# Supporting Information

## Palladium-Catalyzed Cross-Coupling of (Hetero)Aryl or Alkenyl Sulfonates with Aryl Titanium as the Multi-Functional Reagent

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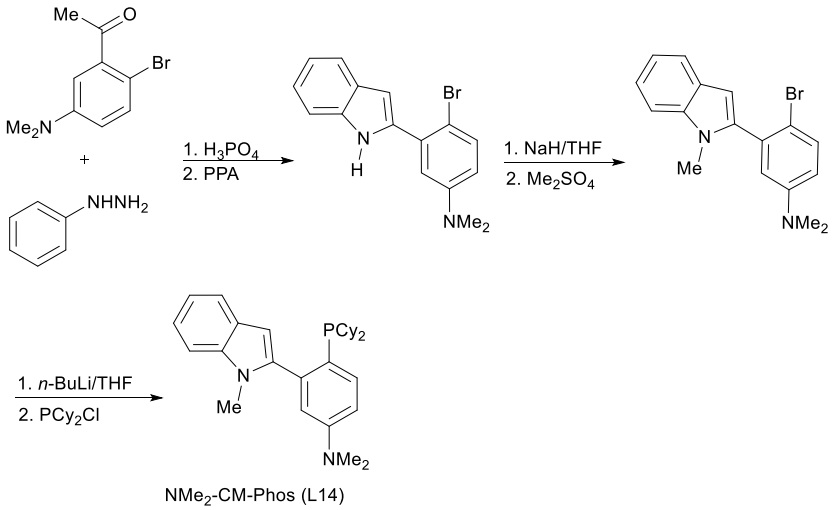
## 1. General considerations

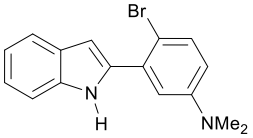
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All cross-coupling reactions were performed in resealable screw cap Schlenk tube (approx. 20 mL volume) in the presence of Teflon-coated magnetic stirrer bar (4.5 mm × 12 mm). Indolylphosphine ligand **L1**[1] and **L13**[2] were prepared according to the reported procedures. Ligands **L2**-**L12** were purchased from commercial suppliers. Alkenyl tosylates and mesylates were synthesized according to the reported procedures.[3] Thin layer chromatography was performed on pre-coated silica gel 60 $F_{254}$ plates. Silica gel (Merck, 230-400 mesh) was used for column chromatography. Melting points were recorded on an uncorrected Büchi Melting Point B-545 instrument. NMR spectra were recorded on a Brüker spectrometer (400 MHz for $^{1}H$, 100 MHz for $^{13}C$, 376 MHz for $^{19}F$ and 162 MHz for $^{31}P$). Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm) or TMS (δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. $^{13}C$ NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). $^{19}F$ NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. $^{31}P$ NMR spectra were referenced to 85% $H_3PO_4$ externally. Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FTICR mass spectrometer (ESI-MS), a Agilent 6540 Qtof MS and a Bruker UltrafleXtreme Maldi-Tof/Tof MS. GC-MS analysis was conducted on a HP 5977A GCD system using a HP5MS column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from HP 7890B GC-FID system. All yields reported refer to isolated yield of compounds estimated to be greater than 95% purity as determined by capillary gas chromatography (GC) or $^{1}H$ NMR. Compounds described in the literature were characterized by comparison of their $^{1}H$, $^{13}C$, $^{31}P$ and/or $^{19}F$ NMR spectra to the previously reported data. E factors were calculated according to the procedure reported by Lipshutz et.al.[4] The procedures in this section are representative, and thus the yields may differ from those reported in tables.

## 2. Preparation of indolylphosphine ligand $NMe_2$-CM-Phos (L14)



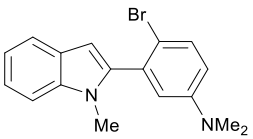

$NMe_2$-CM-Phos (L14)

**4-Bromo-3-(1*H*-indol-2-yl)-*N*,*N*-dimethylaniline**




Fischer indole synthesis of 4-bromo-3-(1*H*-indol-2-yl)-*N*,*N*-dimethylaniline was conducted according to the previous reported procedure.[1, 5] 1-(2-Bromo-5-(dimethyl amino)phenyl)ethanone (5.7 mmol), phenylhydrazine (6.84 mmol), $H_3PO_4$ (2.0 mL) and PPA (20 g) were used to give the desired product as a light yellow powder (1.04 g, 58%). M.p. 113.0–114.9ºC; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.03 (s, 6H), 6.67 (d, *J* = 8.0Hz, 1H). 6.90 (s, 1H), 6.98 (s, 1H), 7.24–7.35 (m, 2H), 7.48 (d, *J* = 8.0Hz, 1H), 7.56 (d, *J* = 8.0Hz, 1H), 7.78 (d, *J* = 8.0Hz, 1H), 8.68 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 40.4, 102.9, 107.4, 110.9, 113.6, 114.9, 119.9, 120.5, 122.2, 128.1, 133.4, 133.9, 135.9, 137.2, 149.6; MS (EI): *m/z* (relative intensity) 314 ($M^+$, 100), 235 (43), 220 (43), 205 (8), 191 (39); HRMS: calcd. for $C_{16}H_{15}N_2BrH^+$: 315.0497, found 315.0495.

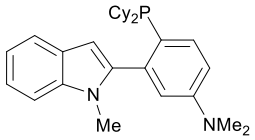
**4-Bromo-*N*,*N*-dimethyl-3-(1-methyl-1*H*-indol-2-yl)aniline**




A 100-mL three-necked round-bottomed flask equipped with dropping funnel is charged with sodium hydride (4.80 mmol, 60 % dispersion in mineral oil) which was washed free of mineral oil with hexane. The dropping funnel was charged with 4-Bromo-3-(1*H*-indol-2-yl) -

*N*,*N*- dimethylaniline (3.20 mmol, 1.00 g) and the setup is evacuated and backfilled with nitrogen three times. Freshly distilled THF (10 mL) was added to the dropping funnel and THF (5.0 mL) was added to the flask. The solution of 4-Bromo-3-(1*H*-indol-2-yl) -*N*,*N*-dimethylaniline was added dropwise to the reaction flask and the reaction mixture was stirred for 15 min at room temperature. $Me_2SO_4$ (3.36 mmol, 0.318 mL) was then added to the mixture dropwise *via* syringe. After the mixture was stirred at room temperature for overnight, solvent was removed by high vacuum. Ethyl acetate and water was added to the mixture and the organic layer was separated. The organic layer was washed with water and brine for three times and concentrated. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) to give the product as a white powder (0.84 g, 80%). M.p. 103–105°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.97 (s, 6H), 3.62 (s, 3H), 6.53 (s, 1H), 6.68 (d, *J* = 7.0Hz, 1H), 6.75 (s, 1H), 7.16 (t, *J* = 6.7Hz, 1H), 7.27 (t, *J* = 7.0Hz, 1H), 7.38 (d, *J* = 7.8Hz, 1H), 7.50 (d, *J* = 8.7Hz, 1H), 7.67 (d, *J* = 7.4Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 30.6, 40.4, 101.4, 109.4, 110.7, 114.0, 116.5, 119.6, 120.6, 121.5, 127.6, 132.7, 134.2, 137.1, 140.7, 143.4; MS (EI): *m/z* (relative intensity) 328 ($M^+$, 100), 249 (42), 233 (31), 204 (44); HRMS: calcd. for $C_{17}H_{17}N_2BrH^+$: 329.0653, found 329.0650.

**4-(Dicyclohexylphosphino)-*N*,*N*-dimethyl-3-(1-methyl-1*H*-indol-2-yl)aniline ($NMe_2$-CM-Phos, L14)**



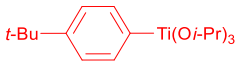

4-Bromo-*N*,*N*-dimethyl-3-(1-methyl-1*H*-indol-2-yl)aniline (1.42 mmol, 0.467 g) was dissolved in freshly distilled THF (10 mL) at room temperature under nitrogen atmosphere. The solution was cooled to –78 °C in dry ice/acetone bath. Titrated *n*-BuLi (1.56 mmol) was added dropwise by syringe. After the reaction mixture was stirred for 30 min at -78 °C, chlorodicyclohexylphosphine (1.56 mmol, 0.344 mL) in THF (3.0 mL) was added. The reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed under high vacuum. The residue was successively washed with cold MeOH and then dried under high vacuum. 4-(Dicyclohexylphosphino)-*N,N*-dimethyl-3-(1-methyl -1*H*-indol-2-yl)aniline was obtained as a white solid (0.44 g, 69%). M.p. 150.6–151.9°C; $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 1.07–1.26 (m, 10H), 1.58–2.10 (m, 12 H), 3.02 (s, 6H), 3.53 (s, 3H), 6.38 (s, 1H), 6.74 (s, 1H), 6.71 (t, *J* = 2.8Hz, 1H), 6.86–6.89 (m, 1H), 7.13 (t, *J* = 7.2Hz, 1H), 7.23 (t, *J* = 7.3Hz, 1H), 7.37 (d, *J* = 8.1Hz, 1H), 7.49 (d, *J* = 8.6Hz, 1H), 7.62 (d, *J* = 7.8Hz, 1H); $^{13}$C

NMR (100 MHz, $CD_2Cl_2$) δ 26.5, 27.2, 30.60, 30.66, 39.8, 102.3, 102.4, 109.1, 112.0, 114.90, 114.97, 119.1, 119.8, 120.6, 121.5, 121.69, 127.7, 133.61, 133.65, 136.4, 141.5, 141.9, 142.6, 142.7, 150.0; $^{31}P$ NMR (162 MHz, $CD_2Cl_2$) δ -12.97; MS (EI): *m/z* (relative intensity) 446 ($M^+$, 47), 431 (9), 363 (100), 281 (96), 265 (18); HRMS: calcd. for $C_{29}H_{39}N_2PH^+$: 447.2929, found 447.2913.

## 3. Preparation of aryl titanium reagents

All aryl titanium reagents were synthesized according or analogous to the reported procedures.[6] A general procedure for the preparation of ArTi(O*i*-Pr)$_3$: A two-necked 250 mL round-bottomed flask equipped with a condenser, a magnetic stir bar, and an addition funnel was charged with magnesium turnings (2.40 g, 100 mmol), and the flask was evacuated under reduced pressure for 2 h. Under a nitrogen atmosphere, THF (100 mL) was added to the flask and aryl bromide (120 mmol) in THF (50 mL) was transferred into the addition funnel. The THF solution of aryl bromide was added slowly to the reaction flask, and the reaction mixture was controlled under gentle reflux using an ice bath if necessary. After the reaction was complete, the resulting Grignard reagent was cooled to 0 °C. In another two-necked 500 mL round bottomed flask under a nitrogen atmosphere, to a solution of Ti(O*i*-Pr)$_4$ (22.4 mL, 75.0 mmol) in 50 mL of THF at 0°C was added $TiCl_4$ (2.8 mL, 25.0 mmol). The resulting solution was warmed to room temperature and stirred for 30 min, giving a ClTi(O*i*-Pr)$_3$ solution (100 mmol). The ClTi(O*i*-Pr)$_3$ solution was cooled to 0 °C, and to this solution was transferred the ice cold Grignard solution via a cannula. The reaction mixture was warmed to room temperature and was allowed to react for 3 h. The volatile material was removed completely under reduced pressure, and under a nitrogen atmosphere, the residue was extracted with *n*-hexane (3 x 200 mL). The combined hexane solution was concentrated and was cooled to -20 °C, furnishing a crystalline product of the corresponding ArTi(O*i*-Pr)$_3$. The characterization data of new 4-*tert*-butylphenyltitanium triisopropoxide is showed below.

4-*tert*-Butylphenyltitanium triisopropoxide

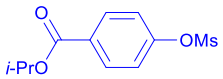



Obtained in 45% as pale yellow crystal; m.p. 74.2-77.0°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 9H), 1.37–1.38 (m, 18H), 4.73–4.77 (m, 3H), 7.23 (d, *J* = 6.8Hz, 2H), 7.61 (d, *J* = 7.1Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 26.3, 31.3, 34.5, 77.3, 123.0, 133.4, 149.7, 182.3; HRMS calcd for $C_{19}H_{34}O_3Ti^+$: 358.1988, found 358.1972.

## 4. Preparation of aryl mesylates and tosylates substrates

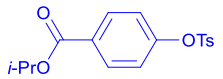
Aryl mesylates and tosylates were prepared according to the literature procedures.[7] A general procedure for the preparation of aryl sulfonates: To a stirred solution of corresponding phenol (10 mmol) in anhydrous dichloromethane (20 mL) cooled to 0 °C was added distilled triethylamine (6.95 mL, 50 mmol). To this was added mesyl chloride (1.94 mL, 15 mmol) dropwise via syringe over 5 min or was added tosyl chloride (2.86 g, 15 mmol) as powder form. The reaction was stirred at room temperature. The reaction was quenched with water and the layer separated when the reaction was completed. The aqueous layer was extracted with dichloromethane and the combined organic solution was dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel using EA/hexane solvent mixtures as the eluent. The organic solution was concentrated and the product was dried to afford the corresponding aryl sulfonates. The characterization data of new isopropyl 4-(mesyloxy)benzoate and isopropyl 4-(tosyloxy)benzoate are showed below.

Isopropyl 4-(mesyloxy)benzoate




Obtained in 82% as white solid; m.p. 49.8-50.6°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.35 (d, $J$ = 6.2Hz, 6H), 3.16 (s, 3H), 5.24 (sept, $J$ = 6.2Hz, 1H), 7.33 (d, $J$ = 8.1Hz, 2H), 8.09 (d, $J$ = 8.4Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.8, 37.7, 68.8, 121.7, 129.9, 131.5, 152.2, 164.7; MS (EI): *m/z* (relative intensity) 258.3 ($M^+$, 23), 216.2 (53), 199.2 (100), 138.2 (93), 121.2 (73), 92.2 (20), 59.2 (27); HRMS calcd for $C_{11}H_{15}O_5S^+$: 259.0635, found 259.0632.

Isopropyl 4-(tosyloxy)benzoate




Obtained in 93% as white solid; m.p. 42.7-44.8°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.35 (d, $J$ = 6.2Hz, 6H), 2.44 (s, 3H), 5.21 (sept, $J$ = 6.2Hz, 1H), 7.04 (d, $J$ = 8.7Hz, 2H), 7.30 (d, $J$ = 8.1Hz, 2H), 7.69 (d, $J$ = 8.2Hz, 2H), 7.96 (d, $J$ = 8.7Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.6, 21.8, 68.7, 122.1, 128.4, 129.6, 129.8, 131.1, 132.0, 145.6, 152.7, 164.9; MS (EI): *m/z* (relative intensity) 334.4 ($M^+$, 27), 292.3 (16), 275.3 (20), 207.3 (9), 155.2 (100), 120.2 (32), 91.2 (90), 65.2 (14); HRMS calcd for $C_{17}H_{19}O_5S^+$: 335.0948, found 335.0955.

## 5. General procedures for palladium-catalyzed cross-coupling reaction of aryl mesylate with different nucleophiles

$Pd(OAc)_2$ (4.5 mg, 0.020 mmol) and **L1** (32.2 mg, 0.080 mmol) were loaded into Schlenk tube with a Teflon-coated magnetic stirrer bar (4.5 mm x 12 mm). The tube was evacuated and backfilled with nitrogen (3 cycles). Precomplexation was applied by adding freshly distilled DCM (1.0 mL) and $Et_3N$ (0.10 mL) into the tube. The solution was stirred and warmed using oil bath (~75 $^oC$) for about 1 min until the solvent started boiling. The solvent in tube was removed under high vacuum. *For cross-coupling reaction using lithium, magnesium and zinc nucleophile,* PhLi (1.25 mL, 2.50 mmol, 2.0 M in dibutyl ether) or *p* -tolylMgBr (2.50 mL, 2.50 mmol, 1.0 M in THF) or *p* -tolylZnCl (2.50 mmol generated from 2.50 mmol *p* -tolylMgBr in 1.0 M THF and 2.50 mmol $ZnCl_2$ in 0.5 M THF) was added into the tube via syringe. The solvent in tube was removed under high vacuum. 4-*tert*-Butylphenyl mesylate (0.114 g, 0.50 mmol) was loaded into the Schlenk tube which was again evacuated and re-filled with nitrogen for three times. *For cross-coupling reaction using boron, silane, stannane and titanium nucleophile,* 4-*tert*-butylphenyl mesylate (0.114 g, 0.50 mmol) and *p*-tolylB$(OH)_2$ (0.339 g, 2.5 mmol) or *p*-tolylBpin (0.545 g, 2.5 mmol), *p*-tolylB$F_3$K (0.495 g, 2.5 mmol) or *p*-tolylSi$(OMe)_3$ (513 $\mu$L, 2.5 mmol) or *p*-tolylS$nBu_3$ (0.953 g, 2.5 mmol) or *p*-tolylTi(O*i*-Pr)$_3$ (0.790 g, 2.5 mmol) were loaded into the Schlenk tube which was again evacuated and re-filled with nitrogen for three times. The Schlenk tube was resealed and magnetically stirred in a preheated 110 $^oC$ oil bath for 3 h. The reaction tube was allowed to reach room temperature. Water, ethyl acetate and dodecane (113 $\mu$L, internal standard) were added to the mixture. The organic solution was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

## 6. General procedure for initial ligand and reaction conditions screening

$Pd(OAc)_2$ (4.5 mg, 0.020 mmol) and ligand (Pd:L =1:4) were loaded into Schlenk tube with a Teflon-coated magnetic stirrer bar (4.5 mm x 12 mm). The tube was evacuated and backfilled with nitrogen (3 cycles). Precomplexation was applied by adding freshly distilled DCM (1.0 mL) and $Et_3N$ (0.10 mL) into the tube. The solution was stirred and warmed using oil bath (~75 ºC) for about 1 min until the solvent started boiling. The solvent in tube was removed under high vacuum. 4-*tert*-Butylphenyl mesylate **1a** (0.114 g, 0.50 mmol) and *p*-tolylTi(O*i*-Pr)$_3$ **2a** (the equivalence was indicated in Table 2) were loaded into the Schlenk tube which was again evacuated and re-filled with nitrogen for three times. The Schlenk tube was resealed and magnetically stirred in a preheated 110 ºC oil bath for the time as indicated in Table 2. The reaction tube was allowed to reach room temperature. Water, ethyl acetate and dodecane (113 $\mu$L, internal standard) were added to the mixture. The organic solution was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

## 7. General procedures for palladium-catalyzed cross-coupling reaction of aryl/heteroaryl and alkenyl mesylates and tosylates with aryl titanium reagents

*General procedure for cross-coupling reaction of aryl/heteroaryl mesylates and tosylates with aryl titanium reagents (Pd catalyst loading equal to or large than 2.0 mol%):* $Pd(OAc)_2$ (Pd loading indicated in Table 3) and $NMe_2$-CM-Phos **L14** (Pd:L =1:4) were loaded in a Schlenk tube with a Teflon-coated magnetic stirrer bar (4.5 mm x 12 mm). The tube was evacuated and backfilled with nitrogen (3 cycles). Precomplexation was applied by adding freshly distilled DCM (1.0 mL) and $Et_3N$ (0.10 mL) into the tube. The solution was stirred and warmed using oil bath (~75 °C) for about 1 min until the solvent started boiling. The solvent in the tube was removed under high vacuum. Aryl/heteroaryl mesylates or tosylates (0.50 mmol) and aryl titanium reagents (the equivalence was indicated in Table 3) were loaded into the tube which was again evacuated and flushed with nitrogen for three times. The tube was resealed and magnetically stirred in a preheated 110 °C oil bath for the time as indicated in Table 3. The tube was cooled and the reaction was quenched by addition of water and ethyl acetate. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic solution was concentrated on a rotary evaporator. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) to give the products.

*General procedure for cross-coupling reaction of alkenyl mesylates and tosylates with aryl titanium reagents (Pd catalyst loading less than 0.50 mol%): Preparation of stock solution*: $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) with $NMe_2$-CM-Phos **L14** (44.6 mg, 0.010 mmol) were loaded into a tube with magnetic stirrer bar (4.5 mm x 12 mm). The tube was evacuated and backfilled with nitrogen (3 cycles). A freshly distilled DCM (10.0 mL) was then added to give the palladium stock solution (0.50 mol% Pd per 1 mL stock solution). A Schlenk tube with a Teflon-coated magnetic stirrer bar (4.5 mm x 12 mm) was evacuated and backfilled with nitrogen (3 cycles). The corresponding volume of the palladium stock solution was transferred to the tube. Precomplexation was applied by adding freshly distilled $Et_3N$ (0.10 mL) into the tube. The solution was stirred and warmed using oil bath (~75 °C) for about 1 minute until the solvent started boiling. The solvent was removed under high vacuum. Alkenyl mesylates or tosylates (0.50 mmol) and aryl titanium reagents (the equivalence was indicated in Table 4) were loaded into the tube which was again evacuated and flushed with nitrogen for three times. The tube was resealed and magnetically stirred in a preheated 110

°C oil bath for the time as indicated in Table 4. The tube was cooled and the reaction was quenched by addition of water and ethyl acetate. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic solution was concentrated on a rotary evaporator. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) to give the products.

## 8. General procedure for a set of parallel experiments between Suzuki-type organoborn and organotitanium nucleophilles

A stock solution of $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) with $NMe_2$-CM-Phos **L14** (17.8 mg, 0.04 mmol) in freshly distilled 10 mL DCM (0.2 mol% Pd per 1.0 mL stock solution) was initially prepared with continuously stirring at room temperature. An array of Schlenk tubes equipped with a Teflon-coated magnetic stir bar (4.5 mm x 12 mm) were evacuated and backfilled with nitrogen (3 cycles). The stock solutions (1.00 mL) and $Et_3N$ (0.10 mL) were transferred accordingly to the each of the tubes *via* syringes. The solution was stirred and warmed using oil bath (~75 $^oC$) for about 1 minute until the solvent started boiling. The solvent was then evaporated under high vacuum.

*For the cross-coupling reaction using organotitanium nucleophile*: 3,4-dihydronaphthalen-2-yl tosylate **4a** (0.150 g, 0.50 mmol) and *p*-tolylTi(O*i*-Pr)$_3$ **2a** (0.316 g, 1.00 mmol) were loaded into the tubes that were further evacuated and flushed with nitrogen for three times. *For the cross-coupling reaction using organoboron nucleophile*: 4-dihydronaphthalen-2-yl tosylate **4a** (0.150 g, 0.50 mmol), *p*-tolyl$B(OH)_2$ (0.123 g, 1.0 mmol) and $K_3PO_4 \bullet H_2O$ (0.345 g, 1.5 mmol) were loaded into the tubes which were further evacuated and flushed with nitrogen for three times. *t*-BuOH (1.5 mL) was then added via syringe. All the tubes were resealed and magnetically stirred in a preheated 110 $^oC$ oil bath for 10 min. The tubes were cooled and the reactions were quenched by addition of water and ethyl acetate. Dodecane (113 $\mu$L, internal standard) was then added into the tubes. The organic solutions were subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

## 9. General procedures and data for palladium-catalyzed cross-coupling reaction of aryl mesylate and alkenyl tosylate using *in situ* generated aryl titanium reagent

*The procedure for cross-coupling reaction of alkenyl tosylate with in situ preparation aryl titanium reagent*:

*Preparation of stock solution*: $Pd(OAc)_2$ (2.3 mg, 0.010 mmol) with $NMe_2$-CM-Phos **L14** (17.8 mg, 0.040 mmol) were loaded into a tube with magnetic stirrer bar (4.5 mm x 12 mm). The tube was evacuated and backfilled with nitrogen (3 cycles). Precomplexation was applied by adding freshly distilled DCM (1.0 mL) and $Et_3N$ (0.10 mL) into the tube. The solution was stirred and warmed using oil bath (~75 °C) for about 1 minute until the solvent started boiling. The solvent was removed under high vacuum. A freshly distilled THF (10.0 mL) was then added to give the palladium stock solution (0.2 mol% Pd per 1 mL stock solution).

A Schlenk tube equipped with a Teflon-coated magnetic stir bar (4.5 mm x 12 mm) was evacuated and backfilled with nitrogen (3 cycles). $ClTi(O\textit{i}\text{-}Pr)_3$ (0.24 mL, 1.00 mmol) and PhLi (0.50 mL, 1.00 mmol, 2.0 M in dibutyl ether) were added successively to the tube at 0 °C and the mixture was then allowed to stand at room temperature and stirred for 30 min. The solvent was then removed under high vacuum. The palladium stock solution (1.0 mL) was transferred to the tube and the solvent was then removed under high vacuum. 3,4-Dihydronaphthalen-2-yl tosylate **4a** (0.15 g, 0.50 mmol) was loaded into the tube which was resealed and magnetically stirred in a preheated 110 °C oil bath for 10 min. The tube was cooled and the reaction was quenched by addition of water and ethyl acetate. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic solution was concentrated on a rotary evaporator. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) to give the products.

*The procedure for cross-coupling reaction of aryl mesylate with in situ preparation aryl titanium reagent*:

*Preparation of stock solution*: $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) with $NMe_2$-CM-Phos **L14** (44.6 mg, 0.10 mmol) were loaded into a tube with magnetic stirrer bar (4.5 mm x 12 mm). The tube was evacuated and backfilled with nitrogen (3 cycles). Precomplexation was applied by adding freshly distilled DCM (1.0 mL) and $Et_3N$ (0.10 mL) into the tube. The palladium complex solution was stirred and warmed using oil bath (~75 °C) for about 1 minute

until the solvent started boiling. The solvent was then evaporated under high vacuum. A freshly distilled THF (1.0 mL) was then added to give the palladium stock solution (5.0 mol% Pd per 1 mL stock solution).

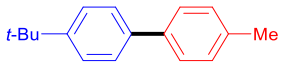
A Schlenk tube equipped with a Teflon-coated magnetic stir bar (4.5 mm x 12 mm) was evacuated and backfilled with nitrogen (3 cycles). $ClTi(O\textit{i}\text{-}Pr)_3$ (0.60 mL, 2.50 mmol) and PhLi (1.25 mL, 2.50 mmol, 2.0 M in dibutyl ether) were added successively to the tube at 0 ºC and the mixture was then allowed to stand at room temperature and stirred for 30 min. The solvent was then removed under high vacuum. The palladium stock solution (0.80 mL) was transferred to the tube and the solvent was then removed under high vacuum. Sesamol mesylate **1g** (0.108 g, 0.50 mmol) was loaded into the tube which was resealed and magnetically stirred in a preheated 110 ºC oil bath for 18 h. The tube was cooled and the reaction was quenched by addition of water and ethyl acetate. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic solution was concentrated on a rotary evaporator. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) to give the products.

## 10. General procedure for large-scale cross-coupling reaction of alkenyl tosylate with aryl titanium reagent

$Pd(OAc)_2$ (4.5 mg, 0.020 mmol) and $NMe_2$-CM-Phos **L14** (35.6 mg, 0.080 mmol) were loaded to a two necked 100 mL round bottom flask which equipped with an air condenser, magnetic stirrer bar (25 mm x 6 mm) and fitted with septum. The flask was carefully evacuated and backfilled with nitrogen (3 cycles). Precomplexation was accomplished by adding freshly distilled DCM (1.0 mL) and $Et_3N$ (0.1 mL) into the flask and the solution was stirred and warmed using oil bath (~75 $^oC$) until the solvent started boiling. The solvent was removed under high vacuum. 3,4-Dihydronaphthalen-2-yl tosylate **4a** (3.00 g, 10.0 mmol) and *m*-anisylTi(O*i*-Pr)$_3$ **2c** (6.64 g, 20.0 mmol) were charged to the flask and the septum was replaced with a glass stopper. The reaction flask was placed in a preheated 110 $^oC$ oil bath for 10 min. The flask was cooled to room temperature. Water was added to quench the reaction. Ethyl acetate was then added to the flask and the mixture was stirred for 5 min. The mixture was filtered through a short pad of sodium sulphate which was then eluted with ethyl acetate. The filtrate was then transferred to separating funnel and the organic layer was washed with water for two times. The organic solution was concentrated on a rotary evaporator. The residue was subjected to flash column chromatography on silica gel (230-400 mesh) to give the 3-(3-methoxyphenyl)-1,2-dihydronaphthalene (2.24 g, 95%).

## 11. Characterization data for coupling products

4-(*tert*-Butyl)-4'-methyl-1,1'-biphenyl (Table 3, **3aa**)[8]

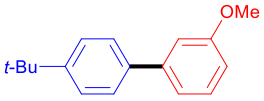



Eluents (Hexane, $R_f$= 0.5) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 2.43 (s, 3H), 7.28 (d, *J* = 6.6Hz, 2H), 7.48-7.57 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.0, 31.3, 34.3, 125.6, 126.5, 126.8, 129.4, 136.6, 138.1, 138.2, 149.9; MS (EI): *m/z* (relative intensity) 224.4 ($M^+$, 45), 209.4 (100), 181.3 (20), 165.3 (15), 90.6 (9).

4-(*tert*-Butyl)-4'-methoxy-1,1'-biphenyl (Table 3, **3ab**)[9]

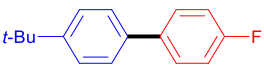

Eluents (Hexane : Dichloromethane = 20:1, $R_f$= 0.3) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 3.87 (s, 3H), 7.00 (d, *J* = 8.6Hz, 2H), 7.48 (d, *J* = 8.3Hz, 2H), 7.55–7.57 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 31.3, 34.4, 55.2, 114.1, 125.6, 126.3, 127.9, 133.6, 137.9, 149.6, 158.9; MS (EI): *m/z* (relative intensity) 240.4 ($M^+$, 47), 225.4 (100), 197.3 (14), 98.7 (14).

4-(*tert*-Butyl)-3'-methoxy-1,1'-biphenyl (Table 3, **3ac** and **3hf**)[10]




Eluents (Hexane : Dichloromethane = 20:1, $R_f$= 0.30) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.39 (s, 9H), 3.88 (s, 3H), 6.90 (d, 8.4Hz, 1H), 7.15 (s, 1H), 7.21 (d, *J* = 7.6Hz, 1H), 7.36 (t, *J* = 8.0Hz, 1H), 7.48 (d, *J* = 8.4Hz, 2H), 7.56 (d, *J* = 8.4Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 31.3, 34.5, 55.2, 112.4, 112.7, 119.5, 125.6, 126.8, 129.6, 138.2, 142.6, 150.4, 159.9; MS (EI): *m/z* (relative intensity) 240.4 ($M^+$, 38), 225.4 (100), 197.3 (15), 98.7 (15).

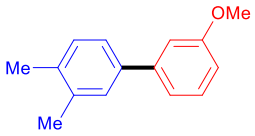
4-(*tert*-Butyl)-4'-fluoro-1,1'-biphenyl (Table 3, **3ad** and **3if**)[11]




Eluents (Hexane, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 9H), 7.16 (t, *J* = 8.8Hz, 2H), 7.54 (d, 8.4Hz, 4H), 7.57–7.61 (m, 2H); $^{13}$C

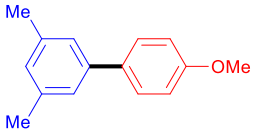
NMR (100 MHz, $CDCl_3$) δ 31.3, 34.4, 115.4 (d, $J$ = 21Hz), 125.7, 126.6, 128.4 (d, $J$ = 8Hz), 137.1 (d, $J$ = 3Hz), 137.3, 150.2, 162.2 (d, $J$ = 244Hz); $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -116.0; MS (EI): *m/z* (relative intensity) 228.4 ($M^+$, 33), 213.3 (100), 195.3 (25), 92.7 (15).

3,4-Dimethyl-3'-methoxy-1,1'-biphenyl (Table 3, **3bc**)



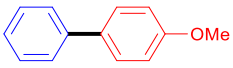

Eluents (Hexane : Dichloromethane = 9:1, $R_f$ = 0.50) was used for flash column chromatography. Colourless liquid; $^1H$ NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.40 (s, 3H), 3.92 (s, 3H), 6.94 (d, $J$ = 8.0Hz, 1H), 7.20 (m, 1H), 7.26 (m, 2H), 7.40 (m, 2H), 7.45 (s, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 19.3, 19.8, 55.1, 112.2, 112.6, 119.4, 124.4, 128.3, 129.5, 129.9, 135.8, 136.8, 138.6, 142.7, 159.8; MS (EI): *m/z* (relative intensity) 212.4 ($M^+$, 100), 197.3 (32), 165.3 (13), 153.2 (13), 128.2 (6); HRMS calcd for $C_{15}H_{16}O$: 212.1196, found 212.1194.

4-Methoxy-3',5'-dimethyl-1,1'-biphenyl (Table 3, **3cb**)[12]



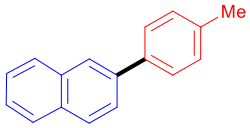

Eluents (Hexane : Dichloromethane = 20:1, $R_f$ = 0.50) was used for flash column chromatography. $^1H$ NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 6H), 3.85 (s, 3H), 6.97 (m, 3H), 7.18 (m, 2H), 7.52 (d, $J$ = 8.7Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 21.4, 55.2, 114.0, 124.6, 128.1, 128.2, 133.9, 138.1, 140.7, 158.9; MS (EI): *m/z* (relative intensity) 212.1 ($M^+$, 100), 197.1 (45), 169.1 (18), 153.1 (9), 128.0 (5).

4-Methoxy-1,1'-biphenyl (Table 3, **3db**)[10]



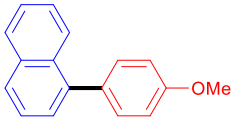

Eluents (Hexane : Dichloromethane = 20:1, $R_f$ = 0.40) was used for flash column chromatography. $^1H$ NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3H), 7.02 (t, $J$ = 8.8Hz, 2H), 7.34 (t, $J$ = 7.3Hz, 1H), 7.46 (t, $J$ = 7.4Hz, 2H), 7.59 (m, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 55.2, 114.1, 126.61, 126.69, 128.1, 128.6, 133.7, 140.7, 159.1; MS (EI): *m/z* (relative intensity) 184.1 ($M^+$, 100), 169.1 (40), 141.1 (27), 115.1 (20), 76.1 (4).

2-(4-Methylphenyl)-naphthalene (Table 3, **3ea**)[13]



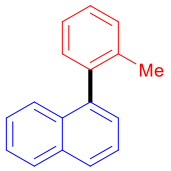

Eluents (Hexane, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H), 7.39 (d, *J* = 7.9Hz, 2H), 7.55-7.61 (m, 2H), 7.74 (d, *J* = 8.1Hz, 2H), 7.84 (d, *J* = 8.5Hz, 1H), 7.94–8.00 (m, 3H), 8.14 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.0, 125.3, 125.5, 125.7, 126.1, 127.2, 127.5, 128.1, 128.3, 129.5, 132.4, 133.7, 137.0, 138.1, 138.4; MS (EI): *m/z* (relative intensity) 218.4 ($M^+$, 100), 202.3 (25), 107.9 (6), 73.1 (6).

1-(4-Methoxyphenyl)-naphthalene (Table 3, **3fb**)[14]



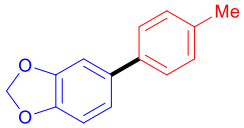

Eluents (Hexane : Dichloromethane = 20:1, $R_f$= 0.30) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 7.11 (d, *J* = 8.6Hz, 2H), 7.48–7.50 (m, 4H), 7.54–7.60 (m, 2H), 7.91 (d, *J* = 8.1Hz, 1H), 7.97 (d, *J* = 7.9Hz, 1H), 8.03 (d, *J* = 8.3Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.2, 113.6, 125.3, 125.6, 125.8, 126.0, 126.8, 127.2, 128.2, 131.0, 131.8, 133.0, 133.8, 139.8, 158.9; MS (EI): *m/z* (relative intensity) 234.3 ($M^+$, 100), 219.3 (32), 189.3 (40), 94.7 (8).

1-(*o*-Tolyl)naphthalene (Table 3, **3fe**)[15]



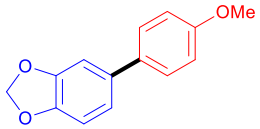

Eluents (Hexane, $R_f$= 0.5) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H), 7.24–7.26 (m, 1H), 7.28–7.40 (m, 5H), 7.45–7.55 (m, 3H), 7.87 (d, *J* = 8.3Hz, 1H), 7.90 (d, *J* = 8.1Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.0, 125.3, 125.5, 125.6, 125.9, 126.1, 126.6, 127.4, 127.5, 128.2, 129.8, 130.4, 132.0, 133.5, 136.8, 139.8, 140.2; MS (EI): *m/z* (relative intensity) 218.3 ($M^+$, 100), 203.3 (53), 189.3 (8), 108.1 (12), 94.8 (7).

5-(4-Methylphenyl)benzo[d][1,3]dioxole (Table 3, **3ga**)[16]



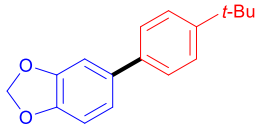

Eluents (Hexane : Dichloromethane = 20:1, $R_f$= 0.30) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 6.02 (s, 2H), 6.93 (d, *J* = 8.0Hz, 1H), 7.09–7.13 (m, 2H), 7.27 (d, *J* = 7.8Hz, 2H), 7.48 (d, *J* = 8.1Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.9,100.9, 107.4, 108.4, 120.2, 126.6, 129.3, 135.5, 136.5, 138.0, 146.7, 148.0; MS (EI): *m/z* (relative intensity) 212.1 ($M^+$, 100), 153.1 (19), 139.1 (13), 105.1 (6), 76.1 (5).

5-(4-Methoxyphenyl)benzo[d][1,3]dioxole (Table 3, **3gb**)[17]



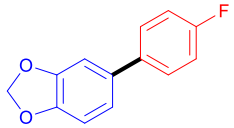

Eluents (Hexane : Dichloromethane = 7:3, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 5.98 (s, 2H), 6.86 (d, *J* = 7.9Hz, 1H), 6.95 (d. *J* = 8.4Hz, 2H), 7.00-7.03 (m, 2H), 7.44 (d, *J* = 8.6Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.3, 101.0, 107.3, 108.4, 114.1, 120.0, 127.8, 133.5, 135.2, 146.5, 148.0, 158.8; MS (EI): *m/z* (relative intensity) 228.3 ($M^+$, 100), 213.3 (63), 185.2 (15), 127.2 (13), 114.1 (6).

5-(4-*tert*-Butylphenyl)benzo[d][1,3]dioxole (Table 3, **3gf**)



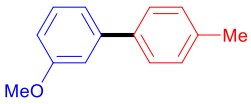

Eluents (Hexane : Dichloromethane = 9:1, $R_f$= 0.50) was used for flash column chromatography. Colourless oily paste; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 9H), 6.02 (s, 2H), 6.93 (d, *J* = 8.0Hz, 1H), 7.11-7.14 (m, 2H), 7.48–7.54 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ31.3, 34.4, 101.0, 107.5, 108.4, 120.3, 125.6, 126.4, 135.4, 138.0, 146.8, 148.0, 149.8; MS (EI): *m/z* (relative intensity) 254.4 ($M^+$, 60), 239.4 (100), 211.3 (14), 181.3 (14), 165.2 (12), 105.3 (17); HRMS calcd. for $C_{17}H_{18}O_2$: 254.1307, found 254.1305.

5-(4-Fluorophenyl)benzo[d][1,3]dioxole (Table 3, **3gd**)[10]



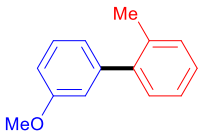

Eluents (Hexane : Dichloromethane = 9:1, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.00 (s, 2H), 6.88 (d, *J* = 7.8Hz, 1H), 7.01 (d, *J* = 8.2Hz, 2H), 7.11 (t, *J* = 8.6Hz, 2H), 7.45–7.47 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 101.1, 107.4, 108.4, 115.4 (d, *J* = 21Hz), 120.3, 128.2 (d, *J* = 8Hz), 134.5, 137.0 (d, *J* = 3Hz), 146.9, 148.0, 162.1 (d, *J* = 244Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ -116.1; MS (EI): *m/z* (relative intensity) 216.2 ($M^+$, 100), 157.2 (27), 107.8 (11), 69.2 (5).

3-Methoxy-4'-methyl-1,1'-biphenyl (Table 3, **3ha**)[16]



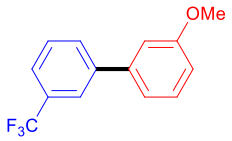

Eluents (Hexane : Dichloromethane = 20:1, $R_f$= 0.40) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H), 4.01 (s, 3H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.30 (s, 1H), 7.35 (d, *J* = 7.6Hz, 1H), 7.41 (d, *J* = 8.0Hz, 2H), 7.51 (t, *J* = 7.6Hz, 1H), 7.67. (d, *J* = 7.6Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.0, 55.1, 112.3, 112.6, 119.4, 126.7, 126.9, 129.4, 129.6, 137.1, 138.1, 142.6; MS (EI): *m/z* (relative intensity) 198.3 ($M^+$, 100), 167.3 (17), 155.3 (13), 115.2 (6).

3-Methoxy-2'-methyl-1,1'-biphenyl (Table 3, **3he**)[18]



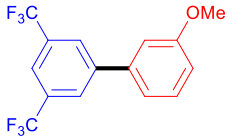

Eluents (Hexane : Dichloromethane = 9:1, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.89 (s, 3H), 6.96–7.00 (m, 3H), 7.32 (m, 4H), 7.40 (t, *J* = 8.4Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.3, 55.1, 112.2, 114.7, 121.6, 125.6, 127.2, 128.9, 129.5, 130.2, 135.2, 141.7, 143.3, 159.2; MS (EI): *m/z* (relative intensity) 198.3 ($M^+$, 100), 183.3 (18), 167.3 (64), 153.2 (25), 128.2 (14), 115.2 (13).

3-Methoxy-3'-(trifluoromethyl)-1,1'-biphenyl (Table 3, **3jc**)[19]



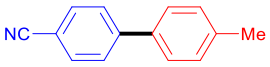

Eluents (Hexane : Dichloromethane = 9:1, $R_f$= 0.30) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), 6.97 (d, *J* = 8.2Hz, 1H), 7.15 (s, 1H), 7.20 (d, *J* = 7.6Hz, 1H), 7.43 (t, *J* = 7.9Hz, 1H), 7.88 (t, *J* = 7.6Hz, 1H), 7.63 (d, *J* = 7.6Hz, 1H) 7.77 (d, *J* = 7.6Hz, 1H), 7.86 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.4, 113.0, 113.3, 119.6, 123.8, 124.0 (m), 124.2 (q, *J* = 270Hz), 129.1, 130.0, 130.4, 131.1 (q, *J* = 34Hz), 141.2, 141.8, 160.1; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.5; MS (EI): *m/z* (relative intensity) 252.3 ($M^+$, 100), 222.3 (21), 209.3 (21), 183.2 (13).

3-Methoxy-3',5'-di(trifluoromethyl)-1,1'-biphenyl (Table 3, **3kc**)[20]



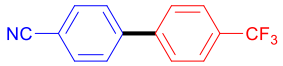

Eluents (Hexane : Dichloromethane = 9:1, $R_f$= 0.40) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 7.01 (d, *J* = 8.2Hz, 1H), 7.13 (s, 1H), 7.19 (d, *J* = 7.6Hz, 1H), 7.43 (t, *J* = 7.9Hz, 1H), 7.88 (s, 1H), 8.02 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.3, 113.1, 114.0, 119.6, 121.0 (m), 123.4 (q, *J* = 270Hz), 127.2, 130.3, 131.9 (q, *J* = 38Hz), 139.6, 143.2, 160.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –62.9; MS (EI): *m/z* (relative intensity) 320.4 ($M^+$, 100), 301.4 (14), 290.3 (29), 277.3 (21), 251.3 (13), 188.2 (7).

4'-Methyl[1,1'-biphenyl]-4-carbonitrile (Table 3, **3la**)[16]



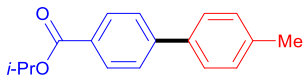

Eluents (Hexane : Ethyl acetate = 9:1, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.32 (d, *J* = 7.9Hz, 2H), 7.51 (d, *J* = 9.2Hz, 2H), 7.66–7.71 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.9, 110.2, 118.8, 126.8, 127.1, 129.6, 132.3, 135.9, 138.5, 145.3; MS (EI): *m/z* (relative intensity) 193.3 ($M^+$, 100), 178.2 (10), 165.2 (20), 91.2 (7).

4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-carbonitrile (Table 3, **3lg**)[21]



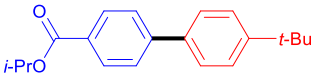

Eluents (Hexane : Ethyl acetate = 9:1, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68–7.77 (m, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 111.9, 118.5, 122.6, 125.3, 126.0 (q, *J* = 4.0Hz), 127.7 (d, *J* = 33Hz), 130.6 (d, *J* = 32Hz), 132.7, 142.6, 144.0; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.6; MS (EI): *m/z* (relative intensity) 247.3 ($M^+$, 100), 228.3 (13), 197.2 (6), 177.2 (10), 151.2 (6), 98.7 (5).

Isopropyl 4'-methyl-[1,1'-biphenyl]-4-carboxylate (Table 3, **3ma**)



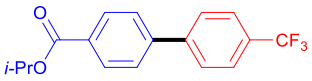

Eluents (Hexane : Ethyl acetate = 9:1, $R_f$= 0.40) was used for flash column chromatography. White solid; m.p. 115.7-117.6°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.41 (d, *J* = 6.2Hz, 6H), 2.42 (s, 3H), 5.30 (sept, *J* = 6.2Hz, 1H), 7.28 (d, *J* = 7.8Hz, 2H), 7.54 (d, *J* = 8.0Hz, 2H), 7.65 (d, *J* = 8.2Hz, 2H), 8.11 (d, *J* = 8.2Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.9, 68.2, 126.6, 127.0, 129.3, 129.6, 129.9, 137.1, 137.7, 145.3, 166.0; MS (EI): *m/z* (relative intensity) 254.4 ($M^+$, 98), 212.3 (100), 195.3 (92), 165.3 (36), 152.2 (40), 97.3 (7); HRMS calcd. for $C_{17}H_{18}NaO_2^+$: 277.1199, found 277.1209.

Isopropyl 4'-(*tert*-butyl)-[1,1'-biphenyl]-4-carboxylate (Table 3, **3mf**)



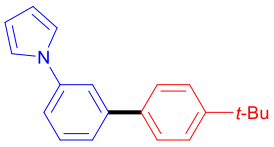

Eluents (Hexane : Ethyl acetate = 9:1, $R_f$= 0.40) was used for flash column chromatography. White solid; m.p. 53.8–56.7°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.40–1.43 (m, 15H), 5.31 (sept, *J* = 6.1Hz, 1H), 7.51 (d, *J* = 6.6Hz, 2H), 7.60 (d, *J* = 8.0Hz, 2H), 7.68 (d, *J* = 8.0Hz, 2H), 8.13 (d, *J* = 8.0Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.9, 31.3, 34.5, 68.2, 125.8, 126.7, 126.9, 129.3, 130.0, 137.1, 145.2, 151.2, 166.0; MS (EI): *m/z* (relative intensity) 296.5 ($M^+$, 38), 281.4 (100), 239.3 (27), 97.2 (10); HRMS calcd. for $C_{20}H_{25}O_2^+$: 297.1849, found 297.1857.

Isopropyl 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate (Table 3, **3mg**)[21]



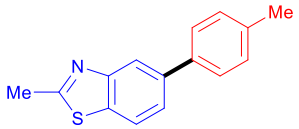

Eluents (Hexane : Ethyl acetate = 20:1, $R_f$ = 0.30) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.40 (d, *J* = 6.2Hz, 6H), 5.29 (sept, *J* = 6.2Hz, 1H), 7.64 (d, *J* = 8.3Hz, 2H), 7.70–7.71 (m, 4H), 8.13 (d, *J* = 8.3Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.8, 68.5, 124.1 (q, *J* = 270Hz), 125.8 (q, *J* = 4Hz), 127.0, 127.5, 130.0 (q, *J* = 32Hz), 130.1, 130.6, 143.5, 143.7, 165.6; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –62.5; MS (EI): *m/z* (relative intensity) 308.4 ($M^+$, 32), 266.3 (70), 249.3 (100), 201.3 (30), 152.2 (35), 59.2 (18).

4-(*tert*-Butylphenyl)-*1H*-benzopyrrole (Table 3, **3nf**)



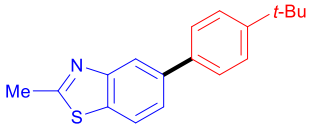

Eluents (Hexane : Ethyl acetate = 10:1, $R_f$ = 0.40) was used for flash column chromatography. White solid; m.p. 123.8-125.2°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.49 (s, 9H), 6.48–6.49 (m, 2H), 7.25 (m, 2H), 7.42–7.44 (m, 1H), 7.53 (d, *J* = 6.2Hz, 2H), 7.60 (d, *J* = 8.3Hz, 2H), 7.66 (d, *J* = 8.3Hz, 2H), 7.72 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 31.3, 34.5, 110.4, 119.0, 119.1, 119.3, 124.2, 125.7, 126.7, 129.7, 137.4, 141.1, 142.6, 150.7; MS (EI): *m/z* (relative intensity) 275.4 ($M^+$, 58), 260.4 (100), 232.3 (13), 116.2 (13); HRMS calcd. for $C_{20}H_{22}N^+$: 276.1747, found 276.1754.

2-Methyl-5-(4-methylphenyl)-benzothiazole (Table 3, **3oa**)[22]



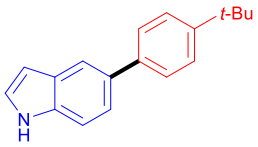

Eluents (Hexane : Ethyl acetate = 9:1, $R_f$ = 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.84 (s, 3H), 7.28 (d, *J* = 7.6Hz, 2H), 7.56–7.59 (m, 3H), 7.83 (d, *J* = 8.4Hz, 1H), 8.18–8.19 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.0, 21.0, 31.7, 120.3, 121.3, 124.0, 127.0, 129.5, 134.1, 137.7, 139.4, 153.9, 167.5; MS (EI): *m/z* (relative intensity) 239.3 ($M^+$, 100), 197.2 (12), 165.2 (12), 152.2 (10), 119.6 (5).

2-Methyl-5-(4-*tert*-butylphenyl)-benzothiazole (Table 3, **3of**)[23]



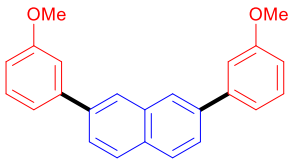

Eluents (Hexane : Ethyl acetate = 9:1, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 9H), 2.88 (s, 3H), 7.54 (d, *J* = 6.5Hz, 2H), 7.61–7.67 (m, 3H), 7.86 (d, *J* = 8.3Hz, 1H), 8.23–8.24 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.0, 34.49, 31.3, 120.4, 121.3, 124.04, 125.8, 126.9, 134.2, 137.7, 139.3, 150.4, 154.0, 167.5; MS (EI): *m/z* (relative intensity) 281.4 ($M^+$, 46), 266.4 (100), 238.3 (13), 119.2 (13).

5-(4-*tert*-Butylphenyl)-*1H*-indole (Table 3, **3pf**)[24]



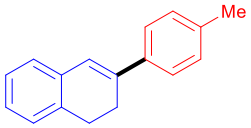

Eluents (Hexane : Ethyl acetate = 9:1, $R_f$= 0.30) was used for flash column chromatography. $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 1.47 (s, 9H), 6.67–6.68 (m, 1H), 7.27–7.29 (m, 1H), 7.49–7.51 (m, 2H), 7.57 (d, *J* = 8.5Hz, 2H), 7.70 (d, *J* = 8.4Hz, 2H) 7.95 (s, 1H), 8.31 (s, 1H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$) δ 31.2, 34.3, 102.6, 111.2, 118.7, 121.5, 125.0, 125.6, 126.7, 128.4, 132.9, 135.3, 139.4, 149.3; MS (EI): *m/z* (relative intensity) 249.4 ($M^+$, 56), 234.4 (100), 204.3 (13), 103.2 (16), 89.2(5).

2,7-Di(3-methoxyphenyl)-naphthalene (Table 3, **3qc**)



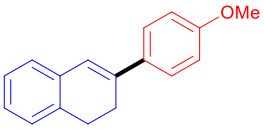

Eluents (Hexane : Dichloromethane = 10:1, $R_f$= 0.30) was used for flash column chromatography. White solid; m.p. 81.2-83.9°C; $^1$H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 6H), 7.01 (d, *J* = 7.3Hz, 2H), 7.36–7.48 (m, 6H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 8.16 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.2, 112.8, 113.0, 119.8, 125.6, 126.0, 128.0, 129.7, 131.8, 133.7, 138.7, 142.4, 159.9; MS (EI): *m/z* (relative intensity) 340.5 ($M^+$, 100), 297.4 (13), 254.4 (6), 170.3 (9); HRMS calcd. for $C_{24}H_{21}O_2^+$: 341.1536, found 341.1540.

3-(4-Methylphenyl)-1,2-dihydronaphthalene (Table 4, **5aa**)[25]



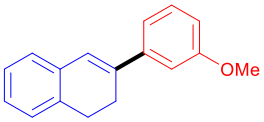

Eluents (Hexane, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 2.84 (t, *J* = 8.2Hz, 2H), 3.06 (t, *J* = 7.6Hz, 2H), 6.95 (s, 1H), 7.23–7.30 (m, 6H), 7.56 (d, *J* = 8.2Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 21.1, 26.2, 28.1, 123.4, 124.9, 126.4, 126.5, 126.7, 127.2, 129.1, 134.6, 134.8, 137.0, 138.1, 138.5; MS (EI): *m/z* (relative intensity) 220.2 ($M^+$, 100), 205.1 (35), 128.1 (17), 105.1 (30).

3-(4-Methoxyphenyl)-1,2-dihydronaphthalene (Table 4, **5ab**)[25]



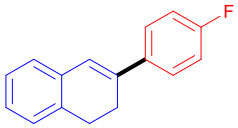

Eluents (Hexane : Dichloromethane = 9:1, $R_f$= 0.25) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.77 (t, *J* = 8.0Hz, 2H), 3.00 (t, *J* = 7.6Hz, 2H), 3.87 (s, 3H), 6.85 (s, 1H), 6.97 (d, *J* = 8.8Hz, 2H), 7.17–7.24 (m, 4H), 7.55 (d, *J* = 8.8Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 26.2, 28.1, 55.2, 113.7, 122.5, 126.24, 126.27, 126.51, 126.55, 127.0, 133.4, 134.4, 134.9, 138.1, 159.0; MS (EI): *m/z* (relative intensity) 236.2 ($M^+$, 100), 221.1 (26), 178.1 (15), 121.1 (26).

3-(3-Methoxyphenyl)-1,2-dihydronaphthalene (Table 4 and Scheme 2, **5ac**)[26]



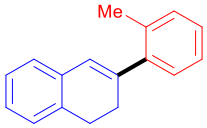

Eluents (Hexane : Dichloromethane = 9:1, $R_f$= 0.25) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.83 (t, *J* = 8.2Hz, 2H), 3.04 (t, *J* = 7.7Hz, 2H), 3.92 (s, 3H), 6.94–6.96 (m, 2H), 7.18–7.26 (m, 6H), 7.38 (t, *J* = 7.9Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 26.3, 28.0, 55.1, 110.9, 112.5, 117.6, 124.5, 126.53, 126.58, 126.9, 127.1, 129.3, 134.5, 134.7, 138.4, 142.5, 159.6; MS (EI): *m/z* (relative intensity) 236.4 ($M^+$, 100), 221.3 (12), 205.3 (14), 189.3 (12), 165.2 (10), 121.2 (37).

3-(4-Fluorophenyl)-1,2-dihydronaphthalene (Table 4, **5ad**)[25]



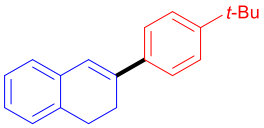

Eluents (Hexane, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.76 (t, *J* = 8.0Hz, 2H), 3.00 (t, *J* = 7.7Hz, 2H), 6.85 (s, 1H), 7.11 (t, *J* = 8.6Hz, 2H), 7.11–7.26 (m, 4H). 7.53–7.57 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 26.3, 28.0, 115.2 (d, *J* = 21Hz), 124.1, 126.5, 126.60, 126.68, 126.99, 127.1, 134.5, 137.1 (d, *J* = 3Hz), 137.5, 160.9, 162.1 (d, *J* = 245Hz); $^{19}$F NMR (376 MHz, $CDCl_3$) δ –114.8; MS (EI): *m/z* (relative intensity) 224.3 ($M^+$, 100), 202.3 (20), 128.2 (17), 109.2 (46).

3-(2-Methylphenyl)-1,2-dihydronaphthalene (Table 4, **5ae**)[25]



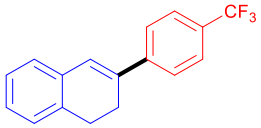

Eluents (Hexane, $R_f$= 0.50) was used for flash column chromatography. Colourless liquid. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 3H), 2.69 (t, *J* = 7.8Hz, 2H), 3.05 (t, *J* = 7.7Hz, 2H), 6.54 (s, 1H), 7.19 (d, *J* = 6.7Hz, 1H), 7.18–7.33 (m, 7H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.4, 28.3, 28.8, 125.7, 126.1, 126.4, 126.5, 126.8, 127.0, 127.2, 128.0, 130.3, 134.5, 134.6, 134.9, 141.1, 142.8; MS (EI): *m/z* (relative intensity) 220.3 ($M^+$, 100), 205.3 (33), 128.2 (25), 105.2 (60).

