Supplementary Material (ESI) for Chemical Communications

Enantioselective aza-Micheal reaction of hydrazide to chalcones through the nonactivated amine moiety conjugated addition

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CONTENTS:

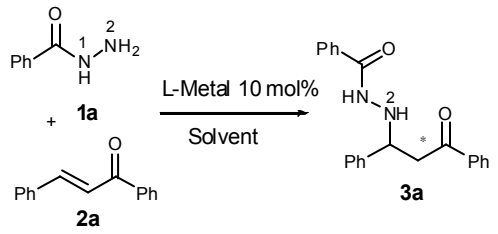
(A) General information:

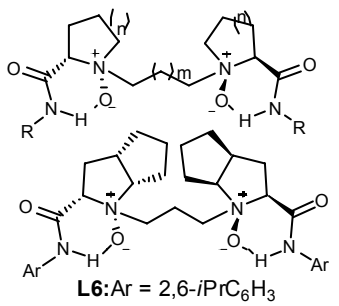
^{1}H NMR spectra were recorded at 400 MHz or 600 MHz on commercial instruments. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz or 150 MHz on commercial instruments with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. All experiments were monitored by analytical thin layer chromatography (TLC). Enantiomeric excesses of products were determined by chiral HPLC analysis on Daicel Chiralcel AD-H/ IA/IB/IC in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (*c*: g/100 mL, in CH_2Cl_2). ESI-HRMS spectra were recorded on a commercial apparatus. The various chalcones were mostly prepared according to the literature procedures except standard one. Hydrazide, dichloromethane were commercially available and purified by usual methods before use. Molecular sieve was dryinged at 500 ^{o}C for 2.5 hours, and the various lewis acids also were commercially available and directly used without further purification. Catalysts **L1-L13** were synthesized according to the previous literatures in our group.[1]

(B) General procedure for the asymmetric aza-Micheal reaction of hydrazide and chalcone

The mixture of ligand **L7** (3.7 mg, 0.006 mmol, 6 mol%), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%), benzoyl hydrazine **1a** (13.6 mg, 0.1 mmol), chalcone **2a** (40.2 mg, 0.20 mmol) and 4ÅMS (60 mg) were stirred in CH_2Cl_2 (2.0 mL) for 16-20 h at 25 ^{o}C. The completion of the reaction was monitored by TLC and purified by flash chromatography on silica gel (Eluent: petroleum ether /ethyl acetate = 3/1) to give the pure product **3a** in 78% yield with 93% *ee*.

(C) Optimization of conditions





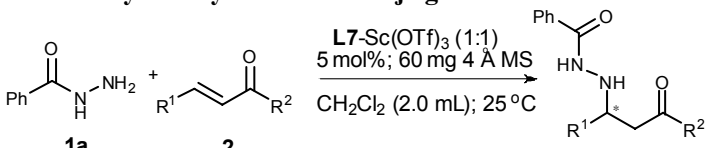
L1: R = 2,6-*i*PrC$_6$H$_3$ n=1 m=1
L2: R = 2,6-Et$_2$C$_6$H$_3$ n=1 m=1
L3: R = 2,6-Me$_2$C$_6$H$_3$ n=1 m=1
L4: R = *t*Bu n=1 m=1
L5: R = 2,6-*i*PrC$_6$H$_3$ n=2 m=1
L7: R = Ph n=1 m=1
L8: R = CH$_2$Ph n=1 m=1
L9: R = adam n=1 m=1
L10: R = CHPh$_2$ n=1 m=1
L11: R = 2,6-*i*PrC$_6$H$_3$ n=1 m=0
L12: R = 2,6-*i*PrC$_6$H$_3$ n=1 m=2
L13: R = Anthtyl n=1 m=1

Entry[a]	L-Metal (L/M)	Add.(Ant.)	**1a**/**2a** (mmol)	Sov. (mL)[b]	Yield[c] (%)	Ee[d] (%)
1	**L1/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	58	78
2	**L2/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	40	45
3	**L3/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	30	18
4	**L4/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	55	54
5	**L5/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	32	41
6	**L6/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	24	75
7	**L7/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	72	-37
8	**L8/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	28	-19
9	**L9/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	78	13
10	**L10/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	33	-44
11	**L11/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	68	1
12	**L12/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	28	34
13	**L13/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	21	-9
14	**L1/La(OTf)$_2$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	34	0
15	**L1/Y(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	78	3
16	**L1/Ca(OTf)$_2$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	30	1
17	**L1/Zn(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.5mL)	22	4
18	**L1/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (0.2mL)	82	26
19	**L1/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (1.0mL)	51	83
20	**L1/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (2.0mL)	48	88
21	**L1/Sc(OTf)$_3$** (1.0/1.0) 10mol%	-	1.0/1.0	$CHCl_3$ (2.0mL)	31	82
22	**L1/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	$CH_2ClClCH_2$ (2.0mL)	40	85
23	**L1/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	EA (2.0mL)	47	68
24	**L1/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	CH_3CN (2.0mL)	60	55
25	**L1/Sc(OTf)$_3$** (1.0/1.0) 10 mol%	-	1.0/1.0	THF (2.0mL)	31	60
26	**L1/Sc(OTf)$_3$** (1.0/1.0) 10mol%	-	1.0/1.0	PhMe (2.0mL)	49	64
27	**L1/Sc(OTf)$_3$** (1.2/1.0) 10 mol%	-	1.0/1.0	CH_2Cl_2 (2.0mL)	52	90
28	**L1/Sc(OTf)$_3$** (1.0/1.2) 10 mol%	-	1.0/1.0	CH_2Cl_2 (2.0mL)	49	80
29	**L1/Sc(OTf)$_3$** (1.2/1.0) 10 mol%	-	2.0/1.0	CH_2Cl_2 (2.0mL)	64	91
30	**L1/Sc(OTf)$_3$** (1.2/1.0) 10 mol%	-	1.5/1.0	CH_2Cl_2 (2.0mL)	57	90
31	**L1/Sc(OTf)$_3$** (1.2/1.0) 10 mol%		1.2/1.0	CH_2Cl_2 (2.0mL)	50	88

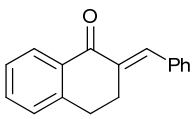
32	**L1/Sc(OTf)$_3$** (1.2/1.0) 10 mol%		1.0/1.5	CH_2Cl_2 (2.0 mL)	54	84
33	**L1/Sc(OTf)$_3$** (1.2/1.0) 10 mol%	3 Å MS 20 mg	2.0/1.0	CH_2Cl_2 (2.0 mL)	62	91
34	**L1/Sc(OTf)$_3$** (1.2/1.0) 10 mol%	4 Å MS 20 mg	2.0/1.0	CH_2Cl_2 (2.0 mL)	66	93
35	**L1/Sc(OTf)$_3$** (1.2/1.0) 10 mol%	5 Å MS 20 mg	2.0/1.0	CH_2Cl_2 (2.0 mL)	67	92
36	**L1/Sc(OTf)$_3$** (1.2/1.0) 10 mol%	4 Å MS 10 mg	2.0/1.0	CH_2Cl_2 (2.0 mL)	58	93
37	**L1/Sc(OTf)$_3$** (1.2/1.0) 10 mol%	4 Å MS 40 mg	2.0/1.0	CH_2Cl_2 (2.0 mL)	69	93
38	**L1/Sc(OTf)$_3$** (1.2/1.0) 10 mol%	4 Å MS 60 mg	2.0/1.0	CH_2Cl_2 (2.0 mL)	73	93
39[e]	**L1/Sc(OTf)$_3$** (1.2/1.0) 5 mol%	4 Å MS 60 mg	2.0/1.0	CH_2Cl_2 (2.0 mL)	78	93

[a] Unless otherwise noted, reactions were carried in one pot, at 25 °C for 12 h. [b] EA = ethyl acetate, THF = tetrahydrofuran, [c] Isolated yield. [d] Determined by HPLC analysis. [e] Reactions were carried for 20 h.

(D) Other substrates for catalytic asymmetric conjugate addition of chalcones and hydrazides

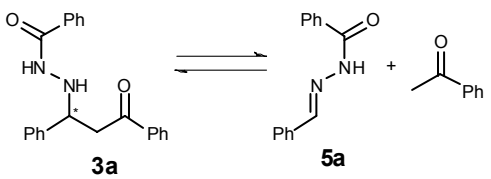


1a **2** **3**

Entry[a]	R^1	R^2	Hydrazide **1**	Yield[b] (%)	Ee[c] (%)	
1	3-$PhOC_6H_4$	Ph	**1a**	78	80	
2	2-Thienyl	Ph	**1a**	51	71	
3	3-$NO_2C_6H_4$	Ph	**1a**	90	71	
4	4-CNC_6H_4	Ph	**1a**	82	72	
5	3-ClC_6H_4	Ph	**1a**	82	80	
6	3-$CF_3C_6H_4$	Ph	**1a**	92	70	
7	2-ClC_6H_4	Ph	**1a**	68	82	
8	CCl_3	Ph	**1a**	99	10	
9	$EtCO_2$	Ph	**1a**	95	19	[a]
10			**1a**	35	0	
11	Ph	Ph	$TsNH\text{-}NH_2$	trace	-	
12[d]	Ph	Ph	$AcNH\text{-}NH_2$	56	81	[a]

Unless otherwise noted, the reactions were carried out with 5 mol% **L7**/Sc(OTf)$_3$ (1.2/1.0), 0.1 mmol hydrazide **1**, and 2.0 equiv chalcones **2** in CH_2Cl_2 (2.0 mL) at 25 °C for 16-20 h. [b] Isolated yield. [c] Determined by HPLC analysis. [d] The reaction was carried out with 0.1 mmol acetylhydrazine **1b** and 2.0 equiv chalcone **2a**, using 10 mol% catalyst.

(E) The discussion for the reactivity and yield issues



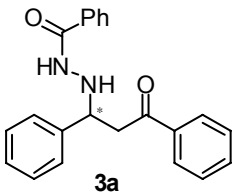
3a **5a**

The electronic property and steric hindrance of the substituted groups at the aromatic ring R^1 had marked influence on reactivity. In addition, another reaction phenomenon in this system was found that a little unknow compound was exited and further confirmed to be hydrazone through reverse Mannich reaction.[2] Under the alkaline condition or heating, the product **3a**

still existed stably, whereas, it was slowly transformed into **5a** in the catalytic environment. Thus, controlling the reaction time was another important factor.

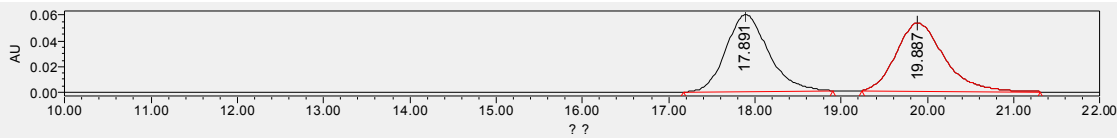
(F) The analytical and spectral characterization data of reaction products

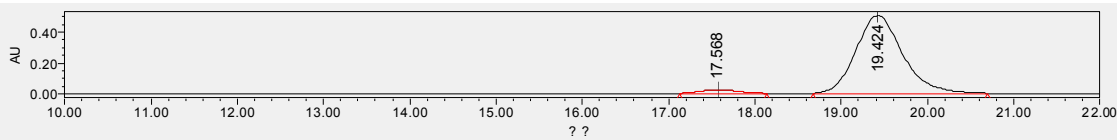
1) Product 3a:



3a

solid; 78% yield, 93% *ee*. $[\alpha]_D^{28}$ = 39.8 (*c* 0.068 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.6 min (minor) and 19.4 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H, Ar-H and NH-C=O), 7.63 – 7.26 (m, 14H, Ar-H), 5.71 (s, 1H, C-NH-N), 4.82 (dd, *J* = 7.8, 5.1 Hz, 1H, N-CH-Ph), 3.46 (qd, *J* = 16.9, 6.5 Hz, 2H -CH_2C=O) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) 198.21, 167.00, 140.84, 136.69, 133.32, 132.85, 131.71, 128.81, 128.64, 128.59, 128.22, 128.05, 127.72, 126.83, 60.92, 44.40 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{20}N_2O_2$ ([M+Na^+]) = 367.1422, Found: 367.1421.





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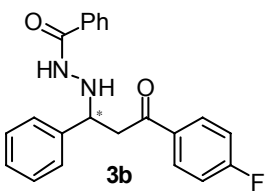
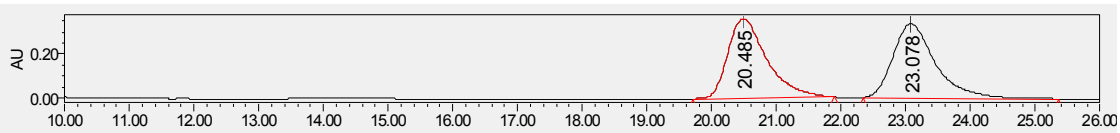
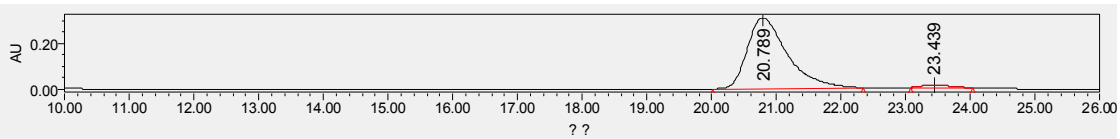


3b

solid; 81% yield, 95% *ee*. $[\alpha]_D^{23}$ = 36.3 (*c* 0.039 in CH_2Cl_2). HPLC DAICEL CHIRALCEL ADH, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 20.8 min (major) and 23.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.6, 5.5 Hz, 2H, Ar-H and NH-C=O), 7.59 – 7.30 (m, 11H, Ar-H), 7.08 (t, *J* = 8.6 Hz, 2H, Ar-H), 5.69 (s, 1H, C-NH-N), 4.81 (dd, *J* = 7.7, 5.2 Hz, 1H, N-CH-Ph), 3.42 (ddd, *J* = 21.8, 16.8, 6.5 Hz, 2H, -CH_2C=O) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) 196.59, 167.06, 164.58, 140.69, 133.14, 132.77, 131.75, 130.92, 130.83, 128.82, 128.59, 128.10, 127.69, 126.82, 115.85, 115.63, 60.85, 44.23 ppm. HRMS (ESI-TOF) calcd for $C_{22}H_{19}FN_2O_2$ ([M+Na^+]) = 385.1328, Found: 385.1332.





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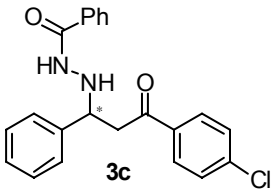
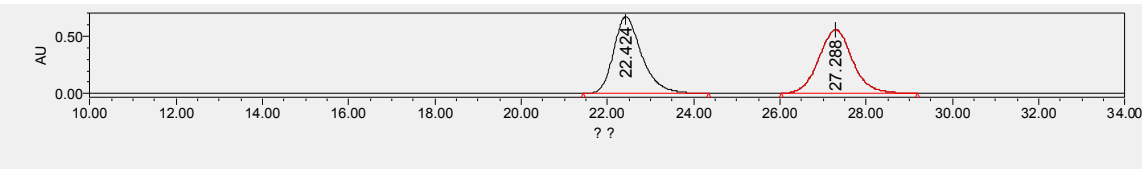
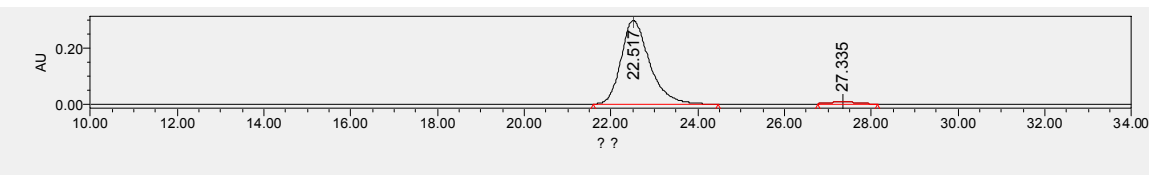


3c

solid; 77% yield, 96% *ee*. $[\alpha]_D^{28}$ = 41.0 (*c* 0.016 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 22.5 min (major) and 27.3 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2H, Ar-H and NH-C=O), 7.61 – 7.27 (m, 13H, Ar-H), 5.68 (s, 1H, C-NH-N), 4.81 (dd, *J* = 7.6, 5.2 Hz, 1H, N-CH-Ph), 3.42 (ddd, *J* = 21.8, 16.8, 6.5 Hz, 2H, -CH_2C=O) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) 196.98, 167.10, 140.62, 139.80, 134.99, 132.74, 131.77, 129.62, 128.95, 128.83, 128.60, 128.12, 127.69, 126.82, 60.80, 44.25 ppm. HRMS (ESI-TOF) calcd for $C_{22}H_{19}ClN_2O_2$ ([M+Na^+]) = 401.1033, Found: 401.1032.





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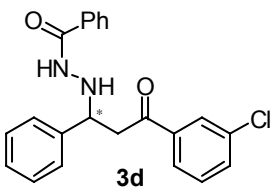
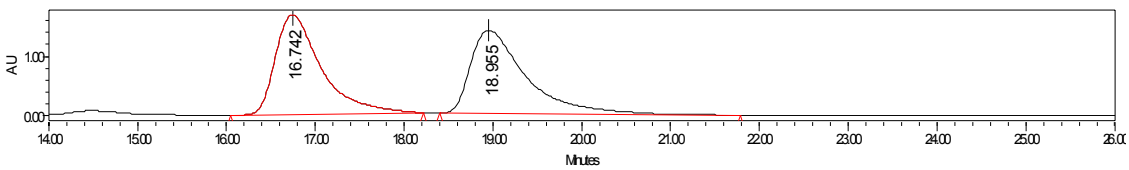
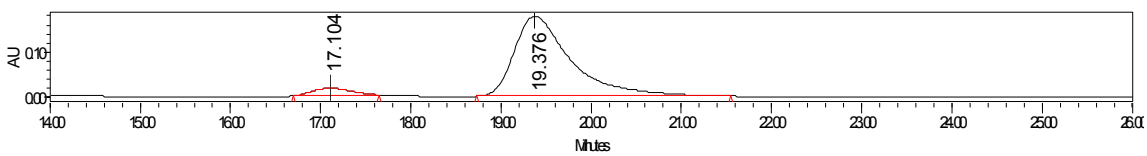


3d

solid; 75% yield, 89% *ee*. $[\alpha]_D^{28}$ = 24.2 (*c* 0.018 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.1 min (minor) and 19.4 min (major); ^{1}H NMR (600 MHz, CDCl3) δ 7.87 (s, 1H, NH-C=O), 7.79 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.63 – 7.54 (m, 3H, Ar-H), 7.48 (dd, *J* = 26.9, 7.7 Hz, 4H, Ar-H), 7.33 (dt, *J* = 32.1, 7.4 Hz, 6H, Ar-H), 4.82 (dd, *J* = 7.4, 5.3 Hz, 1H, N-CH-Ph), 3.71 (dd, *J* = 12.4, 5.1 Hz, 1H, C-NH-N), 3.43 (ddd, *J* = 21.8, 16.9, 6.4 Hz, 2H, -CH_2C=O) ppm. ^{13}C NMR (151 MHz, CDCl3) 196.96, 167.19, 140.52, 138.18, 134.98, 133.24, 132.69, 131.80, 129.97, 128.84, 128.61, 128.31, 128.16, 127.72, 126.85, 60.72, 44.31 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{19}ClN_2O_2$ ([M+Na^+]) = 401.1033, Found: 401.1039.





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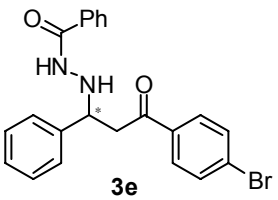
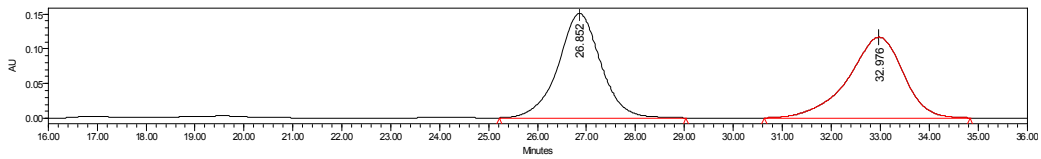
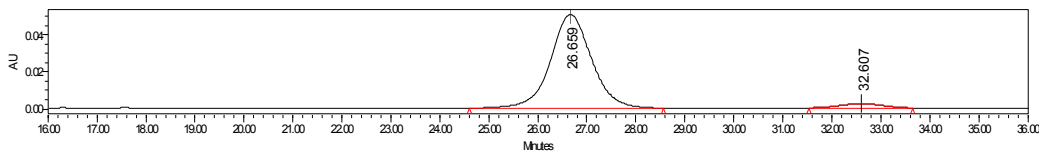


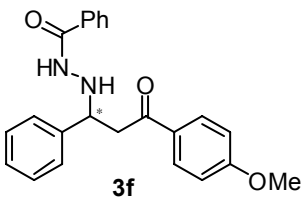
3e

solid; 82% yield, 91% *ee*. $[\alpha]_D^{20}$ = 31.6 (*c* 0.017 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 26.7 min (major) and 32.6 min (minor); ^{1}H NMR (600 MHz, CDCl3) δ 7.78 (d, *J* = 8.2 Hz, 2H, Ar-H and NH-C=O), 7.56 (d, *J* = 8.3 Hz, 4H, Ar-H), 7.47 (t, *J* = 7.6 Hz, 3H, Ar-H), 7.41 (s, 1H, Ar-H), 7.37 (t, *J* = 7.1 Hz, 4H, Ar-H), 7.31 (t, *J* = 7.2 Hz, 1H, Ar-H), 5.68 (s, 1H, C-NH-N), 4.81 (dd, *J* = 7.8, 5.1 Hz, 1H, N-CH-Ph), 3.41 (ddd, *J* = 21.7, 16.8, 6.5 Hz, 2H, -CH_2C=O). ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 197.17, 167.08, 140.62, 135.40, 132.74, 131.96, 131.79, 129.72, 128.86, 128.62, 128.15, 127.69, 126.81, 60.80, 44.25 ppm;HRMS (ESI-TOF) calcd for $C_{22}H_{19}BrN_2O_2$ ([M+Na^+]) = 445.0528, Found: 445.0535.



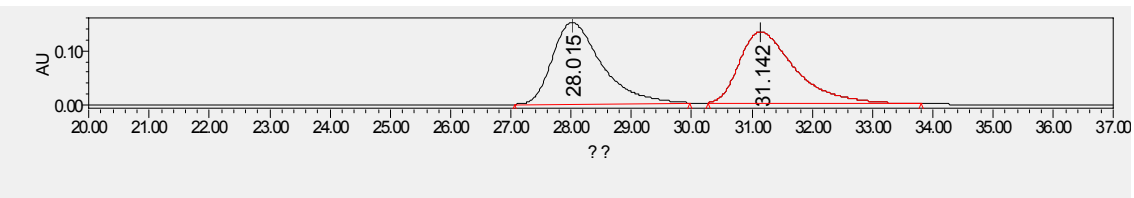


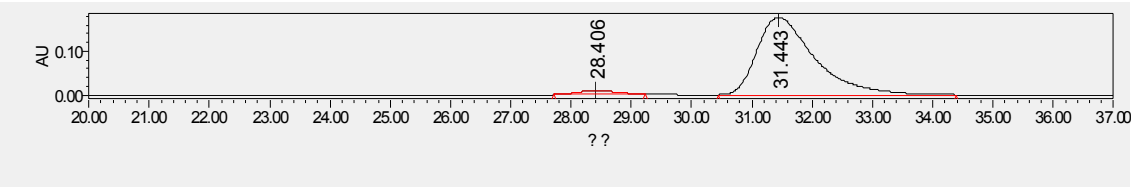
6) Product 3f:



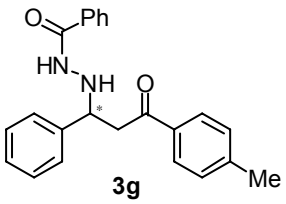
3f

solid; 74% yield, 94% *ee*. $[\alpha]_D^{29}$ = 27.9 (*c* 0.034 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 28.4 min (minor) and 31.4 min (major); ^{1}H NMR (600 MHz, CDCl3) δ 7.92 (d, *J* = 8.8 Hz, 2H, Ar-H and NH-C=O), 7.69 – 7.27 (m, 11H, Ar-H), 6.90 (d, *J* = 8.8 Hz, 2H, Ar-H), 5.71 (s, 1H, C-NH-N), 4.80 (dd, *J* = 7.8, 4.9 Hz, 1H, N-CH-Ph), 3.86 (s, 3H, -OCH_3), 3.40 (ddd, *J* = 21.3, 16.5, 6.5 Hz, 2H, -CH_2C=O)ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 196.78, 166.85, 163.67, 141.01, 132.91, 131.67, 130.56, 129.83, 128.80, 128.58, 128.01, 127.69, 126.82, 113.79, 61.16, 55.49, 44.18. HRMS (ESI-TOF) calcd for $C_{23}H_{22}N_2O_3$ ([M+Na^+]) = 397.1528, Found: 397.1522.



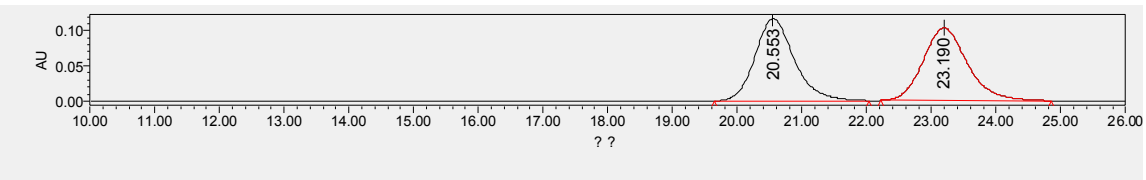


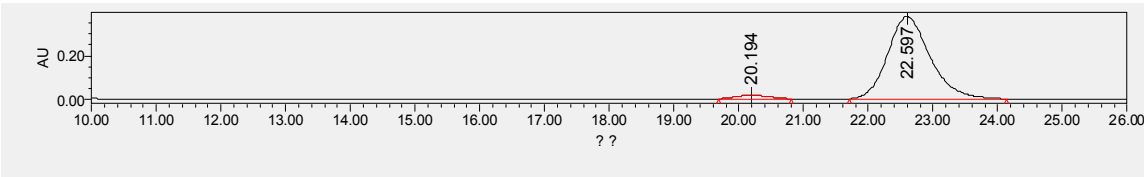
7) Product 3g:



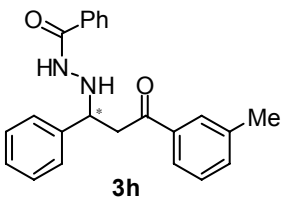
3g

solid; 71% yield, 94% *ee*. $[\alpha]_D^{28}$ = 32.6 (*c* 0.032 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 20.2 min (minor) and 22.6 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H, Ar-H and NH-C=O), 7.64 – 7.31 (m, 12H, Ar-H), 7.17 (d, *J* = 7.5 Hz, 2H, Ar-H and C-NH-N), 4.84 – 4.71 (m, 1H, N-CH-Ph), 3.56 – 3.31 (m, 2H, -CH_2C=O), 2.34 (s, 3H, -CH_3). ppm. ^{13}C NMR (101 MHz, $CDCl_3$) 197.92, 166.96, 144.20, 140.92, 134.24, 132.88, 131.68, 129.33, 128.79, 128.57, 128.36, 128.02, 127.72, 126.85, 61.03, 44.32, 21.66 ppm. HRMS (ESI-TOF) calcd for $C_{23}H_{22}N_2O_2$ ([M+Na^+]) = 381.1579, Found: 381.1591.



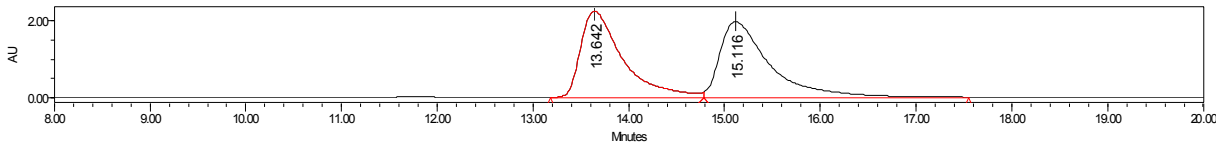


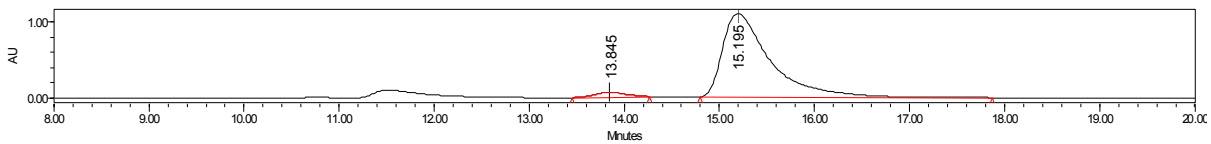
8) Product 3h:



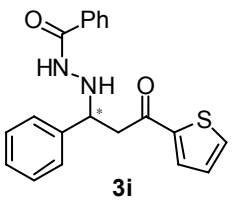
3h

solid; 70% yield, 94% *ee*. $[\alpha]_D^{28}$ = 28.4 (*c* 0.031 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.8 min (minor) and 15.2 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.1 Hz, 2H, Ar-H and NH-C=O), 7.62 – 7.54 (m, 3H, Ar-H), 7.46 (dd, *J* = 15.3, 7.4 Hz, 3H, Ar-H), 7.34 (ddt, *J* = 15.6, 13.4, 6.8 Hz, 7H, Ar-H), 4.81 (dd, *J* = 8.0, 4.9 Hz, 1H, N-CH-Ph), 3.72 (s, 1H, C-NH-N), 3.45 (ddd, *J* = 21.7, 16.8, 6.5 Hz, 2H, -CH_2C=O), 2.37 (s, 3H, -CH_3)ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 198.53, 167.00, 140.83, 138.44, 136.70, 134.12, 132.81, 131.71, 128.80, 128.77, 128.58, 128.51, 128.05, 127.73, 126.85, 125.45, 63.76, 60.98, 44.42ppm; HRMS (ESI-TOF) calcd for $C_{23}H_{22}N_2O_2$ ([M+Na^+]) = 381.1579, Found: 381.1577.



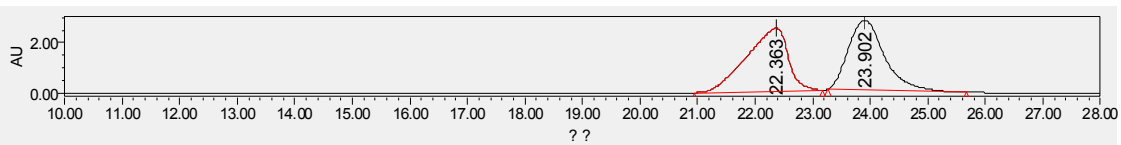


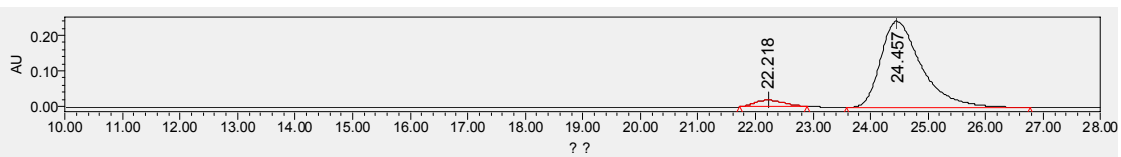
9) Product 3i:



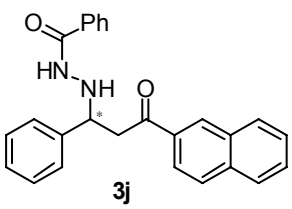
3i

solid; 75% yield, 90% *ee*. $[\alpha]_D^{28}$ = 21.5 (*c* 0.021 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 22.2 min (minor) and 24.5 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 3.7 Hz, 1H, NH-C=O), 7.62 (d, *J* = 4.9 Hz, 1H, Ar-H), 7.56 (t, *J* = 12.9 Hz, 3H, Ar-H), 7.46 (t, *J* = 8.0 Hz, 3H, Ar-H), 7.34 (dt, *J* = 13.9, 6.4 Hz, 5H, Ar-H), 5.61 (s, 1H, C-NH-N), 4.80 (dd, *J* = 7.7, 5.1 Hz, 1H, N-CH-Ph), 3.38 (ddd, *J* = 20.8, 15.9, 6.5 Hz, 2H, -CH_2C=O) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 191.14, 167.07, 144.09, 140.56, 134.25, 132.74, 132.46, 131.76, 128.83, 128.60, 128.21, 128.15, 127.64, 126.84, 63.75, 61.34, 45.28ppm; HRMS (ESI-TOF) calcd for $C_{20}H_{18}SN_2O_2$ ([M+Na^+]) = 373.0987, Found: 373.0981.



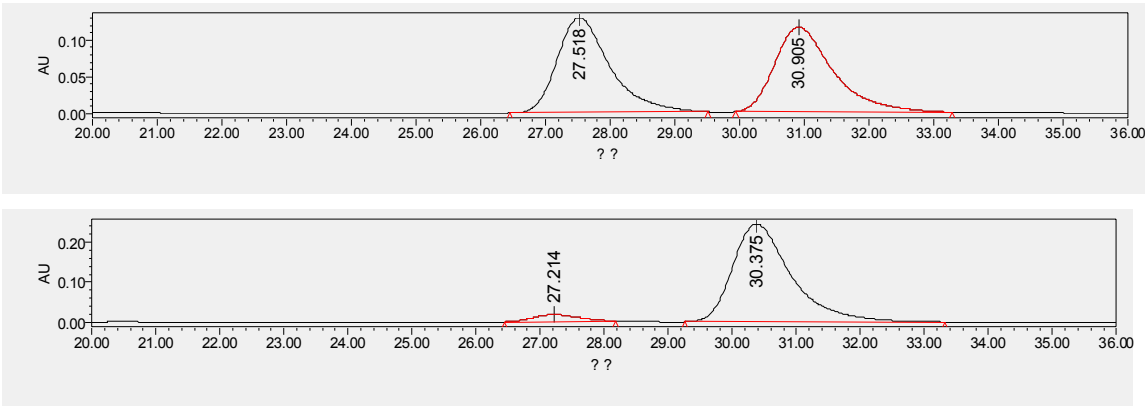


10) Product 3j:

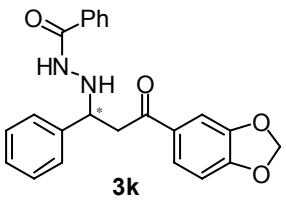


3j

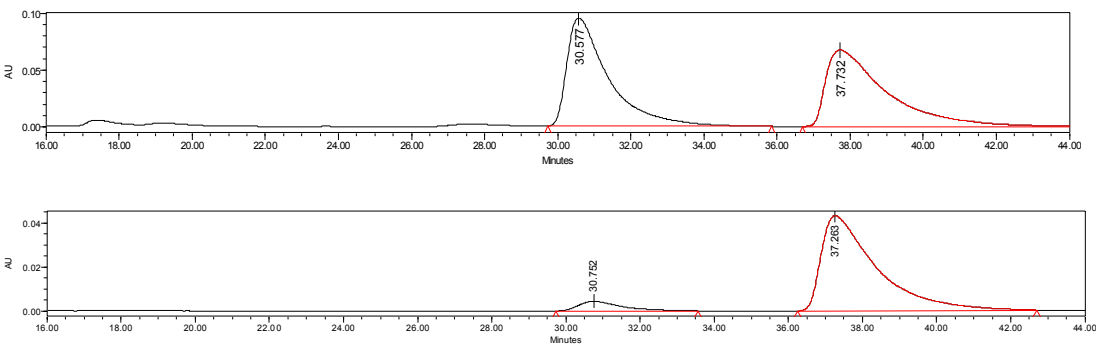
solid; 68% yield, 90% *ee*. $[\alpha]_D^{29}$ = 20.2 (*c* 0.030 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 220 nm, retention time: 11.3 min (minor) and 14.0 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (s, 1H, NH-C=O), 8.02 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.95 – 7.84 (m, 3H, Ar-H), 7.63 – 7.50 (m, 6H, Ar-H), 7.39 (dtt, *J* = 18.4, 14.8, 7.4 Hz, 8H, Ar-H), 5.76 (s, 1H C-NH-N), 4.93 – 4.80 (m, 1H, N-CH-Ph), 3.60 (ddd, *J* = 21.4, 16.6, 6.5 Hz, 2H, -CH_2C=O) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 199.10, 197.98, 140.92, 138.89, 133.53, 131.70, 130.07, 129.95, 129.63, 129.30, 128.84, 128.51, 128.07, 128.01, 127.73, 127.46, 126.81, 64.99, 61.10, 44.50ppm; HRMS (ESI-TOF) calcd for $C_{26}H_{22}N_2O_2$ ([M+Na^+]) = 417.1579, Found: 417.1568.



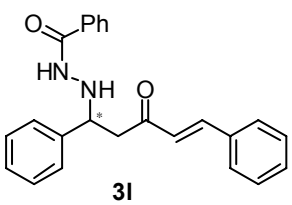
11) Product 3k:



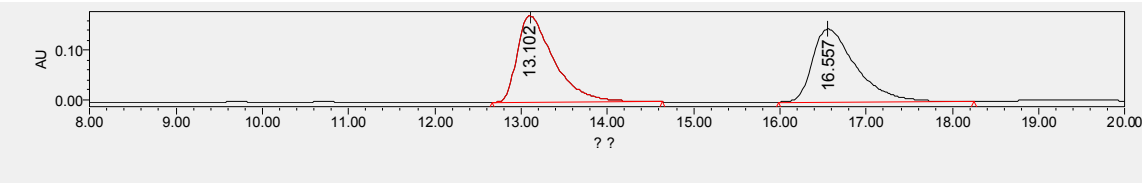
solid; 65% yield, 87% *ee*. $[\alpha]_D^{28}$ = 17.9 (*c* 0.017 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254nm, retention time: 30.8 min (minor) and 37.3 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (dddd, J = 58.6, 26.1, 14.0, 1.9 Hz, 14H, Ar-H and NH-C=O), 6.05 (dd, J = 26.7, 1.7 Hz, 2H, -O-CH_2-O-), 5.71 (s, 1H, C-NH-N), 4.79 (s, 1H, N-CH-Ph), 3.60 – 3.14 (m, 2H, -CH_2C=O) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 196.28, 166.94, 151.98, 148.22, 140.86, 132.84, 131.70, 128.80, 128.58, 128.04, 127.69, 126.83, 124.65, 107.98, 107.87, 101.88, 61.08, 44.17ppm; HRMS (ESI-TOF) calcd for $C_{23}H_{20}N_2O_4$ ([M+Na^+]) = 411.1321, Found: 411.1319.

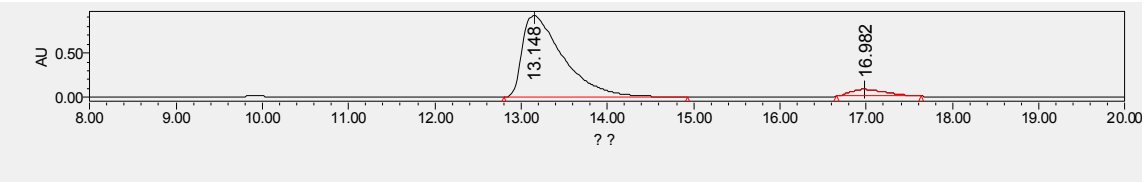


12) Product 3l:

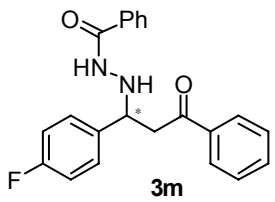


solid; 87% yield, 86% *ee*. $[\alpha]_D^{21}$ = 32.5 (*c* 0.043 in CH_2Cl_2). HPLC DAICEL CHIRALCEL IB, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.1 min (major) and 17.0 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.2 Hz, 3H, Ar-H and NH-C=O), 7.51 – 7.43 (m, 5H, Ar-H), 7.41 – 7.29 (m, 8H, Ar-H), 6.71 (d, J = 16.1 Hz, 1H, =CH-Ar), 5.60 (s, 1H, C-NH-N), 4.75 (dd, J = 7.8, 5.3 Hz, 1H, N-CH-Ph), 3.73 (s, 1H, CO-CH=), 3.16 (ddd, J = 21.3, 16.1, 6.6 Hz, 2H, -CH_2C=O) ppm. ^{13}C NMR (101 MHz, CDCl3) 198.23, 167.05, 143.57, 140.67, 134.27, 132.78, 131.76, 130.67, 128.94, 128.81, 128.62, 128.42, 128.10, 127.69, 126.86, 125.99, 63.77, 61.03, 46.62.ppm; HRMS (ESI-TOF) calcd for $C_{24}H_{22}N_2O_2$ ([M+Na^+]) = 393.1579, Found: 393.1587.

