Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Enantioselective intramolecular propargylic amination using chiral copper-pybox catalyst

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List of Contents of Supporting Information

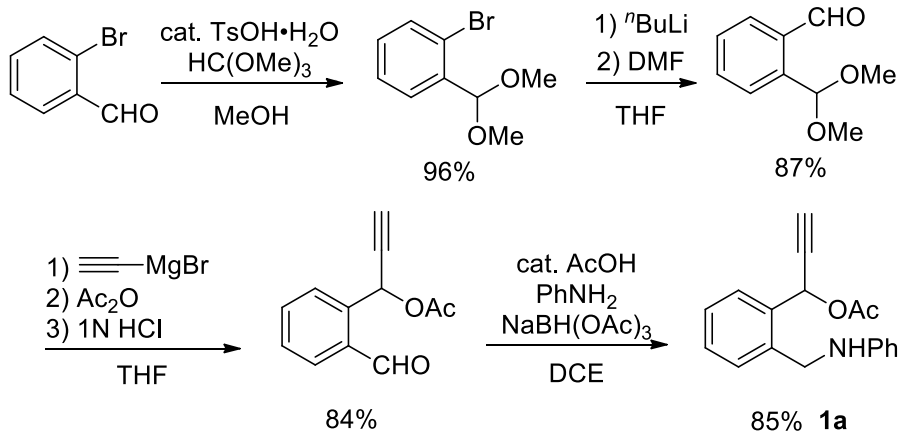
General Methods.

^{1}H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were measured on a JEOL Excalibur 270 spectrometer using $CDCl_3$ as solvent. HPLC analyses were performed on Hitachi L-7100 and GL-7410 apparatuses equipped with a UV detector using 25 cm x 4.6 mm DAICEL Chiralpak AD, IA columns. Elemental analyses were performed at Microanalytical Center of The University of Tokyo. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. Specific rotations were measured on a JASCO DIP-1000 polarimeter.

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods, then distilled under N_2 and degassed before use. Optically pure diphosphines **L1**-**L3**, pybox ligands **L5**, **L9**, CuOTf ▪ $1/2C_6H_6$, aniline, and *N*,*N*'-diphenylethylenediamine are commercially available reagents. Optically pure pybox ligands **L4**,[S1] **L6**,[S2] **L7**,[S3] **L8**,[S2] **L10**,[S3] bis(oxazoline) ligand **L11**,[S4] and propargylic acetate **3**[S5] were prepared according to literature procedures.

General Procedure for the Preparation of Propargylic Acetates.

Scheme S1. Preparation of Propargylic Acetate **1a**



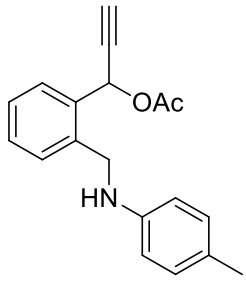
A typical experimental procedure for the preparation of 1-(2-((phenylamino)methyl)phenyl)prop-2-yn-1-yl acetate (**1a**) is described below. In a 50 mL Schlenk flask were placed 2-bromobenzaldehyde (3.80 g, 20.5 mmol) and anhydrous MeOH (20 mL) under N_2. Trimethyl orthoformate (8.75 mL, 80 mmol) and TsOH· H_2O (37.6 mg, 0.20 mmol) were added to the solution and the mixture was stirred at room temperature for 2 h. The resulting mixture was passed through a short silicagel pad to give 1-bromo-2-(dimethoxymethyl)benzene as a colorless oil (4.54 g, 19.6 mmol, 96% isolated yield).

To a solution of 1-bromo-2-(dimethoxymethyl)benzene (4.54 g, 19.6 mmol) in anhydrous THF (60 mL) was added ^{n}BuLi (1.65 M in hexane, 18.0 mL, 29.7 mmol) at -78 ˚C and the mixture was stirred for 30 min. DMF (3.1 mL, 40.0 mmol) was added to the solution and the mixture was stirred at -78 ˚C for 30 min. The solution was allowed to warm to room temperature and stirred for another 1 h. After the reaction mixture was quenched by addition of saturated $NaHCO_3$ aq., the solution was extracted with hexane (20 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (triethylamine-pretreated SiO_2) with hexane/ethyl acetate (90/10) to give 2-(dimethoxymethyl)benzaldehyde as a colorless oil (3.07 g, 17.0 mmol, 87% isolated yield).

To a solution of 2-(dimethoxymethyl)benzaldehyde (1.46 g, 8.09 mmol) in anhydrous THF (45 mL) was added ethynylmagnesium bromide (0.5 M in THF, 24 mL, 12 mmol) at 0 ˚C and the mixture was stirred for 40 min. Acetic anhydride (1.50 mL, 15.9 mmol) was added to the solution and the mixture was allowed to warm to room temperature. After stirring for 1 h, the mixture was acidified by addition of 1N HCl aq. (30 mL) and stirred for 3 h. The solution was extracted with ethyl acetate (15 mL x 3). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2) with hexane/ethyl acetate (85/15) to give 1-(2-formylphenyl)prop-2-yn-1-yl acetate[S6] as a pale yellow oil (1.37 g, 6.7 mmol, 84% isolated yield).

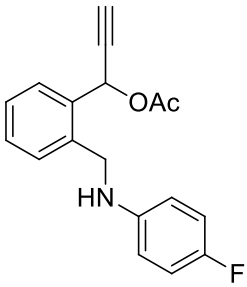
In a 20 mL Schlenk flask were placed 1-(2-formylphenyl)prop-2-yn-1-yl acetate (208 mg, 1.03 mmol), aniline (0.19 mL, 2.1 mmol), and anhydrous dichloroethane (4 mL) under N_2. To the solution was added acetic acid (6 μL, 0.1 mmol) at room temperature and the mixture was stirred for 1 h. Sodium triacetoxyborohydride (283.7 mg, 1.34 mmol) was added to the solution and the mixture was stirred for 4 h. After the reaction mixture was quenched by addition of saturated $NaHCO_3$ aq., the solution was extracted with dichloromethane (5 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2) with hexane/ethyl acetate (85/15) to give 1-(2-((phenylamino)methyl)phenyl)prop-2-yn-1-yl acetate (**1a**) as a brown oil (244.6 mg, 0.876 mmol, 85% isolated yield). ^{1}H NMR δ 7.67-7.63 (m, 1H), 7.46-7.43 (m, 1H), 7.36-7.33 (m, 2H), 7.21-7.15 (m, 2H), 6.76-6.70 (m, 1H), 6.66-6.63 (m, 3H), 4.50 (d, *J* = 14.0 Hz, 1H), 4.43 (d, *J* = 14.0 Hz, 1H), 4.09 (br, 1H), 2.65 (d, *J* = 2.2 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR δ 169.5, 147.9, 136.9, 135.0, 129.4, 129.3, 129.2, 128.3, 128.0, 117.8, 112.9, 80.2, 75.6, 63.0, 45.7, 20.9. HRMS (EI) Calcd. for $C_{18}H_{17}NO_2$ [M]: 279.1259. Found: 279.1249.

Spectroscopic Data of Other Propargylic Acetates



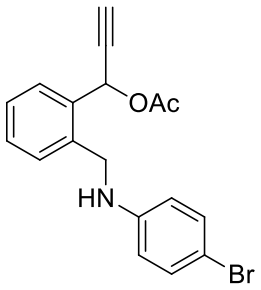
1b

1-(2-(((4-methylphenyl)amino)methyl)phenyl)prop-2-yn-1-yl acetate (**1b**): A brown oil. ^{1}H NMR δ 7.74-7.70 (m, 1H), 7.51-7.48 (m, 1H), 7.42-7.35 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 2H), 4.53 (d, *J* = 14.2 Hz, 1H), 4.46 (d, *J* = 14.2 Hz, 1H), 4.05 (br, 1H), 2.71 (d, *J* = 2.4 Hz, 1H), 2.30 (s, 3H), 2.14 (s, 3H). ^{13}C NMR δ 169.4, 145.6, 137.1, 134.8, 129.6, 129.3, 129.0, 128.2, 127.8, 126.7, 112.9, 80.1, 75.6, 62.9, 45.9, 20.8, 20.3. HRMS (EI) Calcd. for $C_{19}H_{19}NO_2$ [M]: 293.1416. Found: 293.1420.



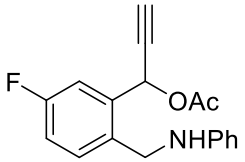
1c

1-(2-(((4-fluorophenyl)amino)methyl)phenyl)prop-2-yn-1-yl acetate (**1c**): A brown solid, m.p. 76.1-78.0 ºC. ^{1}H NMR δ 7.68-7.62 (m, 1H), 7.41-7.28 (m, 3H), 6.90-6.81 (m, 2H), 6.65 (d, *J* = 2.4 Hz, 1H), 6.58-6.50 (m, 2H), 4.42 (d, *J* = 14.0 Hz, 1H), 4.36 (d, *J* = 14.0 Hz, 1H), 4.01 (br, 1H), 2.64 (d, *J* = 2.4 Hz, 1H), 2.05 (s, 3H). ^{13}C NMR δ 169.4, 155.9 (d, $^{1}J_{C\text{-}F}$ = 234.7 Hz), 144.2 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 136.6, 134.9, 129.3, 129.0, 128.3, 128.0, 115.6 (d, $^{2}J_{C\text{-}F}$ = 22.3 Hz), 113.6 (d, $^{3}J_{C\text{-}F}$ = 7.8 Hz), 80.1, 75.7, 62.8, 46.2, 20.8. HRMS (EI) Calcd. for $C_{18}H_{16}FNO_2$ [M]: 297.1165. Found: 297.1177.



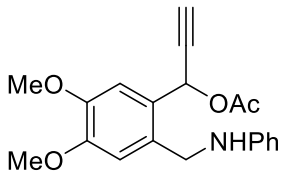
1d

1-(2-(((4-bromophenyl)amino)methyl)phenyl)prop-2-yn-1-yl acetate (**1d**): A pale yellow solid, m.p. 108.1-110.0 ºC. ^{1}H NMR δ 7.65-7.62 (m, 1H), 7.39-7.32 (m, 3H), 7.23 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 2.4 Hz, 1H), 6.50 (d, *J* = 8.9 Hz, 2H), 4.48-4.37 (m, 2H), 4.22 (br, 1H), 2.65 (d, *J* = 2.4 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR δ 169.5, 146.8, 136.3, 135.0, 131.9, 129.4, 129.0, 128.4, 128.1, 114.5, 109.3, 80.1, 75.7, 62.9, 45.7, 20.9. HRMS (EI) Calcd. for $C_{18}H_{16}BrNO_2$ [M]: 357.0364. Found: 357.0369.



1e

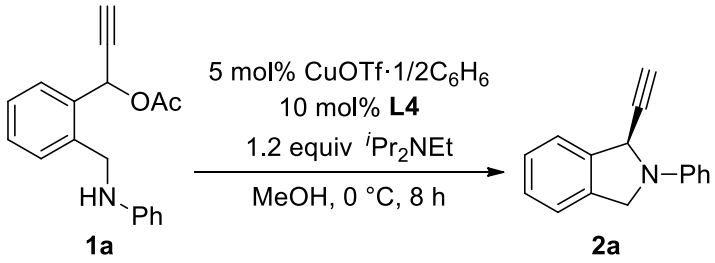
1-(5-fluoro-2-((phenylamino)methyl)phenyl)prop-2-yn-1-yl acetate (**1e**): A brown oil. ^{1}H NMR δ 7.43-7.34 (m, 2H), 7.21-7.15 (m, 2H), 7.06-6.99 (m, 1H), 6.77-6.71 (m, 1H), 6.65-6.62 (m, 3H), 4.44 (d, *J* = 14.2 Hz, 1H), 4.37 (d, *J* = 14.2 Hz, 1H), 4.06 (br, 1H), 2.67 (d, *J* = 2.2 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR δ 169.4, 162.2 (d, $^{1}J_{C\text{-}F}$ = 245.9 Hz), 147.7, 137.2 (d, $^{3}J_{C\text{-}F}$ = 7.3 Hz), 132.3 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 130.9 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 129.3, 117.9, 116.0 (d, $^{2}J_{C\text{-}F}$ = 21.2 Hz), 115.0 (d, $^{2}J_{C\text{-}F}$ = 22.8 Hz), 112.9, 79.6, 76.0, 62.2 (d, $^{4}J_{C\text{-}F}$ = 1.7 Hz), 45.2, 20.8. HRMS (EI) Calcd. for $C_{18}H_{16}NO_2F$ [M]: 297.1165. Found: 297.1173.



1f

1-(4,5-dimethoxy-2-((phenylamino)methyl)phenyl)prop-2-yn-1-yl acetate (**1f**): A yellow oil. ^{1}H NMR δ 7.22-7.16 (m, 3H), 6.94 (s, 1H), 6.76-6.65 (m, 3H), 6.61 (d, *J* = 2.2 Hz, 1H), 4.41 (d, *J* = 13.4 Hz, 1H), 4.32 (d, *J* = 13.4 Hz, 1H), 4.02 (br, 1H), 3.93 (s, 3H), 3.84 (s, 3H), 2.66 (d, *J* = 2.2 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR δ 169.5, 149.6, 148.4, 148.0, 129.6, 129.2, 127.0, 117.8, 112.9, 112.3, 111.5, 80.4, 75.5, 62.7, 56.0, 55.9, 45.6, 20.9. HRMS (EI) Calcd. for $C_{20}H_{21}NO_4$ [M]: 339.1471. Found: 339.1454.

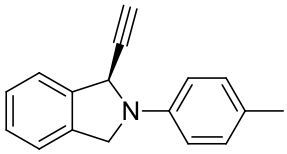
Enantioselective Intramolecular Propargylic Amination of Propargylic Acetates.



1a **2a**

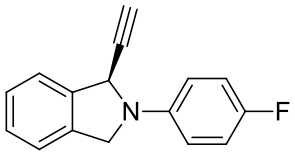
A typical experimental procedure for the reaction of 1-(2-((phenylamino)methyl)phenyl)prop-2-yn-1-yl acetate (**1a**) is described below. In a 20 mL Schlenk flask were placed CuOTf▪1/2C_6H_6 (2.6 mg, 0.010 mmol) and (*S*)-Me-pybox (**L4**) (5.0 mg, 0.020 mmol) under N_2. Anhydrous methanol (1.0 mL) was added, and then the mixture was magnetically stirred at 60 ˚C for 1 h. After the solution was cooled to 0 ˚C, **1a** (55.9 mg, 0.20 mmol) in anhydrous methanol (1.0 mL) and diisopropylethylamine (42 μL, 0.24 mmol) were added under N_2, and the reaction was kept at 0 ˚C for 8 h. The solvent was concentrated under reduced pressure, and the residue was purified by the column chromatography (SiO_2) with hexane/ethyl acetate (93/7) to give 1-ethynyl-2-phenylisoindoline (**2a**) as a white solid (38.2 mg, 0.173 mmol, 87% isolated yield), m.p. 110.1 ˚C (decomp.). ^{1}H NMR δ 7.51-7.48 (m, 1H), 7.39-7.31 (m, 5H), 6.93-6.90 (m, 2H), 6.86-6.80 (m, 1H), 5.61 (br, 1H), 4.82 (dd, *J* = 3.1 and 13.0 Hz, 1H), 4.60 (d, *J* = 13.0 Hz, 1H), 2.41 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR δ 145.9, 138.5, 137.0, 129.2, 128.2, 127.7, 123.1, 122.6, 117.4, 112.9, 82.6, 72.3, 55.1, 53.7. Anal. Calcd. for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.44; H, 6.25; N, 6.32. $[\alpha]^{25}_D$ = − 153.9 (*c* = 0.435, $CHCl_3$). The enantiomeric excess of **2a** was determined by HPLC analysis; DAICEL Chiralpak AD, hexane/^{i}PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 9.4 min (minor) and 12.2 min (major), 93% *ee*.

