Supporting Information

Unexpected Nucleophilic Behaviour of Radicals Generated from α-Iodoketones

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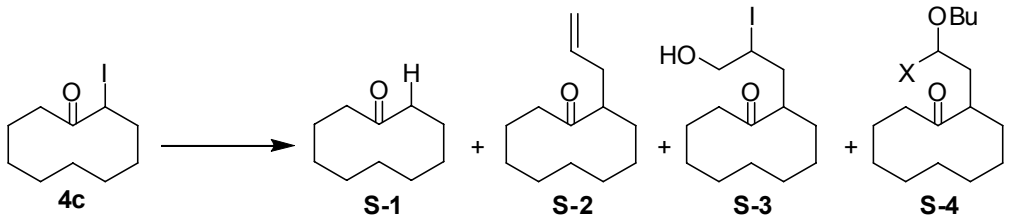
Full notation of reference 14

Gaussian 03, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

General information

- All compounds (Acros, Aldrich and Fluka) were used as received. THF was distilled under argon from sodium benzophenone ketyl. Flash chromatography was performed on silica gel 60 (40-63 μm) (ROCC).
- ^{1}H and ^{13}C-NMR spectra were recorded on a Varian Gemini-2000 (working frequency 300 MHz and 75 MHz, respectively), on a Bruker AC-250 (working frequency 250 MHz and 62.5 MHz, respectively), on a Brucker AC-300 Avance II (working frequency 300 MHz and 75 MHz, respectively) or on a Brucker AM-500 (working frequency 500 MHz and 125 MHz, respectively) at ambient temperature in $CDCl_3$ (Aldrich).
- Mass spectra were recorded on a Finigan TSQ 7000.
- All reactions were carried out under an atmosphere of argon in flame-dried apparatus with magnetic stirring, unless otherwise indicated.
- The identity of known products was confirmed by comparison with literature spectroscopic data. The structure determination of new compounds was made with a help of 2D-COSY, HSQC, HMBC, 2D-NOESY and NOEdiff experiments: **4a,b**,[1] **4d**,[2] **4e**,[3] **4k**,[4] **8**,[5] and **9**[6].
- The α-iodoketones **4a-d,h,i,l**[1] and **4f**[3] were prepared according to published procedures.

Table S-1: The reaction of α-iodoketone **4c** with electron rich olefins.

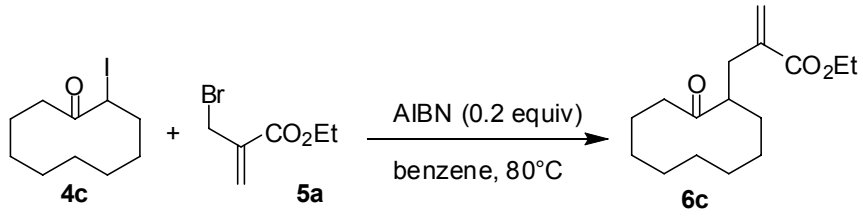


4c **S-1** **S-2** **S-3** **S-4**

Entry	Conditions	Product(s), (Yield(%))[a]
1[b]	nBu$_3$SnH (1.0 equiv), AIBN (0.2 equiv), benzene, Δ, 2h	**4c** (<5%), **S-1** (quant)
2	nBu$_3$Snallyl (1.5 equiv), AIBN (0.2 equiv), benzene, Δ, 12h	**4c** (~50%), **S-1** (<5%), **S-2** (<5%)
3	nBu$_3$Snallyl (1.5 equiv), hν, benzene, r.t., 48h	degradation
4[c]	Sn(allyl)$_4$ (2.0 equiv), AIBN (0.2 equiv), toluene, Δ, 24h	**4c** (41%), **S-1** (<5%), **S-2** (19%)
5	allylMgCl (3.0 equiv), $GaCl_3$ (3.0 equiv), Et_3B (0.5 equiv), H_2O/THF, r.t, 2h	**4c** (<5%), **S-1** (91%), **S-2** (<5%)
6	allylMgCl (3.0 equiv), Cp_2ZrCl_2 (3.0 equiv), Et_3B (0.5 equiv), THF, r.t, 2h	**4c** (<5%), **S-1** (60%), **S-2** (<5%)
7	allylSiMe$_3$ (2.0 equiv), Yb(OTf)$_3$ (1.0 equiv), Et_3B (0.5 equiv), THF, r.t, 2h	**4c** (<5%), **S-1** (95%), **S-2** (<5%)
8	allylOH (5.0 equiv), Et_3B (1.0 equiv), bezene, r.t, 2h	**4c** (<5%), **S-1** (45%), **S-3** (<5%)
9	allylOH (5.0 equiv), Et_3B (1.0 equiv), EtOH, r.t, 2h	**4c** (<5%), **S-1** (80%), **S-3** (<5%)
10	CH_2=CHOBu (10.0 equiv), AIBN (0.2 equiv), toluene, Δ, 3h	degradation
11	CH_2=CHOBu (10.0 equiv), hν, K_2CO_3 (10.0 equiv), MeOH, r.t., 3h	degradation
12	nBu$_3$SnH (1.0 equiv), AIBN (0.2 equiv), toluene/CH_2=CHOBn = 1:1, 90°C, 3h	degradation

[a] Refers to pure, isolated compounds. [b] Reference reaction. To prove that the radical is formed. [c] The reaction proved to be irreproducible. The best obtained result shown.

Table S-2: The addition of **4c** to **5a**. The reaction optimization (part I).

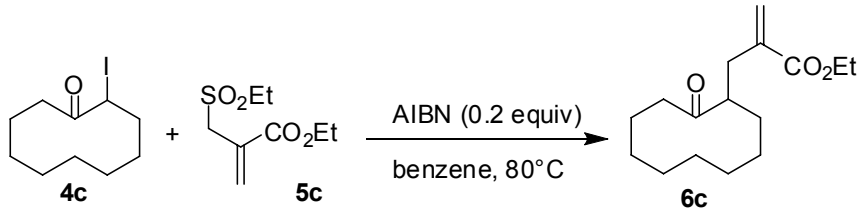


4c **5a** **6c**

Entry	**5a** (equiv)	Bu_6Sn_2 (equiv)	Yield(%)[a]
1	1.2	1.1	60
2	2.0	1.1	67
3	2.0	1.2	70
4	2.0	1.5	70
5	3.0	1.2	90
6	5.0	1.2	93
7	10.0	1.2	95

[a] Refers to pure, isolated compounds.

Table S-2: The addition of **4c** to **5c**. The reaction optimization (part II).

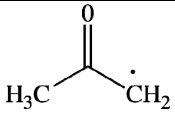
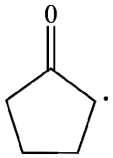
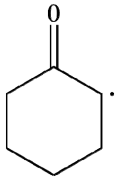


4c + **5c** → **6c**

Entry	**5c** (equiv)	Time (h)	Product(s) (Yield(%))[a]
1	1.0	5	**4c** (62%), **6c** (12%)
2	1.0	15	**4c** (51%), **6c** (19%)
3	2.0	5	**4c** (48%), **6c** (23%)
4	5.0	2	**4c** (10%), **6c** (62%)
5	5.0	10	**4c** (<5%), **6c** (82%)
6	10.0	2	**4c** (<5%), **6c** (89%)

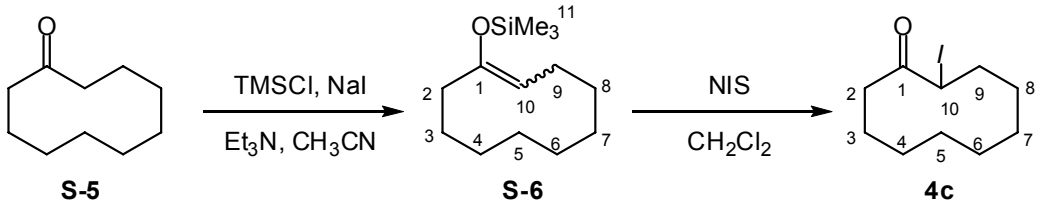
[a] Refers to pure, isolated compounds.

Table S-3: Activation barriers (DE^{π} at 0K and DH^{π} at 298.15 K) and reaction energies (DE_R at 0K and DE_R at 298.15 K) for the addition of the three different radicals to substituted alkenes R-CH=CH_2. All values are in kcal/mol and were obtained at the B3LYP[7]/6-31+G(d)[8] //B3LYP/6-31+G(d) level of theory using the Gaussian03 program.[9]

Radical		R=CH_3	R=OCH_3	R=$COOCH_3$
	DE^{π}	7.1	5.2	5.8
	DH^{π}	6.7	5.3	5.6
	DE_R	−11.8	−14.3	−28.3
	DE_R	−12.1	−14.4	−28.6
	DE^{π}	9.9	7.5	7.4
	DH^{π}	9.5	7.8	7.2
	DE_R	−7.6	−9.4	−12.8
	DE_R	−7.9	−9.4	−13.1
	DE^{π}	13.4	10.7	10.8
	DH^{π}	13.0	11.0	10.6
	DE_R	−7.3	−8.7	−12.8
	DE_R	−7.6	−8.6	−13.1

Synthesis of unknown α-iodoketones

Synthesis of α-iodoketone 4c



S-5 **S-6** **4c**

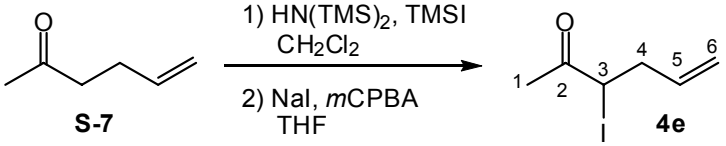
A solution of sodium iodide (3.6 g, 0.024 mol, 1.25 equiv) in acetonitrile (30 mL) was added to neat cyclodecanone **S-5** (3.0 g, 0.020 mol, 1.0 equiv), chloro(trimethyl)silane (2.6 g, 0.024 mol, 1.25 equiv) and triethylamine (2.5 g, 0.024 mol, 1.25 equiv). The reaction mixture was stirred at rt under inert atmosphere for 17h. The organic layer was extracted with pentane (3x20 mL). The pentane layer was dried over $MgSO_4$ and evaporated under reduced pressure to give the desired product **S-6**[10] as colorless liquid (4.25 g, *Z*: *E* 2:1, 99%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 0.10 and 0.13 (2 s, 9H, H-11), 1.2-1.4 (m, 12H, H-4 to 8), 1.93 (t, 2H, *J*= 6 Hz, H-2), 2.03-2.11 and 2.11-2.19 (2 m, 2H, H-9), 4.49 (t, *J*= 8.4 Hz, H-10 *E*) and 4.57 (t, *J*= 7.6 Hz, H-10 *Z*) (1H). ^{13}C-NMR (50 MHz, $CDCl_3$) δ(ppm): 0.5 (C-11), 21.0 (C-3), 21.05 (C-4), 24.9 (C-5), 25.6 (C-6), 26.4 (C-7), 26.7 (C-8), 27.4 (C-9 *Z*), 28.2 (C-9 *E*), 29.0 (C-2 *E*), 37.6 (C-2 *Z*), 107.1 (C-10 *E*), 110.8 (C-10 *Z*), 149.7 (C-1 *Z*), 151.16 (C-1 *E*).

A solution of **S-6** (4.2 g, 18 mmol, 1.0 equiv) in CH_2Cl_2 (70 mL) was cooled to 0°C and N-iodosuccinimide (4.1 g, 18 mmol, 1.0 equiv) was added. The reaction mixture was kept at this temperature for 30 min. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with a saturated aqueous solution of $Na_2S_2O_3$ (2x50 mL) and water (1 x 50 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure. After purification by flash column chromatography (PE : EtOAc, 98:2, Rf=0.3), the desired product **4c** was obtained in 89 % yield (4.5 g) as a slightly yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 1.20-2.20 (m, 13H, one of H-3 and H-4 to 9), 2.50-2.70 (m, 2H, one of H-2 and one of H-3), 2.90-3.00 (m, 1H, one of H-2), 4.90 (dd, *J*= 3.9Hz, *J*= 12Hz, 1H, H-10). ^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 23.6, 24.0, 24.6, 25.3, 25.4, 25.5, 29.2, 35.7, 37.0 (C-2 to C-10), 207.4 (C-1).

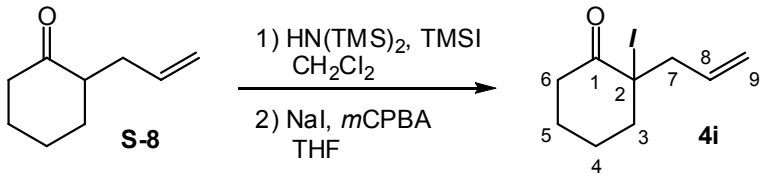
Synthesis of α-iodoketone 4e



A solution of **S-7** (290 µL, 2.5 mmol, 1.0 equiv) in CH_2Cl_2 (13 mL) was cooled to 0°C and $HN(TMS)_2$ (1.04 mL, 5.0 mmol, 2.0 equiv) was added dropwise. After 5 minutes, TMSI (427 µL, 3.0 mmol, 1.2 equiv) was added dropwise. The resulting mixture was stirred at 0°C for 20 minutes and then for an additional 20 minutes at rt. The reaction mixture was again cooled to 0°C before the slow addition of a cold (0°C) solution of NaI (411 mg, 2.75 mmol, 1.1 equiv) and *m*CPBA (475 mg, 2.75 mmol, 1.1 equiv) in THF (16 mL). *This solution was prepared by portion-wise addition of NaI to a cold (0°C) solution of mCPBA in THF*. After 1.5h at 0°C, the mixture was diluted with Et_2O/H_2O = 2:1 (90 mL) and the resulting layers were separated. The aqueous layer was extracted with Et_2O (3x30 mL). The combined organic layers were washed with a saturated aqueous solution of $Na_2S_2O_3$ (30 mL), brine (30 mL), dried over Na_2SO_4 and the solvents were removed under reduced pressure. After purification by flash column chromatography (PE:Et_2O = 10:1), the desired α-iodoketone **4e** (493 mg, 88%)was obtained as a slightly yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 2.42 (s, 3H, H-1), 2.68 (ddd, 1H, *J* = 14.7, 7.4 and 1.1 Hz, one of H-4), 2.80 (ddd,1H, *J* = 14.7, 6.8, 1.0 Hz, one of H-4), 4.51 (t, 1H, *J* = 7.5 Hz, H-3), 5.09-5.19 (m, 2H, H-6), 5.68-5.75 (m, 1H, H-5); ^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 26.4, 31.2, 38.9, 118.6, 135.2, 202.2.

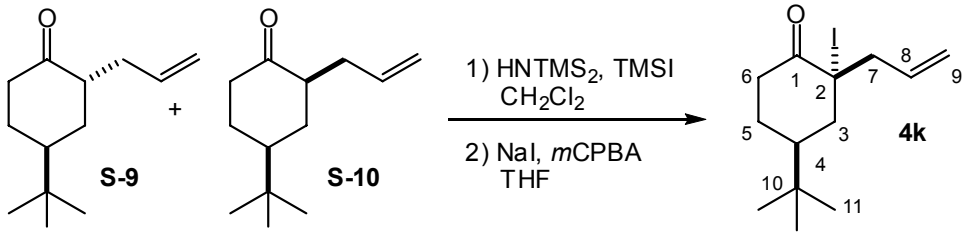
Synthesis of α-iodoketone 4i



Prepared according to the same protocol as α-iodoketone **4e**. After purification by flash column chromatography (P.E.:Et_2O = 20:1), the desired α-iodoketone **4i** (614 mg, 93%) was obtained as a slightly yellow oil.

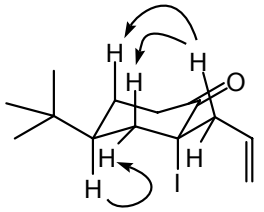
^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 1.42-1.96 (m, 6H, H-3 to H-5), 2.22 (ddd, 1H, *J* = 15.6, 6.0, 3.0 Hz, one of H-6), 2.39 (ddd, 1H, *J* = 15.2, 4.2, 2.2 Hz, one of H-6), 2.73 (dd,1H, *J* = 14.8, 7.0 Hz, one of H-7), 3.05 (dd, 1H, *J* = 14.8, 7.0 Hz, one of H-7), 5.13-5.27 (m, 2H, H-9), 5.79-5.91 (m, 1H, H-8); ^{13}C-NMR (100 MHz, $CDCl_3$) δ(ppm): 23.7, 26.6, 36.5, 41.9, 46.5, 56.4 (C-2), 119.3 (C-9), 135.2 (C-8), 205.1(C-1).

