

Supporting Information

Enantioselective Henry Reaction Catalyzed by Cu^{II}-salt and Bipiperidine

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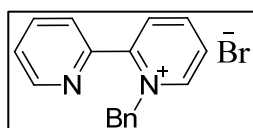
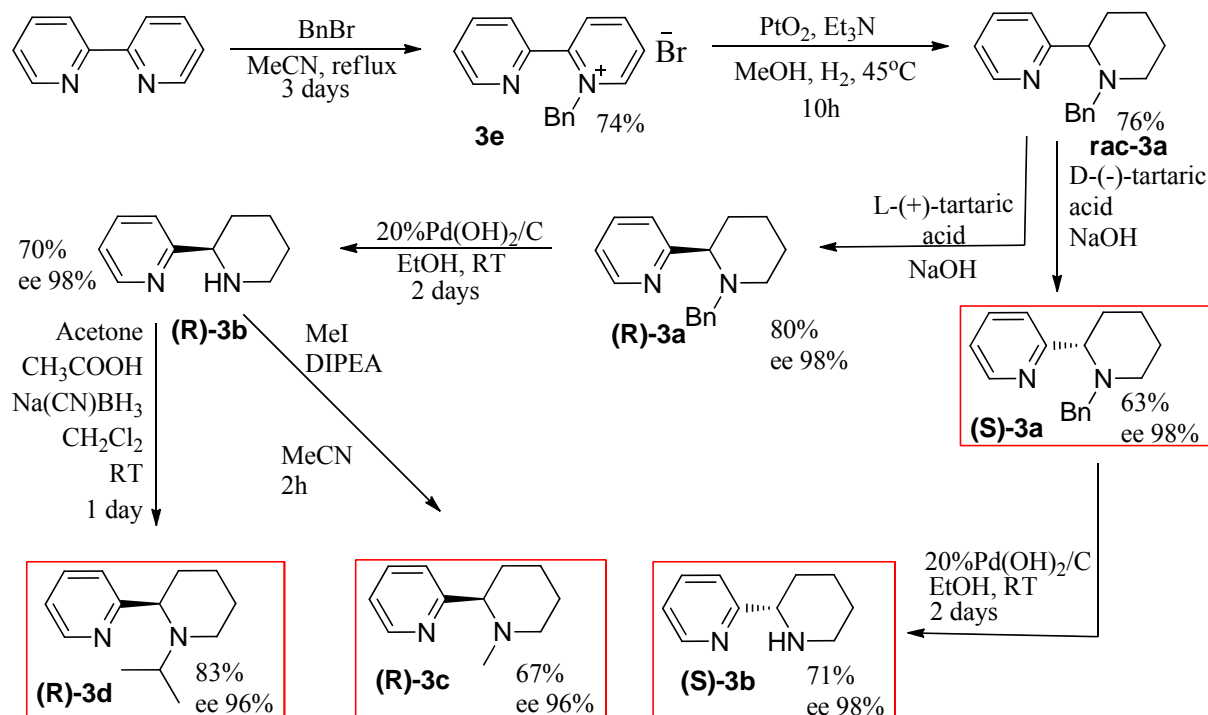
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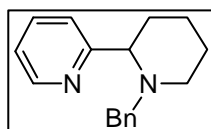
General methods

Full assignment of ¹H and ¹³C chemical shifts is based on the 1D and 2D FT NMR spectra on a 400 MHz instrument. Internal standard (TMS δ=0.00) and solvent peak (CHCl₃ δ=77.00) were used as chemical shift references. Mass spectra were recorded using EI (70 eV). Chiral HPLC was performed using Chiralcel OD-H (250 x 4.6 mm), Chiralcel OJ-H (250 x 4.6 mm), Lux 3u Amylose-2 (250 x 4.6 mm) and Chiralpak AS-H (250 x 4.6 mm) columns. All reactions sensitive to the moisture or oxygen were carried out under Ar atmosphere in oven dried glassware. MeOH was dried by distillation over Na, HPLC grade EtOH was used in asymmetric reactions as received. Precoated silica gel 60 F₂₅₄ plates were used for TLC, whereas for column chromatography silica gel KSK407100 μm was used. Commercial reagents were generally used as received. Petroleum ether used had bp 40-60 °C.

Synthesis of 2-(2'-piperidinyl)pyridine derivatives



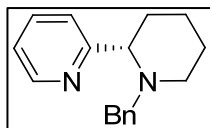
1-benzyl-2-(pyridin-2-yl)pyridinium bromide (3e) was synthesized according to the literature procedure¹ by refluxing 2,2'-bipyridine (1eq) in the presence of benzyl bromide (3eq) in MeCN for three days under argon atmosphere. Crude product was purified by recrystallization from MeCN to yield the product in 74% yield as a white solid; mp: 140°C; IR (KBr) ν = 3038, 2955, 1620, 1567, 1518, 778, 737, 697 cm^{-1} ; ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.43 (dd, *J* = 6.2, 0.9, 14H), 8.82 (tdd, *J* = 5.8, 4.9, 1.4, 2H), 8.37 - 8.27 (m, 2H), 8.03 (td, *J* = 7.8, 1.7, 1H), 7.71 (dt, *J* = 7.9, 0.9, 1H), 7.66 (ddd, *J* = 7.7, 4.8, 1.1, 1H), 7.30 - 7.17 (m, 3H), 6.92 (dd, *J* = 7.9, 1.5, 2H), 6.09 (s, 2H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 151.9, 149.8, 149.7, 147.5, 147.0, 138.3, 133.8, 130.7, 128.8, 128.7, 128.2, 127.7, 126.9, 125.9, 61.0, 40.1, 39.9, 39.7, 39.5, 39.3, 39.1, 38.9.



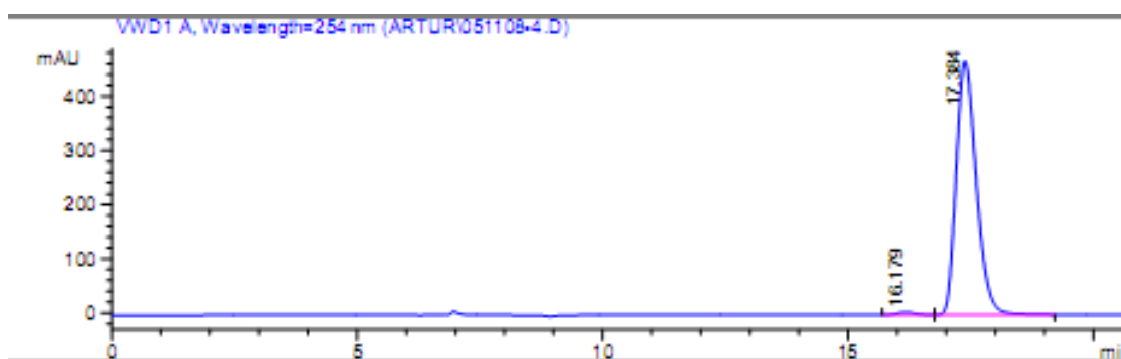
rac-2-(1-benzylpiperidin-2-yl)pyridine (rac-3a). In a 1 L autoclave 1-benzyl-2-(pyridin-2-yl)pyridinium bromide (11,08 g, 33,8 mmol) and triethylamine (4,76 ml, 33,8 mmol) were dissolved in MeOH (564 mL). Platinum(IV)oxide (0.553 g, 2.437 mmol) was added, vessel was sealed and filled with nitrogen before pressurizing with hydrogen up to 20 atm and temperature maintained at 40°C. The reaction was complete after 10h (RP-HPLC), platinum(IV)oxide was filtrated through Celite and the mixture concentrated in vacuo. The crude product was purified by silica gel column chromatography (eluent CH₂Cl₂:*i*PrOH 6%+0,1%Et₃N) affording 6.5 g (76%) of product as a white solid; mp: 65-67°C; IR (KBr) ν 3030, 2934, 2853, 2789, 1588, 1567, 780, 734, 692 cm^{-1} ; MS *m/z* 251 (*M*⁻), 161, 106, 91, 78.; ¹H NMR (400 MHz,

¹ Cheng, Y.-Q.; Bian, Z.; Kang, C.-Q.; Guo, H.-Q.; Gao, L.-X. *Tetrahedron: Asymmetry*, **2008**, *19*, 1572-1575.

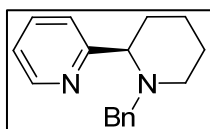
MeOD) δ 8.45 (ddd, $J = 5.0, 1.7, 0.9$ Hz, 1H), 7.83 (td, $J = 7.7, 1.7$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.32 – 7.14 (m, 6H), 3.66 – 3.40 (m, 1H), 2.94 (dd, $J = 15.3, 8.0$ Hz, 2H), 1.99 (td, $J = 11.6, 3.6$ Hz, 1H), 1.85 – 1.74 (m, 2H), 1.67 – 1.51 (m, 3H), 1.48 – 1.31 (m, 1H). ^{13}C NMR (101 MHz, MeOD) δ 165.8, 149.5, 139.8, 139.2, 130.2, 129.3, 128.2, 124.1, 123.6, 71.6, 61.3, 54.2, 36.5, 26.8, 25.9; Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2$ (252.16): C 80.91, H 7.99, N 11.10; found: C 80.87, H 8.04, N 11.08.



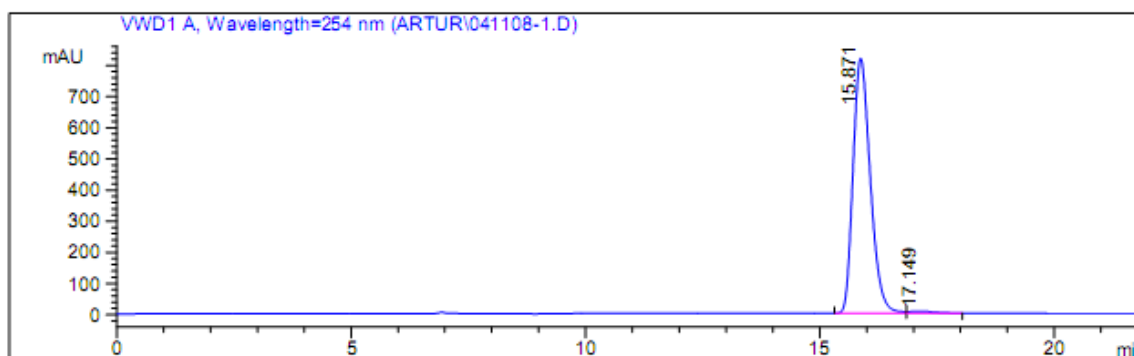
(S)-2-(1-benzylpiperidin-2-yl)pyridine ((S)-3a). In a 250 mL round-bottomed flask D-tartaric acid (1.829 g, 12.19 mmol) was dissolved in the mixture of THF (11.61 mL) and acetonitrile (58.0 mL) to give a colorless solution. After heating the mixture to reflux rac-2-(1-benzyl-2-piperidinyl)pyridine (6.15 g, 24.37 mmol) was added. Mixture was refluxed for 1 hour, the heating was stopped and the mixture was cooled in ice bath. The formed precipitate was filtered out. Wet crystals were suspended in dichloromethane (50 mL) and 15% NaOH solution was added (20mL). The mixture was extracted, water phase back extracted with dichloromethane (3x40mL) and combined organics were dried over Na_2SO_4 . After filtration and concentration crude crystals were recrystallized twice from EtOH/water to yield 1.95g (63%) of product with ee >98% by HPLC analysis (Chiralcel OD-H column, 2% iPrOH in hexane +0,15% Et_2NH , 0.5 mL/min, 254 nm), $t_{\text{R}}=16.18$ (minor) and $t_{\text{R}}=17.38$ (major). ^1H NMR (400 MHz, MeOD) δ 8.45 (ddd, $J = 5.0, 1.7, 0.9$ Hz, 1H), 7.83 (td, $J = 7.7, 1.7$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.32 – 7.14 (m, 6H), 3.66 – 3.40 (m, 1H), 2.94 (dd, $J = 15.3, 8.0$ Hz, 2H), 1.99 (td, $J = 11.6, 3.6$ Hz, 1H), 1.85 – 1.74 (m, 2H), 1.67 – 1.51 (m, 3H), 1.48 – 1.31 (m, 1H). ^{13}C NMR (101 MHz, MeOD) δ 165.8, 149.5, 139.8, 139.2, 130.2, 129.3, 128.2, 124.1, 123.6, 71.6, 61.3, 54.2, 36.5, 26.8, 25.9.



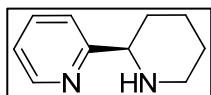
Signaal 1 WDI A, Wavelength=254 nm						
Peak nr	RT [min]	TGUp	Laus [min]	Pindala	Pindala %	Nimi
1	16.179	BV	0.378	115.263	0.863	
2	17.384	VB	0.439	1.324e4	99.137	



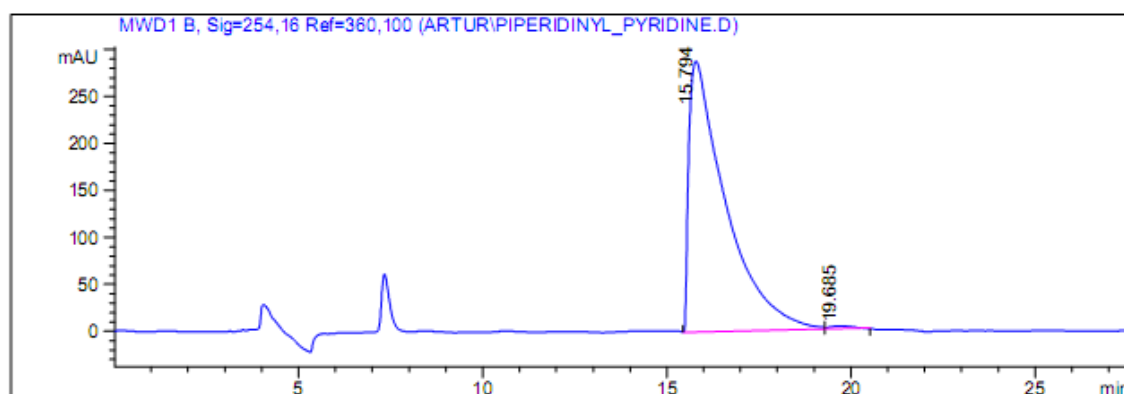
(R)-2-(1-benzylpiperidin-2-yl)pyridine ((R)-3a). Mother liquid from the previous reaction was concentrated, the residue was dissolved in dichloromethane (50 mL) and extracted with 15% NaOH solution. Organic phases were combined, dried over Na₂SO₄ and concentrated. L-tartaric acid (1.829 g, 12.19 mmol) was dissolved in THF (11.61 mL) and acetonitrile (58.0 mL) to give a colourless solution. After heating the mixture to boil enriched 2-(1-benzyl-2-piperidinyl)pyridine was added. The mixture was refluxed for 1 hour, the heating was stopped and the mixture was cooled in ice bath. The formed precipitate was filtered out. Wet crystals were suspended in dichloromethane (50 mL) and 15% NaOH solution was added (20 mL). The mixture was extracted, water phase back extracted with dichloromethane (3x40 mL) and combined organics were dried over Na₂SO₄. Filtration and concentration afforded 2.47g (80%) of product with ee >98% by HPLC analysis (Chiralcel OD-H column, 2% iPrOH in hexane + 0.15% Et₂NH, 0.5 mL/min, 254 nm), t_R=15.87 (major) and t_R=17.15 (minor). ¹H NMR (400 MHz, MeOD) δ 8.45 (ddd, *J* = 5.0, 1.7, 0.9 Hz, 1H), 7.83 (td, *J* = 7.7, 1.7 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.14 (m, 6H), 3.66 – 3.40 (m, 1H), 2.94 (dd, *J* = 15.3, 8.0 Hz, 2H), 1.99 (td, *J* = 11.6, 3.6 Hz, 1H), 1.85 – 1.74 (m, 2H), 1.67 – 1.51 (m, 3H), 1.48 – 1.31 (m, 1H). ¹³C NMR (101 MHz, MeOD) δ 165.8, 149.5, 139.8, 139.2, 130.2, 129.3, 128.2, 124.1, 123.6, 71.6, 61.3, 54.2, 36.5, 26.8, 25.9.



Signaal 1 VWD1 A, Wavelength=254 nm						
Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	15.871	BV	0.398	2.092e4	99.062	
2	17.149	VB	0.485	198.092	0.938	

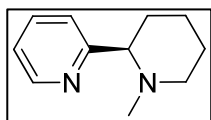


(R)-2-(piperidin-2-yl)pyridine ((R)-3b). In a 25 mL round-bottomed flask (*R*)-2-(1-benzylpiperidin-2-yl)pyridine (0.505 g, 2 mmol) was dissolved in ethanol (20.00 mL) to give a colourless solution. Reaction vessel was filled with Ar and 20% Pd(OH)₂ on carbon (0.04 g, 2.00 mmol) were added. Hydrogen was bubbled through the reaction mixture and after 10 min bubbling was stopped and mixture was stirred under hydrogen atmosphere for 48 h. Reaction was stopped by removing the catalyst via filtration through a pad of Celite. Organic phase was concentrated and crude product was purified by silica gel column chromatography (eluent CH₂Cl₂:MeOH/NH₃ 3%). 229 mg (70%) of product was collected as a yellow viscous oil with ee 98% by HPLC analysis (Chiralpak AS-H column, 1% of *i*PrOH in hexane + 0.1% Et₂NH, 1 mL/min, 254 nm), *t*_R=14.62 (major) and *t*_R=16.55 (minor); IR: $\nu = 3275, 2933, 2852, 1590, 1570, 772, 750 \text{ cm}^{-1}$; MS *m/z*: 161 (*M*⁻ -1), 119, 145, 119, 106, 78.; ¹H NMR (400 MHz, CDCl₃) δ 8.50 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 7.60 (td, *J* = 7.7, 1.8 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.10 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 3.71 (dd, *J* = 10.3, 2.6 Hz, 1H), 3.21 – 3.14 (m, 1H), 2.78 (td, *J* = 11.7, 3.0 Hz, 1H), 2.09 (s, 1H), 1.98 – 1.81 (m, 2H), 1.69 – 1.56 (m, 1H), 1.56 – 1.40 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 163.7, 149.2, 136.8, 122.1, 120.7, 62.7, 47.4, 33.4, 26.3, 25.3.

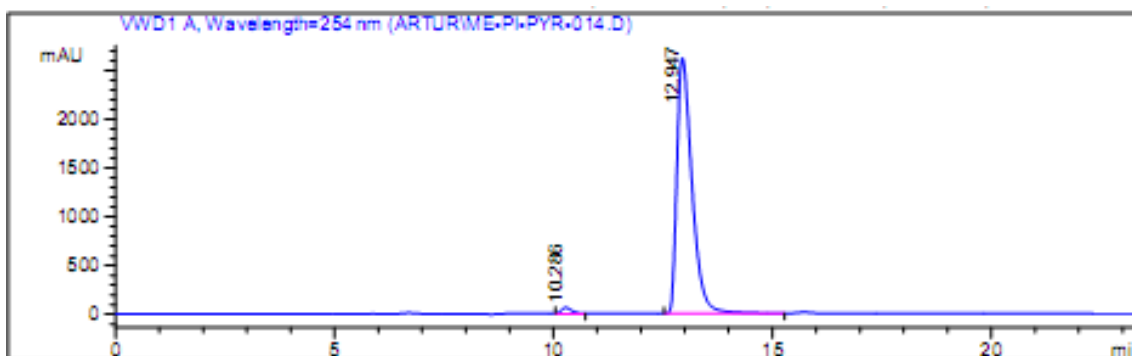


Signaal 1 MWD1 B, Sig=254,16 Ref=360,100

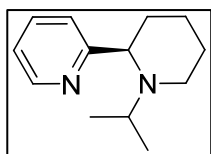
Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	15.794	MF	1.157	2.002e4	99.491	
2	19.685	FM	0.635	102.392	0.509	



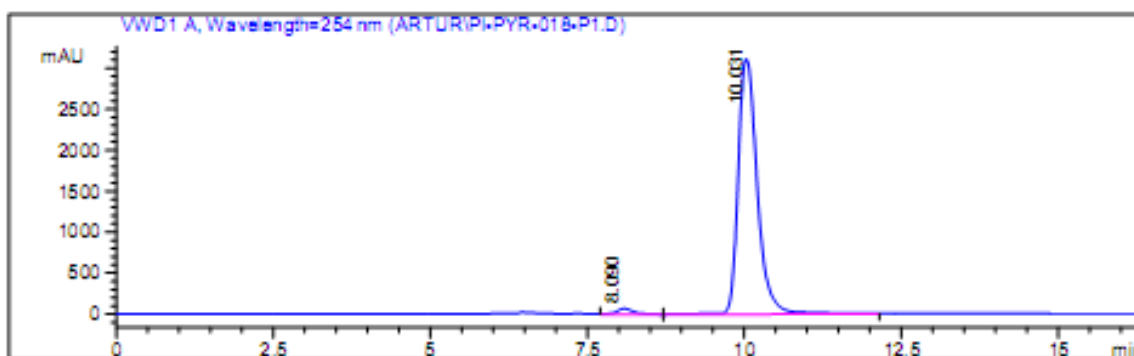
(R)-2-(1-methylpiperidin-2-yl)pyridine ((R)-3c). In a 25 mL round-bottomed flask (*R*)-2-(piperidin-2-yl)pyridine (0.100 g, 0.616 mmol) was dissolved in acetonitrile (6.16 mL) to give a yellow solution. Reaction flask was filled with Ar and cooled to 0 - 5°C. *N,N*-Diisopropylethylamine (0.161 mL, 0.925 mmol) and iodomethane (0.042 mL, 0.678 mmol) were added. Mixture was stirred at 0 - 10°C for 2 h. The reaction mixture was concentrated. Crude product was dissolved in CH₂Cl₂ and extracted with alkaline water solution. Water phase was extracted with CH₂Cl₂ (2 x 10 mL) and combined organic phases were concentrated. Product was purified by silica gel column chromatography (CH₂Cl₂/ MeOH 6%) to yield 73 mg (67%) of product as yellow viscous oil with ee 96% by HPLC analysis (Chiralcel OD-H column, 2% *i*PrOH in hexane + 0.15% Et₂NH, 0.5 mL/min, 254 nm), *t_R*=10.29 (minor) and *t_R*=12.95 (major); IR ν = 2936, 2853, 2782, 1590, 1570, 778, 751 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.50 (ddd, *J* = 4.9, 1.7, 0.9, 1H), 7.60 (td, *J* = 7.7, 1.8, 1H), 7.33 (d, *J* = 7.9, 1H), 7.11 (ddd, *J* = 7.4, 4.9, 1.2, 1H), 2.99 (ddd, *J* = 14.0, 8.1, 2.8, 2H), 2.11 (td, *J* = 11.4, 4.1, 1H), 1.99 (s, 3H), 1.85 - 1.63 (m, 4H), 1.57 (tdd, *J* = 13.1, 11.4, 4.0, 1H), 1.44 - 1.25 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) 164.2, 149.3, 136.7, 122.1, 121.9, 72.5, 57.4, 44.6, 34.7, 26.2, 24.7; HRMS (ESI): calcd. for [M+H]⁺ (C₁₁H₁₇N₂)⁺ requires *m/z* 177.1386, found 177.1383.



