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Supporting Information

Determination of the Electrophilicity Parameters of Diethyl Benzylidenemalonates in DMSO: Reference Electrophiles for Characterizing Strong Nucleophiles

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1. Materials

General. Commercially available DMSO (content of H_2O < 50 ppm) was used without further purification. Stock solutions of KO*t*Bu in DMSO were prepared under nitrogen atmosphere. The employed potassium salts **2a-d** and **2f** were prepared by dissolving the corresponding CH-acid in dry ethanol and subsequent addition of 0.9 equiv. of potassium KO*t*Bu dissolved in dry ethanol. The potassium salts **2a-d** and **2f** precipitated from the reaction mixture. After filtration, they were dried under reduced pressure. The anion of *bis*(p-nitrophenyl)methane (**2e**) was prepared following the procedure described in Ref. [29]

CAUTION: Because of explosion hazards the isolation of 2a–K should be avoided!

2. Instruments

^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 400 (400 MHz, 100.6 MHz), Bruker ARX 300 (300 MHz, 75.5 MHz), or Varian Mercury 200 (200 MHz) NMR spectrometers. Chemical shifts are expressed in ppm and refer to DMSO-d_6 (δ_H 2.49, δ_C 39.7) or to $CDCl_3$ (δ_H 7.26, δ_C 77.0). The coupling constants are in Hz. Abbreviations used are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet).

3. Determination of Rate Constants

The general method for the determination of the rate constants is described in the experimental part of the paper.

The temperature of the solutions was kept constant (20 ± 0.1 °C) during all kinetic experiments by using a circulating bath thermostat.

For evaluation of fast kinetic experiments commercial stopped-flow UV-vis spectrometer systems were used. UV-Vis kinetics of slow reactions was determined by using a diode array spectrophotometer, which was connected to a quartz suprasil immersion probe (5 mm light path). Rate constants k_{obs} (s^{-1}) were obtained by fitting the single exponential function $A_t = A_0\exp(-k_{1\psi}t) + C$ to the observed time-dependent electrophile absorbance. (For the reactions of **1a-c** with the green dinitrobenzhydryl anion **2e**-K^+ the first-order rate constants k_{obs} were determined with **2e**-K^+ as the minor component). Plotting the k_{obs} against the concentrations of the nucleophiles resulted in linear correlations whose slopes correspond to the second-order rate constants k_2 (L mol^{-1} s^{-1}). For stopped-flow experiments two stock solutions were used: A solution of electrophiles **1a-i** in DMSO and a solution of the carbanion **2**, which was either generated by deprotonation of the corresponding parent compound **2**–H with 1.05 equiv. KO*t*Bu in DMSO *in situ* directly before use, or by using the preformed carbanion **2** (potassium salt) in DMSO.

Figure S1 shows that the reaction of electrophile **1b** with the carbanion **2c** was followed at λ = 290 nm. The decay of the absorption of **1b** was accompanied by a development of an absorption band at λ ≈ 360 nm.

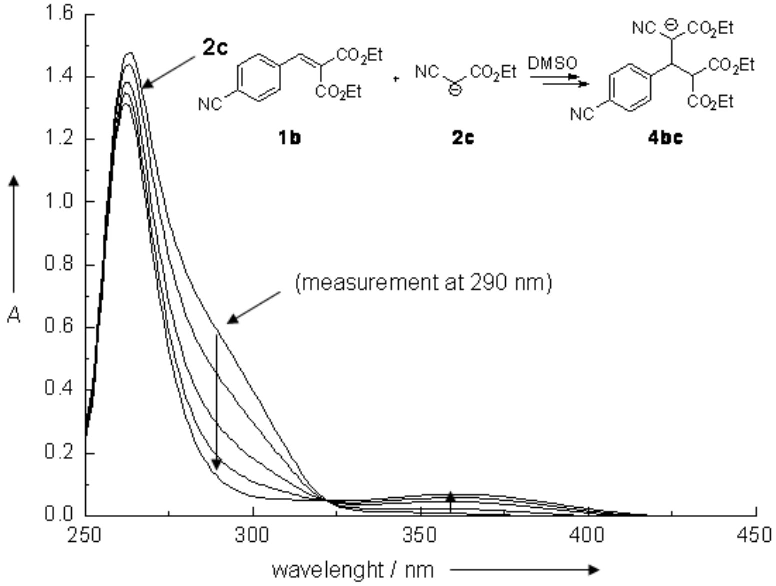


Figure S1: UV-vis spectra during the reaction of electrophile **1b** (4.12×10^{-5} mol L^{-1}) with the carbanion **2c** (3.57×10^{-5} mol L^{-1}) in DMSO at 20°C from an individual measurement.

4.1 Determination of Equilibrium Constants

The equilibrium constants *K* are based on the equation S1 by using the initial absorptions *A* from the electrophiles **1e** and **1f** and the equilibrium absorptions after addition of carbanion **2b** at 20°C in DMSO. It has to be mentioned that the employed values are derived from the kinetic measurements and are not the result from individual titration experiments.

From the initial concentrations, $[E]_0$ and $[C^-]_0$, and the absorbance of the electrophile ($A = \varepsilon[E]d$), the equilibrium concentrations $[E]_{eq}$, and $[C^-]_{eq}$ were calculated. Substitution into equation (S1) yielded the equilibrium constants *K* listed in Table S1 and S2. The equilibrium constants *K* presented herein are based only on the kinetic measurements and have not been repeated.

$$K = \frac{[adduct]_{eq}}{[E]_{eq}[Nu^-]_{eq}} = \frac{[E]_0 - [E]_{eq}}{[E]_{eq}([Nu^-]_0 - [E]_0 + [E]_{eq})} \qquad \text{(S1)}$$

Table S1: Equilibrium constant for the reaction of **1e** with **2b** (DMSO, 20°C)

No.	[**1e**]$_0$ / M	[**2b-K**]$_0$ / M	A_0	A_{eq}	[**1e**]$_{eq}$ / M	[**2b-K**]$_{eq}$ / M	K / M^{-1}
1	9.98×10^{-5}	1.79×10^{-3}	0.788	0.377	4.78×10^{-5}	1.74×10^{-3}	6.26×10^{2}
2	9.71×10^{-5}	2.52×10^{-3}	0.768	0.309	3.99×10^{-5}	2.46×10^{-3}	5.83×10^{2}
3	1.06×10^{-4}	4.13×10^{-3}	0.851	0.268	3.42×10^{-5}	4.06×10^{-3}	5.15×10^{2}
4	1.06×10^{-4}	4.72×10^{-3}	0.857	0.250	3.19×10^{-5}	4.65×10^{-3}	4.98×10^{2}
5	1.12×10^{-4}	6.61×10^{-3}	0.902	0.227	2.95×10^{-5}	6.52×10^{-3}	4.31×10^{2}

$K = 5.31 \times 10^{2}$ M^{-1}

log $K = (2.72 \pm 0.09)$

Table S2: Equilibrium constant for the reaction of **1f** with **2b** (DMSO, 20°C)

No.	[**1f**]$_0$ / M	[**2b-K**]$_0$ / M	A_0	A_{eq}	[**1f**]$_{eq}$ / M	[**2b-K**]$_{eq}$ / M	K / M^{-1}
1	7.95×10^{-5}	1.53×10^{-3}	0.95	0.67	5.60×10^{-5}	1.51×10^{-3}	2.77×10^{2}
2	9.64×10^{-5}	3.98×10^{-3}	1.14	0.59	4.98×10^{-5}	3.93×10^{-3}	2.38×10^{2}
3	9.52×10^{-5}	5.51×10^{-3}	1.13	0.50	4.21×10^{-5}	5.46×10^{-3}	2.31×10^{2}
4	9.20×10^{-5}	7.42×10^{-3}	1.13	0.43	3.47×10^{-5}	7.36×10^{-3}	2.25×10^{2}
5	9.04×10^{-5}	9.23×10^{-3}	1.07	0.38	3.20×10^{-5}	9.17×10^{-3}	1.99×10^{2}

$K = 2.34 \times 10^{2}$ M^{-1}

log $K = (2.37 \pm 0.08)$

4.2 Determination of the Molar Decadic Absorption Coefficients ε in DMSO

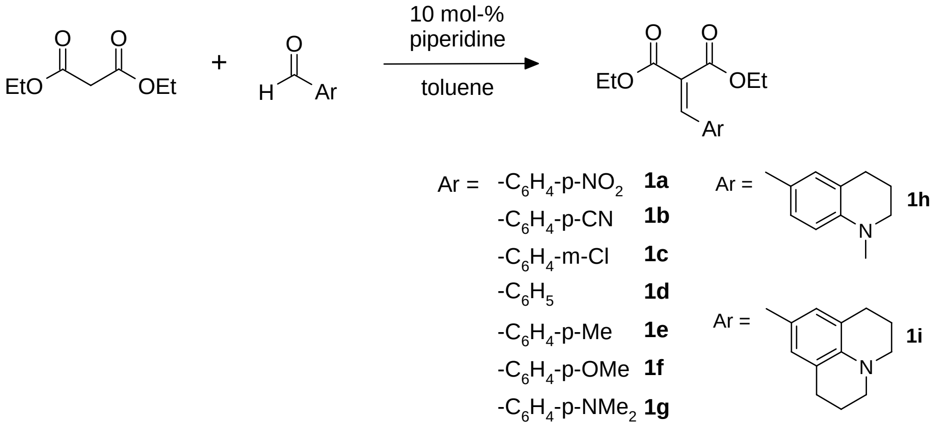
In order to determine the molar decadic absorption coefficients *ε* of electrophiles **1a-i** in DMSO, the absorption coefficients *ε* of the electrophiles **1a-i** were calculated at the absorption maximum on the basis of the Lambert-Beer law $A_{\max} = \varepsilon\, c\, d$ (Table S3). UV-Vis spectra were recorded on a JASCO V-630 spectrometer using a cell of d = 1 cm.

Table S3: Molar decadic absorption coefficients *ε* (L mol^{-1} cm^{-1}) of **1a-i** (DMSO, 20°C)

electrophile	[**1**] / mol L^{-1}	$A_{\max}$ ($\lambda_{\max}$ / nm)	$\varepsilon_{\max}$ [L mol^{-1} cm^{-1}]
1a	3.66×10^{-5}	0.63 (302)	1.72×10^{4}
1b	5.98×10^{-5}	1.35 (283)	2.25×10^{4}
1c	2.93×10^{-5}	0.51 (277)	1.73×10^{4}
1d	5.65×10^{-5}	0.93 (283)	1.65×10^{4}
1e	4.52×10^{-5}	0.94 (295)	2.07×10^{4}
1f	4.53×10^{-5}	1.14 (316)	2.51×10^{4}
1g	3.05×10^{-5}	1.05 (383)	3.28×10^{4}
1h	3.64×10^{-5}	1.23 (395)	3.37×10^{4}
1i	2.93×10^{-5}	0.95 (407)	3.24×10^{4}

5. Synthesis of Diethyl Benzylidenemalonates

Diethyl benzylidenemalonates **1a-i** were prepared according to the protocol by Zabicky (Scheme S1).[23]



Scheme S1: Synthesis of electrophiles **1a**–**i** from diethyl malonate and the corresponding aldehyde via Knoevenagel condensation in toluene.

General Procedure. Diethyl malonate and the corresponding arylaldehyde (1 equiv.) were stirred under reflux in toluene for several hours using piperidine (≈ 10 mol-%) as catalyst. The product formation was followed by TLC. The reaction mixture was consecutively washed with aqueous HCl, aqueous $NaHCO_3$ solution, and water. After drying the solution, the solvent was evaporated. The residue was either distilled (when liquid) or recrystallized from ethanol (when solid) to obtain the purified diethyl benzylidenemalonates. NMR spectra and melting points for the thus obtained compounds **1a–g** were in agreement with literature values.

Diethyl 2-(4-nitro-benzylidene)malonate (1a). From diethyl malonate (16 mmol) and 4-nitrobenzaldehyde: **1a** (3.61 g, 77 %), colorless needles; mp 89.3-89.8 °C (88°C, ref.[S1]) ^1H NMR ($CDCl_3$, 200 MHz): δ 1.28 (t, J = 7.1 Hz, 3 H, CH_3), 1.35 (t, J = 7.1 Hz, 3 H, CH_3), 4.33 (q, J = 7.1 Hz, 4 H, OCH_2), 7.60 (d, J = 8.4 Hz, 2 H, ArH), 7.75 (s, 1 H, =CH), 8.23 (d, J = 8.4 Hz, 2 H, ArH); in agreement with ref.[S1].

[S1] F. Delgado, J. Tamariz, G. Zepeda, M. Landa, R. Miranda, J. Garcia, *Synth. Commun.* **1995**, *25*, 753-759.

Diethyl 2-(4-cyano-benzylidene)malonate (**1b**)**.** From diethyl malonate (39 mmol) and 4-cyanobenzaldehyde: **1b** (6.82 g, 64 %), yellow needles; mp 72-73 °C (73°C, ref.[S2]). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.27 (t, J = 7.1 Hz, 3 H, CH_3), 1.33 (t, J = 7.1 Hz, 3 H, CH_3), 4.31 (q, ^3J = 7.1 Hz, 4 H, OCH_2), 7.53 (d, J = 8.2 Hz, 2 H, ArH), 7.66 (d, J = 8.2 Hz, 2 H, ArH), 7.70 (s, 1 H, =CH).

Diethyl 2-(3-chloro-benzylidene)malonate (**1c**)**.** From diethyl malonate (39 mmol) and 3-chlorobenzaldehyde: **1c** (5.42 g, 50 %), colorless oil; bp 130–134 °C, (8×10^{-3} mbar). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.26 (t, J = 7.0 Hz, 3 H, CH_3), 1.33 (t, J = 7.0 Hz, 3 H, CH_3), 4.30 (q, J = 7.0 Hz, 2 H, OCH_2), 4.34 (q, J = 7.0 Hz, 2 H, OCH_2), 7.30–7.65 (m, 4 H, ArH), 7.65 (s, 1 H, =CH); in agreement with ref.[S3]

Diethyl 2-benzylidenemalonate (**1d**)**.** From diethyl malonate (58 mmol) and benzaldehyde: **1d** (11.2 g, 78 %), colorless oil which crystallized slowly; mp: 31.0-31.2 °C; ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 1.26 (t, J = 7.2 Hz, 3 H, CH_3), 1.31 (t, J = 7.2 Hz, 3 H, CH_3), 4.26 (q, J = 7.2 Hz, 2 H, OCH_2), 4.32 (q, J = 7.2 Hz, 2 H, OCH_2), 7.26–7.46 (m, 5 H, ArH), 7.72 (s, 1 H, =CH), in agreement with ref.[S1]

Diethyl 2-(4-methyl-benzylidene)malonate (1e). From diethyl malonate (68 mmol) and 4-methylbenzaldehyde after crystallization of the crude product from ethyl acetate/petrol ether (2/8) at –32 °C: **1e** (6.91 g, 39 %), colorless solid; mp 47 °C (49–50°C, ref.[S2]). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.29 (t, J = 7.1 Hz, 3 H, CH_3), 1.34 (t, J = 7.1 Hz, 3 H, CH_3), 2.36 (s, 3 H, 4-CH_3), 4.29, 4.34 (2q, J = 7.1 Hz, 2×2 H, OCH_2CH_3), 7.17 (d, J = 7.9 Hz, 2 H, ArH), 7.35 (d, J = 7.9 Hz, 2 H, ArH), 7.70 (s, 1 H, =CH); in agreement with ref.[S4]

Diethyl 2-(4-methoxybenzylidene)malonate (1f). Diethyl malonate (84 mmol) and 4-methoxybenzaldehyde produced a crude product which after distillation (130 °C / 4×10^{-3} mbar) slowly crystallized: **1f** (12.5 g, 53%), solid; mp 38-39 °C (38-40°C, ref[S5]). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.29–1.36 (m, 6 H, $2 \times CH_3$), 3.84 (s, OCH_3), 4.27, 4.38 (2q, ^3J = 7.2 Hz, 2×2 H,

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[S2] G. Deng, J. Yu, X. Yang, H. Xu, *Terahedron*, **1990**, *46*, 5967-5974.

[S3] W. M. Phillips, D. J. Currie, *Can. J. Chem.*, **1969**, *47*, 3137-3146.

[S4] J. K. Kim, P. S. Kwon, T. W. Kwon, S. K. Chung, J. W. Lee, *Synth. Commun*, **1996**, *26*, 535-542.

[S5] P. E. Papadakis, L. M. Hall, R. L. Augustine, *J. Org. Chem.*, **1958**, *23*, 123.

OCH_2CH_3), 6.89 (d, *J* = 8.8 Hz, 2 H, ArH), 7.42 (d, *J* = 8.8 Hz, 2 H, ArCH), 7.67 (s, 1 H, =CH); in agreement with ref.[S1]

Diethyl 2-(4-dimethylamino-benzylidene)malonate (1g). From diethyl malonate (34 mmol) and 4-(dimethylamino)benzaldehyde: **1g** (3.90 g, 39 %), yellow plates; mp 112.1-112.5 °C (from EtOH), in agreement with ref.[S6]. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.30 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.34 (t, *J*= 7.0 Hz, 3 H, CH_3), 3.01 (s, 6 H, NMe_2), 4.26 (q, *J* = 7.0 Hz, 2 H, OCH_2), 4.37 (q, *J*= 7.0 Hz, 2 H, OCH_2), 6.62 (d, *J*= 9.0 Hz, 2 H, ArH), 7.48 (d, *J* = 9.0 Hz, 2 H, ArH), 7.62 (s, 1 H, =CH); in agreement with ref.[S1]

Diethyl 2-(1-methyl-1,2,3,4-tetrahydroquinoline-6-ylmethylene)malonate (1h). Diethyl malonate (1.15 g, 7.18 mmol), 6-formyl-1-methyl-1,2,3,4-tetrahydroquinoline (1.26 g, 7.19 mmol) and piperidine (300 µL) gave a crude product which was washed as described in the general procedure (Supporting Information) and further purified via MPLC (silica gel, dichloromethane/*iso*hexane = 1/1). The fractions were combined, the solvents evaporated in vacuum, and the residue was crystallized from ethanol/*iso*hexane at –5°C: **1h** (1.50 g, 4.7 mmol, 65 %), yellow solid; mp 56.2–56.7 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.22 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.26 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.85 (quint, *J* = 6.3 Hz, 2 H, CH_2), 2.64 (t, *J* = 6.3 Hz, 2 H, CH_2), 2.92 (s, 3 H, NMe), 3.31 (t, *J* = 6.3 Hz, 2 H, NCH_2), 4.17 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.27 (q, *J* = 7.1 Hz, 2 H, OCH_2), 6.57 (d, *J* = 8.7 Hz, 1 H, ArH), 7.02 (s, 1 H, ArH), 7.18 (dd, *J* = 8.8 Hz, 2.3 Hz, 1 H, ArH), 7.45 (s, 1 H, C=CH). ^{13}C NMR (DMSO-d_6, 100.6 MHz): δ 13.7 (q), 14.0 (q), 21.1 (t), 27.0 (t), 38.2 (q, NCH_3), 50.2 (t, NCH_2), 60.5 (t, OCH_2), 60.9 (t, OCH_2), 110.0 (d), 118.1 (s), 118.5 (s), 121.7 (s), 130.1 (d), 130.5 (d), 141.7 (d, =CH), 148.6 (s), 164.2 (s), 167.1 (s). HR-MS: Calcd for $C_{18}H_{23}O_4N$: 317.1627; Found 317.1610. Elemental analysis ($C_{18}H_{23}O_4N$): Calcd: C 68.12 %; H 7.30 %; N 4.41 %. Found C 67.96 %; H 7.28 %; N 4.38 %.

Diethyl 2-((1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinolin-9-yl)methylene)malonate (1i). A mixture of 1,2,3,5,6,7-hexahydropyrido[3.2.1-*ij*]quinoline-9-carbaldehyde (1.00 g, 4.98 mmol), diethyl malonate (0.79 g, 4.93 mmol) and piperidine (350 µL) was stirred in toluene under reflux until TLC indicated full conversion (3 h). After washing the crude reaction mixture as described in the general procedure (Supporting Information), the resulting oily residue was crystalized from

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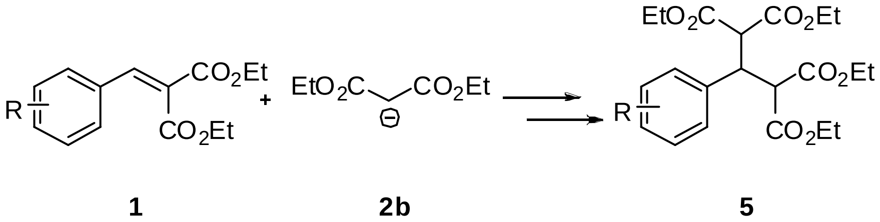
[S6] J. Zabicky, *J. Chem. Soc.* **1961**, 683-687.

EtOAc/*iso*hexane (1:3). The solid was filtered and washed with *iso*hexane: **1i** (1.1 g, 65 %), yellow solid; mp 83.2–83.4 °C. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 1.30 (t, J = 6.2 Hz, 3 H, CH$_3$), 1.35 (t, J = 6.2 Hz, 3 H, CH$_3$), 1.93 (quint, J = 6.2 Hz, 2 × 2 H, CH$_2$), 2.69 (t, ^3J = 5.6 Hz, 2 × 2 H, CH$_2$), 3.23 (t, J = 5.6 Hz, 2 × 2 H, NCH$_2$), 4.25 (q, J = 7.2 Hz, 2 H, OCH$_2$), 4.35 (q, J = 7.2 Hz, 2 H, OCH$_2$), 6.91 (s, 2 H, ArH), 7.52 (s, 1 H, 1 H, C=CH). ^{13}C NMR (CDCl$_3$, 150 MHz): δ 14.0 (q), 14.2 (q), 21.4 (t), 27.6 (t), 49.9 (t, NCH$_2$), 60.9 (t, OCH$_2$), 61.2 (t, OCH$_2$), 118.5 (s), 119.0 (s), 120.6 (s), 129.7 (d), 143.0 (d, =CH), 145.2 (s), 165.3 (s), 168.2 (s). HR-MS: Calcd for $C_{20}H_{25}O_4N$: 343.1784; Found 343.1775. Elemental analysis ($C_{20}H_{25}O_4N$): Calcd: C 69.95 %; H 7.34 %; N 4.08 %. Found C 69.66 %; H 7.35 %; N 4.09 %.

6. Product Studies

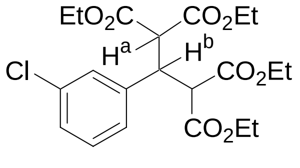
Reactions of 2b-K with Diethyl Benzylidenemalonates 1

General procedure. To a solution of **2b**-K (3.0–7.5 mmol) in dry DMSO (20 mL) a solution of **1** (1.5–2.5 mmol) in dry DMSO was added under nitrogen atmosphere. The reaction mixture was stirred for 5 h at room temperature and consecutively diluted with diethyl ether (25 mL), poured on water (50 mL), cooled with ice, and acidified with acetic acid. After extraction with diethyl ether (3 ×), the combined organic fractions were washed with water (3 × 20 mL) and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the crude product was purified by distillation.



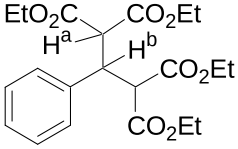
Scheme S2. Reactions of **1** with nucleophile **2b-K** resulting in the formation of products **5**.

Tetraethyl 2-(3-chlorophenyl)propane-1,1,3,3-tetracarboxylate (5cb). From **1c** (0.25 g, 1.5 mmol) and **2b**-K (0.60 g, 3.0 mmol): **5cb** (0.31 g, 47 %), colorless oil; bp 250 °C (4×10^{-2} bar). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.03 (t, J = 7.1, 6 H, 2 × CH_3), 1.21 (t, J = 7.1, 6 H, 2 × CH_3), 3.96 (q, J = 7.1, 2 × 2 H, OCH_2), 4.08–4.15 (m, 7 H), 7.16–7.33 (m, 2 × 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.7 (q), 13.9 (q), 43.4 (d, C^b), 54.8 (d, C^a), 61.4 (t), 61.7 (t), 127.7 (d), 127.8 (d), 129.2 (d), 129.7 (d), 133.7 (s), 139.3 (s), 167.3 (s), 167.7 (s).