Spectroscopic Data and Isolated Yields of Other Products.



2b

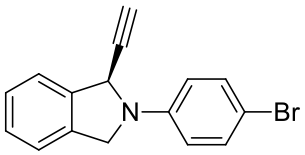
1-ethynyl-2-(4-methylphenyl)isoindoline (**2b**): Isolated yield 79% (with **L4**). A white solid, m.p. 121.4 ˚C (decomp.). ^{1}H NMR δ 7.43-7.40 (m, 1H), 7.30-7.26 (m, 3H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 5.50 (br, 1H), 4.72 (dd, *J* = 3.2 and 13.0 Hz, 1H), 4.49 (d, *J* = 13.0 Hz, 1H), 2.33 (d, *J* = 2.2 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR δ 143.7, 138.6, 137.1, 129.8, 128.2, 127.7, 126.8, 123.0, 122.6, 113.1, 82.6, 72.4, 55.4, 54.0, 20.3. HRMS (EI) Calcd. for $C_{17}H_{15}N$ [M]: 233.1204. Found: 233.1205. $[\alpha]^{25}_{D}$ = − 149.0 (*c* = 0.490, $CHCl_3$). The enantiomeric excess of **2b** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{i}PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.2 min (minor) and 11.5 min (major), 92% *ee*.



2c

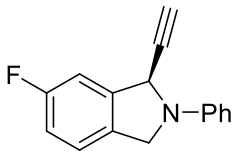
1-ethynyl-2-(4-fluorophenyl)isoindoline (**2c**): Isolated yield 79% (with **L4**). A white solid, m.p. 93.8 ˚C (decomp.). ^{1}H NMR δ 7.50-7.47 (m, 1H), 7.38-7.35 (m, 3H), 7.05 (m, 2H), 6.82 (dd, *J* = 4.3 and 9.2 Hz, 2H), 5.55 (br, 1H), 4.78 (dd, *J* = 3.1 and 12.9 Hz, 1H), 4.54 (d, *J* = 12.9 Hz, 1H), 2.42 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR δ 156.0 (d, $^{1}J_{C\text{-}F}$ = 235.3 Hz), 142.5 (d, $^{4}J_{C\text{-}F}$ = 1.7 Hz), 138.5, 136.9, 128.3, 127.8, 123.1, 122.6, 115.7 (d, $^{2}J_{C\text{-}F}$ = 22.3 Hz), 113.6 (d, $^{3}J_{C\text{-}P}$ = 7.2 Hz), 82.4, 72.5, 55.6, 54.2. Anal. Calcd. for $C_{16}H_{12}FN$: C, 80.99; H, 5.10; N, 5.90. Found: C, 80.83; H, 5.22; N, 5.65. $[\alpha]^{25}_{D}$ = − 150.9 (*c* = 0.470, $CHCl_3$). The enantiomeric excess of **2c** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{i}PrOH = 95/5,

flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.6 min (minor) and 13.7 min (major), 95% *ee*.



2d

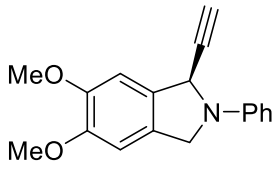
2-(4-bromophenyl)-1-ethynylisoindoline (**2d**): Isolated yield 89% (with **L5**). A white solid, m.p. 163.2 ˚C (decomp.). ^{1}H NMR δ 7.49-7.46 (m, 1H), 7.42-7.34 (m, 5H), 6.76 (d, *J* = 9.2 Hz, 2H), 5.55 (br, 1H), 4.75 (dd, *J* = 3.1 and 12.8 Hz, 1H), 4.54 (d, *J* = 12.8 Hz, 1H), 2.41 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR δ 144.8, 138.2, 136.6, 131.9, 128.3, 127.9, 123.1, 122.6, 114.5, 109.6, 82.0, 72.7, 55.2, 53.7. Anal. Calcd. for $C_{16}H_{12}BrN$: C, 64.45; H, 4.06; N, 4.70. Found: C, 64.23; H, 4.19; N, 4.46. $[\alpha]^{25}_{D}$ = − 146.2 (*c* = 0.455, $CHCl_3$). The enantiomeric excess of **2d** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{i}PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.4 min (minor) and 15.7 min (major), 96% *ee*.



2e

1-ethynyl-6-fluoro-2-phenylisoindoline (**2e**): Isolated yield 81% (with **L4**). A white solid, m.p. 139.8 ˚C (decomp.). ^{1}H NMR δ 7.37-7.23 (m, 3H), 7.19-7.15 (m, 1H), 7.08-7.00 (m, 1H), 6.89-6.80 (m, 3H), 5.56 (br, 1H), 4.74 (dd, *J* = 3.2 and 12.6 Hz, 1H), 4.52 (d, *J* = 12.6 Hz, 1H), 2.42 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR δ 162.7 (d, $^{1}J_{C\text{-}F}$ = 244.8 Hz), 145.8, 140.4 (d, $^{3}J_{C\text{-}F}$ = 8.9 Hz), 132.5 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 129.3, 123.9 (d, $^{3}J_{C\text{-}F}$ = 8.9 Hz), 117.6, 115.6 (d, $^{2}J_{C\text{-}F}$ = 22.9 Hz), 112.9, 110.3 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 81.9, 72.8, 55.1 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 53.2. HRMS (EI) Calcd. for $C_{16}H_{12}NF$ [M]: 237.0954. Found: 237.0950. $[\alpha]^{25}_{D}$ = − 156.8 (*c* = 0.555, $CHCl_3$).

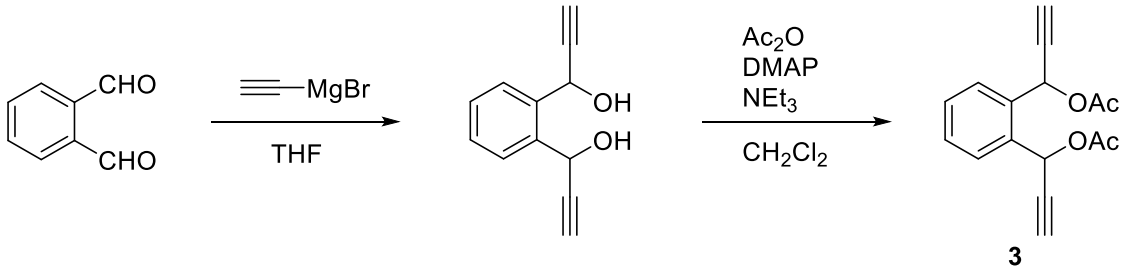
The enantiomeric excess of **2e** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{i}PrOH = 97/3, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 9.5 min (major) and 11.6 min (minor), 98% *ee*.



2f

1-ethynyl-5,6-dimethoxy-2-phenylisoindoline (**2f**): Isolated yield 79% (with **L5**). A white solid, m.p. 149.3 ˚C (decomp.). ^{1}H NMR δ 7.34-7.30 (m, 2H), 6.96 (s, 1H), 6.88-6.78 (m, 4H), 5.52 (br, 1H), 4.73 (dd, *J* = 3.5 and 12.3 Hz, 1H), 4.50 (d, *J* = 12.3 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 2.42 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR δ 149.7, 149.3, 145.9, 130.0, 129.2, 128.6, 117.2, 112.7, 105.7, 105.3, 82.7, 72.3, 56.12, 56.10, 55.2, 53.8. HRMS (EI) Calcd. for $C_{18}H_{17}NO_2$ [M]: 279.1259. Found: 279.1246. $[\alpha]^{25}_{D}$ = − 120.2 (*c* = 0.415, $CHCl_3$). The enantiomeric excess of **2f** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{i}PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 27.0 min (major) and 29.3 min (minor), 96% *ee*.

Preparation of 1,1'-(1,2-phenylene)-bis(prop-2-yne-1,1-diyl) Diacetate (3).

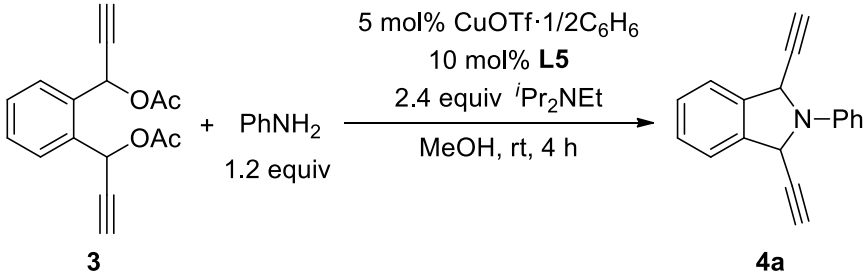


3

To a flame-dried Schlenk flask was placed ethynylmagnesium bromide (0.5 M in THF, 24 mL, 12 mmol). *o*-Phthalaldehyde (405.5 mg, 3.02 mmol) was added at room temperature, and the resulting mixture was stirred at 60 ˚C for 2 h. After the reaction, water (50 mL) was added, and the resulting mixture was extracted with EtOAc (30 mL x 3). The combined organic layer was dried over anhydrous $MgSO_4$. After concentration *in vacuo*, the residue was passed through a short silicagel pad with hexane/EtOAc (7/3) to give 1,1'-(1,2-phenylene)-bis(prop-2-yne-1-ol) as a pale yellow oil (549.4 mg, 2.95 mmol).

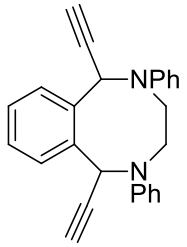
To a flame-dried Schlenk flask were placed CH_2Cl_2 (6.0 mL), DMAP (36.9 mg, 0.302 mmol), NEt_3 (625 μL, 4.55 mmol), and 1,1'-(1,2-phenylene)-bis(prop-2-yne-1-ol) (549.4 mg, 2.95 mmol). Ac_2O (425 μL, 4.53 mmol) dissolved in CH_2Cl_2 (1.0 mL) was added dropwise, and the resulting mixture was stirred at room temperature for 5 h. After the reaction, water (50 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (30 mL x 3). The combined organic layer was dried over anhydrous $MgSO_4$. After concentration *in vacuo*, the residue was purified by column chromatography (SiO_2) with hexane/EtOAc (7/3) to give **3**[S5] as a white solid (716.4 mg, 2.65 mmol, 88% isolated yield).

Double Propargylic Amination of Propargylic Diacetate with Amines.



A typical experimental procedure for the reaction of 1,1'-(1,2-phenylene)-bis(prop-2-yne-1,1-diyl) diacetate (**3**) with aniline is described below. In a 20 mL Schlenk flask were placed CuOTf▪1/2C_6H_6 (2.4 mg, 0.010 mmol) and (*S*)-Ph-pybox (**L5**) (7.3 mg, 0.020 mmol) under N_2. Anhydrous methanol (1.0 mL) was added, and then the mixture was magnetically stirred at 60 ˚C for 1 h. After the solution was cooled to room temperature, **3** (53.0 mg, 0.20 mmol) in anhydrous methanol (1.0 mL), aniline (22 μL, 0.24 mmol), and diisopropylethylamine (84 μL, 0.48 mmol) were added under N_2, and the reaction was kept at room temperature for 4 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2) with hexane/ethyl acetate (93/7) to give 1,3-diethynyl-2-phenylisoindoline (**4a**) as a white solid (33.3 mg, 0.137 mmol, 70% isolated yield, *meso*-**4a**/*dl*-**4a** = 5.0/1). ^{1}H NMR (*meso*-isomer): δ 7.51-7.34 (m, 6H), 7.15-7.07 (m, 2H) 6.91-6.85 (m, 1H), 5.54 (br, 2H), 2.45 (br, 2H). ^{1}H NMR (*dl*-isomer): δ 5.76 (br, 2H), 2.36 (br, 2H). ^{13}C NMR (*meso*-isomer): δ 145.0, 137.6, 129.3, 128.8, 123.1, 118.3, 113.4, 82.4, 72.6, 55.4. ^{13}C NMR (*dl*-isomer): δ 143.7, 137.8, 123.2, 118.6, 115.4, 81.7, 73.3, 54.6. HRMS (EI) Calcd. for $C_{18}H_{13}N$ [M]: 243.1048. Found: 243.1038. The enantiomeric excess of *dl*-**4a** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{i}PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.4 min (minor) and 29.1 min (major), 75% *ee*.

Spectroscopic Data and Isolated Yield of Other Product.



4b

1,6-diethynyl-2,5-diphenyl-1,2,3,4,5,6-hexahydrobenzo[f][1,4]diazocine (**4b**): Isolated yield 68% (*meso*-**4b**/*dl*-**4b** = 7.7/1). A white solid. ^{1}H NMR (*meso*-isomer): δ 7.76-7.73 (m, 2H), 7.36-7.33 (m, 2H) 7.15-7.06 (m, 4H), 6.76-6.65 (m, 6H), 5.70 (d, *J* = 2.2 Hz, 2H), 4.23-4.13 (m, 2H), 3.92-3.82 (m, 2H), 2.44 (d, *J* = 2.2 Hz, 2H). ^{1}H NMR (*dl*-isomer): δ 8.01-7.97 (m, 2H), 5.57 (d, *J* = 2.3 Hz, 2H), 3.97 (br, 4H), 2.66 (d, *J* = 2.3 Hz, 2H). ^{13}C NMR (*meso*-isomer): δ 145.5, 135.8, 130.0, 129.0, 128.2, 117.3, 113.1, 80.1, 77.4, 56.7, 46.8. ^{13}C NMR (*dl*-isomer): δ 129.0, 128.1, 117.2, 112.5, 58.0, 49.1. HRMS (EI) Calcd. for $C_{26}H_{22}N_2$ [M]: 362.1783. Found: 362.1781. The enantiomeric excess of *dl*-**4b** was determined by HPLC analysis; DAICEL Chiralpak IA, hexane/^{i}PrOH = 95/5, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.8 min (minor) and 12.4 min (major), 66% *ee*.

X-ray Diffraction Study of 2d.

Diffraction data for (*R*)-2-(4-bromophenyl)-1-ethynylisoindoline (**2d**) were collected on a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71075 Å) with Varimax optics. Reflections were collected for the 2θ range of 6° to 55°. Intensity data were corrected for numerical absorptions (NUMABS)[S7], and for Lorentz and polarization effects. A correction for secondary extinction[S8] was further applied (coefficient, 19(12)). The structure solution and refinements were carried out by using CrystalStructure package.[S9] The positions of all the non-hydrogen atoms were determined by direct methods (SIR97)[S10] and subsequent Fourier syntheses, and were refined on F_o^2 with all the unique reflections by full-matrix least squares with anisotropic thermal parameters. All the hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Goodness of fit indicator $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$ were all refined to the value of 1.000. The atomic scattering factors were taken from reference S11, and anomalous dispersion effects were included.[S12] The values of $\Delta f'$ and $\Delta f''$ were taken from reference S13. The Flack parameter[S14] for **2d** was refined to the value of 0.010(14), which clearly suggests that the absolute configuration of the major isomer of **2d** is (*R*) as shown in Figure S1, where the ORTEP drawing of **2d** is depicted. Details of the crystals and data collection parameters of **2d** are summarized in Table S1.