Signal 1 WVD1 A, Wavelength=254 nm						
Peak nr	RT [min]	TGUp	Leius [min]	Pindala	Pindala %	Nimi
1	10.286	MM	0.304	1190.327	1.856	
2	12.947	VB	0.365	6.295e4	98.144	

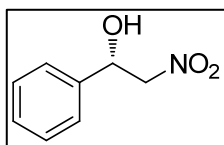


(R)-2-(1-isopropylpiperidin-2-yl)pyridine ((R)-3d). (R)-2-(piperidin-2-yl)pyridine (0.094 g, 0.579 mmol) was dissolved in acetone (2.29 mL) to give a colorless solution. CH₂Cl₂ (2.16 mL) and acetic acid (0.43 mL) were added. The flask was filled with Ar and sodium cyanoborohydride (0.073 g, 1.159 mmol) was added. The mixture was stirred at rt for 24 h. Additional amount of sodium cyanoborohydride (0.073 g, 1.159 mmol) was added and the stirring was continued for 7 h. The reaction was quenched by partitioning the reaction mixture between EtOAc and aq NaHCO₃ solution. Organic phase was extracted with aq NaHCO₃, brine and was dried on Na₂SO₄. Filtration and concentration afforded the crude product that was purified by silica gel column chromatography (eluent CH₂Cl₂:MeOH/NH₃ 30:1). 98 mg (83%) of product was collected as yellow oil with ee 96% by HPLC analysis (Chiralcel OD-H column, 2% iPrOH in hexane +0.15% Et₂NH, 0.5 mL/min, 254 nm), t_R=8.09 (minor) and t_R=10.03 (major); IR ν = 2967, 2934, 2855, 1591, 1570, 781, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.47 (s, 1H), 7.59 (td, *J* = 7.7, 1.8 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.09 (ddd, *J* = 7.4, 4.9, 1.2 Hz, 1H), 3.50 (dd, *J* = 11.0, 2.8 Hz, 1H), 3.00 – 2.89 (m, 1H), 2.63 (hept, *J* = 6.7 Hz, 1H), 2.19 (tt, *J* = 9.5, 4.9 Hz, 1H), 1.81 – 1.64 (m, 3H), 1.63 – 1.49 (m, 2H), 1.40 – 1.24 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.9, 149.2, 136.6, 122.0, 121.9, 67.5, 49.3, 44.0, 35.8, 26.3, 25.3, 21.5, 12.6; HRMS (ESI): calcd. for [M+H]⁺ (C₁₃H₂₁N₂)⁺ requires *m/z* 205.1699, found 205.1698.

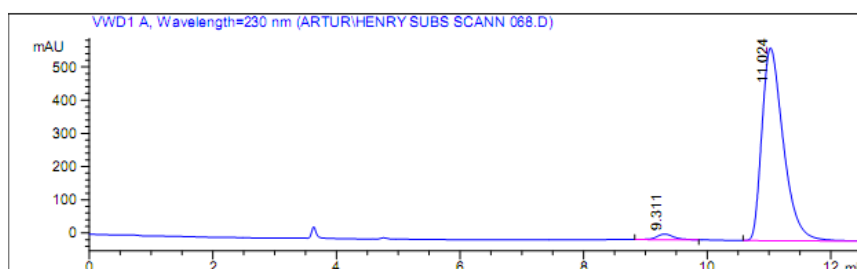


Signaal 1 WVD1 A, Wavelength=254 nm						
Piigi nr	RT [min]	TUUp	Laius [min]	Pindala	Pindala %	Nimi
1	8.090	VV	0.276	1261.742	1.870	
2	10.031	VB	0.327	6.622e4	98.130	

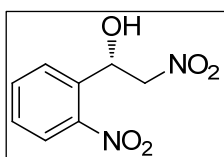
Asymmetric Henry reaction



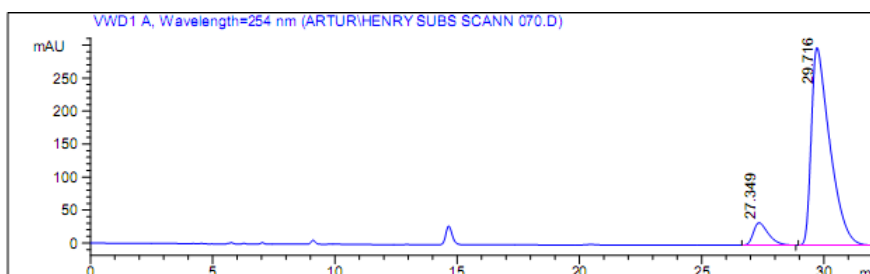
(S)-2-nitro-1-phenylethanol (Table 3, entry 2). 97% of isolated yield, 96% ee by HPLC analysis (Chiralcel OD-H column, 1 mL/min, 15% iPrOH in hexane, 230 nm), (R) t_R =9.31 (minor) and (S) t_R =11.02 (major); $[\alpha]_D^{25} = +12.5$ (c = 2.04 in EtOH), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.33 (m, 5H), 5.47 (dd, $J = 9.6, 3.0$ Hz, 1H), 4.61 (dd, $J = 13.4, 9.6$ Hz, 1H), 4.52 (dd, $J = 13.4, 3.0$ Hz, 1H), 2.85 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.2, 129.2, 129.1, 126.1, 81.4, 71.1.



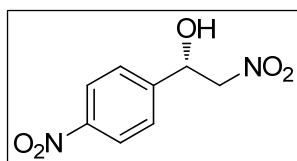
Signaal 1 VWD1 A, Wavelength=230 nm						
Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	9.311	MM	0.313	314.476	2.198	
2	11.024	MM	0.402	1.399e4	97.802	



(S)-2-nitro-1-(2-nitrophenyl)ethanol (Table 3, entry 4). 91% isolated yield, 83% ee by HPLC analysis (Chiralcel OJ-H column, 1 mL/min, 15% iPrOH in hexane, 230 nm), (R) t_R =27.35 (minor) and (S) t_R =29.72 (major); $[\alpha]_D^{25} = -226.2$ (c = 2.25 in EtOH), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; ^1H NMR (400 MHz, CDCl_3) δ 8.08 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.96 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.76 (td, $J = 7.5, 1.0$ Hz, 1H), 7.61 - 7.50 (m, 1H), 6.05 (d, $J = 9.0$ Hz, 1H), 4.87 (dd, $J = 13.8, 2.3$ Hz, 1H), 4.56 (dd, $J = 13.8, 9.1$ Hz, 1H), 3.25 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.6, 134.2, 129.9, 128.9, 125.2, 80.2, 67.0.

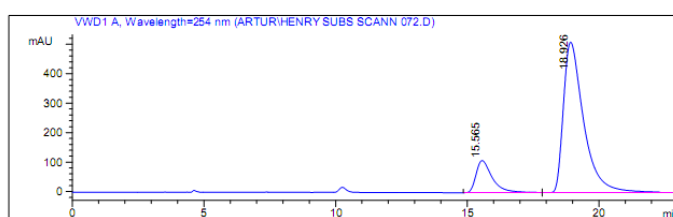


Signaal 1 VWD1 A, Wavelength=254 nm						
Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	27.349	BB	0.659	1479.168	8.554	
2	29.716	BB	0.769	1.581e4	91.446	

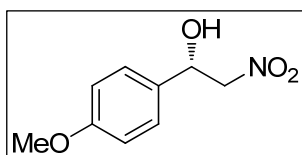


(S)-2-nitro-1-(4-nitrophenyl)ethanol (Table 3, entry 6). 97% isolated yield, 71% ee by HPLC analysis (Chiralcel OD-H column, 1 ml/min, 15% iPrOH in hexane, 254 nm), (R) t_R =15.57 (minor) and (S) t_R =18.93 (major); $[\alpha]_D^{25} = +14.8$ ($c = 2.18$ in EtOH), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.32 – 8.23 (m, 1H), 7.67 – 7.58 (m, 1H), 5.62 (dt, $J = 8.3, 4.1$ Hz, 1H), 4.65 – 4.53 (m, 1H), 3.18 (d, $J = 4.2$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.3, 145.0, 127.1, 124.4, 80.7, 70.1.

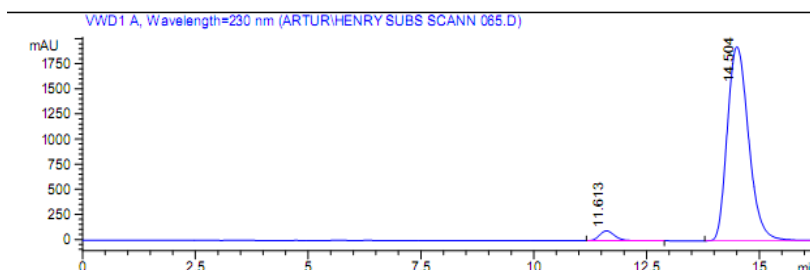
Kuupäev: Thu, 5. Nov. 2009
 Proovi nimi: subs p-Nitro-BA, reaction ->
 Analüüsi meetod: C:\CHEM32\1\METHODS\DEF_LC.M
 lisainfo: Hex:iPrOH 85:15, 1ml/min, 254nm; OD-H



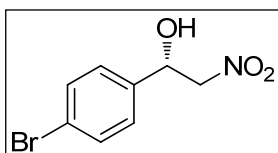
Peigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	15.565	MF	0.715	4682.634	14.640	
2	18.926	FM	0.891	2.730e4	85.360	



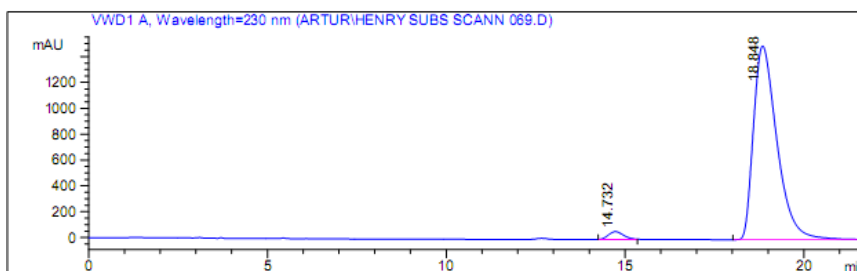
(S)-1-(4-methoxyphenyl)-2-nitroethanol (Table 3, entry 8). 93% isolated yield, 93% ee by HPLC analysis (Chiralcel OD-H column, 1 mL/min, 15% iPrOH in hexane, 230 nm), (R) t_R =11.61 (minor) and (S) t_R =14.50 (major); $[\alpha]_D^{25} = +14.6$ ($c = 1.99$ in EtOH), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 – 7.29 (m, 1H), 6.96 – 6.88 (m, 1H), 5.41 (dd, $J = 9.6, 2.6$ Hz, 1H), 4.61 (dd, $J = 13.2, 9.6$ Hz, 1H), 4.48 (dd, $J = 13.2, 3.1$ Hz, 1H), 3.82 (s, 1H), 2.74 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.2, 130.3, 127.4, 114.6, 81.4, 70.8, 55.5.



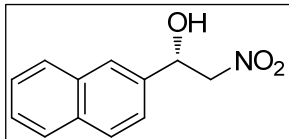
Peigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	11.613	VB	0.368	2393.079	3.607	
2	14.504	BBA	0.520	6.395e4	96.393	



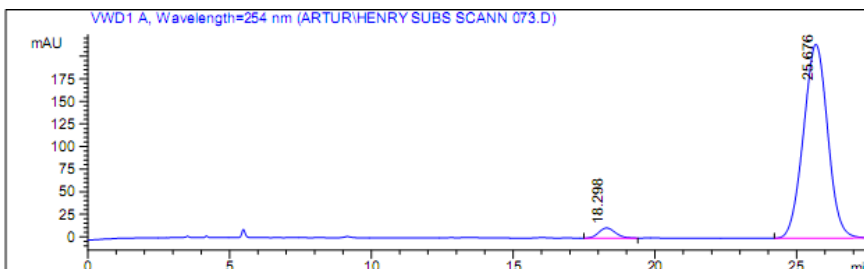
(S)-1-(4-bromophenyl)-2-nitroethanol (Table 3, entry 10). 97% isolated yield, 95% ee by HPLC analysis (Chiralcel OD-H column, 1 mL/min, 10% iPrOH in hexane, 230 nm), (R) t_R =14.73 (minor) and (S) t_R =18.85 (major); $[\alpha]_D^{25} = +16.3$ ($c = 2.04$ in EtOH), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 – 7.51 (m, 2H), 7.33 – 7.27 (m, 2H), 5.44 (dd, $J = 9.3, 2.9$ Hz, 1H), 4.57 (dd, $J = 13.5, 9.3$ Hz, 1H), 4.49 (dd, $J = 13.5, 3.2$ Hz, 1H), 2.90 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.2, 132.4, 127.8, 123.1, 81.0, 70.5.



Signaal 1 VWD1 A, Wavelength=230 nm						
Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	14.732	MM	0.494	1805.812	2.555	
2	18.848	BBA	0.709	6.887e4	97.445	

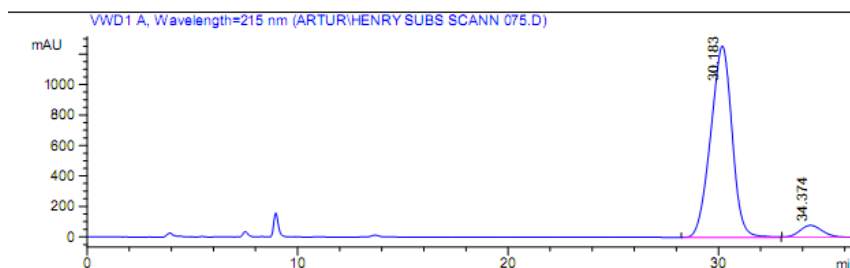
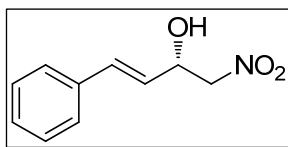


(S)-1-(naphthalen-2-yl)-2-nitroethanol (Table 3, entry 12). 90% isolated yield, 93% ee by HPLC analysis analysis (Chiralcel OD-H column, 1 mL/min, 20% iPrOH in hexane, 254 nm), t_R =18.30 (minor) and t_R =25.68 (major); $[\alpha]_D^{25} = +15.0$ ($c = 1.87$ in EtOH), absolute stereochemistry assigned by comparison of the retention times in HPLC and optical rotation signs with literature data; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 – 7.81 (m, 4H), 7.56 – 7.48 (m, 2H), 7.46 (dd, $J = 8.6, 1.7$ Hz, 1H), 5.61 (d, $J = 9.3$ Hz, 1H), 4.68 (dd, $J = 13.4, 9.5$ Hz, 1H), 4.58 (dd, $J = 13.4, 3.1$ Hz, 1H), 2.96 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 135.5, 133.5, 133.3, 129.2, 128.2, 127.9, 126.9, 126.8, 125.5, 123.3, 81.3, 71.3.

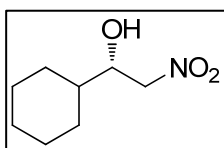


Signaal 1 VWD1 A, Wavelength=254 nm						
Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	18.298	BB	0.632	455.236	3.451	
2	25.676	BB	0.924	1.274e4	96.549	

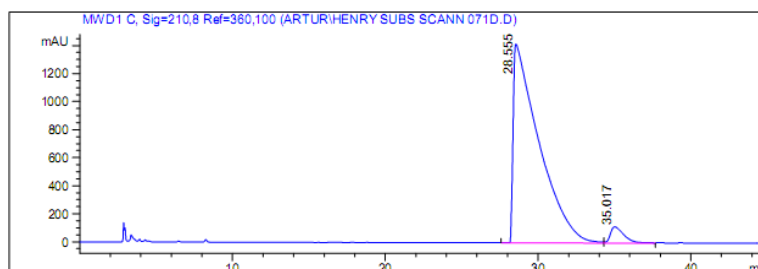
(S,E)-1-nitro-4-phenylbut-3-en-2-ol (Table 3, entry 14). 70% isolated yield, 88% ee by HPLC analysis (Chiralcel OD-H column, 0.8 mL/min, 15% iPrOH in hexane, 215 nm), (S) t_R =30.18 (major) and (R) t_R =34.37 (minor), absolute stereochemistry assigned by comparison of the retention times in HPLC and with literature data; ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.27 (m, 5H), 6.79 (dd, J = 15.9, 1.1 Hz, 1H), 6.15 (dd, J = 15.9, 6.3 Hz, 1H), 5.06 (dd, J = 11.9, 5.8 Hz, 1H), 4.53 (s, 1H), 4.52 (d, J = 1.8 Hz, 1H), 2.63 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 135.6, 133.9, 128.9, 128.7, 126.9, 125.0, 80.0, 69.7.



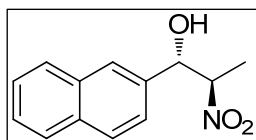
Signaal 1 VWD1 A, Wavelength=215 nm						
Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	30.183	BB	1.100	8.896e4	93.575	
2	34.374	BBA	1.190	6107.897	6.425	



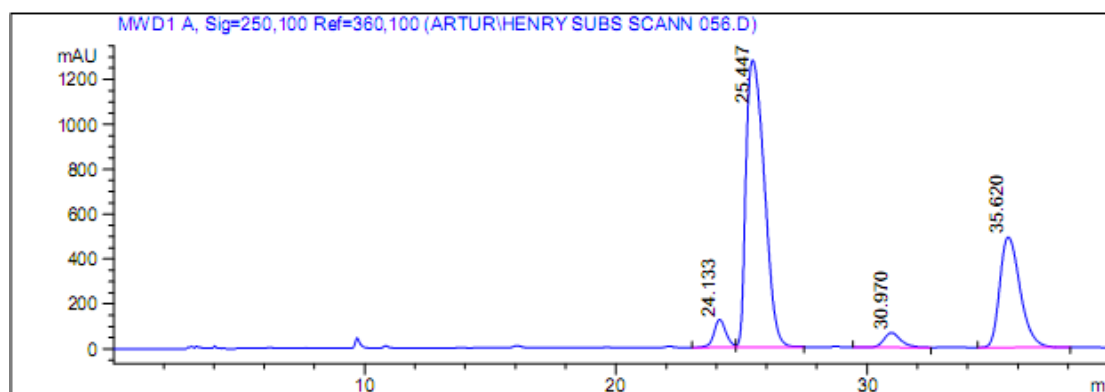
(S)-1-cyclohexyl-2-nitroethanol (Table 3, entry 16). 43% isolated yield, 93% ee by HPLC analysis (Lux 3u Amylose-2 column, 1 mL/min, 2% iPrOH in hexane, 210 nm), (S) t_R =28.56 (major) and (R) t_R =35.02 (minor), absolute stereochemistry assigned by based on other examples in the series; ^1H NMR (400 MHz, CDCl_3) δ 4.42 (dd, J = 13.1, 2.9 Hz, 1H), 4.35 (dd, J = 13.1, 8.9 Hz, 1H), 4.03 (ddd, J = 11.6, 5.8, 2.9 Hz, 1H), 2.48 (d, J = 5.2 Hz, 1H), 1.81 – 1.67 (m, 3H), 1.67 – 1.54 (m, 2H), 1.40 (m, 1H), 1.26 – 0.95 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 79.4, 73.0, 41.5, 28.9, 28.1, 26.2, 26.0, 25.9.



Signaal 1 MWD1 C, Sig=210,8 Ref=360,100						
Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	28.555	VV	1.574	1.663e5	95.938	
2	35.017	VB	0.954	7039.621	4.062	

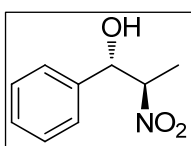


(1S,2R)-1-(naphthalen-2-yl)-2-nitropropan-1-ol (Table 4, entry 2). 86% isolated yield as a mixture of anti : syn (69 : 31), 88% and 80% ee respectively by HPLC analysis (Chiralpak AS-H column, 1 mL/min, 3% ethanol in hexane, 254 nm), anti: $t_R=24.13$ (minor) and $t_R=35.02$ (major), syn: $t_R=30.97$ (minor) and $t_R=35.62$ (major), syn/anti ratio assigned based on chiral HPLC, absolute stereochemistry assigned based on literature data and/or other examples in the series; ^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.79 (m, 5H) (syn/anti), 7.56 – 7.39 (m, 4H) (syn/anti), 5.56 (bs, 1H) (anti), 5.18 (d, $J = 9.0$ Hz, 0.3H) (syn), 4.87 (dq, $J = 9.0, 6.8$ Hz, 0.3H) (syn), 4.79 (qd, $J = 6.8, 3.5$ Hz, 1H) (anti), 2.84 (s, 1H) (anti), 2.71 (s, 0.3H) (syn), 1.51 (d, $J = 6.8$ Hz, 3H) (anti), 1.33 (d, $J = 6.8$ Hz, 1H) (syn). ^{13}C NMR (101 MHz, CDCl_3) δ 135.74 (anti), 135.56 (syn), 133.58 (syn), 133.20 (anti), 133.11 (anti), 133.09 (syn), 129.10 (syn), 128.66 (anti), 128.09 (anti), 128.07 (syn) 127.81 (syn), 127.74 (anti), 126.78 (syn), 126.74 (syn), 126.68 (syn), 126.59 (anti), 126.50 (anti), 125.30 (anti), 123.82 (syn), 123.30 (anti), 88.34 (syn), 87.30 (anti), 76.47 (syn), 73.96 (anti), 16.56 (syn), 12.01 (anti).

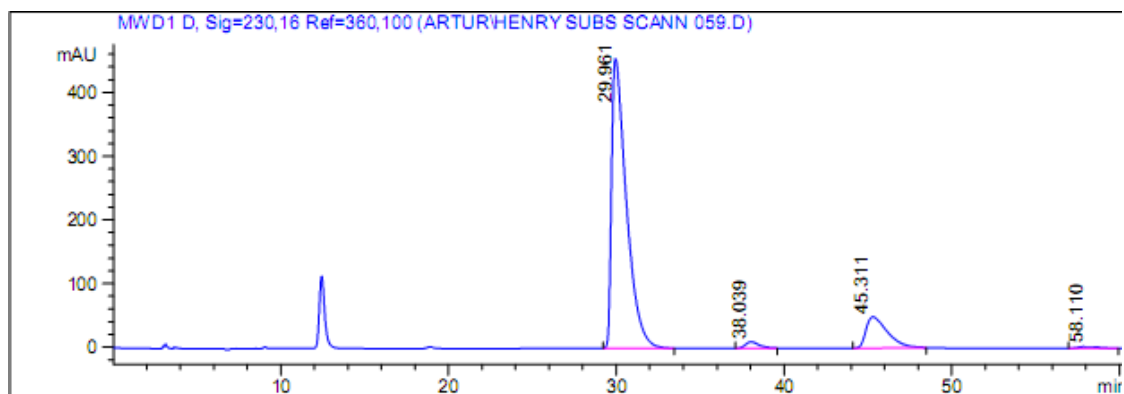


Signaal 1 MWD1 A, Sig=250,100 Ref=360,100

Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	24.133	BV	0.509	4173.939	4.170	
2	25.447	VB	0.849	6.507e4	65.008	
3	30.970	VB	0.709	3046.515	3.044	
4	35.620	VB	0.880	2.780e4	27.778	

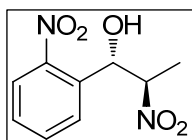


(1S,2R)-2-nitro-1-phenylpropan-1-ol (Table 4, entry 4). 86% isolated yield as a mixture of anti : syn (81 : 19), 96% and 89% ee respectively by HPLC analysis (Chiralpak AS-H column, 1 mL/min, 2% iPrOH in hexane, 210 nm), anti: $t_R=29.96$ (major) and $t_R=38.04$ (minor), syn: $t_R=45.31$ (major) and $t_R=58.10$ (minor), syn/anti ratio assigned based on chiral HPLC, absolute stereochemistry assigned based on literature data and/or other examples in the series; ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.30 (m, 6H) (syn/anti), 5.40 (d, $J = 3.5$ Hz, 1H) (anti), 5.03 (d, $J = 9.0$ Hz, 0.22H) (syn), 4.77 (dq, $J = 9.0, 6.9$ Hz, 0.22H) (syn), 4.70 (qd, $J = 6.8, 3.6$ Hz, 1H) (anti), 2.69 (s, 1H) (anti), 2.55 (s, 1H) (syn), 1.51 (d, $J = 6.8$ Hz, 3H) (anti), 1.32 (d, $J = 6.8$ Hz, 1H) (syn). ^{13}C NMR (101 MHz, CDCl_3) δ 138.39 (anti), 138.28 (syn), 129.26 (syn), 129.05 (syn), 128.77 (anti), 128.56 (anti), 126.93 (syn), 125.95 (anti), 88.40 (syn), 87.43 (anti), 76.30 (syn), 73.88 (anti), 16.49 (syn), 12.08 (anti).