3-(4-*tert*-Butylphenyl)-1,2-dihydronaphthalene (Table 4, **5af**)[25]



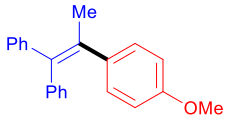

Eluents (Hexane, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.49 (s, 9H), 2.87 (t, *J* = 7.6Hz, 2H), 3.07 (t, *J* = 7.6Hz, 2H), 6.99 (s, 1H), 7.24–7.33 (m, 4H), 7.54 (d, *J* = 8.5Hz, 2H), 7.64 (d, *J* = 8.6Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 26.2, 28.1, 31.2, 34.5, 123.6, 124.8, 125.3, 126.4, 126.5, 126.7, 127.1, 134.7, 134.8, 138.0, 138.3, 150.3; MS (EI): *m/z* (relative intensity) 262.4 ($M^+$, 77), 247.4 (100), 202.3 (7), 131.2 (12), 109.6 (11), 91.2 (6).

3-(4-Trifluoromethylphenyl)-1,2-dihydronaphthalene (Table 4, **5ag**)[25]



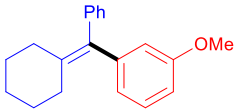

Eluents (Hexane, $R_f$= 0.50) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.72–2.76 (m, 2H), 2.95–2.99 (m, 2H), 6.92 (s, 1H), 7.15–7.62 (m, 4H), 7.65–7.67 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 26.2, 28.0, 124.2 (q, $J$ = 270Hz), 125.2, 125.3 (q, $J$ = 4Hz), 126.3, 126.7, 127.0, 127.3, 127.6, 129.0 (q, $J$ = 32Hz), 134.1, 134.8, 137.1, 144.6; $^{19}$F NMR (376 MHz, $CDCl_3$) δ –62.3; MS (EI): *m/z* (relative intensity) 274.4 ($M^+$, 100), 259.3 (13), 233.3 (19), 202.3 (16), 115.2 (40).

1,1-Diphenyl-2-(4-methoxyphenyl)propene (Table 4, **5bb**)[27]



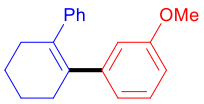

Eluents (Hexane : Dichloromethane = 20:1, $R_f$= 0.30) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 3H), 3.77 (s, 3H), 6.74 (d, $J$ = 8.5Hz, 2H), 6.96 (d, $J$ = 7.2Hz, 2H), 7.04–7.13 (m, 5H), 7.29 (d, $J$ = 6.4Hz, 3H), 7.38 (t, $J$ = 7.2Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 23.2, 55.0, 113.2, 125.6, 126.4, 127.4, 128.0, 129.8, 130.3, 130.8, 135.0, 136.1, 138.7, 143.3, 143.7, 157.8; MS (EI): *m/z* (relative intensity) 300.1 ($M^+$, 100), 285.1 (12), 191.1 (8), 165.1 (6).

1-(Cyclohexylidenephenylmethyl)-3-methoxy-benzene (Table 4, **5cc**)[28]



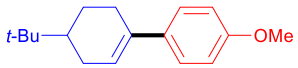

Eluents (Hexane : Dichloromethane = 20:1, $R_f$= 0.30) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.57–1.60, (m, 6H), 2.21–2.24 (m, 4H), 6.67–6.68 (m, 1H), 6.72–6.73 (m, 2H), 7.11–7.17 (m, 4H), 7.22–7.24 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 26.7, 28.64, 28.66, 32.3, 32.4, 55.0, 111.2, 115.5, 122.3, 126.0, 127.8, 128.7, 129.6, 134.3, 139.2, 142.8, 144.5, 159.1; MS (EI): *m/z* (relative intensity) 264.4 ($M^+$, 100), 235.4 (14), 221.3 (20), 115.2 (20), 91.2 (18).

1-Phenyl-2-(3-methoxyphenyl)-cyclohex-1-ene (Table 4, **5dc**)[29]



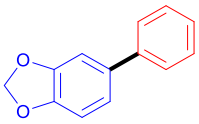

Eluents (Hexane : Dichloromethane = 20:1, $R_f$= 0.30) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.83–1.86 (m, 4H), 2.45–2.49 (m, 4H), 3.56 (s, 3H), 6.52–6.53 (m, 1H), 6.59–6.63 (m, 2H), 7.00–7.07 (m, 4H), 7.09–7.13 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 23.1, 23.2, 31.7, 31.9, 54.8, 111.6, 114.5, 121.3, 125.6, 127.6, 128.4, 128.8, 134.7, 135.1, 143.9, 145.1, 158.8; MS (EI): *m/z* (relative intensity) 264.4 ($M^+$, 100), 221.3 (17), 205.3 (13), 115.2 (7), 91.2 (13).

1-[4'-*tert*-Butylcyclohex-1-enyl]-4-methoxybenzene (Table 4, **5eb**)[30]



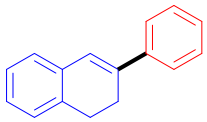

Eluents (Hexane : Dichloromethane = 9:1, $R_f$= 0.40) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 0.9 (s, 9H), 1.34–1.42 (m, 2H), 1.99–2.01 (m, 2H), 2.24–2.28 (m, 1H), 2.38–2.45 (m, 1H), 2.50–2.54 (m, 1H), 3.82 (s, 3H), 6.06–6.07 (m, 1H), 6.87 (d, *J* = 8.5Hz, 2H), 7.34 (d, *J* = 8.5Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 24.4, 27.2, 27.3, 28.8, 32.1, 43.8, 55.1, 113.5, 123.1, 125.8, 134.8, 135.6, 158.3; MS (EI): *m/z* (relative intensity) 244.4 ($M^+$, 88), 187.3 (35), 160.3 (100), 121.2 (42), 57.2 (20).

5-Phenyl-benzo[d][1,3]dioxole (Scheme 3, **3gh**)[10]




Eluents (Hexane : Dichloromethane = 20:1, $R_f$= 0.30) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.02 (s, 2H), 6.93 (d, *J* = 8.0Hz, 1H), 7.10–7.13 (m, 2H), 7.36 (t, *J* = 7.3Hz, 1H), 7.46 (t, *J* = 6.8Hz, 2H), 7.56 (d, *J* = 7.0Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 101.0, 107.6, 108.5, 120.5, 126.82, 126.86, 128.6, 135.5, 140.8, 147.0, 148.0; MS (EI): *m/z* (relative intensity) 198.2 ($M^+$, 100), 139.2 (49), 98.8 (10).

3-Phenyl-1,2-dihydronaphthalene (Scheme 3, **5ah**)[25]



Eluents (Hexane : Dichloromethane = 20:1, $R_f$= 0.30) was used for flash column chromatography. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.85 (t, *J* = 8.0Hz, 2H), 3.05 (t, *J* = 7.6Hz, 2H), 6.96 (s, 1H), 7.22–7.31 (m, 3H), 7.38 (t, J = 7.3Hz, 1H), 7.47 (t, J = 7.8Hz, 2H), 7.64 (d, 7.3Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 26.2, 28.1, 124.3, 125.0, 126.5, 126.9, 127.1, 127.2, 128.4, 134.6, 134.7, 138.6, 141.0; MS (EI): *m/z* (relative intensity) 206.2 ($M^+$, 100), 191.2 (23), 128.2 (35), 91.2 (62).

# 12. X-ray crystallography data of $NMe_2$-CM-Phos L14

Table S1. Crystal data and structure refinement for p.

| | | |
|---|---|---|
| Identification code | BSYU001 | |
| Empirical formula | C29 H39 N2 P | |
| Formula weight | 446.59 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pbca | |
| Unit cell dimensions | a = 15.0158(12) Å | = 90°. |
| | b = 15.6985(10) Å | = 90°. |
| | c = 21.9190(16) Å | = 90°. |
| Volume | 5166.9(6) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.148 $Mg/m^3$ | |
| Absorption coefficient | 0.125 $mm^{-1}$ | |
| F(000) | 1936 | |
| Crystal size | 0.500 x 0.400 x 0.300 $mm^3$ | |
| Theta range for data collection | 2.094 to 25.249°. | |
| Index ranges | -18<=h<=18, -18<=k<=18, -26<=l<=26 | |
| Reflections collected | 93019 | |
| Independent reflections | 4669 [R(int) = 0.0625] | |
| Completeness to theta = 25.242° | 99.9 % | |
| Absorption correction | multi-scan | |
| Max. and min. transmission | 0.7456 and 0.6423 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4669 / 0 / 290 | |
| Goodness-of-fit on $F^2$ | 1.027 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0398, wR2 = 0.1064 | |
| R indices (all data) | R1 = 0.0598, wR2 = 0.1266 | |
| Extinction coefficient | 0.0065(7) | |
| Largest diff. peak and hole | 0.232 and -0.174 $e.Å^{-3}$ | |

Table S2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for p. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 8943(1) | 1522(1) | 3161(1) | 42(1) |
| N(1) | 8361(1) | -56(1) | 2132(1) | 47(1) |
| N(2) | 10731(1) | -1791(1) | 3825(1) | 51(1) |
| C(1) | 8306(1) | 108(1) | 1516(1) | 48(1) |
| C(2) | 7561(2) | 133(1) | 1137(1) | 63(1) |
| C(3) | 7707(2) | 307(2) | 529(1) | 76(1) |
| C(4) | 8547(2) | 445(2) | 306(1) | 76(1) |
| C(5) | 9282(2) | 419(1) | 674(1) | 65(1) |
| C(6) | 9168(2) | 247(1) | 1298(1) | 50(1) |
| C(7) | 9748(2) | 158(1) | 1808(1) | 50(1) |
| C(8) | 9245(1) | -14(1) | 2306(1) | 43(1) |
| C(9) | 7614(2) | -263(2) | 2509(1) | 66(1) |
| C(10) | 9519(1) | -147(1) | 2951(1) | 40(1) |
| C(11) | 9965(1) | -891(1) | 3096(1) | 42(1) |
| C(12) | 10255(1) | -1071(1) | 3693(1) | 41(1) |
| C(13) | 10025(1) | -475(1) | 4144(1) | 46(1) |
| C(14) | 9586(1) | 262(1) | 3995(1) | 46(1) |
| C(15) | 9339(1) | 470(1) | 3401(1) | 40(1) |
| C(16) | 10855(2) | -2444(1) | 3368(1) | 62(1) |
| C(17) | 11022(2) | -1964(2) | 4439(1) | 62(1) |
| C(18) | 9962(1) | 2180(1) | 3299(1) | 45(1) |
| C(19) | 10753(1) | 1824(1) | 2943(1) | 57(1) |
| C(20) | 11549(2) | 2426(2) | 2961(1) | 70(1) |
| C(21) | 11809(2) | 2647(2) | 3606(1) | 74(1) |
| C(22) | 11025(2) | 2986(2) | 3965(1) | 71(1) |
| C(23) | 10244(2) | 2363(1) | 3954(1) | 59(1) |
| C(24) | 8201(1) | 1859(1) | 3790(1) | 46(1) |
| C(25) | 7380(2) | 1294(1) | 3825(1) | 65(1) |
| C(26) | 6742(2) | 1601(2) | 4316(1) | 85(1) |
| C(27) | 6479(2) | 2522(2) | 4215(1) | 92(1) |
| C(28) | 7279(2) | 3095(2) | 4176(1) | 77(1) |
| C(29) | 7927(2) | 2791(1) | 3693(1) | 61(1) |

Table S3. Bond lengths [Å] and angles [°] for p.

| | |
|---|---|
| P(1)-C(15) | 1.8325(17) |
| P(1)-C(24) | 1.8504(19) |
| P(1)-C(18) | 1.8711(19) |
| N(1)-C(1) | 1.379(2) |
| N(1)-C(8) | 1.382(2) |
| N(1)-C(9) | 1.430(3) |
| N(2)-C(12) | 1.367(2) |
| N(2)-C(17) | 1.442(2) |
| N(2)-C(16) | 1.444(2) |
| C(1)-C(2) | 1.394(3) |
| C(1)-C(6) | 1.396(3) |
| C(2)-C(3) | 1.378(3) |
| C(3)-C(4) | 1.371(4) |
| C(4)-C(5) | 1.368(3) |
| C(5)-C(6) | 1.405(3) |
| C(6)-C(7) | 1.422(3) |
| C(7)-C(8) | 1.356(3) |
| C(8)-C(10) | 1.487(2) |
| C(10)-C(11) | 1.384(2) |
| C(10)-C(15) | 1.408(2) |
| C(11)-C(12) | 1.407(2) |
| C(12)-C(13) | 1.404(2) |
| C(13)-C(14) | 1.371(3) |
| C(14)-C(15) | 1.394(2) |
| C(18)-C(23) | 1.524(3) |
| C(18)-C(19) | 1.527(3) |
| C(19)-C(20) | 1.523(3) |
| C(20)-C(21) | 1.507(3) |
| C(21)-C(22) | 1.510(3) |
| C(22)-C(23) | 1.526(3) |
| C(24)-C(25) | 1.520(3) |
| C(24)-C(29) | 1.534(3) |
| C(25)-C(26) | 1.520(3) |
| C(26)-C(27) | 1.514(4) |
| C(27)-C(28) | 1.503(4) |
| C(28)-C(29) | 1.516(3) |

| | |
|---|---|
| C(15)-P(1)-C(24) | 103.89(8) |
| C(15)-P(1)-C(18) | 100.73(8) |
| C(24)-P(1)-C(18) | 102.37(8) |
| C(1)-N(1)-C(8) | 108.55(16) |
| C(1)-N(1)-C(9) | 124.21(16) |
| C(8)-N(1)-C(9) | 127.20(16) |
| C(12)-N(2)-C(17) | 120.75(16) |
| C(12)-N(2)-C(16) | 120.52(15) |
| C(17)-N(2)-C(16) | 118.28(16) |
| N(1)-C(1)-C(2) | 129.5(2) |
| N(1)-C(1)-C(6) | 107.98(16) |
| C(2)-C(1)-C(6) | 122.52(18) |
| C(3)-C(2)-C(1) | 116.9(2) |
| C(4)-C(3)-C(2) | 121.5(2) |
| C(5)-C(4)-C(3) | 121.8(2) |
| C(4)-C(5)-C(6) | 118.9(2) |
| C(1)-C(6)-C(5) | 118.34(19) |
| C(1)-C(6)-C(7) | 106.52(17) |
| C(5)-C(6)-C(7) | 135.1(2) |
| C(8)-C(7)-C(6) | 108.11(19) |
| C(7)-C(8)-N(1) | 108.82(16) |
| C(7)-C(8)-C(10) | 129.76(18) |
| N(1)-C(8)-C(10) | 121.41(16) |
| C(11)-C(10)-C(15) | 120.82(15) |
| C(11)-C(10)-C(8) | 118.09(15) |
| C(15)-C(10)-C(8) | 121.09(15) |
| C(10)-C(11)-C(12) | 122.23(15) |
| N(2)-C(12)-C(13) | 122.08(16) |
| N(2)-C(12)-C(11) | 121.59(15) |
| C(13)-C(12)-C(11) | 116.33(16) |
| C(14)-C(13)-C(12) | 120.97(16) |
| C(13)-C(14)-C(15) | 123.14(16) |
| C(14)-C(15)-C(10) | 116.31(16) |
| C(14)-C(15)-P(1) | 124.38(13) |
| C(10)-C(15)-P(1) | 118.79(12) |
| C(23)-C(18)-C(19) | 109.54(17) |
| C(23)-C(18)-P(1) | 118.94(13) |

| | |
|---|---|
| C(19)-C(18)-P(1) | 110.57(13) |
| C(20)-C(19)-C(18) | 111.70(17) |
| C(21)-C(20)-C(19) | 111.75(19) |
| C(20)-C(21)-C(22) | 111.54(19) |
| C(21)-C(22)-C(23) | 111.45(19) |
| C(18)-C(23)-C(22) | 110.36(17) |
| C(25)-C(24)-C(29) | 110.28(17) |
| C(25)-C(24)-P(1) | 110.99(13) |
| C(29)-C(24)-P(1) | 109.28(13) |
| C(24)-C(25)-C(26) | 111.23(18) |
| C(27)-C(26)-C(25) | 111.3(2) |
| C(28)-C(27)-C(26) | 111.8(2) |
| C(27)-C(28)-C(29) | 111.3(2) |
| C(28)-C(29)-C(24) | 111.98(18) |

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Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for p. The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| P(1) | 50(1) | 40(1) | 37(1) | 1(1) | -3(1) | 2(1) |
| N(1) | 52(1) | 48(1) | 40(1) | -3(1) | -6(1) | 1(1) |
| N(2) | 62(1) | 48(1) | 44(1) | -2(1) | -10(1) | 10(1) |
| C(1) | 65(1) | 39(1) | 41(1) | -4(1) | -13(1) | 4(1) |
| C(2) | 70(1) | 61(1) | 58(1) | -7(1) | -21(1) | 10(1) |
| C(3) | 101(2) | 71(2) | 55(1) | -2(1) | -33(1) | 11(1) |
| C(4) | 114(2) | 72(2) | 41(1) | 4(1) | -17(1) | -1(2) |
| C(5) | 89(2) | 64(1) | 42(1) | -2(1) | -2(1) | -8(1) |
| C(6) | 69(1) | 42(1) | 39(1) | -6(1) | -7(1) | -1(1) |
| C(7) | 56(1) | 55(1) | 40(1) | -6(1) | -3(1) | -1(1) |
| C(8) | 51(1) | 39(1) | 40(1) | -6(1) | -8(1) | 2(1) |
| C(9) | 57(1) | 81(2) | 58(1) | -5(1) | -1(1) | -8(1) |
| C(10) | 42(1) | 42(1) | 37(1) | -2(1) | -3(1) | -3(1) |
| C(11) | 50(1) | 41(1) | 37(1) | -8(1) | -4(1) | 2(1) |
| C(12) | 44(1) | 38(1) | 42(1) | -1(1) | -3(1) | -1(1) |
| C(13) | 62(1) | 45(1) | 32(1) | 1(1) | -5(1) | 0(1) |
| C(14) | 62(1) | 41(1) | 35(1) | -3(1) | -1(1) | 1(1) |
| C(15) | 46(1) | 38(1) | 37(1) | 0(1) | -1(1) | -1(1) |
| C(16) | 69(1) | 51(1) | 66(1) | -10(1) | -12(1) | 16(1) |
| C(17) | 70(2) | 67(1) | 50(1) | 9(1) | -10(1) | 16(1) |
| C(18) | 53(1) | 39(1) | 43(1) | 6(1) | -2(1) | 0(1) |
| C(19) | 53(1) | 62(1) | 55(1) | -1(1) | 3(1) | 0(1) |
| C(20) | 54(1) | 77(2) | 79(2) | 7(1) | 6(1) | -5(1) |
| C(21) | 58(1) | 68(2) | 95(2) | 10(1) | -16(1) | -14(1) |
| C(22) | 79(2) | 64(1) | 69(1) | -6(1) | -14(1) | -22(1) |
| C(23) | 70(1) | 60(1) | 47(1) | -2(1) | -6(1) | -13(1) |
| C(24) | 49(1) | 46(1) | 44(1) | -2(1) | -3(1) | 6(1) |
| C(25) | 57(1) | 65(1) | 73(1) | -6(1) | 7(1) | -4(1) |
| C(26) | 59(2) | 96(2) | 100(2) | -7(2) | 24(1) | -3(1) |
| C(27) | 65(2) | 111(2) | 99(2) | -9(2) | 9(2) | 32(2) |
| C(28) | 82(2) | 70(2) | 77(2) | -13(1) | -2(1) | 31(1) |
| C(29) | 69(2) | 51(1) | 64(1) | -2(1) | -2(1) | 14(1) |

Table S5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for p.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 6991 | 36 | 1288 | 76 |
| H(3A) | 7224 | 331 | 264 | 91 |
| H(4A) | 8620 | 560 | -107 | 91 |
| H(5A) | 9847 | 514 | 514 | 78 |
| H(7A) | 10365 | 208 | 1800 | 61 |
| H(9A) | 7812 | -350 | 2921 | 98 |
| H(9B) | 7192 | 197 | 2499 | 98 |
| H(9C) | 7337 | -773 | 2360 | 98 |
| H(11A) | 10077 | -1285 | 2789 | 51 |
| H(13A) | 10174 | -581 | 4548 | 56 |
| H(14A) | 9446 | 642 | 4307 | 55 |
| H(16A) | 11202 | -2900 | 3537 | 93 |
| H(16B) | 10285 | -2658 | 3242 | 93 |
| H(16C) | 11160 | -2207 | 3023 | 93 |
| H(17A) | 11345 | -2492 | 4447 | 94 |
| H(17B) | 11403 | -1511 | 4576 | 94 |
| H(17C) | 10514 | -2004 | 4703 | 94 |
| H(18A) | 9836 | 2737 | 3118 | 54 |
| H(19A) | 10924 | 1279 | 3115 | 68 |
| H(19B) | 10578 | 1732 | 2522 | 68 |
| H(20A) | 12050 | 2160 | 2758 | 84 |
| H(20B) | 11403 | 2944 | 2742 | 84 |
| H(21A) | 12277 | 3073 | 3599 | 88 |
| H(21B) | 12041 | 2144 | 3807 | 88 |
| H(22A) | 10838 | 3526 | 3793 | 85 |
| H(22B) | 11206 | 3085 | 4384 | 85 |
| H(23A) | 10417 | 1836 | 4153 | 71 |
| H(23B) | 9747 | 2604 | 4178 | 71 |
| H(24A) | 8527 | 1815 | 4176 | 55 |
| H(25A) | 7561 | 714 | 3913 | 78 |
| H(25B) | 7080 | 1296 | 3433 | 78 |
| H(26A) | 6212 | 1247 | 4312 | 102 |

| | | | | |
|---|---|---|---|---|
| H(26B) | 7021 | 1543 | 4712 | 102 |
| H(27A) | 6139 | 2566 | 3840 | 110 |
| H(27B) | 6101 | 2707 | 4548 | 110 |
| H(28A) | 7577 | 3108 | 4569 | 92 |
| H(28B) | 7087 | 3669 | 4080 | 92 |
| H(29A) | 8455 | 3147 | 3701 | 73 |
| H(29B) | 7654 | 2849 | 3294 | 73 |

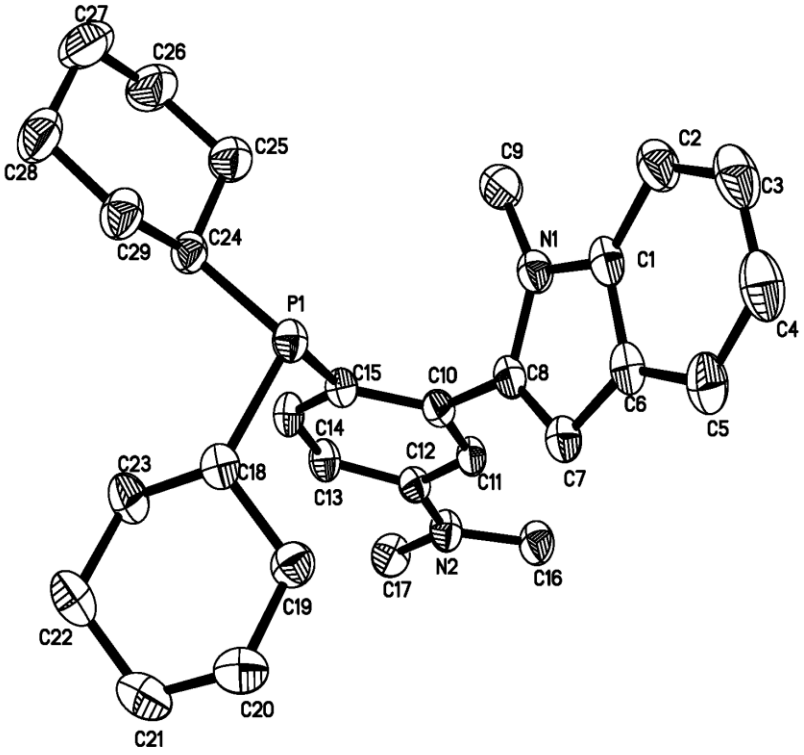
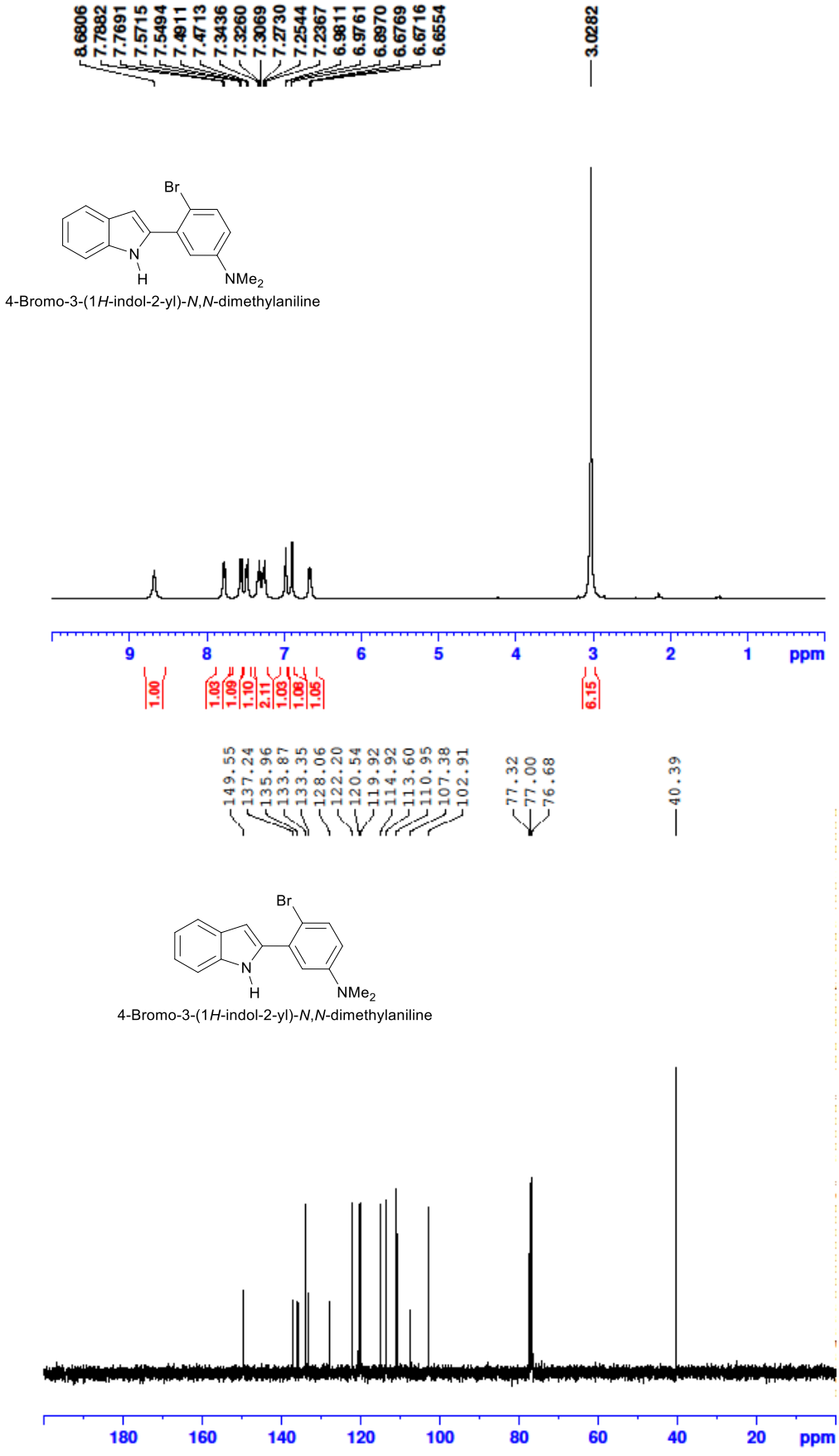
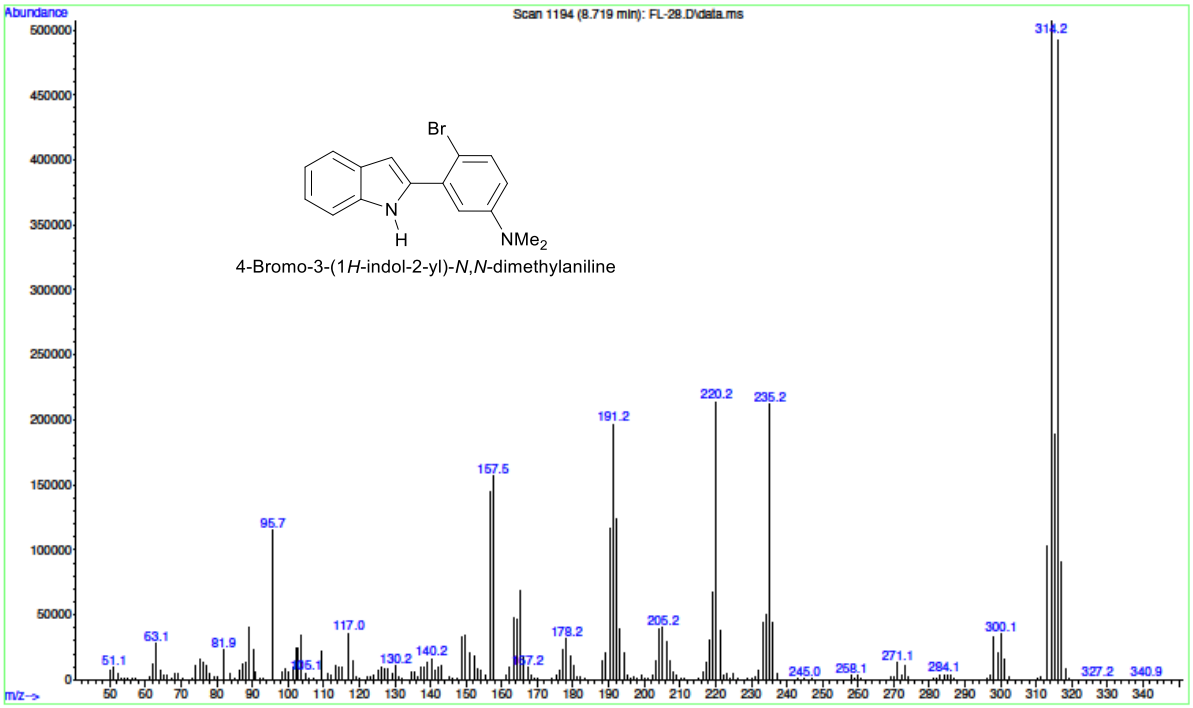
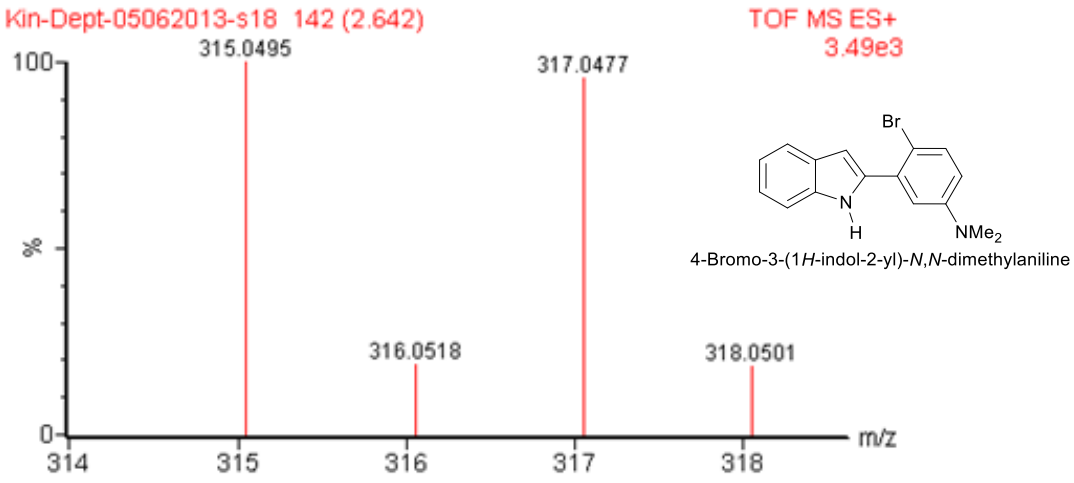



Figure S1. ORTEP drawing of $NMe_2$-CM-Phos (30% probability for the thermal ellipsoid)

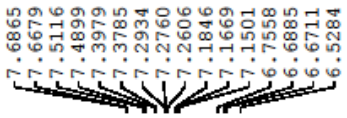
# 13. $^{1}H$, $^{13}C$, $^{19}F$, $^{31}P$ NMR, MS and HRMS spectra

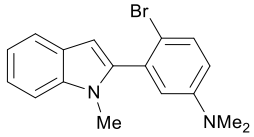




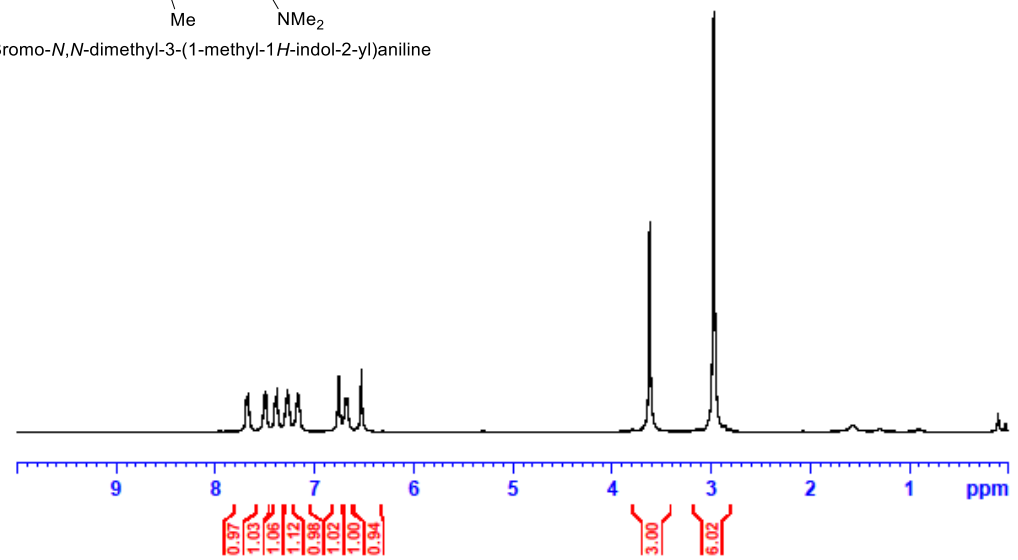



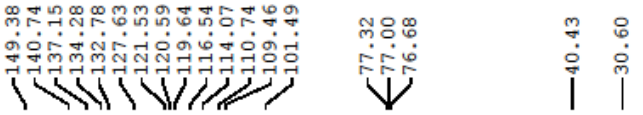

| Mass | Calc. Mass | mDa | PPM | DBE | Score | Formula |
|---|---|---|---|---|---|---|
| 315.0495 | 315.0497 | -0.2 | -0.6 | 9.5 | 1 | C16 H16 N2 Br |

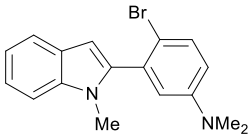


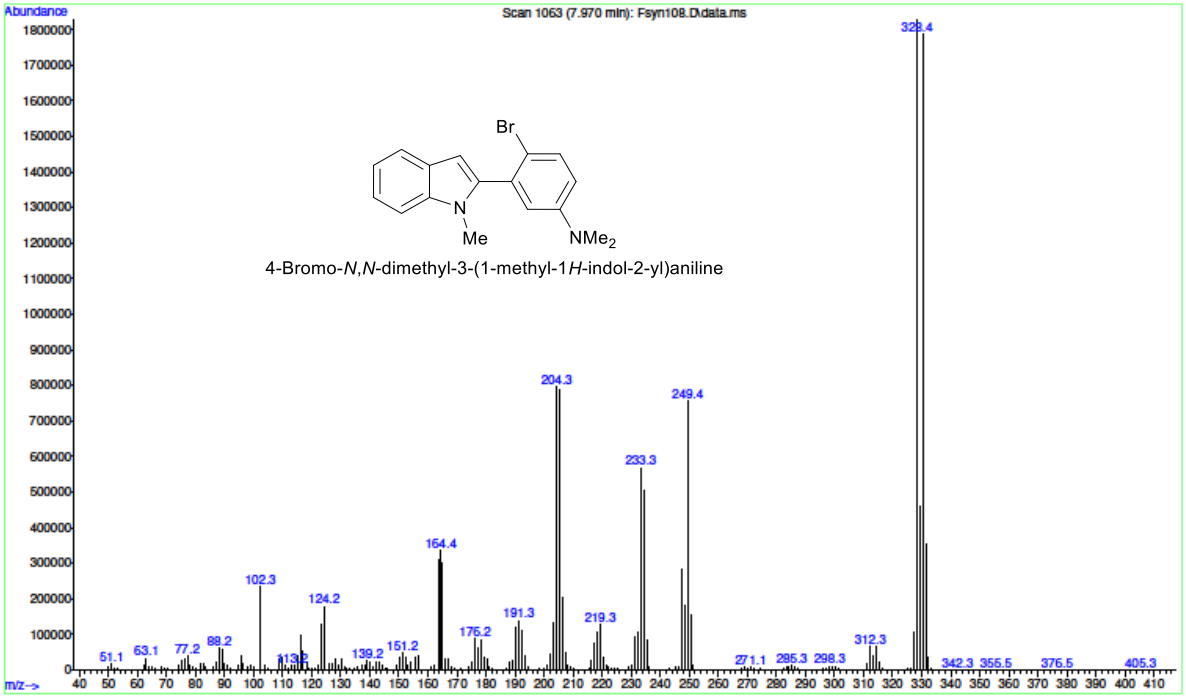

4-Bromo-*N*,*N*-dimethyl-3-(1-methyl-1*H*-indol-2-yl)aniline

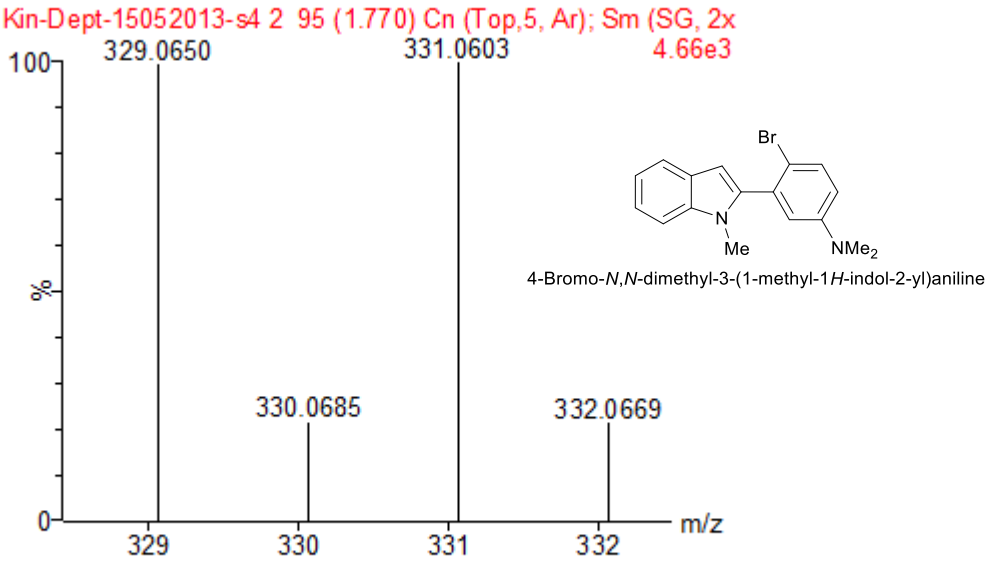


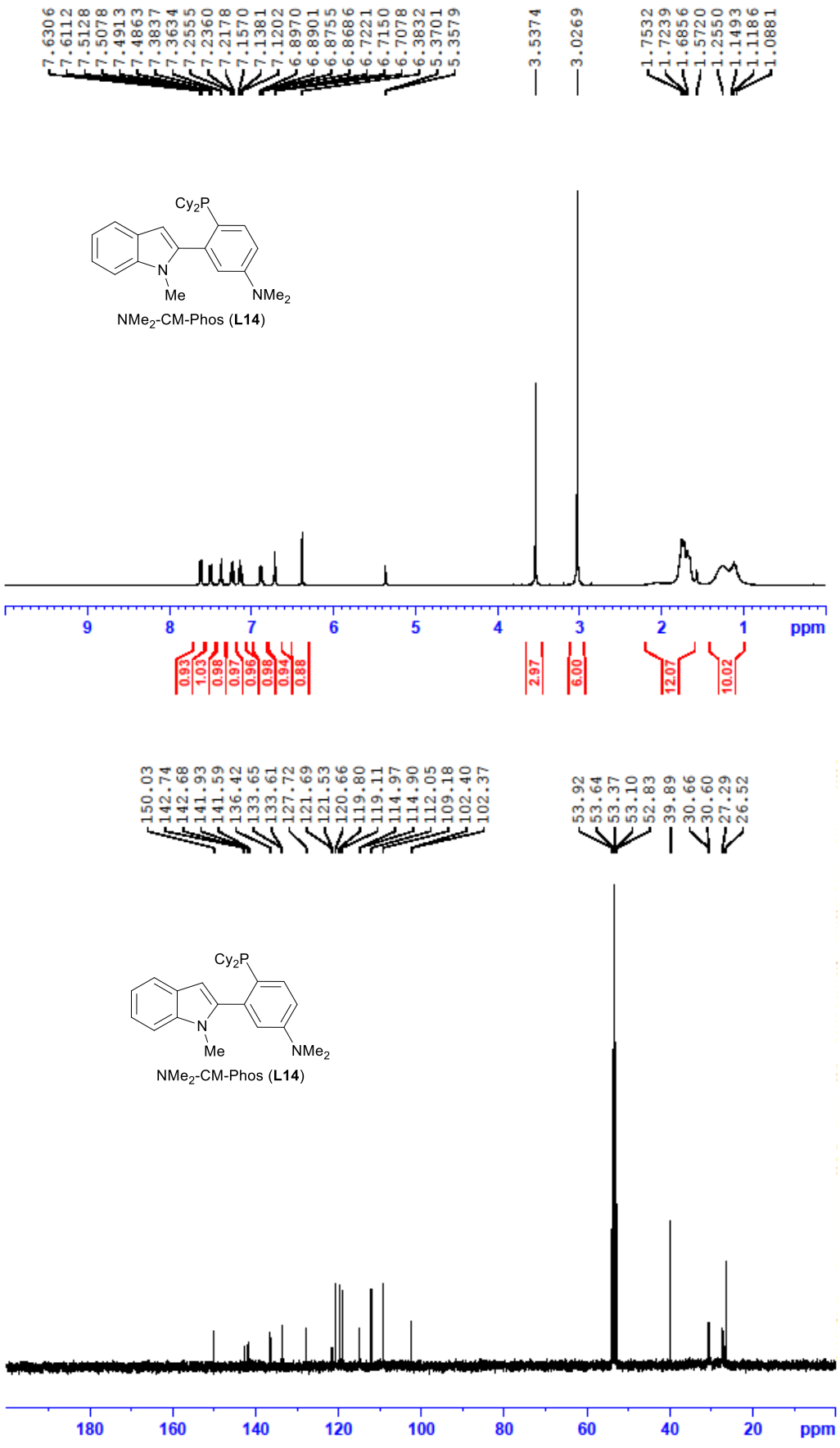



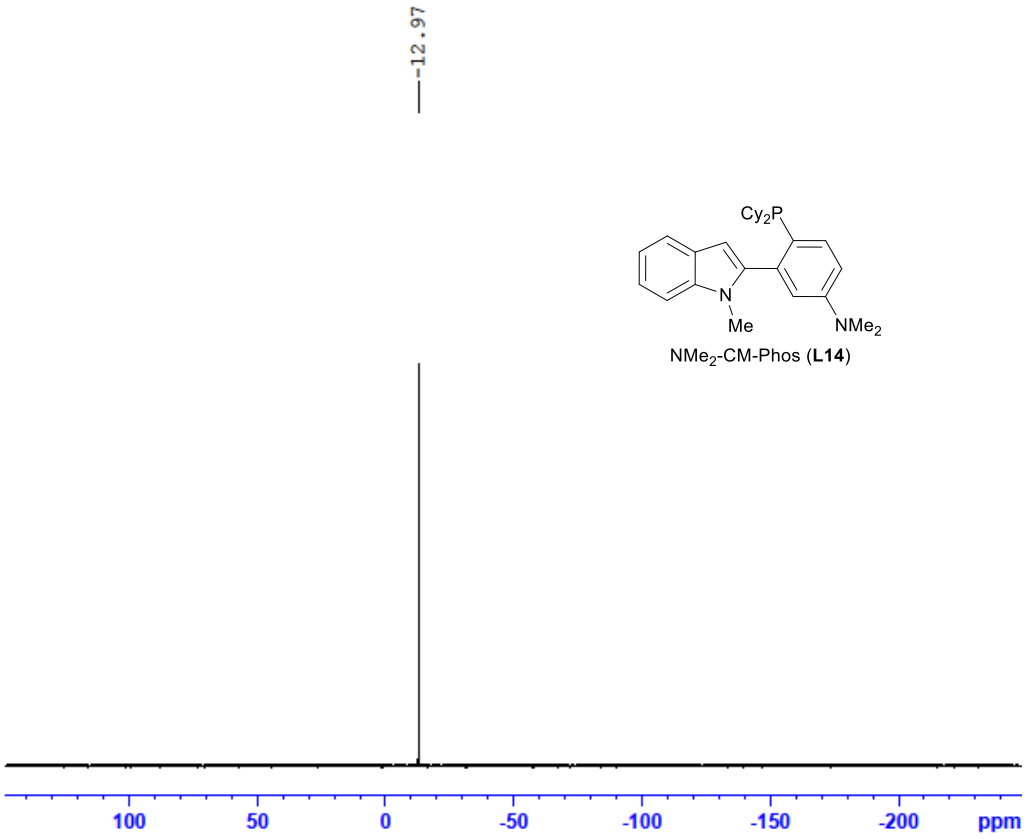

4-Bromo-*N*,*N*-dimethyl-3-(1-methyl-1*H*-indol-2-yl)aniline

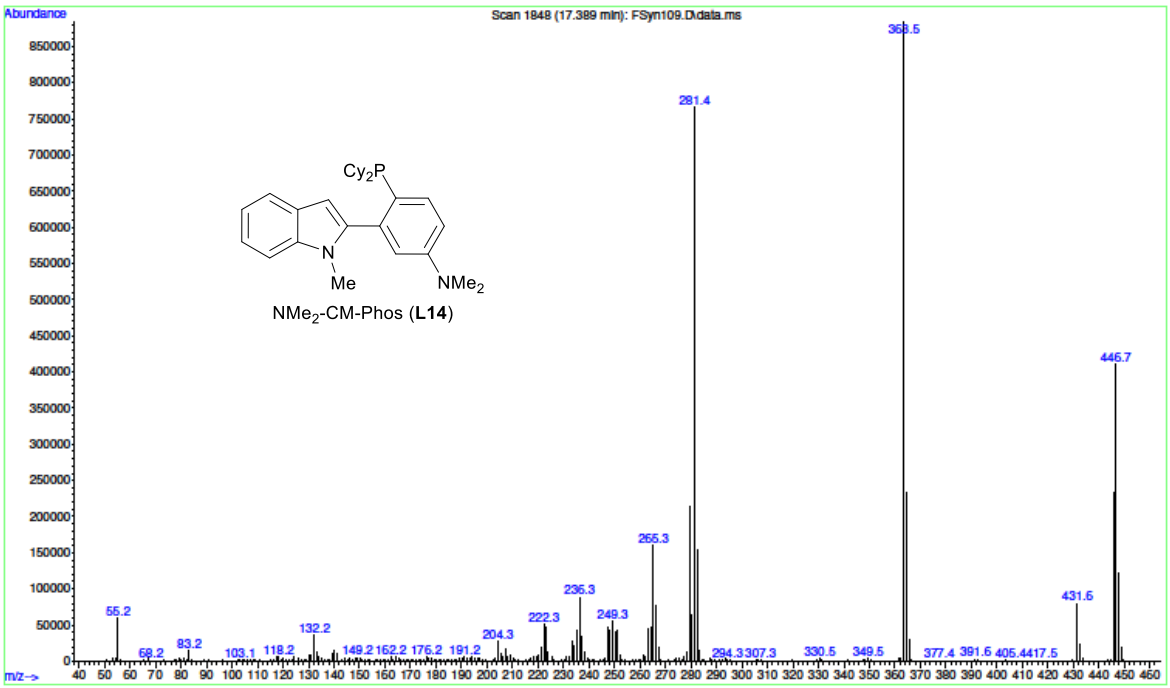


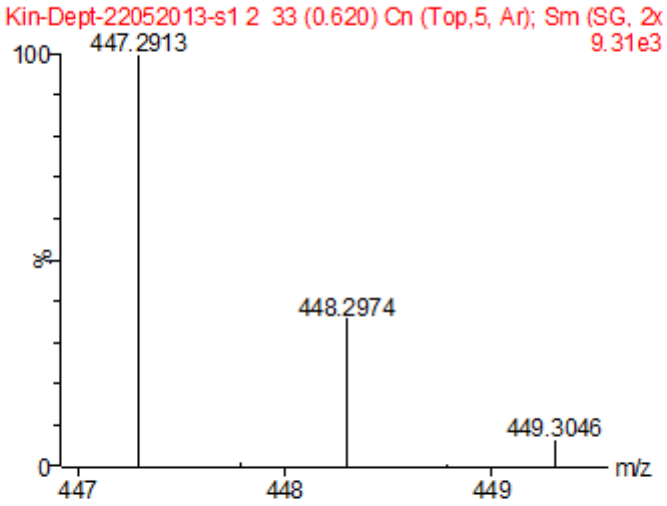



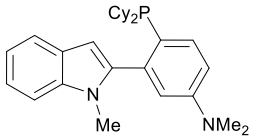

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
|---|---|---|---|---|---|---|
| 329.0650 | 329.0653 | -0.3 | -0.9 | 9.5 | 4.2 | C17 H18 N2 Br |


7.6306
7.6112
7.5128
7.5078
7.4913
7.4863
7.3837
7.3634
7.2555
7.2360
7.2178
7.1570
7.1381
7.1202
6.8970
6.8901
6.8755
6.8686
6.7221
6.7150
6.7078
6.3832
5.3701
5.3579
3.5374
3.0269
1.7532
1.7239
1.6856
1.5720
1.2550
1.1493
1.1186
1.0881
Cy2P
N
Me
NMe2
NMe2-CM-Phos (L14)
9
8
7
6
5
4
3
2
1
ppm
0.93
1.03
0.98
0.97
0.96
0.98
0.94
0.88
2.97
6.00
12.07
10.02
150.03
142.74
142.68
141.93
141.59
136.42
133.65
133.61
127.72
121.69
121.53
120.66
119.80
119.11
114.97
114.90
112.05
109.18
102.40
102.37
53.92
53.64
53.37
53.10
52.83
39.89
30.66
30.60
27.29
26.52
Cy2P
N
Me
NMe2
NMe2-CM-Phos (L14)
180
160
140
120
100
80
60
40
20
ppm


12.97
Cy2P
N
Me
NMe2
NMe2-CM-Phos (L14)
100
50
0
-50
-100
-150
-200
ppm

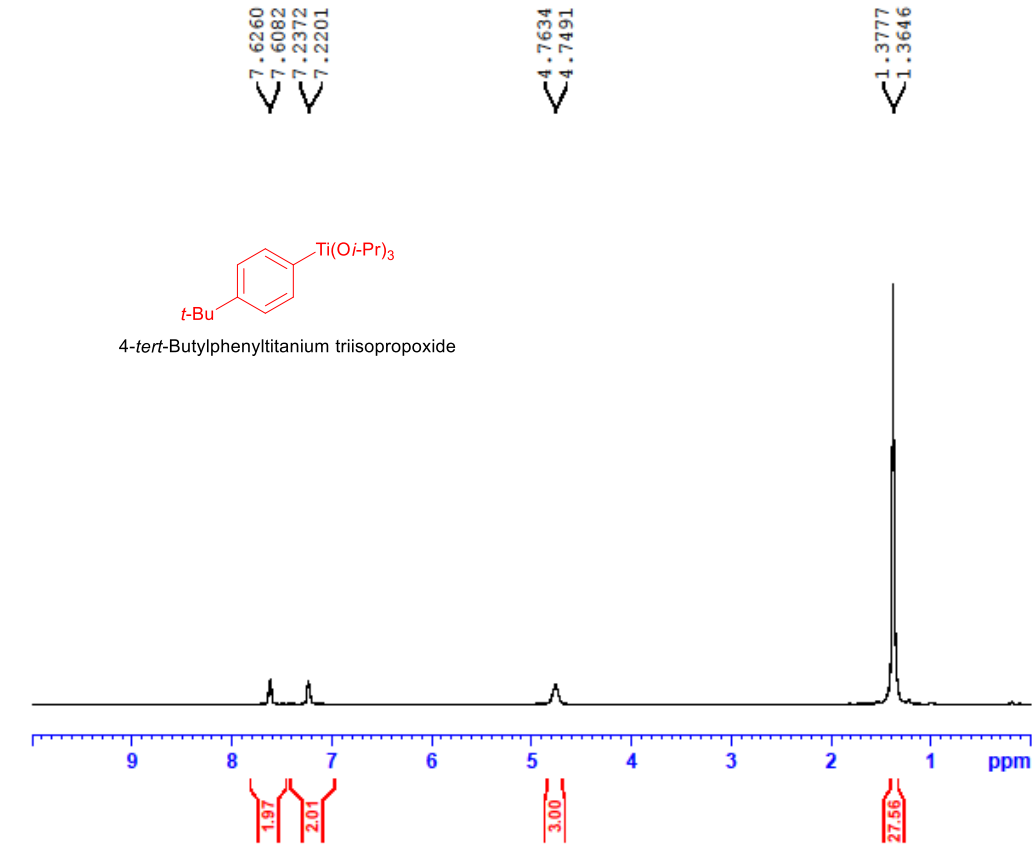

Abundance
Scan 1848 (17.389 min): FSyn109.D\data.ms
Cy2P
N
Me
NMe2
NMe2-CM-Phos (L14)
368.5
281.4
445.7
265.3
236.3
249.3
222.3
204.3
132.2
55.2
431.6
m/z-->



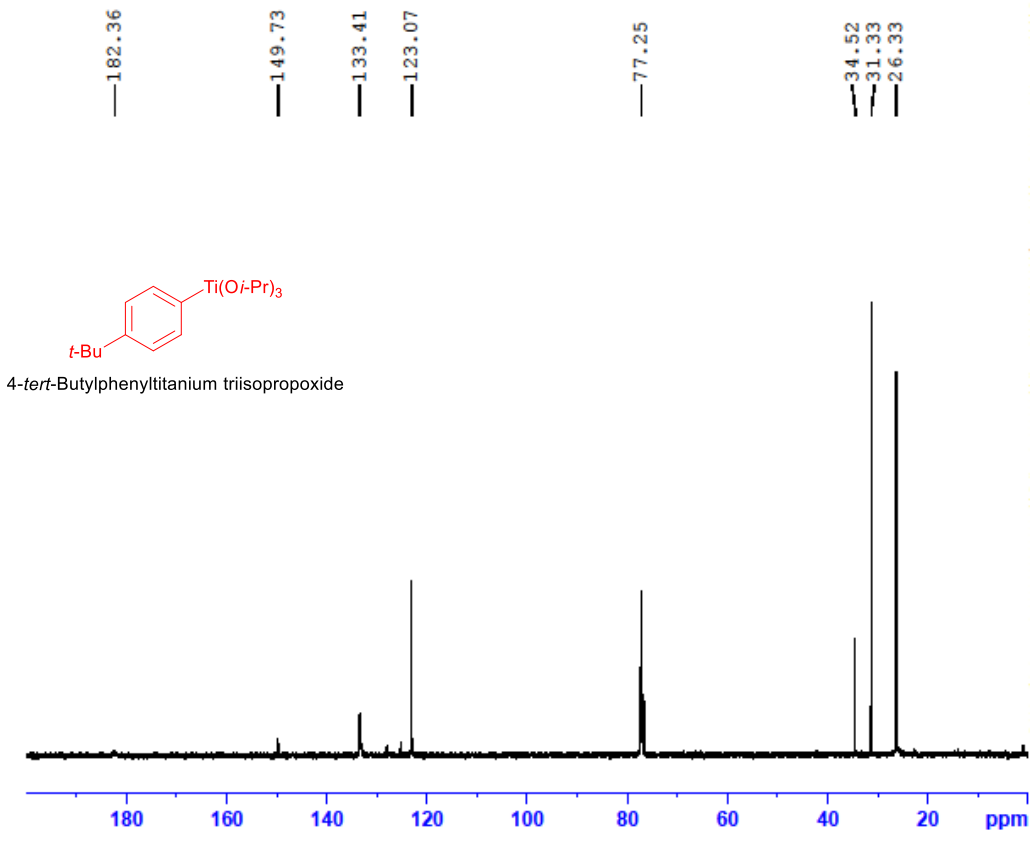




$NMe_2$-CM-Phos (**L14**)