CCDC 989441 (**2d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic Data for **2d**.

	2d
chemical formula	$C_{16}H_{12}BrN$
formula weight	298.18
crystal size	0.42 × 0.11 × 0.08
color, habit	colorless, needle
temperature (°C)	–75
crystal system	orthorhombic
space group	$P2_12_12_1$ (#19)
a (Å)	4.08853(17)
b (Å)	11.1945(6)
c (Å)	27.8189(12)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	1273.25(10)
Z	4
d_{calcd} (g cm^{-3})	1.555
F(000)	600
μ (cm^{-1})	32.173
transmission factors range	0.440–0.773
measured reflections	10532
unique reflections	2885
R_{int}	0.0594
refined parameters	177
$R1$ ($I > 2\sigma(I)$) [a]	0.0365
$wR2$ (all data) [b]	0.0705
residual peaks (e Å^{-3})	+0.531/–0.657
CCDC number	989441

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$, $w = 4F_o^2/q\sigma(F_o^2)$, $q = 1.847$.

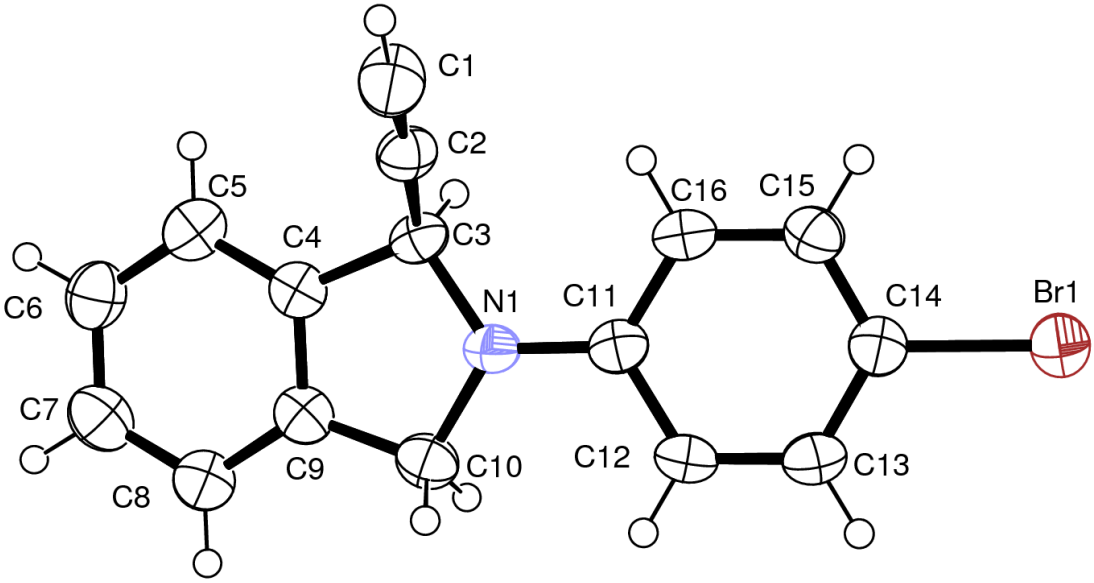


Figure S1. ORTEP drawing of **2d**. Thermal ellipsoids are given at the 50% probability level.

References and Notes

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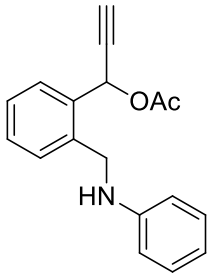
^{1}H and ^{13}C NMR Spectra



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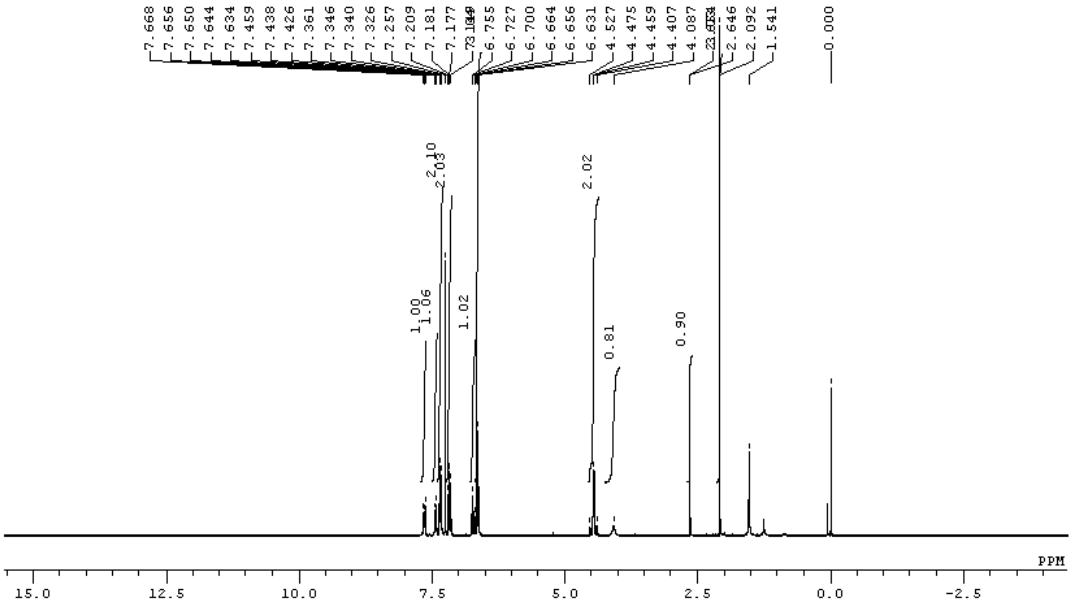

