Supporting Information

Visible Light-Promoted Beckmann Rearrangements: Separating Sequential Photochemical and Thermal Phenomena in a Continuous Flow Reactor

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1. Details of the Flow Set-up

A Vapoutec® E-Series system was used as the flow set-up for the visible light-promoted Beckmann rearrangement (as shown in Figure S1). The UV-150^{TM} flow photoreactor (R_1), the heated coil reactor (R_2), pumps (*P1* and *P2*), two-way valves (*Val 1* and *Val 2*) and the back pressure regulator (*BPR*) are parts of the Vapourtec® system. PFA tubings (i.d. 0.8 mm, o.d. 1.6 mm) were used for the construction of the injection coils (L_1 and L_2) and for the connection of all parts downstream from the pumps. PFA tubings (i.d. 1.58 mm, o.d. 3.18 mm) were used for solvent and inlet of the pumps.

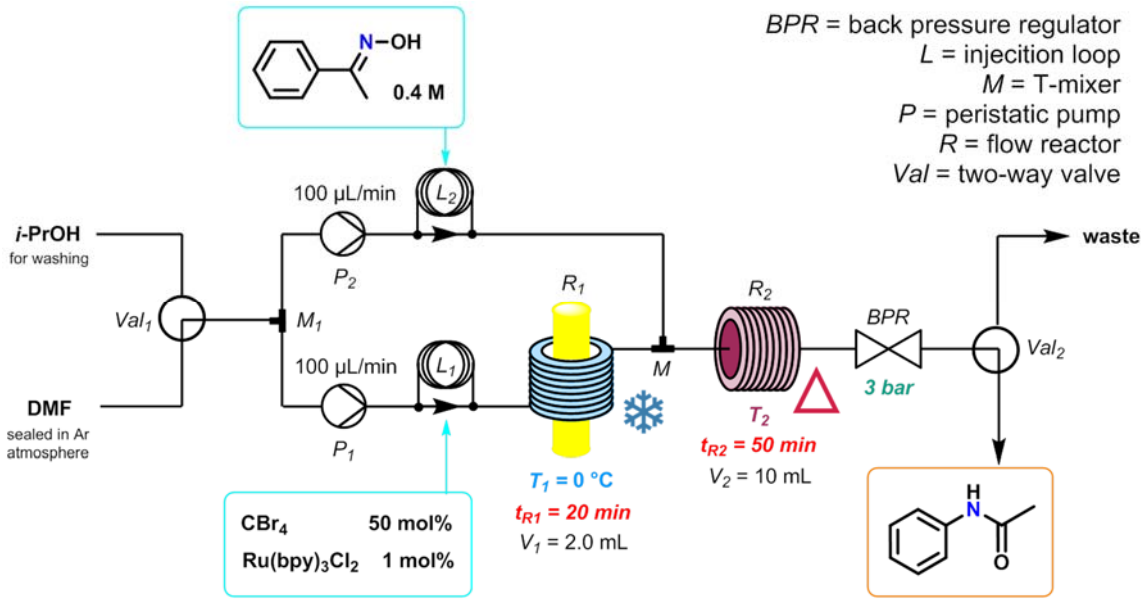


Figure S1: Complete lay-out of the flow set-up.

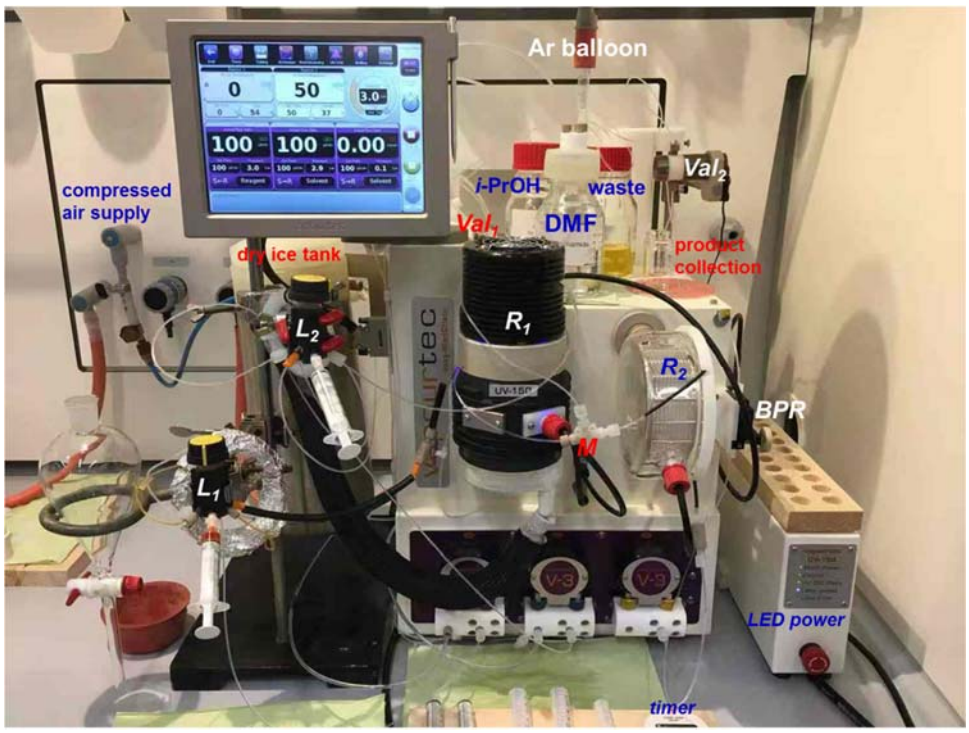


Figure S2: Photograph of the flow set-up (Vapoutec® E-Series system).

The entire flow system was purged with degassed DMF (Ar sparging for 30 min, sealed in Ar atmosphere) before tightening the *BPR*. After using the flow system, the *BPR* was loosened before washing with isopropanol (*i*-PrOH).

2. Construction of Chip Reactor

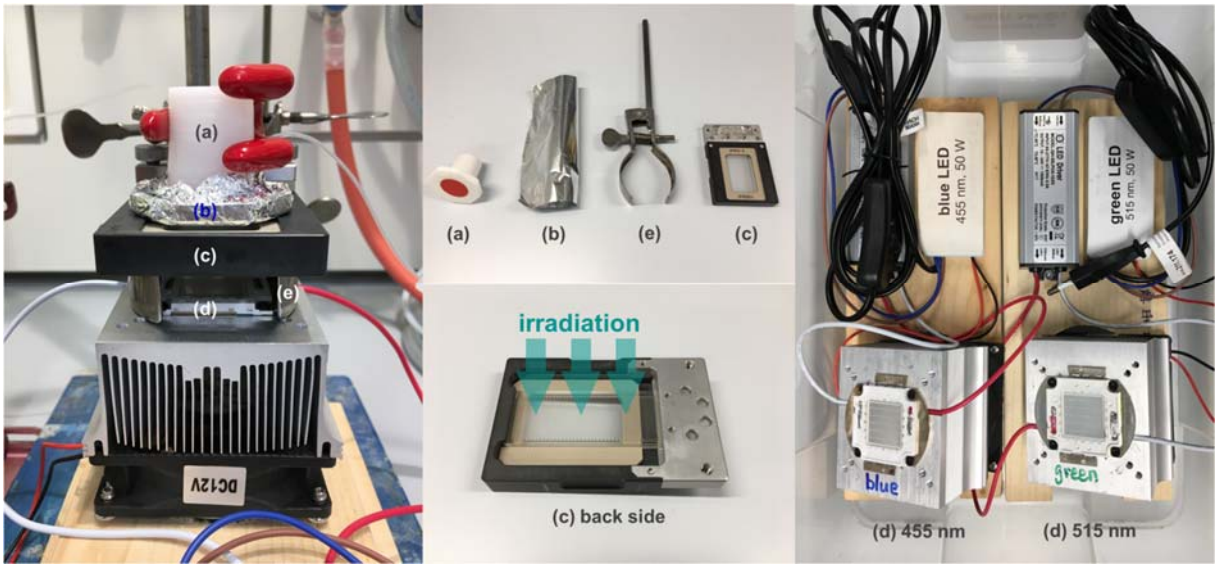


Figure S3: Photograph of all parts for the construction of reactor A and B: (a) plastic stopper; (b) aluminum foil; (c) Syrris ®1000 µL glass chip; (d) 50 W LED with cooler; (e) iron clamp used as spacer between glass chip and LED.

3. General Analytical Methods

NMR spectra were recorded on a 300 MHz instrument (75 MHz for ^{13}C). Chemical shifts (δ) are expressed in ppm downfield from TMS as internal standard. The letters s, d, t, q and m stand for singlet, doublet, triplet, quadruplet and multiplet.

HPLC analysis was carried out on a C18 reversed-phase (RP) analytical column (150 × 4.6 mm, particle size 5 µm) at 37 °C using a mobile phase A (water/MeCN 90:10 (v/v) + 0.1% TFA) and B (MeCN + 0.1% TFA) at a flow rate of 1.5 mL/min. The following gradient was applied: linear increase from solution 30% B to 100% B within 10 min.

GC-MS spectra were recorded using a ThermoFisher Focus GC coupled with a DSQ II (EI, 70 eV). A TR-5MS column (30 m × 0.25 mm × 0.25 µm) was used, with helium as carrier gas (1 mL•min^{-1} constant flow). The injector temperature was set to 280 °C. After 1 min at 50 °C, the temperature was increased by 25 °C•min^{-1} to 300 °C and kept at 300 °C for 3 min.

Emission spectra of the light sources were measured with Avantes® Startline™ AvaSpec-2048 spectrometer.

Carbon monoxide was detected using Chauvin Arnoux® C.A 895 carbon monoxide detector.

Melting points were determined on a Stuart™ SMP3 melting point apparatus.

4. Emission Spectra of the Light Sources

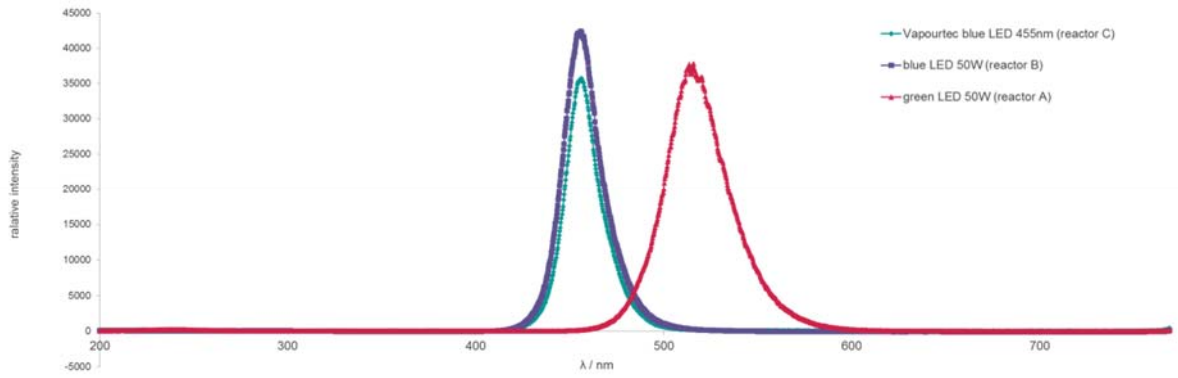
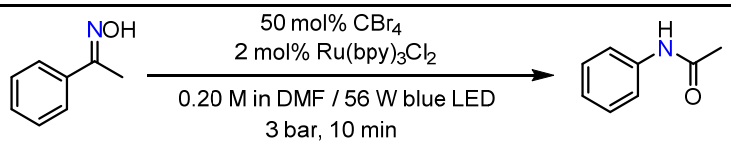


Figure S4: Emission spectra of the light sources.

5. Numeric Data of Figure 2

Table S1: Optimization of reaction temperature (numeric data of Figure 2).



1a **2a**

Entry	*T* / °C	1a / %	2a / %	CBr_4 / %
1	0	81	0	0
2	10	81	0	0
3	20	49	24	0
4	30	22	58	2
5	40	6	79	3
6	50	5	77	8
7	60	5	76	7
8	70	7	73	3

6. Quenching Experiment without Substrate

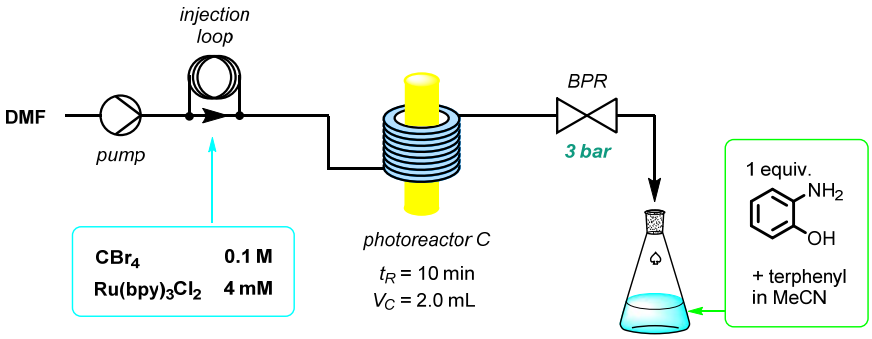


Figure S5: Flow set-up for the quenching experiment.

The flow set-up shown in Figure 1 was used for this experiment (Figure S5). After the stabilization of the temperature and pressure, 500 µL degassed solution was injected for each run. The discharge was collected with a 5 mL volumetric flask with 0.01 mmol *p*-terphenyl and 2-aminophenol (**16**), then diluted to 5.000 mL with acetonitrile for HPLC and GC-MS analysis.

Table S2: Results of the quenching experiment.[a]

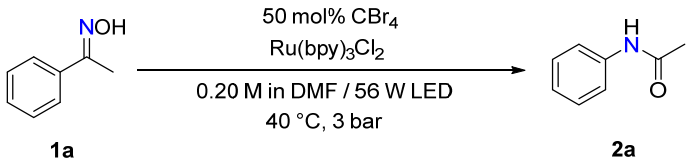
Entry	*T* / °C	Remained CBr_4 / % [b]
1	0	0
2	10	1
3	20	2
4	30	5
5	40	10

[a] The solution of reactants was degassed by Ar sparging for 15 min; 0.5 mL was injected for each run. [b] Determined by HPLC at 254 nm using *p*-terphenyl as internal standard.

The results (Table S2) showed that the conversion of CBr_4 favors low temperature, which is in accordance with Figure 2. A large increase of the triplet life time of Ru(II)* at low temperature (*J. Phys. Chem. A* **2004**, *108*, 9938) makes the quenching more effective. Benzoxazole (**17**) was detected from the samples of all entries; whereas no trace of benzoxazolidinone (**18**) was detected, indicating that bromophosgene (**15**) was not able to survive more than 10 min under the reaction condition.

7. Optimization of Reaction Time and Catalyst Loading

Table S3. Optimization of reaction time and catalyst loading.[a]



1a **2a**

Entry	Time [min]	Catalyst [mol%]	Molar fraction [%][b]		
			1a	**2a**	CBr_4[c]
1	5	2.0	21	58	13
2	7.5	2.0	16	64	10
3	10	2.0	6	79	3
4	15	2.0	5	75	0
5	20	2.0	5	70	0
6	10	1.0	13	71	13
7	20	1.0	3	77	5

[a] The solution of reactants was degassed by Ar sparging for 15 min; 0.5 mL was injected for each run. [b] Determined by HPLC at 254 nm using *p*-terphenyl as internal standard. [c] Unconverted CBr_4 in the reaction mixture.

The influence of reaction time and catalyst loading was investigated at 40 °C (Table S3). The conversion of **1a** stopped increasing when all CBr_4 was consumed (Table S3, entry 3-5), indicating a non-self-propagative mechanism. The reaction rate dropped when the catalyst loading was reduced to 1 mol% (Table S3, entry 6), but prolonging the reaction time to 20 min (Table S3, entry 7) is enough to compensate this conversion loss (Table S3, entry 3).

8. Attempt to Scavenge Bromophosgene

The reaction of Table 3 entry 1 was performed using 2-aminophenol (**16**) in place of oxime (**1a**) (Figure S6), in order to scavenge any trace of bromophosgene (**15**) in the reaction mixture.

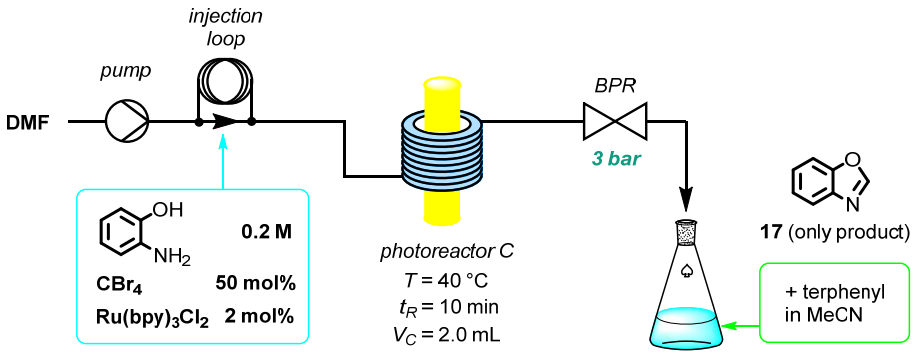


Figure S6: Flow setup for bromophosgene scavenging.

However, benzoxazolidinone (**18**), the condensation product with **15** (a carbonylating reagent), was not detected; this fact ruled out the possibility of OH-activation by **15** during the Beckmann rearrangement. The formation of benzoxazole (**17**) confirmed the presence of V-H reagent (**5A**, a formylating reagent) in the reaction mixture.

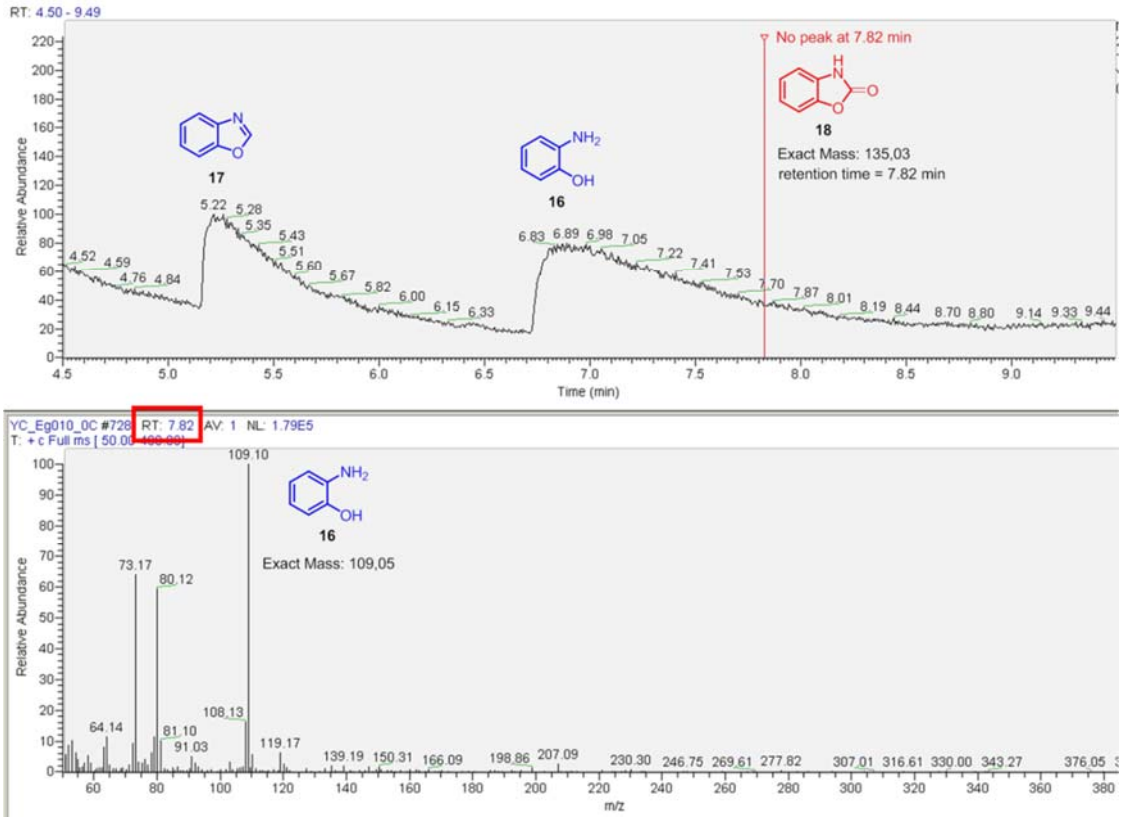


Figure S7: No peak corresponding benzoxazolone (**18**) was given by GC-MS analysis.

9. HPLC Examples

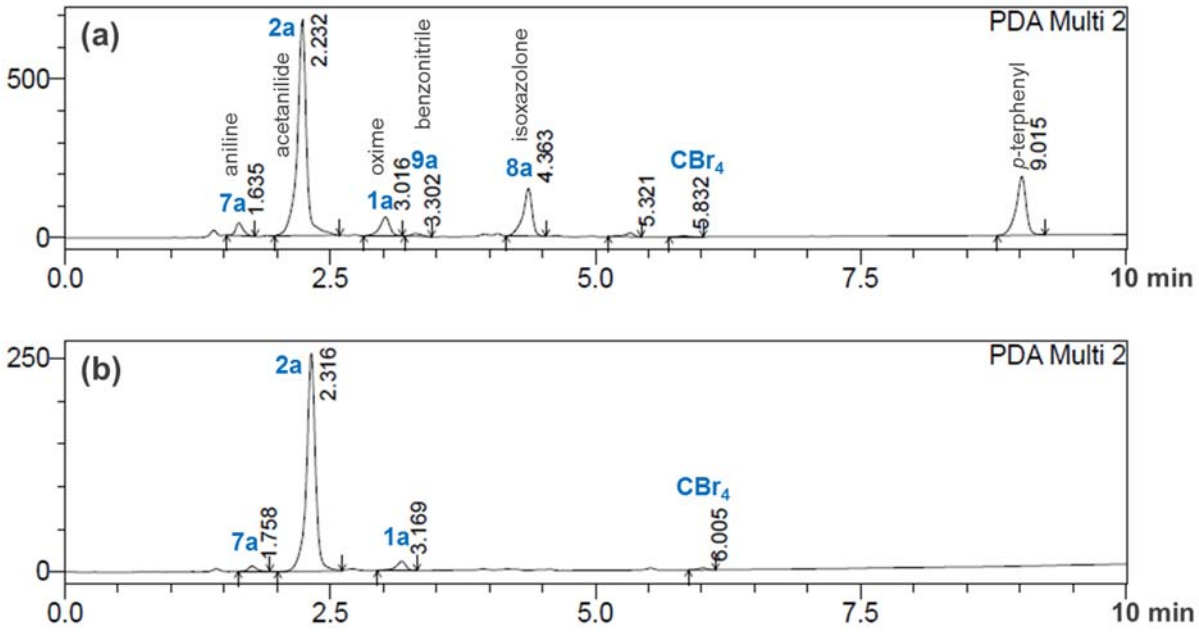
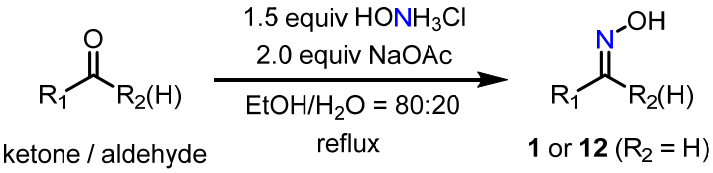


Figure S8: HPLC graphics of the best results from (a) one-pot flow reaction (Table 1, entry 5) and (b) two-step flow reaction (Table 4, entry 1).

10. Substrate Synthesis and Characterization



General Method I (for the Synthesis of Ketoximes) (**1**): 3282 mg (40 mmol) anhydrous NaOAc and 2084 mg (30 mmol) $HONH_3Cl$ were dissolved in 50 mL aqueous ethanol ($EtOH/H_2O$ = 80:20) in a 250 mL round bottomed flask; the mixture was stirred under room temperature. When all solid was dissolved, ketone (20 mmol) was added. The flask was then fitted with a reflux condenser and heated to reflux until the complete conversion of the ketone (monitored by HPLC). The cooled reaction mixture was concentrated *in vacuo*, dissolved in 100 mL Et_2O and washed with 3 × 50 mL distillated water in a separatory funnel. The Et_2O layer was dried over anhydrous Na_2SO_4, concentrated *in vacuo* and dried *in vacuo* overnight to afford the product.

General Method II (for the Synthesis of Aldoximes) (**12**): 3282 mg (40 mmol) anhydrous NaOAc and 2084 mg (30 mmol) $HONH_3Cl$ were dissolved in 50 mL aqueous ethanol ($EtOH/H_2O$ = 80:20) in a 250 mL round bottomed flask; the mixture was stirred under room temperature. When all solid was dissolved, aldehyde (20 mmol) was added. The flask was then fitted with a reflux condenser and heated to reflux until the complete conversion of the aldehyde (monitored by HPLC). The cooled reaction mixture was concentrated *in vacuo*, dissolved in 100 mL Et_2O and washed with 3 × 50 mL distillated water in a separatory funnel. The Et_2O layer was dried over anhydrous Na_2SO_4, concentrated *in vacuo* to afford the crude product. The crude product was purified by flash chromatography on silica (40 – 63 µm) using petroleum ether (PE, 40 – 60 °C) and a 1:1 mixture of dichloromethane and ethyl acetate (DCM/EA) as eluent (gradient: 0 – 40% DCM/EA over 15 CV) to afford the product.

Acetophenone Oxime (**1a**): the product was further purified by flash chromatography on silica (40 – 63 µm) using petroleum ether (PE, 40 – 60 °C) and ethyl acetate (EA) as eluent (gradient: 0 – 15% EA over 3 CV, then maintained at 15% EA over 10 CV), 3282 mg (92%) colorless crystals (mp 59 – 60 °C, lit.[1] 59 – 60 °C) was obtained: ^{1}H NMR (300 MHz, DMSO) δ 11.18 (s, 1H), 7.69 – 7.60 (m, 2H), 7.44 – 7.31 (m, 3H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 153.32, 137.43, 129.03, 128.79, 125.98, 11.99.

Benzophenone Oxime (**1b**): white crystals, mp 143 – 144 °C (lit.[2] 143 – 144 °C); ^{1}H NMR (300 MHz, DMSO) δ 11.33 (s, 1H), 7.58 – 7.17 (m, 10H); ^{13}C NMR (75 MHz, DMSO) δ 155.61, 137.21, 133.98, 129.32, 129.27, 128.82, 128.78, 128.58, 127.41.

4-Methoxyacetophenone Oxime (**1c**): white crystals, mp 86 – 87 °C (lit.[1] 85 – 87 °C); ^{1}H NMR (300 MHz, DMSO) δ 10.99 (s, 1H), 7.69 – 7.48 (m, 2H), 7.03 – 6.82 (m, 2H), 3.76 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 160.07, 152.82, 129.89, 127.28, 114.15, 55.56, 11.90.

3-Methoxyacetophenone Oxime (**1d**): light yellow oily liquid; ^{1}H NMR (300 MHz, DMSO) δ 11.25 (s, 1H), 7.38 – 7.16 (m, 3H), 6.92 (ddd, *J* = 8.0, 2.5, 1.1 Hz, 1H), 3.75 (d, *J* = 4.4 Hz, 3H), 2.16 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 159.63, 153.21, 138.87, 129.81, 118.49, 114.65, 111.20, 55.36, 11.99.

2-Methoxyacetophenone Oxime (**1e**): white solid, mp 85 – 87 °C; major isomer: ^{1}H NMR (300 MHz, DMSO) δ 10.99 (s, 1H), 7.41 – 7.28 (m, 1H), 7.21 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.93 (td, *J* = 7.4, 0.9 Hz, 1H), 3.78 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 157.53, 154.59, 130.25, 129.57, 127.84, 120.65, 111.91, 55.83, 15.74. Apparent signals of the minor isomer: ^{1}H NMR (300 MHz, DMSO) δ 10.30 (s, 1H), 3.74 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 155.78, 151.66, 129.66, 128.87, 125.64, 120.50, 111.78, 21.46; major:minor = 89:11.

