

Supporting Information for
Magnetic Nanoparticle Supported Polyoxometalates (POMs) via
Non-covalent Interaction: Reusable Acid Catalysts and Catalyst
Supports for Chiral Amines

*Xiaoxi Zheng, Long Zhang, Jiuyuan Li, Sanzhong Luo * and Jin-Pei Cheng*

*Beijing National Laboratory for Molecular Sciences (BNLMS), Center for Molecular
Science, Institute of Chemistry and Graduate School, Chinese Academy of Sciences,
Beijing, 100190;*

General Information: Commercial reagents were used as received, unless otherwise stated. ^1H and ^{13}C NMR were recorded on a Bruker-DPX 300 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s= singlet, d= doublet, t= triplet, q= quartet, h= heptet, m= multiplet, br= broad. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). IR spectra were obtained from a Jasco FT/IR-480 Plus instrument using KBr disks. Transmission electron microscope (TEM) images were obtained from a JEOL JEM-2010 instrument. X-ray diffraction (XRD) images were obtained from a Rigaku D/max-2400PC instrument with Cu $K\alpha$ radiation. Elemental analysis (EA) was obtained from ThermoQuest (Flash 1112EA, ITALY). The magnetization curve was obtained by a vibrating sample magnetometer

(JDM-13T, CHINA).

Synthesis of PVP-stabilized magnetite nanoparticles:

Magnetite (Fe_3O_4) particles were prepared in a co-precipitation step based on the procedure of Massart et al.¹ and T. J. Yoon, et al.² $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (22.0 g, 81.4 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (8.0 g, 40.7 mmol) were dissolved in 120 mL deionized water under argon with vigorous stirring at 85 °C. The pH value of the solution was adjusted to 9 by concentrated $\text{NH}_3 \cdot \text{H}_2\text{O}$. After 4 hours, the magnetite precipitates were washed to pH = 7 by deionized water. The black precipitate was collected with a permanent magnet under the reaction flask, and the supernatant was decanted. The sediment was redispersed in 100 mL of deionized water. The PVP aqueous solution (8.8 mL, 25.6 g/L) was added, and stirred for 1 day at room temperature. The PVP-stabilized magnetite nanoparticles were separated by addition of aqueous acetone ($\text{H}_2\text{O}/\text{acetone} = 1/10$, v/v) and centrifugation at 4000 rpm for 10 min. The supernatant solution was removed and the precipitated particles were washed by ethanol twice. The obtained particles were dried in vacuum.

Synthesis of SiO_2 -coated magnetite nanoparticles (SiO_2 -MNP):

SiO_2 -coated magnetite nanoparticles were prepared according to the procedure of Hyeon et al.³ PVP stabilized magnetite nanoparticles (2.0 g) were dispersed in 400 mL ethanol. $\text{NH}_3 \cdot \text{H}_2\text{O}$ (12 mL) and TEOS (4.0 mL) were added successively. After stirring for 24 hours, the black precipitate was collected with a permanent magnet, and rinsed with ethanol three times. The product was dried and stored in vacuum. The

content of nitrogen is less than 0.3 % which is determined by elemental analysis.

Synthesis of amino-functionalized magnetite nanoparticles (MNP-1):

1.0 g SiO₂-coated magnetite nanoparticles were dispersed in 30 mL dry toluene by sonication for 1 hour. 2 mL of (3-aminopropyl) triethoxysilane (10 mmol) was then added and the reaction mixture was refluxed for 24 hours under argon. After being cooled to room temperature, the products were adsorbed on magnet and rinsed twice with 100 mL dry toluene and twice with 100 mL of dry acetone. The obtained particles were dried in vacuum. The loading of the base group is determined to be 1.42 mmol/g by elemental analysis. The loading of amino group can be tuned by changing the loading of (3-aminopropyl) triethoxysilane. The synthesis of MNP-2 has been previously reported (*Green. Chem.* **2009**, *11*, 455).

Synthesis of magnetic polyoxometalates (MNP-1-PW):

Amino-functionalized MNP (179 mg, 0.25 mmol) was dispersed in dry THF (30 mL), and sonicated for 30min. H₃PW₁₂O₄₀ (792 mg, 0.275 mmol) was added with another 1 hour-sonication. The self-assembly catalyst was collected by magnet, and wash twice by THF. After dryness in vacuum, the resulting magnetic POMs (gray powder) were obtained.

Synthesis of MNP-1-PW-A:

MNP-1-PW (900 mg, 0.25 mmol) was dispersed in dry THF (30 mL), and the chiral amine **1** (91.2mg, 0.5mmol) was added, and sonicated for 1 hour. The self-assembly catalyst was collected by magnet, washed twice by THF and dried in vacuum. The loading of the catalyst **MNP-1-PW-A** was 0.55 mmol/g, which was

determined by Elemental Analysis (EA).

General Procedure for Friedel-Crafts reactions:

Catalyst **MNP-1-PW** (0.01 mmol, 5 mol% of the substrate) was dispersed in 0.2 mL THF. The semi-homogeneous solution was stirred for 10 minutes. Chalcone derivative (0.20 mmol) and indole derivative (0.25 mmol) were added. The resulting solution was stirred at room temperature and monitored by TLC. After the indicated reaction time, CH₂Cl₂ (1 mL) was added, and the extracts were easily separated by a magnet. The extracts were combined and concentrated. The residue was purified by FC on silica gel to afford pure product. All of the Friedel-Crafts products are known compounds.⁴

General Procedure for direct aldol reactions:

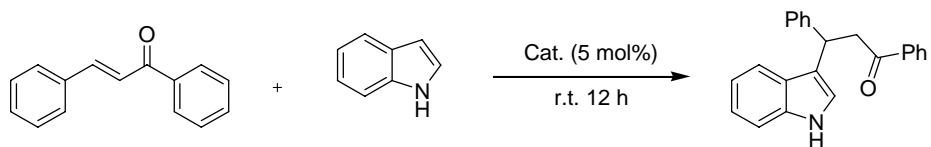
Catalyst **MNP-1-PW-A** (0.013 mmol, 5 mol% of the substrate) was dispersed in 0.20 mL acetone. The semi-homogeneous solution was stirred for 10 minutes, then corresponding aldehyde (0.25 mmol) was added. The resulting solution was stirred at room temperature and monitored by TLC. After the indicated reaction time, CH₂Cl₂ (1 mL) was added, and the extracts were easily separated with the assistance of a magnet. The extracts were combined and concentrated. The residue was purified by FC on silica gel to afford pure product. All of the aldol products are known compounds.⁵ We have also reported the characterizations of these products.⁶

Table S1. XRD of magnetite nanoparticles

Sample	d (nm)					
Prepared Fe ₃ O ₄	0.296	0.252	0.209	0.170	0.161	0.148
Standard Fe ₃ O ₄	0.296	0.253	0.209	0.171	0.161	0.148

A dry powder sample of magnetic nanoparticles was used to analyse the XRD pattern of the nanoparticles. The observed diffraction pattern coincides with the JCPDS database for magnetite. The interlayer spacings (d), calculated using the Bragg equation, agree well with the data for standard magnetite (Table S1).

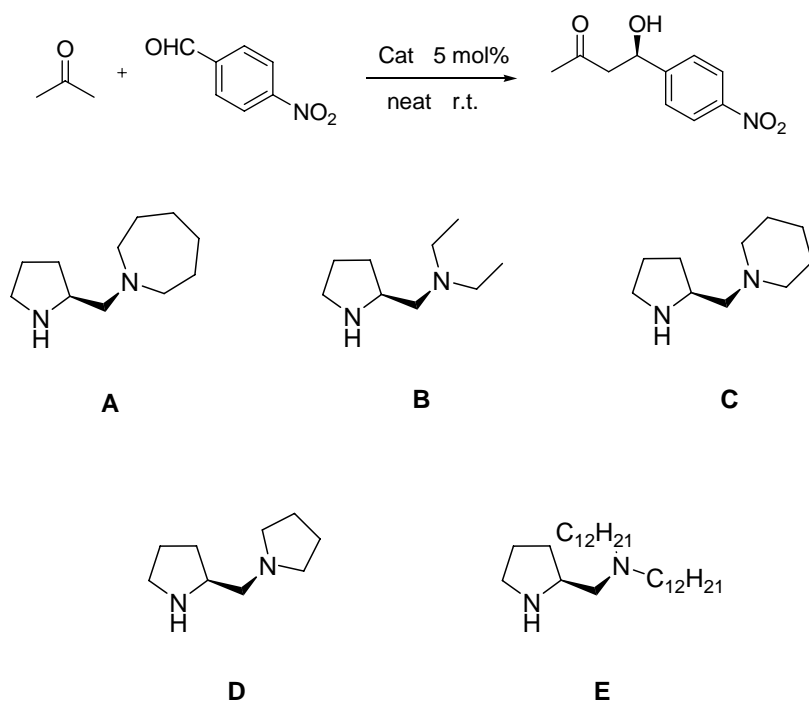
Table S2. Solvent screening of Friedel-Crafts reactions catalyzed by **MNP-1-PW**^a



Entry	Solvent	Yield (%) ^b	Entry	Solvent	Yield (%) ^b
1	MeOH	92	5	DMF	Trace
2	EtOH	90	6	MeCN	55
3	THF	94	7	H ₂ O	85
4	CH ₂ Cl ₂	trace	8	ClCH ₂ CH ₂ Cl	43

^a Reaction condition: indole (0.25 mmol), chalcone (0.20 mmol), solvent (0.2 mL), 12 h. ^b Isolated yield.

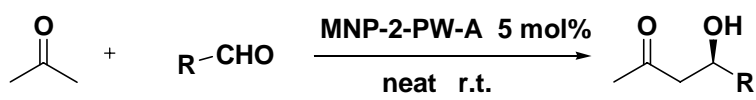
Table S3. Selected screening results for asymmetric direct aldol reaction^a



Entry	Cat.	Time (h)	Yield (%) ^[b]	ee% ^[c]
1	MNP-1-PW-A	13	79	92
2	MNP-1-PW-B	24	77	90
3	MNP-1-PW-C	24	78	86
4	MNP-1-PW-D	24	66	84
5	MNP-1-PW-E	24	71	72

^a Reaction condition: Catalyst (10 mol%), acetone (0.20 mL), aldehyde (0.25 mmol). ^b Isolated yield. ^c Determined by chiral HPLC.