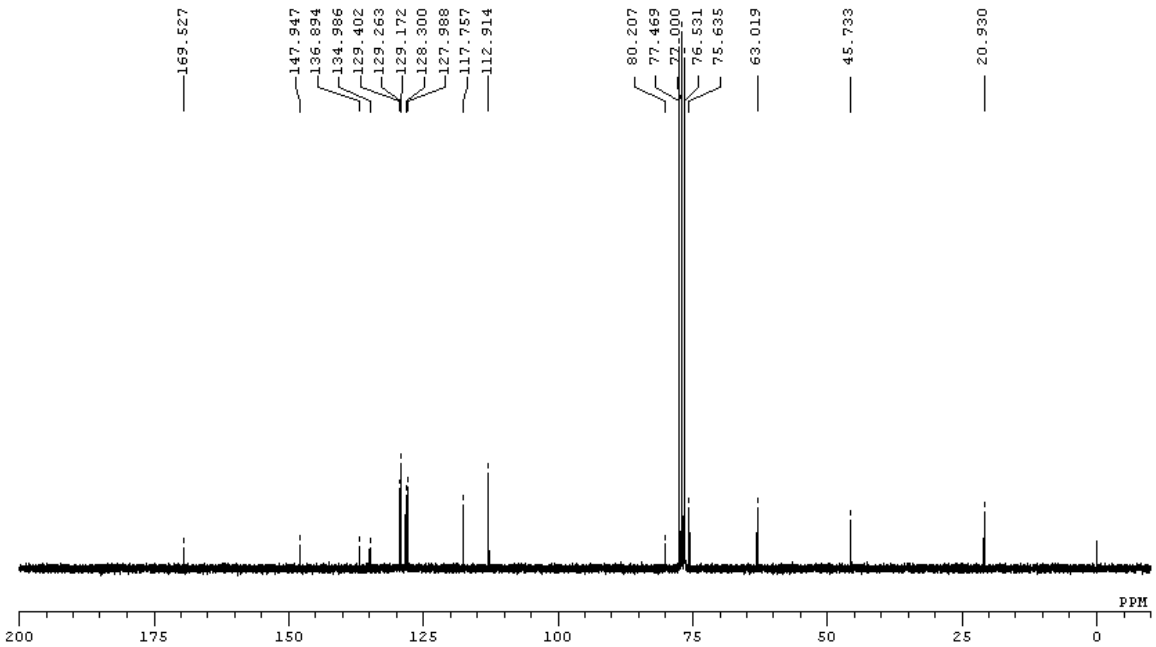

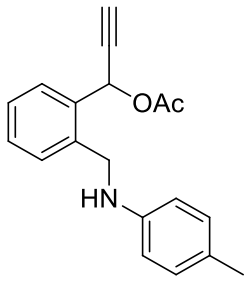
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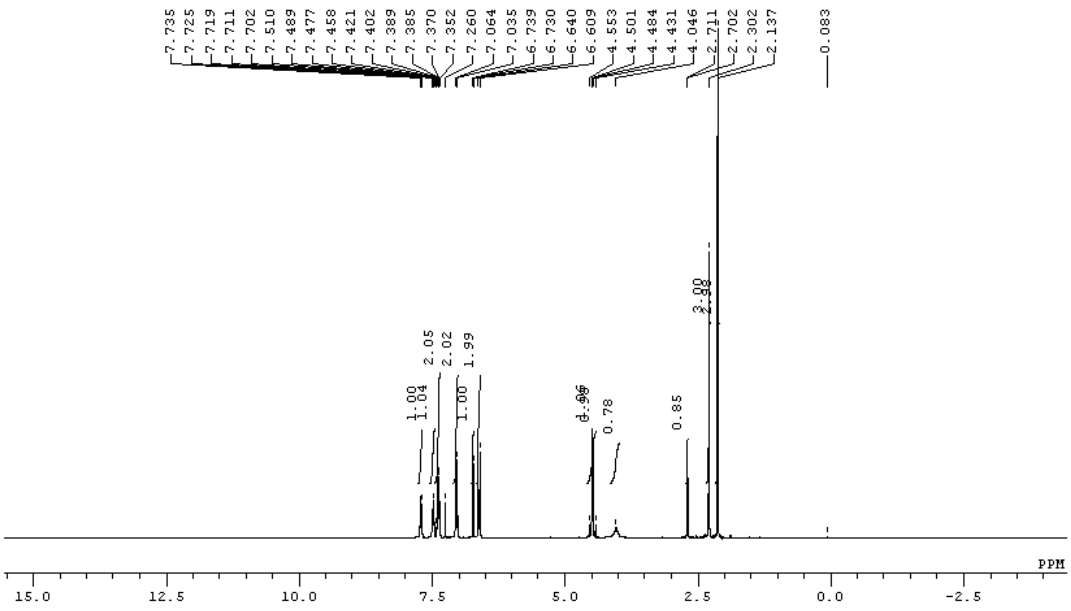
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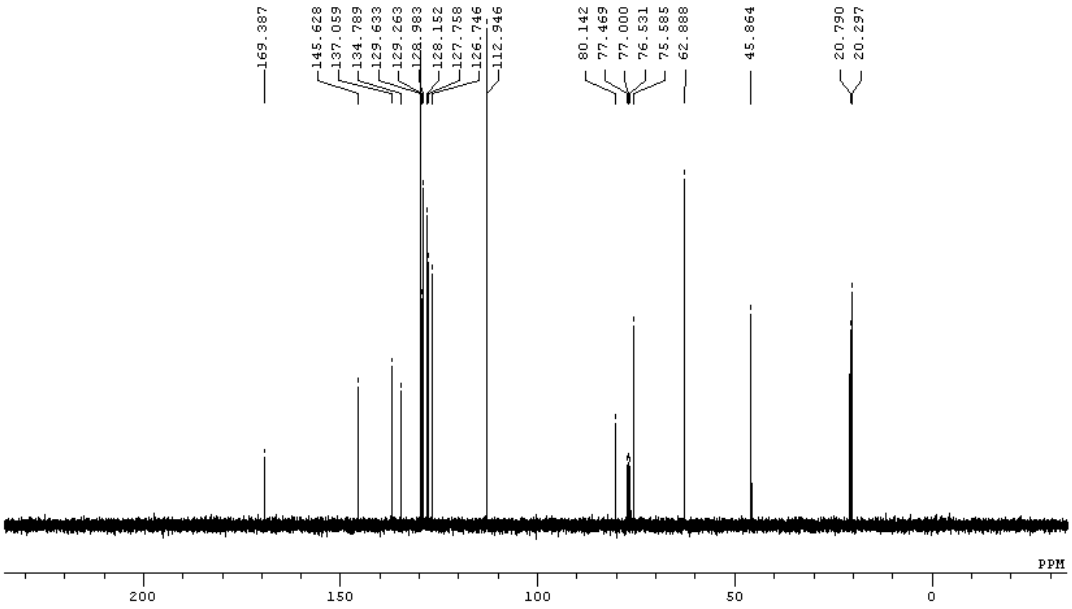
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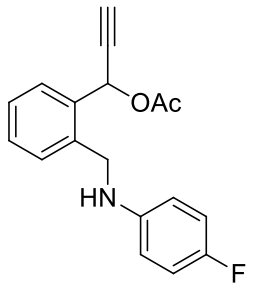
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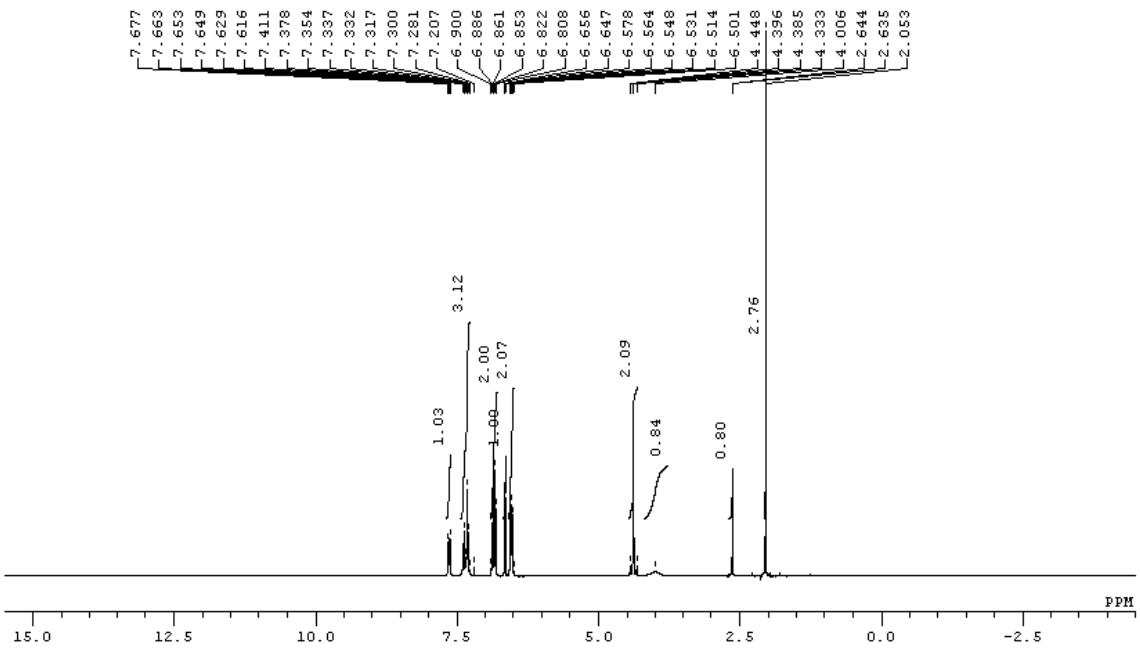
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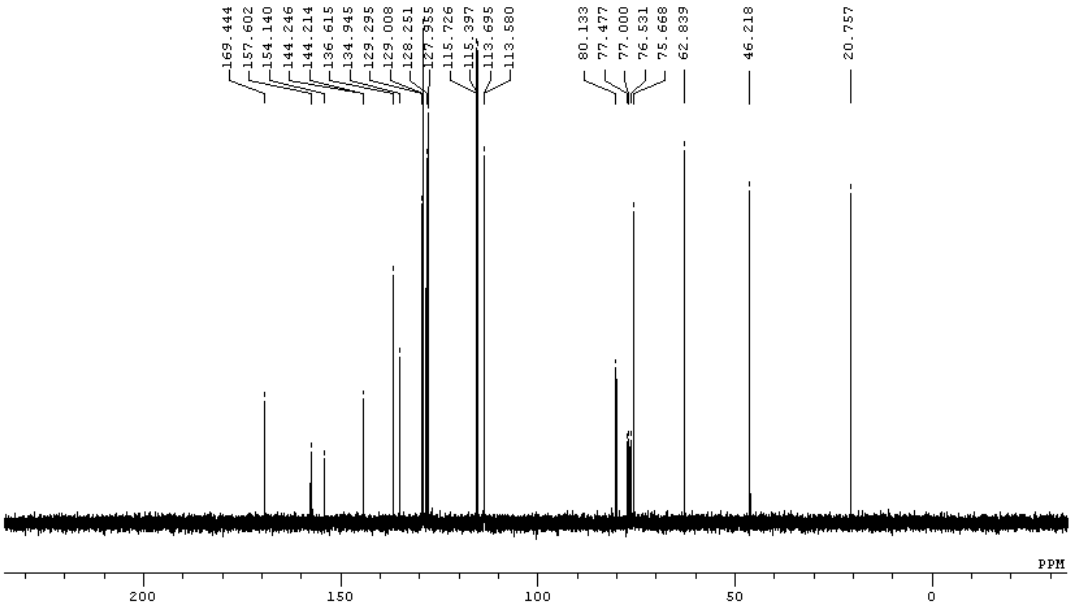
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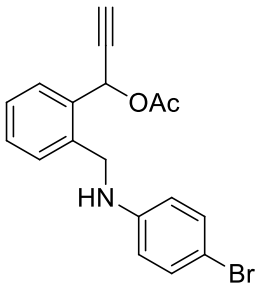
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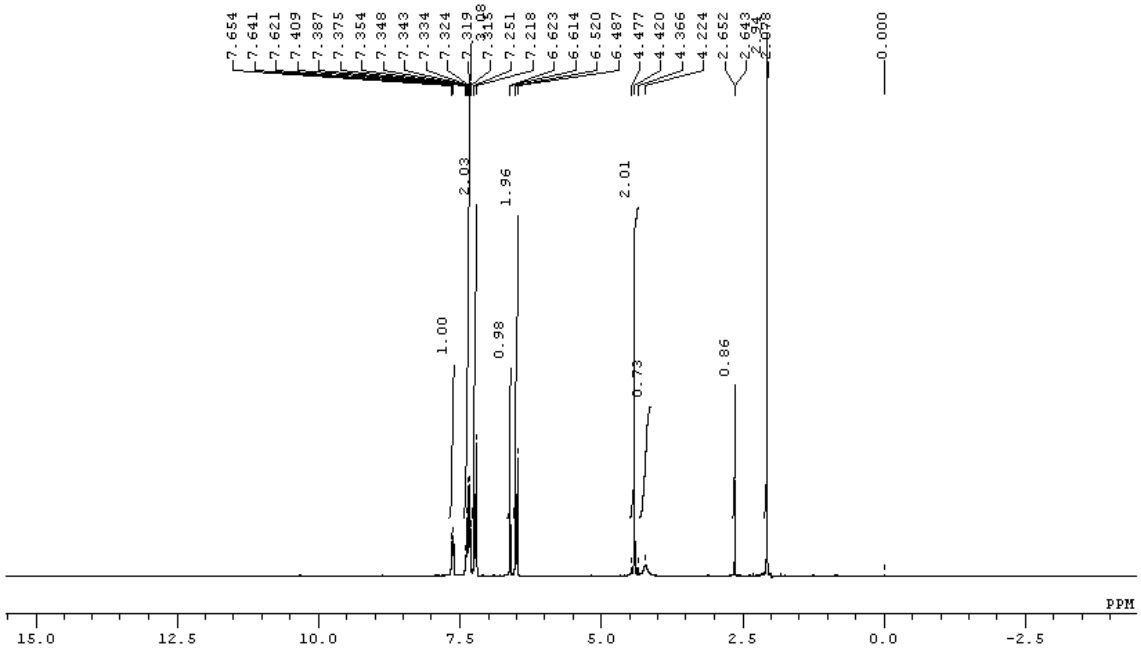
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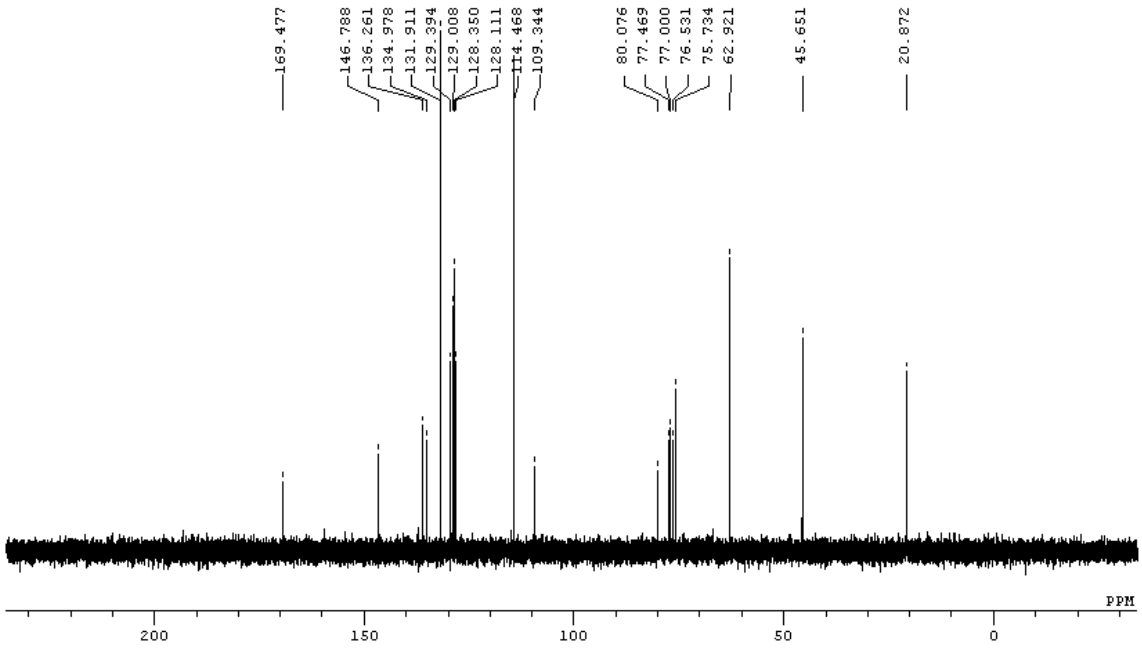
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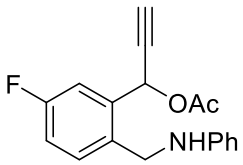
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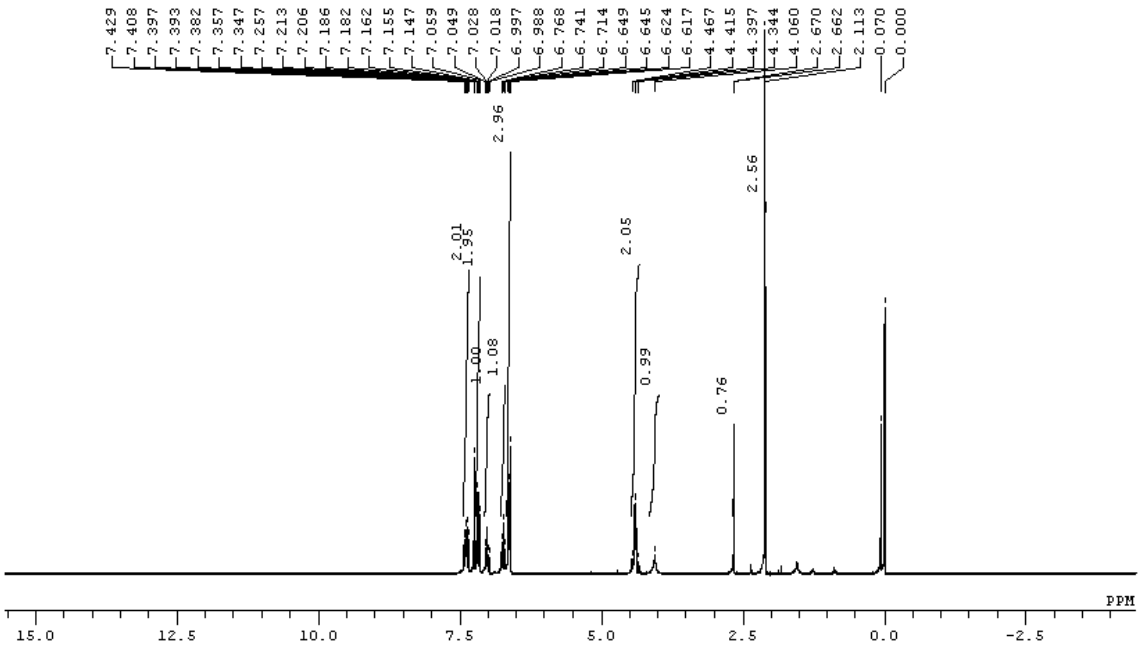
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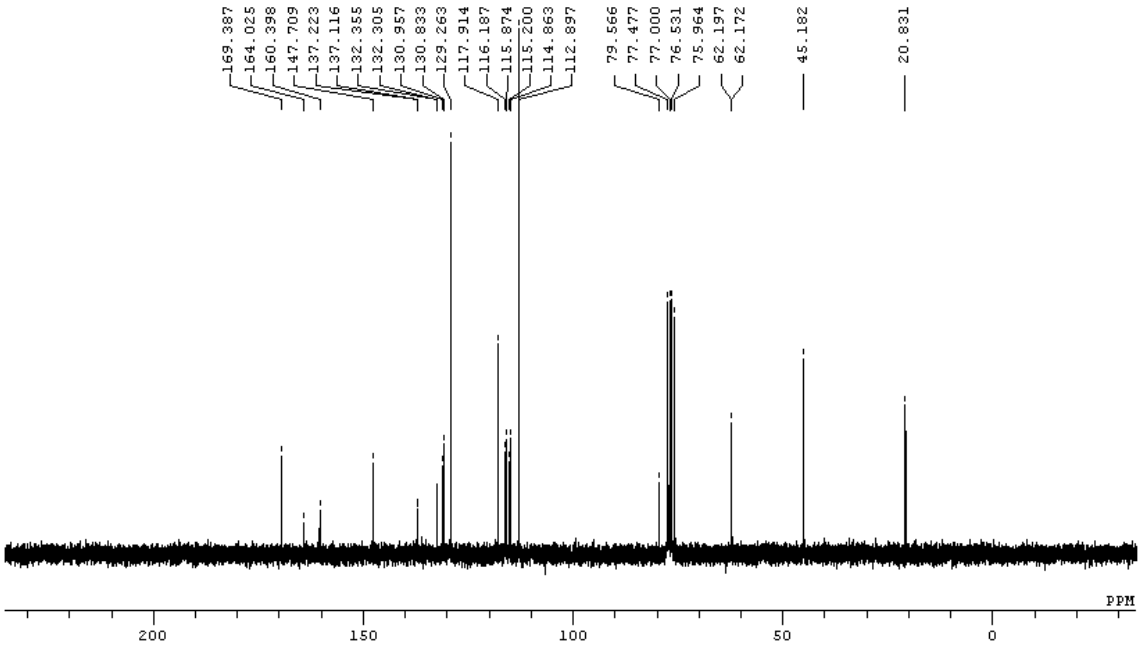
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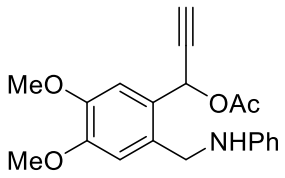
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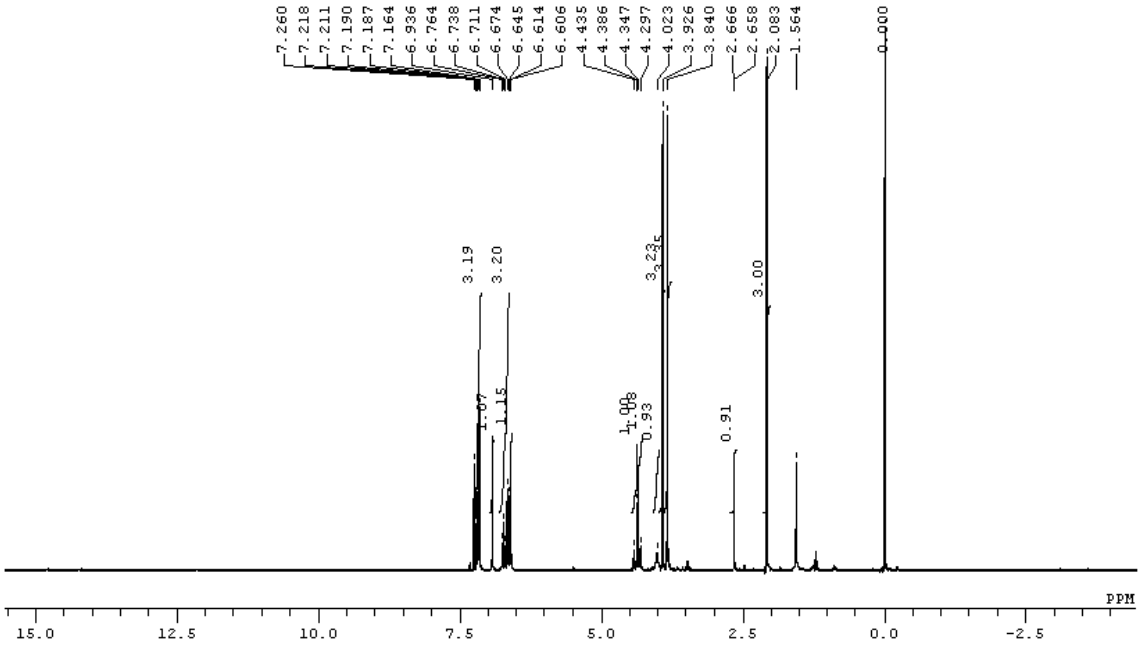
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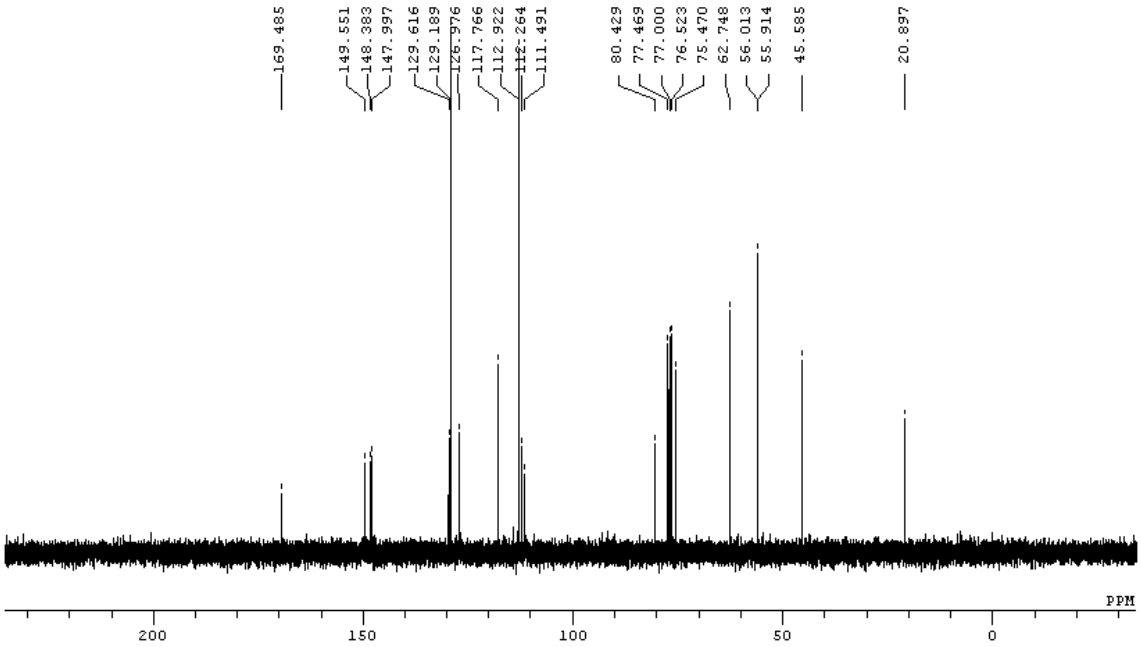
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117.766
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112.264
111.491
80.429
77.469
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76.523
75.470
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55.914
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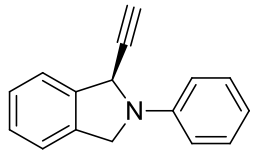
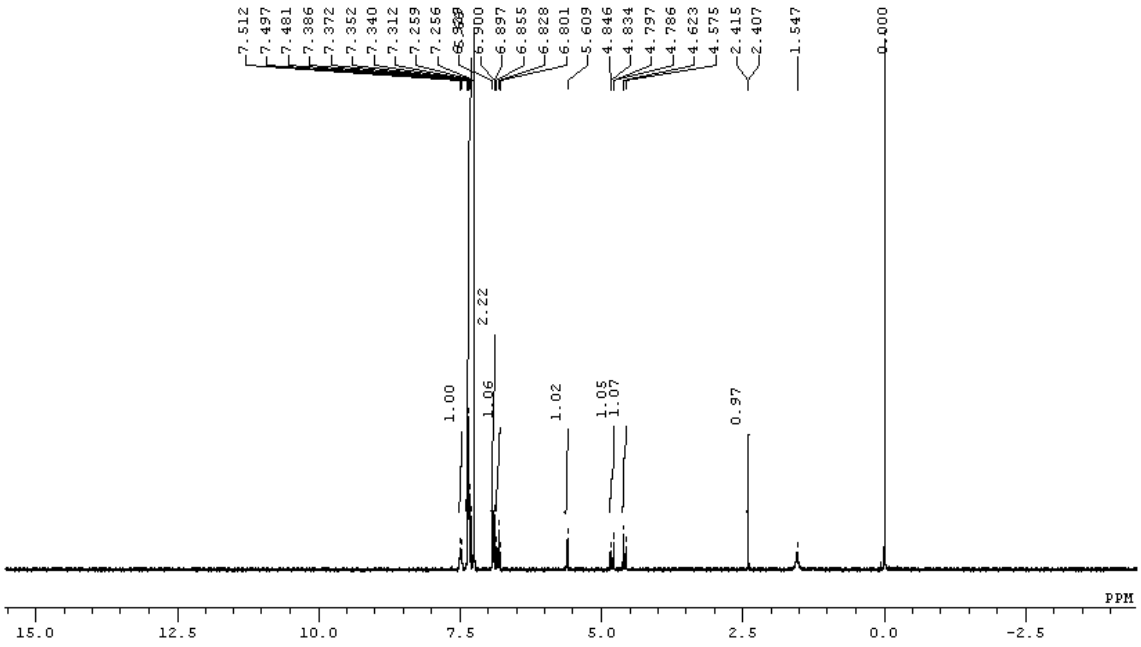
150
100
50
0