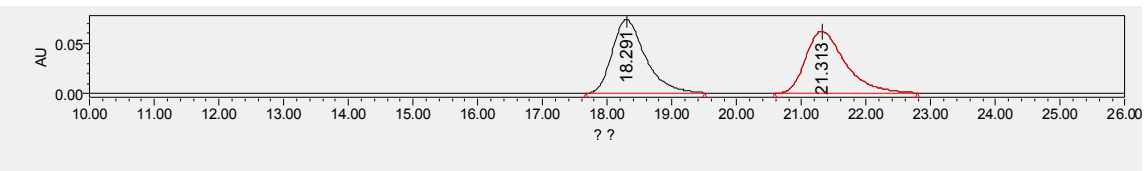


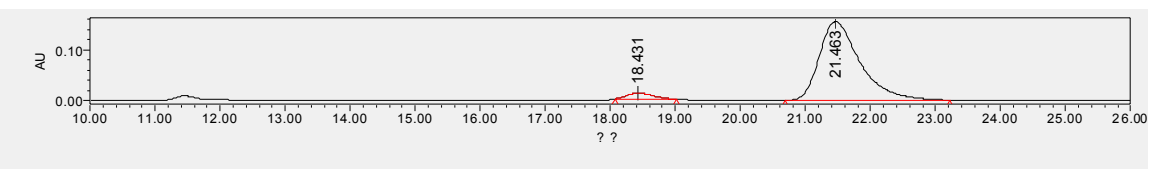


13) Product 3m:

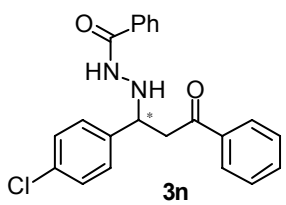


solid; 67% yield, 91% *ee*. $[\alpha]_D^{18}$ = 33.1 (*c* 0.027 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 18.4 min (minor) and 21.5 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H, Ar-H and NH-C=O), 7.61 – 7.31 (m, 11H, Ar-H), 7.04 (t, *J* = 8.6 Hz, 2H, Ar-H), 4.84 – 4.80 (m, 1H, N-CH-Ph), 3.43 (ddd, *J* = 22.1, 16.8, 6.5 Hz, 2H-CH_2C=O) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 197.97, 167.19, 163.22, 161.59, 136.63, 136.59, 133.40, 132.70, 131.82, 129.42, 129.36, 128.67, 128.63, 128.18, 126.82, 115.70, 115.56, 60.22, 44.34 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{19}FN_2O_2$ ([M+Na$^+$]) = 385.1328, Found: 385.1331.

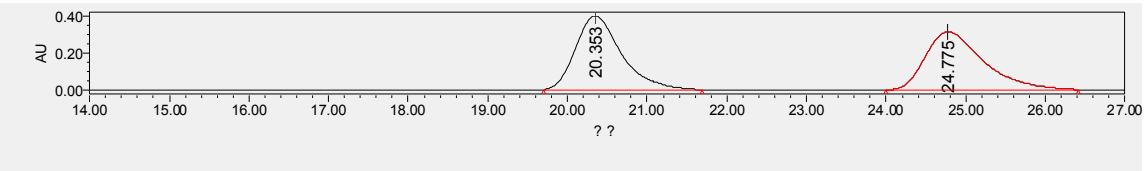


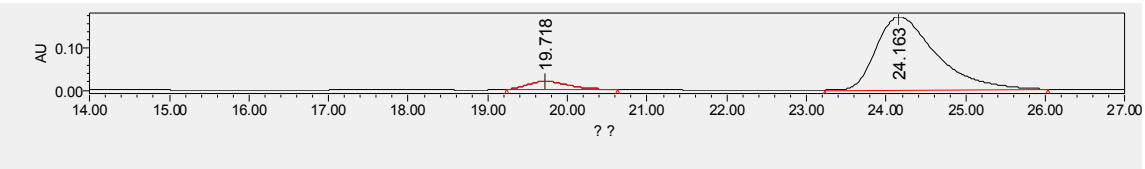


14) Product 3n:

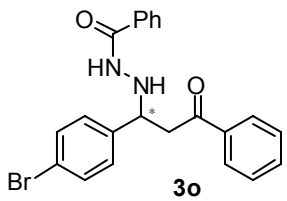


solid; 69% yield, 84% *ee*. $[\alpha]_D^{29}$ = 41.5 (*c* 0.051 in CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 19.7min (minor) and 24.2 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 2H, Ar-H and NH-C=O), 7.57 (dd, *J* = 15.9, 7.6 Hz, 3H, Ar-H), 7.50 – 7.33 (m, 10H, Ar-H), 5.62 (s, 1H, C-NH-N), 4.90 – 4.74 (m, 1H, N-CH-Ph), 3.42 (ddd, *J* = 22.2, 16.8, 6.5 Hz, 2H-CH_2C=O) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 197.75, 167.21, 139.43, 136.58, 133.74, 133.44, 132.65, 131.87, 129.15, 128.95, 128.69, 128.66, 128.18, 126.82, 60.27, 44.23 ppm. HRMS (ESI-TOF) calcd for $C_{22}H_{19}ClN_2O_2$ ([M+Na$^+$]) = 401.1033, Found: 401.1023.



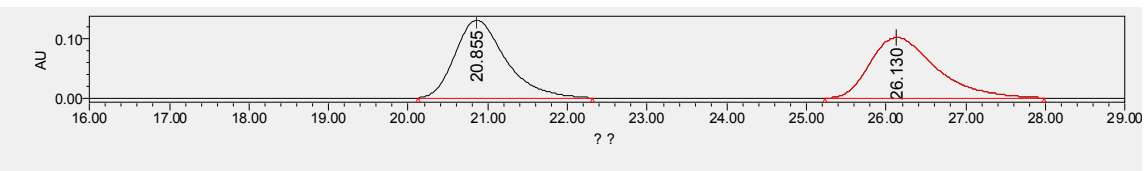


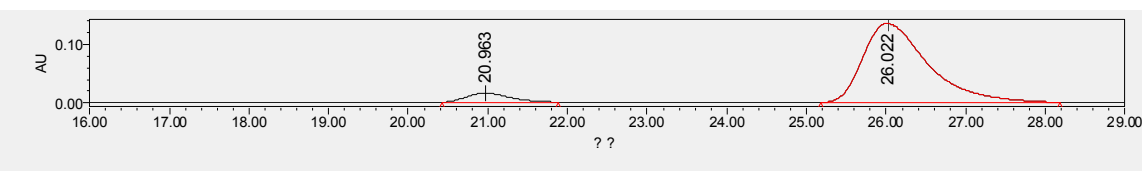
15) Product 3o:



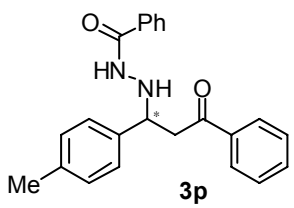
3o

solid; 72% yield, 86% *ee*. $[\alpha]_D^{28}$ = 36.7 (*c* 0.044 in CH_2Cl_2) HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 21.0 min (minor) and 26.0 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 2H, Ar-H and NH-C=O), 7.61 – 7.34 (m, 13H, Ar-H), 5.63 (s, 1H, C-NH-N), 4.84 – 4.75 (m, 1H, N-CH-Ph), 3.42 (ddd, *J* = 22.3, 16.9, 6.5 Hz, 2H, -CH_2C=O) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 197.76, 167.26, 139.93, 136.54, 133.46, 132.61, 131.89, 129.52, 128.69, 128.65, 128.18, 126.85, 121.89, 60.31, 44.14 ppm. HRMS (ESI-TOF) calcd for $C_{22}H_{19}BrN_2O_2$ ([M+Na^+]) = 445.0528, Found: 445.0509.



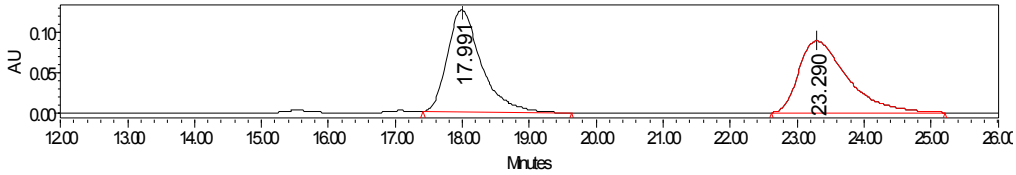


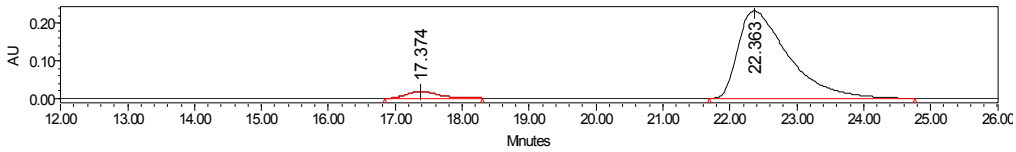
16) Product 3p:



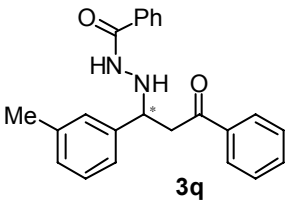
3p

solid; 62% yield, 91% *ee*. $[\alpha]_D^{28}$ = 31.7 (*c* 0.019 in CH_2Cl_2) HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.4 min (minor) and 22.4 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H, Ar-H and NH-C=O), 7.63 – 7.32 (m, 12H, Ar-H), 7.17 (d, *J* = 7.5 Hz, 2H, Ar-H), 4.82 – 4.73 (m, 1H, N-CH-Ph), 3.44 (ddd, *J* = 21.5, 16.8, 6.4 Hz, 2H, -CH_2C=O), 2.34 (s, 3H,-CH_3) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 198.35, 166.95, 137.74, 136.71, 133.30, 132.85, 131.69, 129.47, 128.63, 128.57, 128.23, 127.61, 126.85, 60.67, 44.37, 29.70 ppm; HRMS (ESI-TOF) calcd for $C_{23}H_{22}N_2O_2$ ([M+Na^+]) = 381.1579, Found: 381.1575.

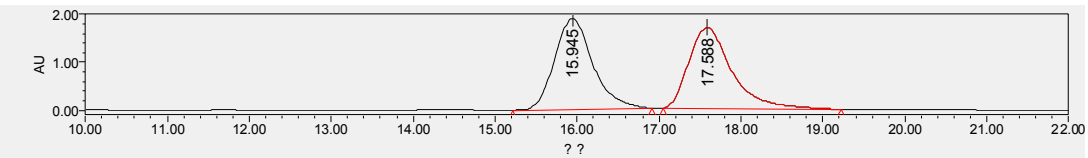


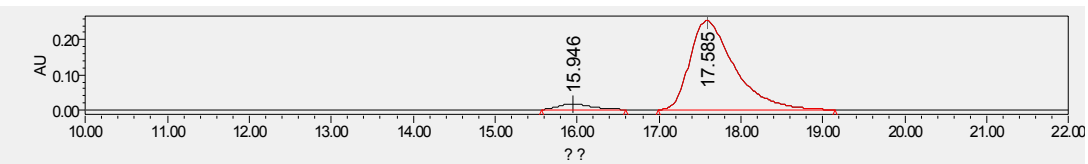


17) Product 3q:

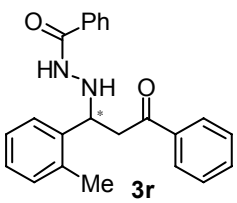


solid; 71% yield, 91% *ee*. $[\alpha]_D^{28}$ = 30.4 (*c* 0.028 in CH_2Cl_2) HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 16.0 min (minor) and 17.6 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.9 Hz, 2H, Ar-H and NH-C=O), 7.65 – 7.33 (m, 9H, Ar-H), 7.30 – 7.20 (m, 4H, Ar-H), 7.11 (d, J = 6.3 Hz, 1H, C-NH-N), 4.78 (dd, J = 8.0, 4.9 Hz, 1H, N-CH-Ph), 3.45 (ddd, J = 21.7, 16.8, 6.5 Hz, 2H, -CH_2C=O), 2.35 (s, 3H,-CH_3) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 198.35, 166.96, 140.69, 138.47, 136.70, 133.31, 132.85, 131.69, 128.82, 128.68, 128.63, 128.57, 128.42, 128.23, 126.86, 124.71, 60.92, 44.36, 29.71ppm; HRMS (ESI-TOF) calcd for $C_{23}H_{22}N_2O_2$ ([M+Na^+]) = 381.1579, Found: 381.1578.

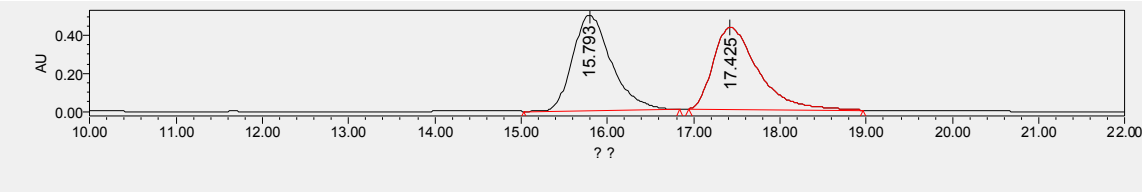


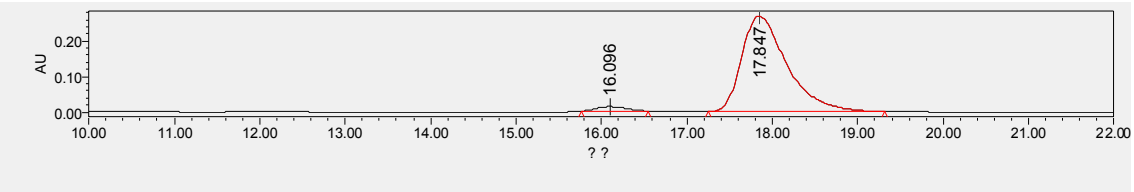


18) Product 3r:

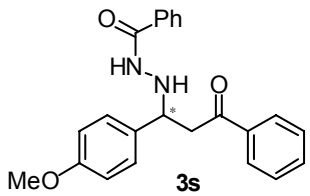


solid; 67% yield, 94% *ee*. $[\alpha]_D^{22}$ = 38.6 (*c* 0.030 in CH_2Cl_2) HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 16.1 min (minor) and 17.8 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H, Ar-H and NH-C=O), 7.60 – 7.26 (m, 12H, Ar-H), 7.12 (d, *J* = 5.8 Hz, 1H, Ar-H), 5.70 (d, *J* = 3.3 Hz, 1H, C-NH-N), 4.84 – 4.73 (m, 1H, N-CH-Ph), 3.45 (ddd, *J* = 21.6, 16.8, 6.5 Hz, 2H, -CH_2C=O), 2.36 (s, 3H, -CH_3) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 198.33, 166.89, 140.77, 138.49, 136.72, 133.31, 132.90, 131.69, 128.82, 128.69, 128.64, 128.59, 128.39, 128.24, 126.83, 124.70, 60.93, 44.46, 21.46 ppm; HRMS (ESI-TOF) calcd for $C_{23}H_{22}N_2O_2$ ([M+Na^+]) = 381.1579, Found: 381.1585.



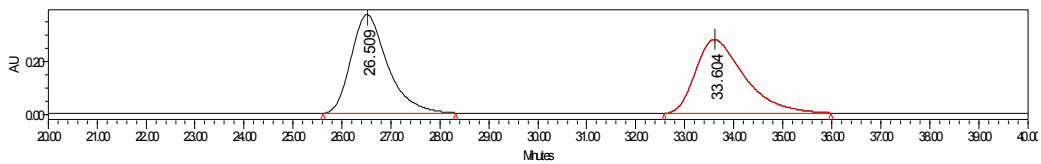


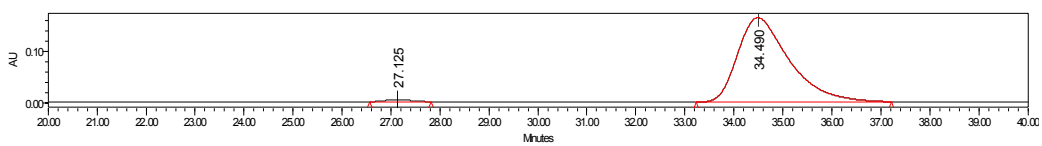
19) Product 3s:



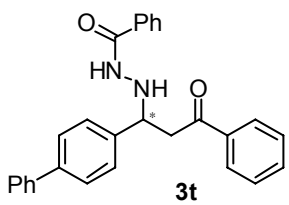
3s

solid; 64% yield, 97% *ee*. $[\alpha]_D^{22}$ = 33.5 (*c* 0.018 in CH_2Cl_2) HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 27.1 min (minor) and 34.5 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 2H, Ar-H and NH-C=O), 7.74 (ddd, *J* = 15.5, 10.5, 8.9 Hz, 1H, Ar-H), 7.62 – 7.33 (m, 11H, Ar-H), 6.88 (d, *J* = 8.5 Hz, 2H, Ar-H and C-NH-N), 4.77 (dd, *J* = 7.8, 5.2 Hz, 1H, N-CH-Ph), 3.79 (s, 3H, $-OCH_3$), 3.44 (ddd, *J* = 21.9, 16.8, 6.5 Hz, 2H, $-CH_2C=O$) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 198.47, 167.08, 159.31, 136.68, 133.33, 132.76, 132.65, 131.73, 128.89, 128.63, 128.58, 128.22, 126.87, 114.12, 63.76, 60.32, 55.27, 44.27 ppm; HRMS (ESI-TOF) calcd for $C_{23}H_{22}N_2O_3$ ([M+Na^+]) = 397.1528, Found: 397.1533.



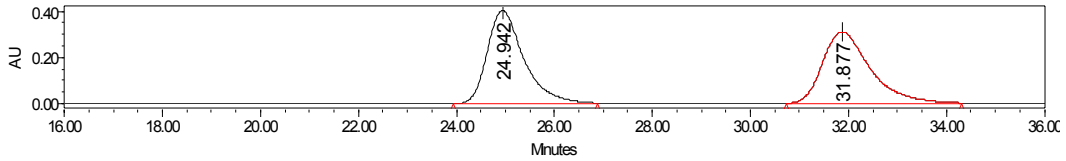


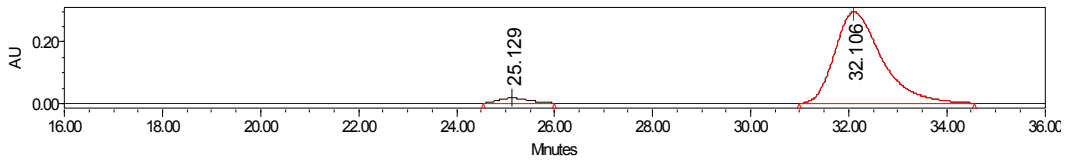
20) Product 3t:



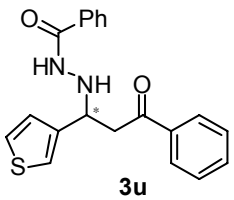
3t

solid; 51% yield, 94% *ee*. $[\alpha]_D^{28}$ = 48.3 (*c* 0.041 in CH_2Cl_2) HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 25.1 min (minor) and 32.1 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H, Ar-H and NH-C=O), 7.62 – 7.34 (m, 18H, Ar-H), 5.73 (s, 1H, C-NH-N), 4.87 (dd, *J* = 7.8, 5.1 Hz, 1H, N-CH-Ph), 3.50 (ddd, *J* = 21.9, 16.8, 6.5 Hz, 2H, $-CH_2C=O$) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 198.20, 167.07, 140.90, 140.65, 139.87, 136.68, 133.37, 132.81, 131.76, 128.81, 128.67, 128.62, 128.24, 128.16, 127.50, 127.40, 127.07, 126.85, 60.65, 44.36 ppm; HRMS (ESI-TOF) calcd for $C_{28}H_{24}N_2O_2$ ([M+Na^+]) = 443.1735, Found: 443.1740.



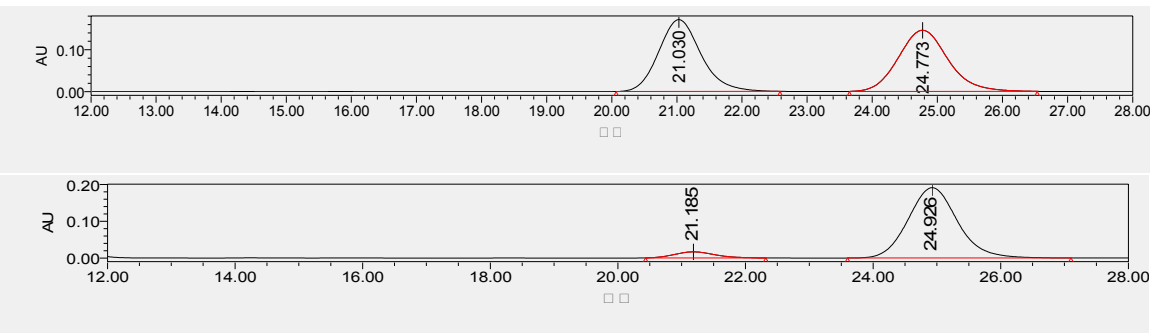


21) Product 3u:

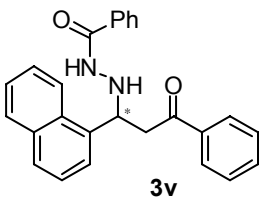


3u

solid; 42% yield, 88% *ee*. $[\alpha]_D^{22}$ = 37.7 (*c* 0.016 in CH_2Cl_2) HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 21.2 min (minor) and 25.0 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.77 (m, 4H, Ar-H and NH-C=O), 7.63 – 7.21 (m, 12H, Ar-H), 5.64 (s, 1H, C-NH-N)), 4.95 (dd, *J* = 7.7, 5.2 Hz, 1H, N-CH-Ph), 3.70 (s, 1H, N-CH-Ph), 3.47 (ddd, *J* = 21.9, 16.8, 6.5 Hz, 2H, -CH_2C=O)ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 198.41, 167.19, 141.60, 136.63, 133.39, 132.68, 131.81, 128.66, 128.62, 128.22, 126.88, 126.65, 126.39, 122.83, 63.76, 56.54, 43.78 ppm; HRMS (ESI-TOF) calcd for $C_{20}H_{18}SN_2O_2$ ([M+Na^+]) = 373.0987, Found: 373.0981.

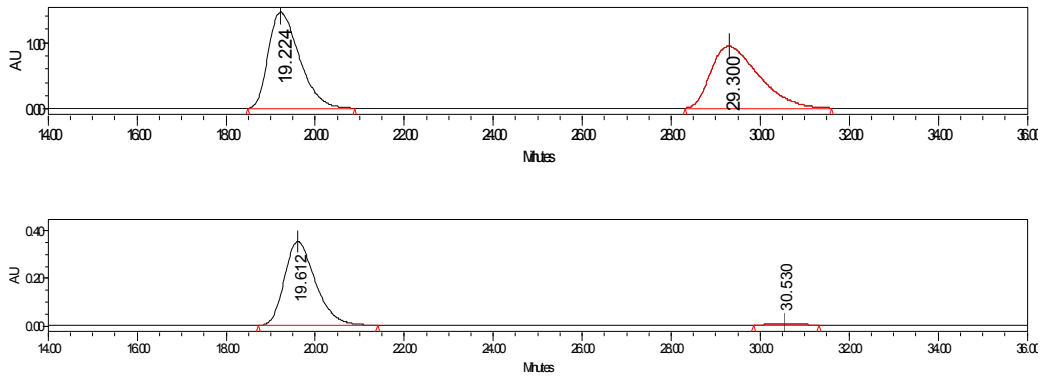


22) Product 3v:

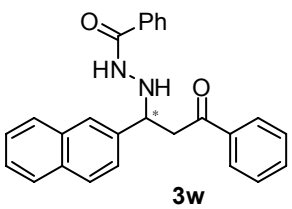


3v

solid; 75% yield, 97% *ee*. $[\alpha]_D^{22}$ = 46.4 (*c* 0.029 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IC, 2-propanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 19.6 min (major) and 30.5 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.7 Hz, 1H, NH-C=O), 7.85 (ddd, *J* = 43.7, 17.1, 7.5 Hz, 5H, Ar-H), 7.66 – 7.26 (m, 13H, Ar-H), 5.72 (dd, *J* = 8.4, 3.2 Hz, 1H, C-NH-N), 3.78 – 3.44 (m, 3H, N-CH-Ph and -CH_2C=O) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) 198.50, 167.13, 136.66, 136.49, 134.12, 133.38, 132.77, 131.65, 131.40, 128.98, 128.64, 128.52, 128.48, 128.28, 126.84, 126.55, 125.84, 125.49, 123.39, 63.76, 43.85ppm; HRMS (ESI-TOF) calcd for $C_{26}H_{22}N_2O_2$ ([M+Na^+]) = 417.1579, Found: 417.1563.

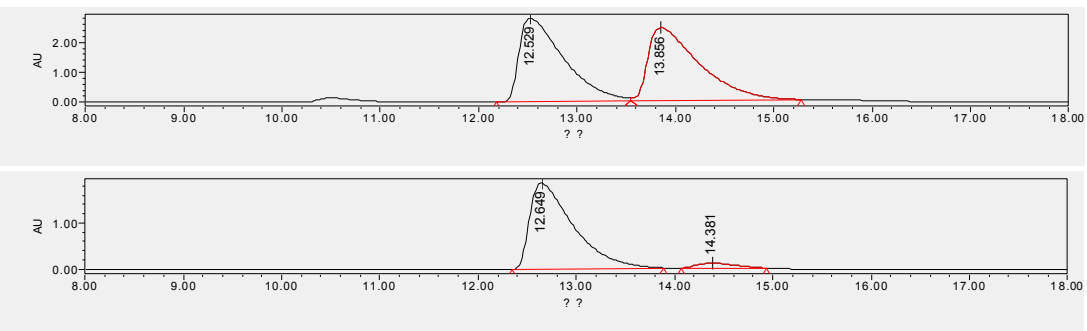


23) Product 3w:

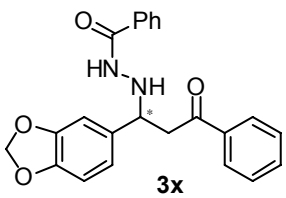


3w

solid; 64% yield, 91% *ee*. $[\alpha]_D^{22}$ = 56.5 (*c* 0.042 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IB, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.7 min (major) and 14.4 min (minor); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.77 (m, 6H, Ar-H and NH-C=O), 7.63 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.59 – 7.36 (m, 8H, Ar-H), 7.29 (t, *J* = 7.6 Hz, 2H, Ar-H), 5.81 (d, J = 6.5 Hz, 1H, C-NH-N), 4.99 (dd, *J* = 7.6, 5.3 Hz, 1H, N-CH-Ph), 3.53 (qd, J = 16.9, 6.5 Hz, 2H, -CH_2C=O) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) 198.13, 167.13, 138.30, 136.67, 133.38, 133.18, 132.75, 131.72, 128.66, 128.24, 128.00, 127.72, 126.91, 126.27, 126.09, 125.42, 61.02, 44.36 ppm; HRMS (ESI-TOF) calcd for $C_{26}H_{22}N_2O_2$ ([M+Na^+]) = 417.1579, Found: 417.1570.



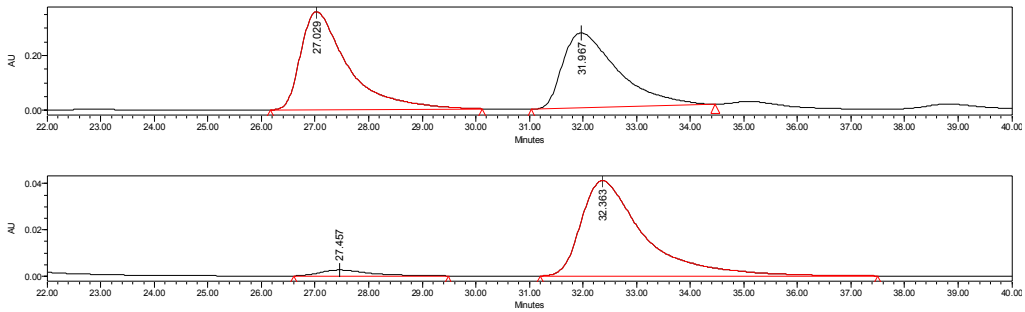
24) Product 3x:



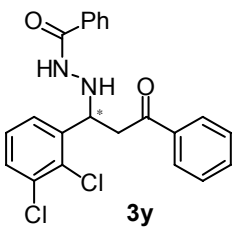
3x

solid; 61% yield, 91% *ee*. $[\alpha]_D^{28}$ = 19.3 (*c* 0.013 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IA, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 27.5 min (minor) and 32.4 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 2H, Ar-H and NH-C=O), 7.64 – 7.34 (m, 9H), 7.00 (s, 1H, Ar-H), 6.90 (d, *J* = 7.9 Hz, 1H, Ar-H), 6.77 (d, *J* = 7.9 Hz, 1H, Ar-H), 5.63 (s, 1H, C-NH-N), 4.73 (dd, *J* = 7.5, 5.4 Hz, 1H, N-CH-Ph), 3.71 (dd, *J* = 13.3, 6.2 Hz, 2H, -O-CH_2-O-), 3.41 (ddd, *J* = 21.9, 16.7, 6.5 Hz, 2H, -CH_2C=O) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 198.18, 167.06, 147.97, 147.27, 133.36, 131.76, 128.65, 128.60, 128.21, 126.86, 121.31, 108.38,

107.76, 101.10, 63.75, 60.66, 44.48 ppm; HRMS (ESI-TOF) calcd for $C_{23}H_{20}N_2O_4$ ([M+Na$^+$]) = 411.1321, Found: 411.1331.

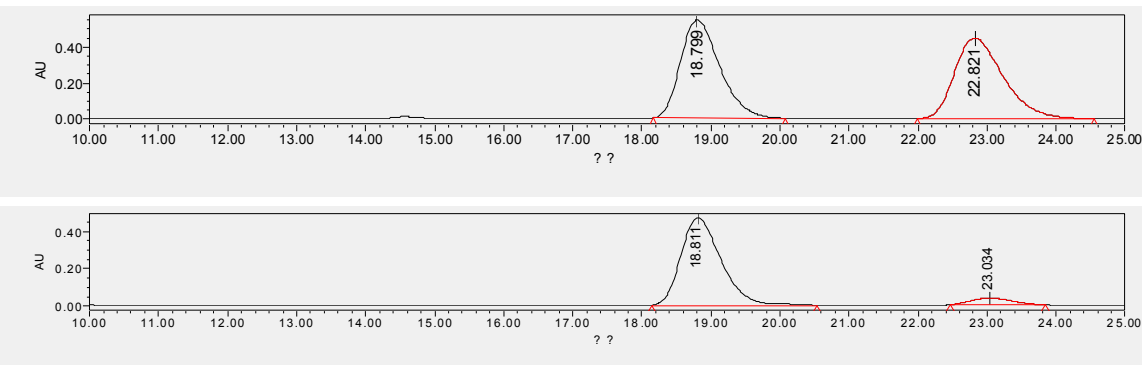


25) Product 3y:

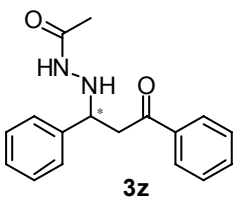


3y

solid; 60% yield, 85% *ee*. $[\alpha]_D^{22}$ = 24.6 (*c* 0.025 in CH_2Cl_2) HPLC DAICEL CHIRALCEL IC, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 18.8 min (minor) and 23.0 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H, Ar-H and NH-C=O), 7.76 - 7.48 (m, 11H, Ar-H), 7.25 (d, *J* = 10.9 Hz, 1H, Ar-H), 5.74 (s, 1H, C-NH-N), 5.25 (s, 1H, N-CH-Ph), 3.41 (d, *J* = 6.4 Hz, 2H, -CH_2C=O) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) 197.77, 167.20, 136.99, 136.39, 134.54, 133.94, 133.55, 132.63, 131.81, 129.65, 129.40, 128.70, 128.60, 128.26, 127.58, 126.94, 56.89, 42.78 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{18}Cl_2N_2O_2$ ([M+Na$^+$]) = 435.0643, Found: 435.0635.

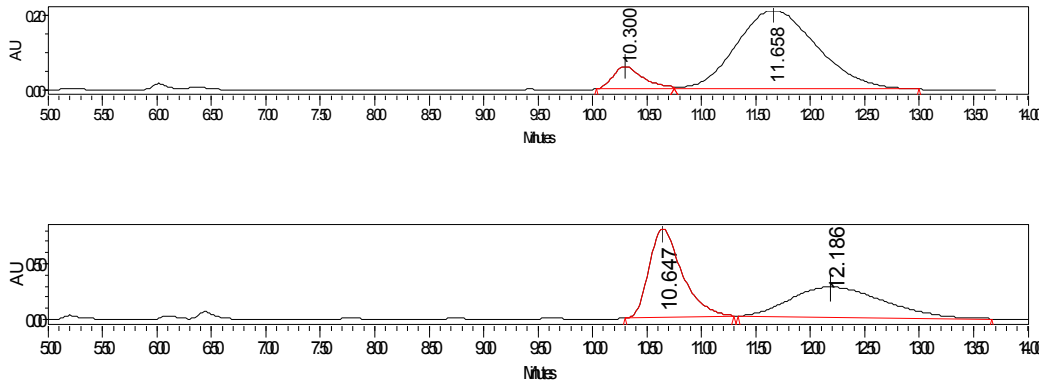


26) Product 3z:



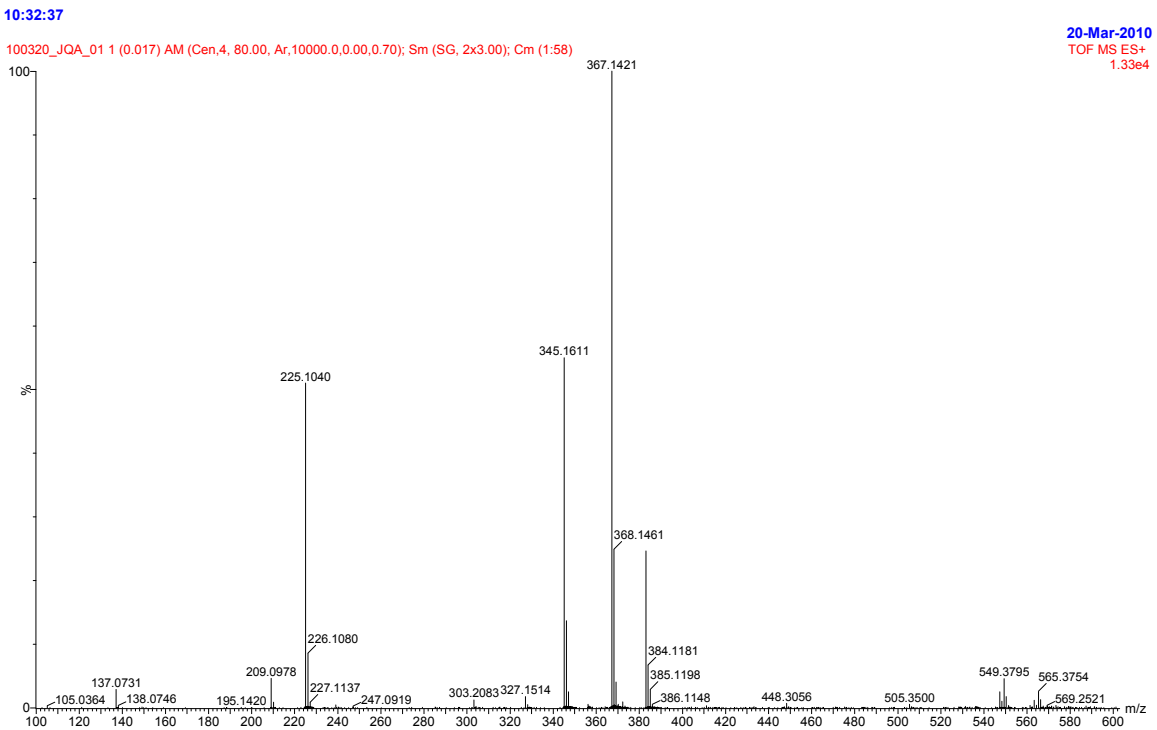
3z

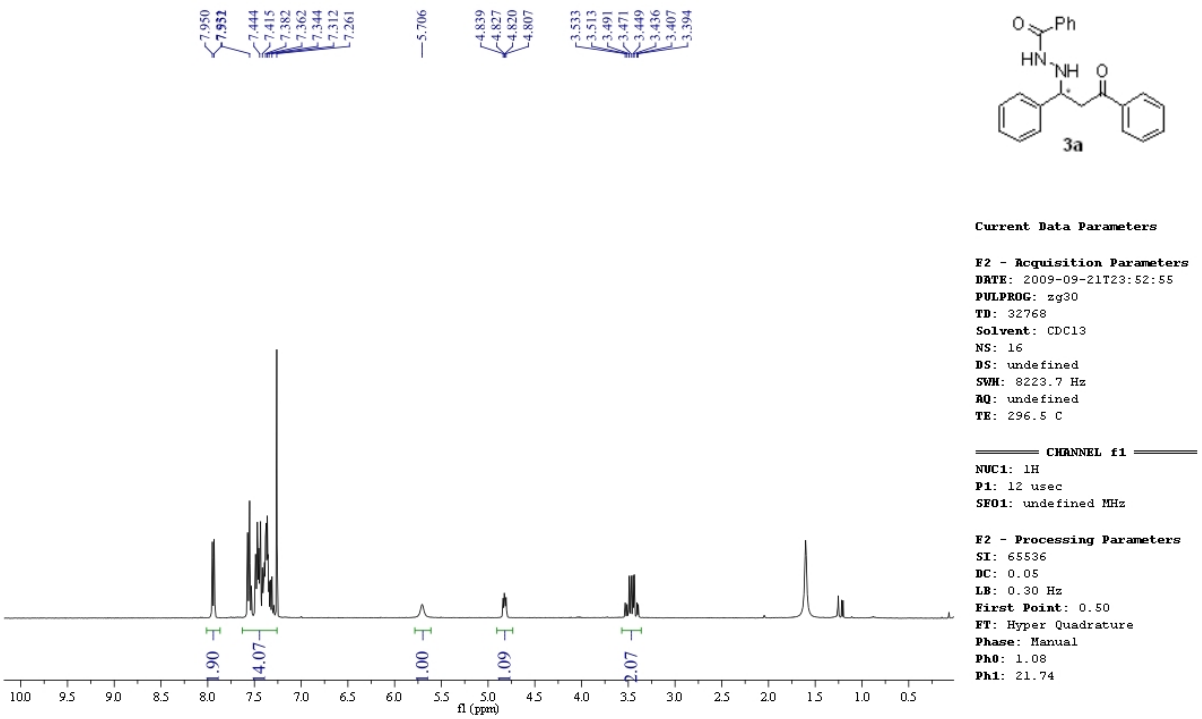
solid; 56% yield, 81% *ee*. $[\alpha]_D^{22}$ = 19.5 (*c* 0.010 in CH_2Cl_2) HPLC DAICEL CHIRALCEL AD-H, 2-propanol/*n*-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 21.0 min (minor) and 26.0 min (major); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 2H, Ar-H and NH-C=O), 7.92 – 7.28 (m, 11H, Ar-H and C-NH-N), 4.74 – 4.64 (m, 1H, N-CH-Ph), 3.36 (dd, *J* = 14.7, 9.2 Hz, 2H, -CH_2C=O), 2.47 – 2.27 (m, 3H,-CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) 198.13, 169.29, 144.90, 128.95, 128.47, 127.67, 126.27, 122.12, 60.66, 44.41 ppm; HRMS (ESI-TOF) calcd for $C_{17}H_{18}N_2O_2$ ([M+Na$^+$]) = 305.1266, Found: 305.1276.