Table S4. MNP-2-PW-A catalyzed aldol reaction of acetone^a

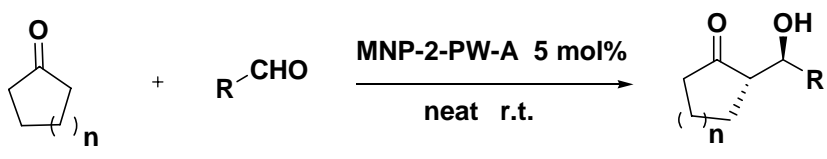


$\text{CH}_3\text{COCH}_3 + \text{R-CHO} \xrightarrow[\text{neat r.t.}]{\text{MNP-2-PW-A 5 mol\%}} \text{CH}_3\text{COCH}_2\text{CH(OH)R}$

Entry	R	Time (h)	Yield (%) ^b	ee (%) ^c
1	2-NO ₂ Ph	12	85	89
2	3-NO ₂ Ph	12	88	88
3	4-CF ₃ Ph	30	81	89
4	4-ClPh	48	75	94
5	2-ClPh	48	77	88
6	2-BrPh	48	77	87
7	4-MeOPh	120	16	89

^a Reaction condition: Catalyst (5 mol%), acetone (0.20 mL), aldehyde (0.25 mmol). ^b Isolated yield. ^c Determined by chiral HPLC.

Table S5. MNP-2-PW-A catalyzed aldol reactions of various aldol donors^a



Entry	n	R	Time (h)	Yield (%) ^b	d.r. ^c (syn:anti)	ee (%) ^d (anti)
1	1	4-NO ₂ Ph	5	95	9:91	98
2	1	2-NO ₂ Ph	5	95	24:76	97
3	1	3-NO ₂ Ph	5	94	16:84	97
4	1	4-CF ₃ Ph	12	86	17:83	96
5	1	4-ClPh	48	83	21:79	97
6	2	2-NO ₂ Ph	8	97	12:88	97
7	2	3-NO ₂ Ph	8	95	14:86	98
8	2	4-NO ₂ Ph	6	95	14:86	99
9	2	4-CF ₃ Ph	11	93	17:83	98
10	2	4-ClPh	48	90	17:83	98
11	2	Ph	72	56	7:93	95

^a Reaction condition: Catalyst (5 mol%), ketone (0.20 mL), aldehyde (0.25 mmol). ^b Isolated yield.

^c Determined by chiral HPLC. ^d Determined by chiral HPLC.

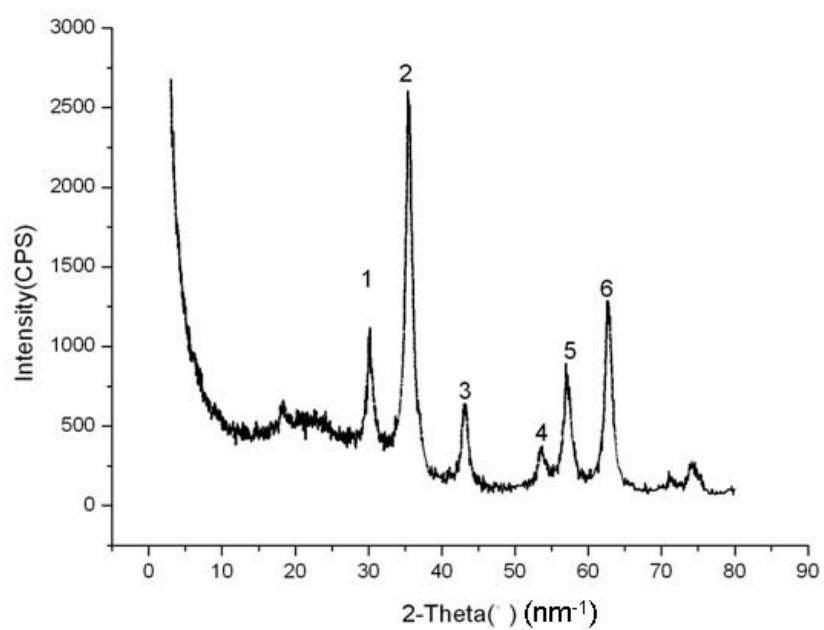
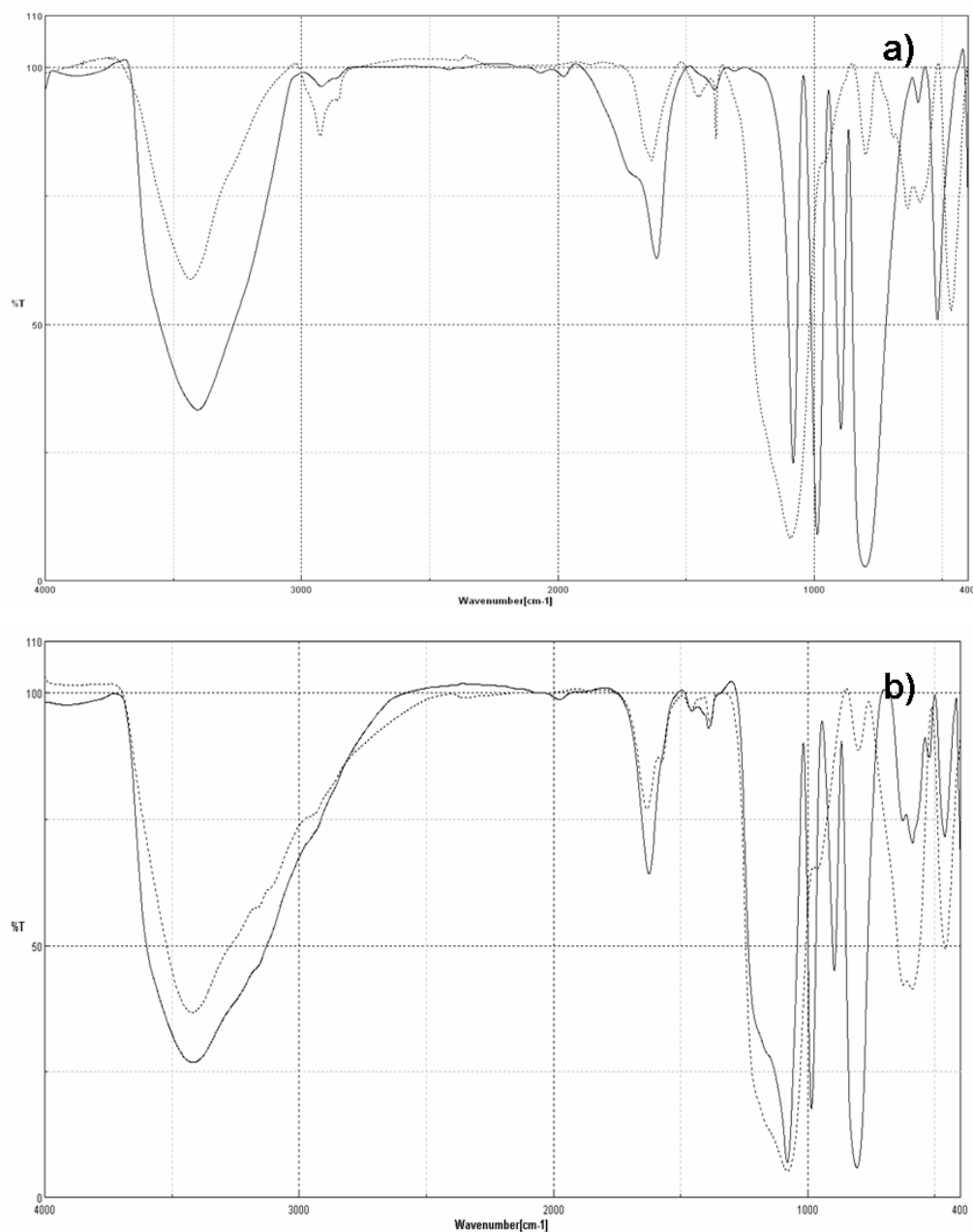


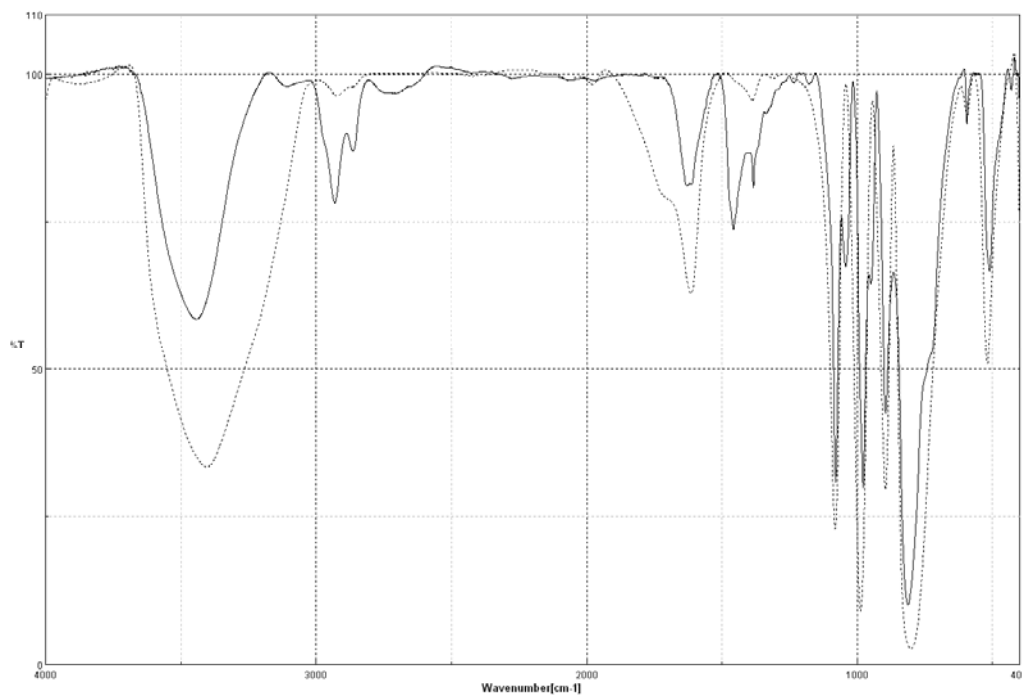
Fig S1. XRD pattern of magnetite nanoparticles.



(a) **MNP-1**(dash line), **MNP-1-PW** (solid line); (b) **MNP-2** (dash line), **MNP-2-PW** (solid line).

Fig. S2 IR spectrum of MNP-1, MNP-2, MNP-1-PW & MNP-2-PW.

The absorption band at 589 cm^{-1} is attributed to the Fe-O bonds. The silica coated particles have stretches at 1092 , 1632 and 3433 cm^{-1} corresponding to the Si-O-Si, and water stretches respectively. The absorption at 987 , 895 , 801 cm^{-1} were for POMs (**MNP-1-PW**, Figure S2, a). The same phenomenon was also appeared between **MNP-2** (Figure S2, b) and **MNP-2-PW** (Figure S2, b).