4-Methylacetophenone Oxime (**1f**): white crystals, mp 85 – 86 °C (lit.[1] 84 – 86 °C); ^{1}H NMR (300 MHz, DMSO) δ 11.09 (s, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 153.16, 138.44, 134.64, 129.36, 125.87, 21.23, 11.95.

[1] S. Prateeptongkum, I. Jovel, R. Jackstell, N. Vogl, C. Weckbecker, M. Beller, *Chem. Commun.* **2009**, *0*, 1990-1992.
[2] E. B. Ayres, C. R. Hauser, *J. Org. Chem.* **1948**, *13*, 116-119.

3-Methylacetophenone Oxime (**1g**): colorless crystals, mp 60 – 61 °C (lit.[3] 57 °C); ^{1}H NMR (300 MHz, DMSO) δ 11.14 (s, 1H), 7.44 (d, *J* = 9.6 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 2.32 (s, 3H), 2.14 (s, 3H).; ^{13}C NMR (75 MHz, DMSO) δ 153.36, 137.85, 137.40, 129.66, 128.67, 126.57, 123.17, 21.52, 12.03.

2-Methylacetophenone Oxime (**1h**): light yellow oily liquid; major isomer: ^{1}H NMR (300 MHz, DMSO) δ 11.05 (s, 1H), 7.33 – 7.11 (m, 5H), 2.29 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 155.37, 138.53, 135.63, 130.83, 128.58, 128.37, 126.08, 20.40, 15.95. Apparent signals of the minor isomer: ^{1}H NMR (300 MHz, DMSO) δ 10.42 (s, 1H), 2.17 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 153.84, 137.36, 134.70, 129.89, 128.11, 126.49, 125.92, 22.01, 19.59; major:minor = 76:24.

4-Bromoacetophenone Oxime (**1i**): white crystals, mp 128 – 129 °C (lit.[1] 128 – 130 °C); ^{1}H NMR (300 MHz, DMSO) δ 11.33 (s, 1H), 7.67 – 7.49 (m, 4H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 152.54, 136.59, 131.73, 128.00, 122.38, 11.79.

4-Chloroacetophenone Oxime (**1j**): white crystals, mp 99 – 100 °C (lit.[1] 97 – 99 °C); ^{1}H NMR (300 MHz, DMSO) δ 11.33 (s, 1H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 152.44, 136.22, 133.71, 128.80, 127.70, 11.82.

3-Chloroacetophenone Oxime (**1k**): white crystals, mp 88 – 89 °C (lit.[1] 88 – 90°C); ^{1}H NMR (300 MHz, DMSO) δ 11.40 (s, 1H), 7.73 – 7.53 (m, 2H), 7.41 (dd, *J* = 3.7, 1.6 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 152.37, 139.53, 133.69, 130.68, 128.82, 125.62, 124.65, 11.87.

2-Chloroacetophenone Oxime (**1l**): white solid powder, mp 87 – 88 °C (lit.[4] 87 – 90 °C, lit.[1] 102 – 104 °C); major isomer: ^{1}H NMR (300 MHz, DMSO) δ 11.29 (s, 1H), 7.54 – 7.30 (m, 4H), 2.10 (s, 1H); ^{13}C NMR (75 MHz, DMSO) δ 154.11, 137.73, 131.92, 130.85, 130.45, 130.10, 127.65, 16.01. Apparent signals of the minor isomer: ^{1}H NMR (300 MHz, DMSO) δ 10.59 (s, 1H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 151.34, 136.36, 130.00, 129.49, 129.12, 127.54, 21.18; major:minor = 81:19.

4-Methylbenzaldehyde Oxime (**12a**): colorless oil; ^{1}H NMR (300 MHz, DMSO) δ 10.96 (s, 1H), 8.06 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 160.53, 148.07, 128.27, 126.06, 114.63, 55.65.

Benzaldehyde Oxime (**12b**): white crystals, mp 68 – 69 °C (lit.[5] 63 – 65 °C); ^{1}H NMR (300 MHz, DMSO) δ 11.24 (s, 1H), 8.14 (s, 1H), 7.70 – 7.54 (m, 2H), 7.49 – 7.30 (m, 3H); ^{13}C NMR (75 MHz, DMSO) δ 148.54, 133.52, 129.70, 129.16, 126.84.

4-Chlorobenzaldehyde Oxime (**12c**): white crystals, mp 112 – 113 °C (lit.[6] 109 – 112 °C); ^{1}H NMR (300 MHz, DMSO) δ 11.37 (s, 1H), 8.15 (s, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, DMSO) δ 147.56, 134.15, 132.46, 129.24, 128.48.

11. Characterization of Isolated Products

Acetanilide (**2a**): 123.9 mg (76%); white crystals, mp 114 – 115 °C (lit.[7] 115 – 116 °C); ^{1}H NMR (300 MHz, DMSO) δ 9.90 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.9 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 168.69, 139.78, 129.08, 123.39, 119.42, 24.44.

Benzanilide (**2b**): 181.1 mg (77%); white crystals, mp 163 – 164 °C (lit.[7] 162 – 164 °C); ^{1}H NMR (300 MHz, DMSO) δ 10.25 (s, 1H), 8.02 – 7.90 (m, 2H), 7.79 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.65 – 7.46 (m, 3H), 7.36 (dd, *J* = 10.7, 5.1 Hz, 2H), 7.16 – 7.04 (m, 1H); ^{13}C NMR (75 MHz, DMSO) δ 166.00, 139.62, 135.44, 131.99, 129.05, 128.83, 128.10, 124.10, 120.81.

4-Methoxyacetanilide (**2c**): 118.6 mg (65%); white crystals, mp 131 – 132 °C (lit.[7] 128 – 130 °C); ^{1}H NMR (300 MHz, DMSO) δ 9.76 (s, 1H), 7.55 – 7.41 (m, 2H), 6.93 – 6.78 (m, 2H), 3.71 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 168.15, 155.46, 132.98, 120.98, 114.21, 55.56, 24.23.

[3] T. Posner, G. Schreiber, *Ber. Dtch. Chem. Ges.* **1924**, *57*, 1127-1137.
[4] T. Weil, H. Stange, Patent: ZA 6800916 (9. Jul. 1968).
[5] J. H. P. Tyman, P. B. Payne, *J. Chem. Res.* **2006**, 691-695.
[6] J. Picha, R. Cibulka, F. Hampl, F. Liska, P. Parik, O. Pytela, *Collect. Czech. Chem. Commun.* **2004**, *69*, 397-413.
[7] V. P. Srivastava, A. K. Yadav, L. D. S. Yadav, *Synlett* **2014**, *25*, 665-670.

3-Methoxyacetanilide (**2d**): 137.8 mg (70%); offwhite crystals, mp 102 – 103 °C (lit.[8] 103 – 103.5 °C, lit.[7] 87 – 89 °C); ^{1}H NMR (300 MHz, DMSO) δ 9.89 (s, 1H), 7.28 (t, *J* = 2.1 Hz, 1H), 7.13 (ddd, *J* = 11.5, 8.5, 4.8 Hz, 2H), 6.60 (ddd, *J* = 8.1, 2.5, 1.1 Hz, 1H), 3.71 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 168.75, 159.92, 140.94, 129.87, 111.73, 108.76, 105.31, 55.37, 24.51.

2-Methoxyacetanilide (**2e**): 123.8 mg (62%); light yellow crystals, mp 87 – 88 °C (lit.[9] 87 – 88 °C); ^{1}H NMR (300 MHz, DMSO) δ 9.10 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.13 – 6.97 (m, 2H), 6.95 – 6.80 (m, 1H), 3.82 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 168.86, 149.96, 127.88, 124.60, 122.43, 120.59, 111.49, 56.01, 24.29.

4-Methylacetanilide (**2f**): 133.7 mg (75%); white crystals, mp 152 – 153 °C (lit.[7] 149 – 150 °C); ^{1}H NMR (300 MHz, DMSO) δ 9.82 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 2.24 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 168.43, 137.28, 132.23, 129.46, 119.42, 24.39, 20.87.

3-Methylacetanilide (**2g**): 136.0 mg (76%); offwhite crystals, mp 66 – 67 °C (lit.[10] 65 – 66 °C); ^{1}H NMR (300 MHz, DMSO) δ 9.83 (s, 1H), 7.49 – 7.28 (m, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 2.26 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 168.62, 139.71, 138.21, 128.92, 124.10, 119.94, 116.63, 24.46, 21.65.

2-Methylacetanilide (**2h**): 94.5 mg (54%); grey crystals, mp 107 – 109 °C (lit.[11] 107 – 110 °C, lit.[10] 110 – 112°C); ^{1}H NMR (300 MHz, DMSO) δ 9.27 (s, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.29 – 6.98 (m, 3H), 2.20 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 168.58, 136.96, 131.97, 130.66, 126.29, 125.43, 125.40, 23.73, 18.32.

4-Bromoacetanilide (**2i**): 146.6 mg (57%); white crystals, mp 169 – 170 °C (lit.[7] 165 – 166 °C); ^{1}H NMR (300 MHz, DMSO) δ 10.07 (s, 1H), 7.64 – 7.52 (m, 2H), 7.51 – 7.39 (m, 2H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 168.91, 139.12, 131.91, 121.28, 114.92, 24.48.

4-Chloroacetanilide (**2j**): 91.4 mg (45%); white crystals, mp 177 – 178 °C (lit.[12] 177 – 178 °C); ^{1}H NMR (300 MHz, DMSO) δ 10.06 (s, 1H), 7.70 – 7.50 (m, 2H), 7.42 – 7.25 (m, 2H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 168.87, 138.71, 129.00, 126.92, 120.90, 24.44.

3-Chloroacetanilide (**2k**): 102.5 mg (50%); offwhite crystals, mp 74 – 75 °C (lit.[12] 72.4 – 73.6 °C, lit.[13] 78 – 79 °C); ^{1}H NMR (300 MHz, DMSO) δ 10.13 (s, 1H), 7.81 (t, *J* = 1.9 Hz, 1H), 7.41 (ddd, *J* = 8.2, 1.8, 1.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 7.9, 0.9 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 169.15, 141.20, 133.47, 130.82, 123.12, 118.82, 117.71, 24.50.

2-Chloroacetanilide (**2l**): 47.7 mg (23%); grey crystals, mp 86 – 88 °C (lit.[10] 85 – 87 °C); ^{1}H NMR (300 MHz, DMSO) δ 9.50 (s, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.48 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.31 (td, *J* = 7.8, 1.5 Hz, 1H), 7.19 (dd, *J* = 7.7, 1.4 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 169.05, 135.53, 129.85, 127.76, 126.85, 126.72, 126.58, 23.78.

4-Methoxybenzonitrile (**13a**): Prepared following the procedure for ketoximes, then isolated by flash chromatography on silica (40 – 63 µm) using petroleum ether (PE, 40 – 60 °C) and ethyl acetate (EA) (gradient: 0 – 15% EA over 20 CV) to afford 106.0 mg (66%) white crystals, mp 59 – 60 °C (lit.[14] 59 – 60 °C); ^{1}H NMR (300 MHz, DMSO) δ 7.78 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 163.16, 134.63, 119.60, 115.59, 103.25, 56.15.

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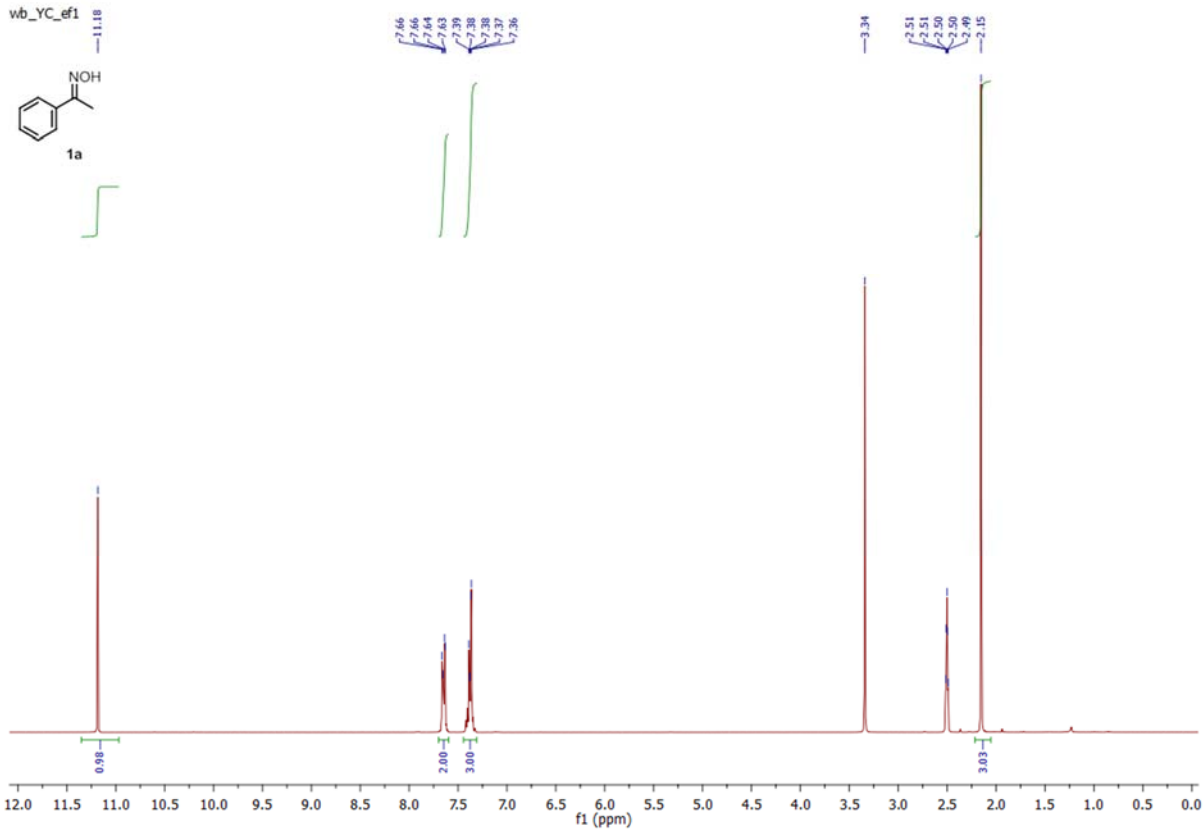
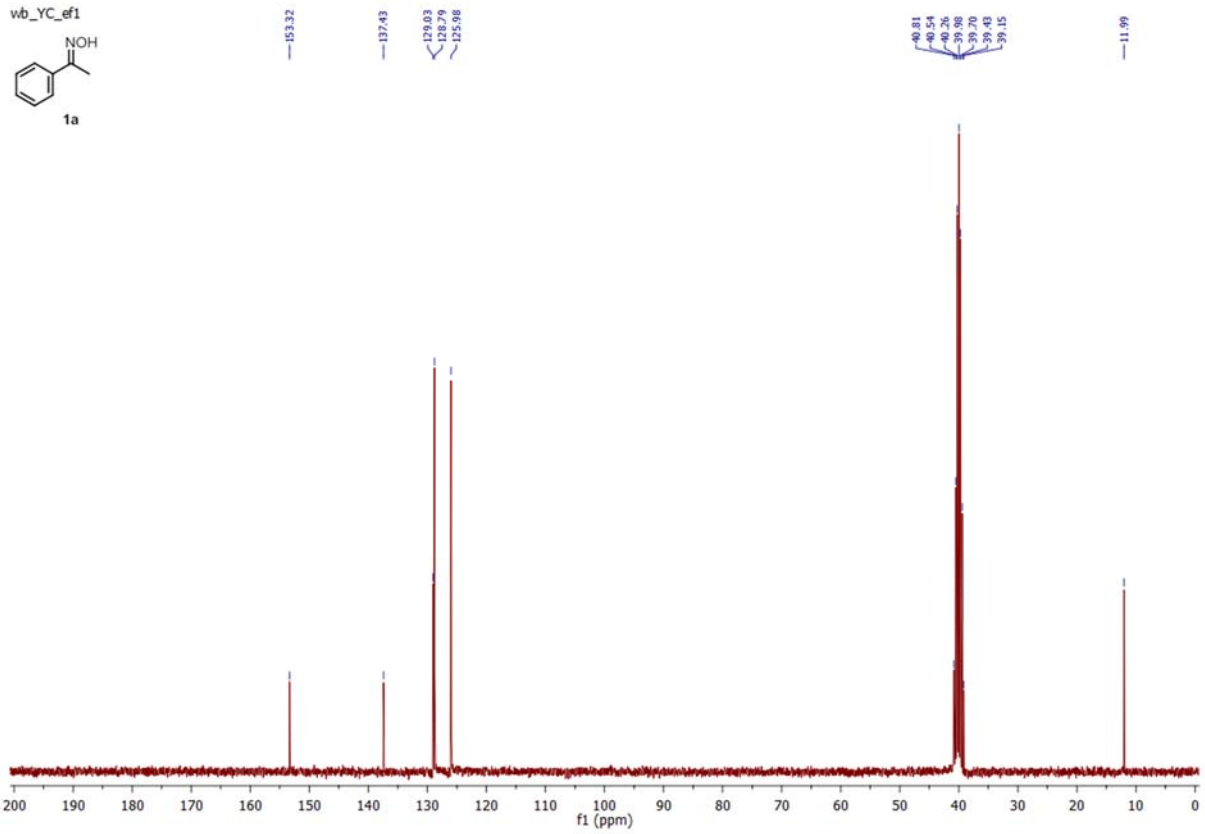
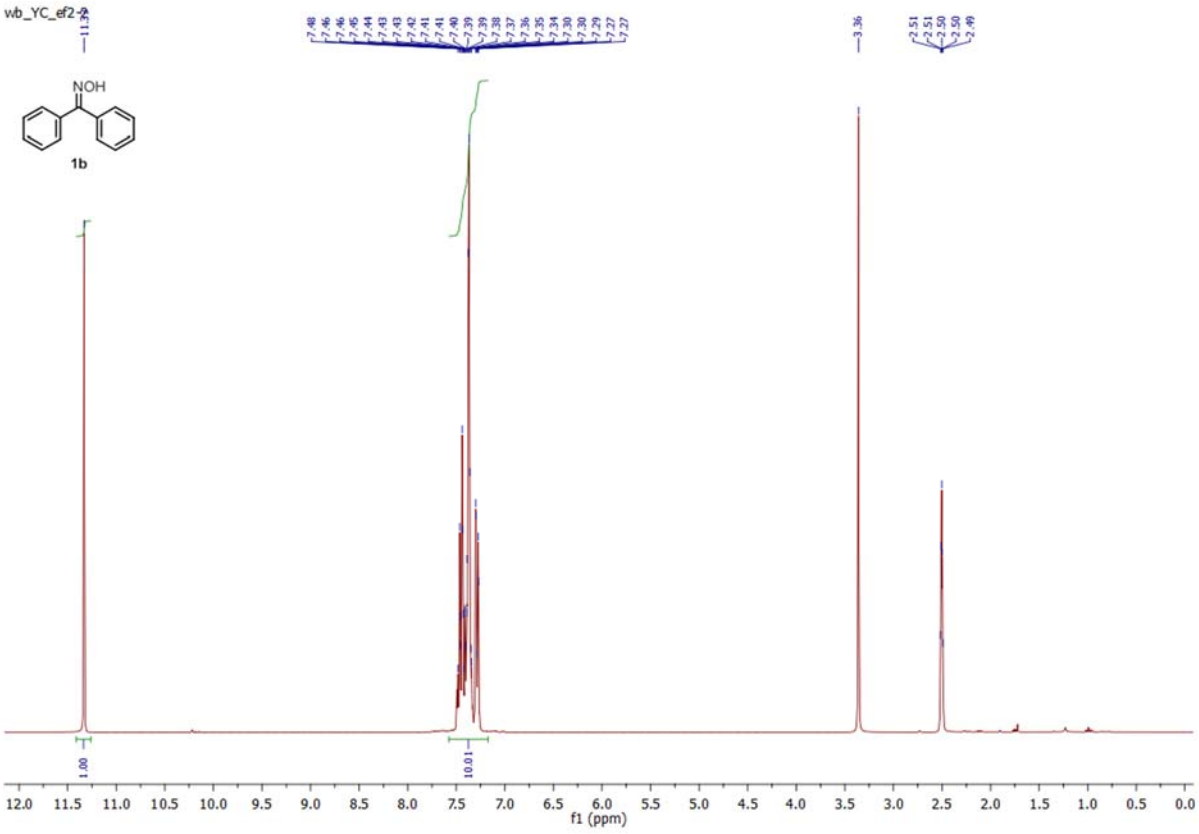
12. Copies of ^{1}H- and ^{13}C-NMR spectra



