Electronic Supplementary Information

C(sp^3)–H Bond Functionalization with Styrenes via Hydrogen-Atom Transfer to an Aqueous Hydroxyl Radical under Photocatalysis

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1. General method

All experiments were performed under an inert gas unless otherwise noted. Photocatalytic reactions were performed in PhotoRedOx Box with LEDs (λ = 365 nm, P205-18-1 365 nm, Fig. S1) purchased from HepatoChem Inc. unless otherwise noted. Spot-type LEDs (λ = 365 nm, HLV-24UV365-4WNRBTNJ) purchased from CCS Inc. were used in a 1 mmol scale reaction. ^{1}H and ^{13}C NMR spectra were measured on a JEOL ECA 600 or 500 (600 or 500 MHz for ^{1}H, 151 or 126 MHz for ^{13}C, 564 MHz for F) at ambient temperature. Chemical shifts are reported as δ in ppm and internally referenced to tetramethylsilane (TMS, 0.0 ppm for ^{1}H), $CDCl_3$ (77.2 ppm for ^{13}C), or benzotrifluoride (-62.6 ppm for ^{19}F). The following abbreviations are used: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet and m = multiplet). GC-MS analyses were performed on Agilent 6850 series network GC system and Agilent 5975C series Mass Selective Detector (EI) [column: HP-5MS capillary column (l = 30 m, d = 0.25 mm, film thickness = 0.25 μm). High-resolution mass spectra (HRMS) were obtained from JMS-700 (FAB, JEOL). IR spectra were obtained from JASCO FT/IR6100. μGC-TCD analyses were conducted in a dual channel micro gas chromatography (μGC) system coupled to a thermal conductivity detector (TCD, Agilent 490). Emission spectroscopy was carried out on a JASCO FP-8500 spectrofluorometer at room temperature using quartz cells (light pass length = 1.0 cm). A Karl Fischer coulometer (MCU-610-DT) was used to check the water content of reagents. Inductively coupled plasma-atomic emission spectrophotometry (ICP-AES) was carried out with Vista Pro (Agilent). For thin–layer chromatography (TLC) analysis through this work, Merck percolated TLC plates (silica gel 60 GF254 0.25 mm) were used. The products were purified by flash chromatography using glass columns with silica gel 60 N (spherical, neutral, diameter: 40–100 μm) purchased from Kanto Chemical or pre-packed Biotage SNAP columns using a Biotage Isolera Automated Flash Chromatography System.

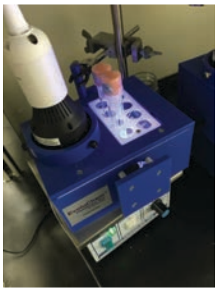


Fig. S1 PhotoRedOx Box with LEDs (λ = 365 nm)

2. Materials

All materials were used directly without further purification. Ethyl acetate (EtOAc), *n*-hexane, mesitylene, *N*,*N*-dimethylformamide (DMF, **2e**), *N*,*N*-dimethyacetamide (DMA, **2f**), potassium acetate (KOAc), potassium carbonate (K_2CO_3), cesium hydroxide monohydrate ($CsOH•H_2O$), acetonitrile-d_3 (**2a**-d_3, 99.9%**)**, deuterium oxide (D_2O, 99.8%), acetonitrile dehydrated -super- (water content = 24 ppm), tetrahydrofuran dehydrated stabilizer free -Super Plus- (THF, **2c**), toluene (**2k**) and benzophenone were purchased from Kanto Chemical. TiO_2 (Aeroxide P25) tripotassium phosphate (K_3PO_4), lithium hydroxide (LiOH) and α-methylstyrene (**1a**), 3,3-dimethyl-2-butanone (**2h**) were purchased from Sigma-Aldrich. 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), 4-fluoro-α-methylstyrene (**1h**), 4-chloro-α-methylstyrene (**1i**), 4-methylstyrene (**1m**), *trans*-anethole (**1o**), 2-methyltetrahydrofuran (**2i**), tetrahydropyran (**2j**), $NaBH_4$, coumarin, umbelliferone, acetone-d_6 (**2b**-d_6, 99.9%**)** and 1,1,2,2-tetrachloroethane were purchased from Tokyo Chemical Industry. *n*-Dodecane, potassium hydroxide (KOH), sodium hydroxide (NaOH), acetonitrile (water content = 2609 ppm, **2a**), acetone super dehydrated (**2b**),1,4-dioxane (**2d**) and $AgNO_3$ were purchased from FUJIFILM Wako Pure Chemical Corporation. Dipotassium hydrogen phosphate (K_2HPO_4) was purchased from nacalai tesque. Propionitrile (**2g**) was purchased from Acros Organics. Chloroform-*d* ($CDCl_3$, 99.8%) was purchased from CIL.

Ag/TiO_2 was synthesized in a manner similar to the literature procedure.[1] Ag(1 wt %)/TiO_2 was prepared as follows: TiO_2(P25, 1.98 g) and $AgNO_3$ (31.5 mg) were added to water (40 mL) and evaporated under vigorous stirring at 353 K for 16 h. The obtained powder was grained gently and calcined at 673 K under air. The heating rate and holding time at 673 K were 1.1 K/min and 2 h, respectively. To a suspension of the powder in water (20 mL), $NaBH_4$ (10 equiv to Ag) in cooled water (5 mL, 0 °C) was added dropwise, and the resulted suspension was stirred for 2 h at room temperature. After the suspension was transferred to a 50 mL Falcon tube and centrifuged (3500 rpm, 30 min), the supernatant was removed by decantation. After water (20 mL) was added to the tube and centrifuged (3500 rpm, 30 min), the supernatant was removed by decantation. This washing process was repeated once more. Drying the solid residue under reduced pressure gave Ag(1 wt %)/TiO_2 (1.86 g). The silver content was 0.9 wt % [determined by ICP-AES, after digestion of the catalyst (10.0 mg) using concd HNO_3 aq (2 mL) at 80 °C for 12 h].

Pt (5 wt %)/TiO_2 was prepared by the same method as Ag/TiO_2. M (5 wt %)/TiO_2 (M = Co, Rh, Ir, Ni, Pd, Cu and Au) were synthesized by the reported procedure.[2] Tetrakis(tetrabutylammonuim)decatungstate (TBADT) was synthesized by the reported procedure.[3]

According to the reported procedure[4], known compounds (**1b**[5], **1d**[6], **1e**[6], **1f**[7], **1g**[8], **1j**[9], **1k**[6], **1l**[9], **1n**[10], **1p**[11] and **1q**[12]) and **1c** were synthesized. **1c** (white solid): ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 5.49 (m, 1H), 5.27–5.26 (m, 1H), 3.06 (s, 3H), 2.19–2.18 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 146.9, 142.0, 139.2, 127.6, 126.6, 116.0, 44.8, 21.8; HRMS (FAB): *m*/*z* calcd. for $C_{10}H_{13}O_2S$ ($[M+H]^+$) 197.0631, found 197.0639. FT-IR (KBr, cm^{-1}): 1295, 1147.

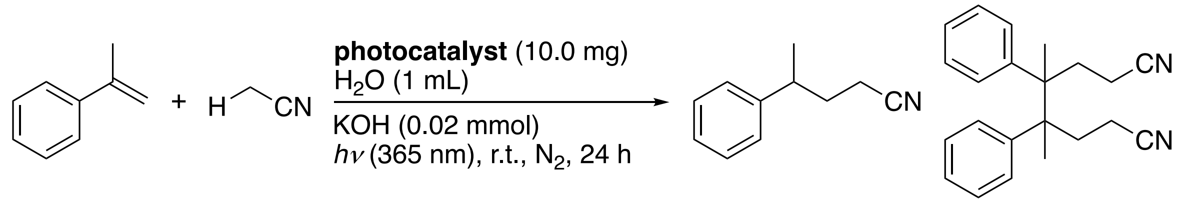
3aa[13], **3da**[13], **3ea**[14], **3ia**[13], **3ma**[13], **3aa’**[15], **3ab**[16], **3mb**[17], **3mc**[18], **5a**[19], **5b**[20] and **6**[21] are known compounds.

3. Optimization

General procedure for optimization

An oven-dried Pyrex glass test tube was charged with a magnetic stirrer bar and photocatalyst. The vessel was sealed with a rubber septum and placed under nitrogen before 1 mL of a stock solution containing **1a** (0.20 mmol) in **2a** and 1 mL of an aqueous solution of base were added. The mixture was sonicated and then stirred under LED-light irradiation (λ = 365 nm). After 24 h, the reaction mixture diluted with ethyl acetate (EtOAc) was analyzed by GC-MS with an internal standard (*n*-dodecane). The mixture was dried over Na_2SO_4. After filtration through a 0.45 μm membrane filter and concentration under reduced pressure (80 mmHg, 40 ºC), an aliquot with an internal standard (mesitylene) was monitored by ^1H NMR analysis.

Table S1. Evaluation of photocatalyst (M/TiO_2)



1a, 0.2 mmol **2a**, 1 mL **3aa** **6**

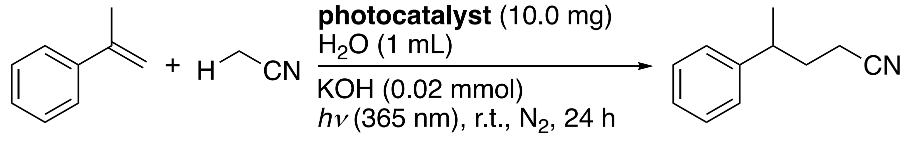
entry	photocatalyst	yield		
		3aa (%)[a]	**6** (%)[a]	H_2 (μmol)[b]
1	TiO_2 (P25)	–[c]	–[c]	1.4
2	Co(5 wt %)/TiO_2	–[c]	–[c]	0.1
3	Rh(5 wt %)/TiO_2	–[c]	12	22.3
4	Ir(5 wt %)/TiO_2	–[c]	<10	17.2
5	Ni(5 wt %)/TiO_2	–[c]	–[c]	0.3
6	Pd(5 wt %)/TiO_2	<5	26	92.1
7	Pt(5 wt %)/TiO_2	<5	26	59.9
8	Cu(5 wt %)/TiO_2	20	33	85.4
9	Ag(5 wt %)/TiO_2	69	<10	2.0
10	Au(5 wt %)/TiO_2	–[c]	<10	3.8

[a] ^1H NMR yield.

[b] Determined by μGC-TCD.

[c] Not detected.

Table S2. Evaluation of Ag loading amount

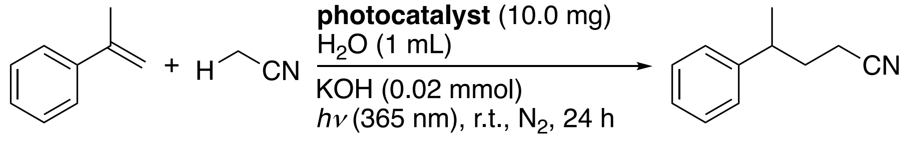


1a, 0.2 mmol **2a**, 1 mL **3aa**

entry	**photocatalyst**	yield of **3aa** (%)[a]
1	Ag(0.5 wt %)/TiO_2	54
2	Ag(1 wt %)/TiO_2	86 (85)[b]
3	Ag(2 wt %)/TiO_2	62
4	Ag(5 wt %)/TiO_2	69

[a] ^1H NMR yield.
[b] Isolated yield.

Table S3. Evaluation of homogeneous photo-induced HAT catalyst

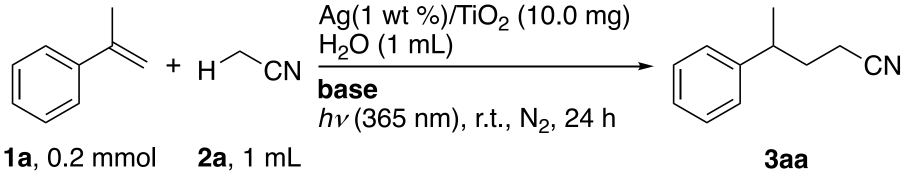


1a, 0.2 mmol **2a**, 1 mL **3aa**

entry	**photocatalyst**	yield of **3aa** (%)[a]
1	Ag(1 wt %)/TiO_2 (10.0 mg)	86 (85)[b]
2	TBADT (4 mol %)	–[c]
3	benzophenone (100 mol %)	–[c]

[a] ^1H NMR yield.
[b] Isolated yield.
[c] Not detected.

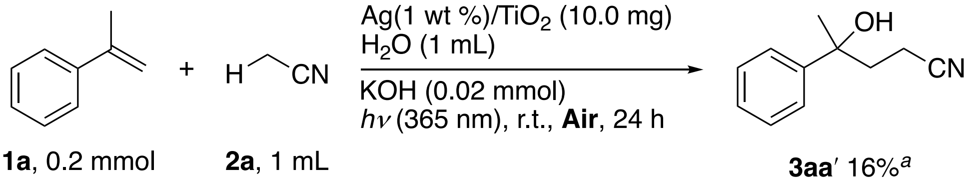
Table S4: Evaluation of base



entry	**base**	yield of **3aa** (%)[a]
1	KOH (0.02 mmol)	86 (85)[b]
2	LiOH (0.02 mmol)	71
3	NaOH (0.02 mmol)	70
4	$CsOH•H_2O$ (0.02 mmol)	78
5	KOAc (0.02 mmol)	17
6	K_2CO_3 (0.02 mmol)	67
7	K_3PO_4 (0.02 mmol)	74
8	K_2HPO_4 (0.02 mmol)	8
9	KOH (0.01 mmol	65
10	KOH (0.04 mmol)	84
11	KOH (0.2 mmol)	78
12	KOH (2 mmol)	35

[a] ^{1}H NMR yield.
[b] Isolated yield.

Scheme S1. Oxidative difunctionalization of **1a** under air



[a] Isolated yield

4. Isolated yields and characterization of products

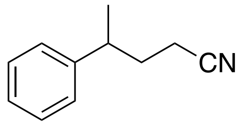
General procedure A

An oven-dried Pyrex glass test tube was charged with a magnetic stirrer bar and Ag(1 wt %)/TiO_2 (10.0 mg). The vessel was sealed with a rubber septum and placed under nitrogen before **1** (0.20 mmol), **2** (1 mL) and an aqueous solution of KOH (0.02 M, 1 mL) were added (**1** that was not volatile was added with the Ag(1 wt %)/TiO_2). The mixture was sonicated and then stirred under LED-light irradiation (λ = 365 nm). After 24 h, the reaction mixture was diluted with EtOAc and dried over Na_2SO_4. After filtration through a 0.45 μm membrane filter and concentration under reduced pressure

(80 mmHg, 40 ºC), the residue was purified by flash column chromatography on silica gel using EtOAc–hexane as the eluent.

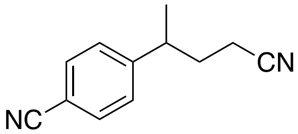
General procedure B

An oven-dried Pyrex glass test tube was charged with a magnetic stirrer bar and Ag(1 wt %)/TiO_2 (10.0 mg). The vessel was sealed with a rubber septum and placed under nitrogen before **1** (0.20 mmol), **2** (1 mL) and an aqueous solution of KOH (0.02 M, 1 mL) were added (**1** that was not volatile was added with the Ag(1 wt %)/TiO_2). The mixture was sonicated and then stirred under LED-light irradiation (λ = 365 nm). After 24 h, the reaction mixture was transferred to a 50 mL Falcon tube that contained EtOAc (10 mL) and water (30 mL). The mixture was centrifuged (3,500 rpm, 3 min) and the organic phase was separated. The aqueous phase was subjected to additional three EtOAc (5 mL) addition–centrifugation–extraction cycles. The combined organic extracts were dried over Na_2SO_4, filtrated, and the filtrate was concentrated under reduced pressure (80 mmHg, 40 ºC). Purification of the residue by flash column chromatography on silica gel using EtOAc–hexane as the eluent afforded pure **3** and **4**, and a mixture of **3** and **4**. The ratio of isomers (**3**/**4**) was determined by ^{1}H NMR analysis after column chromatography.



4-Phenylpentanenitrile (3aa)[13]

According to the general procedure A, **1a** (23.6 mg, 0.200 mmol) and **2a** (1 mL) were used. The desirable product (**3aa**, 27.1 mg, 0.170 mmol, 85%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 (t, J = 7.2 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 7.19 (d, J = 7.2 Hz, 2H), 2.86 (dqd, J = 9.6, 7.2, 5.4 Hz, 1H), 2.22 (ddd, J = 16.8, 7.8, 6.0 Hz, 1H), 2.11 (ddd, J = 16.8, 7.8, 7.8 Hz, 1H), 1.97 (dddd, J = 13.8, 7.8, 7.8, 5.4 Hz, 1H), 1.88 (dddd, J = 13.8, 9.6, 7.8, 6.0 Hz, 1H), 1.31 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.8, 129.0, 127.1, 127.0, 119.8, 39.1, 33.7, 22.1, 15.7; HRMS (FAB): m/z calcd. for $C_{11}H_{14}N$ ($[M+H]^+$) 160.1121, found 160.1127.



4-(4-Cyanobutan-2-yl)benzonitrile (3ba)

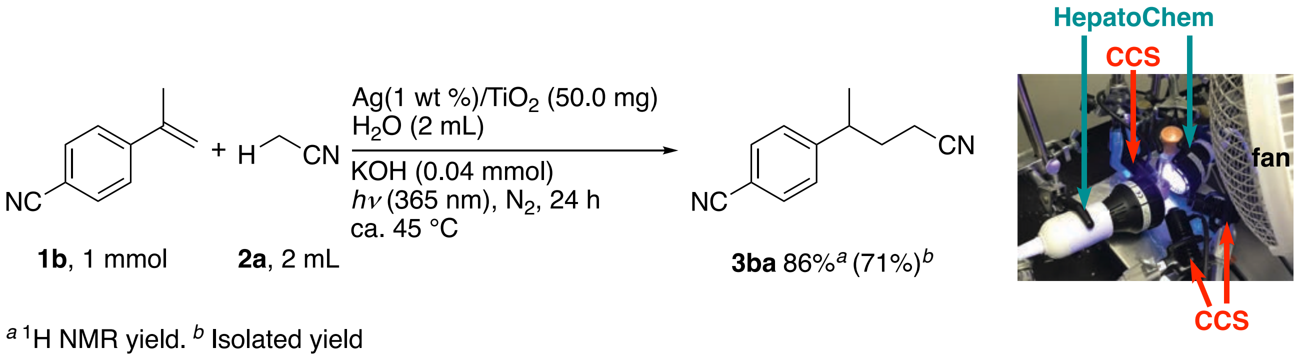
According to the general procedure A, **1b** (28.7 mg, 0.200 mmol) and **2a** (1 mL) were used. The desirable product (**3ba**, 33.8 mg, 0.183 mmol, 92%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/4) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 2.97 (dqd, J = 9.0, 7.2, 6.6 Hz, 1H), 2.28 (ddd, J = 16.8, 7.2, 6.0 Hz, 1H), 2.14 (ddd, J = 16.8, 7.8, 7.8 Hz, 1H), 2.00 (dddd, J = 13.8, 7.8, 7.2, 6.0 Hz, 1H), 1.91 (dddd, J = 13.8, 9.0, 7.8, 6.0 Hz, 1H), 1.33 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.4, 132.8, 128.0, 119.2, 118.9, 111.0, 39.2, 33.2, 21.6, 15.6; HRMS (FAB): m/z calcd. for $C_{12}H_{13}N_2$ ($[M+H]^+$)

185.1073, found 185.1075; FT-IR (neat, NaCl, cm^{-1}): 2245, 2227.

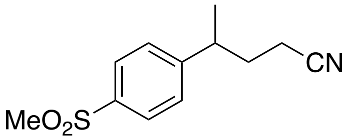
1 mmol scale reaction

An oven-dried Pyrex glass test tube was charged with a magnetic stirrer bar, **1b** (143.9 mg, 1.00 mmol) and Ag(1 wt %)/TiO_2 (50.0 mg). The vessel was sealed with a rubber septum and placed under nitrogen before **2a** (2 mL) and an aqueous solution of KOH (0.02 M, 2 mL) were added. The mixture was sonicated and then stirred under light irradiation with two LEDs (λ = 365 nm, P205-18-1 365 nm) purchased from HepatoChem Inc. and three LEDs (λ = 365 nm, HLV-24UV365-4WNRBTNJ) purchased from CCS Inc. at ca. 45 °C. After 24 h, the aqueous mixture was extracted with four portions of EtOAc (5 mL). The combined organic fractions were dried over Na_2SO_4. After filtration through a 0.45 μm membrane filter and concentration under reduced pressure (80 mmHg, 40 ºC), an aliquot with an internal standard (1,1,2,2-tetrachloroethane) was monitored by ^{1}H NMR analysis. The desirable product (**3ba**, 131.5 mg, 0.71 mmol, 71%) was isolated after flash column chromatography on silica gel (EtOAc/hexane = 1/4) as a colorless oil.

Scheme S2. 1 mmol scale reaction

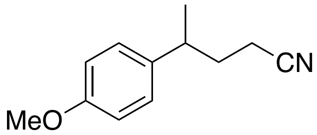


^{a} ^{1}H NMR yield. ^{b} Isolated yield



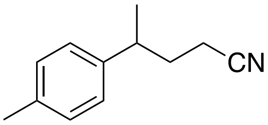
4-(4-Cyanobutan-2-yl)phenyl methyl sulfone (3ca)

According to the general procedure A, **1c** (39.3 mg, 0.200 mmol) and **2a** (1 mL) were used. The desirable product (**3ca**, 39.5 mg, 0.166 mmol, 83%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/1) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92 (d, J = 9.0 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 3.07 (s, 3H), 3.01 (dqd, J = 9.6, 7.2, 6.0 Hz, 1H), 2.29 (ddd, J = 17.4, 7.2, 6.0 Hz, 1H), 2.15 (ddd, J = 17.4, 7.8, 7.8 Hz, 1H), 2.02 (dddd, J = 13.8, 7.8, 7.2, 6.0 Hz, 1H), 1.93 (dddd, J = 13.8, 9.6, 7.8, 6.0 Hz, 1H), 1.35 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 151.4, 139.3, 128.2, 119.2, 44.7, 39.0, 33.2, 21.7, 15.6; HRMS (FAB): m/z calcd. for $C_{12}H_{16}NO_2S$ ([M+H]$^+$) 238.0896, found 238.0904; FT-IR (neat, NaCl, cm^{-1}): 2245, 1307, 1148.



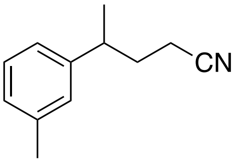
4-(4-Methoxyphenyl)pentanenitrile (3da)[13]

According to the general procedure A, **1d** (29.6 mg, 0.200 mmol), Ag(1 wt %)/TiO_2 (20.0 mg) and **2a** (1 mL) were used. The desirable product (**3da**, 31.9 mg, 0.169 mmol, 84%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/19) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H) 2.81 (dqd, J = 9.6, 7.2, 6.0 Hz, 1H), 2.21 (ddd, J = 17.4, 7.8, 5.4 Hz, 1H), 2.10 (ddd, J = 17.4, 7.8, 7.8 Hz, 1H), 1.95 (dddd, J = 13.2, 7.8, 7.8, 6.0 Hz, 1H), 1.82 (dddd, J = 13.2, 9.6, 7.8, 5.4 Hz, 1H), 1.28 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 158.5, 136.7, 128.0, 119.9, 114.3, 55.4, 38.3, 33.9, 22.3, 15.6; HRMS (FAB): m/z calcd. for $C_{12}H_{16}NO$ ($[M+H]^+$) 190.1226, found 190.1236.



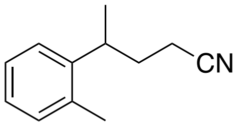
4-(4-Tolyl)pentanenitrile (3ea)[14]

According to the general procedure A, **1e** (26.4 mg, 0.200 mmol) and **2a** (1 mL) were used. The desirable product (**3ea**, 28.8 mg, 0.166 mmol, 83%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.13 (d, J = 7.8 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 2.82 (dqd, J = 9.6, 7.2, 6.0 Hz, 1H), 2.33 (s, 3H), 2.21 (ddd, J = 16.8, 8.4, 5.4 Hz, 1H), 2.10 (ddd, J = 16.8, 7.8, 7.8 Hz, 1H), 1.95 (dddd, J = 13.2, 8.4, 7.8, 6.0 Hz, 1H), 1.85 (dddd, J = 13.2, 9.6, 7.8, 5.4 Hz, 1H), 1.29 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.7, 136.5, 129.6, 127.0, 119.9, 38.7, 33.8, 22.2, 21.2, 15.6; HRMS (FAB): m/z calcd. for $C_{12}H_{16}N$ ($[M+H]^+$) 174.1277, found 174.1279.



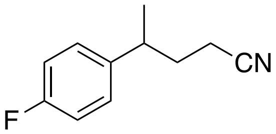
4-(3-Tolyl)pentanenitrile (3fa)

According to the general procedure A, **1f** (26.4 mg, 0.200 mmol) and **2a** (1 mL) were used. The desirable product (**3fa**, 22.2 mg, 0.128 mmol, 64%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 (t, J = 7.8 Hz, 1H), 7.05–7.04 (m, 1H), 6.99–6.97 (m, 2H), 2.81 (dqd, J = 9.6, 6.6, 5.4 Hz, 1H), 2.34 (s, 3H), 2.22 (ddd, J = 16.8, 7.8, 6.0 Hz, 1H), 2.11 (ddd, J = 16.8, 7.8, 7.8 Hz, 1H), 1.96 (dddd, J = 13.8, 7.8, 7.8, 5.4 Hz, 1H), 1.87 (dddd, J = 13.8, 9.6, 7.8, 6.0 Hz, 1H), 1.29 (d, J = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.7, 138.5, 128.8, 127.9, 127.7, 124.1, 119.9, 39.1, 33.7, 22.2, 21.6, 15.7; HRMS (FAB): m/z calcd. for $C_{12}H_{16}N$ ($[M+H]^+$) 174.1277, found 174.1279; FT-IR (neat, NaCl, cm^{-1}): 2247.



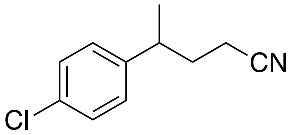
4-(2-Tolyl)pentanenitrile (3ga)

According to the general procedure A, **1g** (26.5 mg, 0.200 mmol), Ag(1 wt %)/TiO_2 (20.0 mg) and **2a** (1 mL) were used. The desirable product (**3ga**, 15.0 mg, 0.087 mmol, 44%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil: ^1H NMR (600 MHz, $CDCl_3$): δ 7.21–7.10 (m, 4H), 3.17 (ddq, J = 8.4, 7.2, 6.6 Hz, 1H), 2.36 (s, 3H), 2.27 (ddd, J = 16.8, 7.2, 6.0 Hz, 1H), 2.17 (ddd, J = 16.8, 7.8, 7.8 Hz, 1H), 2.01–1.92 (m, 2H), 1.25 (d, J = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.9, 136.0, 130.9, 126.7, 126.5, 125.0, 119.9, 33.6, 33.0, 21.7, 19.7, 15.6; HRMS (FAB): m/z calcd. for $C_{12}H_{16}N$ ($[M+H]^+$) 174.1277, found 174.1276; FT-IR (neat, NaCl, cm^{-1}): 2247.



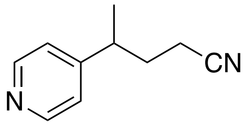
4-(4-Fluorophenyl)pentanenitrile (3ha)

According to the general procedure A, **1h** (27.3 mg, 0.200 mmol), Ag(1 wt %)/TiO_2 (20.0 mg) and **2a** (1 mL) were used. The desirable product (**3ha**, 26.7 mg, 0.151 mmol, 75%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/9) as a colorless oil: ^1H NMR (600 MHz, $CDCl_3$): δ 7.15 (dd, J = 8.4, 5.4 Hz, 2H), 7.01 (dd, J = 8.4, 8.4 Hz, 2H), 2.87 (dqd, J = 9.6, 6.6, 6.0 Hz, 1H), 2.23 (ddd, J = 16.8, 7.8, 5.4 Hz, 1H), 2.10 (ddd, J = 16.8, 7.8, 7.8 Hz, 1H), 1.96 (dddd, J = 13.8, 7.8, 7.8, 6.0 Hz, 1H), 1.84 (dddd, J = 13.8, 9.6, 7.8, 5.4 Hz, 1H), 1.29 (d, J = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.6, 161.0, 140.4, 140.4, 128.5, 128.5, 119.6, 115.8, 115.7, 38.4, 33.8, 22.2, 15.6; ^{19}F NMR (564 MHz, $CDCl_3$): δ –116.1; HRMS (FAB): m/z calcd. for $C_{11}H_{13}FN$ ($[M+H]^+$) 178.1027, found 178.1027; FT-IR (neat, NaCl, cm^{-1}): 2248, 1224.



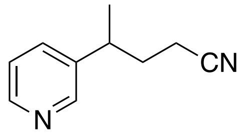
4-(4-Chlorophenyl)pentanenitrile (3ia)[13]

According to the general procedure A, **1i** (15.2 mg, 0.100 mmol), Ag(1 wt %)/TiO_2 (20.0 mg) and **2a** (1 mL) were used. The desirable product (**3ia**, 13.4 mg, 0.069 mmol, 69%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/19) as a colorless oil: ^1H NMR (600 MHz, $CDCl_3$): δ 7.30 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 2.86 (dqd, J = 9.6, 7.2, 6.0 Hz, 1H), 2.24 (ddd, J = 16.8, 7.2, 5.4 Hz, 1H), 2.11 (ddd, J = 16.8, 7.8, 7.8 Hz, 1H), 1.96 (dddd, J = 13.8, 7.8, 7.8, 6.0 Hz, 1H), 1.84 (dddd, J = 13.8, 9.6, 7.8, 5.4 Hz, 1H), 1.29 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.2, 132.7, 129.1, 128.5, 119.5, 38.5, 33.6, 22.0, 15.6; HRMS (FAB): m/z calcd. for $C_{11}H_{13}ClN$ ($[M+H]^+$) 194.0731, found 194.0735.



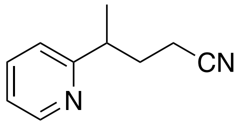
4-(4-Cyanobutan-2-yl)pyridine (3ja)

According to the general procedure A, **1j** (11.8 mg, 0.099 mmol), Ag(1 wt %)/TiO_2 (20.0 mg) and **2a** (1 mL) were used. The desirable product (**3ja**, 11.2 mg, 0.070 mmol, 71%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 2/1) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.56 (d, J = 4.8 Hz, 2H), 7.13 (dd, J = 4.8, 1.2 Hz, 2H), 2.89 (dqd, J = 9.0, 7.2, 6.6 Hz, 1H), 2.29 (ddd, J = 16.8, 7.8, 6.0 Hz, 1H), 2.15 (ddd, J = 16.8, 7.8, 7.8 Hz, 1H), 1.99 (dddd, J = 13.8, 7.8, 7.8, 6.6 Hz, 1H), 1.92 (dddd, J = 13.8, 9.0, 7.8, 6.0 Hz, 1H), 1.33 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 153.7, 150.5, 122.5, 119.2, 38.5, 32.9, 21.2, 15.6; HRMS (FAB): m/z calcd. for $C_{10}H_{13}N_2$ ($[M+H]^+$) 161.1073, found 161.1079; FT-IR (neat, NaCl, cm^{-1}): 2247.



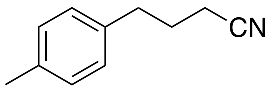
3-(4-Cyanobutan-2-yl)pyridine (3ka)

According to the general procedure A, **1k** (12.0 mg, 0.101 mmol), Ag(1 wt %)/TiO_2 (20.0 mg) and **2a** (1 mL) were used. The desirable product (**3ka**, 8.0 mg, 0.050 mmol, 50%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 2/1) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.51 (d, J = 12.6 Hz, 2H), 7.53 (d, J = 7.8 Hz, 1H), 7.29–7.27 (m, 1H), 2.92 (dqd, J = 9.0, 7.2, 6.6 Hz, 1H), 2.28 (ddd, J = 16.8, 7.8, 6.0 Hz, 1H), 2.17 (ddd, J = 16.8, 7.8, 7.8 Hz, 1H), 2.01 (dddd, J = 13.8, 7.8, 7.8, 6.0 Hz, 1H), 1.92 (dddd, J = 13.8, 9.0, 7.8, 6.0 Hz, 1H), 1.35 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.1, 148.7, 140.1, 134.4, 124.0, 119.3, 36.7, 33.4, 21.8, 15.6; HRMS (FAB): m/z calcd. for $C_{10}H_{13}N_2$ ($[M+H]^+$) 161.1073, found 161.1079; FT-IR (neat, NaCl, cm^{-1}): 2247.



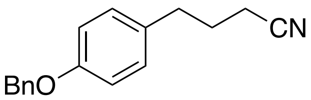
2-(4-Cyanobutan-2-yl)pyridine (3la)

According to the general procedure A, **1l** (23.9 mg, 0.201 mmol), Ag(1 wt %)/TiO_2 (20.0 mg) and **2a** (1 mL) were used. The desirable product (**3la**, 23.8 mg, 0.149 mmol, 74%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/3) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.57–8.56 (m, 1H), 7.64 (td, J = 7.8, 1.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.15 (ddd, J = 7.8, 4.8, 1.2 Hz, 1H), 3.07–3.01 (m, 1H), 2.32–2.26 (m, 1H), 2.21–2.15 (m, 2H), 2.00–1.95 (m, 1H), 1.33 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 163.7, 149.8, 136.9, 122.6, 121.9, 119.8, 40.7, 31.9, 21.0, 15.5; HRMS (FAB): m/z calcd. for $C_{10}H_{13}N_2$ ($[M+H]^+$) 161.1073, found 161.1079; FT-IR (neat, NaCl, cm^{-1}): 2246.



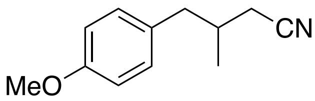
4-(4-Tolyl)butanenitrile (3ma)[13]

According to the general procedure A, **1m** (23.6 mg, 0.200 mmol) and **2a** (1 mL) were used. The desirable product (**3ma**, 21.8 mg, 0.137 mmol, 68%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/19): ^{1}H NMR (500 MHz, CDCl$_3$) as a colorless oil: δ 7.11 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 2.73 (t, J = 7.5 Hz, 2H), 2.32 (s, 3H), 2.30 (t, J = 7.0 Hz, 2H), 1.96 (tt, J = 7.5, 7.0 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 136.8, 136.2, 129.5, 128.5, 119.7, 34.1, 27.2, 21.2, 16.5; HRMS (FAB): m/z calcd. for $C_{11}H_{14}N$ ([M+H]$^+$) 160.1121, found 160.1126.



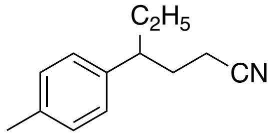
4-(4-(Benzyloxy)phenyl)butanenitrile (3na)

According to the general procedure A, **1n** (42.1 mg, 0.200 mmol), Ag(1 wt %)/TiO$_2$ (50.0 mg) and **2a** (1 mL) were used. The desirable product (**3na**, 35.0 mg, 0.139 mmol, 70%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/9) as a white solid: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.43 (d, J = 7.8 Hz, 2H), 7.38 (t, J = 7.8 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 5.04 (s, 2H), 2.71 (t, J = 7.2 Hz, 2H), 2.29 (t, J = 7.2 Hz, 2H), 1.94 (quin, J = 7.2 Hz, 2H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 157.7, 137.2, 132.2, 129.6, 128.8, 128.1, 127.6, 119.7, 115.2, 70.2, 33.7, 27.3, 16.5; HRMS (FAB): m/z calcd. for $C_{17}H_{17}NO$ (M$^+$) 251.1305, found 251.1318; FT-IR (KBr, cm^{-1}): 2244, 1248, 1015.



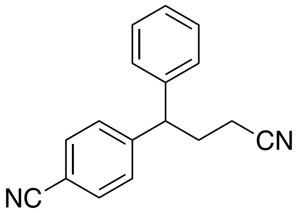
4-(4-Methoxyphenyl)-3-methylbutanenitrile (3oa)

According to the general procedure A, **1o** (14.8 mg, 0.100 mmol), Ag(1 wt %)/TiO$_2$ (20.0 mg) and **2a** (1 mL) were used. The desirable product (**3oa**, 13.1 mg, 0.069 mmol, 69%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/19) as a colorless oil: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.08 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 3.80 (s, 3H), 2.62 (dd, J = 13.8, 7.2 Hz, 1H), 2.58 (dd, J = 13.8, 7.8 Hz, 1H), 2.28 (dd, J = 16.8, 5.4 Hz, 1H), 2.18 (dd, J = 16.2, 6.6 Hz, 1H), 2.13–2.06 (m, 1H), 1.11 (d, J = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 158.5, 131.2, 130.1, 118.9, 114.1, 55.4, 41.3, 32.8, 23.7, 19.6; HRMS (FAB): m/z calcd. for $C_{12}H_{16}NO$ ([M+H]$^+$) 190.1226, found 190.1232; FT-IR (neat, NaCl, cm^{-1}): 2250, 1249, 1036.



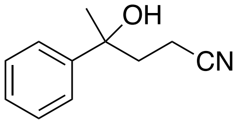
4-(4-Tolyl)hexanenitrile (3pa)

According to the general procedure A, **1p** (29.3 mg, 0.200 mmol), Ag(1 wt %)/TiO_2 (20.0 mg) and **2a** (1 mL) were used. The desirable product (**3pa**, 29.8 mg, 0.159 mmol, 80%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.12 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.55–2.49 (m, 1H), 2.33 (s, 3H), 2.20–2.14 (m, 1H), 2.07–1.99 (m, 2H), 1.85–1.77 (m, 1H), 1.72–1.55 (m, 2H), 0.80 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 139.9, 136.4, 129.6, 127.6, 120.0, 46.5, 32.1, 29.6, 21.2, 15.6, 12.2; HRMS (FAB): *m*/*z* calcd. for $C_{13}H_{18}N$ ($[M+H]^+$) 188.1434, found 188.1437; FT-IR (neat, NaCl, cm^{-1}): 2246.



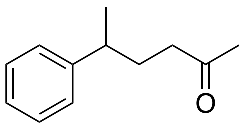
4-(3-Cyano-1-phenylpropan-1-yl)benzonitrile (3qa)

According to the general procedure A, **1q** (41.0 mg, 0.200 mmol) and **2a** (1 mL) were used. The desirable product (**3qa**, 42.9 mg, 0.174 mmol, 87%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/3) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.60 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.22–7.20 (m, 2H), 4.14 (t, *J* = 7.8 Hz, 1H), 2.45–2.36 (m, 2H), 2.33–2.24 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): *δ* 148.5, 141.1, 132.8, 129.3, 128.6, 127.8, 127.7, 119.0, 118.7, 111.0, 49.9, 30.7, 15.9; HRMS (FAB): *m*/*z* calcd. for $C_{17}H_{15}N_2$ ($[M+H]^+$) 247.1230, found 247.1231; FT-IR (neat, NaCl, cm^{-1}): 2247, 2227.



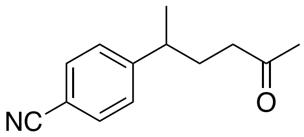
4-Hydroxy-4-phenylpentanenitrile (3aa')[15]

According to the general procedure A, **1a** (23.7 mg, 0.200 mmol) and **2a** (1 mL) were used under air. The product (**3aa'**, 5.7 mg, 0.033 mmol, 16%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/4) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.41–7.36 (m, 4H), 7.30–7.27 (m, 1H), 2.44–2.38 (m, 1H), 2.18–2.15 (m, 2H), 2.12–2.05 (m, 1H), 1.72 (s, 1H), 1.63 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): *δ*; 145.6, 128.8, 127.5, 124.7, 120.3, 73.8, 39.8, 30.9, 12.3; HRMS (FAB): *m*/*z* calcd. for $C_{11}H_{14}NO$ ($[M+H]^+$) 176.1070, found 176.1076.



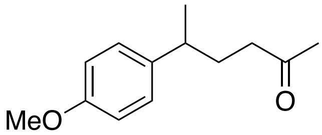
5-Phenylhexan-2-one (3ab)[16]

According to the general procedure A, **1a** (23.6 mg, 0.200 mmol) and **2b** (1 mL) were used. The desirable product (**3ab**, 32.5 mg, 0.184 mmol, 92%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/19) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.29 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 2.68 (dqd, *J* = 9.0, 6.6, 6.0 Hz, 1H), 2.33 (ddd, *J* = 17.4, 9.0, 6.6 Hz, 1H), 2.26 (ddd, *J* = 17.4, 9.0, 5.4 Hz, 1H), 2.05 (s, 3H), 1.90 (dddd, *J* = 13.8, 9.0, 6.6, 6.0 Hz, 1H), 1.82 (dddd, *J* = 13.8, 9.0, 9.0, 5.4 Hz, 1H), 1.26 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): *δ* 209.1, 146.6, 128.6, 127.2, 126.3, 42.0, 39.5, 32.0, 30.1, 22.6; HRMS (FAB): *m*/*z* calcd. for $C_{12}H_{17}O$ ($[M+H]^+$) 177.1274, found 177.1274.



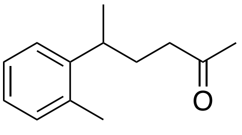
4-(5-Oxohexan-2-yl)benzonitrile (3bb)

According to the general procedure A, **1b** (28.8 mg, 0.201 mmol) and **2b** (1 mL) were used. The desirable product (**3bb**, 37.2 mg, 0.185 mmol, 92%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/5) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.60 (d, *J* = 8.4 Hz, 2H), 7.29–7.28 (m, 2H), 2.77 (dqd, *J* = 8.4, 7.2, 6.6 Hz, 1H), 2.34 (ddd, *J* = 17.4, 9.0, 6.0 Hz, 1H), 2.27 (ddd, *J* = 17.4, 9.0, 6.0 Hz, 1H), 2.08 (s, 3H), 1.91 (dddd, *J* = 14.4, 9.0, 6.6, 6.0 Hz, 1H), 1.83 (dddd, *J* = 14.4, 9.0, 8.4, 6.0 Hz, 1H), 1.26 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): *δ* 208.3, 152.4, 132.5, 128.0, 119.1, 110.2, 41.5, 39.6, 31.5, 30.1, 22.0; HRMS (FAB): *m*/*z* calcd. for $C_{13}H_{16}NO$ ($[M+H]^+$) 202.1226, found 202.1238; FT-IR (neat, NaCl, cm^{-1}): 2229, 1713.



5-(4-Methoxyphenyl)hexan-2-one (3db)

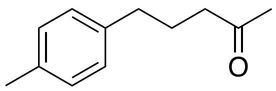
According to the general procedure A, **1d** (29.6 mg, 0.200 mmol), Ag(1 wt %)/TiO_2 (20.0 mg) and **2b** (1 mL) were used. The desirable product (**3db**, 23.2 mg, 0.112 mmol, 56%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/9) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.08 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H), 2.63 (dqd, *J* = 9.6, 7.2, 6.0 Hz, 1H), 2.31 (ddd, *J* = 17.4, 9.6, 6.6 Hz, 1H), 2.25 (ddd, *J* = 17.4, 9.6, 5.4 Hz, 1H), 2.05 (s, 3H), 1.88 (dddd, *J* = 13.8, 9.6, 6.6, 6.0 Hz, 1H), 1.77 (dddd, *J* = 13.8, 9.6, 9.6, 5.4 Hz, 1H), 1.23 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): *δ* 209.2, 158.1, 138.7, 128.0, 114.0, 55.4, 42.0, 38.7, 32.2, 30.1, 22.8; HRMS (FAB): *m*/*z* calcd. for $C_{13}H_{19}O_2$ ($[M+H]^+$) 207.1380, found 207.1378; FT-IR (neat, NaCl, cm^{-1}): 1714, 1247, 1037.



5-(2-Tolyl)hextan-2-one (3gb)

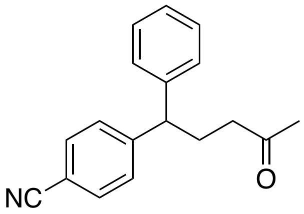
According to the general procedure A, **1g** (26.4 mg, 0.199 mmol), Ag(1 wt %)/TiO_2 (20.0 mg) and **2b** (1 mL) were used. The desirable product (**3gb**, 9.0 mg, 0.047 mmol, 24%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/19) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.18–7.16 (m, 2H), 7.14–7.13 (m, 1H), 7.10–7.07 (m, 1H), 2.99 (sext, *J* = 7.2 Hz, 1H), 2.38–2.28

(m, 2H), 2.31 (s, 3H), 2.06 (s, 3H), 1.88 (td, *J* = 7.8, 7.2 Hz, 2H), 1.21 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): *δ* 209.1, 144.7, 135.7, 130.5, 126.5, 125.9, 125.4, 41.9, 33.9, 31.3, 30.1, 22.0, 19.8; HRMS (FAB): *m*/*z* calcd. for $C_{13}H_{19}O$ ([M+H]$^+$) 191.1430, found 191.1438; FT-IR (neat, NaCl, cm^{-1}): 1713.



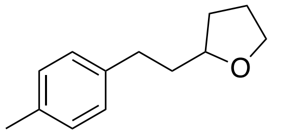
5-(4-Tolyl)pentan-2-one (3mb)[17]

According to the general procedure A, **1m** (23.7 mg, 0.201 mmol) and **2b** (1 mL) were used. The desirable product (**3mb**, 25.3 mg, 0.144 mmol, 72%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/19) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.09 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 2.10 (s, 3H), 1.88 (quin, *J* = 7.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): *δ* 209.0, 138.6, 135.5, 129.2,128.5, 43.0, 34.7, 30.1, 25.5, 21.1; HRMS (FAB): *m*/*z* calcd. for $C_{12}H_{17}O$ ([M+H]$^+$) 177.1274, found 177.1274.



4-(4-Oxo-1phenylpentan-1-yl)benzonitrile (3qb)

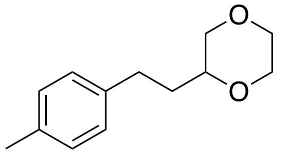
According to the general procedure A, **1q** (41.4 mg, 0.202 mmol) and **2b** (1 mL) were used. The desirable product (**3qb**, 51.0 mg, 0.194 mmol, 96%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/4) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.56 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 9.0 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.20–7.18 (m, 2H), 3.97 (t, *J* = 8.0 Hz, 1H), 2.41–2.38 (m, 2H), 2.34–2.30 (m, 2H), 2.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 208.0, 150.2, 142.7, 132.5, 129.0, 128.7, 128.0, 127.1, 119.0, 110.4, 50.4, 41.6, 30.2, 28.8; HRMS (FAB): *m*/*z* calcd. for $C_{18}H_{18}NO$ ([M+H]$^+$) 264.1383, found 264.1387; FT-IR (neat, NaCl, cm^{-1}): 2229, 1713.



2-(4-Methylphenethyl)tetrahydrofuran (3mc)[18]

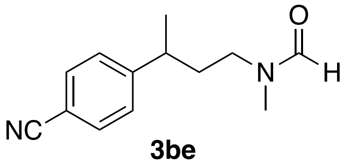
According to the general procedure A, **1m** (23.6 mg, 0.200 mmol), Ag(1 wt %)/TiO_2 (20.0 mg) and **2c** (1 mL) were used. The desirable product (**3mc**, 17.7 mg, 0.093 mmol, 47%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/19) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.11–7.08 (m, 4H), 3.90–3.87 (m, 1H), 3.83–3.79 (m, 1H), 3.75–3.71 (m, 1H), 2.74–2.69

(m, 1H), 2.64–2.59 (m, 1H), 2.31 (s, 3H), 2.00–1.95 (m, 1H), 1.94–1.82 (m, 3H), 1.78–1.72 (m, 1H), 1.50–1.44 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 139.3, 135.3, 129.2, 128.5, 78.8, 67.8, 37.7, 32.4, 31.5, 25.9, 21.2; HRMS (FAB): *m*/*z* calcd. for $C_{13}H_{19}O$ ($[M+H]^+$) 191.1430, found 191.1438.

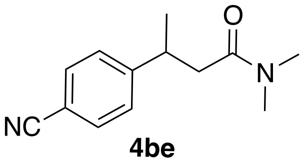


2-(4-Methylphenethyl)-1,4-dioxane (3md)

According to the general procedure A, **1m** (23.7 mg, 0.200 mmol) and **2d** (1 mL) were used. The desirable product (**3md**, 27.3 mg, 0.132 mmol, 66%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/19) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.10–7.06 (m, 4H), 3.79 (dd, *J* = 12.0, 1.8 Hz, 1H), 3.73–3.67 (m, 3H), 3.60 (td, *J* = 12.0, 1.8 Hz, 1H), 3.55–3.51 (m, 1H), 3.29 (t, *J* = 10.2 Hz, 1H), 2.73 (ddd, *J* = 13.8, 10.2, 5.4 Hz, 1H), 2.60 (ddd, *J* = 13.8, 9.6, 7.2 Hz, 1H), 2.31 (s, 3H), 1.72 (dddd, *J* = 13.8, 9.6, 8.4, 5.4 Hz, 1H), 1.62–1.56 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 138.8, 135.5, 129.3, 128.5, 74.8, 71.5, 67.0, 66.7, 33.6, 31.0, 21.2; HRMS (FAB): *m*/*z* calcd. for $C_{13}H_{18}O_2$ (M^+) 206.1301, found 206.1302. FT-IR (neat, NaCl, cm^{-1}): 1123.



