Palladium(II)-Catalyzed C-C Bond Formation of Arylhydrazines with Olefins via Carbon-Nitrogen Bond Cleavage

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Supporting Information

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General Methods

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware under a positive pressure of nitrogen using freshly distilled solvents. Commercial grade solvents and reagents were used without further purification. Hexane, ethyl acetate were fractionally distilled.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate.

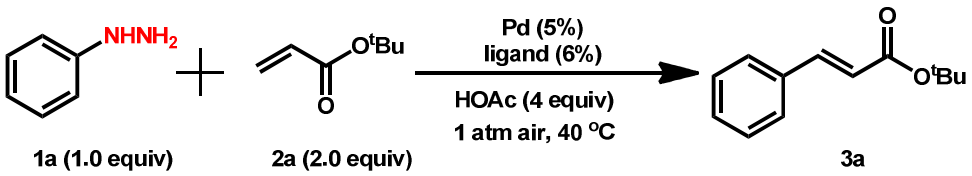
Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

Infrared spectra were recorded on a Bio-Rad FTS 165 FTIR spectrometer. The oil samples were examined under neat conditons.

High Resolution Mass (HRMS) spectra were obtained using Waters Q-Tof Permies Mass Spectrometer.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker Avance DPX 300 and Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.2600, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dddd (doublets of doublets of doublets of doublet); dt (doublets of triplet); or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.0, triplet).

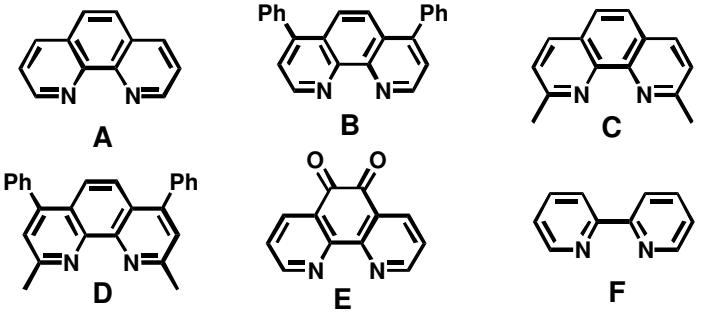
Screening of the optimal conditions:



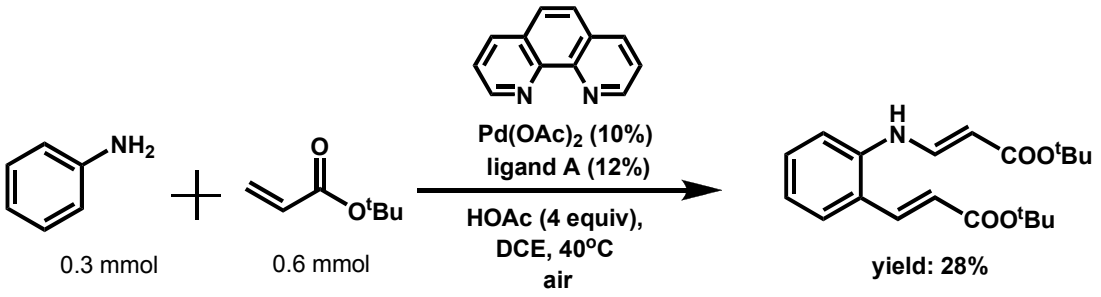
1a (1.0 equiv) 2a (2.0 equiv) 3a

entry	Pd	Ligand	Solvent	Time (h)	yield (**3a**) (%)[b]
1	NO	NO	DCE	2h	trace
2	$Pd(OAc)_2$	NO	DCE	4h	22%
3	$Pd(OAc)_2$	**A**	DCE	2h	68%
4	$PdCl_2$	**A**	DCE	2h	61%
5	$Pd(OCOCF_3)_2$	**A**	DCE	2h	57%
6	$Pd(dba)_2$	**A**	DCE	2h	41%
7	$Pd(OAc)_2$	B	DCE	2h	72%
8	$Pd(OAc)_2$	C	DCE	2h	81%
9	$Pd(OAc)_2$	D	DCE	2h	83%
10	$Pd(OAc)_2$	E	DCE	2h	23%
11	$Pd(OAc)_2$	F	DCE	2h	77%
12	$Pd(OAc)_2$	D	THF	2h	75%
13	$Pd(OAc)_2$	D	toluene	2h	80%
14	$Pd(OAc)_2$	D	CH_3CN	2h	75%
15	$Pd(OAc)_2$	D	DMSO	2h	51%
16	$Pd(OAc)_2$	D	$CHCl_3$	2h	78%
17	$Pd(OAc)_2$	D	PhCl	2h	92%
18	$Pd(OAc)_2$	D	1,4-dioxane	2h	72%
19	$Pd(OAc)_2$	D	MeOH	2h	85%
20[c]	$Pd(OAc)_2$	D	PhCl	2h	91%
21[d]	$Pd(OAc)_2$	D	PhCl	2h	91%
21[d,e]	$Pd(OAc)_2$	D	PhCl/MeOH	2h	92%

[a] Unless noted otherwise, the reactions were carried out on a 0.30 mmol scale of **1a** with 4 equiv of HOAc (1.2 mmol), and 2.0 equiv **2a** (0.6 mmol) in solvent (0.5 mL). [b] Isolated yield. [c] 50mg 4A° MS was added. [d] with 3% $Pd(OAc)_2$. [e] reaction was done in PhCl:MeOH= 4:1(0.4 mL:0.1 mL).

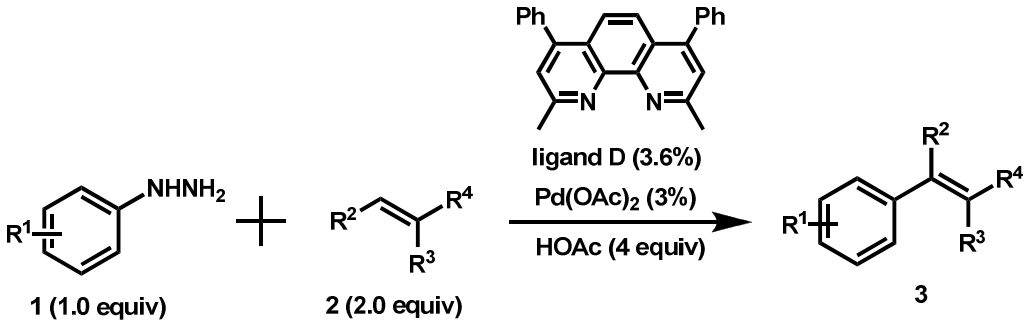


Procedure for Palladium(II)-Catalyzed C-C bond formation of aniline with *tert*-butyl acrylate:



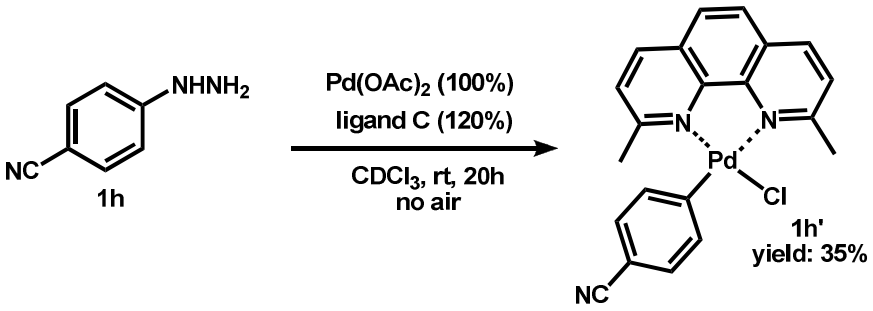
A 5 mL round bottomed flask equipped with a magnetic stirring bar was charged with aniline (0.30 mmol), $Pd(OAc)_2$ (10 mol %, 0.03 mmol), 1,10-phenanthroline (3.6 mol %, 0.036 mmol), *tert*-butyl acrylate (0.60 mmol) and 4 equiv of HOAc (1.2 mmol) a in DCE. The flask was stirred at 40 ^{o}C in air (1 atm) for 12 h and judged by TLC. The reaction mixture was cooled to room temperature, The solvent was removed under the reduced pressure and the residue was purified through column chromatography on silica gel.

General Procedure for Palladium(II)-Catalyzed C-C bond formation of arylhydrazines with olefins:



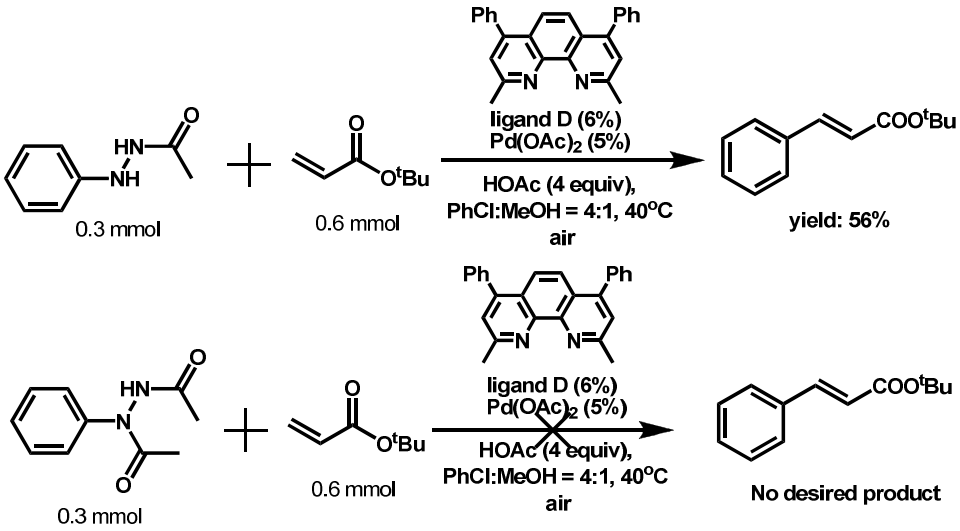
A 5 mL round bottomed flask equipped with a magnetic stirring bar was charged with arylhydrazine (0.30 mmol), $Pd(OAc)_2$ (3 mol %, 0.009 mmol), 2,9-dimethyl-4,7-diphenyl -1,10-phenanthroline (3.6 mol %, 0.0108 mmol), and 4 equiv of HOAc (1.2 mmol) a in Ph / MeOH = 4:1 (0.4 mL:0.1 mL). The flask was stirred at 40 ^{o}C in air (1 atm) for 2-12 h and judged by TLC. The reaction mixture was cooled to room temperature, The solvent was removed under the reduced pressure and the residue was purified through column chromatography on silica gel.

Procedure for synthesis of (2,9-dimethyl-1,10-phenanthroline)-4-cyanophenyl-palladium(II) chloride (1h'):



A solution of preformed $Pd(OAc)_2$ (67.3 mg, 0.3 mmol), 2,9-dimethyl-1,10 -phenanthroline (75 mg, 0.36 mmol) in 2 mL of chloroform-d was treated with the 4-hydrazinylbenzonitrile (40 mg, 0.30 mmol) and the resulting mixture was stirred at room temperature for 12 h in glove-box. The solvent is removed under reduced pressure to a volume of approx. 0.2 mL and the crude product is precipitated by addition of 4 mL of absolute diethylether. The crude product is washed with further diethyl ether and the dried under reduced pressure. It is taken up in 3 mL of dichloromethane and filtered through a pad of Celite. The remaining solution is evaporated to dryness under reduced pressure to leave the product as a white solid.

Procedure for Palladium(II)-Catalyzed C-C bond formation of N'-phenyl- acetohydrazide with *tert*-butyl acrylate:

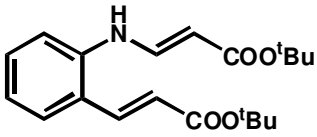


A 5 mL round bottomed flask equipped with a magnetic stirring bar was charged with N'-phenyl-acetohydrazide (0.30 mmol), $Pd(OAc)_2$ (5 mol %, 0.015 mmol), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (6 mol %, 0.018 mmol), *tert*-butyl acrylate (0.60 mmol) and 4 equiv of HOAc (1.2 mmol) in PhCl / MeOH = 4:1 (0.4 mL:0.1 mL). The

flask was stirred at 40 °C in air (1 atm) for 12 h and judged by TLC. The reaction mixture was cooled to room temperature, The solvent was removed under the reduced pressure and the residue was purified through column chromatography on silica gel.

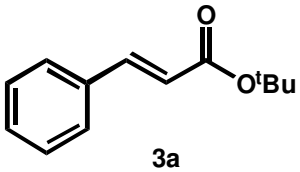
Characterization Data for the product

(*E*)-*tert*-butyl 3-(2-((*E*)-3-tert-butoxy-3-oxoprop-1-enyl)phenylamino)acrylate: This



compound was prepared by the general procedure described above and was obtained as a yellow oil in 28% yield: R_f = 0.65 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.70 (d, 1H, *J* = 12.8 Hz, NH), 7.70 (d, 1H, *J* = 13.2 Hz, ArH), 7.32-7.40 (m, 3H), 7.04-7.10 (m, 3H), 6.06 (d, 1H, *J* = 15.6 Hz, CH), 1.58 (s, 9H, $3CH_3$), 1.50 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 167.9, 146.5, 141.8, 139.7, 129.8, 124.0, 116.5, 112.4, 99.8, 81.4, 79.4, 28.4, 28.3 ppm; HRMS (ESI, m/z): calcd. for $C_{20}H_{27}NO_4H^+$ 346.2018, found 346.2022.

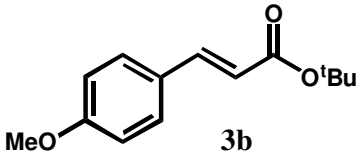
***tert*-butyl cinnamate (3a):** This compound was prepared by the general procedure described



3a

above and was obtained as a yellow oil in 91% yield: R_f = 0.72 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, 1H, *J* = 16.0 Hz, CH), 7.49-7.52 (m, 2H, ArH), 7.36-7.38 (m, 3H, ArH), 6.37 (d, 1H, *J* = 16.0 Hz, CH), 1.54 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 143.5, 134.7, 130.0, 128.8, 128.0, 120.2, 80.5, 28.2 ppm; HRMS (ESI, m/z): calcd. for $C_{13}H_{16}O_2Na^+$ 227.1048, found 227.1042.

(*E*)-*tert*-butyl 3-(4-methoxyphenyl)acrylate (3b): This compound was prepared by the

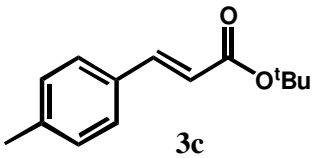


3b

general procedure described above and was obtained as a yellow solid in 90% yield: R_f = 0.70 (hexane : ethyl acetate = 7:1); Mp = 39.5-40.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, 1H, *J* = 16.0 Hz, CH), 7.45 (d, 2H, *J* = 8.4 Hz, ArH), 6.88 (d, 2H, *J* = 8.8 Hz, ArH), 6.24 (d, 1H, *J* = 16.0 Hz, CH), 3.82 (s, 3H, OCH_3), 1.52 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 161.1, 143.2, 129.6, 127.4, 117.7, 114.3, 80.2, 55.3, 28.2 ppm; HRMS (ESI, m/z): calcd. for $C_{14}H_{18}O_3Na^+$ 257.1154, found 257..1158.

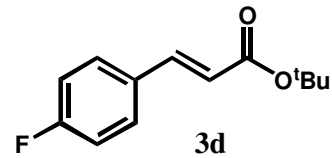
(*E*)-*tert*-butyl 3-p-tolylacrylate (3c): This compound was prepared by the general procedure

described above and was obtained as a yellow oil in 92% yield: R_f = 0.74 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, 1H, *J* = 16.0 Hz, CH), 7.40 (d, 2H, *J* = 8.0 Hz, ArH), 7.17 (d, 2H, *J* = 7.6 Hz, ArH), 6.33 (d, 1H, *J* = 16.0 Hz, CH), 2.36 (s, 3H, CH_3), 1.54 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 143.6, 140.3, 132.0, 129.6, 128.0, 119.1, 80.3, 28.2, 21.4 ppm; HRMS (ESI, m/z): calcd. for $C_{14}H_{18}O_2Na^+$ 241.1204, found 241.1199.



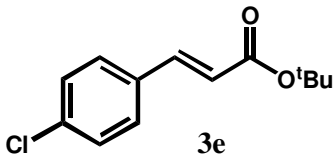
3c

(*E*)-*tert*-butyl 3-(4-fluorophenyl)acrylate (3d): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 85% yield: R_f = 0.75 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, 1H, *J* = 16.0 Hz, CH), 7.46-7.49 (m, 2H, ArH), 7.02-7.07 (m, 2H, ArH), 6.28 (d, 1H, *J* = 16.0 Hz, CH), 1.52 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 163.6 (d, *J* = 237.0 Hz), 142.2, 130.9 (d, *J* = 3.3 Hz), 129.8 (d, *J* = 8.6 Hz), 120.0 (d, *J* = 2.1Hz), 115.9 (d, *J* = 21.9 Hz), 80.6, 28.2 ppm; HRMS (ESI, m/z): calcd. for $C_{13}H_{15}O_2FNa^+$ 245.0954, found 245.0950.



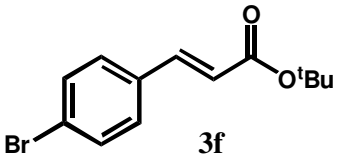
3d

(*E*)-*tert*-butyl 3-(4-chlorophenyl)acrylate (3e): This compound was prepared by the general procedure described above and was obtained as a white solid in 85% yield: R_f = 0.74 (hexane : ethyl acetate = 7:1); Mp = 67.3-68.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, 1H, *J* = 16.0 Hz, CH), 7.42 (d, 2H, *J* = 8.4 Hz, ArH), 7.33 (d, 2H, *J* = 8.4 Hz, ArH), 6.33 (d, 1H, *J* = 16.0 Hz, CH), 1.52 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 142.1, 135.8, 133.2, 129.1, 120.8, 80.7, 28.2 ppm; HRMS (ESI, m/z): calcd. for $C_{13}H_{16}O_2H^+$ 239.0839, found 239.0832.



3e

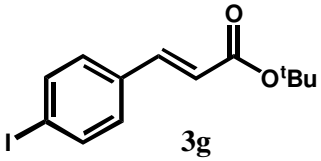
(*E*)-*tert*-butyl 3-(4-bromophenyl)acrylate (3f): This is compound was prepared by the general procedure described above and was obtained as a white solid in 81% yield: R_f = 0.74 (hexane : ethyl acetate = 7:1); Mp = 64.8-65.9 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, 1H, *J* = 16.0 Hz, CH), 7.49 (d, 2H, *J* = 8.0 Hz, ArH), 7.35 (d, 2H, *J* = 8.4 Hz, ArH), 6.34 (d, 1H, *J* = 16.0 Hz, CH), 1.52 (s, 9H, 3CH3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 142.1, 133.6,



3f

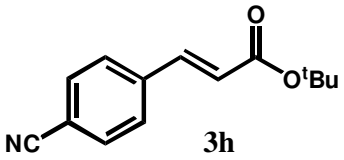
132.1, 129.3, 124.1, 120.9, 80.7, 28.2 ppm; HRMS (ESI, m/z): calcd. for $C_{13}H_{15}O_2Na^+$ 305.0153, found 305.0148.

(*E*)-*tert*-butyl 3-(4-iodophenyl)acrylate (3g): This is compound was prepared by the general procedure described above and was obtained as a yellow solid in 80% yield: R_f = 0.74 (hexane : ethyl acetate = 7:1); Mp = 66.2-67.4 ^oC;^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, 2H, *J* = 8.0 Hz, ArH), 7.48 (d, 1H, *J* = 16.0 Hz, CH), 7.22 (d, 2H, *J* = 8.4 Hz, ArH), 6.36 (d, 1H, *J* = 16.0 Hz, CH), 1.52 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 142.3, 138.0, 134.2, 129.4, 121.0, 96.1, 80.7, 28.2 ppm; HRMS (ESI, m/z): calcd. for $C_{13}H_{15}O_2INa^+$ 353.0015, found 353.0020.



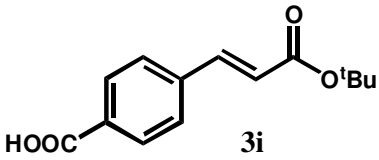
3g

(*E*)-*tert*-butyl 3-(4-cyanophenyl)acrylate (3h): This is compound was prepared by the general procedure described above and was obtained as a white solid in 93% yield: R_f = 0.62 (hexane : ethyl acetate = 7:1); Mp = 154.8-155.9 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 2H, *J* = 8.0 Hz, ArH), 7.58 (d, 2H, *J* = 8.4 Hz, ArH), 7.55 (d, 1H, *J* = 16.0 Hz, CH), 6.44 (d, 1H, *J* = 16.0 Hz, CH), 1.53 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 141.1, 139.0, 132.6, 128.3, 123.8, 118.4, 113.1, 81.2, 28.1 ppm; HRMS (ESI, m/z): calcd. for $C_{14}H_{15}NO_2Na^+$ 252.1000, found 252.0995.



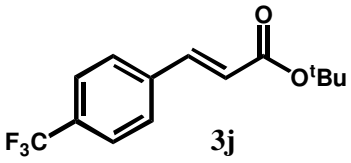
3h

(*E*)-4-(3-*tert*-butoxy-3-oxoprop-1-enyl)benzoic acid (3i): This is compound was prepared by the general procedure described above and was obtained as a white solid in 98% yield: R_f = 0.35 (dichloromethane : ethyl acetate = 3:1); ^1H NMR (400 MHz, $CDCl_3$): δ 10.96 (b, 1H, COOH), 8.11 (d, 2H, *J* = 8.0 Hz, ArH), 7.61 (d, 1H, *J* = 16.0 Hz, CH), 7.59 (d, 2H, *J* = 8.0 Hz, ArH), 6.73 (d, 1H, *J* = 16.0 Hz, CH), 1.54 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 165.8, 142.0, 139.8, 130.7, 130.3, 127.9, 123.0, 81.1, 28.2 ppm; HRMS (ESI, m/z): calcd. for $C_{14}H_{16}O_4Na^+$ 271.0946, found 271.0941



3i

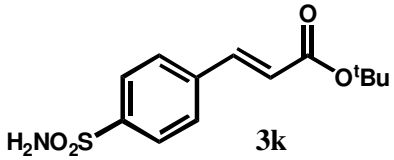
(*E*)-*tert*-buty(E)-tert-butyl 3-(4-(trifluoromethyl)phenyl)acrylate (3j): This is compound was prepared by the general procedure described above and was obtained as a yellow oil in 85% yield: R_f = 0.71 (hexane : ethyl acetate = 7:1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.57-7.63



3j

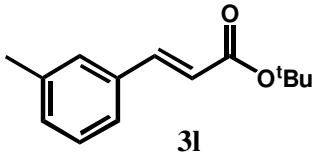
(m, 4H, ArH), 7.59 (d, 1H, *J* = 16.0 Hz, CH), 6.43 (d, 1H, *J* = 16.0 Hz, CH), 1.54 (s, 9H, 3CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 141.6, 138.1, 131.5 (q, *J* = 32.0 Hz), 128.0, 125.8 (q, *J* = 4.0 Hz), 123.9 (q, *J* = 270.0 Hz), 122.8, 81.0, 28.1 ppm; HRMS (ESI, m/z): calcd. for $C_{14}H_{15}O_2F_3Na^+$ 295.0922, found 295.0927.

(*E*)-*tert*-butyl 3-(4-sulfamoylphenyl)acrylate (3k): This is compound was prepared by the general procedure described above and was obtained as a white solid in 85% yield: R_f = 0.46 (dichloromethane : methanol= 7:1); Mp = 91.8-92.9 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.71-7.88 (m, 4H, ArH), 7.58 (d, 1H, *J* = 16.0 Hz, CH), 7.41 (b, 2H, NH_2), 6.63 (d, 1H, *J* = 16.0 Hz, CH), 1.52 (s, 9H, 3CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.7, 145.5, 142.3, 137.8, 129.1, 126.6, 122.9, 80.8, 28.3 ppm; HRMS (ESI, m/z): calcd. for $C_{13}H_{17}NO_4SNa^+$ 306.0776, found 306.0782.



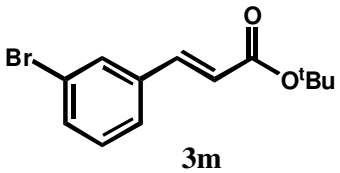
3k

(*E*)-*tert*-butyl 3-m-tolylacrylate (3l): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 93% yield: R_f = 0.74 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 1H, *J* = 16.0 Hz, CH), 7.29-7.31 (m, 2H, ArH), 7.23-7.27 (m, 1H, ArH), 7.16 (d, 1H, *J* = 7.3 Hz, ArH), 6.35 (d, 1H, *J* = 16.0 Hz, CH), 2.35 (s, 3H, CH_3), 1.53 (s, 9H, 3CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 143.7, 138.4, 134.6, 130.8, 128.7, 128.6, 125.2, 120.0, 80.4, 28.2, 21.3 ppm; HRMS (ESI, m/z): calcd. for $C_{14}H_{18}O_2Na^+$ 241.1204, found 241.1202.



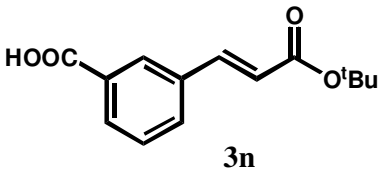
3l

(*E*)-*tert*-butyl 3-(3-bromophenyl)acrylate (3m): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 93% yield: R_f = 0.72 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H, ArH), 7.49 (d, 1H, *J* = 16.0 Hz, CH), 7.47-7.48 (m, 1H, ArH), 7.41 (d, 1H, *J* = 7.7 Hz, ArH), 7.21-7.25 (m, 1H, ArH), 6.36 (d, 1H, *J* = 16.0 Hz, CH), 1.53 (s, 9H, 3CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 141.8, 136.8, 132.7, 130.6, 130.3, 126.6, 123.0, 121.7, 80.8, 28.2 ppm; HRMS (ESI, m/z): calcd. for $C_{13}H_{15}O_2BrNa^+$ 305.0153, found 305.0155.



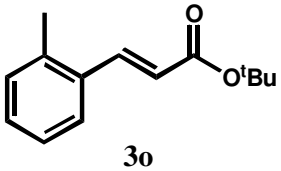
3m

(*E*)-3-(3-*tert*-butoxy-3-oxoprop-1-enyl)benzoic acid (3n): This compound was prepared by the general procedure described above and was obtained as a white solid in 94% yield: R_f = 0.38 (dichloromethane : ethyl acetate = 3:1); Mp = 159.5-160.7 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 10.8 (b, 1H, COOH), 8.26 (s, 1H, ArH), 8.10 (d, 1H, *J* = 7.8 Hz, ArH), 7.73 (d, 1H, *J* = 7.7 Hz, ArH), 7.63 (d, 1H, *J* = 16.0 Hz, CH), 7.49 (t, 1H, *J* = 7.7 Hz, ArH), 6.47 (d, 1H, *J* = 16.0 Hz, CH), 1.54 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 166.0, 142.2, 135.2, 132.9, 131.4, 130.1, 129.5, 129.1, 121.7, 80.9, 28.2 ppm; HRMS (ESI, m/z): calcd. for $C_{14}H_{16}O_4Na^+$ 271.0946, found 271.0937.



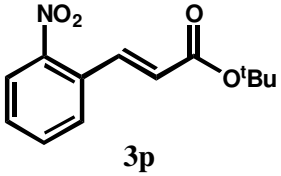
3n

(*E*)-*tert*-butyl 3-o-tolylacrylate (3o): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 73% yield: R_f = 0.71 (hexane : ethyl acetate = 7:1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, 1H, *J* = 16.0 Hz, CH), 7.54 (d, 1H, *J* = 8.3 Hz, ArH), 7.23-7.25 (m, 1H, ArH), 7.17-7.20 (m, 2H, ArH), 6.29 (d, 1H, *J* = 15.9 Hz, CH), 2.43 (s, 3H, CH_3), 1.54 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 141.3, 137.5, 133.6, 130.7, 129.7, 126.4, 126.3, 121.1, 80.5, 28.2, 19.8 ppm; HRMS (ESI, m/z): calcd. for $C_{14}H_{18}O_2Na^+$ 241.1204, found 241.1201.



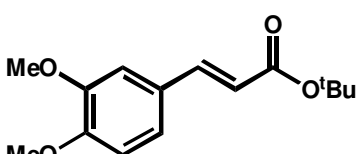
3o

(*E*)-*tert*-butyl 3-(2-nitrophenyl)acrylate (3p): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 75% yield: R_f = 0.65 (hexane : ethyl acetate = 7:1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, 1H, *J* = 16.0 Hz, CH), 7.99-8.00 (m, 1H, ArH), 7.62-7.63 (m, 2H, ArH), 7.49-7.53 (m, 1H, ArH), 6.29 (d, 1H, *J* = 15.9 Hz, CH), 1.53 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 148.4, 138.7, 133.4, 130.8, 130.0, 129.1, 125.3, 124.9, 81.2, 28.1 ppm; HRMS (ESI, m/z): calcd. for $C_{13}H_{15}NO_4Na^+$ 272.0899, found 272.0896.



3p

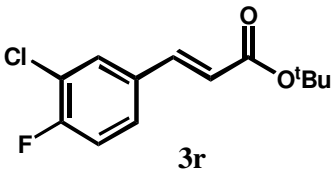
(*E*)-*tert*-butyl 3-(3,4-dimethoxyphenyl)acrylate (3q): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 88% yield: R_f = 0.61 (hexane : ethyl acetate = 7:1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, 1H, *J* = 16.0



3q

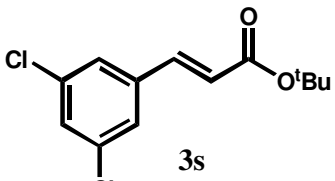
Hz, CH), 7.27 (s, 1H, ArH), 7.24 (d, 1H, *J* = 6.7 Hz, ArH), 7.11 (d, 1H, *J* = 7.8 Hz, ArH), 6.31 (d, 1H, *J* = 15.9 Hz, CH), 2.26 (s, 6H, $2OCH_3$), 1.54 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 143.7, 139.0, 137.0, 132.4, 130.1, 129.2, 125.6, 118.9, 80.3, 28.2, 19.8, 19.7 ppm; HRMS (ESI, m/z): calcd. for $C_{15}H_{20}O_4Na^+$ 287.1259, found 278.1261.