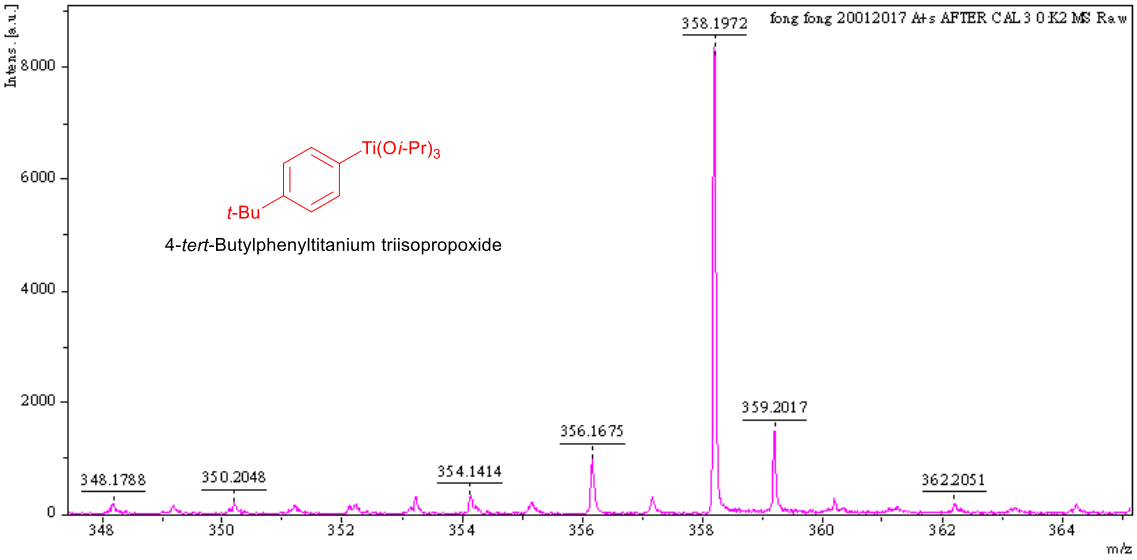
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
|---|---|---|---|---|---|---|
| 447.2913 | 447.2929 | -1.6 | -3.6 | 11.5 | 10.1 | C29 H40 N2 P |




4-*tert*-Butylphenyltitanium triisopropoxide

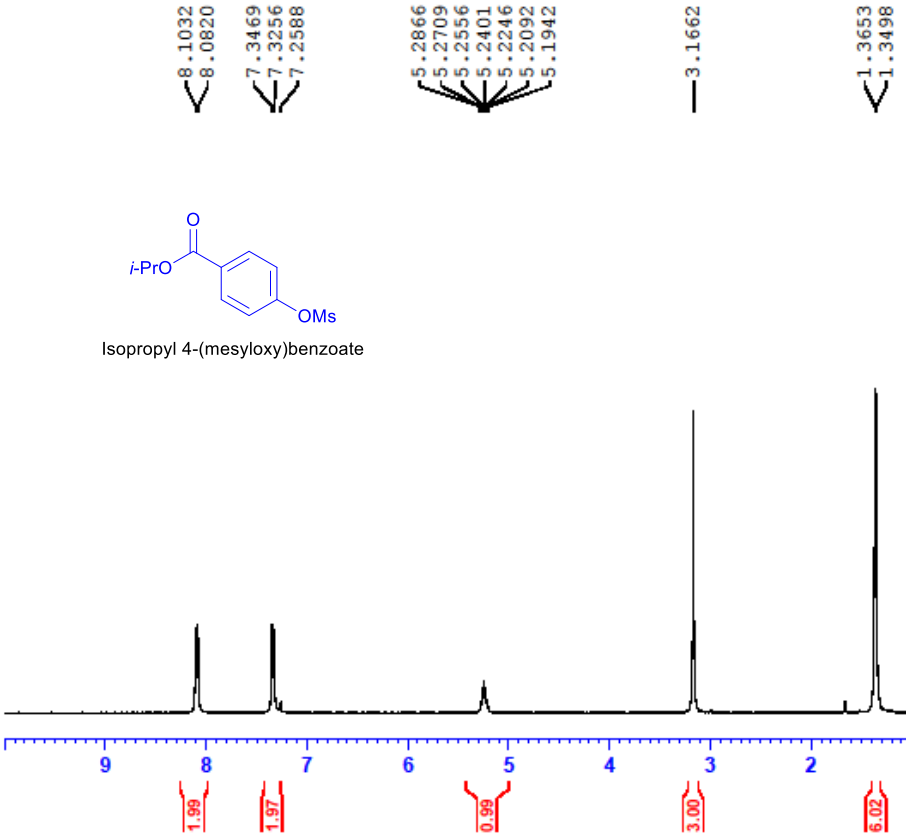



4-*tert*-Butylphenyltitanium triisopropoxide

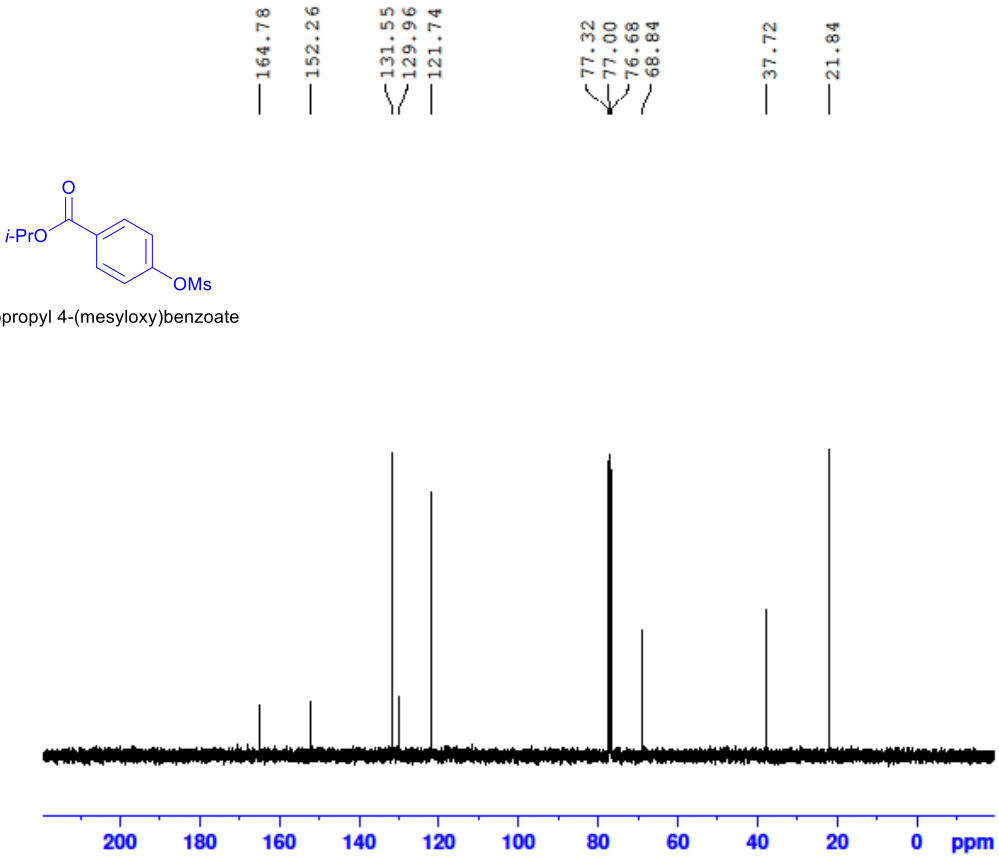



4-*tert*-Butylphenyltitanium triisopropoxide

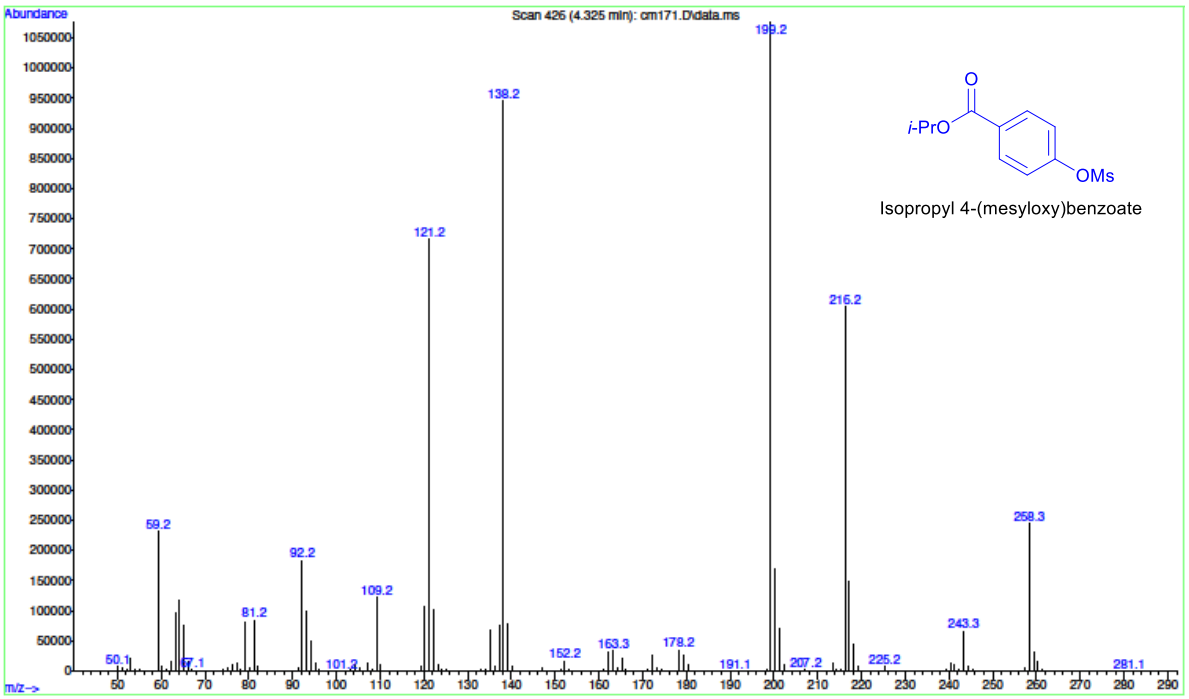
| Mass | Calc. Mass | mDa | PPM | Formula |
|---|---|---|---|---|
| 358.1972 | 358.1988 | -1.6 | -4.5 | C19H34O3Ti |

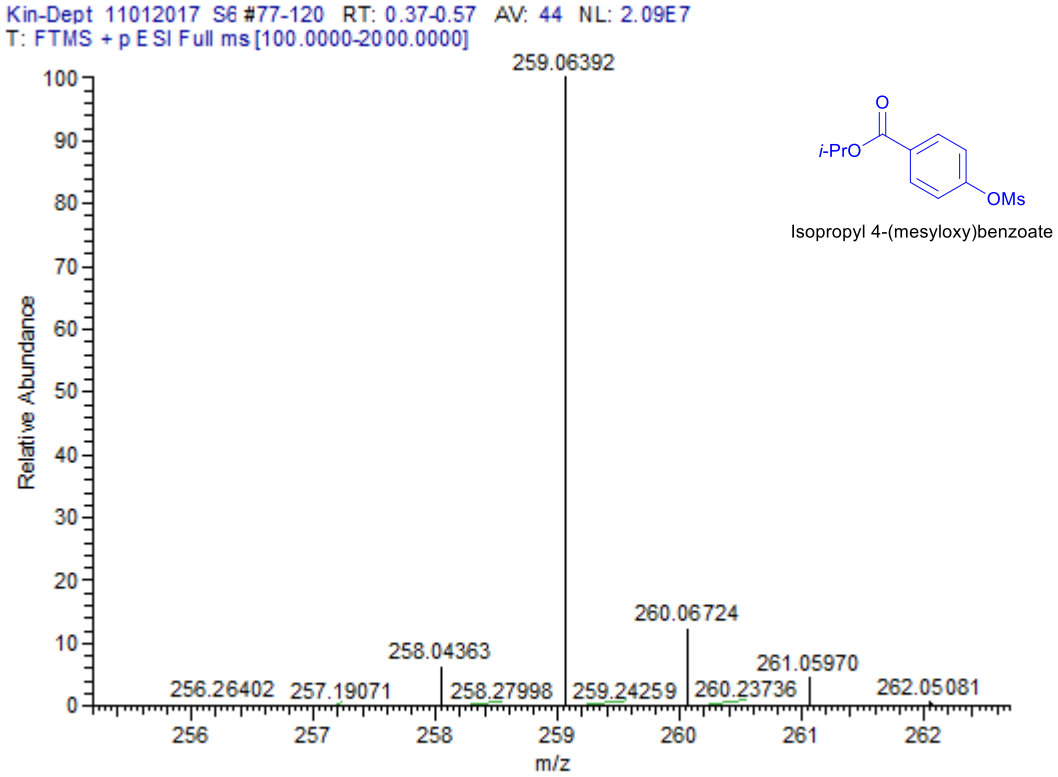



Isopropyl 4-(mesyloxy)benzoate

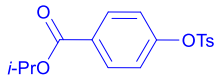



Isopropyl 4-(mesyloxy)benzoate

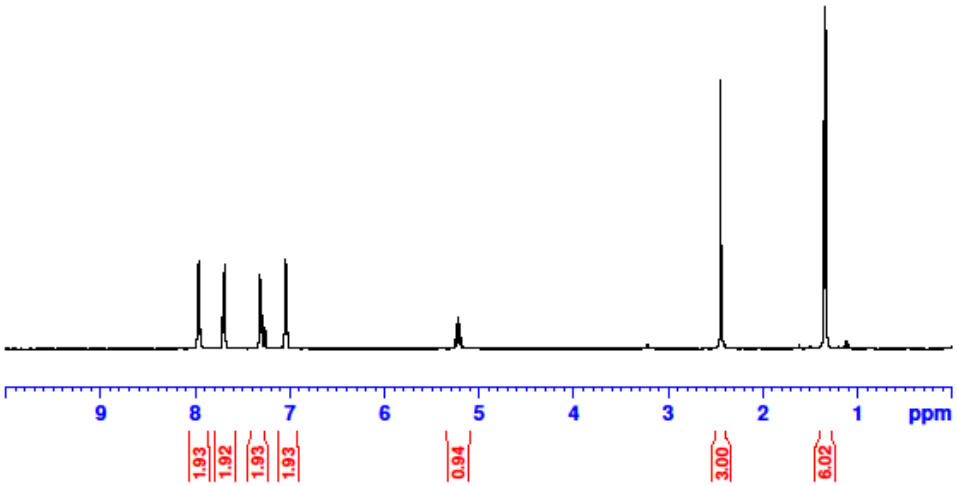


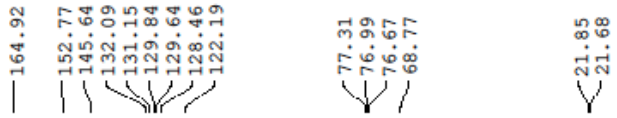



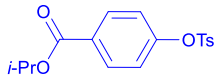

| Mass | Calc. Mass | mDa | PPM | Formula |
|---|---|---|---|---|
| 259.0639 | 259.0635 | 0.4 | 1.6 | C11 H15 O5 S |

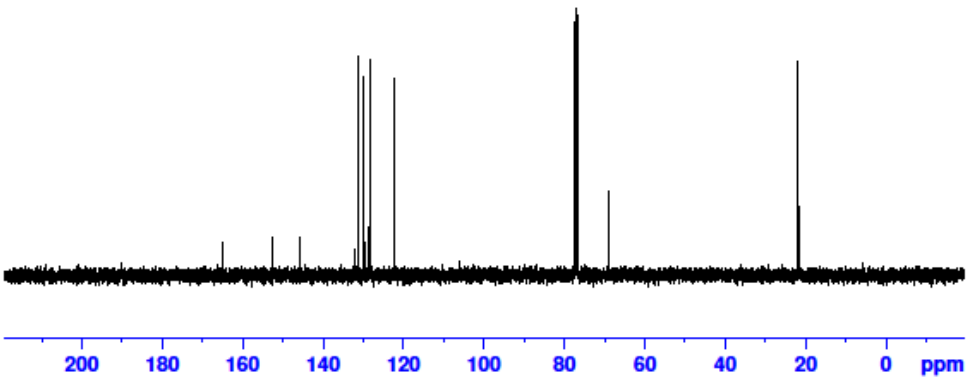

Isopropyl 4-(tosyloxy)benzoate

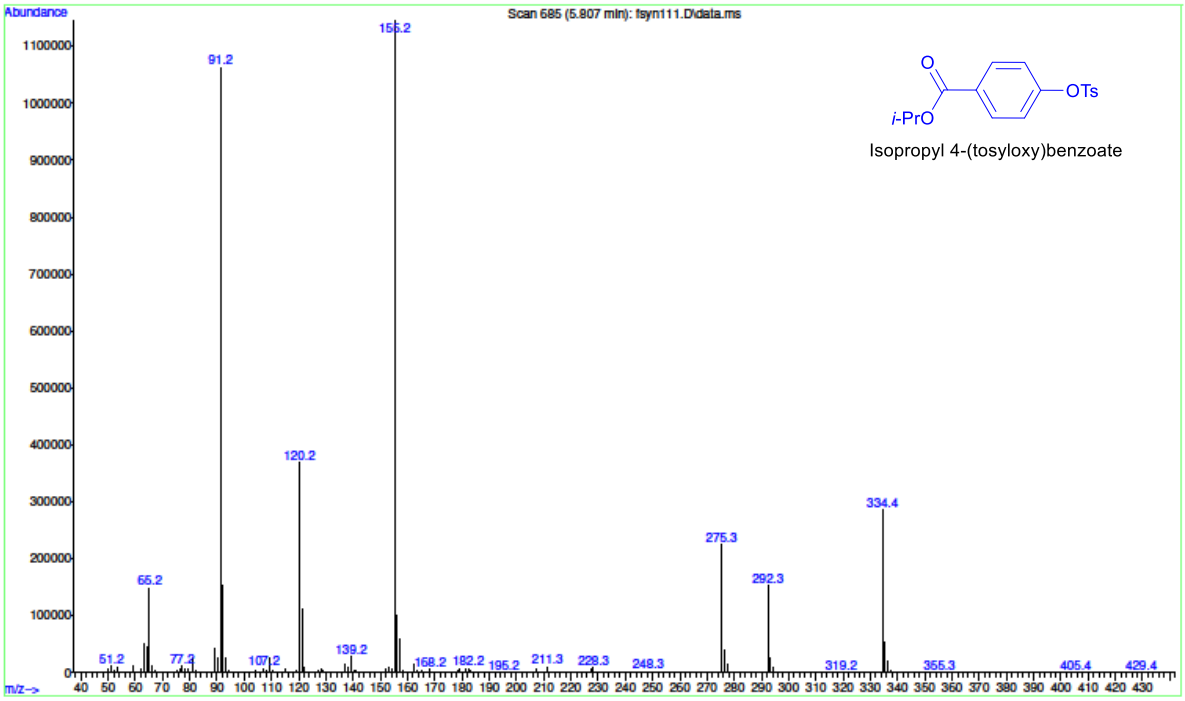


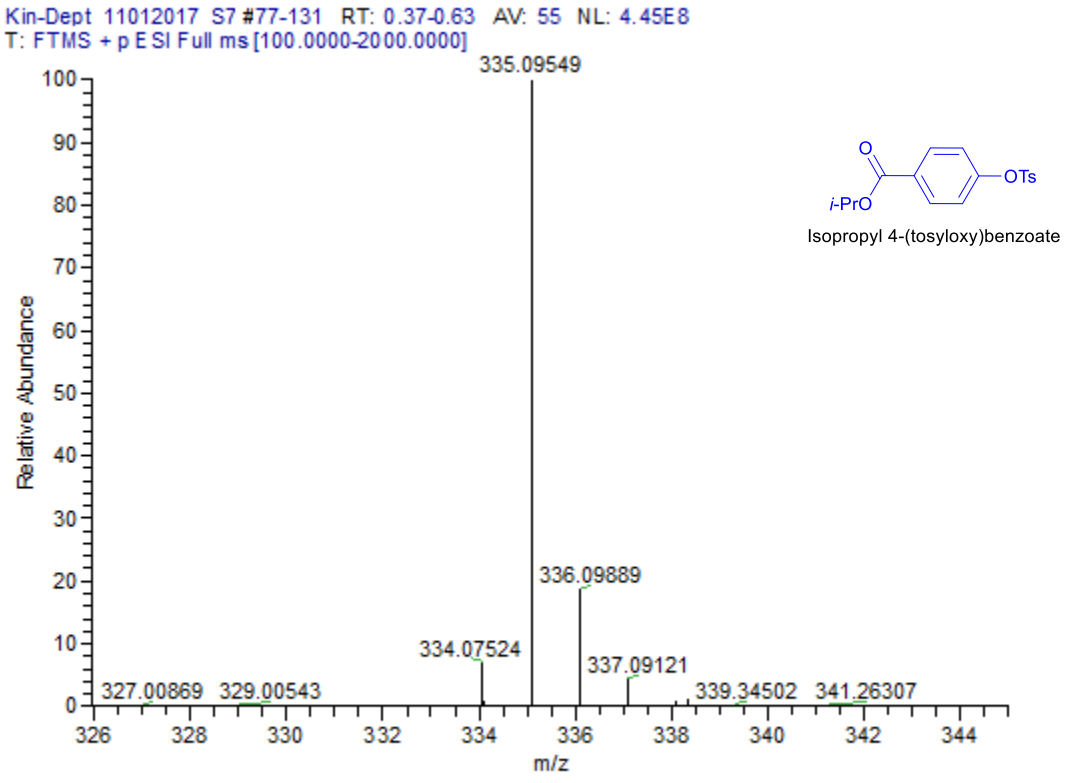




Isopropyl 4-(tosyloxy)benzoate



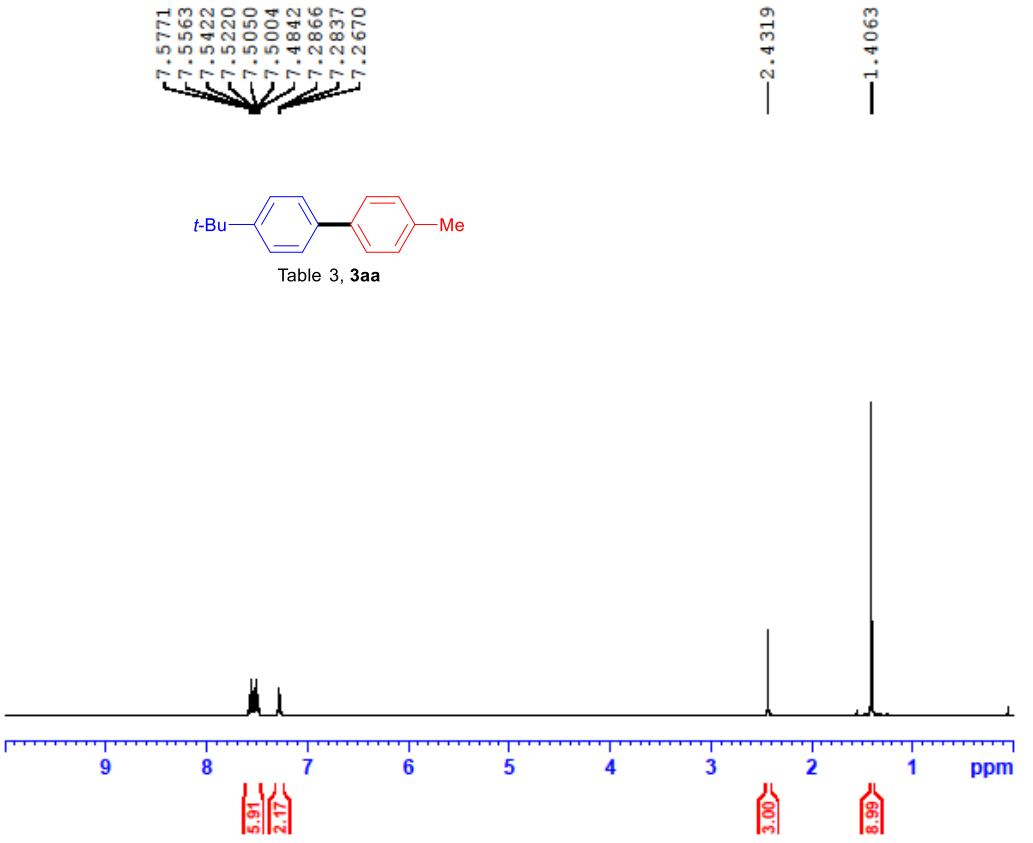


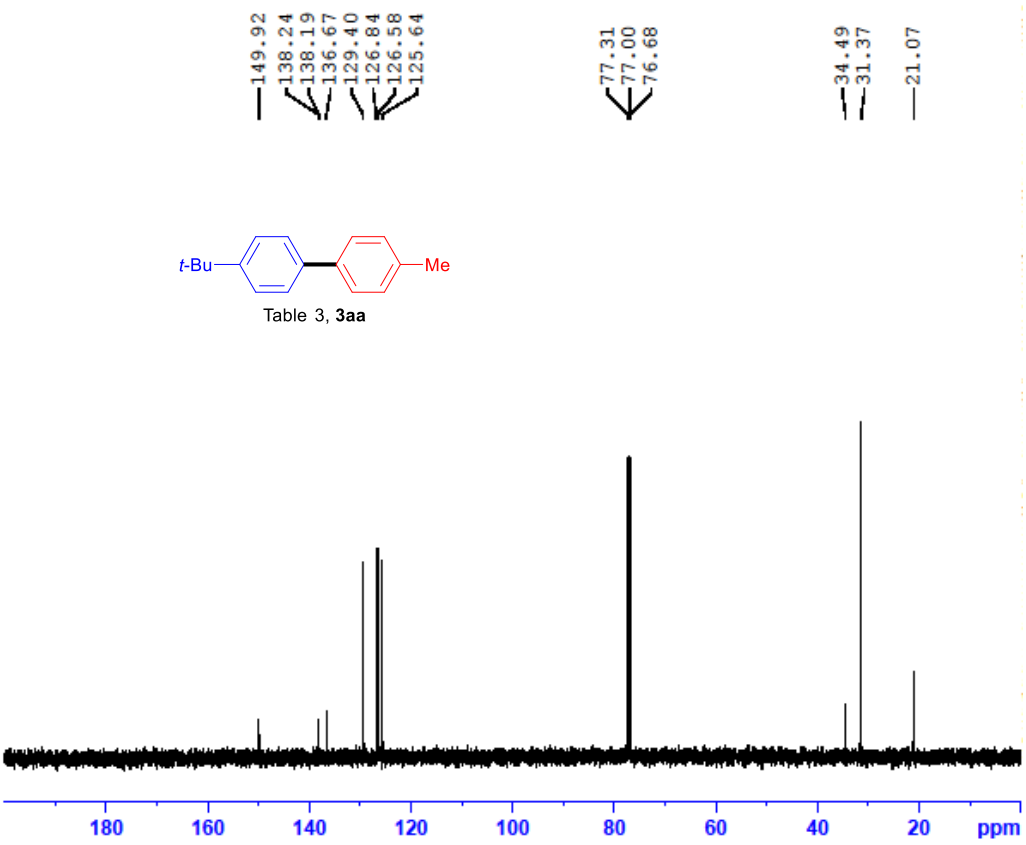

Isopropyl 4-(tosyloxy)benzoate




Isopropyl 4-(tosyloxy)benzoate

| Mass | Calc. Mass | mDa | PPM | Formula |
|---|---|---|---|---|
| 335.0955 | 335.0948 | 0.7 | 2.2 | C17 H19 O5 S |


7.5771
7.5563
7.5422
7.5220
7.5050
7.5004
7.4842
7.2866
7.2837
7.2670
2.4319
1.4063
t-Bu
Me
Table 3, 3aa
9
8
7
6
5
4
3
2
1
ppm
5.91
2.17
3.00
8.99


149.92
138.24
138.19
136.67
129.40
126.84
126.58
125.64
77.31
77.00
76.68
34.49
31.37
21.07
t-Bu
Me
Table 3, 3aa
180
160
140
120
100
80
60
40
20
ppm

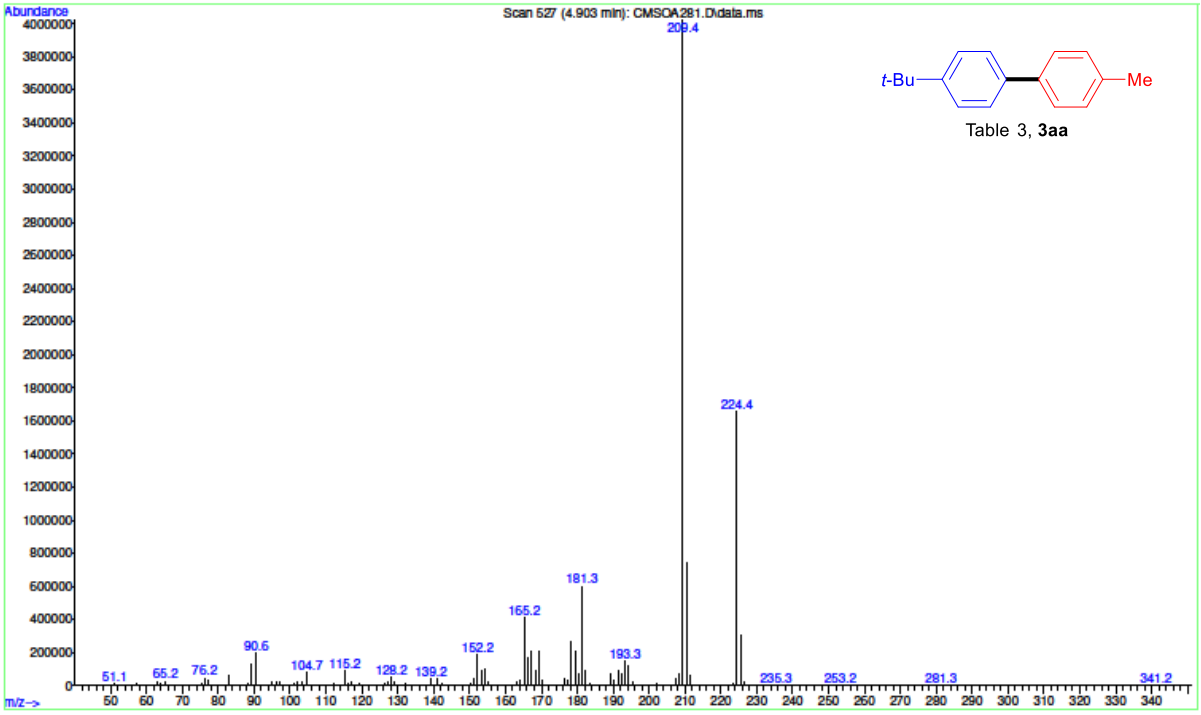

Abundance
Scan 527 (4.903 min): CMSOA281.Dldata.ms
209.4
224.4
181.3
165.2
90.6
152.2
193.3
51.1
65.2
76.2
104.7
115.2
128.2
139.2
235.3
253.2
281.3
341.2
m/z-->
t-Bu
Me

Table 3, **3aa**

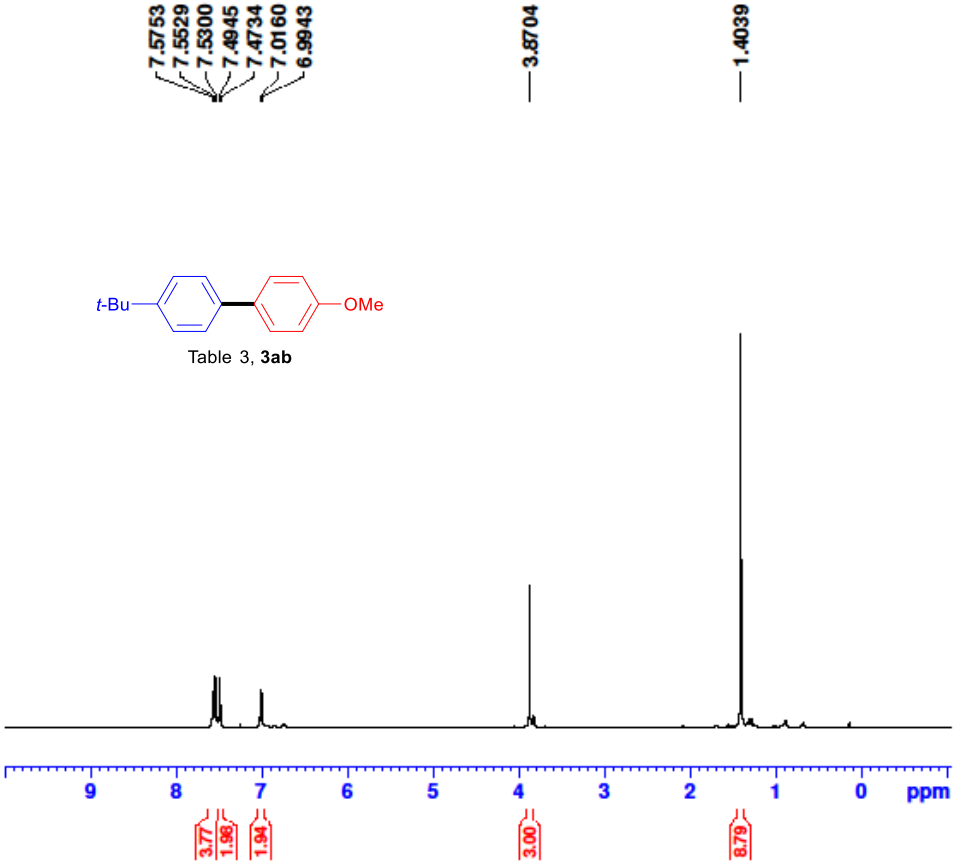



Table 3, **3ab**

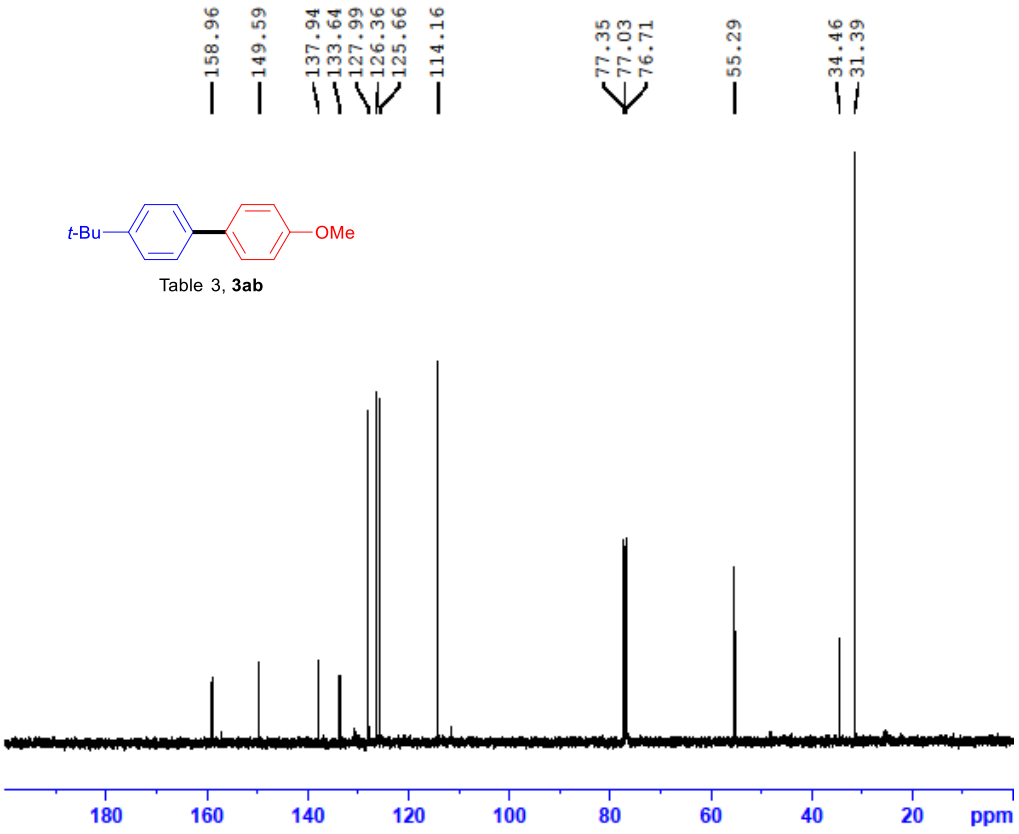



Table 3, **3ab**

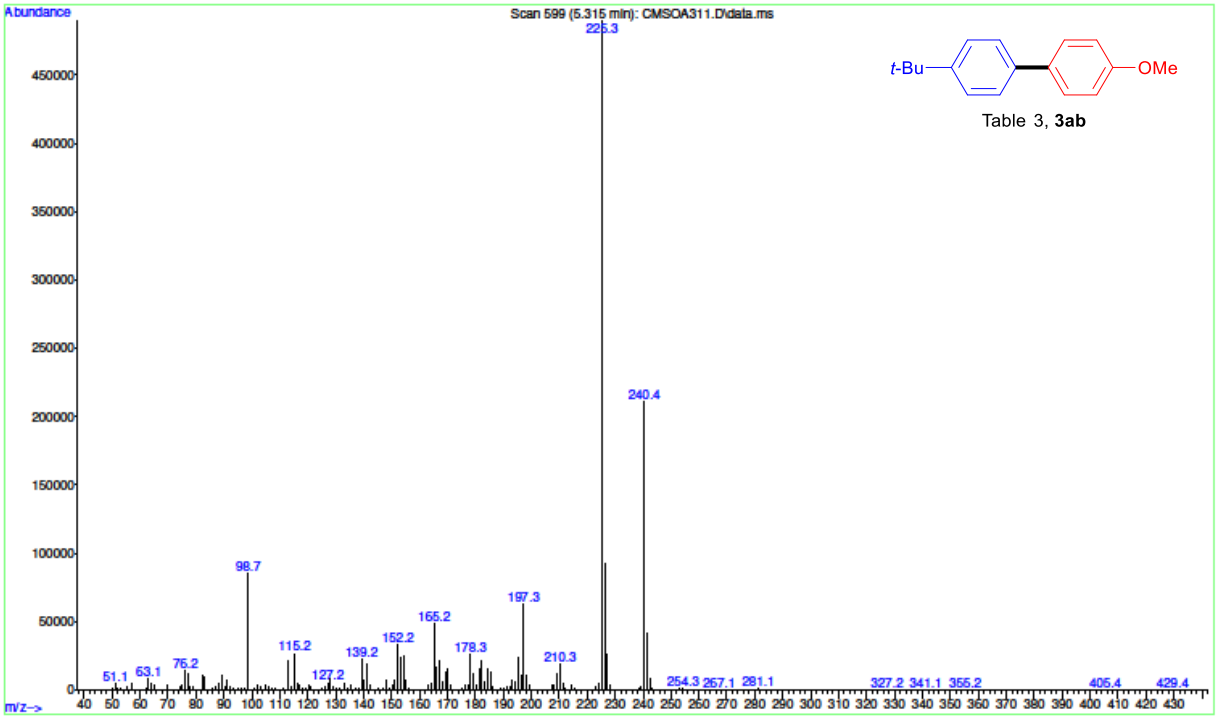

Abundance
Scan 599 (5.315 min): CMSOA311.D\data.ms
225.3
240.4
98.7
197.3
165.2
115.2
152.2
178.3
139.2
210.3
76.2
63.1
51.1
127.2
254.3
267.1
281.1
327.2
341.1
355.2
405.4
429.4
m/z-->
t-Bu
OMe

Table 3, **3ab**

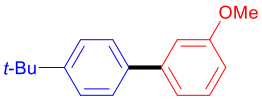
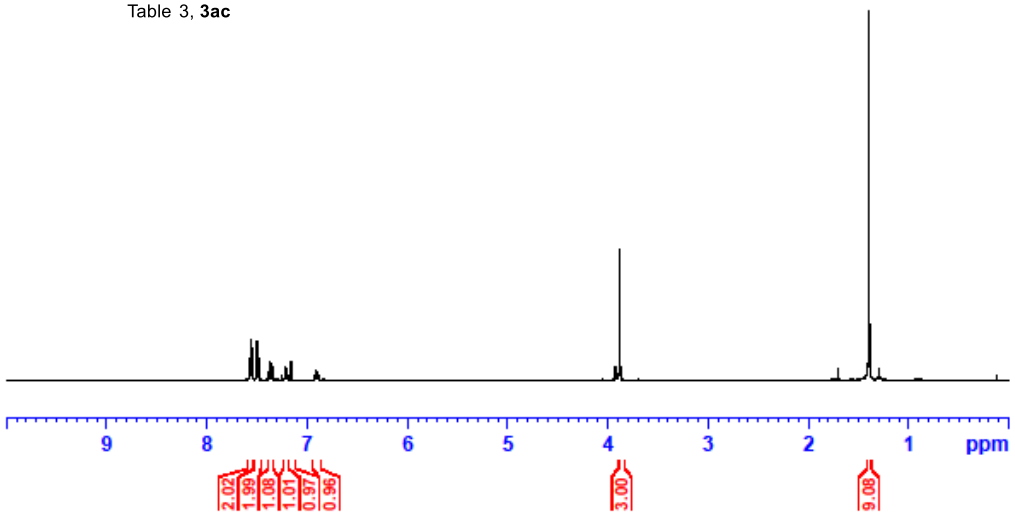
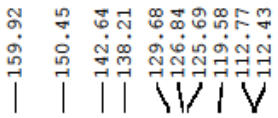




Table 3, **3ac**



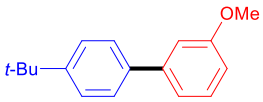
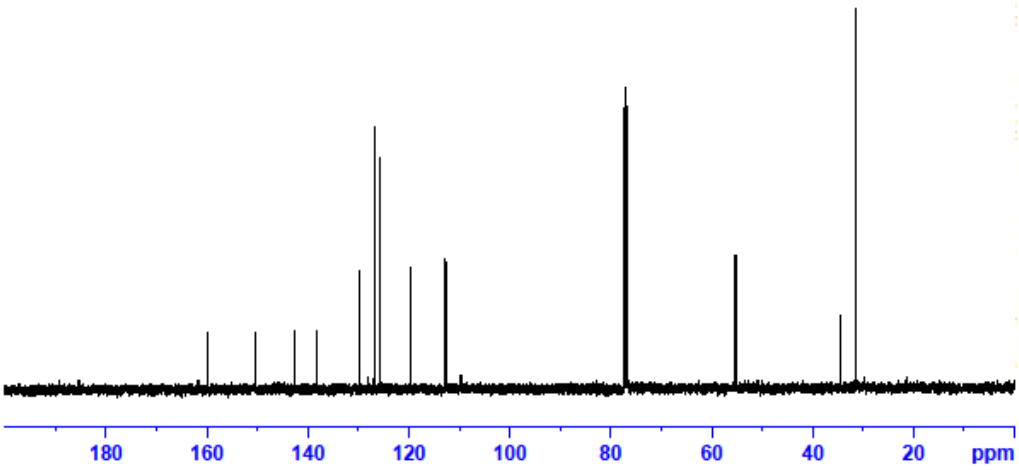




Table 3, **3ac**



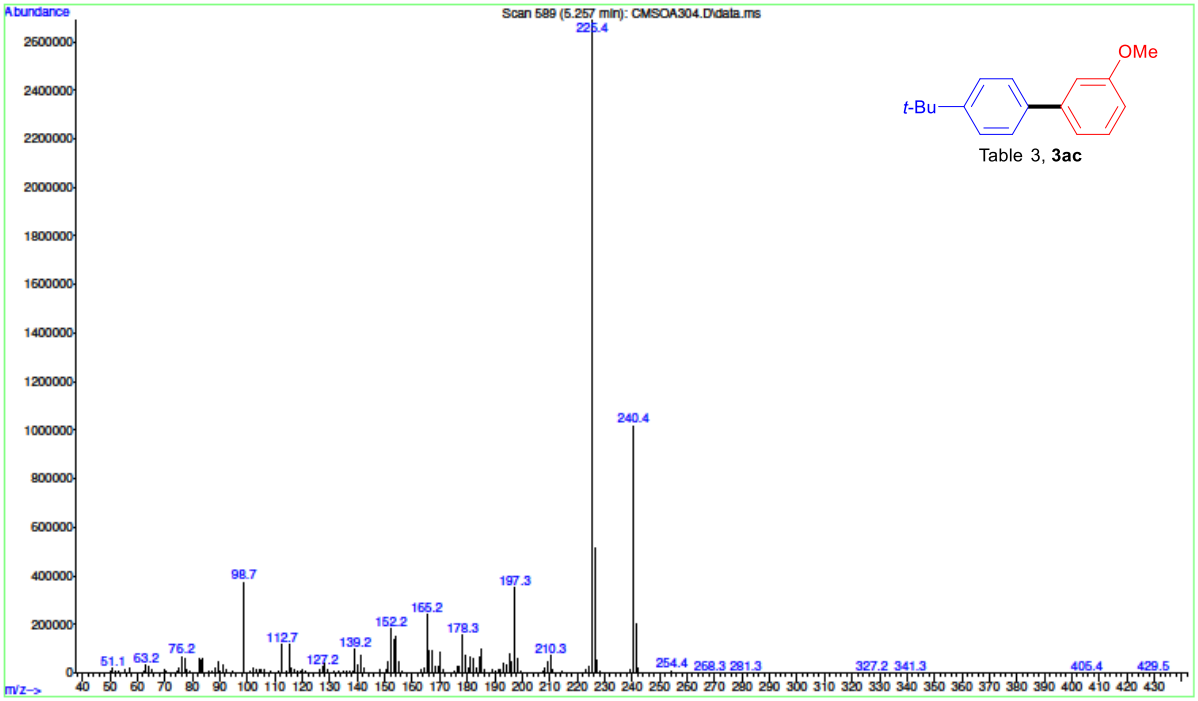
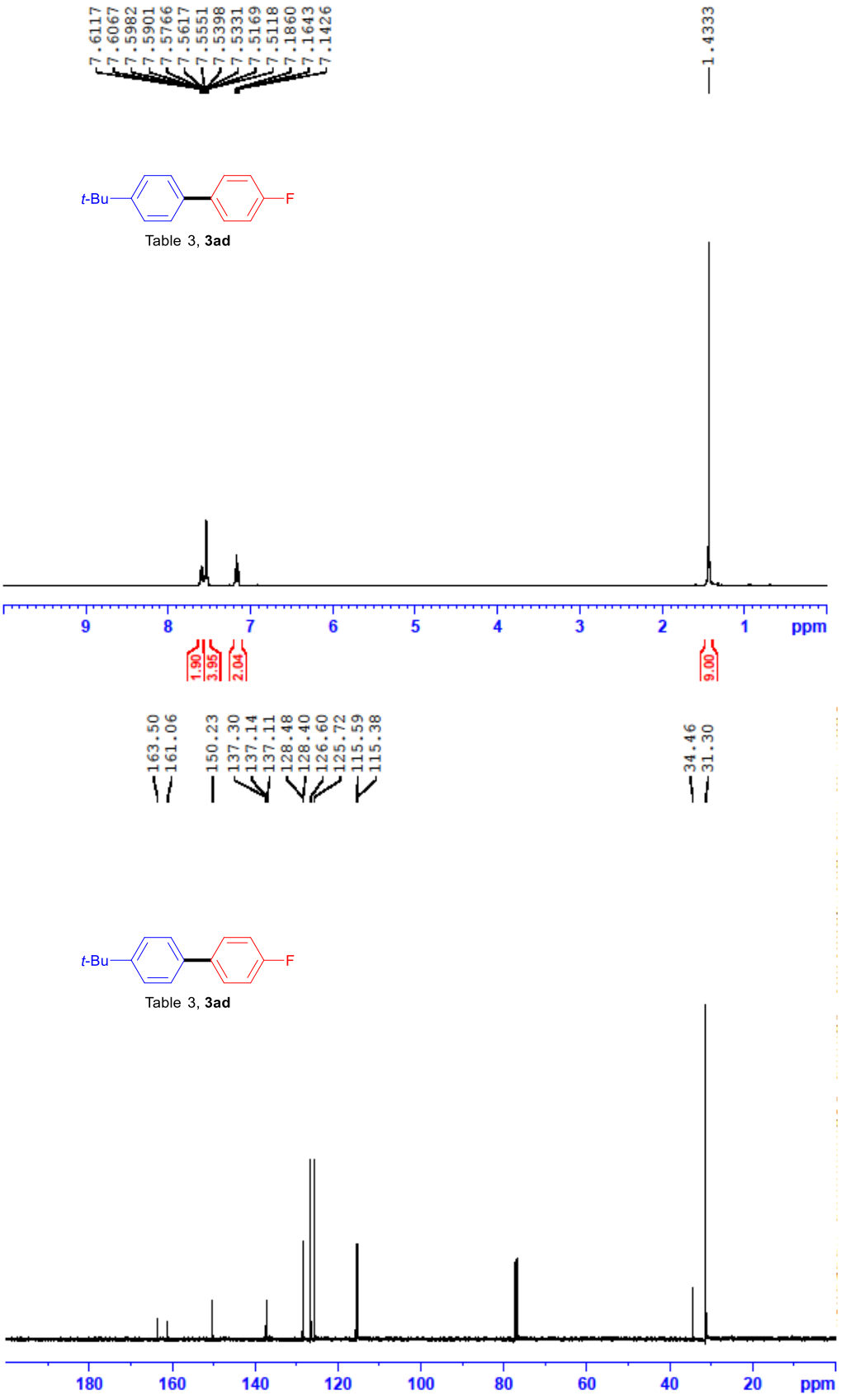

Abundance
Scan 589 (5.257 min): CMSOA304.D\data.ms
225.4
240.4
98.7
197.3
165.2
152.2
178.3
112.7
139.2
76.2
63.2
51.1
127.2
210.3
254.4
268.3
281.3
327.2
341.3
405.4
429.5
m/z-->
OMe
t-Bu

Table 3, **3ac**


7.6117
7.6067
7.5982
7.5901
7.5766
7.5617
7.5551
7.5398
7.5331
7.5169
7.5118
7.1860
7.1643
7.1426
1.4333
t-Bu
F
Table 3, 3ad
9
8
7
6
5
4
3
2
1
ppm
1.90
3.85
2.04
9.00
163.50
161.06
150.23
137.30
137.14
137.11
128.48
128.40
126.60
125.72
115.59
115.38
34.46
31.30
t-Bu
F
Table 3, 3ad
180
160
140
120
100
80
60
40
20
ppm

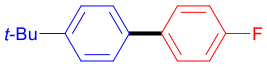



Table 3, **3ad**



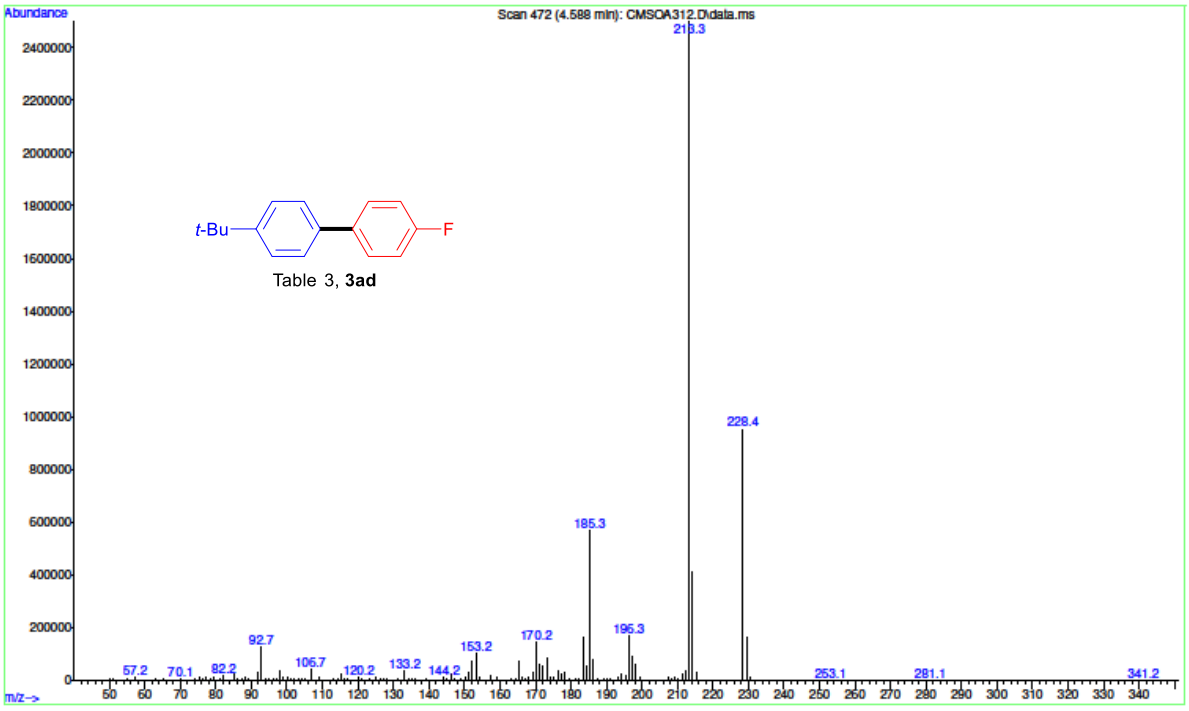







Table 3, **3ad**

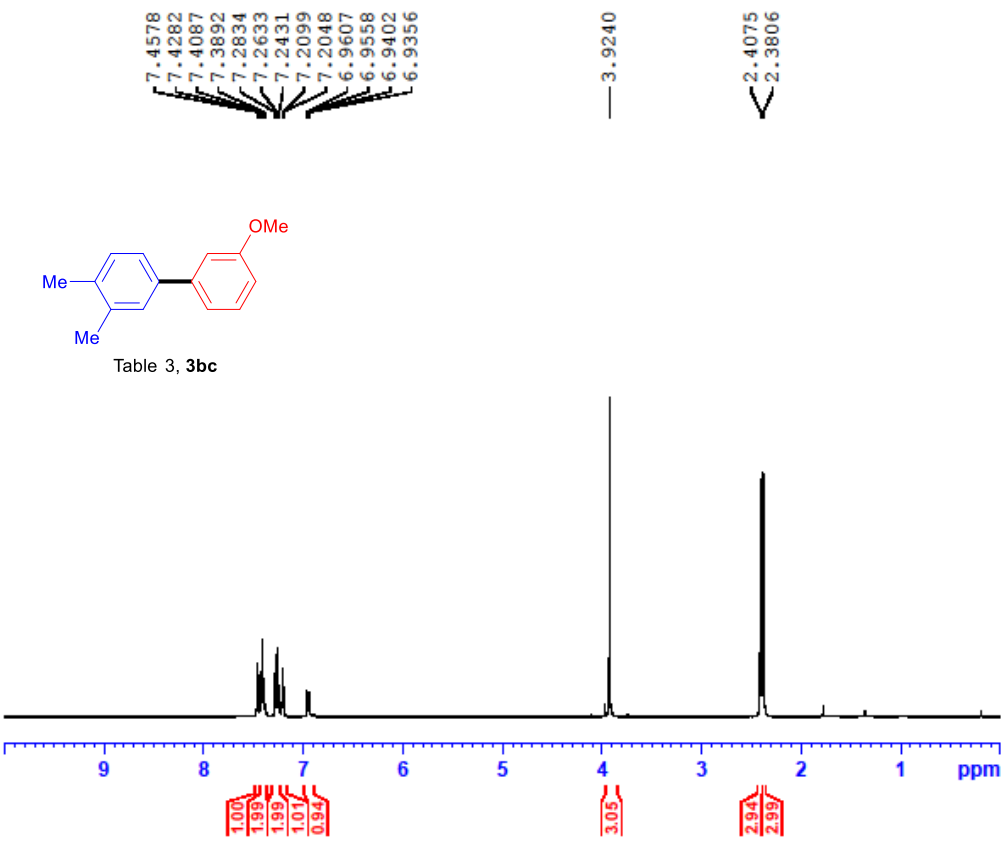



Table 3, **3bc**

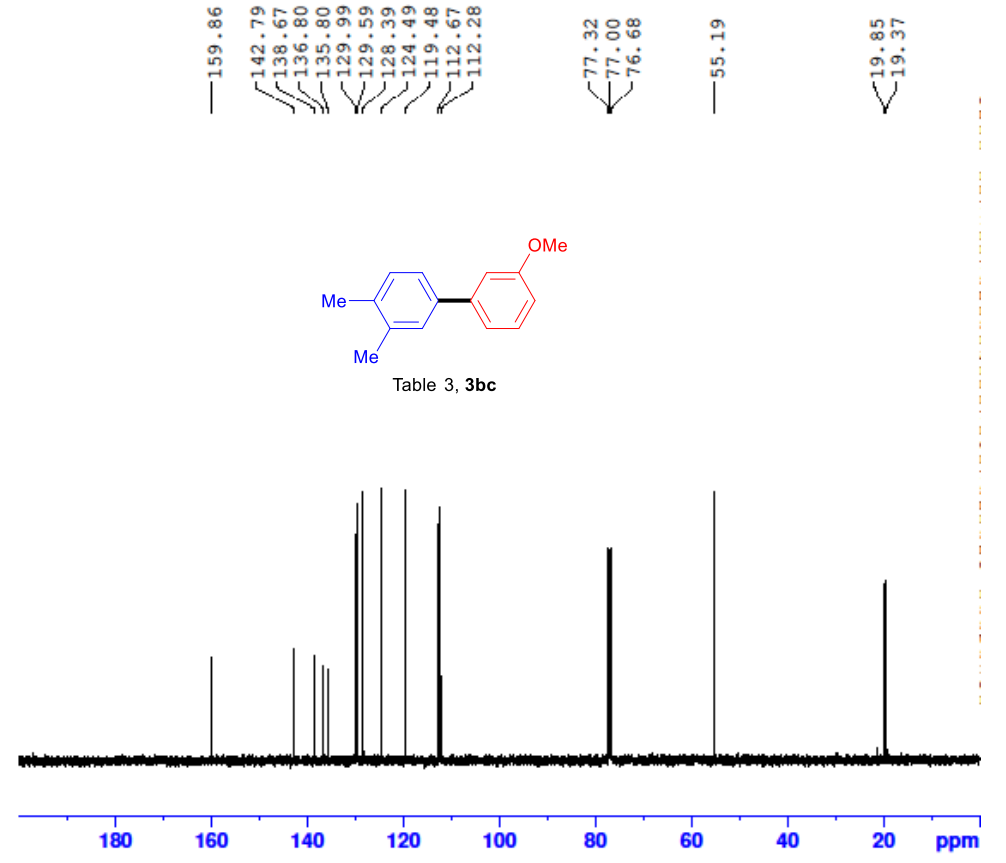



Table 3, **3bc**

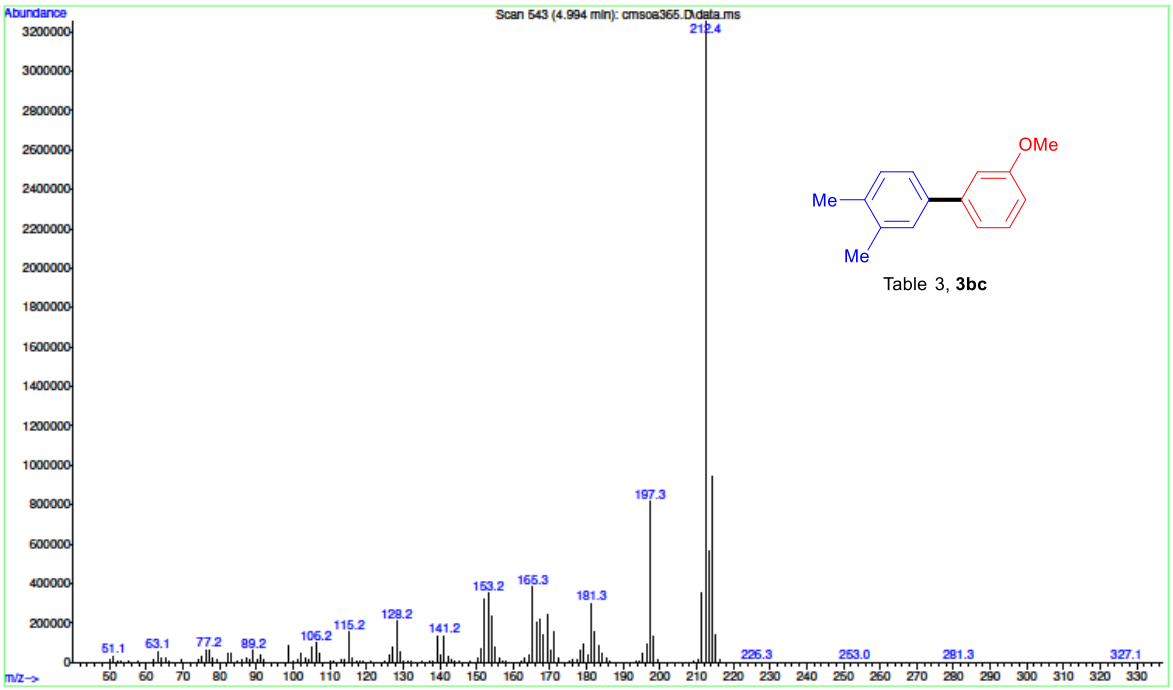



Table 3, **3bc**

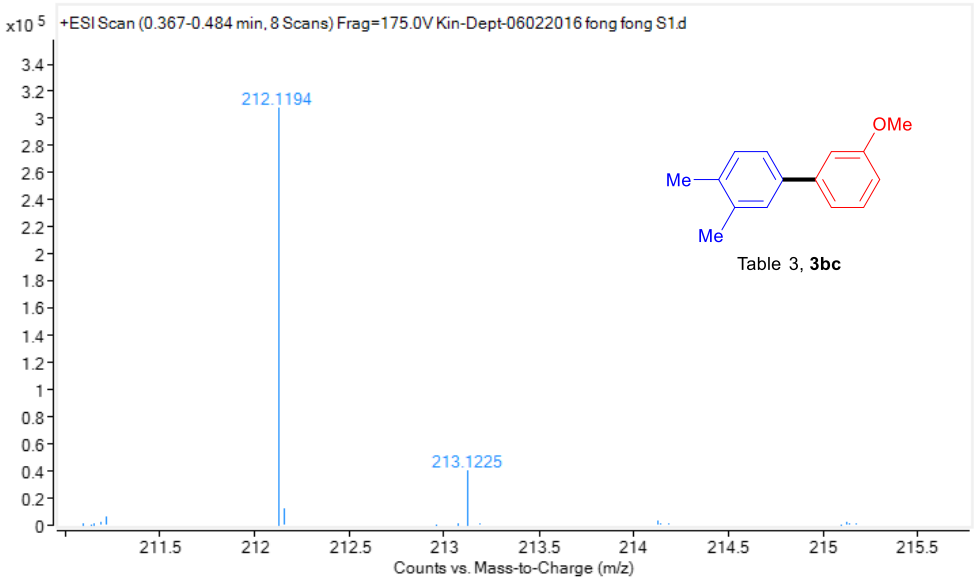



Table 3, **3bc**

| Mass | Calc. Mass | mDa | PPM | Formula |
|---|---|---|---|---|
| 212.1194 | 212.1196 | 0.2 | 0.8 | C15 H16 O |