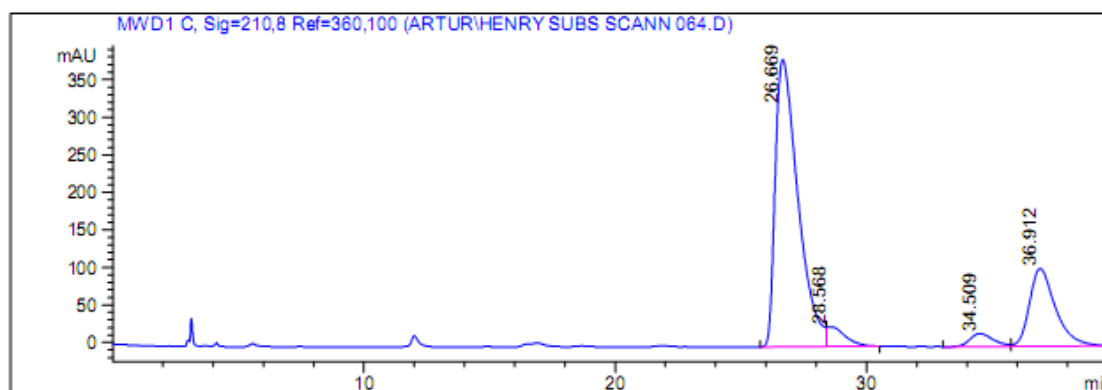


Signaal 1 MWD1 D, Sig=230,16 Ref=360,100

Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	29.961	BB	0.912	2.794e4	84.399	
2	38.039	BB	0.828	574.521	1.736	
3	45.311	BB	1.318	4367.240	13.193	
4	58.110	BB	0.908	222.667	0.673	

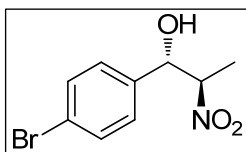


(1S,2R)-2-nitro-1-(2-nitrophenyl)propan-1-ol (Table 4, entry 5). 88% isolated yield as a mixture anti : syn (75 : 25), 89% and 74% ee respectively by HPLC analysis (Chiralpak AS-H column, 1 mL/min, 3% iPrOH in hexane, 210 nm), anti: $t_R=26.67$ (major) and $t_R=28.57$ (minor), syn: $t_R=34.51$ (minor) and $t_R=36.91$ (major), syn/anti ratio assigned based on chiral HPLC, absolute stereochemistry assigned based on literature data and/or other examples in the series; ^1H NMR (400 MHz, CDCl_3) δ 8.11 (dd, $J = 8.2, 1.2$ Hz, 1H) (anti), 8.02 (d, $J = 8.0$ Hz, 0.34H) (syn), 7.94 (dd, $J = 7.9, 0.9$ Hz, 1H) (anti), 7.78 – 7.67 (m, 1.7H) (syn/anti), 7.59 – 7.49 (m, 1.3H) (syn/anti), 6.14 – 6.07 (m, 1H) (anti), 5.73 (t, $J = 6.2$ Hz, 1H) (syn), 5.06 – 4.95 (m, 1.3H) (syn/anti), 3.17 (d, $J = 6.1$ Hz, 0.3H) (syn), 3.13 (d, $J = 4.1$ Hz, 1H) (anti), 1.57 (d, $J = 6.9$ Hz, 1H) (syn), 1.54 (d, $J = 7.0$ Hz, 1H) (anti). ^{13}C NMR (101 MHz, CDCl_3) δ 148.08 (syn), 147.15 (anti), 134.11 (anti), 134.08 (syn), 134.05 (syn), 134.00 (anti), 129.75 (syn), 129.48 (anti), 129.33 (anti), 128.84 (syn), 125.22 (anti), 125.06 (syn), 87.46 (syn), 84.73 (anti), 70.64 (syn), 69.26 (anti), 16.45 (syn), 12.05 (anti).

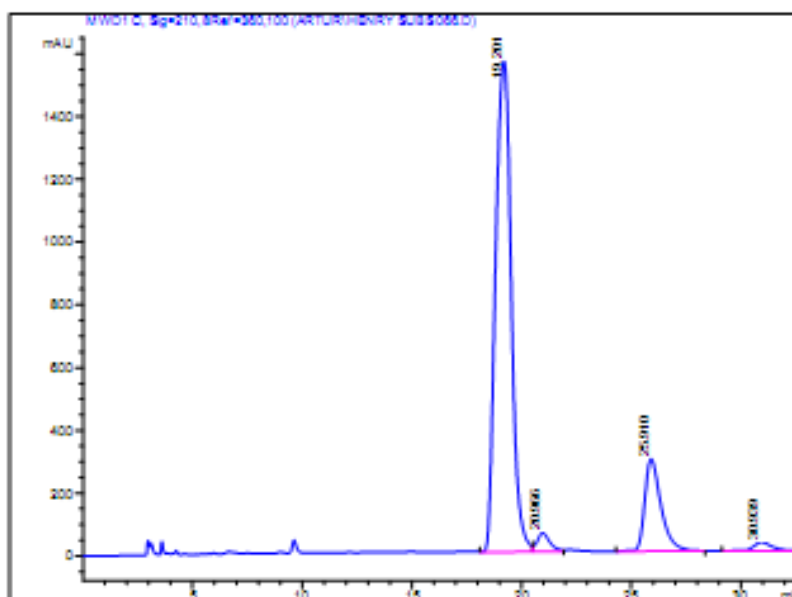


Signaal 1 MWD1 C, Sig=210,8 Ref=360,100

Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	26.669	BV	0.964	2.405e4	70.709	
2	28.568	VB	0.757	1353.191	3.979	
3	34.509	VV	0.945	1113.225	3.273	
4	36.912	VB	1.078	7495.403	22.039	

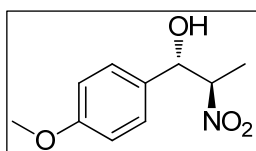


(1S,2R)-1-(4-bromophenyl)-2-nitropropan-1-ol (Table 4, entry 6). 95% isolated yield as a mixture of anti : syn (82 : 18), 94% and 80% ee respectively by HPLC analysis (Chiralpak AS-H column, 1 mL/min, 5% iPrOH in hexane, 210 nm), anti: $t_R=19.20$ (major) and $t_R=20.97$ (minor), syn: $t_R=25.91$ (major) and $t_R=30.94$ (minor), syn/anti ratio assigned based on chiral HPLC, absolute stereochemistry assigned based on literature data and/or other examples in the series; ^1H NMR (400 MHz, CDCl_3) δ 7.58 - 7.45 (m, 2.4H) (syn/anti), 7.31 - 7.20 (m, 2.9H) (syn/anti), 5.37 (t, $J = 3.3$ Hz, 1H) (anti), 5.02 (dd, $J = 8.8, 3.8$ Hz, 0.2H) (syn), 4.77 - 4.69 (m, 0.2H) (syn), 4.65 (qd, $J = 6.8, 3.5$ Hz, 1H) (anti), 2.72 (d, $J = 3.5$ Hz, 1H) (anti), 2.59 (d, $J = 4.0$ Hz, 0.2H) (syn), 1.49 (d, $J = 6.8$ Hz, 1H) (anti), 1.33 (d, $J = 6.9$ Hz, 0.7H) (syn). ^{13}C NMR (101 MHz, CDCl_3) δ 137.33 (anti), 137.23 (syn), 132.20 (syn), 131.93 (anti), 128.56 (syn), 127.67 (anti), 123.28 (syn), 122.56 (anti), 88.07 (syn), 87.12 (anti), 75.57 (syn), 73.22 (anti), 16.38 (syn), 12.02 (anti).

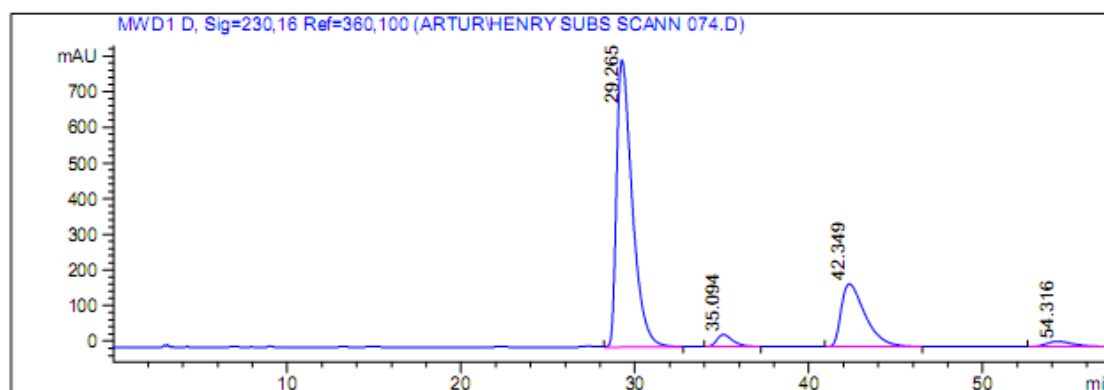


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

[Peak]	RT	Temp	Area	Intens	Intens	Area
[nr]	[min]	[min]	[min]	[%]	[%]	[%]
1	19.201	VV	10.808	7.738e4	80.060	
2	20.966	VV	10.600	2420.492	2.505	
3	25.910	BB	10.774	1.515e4	15.874	
4	30.939	BB	10.917	1701.935	1.761	

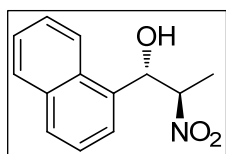


(1*S*,2*R*)-1-(4-methoxyphenyl)-2-nitropropan-1-ol (Table 4, entry 7). 96% isolated yield as a mixture of anti : syn (80 : 20), 92% and 84% ee respectively by HPLC analysis (Chiralpak AS-H column, 1 mL/min, 5% iPrOH in hexane, 210 nm), anti: $t_R=29.27$ (major) and $t_R=35.09$ (minor), syn: $t_R=42.35$ (major) and $t_R=54.32$ (minor), syn/anti ratio assigned based on chiral HPLC, absolute stereochemistry assigned based on literature data and/or other examples in the series; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.31 – 7.25 (m, 3H) (syn/anti), 6.94 – 6.86 (m, 3H) (syn/anti), 5.28 (d, $J = 3.7$ Hz, 1H) (anti), 4.96 (d, $J = 9.1$ Hz, 0.3H) (syn), 4.73 (dq, $J = 9.1, 6.8$ Hz, 0.3H) (syn), 4.66 (qd, $J = 6.8, 4.1$ Hz, 1H) (anti), 3.81 (s, 1H) (syn), 3.80 (s, 3H) (anti), 2.71 (s, 1H) (anti), 2.60 (s, 0.3H) (syn), 1.51 (d, $J = 6.8$ Hz, 3H) (anti), 1.29 (d, $J = 6.8$ Hz, 1H) (syn). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.17 (syn), 159.69 (anti), 130.51 (anti), 130.38 (syn), 128.18 (syn), 127.26 (anti), 114.38 (syn), 114.12 (anti), 88.51 (syn), 87.57 (anti), 75.91 (syn), 73.78 (anti), 55.34 (syn), 55.31 (anti), 16.47 (syn), 12.47 (anti).

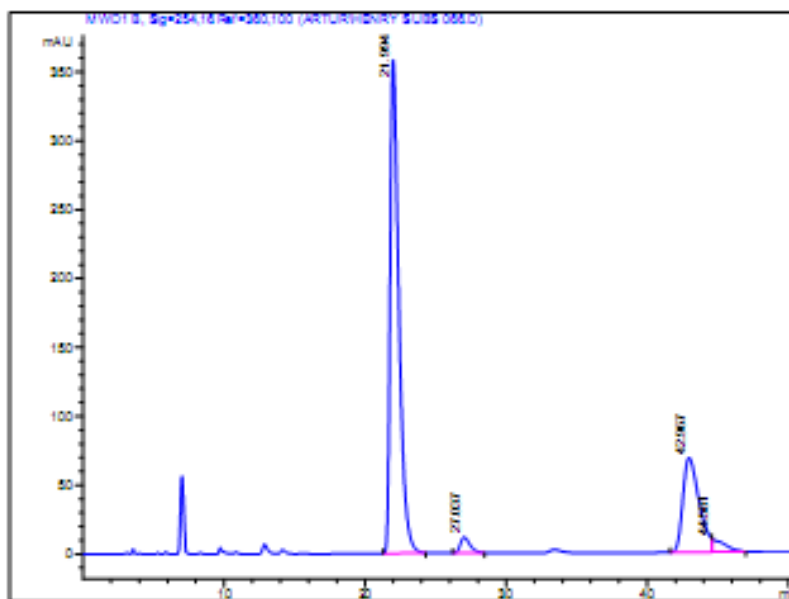


Signaal 1 MWD1 D, Sig=230,16 Ref=360,100

Piigi nr	RT [min]	Tüüp	Laius [min]	Pindala	Pindala %	Nimi
1	29.265	VB	0.956	5.035e4	70.784	
2	35.094	BB	0.992	2218.184	3.118	
3	42.349	BB	1.481	1.698e4	23.868	
4	54.316	BB	1.552	1586.370	2.230	



(1S,2R)-1-(naphthalen-1-yl)-2-nitropropan-1-ol (Table 4, entry 8). 74% isolated yield as a mixture of anti : syn (72 : 28), 93% and 81% ee respectively by HPLC analysis (Chiralpak AS-H column, 1 mL/min, 2% ethanol in hexane, 210 nm), anti: $t_R=21.99$ (major) and $t_R=27.04$ (minor), syn: $t_R=42.97$ (major) and $t_R=44.58$ (minor), syn/anti ratio assigned based on chiral HPLC, absolute stereochemistry assigned based on literature data and/or other examples in the series; ^1H NMR (400 MHz, CDCl_3) δ 8.29 (d, $J = 8.5$ Hz, 0.4H) (syn), 8.01 (d, $J = 8.5$ Hz, 1H) (anti), 7.94 – 7.87 (m, 1.5H) (syn/anti), 7.85 (d, $J = 8.5$ Hz, 1H) (anti), 7.79 (d, $J = 7.2$ Hz, 1H) (anti), 7.64 – 7.46 (m, 5H) (syn/anti), 6.28 (s, 1H) (anti), 5.80 (d, $J = 9.2$ Hz, 0.4H) (syn), 5.13 (dq, $J = 9.2, 6.9$ Hz, 0.4H) (syn), 4.92 (qd, $J = 6.8, 2.4$ Hz, 1H) (anti), 2.71 (s, 1.3H) (syn/anti), 1.44 (d, $J = 6.8$ Hz, 3H) (anti), 1.27 (d, $J = 6.9$ Hz, 1H) (syn). ^{13}C NMR (101 MHz, CDCl_3) δ 134.02 (syn), 133.96 (syn), 133.77 (anti), 133.65 (anti), 130.81 (syn), 129.82 (anti), 129.38 (syn), 129.33 (anti), 129.18 (syn), 129.08 (anti), 127.06 (anti), 126.85 (syn), 126.13 (syn), 125.96 (anti), 125.66 (syn), 125.41 (anti), 125.36 (syn), 124.01 (anti), 123.20 (syn), 121.74 (anti), 88.48 (syn), 85.58 (anti), 73.76 (syn), 70.86 (anti), 16.85 (syn), 11.03 (anti).



Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak nr	RT [min]	T00p	Integ [min]	Area	Area %	Area %
1	21.994	BB	0.649	1.542e4	69.827	
2	27.037	BB	0.712	857.847	2.821	
3	42.967	MF	1.344	8832.080	28.004	
4	44.581	7H	1.004	885.811	2.848	

ESI-MS analysis of the catalytic complex

Ligand **4c** (1.8 mg, 8.56 μmol) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (1.7 mg, 8.56 μmol) were dissolved in EtOH (850 μl) and stirred for 5 min to generate the catalyst. The mixture was diluted (10^{-4} M) and analyzed directly by ESI-MS.

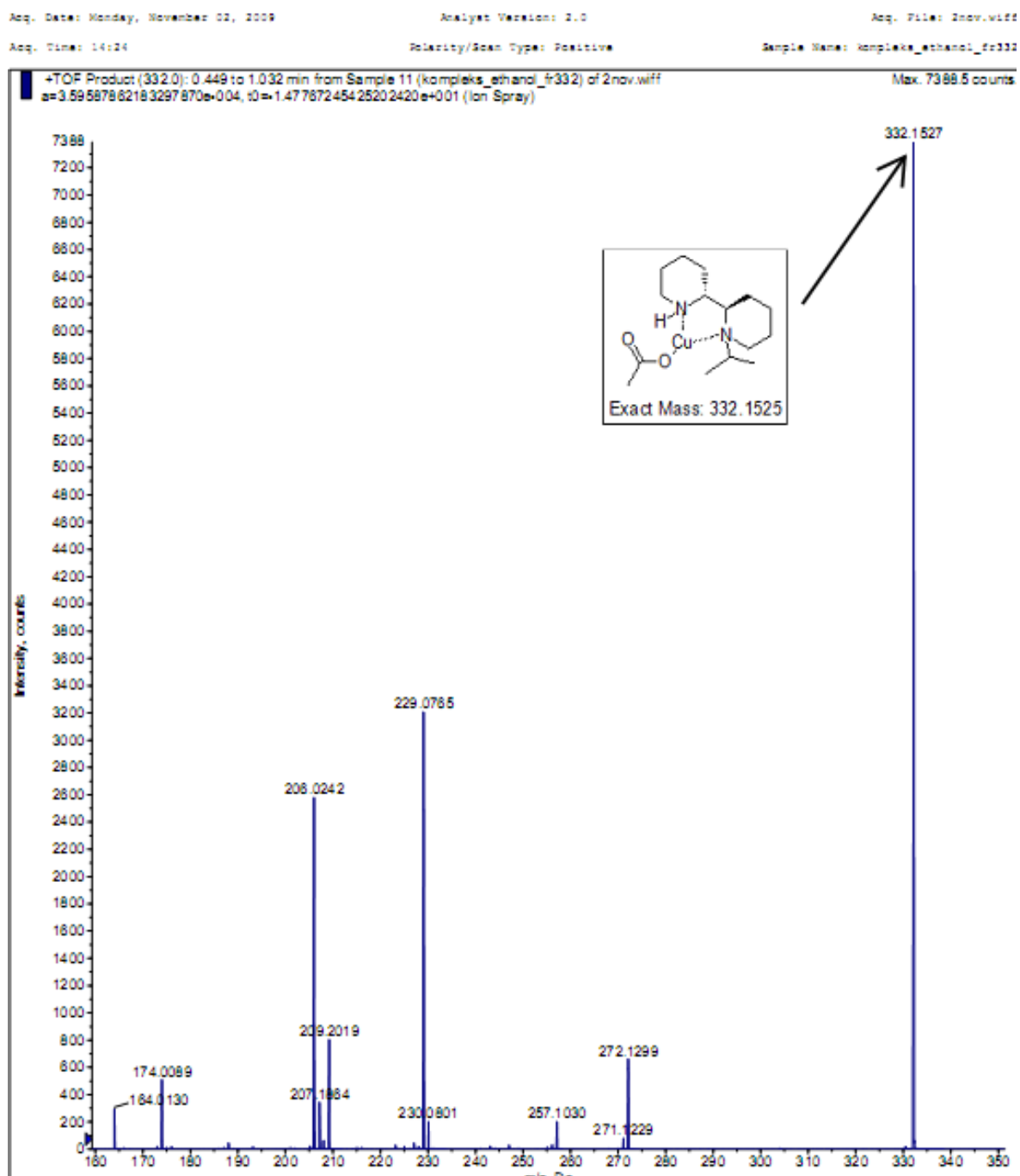


Figure S1. ESI-HRMS analysis of ligand **4c** : $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ complex in ethanol– splitting pattern of peak 332.1527

Computational aspects

Calculations of the geometry and energetic parameters were performed at the B3LYP/6-31+G* in highest level² using Gaussian03 program.³ Continuum solvent effects in case of ethanol were modeled using the Polarized Continuum (overlapping spheres) model (PCM) of Tomasi and coworkers⁴ as implemented in Gaussian.

The calculation procedure is as follows. The initial geometry generated was subjected to conformational analysis with Tinker program package.⁵ The force field chosen was MM3⁶ and the missing copper metal—ligand force field parameters were taken from literature.⁷ The conformers were generated using the SCAN program implemented in Tinker. This program performs a general conformational search for the entire potential energy surface via a basin hopping algorithm,⁸ and it also minimizes geometry of each conformer after its generation. The MM3 force field chosen is known to be quite successful in reproducing molecular IR spectra. All the conformers generated were further minimized using the Gaussian03 program and with the same B3LYP method with initial basis set 6-31G. After removing the duplicate conformers the rest of the stuff was subsequently minimized at the B3LYP/6-31+G* level. Minima were confirmed by the vibrational analysis at the same level of theory and the Gibbs free energy was used to calculate the Boltzmann probability for each conformer.

² Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648-5652

³ Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004

⁴ (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117-129. (b) Miertus, S.; Tomasi, J. *Chem. Phys.* **1982**, *65*, 239-245.

⁵ TINKER version 5.0 was used: <http://dasher.wustl.edu/tinker>.

⁶ Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551–8566.

⁷ Wolohan, P.; Yoo, J.; Welch, M. J.; Reichert, D.E. *J. Med. Chem.* **2005**, *48*, 5561-5569.

⁸ Pappu, R. V.; Hart, R. K.; Ponder, J. W. *J. Phys. Chem. B* **1998**, *102*, 9725–9742.

Energies (in Hartrees) and Boltzmann probabilities of the calculated structures:

Fail	Total energy (in Hartrees)	ΔE kJ/mol	partition function	Boltzmann probability, %
kt1_t_ns_185.log	-2717.565896	0	1	33.17
kt1_t_ns_282.log	-2717.565184	1.87	0.464	15.40
kt1_t_ns_267.log	-2717.564971	2.43	0.369	12.24
kt1_t_ns_261.log	-2717.564945	2.50	0.359	11.90
kt1_t_ns_274.log	-2717.564794	2.89	0.305	10.12
kt1_t_ns_268.log	-2717.564373	4.00	0.194	6.43
kt1_t_ns_95.log	-2717.564293	4.21	0.178	5.90
kt1_t_ns_141.log	-2717.563206	7.06	0.055	1.83
kt1_t_ns_263.log	-2717.562216	9.66	0.019	0.63
kt1_t_ns_228.log	-2717.562201	9.70	0.019	0.62
kt1_t_ns_234.log	-2717.562194	9.72	0.019	0.61
kt1_t_ns_229.log	-2717.562147	9.84	0.018	0.58
kt1_t_ns_98.log	-2717.561285	12.11	0.007	0.23
kt1_t_ns_101.log	-2717.560795	13.39	0.004	0.14
kt1_t_ns_139.log	-2717.560719	13.59	0.004	0.13
kt1_t_ns_102.log	-2717.560343	14.58	0.003	0.08

XYZ coordinates for the calculated conformers

The data below give the coordinates for the calculated structures of bipiperidine derivative **4c** and Cu(OAc)₂ complex described about in XYZ format. In order to view the structures, copy and paste the complete coordinate file. Save the file as filename.xyz and then open this file with molecular viewer.