(*E*)-*tert*-butyl 3-(3-chloro-4-fluorophenyl)acrylate (3r): This compound was prepared by the general procedure described above and was obtained as a yellow oil in 82% yield: R_f = 0.68 (hexane : ethyl acetate = 7:1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, 1H, *J* = 1.8 Hz, *J* = 6.9 Hz, ArH), 7.46 (d, 1H, *J* = 16.0 Hz, CH), 7.34-7.37 (m, 1H, ArH), 7.13 (t, 1H, *J* = 8.6 Hz, ArH), 6.29 (d, 1H, *J* = 16.0 Hz, CH), 1.52 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 158.9 (d, *J* = 252.9 Hz), 140.9, 132.1 (d, *J* = 4.2 Hz), 129.9, 127.8 (d, *J* = 7.4 Hz), 121.7 (d, *J* = 18.3 Hz), 121.4 (d, *J* = 2.2 Hz), 117.0 (d, *J* = 21.6 Hz), 80.9, 28.2 ppm; HRMS (ESI, m/z): calcd. for $C_{13}H_{14}O_2ClFNa^+$ 279.0564, found 279.0566.



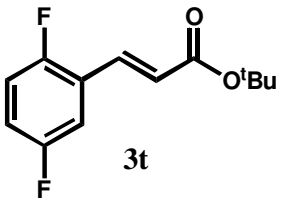
3r

(*E*)-*tert*-butyl 3-(3,5-dichlorophenyl)acrylate (3s): This compound was prepared by the general procedure described above and was obtained as a white solid in 85% yield: R_f = 0.67 (hexane : ethyl acetate = 7:1); Mp = 53.6-54.5 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, 1H, *J* = 16.0 Hz, CH), 7.347 (s, 1H, ArH), 7.349 (s, 1H, ArH), 7.32 (s, 1H, ArH), 6.35 (d, 1H, *J* = 16.0 Hz, CH), 1.52 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 140.4, 137.7, 135.5, 129.5, 126.1, 123.1, 81.1, 28.1 ppm; HRMS (ESI, m/z): calcd. for $C_{13}H_{14}O_2Cl_2Na^+$ 295.0269, found 295.0272.



3s

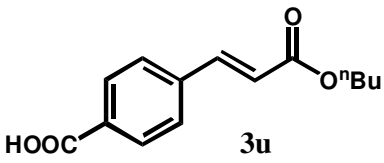
(*E*)-*tert*-butyl 3-(2,5-difluorophenyl)acrylate (3t): This compound was prepared by the general procedure described above and was obtained as a solid in 73% yield: R_f = 0.66 (hexane : ethyl acetate = 7:1); Mp = 50.1-51.0 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, 1H, *J* = 16.0 Hz, CH), 7.17-7.21 (m, 1H, ArH), 7.01-7.06 (m, 2H, ArH), 6.42 (d, 1H, *J* = 16.0 Hz, CH), 1.53 (s, 9H, $3CH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 158.7 (d, *J* = 242.8 Hz), 157.2 (d, *J* = 249.4 Hz), 134.8 (t, *J* = 2.3 Hz), 124.0, 123.9 (d, *J* = 5.8 Hz), 117.8



3t

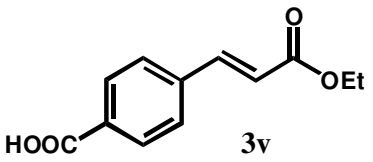
(dd, J = 8.9 Hz, J = 24.4 Hz), 117.3 (dd, J = 8.6 Hz, J = 25.2 Hz), 114.5 (dd, J = 3.5 Hz, J = 24.5 Hz), 81.0, 28.1 ppm; HRMS (ESI, m/z): calcd. for $C_{13}H_{14}F_2O_2Na^+$ 263.0860, found 263.0870.

(*E*)-4-(3-butoxy-3-oxoprop-1-enyl)benzoic acid (3u): This is compound was prepared by the general procedure described above and was obtained as a white solid in 97% yield: R_f = 0.35 (dichloromethane : ethyl acetate = 3:1); Mp = 88.6-89.3 ^oC; ^1H NMR (400 MHz, DMSO-d_6): δ 7.95 (d, 2H, J = 8.0 Hz, ArH), 7.80 (d, 2H, J = 8.0 Hz, ArH), 7.67 (d, 1H, J = 15.9 Hz, CH), 6.70 (d, 1H, J = 16.0 Hz, CH), 4.13 (t, 2H, J = 6.5 Hz, OCH_2), 1.58-1.61 (m, 2H, CH_2), 1.32-1.38 (m, 2H, CH_2), 0.88 (t, 3H, J = 7.3 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.8, 166.0, 143.1, 138.1, 132.1, 129.7, 128.4, 120.4, 63.9, 30.3, 18.7, 13.6 ppm; HRMS (ESI, m/z): calcd. for $C_{14}H_{16}O_4Na^+$ 271.0946, found 271.0940



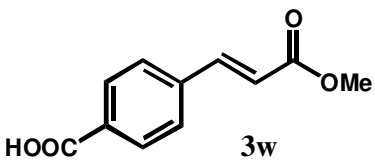
3u

(*E*)-4-(3-ethoxy-3-oxoprop-1-enyl)benzoic acid (3v): This is compound was prepared by the general procedure described above and was obtained as a white solid in 96% yield: R_f = 0.34 (dichloromethane : ethyl acetate = 3:1); Mp = 109.5-110.2 ^oC; ^1H NMR (400 MHz, DMSO-d_6): δ 7.95 (d, 2H, J = 8.0 Hz, ArH), 7.80 (d, 2H, J = 8.0 Hz, ArH), 7.67 (d, 1H, J = 16.0 Hz, CH), 6.70 (d, 1H, J = 16.0 Hz, CH), 4.18 (q, 2H, J = 7.1 Hz, OCH_2), 1.25 (t, 3H, J = 7.1 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.8, 165.9, 143.1, 138.1, 132.1, 129.7, 128.4, 120.5, 60.2, 14.2 ppm; HRMS (ESI, m/z): calcd. for $C_{12}H_{12}O_4Na^+$ 243.0633, found 243.0636



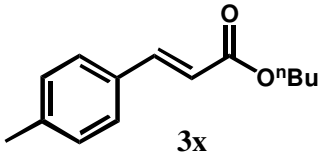
3v

(*E*)-4-(3-methoxy-3-oxoprop-1-enyl)benzoic acid (3w): This is compound was prepared by the general procedure described above and was obtained as a white soild in 98% yield: R_f = 0.32 (dichloromethane : ethyl acetate = 3:1); Mp = 149.6-150.5 ^oC; ^1H NMR (400 MHz, DMSO-d_6): δ 7.95 (d, 2H, J = 8.0 Hz, ArH), 7.80 (d, 2H, J = 8.0 Hz, ArH), 7.68 (d, 1H, J = 15.8 Hz, CH), 6.71 (d, 1H, J = 16.0 Hz, CH), 3.73 (s, 3H, OCH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.8, 166.4, 143.2, 138.1, 132.1, 129.7, 128.4, 120.1, 51.6 ppm; HRMS (ESI, m/z): calcd. for $C_{11}H_{10}O_4Na^+$ 229.0477, found 229.0477



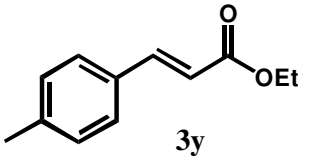
3w

(*E*)-butyl 3-p-tolylacrylate (3x): This is compound was prepared by the general procedure described above and was obtained as a yellow oil in 89% yield: R_f = 0.69 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, 1H, *J* = 15.9 Hz, CH), 7.42 (d, 2H, *J* = 8.0 Hz, ArH), 7.18 (d, 2H, *J* = 8.0 Hz, ArH), 6.40 (d, 1H, *J* = 16.0 Hz, CH), 4.20 (t, 2H, *J* = 6.7 Hz, OCH_2), 2.37 (s, 3H, CH_3), 1.67-1.72 (m, 2H, CH_2), 1.41-1.47 (m, 2H, CH_2), 0.97 (t, 3H, *J* = 7.4 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 144.6, 140.6, 131.8, 129.6, 128.1, 117.2, 64.3, 30.8, 21.4, 19.2, 13.8 ppm; HRMS (ESI, m/z): calcd. for $C_{14}H_{18}O_2Na^+$ 241.1204, found 241.1202



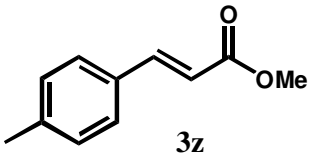
3x

(*E*)-ethyl 3-p-tolylacrylate (3y): This is compound was prepared by the general procedure described above and was obtained as a yellow oil in 86% yield: R_f = 0.68 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, 1H, *J* = 15.9 Hz, CH), 7.42 (d, 2H, *J* = 8.0 Hz, ArH), 7.18 (d, 2H, *J* = 8.0 Hz, ArH), 6.39 (d, 1H, *J* = 16.0 Hz, CH), 4.26 (q, 2H, *J* = 7.1 Hz, OCH_2), 2.37 (s, 3H, CH_3), 1.33 (t, 3H, *J* = 7.1 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 144.6, 140.6, 131.8, 129.6, 128.1, 117.2, 60.4, 21.5, 14.4 ppm; HRMS (ESI, m/z): calcd. for $C_{12}H_{14}O_2Na^+$ 213.0891, found 213.0894



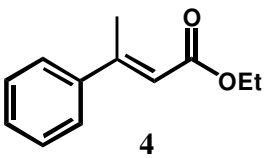
3y

(*E*)-methyl 3-p-tolylacrylate (3z): This is compound was prepared by the general procedure described above and was obtained as a yellow solid in 84% yield: R_f = 0.63 (hexane : ethyl acetate = 7:1); Mp = 53.2-54.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, 1H, *J* = 16.0 Hz, CH), 7.42 (d, 2H, *J* = 8.0 Hz, ArH), 7.19 (d, 2H, *J* = 7.6 Hz, ArH), 6.39 (d, 1H, *J* = 16.0 Hz, CH), 3.80 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 144.9, 140.7, 131.7, 129.6, 128.1, 116.7, 51.6, 21.5 ppm; HRMS (ESI, m/z): calcd. for $C_{11}H_{12}O_2Na^+$ 199.0735, found 199.0732



3z

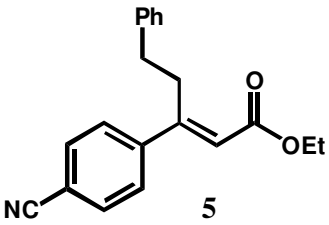
(*E*)-ethyl 3-phenylbut-2-enoate (4): This is compound was prepared by the general procedure described above and was obtained as a yellow oil in 72% yield: R_f = 0.70 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.53 (m, 2H, ArH), 7.36-7.40 (m, 3H, ArH), 6.14 (s,



4

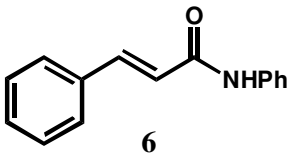
1H, CH), 4.22 (q, 2H, *J* = 7.2 Hz, OCH_2), 2.58 (s, 3H, CH_3), 1.32 (t, 3H, *J* = 7.2 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 155.5, 142.3, 129.0, 128.5, 126.3, 117.2, 59.8, 17.9, 14.4 ppm; HRMS (ESI, m/z): calcd. for $C_{12}H_{14}O_2Na^+$ 213.0888, found 213.0891

(*E*)-ethyl 3-(4-cyanophenyl)-5-phenylpent-2-enoate (5): This is compound was prepared by the general procedure described above and was obtained as a solid in 45% yield: R_f = 0.65 (hexane : ethyl acetate = 7:1); Mp = 51.3-52.5 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, 2H, *J* = 8.2 Hz, ArH), 7.49 (d, 2H, *J* = 8.3 Hz, ArH), 7.23-7.27 (m, 2H, ArH), 7.16-7.18 (m, 3H, ArH), 6.06 (s, 1H, CH), 4.22 (q, 2H, *J* = 7.1 Hz, OCH_2), 3.37-3.41 (m, 2H, CH_2), 2.70-2.74 (m, 2H, CH_2), 1.31 (t, 3H, *J* = 7.1 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) (major): δ 165.7, 157.1, 145.9, 140.8, 132.4, 128.4, 128.4, 127.5, 126.2, 120.3, 118.5, 112.5, 60.3, 35.0, 32.9, 14.3 ppm; HRMS (ESI, m/z): calcd. for $C_{22}H_{23}NO_2Na^+$ 356.1626, found 356.1624



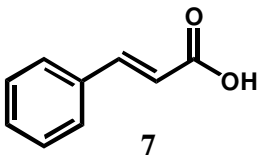
5

N-phenylcinnamamide (6): This is compound was prepared by the general procedure described above and was obtained as a white solid in 78% yield: R_f = 0.35 (hexane : ethyl acetate = 3:1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.35 (b, 1H, NH), 7.72 (d, 1H, *J* = 15.9 Hz, CH), 7.66-7.68 (m, 2H, ArH), 7.38-7.40 (m, 2H, ArH), 7.24-7.30 (m, 5H, ArH), 7.07-7.11 (m, 1H, ArH), 6.67 (d, 1H, *J* = 15.9 Hz, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 142.3, 138.2, 134.6, 130.0, 129.1, 128.8, 128.0, 124.5, 121.2, 120.4 ppm; HRMS (ESI, m/z): calcd. for $C_{15}H_{13}NONa^+$ 246.0895, found 246.0901



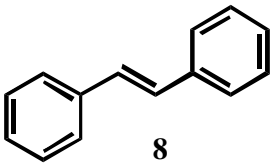
6

cinnamic acid (7): This is compound was prepared by the general procedure described above and was obtained as a white solid in 73% yield: R_f = 0.38 (dichloromethane : ethyl acetate = 2:1); ^1H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, 1H, *J* = 15.9 Hz, CH), 7.42 (d, 2H, *J* = 8.0 Hz, ArH), 7.18 (d, 2H, *J* = 8.0 Hz, ArH), 6.39 (d, 1H, *J* = 16.0 Hz, CH), 4.26 (q, 2H, *J* = 7.1 Hz, OCH_2), 2.37 (s, 3H, CH_3), 1.33 (t, 3H, *J* = 7.1 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 144.6, 140.6, 131.8, 129.6, 128.1, 117.2, 60.4, 21.5, 14.4 ppm; HRMS (ESI, m/z): calcd. for $C_9H_8O_2Na^+$ 171.0422, found 171.0424



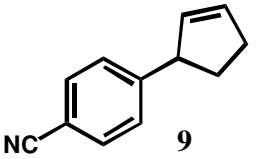
7

(*E*)-1,2-diphenylethene (8): This is compound was prepared by the general procedure described above and was obtained as a white solid in 93% yield: R_f = 0.78 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.57 (m, 4H, ArH), 7.39-7.42 (m, 4H, ArH), 7.29-7.32 (m, 2H, ArH), 7.16 (s, 2H, CH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 128.8, 128.7, 127.7, 126.6 ppm; HRMS (ESI, m/z): calcd. for $C_{14}H_{12}H^+$ 181.1017, found 181.1015

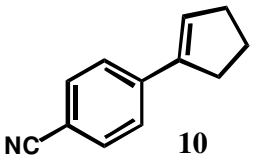


8

4-(cyclopent-2-enyl)benzonitrile (9) and 4-cyclopentenylbenzonitrile (10): This is compound was prepared by the general procedure described above and was obtained as a yellow oil in 80% yield: R_f = 0.58 (hexane : ethyl acetate = 7:1) (**9**:**10** = 80:20); ^{1}H NMR (400 MHz, $CDCl_3$) **(9)**: δ 7.57 (d, 2H, *J* = 8.0 Hz, ArH), 7.28 (d, 2H, *J* = 8.4 Hz, ArH), 6.00-6.01 (m, 1H, CH), 5.72-5.74 (m, 1H, CH), 3.93-3.94 (m, 1H, CH), 2.41-2.51 (m, 3H, CH_2), 1.63-1.72 (m, 1H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 133.4, 132.8, 132.3, 128.0, 119.2, 109.8, 51.4, 33.6, 32.5 ppm; HRMS (ESI, m/z): calcd. for $C_{12}H_{11}NH^+$ 170.0970, found 170.0972; ^{1}H NMR (400 MHz, $CDCl_3$) **(10)**: δ 7.57 (d, 2H, *J* = 8.0 Hz, ArH), 7.34 (d, 2H, *J* = 8.0 Hz, ArH), 3.48-3.52 (m, 1H, CH), 2.83-2.89 (m, 2H, CH_2), 2.71-2.73 (m, 1H, CH_2), 2.41-2.51 (m, 2H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 132.1, 130.7, 129.7, 127.7, 126.0, 109.6, 43.0, 41.2, 32.9 ppm; HRMS (ESI, m/z): calcd. for $C_{12}H_{11}NH^+$ 170.0970, found 170.0972

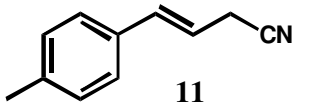


9



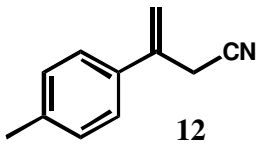
10

(*E*)-4-p-tolylbut-3-enenitrile (11): This is compound was prepared by the general procedure described above and was obtained as a yellow oil in 71% yield: R_f = 0.58 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, 2H, *J* = 7.9 Hz, ArH), 7.14 (d, 2H, *J* = 7.8 Hz, ArH), 6.69 (d, 1H, *J* = 15.8 Hz, CH), 5.99 (td, 1H, *J* = 5.6 Hz, *J* = 15.7 Hz, CH), 3.26 (d, 2H, *J* = 5.5 Hz, CH_2), 2.34 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 134.5, 132.9, 129.4, 126.4, 117.5, 115.7, 21.2, 20.8 ppm; HRMS (ESI, m/z): calcd. for $C_{11}H_{11}NH^+$ 158.0970, found 158.0969



11

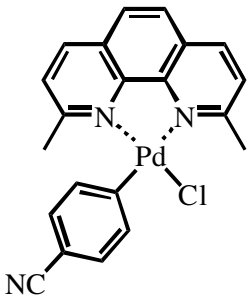
3-*p*-tolylbut-3-enenitrile (12): This is compound was prepared by the general procedure described above and was obtained as a yellow oil in 14% yield: R_f =



12

0.63 (hexane : ethyl acetate = 7:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, 2H, *J* = 8.1 Hz, ArH), 7.18 (d, 2H, *J* = 8.0 Hz, ArH), 5.60 (s, 1H, CH_2), 5.48 (s, 1H, CH_2), 3.52 (s, 2H, CH_2), 2.36 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 136.8, 135.0, 129.4, 125.4, 117.5, 115.2, 23.9, 21.1 ppm; HRMS (ESI, m/z): calcd. for $C_{11}H_{11}NH^+$ 158.0970, found 158.0969.

(2,9-dimethyl-1,10-phenanthroline)- 4-cyanophenyl-palladium(II) chloride (1h'): This is compound was prepared by the general procedure described above and was obtained as a yellow oil in 35% yield: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, 2H, *J* = 8.4 Hz, ArH), 7.86 (s, 2H, ArH), 7.55 (b, 2H, ArH), 7.26-7.29 (m, 2H, ArH), 7.15 (d, 2H, *J* = 8.0 Hz, ArH), 3.27 (b, 3H, CH_3), 2.08 (b, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 153.6, 137.8, 136.8, 128.8, 127.6, 126.7, 125.3, 120.1, 106.7, 28.5, 26.7 ppm; HRMS (ESI, m/z): calcd. for $C_{21}H_{16}ClN_3PdH^+$ 452.0146, found 452.0141.



1h'

Mechanistic study by employing ESI-MS:

Figure 1 shows the ESI-MS spectrum of the reaction mixture of cross-coupling between 4-methoxy phenylhydrazine and *tert*-butyl acrylate. The reaction mixture was injected directly to ESI-MS after reaction time of 2 hours. Aryl palladium ion **14** (m/z 573) and **18** (m/z 932) and four palladiaziridine complexes **13** (m/z 497), **15** (m/z 603), **16** (m/z 709) and **17** (m/z 731) could be detected as stable species (Figure 1).

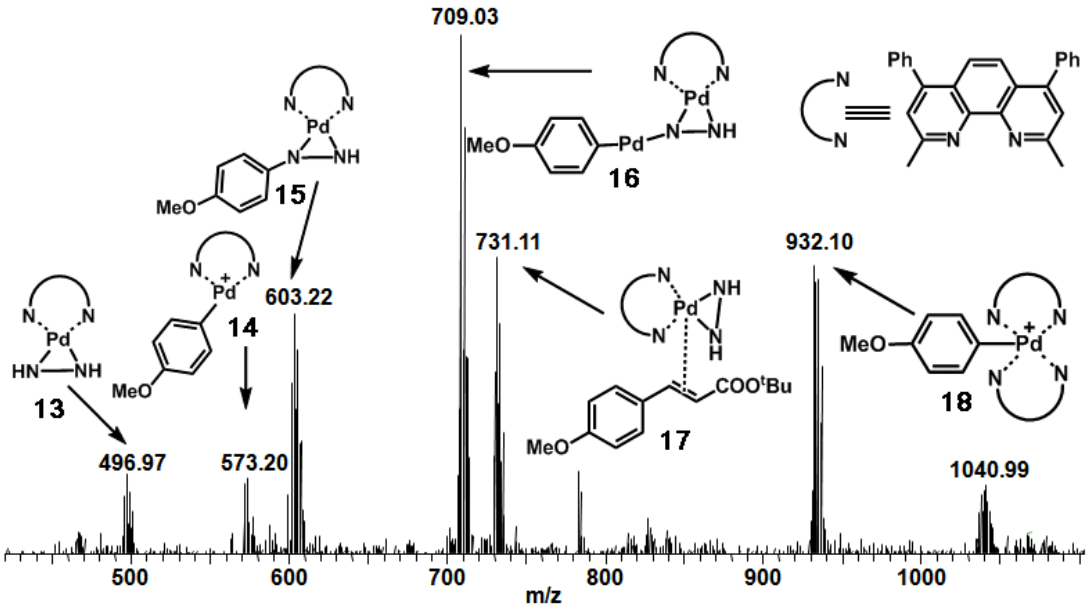
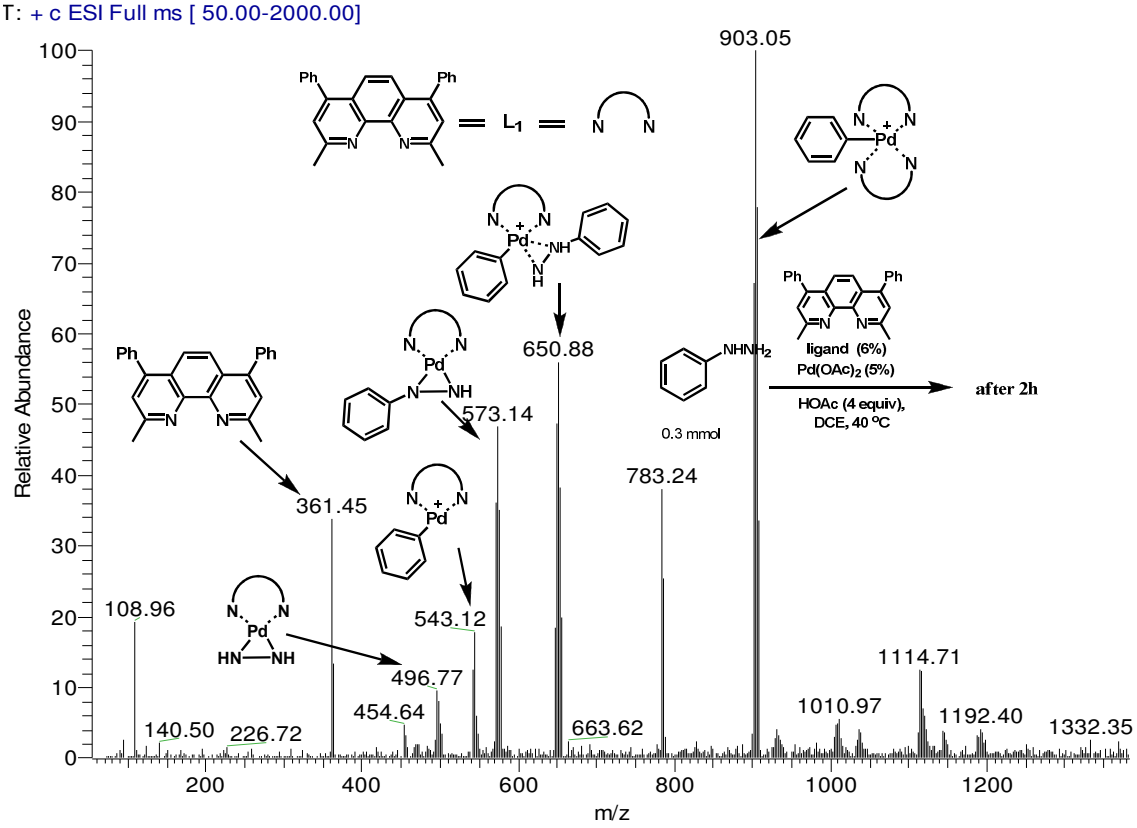
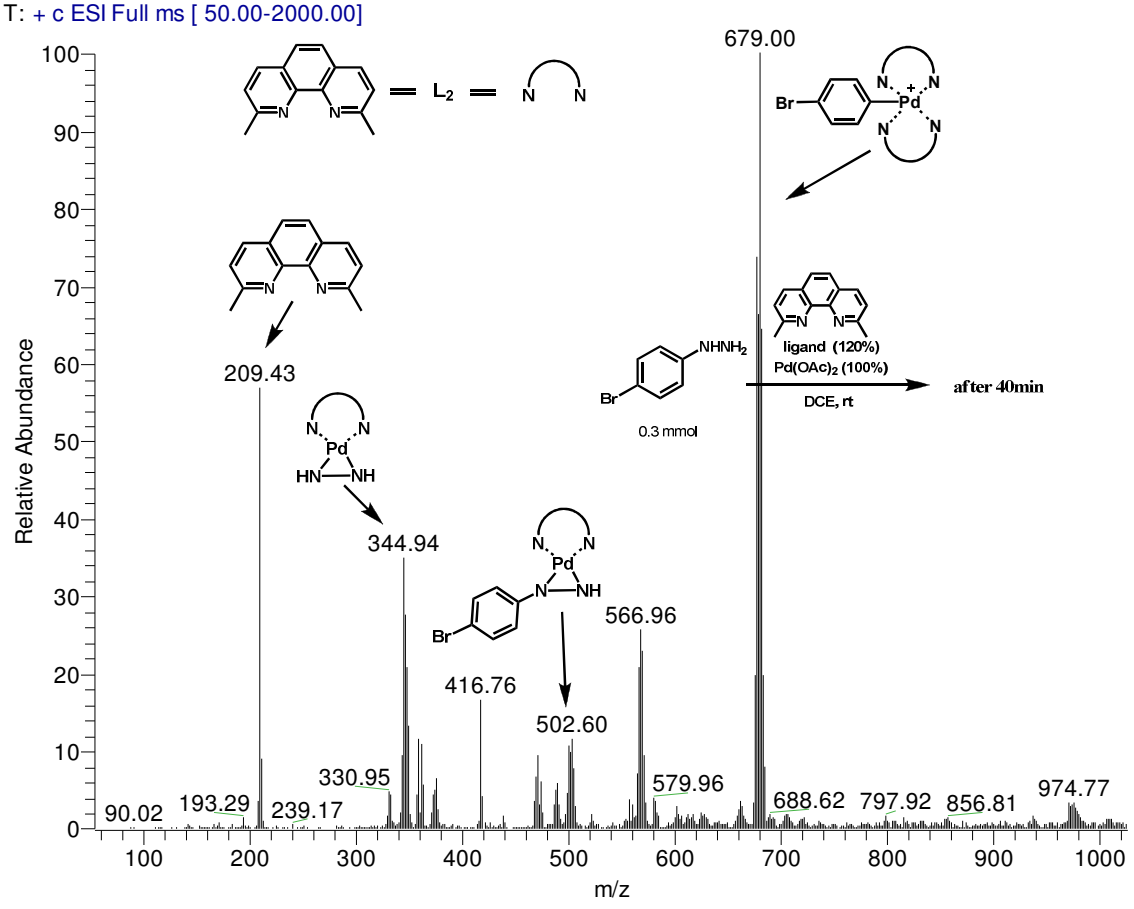


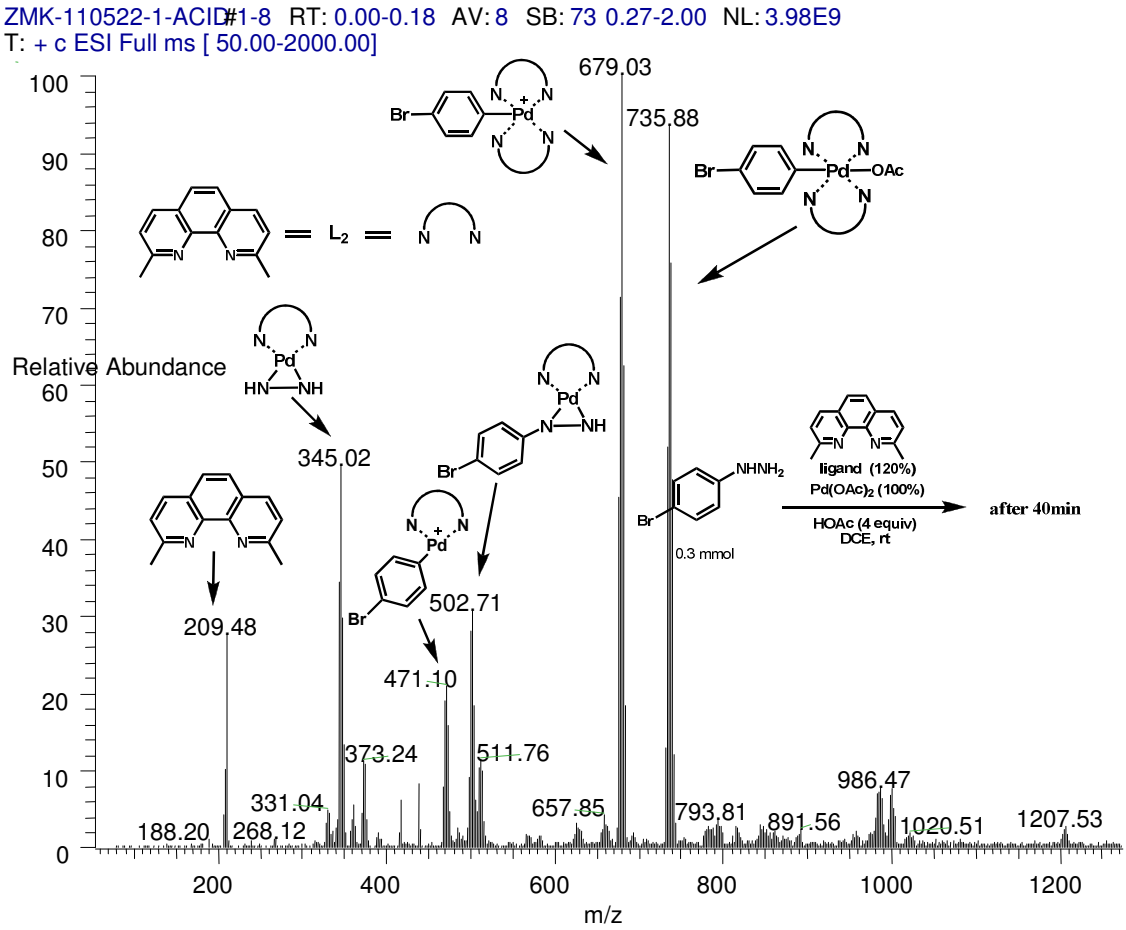
Figure 1. ESI(+)-MS spectrum of the reaction mixture of cross-coupling between 4-methoxy phenylhydrazine and *tert*-butyl acrylate.