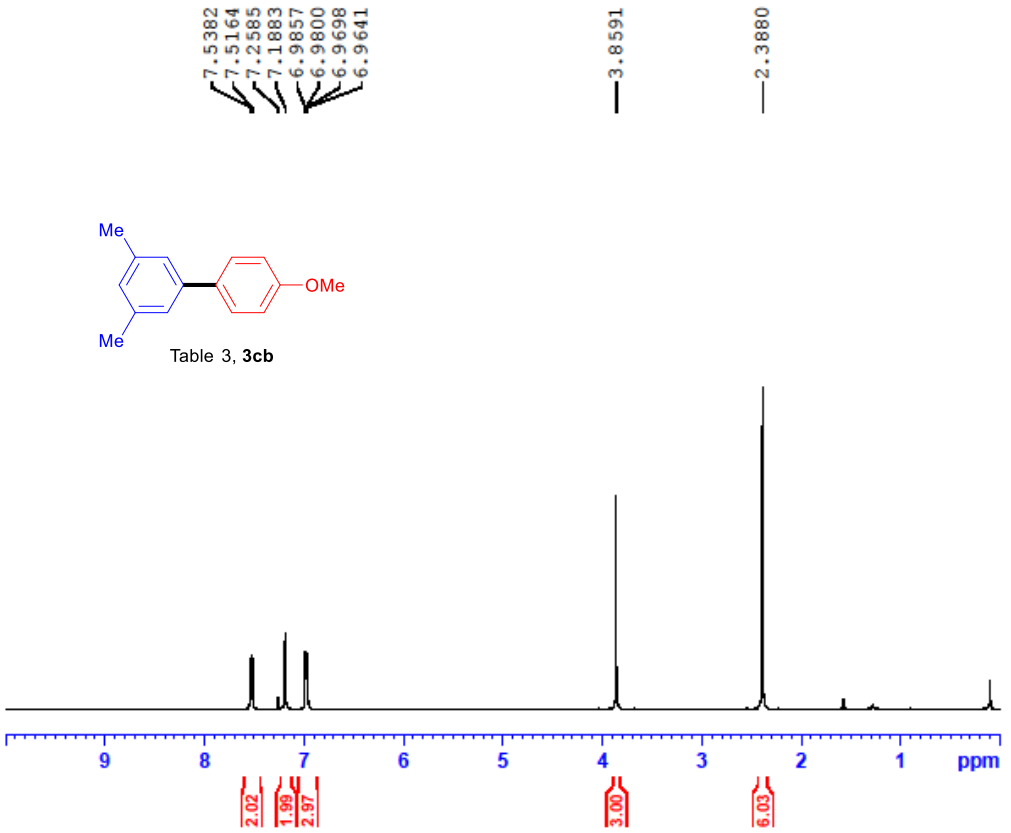



Table 3, **3cb**

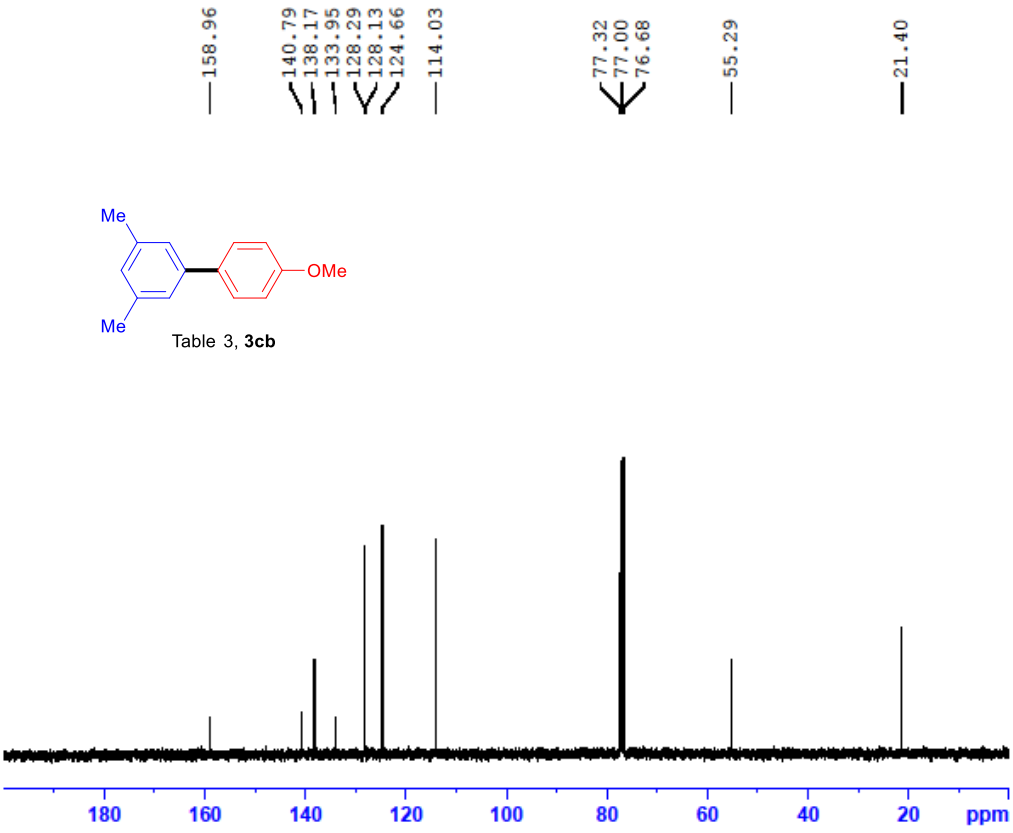



Table 3, **3cb**

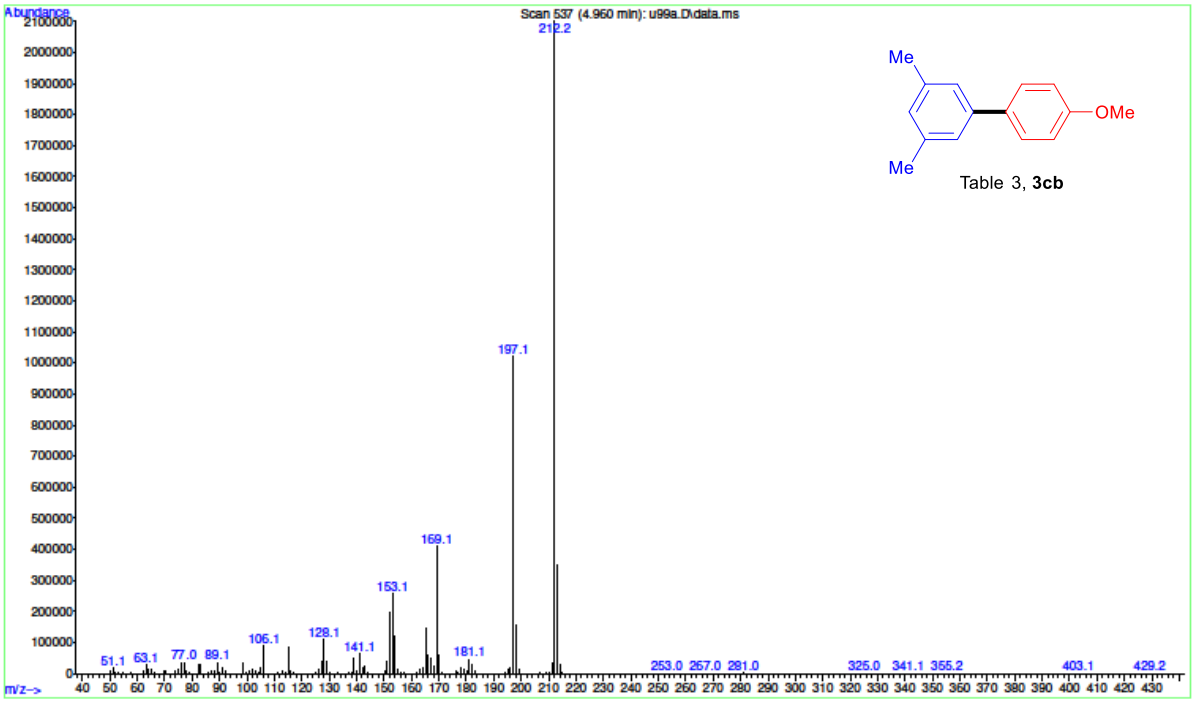

Abundance
Scan 537 (4.960 min): u99a.D\data.ms
212.2
197.1
169.1
153.1
128.1
106.1
141.1
181.1
51.1
63.1
77.0
89.1
253.0
267.0
281.0
325.0
341.1
355.2
403.1
429.2
m/z-->
Me
Me
OMe

Table 3, **3cb**

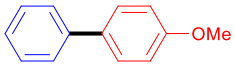
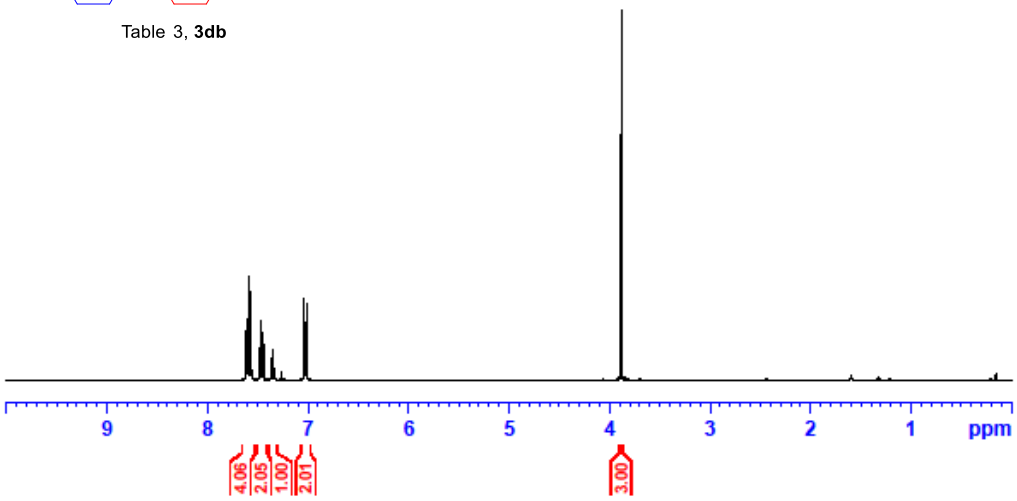




Table 3, **3db**





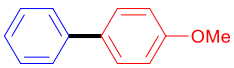
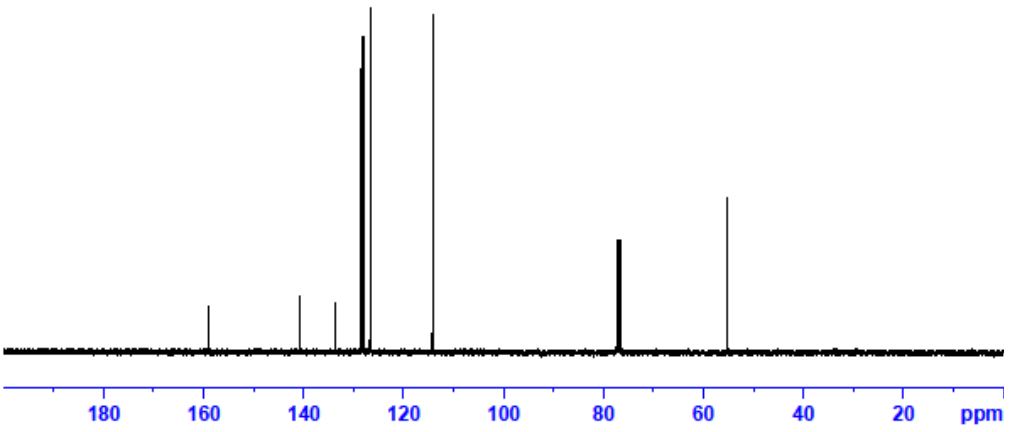



Table 3, **3db**



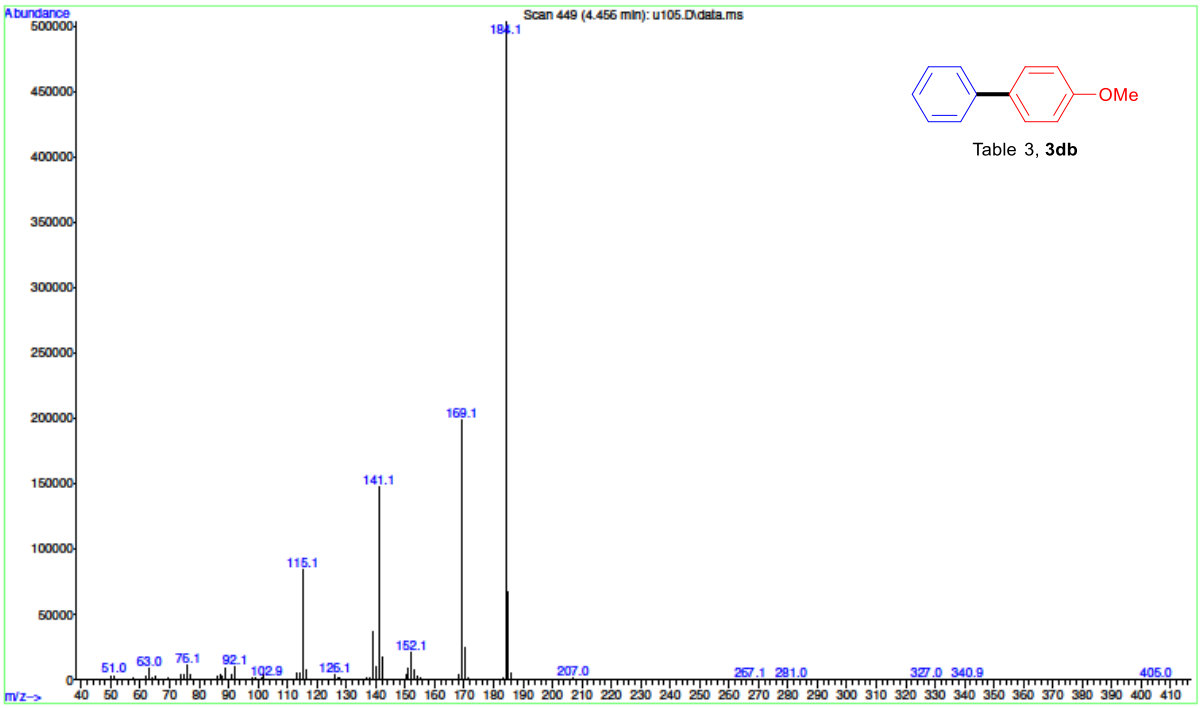
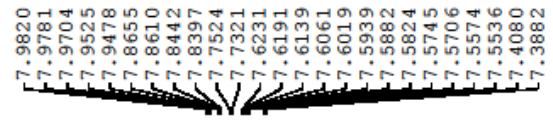
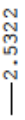

Abundance
Scan 449 (4.456 min): u105.D\data.ms
OMe
m/z-->
184.1
169.1
141.1
115.1
152.1
51.0
63.0
76.1
92.1
102.9
125.1
207.0
257.1
281.0
327.0
340.9
405.0

Table 3, **3db**



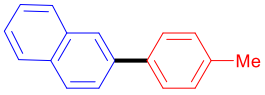
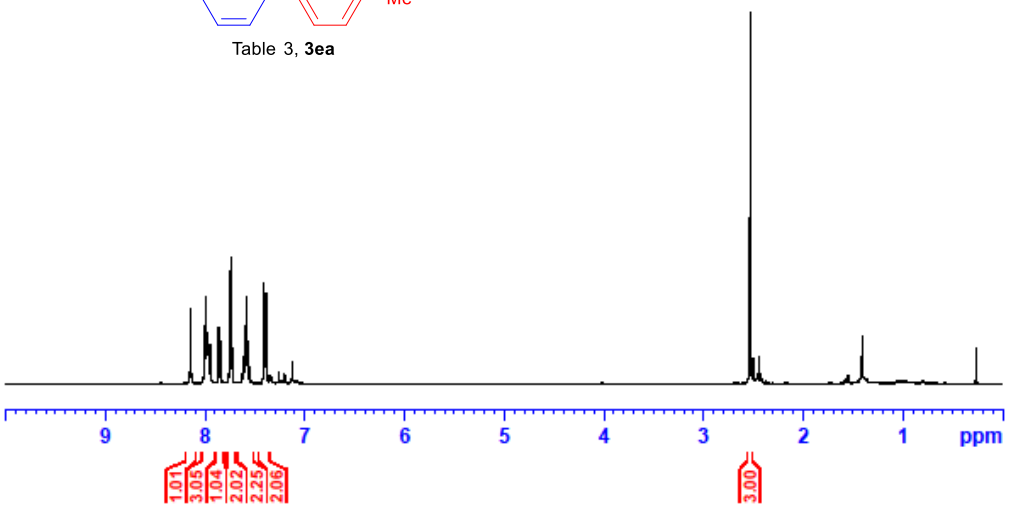
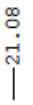




Table 3, **3ea**





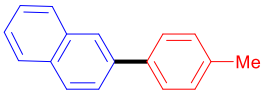
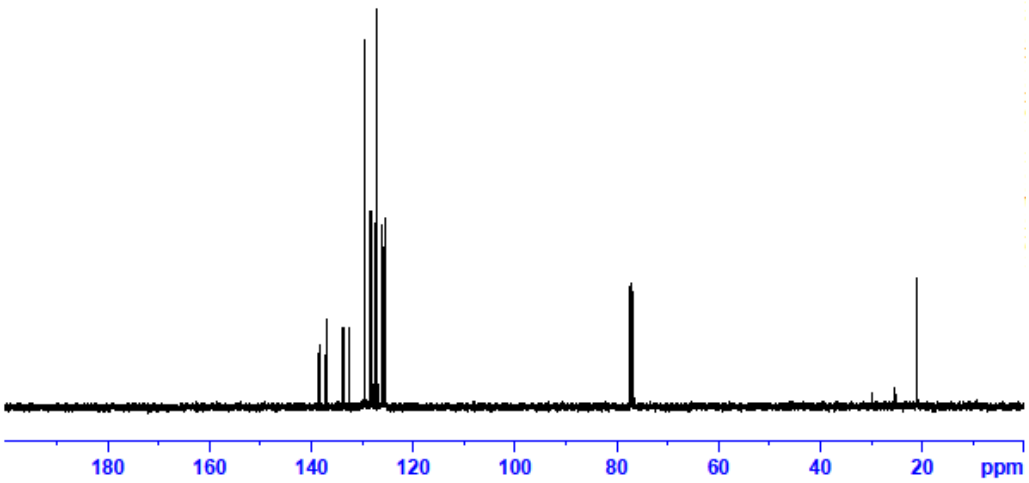
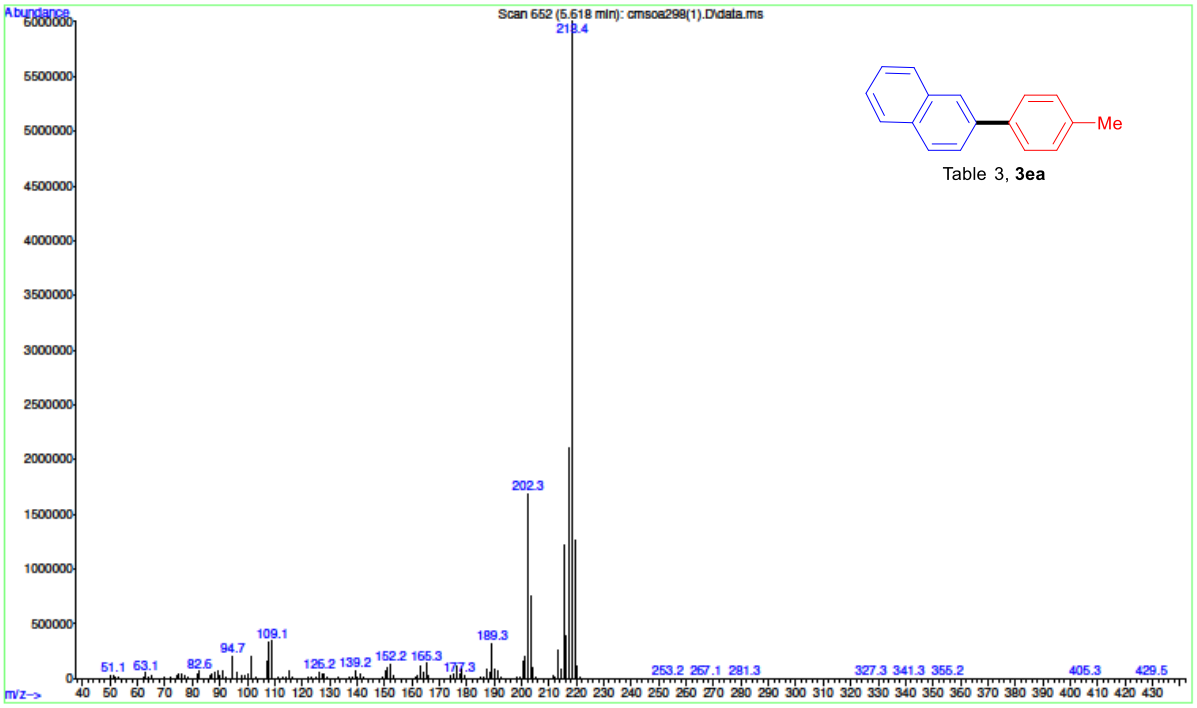




Table 3, **3ea**






Me

Table 3, **3ea**

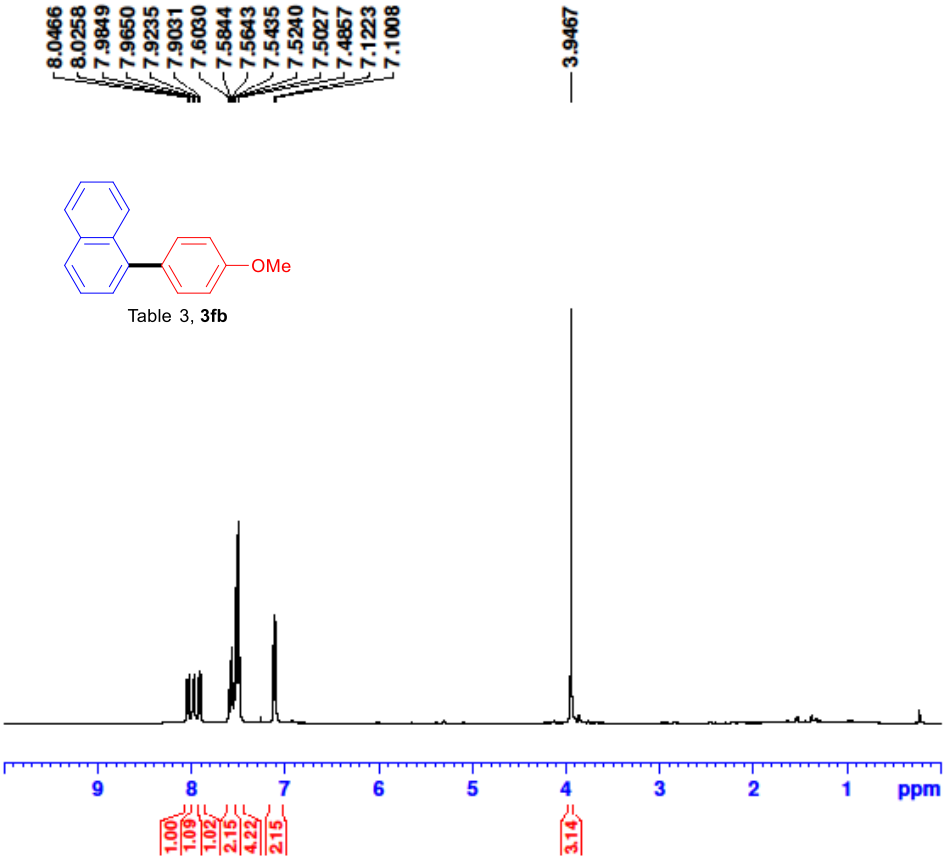
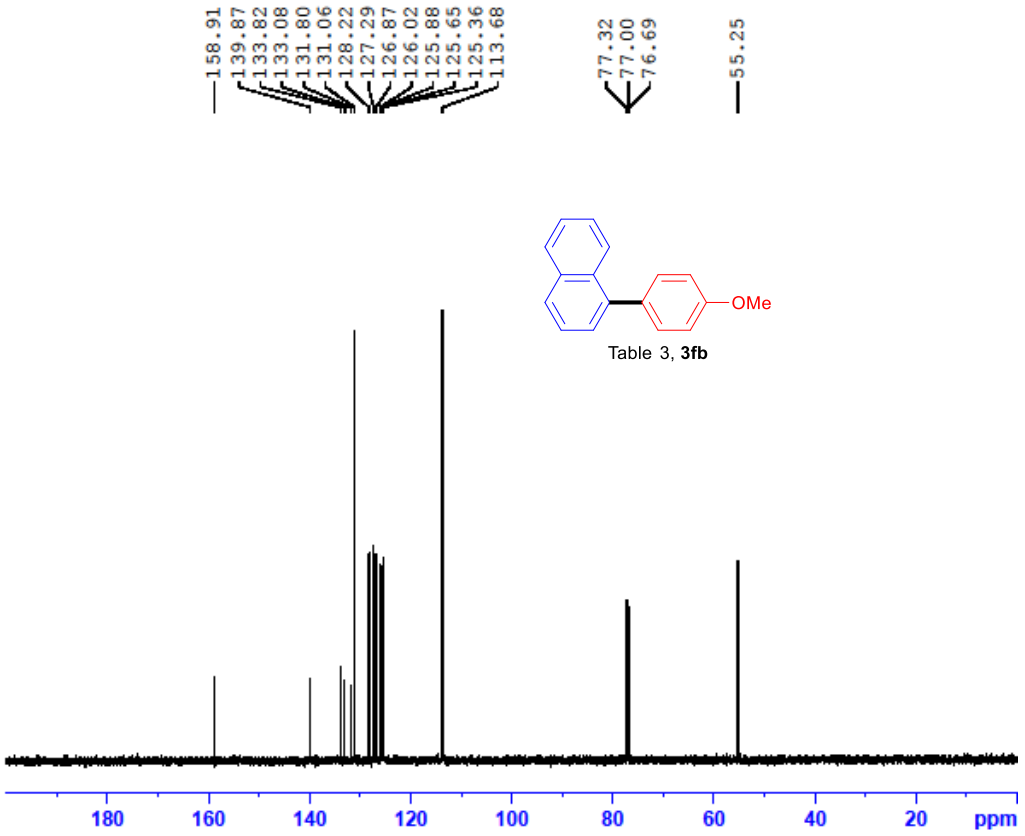
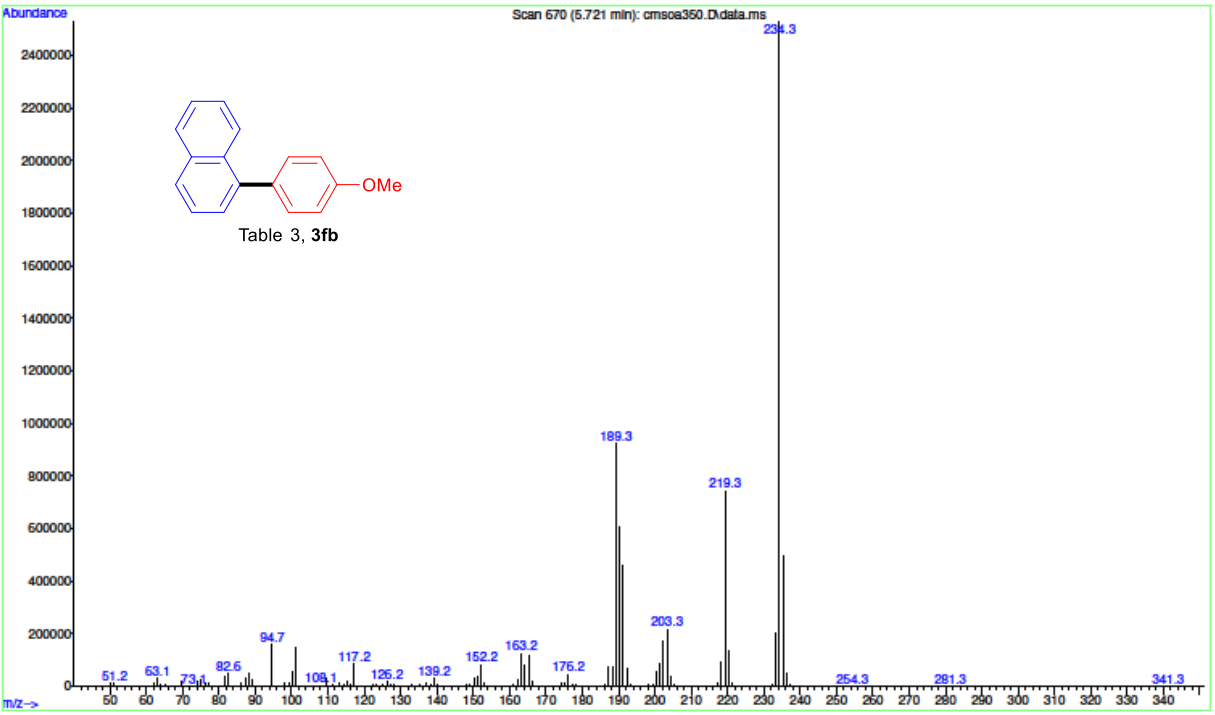
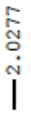

8.0466
8.0258
7.9849
7.9650
7.9235
7.9031
7.6030
7.5844
7.5643
7.5435
7.5240
7.5027
7.4857
7.1223
7.1008
3.9467
OMe
9
8
7
6
5
4
3
2
1
ppm
1.00
1.09
1.02
2.15
4.22
2.15
3.14

Table 3, **3fb**


158.91
139.87
133.82
133.08
131.80
131.06
128.22
127.29
126.87
126.02
125.88
125.65
125.36
113.68
77.32
77.00
76.69
55.25
OMe
Table 3, 3fb
180
160
140
120
100
80
60
40
20
ppm


Abundance
Scan 670 (5.721 min): cmsoa350.D\data.ms
OMe
Table 3, 3fb
m/z-->

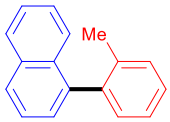
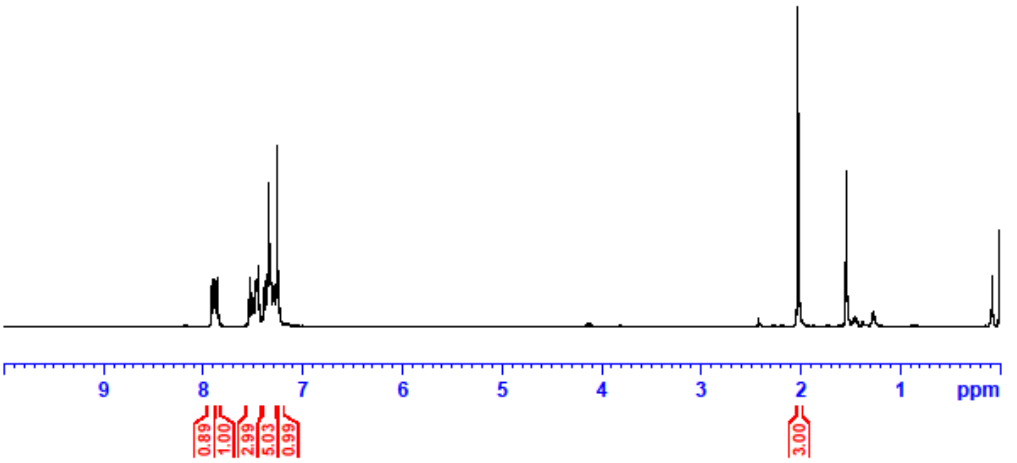
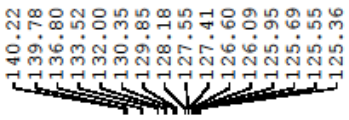




Table 3, **3fe**





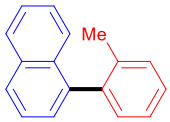
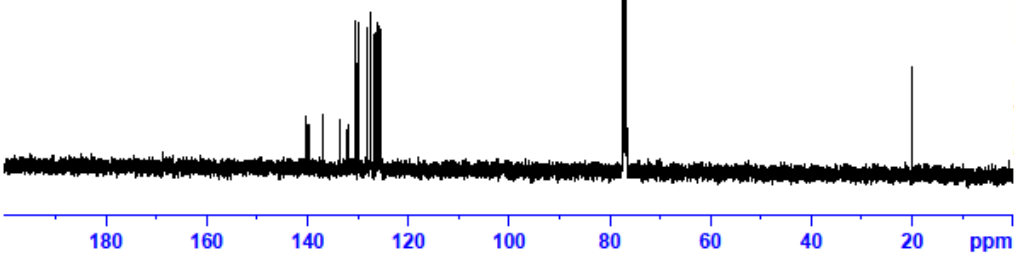
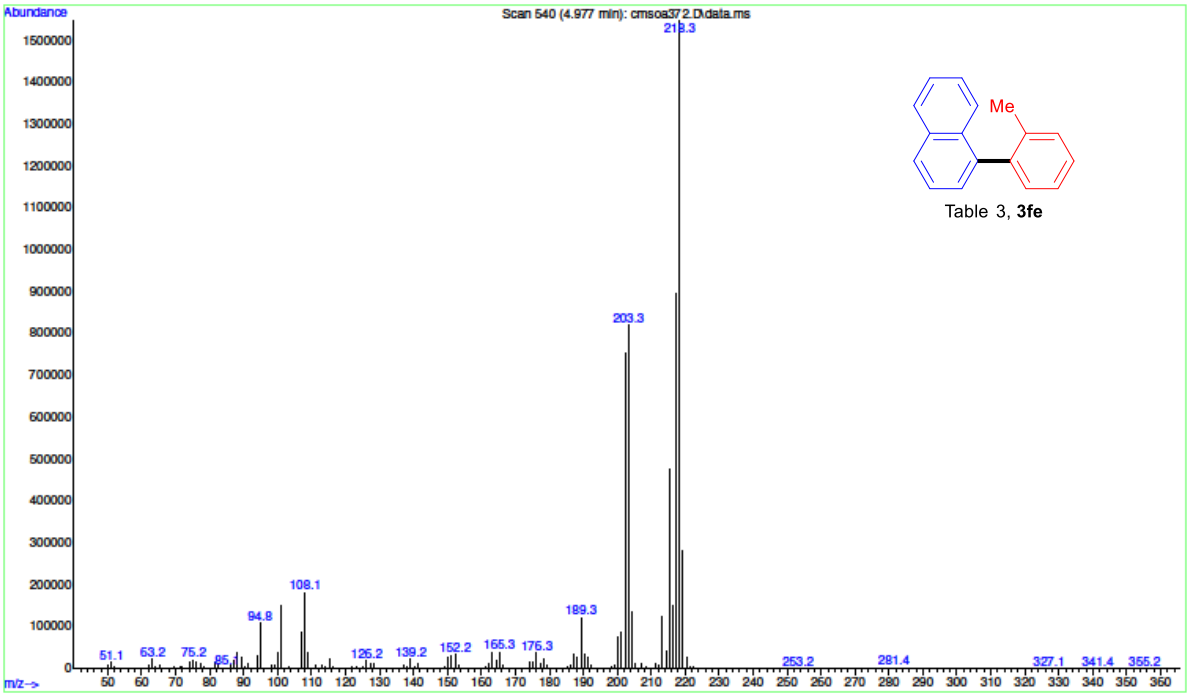




Table 3, **3fe**




Abundance
Scan 540 (4.977 min): cmsoa372.D\data.ms
219.3
203.3
108.1
94.8
189.3
51.1
63.2
75.2
85.1
125.2
139.2
152.2
155.3
176.3
253.2
281.4
327.1
341.4
355.2
m/z-->


Me

Table 3, **3fe**

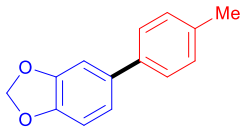
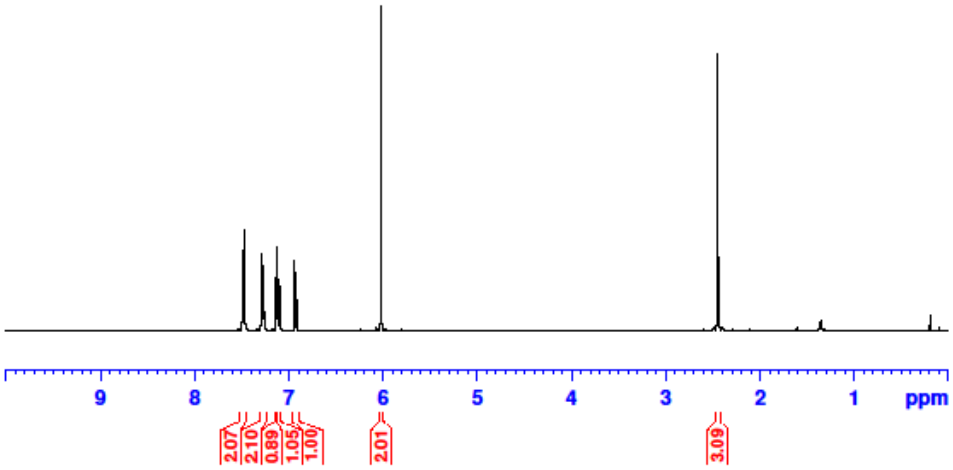
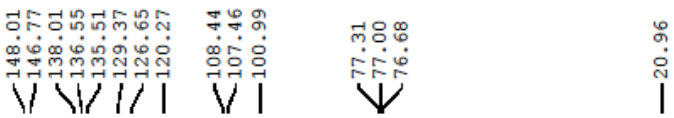




Table 3, **3ga**



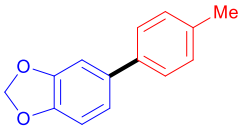
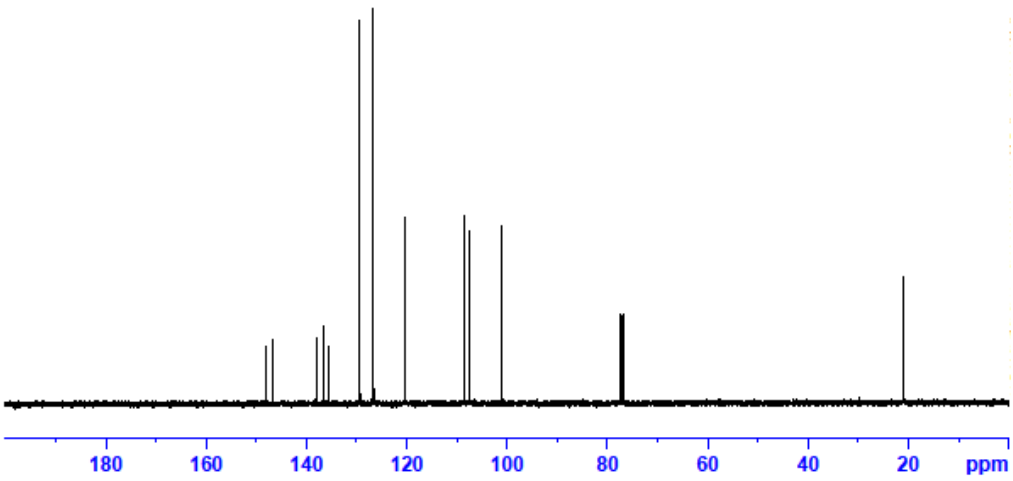




Table 3, **3ga**



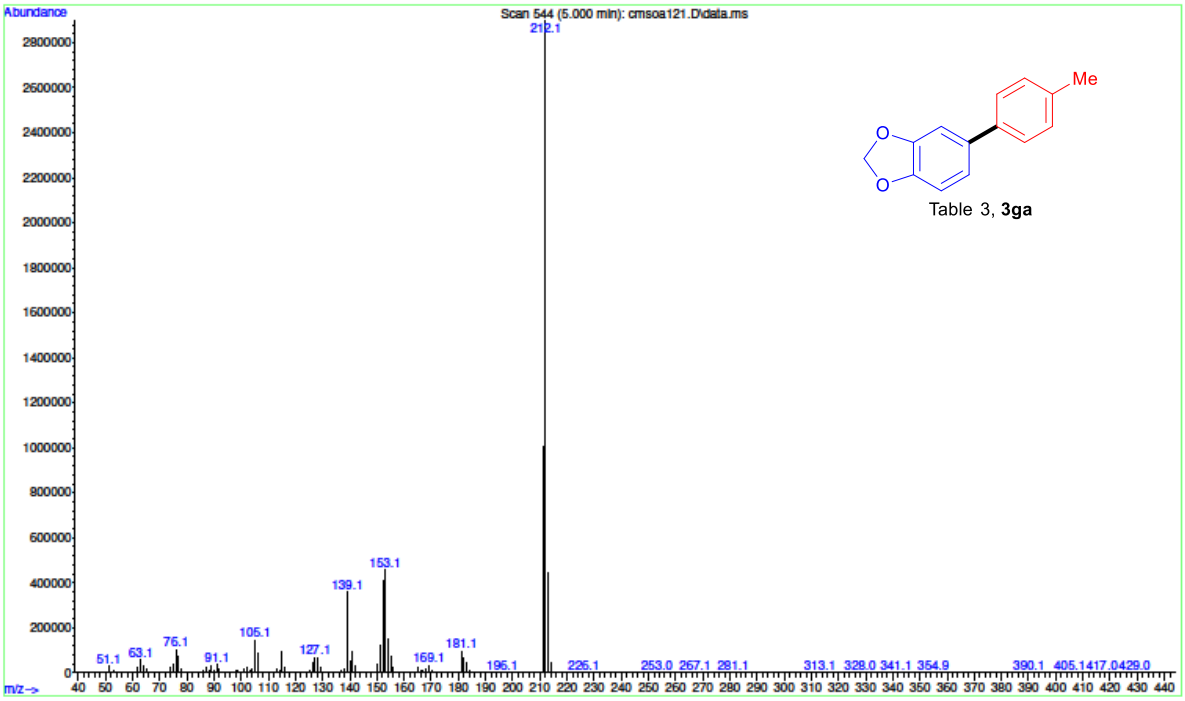

Abundance
Scan 544 (5.000 min): cmsoa121.D\data.ms
212.1
153.1
139.1
105.1
76.1
63.1
51.1
91.1
127.1
169.1
181.1
196.1
226.1
253.0
257.1
281.1
313.1
328.0
341.1
354.9
390.1
405.1
417.0
429.0
m/z-->
Me
O
O

Table 3, **3ga**

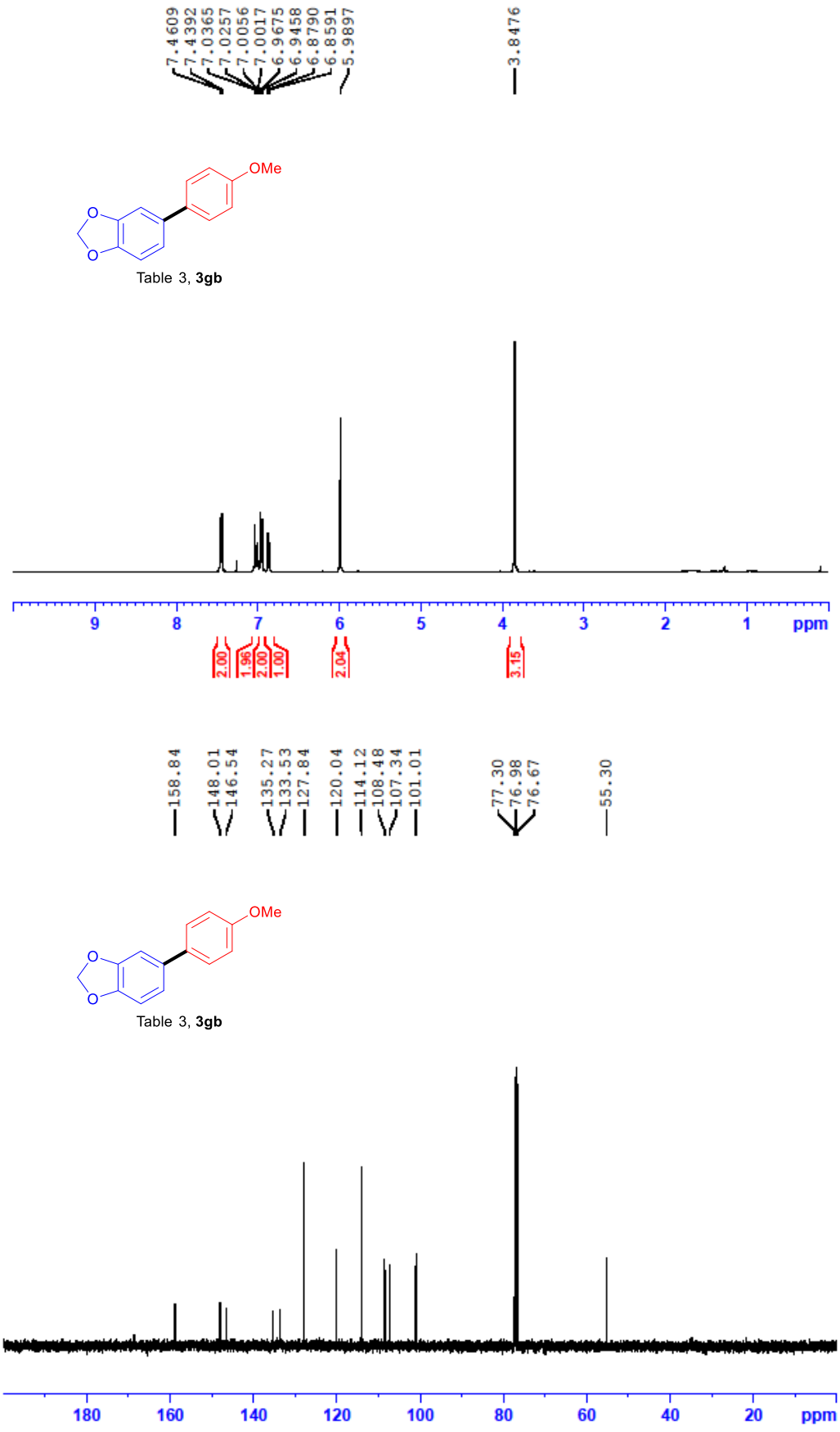



Table 3, **3gb**

Table 3, **3gb**

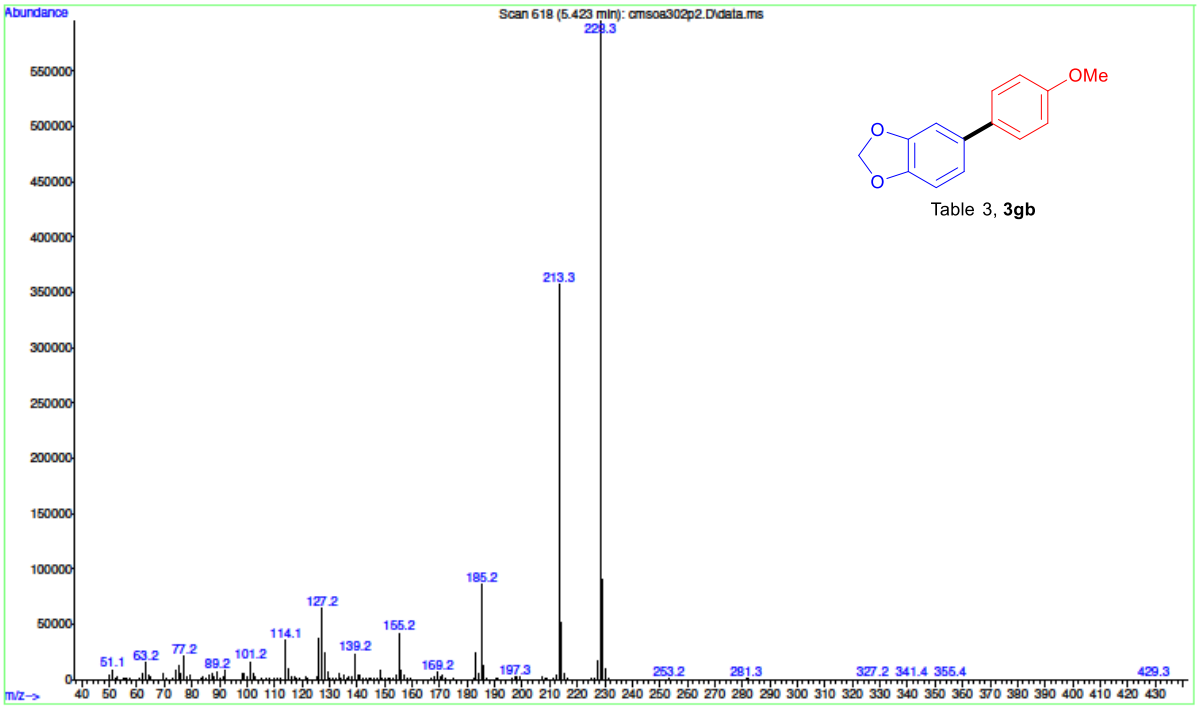
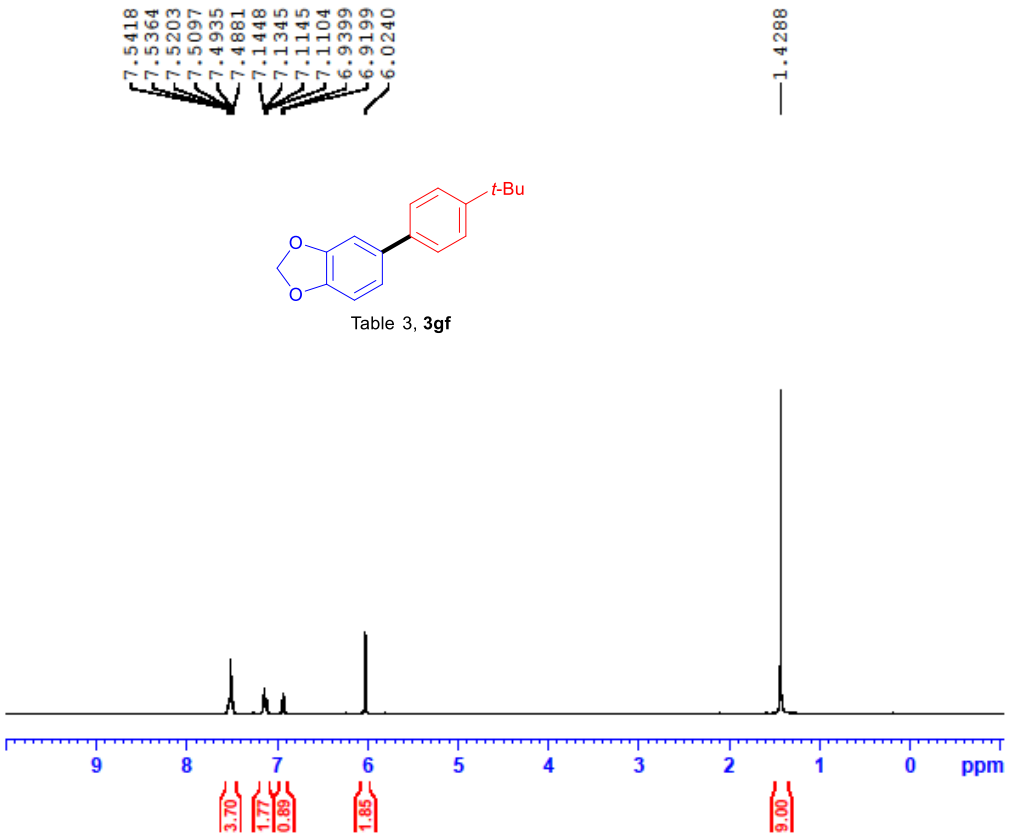
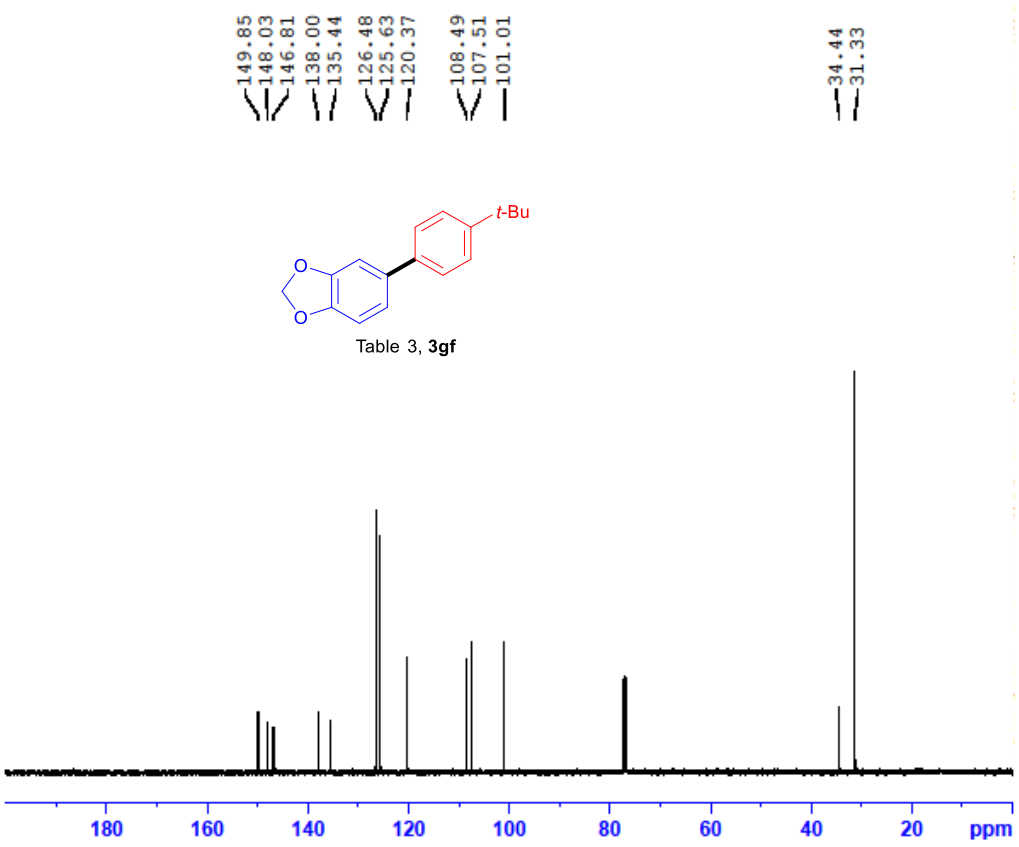