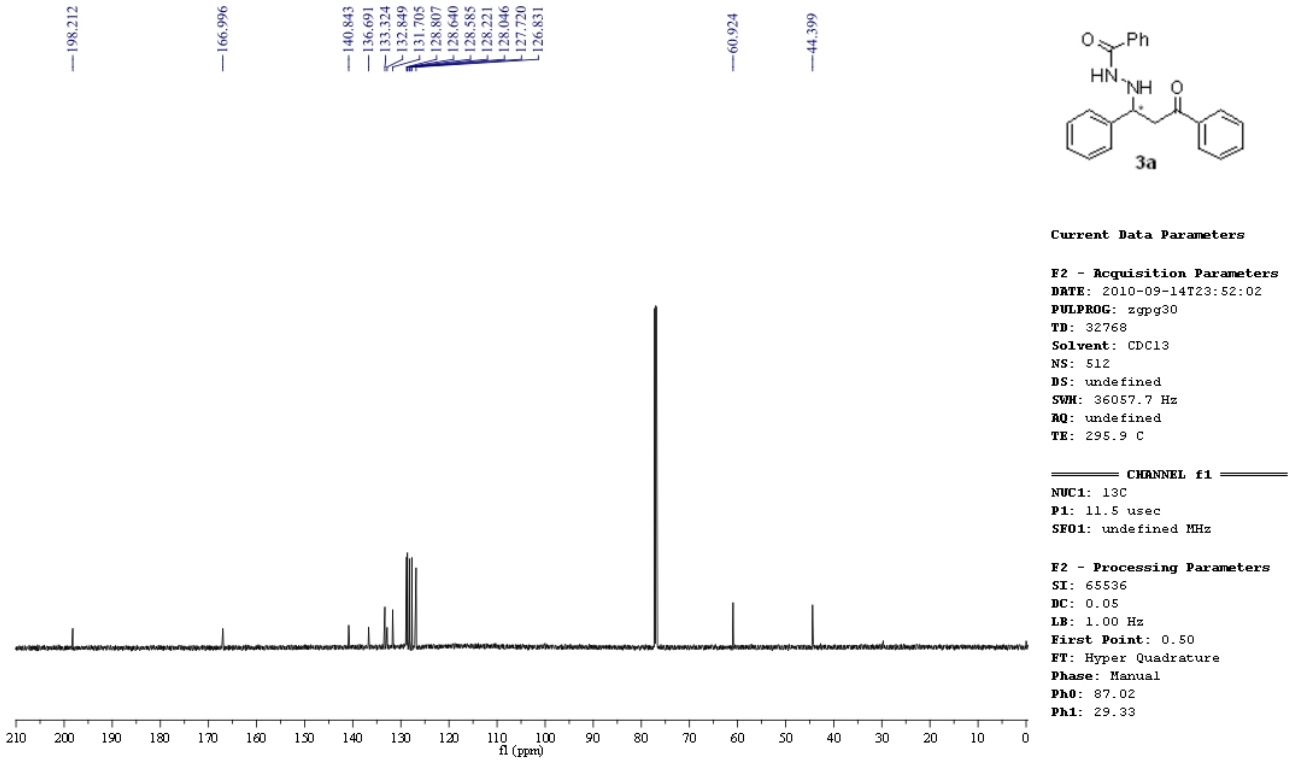
(G) Copies of NMR and MS spectra for products

1) Product 3a:



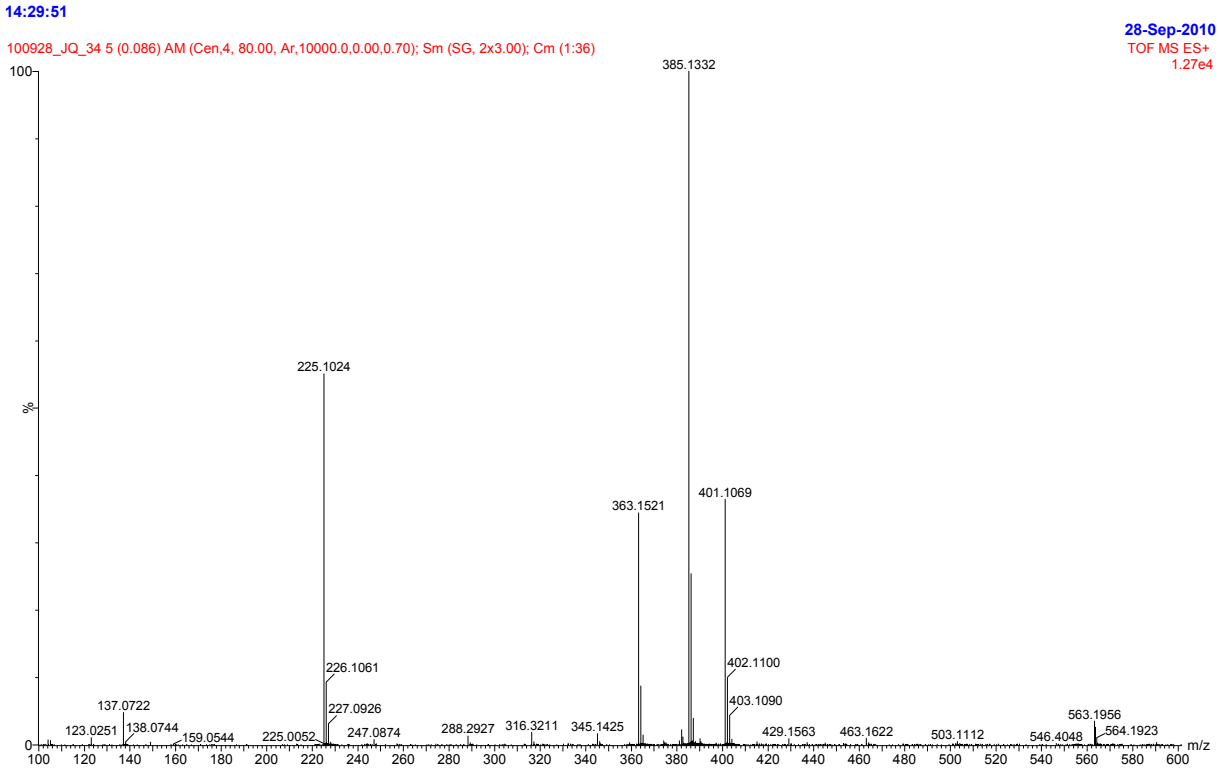


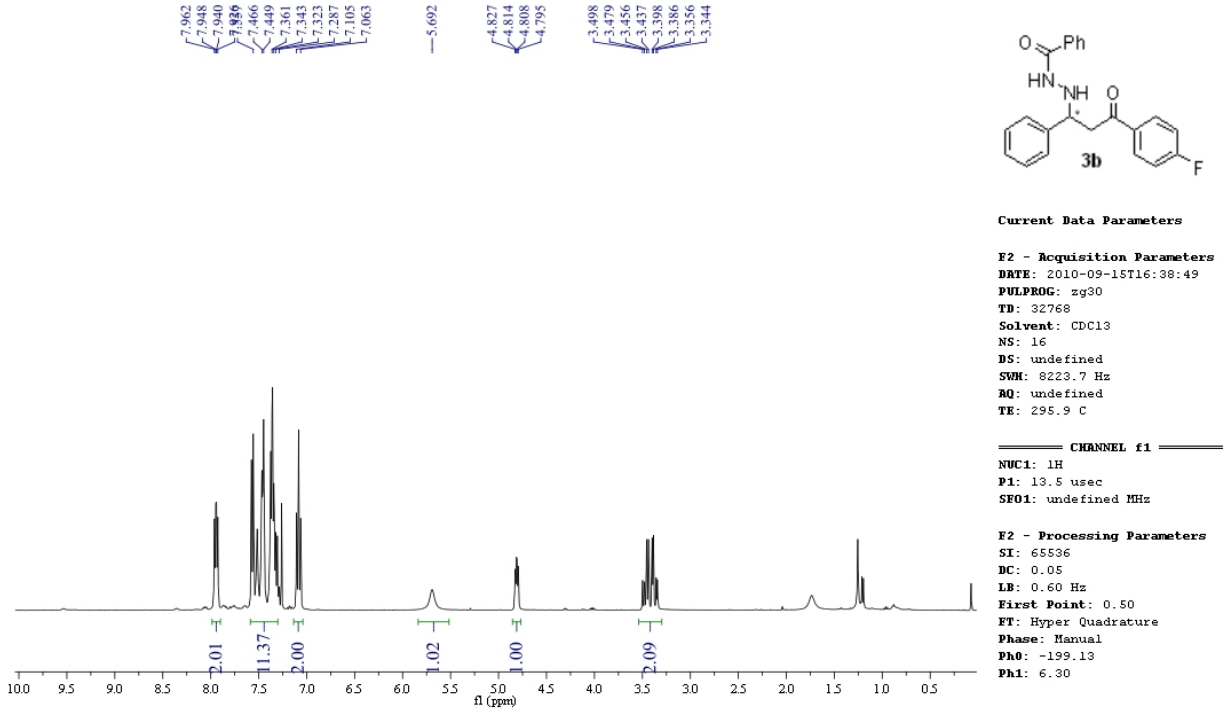
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.63 – 7.26 (m, 14H), 5.71 (s, 1H), 4.82 (dd, *J* = 7.8, 5.1 Hz, 1H), 3.46 (qd, *J* = 16.9, 6.5 Hz, 2H).



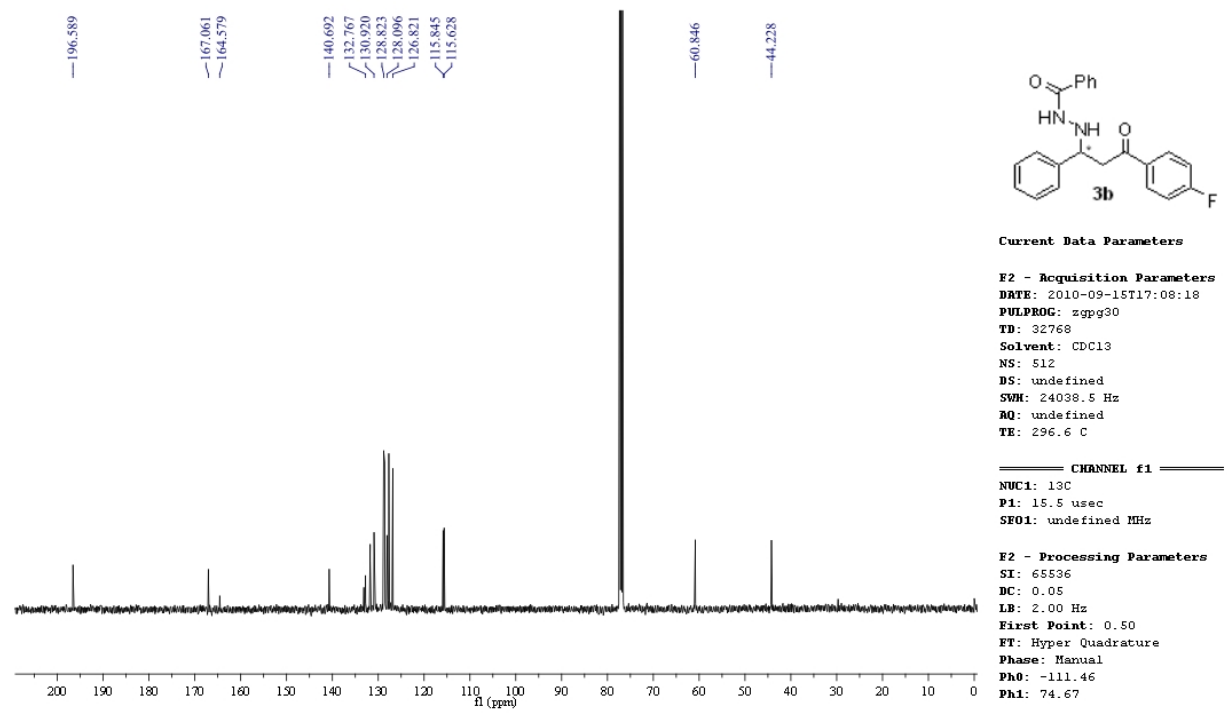
δ_C (151 MHz, $CDCl_3$) 198.21, 167.00, 140.84, 136.69, 133.32, 132.85, 131.71, 128.81, 128.64, 128.59, 128.22, 128.05, 127.72, 126.83, 60.92, 44.40.

2) Product 3b:



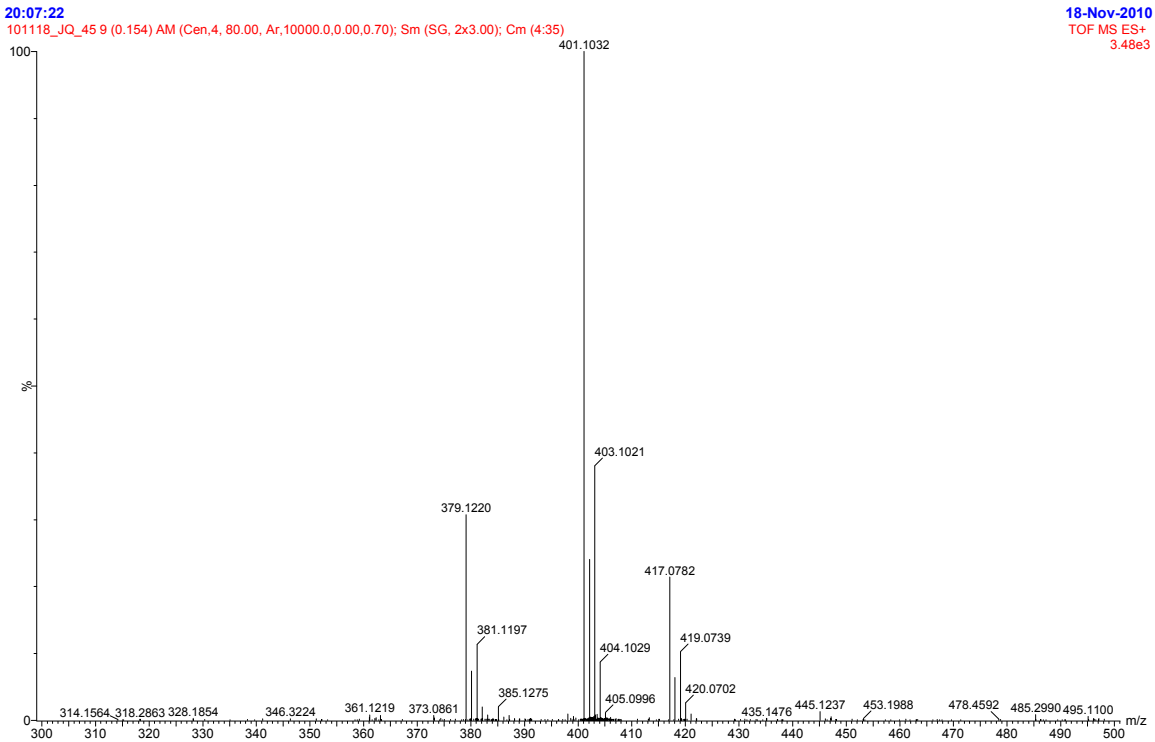


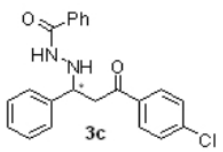
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.59 – 7.30 (m, 11H), 7.08 (t, *J* = 8.6 Hz, 2H), 5.69 (s, 1H), 4.81 (dd, *J* = 7.7, 5.2 Hz, 1H), 3.42 (ddd, *J* = 21.8, 16.8, 6.5 Hz, 2H).

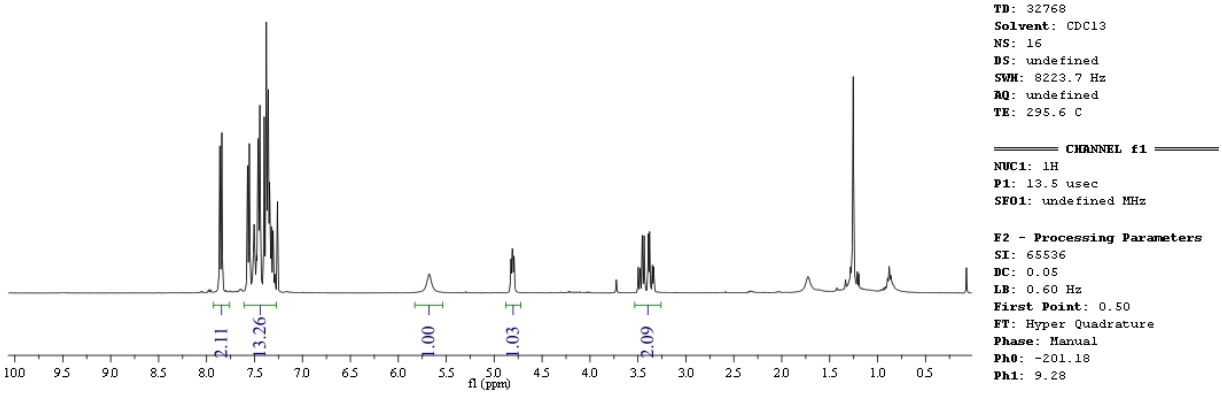


δ $_C$ (101 MHz, $CDCl_3$) 196.59, 167.06, 164.58, 140.69, 133.14, 132.77, 131.75, 130.92, 130.83, 128.82, 128.59, 128.10, 127.69, 126.82, 115.85, 115.63, 60.85, 44.23.

3) Product 3c:







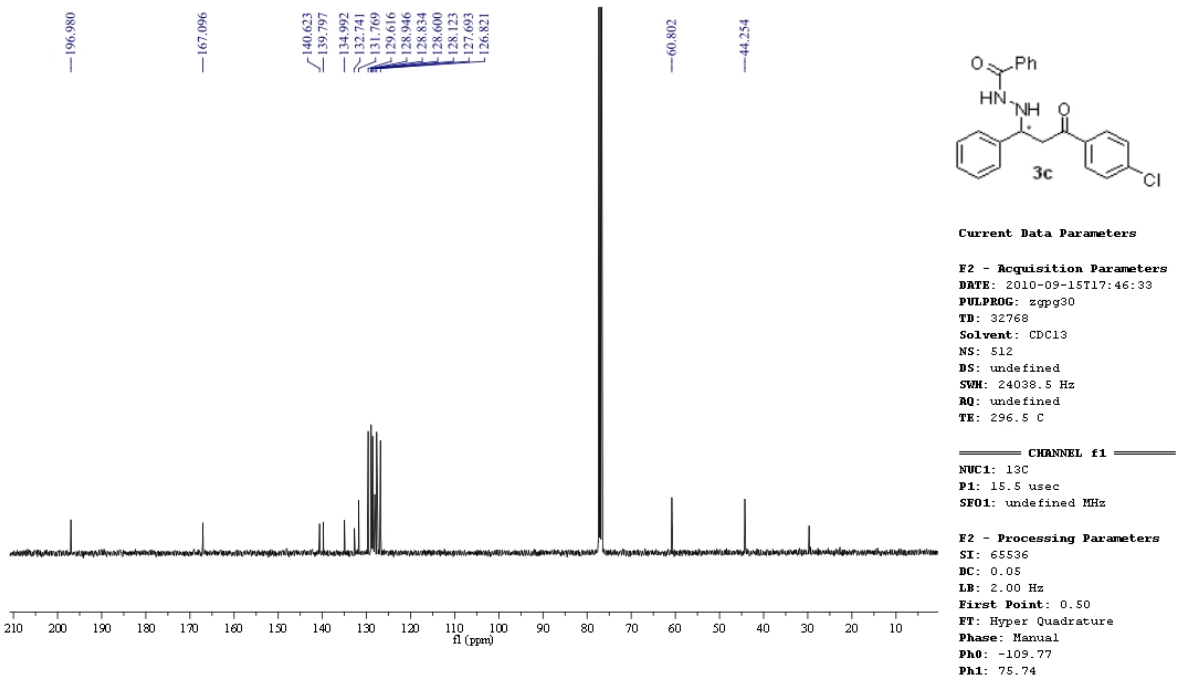
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-09-15T17:17:04
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.6 C

CHANNEL f1
NUC1: 1H
P1: 13.5 usec
SFO1: undefined MHz

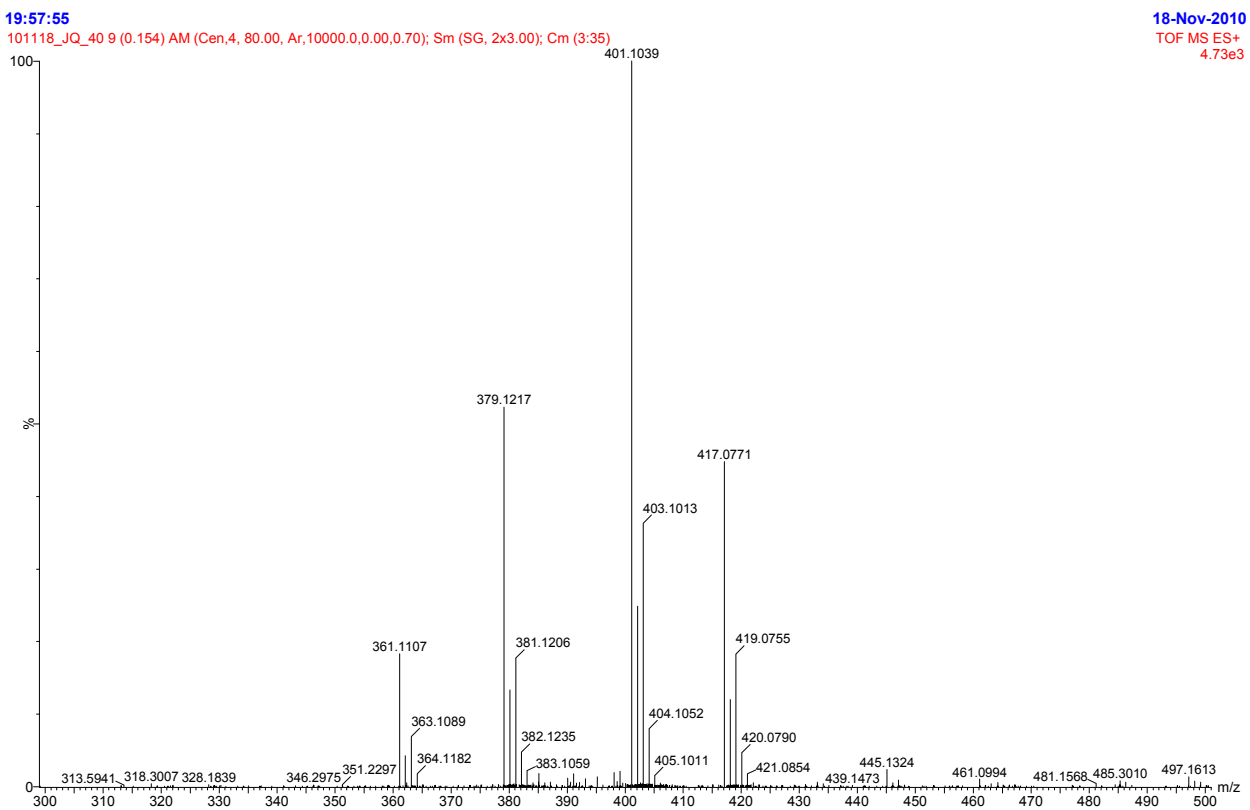
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -201.18
Ph1: 9.28

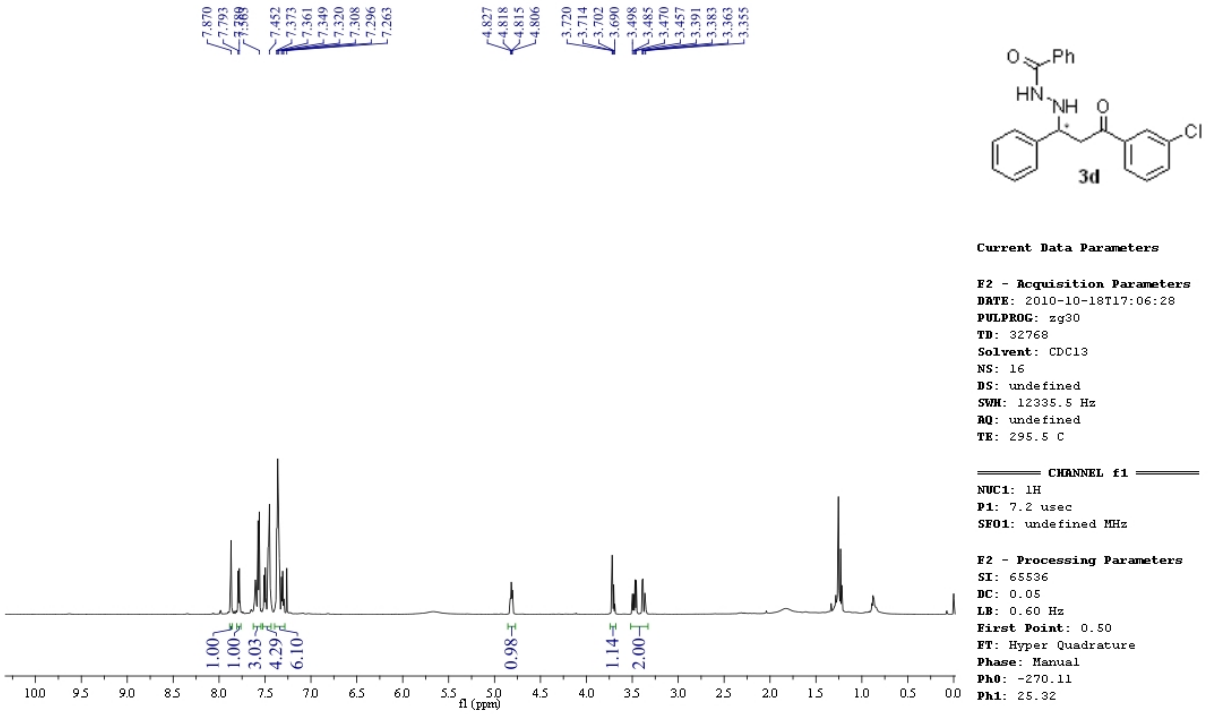
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.5 Hz, 2H), 7.61 – 7.27 (m, 13H), 5.68 (s, 1H), 4.81 (dd, J = 7.6, 5.2 Hz, 1H), 3.42 (ddd, J = 21.8, 16.8, 6.5 Hz, 2H).



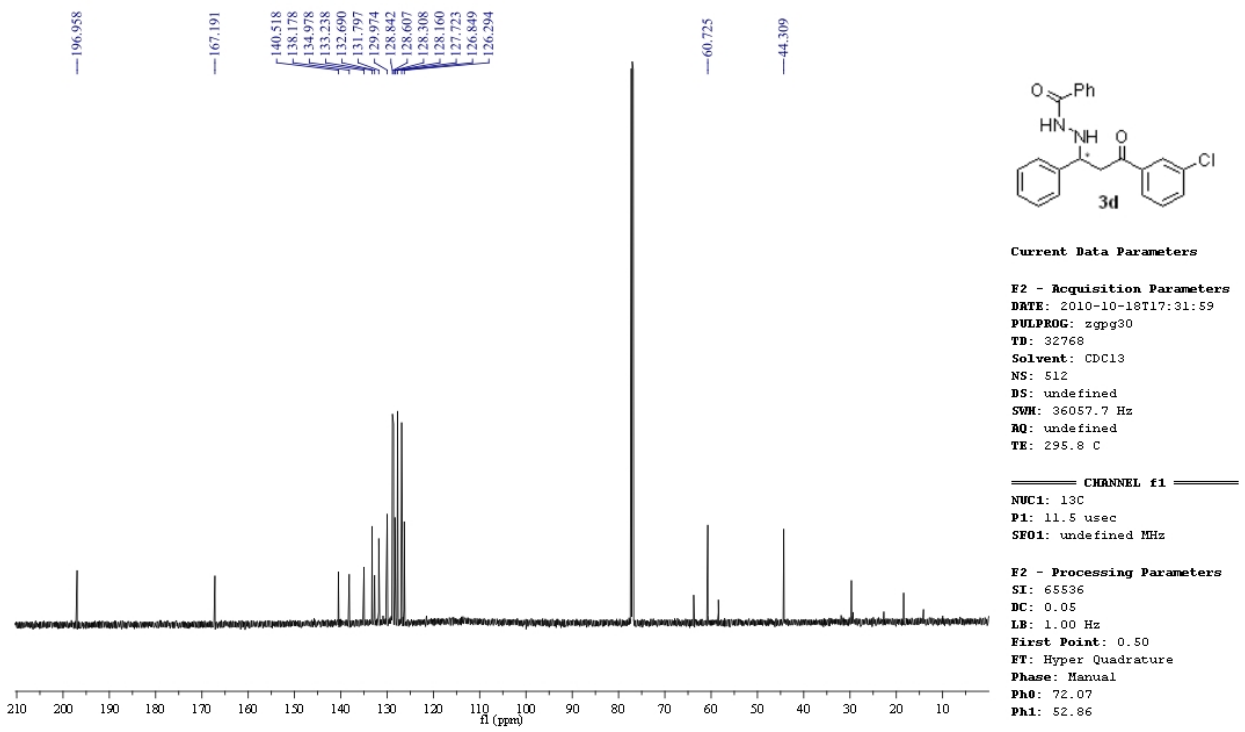
δ_C (101 MHz, $CDCl_3$) 196.98, 167.10, 140.62, 139.80, 134.99, 132.74, 131.77, 129.62, 128.95, 128.83, 128.60, 128.12, 127.69, 126.82, 60.80, 44.25.

4) Product 3d:



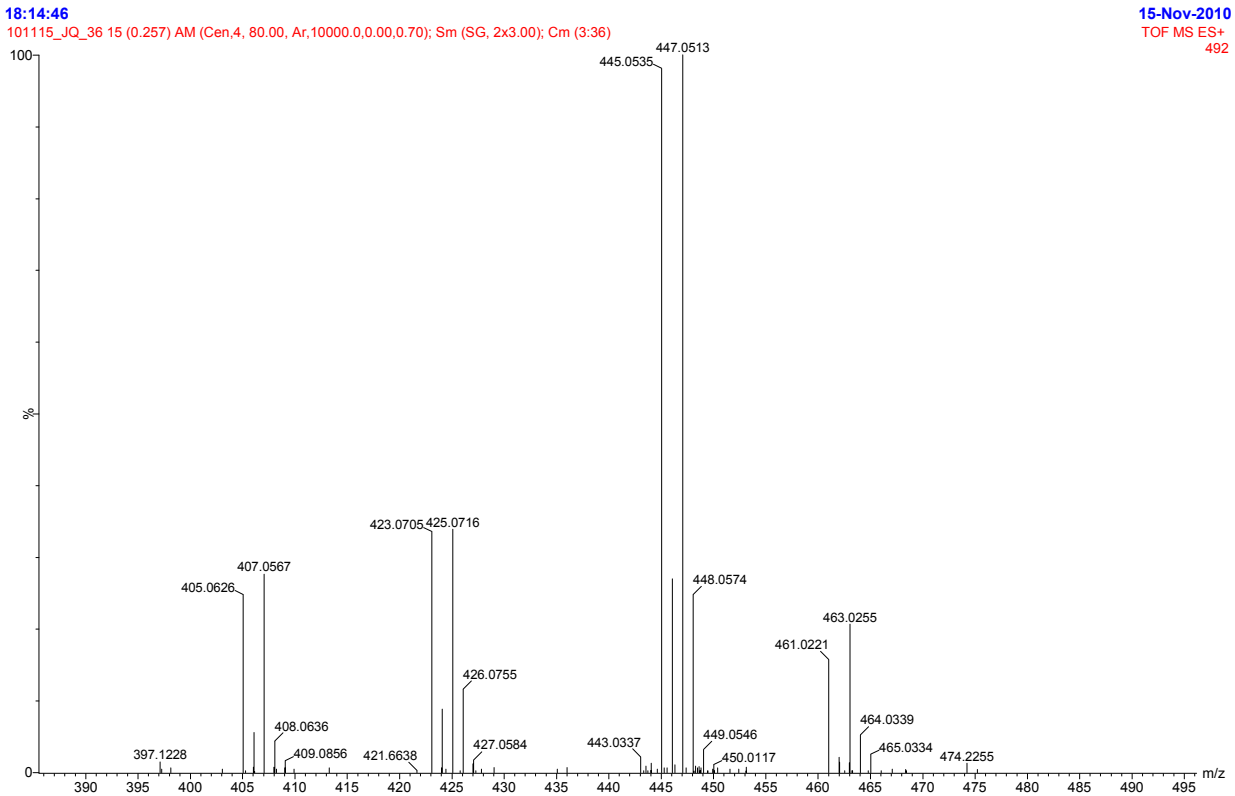


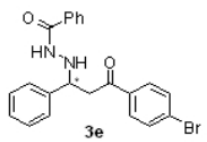
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.48 (dd, *J* = 26.9, 7.7 Hz, 4H), 7.33 (dt, *J* = 32.1, 7.4 Hz, 6H), 4.82 (dd, *J* = 7.4, 5.3 Hz, 1H), 3.71 (dd, *J* = 12.4, 5.1 Hz, 1H), 3.43 (ddd, *J* = 21.8, 16.9, 6.4 Hz, 2H).

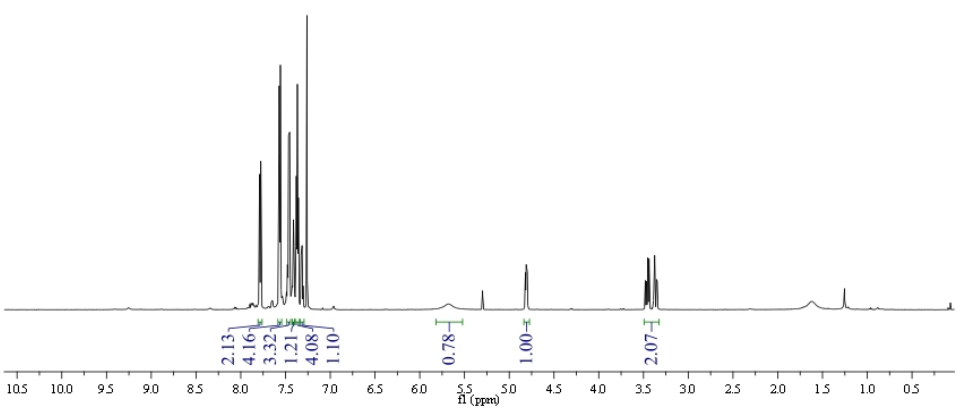


δ_C (151 MHz, $CDCl_3$) 196.96, 167.19, 140.52, 138.18, 134.98, 133.24, 132.69, 131.80, 129.97, 128.84, 128.61, 128.31, 128.16, 127.72, 126.85, 126.29, 60.72, 44.31.

5) Product 3e:







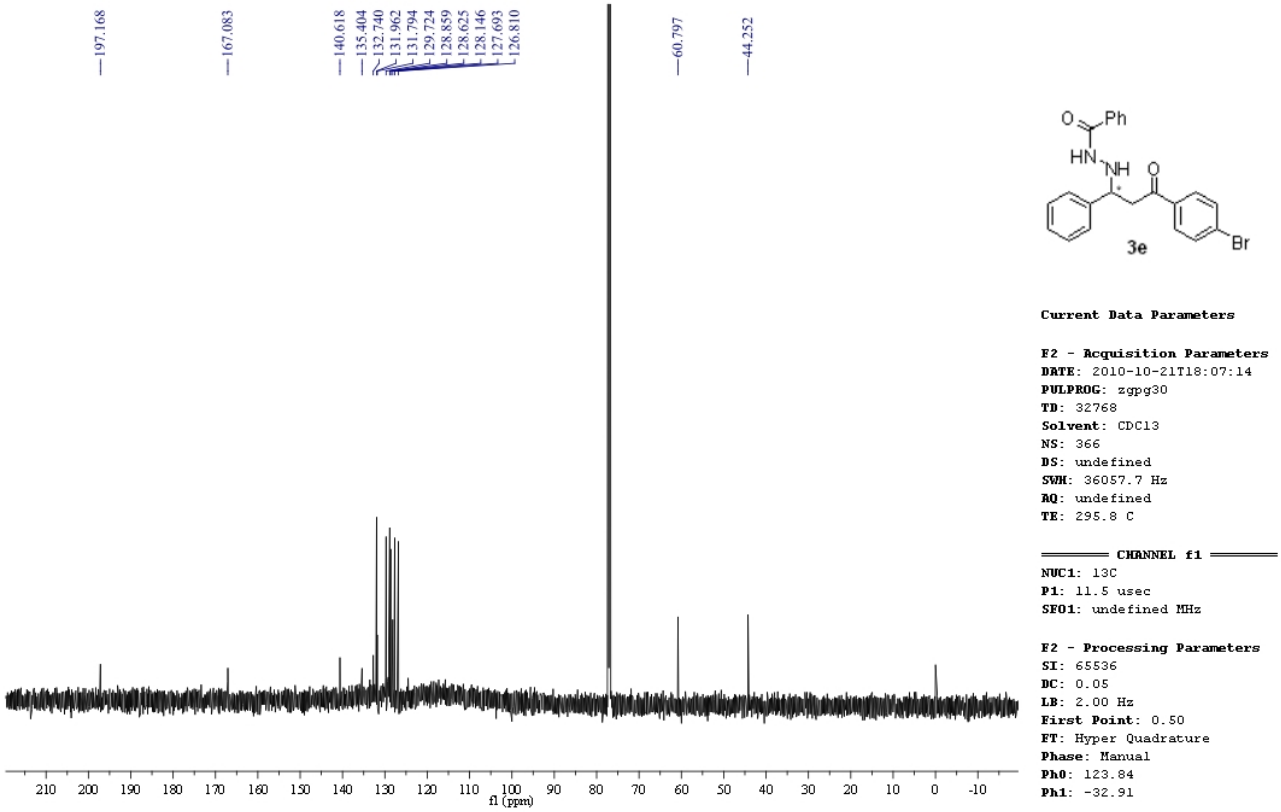
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-10-21T17:48:51
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.8 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

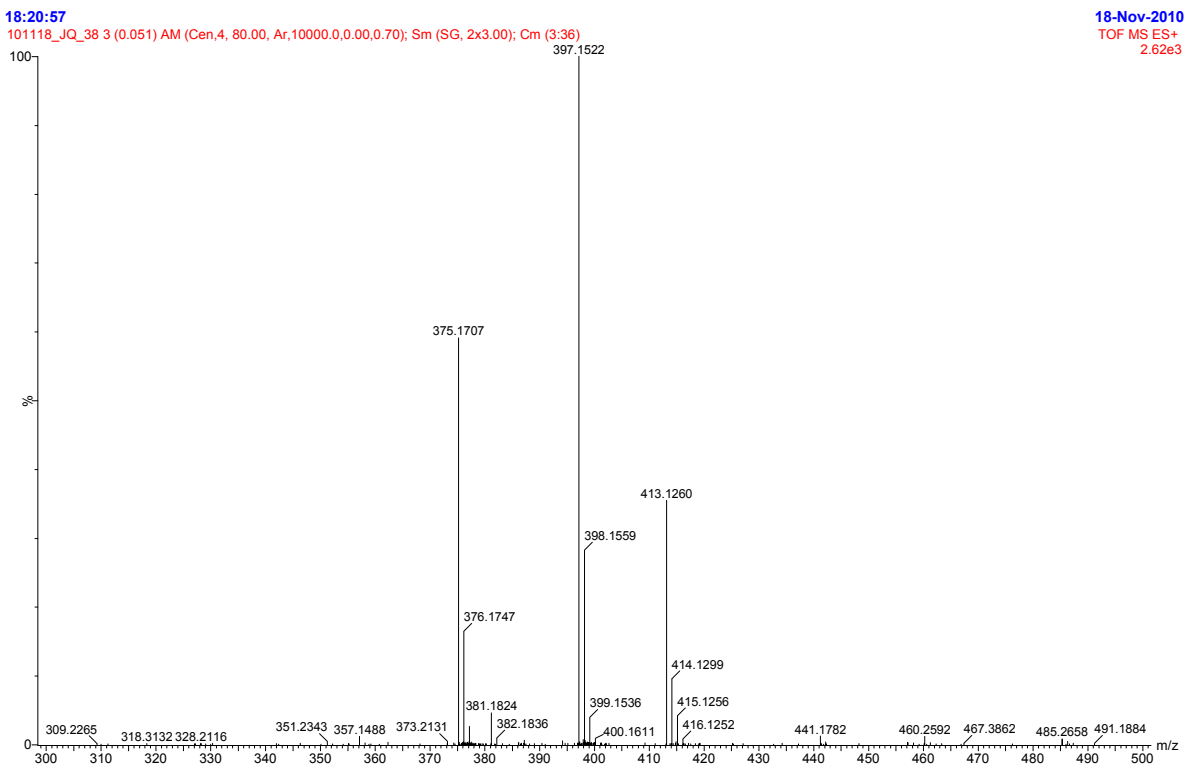
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -162.13
Ph1: 29.19

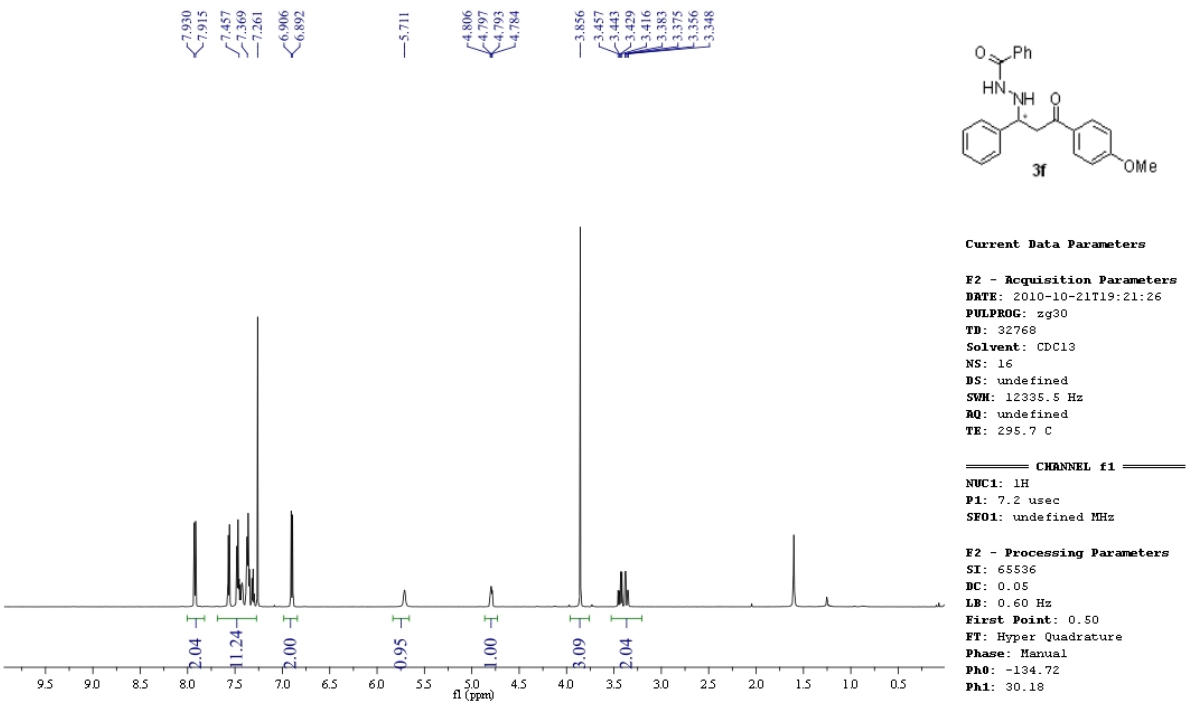
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.3 Hz, 4H), 7.47 (t, J = 7.6 Hz, 3H), 7.41 (s, 1H), 7.37 (t, J = 7.1 Hz, 4H), 7.31 (t, J = 7.2 Hz, 1H), 5.68 (s, 1H), 4.81 (dd, J = 7.8, 5.1 Hz, 1H), 3.41 (ddd, J = 21.7, 16.8, 6.5 Hz, 2H).