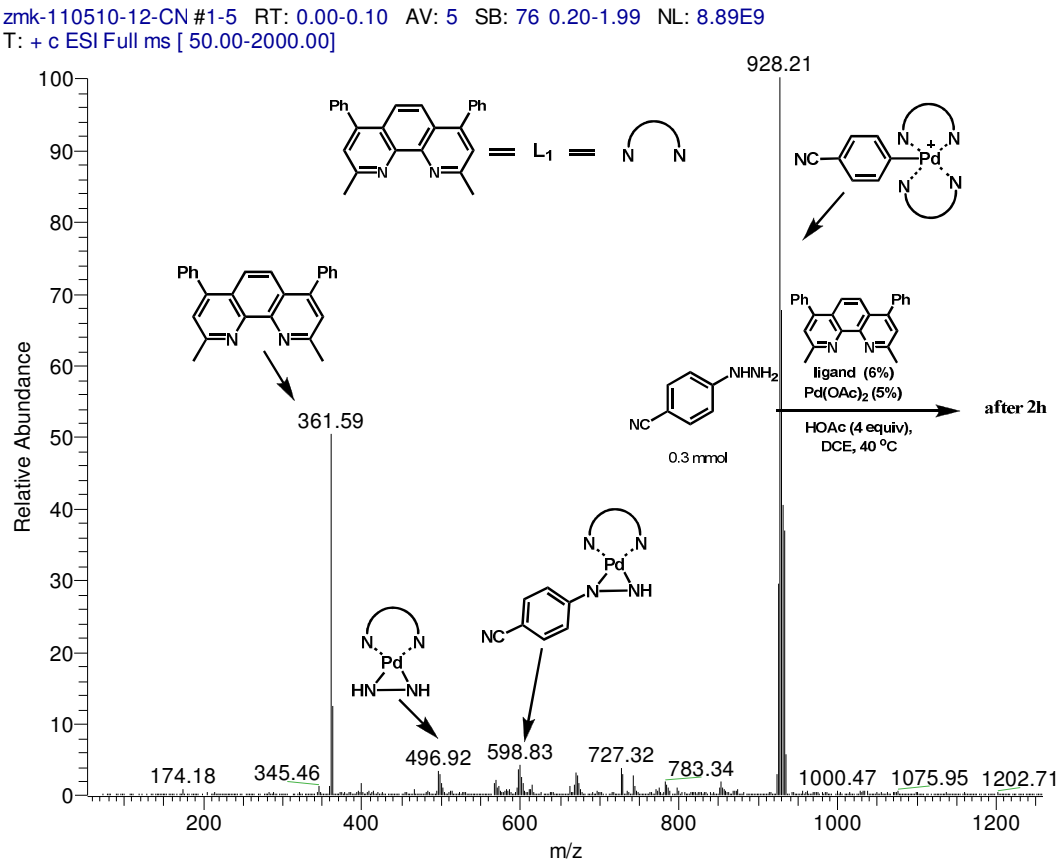
ZMK-110610-2-2H_110610141812 #2-6 RT: 0.03-0.13 AV: 5 SB: 77 0.17-1.98 NL: 3.93E9
T: + c ESI Full ms [50.00-2000.00]



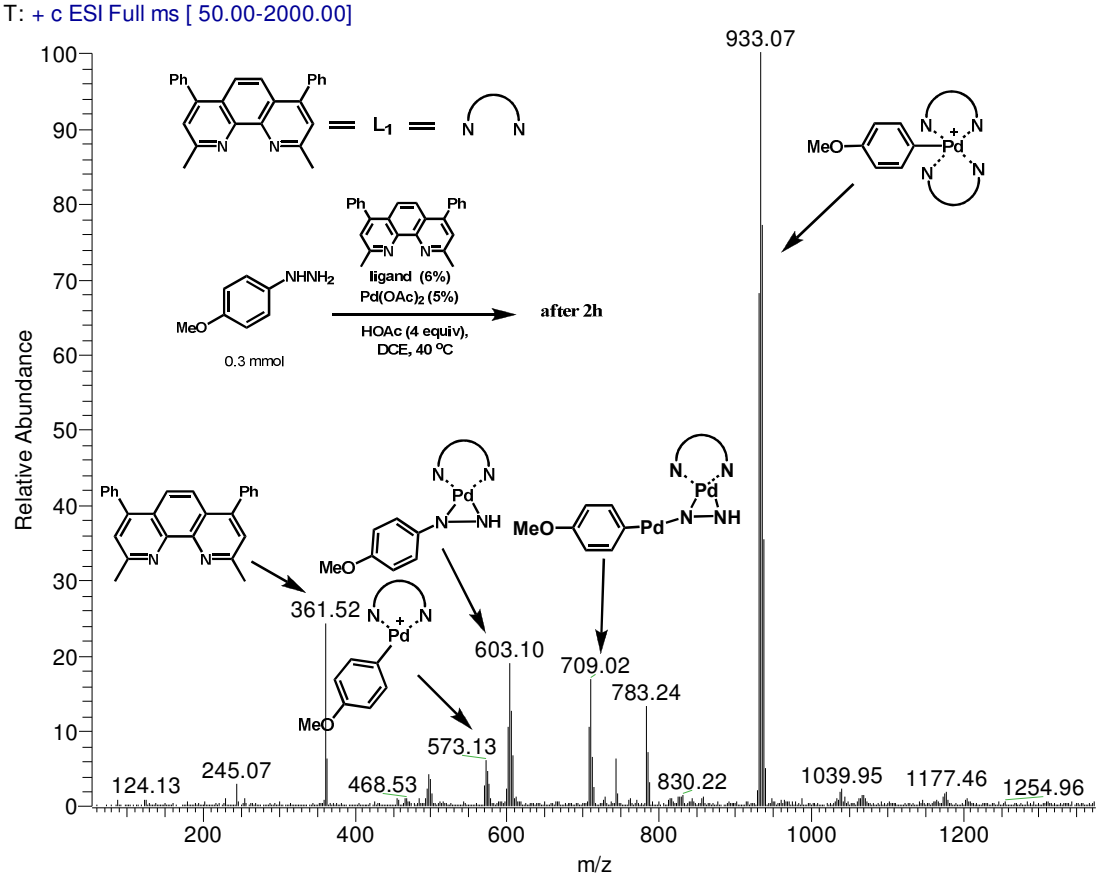
ZMK-110522-2-NO #2-7 RT: 0.03-0.15 AV: 6 SB: 74 0.20-1.94 NL: 4.84E9
T: + c ESI Full ms [50.00-2000.00]



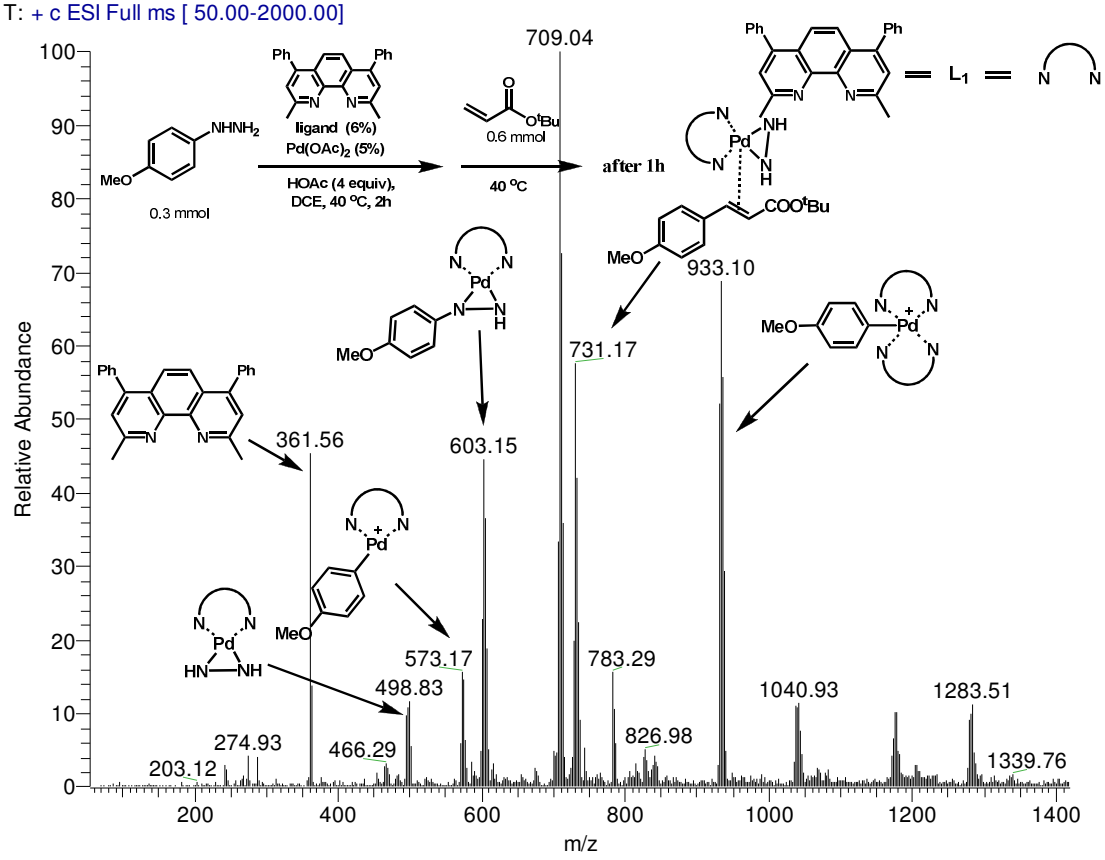

ZMK-110522-1-ACID#1-8 RT: 0.00-0.18 AV: 8 SB: 73 0.27-2.00 NL: 3.98E9
T: + c ESI Full ms [50.00-2000.00]
679.03
735.88
345.02
209.48
502.71
471.10
373.24
511.76
331.04
188.20
268.12
657.85
793.81
891.56
986.47
1020.51
1207.53
Relative Abundance
m/z
L2
ligand (120%)
Pd(OAc)2 (100%)
HOAc (4 equiv)
DCE, rt
after 40min
0.3 mmol


zmk-110510-12-CN #1-5 RT: 0.00-0.10 AV: 5 SB: 76 0.20-1.99 NL: 8.89E9
T: + c ESI Full ms [50.00-2000.00]
928.21
361.59
496.92
598.83
727.32
783.34
174.18
345.46
1000.47
1075.95
1202.71
Relative Abundance
m/z
L1
ligand (6%)
Pd(OAc)2 (5%)
HOAc (4 equiv),
DCE, 40 °C
after 2h
0.3 mmol

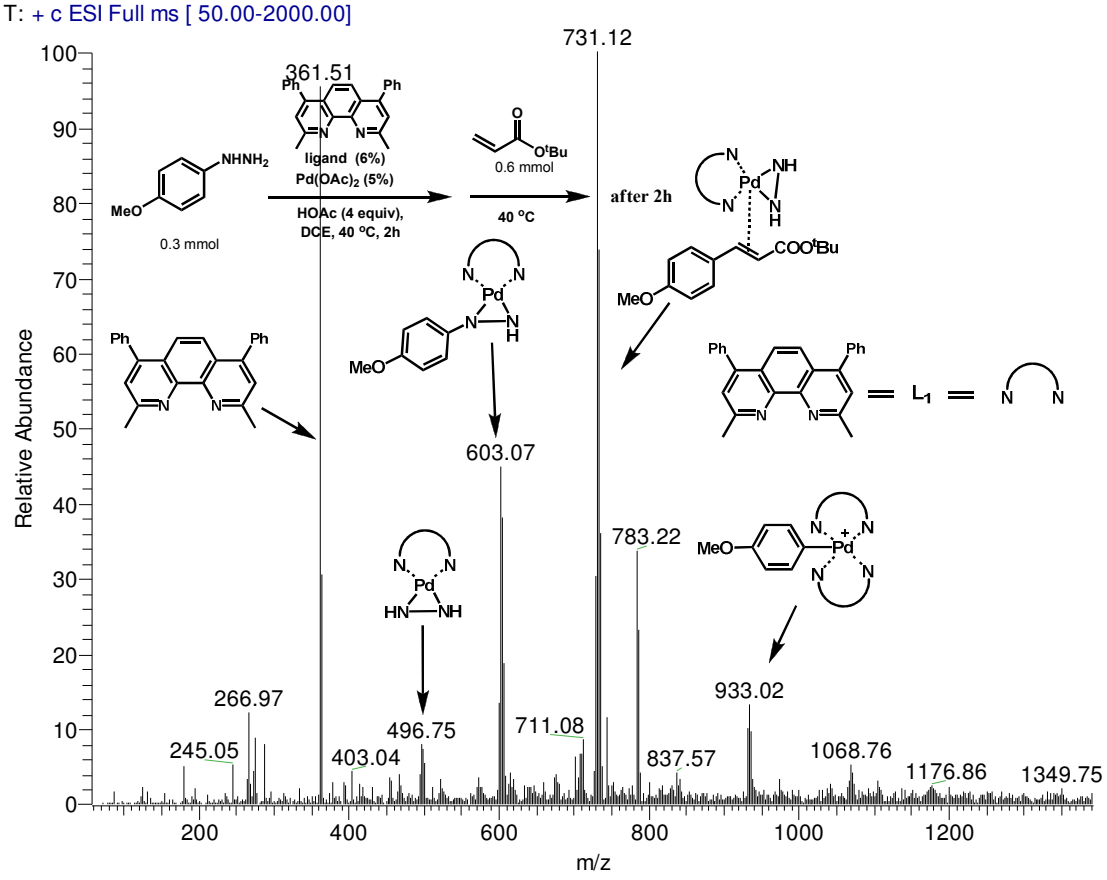
zmk-110609-2-2h_110609145346 #1-7 RT: 0.01-0.16 AV: 7 SB: 74 0.23-1.96 NL: 7.63E9
T: + c ESI Full ms [50.00-2000.00]



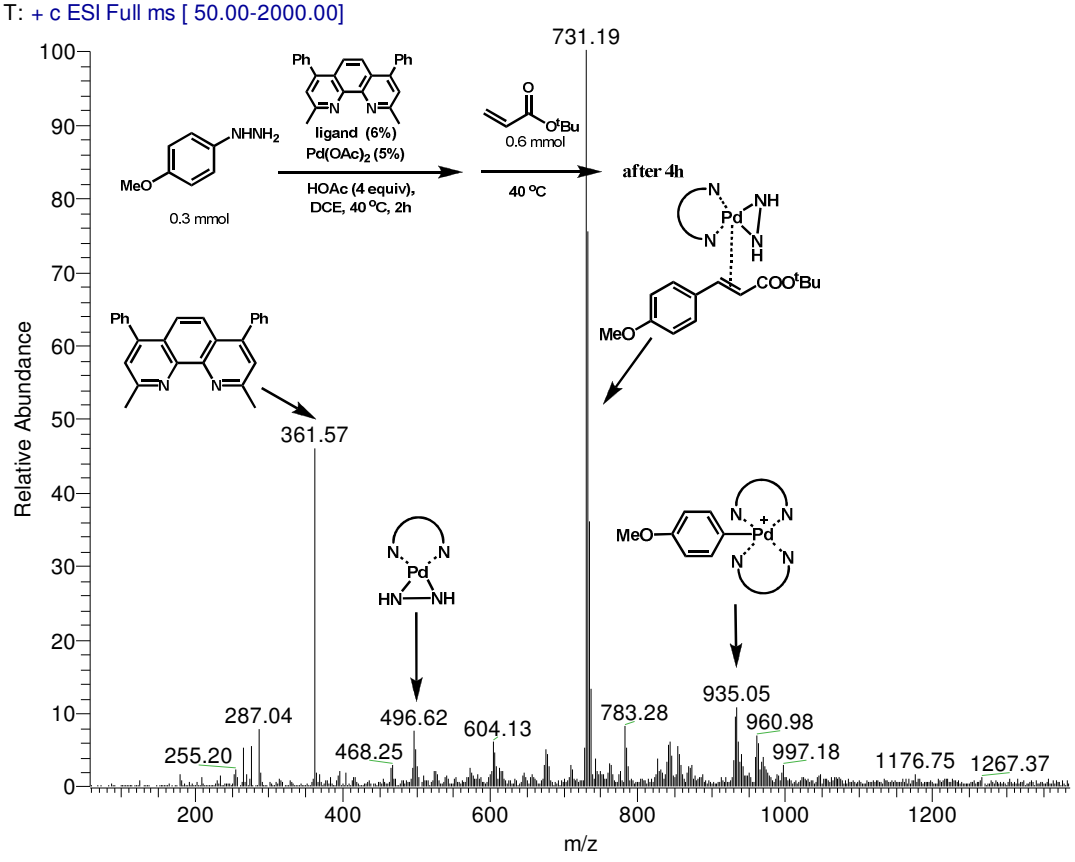
zmk-110609-5-1h_110609162009 #1-8 RT: 0.01-0.18 AV: 8 SB: 72 0.26-1.95 NL: 6.54E9
T: + c ESI Full ms [50.00-2000.00]

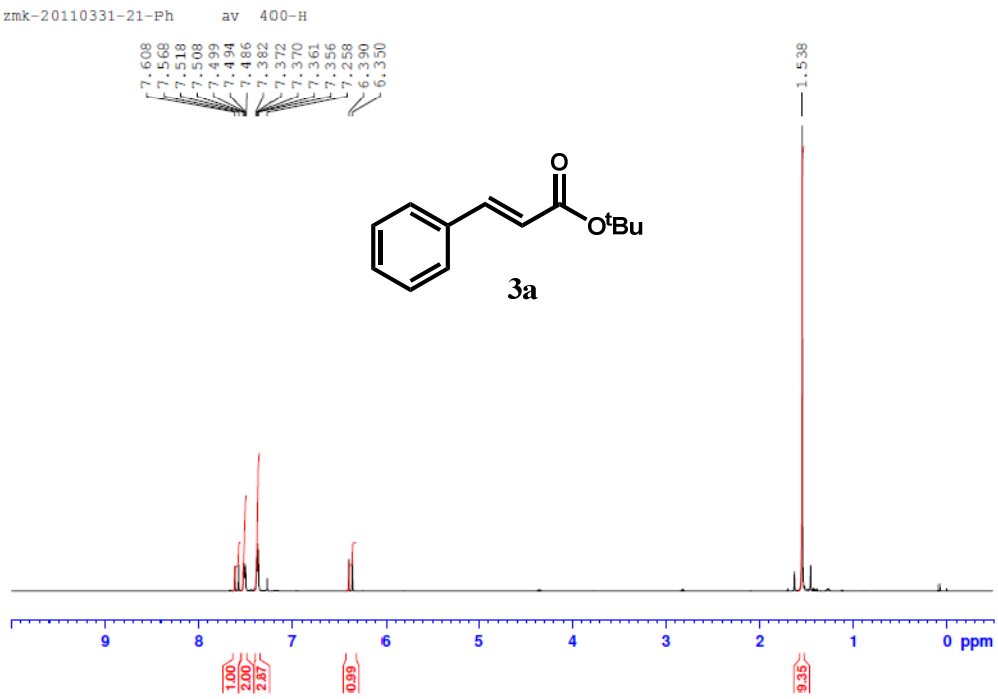


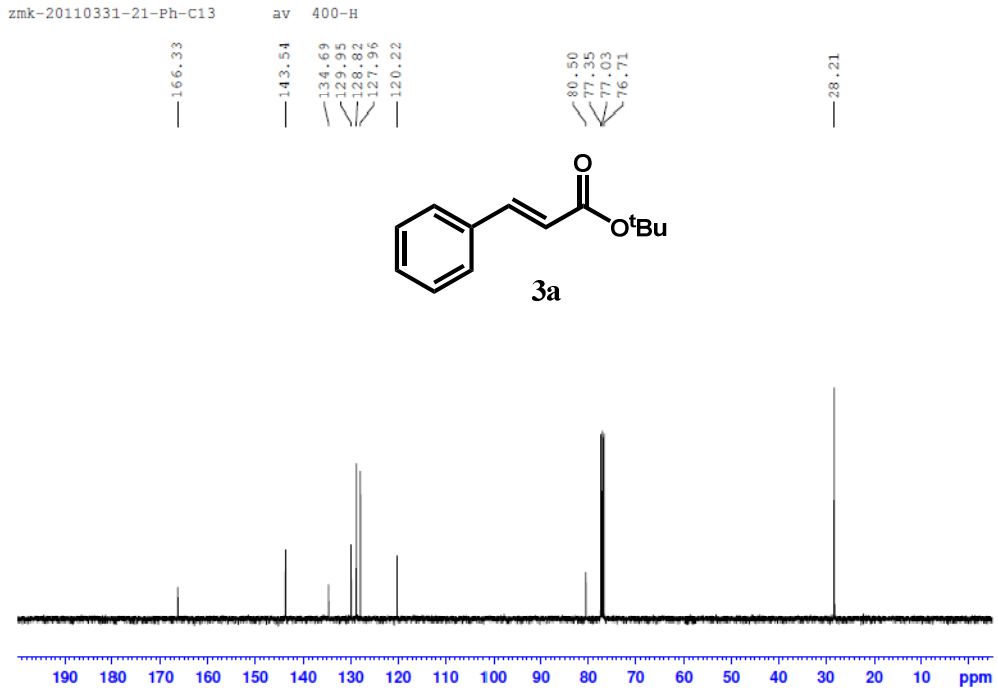
zmk-110609-6-2h_110609173708 #1-6 RT: 0.01-0.14 AV: 6 SB: 75 0.19-1.95 NL: 3.61E9
T: + c ESI Full ms [50.00-2000.00]

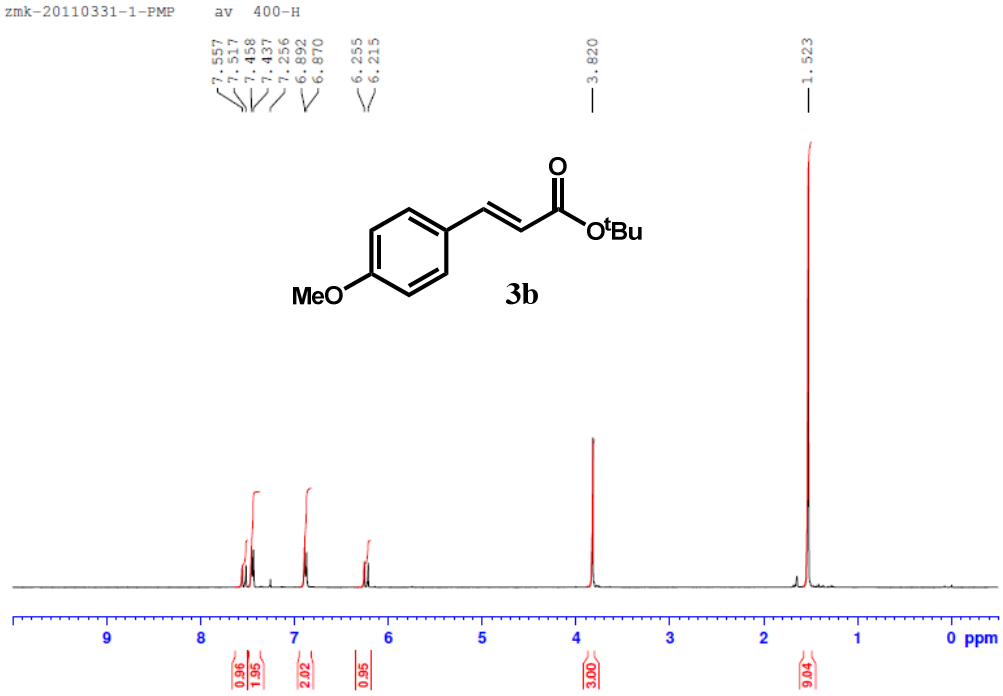


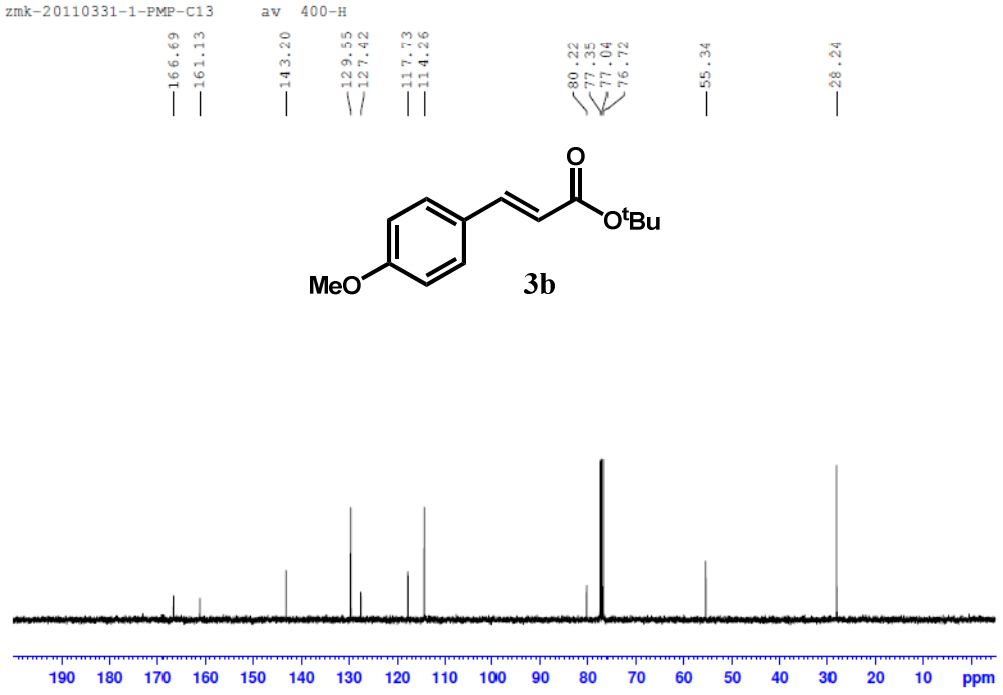
zmk-110609-7-4h_110609195920 #2-7 RT: 0.03-0.16 AV: 6 SB: 77 0.18-1.99 NL: 9.50E9
T: + c ESI Full ms [50.00-2000.00]