File name: **kt1_t_ms_185.xyz**

56

C	-0.43460	3.94700	-1.18890
C	0.40190	2.86600	-0.48440
N	-0.19240	1.50670	-0.71780
C	-1.60250	1.44360	-0.18960
C	-2.49260	2.44150	-0.95050
C	-1.92500	3.87190	-0.79590
C	-2.02720	-0.02780	-0.27630
N	-1.01660	-0.93340	0.43820
C	-1.23870	-2.31890	-0.15740
C	-2.66980	-2.84470	0.06490
C	-3.75190	-1.84590	-0.40120
C	-3.47420	-0.40250	0.08350
C	-1.11980	-1.02290	1.97690
C	0.07120	-1.82310	2.53880
C	-1.18830	0.32760	2.70900
H	-0.22070	1.35620	-1.74230
Cu	0.81830	-0.15710	-0.12100
O	1.74070	-1.93050	-0.24150
C	1.78370	-2.15230	-1.53260
O	1.19500	-1.38120	-2.36640
C	2.54770	-3.36190	-2.01820
O	2.58160	0.75880	-0.31420
C	2.97500	1.04760	0.90410
O	2.23830	0.82490	1.92050
C	4.34420	1.66860	1.06650
H	-0.02650	4.93730	-0.94960
H	-0.33500	3.81690	-2.27720
H	1.42870	2.84570	-0.85200
H	0.43380	3.02680	0.59890
H	-1.54380	1.77580	0.84570
H	-2.53730	2.15880	-2.01370
H	-3.51770	2.40930	-0.56330
H	-2.04110	4.18760	0.25170
H	-2.50970	4.57260	-1.40430
H	-1.90080	-0.29280	-1.33950
H	-0.49600	-2.99810	0.25480
H	-1.02940	-2.22650	-1.22710
H	-2.77170	-3.78760	-0.48870
H	-2.82350	-3.09700	1.12150

H	-4.74070	-2.17750	-0.06160
H	-3.78060	-1.83660	-1.50100
H	-4.16920	0.28410	-0.41320
H	-3.65400	-0.30660	1.16130
H	-2.04290	-1.56690	2.20650
H	-0.07080	-1.94290	3.61860
H	0.16590	-2.82060	2.10580
H	1.00620	-1.28120	2.37210
H	-1.15100	0.12220	3.78490
H	-2.11760	0.87240	2.52540
H	-0.32800	0.95940	2.46800
H	3.35770	-3.04400	-2.68470
H	2.96740	-3.92590	-1.18390
H	1.88400	-4.01050	-2.60100
H	4.25370	2.64170	1.56250
H	4.96380	1.03370	1.71020
H	4.83840	1.79680	0.10250

File name: **kt1_t_ns_282.xyz**

56

C	0.14600	-2.92800	1.35100
C	0.39400	-2.32000	2.73800
N	1.18800	-1.06400	2.63900
C	2.50100	-1.29500	1.96400
C	2.29500	-1.82900	0.54000
C	1.45700	-3.12100	0.57400
C	3.27200	0.02500	2.08900
N	3.45100	0.35100	3.55500
C	3.99900	1.73800	3.65500
C	5.30900	1.96100	2.88700
C	5.14400	1.58900	1.40700
C	4.54100	0.18300	1.23200
C	4.13300	-0.69600	4.43700
C	5.42000	-1.36800	3.92600
C	4.36600	-0.14800	5.85200
H	0.64500	-0.41500	2.04000
C	1.44900	0.17600	4.27700
O	1.50000	1.76600	5.46900
C	0.92300	2.71100	4.81300
O	0.54800	2.59000	3.62200
C	0.70200	4.02800	5.54600
O	-0.31400	-0.37300	5.05900
C	-0.02000	-1.21500	5.98900
O	1.15100	-1.59700	6.22300
C	-1.17800	-1.75900	6.81700
H	-0.38000	-3.88400	1.46900
H	-0.52600	-2.26400	0.78600
H	-0.54500	-2.08100	3.24100
H	0.95200	-3.01300	3.37800

H	3.00400	-2.08000	2.54100
H	1.79100	-1.06300	-0.07000
H	3.26500	-2.02900	0.07100
H	2.04900	-3.91700	1.05100
H	1.24700	-3.45600	-0.44900
H	2.58600	0.81000	1.73100
H	4.09800	2.00400	4.70700
H	3.22900	2.39500	3.23700
H	5.58000	3.02100	2.98500
H	6.12800	1.39100	3.34100
H	6.10600	1.65200	0.88200
H	4.47600	2.32200	0.93000
H	4.25600	0.04600	0.18200
H	5.28700	-0.58500	1.45400
H	3.38800	-1.49400	4.54000
H	5.73600	-2.08900	4.69100
H	5.27300	-1.93100	3.00200
H	6.24300	-0.66400	3.77900
H	4.57400	-0.99400	6.51600
H	3.48700	0.37100	6.24300
H	5.22900	0.52600	5.89700
H	1.18500	4.84100	4.99200
H	-0.37100	4.25000	5.57800
H	1.09500	3.99800	6.56500
H	-1.22000	-2.85000	6.71300
H	-1.00200	-1.54100	7.87700
H	-2.13500	-1.32900	6.51300

File name: **kt1_t_ns_267.xyz**
56

C	0.27900	-2.00900	0.26900
C	0.33600	-1.72100	1.77400
N	1.33000	-0.65400	2.08000
C	2.69800	-1.02100	1.59800
C	2.69700	-1.24400	0.07900
C	1.67000	-2.32700	-0.29900
C	3.63200	0.07700	2.12000
N	3.56300	0.10100	3.63100
C	4.30300	1.31100	4.10800
C	5.75800	1.38900	3.62900
C	5.83400	1.32700	2.09800
C	5.05800	0.12300	1.53700
C	3.87300	-1.19800	4.37800
C	5.09500	-2.02900	3.94400
C	3.92900	-0.95700	5.89300
H	1.03600	0.18500	1.54800
C	1.44400	0.18200	3.96600
O	1.55800	1.47600	5.46000
C	1.24000	2.62500	4.97200

O	1.02300	2.81200	3.75000
C	1.15200	3.78700	5.94700
O	-0.46500	-0.21000	4.39000
C	-0.47200	-1.28600	5.10400
O	0.56700	-1.93100	5.37300
C	-1.82500	-1.76900	5.60100
H	-0.41300	-2.84100	0.08700
H	-0.13800	-1.13000	-0.24500
H	-0.63300	-1.38900	2.15400
H	0.63000	-2.61500	2.33700
H	2.94100	-1.97800	2.07200
H	2.45900	-0.29700	-0.43100
H	3.69600	-1.54800	-0.25300
H	2.01100	-3.29600	0.09400
H	1.62100	-2.42900	-1.39000
H	3.17100	1.03400	1.82400
H	4.23300	1.36000	5.19400
H	3.75100	2.17300	3.71700
H	6.18300	2.33500	3.99200
H	6.35600	0.58800	4.07900
H	6.87800	1.29000	1.76300
H	5.40200	2.25100	1.68500
H	4.97300	0.22700	0.44900
H	5.60700	-0.80400	1.72000
H	2.99300	-1.82700	4.20200
H	5.13100	-2.91700	4.58700
H	5.02700	-2.38600	2.91300
H	6.04200	-1.49600	4.06700
H	3.85500	-1.92800	6.39500
H	3.10100	-0.33700	6.24400
H	4.87500	-0.49700	6.20100
H	1.90200	4.54200	5.68200
H	0.16900	4.26400	5.86300
H	1.31400	3.46500	6.97800
H	-2.06200	-2.73100	5.13000
H	-1.78100	-1.94100	6.68300
H	-2.62100	-1.05500	5.37700

File name: **kt1_t_ns_261.xyz**

56

C	0.40200	-2.26500	0.32800
C	0.44900	-2.15600	1.85900
N	1.22200	-0.95800	2.28200
C	2.61900	-0.98800	1.75200
C	2.61000	-0.99700	0.21800
C	1.80600	-2.20700	-0.29300
C	3.35500	0.17600	2.42600
N	3.29500	-0.01300	3.92800
C	3.85400	1.20800	4.58200

C	5.27200	1.58500	4.13100
C	5.33300	1.74800	2.60600
C	4.75200	0.52500	1.87700
C	3.77200	-1.35100	4.48800
C	5.12700	-1.90700	4.00700
C	3.73500	-1.35000	6.02300
H	0.75600	-0.13300	1.85700
C	1.19200	-0.23100	4.22700
O	0.90000	1.38200	5.27300
C	0.89500	1.46700	6.56400
O	1.19100	0.54500	7.34600
C	0.48800	2.83000	7.12400
O	-0.36600	-1.20900	4.85400
C	-1.54600	-0.84300	4.47200
O	-1.77400	0.02000	3.59900
C	-2.70900	-1.54200	5.17100
H	-0.10700	-3.19700	0.04900
H	-0.21100	-1.43900	-0.06500
H	-0.55400	-2.07500	2.28100
H	0.93300	-3.03500	2.30400
H	3.04900	-1.94200	2.07800
H	2.17200	-0.05800	-0.15500
H	3.63700	-1.04800	-0.16200
H	2.35400	-3.12800	-0.04100
H	1.73600	-2.17200	-1.38700
H	2.73900	1.07500	2.25100
H	3.79900	1.08100	5.66300
H	3.17100	2.02400	4.32800
H	5.53800	2.53000	4.62300
H	6.00500	0.84300	4.47100
H	6.36400	1.92500	2.27600
H	4.75300	2.63900	2.32100
H	4.64700	0.75800	0.81100
H	5.43800	-0.32400	1.94400
H	3.01300	-2.07000	4.16000
H	5.29000	-2.86400	4.51600
H	5.15400	-2.10700	2.93300
H	5.96400	-1.25100	4.26100
H	3.77300	-2.39000	6.36700
H	2.82800	-0.88900	6.42700
H	4.60200	-0.83500	6.45300
H	-0.42800	2.71500	7.71600
H	1.27000	3.19600	7.80000
H	0.31400	3.56400	6.33400
H	-3.24200	-0.80900	5.79000
H	-3.41800	-1.91900	4.42600
H	-2.37000	-2.36300	5.80700

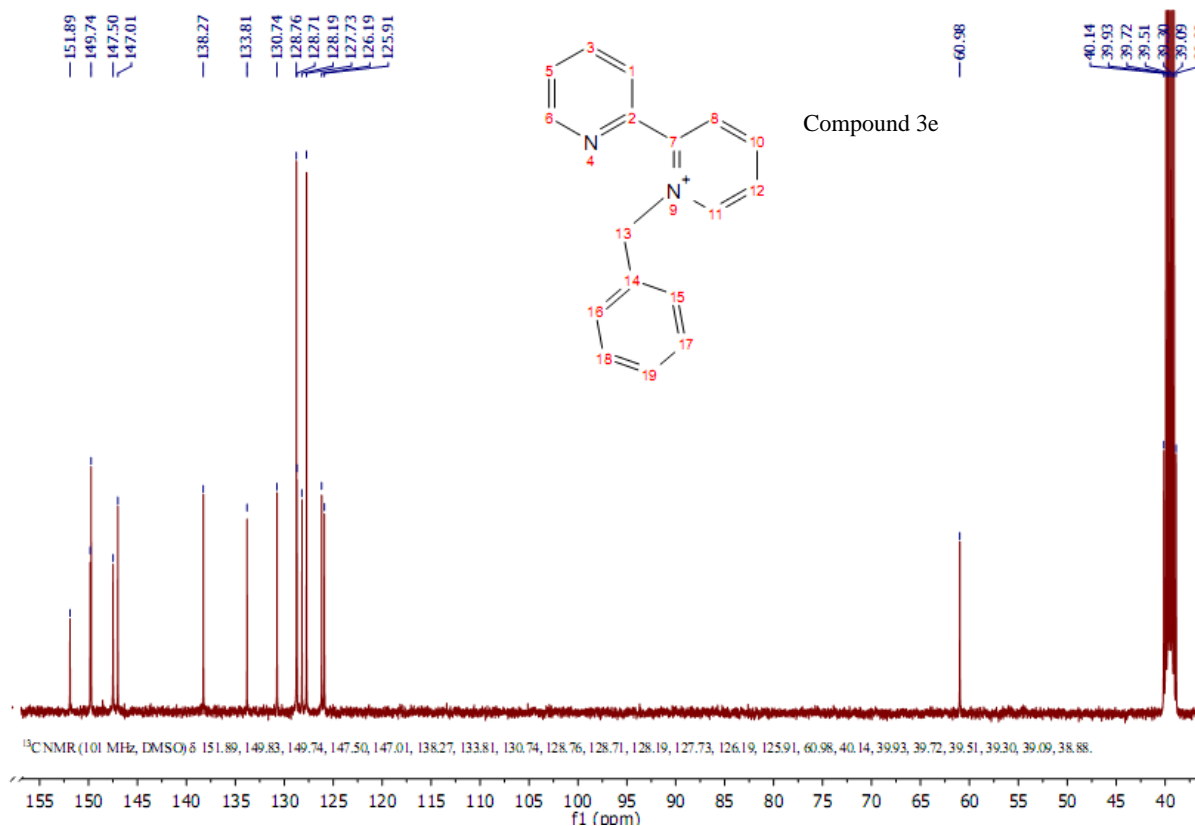
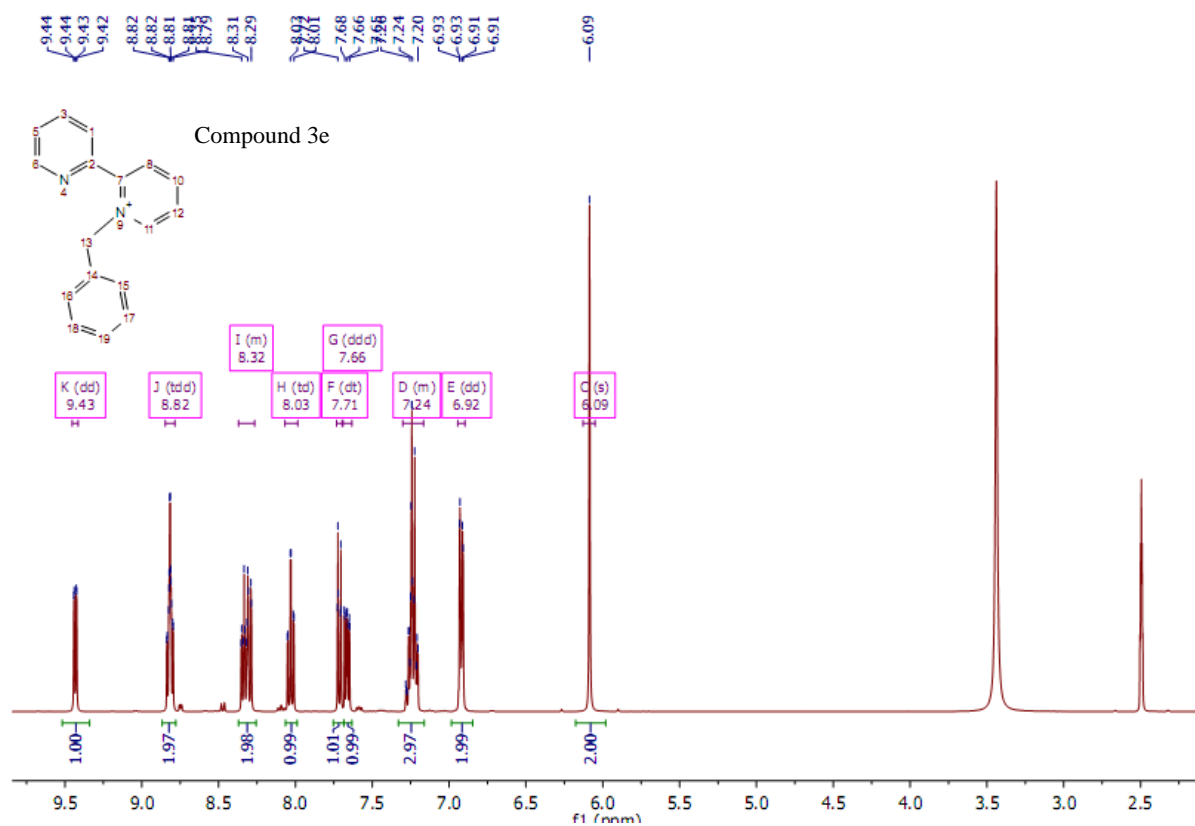
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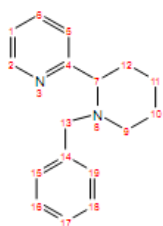
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C	0.40100	-1.67800	-0.03700
C	0.34400	-1.56900	1.49100
N	1.35100	-0.60000	2.00000
C	2.73800	-0.98200	1.59300
C	2.85800	-1.02600	0.06200
C	1.82100	-2.00000	-0.52600
C	3.67900	0.01300	2.29100
N	3.45800	0.03700	3.79600
C	4.00100	1.37000	4.24800
C	5.49600	1.55900	3.93500
C	5.83200	1.28000	2.45900
C	5.17400	-0.01300	1.93600
C	4.12300	-1.07700	4.60600
C	3.68800	-1.01300	6.08000
C	3.88200	-2.50400	4.09600
H	1.13700	0.31700	1.56800
C	1.35600	-0.07500	3.99700
O	1.26300	1.10200	5.61600
C	0.86600	2.23600	5.16000
O	0.69700	2.46000	3.93600
C	0.62100	3.34600	6.17500
O	-0.51700	-0.63400	4.31400
C	-0.54400	-1.80300	4.85500
O	0.48300	-2.47500	5.09900
C	-1.92100	-2.37000	5.18500
H	-0.30900	-2.44700	-0.36800
H	0.06500	-0.72600	-0.47600
H	-0.64000	-1.23600	1.83100
H	0.54900	-2.53700	1.96300
H	2.88200	-1.99600	1.96400
H	2.70800	-0.01500	-0.34900
H	3.86700	-1.34400	-0.22500
H	2.08600	-3.02500	-0.22700
H	1.86200	-1.97300	-1.62300
H	3.31400	1.00000	1.96300
H	3.81000	1.48600	5.31300
H	3.41100	2.13500	3.73600
H	5.75800	2.59500	4.19000
H	6.10700	0.92500	4.58800
H	6.92000	1.23600	2.32100
H	5.47000	2.11700	1.84500
H	5.29200	-0.06100	0.84900
H	5.66600	-0.90500	2.34400
H	5.20400	-0.90300	4.56700
H	4.25900	-1.76400	6.63800
H	3.87600	-0.04700	6.55300
H	2.62500	-1.24900	6.18800

H	4.35200	-3.19300	4.80800
H	4.34400	-2.69900	3.12400
H	2.81700	-2.75200	4.06100
H	1.35300	4.14700	6.01500
H	-0.37400	3.77700	6.01800
H	0.70700	2.98300	7.20200
H	-2.11200	-3.24300	4.54900
H	-1.93900	-2.71400	6.22500
H	-2.71300	-1.63400	5.02800

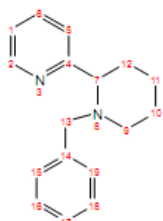
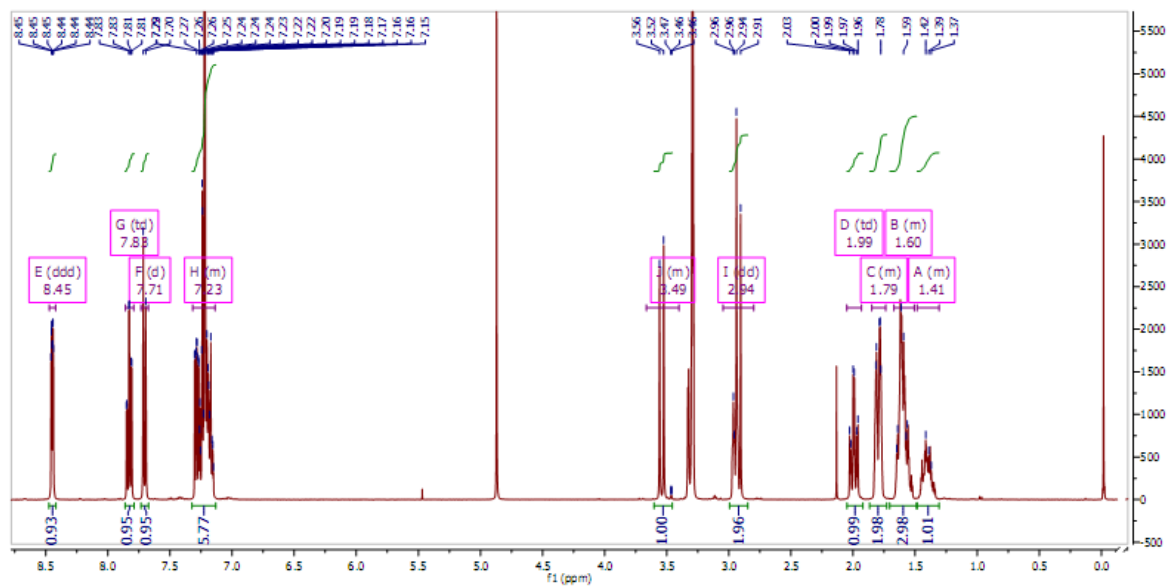
^1H and ^{13}C NMR spectra





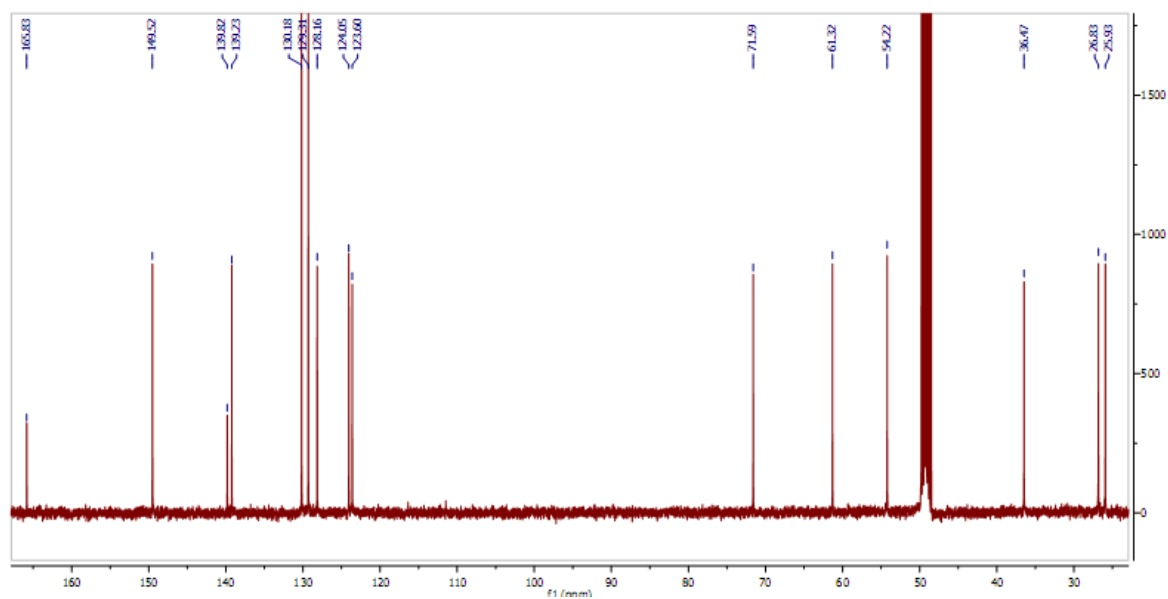
Compound 3a

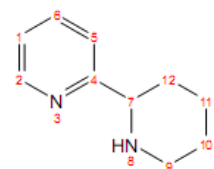
^1H NMR (400 MHz, MeOD) δ 8.45 (ddd, $J = 5.0, 1.7, 0.9$ Hz, 1H), 7.83 (td, $J = 7.7, 1.7$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.32 – 7.14 (m, 6H), 3.66 – 3.40 (m, 1H), 2.94 (dd, $J = 15.3, 8.0$ Hz, 2H), 1.99 (td, $J = 11.6, 3.6$ Hz, 1H), 1.85 – 1.74 (m, 2H), 1.67 – 1.51 (m, 3H), 1.48 – 1.31 (m, 1H).



Compound 3a

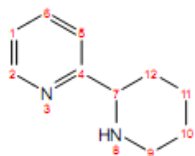
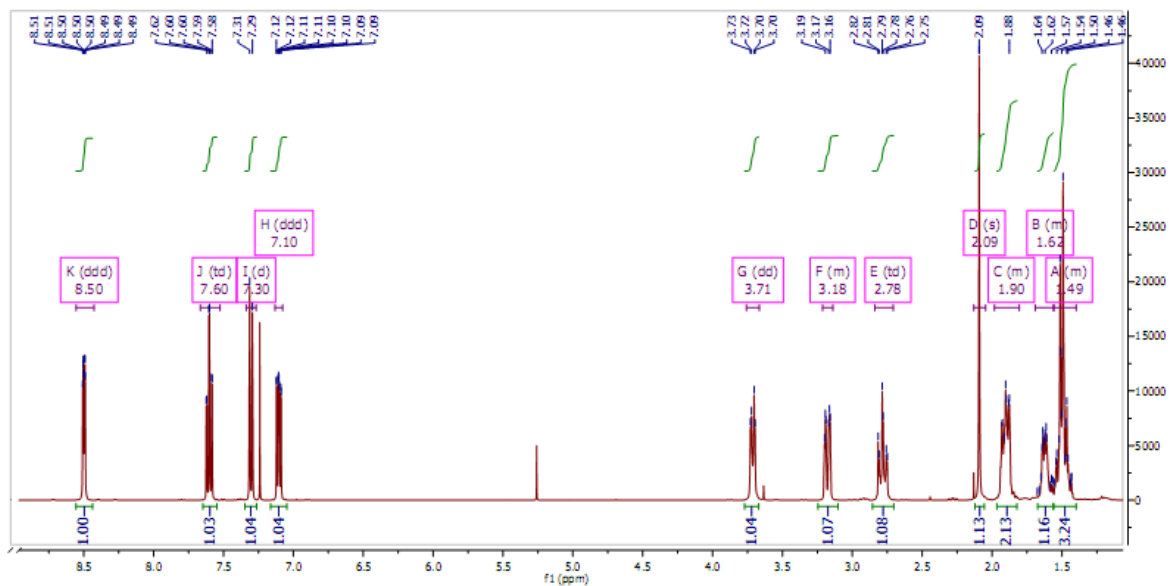
^{13}C NMR (101 MHz, MeOD) δ 165.83, 149.52, 139.82, 139.23, 130.18, 129.31, 128.16, 124.05, 123.60, 71.59, 61.32, 54.22, 36.47, 26.83, 25.93.