3be

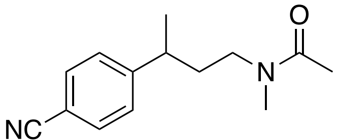


4be

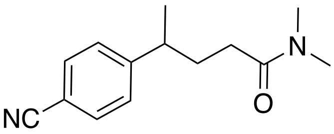
***N*-(3-(4-Cyanophenyl)butan-1-yl)-*N*-methylformamide (3be) and 3-(4-cyanophenyl)-*N,N*-dimethylbutanamide (4be)**

According to the general procedure B, **1b** (28.5 mg, 0.199 mmol) and **2e** (1 mL) were used. The products (**3be**+**4be**, 36.6 mg, 0.169 mmol, 85% total yield, **3be**/**4be** = 1.1:1) were obtained and **3be** (colorless oil, 14.5 mg, 0.067 mmol, 34%) and **4be** (colorless oil, 10.6 mg, 0.049 mmol, 25%) were isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/1): **3be**: ^{1}H NMR (600 MHz, $CDCl_3$) major rotamer: δ 7.87 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.20–3.07 (m, 2H), 2.83 (s, 3H), 2.81–2.75 (m, 1H), 1.91–1.80 (m, 2H), 1.29 (d, *J* = 7.2 Hz, 3H); minor rotamer: δ 7.99 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 3.31 (ddd, *J* = 13.2, 9.0, 6.0 Hz, 1H), 3.20–3.07 (m, 1H), 2.87 (s, 3H), 2.81–2.75 (m, 1H), 1.91–1.80 (m, 2H), 1.30 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): rotameric mixture: δ 162.7, 152.3, 151.5, 132.8, 132.6, 127.9, 127.9, 119.1, 118.9, 110.7, 110.4, 47.7, 42.8, 38.1, 37.4, 35.8, 34.6, 34.5, 29.5, 22.4, 22.2; HRMS (FAB): *m*/*z* calcd. for $C_{13}H_{17}N_2O$ ($[M+H]^+$) 217.1335, found 217.1342; FT-IR (neat, NaCl, cm^{-1}): 2226, 1671.; **4be**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 2H), 3.46 (sext, *J* = 7.2 Hz, 1H), 2.93 (s, 3H), 2.90 (s, 3H), 2.61 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.55 (dd, *J* = 15.6, 7.2 Hz, 1H), 1.32 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ; 171.0, 152.5, 132.5, 128.0, 119.2, 110.2, 41.3, 37.4, 36.6, 35.6, 21.8; HRMS (FAB): *m*/*z* calcd. for $C_{13}H_{17}N_2O$ ($[M+H]^+$) 217.1335, found 217.1344;

FT-IR (neat, NaCl, cm^{-1}): 2226, 1647.



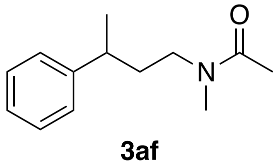
3bf



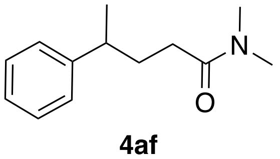
4bf

***N*-(3-(4-Cyanophenyl)butan-1-yl)-*N*-methylacetamide (3bf) and 4-(4-cyanophenyl)-*N*,*N*-dimethylpentanamide (4bf)**

According to the general procedure B, **1b** (28.7 mg, 0.200 mmol) and **2f** (1 mL) were used. **3bf** (colorless oil, 40.1 mg, 0.174 mmol, 87%) and **4bf** (colorless oil, 3.0 mg, 0.013 mmol, 7%) were isolated by flash column chromatography on silica gel (EtOAc): **3bf**: ^{1}H NMR (600 MHz, $CDCl_3$) major rotamer: δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.32 (ddd, *J* = 13.8, 9.0, 5.4 Hz, 1H), 3.25–3.17 (m, 1H), 2.89 (s, 3H), 2.81–2.76 (m, 1H), 2.01 (s, 3H), 1.93–1.78 (m, 2H) 1.28 (d, *J* = 7.2 Hz, 3H); minor rotamer: δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.25–3.17 (m, 1H), 3.07 (ddd, *J* = 15.0, 10.2, 4.8 Hz, 1H), 2.87 (s, 3H), 2.81–2.76 (m, 1H), 1.92 (s, 3H), 1.93–1.78 (m, 2H) 1.31 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): rotameric mixture: δ 170.6, 170.2, 152.6, 151.7, 132.7, 132.5, 127.9, 127.8, 119.2, 118.9, 110.6, 110.1, 49.1, 46.2, 38.3, 38.0, 36.2, 36.1, 34.9, 33.2, 22.4, 22.4, 22.0, 21.2; HRMS (FAB): *m*/*z* calcd. for $C_{14}H_{19}N_2O$ ($[M+H]^+$) 231.1492, found 231.1495; FT-IR (neat, NaCl, cm^{-1}): 2226, 1646.; **4bf**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.92 (s, 3H), 2.87 (s, 3H), 2.85 (dqd, *J* = 9.0, 6.6, 6.0 Hz, 1H), 2.18 (ddd, *J* = 15.6, 9.0, 6.6 Hz, 1H), 2.12 (ddd, *J* = 15.6, 9.0, 6.0 Hz, 1H), 1.99 (dddd, *J* = 13.8, 9.0, 6.6, 6.0 Hz, 1H), 1.90 (dddd, *J* = 13.8, 9.0, 9.0, 6.0 Hz, 1H) 1.28 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ; 172.4, 152.7, 132.5, 128.1, 119.2, 110.2, 39.9, 37.3, 35.6, 33.0, 31.1, 22.2 ;HRMS (FAB): *m*/*z* calcd. for $C_{14}H_{19}N_2O$ ($[M+H]^+$) 231.1492, found 231.1495; FT-IR (neat, NaCl, cm^{-1}): 2226, 1646.



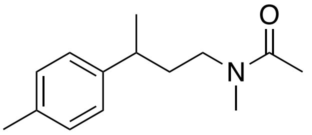
3af



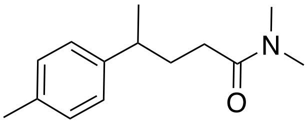
4af

***N*-methyl-*N*-(3-phenylbutan-1-yl)acetamide (3af) and *N*,*N*-dimethyl-4-phenylpentanamide (4af)**

According to the general procedure B, **1a** (23.6 mg, 0.200 mmol) and **2f** (1 mL) were used. The products (**3af**+**4af**, 23.5 mg, 0.114 mmol, 57% total yield, **3af**/**4af** = 4.7:1) were obtained and **3af** (colorless oil, 8.4 mg, 0.041 mmol, 20%) and **4af** (colorless oil, 1.3 mg, 0.006 mmol, 3%) were isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/2): **3af**: ^{1}H NMR (600 MHz, $CDCl_3$) major rotamer: δ 7.33–7.28 (m, 2H), 7.23–7.17 (m, 3H), 3.20–3.14 (m, 1H), 3.06 (ddd, *J* = 15.0, 10.2, 4.8 Hz, 1H), 2.86 (s, 3H), 2.74–2.66 (m, 1H), 1.88 (s, 3H), 1.93–1.76 (m, 2H), 1.29 (d, *J* = 6.6 Hz, 3H); minor rotamer: δ 7.33–7.28 (m, 2H), 7.23–7.17 (m, 3H), 3.39 (ddd, *J* = 13.2, 9.6, 6.0 Hz, 1H), 3.20–3.14 (m, 1H), 2.86 (s, 3H), 2.74–2.66 (m, 1H), 2.01 (s, 3H), 1.93–1.76 (m, 2H), 1.27 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): rotameric mixture: δ 170.5, 147.0, 146.0, 128.9, 128.6, 127.0, 126.9, 126.7, 126.3 49.4, 46.5, 38.1, 37.9, 36.5, 36.3, 35.4, 33.3, 23.0, 22.8, 22.1, 21.2; HRMS (FAB): *m*/*z* calcd. for $C_{13}H_{20}NO$ ($[M+H]^+$) 206.1539, found 206.1547.; FT-IR (neat, NaCl, cm^{-1}): 1647.; **4af**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.8 Hz, 2H), 7.20–7.18 (m, 3H), 2.90 (s, 3H), 2.84 (s, 3H), 2.74 (dqd, *J* = 9.6, 7.2, 5.4 Hz, 1H), 2.19 (ddd, *J* = 15.6, 9.6, 6.6 Hz, 1H), 2.13 (ddd, *J* = 15.6, 9.6, 5.4 Hz, 1H), 1.99 (dddd, *J* = 13.8, 9.6, 6.6, 5.4 Hz, 1H), 1.88 (dddd, *J* = 13.8, 9.6, 9.6, 5.4 Hz, 1H), 1.28 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ; 173.2, 146.9, 128.6, 127.3, 126.3, 39.8, 37.3, 35.5, 33.5, 31.6, 22.8; HRMS (FAB): *m*/*z* calcd. for $C_{13}H_{20}NO$ ($[M+H]^+$) 206.1539, found 206.1547.; FT-IR (neat, NaCl, cm^{-1}): 1648.



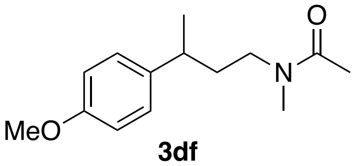
3ef



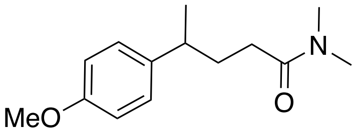
4ef

N-Methyl-N-(3-(4-tolyl)butan-1-yl)acetamide (3ef) and N,N-dimethyl-4-(4-tolyl)pentanamide (4ef)

According to the general procedure B, **1e** (26.4 mg, 0.200 mmol) and **2f** (1 mL) were used. **3ef** (colorless oil, 19.7 mg, 0.090 mmol, 45%) and **4ef** (colorless oil, 5.9 mg, 0.027 mmol, 13%) were isolated by flash column chromatography on silica gel (EtOAc/hexane = 2/3): **3ef**: ^{1}H NMR (600 MHz, $CDCl_3$) major rotamer: δ 7.13–7.07 (m, 4H), 3.18–3.12 (m, 1H), 3.05 (ddd, *J* = 14.4, 10.2, 4.8 Hz, 1H), 2.86 (s, 3H), 2.71–2.62 (m, 1H), 2.33 (s, 3H), 1.90 (s, 3H), 1.91–1.74 (m, 2H), 1.27 (d, *J* = 7.2 Hz, 3H); minor rotamer: δ 7.13–7.07 (m, 4H), 3.38 (ddd, *J* = 13.8, 9.0, 5.4 Hz, 1H), 3.18–3.12 (m, 1H), 2.86 (s, 3H), 2.71–2.62 (m, 1H), 2.31 (s, 3H), 2.01 (s, 3H), 1.91–1.74 (m, 2H) 1.25 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): rotameric mixture: δ 170.5, 144.0, 142.9, 136.1, 135.6, 129.5, 129.3, 126.8, 126.8, 49.4, 46.5, 37.6, 37.4, 36.5, 36.2, 35.4, 33.2, 23.1, 22.9, 22.1, 21.2, 21.1; HRMS (FAB): *m*/*z* calcd. for $C_{14}H_{22}NO$ ($[M+H]^+$) 220.1696, found 220.1700; FT-IR (neat, NaCl, cm^{-1}): 1649.; **4ef**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.10 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.90 (s, 3H), 2.85 (s, 3H), 2.70 (dqd, *J* = 9.6, 6.6, 5.4 Hz, 1H), 2.32 (s, 3H), 2.18 (ddd, *J* = 15.6, 9.6, 6.6 Hz, 1H), 2.13 (ddd, *J* = 15.6, 9.6, 5.4 Hz, 1H), 1.97 (dddd, *J* = 13.8, 9.6, 6.6, 5.4 Hz, 1H), 1.86 (dddd, *J* = 13.8, 9.6, 9.6, 5.4 Hz, 1H), 1.25 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ; 173.2, 143.8, 135.7, 129.3, 127.1, 39.4, 37.3, 35.5, 33.5, 31.6, 22.9, 21.2; HRMS (FAB): *m*/*z* calcd. for $C_{14}H_{22}NO$ ($[M+H]^+$) 220.1696, found 220.1699; FT-IR (neat, NaCl, cm^{-1}): 1648.



3df



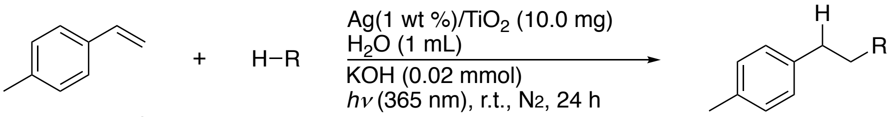
4df

N-(3-(4-methoxyphenyl)butan-1-yl)-N-methylacetamide (3df) and 4-(4-methoxyphenyl)-N,N-dimethylpentanamide (4df)

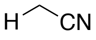
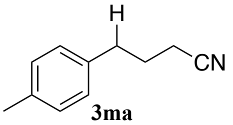
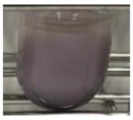
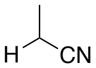
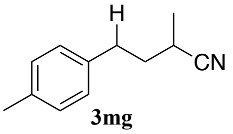
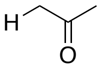
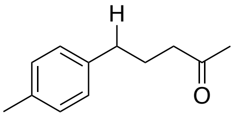
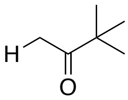
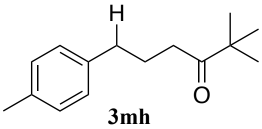
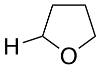
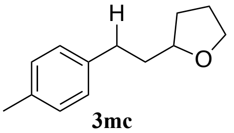
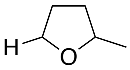
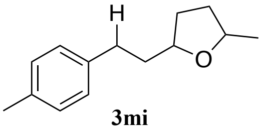
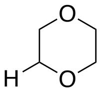
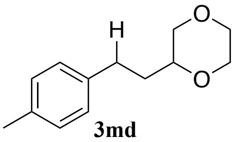
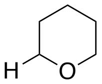
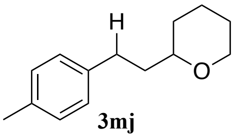
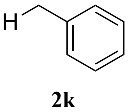
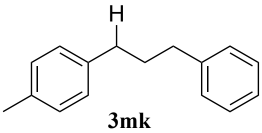
According to the general procedure B, **1d** (29.6 mg, 0.200 mmol) and **2f** (1 mL) were used. The products (**3df**+**4df**, 29.4 mg, 0.125 mmol, 62% total yield, **3df**/**4df** = 4.7:1) were obtained and **3df** (colorless oil, 11.5 mg, 0.049 mmol, 24%) and **4df** (colorless oil, 2.2 mg, 0.009 mmol, 5%) were isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/3): **3df**: ^{1}H NMR (600 MHz, $CDCl_3$) major rotamer: δ 7.13–7.09 (m, 2H), 6.86 (d, J = 8.4 Hz, 2H), 3.80 (s, 3H), 3.18–3.12 (m, 1H), 3.05 (ddd, J = 14.4, 10.8, 4.8 Hz, 1H), 2.86 (s, 3H), 2.70–2.61 (m, 1H), 1.89 (s, 3H), 1.93–1.75 (m, 2H), 1.26 (d, J = 7.8 Hz, 3H); minor rotamer: δ 7.13–7.09 (m, 2H), 6.84 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H), 3.37 (ddd, J = 14.4, 9.0, 6.0 Hz, 1H), 3.18–3.12 (m, 1H), 2.86 (s, 3H), 2.70–2.61 (m, 1H), 2.02 (s, 3H), 1.93–1.75 (m, 2H), 1.24 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): rotameric mixture: δ 170.5, 158.3, 158.0, 139.1, 138.1, 127.9, 127.8, 114.3, 114.0, 55.5, 49.4, 46.6, 37.3, 37.0, 36.7, 36.3, 35.6, 33.3, 23.2, 23.0, 22.1, 21.2; HRMS (FAB): *m*/*z* calcd. for $C_{14}H_{22}NO_2$ ($[M+H]^+$) 236.1645, found 236.1653.; FT-IR (neat, NaCl, cm^{-1}): 1647, 1247, 1034.; **4df**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.10 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H), 2.90 (s, 3H), 2.85 (s, 3H), 2.69 (dqd, J = 9.6, 7.2, 5.4 Hz, 1H), 2.17 (ddd, J = 15.6, 9.6, 6.6 Hz, 1H), 2.12 (ddd, J = 15.6, 9.6, 5.4 Hz, 1H), 1.96 (dddd, J = 13.8, 9.6, 6.6, 5.4 Hz, 1H), 1.83 (dddd, J = 13.8, 9.6, 9.6, 5.4 Hz, 1H), 1.25 (d, J = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ; 173.2, 158.1, 139.0, 128.1, 114.0, 55.4, 39.0, 37.4, 35.5, 33.7, 31.6, 23.0; HRMS (FAB): *m*/*z* calcd. for $C_{14}H_{22}NO_2$ ($[M+H]^+$) 236.1645, found 236.1644.; FT-IR (neat, NaCl, cm^{-1}): 1648, 1247, 1036.

5. Appearances of reaction mixtures

Table S5. Reactivity and water-miscibility of **2**



1m, 0.2 mmol **2**, 1 mL **3**

entry	**2**	product (**3**)	conv. of **1m** (%)^a	yield of **3** (%)^b	appearance before irradiation
1	 **2a**	 **3ma**	–^{c}	68	
2	 **2g**	 **3mg**	<1	–^{d}	
3	 **2b**	 **3mb**	–^{c}	72	
4	 **2h**	 **3mh**	8	–^{d}	
5^e	 **2c**	 **3mc**	–^{c}	47	
6	 **2i**	 **3mi**	<1	–^{d}	
7	 **2d**	 **3md**	–^{c}	66	
8	 **2j**	 **3mj**	5	–^{d}	
9	 **2k**	 **3mk**	<1	–^{d}	

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[a] Determined by GC-MS.
[b] Isolated yield.
[c] Not determined
[d] Not detected.
[e] Ag(1 wt %)/TiO_2 (20.0 mg) was used.

6. Mechanistic study

6-1. Hydroxy radical detection by coumarin fluorescence method[22]

Coumarin is known to react with the hydroxyl radical in water. Among the products, only umbelliferone emits strong fluorescence. If the hydroxyl radical is generated by photocatalysis, umbelliferone should be observed.

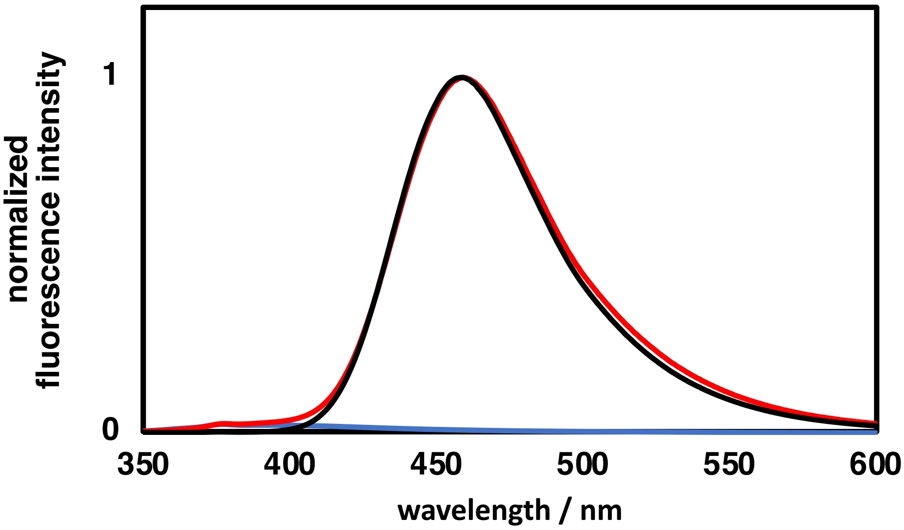
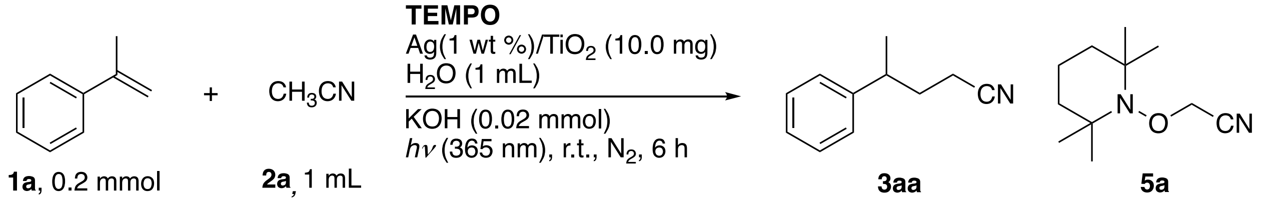


Fig. S2 Normalized fluorescence spectra of a 5 μM umbelliferone aqueous solution (black), a 0.1 mM coumarin aqueous solution (blue), and a sample prepared as follows (red): Ag(1 wt %)/TiO_2 (15.0 mg) was suspended in a test tube containing 3.5 mL of a 0.1 mM coumarin aqueous solution under N_2. The suspension was sonicated and then stirred vigorously under LED light of 365 nm. After the irradiation for 5 min, 0.5 g of KCl was added into the suspension, and then the suspension was kept in dark to precipitate the powder. After 12 h, the clear solution was obtained by decantation and its fluorescence spectrum was measured. All measurements were carried out after N_2 bubbling for 10 min. Excitation wavelength was 322 nm.

6-2. Radical trapping experiment

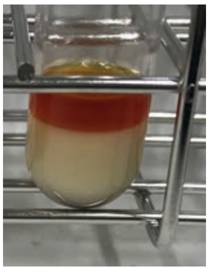
An oven-dried Pyrex glass test tube was charged with a magnetic stirrer bar, Ag(1 wt %)/TiO_2 (10.0 mg) and TEMPO (0.8 mmol). The vessel was sealed with a rubber septum and placed under nitrogen before 1 mL of a stock solution containing **1a** (0.20 mmol) in **2a** or **2b** and 1 mL of an aqueous solution of KOH (0.02 M) were added. The mixture was sonicated and then stirred under LED-light irradiation (λ = 365 nm). After 6 h, the reaction mixture diluted with EtOAc was analyzed by GC-MS with an internal standard (*n*-dodecane). The mixture was dried over Na_2SO_4. After filtration through a 0.45 μm membrane filter and concentration under reduced pressure (80 mmHg, 40 ºC), an aliquot with an internal standard (1,1,2,2-tetrachloroethane) was monitored by ^1H NMR analysis. The residue was purified by flash column chromatography on silica gel using EtOAc–hexane as the eluent.

Table S6. Radical trapping experiment using TEMPO in a **2a**/water system

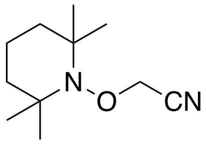


entry	TEMPO	yield[a]	
		3aa (%)	**5a** (mmol)
1	–	74	–
2	0.8 mmol	<5	0.33

[a] ^{1}H NMR yield.



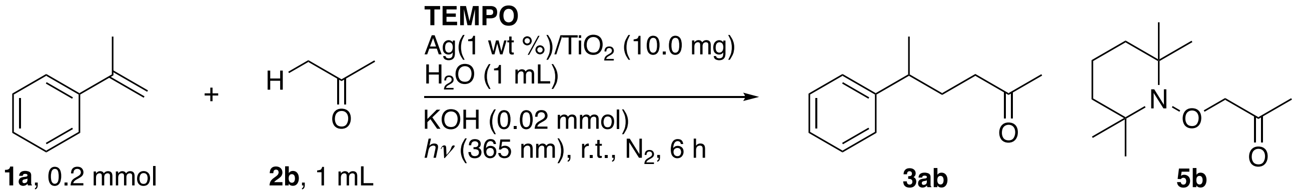
(entry 2, before reaction)



2-(2,2,6,6-Tetramethylpiperidin-1-yloxy)acetonitrile (5a)[19]

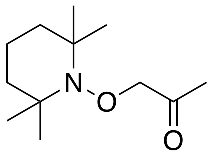
In entry 2, **5a** (59.8 mg, 0.305 mmol) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 3/97) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.52 (s, 2H), 1.57–1.52 (m, 1H), 1.49–1.41 (m, 4H), 1.35–1.31 (m, 1H), 1.20 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ; 116.2, 62.8, 60.5, 39.7, 33.1, 20.1, 17.0; HRMS (FAB): *m*/*z* calcd. for $C_{11}H_{20}N_2O$ (M^+) 196.1570, found 196.1578.

Table S7. Radical trapping experiment using TEMPO in a **2b**/water system



entry	TEMPO	yield[a] 3ab (%)	5b (mmol)
1	–	92	–
2	0.8 mmol	<5	0.34

[a] ^{1}H NMR yield.

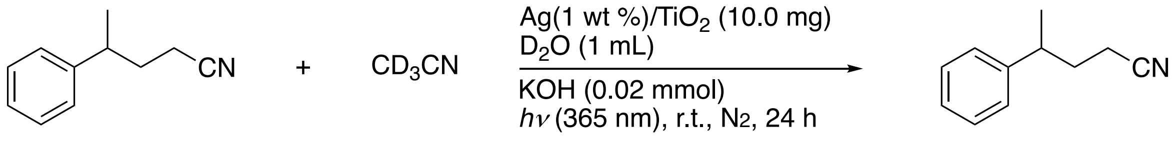


1-(2,2,6,6-Tetramethylpiperidin-1-yloxy)propan-2-one (5b)[20]

In entry 2, **5b** (29.2 mg, 0.137 mmol) was isolated by flash column chromatography on silica gel(EtOAc/hexane = 1/49) as a pale yellow oil: ^{1}H NMR (600 MHz, CDCl$_3$): δ 4.38 (s, 2H), 2.21 (s, 3H) 1.60–1.52 (m, 1H), 1.49–1.42 (m, 4H), 1.36–1.30 (m, 1H), 1.16 (s, 6H), 1.14 (s, 6H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 207.1, 83.4, 60.2, 39.7, 33.0, 27.4, 20.2, 17.1; HRMS (FAB): *m*/*z* calcd. for $C_{12}H_{23}NO_2$ (M^+) 213.1723, found 213.1722.

6-3. Labeling experiments

Labeling experiments were carried out according to general procedure A. Conversions of **1a** were determined by GC-MS. Yields were determined by weight. D/H ratios of the isolated products were calculated based on ^{1}H NMR (600 MHz, $CDCl_3$) analysis of **3aa**: *δ* 7.32 (t, *J* = 7.2 Hz, 2.00H), 2.86 (dqd, *J* = 9.6, 7.2, 5.4 Hz, 1.00H, PhC*H*), 2.22 (ddd, *J* = 16.8, 7.8, 6.0 Hz, 1.04H, CH_2CN), 2.11 (ddd, *J* = 16.8, 7.8, 7.8 Hz, 1.04H, CH_2CN); **3ab**: *δ* 7.29 (t, *J* = 7.2 Hz, 2.00H), 2.68 (dqd, *J* = 9.0, 6.6, 6.0 Hz, 1.01H, PhC*H*), 2.33 (ddd, *J* = 17.4, 9.0, 6.6 Hz, 1.04H, CH_2CO), 2.26 (ddd, *J* = 17.4, 9.0, 5.4 Hz, 1.03H, CH_2CO), 2.05 (s, 2.99H, CH_3CO).



3aa, 0.2 mmol

2a-*d*$_3$, 1 mL

3aa, 91%
no D incorporation

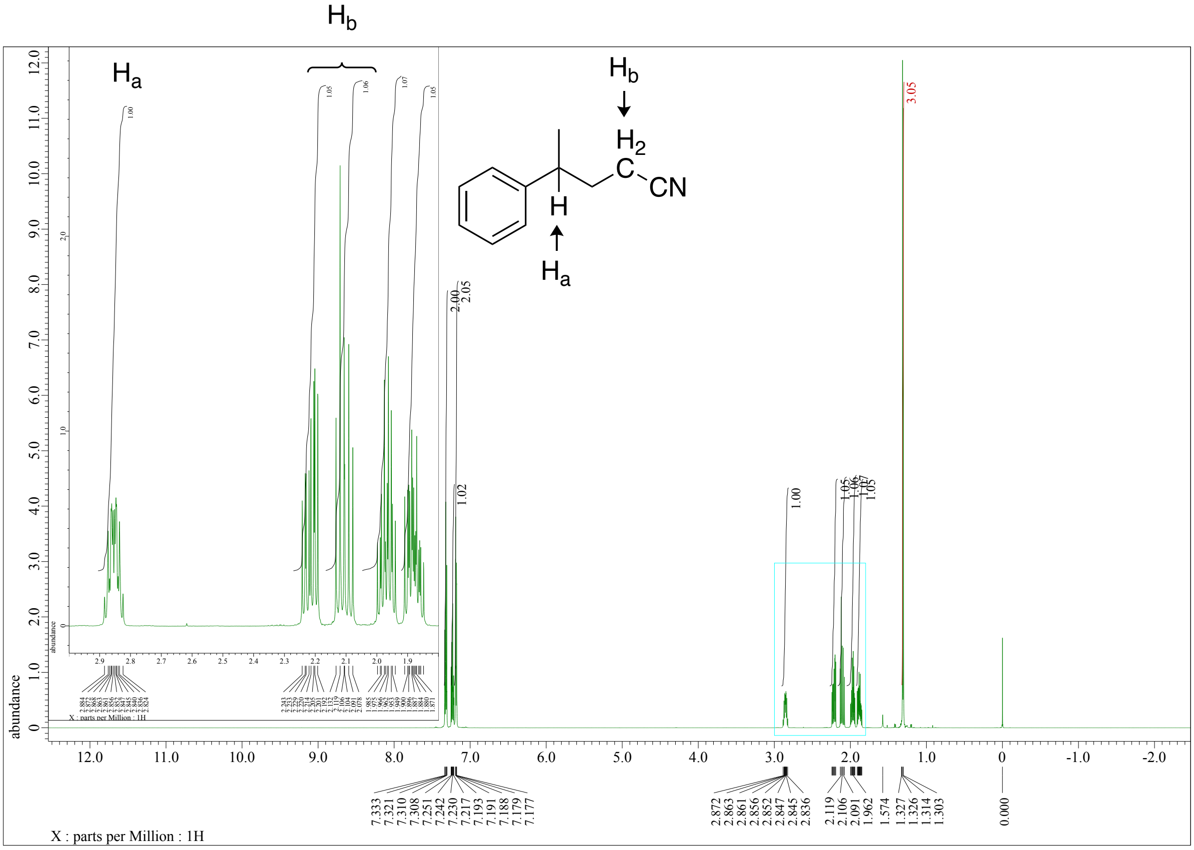
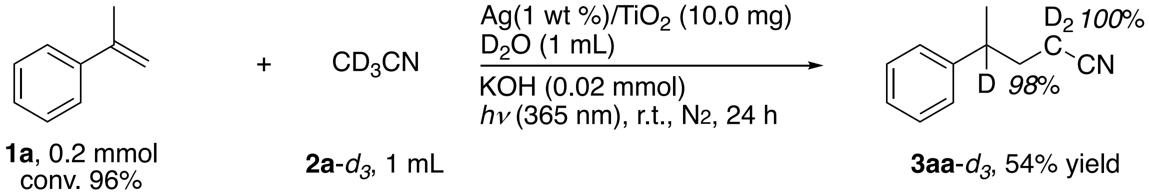


Fig. S3 D labeling experiment using **3aa** in **2a**-*d*$_3$/D_2O-KOH. According to general procedure A, **3aa** (31.8 mg, 0.200 mmol) was used instead of **1**, and **2a**-*d*$_3$ and D_2O were used. **3aa** (29.0 mg, 0.182 mmol, 91%) was recovered by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil.



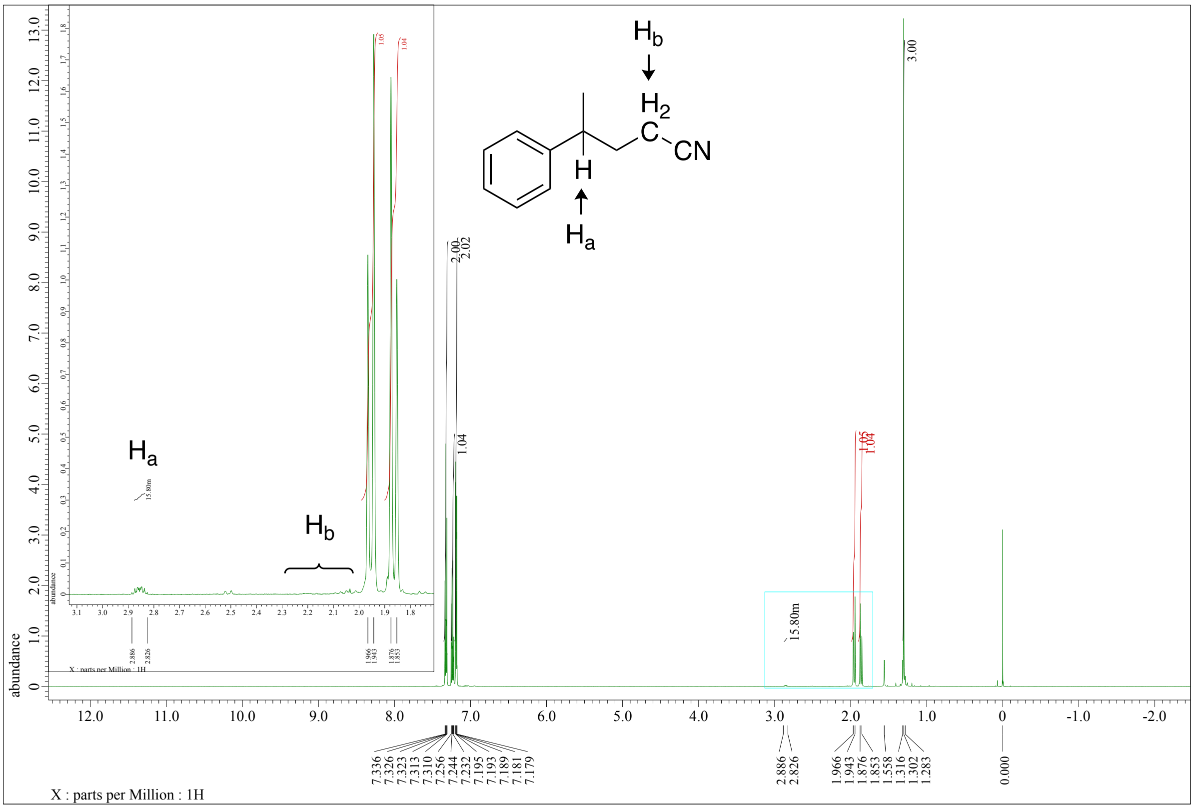
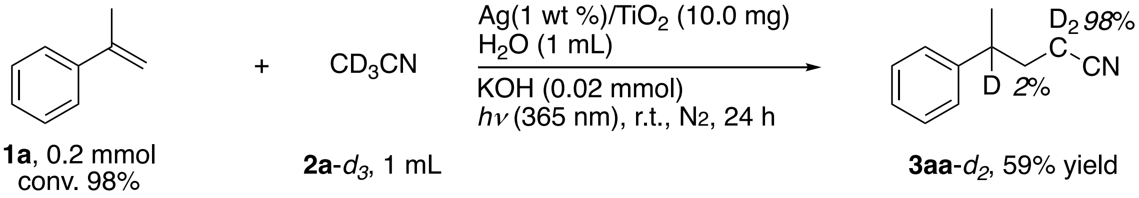


Fig. S4 D labeling experiment using **1a** in **2a**-*d*3/D2O-KOH. According to general procedure A, **1a** (23.6 mg, 0.200 mmol), **2a**-*d*3 and D2O were used. **3aa**-*d*3 (17.6 mg, 0.108 mmol, 54%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil.



1a, 0.2 mmol
conv. 98%

2a-d_3, 1 mL

3aa-d_2, 59% yield

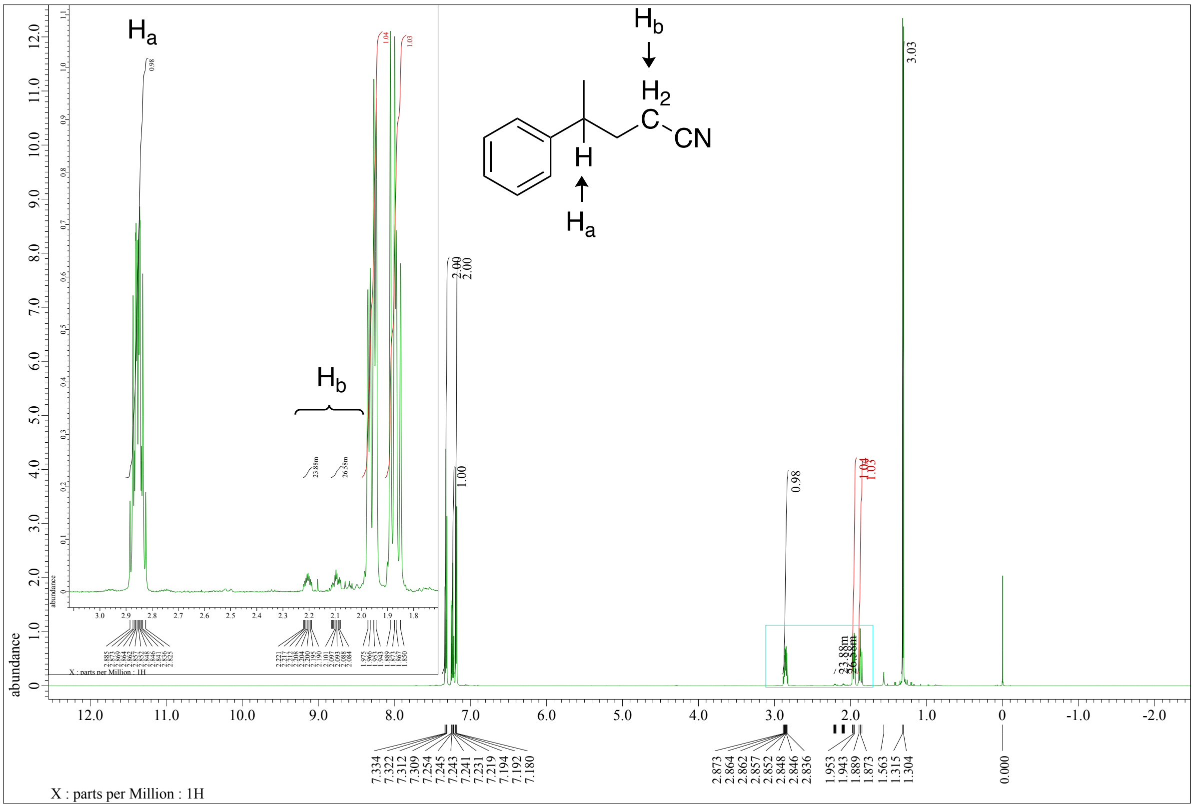
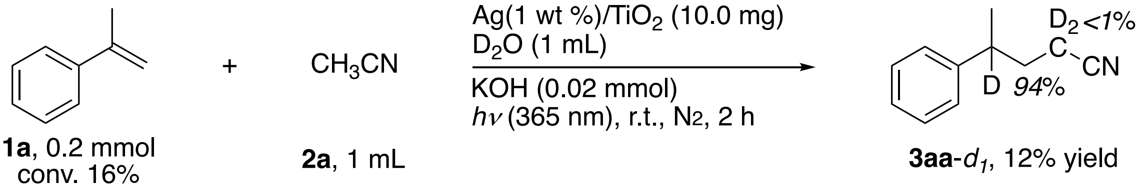


Fig. S5 D labeling experiment using **1a** in **2a**-d_3/H$_2$O-KOH. According to general procedure A, **1a** (23.6 mg, 0.200 mmol), **2a**-d_3 and H$_2$O were used. **3aa**-d_2 (19.1 mg, 0.118 mmol, 59%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil.



1a, 0.2 mmol
conv. 16%

2a, 1 mL

3aa-*d*$_1$, 12% yield

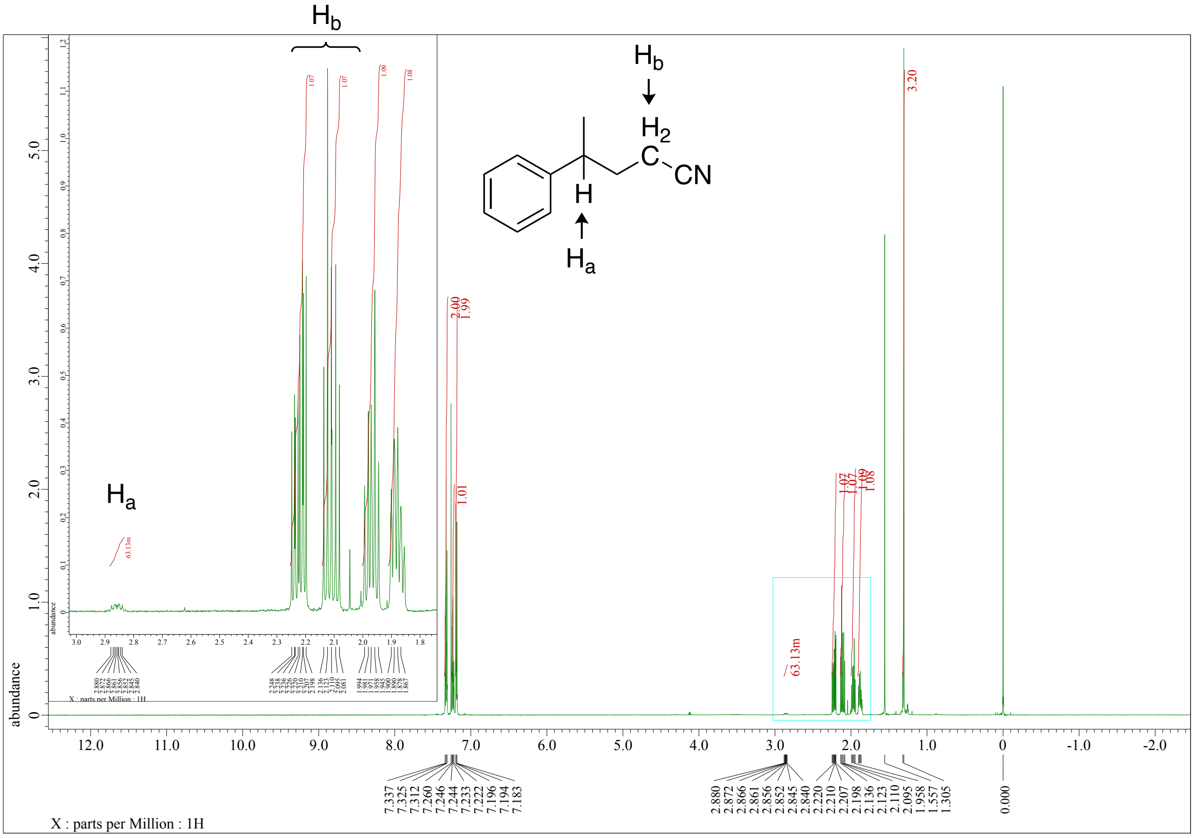
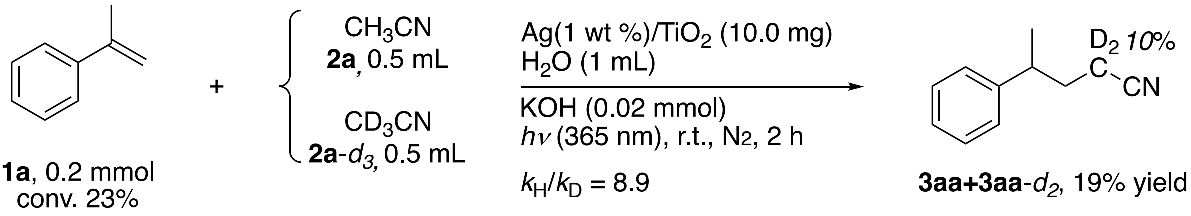


Fig. S6 D labeling experiment using **1a** in **2a**/D$_2$O-KOH. According to general procedure A, **1a** (23.6 mg, 0.200 mmol), **2a** and D$_2$O were used. **3aa**-*d$_1$* (3.7 mg, 0.023 mmol, 12%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil.



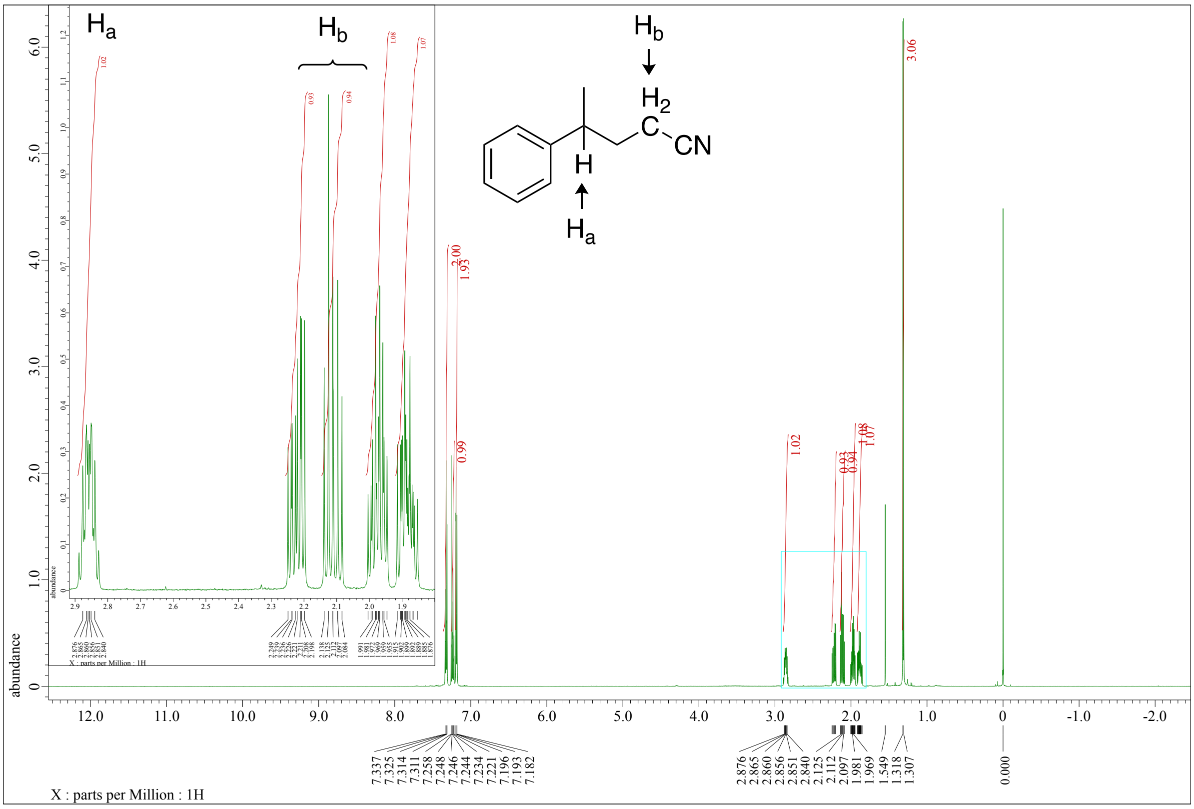
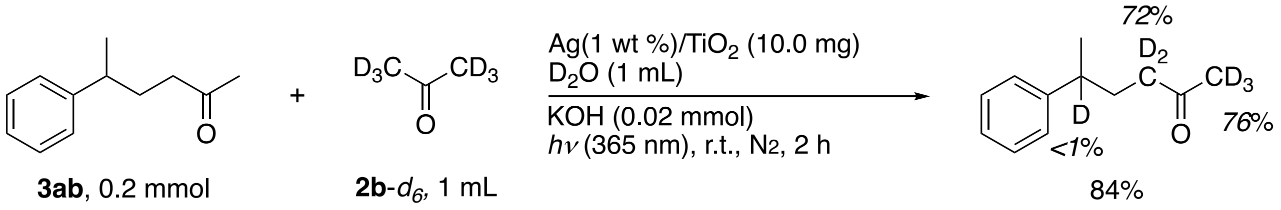


Fig. S7 Kinetic isotope effect experiment using **1a** in **2a**/**2a**-d_3/H_2O-KOH . According to general procedure A, **1a** (23.7 mg, 0.200 mmol), **2a** (0.5 mL), **2a**-d_3 (0.5 mL) and H_2O were used. After 2 h irradiation, the products (**3aa**+**3aa**-d_2, 6.0 mg, 0.038 mmol, 19% total yield, **3aa**/**3aa**-d_2 = 8.9) were obtained by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil.