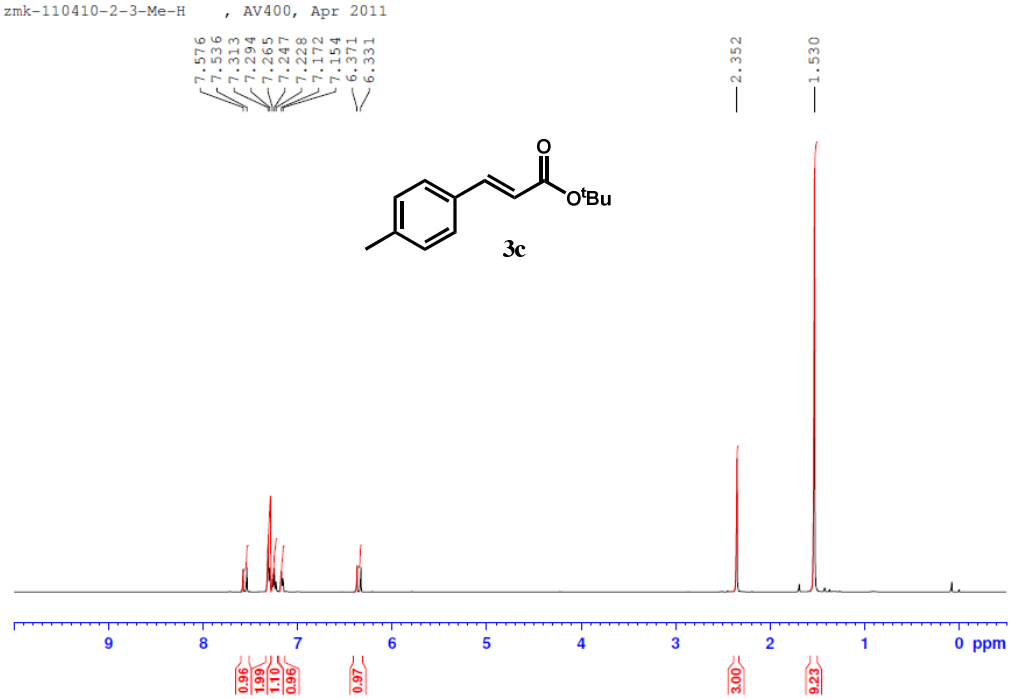


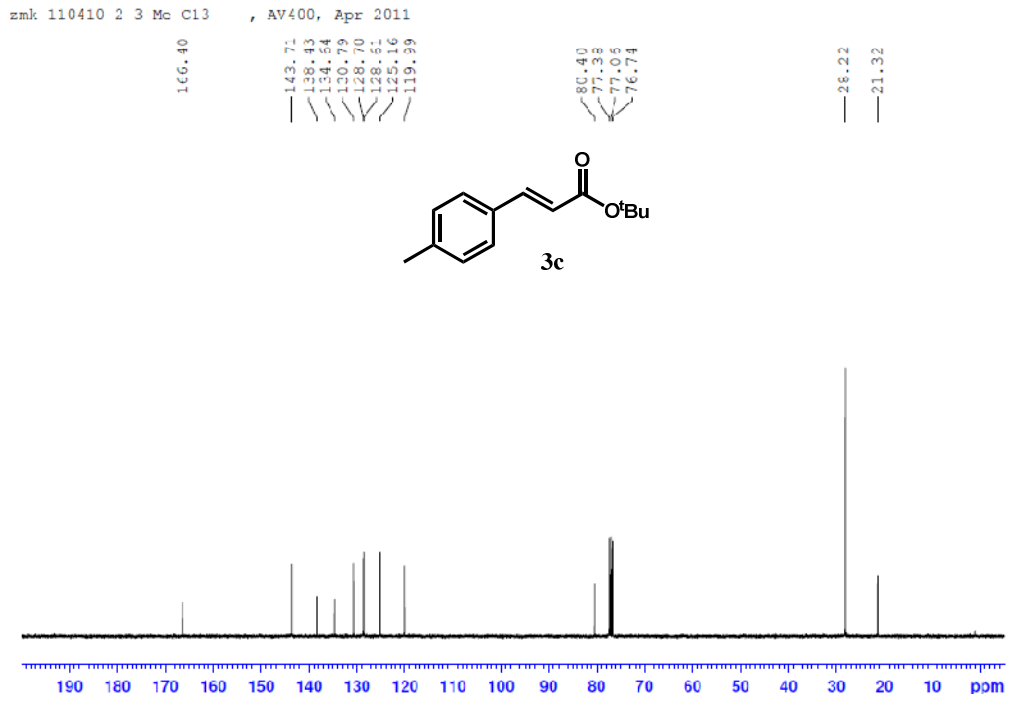

zmk-20110331-21-Ph av 400-H
7.608
7.568
7.518
7.508
7.499
7.494
7.486
7.382
7.372
7.370
7.361
7.356
7.258
6.390
6.350
1.538
O
O^{t}Bu
3a
9
8
7
6
5
4
3
2
1
0 ppm
1.00
2.00
2.07
0.99
9.35

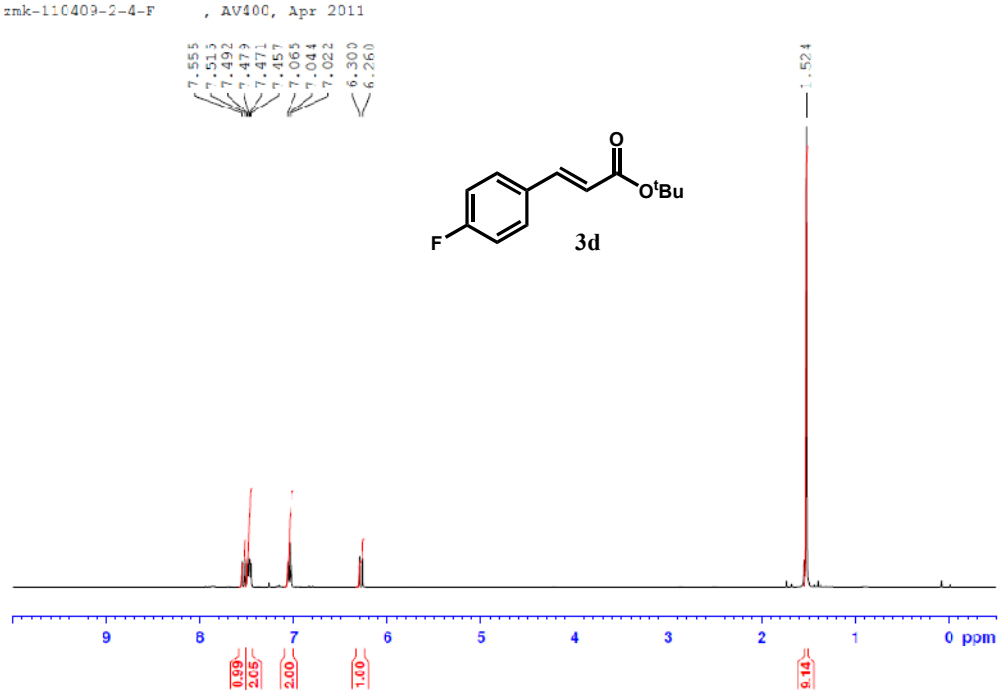

zmk-20110331-21-Ph-C13 av 400-H
166.33
143.54
134.69
129.95
128.82
127.96
120.22
80.50
77.35
77.03
76.71
28.21
O
O^{t}Bu
3a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

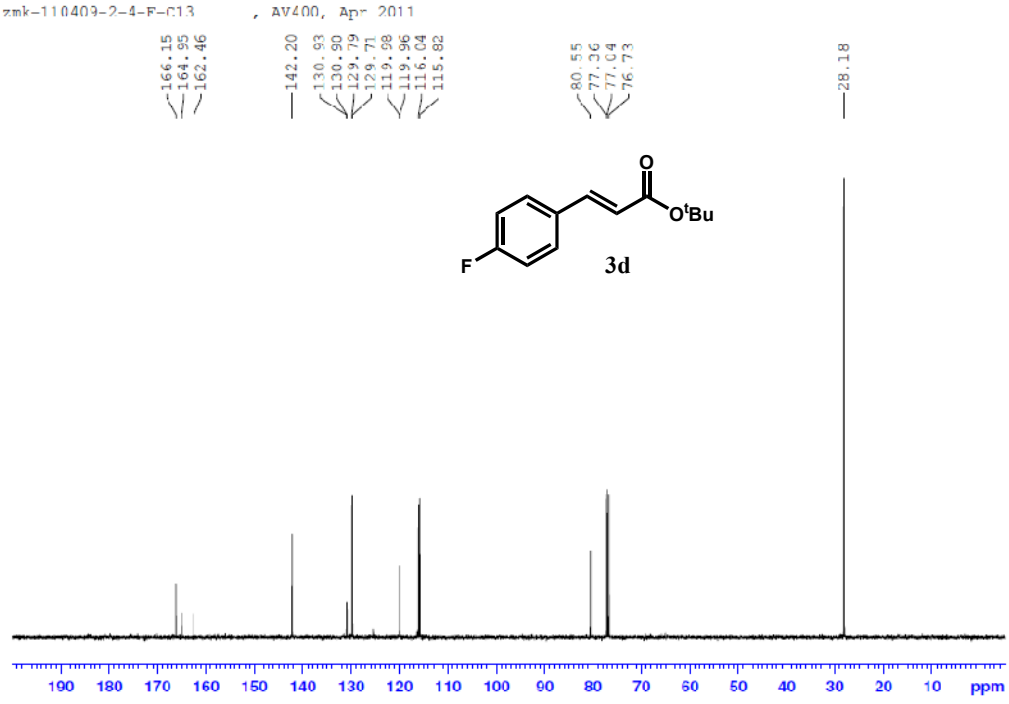

zmk-20110331-1-PMP av 400-H
7.557
7.517
7.458
7.437
7.256
6.892
6.870
6.255
6.215
3.820
1.523
O
OtBu
MeO
3b
9
8
7
6
5
4
3
2
1
0 ppm
0.96
1.95
2.02
0.95
3.00
9.04

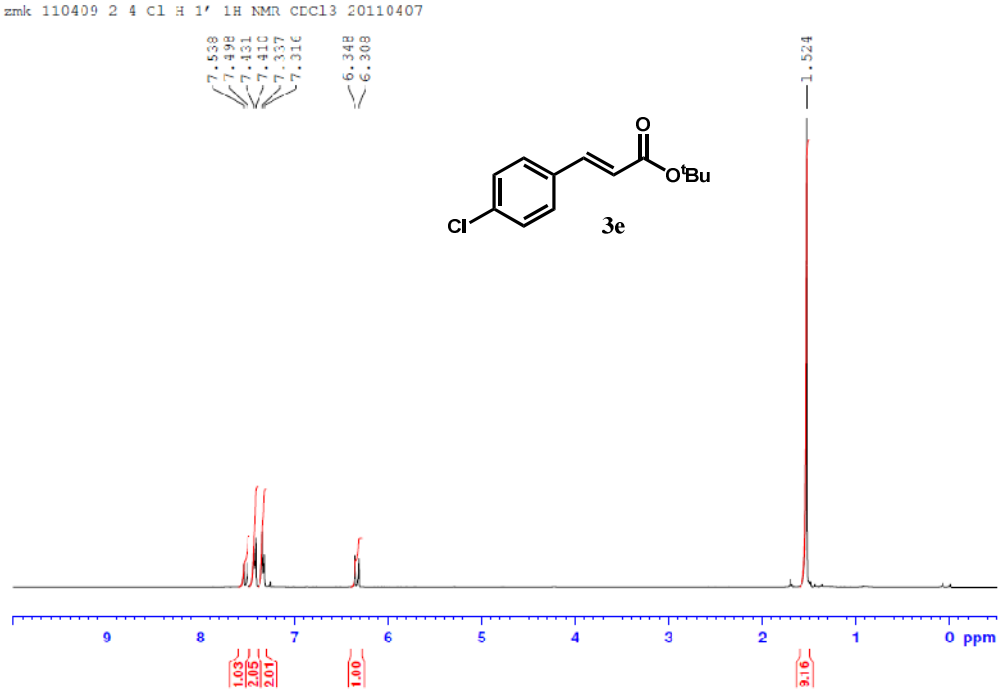

zmk-20110331-1-PMP-C13 av 400-H
166.69
161.13
143.20
129.55
127.42
117.73
114.26
80.22
77.35
77.04
76.72
55.34
28.24
O
OtBu
MeO
3b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

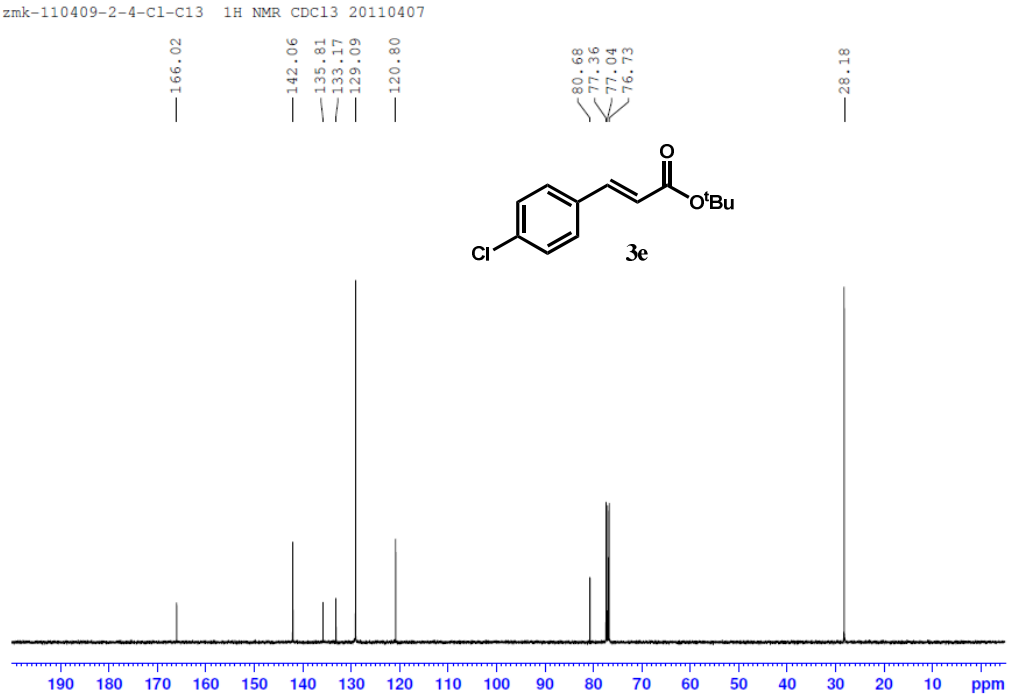

zmk-110410-2-3-Me-H , AV400, Apr 2011
7.576
7.536
7.313
7.294
7.265
7.247
7.228
7.172
7.154
6.371
6.331
2.352
1.530
O
O^{t}Bu
3c
9
8
7
6
5
4
3
2
1
0 ppm
0.96
1.99
1.10
0.96
0.97
3.00
9.23

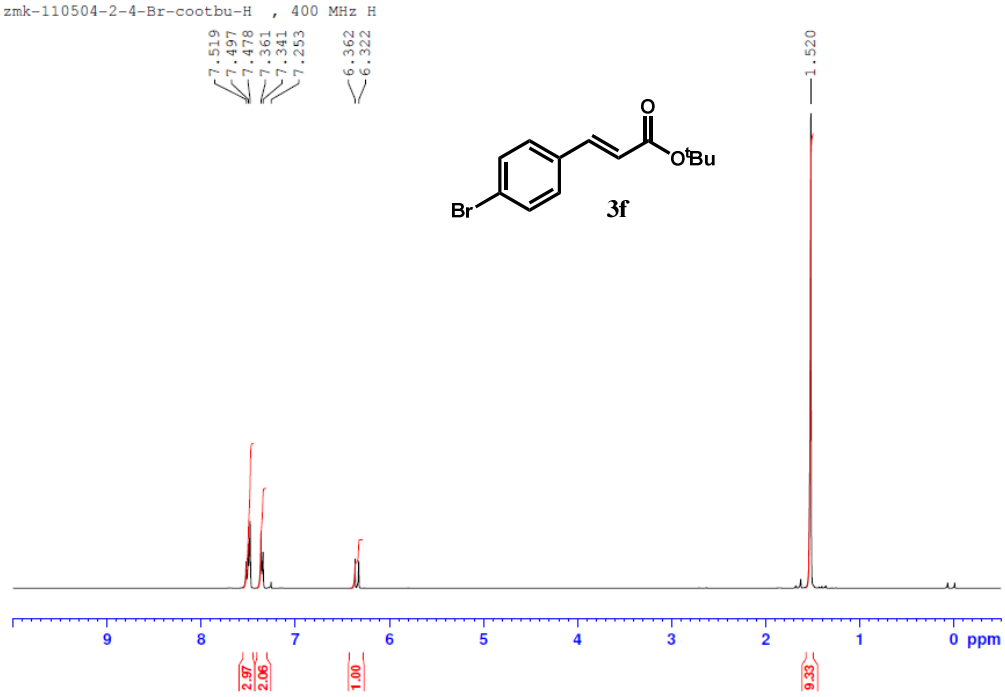

zmk 110410 2 3 Me C13 , AV400, Apr 2011
166.40
143.71
138.43
134.54
120.79
128.70
128.61
125.16
119.99
80.40
77.38
77.05
76.74
28.22
21.32
O
O^{t}Bu
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

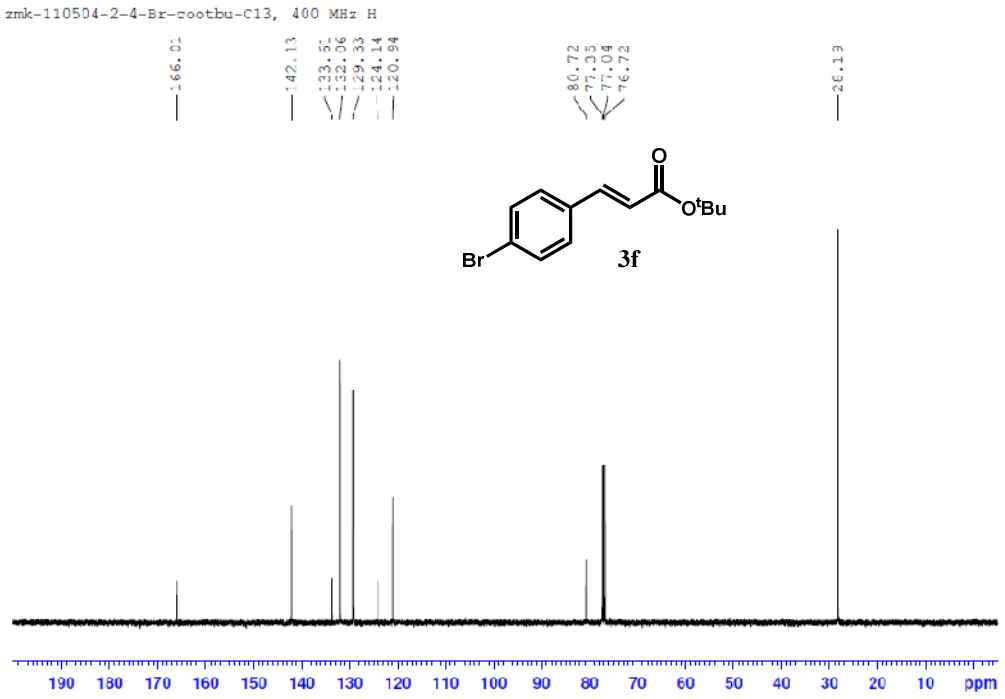

zmk-110409-2-4-F , AV400, Apr 2011
7.555
7.515
7.492
7.479
7.471
7.457
7.065
7.044
7.022
6.300
6.260
1.524
O
O^{t}Bu
F
3d
9
8
7
6
5
4
3
2
1
0 ppm
0.99
2.05
2.00
1.00
9.14

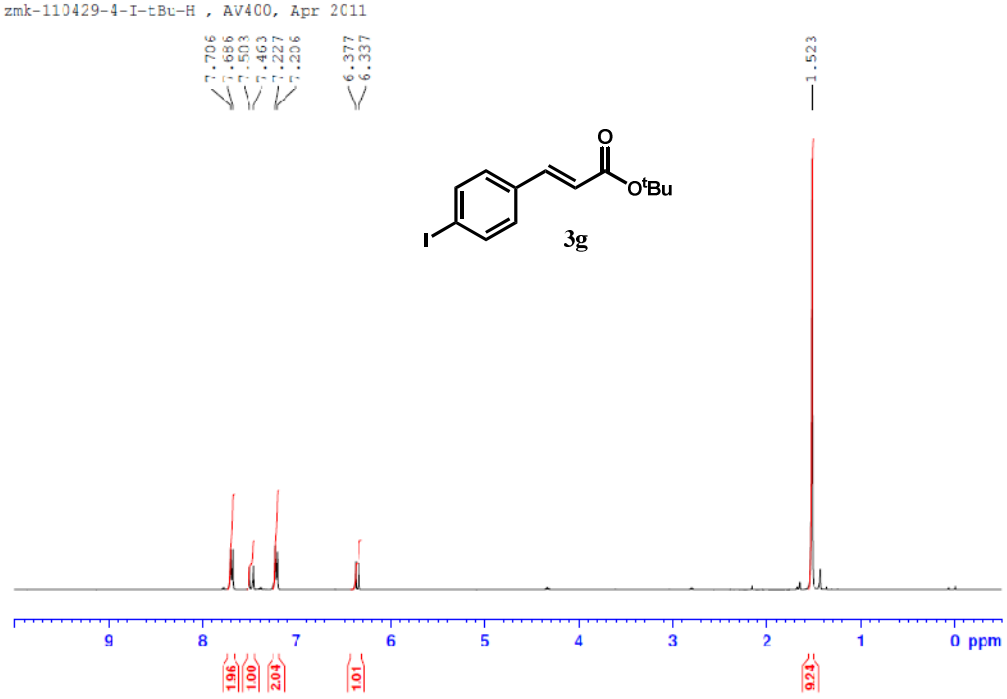

zmk-110409-2-4-F-C13 , AV400, Apr 2011
166.15
164.95
162.46
142.20
130.93
130.90
129.79
129.71
119.98
119.96
116.04
115.82
80.55
77.36
77.04
76.73
28.18
O
O^{t}Bu
F
3d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

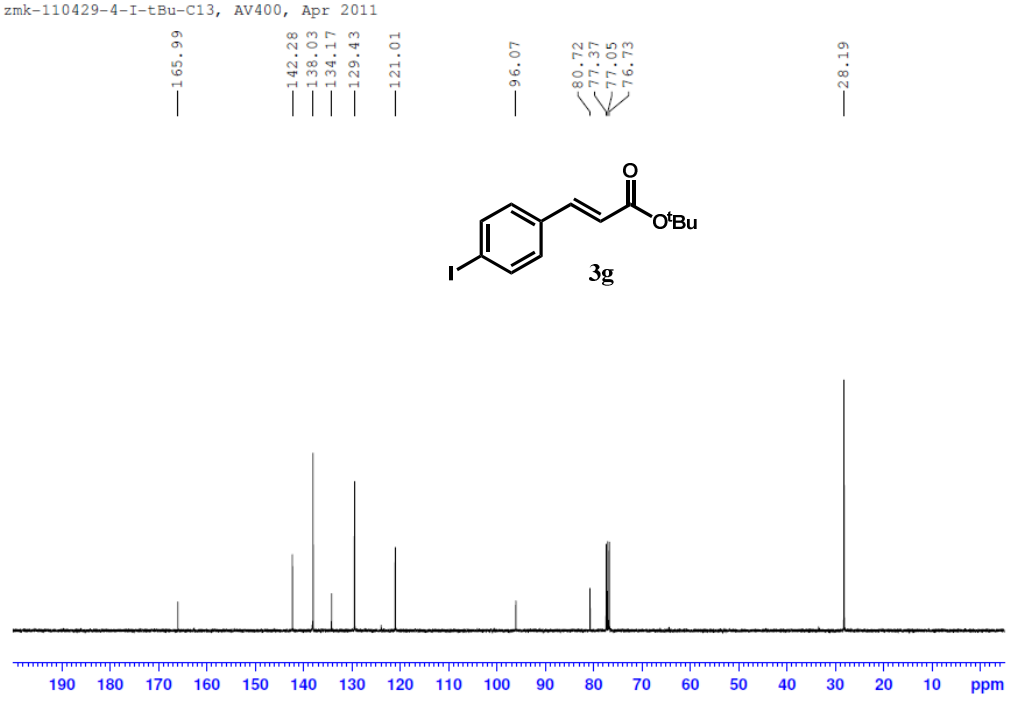

zmk 110409 2 4 Cl H 1' 1H NMR CDCl3 20110407
7.538
7.498
7.431
7.410
7.337
7.316
6.348
6.308
1.524
O
O^{t}Bu
Cl
3e
9
8
7
6
5
4
3
2
1
0 ppm
1.03
2.05
2.01
1.00
9.16

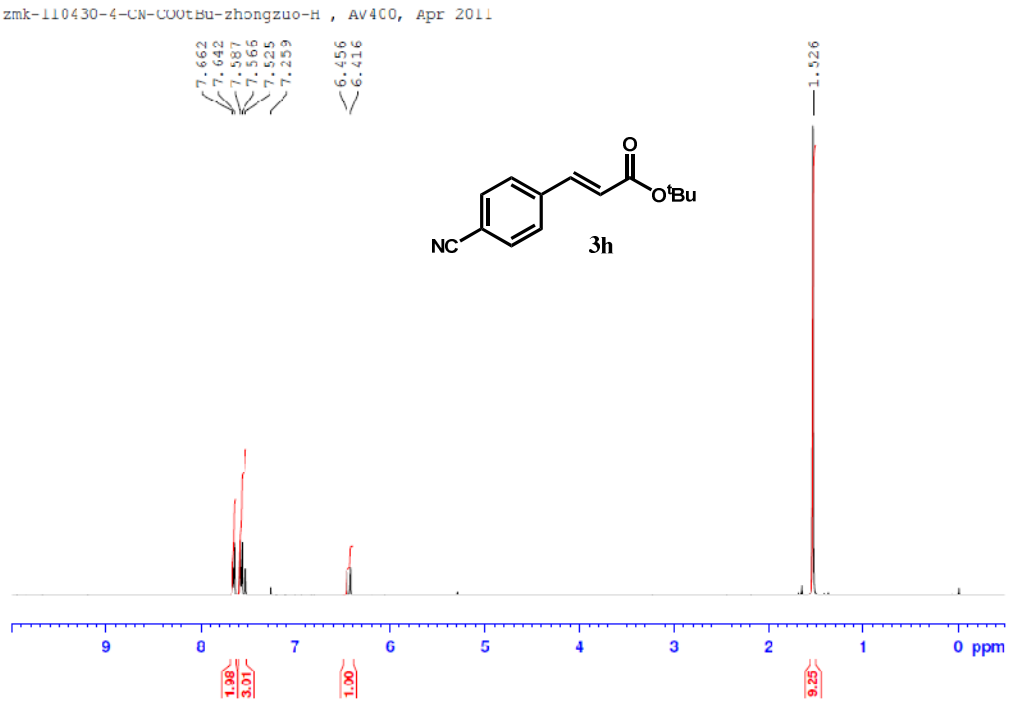

zmk-110409-2-4-Cl-C13 1H NMR CDCl3 20110407
166.02
142.06
135.81
133.17
129.09
120.80
80.68
77.36
77.04
76.73
28.18
O
O^{t}Bu
Cl
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

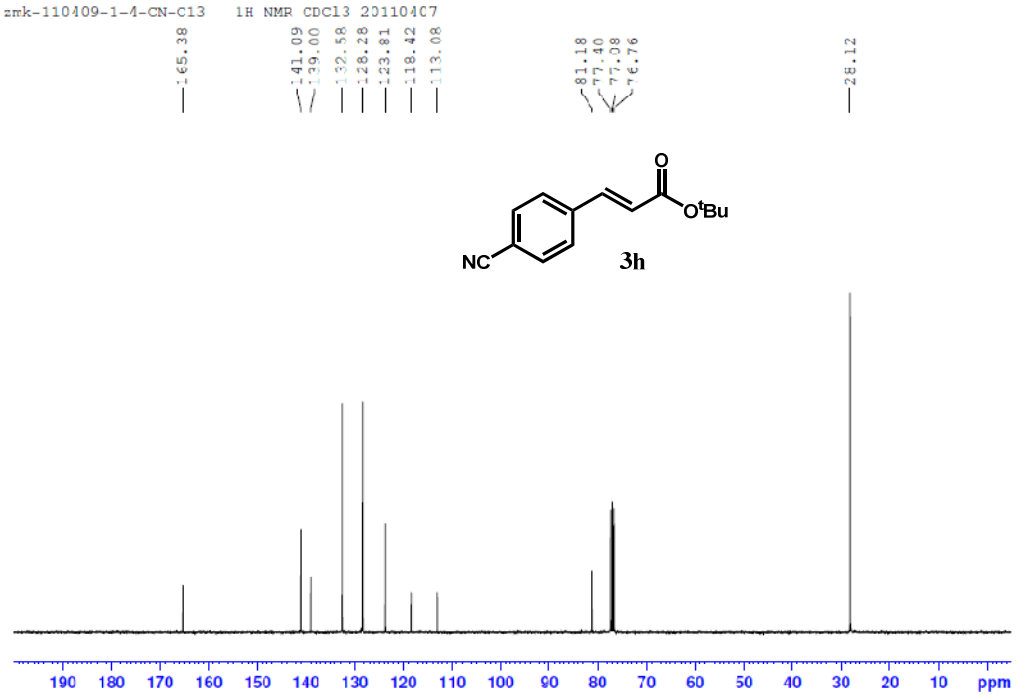

zmk-110504-2-4-Br-cootbu-H , 400 MHz H
7.519
7.497
7.478
7.361
7.341
7.253
6.362
6.322
1.520
O
O^{t}Bu
Br
3f
9
8
7
6
5
4
3
2
1
0 ppm
2.97
2.06
1.00
9.33