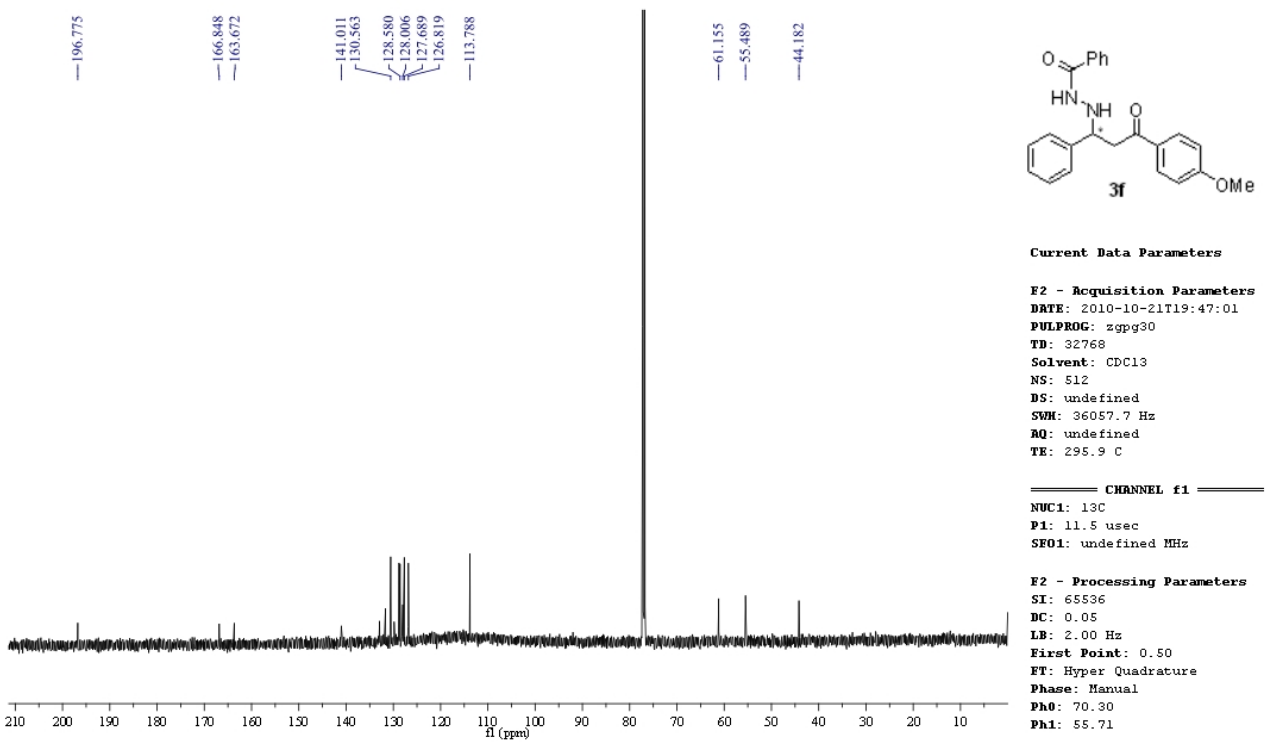
δ_C (151 MHz, $CDCl_3$) 197.17, 167.08, 140.62, 135.40, 132.74, 131.96, 131.79, 129.72, 128.86, 128.62, 128.15, 127.69, 126.81, 60.80, 44.25.

6) Product 3f:



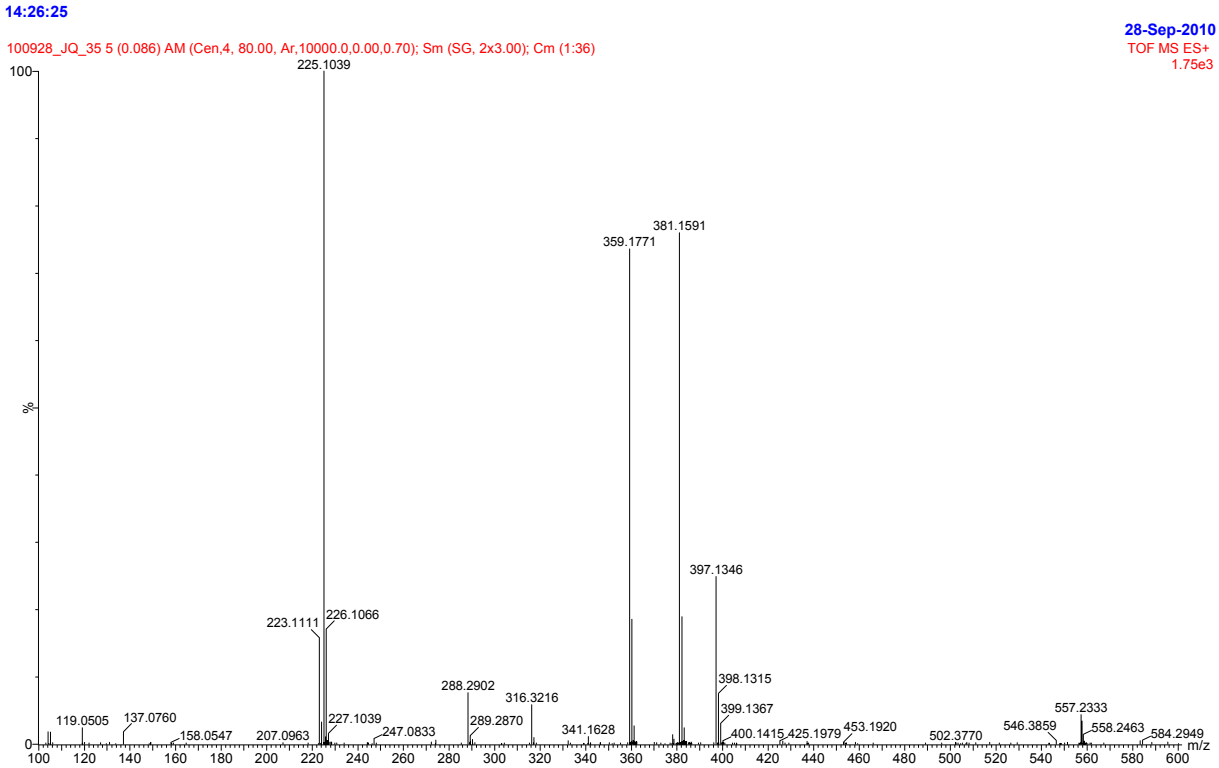


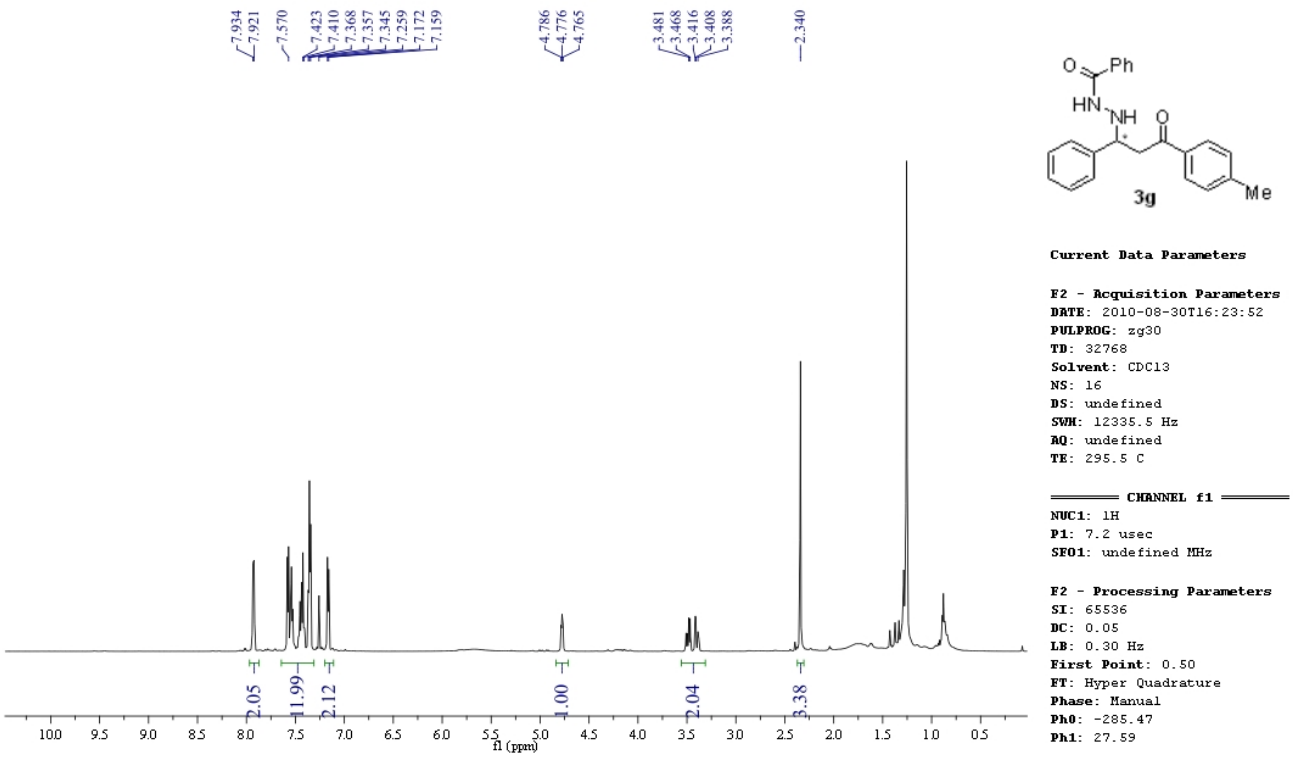
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.69 – 7.27 (m, 11H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.71 (s, 1H), 4.80 (dd, *J* = 7.8, 4.9 Hz, 1H), 3.86 (s, 3H), 3.40 (ddd, *J* = 21.3, 16.5, 6.5 Hz, 2H).



δ_C (151 MHz, $CDCl_3$) 196.78, 166.85, 163.67, 141.01, 132.91, 131.67, 130.56, 129.83, 128.80, 128.58, 128.01, 127.69, 126.82, 113.79, 61.16, 55.49, 44.18.

7) Product 3g:





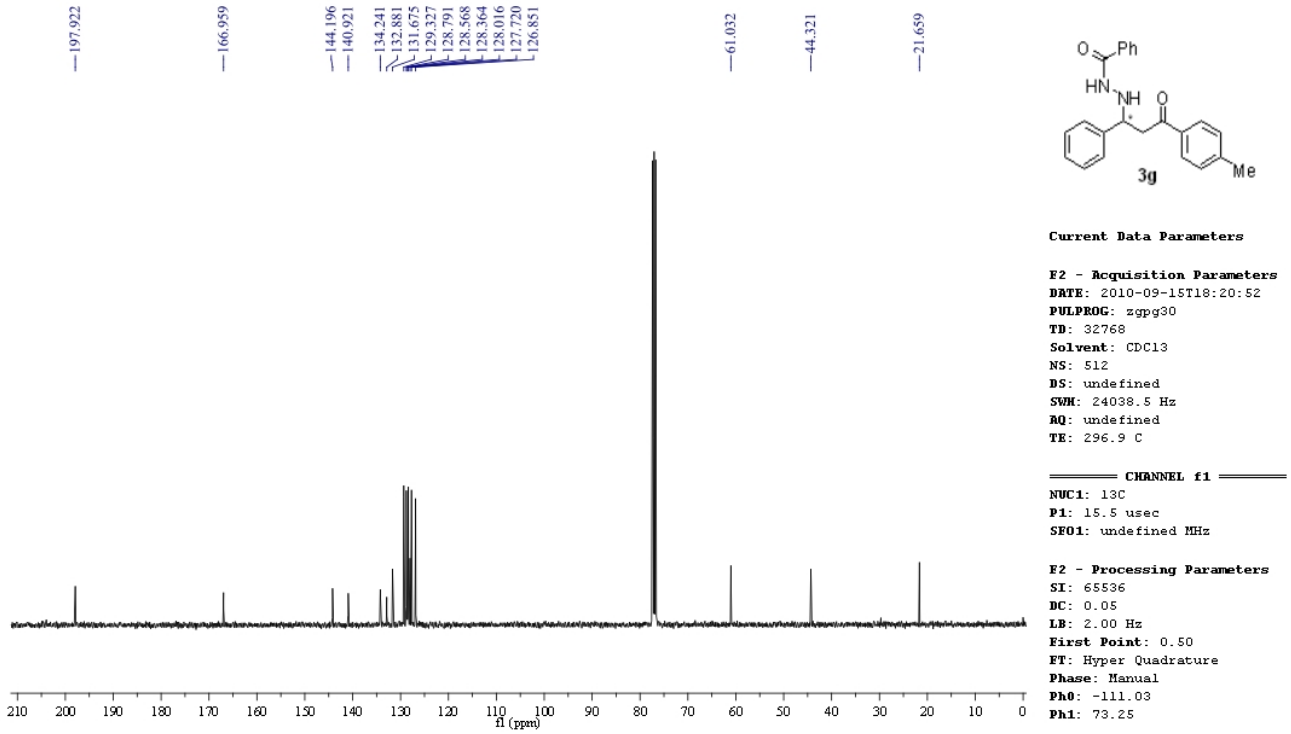
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-08-30T16:23:52
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.5 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

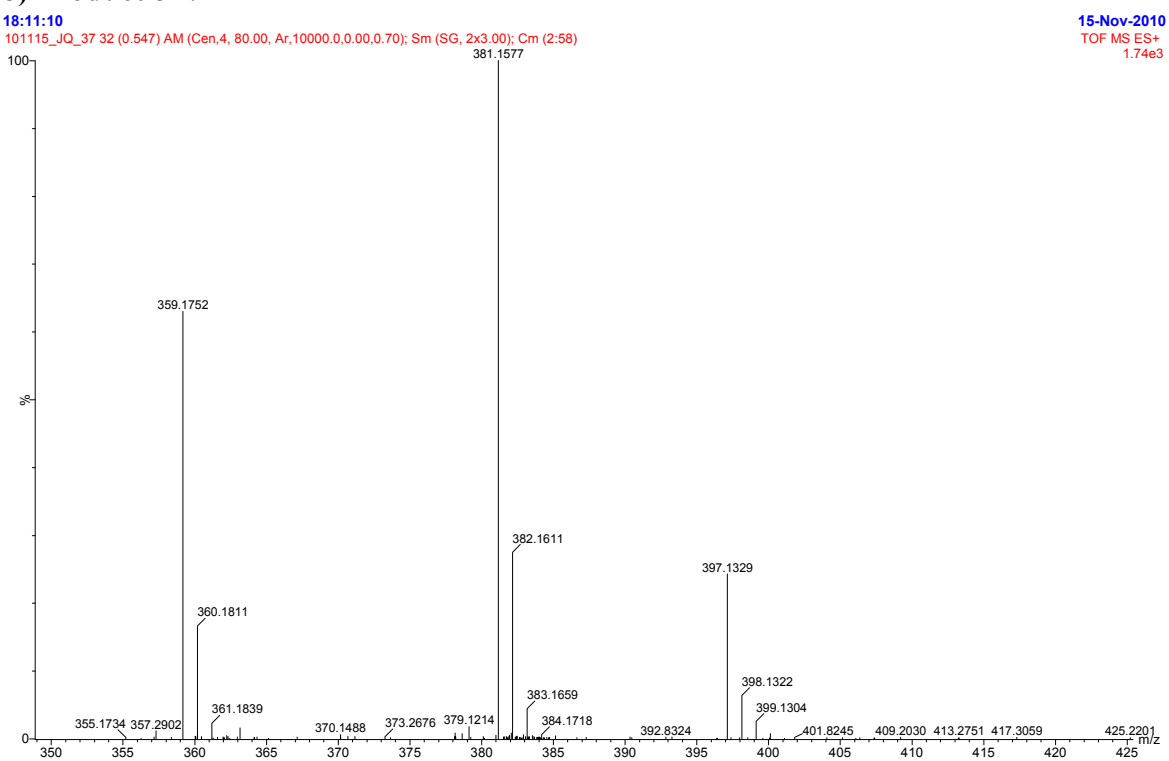
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -285.47
Ph1: 27.59

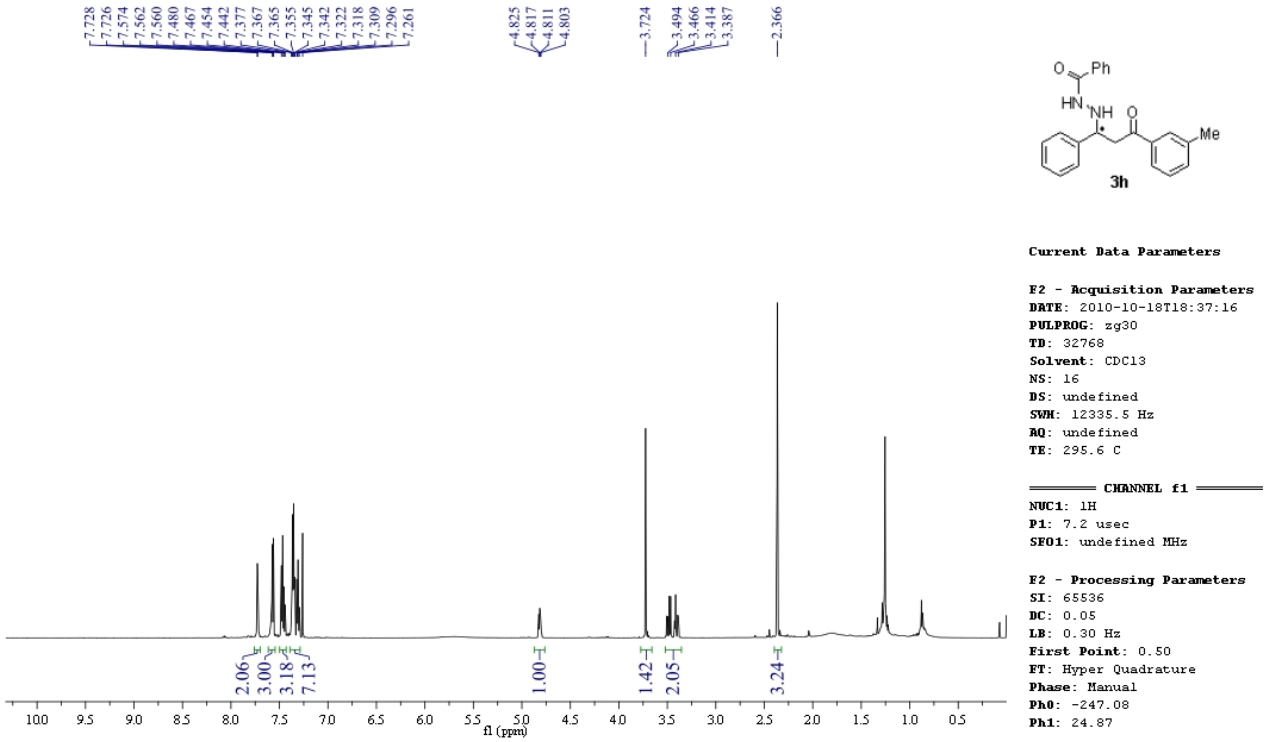
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.64 – 7.31 (m, 12H), 7.17 (d, J = 7.5 Hz, 2H), 4.84 – 4.71 (m, 1H), 3.56 – 3.31 (m, 2H), 2.34 (s, 3H).



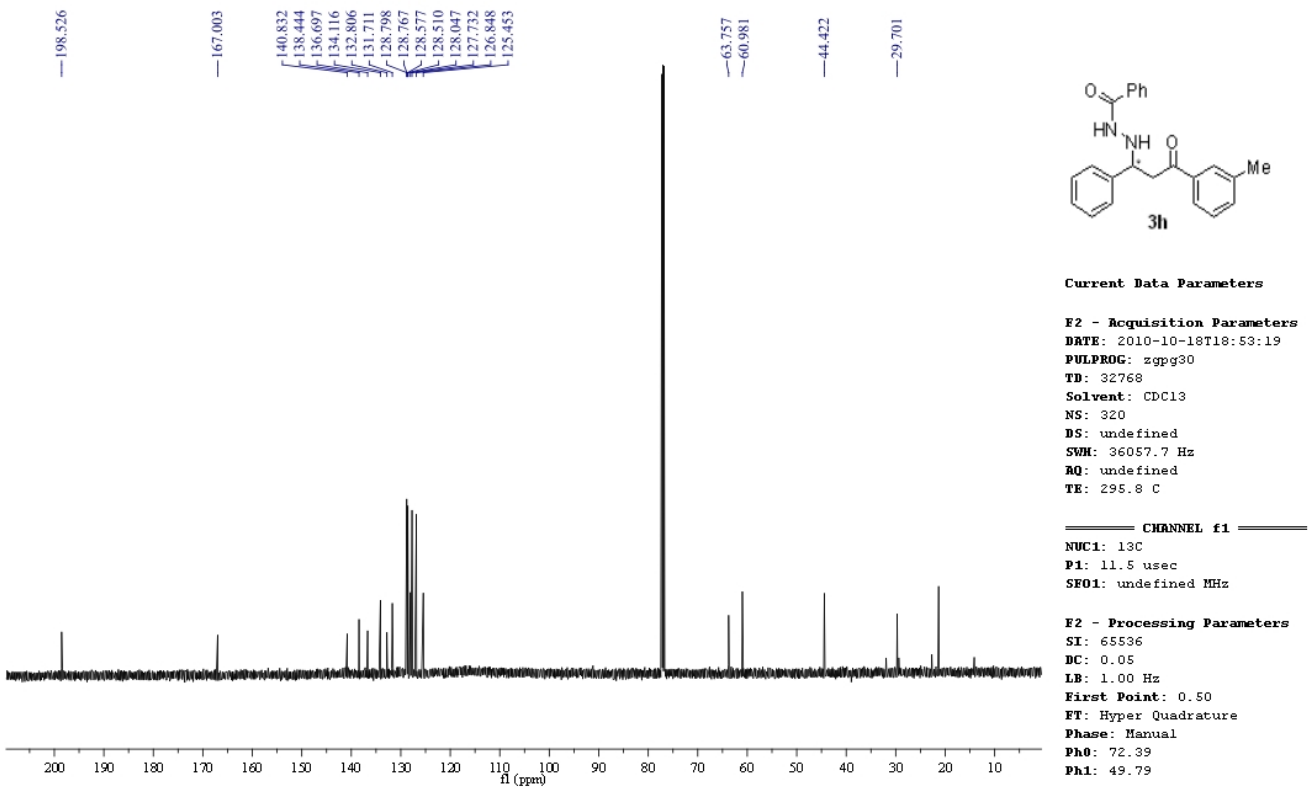
δ_C (101 MHz, $CDCl_3$) 197.92, 166.96, 144.20, 140.92, 134.24, 132.88, 131.68, 129.33, 128.79, 128.57, 128.36, 128.02, 127.72, 126.85, 61.03, 44.32, 21.66.

8) Product 3h:



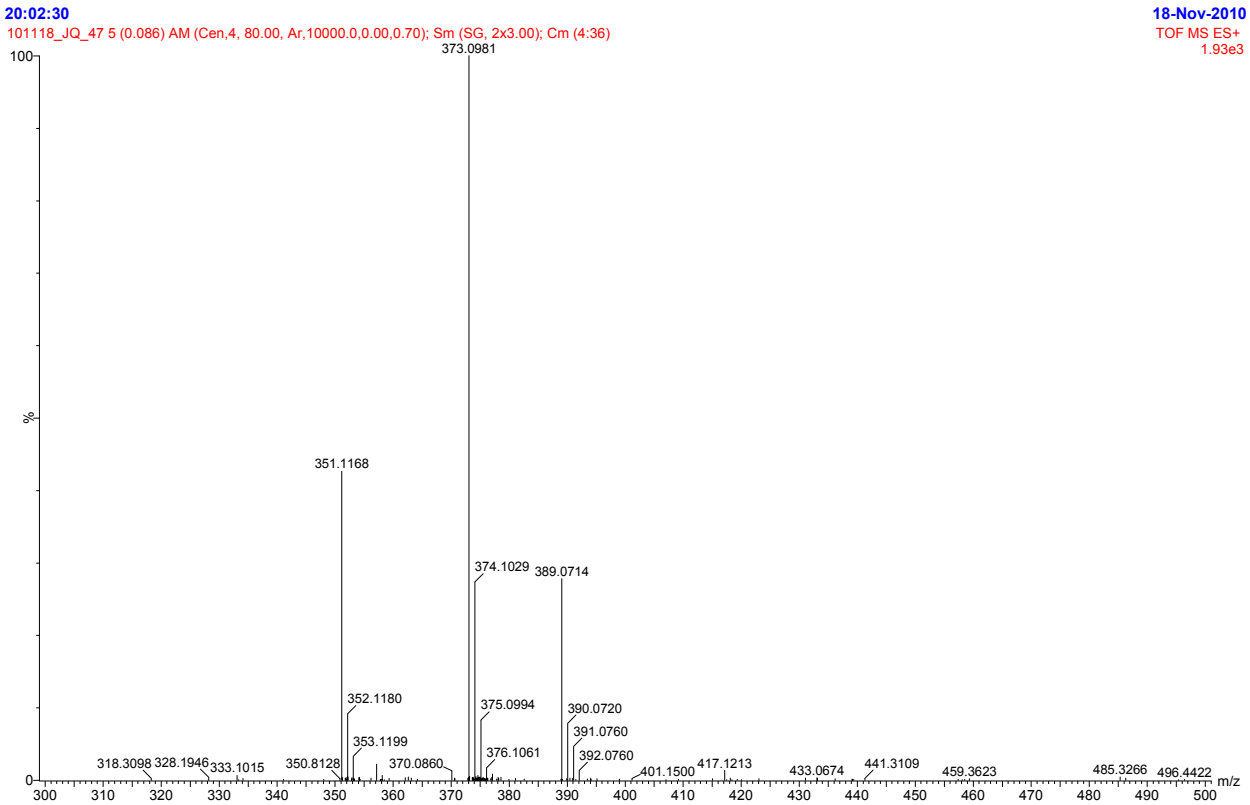


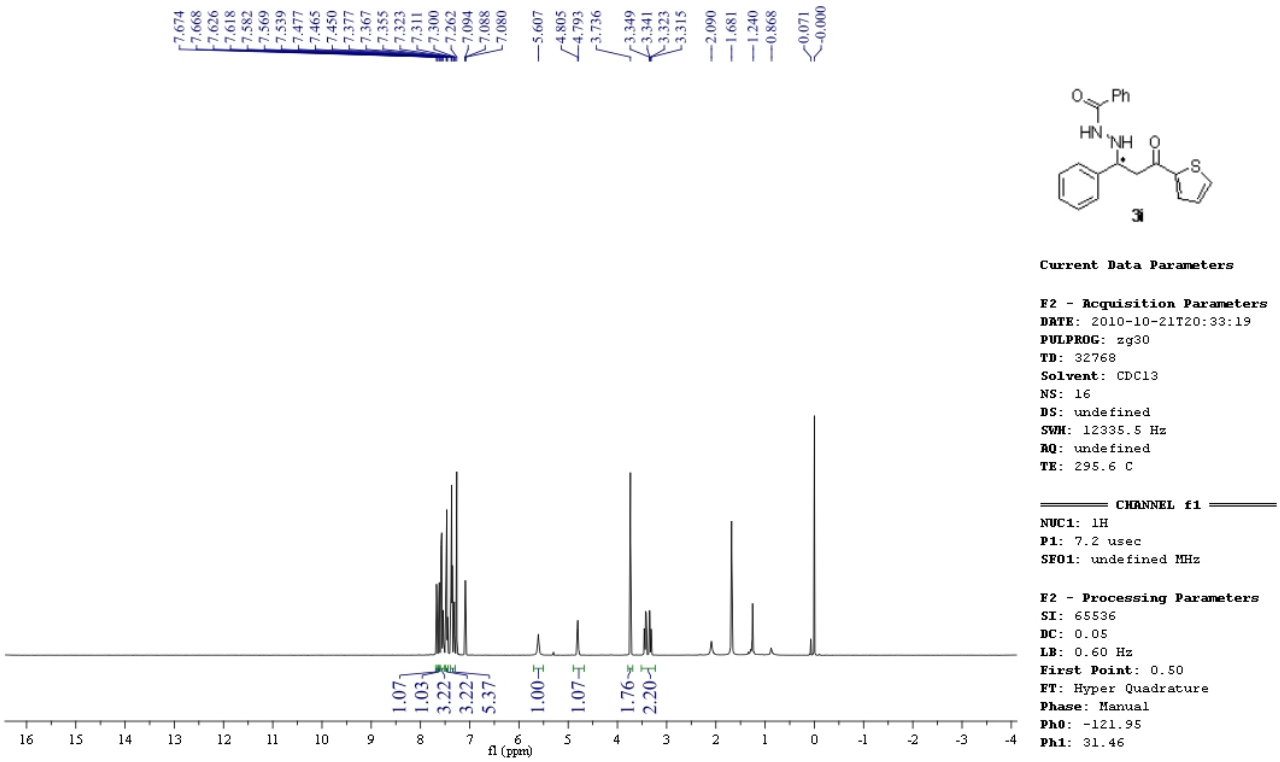
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.1 Hz, 2H), 7.62 – 7.54 (m, 3H), 7.46 (dd, *J* = 15.3, 7.4 Hz, 3H), 7.34 (ddt, *J* = 15.6, 13.4, 6.8 Hz, 7H), 4.81 (dd, *J* = 8.0, 4.9 Hz, 1H), 3.72 (s, 1H), 3.45 (ddd, *J* = 21.7, 16.8, 6.5 Hz, 2H), 2.37 (s, 3H).



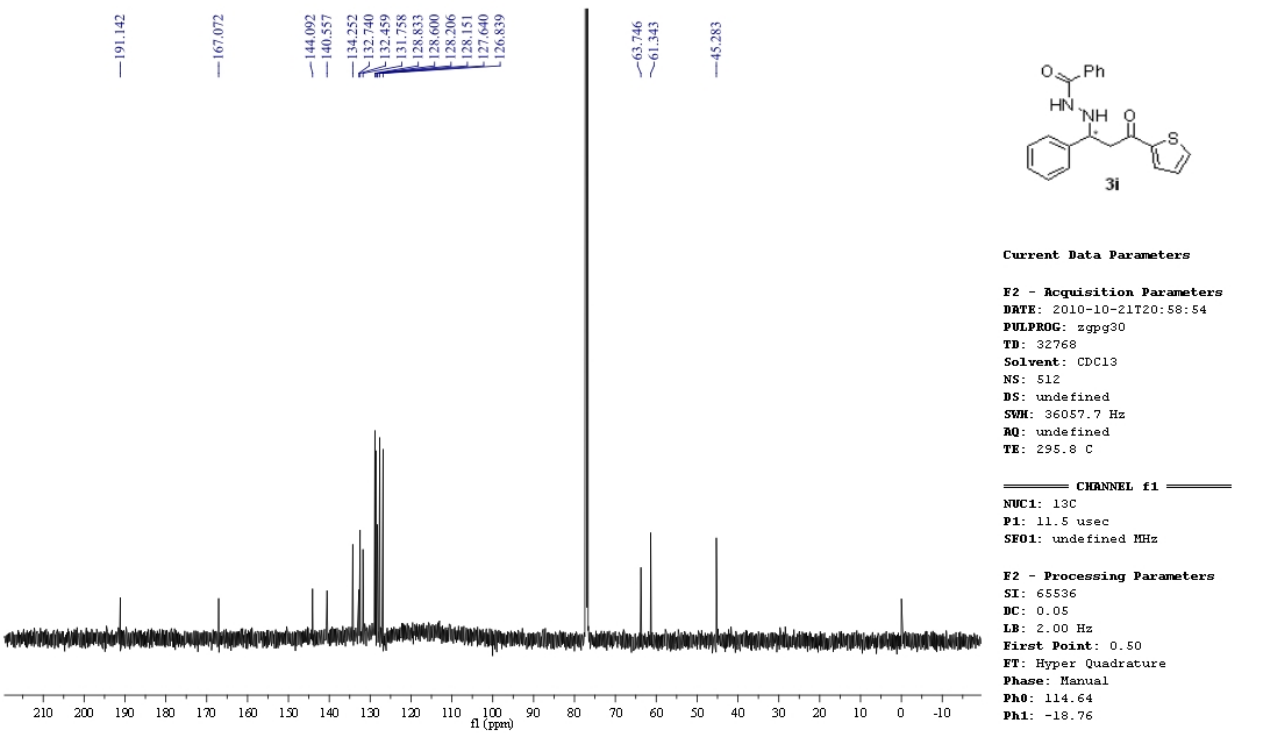
δ_C (151 MHz, $CDCl_3$) 198.53, 167.00, 140.83, 138.44, 136.70, 134.12, 132.81, 131.71, 128.80, 128.77, 128.58, 128.51, 128.05, 127.73, 126.85, 125.45, 63.76, 60.98, 44.42, 29.70.