MNP-1-PW (dash line), MNP-1-PW-A (solid line);

Fig. S3 IR spectrum of MNP-1-PW-A

IR spectra indicated that additional stretches are attributed to the presence of the catalyst. Alkyl C-H stretches are found at 2931 and 2863 cm^{-1} . The amine C-N stretch is found at 1457 cm^{-1} .

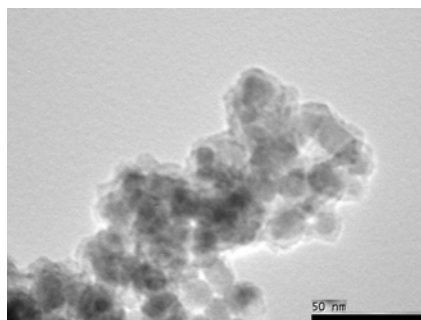
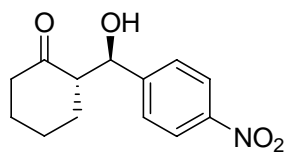


Fig. S4 TEM image of the MNP-1-PW-A.

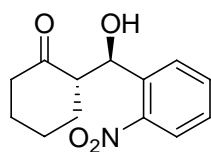
References in ESI:

1. A. Bee , R. Massart and S. Neveu, *J. Magn. Magn. Mater.* 1995, **149**, 6.
2. T.-J. Yoon, J. S. K., B. G. Kim, K. N. Yu, M.-H. Cho and J.-K. Lee, *Angew. Chem. Int. Ed.* 2005, **44**, 1068.
3. M. Shokouhimehr, Y. Piao, J. Kim, Y. Jang and T. Hyeon, *Angew. Chem. Int. Ed.* 2007, **46**, 7039.
4. (a) T. Okuhara, T. Nishimura, H. Watanabe and M. Misono, *J. Mol. Catal.* 1992, **74**, 247; (b) M. Misono and T. Okuhara, *Chemtech.* 1993, November, 23; (c) H. Soeda, T. Okuhara and M. Misono, *Chem. Lett.* 1994, **5**, 909; (d) T. Okuhara, T. Nishimura, K. Ohashi and M. Misono, *Chem. Lett.* 1990, 1201; (e) Y. Izumi, M. Ogawa, W. Nohara and K. Urabe, *Chem. Lett.* 1992, 1987.
5. For examples, see: (a) S. Samanta, J. Liu, R. Dodda, C and G. Zhao, *Org. Lett.* 2005, **7**, 5321; (b) L. Q. Gu, M. L. Yu, X. Y. Wu, Y. Z. Zhang and G. Zhao, *Adv. Synth. Catal.* 2006, **348**, 2223; (c) J. R. Chen, H. H. Lu, X. Y. Li, L. Chen, J. Wan and W. J. Xiao, *Org. Lett.* 2005, **7**, 4543; (d) Y. Y. Wu, Y. Z. Zhang, M. L. Yu, G. S. Zhao and W. Wang, *Org. Lett.* 2006, **8**, 4417; (e) N. Mase, F. Tanaka and C. F. III. Barbas, *Angew. Chem. Int. Ed.* 2004, **43**, 2420.
6. (a) S. Z. Luo, H. Xu, J. Y. Li, L. Zhang and J.-P. Cheng, *J. Am. Chem. Soc.* 2007, **129**, 3074; b) S. Z. Luo, H. Xu, L. Zhang, J. Y. Li and J.-P. Cheng, *Org. Lett.* 2008, **10**, 653.

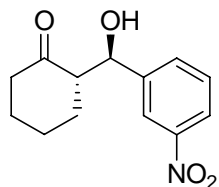
HPLC conditions



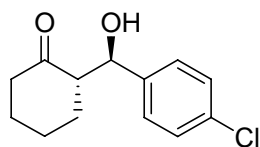
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: Hexane = 20:80), 25°C, 0.5 mL/min; anti: $t_R = 24.50$ (major), $t_R = 31.21$ (minor); syn: $t_R = 21.14$ (minor), $t_R = 24.75$ (major).



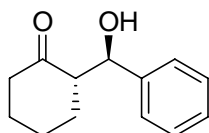
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: Hexane = 5:95), 25°C, 1.0 mL/min; anti: $t_R = 42.65$ (major), $t_R = 45.42$ (minor); syn: $t_R = 21.14$ (minor), $t_R = 24.75$ (major).



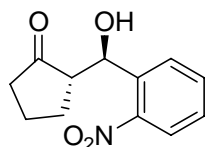
The enantiomeric excess was determined by HPLC with an AS-H column at 254 nm (2-propanol: Hexane = 5:95), 25°C, 0.8 mL/min; anti: $t_R = 57.84$ (major), $t_R = 65.30$ (minor); syn: $t_R = 39.10$ (minor), $t_R = 48.08$ (major).



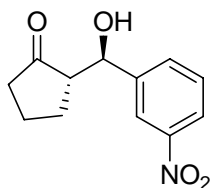
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: Hexane = 10:90), 25°C, 0.5 mL/min; anti: $t_R = 29.81$ (minor), $t_R = 33.80$ (major); syn: $t_R = 19.68$ (minor), $t_R = 22.75$ (major).



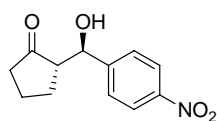
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: Hexane = 10:90), 25°C, 0.8 mL/min; anti: $t_R = 18.08$ (major), $t_R = 20.14$ (minor); syn: $t_R = 14.72$ (minor), $t_R = 17.11$ (major).



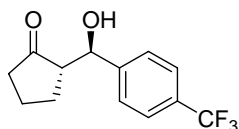
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: Hexane = 5:95), 25°C, 1.0 mL/min; anti: $t_R = 30.48$ (major), $t_R = 33.23$ (minor); syn: $t_R = 21.15$ (minor), $t_R = 24.76$ (major).



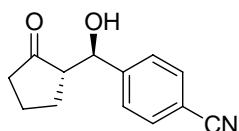
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: Hexane = 5:95), 25°C, 1.0 mL/min; anti: $t_R = 35.44$ (major), $t_R = 53.10$ (minor); syn: $t_R = 25.95$ (minor), $t_R = 29.67$ (major).



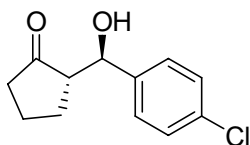
The enantiomeric excess was determined by HPLC with an AS-H column at 254 nm (2-propanol: Hexane = 10:90), 25°C, 0.8 mL/min; anti: $t_R = 45.69$ (major), $t_R = 58.11$ (minor).



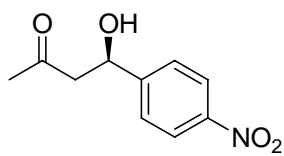
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: Hexane = 5:95), 25°C, 1.0 mL/min; anti: $t_R = 14.495$ (major), $t_R = 16.15$ (minor); syn: $t_R = 9.03$ (minor), $t_R = 11.08$ (major).



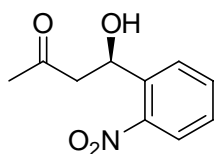
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: Hexane = 5:95), 25°C, 1.0mL/min; anti: $t_R = 47.87$ (major), $t_R = 50.50$ (minor); syn: $t_R = 27.80$ (minor), $t_R = 35.74$ (major).



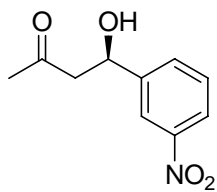
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: Hexane = 5:95), 25°C, 1.0 mL/min; anti: $t_R = 14.21$ (major), $t_R = 16.73$ (minor); syn: $t_R = 8.10$ (minor), $t_R = 11.20$ (major).



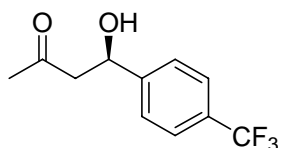
The enantiomeric excess was determined by HPLC with an AS-H column at 254 nm (2-propanol: Hexane = 30:70), 25°C, 0.5 mL/min; $t_R = 24.26$ (minor), $t_R = 32.63$ (major).



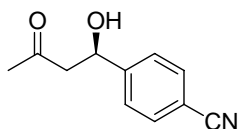
enantiomeric excess was determined by HPLC with an AS-H column at 254 nm (2-propanol: Hexane = 30:70), 25°C, 0.8mL/min; $t_R = 10.46$ (minor), $t_R = 13.75$ (major).



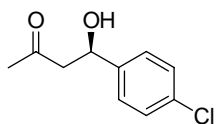
The enantiomeric excess was determined by HPLC with an OJ-H column at 254 nm (2-propanol: Hexane = 30:70), 25°C, 0.5 mL/min; $t_R = 33.33$ (major), $t_R = 38.26$ (minor).



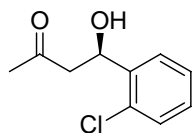
The enantiomeric excess was determined by HPLC with an AS-H column at 254 nm (2-propanol: Hexane = 20:80), 25°C, 0.5 mL/min; $t_R = 12.32$ (major), $t_R = 14.58$ (minor).



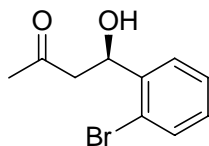
The enantiomeric excess was determined by HPLC with an AS-H column at 254 nm (2-propanol: Hexane = 30:70), 25°C, 0.5 mL/min; $t_R = 22.39$ (major), $t_R = 41.18$ (minor).



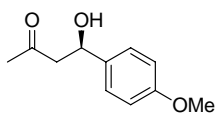
The enantiomeric excess was determined by HPLC with an AS-H column at 254 nm (2-propanol: Hexane = 10:90), 25°C, 0.8 mL/min; $t_R = 10.81$ (major), $t_R = 16.72$ (minor).



The enantiomeric excess was determined by HPLC with an AS-H column at 254 nm (2-propanol: Hexane = 10:90), 25°C, 0.5 mL/min; $t_R = 25.56$ (major), $t_R = 37.47$ (minor).

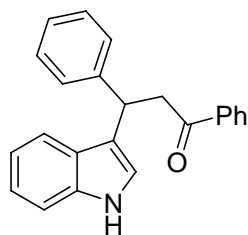


The enantiomeric excess was determined by HPLC with an AS-H column at 254 nm (2-propanol: Hexane = 25:75), 25°C, 0.8 mL/min; $t_R = 9.11$ (minor), $t_R = 11.48$ (major).

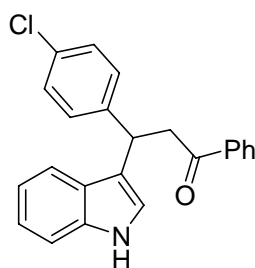


The enantiomeric excess was determined by HPLC with an AS-H column at 254 nm (2-propanol: Hexane = 10:90), 25°C, 0.8 mL/min; $t_R = 39.85$ (major), $t_R = 45.41$ (minor).