Synthesis of α-iodoketone 4k



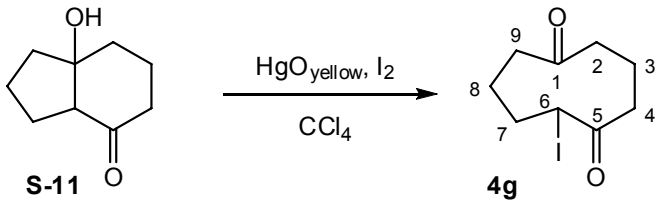
Prepared according to the same protocol as α-iodoketone **4e**. After purification by flash column chromatography (PE:Et_2O = 30:1), the desired α-iodoketone **4k** (736 mg, 92%) was obtained as a slightly yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm): 0.94 (s, 9H, H-11), 1.11-1.21 (m, 1H, H-4), 1.35-1.46 (m, 1H), 1.65 (dt, *J* = 13.5, 6.2 Hz, 1H), 2.01-2.11 (m, 1H), 2.23 (dt, *J* = 15.4, 3.2 Hz, 1H, one of H-3), 2.43 (ddd, *J* = 15.4, 4.2, 2.6 Hz, 1H, one of H-3), 2.76 (dd, *J* = 14.8, 7.0 Hz, 1H, one of H-7), 3.07 (dd, *J* = 14.8, 7.1 Hz, 1H, one of H-7), 3.45-3.58 (m, 1H), 5.18-5.26 (m, 2H, H-9), 5.87 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H, H-8)
^{13}C-NMR (100 MHz, $CDCl_3$) δ(ppm): 27.8 (C-11), 28.1, 34.3 (C-10), 36.4, 43.1, 45.1, 47.0, 61.7 (C-2), 119.5 (C-9), 135.5 (C-8), 205.3 (C-1).



observed NOE effect

Synthesis of α-iodoketone 4g

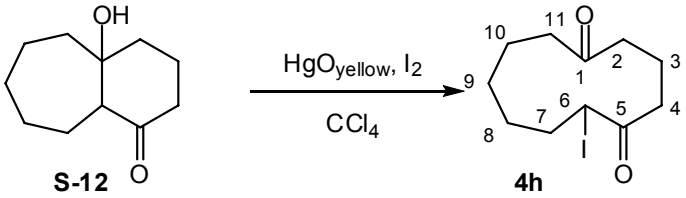


HgO_{yellow} (210 mg, 0.97 mmol, 3 equiv) and iodine (240 mg, 0.95 mmol, 2.9 equiv) were added to a solution of (3a*S**,7a*R**)-7a-hydroxyperhydro-4-indenone **S-11**[11] (50 mg, 0.32 mmol, 1 equiv) in CCl_4 (5 mL). The reaction mixture was stirred at rt under irradiation (visible light) for 3 hours.

The solution was filtrated over Celite® and the filter cake was washed with CH_2Cl_2 (3 x 3 mL). The resulting solution was treated with a saturated aqueous solution of $Na_2S_2O_3$ (2 x 10 mL) and water (2 x 10 mL). The organic layer was separated, dried over $MgSO_4$ and the solvents were removed under reduced pressure. 6-Iodocyclononane-1,5-dione **4g** (85 mg, 93 %) was obtained as a yellow solid (mp = 65-70°C).

IR (film): 2954 cm^{-1} (stretching C-H), 1700 (C=O), 1462, 1442, 1359, 1316, 1100, 732 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm): 1.72-1.85 (m, 1H, one of H-8), 1.89-2.00 (m, 1H, one of H-8), 2.09-2.28 (m, 3H, H-3 and one of H-7), 2.29-2.42 (m, 4H, one of H-4, H-9, one of H-7), 2.49 (ddd, *J* = 10.8 Hz, *J* = 6.0 Hz, *J* = 3.6Hz, 1H, one of H-4), 2.60-2.72 (m, 2H, H-2), 4.37 (dd, *J* = 12.3 Hz, *J* = 3.7 Hz, 1H, H-6). ^{13}C-NMR (125 MHz, $CDCl_3$) δ(ppm): 21.36, 24.46, 29.86 (C-6), 33.95, 34.20, 38.78, 41.60, 207.39 (C-5), 213.85 (C-1). MS (EI, 70 eV) m/z (relative intensity): (M^+) 280 (12 %); (M^+-I) 153 (77%); (153^+-H2O) 135 (92 %); (164^+-C_2H_4) 125 (43 %); 107 (90%); 97 (61%); 84 (42%); 55 (100%).

Synthesis of α-iodoketone 4h

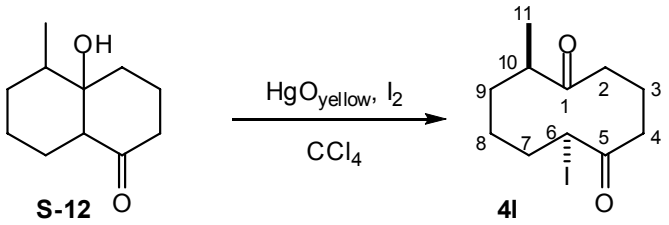


HgO_{yellow} (75 mg, 0.34 mmol, 3 equiv) and iodine (85 mg, 0.33 mmol, 2.9 equiv) were added to a solution of 4a-hydroxyperhydrobenzo[*a*]cyclohepten-1-one **S-12**[11] (21 mg, 0.11 mmol, 1 equiv) in CCl_4 (1.5 mL). The reaction mixture was stirred at rt under irradiation (visible light) for five hours.

The solution was filtrated over Celite® and the filter cake was washed with CH_2Cl_2 (3 x 4 mL). The resulting solution was treated with a saturated aqueous solution of $Na_2S_2O_3$ (2 x 10mL) and water (2 x 10mL). The organic layer was separated, dried over $MgSO_4$ and the solvents were removed under reduced pressure. 6-iodocycloundecane-1,5-dione **4h** (31 mg, 90%) were obtained as a yellow solid (mp = 79-80°C).

IR (film): 2938, 2875 and 2848 cm^{-1} (stretching C-H), 1703 (C=O), 1460, 1436, 1367, 1189, 1087 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$) δ(ppm): 1.08-1.52 (m, 4H), 1.70-2.42 (m, 8H), 2.55-2.69 (m, 2H), 2.77 (ddd, *J* = 17.3, 6.6 , 4.9 Hz, 1H, one of H-2), 2.95 (ddd, *J* = 17.4, 8.2, 5.1 Hz, 1H, one of H-2), 4.28 (dd, *J* =11.5 3.3 Hz, 1H, H-6). ^{13}C-NMR (50 MHz, $CDCl_3$) δ(ppm): 18.30, 22.97, 26.18, 26.88, 30.61 (C-6), 33.84, 34.30, 40.17, 41.63, 207.19 (C-5), 213.46 (C-1). MS (EI, 70 eV) m/z (relative intensity): (M^+) 308 (6 %); (M^+-$H^{\cdot}$) 307 (6 %); (M^+-H_2) 306 (20 %); (M^+-I) 181 (100 %); (181^+-H_2O) 163 (40 %); 97 (35%); 55 (80%).

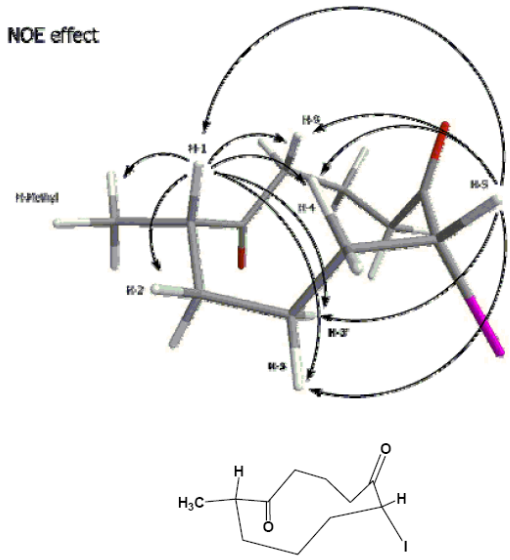
Synthesis of α-iodoketone 4l



HgO_{yellow} (268 mg, 1.23 mmol, 3 equiv) and iodine (304 mg, 1.19 mmol, 2.9 equiv) were added to a solution of 4a-hydroxy-5-methyloctahydro-1(*2H*)-naphtone **S-12**[11] (75 mg, 0.41 mmol, 1 equiv) in CCl_4 (1.5 mL). The reaction mixture was stirred at rt under irradiation (visible light) for 5 hours.

The solution was filtrated over celite® and the filter cake was washed with CH_2Cl_2 (3 x 5 mL). The resulting solution was treated with a saturated aqueous solution of $Na_2S_2O_3$ (2 x 10 mL) and water (2 x 10 mL). The organic layer was separated, dried over $MgSO_4$ and the solvents were removed under reduced pressure. *cis*-6-iodo-10-methylcyclodecane-1,5-dione **4l** (119 mg, 94%) was obtained as a yellow solid (mp = 83-84°C).

IR (film): 3008, 2969, 2940 and 2887 cm^{-1} (stretching C-H), 1702 (C=O), 1466, 1375, 1194, 1083, 905, 740 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm): 1.00 (d, *J*= 6.7 Hz, 3H, H-11), 1.10-1.21 (m, 1H, one of H-8), 1.40-1.54 (m, 1H, one of H-9), 1.63-1.81 (m, 2H, one of H-8 and one of H-9), 1.87-2.01 (m, 1H, one of H-3), 2.04-2.22 (m, 3H, one o f H-3 and H-7), 2.39 (ddd, *J* = 17.6, 5.6 Hz, *J* = 4.0 Hz, 1H, one of H-4), 2.55-2.70 (m, 3H, one of H-2, one of H-4 and H-10), 2.98 (ddd, *J* = 15.0, 10.2 Hz, *J* = 4.0 Hz, 1H, one of H-2), 4.31 (dd, *J* =11.7, 4.0 Hz, 1H, H-6). ^{13}C-NMR (125 MHz, $CDCl_3$) δ(ppm): 16.27 (C-11), 19.26 (C-3), 24.99 (C-8), 31.42 (C-9), 31.64 (C-6), 33.68 (C-2), 35.47 (C-7), 39.79 (C-4), 46.85 (C-10), 207.09 (C-5), 215.39 (C-1). MS (EI, 70 eV) m/z (relative intensity): (M^+) 308 (46 %), (M^+-I) 181 (93 %), 139 (45%), 111 (50%), 97 (52%), 55 (95%), 42 (100%).



General procedure for radical coupling reaction

Method A: A solution of α-iodoketone **4** (0.2 mmol, 1.0 equiv), ethyl 2-(bromomethyl)acrylate **5a** (116 mg, 80 μL, 0.6 mmol, 3.0 equiv), nBu$_6$Sn$_2$ (139 mg, 120 μL, 0.24 mmol, 1.2 equiv) and AIBN (7 mg, 0.04 mmol, 0.2 equiv) in benzene (1 mL) refluxed for 2.5h. The resulting solution was evaporated under reduced pressure and the residue was purified by flash column chromatography.

Method B: A solution of α-iodoketone **4a** (42 mg, 0.2 mmol, 1.0 equiv), ethyl 2-(tributyltinmethyl)acrylate **5b** (121 mg, 0.3 mmol, 1.5 equiv), and AIBN (7 mg, 0.04 mmol, 0.2 equiv) in benzene (1 mL) refluxed for 4h. The resulting solution was evaporated under reduced pressure and the residue was purified by flash column chromatography.

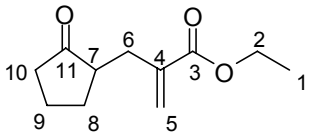
Method C: A solution of α-iodoketone **4** (0.2 mmol, 1.0 equiv), ethyl 2-(ethylsulfonemethyl)acrylate **5c** (413 mg, 0.3 mmol, 10.0 equiv), and AIBN (7 mg, 0.04 mmol, 0.2 equiv) in benzene (1 mL) refluxed for 2h. The resulting solution was evaporated under reduced pressure and the residue was purified by flash column chromatography.

Adduct 6a[12]

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 9:1 → 4:1) to give 35.3 mg (90%) of **6a**.

Method B: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 9:1 → 4:1 , Rf = 0.25) to give 36.1 mg (92%) of **6a**.

Method C: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fractions; P.E : Et_2O = 5:1 → CH_2Cl_2:MeOH = 100:1) to give 37.7 mg (96%) of **6a** and 224 mg (5.4 equiv.) of **5c**.

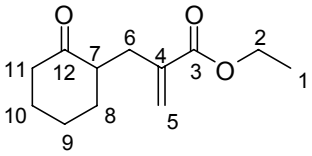


^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm): 1.30 (t, *J* = 7.1 Hz, 3H, H-1), 1.47-1.55 (m, 1H), 1.73-1.82 (m, 1H), 1.97-2.04 (m, 1H), 2.09-2.19 (m, 3H), 2.30-2.36 (m, 2H), 2.83 (ddd, *J* = 14.0, 4.2, 0.8 Hz, 1H, one of H-6), 4.21 (q, J = 7.1 Hz, 2H, H-2), 5.57 (s, 1H, one of H-5), 6.20 (s, 1H, one of H-5); ^{13}C-NMR (125 MHz, $CDCl_3$) δ(ppm): 14.1 (C-1), 20.4, 29.3, 32.0, 37.8 (C-10), 48.3 (C-7), 60.7 (C-2), 126.1 (C-5), 138.8 (C-4), 166.8 (C-3), 219.7 (C-11); MS (CI, CH_4-NO_2) m/z (relative intensity): $[M+H]^+$ 197 (57 %); 151 (100%); 133 (12%); 123 (37%); 105 (24%); 95 (56%); 93 (9%); 79 (34%); 67 (36%); 55 (9%); 43 (9 %).
CAS : 54312-35-5.

Adduct 6b[12]

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 9:1 → 4:1) to give 35.6 mg (85%) of **6b**.

Method C: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 5:1 → CH_2Cl_2:MeOH = 100:1) to give 38.7 mg (92%) of **6b** and 202 mg (4.9 equiv.) of **5c**.

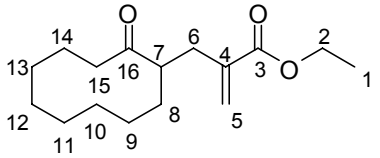


^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 1.25 (t, *J* = 7.1 Hz, 3H, H-1), 1.25-1.34 (partial overlap, m, 1H), 1.55-1.66 (m, 2H), 1.78-1.86 (m, 1H), 1.97-2.12 (m, 3H), 2.22-2.42 (m, 2H), 2.47-2.60 (m, 1H), 2.87 (dd, *J* = 13.8, 4.8 Hz, 1H, one of H-6), 4.15 (q, J = 7.2 Hz, 2H, H-2), 5.52 (d, *J* = 1.5 Hz, 1H, one of H-5), 6.15 (d, *J* = 1.5 Hz, 1H, one of H-5); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ(ppm): 14.2 (C-1), 25.1, 28.1, 32.0, 33.6, 42.1 (C-11), 49.2 (C-7), 60.6 (C-2), 126.5 (C-5), 138.4 (C-4), 166.8 (C-3), 211.8 (C-11); MS (CI, CH_4-NO_2) m/z (relative intensity): $[M+H]^+$ 211 (52 %); $[M]^+$ 210 (8%); 193 (6 %); 182 (8 %); 166 (10 %); 165 (100 %); 164 (9 %); 136 (9 %).

Adduct 6c

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 50:1 → 9:1) to give 37.3 mg (70%) of **6c** as a colorless oil.

Method C: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 10:1 → CH_2Cl_2:MeOH = 100:1) to give 47.5 mg (89%) of **6c** and 241 mg (5.8 equiv) of **5c**.



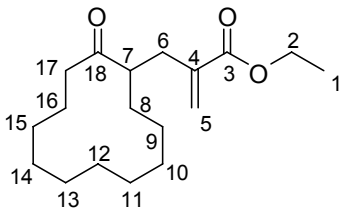
IR: 2927, 2871, 1629, 1472, 1445, 1369, 1326, 1179, 1137, 1026, 950, 819, 737 cm^{-1}

^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 1.28 (t, *J* = 7.2 Hz, 3H, H-1), 1.21-1.93 (m, 16H), 2.20-2.31 (m, 2H), 2.61 (ddd, *J* = 16.2, 9.0, 3.3 Hz, 1H), 2.99-3.10 (m, 1H), 4.18 (q, J = 7.2 Hz, 2H, H-2), 5.48 (s, 1H, one of H-5), 6.12 (d, *J* = 1.5 Hz, 1H, one of H-5); ^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 14.1 (C-1), 23.0, 23.3, 23.5, 24.1. 24.7, 24.8, 25.1, 25.2, 42.3 (C-15), 50.3 (C-7), 60.7 (C-2), 126.9 (C-5), 138.0 (C-4), 166.7 (C-3), 214.7 (C-16)]; MS (CI, CH_4-NO_2) m/z (relative intensity): $[M+H]^+$ 267 (100 %), 249 (23 %), 181 (17 %), 174 (13 %), 162 (8 %); HRMS (CI^+): calculated mass for $C_{16}H_{27}O_3$ (267.1960, $[M+H]^+$), found (267.1947).

Adduct 6d

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 50:1) to give 41.8 mg (71%) of **6d** as a colorless oil.

Method C: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 20:1 → CH_2Cl_2:MeOH = 100:1) to give 51.9 mg (88%) of **6d** and 215 mg (5.2 equiv) of **5c**.