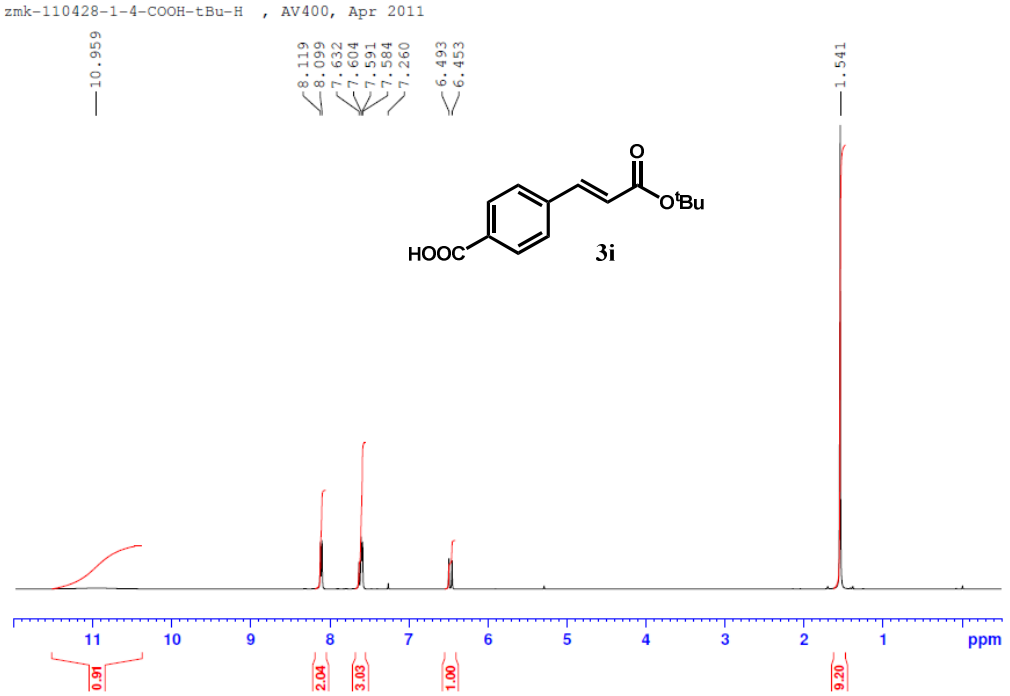

zmk-110504-2-4-Br-cootbu-C13, 400 MHz H
166.01
142.13
133.51
132.06
129.33
124.14
120.94
80.72
77.35
77.04
76.72
28.13
O
O^{t}Bu
Br
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

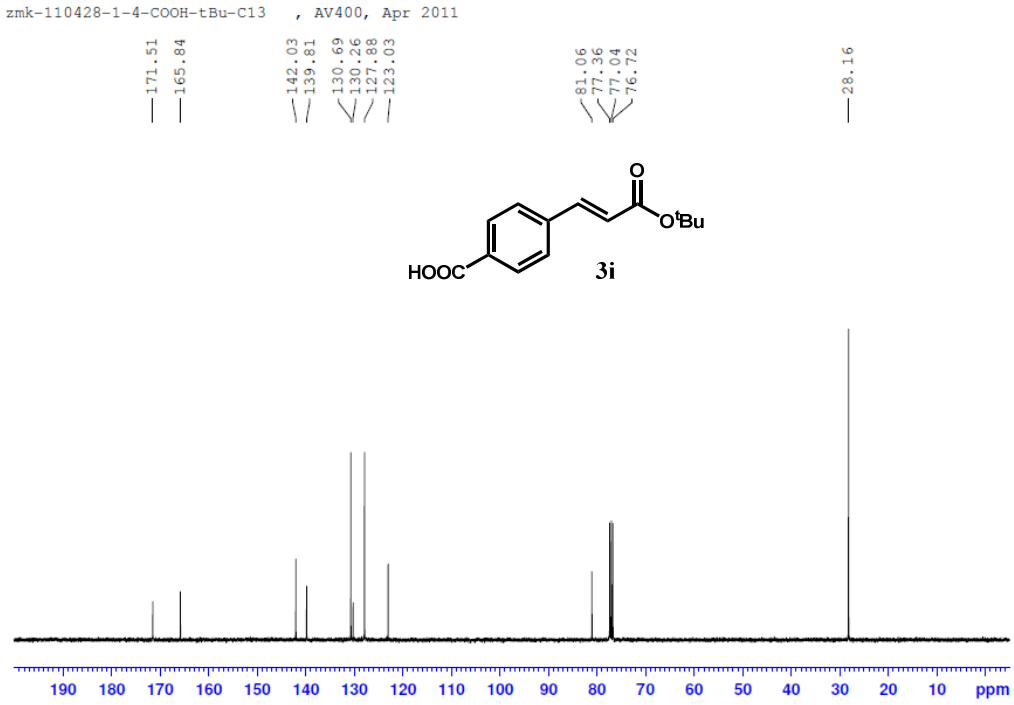

zmk-110429-4-I-tBu-H , AV400, Apr 2011
7.706
7.686
7.503
7.463
7.227
7.206
6.377
6.337
1.523
O
O^{t}Bu
I
3g
9
8
7
6
5
4
3
2
1
0 ppm
1.96
1.00
2.04
1.01
9.24

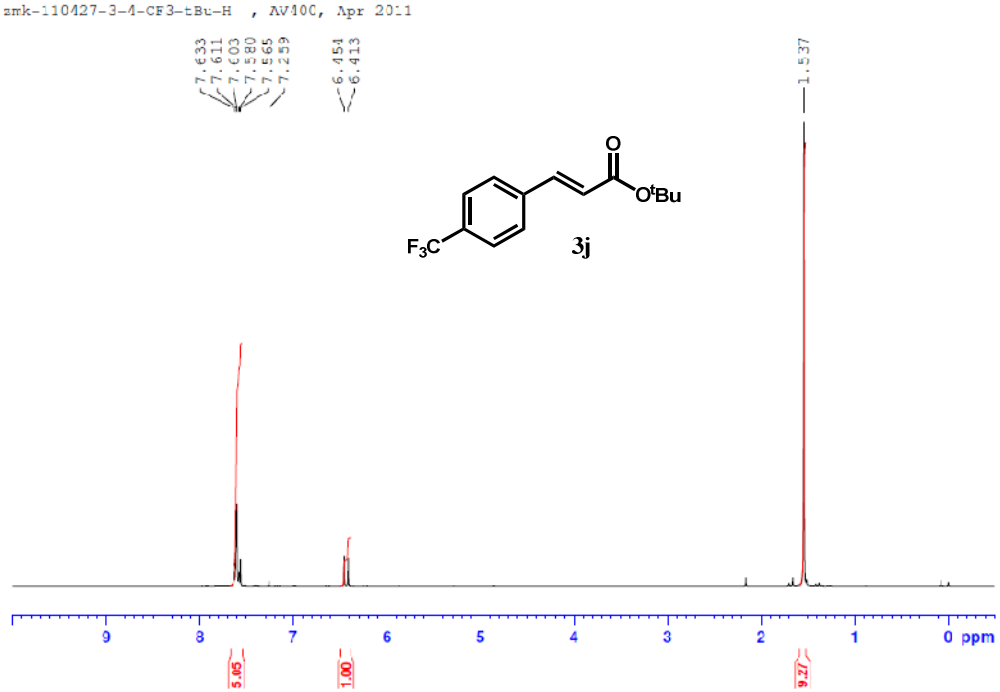

zmk-110429-4-I-tBu-C13, AV400, Apr 2011
165.99
142.28
138.03
134.17
129.43
121.01
96.07
80.72
77.37
77.05
76.73
28.19
O
O^{t}Bu
I
3g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

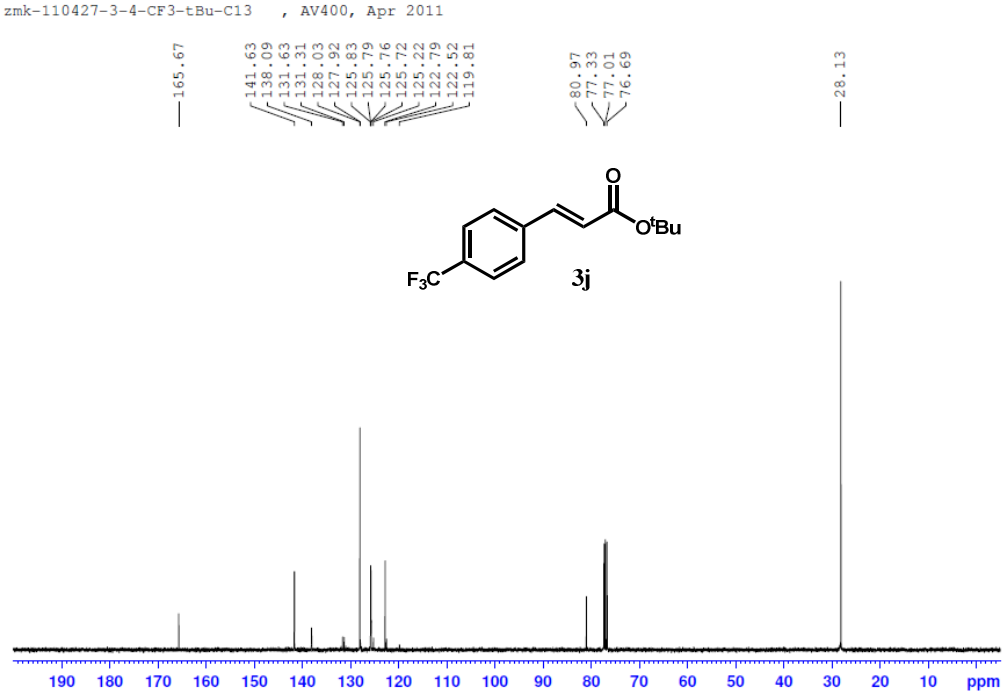

zmk-110430-4-CN-COOtBu-zhongzuo-H , AV400, Apr 2011
7.662
7.642
7.587
7.566
7.525
7.259
6.456
6.416
1.526
O
O'Bu
NC
3h
9
8
7
6
5
4
3
2
1
0 ppm
1.98
3.01
1.00
9.25

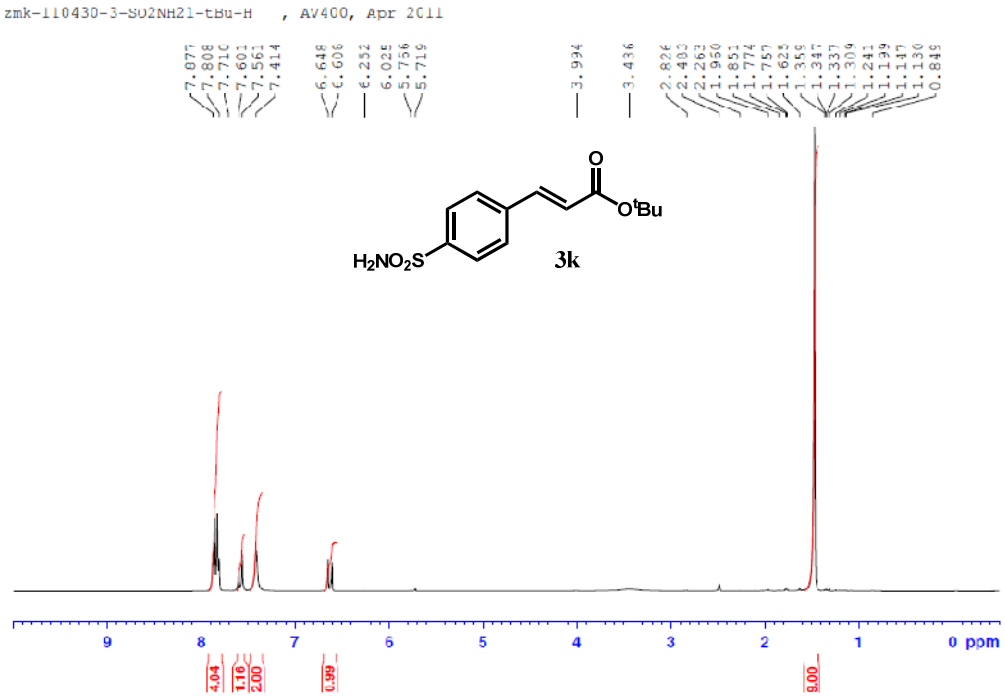

zmk-110409-1-4-CN-C13 1H NMR CDCl3 20110407
165.38
141.09
139.00
132.58
128.28
123.81
118.42
113.08
81.18
77.40
77.08
76.76
28.12
O
O'Bu
NC
3h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

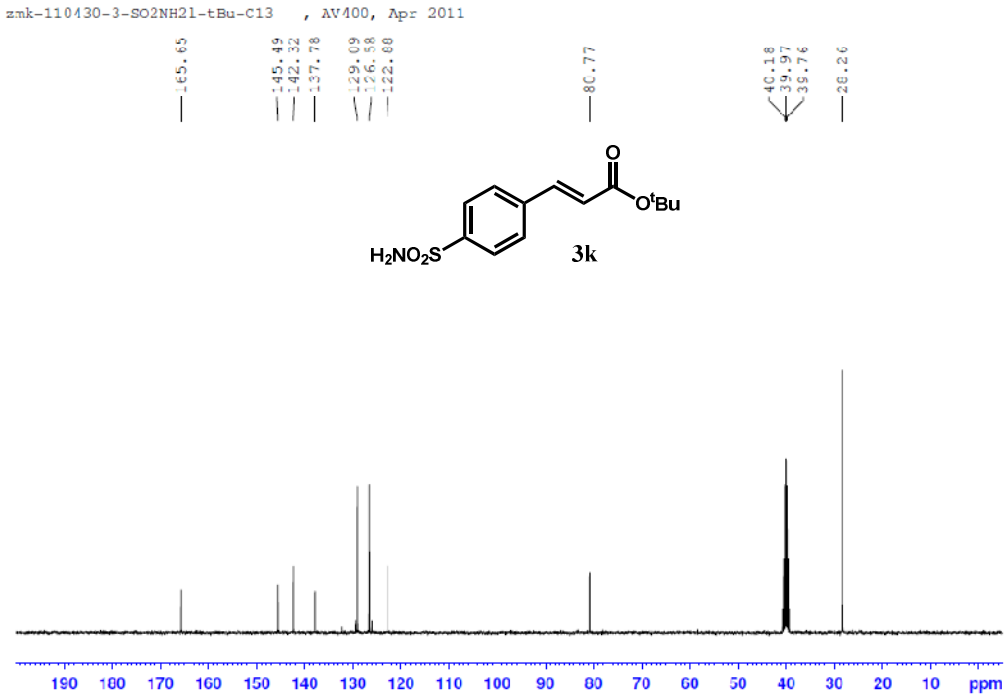

zmk-110428-1-4-COOH-tBu-H , AV400, Apr 2011
10.959
8.119
8.099
7.632
7.604
7.591
7.584
7.260
6.493
6.453
1.541
HOOC
O
O
tBu
3i
11
10
9
8
7
6
5
4
3
2
1
ppm
0.91
2.04
3.03
1.00
9.20

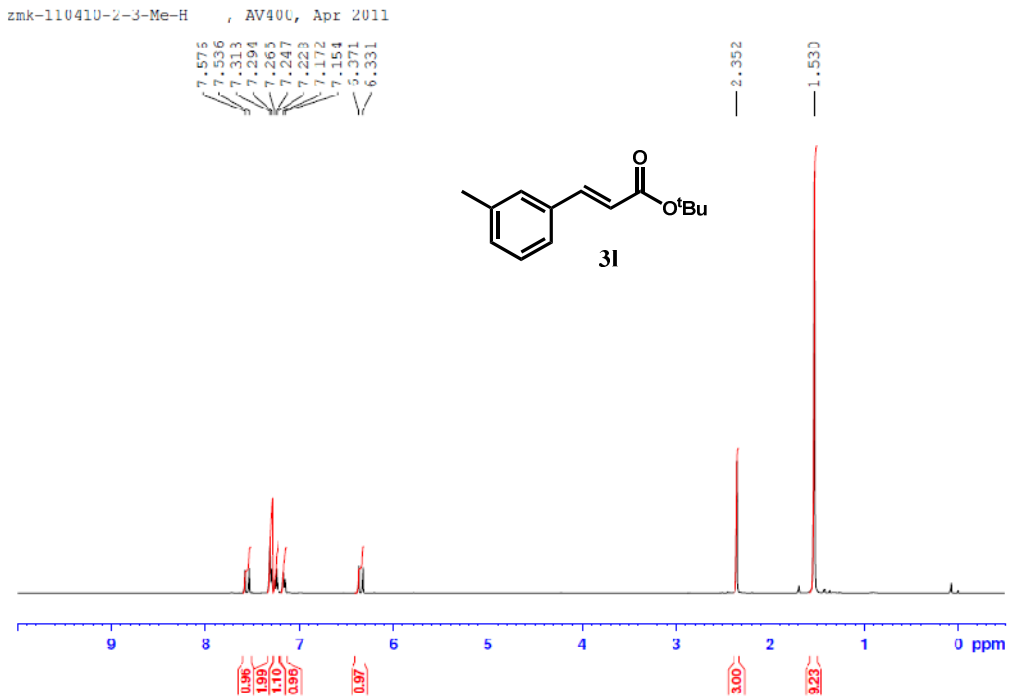

zmk-110428-1-4-COOH-tBu-C13 , AV400, Apr 2011
171.51
165.84
142.03
139.81
130.69
130.26
127.88
123.03
81.06
77.36
77.04
76.72
28.16
HOOC
O
O
tBu
3i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

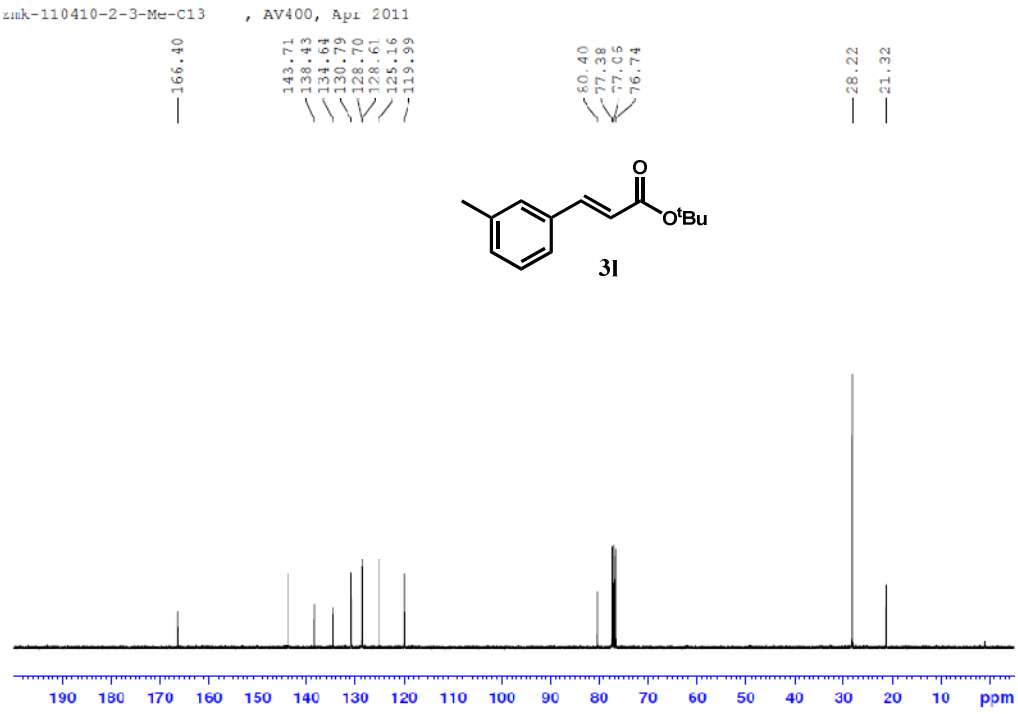

zmk-110427-3-4-CF3-tBu-H , AV400, Apr 2011
7.633
7.611
7.603
7.580
7.565
7.259
6.454
6.413
1.537
O
OtBu
F3C
3j
9
8
7
6
5
4
3
2
1
0 ppm
5.05
1.00
9.27

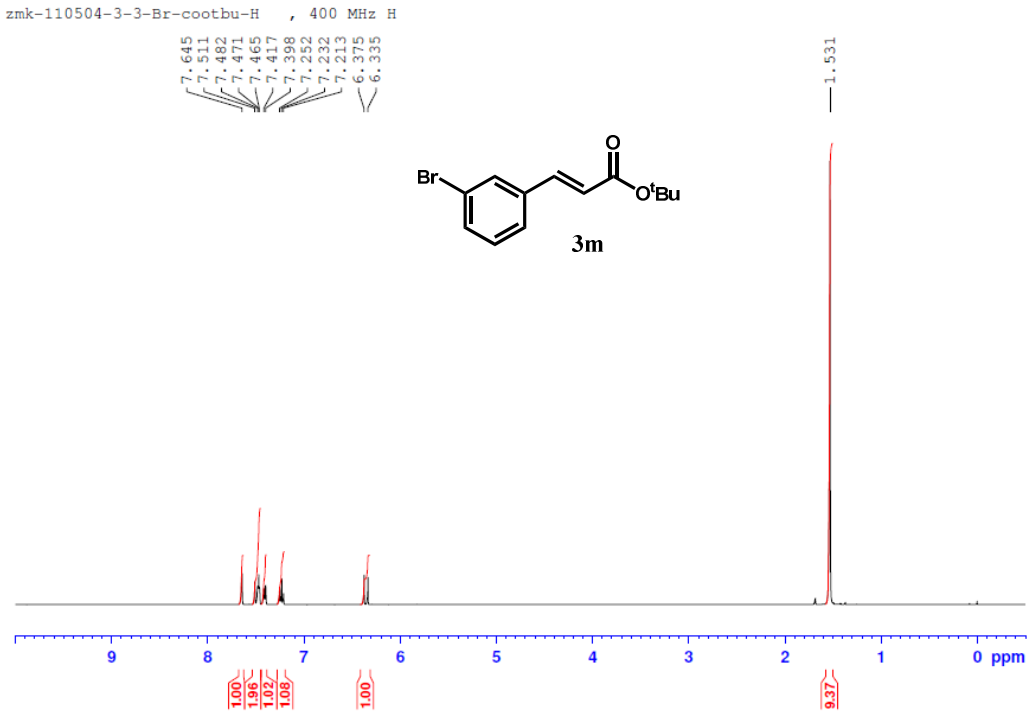

zmk-110427-3-4-CF3-tBu-C13 , AV400, Apr 2011
165.67
141.63
138.09
131.63
131.31
128.03
127.92
125.83
125.79
125.76
125.72
125.22
122.79
122.52
119.81
80.97
77.33
77.01
76.69
28.13
O
OtBu
F3C
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

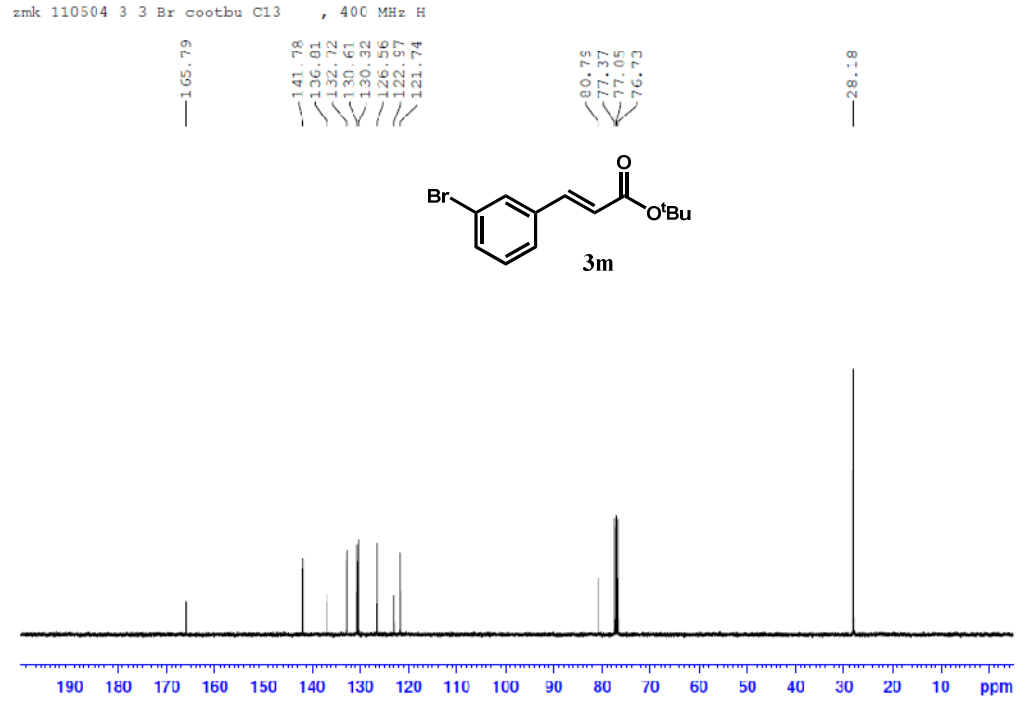

zmk-110430-3-SO2NH2-tBu-H , AV400, Apr 2011
7.677
7.808
7.710
7.601
7.561
7.414
6.648
6.606
6.252
6.025
5.756
5.719
3.994
3.436
2.826
2.493
2.263
1.950
1.851
1.774
1.757
1.625
1.359
1.347
1.337
1.309
1.241
1.139
1.147
1.130
0.849
O
O^{t}Bu
H_2NO_2S
3k
9
8
7
6
5
4
3
2
1
0 ppm
4.04
1.16
2.00
0.99
9.00

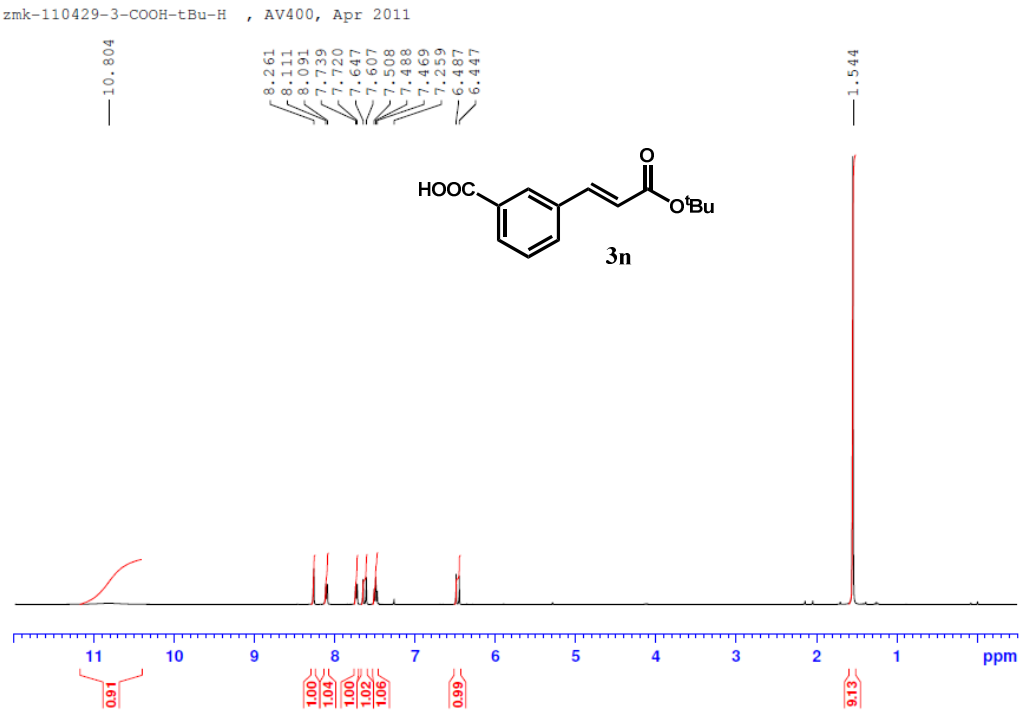

zmk-110430-3-SO2NH2-tBu-C13 , AV400, Apr 2011
165.65
145.49
142.32
137.78
129.09
126.58
122.60
80.77
40.18
39.97
39.76
28.26
O
O^{t}Bu
H_2NO_2S
3k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

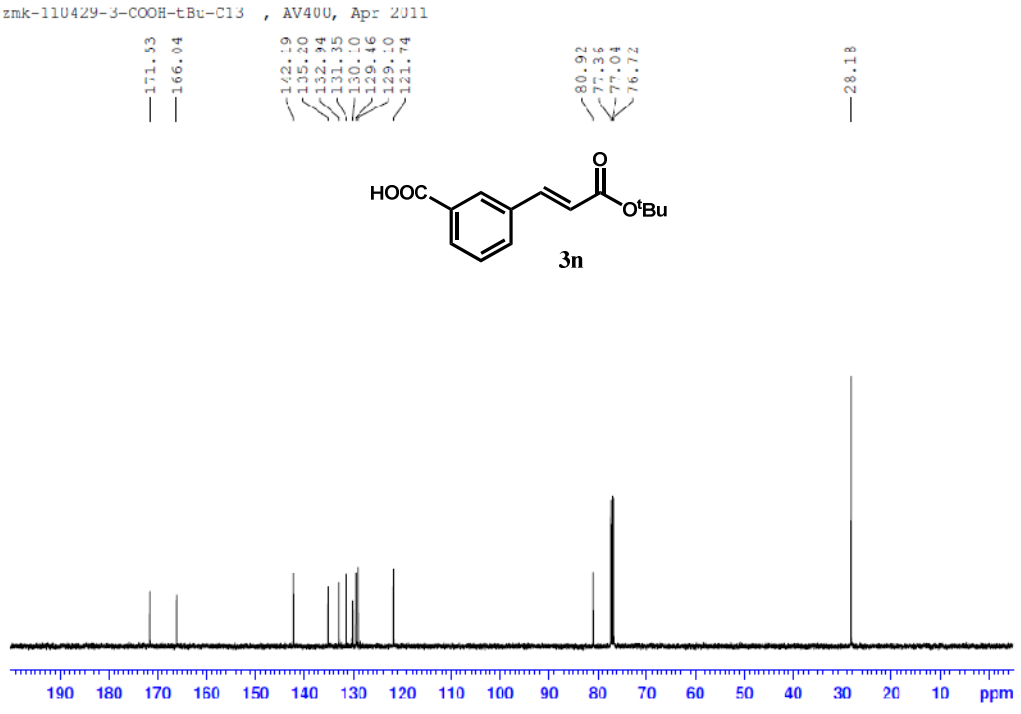

zmk-110410-2-3-Me-H , AV400, Apr 2011
7.575
7.556
7.313
7.294
7.265
7.247
7.223
7.172
7.154
6.371
6.331
2.352
1.530
O
O'Bu
3l
9
8
7
6
5
4
3
2
1
0 ppm
0.96
1.99
1.10
0.96
0.97
3.00
9.23