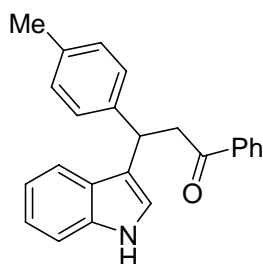
NMR Data:



^1H NMR (300 MHz, CDCl_3): δ 3.64-3.78 (2H, m), 5.05 (1H, t), 6.91-7.51 (14H, m), 7.90 (3H, m); ^{13}C NMR (CDCl_3 , 75 MHz): δ 38.3, 45.3, 111.1, 119.3, 119.4, 121.4, 122.1, 126.2, 127.8, 128.1, 128.4, 128.5, 132.9, 136.6, 137.2, 144.2, 198.6.

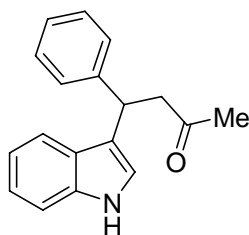


^1H NMR (300 MHz, CDCl_3): δ 3.64-3.83 (2H, m), 5.04 (1H, t), 6.91-7.51 (13H, m), 7.90 (3H, m); ^{13}C NMR (CDCl_3 , 75 MHz): δ 37.7, 45.0, 111.1, 119.0, 119.4, 119.5, 121.3, 122.3, 126.4, 128.0, 128.5, 129.2, 131.9, 133.0, 136.7, 137.1, 142.7, 198.1.

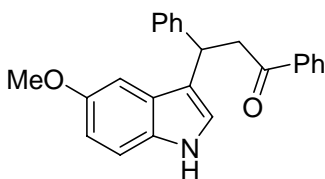


^1H NMR (300 MHz, CDCl_3): δ 2.26 (3H, s), 3.69-3.82 (2H, m), 5.01 (1H, t), 6.92-7.42 (13H, m), 7.89 (3H, m); ^{13}C NMR (CDCl_3 , 75 MHz): δ 20.9, 37.9, 45.3, 111.1, 119.3, 119.5, 121.4, 122.0, 127.6, 128.1, 128.5, 129.1, 132.9, 135.7, 136.7,

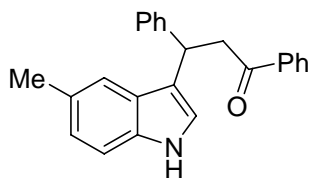
137.2, 141.2, 198.7.



^1H NMR (300 MHz, CDCl_3): δ 2.06 (3H, s), 3.10-3.27 (2H, m), 4.82 (1H, t), 6.92-7.43 (10H, m), 8.07 (1H, s); ^{13}C NMR (CDCl_3 , 75 MHz): δ 30.2, 38.4, 50.3, 111.2, 118.8, 119.4, 121.4, 122.1, 126.3, 126.5, 127.7, 128.4, 136.6, 144.0, 207.5.

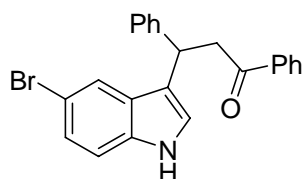


^1H NMR (300 MHz, CDCl_3): δ 3.64-3.81 (5H, m), 5.00 (1H, t), 6.92-7.43 (12H, m), 7.89-7.91 (3H, m); ^{13}C NMR (CDCl_3 , 75 MHz): δ 38.2, 45.2, 55.8, 101.5, 111.8, 112.1, 118.9, 122.2, 126.3, 127.1, 127.8, 128.1, 128.4, 128.6, 131.8, 133.0, 137.2, 144.2, 153.8, 198.8.

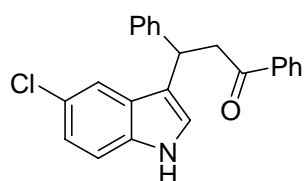


^1H NMR (300 MHz, CDCl_3): δ 2.36 (3H, s), 3.66-3.82 (2H, m), 5.03 (1H, t), 6.91-7.52 (12H, m), 7.90-7.93 (3H, m); ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.4, 38.2, 45.3, 110.7, 119.1, 121.6, 123.8, 126.2, 127.8, 128.0, 128.4, 128.5, 132.9, 144.2,

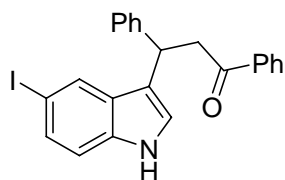
198.5.



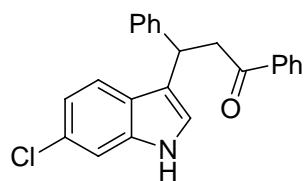
^1H NMR (300 MHz, CDCl_3): δ 3.63-3.80 (2H, m), 4.98 (1H, t), 6.95-7.52 (12H, m), 7.90-8.05 (3H, m); ^{13}C NMR (CDCl_3 , 75 MHz): δ 38.1, 45.2, 112.5, 112.7, 118.9, 122.0, 122.6, 125.0, 126.5, 127.7, 128.0, 128.4, 128.5, 128.6, 133.0, 135.2, 137.0, 143.8, 198.2.



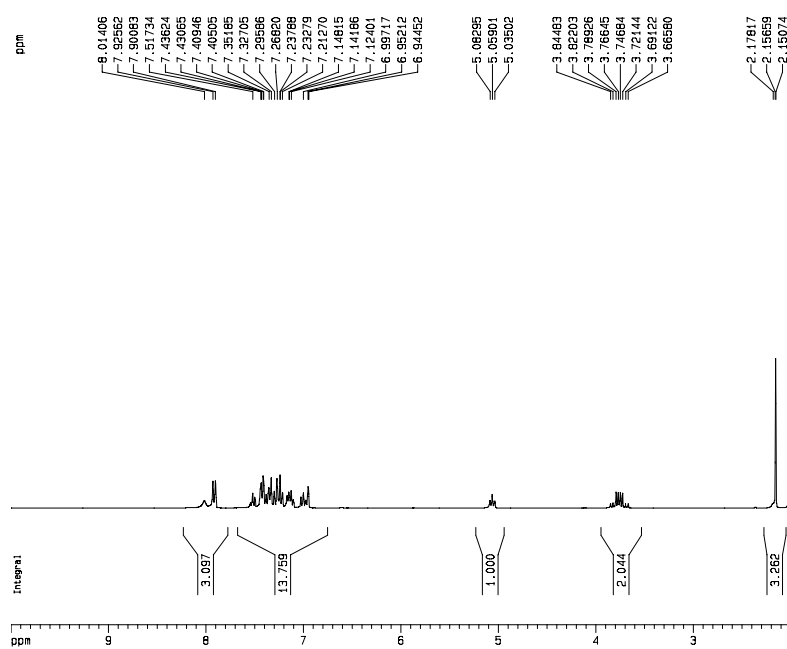
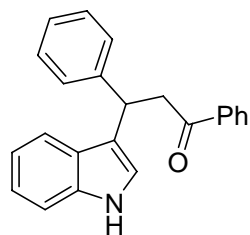
^1H NMR (300 MHz, CDCl_3): δ 3.63-3.80 (2H, m), 4.98 (1H, t), 6.96-7.58 (12H, m), 7.89-8.03 (3H, m); ^{13}C NMR (CDCl_3 , 75 MHz): δ 38.1, 45.2, 112.1, 118.9, 122.5, 122.8, 125.1, 126.5, 127.7, 128.1, 128.5, 128.6, 133.1, 134.9, 137.6, 143.8, 198.4.



^1H NMR (300 MHz, CDCl_3): δ 3.61-3.77 (2H, m), 4.96 (1H, t), 6.985-7.54 (12H, m), 7.73-8.05 (3H, m); ^{13}C NMR (CDCl_3 , 75 MHz): δ 38.0, 45.3, 82.9, 113.1, 118.5, 122.3, 126.5, 127.7, 128.1, 128.2, 128.6, 129.2, 130.5, 133.1, 135.6, 137.0, 143.8, 198.5.



^1H NMR (300 MHz, CDCl_3): δ 3.63-3.82 (2H, m), 5.01 (1H, t), 6.93-7.53 (12H, m),
7.90-7.92 (3H, m); ^{13}C NMR (CDCl_3 , 75 MHz): δ 38.1, 45.1, 111.0, 119.0, 120.1,
120.4, 121.9, 125.7, 126.4, 127.7, 128.0, 128.5, 128.6, 133.0, 136.9, 144.0, 198.4.



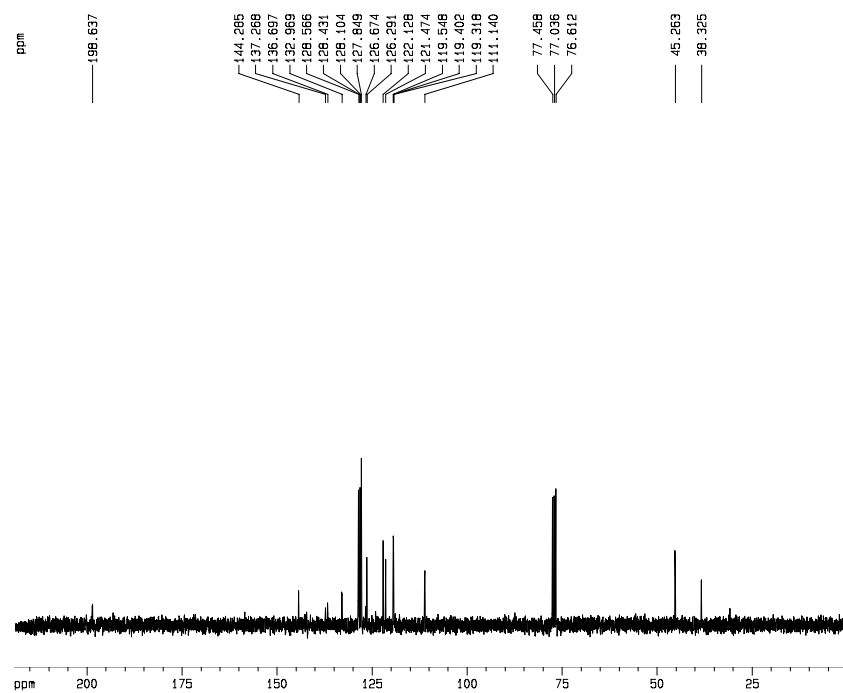
Current Data Parameters
 NAME ZX-08-162-1
 EXPNO 20
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080722
 Time 15.50
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 9
 DS 0
 SWH 8992.806 Hz
 FIDRES 0.137219 Hz
 AQ 3.6438615 sec
 RG 143.7
 DM 55.600 usec
 DE 5.00 usec
 TE 300.5 K
 D1 1.0000000 sec
 MCREST 0.0000000 sec
 MCHWK 0.0150000 sec