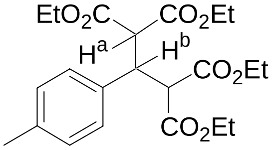


Tetraethyl 2-phenylpropane-1,1,3,3-tetracarboxylate (5db). From **1d (**0.62 g, 2.5 mmol) and **2b**-K (1.49 g,7.5 mmol): **5db** (0.85 g, 83%), colorless oil; bp 175–180 °C (9×10^{-3} bar). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, J = 7.1 Hz, 2 × 3 H, CH_3), 1.21 (t, J = 7.1 Hz, 2 × 3 H, CH_3), 3.91

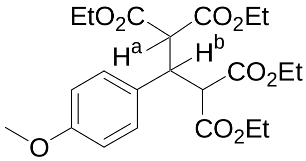
(q, J = 7.1, 2 × 2 H, OCH_2), 4.07-4.21 (m, 7 H), 7.15–7.34 (m, 5 H, ArH); in agreement with ref.[S7]



Tetraethyl 2-*p*-tolylpropane-1,1,3,3-tetracarboxylate (5eb). From **1e** (0.22 g, 1.5 mmol) and **2b**-K (0.60 g, 3.0 mmol): **5eb** (0.31 g, 47%) , colorless oil; with bp 250 °C (4×10^{-2} bar). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (t, J = 7.1 Hz, 2 × 3 H, CH_3), 1.22 (t, J = 7.1 Hz, 2 × 3 H, CH_3), 2.25 (s, 3 H, CH_3), 3.93 (q, J = 7.1 Hz, 2 × 2 H, OCH_2), 4.07–4.22 (m, 7 H), 7.03–7.04 (m, 2 H, ArH), 7.18-7.21 (m, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.7 (q), 13.9 (q), 21.0 (q), 43.5 (d, C^b), 55.3 (d, C^a), 61.2 (t), 61.6 (t), 128.6 (d), 129.2 (d), 134.2 (s), 137.1 (s), 167.5 (s), 168.0 (s); in agreement with ref.[S7]



Tetraethyl 2-(4-methoxyphenyl)propane-1,1,3,3-tetracarboxylate (5fb). From **1f** (0.56 g, 2.0mmol) and **2b**-K (0.79 g, 4.0 mmol): **5fb** (0.68 g, 78%), colorless oil; bp 210–220 °C (1.3×10^{-2} bar). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.04 (t, J = 7.1 Hz, 2 × 3 H, CH_3), 1.23 (t, J = 7.1 Hz, 2 × 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 3.95 (q, J = 7.1 Hz, 2 × 2 H, OCH_2), 4.04–4.18 (m, 7 H), 6.76–6.79 (m, 2 H, ArH), 7.24–7.27 (m, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.6 (q), 13.8 (q), 43.0 (d, C^b), 54.9 (q, OCH_3), 55.1 (d, C^a), 61.1 (t), 61.4 (t), 113.1 (d), 129.0 (s), 130.4 (d), 158.7 (s), 167.4 (s), 167.9 (s); in agreement with ref.[S7]



[S7] R. Fan, W. Wang, D. Pu, J. Wu, *J. Org. Chem.* **2007**, *72*, 5905-5907.

Reactions of 2c-K with Diethyl Benzylidenemalonates 1

General Procedure. Equimolar amounts of **2c-K** and an electrophile **1** were mixed and stirred in dry DMSO-d_6 (3–5 mL). After 5 min samples were taken and analyzed by NMR spectrocopy. Samples for MS were obtained by mixing equimolar amounts (0.2-0.5 mmol) of **2c**-K and **1** in dry EtOH (2 mL).

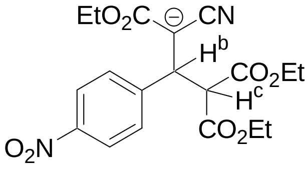
2-Cyano-1,5-diethoxy-4-(ethoxycarbonyl)-3-(4-nitrophenyl)-1,5-dioxopentan-2-yl) potassium (4ac).

Mixture of two tautomers (3:1)

Major tautomer

^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.87 (t, J = 7.1 Hz, 3 H, CH_3), 0.99 (t, J = 7.1 Hz, 3 H, CH_3) 1.16 (t, J = 7.1 Hz, 3 H, CH_3), 3.67–3.87 (m, 2 × 2 H, OCH_2), 4.05 (d, J = 12.3 Hz, 1 H, CH^b), 4.12–4.24 (m, 2 H, OCH_2), 4.22 (d, J = 12.4 Hz, 1 H, CH^a), 7.40 (d, J = 8.8 Hz, 2 H, ArH), 8.08 (d, ^3J = 8.8 Hz, 2 H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 13.5 (q), 13.7 (q), 15.3 (q), 42.6 (d, C^b), 47.4 (s, C^-), 55.4 (d, C^c), 55.7 (t), 60.3 (t), 60.4 (t), 122.9 (d), 127.5 (d), 128.6 (s), 145.0 (s), 153.6 (s), 167.1 (s), 167.7 (s), 168.5 (s). MS (ESI, negative) *m*/*z* (%): 406.13 (15), 405.13 (100), 191.12 (7), 257.08 (10).

Peak assignment in analogy to the neutral compound **4ac**-H from ref.[S8]



2-Cyano-3-(4-cyanophenyl)-1,5-diethoxy-4-(ethoxycarbonyl)-1,5-dioxopentan-2-yl) potassium (4bc).

Mixture of two tautomers (3:1)

NMR spectra refer to the major tautomer

^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.86–0.89 (m, 3 H, CH_3), 0.98–1.01 (m, 3 H, CH_3), 1.15–1.18 (m, 3 H, CH_3), 3.72–3.82 (m, 2 × 2 H, OCH_2), 4.02–4.18 (m, 4 H), 7.35 (d, J = 8.0 Hz, 2 H, ArH), 7.63–7.65 (m, 2 H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 13.3 (q), 13.5 (q), 15.1 (q),

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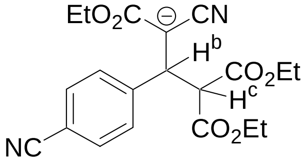
[S8] G. Manickam, G. Sundararajan, *Tetrahedron*, **1999**, *55*, 2721-2736.

42.6 (d, C^b), 47.2 (s, C^-), 55.4 (d, C^c), 55.5 (t), 60.1 (t), 60.2 (t), 107.4 (s, Ar-CN), 118.9 (s), 127.4 (d), 128.6 (s, C^a-*C*N), 131.3 (d), 151.1 (s), 166.9 (s), 167.5 (s), 168.3 (s). MS (ESI, negative) *m*/*z* (%): 385.14 (100, $C_{20}H_{21}O_6N_2$).

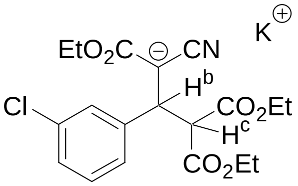


3-(3-Chlorophenyl)-2-cyano-1,5-diethoxy-4-(ethoxycarbonyl)-1,5-dioxopentan-2-yl) potassium (4cc).

Mixture of two tautomers

NMR spectra refer to the major tautomer

^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.87 (t, J = 7.1 Hz, 3 H, CH_3), 1.01 (t, J = 7.1 Hz, 3 H, CH_3), 1.15 (t, J = 7.1 Hz, 3 H, CH_3), 3.69–3.85 (m, 2 × 2 H, OCH_2), 3.96 (d, J = 12.3 Hz, 1 H, CH^c), 4.04-4.12 (m, 3 H, OCH_2 and CH^b), 7.10–7.22 (m, 2 × 2 H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 13.2 (q), 13.5 (q), 15.1 (q), 42.2 (d, C^b), 47.3 (s, C^-), 55.4 (t), 55.9 (d, C^c), 59.9 (t), 60.1 (t), 124.7 (d), 125.2 (d), 126.5 (d), 129.0 (d), 131.7 (s), 147.9 (s), 166.9 (s), 167.5 (s), 168.3 (s). MS (ESI, negative) *m*/*z* (%): 394.11 (100).

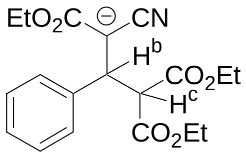


2-Cyano-1,5-diethoxy-4-(ethoxycarbonyl)-1,5-dioxo-3-phenylpentan-2-yl) potassium (4dc).

Mixture of two tautomers

NMR spectra refer to the major tautomer

^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.83 (t, J = 7.1 Hz, 3 H, CH_3), 0.99 (t, J = 7.1 Hz, 3 H, CH_3), 1.15 (t, J = 7.1 Hz, 3 H, CH_3), 3.70–3.78 (m, 2 × 2 H, OCH_2), 3.95 (d, J = 12.4 Hz, 1 H, CH^c), 4.05–4.13 (m, 3 H, OCH_2 and CH^b), 7.03–7.19 (m, 5 H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 13.4 (q), 13.8 (q), 15.4 (q), 42.5 (d, C^b), 47.8 (s, C^-), 55.5 (t), 56.6 (d, C^c), 59.9 (t), 60.1 (t), 125.0 (d), 126.9 (d), 127.2 (d), 129.5 (s), 145.7 (s), 167.4 (s), 167.9 (s), 168.5 (s). MS (ESI, negative) *m*/*z* (%): 360.15 (100, $C_{19}H_{22}NO_6$).

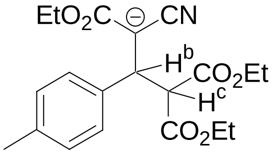


2-Cyano-1,5-diethoxy-4-(ethoxycarbonyl)-1,5-dioxo-3-*p*-tolylpentan-2-yl) potassium (4ec).

Mixture of two tautomers

NMR spectra refer to the major tautomer

^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.86 (t, J = 7.1 Hz, 3 H,CH$_3$), 0.99 (t, J = 7.1 Hz, 3 H, CH$_3$), 1.15 (t, J = 7.1 Hz, 3 H, CH$_3$), 2.21 (s, CH$_3$), 3.67–3.80 (m, 2 × 2 H, OCH$_2$), 3.91 (d, J = 12.3 Hz, 1 H, CH^c), 4.04–4.09 (m, 3 H, OCH$_2$ and CH^b), 6.95 (d, J = 8.0 Hz, ArH), 7.06 (d, J = 8.0 Hz, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 13.5 (q), 13.8 (q), 15.4 (q), 20.5 (q), 42.1 (d, C^b), 47.9 (s, C$^-$), 55.4 (t), 56.7 (d, C^c), 59.9 (t), 60.1 (t), 126.8 (d), 127.8 (d), 129.6 (s), 133.7 (s), 142.7 (s), 167.5 (s), 167.9 (s), 168.5 (s). MS (ESI, positive) m/z (%): 414.13 (100, $C_{20}H_{25}O_6N^{39}K$), 461.16 (80). MS (ESI, negative) *m*/*z* (%): 241.09 (100), 374.16 (8), 386.14 (20).

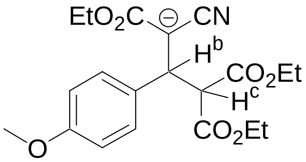


2-Cyano-1,5-diethoxy-4-(ethoxycarbonyl)-3-(4-methoxyphenyl)-1,5-dioxopentan-2-yl) potassium (4fc)

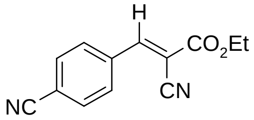
Mixture of two tautomers

NMR spectra refer to the major tautomer

^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.86 (t, J = 7.1 Hz, 3 H, CH$_3$), 0.99 (t, J = 7.1 Hz, 3 H, CH$_3$), 1.14 (t, J = 7.1 Hz, 3 H, CH$_3$), 3.67 (s, OCH$_3$), 3.70–3.78 (m, 2 × 2 H, OCH$_2$), 3.90 (d, J = 12.3 Hz, 1 H, CH^c), 4.02–4.07 (m, 3 H, OCH$_2$ and CH^b), 6.71 (d, J = 8.6 Hz, 2 H, ArH), 7.10 (d, J = 8.6 Hz, 2 H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 13.5 (q), 13.8 (q), 15.4 (q), 41.8 (d, C^b), 48.0 (s, C$^-$), 54.8 (q, OCH$_3$), 55.4 (t), 57.0 (d, C^c), 59.9 (t), 60.1 (t), 112.7 (d), 127.7 (s, CN) 127.9 (d), 129.7 (s), 137.9 (s), 156.9 (s), 167.4 (s), 167.9 (s), 168.5 (s). MS (ESI, negative) *m*/*z* (%): 390.16 (15), 257.09 (100).



Ethyl-(*E*)-2-cyano-3-(4-cyanophenyl)acrylic acid ethyl ester (retro-Michael product). After addition of **1b** (302 mg, 1.11 mmol) to a mixture of **2c-H** (510 µl, 4 mmol) and K_2CO_3 (1.2 g, 19 mmol) in DME/DMSO as solvent mixture the solution was stirred for 1 h at room temperature. The solution turned yellow and after the excess K_2CO_3 was filtered off, and the solution was concentrated under reduced pressure. After extraction with ethyl acetate the solution was washed with sat. aqueous NaCl solution and dried over $MgSO_4$. After evaporation of the solvent, the crude product was crystallized from ethanol: **retro-Michael product** (60 mg, 24 %), yellow needles; mp 172.0–172.5 °C (from EtOH), (168.5.-169.0 °C, ref. [S9]).



retro-Michael product

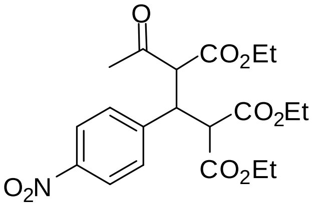
^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.41 (t, J = 7.1 Hz, 3 H, CH_3), 4.41 (q, J = 7.1 Hz, 2 H, OCH_2), 7.79 (d, J = 8.3 Hz, 2 H, ArH), 8.06 (d, J = 8.3 Hz, 2 H, ArH), 8.24 (s, 1 H, =CH), in agreement with ref.[S10]. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (q), 63.3 (t), 106.8 (s), 114.6 (s), 116.0 (s), 117.7 (s), 131.0 (d), 132.8 (d), 135.3 (s), 152.2 (d, =CH), 161.5 (s). HR-MS: Calcd. for ($C_{13}H_{10}N_2O_2$) 226.0742; Found 226.0424

[S9] D. T. Mowry, *J. Am. Chem. Soc.* **1949**, *65*, 992.

[S10] C. N. Robinson, C. D. Slater, J. S. Covington, C. R. Chang *et. al*, *J. Magn. Reson.* **1980**, *41*, 293-301.

Reaction of 2d with Diethyl Benzylidenemalonate 1a

2-Acetyl-4-ethoxycarbonyl-3-(4-nitrophenyl)-pentanedioic acid diethyl ester (5ad). Potassium carbonate (1.38 g, 10 mmol) was added to a mixture of **1a** (293 mg, 1.00 mmol) and **2d-H** (510 µl, 4 mmol) in DMSO (4 mL) at room temperature. After stirring for 2 h, the reaction mixture was diluted with ethyl acetate (40 mL) and poured into 5 % of hydrochloric acid with ice. After extraction with ethyl acetate, the combined organic layers were washed with water and brine and dried (Na_2SO_4). Removal of the solvents in the vacuum gave a residue, which was purified by column chromatography (SiO_2, hexane/ethyl acetate). The crude product (420 mg, 2:1-mixture of diastereomers) was crystallized to yield the major diastereomer: **5ad** (200 mg, 47 %); mp 72 °C (from EtOH).



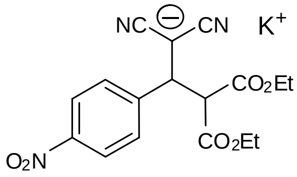
5ad

^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.00 (t, J = 7.2, 3 H), 1.08, (t, J = 7.2 Hz, 3 H), 1.21 (t, J = 7.2 Hz, 3 H), 2.27 (s, 3 H), 3.88 (m, 1 H), 3.91 (q, J = 7.2 Hz, 2 H), 4.00 (q, J = 7.2 Hz, 2 H), 4.11 (q, J = 7.2 Hz, 2 H), 4.39 (m, 2 H), 7.51 (d, J = 8.8 Hz, 2 H), 8.11 (d, J = 8.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.7, 13.8, 13.9, 29.7, 42.6, 54.5, 61.7, 61.8, 61.9, 62.3, 123.1, 130.5, 145.6, 147.2, 167.1, 167.3, 167.6, 200.6. MS (EI, 70 eV) *m*/*z* (%): 423 (M^+, < 1), 380 (2), 377 (5), 364 (12), 334 (14), 304 (8), 288 (21), 248 (90), 218 (30), 203 (20), 176 (50), 160 (58), 133 (33), 115 (54), 102 (21), 43 (100). Elemental analysis ($C_{20}H_{25}NO_9$) Calcd. C 56.73 H 5.95 N 3.31. Found: C 56.68 H 5.84 N 3.26.

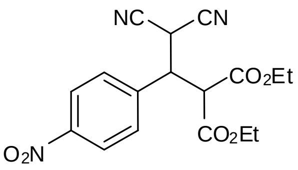
Reactions of 2f–K with Diethyl Benzylidenemalonates 1a.

Diethyl 2-(2,2-dicyano-1-(4-nitrophenyl)ethyl)malonate (5af).

After addition of **1a** (283 mg, 0.965 mmol) to the potassium salt of malononitrile **2f**-K (103 mg, 0.983 mmol) dissolved in dry DMSO-d_6 (5 mL) the solution turned from pale yellow to orange-red. Stirring was continued for 5 min at room temperature. For the NMR spectroscopic characterization of **4af**, a sample of the crude reaction mixture was used. The reaction mixture was poured on cold water and acidified with conc. hydrochloric acid (2 mL). The solution turned yellow and a fine solid precipitated. Since the formed precipitate was too fine to be filtered, it was dissolved in CH_2Cl_2, filtered over a warm cotton batting and evaporated under reduced pressure: **5af** (120 mg, 35 %), pale yellow oil.



4af–K



5af

4af-K: ^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.87 (t, J = 7.1 Hz, 3 H, CH_3), 1.25 (t, J = 7.1 Hz, 3 H, CH_3), 3.66 (d, J = 12.0 Hz, 1 H, CH), 3.78–3.85 (m, 3 H, OCH_2 and CH), 4.19 (q, J = 7.1 Hz, 4 H, OCH_2), 7.39 (d, J = 8.1 Hz, 2 H, ArH), 8.13 (d, J = 8.1 Hz, 2 H, ArH).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 13.4 (q), 13.9 (q), 17.2 (s, C^-), 44.1 (d), 56.7 (d), 60.7 (t), 60.9 (t), 123.3 (d), 127.5 (d), 129.3 (s, CN), 145.5 (s), 152.3 (s), 166.8 (s), 167.0 (s).

5af: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.97 (t, J = 7.1 Hz, 3 H, CH_3), 1.26 (t, J = 7.1 Hz, 3 H, CH_3), 3.90–3.96 (m, 2 H, OCH_2), 4.07 (m, 2 H, 2 × CH), 4.24–4.27 (m, 2 H, OCH_2), 4.95–4.97 (m, 1 H, H^b), 7.60 (d, J = 8.8 Hz, 2 H, ArH), 8.24 (d, J = 8.8 Hz, 2 H, ArH). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 13.7 (q), 27.1 (d), 44.2 (d), 52.9 (d), 62.3 (t), 63.1 (t), 110.7 (s), 110.8 (s), 124.1 (d), 129.7 (d), 140.5 (s) 148.4 (s), 165.3 (s), 166.7 (s).

7. Reactivities of Diethyl Benzylidenemalonates 1a–i

Reactions of electrophile 1a

Table S1: Kinetics of the reaction of **1a** with the nitro ethyl anion **2a** (K^+ salt, DMSO, 20 °C, stopped-flow UV-Vis spectrometer, decrease at $\lambda = 305$ nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a370-1	2.83×10^{-5}	9.61×10^{-4}	1.94×10^{-1}
a370-2	2.83×10^{-5}	1.92×10^{-3}	4.56×10^{-1}
a370-3	2.83×10^{-5}	2.88×10^{-3}	6.74×10^{-1}
a370-4	2.83×10^{-5}	3.77×10^{-3}	8.74×10^{-1}

$k_2 = 2.41 \times 10^2$ L mol^{-1} s^{-1}

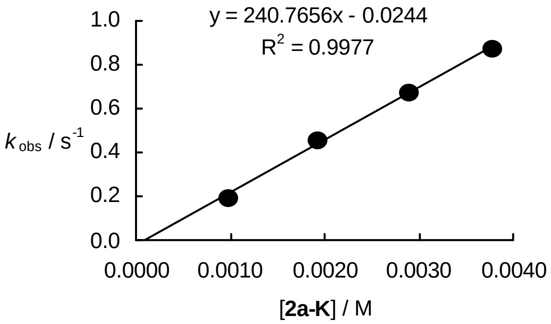
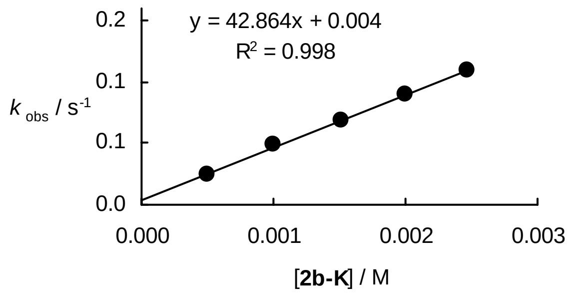
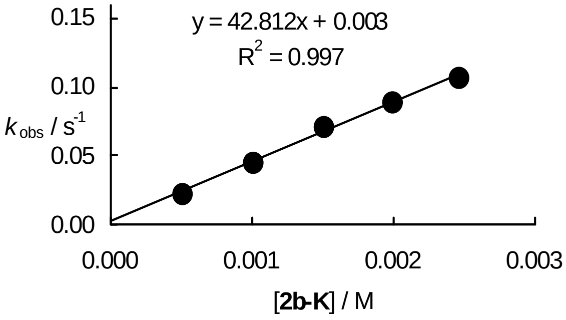


Table S2: Kinetics of the reaction of **1a** with the diethyl malonate anion **2b** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1} (decrease at $\lambda = 325$ nm)	k_{obs} / s^{-1} (increase at $\lambda = 425$ nm)
a338-6	4.09×10^{-5}	5.06×10^{-4}	2.38×10^{-2}	2.43×10^{-2}
a338-2	4.09×10^{-5}	9.99×10^{-4}	4.55×10^{-2}	4.88×10^{-2}
a338-3	4.09×10^{-5}	1.51×10^{-3}	7.10×10^{-2}	6.83×10^{-2}
a338-4	4.09×10^{-5}	2.00×10^{-3}	9.02×10^{-2}	9.04×10^{-2}
a338-5	4.09×10^{-5}	2.47×10^{-3}	1.07×10^{-1}	1.09×10^{-1}





$k_2 = 4.29 \times 10^1$ L mol^{-1} s^{-1}

(from decrease at $\lambda = 325$ nm)

$k_2 = 4.28 \times 10^1$ L mol^{-1} s^{-1}

(from increase at $\lambda = 425$ nm)

Table S3: Kinetics of the reaction of **1a** with the anion of ethyl cyano acetate **2c** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 310 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a320-6	4.94×10^{-5}	1.14×10^{-3}	2.62×10^{-2}
a320-1 [a]	4.94×10^{-5}	1.14×10^{-3}	2.58×10^{-2}
a320-3	4.94×10^{-5}	1.70×10^{-3}	3.70×10^{-2}
a320-5	4.94×10^{-5}	2.13×10^{-3}	4.72×10^{-2}

[a] in the presence of 1 equiv. 18-crown-6.