3ab, 0.2 mmol

2b-d_6, 1 mL

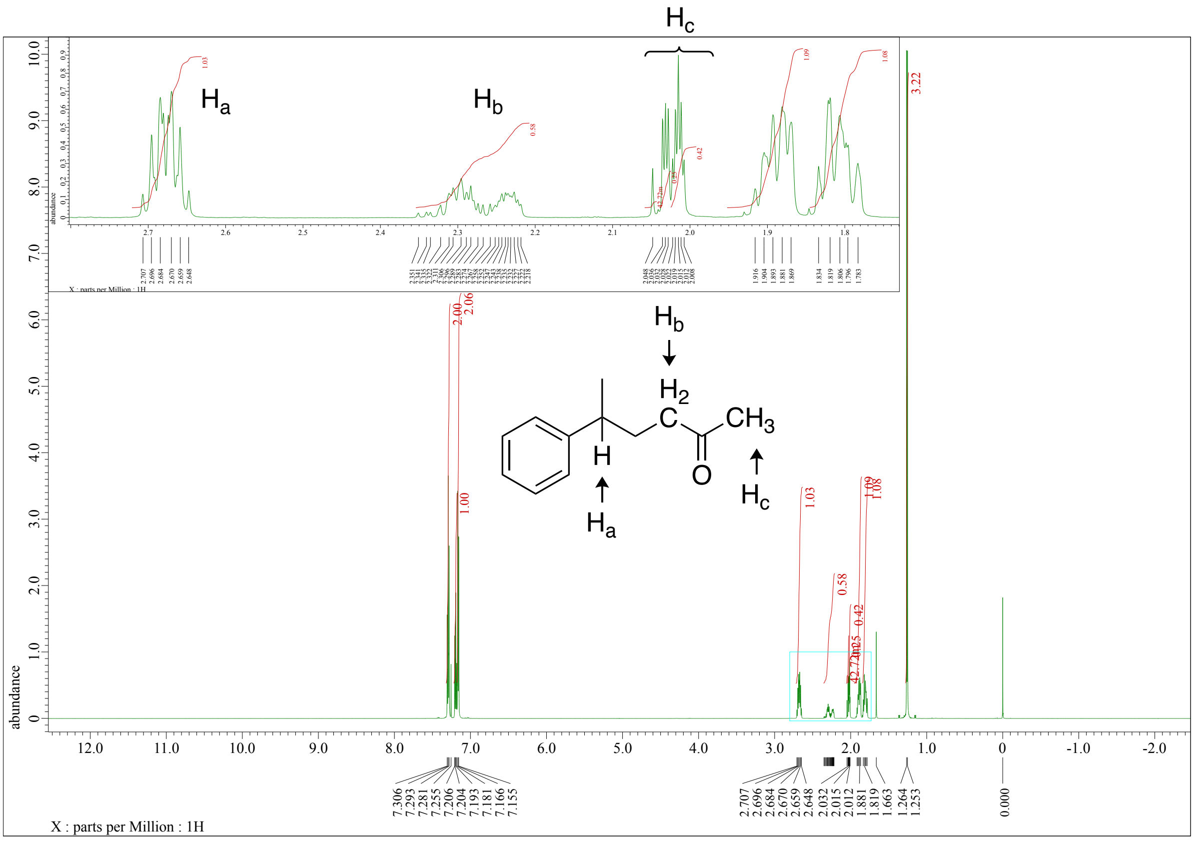
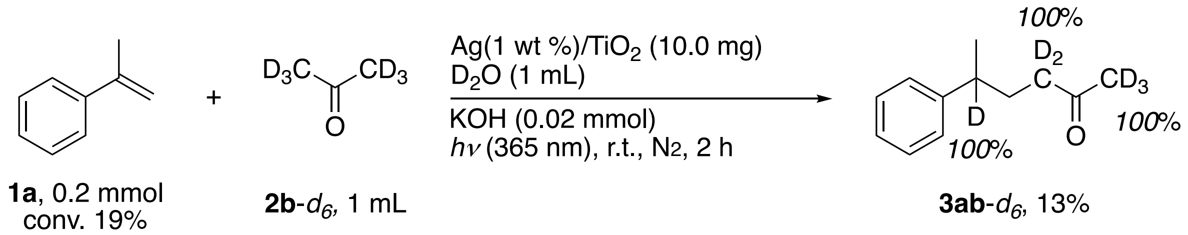


Fig. S8 D labeling experiment using **3ab** in **2b**-d_6/D_2O-KOH. According to general procedure A, **3ab** (35.3 mg, 0.200 mmol) was used instead of **1**, and **2b**-d_6 and D_2O were used. Deuterated **3ab** (30.1 mg, 0.167 mmol, 84%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil.



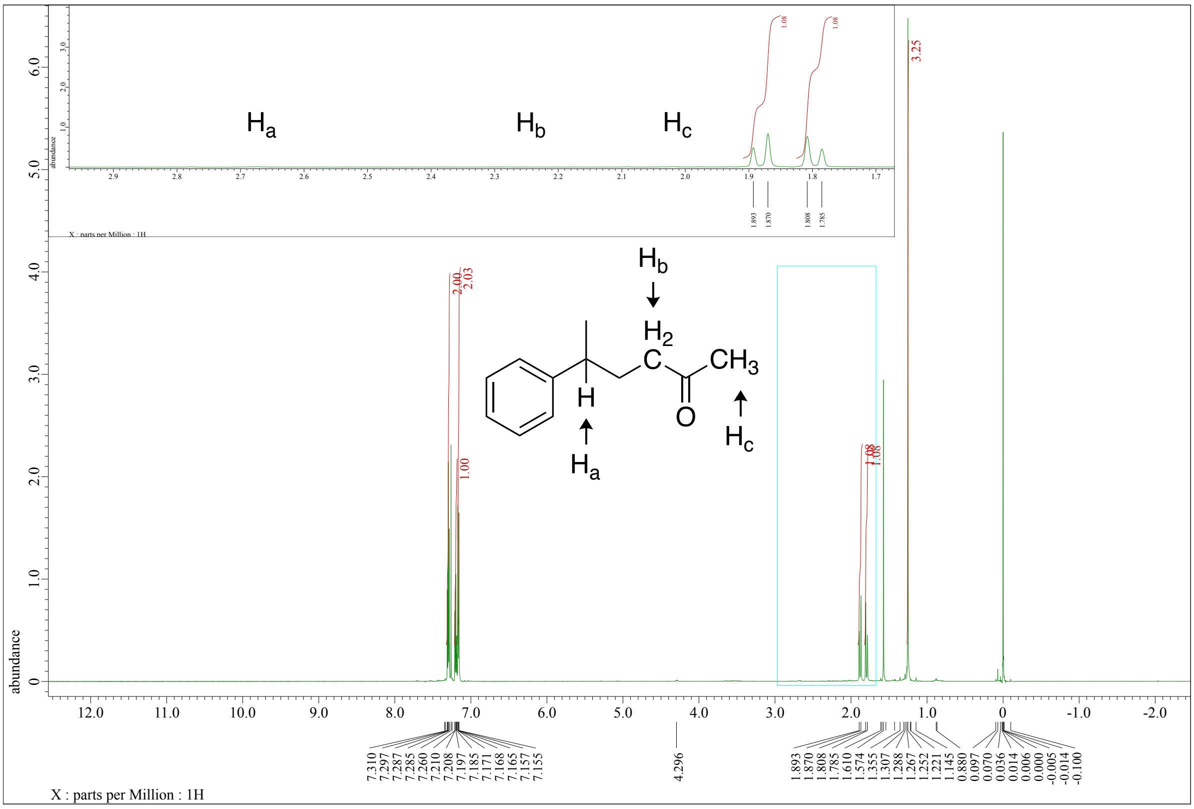
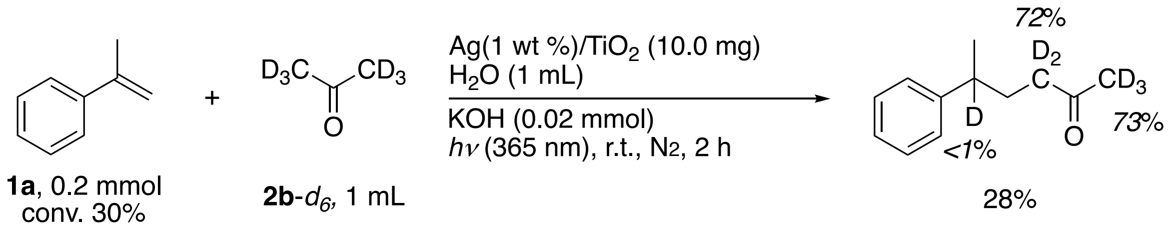


Fig. S9 D labeling experiment using **1a** in **2b**-*d*$_6$/D$_2$O-KOH. According to general procedure A, **1a** (23.7 mg, 0.200 mmol), **2b**-*d*$_6$ and D$_2$O were used. **3ab**-*d*$_6$ (4.6 mg, 0.025mmol, 13%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil.



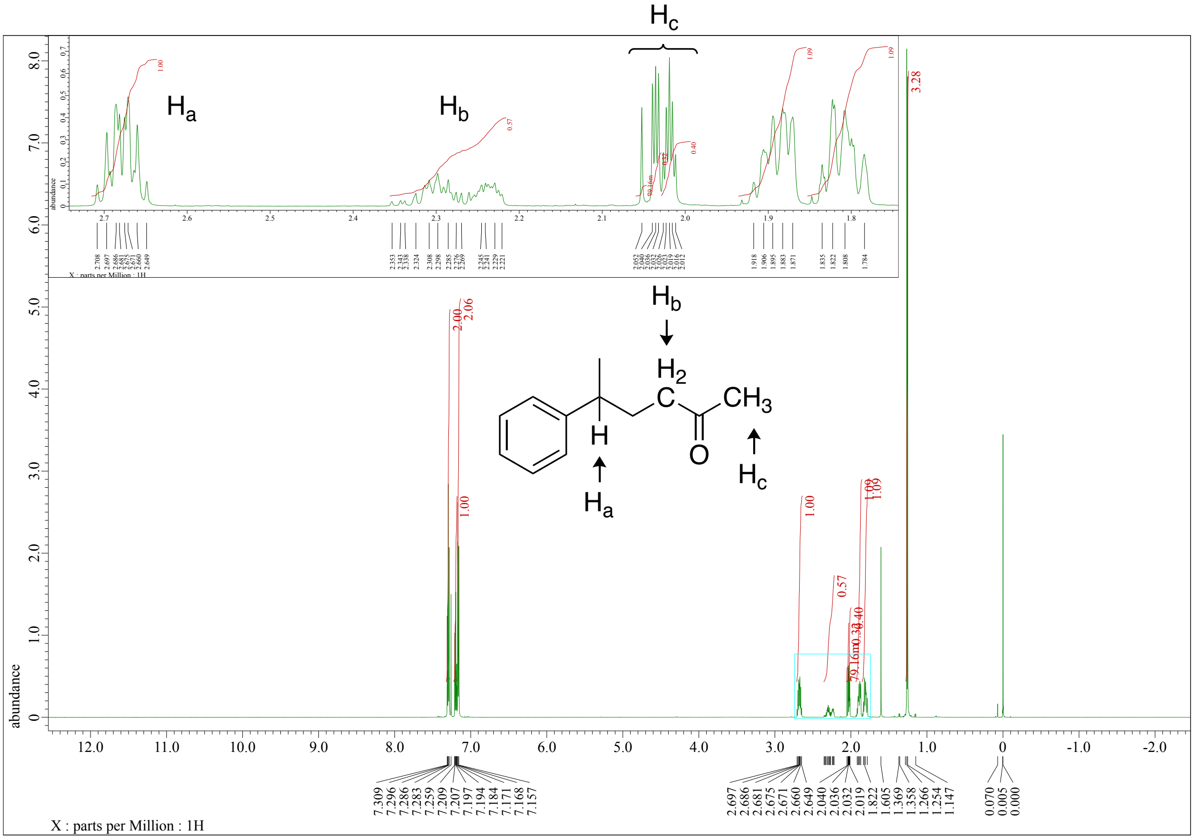
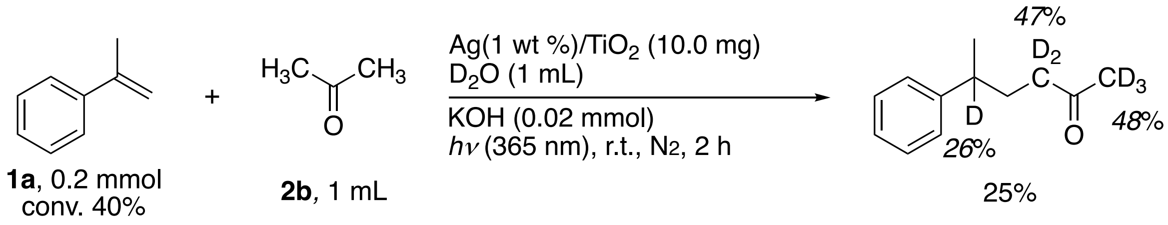


Fig. S10 D labeling experiment using **1a** in **2b**-*d*$_6$/H$_2$O-KOH. According to general procedure A, **1a** (23.7 mg, 0.200 mmol), **2b**-*d*$_6$, and H$_2$O were used. Deuterated **3ab** (9.9 mg, 0.055mmol, 28%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil.



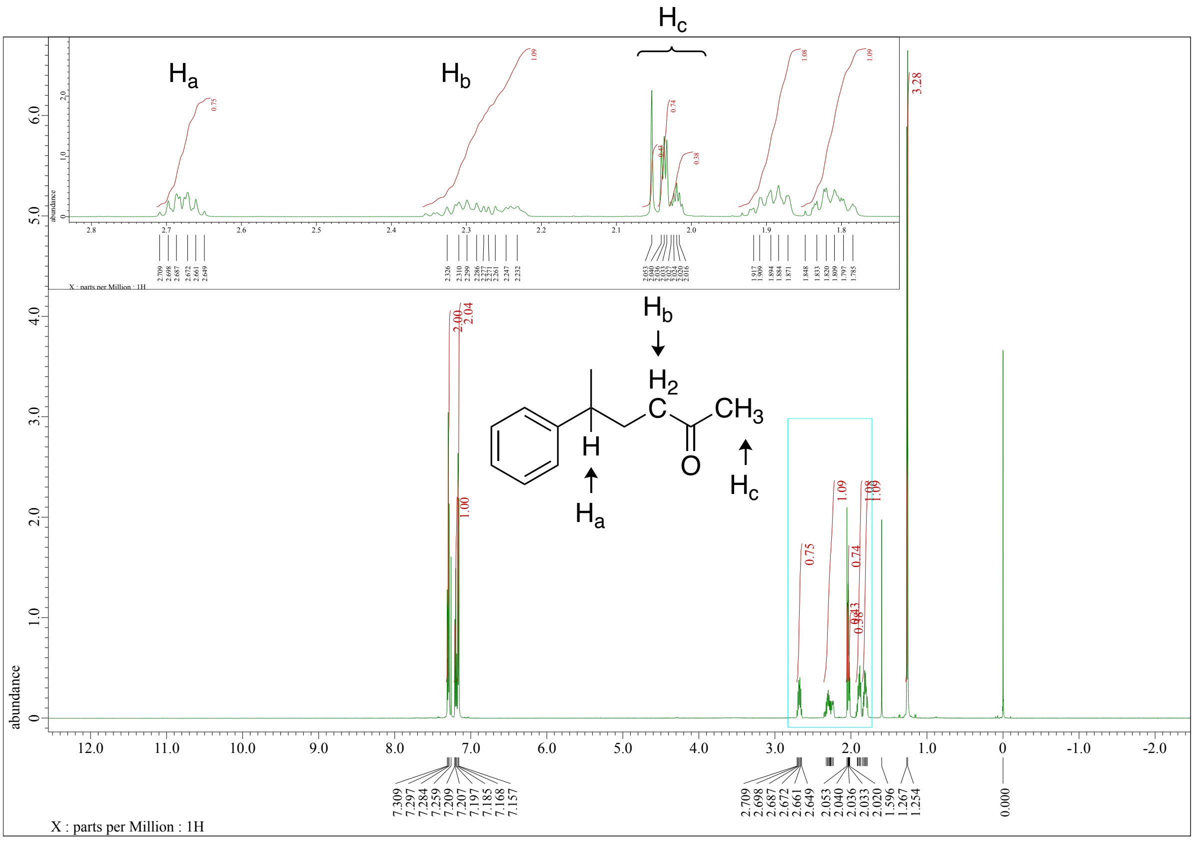
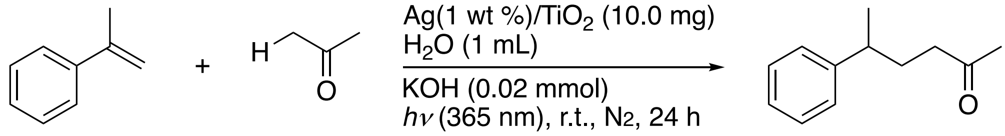


Fig. S11 D labeling experiment using **1a** in **2b**/D_2O-KOH. According to general procedure A, **1a** (23.6 mg, 0.200 mmol), **2b** and D_2O were used. Deuterated **3ab** (9.0 mg, 0.050 mmol, 25%) was isolated by flash column chromatography on silica gel (EtOAc/hexane = 1/24) as a colorless oil.

6-4. Control experiment with 2b

Table S8. Control experiment with **2b**



1a, 0.2 mmol **2b**, 1 mL **3ab**

entry	changes from standard conditions	yield of **3ab** (%)[a]
1	none	>99 (92)[b]
2	without Ag(1 wt %)/TiO_2	–[c]
3	in the dark	–[c]
4	without KOH	25
5[d]	without H_2O	–[c]
6[d]	without H_2O, KOH	–[c]

[a] ^1H NMR yield.
[b] Isolated yield.
[c] Not detected.
[d] Dehydrated acetone (2 mL) was used.

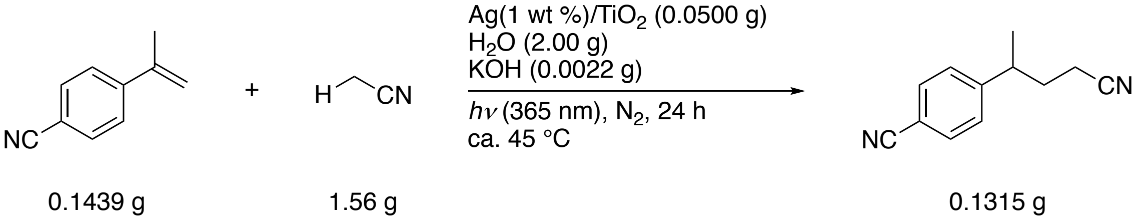
7. Green metrics

Table S9. Green metrics of this work and previous works

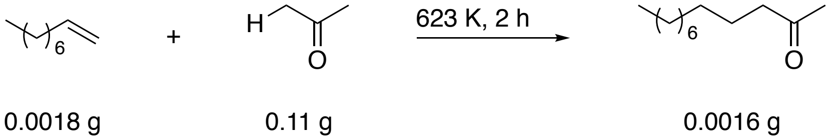
entry	1	2	3	4
reference number in the main text	this work	29	30	25
AE (%)[a]	100	100	100	100
RME (%)[b]	7.7	1.4	1.2	0.9
PMI[c] (reaction)	29	70	86	121
PMI[c] (reactant reagent, catalyst)	13	70	86	121
TON[d]	171[e]	–	9[f]	2[g]

[a] atom economy. [b] reaction mass efficiency. [c] process mass intensity.
[d] turnover number (mol/mol). [e] based on Ag. [f] based on CuI.
[g] based on 4,4’-dichlorobenzophenone.

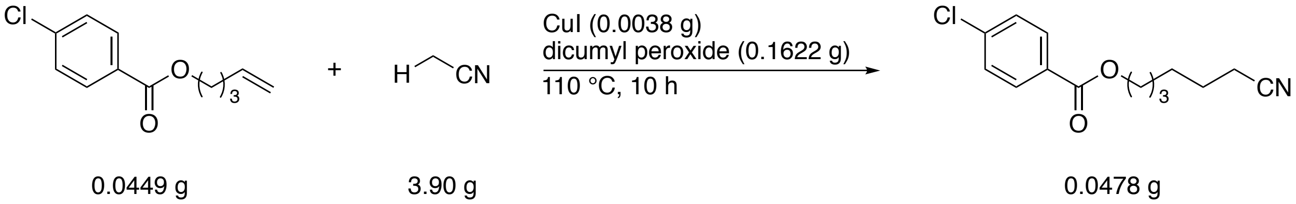
entry 1



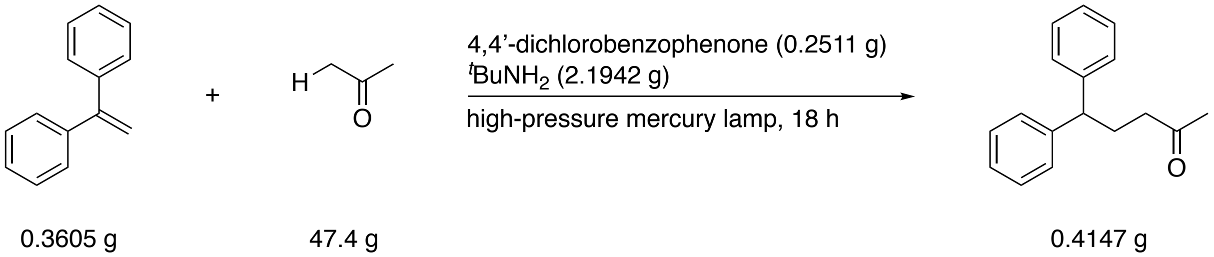
entry 2



entry 3



entry 4



8. Reference

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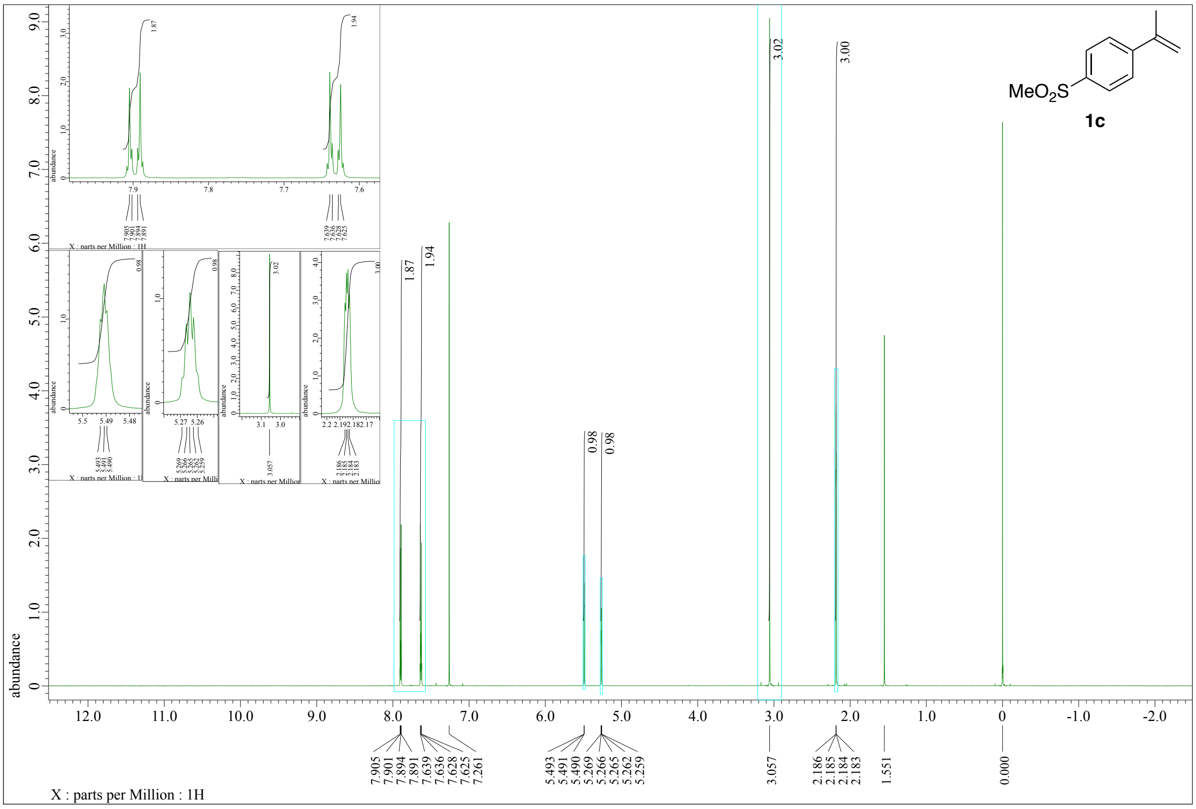
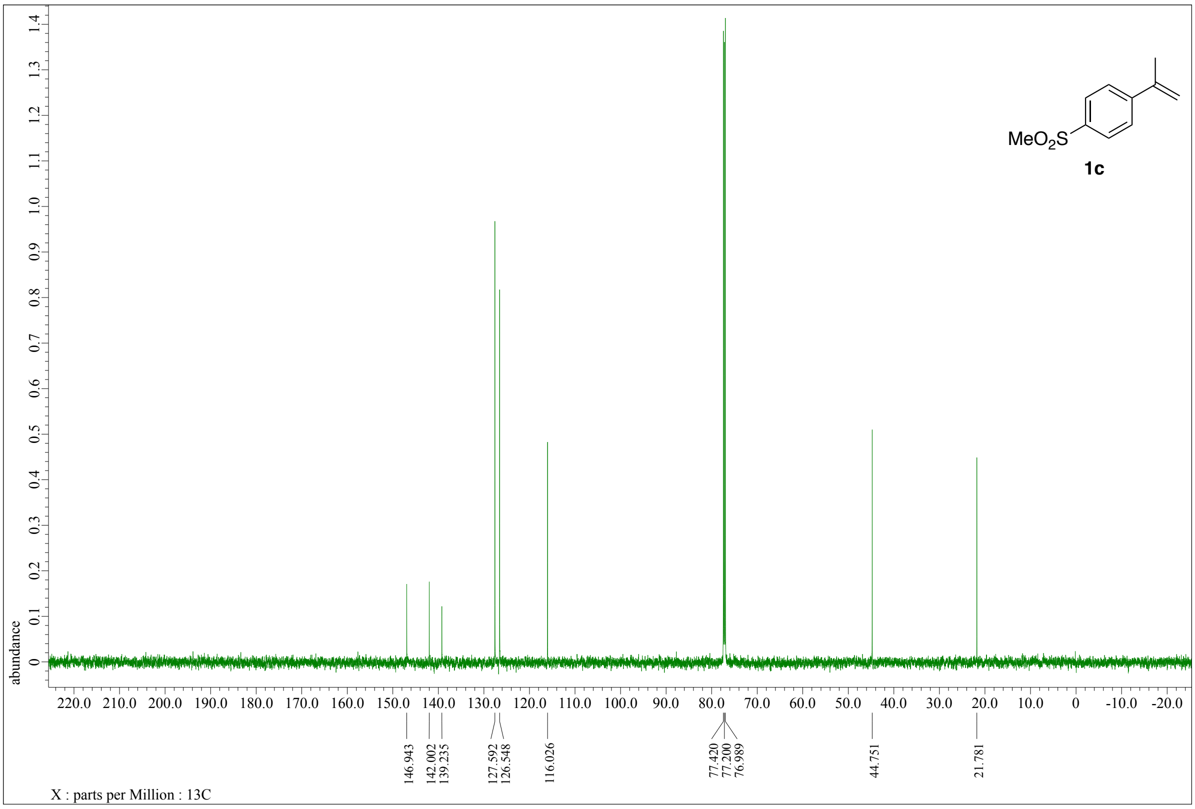
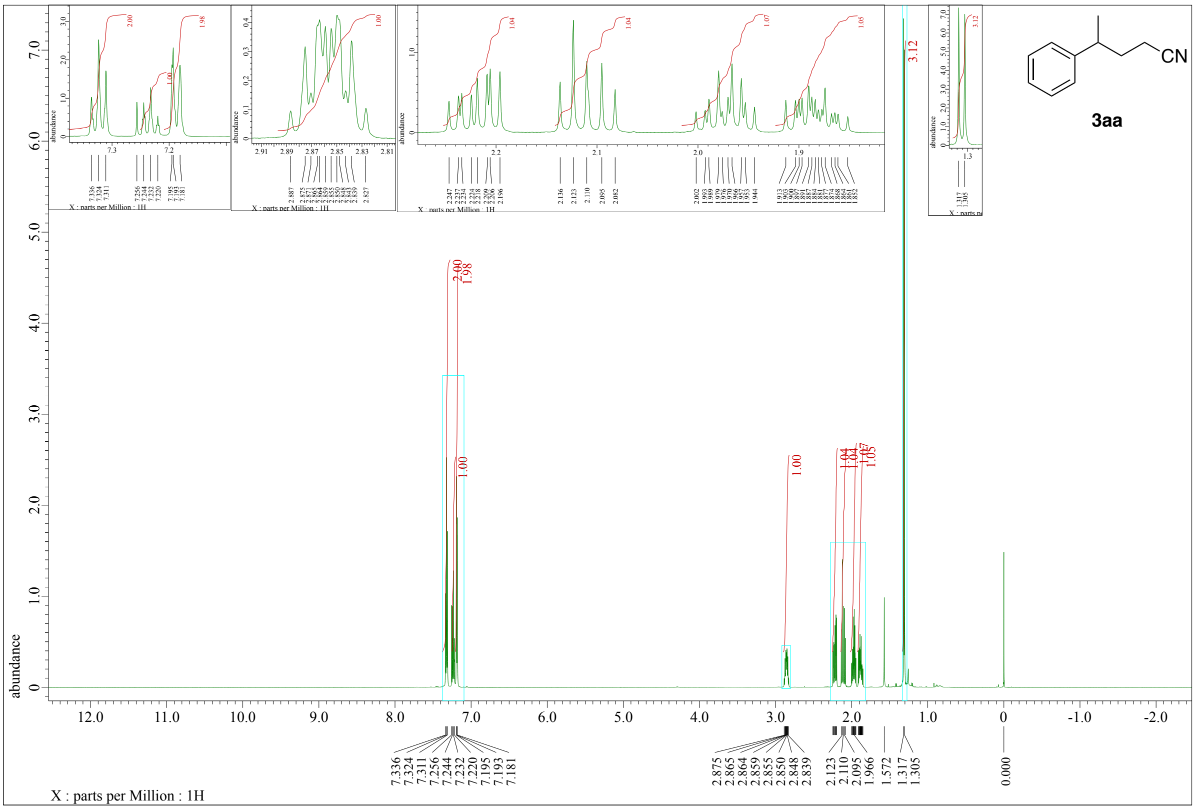
22. J. Zhang and Y. Nosaka, *J. Photochem. Photobiol., A,* 2015, **303–304**, 53–58.

9. Spectral data



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1.00
1.00
1.04
1.04
1.07
1.05
3.12
7.336
7.324
7.311
7.256
7.244
7.232
7.220
7.195
7.193
7.181
2.875
2.865
2.864
2.859
2.855
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2.839
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2.095
1.966
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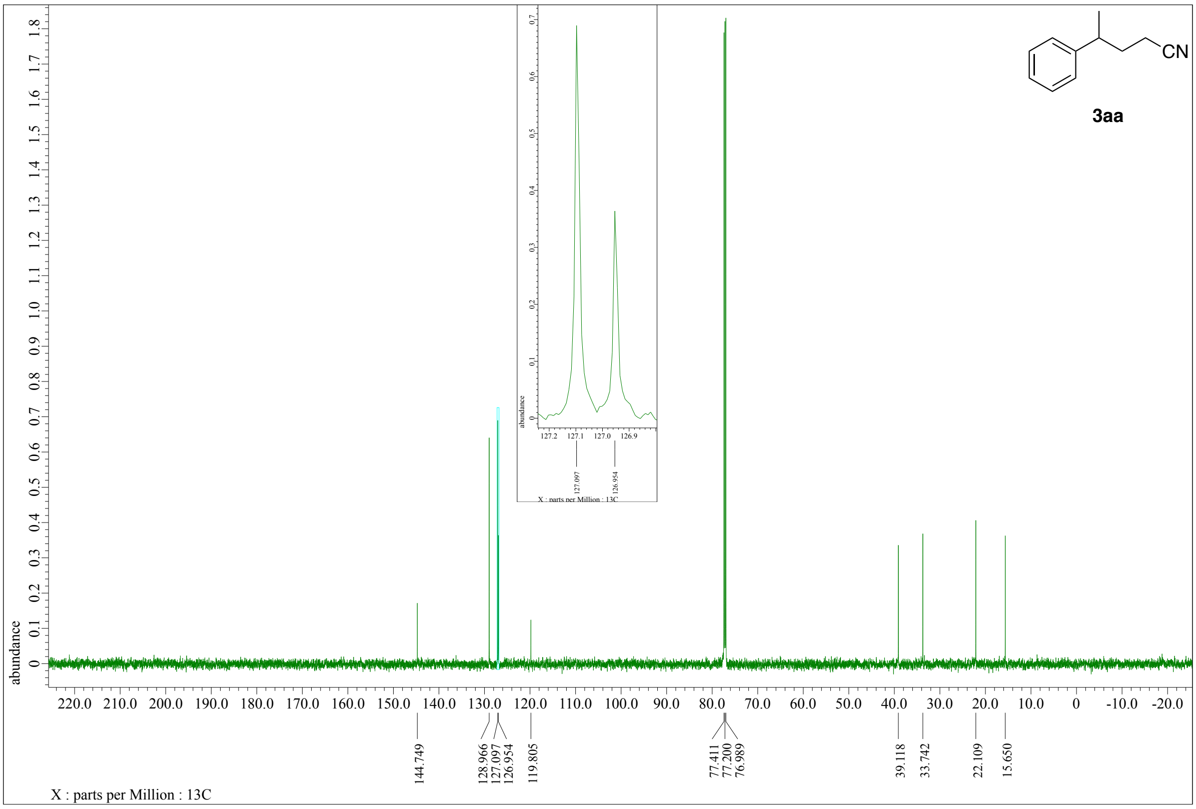
1.305
0.000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3aa
abundance
X : parts per Million : 13C
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126.954
144.749
128.966
127.097
126.954
119.805
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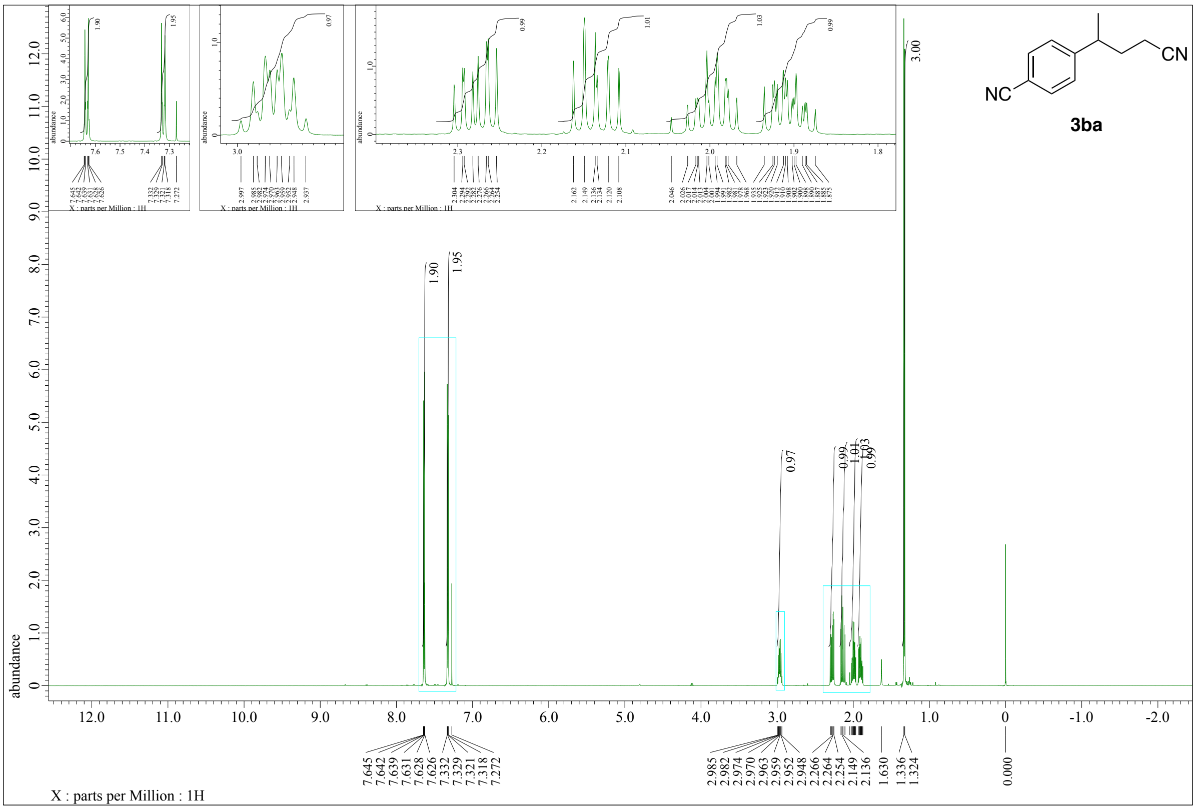
33.742
22.109
15.650



NC
CN
3ba
abundance
X : parts per Million : 1H
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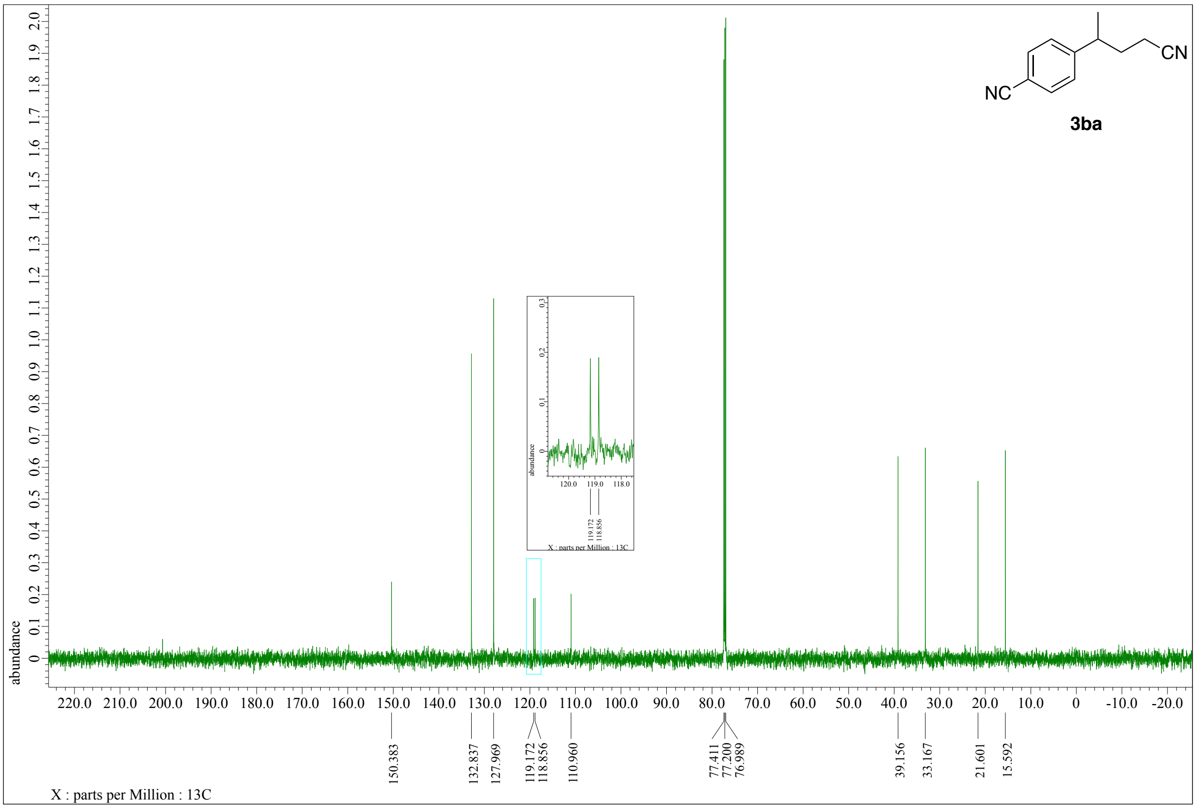
0.97
0.99
1.01
1.03
0.99
3.00
7.645
7.642
7.639
7.631
7.628
7.626
7.332
7.329
7.321
7.318
7.272
2.985
2.982
2.974
2.970
2.963
2.959
2.952
2.948
2.266
2.264
2.254
2.149
2.136
1.630
1.336
1.324
0.000



NC
CN
3ba
abundance
X : parts per Million : 13C
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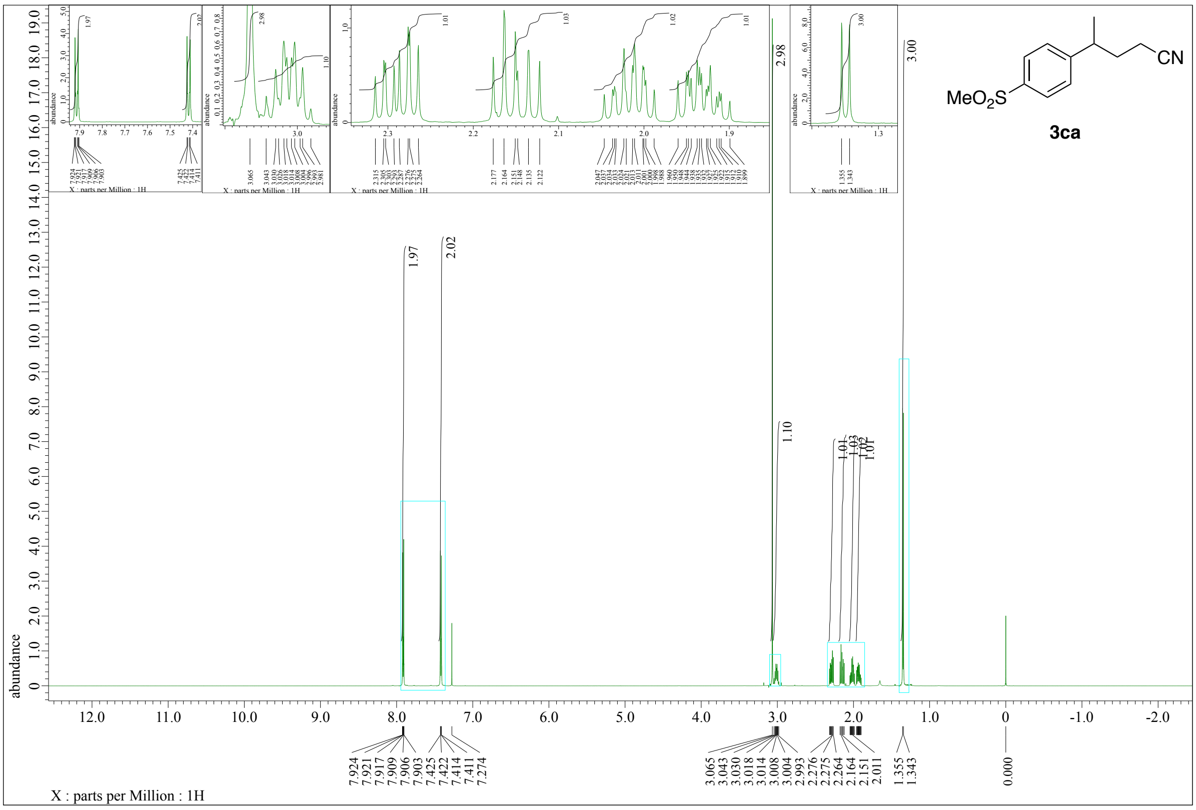
118.856
110.960
77.411
77.200
76.989
39.156
33.167
21.601
15.592


MeO2S
CN
3ca
abundance
X : parts per Million : 1H
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2.98
1.10
1.01
1.03
1.02
1.01
3.00
7.924
7.921
7.917
7.909
7.906
7.903
7.425
7.422
7.414
7.411
7.274
3.065
3.043
3.030
3.018
3.014
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2.276
2.275
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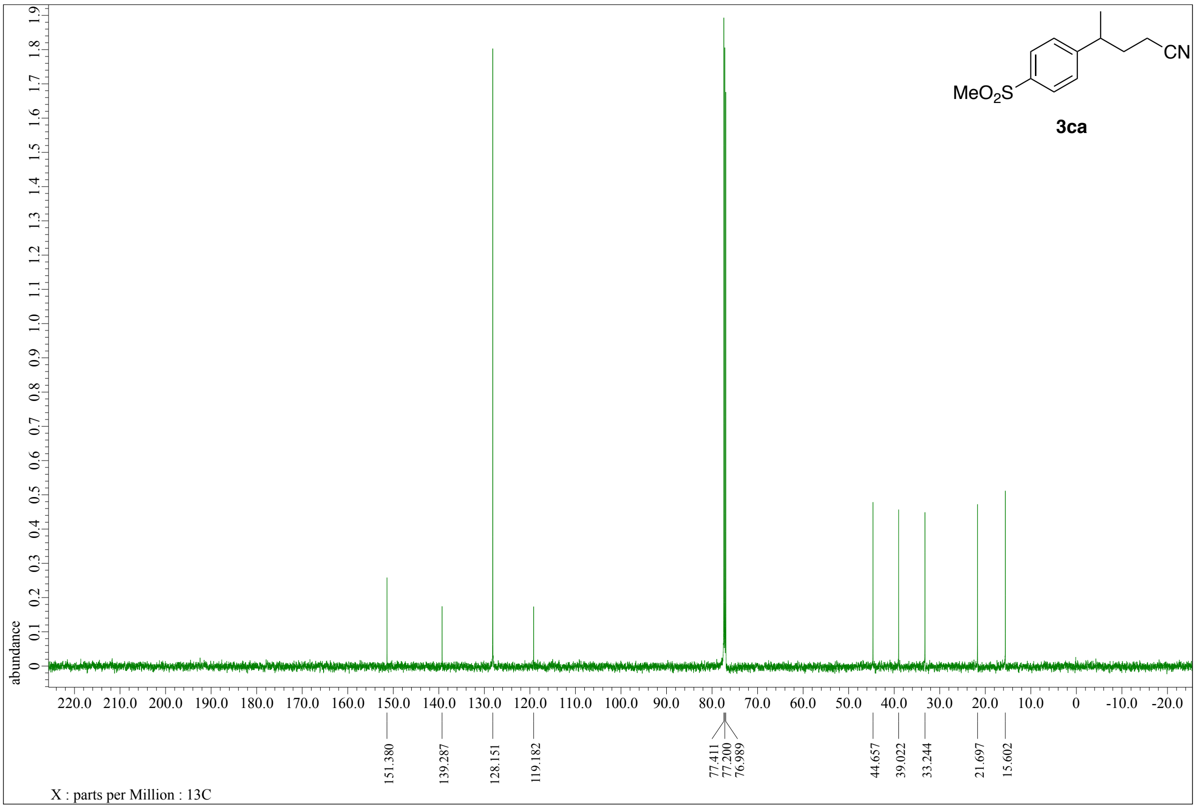
MeO2S
CN
3ca
abundance
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76.989
44.657
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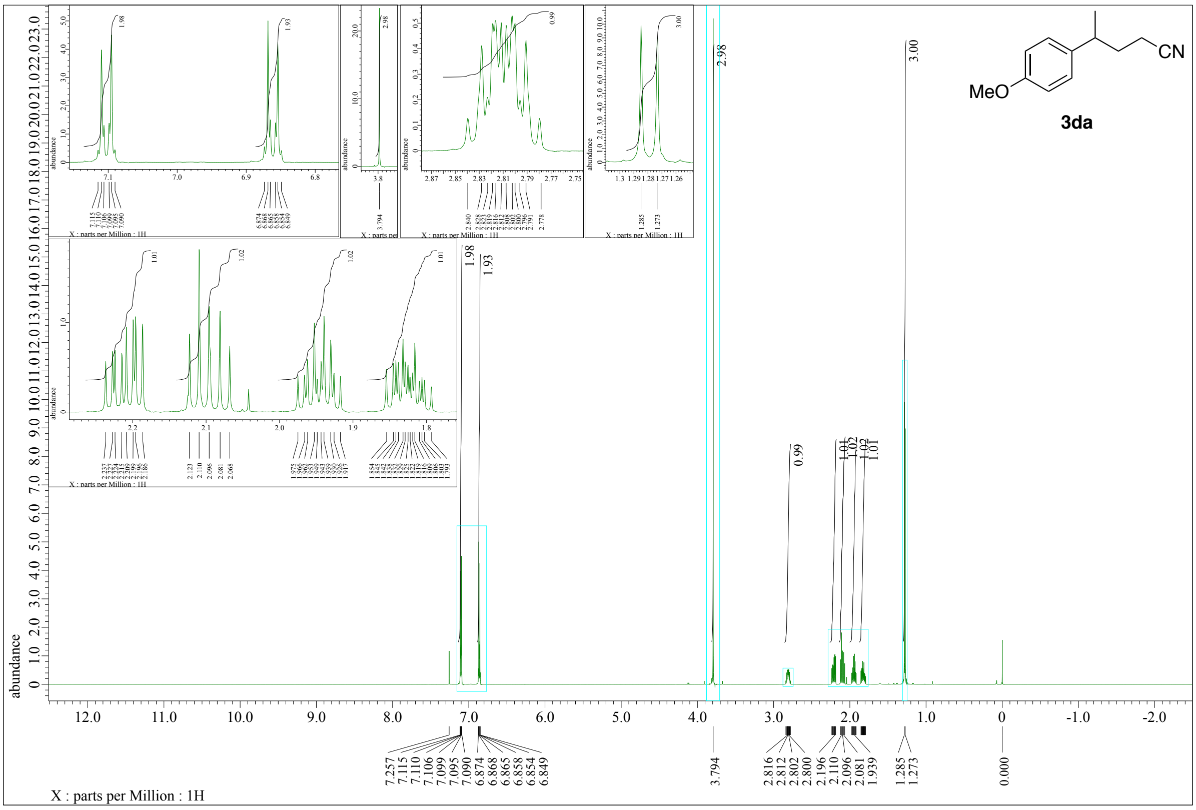
33.244
21.697
15.602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CN
3da
abundance
X : parts per Million : 1H
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1.98
1.93
0.99
1.01
1.02
1.02
1.01
7.257
7.115
7.110
7.106
7.099
7.095
7.090
6.874
6.868
6.865
6.858
6.854
6.849
3.794
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2.800
2.196
2.110
2.096
2.081
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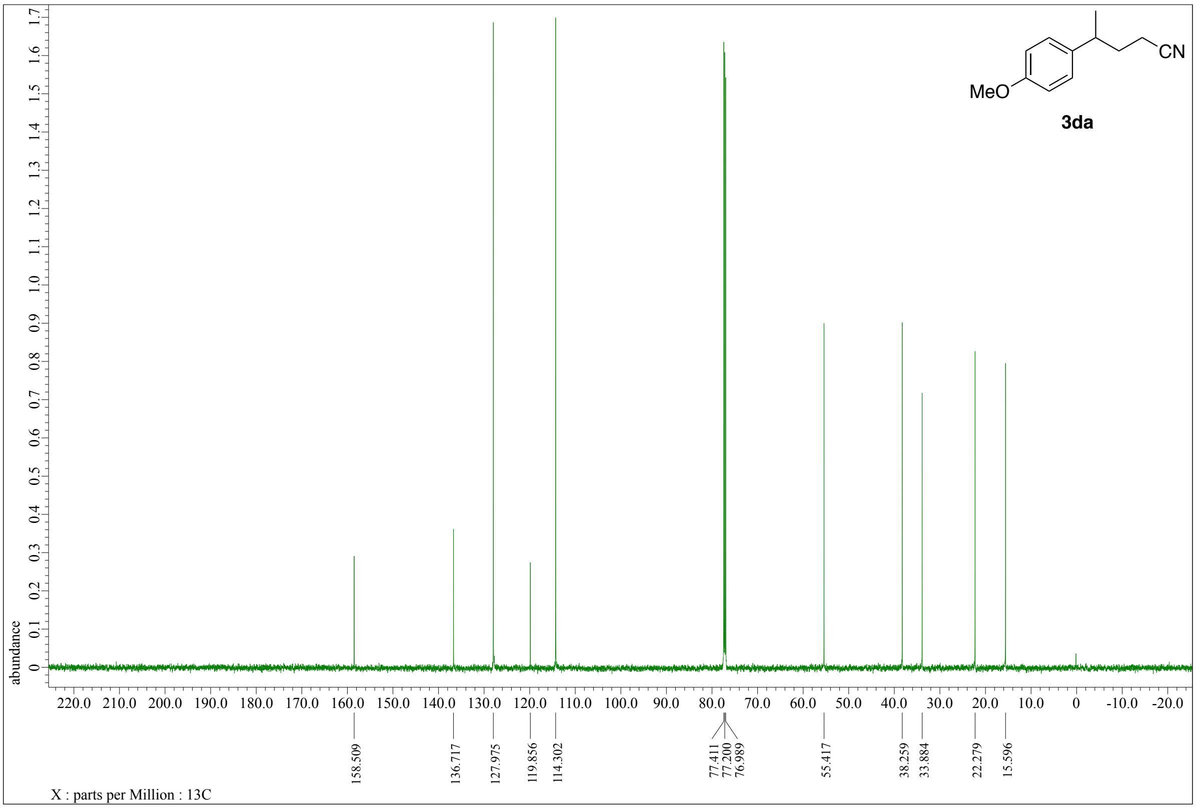
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CN
3da
abundance
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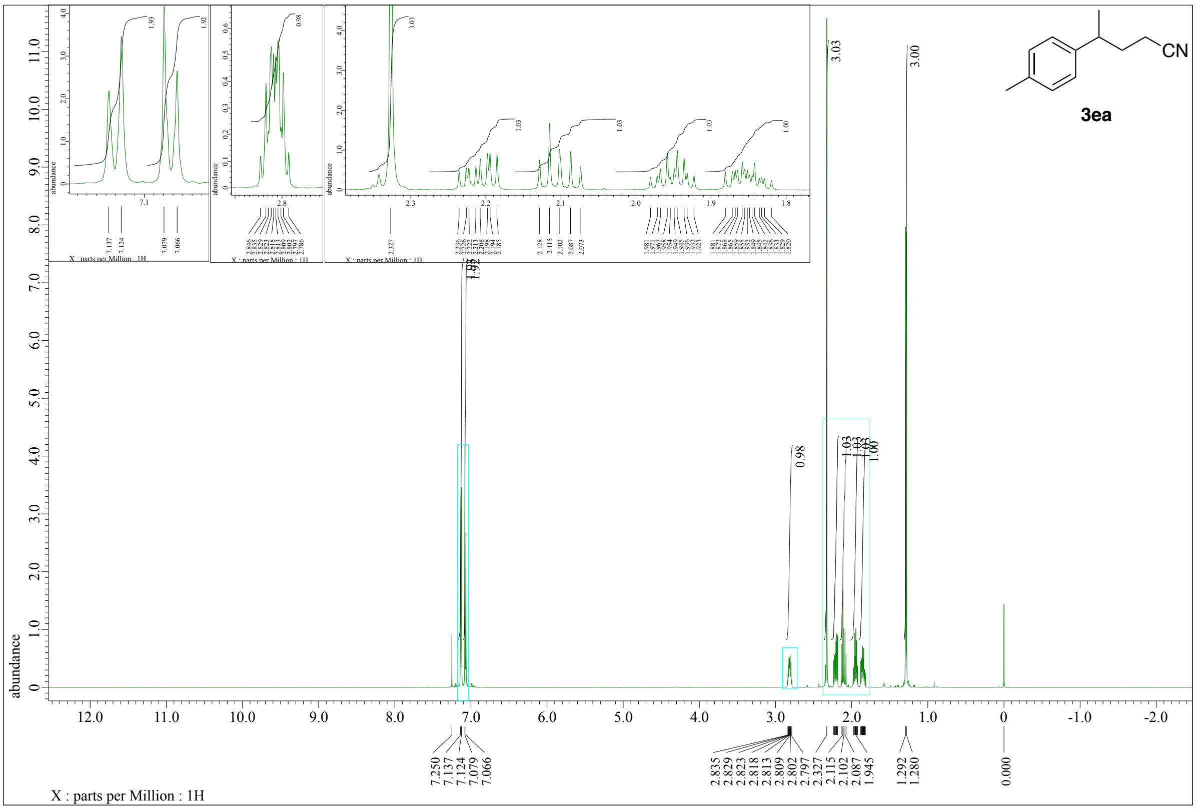
15.596