----- CHANNEL f1 -----
 NUC1 1H
 P1 7.00 usec
 PL1 -1.00 dB
 SF01 300.1324010 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300141 MHz
 WDM EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 4.00 cm
 FIP 10.000 ppm
 F1 3001.30 Hz
 F2 2.000 ppm
 F3 800.25 Hz
 PPMCM 0.40000 ppm/cm
 HZCM 120.08200 Hz/cm



Current Data Parameters
 NAME ZX-08-162-1
 EXPNO 21
 PROCNO 1

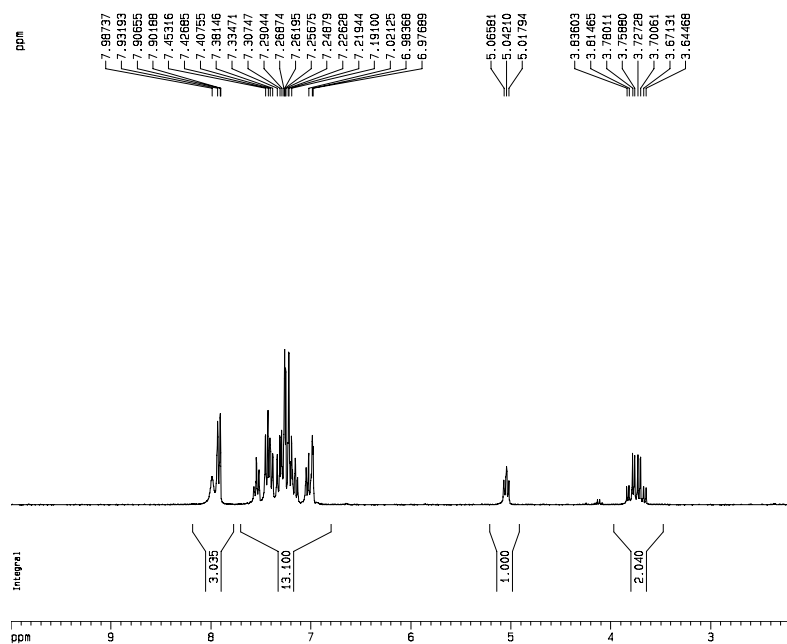
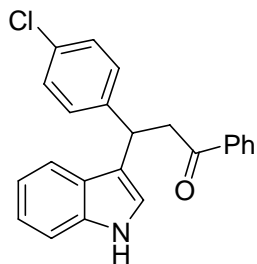
F2 - Acquisition Parameters
 Date_ 20080722
 Time 15.52
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 50
 DS 4
 SWH 17986.811 Hz
 FIDRES 0.274458 Hz
 AQ 1.8219508 sec
 RG 456.1
 DM 27.800 usec
 DE 6.00 usec
 TE 301.0 K
 D1 2.0000000 sec
 S11 0.1300000 sec
 DELTA 1.8999999 sec
 MCREST 0.0000000 sec
 MCHWK 0.0150000 sec

----- CHANNEL f1 -----
 NUC1 13C
 P1 12.50 usec
 PL1 2.00 dB
 SF01 75.4752953 MHz

----- CHANNEL f2 -----
 CPDPRG2 waltz16
 NUC2 1H
 P2PRG2 80.00 usec
 PL2 -1.00 dB
 PL12 20.15 dB
 PL13 15.98 dB
 SF02 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677480 MHz
 WDM EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 4.00 cm
 FIP 220.000 ppm
 F1 16602.80 Hz
 F2 0.000 ppm
 F3 0.00 Hz
 PPMCM 11.66000 ppm/cm
 HZCM 830.14520 Hz/cm



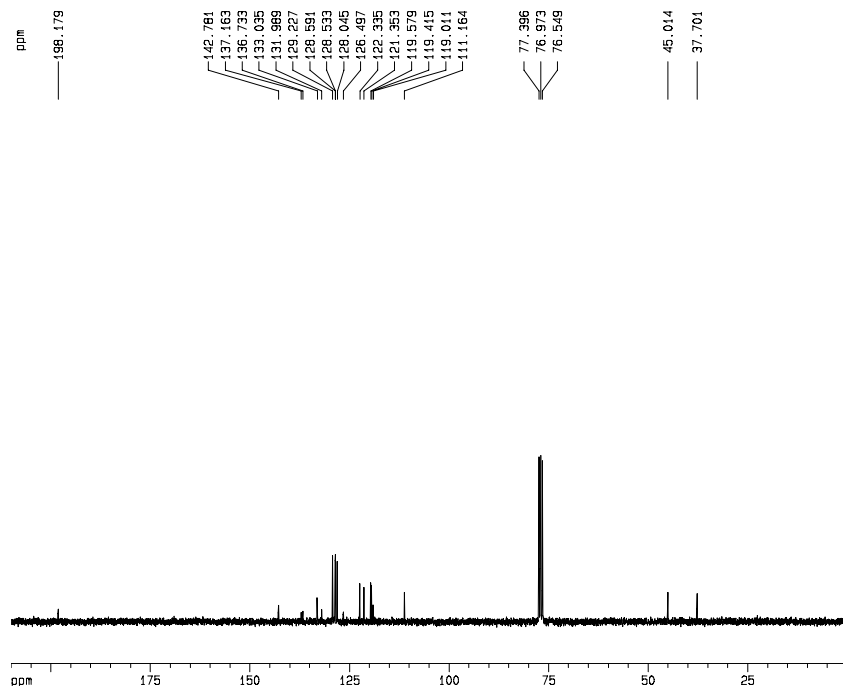
Current Data Parameters
 NAME ZX-08-162-2
 EXPNO 20
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080722
 Time 16.59
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 9
 DS 0
 SWH 8992.806 Hz
 FIDRES 0.137219 Hz
 AQ 3.6438515 sec
 RG 352
 DM 55.600 usec
 DE 6.00 usec
 TE 301.2 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCHWK 0.01500000 sec

***** CHANNEL f1 *****
 NUC1 1H
 P1 7.00 usec
 PL1 -1.00 dB
 SF01 300.1324010 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300091 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 4.00 cm
 F1P 10.000 ppm
 F1 3001.30 Hz
 F2P 2.200 ppm
 F2 660.29 Hz
 PPMCH 0.39000 ppm/cm
 HZCM 117.05070 Hz/cm



Current Data Parameters
 NAME ZX-08-162-2
 EXPNO 30
 PROCNO 1

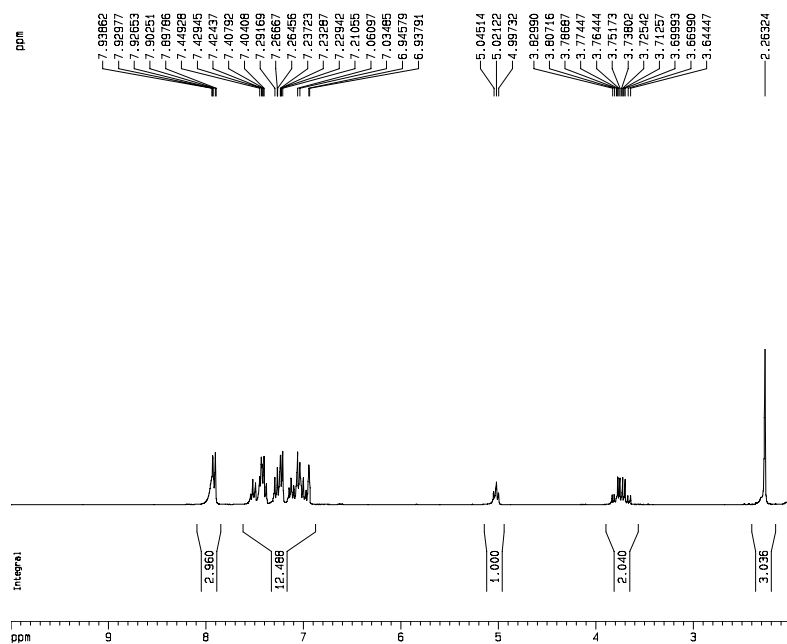
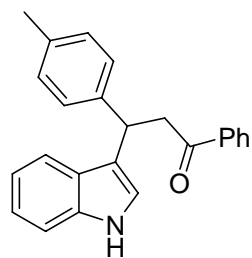
F2 - Acquisition Parameters
 Date_ 20080722
 Time 20.59
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 239
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219209 sec
 RG 812.7
 DM 27.900 usec
 DE 6.00 usec
 TE 301.5 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999999 sec
 MCREST 0.00000000 sec
 MCHWK 0.01500000 sec

***** CHANNEL f1 *****
 NUC1 13C
 P1 12.50 usec
 PL1 2.00 dB
 SF01 75.4752953 MHz

***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -1.00 dB
 PL12 20.16 dB
 PL13 15.98 dB
 SF02 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677490 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 4.00 cm
 F1P 210.000 ppm
 F1 15848.23 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCH 10.50000 ppm/cm
 HZCM 792.41138 Hz/cm



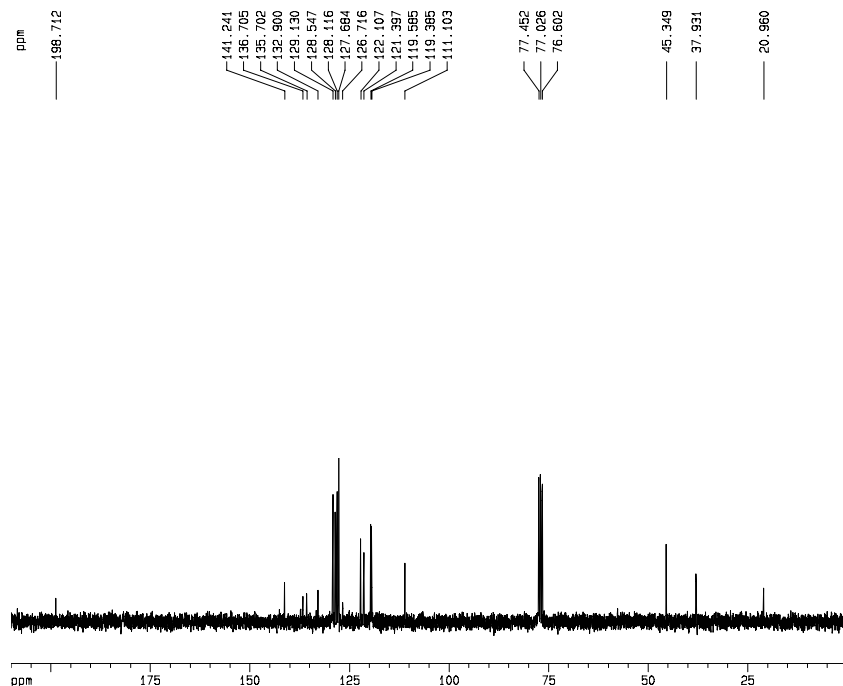
Current Data Parameters
 NAME ZX-08-162-4
 EXPNO 20
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080725
 Time 9.04
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zg30
 TD 69936
 SOLVENT CDCl3
 NS 12
 DS 0
 SWH 8992.806 Hz
 FIDRES 0.137219 Hz
 AQ 3.5438515 sec
 RG 161.3
 DM 55.600 usec
 DE 6.00 usec
 TE 300.4 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCHWK 0.01500000 sec