$k_2 = 2.12 \times 10^1$ L mol^{-1} s^{-1}

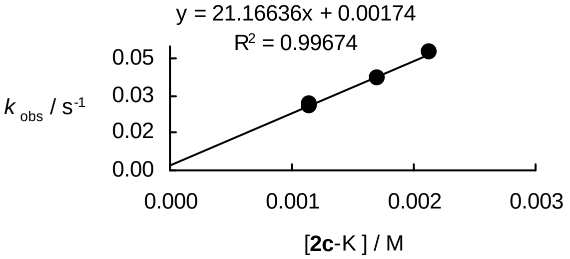


Table S4: Kinetics of the reaction of **1a** with the anion of ethyl cyano acetate **2c** (K^+ salt, in the presence of 1 equiv. of 18-crown-6, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 302 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
72-1	1.29×10^{-4}	9.92×10^{-4}	1.64×10^{-2}
72-2	1.38×10^{-4}	1.97×10^{-3}	3.94×10^{-2}
72-3	1.38×10^{-4}	3.07×10^{-3}	6.52×10^{-2}
72-4	1.37×10^{-4}	4.05×10^{-3}	8.62×10^{-2}
72-5	1.36×10^{-4}	5.05×10^{-3}	1.07×10^{-1}

$k_2 = 2.24 \times 10^1$ L mol^{-1} s^{-1}

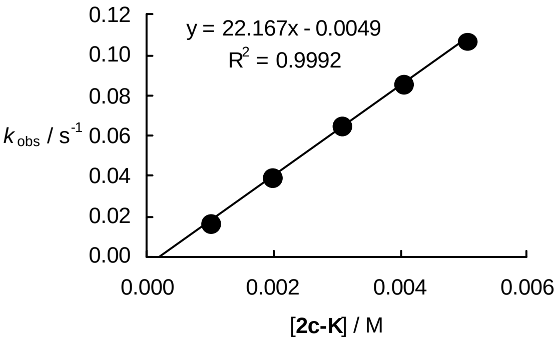


Table S5: Kinetics of the reaction of **1a** with the anion of ethyl aceto acetate **2d** (K^+ salt) in presence of 18-crown-6 (1 equiv.) and the corresponding CH acid **2d-H** (DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 310 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	[**2b-H**]$_0$ / M	k_{obs} / s^{-1}
102-1	7.03×10^{-5}	5.30×10^{-4}	7.03×10^{-5}	4.27×10^{-3}
102-2	6.93×10^{-5}	1.04×10^{-3}	6.93×10^{-5}	7.26×10^{-3}
102-3	6.91×10^{-5}	1.56×10^{-3}	6.91×10^{-5}	1.10×10^{-2}
102-4	6.86×10^{-5}	2.07×10^{-3}	6.86×10^{-5}	1.42×10^{-2}
102-5	6.85×10^{-5}	2.58×10^{-3}	6.85×10^{-5}	1.77×10^{-2}

$k_2 = 6.58$ L mol^{-1} s^{-1}

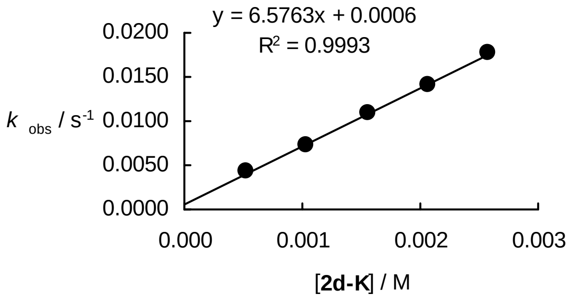
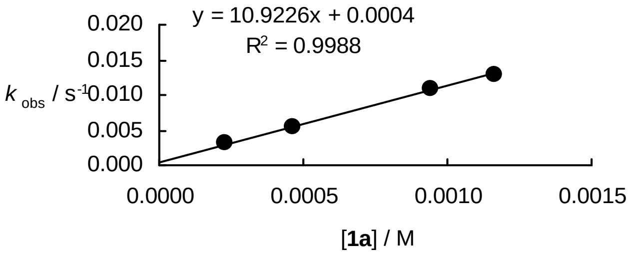


Table S6: Kinetics of the reaction of **1a** with the bis(4-nitrophenyl)methyl anion **2** (K^+ salt, DMSO, 20 ° C, diode array UV-vis spectrometer, decrease at λ = 700 nm).

No.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
a294b-1	2.31×10^{-5}	2.31×10^{-4}	3.02×10^{-3}
a294b-2	2.31×10^{-5}	4.63×10^{-4}	5.34×10^{-3}
a294b-3b	2.31×10^{-5}	9.43×10^{-4}	1.09×10^{-2}
a294b-5	2.31×10^{-5}	1.16×10^{-3}	1.30×10^{-2}

$k_2 = 1.09 \times 10^1$ L mol^{-1} s^{-1}



Reactions of electrophile 1b

Table S7: Kinetics of the reaction **1b** with the nitroethyl anion **2a** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 305 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a342b	1.55×10^{-5}	1.88×10^{-4}	2.64×10^{-2}
a342b-2	1.55×10^{-5}	3.74×10^{-4}	5.49×10^{-2}
a342b-3	1.55×10^{-5}	5.59×10^{-4}	8.15×10^{-2}
a342b-4	1.55×10^{-5}	7.41×10^{-4}	1.03×10^{-1}
a342b-5	1.55×10^{-5}	9.67×10^{-4}	1.42×10^{-1}

$k_2 = 1.45 \times 10^2$ L mol^{-1} s^{-1}

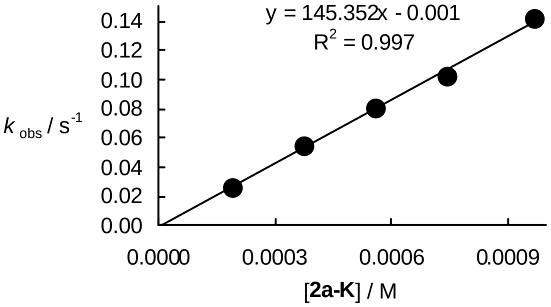


Table S8: Kinetics of the reaction of **1b** with the diethyl malonate anion **2b** (K^+ salt) in the presence of 1.5 to 2.0 equiv. 18-crown-6
(DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 300 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
40-5	6.01×10^{-5}	2.44×10^{-4}	7.01×10^{-3}
40-4	6.00×10^{-5}	4.25×10^{-4}	1.25×10^{-2}
49-3	5.98×10^{-5}	5.43×10^{-4}	1.54×10^{-2}
49-2	6.02×10^{-5}	9.00×10^{-4}	2.54×10^{-2}
49-1	6.04×10^{-5}	1.13×10^{-3}	3.26×10^{-2}

$k_2 = 2.86 \times 10^1$ L mol^{-1} s^{-1}

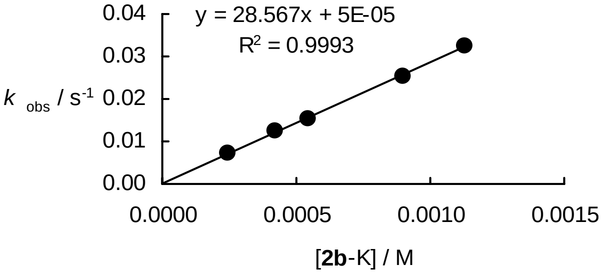


Table S9: Kinetics of the reaction of **1b** with the anion of ethyl cyano acetate **2c** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 290 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a291b-1	4.32×10^{-5}	1.86×10^{-4}	1.73×10^{-3}
a291b-2	4.32×10^{-5}	3.72×10^{-4}	3.64×10^{-3}
a291b-3	4.32×10^{-5}	5.54×10^{-4}	5.38×10^{-3}
a291b-4	4.32×10^{-5}	7.56×10^{-4}	7.41×10^{-3}
a291b-5	4.32×10^{-5}	9.45×10^{-4}	9.14×10^{-3}

$k_2 = 9.77$ L mol^{-1} s^{-1}

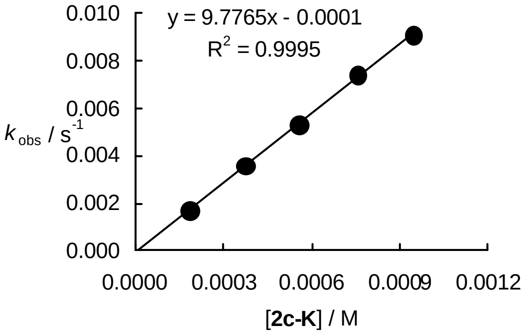


Table S10: Kinetics of the reaction of **1b** with the bis(4-nitrophenyl)methyl anion **2e** (K^+ salt, (DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 620 nm).

No.	$[\mathrm{Nu}^-]_0$ / M	$[\mathrm{E}]_0$ / M	k_{obs} / s^{-1}
a295-1	2.30×10^{-5}	2.28×10^{-4}	1.75×10^{-3}
a295-2	2.30×10^{-5}	4.56×10^{-4}	2.89×10^{-3}
a295-3	2.30×10^{-5}	7.02×10^{-4}	4.81×10^{-3}
a295-4	2.30×10^{-5}	8.96×10^{-4}	5.69×10^{-3}
a295-5	2.30×10^{-5}	1.08×10^{-3}	6.70×10^{-3}

$k_2 = 5.94$ L mol^{-1} s^{-1}

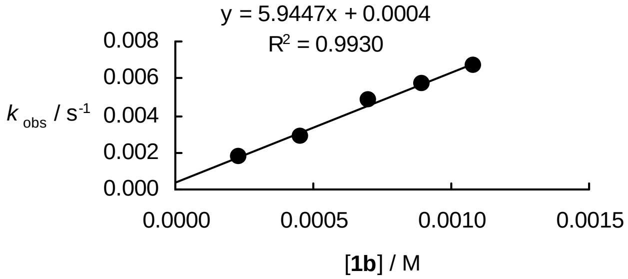
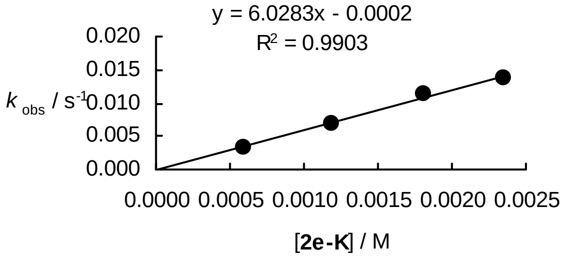


Table S11: Kinetics of the reaction of **1b** with the bis(4-nitrophenyl)methyl anion **2e** (K^+ salt) in the presence of 1 equiv. 18-crown-6
(DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 620 nm).

No.	$[\mathrm{Nu}^-]_0$ / M	$[\mathrm{E}]_0$ / M	k_{obs} / s^{-1}
a323-1	4.98×10^{-5}	5.97×10^{-4}	3.38×10^{-3}
a323-2	4.98×10^{-5}	1.18×10^{-3}	6.77×10^{-3}
a323-3	4.98×10^{-5}	1.81×10^{-3}	1.15×10^{-2}
a323-4	4.98×10^{-5}	2.35×10^{-3}	1.36×10^{-2}

$k_2 = 6.03$ L mol^{-1} s^{-1}



Reactions of electrophile 1c

Table S12: Kinetics of the reaction of **1c** with the nitro ethyl anion **2a** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 305 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a343-1	3.76×10^{-5}	2.89×10^{-4}	1.70×10^{-2}
a343-4	3.76×10^{-5}	4.19×10^{-4}	2.14×10^{-2}
a343-2	3.76×10^{-5}	5.71×10^{-4}	2.70×10^{-2}
a343-6	3.76×10^{-5}	7.18×10^{-4}	3.35×10^{-2}
a343-5	3.76×10^{-5}	8.49×10^{-4}	3.72×10^{-2}

$k_2 = 3.71 \times 10^1$ L mol^{-1} s^{-1}

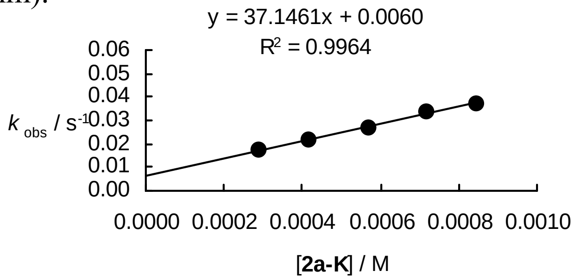


Table S13: Kinetics of the reaction of **1c** with the diethyl malonate anion **2b** (K^+ salt) in the presence of 1.5 equiv. 18-crown-6
(DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 303 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
56-1	2.26×10^{-4}	1.47×10^{-3}	1.02×10^{-2}
56-2	2.26×10^{-4}	1.95×10^{-3}	1.29×10^{-2}
56-3	2.40×10^{-4}	3.06×10^{-3}	2.14×10^{-2}
56-4	2.53×10^{-4}	5.60×10^{-3}	3.81×10^{-2}

$k_2 = 6.81$ L mol^{-1} s^{-1}

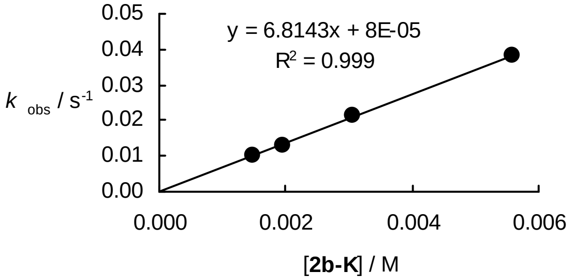


Table S14: Kinetics of the reaction of **1c** with the anion of ethyl cyano acetate **2c** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 305 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a292-1	3.85×10^{-5}	4.69×10^{-4}	1.46×10^{-3}
a292-2	3.85×10^{-5}	7.85×10^{-4}	2.11×10^{-3}
a292-3	3.85×10^{-5}	1.16×10^{-3}	3.21×10^{-3}
a292-4	3.85×10^{-5}	1.56×10^{-3}	4.16×10^{-3}
a292-5	3.85×10^{-5}	2.27×10^{-3}	6.26×10^{-3}

$k_2 = 2.68$ L mol^{-1} s^{-1}

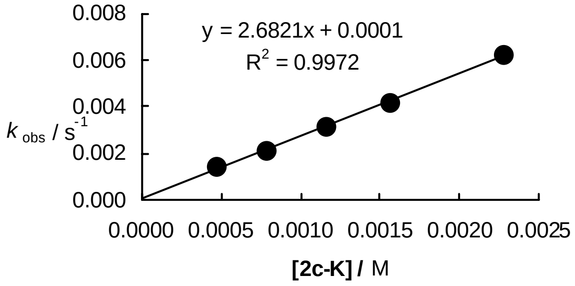


Table S15: Kinetics of the reaction of **1c** with the anion of ethyl cyano acetate **2c** (K^+ salt) in the presence of 1 equiv. 18-crown-6
(DMSO, 20 °C, diode array UV-vis spectrometer, decrease at $\lambda = 290$ nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a318b-2	3.89×10^{-5}	1.22×10^{-3}	3.31×10^{-3}
a318b-3	3.89×10^{-5}	1.84×10^{-3}	4.80×10^{-3}
a318b-4	3.89×10^{-5}	2.44×10^{-3}	6.26×10^{-3}
a318b-5	3.89×10^{-5}	3.15×10^{-3}	8.16×10^{-3}

$k_2 = 2.51$ L mol^{-1} s^{-1}

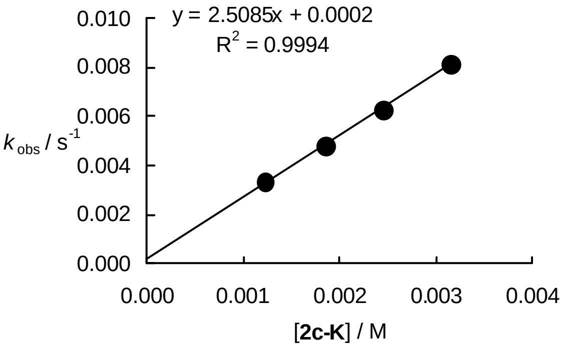
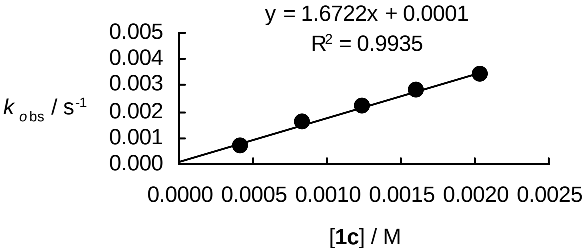


Table S16: Kinetics of the reaction of **1c** with the bis(4-nitrophenyl)methyl anion **2e** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at $\lambda = 785$ nm).

No.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
a297b-1	3.56×10^{-5}	4.12×10^{-4}	6.72×10^{-4}
a297b-2	3.56×10^{-5}	8.33×10^{-4}	1.58×10^{-3}
a297b-3	3.56×10^{-5}	1.24×10^{-3}	2.23×10^{-3}
a297b-4	3.56×10^{-5}	1.60×10^{-3}	2.79×10^{-3}
a297b-5	3.56×10^{-5}	2.04×10^{-3}	3.43×10^{-3}

$k_2 = 1.67$ L mol^{-1} s^{-1}



Reactions of electrophile 1d

Table S17: Kinetics of the reaction of **1d** with the diethyl malonate anion **2b** (K^+ salt) in the presence of 1.6 equiv. 18-crown-6
(DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 303 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
41-1	2.04×10^{-4}	4.18×10^{-3}	2.36×10^{-3}
40-3	1.97×10^{-4}	5.15×10^{-3}	3.04×10^{-3}
40-2	3.00×10^{-4}	5.24×10^{-3}	3.05×10^{-3}
40-4	1.98×10^{-4}	6.83×10^{-3}	3.95×10^{-3}

$k_2 = 5.93 \times 10^{-1}$ L mol^{-1} s^{-1}

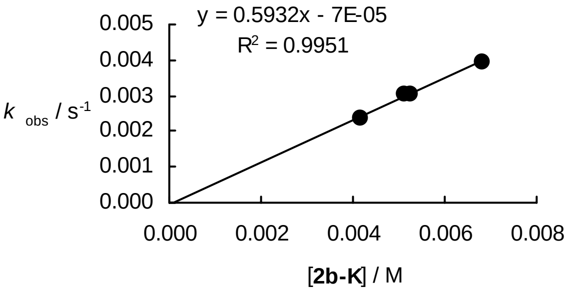
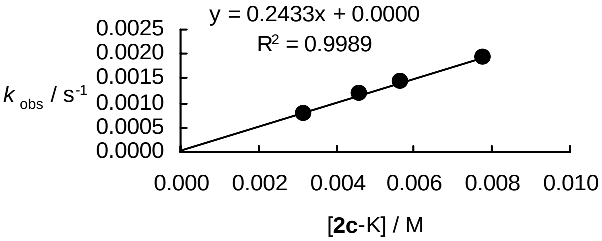


Table S18: Kinetics of the reaction of **1d** with the ethyl cyano acetate anion **2c** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 303 nm)

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a304c-1	4.80×10^{-5}	3.17×10^{-3}	7.87×10^{-4}
a304c-2	4.80×10^{-5}	4.62×10^{-3}	1.17×10^{-3}
a304c-3	4.80×10^{-5}	5.64×10^{-3}	1.42×10^{-3}
a304c-4	4.80×10^{-5}	7.77×10^{-3}	1.91×10^{-3}

$k_2 = 2.43 \times 10^{-1}$ L mol^{-1} s^{-1}



Reactions of electrophile 1e

Table S19: Kinetics of the reaction of **1e** with the nitro ethyl anion **2a** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 316 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a339-1	4.79×10^{-5}	4.91×10^{-4}	1.34×10^{-3}
a339-2	4.79×10^{-5}	9.71×10^{-4}	2.74×10^{-3}
a339-3	4.79×10^{-5}	1.49×10^{-3}	4.27×10^{-3}
a339-4	4.79×10^{-5}	1.92×10^{-3}	5.56×10^{-3}
a339-5	4.79×10^{-5}	2.42×10^{-3}	7.12×10^{-3}

k_2 = 2.99 L mol^{-1} s^{-1}

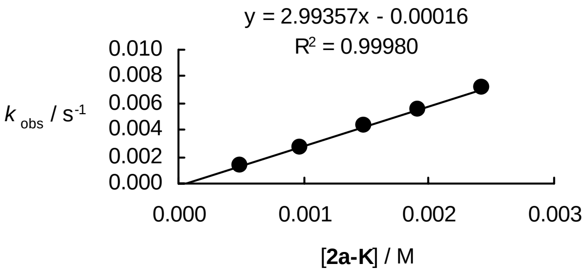


Table S20a: Kinetics of the reaction of **1e** with the diethyl malonate anion **2b** (K^+ salt) in the presence of 1.6 equiv. 18-crown-6
(DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 310 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
50-1	9.98×10^{-5}	1.79×10^{-3}	8.06×10^{-4}
50-2	9.71×10^{-5}	2.52×10^{-3}	9.90×10^{-4}
50-3	1.06×10^{-4}	4.13×10^{-3}	1.38×10^{-3}
50-4	1.06×10^{-4}	4.72×10^{-3}	1.52×10^{-3}
50-5	1.12×10^{-4}	6.61×10^{-3}	1.95×10^{-3}

$k_2 = 2.37 \times 10^{-1}$ L mol^{-1} s^{-1}

$k_{-} = 4 \times 10^{-4}$ s^{-1}

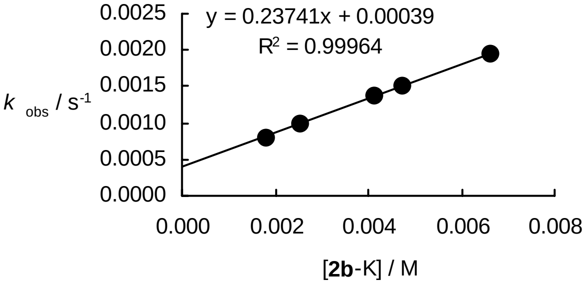


Table S20b: Kinetics of the reaction of **1e** with the diethyl malonate anion **2b** (K^+ salt) in the presence of 2–6 equivalents of **2b**–H
(DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 310 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	[**2b**–H]$_0$ / M	k_{obs} / s^{-1}
371-2	1.00×10^{-4}	3.00×10^{-3}	1.89×10^{-2}	5.58×10^{-4}
371-3	1.00×10^{-4}	4.75×10^{-3}	9.52×10^{-3}	9.63×10^{-4}
371-4	1.00×10^{-4}	4.99×10^{-3}	1.92×10^{-2}	9.93×10^{-4}

$k_2 = 2.23 \times 10^{-1}$ L mol^{-1} s^{-1}

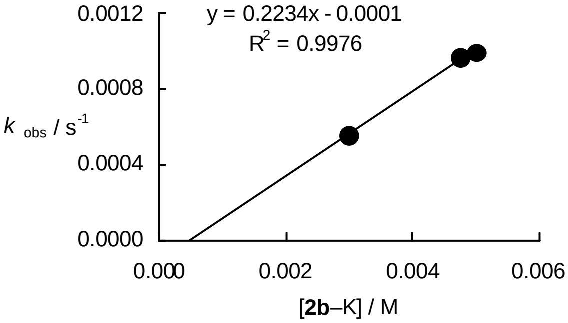
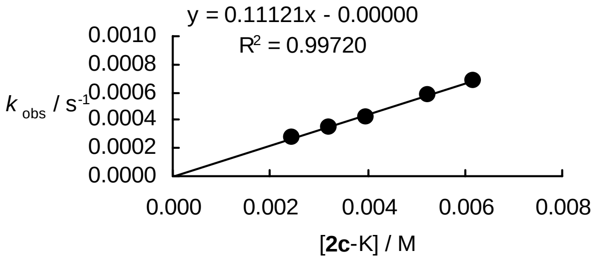


Table S21: Kinetics of the reaction of **1e** with the ethyl cyano acetate anion **2c** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 305 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a315-4	2.91×10^{-5}	2.47×10^{-3}	2.82×10^{-4}
a315-5	2.91×10^{-5}	3.23×10^{-3}	3.51×10^{-4}
a315-3	2.91×10^{-5}	3.98×10^{-3}	4.29×10^{-4}
a315-2	2.91×10^{-5}	5.25×10^{-3}	5.82×10^{-4}
a315-1	2.91×10^{-5}	6.17×10^{-3}	6.87×10^{-4}

$k_2 = 1.11 \times 10^{-1}$ L mol^{-1} s^{-1}



Reactions of electrophile 1f

Table S22: Kinetics of the reaction of **1f** with the nitro ethyl anion **2a** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 316 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a336-1	2.60×10^{-5}	5.84×10^{-4}	1.04×10^{-3}
a336-2	2.60×10^{-5}	1.16×10^{-3}	2.02×10^{-3}
a336-3	2.60×10^{-5}	1.72×10^{-3}	2.95×10^{-3}
a336-4	2.60×10^{-5}	2.28×10^{-3}	4.03×10^{-3}
a336-5	2.60×10^{-5}	2.85×10^{-3}	4.83×10^{-3}

$k_2 = 1.70$ L mol^{-1} s^{-1}

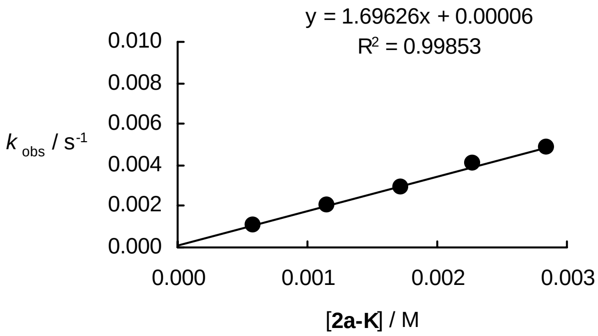


Table S23: Kinetics of the reaction of **1f** with the diethyl malonate anion **2b** (K^+ salt) in the presence of 1.5 equiv. 18-crown-6 (DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 316 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
45-1	7.95×10^{-5}	1.53×10^{-3}	1.23×10^{-3}
45-2	9.64×10^{-5}	3.98×10^{-3}	1.58×10^{-3}
45-3	9.52×10^{-5}	5.51×10^{-3}	1.82×10^{-3}
45-4	9.20×10^{-5}	7.42×10^{-3}	2.08×10^{-3}
45-5	9.04×10^{-5}	9.23×10^{-3}	2.31×10^{-3}

