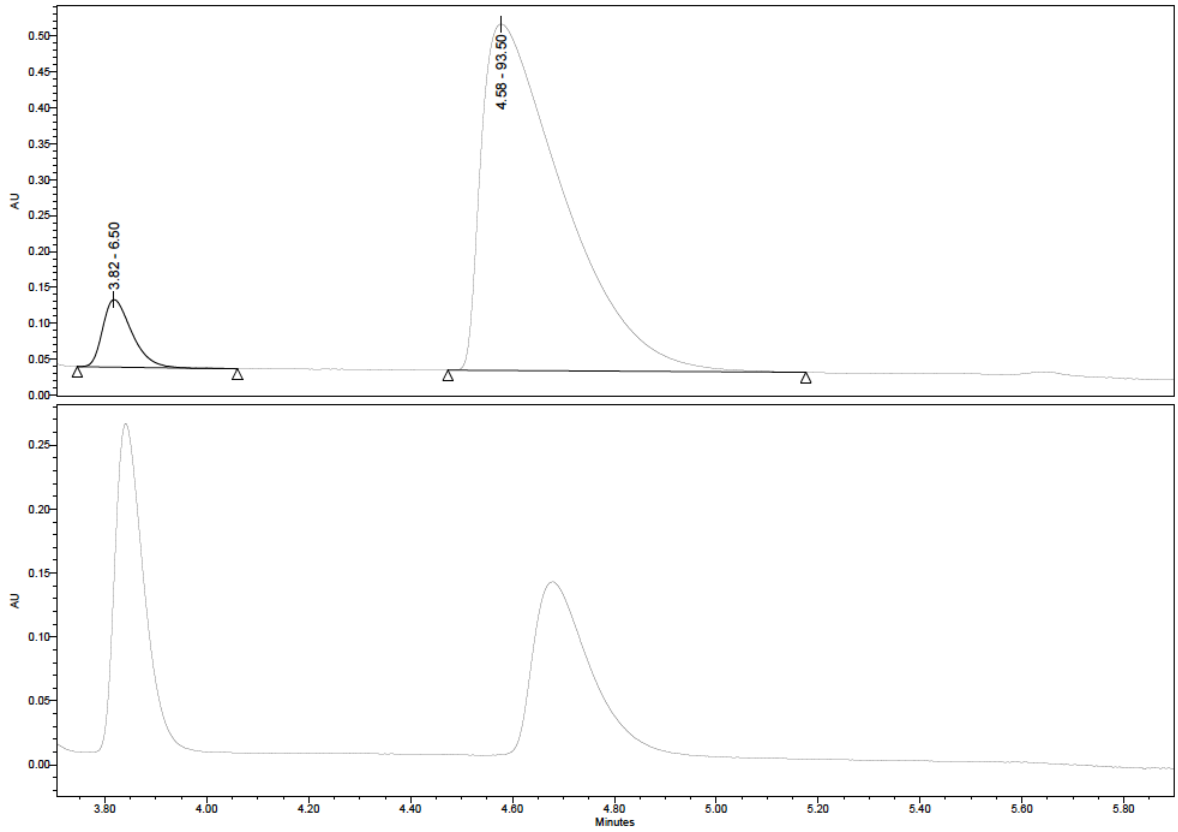
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.25 – 7.17 (m, 4H, $4C_{Ar}H$), 7.16 – 7.08 (m, 4H, $4C_{Ar}H$), 7.06 – 7.00 (m, 2H,$2C_{Ar}H$), 2.58 (dd, *J* = 8.5, 6.8 Hz, 2H, CH_2), 2.55 – 2.34 (m, 2H, CH_2), 2.21 (t, *J* = 8.0 Hz, 2H, $COCH_2CH_2$), 2.05 (s, 2H, $COCH_2C$), 1.78 (t, *J* = 8.0 Hz, 2H, $COCH_2CH_2$), 1.66 – 1.53 (m, 4H, $2CH_2$), 1.48 – 1.16 (m, 4H, $2CH_2$).

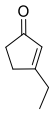
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 219.8, 142.4, 142.4, 128.6 (2C), 128.5 (2C), 128.5 (2C), 128.3 (2C), 126.0, 125.9, 51.2, 42.6, 40.1, 37.4, 36.6, 35.9, 33.4, 32.1, 31.0, 23.9.

HRMS ($APCI^+$) $[C_{23}H_{29}O]^+$ predicted 321.22129, found 321.22137 (Δ 0.26 ppm).

IR υ_{max} (liq): 2930, 2858, 2360, 1739, 1454, 1157, 699.

$[\alpha]_{589}^{25}$ = +2.8 (*c* 1.00, $CHCl_3$)





3-Ethylcyclopent-2-en-1-one

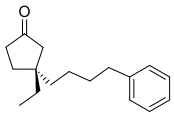
3-Ethylcyclopent-2-en-1-one was synthesized based on the procedure reported by Buchwald.[12]

To a dried round bottom flask containing 3-methoxycyclopent-2-en-1-one (1.5 g, 13.4 mmol, 1.0 eq.) in *t*-BuOMe (26 ml), the reaction of ethylmagnesium bromide (8.9 ml, 26.8 mmol, 2.0 eq., 3 M in Et_2O) was added dropwise at 0 °C. The suspension was stirred at rt for 2 h. Then distilled H_2O (10 ml), $HCl_{(aq.)}$ (2 M, *ca.* 10 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography [SiO_2, pentane/EtOAc = 100:15 to 1:1] to afford 3-ethylcyclopent-2-en-1-one as a viscous oil (252 mg, 17%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 5.94 – 5.87 (m, 1H, C=C*H*), 2.59 – 2.51 (m, 2H, CH_2), 2.43 – 2.33 (m, 4H, 2CH_2), 1.14 (t, *J* = 7.4 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 210.2, 184.6, 128.7, 35.4, 31.5, 26.8, 11.5.

Data was consistent with previously reported values.[12]


(*R*)-3-ethyl-3-(4-phenylbutyl)cyclopentan-1-one **15**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine$_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) 4-phenyl-1-butene$_{(l)}$ (150 mg, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-ethylcyclopent-2-en-1-one (43 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/Et_2O = 5:1] to afford colourless oil of 3-ethyl-3-(4-phenylbutyl)cyclopentan-1-one (64.7 mg, 66%).

SFC analysis indicated an enantiomeric excess of 84% [Chiralpak® IA-3; 1500 psi, 30 °C, flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; λ = 210 nm; minor enantiomer, t_R = 2.63 min; major enantiomer, t_R = 2.85 min].

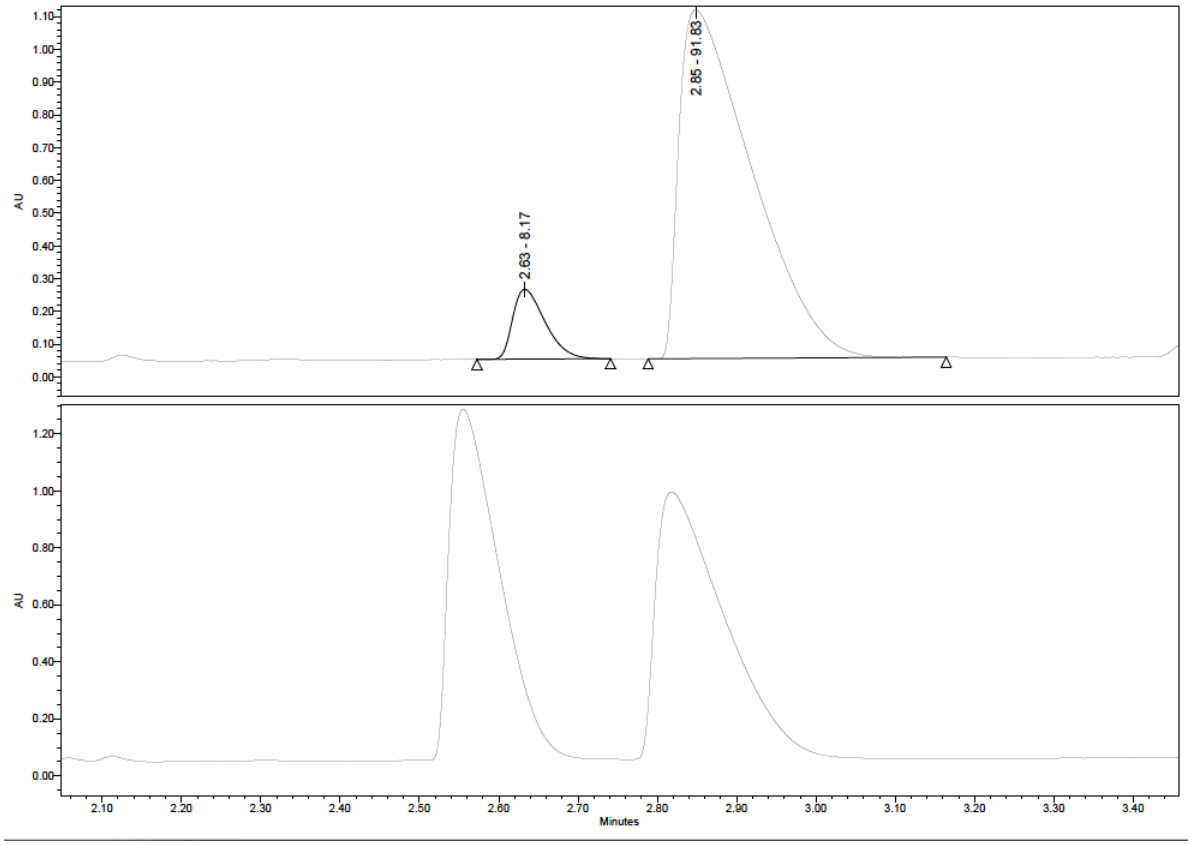
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.24 – 7.15 (m, 2H, 2C$_{Ar}$*H*), 7.14 – 7.06 (m, 3H, 2C$_{Ar}$*H*), 2.59 – 2.48 (m, 2H, ArC*H*$_2$), 2.17 (t, *J* = 8.0 Hz, 2H, COC*H*$_2$CH$_2$), 1.97 (s, 2H, COC*H*$_2$C), 1.77 – 1.62 (m, 2H, COCH$_2$C*H*$_2$), 1.58 – 1.49 (m, 2H, 2C*H*$_2$), 1.42 – 1.12 (m, 6H, 3C*H*$_2$), 0.76 (t, *J* = 7.5 Hz, 3H, C*H*$_3$).

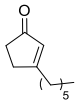
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 220.3, 142.5, 128.4 (2C), 128.4 (2C), 125.8, 50.8, 42.7, 37.1, 36.6, 35.9, 32.8, 32.2, 30.0, 24.0, 8.7.

HRMS (ESI$^+$) $[C_{17}H_{25}O_2]^+$ predicted 245.18999, found 245.19007 (Δ 0.33 ppm).

IR υ_{max} (liq): 3026, 2962, 2931, 2859, 2630, 1740, 1456, 699.

$[\alpha]_{589}^{25}$ = –4.1 (*c* 1.04, $CHCl_3$)





3-Hexylcyclopent-2-en-1-one

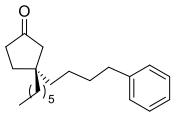
3-Hexylcyclopent-2-en-1-one was synthesized based on the procedure reported by Buchwald.[12]

To a dried round bottom flask containing 3-methoxycyclopent-2-en-1-one (2.0 g, 17.8 mmol, 1.0 eq.) in THF (10 ml), the reaction of hexylmagnesium bromide (44.5 ml, 35.6 mmol, 2.0 eq., 0.8 M in THF) was added dropwise at 0 °C. The suspension was stirred at rt for 2 h. Then distilled H_2O (10 ml), $HCl_{(aq.)}$ (2 M, *ca.* 10 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography [SiO_2, petrol/EtOAc = 1:0 to 10:1] to afford 3-hexylcyclopent-2-en-1-one as a viscous brown oil (1.74 g, 71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 5.96 – 5.91 (m, 1H, C=C*H*), 2.60 – 2.54 (m, 2H, CH_2), 2.44 – 2.36 (m, 4H, 2CH_2), 1.63 – 1.51 (m, 2H, CH_2), 1.39 – 1.13 (m, 6H, 3CH_2), 0.94 – 0.84 (m, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 210.3, 183.3, 35.5, 33.7, 31.7, 31.7, 29.2, 27.2, 22.7, 14.2.

^{1}H and IR spectroscopy was consistent with previously reported values.[13]


(*R*)-3-hexyl-3-(4-phenylbutyl)cyclopentan-1-one **16**

General procedure A: $CuCl_{(s)}$ (4.0 mg, 0.4 mmol, 0.10 eq.), ligand *(R_a)-N*-(di(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine $_{(s)}$ (28.2 mg, 0.04 mmol, 0.11 eq.), Et_2O (2.0 ml), $AgNTf_{2(s)}$ (23.8 mg, 0.06 mmol, 0.15 eq.), DCM (0.40 ml) 4-phenyl-1-butene$_{(l)}$ (150 mg, 1.00 mmol, 2.5 eq.), $ZrHClCp_2$ (206.0 mg, 0.80 mmol, 2.0 eq.), 3-hexylcyclopent-2-en-1-one (70 µl, 0.40 mmol, 1.0 eq.) and $TMSCl_{(l)}$ (0.25 ml, 2.0 mmol, 5.0 eq.)

The crude mixture was treated as describe above and was purified by flash column chromatography [SiO_2, pentane/Et_2O = 100:15] to afford colourless oil of hexyl-3-(4-phenylbutyl)cyclopentan-1-one (65.5 mg, 54%).

SFC analysis indicated an enantiomeric excess of 82% [Chiralpak® ID-3; 1500 psi, 30 °C, flow: 1.5 mL/min; 1% to 30% MeOH in 5 min; λ = 210 nm; minor enantiomer, t_R = 2.61 min; major enantiomer, t_R = 3.17 min].

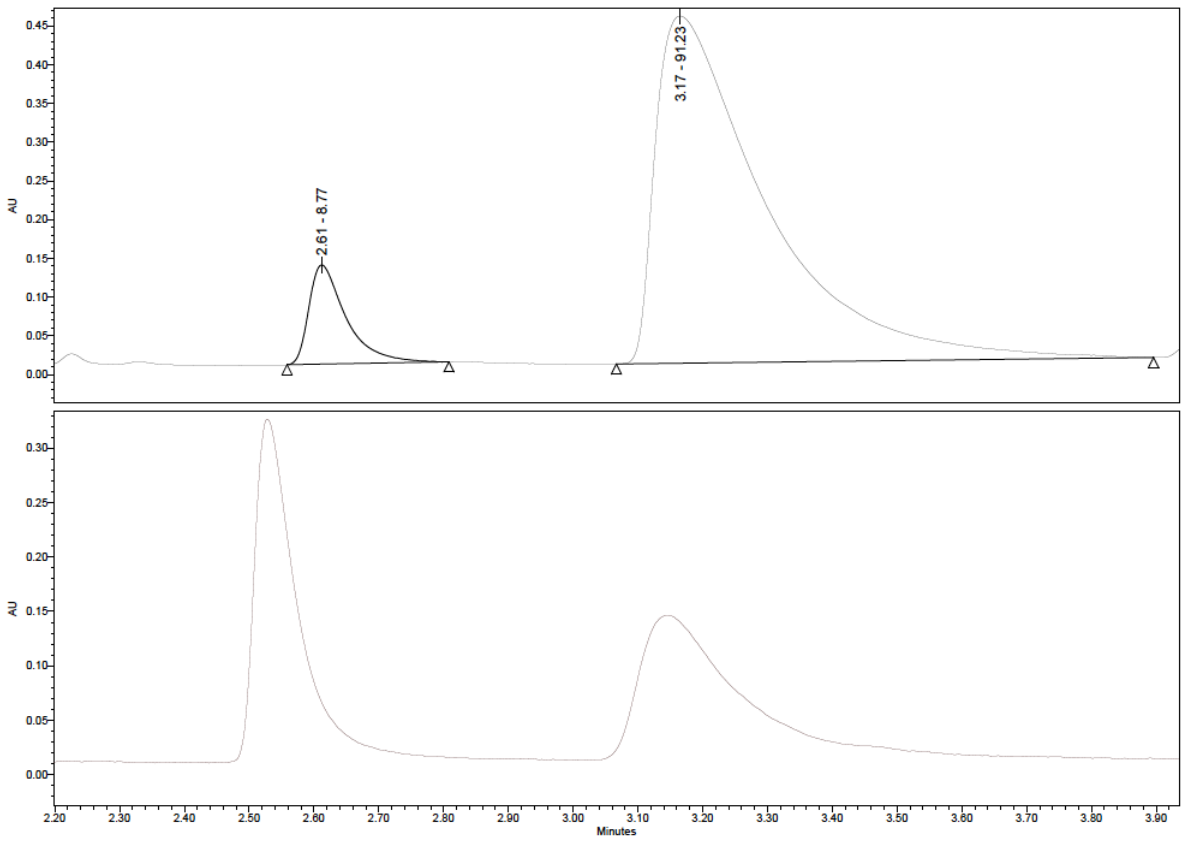
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.25 – 7.16 (m, 2H, $2C_{Ar}H$), 7.13 – 7.06 (m, 3H, $3C_{Ar}H$), 2.59 – 2.50 (m, 2H, $C_{Ar}CH_2$), 2.17 (t, *J* = 8.0 Hz, 2H, $COCH_2CH_2$), 1.98 (s, 2H $COCH_2C$), 1.75 – 1.65 (m, 2H, $COCH_2CH_2$), 1.60 – 1.48 (m, 2H, CH_2), 1.41 – 0.97 (m, 14H, $7CH_2$), 0.88 – 0.76 (m, 3H, CH_3).

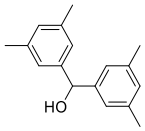
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 220.5, 142.6, 128.5 (2C), 128.4 (2C), 125.8, 51.3, 42.5, 37.8, 37.7, 36.6, 35.9, 33.4, 32.2, 31.9, 30.1, 24.3, 24.0, 22.8, 14.2.

HRMS ($APCI^+$) $[C_{21}H_{33}O]^+$ predicted 301.25259, found 301.25259 (Δ 1.53 ppm).

IR υ_{max} (liq): 2927, 2857, 2360, 1740, 1455, 699.

$[\alpha]_{589}^{25}$ = –3.1 (*c* 1.08, $CHCl_3$)





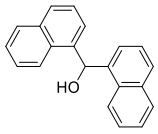
Bis(3,5-dimethylphenyl)methanol

To a dried multi-neck round bottom flask with a condenser attached, $Mg_{(s)}$ (948 mg, 39 mmol, 1.8 eq.), $I_{2(s)}$ (1 crystal) and THF (5 ml) was stirred at 40 ˚C for 30 mins. Then 1-bromo-3,5-dimethylbenzene (4.28 ml, 31.5 mmol, 1.49 eq.) in THF (10 ml) was added and the stirring mixture was heated to reflux (70 ˚C) for 5 h. The mixture was cooled to rt and 3,5-dimethylbenzaldehyde (2.84 g, 21.1 mmol, 1.0 eq.) in THF (15 ml) was added and the condenser was removed. The suspension was stirred at rt for 16 h. Then distilled H_2O (10 ml), $HCl_{(aq.)}$ (2 M, *ca.* 5 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo* to afford bis(3,5-dimethylphenyl)methanol as a white solid (5.02 g, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.03 (br s, 4H, *o*-$C_{Ar}H$), 6.90 (br s, 2H, *p*-$C_{Ar}H$), 5.70 (s, 1H, $CHAr_2$), 2.30 (s, 12H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 144.0 (2C), 138.1 (4C), 129.3 (2C), 124.4 (4C), 76.5 , 21.5 (4C).

Data was consistent with previously reported values.[14]



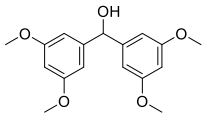
Di(naphthalen-1-yl)methanol

To a dried multi-neck round bottom flask with a condenser attached, $Mg_{(s)}$ (948 mg, 39 mmol, 1.3 eq.), $I_{2(s)}$ (1 crystal) and THF (5 ml) was stirred at 40 ˚C for 30 mins. Then 1-bromonaphthalene (4.40 ml, 31.5 mmol, 1.05 eq.) in THF (10 ml) was added and the stirring mixture was heated to reflux (70 ˚C) for 5 h. The mixture was cooled to rt and 1-naphthaldehyde (4.69 g, 29.9 mmol, 1.0 eq.) in THF (15 ml) was added and the condenser was removed. The suspension was stirred at rt for 16 h. Then distilled H_2O (10 ml), $HCl_{(aq.)}$ (2 M, *ca.* 5 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo* to afford di(naphthalen-1-yl)methanol as a white solid with minor impurity (9.19 g, quantitative yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.10 – 8.03 (m, 2H,$C_{Ar}H$), 7.92 (dd, *J* = 7.7, 1.7 Hz, 2H, $C_{Ar}H$), 7.84 (d, *J* = 8.0 Hz, 2H, $C_{Ar}H$), 7.55 – 7.37 (m, 8H, $C_{Ar}H$), 7.33 (br s, 1H, OC*H*), 2.40 (br s, 1H, O*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 138.5 (2C), 134.0 (2C), 131.2 (2C), 129.0 (2C), 128.7 (2C), 126.6 (2C), 125.9 (2C), 125.6 (2C), 125.1 (2C), 123.8 (2C), 69.8.

Data was consistent with previously reported values.[15]



Bis(3,5-dimethoxyphenyl)methanol

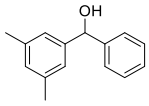
To a dried multi-neck round bottom flask with a condenser attached, $Mg_{(s)}$ (583 mg, 24.3 mmol, 1.8 eq.), $I_{2(s)}$ (1 crystal) and THF (4 ml) was stirred at reflux for 30 mins until the suspension decolourised. Heating was halted before 1-bromo-3,5-dimethoxybenzene (4.34 ml, 20.0 mmol, 1.50 eq.) was added dropwise and the stirring mixture was heated to reflux (70 ˚C) for 3.5 h. The mixture was cooled to rt. To a stirring solution of 3,5-dimethoxybenzaldehyde (2.21 g, 13.3 mmol, 1.0 eq.) in THF (13 ml), the organomagnesium solution was added by syringe at 0 ˚C. The suspension was stirred at rt for 16 h. Then distilled H_2O (10 ml), $HCl_{(aq.)}$ (2 M, *ca.* 5 ml) and

Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_{4(s)}$ and the solvent was removed *in vacuo* to afford bis(3,5-dimethoxyphenyl)methanol as a white solid (3.28 g, 54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 6.55 (d, *J* = 2.2 Hz, 4H, $4C_{Ar}H$), 6.36 (t, *J* = 2.3 Hz, 2H, $2C_{Ar}H$), 5.68 (s, 1H, C*H*), 3.77 (s, 12H, $4CH_3$), 2.18 (s, br, 1H, O*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 161.0 (4C), 146.1 (2C), 104.6 (4C), 99.6 (2C), 76.4, 55.5 (4C).

Data was consistent with previously reported values.[16]



(3,5-Dimethylphenyl)(phenyl)methanol

To a dried multi-neck round bottom flask with a condenser attached, $Mg_{(s)}$ (94.8 mg, 3.9 mmol, 1.8 eq.), $I_{2(s)}$ (1 crystal) and THF (1 ml) was stirred at reflux for 30 mins until the suspension decolourised. Heating was halted before 1-bromo-3,5-dimethybenzene (0.57 ml, 4.3 mmol, 1.4 eq.) was added dropwise and the stirring mixture was heated to reflux (70 ˚C) for 3.5 h. The mixture was cooled to rt. To a stirring solution of benzaldehyde (305 µl, 3.0 mmol, 1.0 eq.) in THF (8 ml), the organomagnesium solution was added by syringe at 0 ˚C. The suspension was stirred at rt for 16 h. Then distilled H_2O (10 ml), $HCl_{(aq.)}$ (2 M, *ca.* 5 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography [SiO_2, pentane/EtOAc = 1:0 to 1:1] to afford (3,5-dimethylphenyl)(phenyl)methanol as a yellow viscous oil (512 mg, 80%).

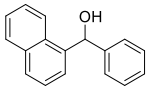
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.44 – 7.40 (m, 2H, $2C_{Ar}H$), 7.39 – 7.34 (m, 2H, $2C_{Ar}H$), 7.31 – 7.27 (m, 1H, $C_{Ar}H$), 7.04 – 7.00 (m, 2H, $2C_{Ar}H$), 6.96 – 6.91 (m, 1H, $C_{Ar}H$), 5.80 (s, 1H, C*H*), 2.32 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.20 (s, br, 1H, O*H*).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 144.1, 143.9, 138.2 (2C), 129.4, 128.6 (2C), 127.6, 126.6 (2C), 124.5 (2C), 76.5, 21.5 (2C).

HRMS ($APCI^+$) $[C_{15}H_{15}O]^+$ predicted 211.11174, found 211.11176 (Δ 0.06 ppm).

IR υ_{max} (film): 3347 (br), 2918, 1602, 701.

^{1}H NMR was consistent with previously reported values.[17]



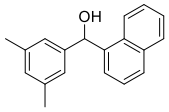
Naphthalen-1-yl(phenyl)methanol

To a dried multi-neck round bottom flask with a condenser attached, $Mg_{(s)}$ (1.30 g, 54.0 mmol, 1.8 eq.), $I_{2(s)}$ (1 crystal) and THF (30 ml) was stirred at reflux for 30 mins until the suspension decolourised. Heating was halted before 1-bromonaphthalene (6.30 ml, 45.0 mmol, 1.5 eq.) was added dropwise and the stirring mixture was heated to reflux (70 ˚C) for 3.5 h. The mixture was cooled to rt. To a stirring solution of benzaldehyde (3.05 ml, 30.0 mmol, 1.0 eq.) in THF (90 ml), the organomagnesium solution was added by syringe at 0 ˚C. The suspension was stirred at rt for 16 h. Then $HCl_{(aq.)}$ (2 M, *ca.* 40 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography [SiO_2, petrol/EtOAc = 1:0 to 85:15] to afford naphthalen-1-yl(phenyl)methanol as a colourless viscous oil (6.53 g, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.10 – 8.04 (m, 1H, $C_{Ar}H$), 7.93 – 7.82 (m, 2H, $2C_{Ar}H$), 7.67 (dt, *J* = 7.2, 1.0 Hz, 1H, $C_{Ar}H$), 7.55 – 7.43 (m, 5H, $5C_{Ar}H$), 7.39 – 7.33 (m, 2H, $2C_{Ar}H$), 7.32 – 7.27 (m, 1H, $C_{Ar}H$), 6.58 (s, 1H, C*H*), 2.33 (s, br, 1H, O*H*).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 143.3, 139.0, 134.1, 130.9, 128.9, 128.7 (2C), 128.7, 127.8 (2C), 127.2, 126.3, 125.8, 125.5, 124.8, 124.1, 73.9.

Data was consistent with previously reported values.[18]



(3,5-Dimethylphenyl)(naphthalen-1-yl)methanol

To a dried multi-neck round bottom flask with a condenser attached, $Mg_{(s)}$ (94.8 mg, 3.9 mmol, 1.8 eq.), $I_{2(s)}$ (1 crystal) and THF (1 ml) was stirred at reflux for 30 mins until the suspension decolourised. Heating was halted before 1-bromo-3,5-dimethybenzene (0.57 ml, 4.3 mmol, 1.4 eq.) was added dropwise and the stirring mixture was heated to reflux (70 ˚C) for 3.5 h. The mixture was cooled to rt. To a stirring solution of naphthaldehyde (469 mg, 3.0 mmol, 1.0 eq.) in THF (8 ml), the organomagnesium solution was added by syringe at 0 ˚C. The suspension was stirred at rt for 16 h. Then distilled H_2O (10 ml), $HCl_{(aq.)}$ (2 M, *ca.* 5 ml) and Et_2O were added to

the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography [SiO_2, pentane/EtOAc = 1:0 to 1:1] to afford (3,5-dimethylphenyl)(naphthalen-1-yl)methanol as a colourless solid (615 mg, 78%).

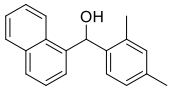
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.12 – 8.04 (m, 1H, $C_{Ar}H$), 7.91 – 7.88 (m, 1H, $C_{Ar}H$), 7.84 (d, *J* = 8.2 Hz, 1H, $C_{Ar}H$), 7.69 (dt, *J* = 7.0, 1.0 Hz, 1H, $C_{Ar}H$), 7.56 – 7.42 (m, 3H, $3C_{Ar}H$), 7.05 (s, 2H, $2C_{Ar}H$), 6.94 (s, 1H, $C_{Ar}H$), 6.53 – 6.49 (m, 1H, C*H*), 2.30 (s, 6H), 2.26 (d, *J* = 3.7 Hz, 1H, O*H*).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 143.2, 139.1, 138.3 (2C), 134.1, 130.9, 129.6, 128.9, 128.5, 126.3, 125.7, 125.5, 125.0 (2C), 124.6, 124.1, 73.8, 21.5 (2C).

HRMS ($APCI^+$) $[C_{19}H_{17}O]^+$ predicted 261.12739, found 261.12735 (Δ –0.16 ppm).

IR υ_{max} (s): 2981, 2360, 2342, 773.

M.P. = 95.0-96.6 ˚C.



(2,4-Dimethylphenyl)(naphthalen-1-yl)methanol

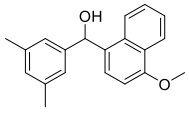
To a dried multi-neck round bottom flask with a condenser attached, $Mg_{(s)}$ (1.30 g, 54.0 mmol, 1.8 eq.), $I_{2(s)}$ (1 crystal) and THF (30 ml) was stirred at reflux for 30 mins until the suspension decolourised. Heating was halted before 1-bromonaphthalene (6.30 ml, 45.0 mmol, 1.5 eq.) was added dropwise and the stirring mixture was heated to reflux (70 ˚C) for 3.5 h. The mixture was cooled to rt. To a stirring solution of 2,4-dimethylbenzaldehyde (4.18 ml, 30.0 mmol, 1.0 eq.) in THF (90 ml), the organomagnesium solution was added by syringe at 0 ˚C. The suspension was stirred at rt for 16 h. Then $HCl_{(aq.)}$ (2 M, *ca.* 40 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography [SiO_2, petrol/EtOAc = 1:0 to 85:15] to afford (2,4-dimethylphenyl)(naphthalen-1-yl)methanol as a colourless residue (4.79 g, 61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.07 – 8.00 (m, 1H, $C_{Ar}H$), 7.93 – 7.88 (m, 1H, $C_{Ar}H$), 7.86 – 7.80 (m, 1H, $C_{Ar}H$), 7.55 – 7.44 (m, 4H, $4C_{Ar}H$), 7.21 (d, *J* = 7.8 Hz, 1H, $C_{Ar}H$), 7.07 (s, 1H, $C_{Ar}H$), 7.00 (d, *J* = 8.0 Hz, 1H, $C_{Ar}H$), 6.74 (s, 1H, C*H*), 2.35 (d, *J* = 1.8 Hz, 6H, $2CH_3$), 2.12 (s, 1H, O*H*).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 138.6, 138.2, 137.5, 135.8, 134.0, 131.6, 131.2, 128.9, 128.5, 127.0 (2C), 126.4, 125.8, 125.5, 124.6, 123.8, 70.1, 21.2, 19.3.

HRMS (ESI^+) $[C_{19}H_{17}O]^+$ predicted 261.12739, found 261.12741 (Δ 0.07 ppm).

IR υ_{max} (s): 2918, 2360, 1655, 1303, 781.



(3,5-Dimethylphenyl)(4-methoxynaphthalen-1-yl)methanol

To a dried multi-neck round bottom flask with a condenser attached, $Mg_{(s)}$ (707 mg, 29.1 mmol, 1.8 eq.), $I_{2(s)}$ (1 crystal) and THF (16 ml) was stirred at reflux for 30 mins until the suspension decolourised. Heating was halted before 1-bromo-3,5-dimethybenzene (5.0 g, 21.1 mmol, 1.3 eq.) was added dropwise and the stirring mixture was heated to reflux (70 ˚C) for 3.5 h. The mixture was cooled to rt. To a stirring solution of 4-methoxy-1-naphthaldehyde (2.18 ml, 16.2 mmol, 1.0 eq.) in THF (40 ml), the organomagnesium solution was added by syringe at 0 ˚C. The suspension was stirred at rt for 16 h. Then distilled H_2O (10 ml), $HCl_{(aq.)}$ (2 M, *ca.* 5 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography [SiO_2, pentane/EtOAc = 1:0 to 8:2] to afford (3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methanol as a colourless oil (985 mg, 21%).

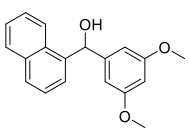
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.58 – 8.51 (m, 1H, $C_{Ar}H$), 8.30 – 8.22 (m, 1H, $C_{Ar}H$), 7.75 – 7.65 (m, 3H, $3C_{Ar}H$), 7.28 – 7.24 (m, 2H,2 $C_{Ar}H$), 7.14 (s, 1H, $C_{Ar}H$), 7.03 (d, *J* = 8.0 Hz, 1H, $C_{Ar}H$), 6.63 (d, *J* = 3.5 Hz, 1H, C*H*), 4.24 (s, 3H, OCH_3), 2.51 (s, 6H, 2CH_3), 2.47 – 2.43 (m, 1H, O*H*).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 155.5, 143.5, 138.1 (2C), 131.9, 131.2, 129.3, 126.8, 126.1, 125.2, 125.1, 124.9 (2C), 123.9, 122.7, 103.1, 73.7, 55.6, 21.5 (2C).

HRMS (ESI^+) $[C_{20}H_{20}O_2{}^{23}Na]^+$ predicted 315.13555, found 315.13565 (Δ 0.32 ppm).

IR υ_{max} (solid): 3287, 2999, 2916, 1585, 767.

M.P. = 103 - 108 ˚C.



(3,5-Dimethoxyphenyl)(naphthalen-1-yl)methanol

To a dried multi-neck round bottom flask with a condenser attached, $Mg_{(s)}$ (1.30 g, 54.0 mmol, 1.8 eq.), $I_{2(s)}$ (1 crystal) and THF (30 ml) was stirred at reflux for 30 mins until the suspension decolourised. Heating was halted before 1-bromonaphthalene (6.30 ml, 45.0 mmol, 1.5 eq.) was added dropwise and the stirring mixture was heated to reflux (70 ˚C) for 3.5 h. The mixture was cooled to rt. To a stirring solution of 3,5-dimethoxybenzaldehyde (4.78 g, 30.0 mmol, 1.0 eq.) in THF (90 ml), the organomagnesium solution was added by syringe at 0 ˚C. The suspension was stirred at rt for 16 h. Then $HCl_{(aq.)}$ (2 M, *ca.* 40 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography [SiO_2, petrol/EtOAc = 1:0 to 85:15] to afford (3,5-dimethoxyphenyl)(naphthalen-1-yl)methanol as a colourless viscous oil (5.05 g, 61%).

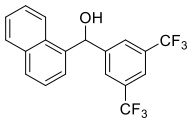
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.09 (d, *J* = 2.5 Hz, 1H, $C_{Ar}H$), 7.90 – 7.85 (m, 1H, $C_{Ar}H$), 7.83 – 7.79 (m, 1H, $C_{Ar}H$), 7.60 (dt, *J* = 7.1, 1.0 Hz, 1H, $C_{Ar}H$), 7.51 – 7.43 (m, 3H, $C_{Ar}H$), 6.59 (d, *J* = 2.4 Hz, 2H, $C2_{Ar}H$), 6.47 (d, *J* = 4.0 Hz, 1H, C*H*), 6.38 (t, *J* = 2.4 Hz, 1H, $C_{Ar}H$), 3.74 (s, 6H, OCH_3), 2.31 (d, *J* = 4.0 Hz, 1H, O*H*).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 161.1 (2C), 145.8, 138.7, 134.1, 131.0, 128.9, 128.7, 126.4, 125.8, 125.5, 124.9, 124.1, 105.3 (2C), 99.6, 73.8, 55.5 (2C).

HRMS (ESI^+) $[C_{19}H_{18}O_3{}^{23}Na]^+$ predicted 317.11482, found 317.11499 (Δ 0.55 ppm).

IR υ_{max} (film): 3421 (br), 2938, 2837, 2360, 1595, 1152, 780.

^{1}H NMR was consistent with previously reported values.[19]



(3,5-Bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methanol

To a stirring solution of 3,5-bis(trifluoromethyl)benzaldehyde (3.40 ml, 20.7 mmol, 1.0 eq.) in THF (21 ml), the premade naphthalen-1-ylmagnesium bromide solution (41 ml, 0.75 M, 31.0 mmol, 1.5 eq.) was added by syringe at 0 ˚C. The suspension was stirred at rt for 16 h. Then $HCl_{(aq.)}$ (2 M, *ca.* 40 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column

chromatography [SiO_2, petrol/EtOAc = 1:0 to 85:15] to afford (3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methanol as a white solid (2.71 g, 35%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.11 – 8.03 (m, 1H, $C_{Ar}H$), 7.95 – 7.85 (m, 4H, $4C_{Ar}H$), 7.81 (s, 1H, $C_{Ar}H$), 7.56 – 7.47 (m, 3H, $3C_{Ar}H$), 7.44 (dd, *J* = 7.2, 1.3 Hz, 1H, $C_{Ar}H$), 6.60 (s, 1H, C*H*), 2.55 (s, 1H, O*H*).

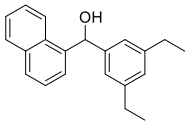
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 145.8, 137.6, 134.4, 131.8 (q, *J* = 33.3 Hz, 2C), 130.7, 129.8, 129.3, 127.0, 127.0 (2C), 126.3, 125.8, 125.5, 123.6, 123.5 (q, *J* = 272.7 Hz, 2C), 121.6 (p, *J* = 3.8 Hz), 73.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ_F: -62.8 (s).

HRMS (ESI^+) $[C_{19}H_{11}OF_6]^+$ predicted 369.07086, found 369.07135 (Δ 1.33 ppm).

IR υ_{max} (s): 2981, 2360, 2342, 1276, 1125, 773.

M.P. = 89.5-94.7 ˚C.



(3,5-Diethylphenyl)(naphthalen-1-yl)methanol

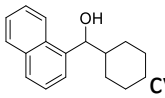
To a stirring solution of 3,5-diethylbenzaldehyde (1.00 g, 6.16 mmol, 1.0 eq.) in THF (6 ml), the premade naphthalen-1-ylmagnesium bromide solution (12.3 ml, 0.75 M, 9.24 mmol, 1.5 eq.) was added by syringe at 0 ˚C. The suspension was stirred at rt for 16 h. Then $HCl_{(aq.)}$ (2 M, *ca.* 40 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography [SiO_2, petrol/EtOAc = 1:0 to 85:15] to afford (3,5-diethylphenyl)(naphthalen-1-yl)methanol as a white solid (1.82 g, quantitative yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.13 – 8.06 (m, 1H, $C_{Ar}H$), 7.91 – 7.83 (m, 1H, $C_{Ar}H$), 7.82 (dt, *J* = 8.2, 1.1 Hz, 1H, $C_{Ar}H$), 7.64 (dt, *J* = 7.2, 1.0 Hz, 1H, $C_{Ar}H$), 7.53 – 7.42 (m, 3H, $3C_{Ar}H$), 7.08 (d, *J* = 1.5 Hz, 2H, $2C_{Ar}H$), 6.97 (d, *J* = 1.8 Hz, 1H, $C_{Ar}H$), 6.52 (d, *J* = 3.9 Hz, 1H C*H*), 2.60 (q, *J* = 7.6 Hz, 4H, $2CH_2$), 2.28 (d, *J* = 3.9 Hz, 1H, O*H*), 1.20 (t, *J* = 7.6 Hz, 6H, $3CH_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 144.7 (2C), 143.3, 139.2, 134.1, 131.0, 128.9, 128.5, 127.0, 126.2, 125.7, 125.5, 124.7, 124.1 (2C), 124.1, 73.9, 29.0 (2C), 15.7 (2C).

HRMS (ESI$^+$) $[C_{21}H_{22}O^{23}Na]^+$ predicted 313.15629, found 313.15631 (Δ 0.08 ppm).

IR υ_{max} (s): 3234 (br), 2964, 2361, 1598, 1456, 782.



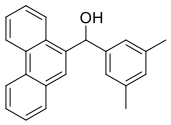
cyclohexyl(naphthalen-1-yl)methanol

To a stirring solution of cyclohexaldehyde (3.50 ml, 30.0 mmol, 1.0 eq.) in THF (52 ml), the premade naphthalen-1-ylmagnesium bromide solution (60 ml, 0.75 M, 45 mmol, 1.5 eq.) was added by syringe at 0 ˚C. The suspension was stirred at rt for 7 d. Then $HCl_{(aq.)}$ (2 M, *ca.* 40 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column chromatography [SiO_2, petrol/EtOAc = 1:0 to 8:2] to afford cyclohexyl(naphthalen-1-yl)methanol as a white solid (3.72 g, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.16 (d, *J* = 8.1 Hz, 1H), 7.90 – 7.85 (m, 1H, $C_{Ar}H$), 7.78 (d, *J* = 8.1, 1.0 Hz, 1H, $C_{Ar}H$), 7.59 (d, *J* = 7.1 Hz, 1H, $C_{Ar}H$), 7.55 – 7.43 (m, 3H, $C_{Ar}H$), 5.20 (dd, *J* = 6.6, 3.1 Hz, 1H, C*H*OH), 2.02 – 1.95 (m, 1H, CH_aH$_b$), 1.95 – 1.87 (m, 2H, OH, CHCH$_2$), 1.81 – 1.73 (m, 1H, CH_aH$_b$), 1.70 – 1.60 (m, 2H, CH_aH$_b$, CH_aH$_b$), 1.46 – 1.38 (m, 1H, CH_aH$_b$), 1.24 – 1.12 (m, 5H, 5CH$_a$$H_b$).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 139.7, 134.0, 131.0, 129.0, 128.0, 125.9, 125.6, 125.4, 124.3, 123.8, 76.3, 44.5, 30.5, 28.4, 26.6, 26.5, 26.2.

Data was consistent with previously reported values.[20]



(3,5-Dimethylphenyl)(phenanthren-9-yl)methanol

To a stirring solution of phenanthren-9-al (1.32 mg, 6.40 mmol, 1.0 eq.) in THF (29 ml), the premade 3,5-dimethylphenylmagnesium bromide solution (16.6 ml, 0.50 M, 8.32 mmol, 1.3 eq.) was added by syringe at 0 ˚C. The suspension was stirred at rt for 2 d. Then $HCl_{(aq.)}$ (2 M, *ca.* 40 ml) and Et_2O were added to the suspension until no effervescence was observed. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by Et_2O three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude mixture was purified by column

chromatography [SiO_2, petrol/EtOAc = 1:0 to 8:2] to afford (3,5-dimethylphenyl)(phenanthren-9-yl)methanol as a white solid (1.73 g, 87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.79 – 8.68 (m, 2H,), 8.08 – 8.02 (m, 1H, $C_{Ar}H$), 8.03 (s, 1H, $C_{Ar}H$), 7.99 – 7.93 (m, 1H, $C_{Ar}H$), 7.75 – 7.59 (m, 3H, $C_{Ar}H$), 7.60 – 7.51 (m, 1H, $C_{Ar}H$), 7.09 (d, *J* = 1.5 Hz, 2H, $C_{Ar}H$), 6.95 (s, 1H, $C_{Ar}H$), 6.49 (s, 1H, C*H*), 2.36 (s, 6H, O*H*), 2.30 (s, 6H, 2CH_3).

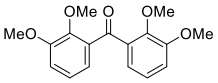
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 154.7, 144.4, 137.9 (2C), 132.5, 131.6, 128.6, 126.6, 126.1, 125.7 (2C), 125.3, 124.8, 123.4, 122.7, 103.5, 59.8, 55.6, 46.8, 23.5, 23.5, 21.5 (2C).

HRMS ($APCI^+$) $[C_{23}H_{19}O]^+$ predicted 311.14304, found 311.14297 (Δ –0.22 ppm).

IR υ_{max} (s): 3291 (br), 2918, 1586, 726.

M.P. = 57 – 60 ˚C.

HRMS (CI^+) $[C_{20}H_{20}NO_2]^+$ predicted 306.1489, found 306.1485 (Δ 1.16 ppm).



Bis(2,3-dimethoxyphenyl)methanone

This procedure has been modified from a procedure developed by Xiao and co-worker.[21] To a dried round bottom flask fitted with a condenser, Pd (231 mg,), and DPPP (165 mg) were add. Flush the flask with $Ar_{(g)}$ and add $AgNO_3$ (1.70 g,), (2,3-dimethoxyphenyl)boronic acid (1.81 g,) and dried acetone (30 ml). Purge the flask with CO 6 times then heat the mixture to 40 ˚C. The reaction was stirrer for 24 h before addition of H_2O (50 ml). The reaction mixture was extracted by DCM three times. The combined organic layer was dried with $Na_2SO_{4(s)}$ and filtered through celite. The solvent was removed *in vacuo*. The product was purified by flash column chromatography [SiO_2, pentane/EtOAc, 5:2 then 5:3] gave yellow viscous oil. The oil was dissolved in minimum amount of Et_2O and filtered under reduced pressure to afford white solid of bis(2,3-dimethoxyphenyl)methanone (265 mg, 9%).

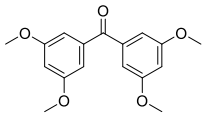
^{1}H NMR (400 MHz, $CDCl_3$) δ_H:7.12 – 6.99 (m, 6H, $C_{Ar}H$), 3.87 (s, 6H, OCH_3), 3.64 (s, 6H, OCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 196.2, 153.0 (2C), 148.0 (2C), 135.5 (2C), 123.7 (2C), 121.3 (2C), 115.3 (2C), 61.5 (2C), 56.1 (2C).

HRMS (ESI^+) $[C_{17}H_{19}O_5]^+$ predicted 303.1227, found 303.1228 (Δ 0.44 ppm).

IR υ_{max} (film): 2933, 2836, 2360, 1594, 1156.

Data was consistent with previously reported values.[21]



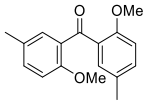
Bis(3,5-dimethoxyphenyl)methanone

In a dried round bottom flask, a mixture of bis(3,5-dimethoxyphenyl)methanol (3.28 g, 10.9 mmol, 1.0 eq.), MnO_2 (28.3 g, 326 mmol, 30.0 eq.) and DCM (18 ml) was stirred vigorously at rt for 72 h. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo* to afford bis(3,5-dimethoxyphenyl)methanoneas an off-white solid (3.06 g, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 6.93 (d, *J* = 2.4 Hz, 4H, $C_{Ar}H$), 6.66 (t, *J* = 2.3 Hz, 2H, $C_{Ar}H$), 3.82 (s, 12H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 196.1, 160.6 (4C), 139.5 (2C), 108.0 (4C), 105.0 (2C), 55.7 (4C).

Data was consistent with previously reported values.[16]



Bis(2-methoxy-5-methylphenyl)methanone

This procedure has been modified from a procedure developed by Xiao and co-worker.[21] To a dried round bottom flask fitted with a condenser, Pd (578 mg, 0.50 mmol, 0.05 eq.), and DPPP (412 mg, 1.0 mmol, 0.10 eq.) were add. Flush the flask with $Ar_{(g)}$ and add $AgNO_3$ (1.70 g, 10 mmol, 1.0 eq.), (2-methoxy-5-methylphenyl)boronic acid (1.66 g, 10 mmol, 1.0 eq.) and dried acetone (30 ml). Purge the flask with CO 6 times then heat the mixture to 40 ˚C. The reaction was stirrer for 24 h before addition of H_2O (50 ml). The reaction mixture was extracted by DCM three times. The combined organic layer was dried with $Na_2SO_{4(s)}$ and filtered through celite. The solvent was removed *in vacuo*. The product was purified by flash column chromatography [SiO_2, pentane/EtOAc, 85:15] gave yellow viscous oil. The oil was frozen and dried under high vacuum to afford white solid of bis(2-methoxy-5-methylphenyl)methanone (286 mg, 11%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.24 – 7.18 (m, 2H, $C_{Ar}H$), 7.14 – 7.06 (m, 2H, $C_{Ar}H$), 6.69 (d, *J* = 8.3 Hz, 2H, $C_{Ar}H$), 3.50 (s, 3H, OCH_3), 2.18 (s, 3H, CH_3).

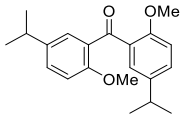
^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 195.5, 156.3 (2C), 133.0 (2C), 130.5 (2C), 130.0 (2C), 129.5(2C), 111.5 (2C), 55.8 (2C), 20.3 (2C).

HRMS (ESI^+) $[C_{17}H_{19}O_3]^+$ predicted 271.1329, found 271.1331 (Δ 0.68 ppm).

IR υ_{max} (film): 3650, 3318, 2980, 1979, 1597.

M.P. = 57.4-61.0 ˚C.

Melting point was consistent with previously reported values.[22]



Bis(5-isopropyl-2-methoxyphenyl)methanone

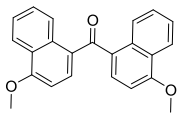
This procedure has been modified from a procedure developed by Xiao and co-worker.[21] To a dried round bottom flask fitted with a condenser, Pd (578 mg, 0.50 mmol, 0.05 eq.), and DPPP (412 mg, 1.0 mmol, 0.10 eq.) were add. Flush the flask with $Ar_{(g)}$ and add $AgNO_3$ (1.70 g, 10 mmol, 1.0 eq.), (2-methoxy-5-isopropylphenyl)boronic acid (1.94 g, 10 mmol, 1.0 eq.) and dried acetone (30 ml). Purge the flask with CO 6 times then heat the mixture to 40 ˚C. The reaction was stirrer for 24 h before addition of H_2O (50 ml). The reaction mixture was extracted by DCM three times. The combined organic layer was dried with $Na_2SO_{4(s)}$ and filtered through celite. The solvent was removed *in vacuo*. The product was purified by flash column chromatography [SiO_2, pentane/EtOAc, 9:1 then 85:15] gave yellow viscous oil of bis(5-isopropyl-2-methoxyphenyl)methanone (372 mg, 11%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.39 (d, *J* = 2.4 Hz, 2H, $C_{Ar}H$), 7.30 (dd, *J* = 2.4, 8.4 Hz, 2H, $C_{Ar}H$), 6.86 (d, *J* = 8.4 Hz, 2H, $C_{Ar}H$), 3.64 (s, 3H, OCH_3), 2.89 (hept, *J* = 6.9 Hz, 1H, C*H*), 1.24 (d, *J* = 6.9 Hz, $CHCH_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 195.8, 156.6 (2C), 140.6 (2C), 130.3(2C), 130.0(2C), 128.3(2C), 111.6 (2C), 55.9 (2C), 33.2 (2C), 24.1 (4C).

HRMS (ESI^+) $[C_{21}H_{27}O_3]^+$ predicted 327.1966, found 327.1953 (Δ -3.84 ppm).

IR υ_{max} (film): 2959, 2870, 1650, 1487, 1255.



Bis(4-methoxynaphthalen-1-yl)methanone

To a dried round bottom flask with a condenser attached, $Mg_{(s)}$ (1.37 g, 56.0 mmol, 10 eq.), $I_{2(s)}$ (1 crystal) and THF (3 ml) was stirred at reflux for 10 mins until the suspension decolourised. Heating was halted before 1-bromo-4-methoxynaphthalene (2.00 g, 8.44 mmol, 1.50 eq.) was added dropwise and the stirring mixture was heated to reflux for 6 h. The mixture was cooled to rt. To a stirring solution of 4-methoxynaphthaldehyde (1.05 g, 5.62 mmol, 1.0 eq.) in THF (4 ml), the organomagnesium solution was added dropwise by syringe at 0 ˚C. The suspension

was stirred at rt for 18h. Then $HCl_{(aq.)}$ (2 M, *ca.* 5 ml) and Et_2O were added to the suspension. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by DCM three times. The combined organic layer was dried with anhydrous $MgSO_4$(s) and the solvent was removed *in vacuo*. The crude reaction mixture was used in the next step without further purification.

In a dried round bottom flask, bis(4-methoxynaphthalen-1-yl)methanol as a crude reaction mixture (1.94 g, 5.62 mmol, 1.0 eq.), MnO_2 (14.7 g, 169 mmol, 30.0 eq.) and DCM (11 ml) were added and stirred vigorously at rt for 72 h. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo*. The crude reaction mixture was purified by flash column chromatography [SiO_2, pentane/EtOAc, 95:5 t0 8:2] to give orange solid. Subsequent recrystallisation of the product in EtOAc and Hexane afforded white crystalline solid of bis(4-methoxynaphthalen-1-yl)methanone product (1.41 g, 74% over two steps).

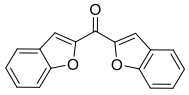
^{1}H NMR (400 MHz, $CDCl_3$) δ_H:8.69 – 8.61 (m, 2H, $C_{Ar}H$), 8.43 – 8.32 (m, 2H, $C_{Ar}H$), 7.65 – 7.49 (m, 6H, $C_{Ar}H$), 6.69 (d, *J* = 8.2 Hz, 2H, $C_{Ar}H$), 4.02 (s, 6H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 198.3, 158.5, 132.9, 132.6, 130.2, 128.3, 126.0, 125.9, 125.8, 122.3, 102.2, 55.8.

HRMS (ESI^+) $[C_{20}H_{28}O_4]^+$ predicted 343.13287, found 343.13293 (Δ -0.19 ppm).

IR υ_{max} (film): 2970, 1669, 1265, 1092.

MP. = 152-154 ˚C.


Di(benzofuran-2-yl)methanone

To a dried round bottom flask with a condenser attached, $Mg_{(s)}$ (822 mg, 33.8 mmol, 10 eq.), $I_{2(s)}$ (1 crystal) and THF (2.5 ml) was stirred at reflux for 10 mins until the suspension decolourised. Heating was halted before 2-bromobenzofuran (0.94 g, 5.08 mmol, 1.50 eq.) was added dropwise and the stirring mixture was heated to reflux for 2.5 h. The mixture was cooled to rt. To a stirring solution of benzofuran-2-carbaldehyde (495 mg, 3.38 mmol, 1.0 eq.) in THF (2 ml), the organomagnesium solution was added dropwise by syringe at 0 ˚C. The suspension was stirred at rt for 20h. Then $HCl_{(aq.)}$ (2 M, *ca.* 5 ml) and Et_2O were added to the suspension. The mixture was partitioned between the aqueous and organic layer. The aqueous layer was extracted by DCM three times. The combined organic layer was dried with anhydrous $MgSO_4$(s)

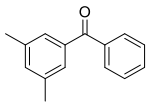
and the solvent was removed *in vacuo*. The crude reaction mixture was used in the next step without further purification.

In a dried round bottom flask, di(benzofuran-2-yl)methanol as a crude reaction mixture (1.00 g, 3.38 mmol, 1.0 eq.), MnO_2 (8.82 g, 101 mmol, 30.0 eq.) and DCM (6 ml) were added and stirred vigorously at rt for 72 h. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo*. The crude reaction mixture was purified by flash column chromatography [SiO_2, pentane/EtOAc, 95:5 t0 8:2] to give orange solid product (275 mg, 31% over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H:8.04 (d, *J* = 1.0 Hz, 2H, C_{Ar}*H*CC=O), 7.82 –7.78 (m, 2H, C_{Ar}*H*), 7.70 – 7.66 (m, 2H, C_{Ar}*H*), 7.56 – 7.51 (m, 2H, C_{Ar}*H*), 7.39 – 7.34 (m, 2H, C_{Ar}*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 171.7, 156.0 (2C), 151.8 (2C), 128.8 (2C), 127.2 (2C), 124.3 (2C), 123.7 (2C), 116.3 (2C), 112.6 (2C).

Data was consistent with previously reported values.[23]



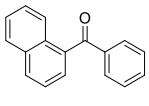
(3,5-Dimethylphenyl)(phenyl)methanone

In a dried round bottom flask, (3,5-dimethylphenyl)(phenyl)methanol (440 mg, 2.07 mmol, 1.0 eq.), MnO_2 (5.40 g, 62.1 mmol, 30.0 eq.) and DCM (9 ml) was stirred vigorously at rt for 4 days. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo* to afford (3,5-dimethylphenyl)(phenyl)methanone as a colourless residue (412 mg, 94%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.83 – 7.77 (m, 2H, 2C_{Ar}*H*), 7.62 – 7.55 (m, 1H, C_{Ar}*H*), 7.48 (dd, *J* = 8.3, 7.0 Hz, 2H, 2C_{Ar}*H*), 7.42 – 7.38 (m, 2H, 2C_{Ar}*H*), 7.26 – 7.20 (m, 1H, C_{Ar}*H*), 2.38 (d, *J* = 0.8 Hz, 6H, 3C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 197.3, 138.1, 138.1 (2C), 137.9, 134.2, 132.4 (2C), 130.2 (2C), 128.3 (2C), 127.9, 21.4 (2C).

Data was consistent with previously reported values.[24]



Naphthalen-1-yl(phenyl)methanone

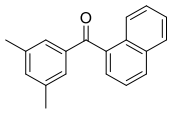
In a dried round bottom flask, naphthalen-1-yl(phenyl)methanol (6.53 g, 27.9 mmol, 1.0 eq.), MnO_2 (48.5 g, 558 mmol, 20.0 eq.) and DCM (100 ml) was stirred vigorously at rt for 3 days. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo* to afford naphthalen-1-yl(phenyl)methanone as a viscous yellow oil (6.06 g, 94%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.11 (d, *J* = 8.3 Hz, 1H, $C_{Ar}H$), 8.01 (dt, *J* = 8.2, 1.1 Hz, 1H, $C_{Ar}H$), 7.93 (dd, *J* = 7.8, 1.7 Hz, 1H, $C_{Ar}H$), 7.90 – 7.85 (m, 2H, $2C_{Ar}H$), 7.64 – 7.57 (m, 2H, $2C_{Ar}H$), 7.57 – 7.43 (m, 5H, $5C_{Ar}H$).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 198.1, 138.5, 136.5, 133.8, 133.3, 131.4, 131.1, 130.5 (2C), 128.6 (2C), 128.5, 127.9, 127.4, 126.6, 125.8, 124.4.

HRMS (ESI^+) $[C_{17}H_{13}O]^+$ predicted 233.09609, found 233.09608 (Δ -0.03 ppm).

IR υ_{max} (film): 3057, 2360, 1655, 1248, 774, 711.



(3,5-Dimethylphenyl)(naphthalen-1-yl)methanone

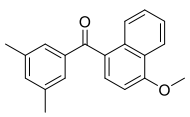
In a dried round bottom flask, (3,5-dimethylphenyl)(naphthalen-1-yl)methanol (610 mg, 2.33 mmol, 1.0 eq.), MnO_2 (6.06 g, 69.8 mmol, 30.0 eq.) and DCM (5 ml) was stirred vigorously at rt for 4 days. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo* to afford (3,5-dimethylphenyl)(naphthalen-1-yl)methanone as a colourless residue (531 mg, 88%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.08 (d, *J* = 8.2 Hz, 1H, $C_{Ar}H$), 8.00 (d, *J* = 8.0 Hz, 1H, $C_{Ar}H$), 7.94 – 7.91 (m, 1H, $C_{Ar}H$), 7.59 – 7.44 (m, 4H, $C_{Ar}H$), 7.47 (s, 2H, *o*-$C_{Ar}H$), 7.24 (s, 1H, *p*-$C_{Ar}H$), 2.34 (s, 6H, $2CH_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 198.6, 138.6, 138.3 (2C), 136.9, 135.1, 133.9, 131.2, 131.1, 128.5, 128.3 (2C), 128.0, 127.7, 127.3, 126.5, 125.9, 124.5, 21.3 (2C).

HRMS (ESI^+) $[C_{19}H_{17}O]^+$ predicted 261.12739, found 261.12741 (Δ 0.07 ppm).

IR υ_{max} (film): 2917, 2360, 1655, 1303, 781.



(3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methanone

In a dried round bottom flask, (3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methanol (985 mg, 3.40 mmol, 1.0 eq.), MnO_2 (8.79 g, 10.2 mmol, 30.0 eq.) and DCM (15 ml) was stirred vigorously at rt for 4 days. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo* to afford (3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methanone as a colourless solid (861 mg, 88%).

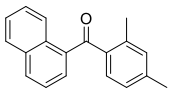
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.35 (dt, *J* = 8.0, 1.6 Hz, 2H, 2$C_{Ar}H$), 7.62 – 7.49 (m, 3H, 3$C_{Ar}H$), 7.45 (s, 2H, *o*-$C_{Ar}H$), 7.22 (s, 1H, *p*-$C_{Ar}H$), 6.80 (d, *J* = 8.0 Hz, 1H, C*H*), 4.08 (d, *J* = 1.3 Hz, 3H, OCH_3), 2.36 (s, 6H, 2CH_3)

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 197.9, 158.3 (2C), 139.7, 138.0, 134.4, 132.8, 131.2, 128.7, 128.2 (2C), 128.1, 125.9, 125.9 (2C), 122.3, 102.1, 55.9, 21.4 (2C).

HRMS (ESI$^+$) $[C_{20}H_{18}O_2{}^{23}Na]^+$ predicted 313.11990, found 313.1975 (Δ –0.48 ppm).

IR υ_{max} (s): 2981, 2360, 1647, 1227, 770.

MP. = 126 - 132 ˚C


(2,4-Dimethylphenyl)(naphthalen-1-yl)methanone

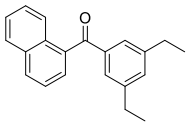
In a dried round bottom flask, 2,4-dimethylphenyl)(naphthalen-1-yl)methanol (4.79 g, 18.3 mmol, 1.0 eq.), MnO_2 (31.8 g, 36.6 mmol, 20.0 eq.) and DCM (92 ml) was stirred vigorously at rt for 3 days. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo* to afford (2,4-dimethylphenyl)(naphthalen-1-yl)methanone as a viscous yellow oil (4.80 g, quantitative yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.49 – 8.43 (m, 1H, $C_{Ar}H$), 8.09 – 7.97 (m, 1H, $C_{Ar}H$), 8.01 – 7.89 (m, 1H, $C_{Ar}H$), 7.68 – 7.54 (m, 3H, 3$C_{Ar}H$), 7.52 – 7.45 (m, 1H, $C_{Ar}H$), 7.35 – 7.27 (m, 1H, $C_{Ar}H$), 7.18 (s, 1H, $C_{Ar}H$), 7.06 – 6.98 (m, 1H, $C_{Ar}H$), 2.54 (s, 3H, CH_3), 2.42 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 200.1, 141.9, 139.0, 137.4, 136.6, 134.0, 132.5, 132.1, 131.5, 131.1, 129.5, 128.5, 127.7, 126.5, 126.2, 125.9, 124.5, 21.6, 21.0.

HRMS (ESI$^+$) $[C_{19}H_{17}O]^+$ predicted 261.12739, found 261.12744 (Δ 0.19 ppm).

IR υ_{max} (film): 2922, 2361, 1653, 777.



(3,5-Diethylphenyl)(naphthalen-1-yl)methanone

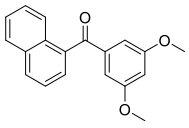
In a dried round bottom flask, (3,5-diethylphenyl)(naphthalen-1-yl)methanol (1.79 g, 6.2 mmol, 1.0 eq.), MnO_2 (10.7 g, 123 mmol, 20.0 eq.) and DCM (30 ml) was stirred vigorously at rt for 3 days. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo* to afford (3,5-diethylphenyl)(naphthalen-1-yl)methanone as a viscous colourless oil (1.72 g, 97%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.17 – 8.11 (m, 1H, $C_{Ar}H$), 8.03 (dt, *J* = 7.9, 1.1 Hz, 1H, $C_{Ar}H$), 7.99 – 7.92 (m, 1H, $C_{Ar}H$), 7.63 – 7.49 (m, 5H, $5C_{Ar}H$), 7.31 – 7.29 (m, 1H, $C_{Ar}H$), 7.28 (s, 1H, *p*-$C_{Ar}H$), 2.73 – 2.63 (m, 4H, $2CH_2$), 1.25 (t, *J* = 7.6 Hz, 6H, $2CH_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 198.4, 144.6 (2C), 138.5, 136.8, 133.7, 132.7, 131.0, 128.3, 127.6, 127.4 (2C), 127.1, 126.4, 125.8, 124.3, 28.7 (2C), 15.5 (2C).

HRMS (ESI^+) $[C_{21}H_{20}O^{23}Na]^+$ predicted 311.14064, found 311.14053 (Δ –0.33 ppm).

IR υ_{max} (film): 2964, 2931, 2360, 1655, 780.



(3,5-Dimethoxyphenyl)(naphthalen-1-yl)methanone

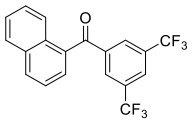
In a dried round bottom flask, (3,5-dimethoxyphenyl)(naphthalen-1-yl)methanol (7.07 g, 26.0 mmol, 1.0 eq.), MnO_2 (45.5 g, 523 mmol, 20.0 eq.) and DCM (130 ml) was stirred vigorously at rt for 3 days. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo* to afford (3,5-dimethoxyphenyl)(naphthalen-1-yl)methanone as a viscous colourless oil (7.08 g, 93%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.12 – 8.08 (m, 1H, $C_{Ar}H$), 8.00 (d, *J* = 8.4 Hz, 1H, $C_{Ar}H$), 7.94 – 7.90 (m, 1H, $C_{Ar}H$), 7.61 – 7.58 (m, 1H, $C_{Ar}H$), 7.56 – 7.47 (m, 3H, $3C_{Ar}H$), 7.01 (d, *J* = 2.2 Hz, 2H, $C_{Ar}H$), 6.70 (q, *J* = 2.3, 1.7 Hz, 1H, $C_{Ar}H$), 3.80 (s, 6H, $2CH_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 197.7, 160.9 (2C), 140.4, 136.4, 133.9, 131.4, 131.1, 128.5, 127.9, 127.4, 126.6, 125.8, 124.4, 108.4 (2C), 105.8, 55.7 (2C).

HRMS (ESI^+) $[C_{19}H_{17}O_3]^+$ predicted 293.11722, found 293.11697 (Δ –0.84 ppm).

IR υ_{max} (film): 2938, 2837, 2360, 1656, 1589, 1154, 780.



(3,5-Bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methanone

In a dried round bottom flask, (3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methanol (2.69 g, 7.27 mmol, 1.0 eq.), MnO_2 (12.6 g, 145 mmol, 20.0 eq.) and DCM (35 ml) was stirred vigorously at rt for 3 days. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo* to afford (3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methanone as a white solid (2.57 g, 96%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.33 – 8.28 (m, 2H, 2$C_{Ar}H$), 8.23 – 8.17 (m, 1H, $C_{Ar}H$), 8.15 – 8.06 (m, 2H, 4$C_{Ar}H$), 8.01 – 7.95 (m, 1H, $C_{Ar}H$), 7.65 – 7.52 (m, 4H, 4$C_{Ar}H$).

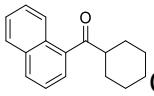
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 194.8, 140.4, 134.1, 134.1, 133.1, 132.4 (q, *J* = 34.0 Hz, 2C), 132.4, 130.3 (q, *J* = 4.0 Hz, 2C), 129.0, 128.9, 128.2, 127.2, 126.4 – 126.3 (m), 125.4, 124.4, 123.0 (q, *J* = 273.1 Hz, 2C).

^{19}F NMR (471 MHz, $CDCl_3$) δ_F: –62.9 (s).

HRMS ($APCI^+$) $[C_{19}H_{11}OF_6]^+$ predicted 349.07086, found 349.07086 (Δ –0.01 ppm).

IR υ_{max} (s): 2981, 2360, 1662, 1122.

M.P. = 87.0 - 89.5 ˚C.



Cyclohexyl(naphthalen-1-yl)methanone

In a dried round bottom flask, cyclohexyl(naphthalen-1-yl)methanol (940 mg, 3.91 mmol, 1.0 eq.), MnO_2 (11.7 g, 135 mmol, 34.5 eq.) and DCM (20 ml) was stirred vigorously at rt for 13 d. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo*. The crude reaction mixture was purified by flash column chromatography [SiO_2, petrol/EtOAc, 1:0 t0 9:1] to give cyclohexyl(naphthalen-1-yl)methanone as a white solid (782 g, 84%).

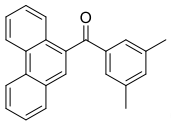
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.29 – 8.23 (m, 1H, $C_{Ar}H$), 7.95 (dt, *J* = 8.1, 1.1 Hz, 1H, $C_{Ar}H$), 7.90 – 7.82 (m, 1H, $C_{Ar}H$), 7.71 (dd, *J* = 7.1, 1.2 Hz, 1H, $C_{Ar}H$), 7.60 – 7.45 (m, 3H, $C_{Ar}H$), 3.20 (tt, *J* = 11.4, 3.4 Hz, 1H, C*H*), 1.99 – 1.89 (m, 2H, 2C$H_a$$H_b$), 1.88 – 1.79 (m, 2H, 2C$H_a$$H_b$), 1.75 – 1.67 (m, 1H, C$H_a$$H_b$), 1.60 – 1.49 (m, 2H, 2$CH_a$$H_b$), 1.42 – 1.22 (m, 3H, 3$CH_a$$H_b$).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 208.7, 137.4, 134.0, 131.6, 130.6, 128.5, 127.6, 126.5, 125.8, 125.8, 124.5, 49.9, 29.1 (2C), 26.1, 25.9 (2C).

HRMS (ESI$^+$) $[C_{17}H_{19}O]^+$ predicted 239.14304, found 239.14311 (Δ 0.29 ppm).

IR υ_{max} (s): 2981, 2360, 774.

M.P. = 61.1 – 62.9 ˚C.



(3,5-Dimethylphenyl)(phenanthren-9-yl)methanone

In a dried round bottom flask, (3,5-dimethylphenyl)(phenanthren-9-yl)methanol (1.71 g, 5.37 mmol, 1.0 eq.), MnO_2 (14.3 g, 164 mmol, 30 eq.) and DCM (27 ml) was stirred vigorously at rt for 3 d. The mixture was filtered in celite/DCM and the solvent was removed *in vacuo*. The crude reaction mixture was purified by flash column chromatography [SiO_2, petrol/EtOAc, 1:0 t0 8:2] to give (3,5-dimethylphenyl)(phenanthren-9-yl)methanone as a white solid (1.34 g, 79%).

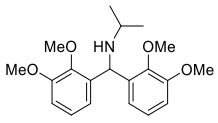
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.69 – 8.60 (m, 2H, $C_{Ar}H$), 8.01 (dd, *J* = 8.3, 1.2 Hz, 1H, $C_{Ar}H$), 7.79 (dd, *J* = 7.9, 1.3 Hz, 1H, $C_{Ar}H$), 7.73 (s, 1H, $C_{Ar}H$), 7.68 – 7.44 (m, 6H, $C_{Ar}H$), 7.17 – 7.13 (m, 1H, $C_{Ar}H$), 2.24 (s, 6H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 198.5, 138.5, 138.4 (2C), 135.9, 135.3, 131.4, 130.7, 130.3, 129.6, 129.6, 128.9, 128.3 (3C), 127.3, 127.3, 127.2, 126.8, 123.0, 122.8, 21.3 (2C).

HRMS (ESI$^+$) $[C_{23}H_{19}O]^+$ predicted 311.14304, found 311.14304 (Δ –0.02 ppm).

IR υ_{max} (s): 2918, 2165, 1655, 747, 724.

M.P. = 100 – 103 ˚C.



N-(bis(2,3-dimethoxyphenyl)methyl)propan-2-amine

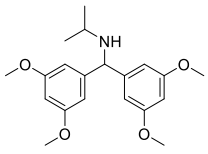
General procedure B: bis(2,3-dimethoxyphenyl)methanone (211 mg, 0.70 mmol, 1.0 eq.), DCM (2.0 ml) $TiCl_4$ solution in DCM (0.77 ml, 1.0 M, 0.77 mmol, 1.1 eq.), isopropylamine (0.18 ml, 2.10 mmol, 3.0 eq.) $NaB(CN)H_3$ (220 mg, 3.50 mmol, 5.0 eq.) in THF (3.5 ml), anhydrous MeOH (0.4 ml), reaction duration 18 h. *N*-(bis(2,3-dimethoxyphenyl)methyl)propan-2-amine was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.05 – 6.92 (m, 4H, CH_{Ar}), 6.80 (dd, *J* = 7.7, 1.9 Hz, 2H, CH_{Ar}), 5.68 (s, 1H, C*H*Ar), 3.84 (s, 6H, OCH_3), 3.70 (s, 6H, OCH_3), 2.75 (hept, *J* = 6.2 Hz, 1H, C*H*Me), 1.09 (d, *J* = 6.2 Hz, 6H, CHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 152.8 (2C), 146.9 (2C), 137.9 (2C), 123.8 (2C), 120.6 (2C), 110.9 (2C), 60.3 (2C), 55.8 (2C), 51.9, 46.5, 23.2 (2C).

HRMS (ESI^+) $[C_{20}H_{28}O_4]^+$ predicted 346.2013, found 346.2011 (Δ -0.68 ppm).

IR υ_{max} (film): 2961, 2361, 1478, 1266.



N-(bis(3,5-dimethoxyphenyl)methyl)propan-2-amine

General procedure B: bis(3,5-dimethoxyphenyl)methanone (1.06 g, 3.5 mmol, 1.0 eq.), DCM (10 ml) $TiCl_4$ solution in DCM (3.85 ml, 1.0 M, 3.85 mmol, 1.1 eq.), isopropylamine (0.90 ml, 10.5 mmol, 3.0 eq.), $NaB(CN)H_3$ (1.10 g, 17.5 mmol, 5.0 eq.) in THF (17.5 ml), anhydrous MeOH (2.0 ml), reaction duration 17 h. *N*-(bis(3,5-dimethoxyphenyl)methyl)propan-2-amine was used without further purification (1.33 g, quantitative yield).

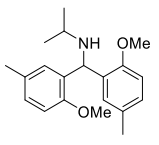
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 6.57 (d, *J* = 2.3 Hz, 4H, $C_{Ar}H$), 6.30 (t, *J* = 2.3 Hz, 2H, $C_{Ar}H$), 4.79 (s, 1H, C*H*Ar), 3.76 (s, 14H, OCH_3), 2.75 (hept, *J* = 6.3 Hz, 1H, C*H*Me), 1.07 (d, *J* = 6.3 Hz, 6H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 160.9 (4C), 147.0 (2C), 105.5 (4C), 98.7 (2C), 64.6, 55.4 (4C), 46.4, 23.4 (2C).

HRMS (Cl^+) $[C_{20}H_{27}NO_4]^+$ predicted 345.1940, found 346.2017 (Δ -0.74 ppm).

IR υ_{max} (film): 3019, 2957, 1596, 1460, 830.

MP. = 61.9 - 63.5 ˚C



N-(bis(2-methoxy-5-methylphenyl)methyl)propan-2-amine

General procedure B: bis(2-methoxy-5-methylphenyl)methanone (286 mg, 1.06 mmol, 1.0 eq.), DCM (3.0 ml) $TiCl_4$ solution in DCM (1.16 ml, 1.0 M, 1.16 mmol, 1.1 eq.), isopropylamine

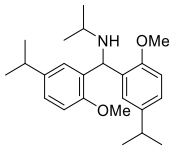
(0.27 ml, 3.18 mmol, 3.0 eq.), $NaB(CN)H_3$ (333 mg, 5.30 mmol, 5.0 eq.) in THF (5.3 ml), anhydrous MeOH (0.61 ml), reaction duration 16 h. *N*-(bis(2-methoxy-5-methylphenyl)methyl)propan-2-amine was used without further purification (273 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.15-7.12 (m, *J* = 2.3 Hz, 2H, $C_{Ar}H$), 6.97 (dd, *J* = 8.3, 2.3 Hz, 2H, $C_{Ar}H$), 6.73 (d, *J* = 8.2 Hz, 2H, $C_{Ar}H$), 5.55 (s, 1H, C*H*Ar), 3.75 (s, 6H, OCH_3), 2.72 (hept, *J* = 6.3 Hz, 1H, C*H*Me), 2.26 (s, 6H, CH_3), 1.85(s, br, 1H, N*H*), 1.09 (d, *J* = 6.3 Hz, 6H, CHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 155.3 (2C), 131.9 (2C), 129.6 (2C), 129.3 (2C), 127.8 (2C), 111.0 (2C), 55.9 (2C), 52.5, 46.4, 23.3 (2C), 20.9 (2C).

HRMS (ESI$^+$) $[C_{20}H_{28}O_2N]^+$ predicted 314.2115, found 314.2114 (Δ -0.10 ppm).

IR υ_{max} (film): 2956, 2833, 1610, 1242, 1034, 804.



N-(bis(5-isopropyl-2-methoxyphenyl)methyl)propan-2-amine

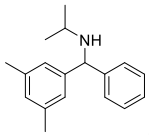
General procedure B: bis(5-isopropyl-2-methoxyphenyl)methanone (372 mg, 1.14 mmol, 1.0 eq.), DCM (3.3 ml) $TiCl_4$ solution in DCM (1.25 ml, 1.0 M, 1.25 mmol, 1.1 eq.), isopropylamine (0.29 ml, 1.14 mmol, 1.0 eq.), $NaB(CN)H_3$ (392 mg, 5.70 mmol, 5.0 eq.) in THF (5.7 ml), anhydrous MeOH (0.65 ml), reaction duration 16 h. N-(bis(5-isopropyl-2-methoxyphenyl)methyl)propan-2-amine was used without further purification (260 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.33 - 7.31 (m, 2H, $C_{Ar}H$), 7.12 – 7.04 (m, 2H, $C_{Ar}H$), 6.83-6.78 (m, 2H, $C_{Ar}H$), 5.59 (s, 1H, C*H*Ar), 3.81 (s, 6H,OCH_3), 2.91 (hept, *J* = 7.0 Hz, 2H, C*H*Me), 2.80 (hept, *J* = 6.4 Hz, NC*H*Me), 2.36 (s, br, 1H, N*H*), 1.28 (d, *J* = 6.9 Hz, 12H, CHCH_3), 1.17 (d, *J* = 6.2 Hz, 6H, NCHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 155.5 (2C), 140.4 (2C), 131.2 (2C), 127.0 (2C), 125.0 (2C), 110.64 (2C), 55.5 (2C), 53.9 (2C), 46.2 , 33.5 (2C), 24.3 (2C), 24.3 (2C), 23.2 (2C).

HRMS (ESI$^+$) $[C_{24}36O_2N]^+$ predicted 370.2741, found 370.2733 (Δ -2.16 ppm).

IR υ_{max} (film): 2956, 2834, 1497, 1244, 1031, 810.



N-((3,5-dimethylphenyl)(phenyl)methyl)propan-2-amine

General procedure B: (3,5-dimethylphenyl)(phenyl)methanone (400 mg, 1.90 mmol, 1.0 eq.), DCM (5.4 ml) $TiCl_4$ solution in DCM (2.09 ml, 1.0 M, 2.09 mmol, 1.1 eq.), isopropylamine (0.49 ml, 5.71 mmol, 3.0 eq.), $NaB(CN)H_3$ (143 mg, 2.28 mmol, 1.2 eq.) in THF (2.2 ml), anhydrous MeOH (1.08 ml), reaction duration 18 h. Following the work up procedure, *N*-((3,5-dimethylphenyl)(phenyl)methyl)propan-2-amine was obtained as colourless viscous oil (269 mg, 56%).

The two enantiomers of *N*-((3,5-dimethylphenyl)(phenyl)methyl)propan-2-amine was separated by chiral UPC^2 [Chiralcel® OJ-H; flow: 2 mL/min; 8% Heptane:IPA, 20 mM NH_3; λ = 230 nm; enantiomer (–)-(3-methyl-3-(4-phenylhexyl)cyclopentanone, t_R = 4.02 min; enantiomer (+)-(*S*)-3-methyl-3-(4-phenylhexyl)cyclopentanone, t_R = 4.58 min].

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.42 – 7.39 (m, 2H, 2$C_{Ar}H$), 7.31 (dd, *J* = 8.4, 6.9 Hz, 3H, 3$C_{Ar}H$), 7.23 – 7.19 (m, 1H, $C_{Ar}H$), 7.00 (s, 2H, 2$C_{Ar}H$), 6.85 (s, 1H, $C_{Ar}H$), 4.91 (s, 1H, ArCH), 2.76 (hept, *J* = 6.3 Hz, 1H, NC$H$$CH_3$), 2.29 (s, 6H, Ar($CH_3$)$_2$), 1.10 (d, *J* = 6.3 Hz, 6H, CHCH_3), 1.10 (d, *J* = 6.3 Hz, 6H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 144.9, 144.7, 138.0 (2C), 128.7, 128.5 (2C), 127.5 (2C), 126.8, 125.2 (2C), 64.4, 46.3, 23.5, 23.3, 21.5 (2C).

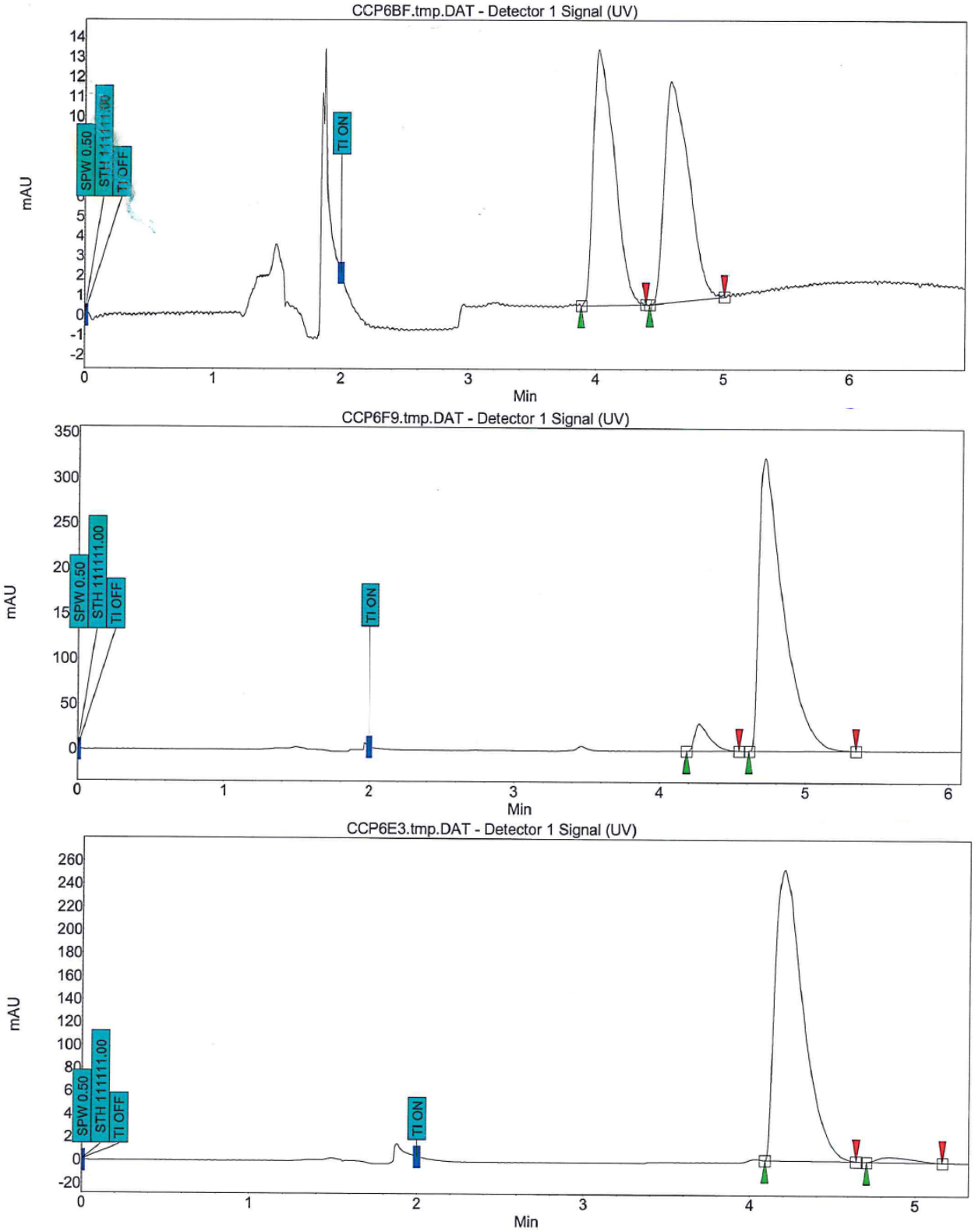
HRMS (APCI$^+$) $[C_{18}H_{22}N]^+$ predicted 252.17468, found 252.17473 (Δ 0.21 ppm).

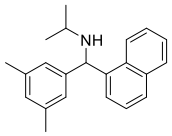
IR υ_{max} (film): 2960, 2920, 1599, 1167, 707.

(–)-*N*-((3,5-dimethylphenyl)(phenyl)methyl)propan-2-amine (79.6 mg, 95.5% ee): $[\boldsymbol{\alpha}]_{589}^{25}$= –0.7 (*c* 0.88, $CHCl_3$).

(+)-*N*-((3,5-dimethylphenyl)(phenyl)methyl)propan-2-amine (82.1 mg, – 89% ee): $[\boldsymbol{\alpha}]_{589}^{25}$= +1.5 (*c* 1.04, $CHCl_3$).

B5R9_OJ-H_8(Heptane-IPA_80-20)_NH31:





N-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine

General procedure B: (3,5-dimethylphenyl)(naphthalen-1-yl)methanone (520 mg, 2.00 mmol, 1.0 eq.), DCM (5.7 ml) $TiCl_4$ solution in DCM (2.20 ml, 1.0 M, 2.20 mmol, 1.1 eq.), isopropylamine (0.52 ml, 5.99 mmol, 3.0 eq.), $NaB(CN)H_3$ (151 mg, 2.28 mmol, 1.2 eq.) in THF (2.5 ml), anhydrous MeOH (1.14 ml), reaction duration 18 h. Following the work up procedure, *N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine was obtained as light pink viscous oil (355 mg, 59%).

The two enantiomers of *N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine was separated by chiral UPLC [Chiralcel® OJ; flow: 2 mL/min; MeOH, 20 mM NH_3; λ = 300 nm; enantiomer (–)-*N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine, t_R = 0.43 min; enantiomer (+)-*N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine, t_R = 0.59 min].

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.21 – 8.15 (m, 1H, $C_{Ar}H$), 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H, $C_{Ar}H$), 7.78 – 7.72 (m, 1H, $C_{Ar}H$), 7.70 (dt, *J* = 7.3, 0.9 Hz, 1H, $C_{Ar}H$), 7.51 – 7.40 (m, 3H, $C_{Ar}H$), 7.00 (d, *J* = 1.6 Hz, 2H, $C_{Ar}H$), 6.86 – 6.81 (m, 1H, $C_{Ar}H$), 5.68 (s, 1H ArC*H*), 2.86 (hept, *J* = 6.3 Hz, 1H, NC*H*CH_3), 2.26 (s, 6H, Ar(CH_3)$_2$), 1.14 (d, *J* = 6.3 Hz, 3H, CHCH_3), 1.12 (d, *J* = 6.3 Hz, 3H, CHCH_3).

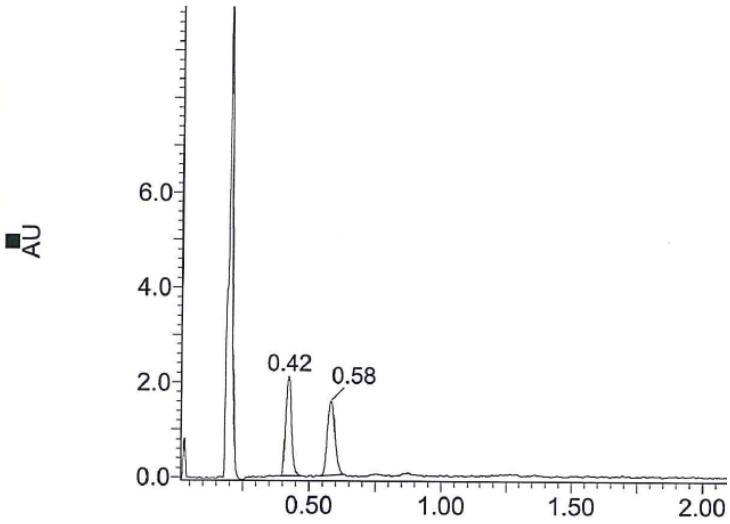
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 144.1, 139.6, 138.0 (2C), 134.2, 131.6, 129.0, 128.8, 127.5, 126.0, 125.7 (2C), 125.7, 125.4, 125.1, 123.7, 60.0, 46.9, 23.5, 23.4, 21.5 (2C).

HRMS ($APCI^+$) $[C_{22}H_{24}N]^+$ predicted 302.19033, found 302.19019 (Δ –0.47 ppm).

IR υ_{max} (film): 2959, 1599, 1467, 778.

(–)-*N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine (112 mg, >99.9% ee): $[\alpha]_{589}^{25}$ = –104.5 (*c* 1.82, $CHCl_3$).

(+)-*N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine (121 mg, 97.0% ee): $[\alpha]_{589}^{25}$ = +74.3 (*c* 1.70, $CHCl_3$).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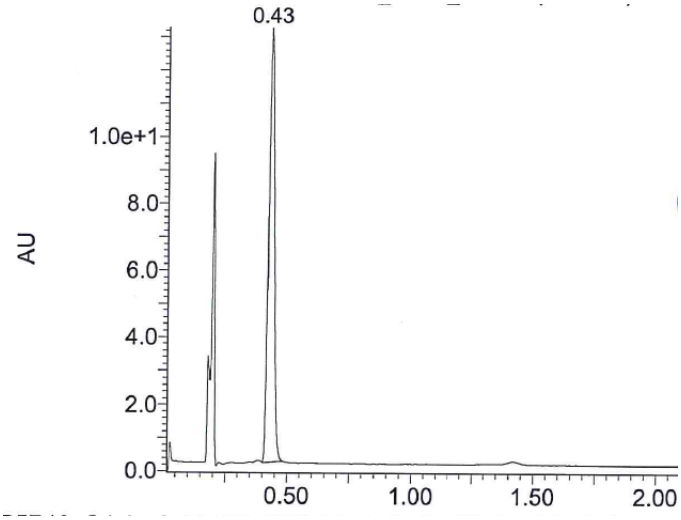
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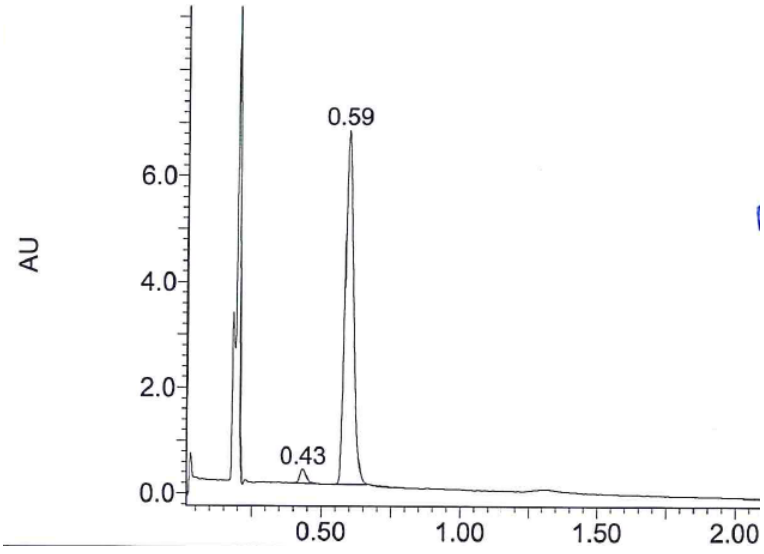
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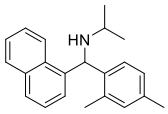


N-((2,4-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine

General procedure B: (2,4-dimethylphenyl)(naphthalen-1-yl)methanone (1.00 g, 3.84 mmol, 1.0 eq.), DCM (11 ml) $TiCl_4$ solution in DCM (4.23 ml, 1.0 M, 4.23 mmol, 1.1 eq.), isopropylamine (0.99 ml, 11.5 mmol, 3.0 eq.), $NaB(CN)H_3$ solution in THF (17.3 ml, 1.0 M, 17.3 mmol, 4.5 eq.), anhydrous MeOH (2.1 ml), reaction duration 2 d. Following the work up procedure, *N*-((2,4-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine was obtained as colourless viscous oil (684 mg, 59%).