***** CHANNEL f1 *****
 NUC1 1H
 P1 7.00 usec
 PL1 -1.00 dB
 SFO1 300.1324010 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300148 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 4.00 cm
 F1P 10.000 ppm
 F1 3001.30 Hz
 F2P 2.000 ppm
 F2 600.26 Hz
 PPMCH 0.40000 ppm/cm
 HZCM 120.05200 Hz/cm



Current Data Parameters
 NAME ZX-08-162-4
 EXPNO 21
 PROCNO 1

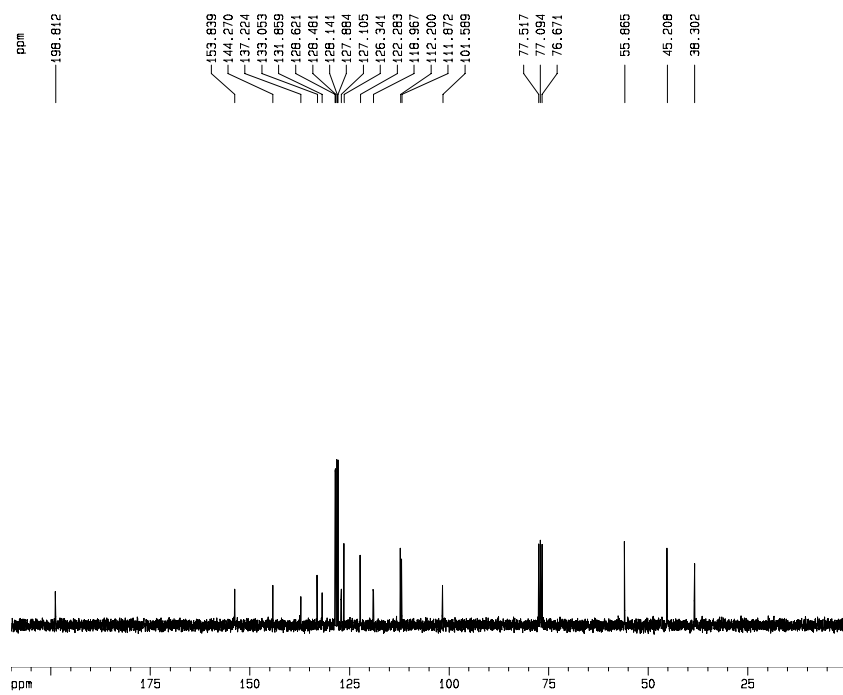
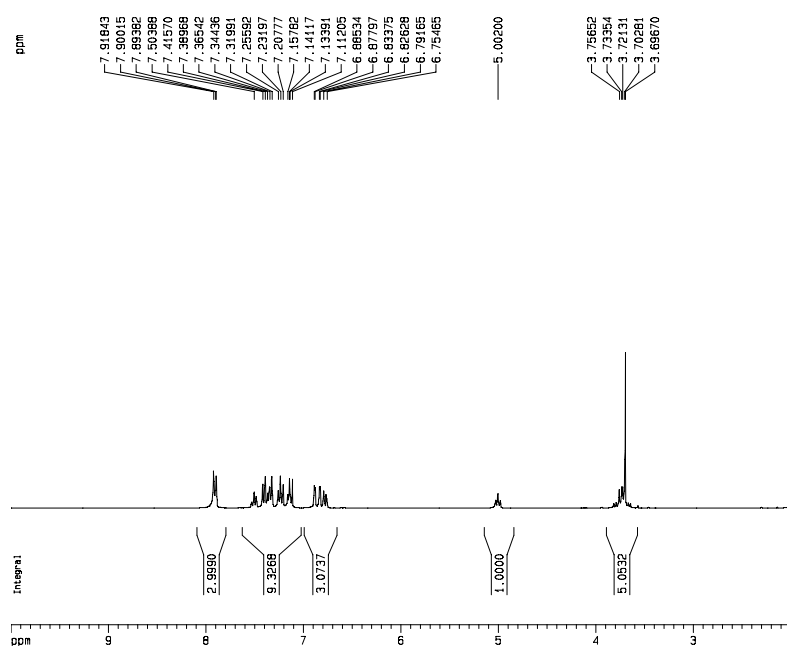
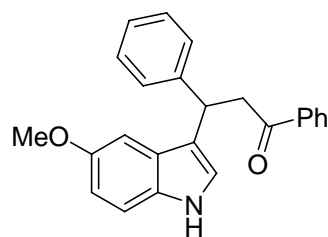
F2 - Acquisition Parameters
 Date_ 20080725
 Time 9.06
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zgpg30
 TD 65936
 SOLVENT CDCl3
 NS 64
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 456.1
 DM 27.900 usec
 DE 6.00 usec
 TE 300.6 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999999 sec
 MCREST 0.00000000 sec
 MCHWK 0.01500000 sec

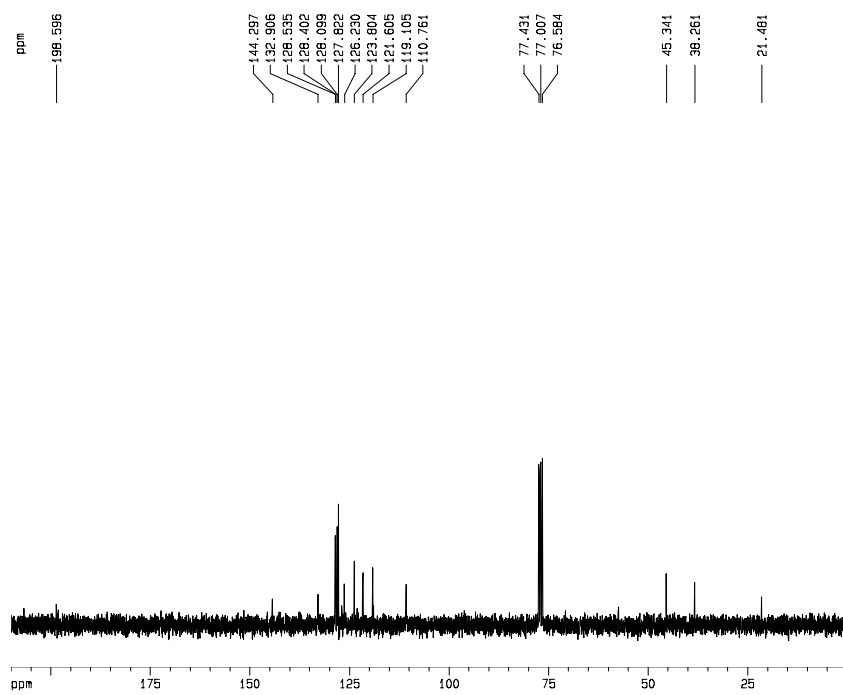
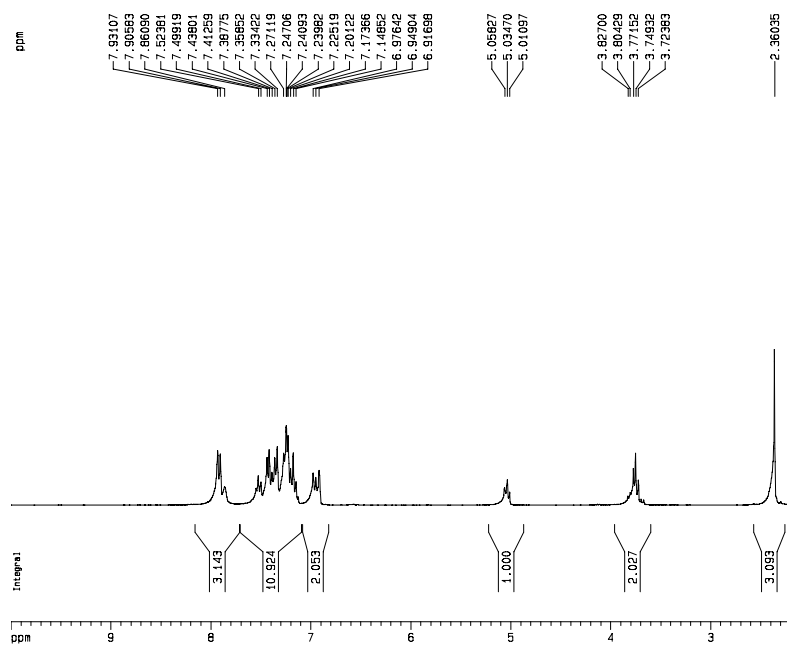
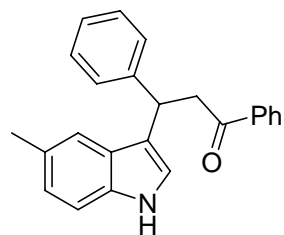
***** CHANNEL f1 *****
 NUC1 13C
 P1 12.50 usec
 PL1 2.00 dB
 SFO1 75.4752953 MHz

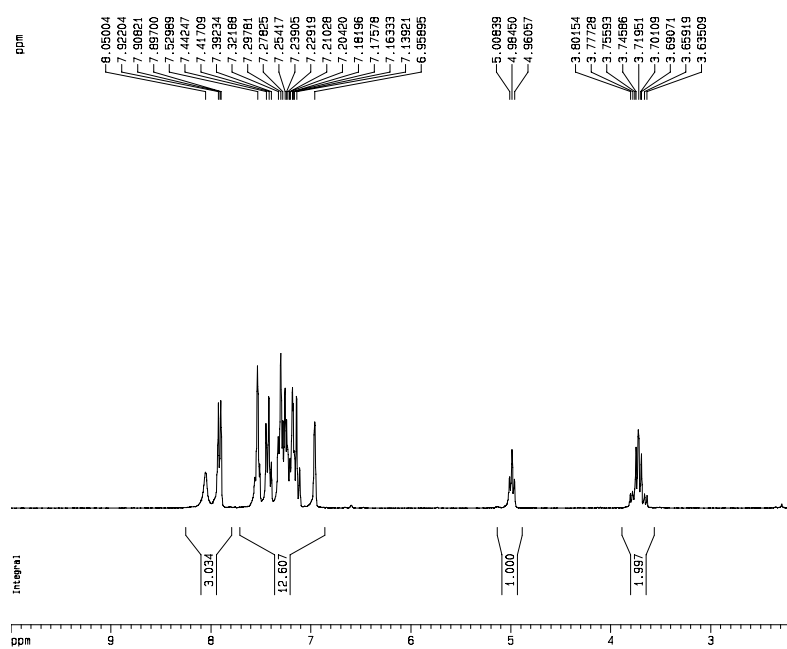
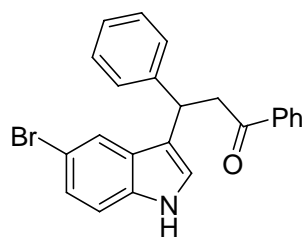
***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -1.00 dB
 PL12 20.16 dB
 PL13 15.38 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677490 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 4.00 cm
 F1P 210.000 ppm
 F1 15848.23 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCH 10.50000 ppm/cm
 HZCM 792.41138 Hz/cm