IR: 2932 and 2864 cm^{-1} (stretching C-H), 1718 cm^{-1} (C=O), 1628 cm^{-1} (C=C-C=O), 1469, 1411, 1368, 1326, 1188, 1140, 1025, 946 cm^{-1}

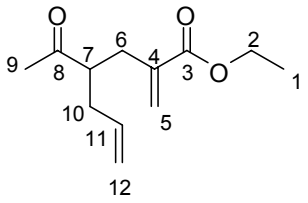
^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm): 1.05-1.38 (m, 17H), 1.47-1.83 (m, 4H), 2.19-2.40 (m, 2H), 2.53-2.73 (m, 2H), 2.82-2.97 (m, 1H), 4.18 (q, *J* = 7.5 Hz, 2H, H-2), 5.52 (d, *J* = 1.2 Hz, 1H, one of H-5), 6.15 (d, *J* = 1.6 Hz, 1H, one of H-5); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ(ppm): 14.1 (C-1), 21.9, 22.2, 23.7, 23.9

(2 C), 24.0, 25.6, 25.9, 29.1, 33.4, 38.2 (C-6 and C-8 to C-17), 49.6 (C-7), 60.7 (C-2), 126.6 (C-5), 138.3 (C-4), 166.8 (C-3), 213.7 (C-18); MS (APCI) m/z (relative intensity): (M^++1) 295 (100 %); 250 (16 %); 249 (95 %); HRMS (EI+) : calculated mass for $C_{18}H_{30}O_3$ (294.2195, $[M]^+$), found (294.2193).

Adduct 6e

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 20:1 → 10:1 → 5:1) to give 33.6 mg (80%) of **6e** as a colorless oil.

Method C: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 10:1 → CH_2Cl_2:MeOH = 100:1) to give 36.3 mg (86%) of **6e** and 210 mg (4.9 equiv) of **5c**.



^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 1.31 (t, *J* = 7.3 Hz, 3H, H-1), 2.13 (s, 3H, H-9), 2.16-2.45 (m, 3H, H-10 and one of H6), 2.60 (dd, *J* = 14.0, 7.9 Hz, 1H, one of H-6), 2.88 (tt, *J* = 7.4, 6.4 Hz, 1H, H-7), 4.21 (q, *J* = 7.3 Hz, 2H, H-2), 5.02 (s, 1H, one of H-12), 5.07 (d, *J* = 7.0 Hz, 1H, one of H-12), 5.55 (s, 1H, one of H-5), 5.64-5.77 (m, 1H, H-11), 6.19 (d, *J* = 0.9 Hz, 1H, one of H-5); ^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 14.4 (C-1), 30.3 (C-9), 33.7 (C-6), 35.7 (C-10), 51.0 (C-7), 61.0 (C-2), 117.5 (C-12), 127.4 (C-5), 135.2 (C-11), 138.2 (C-4), 167.0 (C-3), 211.2 (C-8).

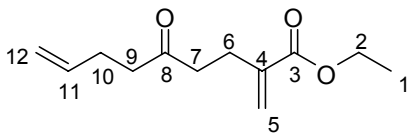
MS (APCI) m/z (relative intensity): (M^+) 210 (42 %), 165 (9 %), 138 (14 %), 106 (11 %), 85 (100 %), 84 (17 %), 65 (32 %), 60 (33 %).

HRMS (ESI): calculated mass for $C_{12}H_{19}O_3$ (211.1334, $[M+H]^+$), found (211.1338).

Adduct 6f

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 20:1 → 10:1 → 5:1) to give 34.9 mg (83%) of **6f** as a colorless oil.

Method C: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 10:1 → CH_2Cl_2:MeOH = 100:1) to give 38.2 mg (91%) of **6f** and 236 mg (5.8 equiv) of **5c**.

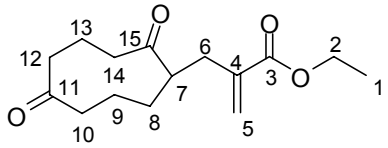


^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 1.31 (t, *J* = 7.1 Hz, 3H, H-1), 2.30-2.37 (m, 2H, H-10), 2.50-2.54 (m, 2H, H-9), 2.57-2.67 (m, 4H, H-6 and H-7), 4.21 (q, *J* = 7.1 Hz, 2H, H-2), 4.97-5.06 (m, 2H, H-12), 5.58 (s, 1H, one of H-5), 5.74-5.87 (m, 1H, H-11), 6.17 (s, 1H, one of H-5); ^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 14.4 (C-1), 26.4 (C-10), 27.9 (C-6), 41.8 and 42.0 (C-7 and C-9), 60.9 (C-2), 115.5 (C-12), 125.8 (C-5), 137.3 (C-11), 139.7 (C-4), 167.0 (C-3), 209.2 (C-8); MS (APCI) m/z (relative intensity): (M^++1) 211 (100 %), 197 (26 %), 165 (77 %), 163 (42 %), 149 (52 %), 147 (29 %), 135 (33 %), 109 (32 %). HRMS (ESI): calculated mass for $C_{12}H_{19}O_3$ (211.1334, $[M+H]^+$), found (211.1337).

Adduct 6g

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 9:1 → 3:1) to give 37.2 mg (70%) of **6g** as a colorless oil.

Method C: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 5:1 → CH_2Cl_2:MeOH = 100:1) to give 47.4 mg (89%) of **6g** and 253 mg (6.1 equiv) of **5c**.



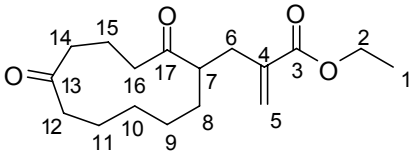
IR: 2929 cm^{-1} (stretching C-H), 1707 cm^{-1} (C=O), 1630 cm^{-1} (C=C-C=O), 1444, 1370, 1189, 1146, 1108, 1024, 908, 734, 649 cm^{-1}

^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 1.31 (t, *J* = 7.2 Hz, 3H, H-1), 1.62-1.86 (m, 5H), 2.04-2.14 (m, 2H), 2.22-2.55 (m, 7H), 2.75-2.85 (m, 1H, H-7), 4.20 (q, *J* = 6.9 Hz, 2H, H-2), 5.49 (d, *J* = 1.2 Hz, 1H, one of H-5), 6.16 (d, *J* = 1.5 Hz, 1H, one of H-5); ^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 14.2 (C-1), 20.9, 21.2 (C-9 and C-13), 29.4, 34.4 (C-6 and C-8), 38.8, 43.4 (C-10, C-12 and-14), 51.2 (C-7), 60.9 (C-2), 127.0 (C-5), 137.9 (C-4), 166.6 (C-3), 214.8 (C-11), 216.3 (C-15); MS (ESI) m/z (relative intensity): (M^+) 266 (100 %); 249 (23 %), 244 (8 %), 115 (29 %), 83 (9 %); HRMS (EI+) : calculated mass for $C_{15}H_{22}O_4$ (266.1518, $[M]^+$), found (266.1506).

Adduct 6h

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 9:1 → 3:1) to give 37.6 mg (67%) of **6h** as a colorless oil.

Method C: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 5:1 → CH_2Cl_2:MeOH = 100:1) to give 50.7 mg (90%) of **6h** and 172 mg (4.2 equiv) of **5c**.



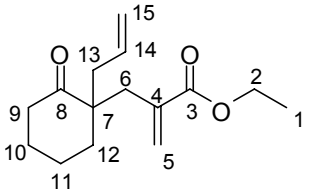
IR: 2935 cm^{-1} (stretching C-H), 1708 cm^{-1} (C=O), 1629 cm^{-1} (C=C-C=O), 1463, 1369, 1255, 1182, 1025, 949, 872, 819, 727 cm^{-1}

^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm): 1.26 (t, *J* = 7.1 Hz, 3H, H-1), 1.18-1.32 (m, 3H), 1.44-1.56 (m, 2H), 1.62-1.75 (m, 2H), 1.80-1.94 (m, 2H), 2.06-2.88 (m, 10H), 4.16 (q, *J* = 7.1 Hz, 2H, H-2), 5.45 (d, *J* = 1.2 Hz, 1H, one of H-5), 6.10 (s, 1H, one of H-5); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ(ppm): 14.1 (C-1), 17.3, 23.0, 24.3, 26.9, 29.3, 34.2, 38.6, 39.3, 42.2 (C-6, C-8 to C-12 and C-14 to C-16), 51.1 (C-7), 60.7 (C-2), 126.6 (C-5), 138.1 (C-4), 166.6 (C-3), 214.0, 215.2 (C-13 and C-17); MS (APCI) m/z (relative intensity): (M^+) 294 (11 %); 277 (100 %); 259 (11 %); 249 (17 %); 248 (20 %); 239 (40 %); 225 (21 %); HRMS (CI+) : calculated mass for $C_{17}H_{26}O_4$ (294.1831, $[M]^+$), found (294.1829)

Adduct 6i

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 20:1 → 10:1 → 5:1) to give 31.6 mg (63%) of **6i** as a colorless oil.

Method C: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 10:1 → CH_2Cl_2:MeOH = 100:1) to give 39.7 mg (79%) of **6i** and 186 mg (4.5 equiv) of **5c**.

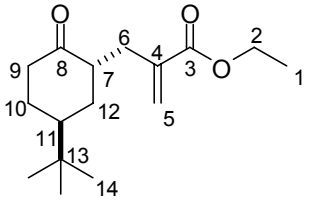


^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 1.29 (t, *J* = 7.1 Hz, 3H, H-1), 1.66-1.85 (m, 6H, H-10 – H-12), 2.21-2.40 (m, 3H, H-9 and one of H-13), 2.50-2.61 (m, overlapped, 1H, one of H-13), 2.53 (d, *J* = 14.0 Hz, 1H, one of H-6), 2.85 (d, *J* = 14.0 Hz, 1H, one of H-6), 4.18 (q, *J* = 7.2 Hz, 2H, H-2), 5.01-5.08 (m, 2H, H-15), 5.56 (s, 1H, one of H-5), 5.56-5.72 (m, 1H, H-14), 6.24 (d, *J* = 1.5 Hz, 1H, one of H-5); ^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 14.4 (C-1), 21.0 (C-11), 26.9 (C-10), 36.2 (C-13), 36.5 (C-9), 39.4 (C-6), 39.7 (C-12), 52.0 (C-7), 61.1 (C-2), 118.4 (C-15), 128.7 (C-5), 134.0 (C-14), 137.4 (C-4), 167.9 (C-3), 213.9 (C-8); MS (APCI) m/z (relative intensity): [M^++H] 251 (100 %), 252 (11%), 206 (9%), 205 (66%), 187 (13%), 163 (7%), 159 (11%); HRMS (ESI): calculated mass for $C_{15}H_{23}O_3$ (251.1647, $[M+H]^+$); found (251.1658).

Adduct 6j

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 20:1 → 10:1 → 5:1) to give 38.4 mg (72%) of **6j** as a colorless oil.

Method C: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 10:1 → CH_2Cl_2:MeOH = 100:1) to give 48.5 mg (91%) of **6j** and 214 mg (5.0 equiv) of **5c**.

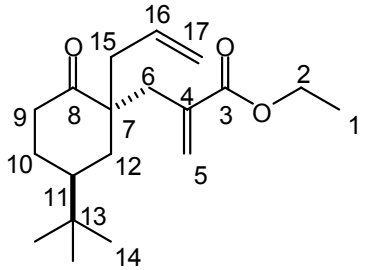


^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm): 0.87 (s, 9H, H-14), 1.28 (t, *J* = 7.1 Hz, 3H, H-1), 1.49 (td, *J* = 12.7, 4.5 Hz, 1H, H-11), 1.55-1.68 (m, 3H, H-7 and H-12), 1.77 (ddd, *J* = 12.4, 6.5, 3.4 Hz, 1H, one of H-10), 1.98 (dddd, *J* = 12.2, 5.9, 3.0, 2.9 Hz, 1H, one of H-10), 2.31 (dt, *J* = 12.4, 3.0 Hz, 1H, one of H-9), 2.41 (dd, *J* = 13.7, 7.5 Hz, 1H, one of H-6), 2.73 (dt, *J* = 12.8, 5.7 Hz, 1H, one of H-9), 2.76 (dd, *J* = 14.0, 7.7 Hz, 1H, one of H-6), 4.18 (q, *J* = 7.1 Hz, 2H, H-2), 5.57 (s, 1H, one of H-5), 6.20 (s, 1H, on e of H-5); ^{13}C-NMR (125 MHz, $CDCl_3$) δ(ppm): 14.3 (C-1), 26.6 (C-10), 27.5 (C-14), 31.1 (C-12), 32.6 (C-13), 33.7 (C-6), 38.7 (C-9), 41.5 (C-11), 48.1 (C-7), 61.0 (C-2), 126.9 (C-5), 138.3 (C-4), 166.8 (C-3), 213.3 (C-8); MS (APCI) m/z (relative intensity): (M^++1) 266 (100 %), 267 (10%), 237 (54%), 205 (45%), 153 (15%); HRMS (ESI): $C_{16}H_{26}NaO_3$ [M+Na^+] calculated mass (289.1780); found mass (289.1783).

Adduct 6k

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 20:1 → 10:1 → 5:1) to give 9.8 mg (16%) of **6k** as a colorless oil.

Method C: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 10:1 → CH_2Cl_2:MeOH = 100:1) to give 33.7 mg (55%) of **6k**.

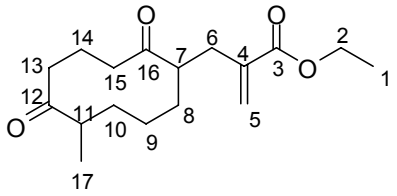


^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm): 0.89 (s, 9H, H-14), 1.29 (t, *J* = 7.1 Hz, 3H, H-1), 1.47 (td, *J* = 12.5, 4.7 Hz, 1H, H-11), 1.59-2.02 (m, 4H, H-12 and H-10), 2.31-2.43 (m, 3H, H-9 and one of H-15), 2.42 (d, *J* = 13.9, 1H, one of H-6), 2.49-2.59 (m, 1H, one of H-15), 2.81 (dd, *J* = 14.0, 1H, one of H-6), 4.18 (q, *J* =

7.1 Hz, 2H, H-2), 5.03-5.11 (m, 2H, H-17), 5.58 (s, 1H, one of H-5), 5.63-5.72 (m, 1H, H-16), 6.25 (s, 1H, one of H-5); ^{13}C-NMR (125 MHz, $CDCl_3$) δ(ppm): 14.3 (C-1), 26.5 (C-10), 27.4 (C-14), 32.7 (C-13), 36.1 (C-12), 38.1 (C-6), 39.2 (C-9), 41.6 (C-11), 52.3 (C-7), 61.0 (C-2), 119.1 (C-17), 126.9 (C-5), 135.8 (C-16), 138.3 (C-4), 168.2 (C-3), 213.7 (C-8); MS (APCI) m/z (relative intensity): (M^++1) 307 (100 %), 267 (21%), 209 (51%), 153 (42%), 113 (21%), 96 (9%); HRMS (ESI): $C_{19}H_{30}NaO_3$ [M+Na^+] calculated mass (329.2093); found mass (329.2099).

Adduct 6l

Method A: The crude was purified by (ϕ1.5 cm, 9 cm of SiO_2, 10 mL fracions; P.E : Et_2O = 100:0 → 9:1 → 3:1) to give 27.1 mg (46%) of *syn*-**6l** and 8.2 mg (14%) of *anti*-**6l**.



Syn-**6l**

IR: 2958, 2931 and 2872 cm^{-1} (stretching C-H), 1714 and 1695 cm^{-1} (C=O), 1629 cm^{-1} (C=C-C=O), 1465, 1370, 1272, 1202, 1095, 1026, 953, 861, 818, 736, 703 cm^{-1}

^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm): 0.92 (d, *J* = 6.7 Hz, 3H, H-17), 1.26 (t, *J* = 7.1 Hz, 3H, H-1), 1.17-1.47 (m, 6H, H-8, H-9 and H-10), 1.83-2.00 (m, 2H, H-14), 2.07-2.29 (m, 3H, one of each H-6, H-13 and H-15), 2.45-2.62 (m, 2H, one of H-6 and H-11), 2.67-2.94 (m, 3H, H-7 and one of each H-13 and H-15), 4.16 (q, *J* = 7.1 Hz, 2H, H-2), 5.47 (s, 1H, one of H-5), 6.10 (d, *J* = 1.6 Hz, 1H, one of H-5); ^{13}C-NMR (62.5 MHz, $CDCl_3$) δ(ppm): 14.1 (C-1), 14.7 (C-17), 17.8 (C-14), 20.7 (C-9), 30.2 (C-8), 31.9 (C-10), 33.0 (C-6), 37.9 (C-13), 40.2 (C-15), 47.0 (C-11), 51.5 (C-7), 60.7 (C-2), 126.8 (C-5), 138.1 (C-4), 166.7 (C-3), 215.3 (C-16), 216.3 (C-12); MS (APCI) m/z (relative intensity): $[M]^+$ 294 (7 %), 277 (15%), 259 (46%), 249 (100%), 231 (95%), 213 (58%), 203 (30%), 195 (16%), 185 (38%); HRMS (EI^+) : calculated mass for $C_{17}H_{26}O_4$ (294.1831, $[M]^+$); found mass (294.1828).