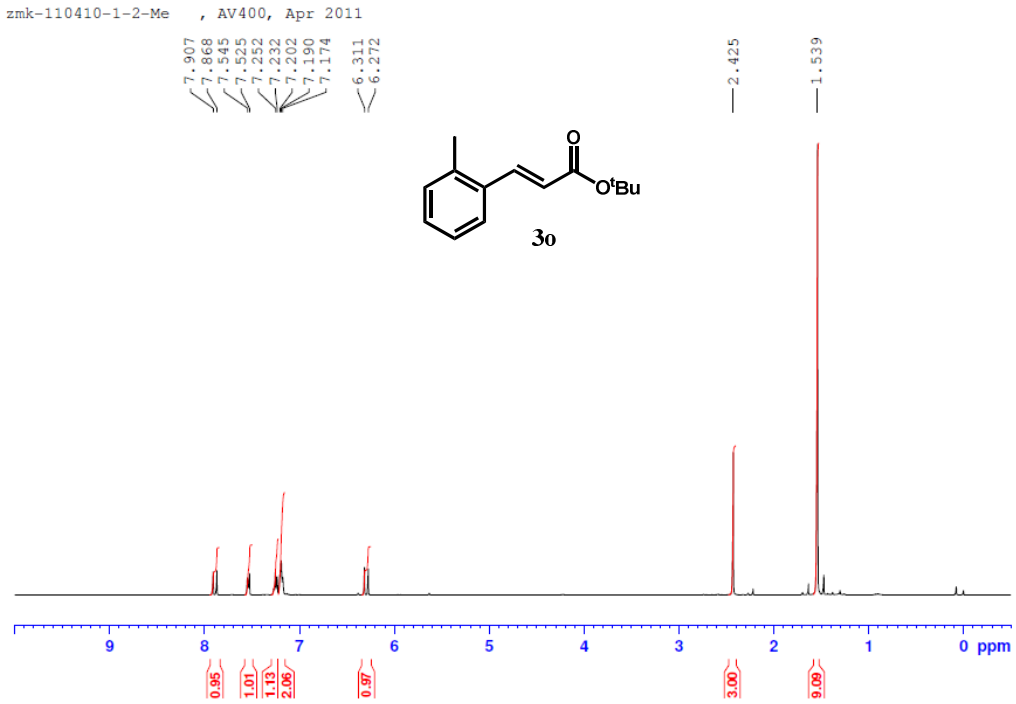

zmk-110410-2-3-Me-C13 , AV400, Apr 2011
166.40
143.71
138.43
134.64
130.79
128.70
128.61
125.16
119.99
60.40
77.38
77.05
76.74
28.22
21.32
O
O'Bu
3l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


zmk-110504-3-3-Br-cootbu-H , 400 MHz H
7.645
7.511
7.482
7.471
7.465
7.417
7.398
7.252
7.232
7.213
6.375
6.335
1.531
Br
O
O
tBu
3m
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.96
1.02
1.08
1.00
9.37

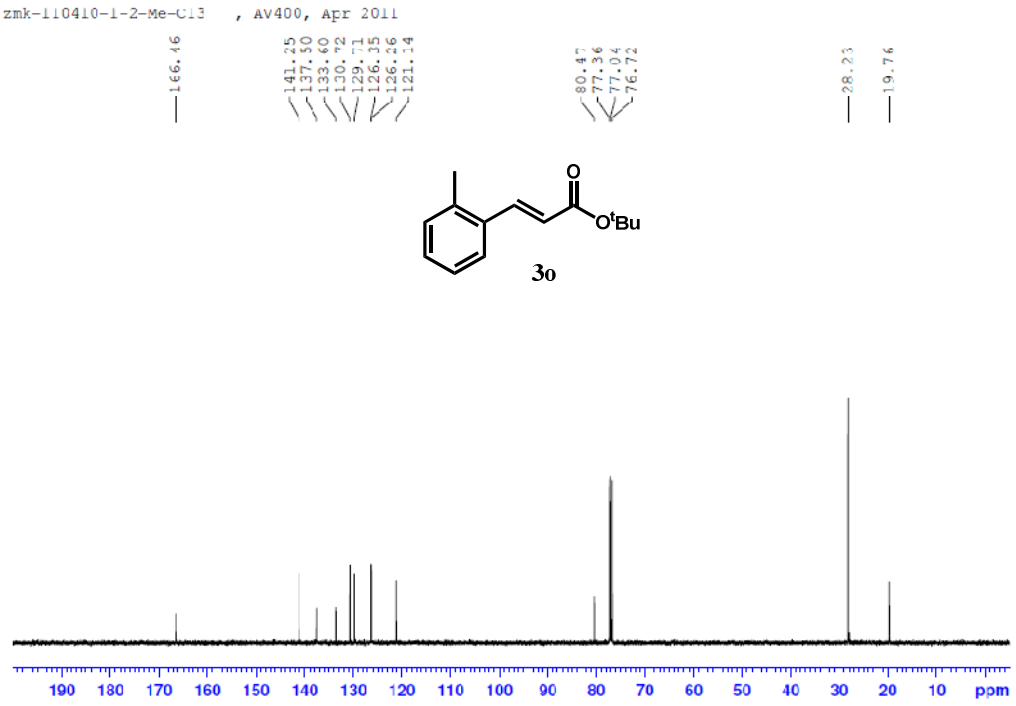

zmk 110504 3 3 Br cootbu C13 , 400 MHz H
165.79
141.78
136.81
132.72
130.61
130.32
126.56
122.97
121.74
80.75
77.37
77.05
76.73
28.18
Br
O
O
tBu
3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


zmk-110429-3-COOH-tBu-H , AV400, Apr 2011
10.804
8.261
8.111
8.091
7.739
7.720
7.647
7.607
7.508
7.488
7.469
7.259
6.487
6.447
1.544
HOOC
O
O
tBu
3n
11
10
9
8
7
6
5
4
3
2
1
ppm
0.91
1.00
1.04
1.00
1.02
1.06
0.99
9.13

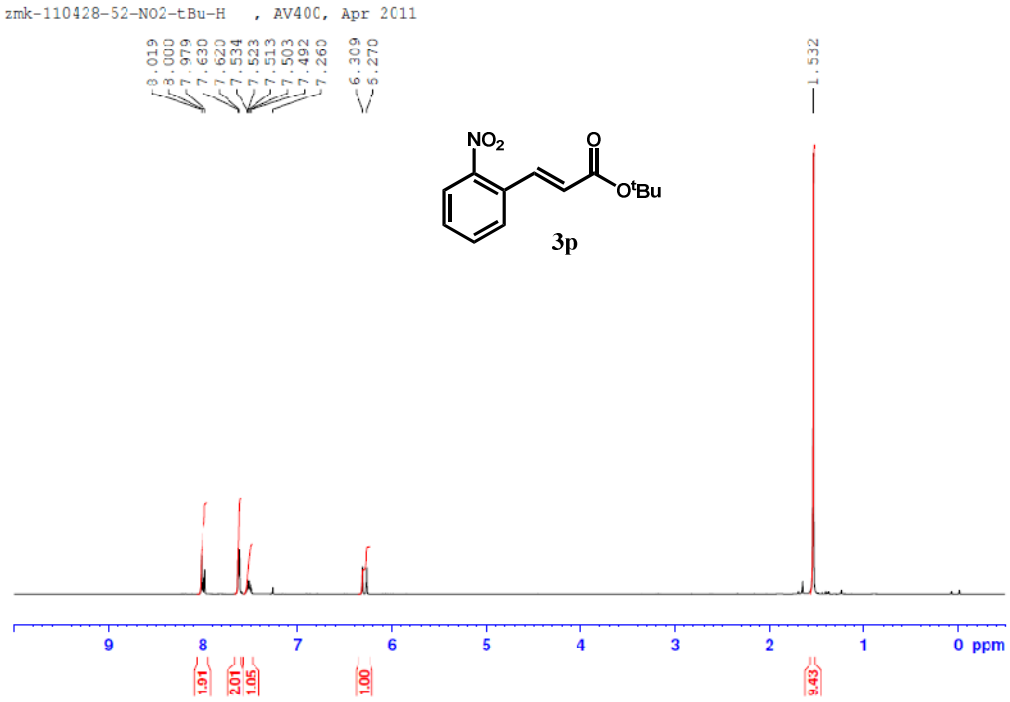

zmk-110429-3-COOH-tBu-C13 , AV400, Apr 2011
171.53
166.04
142.9
135.20
132.94
131.35
130.10
129.46
129.10
121.74
80.92
77.36
77.04
76.72
28.18
HOOC
O
O
tBu
3n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

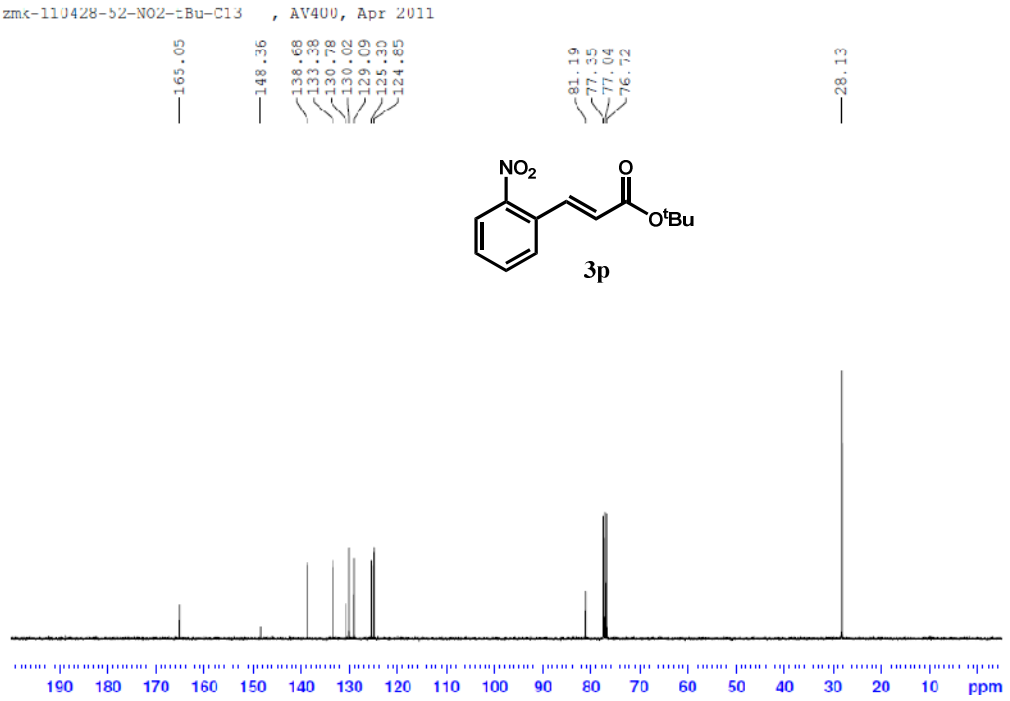

zmk-110410-1-2-Me , AV400, Apr 2011
7.907
7.868
7.545
7.525
7.252
7.232
7.202
7.190
7.174
6.311
6.272
2.425
1.539
O
O^{t}Bu
9 8 7 6 5 4 3 2 1 0 ppm
0.95
1.01
1.13
2.06
0.97
3.00
9.09

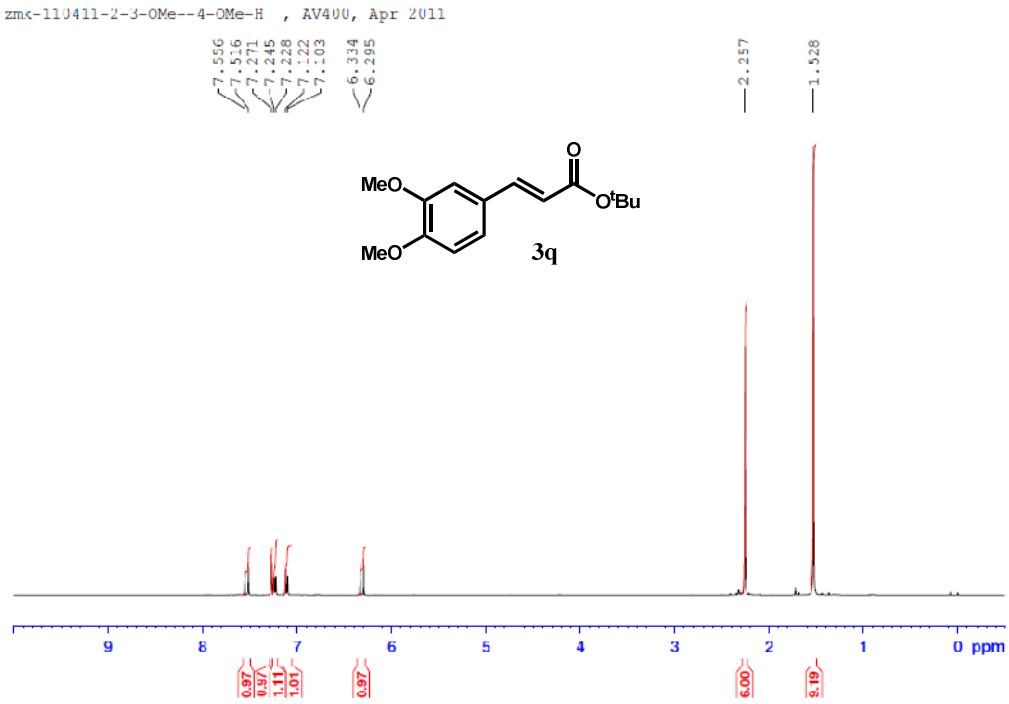
3o

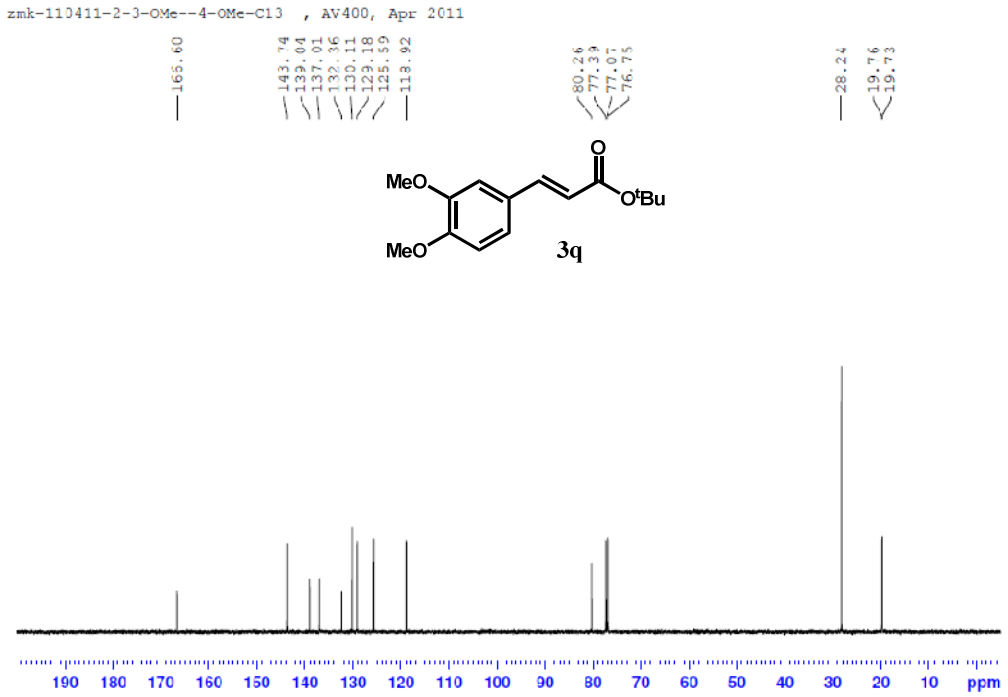

zmk-110410-1-2-Me-C13 , AV400, Apr 2011
166.46
141.25
137.50
133.60
130.72
129.71
126.35
126.26
121.14
80.47
77.36
77.04
76.72
28.23
19.76
O
O^{t}Bu
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

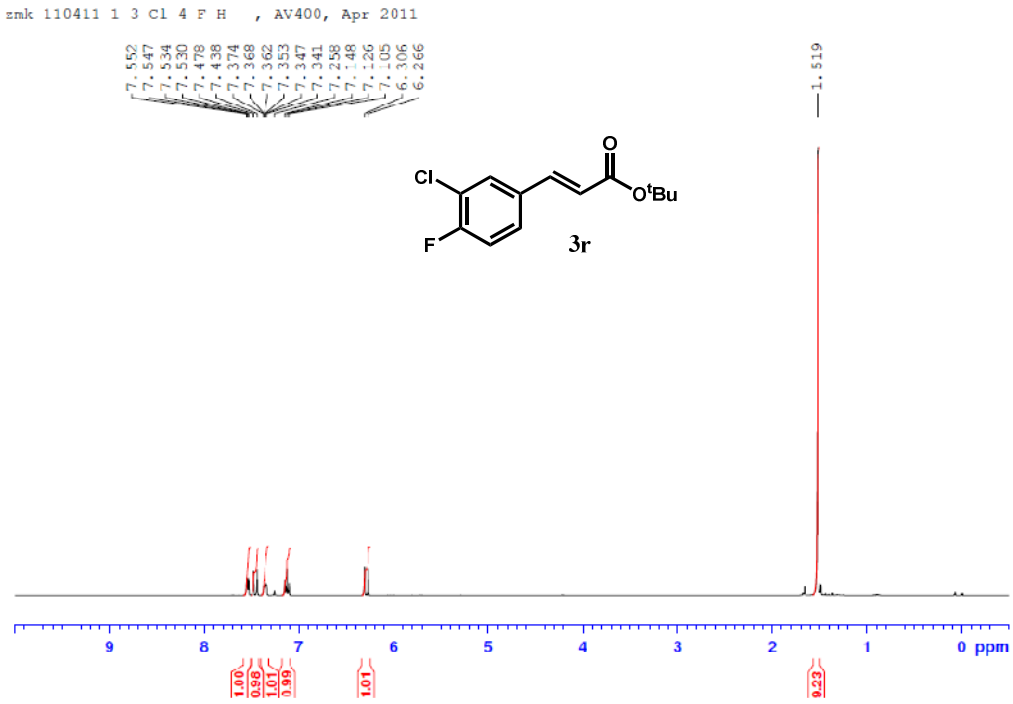
3o

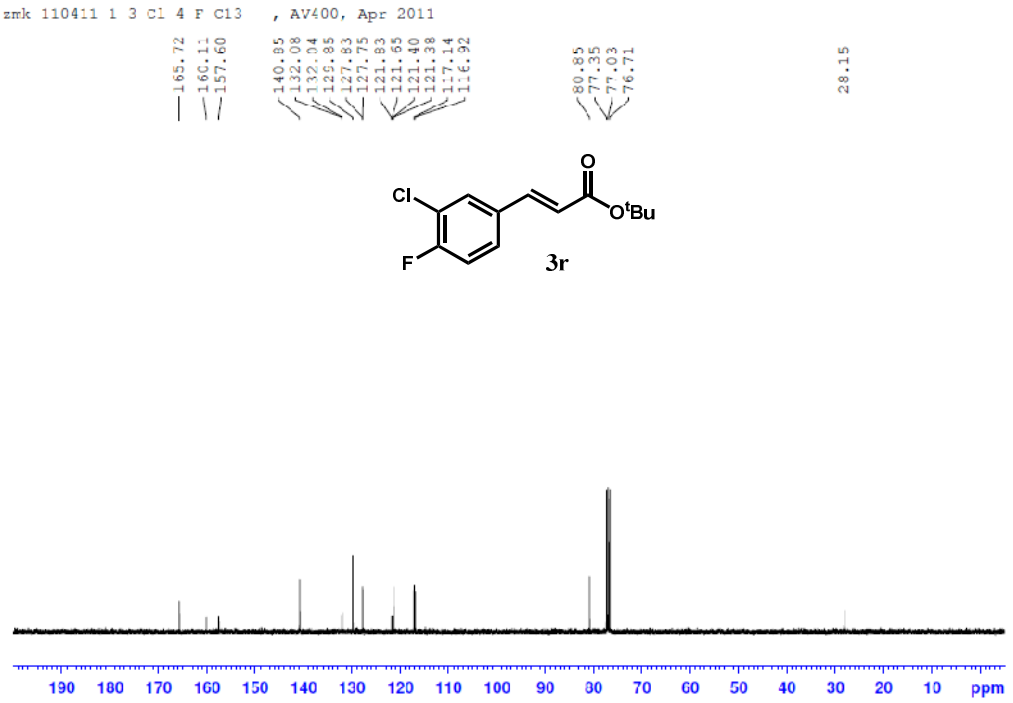

zmk-110428-52-NO2-tBu-H , AV400, Apr 2011
8.019
8.000
7.979
7.630
7.620
7.534
7.523
7.513
7.503
7.492
7.260
6.309
5.270
1.532
NO2
O
OtBu
3p
9
8
7
6
5
4
3
2
1
0 ppm
1.01
2.01
1.05
1.00
9.43


zmk-110428-52-NO2-tBu-C13 , AV400, Apr 2011
165.05
148.36
138.68
133.38
130.78
130.02
129.09
125.30
124.85
81.19
77.35
77.04
76.72
28.13
NO2
O
OtBu
3p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

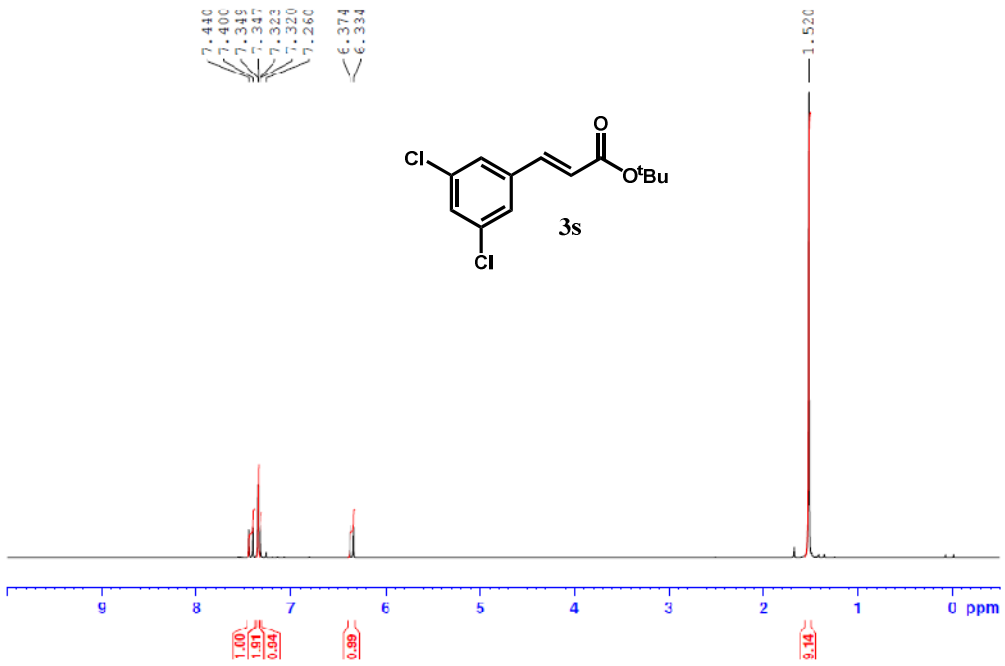

zmk-110411-2-3-OMe--4-OMe-H , AV400, Apr 2011
7.556
7.516
7.271
7.245
7.228
7.222
7.103
6.334
6.295
2.257
1.528
MeO
MeO
O
O
tBu
3q
9
8
7
6
5
4
3
2
1
0 ppm
0.97
0.97
1.11
1.01
0.97
6.00
9.19


zmk-110411-2-3-OMe--4-OMe-C13 , AV400, Apr 2011
166.60
143.74
139.04
137.01
132.36
130.11
129.18
125.59
118.92
80.26
77.33
77.07
76.75
28.24
19.76
19.73
MeO
MeO
O
O
tBu
3q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

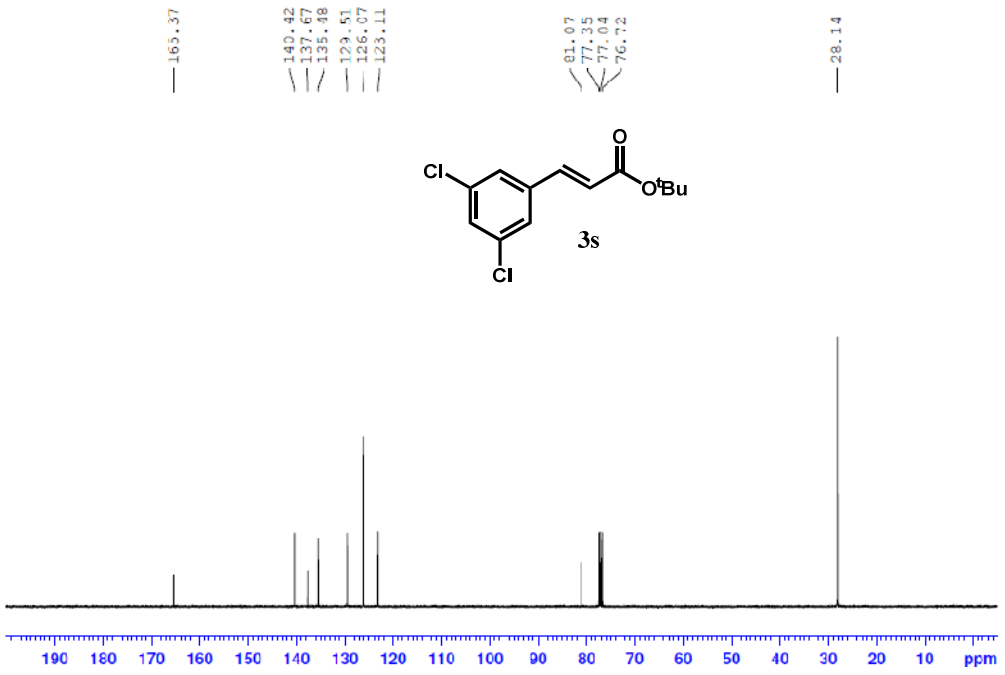

zmk 110411 1 3 Cl 4 F H , AV400, Apr 2011
7.552
7.547
7.534
7.530
7.478
7.438
7.374
7.368
7.362
7.353
7.347
7.341
7.258
7.148
7.126
7.105
6.306
6.266
1.519
Cl
F
O
O^{t}Bu
3r
9
8
7
6
5
4
3
2
1
0 ppm
1.00
0.88
1.01
0.99
1.01
9.23

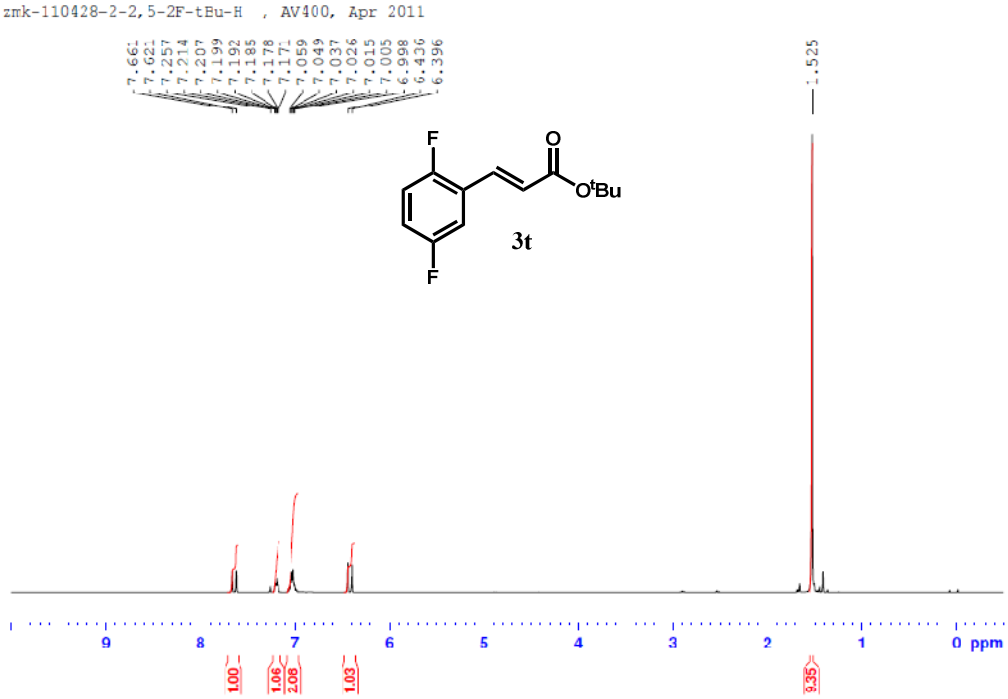

zmk 110411 1 3 Cl 4 F Cl3 , AV400, Apr 2011
165.72
160.11
157.60
140.85
132.08
132.04
129.85
127.83
127.75
121.83
121.65
121.40
121.38
117.14
116.92
80.85
77.35
77.03
76.71
28.15
Cl
F
O
O^{t}Bu
3r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