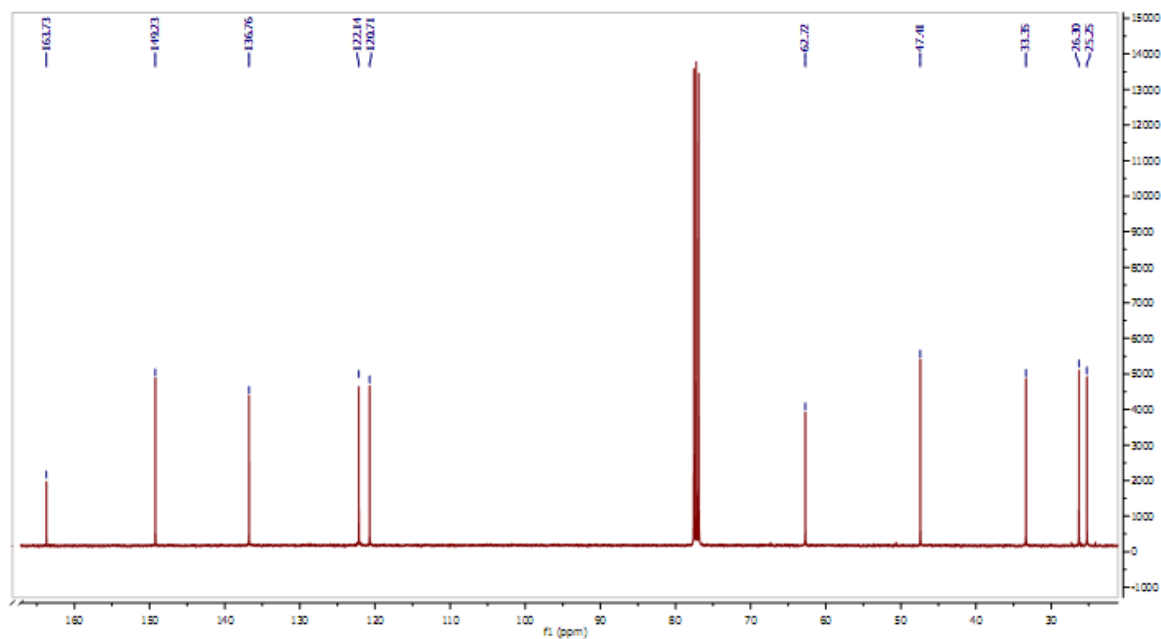
Compound 3b

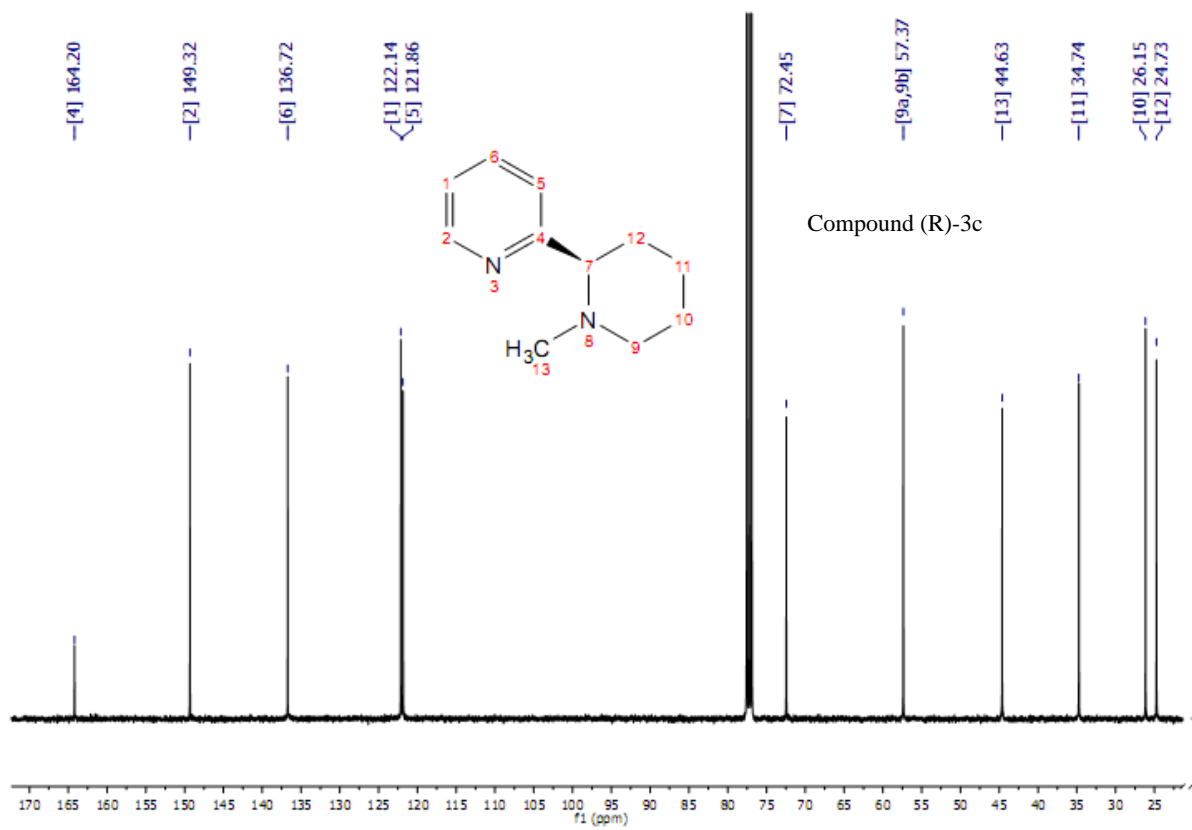
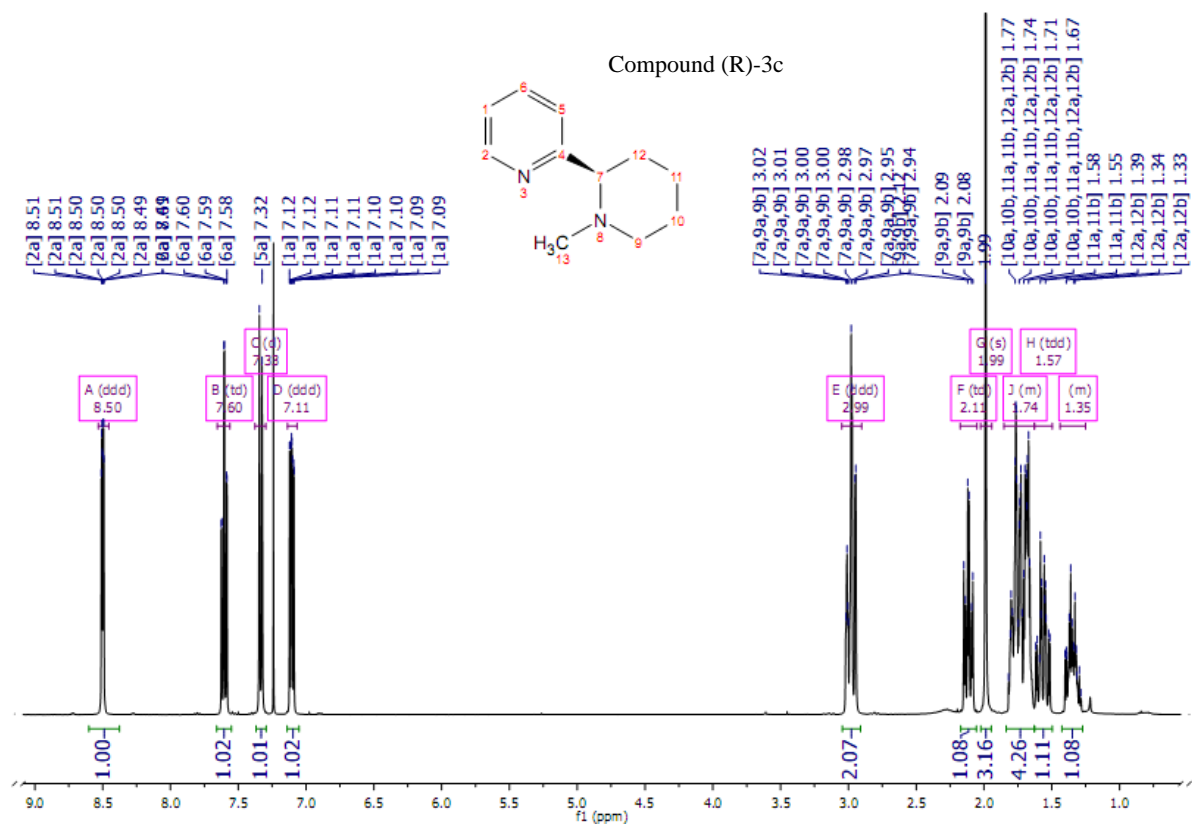
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.50 (ddd, $J = 4.8, 1.7, 0.9$ Hz, 1H), 7.60 (td, $J = 7.7, 1.8$ Hz, 1H), 7.30 (d, $J = 7.9$ Hz, 1H), 7.10 (ddd, $J = 7.5, 4.9, 1.1$ Hz, 1H), 3.71 (dd, $J = 10.3, 2.6$ Hz, 1H), 3.21 – 3.14 (m, 1H), 2.78 (td, $J = 11.7, 3.0$ Hz, 1H), 2.09 (s, 1H), 1.98 – 1.81 (m, 2H), 1.69 – 1.56 (m, 1H), 1.56 – 1.40 (m, 3H).



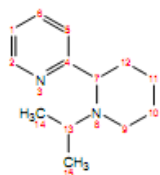
Compound 3b

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.73, 149.23, 136.76, 122.14, 120.71, 62.72, 47.41, 33.35, 26.30, 25.25.

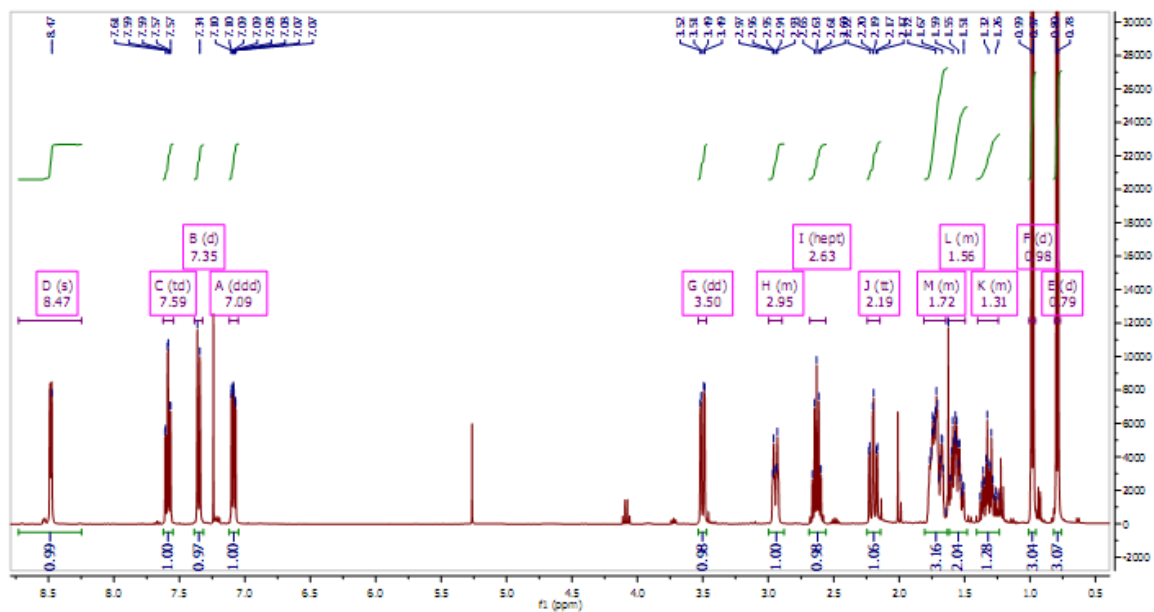




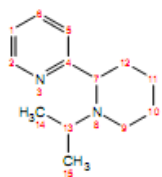
Compound 3d



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.47 (s, 1H), 7.59 (td, $J = 7.7, 1.8$ Hz, 1H), 7.35 (d, $J = 7.9$ Hz, 1H), 7.09 (ddd, $J = 7.4, 4.9, 1.2$ Hz, 1H), 3.50 (dd, $J = 11.0, 2.8$ Hz, 1H), 3.00 – 2.89 (m, 1H), 2.63 (hept, $J = 6.7$ Hz, 1H), 2.19 (tt, $J = 9.5, 4.9$ Hz, 1H), 1.81 – 1.64 (m, 3H), 1.63 – 1.49 (m, 2H), 1.40 – 1.24 (m, 1H), 0.98 (d, $J = 6.8$ Hz, 3H), 0.79 (d, $J = 6.5$ Hz, 3H).



Compound 3d



$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.93, 149.19, 136.57, 122.00, 121.88, 67.50, 49.33, 43.98, 35.81, 26.29, 25.29, 21.46, 12.61.

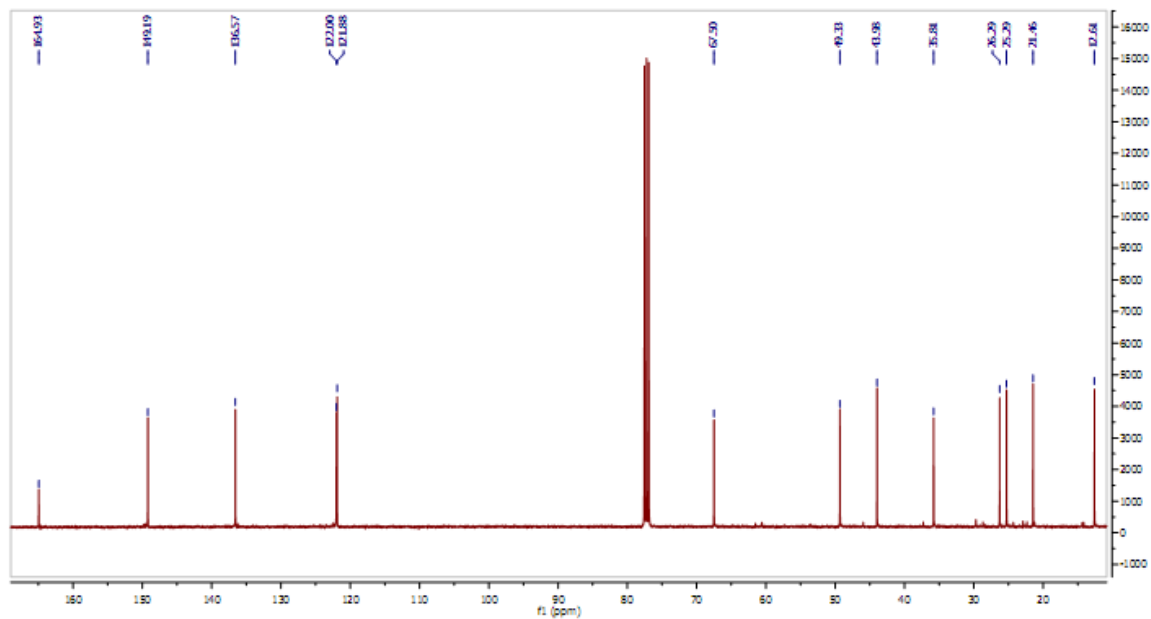
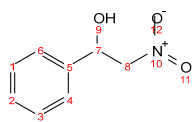
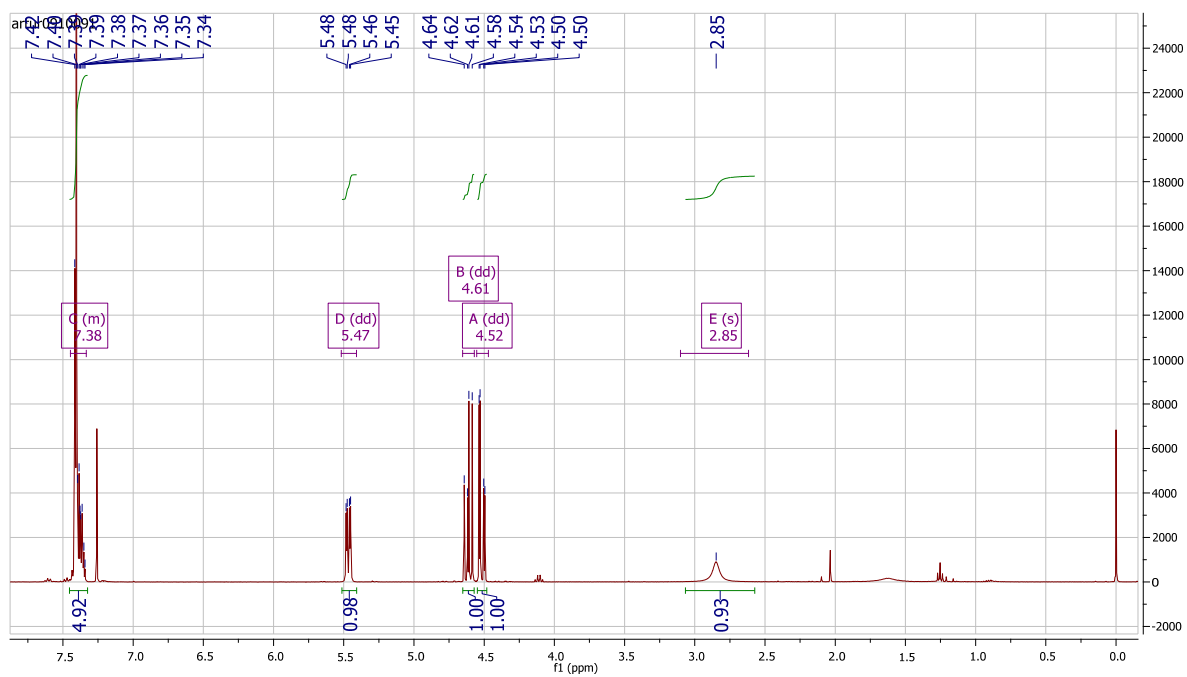


Table 3, entry 2



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 – 7.33 (m, 5H), 5.47 (dd, $J = 9.6, 3.0$ Hz, 1H), 4.61 (dd, $J = 13.4, 9.6$ Hz, 1H), 4.52 (dd, $J = 13.4, 3.0$ Hz, 1H), 2.85 (s, 1H).



$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.21, 129.19, 129.14, 126.07, 81.35, 71.14.

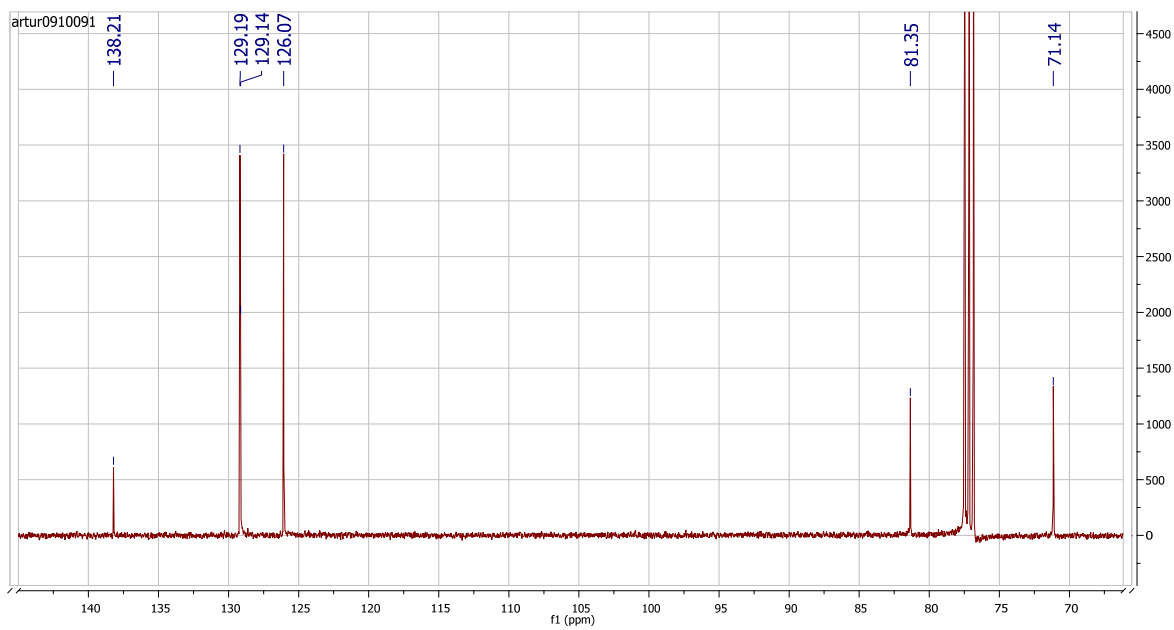
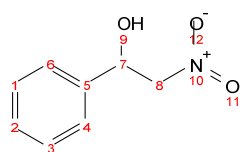
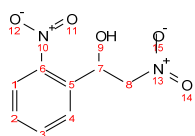
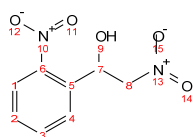
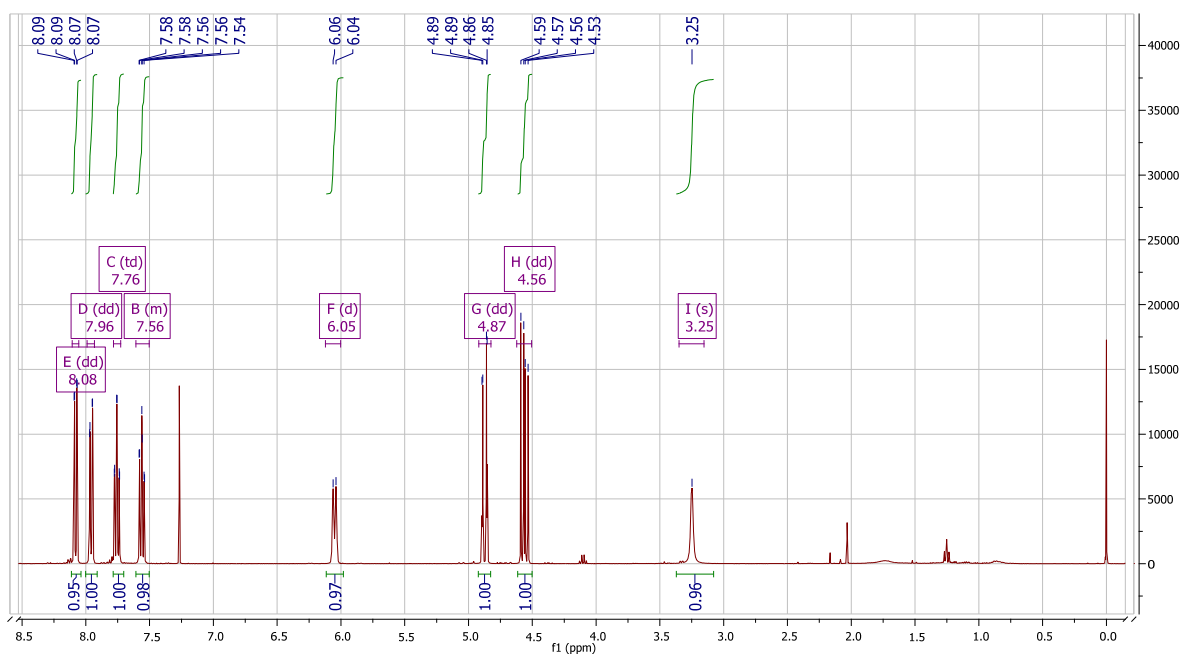


Table 3, entry 4



^1H NMR (400 MHz, CDCl_3) δ 8.08 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.96 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.76 (td, $J = 7.5, 1.0$ Hz, 1H), 7.61 – 7.50 (m, 1H), 6.05 (d, $J = 9.0$ Hz, 1H), 4.87 (dd, $J = 13.8, 2.3$ Hz, 1H), 4.56 (dd, $J = 13.8, 9.1$ Hz, 1H), 3.25 (s, 1H).