The two enantiomers of *N*-((2,4-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine was separated by chiral UPC^2 [Chiralcel® OD-H; flow: 2 mL/min; 8% MeOH:MeCN 1:1, 0.2% *N,N*-dimethylisopropylamine; λ = 280 nm; enantiomer (+)-*N*-((2,4-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine, t_R = 5.85 min; enantiomer (–)-*N*-((2,4-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine, t_R = 6.41 min].

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.01 (d, *J* = 8.2 Hz, 1H, $C_{Ar}H$), 7.76 (dd, *J* = 7.8, 1.6 Hz, 1H, $C_{Ar}H$), 7.65 (dd, *J* = 6.7, 2.7 Hz, 1H, $C_{Ar}H$), 7.42 – 7.27 (m, 4H, $C_{Ar}H$), 7.17 – 7.10 (m, 1H, $C_{Ar}H$), 6.92 (d, *J* = 1.8 Hz, 1H, $C_{Ar}H$), 6.88 (dd, *J* = 7.9, 1.8 Hz, 1H, $C_{Ar}H$), 5.80 (s, 1H, ArC*H*), 2.88 (hept, *J* = 6.3 Hz, 1H, NC*H*CH_3), 2.23 (s, 3H, ArCH_3), 2.21 (s, 3H, ArCH_3), 1.28 (s, br, 1H, N*H*), 1.09 (d, *J* = 6.2 Hz, 3H, CHCH_3), 1.03 (d, *J* = 6.3 Hz, 3H, CHCH_3).

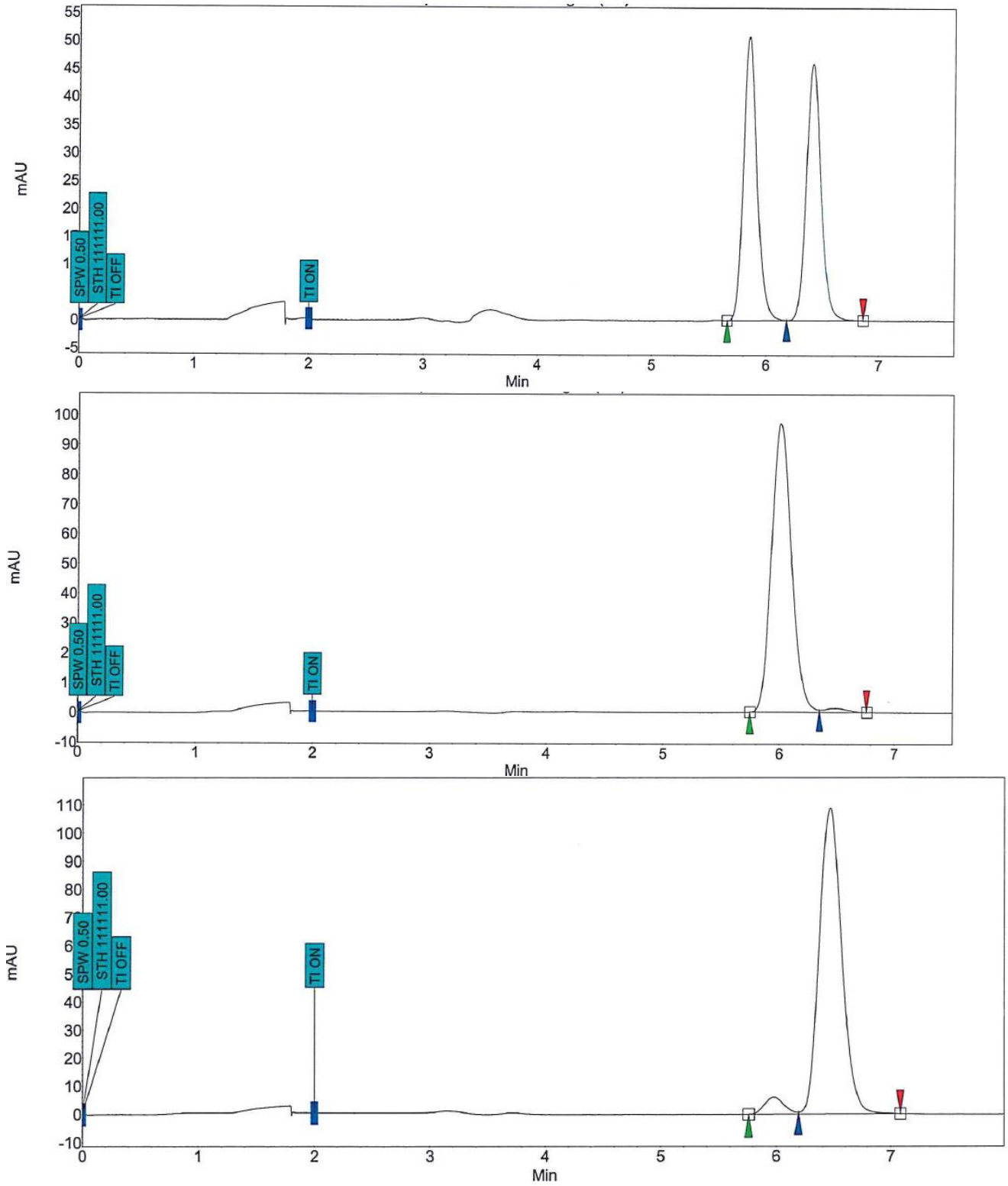
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 139.2, 138.7, 136.4, 135.8, 134.2, 131.8, 131.6, 129.0, 127.6, 127.6, 126.7, 126.2, 125.6, 125.5, 125.4, 123.2, 55.9, 47.1, 23.5, 23.3, 21.1, 19.4.

HRMS (ESI$^+$) $[C_{22}H_{26}N]^+$ predicted 304.20598, found 304.20593 (Δ –0.14 ppm).

IR υ_{max} (film): 2960, 1465, 1166, 777.

(–)-*N*-((2,4-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine (97% ee): $[\alpha]_{589}^{25}$= –39.8 (*c* 1.18, $CHCl_3$).

(+)-*N*-((2,4-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine (91% ee): $[\alpha]_{589}^{25}$= +28.3 (*c* 0.93, $CHCl_3$).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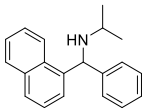


N-(naphthalen-1-yl(phenyl)methyl)propan-2-amine

General procedure B: naphthalen-1-yl(phenyl)methanone (2.32 g, 10.0 mmol, 1.0 eq.), DCM (29 ml) $TiCl_4$ solution in DCM (3.67 ml, 1.0 M, 3.67 mmol, 0.37 eq.), isopropylamine (4.3 ml, 50 mmol, 5.0 eq.), $NaB(CN)H_3$ solution in THF (50 ml, 1.0 M, 50.0 mmol, 5.0 eq.) anhydrous MeOH (5.71 ml), reaction duration 2 d. Following the work up procedure, *N*-(naphthalen-1-yl(phenyl)methyl)propan-2-amine was obtained as light pink viscous oil (536 mg, 19%).

The two enantiomers of *N*-(naphthalen-1-yl(phenyl)methyl)propan-2-amine was separated by chiral UPLC [Chiralcel® OD-H; flow: 2 mL/min; 30% MeOH, 20 mM NH_3; λ = 280 nm; enantiomer (–)-*N*-(naphthalen-1-yl(phenyl)methyl)propan-2-amine t_R = 2.84 min; enantiomer (+)-*N*-(naphthalen-1-yl(phenyl)methyl)propan-2-amine, t_R = 3.68 min].

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.25 – 8.21 (m, 1H, $C_{Ar}H$), 7.92 – 7.88 (m, 1H, $C_{Ar}H$), 7.82 – 7.79 (m, 1H, $C_{Ar}H$), 7.74 (d, *J* = 7.1 Hz, 1H, $C_{Ar}H$), 7.54 – 7.45 (m, 5H, $5C_{Ar}H$), 7.36 – 7.31 (m, 2H, $2C_{Ar}H$), 7.27 – 7.22 (m, 1H, $C_{Ar}H$), 5.81 (s, 1H, ArC*H*), 2.94 (hept, *J* = 6.3 Hz, 1H, NC*H*CH_3), 1.57 (s, br, 1H, N*H*), 1.21 (d, *J* = 6.3 Hz, 3H, CHCH_3), 1.18 (d, *J* = 6.3 Hz, 3H, CHCH_3).

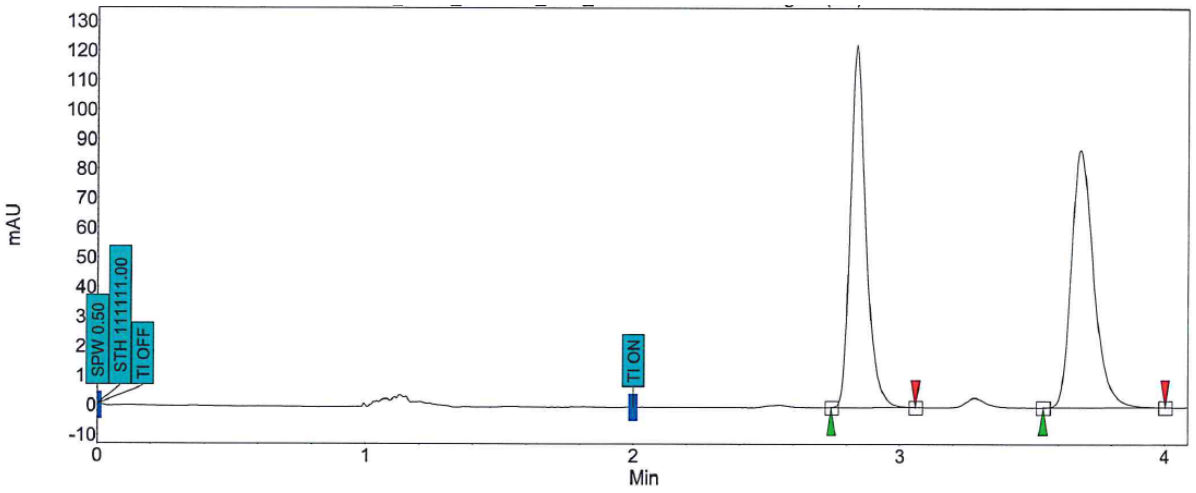
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 144.2, 139.6, 134.2, 131.5, 129.0, 128.6 (2C), 128.0 (2C), 127.7, 127.0, 126.1, 125.6, 125.4, 125.2, 123.6, 60.1, 46.9, 23.4 (2C).

HRMS (ESI^+) $[C_{20}H_{22}N]^+$ predicted 276.17468, found 276.17459 (Δ –0.31 ppm).

IR υ_{max} (film): 2959, 2924, 2855, 1465, 708.

(–)-*N*-(naphthalen-1-yl(phenyl)methyl)propan-2-amine (99.7% ee): $[\alpha]_{589}^{25}$ = –51.9 (*c* 0.94, $CHCl_3$).

(+)-*N*-(naphthalen-1-yl(phenyl)methyl)propan-2-amine (99.7% ee): $[\alpha]_{589}^{25}$ = +62.2 (*c* 1.03 $CHCl_3$).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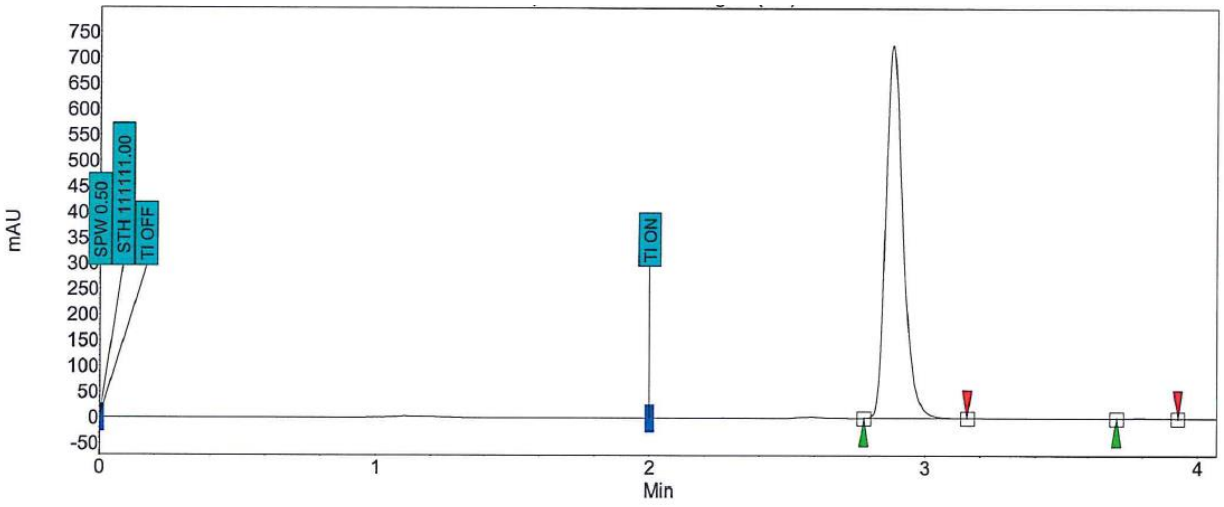
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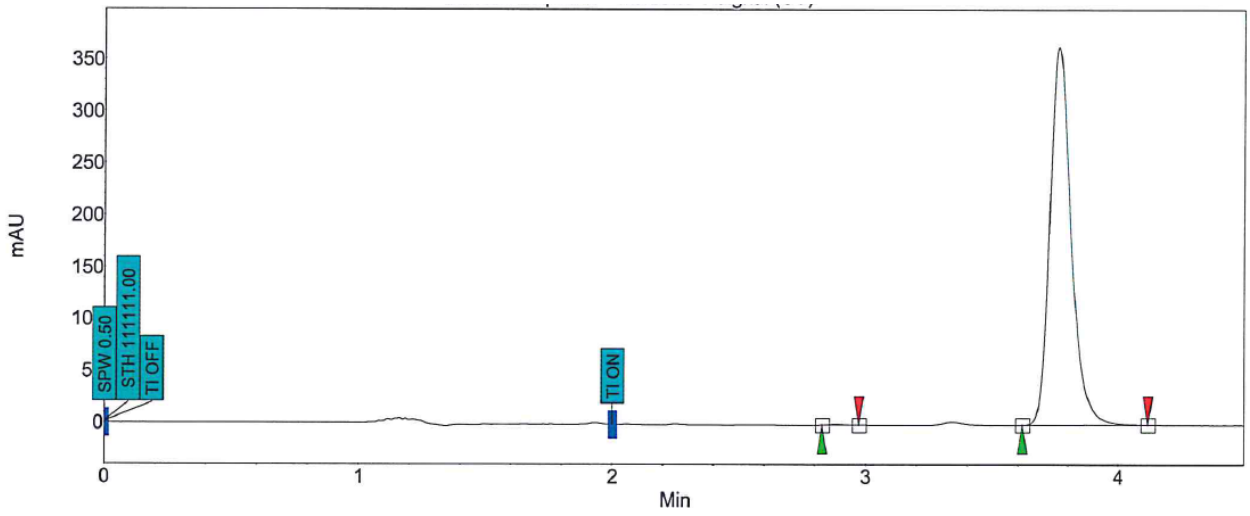
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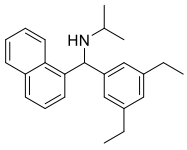


N-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine

General procedure B: (3,5-diethylphenyl)(naphthalen-1-yl)methanone (1.70 g, 5.90 mmol, 1.0 eq.), DCM (17 ml) $TiCl_4$ solution in DCM (7.8 ml, 1.0 M, 7.80 mmol, 1.1 eq.), isopropylamine (1.52 ml, 17.7 mmol, 3.0 eq.), $NaB(CN)H_3$ solution in THF (20.7 ml, 1.0 M, 20.7 mmol, 3.5 eq.), anhydrous MeOH (3.37 ml), reaction duration 2 d. Following the work up procedure, *N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine was obtained as light pink viscous oil (1.34 g, 68%).

The two enantiomers of *N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine was separated by chiral UPLC [Chiralcel® OD-H; flow: 2 mL/min; 20% MeOH, 20 mM NH_3; λ = 280 nm; enantiomer (–)-*N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine, t_R = 3.22 min; enantiomer (+)-*N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine, t_R = 3.97 min].

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.25 (d, *J* = 8.2 Hz, 1H, $C_{Ar}H$), 7.85 (dd, *J* = 7.9, 1.6 Hz, 1H, $C_{Ar}H$), 7.76 – 7.73 (m, 1H, $C_{Ar}H$), 7.70 – 7.65 (m, 1H, $C_{Ar}H$), 7.52 – 7.41 (m, 3H, $3C_{Ar}H$), 7.08 (d, *J* = 1.6 Hz, 2H, $2C_{Ar}H$), 6.90 (d, *J* = 1.7 Hz, 1H, $C_{Ar}H$), 5.73 (s, 1H, ArC*H*), 2.88 (hept, *J* = 6.3 Hz, 1H, NC*H*CH_3), 2.59 (q, *J* = 7.6 Hz, 4H, $2CH_2CH_3$), 1.45 (s, br, 1H, N*H*), 1.20 (t, *J* = 7.6 Hz, 6H, $2CH_2CH_3$), 1.16 (d, *J* = 6.3 Hz, 3H, $CHCH_3$), 1.13 (d, *J* = 6.2 Hz, 3H, $CHCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 144.4, 144.0, 139.9, 134.2, 131.7, 129.0, 127.5, 126.1, 126.0, 125.7, 125.4, 125.2, 124.9 (2C), 123.7, 60.2, 46.9, 29.0 (2C), 23.5, 23.5, 15.7 (2C).

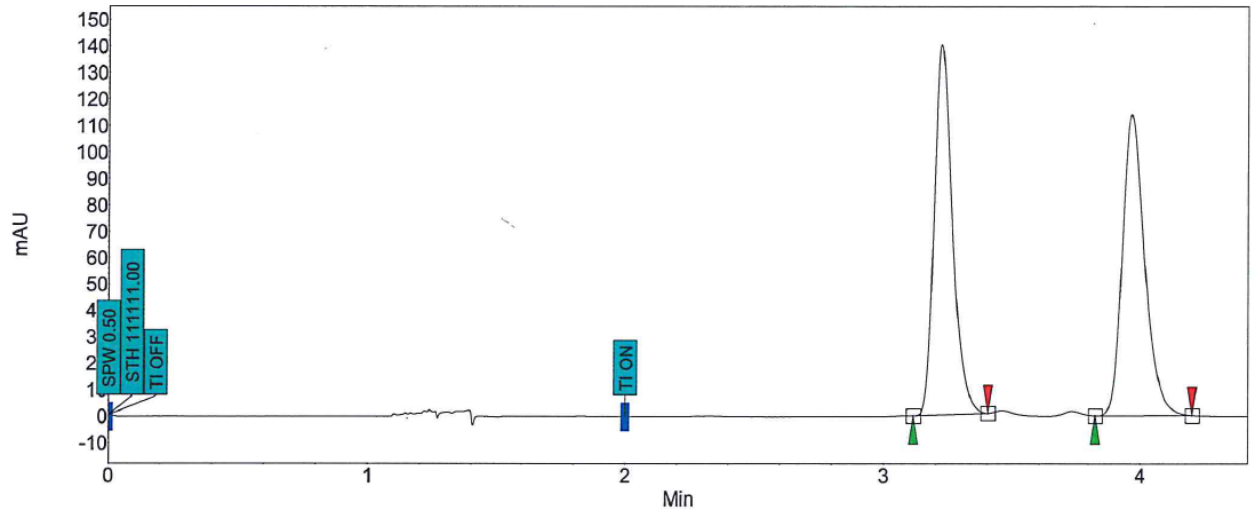
HRMS (ESI^+) $[C_{24}H_{30}N]^+$ predicted 332.23728, found 332.23718 (Δ –0.28 ppm).

IR υ_{max} (film): 2962, 2930, 1598, 1459, 778.

(–)-*(S)*-*N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine (**L26S-amine**) (99.4% ee): $[\alpha]_{589}^{25}$ = –201.3 (*c* 2.80, $CHCl_3$).

(+)-*(R)*-*N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine (98.5% ee): $[\alpha]_{589}^{25}$ = +166.7 (*c* 2.36, $CHCl_3$).

The absolute stereochemistry of **L26S-amine** was proven by X-ray crystallography of its HCl salt. (See additional supporting information for crystallography data).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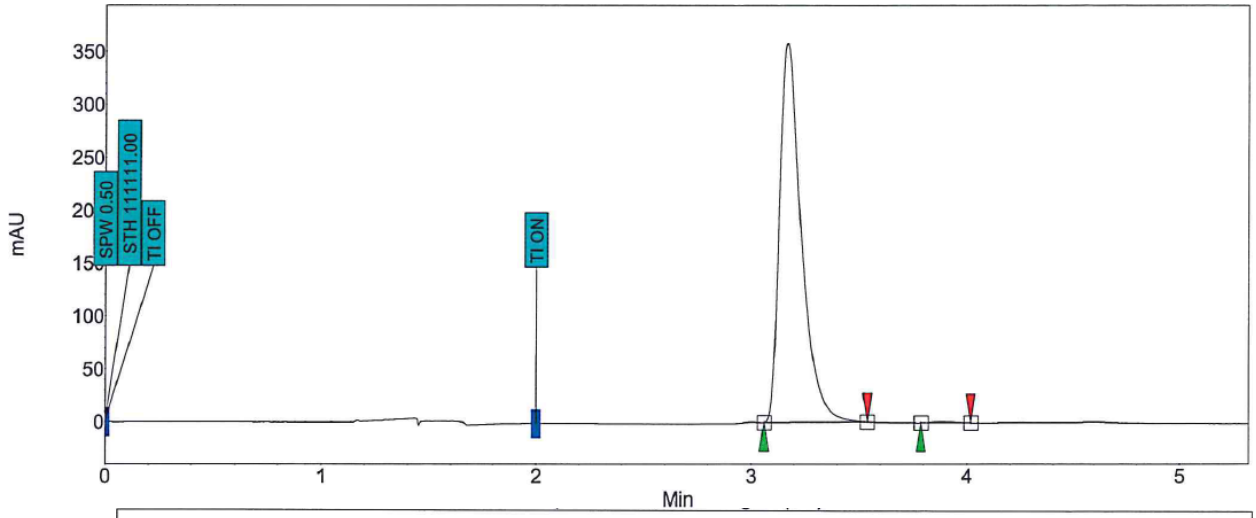
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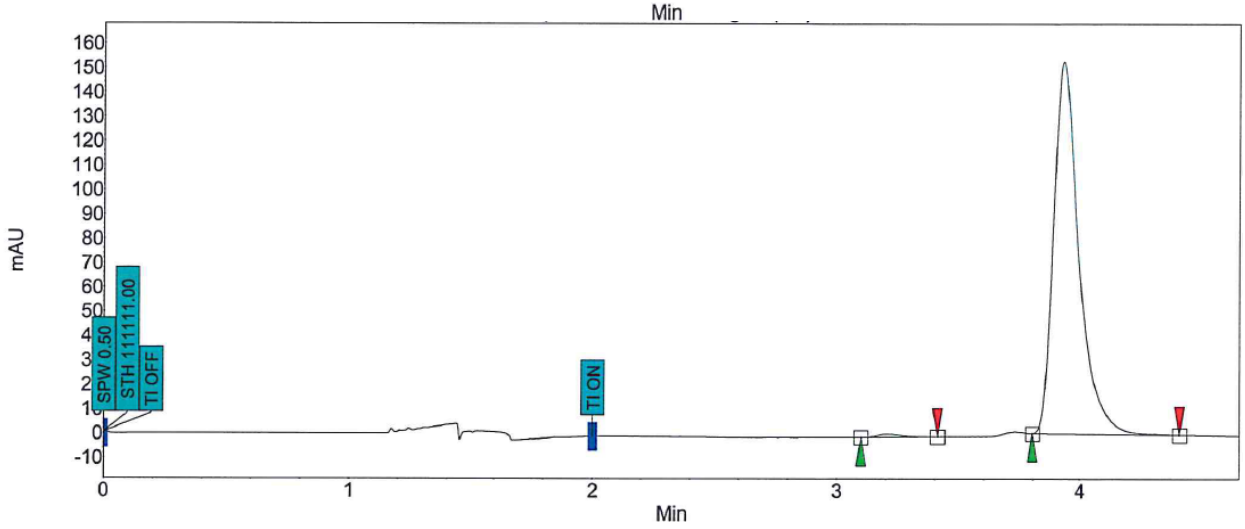
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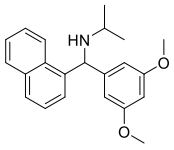


N-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)propan-2-amine

General procedure B: (3,5-dimethoxyphenyl)(naphthalen-1-yl)methanone (3.61 g, 12.4 mmol, 1.0 eq.), DCM (35 ml) $TiCl_4$ solution in DCM (13.6 ml, 1.0 M, 13.6 mmol, 1.1 eq.), isopropylamine (3.2 ml, 37.1 mmol, 3.0 eq.), $NaB(CN)H_3$ solution in THF (37.1 ml, 1.0 M, 37.1 mmol, 3.0 eq.), anhydrous MeOH (7.1 ml), reaction duration 2 d. Following the work up procedure, *N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)propan-2-amine was obtained as colourless viscous oil (3.18 g, 77%).

The two enantiomers of *N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)propan-2-amine was separated by chiral UPLC [Chiralcel® OJ; flow: 2 mL/min; 5% MeOH, 20 mM NH_3; λ = 300 nm; enantiomer (–)-*N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)propan-2-amine, t_R = 0.52 min; enantiomer (+)-*N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)propan-2-amine, t_R = 0.96 min].

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.21 (d, *J* = 8.2 Hz, 1H, $C_{Ar}H$), 7.85 (dd, *J* = 7.8, 1.8 Hz, 1H, $C_{Ar}H$), 7.74 (d, *J* = 8.1 Hz, 1H, $C_{Ar}H$), 7.63 (d, *J* = 7.1 Hz, 1H, $C_{Ar}H$), 7.52 – 7.41 (m, 3H, $C_{Ar}H$), 6.61 (d, *J* = 2.4 Hz, 2H, 2*o*-$C_{Ar}H$), 6.32 (t, *J* = 2.3 Hz, 1H, *p*-$C_{Ar}H$), 5.67 (s, 1H, Ar*H*), 3.74 (s, 6H, 2OCH_3), 2.90 (hept, *J* = 6.3 Hz, 1H, NC*H*CH_3), 1.44 (s, br, 1H, N*H*), 1.16 (d, *J* = 6.3 Hz, 3H, CHCH_3), 1.12 (d, *J* = 6.3 Hz, 3H, CHCH_3).

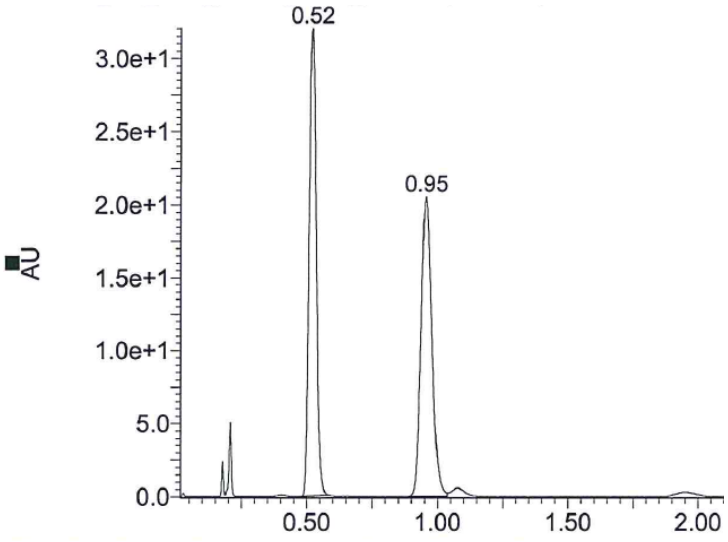
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 161.0 (2C), 146.8, 139.5, 134.2, 131.5, 129.0, 127.7, 126.1, 125.7, 125.5, 125.3, 123.6, 106.3 (2C), 98.7, 60.3, 55.4 (2C), 47.0, 23.6, 23.3.

HRMS (ESI^+) $[C_{22}H_{26}O_2N]^+$ predicted 336.19581, found 336.19586 (Δ 0.17 ppm).

IR υ_{max} (film): 2959, 2836, 1593, 1152, 779.

(–)-*N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)propan-2-amine (>99.9% ee): $[\alpha]_{589}^{25}$= –200.0 (*c* 2.55, $CHCl_3$).

(+)-*N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)propan-2-amine (99.1% ee): $[\alpha]_{589}^{25}$= +252.8 (*c* 3.43, $CHCl_3$).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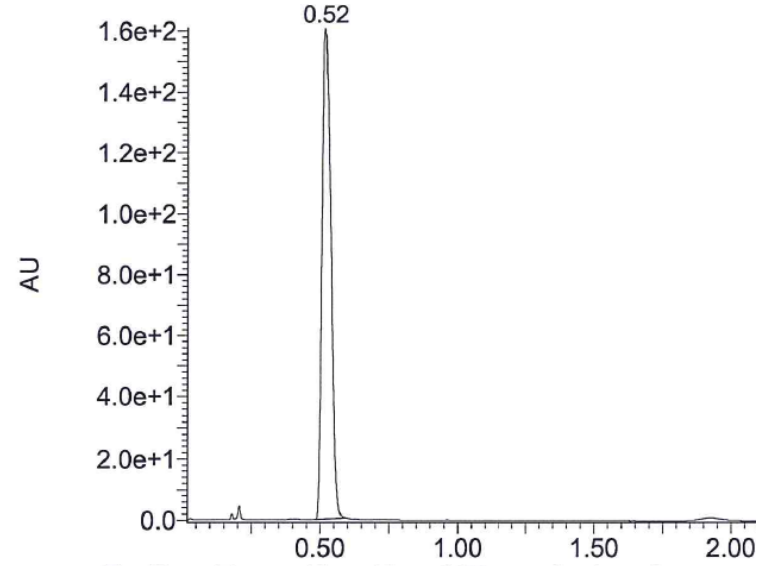
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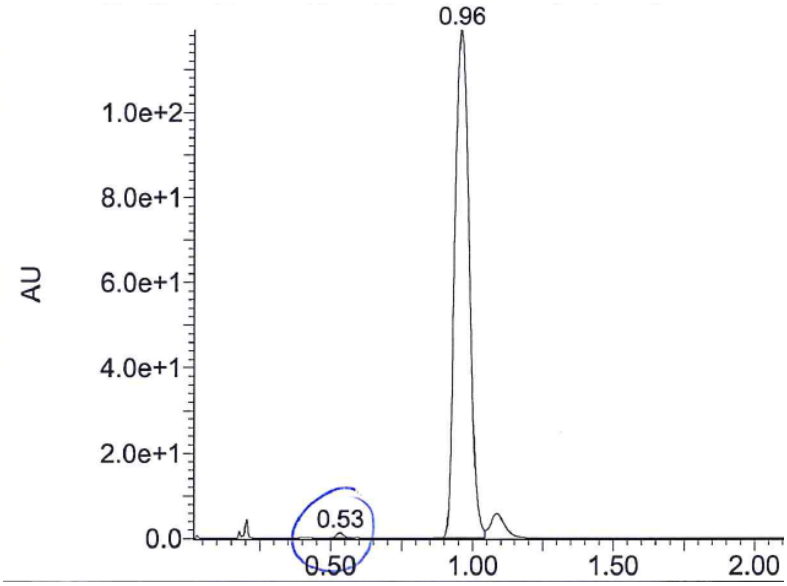
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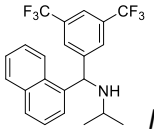


N-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)propan-2-amine

General procedure B: (3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methanone (2.55 g, 6.92 mmol, 1.0 eq.), DCM (24 ml) $TiCl_4$ solution in DCM (7.6 ml, 1.0 M, 7.60 mmol, 1.1 eq.), isopropylamine (1.8 ml, 20.8 mmol, 3.0 eq.), $NaB(CN)H_3$ solution in THF (20.8 ml, 1.0 M, 20.8 mmol, 3.0 eq.), anhydrous MeOH (4.0 ml), reaction duration 2 d. Following the work up procedure, *N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)propan-2-amine was obtained as light pink viscous oil (2.53 g, 89%).

The two enantiomers of *N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)propan-2-amine was separated by chiral UPLC [Chiralcel® OD-H; flow: 2 mL/min; 5% MeOH, 20 mM NH_3; λ = 280 nm; enantiomer (–)-*N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)propan-2-amine, t_R = 3.03 min; enantiomer (+)-*N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)propan-2-amine, t_R = 3.74 min].

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.16 (d, *J* = 8.3 Hz, 1H, $C_{Ar}H$), 7.98 (s, 2H, $2C_{Ar}H$), 7.90 (dd, *J* = 8.0, 1.5 Hz, 1H, $C_{Ar}H$), 7.81 (d, *J* = 7.9 Hz, 1H, $C_{Ar}H$), 7.75 (s, 1H, $C_{Ar}H$), 7.59 – 7.40 (m, 4H, $4C_{Ar}H$), 5.84 (d, *J* = 2.5 Hz, 1H, Ar*CH*), 2.79 (hept, *J* = 6.3 Hz, 1H, N*CH*CH_3), 1.09 (d, *J* = 6.3 Hz, 3H, CHCH_3), 1.02 (d, *J* = 6.3 Hz, 3H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 147.4, 138.4, 134.4, 131.7 (q, *J* = 33.2 Hz, 2C), 131.1, 129.4, 128.6, 128.1 (q, *J* = 4.0 Hz, 2C), 126.7, 125.9, 125.8, 125.7, 124.6 (q, *J* = 273.9 Hz, 2C), 122.9, 121.2-121.0 (m), 59.9, 47.6, 23.5, 23.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ_F: –62.7 (s).

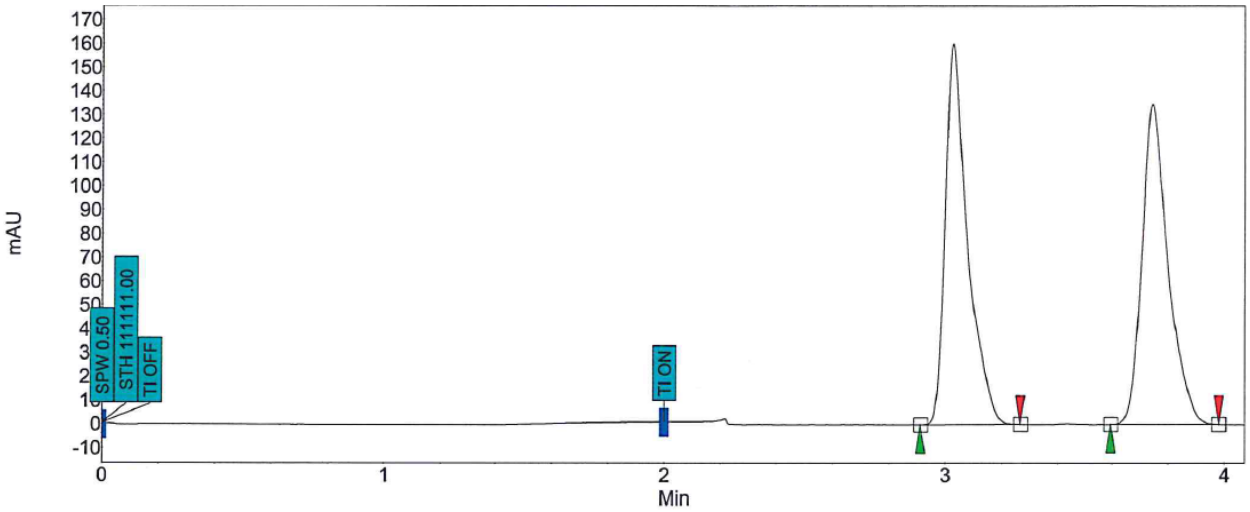
HRMS (ESI^+) $[C_{22}H_{20}NF_6]^+$ predicted 412.14945, found 412.15002 (Δ 1.4 ppm).

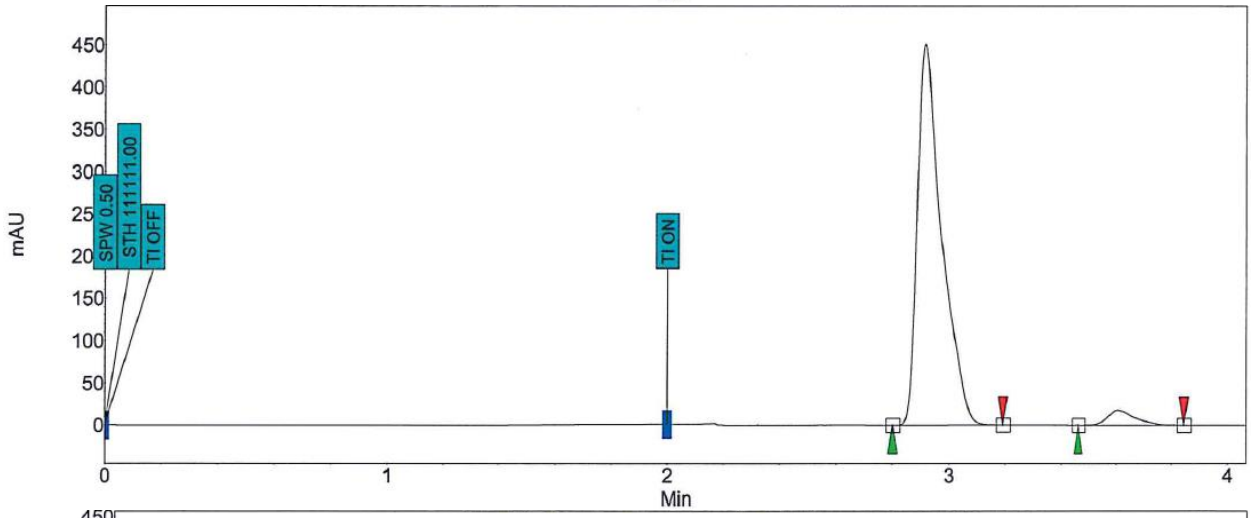
IR υ_{max} (film): 2965, 1371, 1275, 1126, 778.

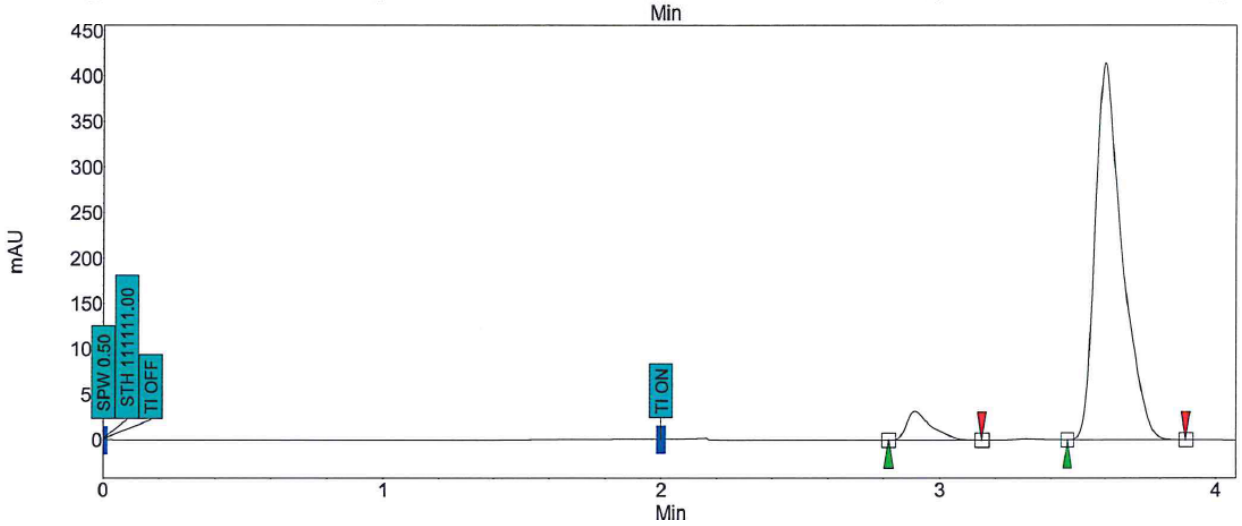
(–)-*(S)*-*N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)propan-2-amine (**L28S-amine**) (91.4% ee): $[\alpha]_{589}^{25}$ = –408.9 (*c* 4.23, $CHCl_3$).

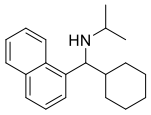
(+)-*N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)propan-2-amine (99.2% ee): $[\alpha]_{589}^{25}$ = +361.0 (*c* 3.49, $CHCl_3$).

The absolute stereochemistry of **L28S-amine** was proven by X-ray crystallography of its HCl salt. (See additional supporting information for crystallography data).









N-(cyclohexyl(naphthalen-1-yl)methyl)propan-2-amine

General procedure B: cyclohexyl(naphthalen-1-yl)methanone (2.41 g, 8.98 mmol, 1.0 eq.), DCM (26 ml) $TiCl_4$ solution in DCM (9.9 ml, 1.0 M, 9.90 mmol, 1.1 eq.), isopropylamine (2.3 ml, 26.9 mmol, 3.0 eq.), $NaB(CN)H_3$ solution in THF (26.9 ml, 1.0 M, 26.9 mmol, 3.0 eq.), anhydrous MeOH (5.1 ml), reaction duration 4 d. Following the work up procedure and purification by flash column chromatography [Basic Al_2O_3, petrol/EtOAc, 1:0 to 7:3], *N*-(cyclohexyl(naphthalen-1-yl)methyl)propan-2-amine was obtained as colourless oil (1.47 g, 58%).

The two enantiomers of *N*-(cyclohexyl(naphthalen-1-yl)methyl)propan-2-amine was separated by chiral UPLC [Chiralpak® AS-H; flow: 2 mL/min; 15% MeOH, 20 mM NH_3; λ = 280 nm; enantiomer (–)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)propan-2-amine, t_R = 2.77 min; enantiomer (+)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)propan-2-amine, t_R = 3.29 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.23 (s, br, 1H, $C_{Ar}H$), 7.93 – 7.86 (m, 1H, $C_{Ar}H$), 7.80 – 7.73 (m, 1H, $C_{Ar}H$), 7.67 – 7.43 (m, 4H, $C_{Ar}H$), 4.42 (s, br, 1H, ArC*H*), 2.54 (hept, *J* = 6.2 Hz, 1H, NC*H*CH_3), 1.99 (s, br, 1H, N*H*), 1.76 (d, *J* = 12.8 Hz, 2H, CH_2), 1.69 – 1.56 (m, 2H, CH_2), 1.41 (s, br, 2H, 1C$H_a$$CH_b$, C*H*), 1.23 – 1.04 (m, 5H, CH_aCH_b, 2CH_2), 1.03 (d, *J* = 6.1 Hz, 3H, CHCH_3), 0.97 (d, *J* = 6.3 Hz, 3H, CHCH_3).

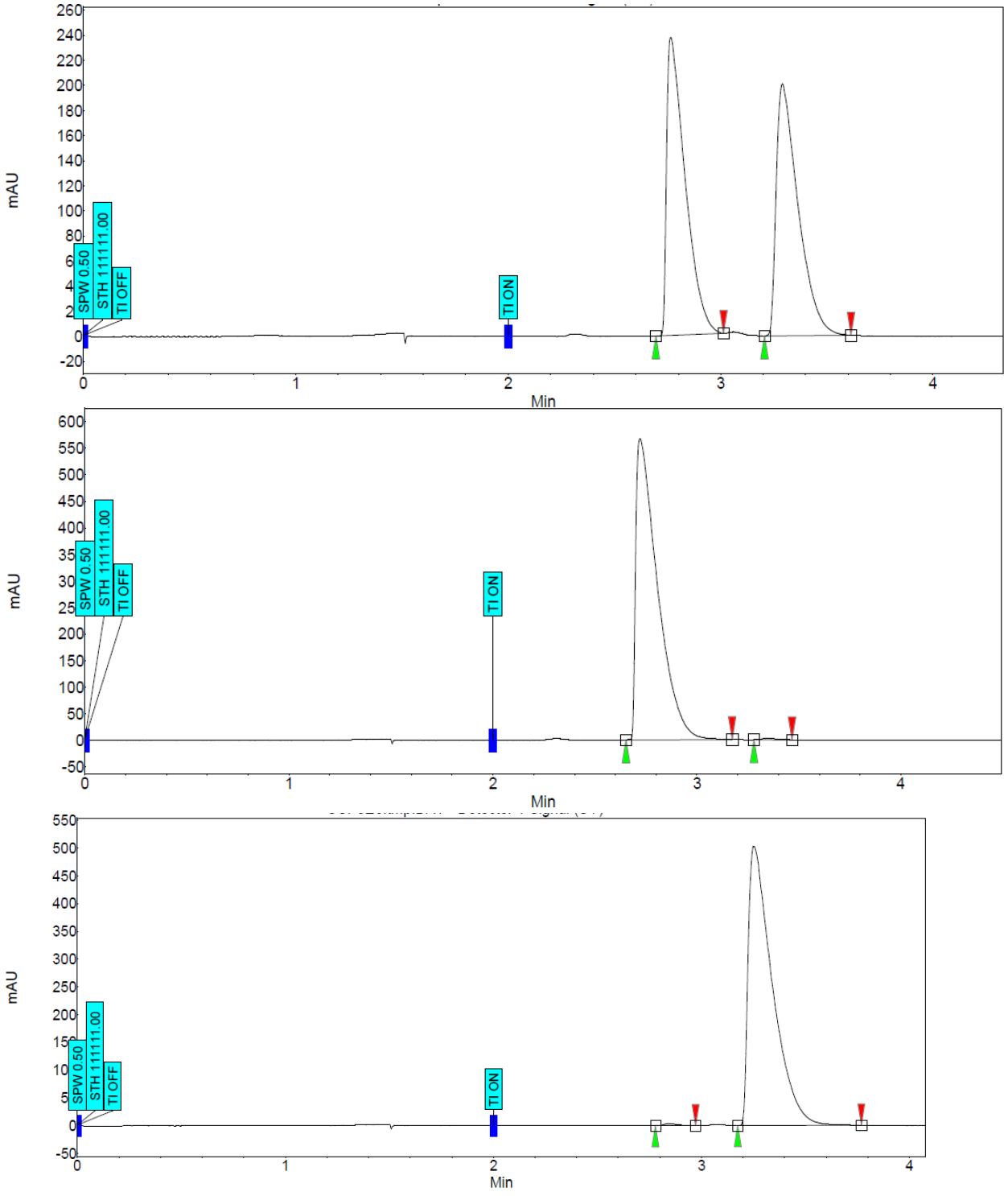
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 140.3 (br), 134.0, 132.6, 129.1, 126.9, 125.6, 125.5, 125.2 (2C), 123.8 (br), 59.1 (br), 46.3, 44.9 (br), 30.9, 29.8 (br), 26.7, 26.7, 26.5, 24.6, 22.5.

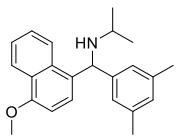
HRMS ($APCI^+$) $[C_{20}H_{28}N]^+$ predicted 282.22163, found 282.22165 (Δ 0.08 ppm).

IR υ_{max} (film): 3059, 2959, 2922, 776.

(–)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)propan-2-amine (99.3% ee): $[\alpha]_{589}^{25}$ = –139 (*c* 2.22, $CHCl_3$).

(+)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)propan-2-amine (99.1% ee): $[\alpha]_{589}^{25}$ = +113 (*c* 1.62, $CHCl_3$).





N-((3,5-dimethylphenyl)(2-methoxynaphthalen-1-yl)methyl)propan-2-amine

General procedure B: (3,5-dimethylphenyl)(2-methoxynaphthalen-1-yl)methanone (860 mg, 2.96 mmol, 1.0 eq.), DCM (8.5 ml) $TiCl_4$ solution in DCM (3.26 ml, 1.0 M, 3.26 mmol, 1.1 eq.), isopropylamine (0.76 ml, 8.89 mmol, 3.0 eq.), $NaB(CN)H_3$ solution in THF (8.9 ml, 1.0 M, 8.89 mmol, 3.0 eq.), anhydrous MeOH (1.69 ml), reaction duration 2 d. Following the work up procedure, *N*-((3,5-dimethylphenyl)(2-methoxynaphthalen-1-yl)methyl)propan-2-amine was obtained as brown residue (827 mg, 84%).

The two enantiomers of *N*-((3,5-dimethylphenyl)(2-methoxynaphthalen-1-yl)methyl)propan-2-amine was separated by chiral UPLC [Chiralcel® OD-H; flow: 2 mL/min; 40% MeOH, 20 mM NH_3; λ = 300 nm; enantiomer (–)-*N*-((3,5-dimethylphenyl)(2-methoxynaphthalen-1-yl)methyl)propan-2-amine, t_R = 2.39 min; enantiomer (+)-*N*-((3,5-dimethylphenyl)(2-methoxynaphthalen-1-yl)methyl)propan-2-amine, t_R = 3.20 min].

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.34 – 8.28 (m, 1H, $C_{Ar}H$), 8.17 – 8.11 (m, 1H, $C_{Ar}H$), 7.56 (dd, *J* = 8.0, 0.6 Hz, 1H, $C_{Ar}H$), 7.53 – 7.41 (m, 2H, $C_{Ar}H$), 7.04 – 7.00 (m, 2H, $C_{Ar}H$), 6.87 – 6.80 (m, 2H, $C_{Ar}H$), 5.61 (s, 1H, ArC*H*), 4.00 (s, 3H, OCH_3), 2.88 (hept, *J* = 6.3 Hz, 1H, NC*H*CH_3), 2.28 (s, 6H, ArCH_3), 1.44 (s, 1H, N*H*), 1.16 (d, *J* = 6.3 Hz, 3H, CHCH_3), 1.13 (d, *J* = 6.3 Hz, 3H, CHCH_3).

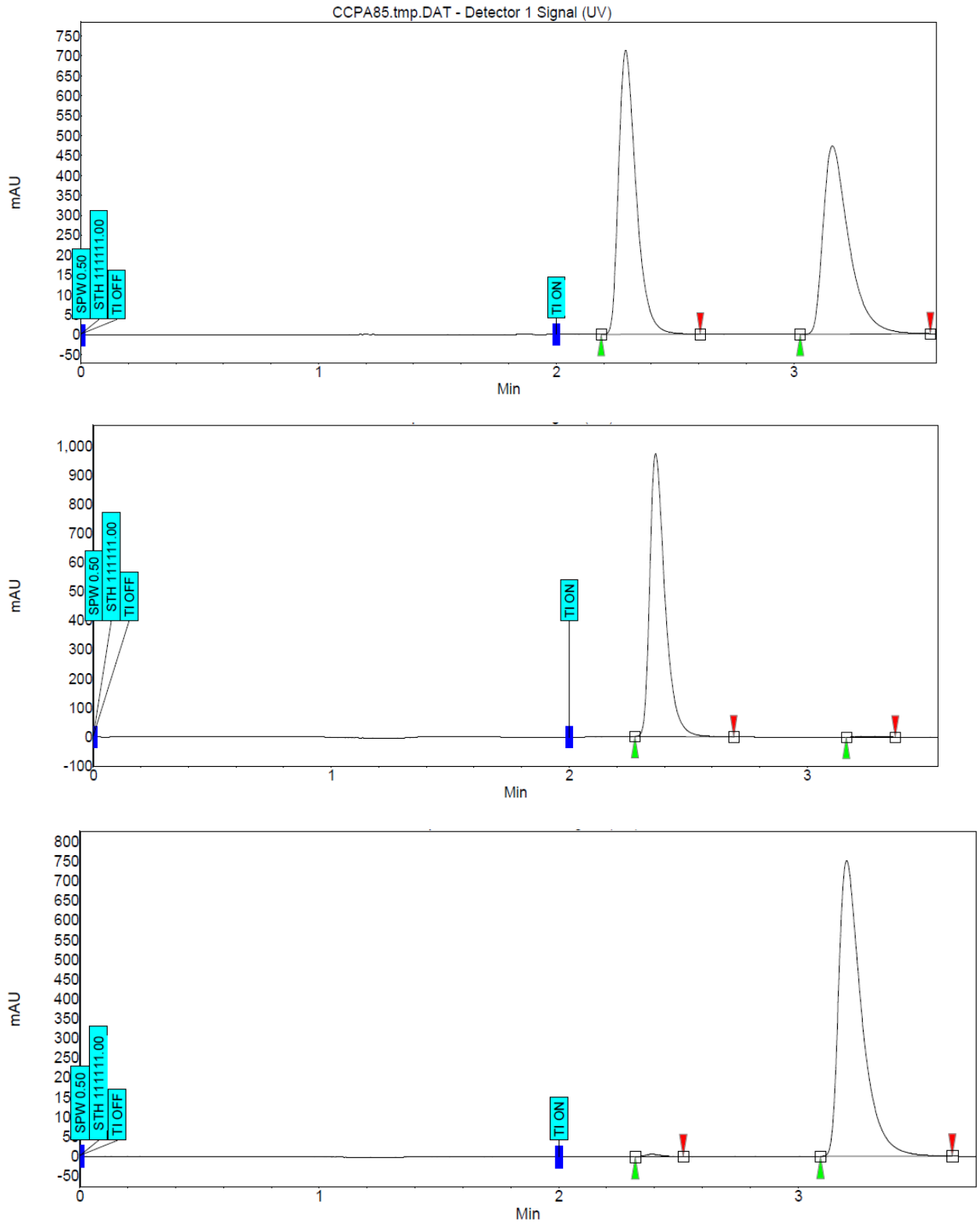
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 154.7, 144.4, 137.9 (2C), 132.5, 131.6, 128.6, 126.6, 126.1, 125.7 (2C), 125.3, 124.8, 123.4, 122.7, 103.5, 59.8, 55.6, 46.8, 23.5, 23.5, 21.5 (2C).

HRMS (ESI^+) $[C_{23}H_{27}ON^{23}Na]^+$ predicted 356.19849, found 356.19836 (Δ –0.34 ppm).

IR υ_{max} (film): 2959, 1586, 1091, 760.

(–)-*N*-((3,5-dimethylphenyl)(2-methoxynaphthalen-1-yl)methyl)propan-2-amine (99.1% ee): $[\alpha]_{589}^{25}$ = –27.6 (*c* 1.53, $CHCl_3$).

(+)-*N*-((3,5-dimethylphenyl)(2-methoxynaphthalen-1-yl)methyl)propan-2-amine (98.8% ee): $[\alpha]_{589}^{25}$ = +30.7 (*c* 1.67, $CHCl_3$).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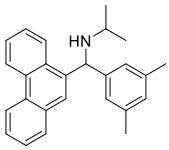


N-((3,5-dimethylphenyl)(phenanthren-9-yl)methyl)propan-2-amine

General procedure B: (3,5-dimethylphenyl)(phenanthren-9-yl)methanone (1.36 g, 4.30 mmol, 1.0 eq.), DCM (12 ml) $TiCl_4$ solution in DCM (12.0 ml, 1.0 M, 12.0 mmol, 1.1 eq.), isopropylamine (1.11 ml, 12.9 mmol, 3.0 eq.), $NaB(CN)H_3$ solution in THF (12.9 ml, 1.0 M, 12.9 mmol, 3.0 eq.), anhydrous MeOH (2.5 ml), reaction duration 2 d. Following the work up, *N*-((3,5-dimethylphenyl)(phenanthren-9-yl)methyl)propan-2-amine was obtained as orange residue (1.34 g, 88%).

The two enantiomers of *N*-((3,5-dimethylphenyl)(phenanthren-9-yl)methyl)propan-2-amine was separated by chiral UPLC [Chiralpak® IB; flow: 2 mL/min; 20% MeOH, 20 mM NH_3; λ = 300 nm; enantiomer (+)-*N*-((3,5-dimethylphenyl)(phenanthren-9-yl)methyl)propan-2-amine, t_R = 0.53 min; enantiomer (–)-*N*-((3,5-dimethylphenyl)(phenanthren-9-yl)methyl)propan-2-amine, t_R = 0.94 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.76 – 8.64 (m, 2H, $C_{Ar}H$), 8.18 (dd, *J* = 8.2, 1.4 Hz, 1H, $C_{Ar}H$), 8.07 (s, 1H, $C_{Ar}H$), 7.98 – 7.94 (m, 1H, $C_{Ar}H$), 7.68 – 7.50 (m, 4H), 7.07 – 7.01 (m, 2H, $C_{Ar}H$), 6.88 – 6.82 (m, 1H, $C_{Ar}H$), 5.66 (s, 1H, ArC*H*), 2.94 (hept, *J* = 6.3 Hz, 1H C*H*CH_3), 2.26 (s, 6H, ArCH_3), 1.18 (dd, *J* = 7.2, 6.3 Hz, 6H, CHCH_3).

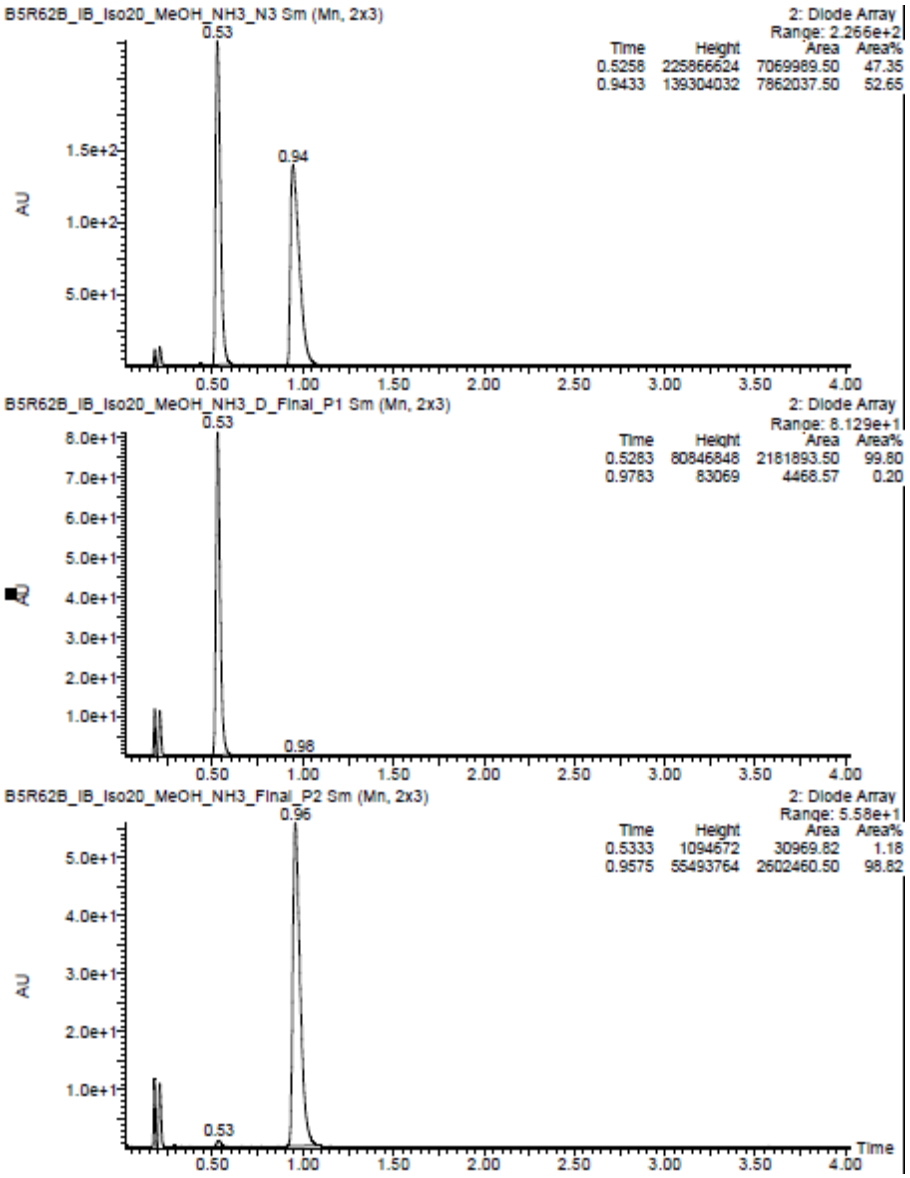
^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 143.9, 138.1 (2C), 137.3, 131.9, 131.1, 131.0, 130.1, 129.0, 128.9, 126.7, 126.7, 126.4, 126.1, 125.8 (3C), 124.6, 123.3, 122.5, 60.6, 47.1, 23.7, 23.4, 21.5 (2C).

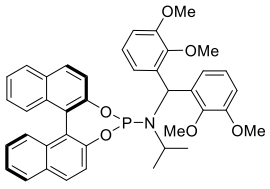
HRMS (ESI^+) $[C_{26}H_{28}N]^+$ predicted 354.22163, found 354.22178 (Δ 0.43 ppm).

IR υ_{max} (film): 2961, 1600, 1091, 726.

(+)-*N*-((3,5-dimethylphenyl)(phenanthren-9-yl)methyl)propan-2-amine (99.6% ee): $[\alpha]_{589}^{25}$= +21.2 (*c* 1.00, $CHCl_3$).

(–)-*N*-((3,5-dimethylphenyl)(phenanthren-9-yl)methyl)propan-2-amine (97.6% ee): $[\alpha]_{589}^{25}$= –130 (*c* 3.00, $CHCl_3$).





(R_a)-N-(bis(2,3-dimethoxyphenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L15**

General procedure C: $PCl_{3(l)}$ (62 µl, 0.71 mmol, 1.1 eq.) in DCM (2.5 ml), Et_3N (0.45 ml, 3.20 mmol, 5.0 eq.), *N*-(bis(2,3-dimethoxyphenyl)methyl)propan-2-amine (223 mg, 0.64 mmol, 1.0 eq.) in DCM (2.0 ml), *(R)*-binol (238 mg, 0.83 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [SiO_2, petrol/DCM/Et_3N, 90:9:1 then 78:21:1] to afford a mixture *N*-(bis(2,3-dimethoxyphenyl)methyl)propan-2-amine and Et_3N. To remove the residue

Et_3N, small amount of MeCN and DCM was added to the mixture and the solvents were removed *in vacuo* to afford white solid of *(R_a)-N*-(bis(2,3-dimethoxyphenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (324 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.94 – 7.84 (m, 4H, CH_{Ar}), 7.57 (d, *J* = 8.8 Hz, 1H, CH_{Ar}), 7.47 (dd, *J* = 8.7, 0.9 Hz, 1H, CH_{Ar}), 7.39 (m, 3H, CH_{Ar})7.32 – 7.16 (m, 4H, CH_{Ar}), 7.14 – 7.02 (m, 3H, CH_{Ar}), 6.92 – 6.87 (m, 2H, CH_{Ar}), 6.42 (d, *J* = 16.8 Hz, 1H, C*H*Ar), 3.92 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.55 (qq, *J* = 6.6, 6.7 Hz, 1H, C*H*Me_2), 1.02 (d, *J* = 6.7 Hz, 3H, CHCH_3), 0.89 (d, *J* = 6.6 Hz, 3H, CHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 153.0, 152.8, 150.8 (d, *J* = 6.9 Hz), 150.3, 146.5, 146.3, 137.7 (d, *J* = 7.2 Hz), 137.2 (d, *J* = 5.4 Hz), 132.9, 132.8, 131.4, 130.6, 130.1, 129.4, 128.3, 128.3, 127.2, 125.9, 125.8, 124.7, 124.3, 124.2, 123.4, 123.4, 123.1, 123.0, 123.0, 122.9, 122.7, 121.9 (d, *J* = 2.0 Hz), 111.8, 111.5, 60.1, 60.0, 56.0, 55.9, 49.3 (d, *J* = 25.2 Hz), 47.1 (d, *J* = 5.0 Hz), 23.2, 22.1.

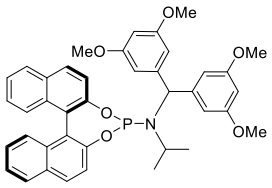
^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 148.8.

IR υ_{max} (film): 2934, 2833, 2360, 1588, 1477.

HRMS (Cl^+) $[C_{40}H_{38}NO_6P]^+$ predicted 659.2437, found 660.2532 (Δ -1.79 ppm).

MP. = 140-144˚C.

$[\alpha]_{589}^{25}$= +29.3 (*c* 1.0, $CHCl_3$).



(R_a)-N-(bis(3,5-dimethoxyphenyl)methyl)-N-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine **L16**

General procedure C: $PCl_{3(l)}$ (34 µl, 3.85 mmol, 1.1 eq.) in DCM (10 ml), Et_3N (2.44 ml, 17.5 mmol, 5.0 eq.), *N*-(bis(3,5-dimethoxyphenyl)methyl)propan-2-amine (1.21 g, 3.5 mmol, 1.0 eq.) in DCM (13 ml), *(S)*-binol (1.30 g, 4.55 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [SiO_2, petrol/DCM/Et_3N, 78:21:1 then 70:29:1] to afford a mixture of *N*-(bis(3,5-dimethoxyphenyl)methyl)propan-2-amine and Et_3N. To remove the residue Et_3N,

small amount of MeCN and DCM was added to the mixture and the solvents were removed *in vacuo* to afford white solid of N-(bis(3,5-dimethoxyphenyl)methyl)-N-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (2.09 g, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.95 – 7.78 (m, 4H, $C_{Ar}H$), 7.47 – 7.27 (m, 4H, $C_{Ar}H$), 7.29 – 7.10 (m, 4H, $C_{Ar}H$), 6.78 – 6.71 (m, 2H, $C_{Ar}H$), 6.60 – 6.53 (m, 2H, $C_{Ar}H$), 6.49 – 6.39 (m, 2H, $C_{Ar}H$), 5.56 (dd, *J* = 17.9, 3.5 Hz, 1H, C*H*Ar), 3.80 (s, 6H, OCH_3), 3.79 (s, 6H, OCH_3), 3.68 – 3.54 (m, 1H, C*H*Me), 1.13 – 1.00 (m, 6H, CHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 160.9, 160.7, 150.5, 150.5, 149.8, 146.06 (d, *J* = 6.0 Hz), 145.76 (d, *J* = 3.4 Hz), 137.9, 132.8, 132.7, 131.4, 130.6, 130.3, 129.5, 129.1, 128.4, 128.3, 128.3, 127.1, 127.1, 126.1, 126.0, 124.8, 124.5, 124.05 (d, *J* = 5.3 Hz), 122.3, 122.1, 121.8, 107.34 (d, *J* = 4.5 Hz), 106.91 (d, *J* = 4.0 Hz), 99.3, 98.9, 60.96 (d, *J* = 24.7 Hz, 2),55.4 (2C), 55.3 (2C), 47.0, 23.0, 22.9.

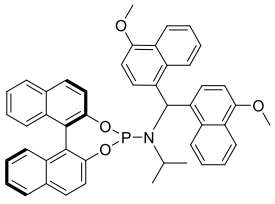
^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 149.5.

IR υ_{max} (film): 2933, 2836, 2360, 1594, 1156.

HRMS (CI^+) $[C_{40}H_{38}NO_6P]^+$ predicted 659.2437, found 660.2513 (Δ -0.56 ppm).

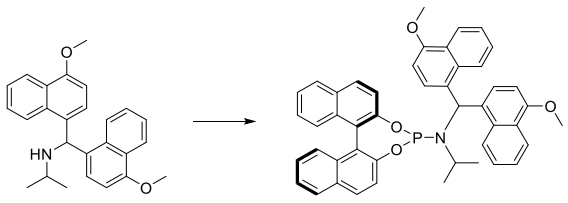
MP. = 114-118˚C.

$[\alpha]_{589}^{25}$= +111.3 (*c* 1.0, $CHCl_3$).



(R_a)-N-(bis(4-methoxynaphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L17**

General procedure B: bis(4-methoxynaphthalen-1-yl)methanone (1.41 g, 4.12 mmol, 1.0 eq.), DCM (12 ml), $TiCl_4$ solution in DCM (1.0 M, 4.53 ml, 4.53 mmol, 1.1 eq.), isopropylamine (2.12 ml, 24.8 mmol, 6.0 eq.), $NaB(CN)H_3$ (2.59 g, 41.2 mmol, 10.0 eq.) in THF (20.6 ml), anhydrous MeOH (2.3 ml), reaction duration 40 h. The amine was used without further purification.



Freshly distilled $PCl_{3(l)}$ (160 µl, 1.88 mmol, 1.1 eq.) was diluted in DCM (5.0 ml) and cooled in an ice bath. Et_3N (1.19 ml, 8.55 mmol, 5 eq.) was added dropwise to the cooled, stirring solution of PCl_3. The ice bath was removed and the solution was left to slowly warm up to rt over 10 mins. The crude mixture of N-(bis(4-methoxynaphthalen-1-yl)methyl)propan-2-amine (660 mg, 1.71 mmol, 1.0 eq.) in DCM (3 ml) was added dropwise to the stirred solution of Et_3N. The reaction mixture was stirred at rt for 5 h before *(R)*-binol (639 mg, 2.23 mmol, 1.3 eq.) was added and the mixture was continued to stir at rt for 14 h. The mixture was filtered through celite/DCM and solvent was evaporated under reduced pressure. The crude mixture was purified by flash column chromatography [SiO_2, petrol/DCM/Et_3N, 90:9:1 then 80:19:1] to afford *N*-(bis(4-methoxynaphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine as a white solid (1.14 g, 39 %over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.39 – 8.31 (m, 2H, $C_{Ar}H$), 8.28 (s, br, 1H, $C_{Ar}H$), 8.04 (s, br, 1H, $C_{Ar}H$), 7.86 – 7.79 (m, 4H, $C_{Ar}H$), 7.72 – 7.65 (m, 1H, $C_{Ar}H$), 7.57 – 7.43 (m, 4H, $C_{Ar}H$), 7.39 – 7.29 (m, 4H, $C_{Ar}H$), 7.30 – 7.10 (m, 4H, $C_{Ar}H$), 7.00 (d, *J* = 11.6 Hz, 1H, ArC*H*), 6.84 (d, *J* = 8.1 Hz, 1H, $C_{Ar}H$), 6.71 (d, *J* = 8.1 Hz, 1H, $C_{Ar}H$), 3.92 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.75 (q, *J* = 6.6, 6.0 Hz, 1H, C*H*CH_3), 1.14 (s, br 3H, CHCH_3), 0.96 (s, br, 3H, CHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 155.2, 155.2, 149.8, 132.7(2C), 132.6, 132.0 (br), 131.8, 131.2, 130.5 (br), 130.3, 130.0(2C), 129.6 (br), 129.2 (2C), 128.8 (br), 128.2, 128.1, 127.0, 127.0, 126.7, 126.6, 126.1, 126.0, 125.8, 125.7, 124.9, 124.9, 124.5, 124.1, 124.0 (d, *J* = 5.5 Hz), 123.4, 123.2, 122.8, 122.6, 122.4, 121.4 (br), 102.9, 102.8, 55.4, 55.4, 54.2 (d, *J* = 27.4 Hz), 47.8, 24.0, 23.1.

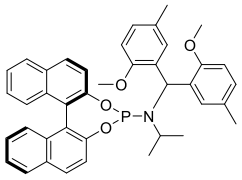
^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 148.0.

IR υ_{max} (film): 3069, 2935, 1622, 1462, 945.

HRMS (EI^+) $[C_{46}H_{38}NO_4P]^+$ predicted 699.2538, found 699.2547 (Δ -0.72 ppm).

M.P. = 196 - 202 ˚C.

$[\alpha]_{589}^{25}$ = –36.6 (*c* 1.0, $CHCl_3$)



(R_a)-N-(bis(2-methoxy-5-methylphenyl)methyl)-N-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine **L18**

General procedure C: $PCl_{3(l)}$ (74 µl, 0.85 mmol, 1.1 eq.) in DCM (2.5 ml), Et_3N (0.54 ml, 3.88 mmol, 5.0 eq.), *N*-(bis(2-methoxy-5-methylphenyl)methyl)propan-2-amine (243 mg, 0.78 mmol, 1.0 eq.) in DCM (2.5 ml), *(R)*-binol (289 mg, 1.01 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [SiO_2, petrol/DCM/Et_3N, 90:9:1 then 80:19:1] and filtered through a small amount of silica gel/$CHCl_3$ to remove impurity. The purification process yielded white solid of N-(bis(2-methoxy-5-methylphenyl)methyl)-N-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (258 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 7.95 – 7.86 (m, 4H, $C_{Ar}H$), 7.50 – 7.18 (m, 8H, $C_{Ar}H$), 7.16 – 7.05 (m, 4H, $C_{Ar}H$), 6.83 (m, 2H, $C_{Ar}H$), 6.34 (d, *J* = 16.9 Hz, 1H, C*H*Ar), 3.91 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.58 – 3.47 (m, 1H, C*H*Me), 2.34 (s, 3H, CCH_3), 2.33 (s, 3H, CCH_3), 0.96 (d, *J* = 6.6 Hz, 3H, CHCH_3), 0.88 (d, *J* = 6.5 Hz, 3H, CHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 154.7, 154.5, 151.0, 150.9, 150.3, 132.9, 132.8, 131.5, 131.4 (2C), 131.3, 131.0, 130.9, 130.5, 130.1, 129.4, 128.9, 128.6, 128.6, 128.3 (2C), 127.2, 127.1, 125.9, 125.8, 124.6, 124.3, 124.2, 122.6, 122.5, 121.8, 110.7, 55.6 (2C), 49.1 (d, *J* = 30.0 Hz), 47.23 (d, *J* = 5.4 Hz), 23.0, 22.0, 21.1, 21.1.

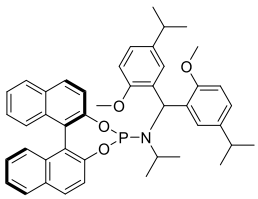
^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 149.3.

IR υ_{max} (film): 2971, 2834, 2360, 1590, 1499.

HRMS (Cl^+) $[C_{40}H_{38}NO_4P]^+$ predicted 627.2538, found 628.2613 (Δ 4.55 ppm).

MP. = 138-144˚C.

$[\alpha]_{589}^{25}$ = –86.1 (*c* 1.00, $CHCl_3$).



(R_a)-N-(bis(5-isopropyl-2-methoxyphenyl)methyl)-N-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine **L19**

General procedure C: $PCl_{3(l)}$ (68 µl, 0.77 mmol, 1.1 eq.) in DCM (2.0 ml), Et_3N (0.49 ml, 3.52 mmol, 5.0 eq.), *N*-(bis(5-isopropyl-2-methoxyphenyl)methyl)propan-2-amine (260 mg, 0.70 mmol, 1.0 eq.) in DCM (2.7 ml), *(R)*-binol (262 mg, 0.92 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [SiO_2, petrol/DCM/Et_3N, 90:9:1 then 80:19:1] to afford white solid of N-(bis(5-isopropyl-2-methoxyphenyl)methyl)-N-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (498 mg, quantitative yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.05 – 7.93 (m, 4H, $C_{Ar}H$), 7.65 – 7.55 (m, 1H, $C_{Ar}H$), 7.57 – 7.18 (m, 11H, $C_{Ar}H$), 6.99 – 6.90 (m, 2H, $C_{Ar}H$), 6.53 (dd, *J* = 16.7, 2.0 Hz, 1H, C*H*Ar), 4.00 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 3.72 – 3.59 (m, 1H, NC*H*Me), 3.07 – 2.93 (m, 2H, CC*H*Me), 1.36 (m, 12H, CCHCH_3), 1.14 (d, *J* = 6.8 Hz, 3H, NCHCH_3), 1.00 (d, *J* = 6.6 Hz, 3H, NCHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 154.9, 154.7, 151.1, 151.1, 150.4, 140.1, 140.0, 133.0, 132.8, 131.3, 131.3, 131.1, 131.0, 130.5, 130.1, 129.3, 129.1, 129.0, 128.9, 128.8, 128.3, 128.3, 127.2, 127.2, 125.9, 125.9, 125.8, 124.6, 124.3, 124.3, 122.7, 121.8, 110.5, 110.5, 49.1 (d, *J* = 29.6 Hz, 25), 47.2 (d, *J* = 5.5 Hz, 26), 33.5, 33.5, 24.6, 24.4, 24.4, 24.2, 23.1, 22.0.

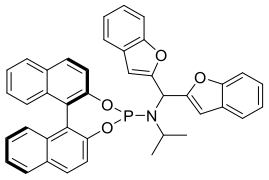
^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 149.7.

IR υ_{max} (film): 3055, 2957, 2834, 1497.

HRMS (Cl^+) $[C_{44}H_{46}NO_4P]^+$ predicted 683.3164, found 684.3235 (Δ -1.63 ppm).

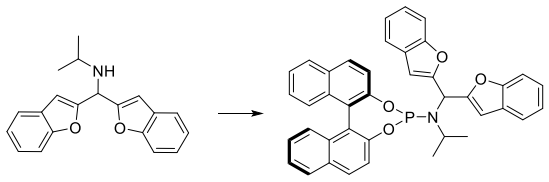
MP. = 218-219˚C.

$[\alpha]_{589}^{25}$ = –78.6 (*c* 1.0, $CHCl_3$).



(R_a)-N-(di(benzofuran-2-yl)methyl)-*N*-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine **L20**

General procedure B: Di(benzofuran-2-yl)methanone (278 mg, 1.06 mmol, 1.0 eq.), DCM (4 ml), $TiCl_4$ solution in DCM (1.0 M, 1.17 ml, 1.17 mmol, 1.1 eq.), isopropylamine (273 µl, 3.18 mmol, 3.0 eq.), $NaB(CN)H_3$ (333 mg, 5.30 mmol, 5.0 eq.) in THF (5.3 ml), anhydrous MeOH (0.61 ml), reaction duration 40 h. The amine was used without further purification.



Freshly distilled $PCl_{3(l)}$ (90 µl, 1.03 mmol, 1.1 eq.) was diluted in DCM (3.0 ml) and cooled in an ice bath. Et_3N (0.66 ml, 4.70 mmol, 5 eq.) was added dropwise to the cooled, stirring solution of

PCl_3. The ice bath was removed and the solution was left to slowly warm up to rt over 10 mins. The crude mixture of N-(di(benzofuran-2-yl)methyl)propan-2-amine (286 mg, 0.94 mmol, 1.0 eq.) in DCM (3.0 ml) was added dropwise to the stirred solution of Et_3N. The reaction mixture was stirred at rt for 5 h before *(R)*-binol (349 mg, 1.22 mmol, 1.3 eq.) was added and the mixture was continued to stir at rt for 17 h. The mixture was filtered through celite/DCM and solvent was evaporated under reduced pressure. The crude mixture was purified by flash column chromatography [SiO_2, petrol/DCM/Et_3N, 80:19:1] to afford *N*-(di(benzofuran-2-yl)methyl)-*N*-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine as a white solid (181 mg, 31 %over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.01 – 7.83 (m, 3H, $C_{Ar}H$), 7.69 – 7.50 (m, 6H, $C_{Ar}H$), 7.48 – 7.16 (m, 11H, $C_{Ar}H$), 6.69 (s, 1H, $C_{Ar}H$), 6.61 (s, 1H, $C_{Ar}H$), 5.93 (d, *J* = 13.0 Hz, 1H, ArC*H*), 3.84 – 3.70 (m, 1H, C*H*CH_3), 1.34 (d, *J* = 6.8 Hz, 3H, CHCH_3), 1.18 (d, *J* = 6.6 Hz, 3H, CHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 156.3 (br), 156.1 (br), 155.1, 154.9, 149.7, 149.7 , 132.9, 132.7, 131.5, 130.8, 130.4, 129.6, 128.4, 128.3 (2C), 128.3, 127.2, 127.2, 126.1, 126.1, 124.9, 124.6, 124.5, 124.4, 124.1 (d, *J* = 6 Hz), 123.0, 122.9, 122.4 (2C), 122.1 (d, *J* = 2 Hz), 121.3, 121.2, 111.4, 111.4, 106.4 (d, *J* = 4 Hz), 105.9 (d, *J* = 2 Hz), 50.0 (d, *J* = 18 Hz), 47.7 (d, *J* = 8 Hz), 23.7, 23.7.

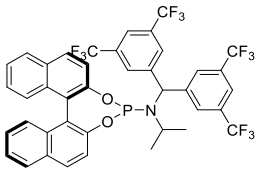
^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 148.4.

IR υ_{max} (film): 2972, 1619, 1503, 946, 731.

HRMS (CI^+) $[C_{40}H_{31}NO_4P]^+$ predicted 620.1985, found 620.1929 (Δ -9.0 ppm).

M.P. = 98.0 - 108 ˚C.

$[\alpha]_{589}^{25}$ = –132.5 (*c* 1.0, $CHCl_3$)



(R_a)-N-(bis(3,5-bis(trifluoromethyl)phenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L21**

General procedure C: $PCl_{3(l)}$ (1.17 µl, 13.4 mmol, 1.1 eq.) in DCM (11.0 ml), Et_3N (8.5 ml, 61.0 mmol, 5.0 eq.), *N*-(bis(3,5-bis(trifluoromethyl)phenyl)methyl)propan-2-amine (6.07 g, 12.2 mmol, 1.0 eq.) in DCM (50.0 ml), *(R)*-binol (4.55 mg, 15.9 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of *(R_a)-N*-(bis(3,5-bis(trifluoromethyl)phenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (3.41 g, 78%).

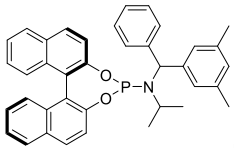
^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.09 – 7.92 (m, 7H, $C_{Ar}H$), 7.91 (s, 2H, $C_{Ar}H$), 7.86 (d, *J* = 8.8 Hz, 1H, $C_{Ar}H$), 7.56 – 7.43 (m, 4H, $C_{Ar}H$), 7.40 – 7.24 (m, 4H, $C_{Ar}H$), 6.02 (d, *J* = 15.4 Hz, 1H, ArC*H*), 3.70 (h, *J* = 6.5 Hz, 1H, C*H*CH_3), 1.30 (d, *J* = 6.7 Hz, 3H, CHC*H*$_3$), 1.04 (d, *J* = 6.5 Hz, 3H, CHC*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C:

^{31}P NMR {^{1}H} (162 MHz, $CDCl_3$) δ_P: 146.3 (s).

$[\alpha]_{589}^{25}$= –159 (*c* 1.00, $CHCl_3$)

Data was consistent with previously reported values.[6]



(R_a,R or *S)-N*-((3,5-dimethylphenyl)(phenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L22a**

General procedure C: $PCl_{3(l)}$ (30 µl, 0.35 mmol, 1.1 eq.) in DCM (1.0 ml), Et_3N (0.22 ml, 1.58 mmol, 5.0 eq.), (–)-*N*- ((3,5-dimethylphenyl)(phenyl)methyl)propan-2-amine (80 mg, 0.32 mmol, 1.0 eq.) in DCM (1.0 ml), *(R)*-binol (118 mg, 0.41 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 85:15] to afford white solid of *N*-((3,5-dimethylphenyl)(phenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (37 mg, 20%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.93 – 7.84 (m, 3H, $C_{Ar}H$), 7.79 (d, *J* = 8.8 Hz, 1H, $C_{Ar}H$), 7.43 – 7.23 (m, 12H, $C_{Ar}H$), 7.22 – 7.17 (m, 1H, $C_{Ar}H$), 7.09 (s, 2H, $C_{Ar}H$), 6.95 (s, 1H, $C_{Ar}H$), 5.62 (d, *J* = 17.1 Hz, 1H, ArC*H*), 3.62 – 3.52 (m, 1H, C*H*CH_3), 2.35 (s, 6H, ArC*H*$_3$), 1.06 (d, *J* = 6.8 Hz, 3H, CHC*H*$_3$), 0.97 (d, *J* = 6.5 Hz, 3H, CHC*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 150.6 (d, *J* = 7.1 Hz), 150.1, 143.9 (d, *J* = 5.9 Hz), 143.4 (d, *J* = 3.9 Hz), 137.8 (2C), 132.9 (d, *J* = 1.8 Hz), 132.8, 131.5, 130.6, 130.3, 129.4, 129.2, 129.2, 128.7, 128.4, 128.3, 128.2 (2C), 127.3, 127.2, 127.0, 126.8, 126.8, 126.0, 125.9, 124.8, 124.4, 124.1 (d, *J* = 5.4 Hz), 122.6 (d, *J* = 2.1 Hz), 122.3, 121.9 (d, *J* = 2.3 Hz), 60.8 (d, *J* = 24.3 Hz), 47.0, 23.3, 23.1, 21.7 (2C).

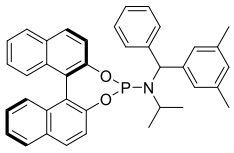
^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 149.6 (d, 17.1 Hz).

IR υ_{max} (film): 3058, 2973, 2926, 1591,1232, 948.

HRMS (CI^+) $[C_{38}H_{35}NO_2P]^+$ predicted 568.2400, found 568.2403 (Δ –0.54 ppm).

M.P. = 89 – 93 ˚C.

$[\alpha]_{589}^{25}$= –163 (*c* 1.00, $CHCl_3$)



(R_{α},R or *S)-N*-((3,5-dimethylphenyl)(phenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L22b**

General procedure C: $PCl_{3(l)}$ (30 µl, 0.35 mmol, 1.1 eq.) in DCM (1.0 ml), Et_3N (0.22 ml, 1.58 mmol, 5.0 eq.), (+)-*N*- ((3,5-dimethylphenyl)(phenyl)methyl)propan-2-amine (82 mg, 0.32 mmol, 1.0 eq.) in DCM (1.0 ml), *(R)*-binol (118 mg, 0.41 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 85:15] to afford white solid of *N*-((3,5-dimethylphenyl)(phenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (65 mg, 35%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.97 – 7.87 (m, 3H, $C_{Ar}H$), 7.84 (d, *J* = 8.7 Hz, 1H, $C_{Ar}H$), 7.51 – 7.21 (m, 14H, $C_{Ar}H$), 6.98 (s, 2H, $C_{Ar}H$), 6.94 (s, 1H, $C_{Ar}H$), 5.65 (d, *J* = 17.9 Hz, 1H, ArC*H*), 3.61 (qq, *J* = 6.7, 6.6 Hz, 1H, C*H*CH_3), 2.36 (s, 6H, ArCH_3), 1.09 (d, *J* = 6.7 Hz, 3H, CHCH_3), 0.99 (d, *J* = 6.6 Hz, 3H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 150.7 (d, *J* = 7.3 Hz), 150.0, 143.9 (d, *J* = 4.6 Hz), 143.6 (d, *J* = 5.4 Hz), 137.7 (2C), 132.9 (d, *J* = 1.8 Hz), 132.9, 131.4, 130.6, 130.3, 129.5, 129.1, 129.0, 128.7, 128.4 (3C), 128.3, 127.3, 127.2, 127.1, 126.9, 126.9, 126.0, 125.9, 124.8 (d, *J* = 2.8 Hz), 124.4, 124.2 (d, *J* = 5.5 Hz), 122.5 (d, *J* = 2.0 Hz), 122.4, 121.8 (d, *J* = 2.3 Hz), 60.8 (d, *J* = 25.4 Hz), 46.9, 23.2, 23.0 (d, *J* = 2.7 Hz), 21.7 (2C).

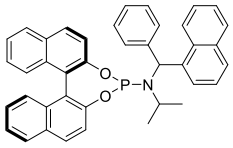
^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 149.4 (d, *J* = 17.9 Hz).

IR υ_{max} (film): 3057, 2972, 2927, 1591,1231, 948.

HRMS (Cl^+) $[C_{38}H_{35}NO_2P]^+$ predicted 568.2400, found 568.2378 (Δ 3.86 ppm).

M.P. = 82 – 88 ˚C.

$[\alpha]_{589}^{25}$= –39.1 (*c* 0.50, $CHCl_3$)



(R_a,R or *S)-N*-isopropyl-*N*-(naphthalen-1-yl(phenyl)methyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L23a**

General procedure C: $PCl_{3(l)}$ (64 µl, 0.74 mmol, 1.1 eq.) in DCM (0.5 ml), Et_3N (0.47 ml, 3.35 mmol, 5.0 eq.), (–)-*N*-(naphthalen-1-yl(phenyl)methyl)propan-2-amine (185 mg, 0.67 mmol, 1.0 eq.) in DCM (2.4 ml), *(R)*-binol (249 mg, 0.87 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of (R_a, *R* or *S*)-*N*-isopropyl-*N*-(naphthalen-1-yl(phenyl)methyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine with trace of grease (268 mg, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.05 (d, *J* = 7.2 Hz, 1H, $C_{Ar}H$), 7.97 – 7.81 (m, 7H, $C_{Ar}H$), 7.65 (t, *J* = 7.7 Hz, 1H, $C_{Ar}H$), 7.53 (dd, *J* = 8.8, 3.8 Hz, 2H, $C_{Ar}H$), 7.50 – 7.16 (m, 13H, $C_{Ar}H$), 6.46 (d, *J* = 16.3 Hz, 1H, ArC*H*), 3.80 – 3.71 (m, 1H, C*H*CH_3), 1.32 (d, *J* = 6.6 Hz, 3H, CHCH_3), 0.70 (d, *J* = 6.6 Hz, 3H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 150.5 (d, *J* = 8.2 Hz), 150.1, 143.0 (d, *J* = 9.9 Hz), 138.6 (d, *J* = 1.6 Hz), 134.0, 132.9 (2C), 132.9, 131.5, 131.0, 130.6, 130.4, 129.7 (d, *J* = 3.5 Hz, 2C), 129.0, 128.4 (2C), 128.4, 128.3, 128.2, 127.4, 127.3, 127.2, 126.6 (d, *J* = 7.6 Hz), 126.3, 126.1, 126.0, 125.6, 125.5, 124.8, 124.5, 124.2 (d, *J* = 5.4 Hz), 123.7, 122.5 (d, *J* = 2.0 Hz), 122.4, 121.8 (d, *J* = 2.3 Hz), 57.2 (d, *J* = 28.0 Hz), 46.7 (d, *J* = 4.1 Hz), 23.4, 22.9.

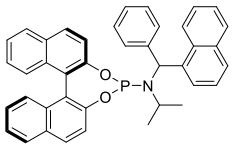
^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 149.2 (d, *J* = 16.1 Hz).

IR υ_{max} (film): 3059, 2971, 2972, 1591,1231, 948.

HRMS (Cl^+) $[C_{40}H_{33}NO_2P]^+$ predicted 590.2243, found 590.2248 (Δ –0.78 ppm).

M.P. = 108 – 118 ˚C.

$[\alpha]_{589}^{25}$= 21.3 (*c* 1.00, $CHCl_3$)



(R_a, R or *S)- N*-isopropyl-*N*-(naphthalen-1-yl(phenyl)methyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L23b**

General procedure C: $PCl_{3(l)}$ (64 µl, 0.74 mmol, 1.1 eq.) in DCM (0.5 ml), Et_3N (0.47 ml, 3.35 mmol, 5.0 eq.), (+)-*N*-(naphthalen-1-yl(phenyl)methyl)propan-2-amine (177 mg, 0.64 mmol,

1.0 eq.) in DCM (2.4 ml), *(R)*-binol (249 mg, 0.87 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of (*R_a*, *R* or *S*)-*N*-isopropyl-*N*-(naphthalen-1-yl(phenyl)methyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (125 mg, 32%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.30 (d, *J* = 7.1 Hz, 1H, $C_{Ar}H$), 7.94 – 7.85 (m, 4H, $C_{Ar}H$), 7.76 – 7.66 (m, 2H, $C_{Ar}H$), 7.51 – 7.30 (m, 8H, $C_{Ar}H$), 7.30 – 7.03 (m, 9H, $C_{Ar}H$), 6.41 (d, *J* = 13.3 Hz, 1H, ArC*H*), 3.64 (h, *J* = 6.4 Hz, 1H, C*H*CH_3), 1.12 (d, *J* = 6.4 Hz, 3H, CHCH_3), 1.04 (s, br, 3H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 150.4, 149.9, 142.6 (d, *J* = 8.2 Hz), 139.1, 134.0, 132.9, 132.7, 131.5, 131.0, 130.5, 130.3, 129.8 (d, *J* = 3.0 Hz, 2C), 129.3, 128.8, 128.4, 128.3, 128.3 (2C), 128.1, 127.3, 127.2, 127.1, 126.1 (2C), 126.0, 125.9, 125.6, 125.4, 124.8, 124.3, 124.2 (d, *J* = 5.3 Hz), 123.7, 122.5 (d, *J* = 1.9 Hz), 122.0, 121.7 (d, *J* = 2.3 Hz), 57.8 (d, *J* = 20.4 Hz), 47.8, 23.9, 23.2.