$k_2 = 1.41 \times 10^{-1}$ L mol^{-1} s^{-1}, $k_{-} = 1 \times 10^{-3}$ s^{-1}

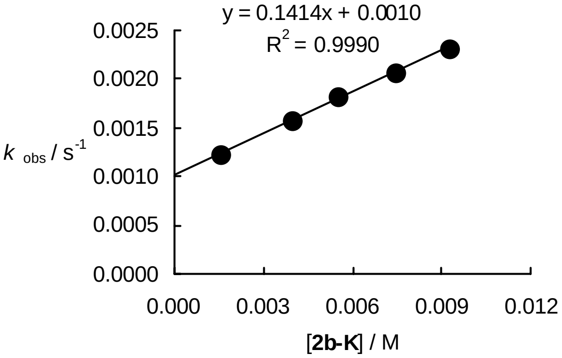
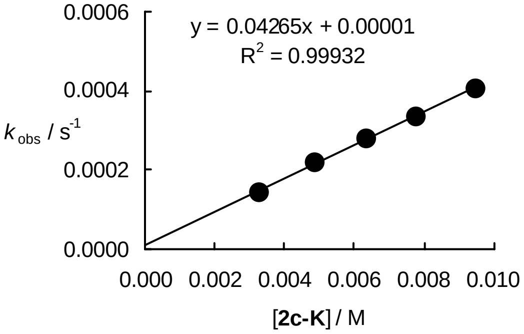


Tabelle S24: Kinetics of the reaction of **1f** with the ethyl cyano acetate anion **2c** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 315 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a316-1	3.98×10^{-5}	3.24×10^{-3}	1.44×10^{-4}
a316-2	3.98×10^{-5}	4.85×10^{-3}	2.20×10^{-4}
a316-3	3.98×10^{-5}	6.33×10^{-3}	2.81×10^{-4}
a316-4	3.98×10^{-5}	7.77×10^{-3}	3.39×10^{-4}
a316-5	3.98×10^{-5}	9.44×10^{-3}	4.11×10^{-4}

$k_2 = 4.27 \times 10^{-2}$ L mol^{-1} s^{-1}



Reactions of electrophile 1g

Table S25: Kinetics for the reaction of **1g** with the nitro ethyl anion **2a** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 383 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a333-1	4.20×10^{-5}	1.39×10^{-3}	2.62×10^{-4}
a333-2	4.20×10^{-5}	2.56×10^{-3}	4.60×10^{-4}
a333-3	4.20×10^{-5}	3.43×10^{-3}	6.13×10^{-4}
a333-4	4.20×10^{-5}	4.21×10^{-3}	7.49×10^{-4}
a333-5	4.20×10^{-5}	4.73×10^{-3}	8.13×10^{-4}

$k_2 = 1.68 \times 10^{-1}$ L mol^{-1} s^{-1}

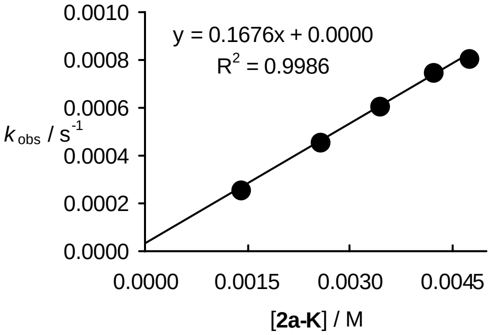
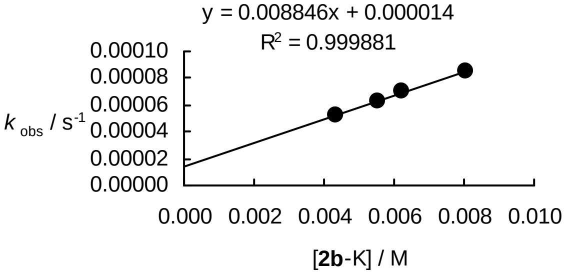


Table S26: Kinetics for the reaction of **1g** with the diethyl malonate anion **2b** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 380 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	[**2b-H**] / M	k_{obs} / s^{-1}
a371b-1	4.41×10^{-5}	4.35×10^{-3}	2.13×10^{-2}	5.29×10^{-5}
a371b-2	4.41×10^{-5}	5.55×10^{-3}	1.77×10^{-2}	6.33×10^{-5}
a371b-3	4.41×10^{-5}	6.22×10^{-3}	1.82×10^{-2}	6.96×10^{-5}
a371b-4	4.41×10^{-5}	8.07×10^{-3}	2.23×10^{-2}	8.58×10^{-5}

$k_2 = 8.85 \times 10^{-3}$ L mol^{-1} s^{-1}



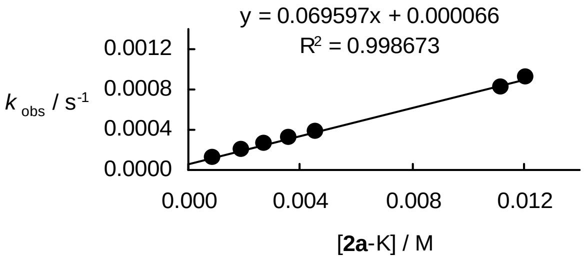
Reactions of electrophile 1h

Table S27: Kinetics for the reaction of **1h** with the nitro ethyl anion **2a** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 395 nm).

No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a348-1	3.59×10^{-5}	9.18×10^{-4}	1.25×10^{-4}
a348-2	3.59×10^{-5}	1.89×10^{-3}	2.03×10^{-4}
a348-3	3.59×10^{-5}	2.72×10^{-3}	2.58×10^{-4}
a348-4	3.59×10^{-5}	3.65×10^{-3}	3.15×10^{-4}
a348-5	3.59×10^{-5}	4.60×10^{-3}	3.91×10^{-4}
a348b*	4.00×10^{-5}	1.12×10^{-2}	8.24×10^{-4}
a348b-8**	4.00×10^{-5}	1.21×10^{-2}	9.27×10^{-4}

$k_2 = 6.96 \times 10^{-2}$ L mol^{-1} s^{-1}

**Addition of 1 equiv. CH-acid, * 0.05 equiv. CH-acid

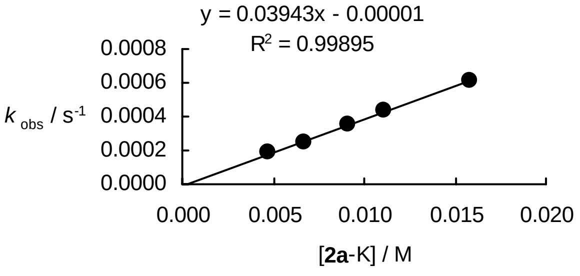


Reactions of electrophile 1i

Table S28: Kinetics for the reaction of **1i** with the nitro ethyl anion **2a** (K^+ salt, DMSO, 20 °C, diode array UV-vis spectrometer, decrease at λ = 409 nm).

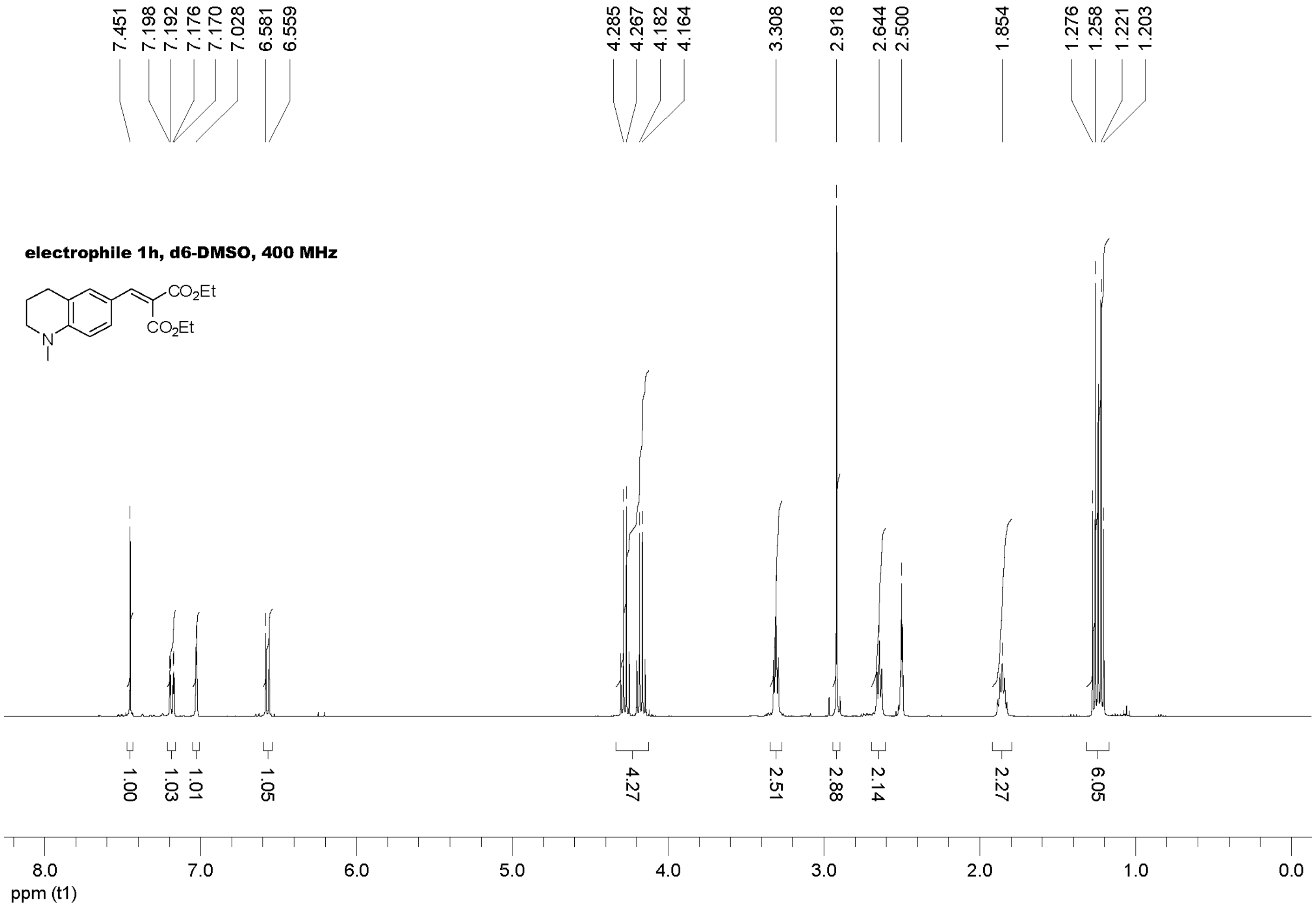
No.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a340-1	2.33×10^{-5}	4.77×10^{-3}	1.84×10^{-4}
a340-2	2.33×10^{-5}	6.66×10^{-3}	2.51×10^{-4}
a340-3	2.33×10^{-5}	9.13×10^{-3}	3.51×10^{-4}
a340-5	2.33×10^{-5}	1.11×10^{-2}	4.39×10^{-4}
a340-5	2.33×10^{-5}	1.58×10^{-2}	6.13×10^{-4}

$k_2 = 3.94 \times 10^{-2}$ L mol^{-1} s^{-1}

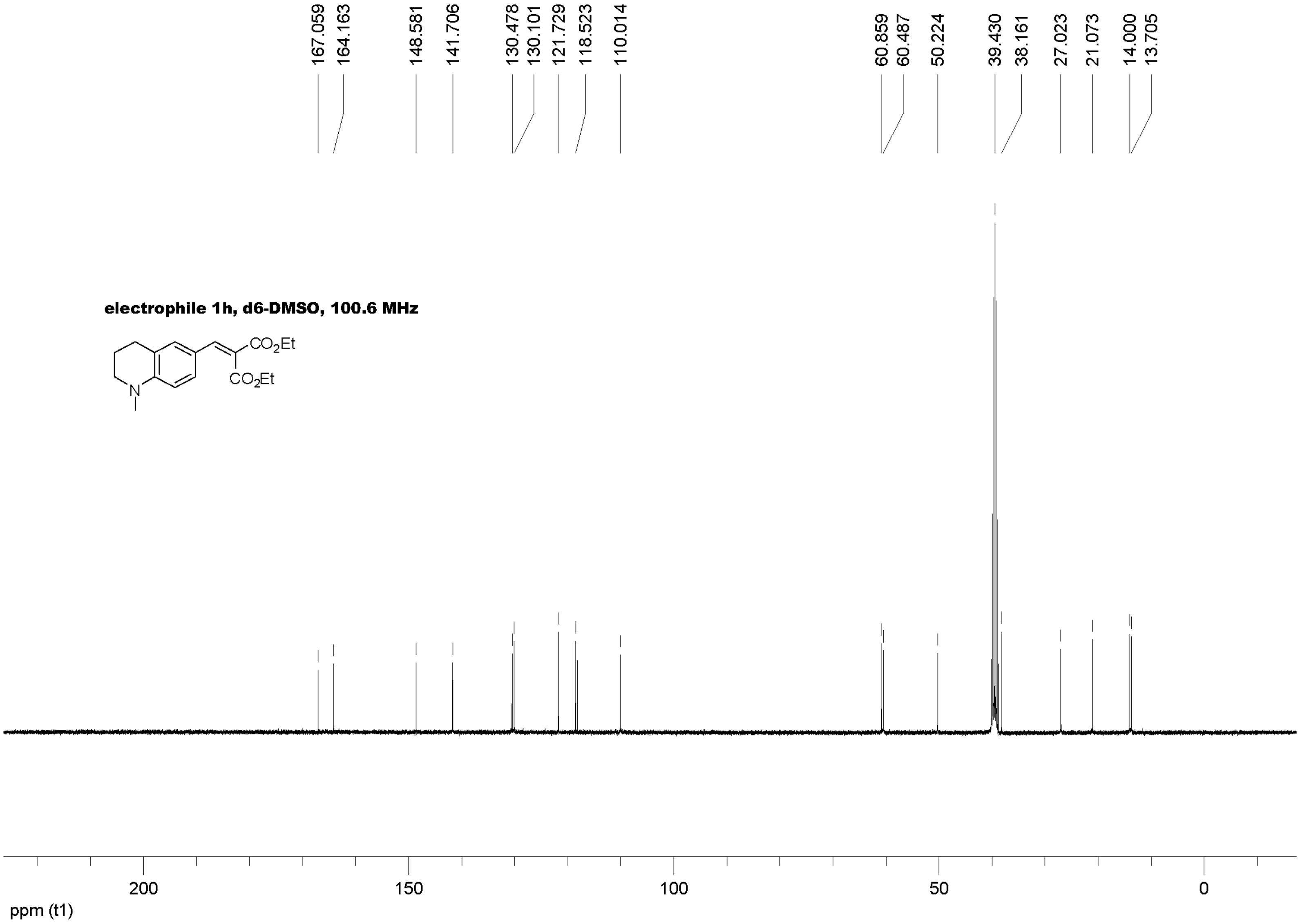


8. Copies of NMR spectra

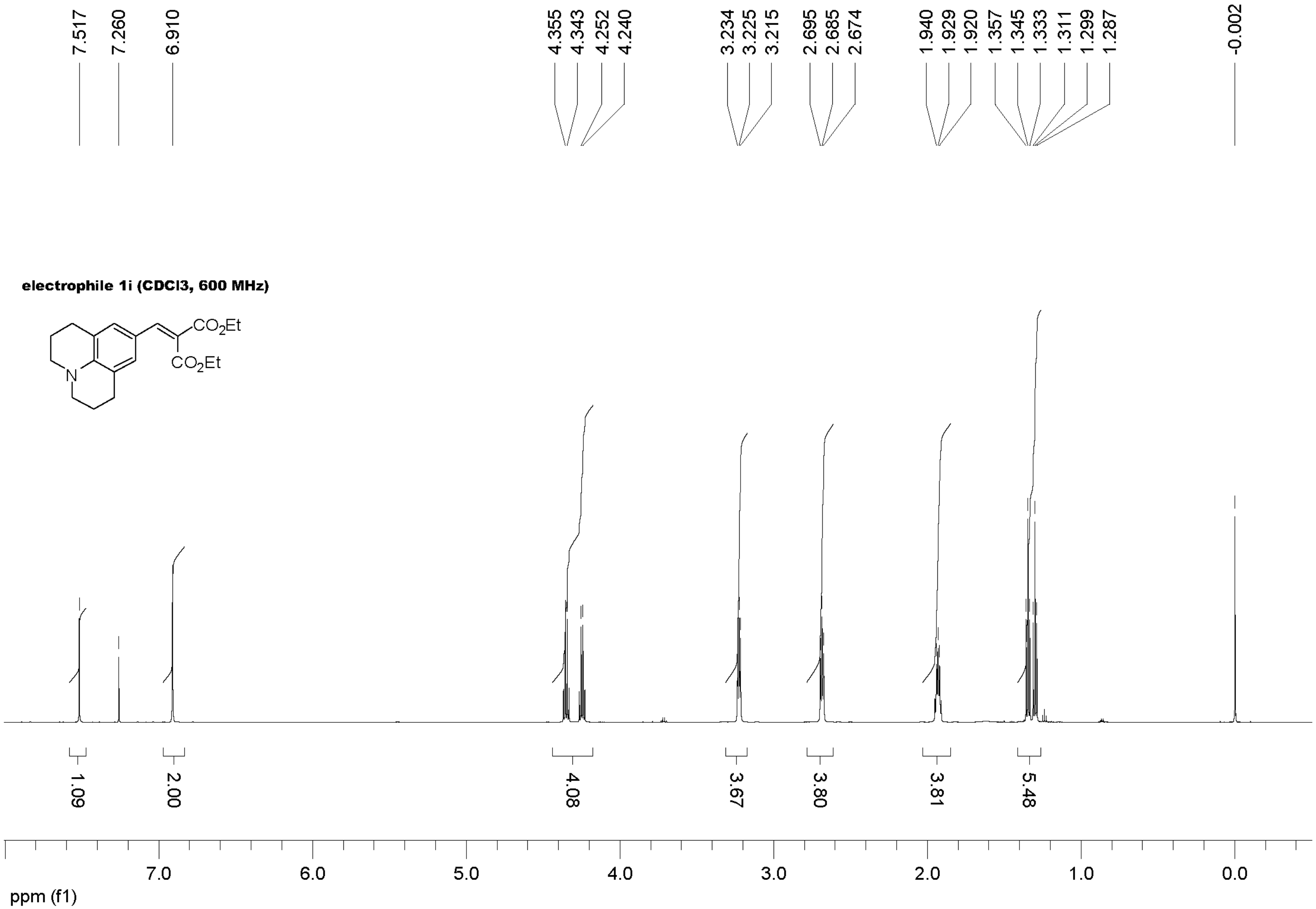
1h (^{1}H NMR, DMSO-d_6)



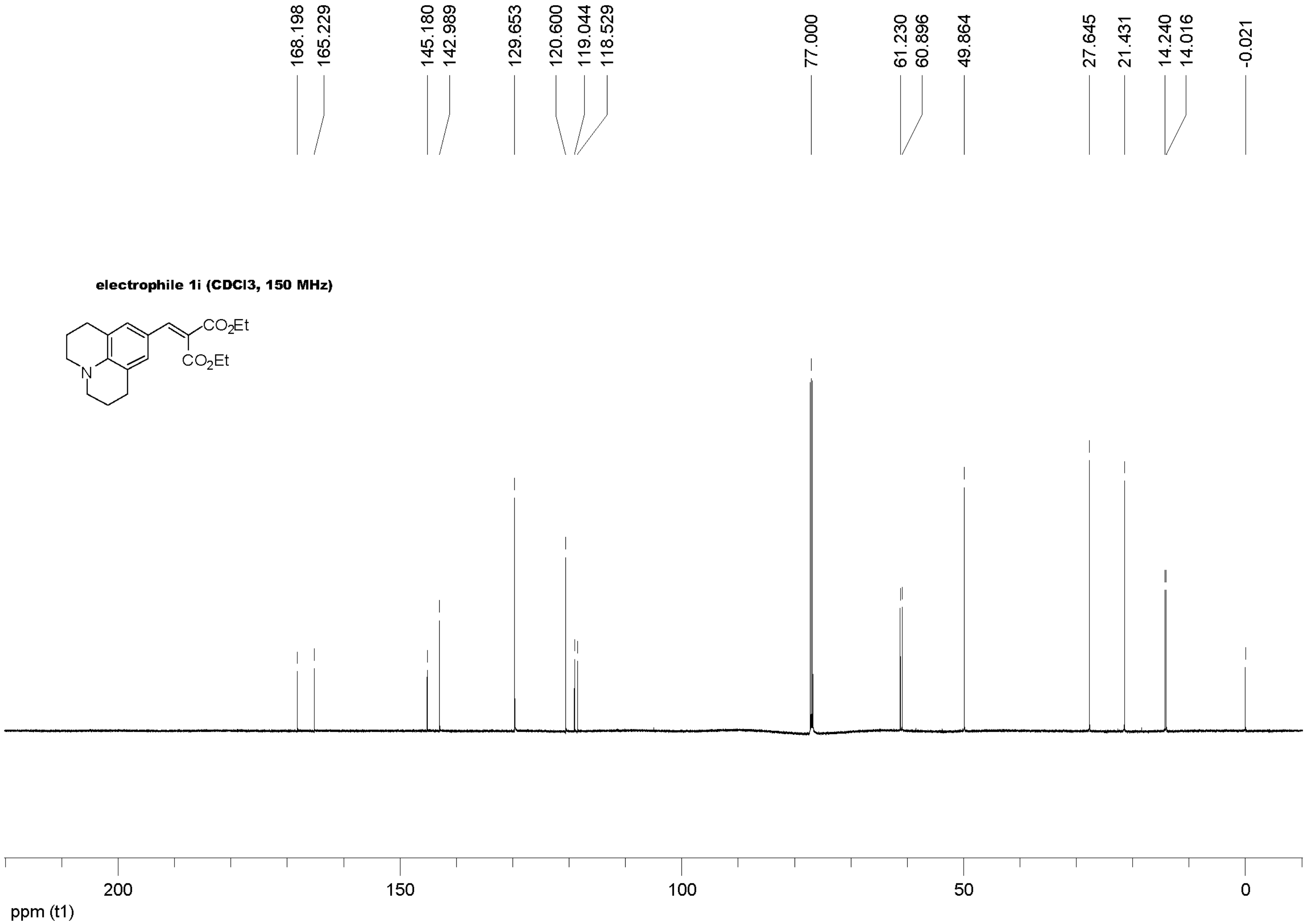
1h (^{13}C NMR, DMSO-d_6)