3ea
CN
abundance
X : parts per Million : 1H
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7.079
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2.829
2.823
2.818
2.813
2.809
2.802
2.797
2.327
2.115
2.102
2.087
1.945
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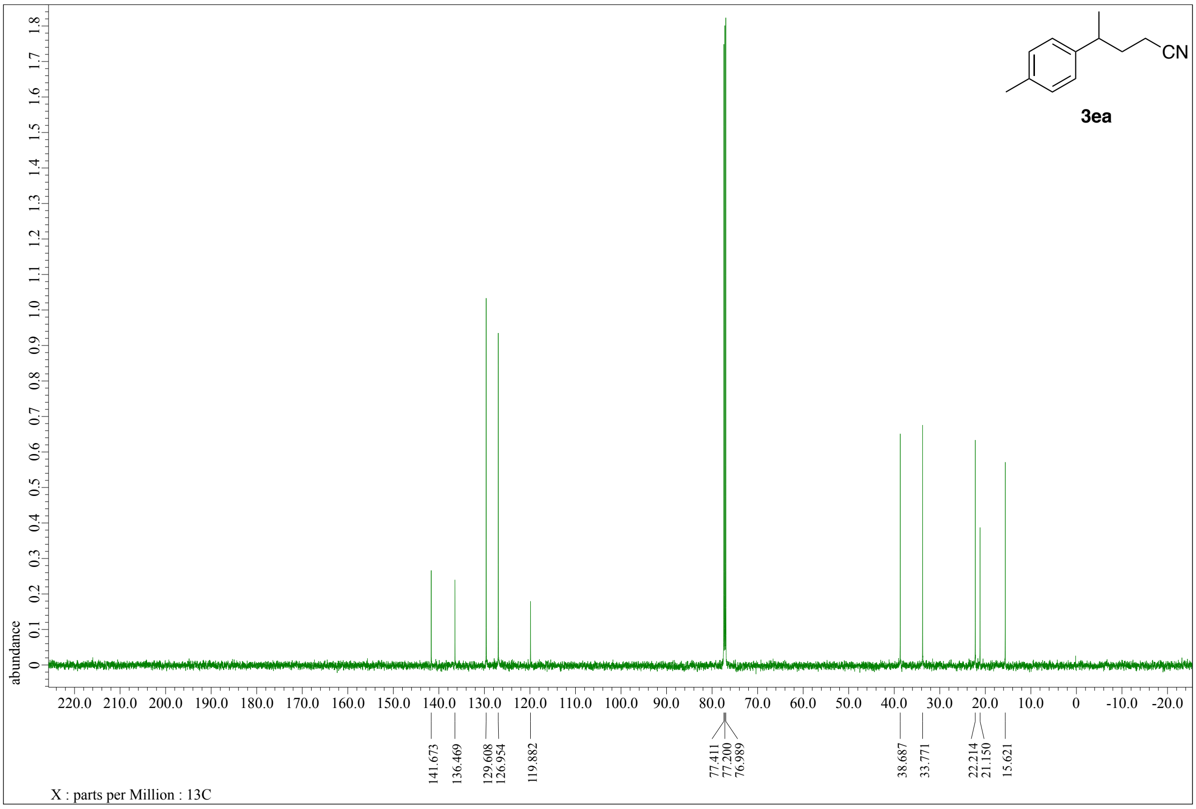
1.93
1.92
0.98
3.03
1.03
1.03
1.03
1.00
3.00


3ea
CN
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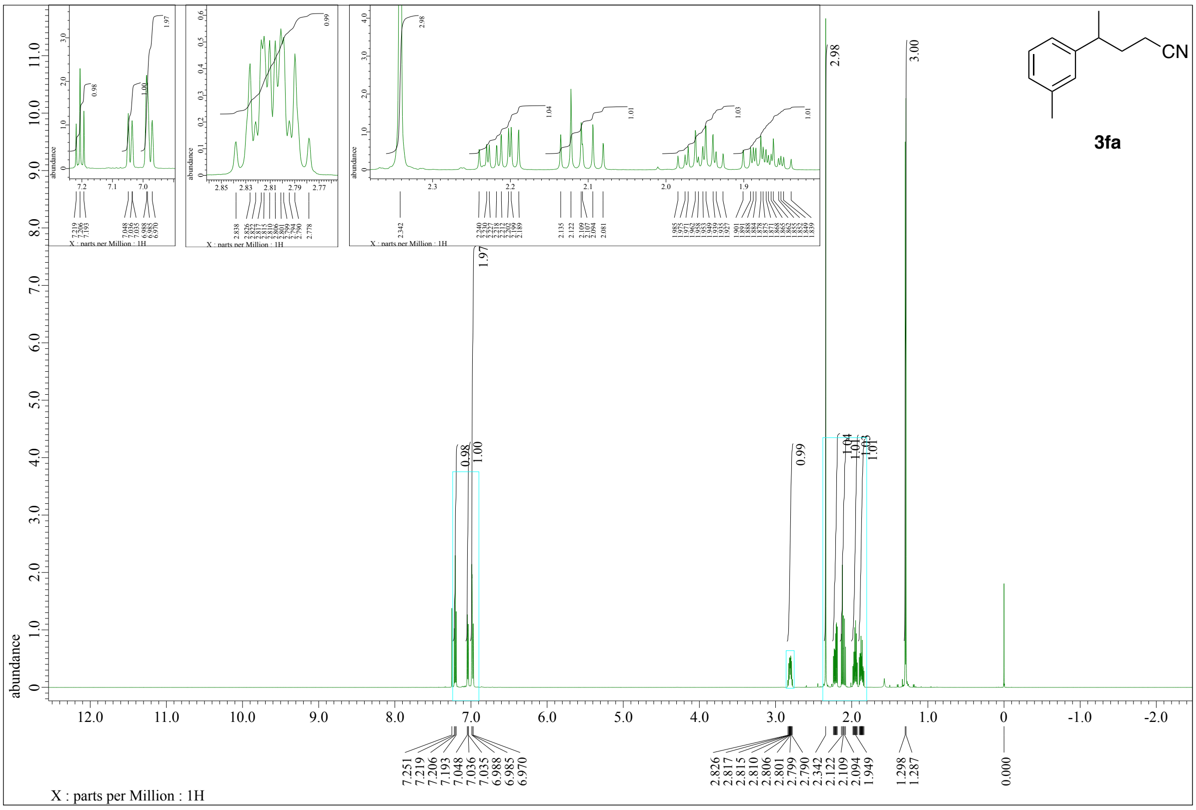
15.621


CN
3fa
abundance
X : parts per Million : 1H
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
2.98
3.00
1.97
0.98
1.00
0.99
1.04
1.01
1.03
1.01
7.251
7.219
7.206
7.193
7.048
7.036
7.035
6.988
6.985
6.970
2.826
2.817
2.815
2.810
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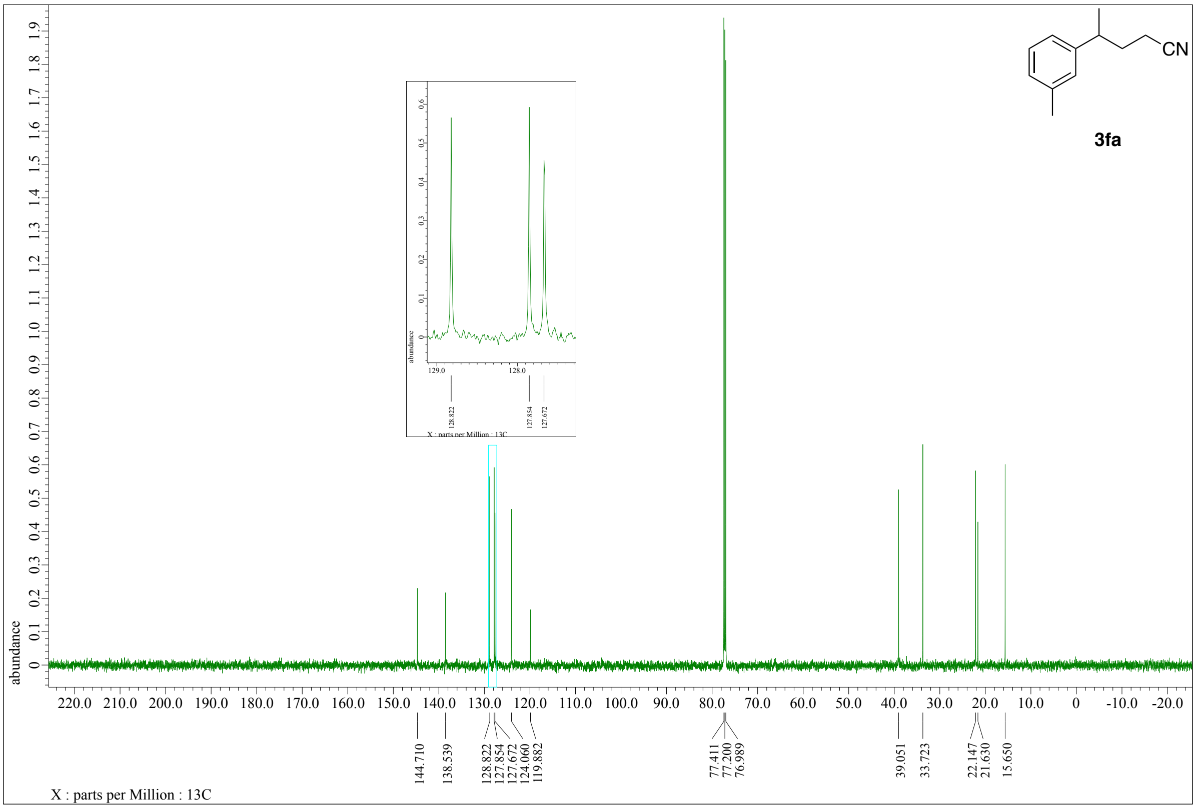
1.287
0.000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3fa
abundance
X : parts per Million : 13C
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180.0
170.0
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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
144.710
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128.822
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119.882
77.411
77.200
76.989
39.051
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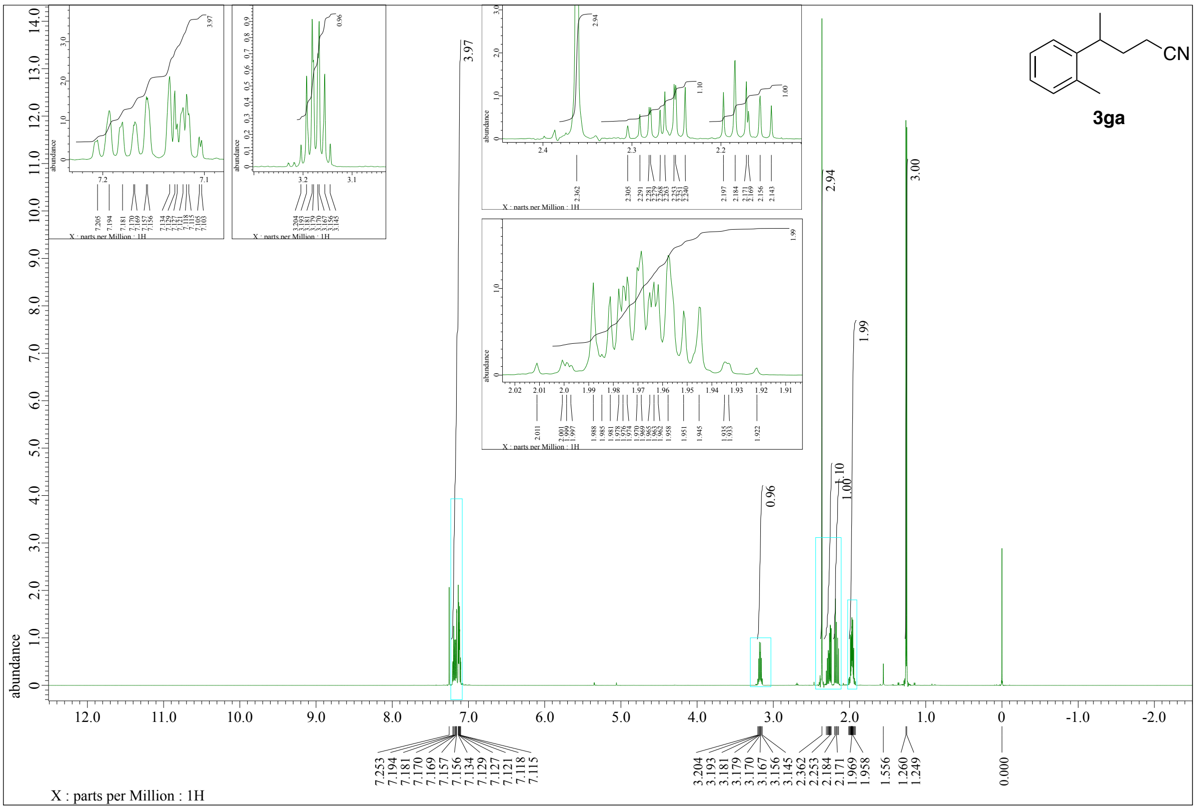
21.630
15.650


CN
3ga
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1.00
3.00
1.99
7.253
7.194
7.181
7.170
7.169
7.157
7.156
7.134
7.129
7.127
7.121
7.118
7.115
3.204
3.193
3.181
3.179
3.170
3.167
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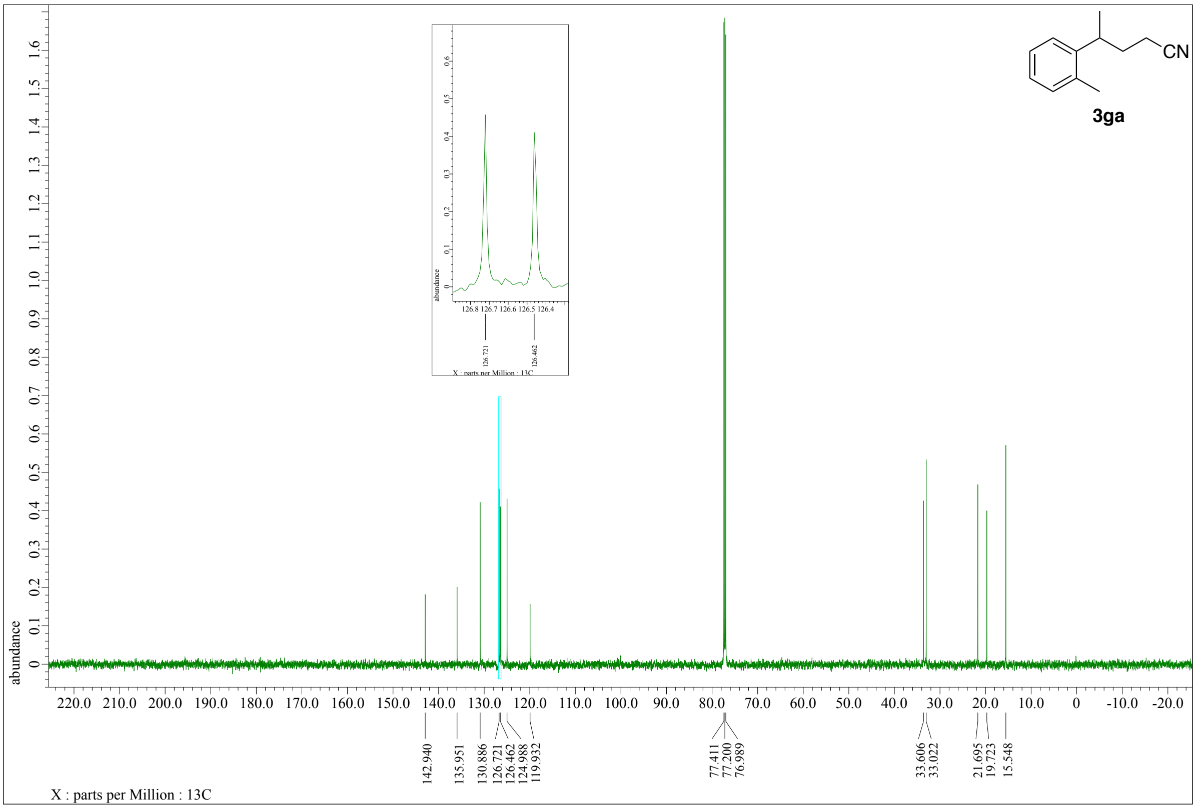
CN
3ga
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X : parts per Million : 13C
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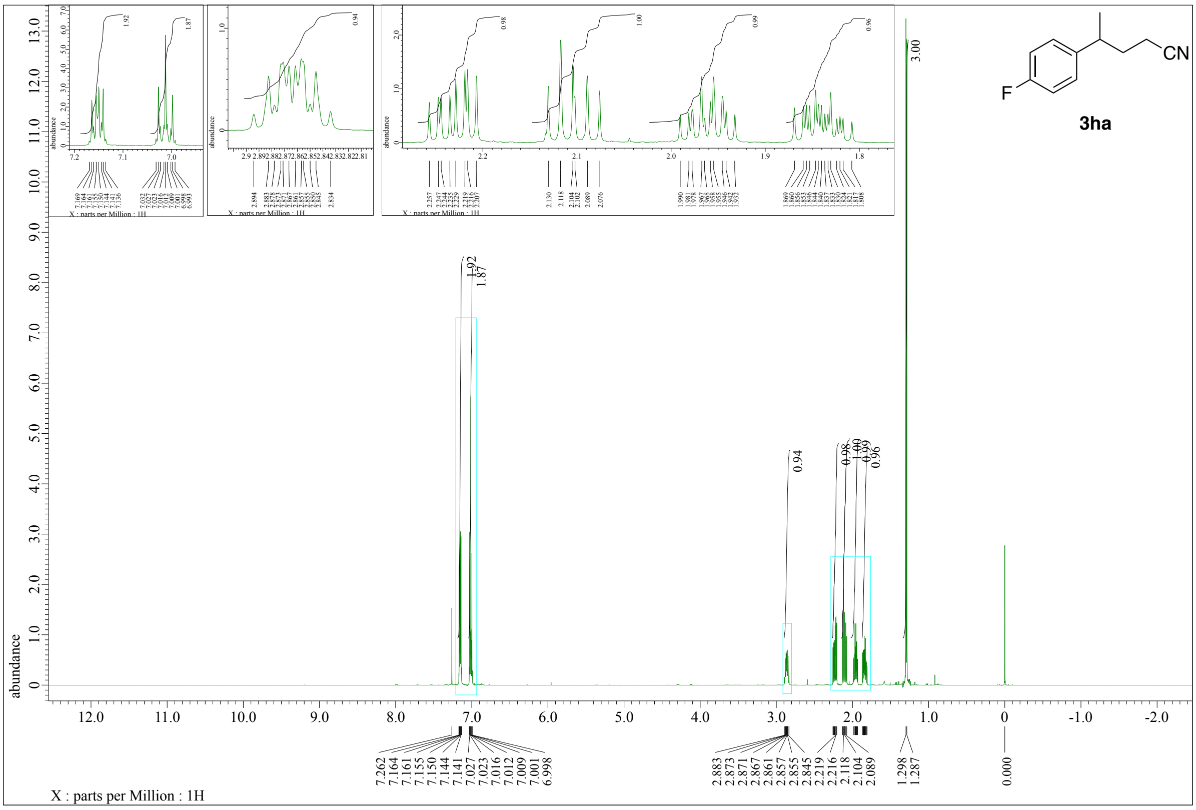
21.695
19.723
15.548


3ha
F
CN
abundance
X : parts per Million : 1H
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1.87
0.94
0.98
1.00
0.99
0.96
3.00
7.262
7.164
7.161
7.155
7.150
7.144
7.141
7.027
7.023
7.016
7.012
7.009
7.001
6.998
2.883
2.873
2.871
2.867
2.861
2.857
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2.845
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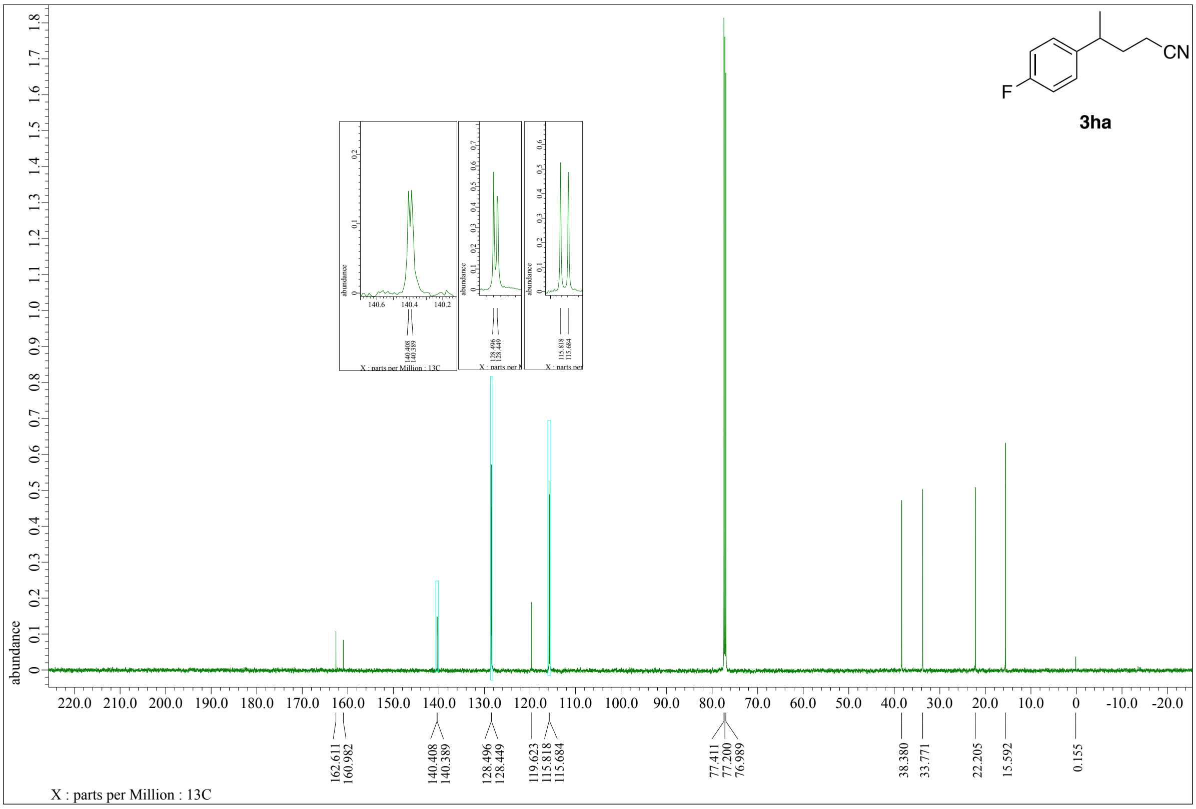
2.216
2.118
2.104
2.089
1.298
1.287
0.000


3ha
F
CN
abundance
X : parts per Million : 13C
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76.989
38.380
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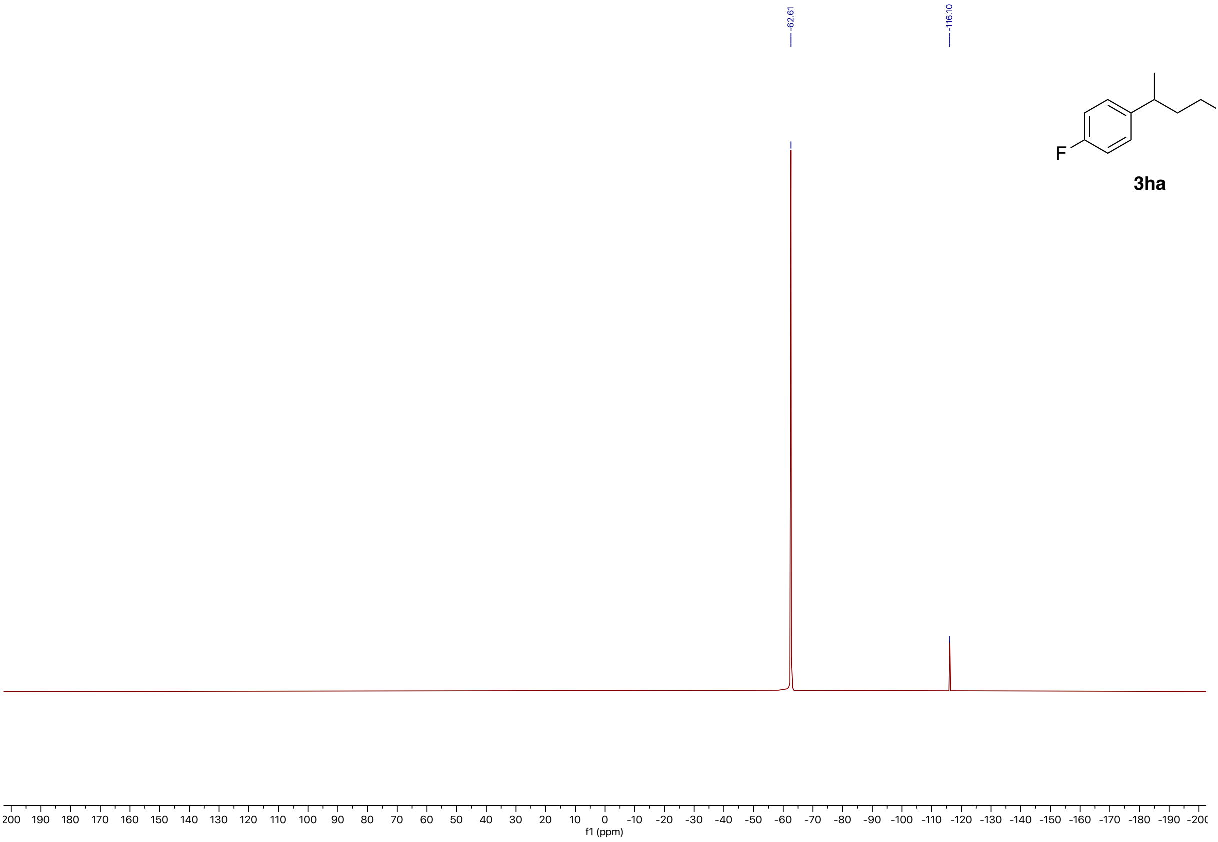
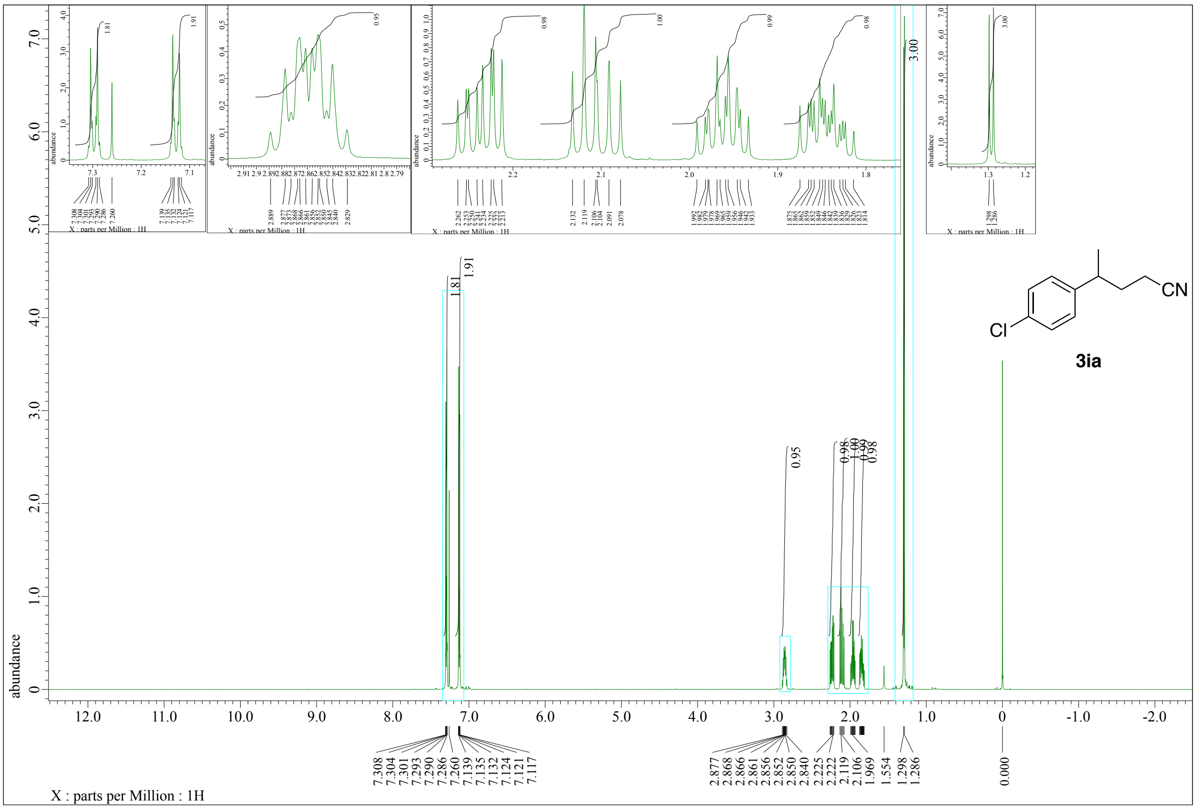
0.155


-62.61
-116.10
F
CN
3ha
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


abundance
0
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2.0
3.0
4.0
5.0
6.0
7.0
1.81
1.91
0.95
0.98
1.00
0.99
0.98
3.00
Cl
CN
3ia
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.308
7.304
7.301
7.293
7.290
7.286
7.260
7.139
7.135
7.132
7.124
7.121
7.117
2.877
2.868
2.866
2.861
2.856
2.852
2.850
2.840
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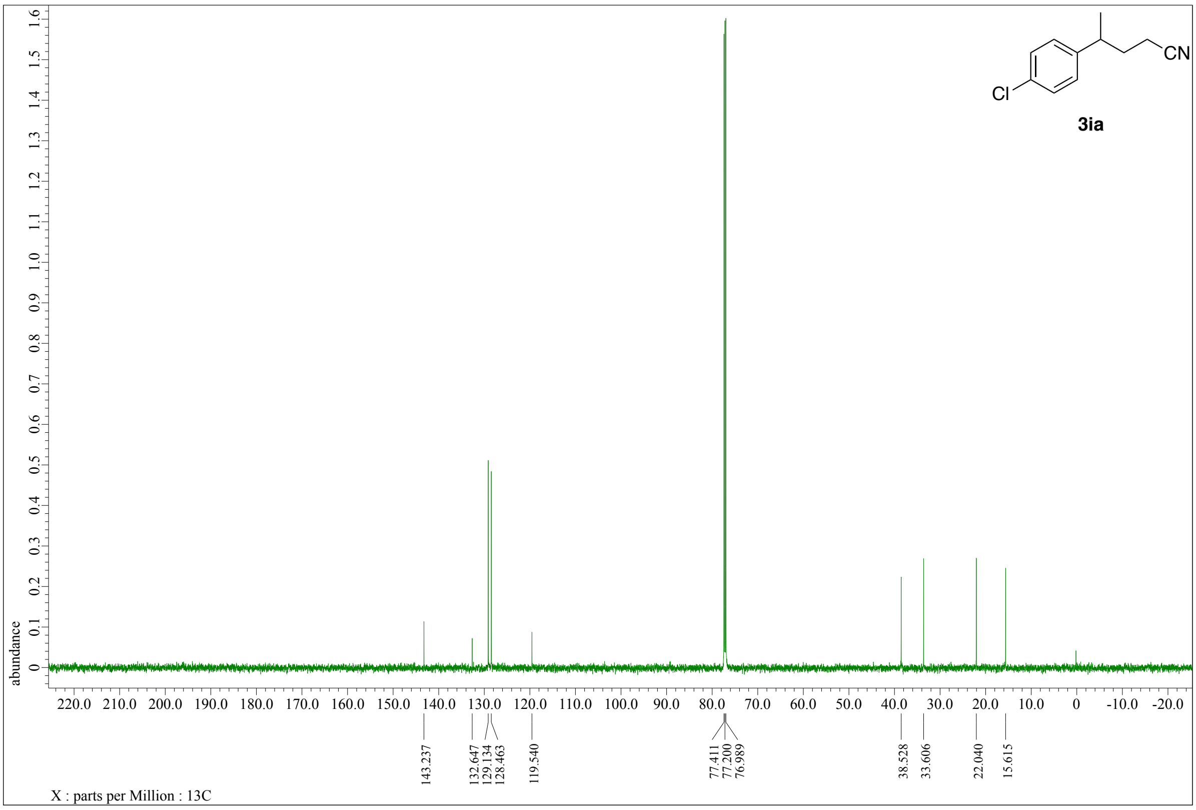
2.222
2.119
2.106
1.969
1.554
1.298
1.286
0.000
X : parts per Million : 1H


3ia
Cl
CN
abundance
X : parts per Million : 13C
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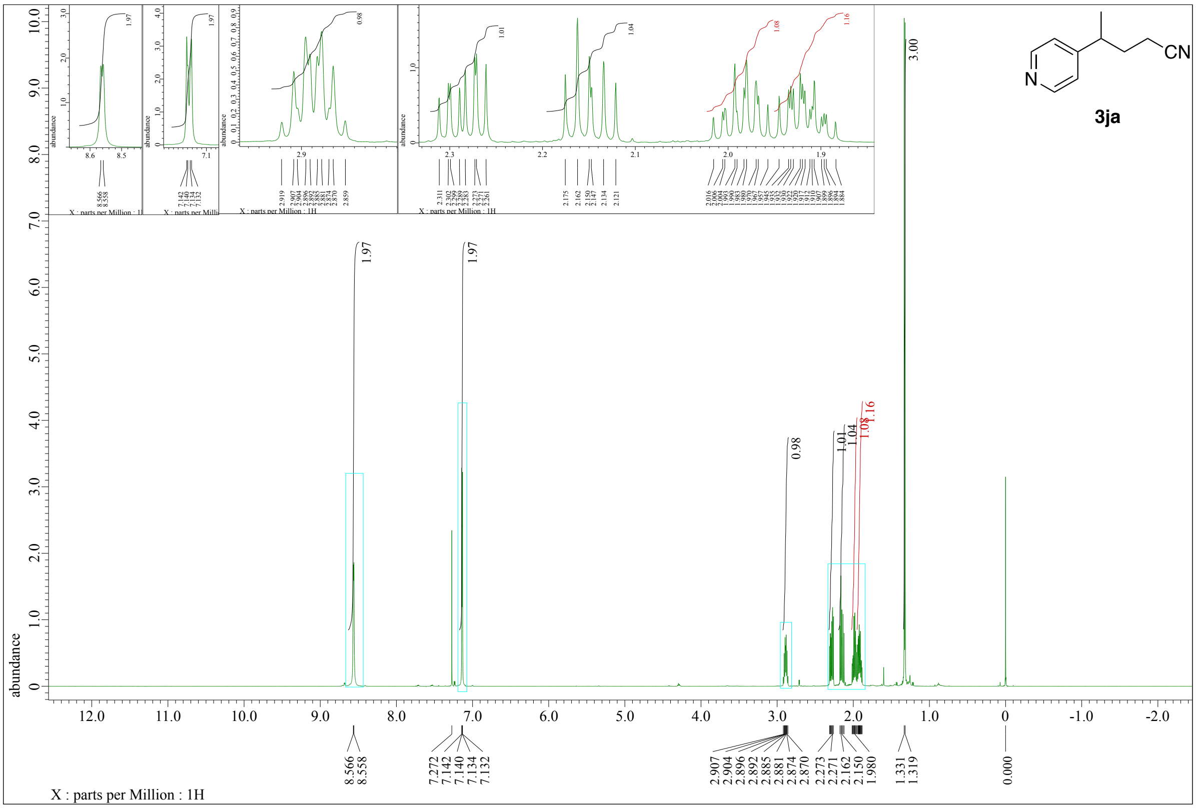
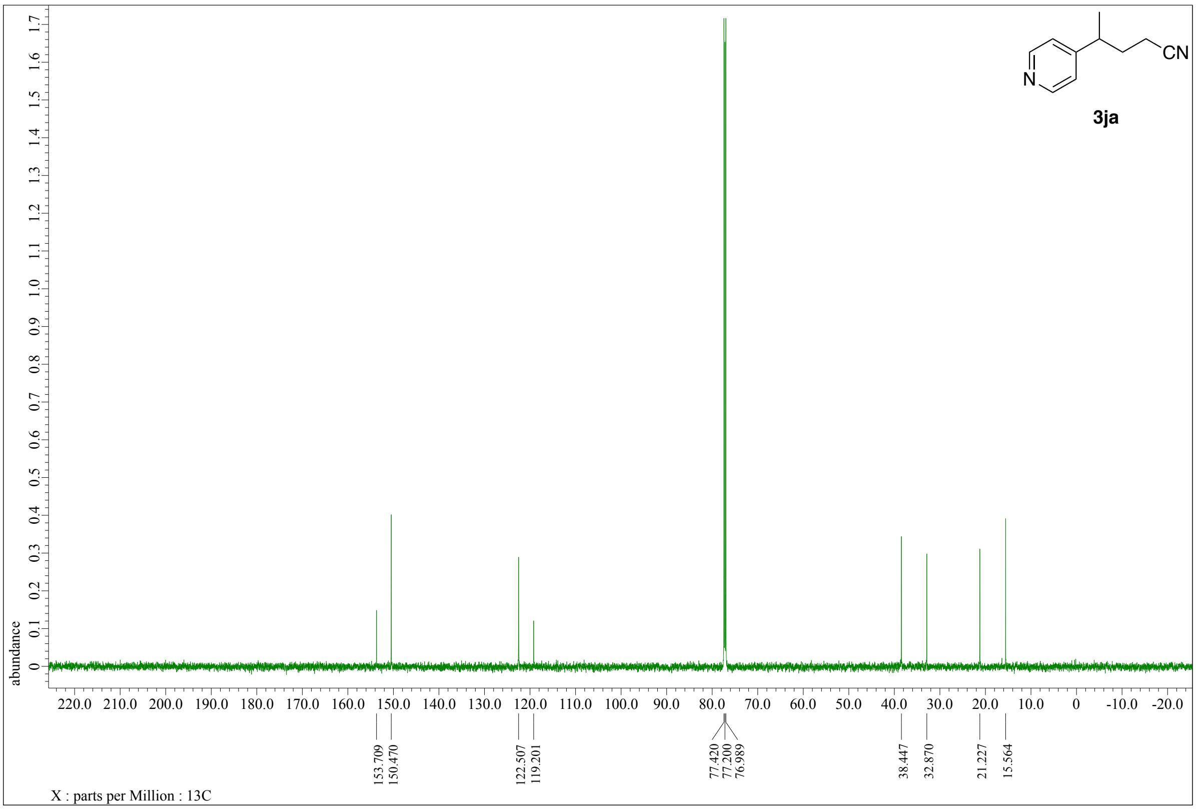
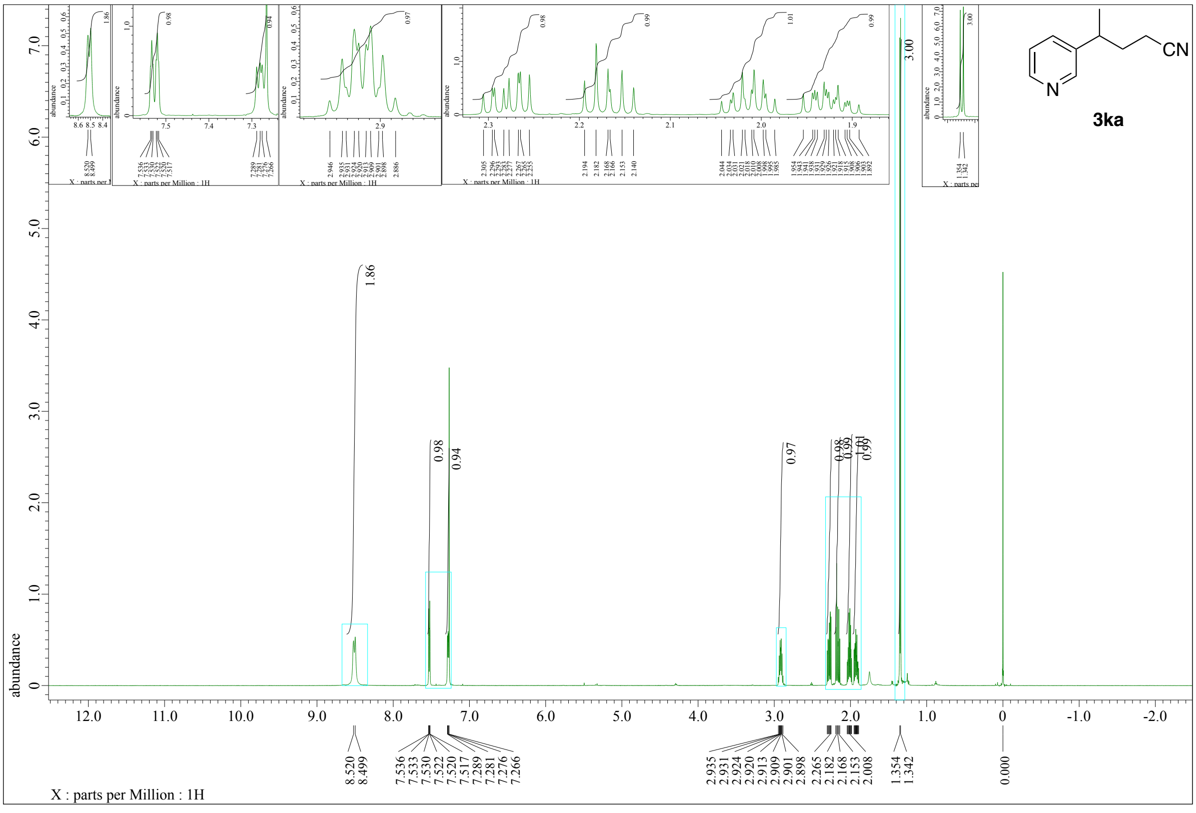
76.989
38.528
33.606
22.040
15.615

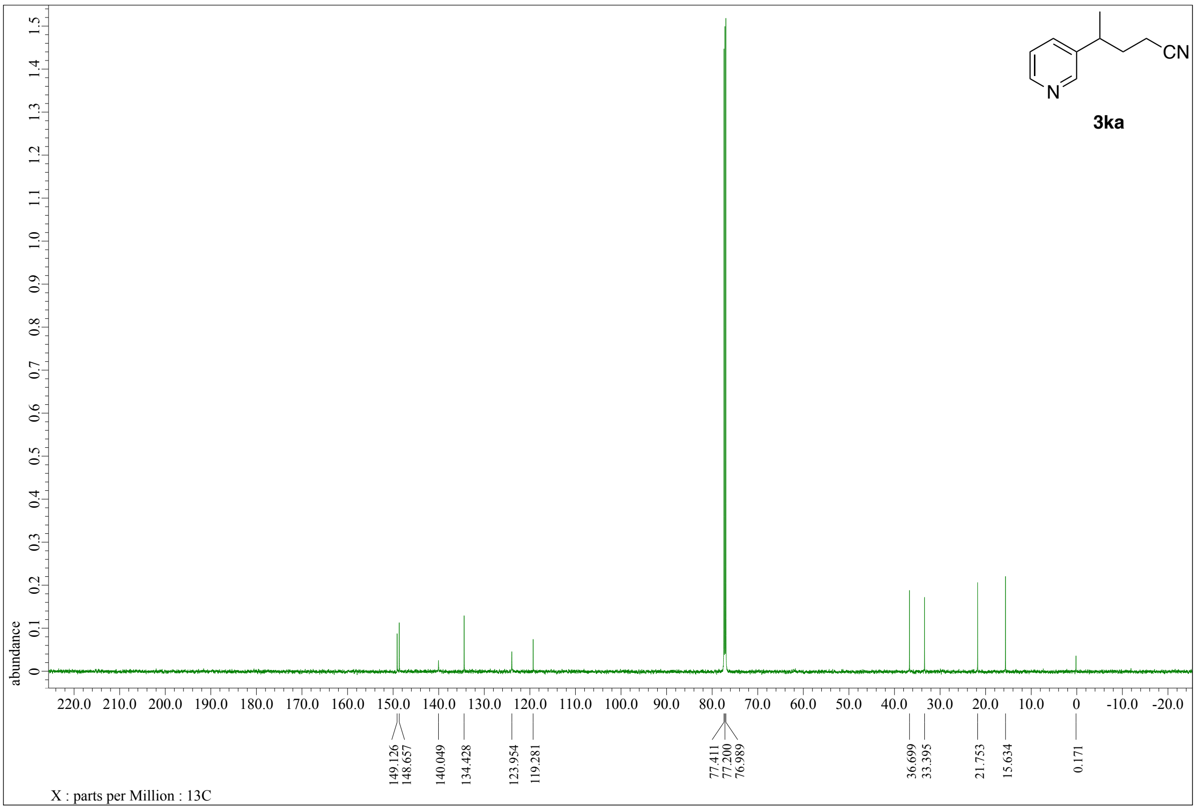

3ja
N
CN
abundance
X : parts per Million : 1H
1.97
1.97
0.98
1.01
1.04
1.08
1.16
3.00
8.566
8.558
7.272
7.142
7.140
7.134
7.132
2.907
2.904
2.896
2.892
2.885
2.881
2.874
2.870
2.273
2.271
2.162
2.150
1.980
1.331
1.319
0.000