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7.40
7.39
7.39
7.38
7.37
7.36
7.35
7.34
7.30
7.30
7.29
7.27
7.27
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2.51
2.50
2.50
2.49
1.00
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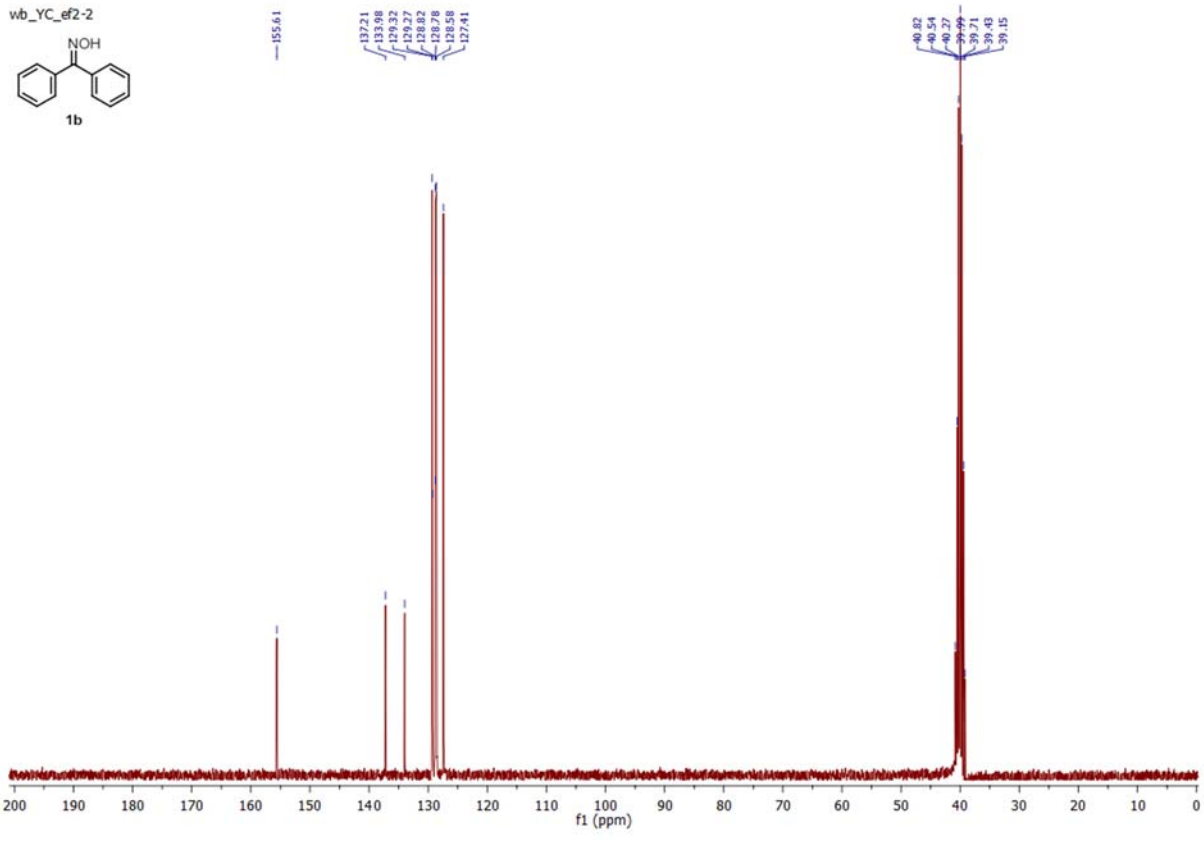
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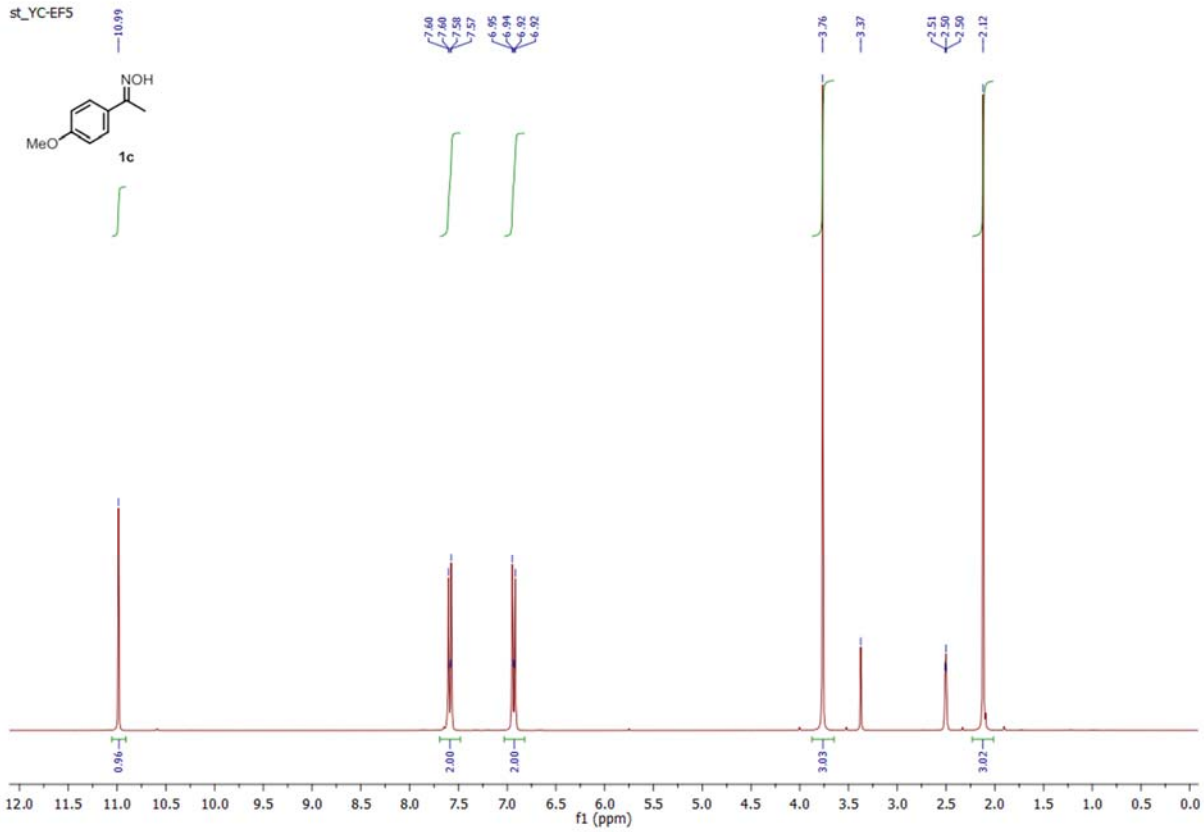
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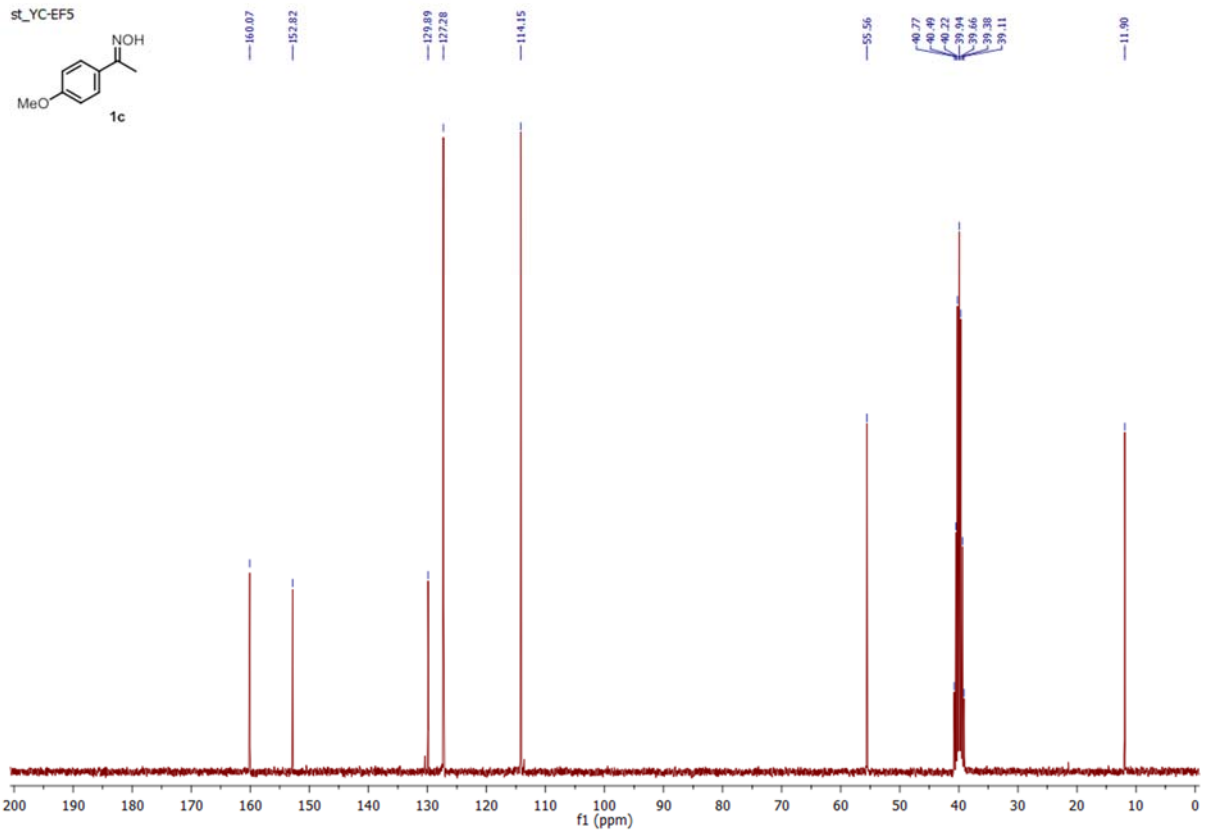
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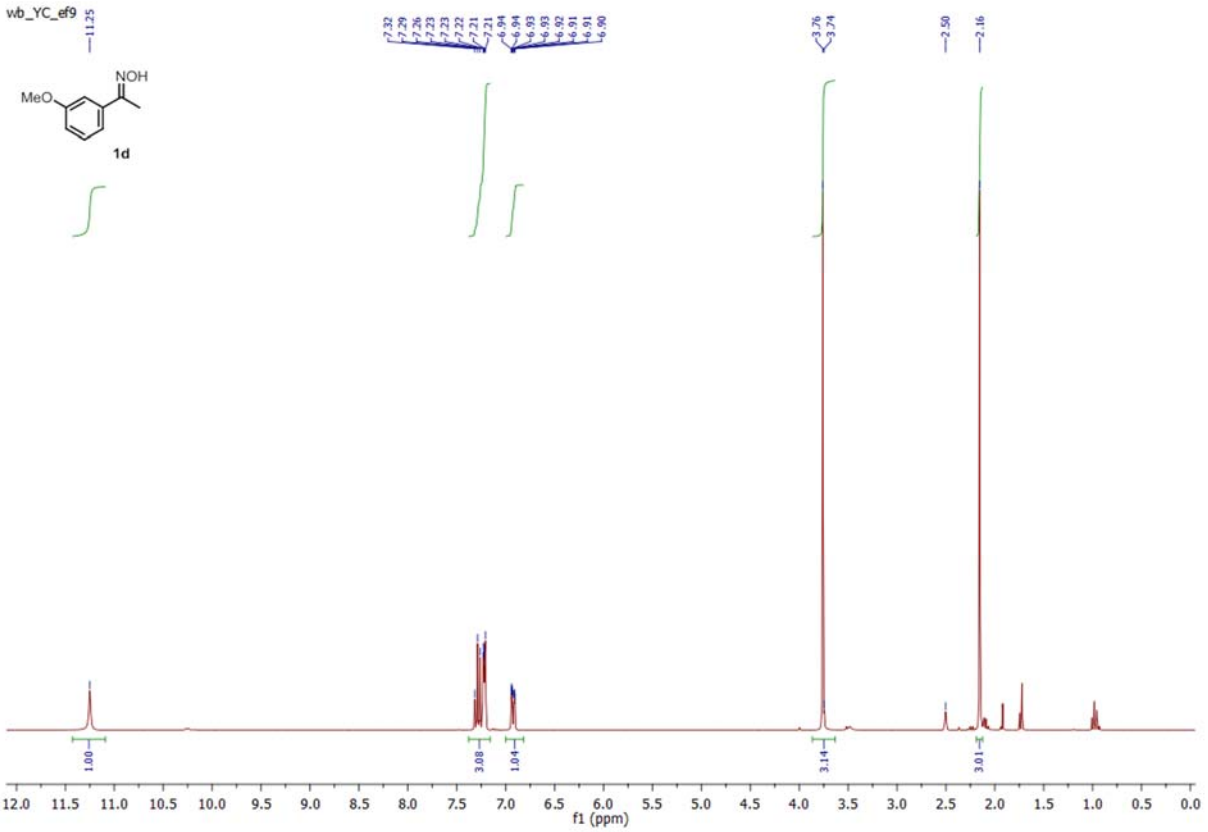
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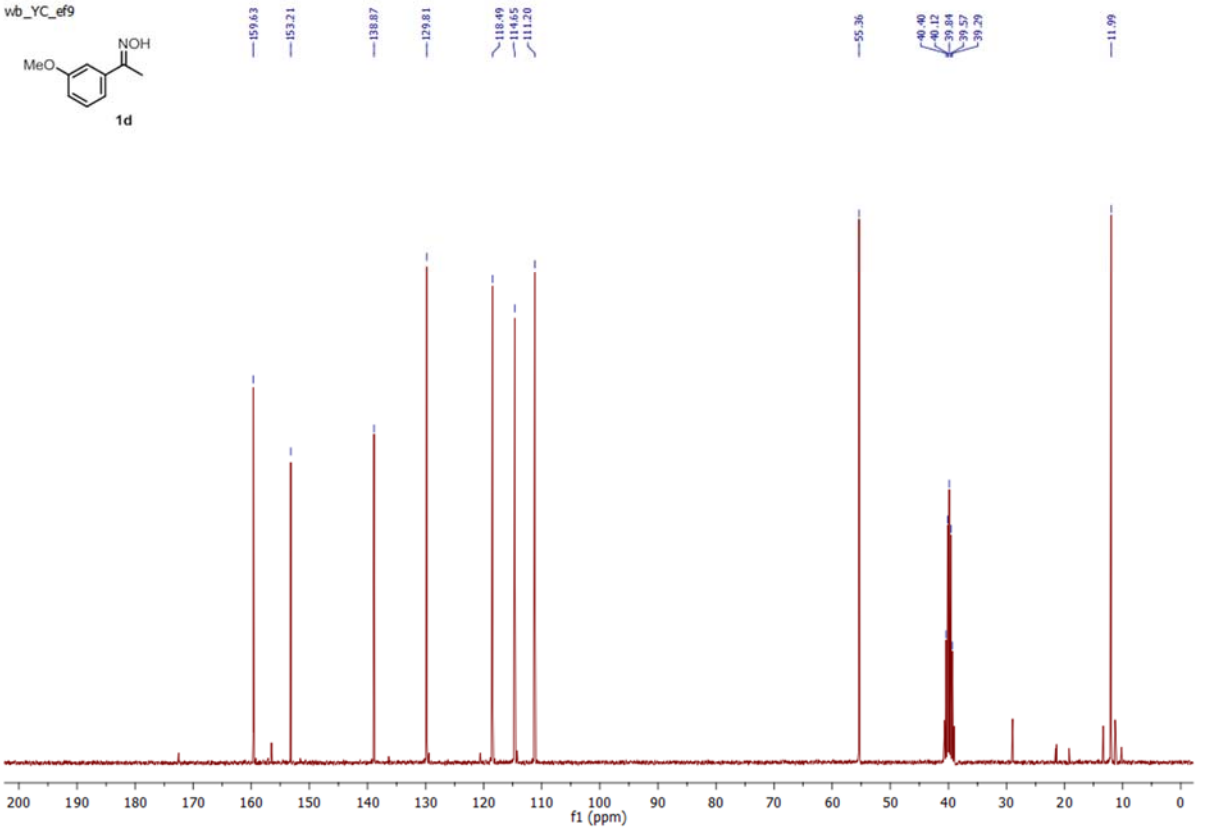
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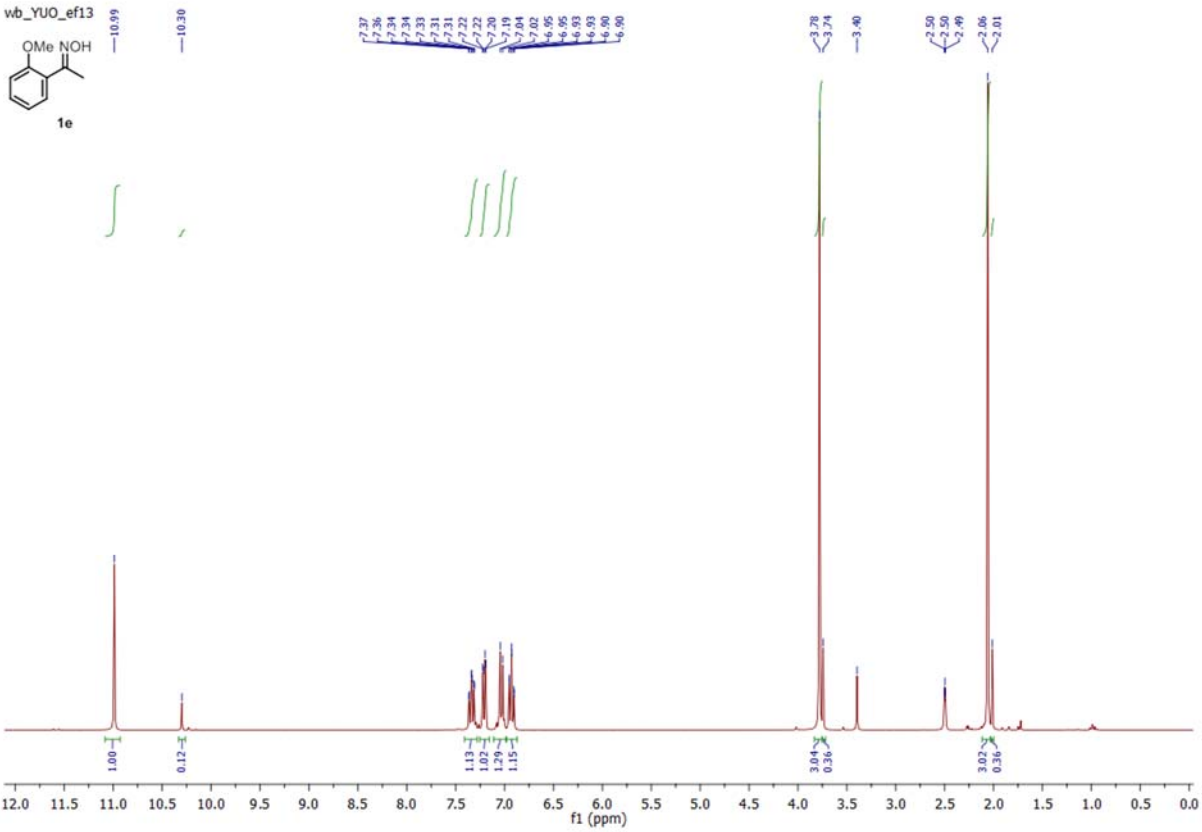
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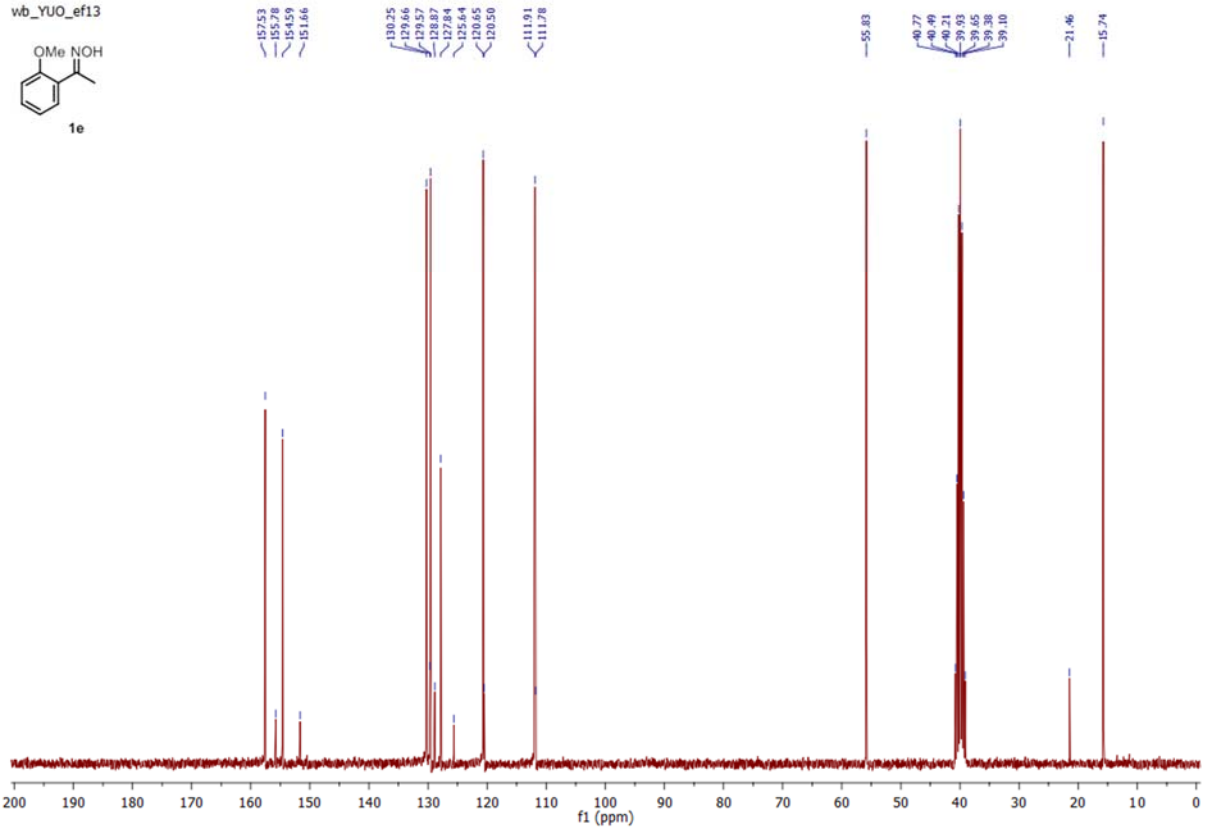
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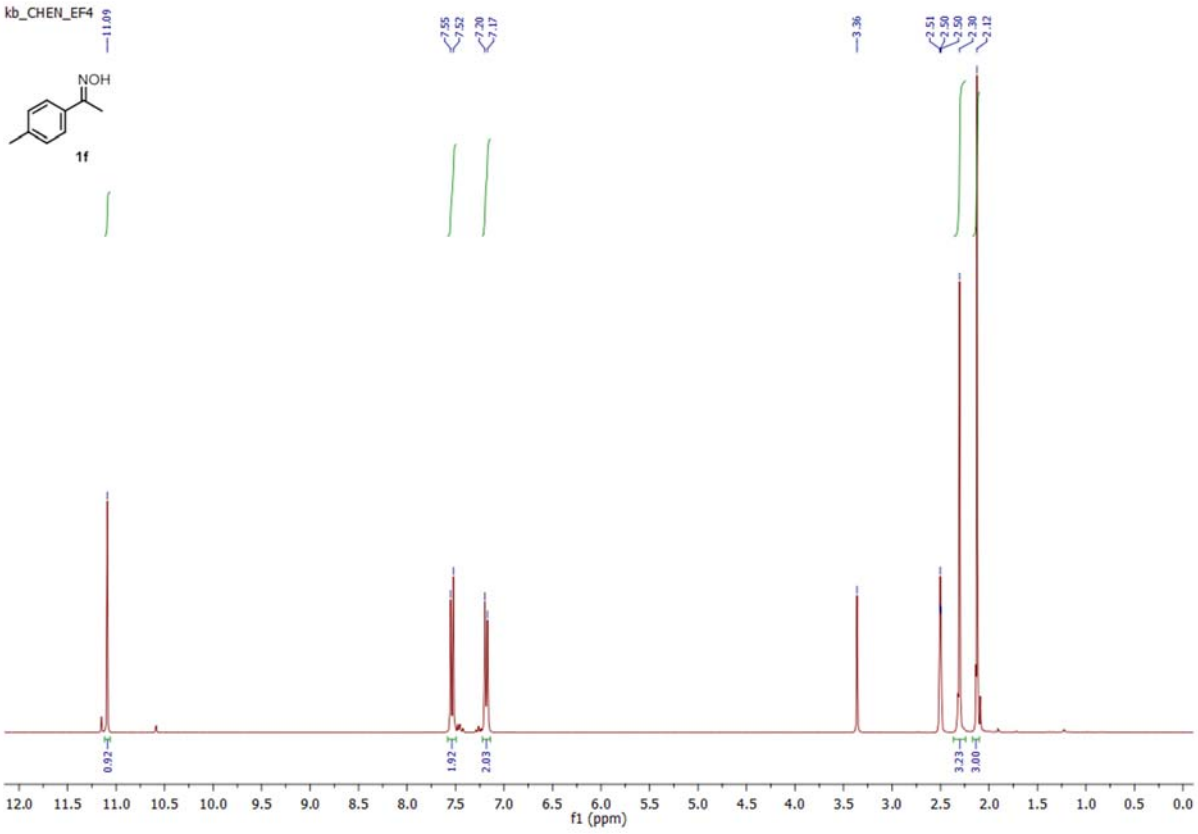
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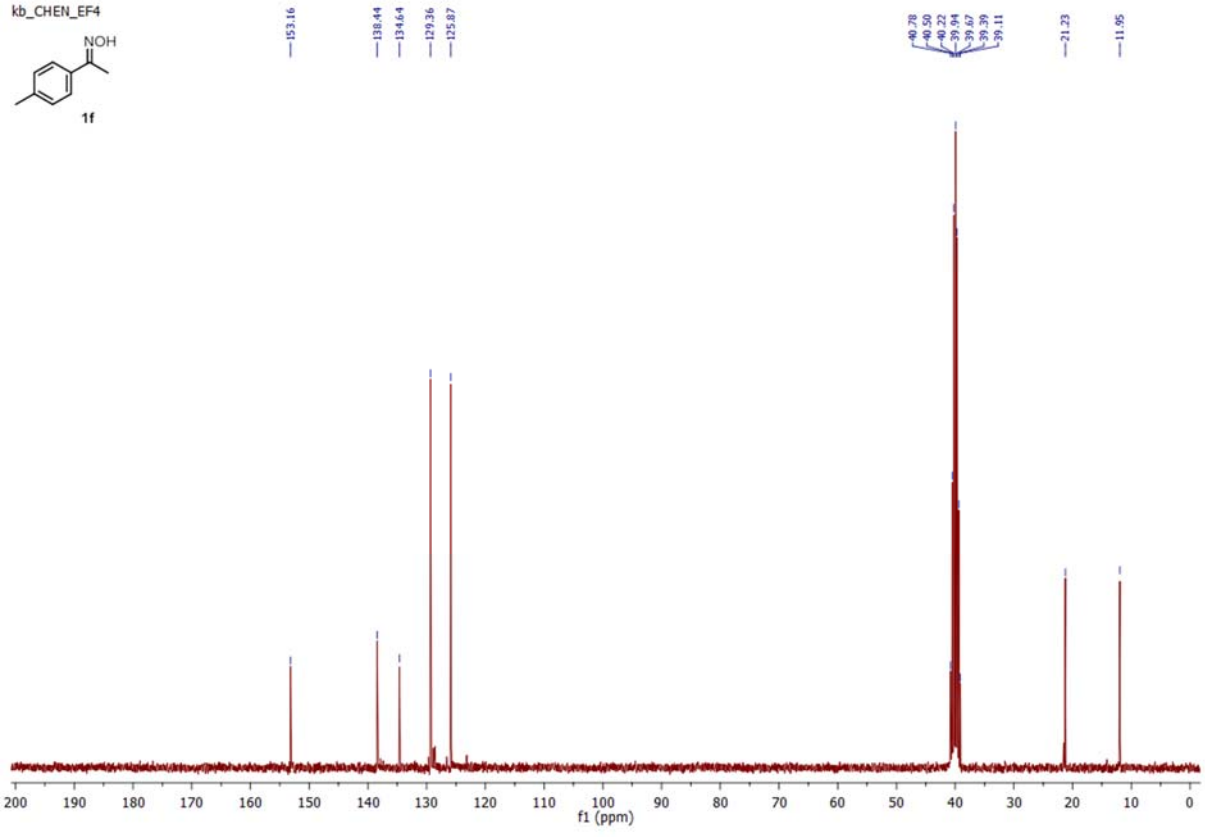
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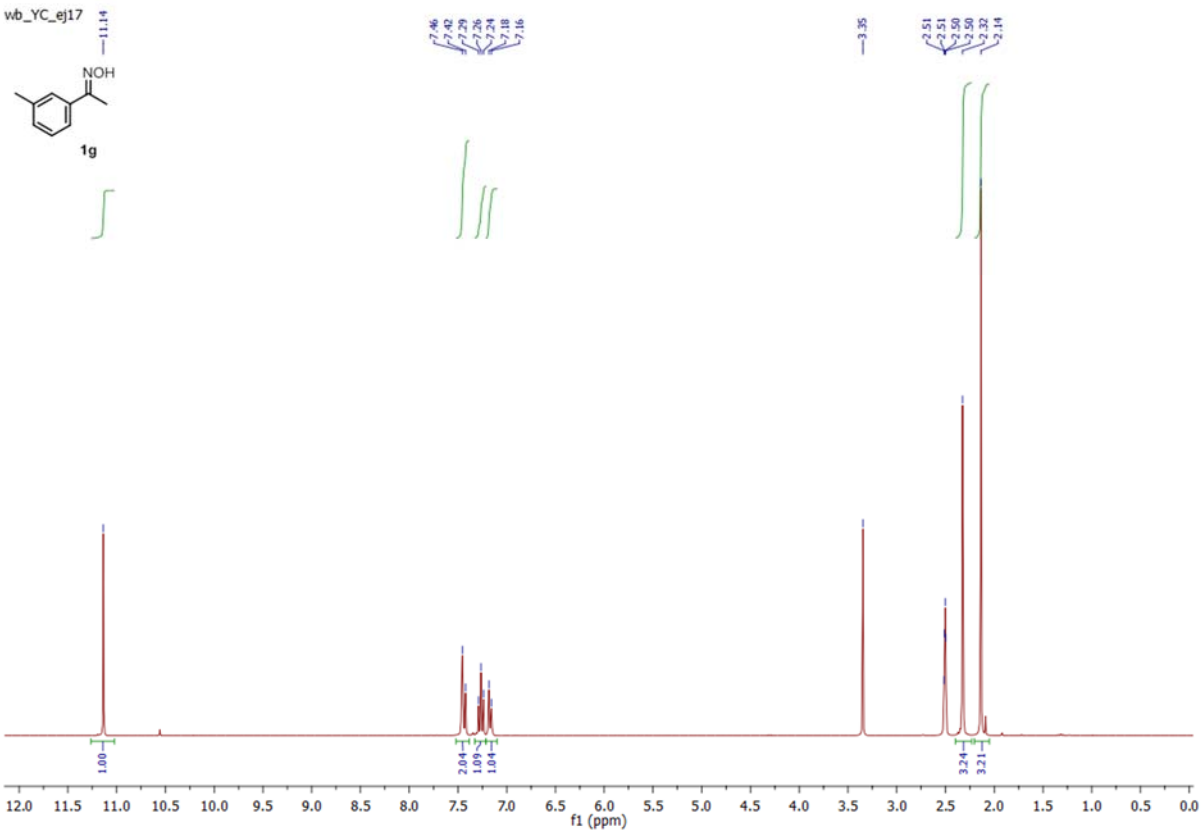
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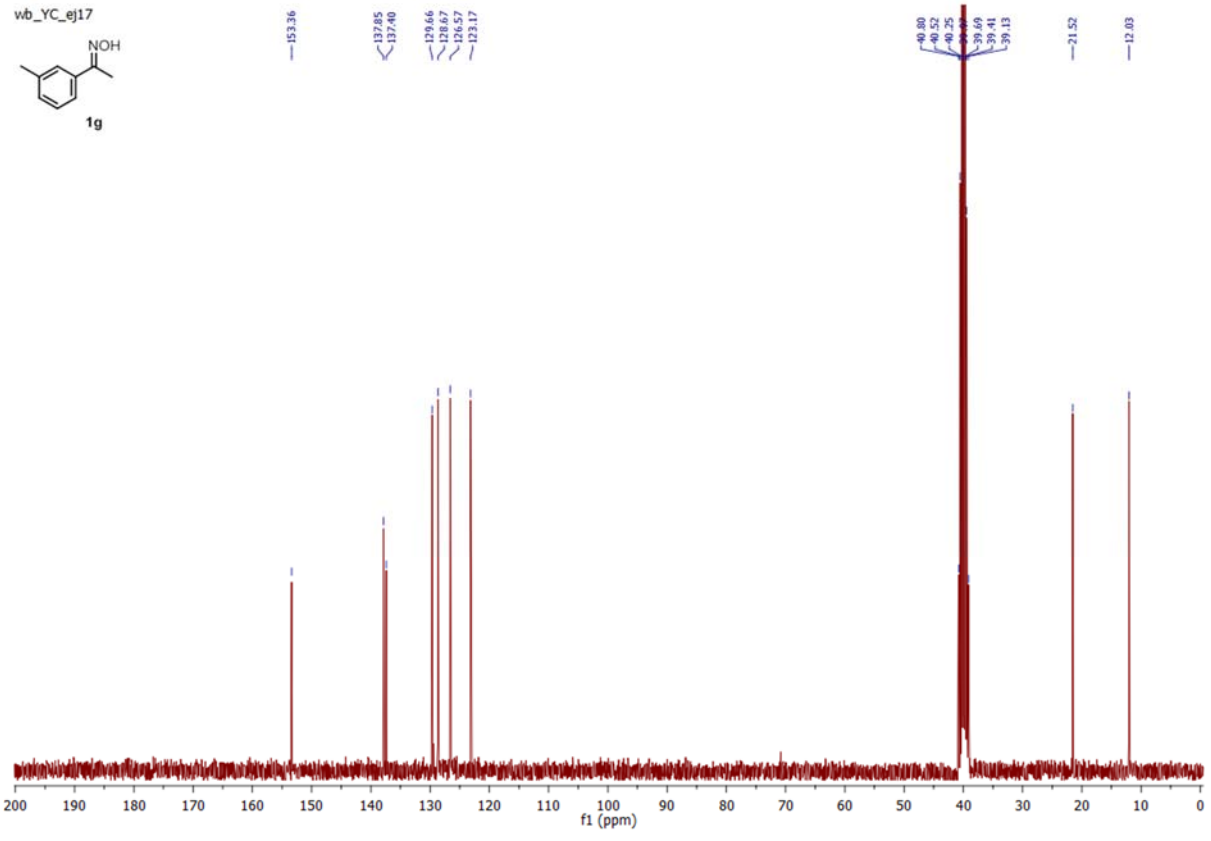
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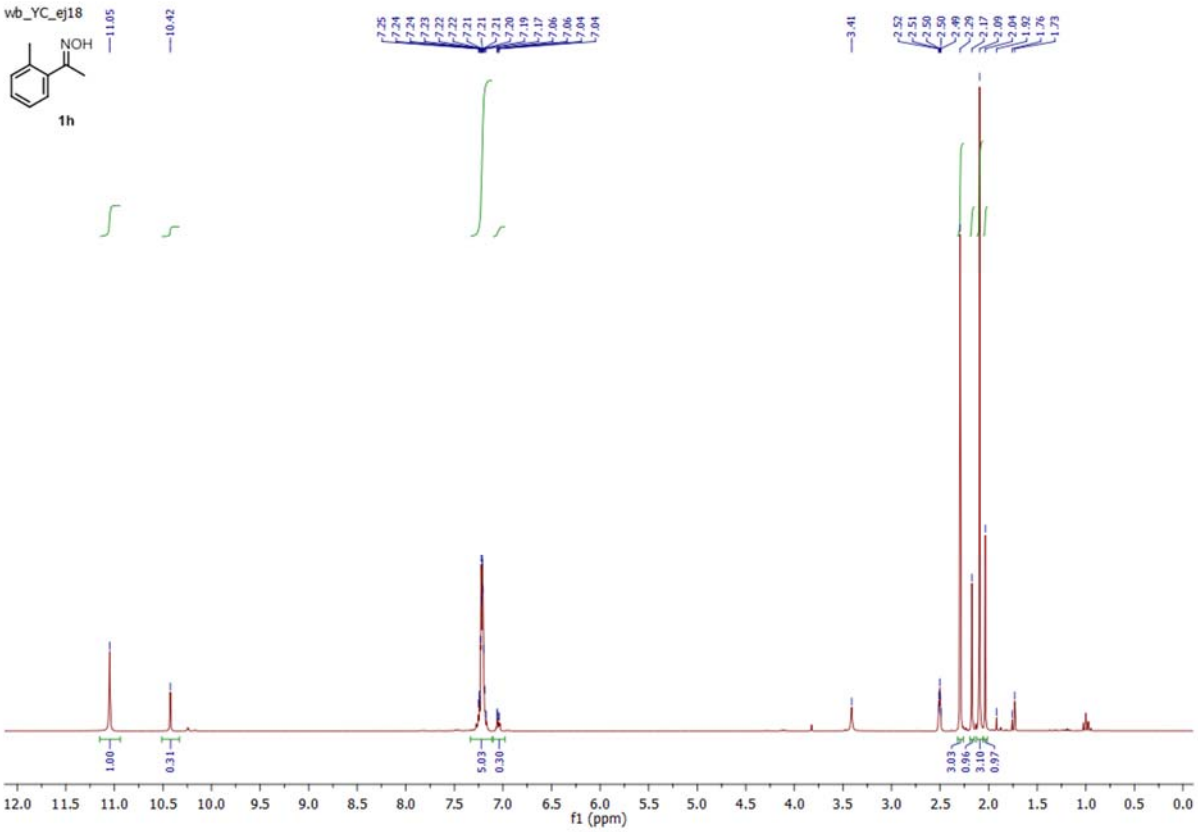