^{13}C NMR (101 MHz, CDCl_3) δ 134.61, 134.17, 129.91, 128.89, 125.23, 80.23, 66.98.

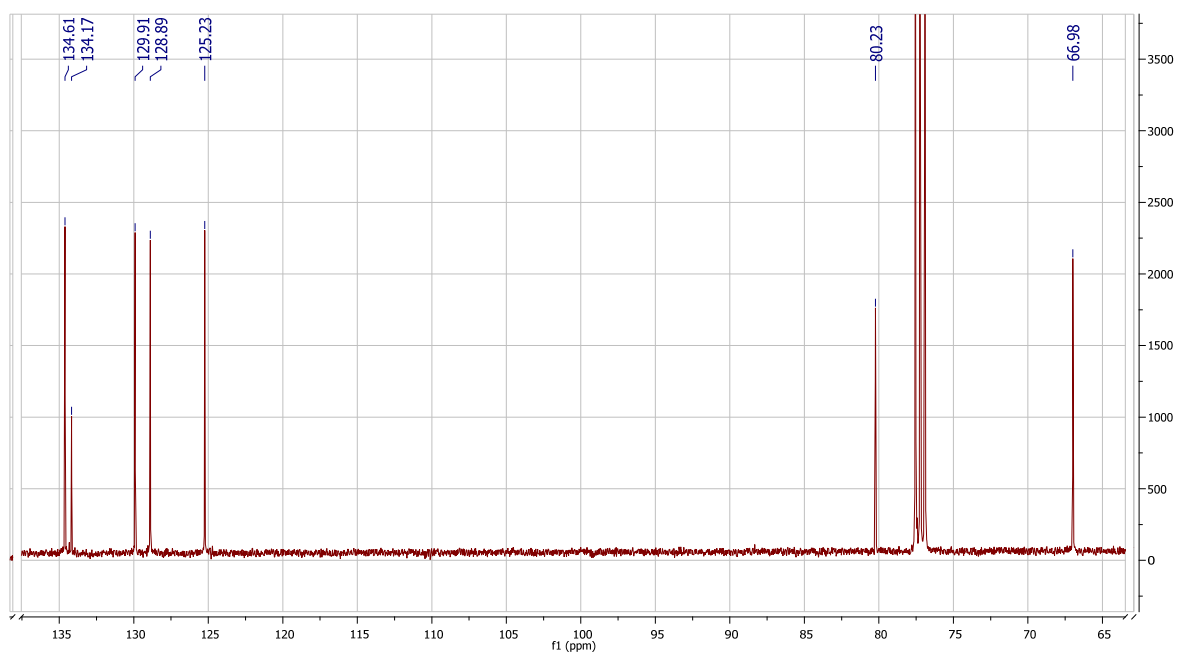
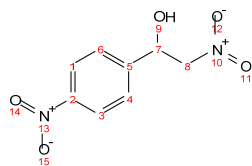
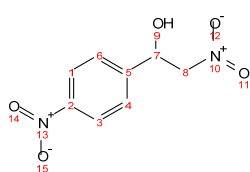
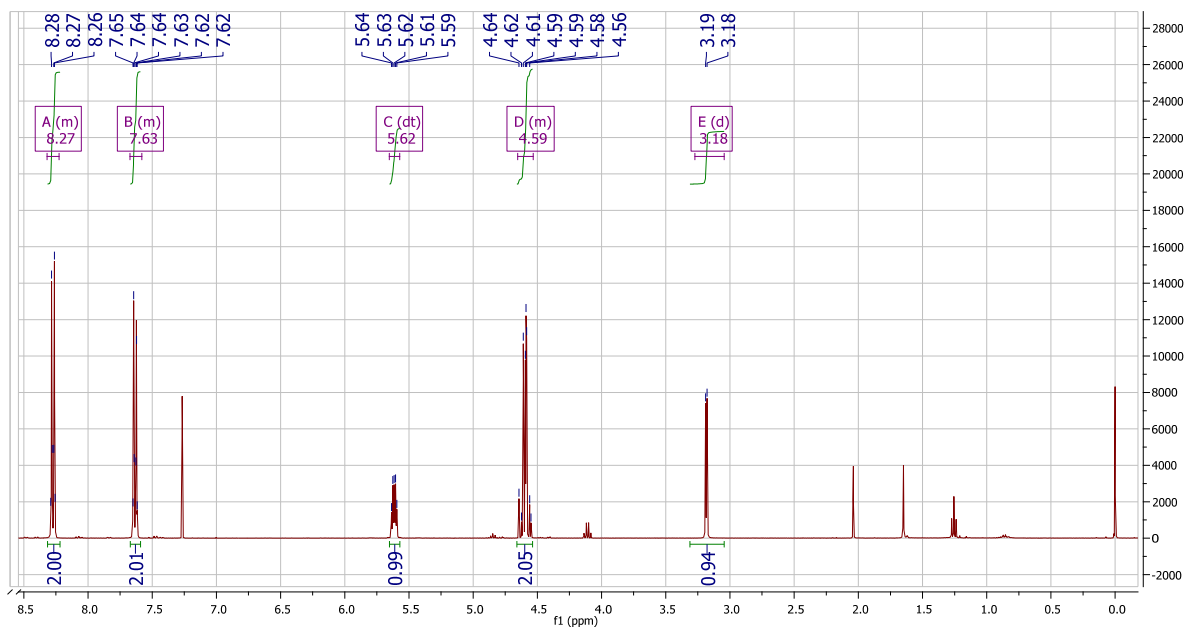


Table 3, entry 6



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.32 – 8.23 (m, 1H), 7.67 – 7.58 (m, 1H), 5.62 (dt, J = 8.3, 4.1 Hz, 1H), 4.65 – 4.53 (m, 1H), 3.18 (d, J = 4.2 Hz, 1H).



$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.29, 145.04, 127.08, 124.35, 80.71, 70.09.

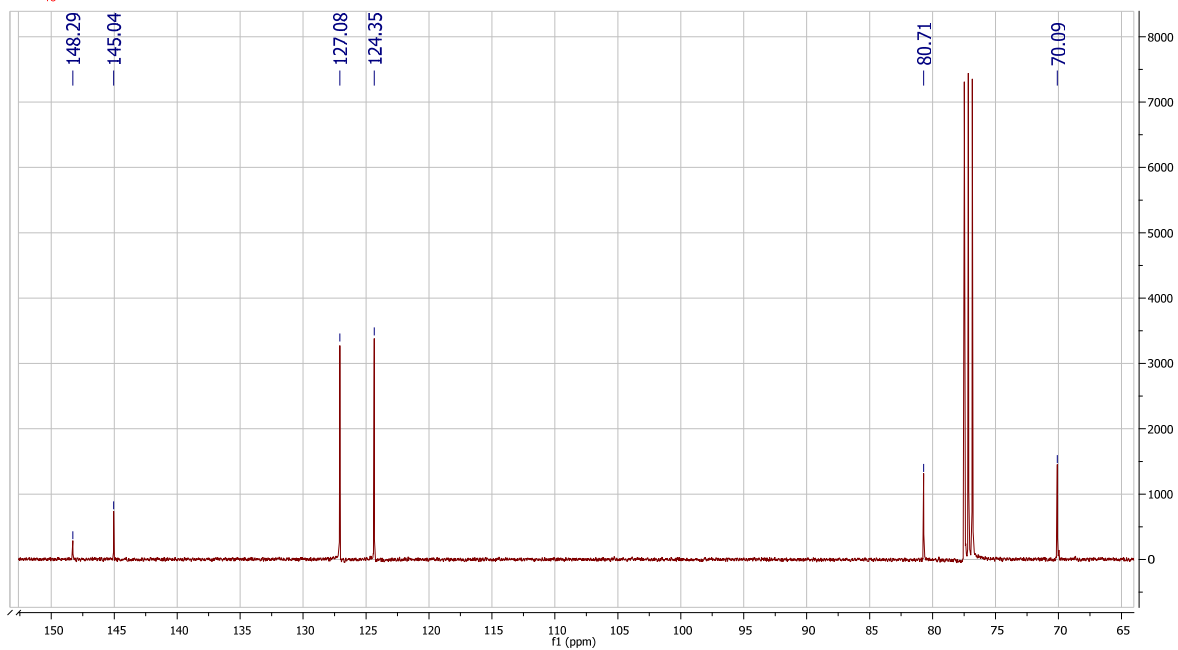
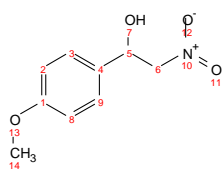
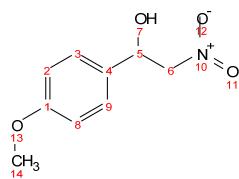
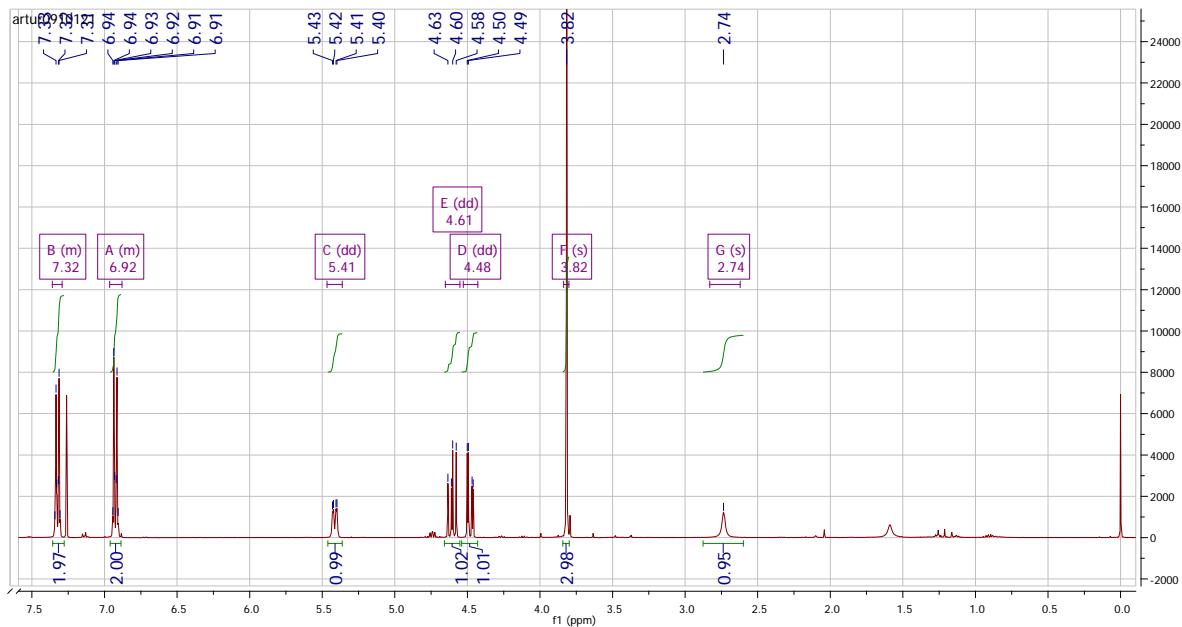


Table 3, entry 8



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 – 7.29 (m, 1H), 6.96 – 6.88 (m, 1H), 5.41 (dd, $J = 9.6, 2.6$ Hz, 1H), 4.61 (dd, $J = 13.2, 9.6$ Hz, 1H), 4.48 (dd, $J = 13.2, 3.1$ Hz, 1H), 3.82 (s, 1H), 2.74 (s, 1H).



$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.21, 130.30, 127.43, 114.55, 81.38, 70.82, 55.50.

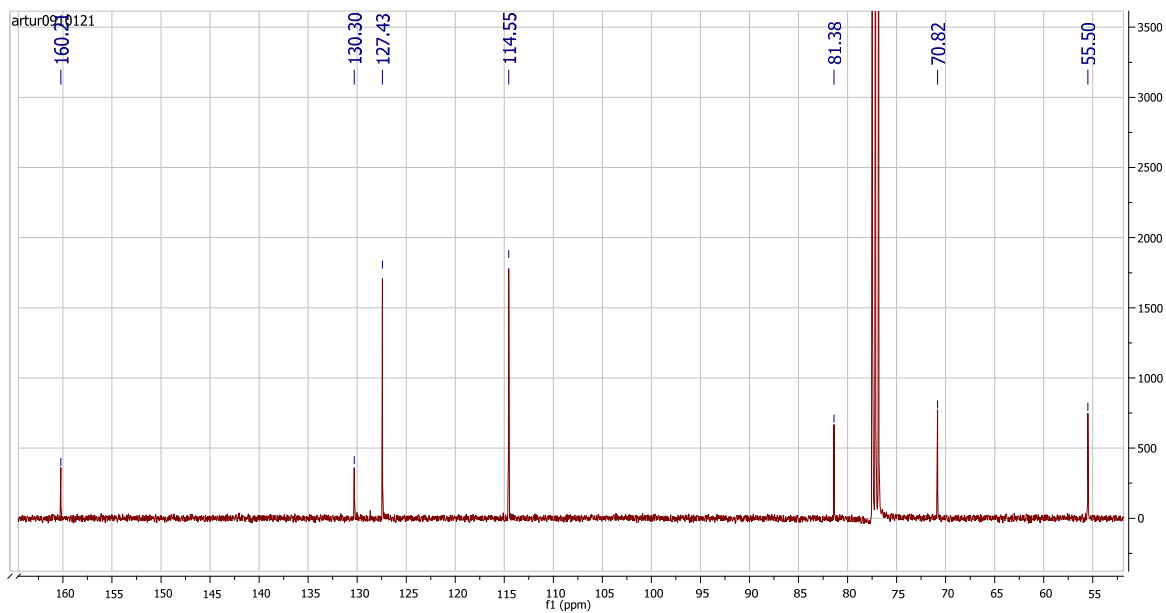
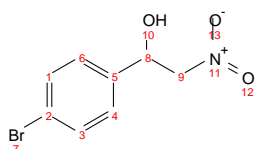
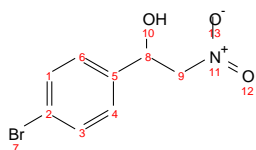
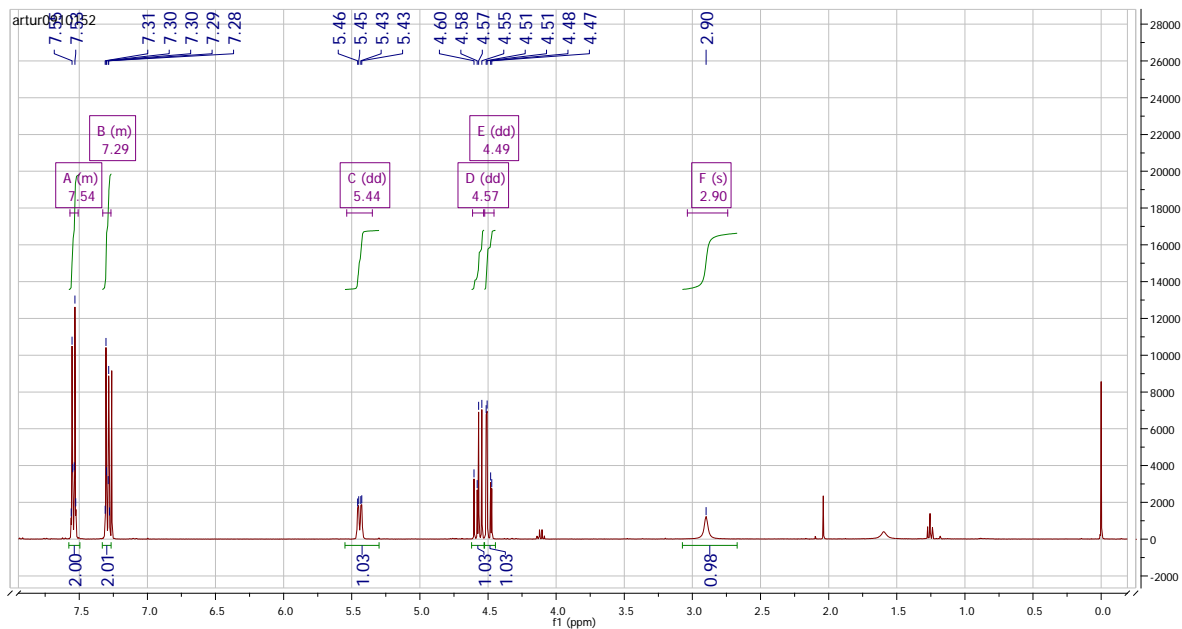


Table 3, entry 10



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.57 – 7.51 (m, 2H), 7.33 – 7.27 (m, 2H), 5.44 (dd, $J = 9.3$, 2.9 Hz, 1H), 4.57 (dd, $J = 13.5$, 9.3 Hz, 1H), 4.49 (dd, $J = 13.5$, 3.2 Hz, 1H), 2.90 (s, 1H).



$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.15, 132.35, 127.76, 123.13, 81.04, 70.48.

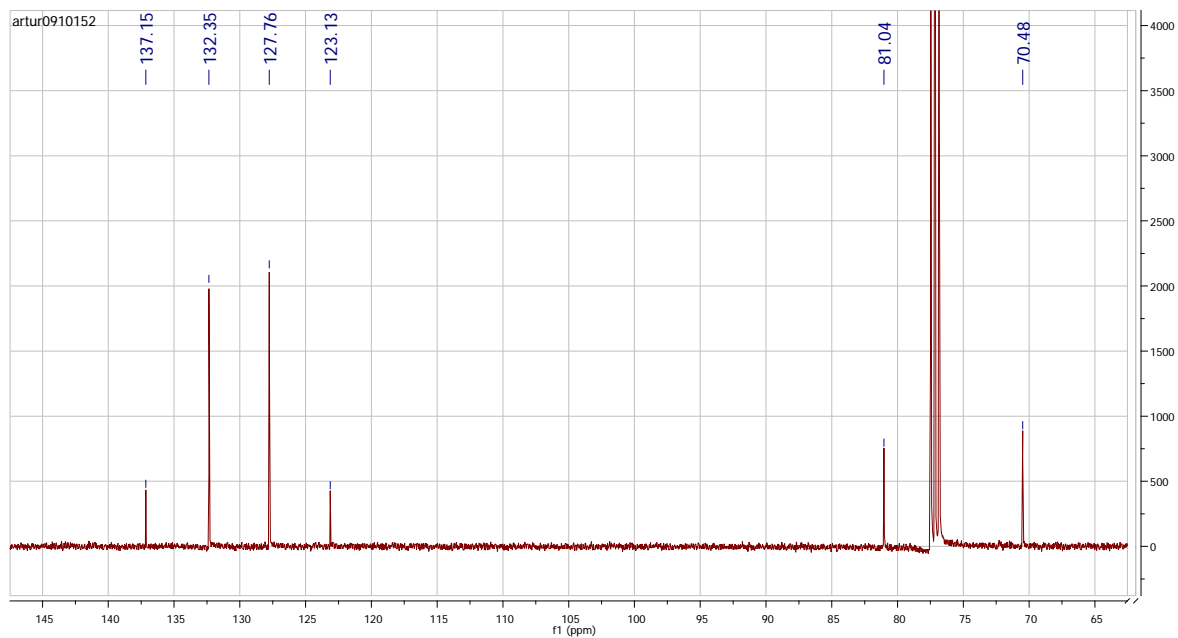
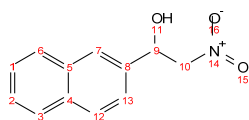
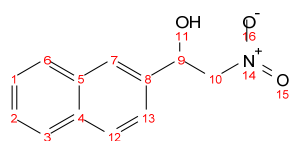
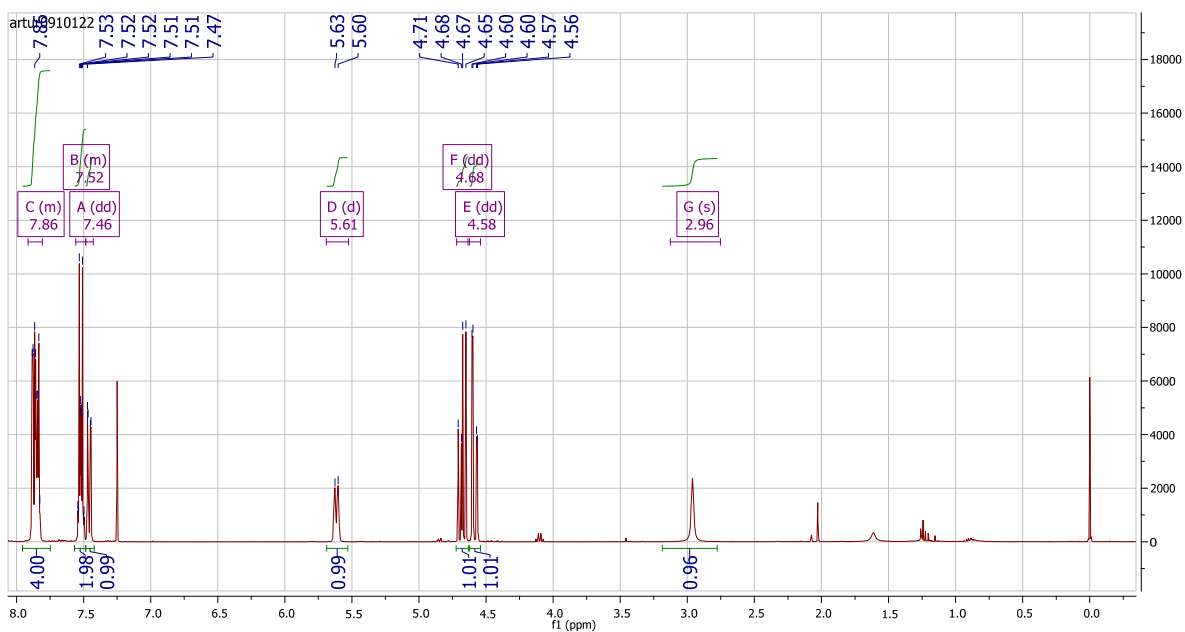


Table 3, entry 12



^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.81 (m, 4H), 7.56 – 7.48 (m, 2H), 7.46 (dd, $J = 8.6, 1.7$ Hz, 1H), 5.61 (d, $J = 9.3$ Hz, 1H), 4.68 (dd, $J = 13.4, 9.5$ Hz, 1H), 4.58 (dd, $J = 13.4, 3.1$ Hz, 1H), 2.96 (s, 1H).



^{13}C NMR (101 MHz, CDCl_3) δ 135.50, 133.54, 133.31, 129.16, 128.20, 127.93, 126.87, 126.83, 125.46, 123.32, 81.31, 71.29.