2a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7.259
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6.897
6.855
6.828
6.801
5.609
4.846
4.834
4.797
4.786
4.623
4.575
2.415
2.407
1.547
0.000
2.22
1.00
1.06
1.02
1.05
1.07
0.97
PPM
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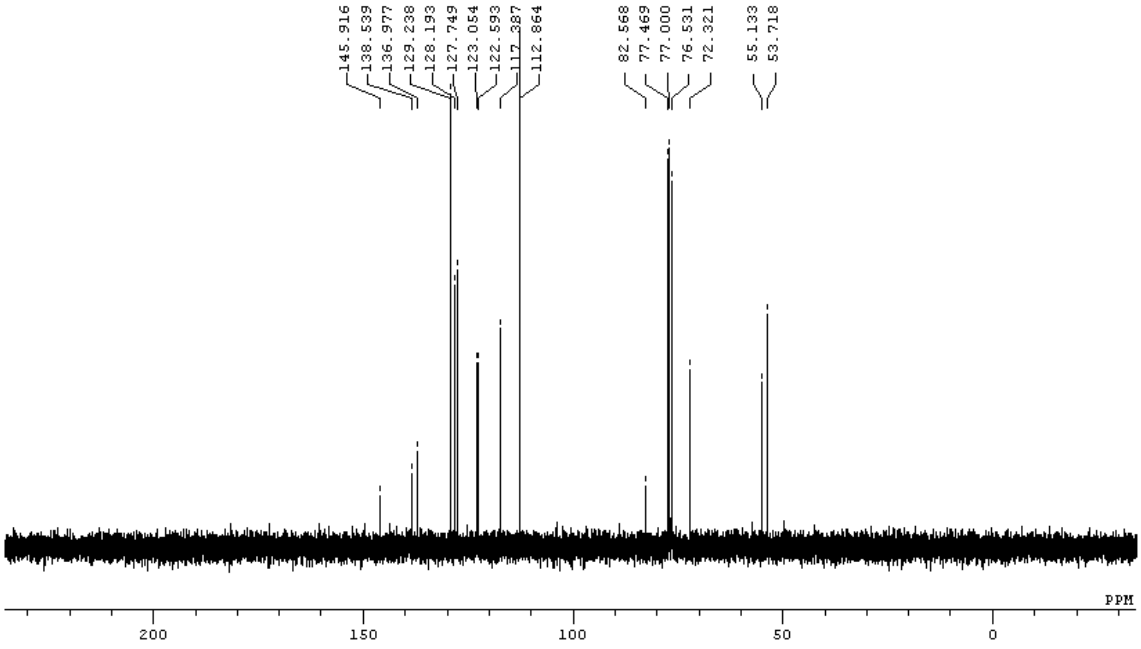
7.5
5.0
2.5
0.0
-2.5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76.531
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PPM
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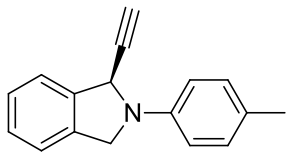
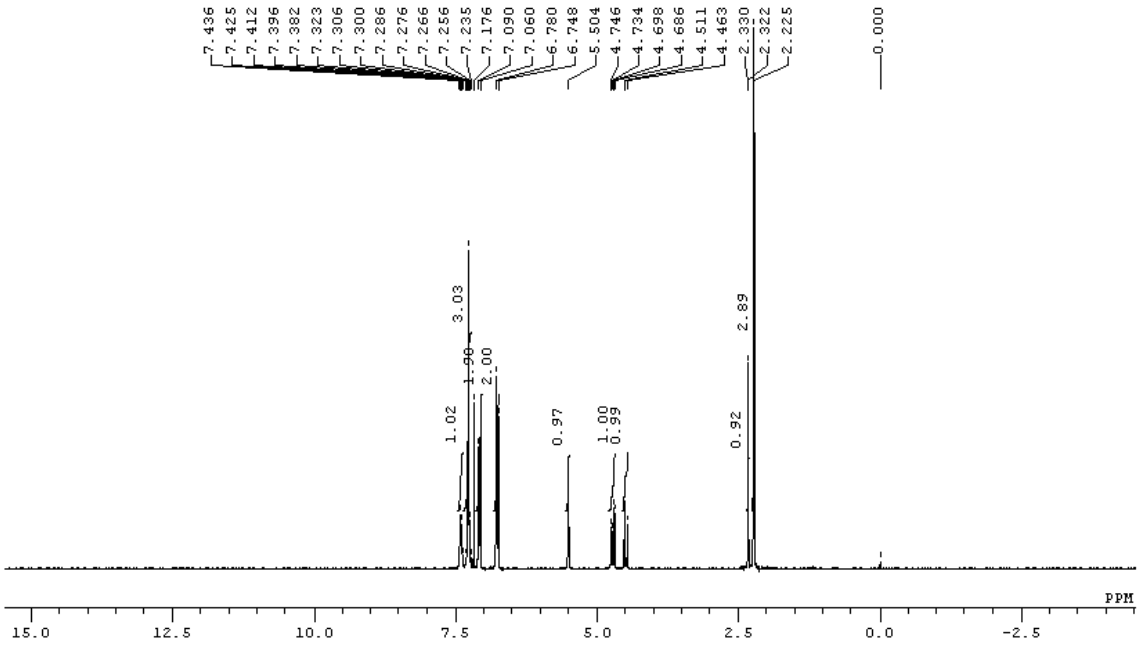
150
100
50
0



2b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7.276
7.266
7.256
7.235
7.176
7.090
7.060
6.780
6.748
5.504
4.746
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4.698
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4.511
4.463
2.330
2.322
2.225
0.000
3.03
1.96
2.00
1.02
0.97
1.00
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7.5
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0.0
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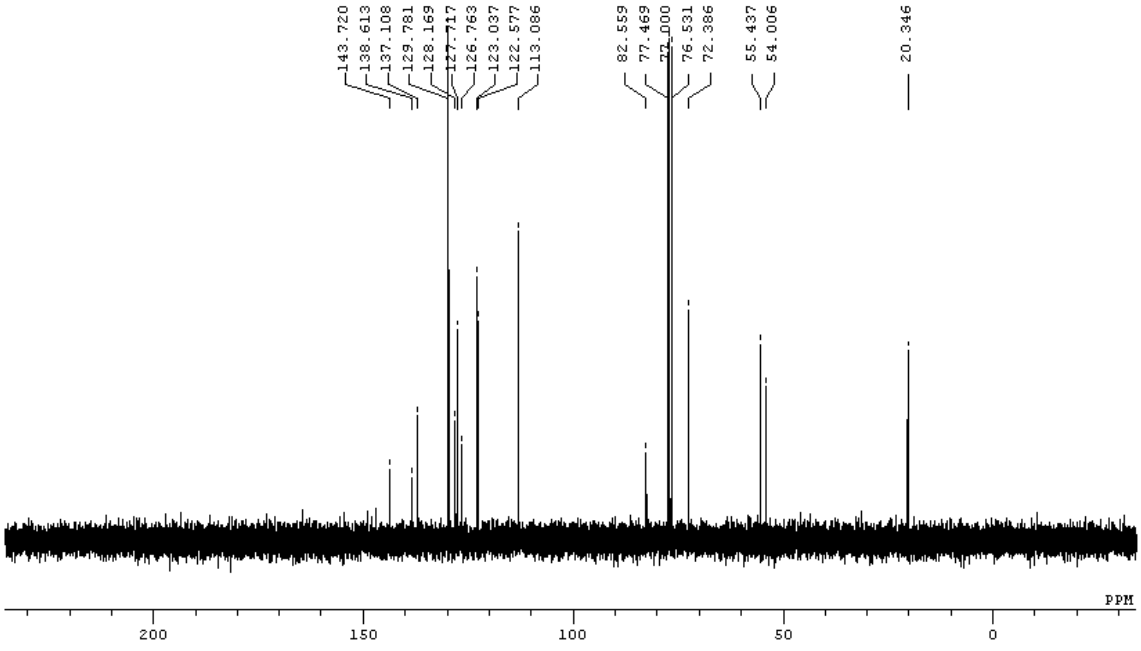
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129.781
128.169
127.717
126.763
123.037
122.577
113.086
82.559
77.469
77.000
76.531
72.386
55.437
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20.346
PPM
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100
50
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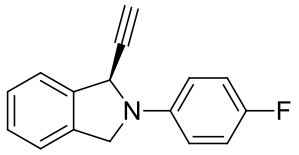
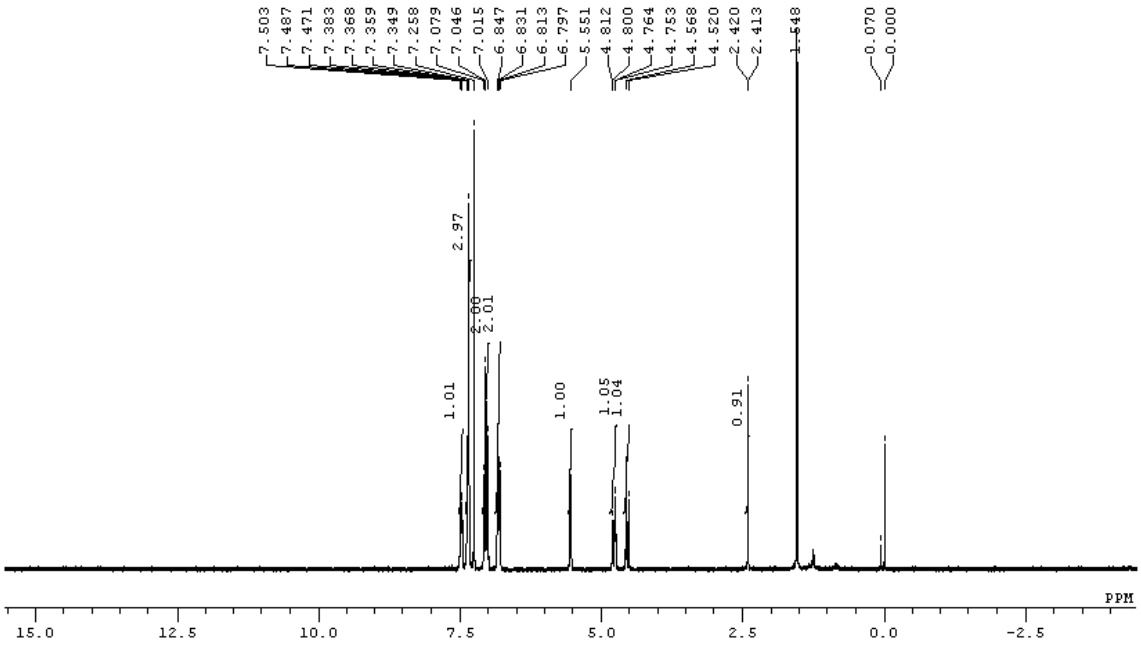