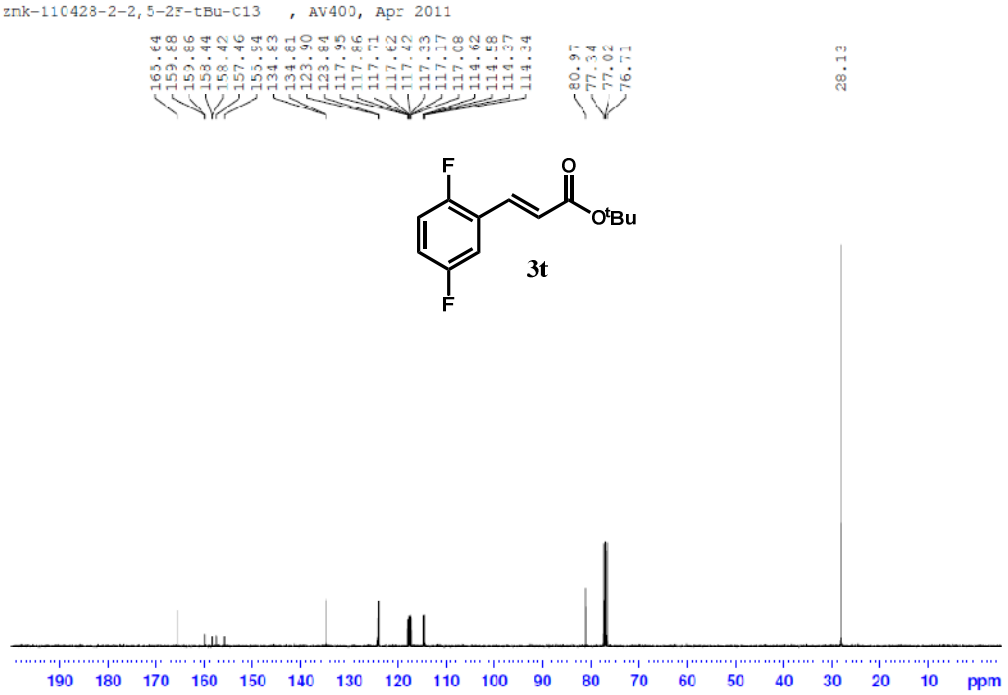
zmk-110427-4-3,5-2Cl-tBu-H , AV400, Apr 2011

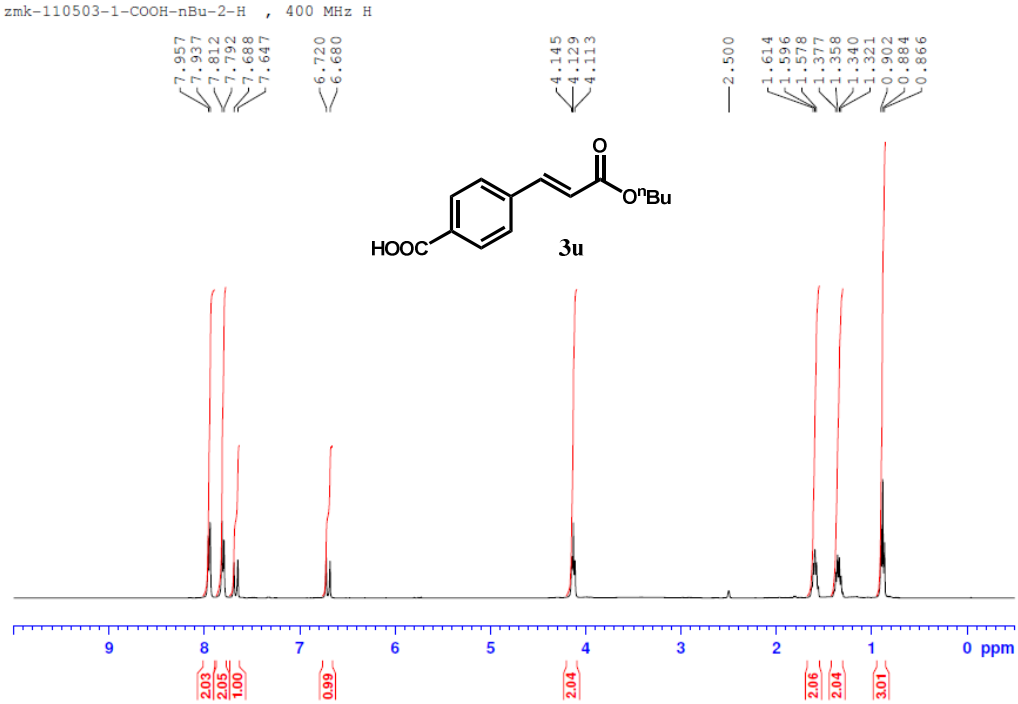


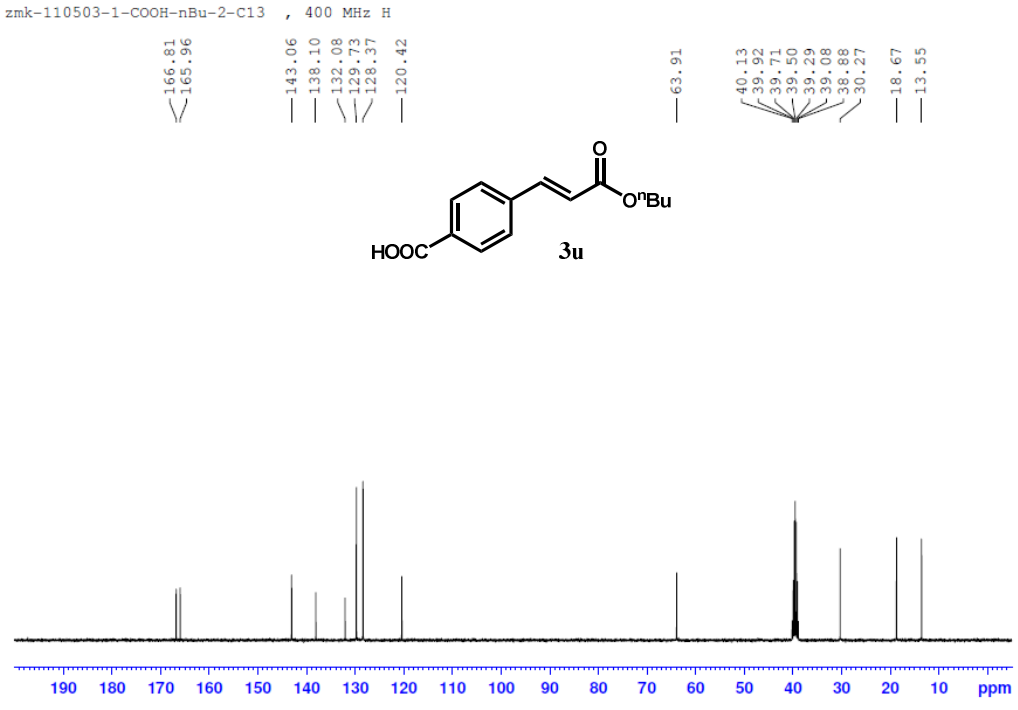
zmk-110427-4-3,5-2Cl-tBu-C13 , AV400, Apr 2011

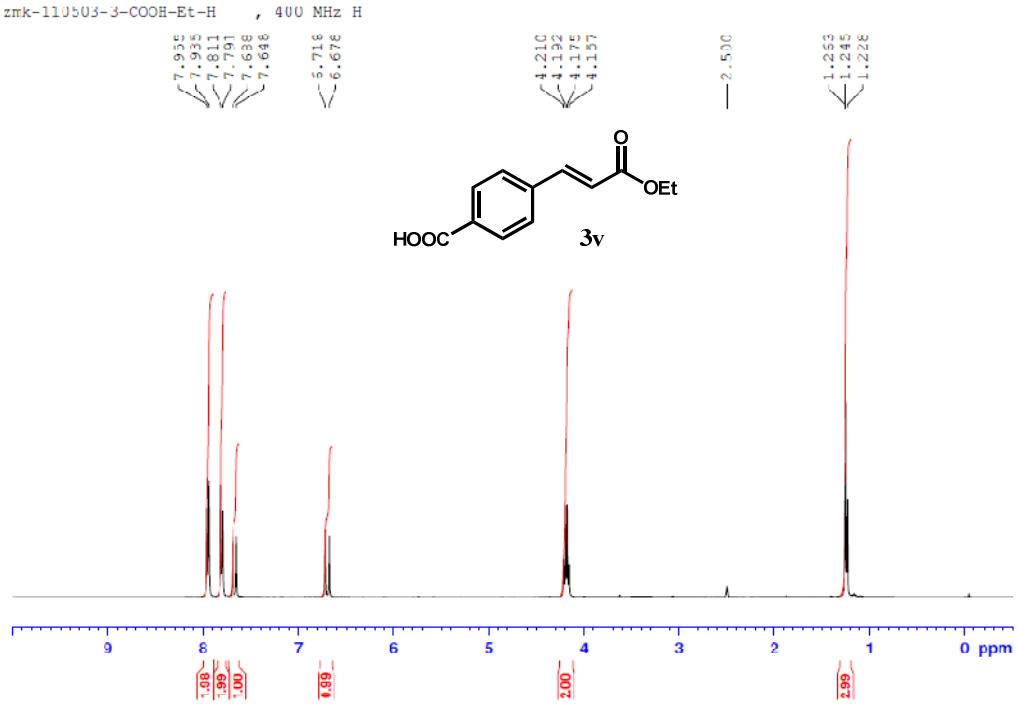


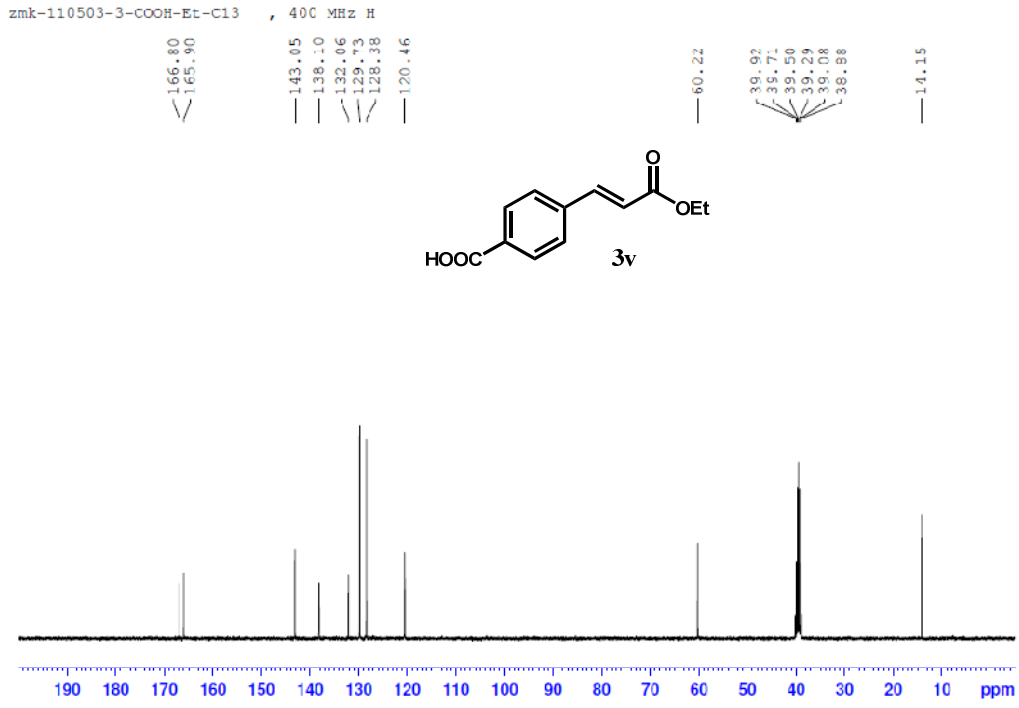

zmk-110428-2-2,5-2F-tBu-H , AV400, Apr 2011
7.661
7.622
7.257
7.214
7.207
7.199
7.192
7.185
7.178
7.172
7.059
7.049
7.037
7.026
7.015
7.005
6.998
6.436
6.396
1.525
F
O
OtBu
F
3t
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.06
2.06
1.03
9.35

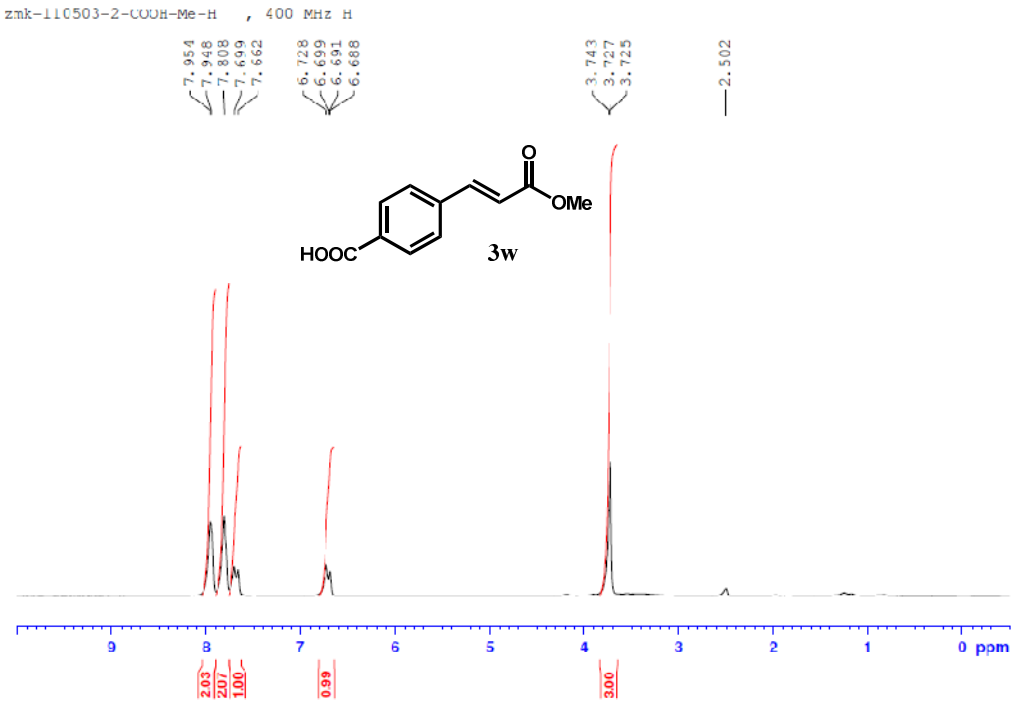

znk-110428-2-2,5-2F-tBu-C13 , AV400, Apr 2011
165.64
159.88
159.86
158.44
158.42
157.46
155.54
134.83
134.81
123.90
123.84
117.95
117.86
117.71
117.62
117.42
117.33
117.17
117.08
114.62
114.58
114.37
114.34
80.97
77.34
77.02
76.71
28.13
F
O
OtBu
F
3t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

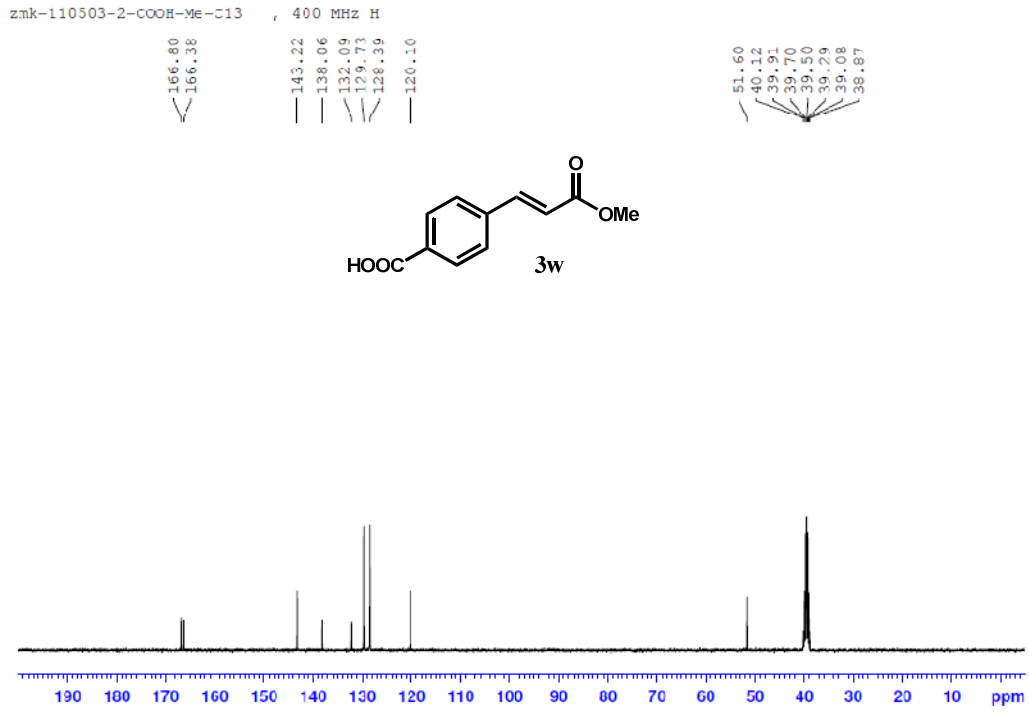

zmk-110503-1-COOH-nBu-2-H , 400 MHz H
7.957
7.937
7.812
7.792
7.688
7.647
6.720
6.680
4.145
4.129
4.113
2.500
1.614
1.596
1.578
1.377
1.358
1.340
1.321
0.902
0.884
0.866
O
O^{n}Bu
HOOC
3u
9
8
7
6
5
4
3
2
1
0 ppm
2.03
2.05
1.00
0.99
2.04
2.06
2.04
3.01

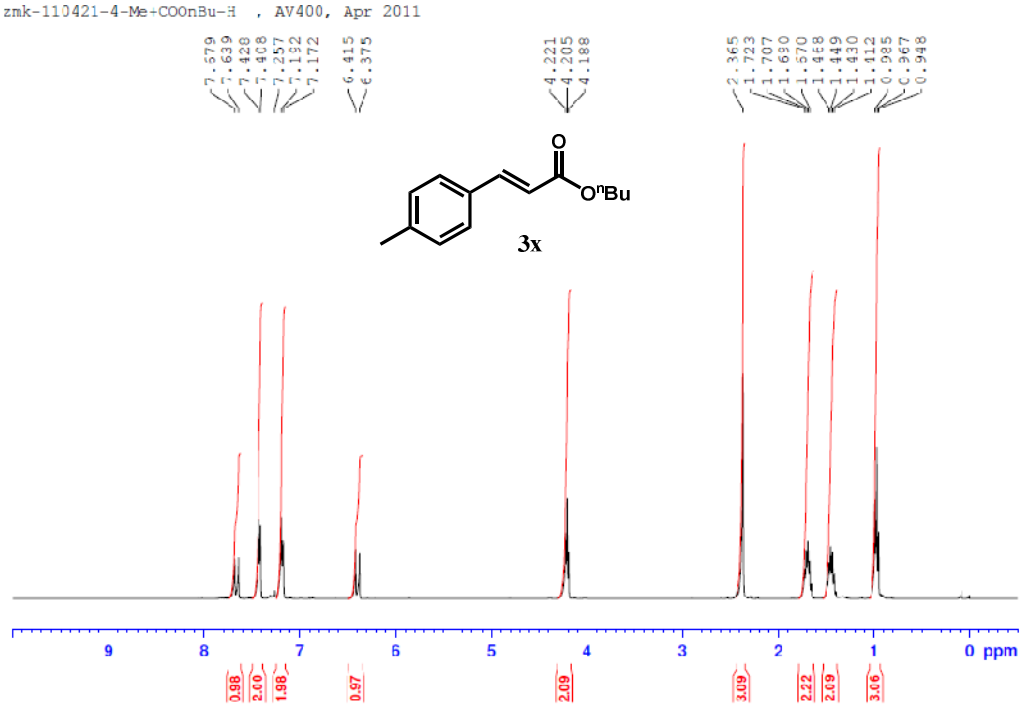

zmk-110503-1-COOH-nBu-2-C13 , 400 MHz H
166.81
165.96
143.06
138.10
132.08
129.73
128.37
120.42
63.91
40.13
39.92
39.71
39.50
39.29
39.08
38.88
30.27
18.67
13.55
O
O^{n}Bu
HOOC
3u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

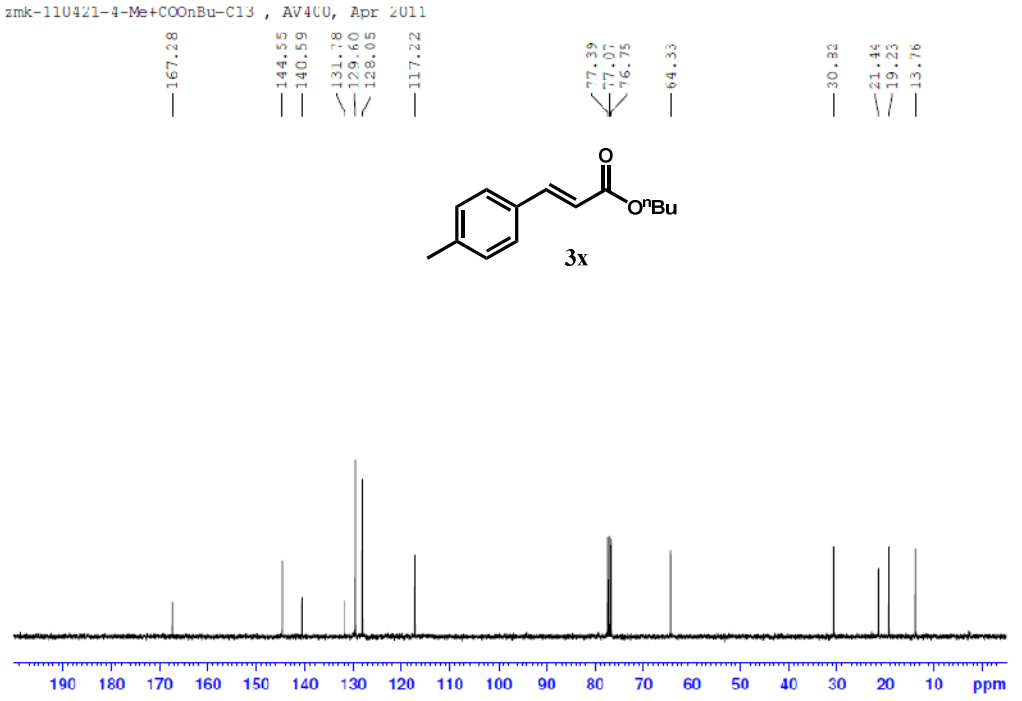

zmk-110503-3-COOH-Et-H , 400 MHz H
7.935
7.811
7.791
7.638
7.648
6.718
6.678
4.210
4.192
4.175
4.157
2.500
1.253
1.245
1.228
HOOC
OEt
O
3v
9
8
7
6
5
4
3
2
1
0 ppm
1.08
1.99
1.00
0.99
2.00
2.99

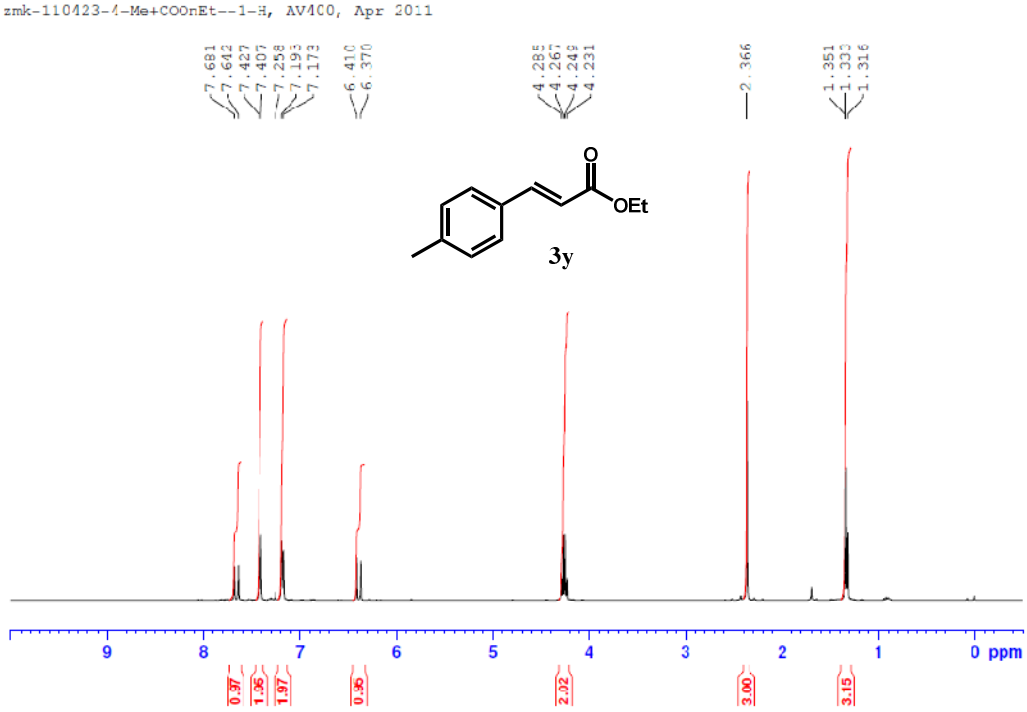

zmk-110503-3-COOH-Et-C13 , 400 MHz H
166.80
165.90
143.65
138.10
132.06
129.73
128.38
120.46
60.22
39.92
39.71
39.50
39.29
39.08
38.88
14.15
HOOC
OEt
O
3v
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

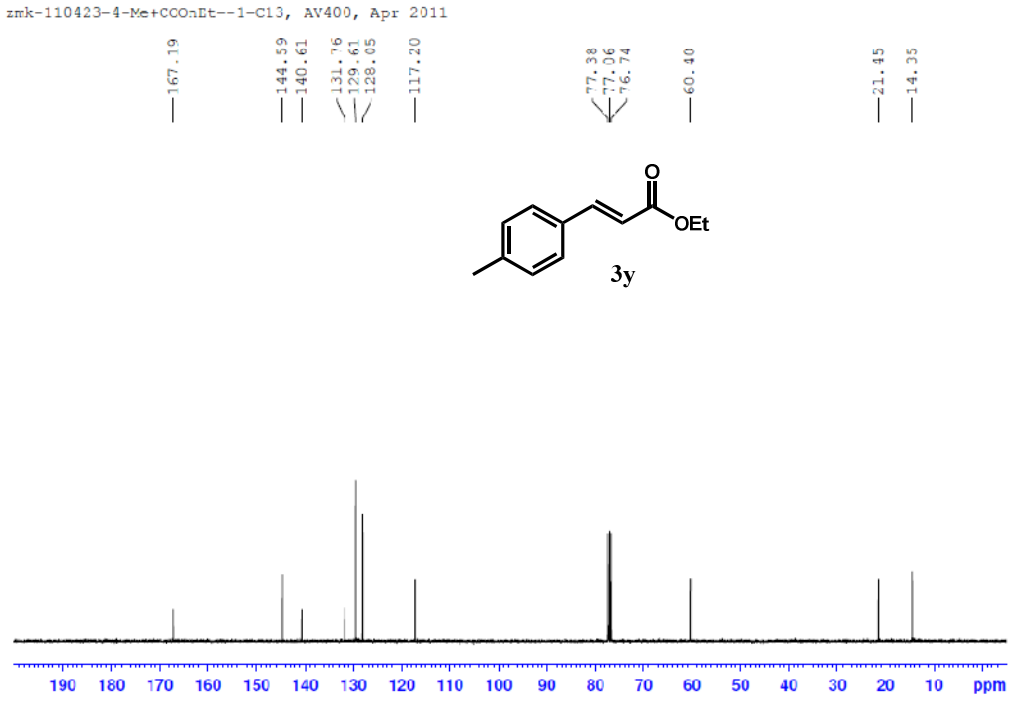

zmk-110503-2-COOH-Me-H , 400 MHz H
7.954
7.948
7.808
7.699
7.662
6.728
6.699
6.691
6.688
3.743
3.727
3.725
2.502
O
OMe
HOOC
3w
9
8
7
6
5
4
3
2
1
0 ppm
2.03
2.07
1.00
0.99
3.00

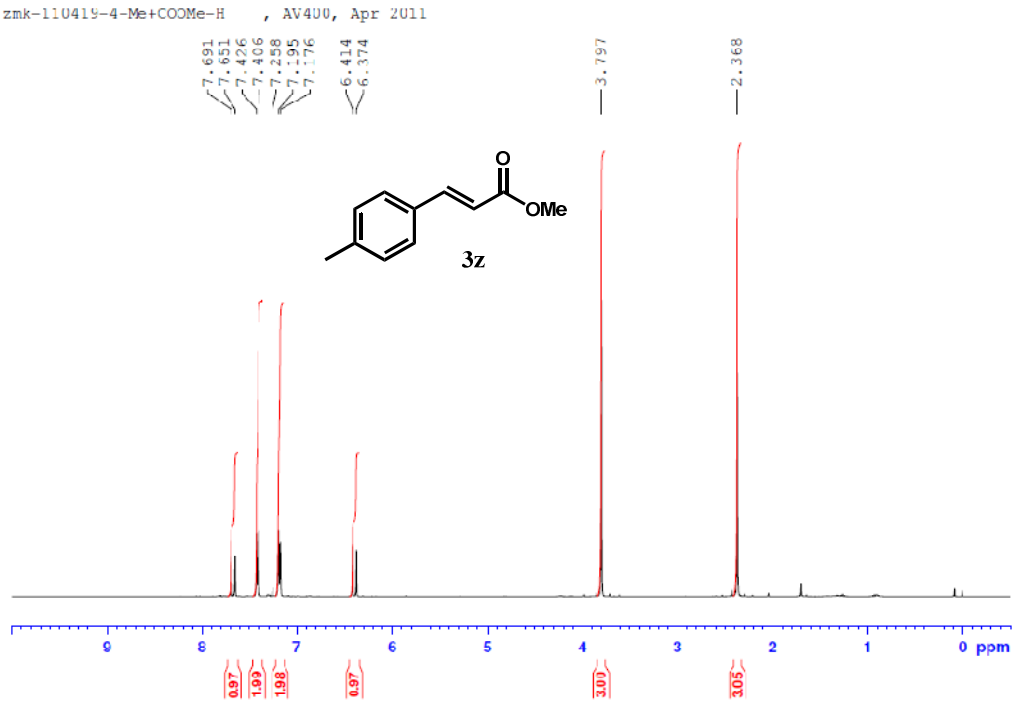

zmk-110503-2-COOH-Me-C13 , 400 MHz H
166.80
166.38
143.22
138.06
132.09
129.73
128.39
120.10
51.60
40.12
39.91
39.70
39.50
39.29
39.08
38.87
O
OMe
HOOC
3w
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