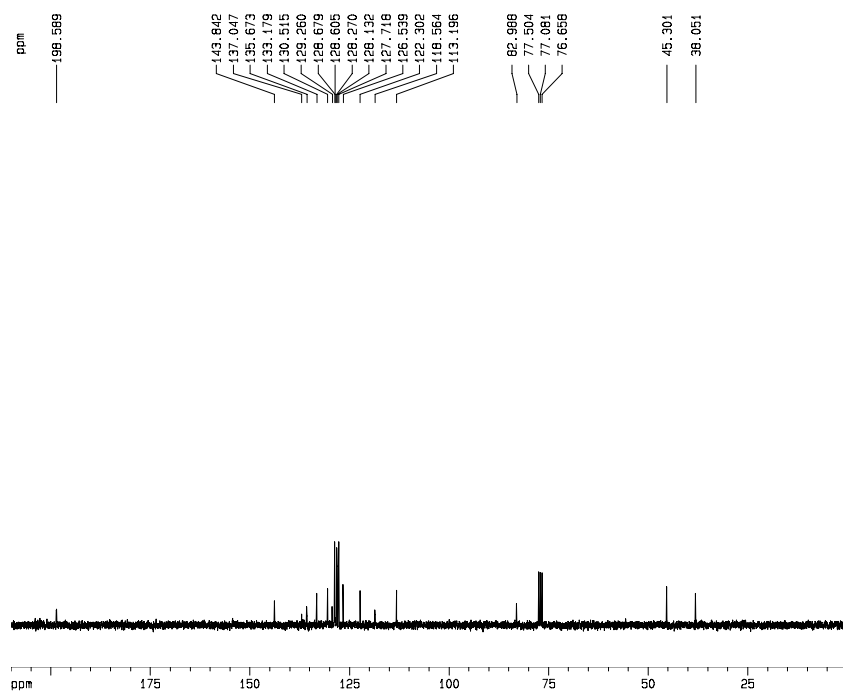
Current Data Parameters
NAME ZX-08-170-3
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080729
Time 15.25
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 3
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438615 sec
RG 203.2
DM 55.600 usec
DE 5.00 usec
TE 301.4 K
D1 1.0000000 sec
MCREST 0.0000000 sec
MORAK 0.0150000 sec

----- CHANNEL f1 -----
NUC1 1H
P1 7.00 usec
PL1 -1.00 dB
SF01 300.1324010 MHz

F2 - Processing parameters
SI 32768
SF 300.1300119 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 4.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P 2.200 ppm
F2 860.25 Hz
P0PCMH 0.35000 ppm/cm
HZCM 117.08070 Hz/cm



Current Data Parameters
NAME ZX-08-170-5
EXPNO 11
PROCNO 1

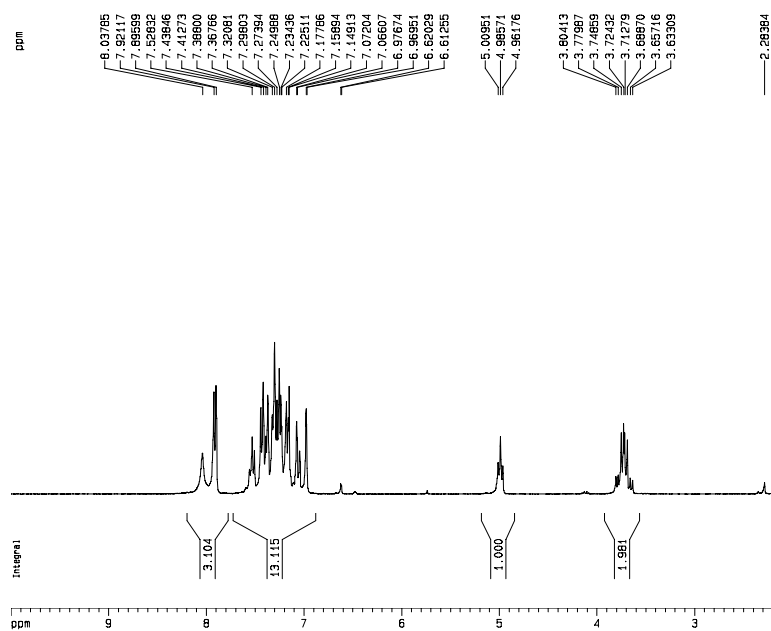
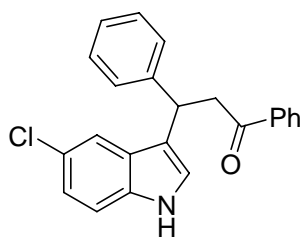
F2 - Acquisition Parameters
Date_ 20080729
Time 15.45
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 13
DS 4
SWH 17985.811 Hz
FIDRES 0.274458 Hz
AQ 1.8219508 sec
RG 456.1
DM 27.800 usec
DE 6.00 usec
TE 301.5 K
D1 2.0000000 sec
S11 0.0300000 sec
DELTA 1.8999999 sec
MCREST 0.0000000 sec
MORAK 0.0150000 sec

----- CHANNEL f1 -----
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SF01 75.4752953 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
P2P2 80.00 usec
PL2 -1.00 dB
PL12 20.15 dB
PL13 15.98 dB
SF02 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677430 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 2.00 cm
F1P 210.000 ppm
F1 15846.23 Hz
F2P 0.000 ppm
F2 0.00 Hz
P0PCMH 10.50000 ppm/cm
HZCM 792.41136 Hz/cm

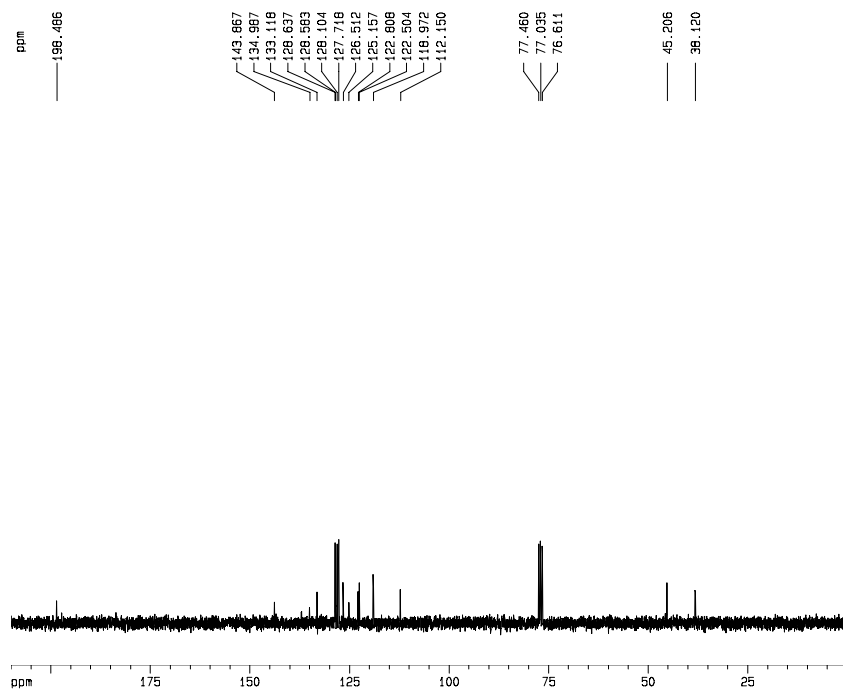


Current Data Parameters
 NAME ZXX-08-170-4
 EXPNO 10
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20080729
 Time 15.36
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 3
 DS 0
 SWH 8992.805 Hz
 FIDRES 0.137218 Hz
 AQ 3.6438615 sec
 RG 143.7
 DM 55.600 usec
 DE 5.00 usec
 TE 301.5 K
 D1 1.0000000 sec
 MCREST 0.0000000 sec
 MCHK 0.0150000 sec

***** CHANNEL f1 *****
 NUC1 1H
 P1 7.00 usec
 PL1 -1.00 dB
 SFO1 300.1324010 MHz

F2 - Processing parameters
 SI 32768
 SF 300.130130 MHz
 MDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 4.00 cm
 F1P 10.000 ppm
 F1 3001.30 Hz
 F2P 2.200 ppm
 F2 660.29 Hz
 PPMCM 0.39000 ppm/cm
 HZCM 117.05070 Hz/cm



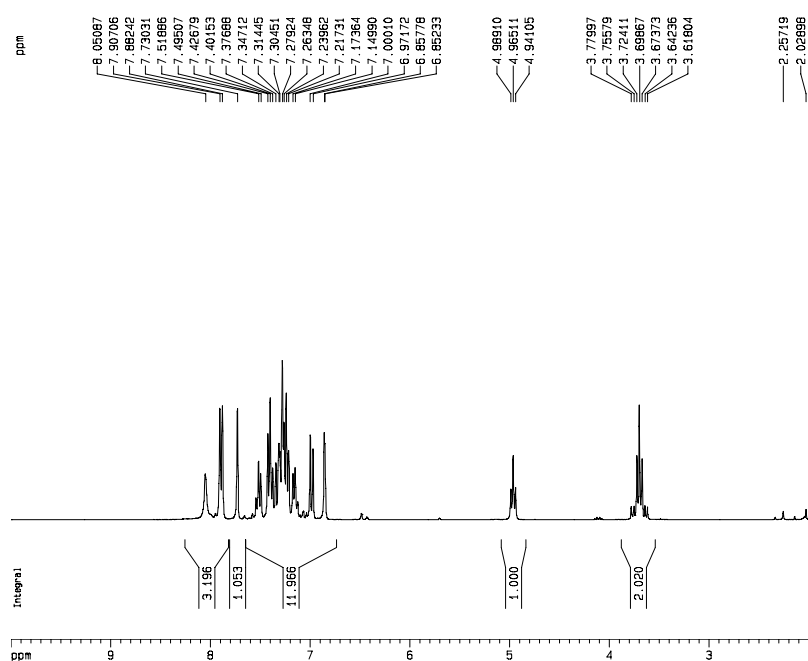
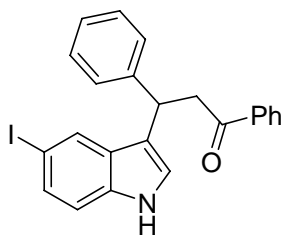
Current Data Parameters
 NAME ZXX-08-170-4
 EXPNO 11
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20080729
 Time 15.38
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 20
 DS 4
 SWH 17985.811 Hz
 FIDRES 0.274458 Hz
 AQ 1.0219508 sec
 RG 574.7
 DM 27.800 usec
 DE 6.00 usec
 TE 301.7 K
 D1 2.0000000 sec
 S11 0.1300000 sec
 DELTA 1.8999999 sec
 MCREST 0.0000000 sec
 MCHK 0.0150000 sec