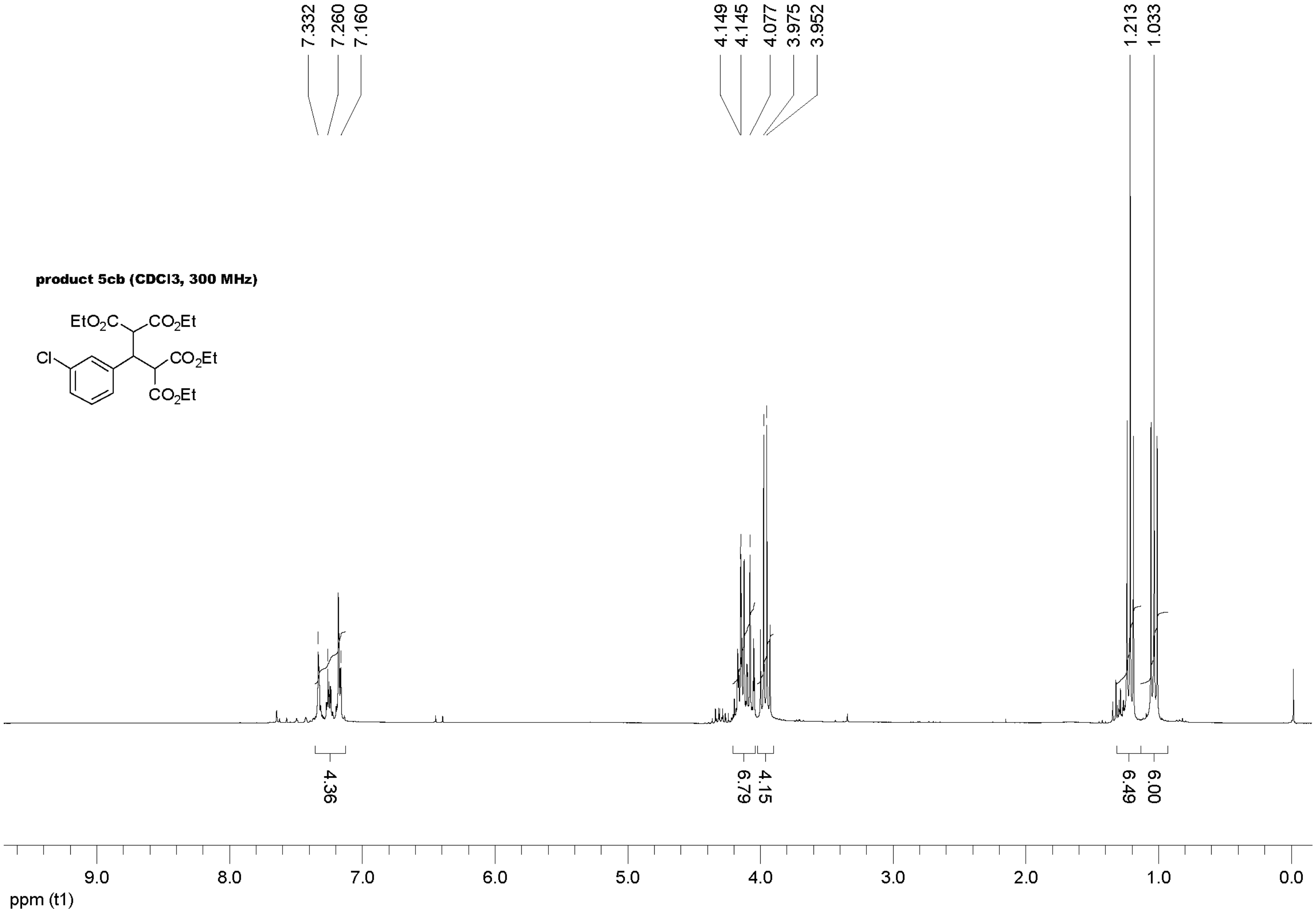
1i (^{1}H NMR, $CDCl_3$)



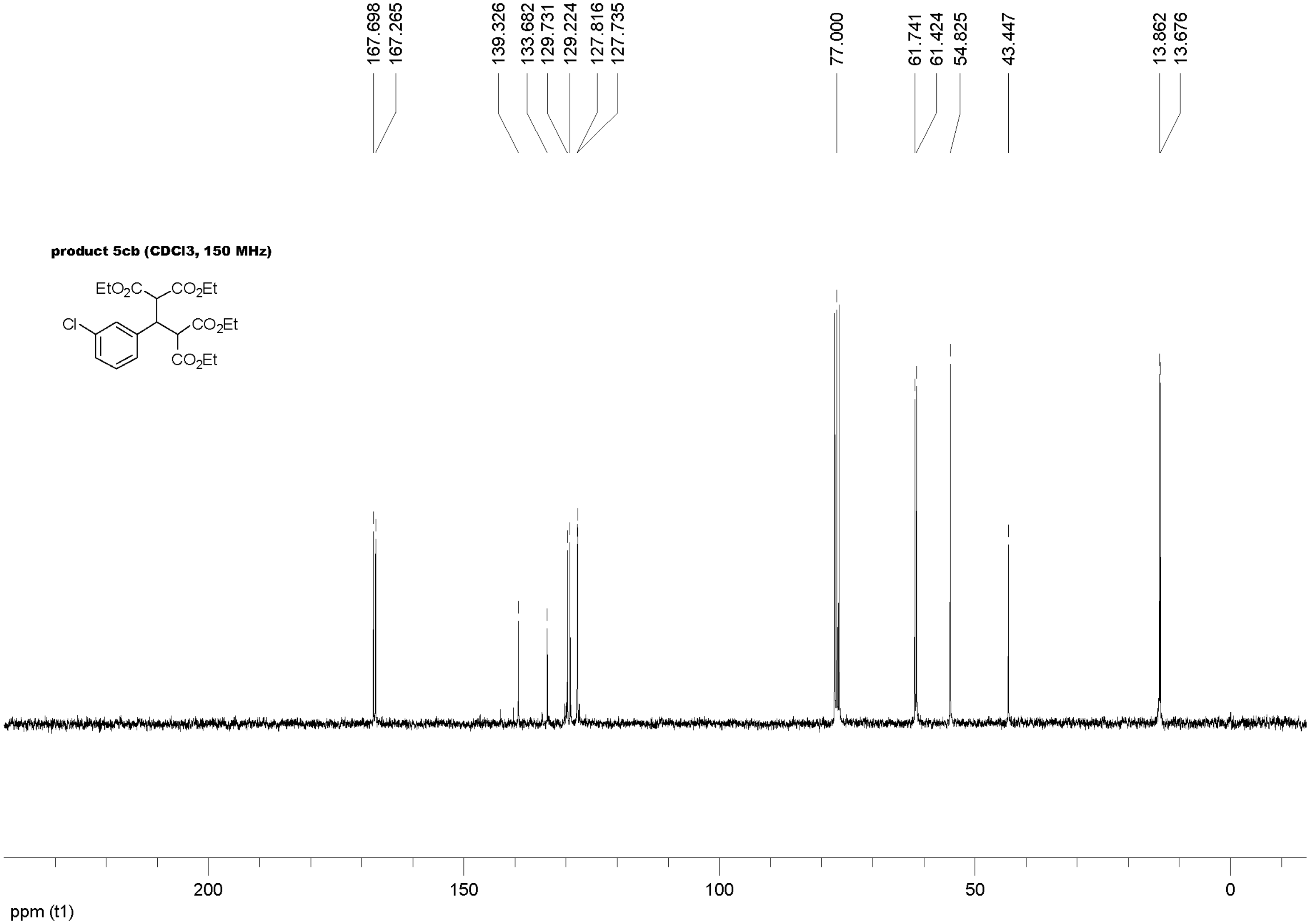
1i (^{13}C NMR, CDCl$_3$)



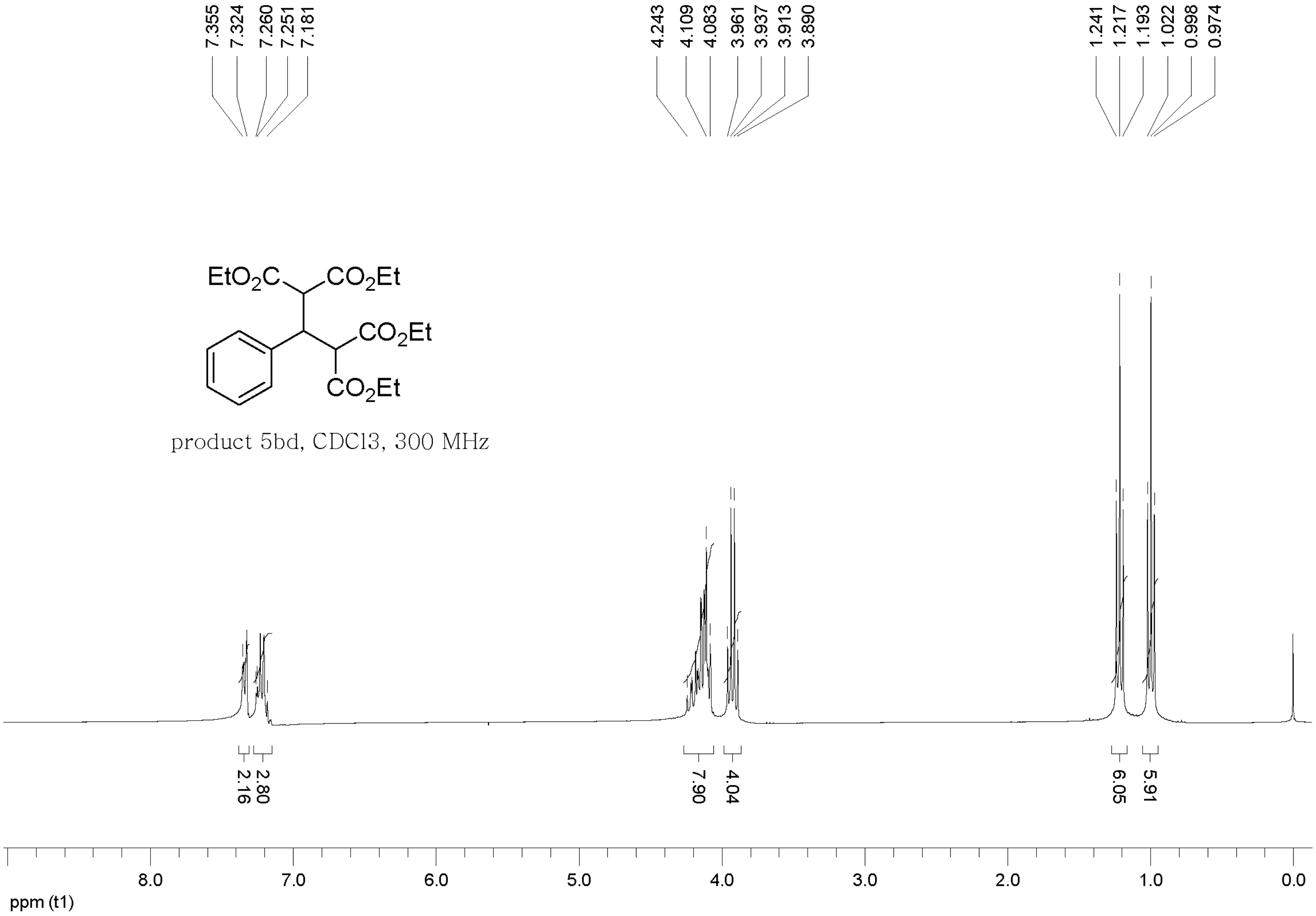
5cb (^{1}H NMR, $CDCl_3$)



5cb (^{13}C NMR, CDCl$_3$)

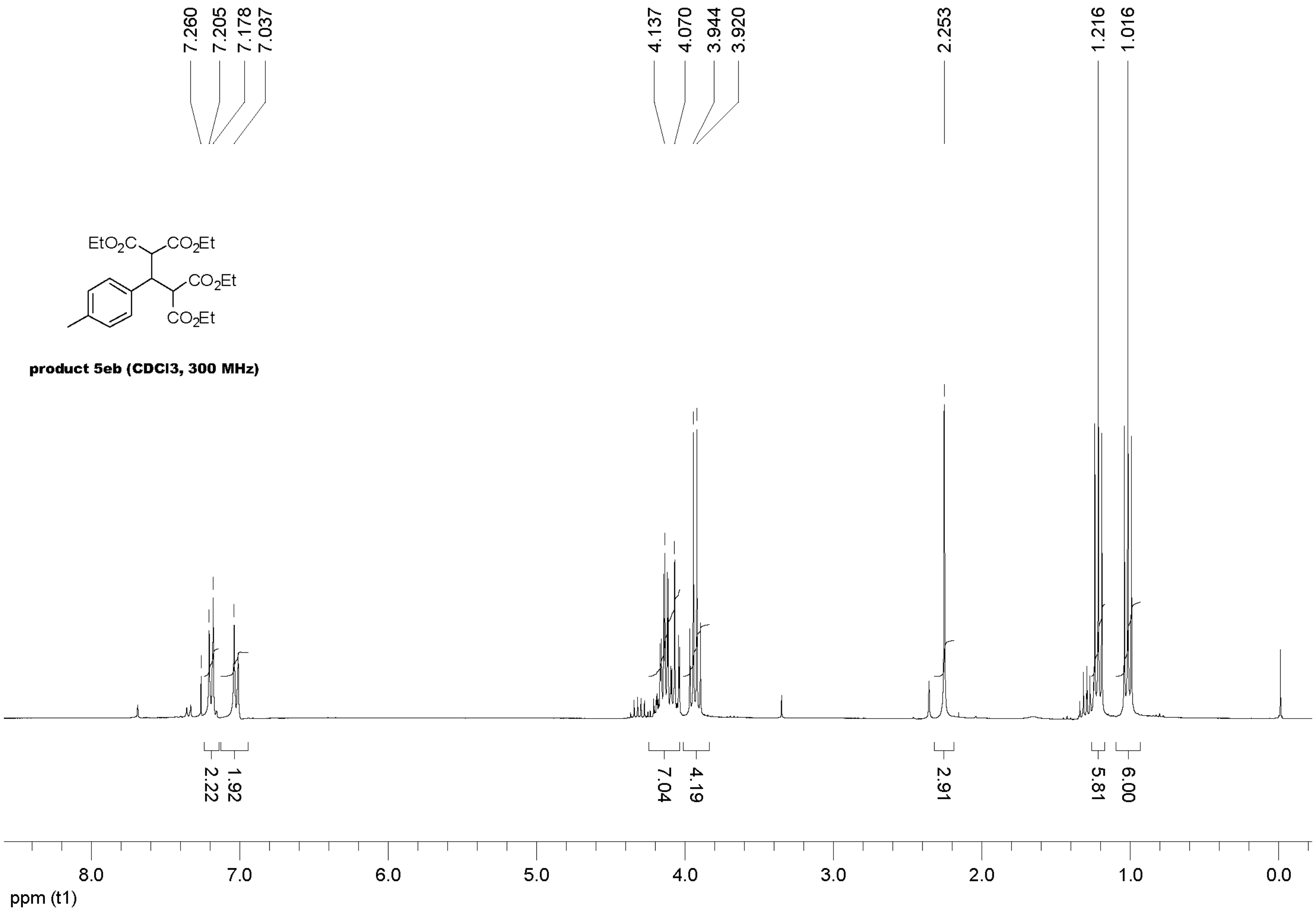


5db (^{1}H NMR, $CDCl_3$)

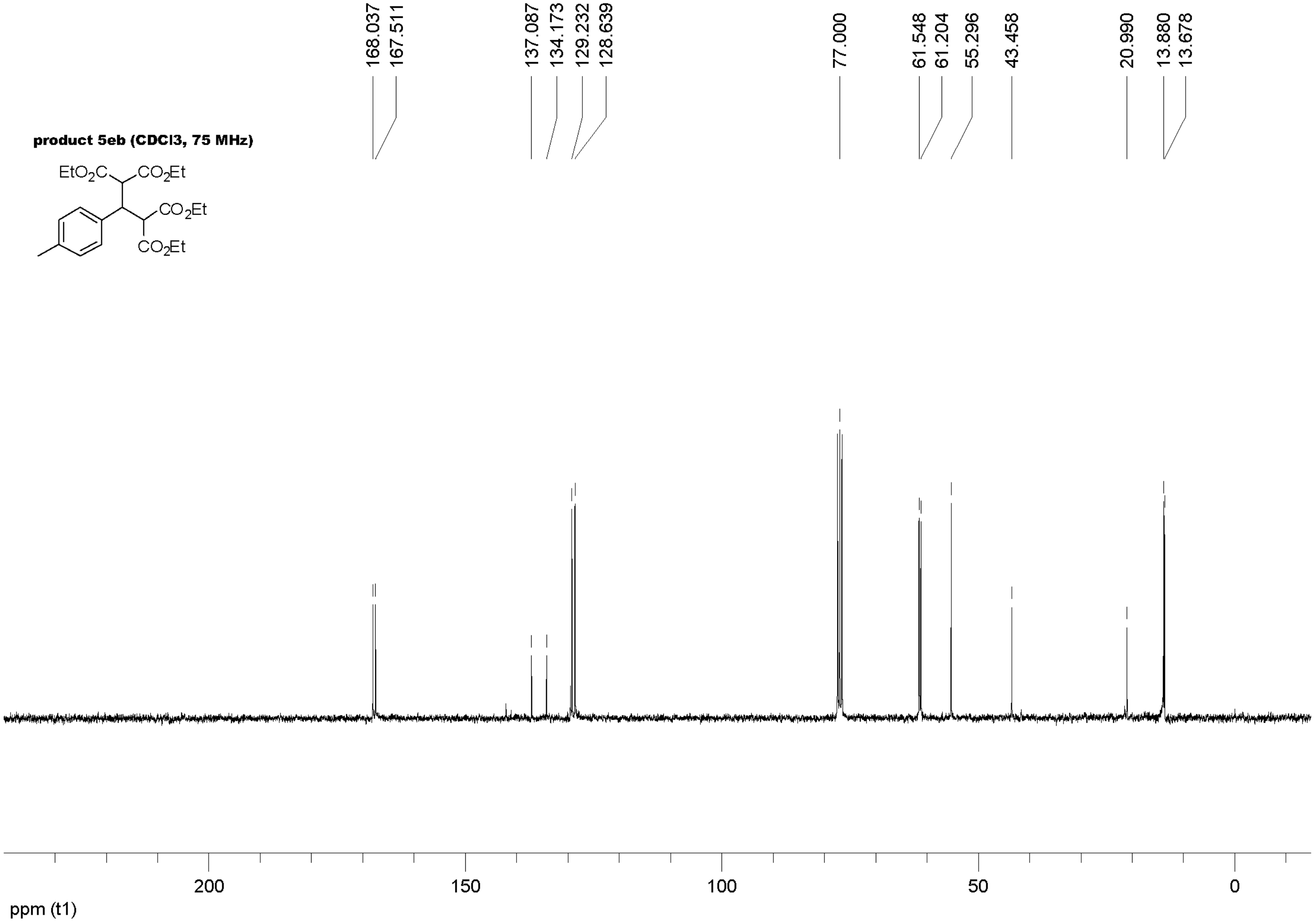


product 5bd, CDCl3, 300 MHz

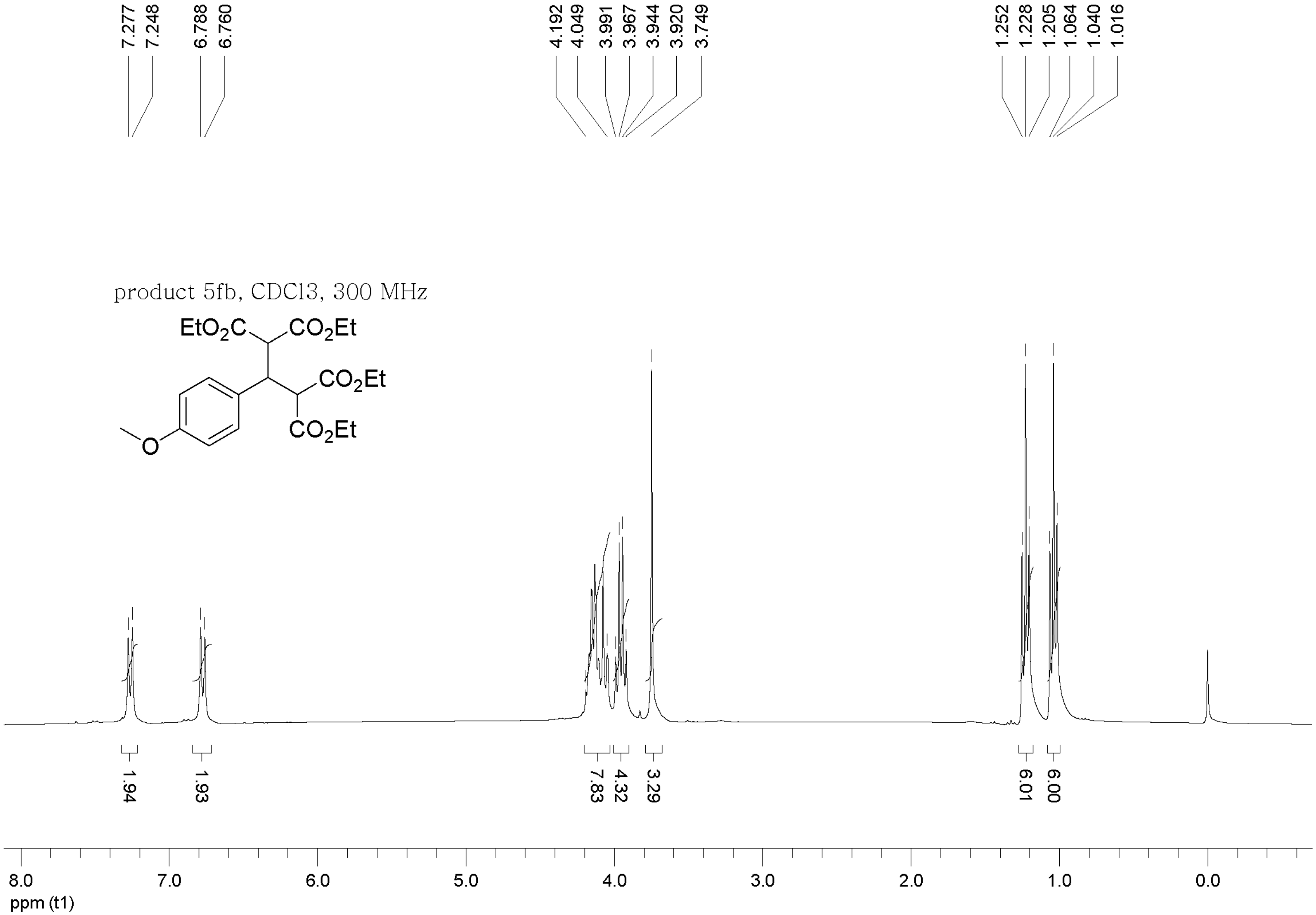
5eb (^{1}H NMR, $CDCl_3$)



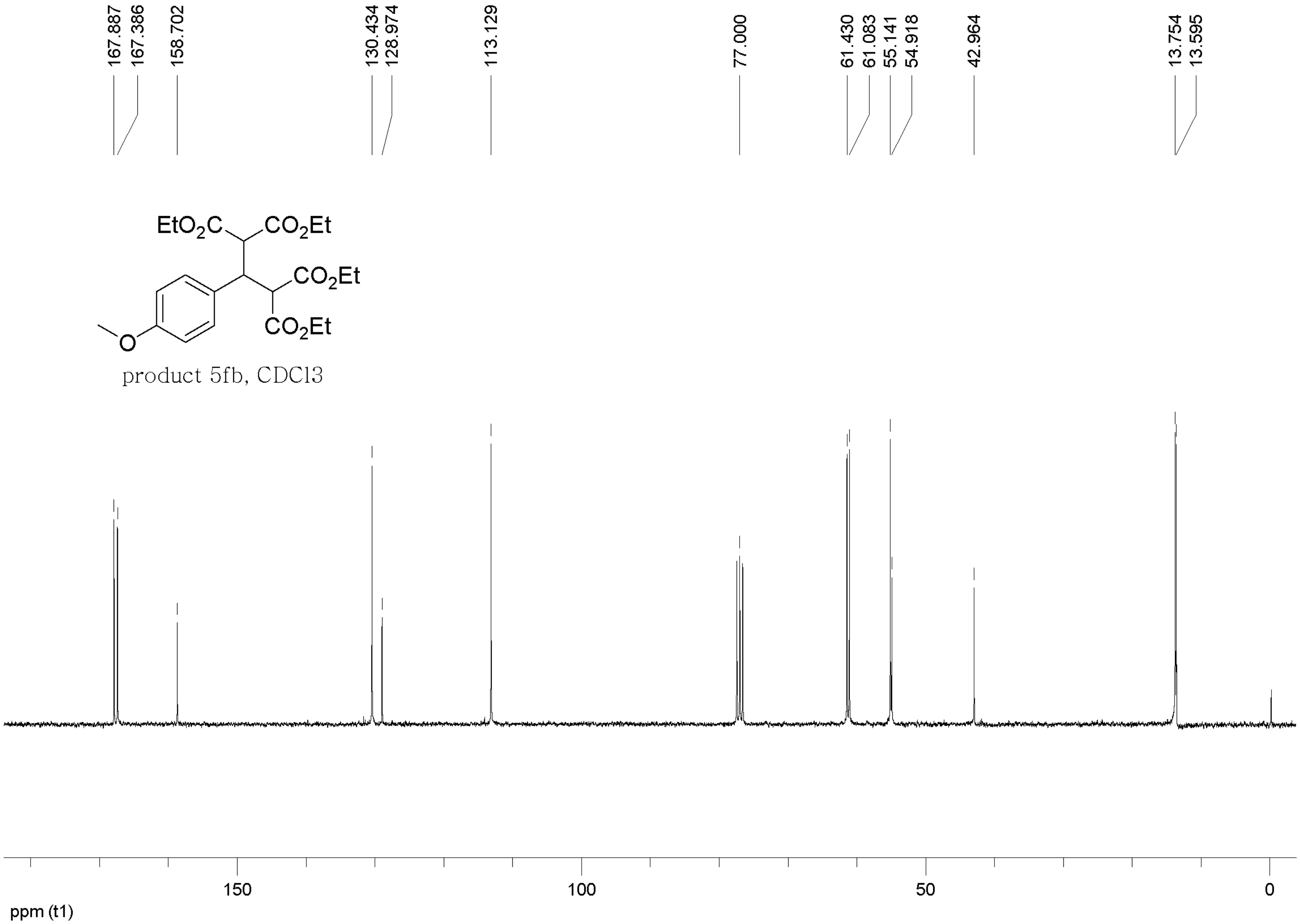
5eb (^{13}C NMR, CDCl$_3$)