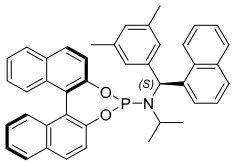
^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 149.8 (s, br)

IR υ_{max} (film): 3056, 2972, 1591,1231, 947.

HRMS (CI^+) $[C_{40}H_{33}NO_2P]^+$ predicted 590.2243, found 590.2226 (Δ 2.96 ppm).

(**M.P.** is unobtainable due to thermal decomposition.)

$[\alpha]_{589}^{25}$ = –156.9 (*c* 1.00, $CHCl_3$)



(R_a,S)-*N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L24S**

General procedure C: $PCl_{3(l)}$ (31 µl, 0.35 mmol, 1.1 eq.) in DCM (1.0 ml), Et_3N (0.22 ml, 1.58 mmol, 5.0 eq.), (–)-*N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine (90.2 mg, 0.30 mmol, 1.0 eq.) in DCM (1.0 ml), *(R)*-binol (120 mg, 0.41 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of *N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (62.2 mg, 34%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.01 – 7.83 (m, 8H, $C_{Ar}H$), 7.67 – 7.60 (m, 1H, $C_{Ar}H$), 7.55 – 7.34 (m, 7H, $C_{Ar}H$), 7.28 – 7.16 (m, 3H, $C_{Ar}H$), 6.94 (s, 2H, $C_{Ar}H$), 6.86 (s, 1H, $C_{Ar}H$), 6.39 (d, *J* = 15.8 Hz, 1H, ArC*H*), 3.79 – 3.69 (m, 1H, C*H*CH_3), 2.26 (s, 6H, ArCH_3), 1.28 (d, *J* = 6.3 Hz, 3H, CHCH_3), 0.68 (d, *J* = 6.5 Hz, 3H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 150.5 (d, *J* = 7.8 Hz), 150.2, 142.8 (d, *J* = 9.8 Hz), 138.8 (d, *J* = 1.9 Hz), 137.7 (2C), 133.9, 132.9 (d, *J* = 2.1 Hz, 2C), 131.4, 131.2 (d, *J* = 1.7 Hz), 130.6, 130.3, 129.5, 129.1, 128.9, 128.3, 128.3, 128.1, 127.6, 127.6, 127.3, 127.1, 126.8 (d, *J* = 7.7 Hz), 126.2, 126.0, 126.0, 125.5, 125.4, 124.8, 124.5, 124.2 (d, *J* = 5.4 Hz), 123.8, 122.6 (d, *J* = 1.9 Hz), 122.3, 121.9 (d, *J* = 2.2 Hz), 57.1 (d, *J* = 27.4 Hz), 46.6 (d, *J* = 3.9 Hz), 23.4, 22.9, 21.6 (2C).

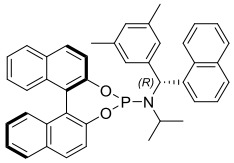
^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 149.5 (d, *J* = 15.9 Hz).

IR υ_{max} (film): 3053, 2971, 2927, 1591,1231, 948.

HRMS (Cl^+) $[C_{42}H_{36}NO_2P]^+$ predicted 618.2556, found 618.2582 (Δ –4.14 ppm).

M.P. = 118 – 122 ˚C.

$[\alpha]_{589}^{25}$= 51.4 (*c* 1.00, $CHCl_3$)



(R_a,R)-*N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L24R**

General procedure C: $PCl_{3(l)}$ (31 µl, 0.35 mmol, 1.1 eq.) in DCM (1.0 ml), Et_3N (0.22 ml, 1.58 mmol, 5.0 eq.), (+)-*N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine (97.8 mg, 0.30 mmol, 1.0 eq.) in DCM (1.0 ml), *(R)*-binol (120 mg, 0.41 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of (R_a, *R* or *S*)-*N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (136 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.25 (d, *J* = 7.2 Hz, 1H, $C_{Ar}H$), 7.96 – 7.86 (m, 4H, $C_{Ar}H$), 7.78 – 7.68 (m, 2H, $C_{Ar}H$), 7.65 – 7.31 (m, 8H, $C_{Ar}H$), 7.30 – 7.17 (m, 4H, $C_{Ar}H$), 6.86 (s, 1H, $C_{Ar}H$), 6.83 (s, 2H, $C_{Ar}H$), 6.34 (d, *J* = 13.9 Hz, 1H, ArC*H*), 3.62 (h, *J* = 6.5 Hz, 1H, C*H*CH_3), 2.24 (s, 6H, ArCH_3), 1.13 (d, *J* = 6.2 Hz, 3H, CHCH_3), 0.94 (s, br, 3H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 150.6, 150.0, 142.5 (d, *J* = 7.7 Hz), 139.4, 137.6 (2C), 134.0, 132.9 (d, *J* = 1.6 Hz), 132.7, 131.4, 131.1, 130.5, 130.2, 129.3, 129.0, 128.8, 128.4, 128.3, 128.0, 127.6 (d, *J* = 3.1 Hz, 2C), 127.2, 127.2, 126.4, 126.1, 126.0, 125.8, 125.5, 125.5, 124.7, 124.3, 124.2 (d, *J* = 5.3 Hz), 123.7, 122.6 (d, *J* = 1.9 Hz), 122.1, 121.7 (d, *J* = 2.3 Hz), 57.6 (d, *J* = 22.3 Hz), 47.7, 23.7 (br), 23.1 (br), 21.6 (2C).

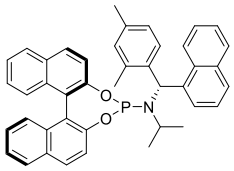
^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 150.0 (s, br).

IR υ_{max} (film): 3053, 2969, 1591,1230, 947.

HRMS (CI^+) $[C_{42}H_{36}NO_2P]^+$ predicted 618.2556, found 618.2538 (Δ 2.98 ppm).

(**M.P.** is unobtainable due to thermal decomposition.)

$[\alpha]_{589}^{25}$ = –228 (*c* 1.00, $CHCl_3$)



(*R*$_a$,*R*)-*N*-(-(2,4-dimethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L25R**

General procedure C: $PCl_{3(l)}$ (82 µl, 0.94 mmol, 1.1 eq.) in DCM (1.3 ml), Et_3N (0.59 ml, 4.26 mmol, 5.0 eq.), (+)-(*R*)-*N*-((2,4-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine (258 mg, 0.85 mmol, 1.0 eq.) in DCM (3.0 ml), *(R)*-binol (317 mg, 1.11 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of (*R*$_a$,)-*N*-((*R*)-(2,4-dimethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (357 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.03 (s, br, 1H, $C_{Ar}H$), 7.92 – 7.74 (m, 6H, $C_{Ar}H$), 7.71 (s, br, 1H, $C_{Ar}H$), 7.56 – 7.40 (m, 4H, $C_{Ar}H$), 7.39 – 7.31 (m, 3H, $C_{Ar}H$), 7.27 – 7.09 (m, 5H, $C_{Ar}H$), 7.03 (s, 1H, $C_{Ar}H$), 6.93 (d, *J* = 7.9 Hz, 1H, $C_{Ar}H$), 6.52 (d, *J* = 12.5 Hz, 1H, ArC*H*), 3.75 – 3.65 (m, 1H, C*H*CH_3), 2.41 (s, 3H, ArCH_3), 2.31 (s, 3H, ArCH_3), 1.09 (d, *J* = 6.8 Hz, 3H, CHCH_3), 0.90 (d, *J* = 6.6 Hz, 3H. CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 150.6 (d, *J* = 7.3 Hz), 150.0, 138.8, 138.7 (d, *J* = 6.4 Hz), 137.0, 135.6, 134.2, 132.9, 132.8, 131.7, 131.4, 131.1, 130.6 (d, *J* = 5.2 Hz), 130.4, 130.2, 129.3, 129.1, 128.3 (4C), 127.2, 127.1, 126.5, 126.2, 126.0, 125.9, 125.6, 125.1, 124.7, 124.3, 124.2 (d, *J* = 5.5 Hz), 123.5, 122.6, 122.4, 121.6, 55.1 (d, *J* = 27.1 Hz), 47.9, 24.2, 23.0, 21.2, 20.0.

^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 147.8 (d, *J* = 12.2 Hz).

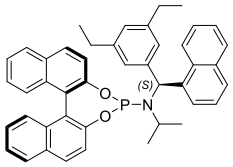
IR υ_{max} (film): 3058, 2973, 1591, 1231, 947.

HRMS (CI^+) $[C_{42}H_{37}NO_2P]^+$ predicted 618.2556, found 618.2565 (Δ –1.39 ppm).

M.P. = 80 – 85 ˚C.

$[\alpha]_{589}^{25}$ = 38.2 (*c* 2.00, $CHCl_3$)

For the other diasteromer: (R_a,*S*)-*N*-(-(2,4-dimethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine: $[\alpha]_{589}^{25}$= –174.7 (*c* 1.00, $CHCl_3$)



(R_a,*S*)- *N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L26S**

General procedure C: $PCl_{3(l)}$ (167 µl, 1.91 mmol, 1.1 eq.) in DCM (2.7 ml), Et_3N (1.21 ml, 8.68 mmol, 5.0 eq.), (–)-*(S)*-*N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine (556 mg, 1.68 mmol, 1.0 eq.) in DCM (6.0 ml), *(R)*-binol (646 mg, 2.26 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of (R_a,*S*)- *N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (992 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.87 – 7.70 (m, 8H, $C_{Ar}H$), 7.51 (t, *J* = 7.7 Hz, 1H, $C_{Ar}H$), 7.42 – 7.21 (m, 7H, $C_{Ar}H$), 7.20 – 7.03 (m, 3H, $C_{Ar}H$), 6.88 (s, 2H, $C_{Ar}H$), 6.79 (s, 1H, $C_{Ar}H$), 6.31 (d, *J* = 15.7 Hz, 1H, Ar*CH*), 3.63 (qq, *J* = 6.6 Hz, 1H, *CH*CH_3), 2.47 (q, *J* = 7.6 Hz, 4H CH_2CH_3), 1.17 (d, *J* = 6.6 Hz, 3H, CHCH_3), 1.07 (t, *J* = 7.6 Hz, 6H, CH_2CH_3), 0.60 (d, *J* = 6.6 Hz, 3H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 150.6 (d, *J* = 8.0 Hz), 150.2, 144.1, 143.0 (d, *J* = 9.1 Hz, 2C), 138.9 (d, *J* = 2.2 Hz), 133.9, 133.3 – 132.7 (m, 2C), 131.4, 131.2 (d, *J* = 1.8 Hz), 130.6, 130.3, 129.5, 128.9, 128.3, 128.3, 128.1, 127.3, 127.2, 126.9 (d, *J* = 7.7 Hz), 126.7, 126.6, 126.4, 126.2, 126.0, 126.0, 125.5, 125.4, 124.8, 124.4, 124.2 (d, *J* = 5.4 Hz), 123.9, 122.6 (d, *J* = 2.0 Hz), 122.4, 121.8 (d, *J* = 2.3 Hz), 57.3 (d, *J* = 27.4 Hz), 46.7 (d, *J* = 3.5 Hz), 29.0 (2C), 23.4, 22.9, 15.7 (2C).

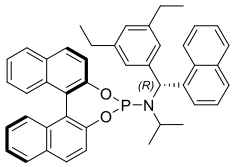
^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 149.7 (d, *J* = 15.7 Hz).

IR υ_{max} (film): 3054, 2965, 2931, 1592, 1231, 948.

HRMS (CI^+) $[C_{44}H_{41}NO_2P]^+$ predicted 646.2869, found 646.2845 (Δ 3.79 ppm).

M.P. = 74 – 78 ˚C.

$[\alpha]_{589}^{25}$= 34.4 (*c* 1.00, $CHCl_3$)



(R_a,*R*)- *N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L26R**

General procedure C: $PCl_{3(l)}$ (167 µl, 1.91 mmol, 1.1 eq.) in DCM (2.7 ml), Et_3N (1.21 ml, 8.68 mmol, 5.0 eq.), (+)-*(R)*-*N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine (575 mg, 1.74 mmol, 1.0 eq.) in DCM (6.0 ml), *(R)*-binol (646 mg, 2.26 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of (R_a,*R*)- *N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (522 mg, 47%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.14 (d, *J* = 7.1 Hz, 1H, $C_{Ar}H$), 7.83 – 7.74 (m, 4H, $C_{Ar}H$), 7.65 – 7.56 (m, 2H, $C_{Ar}H$), 7.54 (s, br, 1H, $C_{Ar}H$), 7.42 (s, br, 1H, $C_{Ar}H$), 7.34 – 7.05 (m, 11H, $C_{Ar}H$), 6.81 – 6.76 (m, 3H, $C_{Ar}H$), 6.27 (d, *J* = 14.2 Hz, 1H, ArC*H*), 3.57 – 3.46 (m, 1H, C*H*CH_3), 2.45 (q, *J* = 7.5 Hz, 4H, CH_2CH_3), 1.06 (t, *J* = 7.6 Hz, 6H, CH_2CH_3), 1.01 (d, *J* = 6.4 Hz, 3H, CHCH_3), 0.85 (s, br, 3H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 150.6 (d, *J* = 6.4 Hz), 150.0, 144.1 (2C), 142.6 (d, *J* = 7.7 Hz), 139.4, 133.9, 132.9 (d, *J* = 1.7 Hz), 132.7, 131.4, 131.2, 130.5, 130.2, 129.3, 128.8, 128.4, 128.3, 128.0, 127.2, 127.1, 126.6 (d, *J* = 3.2 Hz, 2C), 126.5, 126.4, 126.1, 126.0, 125.8, 125.5, 125.4, 124.7, 124.3, 124.2 (d, *J* = 5.2 Hz), 123.8, 122.5 (d, *J* = 2.0 Hz), 122.1, 121.8 (d, *J* = 2.2 Hz), 57.7 (d, *J* = 22.8 Hz), 47.7, 28.9 (2C), 23.6, 23.0, 15.8 (2C).

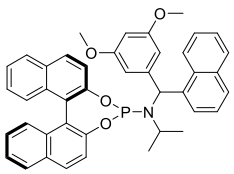
^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 150.5 (s, br).

IR υ_{max} (film): 3055, 2965, 2930, 1592, 1231, 948.

HRMS (Cl^+) $[C_{44}H_{41}NO_2P]^+$ predicted 646.2869, found 646.2859 (Δ 1.62 ppm).

(**M.P.** is unobtainable due to thermal decomposition.)

$[\alpha]_{589}^{25}$ = –104.1 (*c* 0.50, $CHCl_3$)



(R_a,*R* or *S)*-*N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L27a**

General procedure C: $PCl_{3(l)}$ (366 µl, 4.19 mmol, 1.1 eq.) in DCM (3.0 ml), Et_3N (2.66 ml, 19.1 mmol, 5.0 eq.), (–)-*N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)propan-2-amine (1.28 g, 3.81 mmol, 1.0 eq.) in DCM (8.0 ml), *(R)*-binol (1.42 mg, 4.95 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of (*R_a*,*S*)-*N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (2.28 g, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.86 – 7.71 (m, 8H, $C_{Ar}H$), 7.48 (t, *J* = 7.7 Hz, 1H, $C_{Ar}H$), 7.41 – 7.21 (m, 7H, $C_{Ar}H$), 7.18 – 7.04 (m, 3H, $C_{Ar}H$), 6.42 (d, *J* = 2.2 Hz, 2H, $C_{Ar}H$), 6.27 (d, *J* = 15.3 Hz, 1H, ArC*H*), 6.23 (t, *J* = 2.2 Hz, 1H, $C_{Ar}H$), 3.71 – 3.59 (m, 1H, C*H*CH_3), 3.60 (s, 6H, OCH_3), 1.20 (d, *J* = 6.6 Hz, 3H, CHCH_3), 0.59 (d, *J* = 6.6 Hz, 3H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 160.8 (2C), 150.6 (d, *J* = 7.9 Hz), 150.0, 145.6 (d, *J* = 9.0 Hz), 138.3 (d, *J* = 2.3 Hz), 133.9, 132.9 (2C), 131.5, 131.2 (d, *J* = 1.6 Hz), 130.6, 130.4, 129.5, 129.0, 128.4, 128.3 (2C), 127.3, 127.1, 126.9 (d, *J* = 7.5 Hz), 126.3, 126.1, 126.0, 125.6, 125.4, 124.8, 124.5, 124.2 (d, *J* = 5.4 Hz), 123.6, 122.5, 122.5, 122.3, 121.7 (d, *J* = 2.3 Hz), 108.3 (2C), 98.8, 57.2 (d, *J* = 26.6 Hz), 55.4 (2C), 46.8 (d, *J* = 2.7 Hz), 23.4, 22.9.

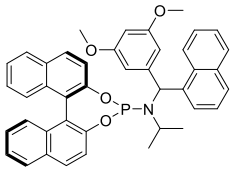
^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 148.7 (d, *J* = 15.3 Hz).

IR υ_{max} (film): 3058, 2970, 2836, 1593, 1231, 947.

HRMS (Cl^+) $[C_{42}H_{37}NO_4P]^+$ predicted 650.2455, found 650.2400 (Δ 2.27 ppm).

M.P. = 116 – 121 ˚C.

$[\alpha]_{589}^{25}$= 24.4 (*c* 1.00, $CHCl_3$)



(R_a,R or *S)*-*N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L27b**

General procedure C: $PCl_{3(l)}$ (366 µl, 4.19 mmol, 1.2 eq.) in DCM (3.0 ml), Et_3N (2.66 ml, 19.1 mmol, 5.3 eq.), (+)-*N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)propan-2-amine (1.20 g, 3.59 mmol, 1.0 eq.) in DCM (8.0 ml), *(R)*-binol (1.42 mg, 4.95 mmol, 1.4 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of (*R_a*,*R*)-*N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (2.02 g, 87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.15 – 8.09 (m, 1H, $C_{Ar}H$), 7.84 – 7.75 (m, 4H, $C_{Ar}H$), 7.57 (t, *J* = 7.7 Hz, 2H, $C_{Ar}H$), 7.50 – 6.85 (m, 12H, $C_{Ar}H$), 6.33 (s, 2H, $C_{Ar}H$), 6.22 (d, *J* = 14.5 Hz, 2H, $C_{Ar}H$, ArC*H*), 3.60 (s, 6H, 2OCH_3), 3.57 – 3.50 (m, 1H, C*H*CH_3), 1.04 (d, *J* = 6.4 Hz, 3H, CHCH_3), 0.90 (s, 3H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 160.7 (2C), 150.4, 149.9, 145.2 (d, *J* = 7.4 Hz), 138.8, 133.9, 132.9, 132.6, 131.5, 131.1, 130.5, 130.3, 129.3, 128.8, 128.4, 128.3, 128.2, 127.2, 127.1, 126.2, 126.2, 126.1, 125.9, 125.6, 125.4, 124.8, 124.3, 124.1, 123.5, 122.4 (d, *J* = 1.9 Hz), 122.0, 121.7 (d, *J* = 2.2 Hz), 108.3 (2C), 98.9, 57.7 (d, *J* = 20.6 Hz), 55.3 (2C), 47.8, 23.8, 23.1.

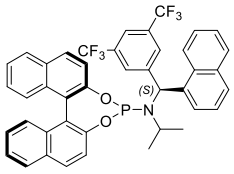
^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 149.4 (s,br).

IR υ_{max} (film): 3055, 2969, 2836, 1594, 1231, 947.

(**HRMS** cannot be obtained by ESI, EI, CI and APCI ionisation methods.)

(**M.P.** is unobtainable due to thermal decomposition.)

$[\alpha]_{589}^{25}$ = –125 (*c* 0.50, $CHCl_3$)



(*R*$_a$,*S*)-*N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L28S**

General procedure C: $PCl_{3(l)}$ (210 µl, 2.41 mmol, 1.1 eq.) in DCM (3.0 ml), Et_3N (1.53 ml, 10.9 mmol, 5.0 eq.), (–)-*(S)*-*N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)propan-2-amine (902 mg, 2.19 mmol, 1.0 eq.) in DCM (8.0 ml), *(R)*-binol (816 mg, 2.85 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of (*R*$_a$,*S*)-*N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (1.29 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.98 – 7.83 (m, 11H, $C_{Ar}H$), 7.65 (t, *J* = 7.7 Hz, 1H, $C_{Ar}H$), 7.55 – 7.34 (m, 7H, $C_{Ar}H$), 7.31 – 7.17 (m, 3H, $C_{Ar}H$), 6.60 (d, *J* = 15.6 Hz, 1H, ArC*H*), 3.85 – 3.76 (m, 1H, C*H*CH_3), 1.32 (d, *J* = 6.6 Hz, 3H, CH_3), 0.76 (d, *J* = 6.6 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 150.0 (d, *J* = 7.6 Hz), 149.6, 146.6 (d, *J* = 2.9 Hz), 136.3, 134.1, 132.9 (2C), 131.8 (q, *J* = 33.3 Hz, 2C), 131.6, 130.8, 130.7, 130.6, 129.8, 129.5 (2C), 129.4, 129.2, 128.4 (2C), 127.4, 127.3, 127.2, 126.8, 126.3, 126.2, 126.0, 125.5, 125.0, 124.7, 124.0 (d, *J* = 4.9

Hz), 123.4 (q, *J* = 273.9 Hz, 2C), 123.0, 122.2, 121.8 (2C), 121.6 – 121.2 (m), 56.7 (d, *J* = 26.2 Hz), 47.1, 23.3, 23.1.

^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 148.5 (s).

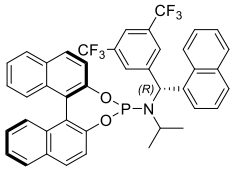
^{19}F NMR (471 MHz, $CDCl_3$) δ_F: –62.6 (s).

IR υ_{max} (film): 3062, 1591, 1231, 948.

HRMS (CI^+) $[C_{42}H_{31}F_6NO_2P]^+$ predicted 726.1991, found 726.1967 (Δ 3.33 ppm).

M.P. = 126 – 128 ˚C.

$[\alpha]_{589}^{25}$ = –2.3 (*c* 0.25, $CHCl_3$)



(*R*$_a$,*R*)-*N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L28R**

General procedure C: $PCl_{3(l)}$ (118 µl, 1.35 mmol, 1.1 eq.) in DCM (2.0 ml), Et_3N (0.86 ml, 6.15 mmol, 5.0 eq.), (+)-*(R)*-*N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)propan-2-amine (506 mg, 1.23 mmol, 1.0 eq.) in DCM (4.0 ml), *(R)*-binol (458 mg, 1.60 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of (*R*$_a$,*R*)-*N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (536 mg, 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 8.11 (d, *J* = 7.2 Hz, 1H, $C_{Ar}H$), 7.91 – 7.78 (m, 4H, $C_{Ar}H$), 7.69 (s, 1H, $C_{Ar}H$),), 7.64 (t, *J* = 7.7 Hz, 2H, $C_{Ar}H$), 7.59 (s, 2H, $C_{Ar}H$)7.44 (s, br, 1H, $C_{Ar}H$), 7.41 – 7.34 (m, 1H, $C_{Ar}H$), 7.33 – 7.22 (m, 4H, $C_{Ar}H$), 7.22 – 7.09 (m, 5H, $C_{Ar}H$), 7.08 (s, br, 1H, $C_{Ar}H$), 6.41 (d, *J* = 14.5 Hz, 1H, ArC*H*), 3.58 – 3.48 (m, 1H, C*H*CH_3), 1.04 (d, *J* = 6.5 Hz, 3H, C*H*$_3$), 0.91 (s, 3H, C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 150.0 (d, *J* = 7.5 Hz), 149.5, 146.1 (d, *J* = 7.5 Hz), 136.8, 134.1, 132.9 (d, *J* = 1.7 Hz), 132.7, 131.7 (q, *J* = 31.8 Hz, 2C), 131.6, 130.7, 130.6 (2C), 129.5 (3C), 129.3, 129.1, 128.5, 128.3, 127.2, 127.2, 126.7 (2C), 126.2, 126.1, 126.0, 125.6, 125.0, 124.6, 124.0 (d, *J* = 5.2 Hz), 123.4 (q, *J* = 272.9 Hz, 2C), 122.7, 122.1 (d, *J* = 2.0 Hz), 121.8 (d, *J* = 2.3 Hz), 121.7, 121.48 – 121.24 (m), 56.9 (d, *J* = 22.5 Hz), 47.9, 23.6, 23.0.

^{31}P NMR (202 MHz, $CDCl_3$) δ_P: 148.0 (s).

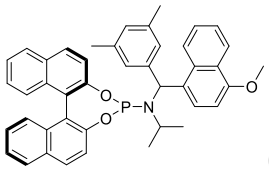
^{19}F NMR (471 MHz, $CDCl_3$) δ_F: -62.8 (s).

IR υ_{max} (film): 3061, 1591, 1231, 949.

HRMS (Cl^+) $[C_{42}H_{31}F_6NO_2P]^+$ predicted 726.1991, found 726.2019 (Δ –3.85 ppm).

M.P. = 125 – 130 ˚C.

$[\alpha]_{589}^{25}$= –103 (*c* 0.50, $CHCl_3$)



(*R_a*,*R or S*)-*N*-((3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L29a**

General procedure C: $PCl_{3(l)}$ (97 µl, 1.11 mmol, 1.1 eq.) in DCM (1.0 ml), Et_3N (1.48 ml, 5.05 mmol, 5.0 eq.), (–)-*N*-((3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methyl)propan-2-amine (337 mg, 1.01 mmol, 1.0 eq.) in DCM (4.0 ml), *(R)*-binol (376 mg, 1.31 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of ((*R_a*,*R or S*)-*N*-((3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (489 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.41 – 8.32 (m, 1H, $C_{Ar}H$), 7.97 – 7.83 (m, 5H, $C_{Ar}H$), 7.76 (d, *J* = 8.1 Hz, 1H, $C_{Ar}H$), 7.54 – 7.33 (m, 7H, $C_{Ar}H$), 7.32 – 7.13 (m, 3H, $C_{Ar}H$), 7.01 – 6.91 (m, 3H, $C_{Ar}H$), 6.87 (s, 1H, $C_{Ar}H$), 6.29 (d, *J* = 15.7 Hz, 1H, ArC*H*), 4.07 (s, 3H, OCH_3), 3.79 – 3.66 (m, 1H, C*H*CH_3), 2.28 (s, 6H, Ar(CH_3)$_2$), 1.24 (d, *J* = 6.6 Hz, 3H, CHCH_3), 0.76 (d, *J* = 6.6 Hz, 3H, CHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 155.0, 150.6 (d, *J* = 7.9 Hz), 150.1, 143.4 (d, *J* = 8.9 Hz), 137.6 (2C), 132.9 (2C), 132.0, 131.4, 130.5, 130.4 (d, *J* = 2.7 Hz), 130.2, 129.5, 128.9, 128.3 (2C), 127.5, 127.4, 127.3, 127.2, 127.1, 126.7, 126.0, 125.9, 125.9, 124.9, 124.7, 124.4, 124.2 (d, *J* = 5.2 Hz), 123.6, 122.7, 122.6, 122.4, 121.8, 103.2, 56.9 (d, *J* = 27.9 Hz), 55.6, 46.7, 23.3, 23.0, 21.7 (2C).

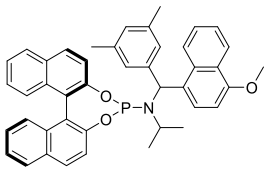
^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 149.5 (s).

IR υ_{max} (film): 2970, 1588, 1231, 947.

(**HRMS** cannot be obtained by ESI, EI, CI and APCI ionisation methods.)

M.P. = 140 – 142 ˚C.

$[\alpha]_{589}^{25}$= 15.8 (*c* 0.50, $CHCl_3$)



(*R*$_a$,*R or S*)-*N*-((3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L29b**

General procedure C: $PCl_{3(l)}$ (97 µl, 1.11 mmol, 1.1 eq.) in DCM (1.0 ml), Et_3N (1.48 ml, 5.05 mmol, 5.0 eq.), (+)-*N*-((3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methyl)propan-2-amine (332 mg, 0.99 mmol, 1.0 eq.) in DCM (4.0 ml), *(R)*-binol (376 mg, 1.31 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of ((*R*$_a$,*R or S*)-*N*-((3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (603 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.36 (dd, *J* = 8.4, 1.3 Hz, 1H, $C_{Ar}H$), 8.07 (d, *J* = 8.1 Hz, 1H, $C_{Ar}H$), 7.94 – 7.84 (m, 2H, $C_{Ar}H$), 7.75 (d, *J* = 8.1 Hz, 1H, $C_{Ar}H$), 7.57 (s, br, 2H, $C_{Ar}H$), 7.48 – 7.13 (m, 10H, $C_{Ar}H$), 7.03 (d, *J* = 8.1 Hz, 1H, $C_{Ar}H$), 6.85 (s, 3H, $C_{Ar}H$), 6.23 (d, *J* = 14.3 Hz, 1H, ArC*H*), 4.11 (s, 3H, OCH_3), 3.66 – 3.53 (m, 1H, C*H*CH_3), 2.25 (s, 6H, Ar(CH_3)$_2$), 1.10 (d, *J* = 6.4 Hz, 3H, CHCH_3), 0.94 (s, br, 3H, CHCH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 155.1, 150.7 (d, *J* = 6.8 Hz), 150.0, 143.0, 137.5 (2C), 132.9 (d, *J* = 1.7 Hz), 132.7, 131.9, 131.4, 131.1 (d, *J* = 1.9 Hz), 130.5, 130.2, 129.3, 128.8, 128.4, 128.3, 127.5, 127.4, 127.2, 127.2, 126.7, 126.0, 125.8, 124.9, 124.7, 124.3, 124.2 (d, *J* = 5.4 Hz), 123.5, 122.6, 122.6, 122.6, 122.2, 121.7 (d, *J* = 2.2 Hz), 103.2, 57.3 (d, *J* = 23.2 Hz), 55.7, 47.6, 23.7, 22.9, 21.6 (2C).

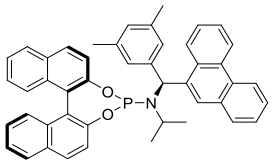
^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 150.7 (s).

IR υ_{max} (film): 2970, 1588, 1231, 947.

(**HRMS** cannot be obtained by ESI, EI, CI and APCI ionisation methods.)

M.P. = 154 – 158 ˚C and 164 – 166 ˚C.

$[\alpha]_{589}^{25}$ = –65.4 (*c* 0.43, $CHCl_3$)



(R_a,*S*)-*N*-(3,5-dimethylphenyl)(phenanthren-9-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L30S**

General procedure C: $PCl_{3(l)}$ (131 µl, 1.50 mmol, 1.1 eq.) in DCM (2.8 ml), Et_3N (0.95 ml, 6.79 mmol, 5.0 eq.), (+)-(*S*)-*N*-((3,5-dimethylphenyl)(phenanthren-9-yl)methyl)propan-2-amine (480 mg, 1.36 mmol, 1.0 eq.) in DCM (4.0 ml), *(R)*-binol (507 mg, 1.77 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [SiO_2, petrol/DCM/Et_3N, 80:20:1] to afford white solid of (R_a,*S*)-*N*-(3,5-dimethylphenyl)(phenanthren-9-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (779 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.89 – 8.77 (m, 2H, $C_{Ar}H$), 8.46 (s, 1H, $C_{Ar}H$), 8.24 – 8.15 (m, 1H, $C_{Ar}H$), 8.11 – 7.93 (m, 5H, $C_{Ar}H$), 7.84 – 7.66 (m, 4H, $C_{Ar}H$), 7.66 – 7.41 (m, 5H, $C_{Ar}H$), 7.41 – 7.23 (m, 3H, $C_{Ar}H$), 7.10 (s, 2H, $C_{Ar}H$), 6.95 (s, 1H, $C_{Ar}H$), 6.45 (d, *J* = 16.5 Hz, 1H, ArC*H*), 3.95 – 3.83 (m, 1H, C*H*CH_3), 2.34 (s, 6H, Ar(CH_3)$_2$), 1.43 (d, *J* = 6.6 Hz, 3H, CHCH_3), 0.80 (d, *J* = 6.6 Hz, 3H, CHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 150.6, 150.5, 150.2, 142.4, 142.3, 137.7 (2C), 137.2, 132.9 (2C), 131.6, 131.4, 130.8, 130.6, 130.4, 130.4, 129.5, 129.2, 129.2, 128.4, 128.3, 127.8 (d, *J* = 2.7 Hz), 127.7, 127.3, 127.1, 126.9, 126.9, 126.8, 126.3, 126.1, 126.0, 124.8, 124.6, 124.5, 124.2 (d, *J* = 5.5 Hz), 123.3, 122.6, 122.5, 122.3, 121.8 (d, *J* = 2.3 Hz), 57.3 (d, *J* = 28.0 Hz), 46.6 (d, *J* = 4.5 Hz), 23.3, 22.8, 21.6 (2C).

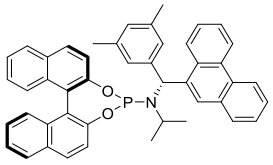
^{31}P NMR {^{1}H} (162 MHz, $CDCl_3$) δ_P: 149.7 (s).

IR υ_{max} (film): 3054, 2971, 1951, 1591, 1231, 948.

(**HRMS** cannot be obtained by ESI, EI, CI and APCI ionisation methods. The structure is confirmed by X-ray crystallography.)

M.P. = 176 – 177 ˚C.

$[\alpha]_{589}^{25}$= 86.4 (*c* 1.00, $CHCl_3$)



(R_a,*R*)-*N*-(3,5-dimethylphenyl)(phenanthren-9-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L30R**

General procedure C: $PCl_{3(l)}$ (131 µl, 1.50 mmol, 1.1 eq.) in DCM (2.8 ml), Et_3N (0.95 ml, 6.79 mmol, 5.0 eq.), (–)-(*R*)-*N*-((3,5-dimethylphenyl)(phenanthren-9-yl)methyl)propan-2-amine (480 mg, 1.36 mmol, 1.0 eq.) in DCM (4.0 ml), *(R)*-binol (507 mg, 1.77 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [SiO_2, petrol/DCM/Et_3N, 80:20:1] to afford white solid of (*R*$_a$,*R*)-*N*-(3,5-dimethylphenyl)(phenanthren-9-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (832 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.71 – 8.63 (m, 2H, $C_{Ar}H$), 8.56 (s, 1H, $C_{Ar}H$), 8.11 – 8.02 (m, 1H, $C_{Ar}H$), 7.85 – 7.74 (m, 2H, $C_{Ar}H$), 7.67 – 7.54 (m, 3H, $C_{Ar}H$), 7.47 (t, *J* = 7.7 Hz, 2H, $C_{Ar}H$), 7.34 – 7.05 (m, 10H, $C_{Ar}H$), 6.80 (s, 2H, $C_{Ar}H$), 6.76 (s, 1H, $C_{Ar}H$), 6.21 (d, *J* = 14.1 Hz, 1H, ArC*H*), 3.56 (h, *J* = 6.5 Hz, 1H, C*H*CH_3), 2.12 (s, 6H, Ar(CH_3)$_2$), 1.07 (d, *J* = 6.3 Hz, 3H, CHCH_3), 0.87 (s, br, 3H, CHCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 150.5, 150.0, 141.9, 137.9, 137.7 (2C), 132.9, 132.7, 131.8, 131.4, 130.8, 130.5, 130.4 (2C), 130.3, 129.4, 129.1, 129.1, 128.4, 128.3, 127.7, 127.7, 127.2 (2C), 127.1, 127.0, 126.8, 126.8, 126.3, 126.0, 125.9, 124.8, 124.5, 124.3, 124.2 (d, *J* = 5.0 Hz), 123.2, 122.7, 122.6, 122.0, 121.8, 57.9 (d, *J* = 22.2 Hz), 47.7, 23,7, 23,1, 21.6 (2C).

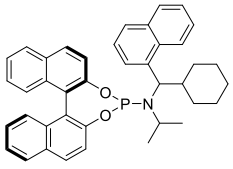
^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 150.1 (d, *J* = 148.6 Hz).

IR υ_{max} (film): 3058, 2970, 2930, 1591, 1231, 947.

(**HRMS** cannot be obtained by ESI, EI, CI and APCI ionisation methods.)

M.P. = 177 – 179 ˚C.

$[\alpha]_{589}^{25}$ = –132 (*c* 1.00, $CHCl_3$)



(*R*$_a$,*R or S*)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L31a**

General procedure C: $PCl_{3(l)}$ (204 µl, 2.34 mmol, 1.1 eq.) in DCM (3.0 ml), Et_3N (1.48 ml, 10.65 mmol, 5.0 eq.), (–)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)propan-2-amine (599 mg, 2.13 mmol, 1.0 eq.) in DCM (7.0 ml), *(R)*-binol (793 mg, 2.77 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of ((*R*$_a$,*R or S*)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (1.09 g, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.24 – 8.16 (m, 2H, $C_{Ar}H$), 8.07 (d, *J* = 8.7 Hz, 1H, $C_{Ar}H$), 8.01 – 7.88 (m, 4H, $C_{Ar}H$), 7.84 (d, *J* = 8.0 Hz, 1H, $C_{Ar}H$), 7.76 – 7.62 (m, 2H, $C_{Ar}H$), 7.62 – 7.35 (m, 7H, $C_{Ar}H$), 7.33 – 7.23 (m, 2H, $C_{Ar}H$), 4.99 – 4.87 (m, 1H, ArC*H*), 3.63 – 3.48 (m, 1H, C*H*CH_3), 3.05 – 2.98 (m, 1H, CH_aH_b), 2.49 – 2.41 (m, 1H, ArCHC*H*), 2.01 – 1.94 (m, 1H, CH_aH_b), 1.70 (d, *J* = 11.9 Hz, 1H, CH_aH_b), 1.55 – 1.48 (m, 1H, CH_aH_b), 1.40 – 1.14 (m, 6H, CH_2, CH_aH_b, CH_3), 1.12 – 0.86 (m, 3H, CH_2, CH_aH_b), 0.32 (d, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 150.9 (d, *J* = 8.4 Hz), 150.3, 142.9, 133.7, 133.0, 132.9, 131.9, 131.5, 130.6, 130.5, 129.6, 129.3, 128.4, 128.3, 127.4, 127.3 (2C), 127.2, 126.1, 126.0 (3C), 125.3, 124.3 (d, *J* = 5.5 Hz), 124.3, 124.2, 123.1, 122.6, 122.5, 121.6, 57.6 (d, *J* = 19.5 Hz), 46.4 (d, *J* = 4.7 Hz), 45.0 (d, *J* = 25.4 Hz), 32.0, 31.5, 26.7 (2C), 26.6, 22.9, 21.5.

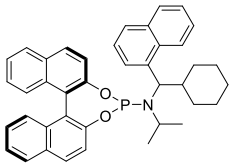
^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 147.3 (s).

IR υ_{max} (film): 3056, 2923, 2850, 1592, 1232, 947.

HRMS (Cl^+) $[C_{40}H_{39}NO_2P]^+$ predicted 596.2713, found 596.2723 (Δ –1.69 ppm).

M.P. = 165 – 167 ˚C.

$[\alpha]_{589}^{25}$ = –95.2 (*c* 1.00, $CHCl_3$)



(*R_a*,*R or S*)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L31b**

General procedure C: $PCl_{3(l)}$ (204 µl, 2.34 mmol, 1.1 eq.) in DCM (3.0 ml), Et_3N (1.48 ml, 10.65 mmol, 5.0 eq.), (+)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)propan-2-amine (594 mg, 2.11 mmol, 1.0 eq.) in DCM (7.0 ml), *(R)*-binol (793 mg, 2.77 mmol, 1.3 eq.) The crude mixture was purified by flash column chromatography [Basic Al_2O_3, petrol/DCM, 4:1] to afford white solid of ((*R_a*,*R or S*)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine (1.21 g, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 8.27 (dd, *J* = 7.4, 3.7 Hz, 1H, $C_{Ar}H$), 8.20 (d, *J* = 8.5 Hz, 1H, $C_{Ar}H$), 8.05 (d, *J* = 8.7 Hz, 1H, $C_{Ar}H$), 8.01 – 7.90 (m, 2H, $C_{Ar}H$), 7.91 – 7.81 (m, 2H, $C_{Ar}H$), 7.76 – 7.67 (m, 2H, $C_{Ar}H$), 7.65 – 7.52 (m, 3H, $C_{Ar}H$), 7.55 – 7.43 (m, 2H, $C_{Ar}H$), 7.47 – 7.35 (m, 2H, $C_{Ar}H$), 7.33 – 7.23 (m, 2H, $C_{Ar}H$), 7.11 (d, *J* = 8.8 Hz, 1H, $C_{Ar}H$), 4.82 (dd, *J* = 16.3, 10.9 Hz, 1H, ArC*H*), 3.52 – 3.39 (m, 1H, C*H*CH_3), 2.74 (d, *J* = 13.0 Hz, 1H, CH_aH_b), 2.50 – 2.35 (m, 1H, ArCHC*H*), 2.06 – 1.96

(m, 1H, CH_aH$_b$), 1.78 – 1.68 (m, 1H, CH$_a$$H_b$), 1.56 – 1.33 (m, 2H, CH$_2$), 1.34 – 1.15 (m, 2H, CH_aH$_b$, CH$_a$$H_b$), 1.13 – 0.85 (m, 6H, CH$_a$$H_b$, C$H_2$, CH_3), 0.41 (d, *J* = 6.8 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 150.7 (d, *J* = 6.4 Hz), 150.2, 142.6, 133.6, 133.0, 132.7, 131.8, 131.5, 130.6, 130.4, 129.5, 129.3, 128.4, 128.3, 127.3, 127.2, 127.2, 126.1, 126.0, 125.9, 125.9, 125.5 (d, *J* = 12.7 Hz), 125.2, 124.8, 124.4, 124.3 (d, *J* = 5.0 Hz),123.4, 122.6, 122.4, 121.9, 58.2 (d, *J* = 18.6 Hz), 46.2, 44.4 (d, *J* = 27.1 Hz), 31.9 (d, *J* = 4.8 Hz), 31.5, 26.7, 26.6, 26.5, 22.2, 21.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ_P: 149.3 (s).

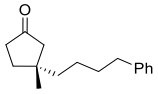
IR υ_{max} (film): 3057, 2930, 1591, 1232, 948.

HRMS (Cl^+) $[C_{40}H_{39}NO_2P]^+$ predicted 596.2713, found 596.2728 (Δ –2.53 ppm).

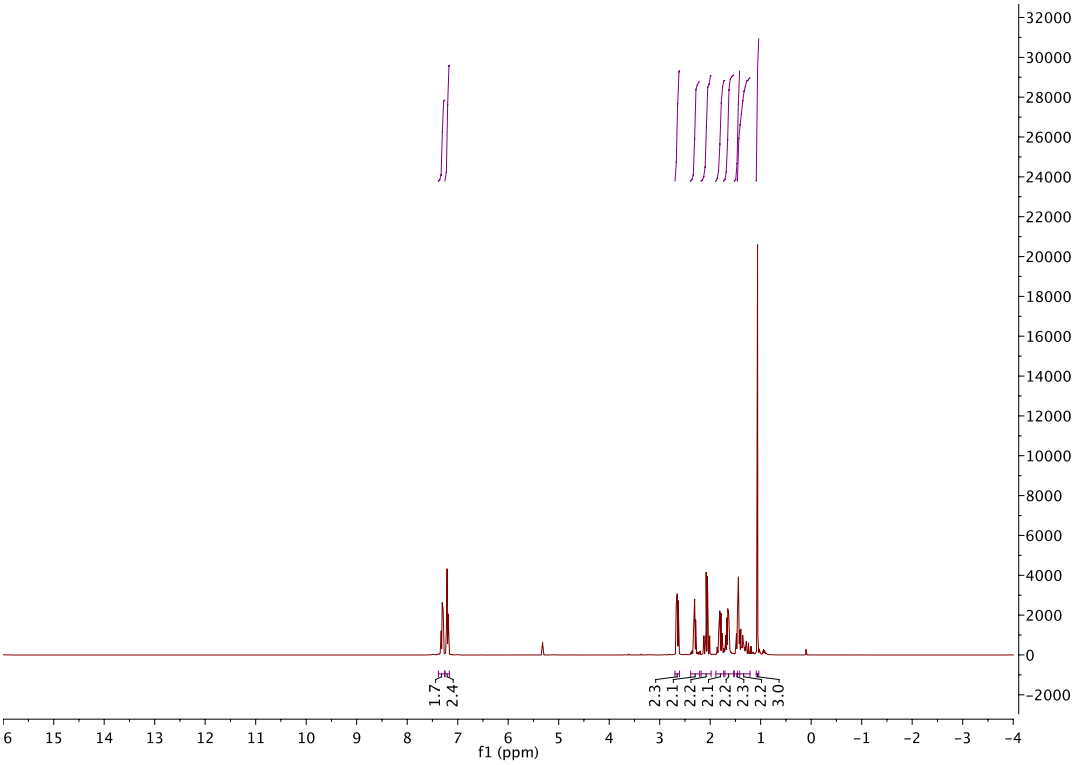
M.P. = 168 – 170 ˚C.

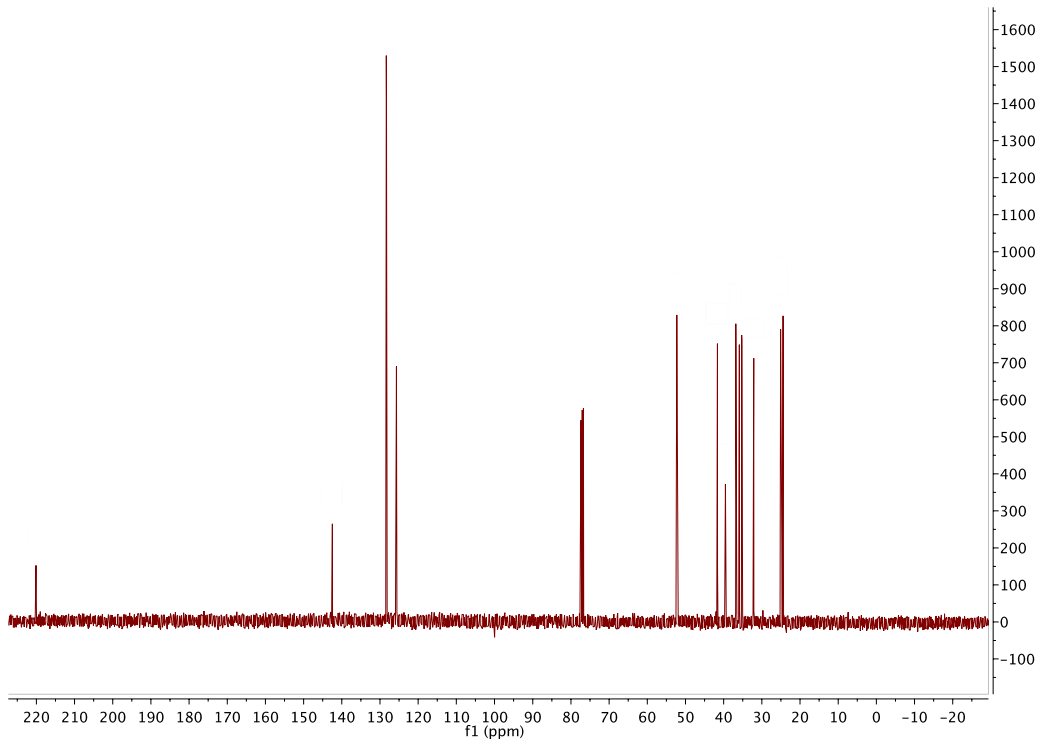
$[\alpha]_{589}^{25}$= –178 (*c* 1.00, $CHCl_3$)

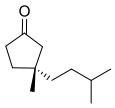
NMR Spectra



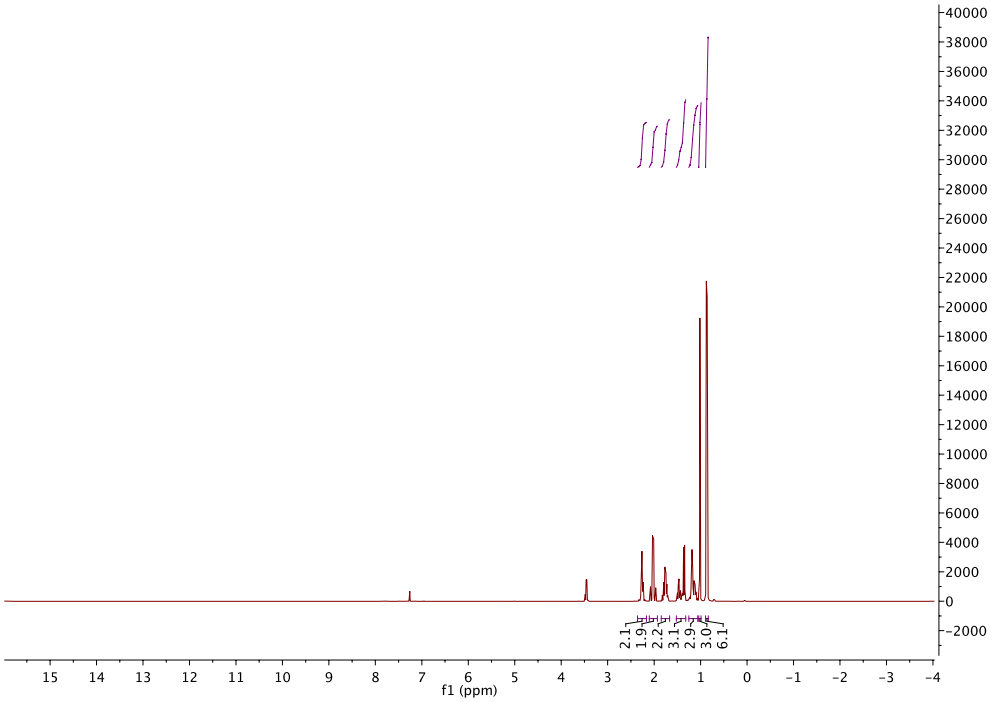
(+)-*(R)*-3-methyl-3-(4-phenylbutyl)cyclopentan-1-one **3**

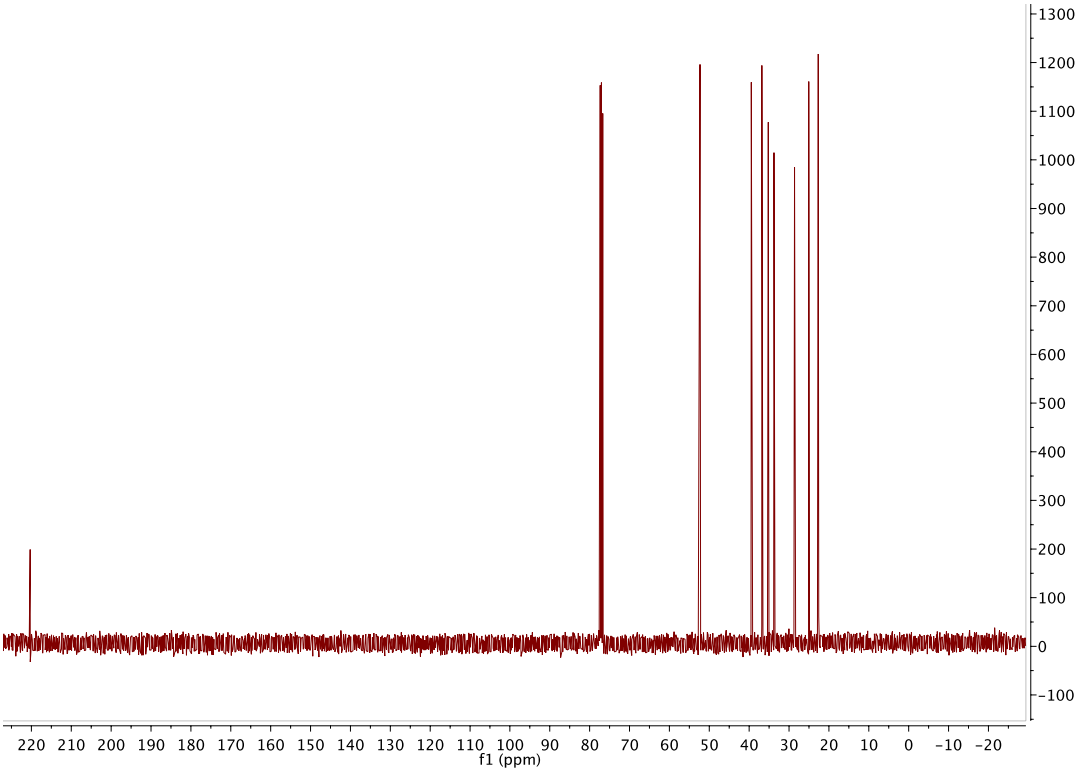


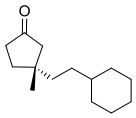




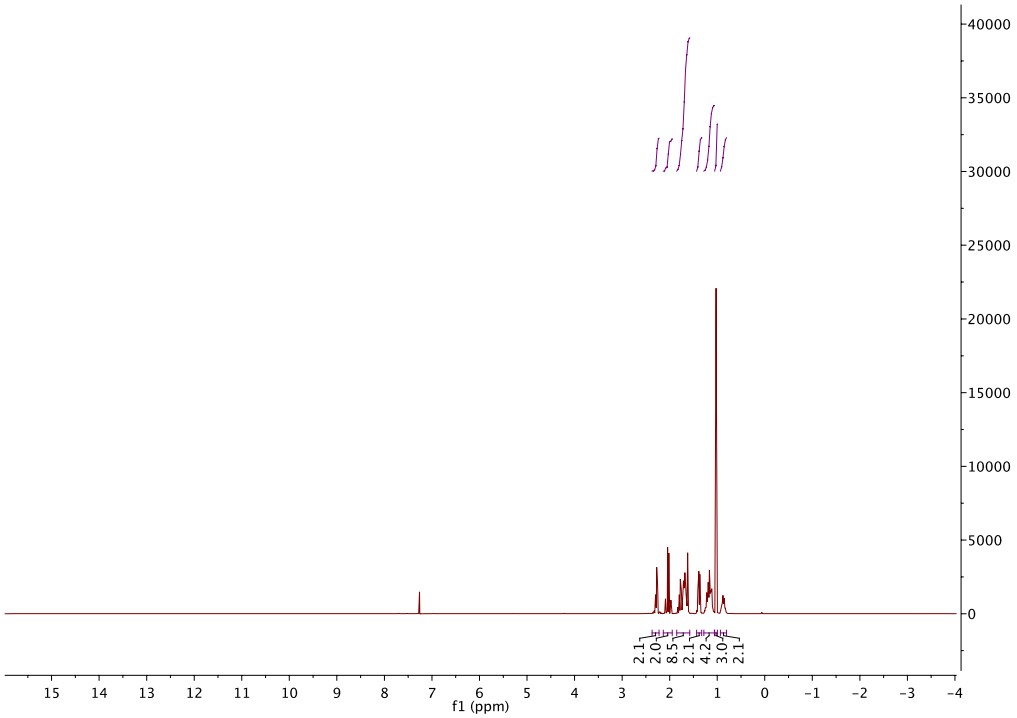
(*R*)-3-isopentyl-3-methylcyclopentan-1-one **5**

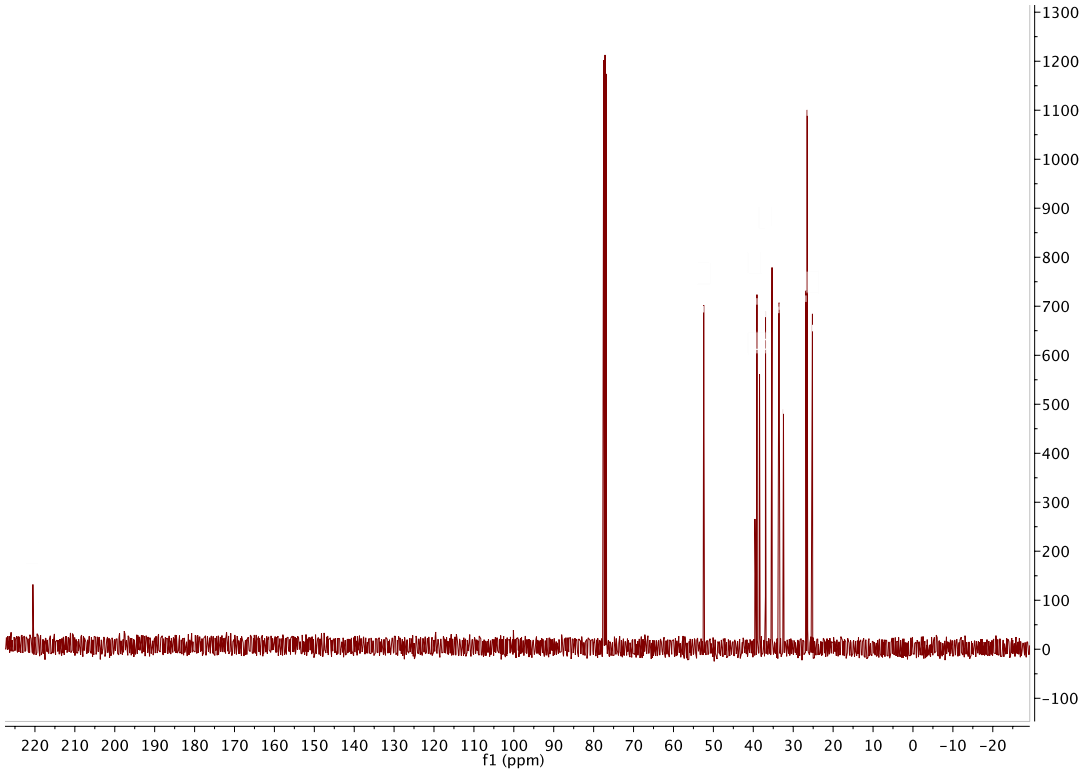


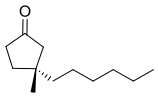




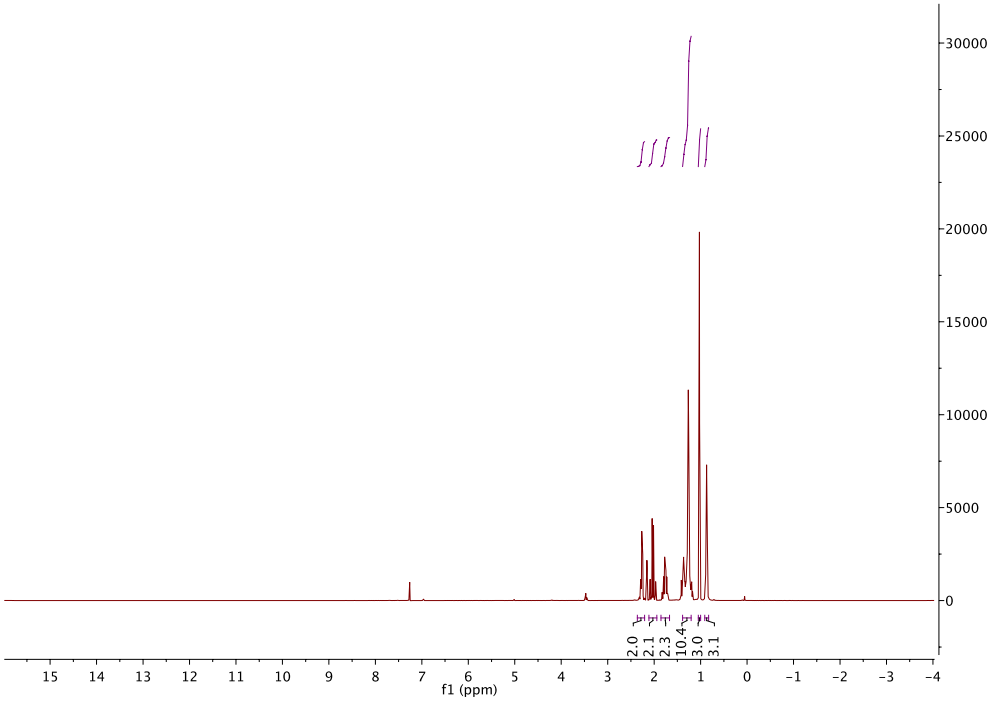
(*R*)-3-(2-cyclohexylethyl)-3-methylcyclopentan-1-one **6**

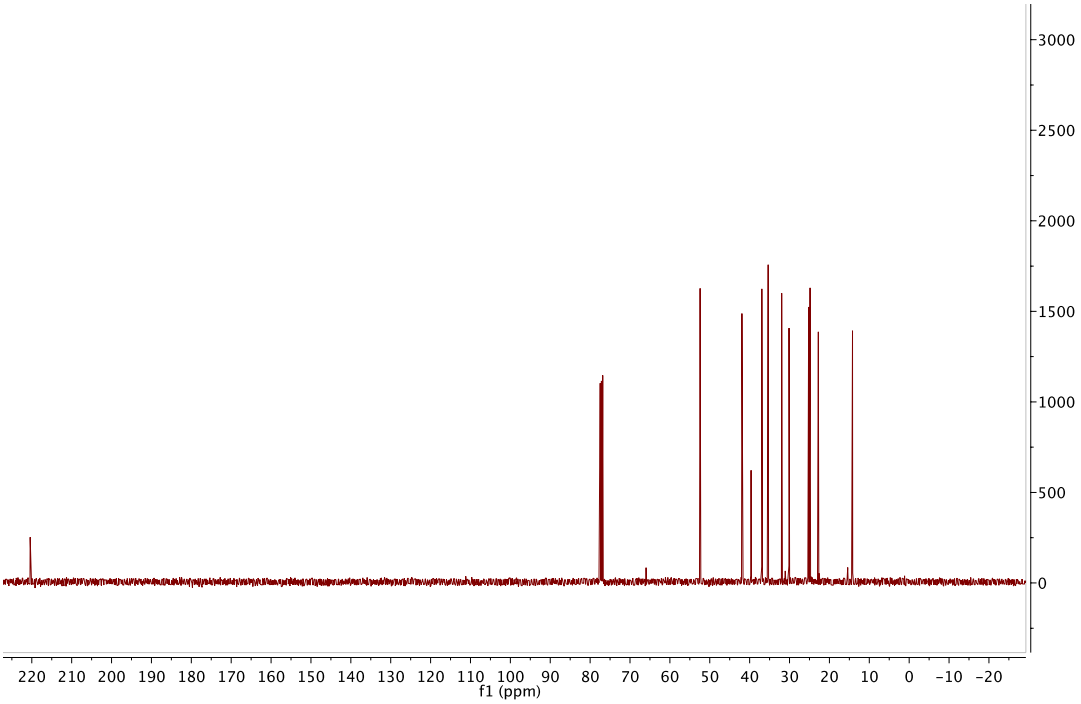




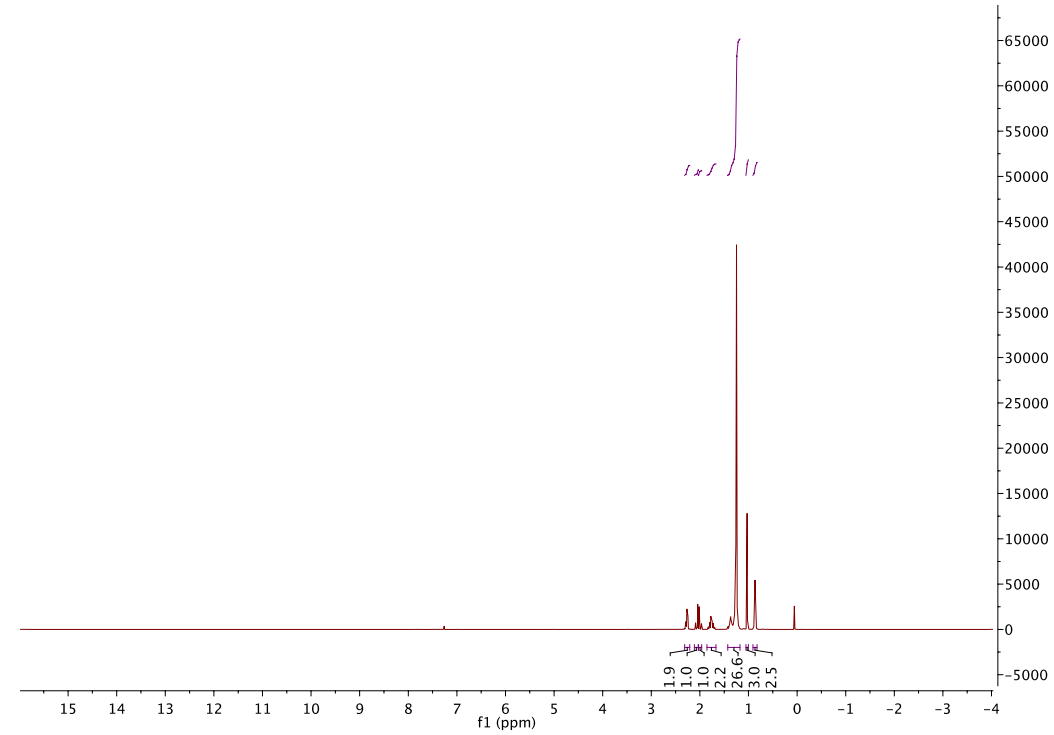


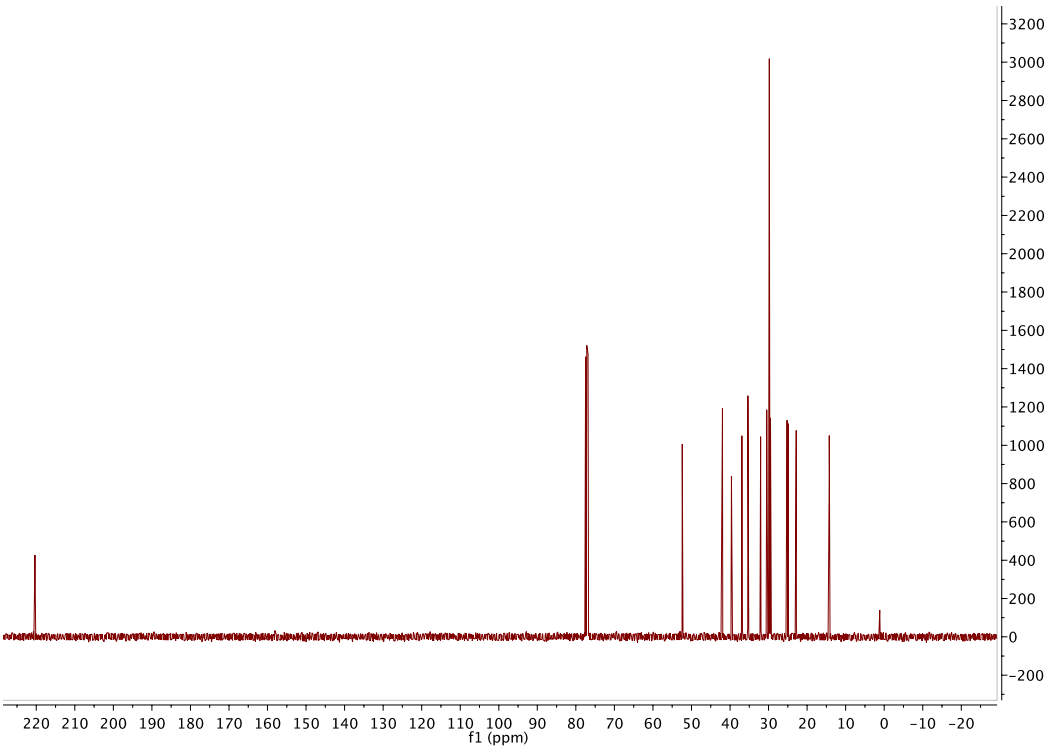
(*R*)-3-hexyl-3-methylcyclopentan-1-one **7**

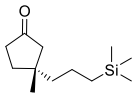




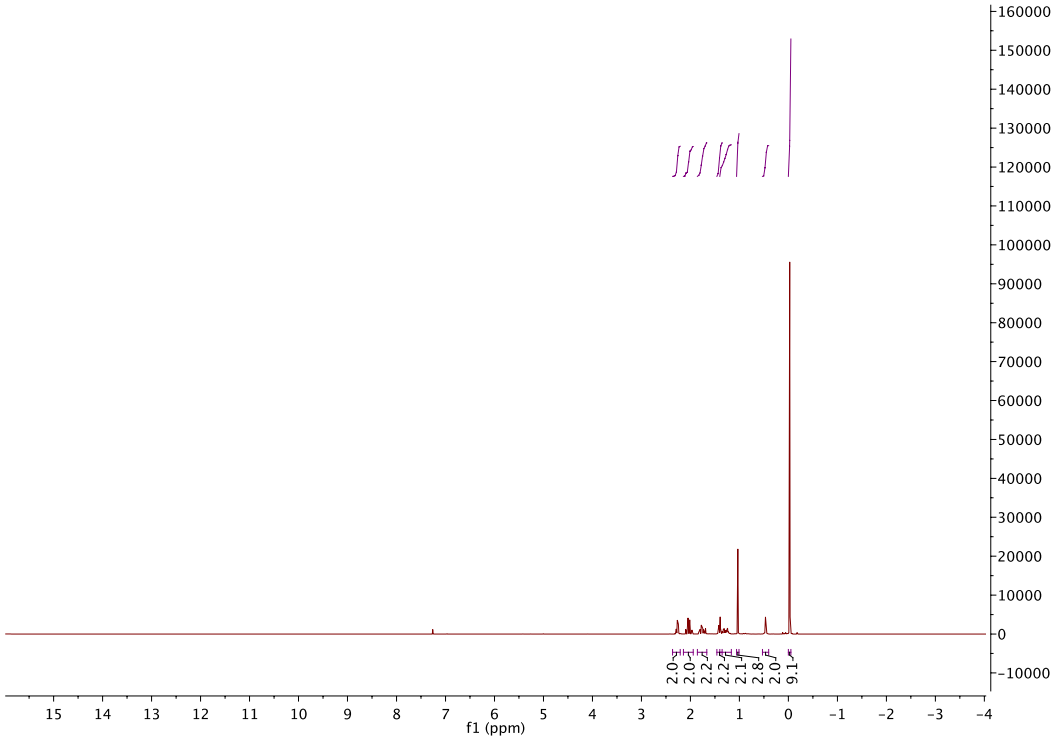
(*R*)-3-methyl-3-tetradecylcyclopentan-1-one **8**

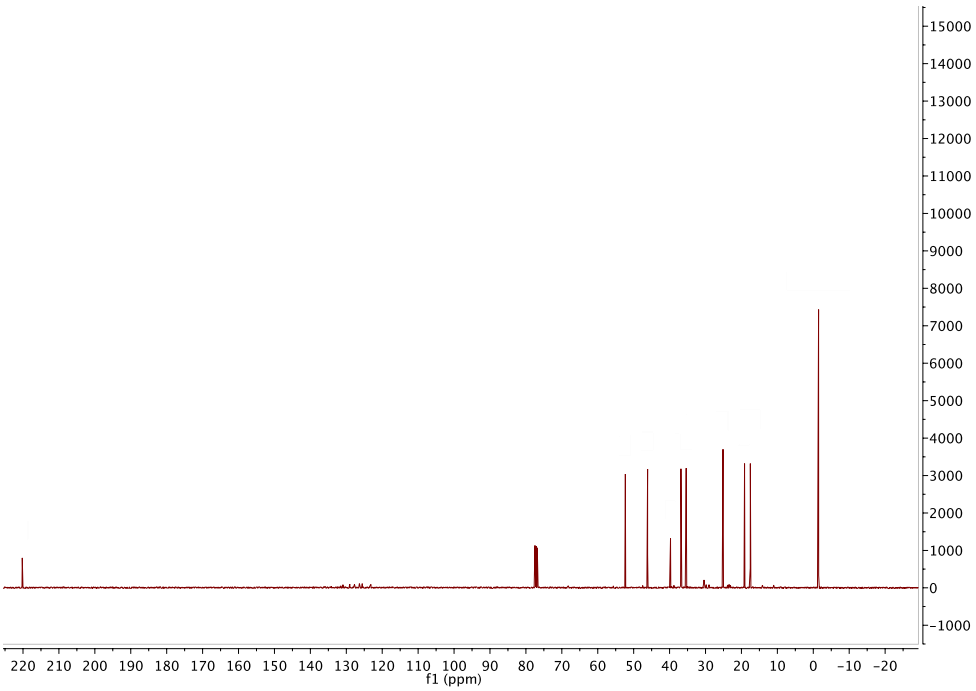


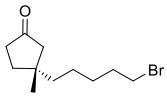




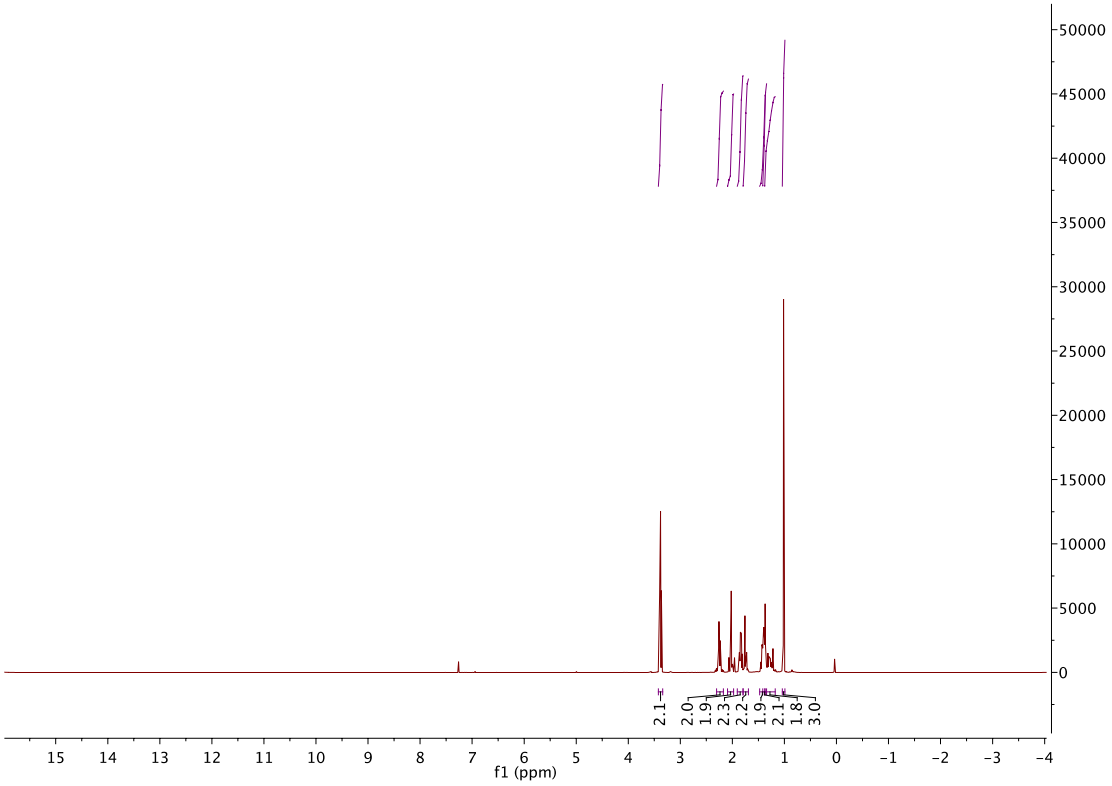
(S)-3-methyl-3-(3-(trimethylsilyl)propyl)cyclopentan-1-one **9**

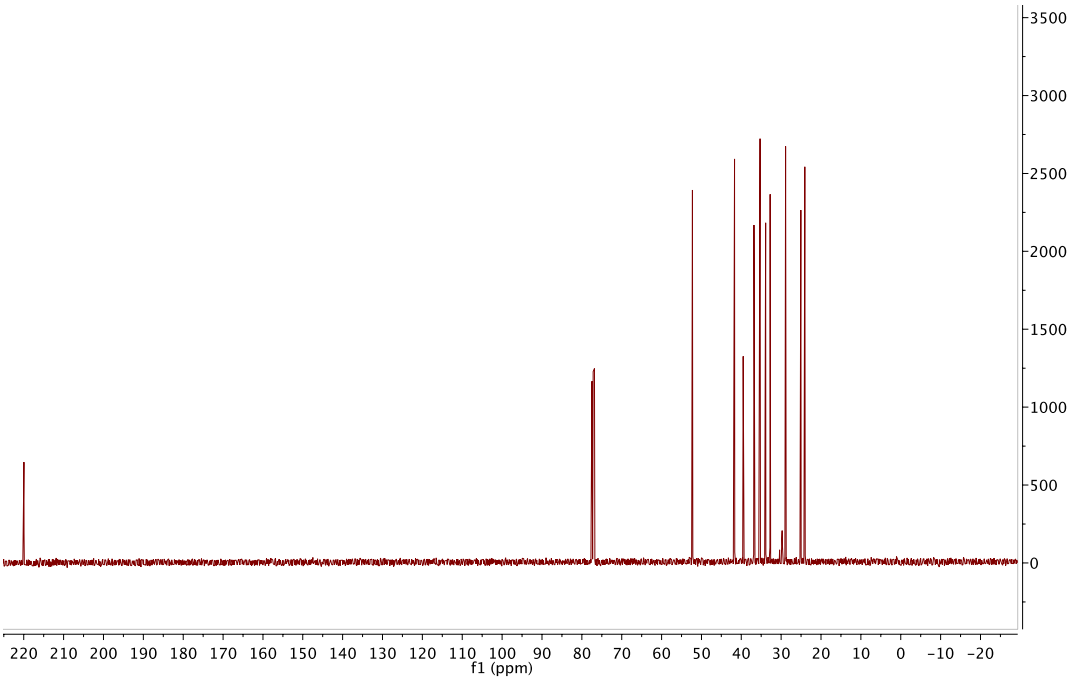


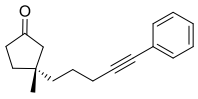




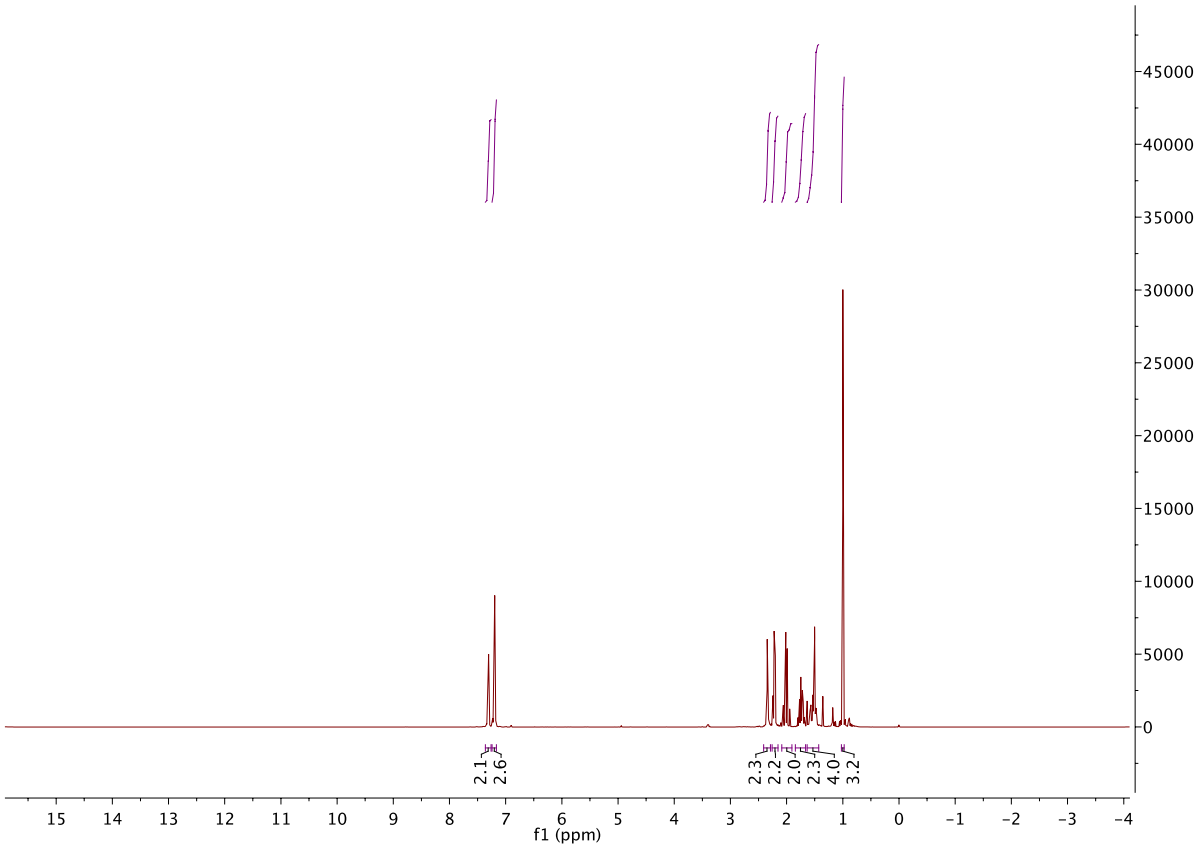
(R)-3-(5-bromopentyl)-3-methylcyclopentan-1-one **10**

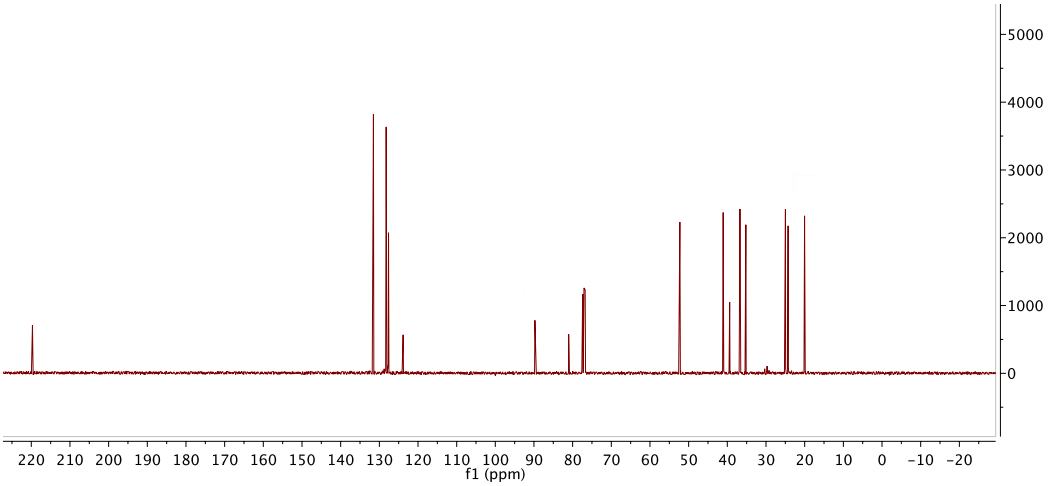


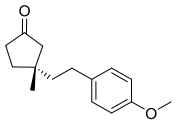




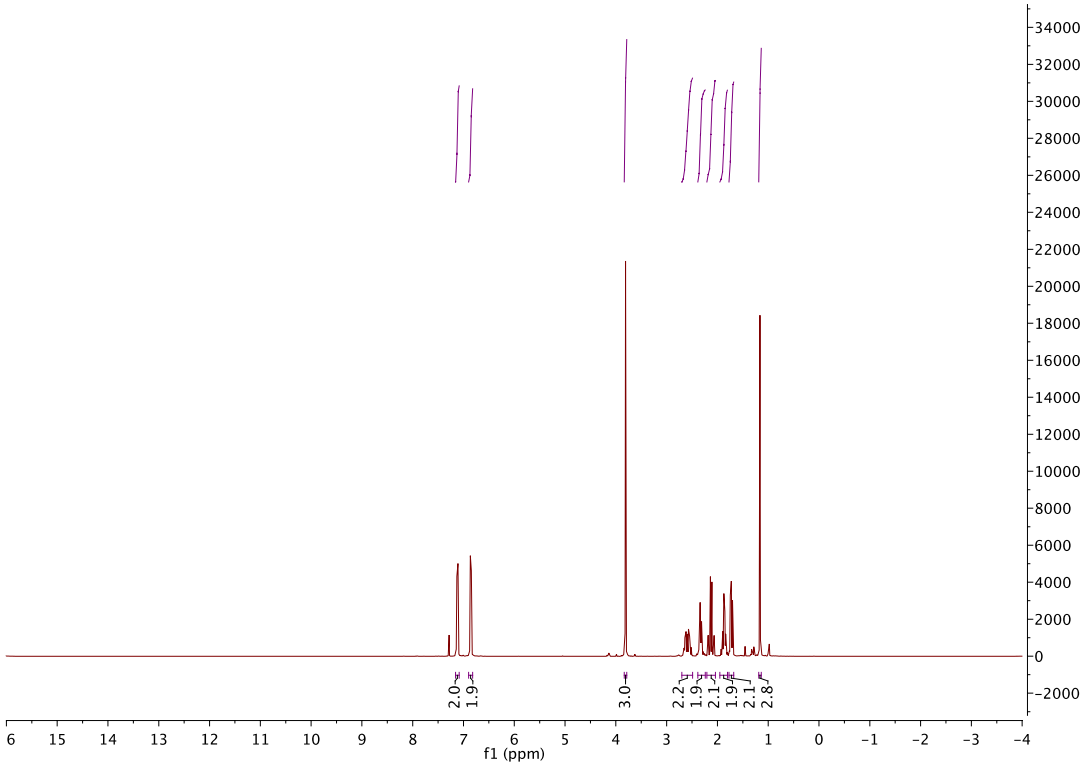
(*R*)-3-methyl-3-(5-phenylpent-4-yn-1-yl)cyclopentan-1-one **11**

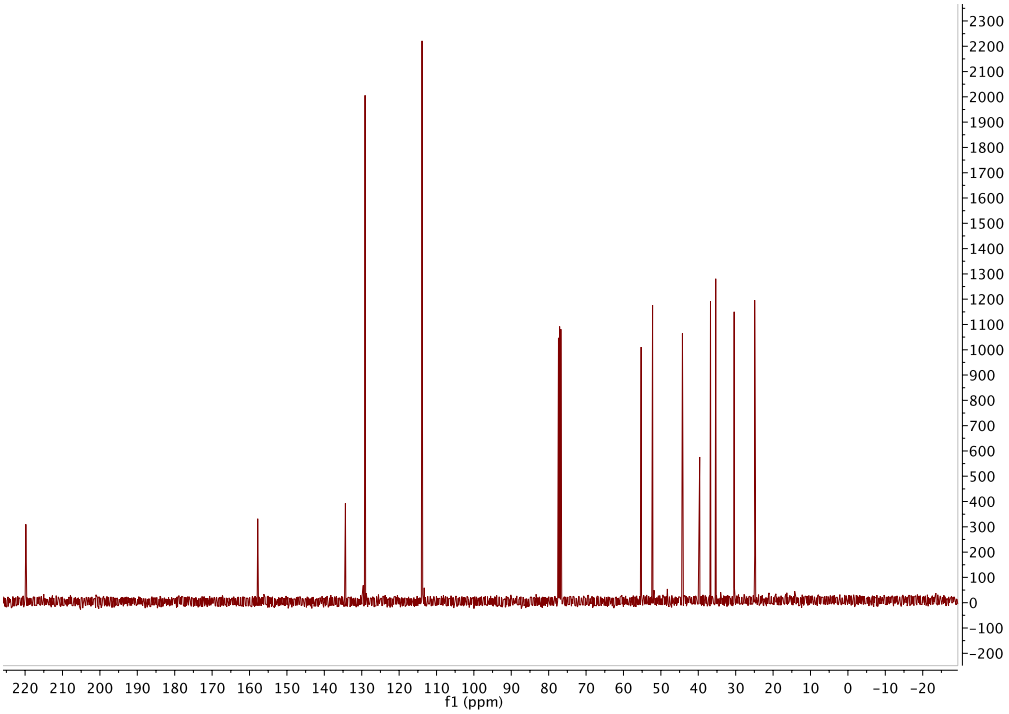


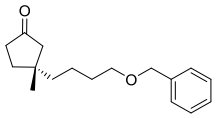




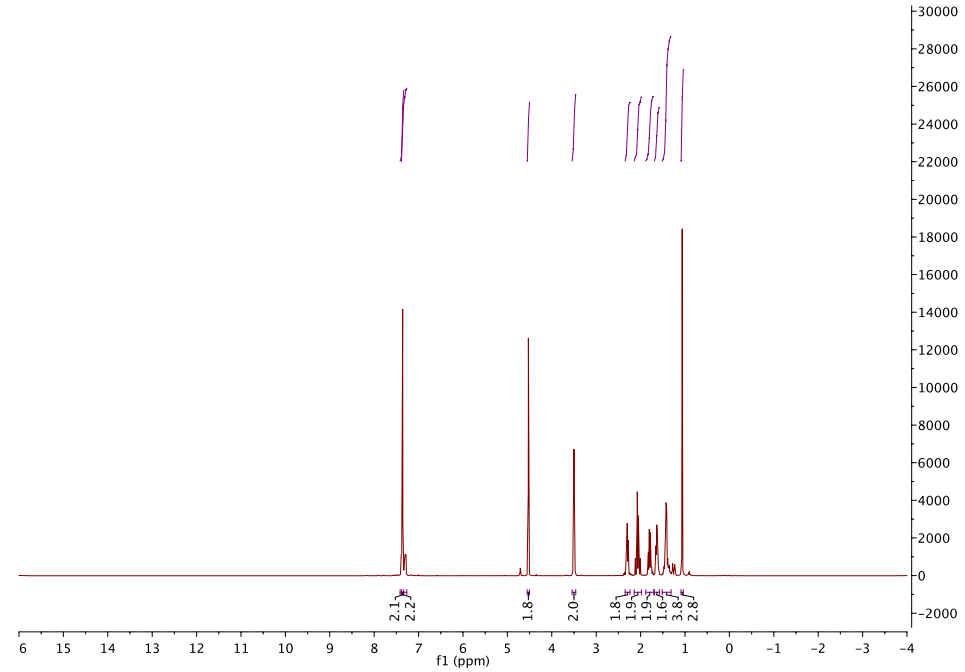
(*R*)-3-(4-methoxyphenethyl)-3-methylcyclopentan-1-one **12**