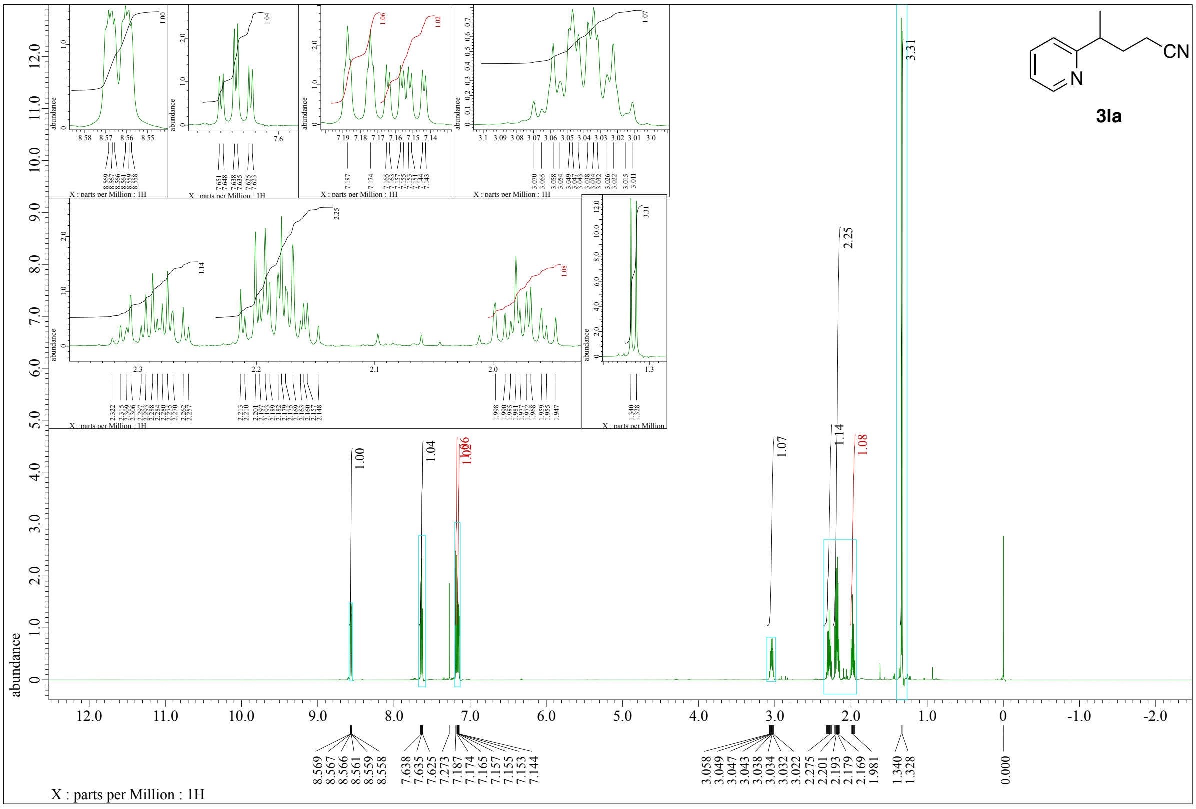

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
153.709
150.470
122.507
119.201
77.420
77.200
76.989
38.447
32.870
21.227
15.564
X : parts per Million : 13C
N
CN

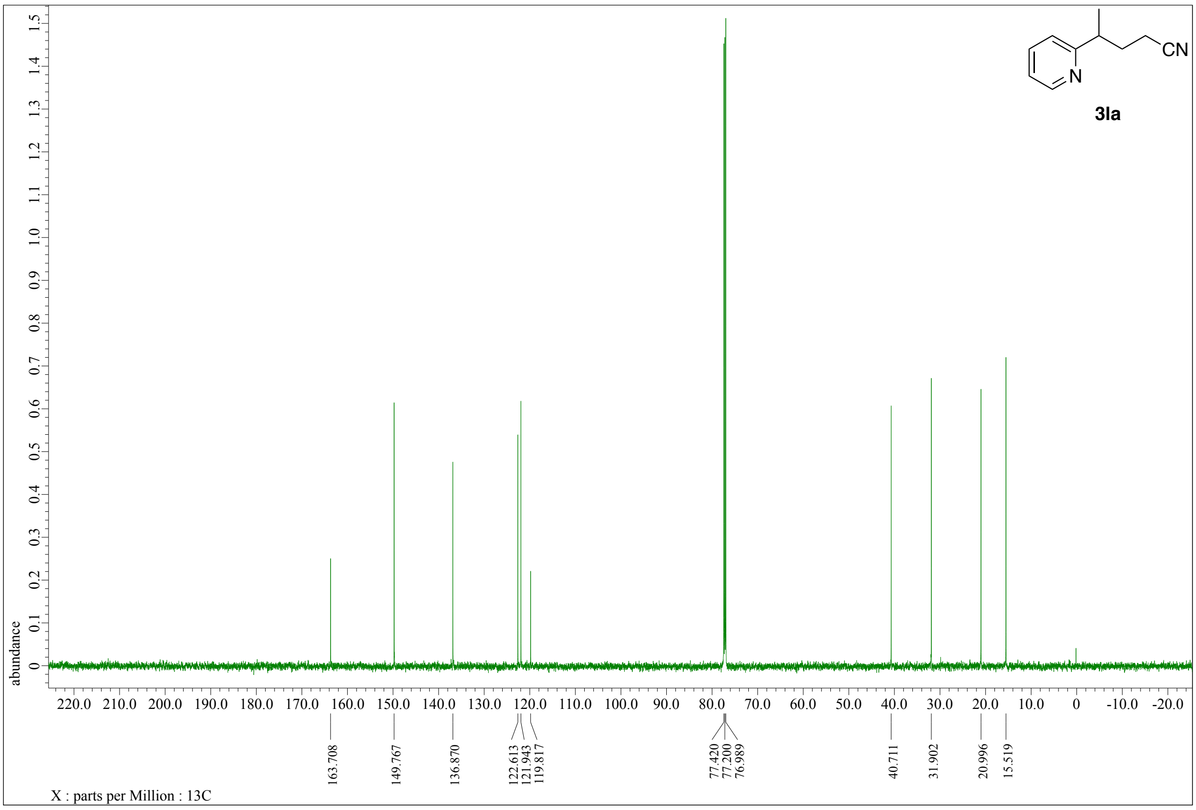
3ja


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
1.86
0.98
0.94
0.97
0.98
0.99
1.01
0.99
3.00
8.520
8.499
7.536
7.533
7.530
7.522
7.520
7.517
7.289
7.281
7.276
7.266
2.935
2.931
2.924
2.920
2.913
2.909
2.901
2.898
2.265
2.182
2.168
2.153
2.008
1.354
1.342
0.000
X : parts per Million : 1H
N
CN

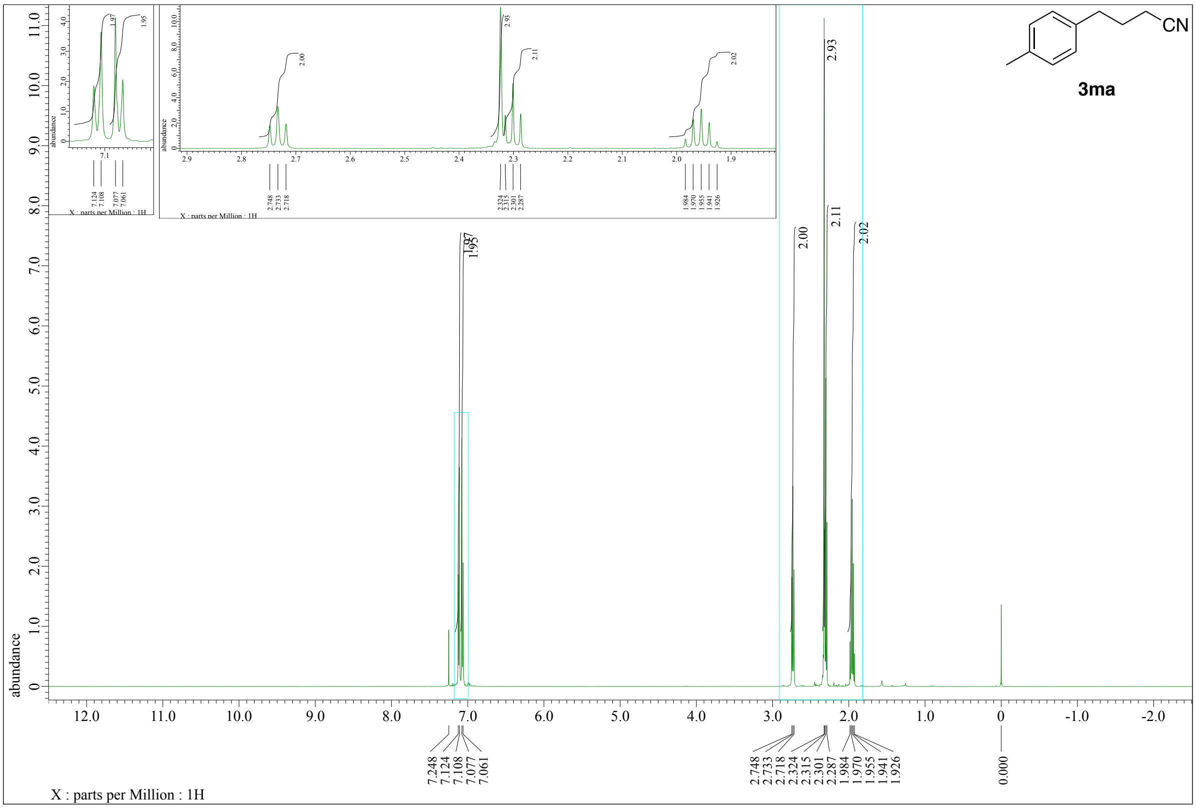
3ka


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
149.126
148.657
140.049
134.428
123.954
119.281
77.411
77.200
76.989
36.699
33.395
21.753
15.634
0.171
X : parts per Million : 13C
N
CN
3ka

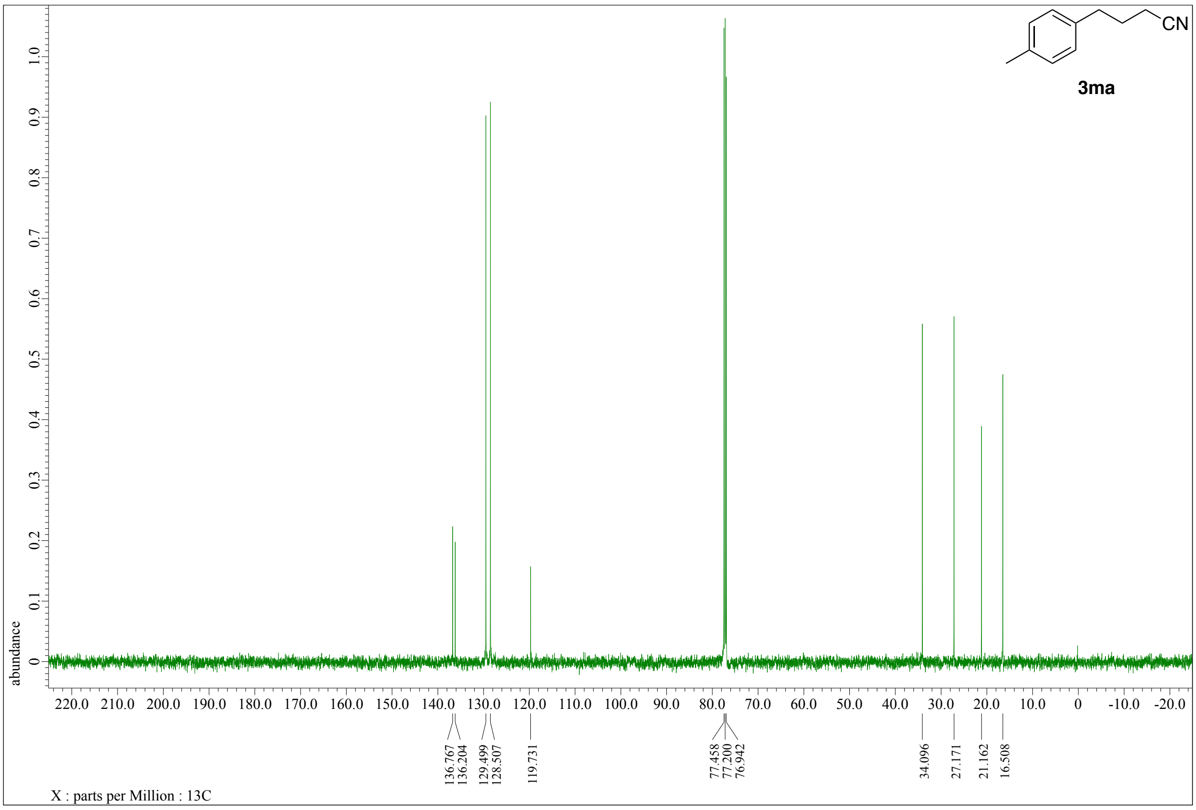

abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
1.00
1.04
1.06
1.02
1.07
1.14
2.25
1.08
3.31
8.569
8.567
8.566
8.561
8.559
8.558
7.638
7.635
7.625
7.273
7.187
7.174
7.165
7.157
7.155
7.153
7.144
3.058
3.049
3.047
3.043
3.038
3.034
3.032
3.022
2.275
2.201
2.193
2.179
2.169
1.981
1.340
1.328
0.000
X : parts per Million : 1H
N
CN
3la

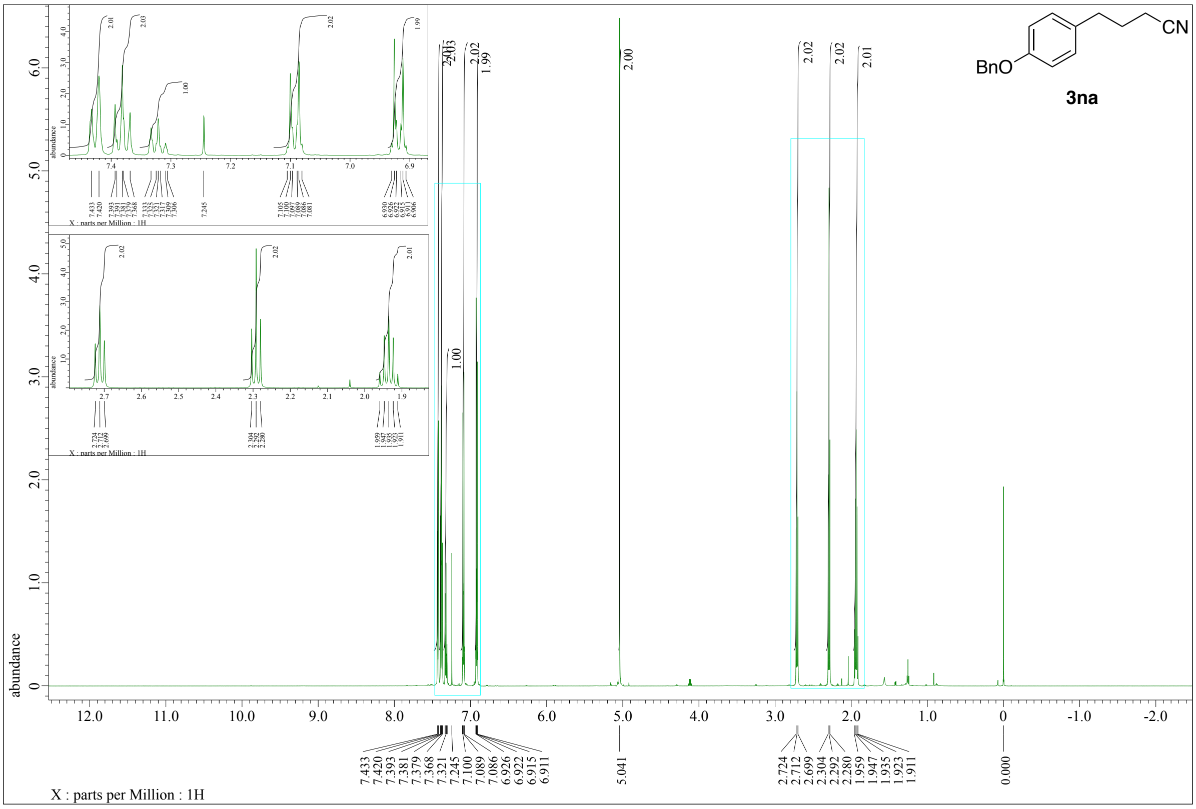

abundance
X : parts per Million : 13C
163.708
149.767
136.870
122.613
121.943
119.817
77.420
77.200
76.989
40.711
31.902
20.996
15.519
CN
N

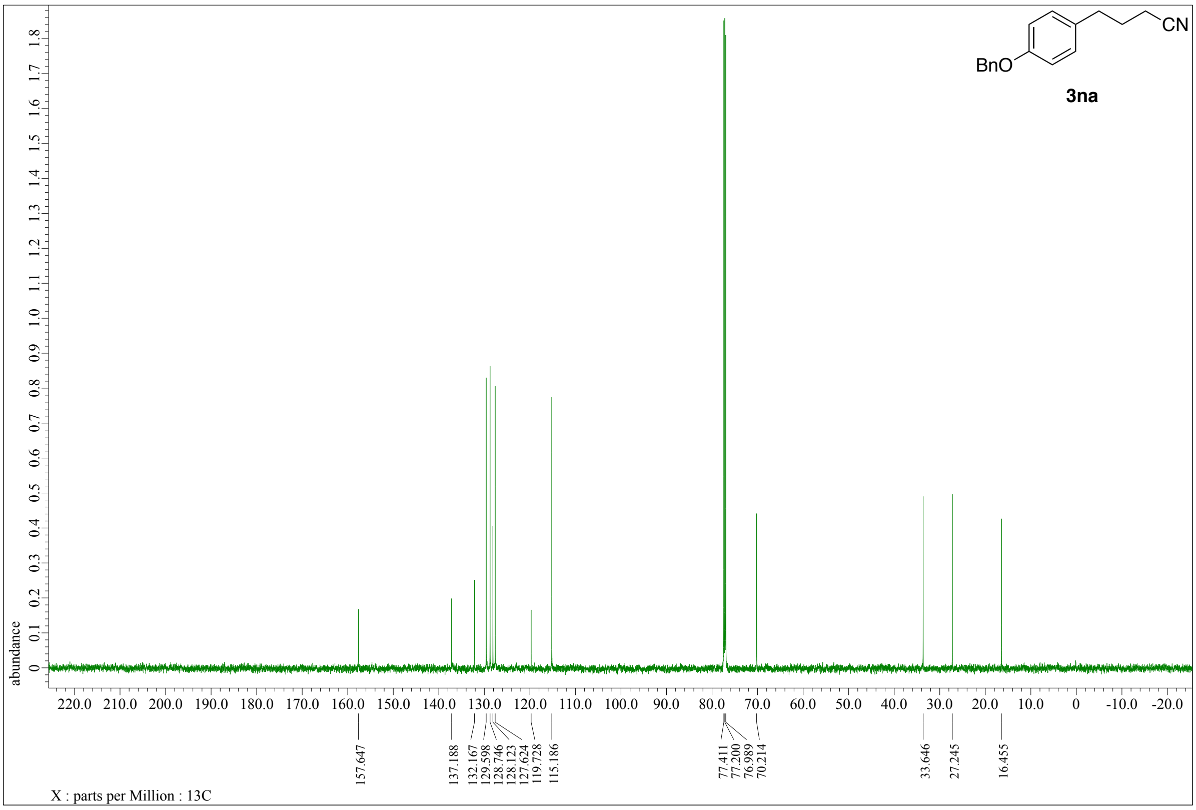
3la

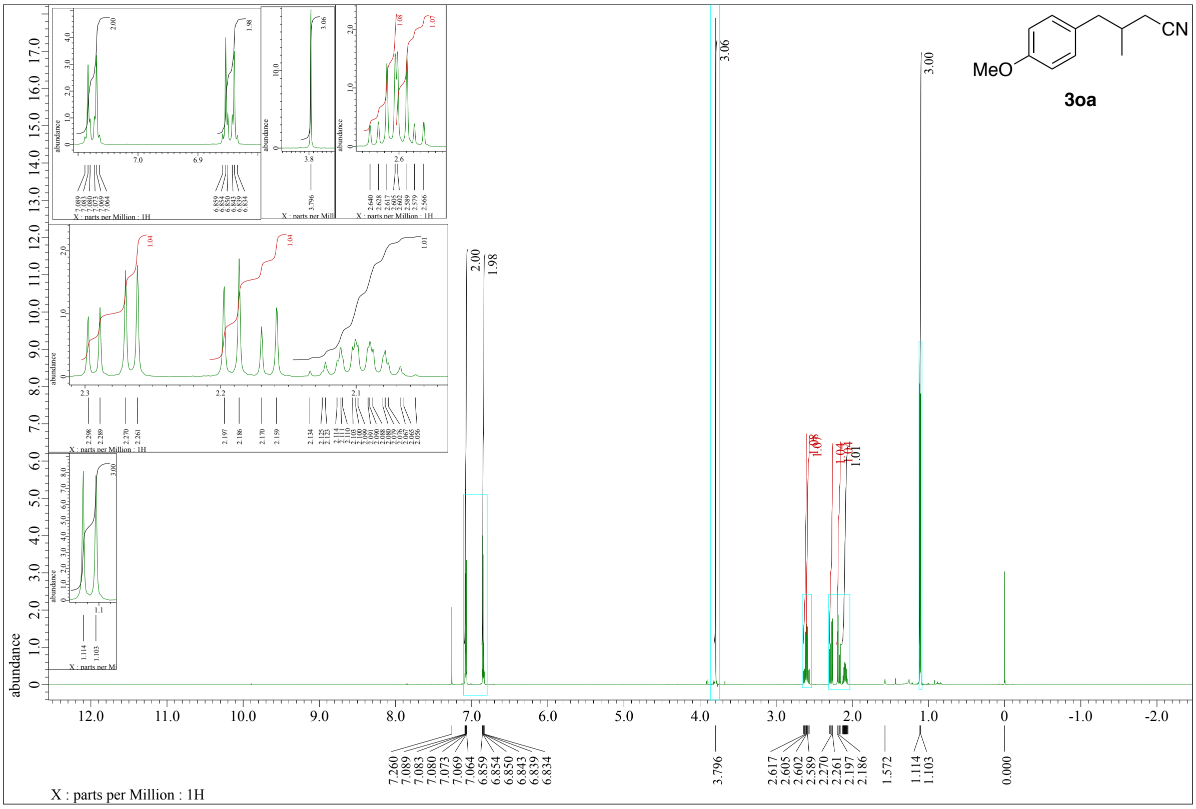

abundance
X : parts per Million : 1H
7.248
7.124
7.108
7.077
7.061
2.748
2.733
2.718
2.324
2.315
2.301
2.287
1.984
1.970
1.955
1.941
1.926
0.000
1.97
1.95
2.00
2.93
2.11
2.02
CN

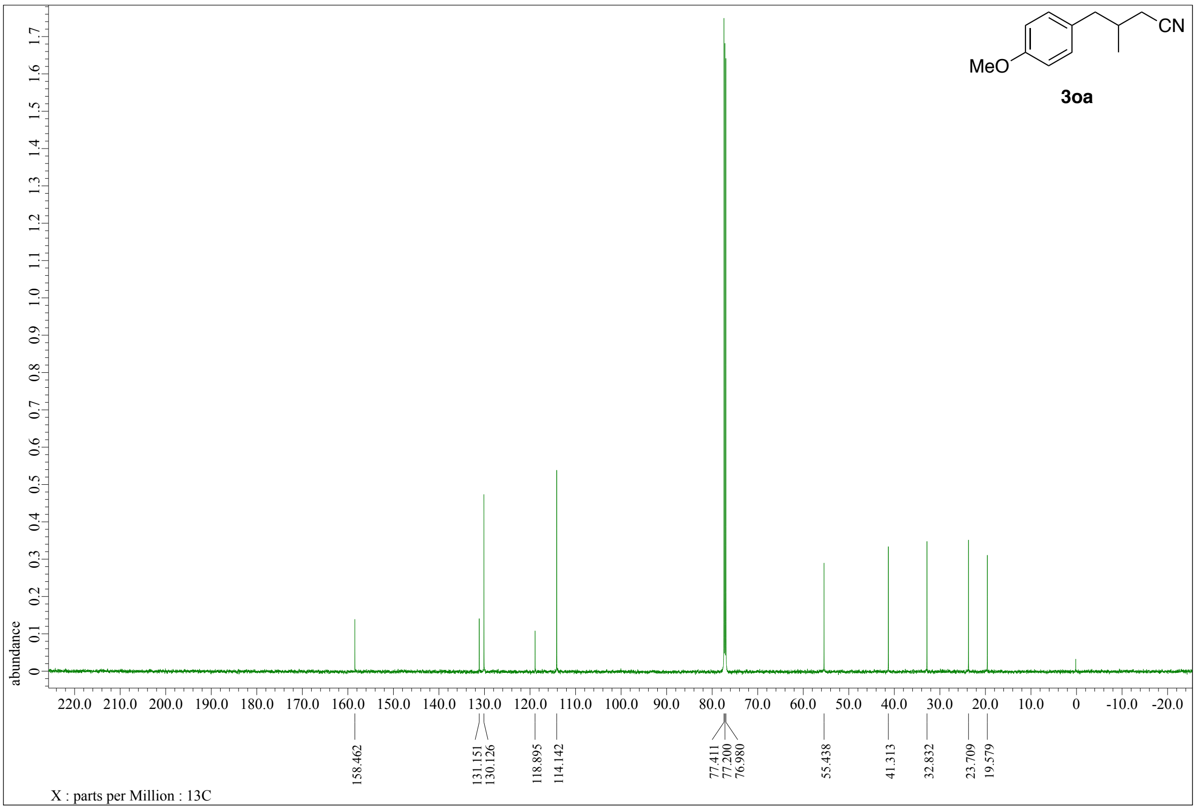
3ma


CN
3ma
abundance
X : parts per Million : 13C
136.767
136.204
129.499
128.507
119.731
77.458
77.200
76.942
34.096
27.171
21.162
16.508

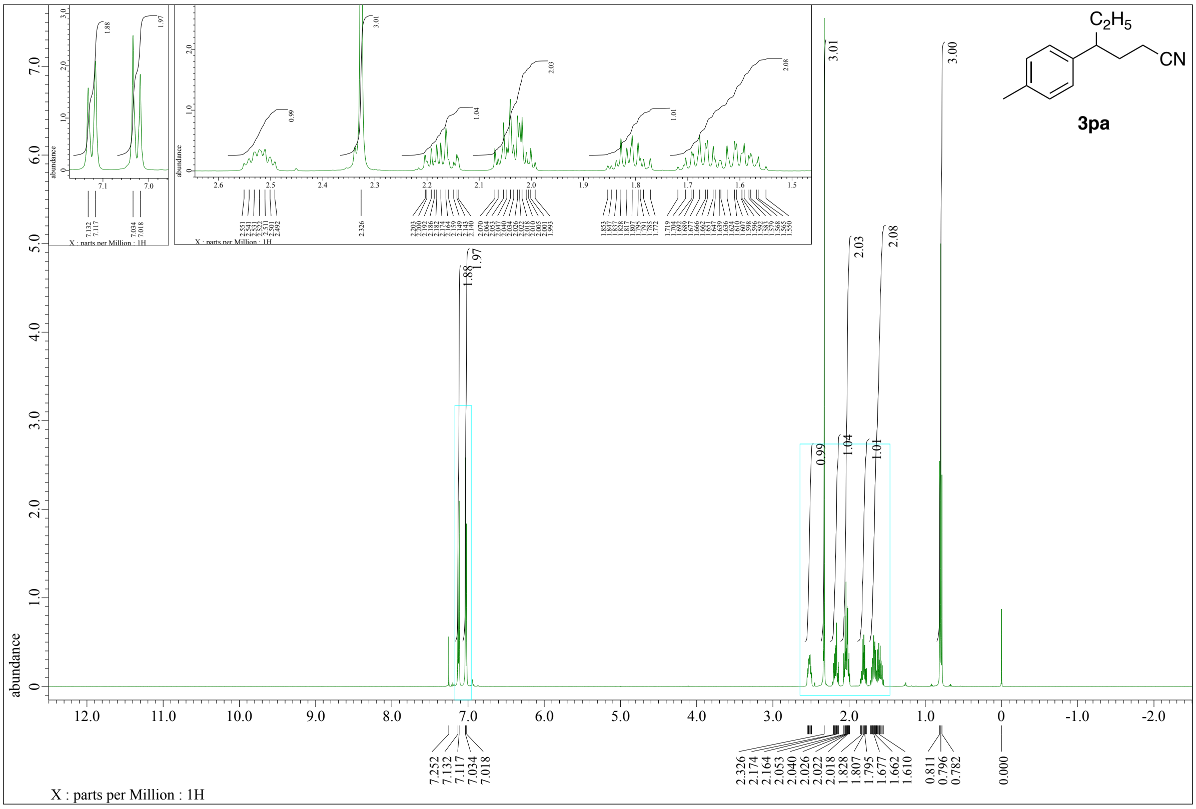

CN
BnO
3na
abundance
X : parts per Million : 1H
2.01
2.03
1.00
2.02
1.99
2.00
2.02
2.02
2.01
7.433
7.420
7.393
7.381
7.379
7.368
7.321
7.245
7.100
7.089
7.086
6.926
6.922
6.915
6.911
5.041
2.724
2.712
2.699
2.304
2.292
2.280
1.959
1.947
1.935
1.923
1.911
0.000


BnO
CN
3na
abundance
X : parts per Million : 13C
157.647
137.188
132.167
129.598
128.746
128.123
127.624
119.728
115.186
77.411
77.200
76.989
70.214
33.646
27.245
16.455

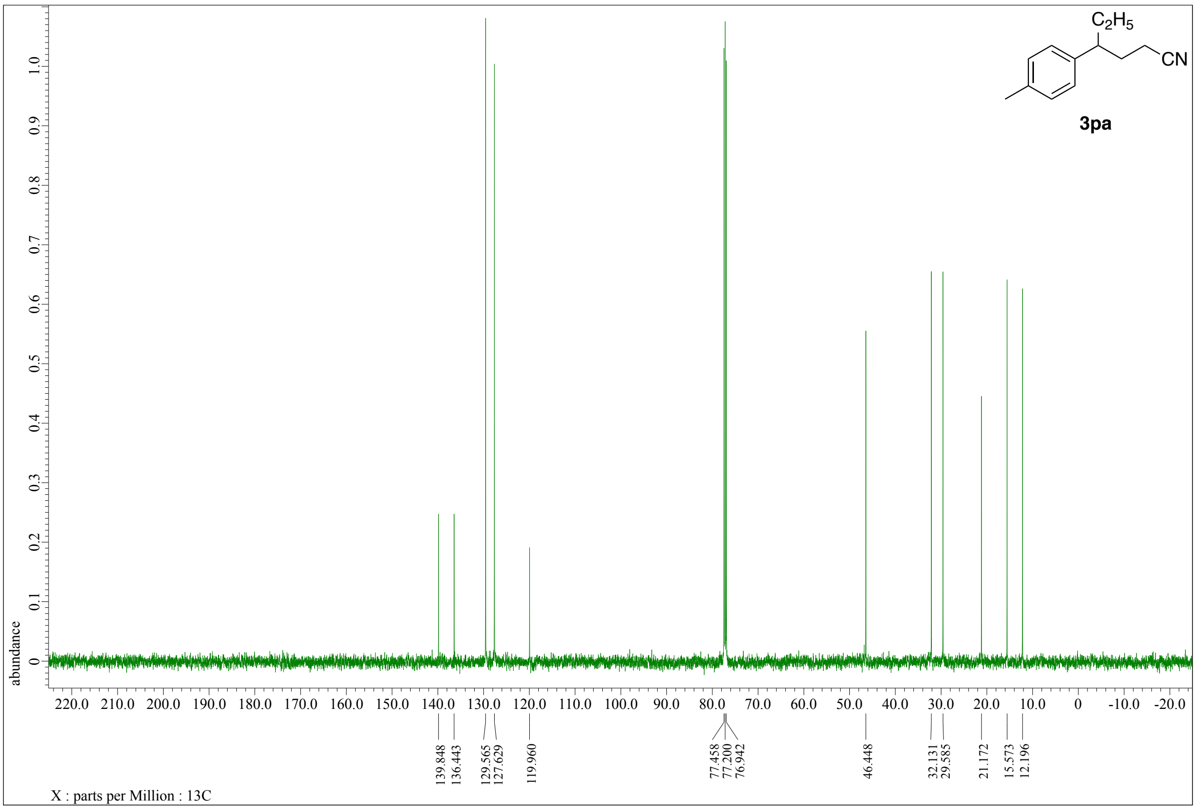

MeO
CN
3oa
abundance
X : parts per Million : 1H
2.00
1.98
3.06
1.08
1.07
1.04
1.04
1.01
3.00
7.260
7.089
7.083
7.080
7.073
7.069
7.064
6.859
6.854
6.850
6.843
6.839
6.834
3.796
2.617
2.605
2.602
2.589
2.270
2.261
2.197
2.186
1.572
1.114
1.103
0.000


3oa

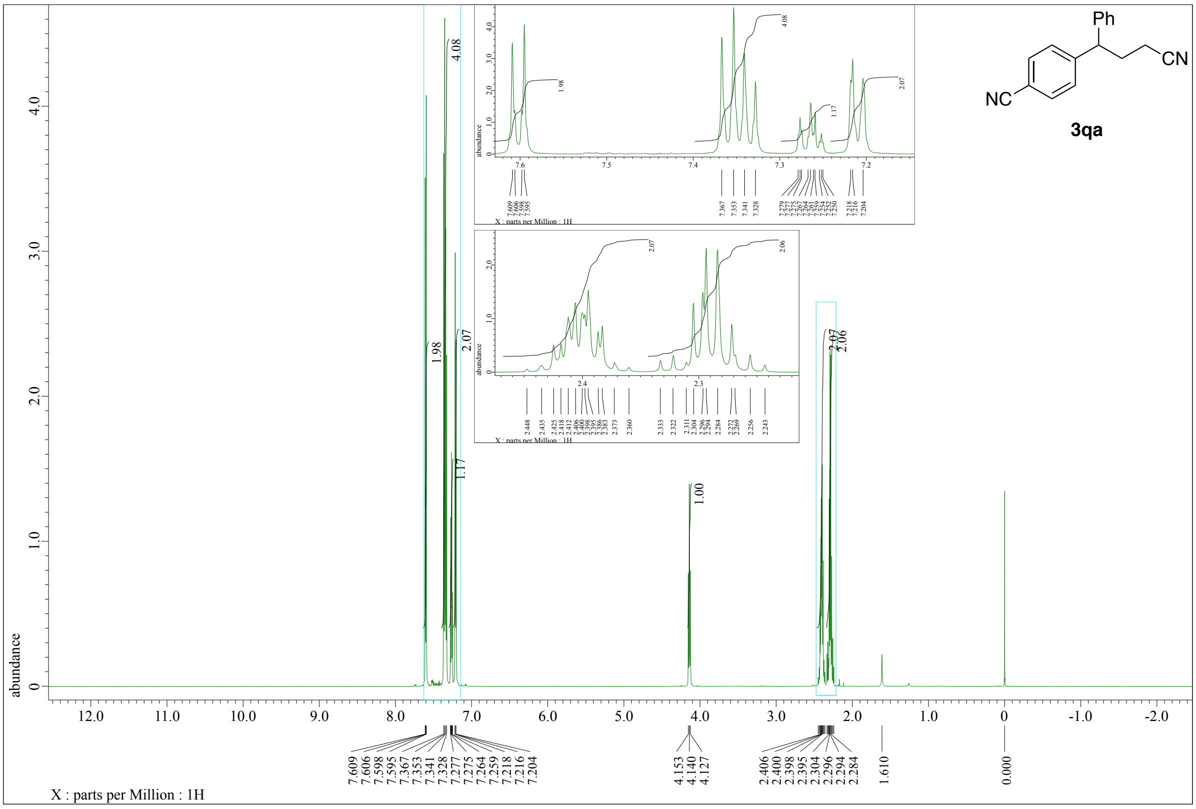
MeO
CN
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
158.462
131.151
130.126
118.895
114.142
77.411
77.200
76.980
55.438
41.313
32.832
23.709
19.579
X : parts per Million : 13C


3pa

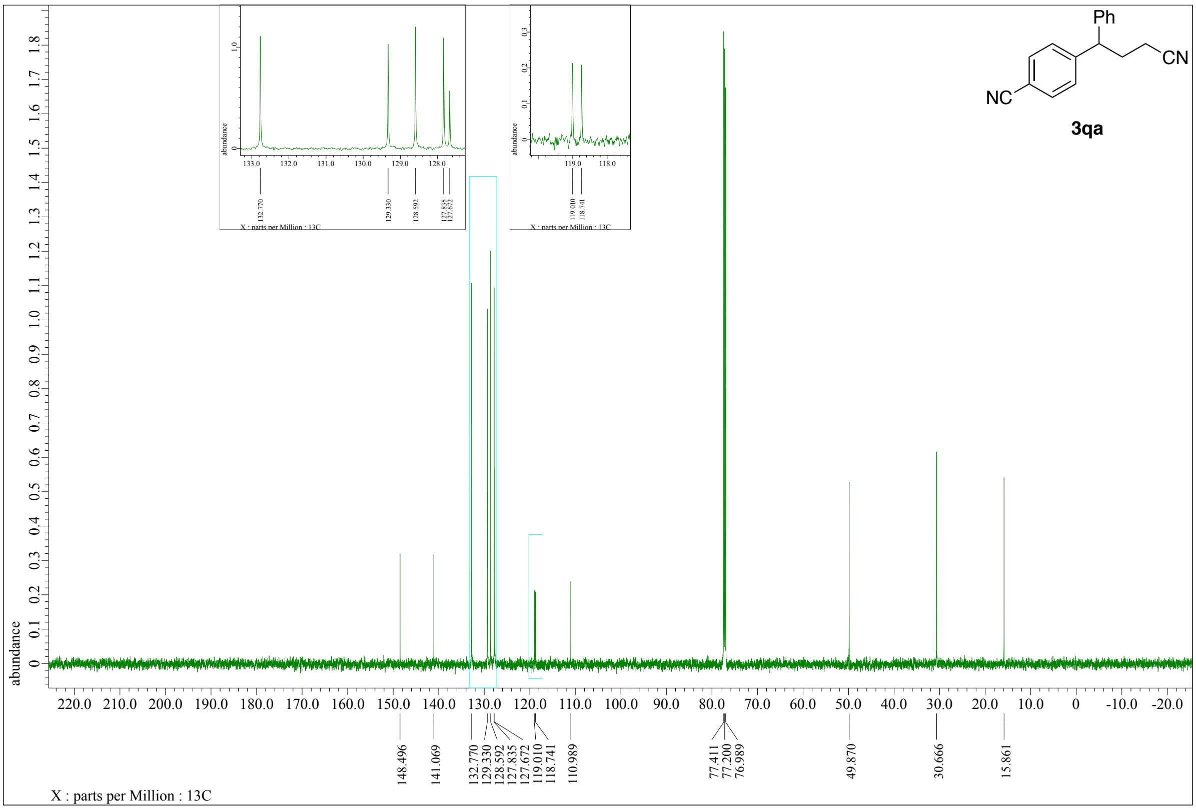
C_2H_5
CN
abundance
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
1.88
1.97
0.99
3.01
1.04
2.03
1.01
2.08
3.00
7.252
7.132
7.117
7.034
7.018
2.326
2.174
2.164
2.053
2.040
2.026
2.022
2.018
1.828
1.807
1.795
1.677
1.662
1.610
0.811
0.796
0.782
0.000
X : parts per Million : 1H


abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
139.848
136.443
129.565
127.629
119.960
77.458
77.200
76.942
46.448
32.131
29.585
21.172
15.573
12.196
X : parts per Million : 13C
C_2H_5
CN

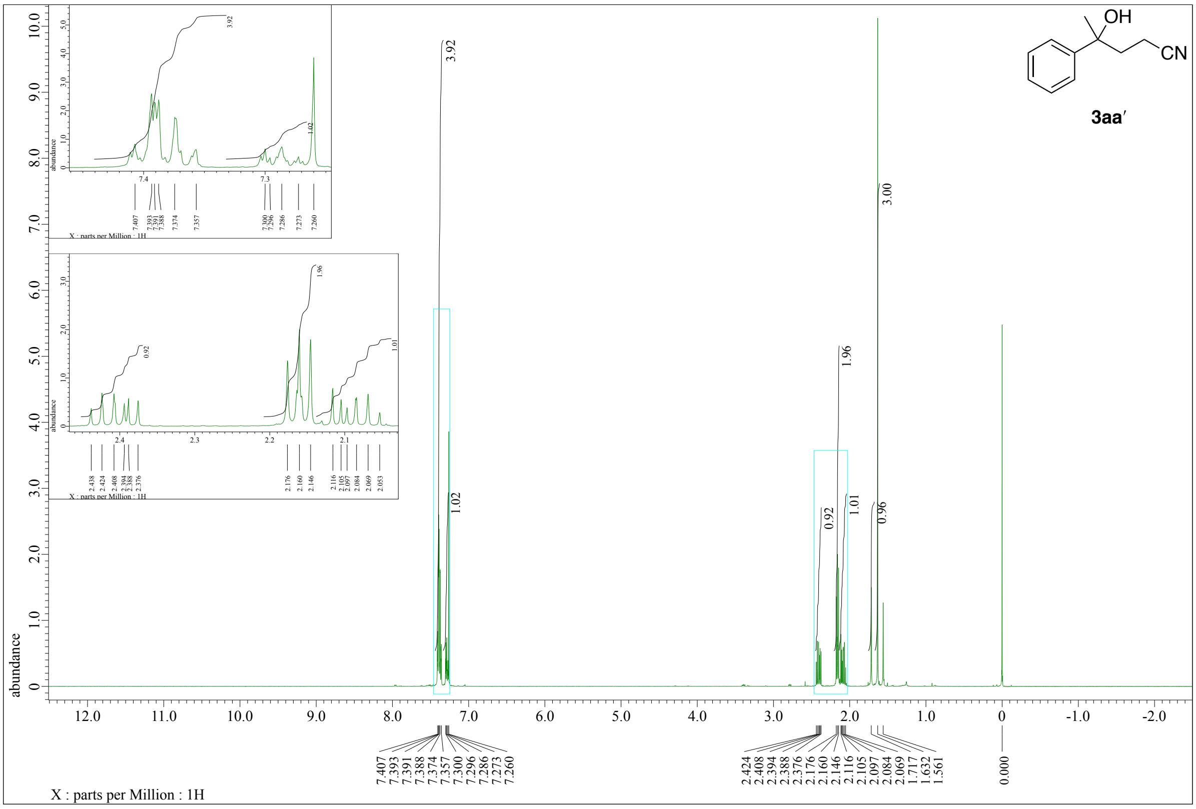
3pa


abundance
0
1.0
2.0
3.0
4.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
1.98
4.08
2.07
1.17
1.00
2.07
2.06
7.609
7.606
7.598
7.595
7.367
7.353
7.341
7.328
7.277
7.275
7.264
7.259
7.218
7.216
7.204
4.153
4.140
4.127
2.406
2.400
2.398
2.395
2.304
2.296
2.294
2.284
1.610
0.000
X : parts per Million : 1H
Ph
CN
NC

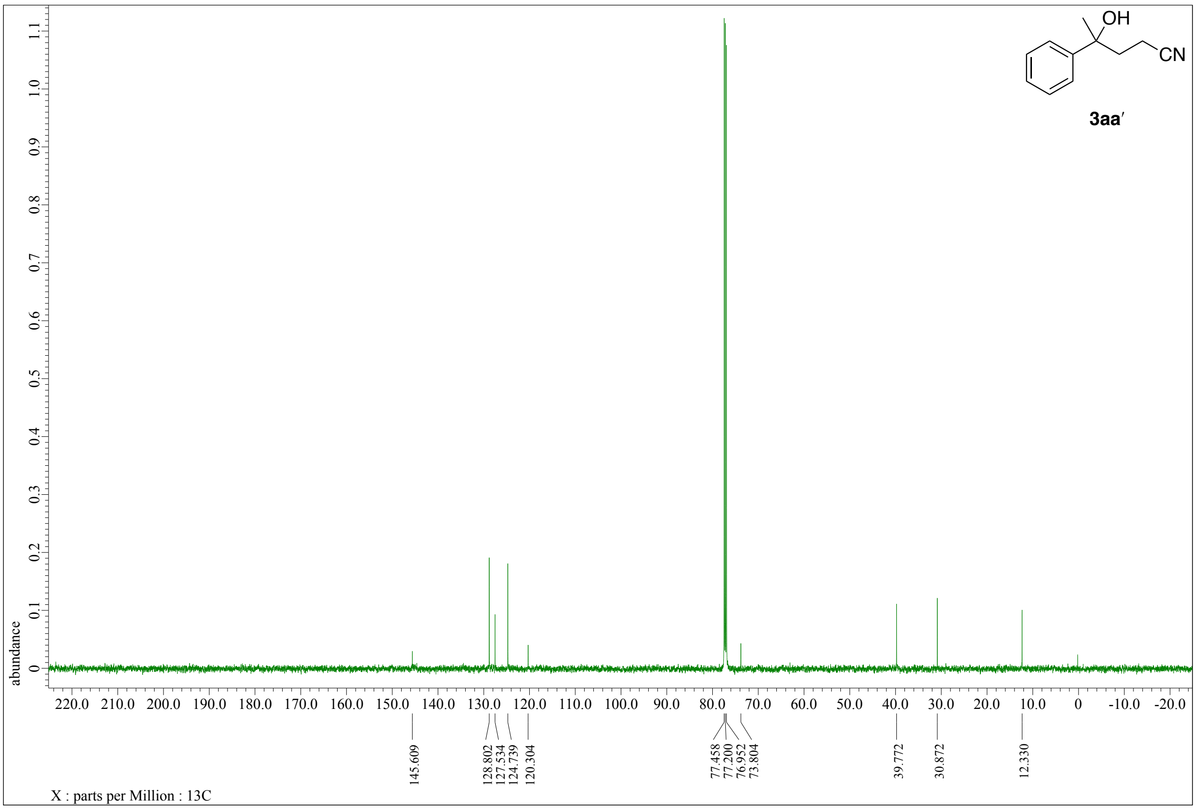
3qa

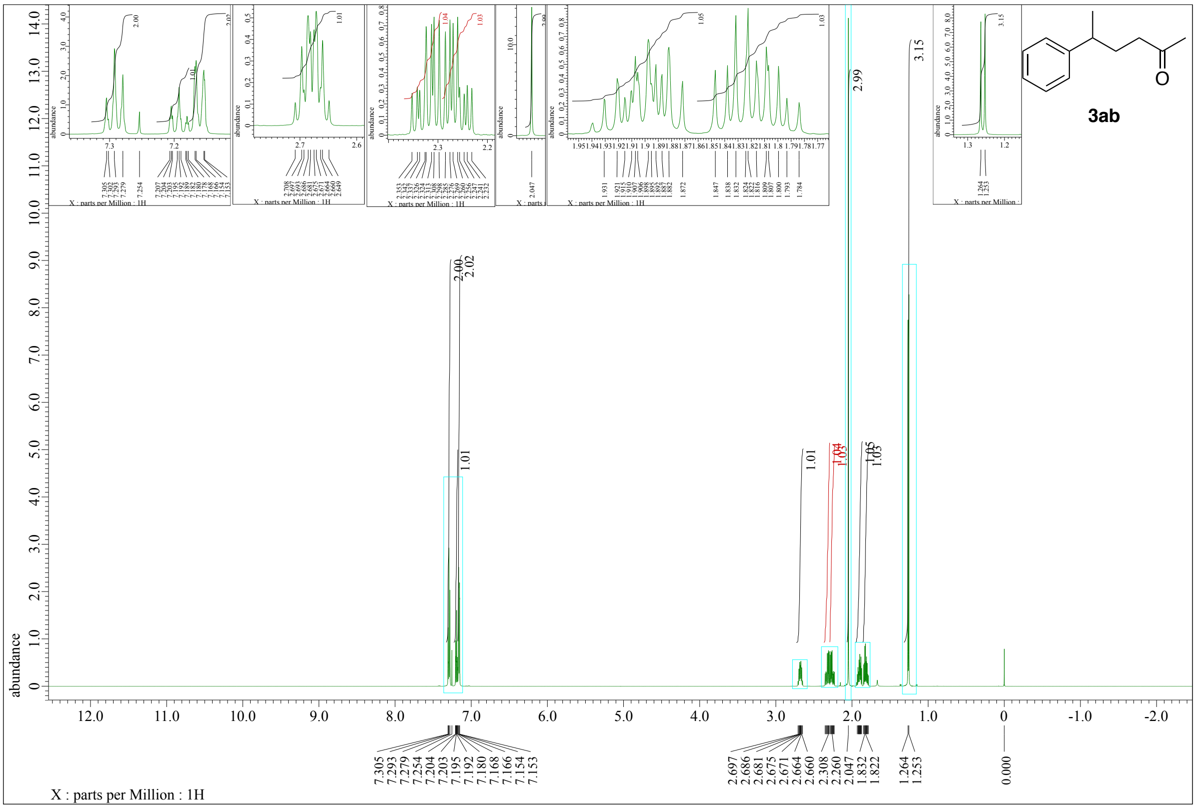

abundance
X : parts per Million : 13C
148.496
141.069
132.770
129.330
128.592
127.835
127.672
119.010
118.741
110.989
77.411
77.200
76.989
49.870
30.666
15.861
Ph
CN
NC