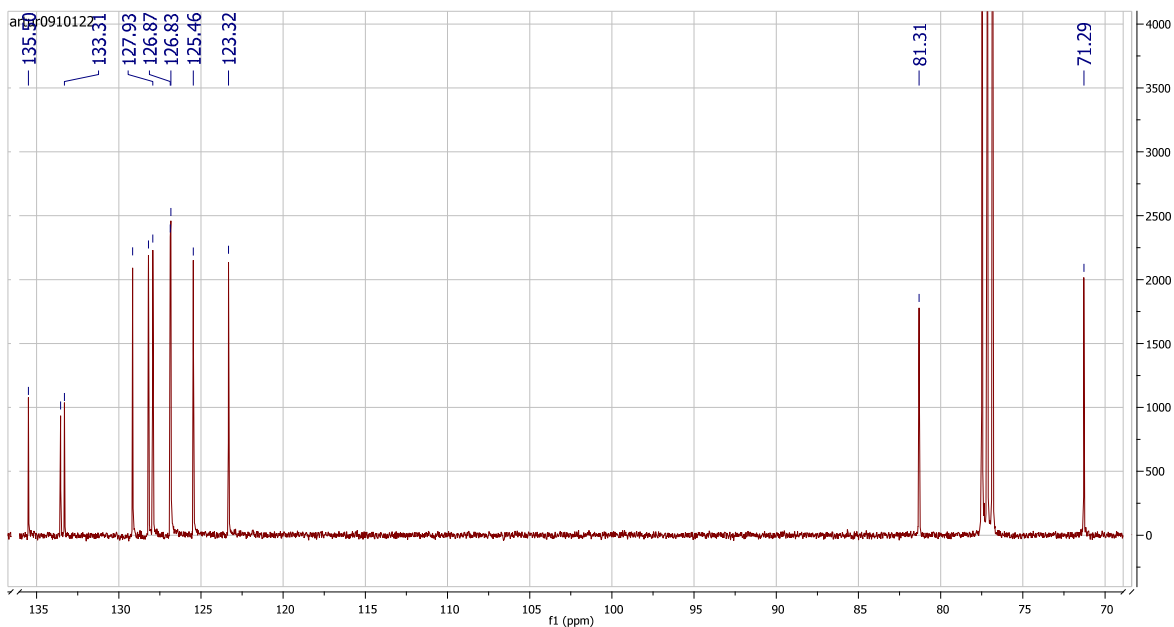
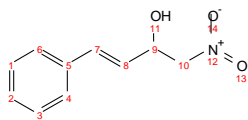
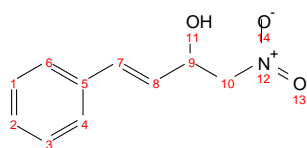
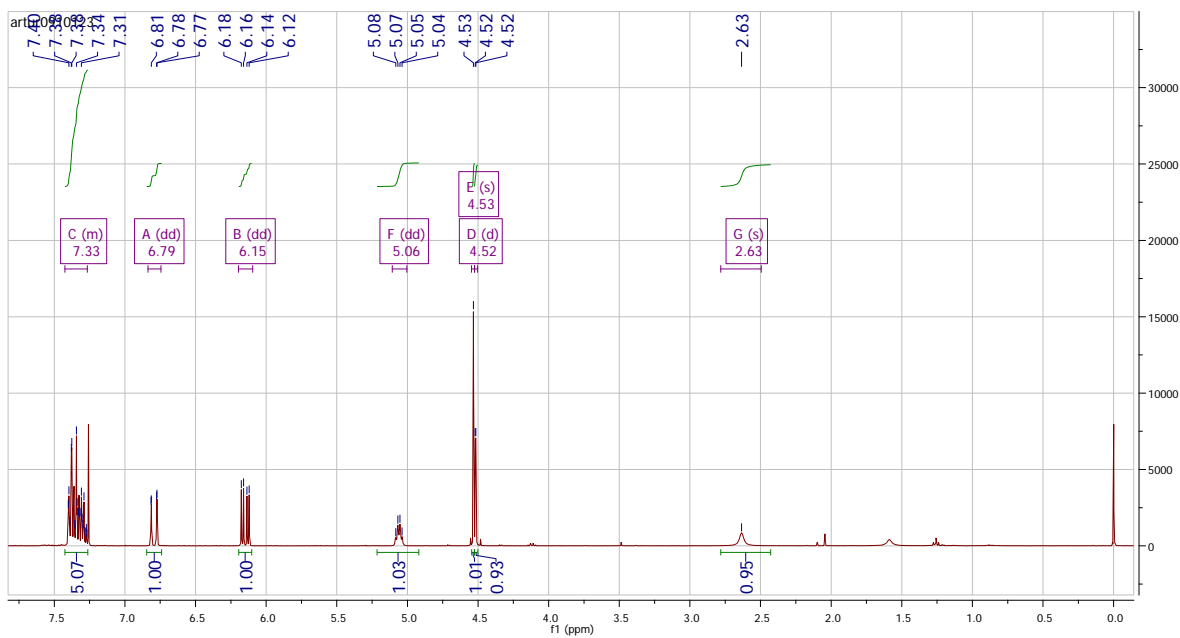


Table 3, entry 14



^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.27 (m, 5H), 6.79 (dd, $J = 15.9, 1.1$ Hz, 1H), 6.15 (dd, $J = 15.9, 6.3$ Hz, 1H), 5.06 (dd, $J = 11.9, 5.8$ Hz, 1H), 4.53 (s, 1H), 4.52 (d, $J = 1.8$ Hz, 1H), 2.63 (s, 1H).



^{13}C NMR (101 MHz, CDCl_3) δ 135.62, 133.88, 128.89, 128.70, 126.87, 125.01, 79.98, 69.73.

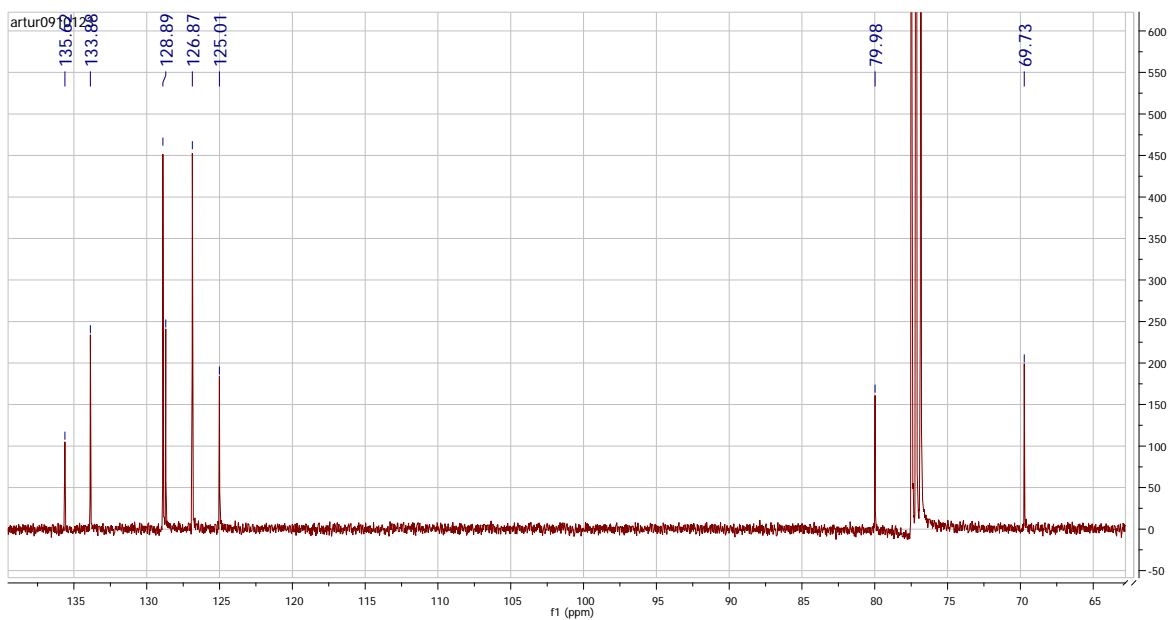
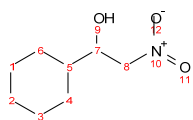
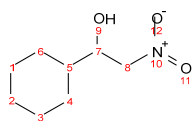
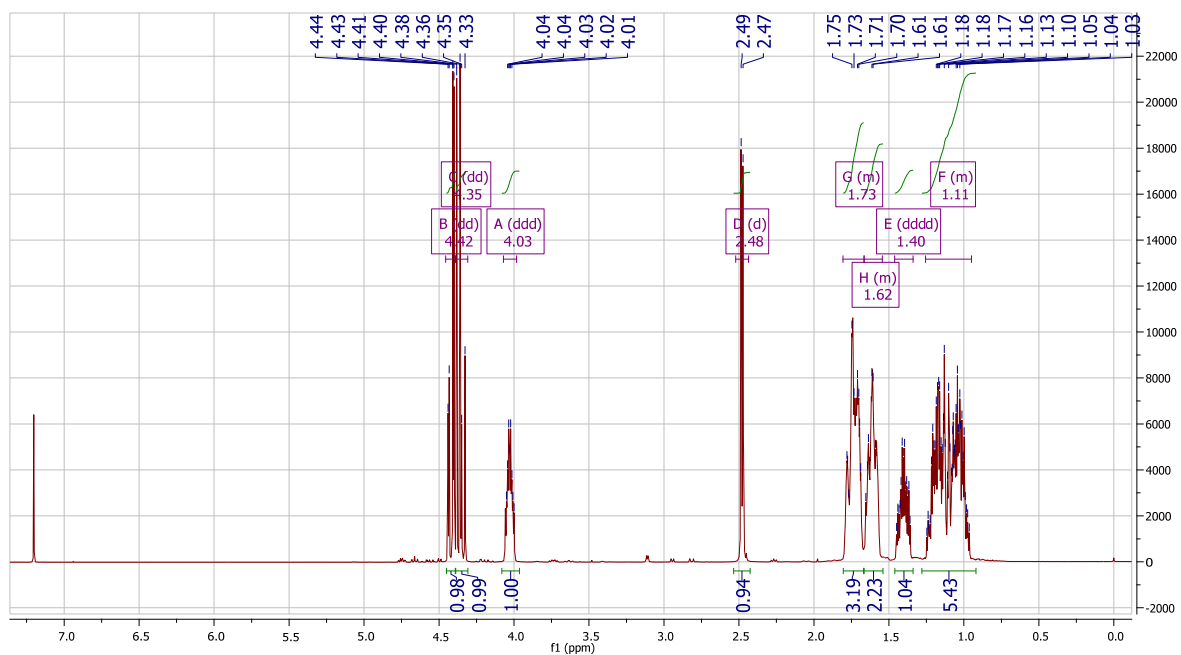


Table 3, entry 16



^1H NMR (400 MHz, CDCl_3) δ 4.42 (dd, $J=13.1, 2.9$ Hz, 1H), 4.35 (dd, $J=13.1, 8.9$ Hz, 1H), 4.03 (ddd, $J=11.6, 5.8, 2.9$ Hz, 1H), 2.48 (d, $J=5.2$ Hz, 1H), 1.81 – 1.67 (m, 3H), 1.67 – 1.54 (m, 2H), 1.40 (dddd, $J=14.9, 11.8, 6.3, 3.3$ Hz, 1H), 1.26 – 0.95 (m, 5H).



^{13}C NMR (101 MHz, CDCl_3) δ 79.44, 72.97, 41.53, 28.92, 28.07, 26.20, 26.00, 25.86.

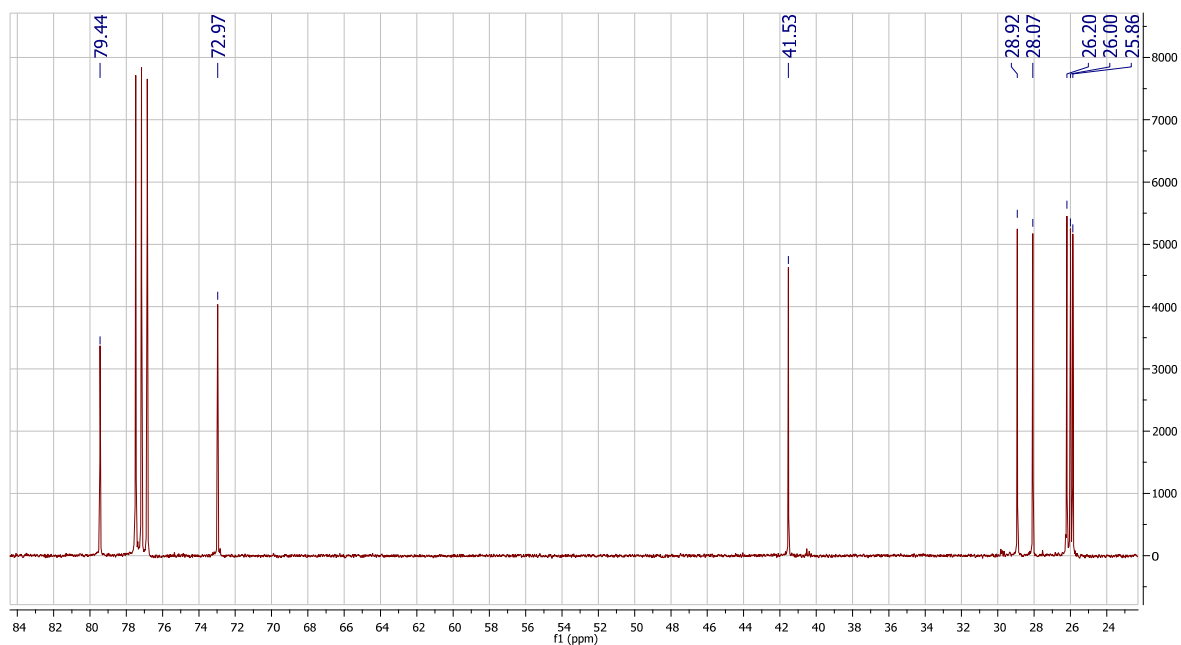
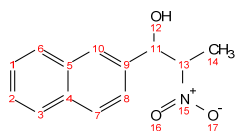
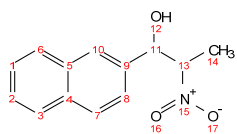
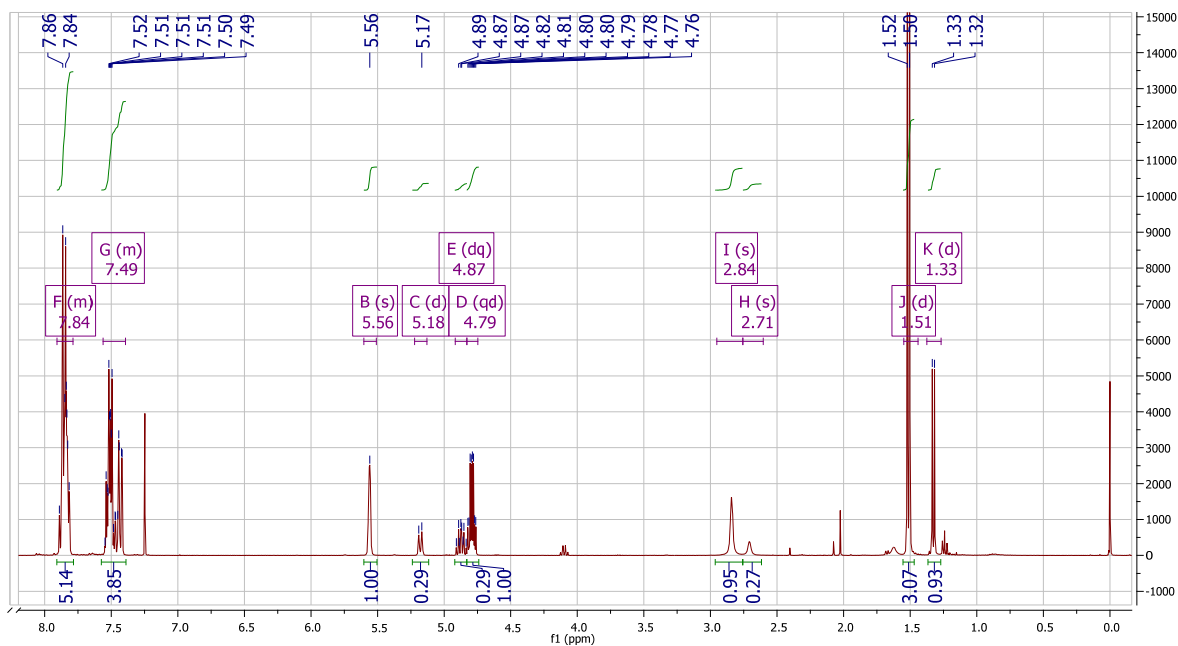


Table 4, entry 2



¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.79 (m, 5H)(syn/anti), 7.56 – 7.39 (m, 4H)(syn/anti), 5.56 (bs, 1H)(anti), 5.18 (d, *J* = 9.0 Hz, 0.3H)(syn), 4.87 (dq, *J* = 9.0, 6.8 Hz, 0.3H)(syn), 4.79 (qd, *J* = 6.8, 3.5 Hz, 1H)(anti), 2.84 (s, 1H)(anti), 2.71 (s, 0.3H)(syn), 1.51 (d, *J* = 6.8 Hz, 3H)(anti), 1.33 (d, *J* = 6.8 Hz, 1H)(syn).



¹³C NMR (101 MHz, CDCl₃) δ 135.74(anti), 135.56(syn), 133.58(syn), 133.20(anti), 133.11(anti), 133.09(syn), 129.10(syn), 128.66(anti), 128.09(anti), 128.07(syn), 127.81(syn), 127.74(anti), 126.78(syn), 126.74(syn), 126.68(syn), 126.59(anti), 126.50(anti), 125.30(anti), 123.82(syn), 123.30(anti), 88.34(syn), 87.30(anti), 76.47(syn), 73.96(anti), 16.56(syn), 12.01(anti).

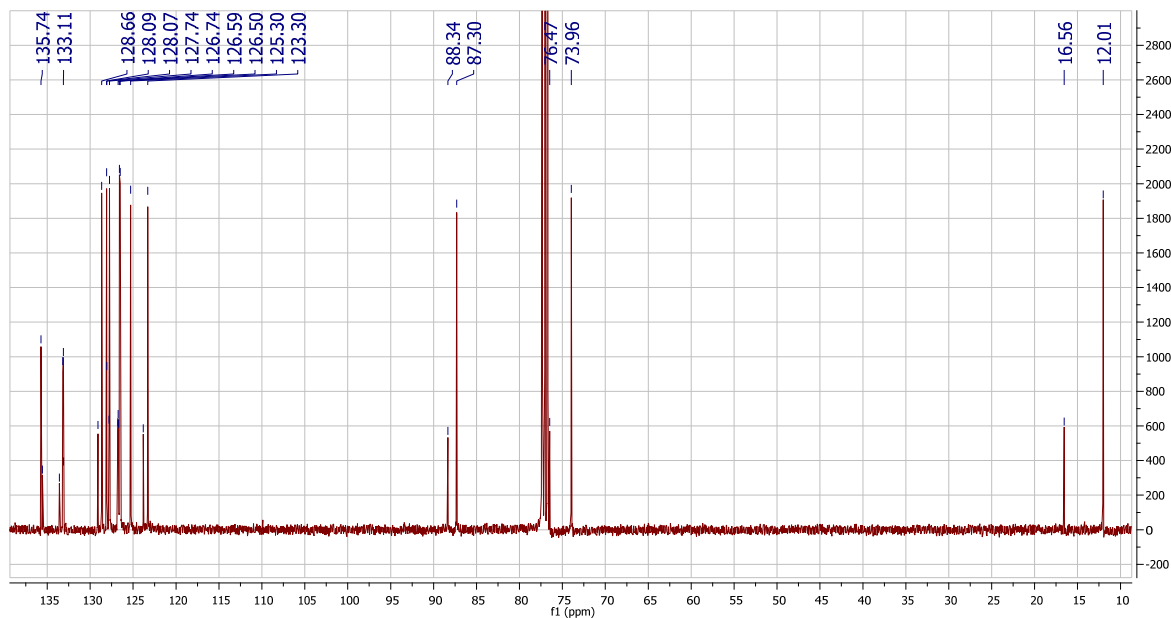
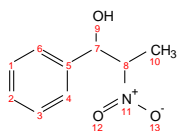
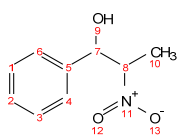
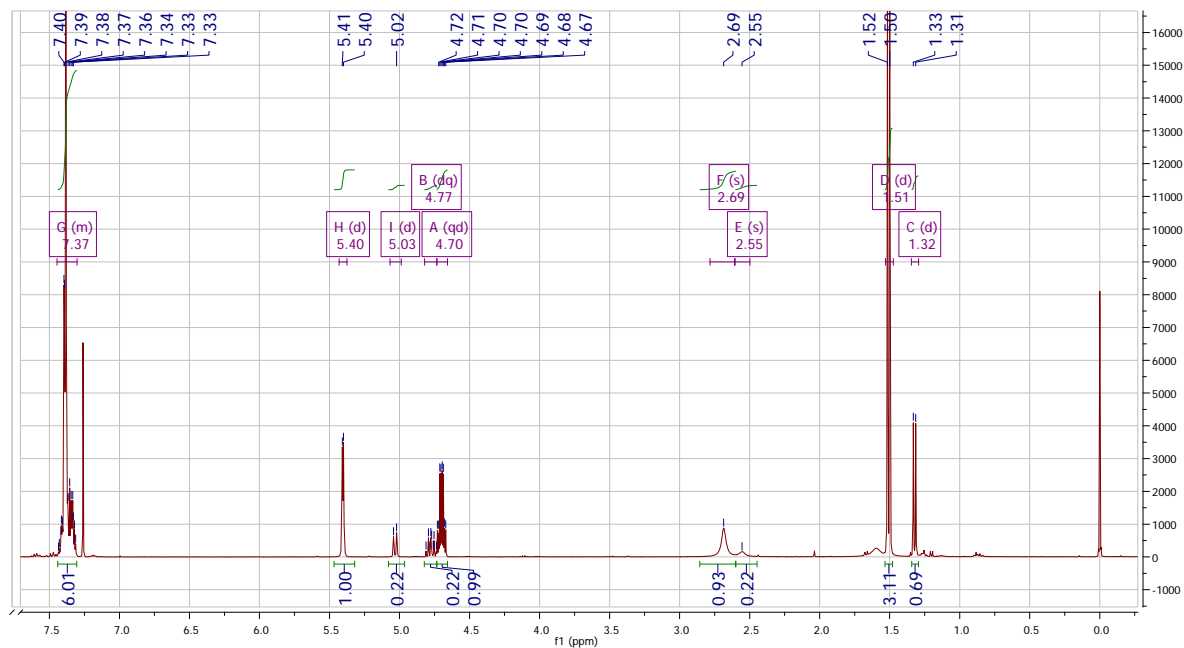


Table 4, entry 4



^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.30 (m, 6H)(syn/anti), 5.40 (d, J = 3.5 Hz, 1H)(anti), 5.03 (d, J = 9.0 Hz, 0.22H)(syn), 4.77 (dq, J = 9.0, 6.9 Hz, 0.22H)(syn), 4.70 (qd, J = 6.8, 3.6 Hz, 1H)(anti), 2.69 (s, 1H)(anti), 2.55 (s, 1H)(syn), 1.51 (d, J = 6.8 Hz, 3H)(anti), 1.32 (d, J = 6.8 Hz, 1H)(syn).



^{13}C NMR (101 MHz, CDCl_3) δ 138.39(anti), 138.28(syn), 129.26(syn), 129.05(syn), 128.77(anti), 128.56(anti), 126.93(syn), 125.95(anti), 88.40(syn), 87.43(anti), 76.30(syn), 73.88(anti), 16.49(syn), 12.08(anti).