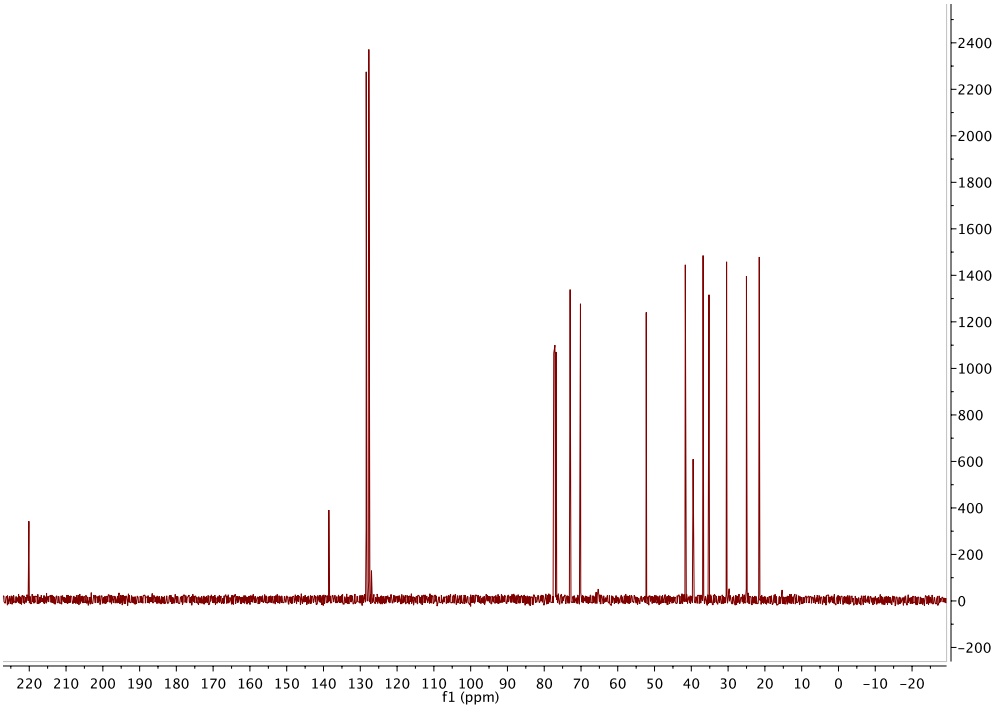


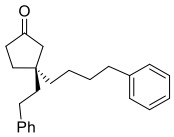




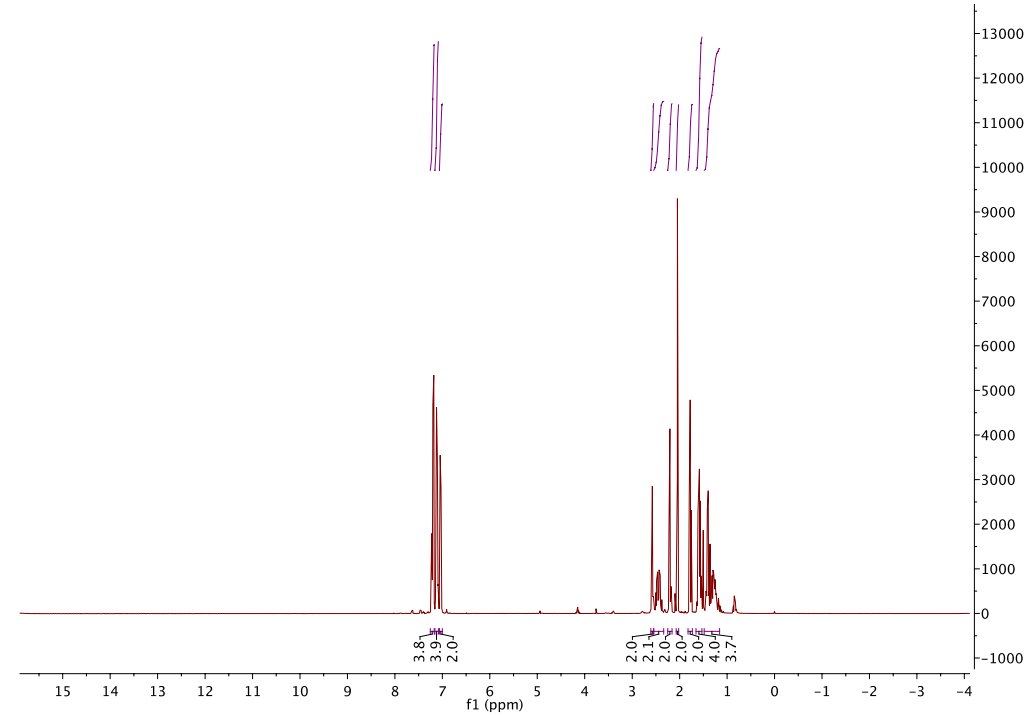
(*R*)-3-(4-(benzyloxy)butyl)-3-methylcyclopentan-1-one **13**

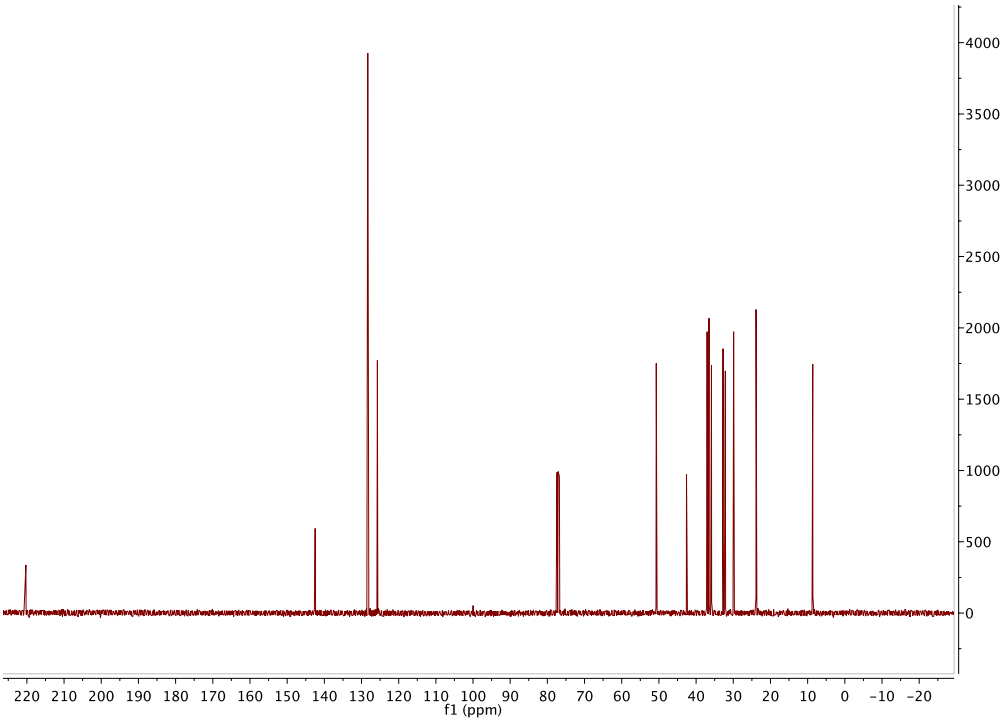


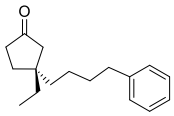




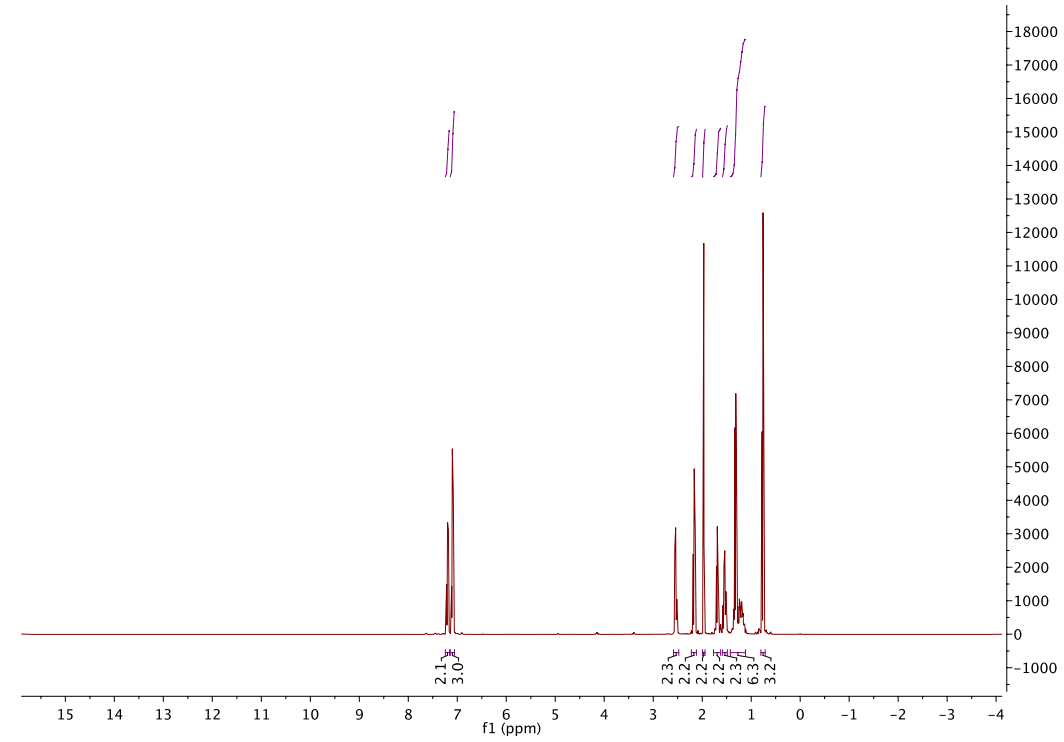
(*S*)-3-phenethyl-3-(4-phenylbutyl)cyclopentan-1-one **14**

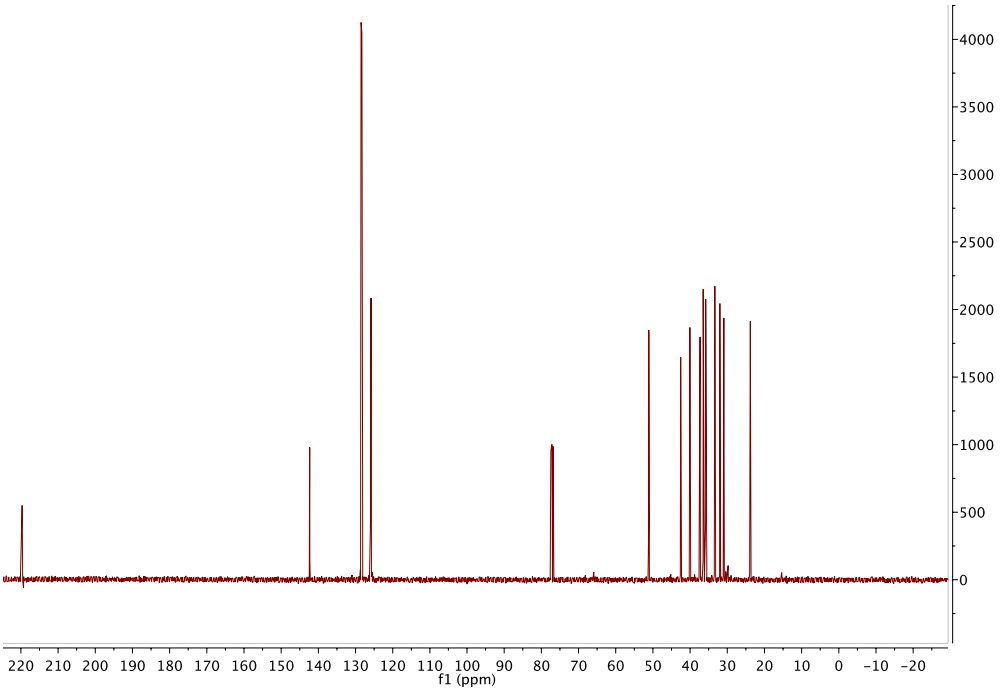


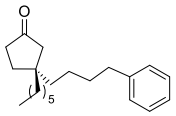




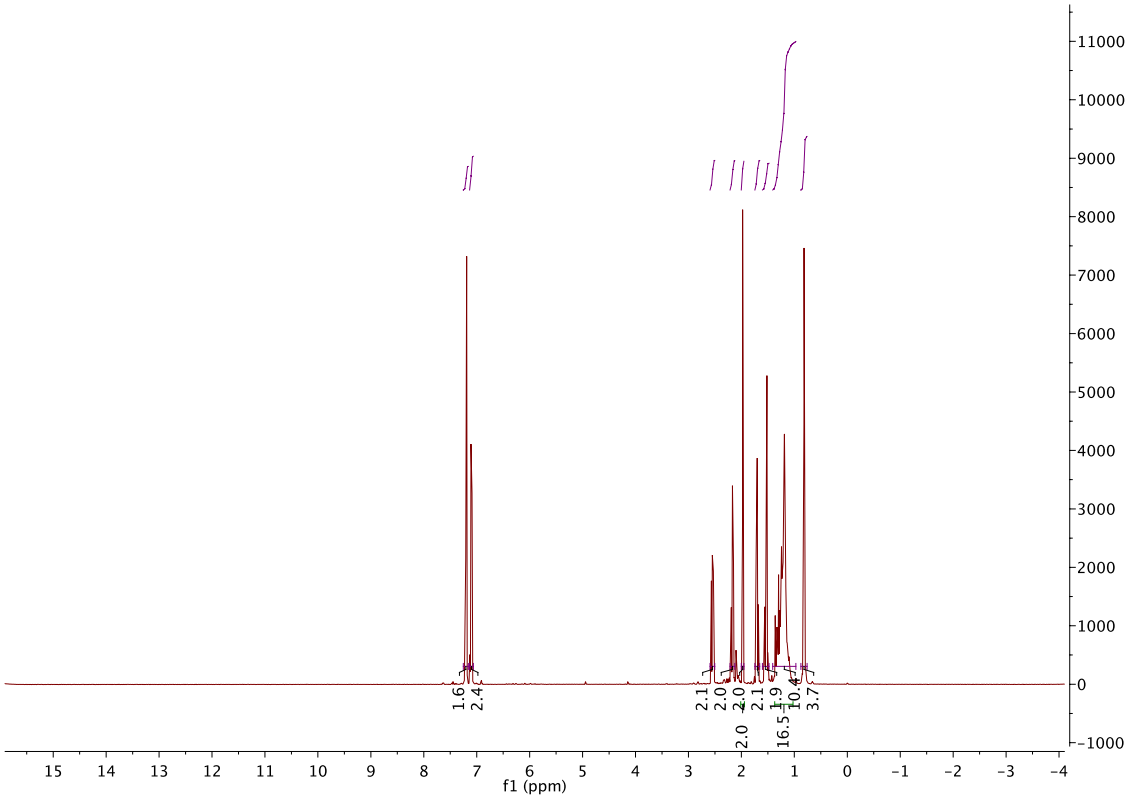
(*R*)-3-ethyl-3-(4-phenylbutyl)cyclopentan-1-one **15**

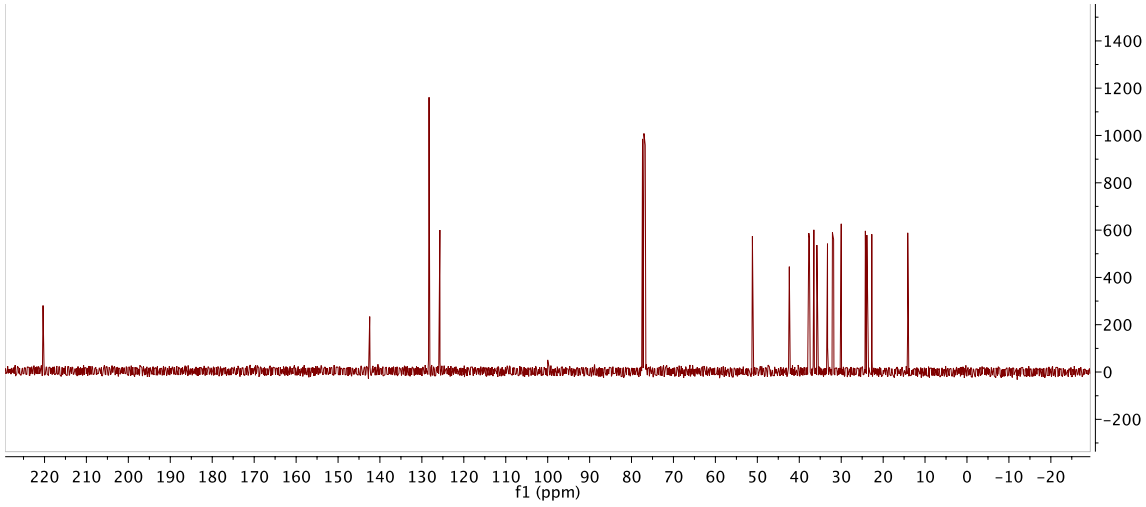


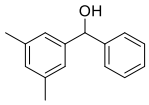




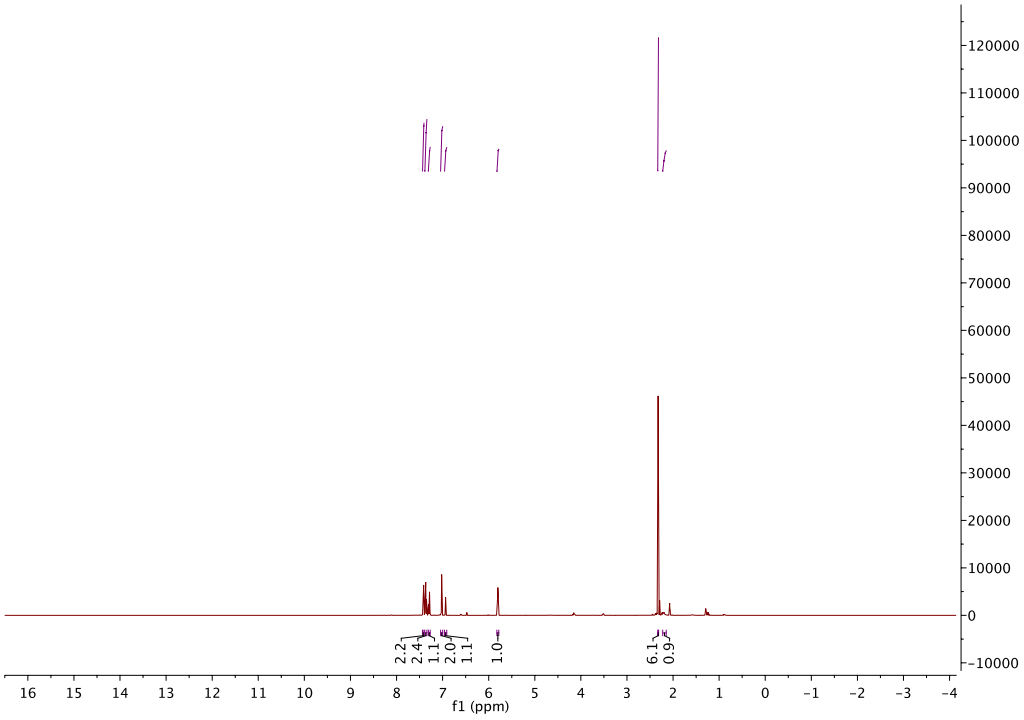
(*R*)-3-hexyl-3-(4-phenylbutyl)cyclopentan-1-one **16**

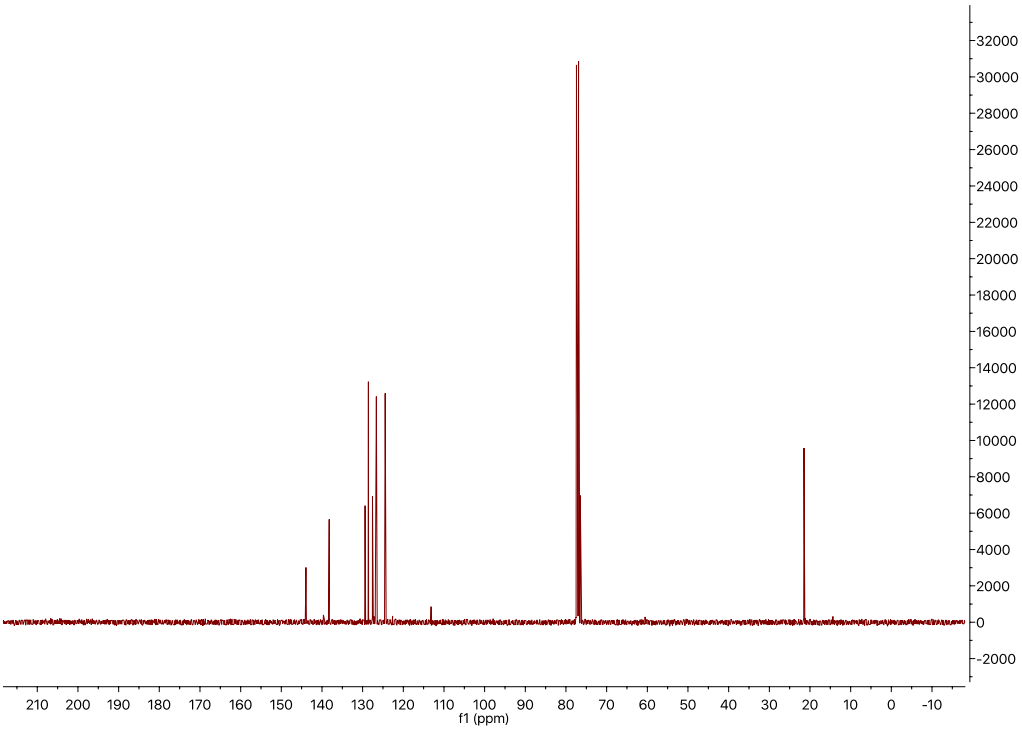


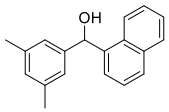




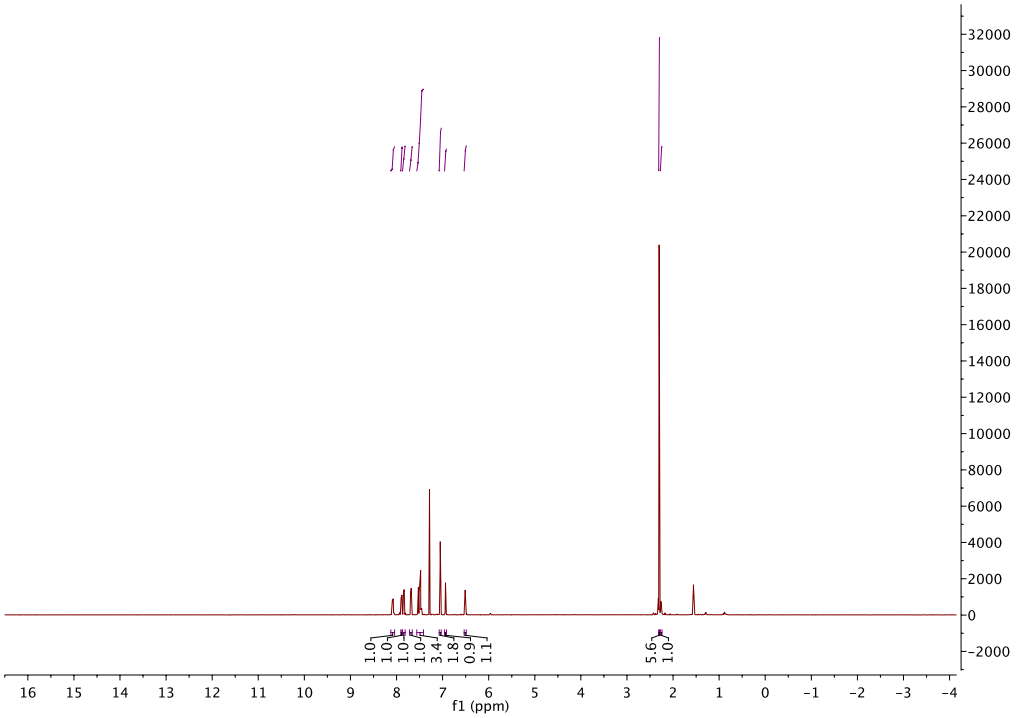
(3,5-dimethylphenyl)(phenyl)methanol

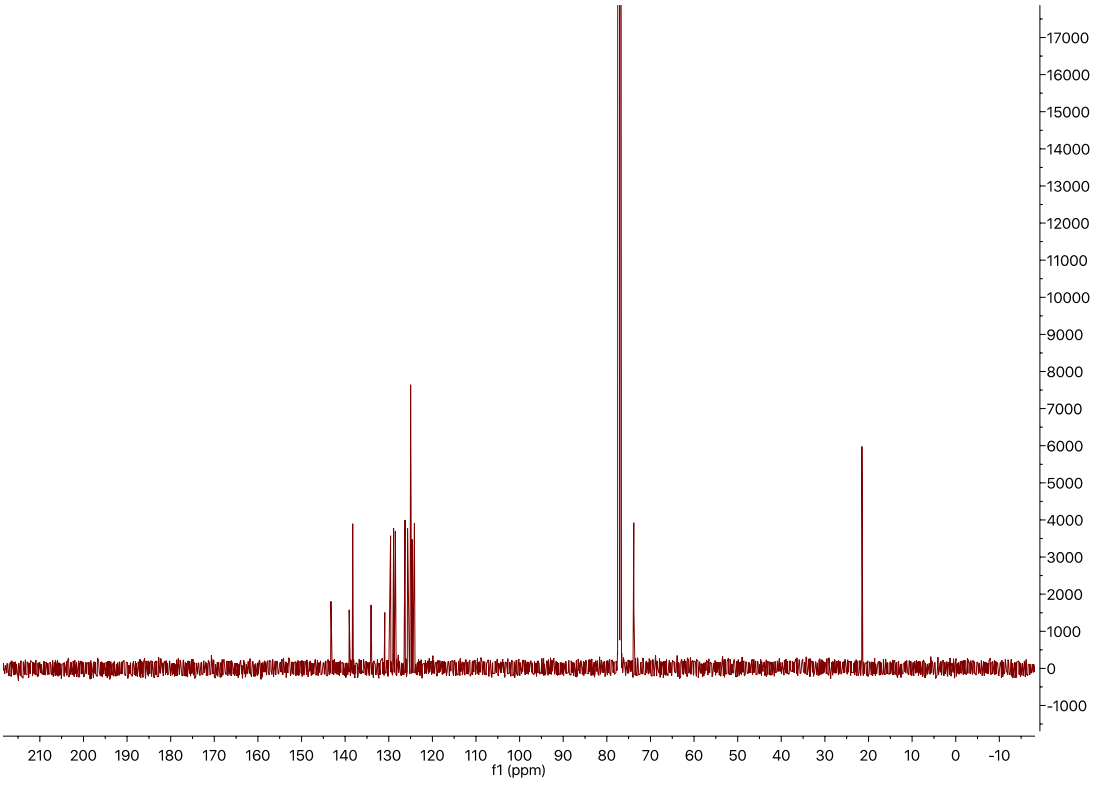


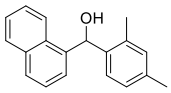




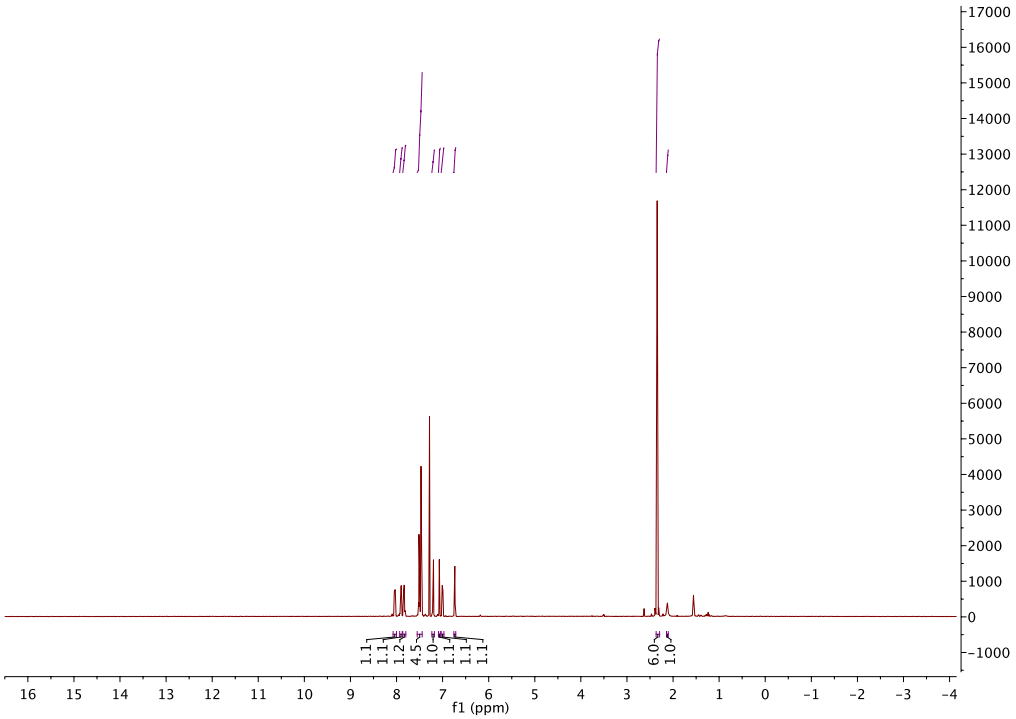
(3,5-dimethylphenyl)(naphthalen-1-yl)methanol

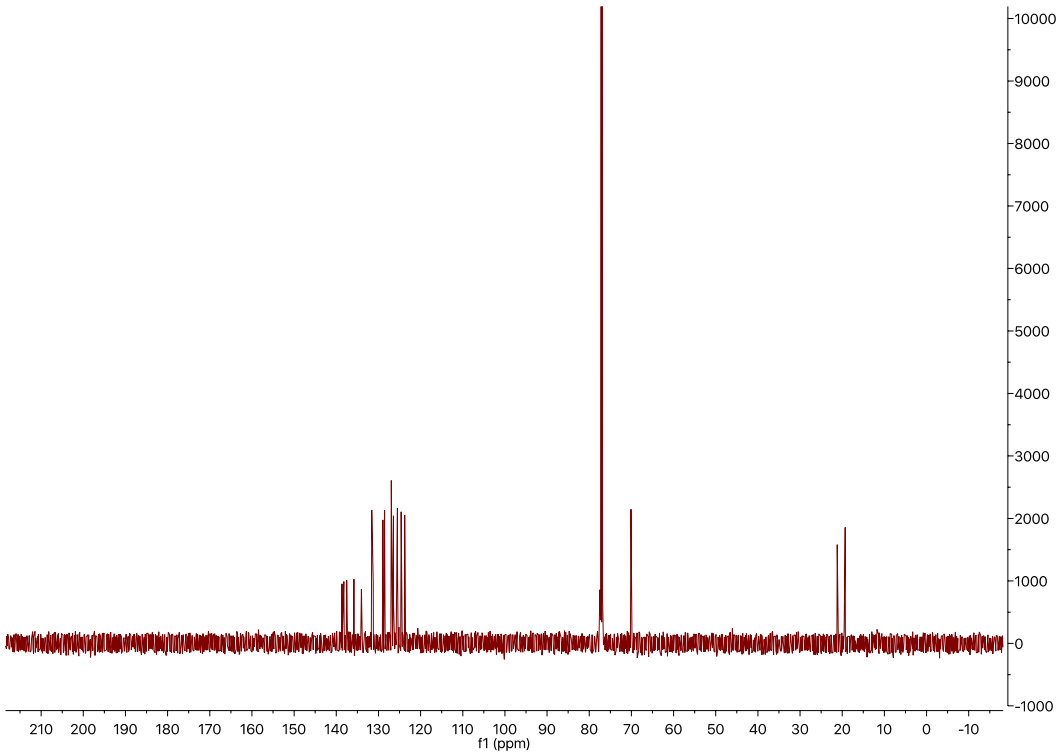


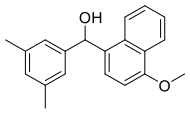




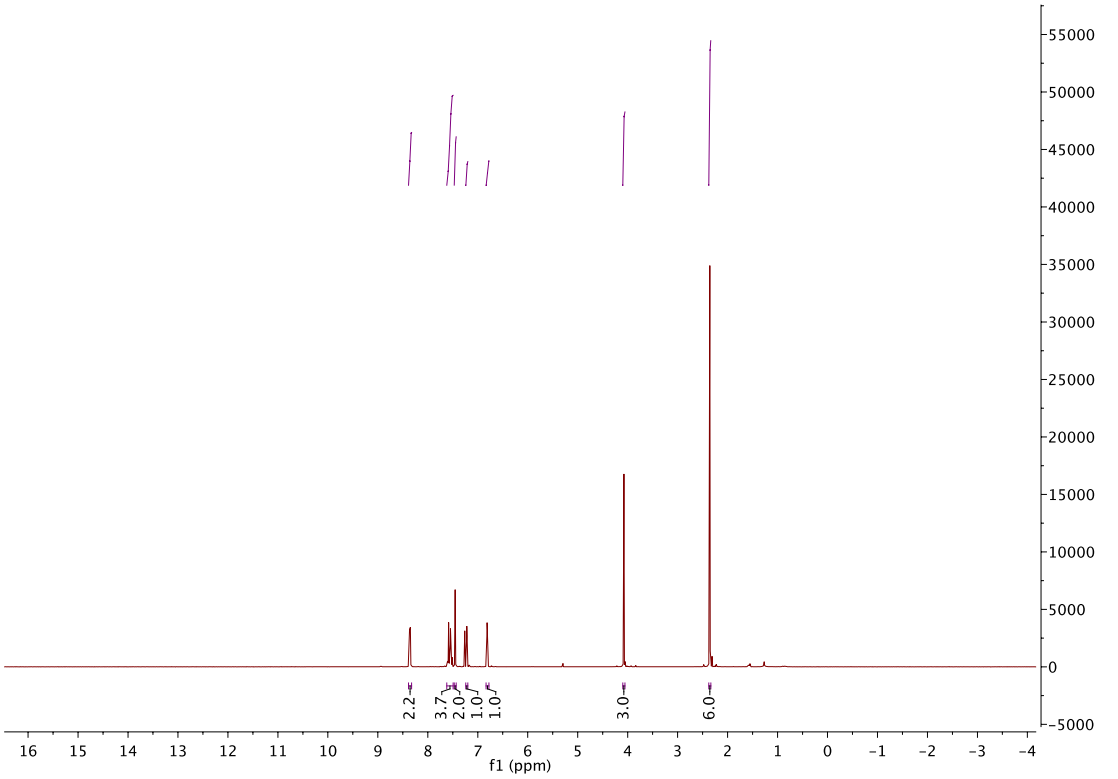
(2,4-dimethylphenyl)(naphthalen-1-yl)methanol

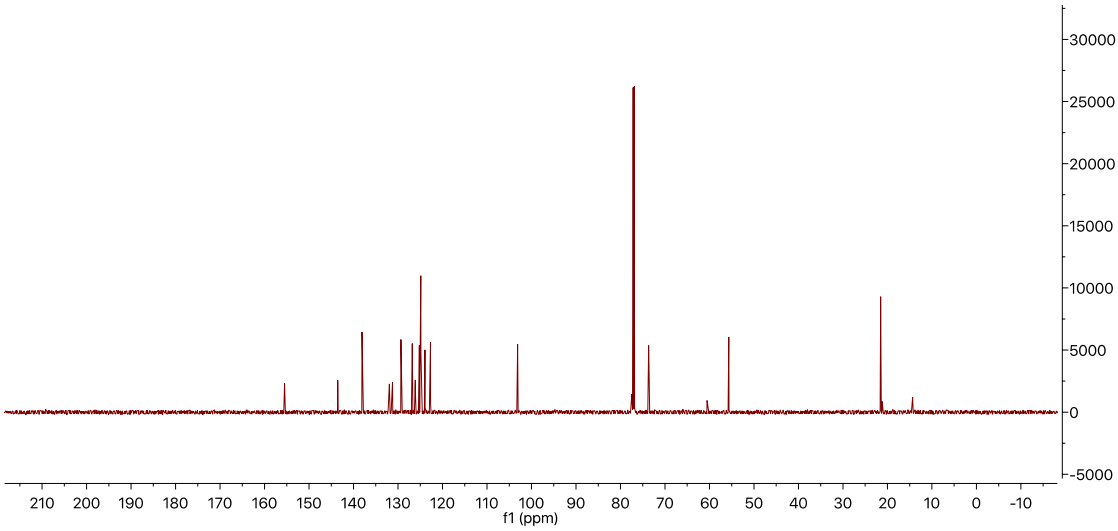


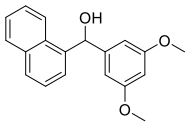




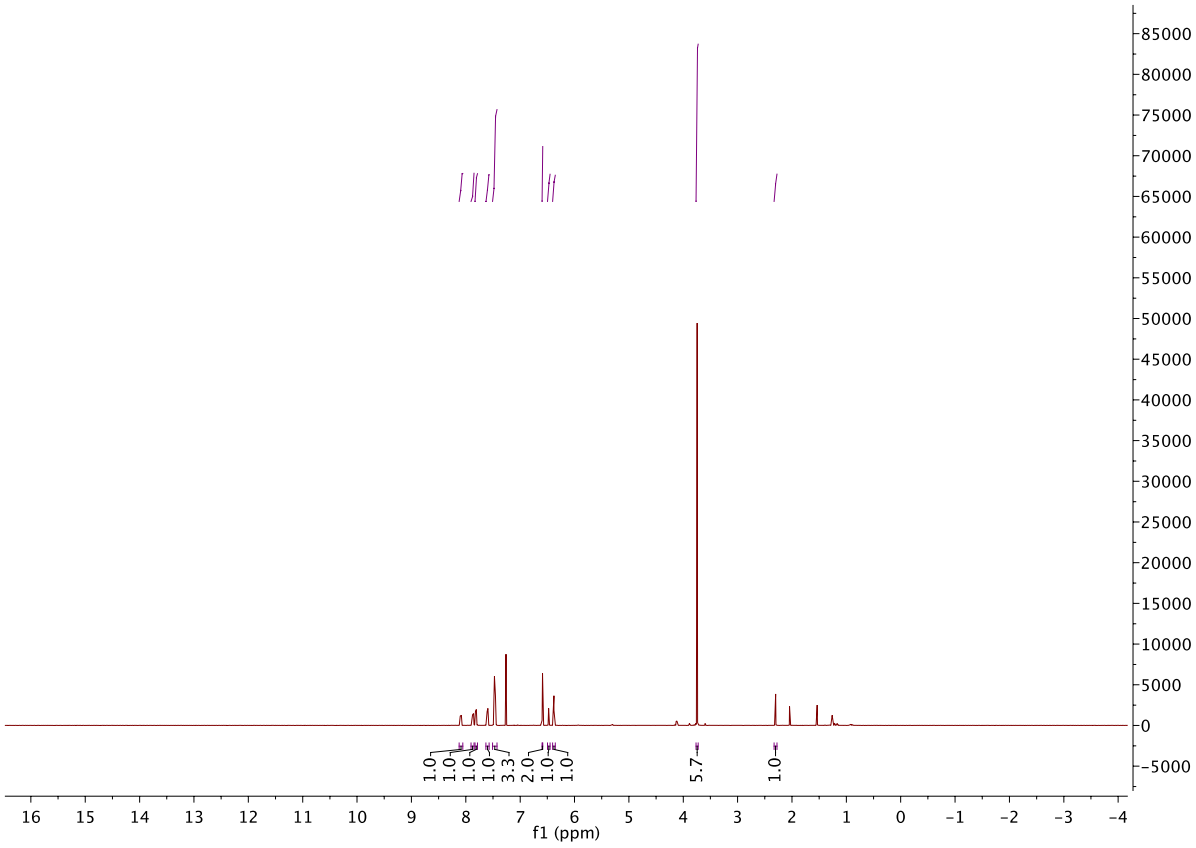
(3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methanol

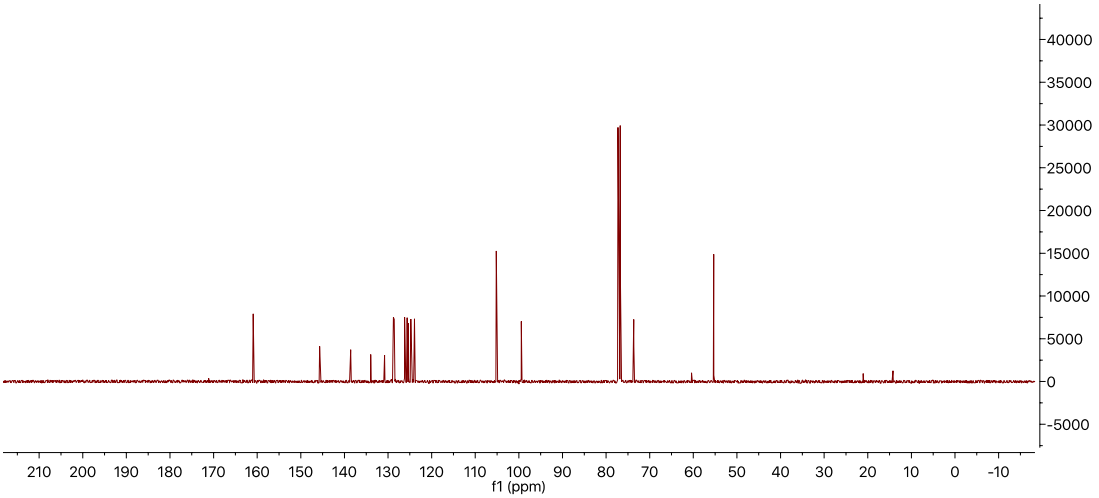


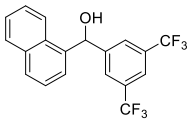




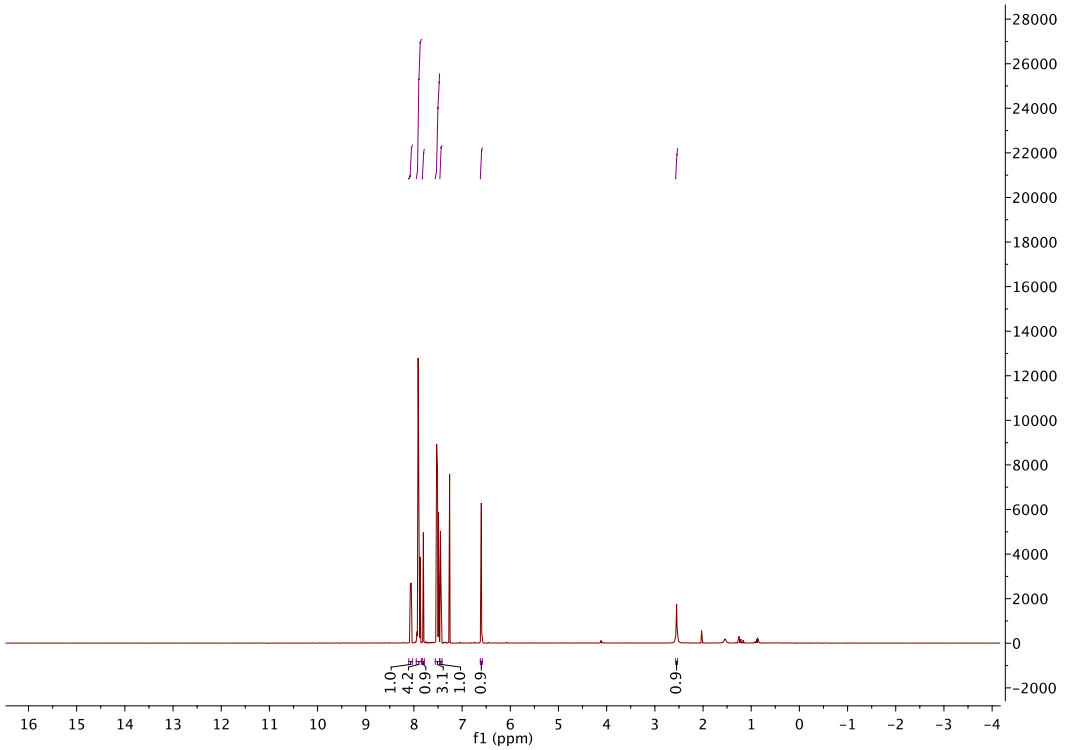
(3,5-dimethoxyphenyl)(naphthalen-1-yl)methanol

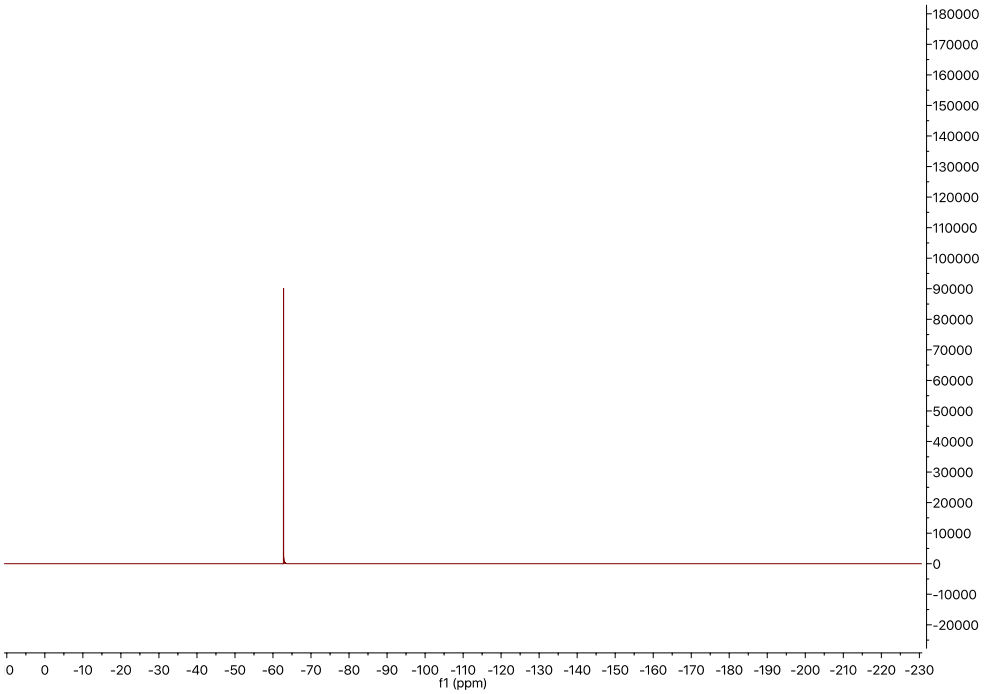


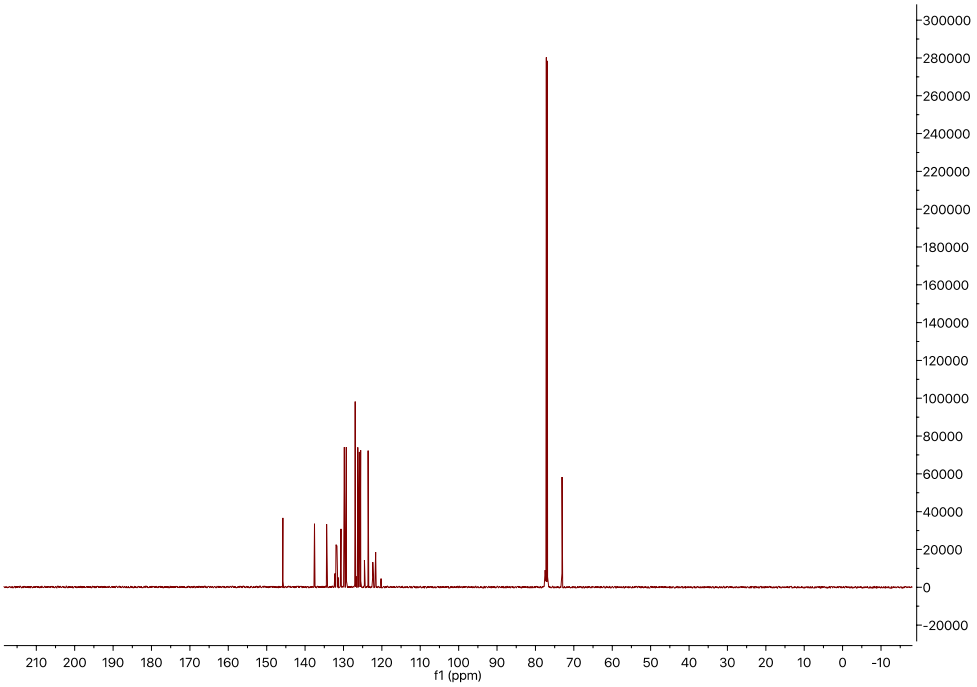


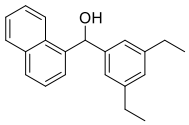


(3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methanol

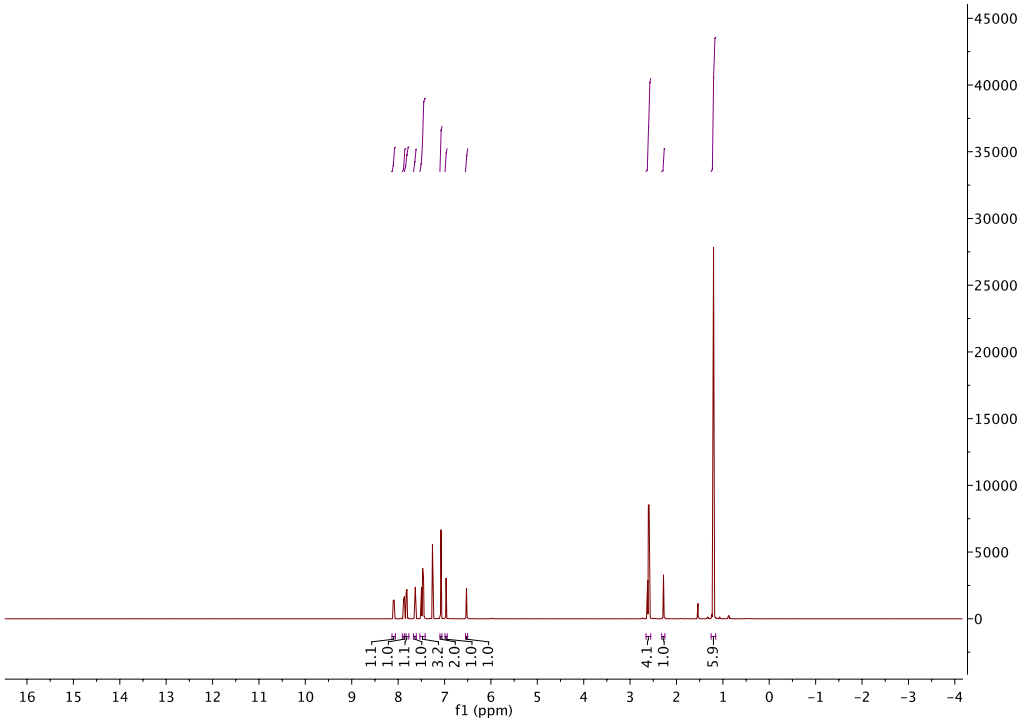


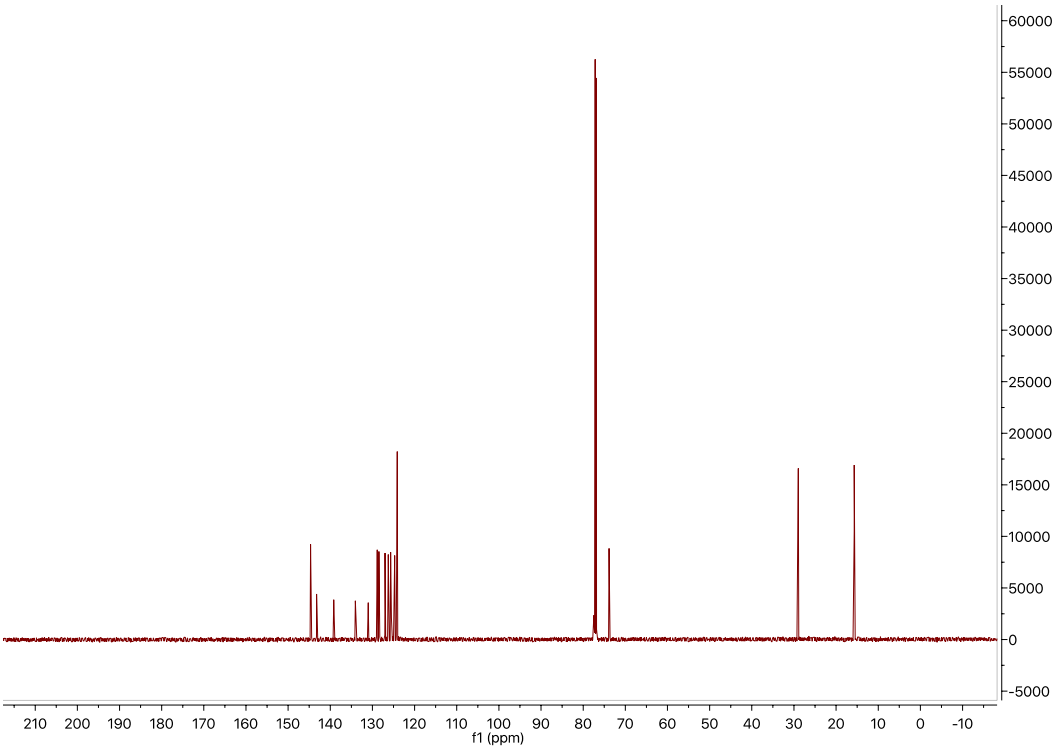


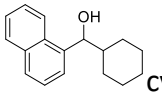




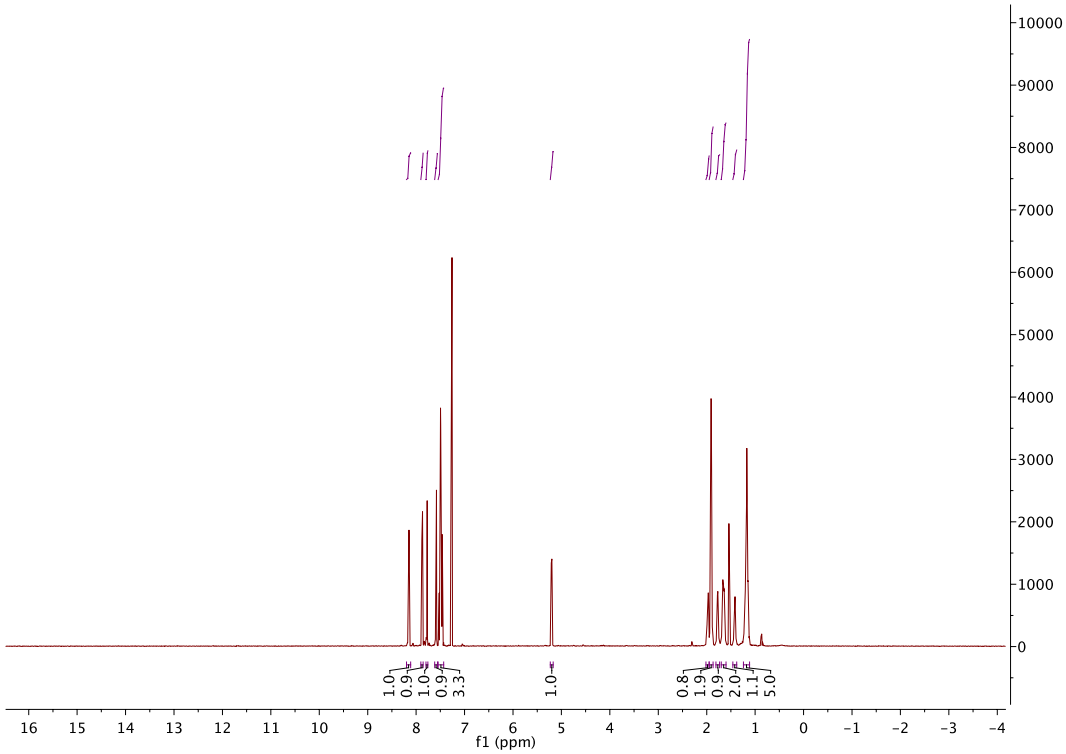
(3,5-diethylphenyl)(naphthalen-1-yl)methanol

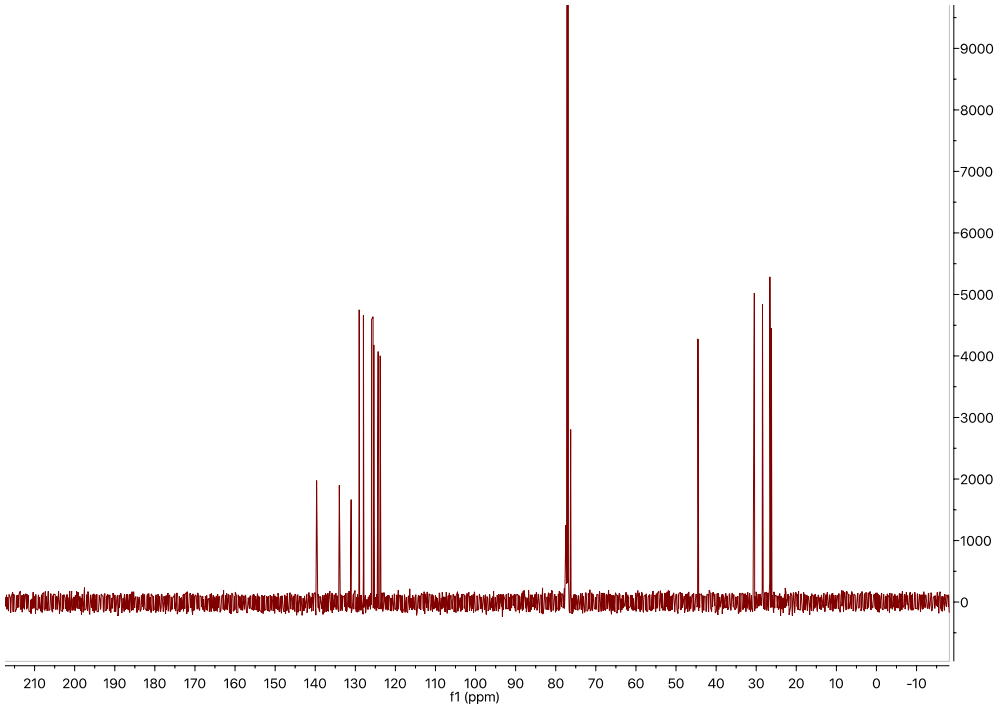


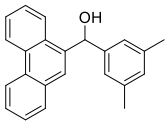




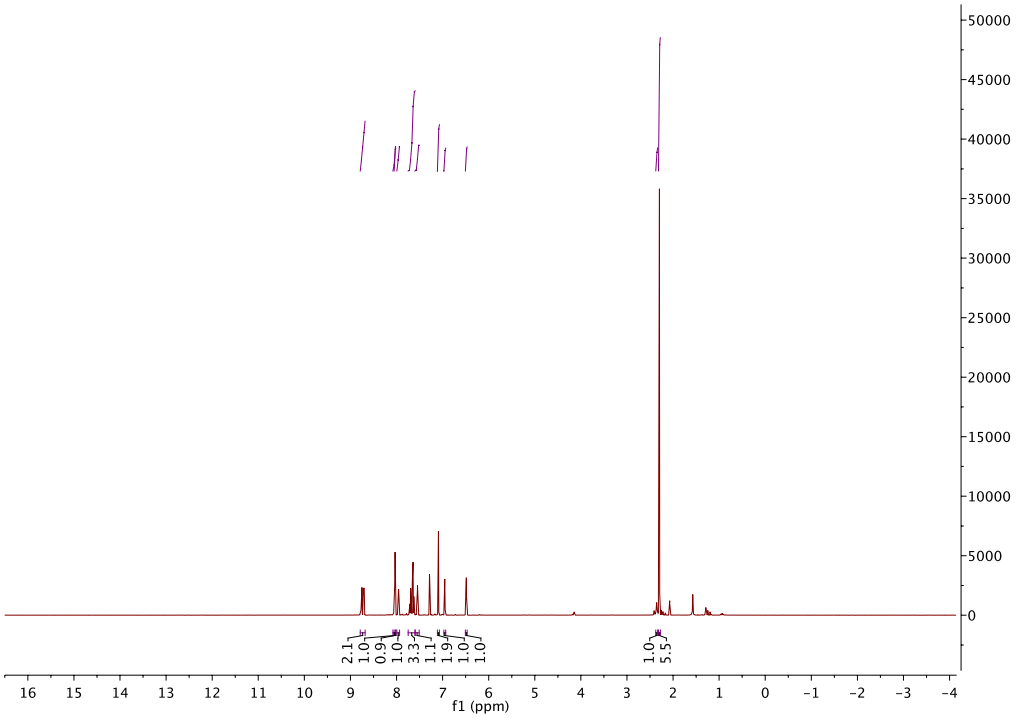
cyclohexyl(naphthalen-1-yl)methanol

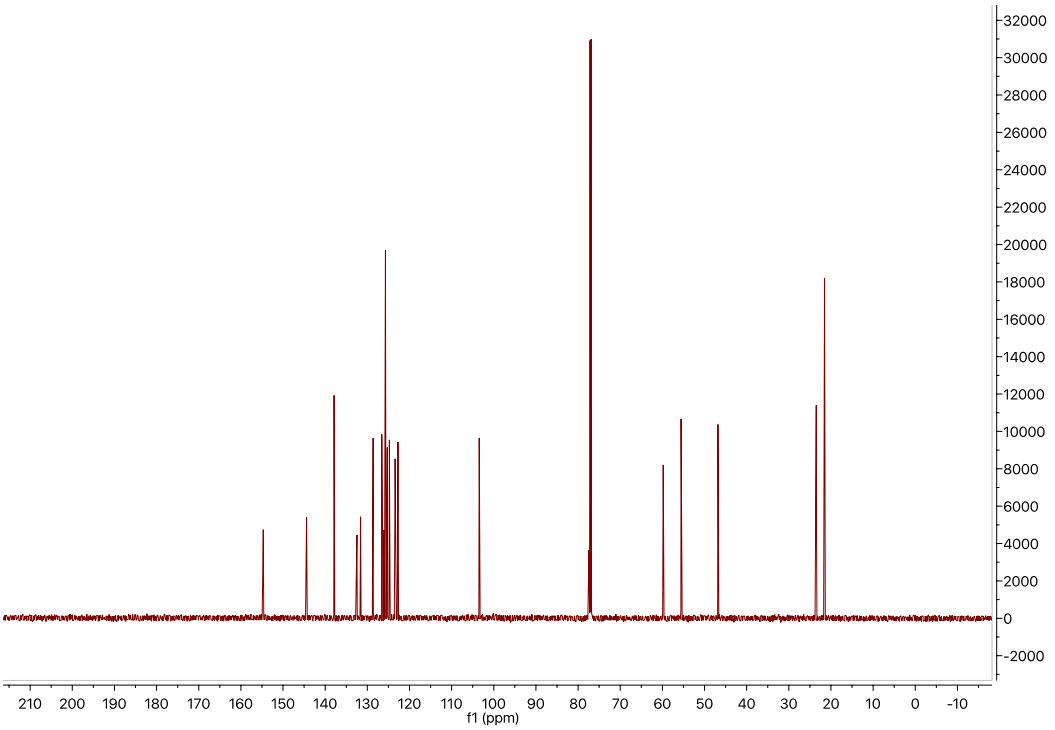


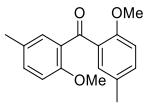




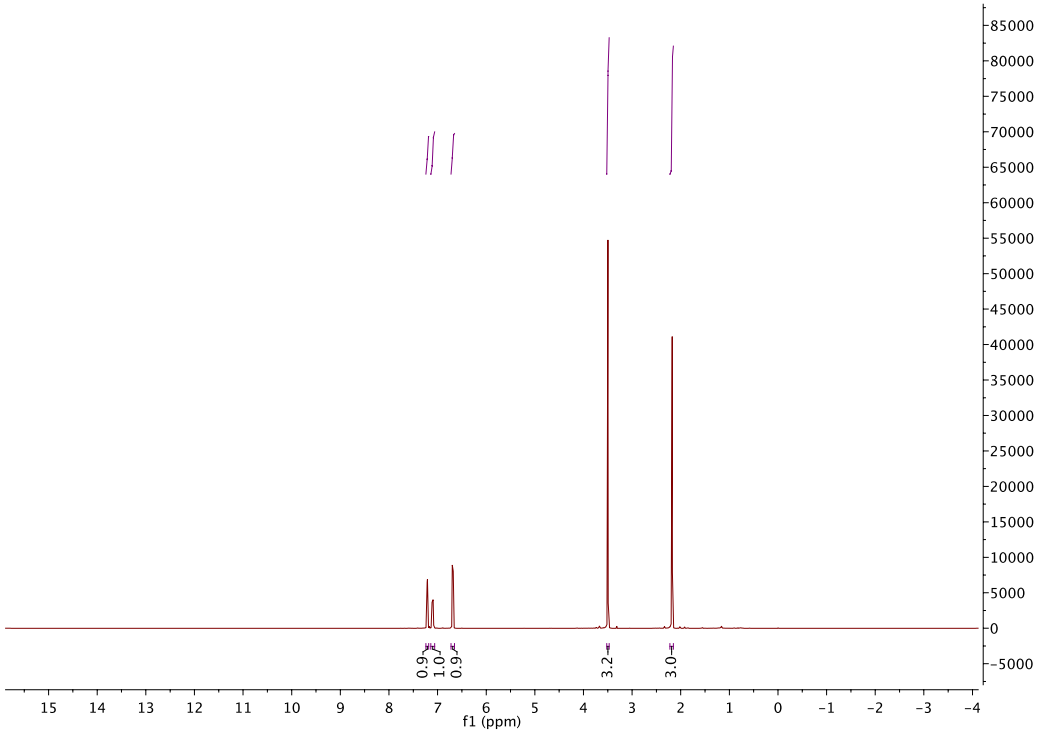
(3,5-dimethylphenyl)(phenanthren-9-yl)methanol

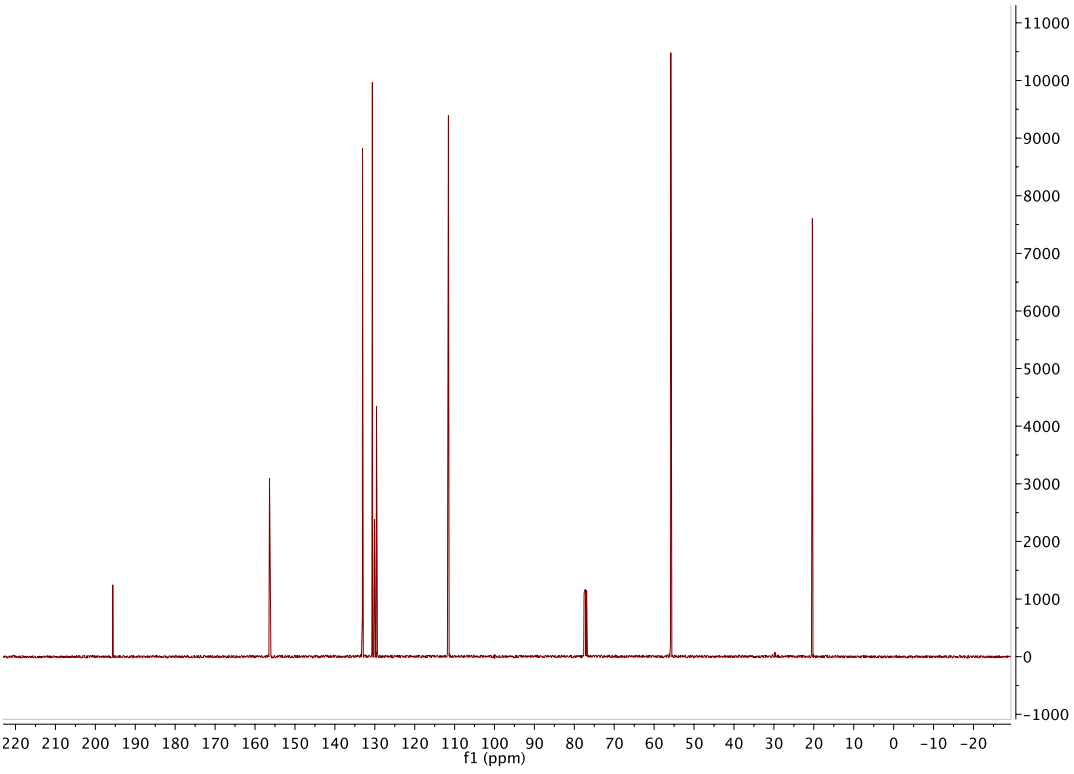


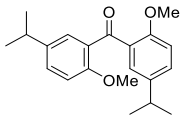




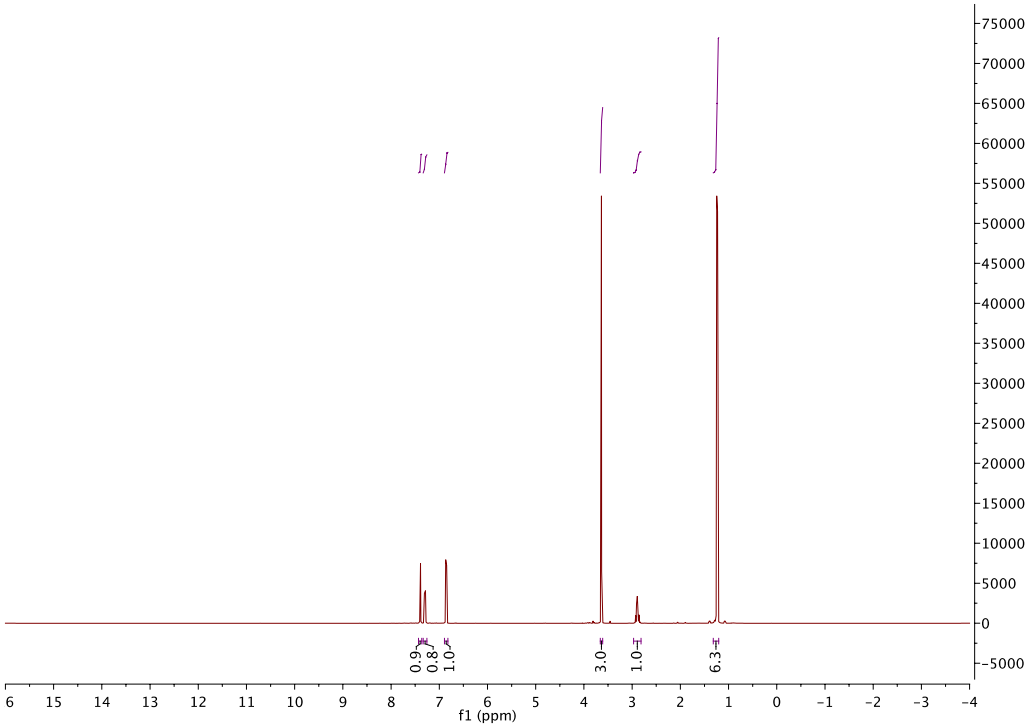
bis(2-methoxy-5-methylphenyl)methanone

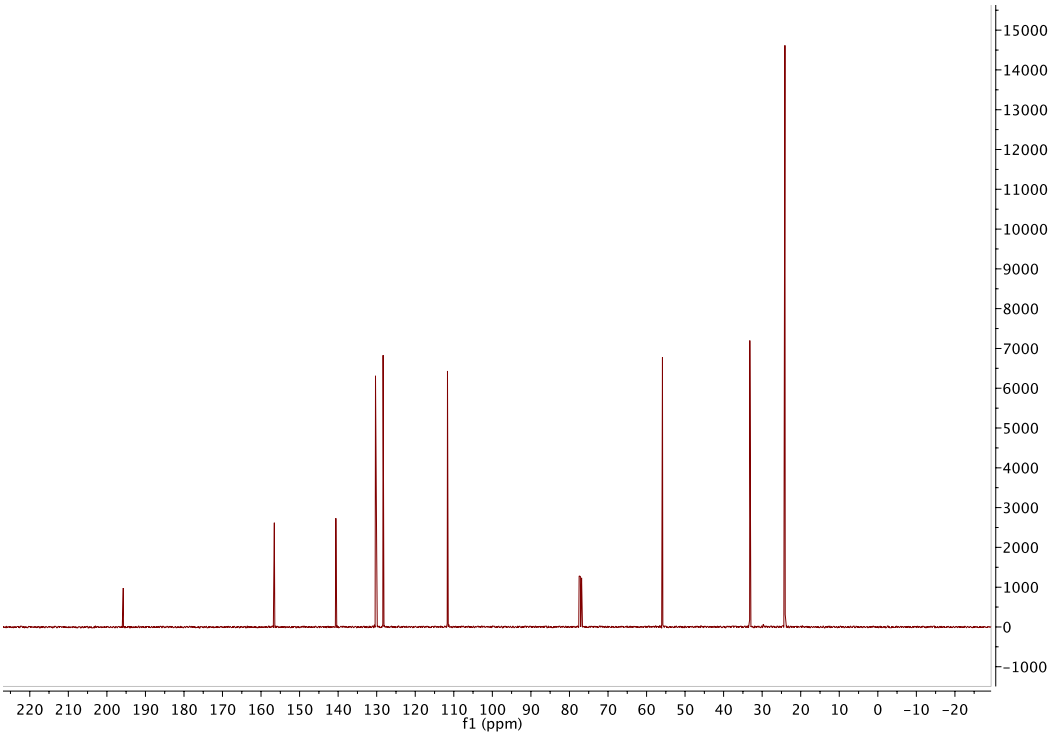


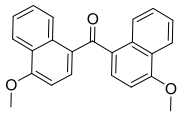




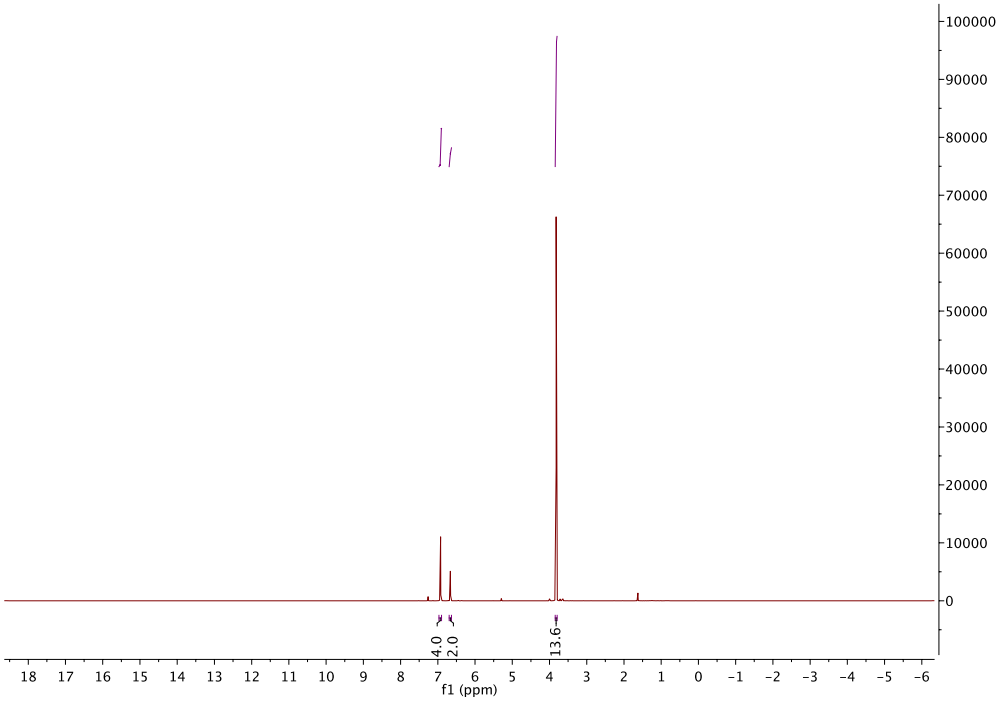
bis(5-isopropyl-2-methoxyphenyl)methanone

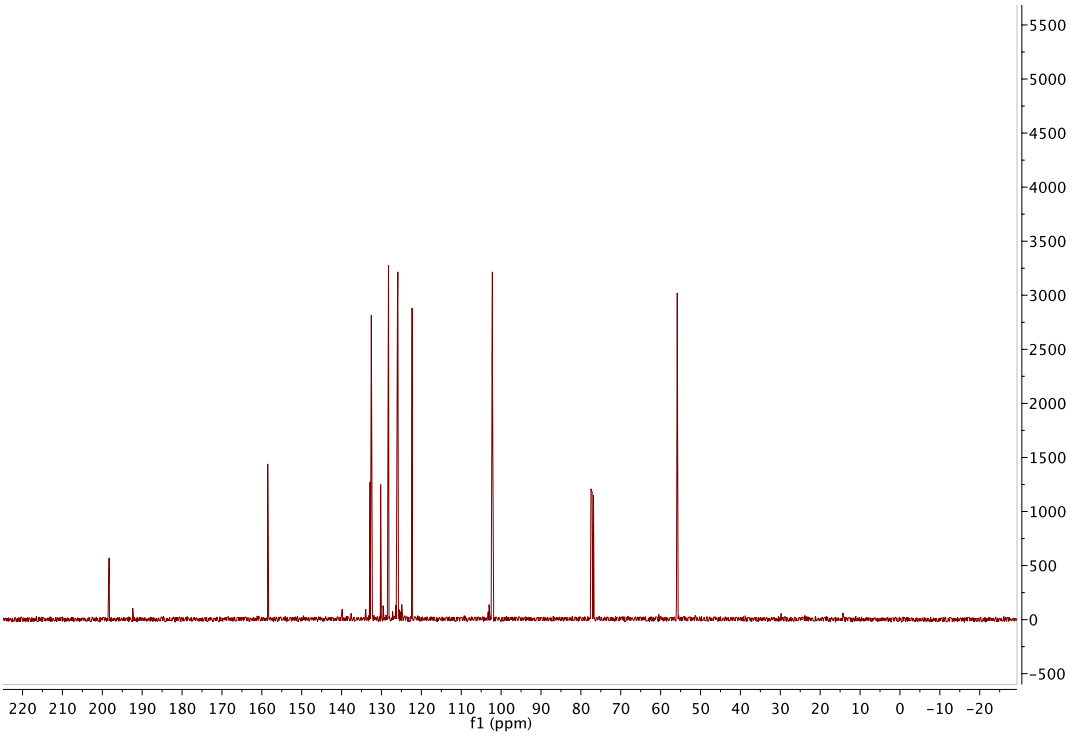


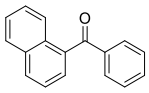




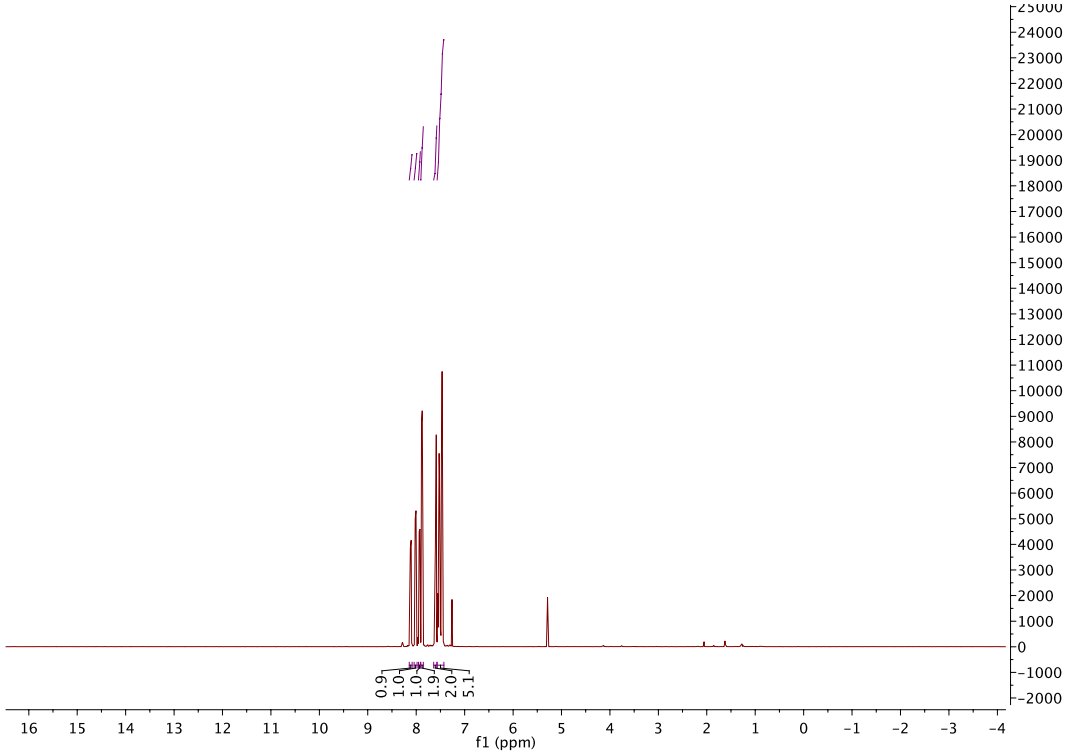
bis(4-methoxynaphthalen-1-yl)methanone

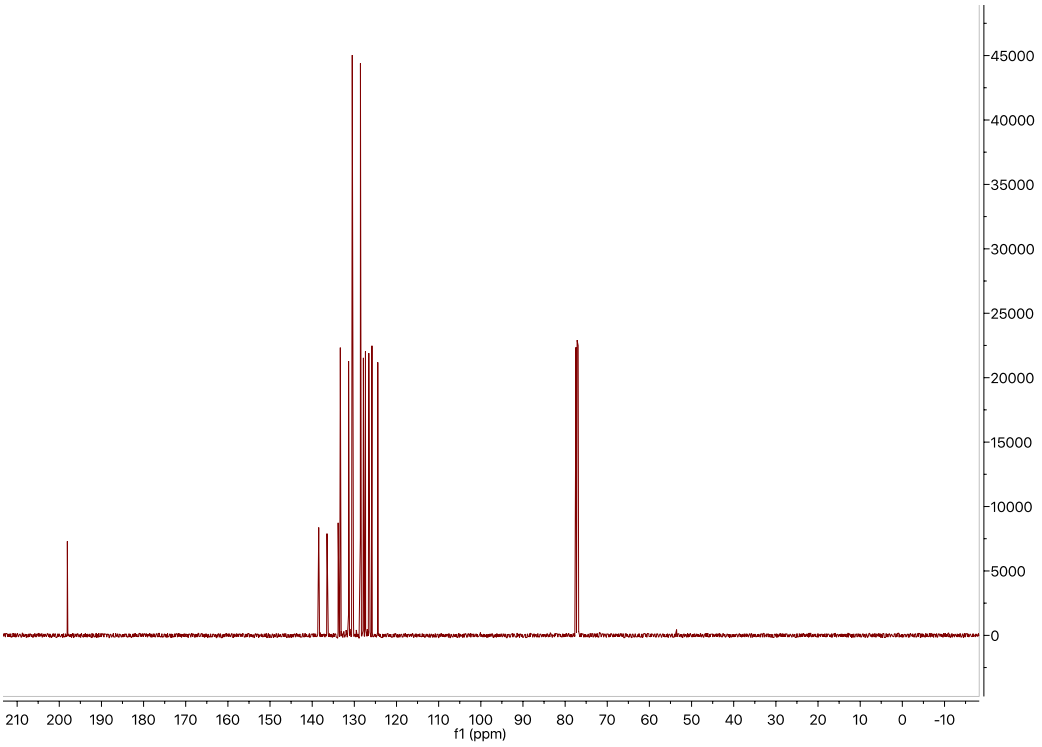


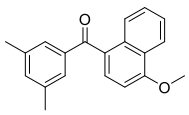




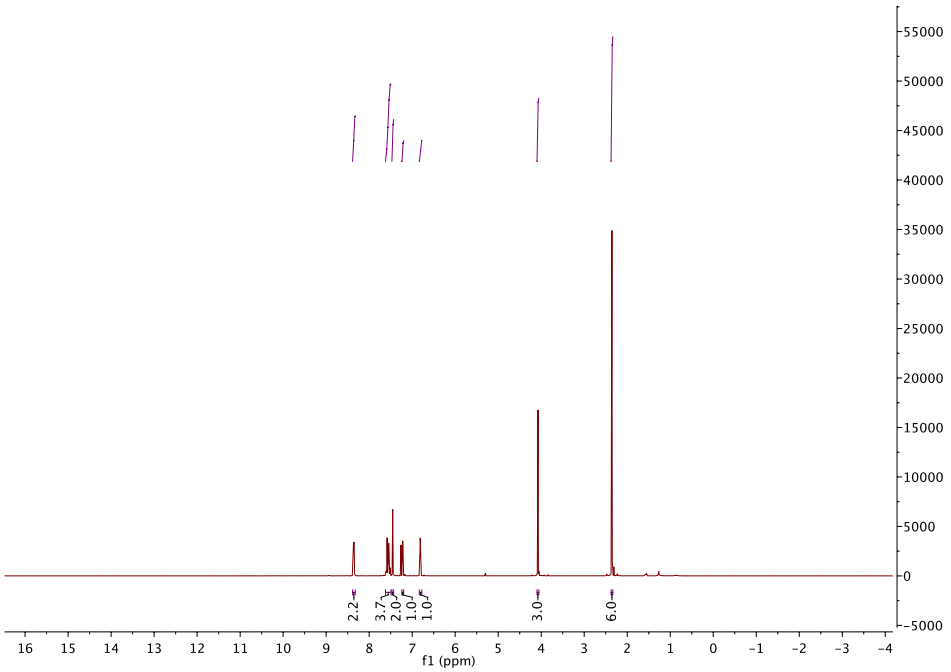
naphthalen-1-yl(phenyl)methanone

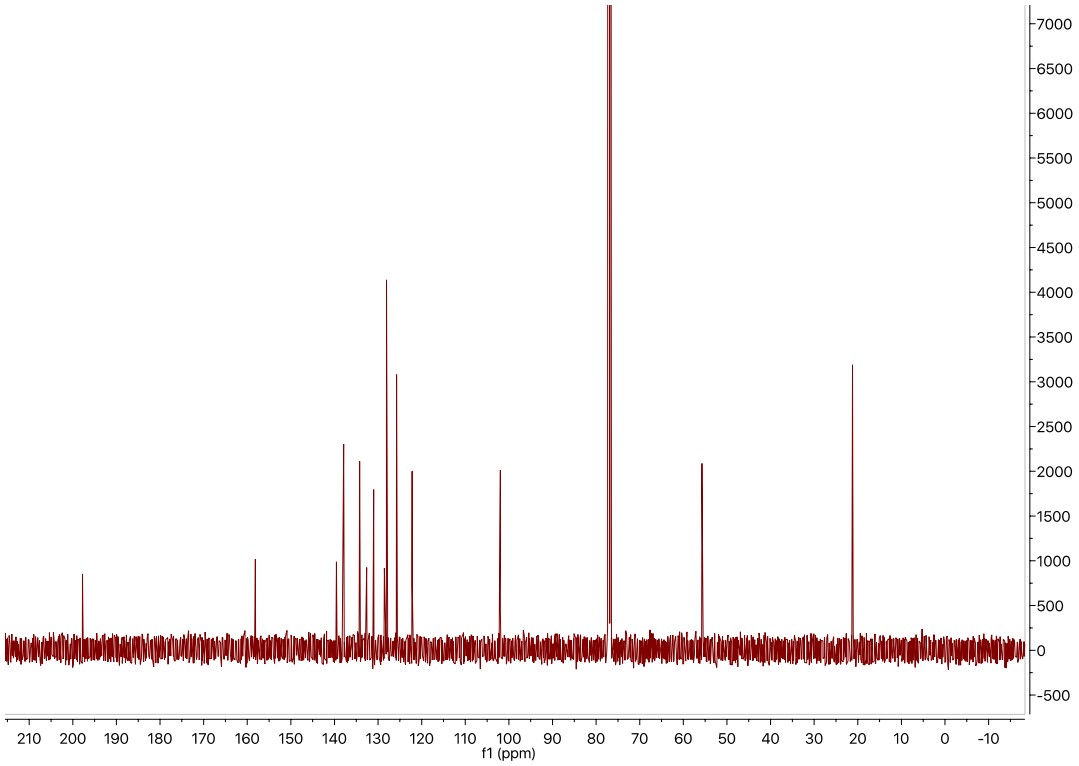


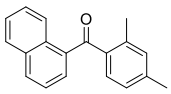




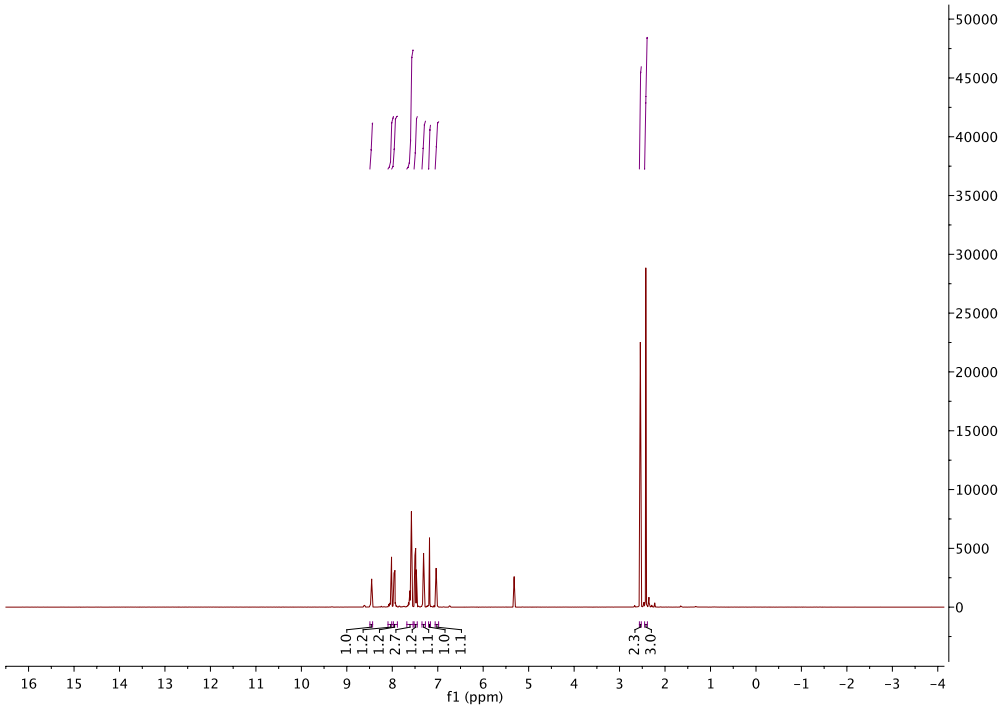
(3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methanone