Abundance
Scan 618 (5.423 min): cmsoa302p2.D\data.ms
228.3
213.3
185.2
127.2
155.2
114.1
139.2
77.2
63.2
51.1
89.2
101.2
169.2
197.3
253.2
281.3
327.2
341.4
355.4
429.3
m/z-->
OMe
O
O

Table 3, **3gb**


7.5418
7.5364
7.5203
7.5097
7.4935
7.4881
7.1448
7.1345
7.1145
7.1104
6.9399
6.9199
6.0240
1.4288
t-Bu
O
O
Table 3, 3gf
9
8
7
6
5
4
3
2
1
0
ppm
3.70
1.77
0.89
1.85
9.00


149.85
148.03
146.81
138.00
135.44
126.48
125.63
120.37
108.49
107.51
101.01
34.44
31.33
t-Bu
O
O
Table 3, 3gf
180
160
140
120
100
80
60
40
20
ppm

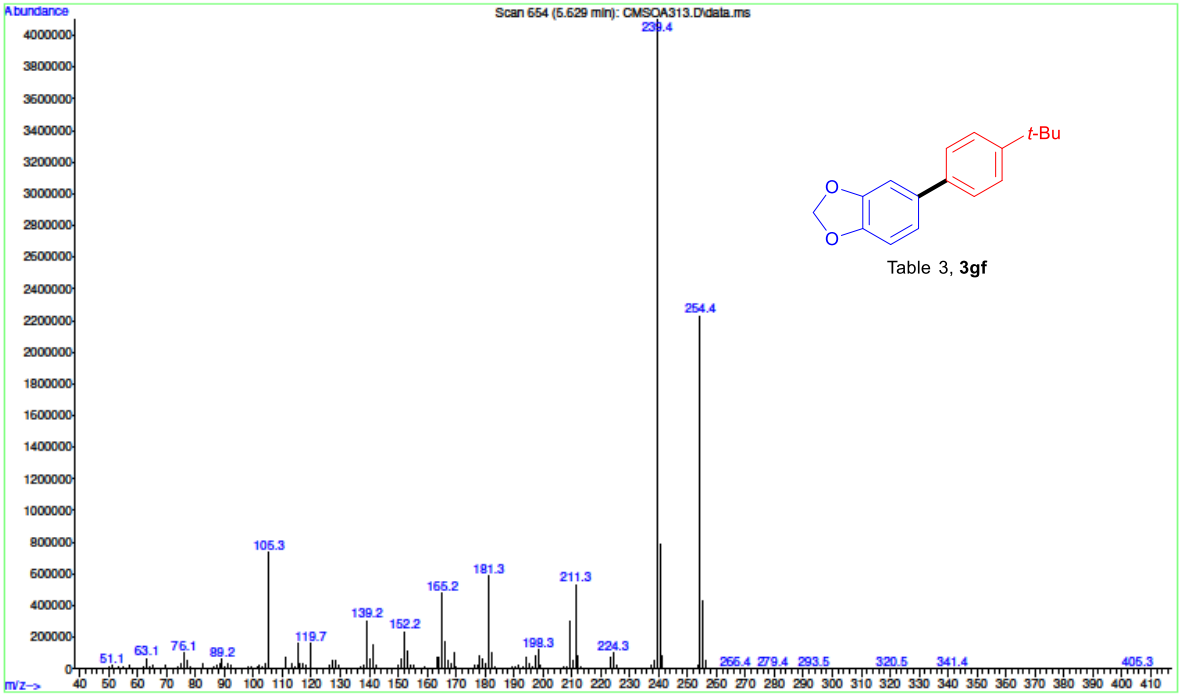






Table 3, **3gf**

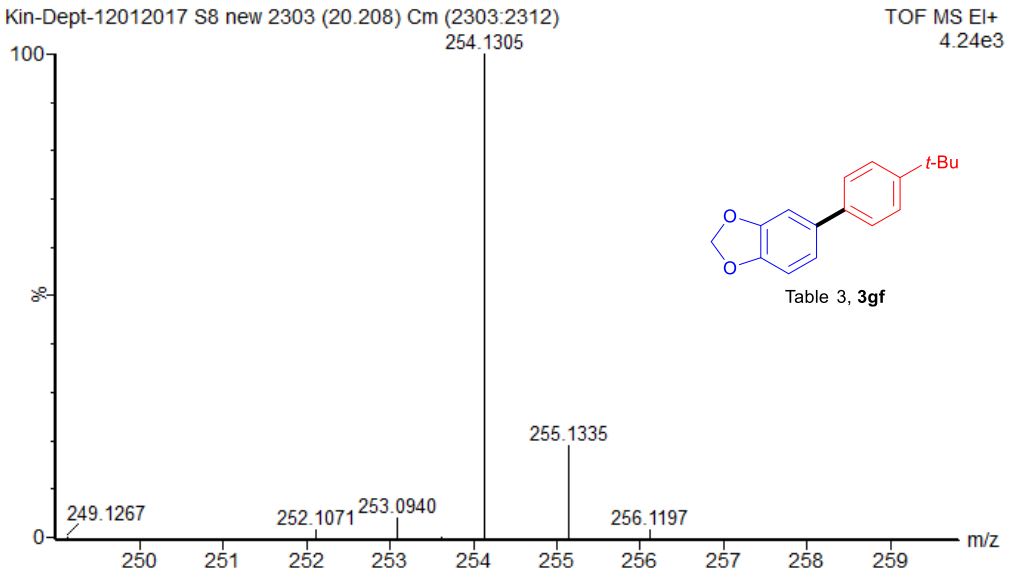
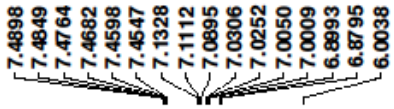






Table 3, **3gf**

| Mass | Calc. Mass | mDa | PPM | Formula |
|---|---|---|---|---|
| 254.1305 | 254.1307 | -0.2 | -0.8 | C17 H18 O2 |



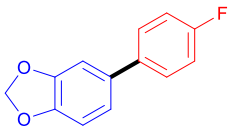
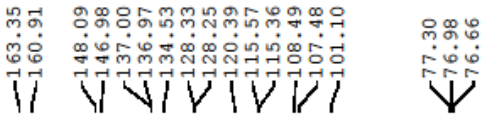




Table 3, **3gd**



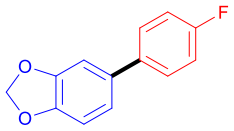
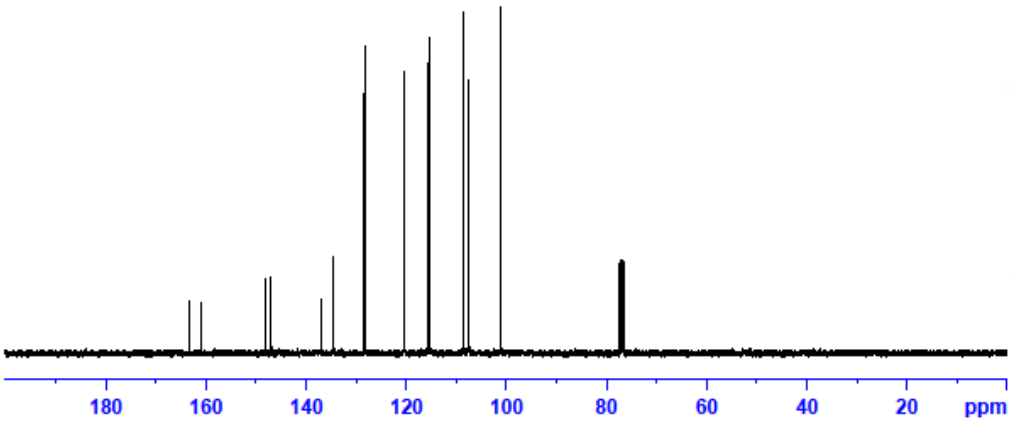




Table 3, **3gd**



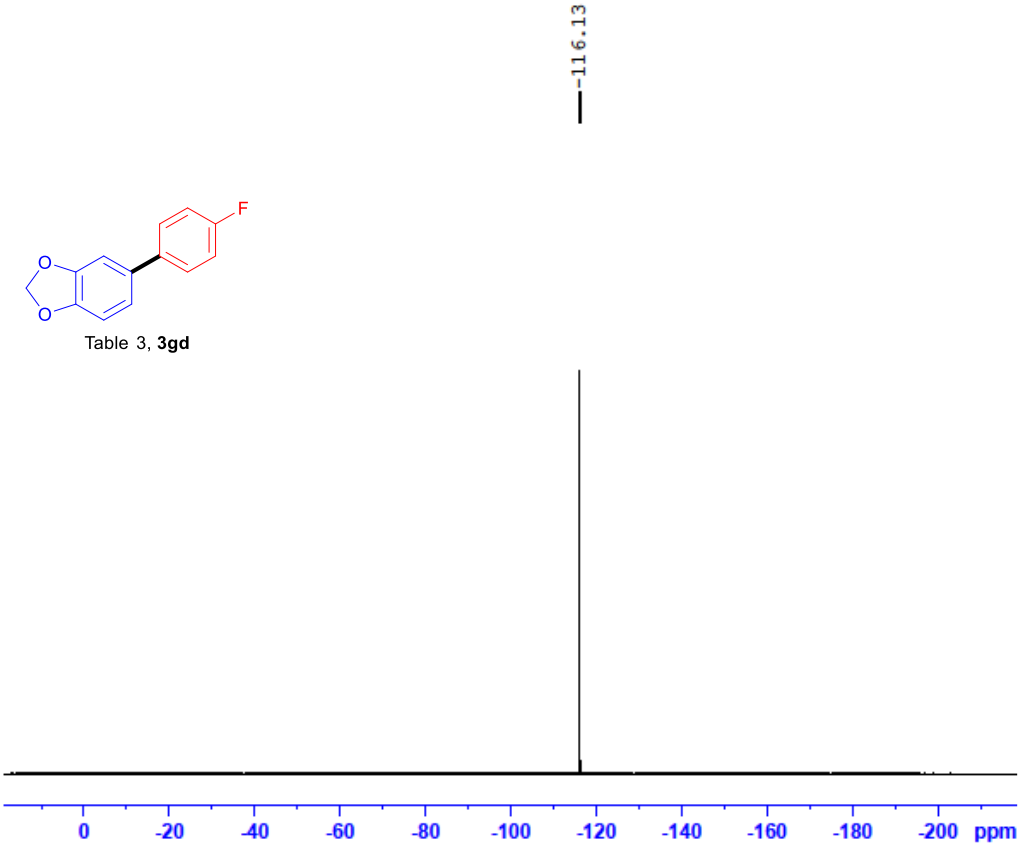



Table 3, **3gd**

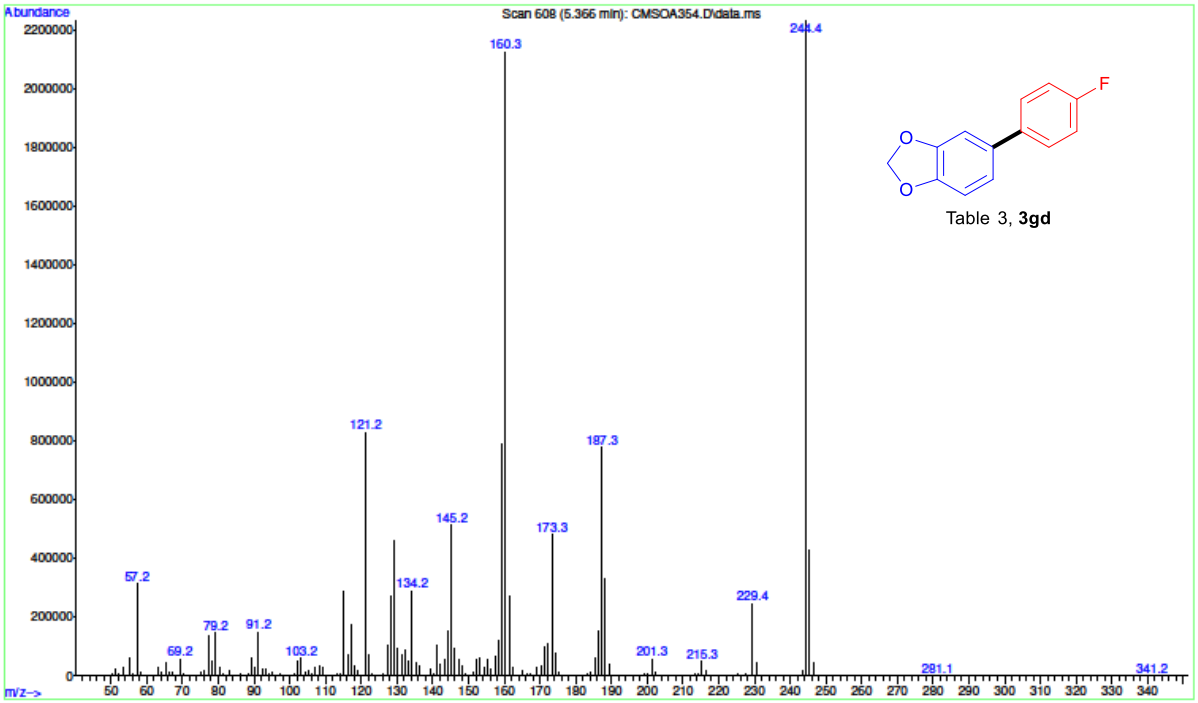



Table 3, **3gd**

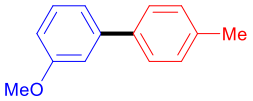
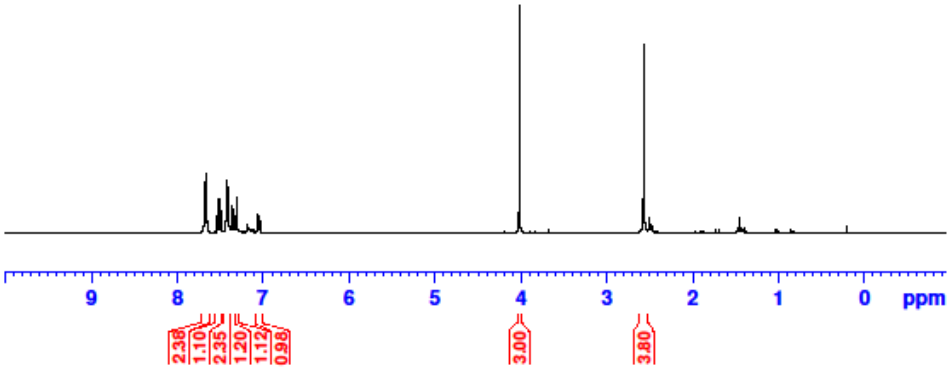
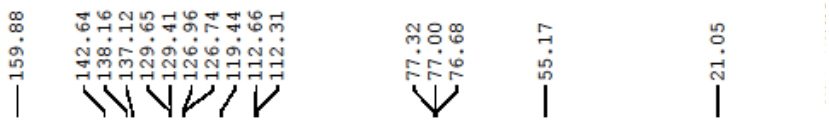




Table 3, **3ha**



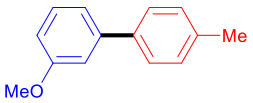
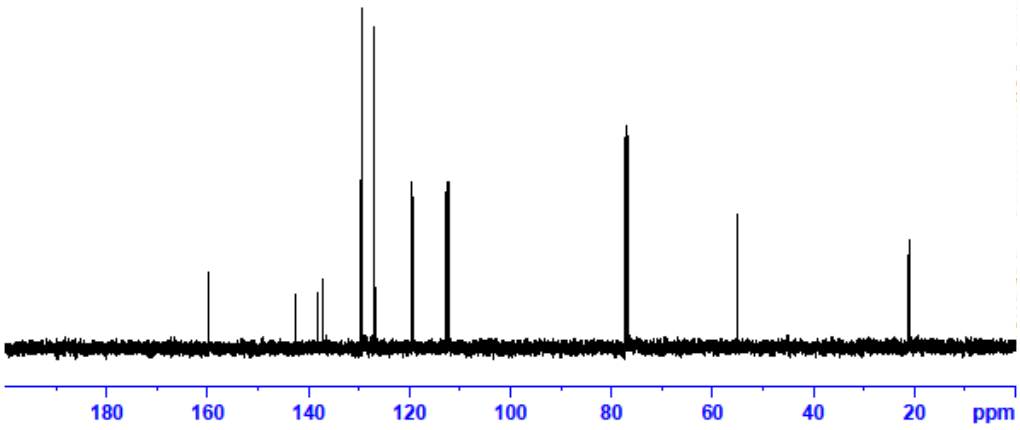
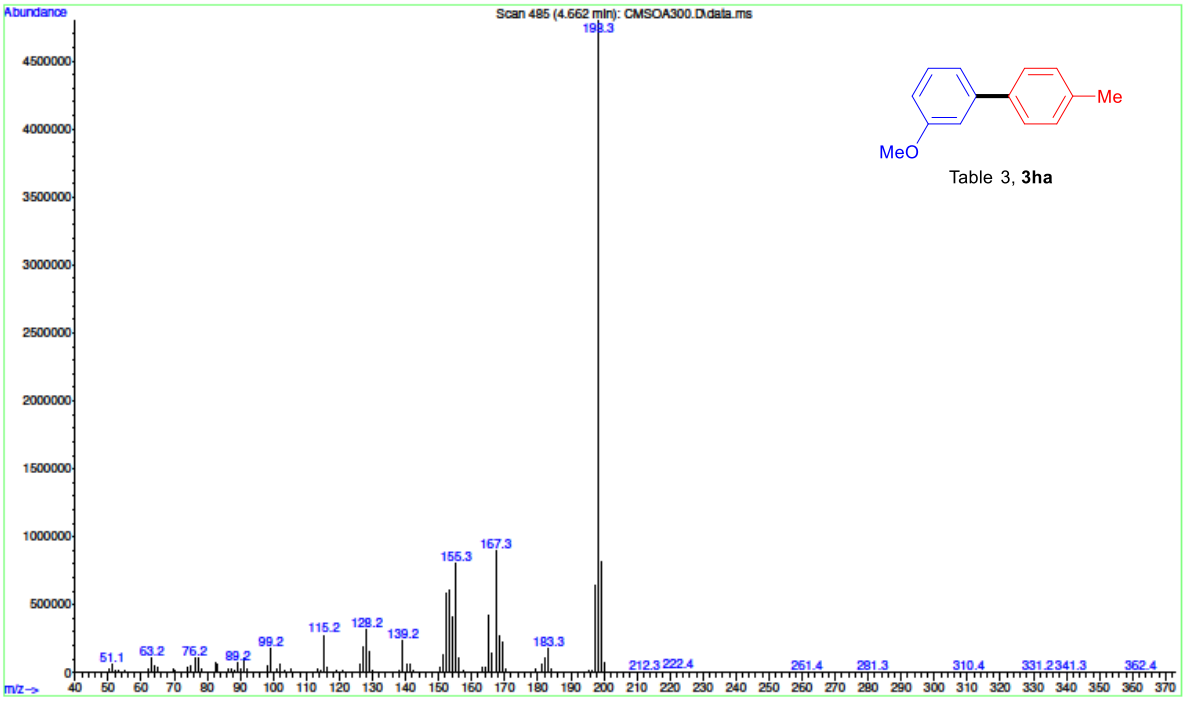




Table 3, **3ha**

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198.3
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
m/z-->
155.3
167.3
115.2
128.2
139.2
99.2
183.3
51.1
63.2
76.2
89.2
212.3
222.4
251.4
281.3
310.4
331.2
341.3
352.4
Me
MeO

Table 3, **3ha**

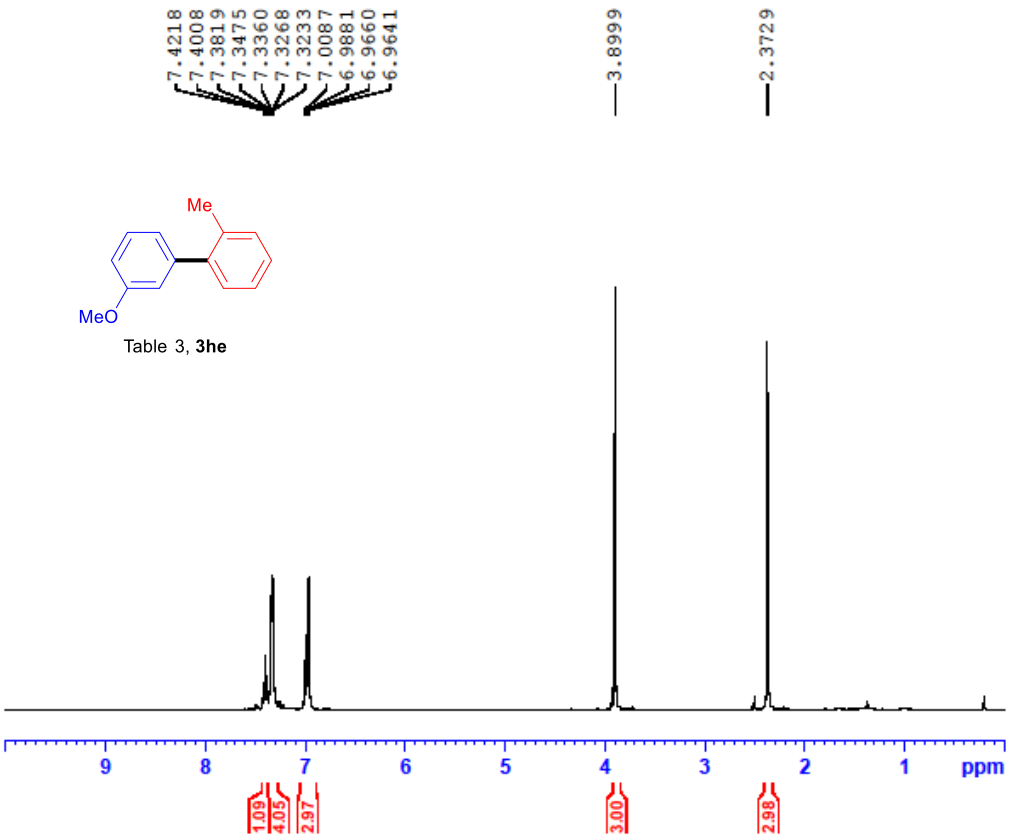



Table 3, **3he**

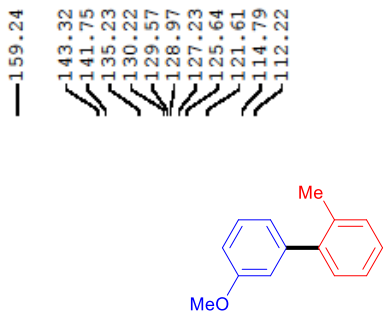
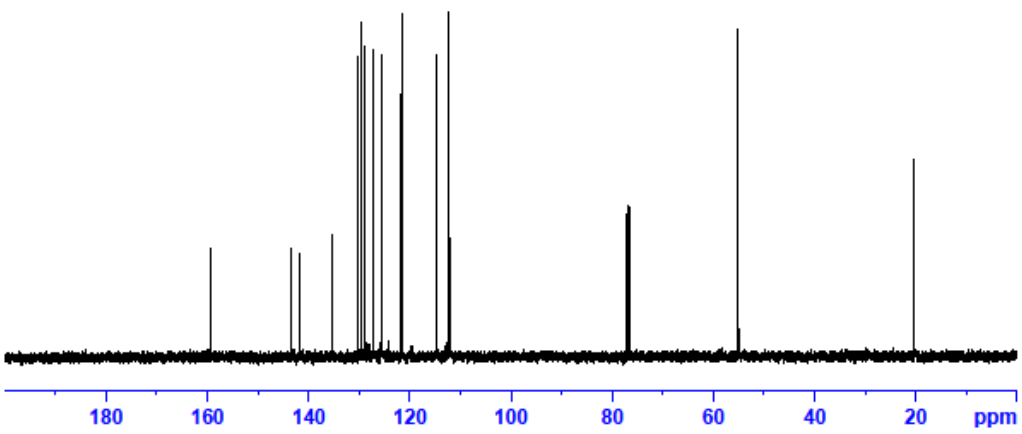



Table 3, **3he**



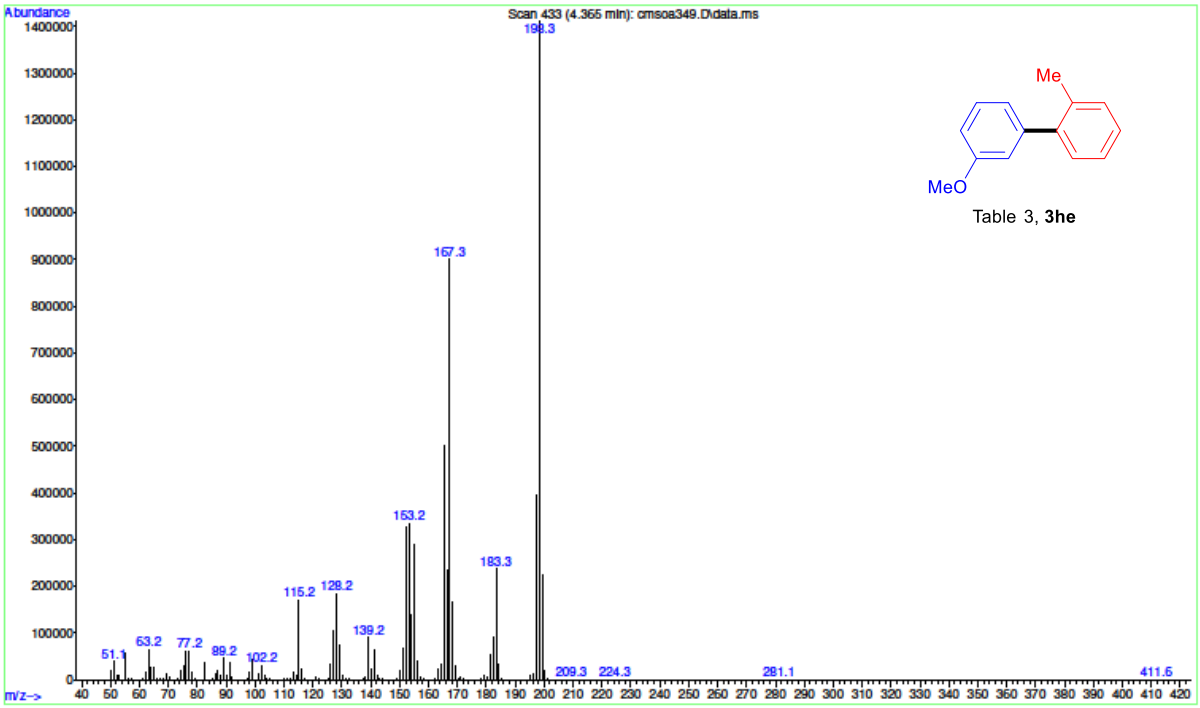

Abundance
Scan 433 (4.365 min): cmsoa349.D\data.ms
198.3
167.3
153.2
183.3
115.2
128.2
139.2
63.2
77.2
89.2
102.2
51.1
209.3
224.3
281.1
411.6
m/z-->
Me
MeO

Table 3, **3he**

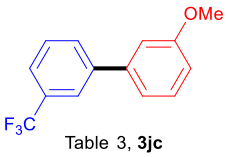
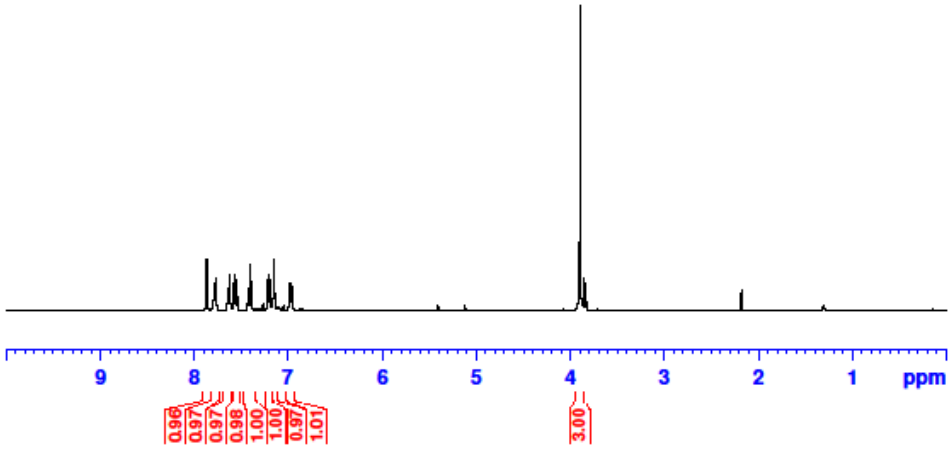




Table 3, **3jc**





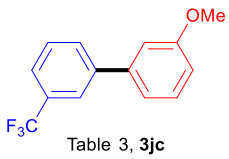
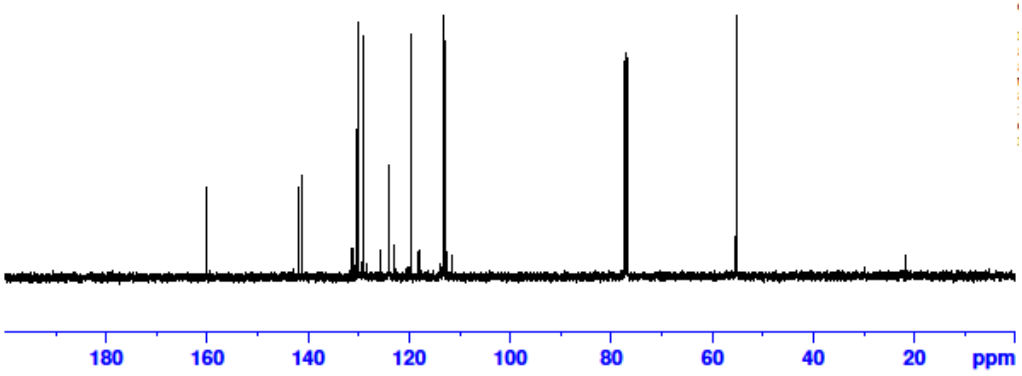



Table 3, **3jc**



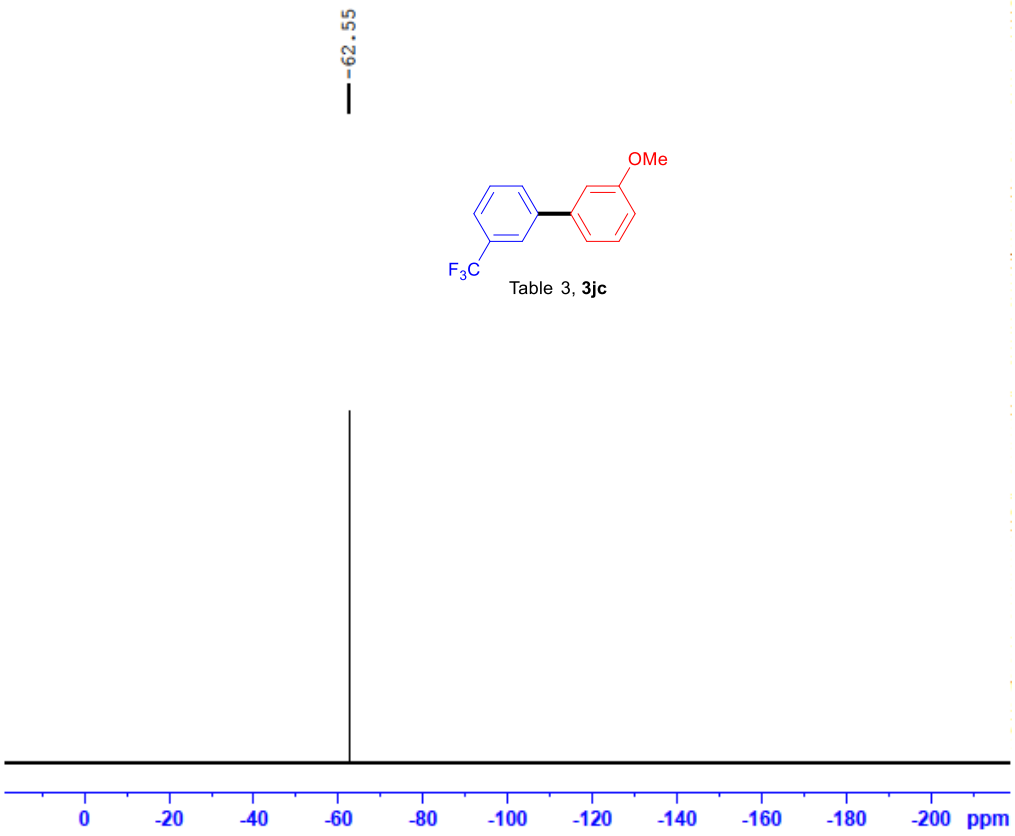



Table 3, **3jc**

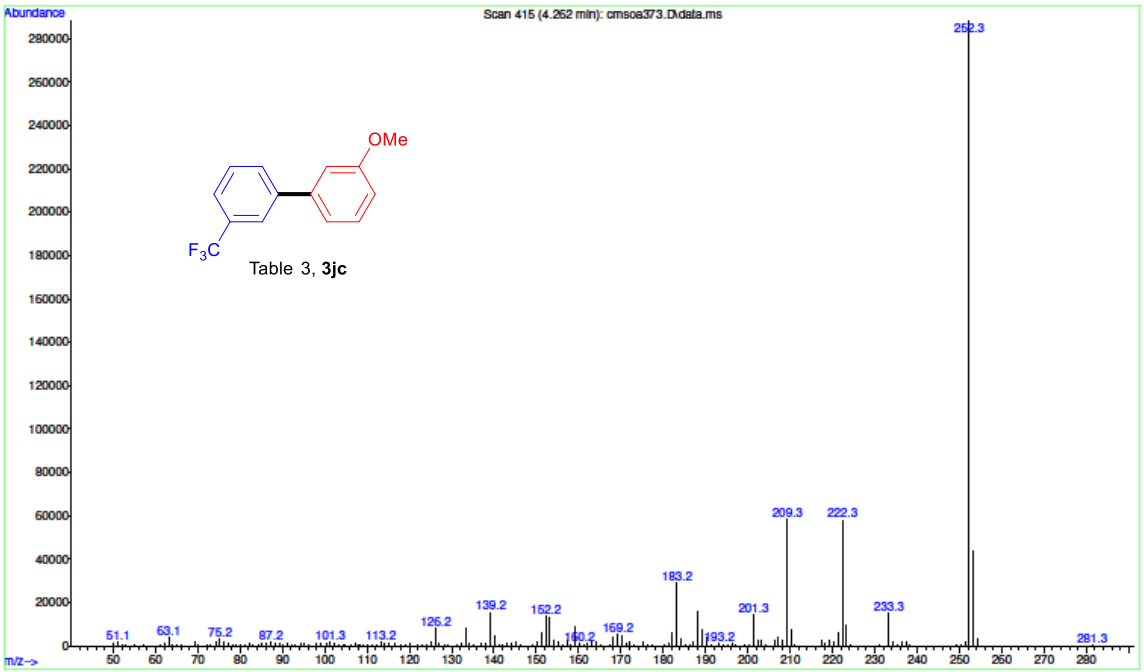
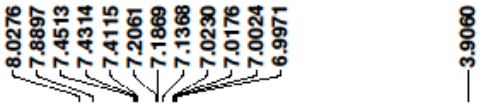



Table 3, **3jc**



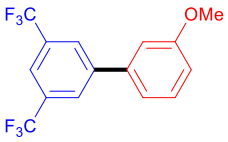
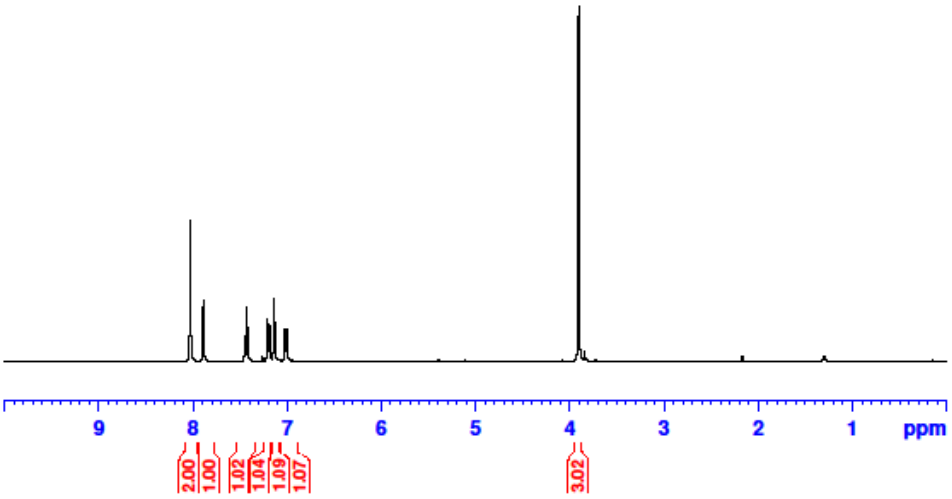
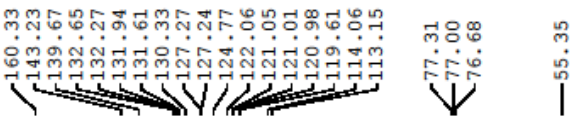




Table 3, **3kc**



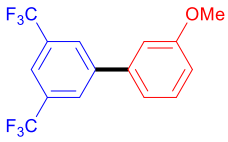
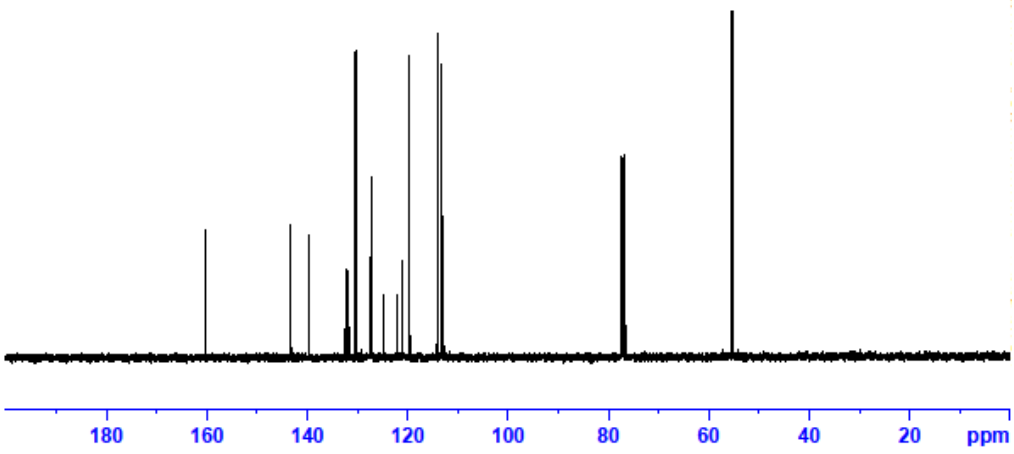




Table 3, **3kc**



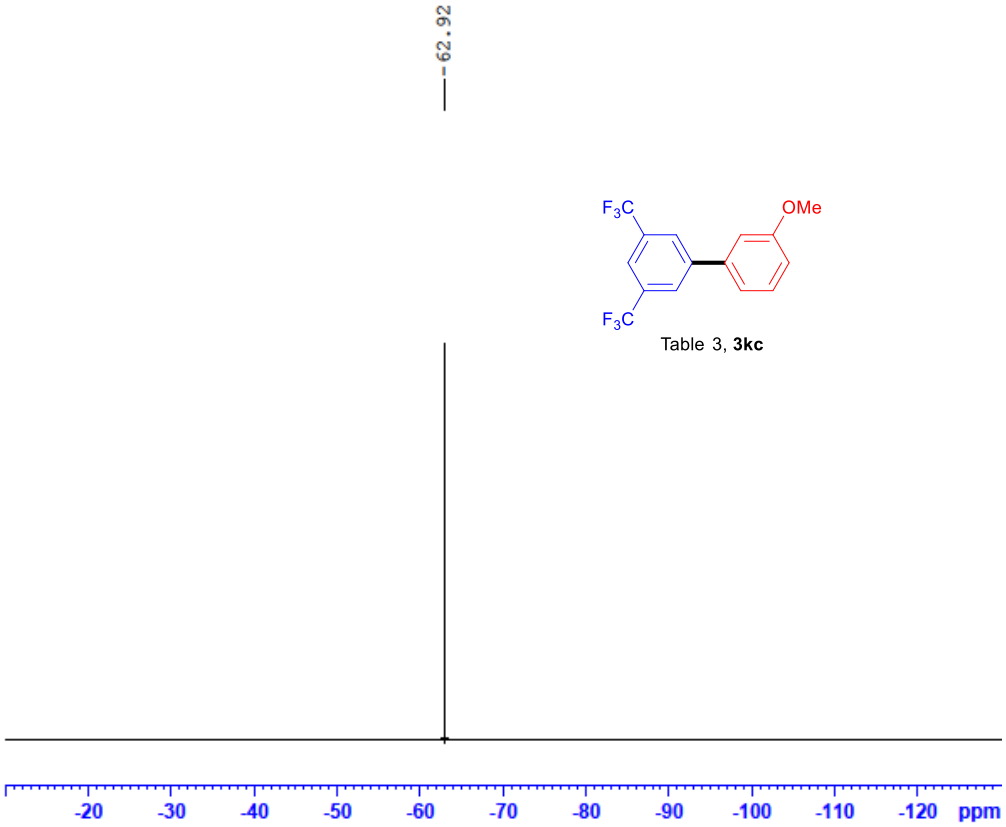



Table 3, **3kc**

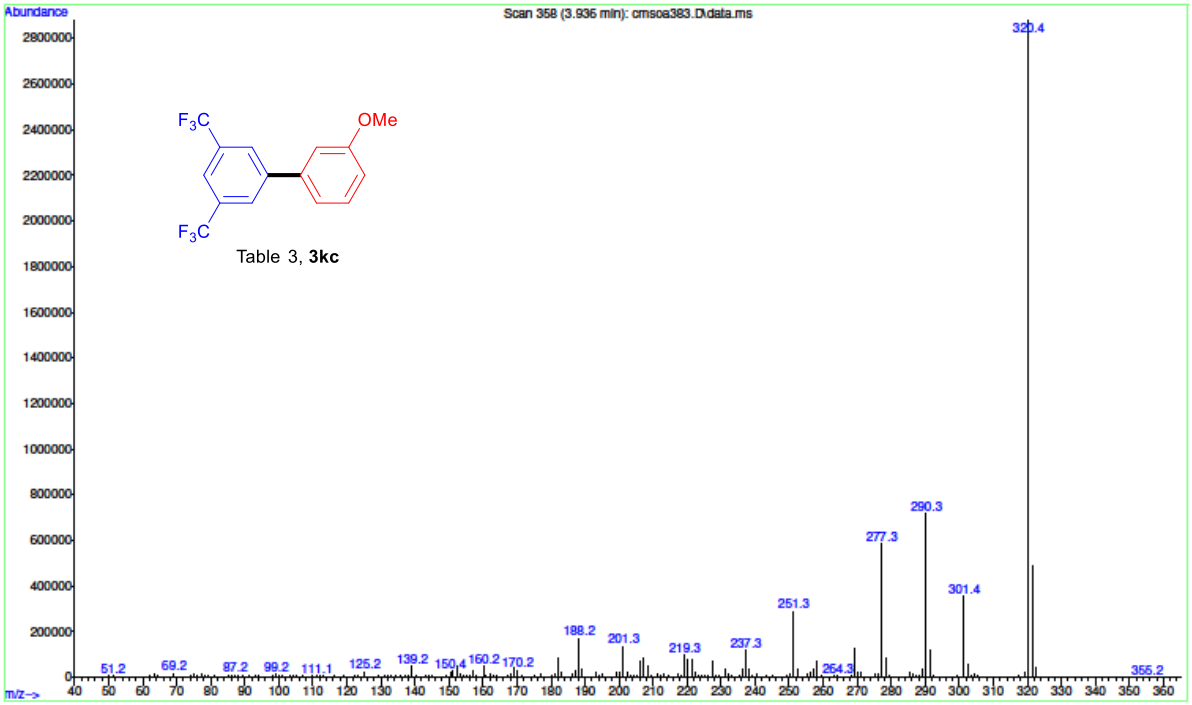



Table 3, **3kc**

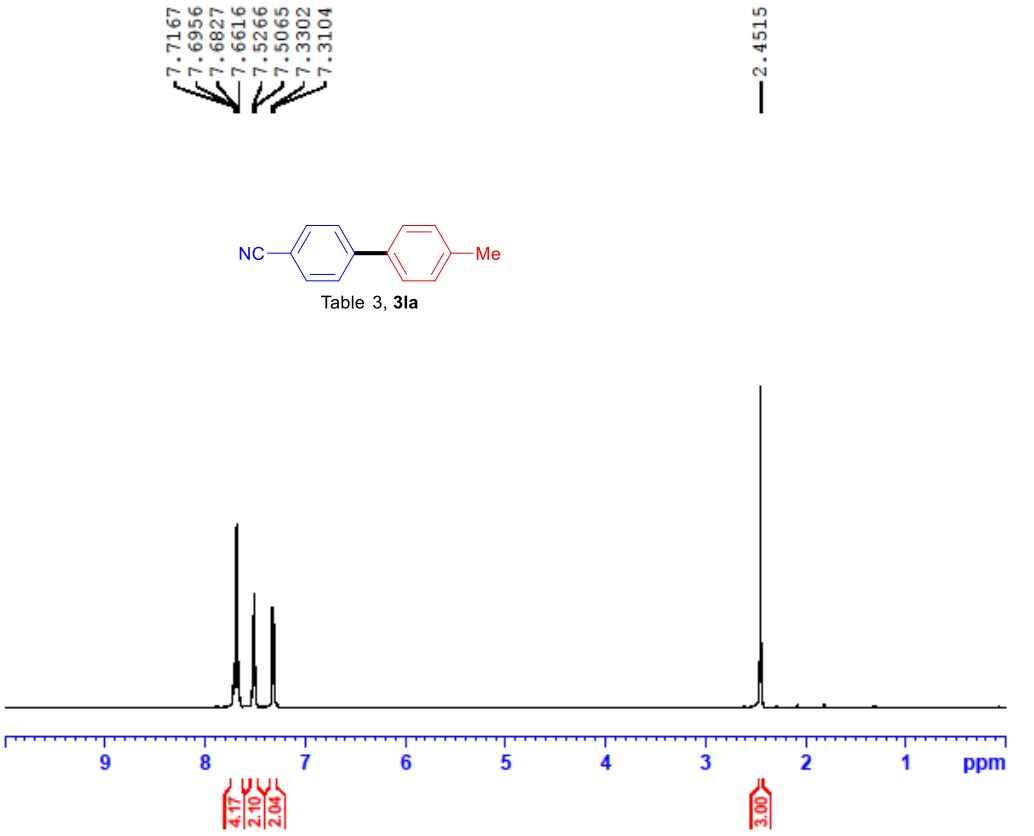



Table 3, **3la**

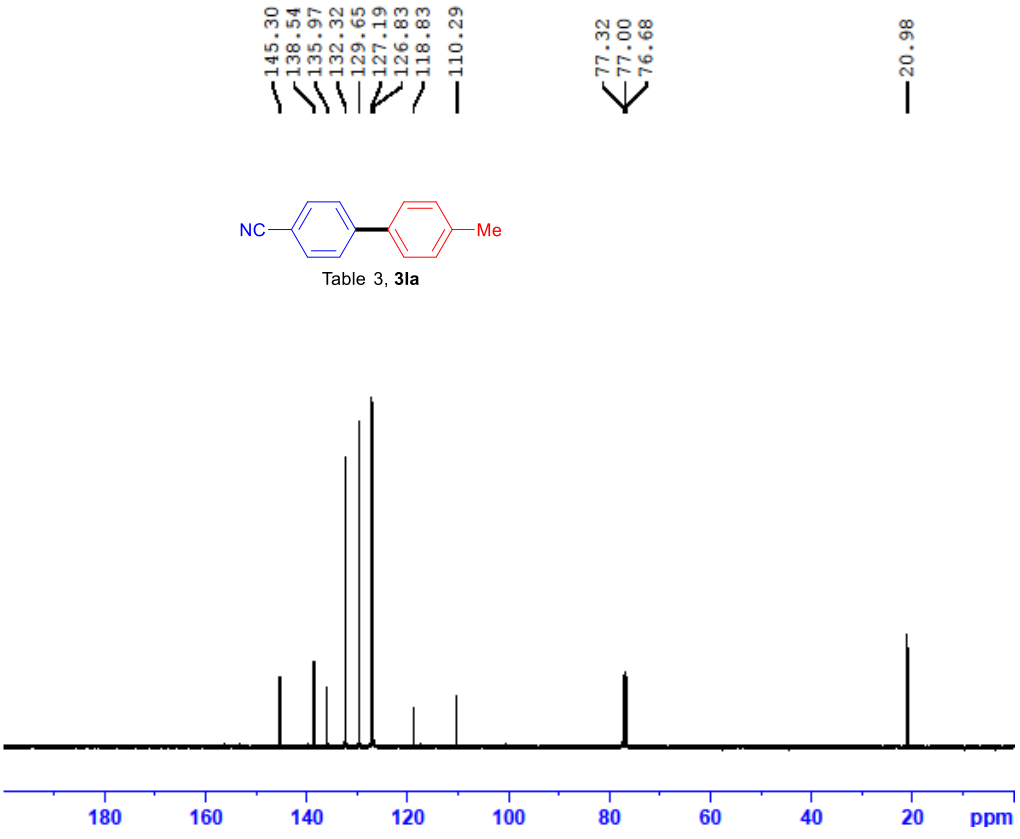



Table 3, **3la**

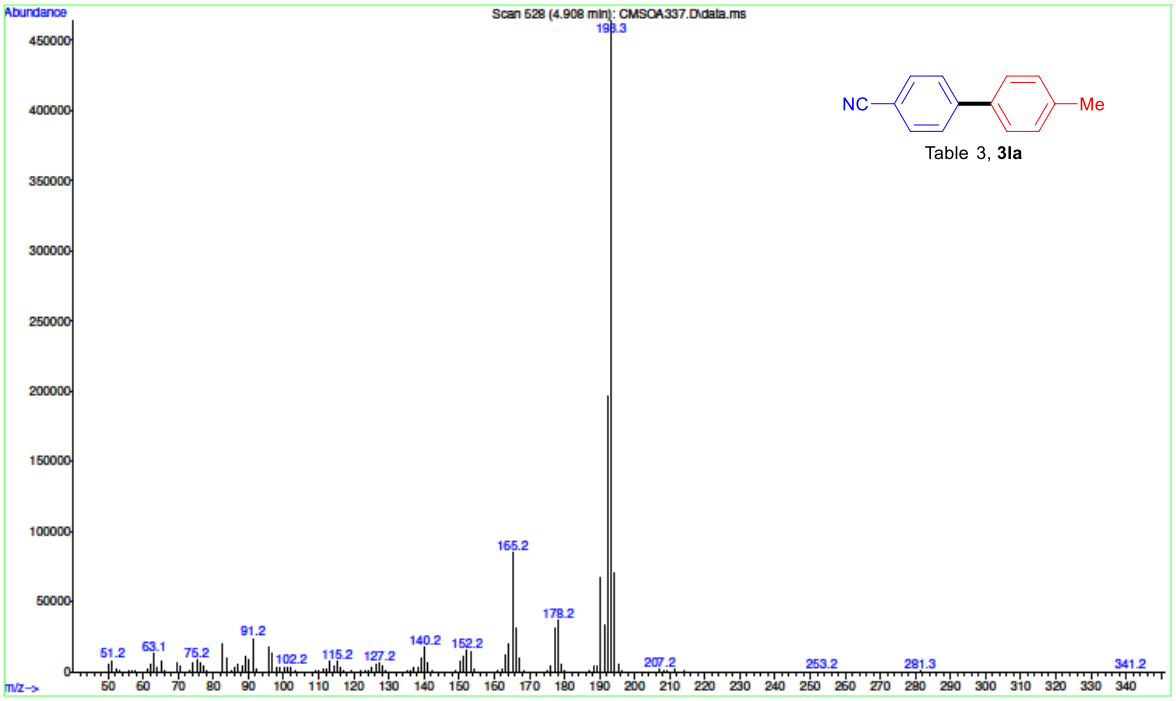
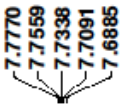

Abundance
Scan 528 (4.908 min): CMSOA337.D\data.ms
193.3
NC
Me
165.2
178.2
91.2
51.2
63.1
75.2
102.2
115.2
127.2
140.2
152.2
207.2
253.2
281.3
341.2
m/z-->

Table 3, **3la**



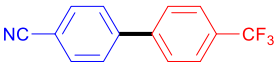




Table 3, **3lg**

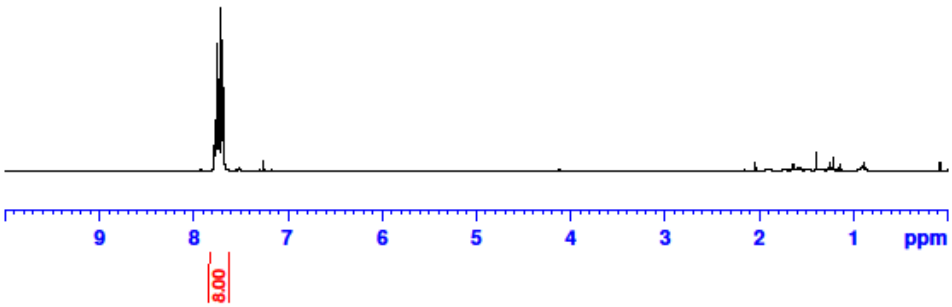
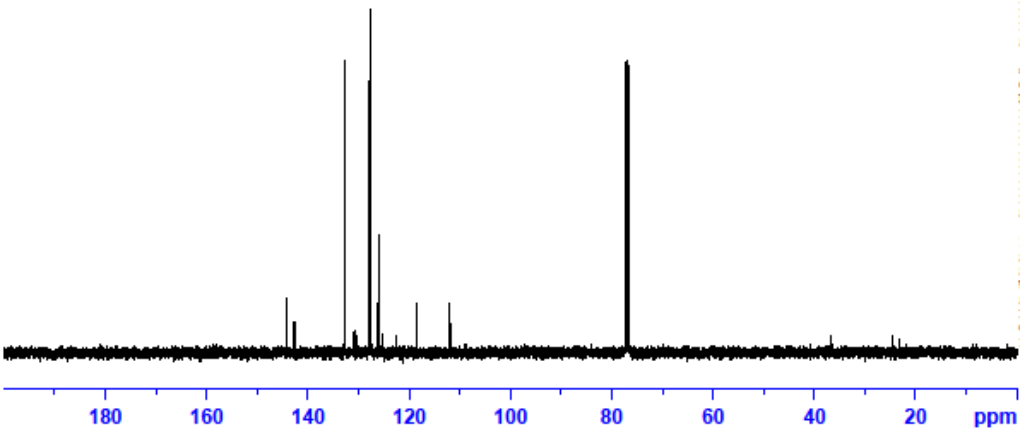