9) Product 3i:


20:02:30
18-Nov-2010
101118_JQ_47 5 (0.086) AM (Cen,4, 80.00, Ar,10000.0,0.00,0.70); Sm (SG, 2x3.00); Cm (4:36)
TOF MS ES+
1.93e3
100
%
0
373.0981
351.1168
374.1029
389.0714
352.1180
375.0994
390.0720
391.0760
353.1199
376.1061
392.0760
318.3098
328.1946
333.1015
350.8128
370.0860
401.1500
417.1213
433.0674
441.3109
459.3623
485.3266
496.4422
300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500
m/z

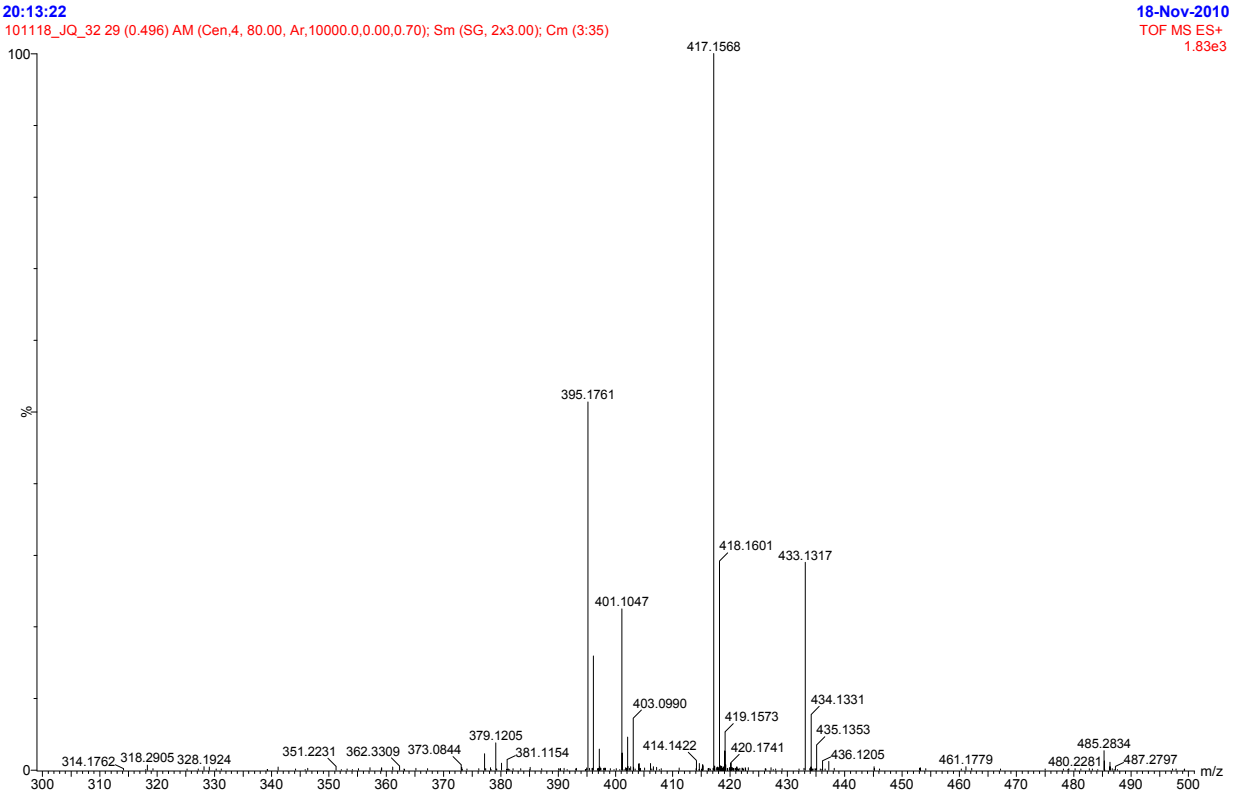


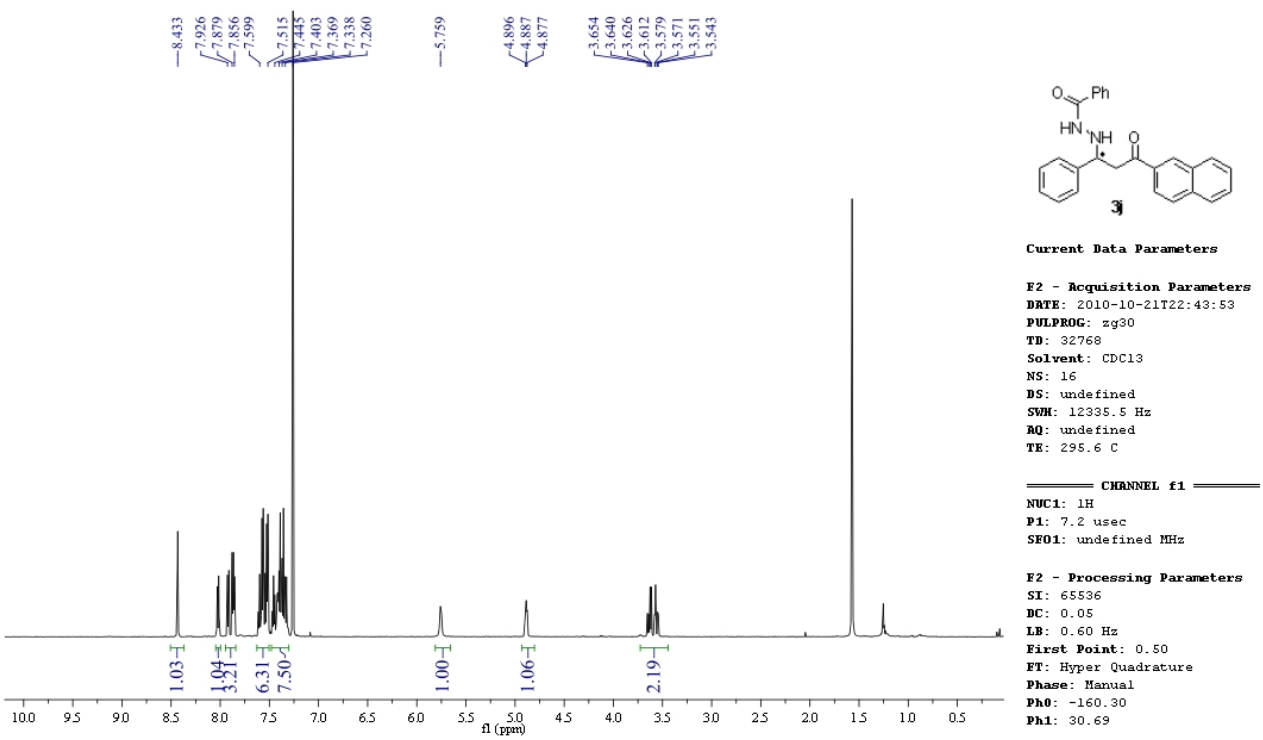
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 3.7 Hz, 1H), 7.62 (d, *J* = 4.9 Hz, 1H), 7.56 (t, *J* = 12.9 Hz, 3H), 7.46 (t, *J* = 8.0 Hz, 3H), 7.34 (dt, *J* = 13.9, 6.4 Hz, 5H), 5.61 (s, 1H), 4.80 (dd, *J* = 7.7, 5.1 Hz, 1H), 3.74 (s, 2H), 3.38 (ddd, *J* = 20.8, 15.9, 6.5 Hz, 2H).



δ_C (151 MHz, $CDCl_3$) 191.14, 167.07, 144.09, 140.56, 134.25, 132.74, 132.46, 131.76, 128.83, 128.60, 128.21, 128.15, 127.64, 126.84, 63.75, 61.34, 45.28.

10) Product 3j:





3j

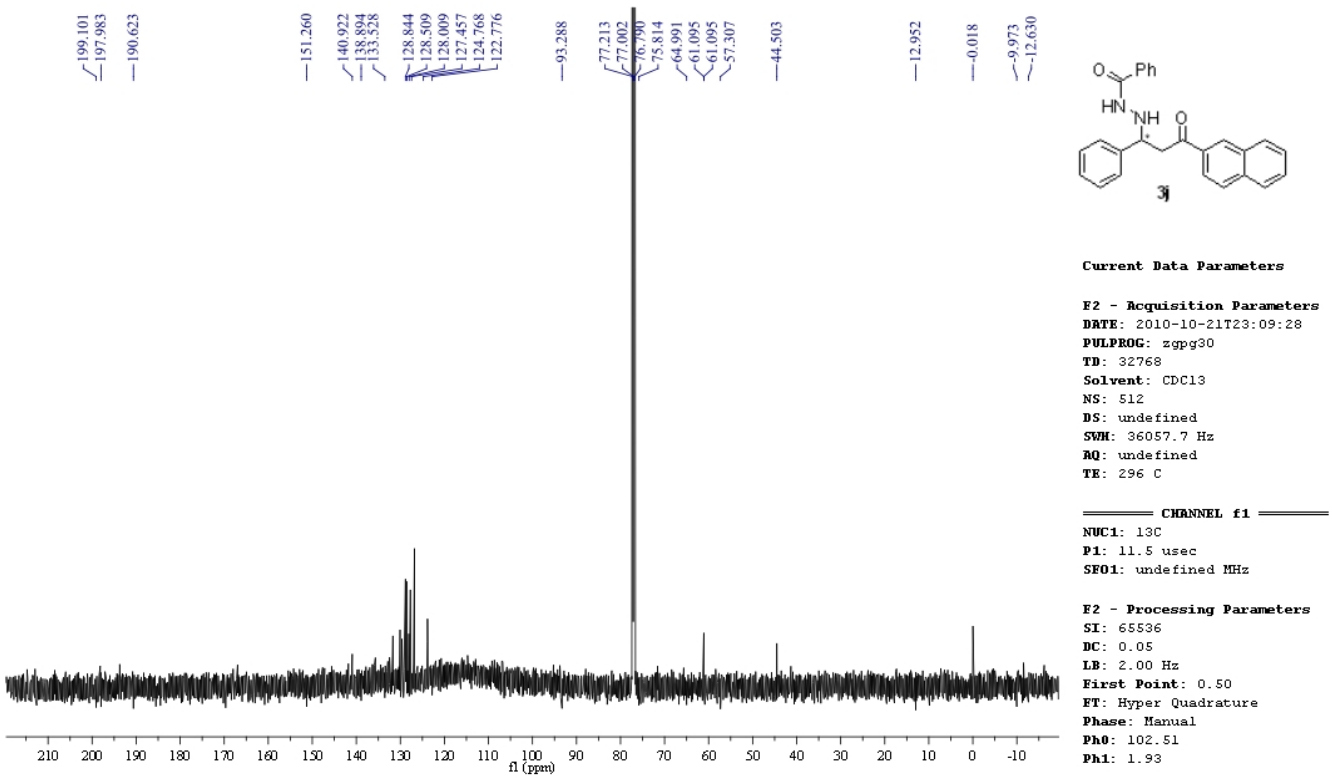
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-10-21T22:43:53
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.6 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

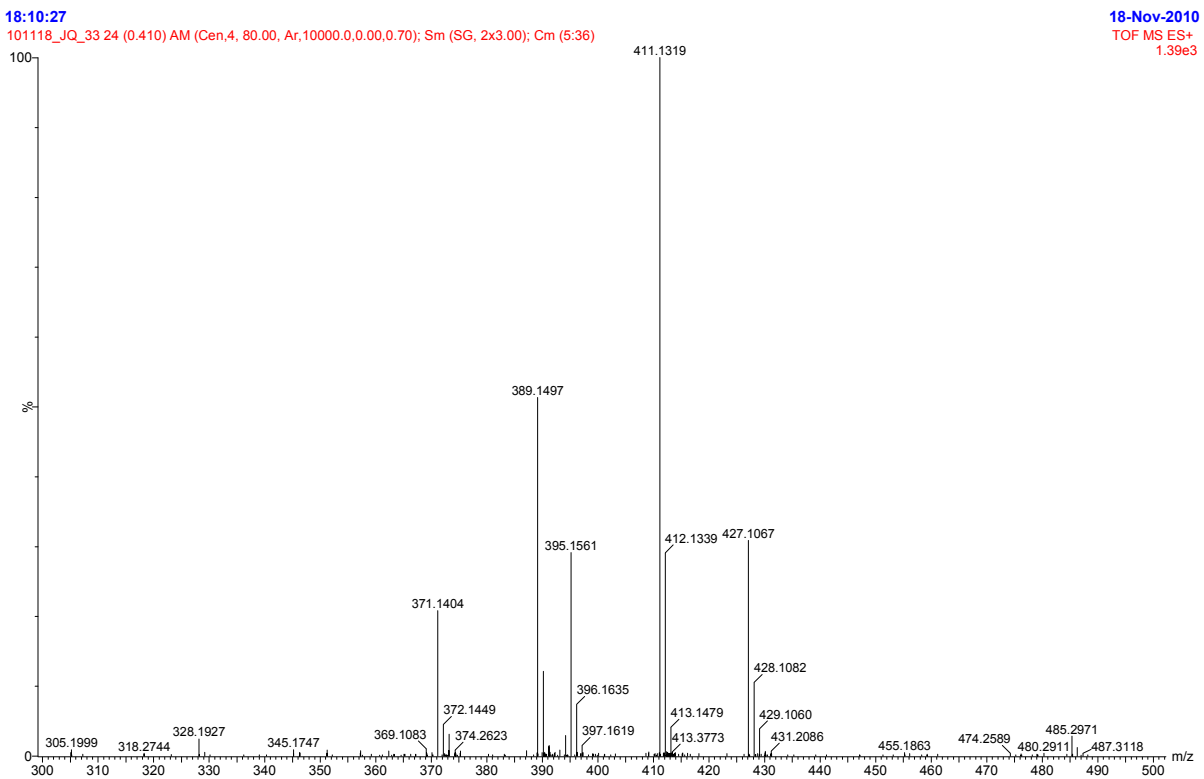
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -160.30
Ph1: 30.69

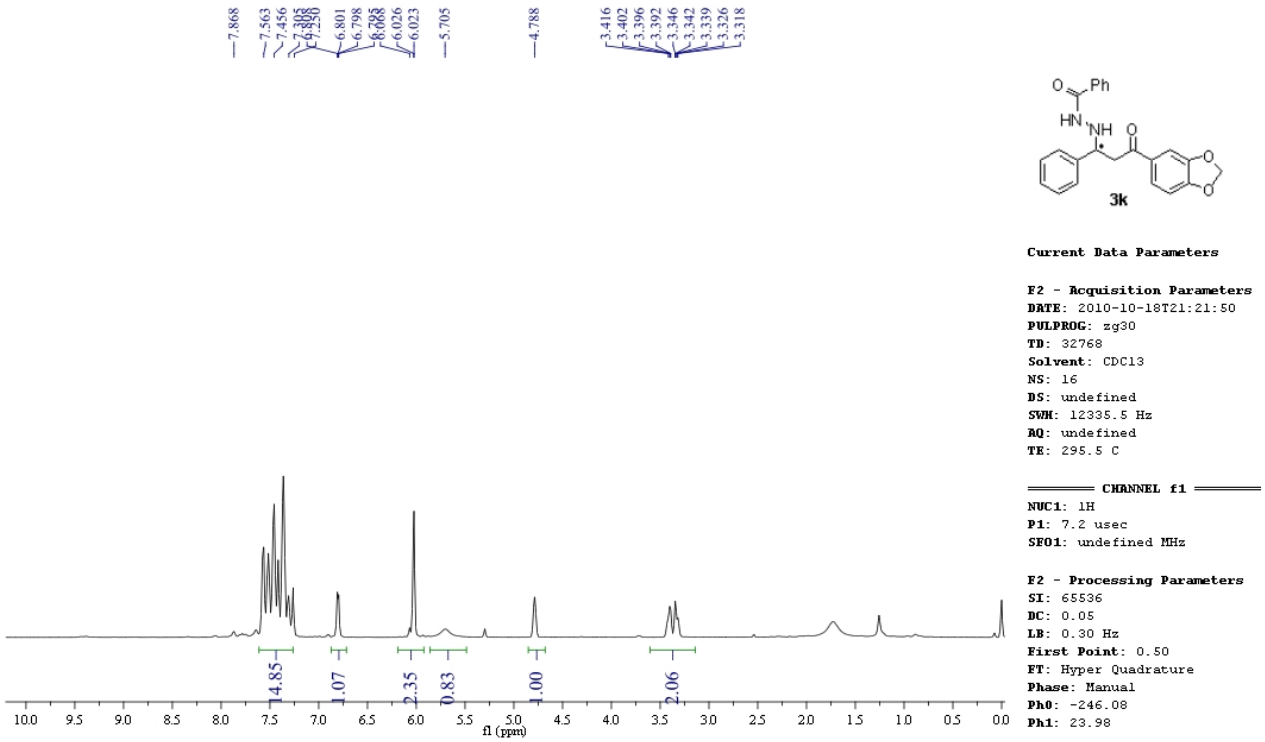
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.02 (d, J = 8.6 Hz, 1H), 7.95 – 7.84 (m, 3H), 7.63 – 7.50 (m, 6H), 7.39 (dtt, J = 18.4, 14.8, 7.4 Hz, 8H), 5.76 (s, 1H), 4.93 – 4.80 (m, 1H), 3.60 (ddd, J = 21.4, 16.6, 6.5 Hz, 2H).



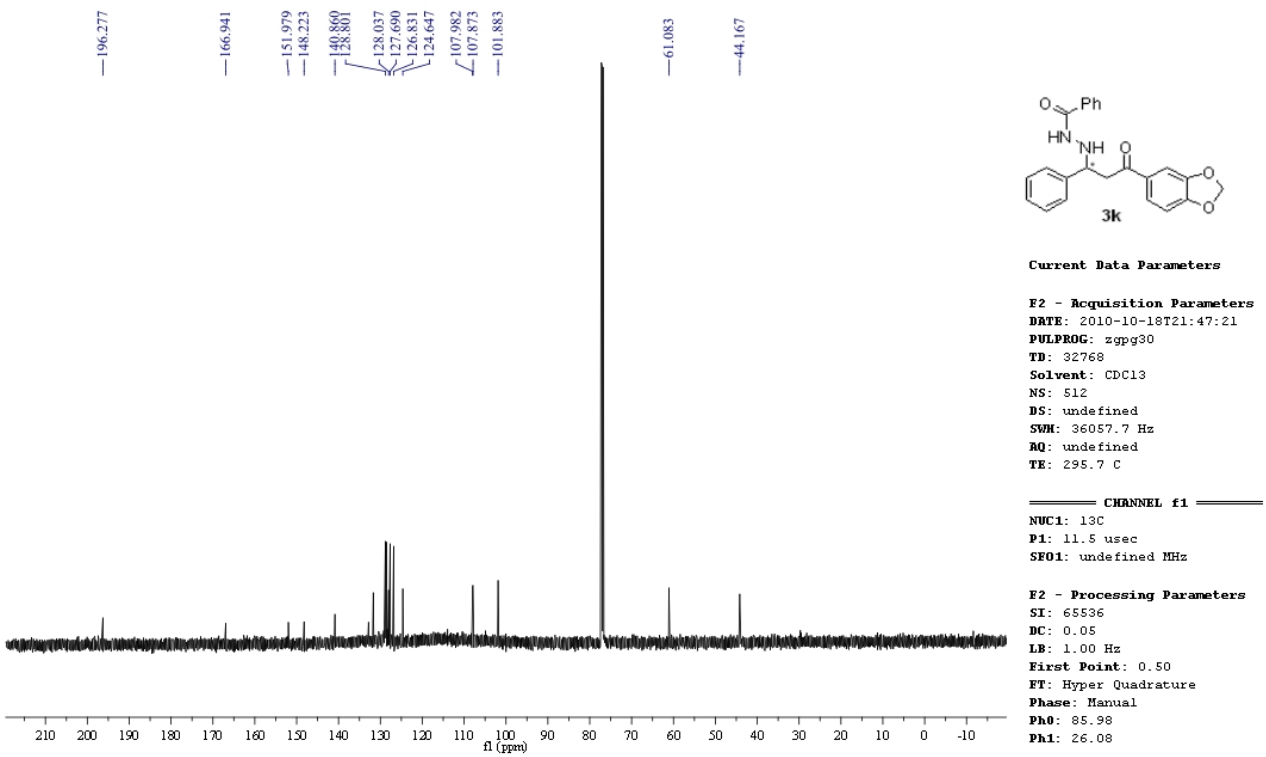
δ_C (151 MHz, $CDCl_3$) 199.10, 197.98, 190.62, 151.26, 140.92, 138.89, 133.53, 131.70, 131.70, 131.32, 130.07, 130.07, 129.95, 129.63, 129.30, 128.84, 128.84, 128.58, 128.58, 128.51, 128.07, 128.07, 128.01, 127.73, 127.73, 127.46, 126.81, 126.81, 124.77, 123.83, 123.83, 122.78, 93.29, 77.21, 77.00, 76.79, 75.81, 64.99, 61.10, 61.10, 57.31, 44.50, 12.95, -0.02, -9.97, -12.63.

11) Product 3k:



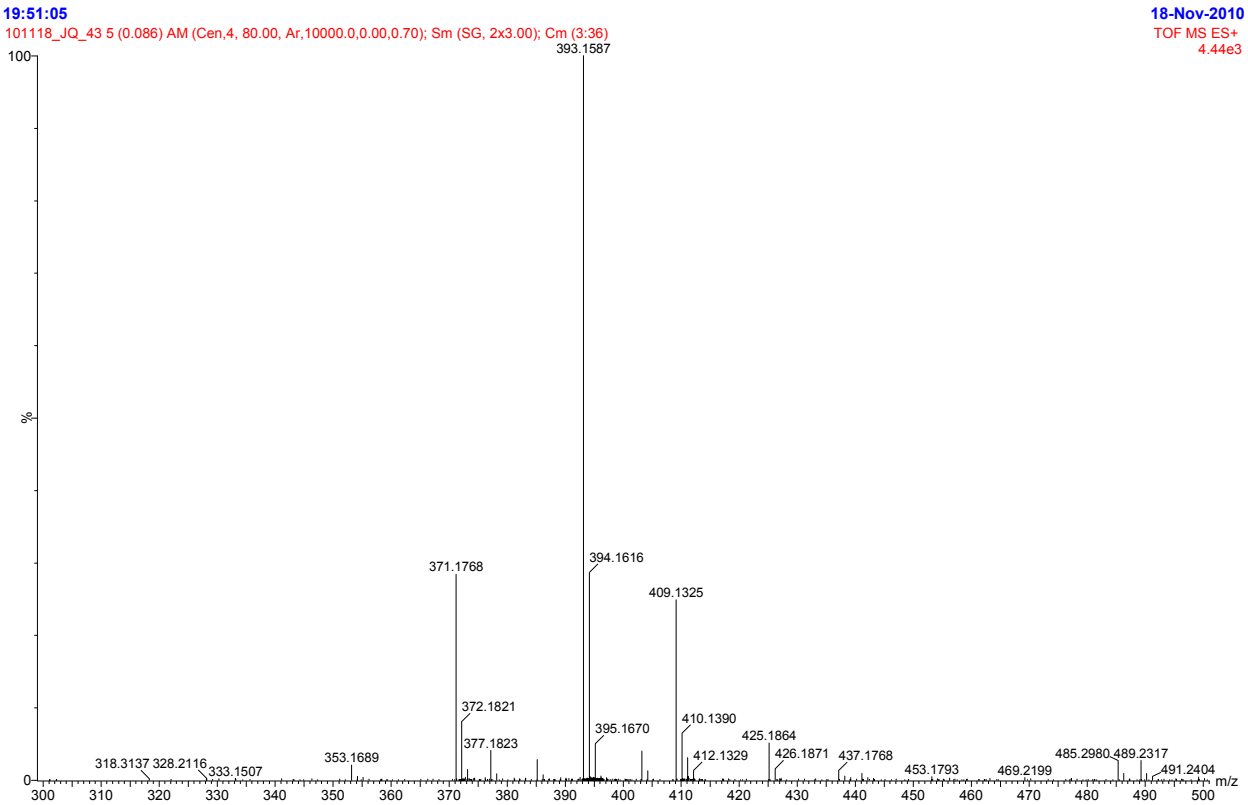


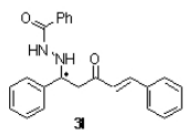
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (dddd, J = 58.6, 26.1, 14.0, 1.9 Hz, 15H), 6.87 – 6.72 (m, 1H), 6.05 (dd, J = 26.7, 1.7 Hz, 2H), 5.71 (s, 1H), 4.79 (s, 1H), 3.60 – 3.14 (m, 2H).



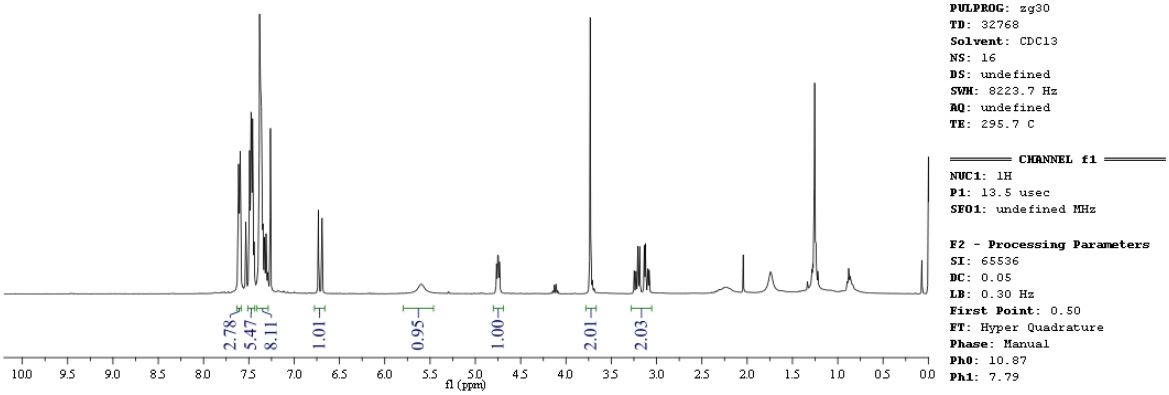
δ_C (151 MHz, $CDCl_3$) 196.28, 166.94, 151.98, 148.22, 140.86, 132.84, 131.70, 128.80, 128.58, 128.04, 127.69, 126.83, 124.65, 107.98, 107.87, 101.88, 61.08, 44.17.

12) Product 3l:



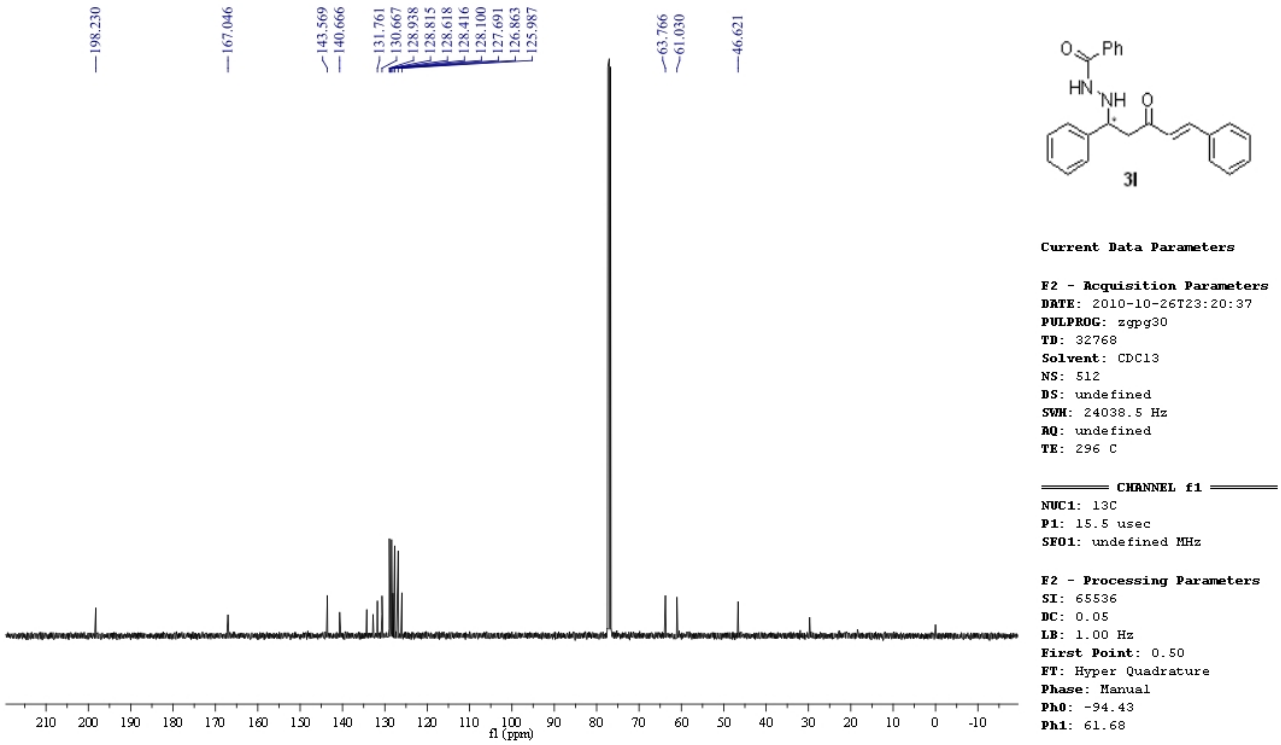


3l



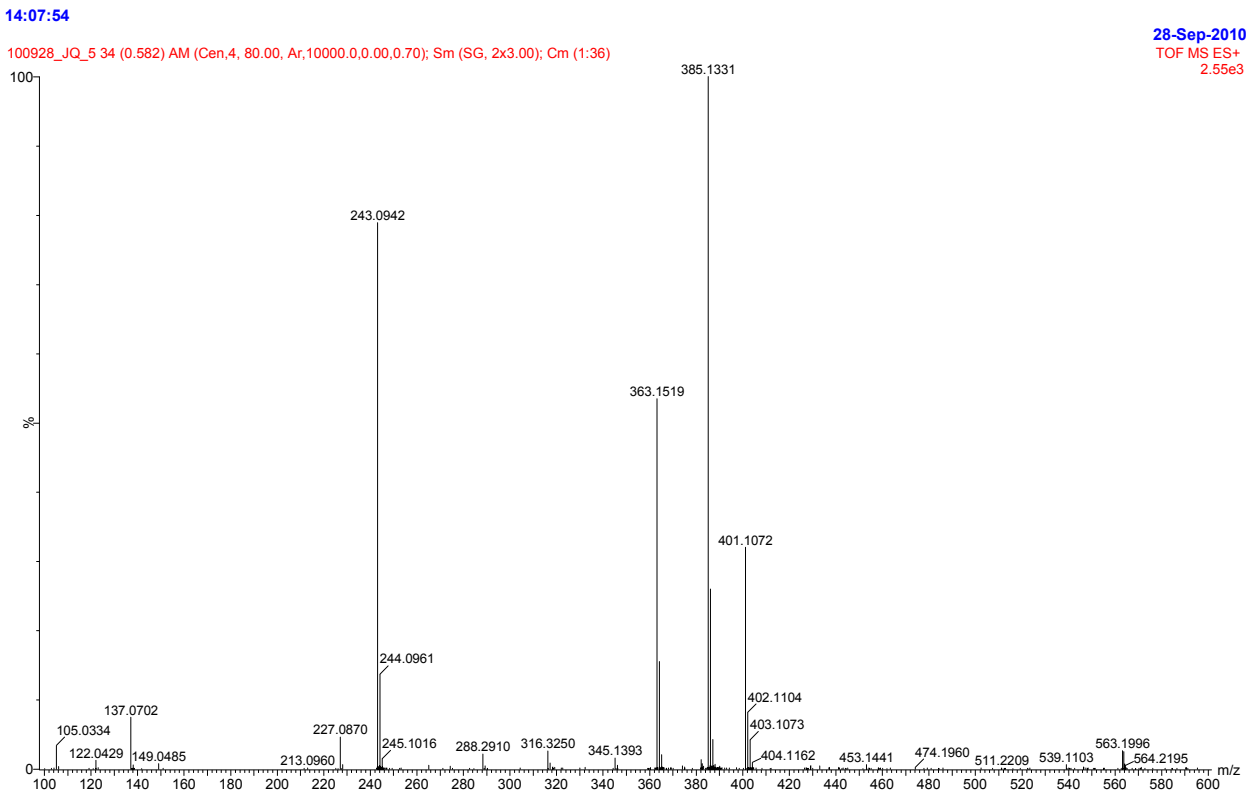

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-10-26T22:51:13
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.7 C