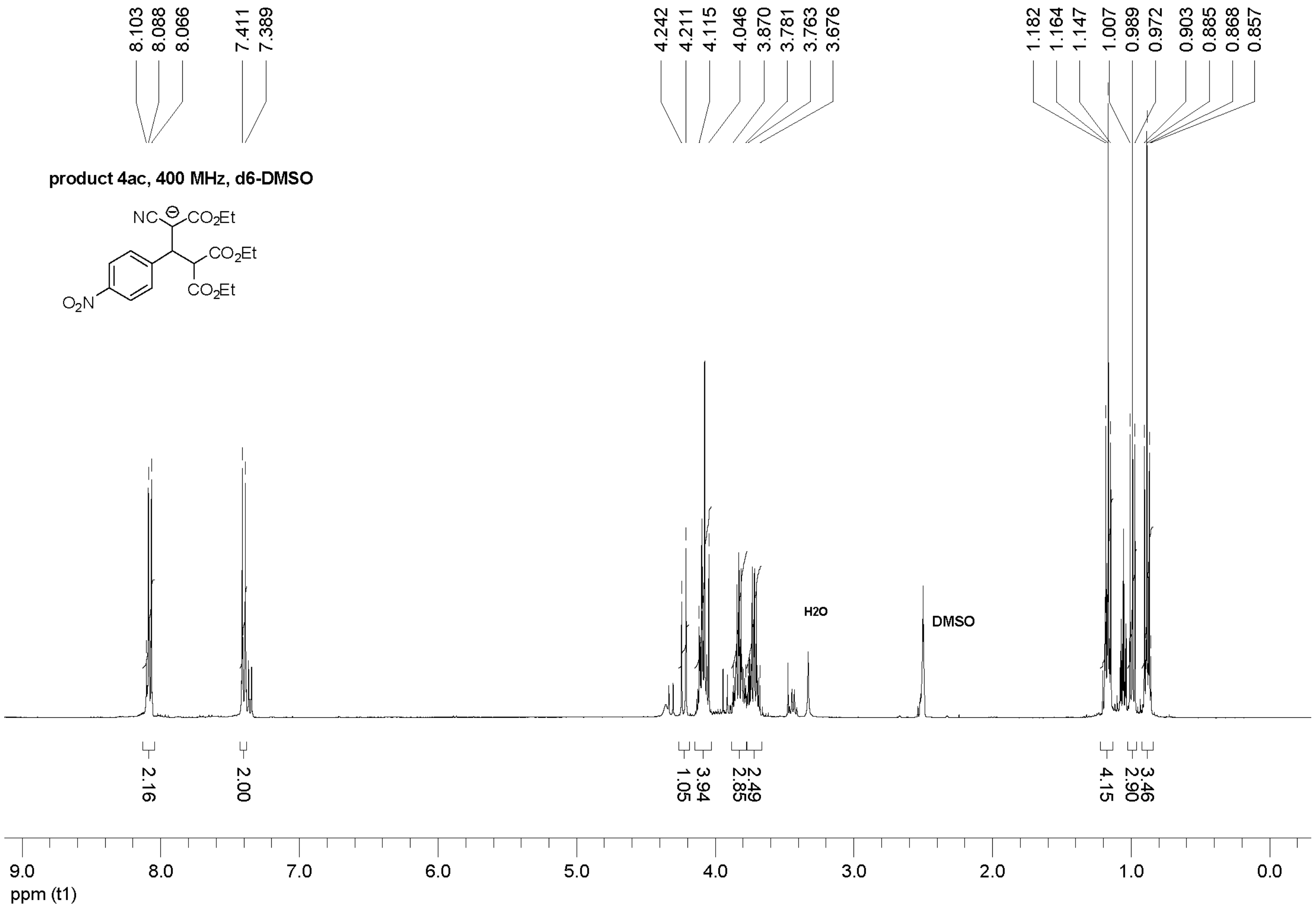
5fb (^{1}H NMR, $CDCl_3$)



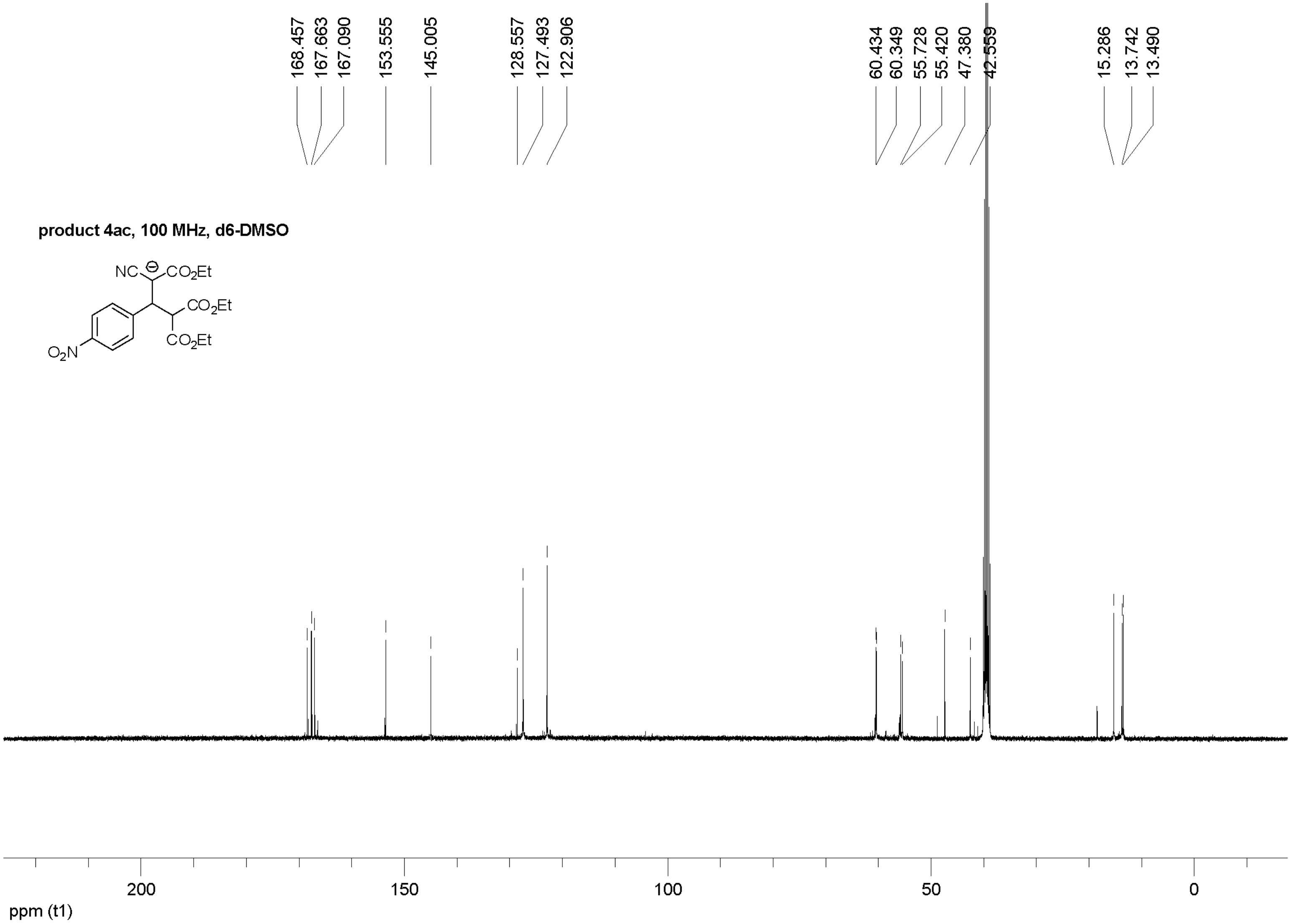
5fb (^{13}C NMR, $CDCl_3$)



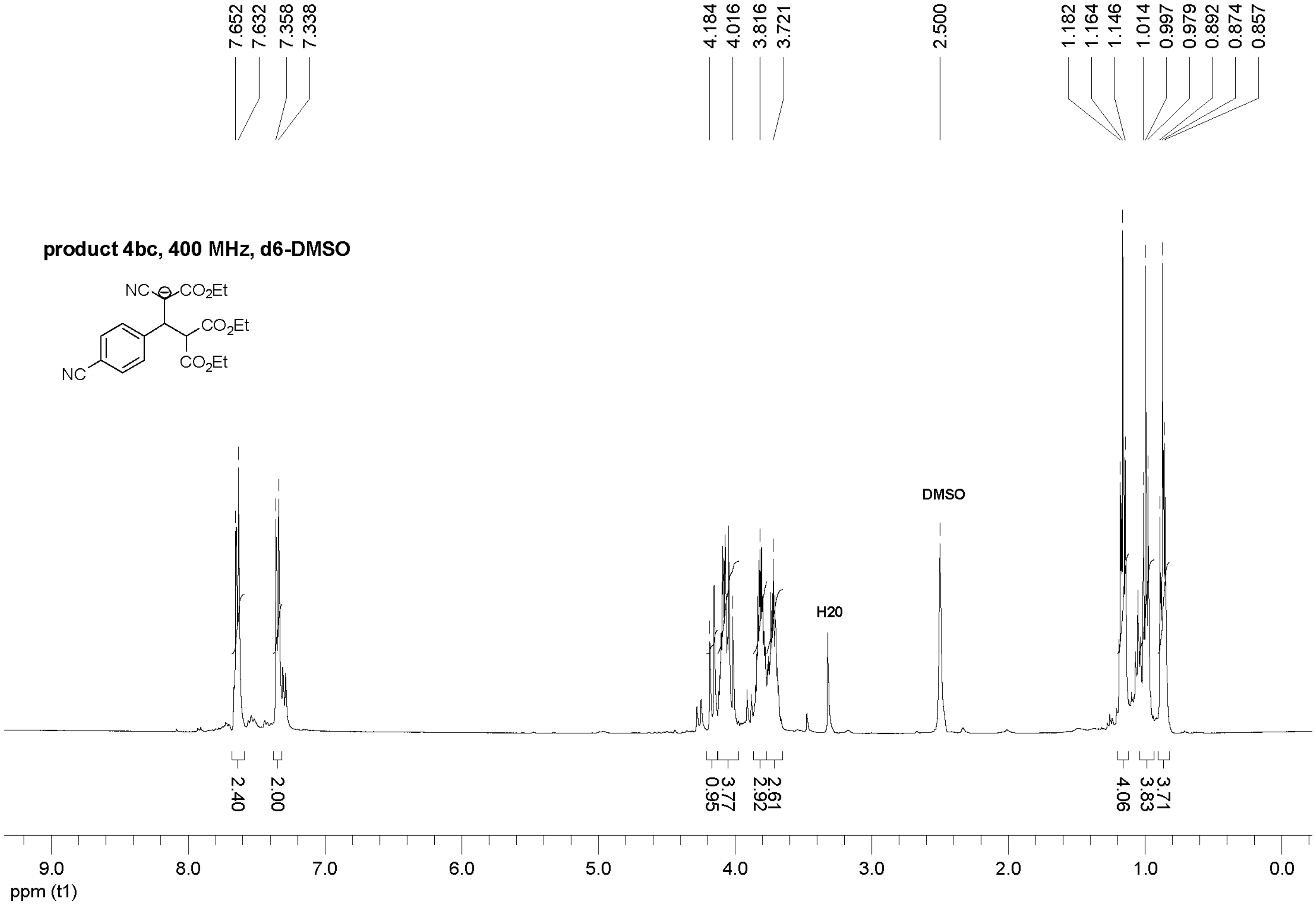
4ac-K^+ (^1H NMR, DMSO-d_6)



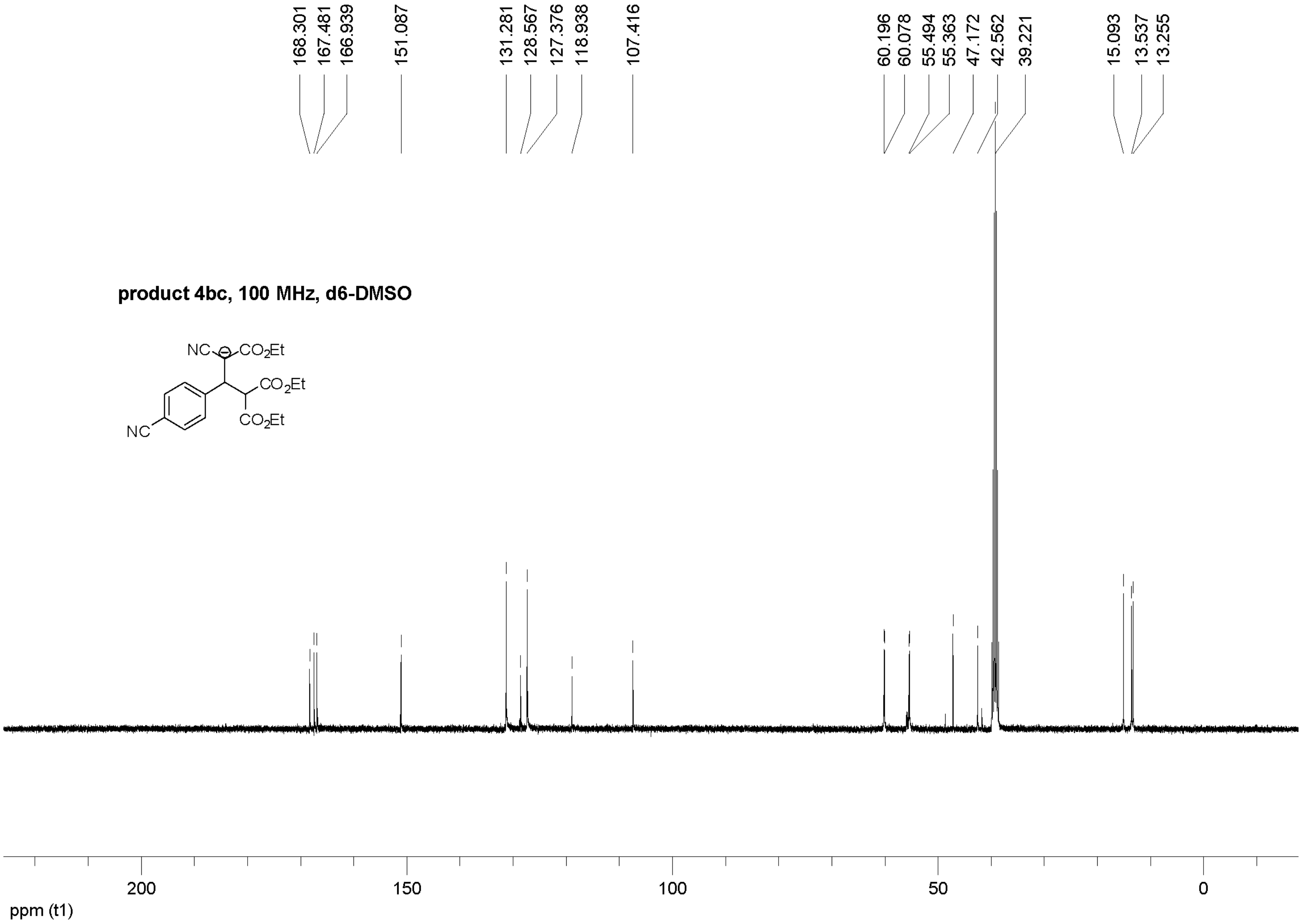
4ac-K$^+$ (^{13}C NMR, DMSO-d_6)



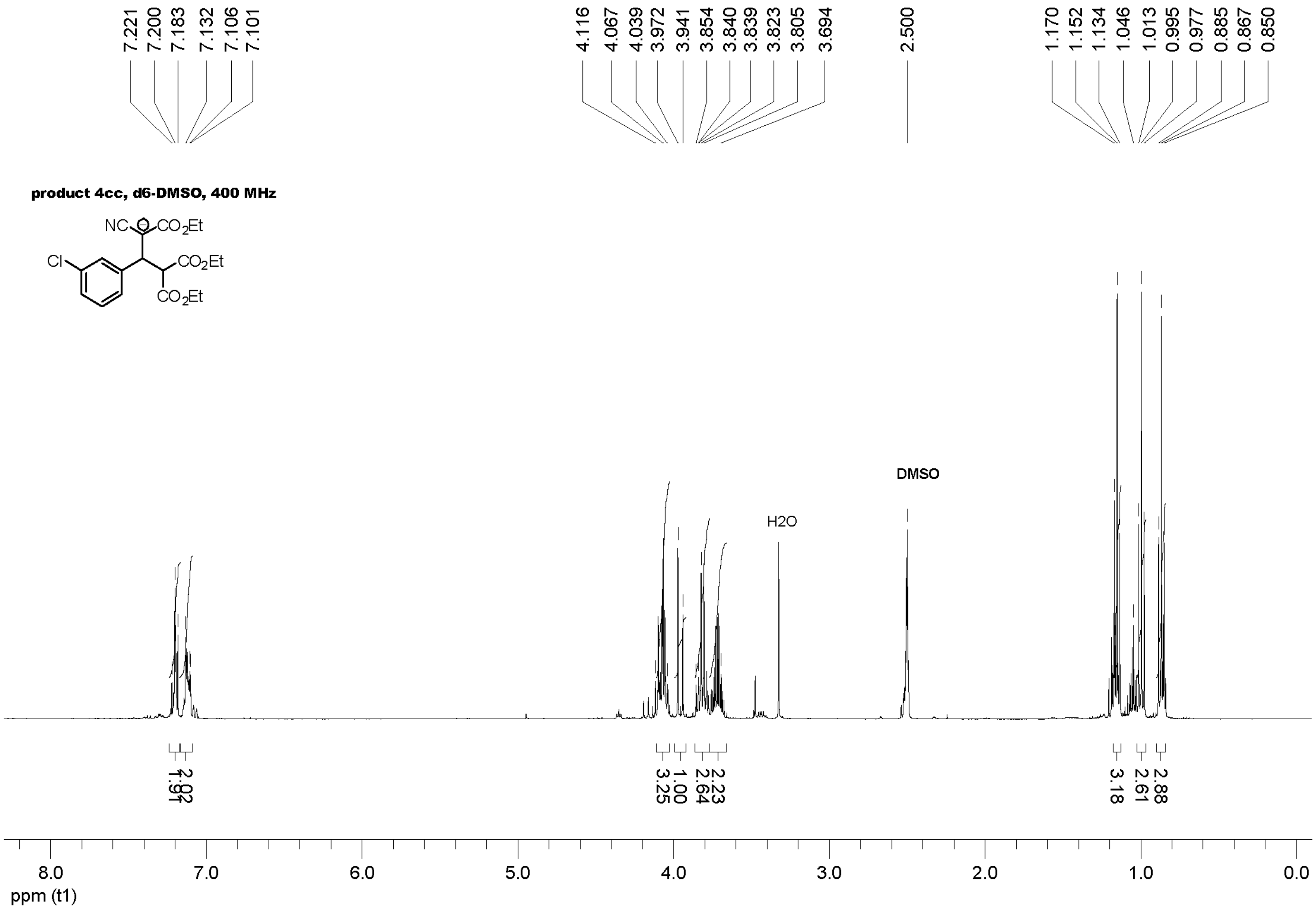
4bc-K^+ (^1H NMR, DMSO-d_6)



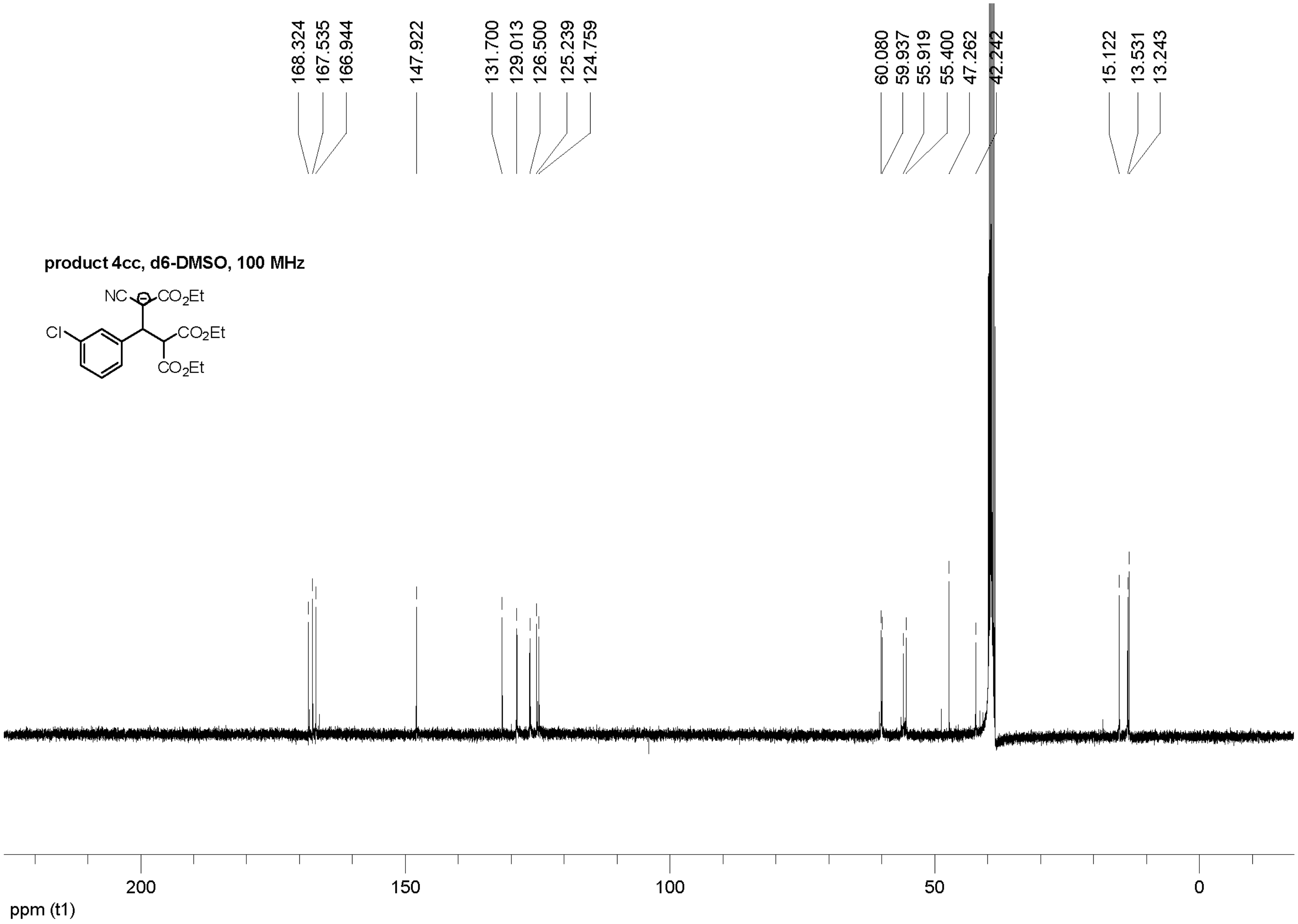
4bc-K$^+$ (^{13}C NMR, DMSO-d_6)