Table 3, **3lg**



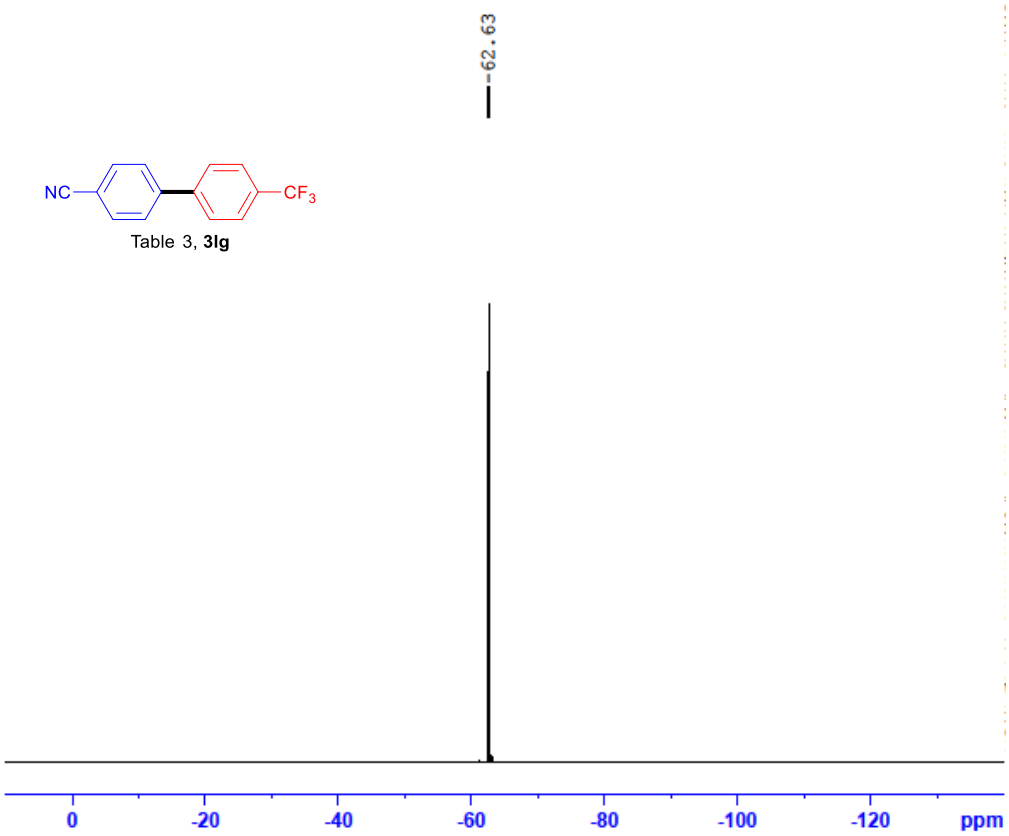



Table 3, **3lg**

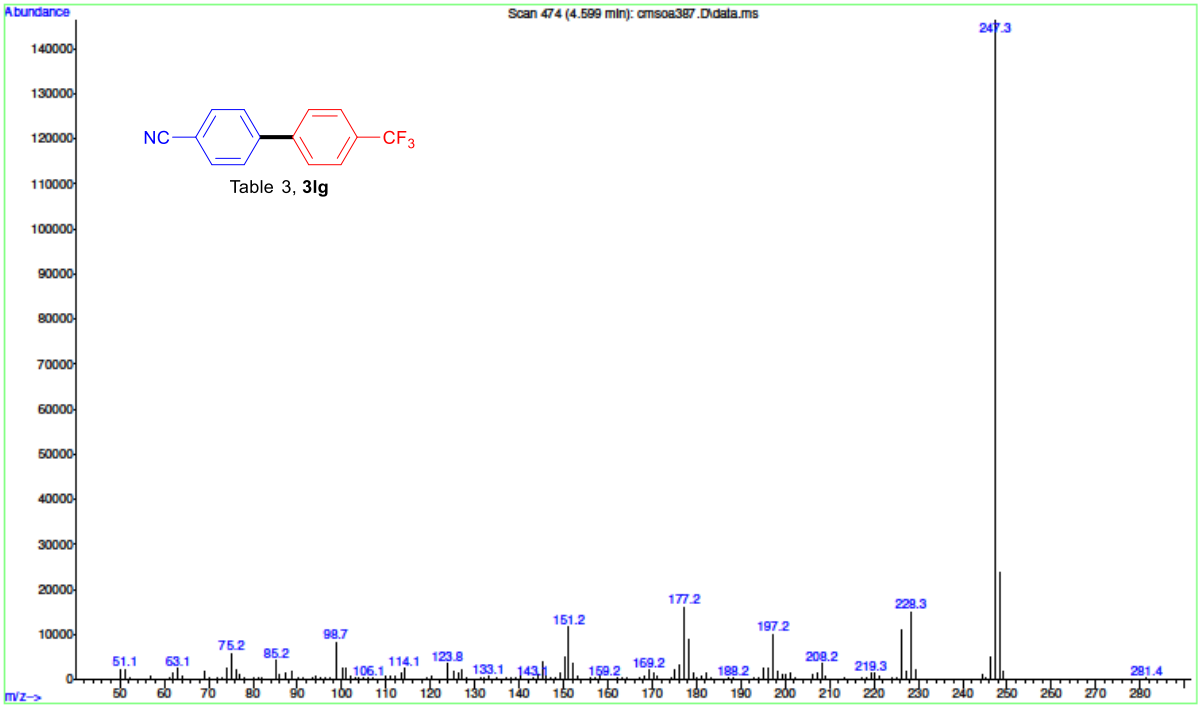
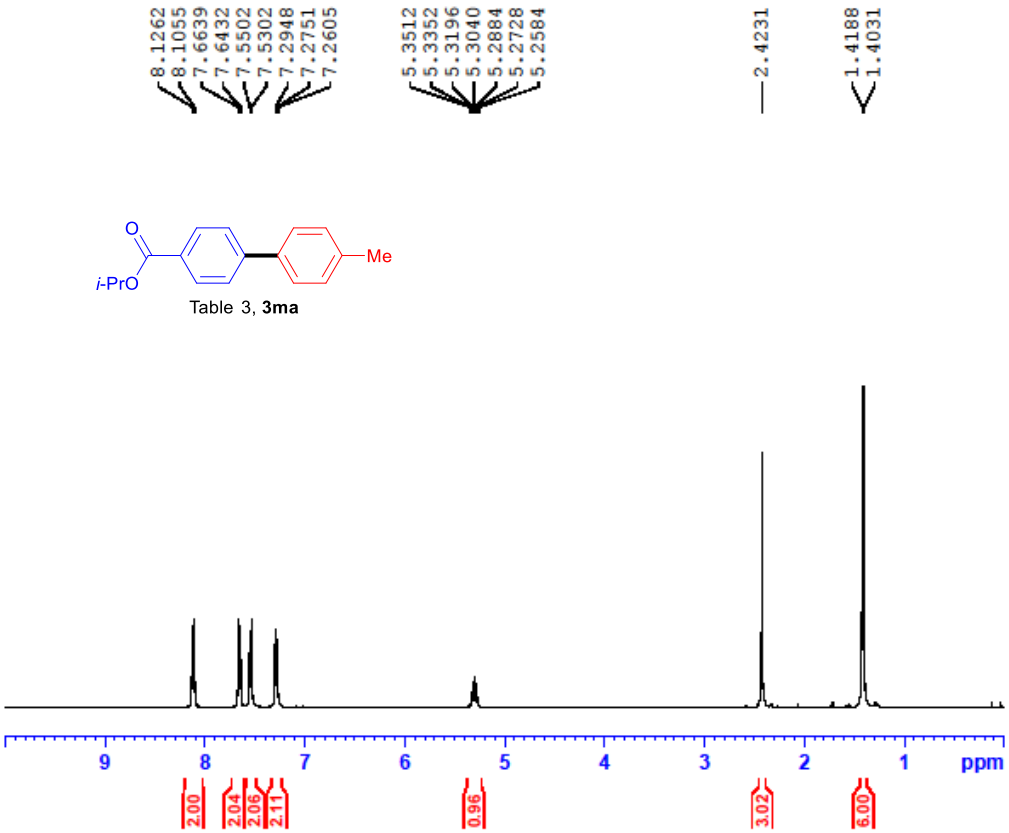
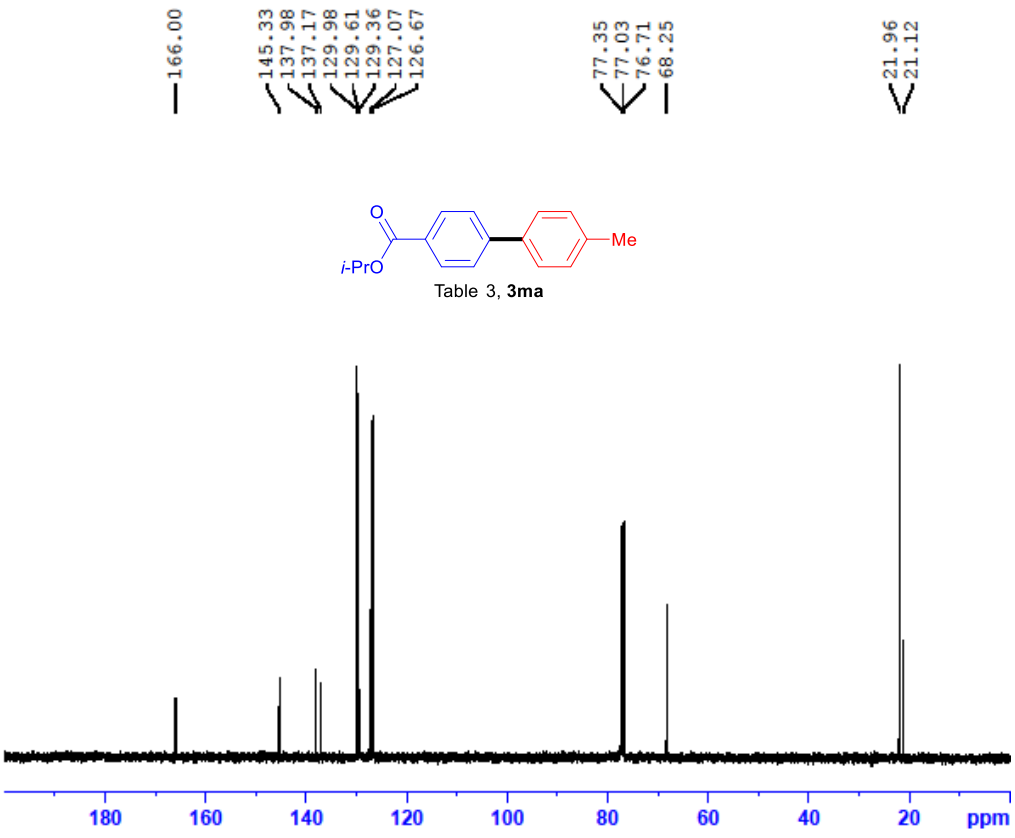
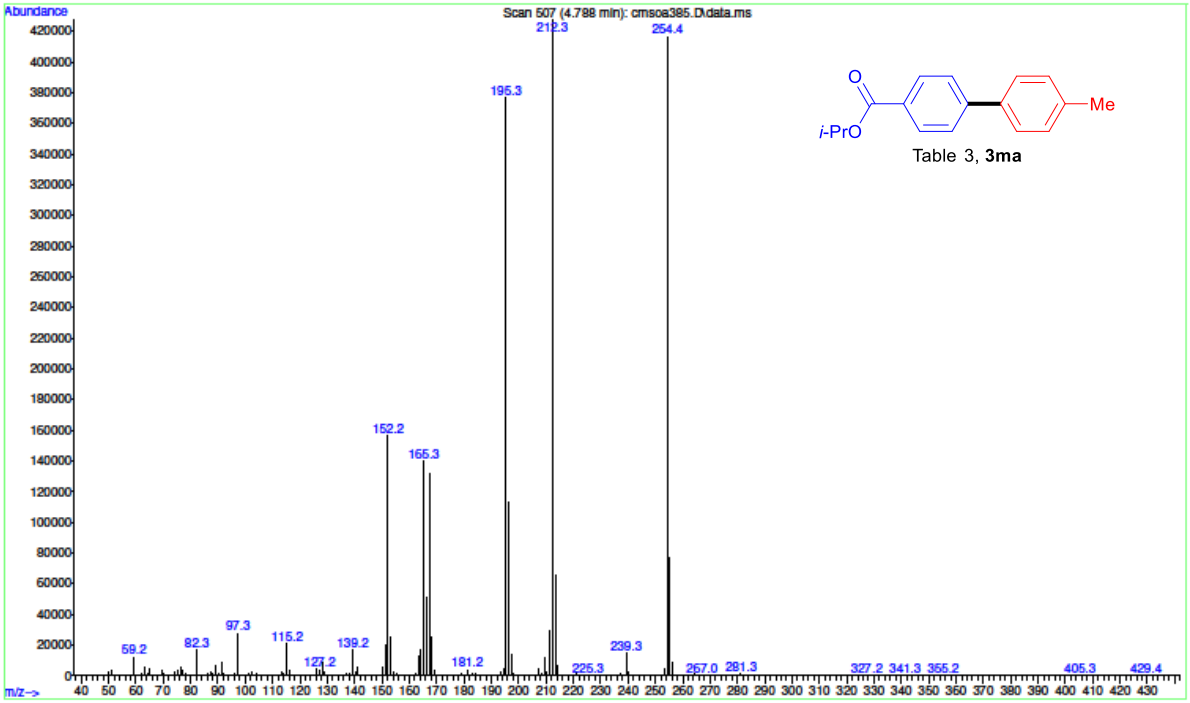
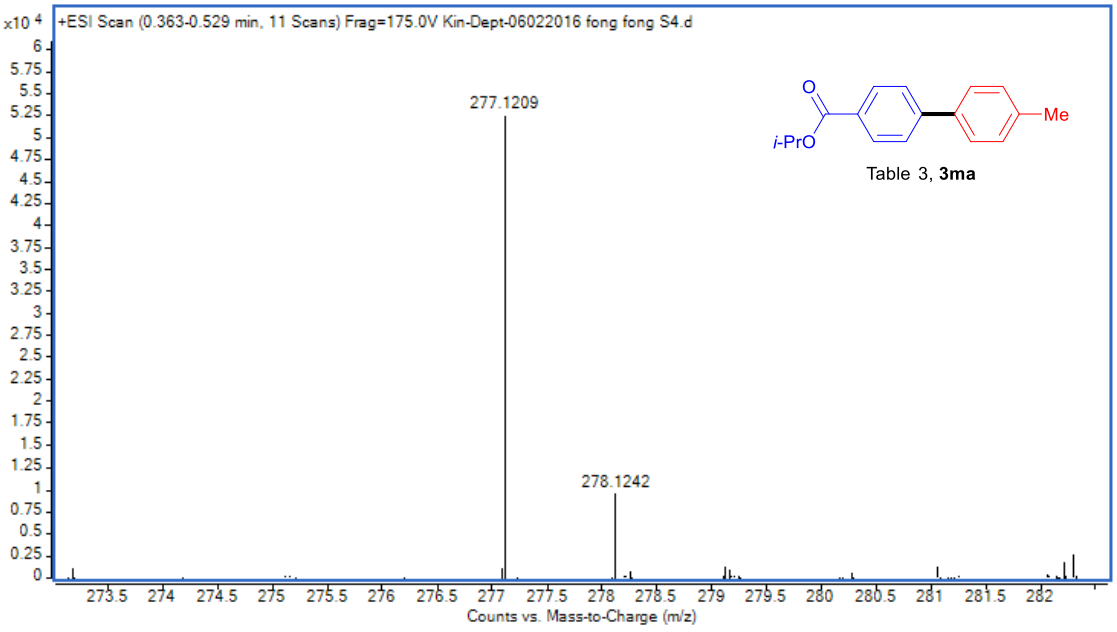



Table 3, **3lg**

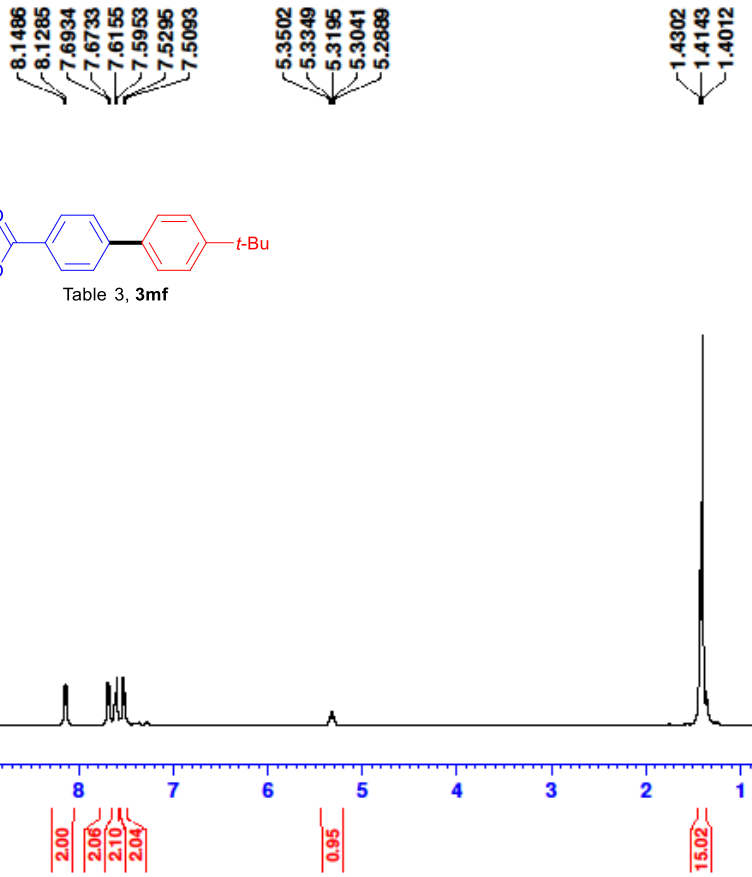

8.1262
8.1055
7.6639
7.6432
7.5502
7.5302
7.2948
7.2751
7.2605
5.3512
5.3352
5.3196
5.3040
5.2884
5.2728
5.2584
2.4231
1.4188
1.4031
O
i-PrO
Me
Table 3, 3ma
9
8
7
6
5
4
3
2
1
ppm
2.00
2.04
2.06
2.11
0.96
3.02
6.00

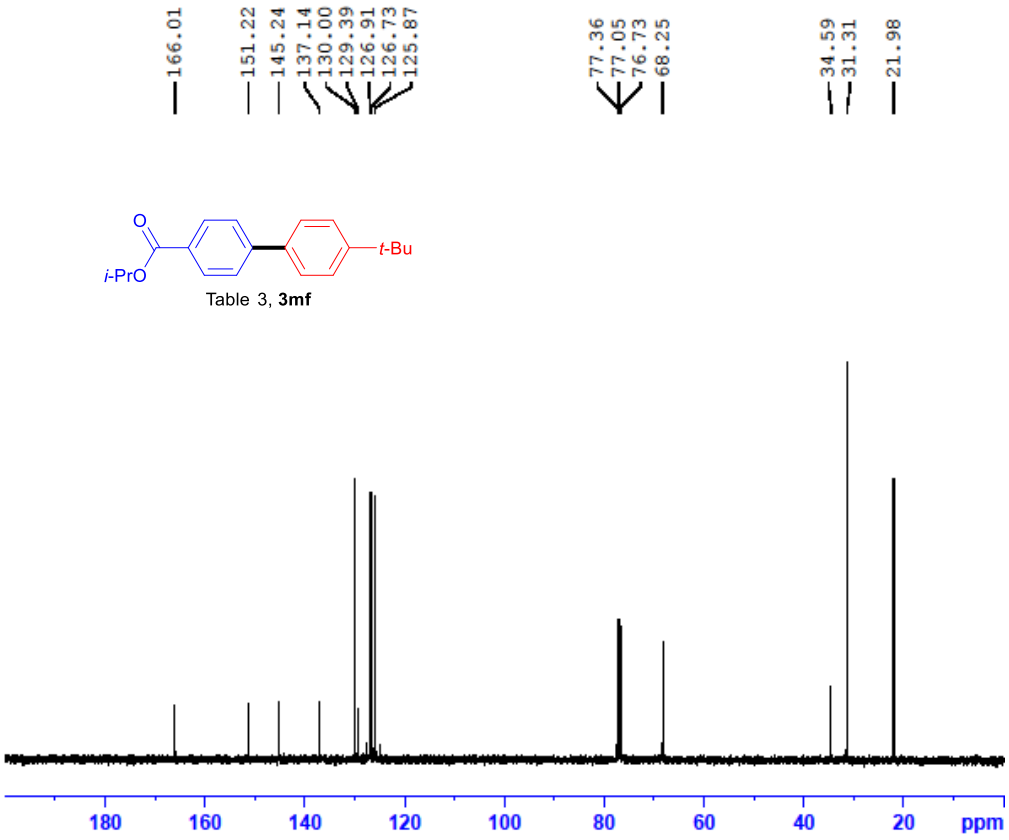

166.00
145.33
137.98
137.17
129.98
129.61
129.36
127.07
126.67
77.35
77.03
76.71
68.25
21.96
21.12
O
i-PrO
Me
Table 3, 3ma
180
160
140
120
100
80
60
40
20
ppm




| Mass | Calc. Mass | mDa | PPM | Formula |
|---|---|---|---|---|
| 277.1209 | 277.1199 | 1.0 | | C17 H18 Na O2 |


8.1486
8.1285
7.6934
7.6733
7.6155
7.5953
7.5295
7.5093
5.3502
5.3349
5.3195
5.3041
5.2889
1.4302
1.4143
1.4012
O
i-PrO
t-Bu
Table 3, 3mf
9
8
7
6
5
4
3
2
1
ppm
2.00
2.06
2.10
2.04
0.95
15.02


166.01
151.22
145.24
137.14
130.00
129.39
126.91
126.73
125.87
77.36
77.05
76.73
68.25
34.59
31.31
21.98
O
i-PrO
t-Bu
Table 3, 3mf
180
160
140
120
100
80
60
40
20
ppm

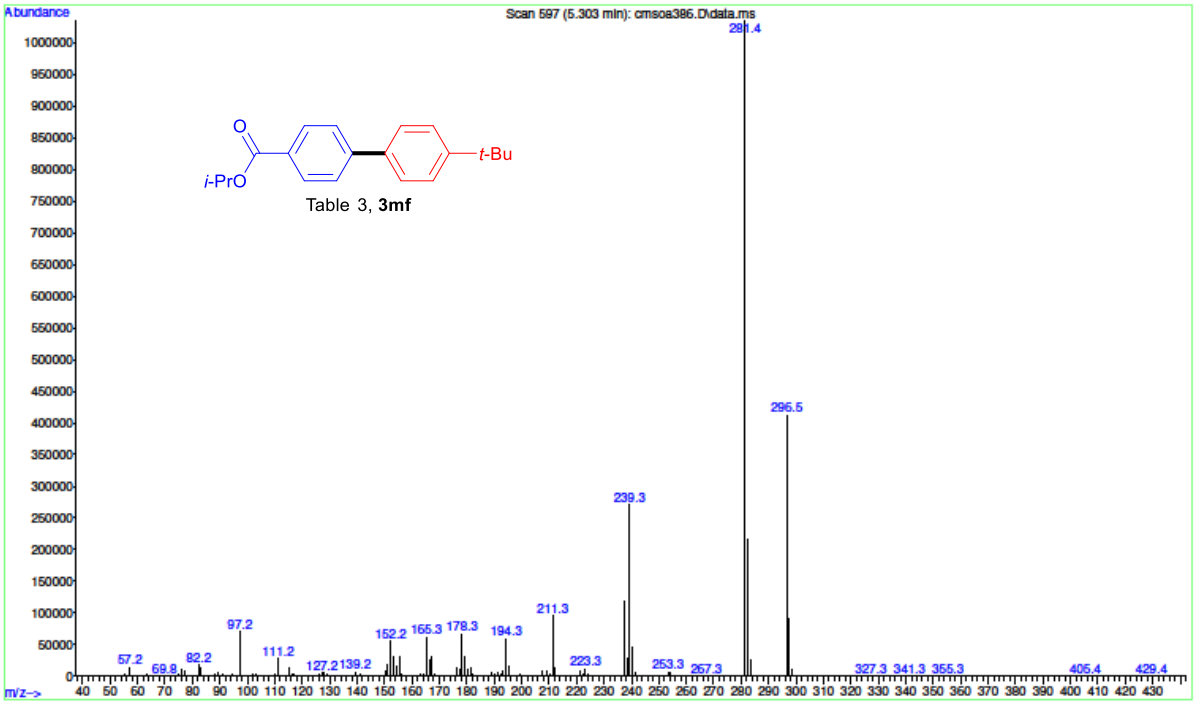






Table 3, **3mf**

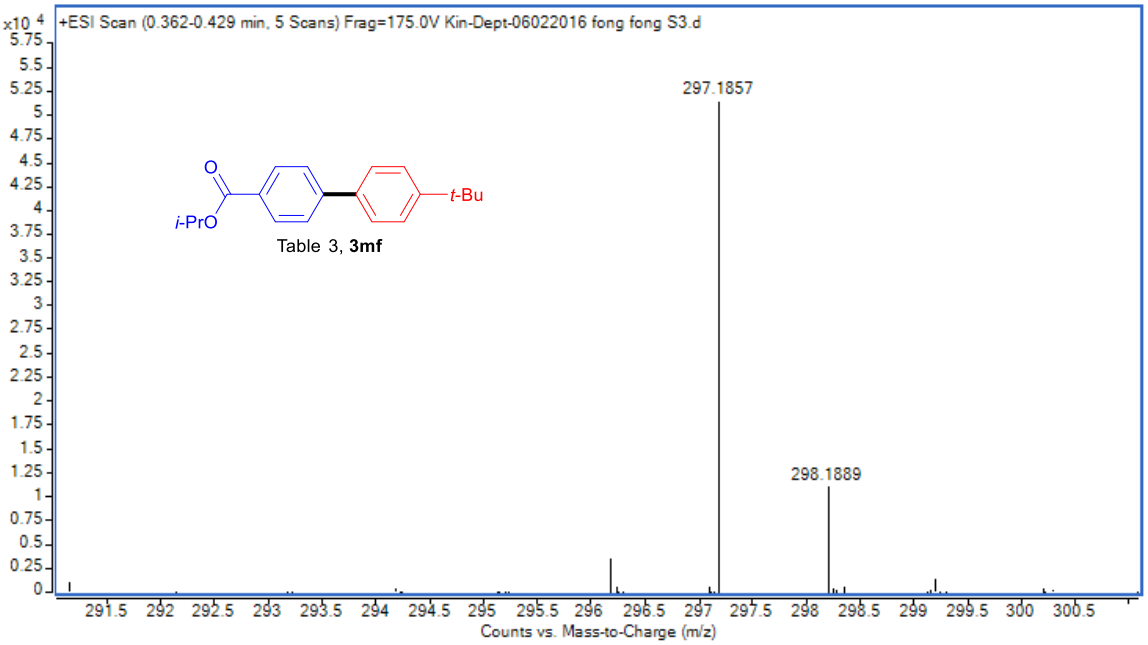






Table 3, **3mf**

| Mass | Calc. Mass | mDa | PPM | Formula |
|---|---|---|---|---|
| 297.1857 | 297.1849 | 0.8 | 2.7 | C20 H25 O2 |

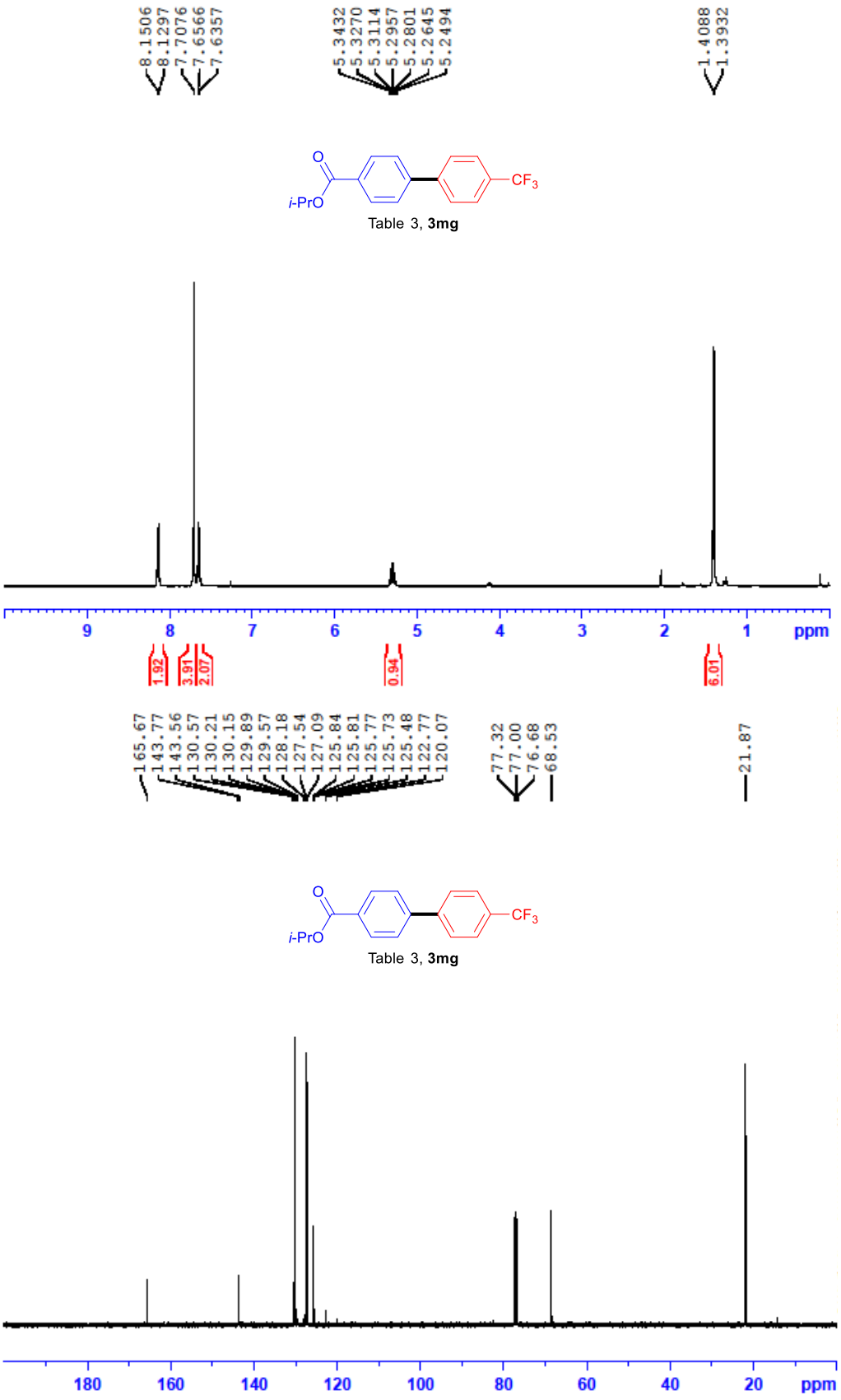
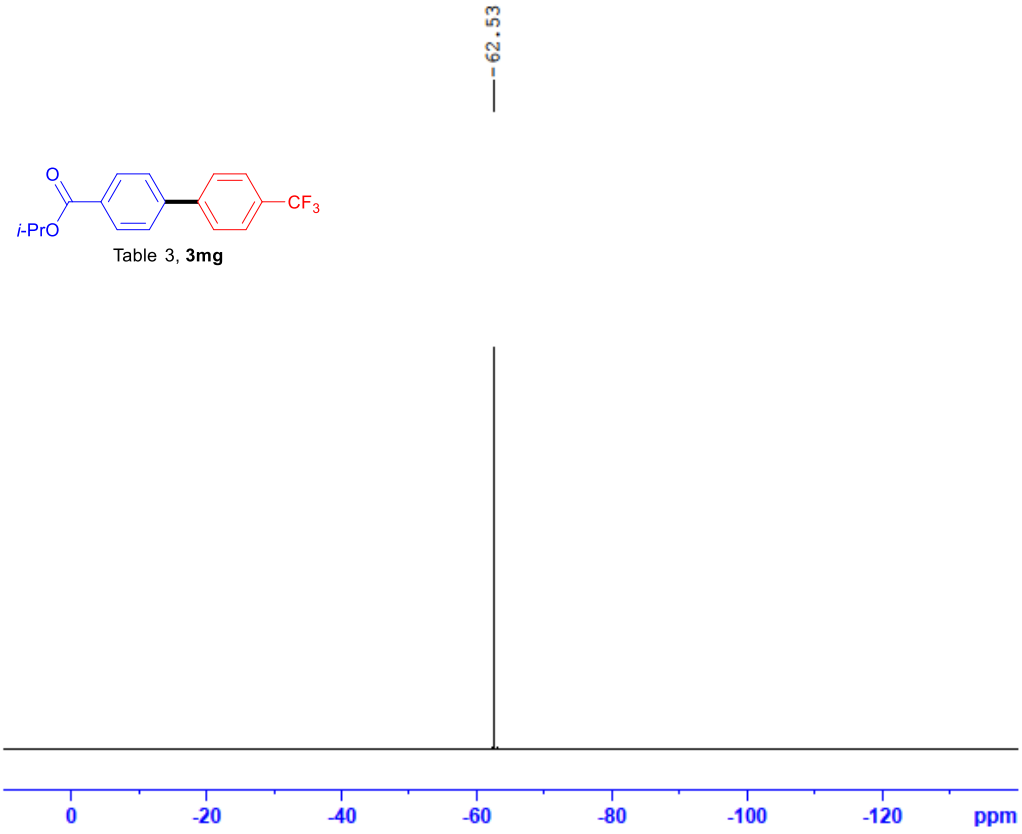
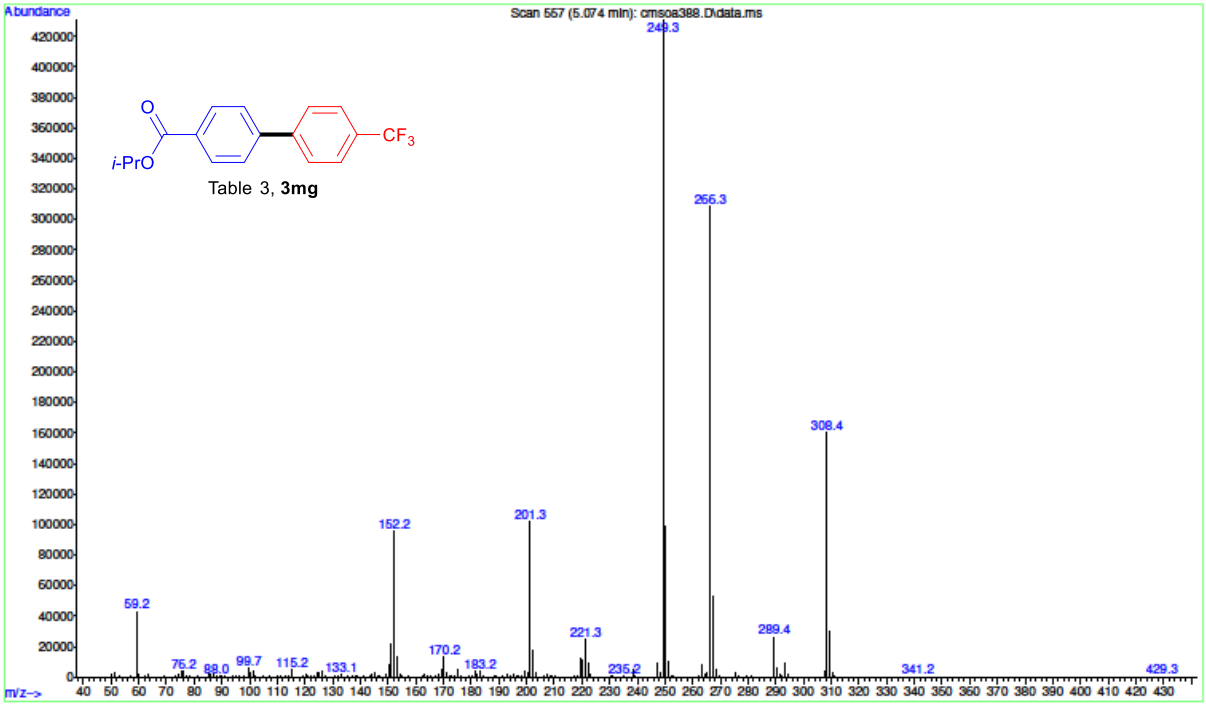



Table 3, **3mg**

Table 3, **3mg**


-62.53
i-PrO
CF3
Table 3, 3mg
0
-20
-40
-60
-80
-100
-120
ppm


Abundance
Scan 557 (5.074 min): cmsoa388.Dldata.ms
i-PrO
CF3
Table 3, 3mg
249.3
266.3
308.4
152.2
201.3
59.2
221.3
289.4
170.2
183.2
76.2
88.0
99.7
115.2
133.1
235.2
341.2
429.3
m/z-->

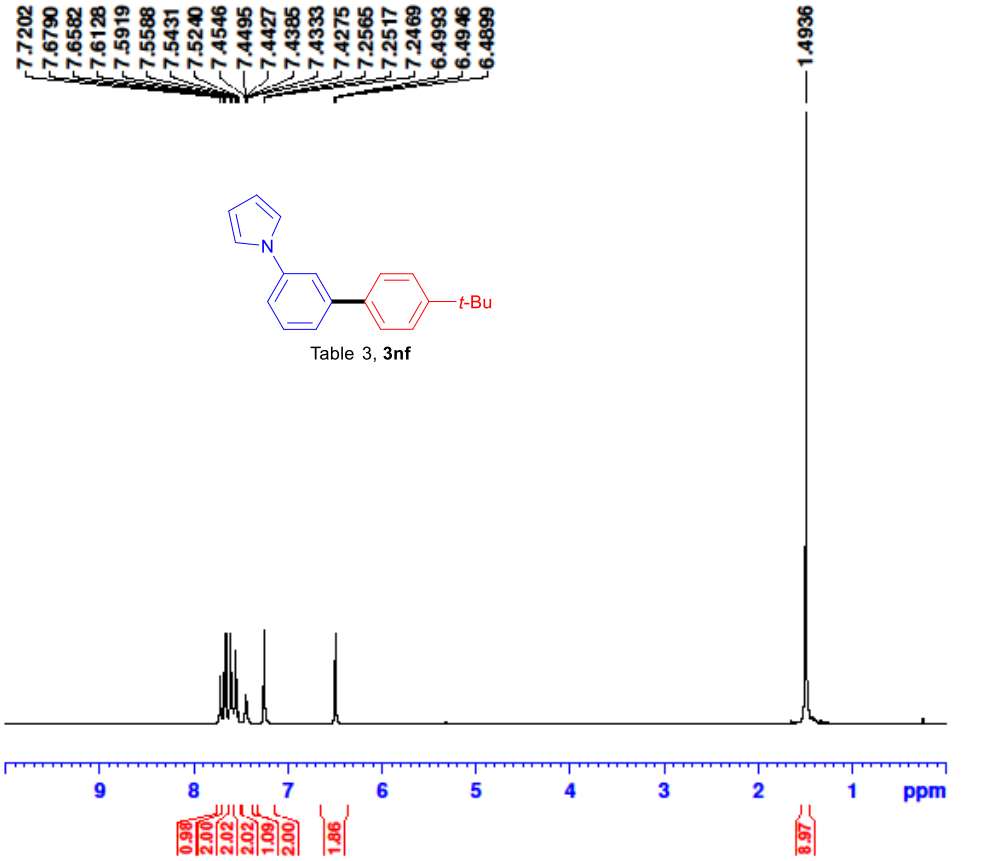
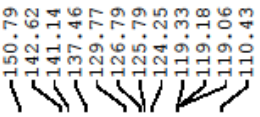



Table 3, **3nf**



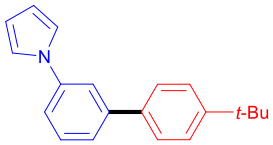
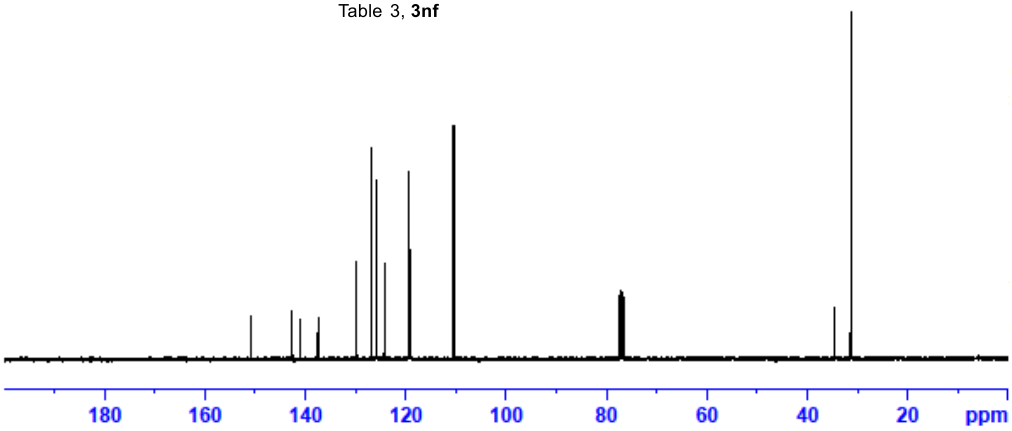
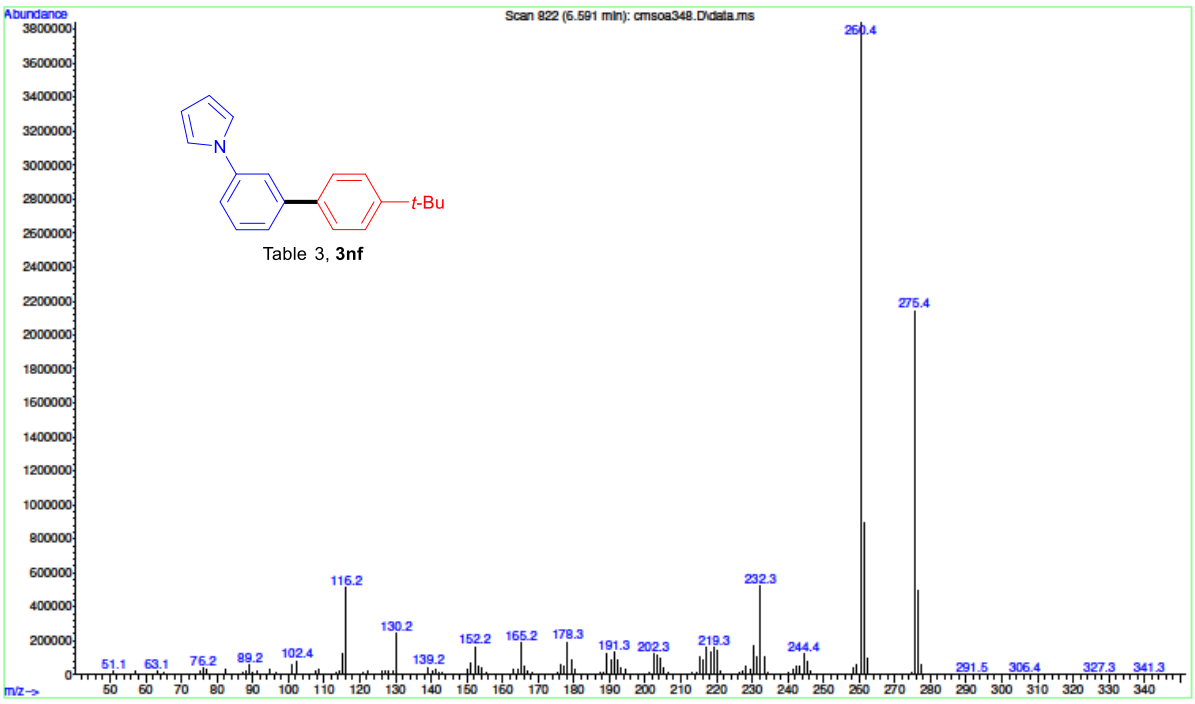
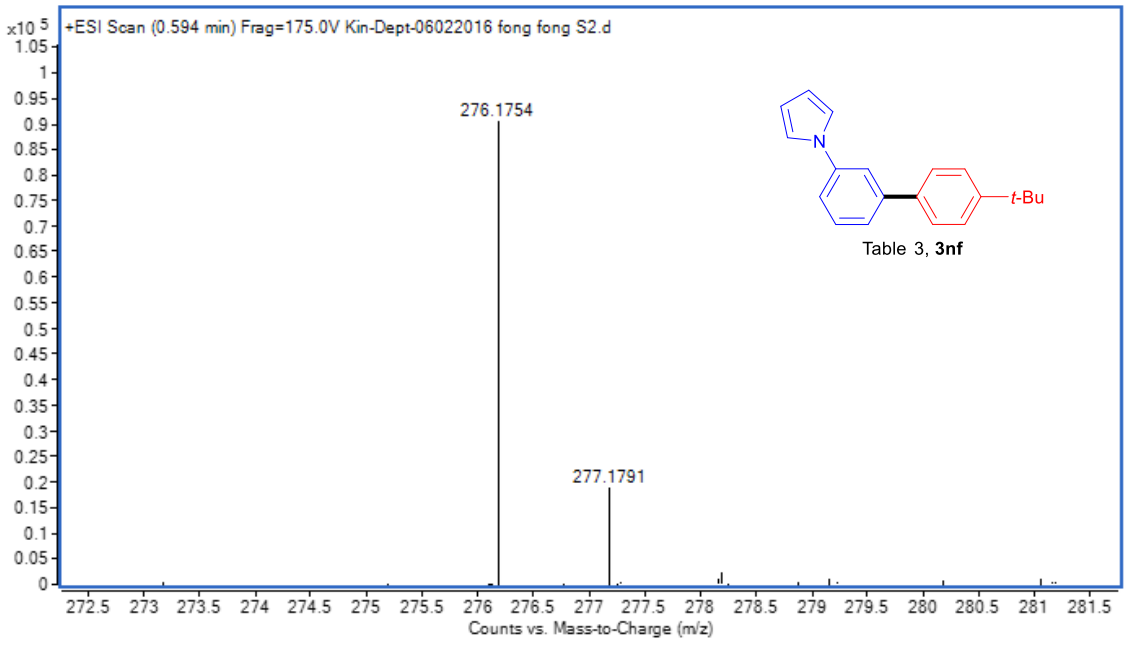



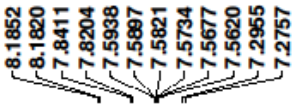

Table 3, **3nf**

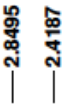





| Mass | Calc. Mass | mDa | PPM | Formula |
|---|---|---|---|---|
| 276.1754 | 276.1747 | 0.7 | 2.6 | C20 H22 N |



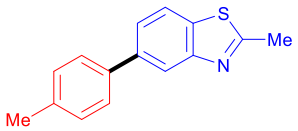
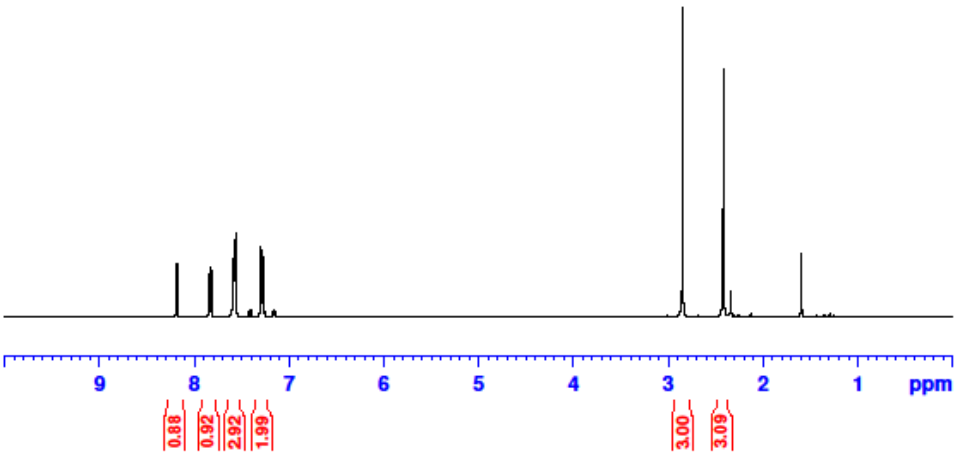
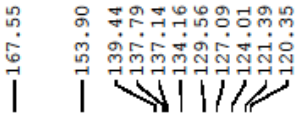
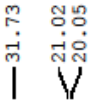




Table 3, **3oa**



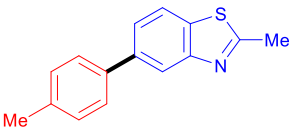
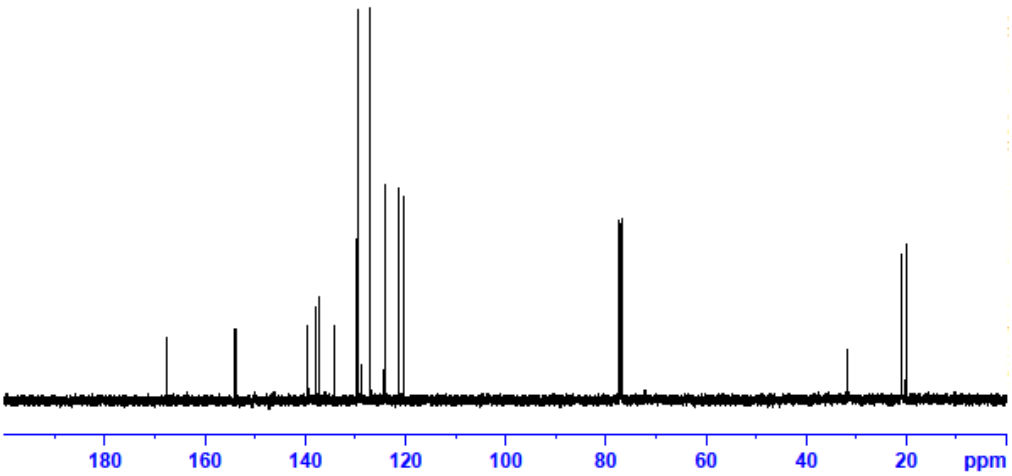




Table 3, **3oa**



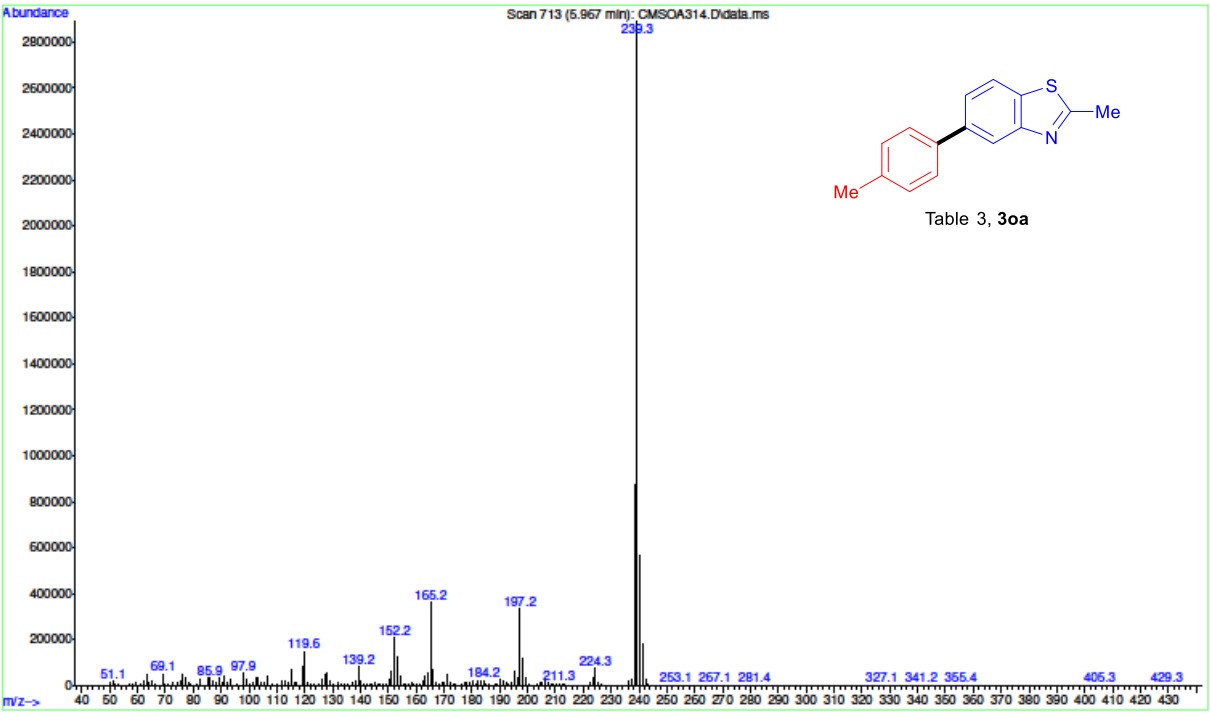

Abundance
Scan 713 (5.967 min): CMSOA314.D\data.ms
239.3
165.2
197.2
152.2
119.6
139.2
224.3
51.1
69.1
85.9
97.9
184.2
211.3
253.1
267.1
281.4
327.1
341.2
355.4
405.3
429.3
m/z-->
S
Me
N
Me