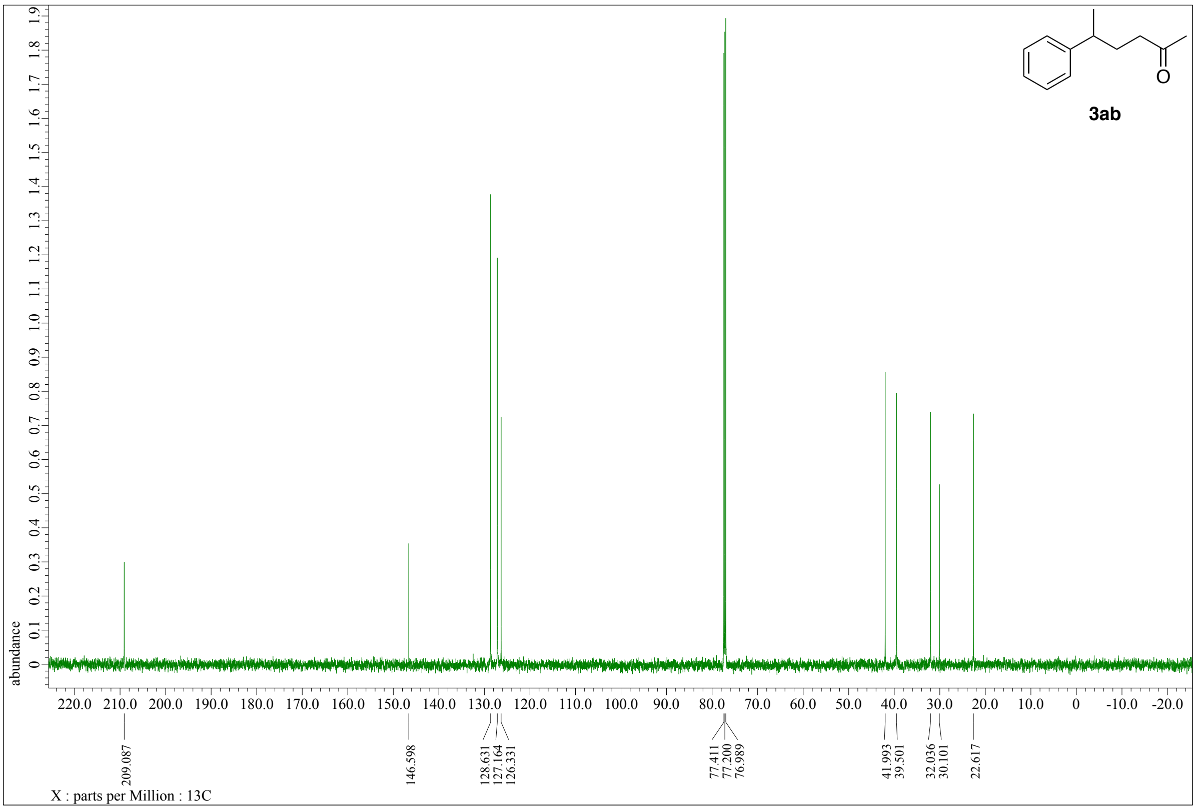
3qa

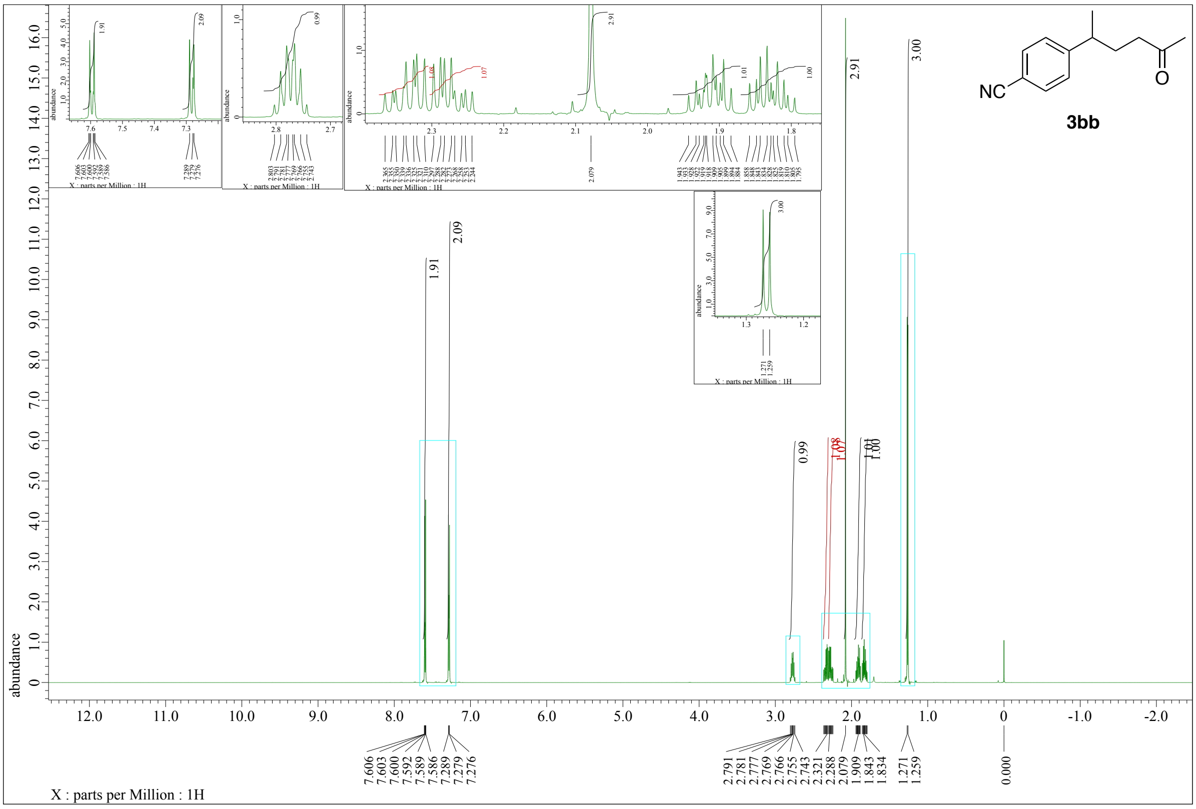

abundance
X : parts per Million : 1H
3.92
1.02
1.96
0.92
1.01
0.96
3.00
7.407
7.393
7.391
7.388
7.374
7.357
7.300
7.296
7.286
7.273
7.260
2.424
2.408
2.394
2.388
2.376
2.176
2.160
2.146
2.116
2.105
2.097
2.084
2.069
1.717
1.632
1.561
0.000
OH
CN

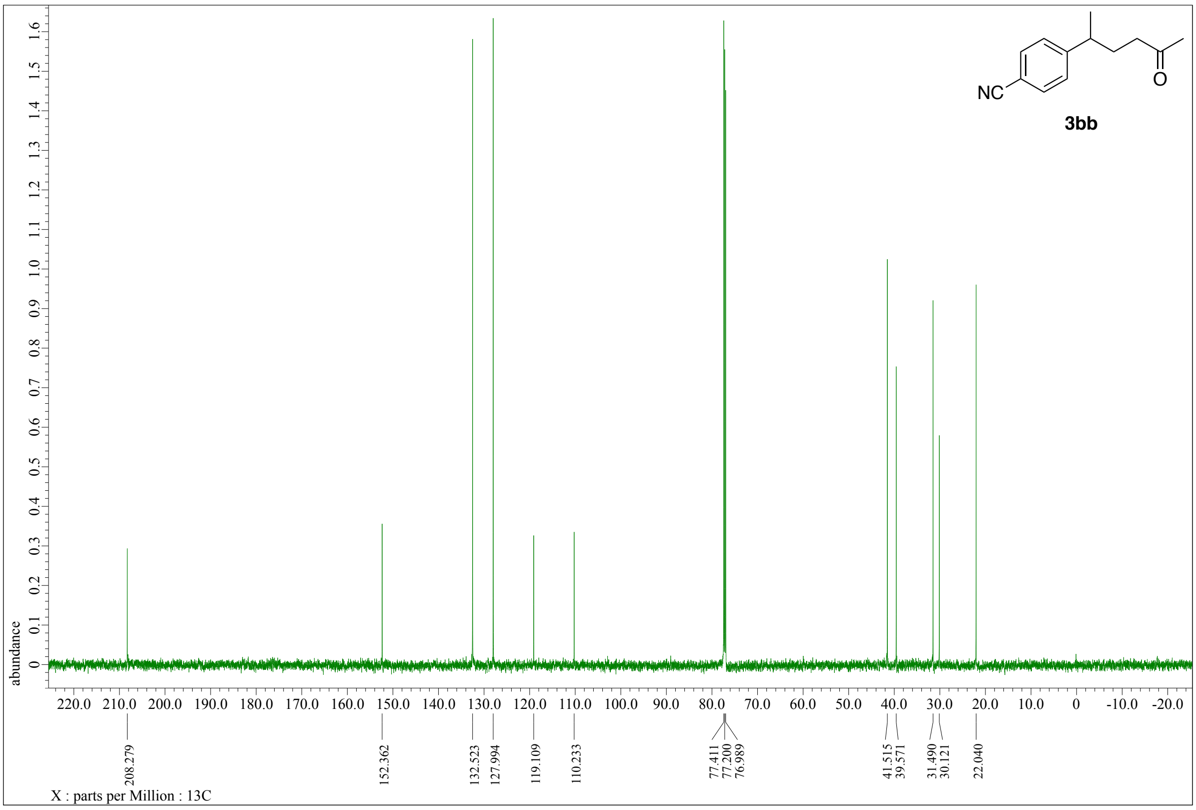
3aa′


OH
CN
3aa′
abundance
X : parts per Million : 13C
145.609
128.802
127.534
124.739
120.304
77.458
77.200
76.952
73.804
39.772
30.872
12.330

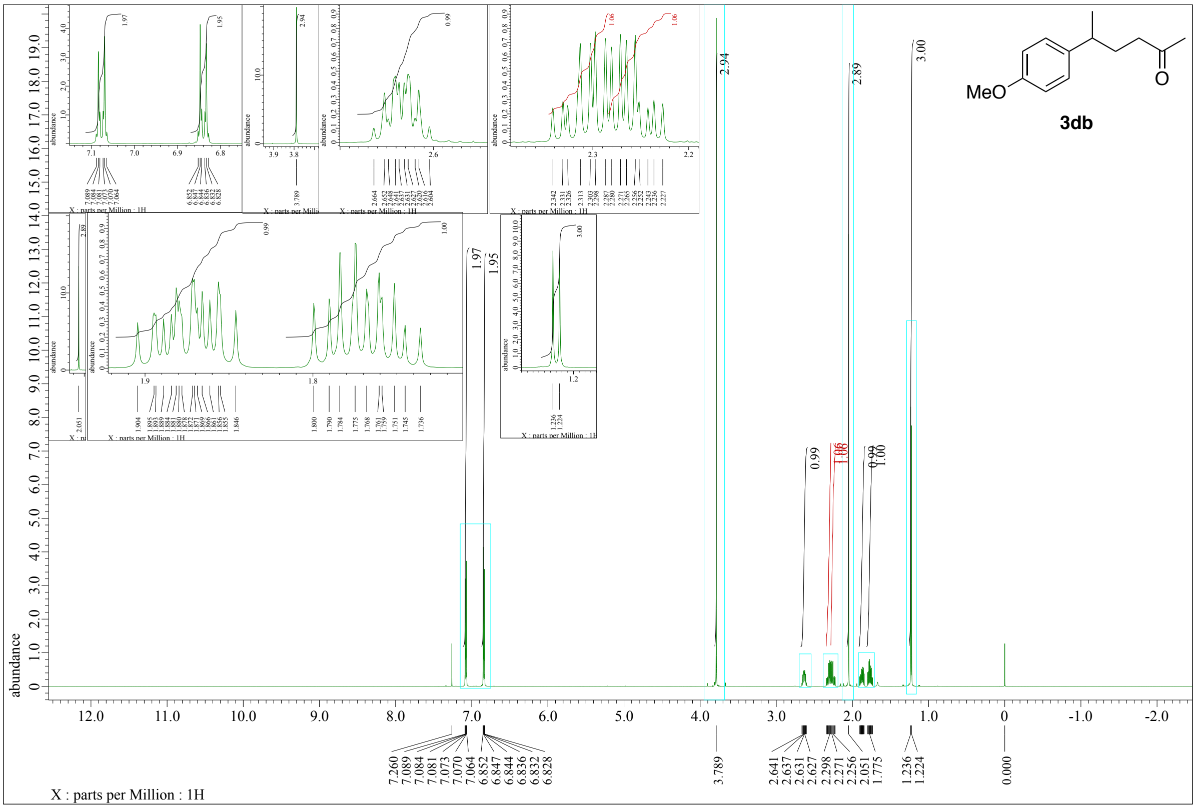

O
3ab
abundance
X : parts per Million : 1H
2.00
2.02
1.01
1.01
1.04
1.03
1.05
1.03
2.99
3.15
7.305
7.293
7.279
7.254
7.204
7.203
7.195
7.192
7.180
7.168
7.166
7.154
7.153
2.697
2.686
2.681
2.675
2.671
2.664
2.660
2.308
2.260
2.047
1.832
1.822
1.264
1.253
0.000


3ab
O
abundance
X : parts per Million : 13C
209.087
146.598
128.631
127.164
126.331
77.411
77.200
76.989
41.993
39.501
32.036
30.101
22.617

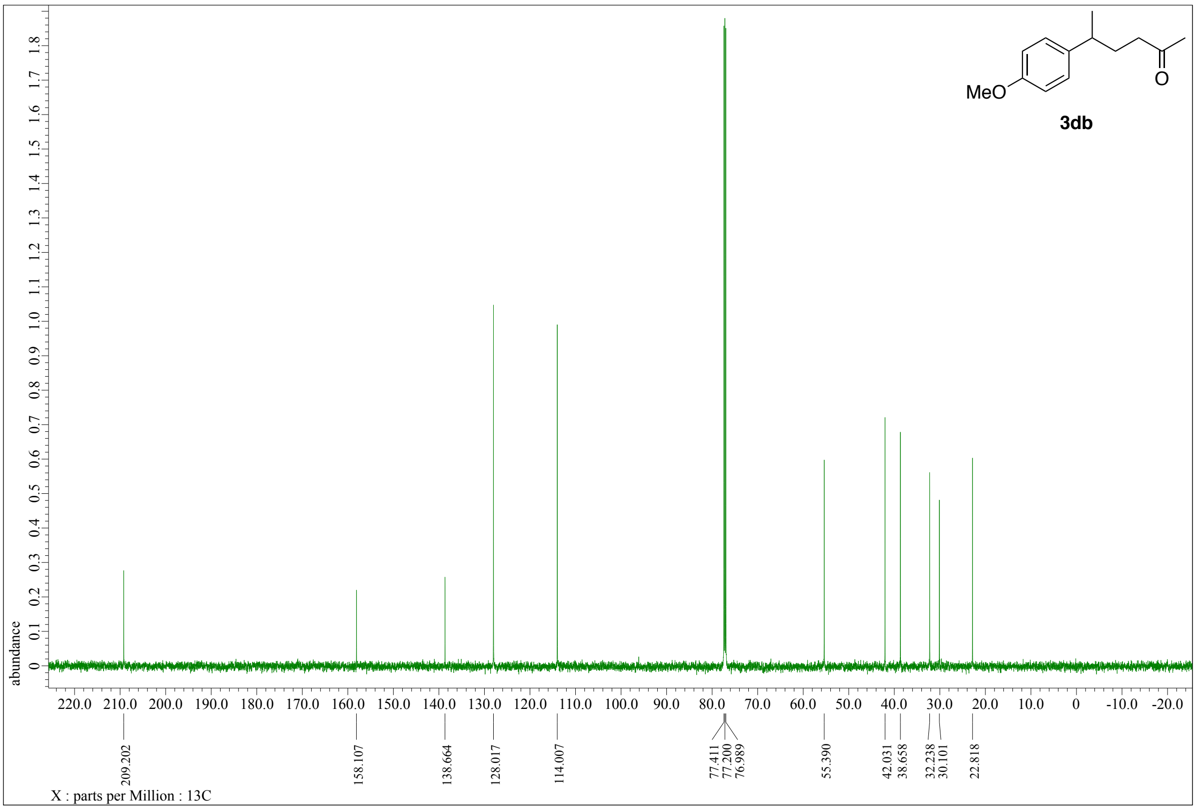

3bb
NC
O
abundance
X : parts per Million : 1H
1.91
2.09
0.99
1.08
1.07
2.91
1.01
1.00
3.00
7.606
7.603
7.600
7.592
7.589
7.586
7.289
7.279
7.276
2.791
2.781
2.777
2.769
2.766
2.755
2.743
2.321
2.288
2.079
1.909
1.843
1.834
1.271
1.259
0.000

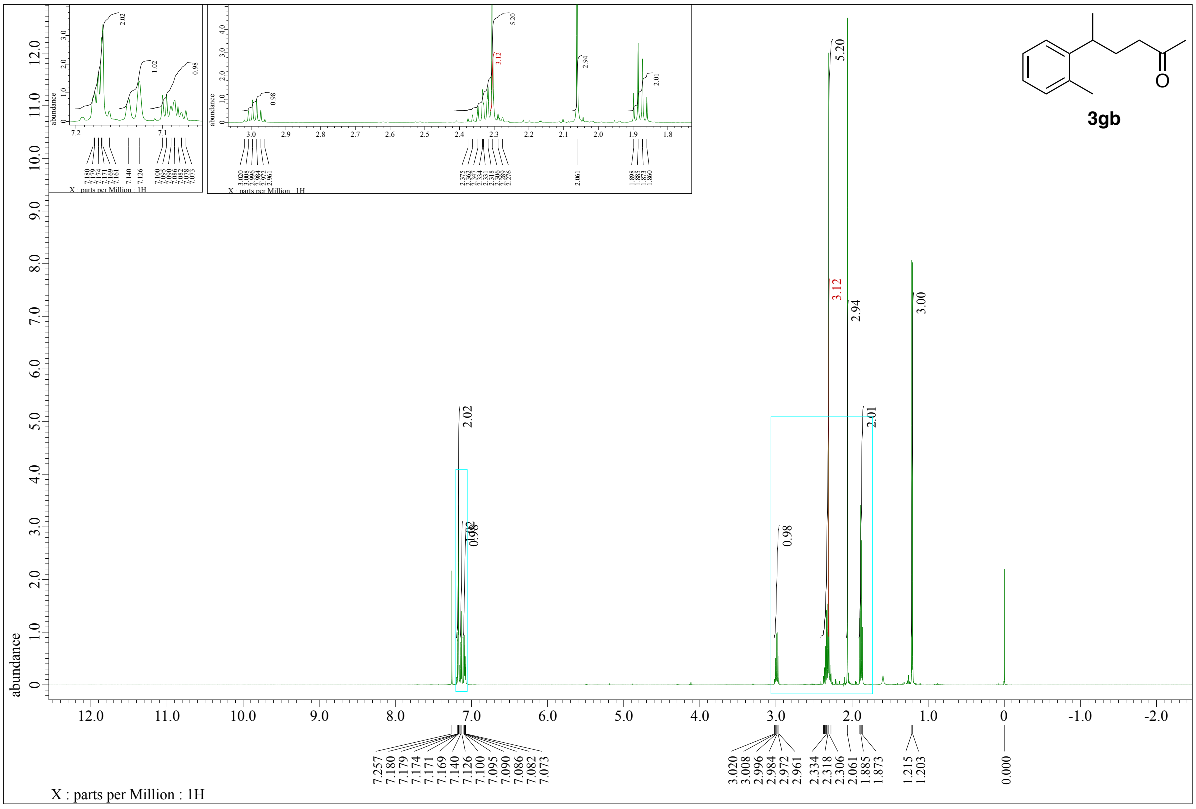


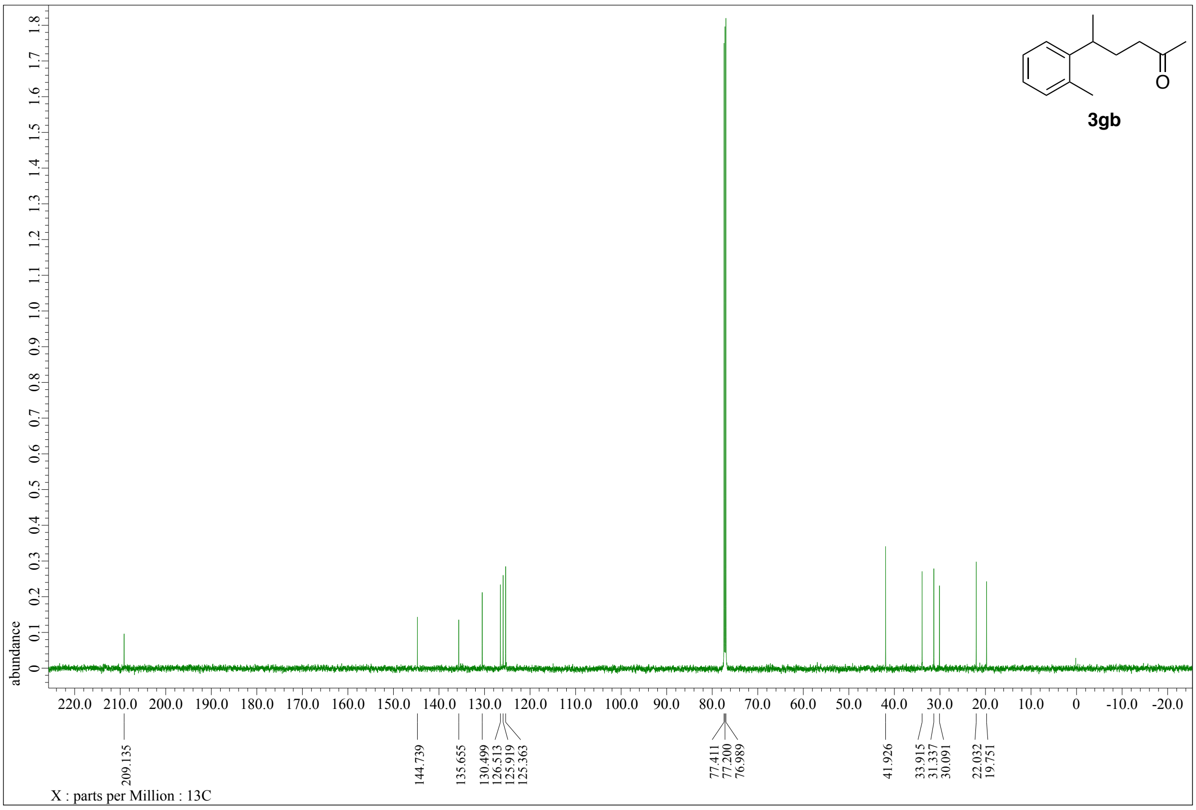
3bb
NC
O
abundance
X : parts per Million : 13C
208.279
152.362
132.523
127.994
119.109
110.233
77.411
77.200
76.989
41.515
39.571
31.490
30.121
22.040



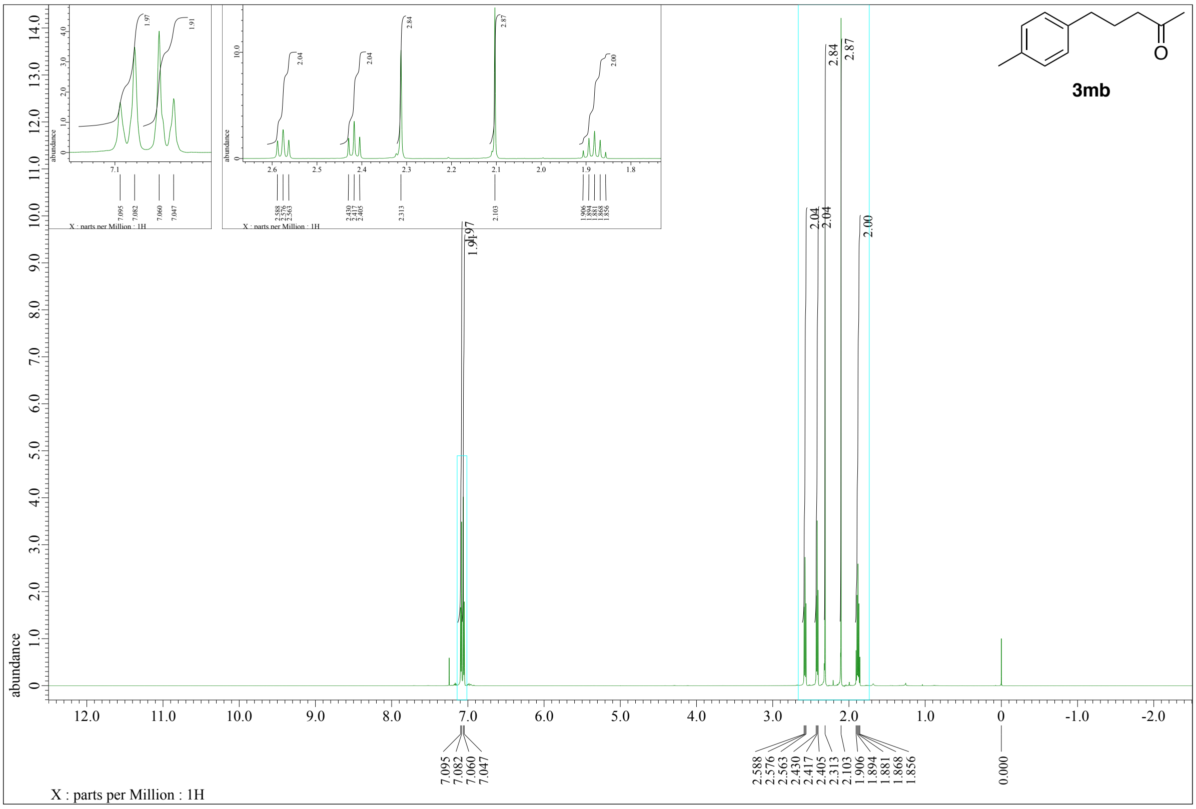
3db
MeO
O
abundance
X : parts per Million : 1H
1.97
1.95
2.94
0.99
1.06
1.06
2.89
0.99
1.00
3.00
7.260
7.089
7.084
7.081
7.073
7.070
7.064
6.852
6.847
6.844
6.836
6.832
6.828
3.789
2.641
2.637
2.631
2.627
2.298
2.281
2.271
2.256
2.051
1.775
1.236
1.224
0.000


MeO
O
3db
abundance
X : parts per Million : 13C
209.202
158.107
138.664
128.017
114.007
77.411
77.200
76.989
55.390
42.031
38.658
32.238
30.101
22.818

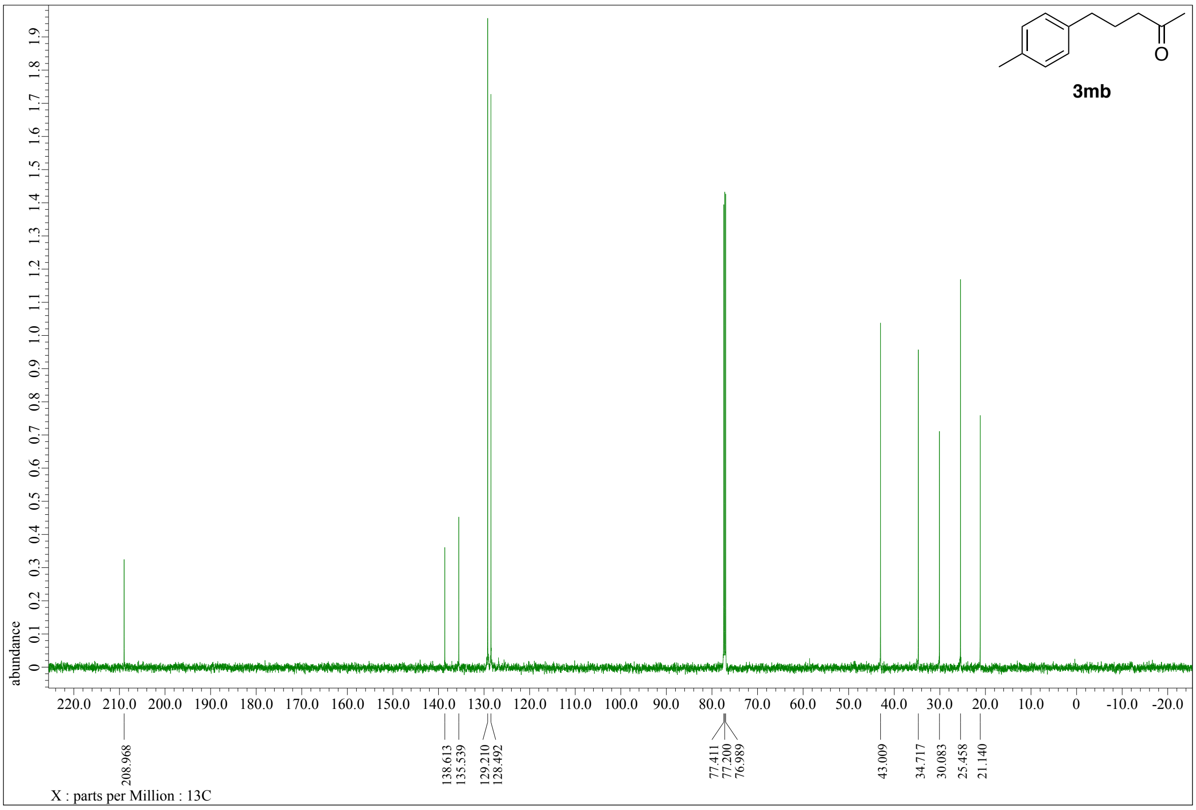

O
3gb
abundance
X : parts per Million : 1H
2.02
0.98
0.98
3.12
5.20
2.94
2.01
3.00
7.257
7.180
7.179
7.174
7.171
7.169
7.140
7.126
7.100
7.095
7.090
7.086
7.082
7.073
3.020
3.008
2.996
2.984
2.972
2.961
2.334
2.318
2.306
2.061
1.885
1.873
1.215
1.203
0.000


abundance
X : parts per Million : 13C
209.135
144.739
135.655
130.499
126.513
125.919
125.363
77.411
77.200
76.989
41.926
33.915
31.337
30.091
22.032
19.751
O

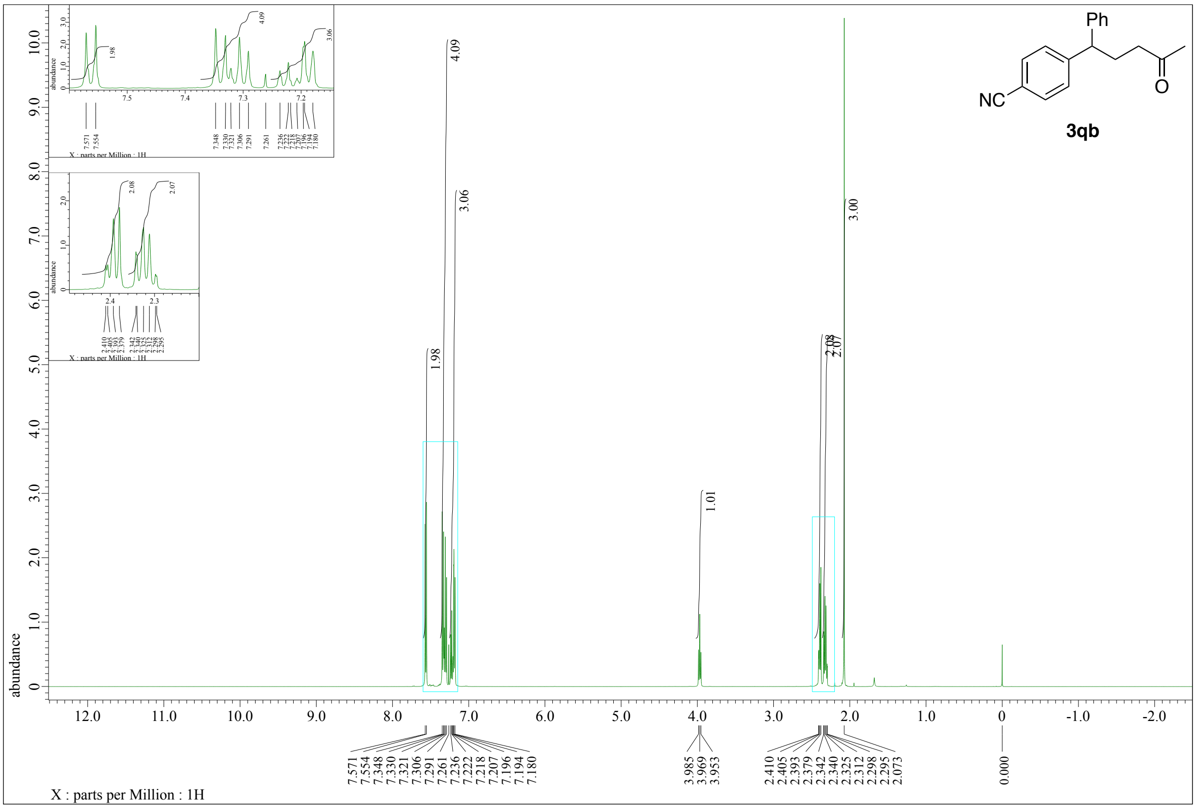
3gb


abundance
X : parts per Million : 1H
1.97
1.91
2.04
2.04
2.84
2.87
2.00
7.095
7.082
7.060
7.047
2.588
2.576
2.563
2.430
2.417
2.405
2.313
2.103
1.906
1.894
1.881
1.868
1.856
0.000
O

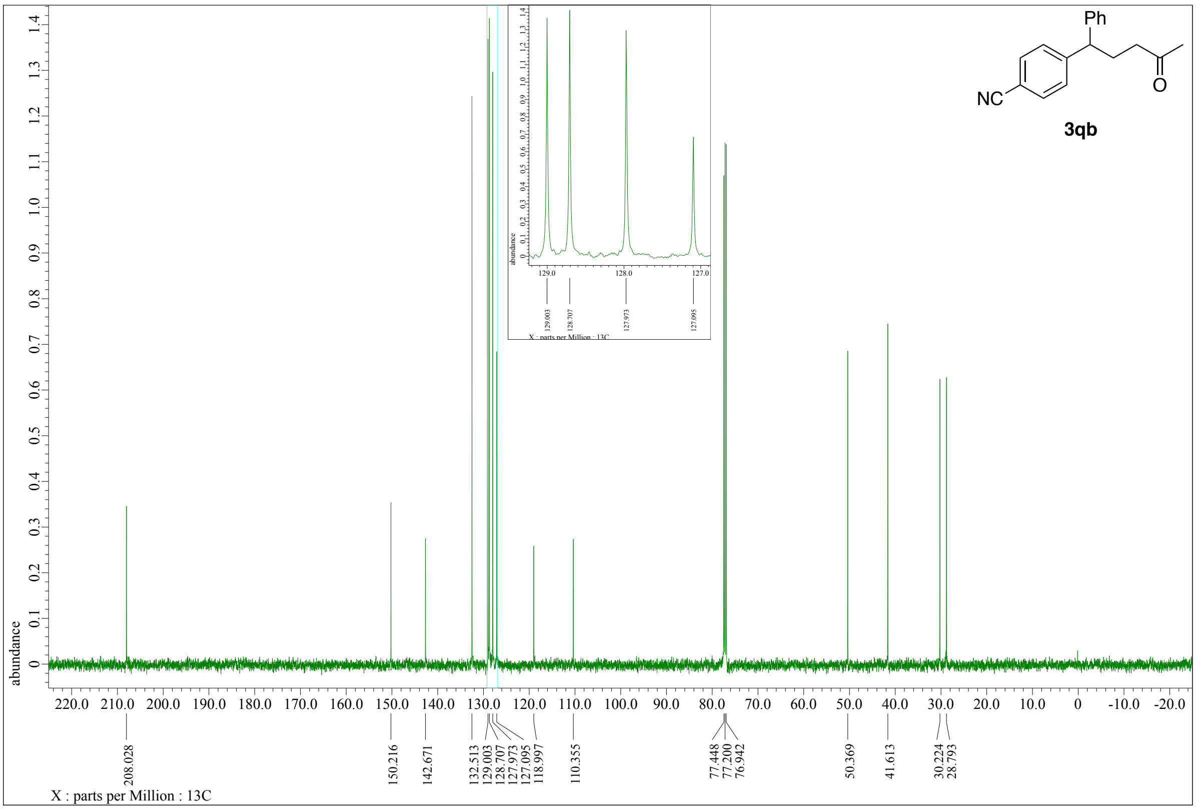
3mb


O
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
208.968
138.613
135.539
129.210
128.492
77.411
77.200
76.989
43.009
34.717
30.083
25.458
21.140
X : parts per Million : 13C

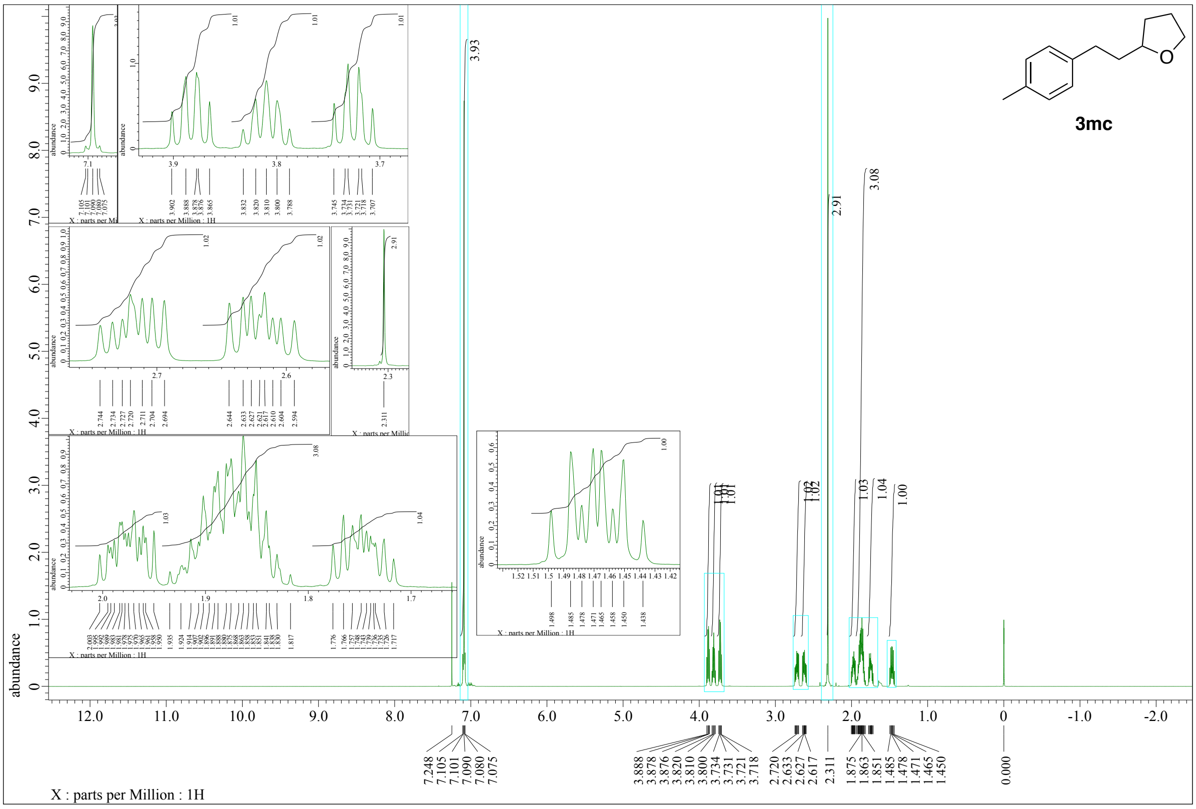
3mb


Ph
NC
O
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
1.98
4.09
3.06
1.01
2.08
2.07
3.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.571
7.554
7.348
7.330
7.321
7.306
7.291
7.261
7.236
7.222
7.218
7.207
7.196
7.194
7.180
3.985
3.969
3.953
2.410
2.405
2.393
2.379
2.342
2.340
2.325
2.312
2.298
2.295
2.073
0.000
X : parts per Million : 1H

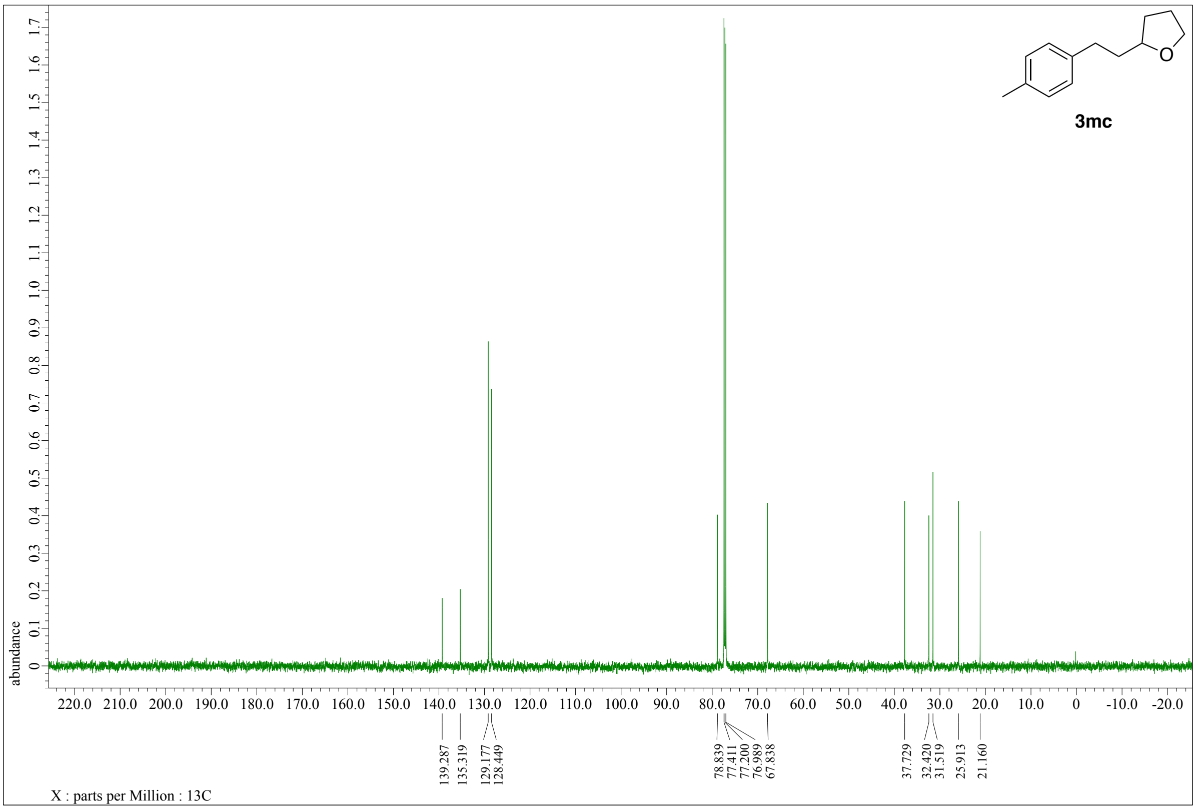
3qb

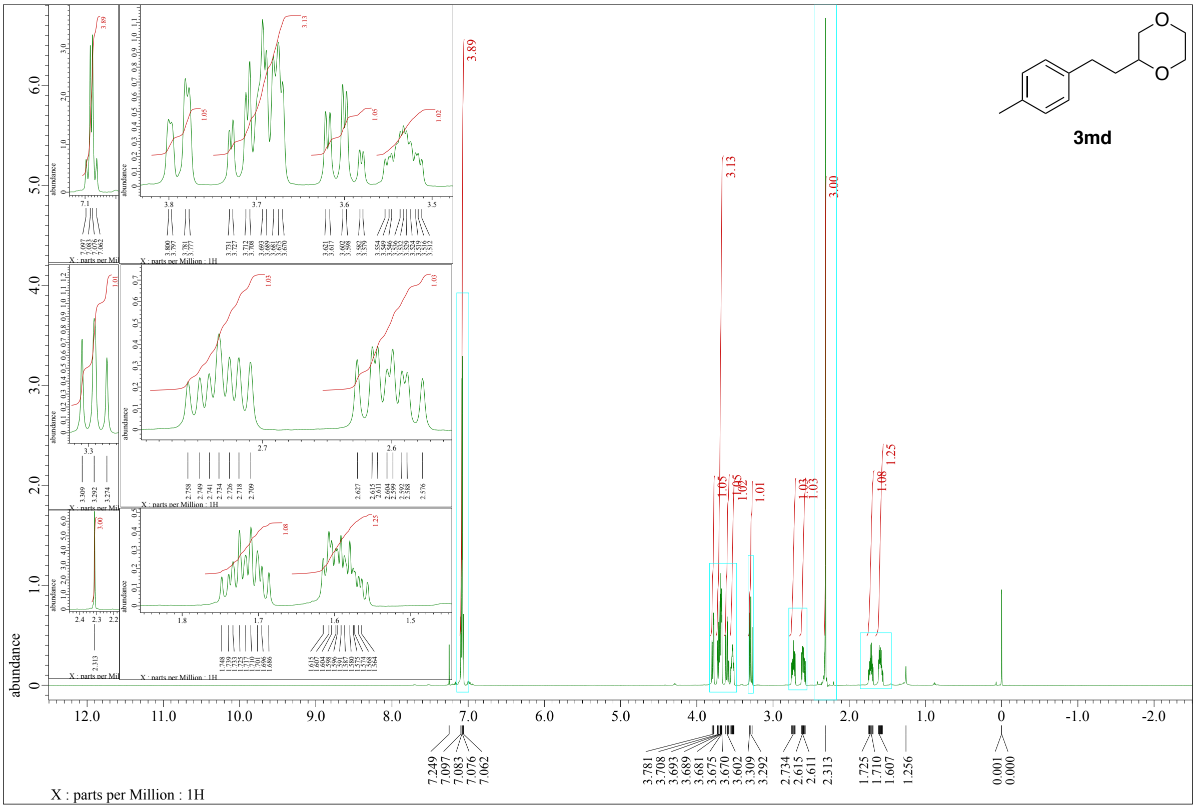

Ph
NC
O
abundance
X : parts per Million : 13C
208.028
150.216
142.671
132.513
129.003
128.707
127.973
127.095
118.997
110.355
77.448
77.200
76.942
50.369
41.613
30.224
28.793

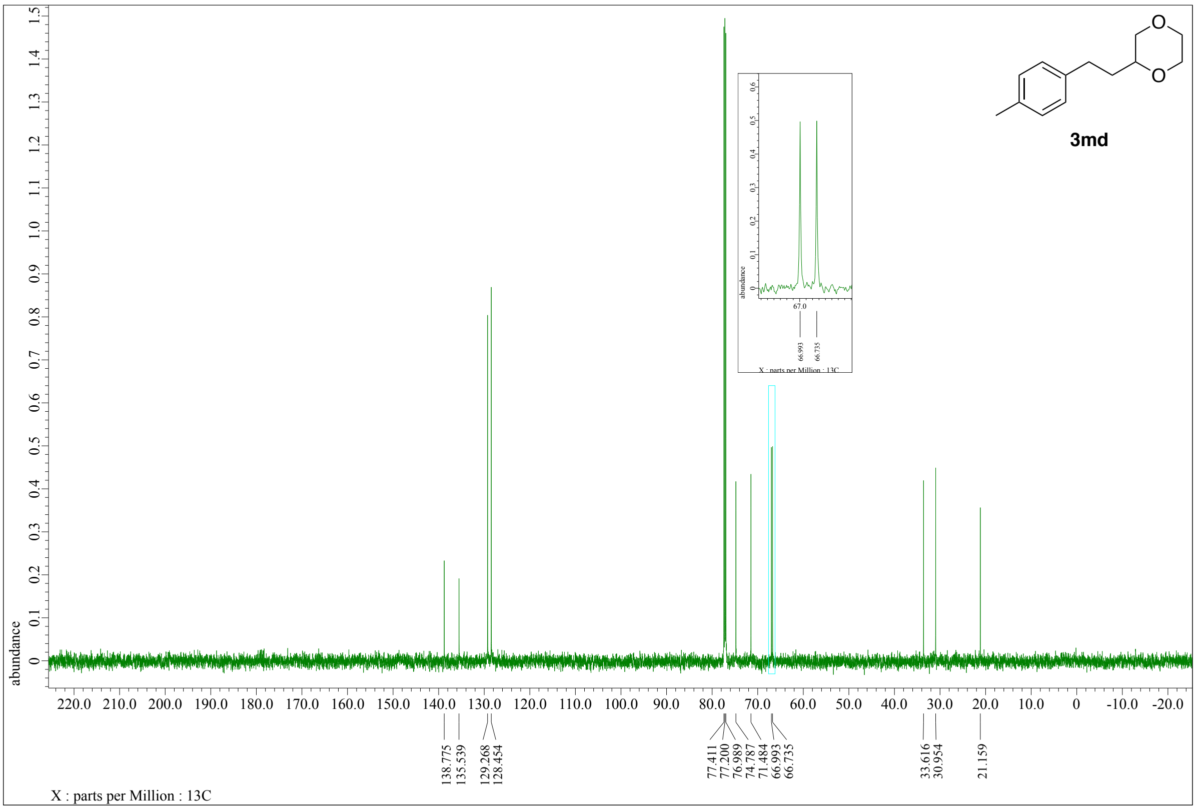
3qb


O
abundance
X : parts per Million : 1H
3.93
2.91
3.08
1.01
1.01
1.01
1.02
1.02
1.03
1.04
1.00
7.248
7.105
7.101
7.090
7.080
7.075
3.888
3.878
3.876
3.820
3.810
3.800
3.734
3.731
3.721
3.718
2.720
2.633
2.627
2.617
2.311
1.875
1.863
1.851
1.485
1.478
1.471
1.465
1.450
0.000