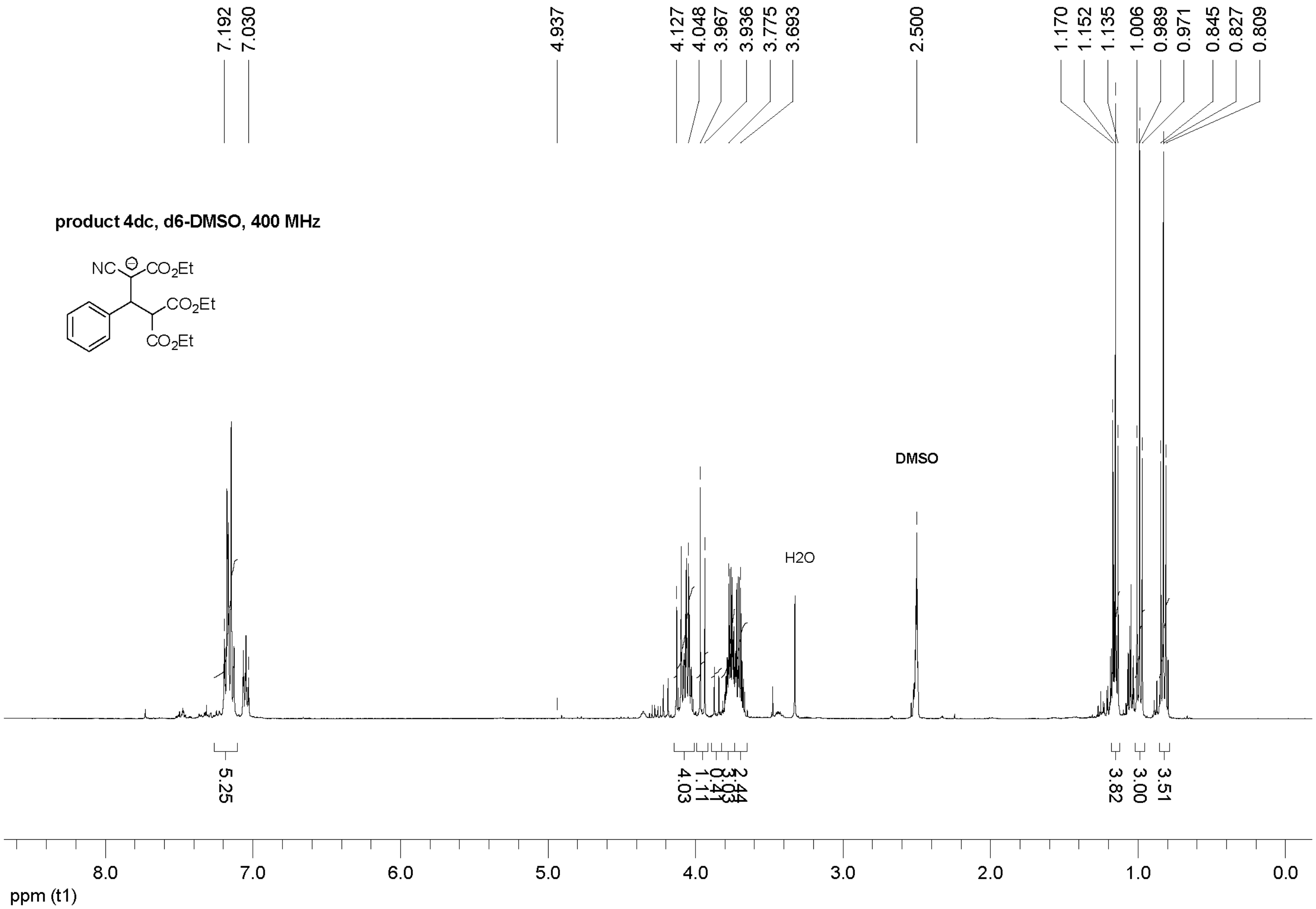
4cc-K$^+$ (^{1}H NMR, DMSO-d_6)



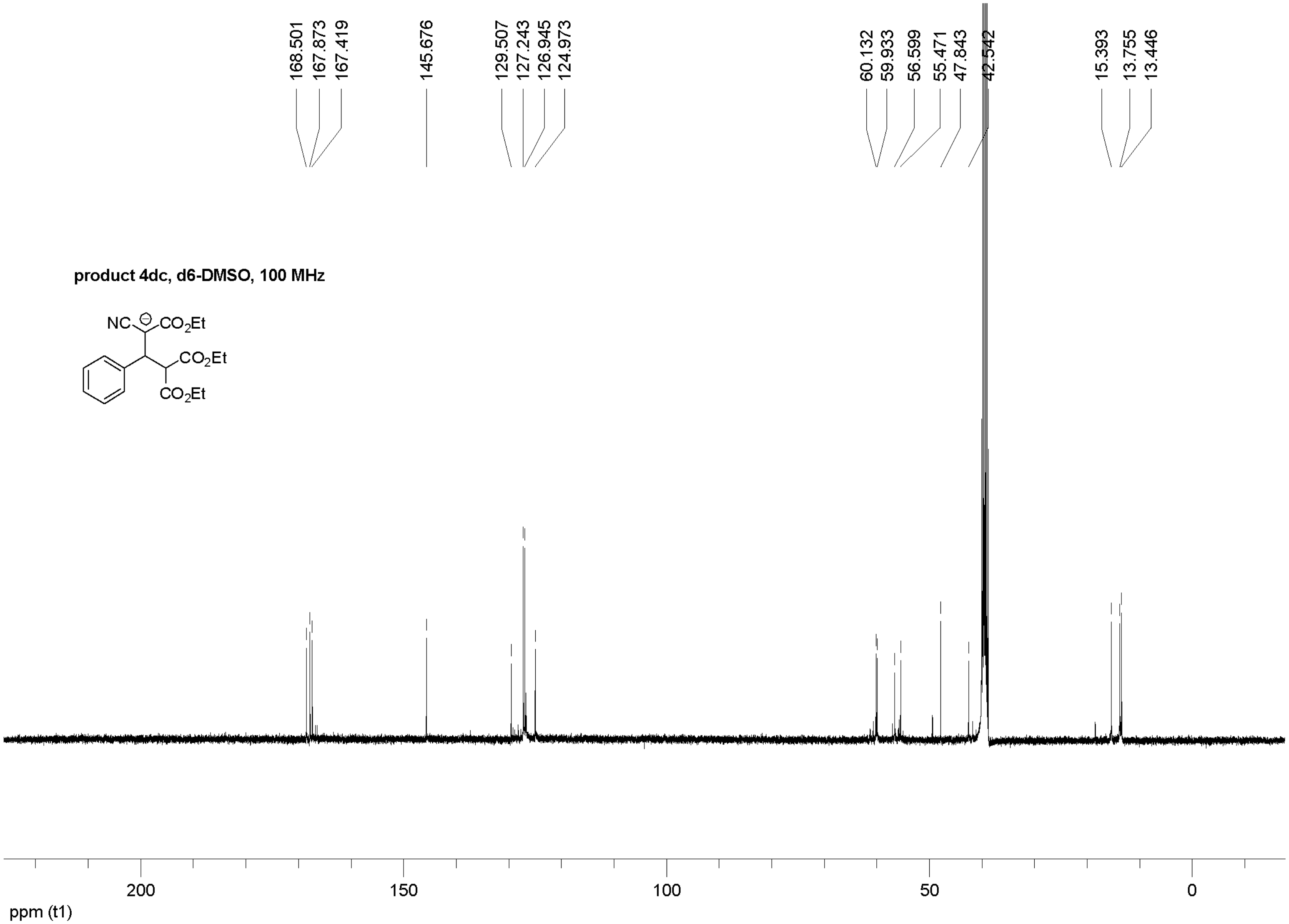
4cc-K$^+$ (^{13}C NMR, DMSO-d_6)



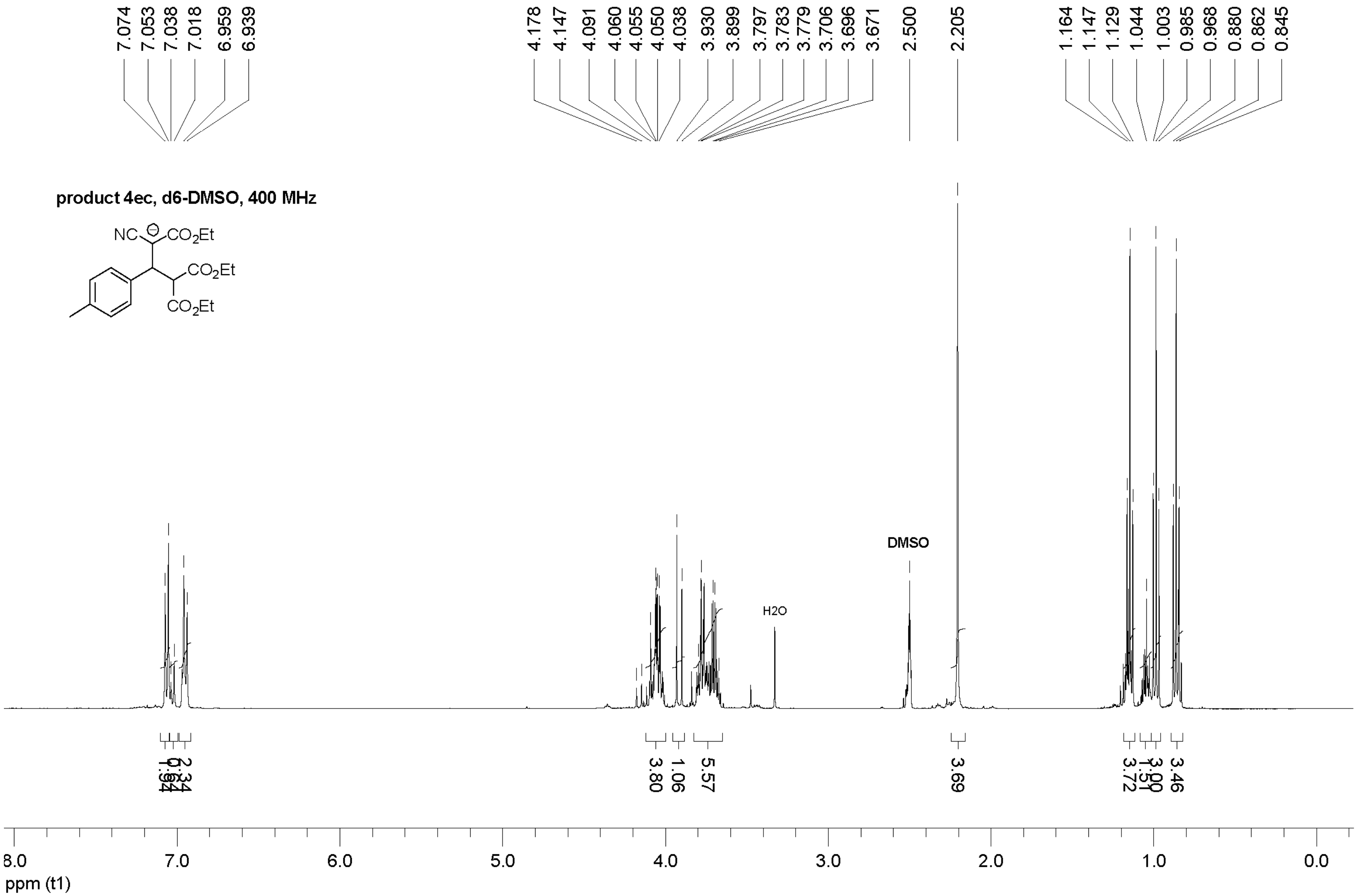
4dc-K$^+$ (^{1}H NMR, DMSO-d_6)



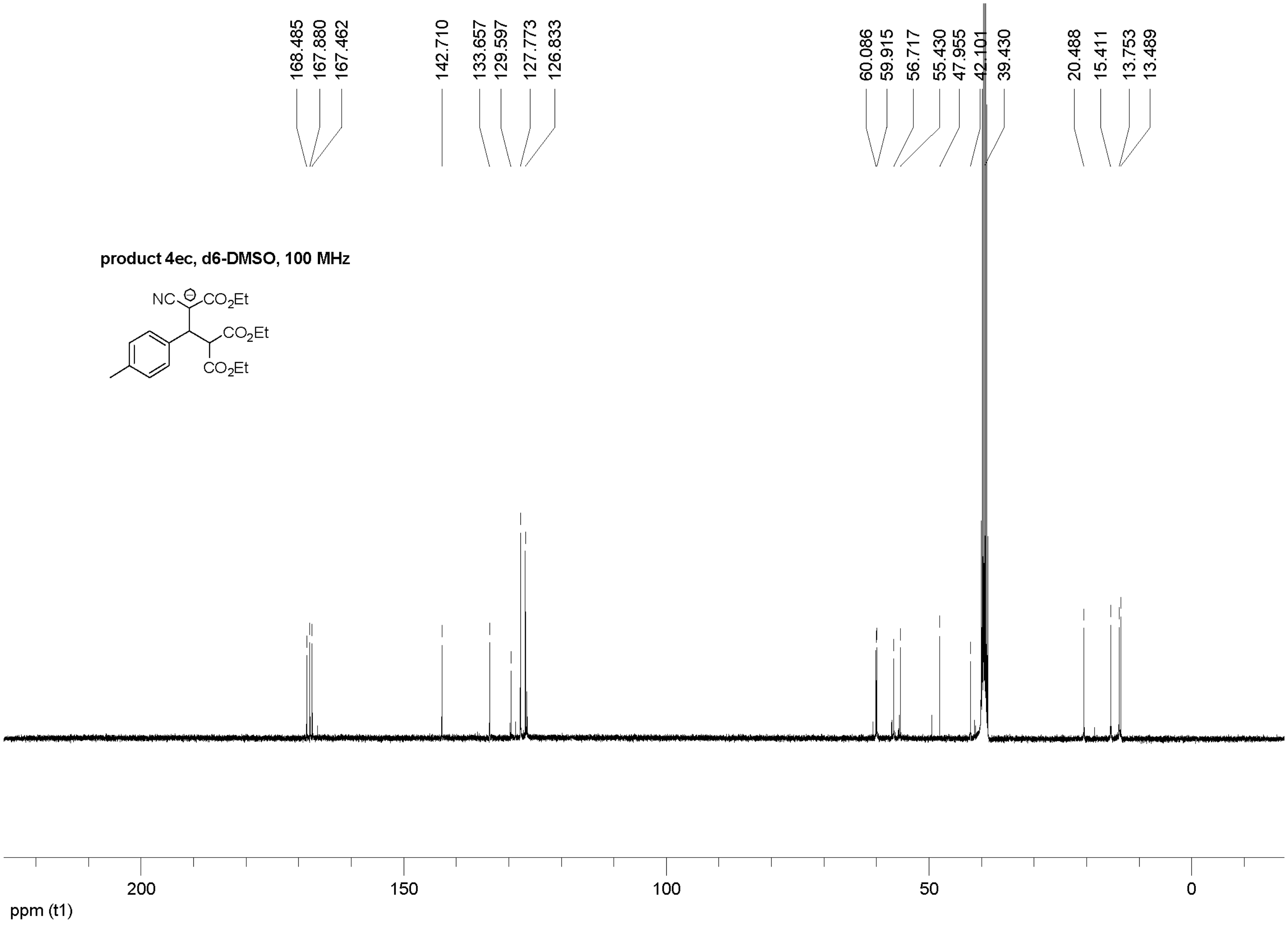
4dc-K$^+$ (^{13}C NMR, DMSO-*d*$_6$)



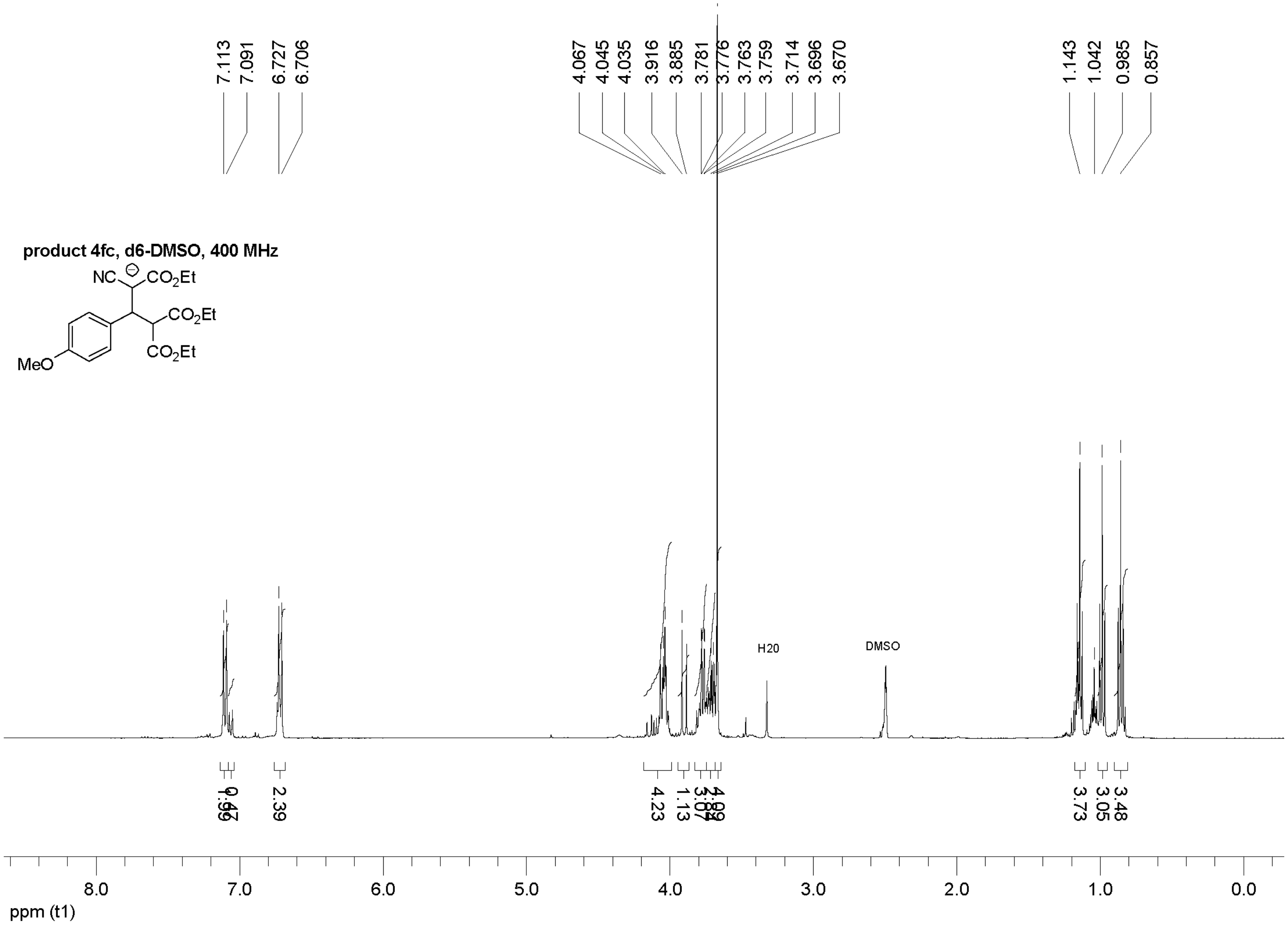
4ec-K$^+$ (^{1}H NMR, DMSO-d_6)



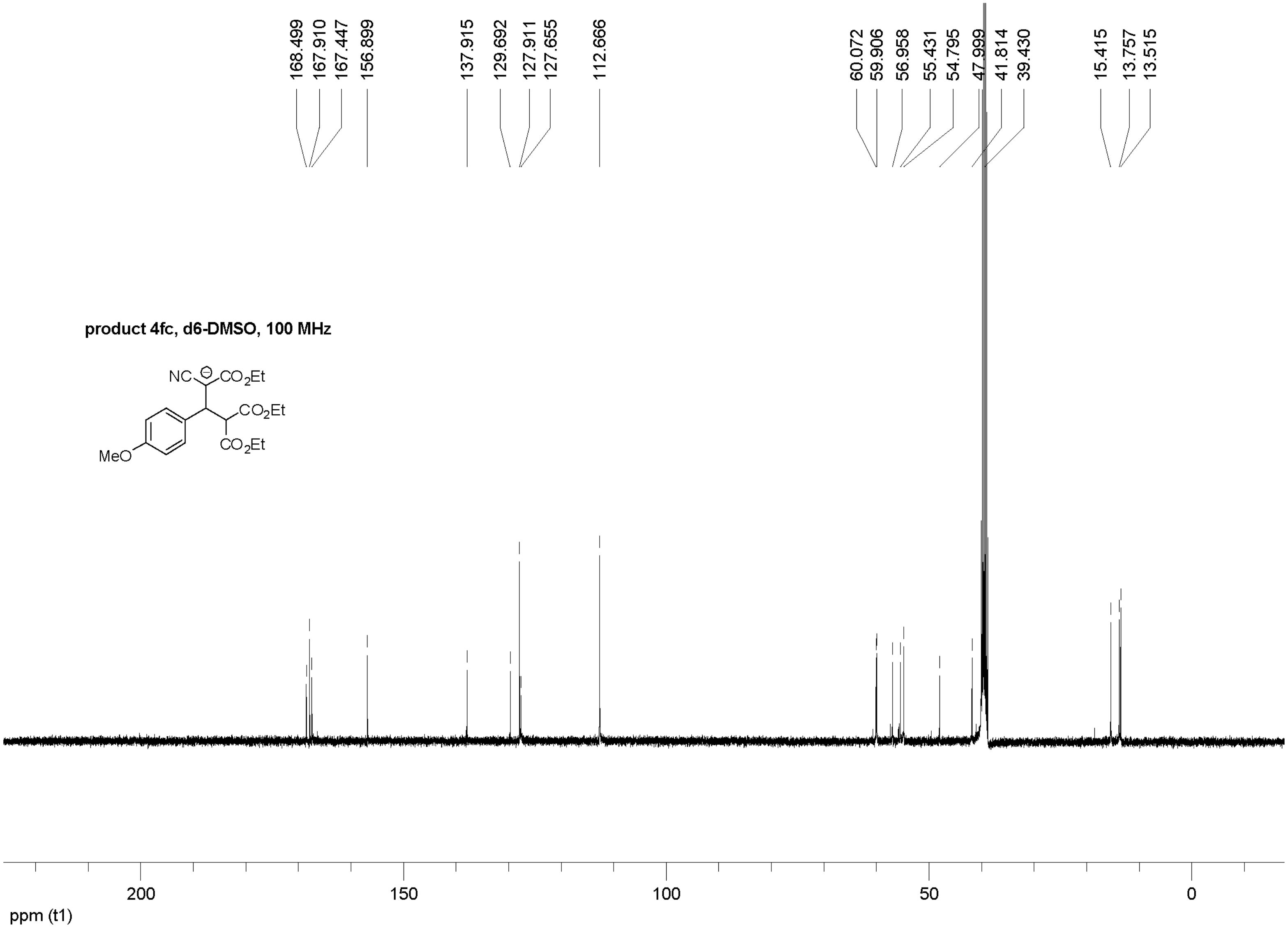
4ec-K$^+$ (^{13}C NMR, DMSO-d_6)



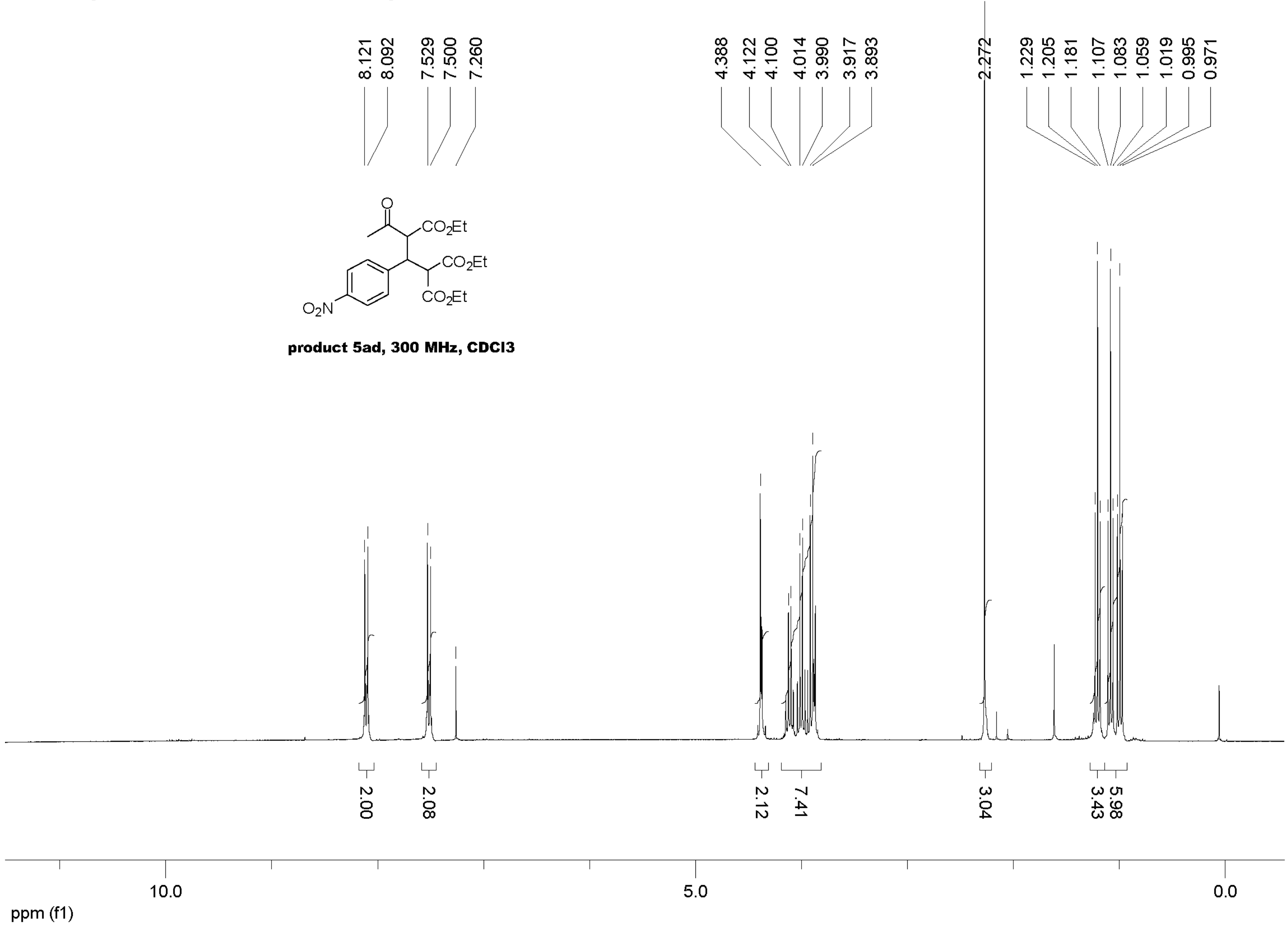
4fc-K$^+$ (^{1}H NMR, DMSO-d_6)