CHANNEL f1
NUC1: 1H
P1: 13.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 10.87
Ph1: 7.79
```

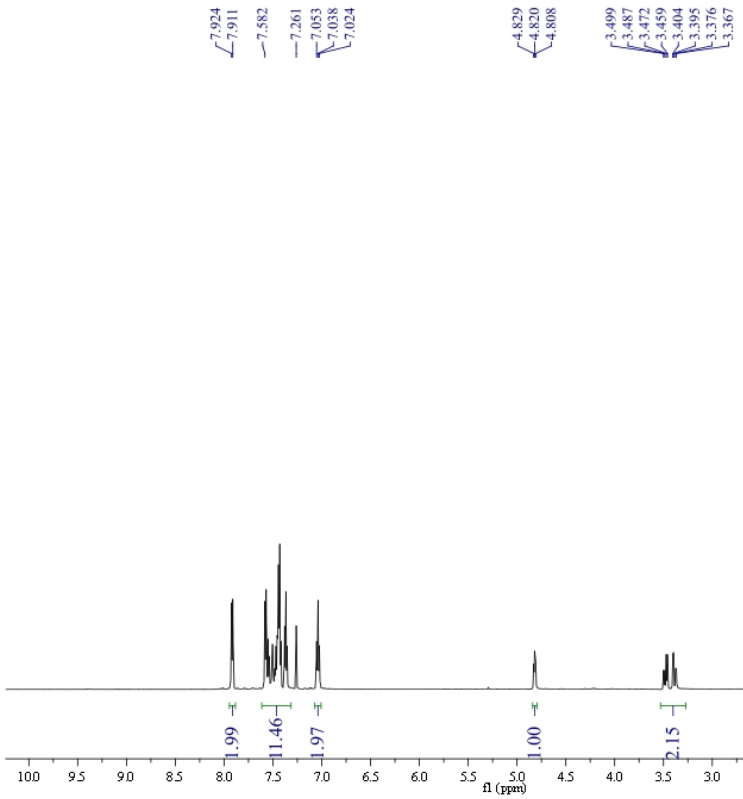
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.2 Hz, 3H), 7.51 – 7.43 (m, 5H), 7.41 – 7.29 (m, 8H), 6.71 (d, J = 16.1 Hz, 1H), 5.60 (s, 1H), 4.75 (dd, J = 7.8, 5.3 Hz, 1H), 3.73 (s, 2H), 3.16 (ddd, J = 21.3, 16.1, 6.6 Hz, 2H).

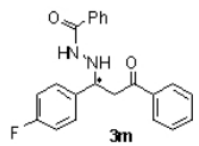


δ_C (101 MHz, $CDCl_3$) 198.23, 167.05, 143.57, 140.67, 134.27, 132.78, 131.76, 130.67, 128.94, 128.81, 128.62, 128.42, 128.10, 127.69, 126.86, 125.99, 63.77, 61.03, 46.62.

13) Product 3m:







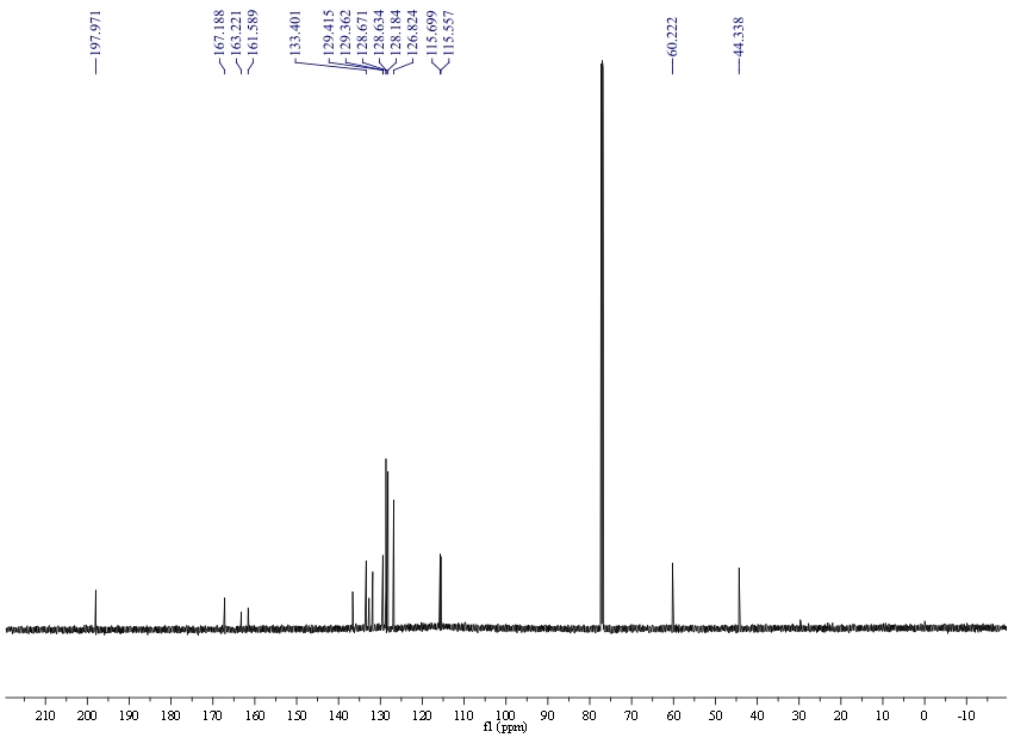
Current Data Parameters

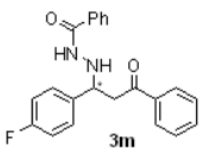
F2 - Acquisition Parameters
DATE: 2010-07-28T16:38:42
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 297.4 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -279.72
Ph1: 12.69

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.61 – 7.31 (m, 11H), 7.04 (t, *J* = 8.6 Hz, 2H), 4.84 – 4.80 (m, 1H), 3.43 (ddd, *J* = 22.1, 16.8, 6.5 Hz, 2H).





Current Data Parameters

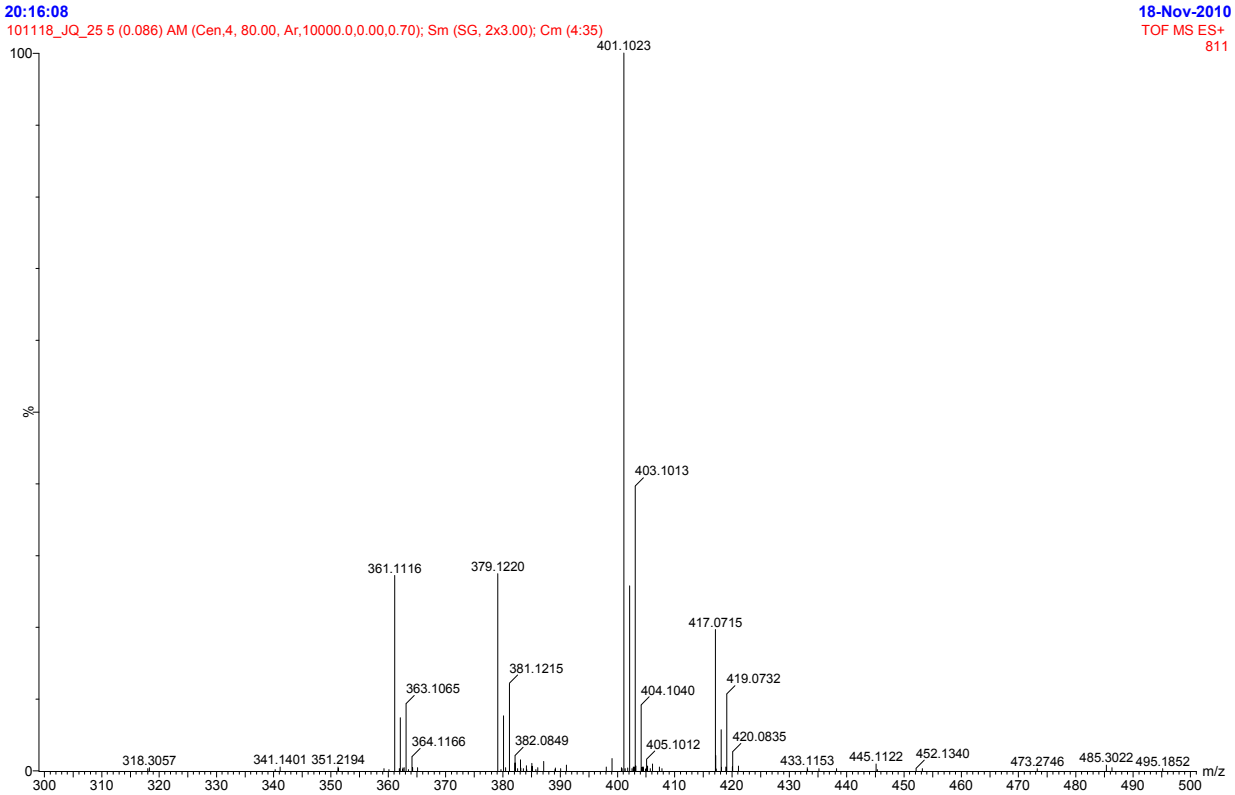
F2 - Acquisition Parameters
DATE: 2010-07-28T16:55:13
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 298 C

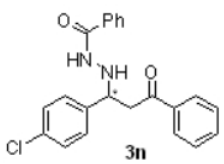
CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

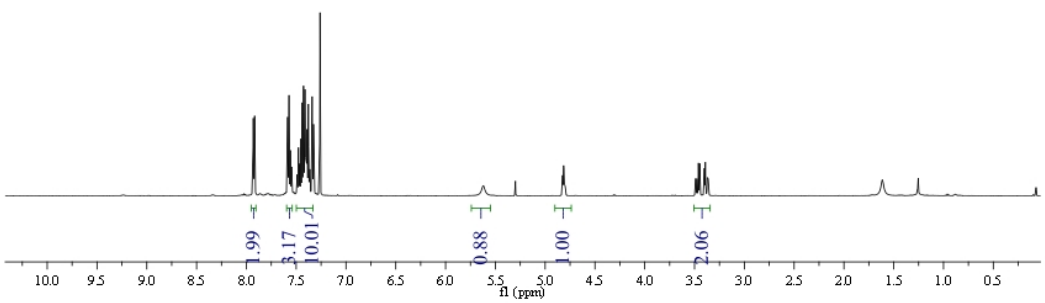
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 80.43
Ph1: 38.75

δ_C (151 MHz, $CDCl_3$) 197.97, 167.19, 163.22, 161.59, 136.63, 136.59, 133.40, 132.70, 131.82, 129.42, 129.36, 128.67, 128.63, 128.18, 126.82, 115.70, 115.56, 60.22, 44.34.

14) Product 3n:







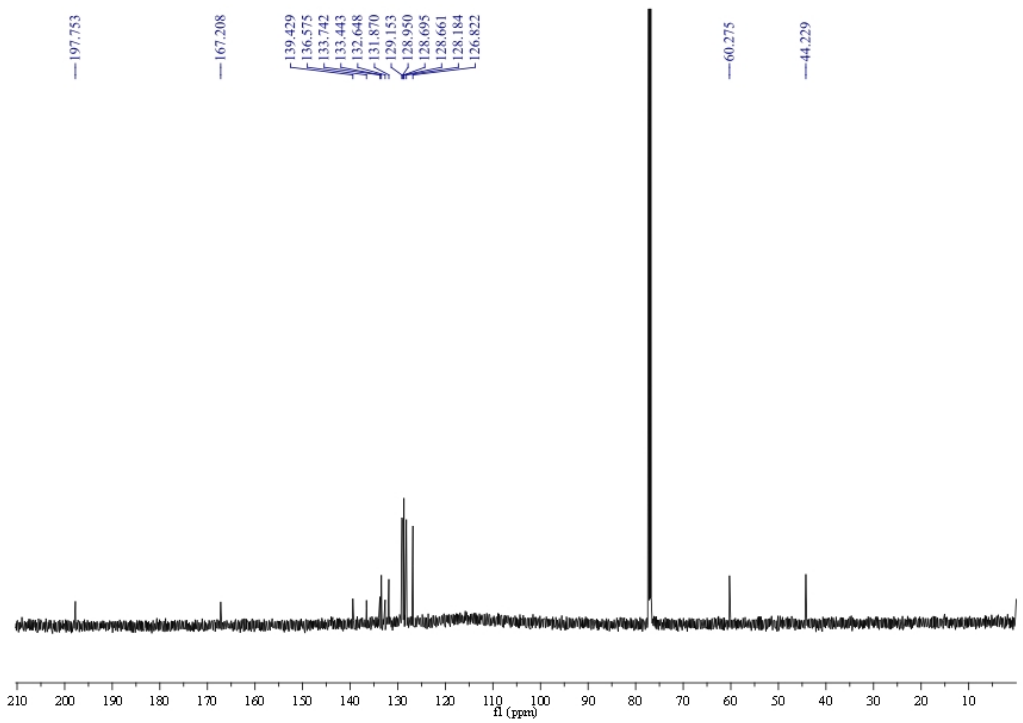
Current Data Parameters

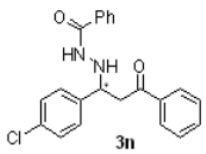
F2 - Acquisition Parameters
DATE: 2010-10-21T18:15:48
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.7 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.60 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -163.88
Ph1: 28.37

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, J = 7.9 Hz, 2H), 7.57 (dd, J = 15.9, 7.6 Hz, 3H), 7.50 – 7.33 (m, 10H), 5.62 (s, 1H), 4.90 – 4.74 (m, 1H), 3.42 (ddd, J = 22.2, 16.8, 6.5 Hz, 2H).





Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-10-21T18:41:23
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 295.9 C

CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 2.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 72.98
Ph1: 51.20

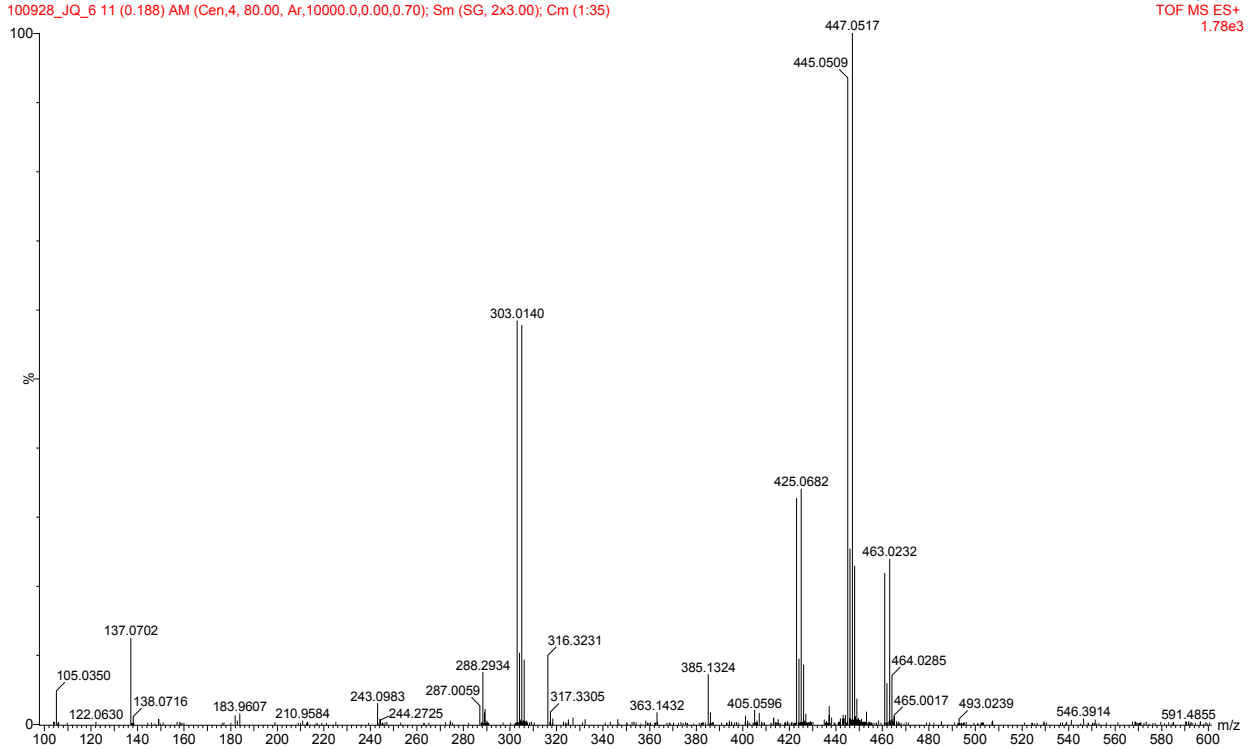
δ_C (151 MHz, $CDCl_3$) 197.75, 167.21, 139.43, 136.58, 133.74, 133.44, 132.65, 131.87, 129.15, 128.95, 128.69, 128.66, 128.18, 126.82, 60.27, 44.23.

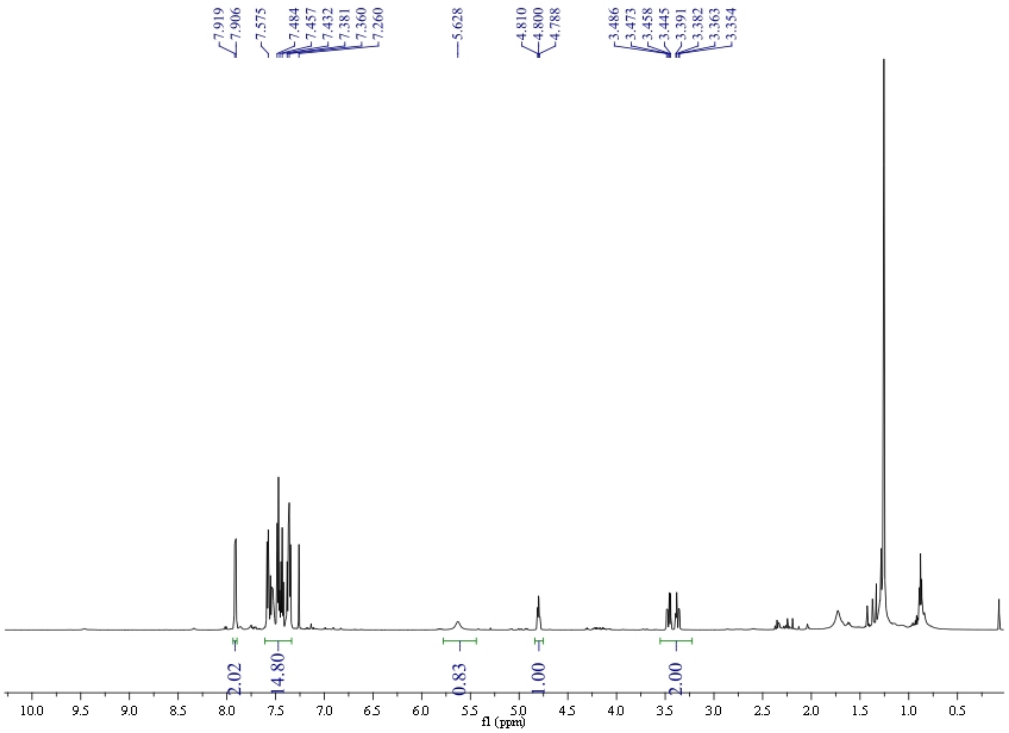
15) Product 3o:

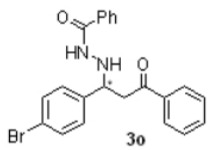
14:11:10

28-Sep-2010
TOF MS ES+
1.78e3

100928_JQ_6 11 (0.188) AM (Cen,4, 80.00, Ar,10000.0,0.00,0.70); Sm (SG, 2x3.00); Cm (1:35)







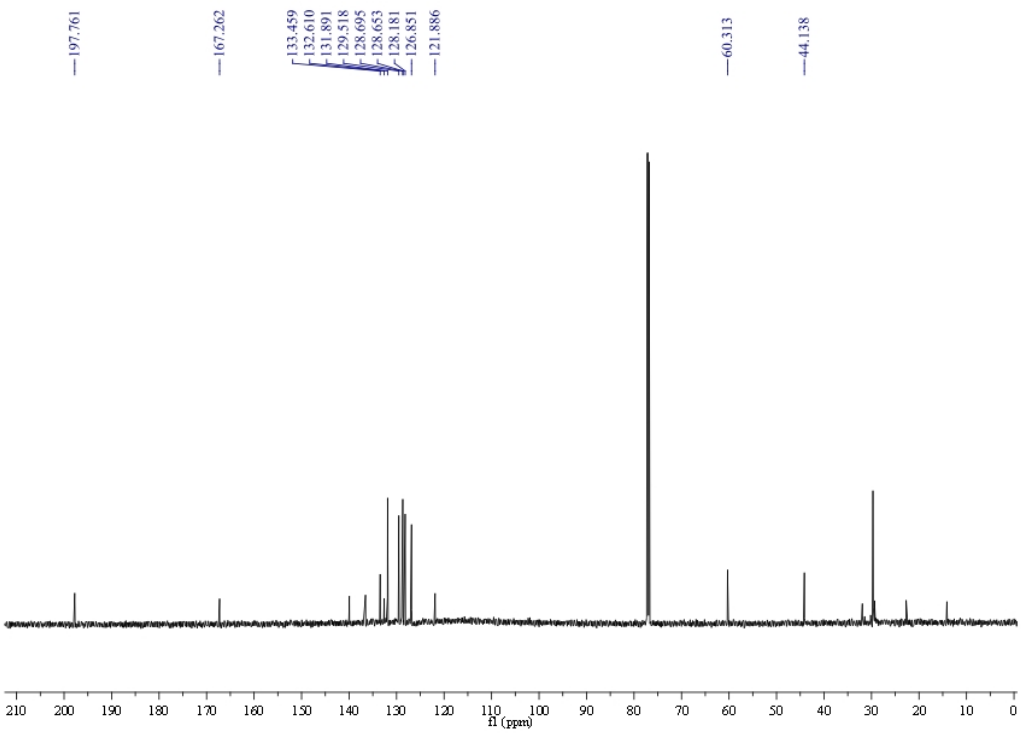
Current Data Parameters

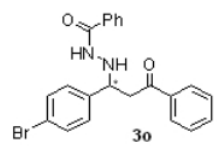
F2 - Acquisition Parameters
DATE: 2010-08-30T17:24:45
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.7 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -257.44
Ph1: 25.80

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, J = 7.9 Hz, 2H), 7.61 – 7.34 (m, 15H), 5.63 (s, 1H), 4.84 – 4.75 (m, 1H), 3.42 (ddd, J = 22.3, 16.9, 6.5 Hz, 2H).





Current Data Parameters

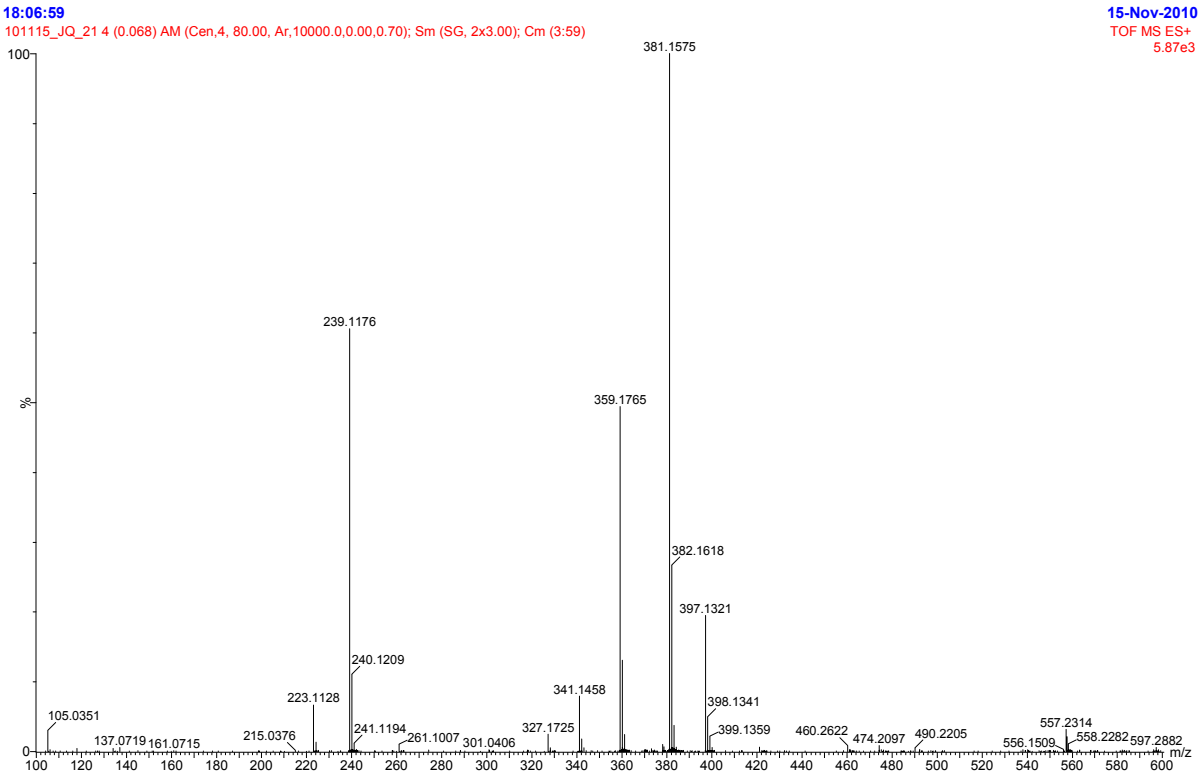
F2 - Acquisition Parameters
DATE: 2010-08-30T17:50:16
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 296 C

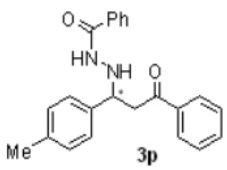
CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

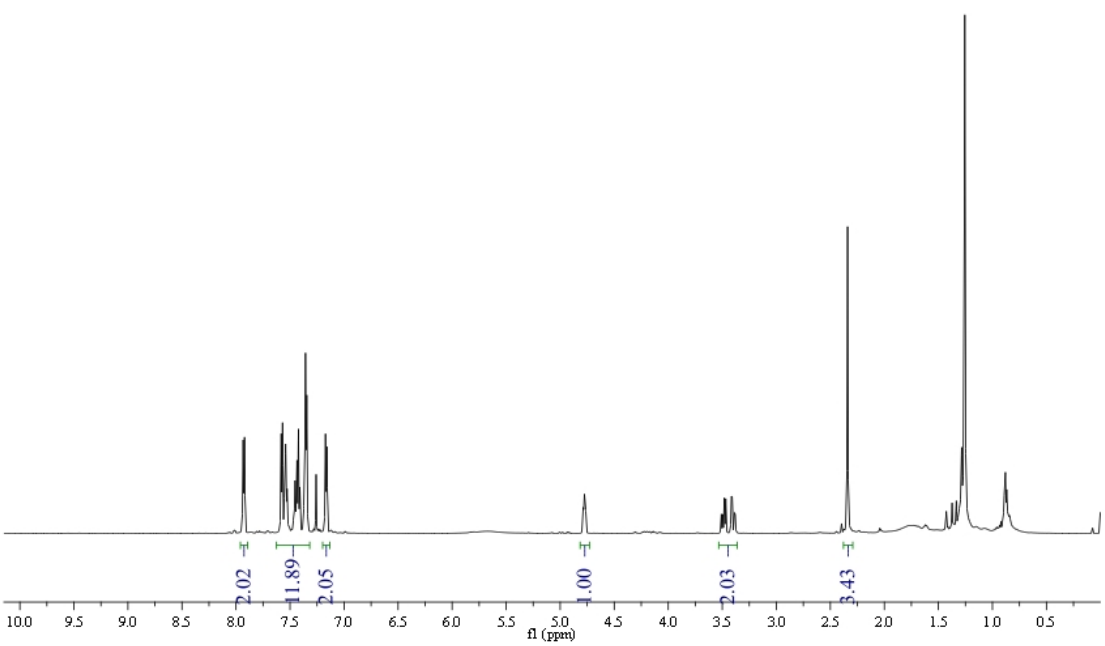
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 2.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 84.56
Ph1: 36.13

δ_C (151 MHz, $CDCl_3$) 197.76, 167.26, 139.93, 136.54, 133.46, 132.61, 131.89, 129.52, 128.69, 128.65, 128.18, 126.85, 121.89, 60.31, 44.14.

16) Product 3p:







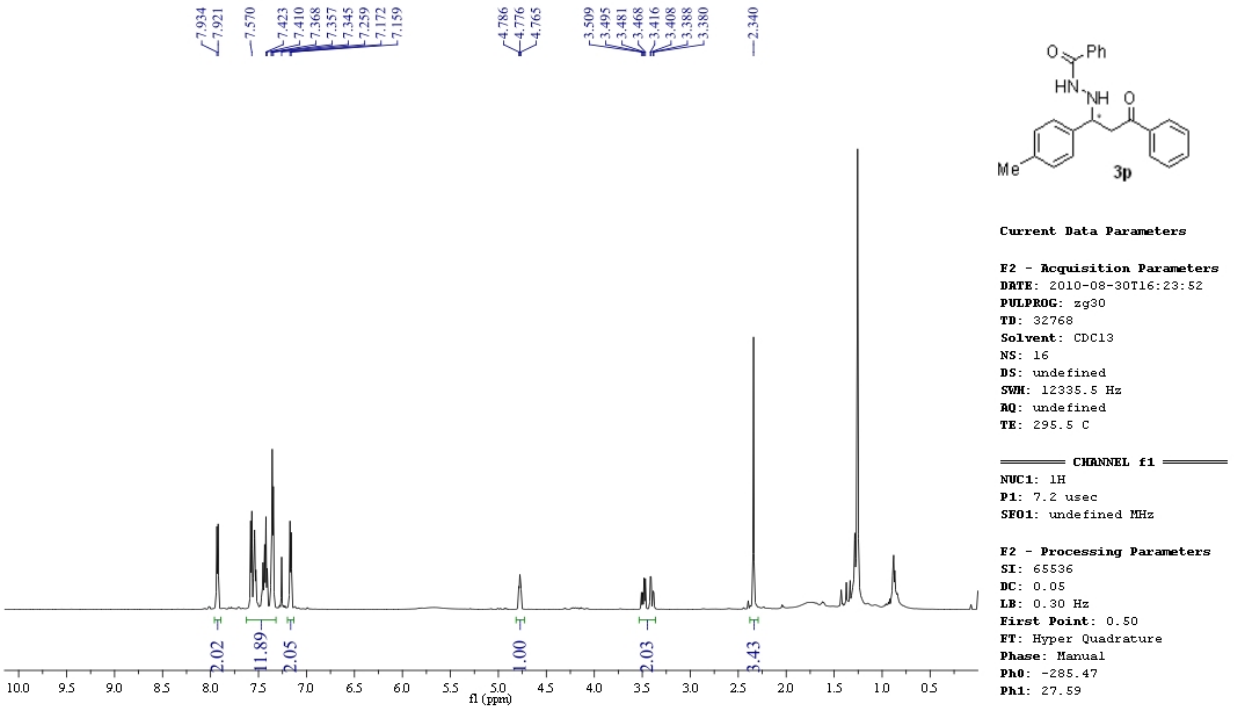
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-08-30T16:23:52
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.5 C

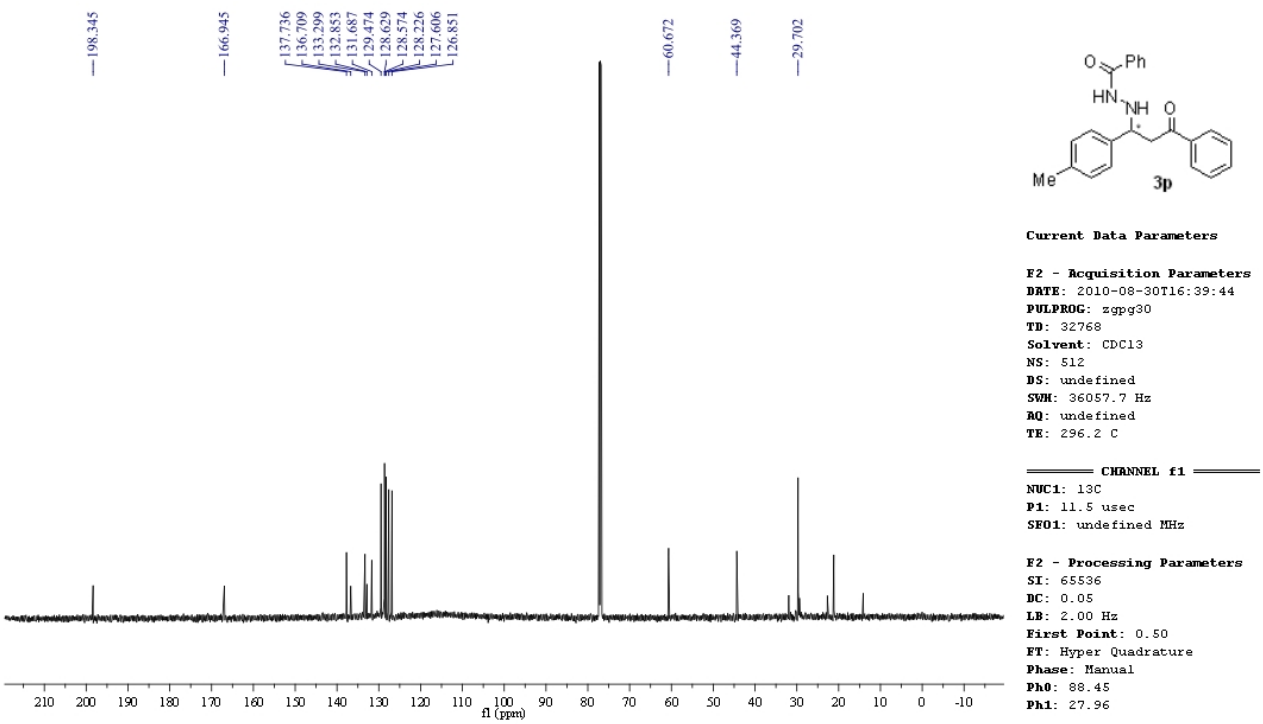
CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -285.47
Ph1: 27.59

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.63 – 7.32 (m, 12H), 7.17 (d, J = 7.5 Hz, 2H), 4.82 – 4.73 (m, 1H), 3.44 (ddd, J = 21.5, 16.8, 6.4 Hz, 2H), 2.34 (s, 3H).