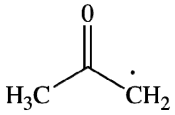
Anti-**6l**

IR: 2960, 2934 and 2874 cm^{-1} (stretching C-H), 1710 cm^{-1} (C=O), 1629 cm^{-1} (C=C-C=O), 1446, 1370, 1328, 1305, 1179, 1148, 1054, 915, 733 cm^{-1}

^{1}H-NMR (300 MHz, $CDCl_3$) δ(ppm): 0.80 (d, *J* = 7.2 Hz, 3H, H-17), 0.77-1.06 (m, 3H), 1.27 (t, *J* = 7.0 Hz, 3H, H-1), 1.13-1.39 (m, 3H), 1.70-1.79 (m, 2H), 1.81-1.96 (m, 1H), 1.96-2.13 (m, 1H), 2.47-2.60 (m, 2H), 2.62-2.75 (m, 2H), 4.14 (q, *J* = 7.0 Hz, 2H, H-2), 5.47 (s, 1H, one of H-5), 6.10 (d, *J* = 0.9 Hz, 1H,

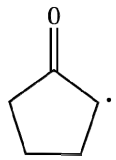
one of H-5); ^{13}C-NMR (75 MHz, $CDCl_3$) δ(ppm): 14.0, 14.1 (C-1 and C-17), 16.9, 22.4, 24.7, 32.2, 35.5, 38.0, 39.4 (C-6, C-8 to C-10 and C-13 to C-15), 39.4 (C-11), 61.0 (C-7), 67.7 (C-2), 128.3 (C-5), 136.0 (C-4), 166.8 (C-3), 210.0 (C-12 and C-16); MS (APCI) m/z (relative intensity): $[M]^+$ 294 (12 %); 277 (67 %); 259 (18 %); 249 (39 %); 231 (100 %); 213 (55 %); 203 (18 %); 195 (8 %); 185 (21 %).
HRMS (EI^+) : calculated mass $C_{17}H_{26}O_4$ (294.1831, $[M]^+$); found mass (294.1841).

I. Structural data for Table 3 : B3LYP/6-311+G(d,p) geometries (Cartesian coordinates, all values in Å)



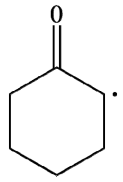
C	–0.084943	0.118290	-0.000017
C	1.358019	-0.356523	-0.000005
H	1.560589	-0.972275	0.881711
H	1.560316	-0.973423	-0.880975
H	2.025623	0.503855	-0.000637
C	–1.130682	-0.870639	0.000000
H	–0.916907	-1.933385	-0.000014
H	–2.161112	-0.537704	0.000037
O	–0.365359	1.320770	0.000001

E(UB3LYP) = –192.556539 a.u.



C	−1.387199	−0.719351	−0.195342
C	−1.377568	0.806767	0.102337
C	0.052881	1.193395	−0.025315
C	0.917142	0.040153	−0.000406
C	0.033407	−1.204363	0.152665
H	−2.168226	−1.243976	0.356950
H	−1.580203	−0.874686	−1.260239
H	−1.730790	1.011153	1.126359
H	−2.037746	1.380582	−0.556608
H	0.430023	2.207362	−0.080643
H	0.396340	−2.020096	−0.474520
H	0.103220	−1.541040	1.193908
O	2.144426	0.047636	−0.063605

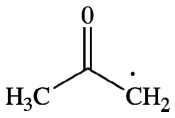
E (UB3LYP= −270.000097 a.u.



C	–4.946029	–0.916357	–0.079752
C	–3.412256	–0.983210	–0.146394
C	–2.744595	0.274568	0.296718
C	–3.403668	1.333813	1.007381
C	–4.893935	1.195561	1.303269
C	–5.407568	–0.248617	1.220107
H	–3.050779	–1.804575	0.495619
H	–3.070723	–1.249875	–1.154602
H	–5.323022	–0.341697	–0.934049
H	–5.362905	–1.923276	–0.169800
H	–5.080027	1.641742	2.283247
H	–5.423255	1.823052	0.574531
H	–5.034164	–0.823487	2.076755
H	–6.499044	–0.260501	1.290667
H	–1.681813	0.409676	0.118712
O	–2.779301	2.343951	1.360115

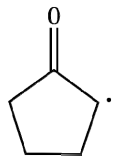
E (UB3LYP) = –309.329556 a.u.

II. Structural data for Table S-3 : B3LYP/6-31+G(d) geometries (Cartesian coordinates, all values in Å)



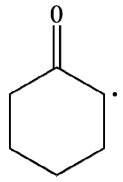
C	0.065059	0.124266	–0.031240
C	–0.069478	0.090962	1.402885
H	0.997180	–0.206284	–0.478131
O	0.869817	–0.312245	2.108435
C	–1.375662	0.561992	2.023578
H	–1.543341	1.624615	1.805839
H	–2.228420	0.007516	1.612672
H	–1.339198	0.421039	3.105941
H	–0.737403	0.470125	–0.677188

E(UB3LYP) = –192.506355 a.u.
Zero Point Vibrational Energy = 0.070516 a.u.
H(298.15K) = –192.429756 a.u.



C	–0.000257	–0.000305	-0.000048
C	–0.000624	0.001022	1.556898
C	1.445793	0.001201	1.919160
C	2.272490	–0.365222	0.795173
C	1.350329	–0.629619	–0.402834
H	–0.863263	–0.529949	–0.414892
H	–0.048380	1.034479	–0.359407
H	–0.489377	–0.907257	1.953269
H	–0.552899	0.846366	1.988786
H	1.850077	0.198866	2.907681
H	1.777791	–0.224239	–1.324987
H	1.267091	–1.717853	–0.536581
O	3.504255	–0.473119	0.797870

E(UB3LYP) = –269.933906 a.u.
Zero Point Vibrational Energy = 0.108190 a.u.
H(298.15K) = –269.819311 a.u.



O	−0.022212	−0.238500	0.010104
C	−0.007226	−0.026671	1.237896
C	1.313524	0.031126	2.001850
C	−1.232644	0.185509	1.958896
C	1.153846	−0.147751	3.520162
H	1.768669	1.010022	1.787290
H	1.984458	−0.719330	1.568950
C	−1.309931	0.424723	3.432449
H	−2.149272	0.125339	1.375306
C	0.050232	0.769038	4.064397
H	2.107282	0.058535	4.021952
H	0.902208	−1.194658	3.745903
H	−2.054818	1.206059	3.645074
H	−1.716736	−0.487226	3.907883
H	−0.019642	0.690385	5.156038
H	0.304069	1.814599	3.838317

E(UB3LYP) = −309.253997 a.u.
Zero Point Vibrational Energy = 0.137634 a.u.
H(298.15K) = −309.108979 a.u.

H_3C-CH=CH_2:

H	–0.007402	0.029111	–0.002415
C	0.045052	–0.118451	1.075335
C	1.198545	–0.013765	1.742875
H	–0.888112	–0.355560	1.580309
H	1.196201	–0.171503	2.823017
C	2.531549	0.308965	1.127765
H	3.257245	–0.494853	1.312852
H	2.450355	0.452746	0.044475
H	2.956583	1.223680	1.563331

E(RB3LYP) = –117.913924 a.u.
Zero Point Vibrational Energy = 0.079826 a.u.
H(298.15K) = –117.829064 a.u.

H_3CO-CH=CH_2:

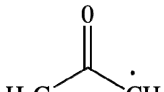
H	0.075194	0.082147	–0.016595
C	0.057937	–0.096343	1.054178
C	1.174586	–0.069372	1.786986
H	–0.893745	–0.302170	1.530559
H	1.169472	–0.247054	2.863487
O	2.401073	0.176974	1.244655
C	3.486732	0.210980	2.165192
H	4.384560	0.405876	1.575767
H	3.354879	1.014228	2.902811
H	3.595074	–0.750971	2.684592

E(RB3LYP) = –193.121169 a.u.
Zero Point Vibrational Energy = 0.084387 a.u.
H(298.15K) = –193.031397 a.u.

$H_3COOC\text{-}CH{=}CH_2$:

H	–0.007689	0.048490	0.002802
C	0.028725	–0.084099	1.079825
C	1.182569	–0.033980	1.755195
H	–0.912154	–0.261000	1.594153
H	1.220007	–0.166813	2.832811
C	2.514261	0.200333	1.144458
O	3.547939	0.236875	1.787950
O	2.468916	0.368744	–0.197242
C	3.733926	0.598436	–0.842956
H	3.501080	0.705890	–1.902806
H	4.199973	1.508320	–0.455166
H	4.405290	–0.248651	–0.678256

E(RB+HF-LYP) = –306.481830 a.u.
Zero Point Vibrational Energy = 0.095588 a.u.
H(298.15K) = –306.378656 a.u.

1. Addition of  to H_3C-CH=CH_2

(a) Transition state:

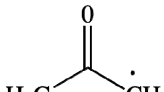
C	0.016370	0.012309	–0.070724
C	–0.024663	0.149983	1.376389
H	0.996503	–0.011091	–0.535595
O	0.971311	–0.079219	2.073619
H	–1.324992	–2.132404	0.268097
C	–0.398087	–2.180751	–0.299947
C	–0.443070	–2.439737	–1.645834
H	0.497013	–2.401437	0.273759
H	0.492584	–2.641932	–2.168254
C	–1.678328	–2.361770	–2.489025
H	–1.826503	–3.289848	–3.058720
H	–2.574417	–2.187909	–1.882664
H	–1.606530	–1.552759	–3.231895
C	–1.339966	0.571380	2.020609
H	–1.410718	1.667507	2.018747
H	–2.211397	0.186801	1.477920
H	–1.368827	0.231391	3.059172
H	–0.802582	0.399708	–0.670928

E(UB3LYP) = –310.411324 a.u.
Zero Point Vibrational Energy = 0.152741 a.u.
H(298.15K) = –310.248100 a.u.

(b) Product:

C	–0.004133	–0.008072	0.001835
C	–0.010672	–0.016104	1.524343
H	1.036952	–0.012253	–0.337867
O	0.810464	–0.665257	2.151577
H	–1.757962	–1.295342	–0.176531
C	–0.725546	–1.281093	–0.556928
C	–0.733551	–1.338578	–2.049847
H	–0.212766	–2.156609	–0.139575
H	0.157361	–1.716242	–2.549401
C	–1.760970	–0.626502	–2.868021
H	–1.813672	–1.025160	–3.888124
H	–2.761269	–0.706479	–2.419190
H	–1.548874	0.454907	–2.965517
C	–1.096685	0.782498	2.222044
H	–0.919742	1.855761	2.067755
H	–2.082466	0.559824	1.793782
H	–1.097926	0.567856	3.293133
H	–0.497506	0.891657	–0.385305

E(UB3LYP) = –310.444021 a.u.
Zero Point Vibrational Energy = 0.155347 a.u.
H(298.15K) = –310.278177 a.u.

2. Addition of  to H_3CO-CH=CH_2

(a) Transition state:

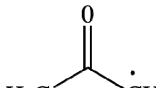
C	−0.069897	0.040717	−0.095364
C	−0.007874	0.178135	1.345132
H	0.873695	0.025461	−0.630876
O	1.046282	−0.012979	1.969559
H	−1.426637	−2.122583	0.262514
C	−0.499678	−2.194203	−0.297328
C	−0.544740	−2.479087	−1.632159
H	0.400715	−2.435164	0.255393
H	0.347078	−2.716099	−2.212167
O	−1.697481	−2.357486	−2.333853
C	−1.620682	−2.664031	−3.726515
H	−2.618021	−2.491836	−4.133679
H	−0.899680	−2.008339	−4.231285
H	−1.338229	−3.713430	−3.878146
H	−0.945564	0.381318	−0.640714
C	−1.284746	0.547973	2.092013
H	−1.333150	1.639318	2.205506
H	−2.190002	0.229847	1.562523
H	−1.266858	0.109150	3.093745

E(UB3LYP) = –385.622089 a.u.
Zero Point Vibrational Energy = 0.157694 a.u.
H(298.15K) = –385.452732 a.u.

(b) Product:

C	−0.029202	−0.024947	−0.009138
C	0.000323	−0.005367	1.511208
H	1.002931	0.003741	−0.373644
O	0.908831	−0.535868	2.130887
H	−1.737182	−1.386906	−0.113639
C	−0.721037	−1.328936	−0.527727
C	−0.795215	−1.413411	−2.011795
H	−0.162512	−2.192858	−0.149341
H	0.079827	−1.685030	−2.606473
O	−1.670976	−0.542794	−2.596049
C	−1.717271	−0.580686	−4.019216
H	−2.422051	0.192433	−4.331116
H	−0.727063	−0.369454	−4.446203
H	−2.064047	−1.561968	−4.367508
H	−0.571907	0.842162	−0.402708
C	−1.161101	0.666901	2.220822
H	−1.102095	1.753355	2.068450
H	−2.121223	0.340948	1.801144
H	−1.127987	0.452352	3.291482

E(UB3LYP) = −385.656725 a.u.
Zero Point Vibrational Energy = 0.161349 a.u.
H(298.15K) = −385.484094 a.u.

3. Addition of  to $H_3COOC-CH=CH_2$

(a) Transition state:

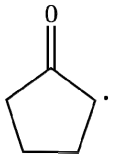
C	−0.107724	0.022851	−0.092111
C	−0.034823	0.188252	1.354092
H	0.821771	0.070241	−0.649517
O	1.046021	0.102815	1.946725
H	−1.135564	−2.288495	0.461151
C	−0.279568	−2.280612	−0.205450
C	−0.442063	−2.572648	−1.530726
H	0.701827	−2.347637	0.253327
H	0.412683	−2.706348	−2.187324
C	−1.741595	−2.692346	−2.213153
O	−1.861793	−2.993543	−3.389356
O	−2.799864	−2.434960	−1.402325
C	−4.098019	−2.567216	−2.009505
H	−4.811527	−2.327506	−1.220463
H	−4.199975	−1.872982	−2.847995
H	−4.247830	−3.589054	−2.368330
C	−1.326087	0.466441	2.108677
H	−1.605247	1.521240	1.982969
H	−2.159130	−0.136387	1.728123
H	−1.181146	0.271841	3.173953
H	−1.025329	0.256460	−0.623917

E(UB3LYP) = −498.980977 a.u.
Zero Point Vibrational Energy = 0.168166 a.u.
H(298.15K) = −498.799562 a.u.

(b) Product:

C	−0.422221	0.067103	0.259037
C	−0.465819	−0.222418	1.756744
H	0.629664	0.262202	0.001141
O	−0.717120	−1.332819	2.190114
H	−2.056208	−1.201522	−0.393666
C	−0.991942	−1.077026	−0.603621
C	−0.765519	−0.848476	−2.057076
H	−0.495504	−2.007011	−0.292782
H	0.249085	−0.810856	−2.444365
C	−1.790908	−0.651397	−3.061628
O	−1.556408	−0.471824	−4.253592
O	−3.057312	−0.682211	−2.557760
C	−4.111335	−0.502500	−3.518099
H	−5.037816	−0.560688	−2.946907
H	−4.021157	0.469696	−4.009785
H	−4.076303	−1.288545	−4.276876
C	−0.177074	0.948099	2.678090
H	0.699863	1.512098	2.341547
H	−1.028706	1.639724	2.662747
H	−0.026541	0.591287	3.698230
H	−0.949828	1.009285	0.061469

E(UB+HF−LYP) = −499.037799 a.u.
Zero Point Vibrational Energy = 0.170671 a.u.
H(298.15K) = −498.854069 a.u.

4. Addition of  to $H_3C-CH=CH_2$

(a) Transition state:

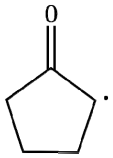
C	−0.066965	0.253363	0.562118
C	0.196436	−0.693539	1.763413
C	1.685319	−0.605371	1.978009
C	2.328104	−0.197716	0.726138
C	1.228370	0.195038	−0.272106
H	−0.958265	−0.032453	−0.005735
H	−0.231382	1.274631	0.927578
H	−0.079339	−1.728907	1.500960
H	−0.392405	−0.434061	2.650743
H	2.208062	−1.285675	2.643123
H	1.480396	1.127087	−0.789384
H	1.179511	−0.591749	−1.038843
O	3.536652	−0.165046	0.498353
H	1.701923	1.890525	2.490542
C	2.147187	1.173270	3.178002
C	1.591829	1.016525	4.428209
H	3.203531	0.974828	3.020629
H	2.137114	0.430287	5.168878
C	0.240162	1.517689	4.835786
H	0.309653	2.145693	5.735913
H	−0.228674	2.113334	4.044522
H	−0.440893	0.691807	5.091908

E(UB3LYP) = −387.834188 a.u.
Zero Point Vibrational Energy = 0.190131 a.u.
H(298.15K) = −387.633200 a.u.

(b) Product:

C	−0.114021	−0.307284	0.036780
C	−0.015849	−0.249713	1.581214
C	1.473036	0.032911	1.879764
C	2.216721	−0.550016	0.667261
C	1.202951	−0.972860	−0.396551
H	−1.002355	−0.847922	−0.305777
H	−0.174768	0.707700	−0.377120
H	−0.303867	−1.222047	2.002786
H	−0.680149	0.502628	2.019745
H	1.825562	−0.484571	2.781437
H	1.556401	−0.714521	−1.399878
H	1.123004	−2.069905	−0.355785
O	3.425013	−0.641467	0.569834
H	1.468021	2.095791	1.153872
C	1.818927	1.536243	2.035914
C	1.260614	2.152384	3.278388
H	2.920946	1.623252	2.018138
H	1.229226	1.542105	4.180495
C	1.093503	3.630882	3.409406
H	0.487667	3.896436	4.283451
H	2.063594	4.150239	3.522586
H	0.616660	4.065669	2.519033

E(UB3LYP) = −387.863815 a.u.
Zero Point Vibrational Energy = 0.191878 a.u.
H(298.15K) = −387.660891 a.u.