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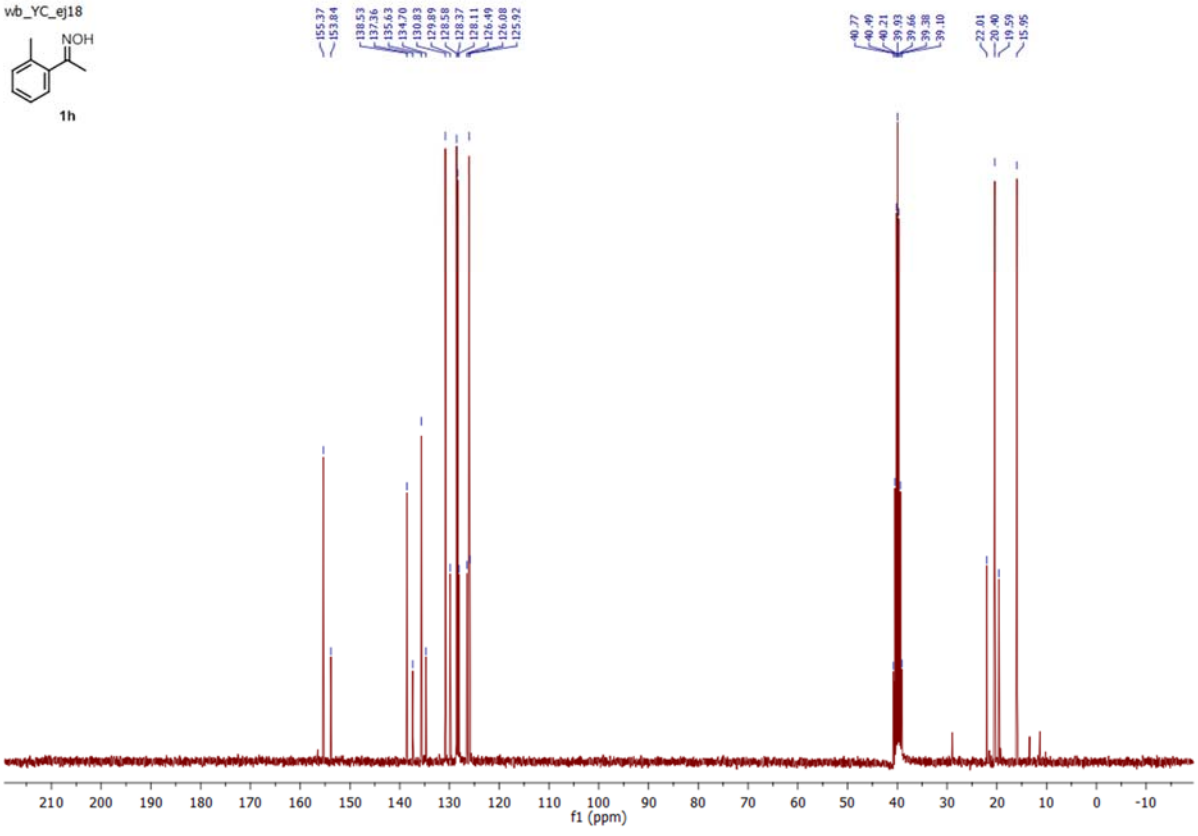
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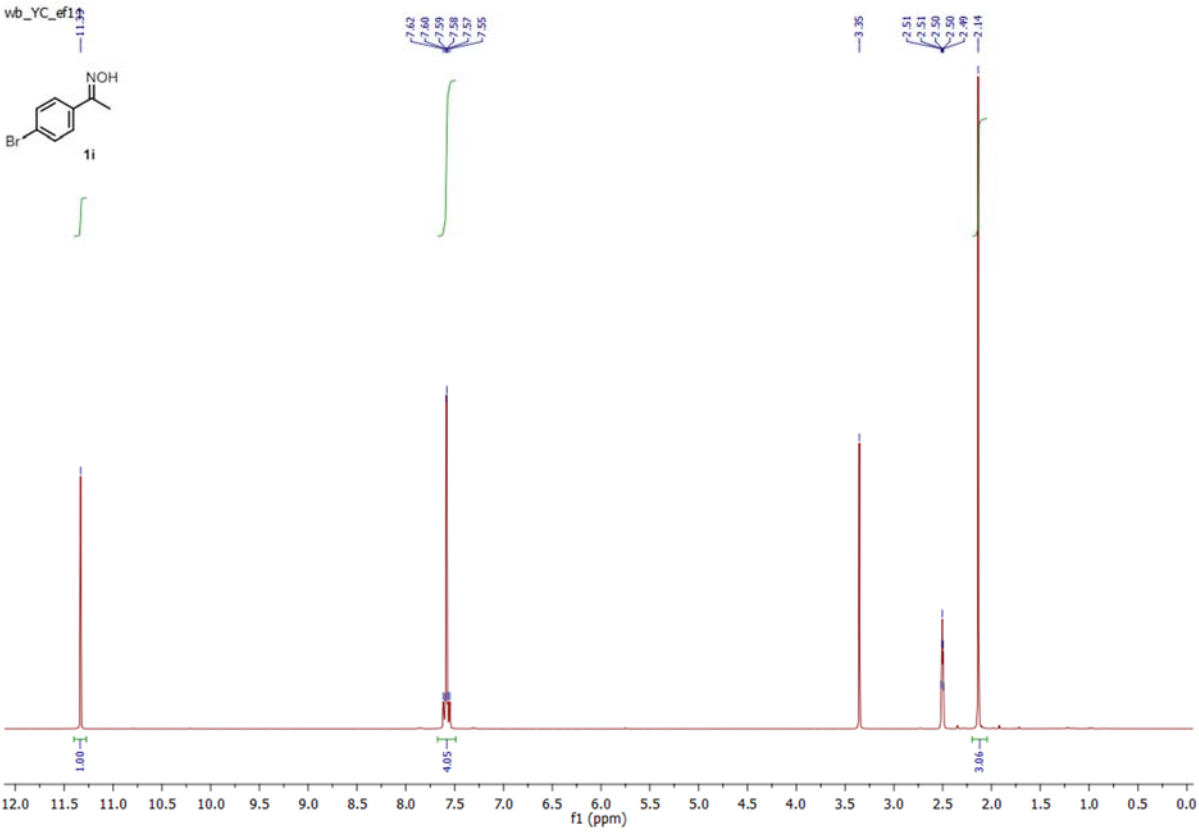
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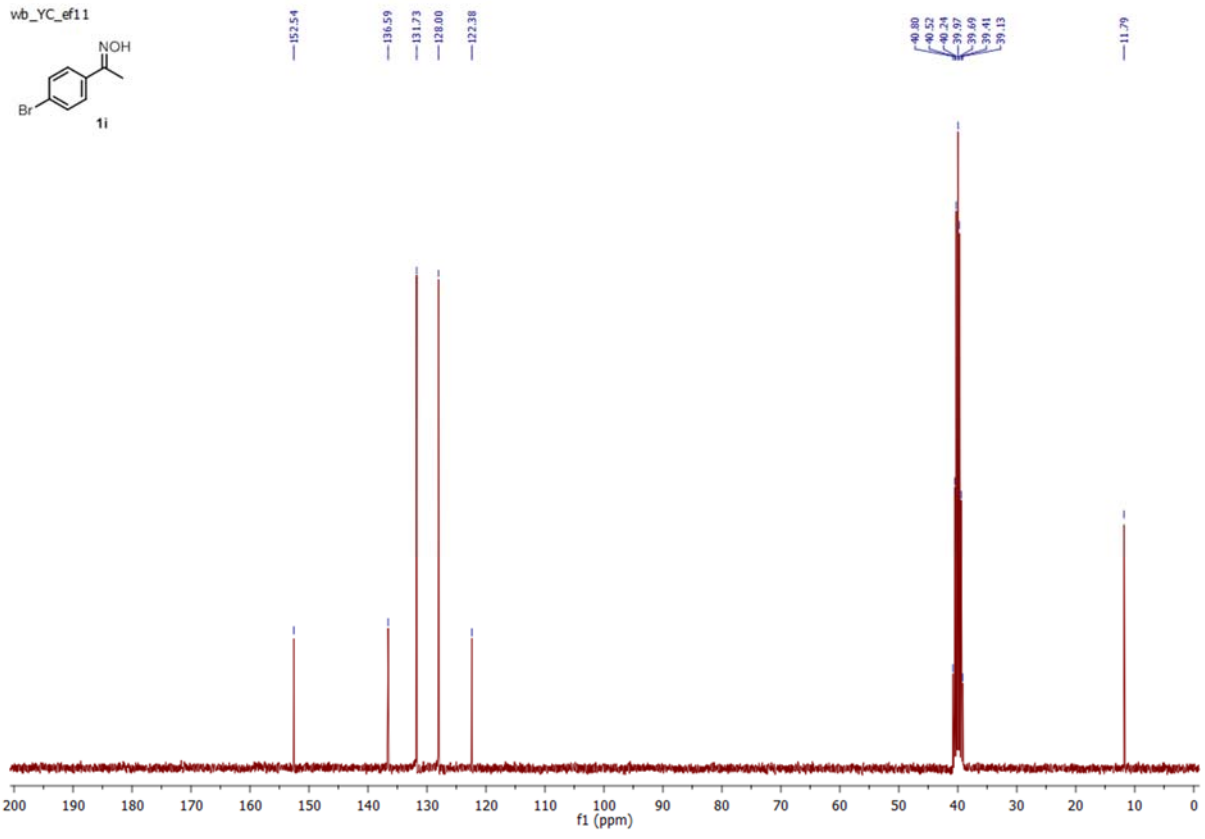
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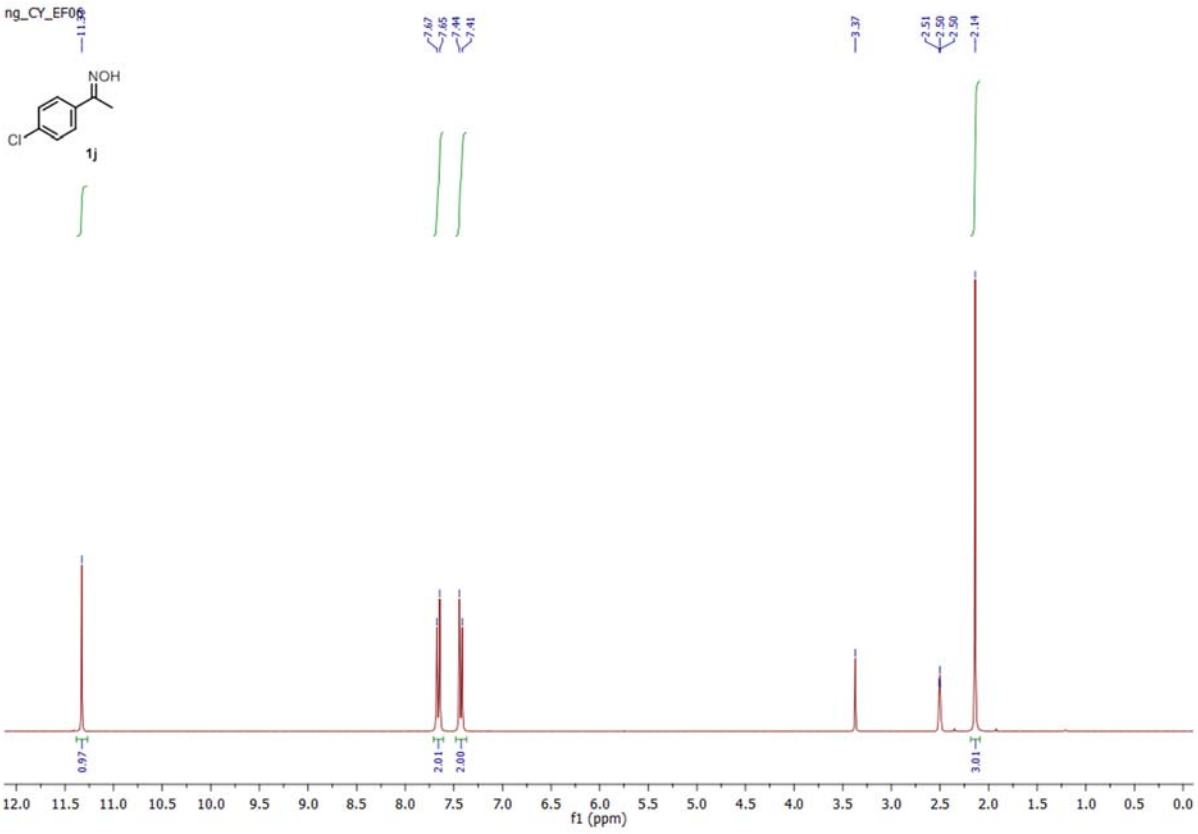
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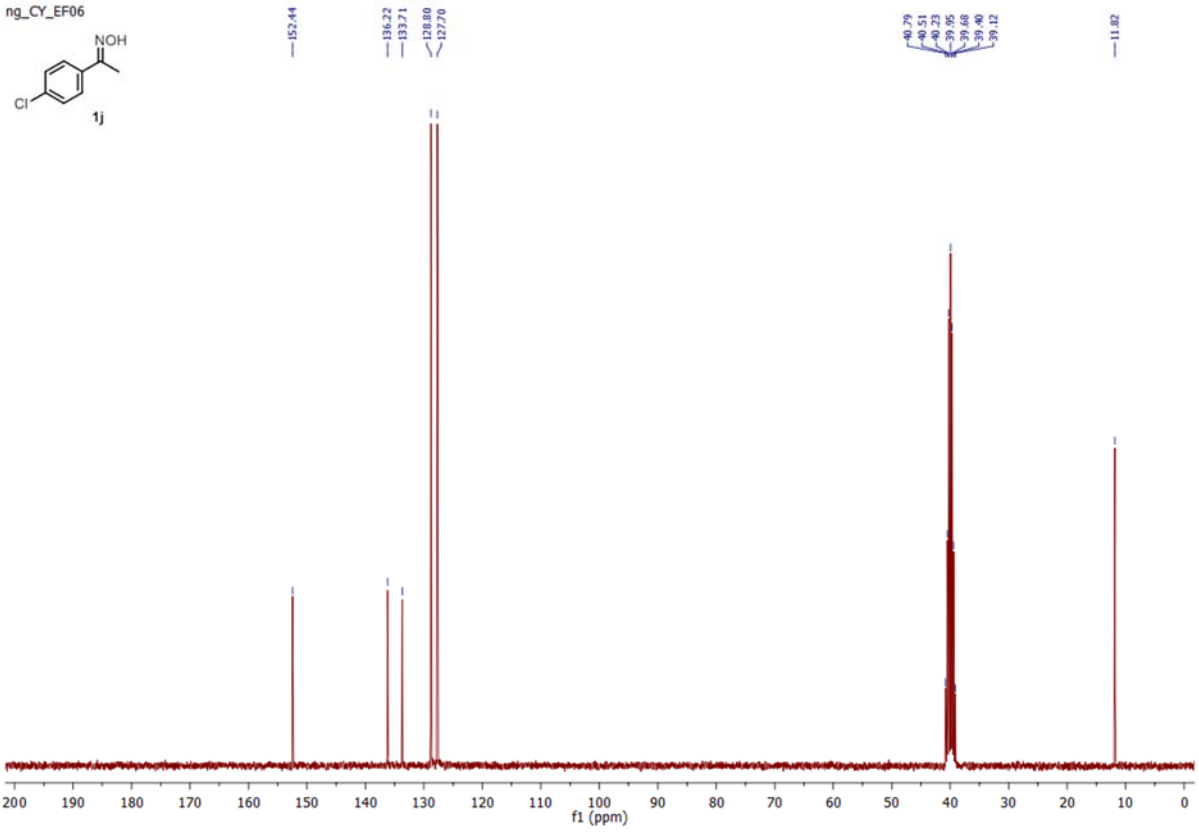
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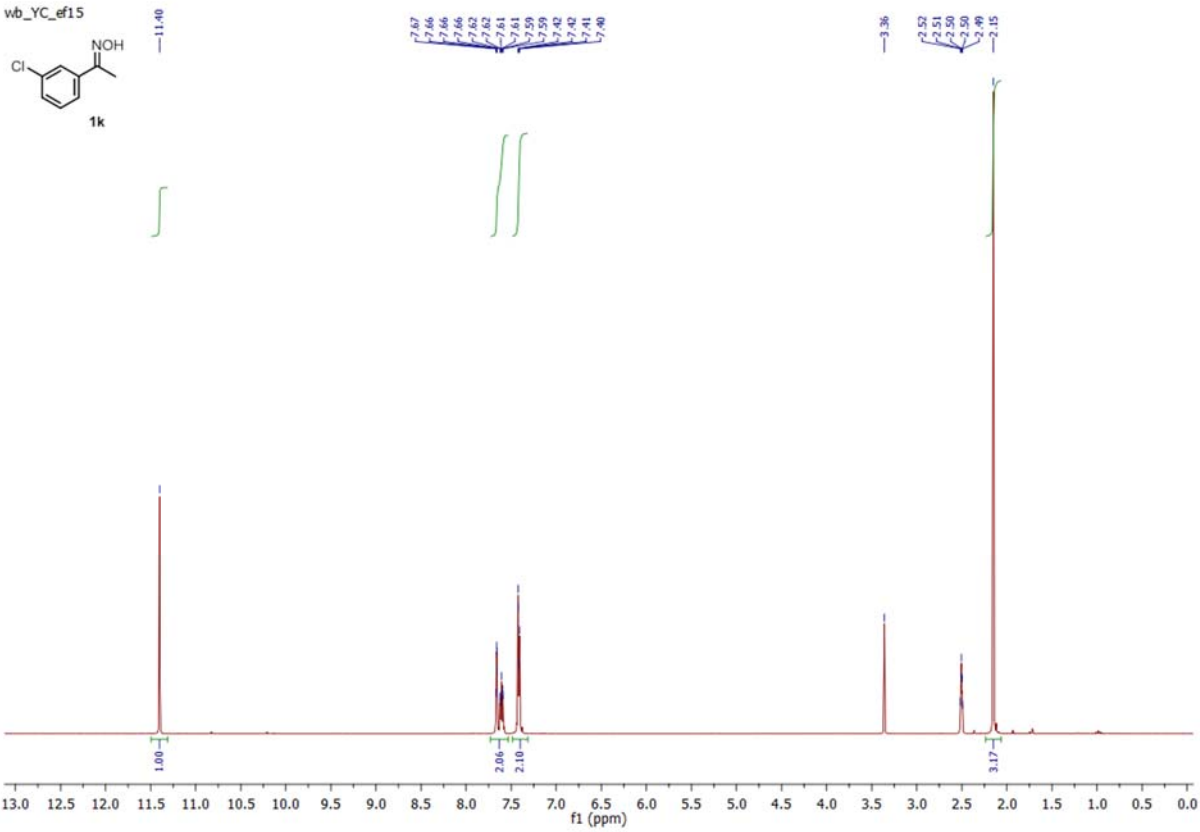
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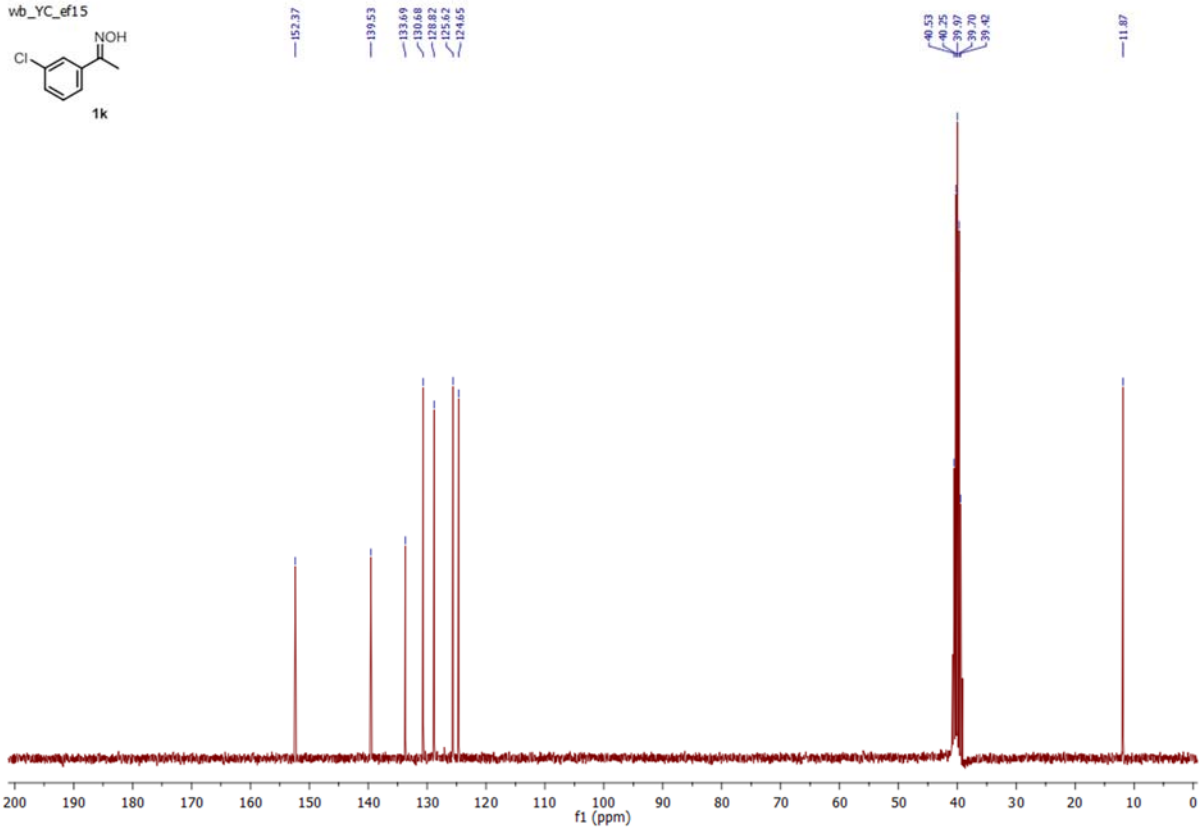
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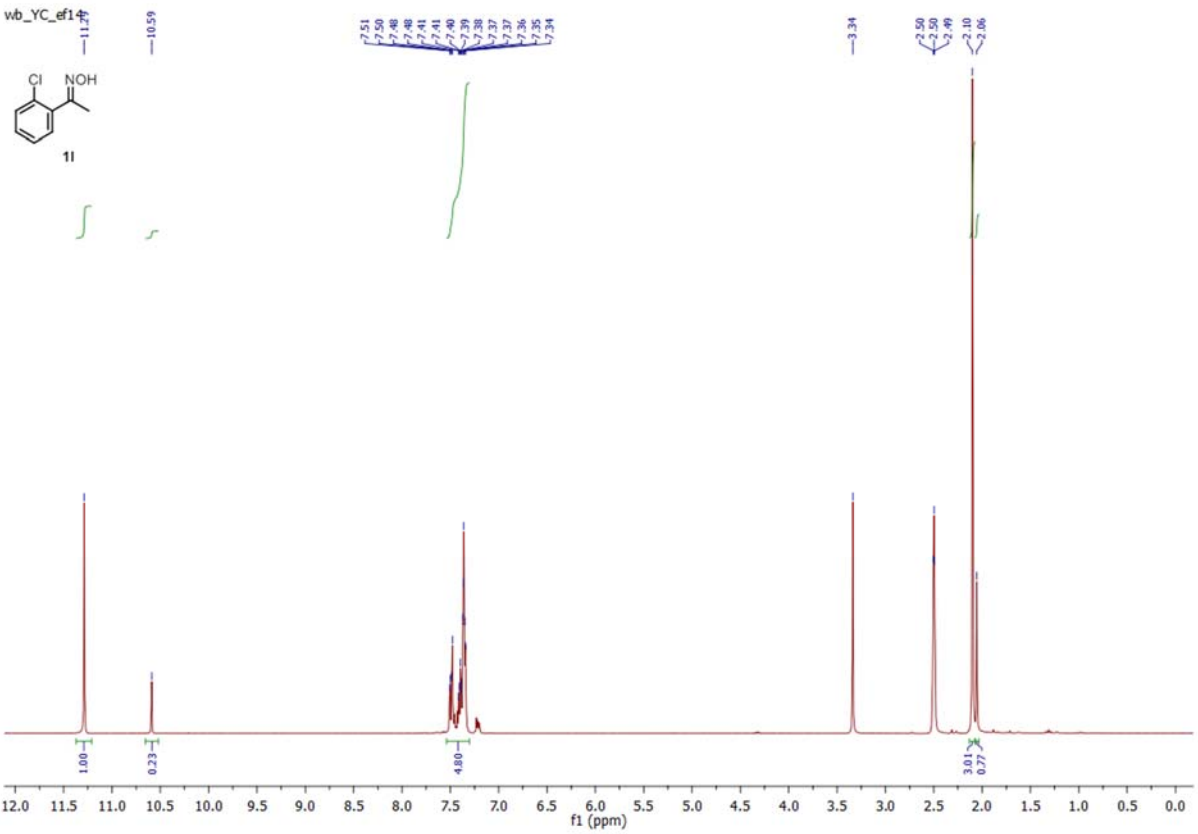
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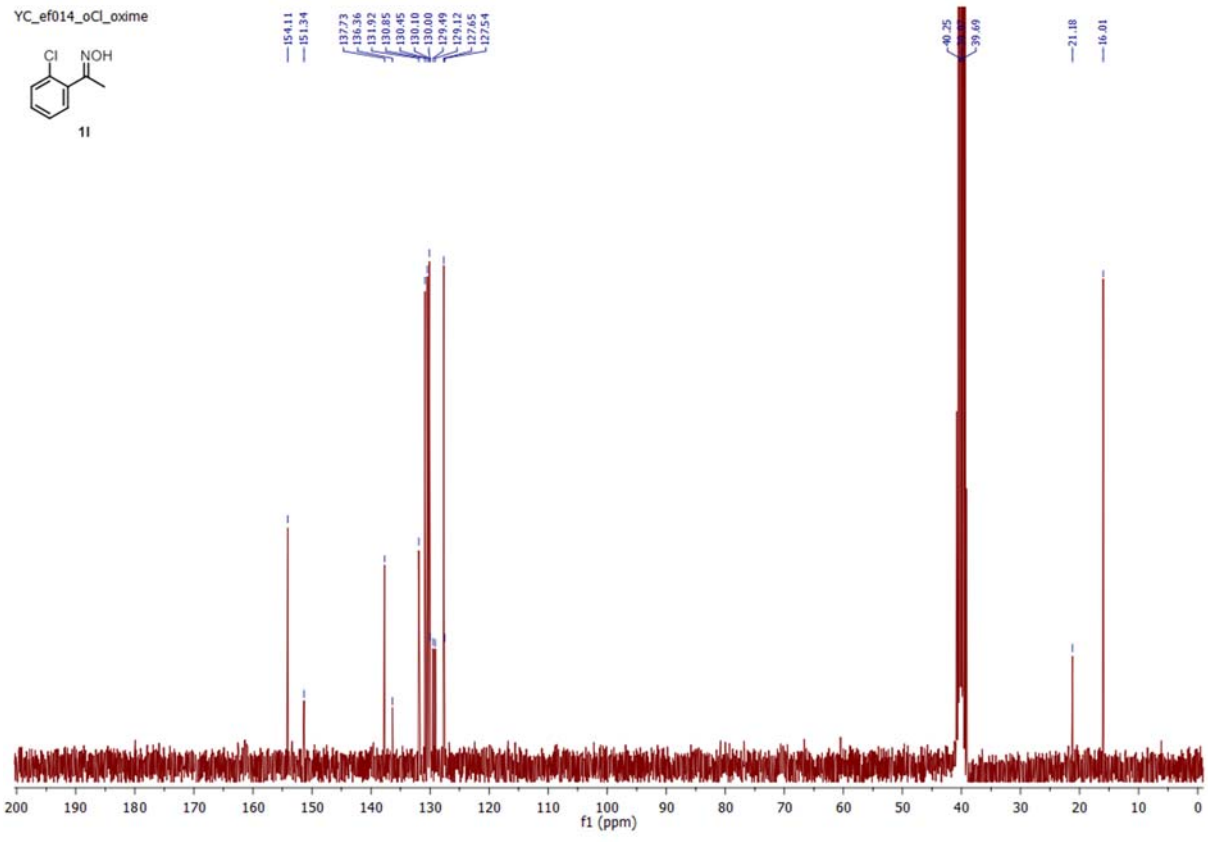
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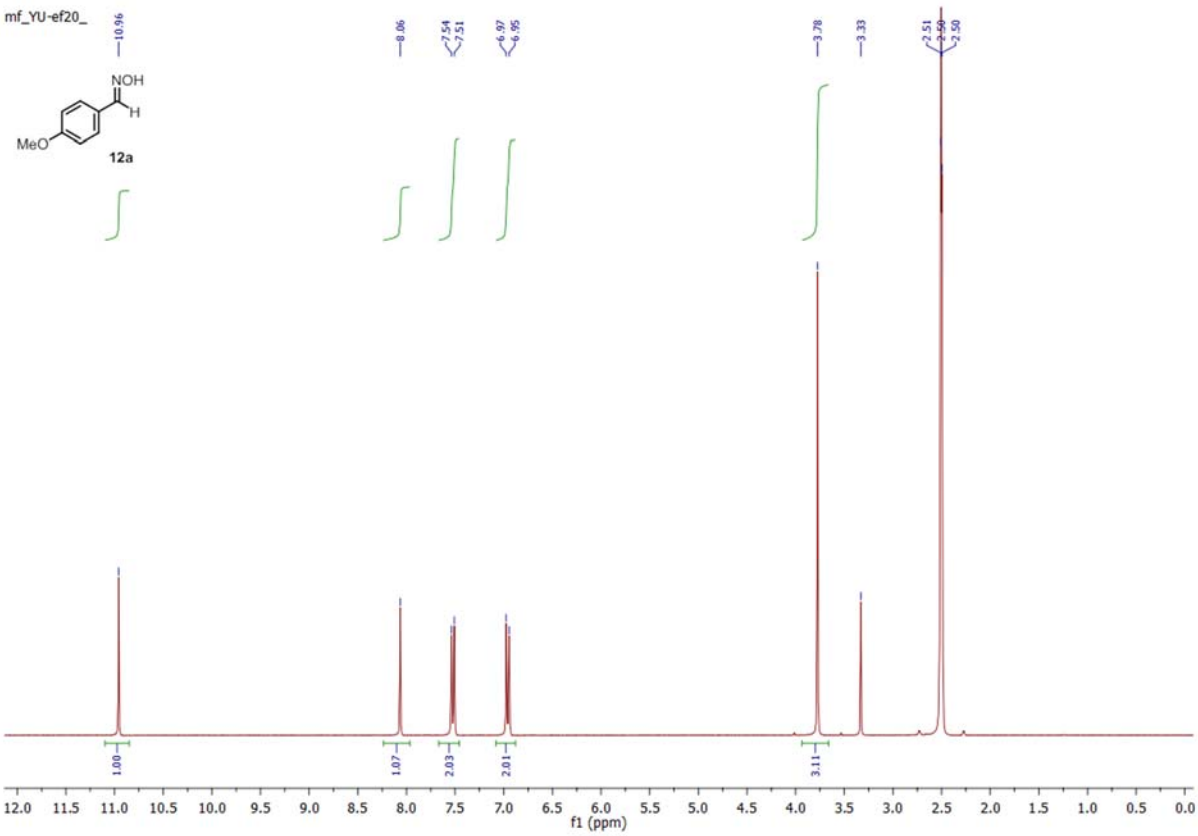
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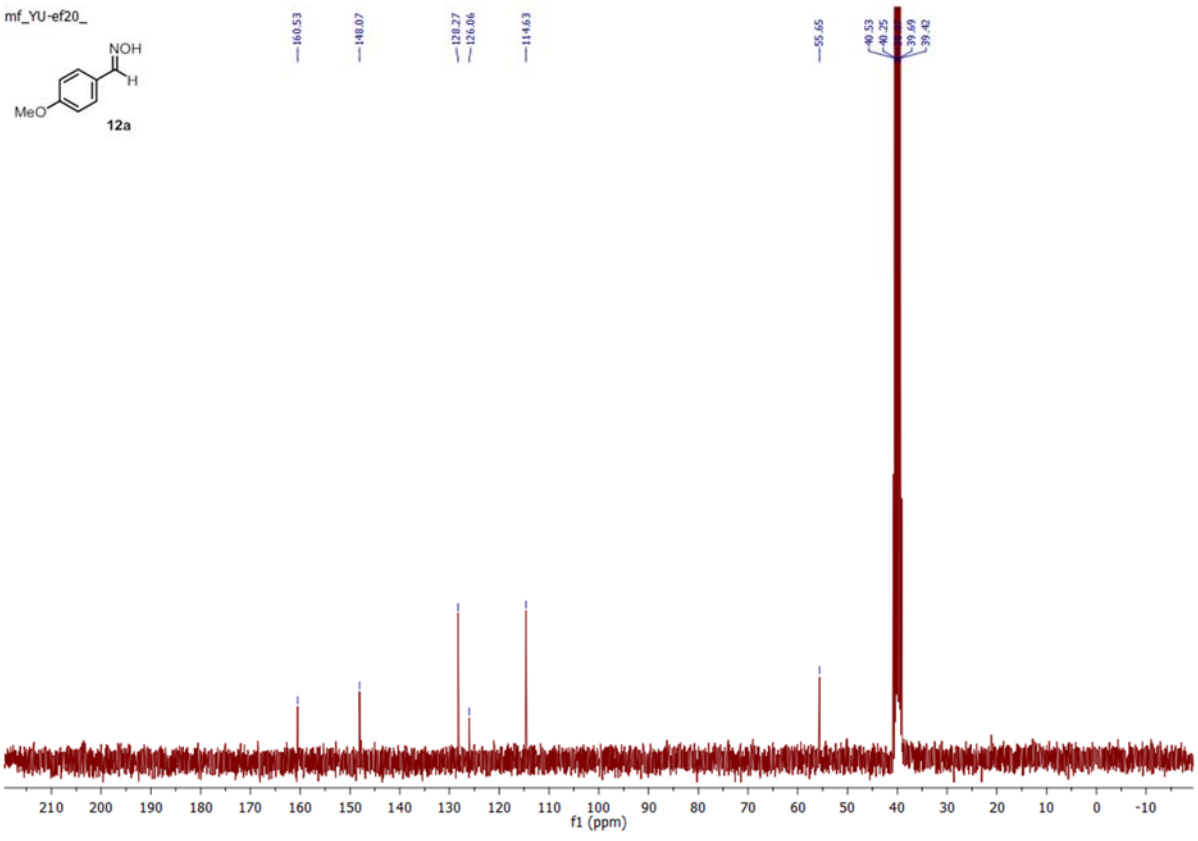
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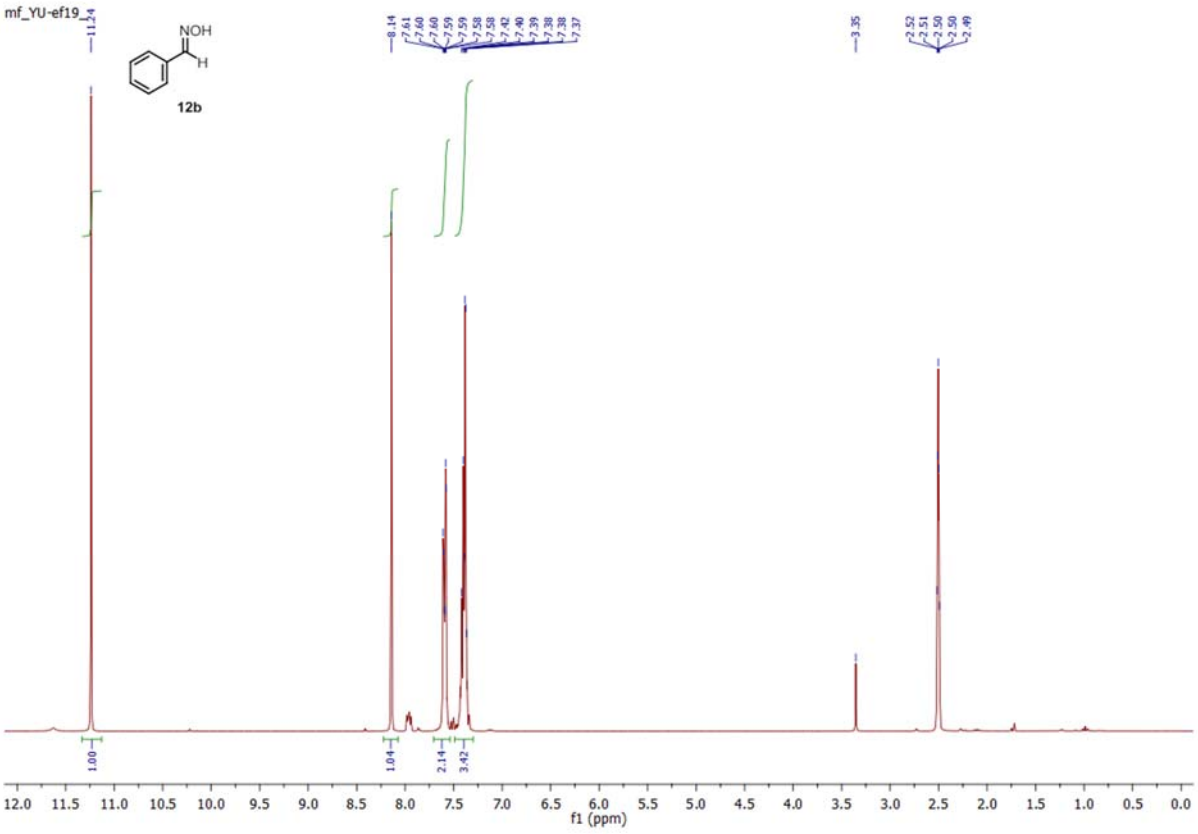
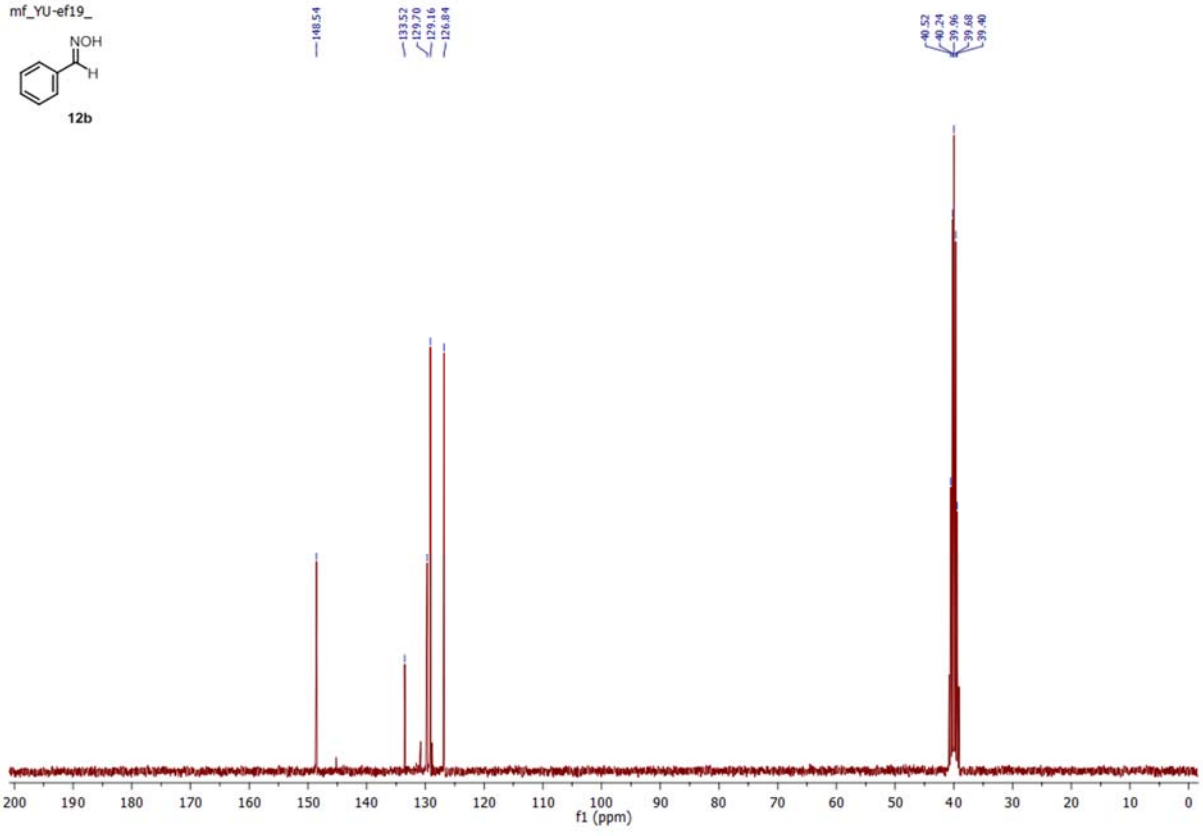
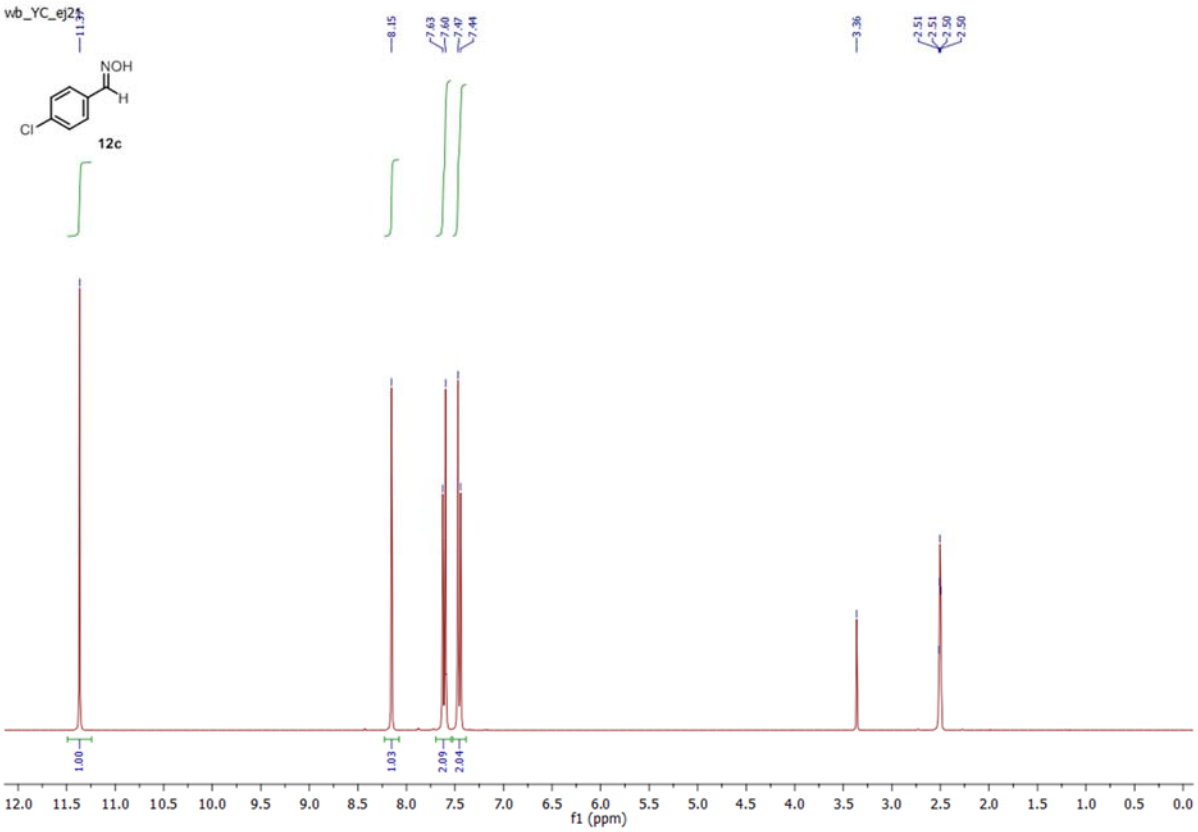
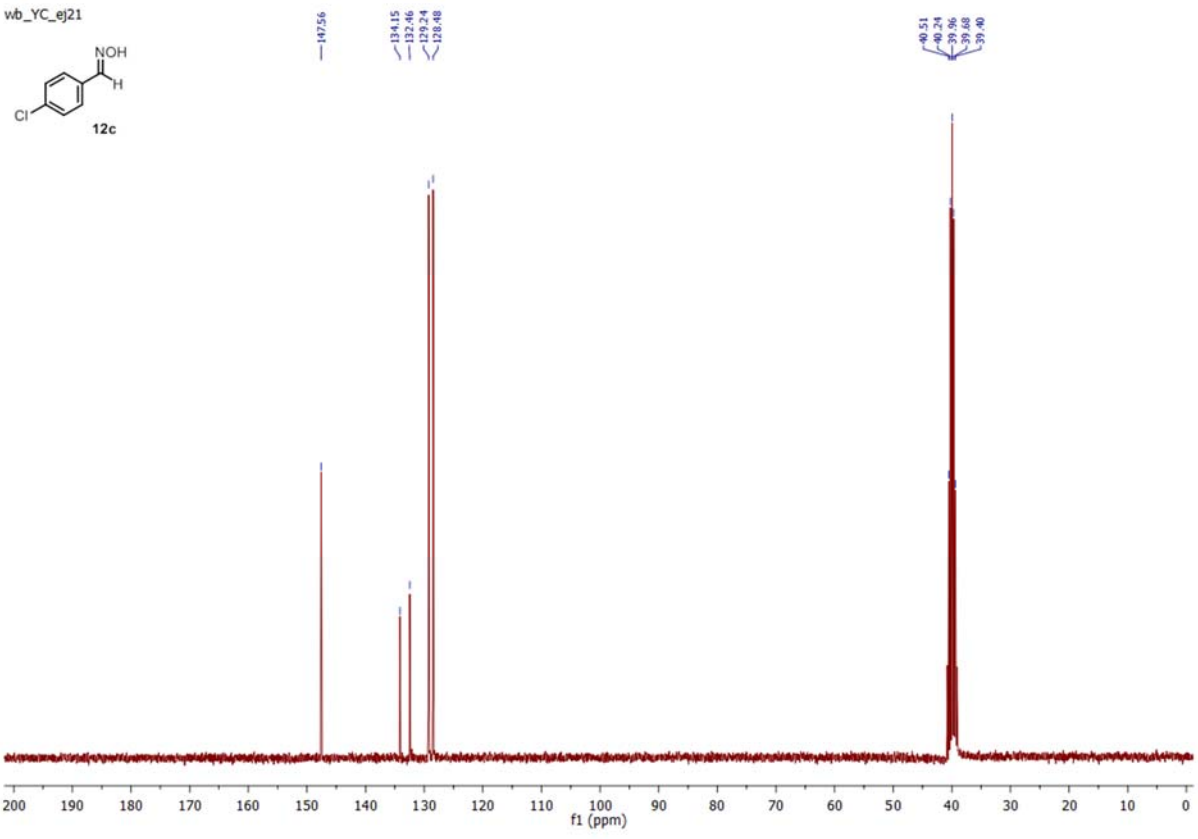
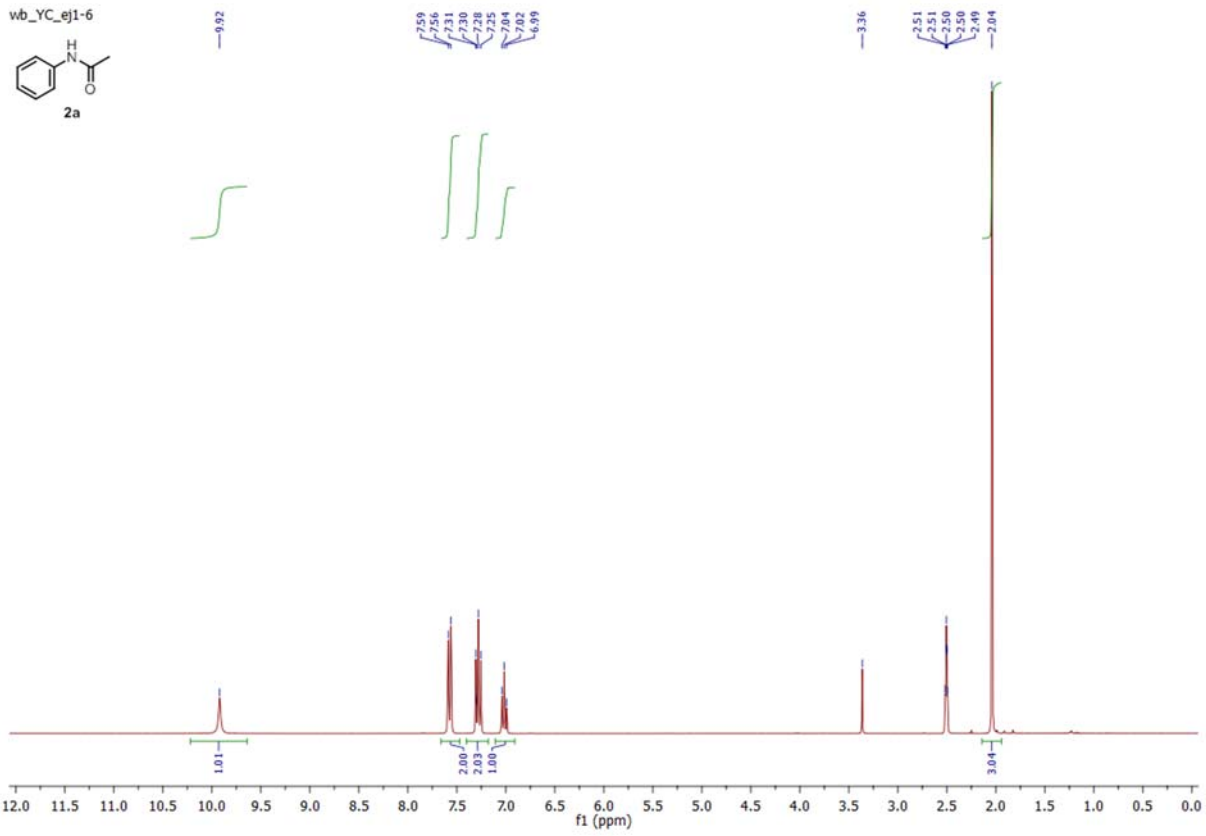
12a
f1 (ppm)