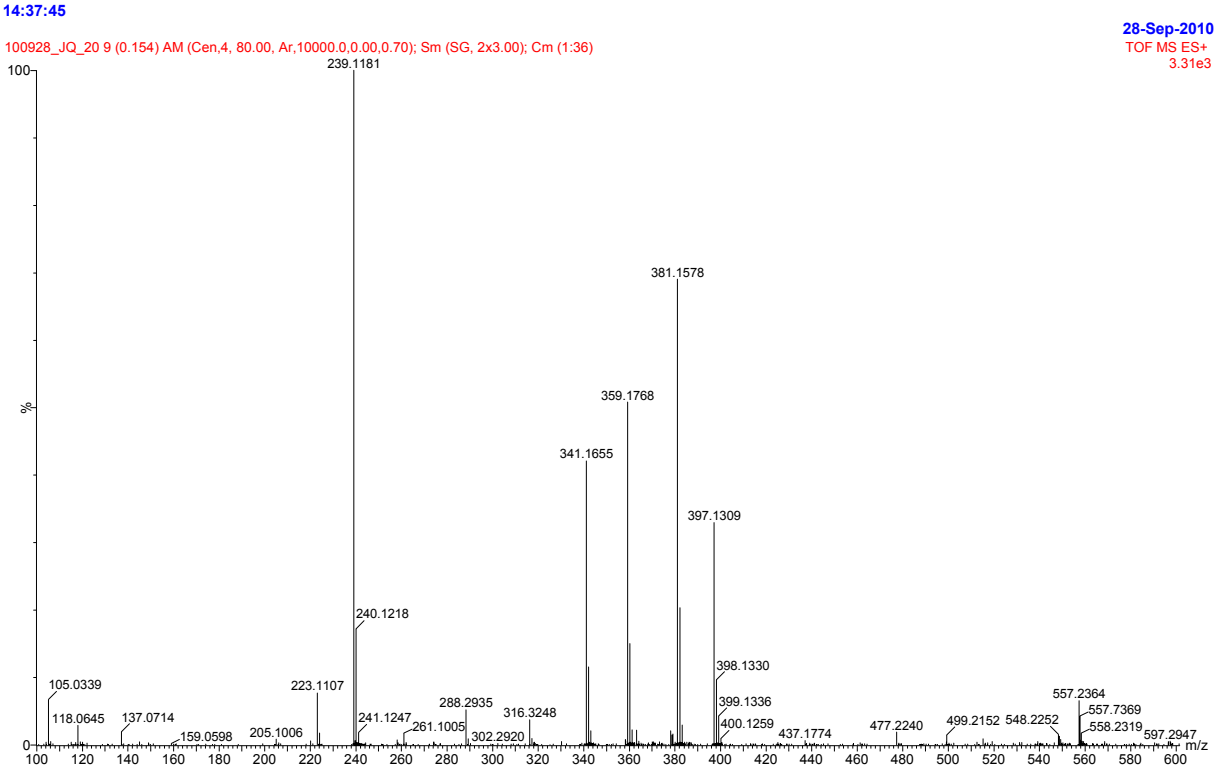


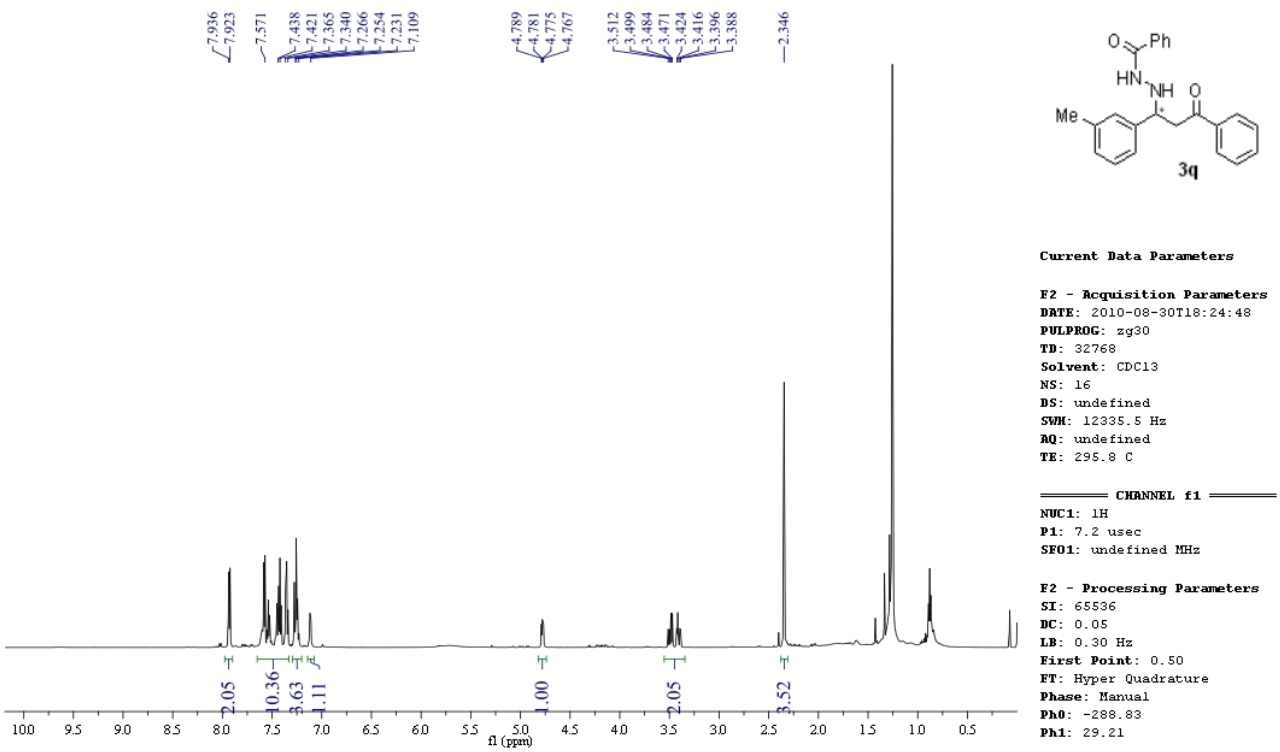
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.63 – 7.32 (m, 12H), 7.17 (d, *J* = 7.5 Hz, 2H), 4.82 – 4.73 (m, 1H), 3.44 (ddd, *J* = 21.5, 16.8, 6.4 Hz, 2H), 2.34 (s, 3H).



δ_C (151 MHz, $CDCl_3$) 198.35, 166.95, 137.74, 136.71, 133.30, 132.85, 131.69, 129.47, 128.63, 128.57, 128.23, 127.61, 126.85, 60.67, 44.37, 29.70.

17) Product 3q:





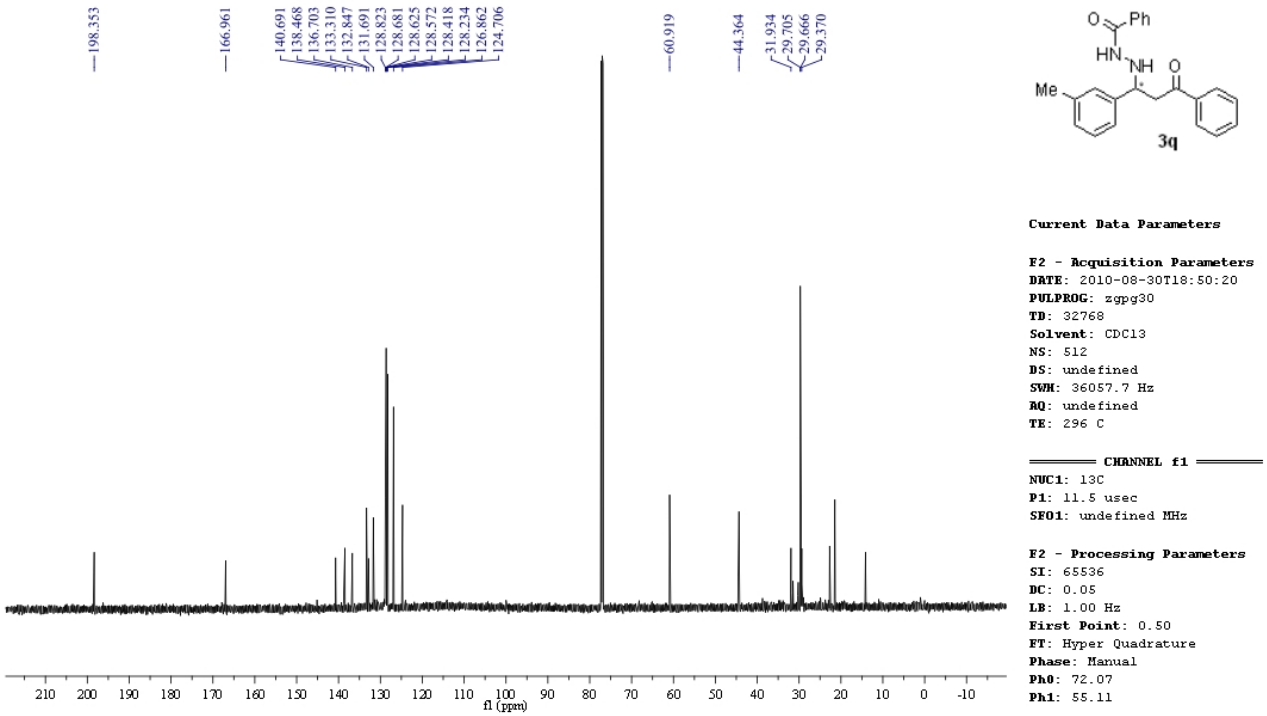
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-08-30T18:24:48
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.8 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

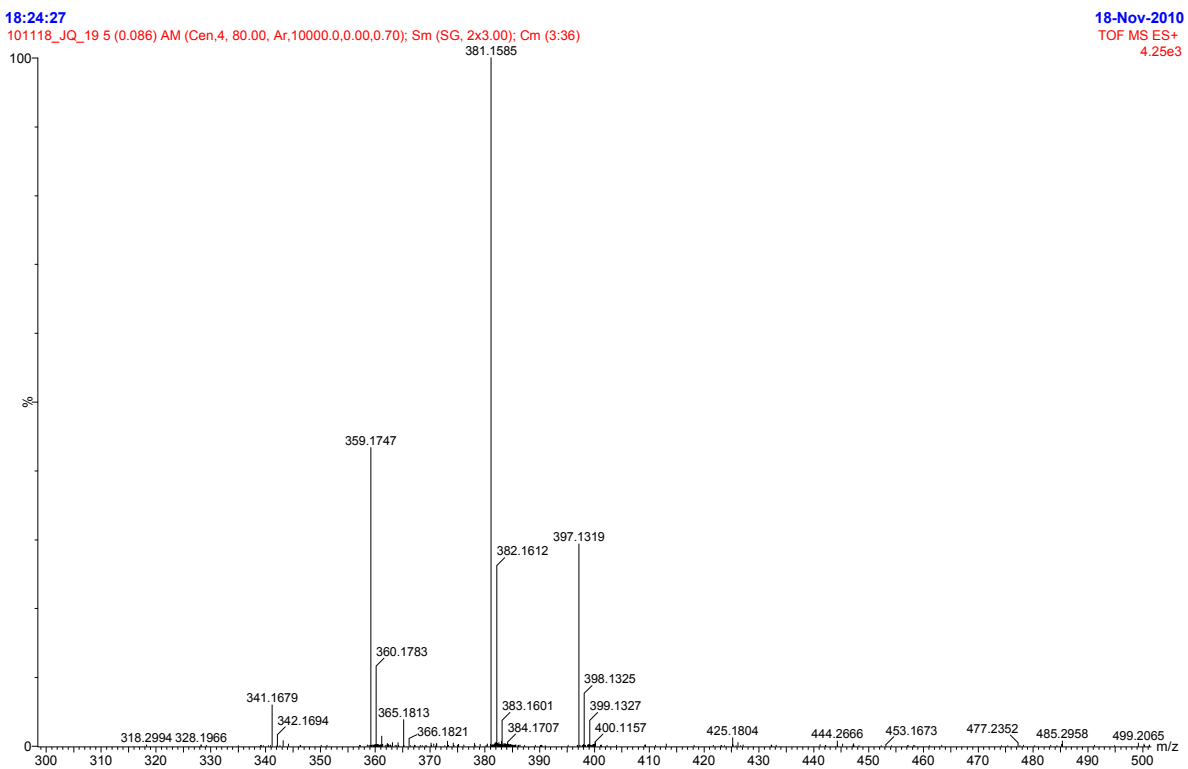
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -288.83
Ph1: 29.21

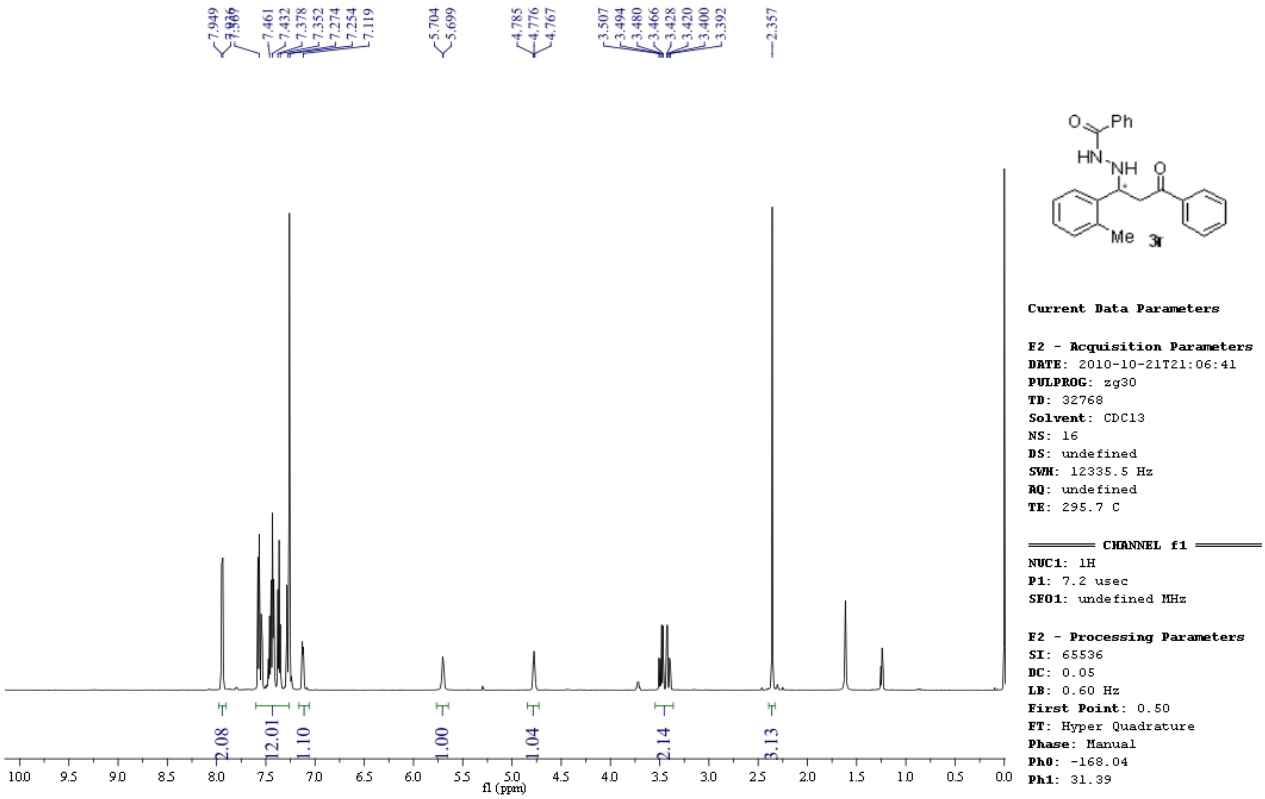
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.9 Hz, 2H), 7.65 – 7.33 (m, 10H), 7.30 – 7.20 (m, 4H), 7.11 (d, J = 6.3 Hz, 1H), 4.78 (dd, J = 8.0, 4.9 Hz, 1H), 3.45 (ddd, J = 21.7, 16.8, 6.5 Hz, 2H), 2.35 (s, 4H).



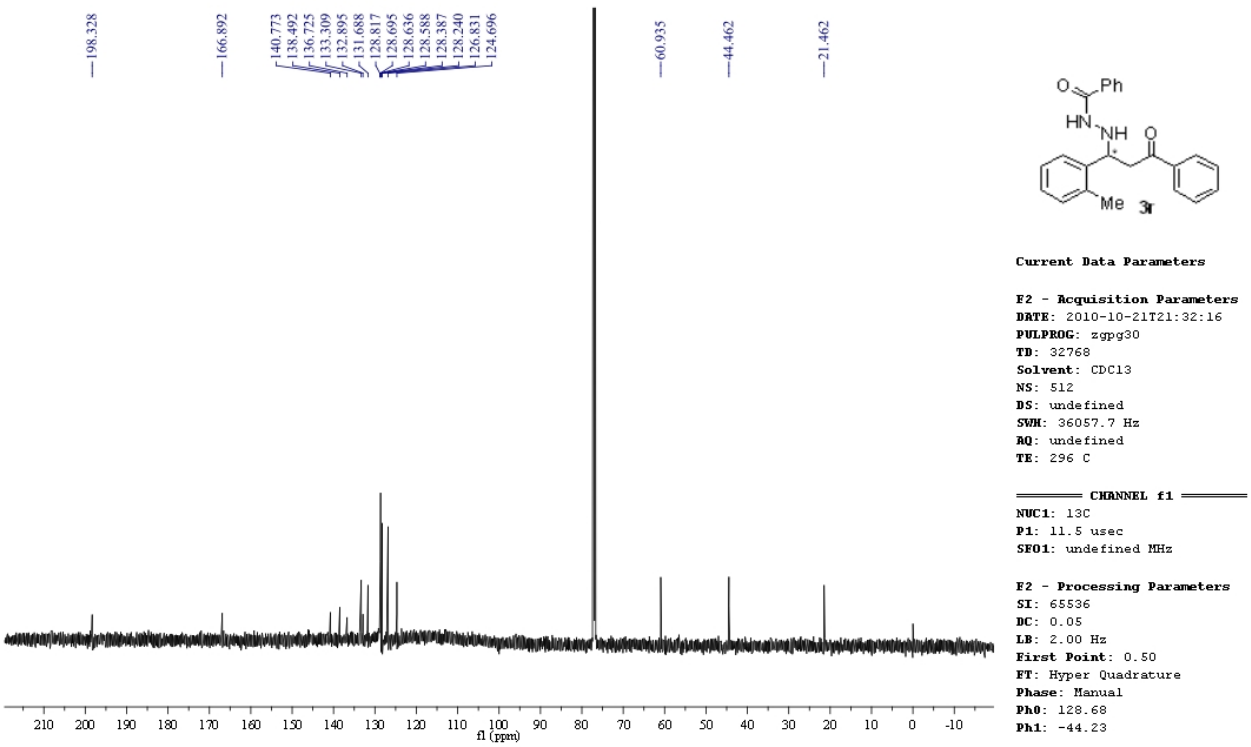
δ_C (151 MHz, $CDCl_3$) 198.35, 166.96, 140.69, 138.47, 136.70, 133.31, 132.85, 131.69, 128.82, 128.68, 128.63, 128.57, 128.42, 128.23, 126.86, 124.71, 60.92, 44.36, 31.93, 29.71, 29.67, 29.37.

18) Product 3r:



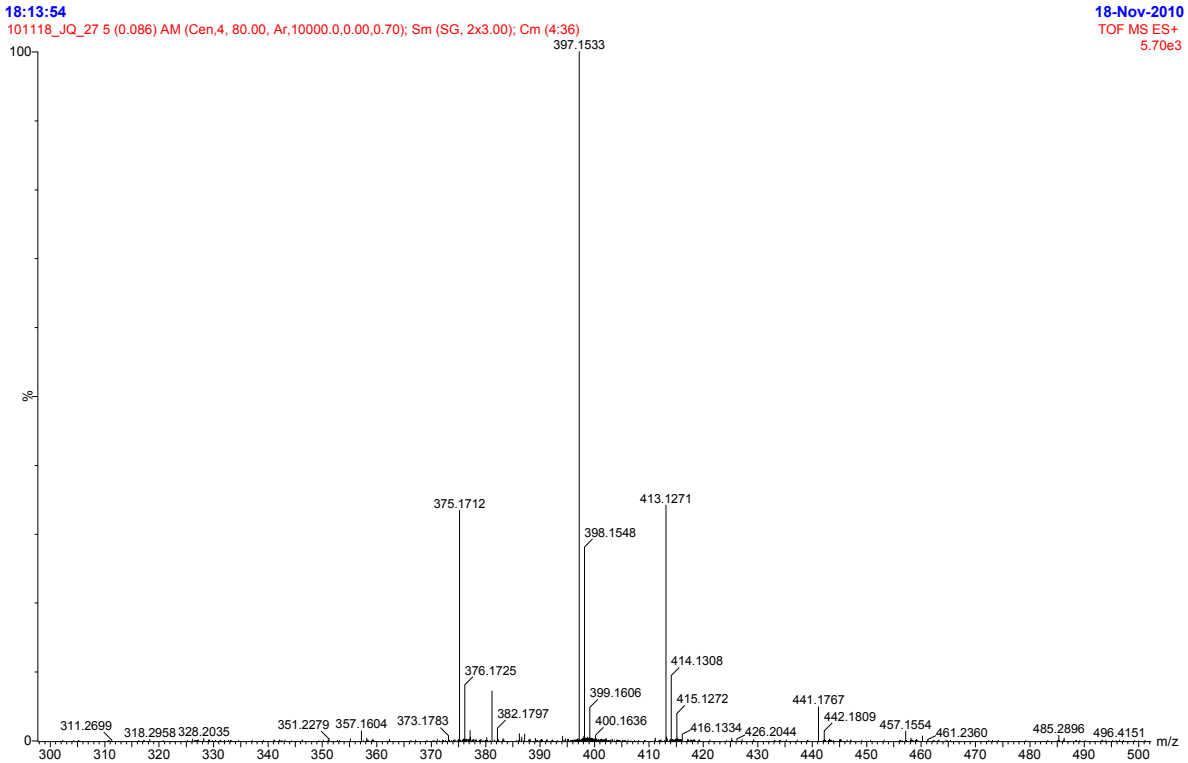


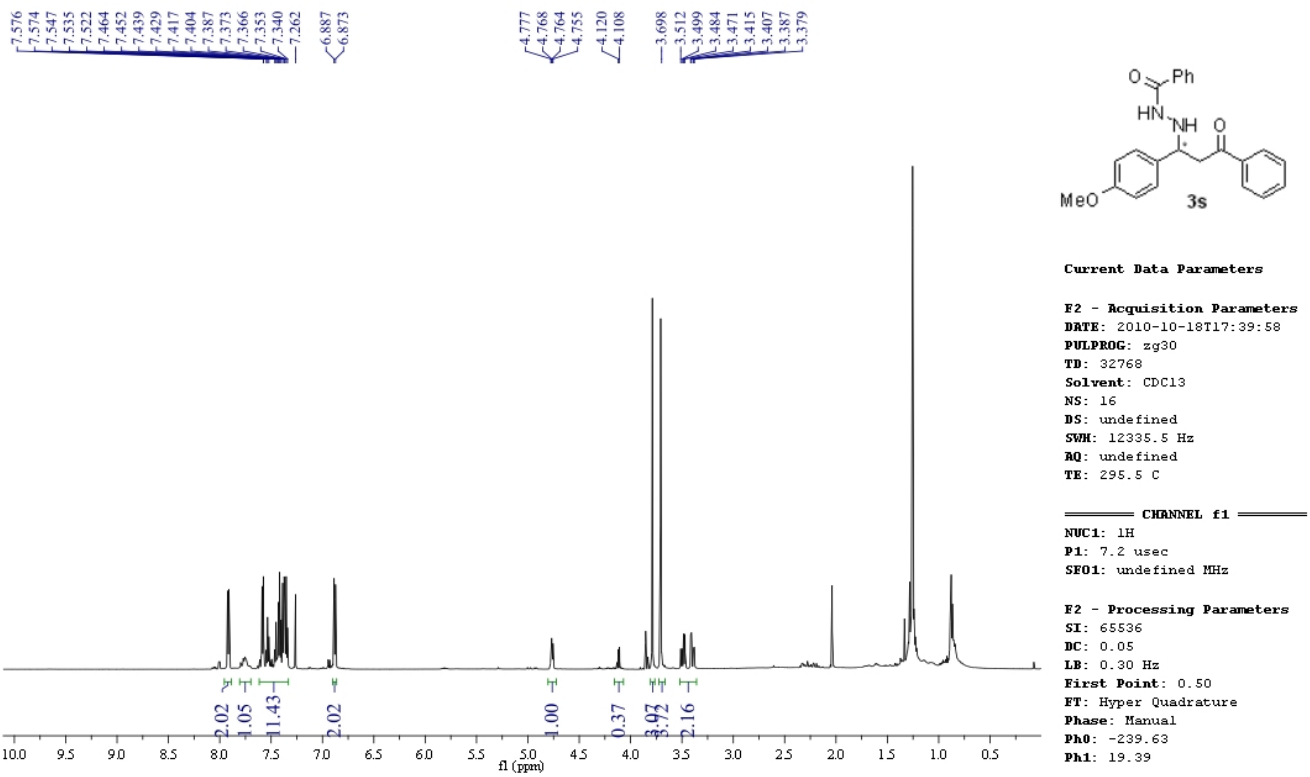
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.60 – 7.26 (m, 12H), 7.12 (d, *J* = 5.8 Hz, 1H), 5.70 (d, *J* = 3.3 Hz, 1H), 4.84 – 4.73 (m, 1H), 3.45 (ddd, *J* = 21.6, 16.8, 6.5 Hz, 2H), 2.36 (s, 3H).



δ_C (151 MHz, $CDCl_3$) 198.33, 166.89, 140.77, 138.49, 136.72, 133.31, 132.90, 131.69, 128.82, 128.69, 128.64, 128.59, 128.39, 128.24, 126.83, 124.70, 60.93, 44.46, 21.46.

19) Product 3s:





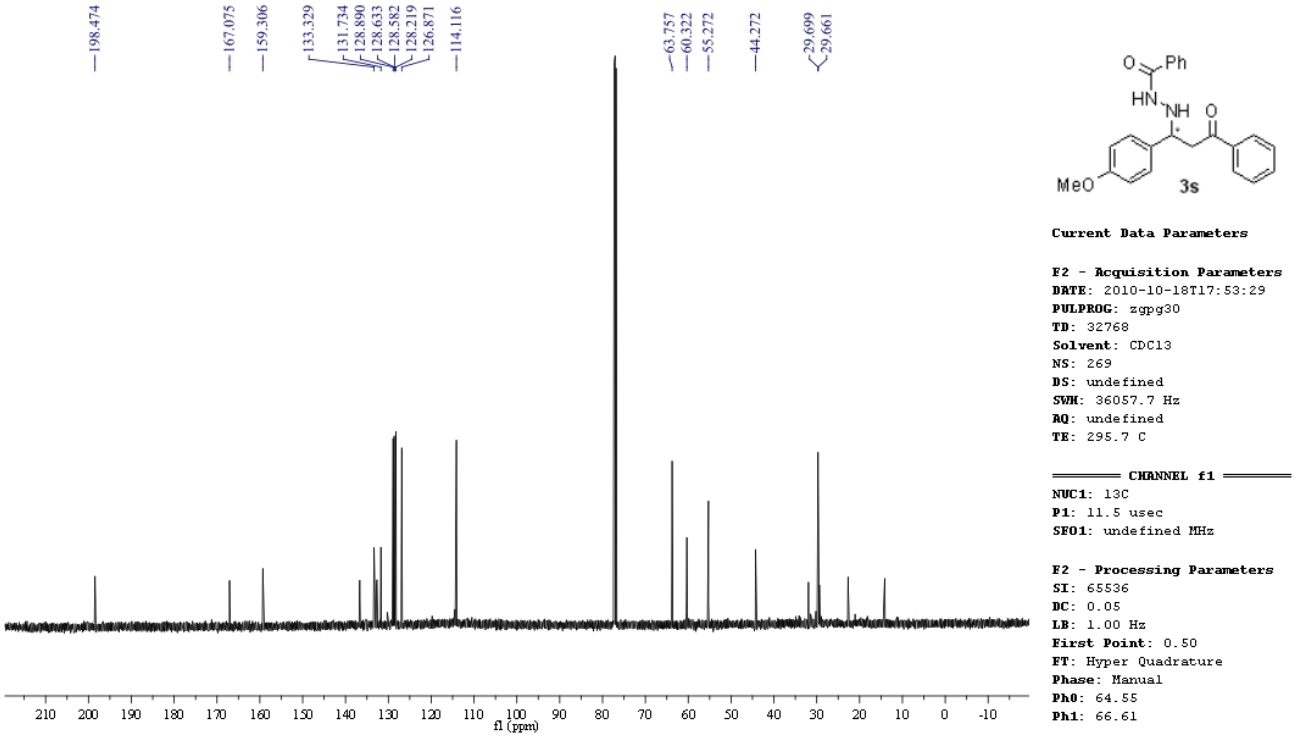
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-10-18T17:39:58
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295.5 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

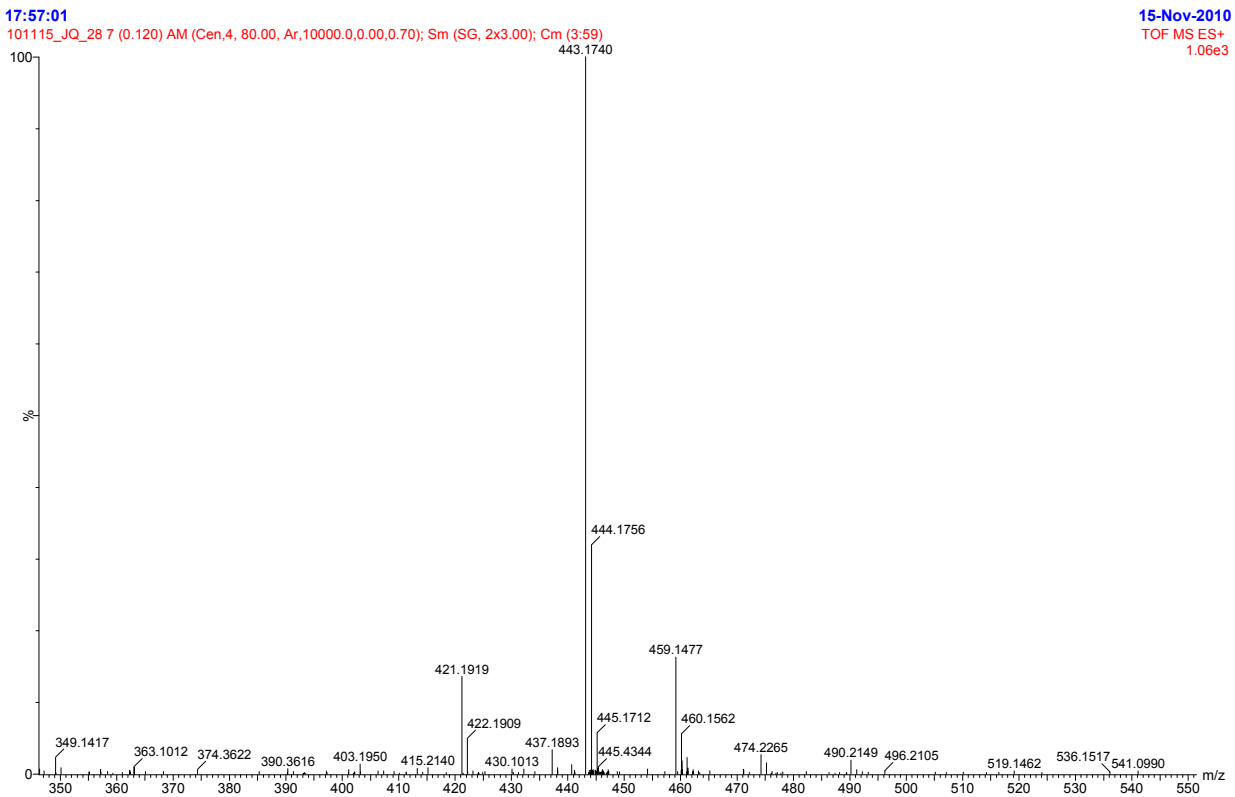
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -239.63
Ph1: 19.39

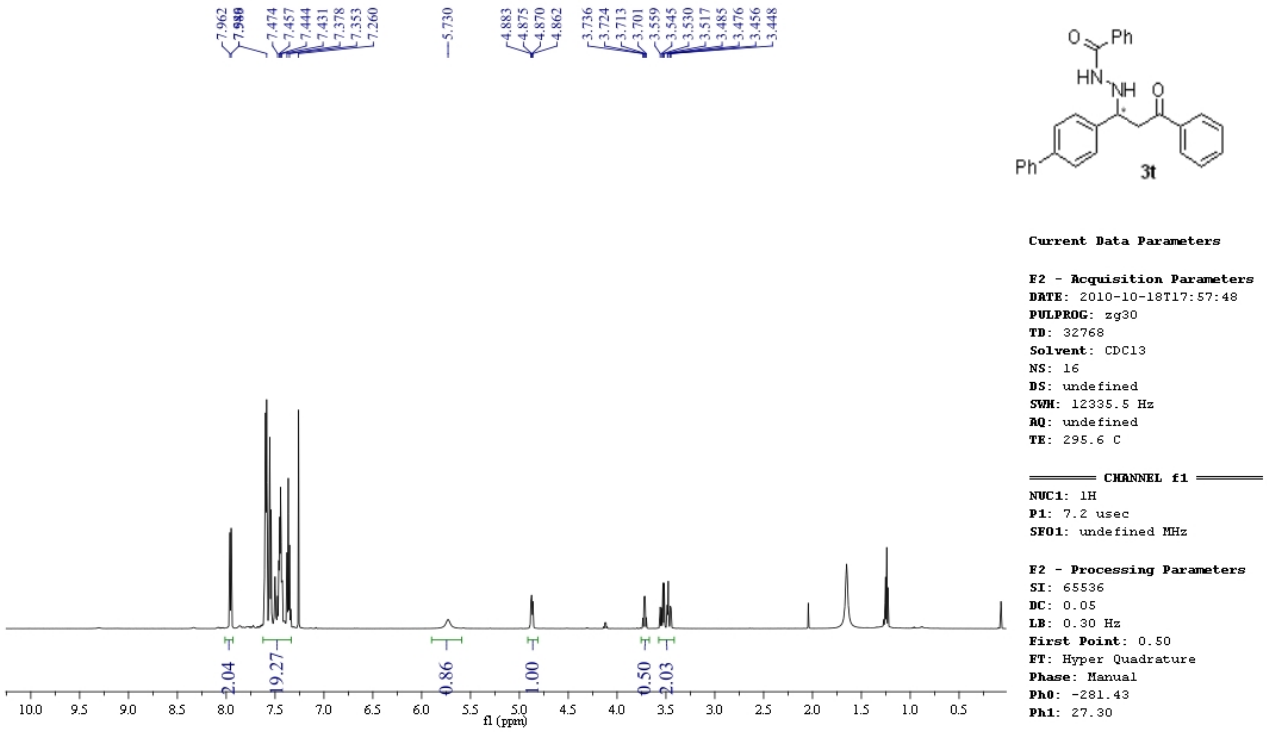
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.74 (ddd, *J* = 15.5, 10.5, 8.9 Hz, 1H), 7.62 – 7.33 (m, 11H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.77 (dd, *J* = 7.8, 5.2 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 0H), 3.79 (s, 3H), 3.70 (d, *J* = 5.6 Hz, 4H), 3.44 (ddd, *J* = 21.9, 16.8, 6.5 Hz, 2H).



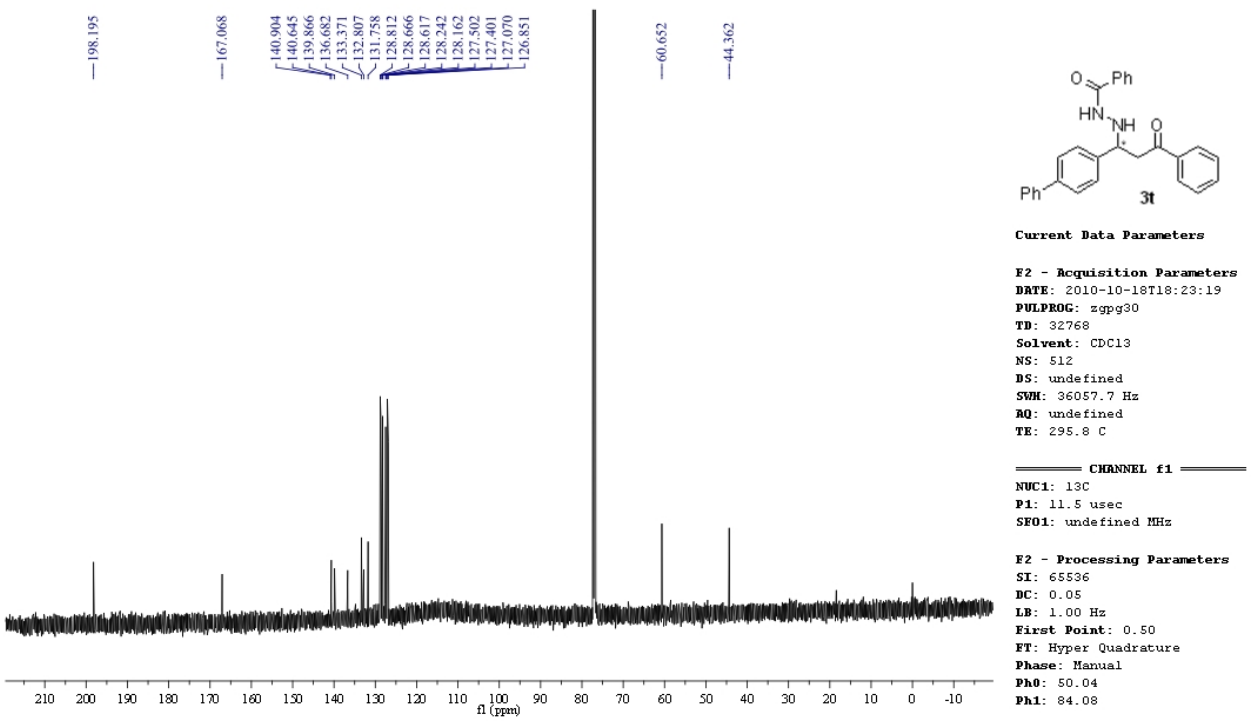
δ_C (151 MHz, $CDCl_3$) 198.47, 167.08, 159.31, 136.68, 133.33, 132.76, 132.65, 131.73, 128.89, 128.63, 128.58, 128.22, 126.87, 114.12, 63.76, 60.32, 55.27, 44.27, 29.70, 29.66.

20) Product 3t:



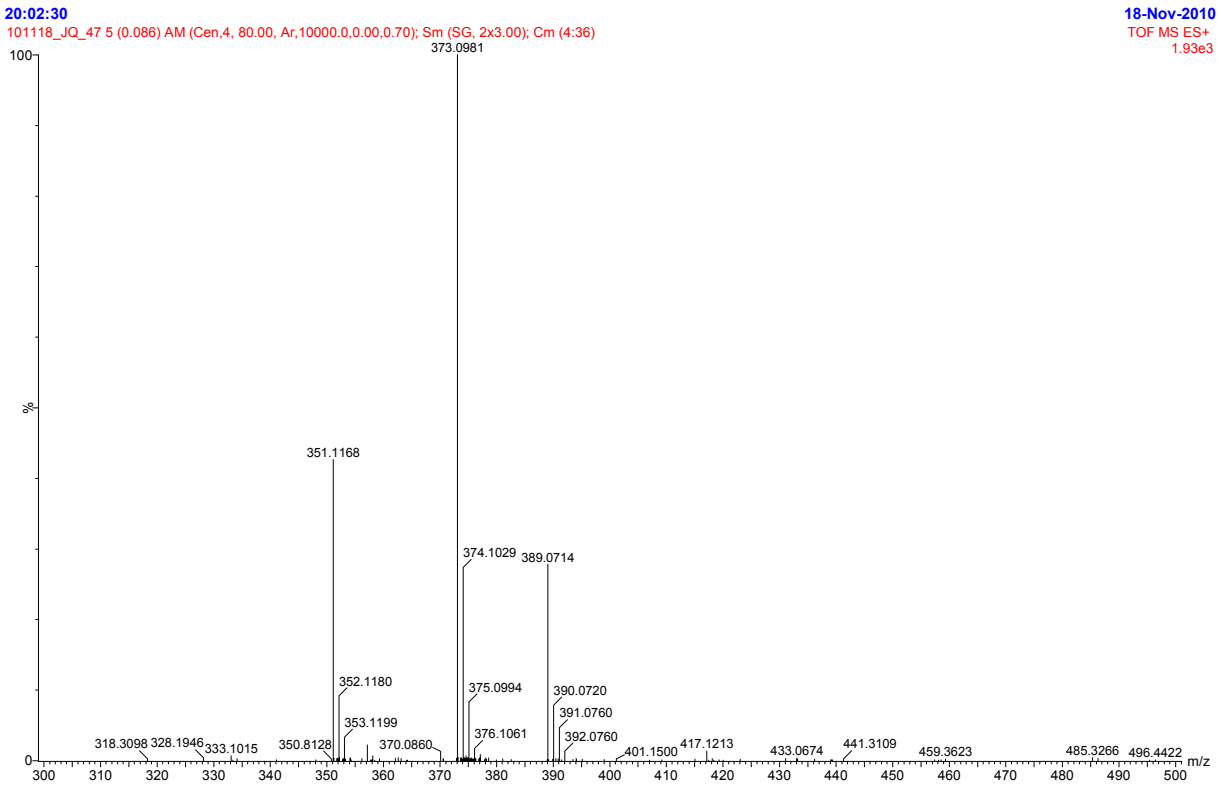


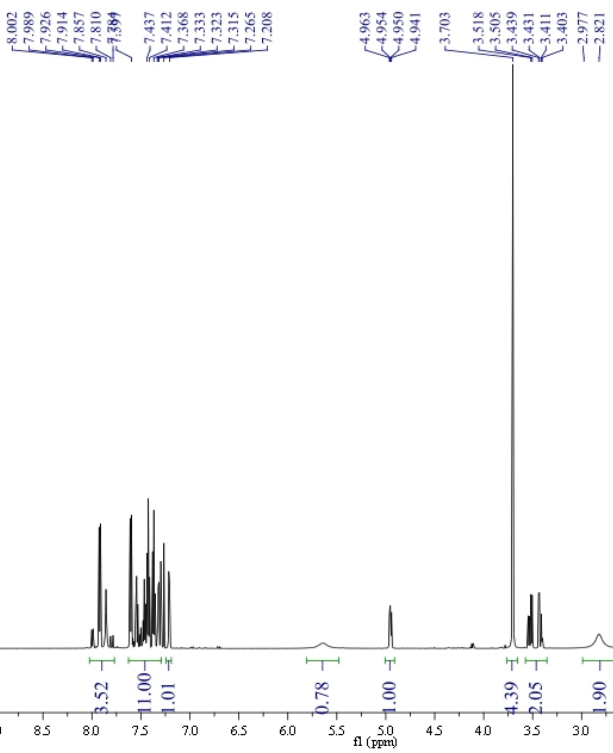
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.62 – 7.34 (m, 19H), 5.73 (s, 1H), 4.87 (dd, *J* = 7.8, 5.1 Hz, 1H), 3.72 (q, *J* = 7.0 Hz, 1H), 3.50 (ddd, *J* = 21.9, 16.8, 6.5 Hz, 2H).

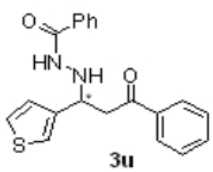


δ_C (151 MHz, $CDCl_3$) 198.20, 167.07, 140.90, 140.65, 139.87, 136.68, 133.37, 132.81, 131.76, 128.81, 128.67, 128.62, 128.24, 128.16, 127.50, 127.40, 127.07, 126.85, 60.65, 44.36.

21) Product 3u:







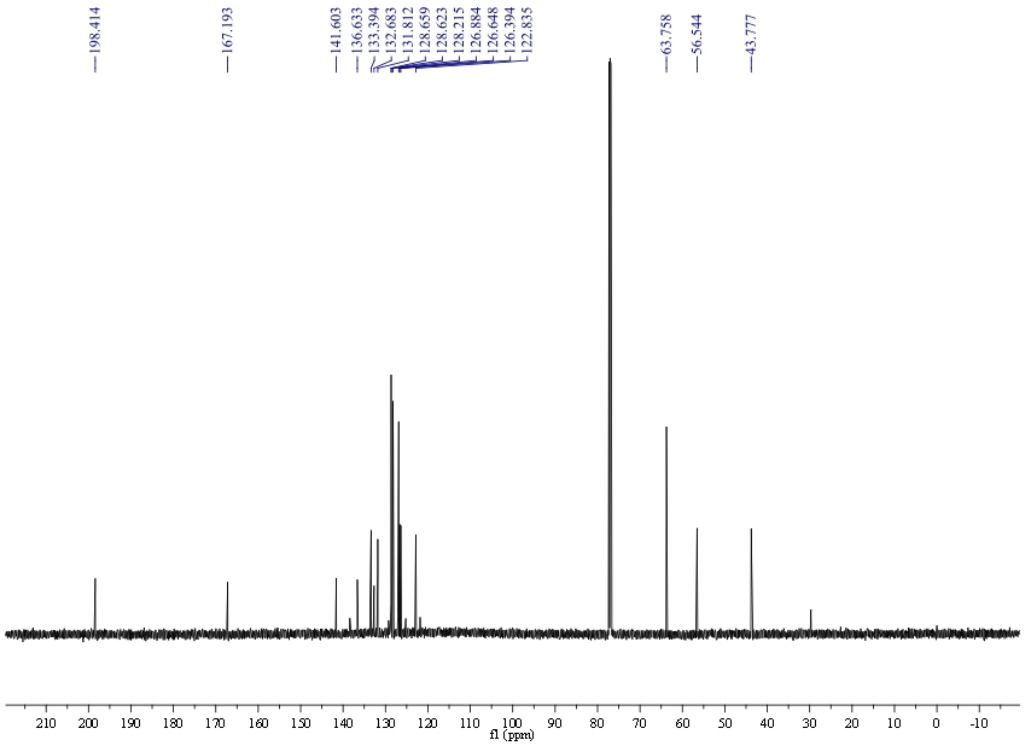
Current Data Parameters

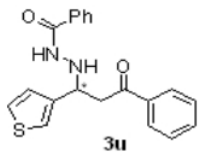
F2 - Acquisition Parameters
DATE: 2010-10-26T16:48:13
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 12335.5 Hz
AQ: undefined
TE: 295 C

CHANNEL f1
NUC1: 1H
P1: 7.2 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: -0.40 Hz
Gauss: 1.00
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -327.04
Ph1: 25.45

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.77 (m, 4H), 7.63 – 7.29 (m, 11H), 7.21 (d, J = 4.9 Hz, 1H), 5.64 (s, 1H), 4.95 (dd, J = 7.7, 5.2 Hz, 1H), 3.70 (s, 4H), 3.47 (ddd, J = 21.9, 16.8, 6.5 Hz, 2H), 2.90 (d, J = 93.2 Hz, 2H).





Current Data Parameters

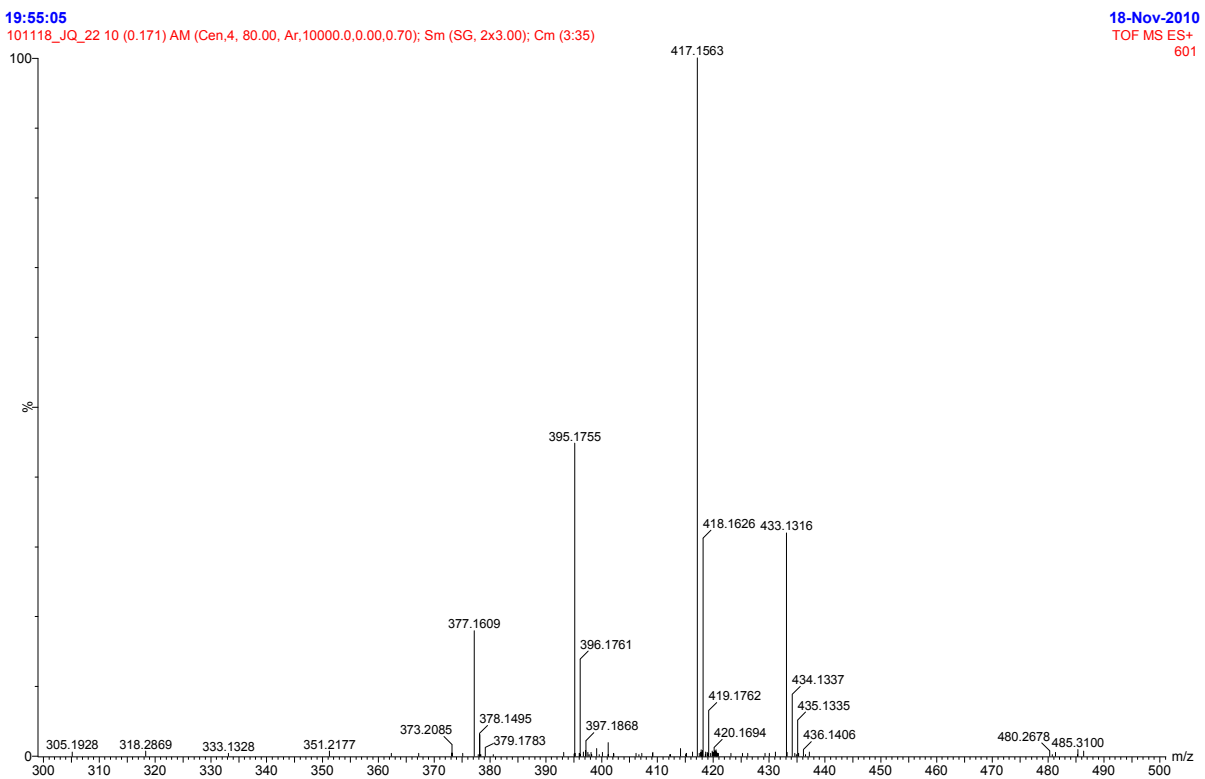
F2 - Acquisition Parameters
DATE: 2010-10-26T17:01:08
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 36057.7 Hz
AQ: undefined
TE: 295.3 C

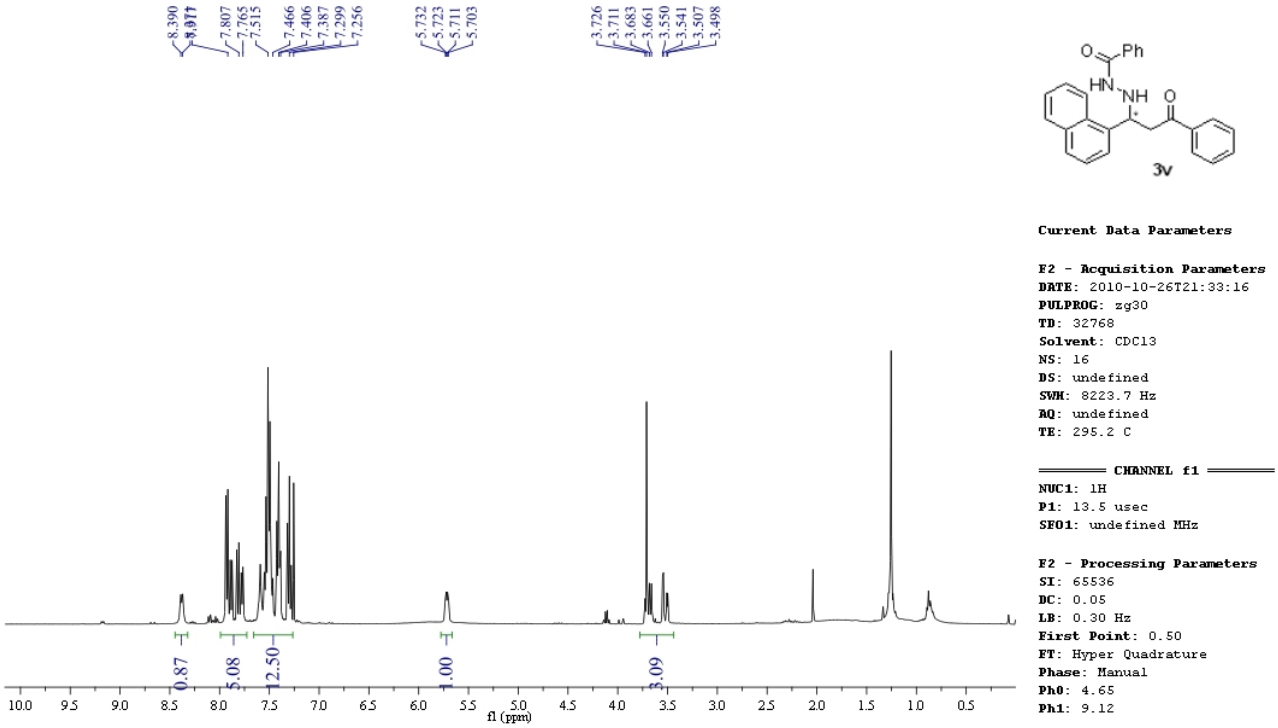
CHANNEL f1
NUC1: 13C
P1: 11.5 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 81.92
Ph1: 36.92