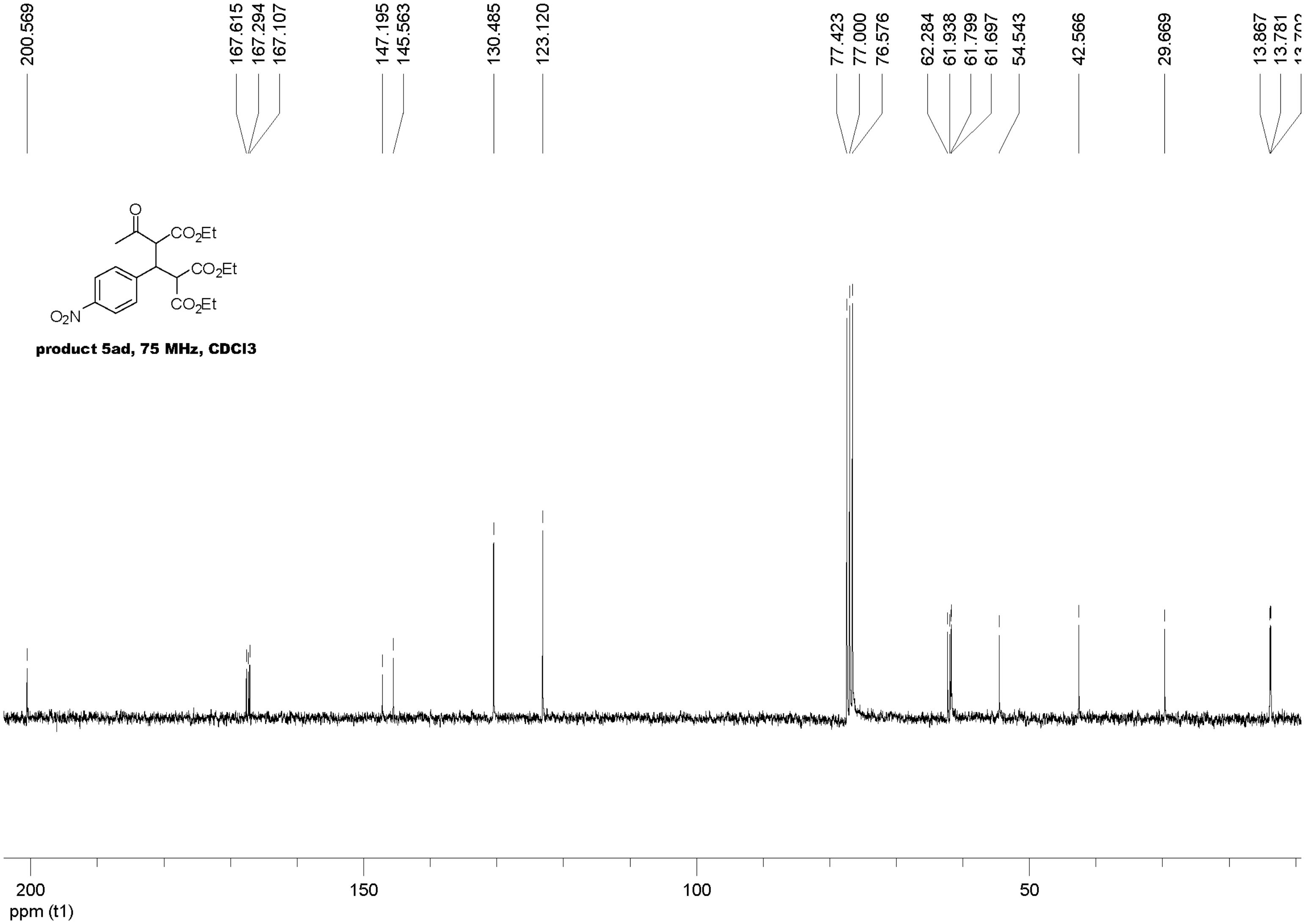
4fc-K$^+$ (^{13}C NMR, DMSO-d_6)



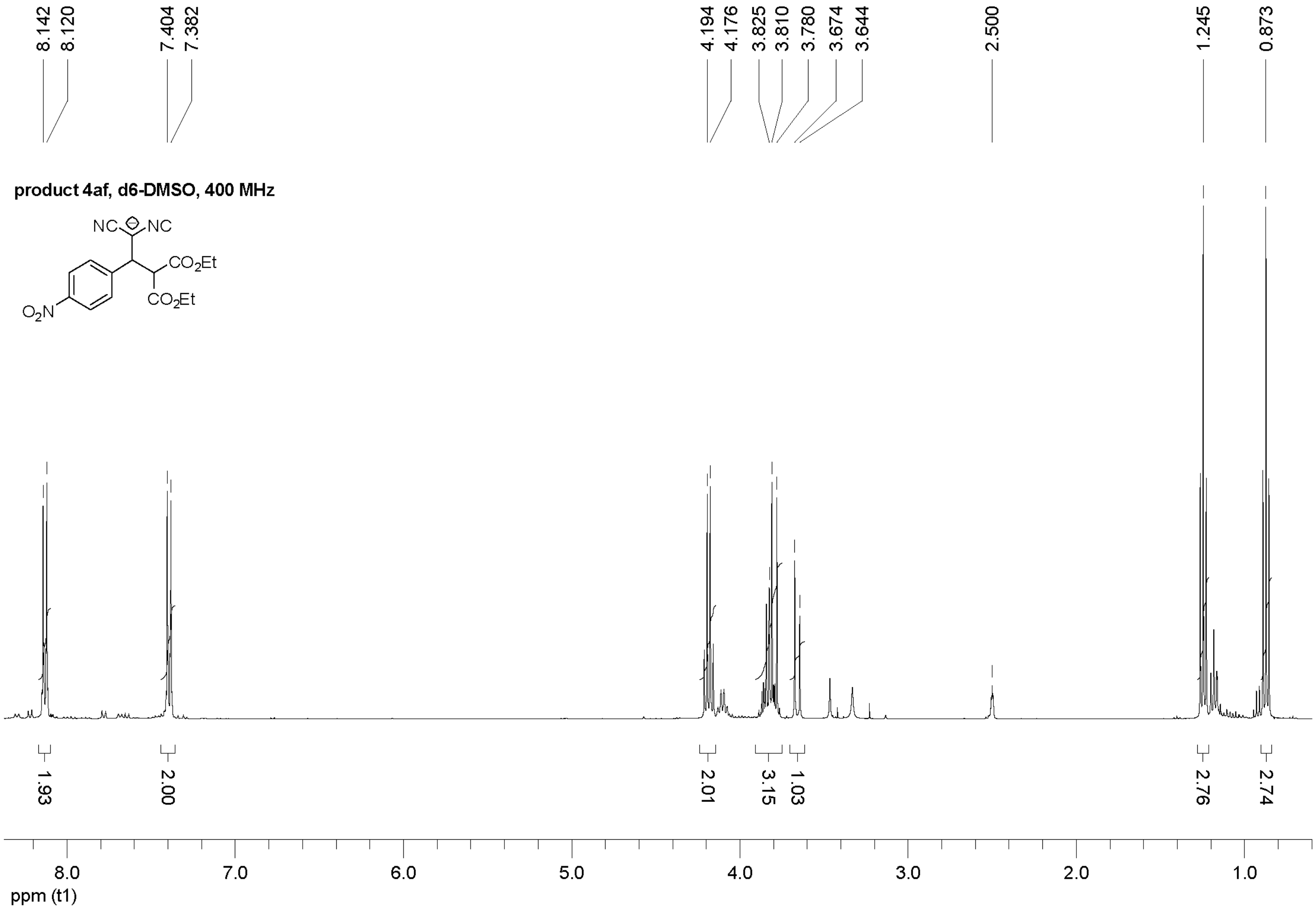
5ad (^{1}H NMR, $CDCl_3$)



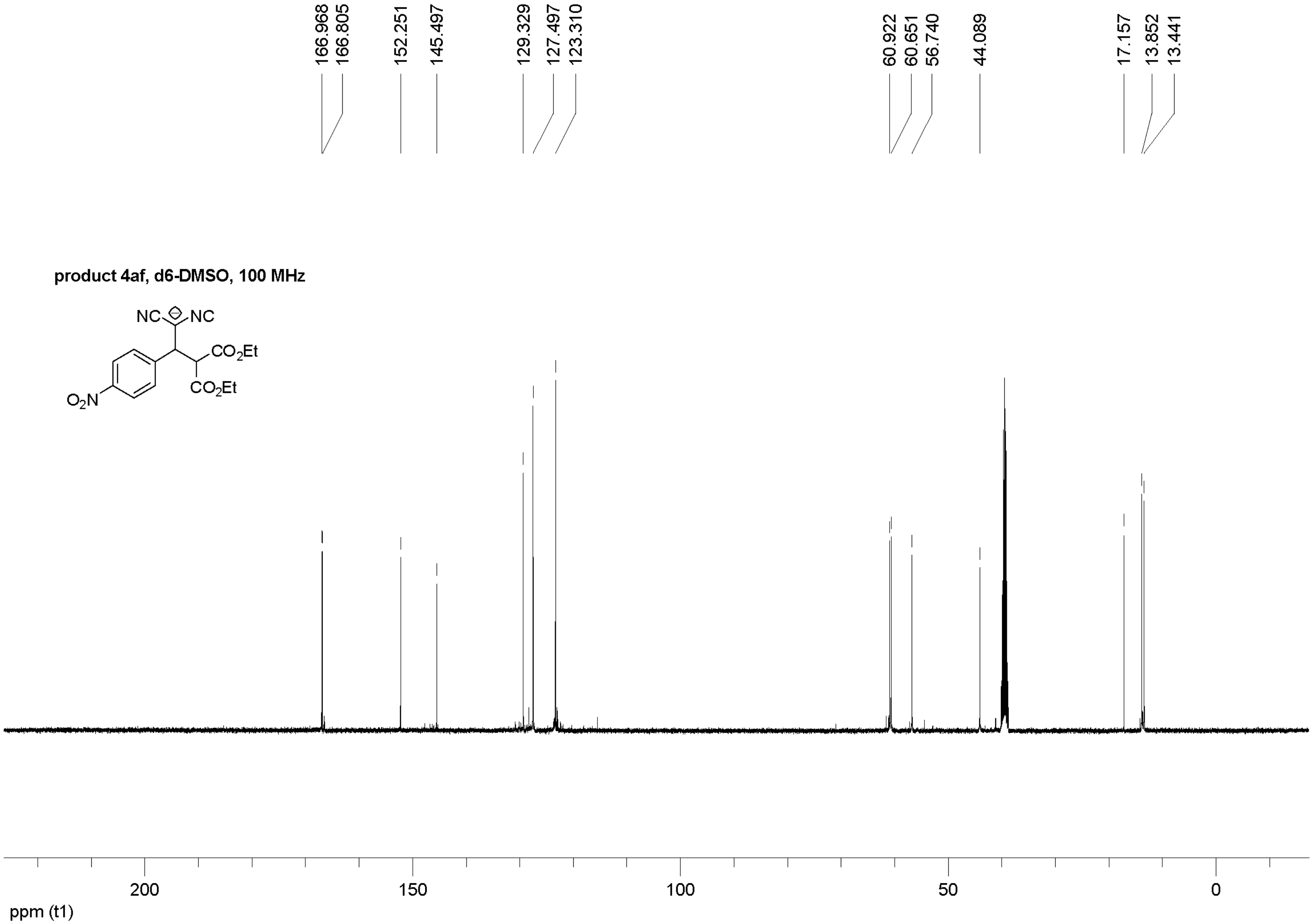
5ad (^{13}C NMR, CDCl$_3$)



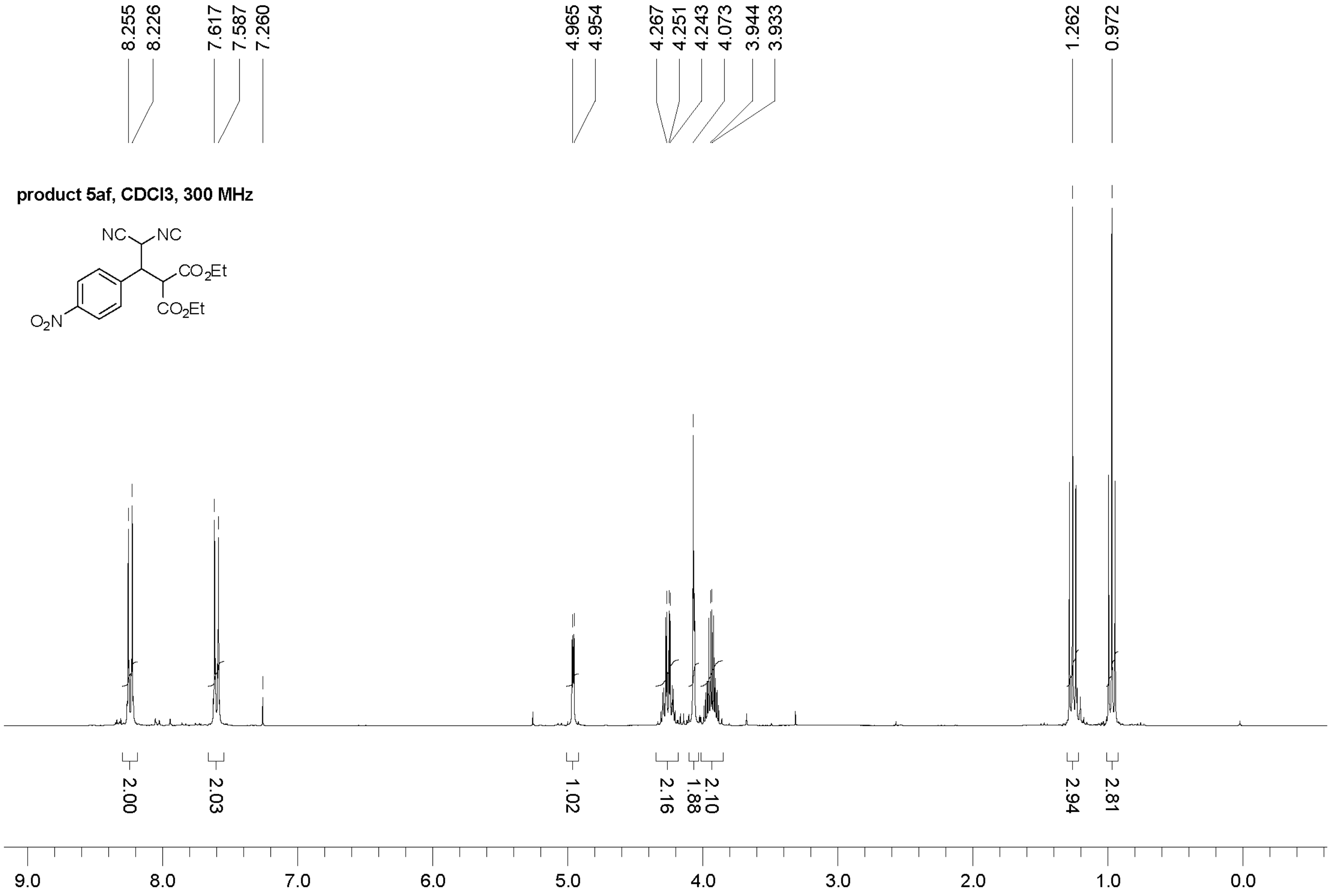
4af-K$^+$ (^{1}H NMR, DMSO-d_6)



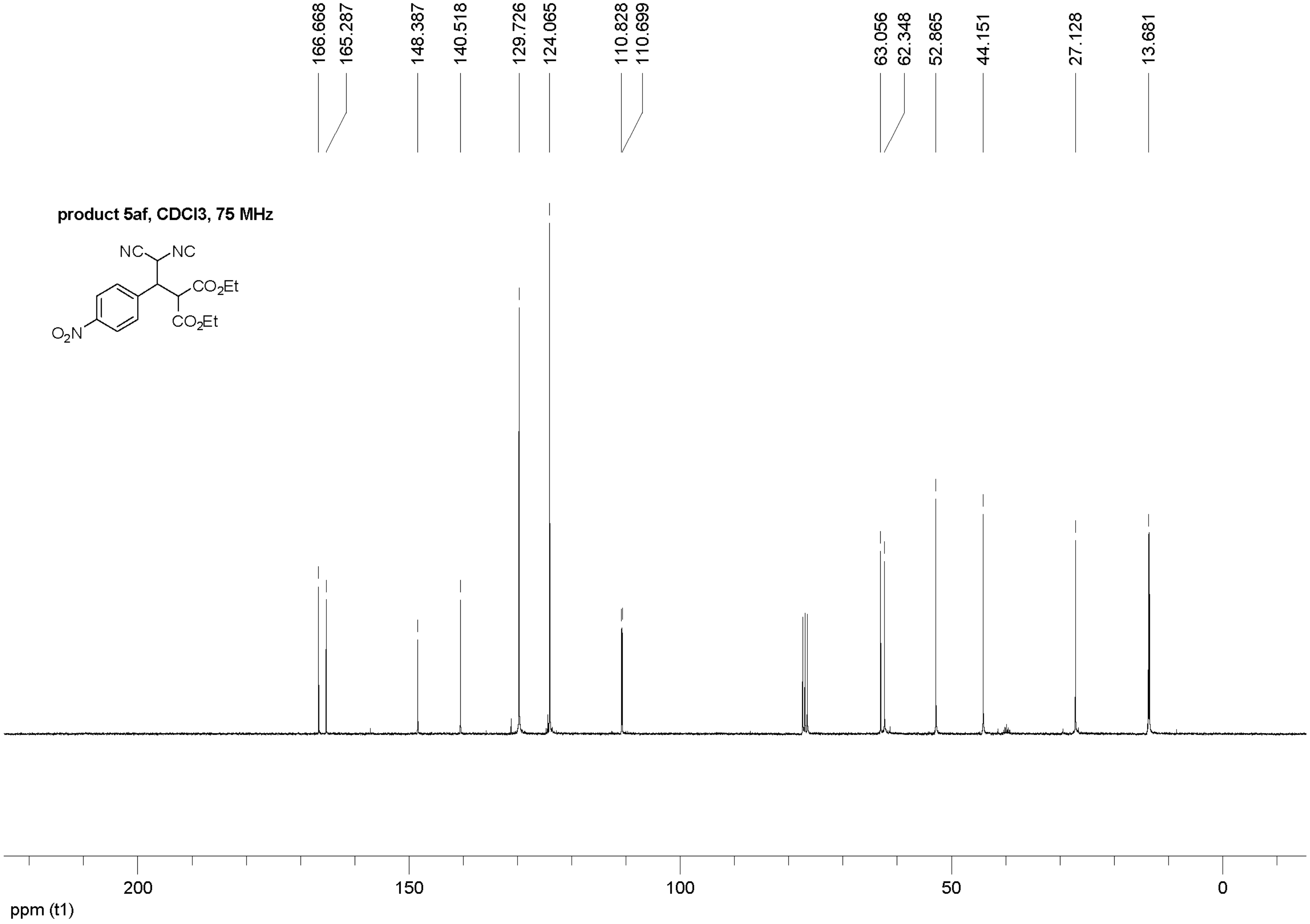
4af-K$^+$ (^{13}C NMR, DMSO-d_6)



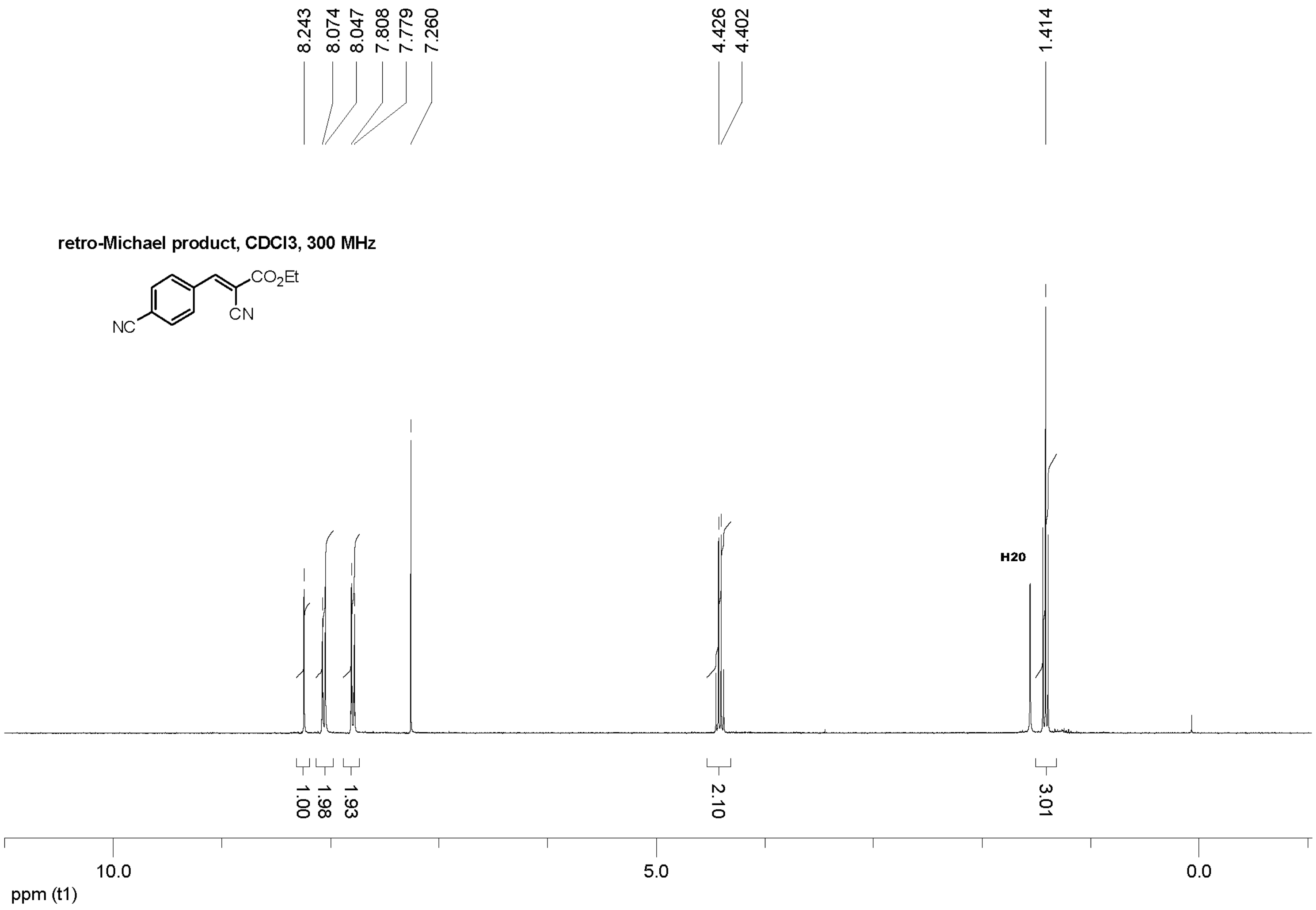
5af (^{1}H NMR, $CDCl_3$)



5af (^{13}C NMR, CDCl$_3$)



retro-Michael product
^{1}H-NMR



retro-Michael product
^{13}C-NMR