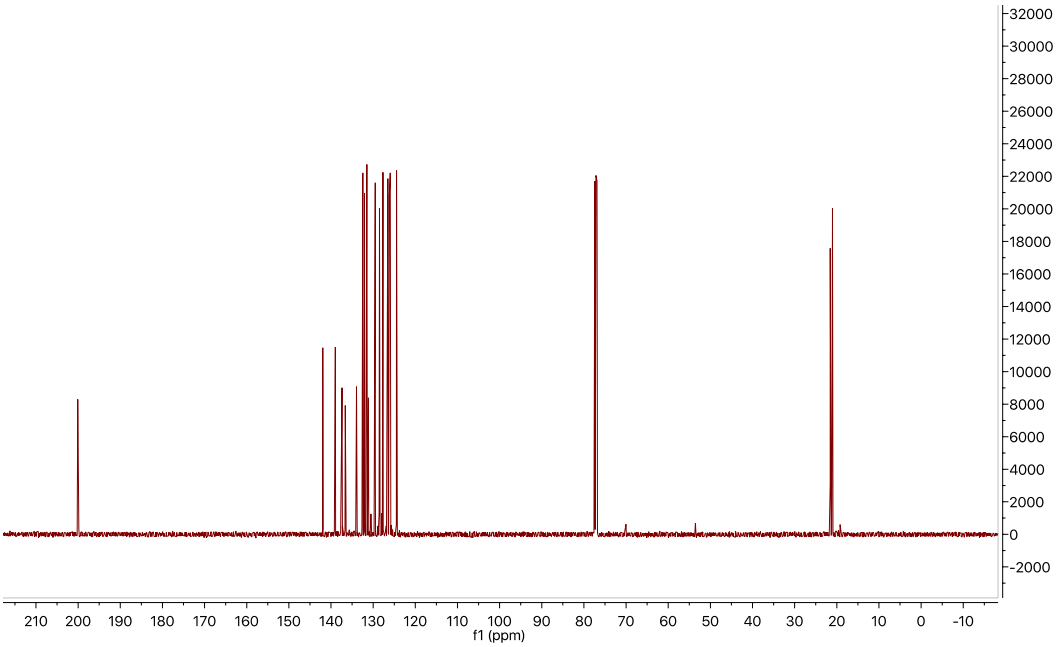


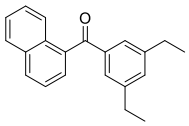




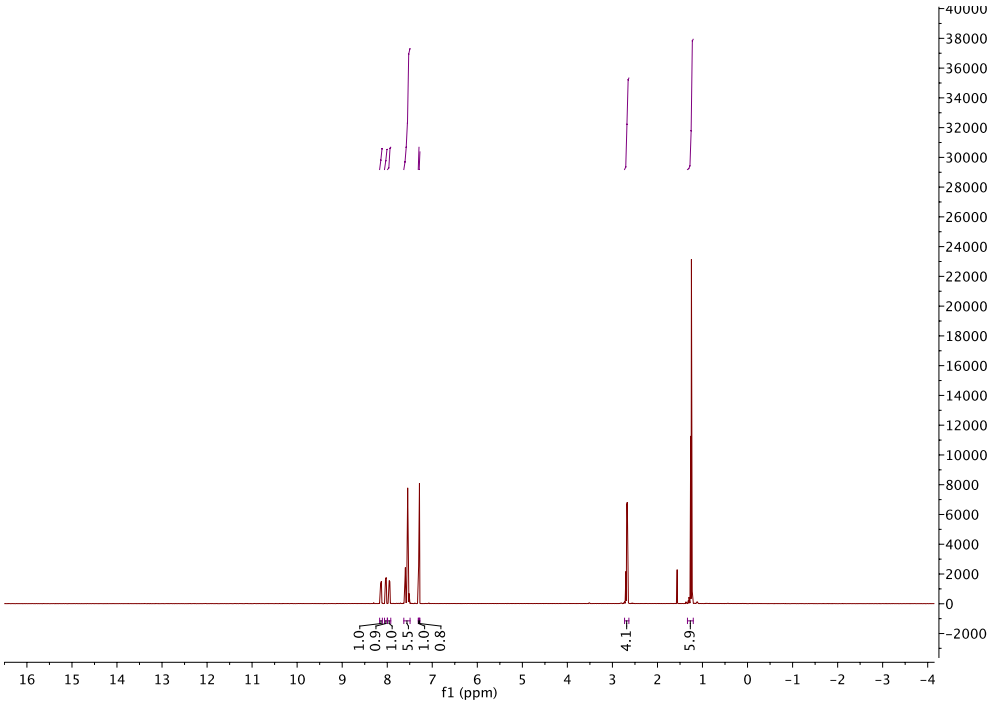
(2,4-dimethylphenyl)(naphthalen-1-yl)methanone

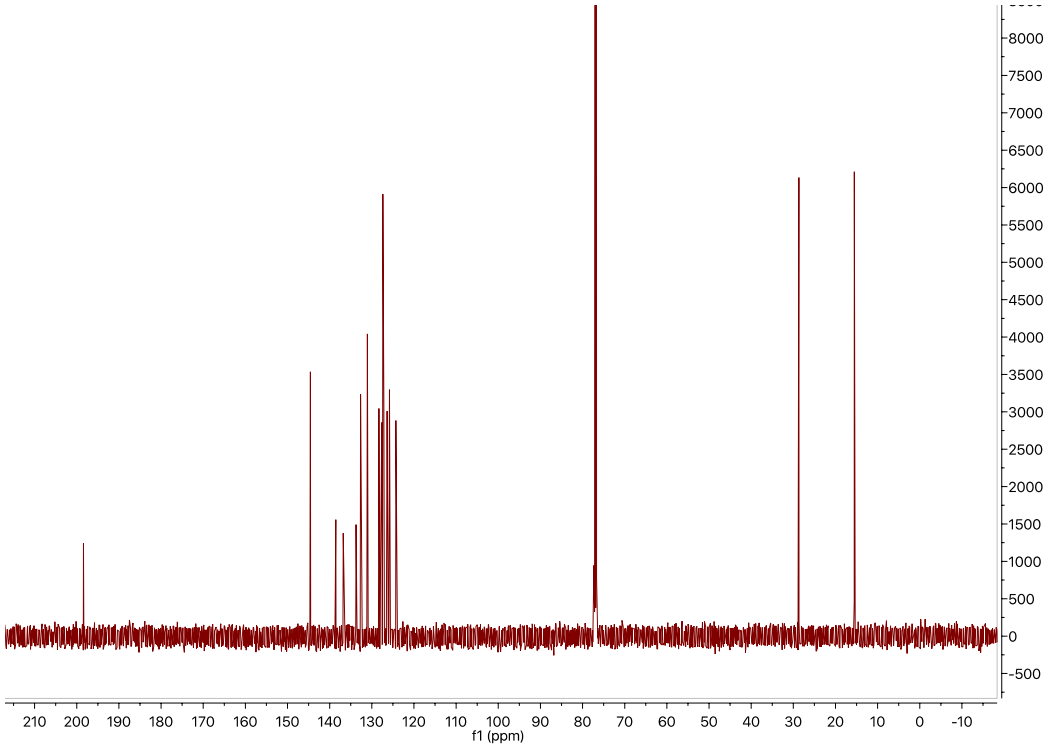


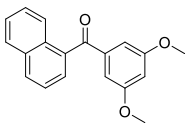




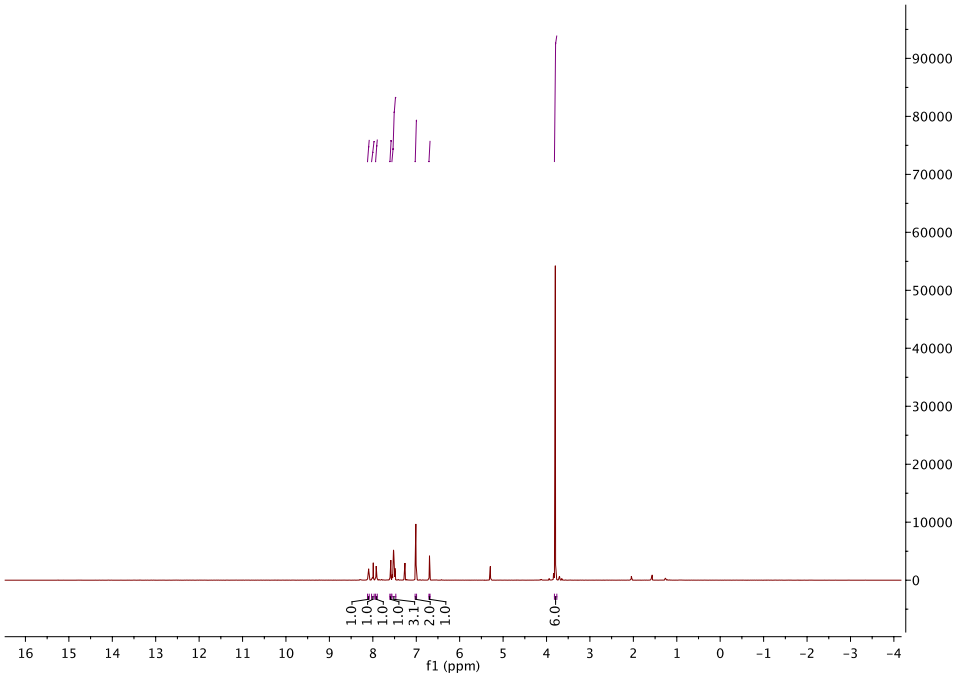
(3,5-diethylphenyl)(naphthalen-1-yl)methanone

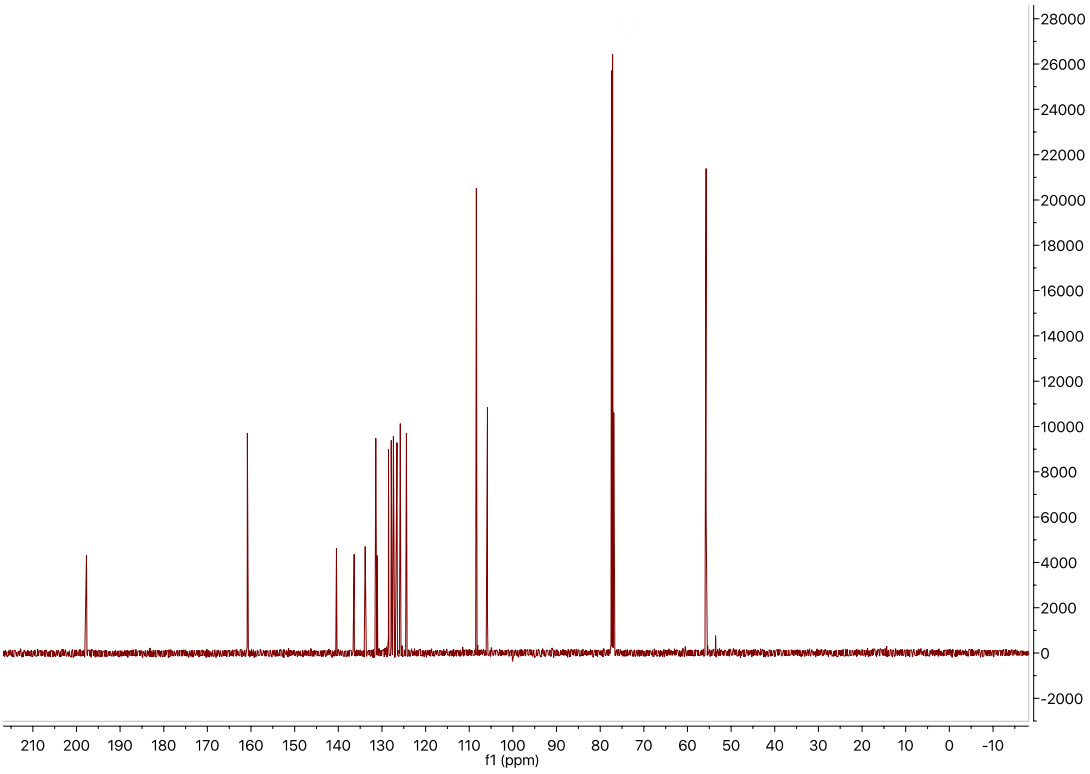


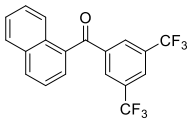




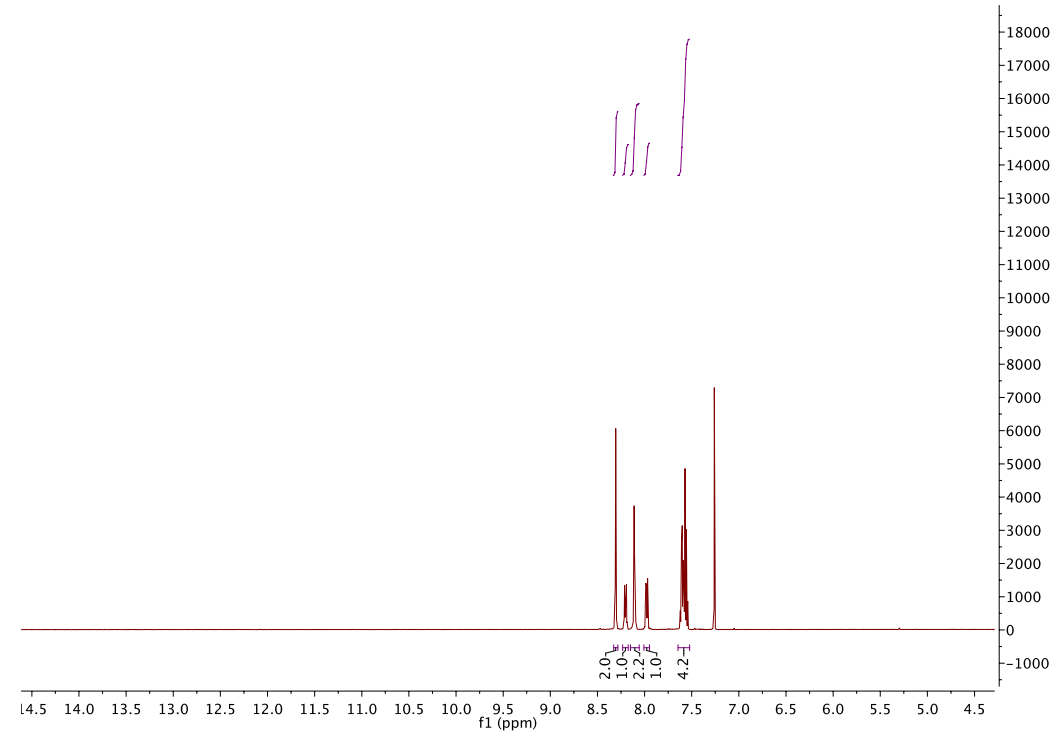
(3,5-dimethoxyphenyl)(naphthalen-1-yl)methanone

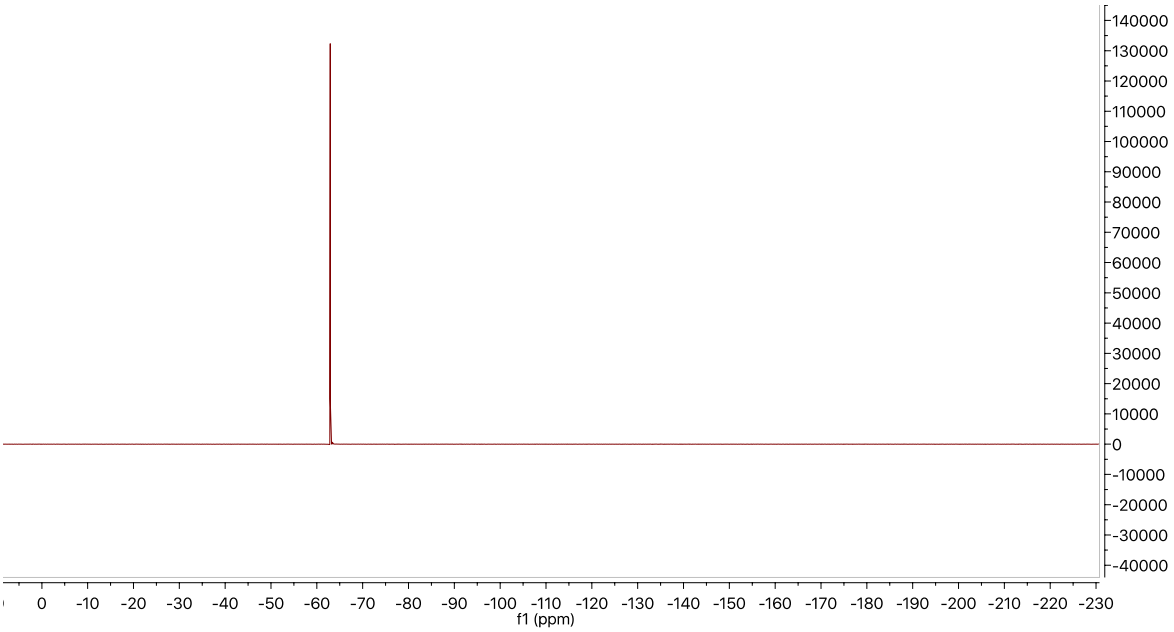






(3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methanone

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-20000
-30000
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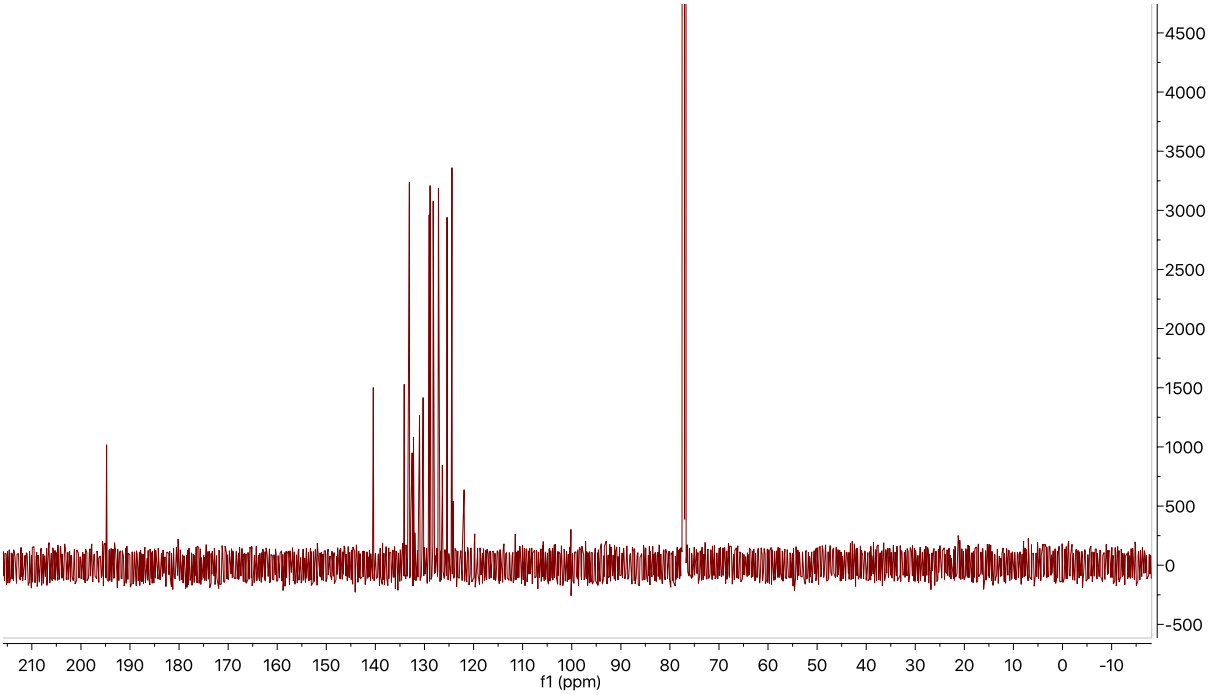
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)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4000
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3000
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-500
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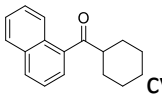
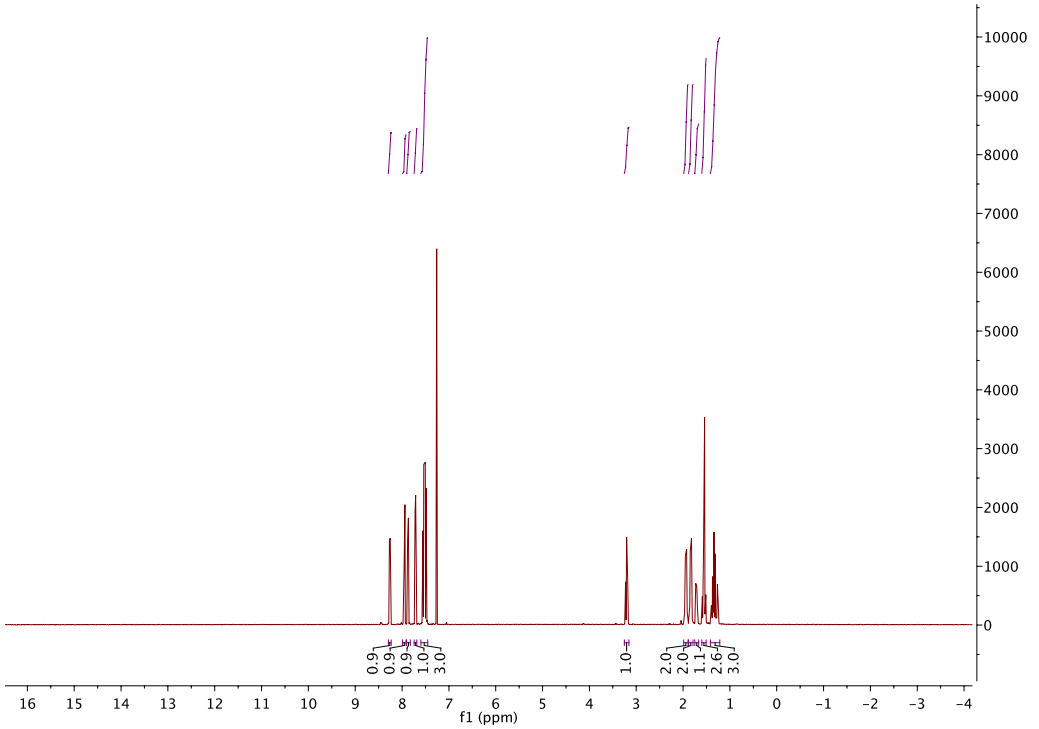
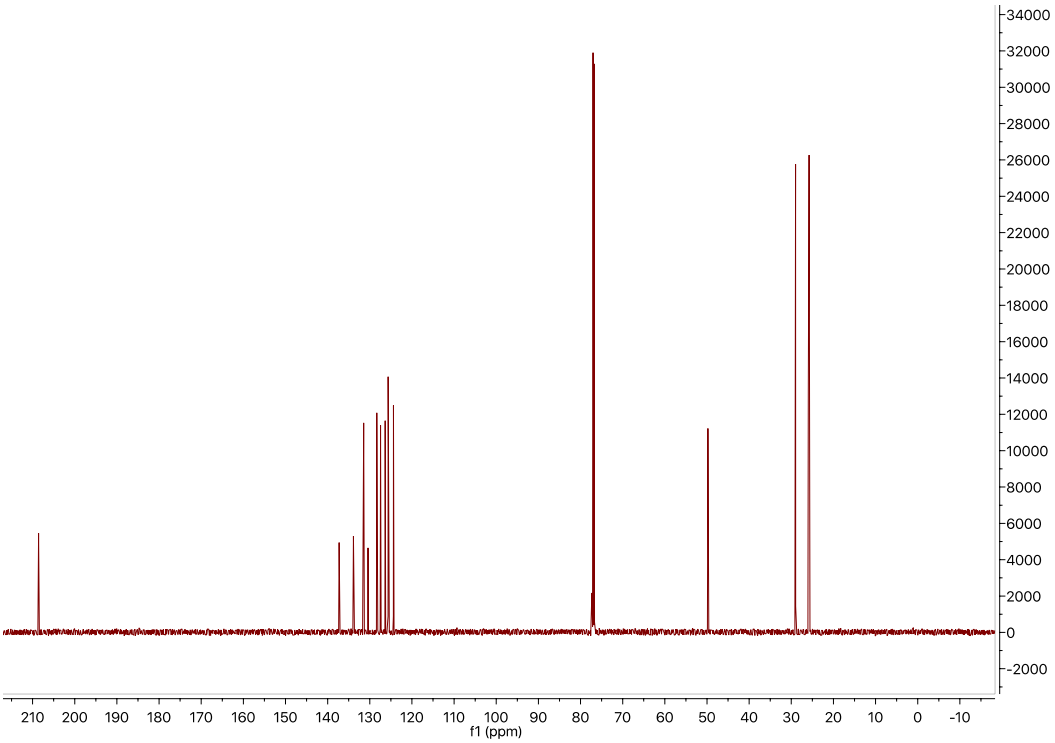
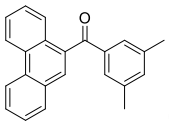
f1 (ppm)



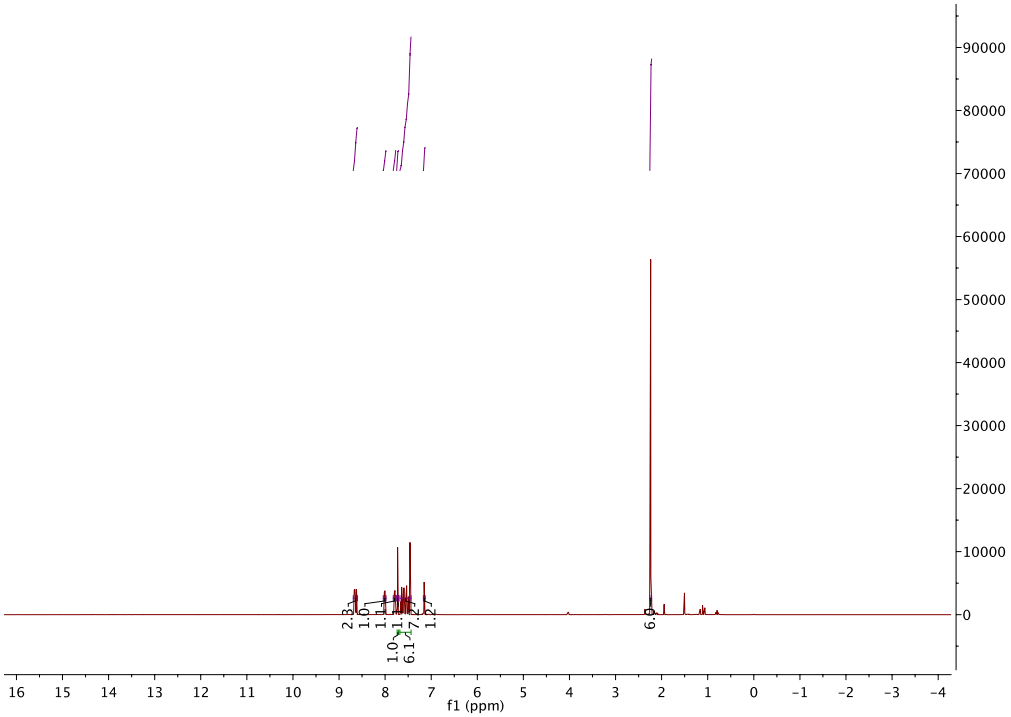
cyclohexyl(naphthalen-1-yl)methanone

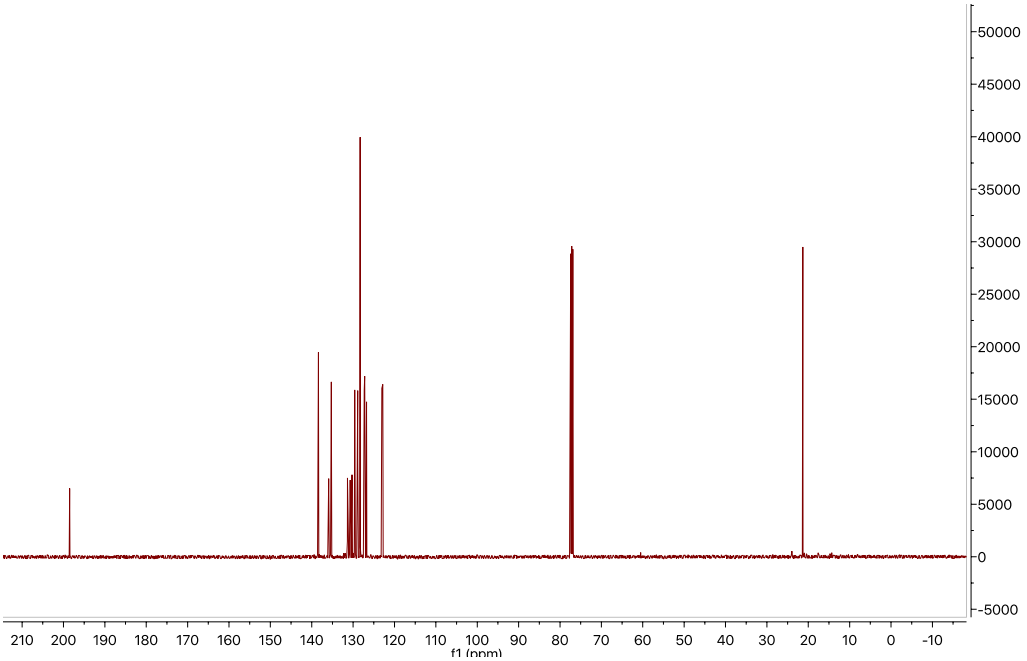


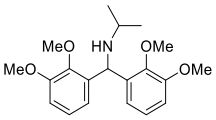




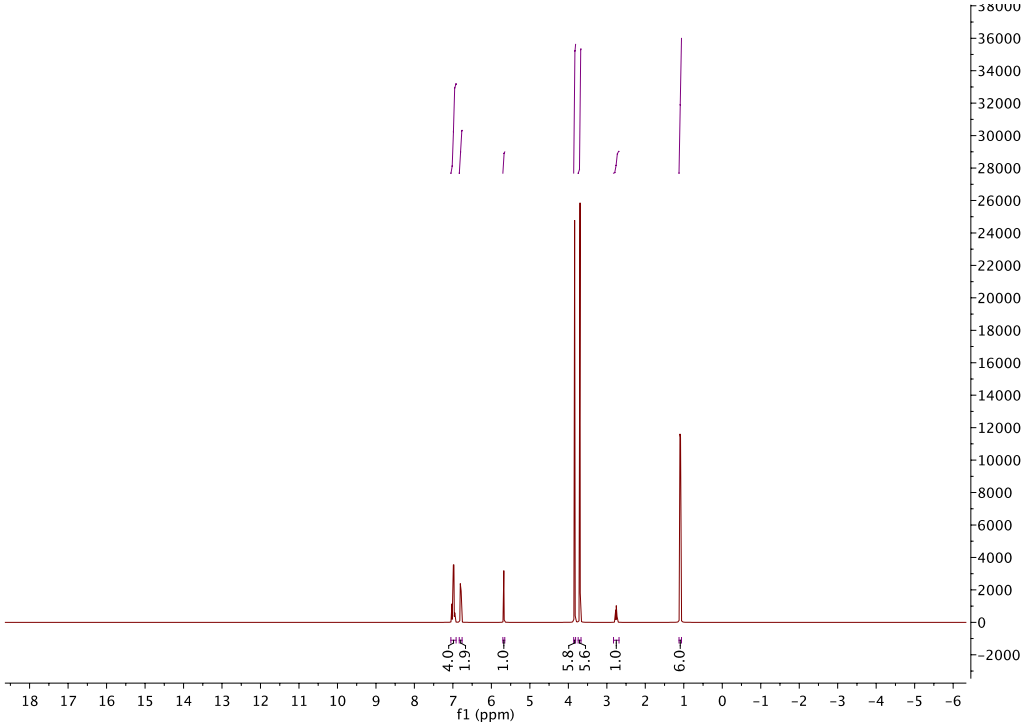
(3,5-dimethylphenyl)(phenanthren-9-yl)methanone

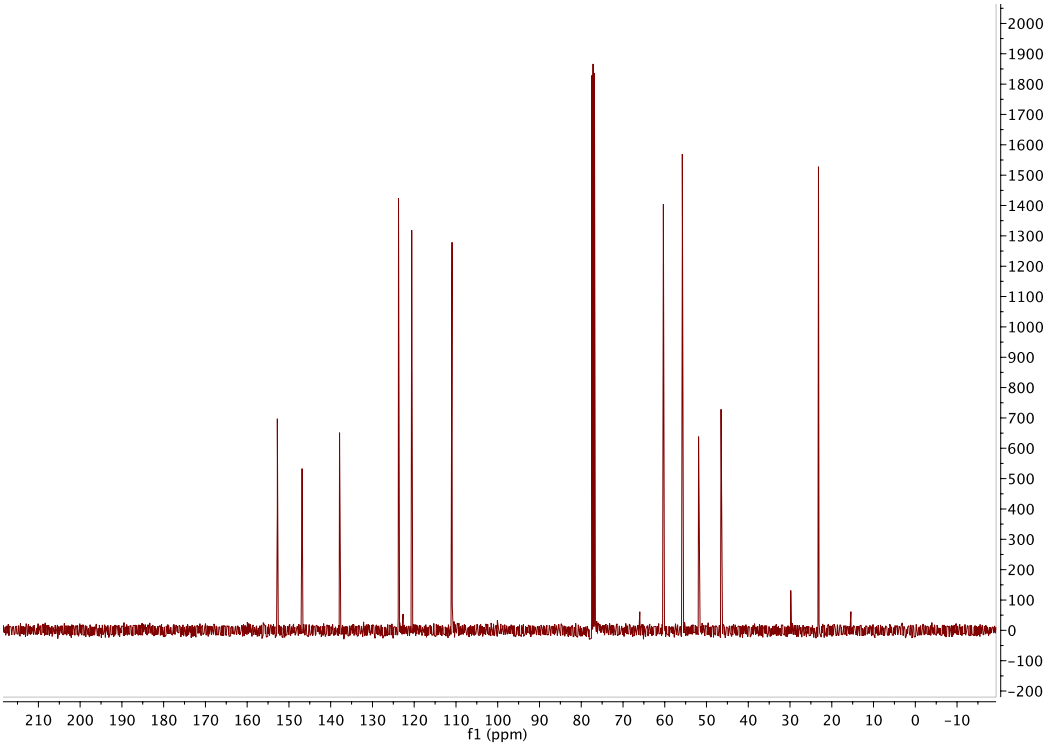


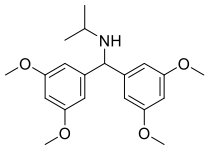




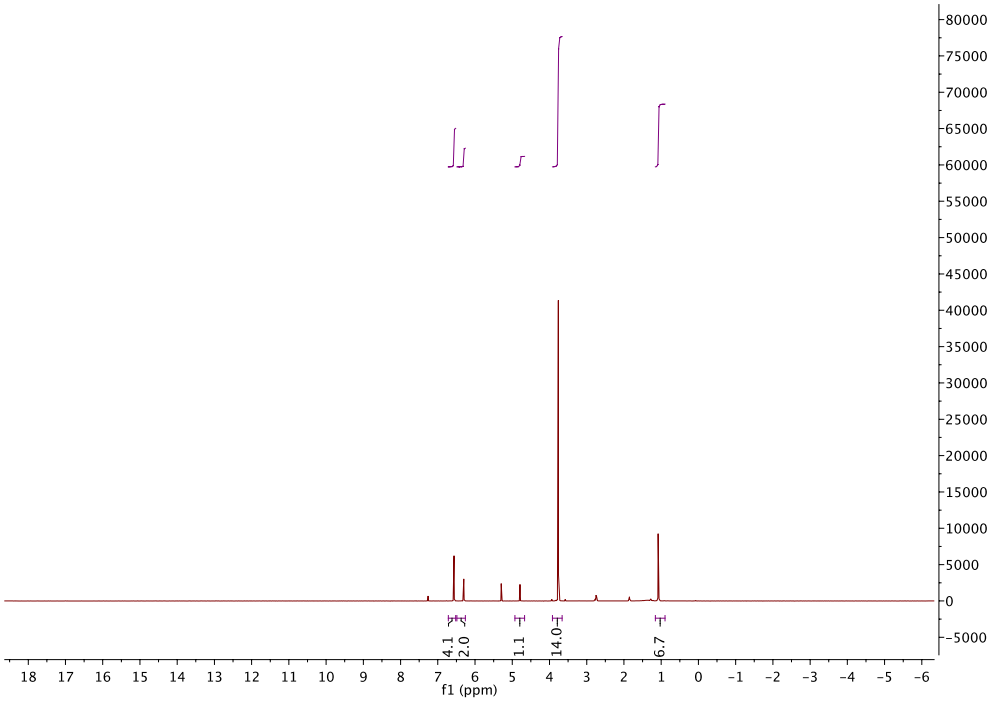
N-(bis(2,3-dimethoxyphenyl)methyl)propan-2-amine

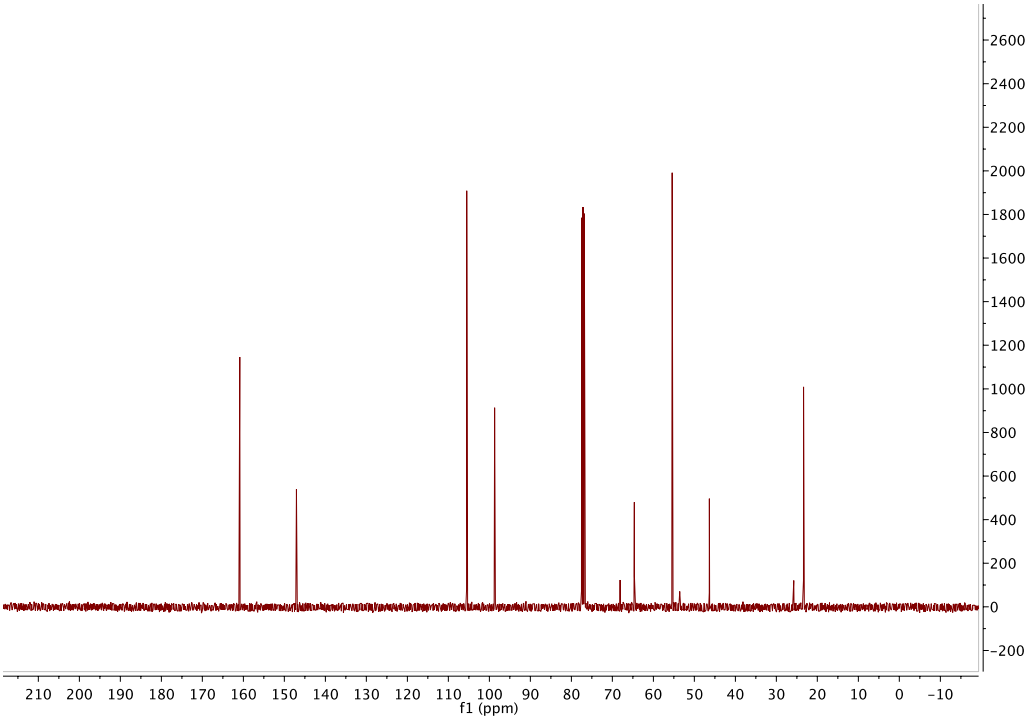


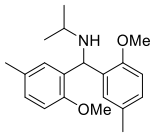




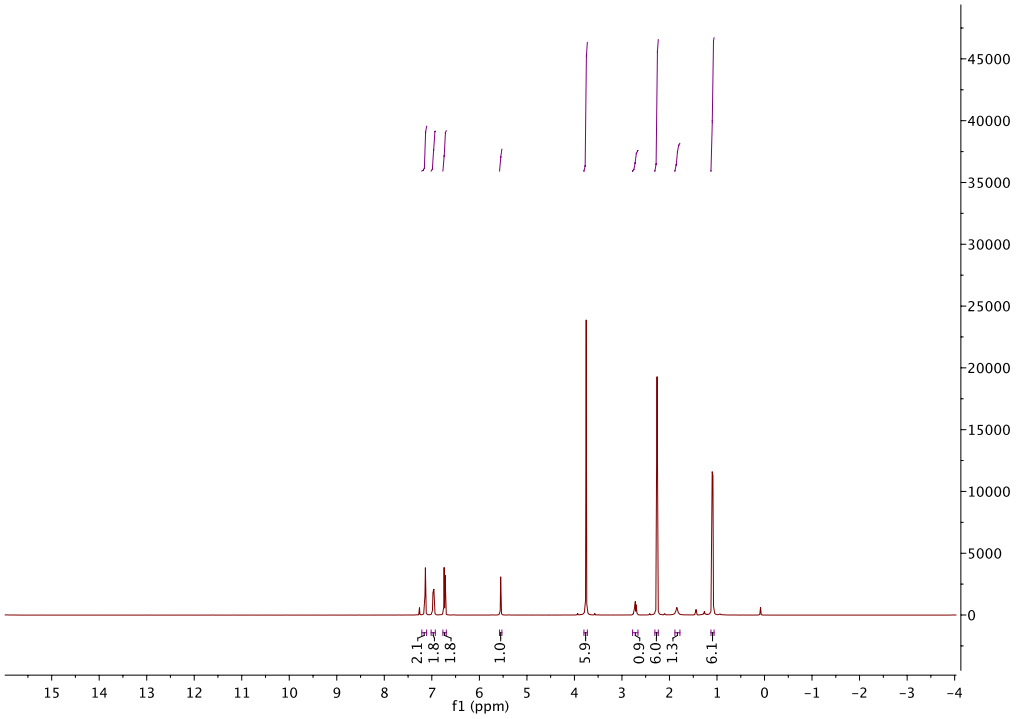
N-(bis(3,5-dimethoxyphenyl)methyl)propan-2-amine

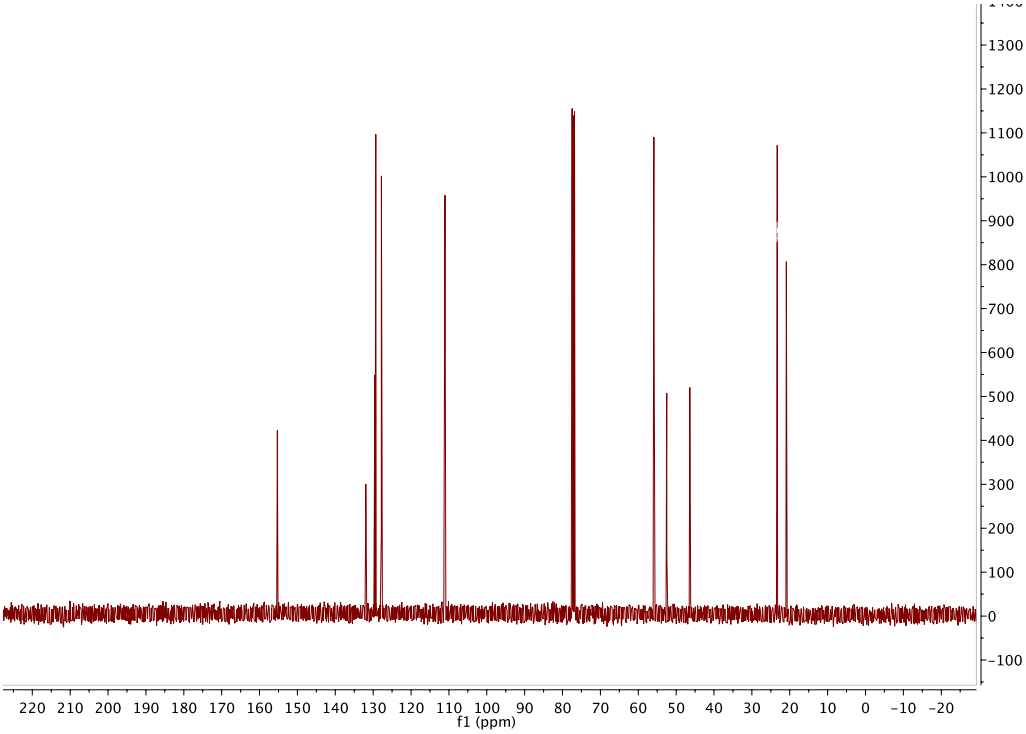


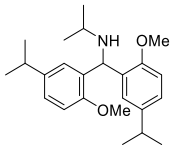




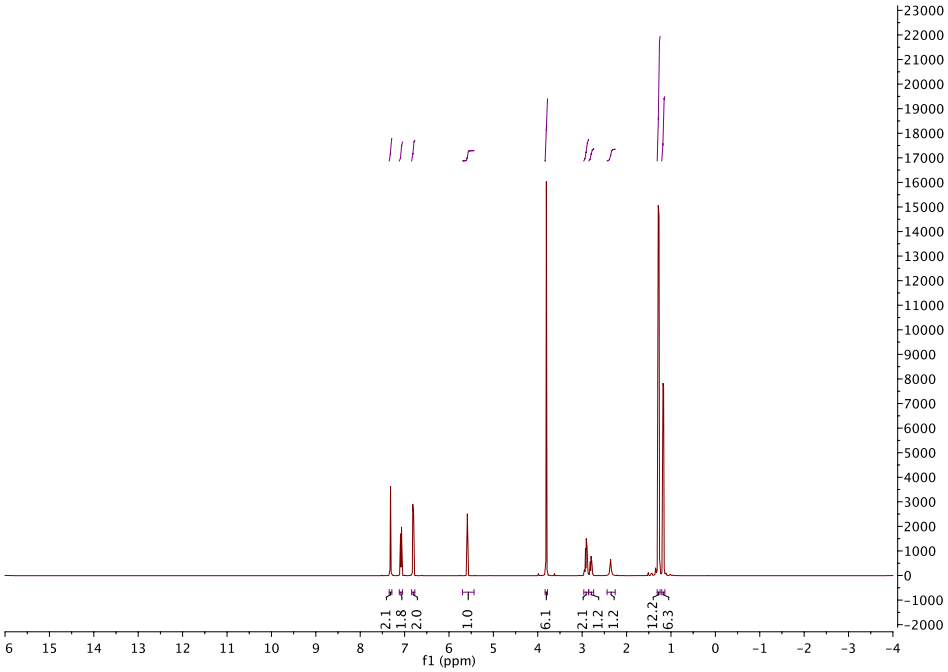
N-(bis(2-methoxy-5-methylphenyl)methyl)propan-2-amine

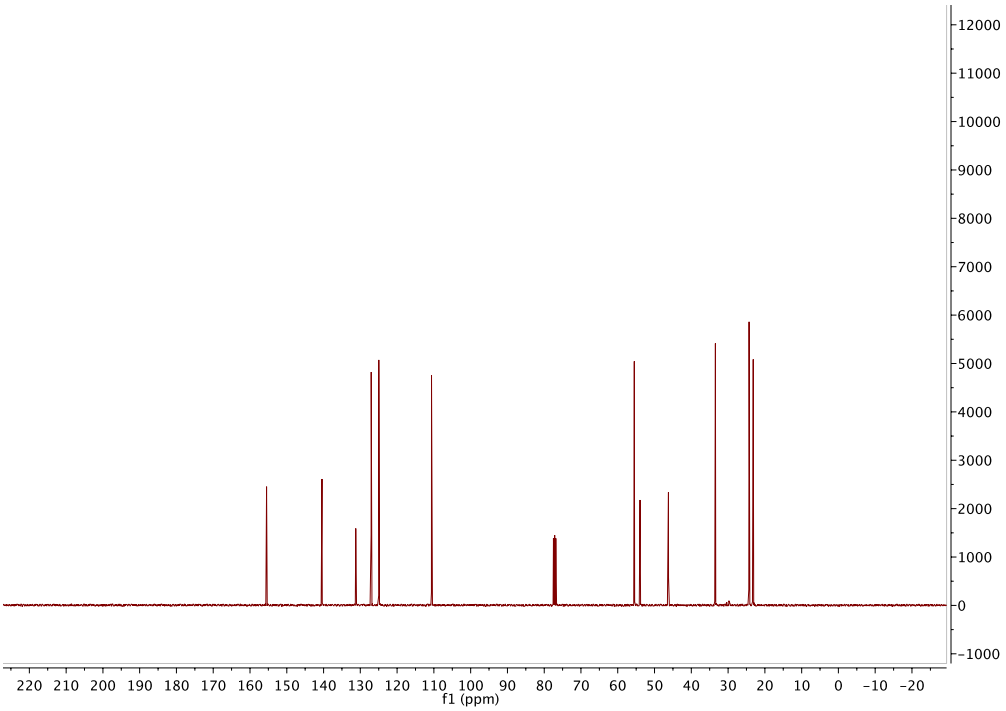


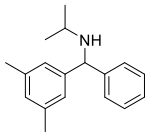




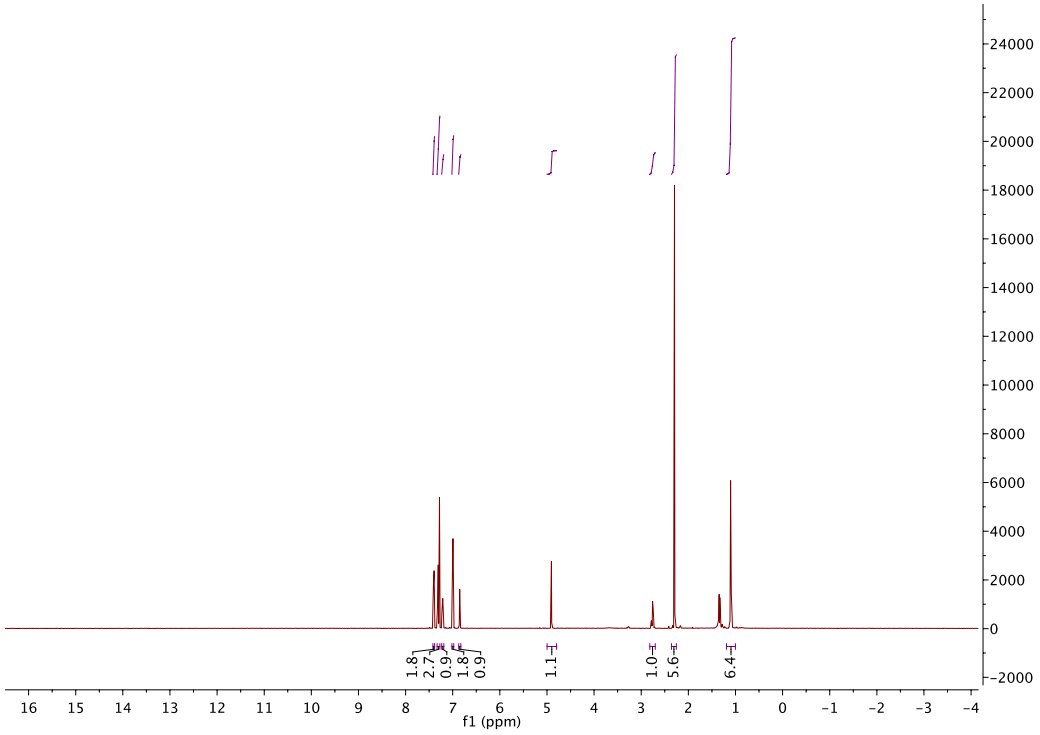
N-(bis(5-isopropyl-2-methoxyphenyl)methyl)propan-2-amine

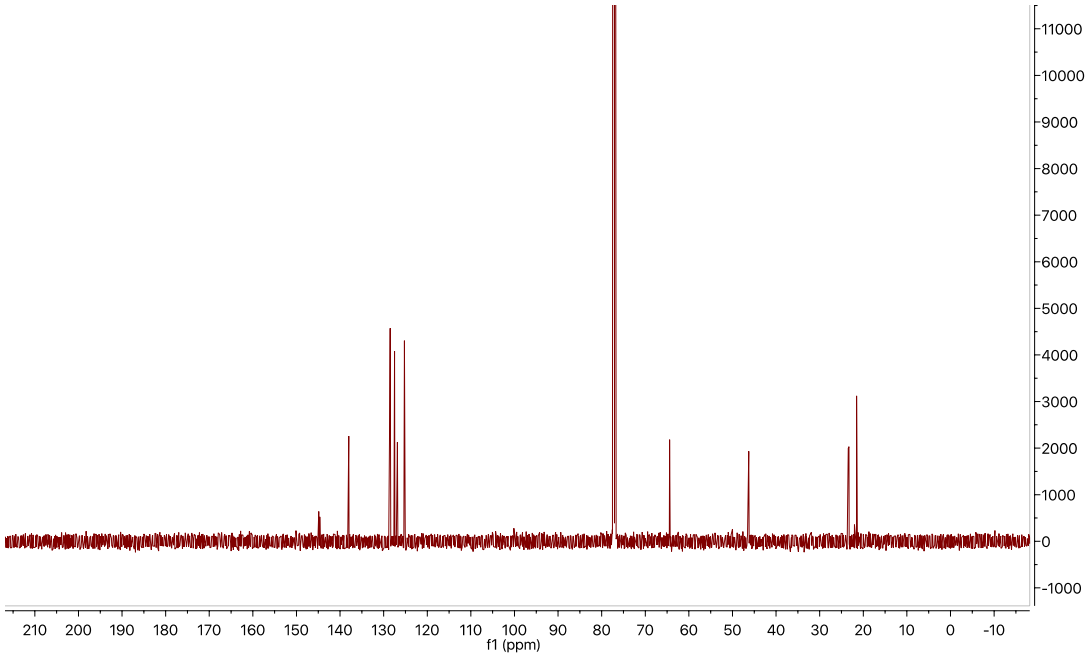


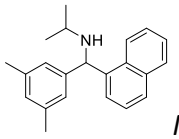




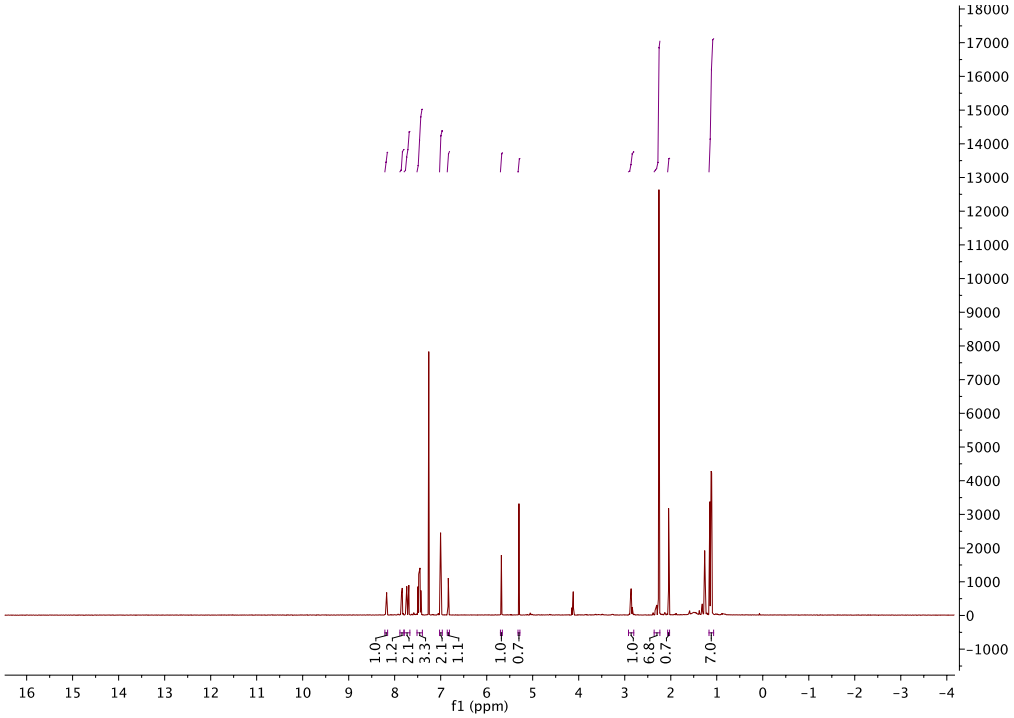
N-((3,5-dimethylphenyl)(phenyl)methyl)propan-2-amine

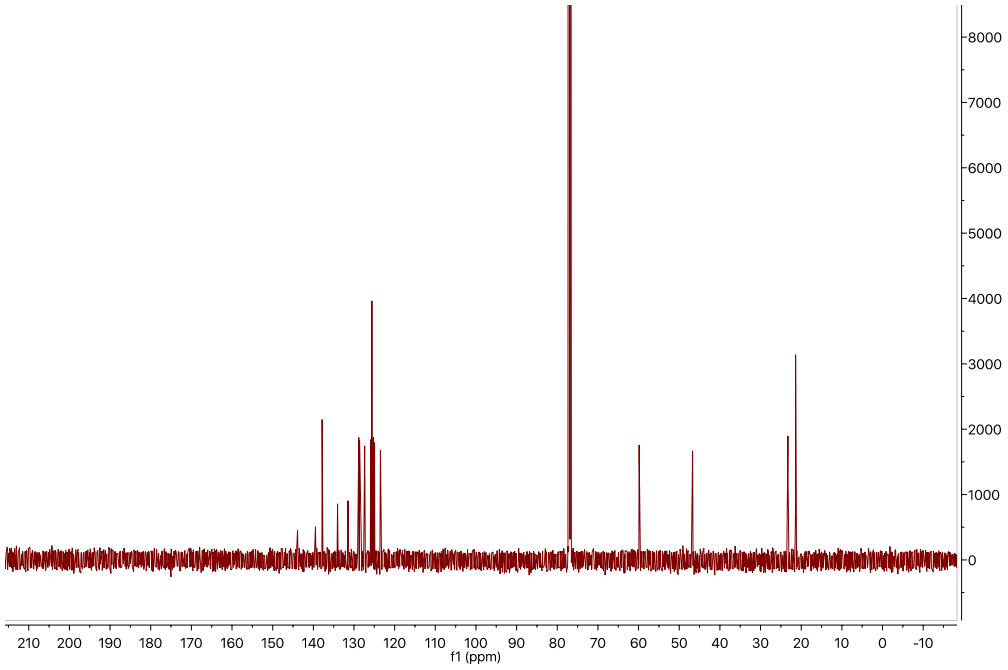


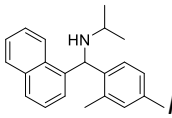




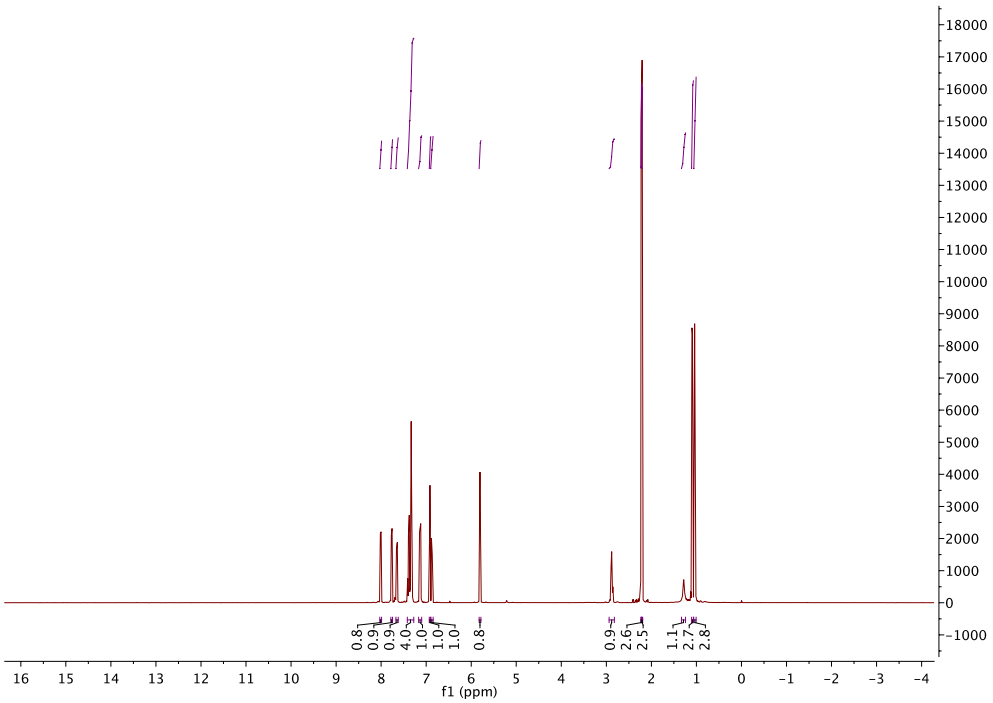
N-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine

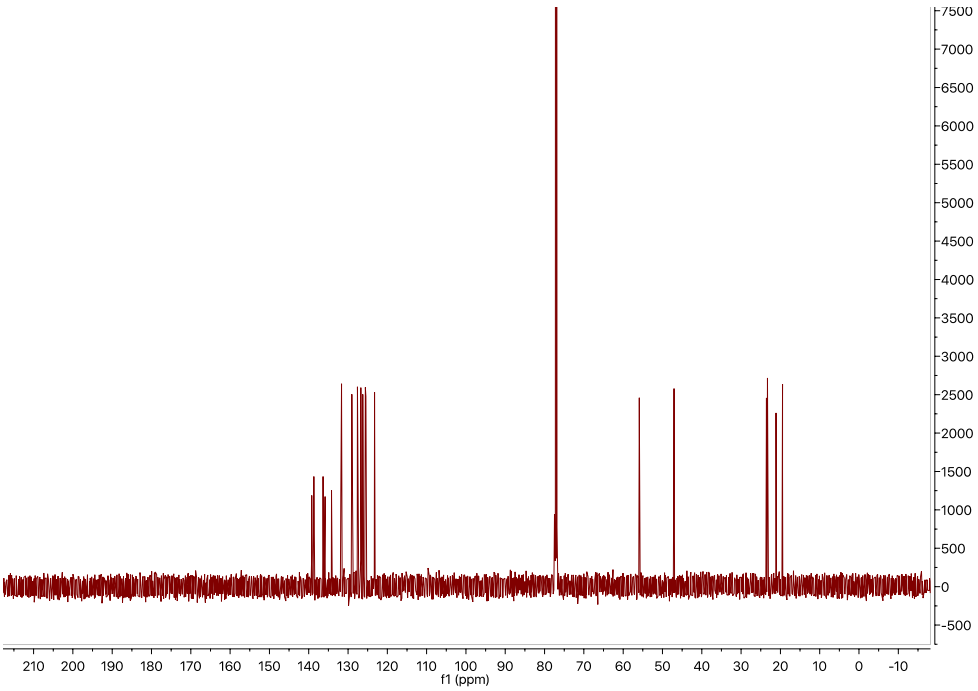


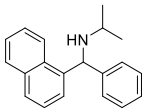




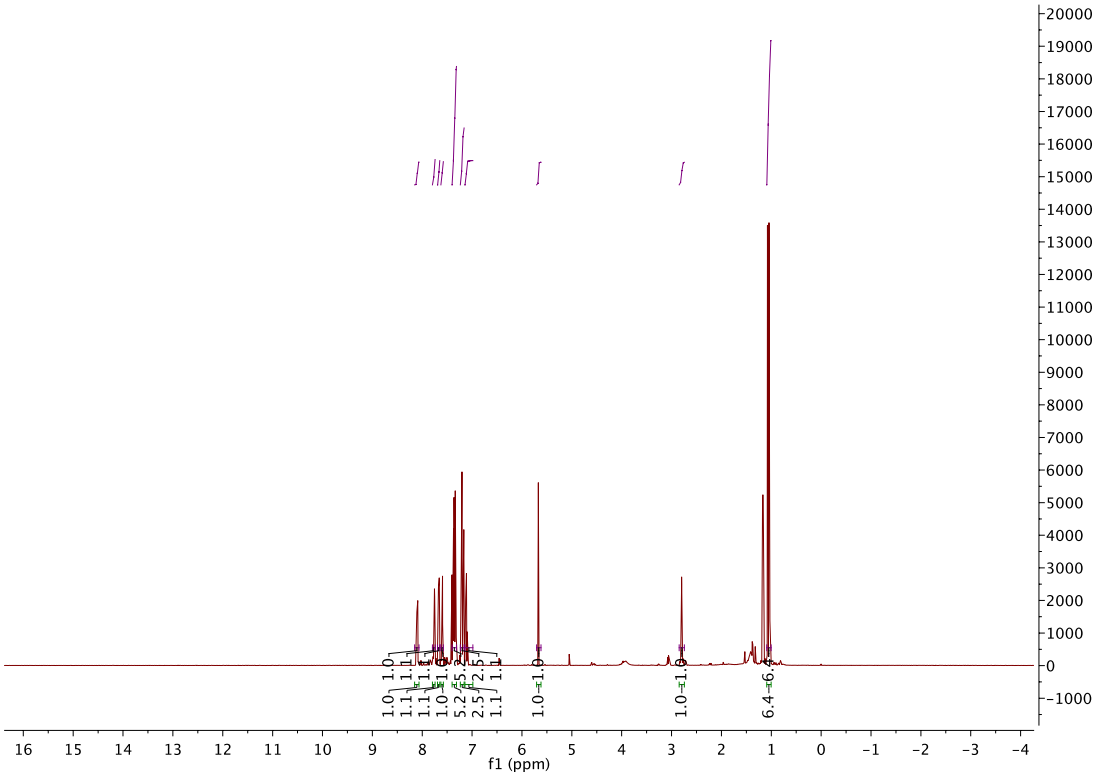
N-((2,4-dimethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine

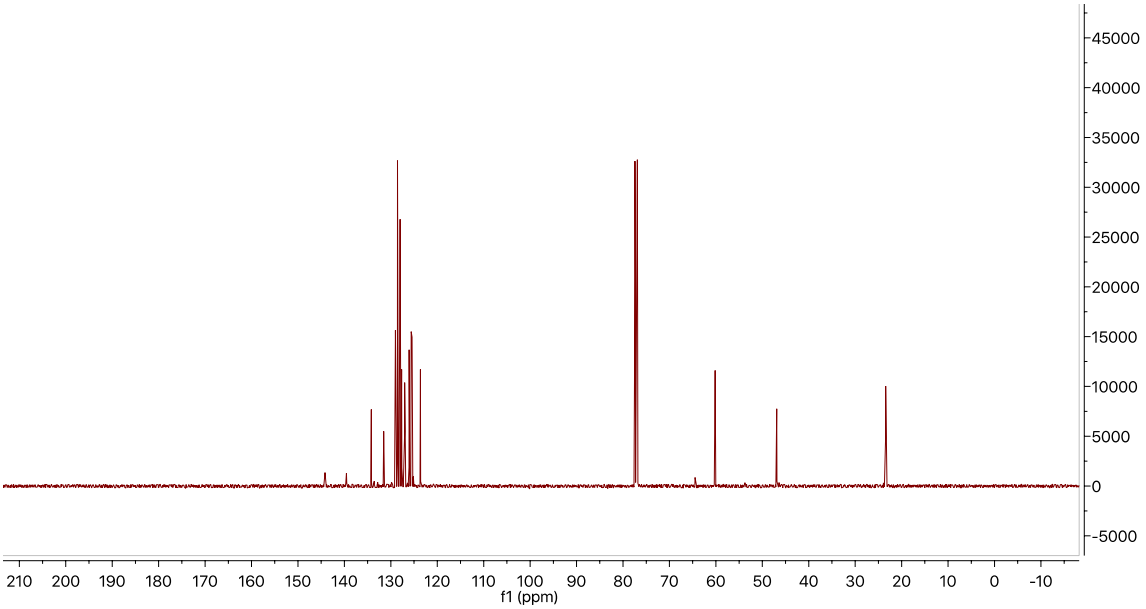


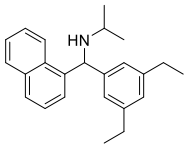




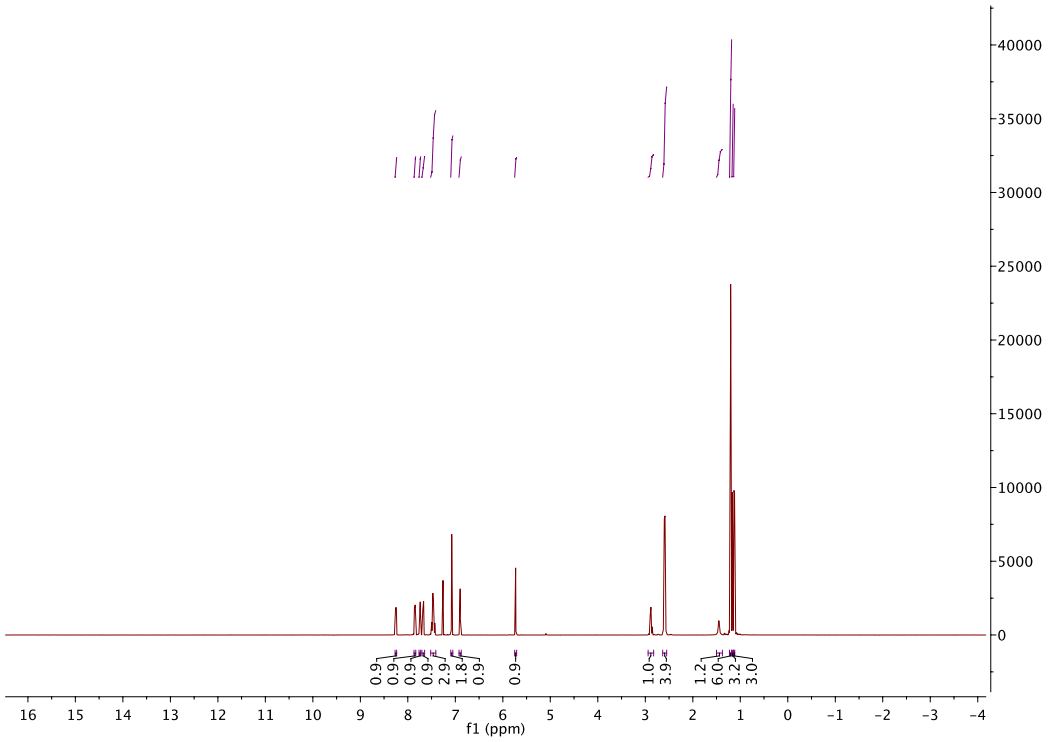
N-(naphthalen-1-yl(phenyl)methyl)propan-2-amine

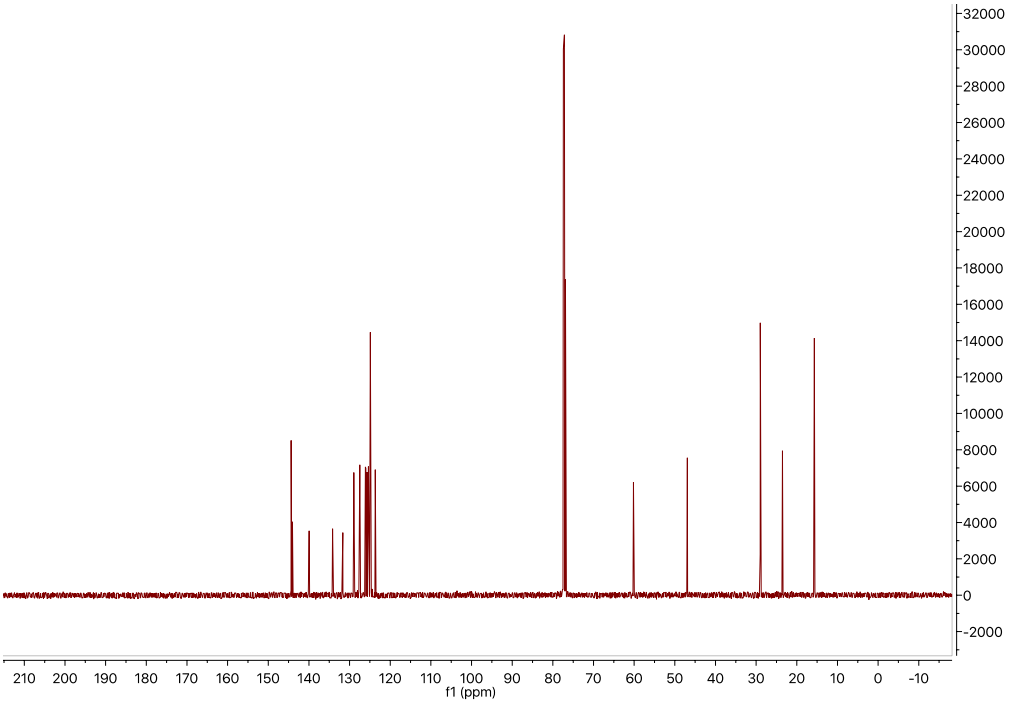


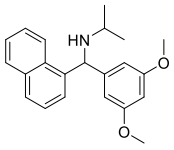




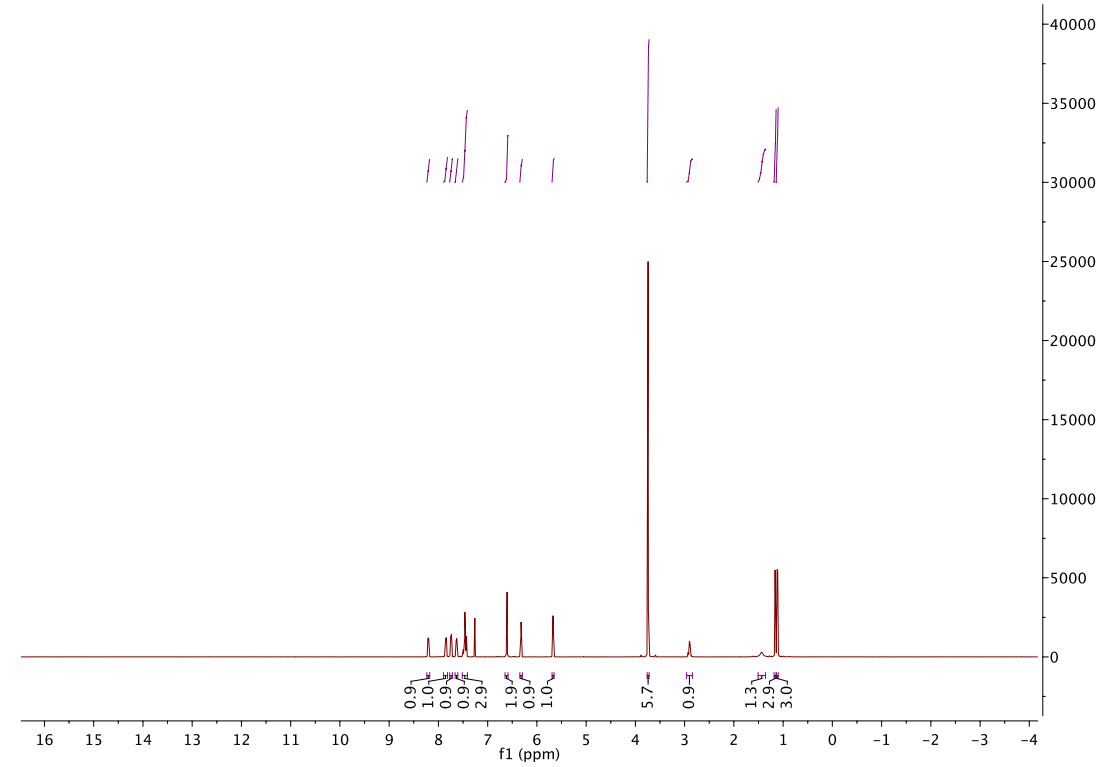
N-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)propan-2-amine

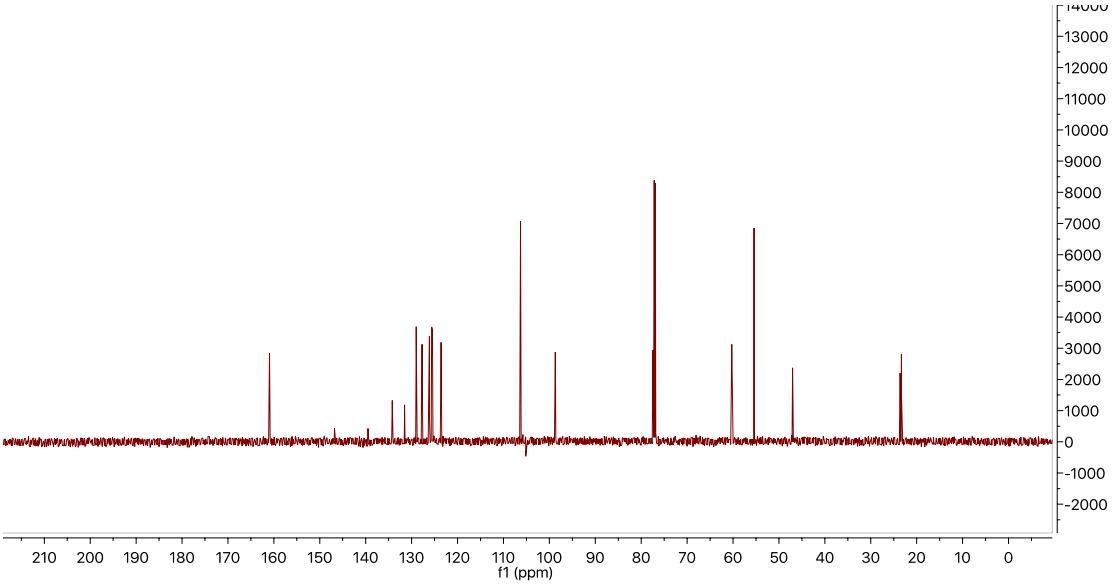


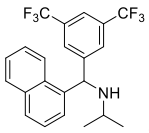




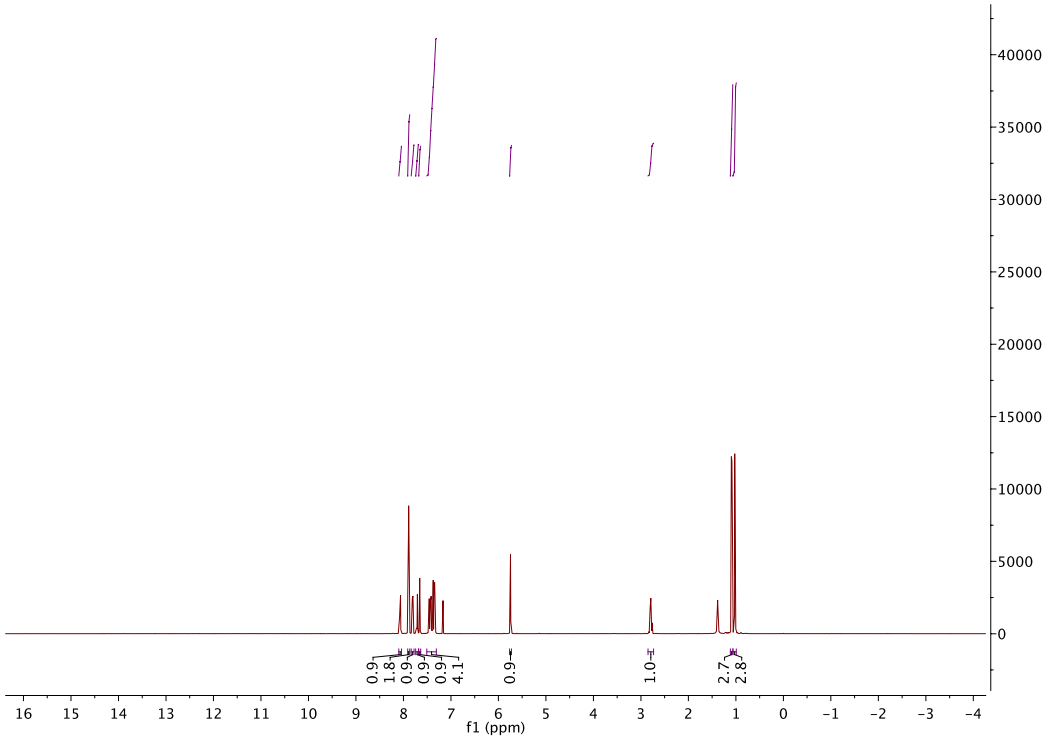
N-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)propan-2-amine

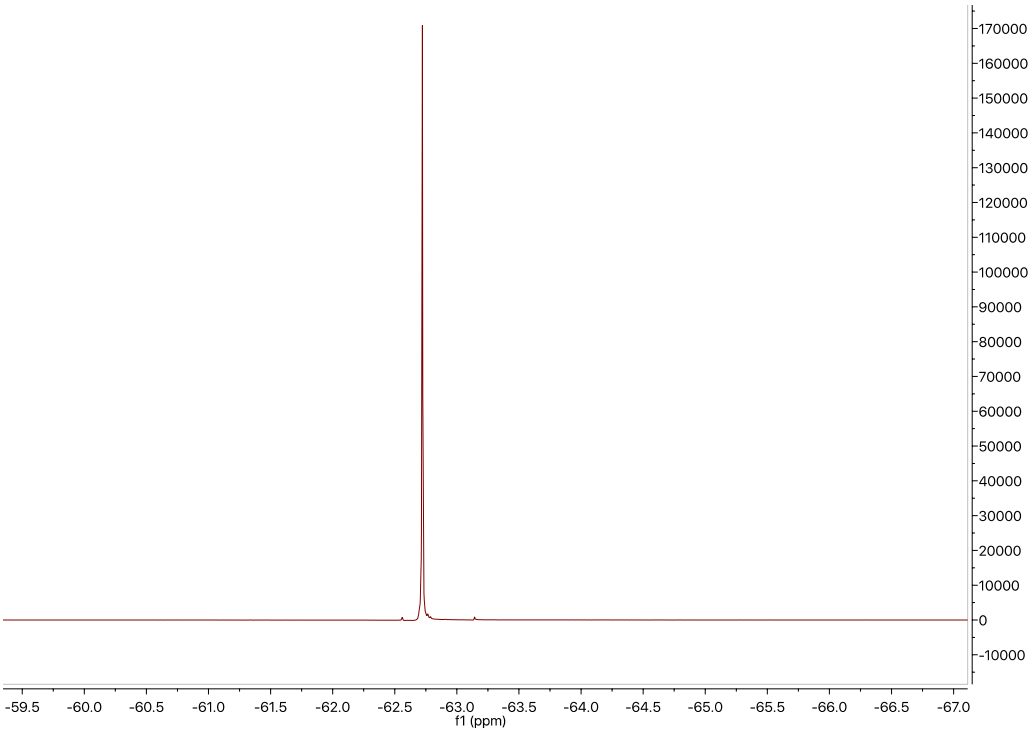


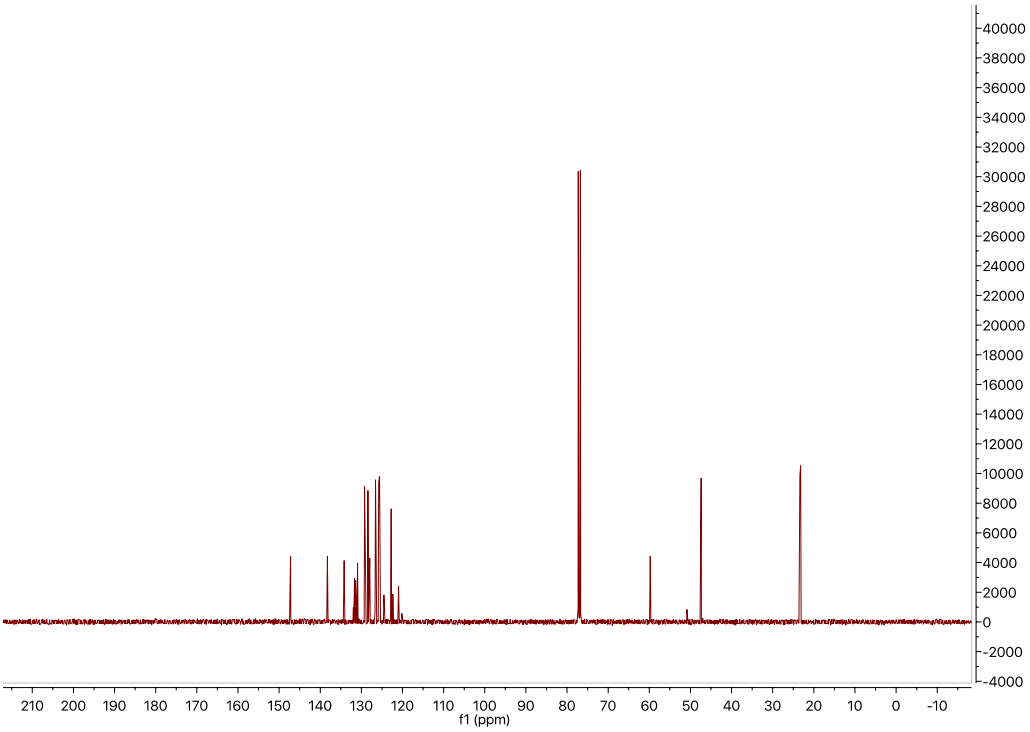


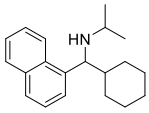


N-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)propan-2-amine

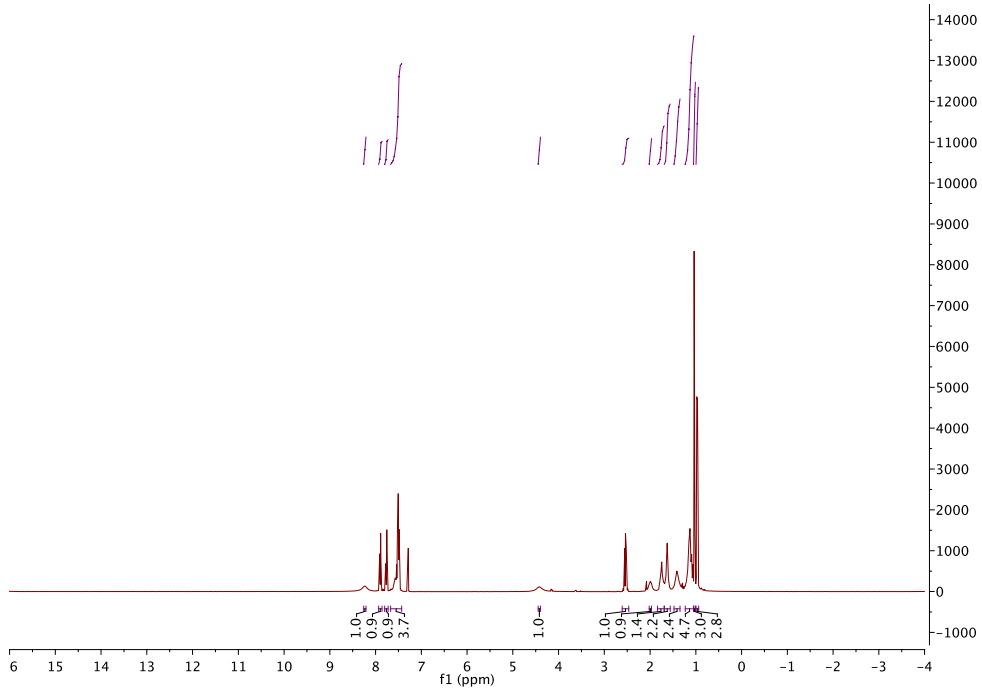


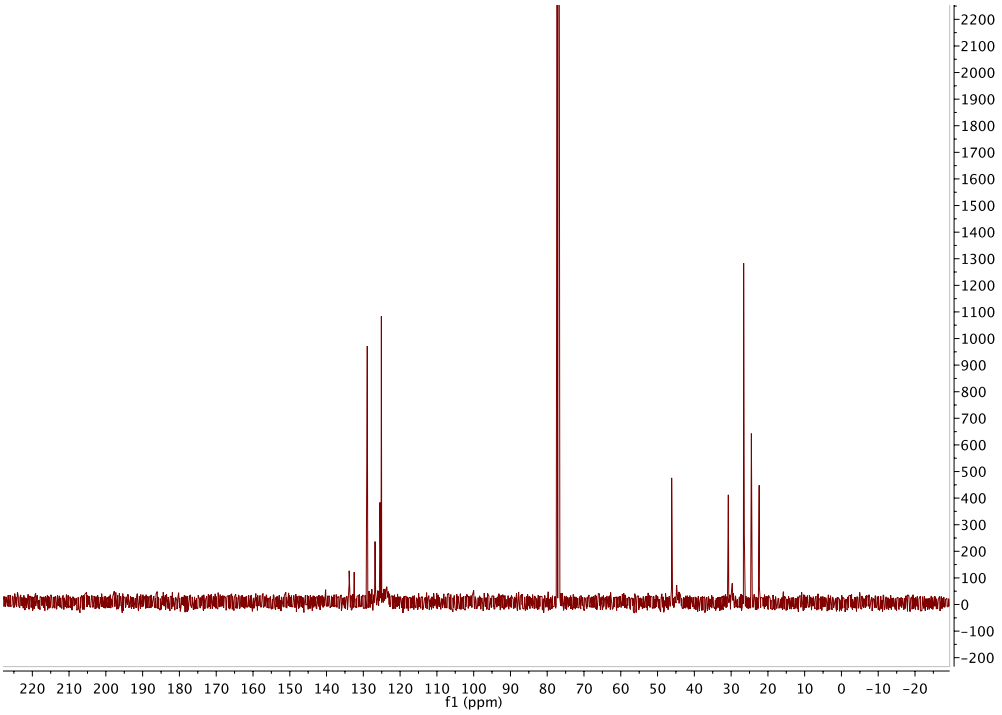


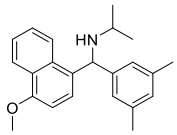




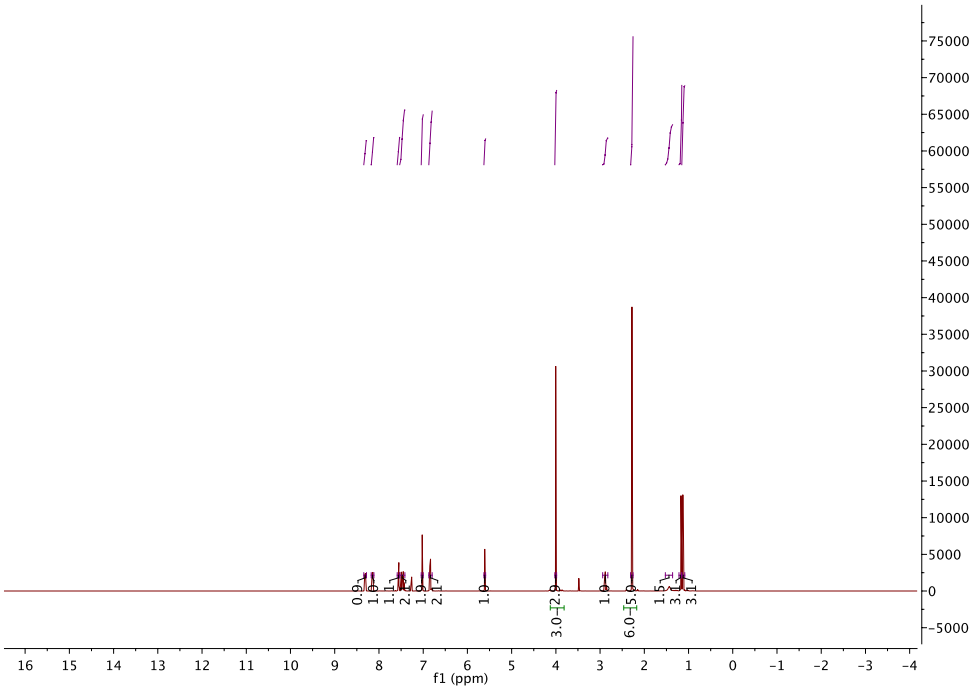
N-(cyclohexyl(naphthalen-1-yl)methyl)propan-2-amine

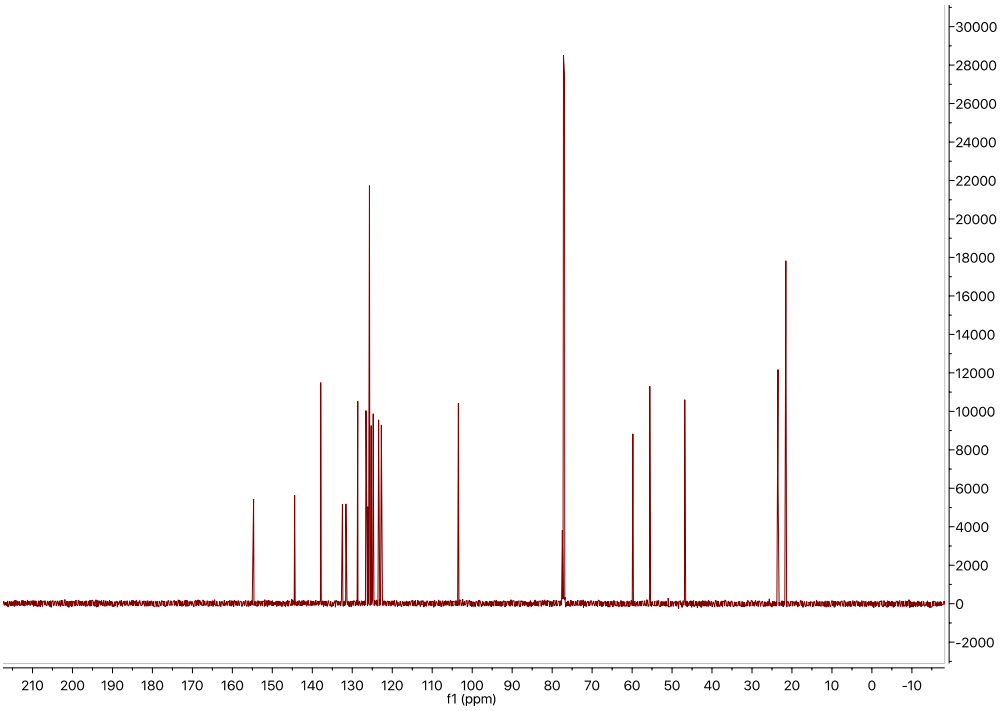


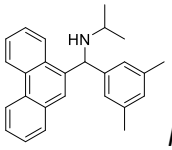




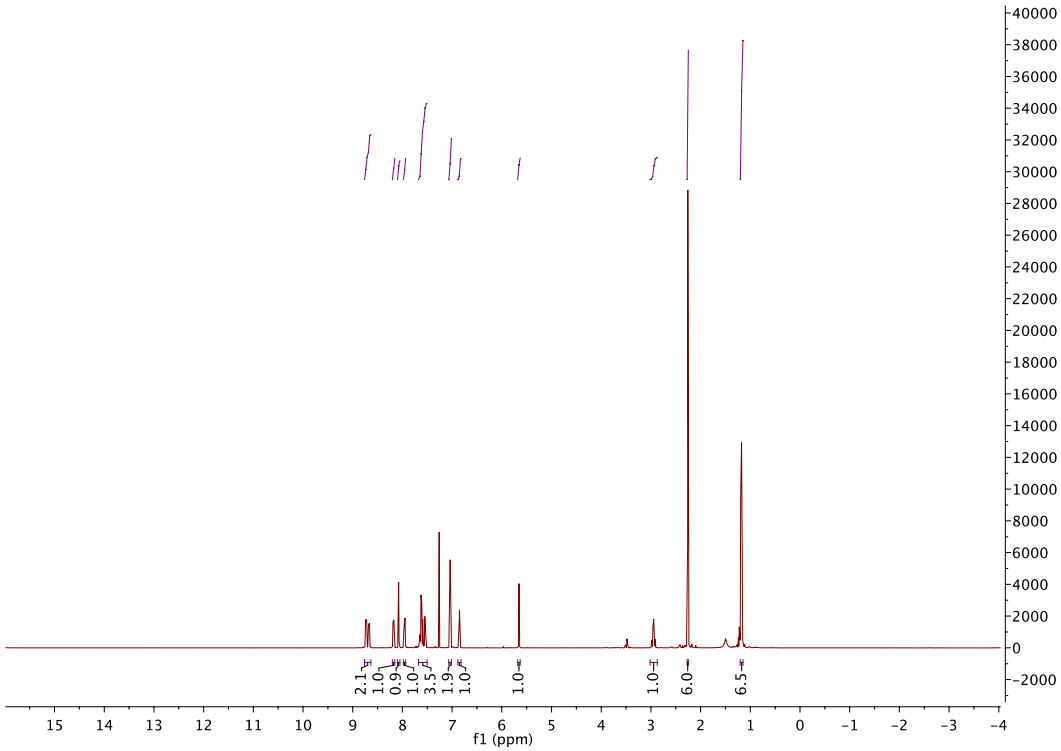
N-((3,5-dimethylphenyl)(2-methoxynaphthalen-1-yl)methyl)propan-2-amine