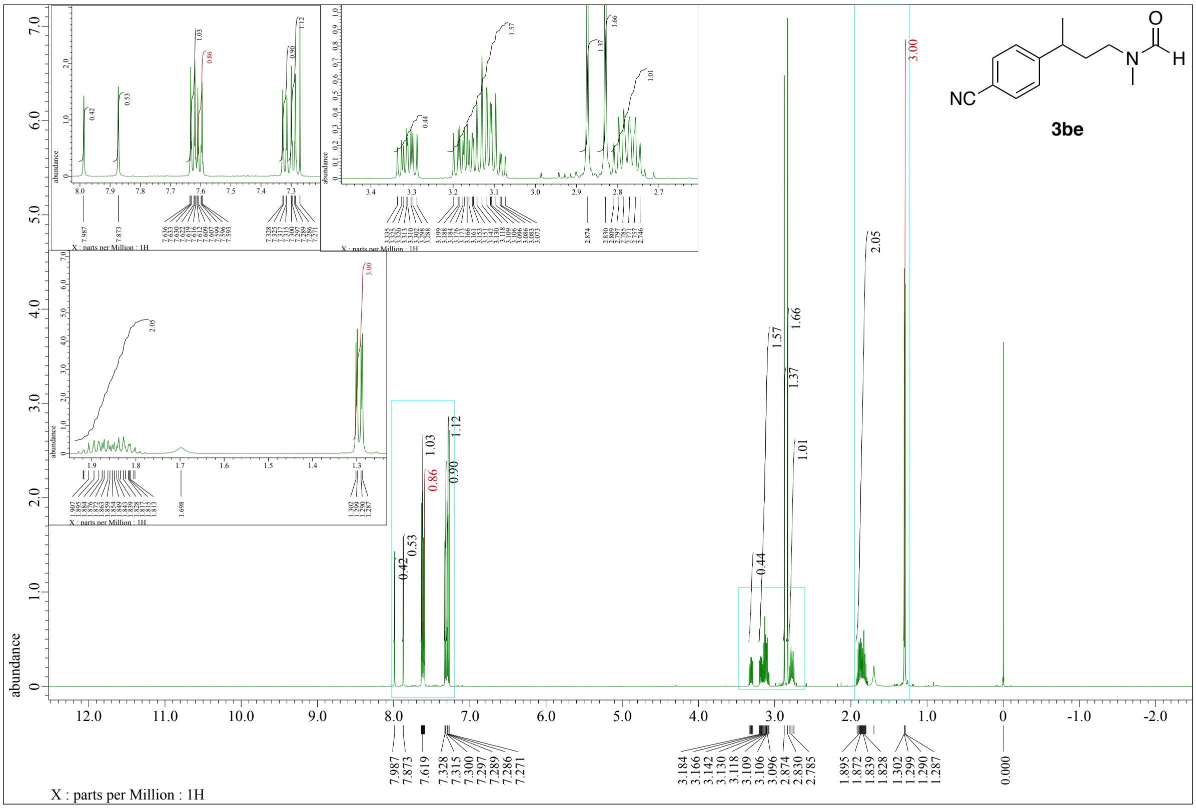
3mc


3mc
abundance
X : parts per Million : 13C
139.287
135.319
129.177
128.449
78.839
77.411
77.200
76.989
67.838
37.729
32.420
31.519
25.913
21.160

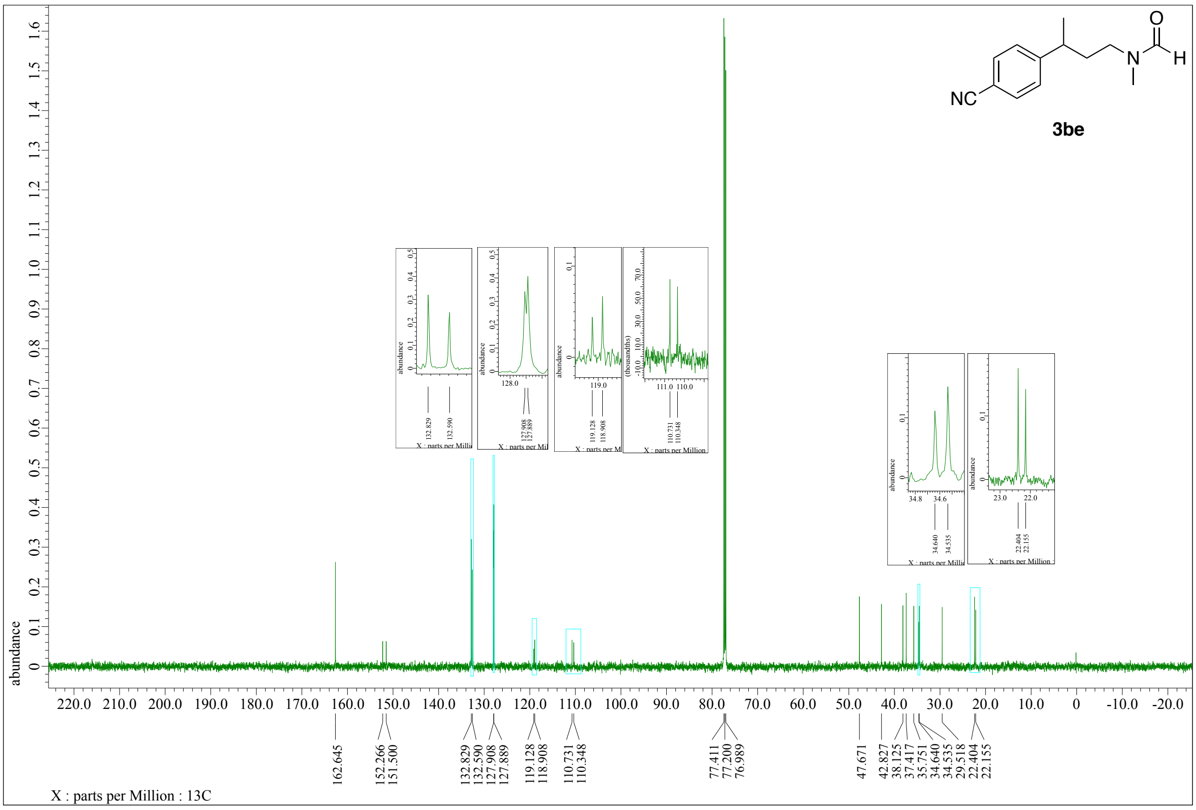

3md
abundance
X : parts per Million : 1H
3.89
3.13
3.00
1.05
1.05
1.02
1.01
1.03
1.03
1.08
1.25
7.249
7.097
7.083
7.076
7.062
3.781
3.708
3.693
3.689
3.681
3.675
3.670
3.602
3.309
3.292
2.734
2.615
2.611
2.313
1.725
1.710
1.607
1.256
0.001
0.000

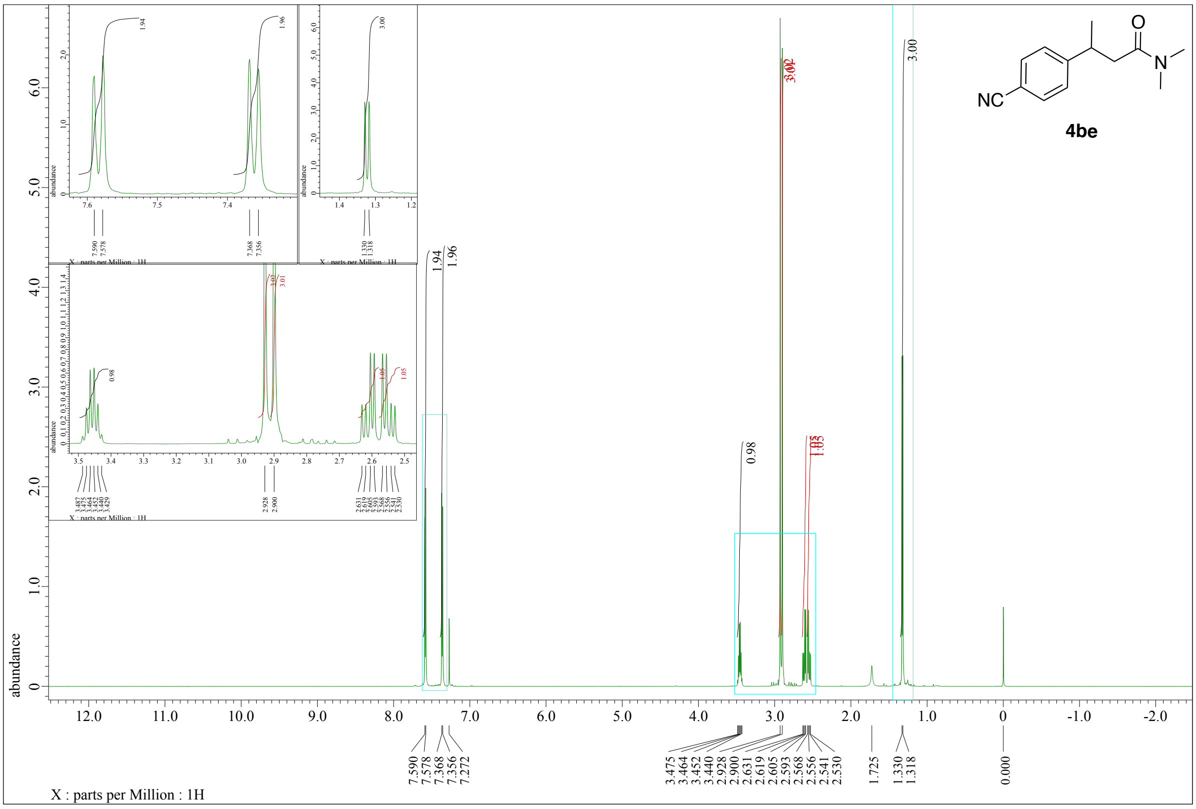

abundance
X : parts per Million : 13C
138.775
135.539
129.268
128.454
77.411
77.200
76.989
74.787
71.484
66.993
66.735
33.616
30.954
21.159
67.0

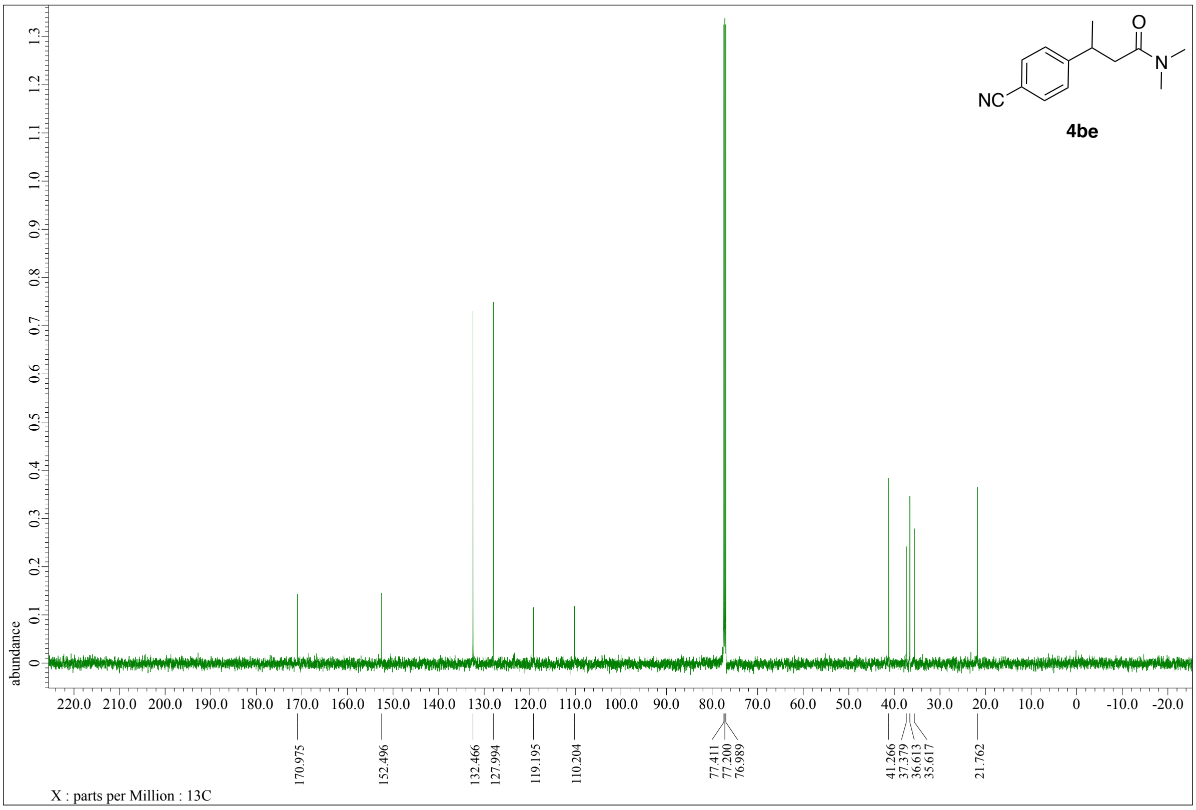
3md


abundance
X : parts per Million : 1H
NC
N
O
H
0.42
0.53
0.86
1.03
0.90
1.12
0.44
1.57
1.37
1.66
1.01
2.05
3.00
7.987
7.873
7.619
7.328
7.315
7.300
7.297
7.289
7.286
7.271
3.184
3.166
3.142
3.130
3.118
3.109
3.106
3.096
2.874
2.830
2.785
1.895
1.872
1.839
1.828
1.302
1.299
1.290
1.287
0.000

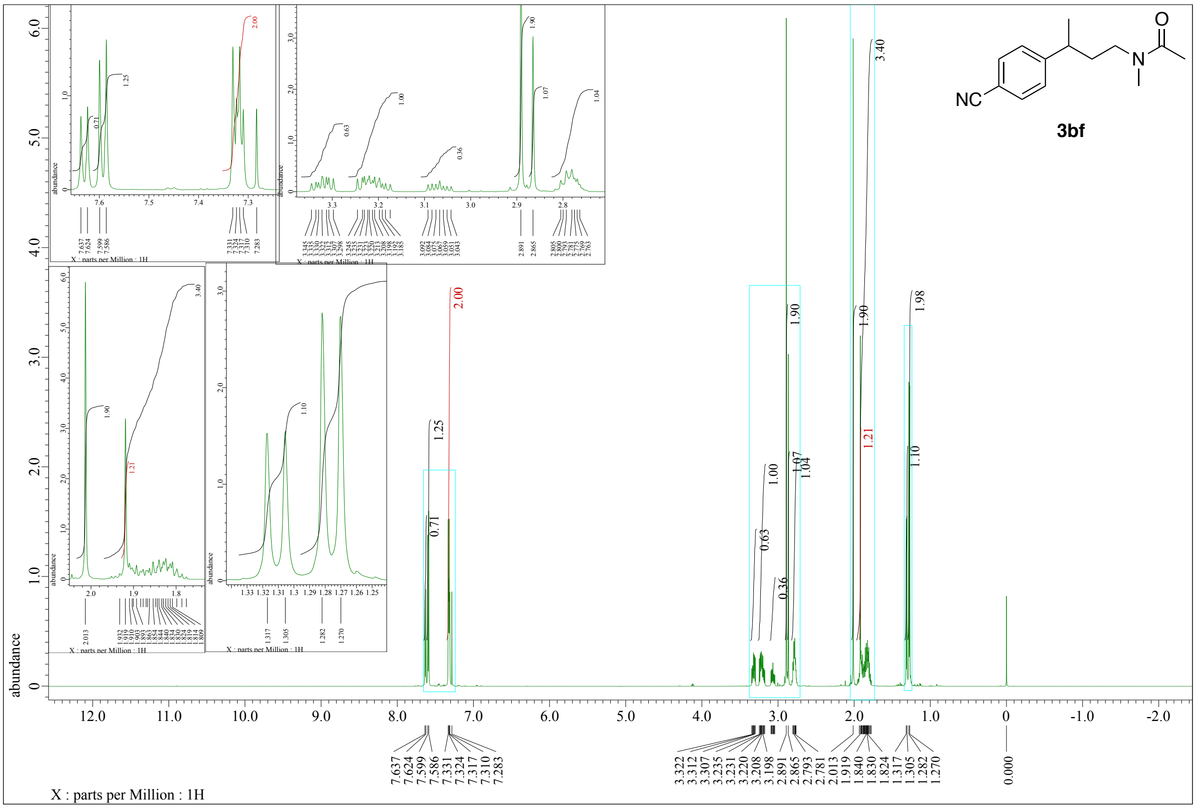
3be


3be
NC
N
O
H
abundance
X : parts per Million : 13C
162.645
152.266
151.500
132.829
132.590
127.908
127.889
119.128
118.908
110.731
110.348
77.411
77.200
76.989
47.671
42.827
38.125
37.417
35.751
34.640
34.535
29.518
22.404
22.155

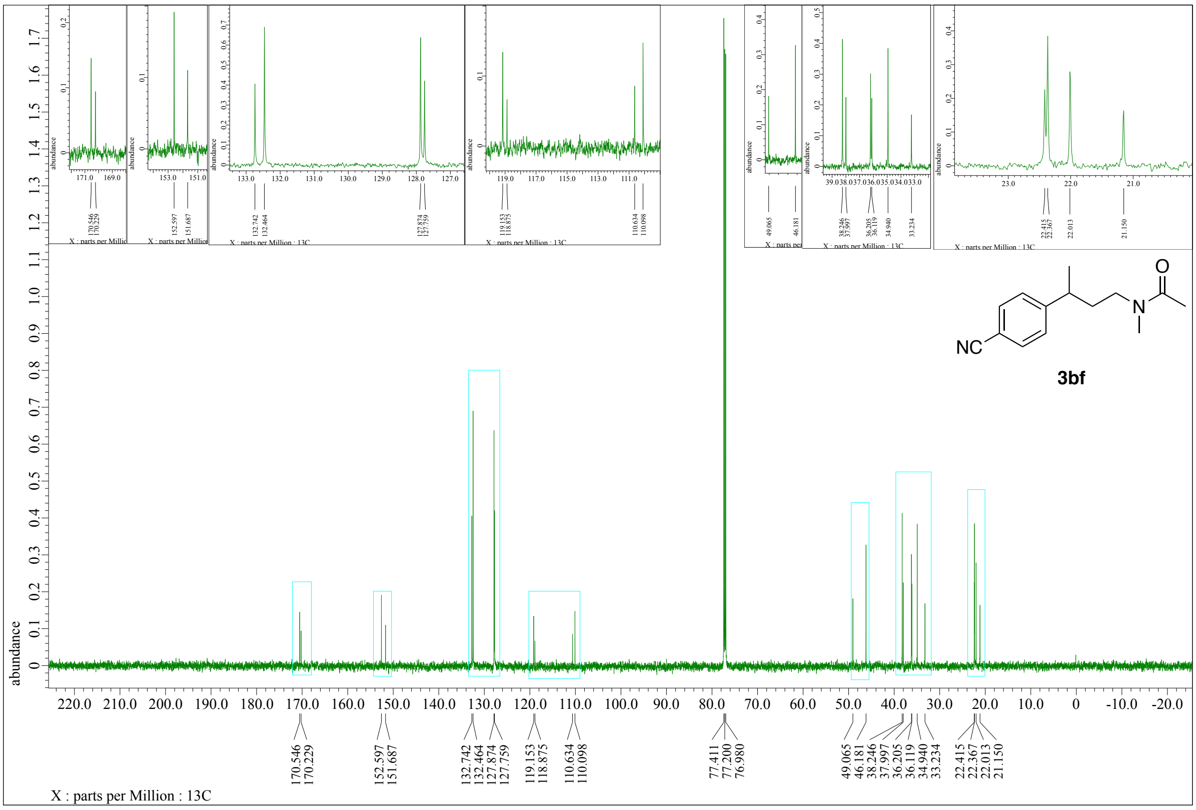

4be
NC
N
O
abundance
X : parts per Million : 1H
1.94
1.96
0.98
3.02
3.01
1.05
1.05
3.00
7.590
7.578
7.368
7.356
7.272
3.475
3.464
3.452
3.440
2.928
2.900
2.631
2.619
2.605
2.593
2.568
2.556
2.541
2.530
1.725
1.330
1.318
0.000

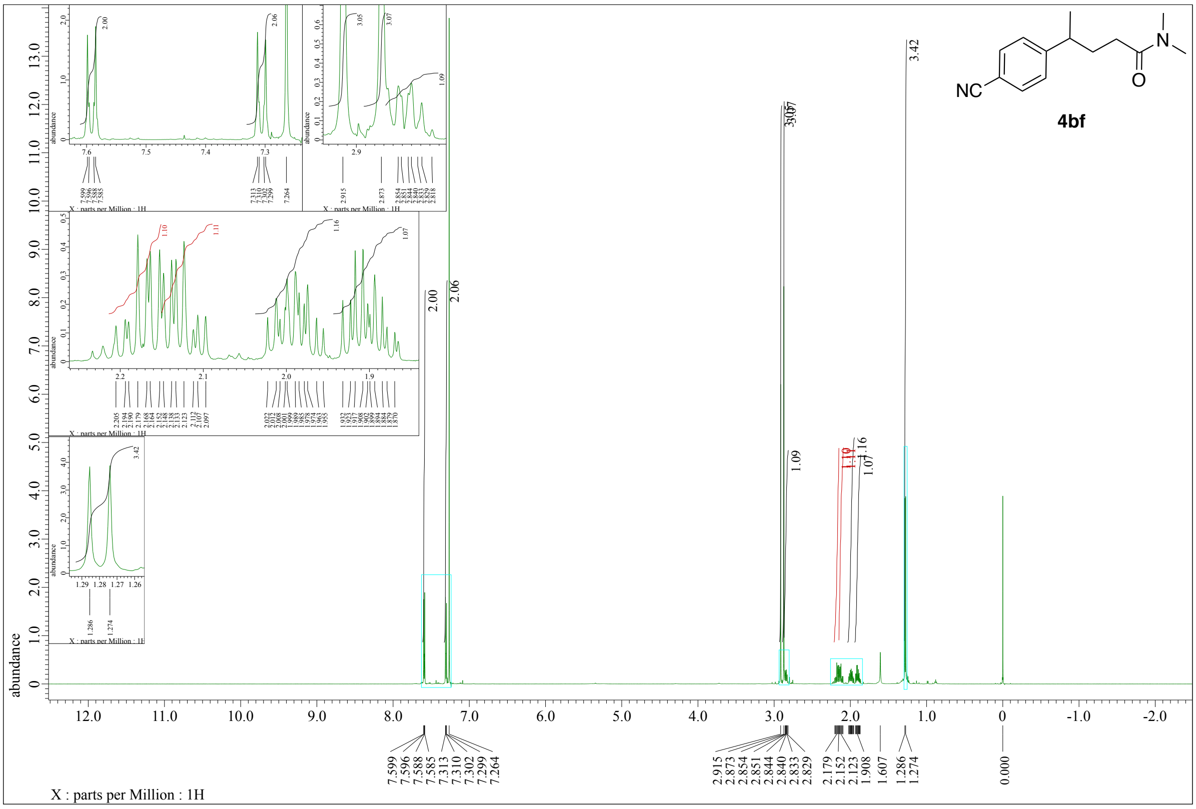

abundance
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
170.975
152.496
132.466
127.994
119.195
110.204
77.411
77.200
76.989
41.266
37.379
36.613
35.617
21.762
X : parts per Million : 13C
NC
O
N

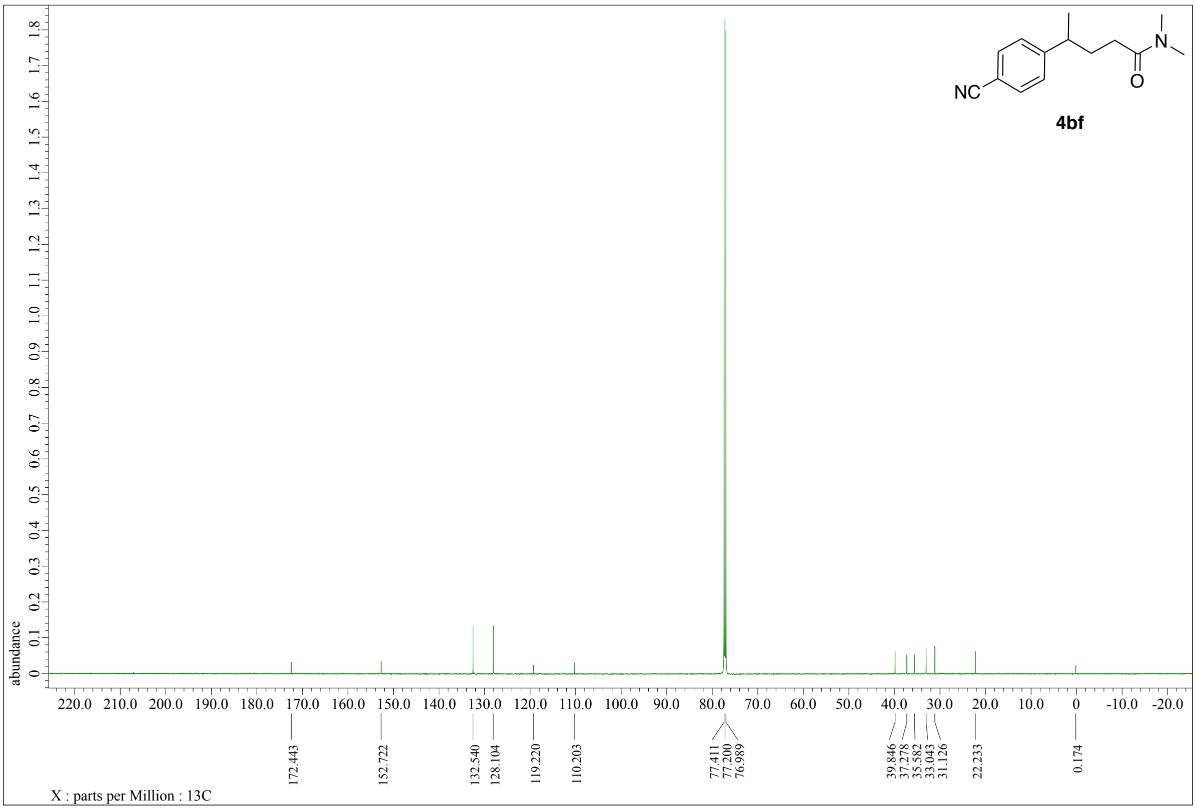
4be


abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
0.71
1.25
2.00
0.63
1.00
0.36
1.90
1.07
1.04
1.90
1.21
3.40
1.98
1.10
7.637
7.624
7.599
7.586
7.331
7.324
7.317
7.310
7.283
3.322
3.312
3.307
3.235
3.231
3.220
3.208
3.198
2.891
2.865
2.793
2.781
2.013
1.919
1.840
1.830
1.824
1.317
1.305
1.282
1.270
0.000
X : parts per Million : 1H
NC
O
N

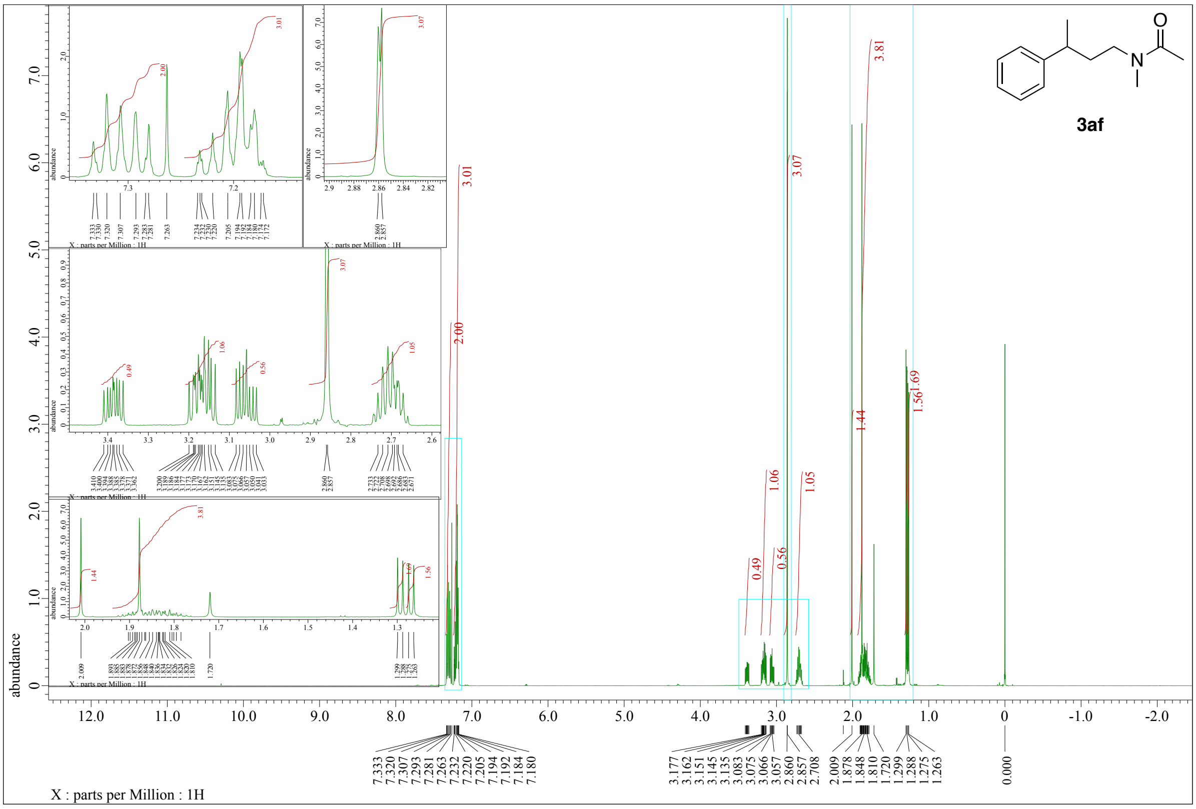
3bf


abundance
X : parts per Million : 13C
NC
N
O
3bf
170.546
170.229
152.597
151.687
132.742
132.464
127.874
127.759
119.153
118.875
110.634
110.098
77.411
77.200
76.980
49.065
46.181
38.246
37.997
36.205
36.119
34.940
33.234
22.415
22.367
22.013
21.150

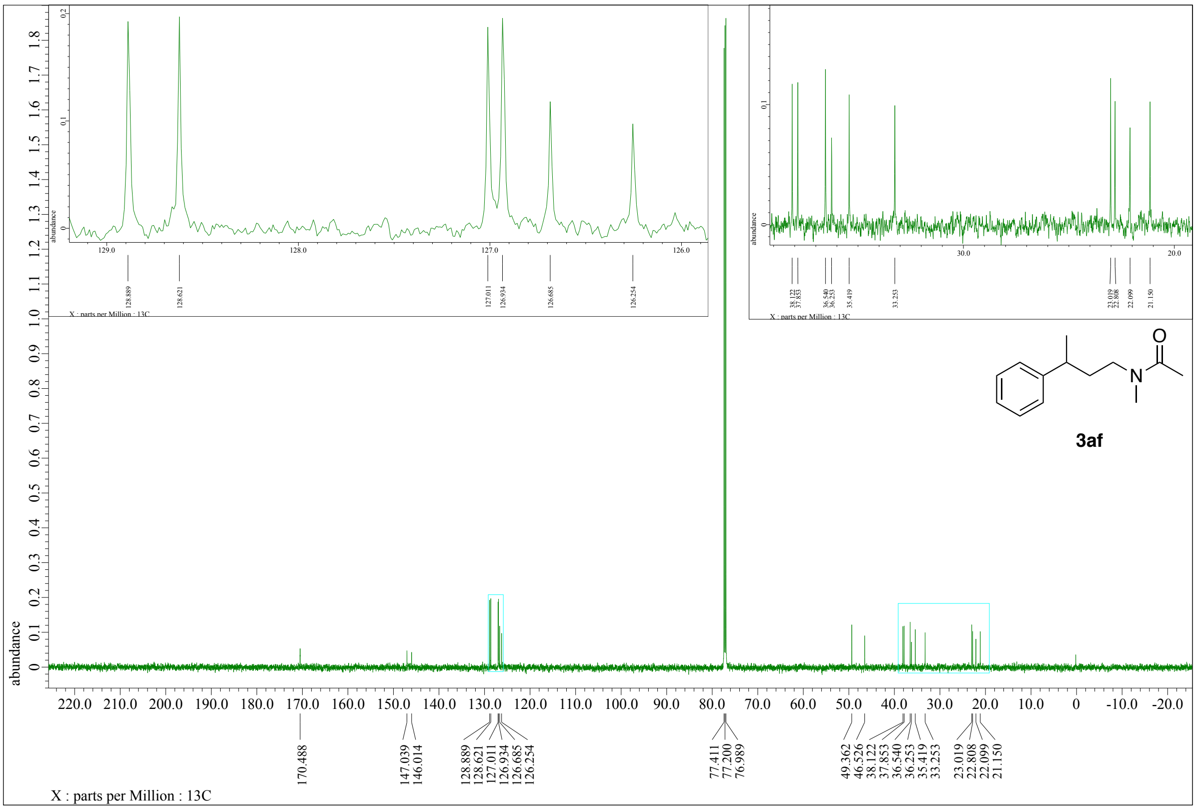

abundance
X : parts per Million : 1H
NC
N
O
4bf
2.00
2.06
3.05
3.07
1.09
1.10
1.11
1.16
1.07
3.42
7.599
7.596
7.588
7.585
7.313
7.310
7.302
7.299
7.264
2.915
2.873
2.854
2.851
2.844
2.840
2.833
2.829
2.179
2.152
2.123
1.908
1.607
1.286
1.274
0.000

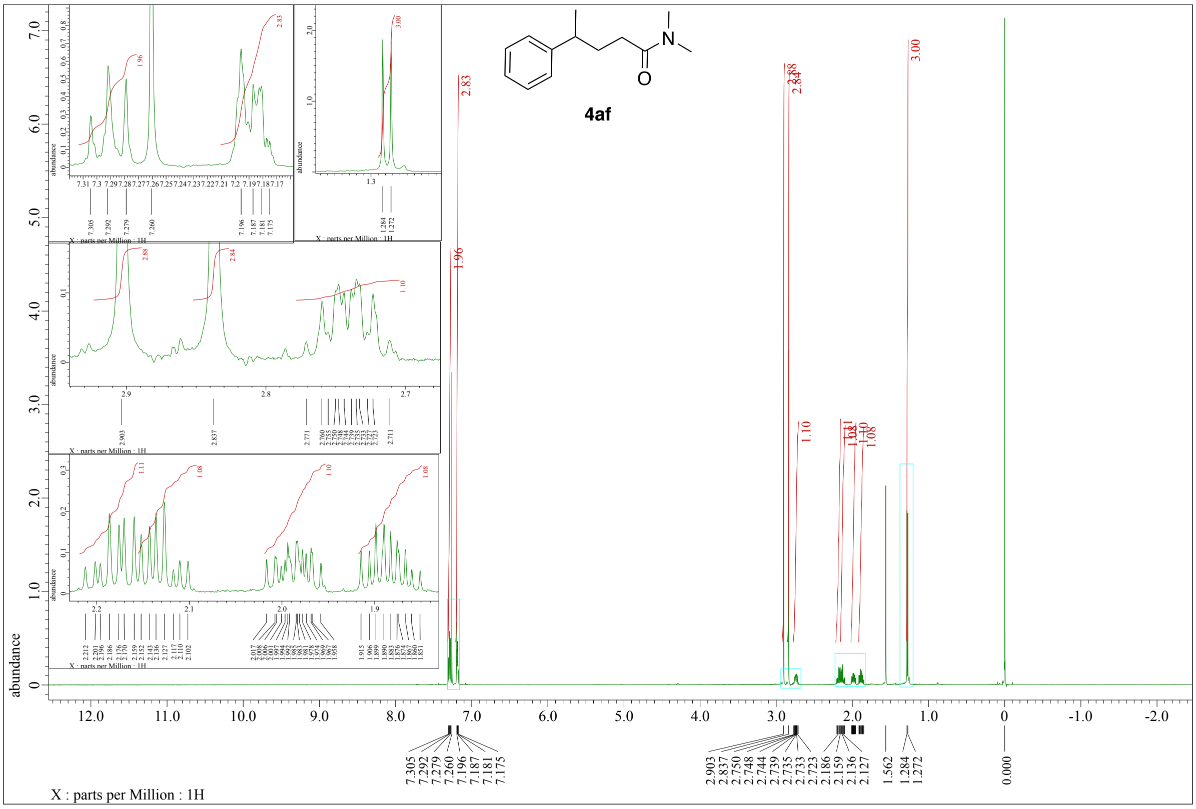

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
172.443
152.722
132.540
128.104
119.220
110.203
77.411
77.200
76.989
39.846
37.278
35.582
33.043
31.126
22.233
0.174
X : parts per Million : 13C
NC
N
O

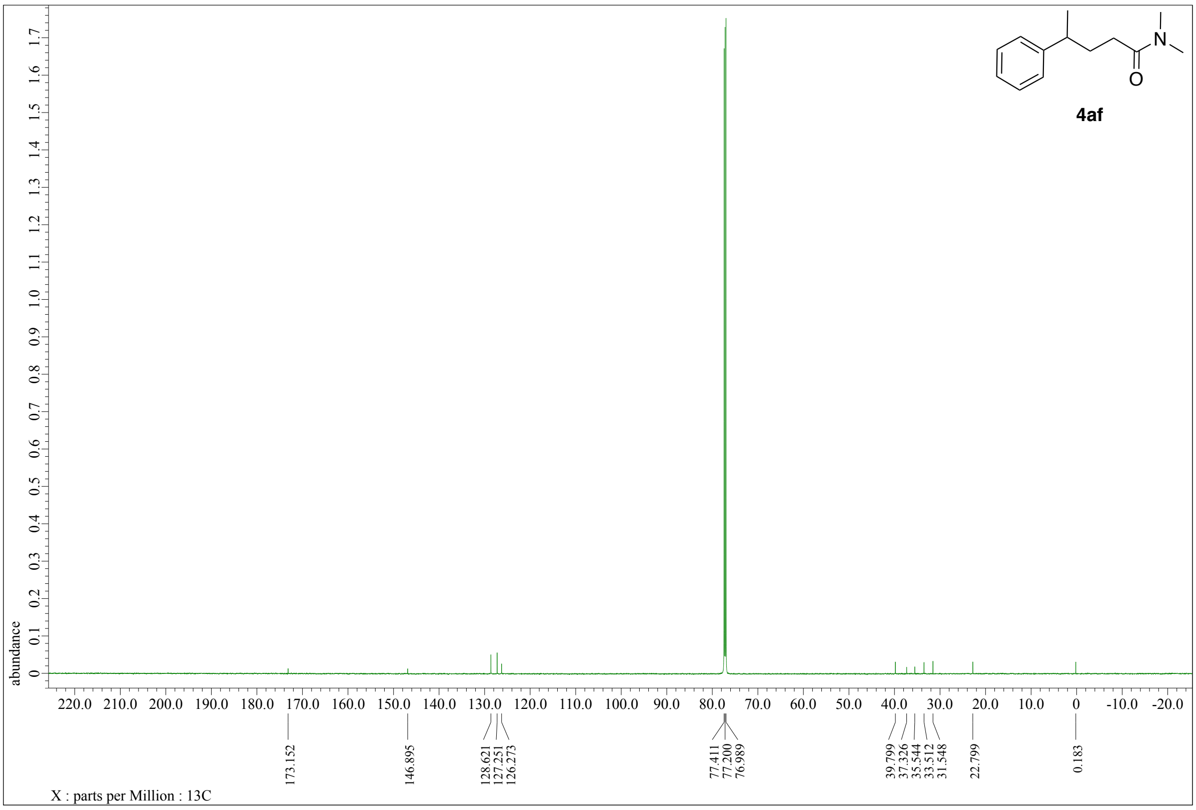
4bf


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
3.01
2.00
0.49
1.06
0.56
1.05
3.07
1.44
3.81
1.56
1.69
7.333
7.320
7.307
7.293
7.281
7.263
7.232
7.220
7.205
7.194
7.192
7.184
7.180
3.177
3.162
3.151
3.145
3.135
3.083
3.075
3.066
3.057
2.860
2.857
2.708
2.009
1.878
1.848
1.810
1.720
1.299
1.288
1.275
1.263
0.000
X : parts per Million : 1H
O
N

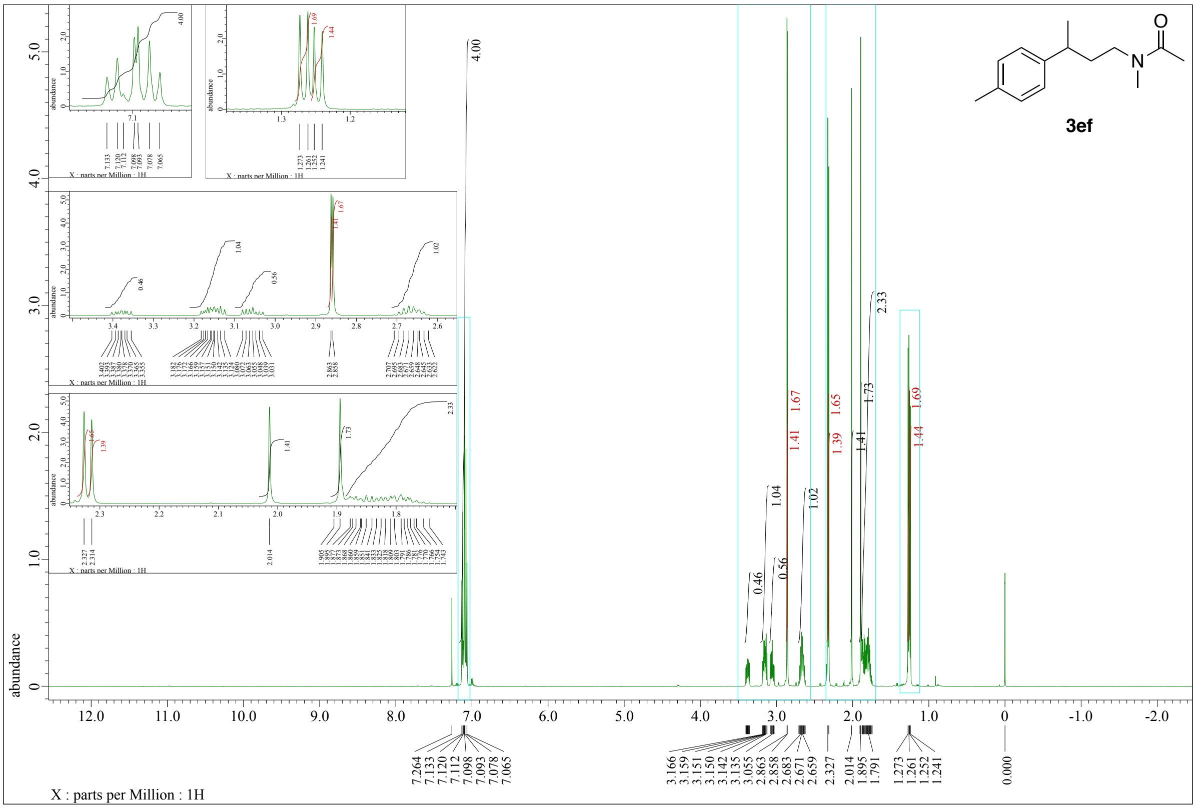
3af


3af
abundance
X : parts per Million : 13C
170.488
147.039
146.014
128.889
128.621
127.011
126.934
126.685
126.254
77.411
77.200
76.989
49.362
46.526
38.122
37.853
36.540
36.253
35.419
33.253
23.019
22.808
22.099
21.150

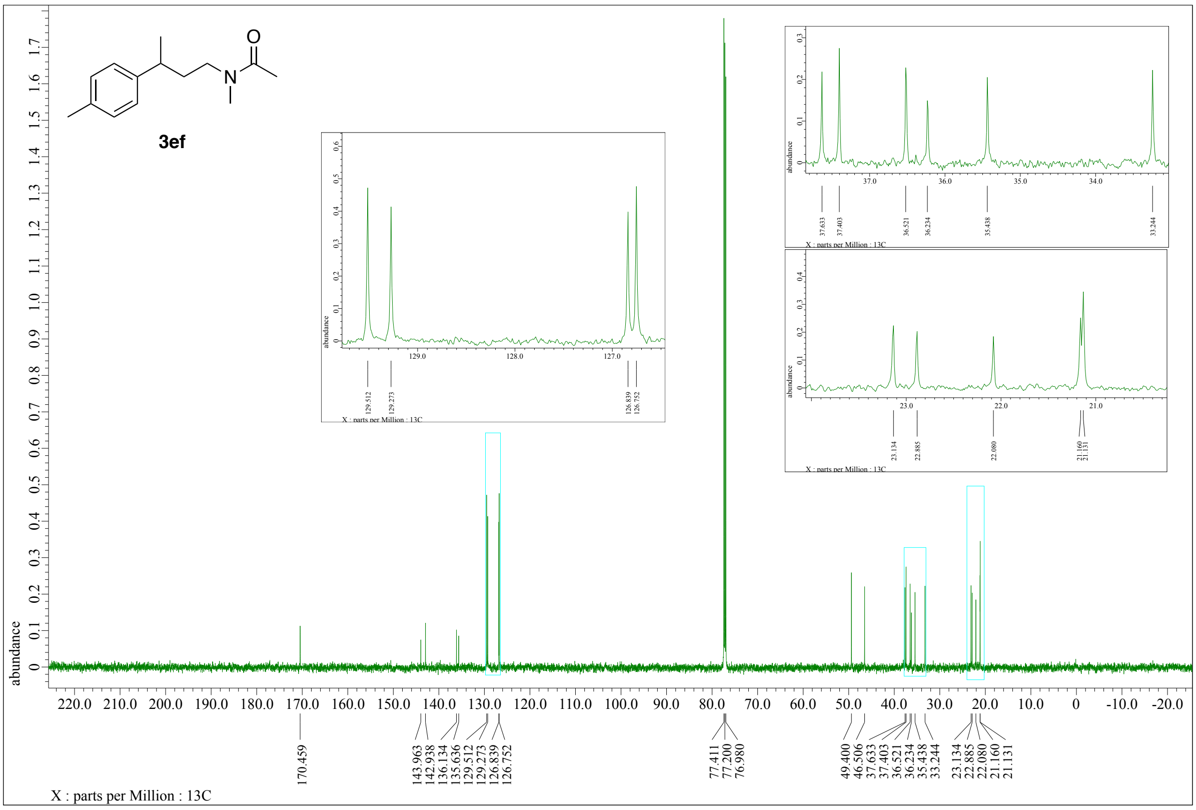

4af
abundance
X : parts per Million : 1H
1.96
2.83
2.88
2.84
1.10
1.11
1.08
1.10
1.08
3.00
7.305
7.292
7.279
7.260
7.196
7.187
7.181
7.175
2.903
2.837
2.750
2.748
2.744
2.739
2.735
2.733
2.723
2.186
2.159
2.136
2.127
1.562
1.284
1.272
0.000

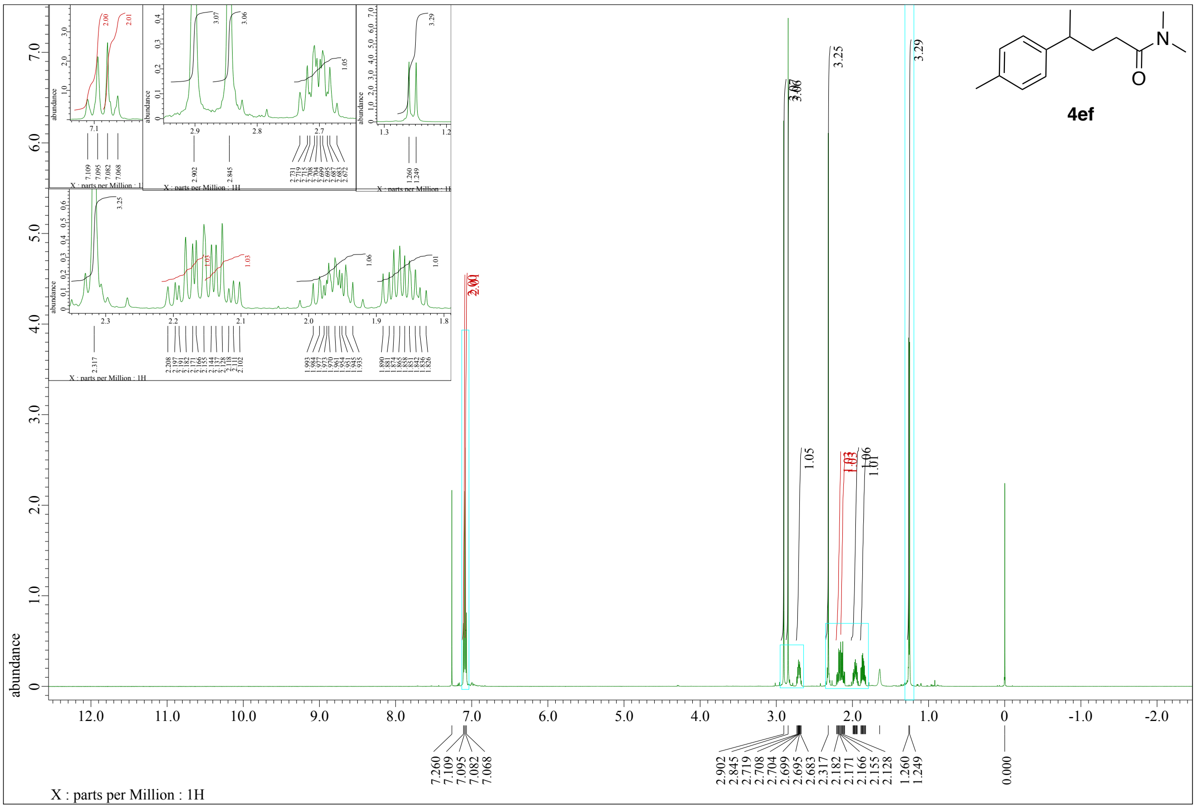


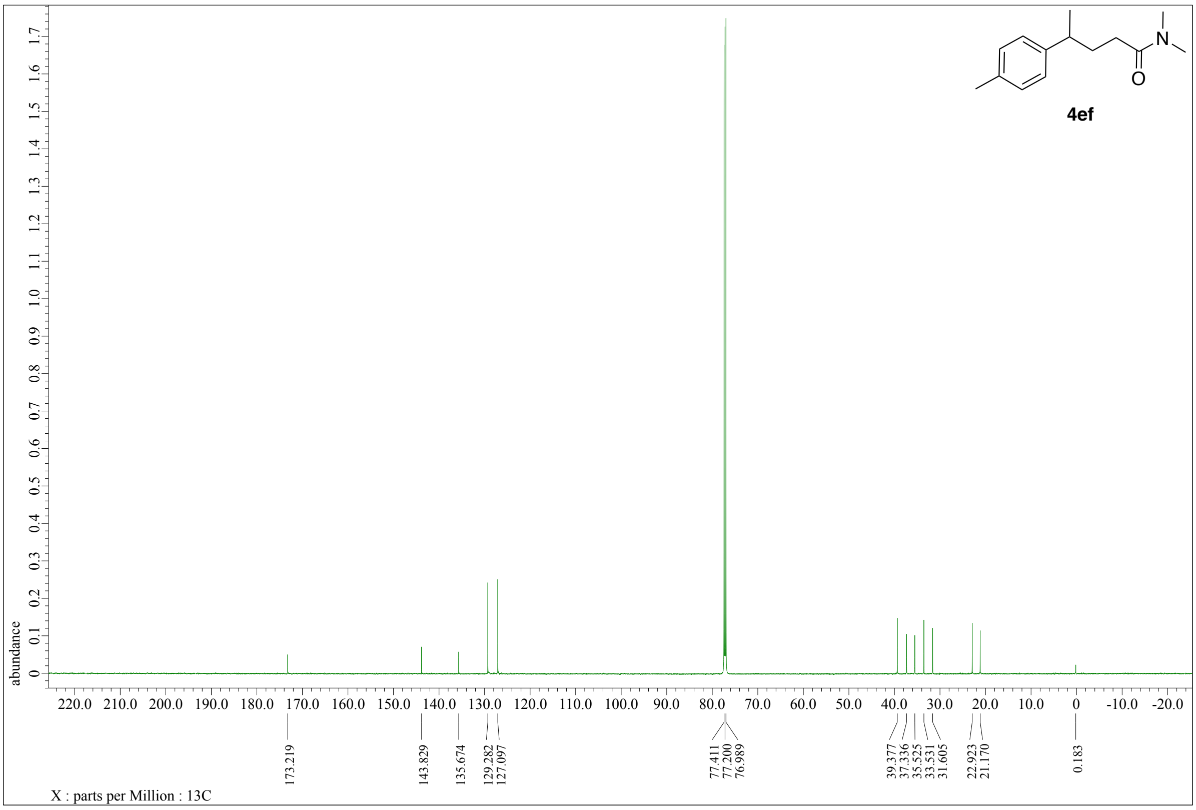
4af
abundance
X : parts per Million : 13C
173.152
146.895
128.621
127.251
126.273
77.411
77.200
76.989
39.799
37.326
35.544
33.512
31.548
22.799
0.183