Table 3, **3oa**

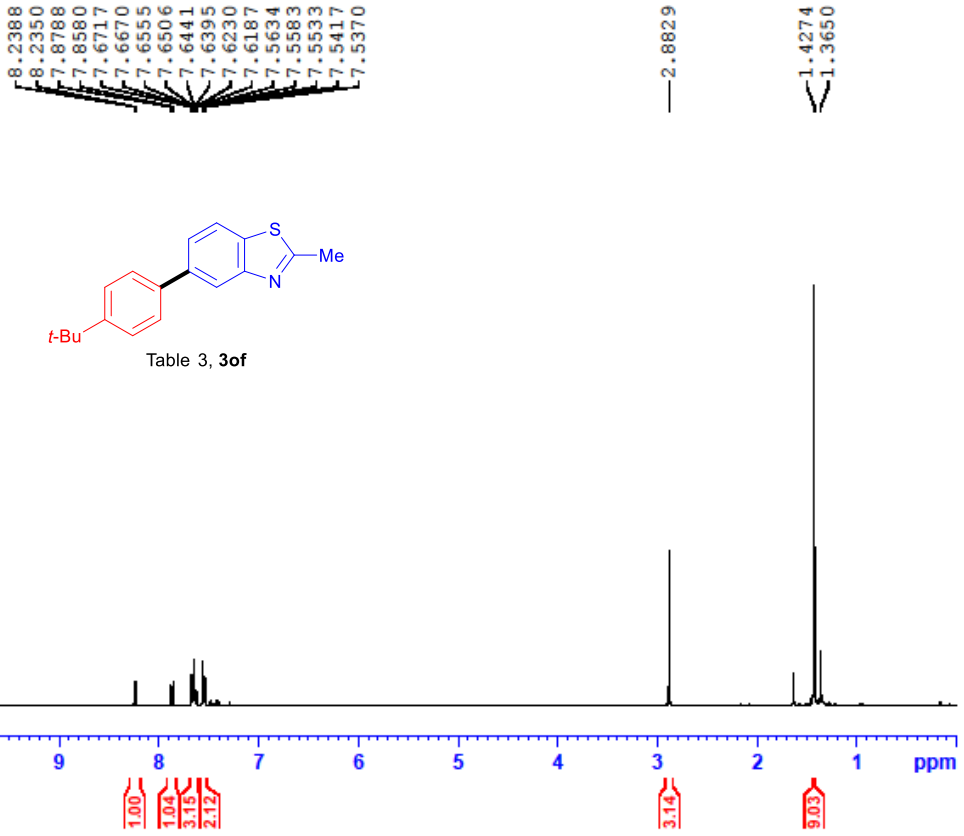



Table 3, **3of**

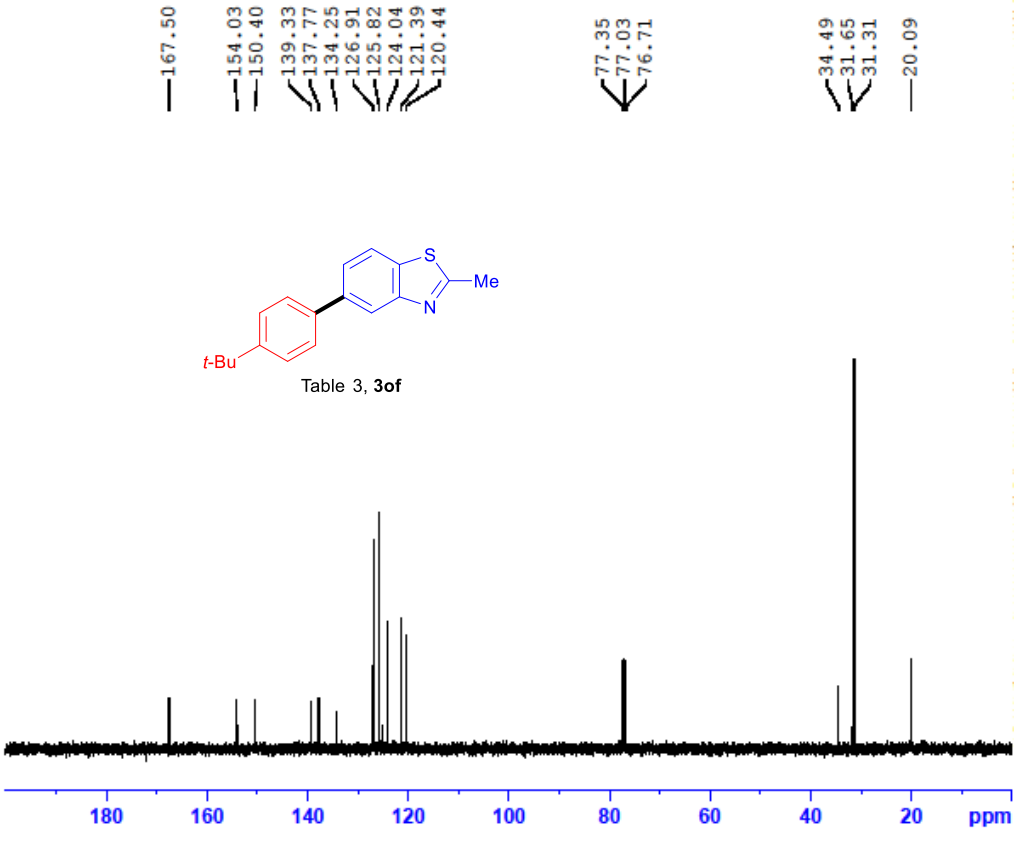



Table 3, **3of**

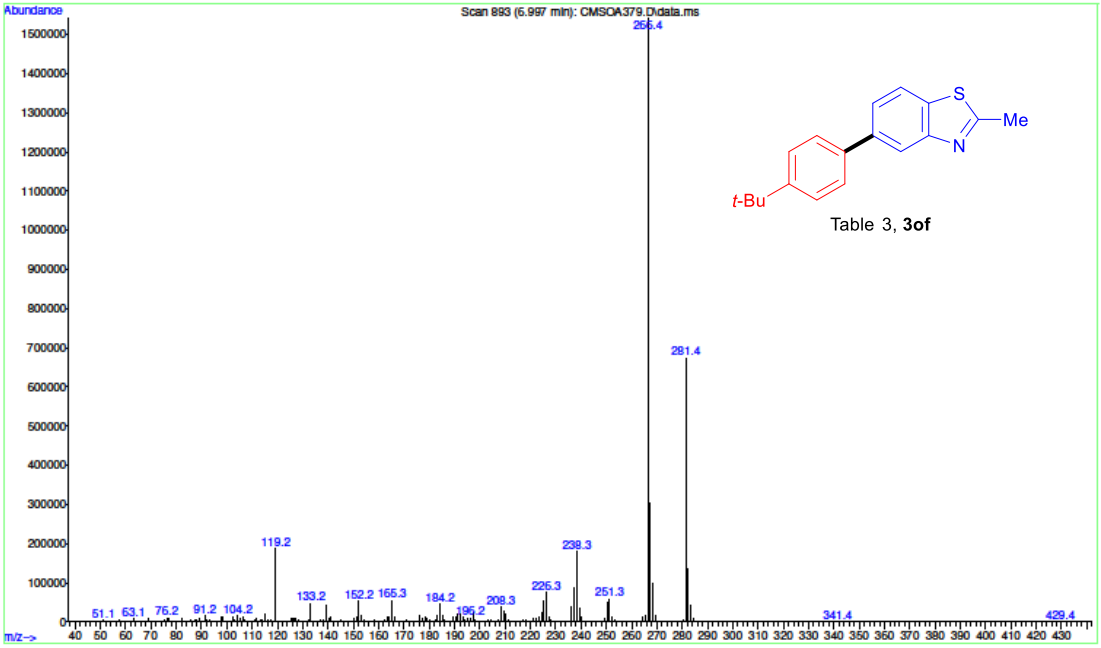

Abundance
Scan 893 (6.997 min): CMSOA379.D\data.ms
256.4
281.4
119.2
238.3
225.3
251.3
133.2
152.2
165.3
184.2
208.3
51.1
63.1
75.2
91.2
104.2
341.4
429.4
m/z-->
S
Me
N
t-Bu

Table 3, **3of**

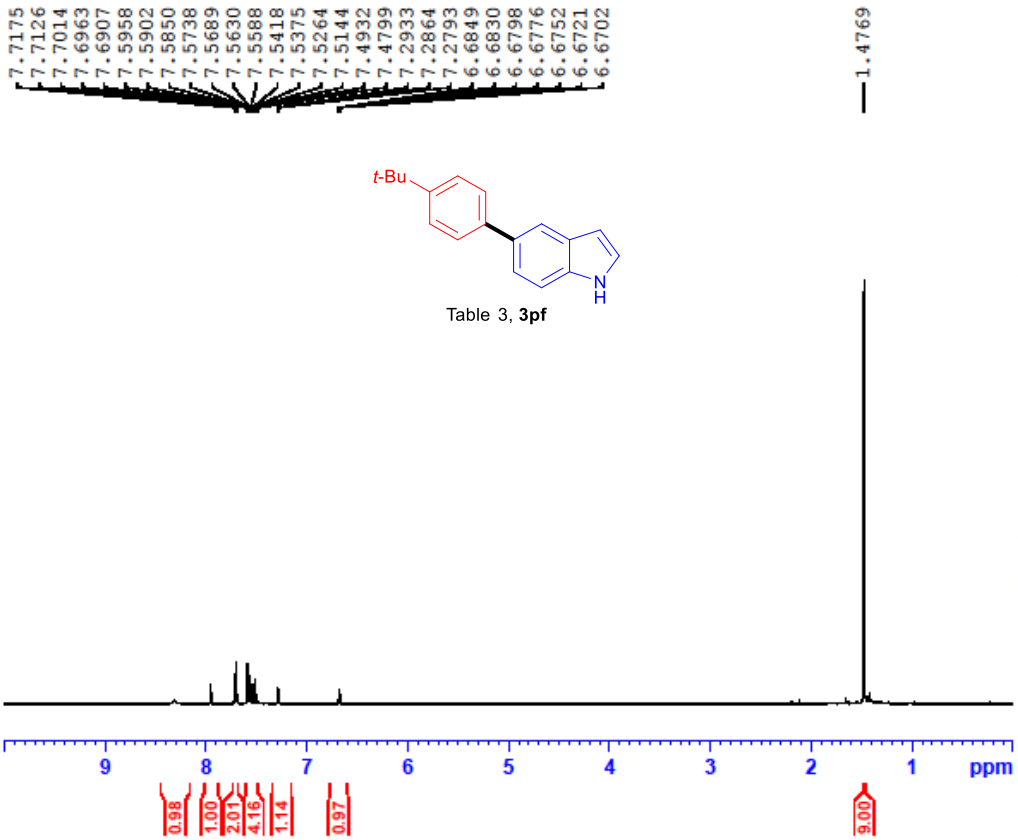



Table 3, **3pf**

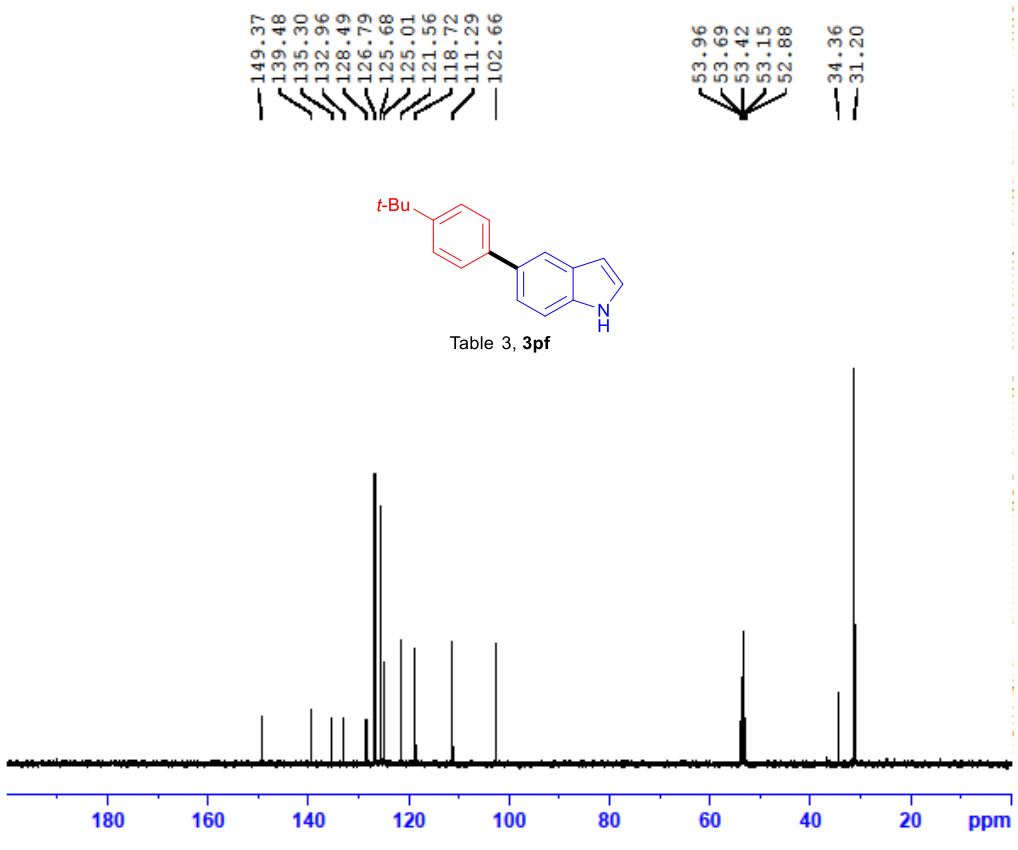



Table 3, **3pf**

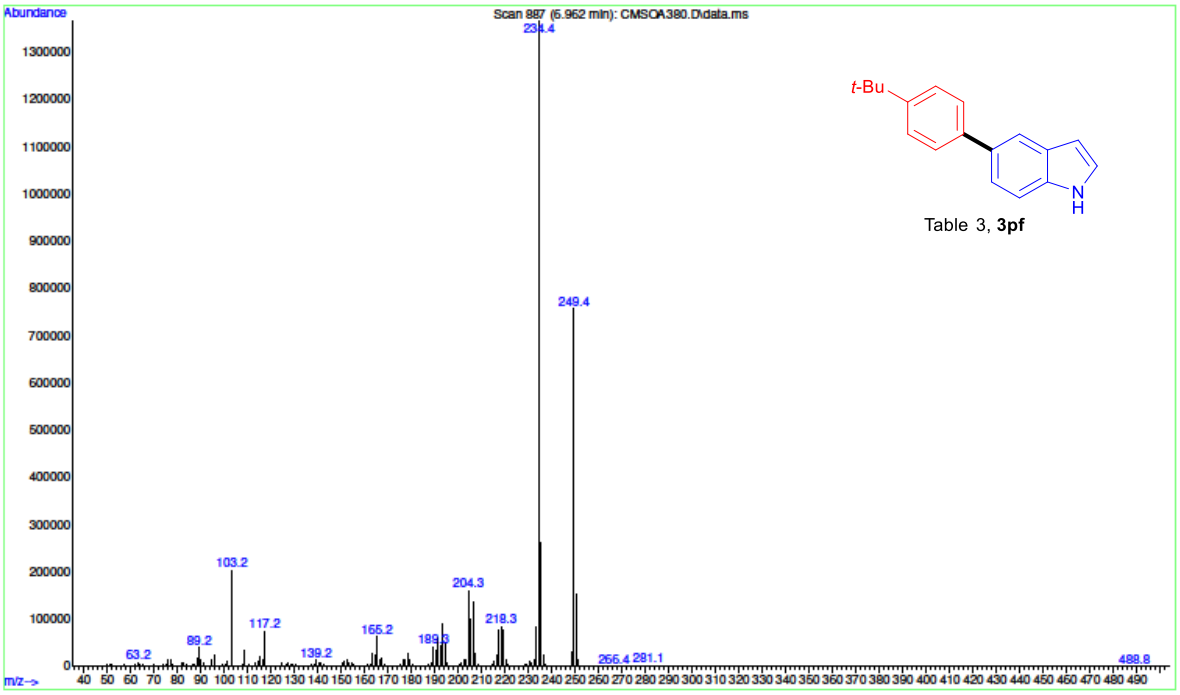
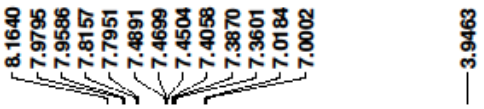

Abundance
Scan 887 (6.962 min): CMSCA380.D\data.ms
234.4
249.4
103.2
204.3
117.2
218.3
155.2
189.3
89.2
63.2
139.2
255.4
281.1
488.8
m/z-->
t-Bu
N
H

Table 3, **3pf**



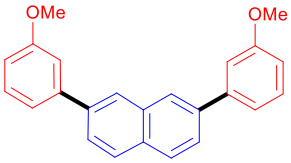
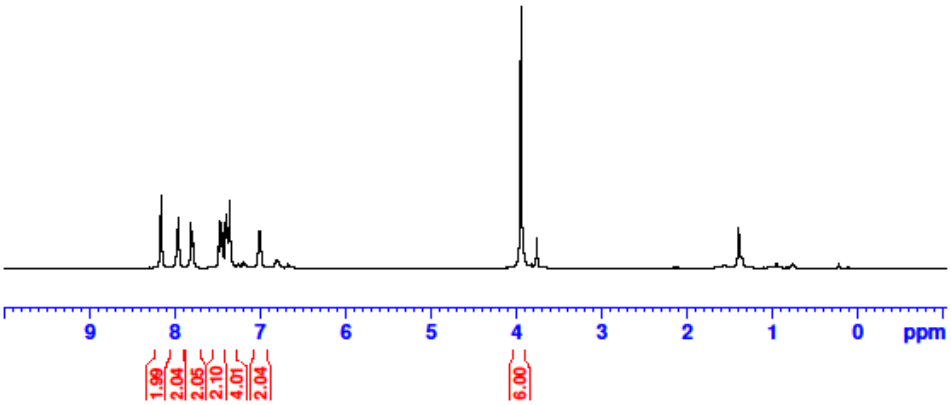




Table 3, **3qc**





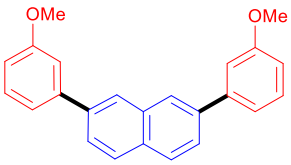
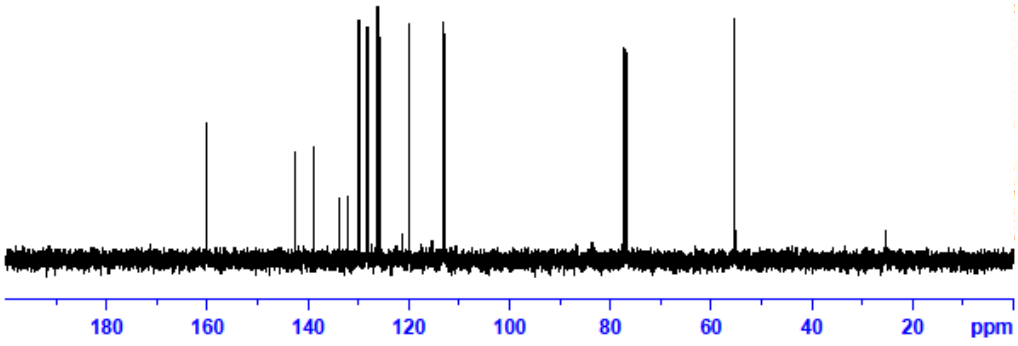
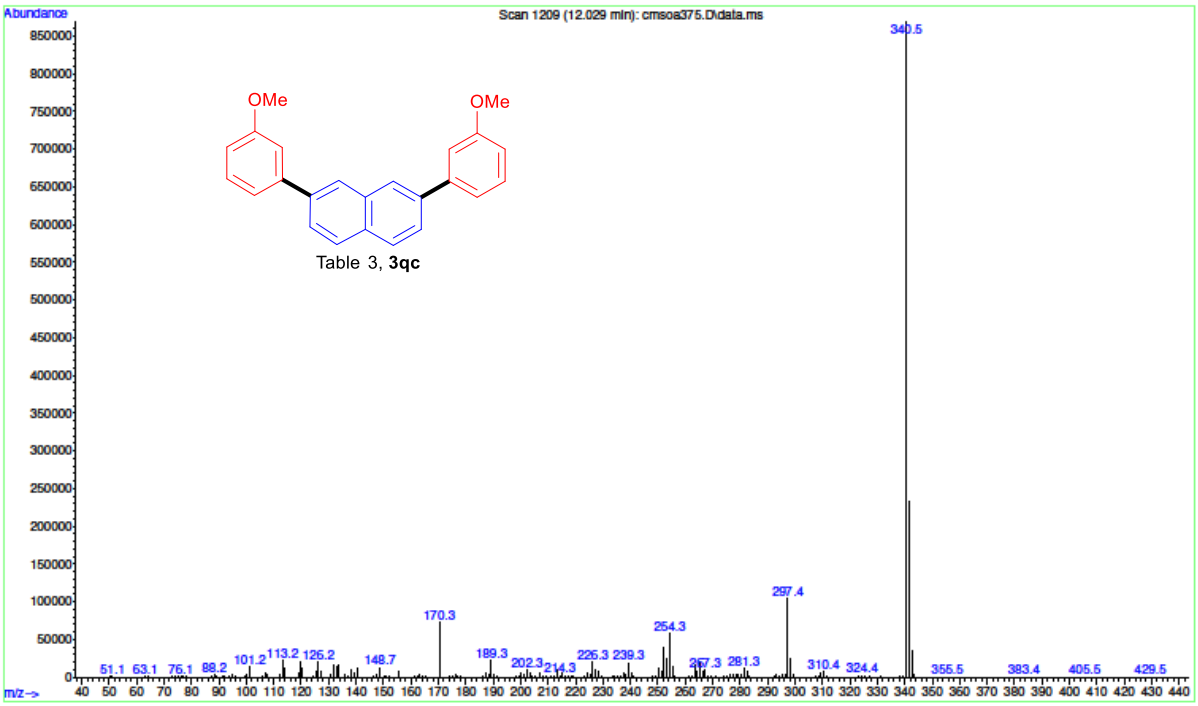
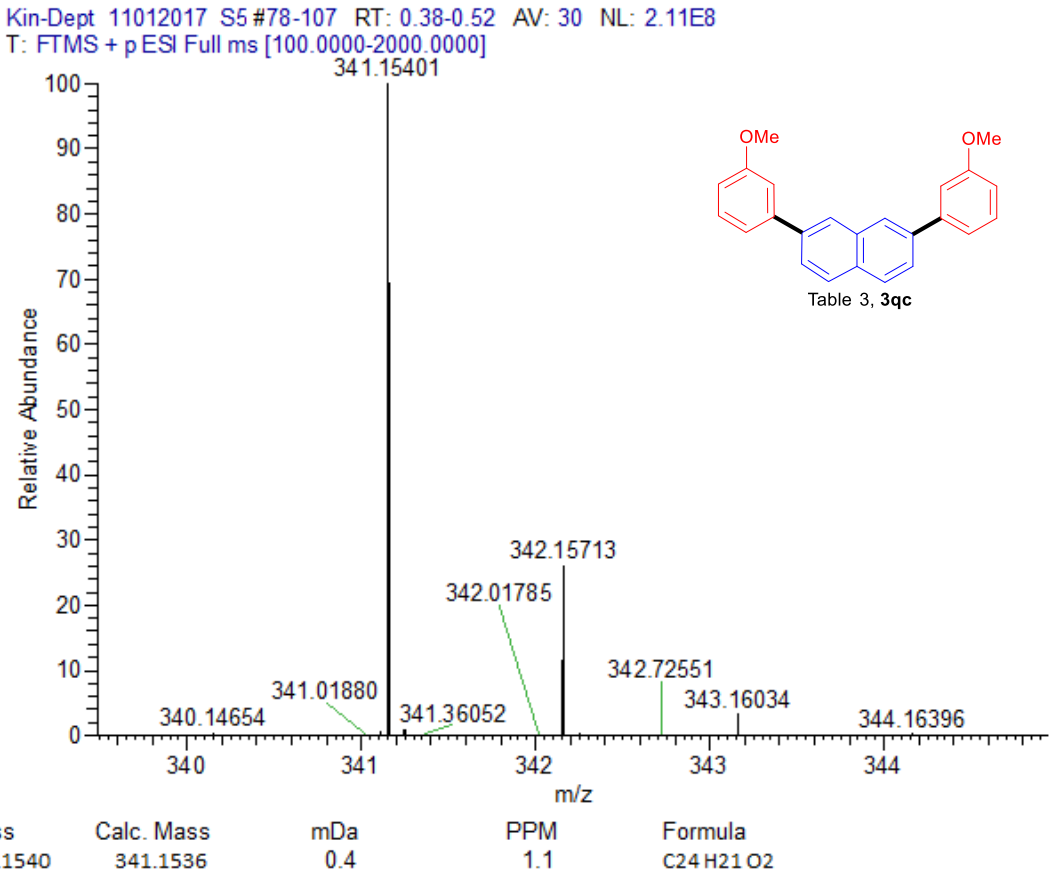



Table 3, **3qc**






| Mass | Calc. Mass | mDa | PPM | Formula |
|---|---|---|---|---|
| 341.1540 | 341.1536 | 0.4 | 1.1 | C24 H21 O2 |

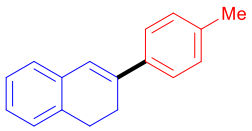
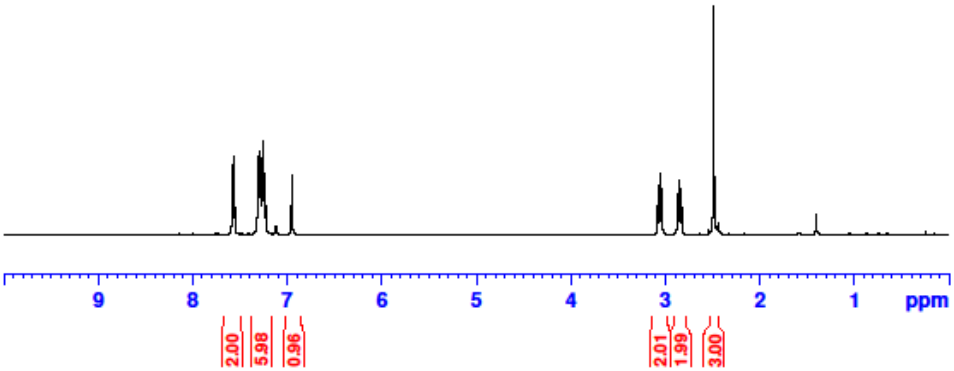
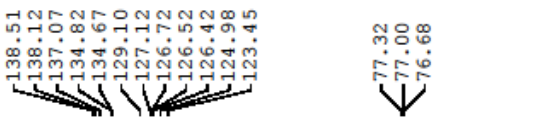




Table 4, **5aa**



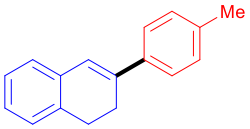
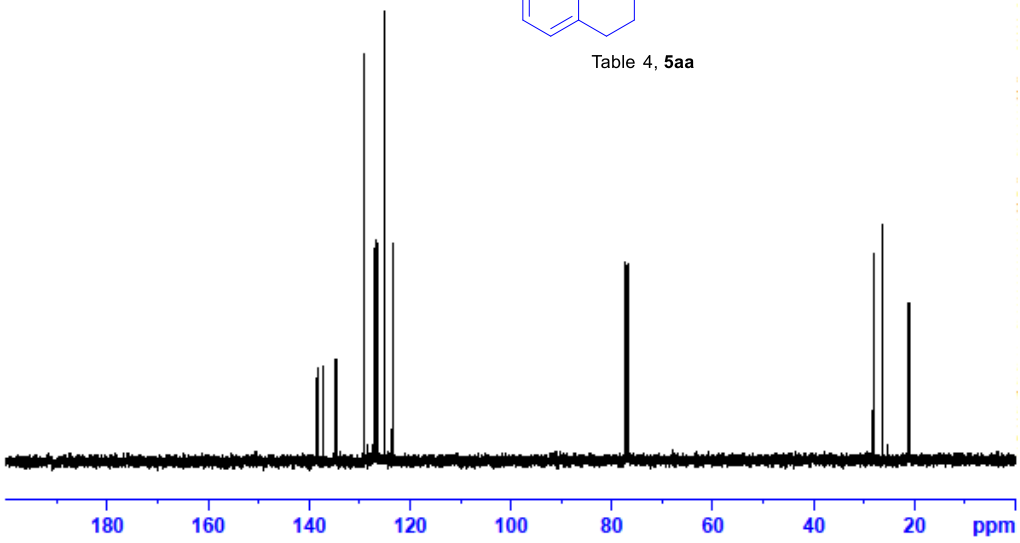




Table 4, **5aa**



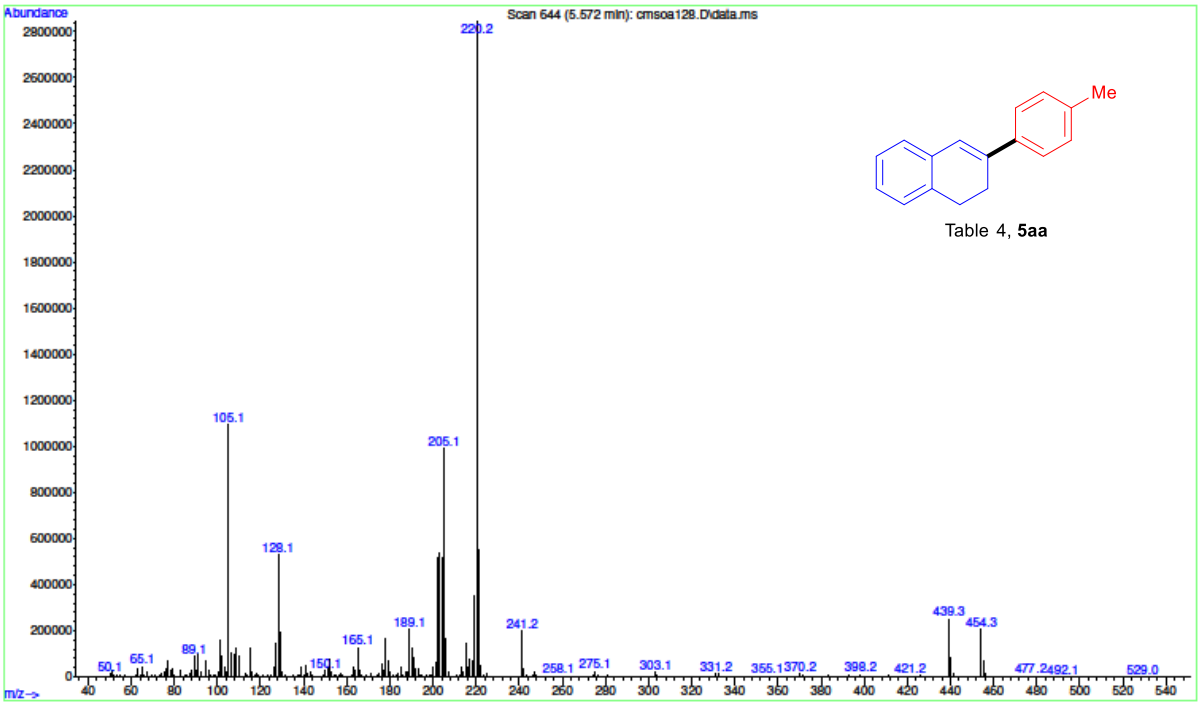
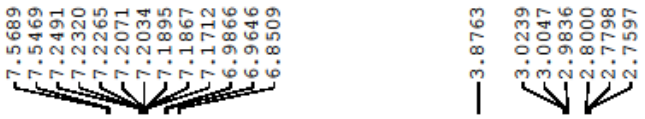

Abundance
Scan 644 (5.572 min): cmsoa128.D\data.ms
220.2
105.1
205.1
128.1
189.1
241.2
165.1
89.1
439.3
454.3
Me
m/z-->

Table 4, **5aa**



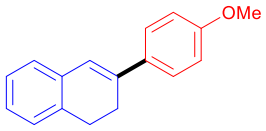
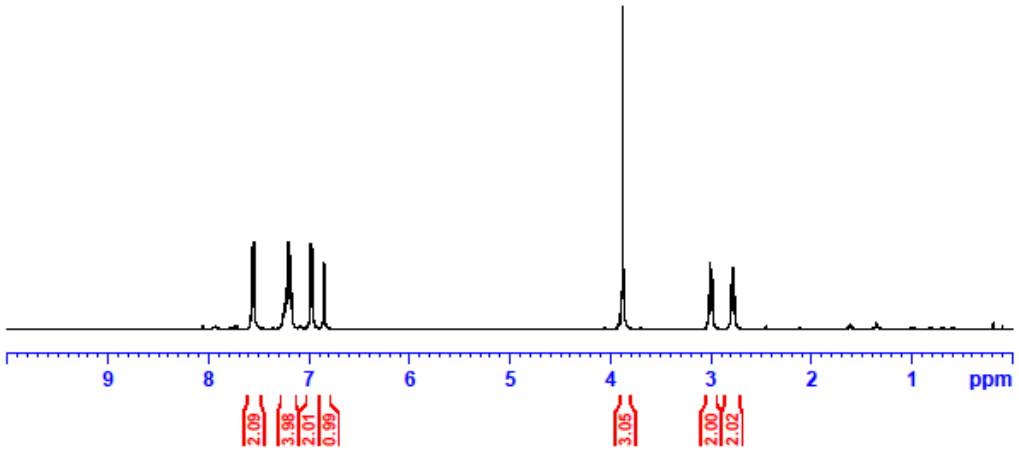




Table 4, **5ab**





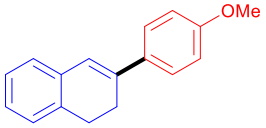
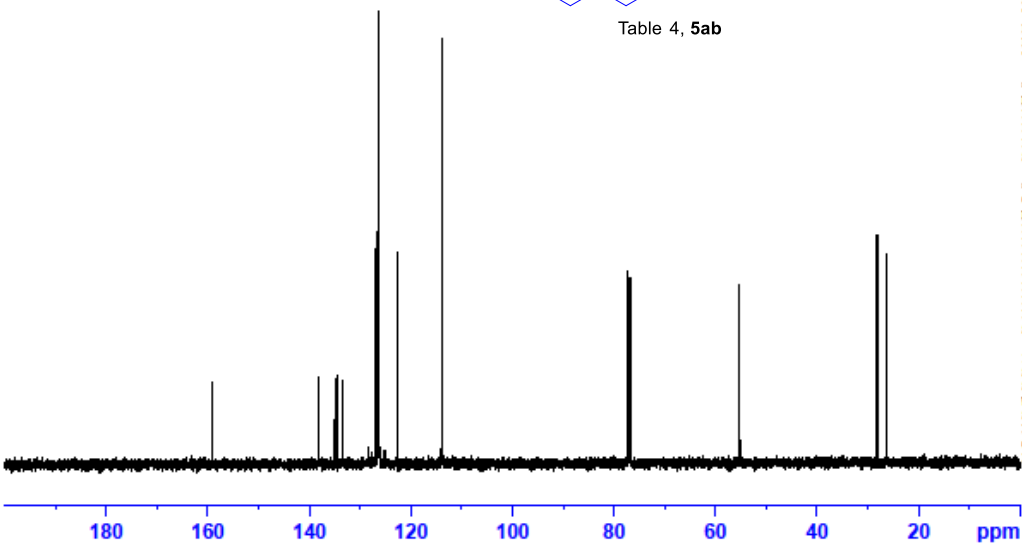



Table 4, **5ab**



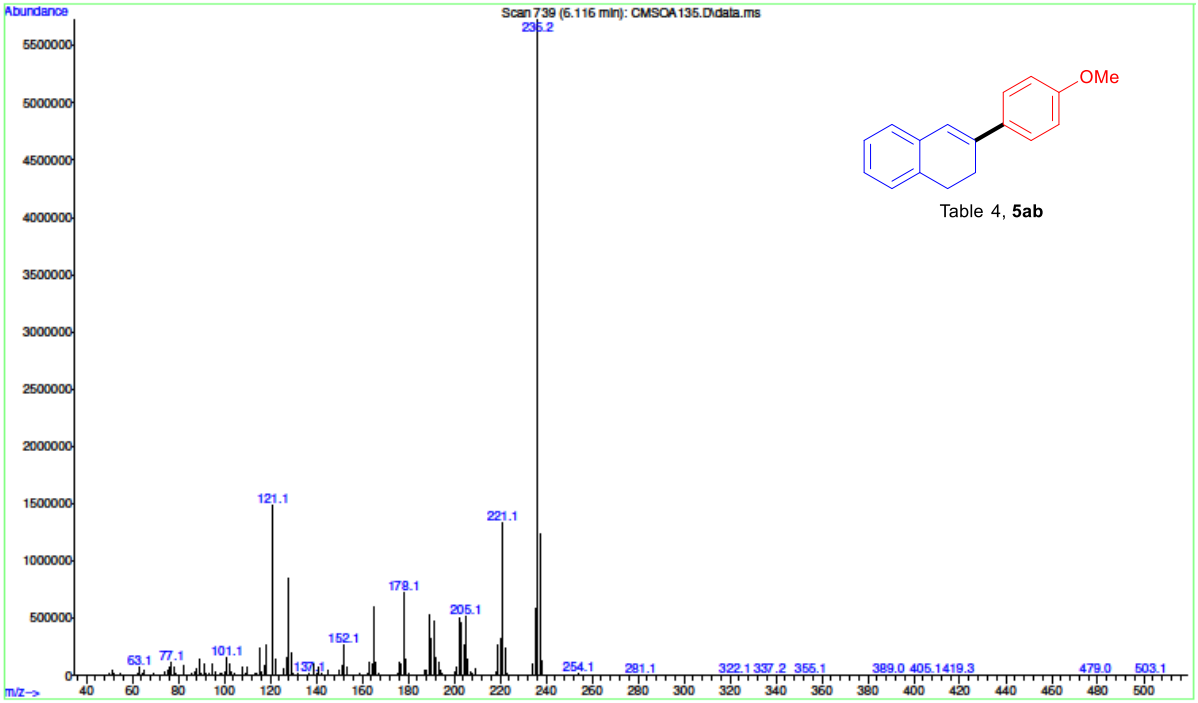
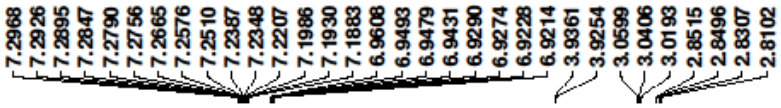

Abundance
Scan 739 (6.116 min): CMSOA135.D\data.ms
236.2
OMe
121.1
221.1
178.1
205.1
152.1
101.1
77.1
63.1
254.1
281.1
322.1
337.2
355.1
389.0
405.1
419.3
479.0
503.1
m/z-->

Table 4, **5ab**



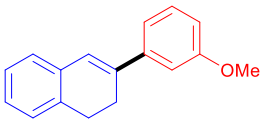
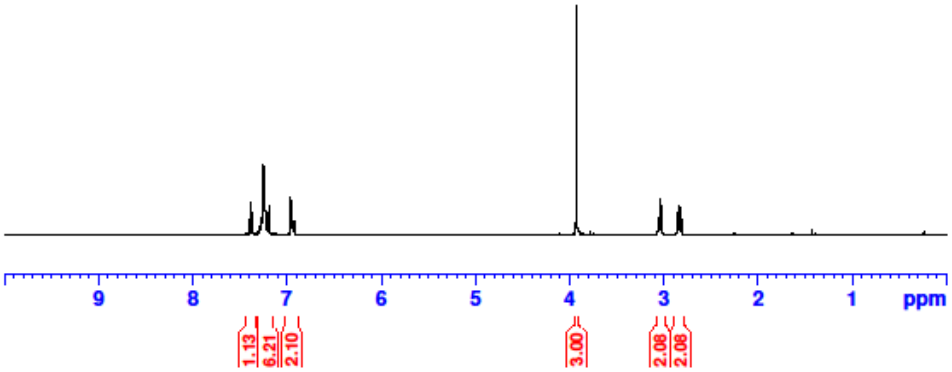
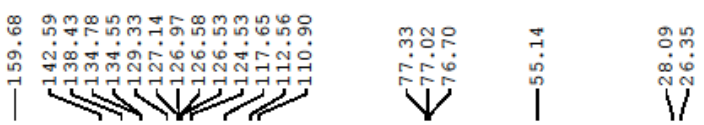




Table 4, **5ac**



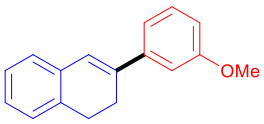
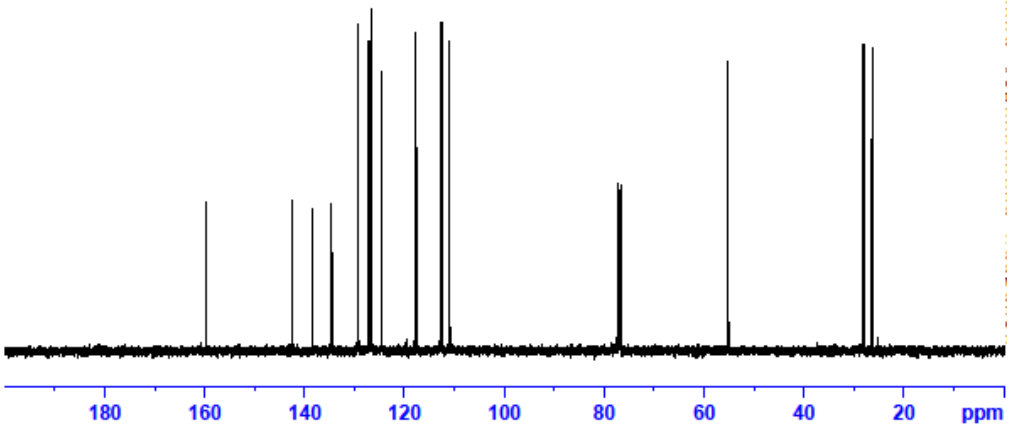




Table 4, **5ac**



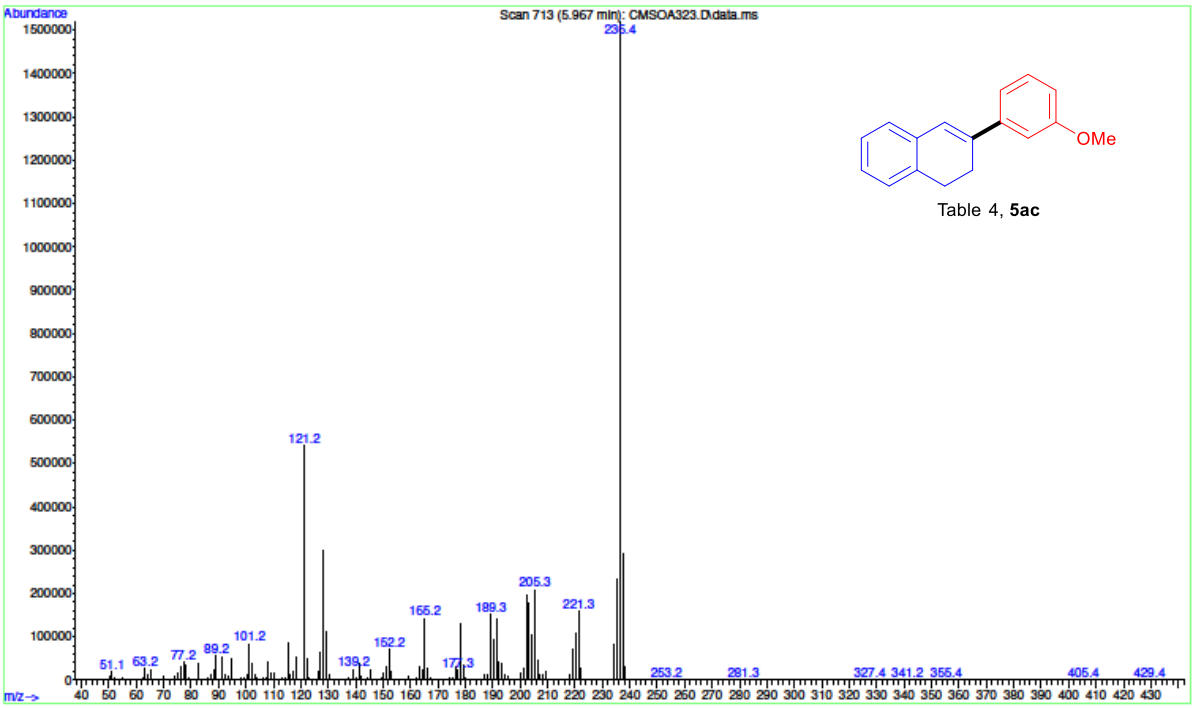
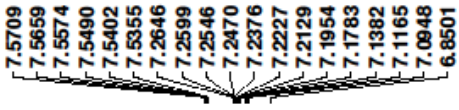

Abundance
Scan 713 (5.967 min): CMSOA323.D\data.ms
235.4
121.2
205.3
165.2
199.3
221.3
101.2
152.2
89.2
77.2
63.2
51.1
138.2
177.3
253.2
281.3
327.4
341.2
355.4
405.4
429.4
m/z-->
OMe

Table 4, **5ac**



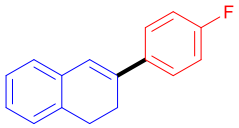
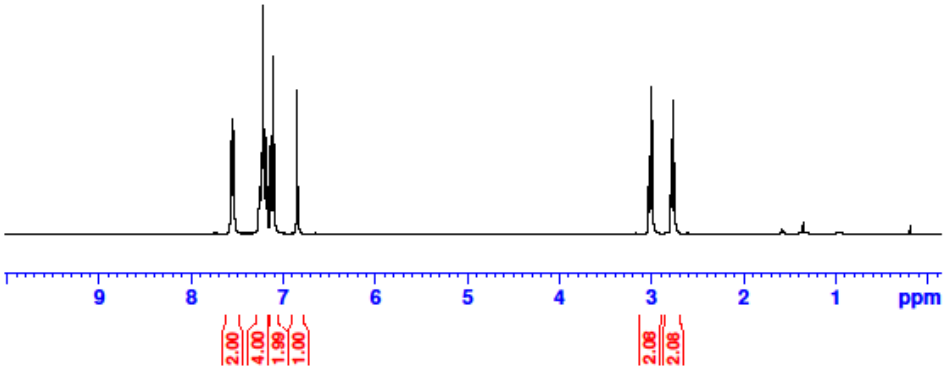
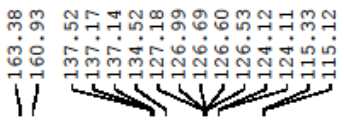
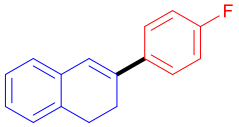




Table 4, **5ad**

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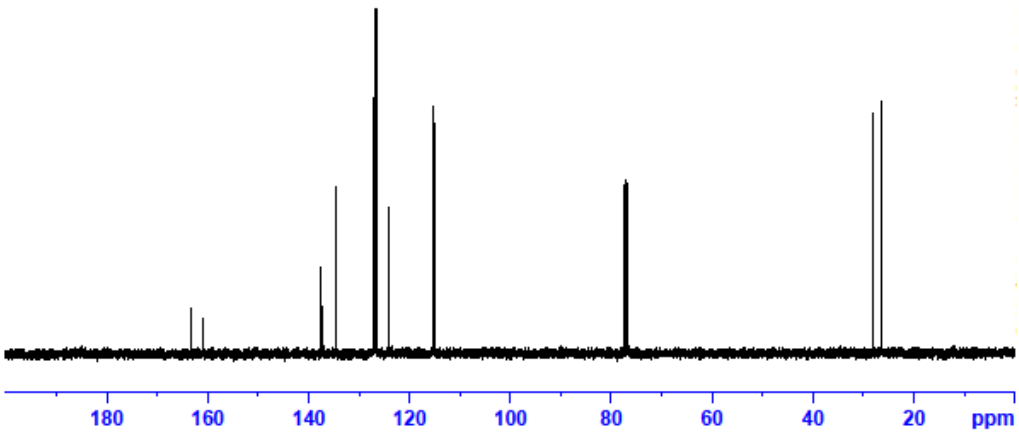

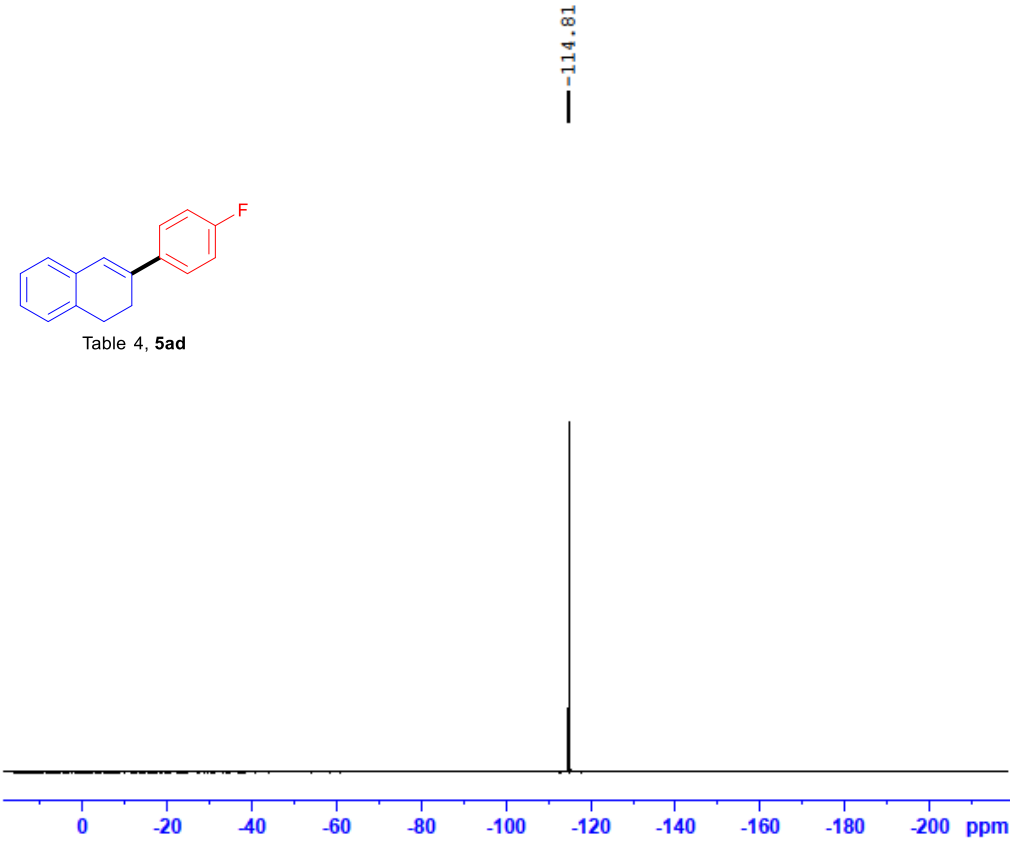


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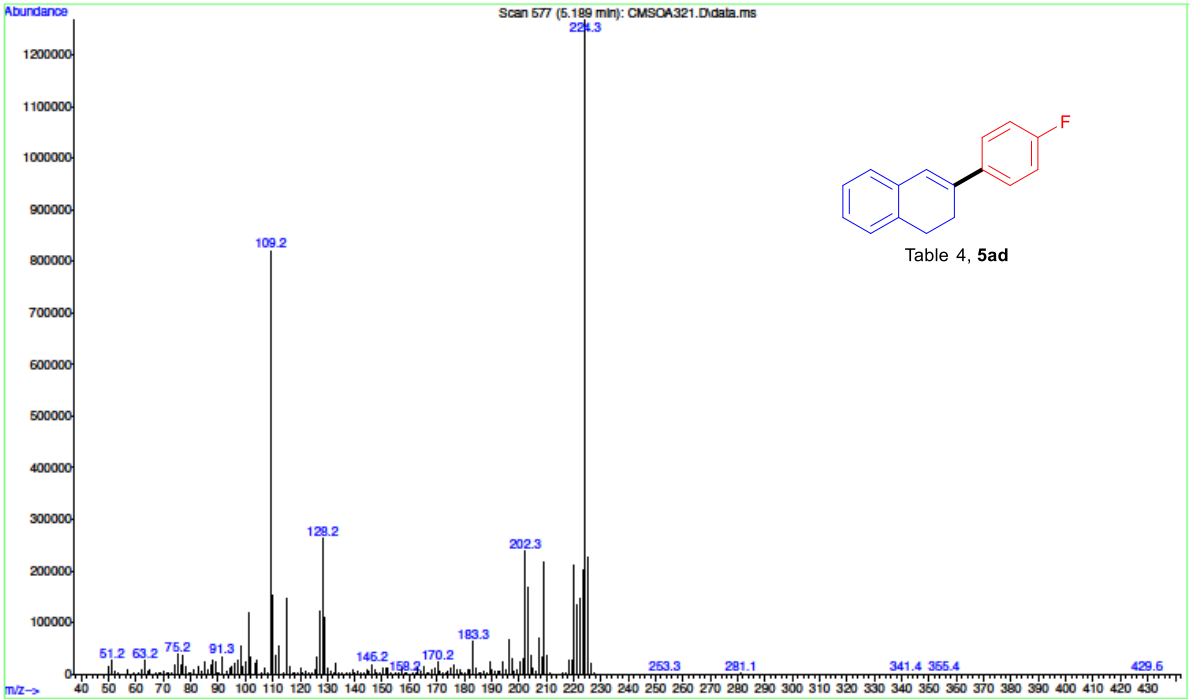


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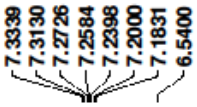


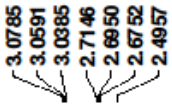


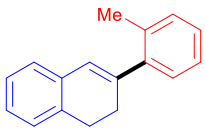


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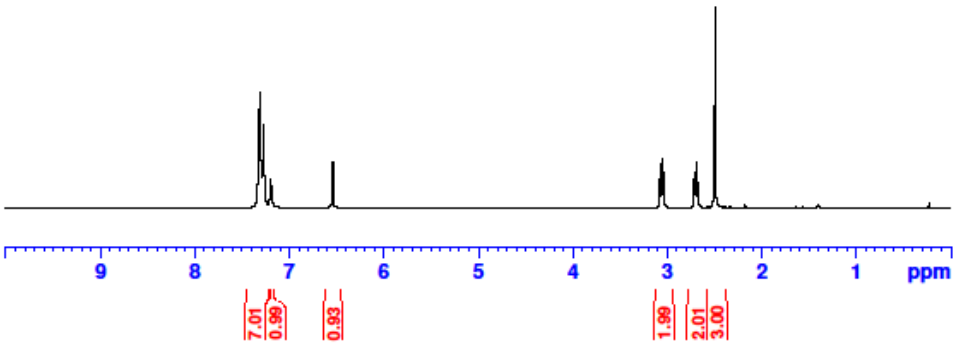


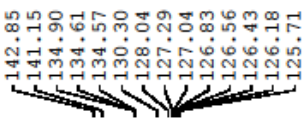


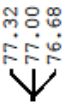


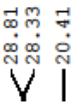


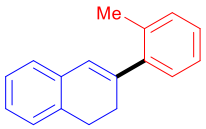


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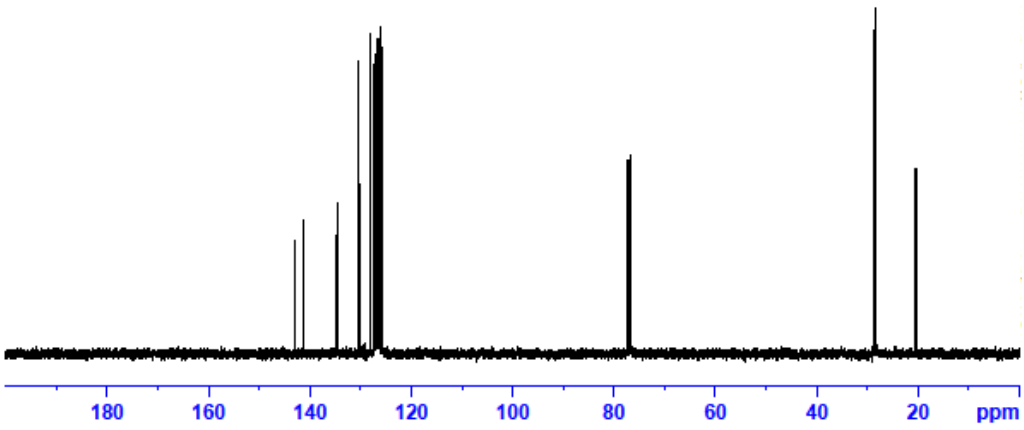

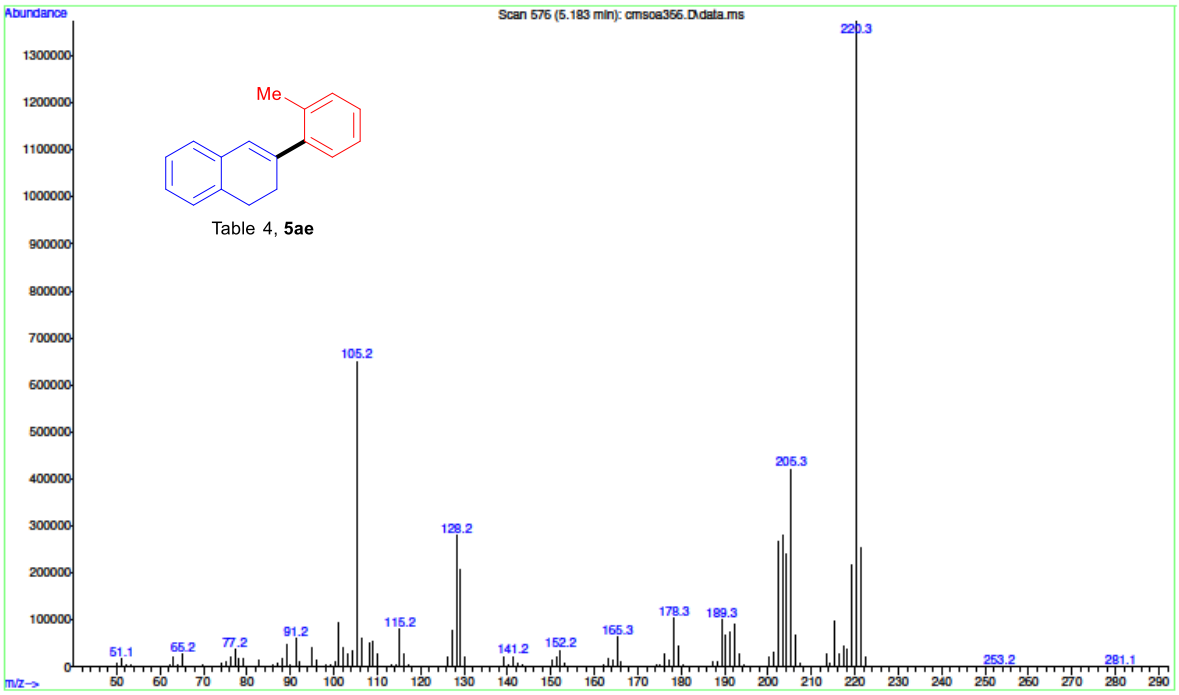
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128.2
115.2
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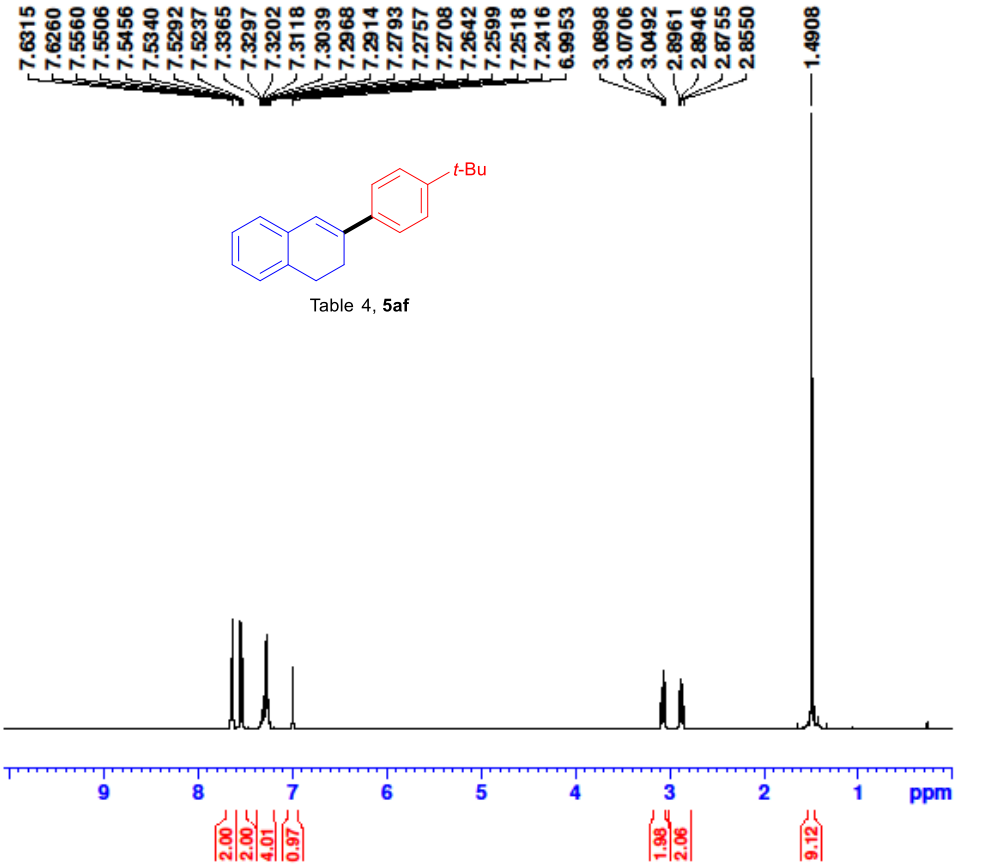
51.1
141.2
152.2
165.3
178.3
189.3
253.2
281.1
m/z-->