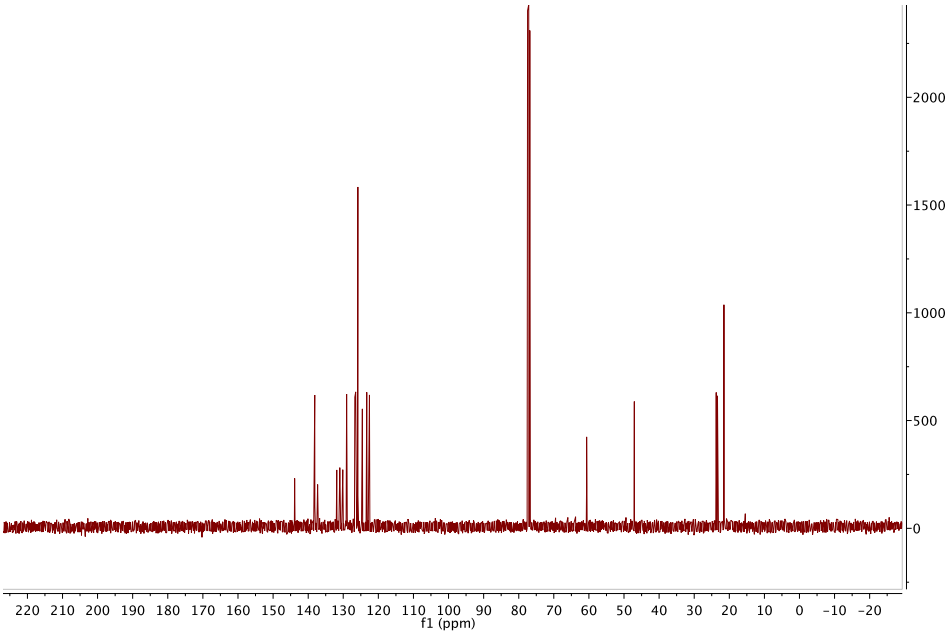


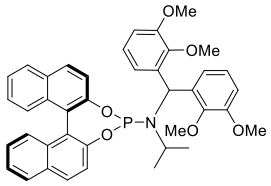




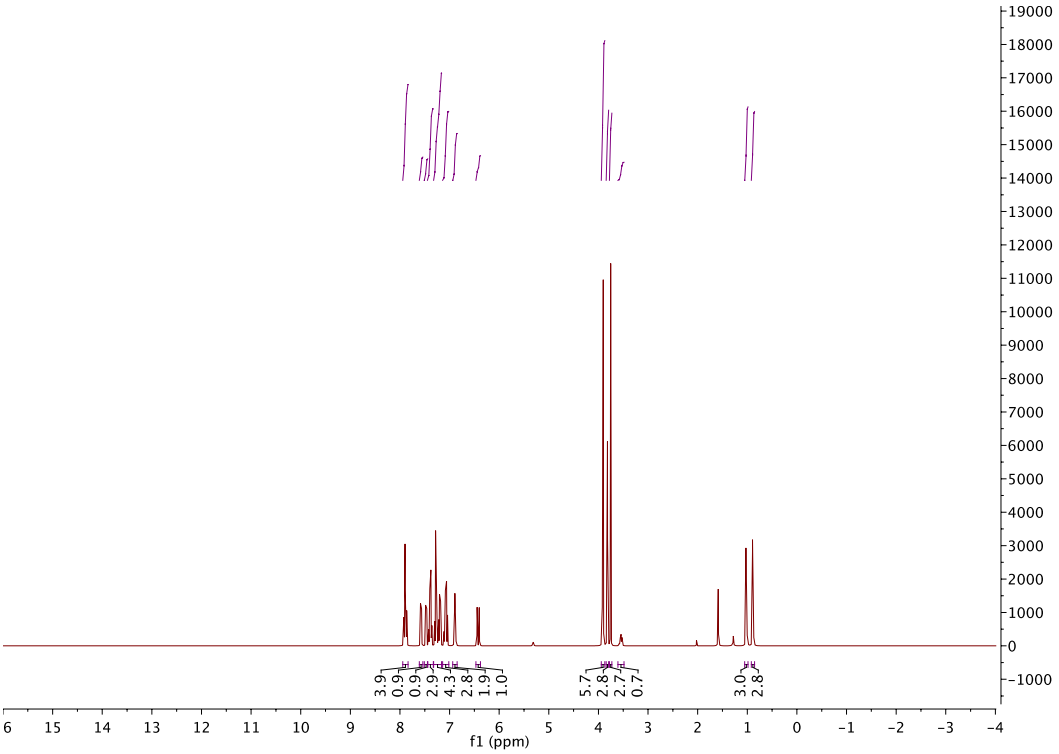
N-((3,5-dimethylphenyl)(phenanthren-9-yl)methyl)propan-2-amine

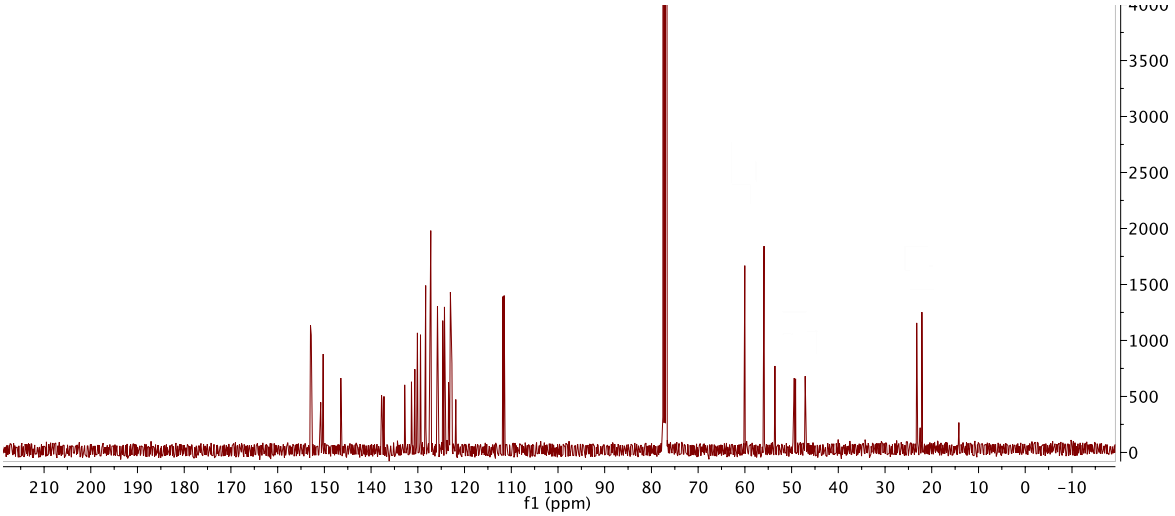


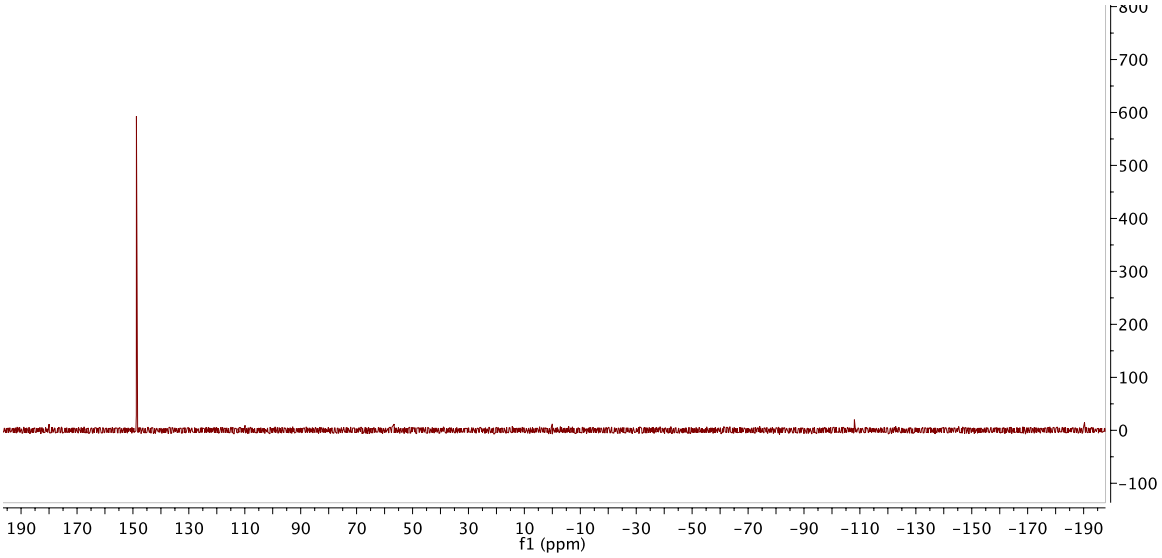


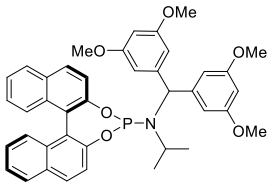


(R_a)-N-(bis(2,3-dimethoxyphenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L15**

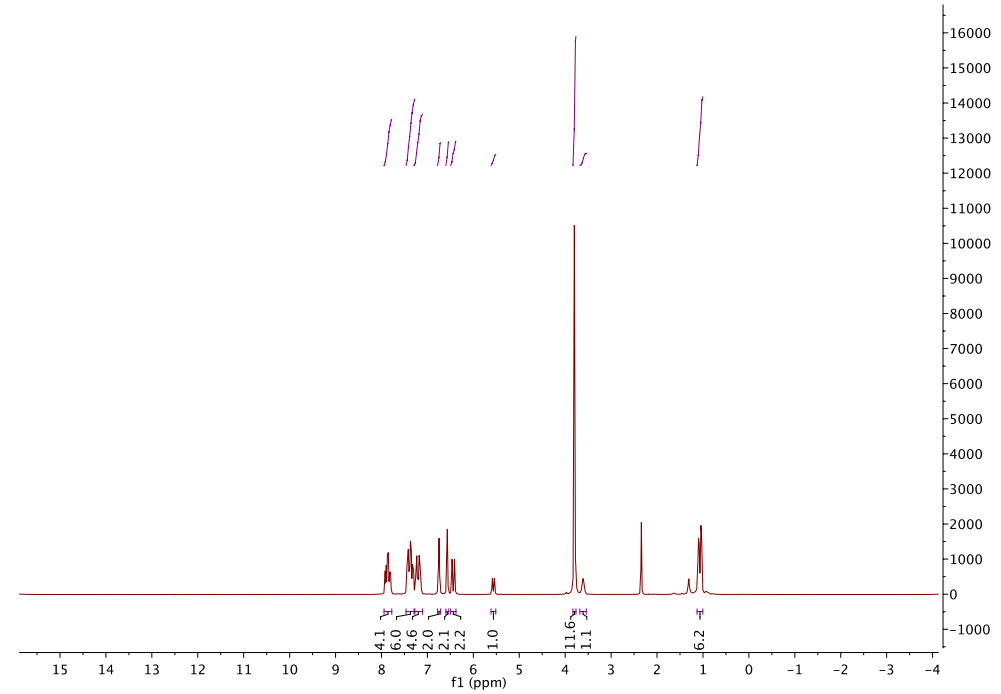


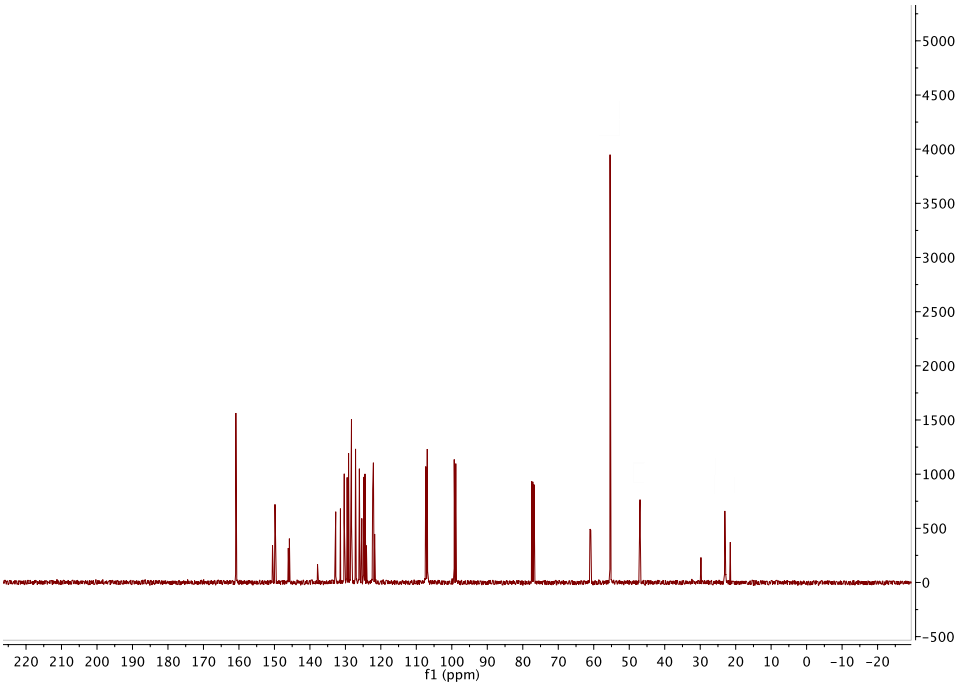


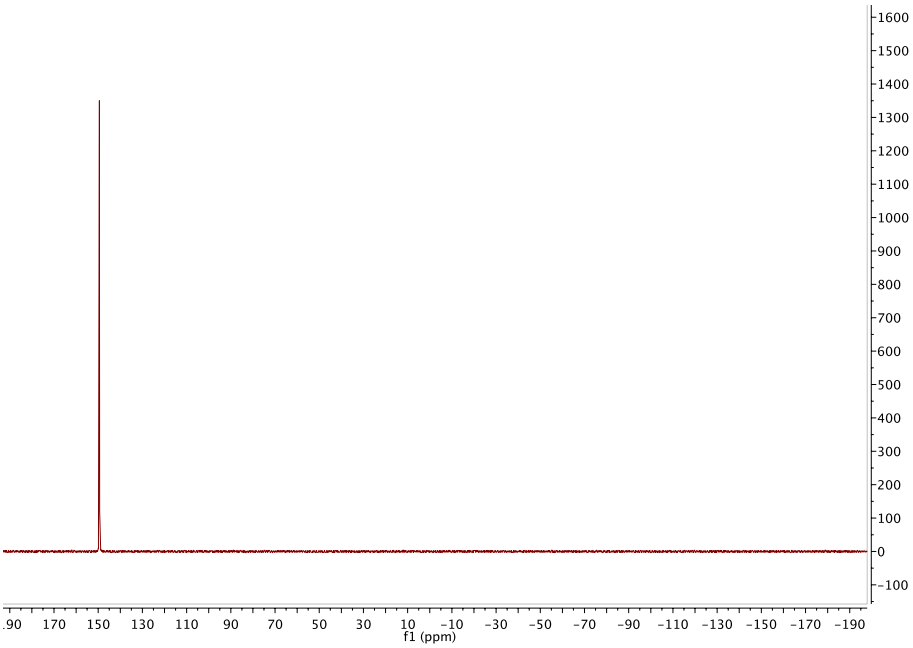


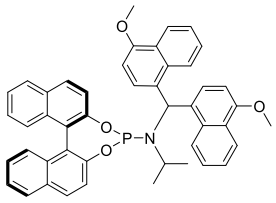


(R_a)-N-(bis(3,5-dimethoxyphenyl)methyl)-N-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine **L16**

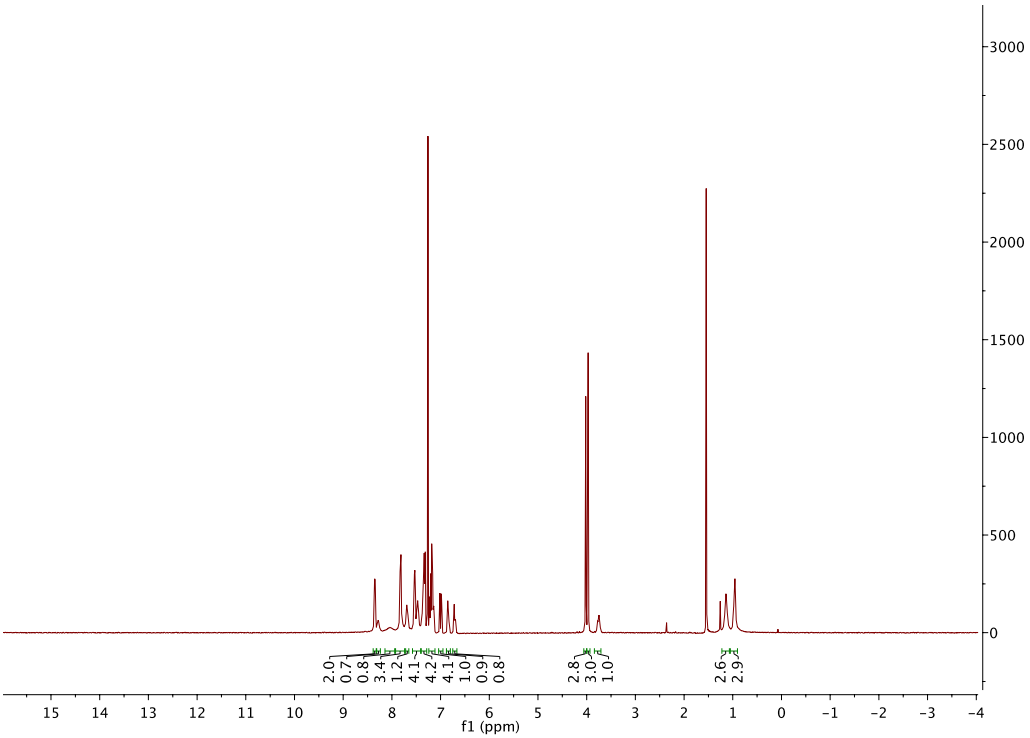

4.1
6.0
4.6
2.0
2.1
2.2
1.0
11.6
1.1
6.2
f1 (ppm)

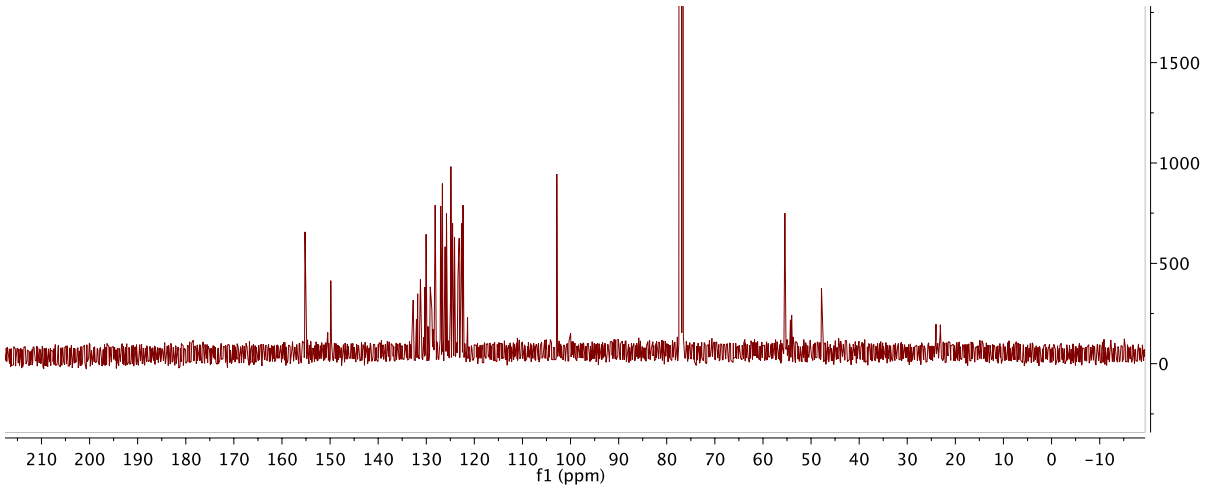

f1 (ppm)

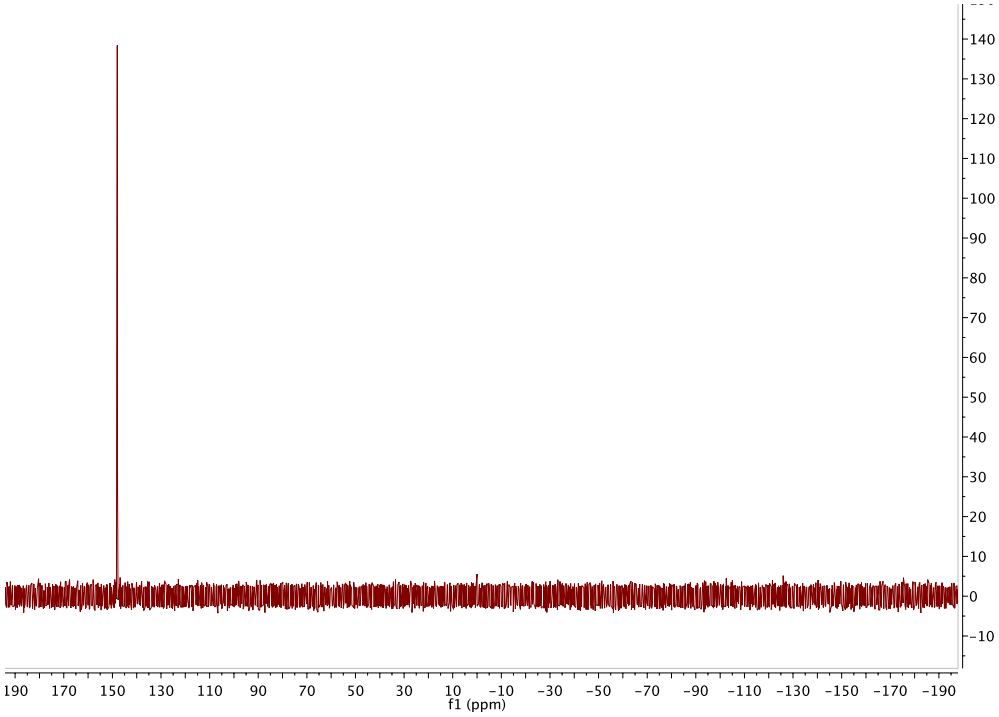


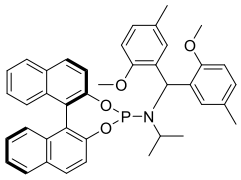


(R_a)-N-(bis(4-methoxynaphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L17**

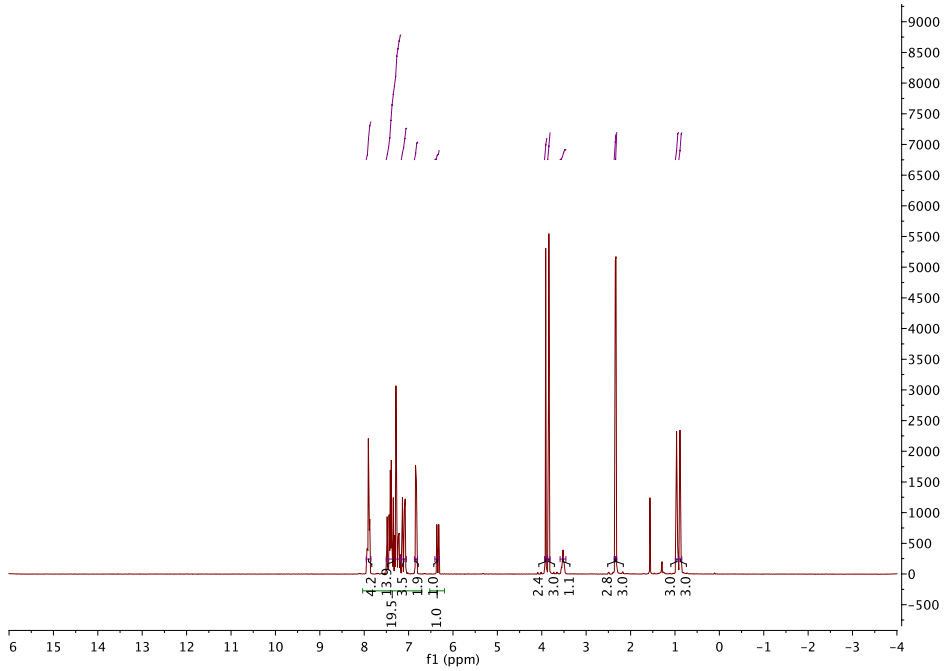


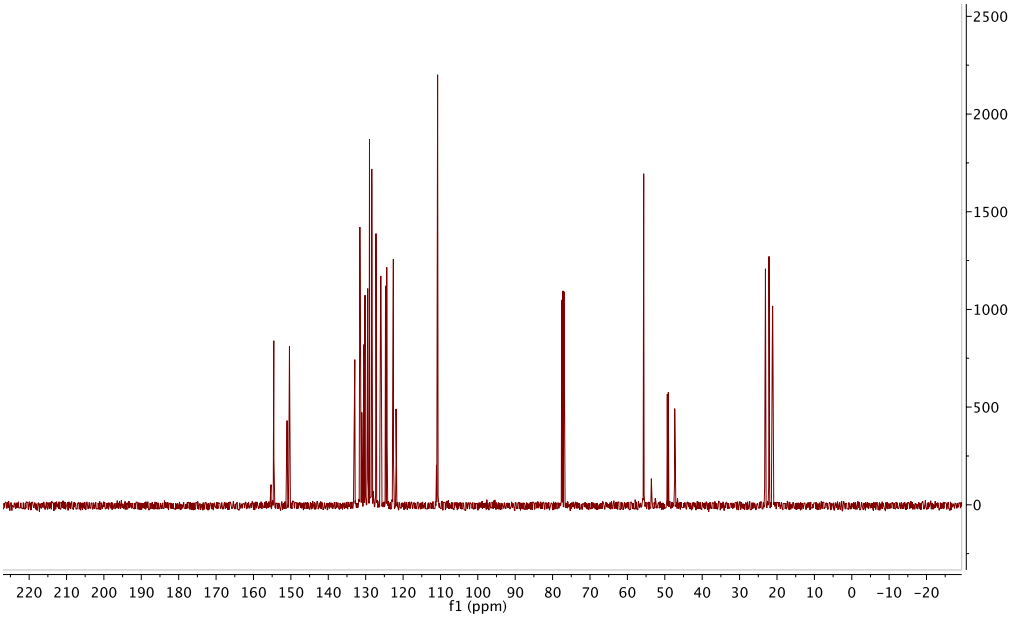

1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

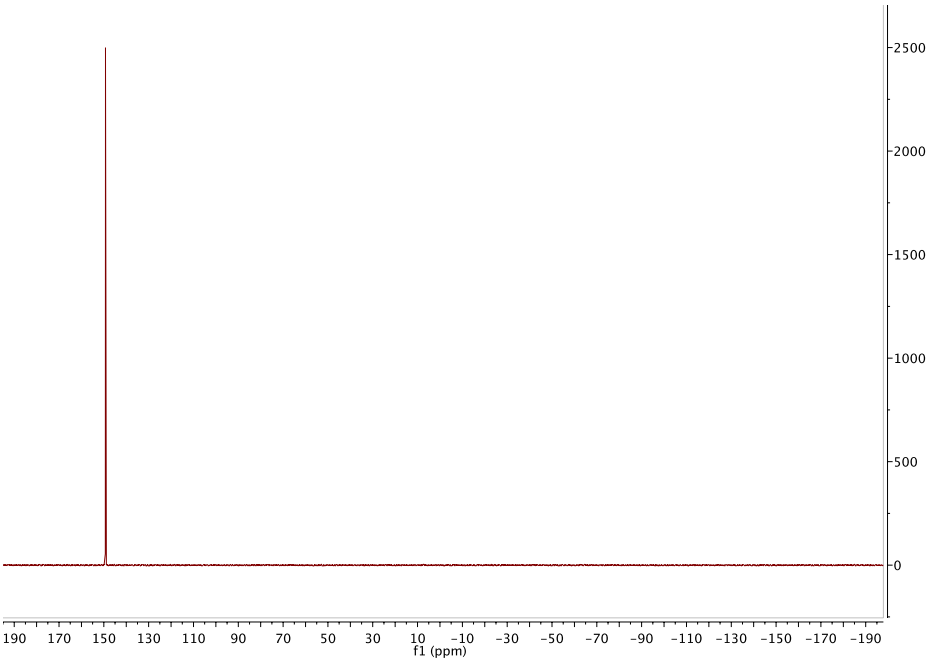

140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)

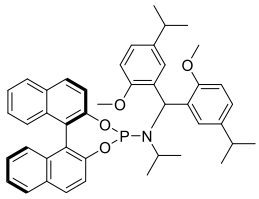


(R_a)-N-(bis(2-methoxy-5-methylphenyl)methyl)-N-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine **L18**

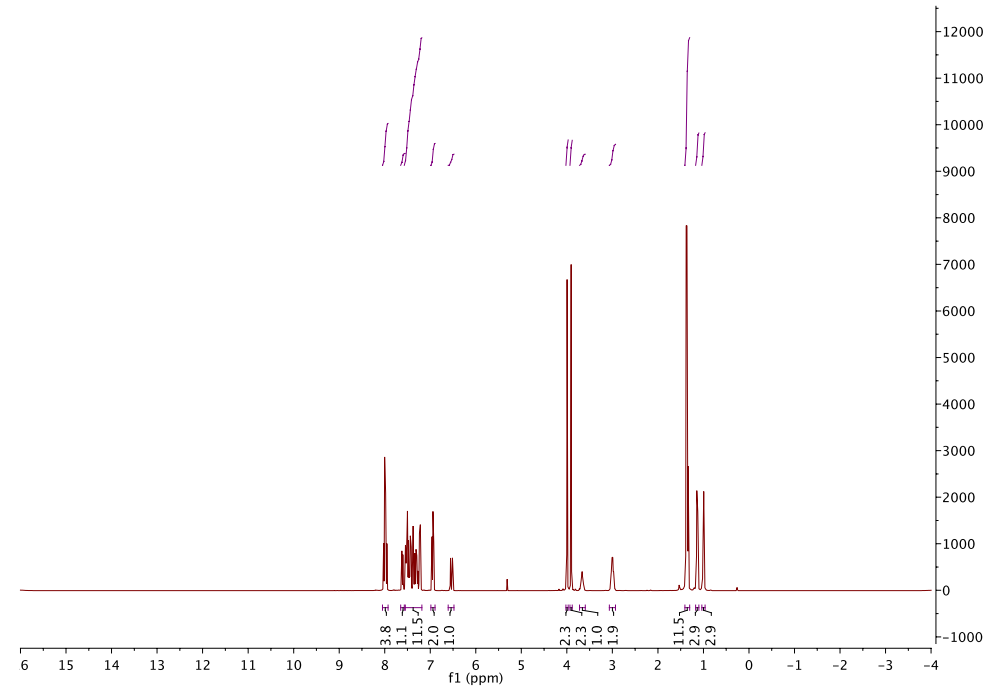


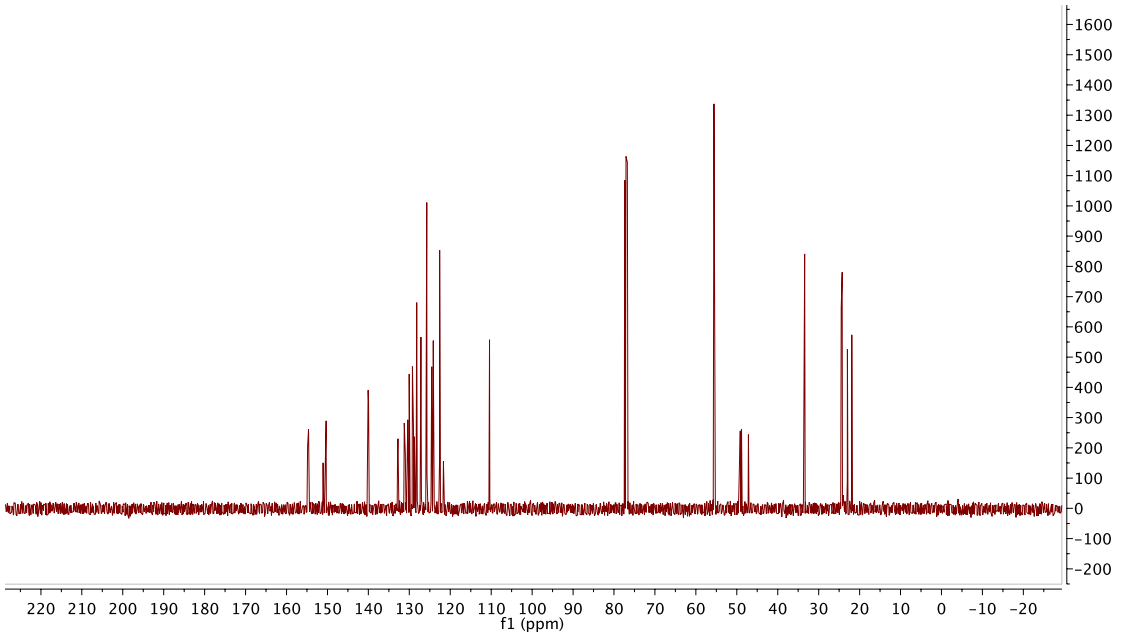






(R_a)-N-(bis(5-isopropyl-2-methoxyphenyl)methyl)-N-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine **L19**

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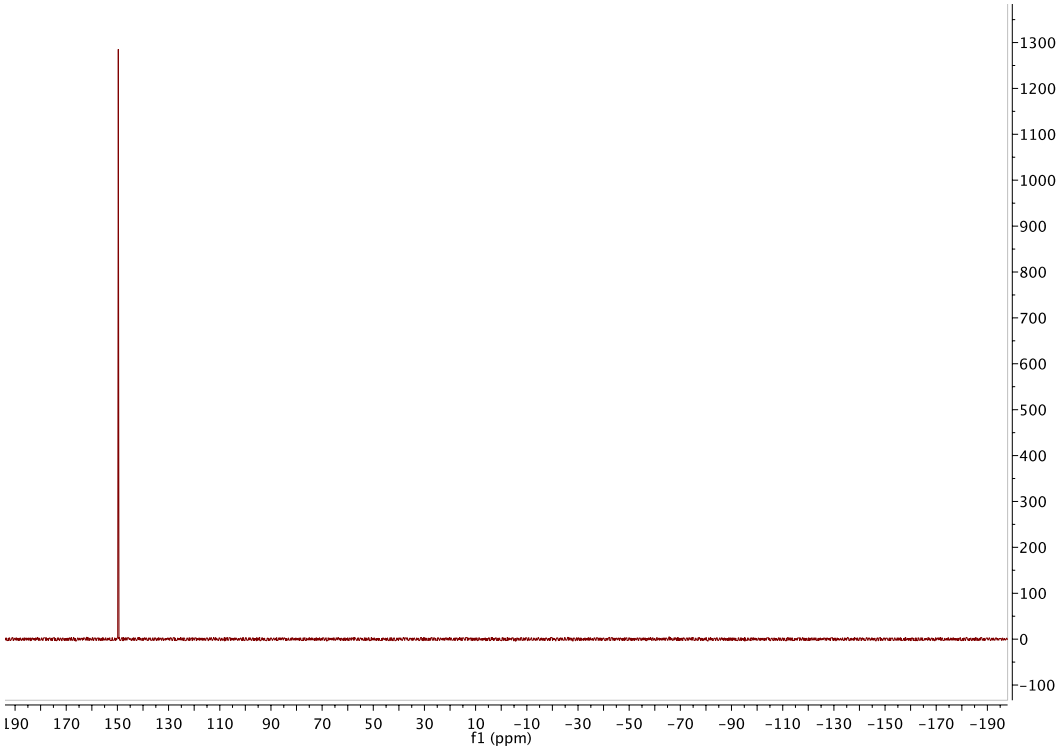
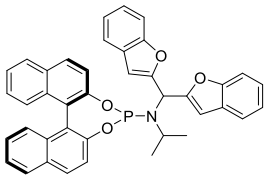
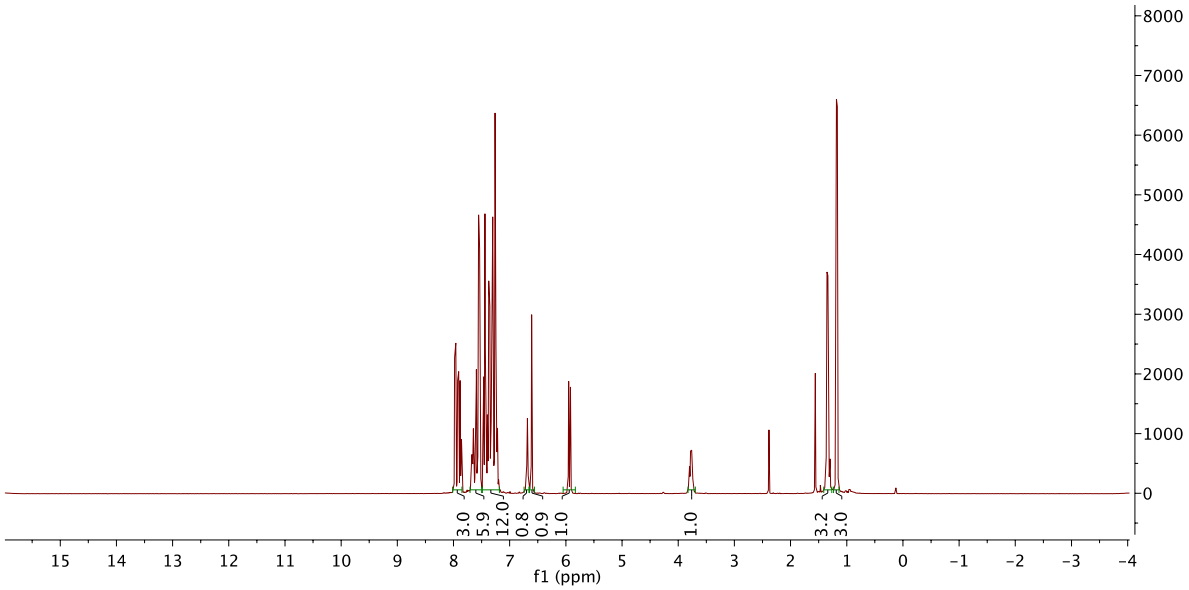
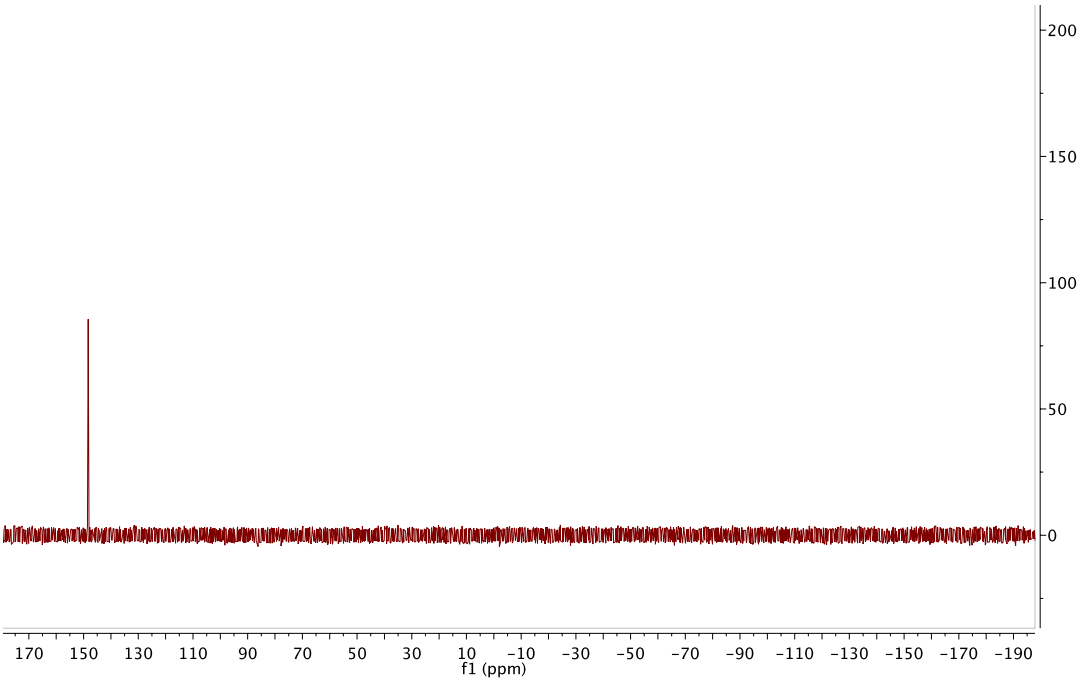
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

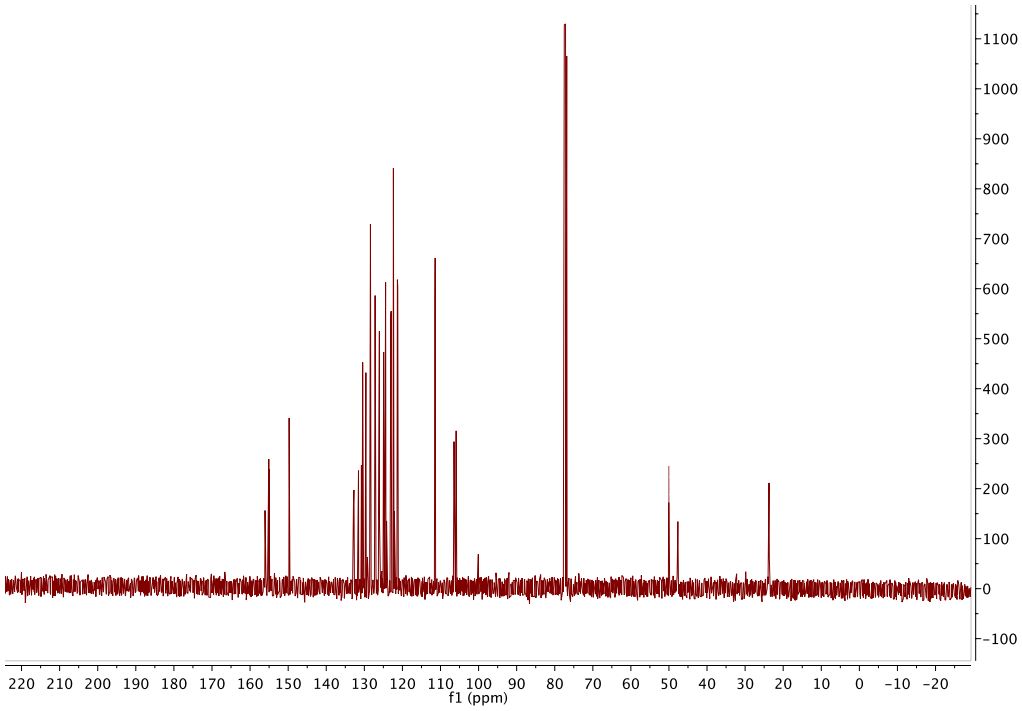

1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)

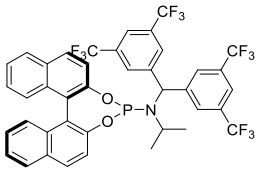


(R_a)-N-(di(benzofuran-2-yl)methyl)-*N*-isopropyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine **L20**

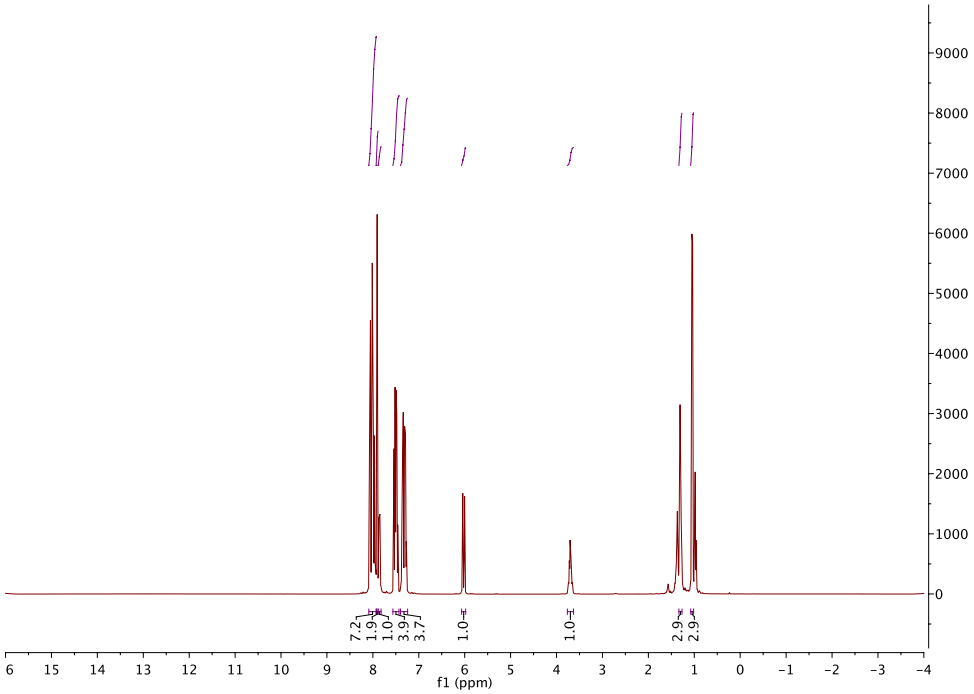


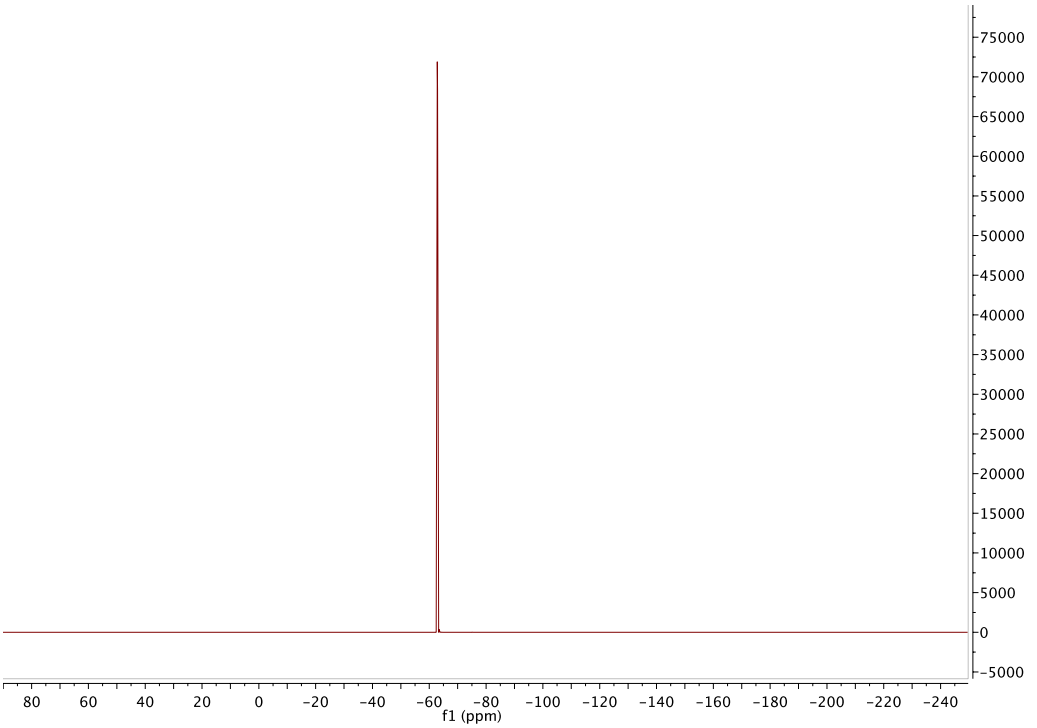


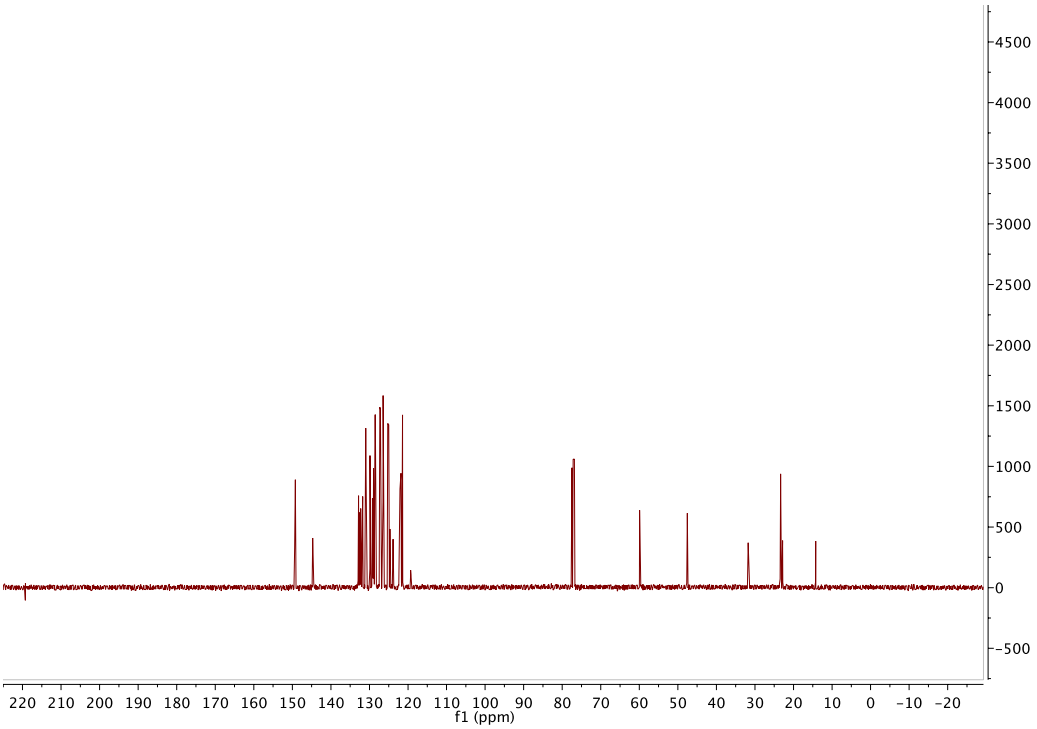


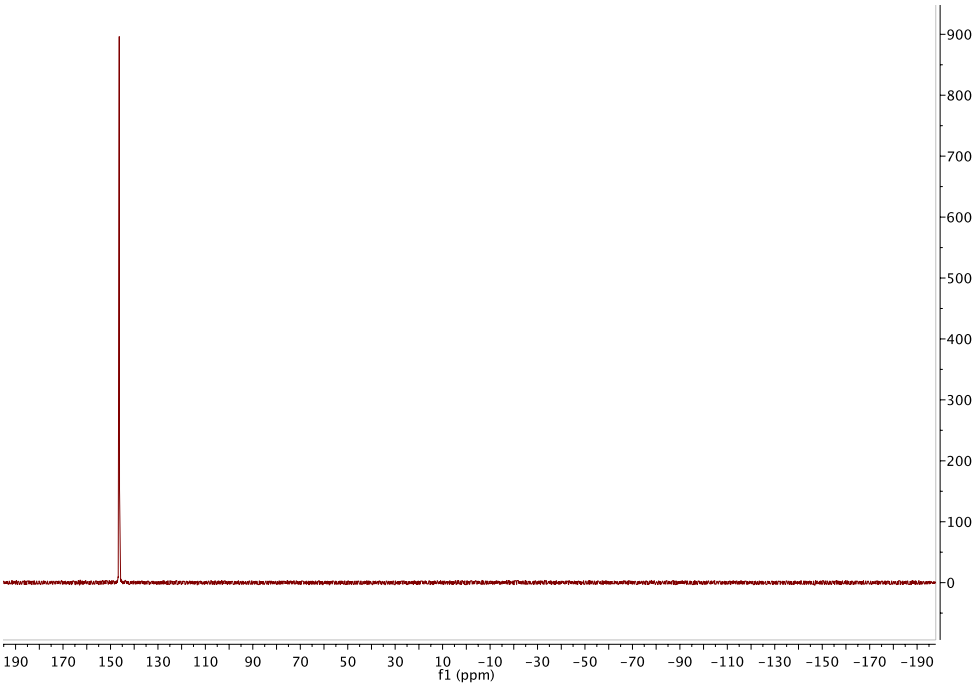


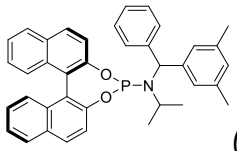
(R_a)-N-(bis(3,5-bis(trifluoromethyl)phenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L21**



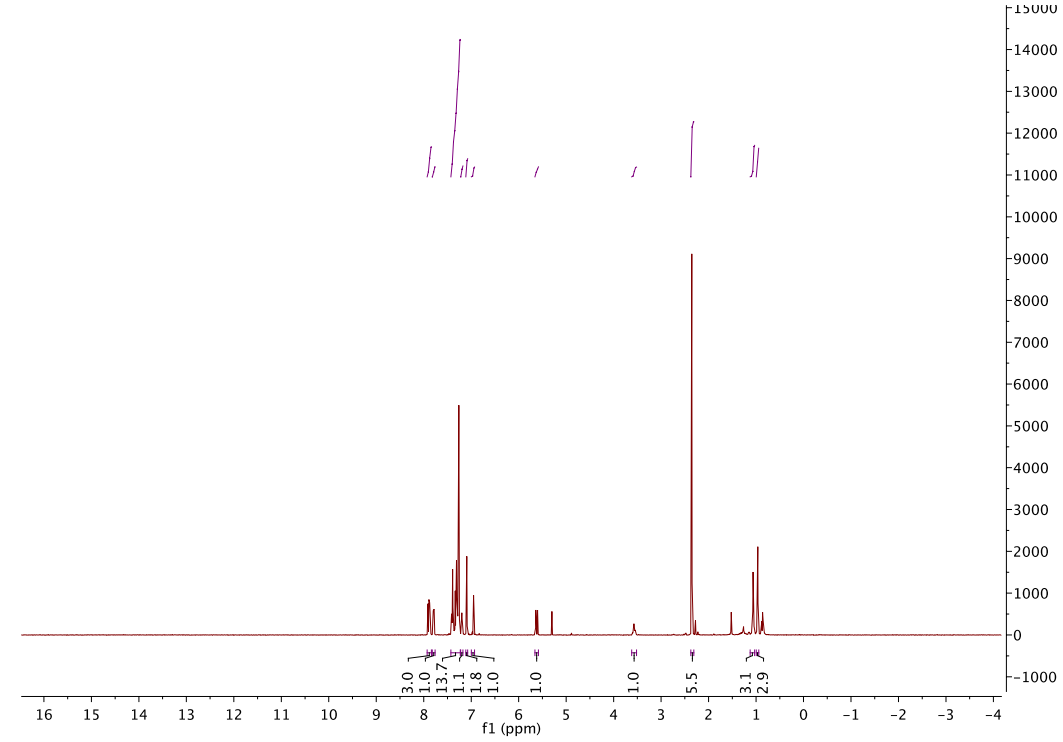

75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)

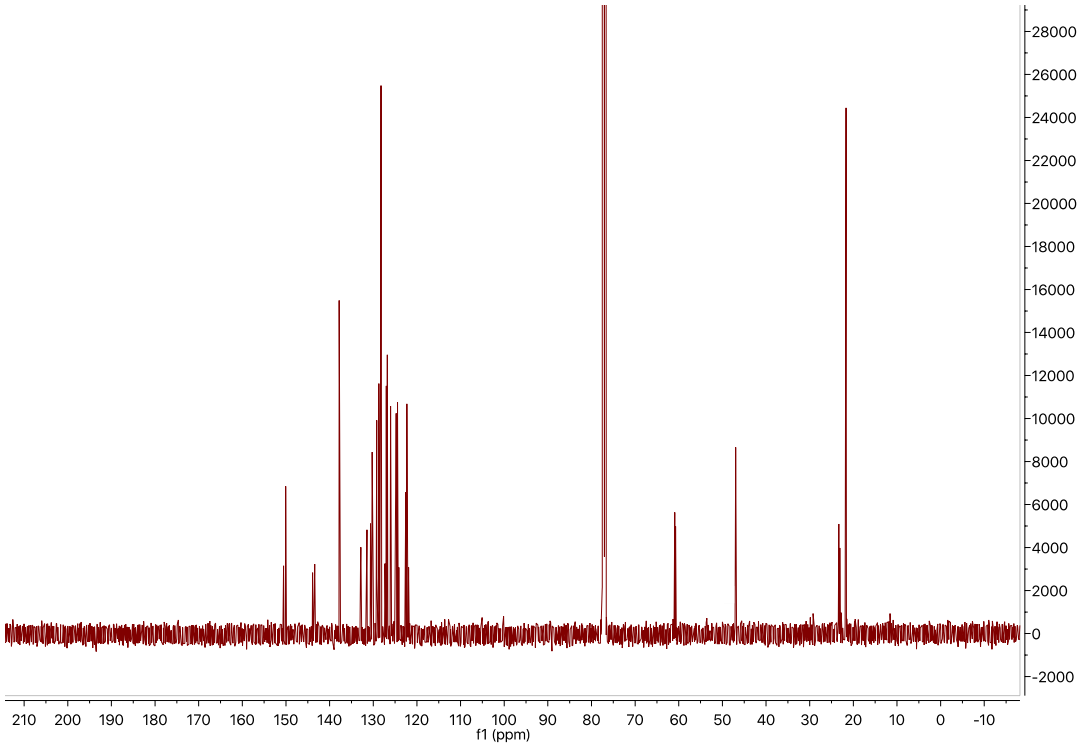

4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)





(R_a,R or *S)-N*-((3,5-dimethylphenyl)(phenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L22a**

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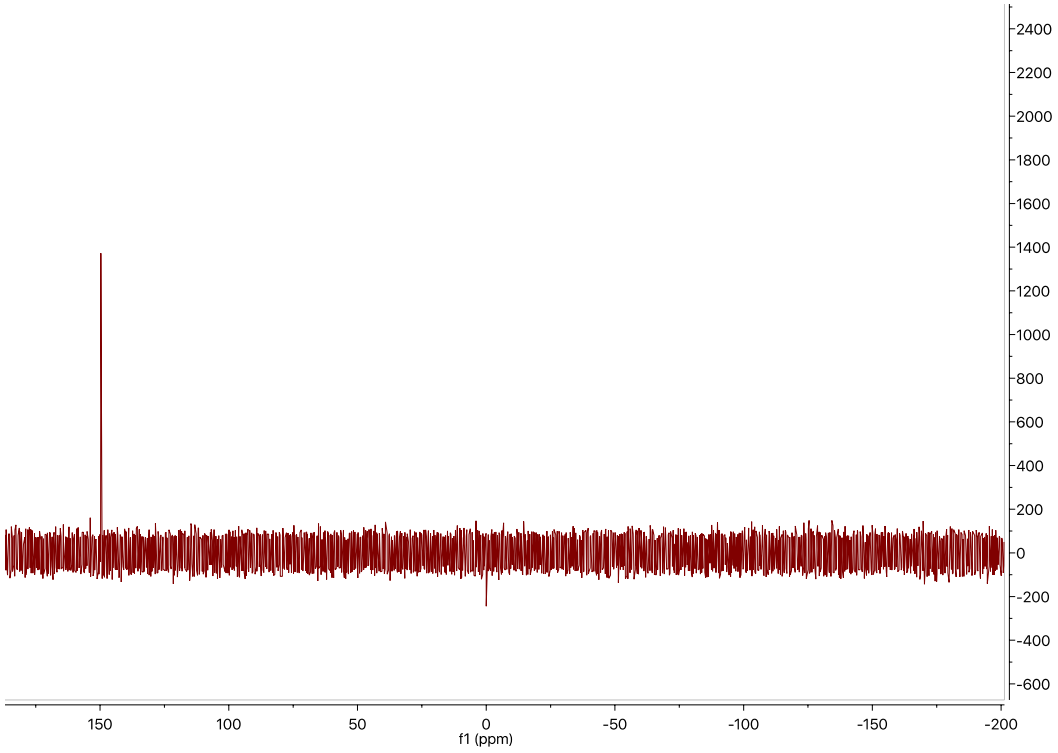
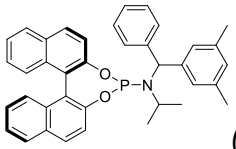
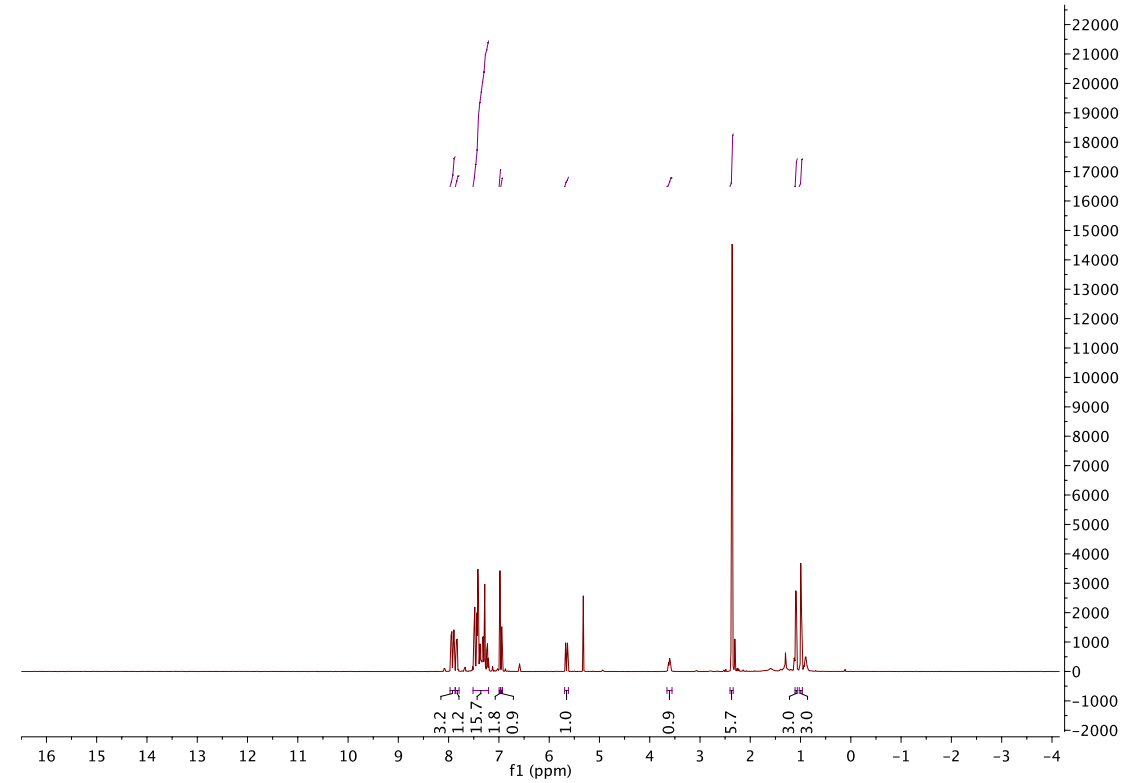
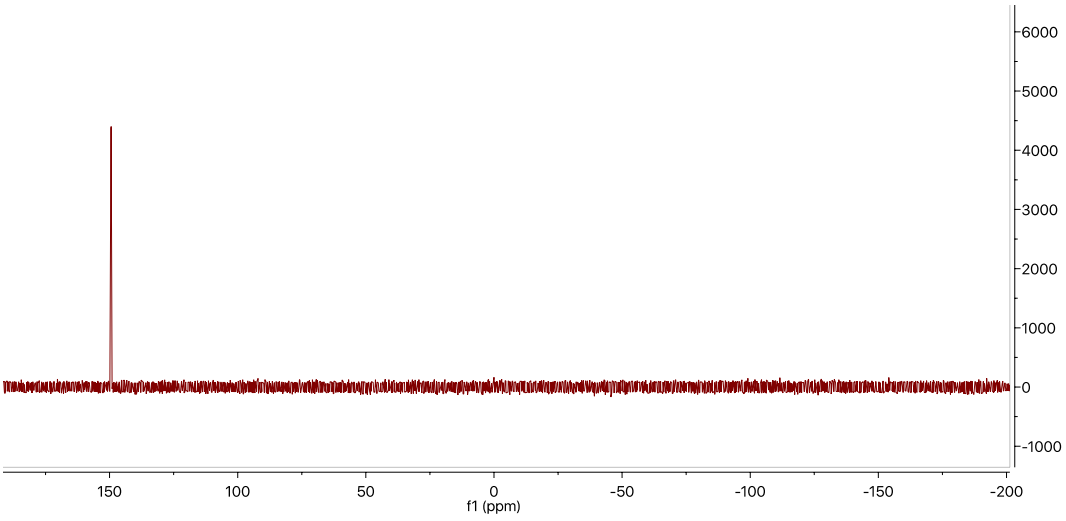
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

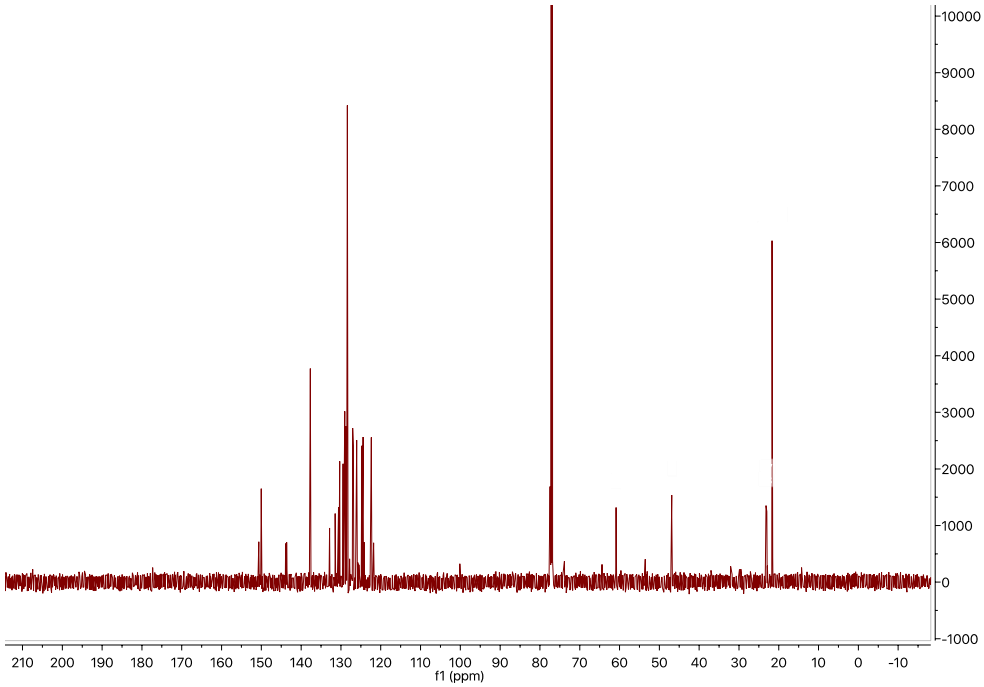

2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
150 100 50 0 -50 -100 -150 -200
f1 (ppm)

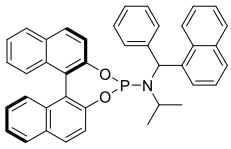


(R_a,R or *S)-N*-((3,5-dimethylphenyl)(phenyl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L22b**

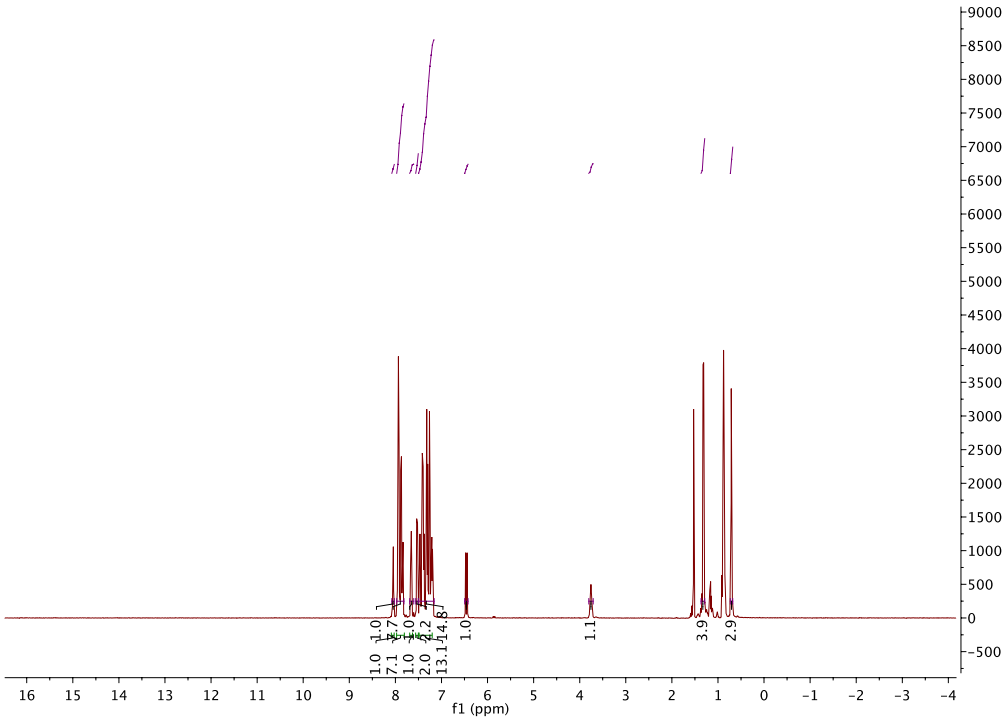


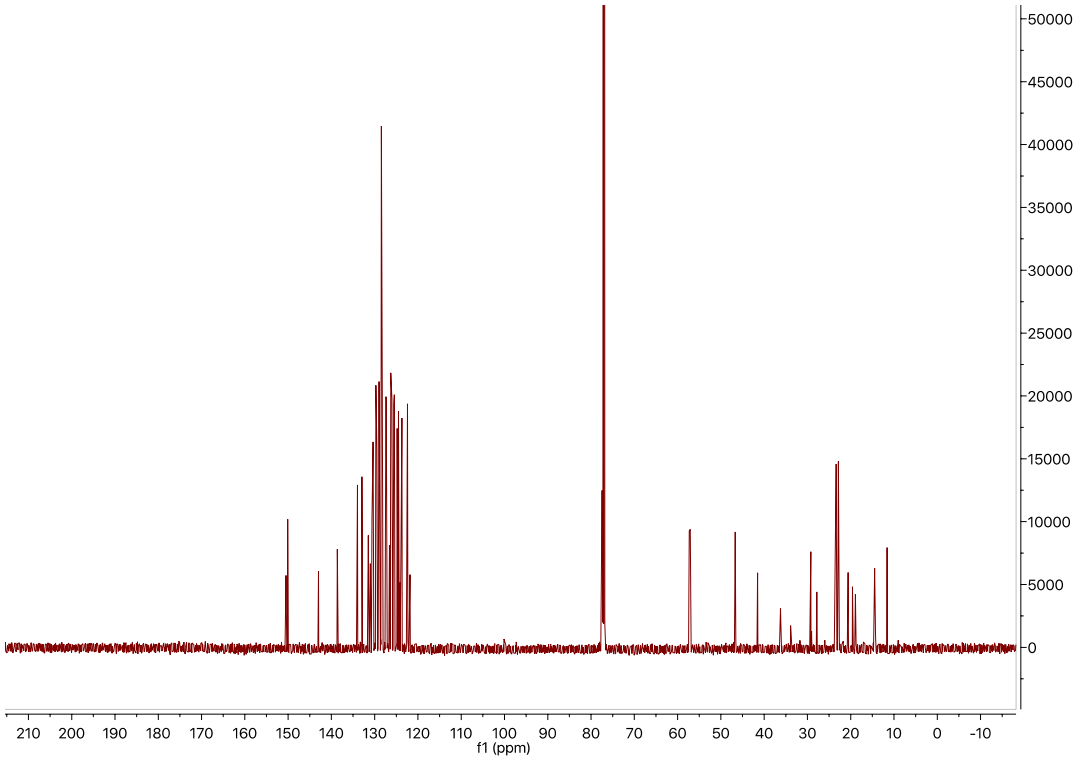






(R_a,R or *S)-N*-isopropyl-*N*-(naphthalen-1-yl(phenyl)methyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L23a**

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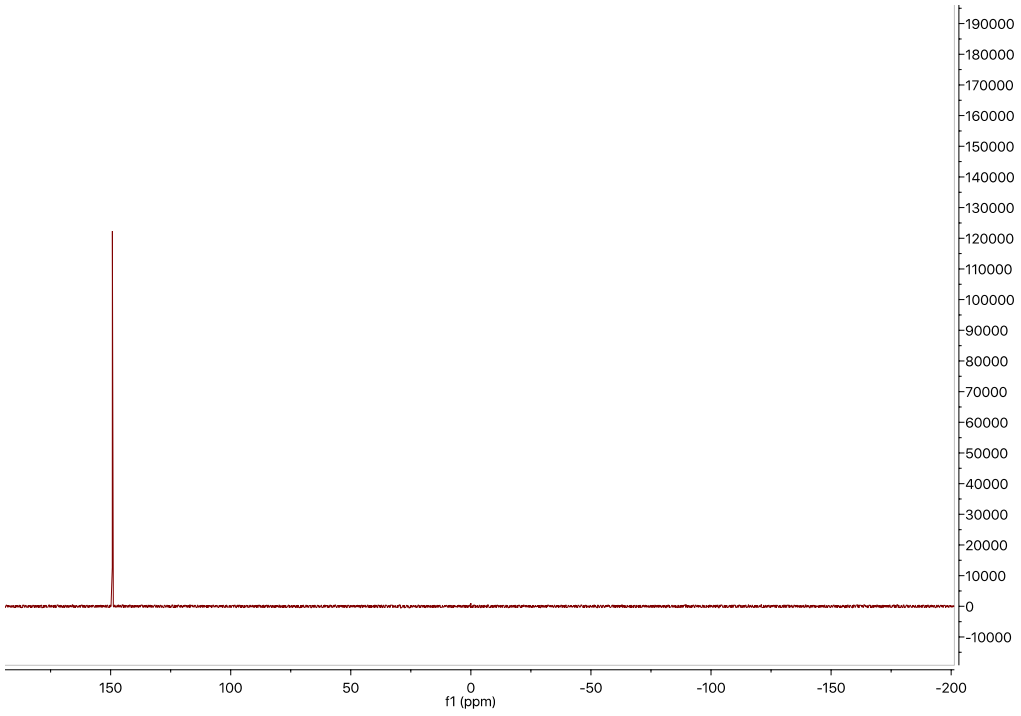
f1 (ppm)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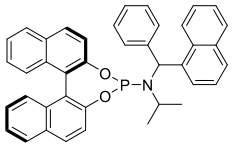
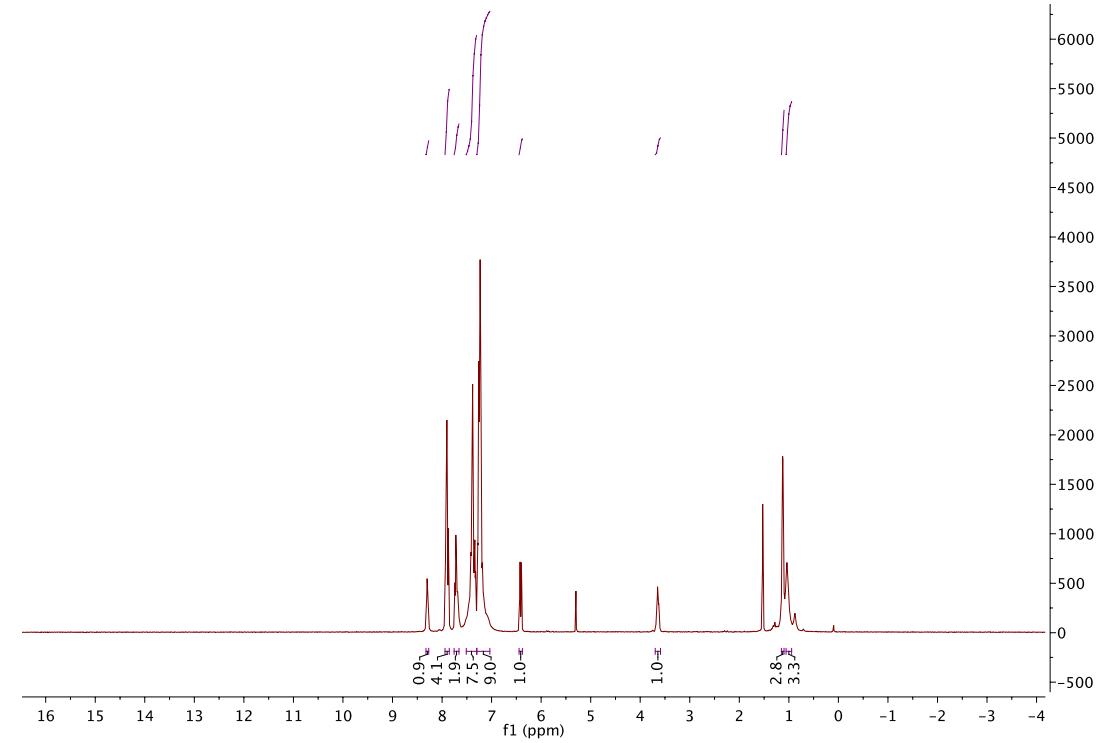
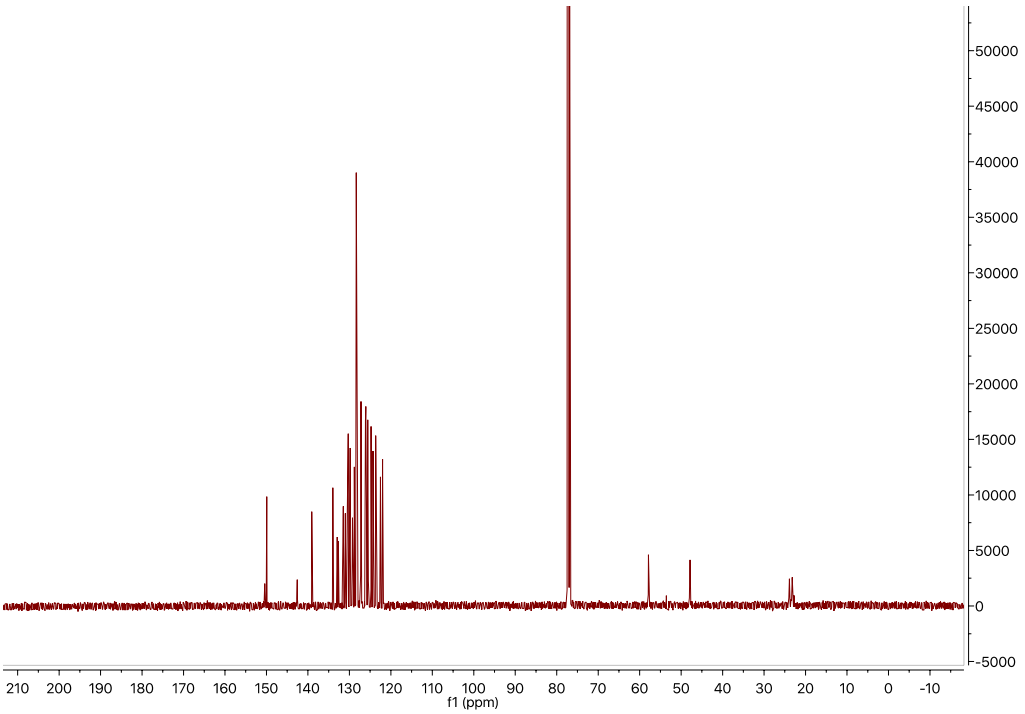
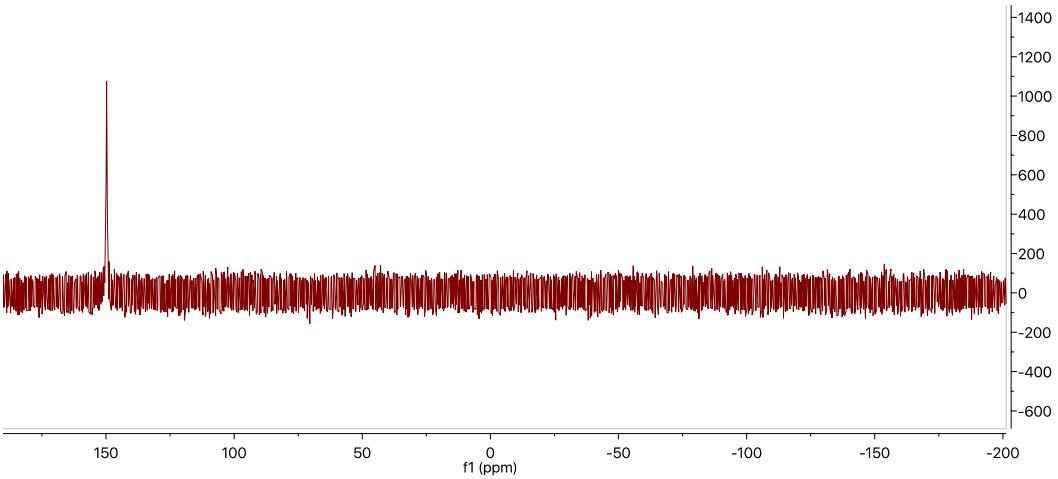
f1 (ppm)

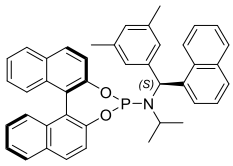


(R_a, R or *S)*- *N*-isopropyl-*N*-(naphthalen-1-yl(phenyl)methyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L23b**

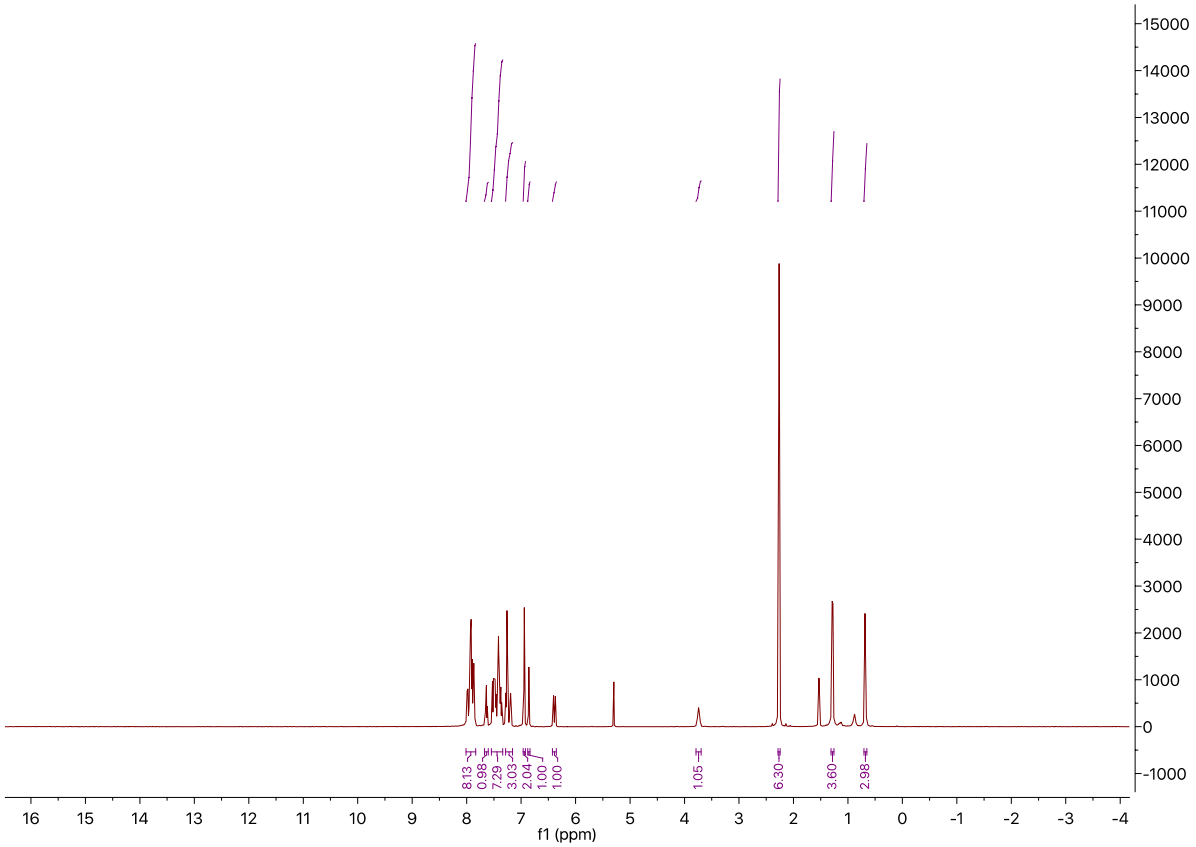


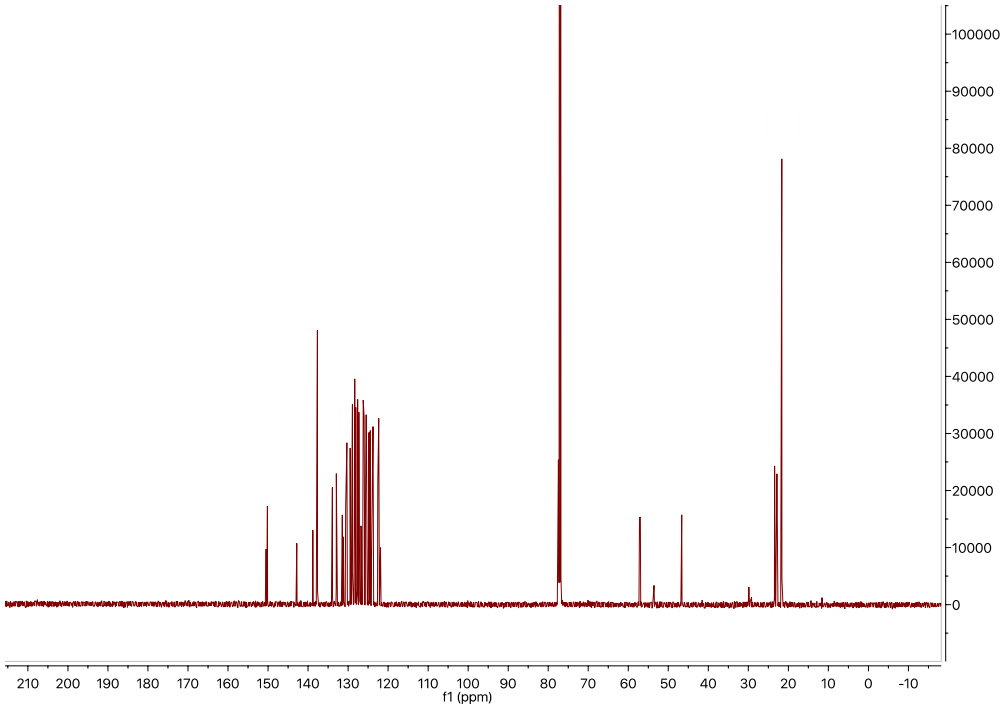






(R_a,S)-N-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L24S**

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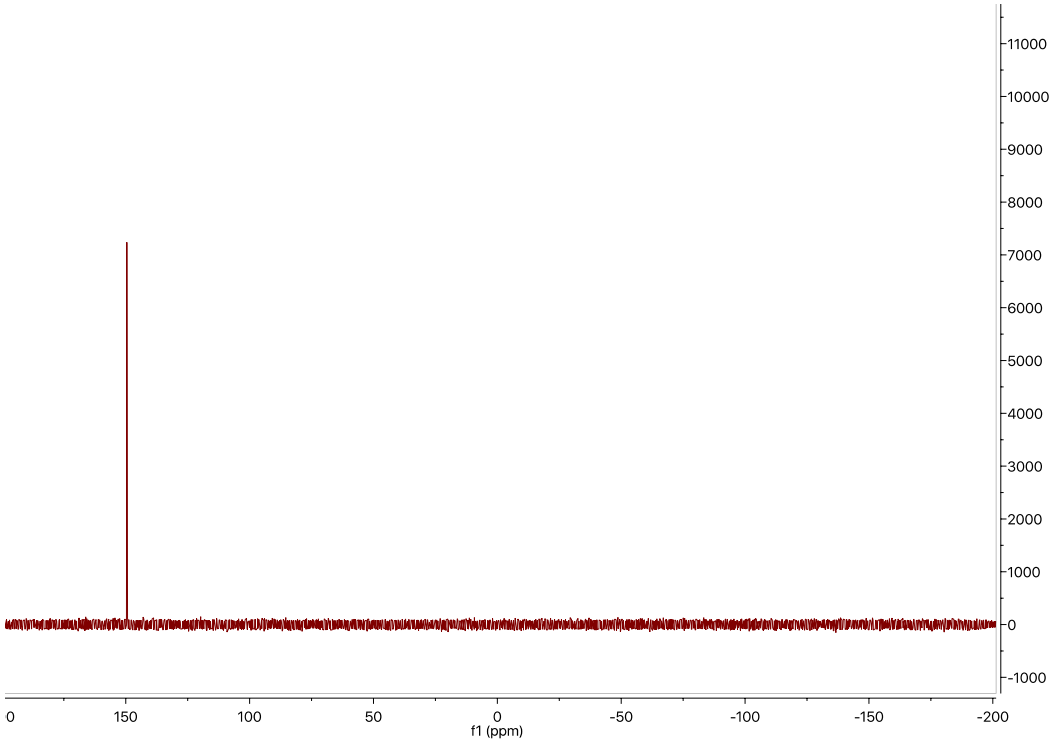
f1 (ppm)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1000
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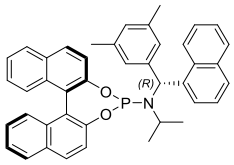
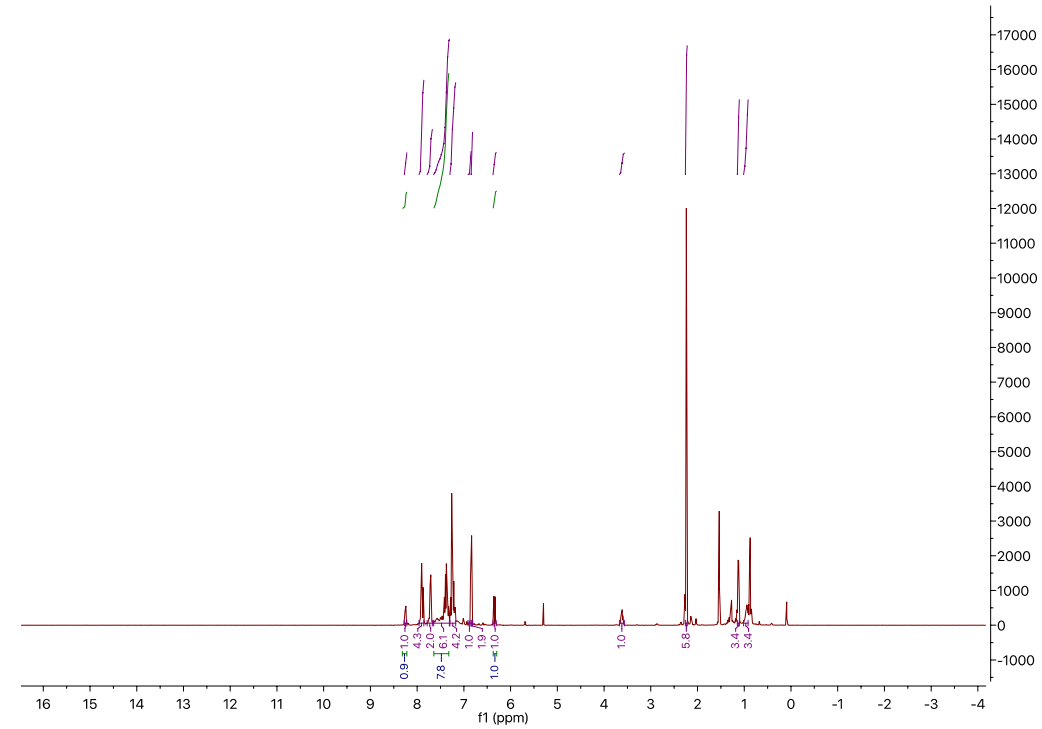
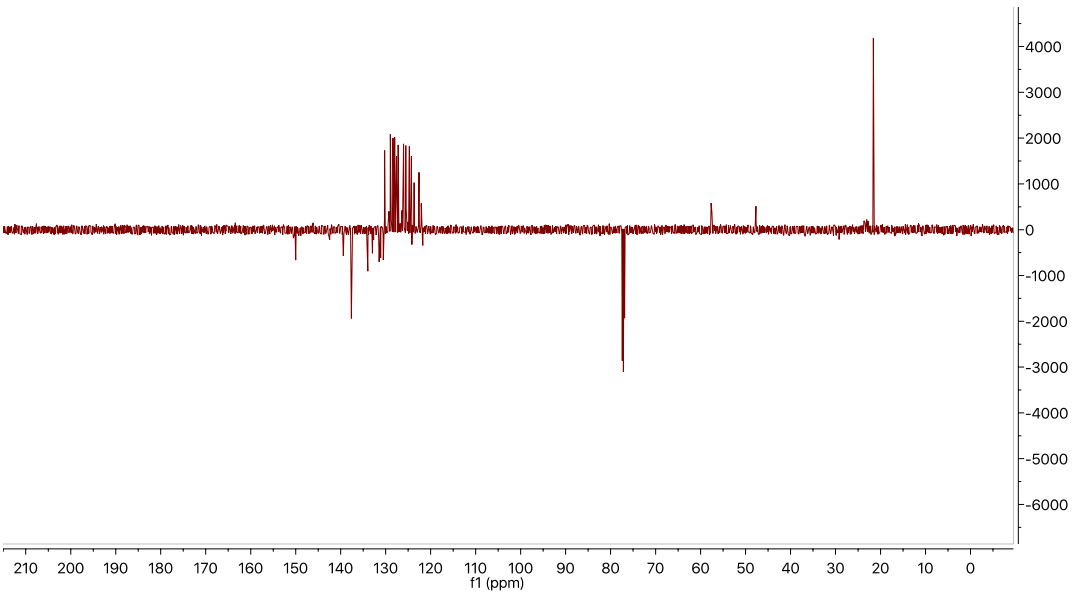
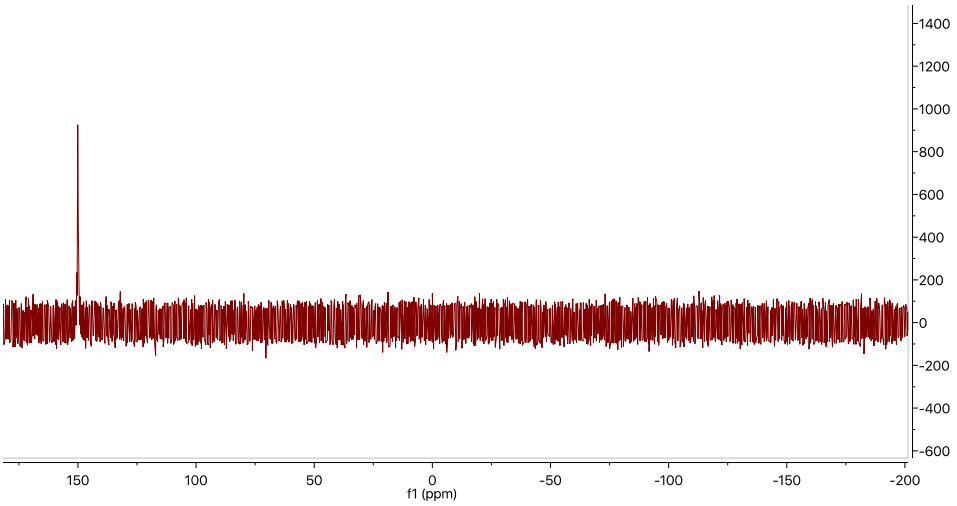
0 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