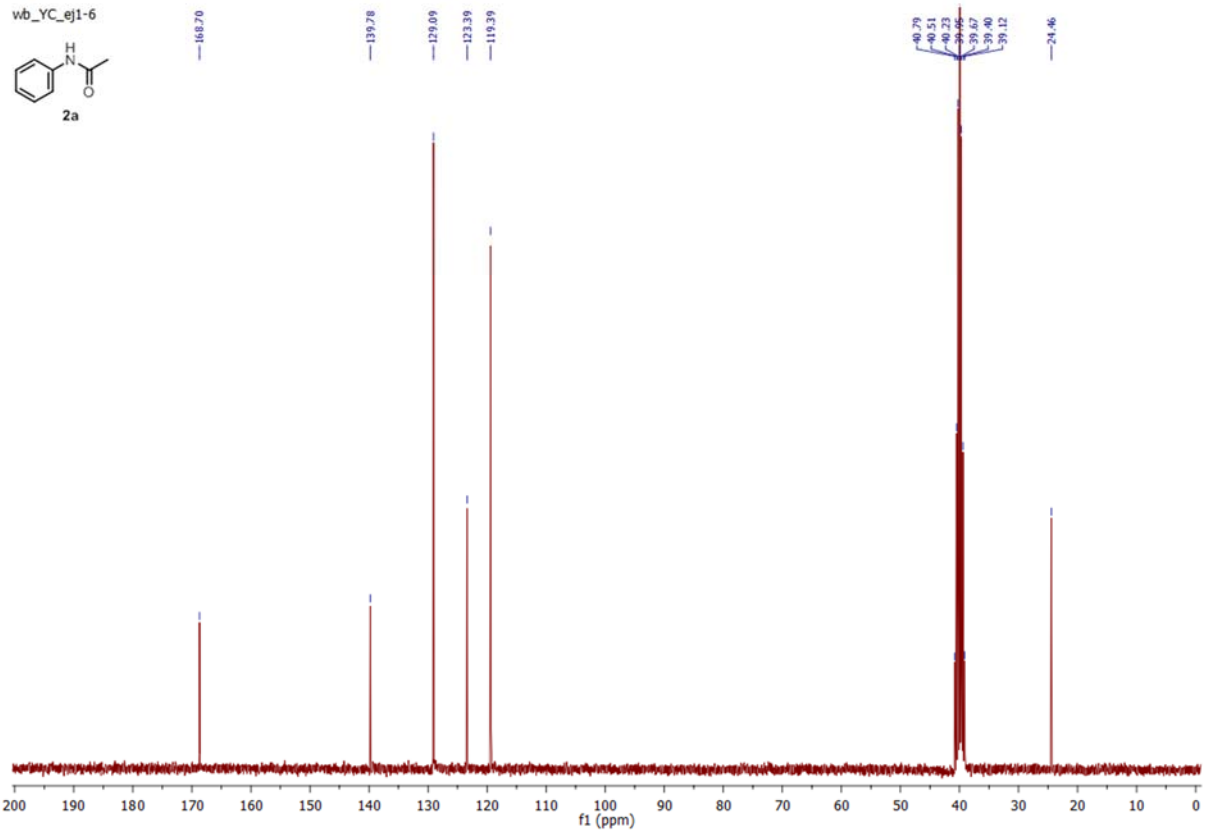

mf_YU-ef19_
NOH
H
12b
11.24
8.14
7.61
7.60
7.60
7.59
7.59
7.58
7.58
7.42
7.40
7.39
7.38
7.38
7.37
3.35
2.52
2.51
2.50
2.50
2.49
1.00
1.04
2.14
3.42
f1 (ppm)