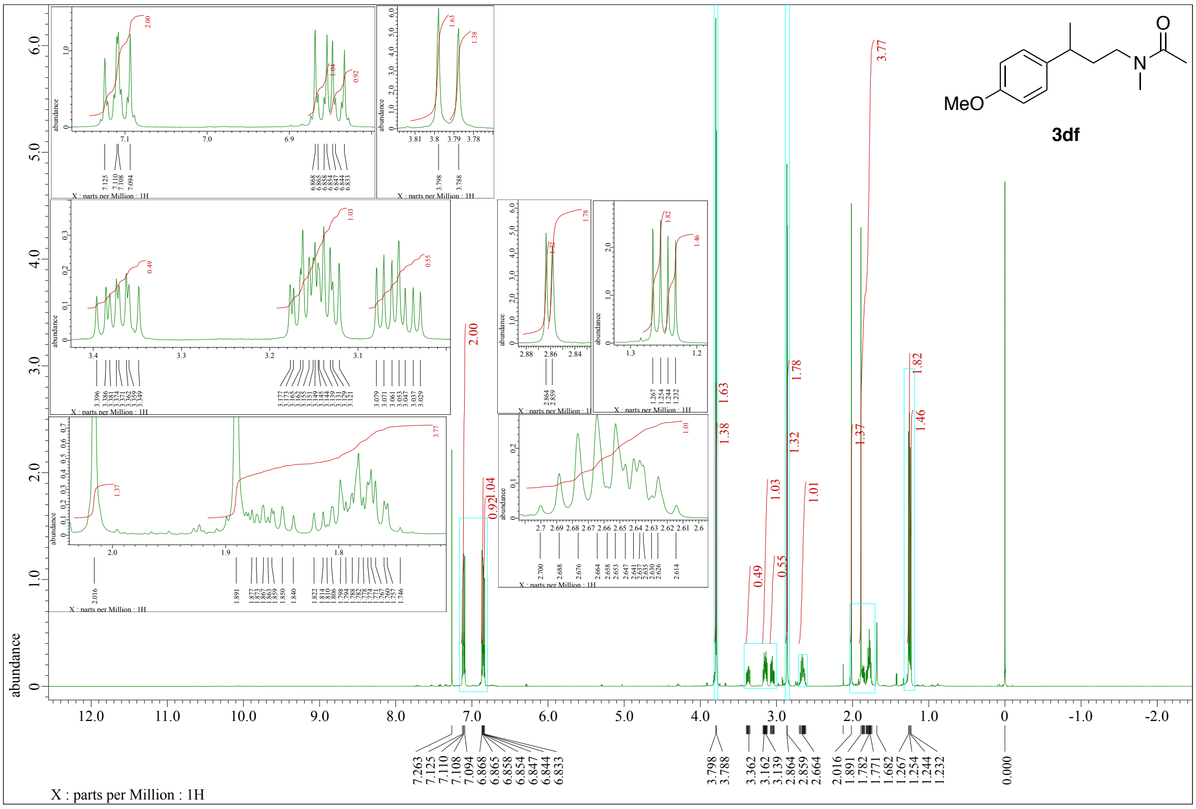
3ef
abundance
X : parts per Million : 1H
4.00
0.46
1.04
0.56
1.02
1.41
1.67
1.39
1.65
1.41
1.73
2.33
1.69
1.44
7.264
7.133
7.120
7.112
7.098
7.093
7.078
7.065
3.166
3.159
3.151
3.150
3.142
3.135
3.055
2.863
2.858
2.683
2.671
2.659
2.327
2.014
1.895
1.791
1.273
1.261
1.252
1.241
0.000


3ef
abundance
X : parts per Million : 13C
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
170.459
143.963
142.938
136.134
135.636
129.512
129.273
126.839
126.752
77.411
77.200
76.980
49.400
46.506
37.633
37.403
36.521
36.234
35.438
33.244
23.134
22.885
22.080
21.160
21.131

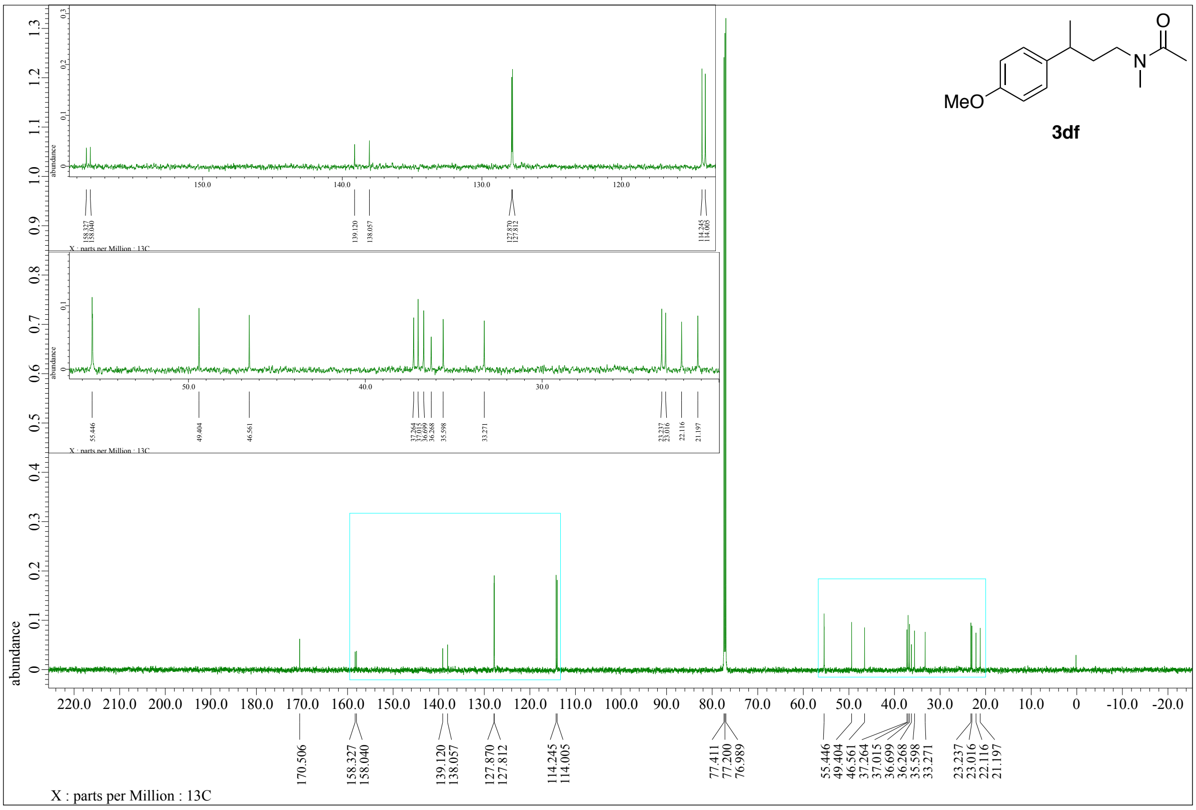

4ef
abundance
X : parts per Million : 1H
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
2.00
2.01
3.07
3.06
3.25
1.05
1.03
1.03
1.06
1.01
3.29
7.260
7.109
7.095
7.082
7.068
2.902
2.845
2.719
2.708
2.704
2.699
2.695
2.683
2.317
2.182
2.171
2.166
2.155
2.128
1.260
1.249
0.000


abundance
X : parts per Million : 13C
173.219
143.829
135.674
129.282
127.097
77.411
77.200
76.989
39.377
37.336
35.525
33.531
31.605
22.923
21.170
0.183

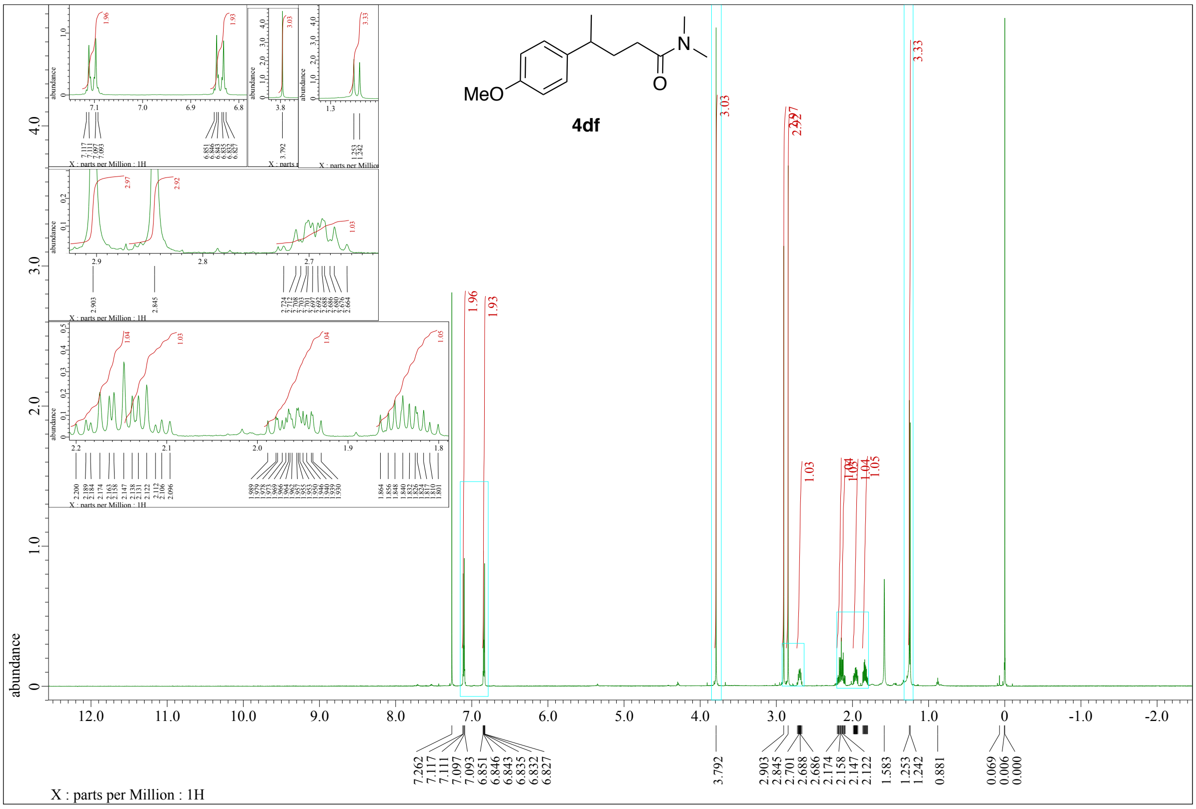
4ef


abundance
X : parts per Million : 1H
MeO
2.00
0.92
1.04
1.63
1.38
0.49
1.03
0.55
1.78
1.32
1.01
1.37
3.77
1.82
1.46
7.263
7.125
7.110
7.108
7.094
6.868
6.865
6.858
6.854
6.847
6.844
6.833
3.798
3.788
3.362
3.162
3.139
2.864
2.859
2.664
2.016
1.891
1.782
1.771
1.682
1.267
1.254
1.244
1.232
0.000

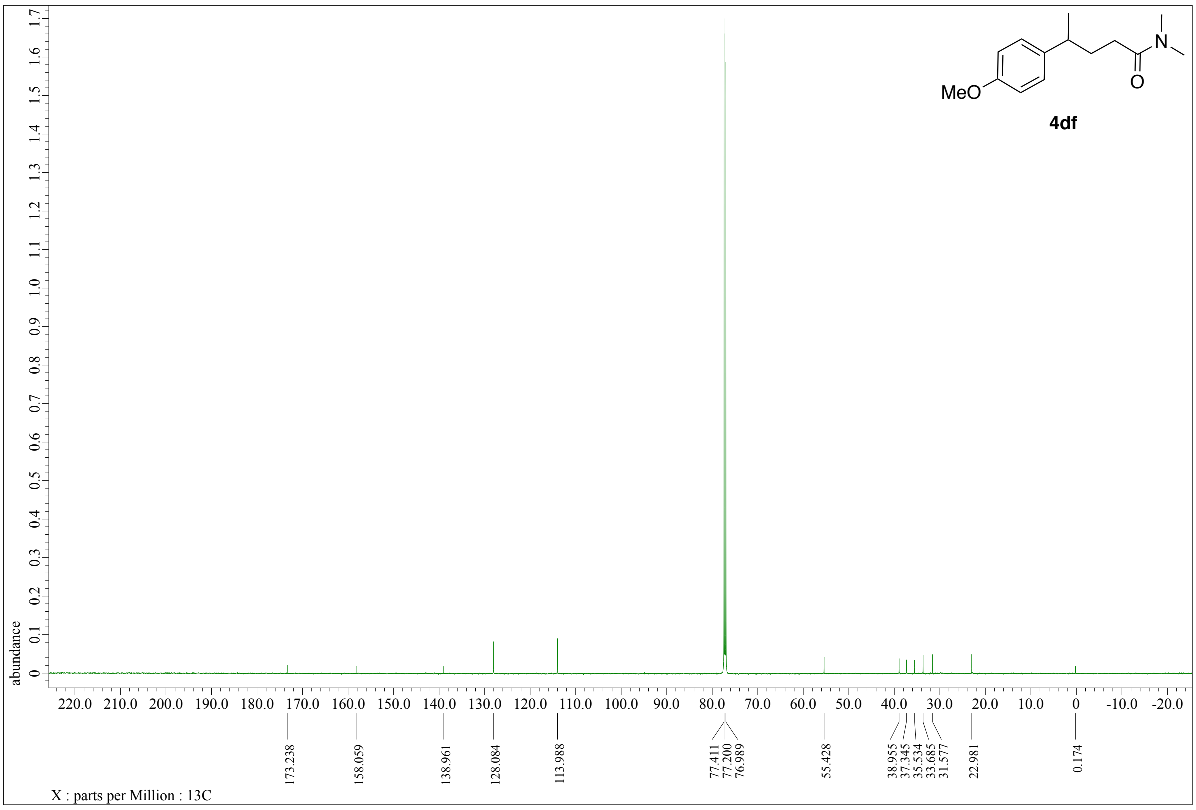
3df

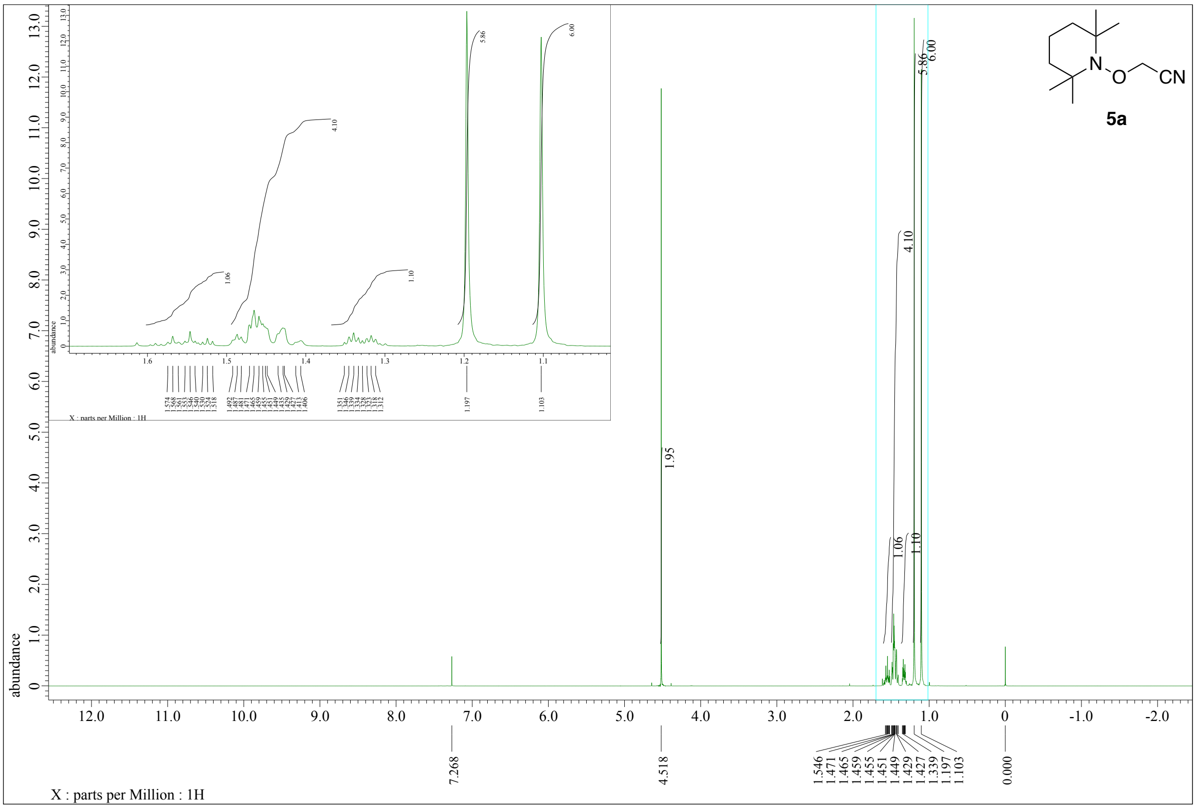

MeO
N
O
abundance
X : parts per Million : 13C
170.506
158.327
158.040
139.120
138.057
127.870
127.812
114.245
114.005
77.411
77.200
76.989
55.446
49.404
46.561
37.264
37.015
36.699
36.268
35.598
33.271
23.237
23.016
22.116
21.197

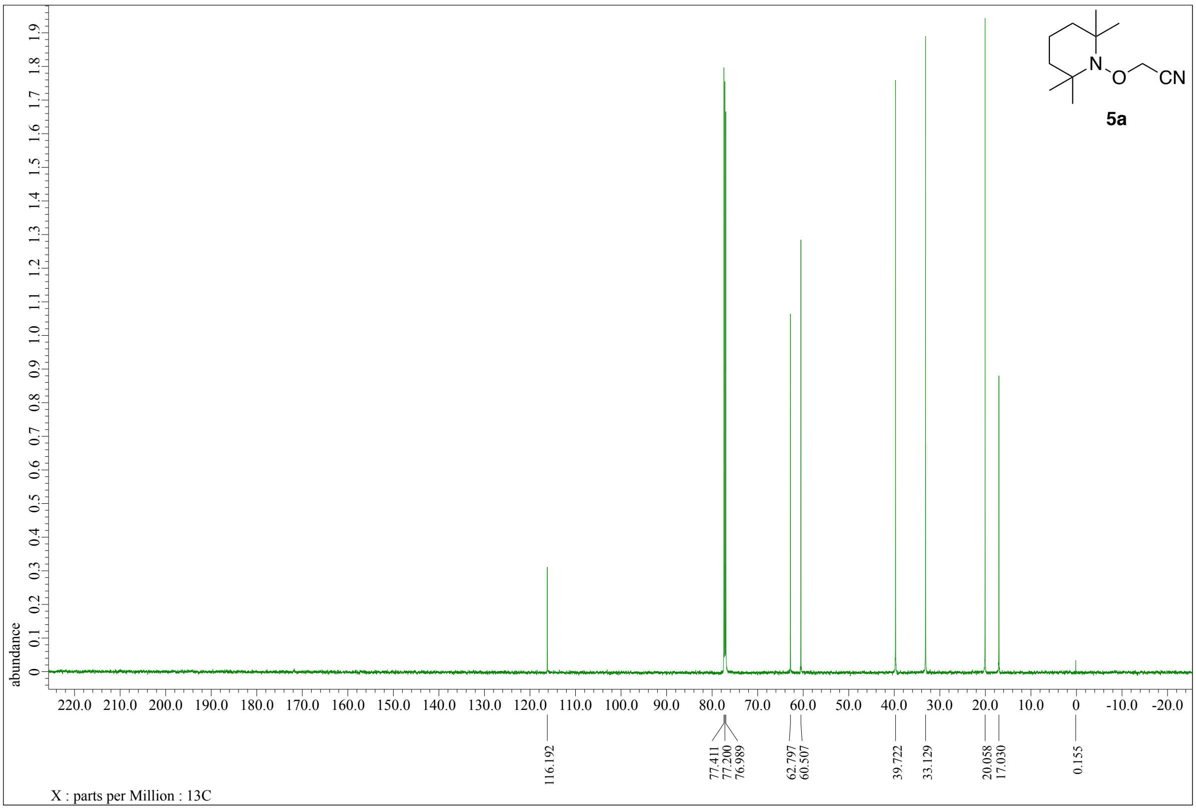
3df

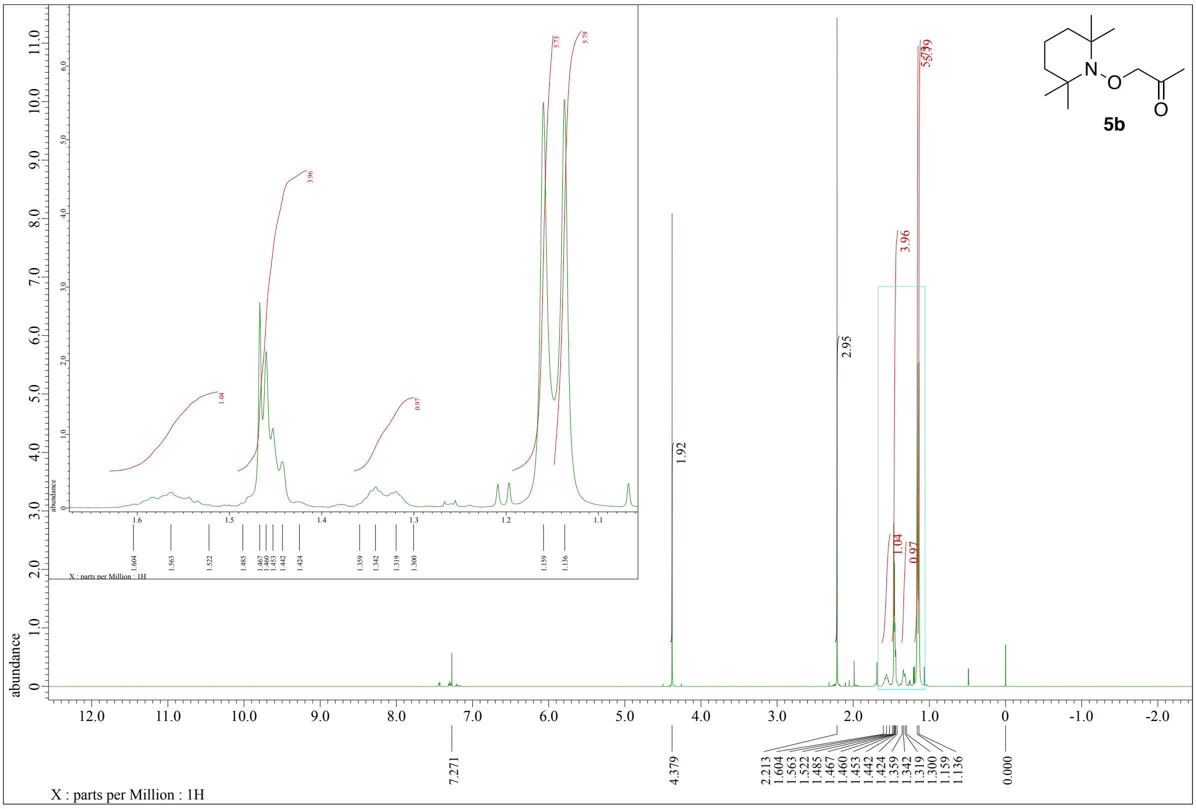

MeO
N
O
abundance
X : parts per Million : 1H
1.96
1.93
3.03
2.97
2.92
1.03
1.04
1.03
1.04
1.05
3.33
7.262
7.117
7.111
7.097
7.093
6.851
6.846
6.843
6.835
6.832
6.827
3.792
2.903
2.845
2.701
2.688
2.686
2.174
2.158
2.147
2.122
1.583
1.253
1.242
0.881
0.069
0.006
0.000

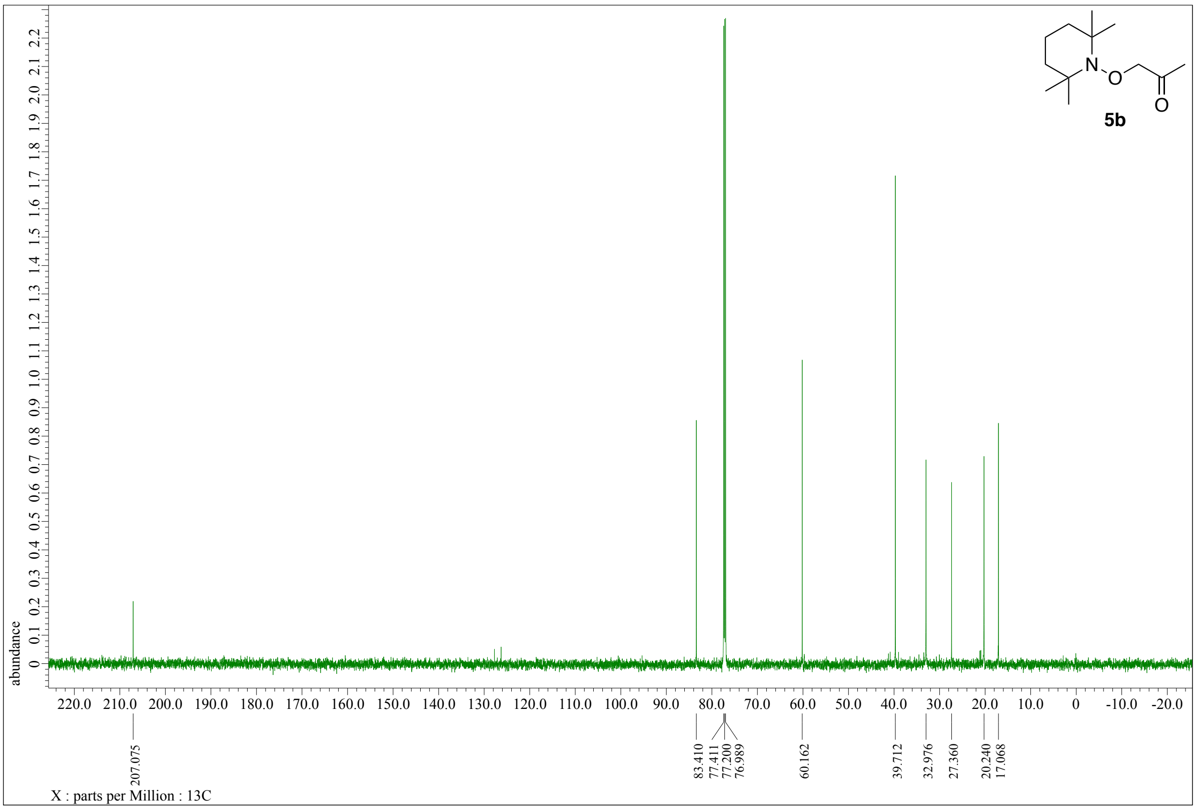
4df

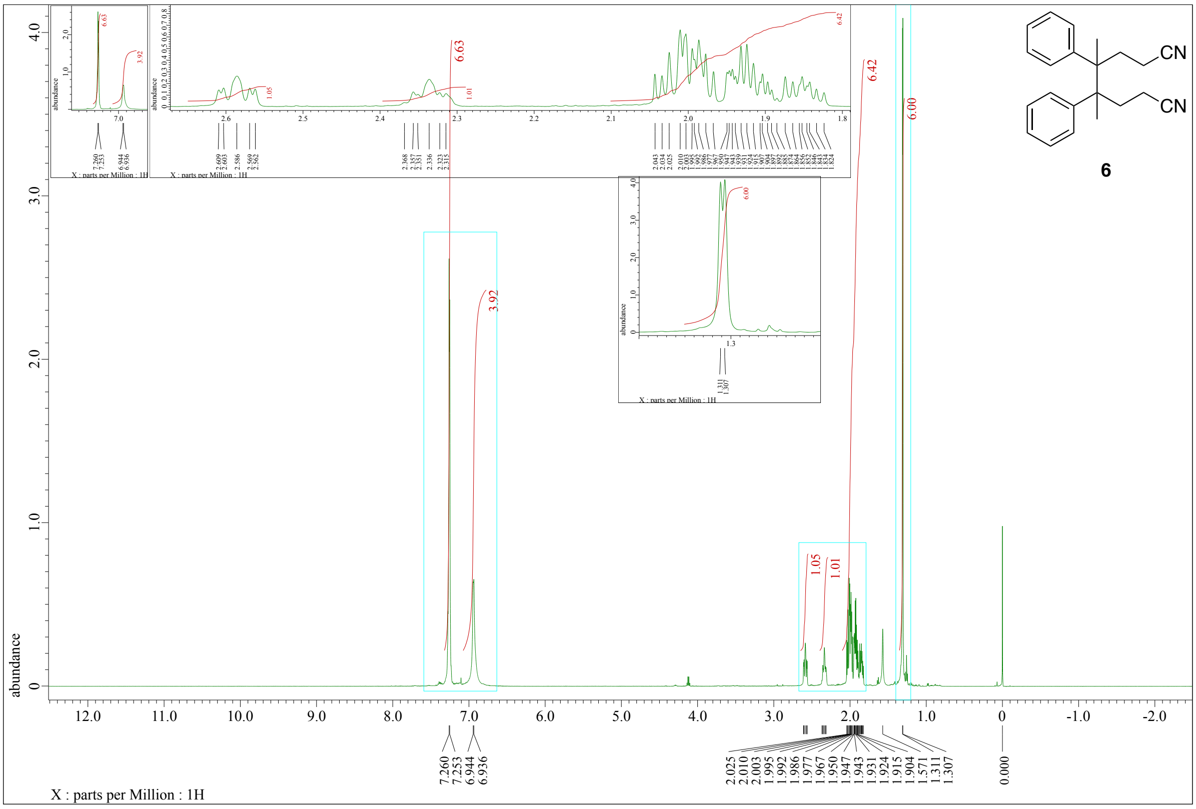

MeO
N
O
4df
abundance
X : parts per Million : 13C
173.238
158.059
138.961
128.084
113.988
77.411
77.200
76.989
55.428
38.955
37.345
35.534
33.685
31.577
22.981
0.174

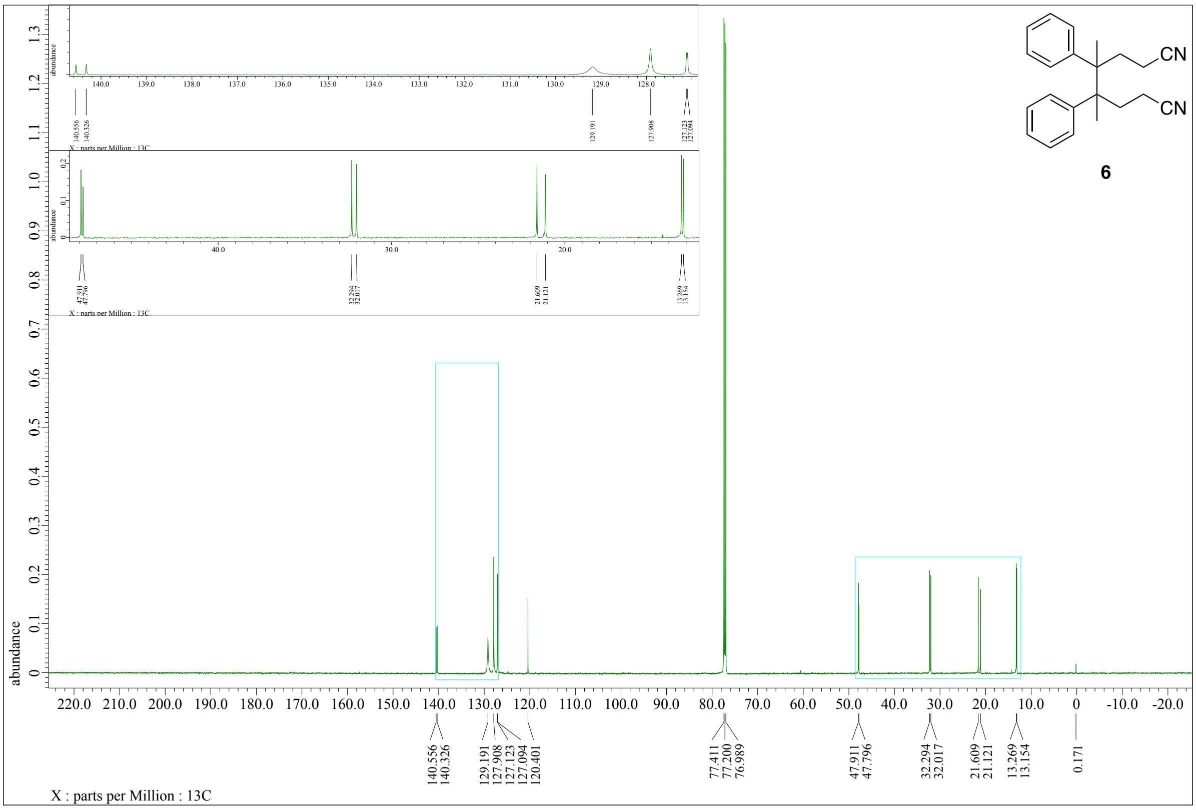

N
O
CN
5a
abundance
X : parts per Million : 1H
1.95
1.06
4.10
1.10
5.86
6.00
7.268
4.518
1.546
1.471
1.465
1.459
1.455
1.451
1.449
1.429
1.427
1.339
1.197
1.103
0.000


5a
N
O
CN
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
116.192
77.411
77.200
76.989
62.797
60.507
39.722
33.129
20.058
17.030
0.155
X : parts per Million : 13C

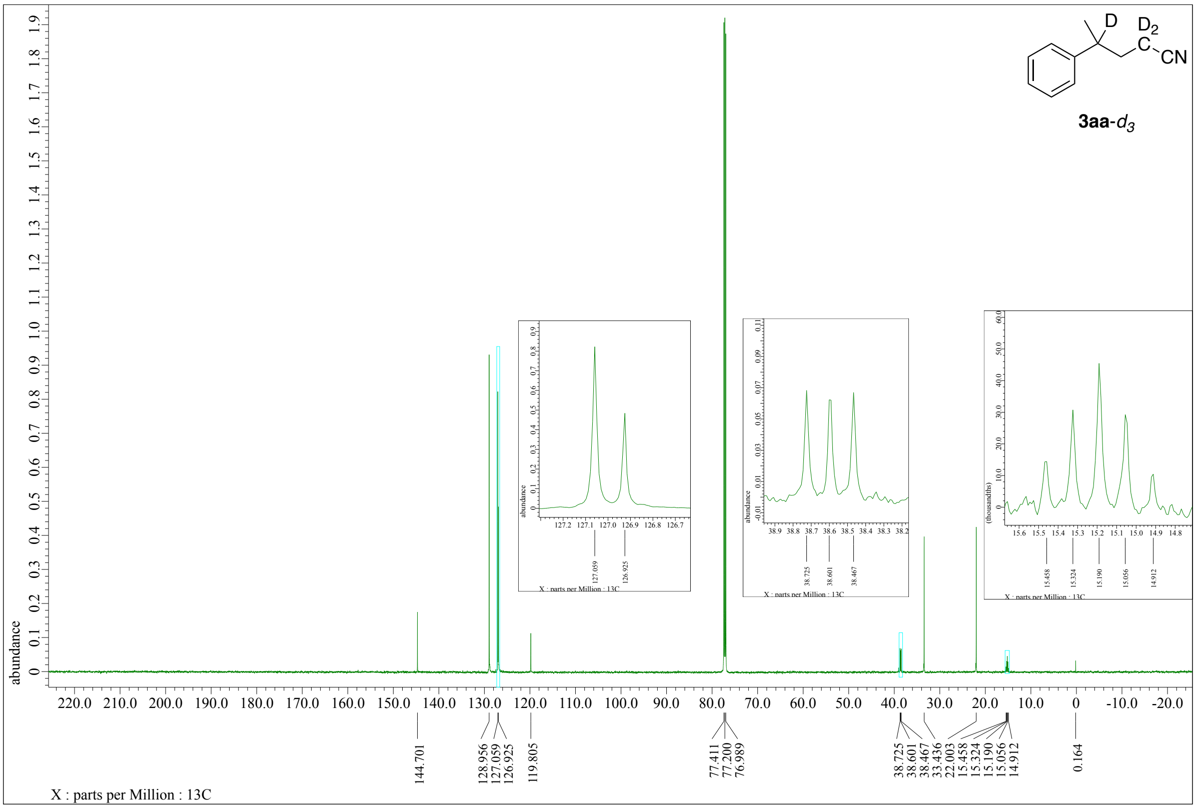

5b
N
O
O
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
1.92
2.95
3.96
1.04
0.97
5.73
5.79
7.271
4.379
2.213
1.604
1.563
1.522
1.485
1.467
1.460
1.453
1.442
1.424
1.359
1.342
1.319
1.300
1.159
1.136
0.000
X : parts per Million : 1H
1.00
3.96
0.97
5.73
5.79
1.6
1.5
1.4
1.3
1.2
1.1
X : parts per Million : 1H


5b
N
O
O
abundance
207.075
83.410
77.411
77.200
76.989
60.162
39.712
32.976
27.360
20.240
17.068
X : parts per Million : 13C

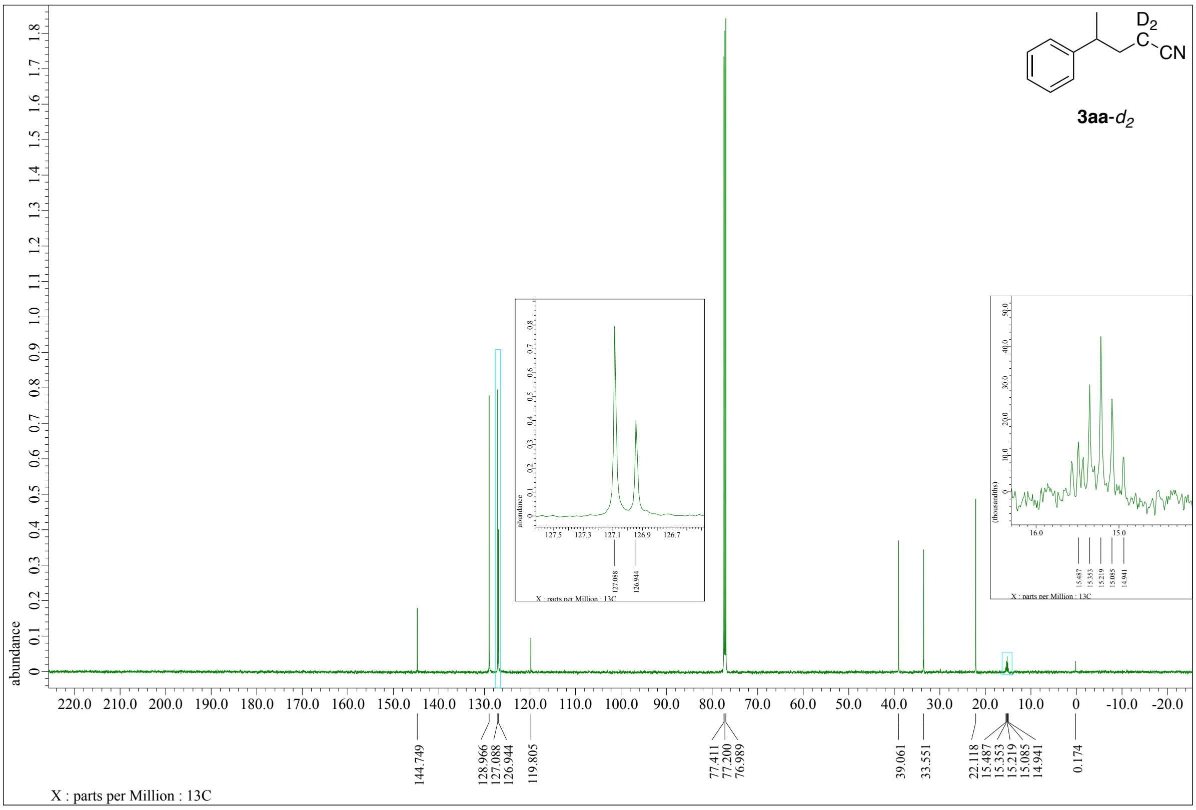

6
CN
CN
abundance
6.63
3.92
1.05
1.01
6.42
6.00
7.260
7.253
6.944
6.936
2.025
2.010
2.003
1.995
1.992
1.986
1.977
1.967
1.950
1.947
1.943
1.931
1.924
1.915
1.904
1.571
1.311
1.307
0.000
X : parts per Million : 1H


CN
CN
abundance
X : parts per Million : 13C
140.556
140.326
129.191
127.908
127.123
127.094
120.401
77.411
77.200
76.989
47.911
47.796
32.294
32.017
21.609
21.121
13.269
13.154
0.171

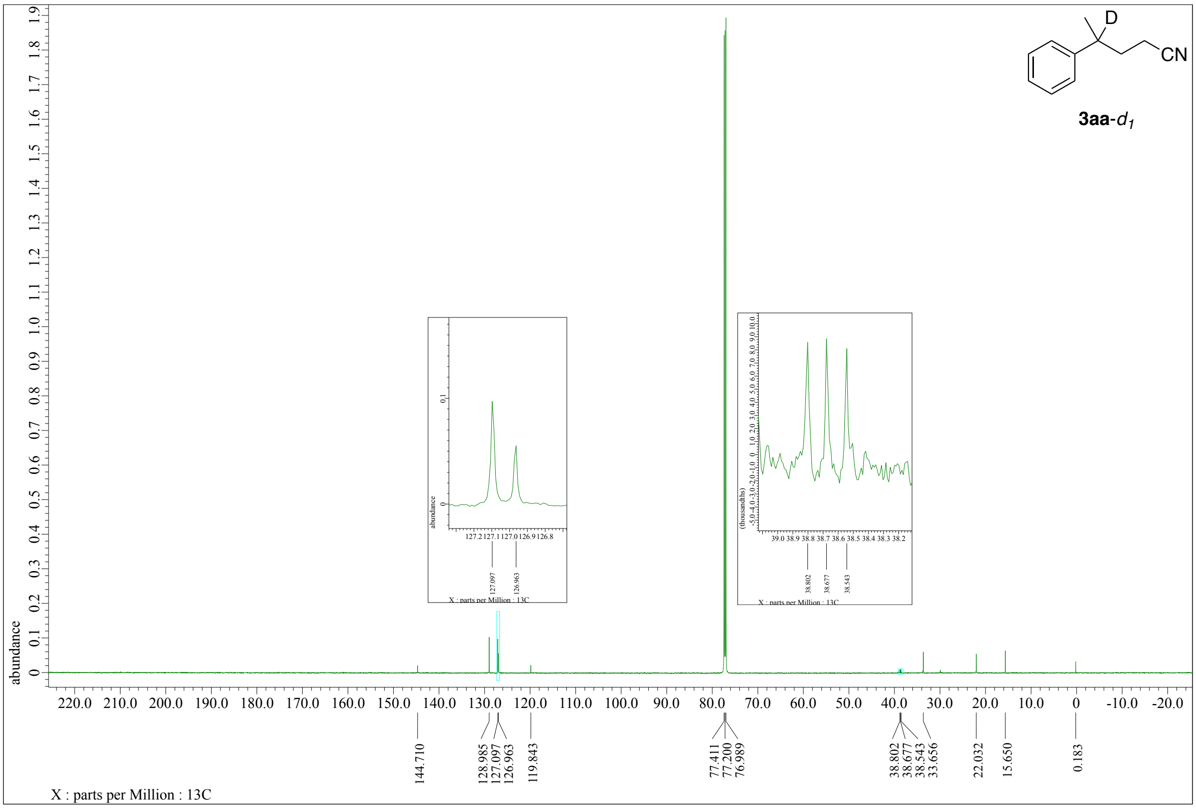
6


D
D_2
C
CN
abundance
X : parts per Million : 13C
144.701
128.956
127.059
126.925
119.805
77.411
77.200
76.989
38.725
38.601
38.467
33.436
22.003
15.458
15.324
15.190
15.056
14.912
0.164

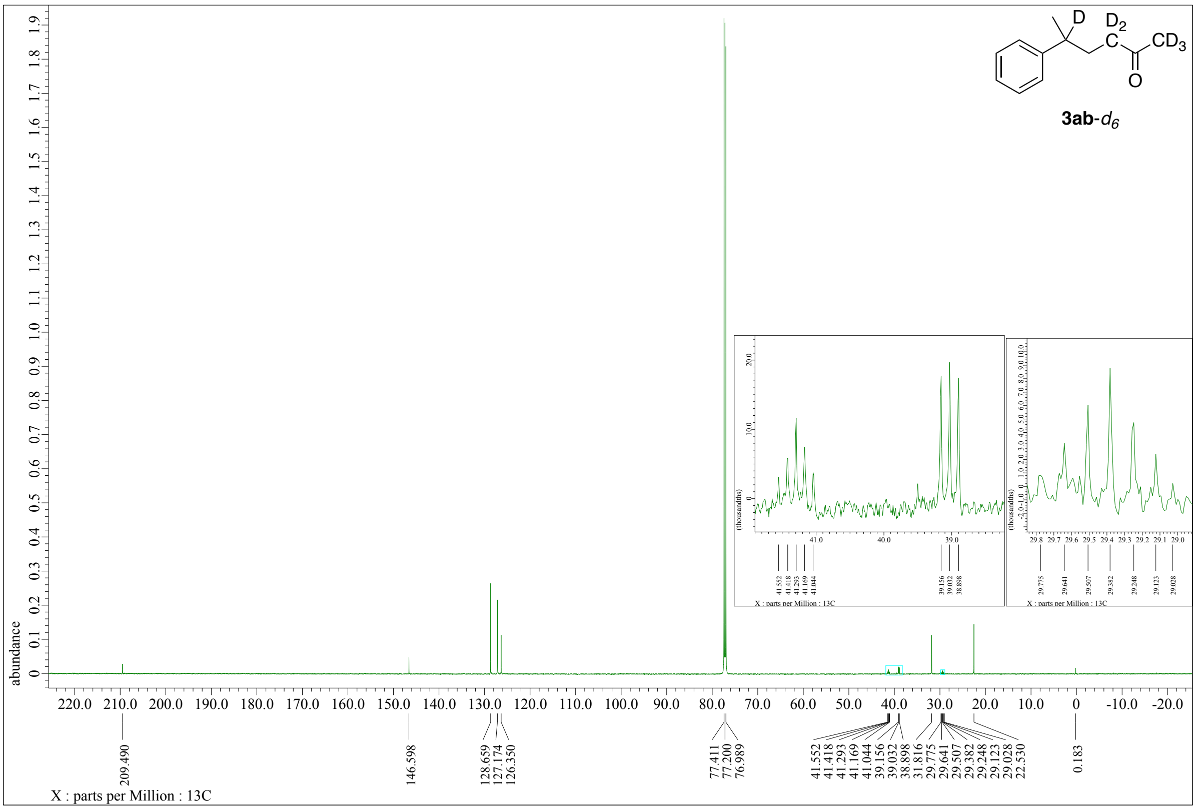
3aa-*d*$_3$



D2
C
CN
3aa-d2
abundance
X : parts per Million : 13C
144.749
128.966
127.088
126.944
119.805
77.411
77.200
76.989
39.061
33.551
22.118
15.487
15.353
15.219
15.085
14.941
0.174



D
CN
3aa-d1
abundance
X : parts per Million : 13C
144.710
128.985
127.097
126.963
119.843
77.411
77.200
76.989
38.802
38.677
38.543
33.656
22.032
15.650
0.183


3ab-*d*$_6$
D
D$_2$
C
CD$_3$
O
abundance
X : parts per Million : 13C
209.490
146.598
128.659
127.174
126.350
77.411
77.200
76.989
41.552
41.418
41.293
41.169
41.044
39.156
39.032
38.898
31.816
29.775
29.641
29.507
29.382
29.248
29.123
29.028
22.530
0.183
(thousandths)