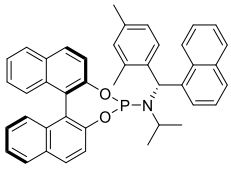


(R_a,R)-*N*-((3,5-dimethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L24R**

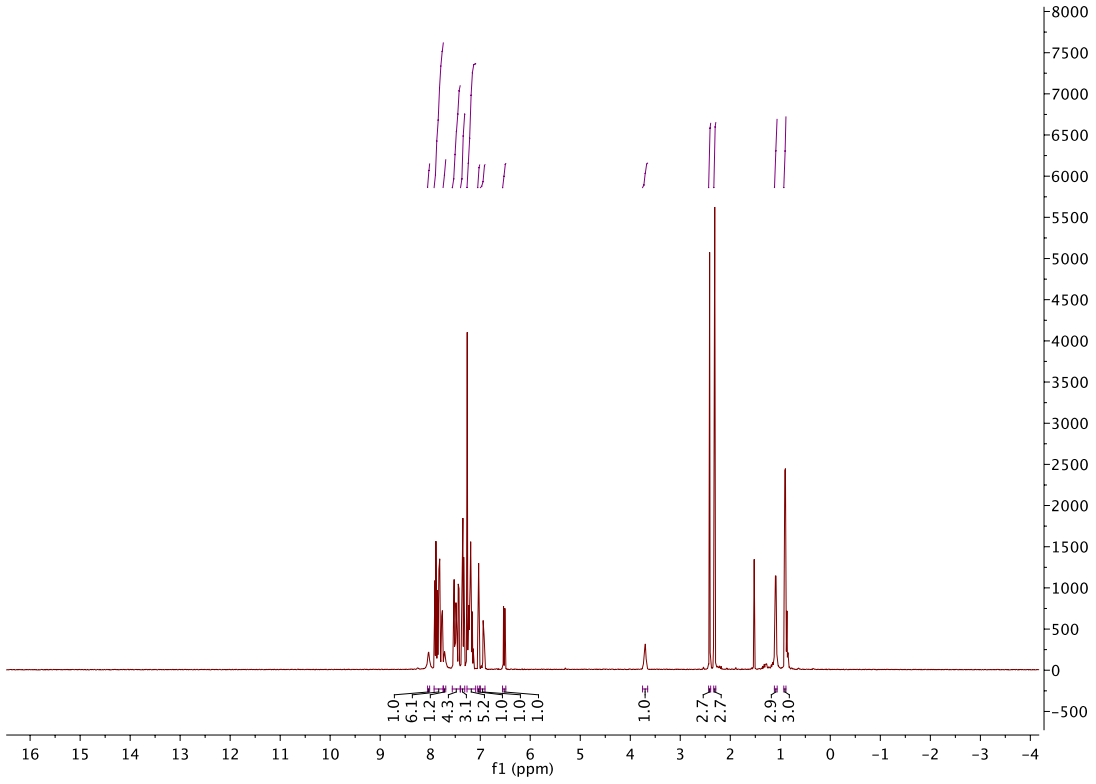


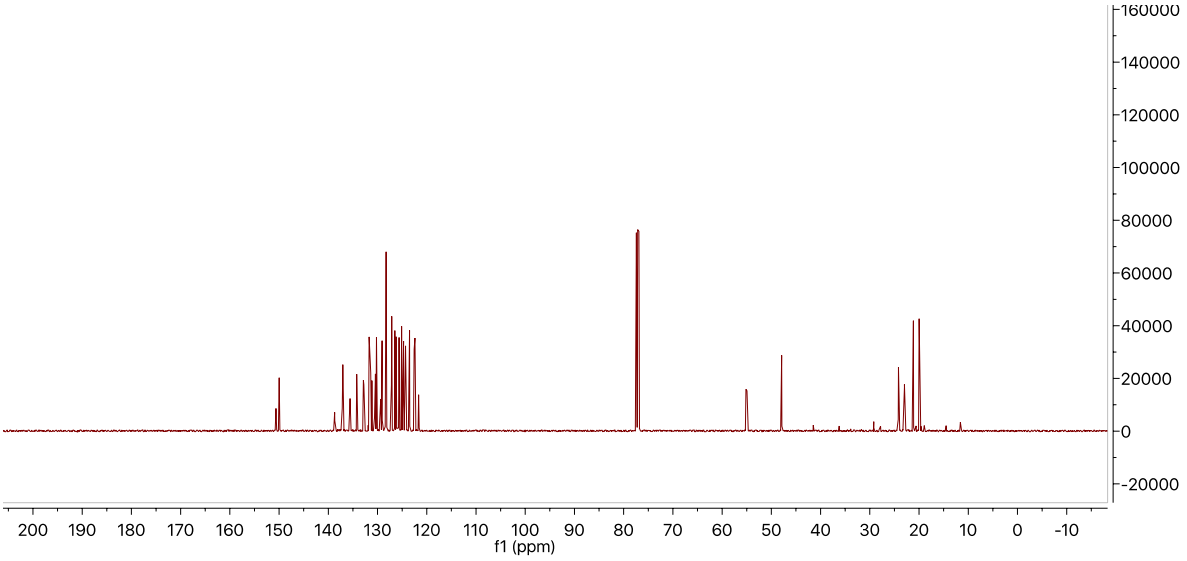






(R_a,*R*)-*N*-(-(2,4-dimethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L25R**

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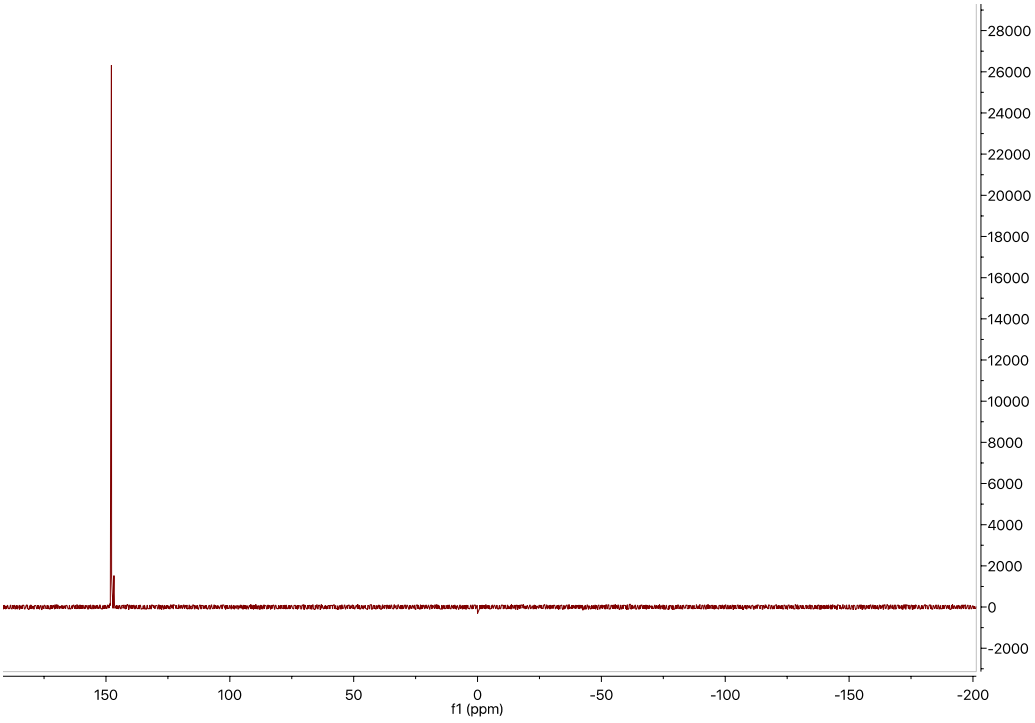
f1 (ppm)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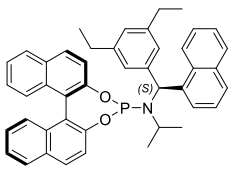
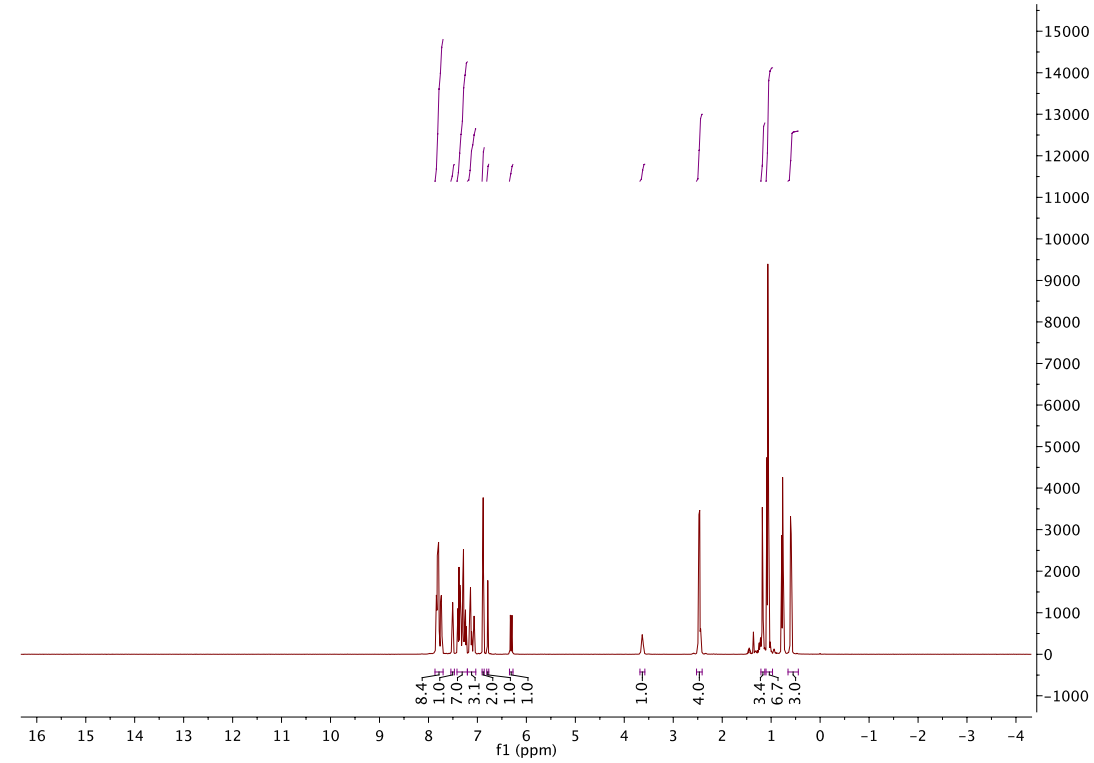
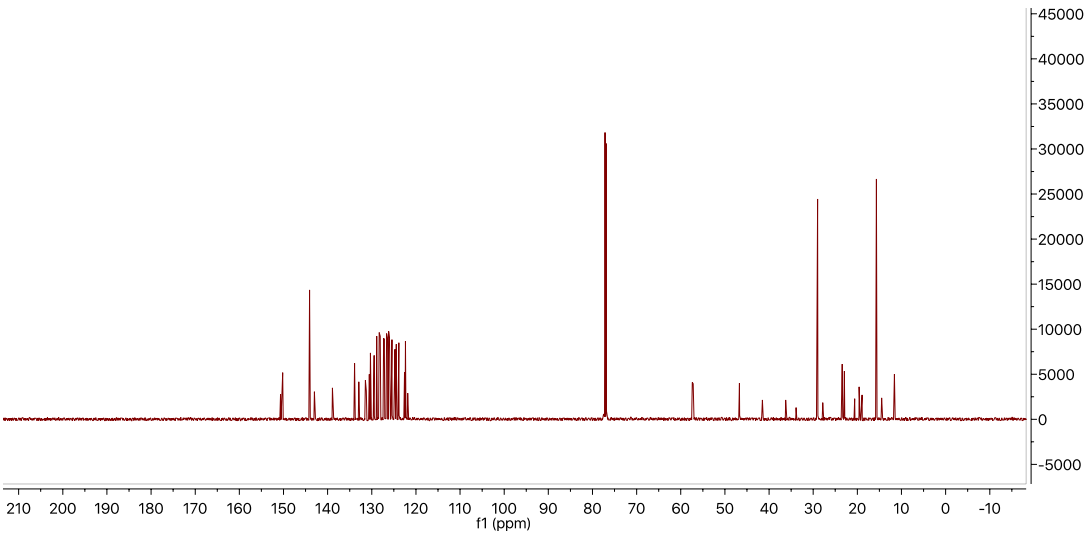
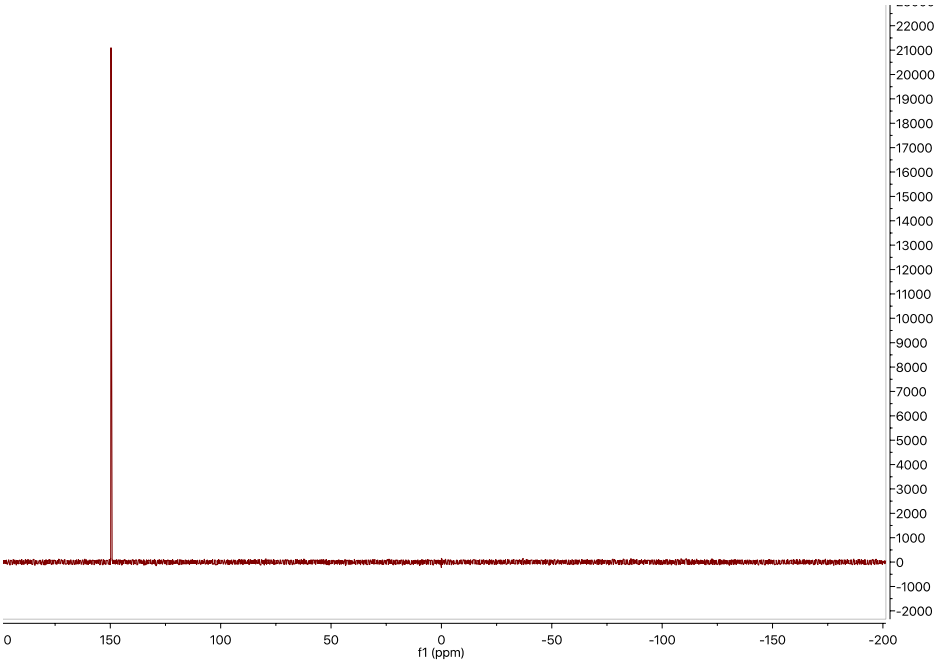
f1 (ppm)

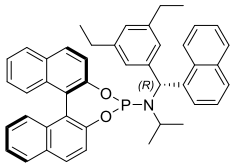


(R_a, *R* or *S*)- *N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L26S**

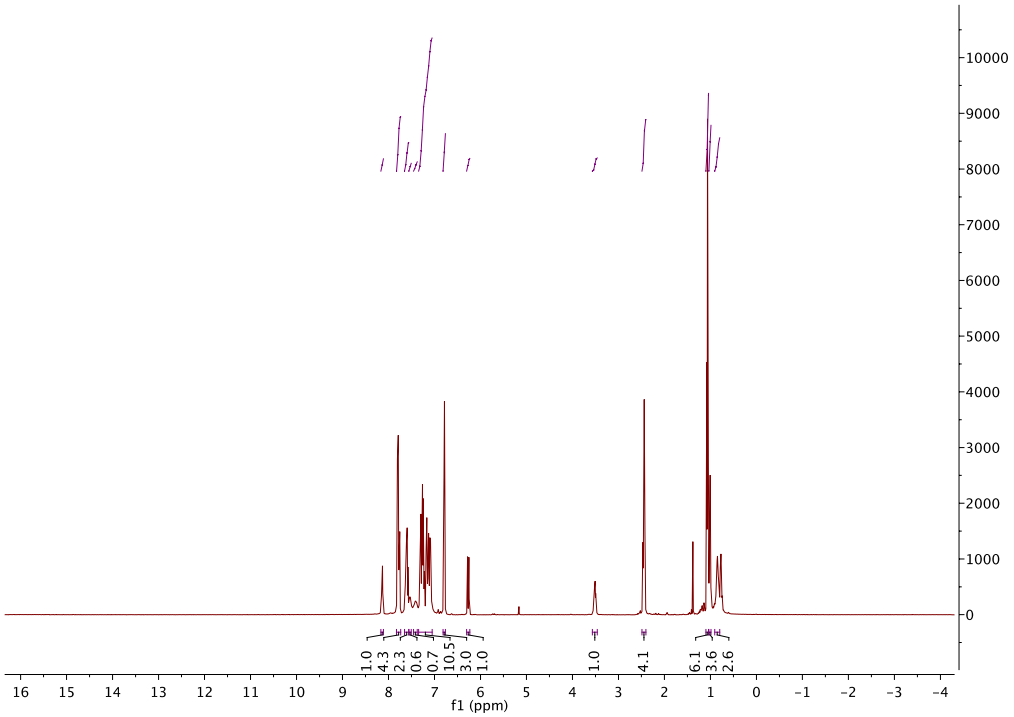


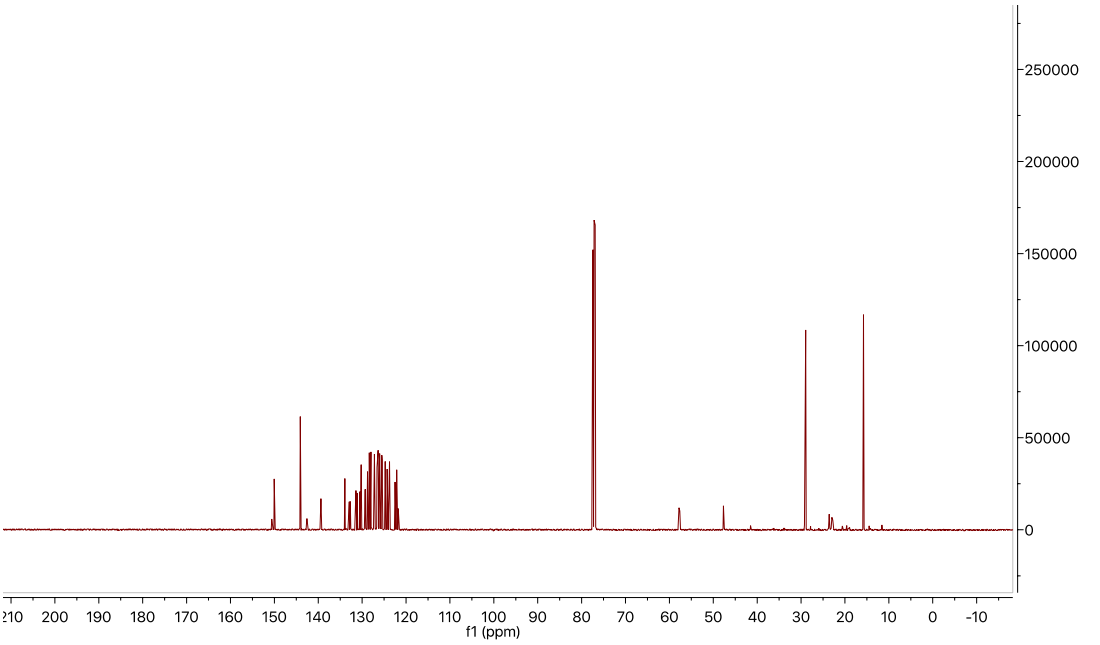






(*R*$_a$, *R* or *S*)- *N*-((3,5-diethylphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L26R**

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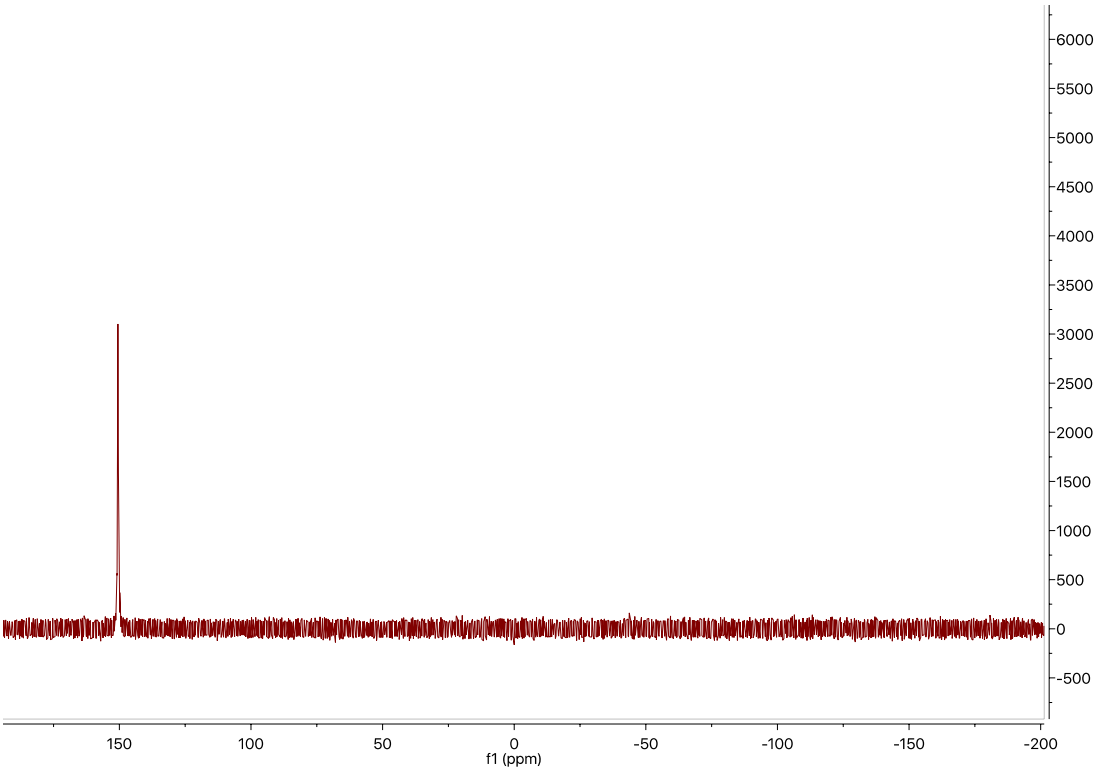
f1 (ppm)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2500
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1500
1000
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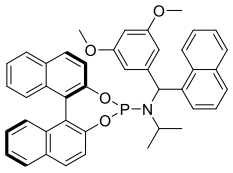
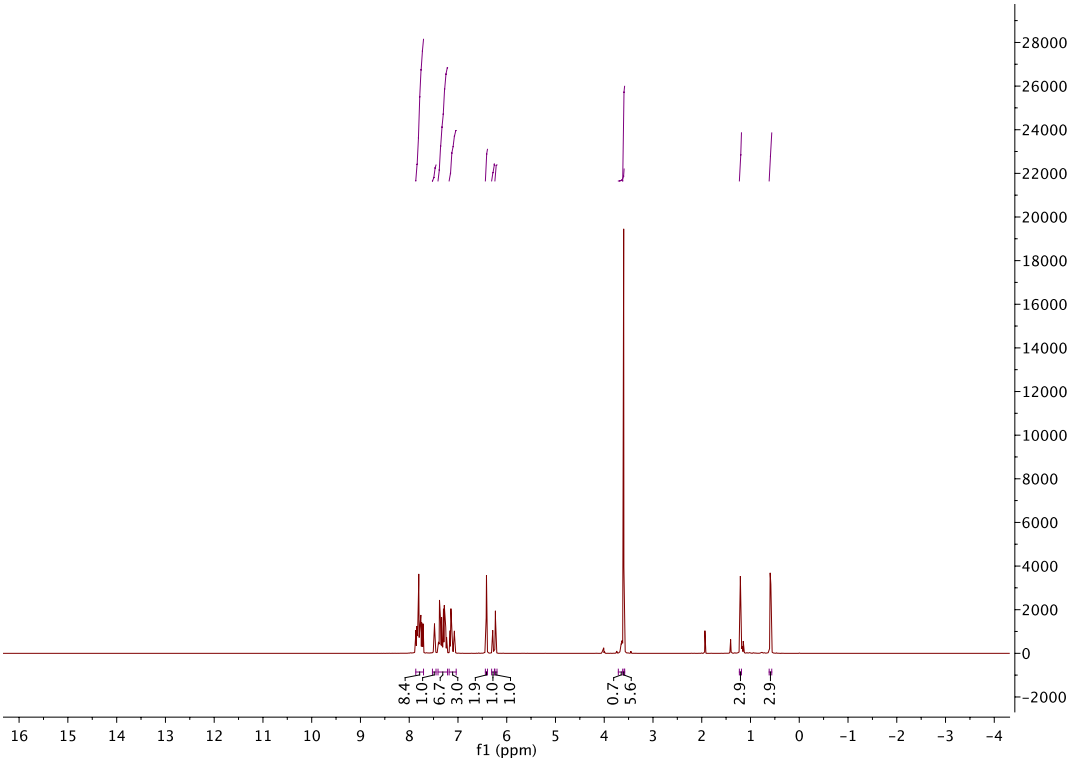
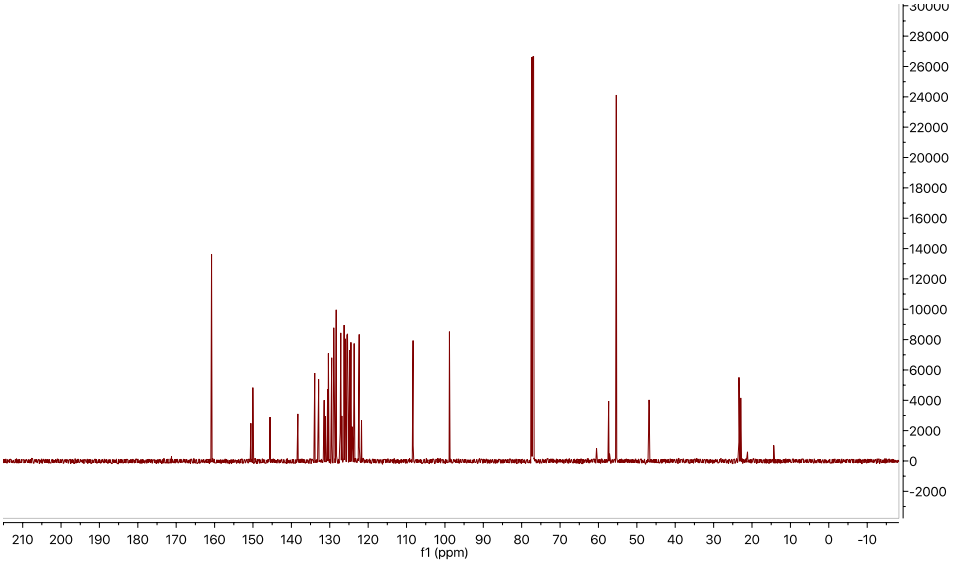
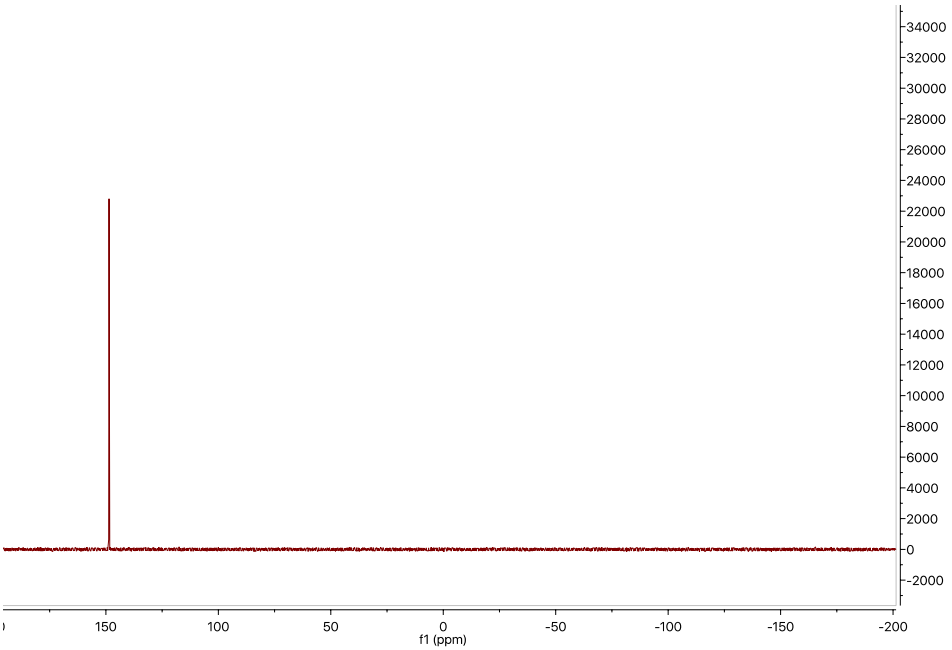
-500
150 100 50 0 -50 -100 -150 -200
f1 (ppm)

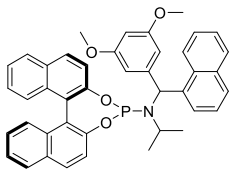


(R_a, R or *S)-N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L27a**

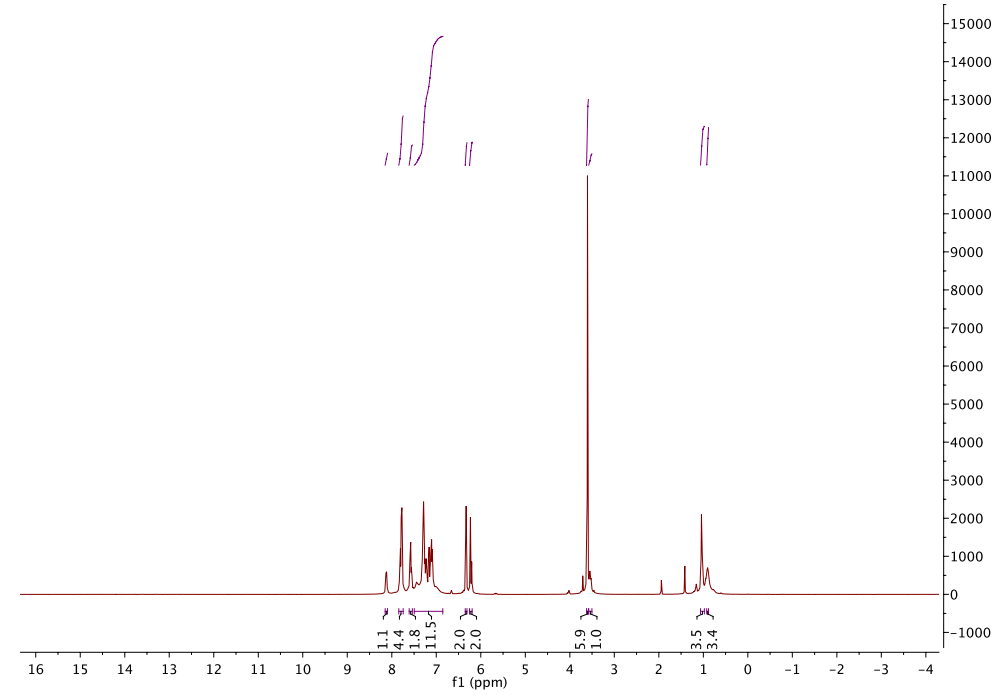


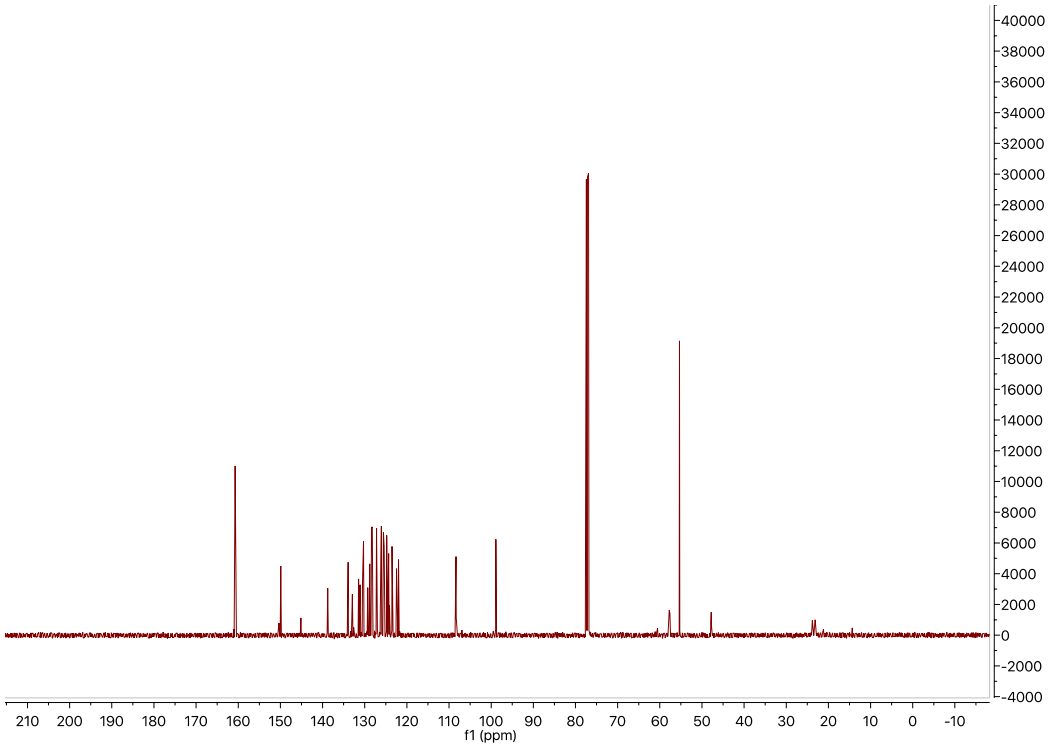






(R_a,R or *S)-N*-((3,5-dimethoxyphenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L27b**

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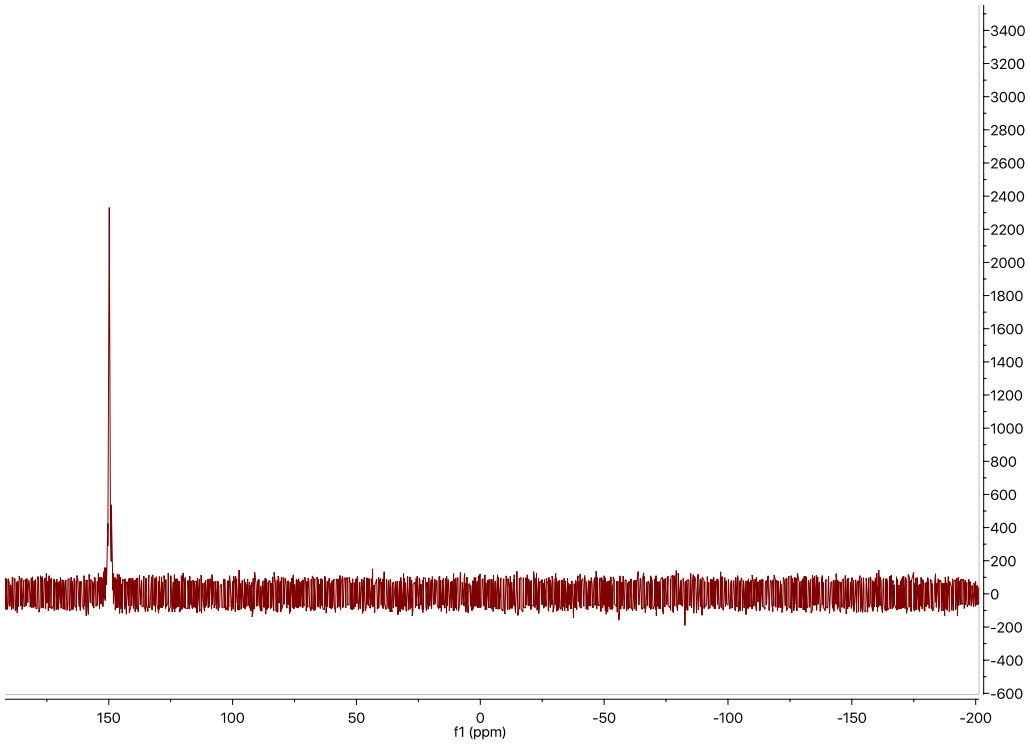
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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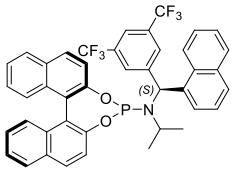
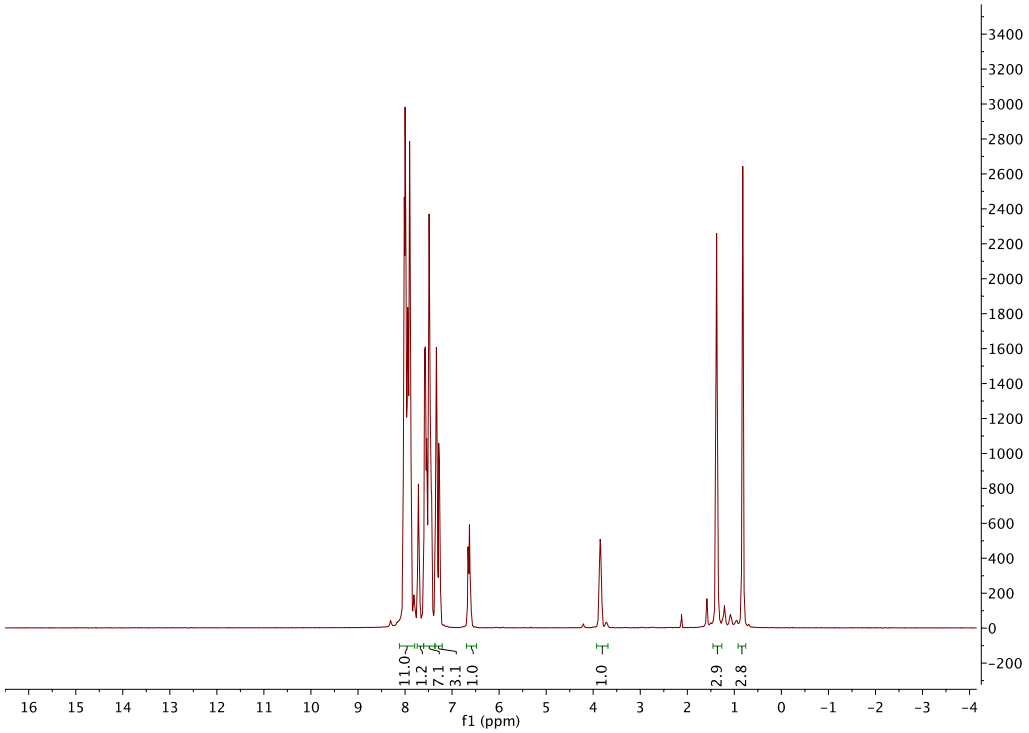
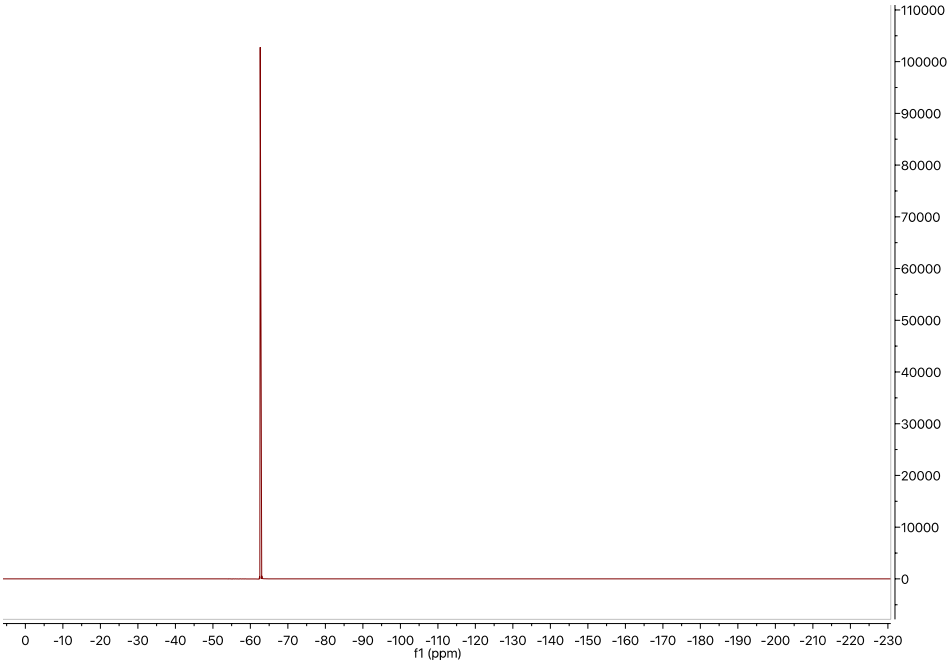
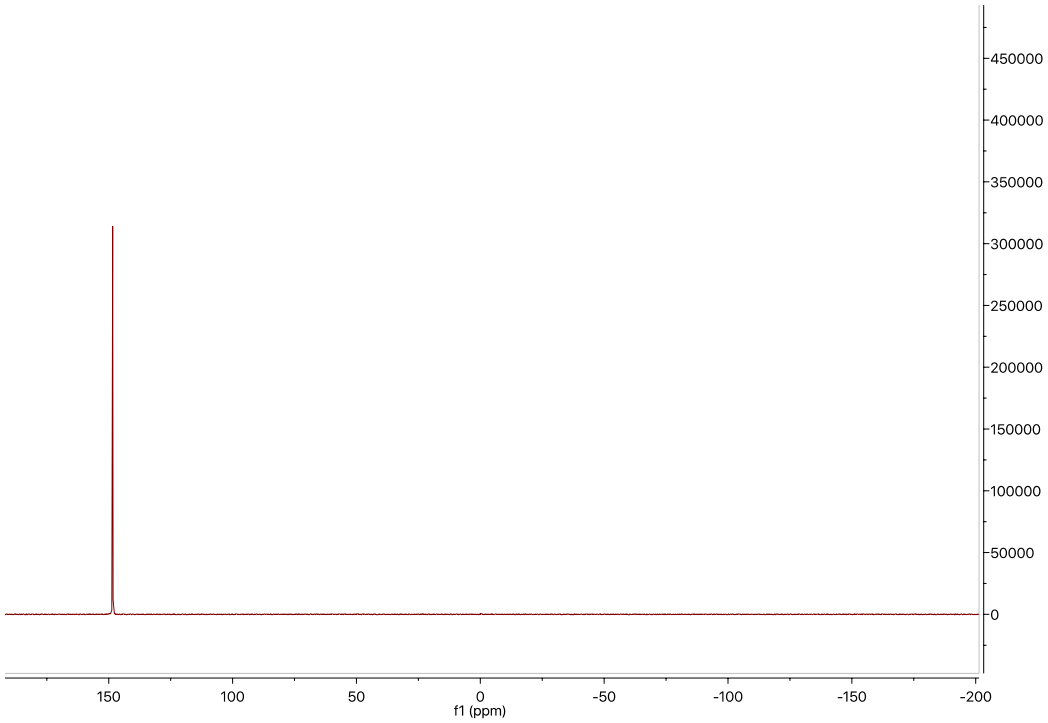
f1 (ppm)



(R_a,*R or S*)-*N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L28S**



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50
0
-50
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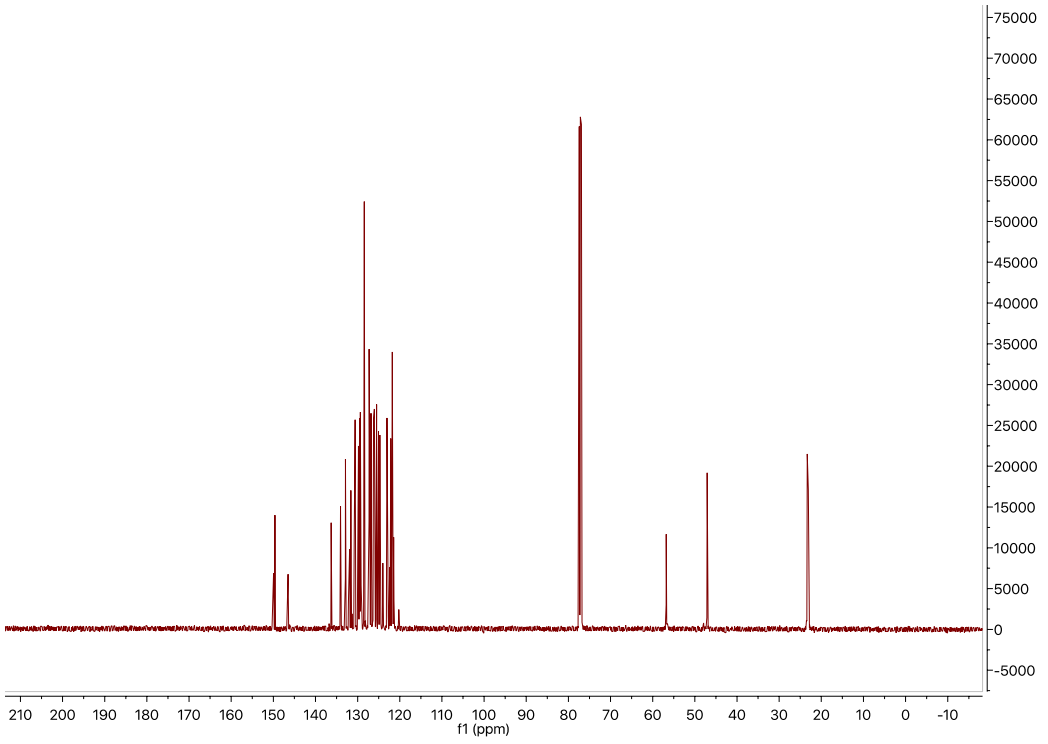
-200
f1 (ppm)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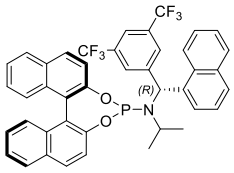
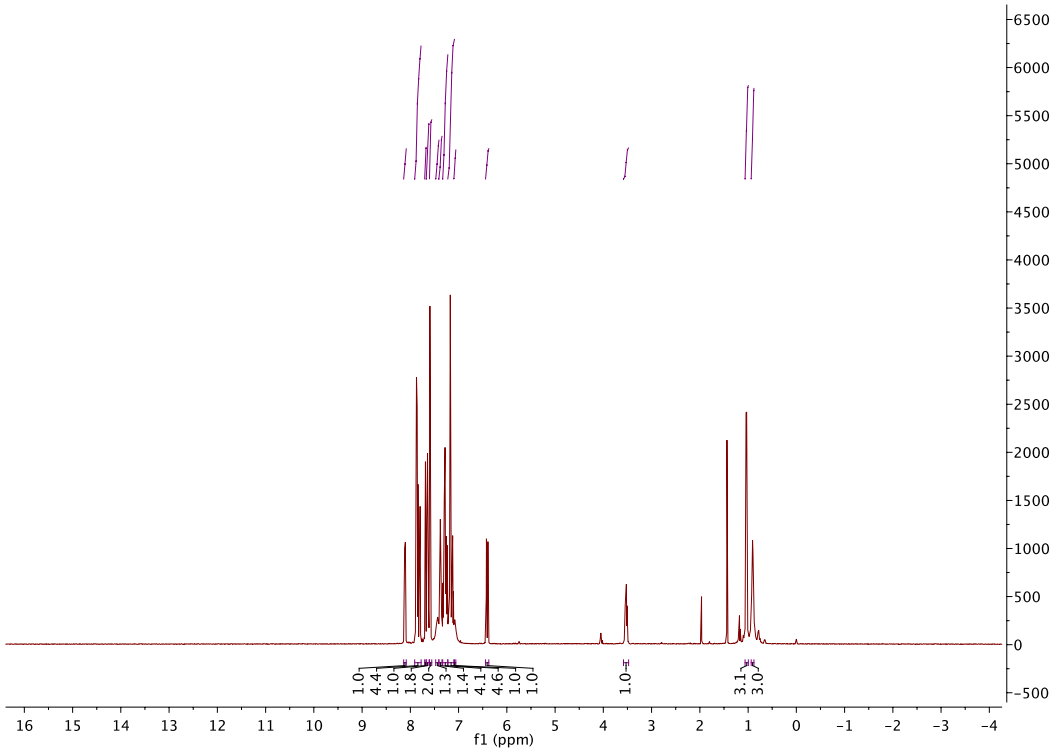
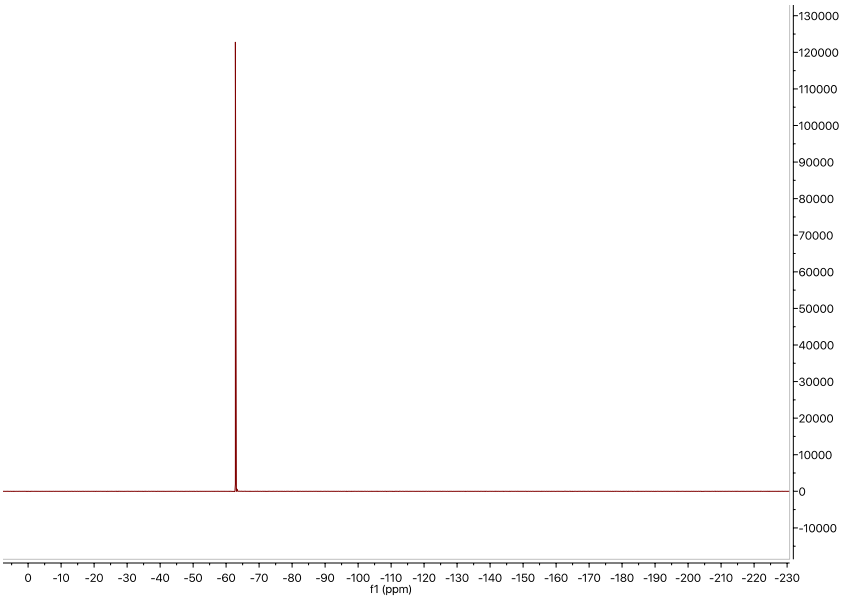
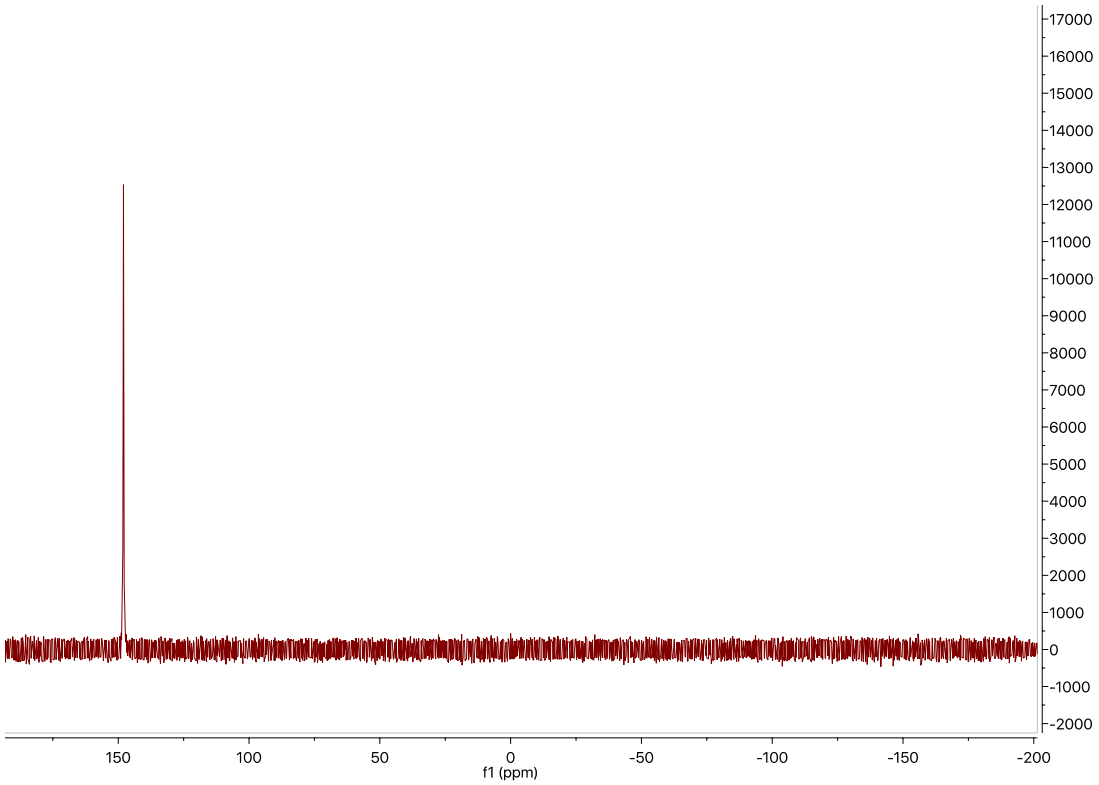
f1 (ppm)



(R_a, *R or S*)- *N*-((3,5-bis(trifluoromethyl)phenyl)(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L28R**



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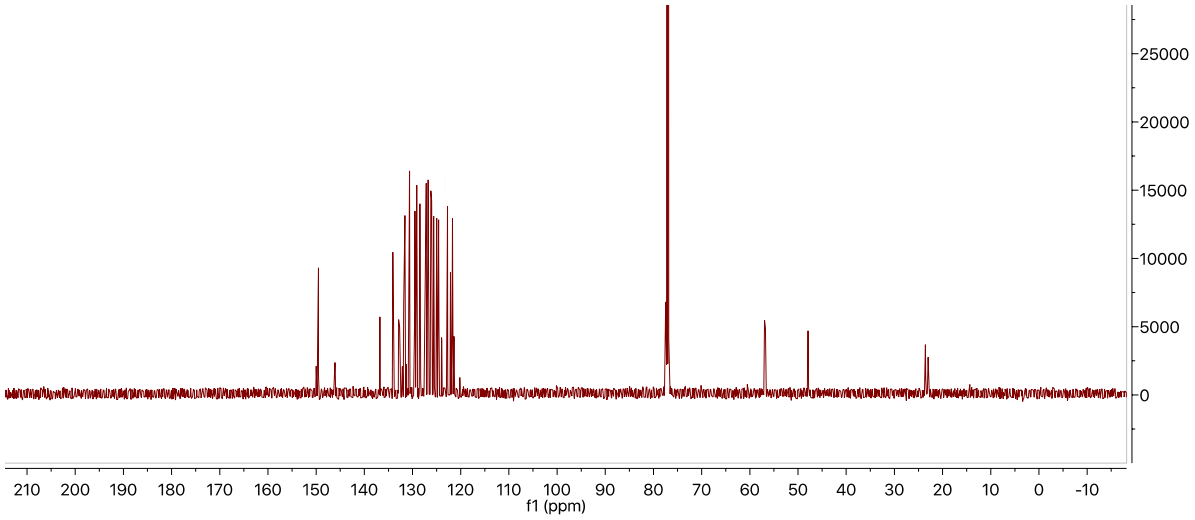
-200
f1 (ppm)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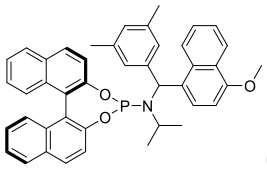
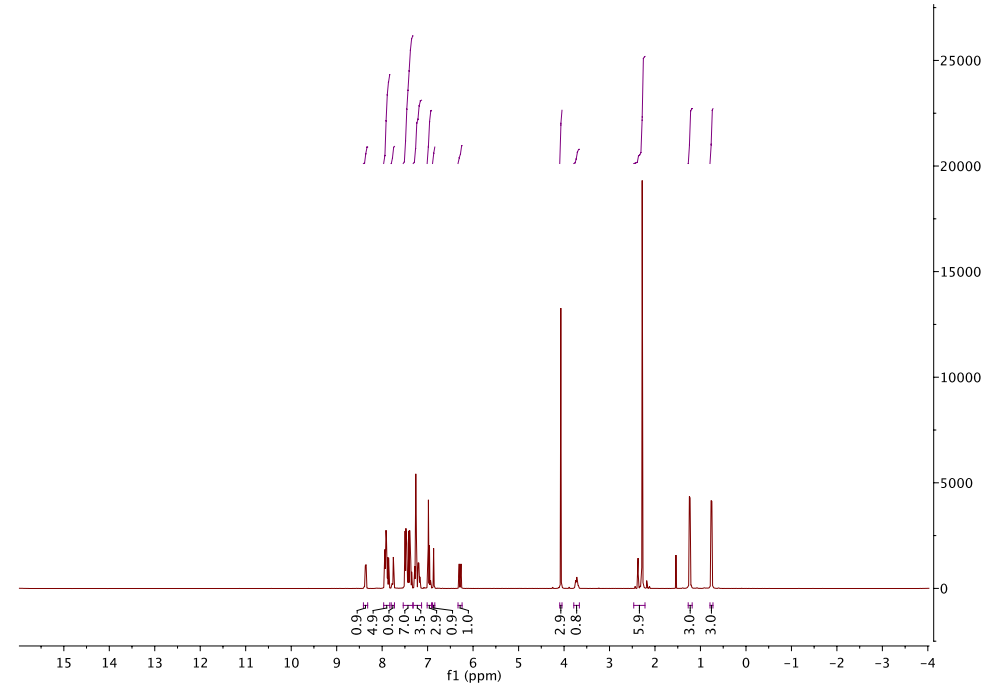
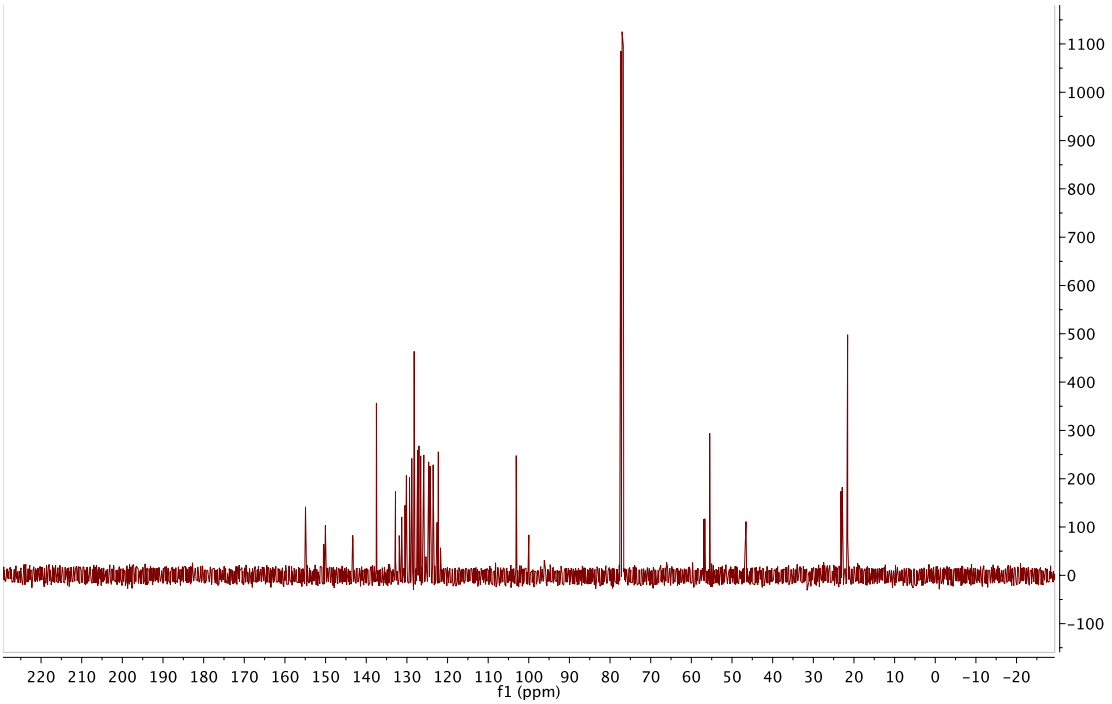
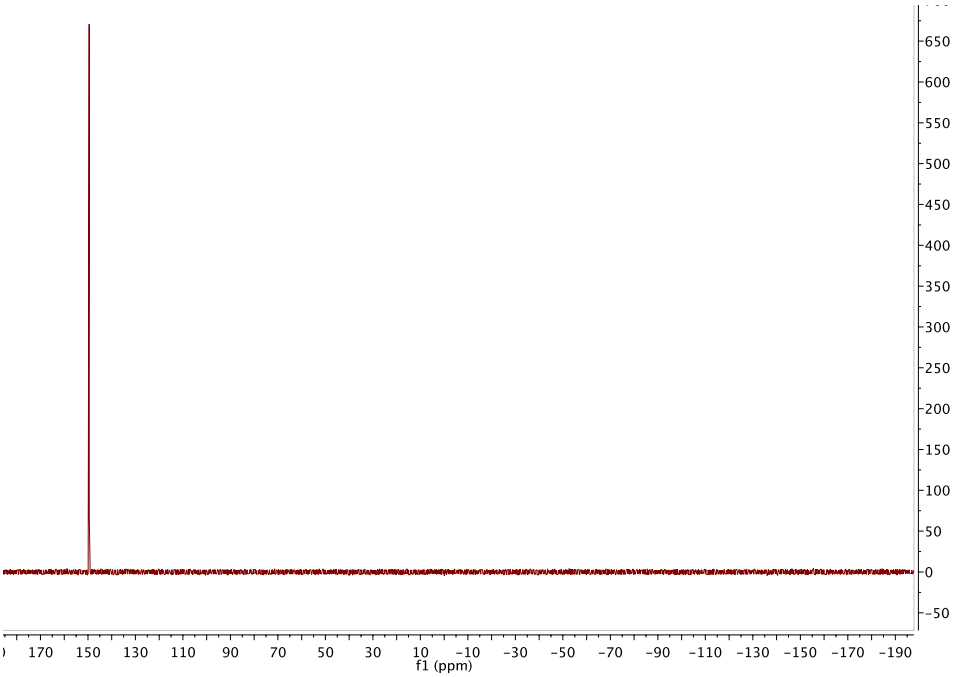
f1 (ppm)

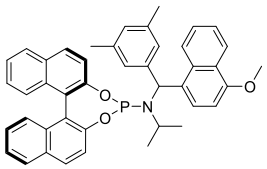


(R_a,*R or S*)-*N*-((3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L29a**

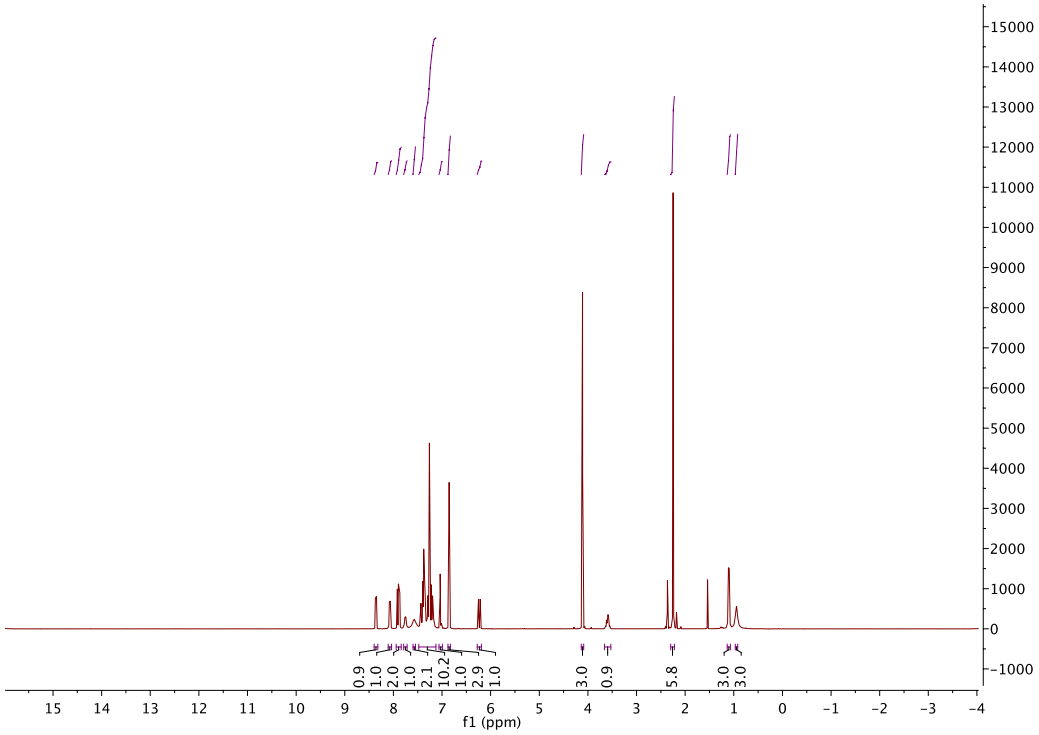


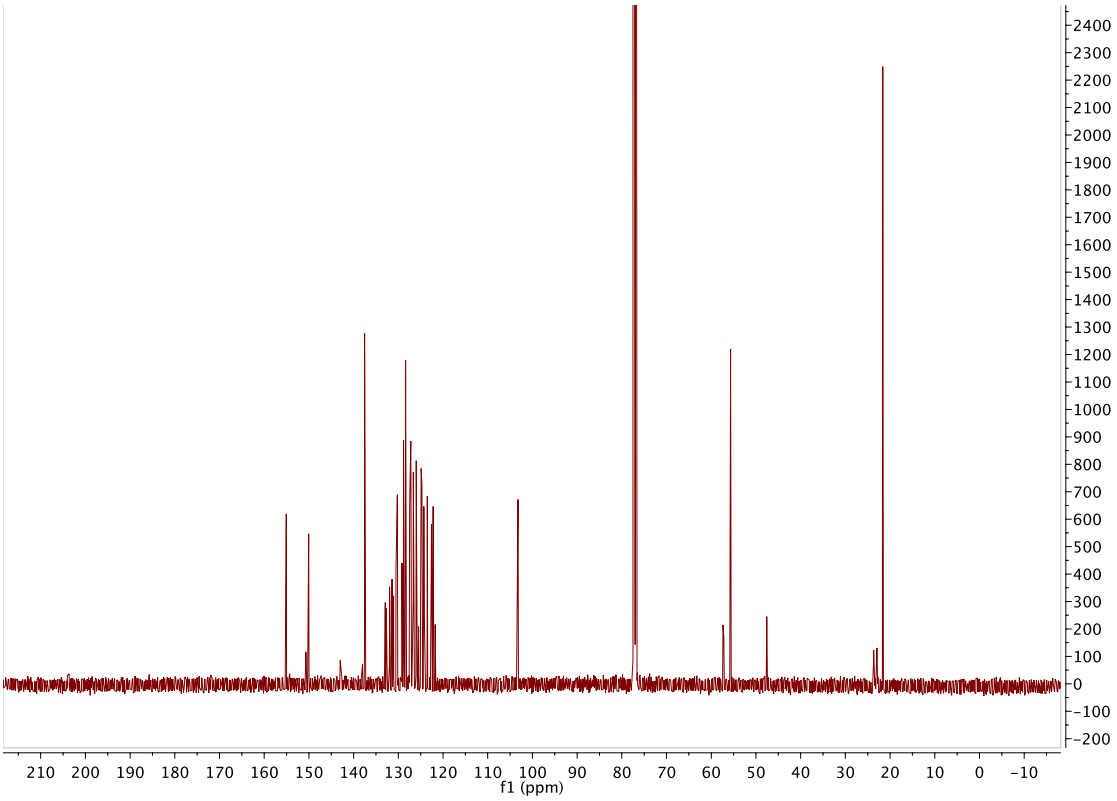






(R_a,*R or S*)-*N*-((3,5-dimethylphenyl)(4-methoxynaphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L29b**

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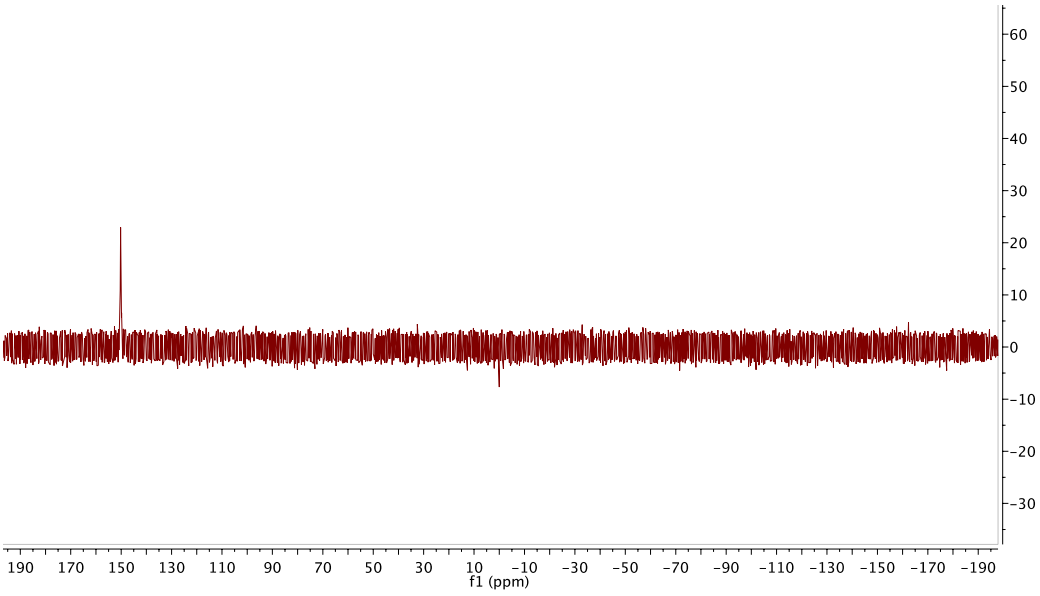
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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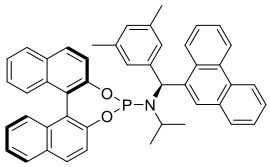
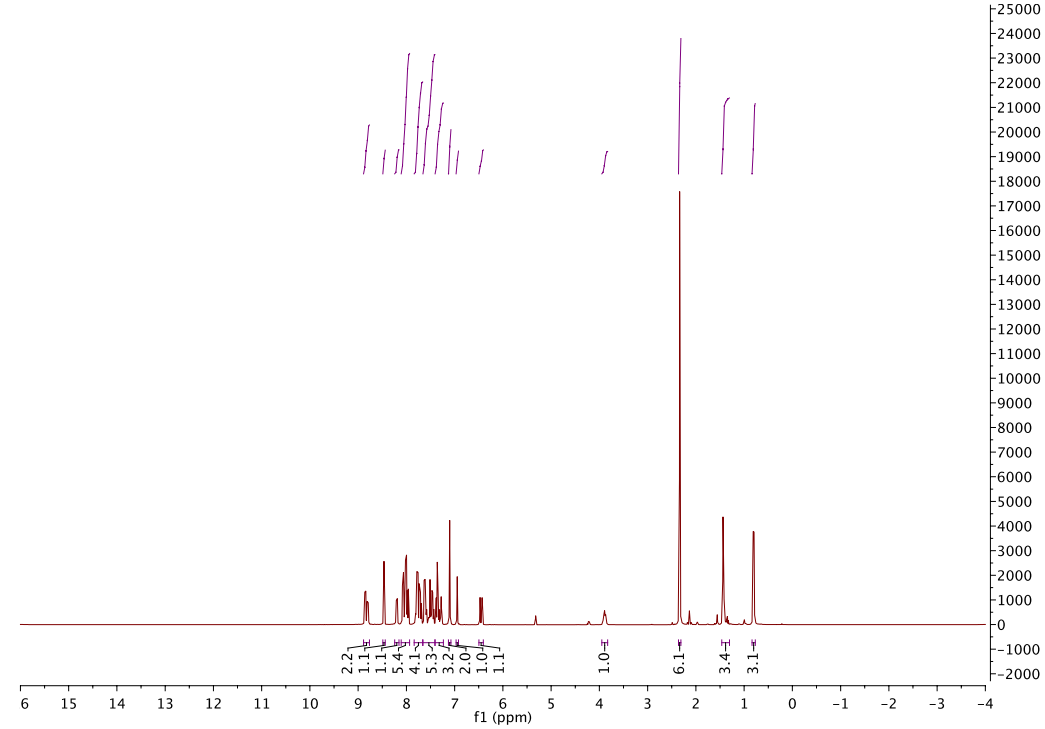
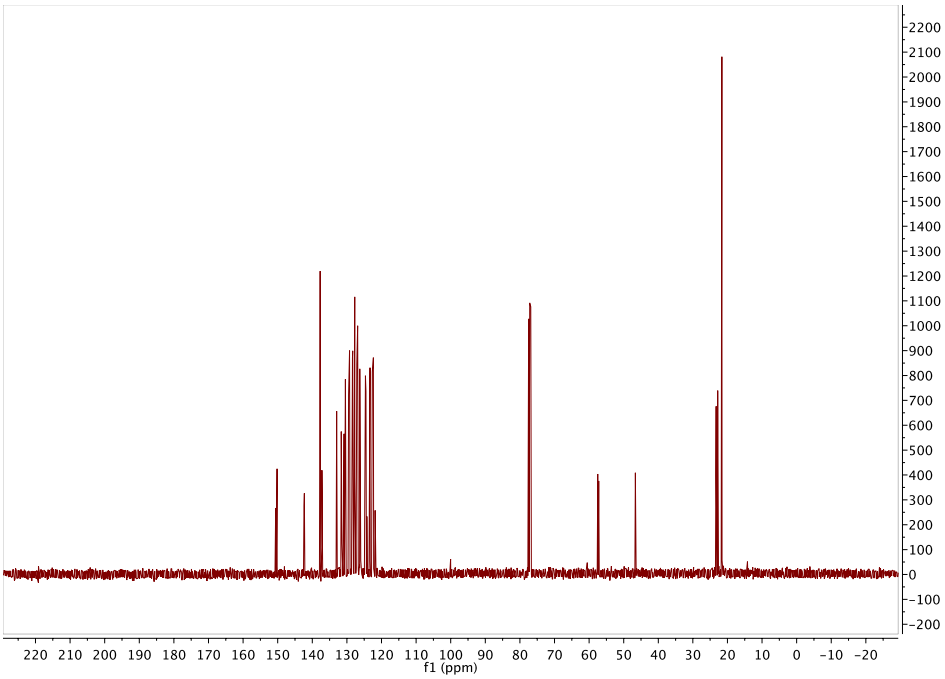
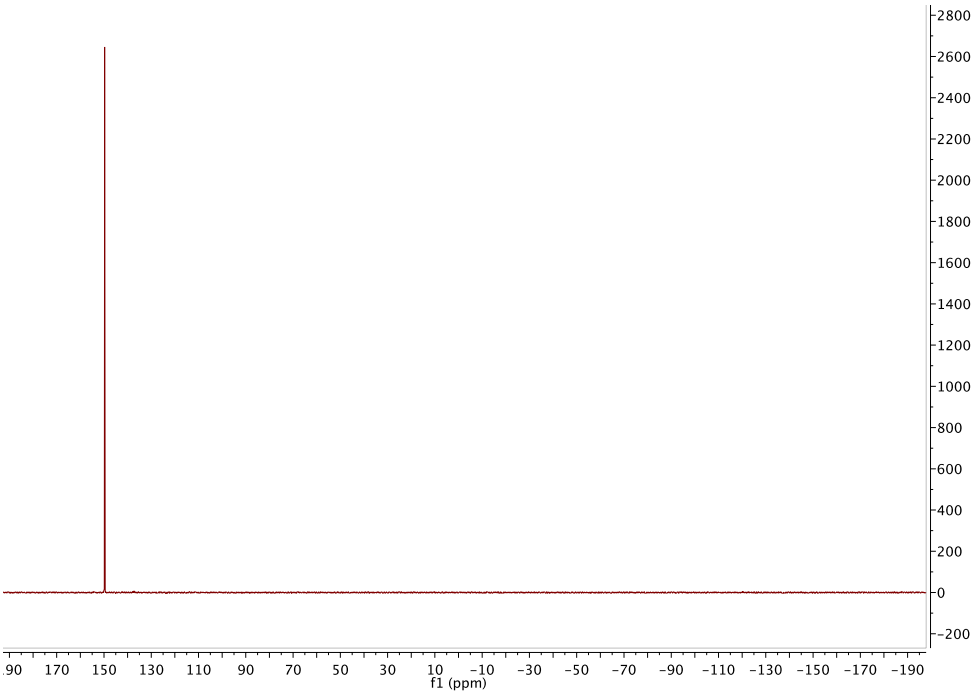
190 170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190
f1 (ppm)

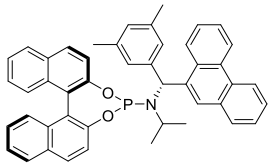


(R_a,*S*)-*N*-(3,5-dimethylphenyl)(phenanthren-9-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L30S**

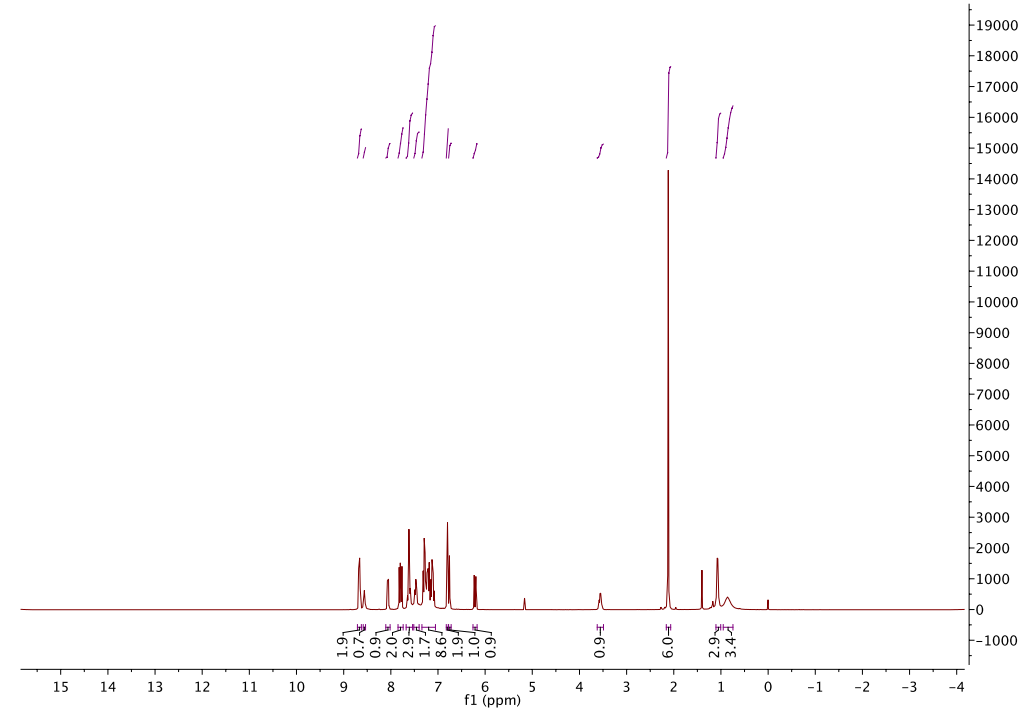


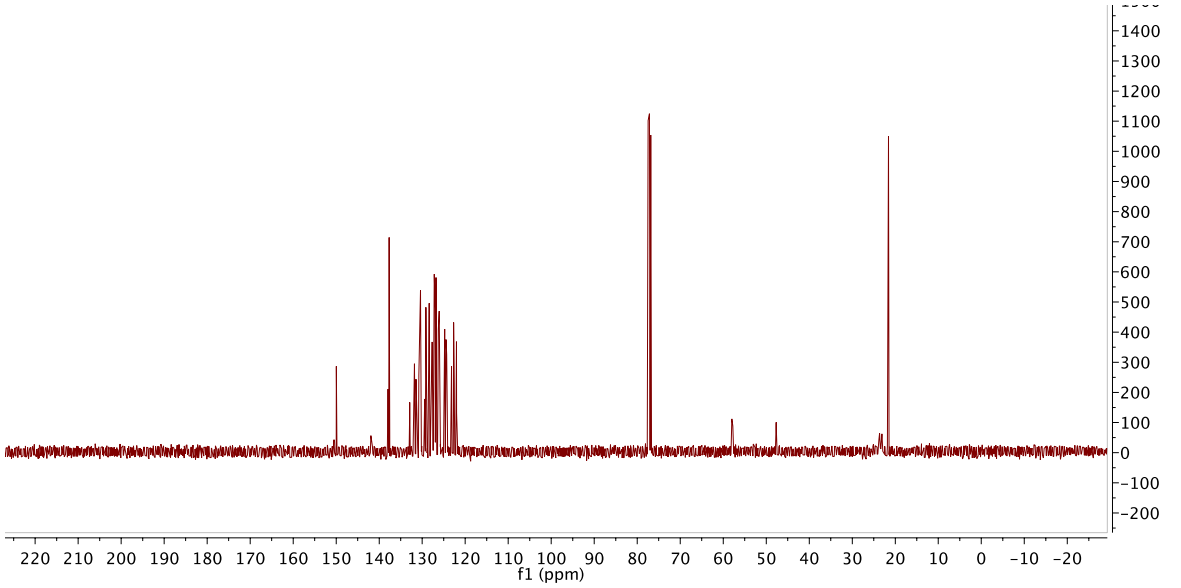






(R_a,*R*)-*N*-(3,5-dimethylphenyl)(phenanthren-9-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L30R**

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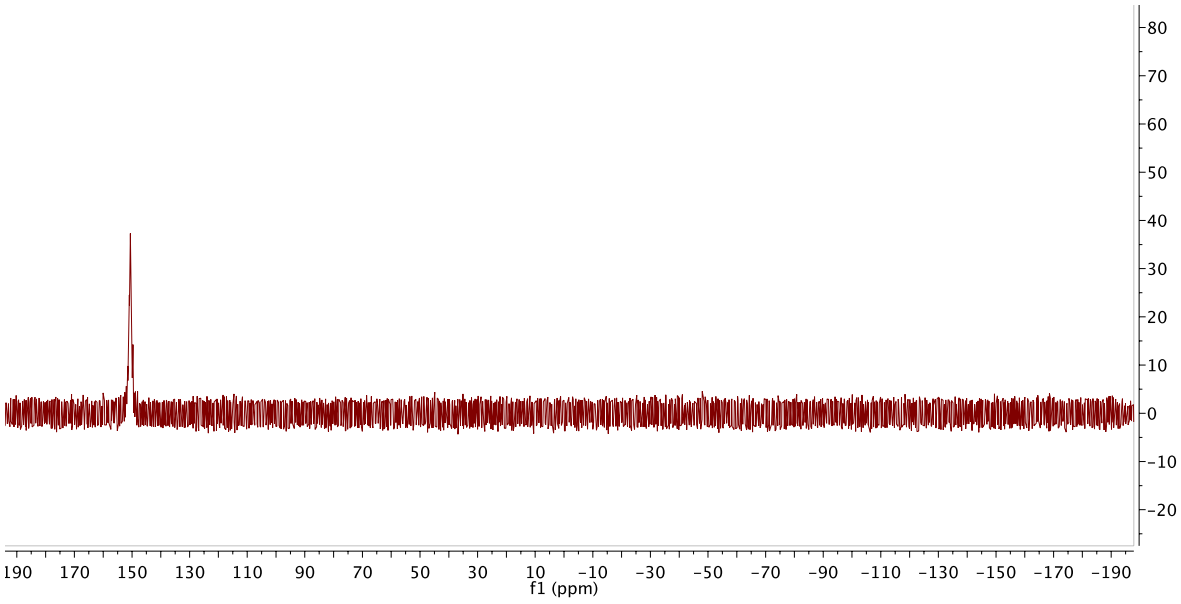
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)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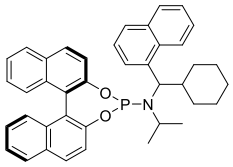
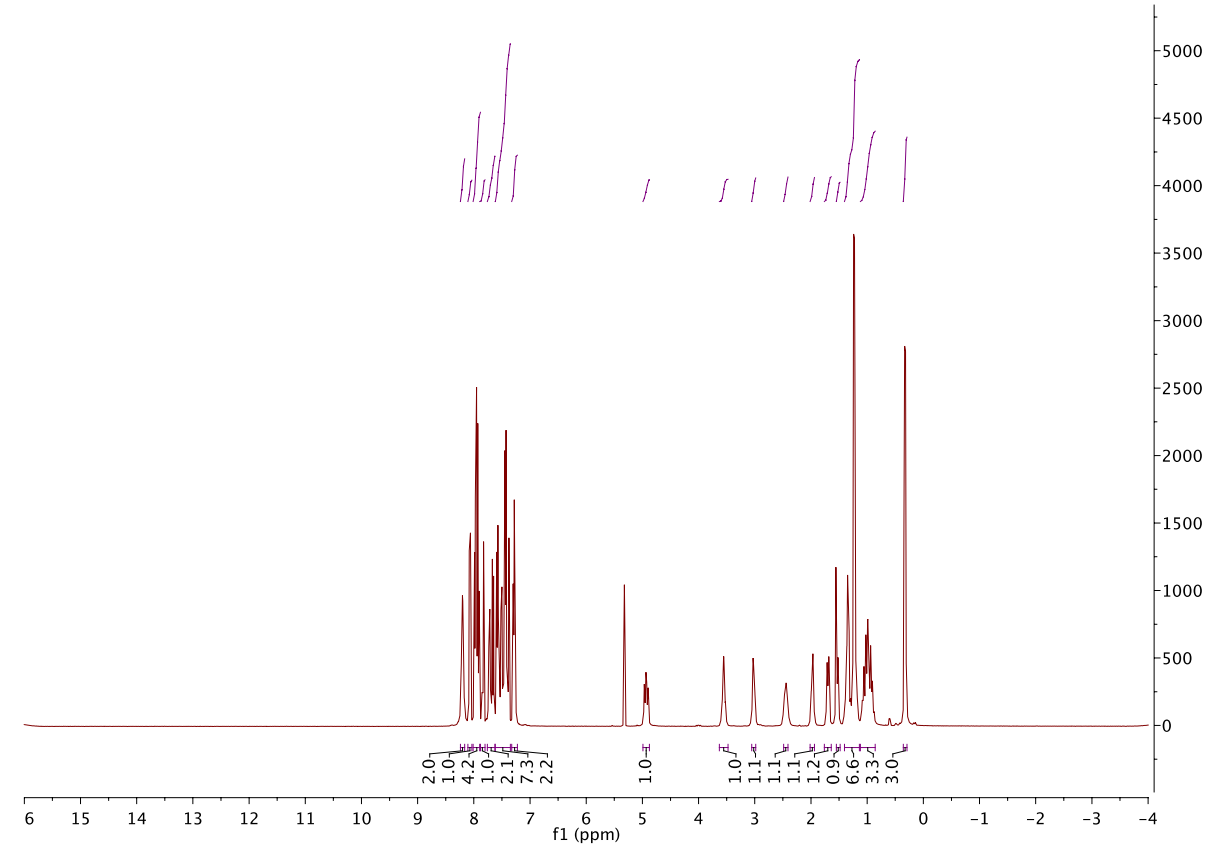
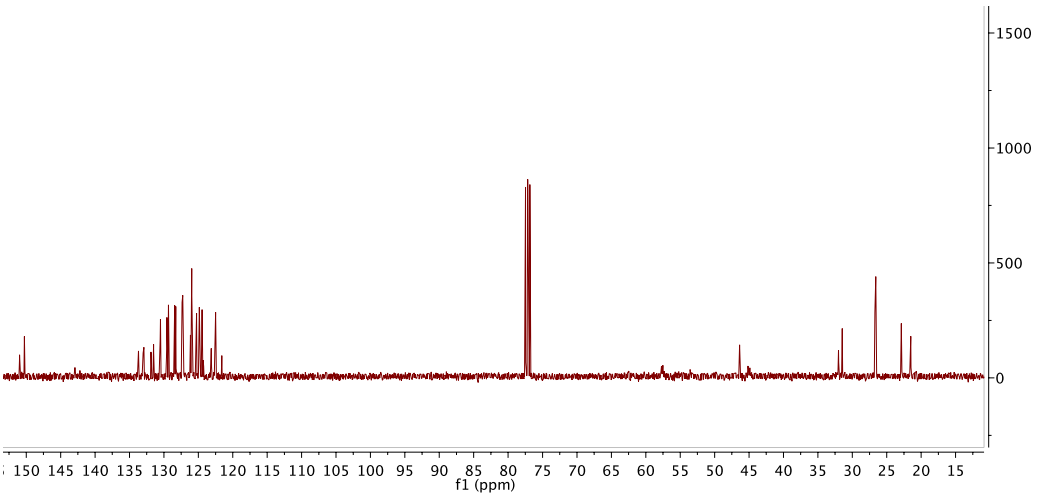
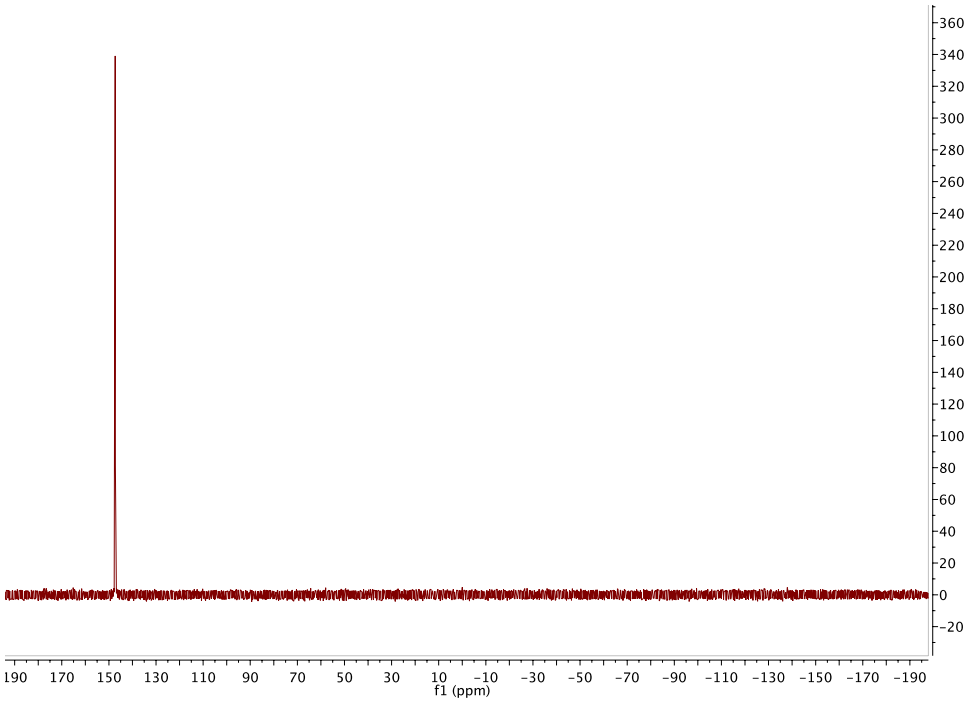
f1 (ppm)

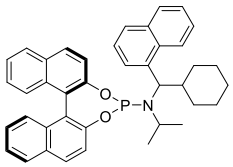


(*R*$_a$,*R or S*)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L31a**

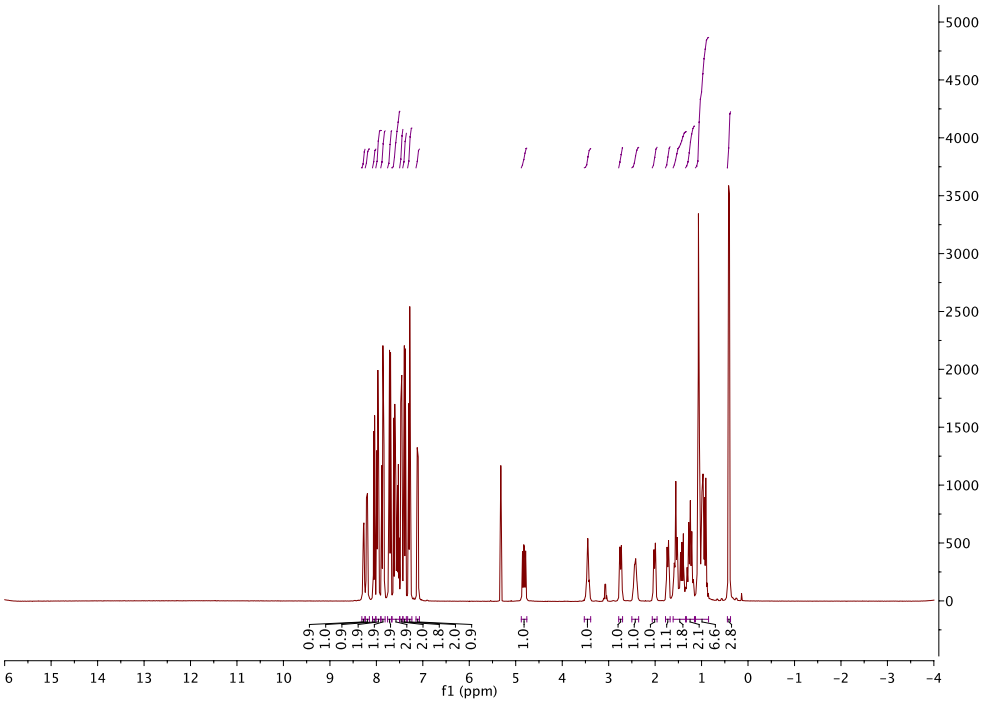


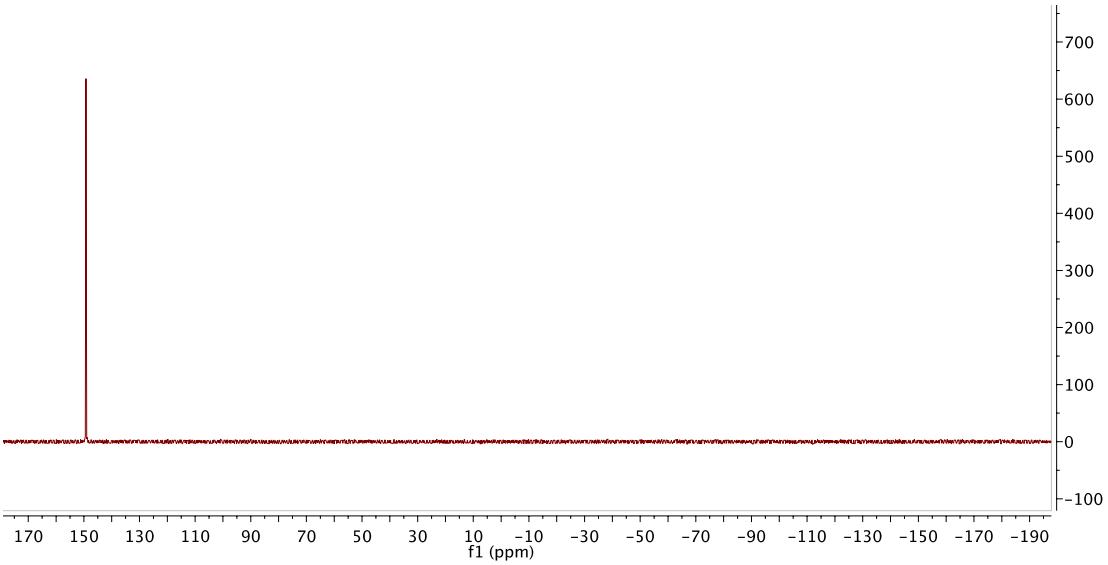






(R_a,*R or S*)-*N*-(cyclohexyl(naphthalen-1-yl)methyl)-*N*-isopropyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **L31b**

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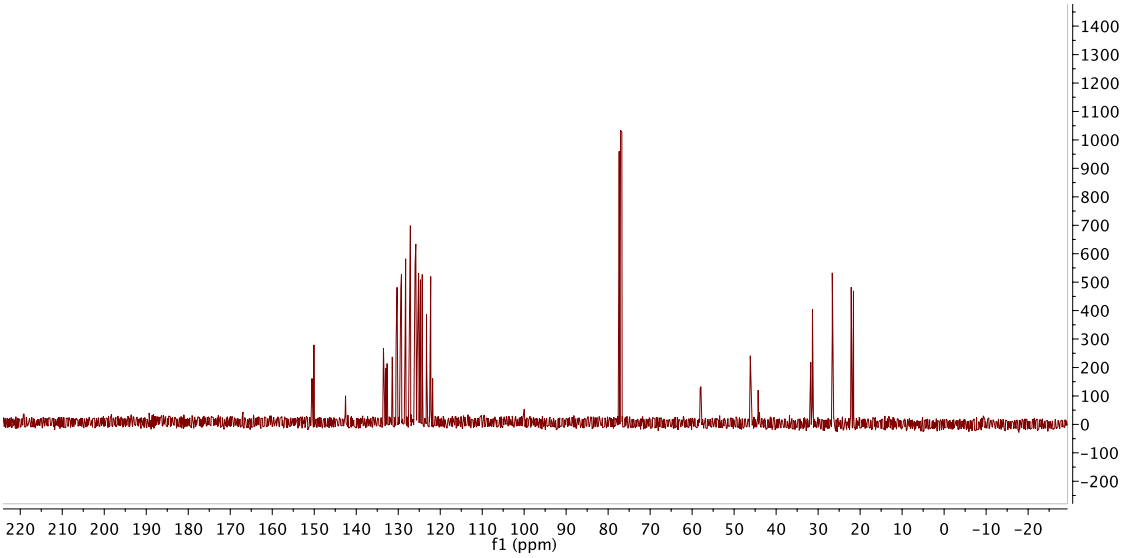
f1 (ppm)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f1 (ppm)

Computational section

Quantitative Structure – Selectivity Relationship (QSSR)

The quantitative relationship between the experimentally observed enantioselectivities of ACA and the chemical descriptors of the corresponding ligands were analysed in *R*-statistics package in the form of multiple linear least squares regression.[25] Ligand geometries were optimised with *Gaussian09*[26] at the SMD(CH_2Cl_2)-B97D/6-31G(d) level of theory, from which steric and quantum chemical electronic descriptors were obtained as described below.[27,28] For **Model I** (first generation ligands, n = 11), 28 chemical descriptors were computed based on optimised ligand structures or only aryl rings capped with a methyl group. For **Model II** (first and second generation ligands, n = 30), 12 relevant chemical descriptors based on aryl rings were computed. Each descriptor (x_i) was scaled to dimensionless values (x) using the equation below.

$$x = \frac{x_i - \bar{x}}{s}$$

Where $\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i$ (sample mean of x), N = number of data points,

$s = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2}$ (sample standard deviation of x).