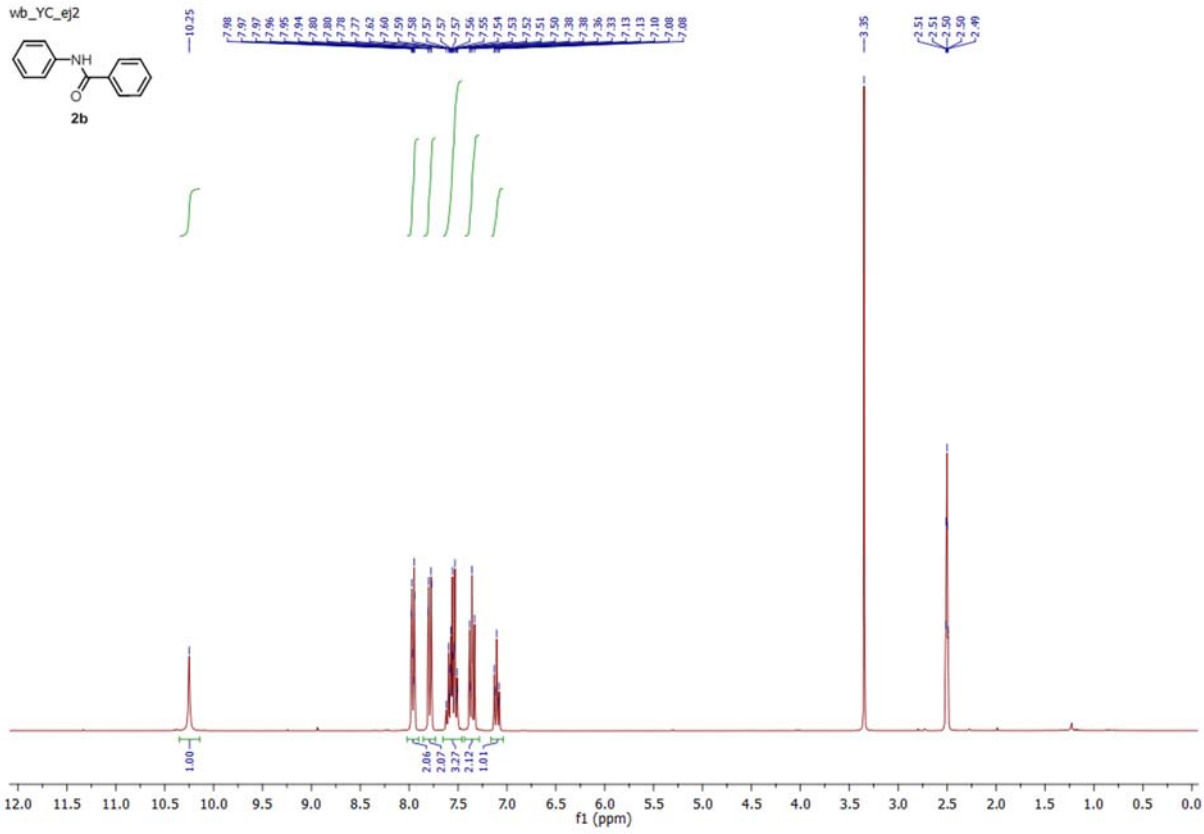

mf_YU-ef19_
NOH
H
12b
148.54
133.52
129.70
129.16
126.84
40.52
40.24
39.96
39.68
39.40
f1 (ppm)

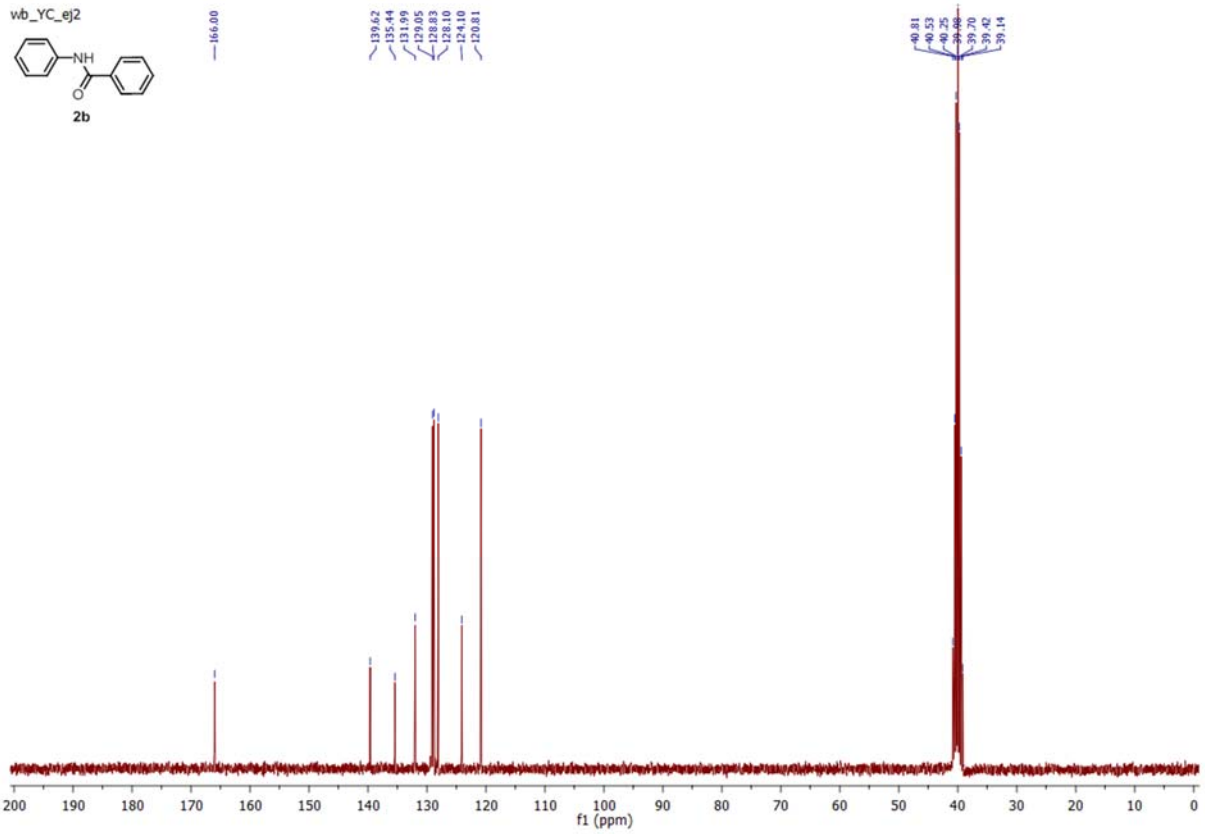

wb_YC_ej21
11.37
8.15
7.63
7.60
7.47
7.44
3.36
2.51
2.51
2.50
2.50
NOH
H
Cl
12c
1.00
1.03
2.09
2.04
f1 (ppm)

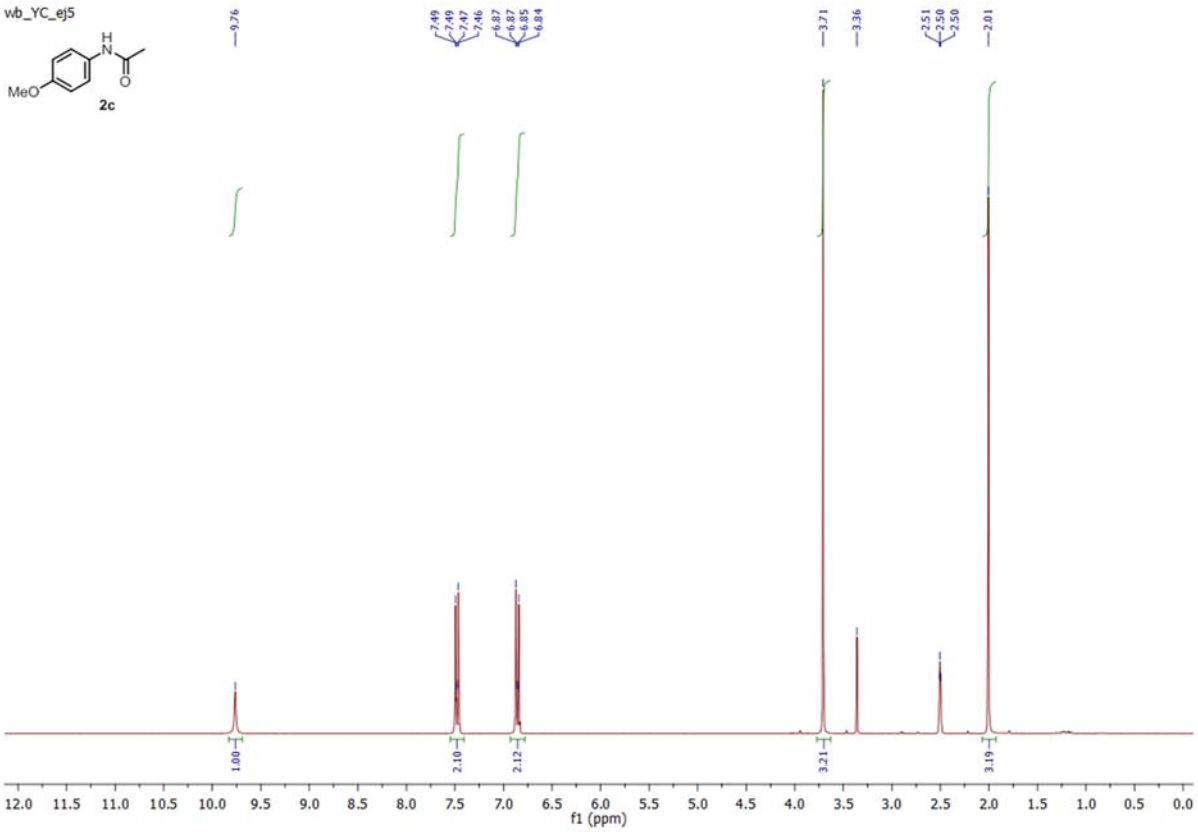

wb_YC_ej21
147.56
134.15
132.46
129.24
128.48
40.51
40.24
39.96
39.68
39.40
NOH
H
Cl
12c
f1 (ppm)

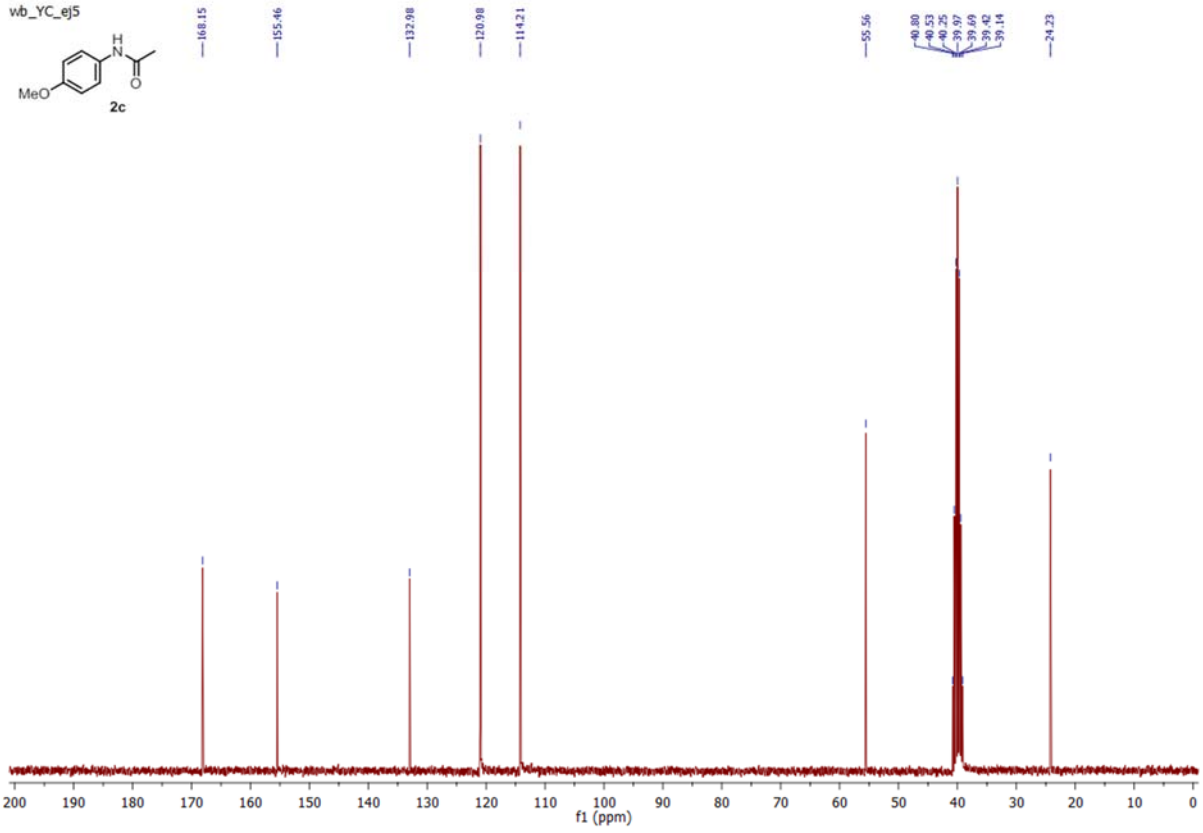

wb_YC_ej1-6
2a
9.92
7.59
7.56
7.31
7.30
7.28
7.25
7.04
7.02
6.99
3.36
2.51
2.51
2.50
2.50
2.49
2.04
1.01
2.00
2.03
1.00
3.04
f1 (ppm)

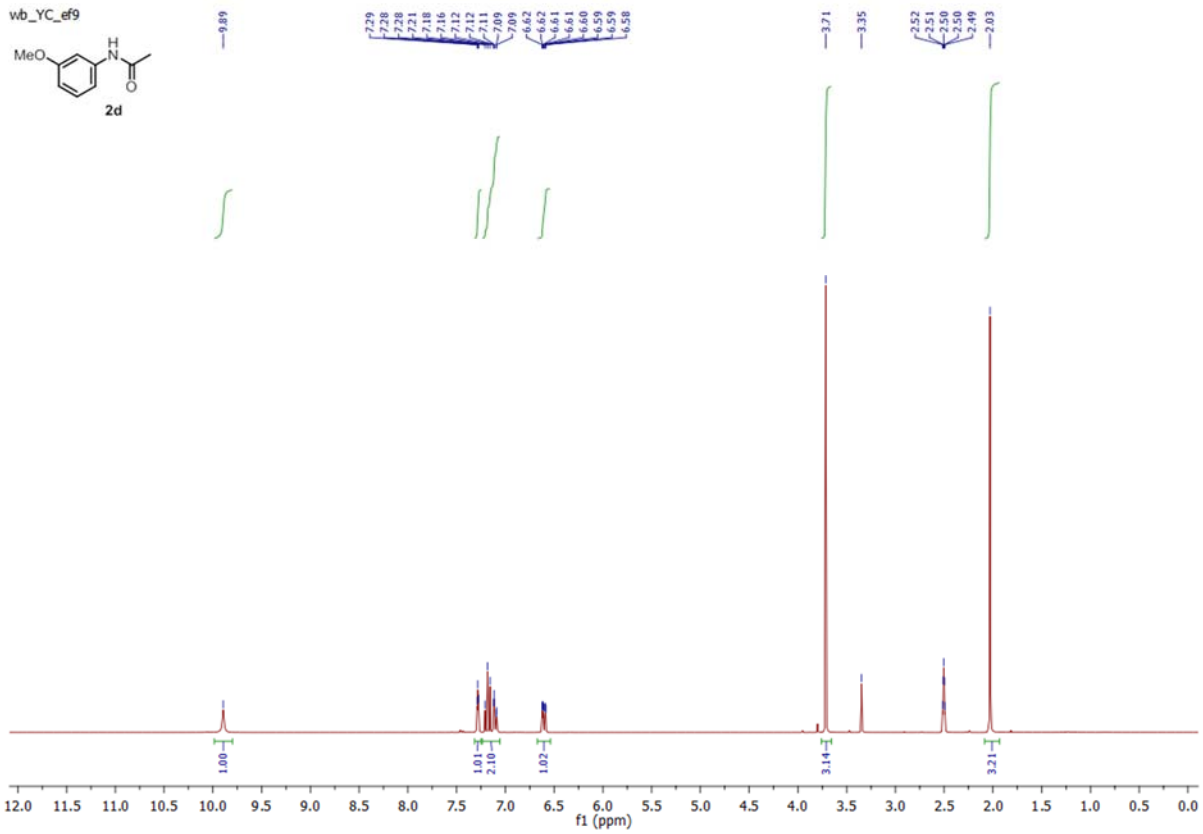

wb_YC_ej1-6
2a
168.70
139.78
129.09
123.39
119.39
40.79
40.51
40.23
39.95
39.67
39.40
39.12
24.46
f1 (ppm)

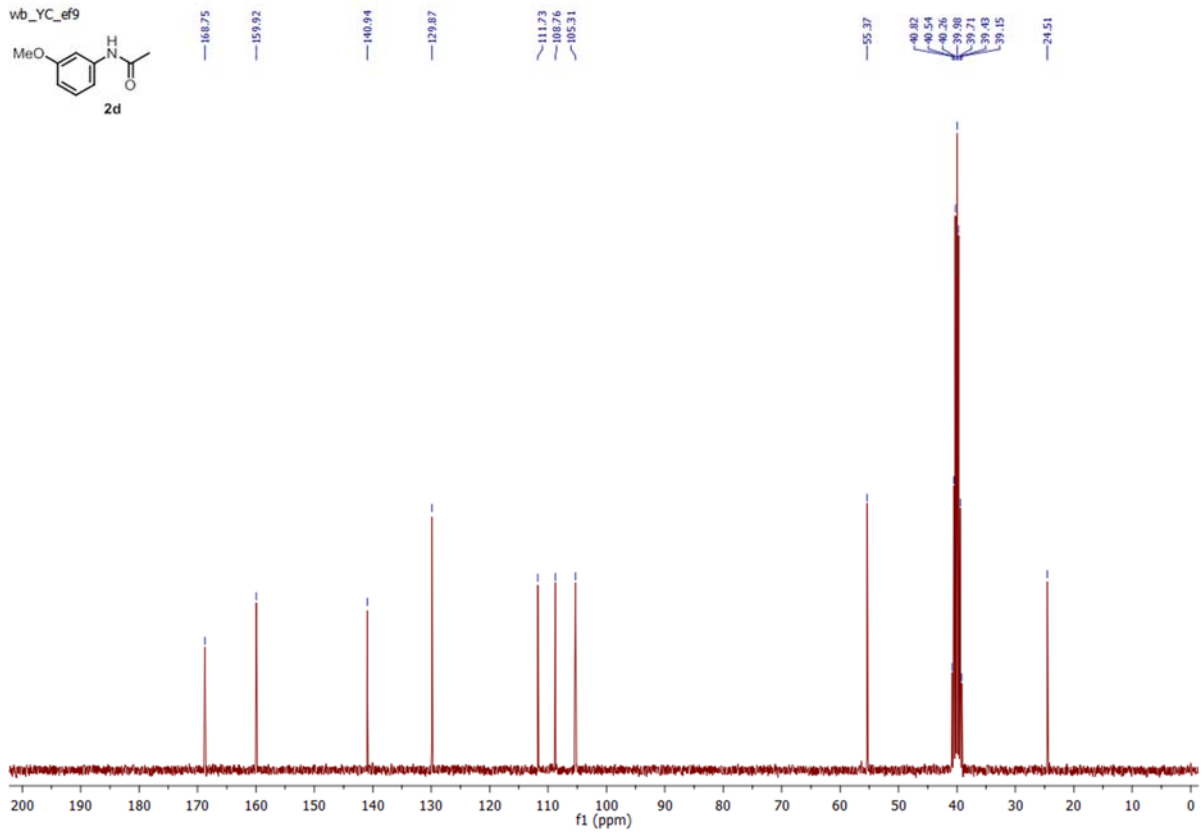

wb_YC_ej2
NH
O
2b
10.25
7.98
7.97
7.97
7.96
7.95
7.94
7.80
7.80
7.78
7.77
7.62
7.60
7.59
7.58
7.57
7.57
7.57
7.56
7.55
7.54
7.53
7.52
7.51
7.50
7.38
7.38
7.36
7.33
7.13
7.10
7.08
7.08
3.35
2.51
2.51
2.50
2.50
2.50
2.49
1.00
2.06
2.07
3.27
2.12
1.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

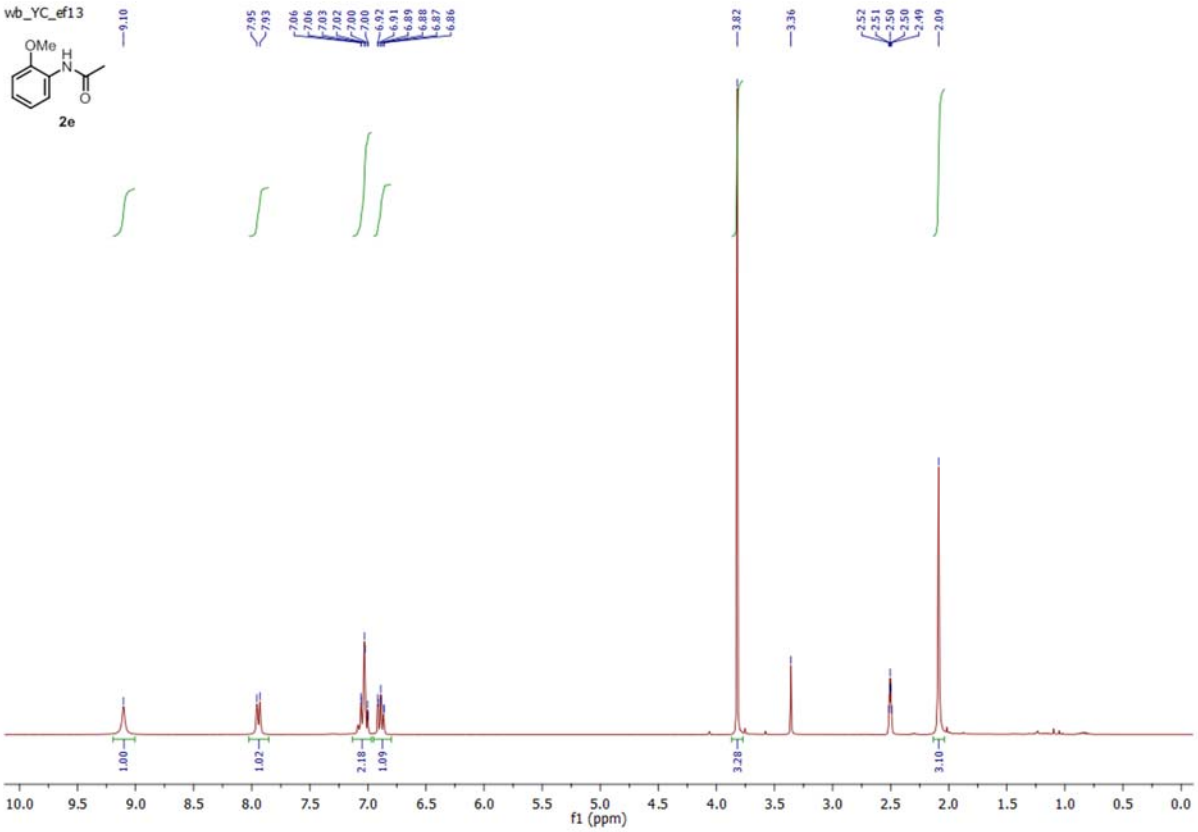

wb_YC_ej2
NH
O
2b
166.00
139.62
135.44
131.99
129.05
128.83
128.10
124.10
120.81
40.81
40.53
40.25
39.98
39.70
39.42
39.14
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

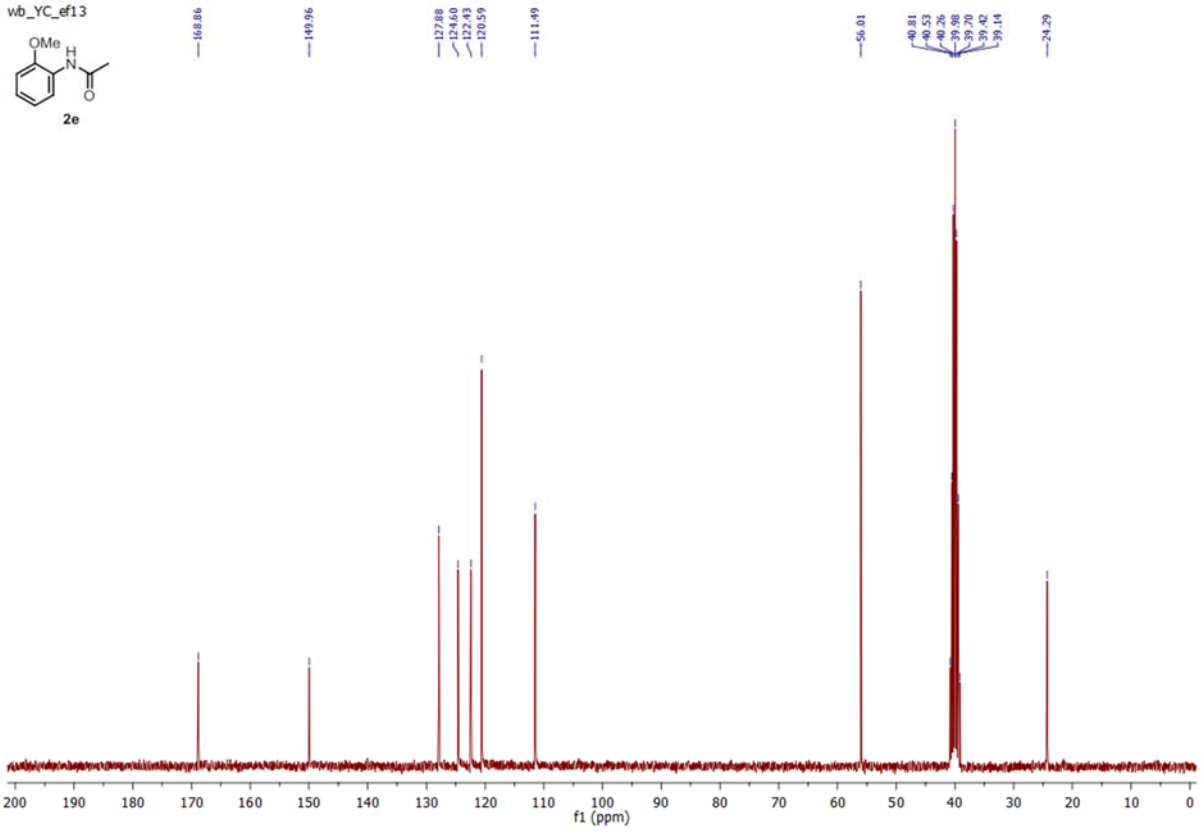

wb_YC_ej5
MeO
2c
9.76
7.49
7.49
7.47
7.47
7.46
6.87
6.87
6.85
6.84
3.71
3.36
2.51
2.50
2.50
2.01
1.00
2.10
2.12
3.21
3.19
f1 (ppm)