N
F

2c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7.471
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7.349
7.258
7.079
7.046
7.015
6.847
6.831
6.813
6.797
5.551
4.812
4.800
4.764
4.753
4.568
4.520
2.420
2.413
1.548
0.070
0.000
2.97
2.00
2.01
1.01
1.00
1.05
1.04
0.91
PPM
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12.5
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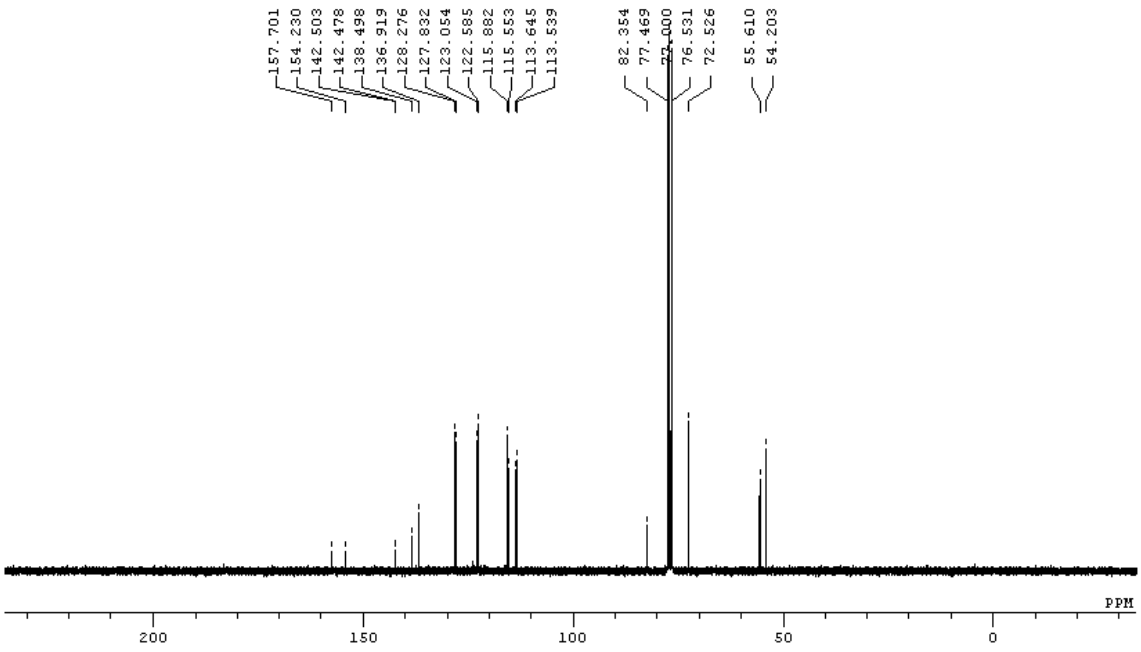
7.5
5.0
2.5
0.0
-2.5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142.503
142.478
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136.919
128.276
127.832
123.054
122.585
115.882
115.553
113.645
113.539
82.354
77.469
77.000
76.531
72.526
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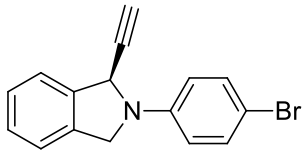
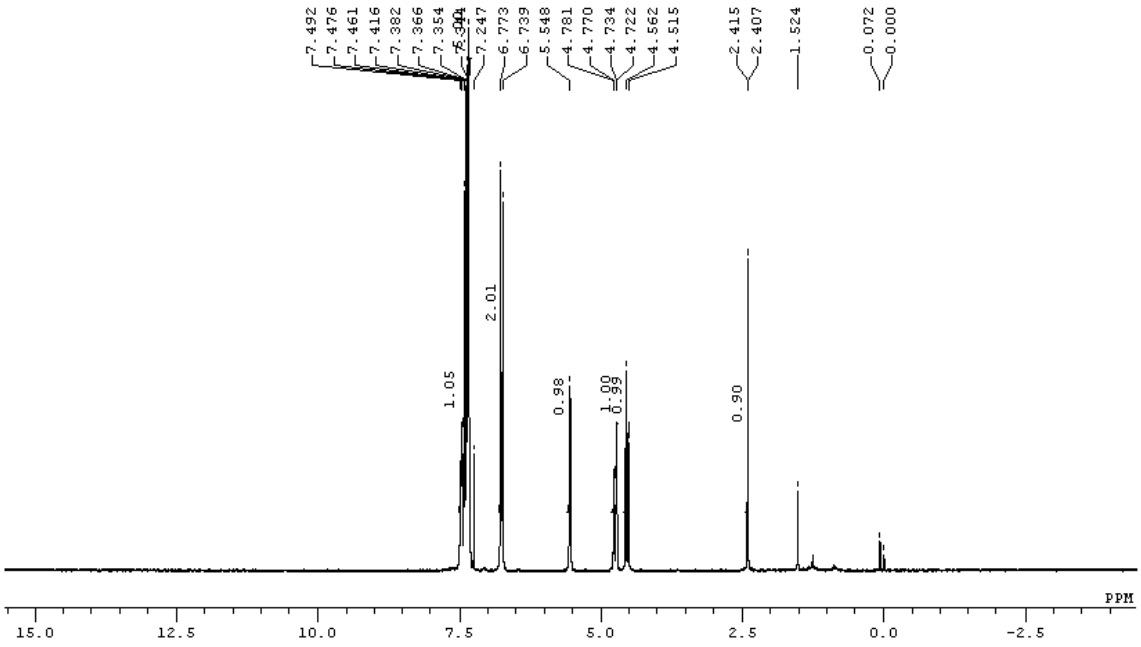
54.203
PPM
200
150
100
50
0


N
Br

2d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7.366
7.354
7.247
6.773
6.739
5.548
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4.770
4.734
4.722
4.562
4.515
2.415
2.407
1.524
0.072
0.000
1.05
2.01
0.98
1.00
0.99
0.90
PPM
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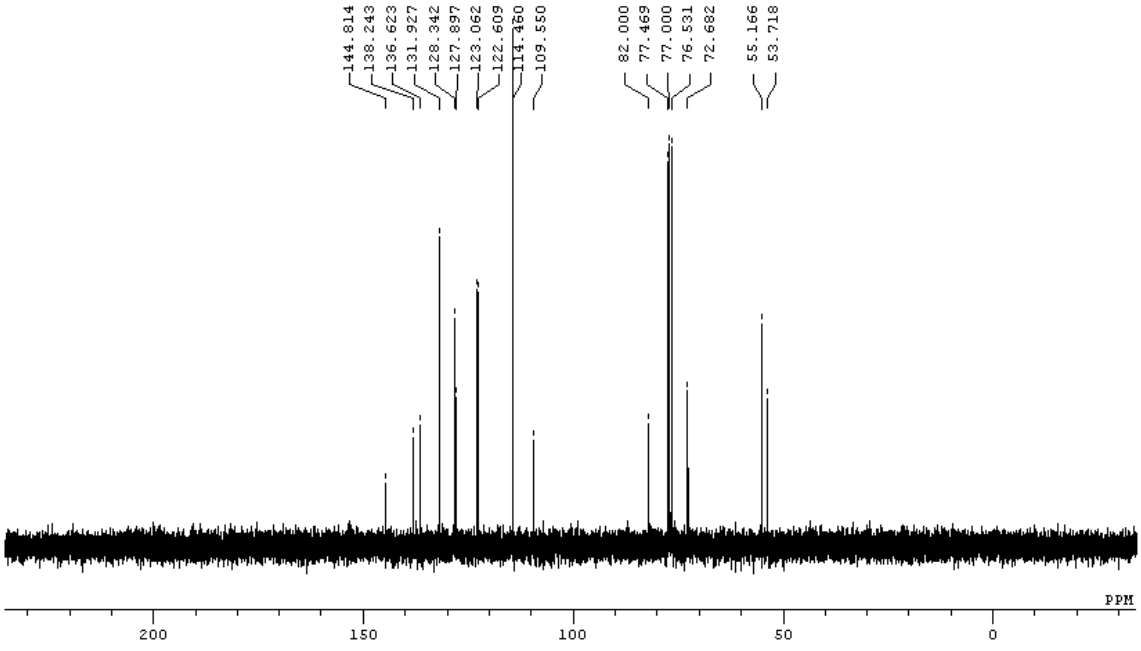
10.0
7.5
5.0
2.5
0.0
-2.5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131.927
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127.897
123.062
122.609
114.460
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82.000
77.469
77.000
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72.682
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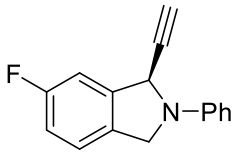
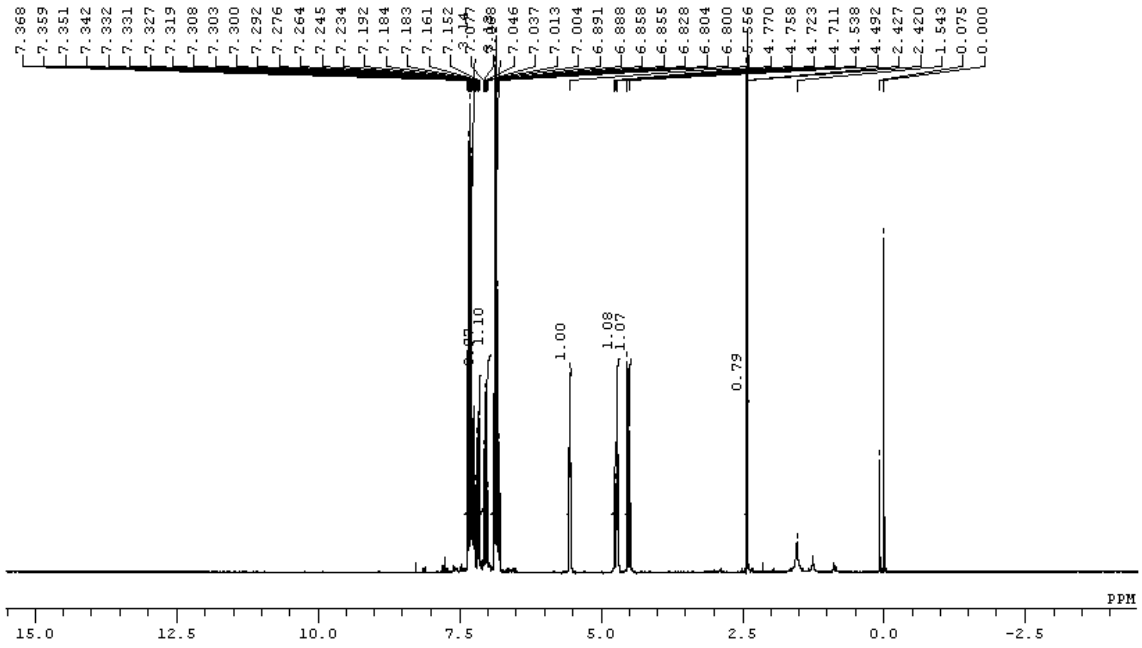
53.718
PPM
200
150
100
50
0


F
N–Ph

2e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7.276
7.264
7.245
7.234
7.192
7.184
7.183
7.161
7.152
7.046
7.037
7.013
7.004
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6.888
6.858
6.855
6.828
6.804
6.800
5.556
4.770
4.758
4.723
4.711
4.538
4.492
2.427
2.420
1.543
0.075
0.000
1.10
1.00
1.08
1.07
0.79
PPM
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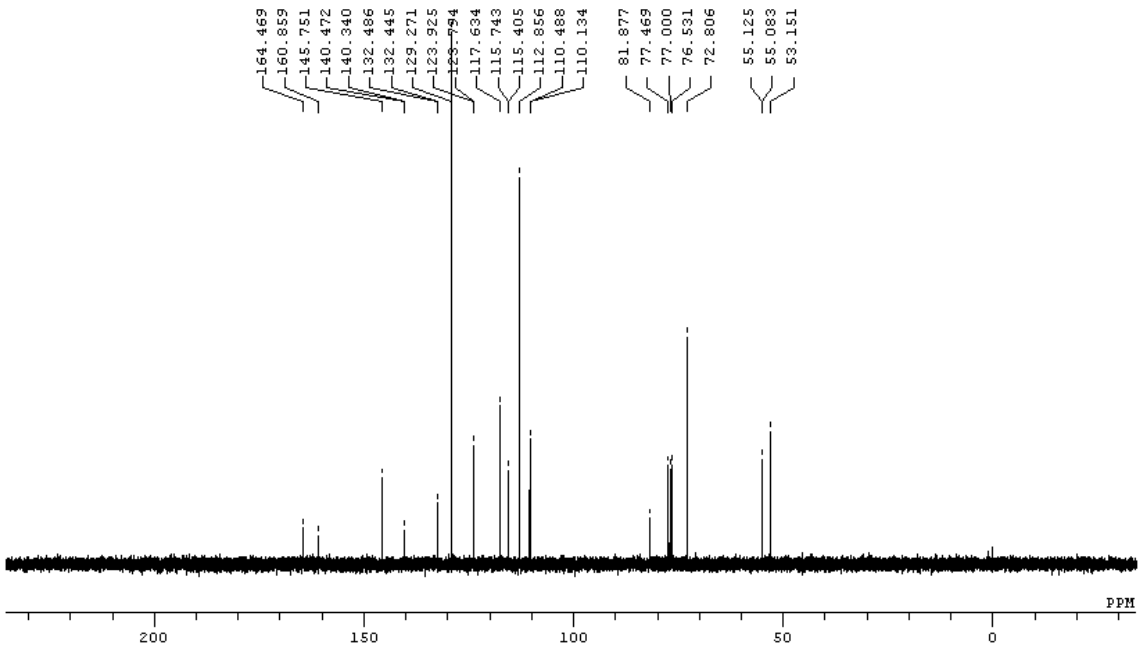
7.5
5.0
2.5
0.0
-2.5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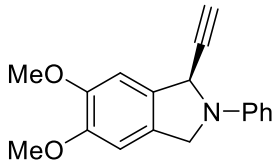
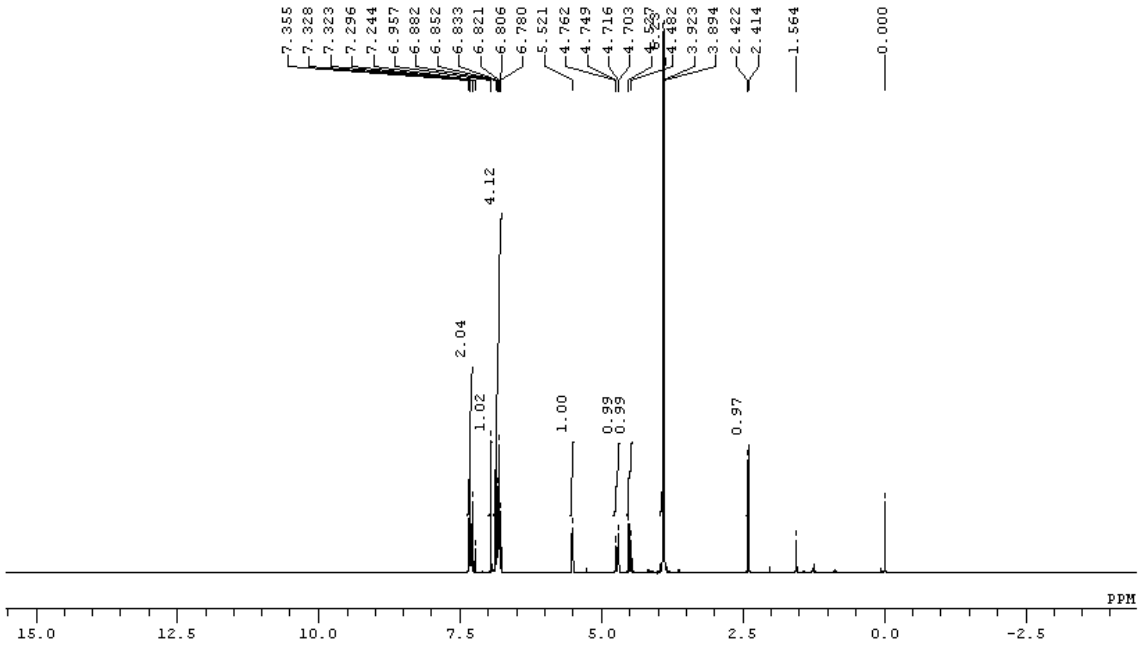
123.794
117.634
115.743
115.405
112.856
110.488
110.134
81.877
77.469
77.000
76.531
72.806
55.125
55.083
53.151
PPM
200
150
100
50
0