5. Addition of  to $H_3CO-CH=CH_2$

(a) Transition state:

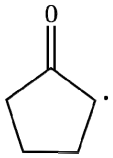
C	−0.094864	0.224805	0.771281
C	0.327212	−0.692605	1.951052
C	1.829782	−0.600396	1.962049
C	2.308002	−0.204464	0.642047
C	1.089474	0.171116	−0.215473
H	−1.043332	−0.086604	0.321392
H	−0.234082	1.249135	1.138103
H	0.016412	−1.733910	1.759433
H	−0.137001	−0.399231	2.900398
H	2.444452	−1.247627	2.579978
H	1.265978	1.102411	−0.764878
H	0.954876	−0.620542	−0.966853
O	3.480661	−0.163887	0.263709
H	1.869298	1.930665	2.405570
C	2.387573	1.251976	3.075859
C	1.945953	1.142183	4.368424
H	3.435291	1.067573	2.866893
H	2.506856	0.618407	5.142218
O	0.704880	1.569891	4.717255
C	0.360837	1.433932	6.095658
H	−0.669292	1.780491	6.191222
H	0.426680	0.385234	6.413783
H	1.015959	2.052489	6.722192

E(UB3LYP) = −463.045322 a.u.
Zero Point Vibrational Energy = 0.194837 a.u.
H(298.15K) = −462.838306 a.u.

(b) Product:

C	0.010508	−0.020758	−0.037068
C	−0.009257	0.035488	1.510271
C	1.477164	0.028539	1.926428
C	2.183617	−0.722379	0.787471
C	1.200796	−0.938337	−0.364204
H	−0.936013	−0.379859	−0.454198
H	0.184113	0.981948	−0.448637
H	−0.506598	−0.862595	1.901924
H	−0.551177	0.904271	1.893783
H	1.653996	−0.513107	2.863453
H	1.683849	−0.760584	−1.330535
H	0.901661	−1.997383	−0.344239
O	3.349544	−1.068057	0.798907
H	1.929905	2.036075	1.165608
C	2.121079	1.450640	2.074995
C	1.662420	2.229188	3.257098
H	3.206533	1.307868	2.146540
H	1.917297	1.915504	4.271875
O	0.477311	2.898336	3.116674
C	0.052301	3.630657	4.261961
H	−0.913168	4.074191	4.010961
H	−0.062961	2.965037	5.128862
H	0.773361	4.422348	4.502889

E(UB3LYP) = −463.075438 a.u.
Zero Point Vibrational Energy = 0.197905 a.u.
H(298.15K) = −462.865643 a.u.

6. Addition of  to $H_3COOC-CH=CH_2$

(a) Transition state:

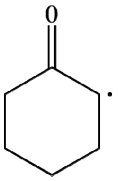
C	−0.212616	−0.080218	0.875230
C	0.489688	−1.041332	1.870684
C	1.910042	−0.557827	1.906424
C	2.207276	0.177359	0.669726
C	0.896455	0.340733	−0.110706
H	−1.069159	−0.548744	0.380723
H	−0.585998	0.793737	1.420784
H	0.472285	−2.076086	1.487213
H	0.009808	−1.072050	2.855340
H	2.698890	−1.098385	2.419934
H	0.797934	1.358583	−0.502492
H	0.942731	−0.332112	−0.979215
O	3.310592	0.582498	0.313408
H	1.448080	1.872273	2.714450
C	2.083251	1.215540	3.299751
C	1.663450	0.789773	4.534745
H	3.140775	1.227304	3.055623
H	2.331671	0.250148	5.199780
C	0.307889	0.964556	5.073857
O	−0.039169	0.571399	6.176958
O	−0.529963	1.622728	4.228628
C	−1.858467	1.859063	4.726927
H	−2.375454	2.394235	3.929605
H	−2.360275	0.912534	4.946100
H	−1.821814	2.464395	5.636755

E(UB3LYP) = −576.405676 a.u.
Zero Point Vibrational Energy = 0.205580 a.u.
H(298.15K) = −576.186453 a.u.

(b) Product:

C	−0.014802	−0.115921	−0.014865
C	−0.000910	−0.073864	1.532899
C	1.492119	0.002701	1.921360
C	2.228175	−0.648235	0.734903
C	1.225621	−0.949496	−0.377617
H	−0.944864	−0.534917	−0.411784
H	0.082863	0.898558	−0.422410
H	−0.438281	−0.999891	1.928504
H	−0.589092	0.757189	1.935521
H	1.720463	−0.575792	2.825415
H	1.660659	−0.748287	−1.361527
H	1.003057	−2.026749	−0.336161
O	3.423234	−0.861086	0.696919
H	1.804865	2.072574	1.258529
C	2.037046	1.447949	2.126553
C	1.520147	2.078104	3.371502
H	3.134195	1.367344	2.186492
H	1.679517	1.581380	4.325170
C	0.805474	3.335275	3.465248
O	0.411870	3.821290	4.521539
O	0.606782	3.938626	2.258289
C	−0.085816	5.196776	2.300044
H	−0.145241	5.529030	1.262877
H	−1.086410	5.069871	2.723195
H	0.469222	5.919014	2.905379

E(UB3LYP) = −576.440831 a.u.
Zero Point Vibrational Energy = 0.208541 a.u.
H(298.15K) = −576.218826 a.u.

7. Addition of  **to $H_3C-CH=CH_2$**

(a) Transition state:

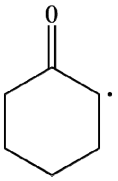
O	0.036190	−0.003665	0.030120
H	0.026529	−0.000551	3.482738
C	1.039414	−0.037246	3.083217
C	2.066060	−0.417729	3.927900
H	1.245686	0.658759	2.274968
H	3.092595	−0.277050	3.587307
C	−0.314390	−0.873333	0.836250
C	−1.800620	−1.180542	1.022081
C	0.669681	−1.597058	1.646920
C	−2.112783	−2.181984	2.143886
H	−2.153925	−1.574986	0.058329
H	−2.325392	−0.227022	1.163264
C	0.306129	−2.883698	2.371609
H	1.675386	−1.534485	1.239479
C	−1.131821	−3.358763	2.089108
H	−3.148739	−2.531904	2.051995
H	−2.038077	−1.690542	3.125275
H	1.021954	−3.669677	2.094289
H	0.424321	−2.750717	3.455931
H	−1.410006	−4.135350	2.812779
H	−1.183403	−3.822814	1.093355
C	1.889340	−1.104600	5.246748
H	2.427611	−0.568687	6.042193
H	0.834471	−1.167158	5.537044
H	2.301431	−2.125642	5.234817

E(UB3LYP) = −427.148772 a.u.
Zero Point Vibrational Energy = 0.219614 a.u.
H(298.15K) = −426.917240 a.u.

(b) Product:

O	−0.240939	−0.114729	0.212504
H	−0.128534	−0.312925	3.077612
C	0.923907	−0.210167	2.770937
C	1.816291	−0.244792	3.971064
H	0.970555	0.781150	2.284287
H	2.849618	−0.566259	3.838266
C	0.519532	−1.051672	0.393904
C	0.784676	−2.092687	−0.685198
C	1.253668	−1.278390	1.717431
C	0.540155	−3.523475	−0.158241
H	1.837234	−2.000643	−0.995068
H	0.158309	−1.863219	−1.552722
C	0.983620	−2.725284	2.207801
H	2.329911	−1.215968	1.477755
C	1.314568	−3.779241	1.142159
H	0.820839	−4.252575	−0.928666
H	−0.535479	−3.658464	0.024519
H	1.562017	−2.903707	3.122323
H	−0.077032	−2.807532	2.489947
H	1.084731	−4.781884	1.525546
H	2.395428	−3.764116	0.934795
C	1.459593	0.493510	5.219781
H	2.099676	0.206112	6.062081
H	1.562227	1.588388	5.097941
H	0.413866	0.316194	5.509456

E(UB3LYP) = −427.183381 a.u.
Zero Point Vibrational Energy = 0.221245 a.u.
H(298.15K) = −426.950114 a.u.

8. Addition of  **to $H_3CO-CH=CH_2$**

(a) Transition state:

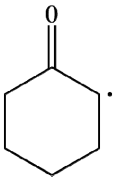
O	−0.004165	−0.011465	−0.030574
H	0.029029	−0.114603	3.417324
C	1.040578	−0.032348	3.029647
C	2.081195	−0.341185	3.875315
H	1.209911	0.724677	2.271438
H	3.121062	−0.118365	3.638264
C	−0.243095	−0.936320	0.759059
C	−1.688090	−1.380569	0.992484
C	0.823300	−1.586319	1.513658
C	−1.865000	−2.413509	2.115992
H	−2.040485	−1.800030	0.038727
H	−2.292677	−0.480537	1.163038
C	0.614453	−2.913487	2.222013
H	1.811830	−1.399124	1.101841
C	−0.792802	−3.503721	2.006825
H	−2.870687	−2.849931	2.064671
H	−1.789309	−1.925424	3.098701
H	1.374804	−3.629735	1.879464
H	0.789970	−2.793346	3.300913
H	−0.971650	−4.303275	2.736905
H	−0.854531	−3.966007	1.010750
O	1.867643	−1.084223	4.992532
C	3.018541	−1.356952	5.791434
H	2.676554	−1.973961	6.623716
H	3.774287	−1.904633	5.213585
H	3.451420	−0.425575	6.178107

E(UB3LYP) = −502.360602 a.u.
Zero Point Vibrational Energy = 0.224585 a.u.
H(298.15K) = −502.122893 a.u.

(b) Product:

O	−0.039262	−0.015281	0.017511
H	0.011462	0.012333	2.910449
C	1.063992	0.004943	2.598716
C	1.938010	0.051305	3.804893
H	1.218256	0.924738	2.022460
H	3.005808	0.269630	3.726264
C	0.608574	−1.010843	0.296630
C	0.770983	−2.165016	−0.684411
C	1.299413	−1.198995	1.650972
C	0.374862	−3.512016	−0.041606
H	1.829949	−2.209283	−0.982923
H	0.179543	−1.946911	−1.579130
C	0.874151	−2.561288	2.256761
H	2.378909	−1.265052	1.429289
C	1.107488	−3.729871	1.288727
H	0.585425	−4.329658	−0.742453
H	−0.710564	−3.520110	0.133090
H	1.414996	−2.720596	3.195474
H	−0.192633	−2.510262	2.521508
H	0.774502	−4.667960	1.751652
H	2.186292	−3.840420	1.099579
O	1.567008	−0.743853	4.856386
C	2.396841	−0.652530	6.009061
H	2.002298	−1.362933	6.738391
H	3.435773	−0.916552	5.764456
H	2.368365	0.362440	6.426329

E(UB3LYP) = −502.394255 a.u.
Zero Point Vibrational Energy = 0.227277 a.u.
H(298.15K) = −502.154097 a.u.

9. Addition of  **to $H_3COOC-CH=CH_2$**

(a) Transition state:

O	0.767734	−0.445484	−0.803238
H	0.135271	−0.213514	2.480705
C	1.137791	0.171469	2.321654
C	1.998964	0.256918	3.394774
H	1.266375	0.843126	1.478709
H	2.945213	0.783778	3.310800
C	1.778581	−0.355996	4.709112
O	2.556661	−0.255111	5.645787
O	0.605946	−1.042459	4.796421
C	0.318821	−1.622222	6.080834
H	−0.645349	−2.118681	5.965265
H	1.093802	−2.341768	6.359270
H	0.261981	−0.843310	6.846189
C	0.738148	−1.335526	0.051368
C	−0.443923	−2.298677	0.125493
C	1.829545	−1.477720	1.026412
C	−0.409707	−3.252849	1.328850
H	−0.430433	−2.874030	−0.811651
H	−1.364546	−1.702356	0.095354
C	2.022639	−2.749127	1.826076
H	2.723677	−0.921922	0.755893
C	0.994310	−3.847117	1.489469
H	−1.154512	−4.046360	1.190805
H	−0.688217	−2.719048	2.248377
H	3.043425	−3.120623	1.660171
H	1.966572	−2.523687	2.899104
H	1.008915	−4.612358	2.274937
H	1.279493	−4.350512	0.554372

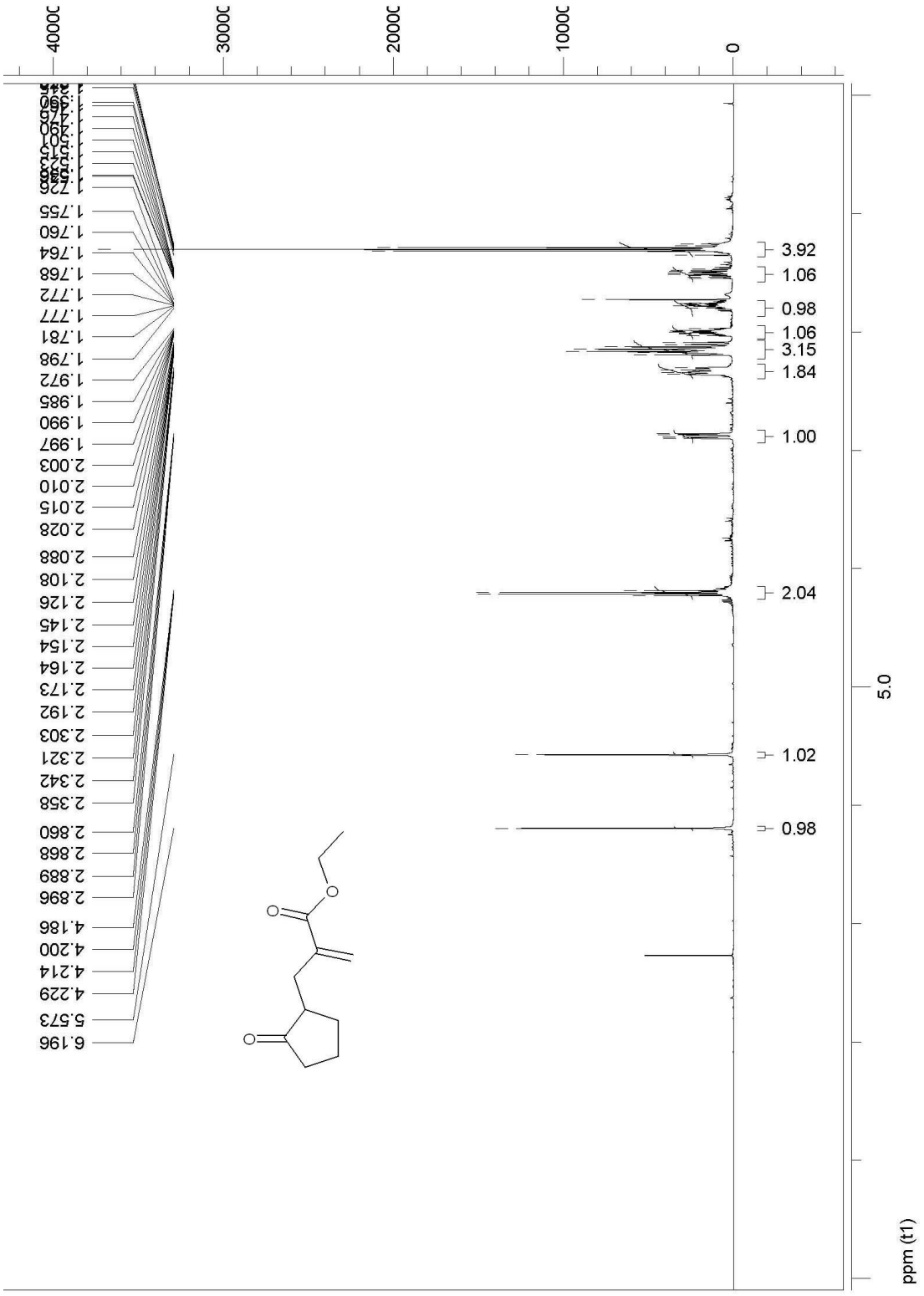
E(UB3LYP) = −615.720695 a.u.
Zero Point Vibrational Energy = 0.235263 a.u.
H(298.15K) = −615.470765 a.u.