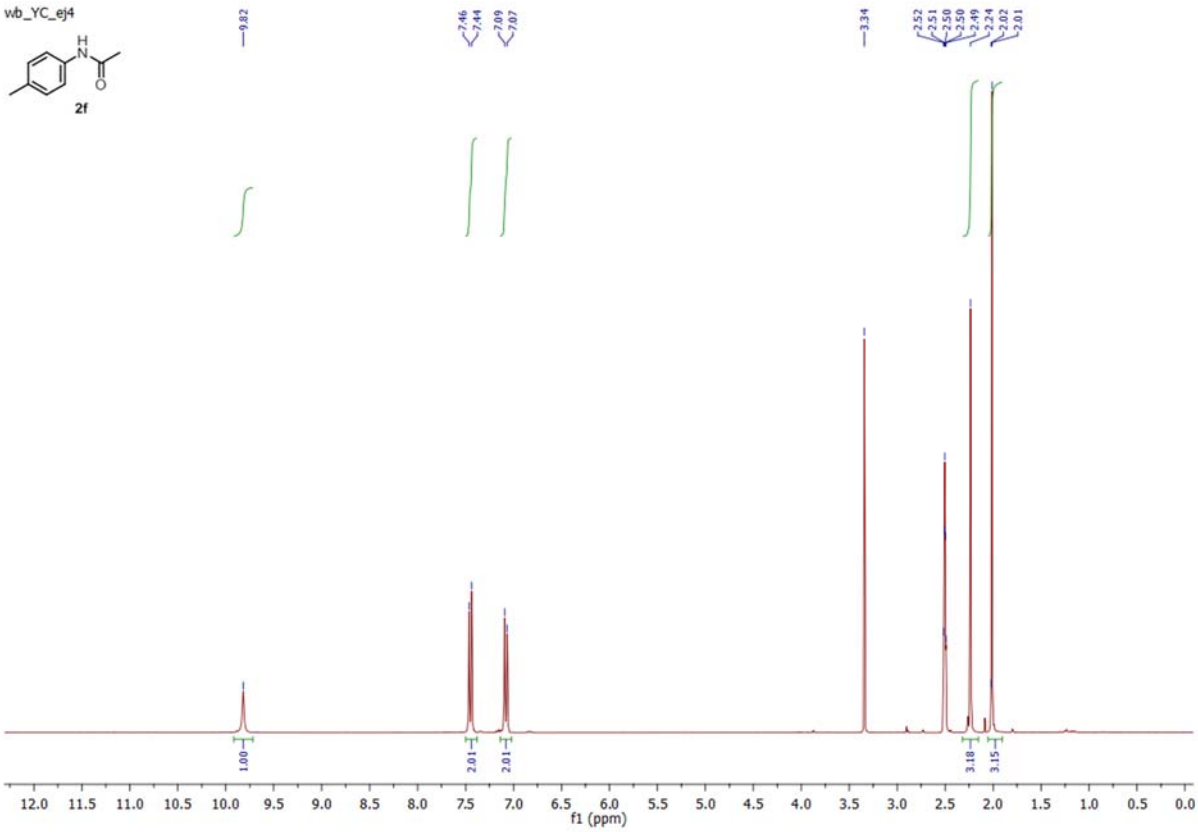

wb_YC_ej5
MeO
2c
168.15
155.46
132.98
120.98
114.21
55.56
40.80
40.53
40.25
39.97
39.69
39.42
39.14
24.23
f1 (ppm)

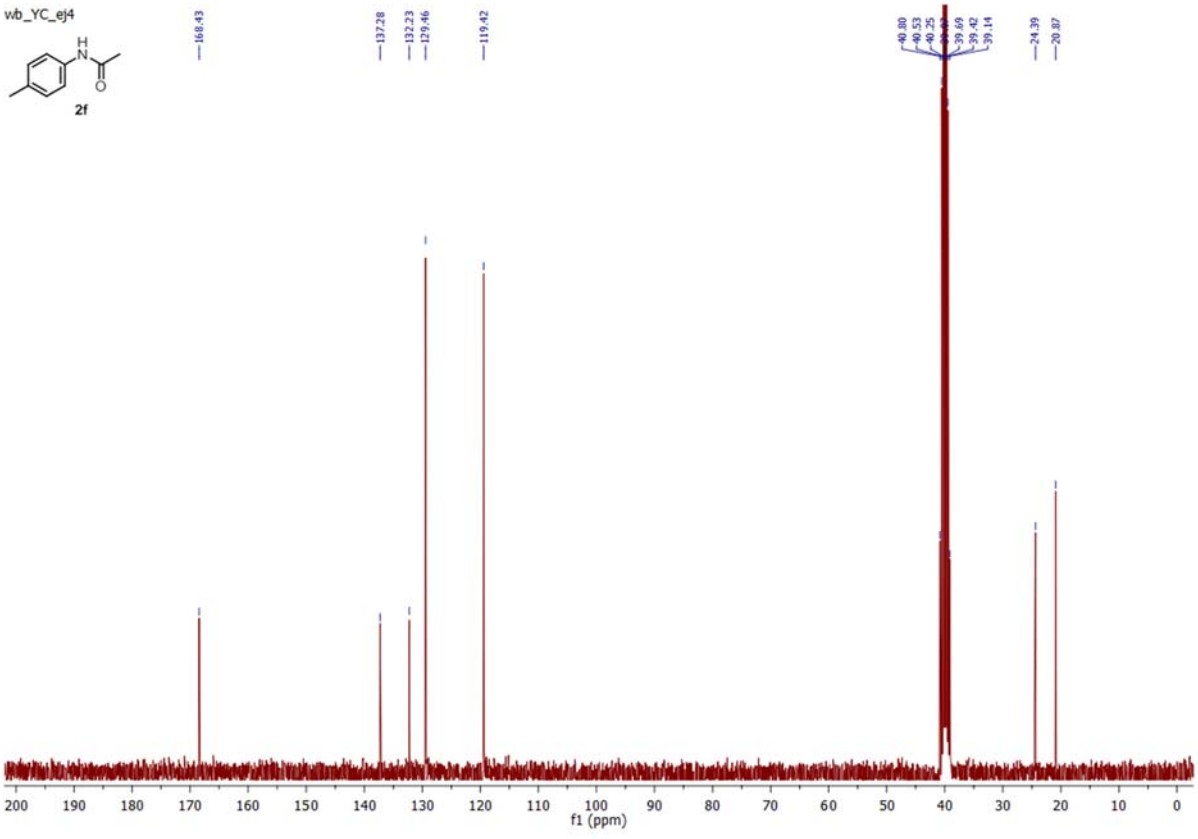

wb_YC_ef9
MeO
H
N
O
2d
9.89
7.29
7.28
7.28
7.21
7.18
7.16
7.12
7.12
7.11
7.09
7.09
6.62
6.62
6.61
6.61
6.60
6.59
6.59
6.58
3.71
3.35
2.52
2.51
2.50
2.50
2.49
2.03
1.00
1.01
2.10
1.02
3.14
3.21
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

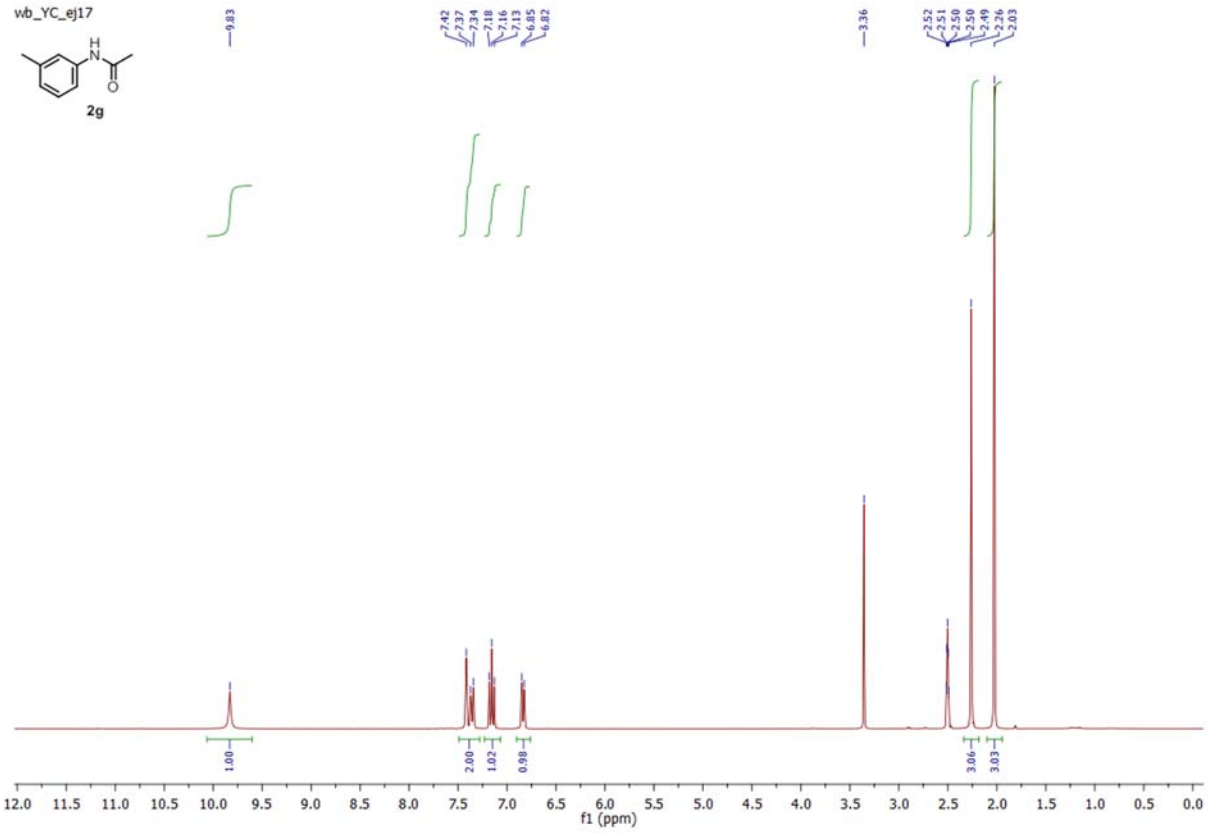

wb_YC_ef9
MeO
H
N
O
2d
168.75
159.92
140.94
129.87
111.73
108.76
105.31
55.37
40.82
40.54
40.26
39.98
39.71
39.43
39.15
24.51
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

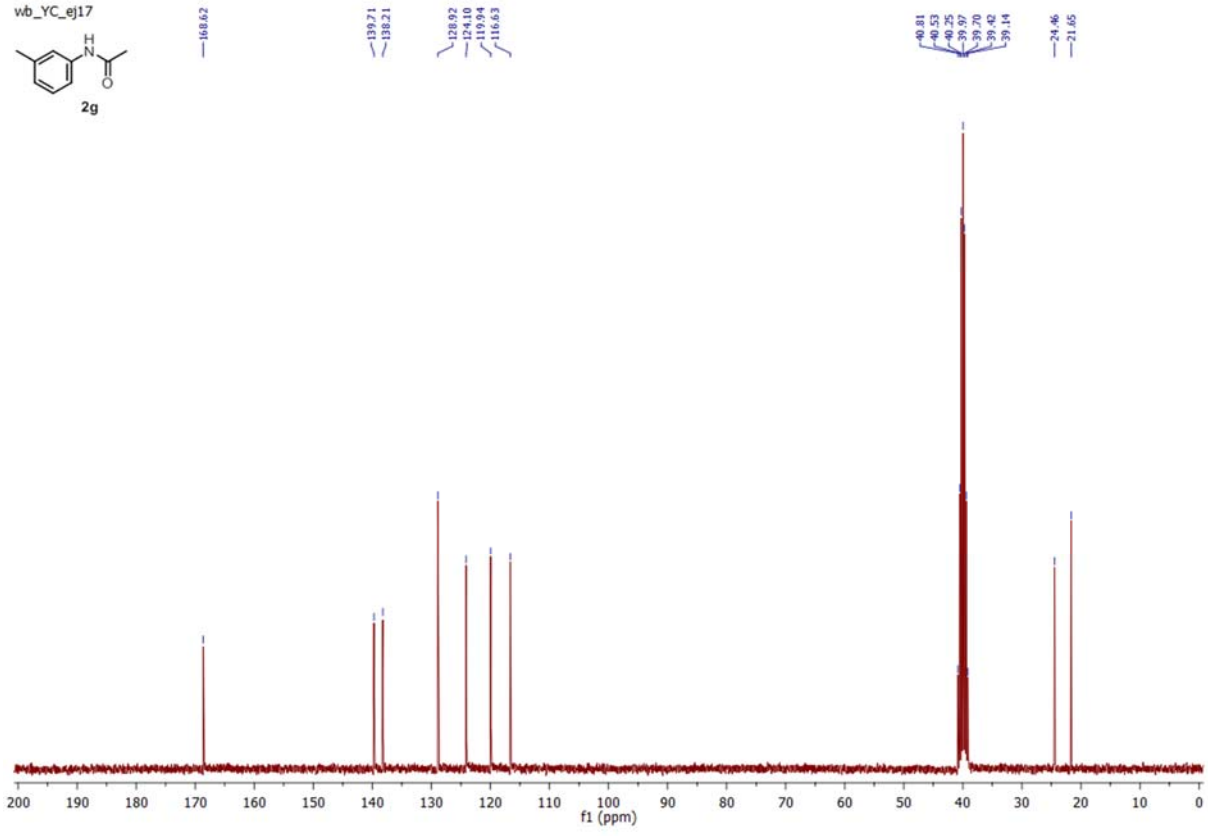

wb_YC_ef13
OMe
H
N
O
2e
9.10
7.95
7.93
7.06
7.06
7.03
7.02
7.00
7.00
6.92
6.91
6.89
6.88
6.87
6.86
3.82
3.36
2.52
2.51
2.50
2.50
2.49
2.09
1.00
1.02
2.18
1.09
3.28
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

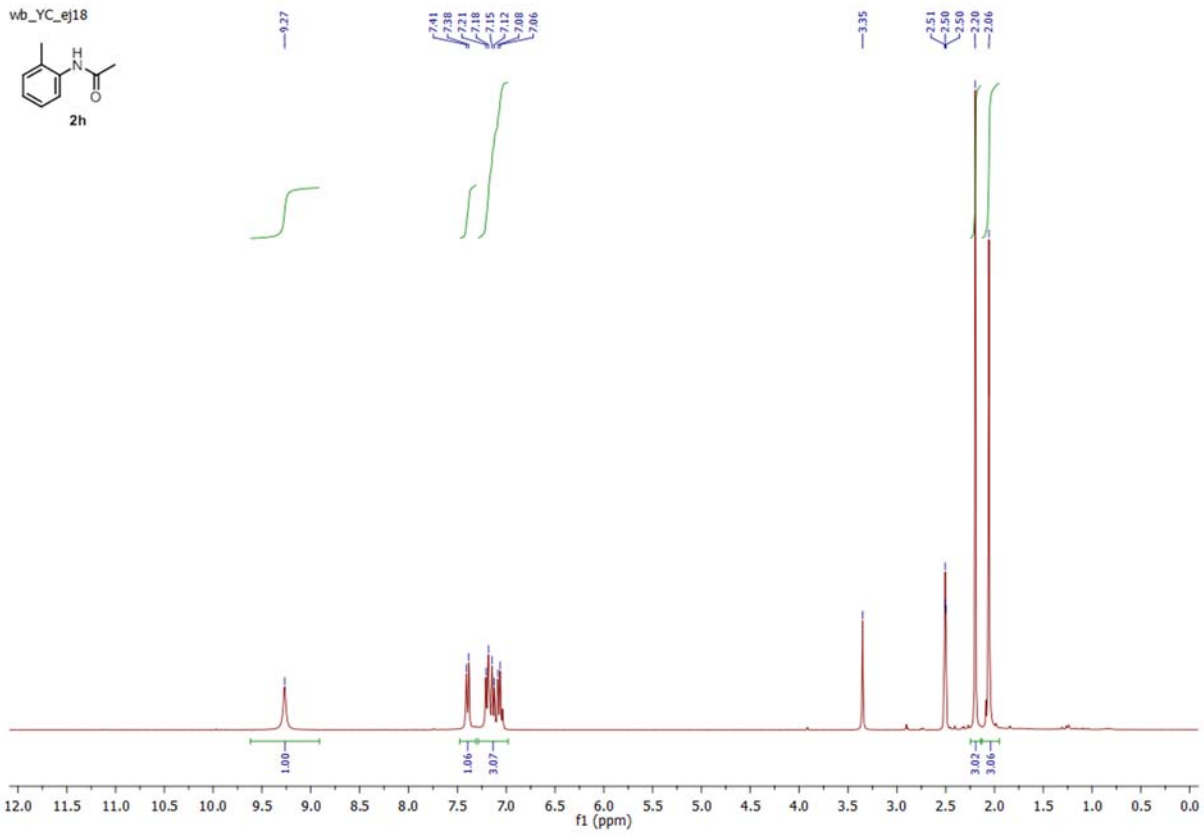

wb_YC_ef13
OMe
H
N
O
2e
168.86
149.96
127.88
124.60
122.43
120.59
111.49
56.01
40.81
40.53
40.26
39.98
39.70
39.42
39.14
24.29
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

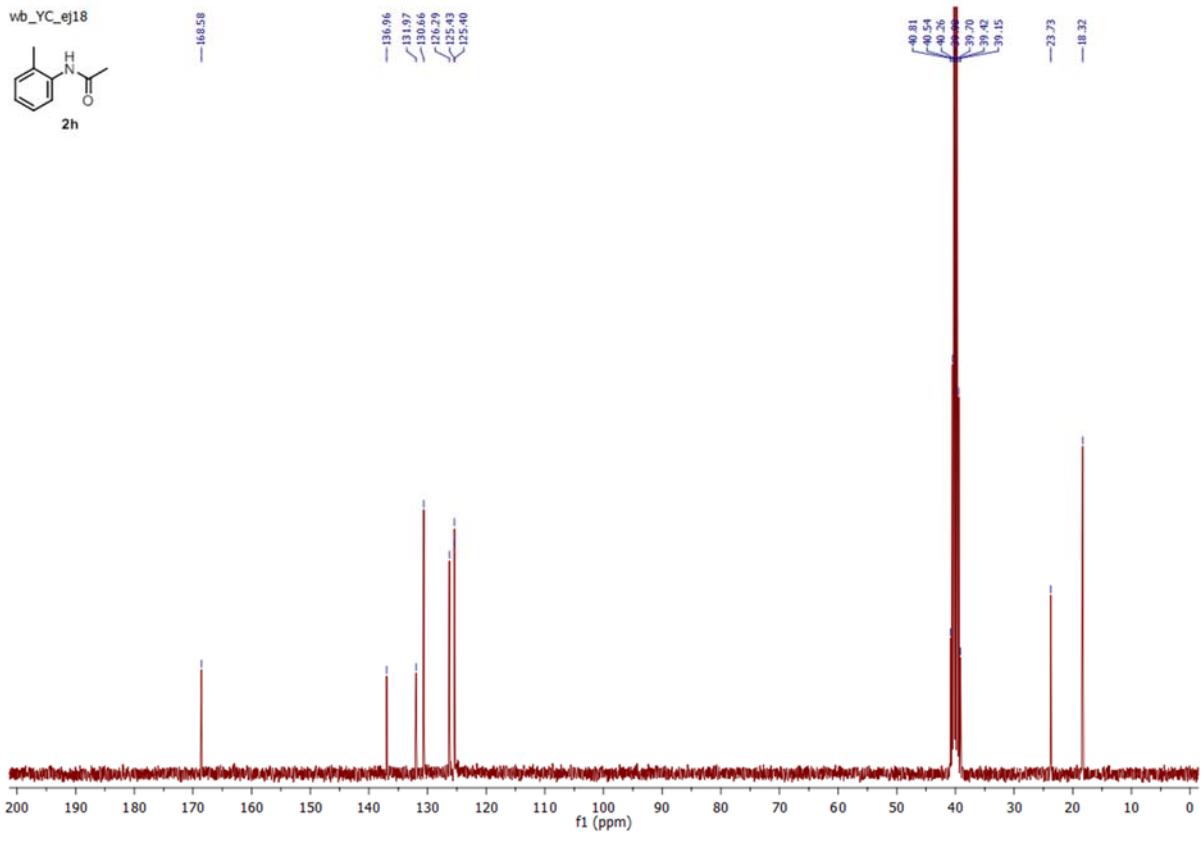

wb_YC_ej4
2f
9.82
7.46
7.44
7.09
7.07
3.34
2.52
2.51
2.50
2.50
2.49
2.24
2.02
2.01
1.00
2.01
2.01
3.18
3.15
f1 (ppm)

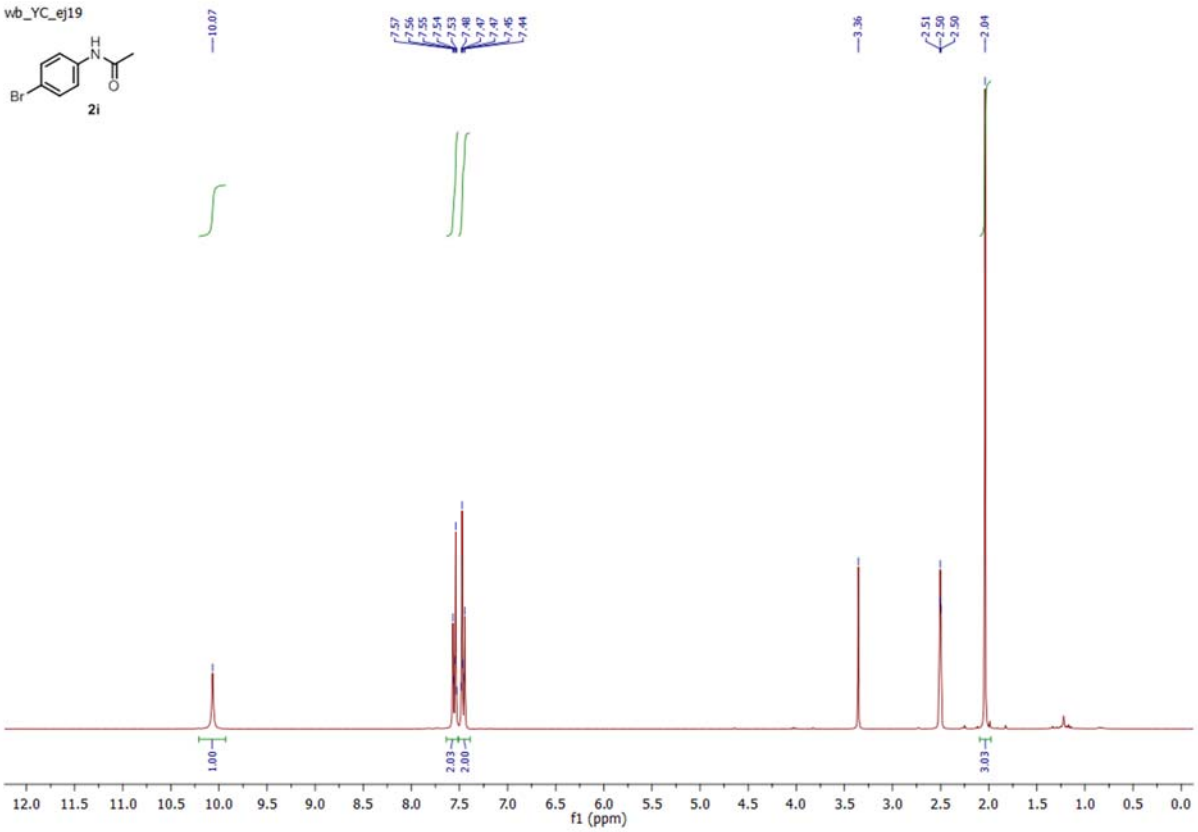

wb_YC_ej4
2f
168.43
137.28
132.23
129.46
119.42
40.80
40.53
40.25
39.69
39.42
39.14
24.39
20.87
f1 (ppm)

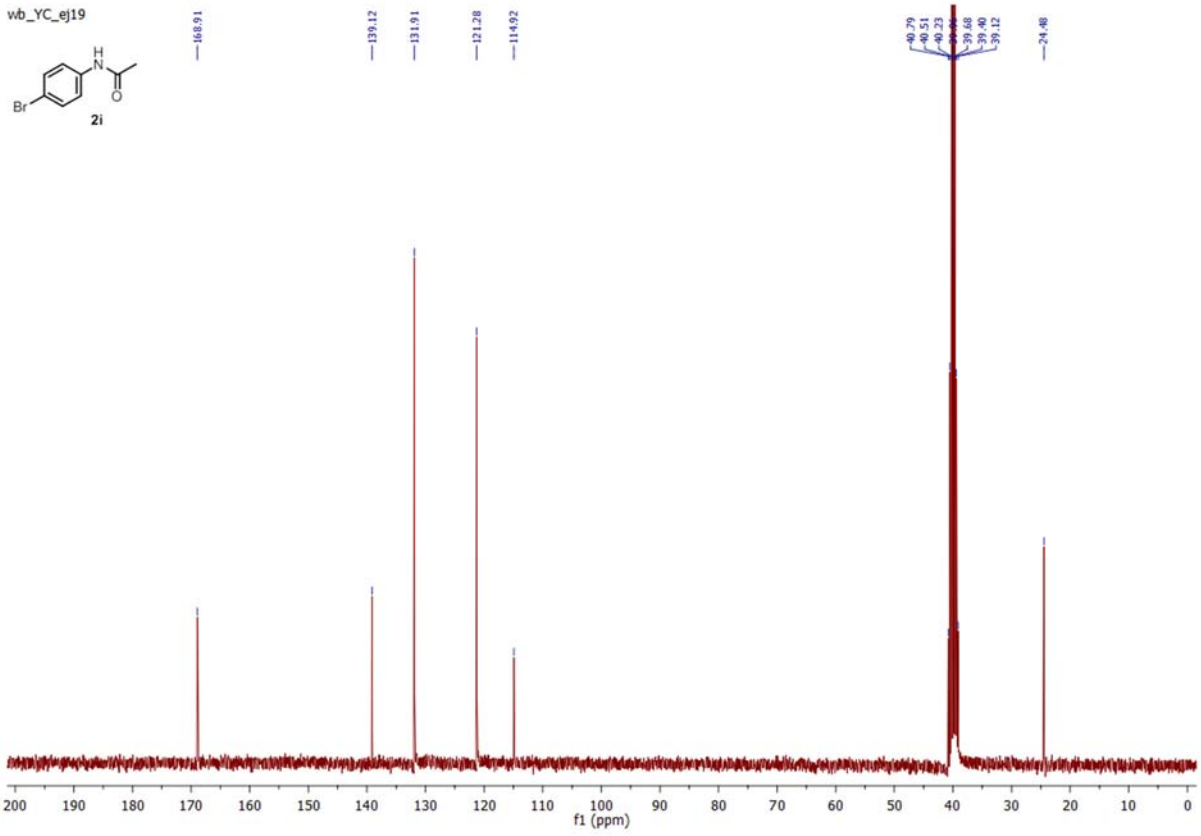

wb_YC_ej17
2g
9.83
7.42
7.37
7.34
7.18
7.16
7.13
6.85
6.82
3.36
2.52
2.51
2.50
2.50
2.49
2.26
2.03
1.00
2.00
1.02
0.98
3.06
3.03
f1 (ppm)