Chemical descriptors considered in a selection process are:

1. HOMO energies of aryl substituents ($\mathbf{E_{HOMO}}$) were calculated at the B3LYP/6-31g(d) level of theory with a methyl group at the disconnection point from the rest of the ligand (**Figure S2**). For substituents that possess multiple stable conformations, their HOMO energies are reported as an averaged value weighed by their corresponding Boltzmann factors at 298 K.
2. The first and second generation Sterimol parameters: **L**, **B1**, **B2**, **B3**, **B4** and **B5**, were derived from *Molecular Modelling Pro Plus 7.0*[29] for the optimised structures of methyl capped aryl rings (B3LYP/6-31g(d), **Figure S2**) unless stated otherwise. Exponential term of B1 is also calculated ($\mathbf{e^{B1}}$).
3. Dihedral angles for P-N-C-C_{Ar} (**dih**), Gauge-Including Atomic Orbital (GIAO) magnetic shielding tensors of ^{31}P atoms (**NMR**) and atomic natural charges on P, N, α-C to N, *ipso*-C, *ortho*-C and *para*-C atoms (**P**, **N**, **aC**, **bC1**, **bC2**, **gC1**, and **gC2** respectively), were obtained by Gaussian 09[30] at B3LYP/6-31G(d,p) from optimised ligand structures (B97D/6-31G(d) with CH_2Cl_2-SMD solvation). Averaged charges of the two *ortho*-Cs and *para*-Cs are represented as **bCav** and **gCav** repectively.

4. QSAR descriptors obtained from Spartan 14[30] on optimised ligand structures (ωB97X-D/6-31G(d)): Molecular orbital energy (**MO**), Natural charges (**Nat**), and Mulliken charge (**Mul**) on Phosphorus, accessible area (**AccArea**), polar area (**Pol**), accessible polar area (**AccPol**), maximum and minimum ionisation potential (**MaxIE** and **MinIE**), local ionisation potential (**loc**) and polarisability (**pol**).

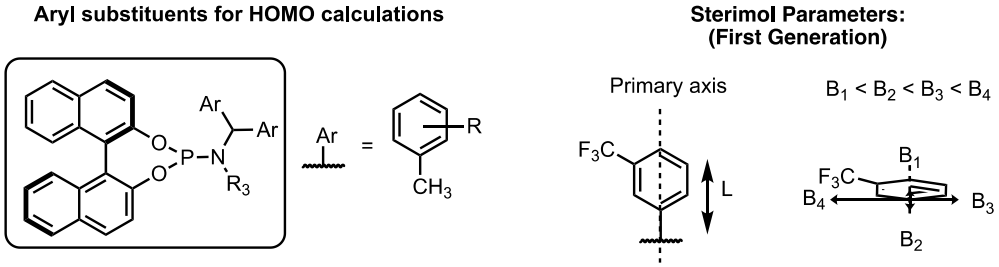

Figure.S2 Aryl substituents with methyl group instead of the rest of the ligand and Sterimol parameters L, B1, B2, B3 and B4.

Lig	dih	NMR	P	N	aC	bC1	bC2	bCav	gC1	gC2	gCav	MO	Nat	Mul	AccArea
L5	-1.458	-0.675	0.359	-2.183	-1.166	1.370	1.161	1.273	1.584	-0.468	0.118	-0.129	-0.277	-1.930	-1.236
L6	0.906	0.467	-0.205	-0.113	0.117	0.040	-0.038	0.002	-0.751	-0.483	-0.662	-2.451	-0.447	0.345	-1.225
L7	0.868	0.193	-0.205	0.301	0.544	-0.403	-0.403	-0.404	-0.650	-0.444	-0.596	-0.132	-0.362	0.453	-0.462
L8	0.851	0.173	0.077	0.301	0.758	0.582	0.744	0.663	-0.776	-0.512	-0.695	0.135	-0.277	0.561	0.165
L9	1.030	0.022	0.359	-0.113	0.972	0.927	0.796	0.866	-0.801	-0.516	-0.707	0.122	-0.277	1.211	2.263
L10	-1.196	-0.609	0.359	-0.113	-1.380	1.124	1.318	1.222	1.496	-0.502	0.060	1.190	-0.277	0.778	0.618
L11	0.837	0.706	-0.205	0.301	0.758	0.040	0.066	0.053	-0.387	-0.497	-0.554	-0.126	-0.447	0.453	1.141
L12	0.911	2.130	-0.205	-0.527	-0.097	0.434	0.275	0.358	-0.475	-0.416	-0.513	Nd	2.942	-0.630	-0.791
L13	-0.844	-0.259	-0.487	-0.113	0.972	-1.487	-1.498	-1.497	-0.512	-0.396	-0.509	1.208	-0.447	0.345	-0.110
L14	-0.840	0.038	-2.180	2.371	-2.021	-1.881	-2.019	-1.955	-0.500	2.237	1.759	0.183	-0.870	0.345	-0.515
L15	-1.065	-2.187	2.334	-0.113	0.544	-0.748	-0.403	-0.582	1.771	1.997	2.299	Nd	0.739	-1.930	0.153

Lig	Pol Area	Acc Pol Area	MaxIE	MinIE	Loc	Polz	L	B1	e^{B1}	B5	B3	B4	E_{HOMO}	ΔΔG
L5	-0.160	-0.068	-0.346	0.189	0.170	-1.162	-0.93	-0.46	-0.38	-1.22	-0.45	-1.22	-0.88	3.15
L6	-0.561	-0.492	-0.579	0.221	0.386	-1.014	-0.93	-0.46	-0.38	-1.22	-0.45	-1.22	-0.88	3.45
L7	-0.390	-0.401	-0.731	0.102	0.329	-0.044	0.35	-0.01	-0.17	-1.21	-0.50	-1.23	-0.20	3.01
L8	-0.334	-0.362	-0.734	0.153	0.322	-0.044	-0.72	-0.46	-0.38	0.11	1.28	0.13	-0.30	5.71
L9	-0.488	-0.860	-0.771	0.469	0.339	2.786	0.47	3.12	3.15	1.23	2.75	1.13	-0.20	1.02
L10	0.132	0.292	-0.683	-0.046	0.381	-0.531	-0.91	-0.46	-0.38	1.14	-0.40	1.22	1.00	5.56
L11	0.107	0.522	-0.175	0.079	0.396	0.351	1.74	-0.46	-0.38	-0.10	-0.35	-0.06	0.94	4.13
L12	-2.076	-1.858	1.553	2.157	-1.609	-0.131	-0.11	-0.27	-0.30	0.54	-0.45	0.59	-2.21	0.18
L13	1.754	1.973	2.068	-0.708	1.449	-0.360	1.90	-0.15	-0.24	-1.21	-0.48	-1.23	1.04	3.15
L14	1.606	1.412	1.096	-0.288	0.177	-0.308	-0.96	-0.36	-0.34	1.13	-0.44	1.21	0.85	4.67

L15	0.409	-0.158	-0.700	-2.327	-2.340	0.458	0.10	-0.03	-0.19	0.83	-0.50	0.65	0.83	4.02

Table S2. Experimental enantiomeric excess (ΔΔG in kJ/mol) and ligand descriptors (scaled to dimensionless values over 11 ligands) for the first generation ligands.

Lig	**ΔΔG**	**R1**	**R2**	**R1L**	**R1B1**	**R1B5**	**R1B3**	**R1B4**	**R2L**	**R2B1**	**R2B5**	**R2B3**	**R2B4**
L5	3.15	-0.62396	-0.60743	-0.67	-0.42	-1.7	-0.69	-1.68	-0.71	-0.43	-1.68	-0.69	-1.67
L6	3.45	-0.62396	-0.60743	-0.67	-0.42	-1.7	-0.69	-1.68	-0.71	-0.43	-1.68	-0.69	-1.67
L7	3.01	-0.14635	-0.12569	0.72	0.23	-1.69	-0.73	-1.69	0.67	0.22	-1.67	-0.73	-1.68
L8	5.71	-0.21826	-0.19822	-0.44	-0.42	-0.24	0.92	-0.24	-0.48	-0.43	-0.21	0.92	-0.21
L9	1.02	-0.14188	-0.12118	0.84	4.73	0.98	2.28	0.82	0.80	4.74	1.03	2.28	0.87
L10	5.56	0.70819	0.73625	-0.64	-0.42	0.88	-0.64	0.93	-0.69	-0.43	0.93	-0.64	0.98
L11	4.13	0.66356	0.69123	2.22	-0.42	-0.47	-0.59	-0.44	2.17	-0.43	-0.44	-0.59	-0.41
L12	0.18	-1.57372	-1.56541	0.22	-0.15	0.22	-0.69	0.25	0.18	-0.16	0.27	-0.69	0.29
L13	3.15	0.73646	0.76476	2.39	0.02	-1.69	-0.71	-1.69	2.35	0.01	-1.67	-0.71	-1.68
L14	4.67	0.60354	0.6307	-0.70	-0.28	0.87	-0.68	0.91	-0.74	-0.29	0.92	-0.68	0.97
L15	4.02	0.58811	0.61513	0.45	0.19	0.55	-0.73	0.32	0.41	0.18	0.59	-0.73	0.36
L22a	3.29	-0.62396	-0.19822	-0.67	-0.42	-1.70	-0.69	-1.68	-0.48	-0.43	-0.21	0.92	-0.21
L22b	4.75	-0.21826	-0.60743	-0.44	-0.42	-0.24	0.92	-0.24	-0.71	-0.43	-1.68	-0.69	-1.67
L23a	3.94	-0.62396	0.73625	-0.67	-0.42	-1.70	-0.69	-1.68	-0.69	-0.43	0.93	-0.64	0.98
L23b	4.22	0.70819	-0.60743	-0.64	-0.42	0.88	-0.64	0.93	-0.71	-0.43	-1.68	-0.69	-1.67
L24S	4.99	-0.21826	0.73625	-0.44	-0.42	-0.24	0.92	-0.24	-0.69	-0.43	0.93	-0.64	0.98
L24R	5.39	0.70819	-0.19822	-0.64	-0.42	0.88	-0.64	0.93	-0.48	-0.43	-0.21	0.92	-0.21
L25R	5.54	0.70819	0.07842	-0.64	-0.42	0.88	-0.64	0.93	0.67	-0.09	-0.22	-0.65	-0.20
L26S*	5.54	-0.24579	0.73625	-0.70	-0.15	0.61	1.76	0.43	-0.69	-0.43	0.93	-0.64	0.98
L26R*	6.05	0.70819	-0.22599	-0.64	-0.42	0.88	-0.64	0.93	-0.74	-0.16	0.65	1.76	0.48
L27a	4.86	0.9036	0.73625	0.42	0.57	0.78	1.26	0.82	-0.69	-0.43	0.93	-0.64	0.98
L27b	4.03	0.70819	0.93335	-0.64	-0.42	0.88	-0.64	0.93	0.38	0.56	0.82	1.26	0.87
L28S	2.3	-2.43421	0.73625	0.21	1.79	0.25	1.47	0.14	-0.69	-0.43	0.93	-0.64	0.98
L28R	4.63	0.70819	-2.43335	-0.64	-0.42	0.88	-0.64	0.93	0.16	1.78	0.29	1.47	0.18
L29a	5.25	-0.21826	1.48062	-0.44	-0.42	-0.24	0.92	-0.24	2.32	0.25	0.93	-0.63	0.97
L29b	6.45	1.44618	-0.19822	2.37	0.26	0.88	-0.63	0.91	-0.48	-0.43	-0.21	0.92	-0.21
L30S	6.83	-0.21826	0.79178	-0.44	-0.42	-0.24	0.92	-0.24	2.12	-0.43	0.93	2.14	0.98
L30R	6.68	0.76324	-0.19822	2.16	-0.42	0.88	2.14	0.93	-0.48	-0.43	-0.21	0.92	-0.21
L31a	1.56	0.70819	-3.24726	-0.64	-0.42	0.88	-0.64	0.93	-0.66	0.69	-1.16	-0.88	-1.14
L31b	0.87	-3.24114	0.73625	-0.61	0.70	-1.18	-0.88	-1.16	-0.69	-0.43	0.93	-0.64	0.98

Table S3. Experimental enantiomeric excess (ΔΔG in kJ/mol) and ligand descriptors (scaled to dimensionless values over 30 ligands) for the first and second generations ligands. *Conformation of diethyl aryl that is 0.009 kJ/mol higher than the most stable conformation was used to extract Sterimol parameter.

Priority assignment of R^i groups in the diastereomeric ligands

For ligands where aryls are identical (R1 = R2, **L5** – **L15**), each electronic and steric descriptor for R1 and R2 are the same. When aryls are not identical (R1 ≠ R2, **L22** – **L31**), we have to assign one of the aryl substituents as R1 and the other as R2, each with a different set of descriptors specific to the identity of the aryls. From the DFT calculations of the stereodetermining carbocupration TSs (see later under Density functional theory (DFT) calculations), the lowest energy **TS-1** places the black aryl ring next to copper metal and the blue aryl ring away from the metal and the enone (Figure S3). With this information, we assigned R1 as the aryl that is next to the copper in the conformation shown in **TS-1** (black aryl ring, Figure S3). Consequently, this means that R2 is the blue ring, pointing away from the metal. In doing this we assume that such TS conformation is the most favoured in energy regardless of the structure of the ligands. Considering that the structure of each ligand differs only on the aryl moiety, we anticipate that this underlying assumption holds for all ligands examined.

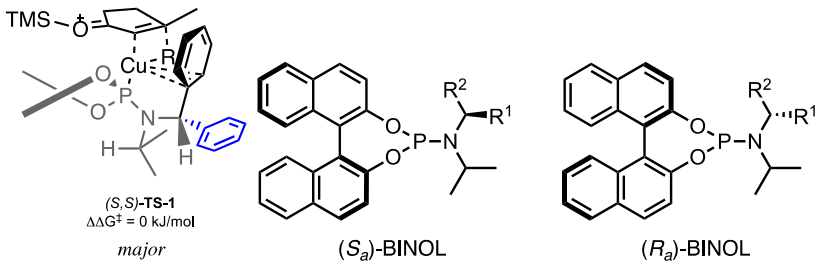

Figure S3. The lowest energy TS: **TS-1** with ligand **L6** and the represention of Ar^1 with (R_a)- and (S_a)-BINOL.

(R_a)-BINOL was employed for all the diastereomeric ligands synthesised in this paper. Where X-ray crystal structures of ligands can be obtained, assignment was done according to the representation shown in Figure S3 (structure on the RHS with (R_a)-BINOL). X-ray structures of **L24R**, **L25R**, **L30, L26S-amine** and **L28S-amine** can be founded in a separate supporting document.

In most cases, however, the X-ray structures were not available. We assigned aryl rings as R1 and R2 based on the experimental enantiomeric excess of the subsequent conjugate addition products. Comparing % *ee* of the ACA product induced by a pair of diastereomeric ligands, we assume ligand that induces higher % *ee* is where the aryl close to metal (black ring) has higher HOMO energy, which is then assigned as R1. This assumption is based on the information from **Model I** where HOMO give a positive correlation with the % *ee*.

Construction of regression models

Next is to select parameters to be included in a model using data from **Table S2**. This was done using an automated stepwise forward regression incorporated in *R* to obtain a starting model (**Model I-0**). The parameters were excluded from this model until the resultant correlation has a good fit (R^2 ≈ 1) with least parameter used (**Model I-1 = Model I** showed in **Figure 1**, manuscript). Further exclusion of parameters (**Model I-2**, Figure S4 and **Model I-3**) resulted in a reduction in R^2 to 0.86 and 0.76 respectively. Leave-one-out cross-validation (LOOCV) was carried out for **Model I** giving the cross-validated correlation coefficient (q^2) of 0.87, higher than recommended value of 0.5.[31] Models with cross-terms were also explored but the resultant models contain parameters which are not statistically significant, therefore those models were discarded.

Stepwise forward regression:

```
null=lm(ddG~1)
full=lm(ddG ~ dih + NMR + P + N + aC + bC1 + bC2 + bCav + gC1 + gC2 + gCav + MO + Nat + Mul
        + AccArea + MinIE + Loc + PolArea + AccPolArea + MaxIE + Polz + L + B1 + eB1 + B5 + B3
+ B4 + R1)

step(null, scope=list(lower=null, upper=full), direction="forward")

Step:  AIC=-Inf
```

Model I-0: ddG ~ R1 + L + B1 + B3 + gC2 + MaxEI + eB1 + bC2 + P + dih

Multiple Linear least squared regression of Model I-1:

Model I-1 <- lm(ddG ~ R1 + L + B1 + B3)

Coefficients:	**Estimate**	**Std. Error**	**t value**	**Pr(>|t|)**	
(Intercept)	3.3908	0.1599	21.205	7.17E-07	***
R1	1.2206	0.1724	7.078	0.0004	***
L	-0.5441	0.1822	-2.986	0.0244	*
B1	-1.72	0.3043	-5.652	0.0013	**
B3	1.3033	0.2969	4.39	0.0046	**

Signif. codes: 0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

Residual standard error: 0.5303 on 6 degrees of freedom
Multiple R-squared: 0.942,   Adjusted R-squared: 0.9033
F-statistic: 24.34 on 4 and 6 DF, p-value: 0.0007484

Multiple Linear least squared regression of Model I-2:

Model I-2 <- lm(ddG ~ R1 + B1 + B3)

Coefficients:	Estimate	Std. Error	t value	Pr(>|t|)	
(Intercept)	3.3908	0.2334	14.526	1.75E-06	***
R1	1.036	0.235	4.408	0.0031	**
B1	-2.0283	0.4179	-4.854	0.0019	**
B3	1.5267	0.4194	3.64	0.0083	**

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.7742 on 7 degrees of freedom
Multiple R-squared: 0.8557, Adjusted R-squared: 0.7938
F-statistic: 13.83 on 3 and 7 DF, p-value: 0.002505

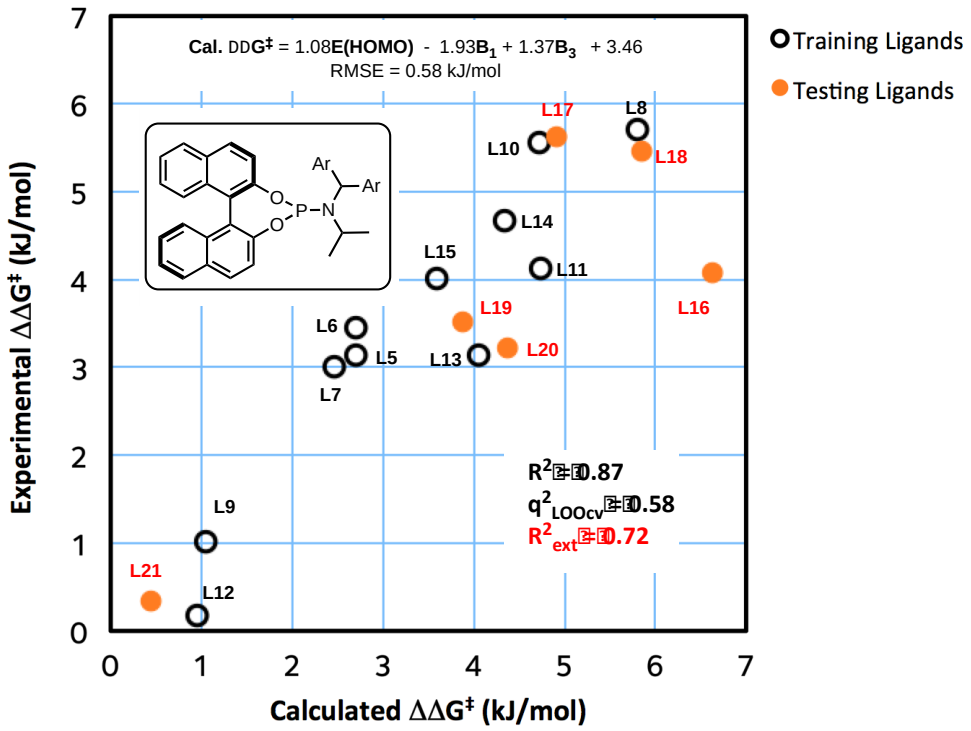

Figure S4. Model I-1

Multiple Linear least squared regression of Model I-3:

Model I-3 <- lm(ddG ~ R1 + L + B1)

Coefficients:	**Estimate**	**Std. Error**	**t value**	**Pr(>|t|)**	
(Intercept)	3.3908	0.3038	11.16	1.03E-05	***
R1	1.2153	0.3276	3.709	0.00756	**
L	-0.7456	0.335	-2.226	0.06136	.
B1	-0.5974	0.3135	-1.906	0.09838	.

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 1.008 on 7 degrees of freedom
Multiple R-squared: 0.7555, Adjusted R-squared: 0.6507
F-statistic: 7.21 on 3 and 7 DF, p-value: 0.01514

Selection of parameters for the combined training ligands (n = 30) was carried out in the same way using data from Table S3. The starting model (**Model II-0**) was derived by forward selection. Based on this, three models with good fit are listed: **Model II-1** with R^2 = 0.85 (Figure S5), **Model II-2** with R^2 = 0.83 (**Figure 1**, **manuscript**) and **Model II-3** with R^2 = 0.75 (Figure S6). The fit of **Model II-2** only slightly increases compared to **Model II-1** when including one more parameter. To help selecting the best model, Leave-one-out cross-validation (LOOCV) was carried out giving the cross-validated correlation coefficient (q^2) of 0.71, 0.66 and 0.65 for **Model II-1,II-2** and **II-3** respectively. Balancing the fit with the number of parameters used, q^2 and its significance (see later under Analysis of variance), we selected model **Model II-2** as the best model (shown as **Model II** in **Figure 3**, manuscript). Once again non-linear models containing cross-terms were discarded on the ground of significance.

Stepwise forward regression:

null=lm(ddG~1)
full=lm(ddG ~ R1 + R2 + R1L + R1B1+ R1B5 + R1B3 + R1B4 + R2L + R2B1 + R2B5 + R2B3 + R2B4)
step(null, scope=list(lower=null, upper=full), direction="forward")

Step: AIC=-13.14
ddG ~ R1 + R2B1 + R2B3 + R1B3 + R1L + R2 + R1B1

Multiple Linear least squared regression of Model II-1:

Model II-1 <- lm(ddG ~ R1 + R2B3 + R1B3 + R2 + R1B1 +R2L)

Coefficients:	**Estimate**	**Std. Error**	**t value**	**Pr(>|t|)**	
(Intercept)	4.1723	0.1365	30.576	< 2e-16	***
R1	0.7929	0.1509	5.253	2.50E-05	***
R2B3	0.5499	0.1525	3.607	0.001485	**
R1B3	0.6147	0.1605	3.829	0.000859	***
R2	0.6952	0.1509	4.607	0.000124	***
R1B1	-1.0622	0.1641	-6.473	1.32E-06	***

R2L	-0.297	0.1475	-2.013	0.055949	.

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.7474 on 23 degrees of freedom
Multiple R-squared: 0.8517, Adjusted R-squared: 0.813
F-statistic: 22.01 on 6 and 23 DF, p-value: 1.852e-08

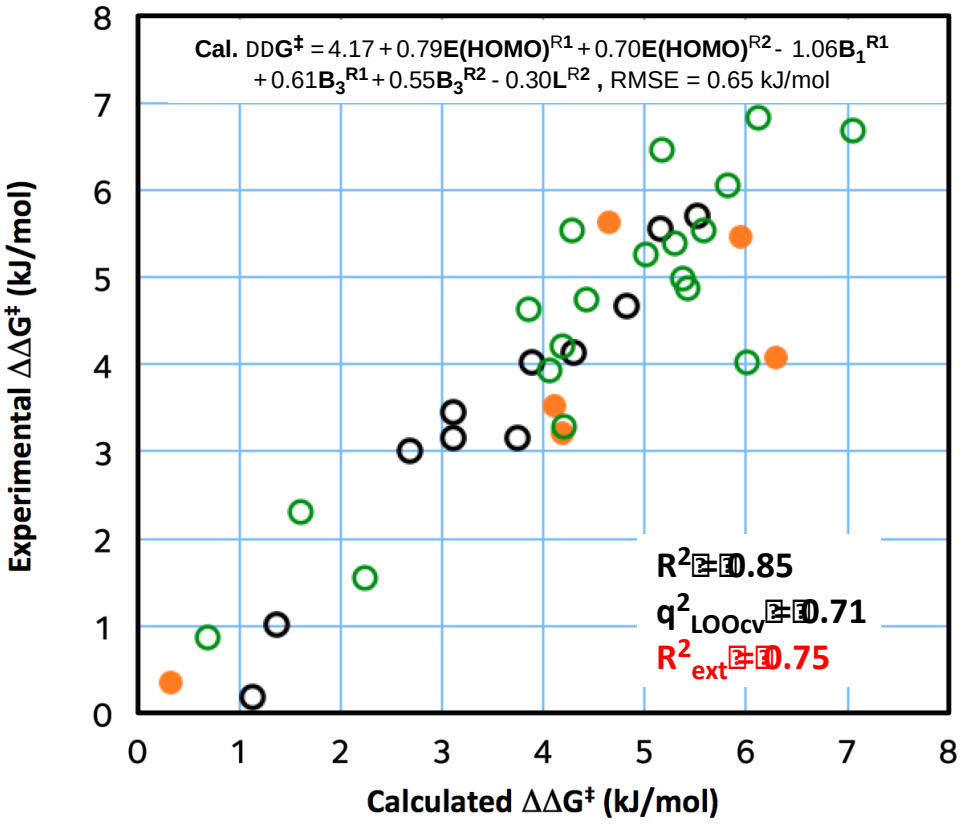

Figure S5. Model II-1

Multiple Linear least squared regression of Model II-2:

Model II-2 <- lm(ddG ~ R1 + R2B3 + R1B3 + R2 + R1B1)

Coefficients:	Estimate	Std. Error	t value	Pr(>|t|)	
(Intercept)	4.172	0.1449	28.797	< 2e-16	***
R1	0.7404	0.1578	4.691	9.12E-05	***
R2B3	0.5136	0.1607	3.196	0.003881	**
R1B3	0.6497	0.1694	3.835	0.000798	***
R2	0.5946	0.1512	3.933	0.000624	***
R1B1	-1.095	0.1734	-6.317	1.57E-06	***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.7935 on 24 degrees of freedom
Multiple R-squared: 0.8255, Adjusted R-squared: 0.7892
F-statistic: 22.71 on 5 and 24 DF, p-value: 2.214e-08

Multiple Linear least squared regression of Model II-3:

Model II-3 <- lm(ddG ~ R1 + R1B3 + R2 + R1B1)
Call:
lm(formula = ddG ~ R1 + R1B3 + R2 + R1B1, data = all)

Coefficients:	Estimate	Std. Error	t value	Pr(>|t|)	
(Intercept)	4.172	0.1695	24.617	< 2e-16	***
R1	0.8911	0.1762	5.057	3.22E-05	***
R1B3	0.7411	0.1953	3.794	0.000839	***
R2	0.5307	0.1753	3.027	0.005655	**
R1B1	-0.9566	0.1964	-4.872	5.20E-05	***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.9283 on 25 degrees of freedom
Multiple R-squared: 0.7513, Adjusted R-squared: 0.7115
F-statistic: 18.88 on 4 and 25 DF, p-value: 2.899e-07

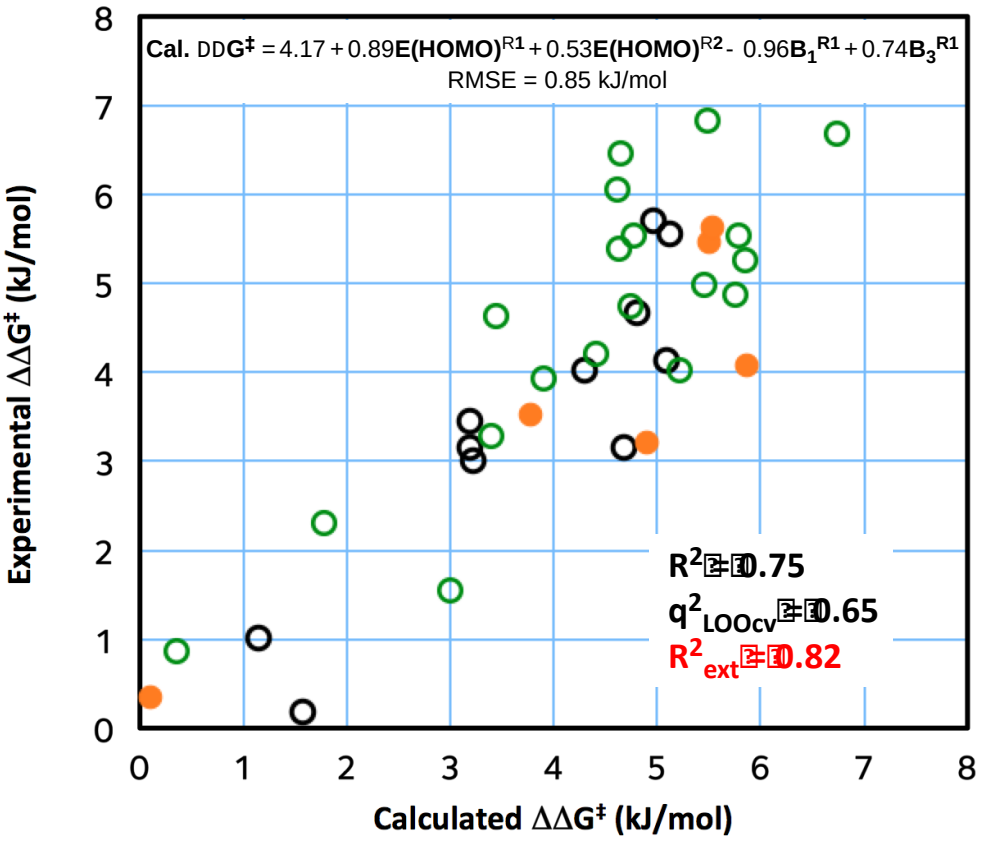

Figure S6. Model II-3

Analysis of variance

Once the models with best fits are identified, the significance of each parameter was tested by analysis of variance (ANOVA) which is an algorithm implemented in *R* statistical package. A parameter is significant at 5% level of confidence if its F value is higher than the critical value for the given degree of freedom. For **Model I**, all parameters are significant within 5% level of confidence.

Analysis of Variance Table of Model I:

Degree of freedom: 6, Critical value (P = 0.05)= **5.9874**.

	F value	Pr(>F)
R1	72.257	0.0001451 ***
L	48.808	0.0004280 ***
B1	25.652	0.0022997 **
B3	25.382	0.0023614 **

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

For **Model II-1**, 4 out of 6 parameters are significant within 5% level of confidence. $\mathbf{L^{R2}}$ and $\mathbf{B_3^{R2}}$ lie in the borderline. For **Model II-2**, 5 out of 6 parameters are significant within 5% level of

confidence. Only B_3^{R2} lies in the borderline. For **Model II-3**, all parameters are significant within 5% level of confidence.

Analysis of Variance Table of Model II-1:

Degree of freedom: 23, Critical value (P = 0.05)= **4.2793**.

	F value	Pr(>F)
R1	53.5720	1.905e-07 ***
R2B3	4.1899	0.0522588 .
R1B3	7.7430	0.0105838 *
R2	17.5405	0.0003523 ***
R1B1	44.9750	7.681e-07 ***
R2L	4.0527	0.0559493 .

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Analysis of Variance Table of Model II-2:

Degree of freedom: 24, Critical value (P = 0.05) = **4.2597**.

	F value	Pr(>F)
R1	47.5268	3.953e-07 ***
R2B3	3.7171	0.0657724 .
R1B3	6.8693	0.0149777 *
R2	15.5612	0.0006058 ***
R1B1	39.9000	1.572e-06 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Analysis of Variance Table of Model II-3:

Degree of freedom: 25, Critical value (P = 0.05) = **4.2417**.

	F value	Pr(>F)
R1	34.7293	3.779e-06 ***
R1B3	6.7852	0.015256 *
R2	10.2816	0.003657 **
R1B1	23.7336	5.195e-05 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Density functional theory (DFT) calculations

Transition structures (TS) were optimised with *Gaussian09*.[26] Geometry optimisations were carried out with B97D functional and the 6-31G(d) basis set for C, H, N, O, P, Si atoms and the LANL2DZ effective core potential/valence double zeta basis set for Cu.[28] Single point energy corrections were obtained at the B97D/def2-TZVPP level of theory with dichloromethane solvation described by an implicit Solvation Model based on Density (SMD).[27,32] All the transition structures possess a single imaginary harmonic vibrational frequency. The enantiomeric excess was calculated at 273 K from the Boltzmann ensemble of all competing transition structures.[33] Graphics were generated by Pymol.[34] Non-covalent interaction index (NCI) was computed from the promolecular density (molecular density calculated from the sum

of atomic density) using NCIPLOT, treating the ligand separately from the rest of the transition state complex.[35] All energetic terms were reported in kJ/mol.

Transition States	ΔΔG (kJ/mol)	Product	Boltzmann factor (273 K)
***(S,S)*-TS-1**	0.00	*(-)*-**3**	1.00
***(S,R)*-TS-2**	2.2(1)	*(+)*-**3**	0.38
***(S,S)*-TS-3**	2.8(8)	*(-)*-**3**	0.28
***(S,S)*-TS-4**	2.9(4)	*(-)*-**3**	0.27
***(S,R)*-TS-5**	7.0(4)	*(+)*-**3**	0.05
***(S,S)*-TS-6**	7.6(4)	*(-)*-**3**	0.03
***(S,R)*-TS-7**	10.2(5)	*(+)*-**3**	0.01
***(S,R)*-TS-8**	11.8(2)	*(+)*-**3**	0.01

Table S4. Transition states and their relative Gibbs Free energy with L6 (S_o-Binol).

The total of 8 relevant TSs of the stereodetermining carbocupration step were calculated. In these structures, the excess Lewis acid activates the carbonyl for conjugate addition through trimethylsilylation of the oxygen atom. This precludes the involvement of higher-order oligomeric Cu-phosphoramidite species in this step, anticipated in the absence of TMSCl.[36] The involvement of a Cu-phosphoramidite complex is consistent with our experimental studies showing the absence of non-linear effects for scalemic ligand mixtures.[6] This step is irreversible, consistent with it being the enantiodetermining step.

The TSs energies and their corresponding Boltzmann factors are tabulated in Table S4. The key bond distances **(Å)** in the two lowest energy TSs; **TS-1** (lead to major enantiomer of product) and **TS-2** (lead to the minor enantiomer of product) are shown in red in Figure S7. The distances (Å) between copper and the *ipso*- and *ortho*-carbon are shown in grey. These distances show closer proximity of the copper and one other aryl ring in (*S*,*S*)-**TS**s compared to those in (*S*,*R*)-**TS**s. The averaged Cu-C distance in (*S*,*S*)-**TS-1** is 3.00 Å, which is 0.39 Å shorter than (*S*,*R*)-**TS-2** (3.39 Å). In all four of the (*S*,*S*)-**TS** structures, the Cu-C distances are closer than the sum of the two van der Waals radii of each element (vdW radii: C 1.70 Å , Cu 1.40 Å).

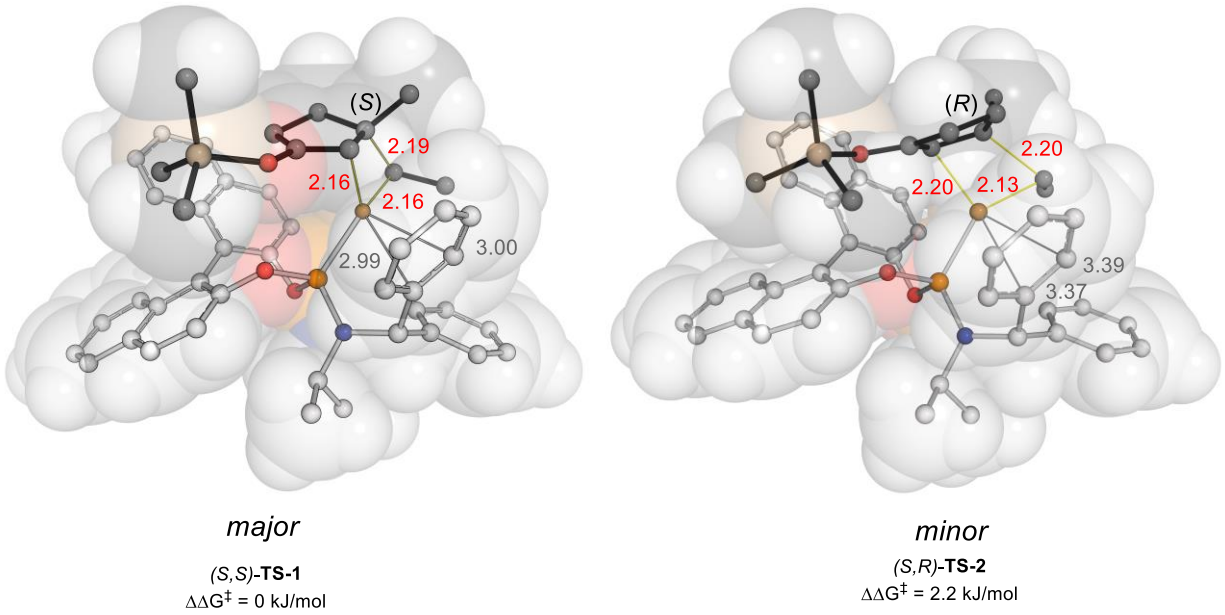

Figure S7. Transition states (*S*,*S*)-**TS-1** and (*S*,*R*)-**TS-2** and the key distances (Å).

To quantitatively probe the Cu-C interaction, a non-covalent interaction isosurface (NCI plot) of the lowest energy TS (**TS-1**) was carried out. The plot highlights the strongest favourable interaction between Cu and P atom as purple area and the weaker interaction between Cu-C as blue area. We previously reported quantitative analysis of this type of interaction in a related system.[6]

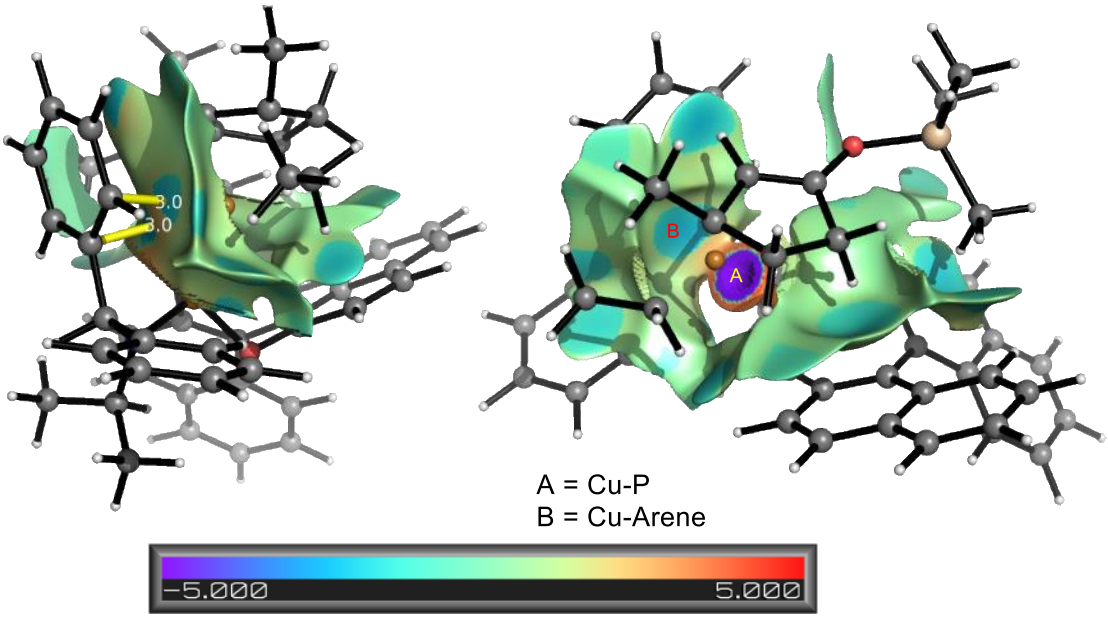

Figure S8. NCI index of the lowest energy transition state (*S*,*S*)-**TS-1.**

Cartesian Coordinates

All TS geometry were optimised at B97D/6-31G(d) and LANL2DZ(ecp) for Cu.

(*S*,*S*)-TS-1

Cu	-1.75715900	1.04968800	0.50436000
C	-2.43335900	1.86758600	2.38365800
C	-1.60499700	3.22065000	0.87783300
C	-0.20739100	3.50929500	1.48960700
C	0.83594300	2.95850500	0.47909800
C	-1.33017000	2.89311800	-0.54584700
H	-0.10303700	4.60454500	1.56762400
H	-0.07158400	3.09057100	2.49487500
H	1.68775200	3.64153000	0.34321900
H	1.25301300	1.98489400	0.78601500
H	-2.08656700	2.88954300	-1.32984700
C	0.02506100	2.80308100	-0.79475800
O	0.53135400	2.59785400	-2.00012400
C	-3.94136700	1.62173700	2.38325300
H	-4.19689100	0.63994600	1.96162300
H	-4.32629700	1.64651800	3.41934700
H	-4.48567400	2.39527200	1.82060300
O	0.59559400	-0.48720200	-1.00578000
P	-0.71822100	-0.84678500	-0.03314200
O	0.04805200	-1.66950500	1.21484700
C	2.59424400	-1.35730000	0.07320500
C	1.76062500	-1.26378700	-1.04496500
C	0.96749100	-0.84246000	1.88107800
C	2.23324100	-0.64303200	1.32861600
C	2.67918400	0.93272300	3.21020500
C	3.11414900	0.29269900	1.98700700
C	1.39781900	0.62352900	3.75205400
C	0.54620400	-0.24376300	3.09281200
H	1.09571400	1.08743300	4.69327000
C	3.77372000	-2.18208600	-0.03248300
C	3.25268200	-2.57249600	-2.42543800
C	2.08344700	-1.84614500	-2.29510300
H	3.52174100	-3.01659900	-3.38586900
C	4.11182500	-2.77540100	-1.30707100
C	3.53598900	1.87529200	3.85150100
C	4.38805200	0.65578900	1.45670600
C	5.19268400	1.58318400	2.10102800
H	6.16136900	1.84488200	1.67176800
C	4.77021000	2.19639300	3.31148800
H	5.41767600	2.91922300	3.81036200
C	4.61144400	-2.46908600	1.08606700
C	5.28744500	-3.57440000	-1.41832100
C	6.09244700	-3.81072000	-0.31624600
H	6.98710600	-4.42802600	-0.41084100
C	5.74088000	-3.26147700	0.94637500
H	6.36238300	-3.47109400	1.81861300
H	3.19552300	2.34077200	4.77913000
H	4.72314300	0.20030300	0.52828900
H	4.35115200	-2.06294000	2.06199200
H	5.53248100	-4.00723000	-2.39069800
H	1.40312400	-1.69697600	-3.13296000
H	-0.43549300	-0.50091100	3.49028400
N	-1.62038200	-2.05103500	-0.73262000
C	-3.07473100	-1.82077000	-0.94103500
H	-3.36384200	-2.54196300	-1.72097600
C	-1.05567000	-3.40447400	-1.03550600
H	-0.00135600	-3.36548400	-0.72804600
C	-3.34325700	-0.42983800	-1.55506900

C	-4.27915400	0.47385400	-1.01047700
C	-2.67428100	-0.07806900	-2.74760800
C	-4.55454000	1.69254600	-1.65852900
H	-4.82304600	0.20763000	-0.10635200
C	-2.95131800	1.13252000	-3.39291200
H	-1.93773200	-0.76631400	-3.16494800
C	-3.90241600	2.01998200	-2.85550100
H	-5.29489100	2.37183000	-1.23180500
H	-2.43177600	1.38304800	-4.31930600
H	-4.12834500	2.95736000	-3.36671900
C	-3.94300400	-2.12506400	0.28051500
C	-5.27604700	-2.52082600	0.05762500
C	-3.49482400	-1.96760200	1.60258400
C	-6.14818700	-2.74608300	1.13184300
H	-5.63229800	-2.64571300	-0.96828600
C	-4.36418400	-2.19755600	2.68204000
H	-2.46070600	-1.69415700	1.80603000
C	-5.69331900	-2.58232100	2.45134800
H	-7.17717900	-3.05504100	0.94010200
H	-3.99707700	-2.08149400	3.70370300
H	-6.36641800	-2.76429000	3.29069900
C	-1.09834300	-3.68966000	-2.54571400
H	-0.58220800	-4.63967400	-2.75234100
H	-2.13184200	-3.78737300	-2.91425100
H	-0.59624600	-2.88925900	-3.10847500
C	-1.75512500	-4.49703200	-0.21239800
H	-1.68414600	-4.27710900	0.86164500
H	-2.81948200	-4.57545200	-0.48140400
H	-1.27675700	-5.46810100	-0.41319000
Si	2.14634200	2.73018500	-2.62892000
C	2.04558300	1.73364600	-4.22587300
H	1.22665100	2.08877900	-4.87226400
H	2.98588400	1.81441400	-4.79671800
H	1.87568100	0.66707400	-4.00618400
C	2.45081300	4.57244000	-2.92012200
H	2.42323800	5.14237400	-1.97582900
H	3.44271600	4.73519500	-3.37517500
H	1.69587600	5.00370700	-3.59763400
C	3.40888800	1.99151400	-1.43854400
H	3.13403200	0.96960600	-1.14244500
H	4.38836300	1.93594100	-1.94538000
H	3.54604600	2.58213100	-0.52101600
C	-2.69004200	4.26925000	1.05792800
H	-2.34987200	5.19542700	0.56328600
H	-2.89720300	4.49738200	2.11336700
H	-3.62564100	3.95683300	0.57196700
H	-2.15532400	2.69920100	3.03314900
H	-1.85296800	1.00082300	2.74464600

(*R*,*S*)-TS-2

Cu	-1.48696900	-1.15305900	-0.49410500
C	-3.04560300	-2.41216900	-1.21010100
C	-1.19592000	-3.33392700	-0.44630800
C	-1.56053400	-3.70721800	1.01708500
C	-0.57028000	-2.92112100	1.92429500
C	0.11764000	-2.65046700	-0.35490800
H	-2.60816300	-3.49417800	1.26620800
H	-1.40061900	-4.79116400	1.13825700
H	-1.04378800	-2.03813400	2.38653200
H	-0.16967100	-3.53906600	2.74267200
H	0.76286200	-2.46167000	-1.21014300
C	0.51693100	-2.48860800	0.95467900
O	1.70434100	-2.00963700	1.29823400
C	-3.09773100	-2.24233800	-2.72572000

H	-4.14660600	-2.28038200	-3.07099100
H	-2.68745400	-1.27119700	-3.04259800
H	-2.54845300	-3.03448000	-3.25298700
O	0.45580900	0.90911900	0.87506400
P	-0.81743200	0.94644000	-0.21076400
O	-0.05881200	1.50463000	-1.58997900
C	2.49404300	1.34077100	-0.38594700
C	1.66778800	1.58426000	0.71440500
C	0.83758400	0.52258200	-2.05985900
C	2.08100500	0.37874700	-1.44494300
C	2.46509900	-1.57222100	-2.95296200
C	2.90423900	-0.73069600	-1.86100200
C	1.21341800	-1.31275000	-3.58440300
C	0.39360000	-0.29634700	-3.12738200
H	0.90008100	-1.94307700	-4.41907600
C	3.73216600	2.07980300	-0.47398600
C	3.26079100	3.08699500	1.74204200
C	2.04061800	2.43915300	1.78132900
H	3.56846900	3.73426500	2.56568400
C	4.12555100	2.94011900	0.61979500
C	3.27553300	-2.67495300	-3.35640000
C	4.12163800	-1.06732300	-1.19954500
C	4.87757300	-2.15534100	-1.60679500
H	5.80382400	-2.39522300	-1.08149000
C	4.46048200	-2.96260200	-2.70002400
H	5.07113300	-3.81030000	-3.01471600
C	4.58276800	2.02152300	-1.61839200
C	5.36105200	3.64812300	0.54812100
C	6.17571400	3.54393500	-0.56680500
H	7.11712900	4.09339400	-0.61411400
C	5.77211500	2.73309100	-1.66163000
H	6.40140800	2.67449200	-2.55133100
H	2.93606000	-3.29305900	-4.19050600
H	4.44986200	-0.46125800	-0.35897700
H	4.28605100	1.41375300	-2.47101100
H	5.64450900	4.28555300	1.38847300
H	1.36135400	2.54897200	2.62628200
H	-0.57639900	-0.09010200	-3.58036200
N	-1.82793500	2.20888600	0.15583300
C	-3.21000600	1.90552700	0.61355900
H	-3.53364100	2.81043900	1.15087800
C	-1.39389300	3.63963500	0.07120700
H	-0.38857400	3.62422400	-0.37238600
C	-3.21053100	0.77631700	1.66681900
C	-4.04657000	-0.35114900	1.57650000
C	-2.37590600	0.91267200	2.79646400
C	-4.03367300	-1.33393400	2.58102600
H	-4.73012900	-0.44736200	0.73391800
C	-2.37085800	-0.05829000	3.80520400
H	-1.72579900	1.78479400	2.87258300
C	-3.19656500	-1.19226800	3.69782700
H	-4.69410500	-2.19911200	2.49598600
H	-1.72529000	0.06953300	4.67501500
H	-3.19607900	-1.94876500	4.48462500
C	-4.21050900	1.68994300	-0.52269000
C	-5.57162200	1.93481000	-0.25539800
C	-3.84579800	1.20489600	-1.78929200
C	-6.55045200	1.68769000	-1.22809900
H	-5.86351900	2.31225100	0.72803000
C	-4.82269700	0.95913300	-2.76805700
H	-2.79621100	1.04337300	-2.03153600
C	-6.17740400	1.19446700	-2.48997100
H	-7.60010900	1.88589700	-1.00458000
H	-4.52124600	0.59145100	-3.75055300
H	-6.93533100	1.00780200	-3.25248600
C	-1.28958500	4.27095800	1.46944600

H	-0.91673000	5.30285400	1.38021600
H	-2.26926400	4.31261300	1.97127300
H	-0.59105300	3.70164500	2.09976300
C	-2.32142300	4.42864500	-0.86567000
H	-2.35696100	3.96061900	-1.85936200
H	-3.34603800	4.47146500	-0.46532500
H	-1.94978900	5.45990600	-0.96627100
Si	2.39354500	-1.72089700	2.86620200
C	3.95816000	-0.74545200	2.48407400
H	3.72977300	0.20922400	1.98747200
H	4.50727400	-0.52239300	3.41454100
H	4.62791200	-1.32545600	1.82939500
C	1.14879600	-0.73579900	3.89424100
H	0.34208000	-1.37643500	4.28246600
H	1.65056700	-0.26539500	4.75704800
H	0.68845500	0.05727100	3.28614100
C	2.78746000	-3.40117900	3.63871800
H	3.44483100	-3.99490700	2.98230500
H	3.31089800	-3.26780400	4.60115200
H	1.88095100	-3.99614800	3.83798100
C	-1.21539200	-4.45506800	-1.47272700
H	-2.20155800	-4.92924500	-1.58129400
H	-0.49843900	-5.22181500	-1.13146000
H	-0.87660100	-4.10091400	-2.45644800
H	-3.48814200	-3.34836200	-0.86333200
H	-3.59381200	-1.60430400	-0.69218200

(S,S)-TS-3

Cu	-1.96000	-1.31700	-0.30300
C	-2.58100	-3.15900	-1.19400
H	-3.59800	-3.44600	-0.92200
H	-2.67200	-2.35500	-1.95500
C	-1.94500	-3.12600	0.95500
C	-0.46700	-3.59100	0.98600
C	0.35100	-2.42900	1.60700
C	-1.98100	-1.90200	1.79900
H	-0.41400	-4.47800	1.63900
H	-0.07300	-3.88600	0.00800
H	1.06300	-2.78500	2.36600
H	0.93200	-1.86400	0.86000
H	-2.89700	-1.46400	2.19600
C	-0.71300	-1.53600	2.21500
O	-0.46500	-0.51500	3.02400
C	-1.74900	-4.29200	-1.76400
H	-2.22500	-4.68000	-2.68300
H	-0.73700	-3.95600	-2.03100
H	-1.65500	-5.13700	-1.06500
O	0.42000	0.68500	0.22900
P	-0.64800	0.35700	-1.02700
O	0.42800	0.13000	-2.28800
C	2.64100	0.85500	-0.68900
C	1.58200	1.43000	0.01400
C	1.39400	-0.85400	-2.00500
C	2.48900	-0.53600	-1.20000
C	3.17300	-2.92700	-1.37500
C	3.38700	-1.60200	-0.83300
C	2.07500	-3.15800	-2.25400
C	1.18400	-2.14200	-2.55300
H	1.93700	-4.15500	-2.67700
C	3.82500	1.64500	-0.89800
C	2.80600	3.46200	0.45200
C	1.65000	2.71700	0.60000
H	2.88400	4.45400	0.90200
C	3.90700	2.96100	-0.30400

C	4.05100	-3.98600	-1.00100
C	4.45500	-1.41900	0.09500
C	5.28200	-2.47500	0.44800
H	6.09100	-2.31100	1.16200
C	5.08800	-3.76800	-0.10900
H	5.75300	-4.58600	0.17200
C	4.91900	1.19300	-1.69500
C	5.08300	3.74300	-0.49800
C	6.13500	3.26500	-1.26300
H	7.02900	3.87300	-1.40800
C	6.04400	1.98300	-1.87100
H	6.86700	1.61900	-2.48800
H	3.88400	-4.97700	-1.43000
H	4.61500	-0.43500	0.53200
H	4.85800	0.21500	-2.17000
H	5.13400	4.73200	-0.03800
H	0.79000	3.08400	1.16000
H	0.32800	-2.29800	-3.20800
N	-1.40900	1.74900	-1.52200
C	-2.83000	1.97300	-1.11800
H	-3.20000	2.71900	-1.83700
C	-0.68800	2.87500	-2.20300
H	0.37700	2.60600	-2.19100
C	-2.98900	2.57800	0.27700
C	-3.80700	3.71100	0.43500
C	-2.38700	2.01100	1.41700
C	-4.00900	4.28200	1.70100
H	-4.28400	4.15300	-0.44300
C	-2.59100	2.57500	2.68600
H	-1.75900	1.12600	1.33800
C	-3.39900	3.71500	2.83100
H	-4.64000	5.16700	1.80300
H	-2.11800	2.11700	3.55400
H	-3.55300	4.15800	3.81700
C	-3.68500	0.71700	-1.35900
C	-3.84400	0.26300	-2.68600
C	-4.35500	0.03100	-0.32200
C	-4.67900	-0.82400	-2.97600
H	-3.31600	0.78000	-3.48900
C	-5.18900	-1.06700	-0.61600
H	-4.26900	0.38900	0.70300
C	-5.36100	-1.48900	-1.94000
H	-4.80900	-1.14600	-4.01100
H	-5.71200	-1.57500	0.19600
H	-6.02000	-2.32800	-2.16900
C	-0.85200	4.20900	-1.46100
H	-0.20500	4.96100	-1.93900
H	-1.88900	4.57300	-1.50800
H	-0.56700	4.11400	-0.40600
C	-1.14200	2.96300	-3.67000
H	-0.94600	2.01400	-4.18800
H	-2.21700	3.19500	-3.74000
H	-0.59300	3.76800	-4.18400
Si	0.95400	-0.16400	3.98000
C	0.61700	1.59600	4.56200
H	-0.28900	1.65000	5.18800
H	1.46200	1.97600	5.16100
H	0.48100	2.27400	3.70300
C	0.95100	-1.42400	5.39000
H	1.07200	-2.45500	5.01800
H	1.78200	-1.22600	6.08800
H	0.01200	-1.37900	5.96500
C	2.54600	-0.25900	2.96900
H	2.55200	0.46700	2.14500
H	3.39100	-0.01100	3.63600
H	2.74500	-1.25400	2.54500

C	-2.99600	-4.16200	1.31900
H	-2.79300	-4.50100	2.35000
H	-2.97100	-5.04100	0.66000
H	-4.00700	-3.72900	1.29500

(S,S)-TS-4

Cu	1.94700	-0.99200	0.29800
C	3.04800	-1.71400	1.99800
H	3.98000	-2.22200	1.73600
H	3.23400	-0.62300	1.90100
C	1.83500	-3.15100	0.79600
C	0.45800	-3.29300	1.49900
C	-0.62100	-2.90300	0.44800
C	1.52200	-2.91500	-0.63300
H	0.33700	-4.34800	1.79600
H	0.36900	-2.68800	2.40700
H	-1.42100	-3.65700	0.37800
H	-1.11200	-1.94300	0.67200
H	2.25500	-2.97600	-1.43400
C	0.16100	-2.81600	-0.84900
O	-0.37200	-2.67100	-2.05100
C	2.56700	-1.99400	3.41000
H	3.33000	-1.67100	4.14100
H	1.64100	-1.44400	3.63400
H	2.37300	-3.06200	3.58900
O	-0.62200	0.46600	-1.03400
P	0.68300	0.82500	-0.05200
O	-0.10600	1.57700	1.22600
C	-2.63600	1.30200	0.04600
C	-1.79200	1.23900	-1.06600
C	-1.02800	0.72600	1.85300
C	-2.29000	0.55000	1.28500
C	-2.76000	-1.07300	3.11900
C	-3.18100	-0.39900	1.91000
C	-1.47800	-0.79100	3.67600
C	-0.61600	0.08700	3.04600
H	-1.18400	-1.28600	4.60400
C	-3.81100	2.13600	-0.04700
C	-3.26400	2.59500	-2.42200
C	-2.10000	1.85800	-2.30200
H	-3.52100	3.06800	-3.37100
C	-4.13200	2.77000	-1.30600
C	-3.62900	-2.02300	3.73200
C	-4.45300	-0.73900	1.36100
C	-5.27100	-1.67400	1.97700
H	-6.23800	-1.91800	1.53500
C	-4.86300	-2.31900	3.17600
H	-5.52100	-3.04700	3.65300
C	-4.65700	2.39500	1.07200
C	-5.30100	3.58000	-1.40500
C	-6.11500	3.78900	-0.30400
H	-7.00400	4.41600	-0.38800
C	-5.78000	3.20000	0.94500
H	-6.40800	3.38800	1.81700
H	-3.30000	-2.51400	4.65000
H	-4.77700	-0.26100	0.44000
H	-4.40900	1.95900	2.03700
H	-5.53400	4.04400	-2.36600
H	-1.41200	1.73000	-3.13700
H	0.36800	0.32100	3.45100
N	1.54200	2.09500	-0.69600
C	3.00800	1.92600	-0.87400
H	3.29200	2.67100	-1.63300
C	0.93700	3.44000	-0.95000

H	-0.12100	3.34900	-0.66900
C	3.33800	0.55600	-1.50900
C	4.25500	-0.35200	-0.93200
C	2.75600	0.23200	-2.75500
C	4.60600	-1.53700	-1.60900
H	4.73700	-0.10600	0.01300
C	3.10700	-0.94500	-3.42400
H	2.03200	0.92000	-3.19300
C	4.04500	-1.83000	-2.85800
H	5.33200	-2.21600	-1.15800
H	2.65800	-1.17100	-4.39300
H	4.33100	-2.73900	-3.39000
C	3.84400	2.22200	0.37200
C	5.18500	2.60800	0.18600
C	3.36200	2.05500	1.68200
C	6.03400	2.81100	1.28300
H	5.56700	2.74100	-0.83000
C	4.20900	2.26000	2.78400
H	2.31800	1.80200	1.85600
C	5.54700	2.63200	2.58900
H	7.07000	3.11300	1.11900
H	3.81500	2.14000	3.79500
H	6.20300	2.79500	3.44600
C	1.00200	3.79300	-2.44500
H	0.45400	4.73100	-2.62300
H	2.03900	3.94700	-2.78400
H	0.54500	3.00000	-3.05400
C	1.57700	4.52100	-0.06600
H	1.48400	4.25800	0.99700
H	2.64500	4.64500	-0.30200
H	1.07200	5.48300	-0.24300
Si	-1.99900	-2.79500	-2.65000
C	-1.95100	-1.72900	-4.20400
H	-1.14300	-2.04300	-4.88400
H	-2.90400	-1.80100	-4.75600
H	-1.79200	-0.67100	-3.94200
C	-2.28000	-4.62800	-3.01400
H	-2.22000	-5.23600	-2.09600
H	-3.28000	-4.78800	-3.45300
H	-1.53500	-5.01700	-3.72700
C	-3.24900	-2.12800	-1.40500
H	-2.98800	-1.11300	-1.07800
H	-4.24000	-2.07400	-1.88900
H	-3.35700	-2.75500	-0.50700
C	2.84900	-4.25900	1.03000
H	2.39600	-5.20500	0.68400
H	3.12100	-4.37800	2.08800
H	3.76400	-4.08700	0.44400

(S,R)-TS-5

Cu	1.36200	1.49100	-0.01400
C	2.80600	3.02900	0.11100
C	0.98500	3.15900	1.37300
C	1.51500	2.68300	2.75200
C	0.70500	1.40400	3.10500
C	-0.27900	2.41100	1.16800
H	2.60000	2.51600	2.76400
H	1.29200	3.47400	3.48700
H	1.27600	0.48100	2.90500
H	0.40300	1.37400	4.16300
H	-1.02800	2.68300	0.42700
C	-0.49400	1.49300	2.17200
O	-1.61100	0.79200	2.29500

C	2.71700	3.76900	-1.22100
H	3.71200	4.16100	-1.49500
H	2.40100	3.10400	-2.03900
H	2.02400	4.62100	-1.17400
O	-0.33100	-1.10200	0.18500
P	0.82100	-0.49900	-0.87900
O	-0.09800	-0.31100	-2.26400
C	-2.49600	-0.92800	-0.91400
C	-1.55000	-1.66600	-0.19900
C	-1.02200	0.73200	-2.04100
C	-2.19300	0.46900	-1.33100
C	-2.69800	2.90700	-1.48800
C	-3.04000	1.58800	-1.00000
C	-1.51100	3.08900	-2.25700
C	-0.66600	2.02200	-2.50900
H	-1.26700	4.08700	-2.62500
C	-3.73300	-1.58100	-1.27100
C	-2.99700	-3.59700	-0.02900
C	-1.78700	-2.98900	0.24900
H	-3.19900	-4.61000	0.32400
C	-3.99000	-2.92200	-0.79600
C	-3.53000	4.01500	-1.14600
C	-4.17600	1.45600	-0.14700
C	-4.95300	2.55700	0.17800
H	-5.81500	2.43400	0.83500
C	-4.63800	3.84600	-0.33300
H	-5.26500	4.70100	-0.07500
C	-4.71300	-0.96700	-2.10700
C	-5.22200	-3.56000	-1.12500
C	-6.16300	-2.92200	-1.91500
H	-7.10100	-3.42000	-2.16500
C	-5.89700	-1.62000	-2.41700
H	-6.62800	-1.12900	-3.06200
H	-3.26700	5.00200	-1.53300
H	-4.42100	0.47700	0.25600
H	-4.52300	0.02600	-2.50900
H	-5.40100	-4.57000	-0.74900
H	-1.00900	-3.49700	0.81800
H	0.26000	2.13700	-3.07400
N	1.82500	-1.76100	-1.25700
C	3.27800	-1.71500	-0.94900
H	3.71300	-2.50400	-1.58400
C	1.24800	-3.05400	-1.75300
H	0.15800	-2.91900	-1.76400
C	3.61600	-2.09400	0.49500
C	2.84500	-1.68200	1.59600
C	4.78100	-2.84700	0.73300
C	3.22800	-2.01300	2.90400
H	1.92000	-1.12700	1.44300
C	5.17200	-3.17700	2.03900
H	5.38800	-3.17300	-0.11600
C	4.39500	-2.75900	3.13100
H	2.60500	-1.69900	3.74500
H	6.07800	-3.76400	2.20200
H	4.69100	-3.02100	4.14900
C	3.93800	-0.40600	-1.42400
C	4.98300	0.19800	-0.70200
C	3.58100	0.12900	-2.68100
C	5.65500	1.31800	-1.22300
H	5.28200	-0.20900	0.26400
C	4.25100	1.24500	-3.19900
H	2.78200	-0.34300	-3.25500
C	5.29300	1.84500	-2.47100
H	6.46500	1.77300	-0.65000
H	3.96800	1.63900	-4.17700
H	5.82100	2.70800	-2.87800

C	1.57300	-4.21500	-0.80200
H	1.04500	-5.11900	-1.14200
H	2.65100	-4.43300	-0.78800
H	1.26000	-3.97800	0.22400
C	1.69900	-3.31800	-3.19800
H	1.38700	-2.49100	-3.85300
H	2.79200	-3.43400	-3.26700
H	1.24100	-4.25000	-3.56300
Si	-2.06500	-0.40400	3.47100
C	-3.68000	-1.08100	2.77900
H	-3.54100	-1.55100	1.79500
H	-4.10600	-1.83700	3.46000
H	-4.41900	-0.27100	2.67400
C	-0.68200	-1.69200	3.58400
H	0.13500	-1.35400	4.24100
H	-1.07100	-2.63600	4.00100
H	-0.26000	-1.90900	2.59100
C	-2.33800	0.48100	5.12000
H	-3.08200	1.28800	5.01700
H	-2.71800	-0.22700	5.87600
H	-1.41200	0.92400	5.52400
C	0.83000	4.65700	1.16700
H	1.77400	5.21100	1.27500
H	0.12500	5.02200	1.93400
H	0.39300	4.88100	0.18400
H	3.21000	3.64400	0.91700
H	3.45000	2.13100	0.05100

(S,S)-TS-6

Cu	0.75600	0.75800	0.88000
C	0.09900	1.88000	2.56900
C	1.55100	2.74300	1.09700
C	2.82400	2.73300	1.98900
C	3.99200	2.23900	1.09400
C	1.98200	2.17100	-0.21500
H	3.01400	3.74700	2.37300
H	2.70100	2.07100	2.85500
H	4.73900	3.02800	0.92100
H	4.53300	1.37900	1.51700
H	1.38900	2.23300	-1.12700
C	3.33500	1.89600	-0.22500
O	4.00100	1.48900	-1.29900
C	-1.37400	2.19800	2.34500
H	-1.87800	2.30700	3.32400
H	-1.51400	3.14400	1.80400
H	-1.89200	1.40700	1.78800
O	-1.93500	-0.99000	1.21600
P	-0.57700	-0.93700	0.24300
O	-1.26300	-0.69800	-1.26700
C	-3.84000	-0.36800	-0.16800
C	-3.23800	-1.22600	0.75400
C	-1.84500	0.58500	-1.30900
C	-3.08800	0.79400	-0.71500
C	-2.80500	3.21500	-1.24000
C	-3.57000	2.15000	-0.62800
C	-1.58700	2.90900	-1.91500
C	-1.10000	1.61500	-1.93400
H	-1.03700	3.71600	-2.40500
C	-5.18000	-0.67900	-0.60600
C	-5.22400	-2.58600	0.97700
C	-3.91700	-2.32100	1.34300
H	-5.76400	-3.41900	1.43100
C	-5.88100	-1.79200	-0.00600
C	-3.27200	4.55900	-1.13700
C	-4.74900	2.49500	0.09600

C	-5.16600	3.81400	0.19000
H	-6.06800	4.05500	0.75500
C	-4.43100	4.85600	-0.43800
H	-4.77700	5.88800	-0.36200
C	-5.84100	0.05300	-1.63800
C	-7.21000	-2.09200	-0.42400
C	-7.83000	-1.34400	-1.41200
H	-8.84700	-1.58400	-1.72700
C	-7.13100	-0.27200	-2.02800
H	-7.61300	0.30100	-2.82300
H	-2.69200	5.35100	-1.61500
H	-5.31800	1.70600	0.58500
H	-5.31800	0.87200	-2.12800
H	-7.72700	-2.93100	0.04600
H	-3.39600	-2.92400	2.08600
H	-0.16800	1.35200	-2.43500
N	0.01700	-2.48300	0.13200
C	1.42500	-2.75800	0.51900
H	1.43500	-3.81700	0.81900
C	-0.82700	-3.60700	-0.38400
H	-1.79200	-3.15600	-0.65700
C	1.81400	-1.97500	1.78600
C	2.97000	-1.17400	1.86400
C	1.00500	-2.11800	2.93500
C	3.31500	-0.54800	3.07700
H	3.61200	-1.07100	0.99000
C	1.33700	-1.47400	4.13200
H	0.10700	-2.73500	2.87600
C	2.50100	-0.68800	4.20900
H	4.23400	0.03600	3.14200
H	0.70000	-1.59900	5.01000
H	2.77600	-0.20300	5.14700
C	2.40600	-2.62700	-0.64700
C	3.44900	-3.56500	-0.76400
C	2.29300	-1.61200	-1.61100
C	4.34400	-3.51100	-1.84300
H	3.54400	-4.35500	-0.01500
C	3.18500	-1.55400	-2.69200
H	1.48900	-0.88000	-1.54500
C	4.20700	-2.50900	-2.81700
H	5.13600	-4.25700	-1.93000
H	3.07200	-0.76800	-3.43900
H	4.89100	-2.47400	-3.66700
C	-1.08600	-4.65100	0.71400
H	-1.80400	-5.39900	0.34400
H	-0.16500	-5.18800	0.99400
H	-1.50600	-4.17600	1.61200
C	-0.21500	-4.22600	-1.65000
H	-0.06000	-3.45800	-2.42000
H	0.75500	-4.69800	-1.43100
H	-0.89400	-4.99900	-2.04200
Si	5.69800	1.10000	-1.45700
C	6.04500	-0.42800	-0.40100
H	5.36000	-1.25400	-0.65000
H	7.07400	-0.78400	-0.58100
H	5.96100	-0.21400	0.67700
C	5.90500	0.80500	-3.30500
H	5.62500	1.70300	-3.88000
H	6.96000	0.57900	-3.53500
H	5.29300	-0.03600	-3.65700
C	6.74000	2.58300	-0.90700
H	6.34100	3.53100	-1.30600
H	6.82200	2.67500	0.18700
H	7.76400	2.47000	-1.30300
C	0.78900	4.05000	0.95900
H	0.46300	4.45300	1.92800

H	-0.09000	3.92600	0.31100
H	1.46100	4.78800	0.48600
H	0.27600	0.88900	3.03200
H	0.59300	2.61900	3.20300

(S,R)-TS-7

Cu	1.43000	1.26200	-0.30800
C	2.86400	2.78300	-0.59900
C	1.23200	3.12300	0.85600
C	1.72100	2.64000	2.25400
C	0.60700	1.70600	2.81000
C	-0.12500	2.54500	0.68600
H	2.68900	2.12600	2.21100
H	1.85300	3.51800	2.90400
H	0.93500	0.66100	2.92100
H	0.25600	2.03200	3.80200
H	-0.80000	2.81700	-0.12400
C	-0.50800	1.81100	1.78500
O	-1.71300	1.27600	1.93800
C	4.10800	2.92100	0.26100
H	4.97600	3.18100	-0.37100
H	4.00300	3.70900	1.02200
H	4.34800	1.97600	0.77200
O	-0.42800	-1.17400	0.47000
P	0.74500	-0.82900	-0.67300
O	-0.14800	-0.95200	-2.08300
C	-2.58000	-1.02600	-0.68300
C	-1.70200	-1.67700	0.18900
C	-0.97700	0.18900	-2.14200
C	-2.15900	0.20700	-1.40300
C	-2.43500	2.57700	-2.12700
C	-2.89800	1.44400	-1.35700
C	-1.24200	2.46600	-2.90100
C	-0.50300	1.29600	-2.89300
H	-0.90800	3.32700	-3.48500
C	-3.87400	-1.63000	-0.90900
C	-3.32400	-3.38100	0.75700
C	-2.06100	-2.84300	0.91100
H	-3.61700	-4.26900	1.32000
C	-4.25400	-2.80300	-0.15400
C	-3.15600	3.80700	-2.06600
C	-4.04500	1.61700	-0.52800
C	-4.71600	2.82900	-0.48200
H	-5.59000	2.93700	0.16300
C	-4.27700	3.93300	-1.26200
H	-4.82000	4.87900	-1.22100
C	-4.79500	-1.13200	-1.87900
C	-5.54200	-3.38200	-0.35400
C	-6.42200	-2.85200	-1.28200
H	-7.40400	-3.30400	-1.43100
C	-6.03500	-1.72600	-2.05800
H	-6.71800	-1.32700	-2.81000
H	-2.80100	4.64900	-2.66400
H	-4.38600	0.78200	0.07800
H	-4.51400	-0.27800	-2.49100
H	-5.81300	-4.26200	0.23300
H	-1.32900	-3.28500	1.58600
H	0.42500	1.19000	-3.45500
N	1.75900	-2.13900	-0.67600
C	3.23100	-1.94400	-0.60400
H	3.65400	-2.89500	-0.96300
C	1.22400	-3.53600	-0.71100
H	0.13000	-3.44500	-0.65700
C	3.75600	-1.74800	0.82000

C	3.05800	-1.02700	1.80400
C	5.03000	-2.25600	1.13800
C	3.62200	-0.80300	3.06900
H	2.05100	-0.66300	1.60300
C	5.60100	-2.03600	2.40000
H	5.58200	-2.82100	0.38200
C	4.89900	-1.30200	3.37100
H	3.05800	-0.24800	3.82200
H	6.58800	-2.44100	2.62700
H	5.33700	-1.13300	4.35600
C	3.72600	-0.87000	-1.59900
C	3.14300	-0.79500	-2.88300
C	4.81000	-0.02500	-1.30100
C	3.60800	0.12800	-3.82900
H	2.31800	-1.46000	-3.13700
C	5.28600	0.89000	-2.25500
H	5.28700	-0.07400	-0.32300
C	4.68200	0.98000	-3.51700
H	3.14300	0.17000	-4.81600
H	6.12900	1.53600	-2.00300
H	5.05200	1.69400	-4.25600
C	1.69700	-4.33200	0.51500
H	1.23500	-5.33100	0.50400
H	2.79000	-4.46200	0.51000
H	1.41800	-3.81500	1.44400
C	1.56900	-4.22000	-2.04300
H	1.16400	-3.64200	-2.88700
H	2.65700	-4.32800	-2.17600
H	1.12800	-5.22900	-2.06400
Si	-2.37900	0.45400	3.31900
C	-4.02800	-0.20400	2.69200
H	-3.89900	-0.87700	1.83300
H	-4.53900	-0.76900	3.49000
H	-4.68900	0.62400	2.39200
C	-1.19100	-0.92000	3.85700
H	-0.40200	-0.54500	4.52900
H	-1.74400	-1.70500	4.40200
H	-0.70900	-1.39000	2.98700
C	-2.62500	1.74000	4.68500
H	-3.23900	2.58400	4.32900
H	-3.14800	1.28800	5.54500
H	-1.67100	2.14800	5.06000
C	1.28500	4.62700	0.62200
H	2.30200	5.03500	0.70000
H	0.66200	5.10200	1.40100
H	0.86400	4.89300	-0.35800
H	3.04100	1.99100	-1.36100
H	2.59000	3.68700	-1.14700

(S,R)-TS-8

Cu	-1.60600	-1.01000	-0.54500
C	-3.06300	-2.19600	-1.55900
C	-1.35400	-3.22700	-0.62800
C	-1.75800	-3.63100	0.81500
C	-0.74200	-2.93400	1.76300
C	-0.02100	-2.59000	-0.49300
H	-2.79300	-3.37100	1.06100
H	-1.66300	-4.72600	0.89800
H	-1.17900	-2.05100	2.26100
H	-0.37900	-3.60600	2.55500
H	0.63500	-2.38400	-1.33500
C	0.37200	-2.50600	0.82300
O	1.57300	-2.08700	1.20200
C	-4.25900	-2.93900	-0.98500

H	-5.13100	-2.82000	-1.65200
H	-4.07600	-4.01700	-0.87100
H	-4.54300	-2.54200	-0.00100
O	0.51700	0.87200	0.89900
P	-0.73900	1.01300	-0.19300
O	0.06300	1.57600	-1.54600
C	2.58900	1.25600	-0.32300
C	1.76000	1.49700	0.77600
C	0.91800	0.57200	-2.04300
C	2.14700	0.35300	-1.42100
C	2.46800	-1.55100	-3.00200
C	2.92900	-0.77300	-1.87200
C	1.23600	-1.21500	-3.63500
C	0.45200	-0.18500	-3.14500
H	0.90700	-1.79900	-4.49700
C	3.85900	1.94300	-0.37000
C	3.40500	2.88900	1.87600
C	2.15700	2.29500	1.87800
H	3.73000	3.49200	2.72700
C	4.27600	2.74400	0.75900
C	3.23900	-2.66800	-3.44300
C	4.12500	-1.18500	-1.21400
C	4.84200	-2.28400	-1.66000
H	5.75300	-2.58200	-1.13800
C	4.40500	-3.02900	-2.79000
H	4.98600	-3.88600	-3.13400
C	4.71900	1.89100	-1.50700
C	5.54200	3.39900	0.72700
C	6.36500	3.30100	-0.38200
H	7.33000	3.80900	-0.39900
C	5.93900	2.55000	-1.51100
H	6.57600	2.49800	-2.39600
H	2.88300	-3.23700	-4.30500
H	4.46900	-0.62800	-0.34600
H	4.40700	1.32900	-2.38600
H	5.84300	3.99200	1.59400
H	1.47100	2.40500	2.71800
H	-0.50600	0.07600	-3.59600
N	-1.68600	2.31700	0.20000
C	-3.09800	2.05100	0.58100
H	-3.42100	2.95500	1.12100
C	-1.18500	3.72600	0.19300
H	-0.16500	3.68000	-0.21300
C	-3.17600	0.90000	1.60700
C	-3.94300	-0.26200	1.40100
C	-2.45700	1.03400	2.81300
C	-3.99500	-1.26500	2.38500
H	-4.52300	-0.36900	0.48600
C	-2.50300	0.03200	3.79100
H	-1.85500	1.92900	2.97600
C	-3.27500	-1.12400	3.58000
H	-4.61200	-2.15000	2.22000
H	-1.94400	0.15600	4.72000
H	-3.32300	-1.90100	4.34600
C	-4.04500	1.88200	-0.61000
C	-5.43000	1.98700	-0.37200
C	-3.60300	1.58700	-1.91100
C	-6.35400	1.77800	-1.40400
H	-5.78300	2.22100	0.63600
C	-4.52700	1.37900	-2.95000
H	-2.53700	1.55400	-2.13200
C	-5.90400	1.46500	-2.69900
H	-7.42300	1.86300	-1.20100
H	-4.16600	1.16400	-3.95700
H	-6.62100	1.30800	-3.50600
C	-1.10900	4.29100	1.62000

H	-0.69900	5.31300	1.59300
H	-2.10600	4.34400	2.08700
H	-0.45500	3.66900	2.24800
C	-2.03600	4.59900	-0.74300
H	-2.03700	4.18900	-1.76200
H	-3.07800	4.65900	-0.39200
H	-1.62500	5.62000	-0.76700
Si	2.24600	-1.91200	2.79300
C	3.87900	-1.02800	2.48000
H	3.72300	-0.04000	2.02300
H	4.42500	-0.88300	3.42700
H	4.52000	-1.62300	1.81000
C	1.05300	-0.88900	3.84400
H	0.16100	-1.46600	4.13600
H	1.55100	-0.55000	4.76900
H	0.71300	-0.00200	3.28900
C	2.51300	-3.64700	3.49800
H	3.15700	-4.24800	2.83500
H	3.00900	-3.59200	4.48300
H	1.56600	-4.19500	3.63800
C	-1.38200	-4.32400	-1.68400
H	-2.37700	-4.76400	-1.83300
H	-0.70000	-5.12200	-1.34400
H	-1.00900	-3.94900	-2.64900
H	-3.33500	-1.11900	-1.64800
H	-2.77200	-2.52700	-2.56000

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