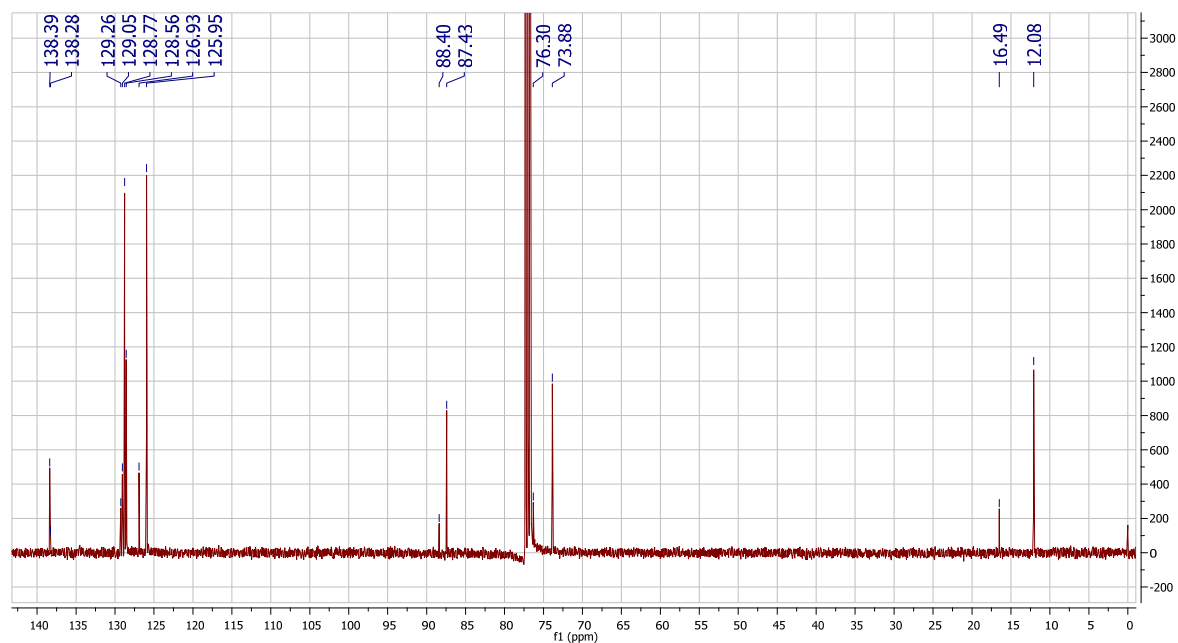
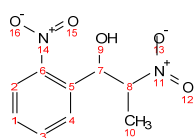
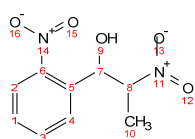
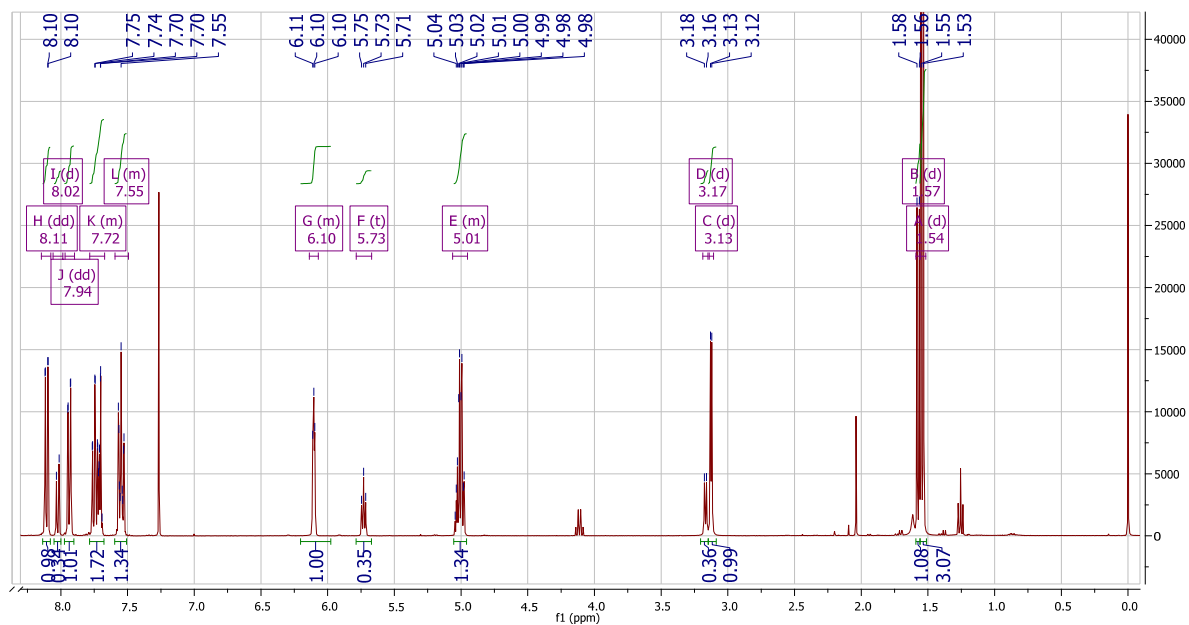


Table 4, entry 5



^1H NMR (400 MHz, CDCl_3) δ 8.11 (dd, $J=8.2, 1.2$ Hz, 1H)(anti), 8.02 (d, $J=8.0$ Hz, 0.34H)(syn), 7.94 (dd, $J=7.9, 0.9$ Hz, 1H)(anti), 7.78 – 7.67 (m, 1.7H)(syn/anti), 7.59 – 7.49 (m, 1.3H)(syn/anti), 6.14 – 6.07 (m, 1H)(anti), 5.73 (t, $J=6.2$ Hz, 1H)(syn), 5.06 – 4.95 (m, 1.3H)(syn/anti), 3.17 (d, $J=6.1$ Hz, 0.3H)(syn), 3.13 (d, $J=4.1$ Hz, 1H)(anti), 1.57 (d, $J=6.9$ Hz, 1H)(syn), 1.54 (d, $J=7.0$ Hz, 1H)(anti).



^{13}C NMR (101 MHz, CDCl_3) δ 148.08(syn), 147.15(anti), 134.11(anti), 134.08(syn), 134.05(syn), 134.00(anti), 129.75(syn), 129.48(anti), 129.33(anti), 128.84(syn), 125.22(anti), 125.06(syn), 87.46(syn), 84.73(anti), 70.64(syn), 69.26(anti), 16.45(syn), 12.05(anti).

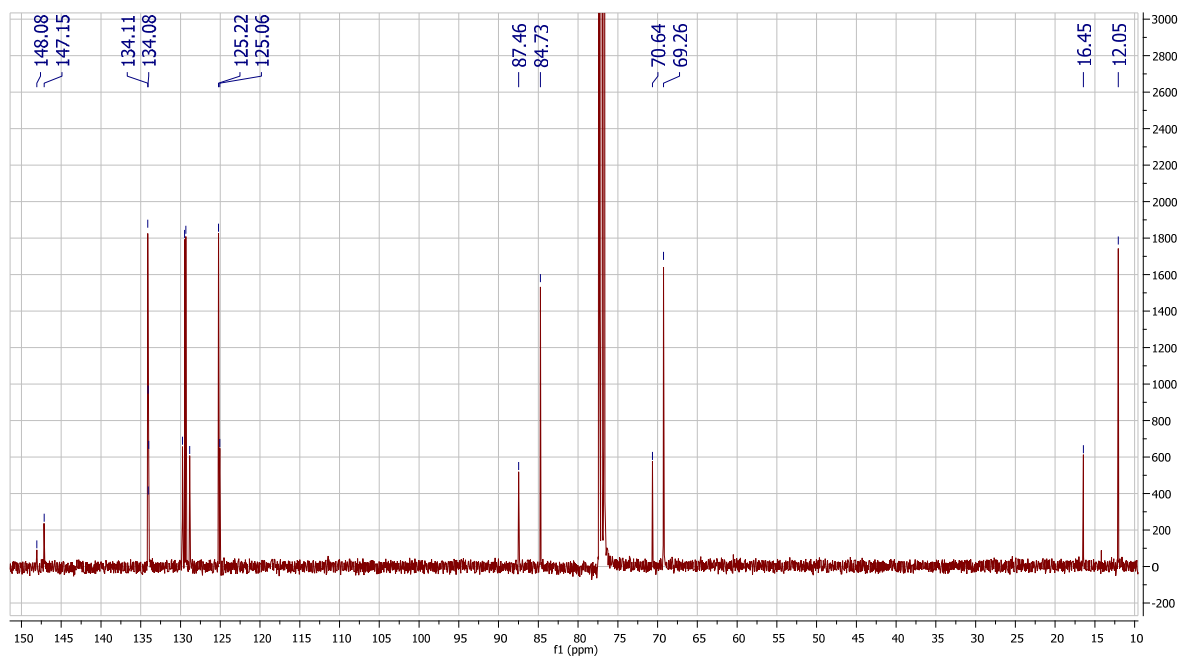
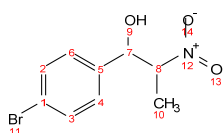
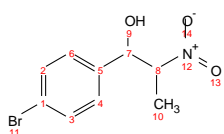
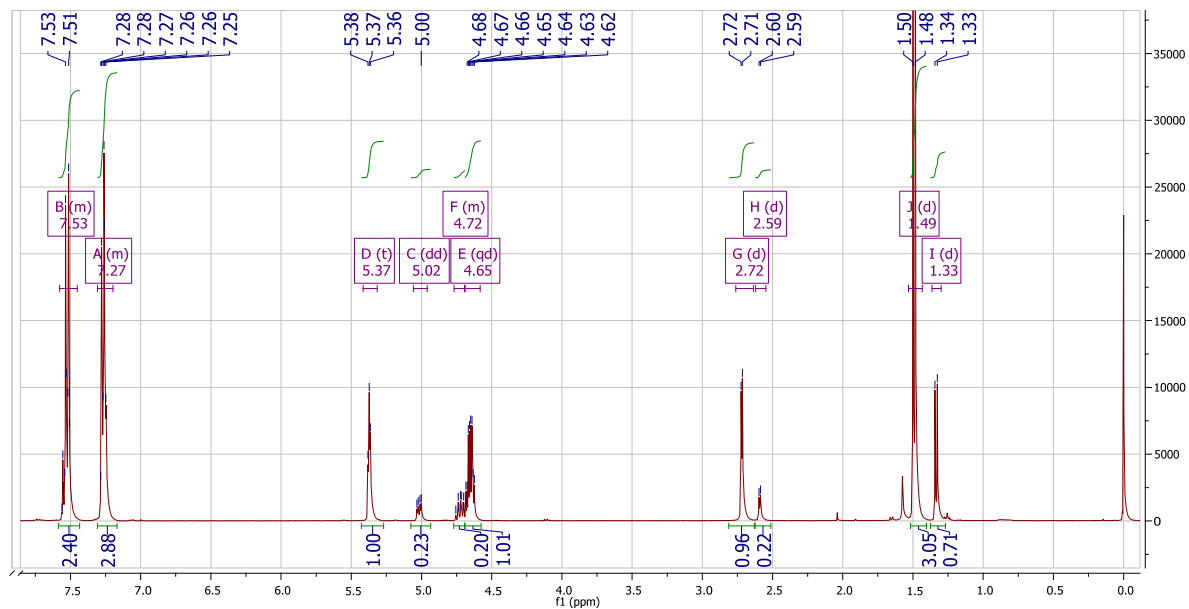


Table 4, entry 6



^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.45 (m, 2.4H)(syn/anti), 7.31 – 7.20 (m, 2.9H)(syn/anti), 5.37 (t, $J = 3.3$ Hz, 1H)(anti), 5.02 (dd, $J = 8.8, 3.8$ Hz, 0.2H)(syn), 4.77 – 4.69 (m, 0.2H)(syn), 4.65 (qd, $J = 6.8, 3.5$ Hz, 1H)(anti), 2.72 (d, $J = 3.5$ Hz, 1H)(anti), 2.59 (d, $J = 4.0$ Hz, 0.2H)(syn), 1.49 (d, $J = 6.8$ Hz, 1H)(anti), 1.33 (d, $J = 6.9$ Hz, 0.7H)(syn).



^{13}C NMR (101 MHz, CDCl_3) δ 137.33(anti), 137.23(syn), 132.20(syn), 131.93(anti), 128.56(syn), 127.67(anti), 123.28(syn), 122.56(anti), 88.07(syn), 87.12(anti), 75.57(syn), 73.22(anti), 16.38(syn), 12.02(anti).

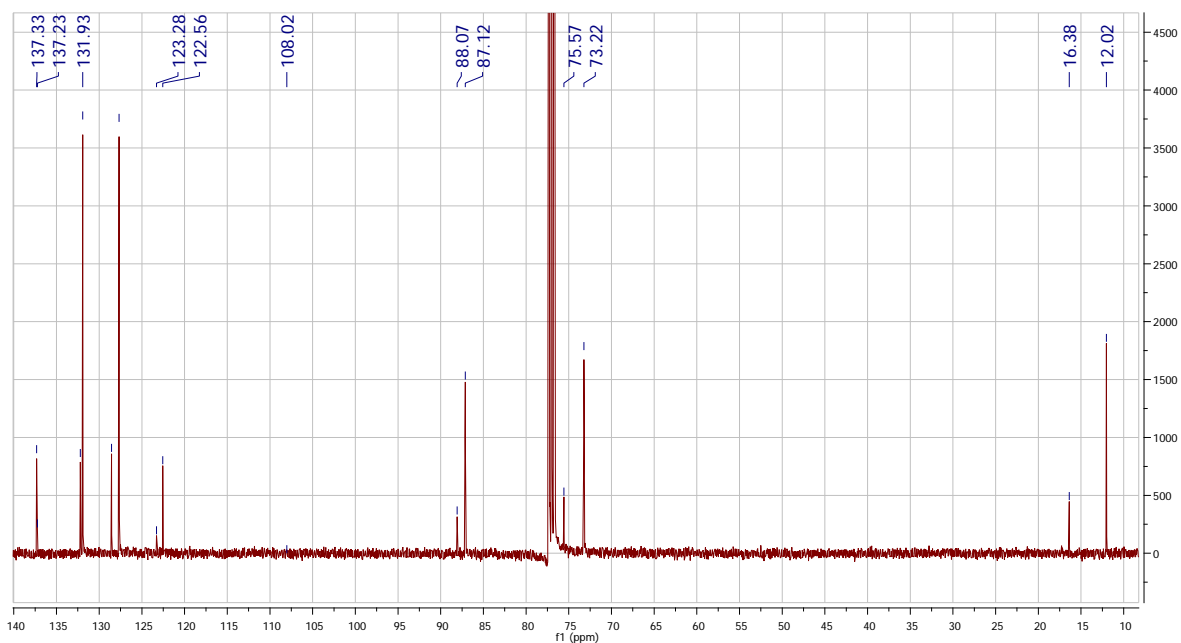
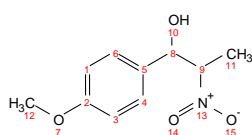
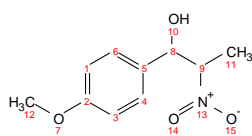
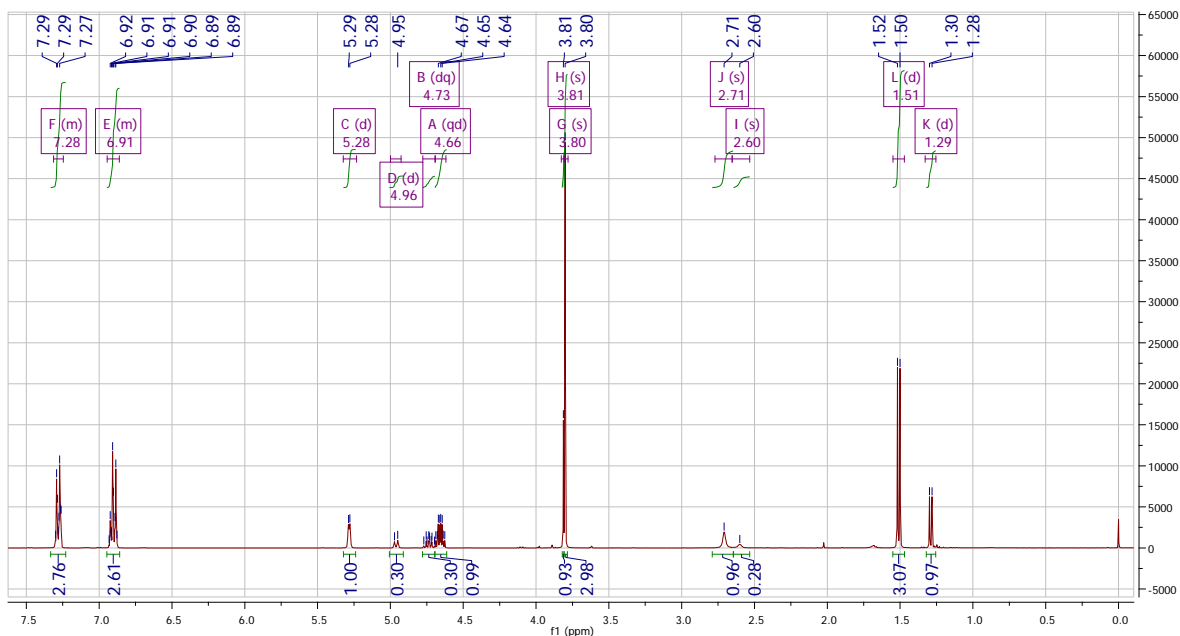


Table 4, entry 7



^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.25 (m, 3H)(syn/anti), 6.94 – 6.86 (m, 3H)(syn/anti), 5.28 (d, $J = 3.7$ Hz, 1H)(anti), 4.96 (d, $J = 9.1$ Hz, 0.3H)(syn), 4.73 (dq, $J = 9.1, 6.8$ Hz, 0.3H)(syn), 4.66 (qd, $J = 6.8, 4.1$ Hz, 1H)(anti), 3.81 (s, 1H)(syn), 3.80 (s, 3H)(anti), 2.71 (s, 1H)(anti), 2.60 (s, 0.3H)(syn), 1.51 (d, $J = 6.8$ Hz, 3H)(anti), 1.29 (d, $J = 6.8$ Hz, 1H)(syn).



^{13}C NMR (101 MHz, CDCl_3) δ 160.17(sy n), 159.69(anti), 130.51(anti), 130.38(syn), 128.18(syn), 127.26(anti), 114.38(syn), 114.12(anti), 88.51(syn), 87.57(anti), 75.91(syn), 73.78(anti), 55.34(syn), 55.31(anti), 16.47(syn), 12.47(anti).

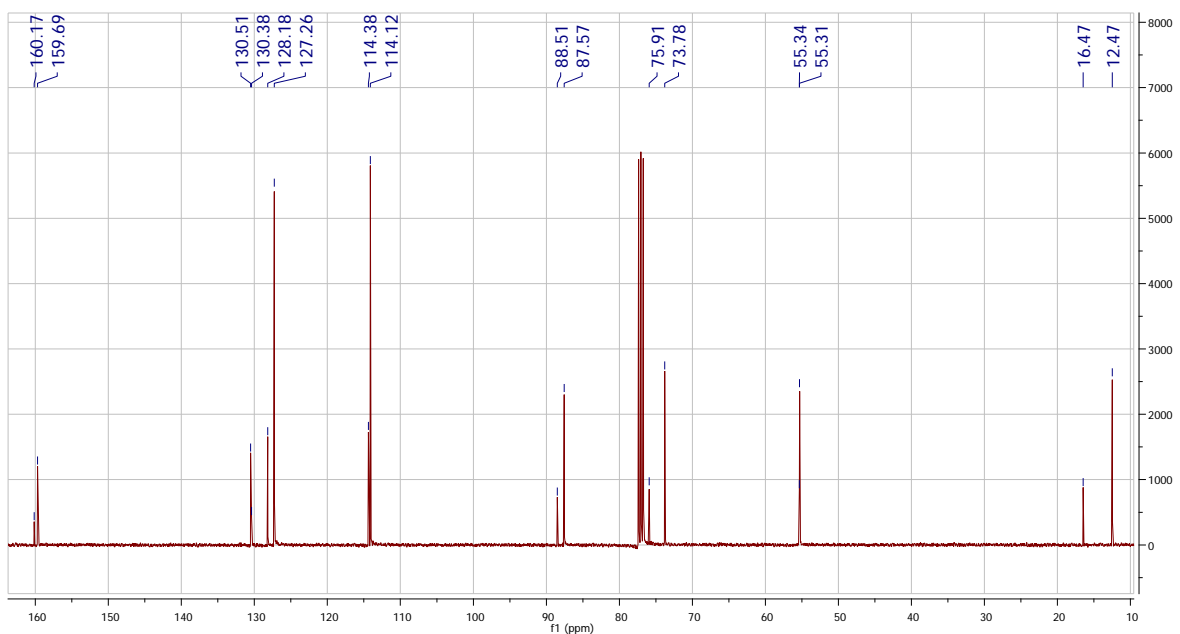
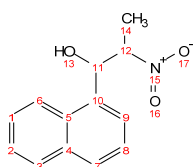
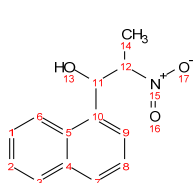
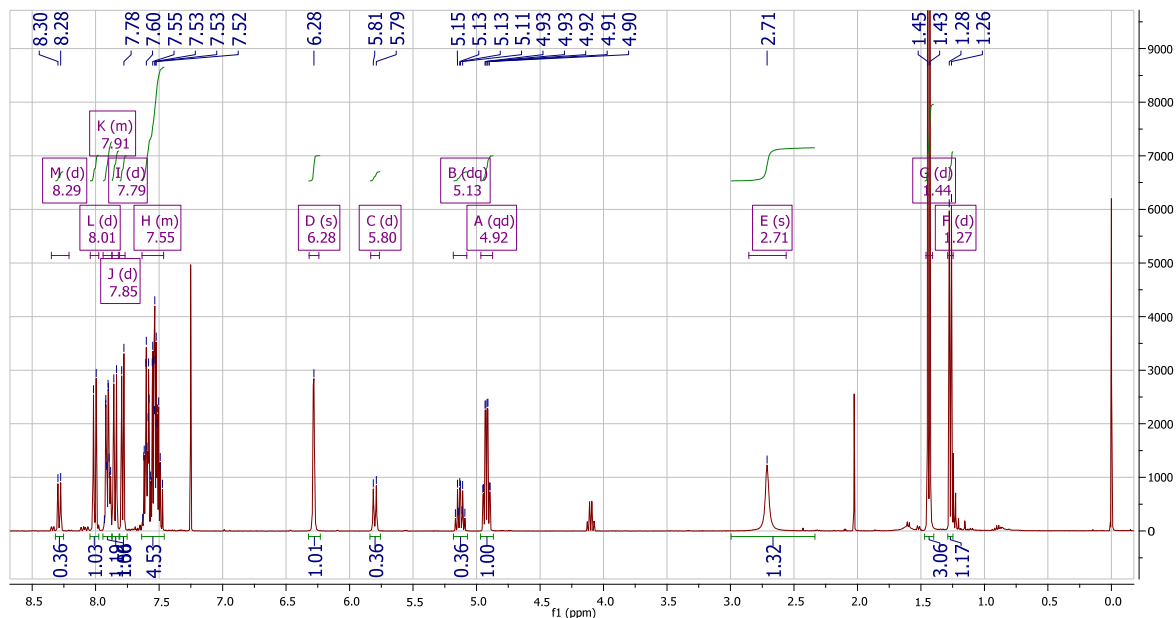


Table 4, entry 8



^1H NMR (400 MHz, CDCl_3) δ 8.29 (d, $J = 8.5$ Hz, 0.4H)(syn), 8.01 (d, $J = 8.5$ Hz, 1H)(anti), 7.94 – 7.87 (m, 1.5H)(syn/anti), 7.85 (d, $J = 8.5$ Hz, 1H)(anti), 7.79 (d, $J = 7.2$ Hz, 1H)(anti), 7.64 – 7.46 (m, 5H)(syn/anti), 6.28 (s, 1H)(anti), 5.80 (d, $J = 9.2$ Hz, 0.4H)(syn), 5.13 (dq, $J = 9.2, 6.9$ Hz, 0.4H)(syn), 4.92 (qd, $J = 6.8, 2.4$ Hz, 1H)(anti), 2.71 (s, 1.3H)(syn/anti), 1.44 (d, $J = 6.8$ Hz, 3H)(anti), 1.27 (d, $J = 6.9$ Hz, 1H)(syn).



^{13}C NMR (101 MHz, CDCl_3) δ 134.02(syn), 133.96(syn), 133.77(anti), 133.65(anti), 130.81(syn), 129.82(anti), 129.38(syn), 129.33(anti), 129.18(syn), 129.08(anti), 127.06(anti), 126.85(syn), 126.13(syn), 125.96(anti), 125.66(syn), 125.41(anti), 125.36(syn), 124.01(anti), 123.20(syn), 121.74(anti), 88.48(syn), 85.58(anti), 73.76(syn), 70.86(anti), 16.85(syn), 11.03(anti).