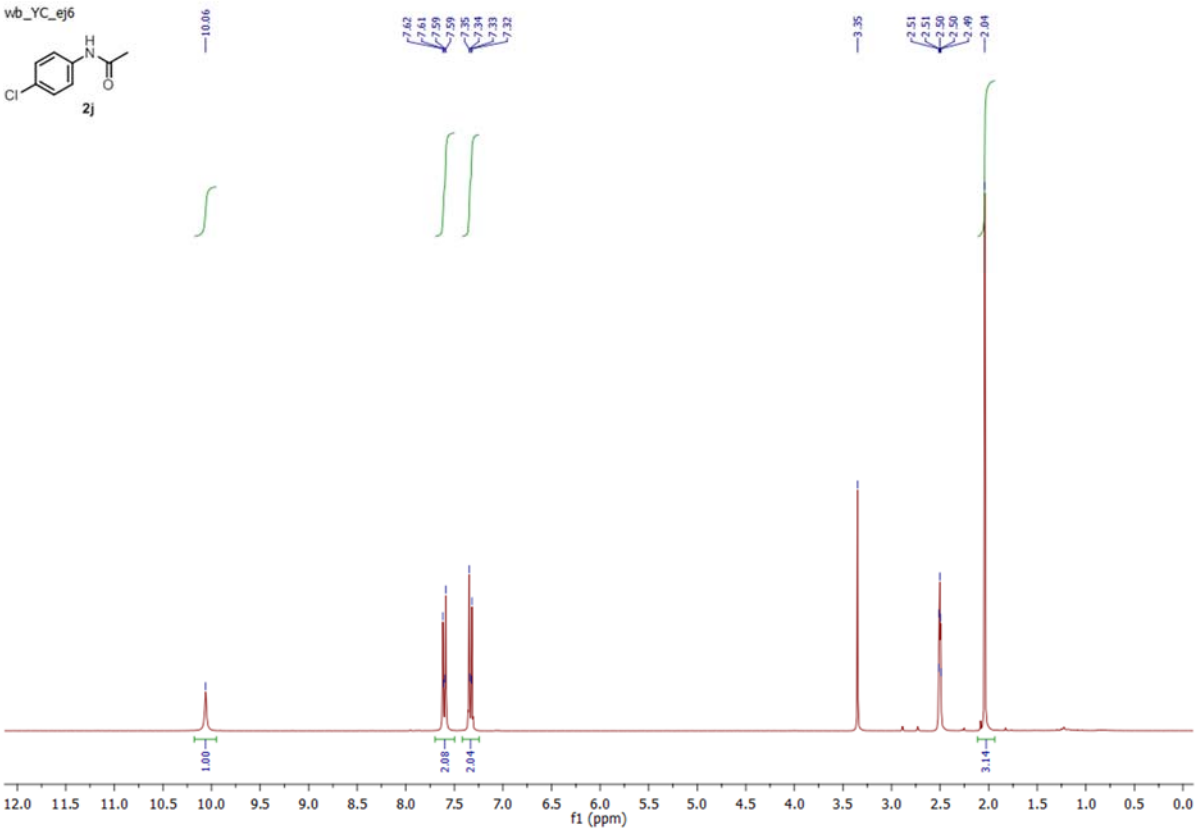

wb_YC_ej17
2g
168.62
139.71
138.21
128.92
124.10
119.94
116.63
40.81
40.53
40.25
39.97
39.70
39.42
39.14
24.46
21.65
f1 (ppm)

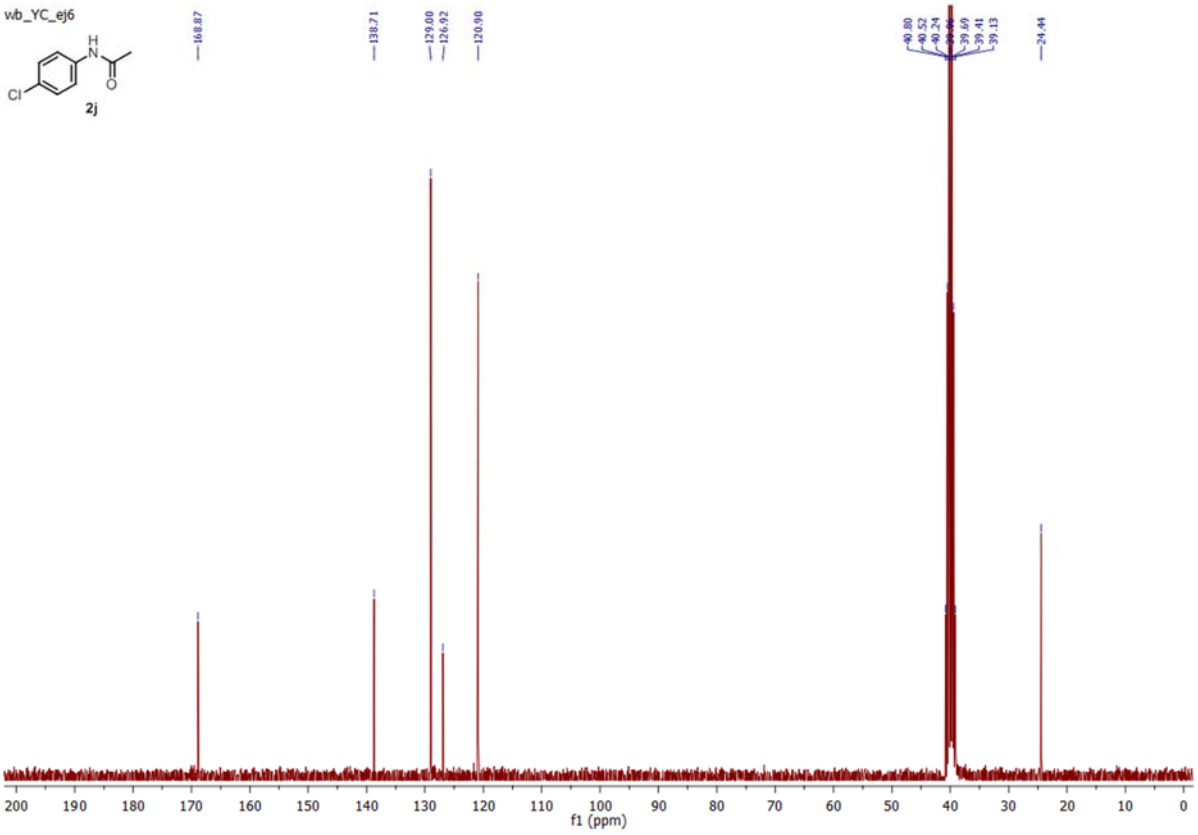

wb_YC_ej18
2h
9.27
7.41
7.38
7.21
7.18
7.15
7.12
7.08
7.06
3.35
2.51
2.50
2.50
2.20
2.06
1.00
1.06
3.07
3.02
3.06
f1 (ppm)

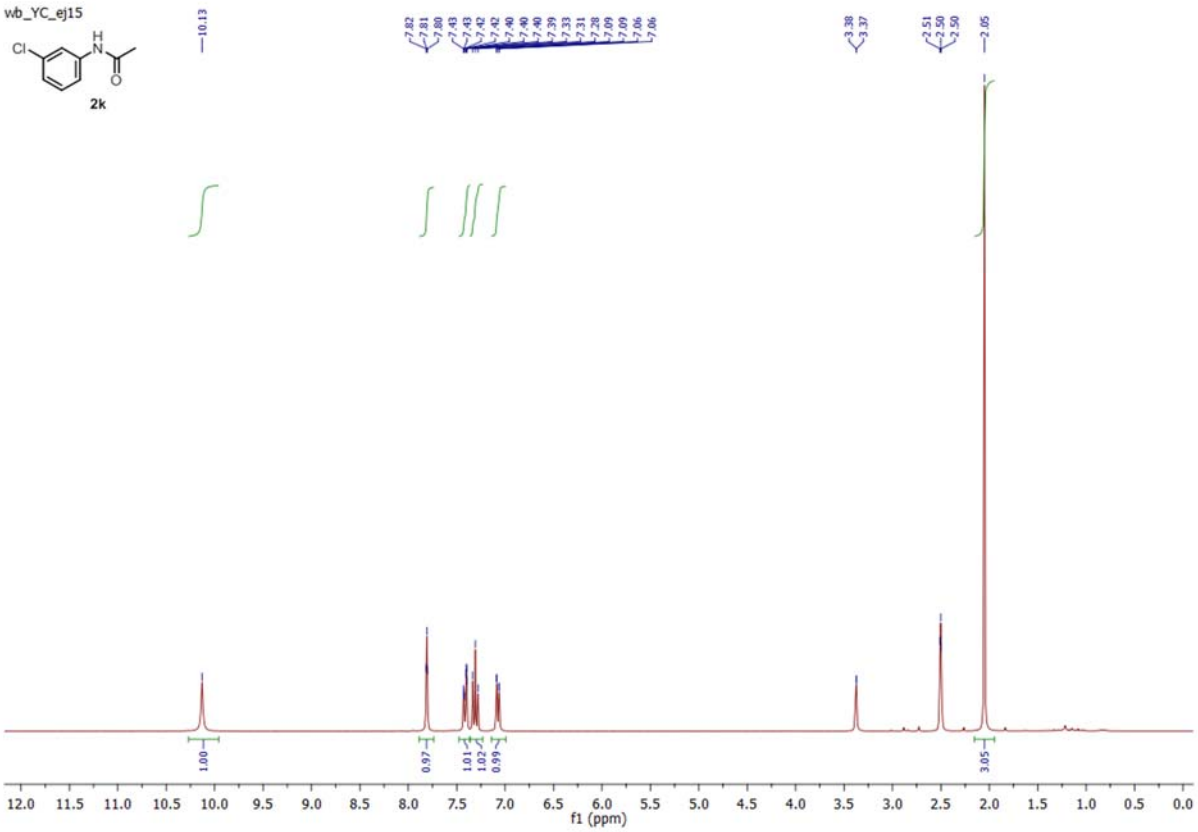

wb_YC_ej18
2h
168.58
136.96
131.97
130.66
126.29
125.43
125.40
40.81
40.54
40.26
39.70
39.42
39.15
23.73
18.32
f1 (ppm)

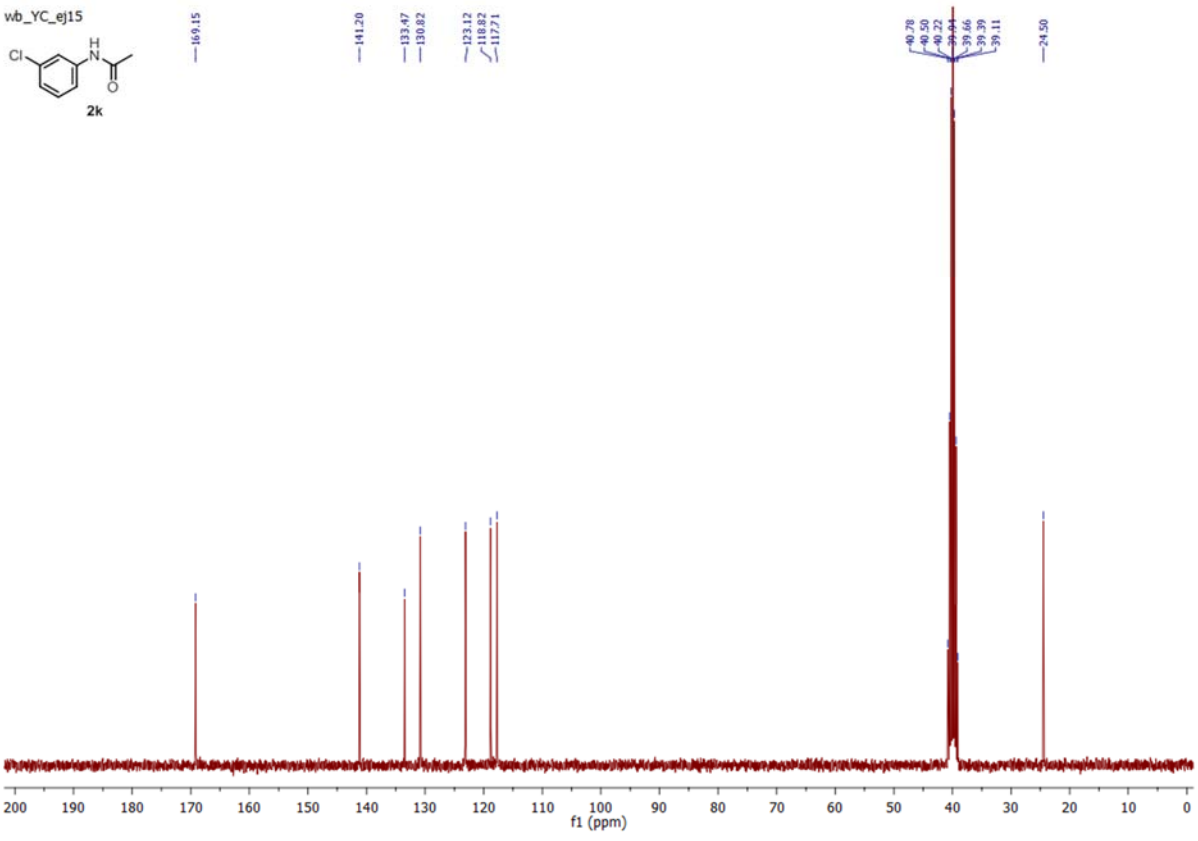

wb_YC_ej19
2i
10.07
7.57
7.56
7.55
7.54
7.53
7.48
7.47
7.47
7.45
7.44
3.36
2.51
2.50
2.50
2.04
1.00
2.03
2.00
3.03
f1 (ppm)

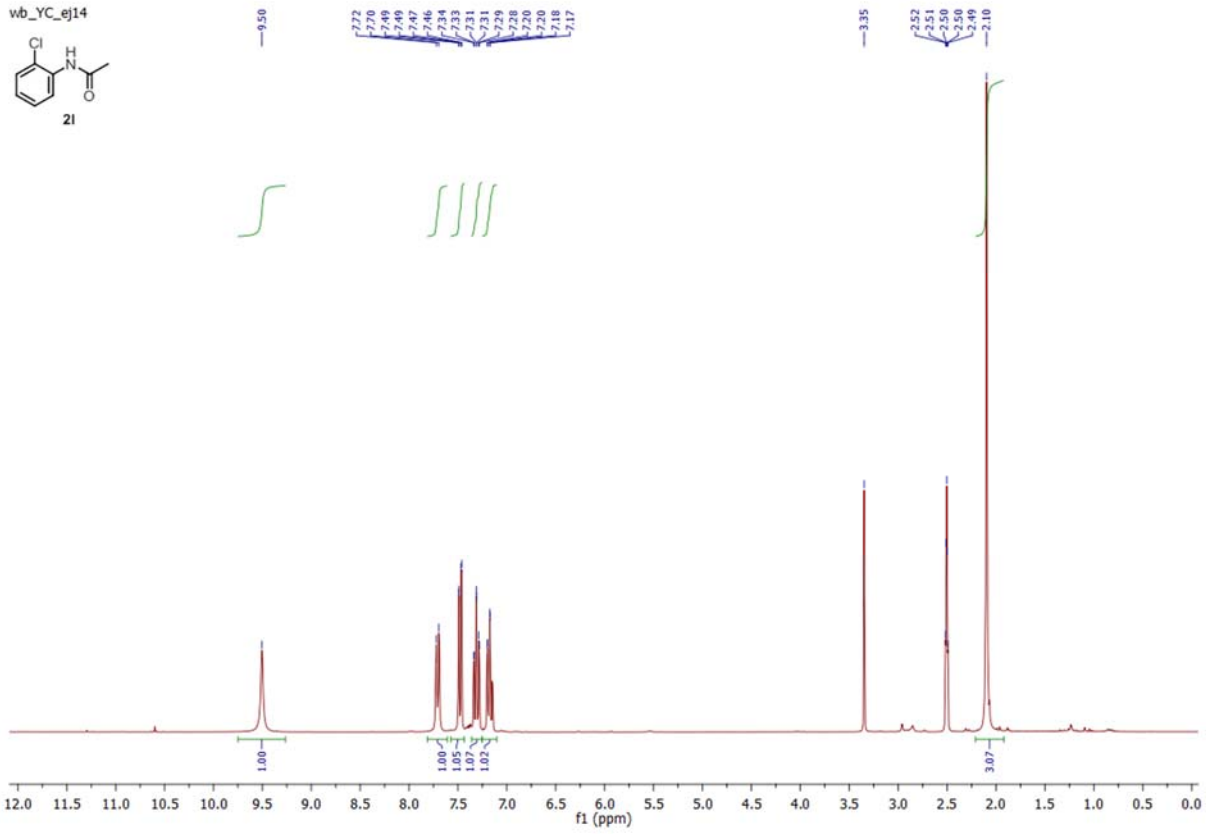

wb_YC_ej19
2i
168.91
139.12
131.91
121.28
114.92
40.79
40.51
40.23
39.68
39.40
39.12
24.48
f1 (ppm)

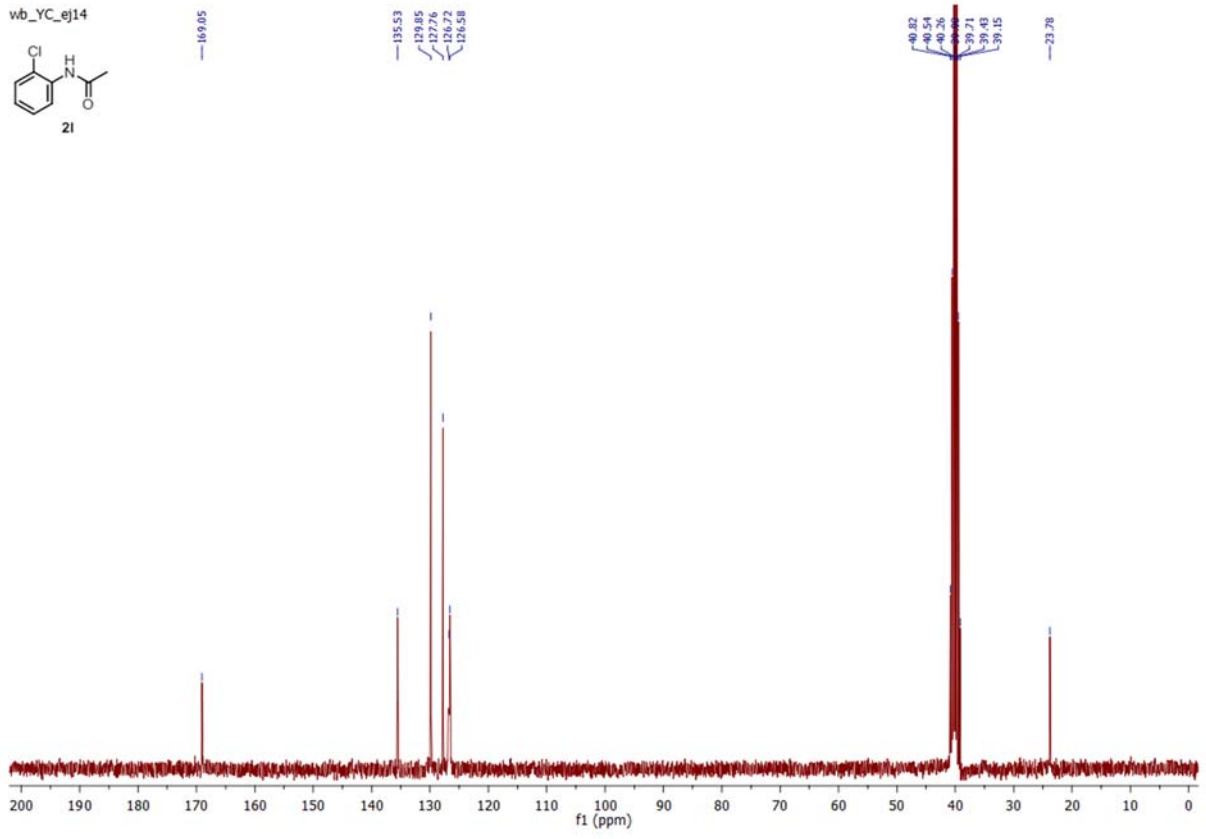

wb_YC_ej6
2j
10.06
7.62
7.61
7.59
7.59
7.35
7.34
7.33
7.32
3.35
2.51
2.51
2.50
2.50
2.49
2.04
1.00
2.08
2.04
3.14
f1 (ppm)

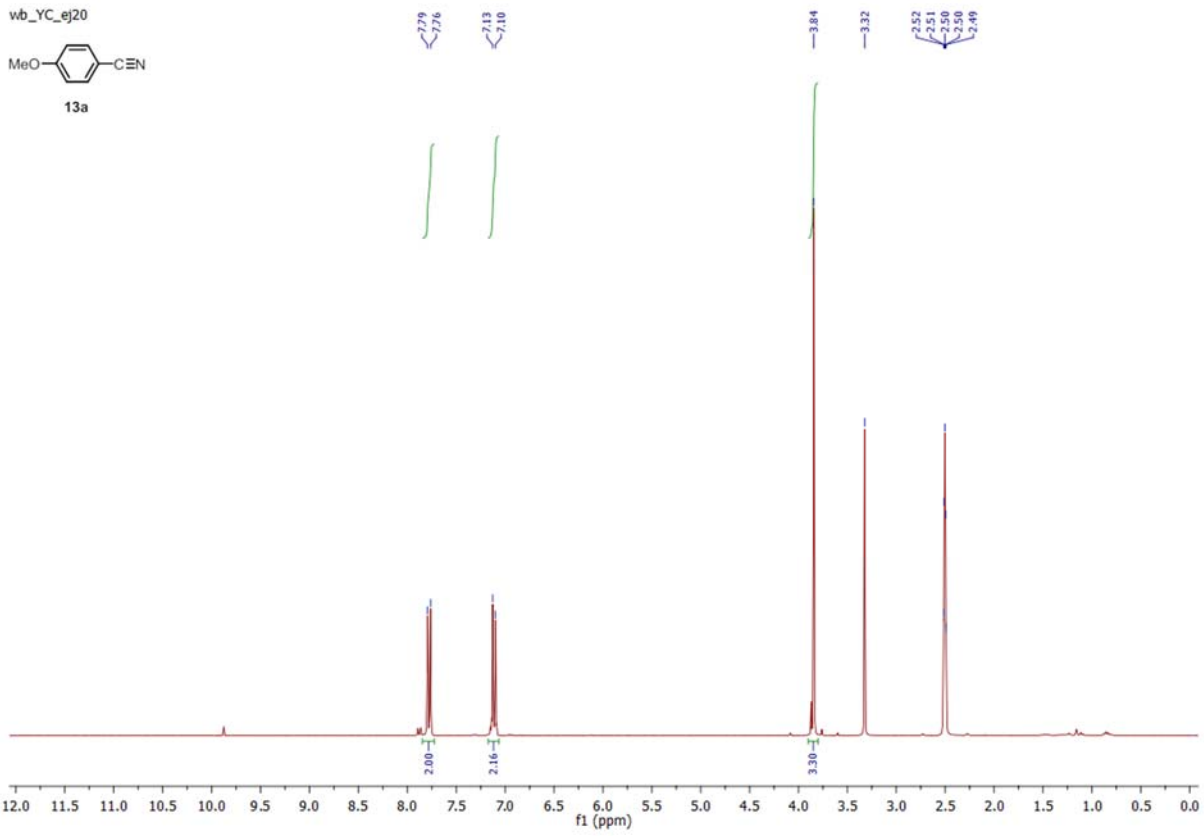

wb_YC_ej6
2j
168.87
138.71
129.00
126.92
120.90
40.80
40.52
40.24
39.69
39.41
39.13
24.44
f1 (ppm)

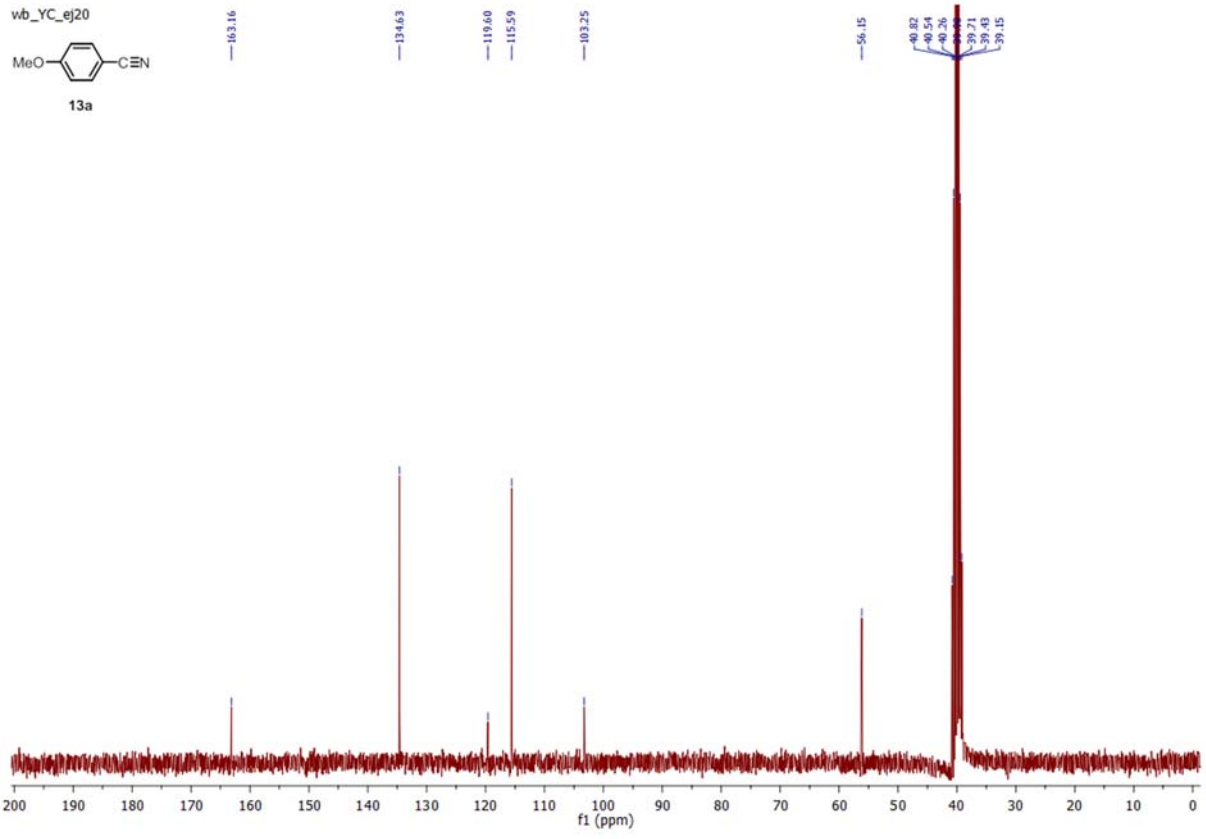

wb_YC_ej15
2k
10.13
7.82
7.81
7.80
7.43
7.43
7.42
7.42
7.40
7.40
7.40
7.40
7.39
7.33
7.31
7.28
7.09
7.09
7.06
7.06
3.38
3.37
2.51
2.50
2.50
2.05
1.00
0.97
1.01
1.02
0.99
3.05
f1 (ppm)


wb_YC_ej15
2k
169.15
141.20
133.47
130.82
123.12
118.82
117.71
40.78
40.50
40.22
39.94
39.66
39.39
39.11
24.50
f1 (ppm)


wb_YC_ej14
2l
9.50
7.72
7.70
7.49
7.49
7.47
7.46
7.34
7.33
7.31
7.31
7.29
7.28
7.20
7.18
7.17
3.35
2.52
2.51
2.50
2.50
2.49
2.10
1.00
1.00
1.05
1.07
1.02
3.07
f1 (ppm)


wb_YC_ej14
2l
169.05
135.53
129.85
127.76
126.72
126.58
40.82
40.54
40.26
39.71
39.43
39.15
23.78
f1 (ppm)


wb_YC_ej20
MeO
CN
13a
7.79
7.76
7.13
7.10
3.84
3.32
2.52
2.51
2.50
2.50
2.49
2.00
2.16
3.30
f1 (ppm)


wb_YC_ej20
MeO
CN
13a
163.16
134.63
119.60
115.59
103.25
56.15
40.82
40.54
40.26
39.71
39.43
39.15
f1 (ppm)