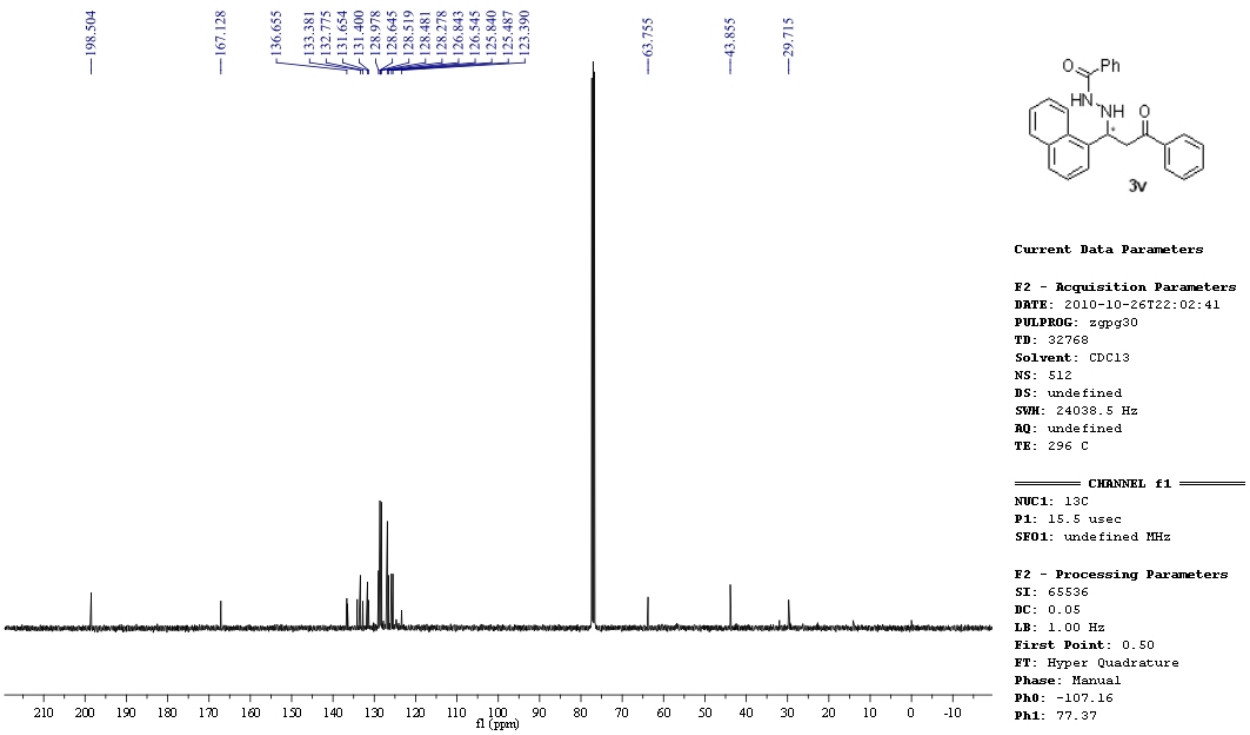
δ_C (151 MHz, $CDCl_3$) 198.41, 167.19, 141.60, 136.63, 133.39, 132.68, 131.81, 128.66, 128.62, 128.22, 126.88, 126.65, 126.39, 122.83, 63.76, 56.54, 43.78.

22) Product 3v:



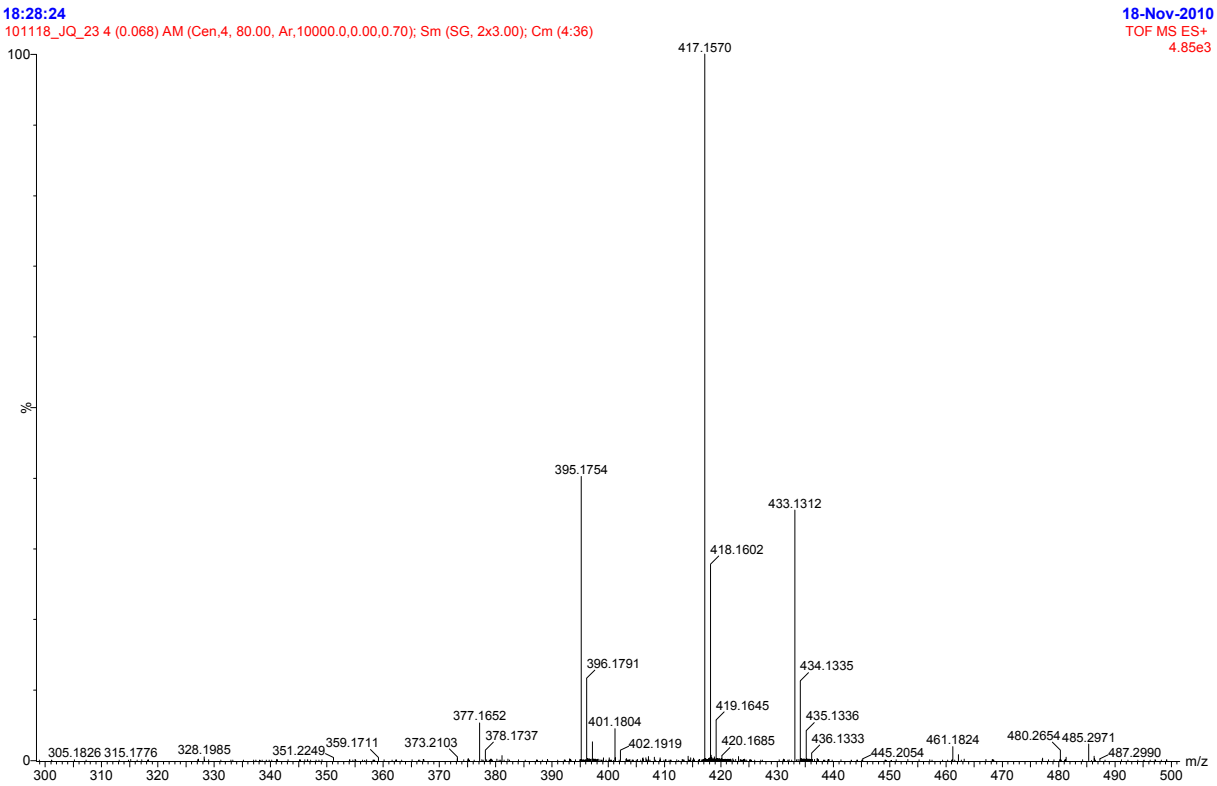


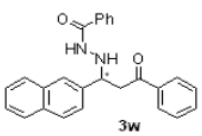
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.7 Hz, 1H), 7.85 (ddd, *J* = 43.7, 17.1, 7.5 Hz, 5H), 7.66 – 7.26 (m, 13H), 5.72 (dd, *J* = 8.4, 3.2 Hz, 1H), 3.78 – 3.44 (m, 3H).

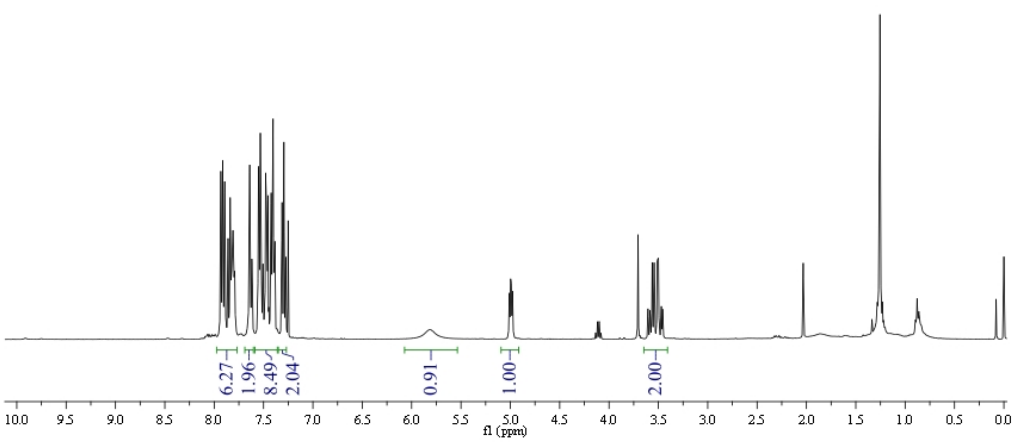


δ_C (101 MHz, $CDCl_3$) 198.50, 167.13, 136.66, 136.49, 134.12, 133.38, 132.77, 131.65, 131.40, 128.98, 128.64, 128.52, 128.48, 128.28, 126.84, 126.55, 125.84, 125.49, 123.39, 63.76, 43.85, 29.71.

23) Product 3w:







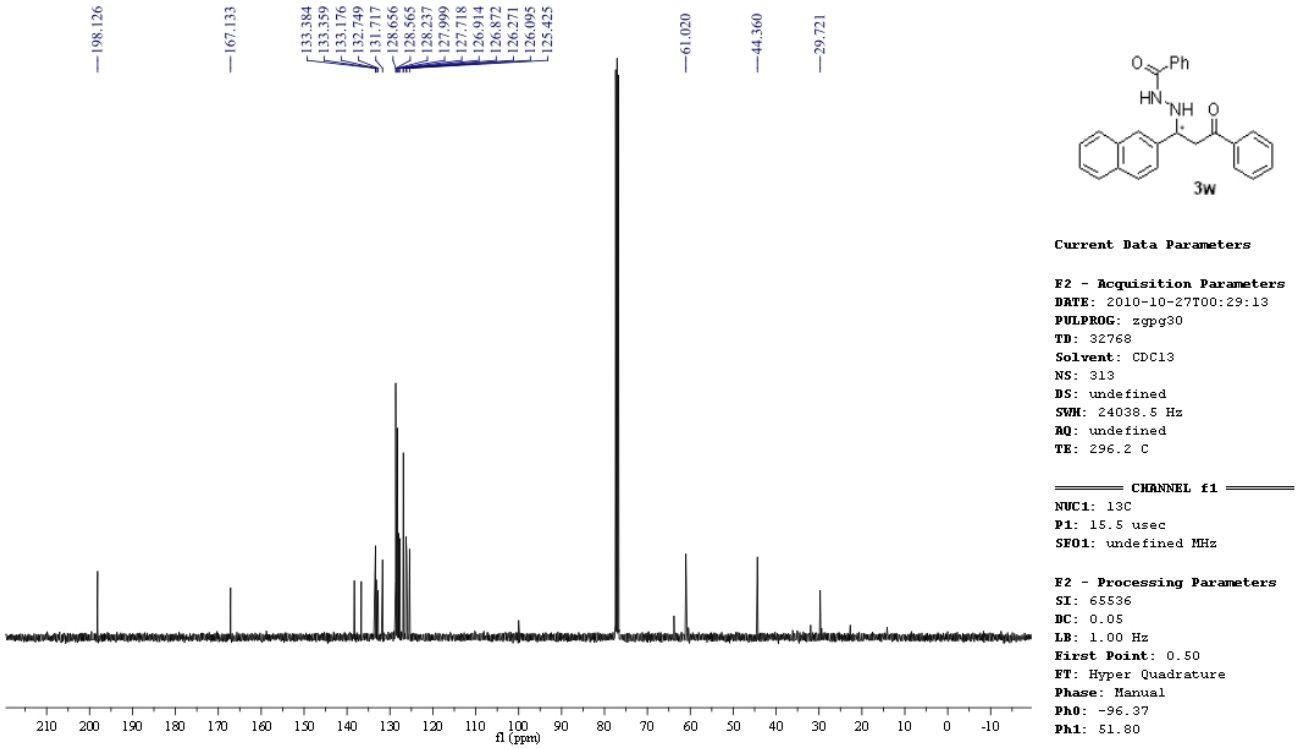
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2010-10-27T00:11:08
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.5 C

CHANNEL f1
NUC1: 1H
P1: 13.5 usec
SFO1: undefined MHz

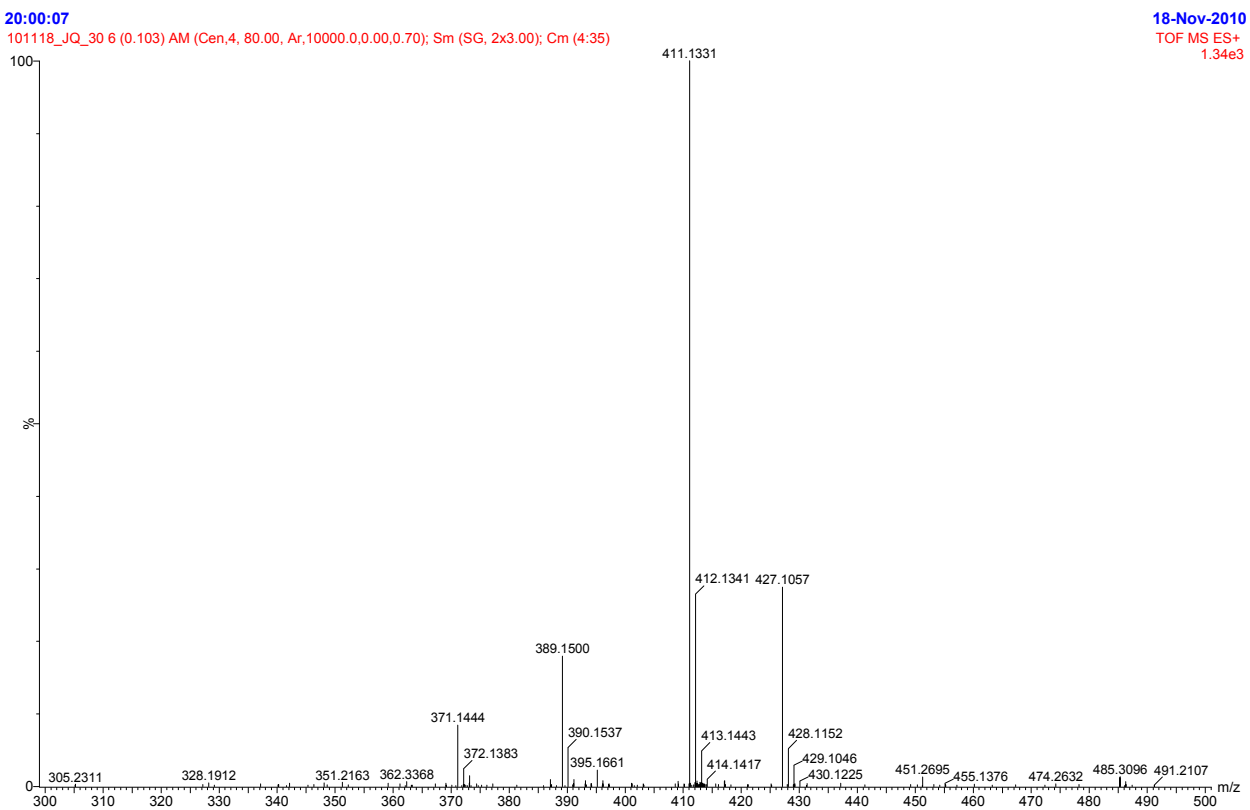
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -0.55
Ph1: 15.13

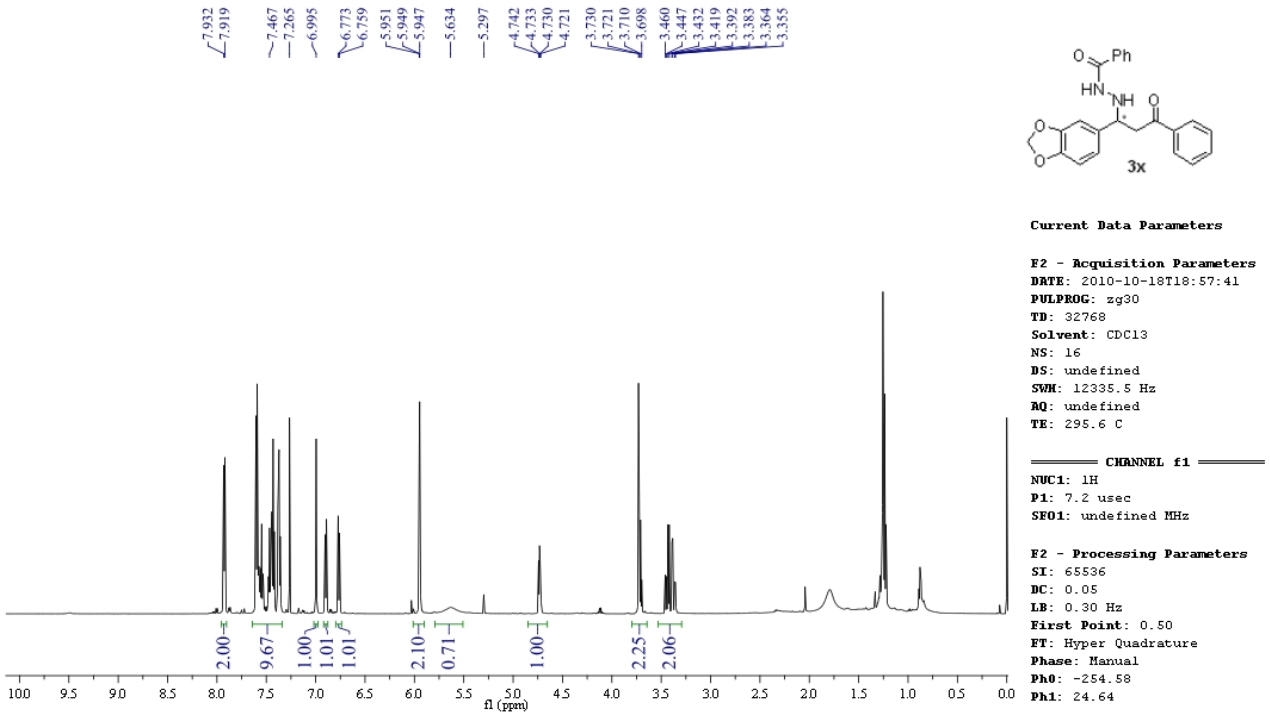
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.77 (m, 6H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.59 – 7.36 (m, 8H), 7.29 (t, *J* = 7.6 Hz, 2H), 5.81 (d, *J* = 6.5 Hz, 1H), 4.99 (dd, *J* = 7.6, 5.3 Hz, 1H), 3.53 (qd, *J* = 16.9, 6.5 Hz, 2H).



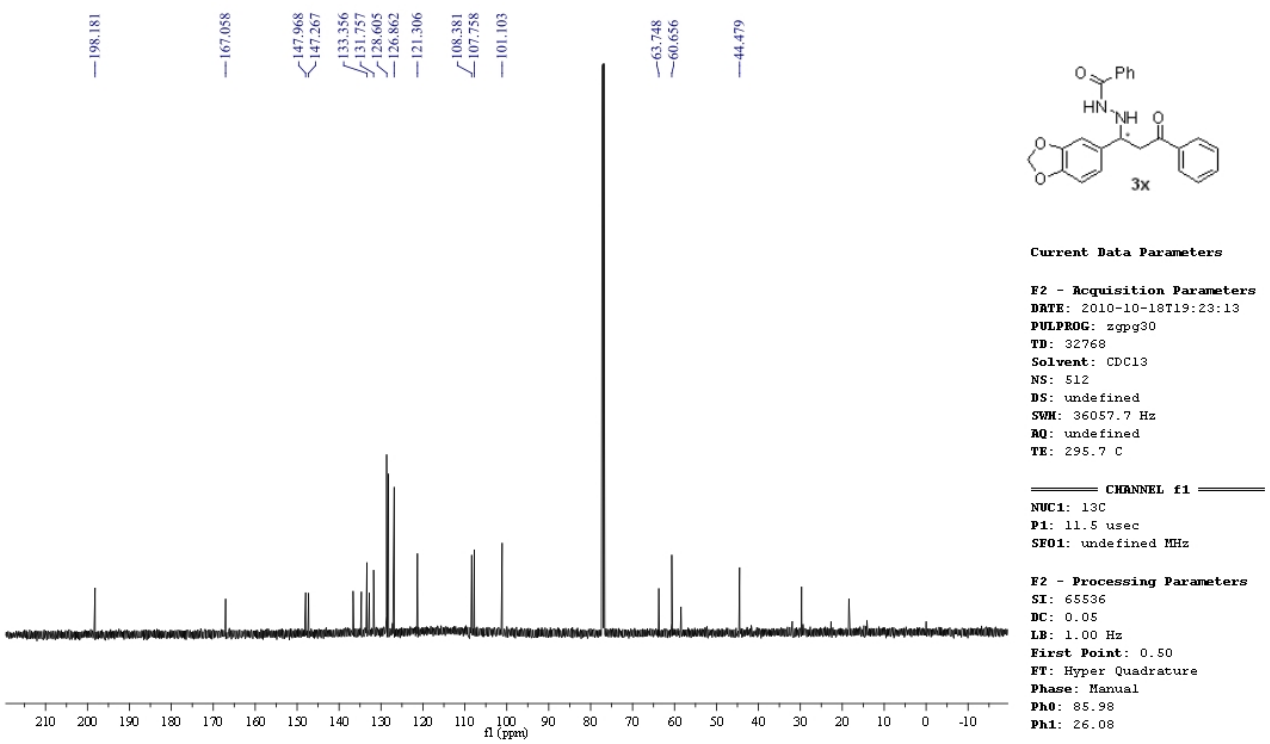
δ_C (101 MHz, $CDCl_3$) 198.13, 167.13, 138.30, 136.67, 133.38, 133.36, 133.18, 132.75, 131.72, 128.66, 128.57, 128.24, 128.00, 127.72, 126.91, 126.87, 126.27, 126.09, 125.42, 61.02, 44.36, 29.72.

24) Product 3x:



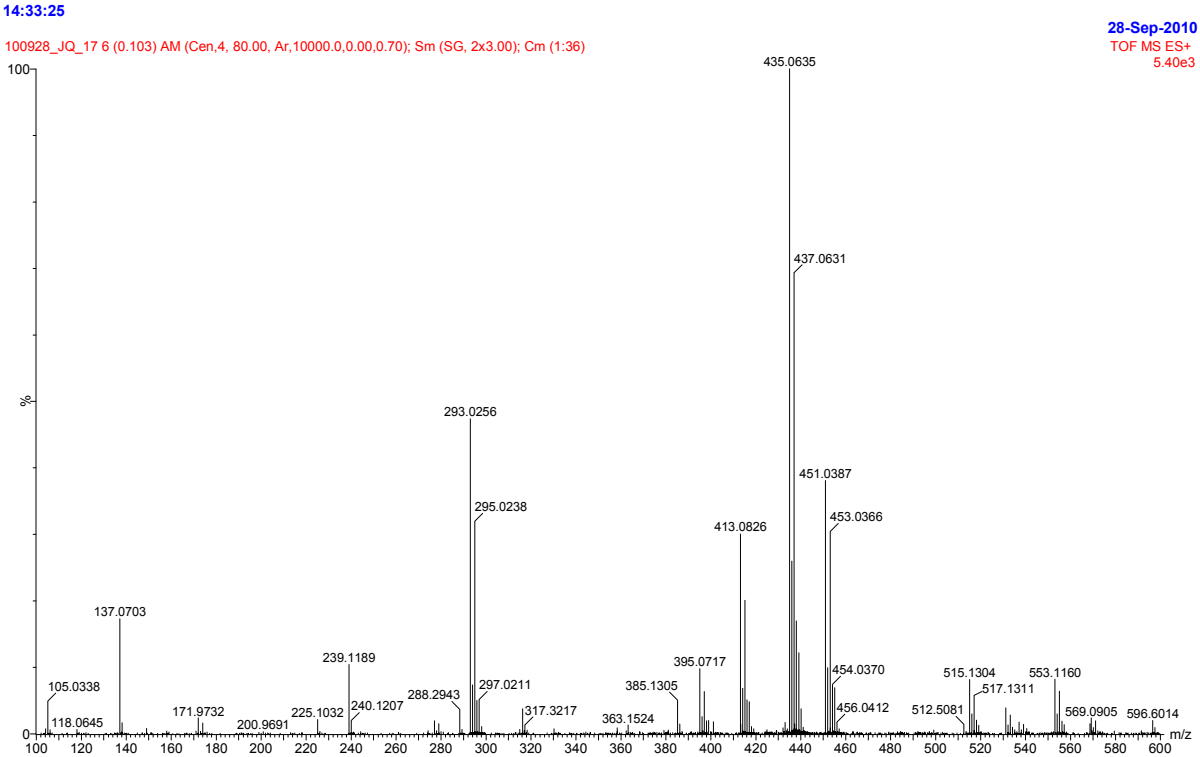


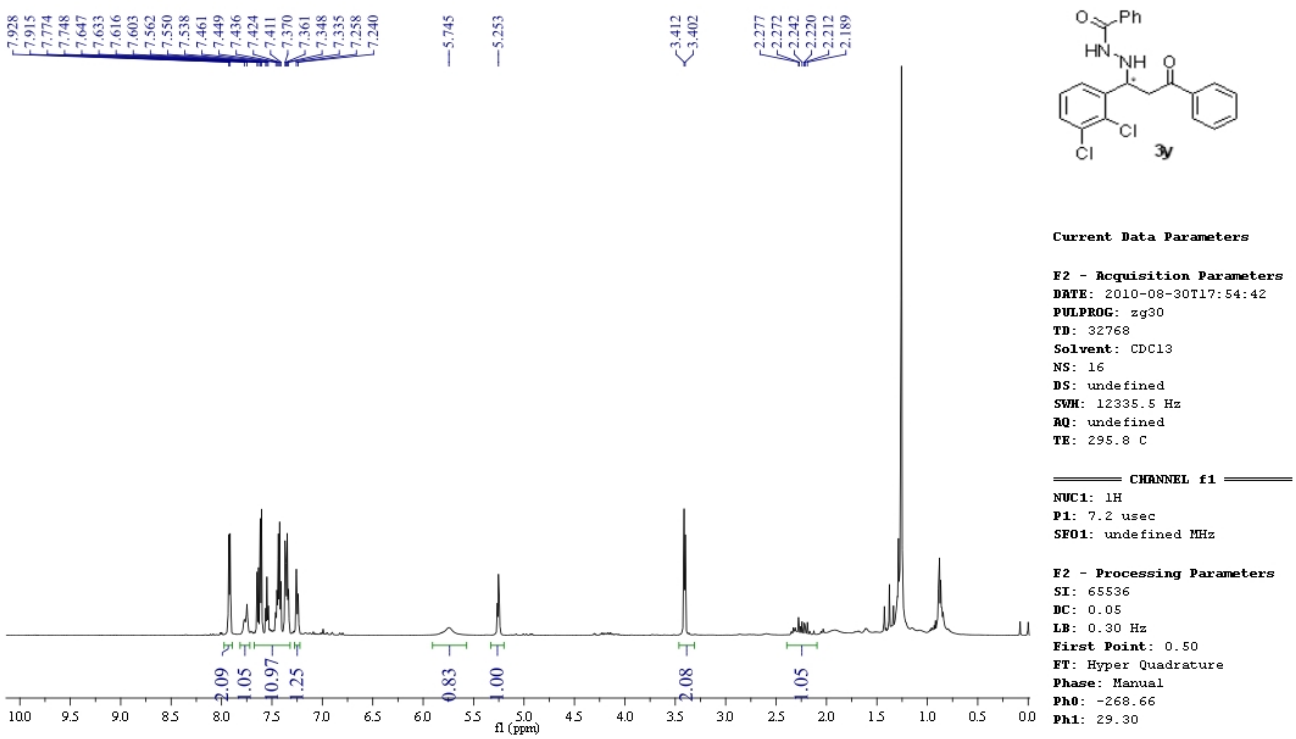
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 2H), 7.64 – 7.34 (m, 10H), 7.00 (s, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.01 – 5.90 (m, 2H), 5.63 (s, 1H), 4.73 (dd, *J* = 7.5, 5.4 Hz, 1H), 3.71 (dd, *J* = 13.3, 6.2 Hz, 2H), 3.41 (ddd, *J* = 21.9, 16.7, 6.5 Hz, 2H).



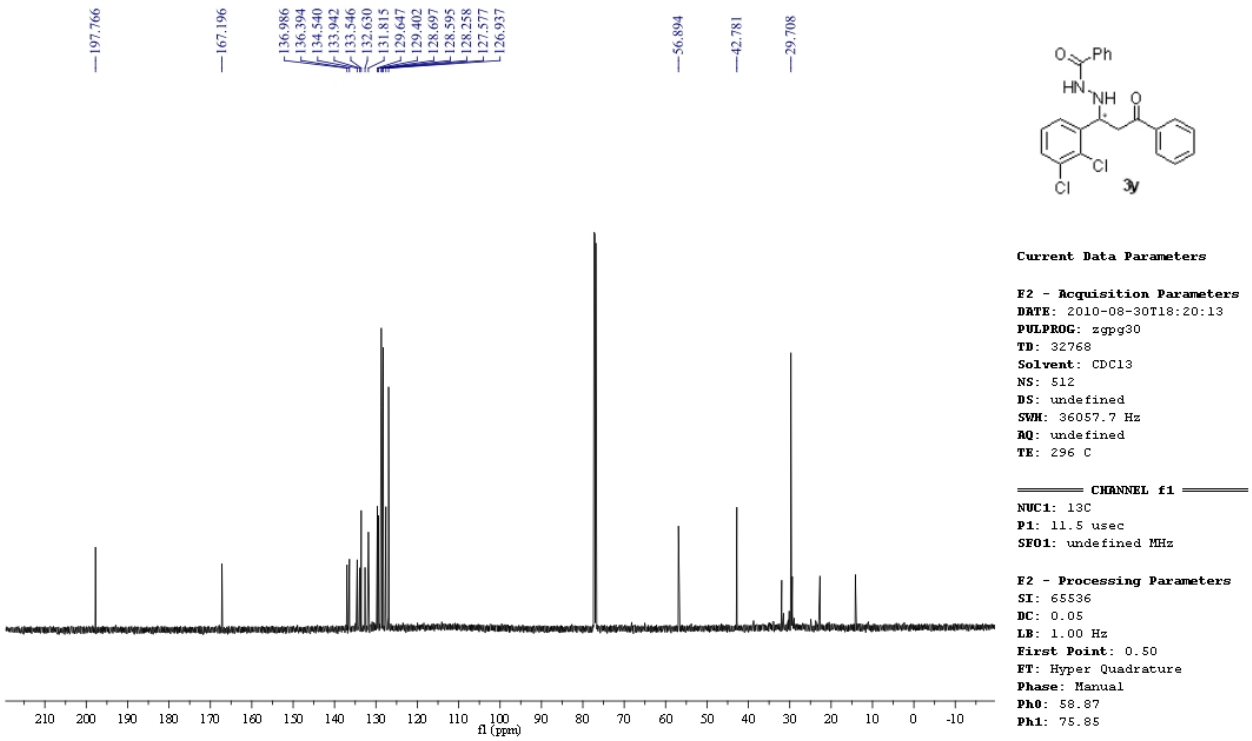
δ_C (151 MHz, $CDCl_3$) 198.18, 167.06, 147.97, 147.27, 136.65, 134.67, 133.36, 132.78, 131.76, 128.65, 128.60, 128.21, 126.86, 121.31, 108.38, 107.76, 101.10, 63.75, 60.66, 44.48.

25) Product 3y:



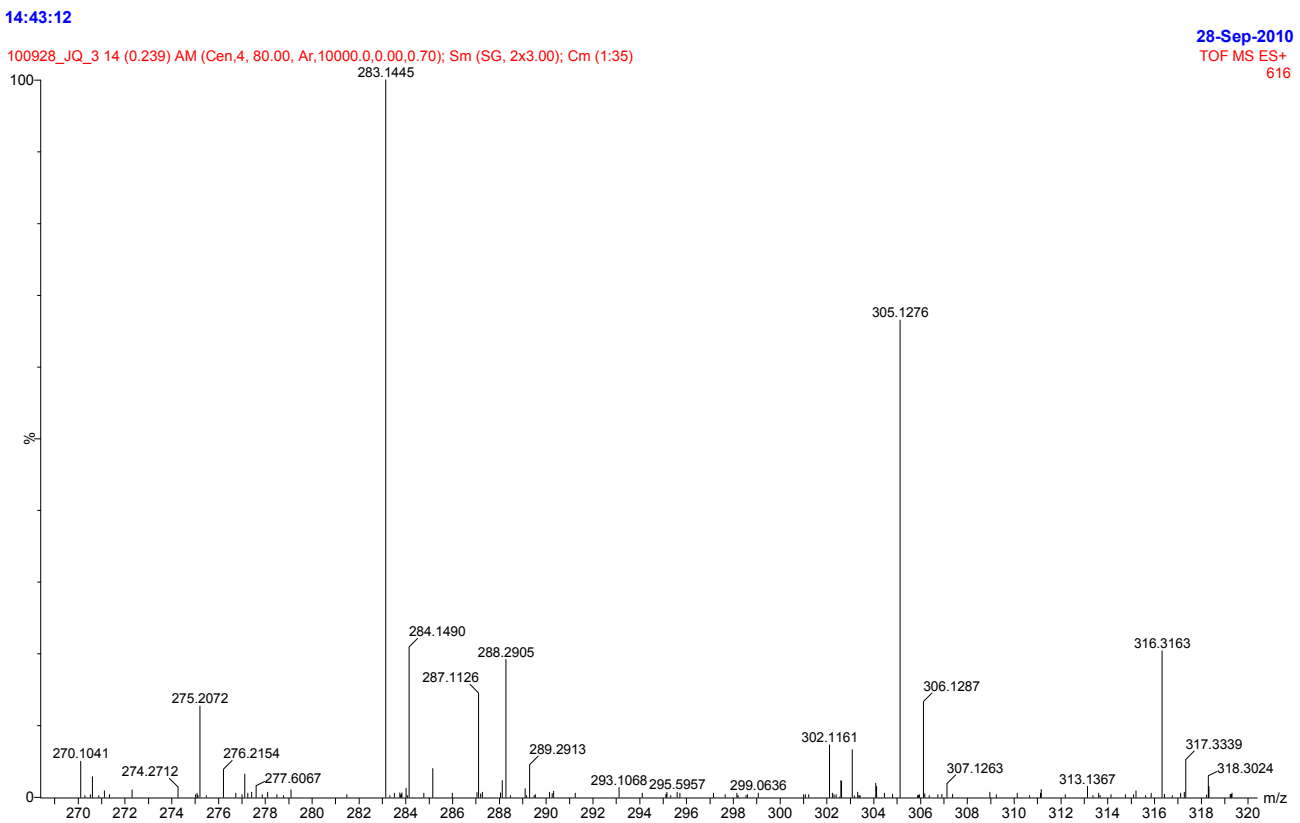


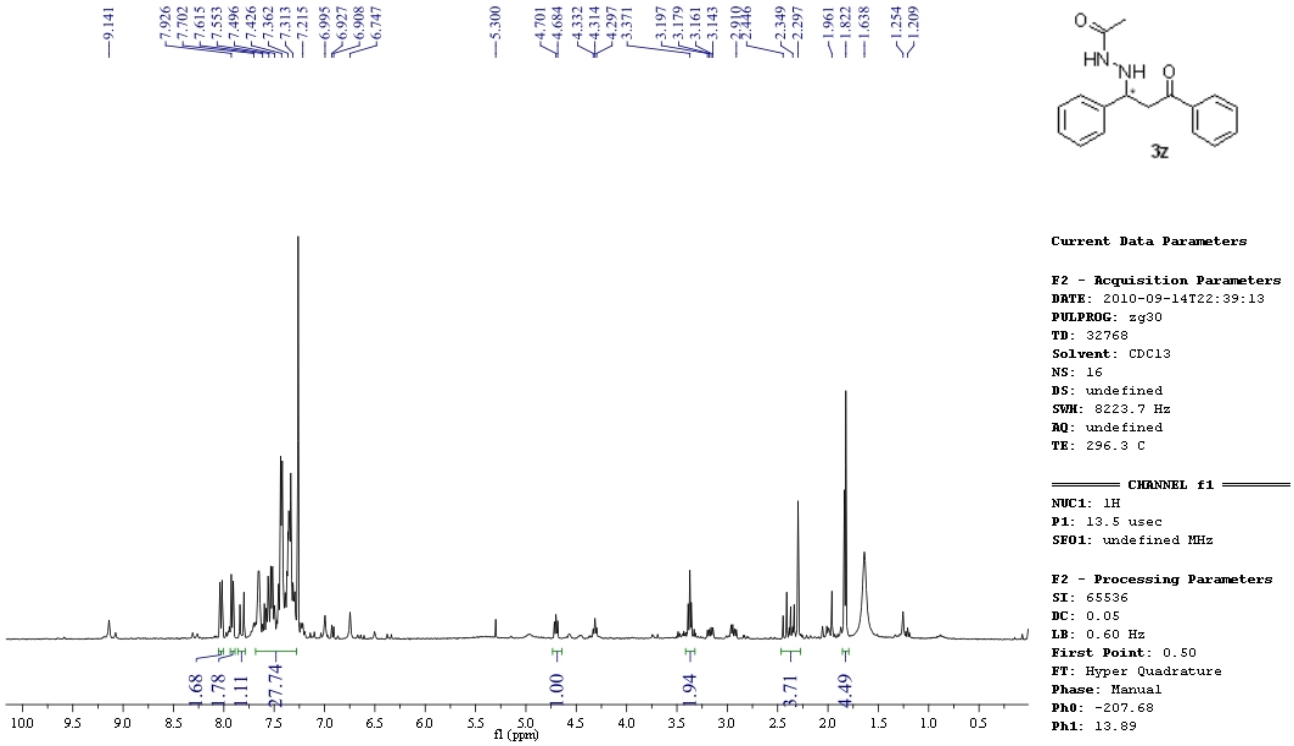
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, J = 7.6 Hz, 2H), 7.76 (d, J = 15.5 Hz, 1H), 7.48 (dddd, J = 53.1, 20.5, 17.0, 7.9 Hz, 11H), 7.25 (d, J = 10.9 Hz, 1H), 5.74 (s, 1H), 5.25 (s, 1H), 3.41 (d, J = 6.4 Hz, 2H), 2.39 – 2.09 (m, 1H).



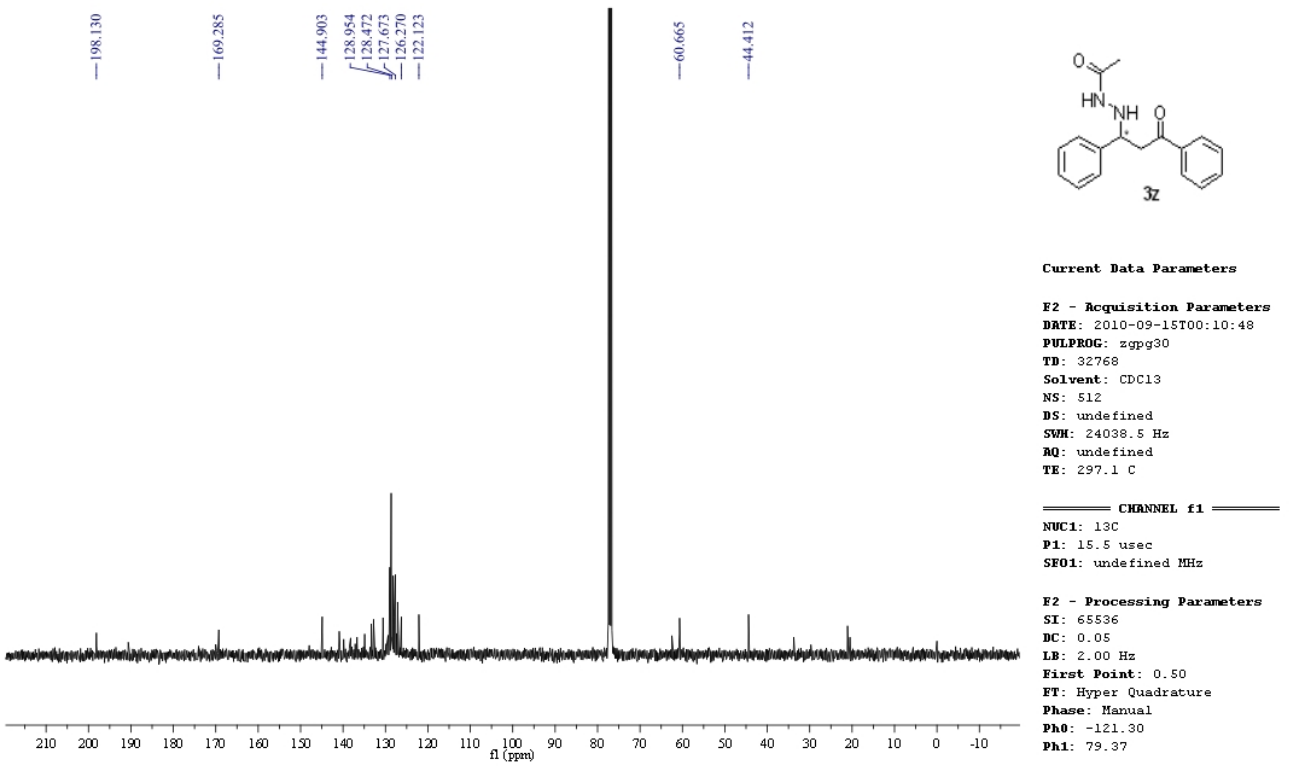
δ_C (151 MHz, $CDCl_3$) 197.77, 167.20, 136.99, 136.39, 134.54, 133.94, 133.55, 132.63, 131.81, 129.65, 129.40, 128.70, 128.60, 128.26, 127.58, 126.94, 56.89, 42.78, 29.71.

26) Product 3z:





^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 2H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 15.7 Hz, 1H), 7.68 – 7.28 (m, 28H), 4.74 – 4.64 (m, 1H), 3.36 (dd, *J* = 14.7, 9.2 Hz, 2H), 2.47 – 2.27 (m, 4H), 1.83 (d, *J* = 6.0 Hz, 4H).



δ_C (101 MHz, $CDCl_3$) 198.13, 169.29, 144.90, 134.90, 133.32, 132.82, 130.58, 128.98, 128.95, 128.74, 128.65, 128.53, 128.47, 128.17, 128.10, 127.95, 127.67, 127.37, 127.14, 126.95, 126.27, 122.12, 60.66, 44.41.

(H) The information of single crystal X-ray diffraction analysis.

CCDC 801220 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./ data_request/cif.

Datablock: 101110_S1_JJ

Bond precision: C-C = 0.0049 A Wavelength=0.71070

Cell: a=12.6570(9) b=5.2425(3) c=14.9418(10)
alpha=90 beta=105.291 (7) gamma=90

Temperature: 294 K

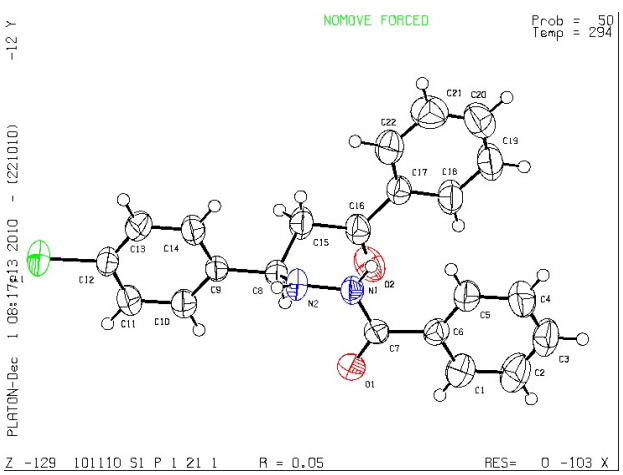
	Calculated	Reported
Volume	956.36(11)	956.35(11)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C22 H19 Cl N2 O2	C22 H19 Cl N2 O2
Sum formula	C22 H19 Cl N2 O2	C22 H19 Cl N2 O2
Mr	378.84	378.84
Dx,g cm-3	1.316	1.316
Z	2	2
Mu (mm-1)	0.219	0.219
F000	396.0	396.0
F000'	396.45	
h,k,lmax	15,6,18	15,6,18
Nref	2189[3929]	3162
Tmin,Tmax	0.912,0.941	0.982,1.000
Tmin'	0.912	

Correction method= MULTI-SCAN

Data completeness= 1.44/0.80 Theta(max)= 26.370

R(reflections)= 0.0464(2489) wR2(reflections)= 0.1209(3162)

S = 1.045 Npar= 244



(I) References

(1) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, *Synlett.* 2005, 2445

(2) G. T. Notte and J. L. Leighton, *J. Am. Chem. Soc.*, 2008, **130**, 6676;