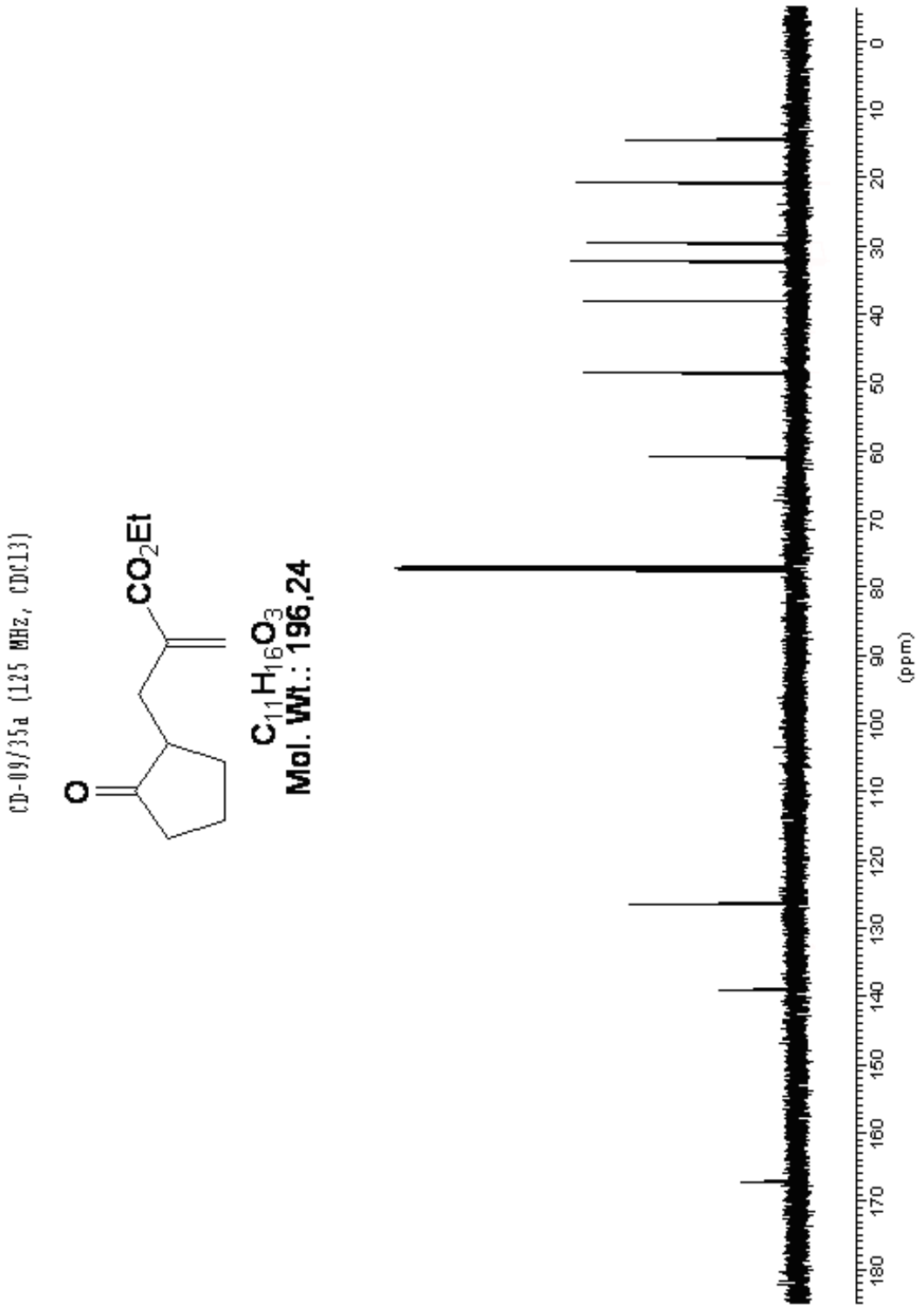
(b) Product:

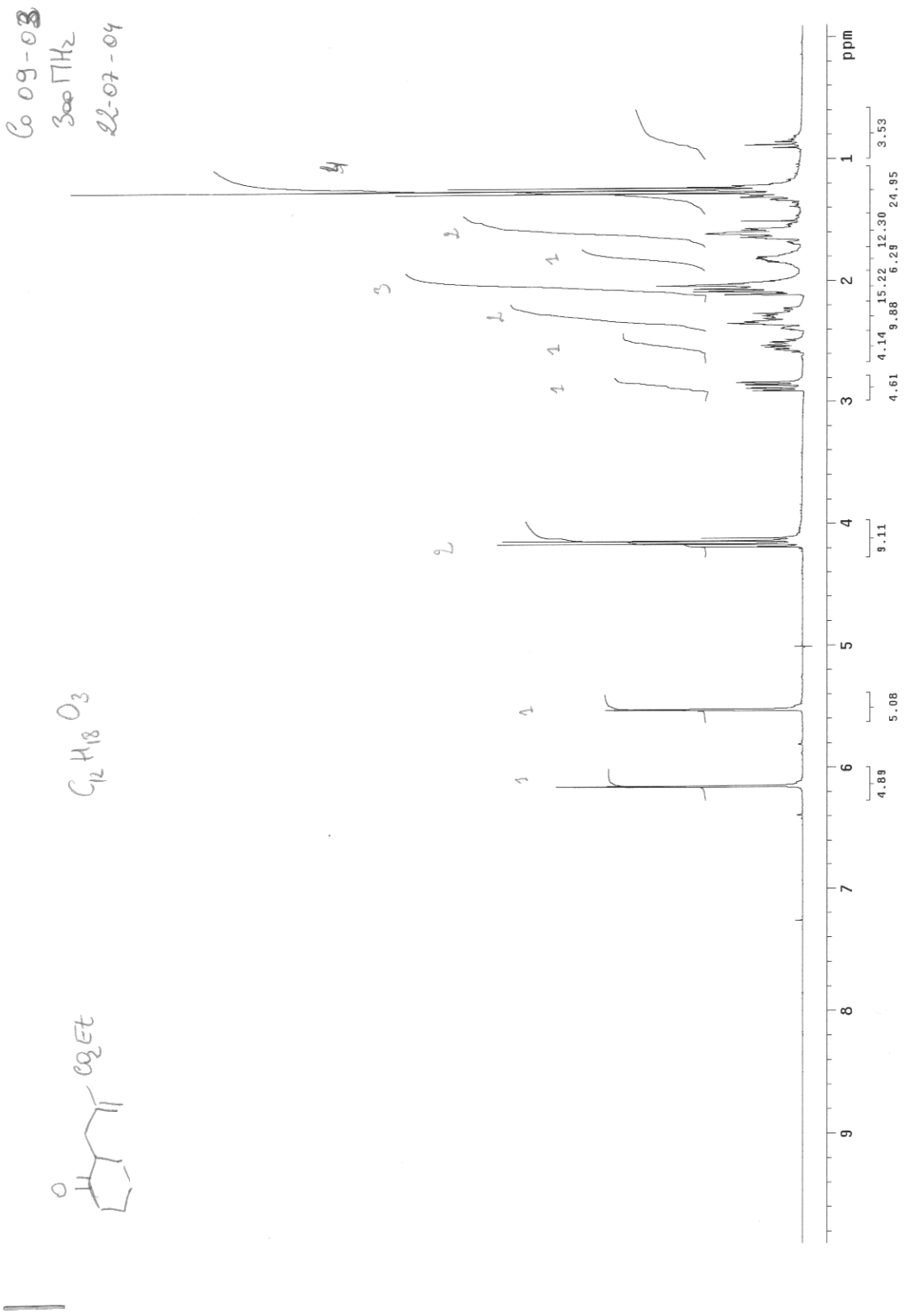
O	0.152215	0.014487	−0.162970
H	0.182540	0.312492	2.719678
C	1.224401	0.185192	2.409958
C	2.134572	0.243346	3.586810
H	1.436969	1.038161	1.743401
H	3.173744	−0.058753	3.479225
C	1.795554	0.734299	4.907107
O	2.590621	0.790881	5.841690
O	0.497110	1.131887	5.020222
C	0.111054	1.636700	6.308198
H	−0.940230	1.909652	6.208537
H	0.239406	0.868139	7.075967
H	0.713106	2.510555	6.573233
C	0.698629	−1.006036	0.220763
C	0.742534	−2.267381	−0.629639
C	1.383876	−1.108212	1.587518
C	0.258752	−3.504034	0.157294
H	1.787199	−2.426600	−0.939589
H	0.149282	−2.096959	−1.533179
C	0.880745	−2.369118	2.336404
H	2.455134	−1.264386	1.370506
C	1.005882	−3.643651	1.490509
H	0.387945	−4.403403	−0.457382
H	−0.819224	−3.408024	0.350214
H	1.438724	−2.474479	3.275179
H	−0.172192	−2.215052	2.615767
H	0.616459	−4.501767	2.052995
H	2.068660	−3.853226	1.296370

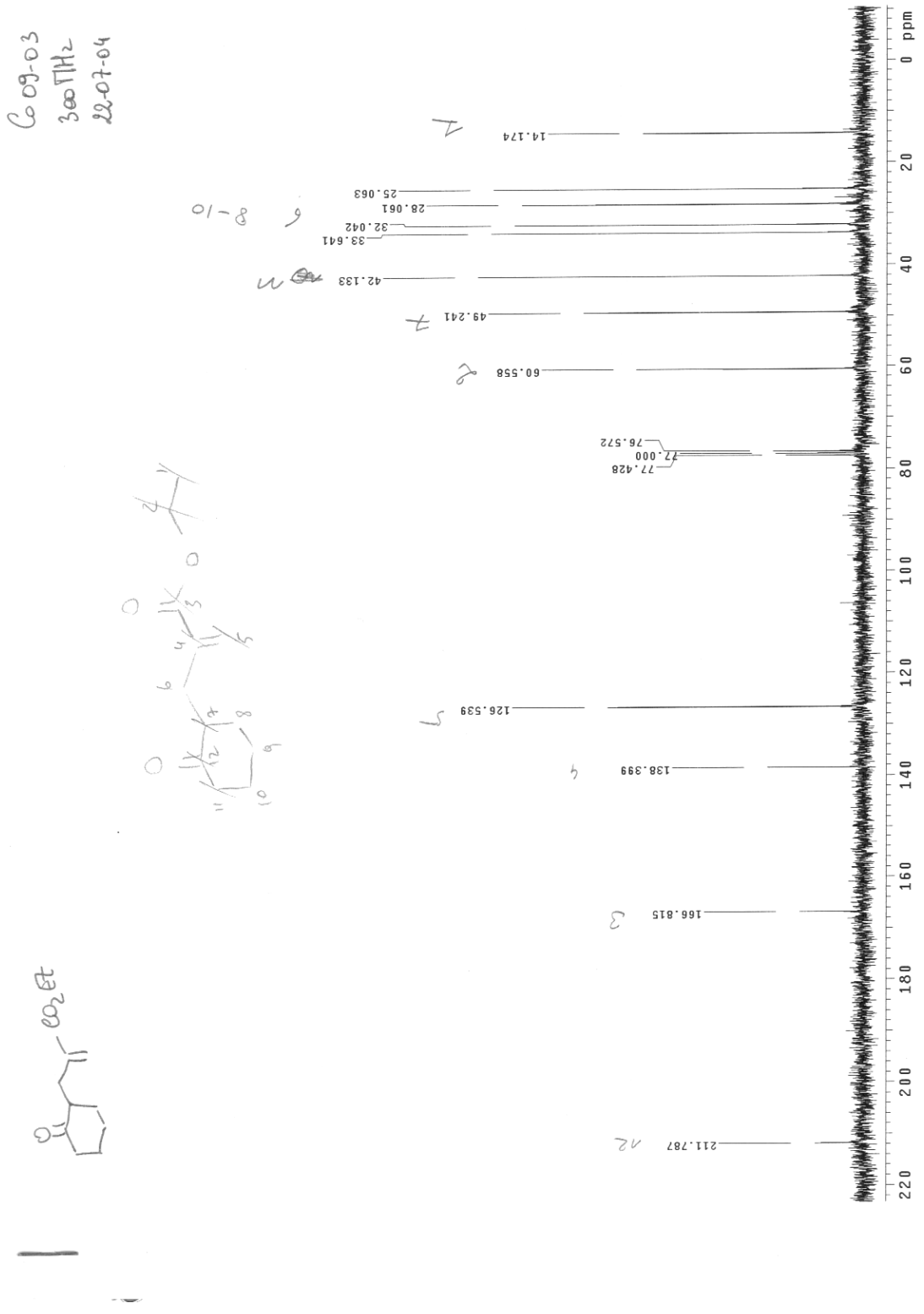
E(UB3LYP) = −615.760767 a.u.
Zero Point Vibrational Energy = 0.237720 a.u.
H(298.15K) = −615.508538 a.u.