Table 4, **5ae**

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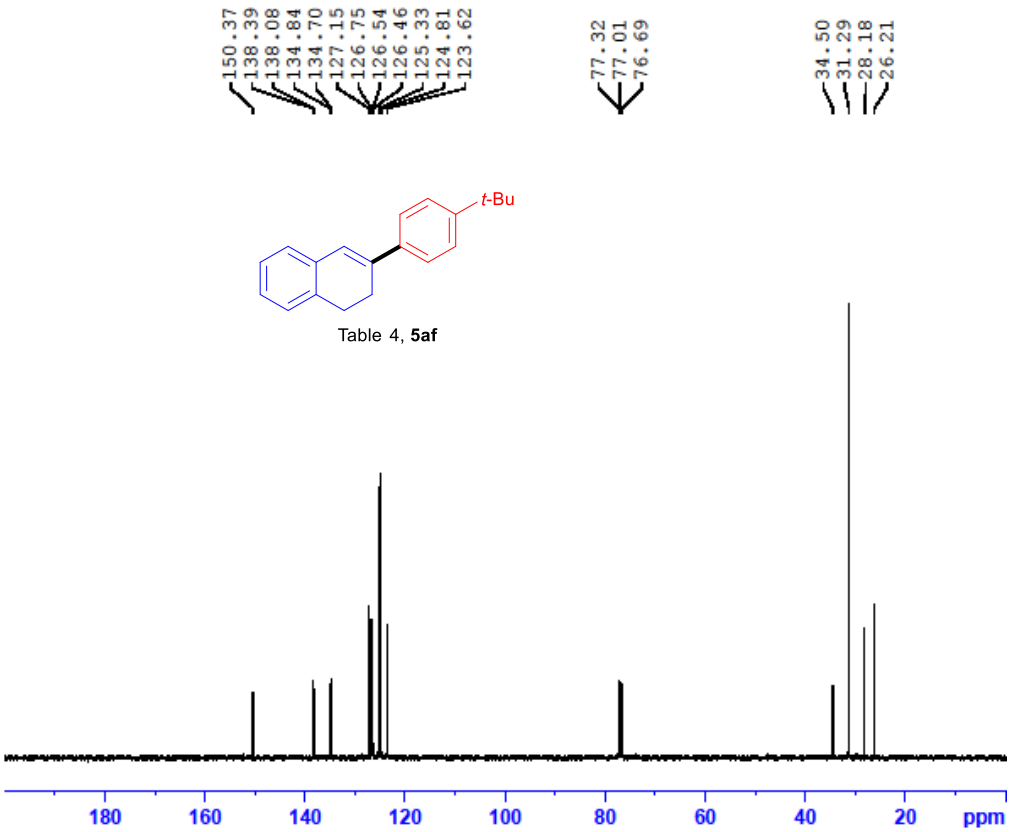


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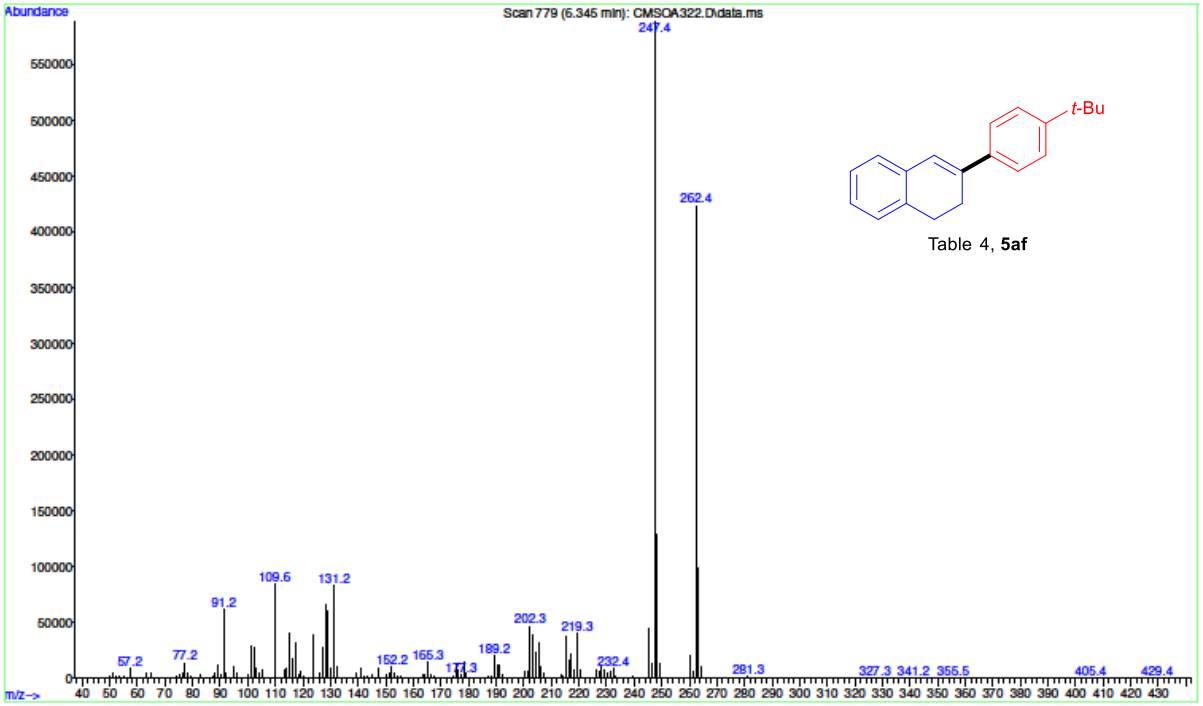
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77.2
152.2
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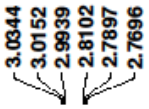
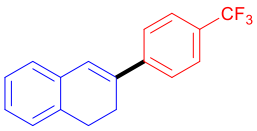
327.3
341.2
355.5
405.4
429.4
m/z-->


*t*-Bu

Table 4, **5af**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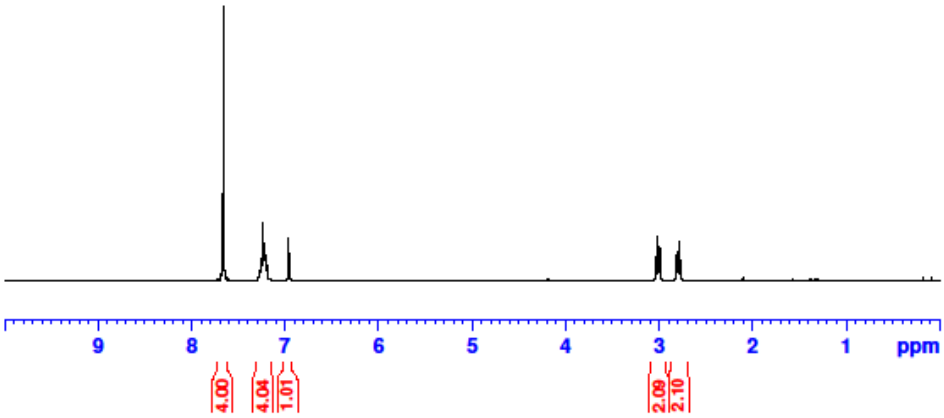


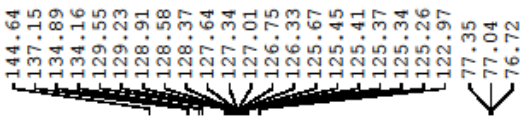


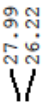


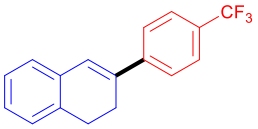


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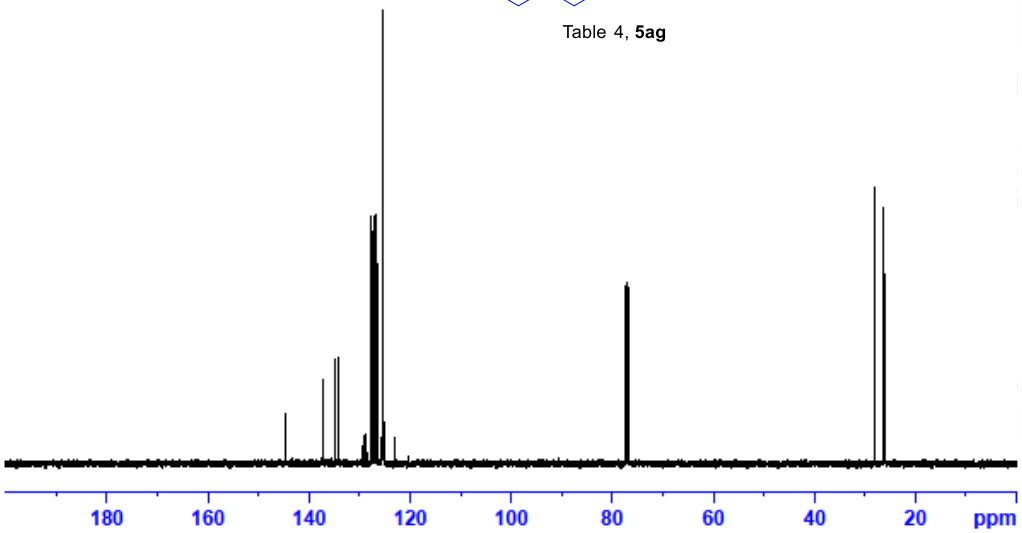

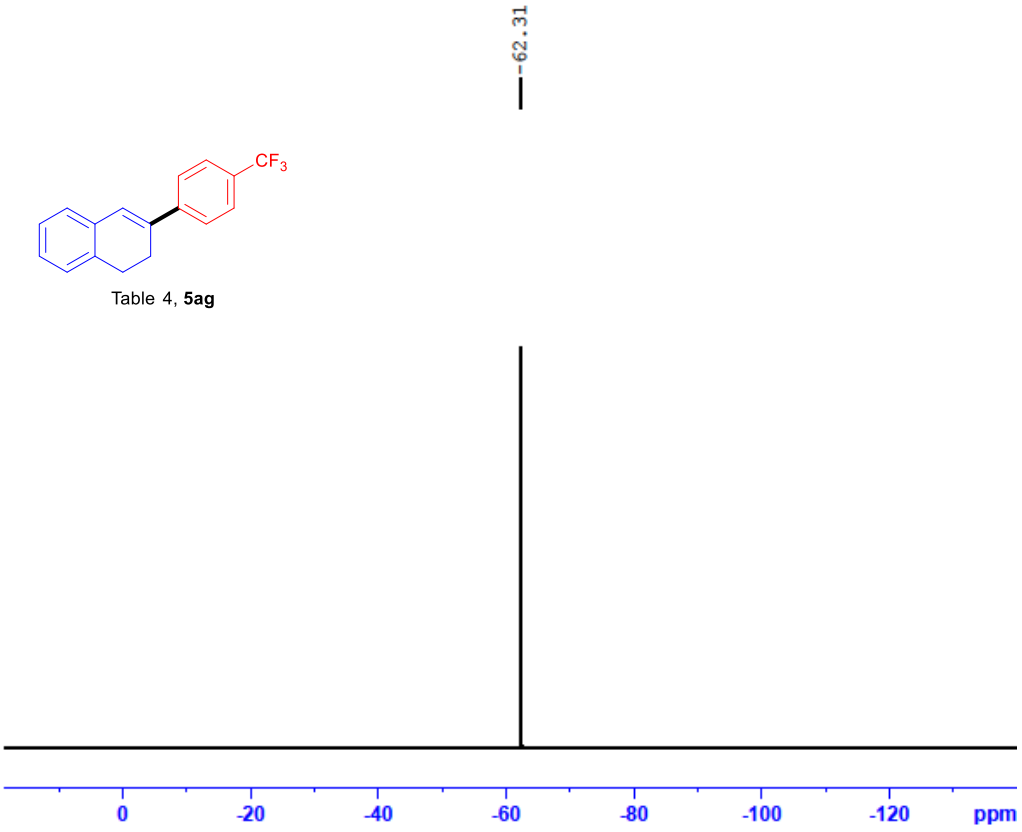


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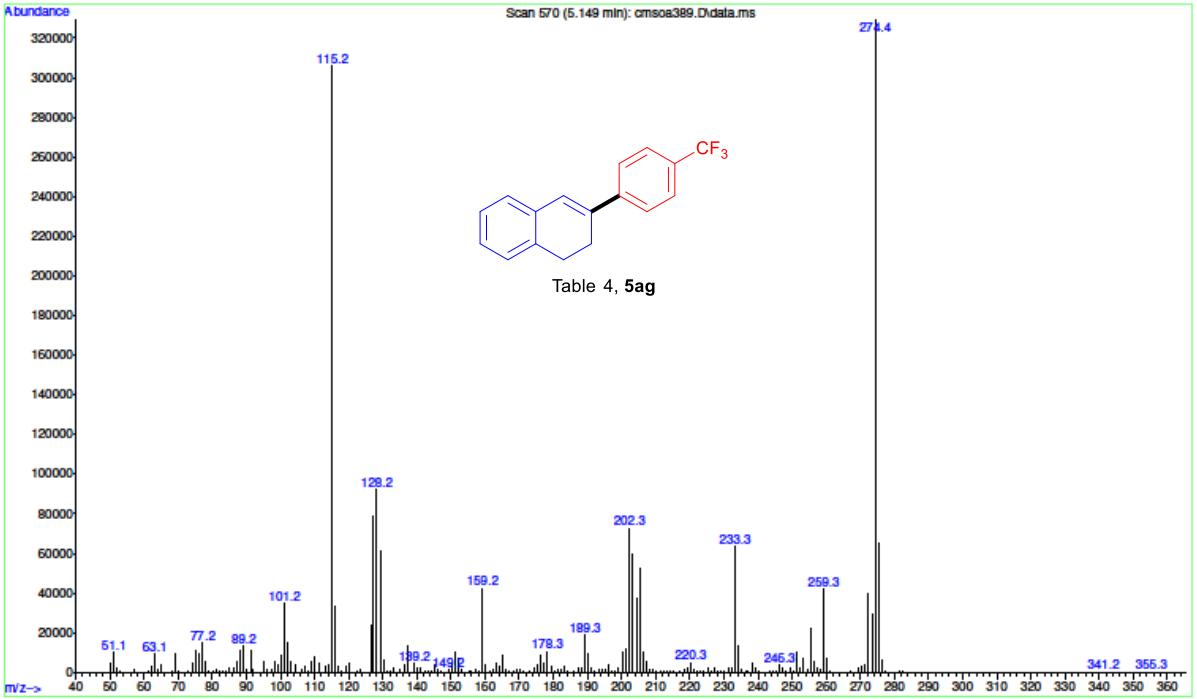


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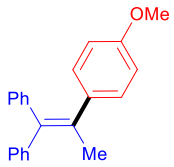


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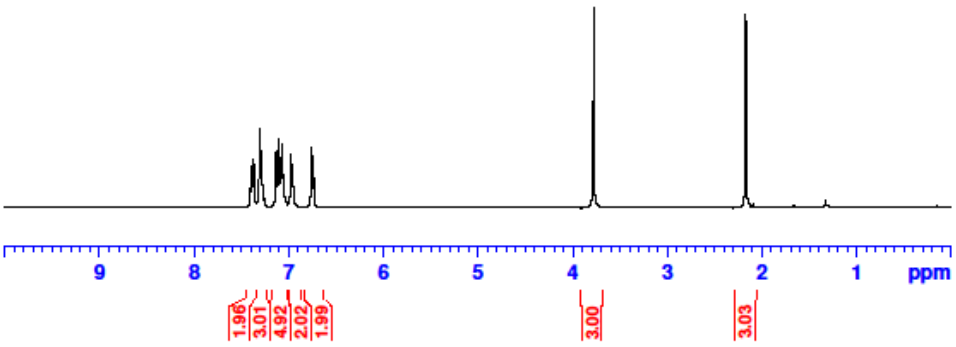



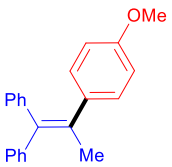


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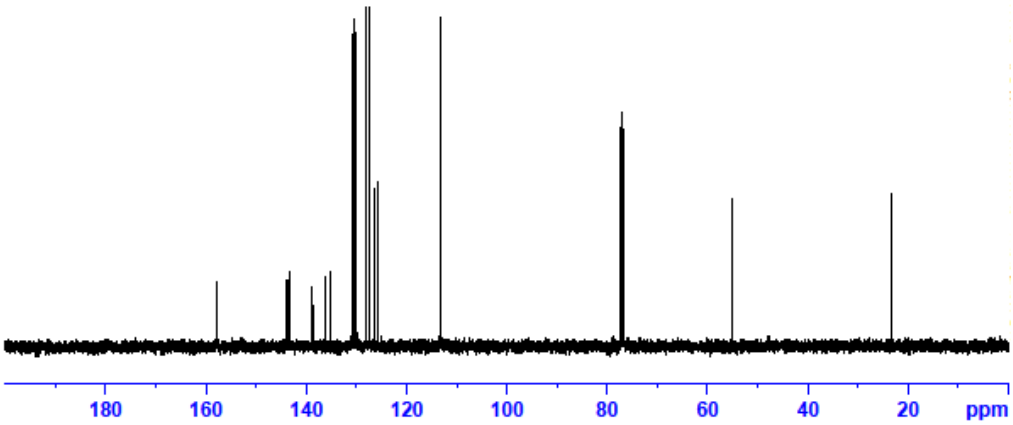

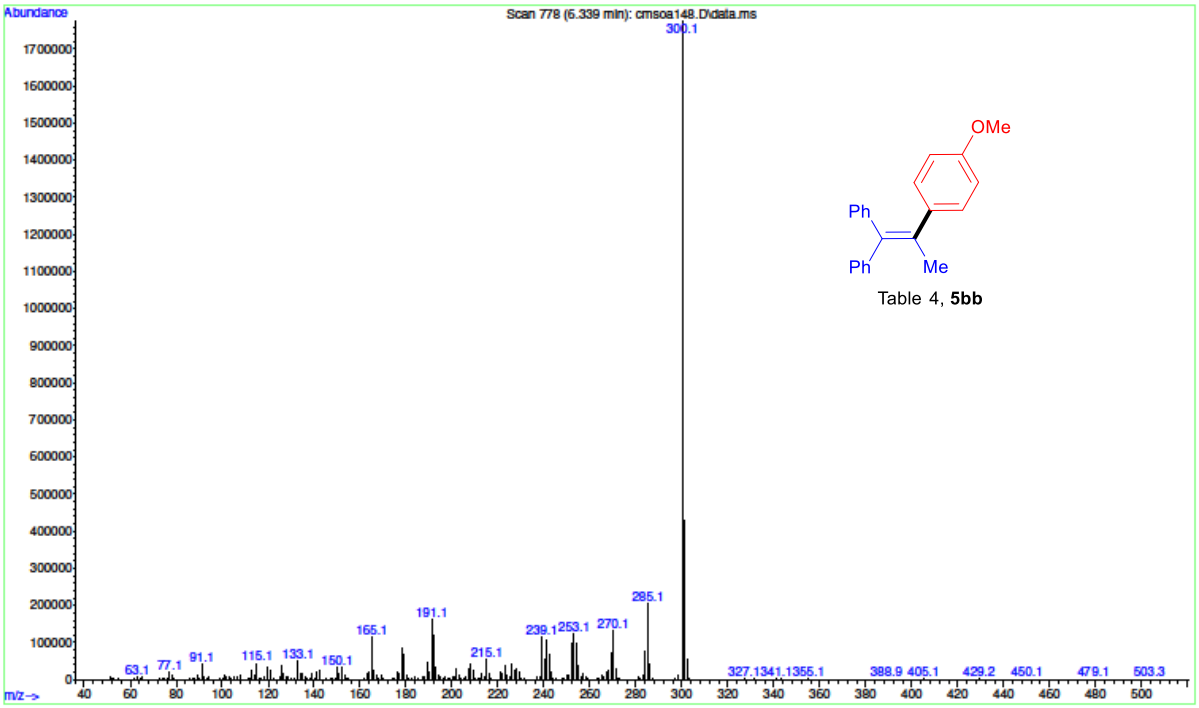
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253.1
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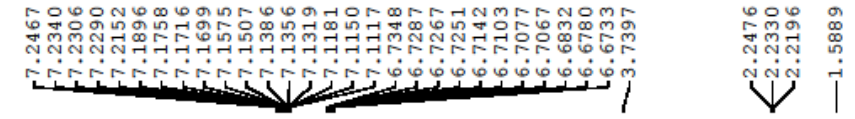
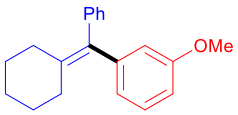
133.1
150.1
63.1
77.1
m/z-->
OMe
Ph
Ph
Me

Table 4, **5bb**

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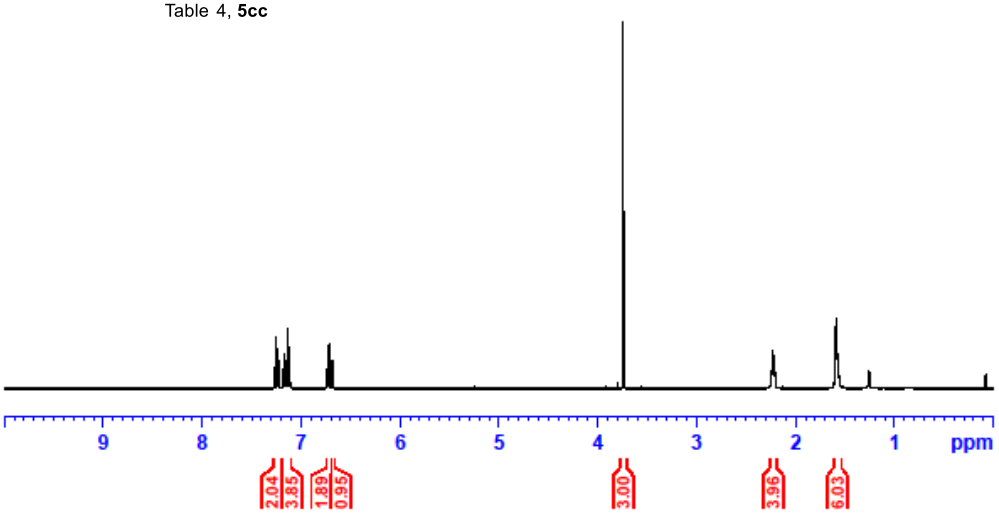


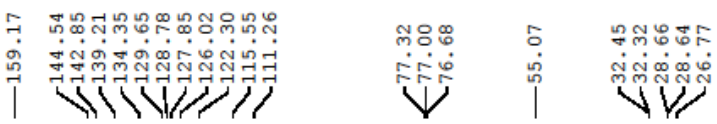


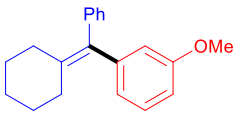


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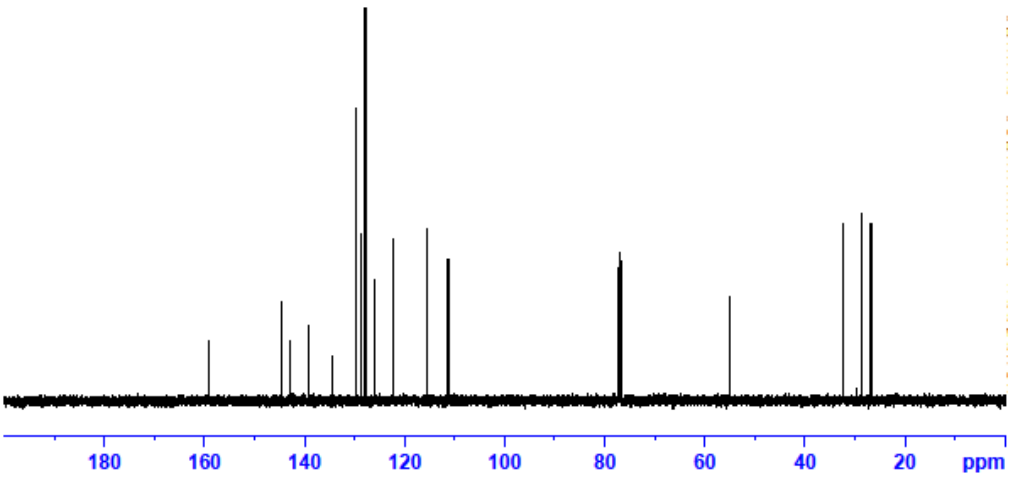

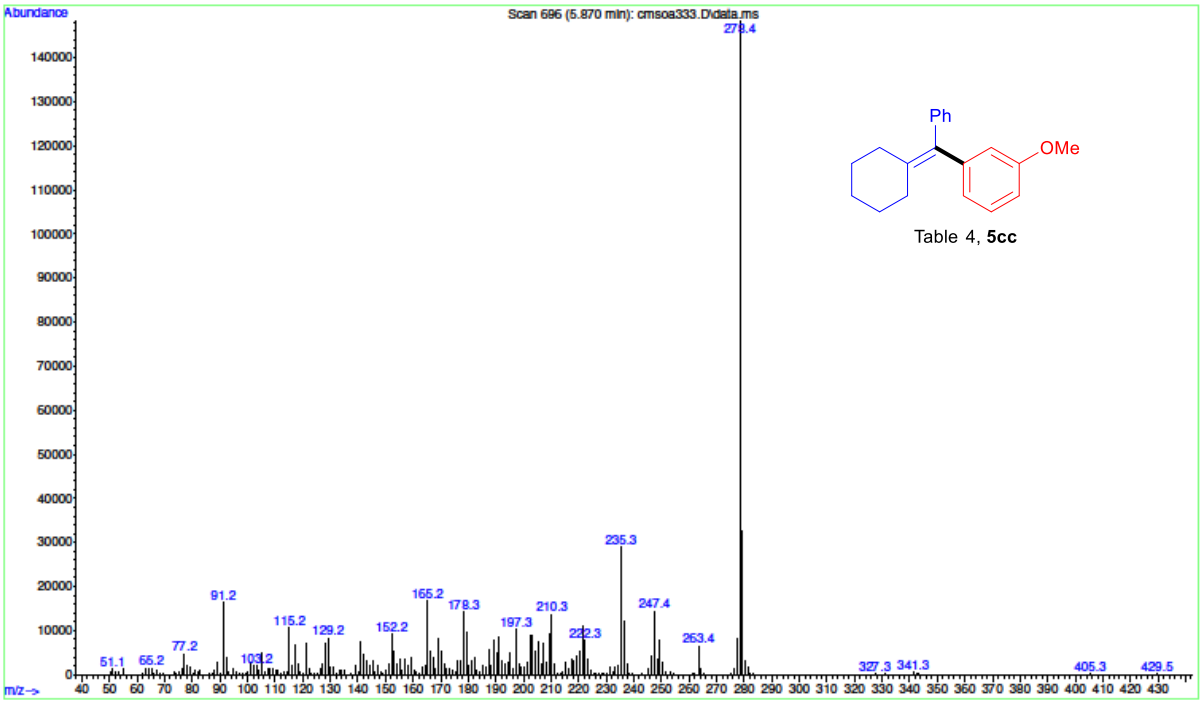
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405.3
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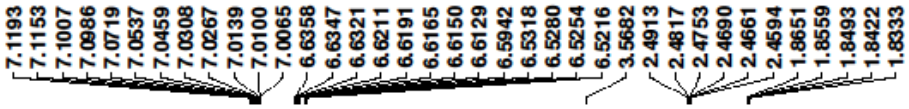
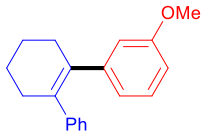
m/z-->

Table 4, **5cc**

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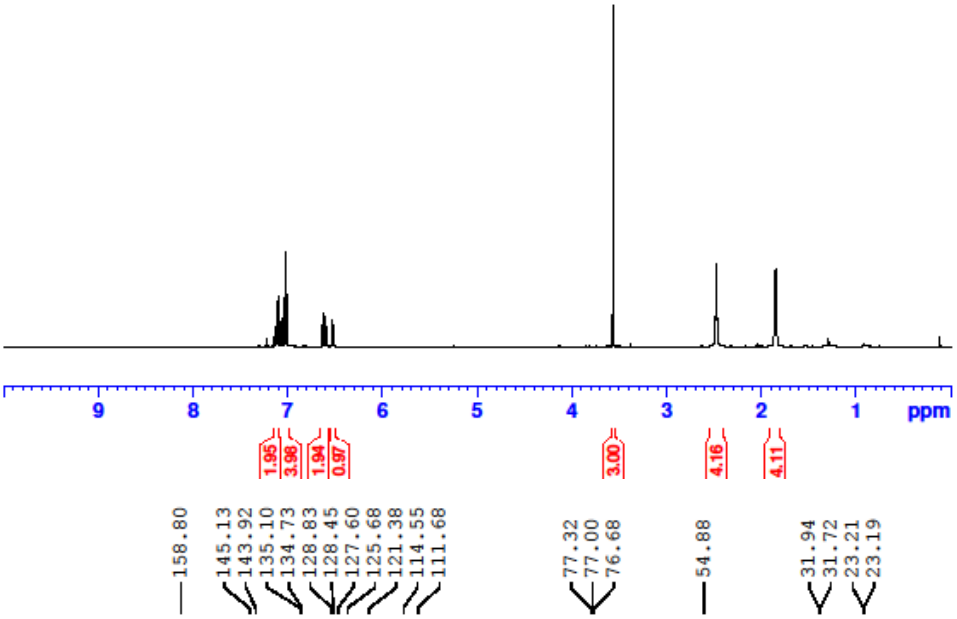





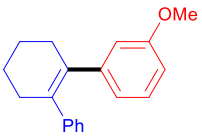


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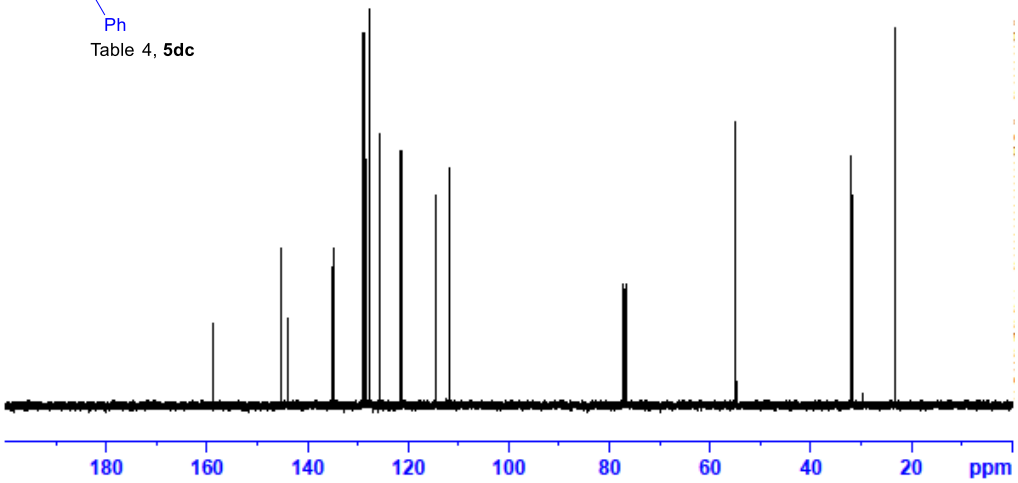

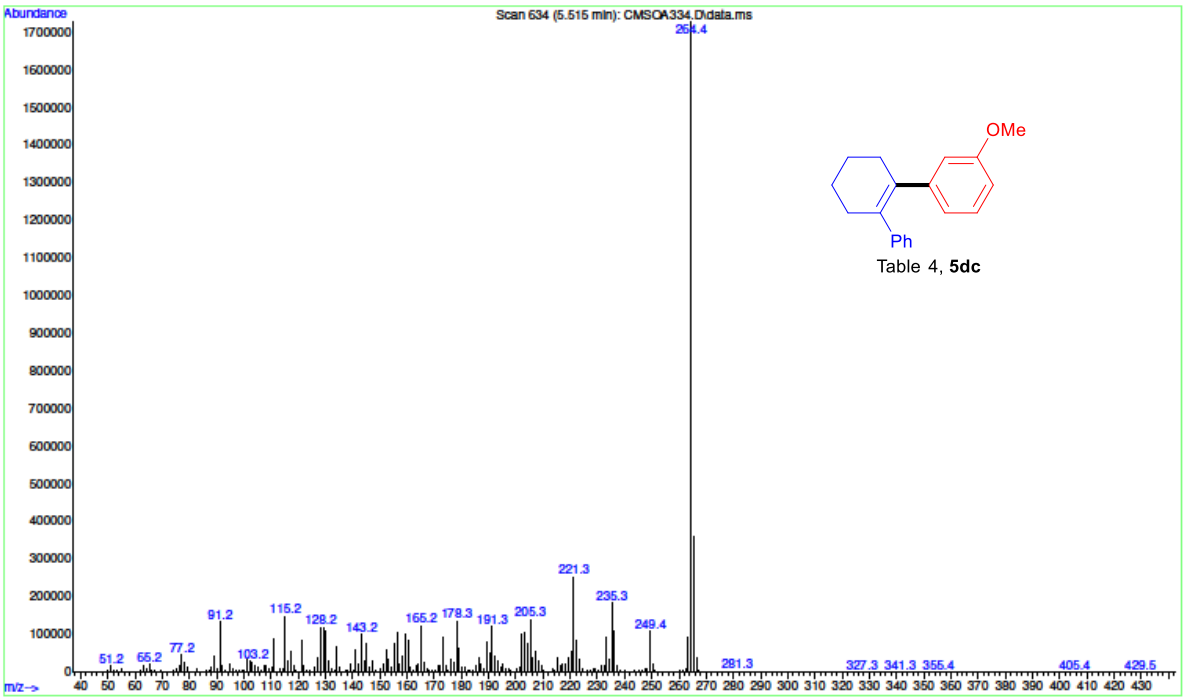
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341.3
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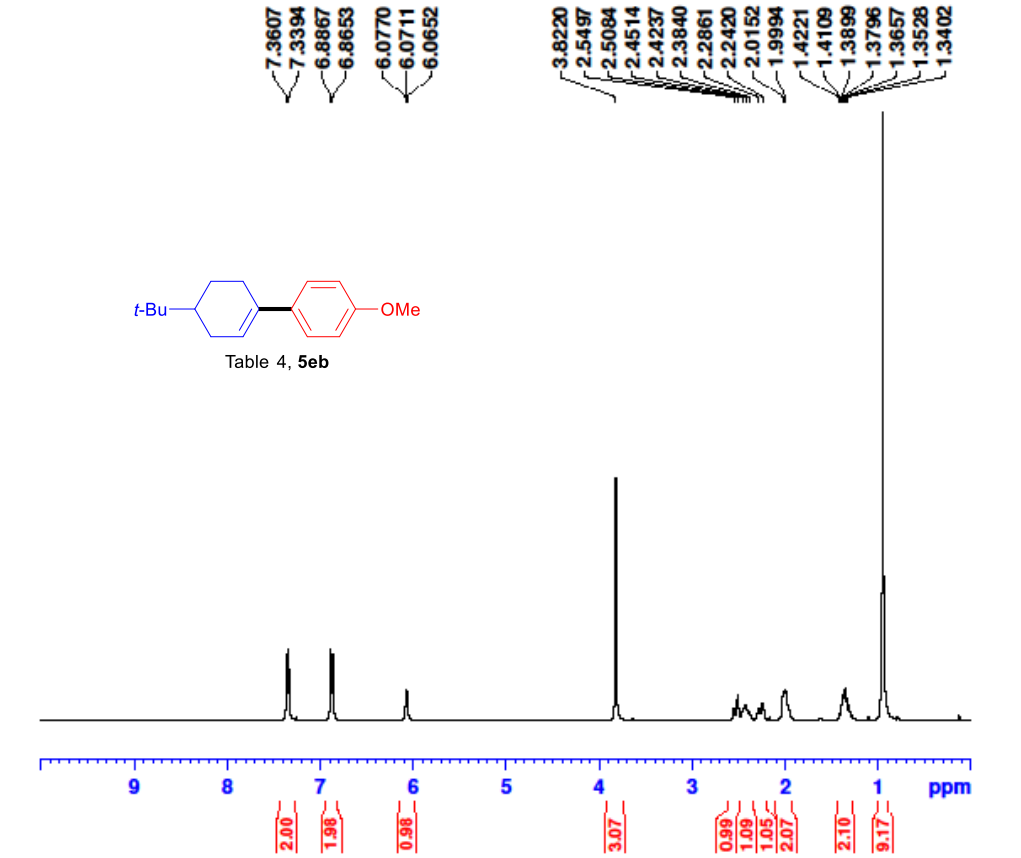
405.4
429.5
m/z-->

Table 4, **5dc**

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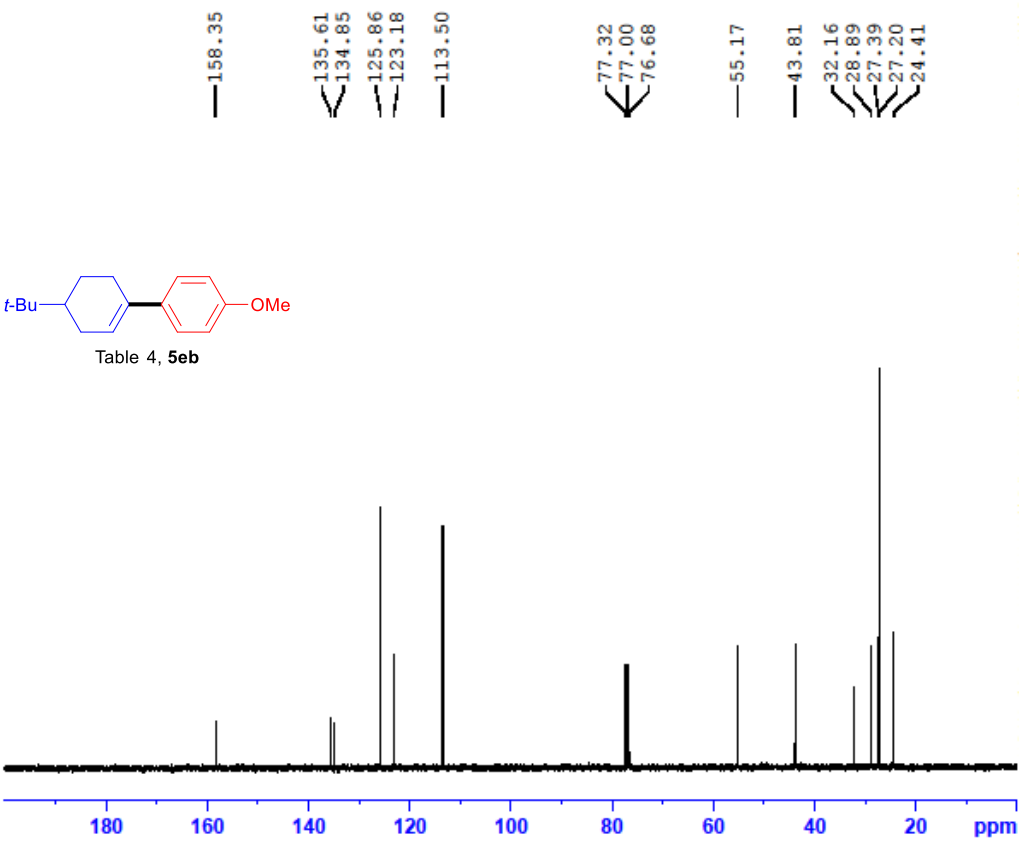


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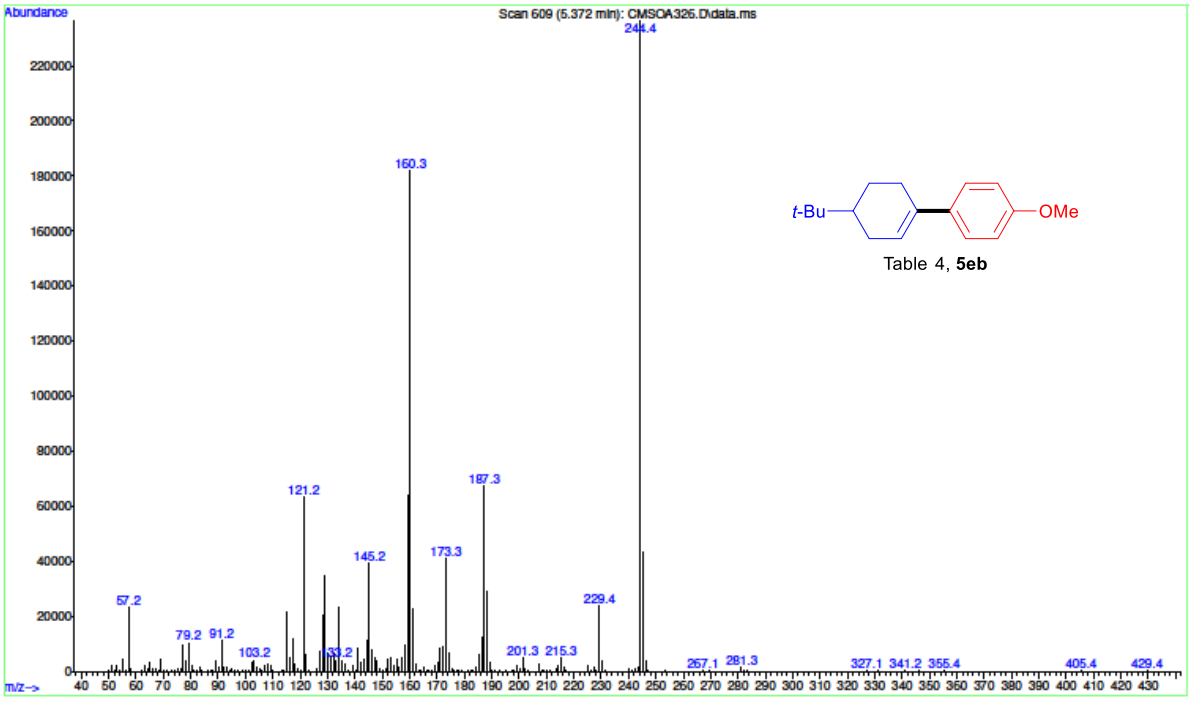
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103.2
201.3
215.3
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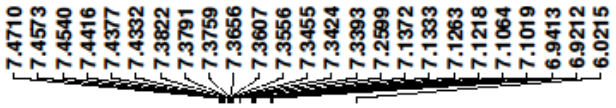
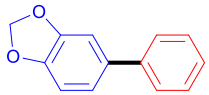
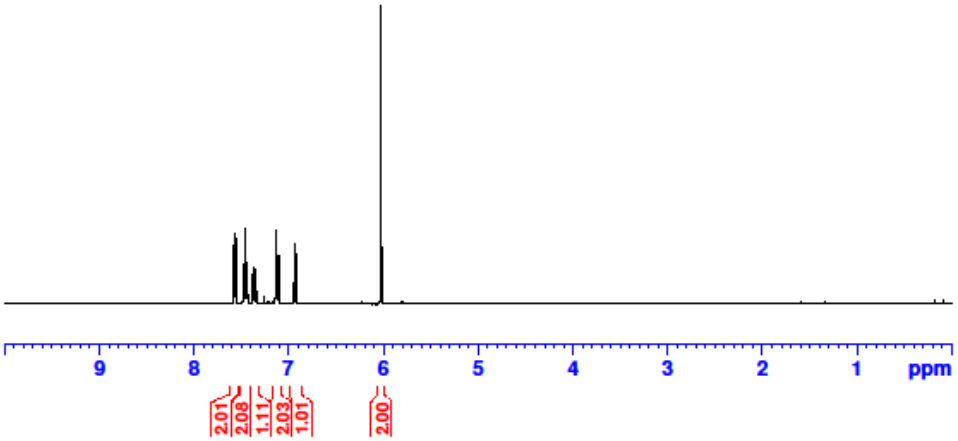
327.1
341.2
355.4
405.4
429.4
m/z-->
t-Bu
OMe

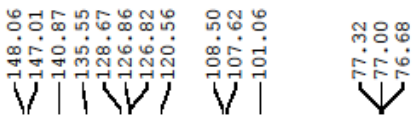
Table 4, **5eb**

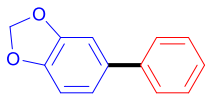


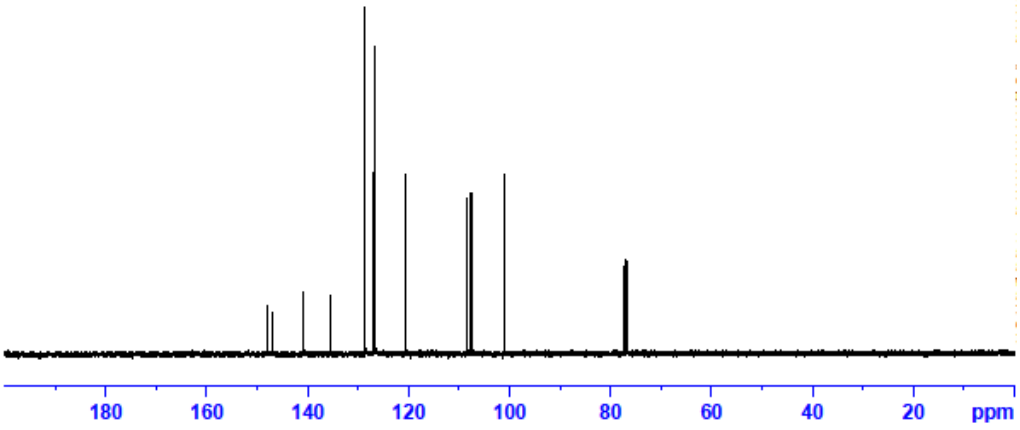
Scheme 3, **3gh**

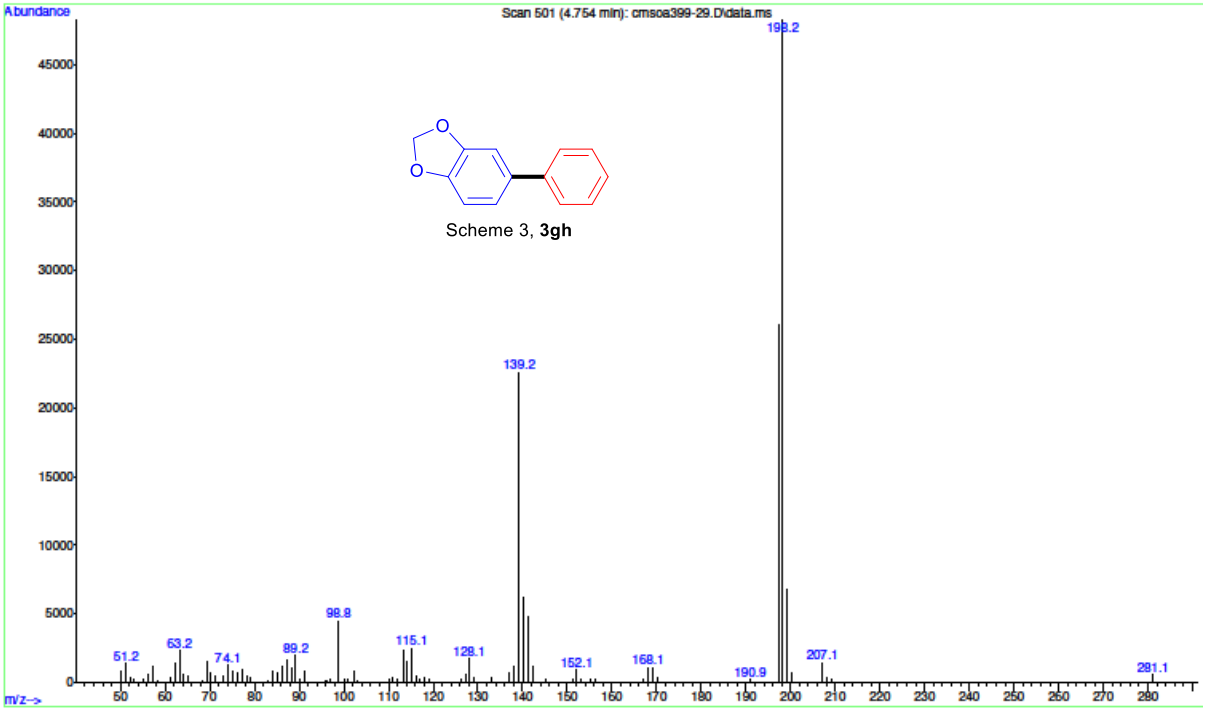


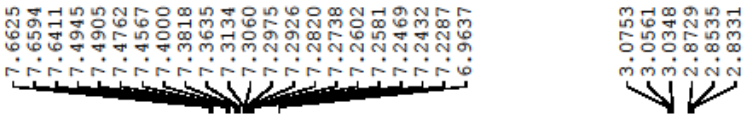



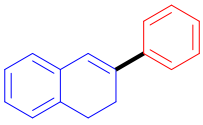
Scheme 3, **3gh**



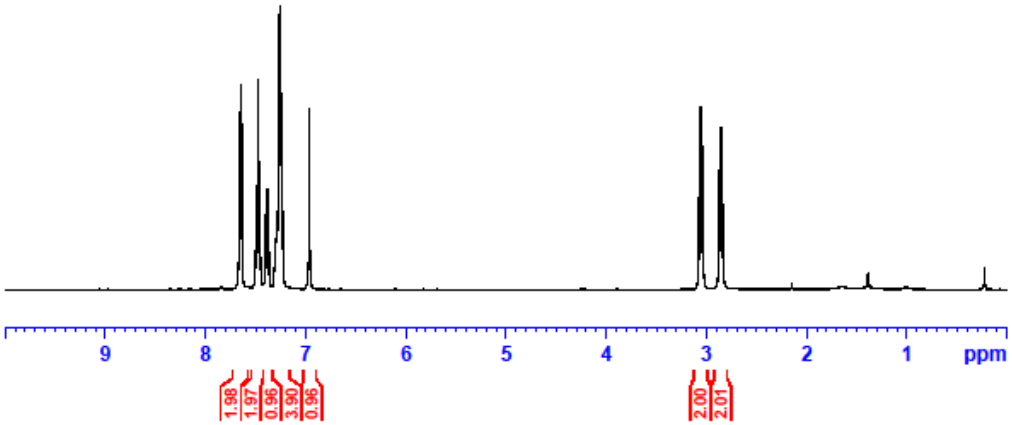

Abundance
Scan 501 (4.754 min): cmsoa399-29.D\data.ms
199.2
139.2
98.8
115.1
89.2
63.2
74.1
51.2
128.1
152.1
168.1
190.9
207.1
281.1
m/z-->

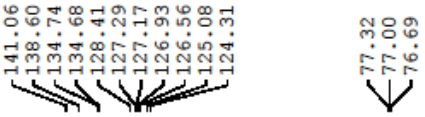
Scheme 3, **3gh**

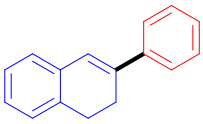


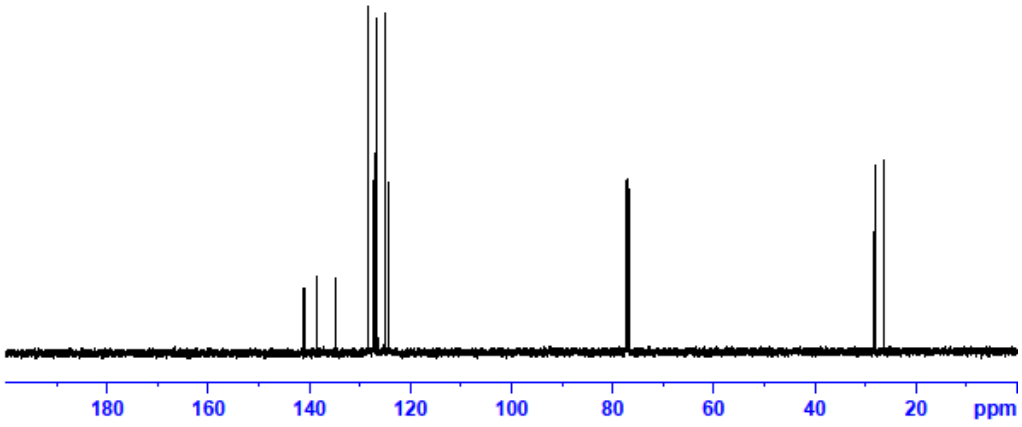
Scheme 3, **5ah**

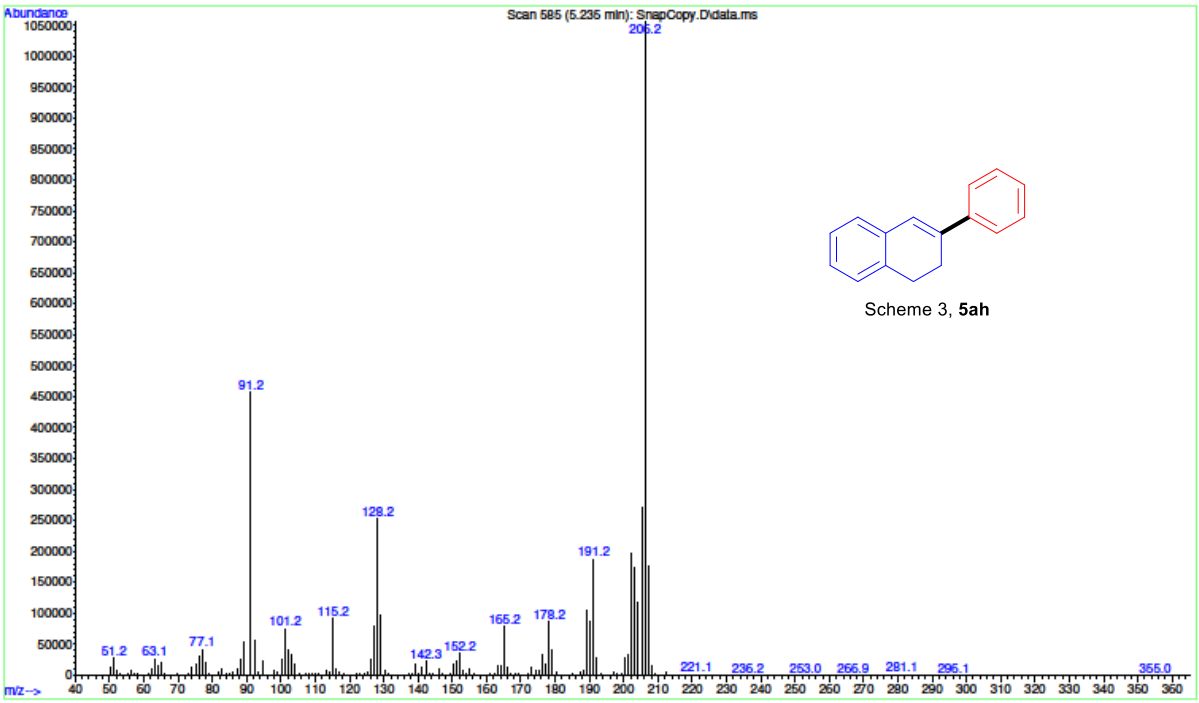


Scheme 3, **5ah**




Abundance
Scan 585 (5.235 min): SnapCopy.D\data.ms
206.2
91.2
128.2
191.2
115.2
101.2
165.2
178.2
77.1
51.2
63.1
152.2
142.3
221.1
236.2
253.0
266.9
281.1
296.1
355.0
m/z-->

Scheme 3, **5ah**

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