MeO
MeO
N–Ph

2f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6.852
6.833
6.821
6.806
6.780
5.521
4.762
4.749
4.716
4.703
4.527
4.482
3.923
3.894
2.422
2.414
1.564
0.000
4.12
2.04
1.02
1.00
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0.99
0.97
PPM
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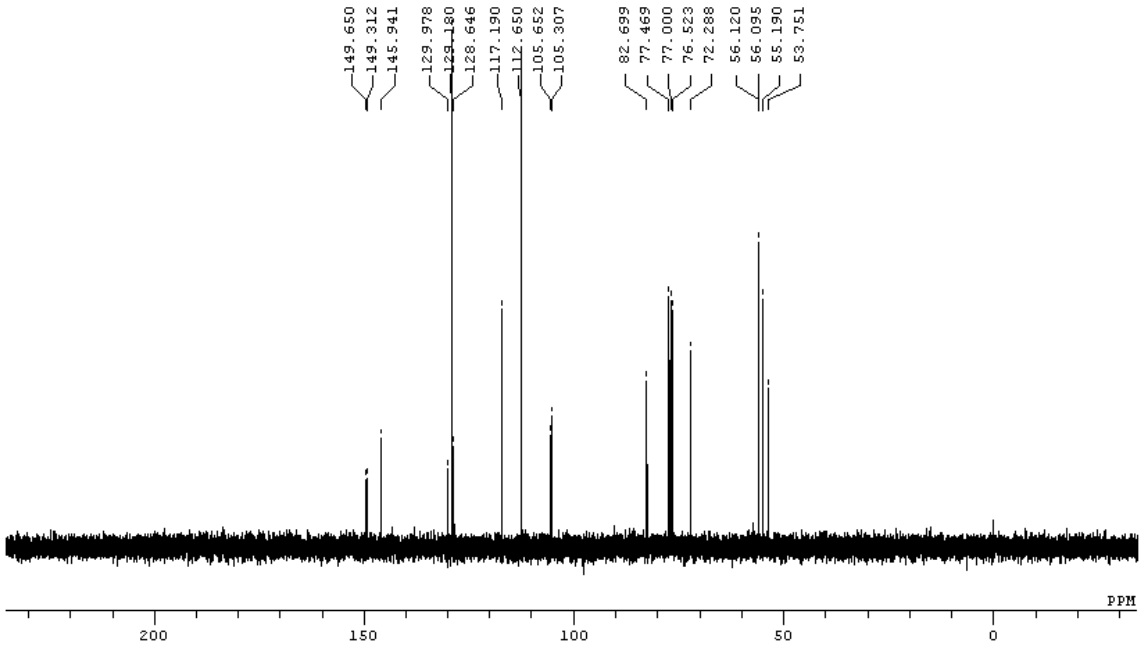
10.0
7.5
5.0
2.5
0.0
-2.5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112.650
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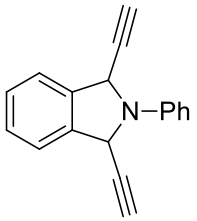
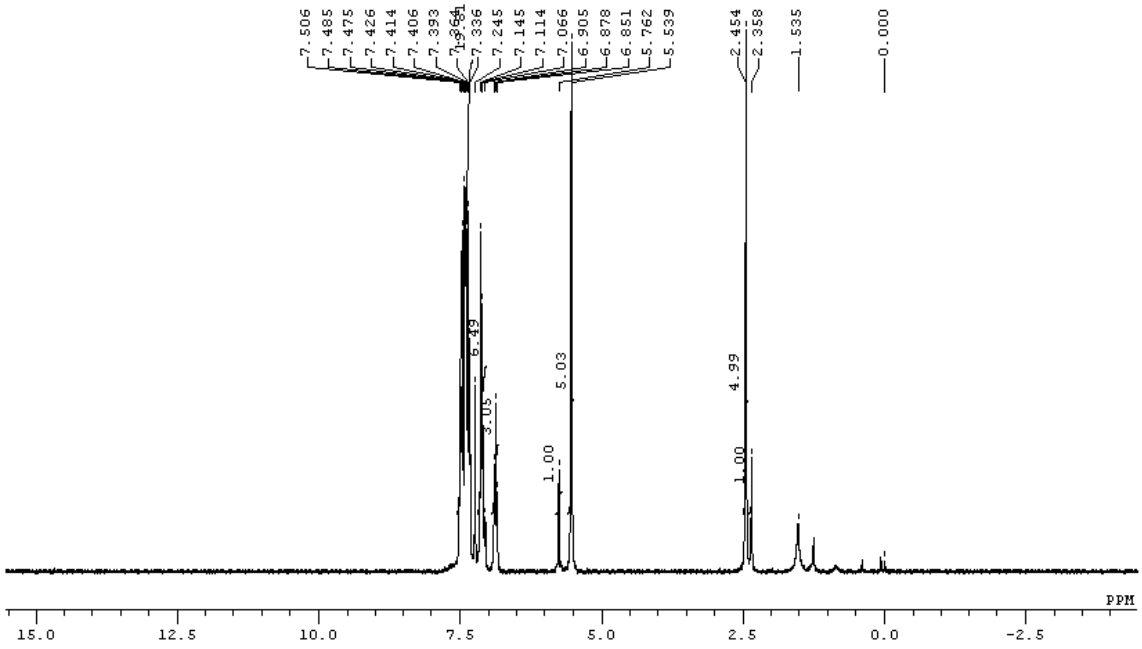
76.523
72.288
56.120
56.095
55.190
53.751
PPM
200
150
100
50
0


N–Ph

4a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7.393
7.361
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7.245
7.145
7.114
7.066
6.905
6.878
6.851
5.762
5.539
2.454
2.358
1.535
0.000
6.49
3.05
5.03
1.00
4.99
1.00
PPM
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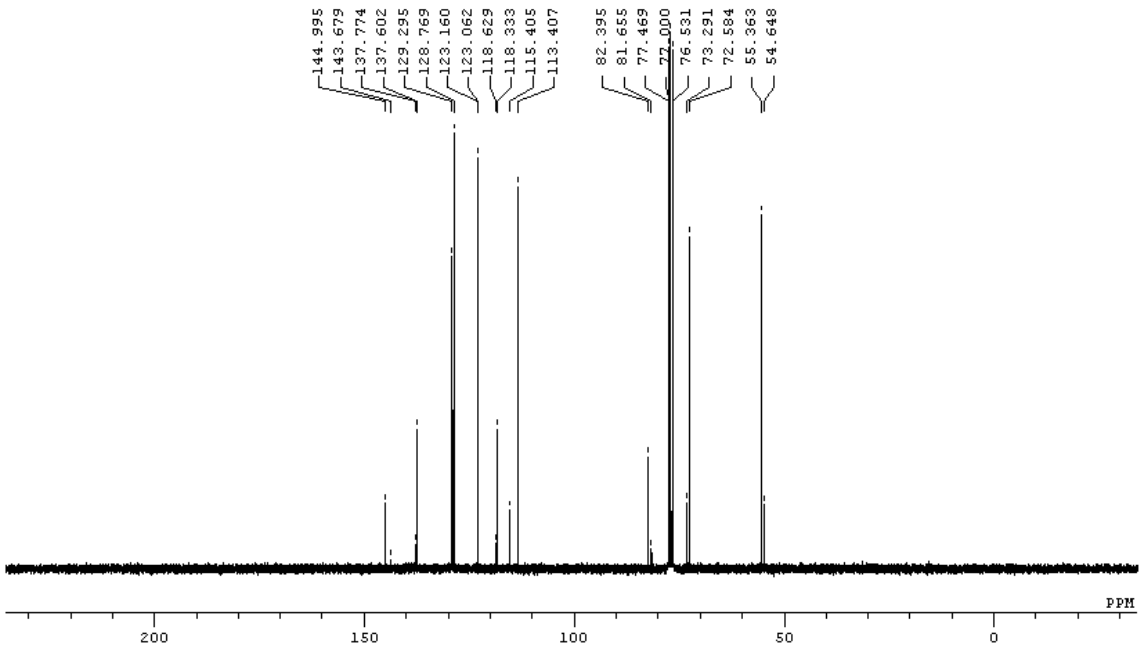
10.0
7.5
5.0
2.5
0.0
-2.5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123.062
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118.333
115.405
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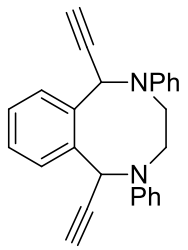
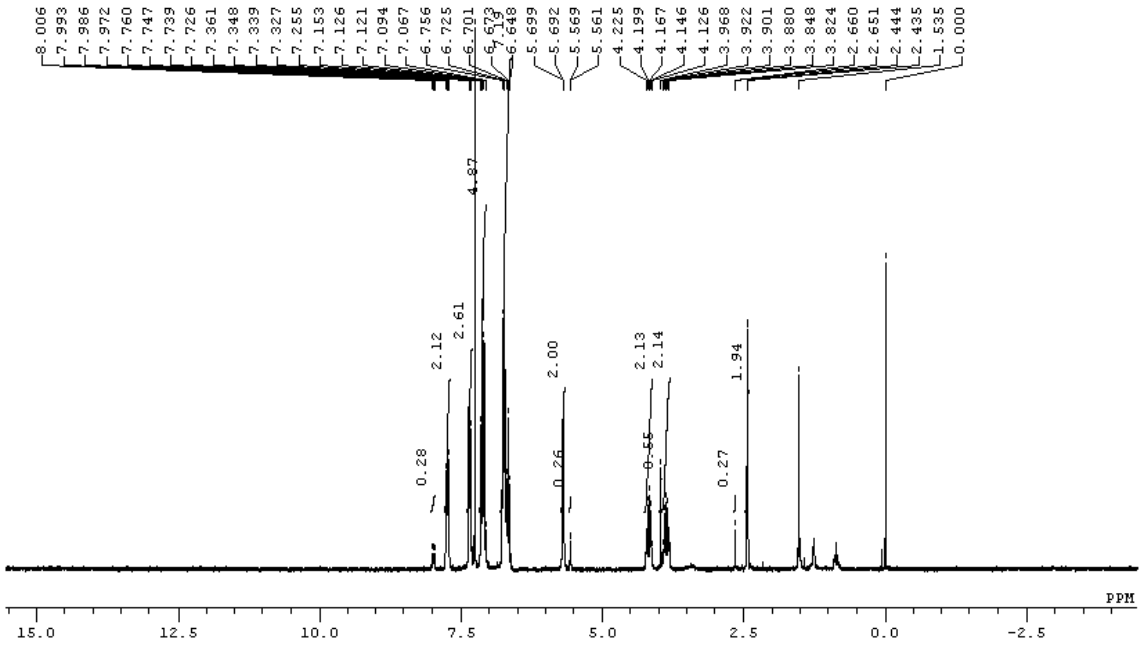
82.395
81.655
77.469
77.000
76.531
73.291
72.584
55.363
54.648
PPM
200
150
100
50
0


NPh
N
Ph

4b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7.153
7.126
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7.067
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4.199
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4.126
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PPM
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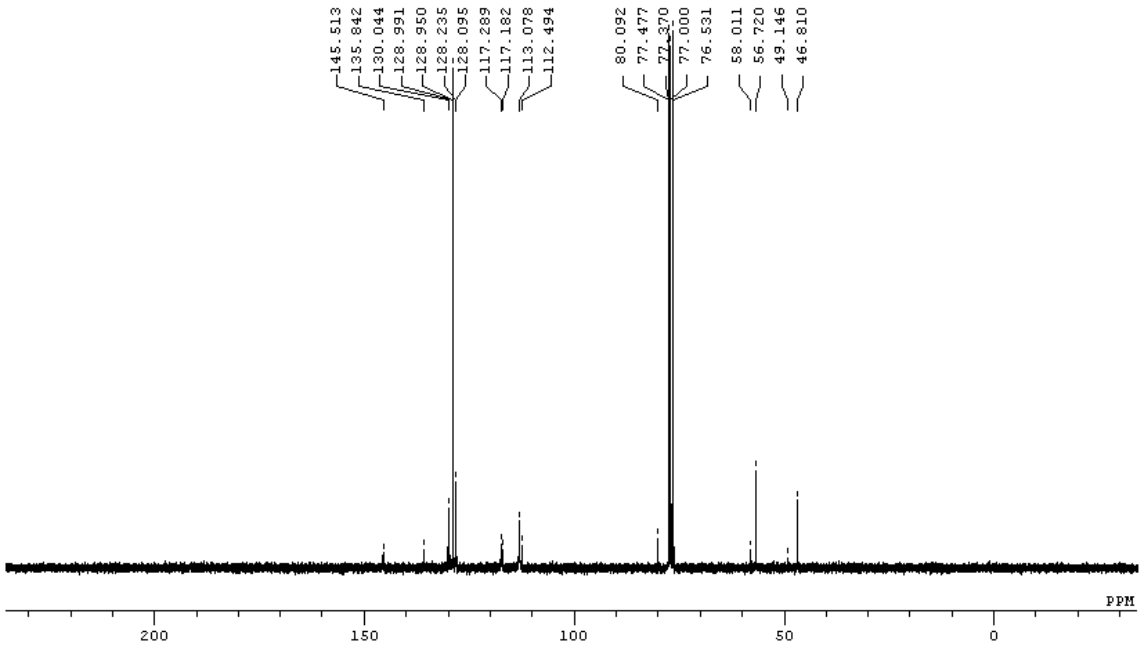
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112.494
80.092
77.477
77.370
77.000
76.531
58.011
56.720
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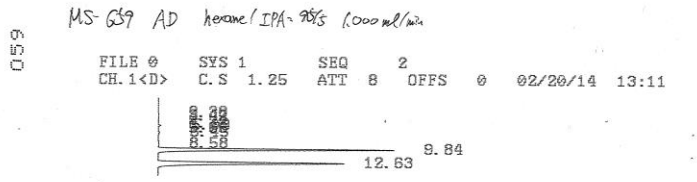
46.810
PPM
200
150
100
50
0

Charts of Propargylic Aminated Products by HPLC Analysis

2a(rac)



D-7500 INTEGRATOR REPORT

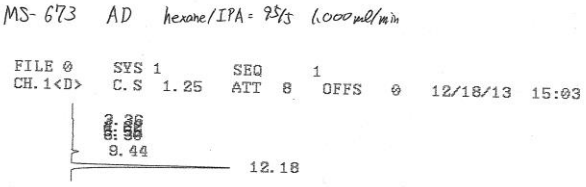
ANALYZED: 02/20/14 13:11 REPORTED: 02/20/14 13:26
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL>
OPERATOR:
SEQ : 2