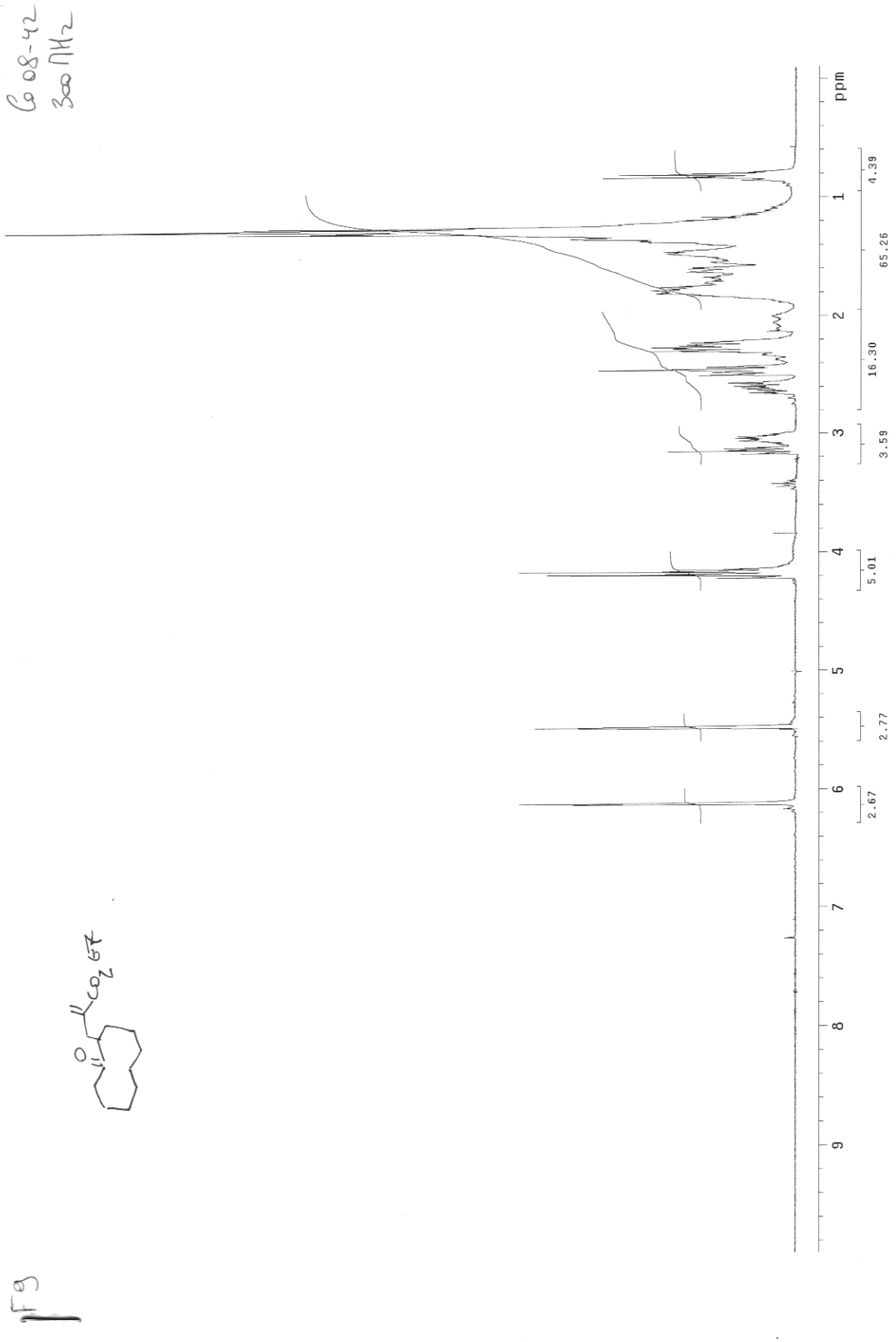
^{1}H and ^{13}C-NMR spectras

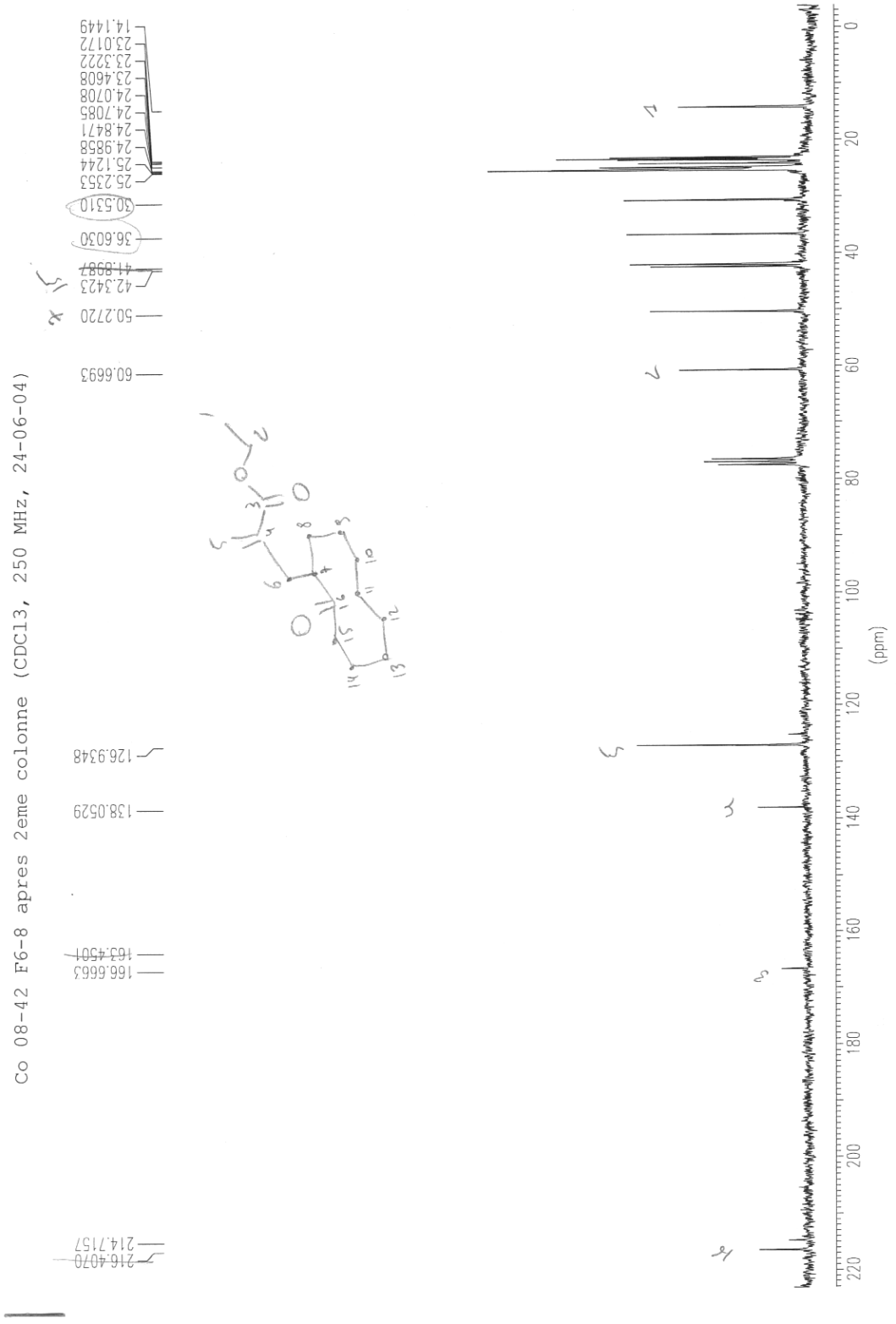


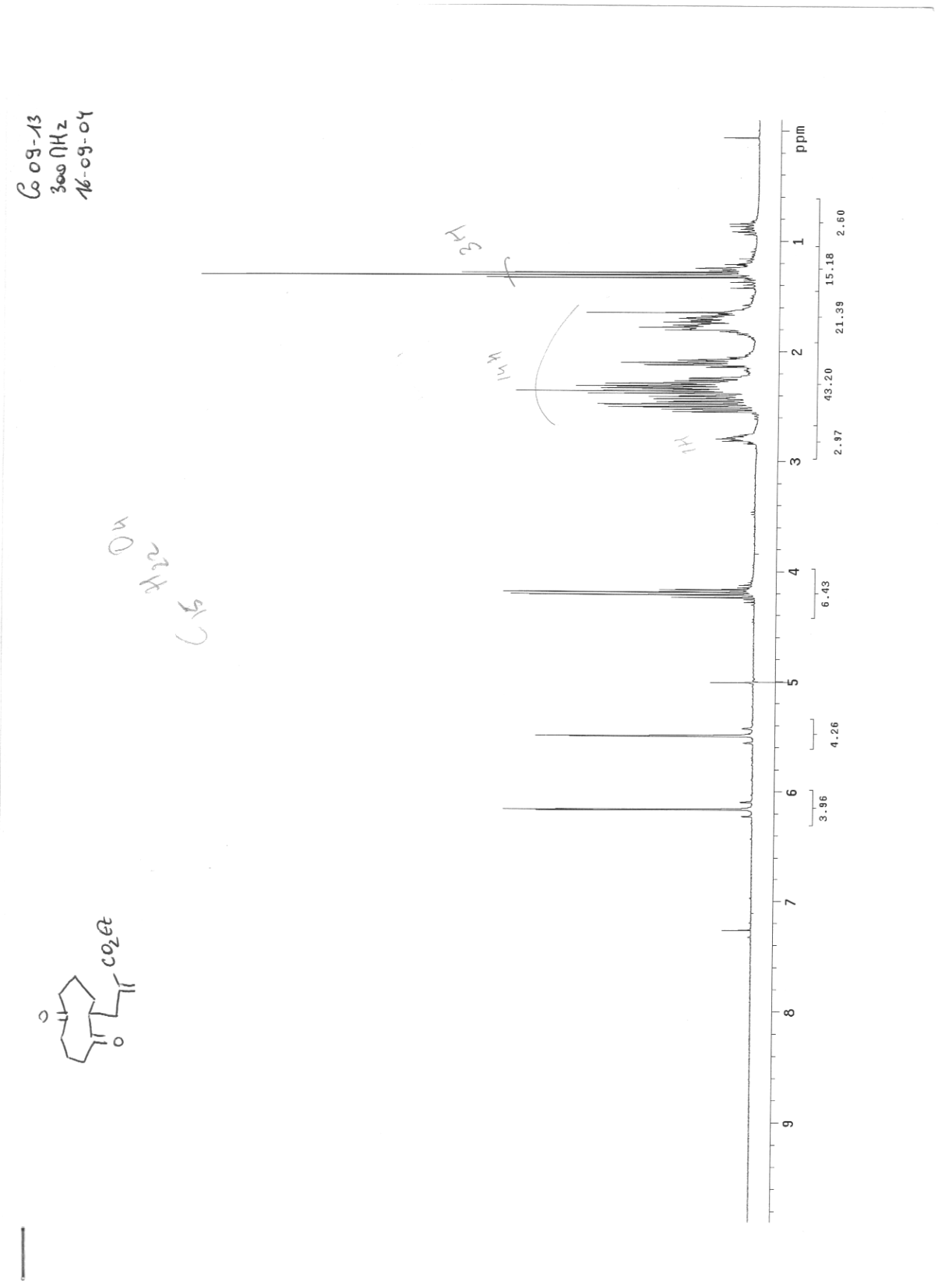

CD-09/35a (125 MHz, CDCl3)
O
CO2Et
C11H16O3
Mol. Wt.: 196,24
(ppm)

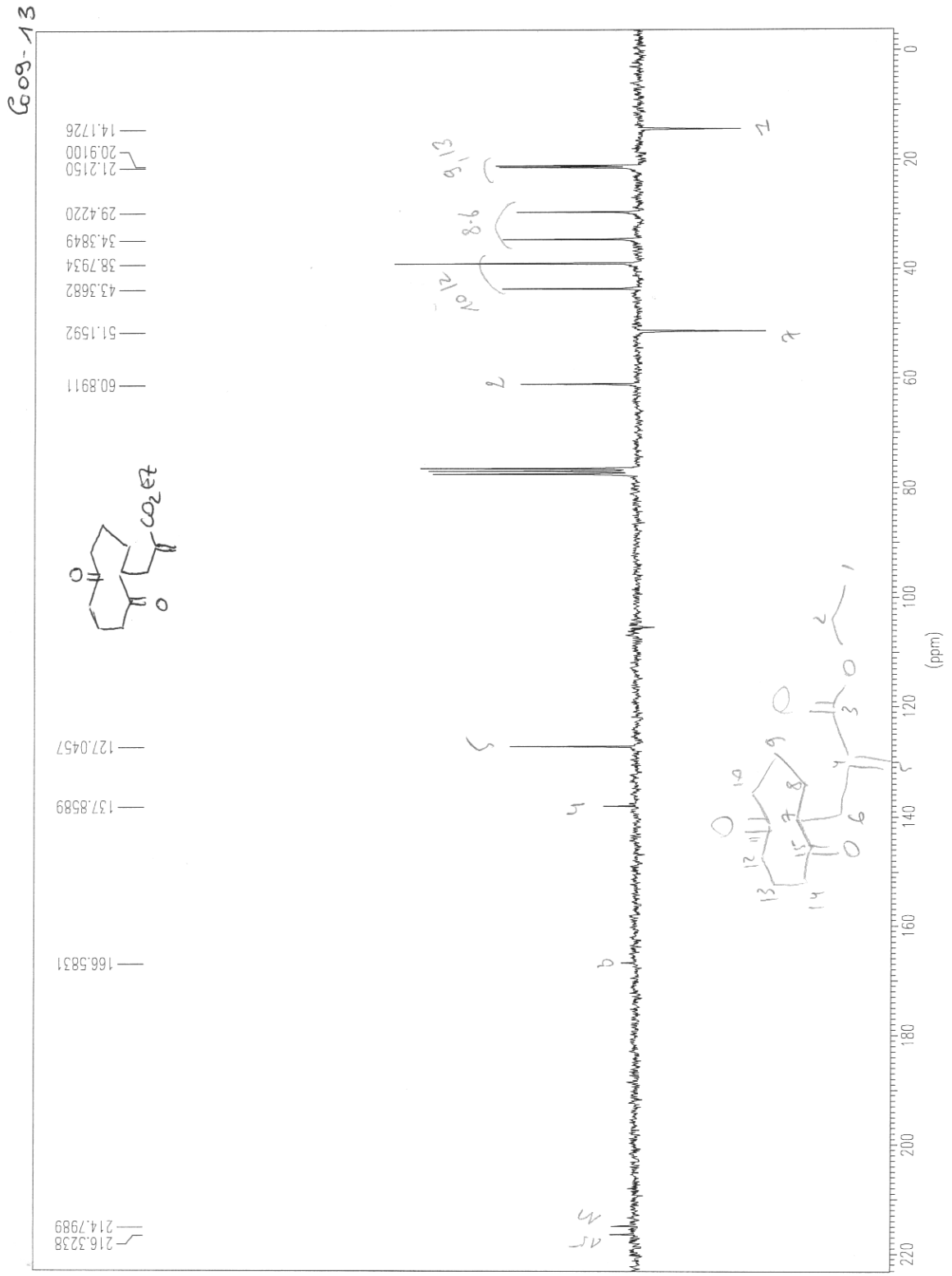

Co 09-03
300 MHz
22-07-04
$C_{12}H_{18}O_3$
CO_2Et
O
ppm
1
2
3
4
5
6
7
8
9
4.89
5.08
9.11
4.61
4.14
9.88
15.22
6.29
12.30
24.95
3.53

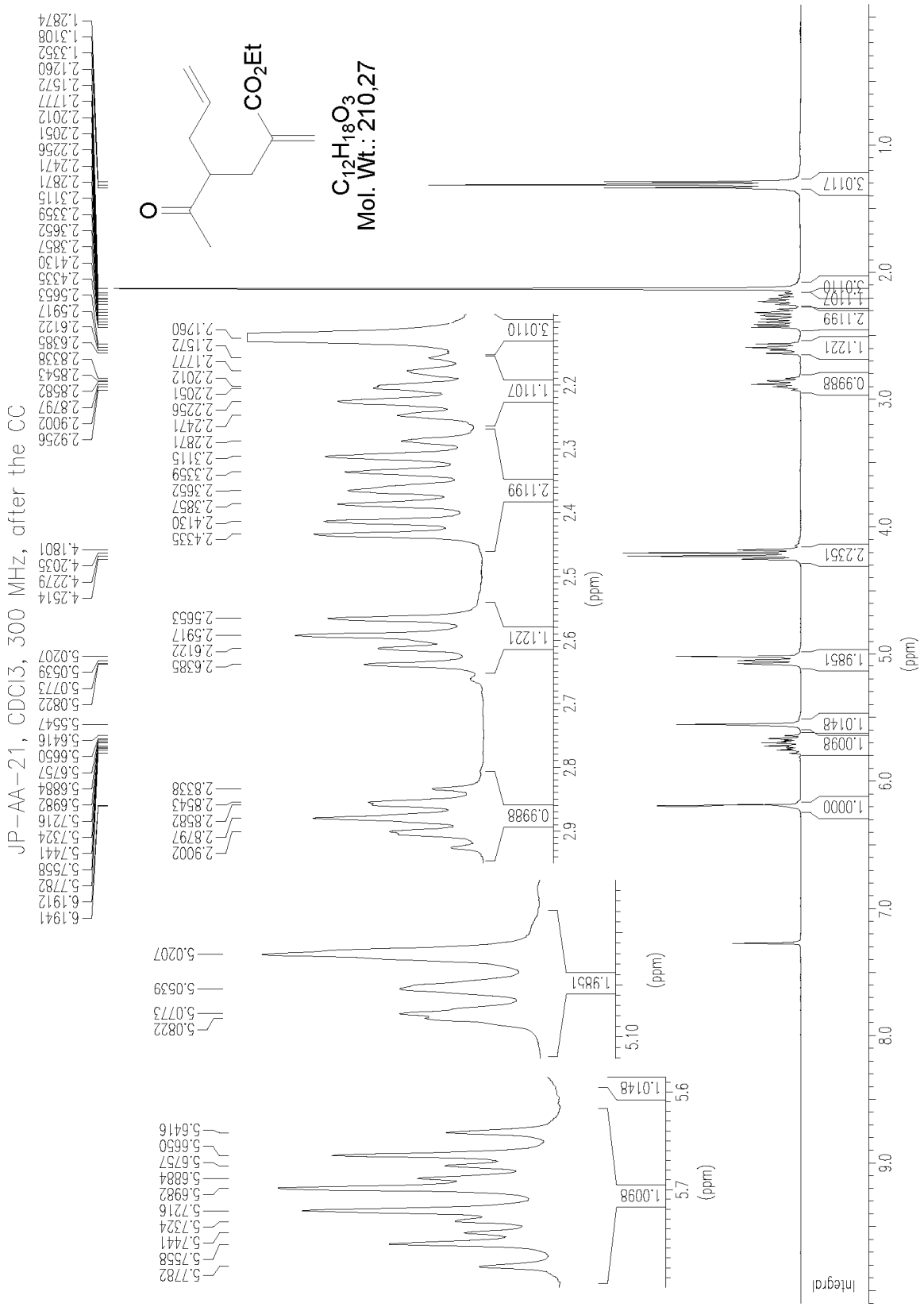

14.174
25.063
28.061
32.042
33.641
42.133
49.241
60.558
76.572
77.000
77.428
126.539
138.399
166.815
211.787
0 ppm
20
40
60
80
100
120
140
160
180
200
220