***** CHANNEL f1 *****
 NUC1 13C
 P1 12.50 usec
 PL1 2.00 dB
 SFO1 75.4752953 MHz

***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 P2P2 80.00 usec
 PL2 -1.00 dB
 PL12 20.15 dB
 PL13 15.98 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.467430 MHz
 MDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 2.00 cm
 F1P 210.000 ppm
 F1 15846.03 Hz
 F2 0.000 ppm
 F2 0.00 Hz
 PPMCM 10.50000 ppm/cm
 HZCM 792.41136 Hz/cm



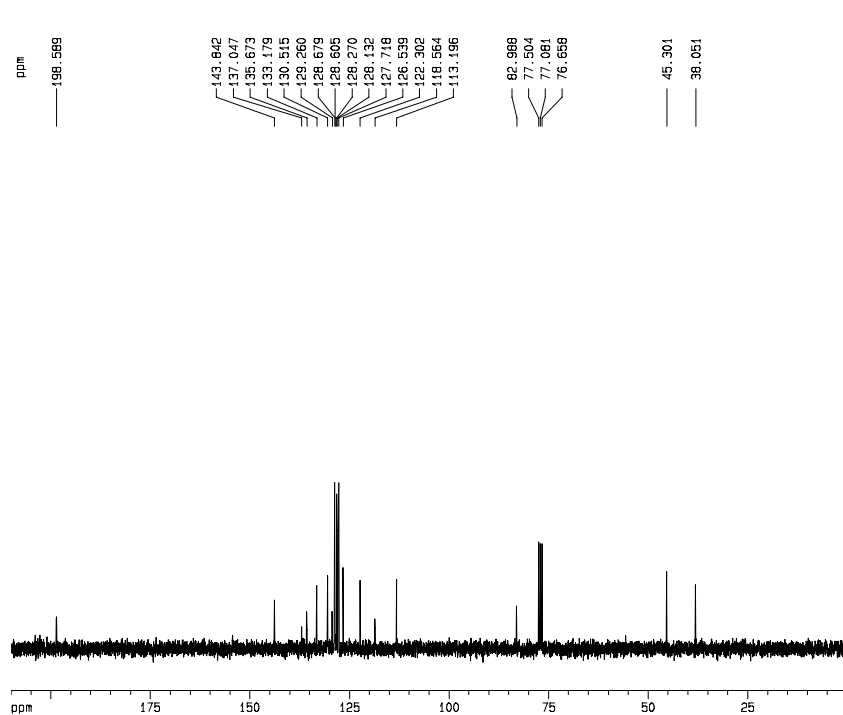
Current Data Parameters
 NAME ZXX-08-170-5
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080729
 Time 16.44
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zg30
 ID 62836
 SOLVENT CDCl3
 NS 4
 DS 0
 SWH 8992.806 Hz
 FIDRES 0.137219 Hz
 AQ 3.6439515 sec
 RG 114
 DW 58.600 usec
 DE 6.00 usec
 TE 301.2 K
 D1 1.0000000 sec
 MCREST 0.0000000 sec
 MCMRK 0.0150000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.00 usec
 PL1 -1.00 dB
 SFO1 300.1324010 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300179 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 4.00 cm
 FIP 10.000 ppm
 F1 3001.30 Hz
 F2P 2.000 ppm
 F2 600.26 Hz
 PPMCM 0.40000 ppm/cm
 HZCM 120.05200 Hz/cm



Current Data Parameters
 NAME ZXX-08-170-5
 EXPNO 11
 PROCNO 1

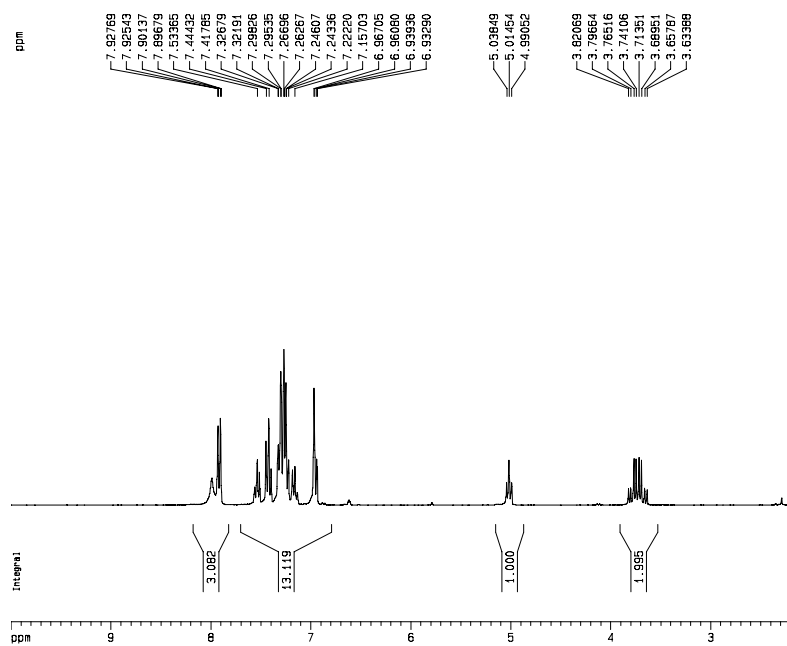
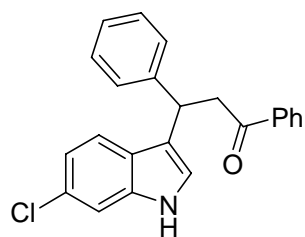
F2 - Acquisition Parameters
 Date_ 20080729
 Time 16.45
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zgpg30
 ID 62836
 SOLVENT CDCl3
 NS 13
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 456.1
 DW 27.800 usec
 DE 6.00 usec
 TE 301.5 K
 D1 2.0000000 sec
 d11 0.0300000 sec
 DELTA 1.8999999 sec
 MCREST 0.0000000 sec
 MCMRK 0.0150000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 12.50 usec
 PL1 2.00 dB
 SFO1 75.4752953 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -1.00 dB
 PL12 20.16 dB
 PL13 16.38 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677490 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 4.00 cm
 FIP 210.000 ppm
 F1 15848.23 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCM 10.50000 ppm/cm
 HZCM 792.41138 Hz/cm



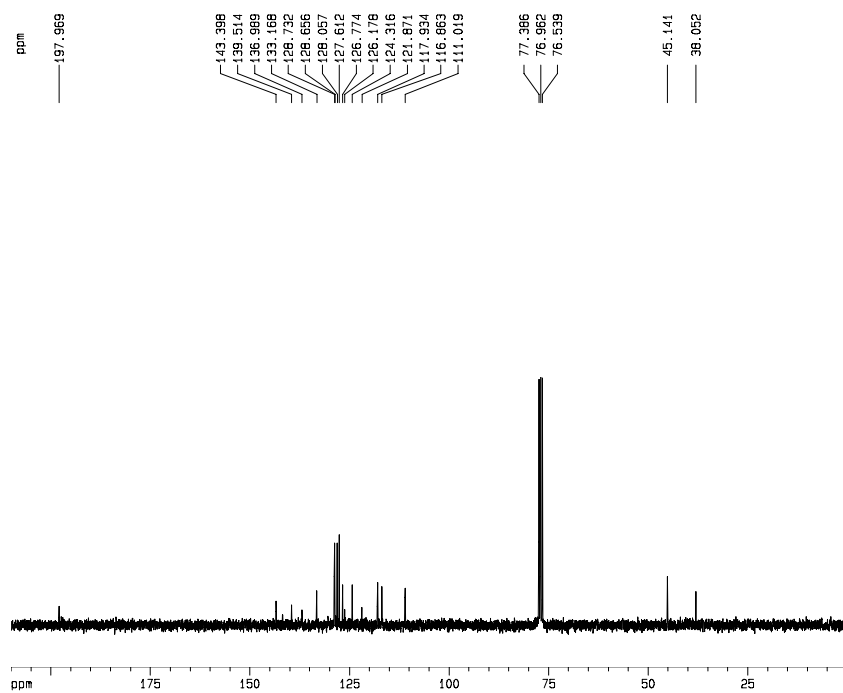
Current Data Parameters
 NAME ZX-08-170-6
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080729
 Time 15.51
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 5
 DS 0
 SWH 8992.806 Hz
 FIDRES 0.137219 Hz
 AQ 3.6438615 sec
 RG 203.2
 DM 55.600 usec
 DE 5.00 usec
 TE 301.0 K
 D1 1.0000000 sec
 MCREST 0.0000000 sec
 MCHWK 0.0150000 sec

----- CHANNEL f1 -----
 NUC1 1H
 P1 7.00 usec
 PL1 -1.00 dB
 SF01 300.1324010 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300106 MHz
 WDM EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 4.00 cm
 FIP 10.000 ppm
 F1 3001.30 Hz
 FAP 2.200 ppm
 F2 860.23 Hz
 PPMCM 0.35000 ppm/cm
 HZCM 117.08070 Hz/cm



Current Data Parameters
 NAME ZX-08-170-6
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20080730
 Time 14.57
 INSTRUM spect
 PROBHD 5 mm DUL 13C-1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 350
 DS 4
 SWH 17886.811 Hz
 FIDRES 0.274458 Hz
 AQ 1.8219508 sec
 RG 512
 DM 27.800 usec
 DE 6.00 usec
 TE 301.2 K
 D1 2.0000000 sec
 S11 0.0300000 sec
 DELTA 1.8999999 sec
 MCREST 0.0000000 sec
 MCHWK 0.0150000 sec

----- CHANNEL f1 -----
 NUC1 13C
 P1 12.50 usec
 PL1 2.00 dB
 SF01 75.4752953 MHz

----- CHANNEL f2 -----
 CPDPRG2 waltz16
 NUC2 1H
 P2P2 80.00 usec
 PL2 -1.00 dB
 PL12 20.15 dB
 PL13 15.98 dB
 SF02 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677480 MHz
 WDM EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 5.00 cm
 FIP 210.000 ppm
 F1 15846.23 Hz
 F2 0.000 ppm
 F2 0.00 Hz
 PPMCM 10.50000 ppm/cm
 HZCM 792.41136 Hz/cm