FILE : 0
CALC-METHOD: AR/HI% <AREA>
MODULE T-PROG :
COMPONENT TBL : 0
DETECTOR= 1

NO.	RT	AREA	CONC	BC
8	9.84	2072754	50.194	BB
9	12.63	2056724	49.806	BB
TOTAL		4129478	100.000	

PEAK REJ : 50000

2a



D-7500 INTEGRATOR REPORT

ANALYZED: 12/18/13 15:03 REPORTED: 12/18/13 15:20
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL>
OPERATOR:
SEQ : 1

FILE : 0
CALC-METHOD: AR/HI% <AREA>
MODULE T-PROG :
COMPONENT TBL : 0
DETECTOR= 1

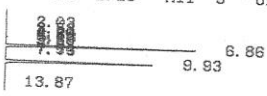
NO.	RT	AREA	CONC	BC
5	9.44	60380	3.370	VB
6	12.18	1731319	96.630	BB
TOTAL		1791699	100.000	

PEAK REJ : 50000

2b(rac)

MS-523 IA hexane/IPA = 95/5 1.000 ml/min

FILE 0 SYS 1 SEQ 2
CH.1<D> C.S 1.25 ATT 9 OFFS 0 07/18/13 20:19



D-7500 INTEGRATOR REPORT

ANALYZED: 07/18/13 20:19 REPORTED: 07/18/13 20:35
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL> OPERATOR:
SEQ : 2

FILE : 0
CALC-METHOD: AR/HI% <AREA> MODULE T-PROG :
COMPONENT TBL : 0 DETECTOR= 1

NO.	RT	AREA	CONC	BC
7	6.86	1738923	50.048	BV
10	9.93	1735572	49.952	BB
TOTAL		3474495	100.000	
PEAK REJ :		50000		

2b

MS-5[illegible] IA hexane/IPA = 95/5 1.000 ml/[illegible]

FILE 0 SYS 1 SEQ 1
CH.1<D> C.S 1.25 ATT 8 OFFS 0 07/19/13 20:11

D-7500 INTEGRATOR REPORT

ANALYZED: 07/19/13 20:11 REPORTED: 07/19/13 20:26
SYSTEM : 1
METHOD :
CHANNEL : 1 <DIGITAL> OPERATOR:
SEQ : 1

FILE : 0
CALC-METHOD: AR/HI% <AREA> MODULE T-PROG :
COMPONENT TBL : 0 DETECTOR= 1

NO.	RT	AREA	CONC	BC
5	7.23	92457	3.805	BB
8	11.49	2337592	96.195	VB
TOTAL		2430049	100.000	
PEAK REJ :		50000		

2c(rac)

MS-536 IA hexane/IPA=95/5 1.000 ml/min

```
FILE 0    SYS 1        SEQ     1
CH.1<D>   C.S  1.25    ATT  8   OFFS   0   07/24/13  20:00

                                    7.38
                                   13.10
 17.38
```

D-7500 INTEGRATOR REPORT

```
ANALYZED: 07/24/13  20:00                  REPORTED: 07/24/13  20:21
SYSTEM  : 1
METHOD  :                          OPERATOR:
CHANNEL : 1 <DIGITAL>              SEQ     :      1

FILE    : 0                        MODULE T-PROG :          DETECTOR= 1
CALC-METHOD: AR/HI%  <AREA>        COMPONENT TBL :   0

  NO.      RT         AREA        CONC  BC
    6    7.38      2603234      50.388  BB
    9   13.10      2563137      49.612  BB
TOTAL
                   5166371     100.000
PEAK REJ :           50000
```

2c

MS-685 IA hexane/IPA=95/5 1.000 ml/min

```
FILE 0    SYS 1        SEQ     1
CH.1<D>   C.S  1.25    ATT  8   OFFS   0   01/17/14  14:00

 10.44
                                   13.68
```

D-7500 INTEGRATOR REPORT

```
ANALYZED: 01/17/14  14:00                  REPORTED: 01/17/14  14:21
SYSTEM  : 1
METHOD  :                          OPERATOR:
CHANNEL : 1 <DIGITAL>              SEQ     :      1

FILE    : 0                        MODULE T-PROG :          DETECTOR= 1
CALC-METHOD: AR/HI%  <AREA>        COMPONENT TBL :   0

  NO.      RT         AREA        CONC  BC
    6    7.66       48387      2.673  BB
    8   13.68     1689114     97.327  BB
TOTAL
                   1735511     100.000
PEAK REJ :           10000
```

2d(rac)

MS-491 IA hexane/IPA = 95/5 1.000 ml/min

```
FILE 0    SYS 1       SEQ     1
CH.1<D>   C.S  1.25   ATT  8   OFFS   0   06/06/13  14:44

          0.56
          8.28
         10.07
         14.61
         18.14
         22.56
         26.20
```

D-7500 INTEGRATOR REPORT

```
ANALYZED: 06/06/13  14:44                 REPORTED: 06/06/13  15:15
SYSTEM  : 1
METHOD  :                        OPERATOR:
CHANNEL : 1 <DIGITAL>            SEQ     :      1

FILE    : 0                      MODULE T-PROG :          DETECTOR= 1
CALC-METHOD: AR/HI%  <AREA>      COMPONENT TBL :   0

  NO.      RT        AREA       CONC  BC
   11    8.28     1239415     50.013  BB
   15   14.61     1238754     49.987  BB
TOTAL
                  2478169    100.000
PEAK REJ :       50000
```

2d

MS-507 IA h/I = 95/5 1.000 ml/min

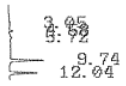
```
FILE 0    SYS 1       SEQ     2
CH.1<D>   C.S  1.25   ATT  7   OFFS   0   07/03/13  12:45

          1.93
          5.20
          8.54
         15.71
```

D-7500 INTEGRATOR REPORT

```
ANALYZED: 07/03/13  12:45                 REPORTED: 07/03/13  13:05
SYSTEM  : 1
METHOD  :                        OPERATOR:
CHANNEL : 1 <DIGITAL>            SEQ     :      2

FILE    : 0                      MODULE T-PROG :          DETECTOR= 1
CALC-METHOD: AR/HI%  <AREA>      COMPONENT TBL :   0

  NO.      RT        AREA       CONC  BC
    5    8.44       22067      2.060  BB
    6   15.71     1048952     97.940  BB
TOTAL
                  1071019    100.000
PEAK REJ :       20000
```

2e(rac)

```
FILE 0    SYS 1       SEQ     2
CH.1<D>   C.S  1.25   ATT  5   OFFS   0   05/02/14  15:31
```



D-7500 INTEGRATOR REPORT

```
ANALYZED: 05/02/14  15:31                 REPORTED: 05/02/14  15:47
SYSTEM  : 1
METHOD  :                          OPERATOR:
CHANNEL : 1 <DIGITAL>              SEQ     :      2

FILE    : 0                        MODULE T-PROG :          DETECTOR= 1
CALC-METHOD: AR/HI%  <AREA>        COMPONENT TBL :   0

  NO.      RT        AREA       CONC  BC
    4   9.74        23048     50.471  BB
    5  12.04        22618     49.529  BB
TOTAL
                     45666    100.000
PEAK REJ :       20000
```

2014. 5/2

PN-265 IA hex/IPA = 97/3 1000 ml/min.

2e

```
FILE 0    SYS 1       SEQ     2
CH.1<D>   C.S  1.25   ATT  6   OFFS   0   05/06/14  17:19
```

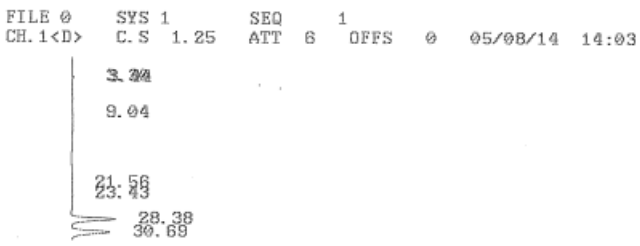
D-7500 INTEGRATOR REPORT

```
ANALYZED: 05/06/14  17:19                 REPORTED: 05/06/14  17:34
SYSTEM  : 1
METHOD  :                          OPERATOR:
CHANNEL : 1 <DIGITAL>              SEQ     :      2

FILE    : 0                        MODULE T-PROG :          DETECTOR= 1
CALC-METHOD: AR/HI%  <AREA>        COMPONENT TBL :   0

  NO.      RT        AREA       CONC  BC
    2   4.18         5794      0.964  BB
    4   9.48       589843     98.088  BB
    5  11.56         5706      0.949  BB
TOTAL
                    601343    100.000
PEAK REJ :        5000
```

2014. 5/6

PN-269 IA hex/IPA = 97/3, 1.000 ml/min

2f(rac)



D-7500 INTEGRATOR REPORT

ANALYZED: 05/08/14 14:03 REPORTED: 05/08/14 14:36
SYSTEM : 1
METHOD : OPERATOR:
CHANNEL : 1 <DIGITAL> SEQ : 1

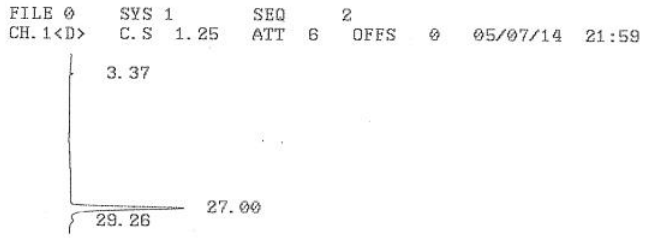
FILE : 0 MODULE T-PROG : DETECTOR= 1
CALC-METHOD: AR/HI% <AREA> COMPONENT TBL : 0

NO.	RT	AREA	CONC	BC
6	28.38	170956	50.413	BB
7	30.69	168152	49.587	BB
TOTAL		339108	100.000	

PEAK REJ : 30000

PN-268
IA, hex/IPA = 95/5, 1.000 ml/min.

2f



D-7500 INTEGRATOR REPORT

ANALYZED: 05/07/14 21:59 REPORTED: 05/07/14 22:33
SYSTEM : 1
METHOD : OPERATOR:
CHANNEL : 1 <DIGITAL> SEQ : 2

FILE : 0 MODULE T-PROG : DETECTOR= 1
CALC-METHOD: AR/HI% <AREA> COMPONENT TBL : 0

NO.	RT	AREA	CONC	BC
2	27.00	435741	97.918	BB
3	29.26	9267	2.082	BB
TOTAL		445008	100.000	

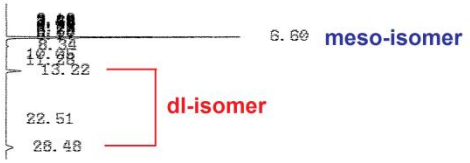
PEAK REJ : 9000

2014. 5/7
PN-272
IA, hex/IPA = 95/5, 1.000 ml/min

4a(rac)

MS 1729 IA hexane/IPA = 95/5 1.000 ml/min

```
FILE 0    SYS 1       SEQ     1
CH.1<D>   C.S  1.25   ATT  9   OFFS   0   02/21/14  11:48
```

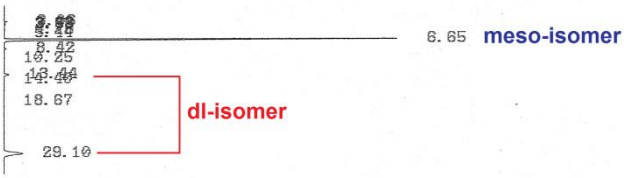



```
                    D-7500 INTEGRATOR REPORT

ANALYZED: 02/21/14  11:48                  REPORTED: 02/21/14  12:20
SYSTEM   : 1
METHOD   :                          OPERATOR:
CHANNEL  : 1 <DIGITAL>              SEQ     :      1

FILE     : 0                        MODULE T-PROG :          DETECTOR= 1
CALC-METHOD: AR/HI%  <AREA>         COMPONENT TBL :   0

  NO.      RT        AREA       CONC  BC
   10    6.60     2130246     80.970  BV
   14   13.22      258415      9.822  VB
   16   28.48      242247      9.208  VB
TOTAL
                  2630908    100.000
PEAK REJ :      200000
```

4a

MS 660 IA hexane/IPA = 95/5 1.000 ml/min

```
FILE 0    SYS 1       SEQ     2
CH.1<D>   C.S  1.25   ATT  9   OFFS   0   02/22/14  15:53
```

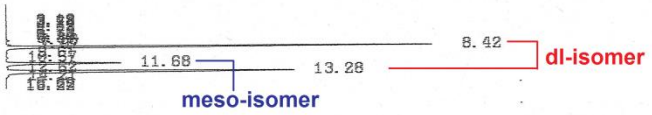



```
                    D-7500 INTEGRATOR REPORT

ANALYZED: 02/22/14  15:53                  REPORTED: 02/22/14  16:27
SYSTEM   : 1
METHOD   :                          OPERATOR:
CHANNEL  : 1 <DIGITAL>              SEQ     :      2

FILE     : 0                        MODULE T-PROG :          DETECTOR= 1
CALC-METHOD: AR/HI%  <AREA>         COMPONENT TBL :   0

  NO.      RT        AREA       CONC  BC
    7    6.65     3595306     84.748  BB
   10   13.44       80786      1.904  BV
   13   29.10      566278     13.348  BB
TOTAL
                  4242370    100.000
PEAK REJ :      30000
```

4b(rac)

MS-730-B IA hexane/IPA = 95/5 1.000ml/min

```
FILE 0    SYS 1       SEQ    1
CH.1<D>   C.S  1.25   ATT 10   OFFS   0   02/21/14  21:38
```



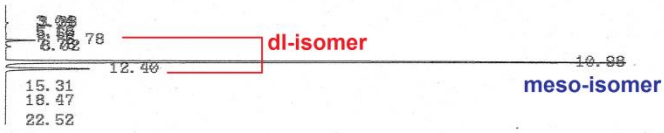
D-7500 INTEGRATOR REPORT

```
ANALYZED: 02/21/14  21:38                REPORTED: 02/21/14  21:56
SYSTEM   : 1
METHOD   :                        OPERATOR:
CHANNEL  : 1 <DIGITAL>            SEQ     :      1

FILE     : 0                      MODULE T-PROG :          DETECTOR= 1
CALC-METHOD: AR/HI%  <AREA>       COMPONENT TBL :   0

  NO.      RT        AREA       CONC  BC
   10    8.42     9934813     42.169  VV
   13   11.68     3530165     14.984  VV
   15   13.28    10094476     42.847  VV
TOTAL
                 23559454    100.000
PEAK REJ :       100000
```

4b

MS-486 IA h/I = 95/5 1.000ml/min

```
FILE 0    SYS 1       SEQ    2
CH.1<D>   C.S  1.25   ATT  6   OFFS   0   06/07/13  17:48
```



D-7500 INTEGRATOR REPORT

```
ANALYZED: 06/07/13  17:49                REPORTED: 06/07/13  18:22
SYSTEM   : 1
METHOD   :                        OPERATOR:
CHANNEL  : 1 <DIGITAL>            SEQ     :      2

FILE     : 0                      MODULE T-PROG :          DETECTOR= 1
CALC-METHOD: AR/HI%  <AREA>       COMPONENT TBL :   0

  NO.      RT        AREA       CONC  BC
    2    3.38        5352     0.371  BB
    5    6.78       34524     2.396  BB
    7    8.02        8846     0.614  VB
    8   10.98     1218714    84.585  BV
    9   12.40      171270    11.887  VB
   10   15.31        2111     0.147  BB
TOTAL
                  1440817   100.000
PEAK REJ :        2000
```