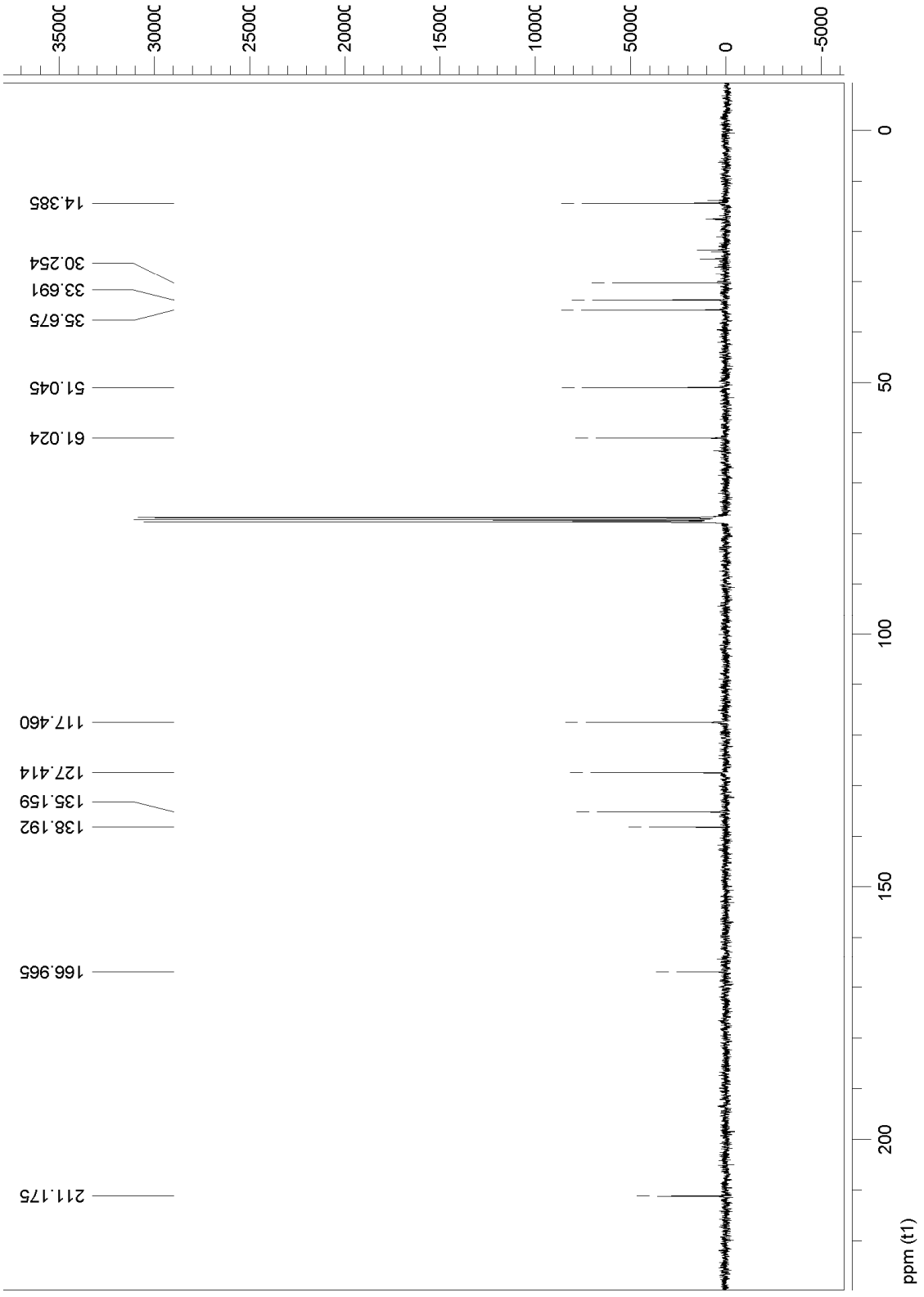

Co 08-42
300 MHz
ppm
1
2
3
4
5
6
7
8
9
4.39
65.26
16.30
3.59
5.01
2.77
2.67

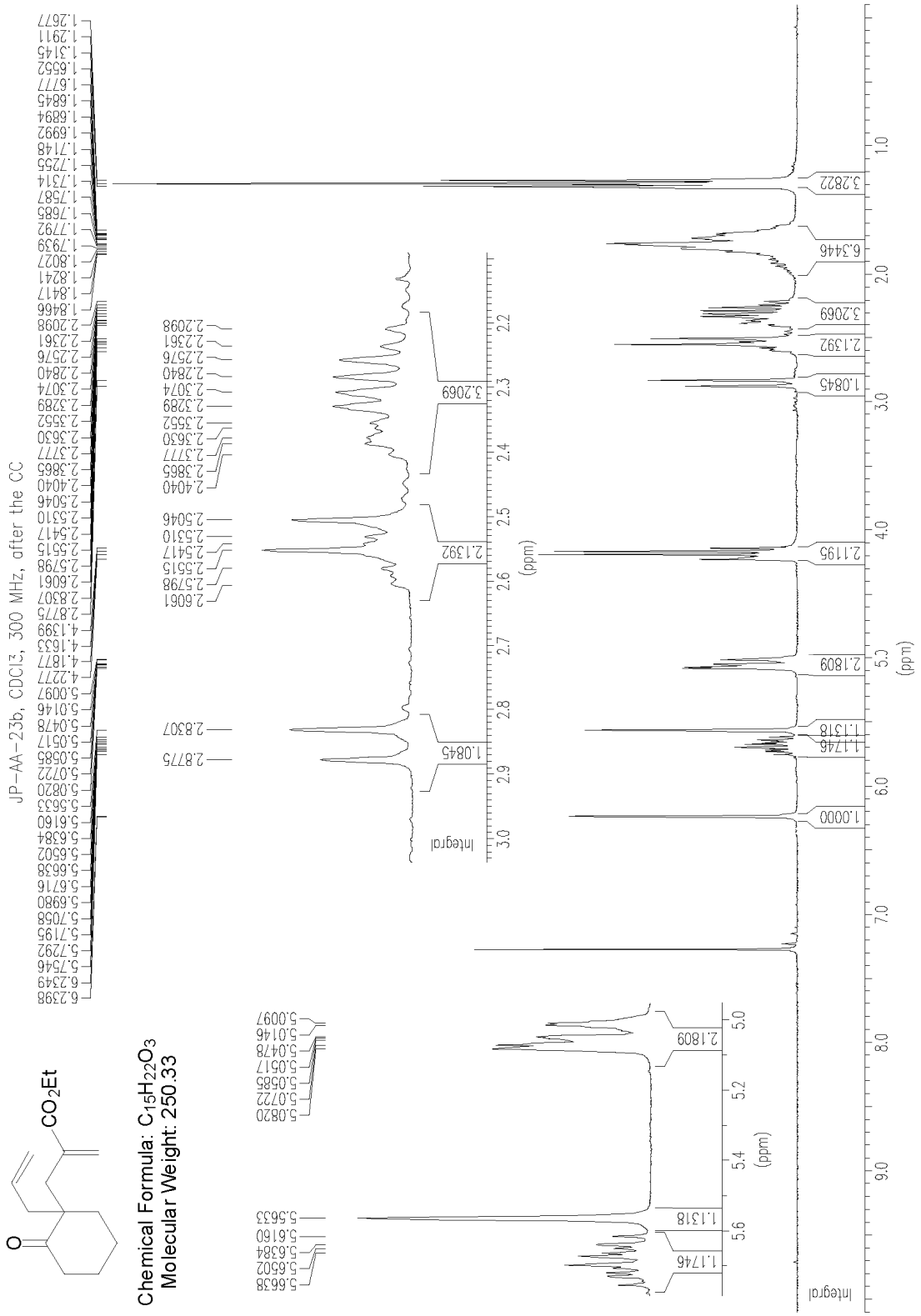

Co 08-42 F6-8 apres 2eme colonne (CDCl3, 250 MHz, 24-06-04)
14.1449
23.0172
23.3222
23.4608
24.0708
24.7085
24.8471
24.9858
25.1244
25.2353
30.5310
36.6030
41.8987
42.3423
50.2720
60.6693
126.9348
138.0529
163.4501
166.6663
214.7157
216.4070
(ppm)

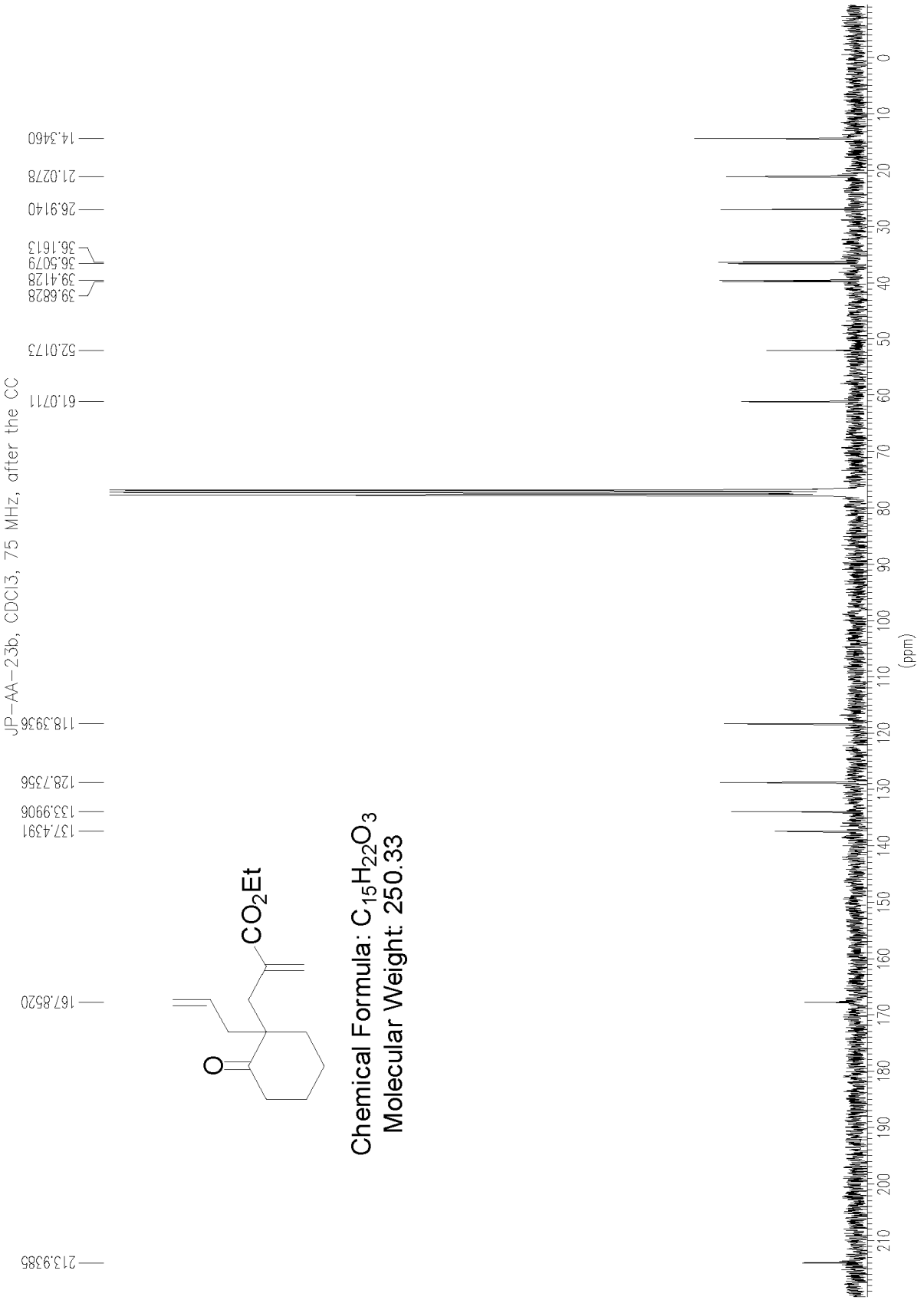

C09-13
300 MHz
16-09-04
ppm
2.60
15.18
21.39
43.20
2.97
6.43
4.26
3.96
CO2Et
O
O

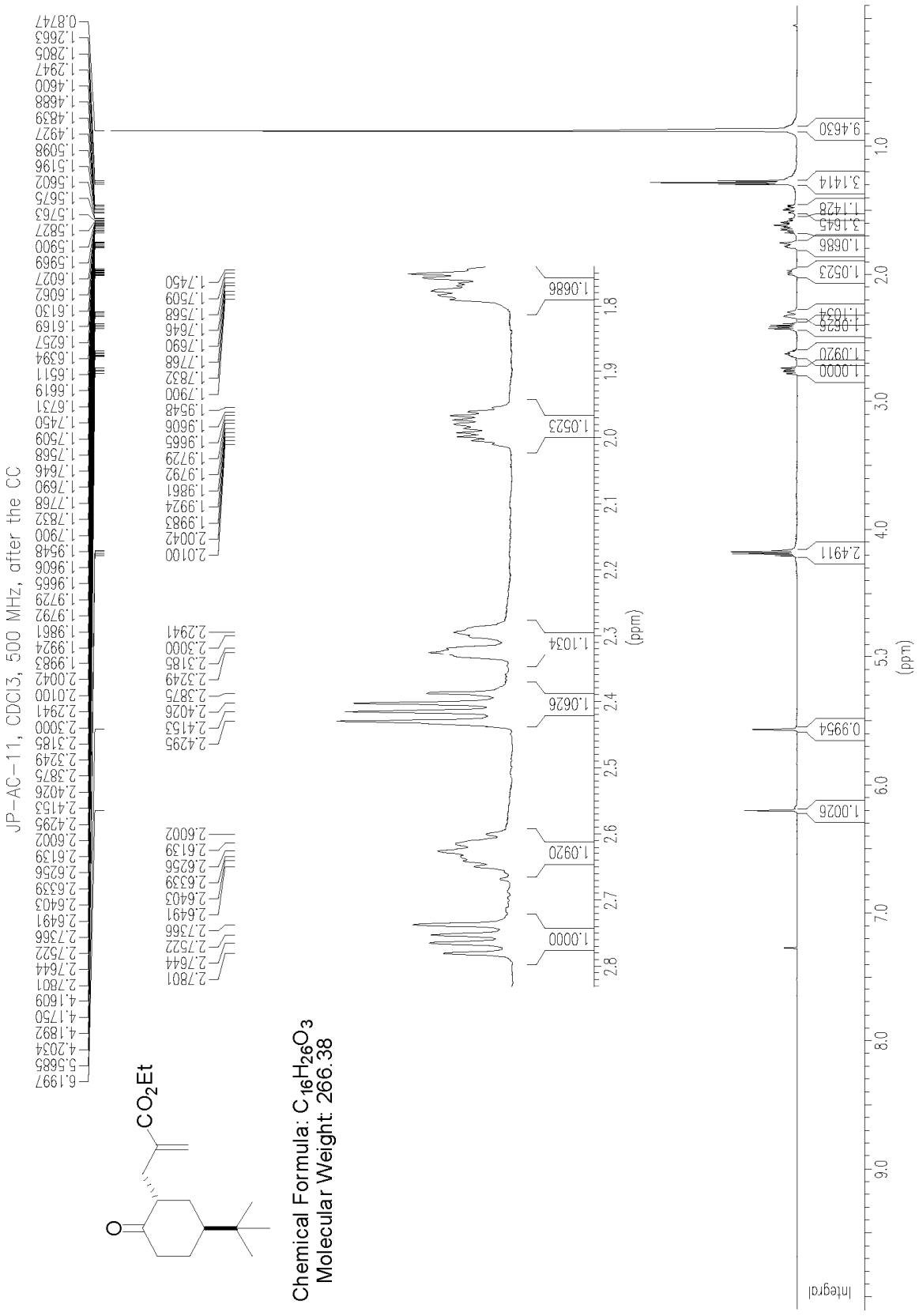

G09-13
14.1726
20.9100
21.2150
29.4220
34.3849
38.7934
43.3682
51.1592
60.8911
127.0457
137.8589
166.5831
214.7989
216.3238
(ppm)

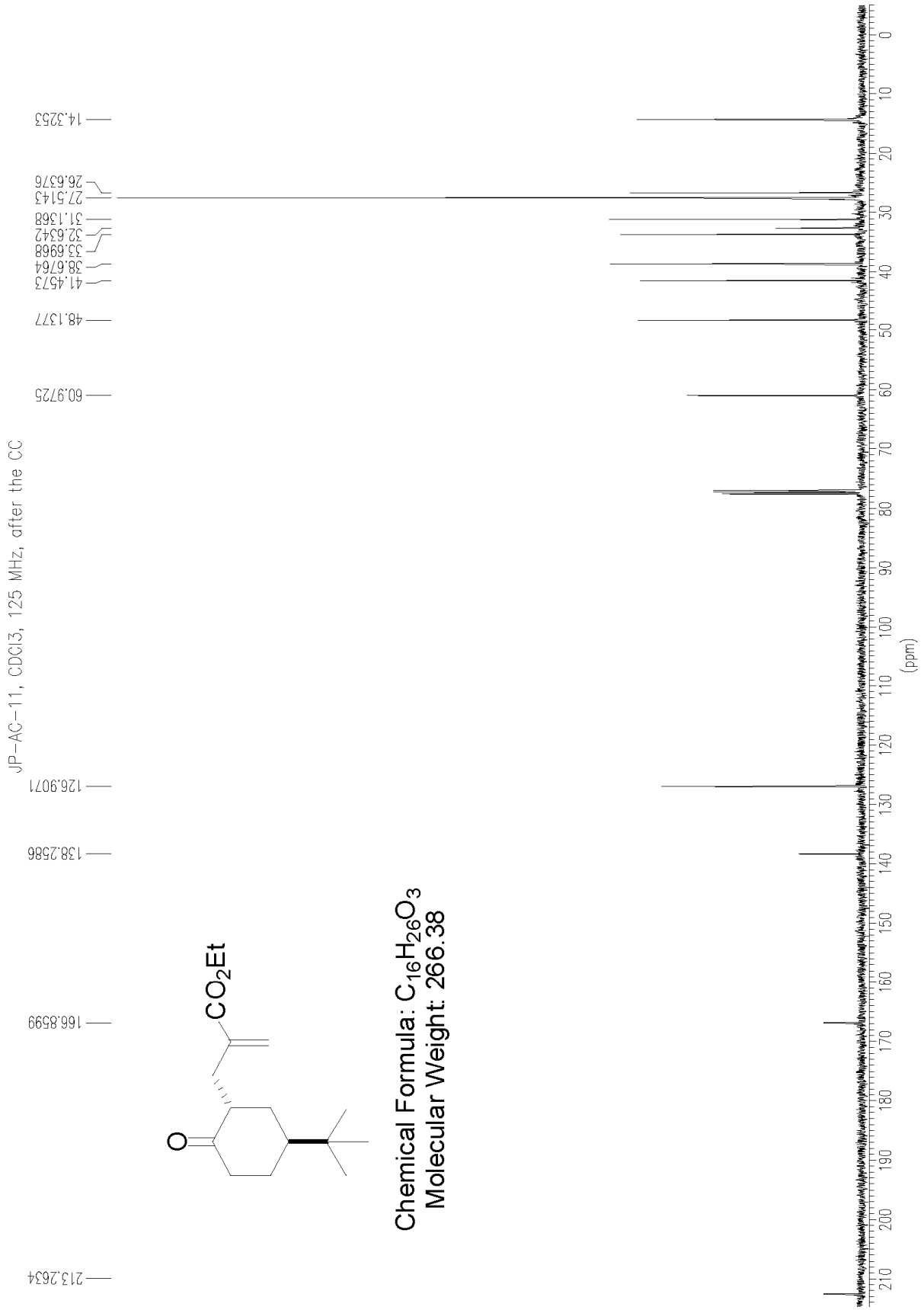

JP-AA-21, CDCl3, 300 MHz, after the CC
O
CO2Et
C12H18O3
Mol. Wt.: 210,27
Integral
(ppm)


35000
30000
25000
20000
15000
10000
5000
0
-5000
14.385
30.254
33.691
35.675
51.045
61.024
117.460
127.414
135.159
138.192
166.965
211.175
0
50
100
150
200
ppm (t1)


JP-AA-23b, CDCl3, 300 MHz, after the CC
Chemical Formula: C15H22O3
Molecular Weight: 250.33
CO2Et
O
(ppm)
Integral
3.2822
6.3446
3.2069
2.1392
1.0845
2.1195
2.1809
1.1318
1.1746
1.0000


JP-AA-23b, CDCl3, 75 MHz, after the CC
14.3460
21.0278
26.9140
36.1613
36.5079
39.4128
39.6828
52.0173
61.0711
118.3936
128.7356
133.9906
137.4391
167.8520
213.9385
CO2Et
O
Chemical Formula: C15H22O3
Molecular Weight: 250.33
(ppm)


JP-AC-11, CDCl3, 500 MHz, after the CC
Chemical Formula: C16H26O3
Molecular Weight: 266.38
CO2Et
O
Integral
(ppm)


JP-AC-11, CDCl3, 125 MHz, after the CC
14.3253
26.6376
27.5143
31.1368
32.6342
33.6968
38.6764
41.4573
48.1377
60.9725
126.9071
138.2586
166.8599
213.2634
CO2Et
O
Chemical Formula: C16H26O3
Molecular Weight: 266.38
(ppm)

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