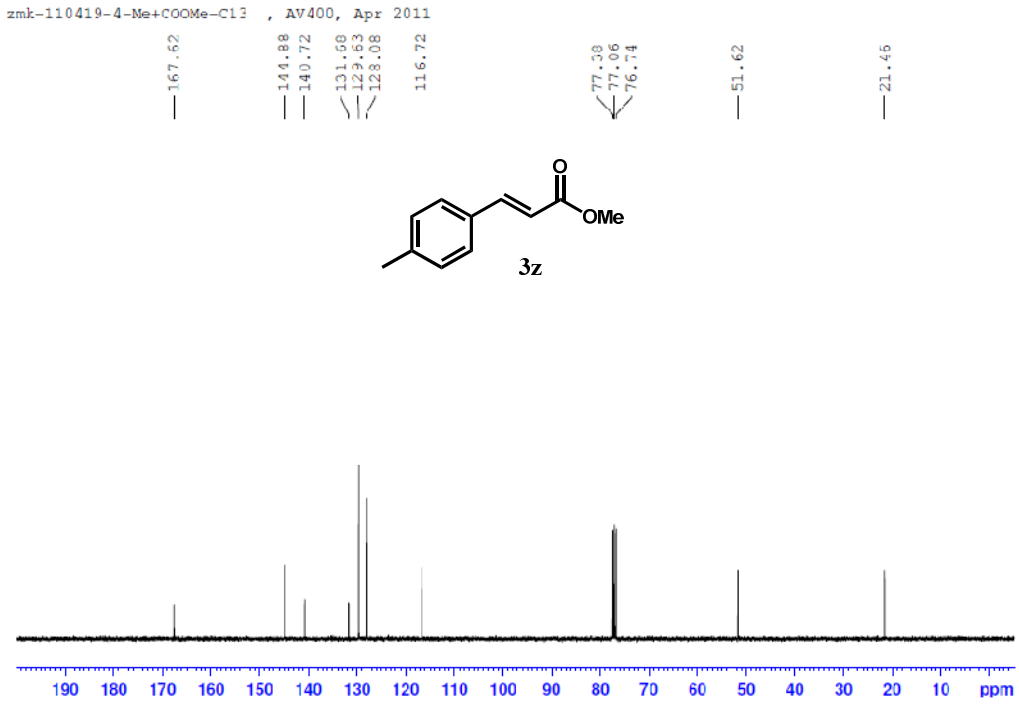

zmk-110421-4-Me+COOnBu-H , AV400, Apr 2011
7.579
7.639
7.428
7.408
7.257
7.192
7.172
6.415
6.375
4.221
4.205
4.188
2.365
1.723
1.707
1.690
1.570
1.468
1.449
1.430
1.412
0.985
0.967
0.948
O
OnBu
3x
9
8
7
6
5
4
3
2
1
0 ppm
0.98
2.00
1.98
0.97
2.09
3.09
2.22
2.09
3.06


zmk-110421-4-Me+COOnBu-C13 , AV400, Apr 2011
167.28
144.55
140.59
131.78
129.60
128.05
117.22
77.39
77.07
76.75
64.33
30.82
21.44
19.23
13.76
O
OnBu
3x
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

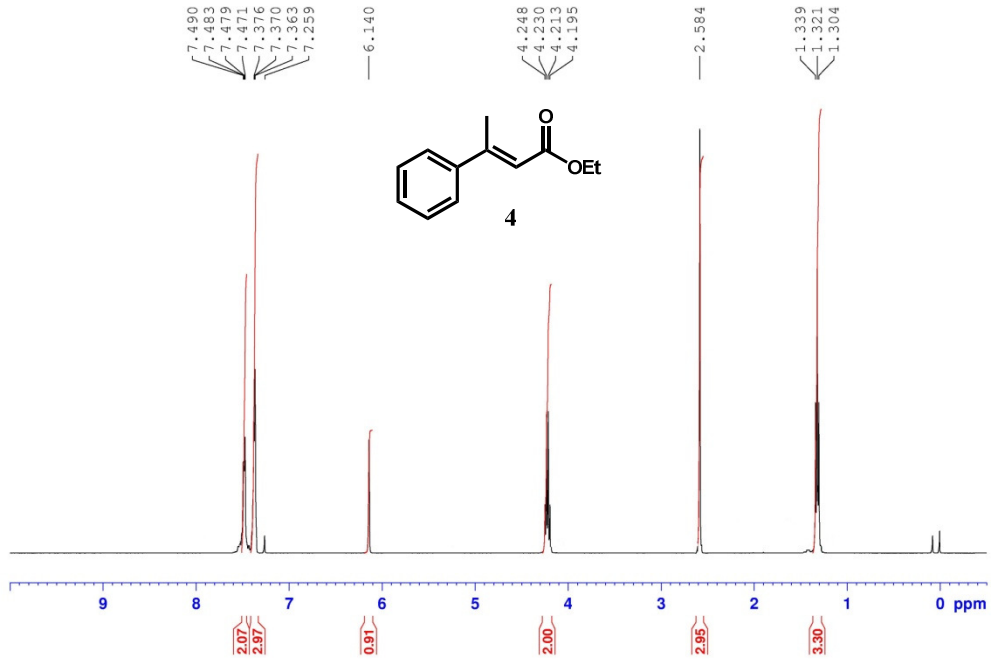

zmk-110423-4-Me+COOnEt--1-H, AV400, Apr 2011
7.681
7.642
7.427
7.407
7.258
7.195
7.173
6.410
6.370
4.285
4.267
4.249
4.231
2.366
1.351
1.333
1.316
OEt
3y
9
8
7
6
5
4
3
2
1
0 ppm
0.97
1.36
1.97
0.36
2.02
3.00
3.15


zmk-110423-4-Me+COOnEt--1-C13, AV400, Apr 2011
167.19
144.59
140.61
131.76
129.61
128.05
117.20
77.38
77.06
76.74
60.40
21.45
14.35
OEt
3y
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

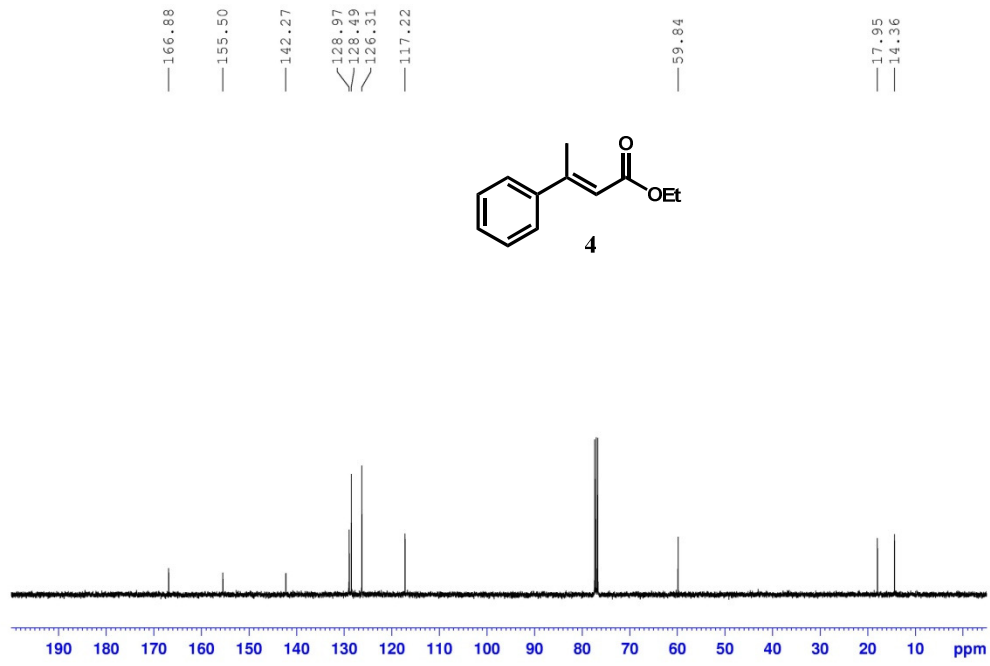

zmk-110419-4-Me+COOMe-H , AV400, Apr 2011
7.691
7.651
7.426
7.406
7.258
7.195
7.176
6.414
6.374
3.797
2.368
O
OMe
3z
9
8
7
6
5
4
3
2
1
0 ppm
0.97
1.99
1.98
0.97
3.01
3.05

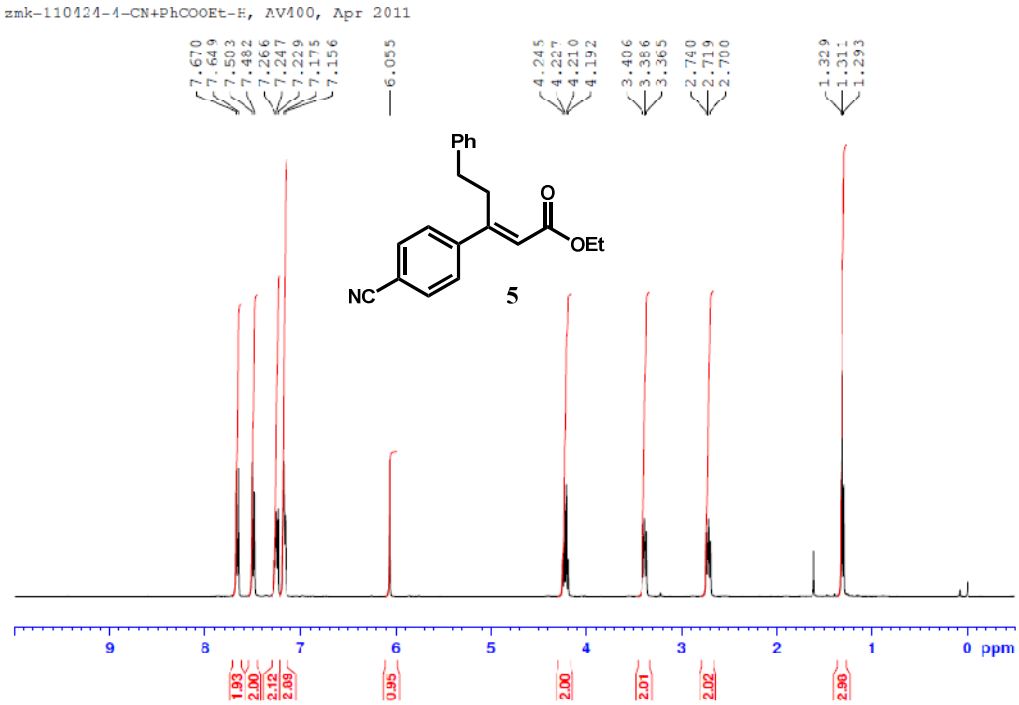

zmk-110419-4-Me+COOMe-C13 , AV400, Apr 2011
167.62
144.88
140.72
131.60
129.63
128.08
116.72
77.38
77.06
76.74
51.62
21.46
O
OMe
3z
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

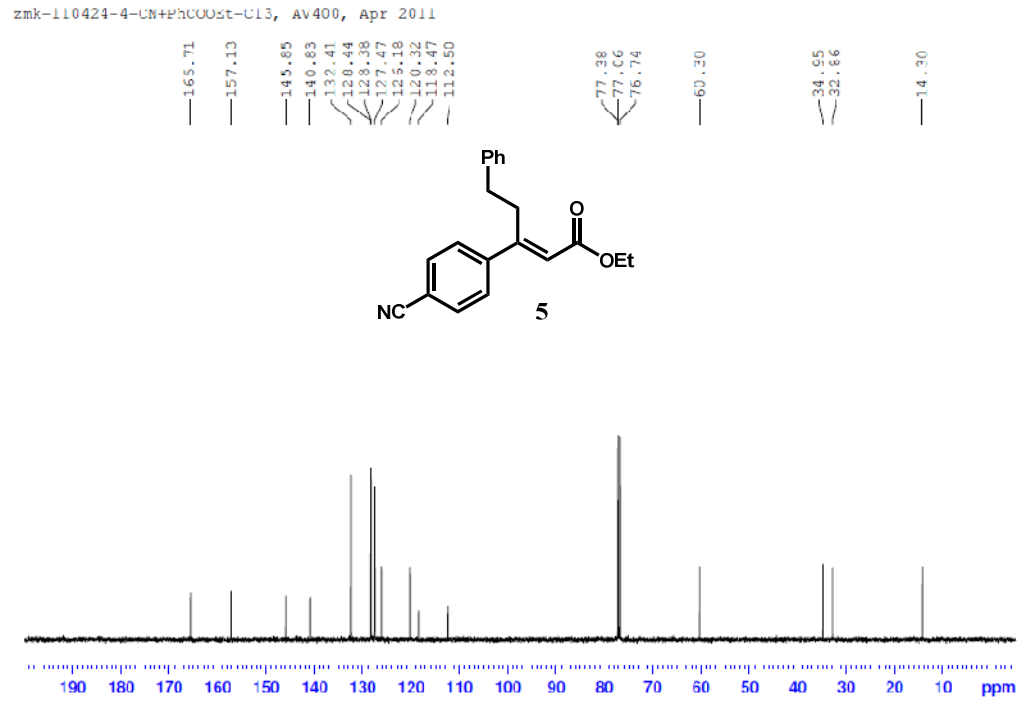
zmk-110430-PhMe-Et-H , AV400, Apr 2011

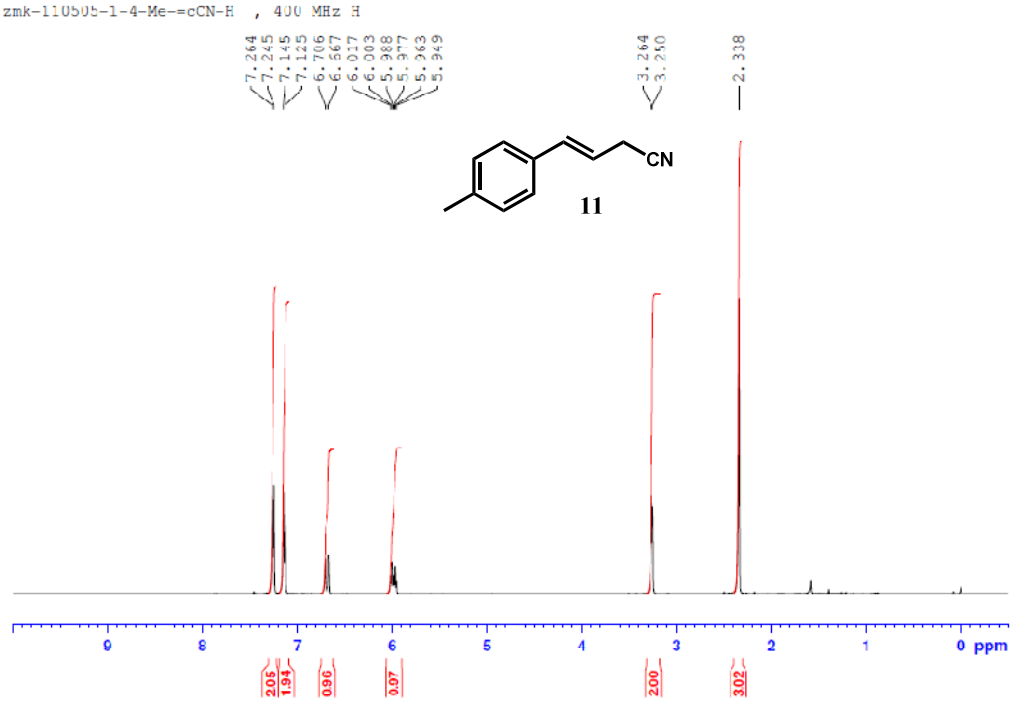


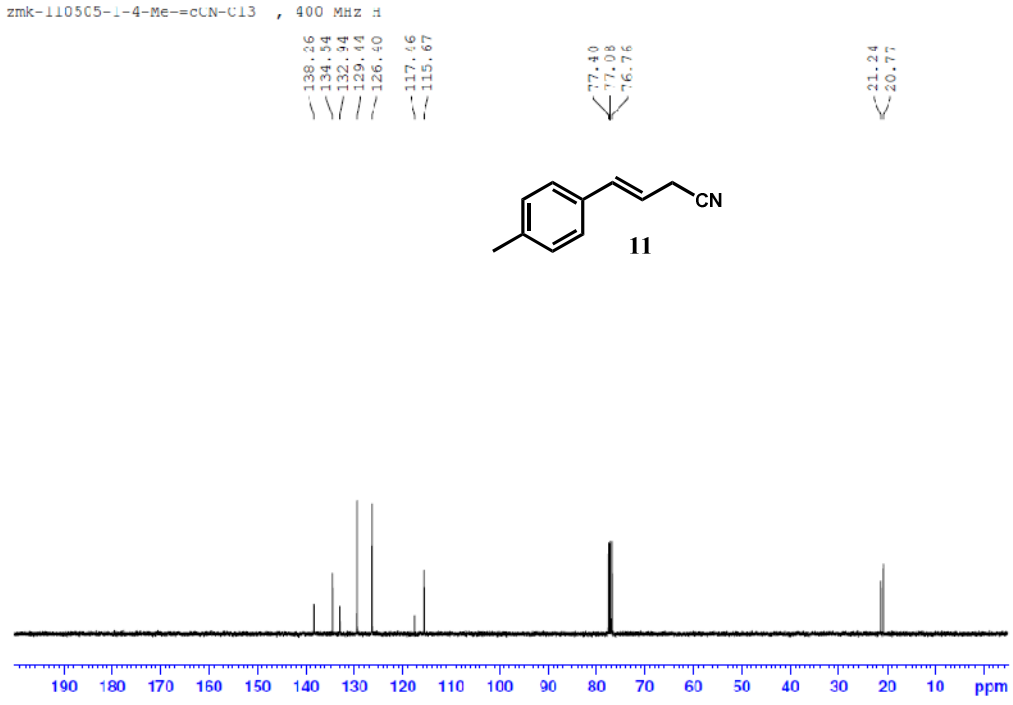
zmk-110430-PhMe-Et-C13 , AV400, Apr 2011

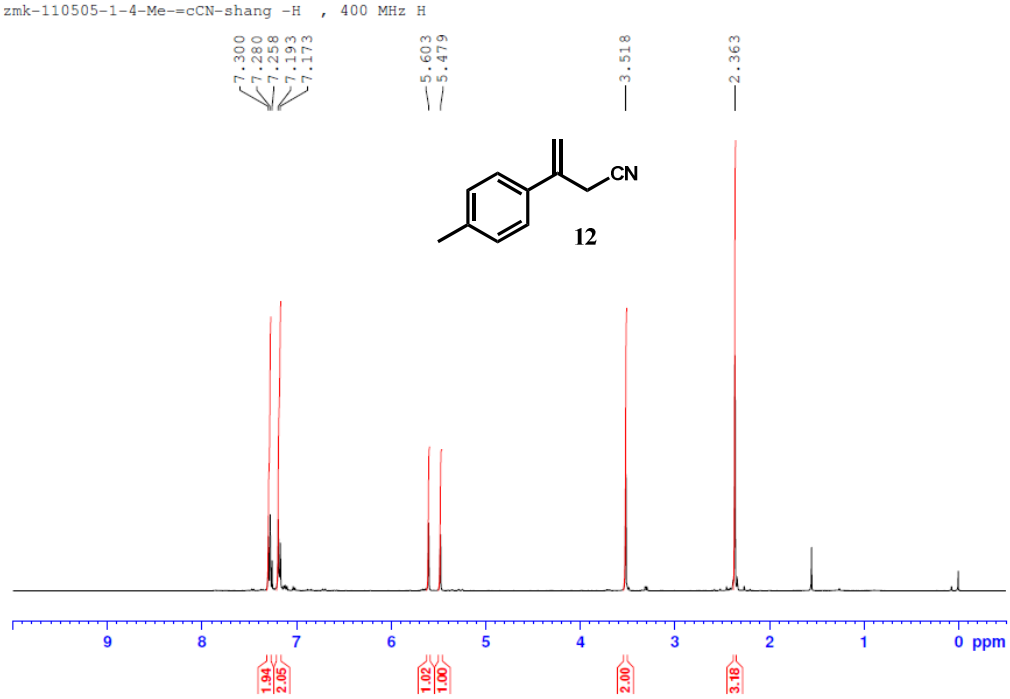


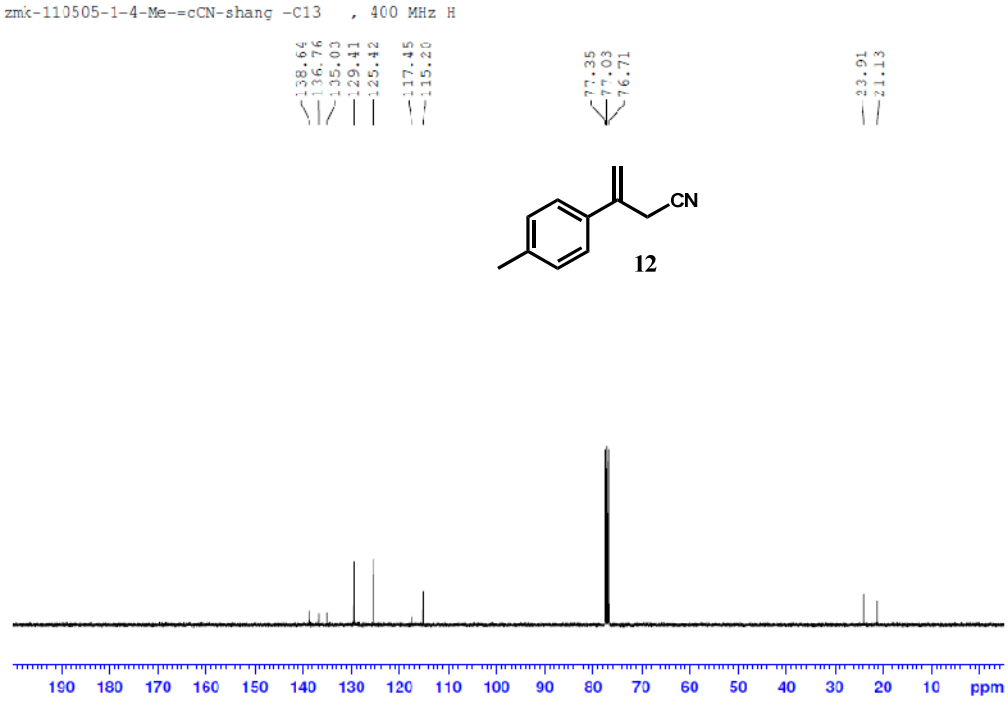

zmk-110424-4-CN+PhCOOEt-H, AV400, Apr 2011
7.670
7.649
7.503
7.482
7.266
7.247
7.229
7.175
7.156
6.055
4.245
4.227
4.210
4.192
3.406
3.386
3.365
2.740
2.719
2.700
1.329
1.311
1.293
Ph
O
OEt
NC
5
9
8
7
6
5
4
3
2
1
0 ppm
1.93
2.00
2.12
2.09
0.95
2.00
2.01
2.02
2.90

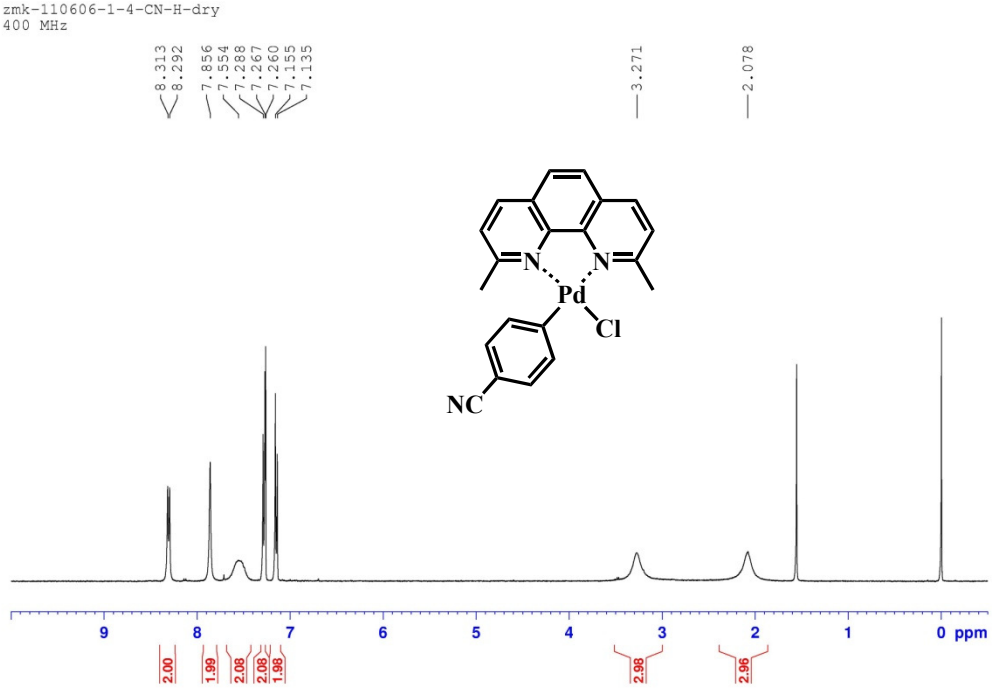

zmk-110424-4-CN+PhCOOEt-C13, AV400, Apr 2011
165.71
157.13
145.85
140.83
132.41
128.44
128.38
127.47
125.18
120.32
118.47
112.50
77.38
77.06
76.74
60.30
34.95
32.66
14.30
Ph
O
OEt
NC
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

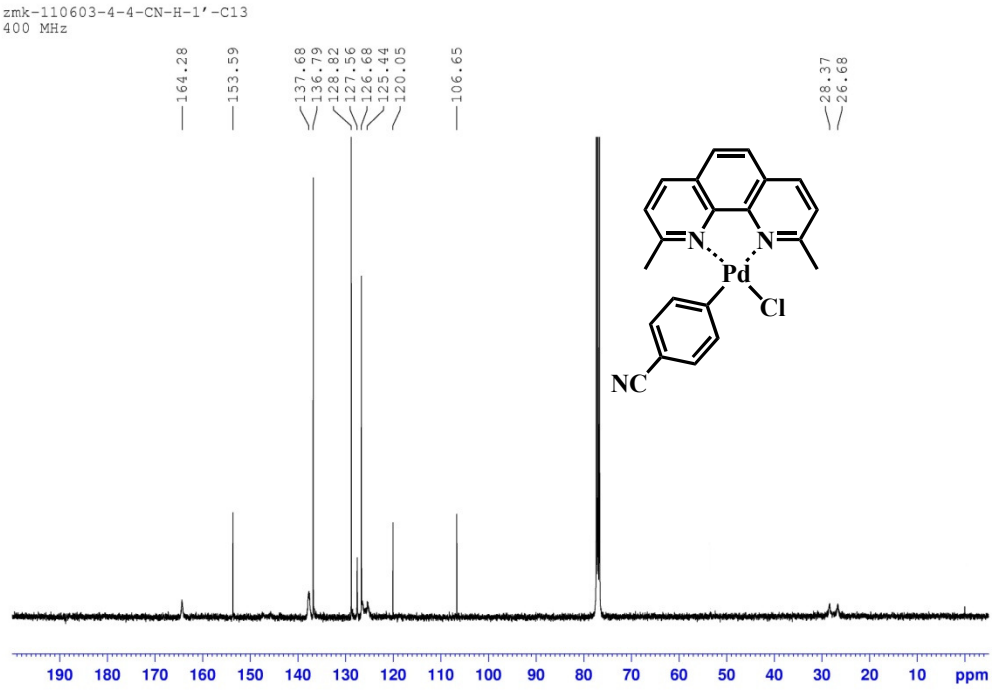

zmk-110505-1-4-Me-=cCN-H , 400 MHz H
7.264
7.245
7.145
7.125
6.706
6.567
6.017
6.003
5.988
5.977
5.963
5.949
3.264
3.250
2.338
CN
11
9
8
7
6
5
4
3
2
1
0 ppm
2.05
1.94
0.96
0.97
2.00
3.02


zmk-110505-1-4-Me-=cCN-C13 , 400 MHz H
138.26
134.54
132.94
129.44
126.40
117.66
115.67
77.40
77.08
76.76
21.24
20.77
CN
11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


zmk-110505-1-4-Me-=cCN-shang -H , 400 MHz H
7.300
7.280
7.258
7.193
7.173
5.603
5.479
3.518
2.363
CN
12
9
8
7
6
5
4
3
2
1
0 ppm
1.94
2.05
1.02
1.00
2.00
3.18


zmk-110505-1-4-Me-=cCN-shang -C13 , 400 MHz H
138.64
136.76
135.03
129.41
125.42
117.45
115.20
77.35
77.03
76.71
23.91
21.13
CN
12
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


zmk-110606-1-4-CN-H-dry
400 MHz
8.313
8.292
7.856
7.554
7.288
7.267
7.260
7.155
7.135
3.271
2.078
N
N
Pd
Cl
NC
9
8
7
6
5
4
3
2
1
0 ppm
2.00
1.99
2.08
2.08
1.90
2.98
2.96


zmk-110603-4-4-CN-H-1'-C13
400 MHz
164.28
153.59
137.68
136.79
128.82
127.56
126.68
125.44
120.05
106.65
28.37
26.68
N
N
Pd
Cl
NC
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm