– Supporting Information –

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Nucleophilicities of the Anions of Arylacetonitriles and Arylpropionitriles in Dimethyl Sulfoxide

Oliver Kaumanns,[a] *Roland Appel,*[a] *Tadeusz Lemek,*[a,b] *Florian Seeliger,*[a,c] *and Herbert Mayr*[*a]

[a] Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, Butenandtstr. 5-13 (Haus F), 81377 München, Germany

[b] Current address: Department of Chemistry, Agricultural University of Cracow, Cracow, Poland

[c] Current address: Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, USA

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1. General

Materials. 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. Phenylacetonitriles are commercially available compounds and have been used without further purification. Compounds **2a**–**c** were prepared by methylation of the corresponding phenylacetonitriles by using methyl iodide as described in ref.[S1]

NMR spectroscopy. In the ^{1}H and ^{13}C NMR spectra chemical shifts are expressed in ppm and refer to DMSO-d_6 (δ_H 2.50, δ_C 39.4) or to $CDCl_3$ (δ_H 7.26, δ_C 77.0) as internal standard. The coupling constants are in Hz. Abbreviations used are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet).

2. Determination of Rate Constants

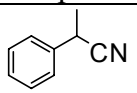
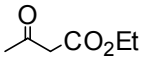
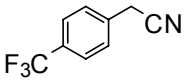
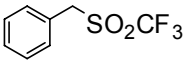
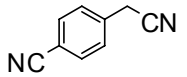
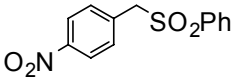
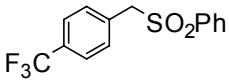
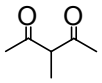
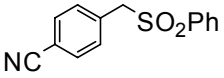
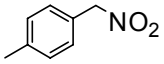
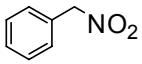
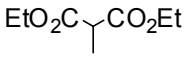
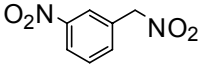
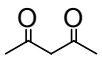
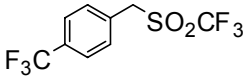
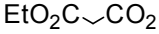
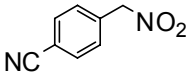
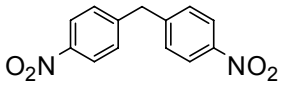
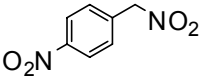
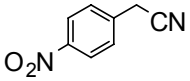
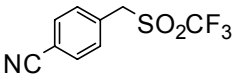
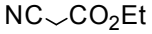
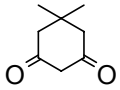
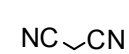
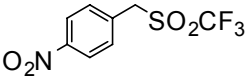
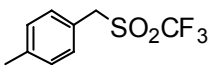
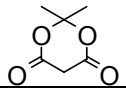
The general method for the determination of the rate constants is described in the experimental part of the paper. The temperature of the solutions was kept constant (20 ± 0.1 °C) during all kinetic experiments by using a circulating bath thermostat.

For fast kinetic experiments ($\tau_{½}$ < 15 s), standard stopped-flow UV-vis-spectrophotometer systems were used in their double mixing mode. Kinetics of slow reactions ($\tau_{½}$ > 15 s) were determined by UV-vis spectrometry using a diode array spectrophotometer which was connected to an insertion probe via fibre optic cables.

Rate constants k_{obs} (s^{-1}) were obtained by fitting the single exponential function $A_t = A_0 \exp(-k_{obs}t) + C$ to the observed time-dependent absorbance of the minor component. Plotting 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 with **1c** and **2c** two stock solutions were used: A solution of electrophiles **3a–u** in DMSO and a solution of the carbanions **1c** and **2c** in DMSO generated by deprotonation of the corresponding CH acid with KO*t*Bu, P_2-*t*Bu, or P_4-*t*Bu or, in case of **2c**, by dissolving the corresponding preformed potassium salt (**2c**-K). Due to their high reactivities and slow decomposition in DMSO solution, the carbanions **1a**,**b** and **2a**,**b** were generated by using the double-mixing mode of conventional stopped-flow instruments. In the first mixing step, solutions of the CH acids (**1a**,**b**)-H or (**2a**,**b**)-H were mixed with solutions of the base to generate the corresponding carbanions. After an age time the thus generated carbanion solutions were mixed with the electrophile solutions in the second mixer. Conditions different from those mentioned here, will be described explicitly in the corresponding tables.

3. Nucleophilicities for Different Carbanions and The Acidities of Their Conjugate CH Acids in DMSO

Table S1: Nucleophilicities *N* for Different Types of Carbanions and the Aciditiy Constants pK_a of their Conjugate CH Acids in DMSO.

Compound	*N*	pK_a	Compound	*N*	pK_a
	29.14	23.00[Bor88]		18.82	14.20[Bor81]
	27.29	18.10[Bor86]		18.67	14.62[Gou03]
	25.11	16.00[Bor88]		18.50	15.80[Bor88a]
	24.30	20.20[Bor88a]		18.38	15.07[Olm80]
	22.60	18.50[Bor88a]		18.31	12.33[Kee79]
	21.54	16.70[Bor94]		18.29	12.20[Bor94]
	21.13	18.70[Bor88d]		18.06	10.04[Kee79]
	20.71	17.20[Olm80]		17.64	13.33[Olm80]
	20.61	16.80[Bor94]		17.33	11.95[Gou03]
	20.22	16.37[Olm80]		16.96	9.31[Kee79]
	19.92	15.10[Bor88b]		16.29	8.62[Kee79]
	19.68	12.30[Bor88]		16.28	10.70[Bor88]
	19.62	13.10[Bor88c]		16.27	11.16[Olm80]
	19.36	11.10[Bor89]		14.49	9.46[Gou03]
	19.35	15.40[Bor88]		13.91	7.33[Arn87]

[Arn87] Arnett, E. M.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 809-812.
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[Bor88a] Bordwell, F. G.; Bausch, M. J.; Branca, J. C.; Harrelson, J. A., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 225-239.
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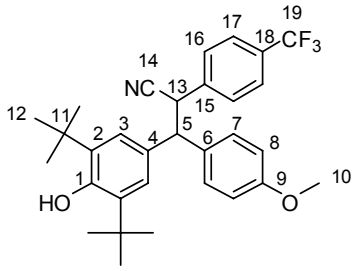
4. Product Studies

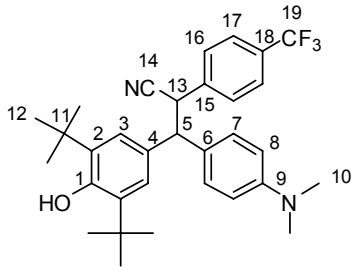
Products 4 from the reactions of the nucleophiles 1a–c with the electrophiles 3c–f

General Method. Compounds (**1a–c**)-H were mixed with 1.0–1.9 equivalents of KO*t*Bu or NaOMe in dry methanol or in methanol/DMSO mixtures. After some minutes the electrophiles **3c**–**f** were added. The reaction mixtures were then stirred for 1 h at ambient temperature. Subsequently aqueous acetic acid solution (1 %) was added. The reaction mixture was then extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure yielded the crude products which were purified by chromatography (SiO_2, *i*hex/EtOAc) and characterized by MS and NMR spectroscopy. Signal assignments are based on additional DEPT, COSY, gHMBC and gHSQC experiments. Diastereomeric ratios (*dr*) were determined on the basis of the integrals in the ^{1}H NMR spectra. The signals of the ^{13}C NMR spectra are given in higher precision because some of the signals of the corresponding diastereomers have very similar chemical shifts.

3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-3-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)-propionitrile (4ad). From **1a**-H (25.0 mg, 135 µmol), KO*t*Bu (22.8 mg, 203 µmol), and **3d** (82.0 mg, 253 µmol) in a 1:2 (v/v) MeOH/DMSO mixture (10.5 mL): 50.0 mg, (98.1 µmol, 73 %); colorless oil (*dr* 1:1.4). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.31, 1.36 (2s, 18 H, 12-H), 3.78, 3.81 (2s, 3 H, 10-H), 4.19, 4.20 (2d, ^3J = 8.9 Hz, ^3J = 7.3 Hz, 1 H, 5-H), 4.40 (d, ^3J = 8.9 Hz, 0.58 H, 13-H), 4.54 (d, ^3J = 7.3 Hz, 0.42 H, 13-H), 5.09, 5.15 (2s, 1 H, OH), 6.79-6.83 (m, 2 H, 3-H, 8-H), 6.88-6.91 (m, 2 H, 3-H, 8-H), 7.13-7.26 (m, 4 H, 7-H, 16-H), 7.49-7.52 ppm (m, 2 H, 17-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 30.10, 30.18 (2q, C-12), 34.26, 34.30 (2s, C-11), 43.58, 43.80 (2d, C-13), 55.23 (q, C-10, both diastereomers), 55.76, 56.24 (2d, C-5), 113.97, 114.08 (2d, C-8), 119.46, 119.67 (2s, C-14), 122.00 (s, C-18, signal for the other diastereomer superimposed), 124.67, 125.37 (2d, C-3), 125.44, 125.48 (2d, C-17), 128.69, 128.77, 128.96, 129.38 (4d, C-7, C-16), 130.23, 130.27 (2q, C-19), 130.28 (s, C-6, signal for the other diastereomer superimposed), 131.73, 132.44 (2s, C-4), 135.71, 135.93 (2s, C-2), 139.29 (s, C-15, signal for the other diastereomer superimposed), 152.82, 153.16 (2s, C-1), 158.58, 158.88 ppm (2s, C-9). HR-MS (ESI) [M – H$^+$]: calcd 508.2458 ($C_{31}H_{33}F_3NO_2^-$); found 508.2461. R_f (*i*hex/EtOAc 4:1) = 0.50.

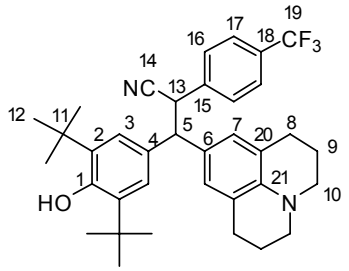


3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-3-(4-(dimethylamino)phenyl)-2-(4-(trifluoromethyl)-phenyl)propionnitrile (4ae). From **1a**-H (30.0 mg, 162 µmol), KO*t*Bu (27.0 mg, 241 µmol), and **3e** (82.0 mg, 243 µmol) in a 1:2 (v/v) MeOH/DMSO mixture (10.5 mL): 68.0 mg (130 µmol, 80 %); orange foam (*dr* 1:1.4). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.31, 1.37 (2s, 18 H, 12-H), 2.92, 2.95 (2s, 6 H, 10-H), 4.13-4.16 (m, 1 H, 5-H), 4.39 (d, ^{3}J = 8.8 Hz, 0.58 H, 13-H), 4.54 (d, ^{3}J = 7.3 Hz, 0.42 H, 13-H), 5.06, 5.12 (2s, 1 H, OH), 6.64, 6.71 (2d, 2 × ^{3}J = 8.6 Hz, 2 H, 8-H), 6.82, 6.92 (2s, 2 H, 3-H), 7.12-7.26 (m, 4 H, 7-H, 16-H), 7.49-7.51 ppm (m, 2 H, 17-H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 30.12, 30.20 (2q, C-12), 34.24, 34.28 (2s, C-11), 40.50 (q, C-10, both diastereomers), 43.76, 44.04 (2d, C-13), 55.84, 56.30 (2d, C-5), 112.52, 112.60 (2d, C-8), 119.67, 119.91 (2s, C-14), 122.94, 122.95 (2s, C-18), 124.67 (d, C-3), 125.31 (d, C-17, signals for the other diastereomer superimposed), 125.35 (d, C-3), 127.30, 128.02 (2s, C-6), 128.56, 128.70, 128.79, 128.95 (4d, C-7, C-16), 129.79 (s, C-4), 130.05, 130.10 (2q, C-19), 130.77 (s, C-4), 135.55, 135.77 (2s, C-2), 139.57, 139.59 (2s, C-15), 149.54, 149.80 (2s, C-9), 152.66, 153.00 ppm (2s, C-1). HR-MS (ESI) [M + H$^+$]: calcd 523.2931 ($C_{32}H_{38}F_3N_2O^+$); found 523.2914. R_f (*i*hex/EtOAc 4:1) = 0.38.

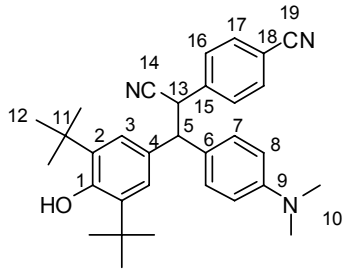


3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-3-(1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-9-yl)-2-(4-(trifluoromethyl)phenyl)propionitrile (**4af).** From **1a**-H (30.0 mg, 162 µmol), KO*t*Bu (27.0 mg, 241 µmol), and **3f** (95.0 mg, 244 µmol) in a 1:2 (v/v) MeOH/DMSO mixture (10.5 mL): 66.0 mg (115 µmol, 71 %); red foam (*dr* 1:1.8). ^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 1.30,

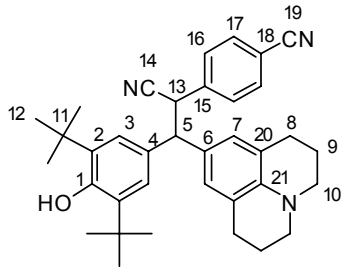
1.37 (2s, 18 H, 12-H), 1.93-2.00 (m, 4 H, 9-H), 2.66-2.78 (m 4 H, 8-H), 3.10-3.14 (m, 4 H, 10-H), 3.98-4.01 (m, 1 H, 5-H), 4.31 (d, ^3J = 9.7 Hz, 0.64 H, 13-H), 4.51 (d, ^3J = 6.6 Hz, 0.35 H, 13-H), 5.03, 5.12 (2s, 1 H, OH), 6.71, 6.76 (2s, 2 H, 7-H), 6.77, 6.90 (2s, 2 H, 3-H), 7.12, 7.15 (2d, 2 × ^3J = 8.0 Hz, 2 H, 16-H), 7.48, 7.51 ppm (2d, 2 × $^3J_{7.48}$ = 8.1 Hz, 2 H, 17-H). ^{13}C-NMR ($CDCl_3$, 151 MHz): δ = 22.04, 22.09 (2t, C-9), 27.68, 27.72 (2t, C-8) 30.08, 30.19 (2q, C-12), 34.20, 34.28 (2s, C-11), 43.96, 44.22 (2d, C-13), 49.91, 49.95 (2t, C-10), 55.11, 55.76 (2d, C-5), 119.73, 120.09 (2s, C-14), 121.50, 121.57 (2s, C-18), 122.94, 122.99 (2s, C-20), 124.69 (d, C-3), 125.18, 125.20 (2d, C-17), 125.52 (d, C-3), 126.35, 126.57 (2s, C-7), 126.67, 127.24 (2s, C-6), 128.66, 128.79 (2d, C-16), 129.58 (s, C-4), 129.96, 129.98 (2q, C-19), 130.71 (s, C-4), 135.40, 135.64 (2s, C-2), 139.78, 139.81 (2s, C-15), 141.92, 142.25 (2s, C-21), 152.57, 152.97 ppm (2s, C-1). HR-MS (ESI) [M + H$^+$]: calcd 575.3244 ($C_{36}H_{42}F_3N_2O^+$); found 575.3229. R_f (*i*hex/EtOAc 4:1) = 0.41.



4-(1-Cyano-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-(dimethylamino)phenyl)ethyl)-benzonitrile (**4be**)**.** From **1b**-H (25.0 mg, 176 µmol), NaOMe (10.0 mg, 185 µmol), and **3e** (59.0 mg, 175 µmol) in MeOH (10 mL): 65.4 mg (136 µmol, 77 %); red foam (*dr* 1:1.2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.34, 1.39 (2s, 18 H, 12-H), 2.91, 2.94 (2s, 6 H, 10-H), 4.12-4.16 (m, 1 H, 5-H), 4.43 (d, ^3J = 8.4 Hz, 0.57 H, 13-H), 4.51 (d, ^3J = 7.9 Hz, 0.47 H, 13-H), 5.10, 5.14 (2s, 1 H, OH), 6.60-6.70 (m, 2 H, 8-H.), 6.89, 6.97 (2s, 2 H, 3-H), 7.05-7.20 (m, 4 H, 7-H, 16-H), 7.51-7.55 ppm (m, 2 H, 17-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 30.15, 30.22 (2q, C-12), 34.26, 34.29 (2s, C-11), 40.40, 40.41 (2q, C-10), 44.01, 44.19 (2d, C-13), 55.84, 56.10 (2d, C-5), 111.76, 111.77 (2s, C-18), 112.43, 112.48 (2d, C-8), 118.19, 118.25 (2s, C-19), 119.35, 119.48 (2s, C-14), 124.54, 125.08 (2d, C-3), 126.84, 127.56 (2s, C-6), 128.53, 128.97 (2d, C-7), 129.12, 129.16 (2d, C-16), 129.78, 130.64 (2s, C-4), 132.07, 132.12 (2d, C-17), 135.69, 135.90 (2s, C-2), 140.84, 140.86 (2s, C-15), 149.54, 149.80 (2d, C-9), 152.72, 153.03 ppm (2s, C-1). HR-MS (ESI) [M + H$^+$]: calcd 480.3010 ($C_{32}H_{38}N_3O^+$); found 480.2995. R_f (*i*hex/EtOAc 4:1) = 0.30.

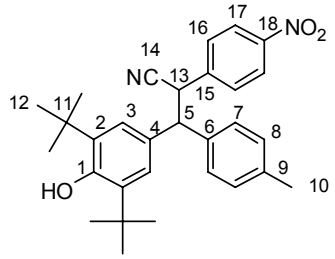


4-(1-Cyano-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]-quinolin-9-yl)ethylbenzonitrile (4bf). From **1b**-H (25.0 mg, 176 µmol), NaOMe (11.0 mg, 204 µmol), and **3f** (69.0 mg, 177 µmol) in MeOH (10 mL): 47.0 mg (88.4 µmol, 50 %); red foam (*dr* 1:1.4). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.32, 1.37 (2s, 18 H, 12-H), 1.91-1.98 (m, 4 H, 9-H), 2.65-2.77 (m, 4 H, 8-H), 3.09-3.13 (m, 4 H, 10-H), 3.96-4.01 (m, 1 H, 5-H), 4.33 (d, ^{3}J = 9.2 Hz, 0.59 H, 13-H), 4.48 (d, ^{3}J = 6.9 Hz, 0.42 H, 13-H), 5.05, 5.12 (2s, 1 H, OH), 6.65, 6.71 (2s, 2 H, 7-H), 6.81, 6.93 (2s, 2 H, 3-H), 7.13, 7.16 (2d, 2 × ^{3}J = 8.1 Hz, 2 H, 16-H), 7.51, 7.54 ppm (2d, 2 × ^{3}J = 8.1 Hz, 2 H, 17-H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 21.98, 22.03 (2t, C-9), 27.68, 27.72 (2t, C-8), 30.14, 30.23 (2q, C-12), 34.25, 34.30 (2s, C-11), 44.26, 44.41 (2d, C-13), 49.87, 49.91 (2t, C-10), 56.06, 56.57 (2d, C-5), 111.64, 111.68 (2s, C-18), 118.23, 118.30 (2s, C-19), 119.41, 119.67 (2s, C-14), 121.50, 121.54 (2s, C-20), 124.58, 125.30 (2d, C-3), 126.26 (s, C-6), 126.30, 126.57 (2d, C-7), 126.83 (s, C-6), 129.10, 129.20 (2d, C-16), 129.58, 130.59 (2s, C-4), 131.96, 132.04 (2d, C-17), 135.54, 135.77 (2s, C-2), 141.07, 141.10 (2s, C-15), 141.96, 142.30 (2s, C-21), 152.66, 153.02 ppm (2s, C-1). HR-MS (ESI) [M + H$^+$]: calcd 532.3322 ($C_{36}H_{42}N_3O^+$); found 532.3310. R_f (*i*hex/EtOAc 4:1) = 0.45.

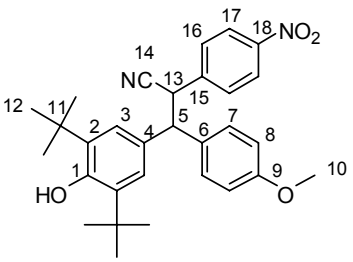


3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-2-(4-nitrophenyl)-3-*p*-tolylpropionitrile (4cc). From **1c**-H (50.0 mg, 308 µmol), NaOMe (18.3 mg, 339 µmol), and **3c** (95.3 mg, 309 µmol) in MeOH (10 mL): 126 mg (268 µmol, 87 %); colorless foam (*dr* 1:1.2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.32, 1.38 (2s, 18 H, 12-H), 2.29, 3.34 (2s, 3 H, 10-H), 4.20-4.24 (m, 1 H, 5-H), 4.52 (d, ^{3}J = 8.7 Hz, 0.52 H, 13-H), 4.59 (d, ^{3}J = 8.1 Hz, 0.45 H, 13-H), 5.13, 5.18 (2s, 1 H, OH), 6.86, 6.98

(2s, 2 H, 3-H), 7.06-7.12 (m, 2 H, 7-H.), 7.14-7.21 (m, 2 H, 8-H.), 7.21-7.27 (m, 2 H, 16-H), 8.09-8.11 ppm (m, 2 H, 17-H.). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 20.98, 21.07 (2q, C-10), 30.11, 30.19 (2q, C-12), 34.27, 34.32 (2s, C-11), 43.46, 43.56 (2d, C-13), 55.19, 55.53 (2d, C-5), 119.12, 119.20 (2s, C-14), 123.58, 123.65 (2d, C-17), 124.57, 125.11 (2d, C-3), 127.68, 128.10 (2d, C-7), 129.22 (s, C-4), 129.29, 129.30 (2d, C-16), 129.41, 129.46 (2d, C-8), 129.89 (s, C-4), 135.84, 136.04 (2s, C-2), 136.19 (s, C-6), 136.85, 137.04 (2s, C-9), 137.34 (s, C-6), 142.40, 142.44 (2s, C-15), 147.42, 147.44 (2s, C-18), 152.95, 153.25 ppm (2s, C-1). HR-MS (ESI) [M – H^+]: calcd 469.2485 ($C_{30}H_{33}N_2O_3^-$); found 469.2490. R_f (*i*hex/EtOAc 4:1) = 0.34.



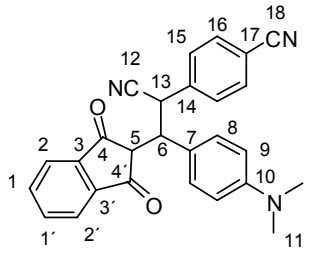
3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-3-(4-methoxyphenyl)-2-(4-nitrophenyl)-propionitrile (4cd). From **1c**-H (25.0 mg, 154 µmol), NaOMe (8.3 mg, 154 µmol), and **3d** (50.0 mg, 154 µmol) in MeOH (10 mL): 71.0 mg (146 µmol, 95 %); yellow foam (*dr* 1:1.2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.32, 1.38 (2s, 18 H, 12-H), 3.76, 3.80 (2s, 3 H, 10-H), 4.19-4.24 (m, 1 H, 5-H), 4.51 (d, ^3J = 8.4 Hz, 0.50 H, 13-H), 4.57 (d, ^3J = 8.1 Hz, 0.47 H, 13-H), 5.13, 5.17 (2s, 1 H, OH), 6.78-6.81 (m, 1 H, 8-H.), 6.85-6.89 (m, 2.20 H, 8-H, 3-H), 6.97 (s, 1 H, 3-H), 7.10-7.13 (m, 1 H, 7-H), 7.19-7.27 (m, 3 H, 7-H, 16-H) 8.07-8.11 ppm (m, 2 H, 17-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 30.15, 30.23 (2q, C-12), 34.32, 34.35 (2s, C-11), 43.64, 43.73 (2d, C-13), 55.22, 55.23 (2q, C-10), 55.82, 56.07 (2d, C-5), 114.07, 114.12 (2d, C-8), 119.13, 119.20 (2s, C-14), 123.61, 123.66 (2d, C-17), 124.55, 125.10 (2d, C-3), 128.95, 129.32, 129.43 (3d, C-7, C-16, peak for the other diastereomer superimposed), 129.35, 130.12 (s, C-4), 131.30, 132.00 (2s, C-6), 135.93, 136.12 (2s, C-2), 142.44, 142.47 (2s, C-15), 147.48, 147.50 (2s, C-18), 152.96, 153.26 (2s, C-1), 158.69, 158.99 ppm (2d, C-9). HR-MS (ESI) [M –H^+]: calcd 485.2435 ($C_{30}H_{33}N_2O_4^-$); found 485.2440. R_f (*i*hex/EtOAc 4:1) = 0.38.



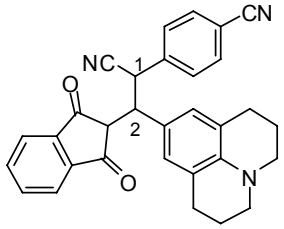
Products 4 from the reactions of the nucleophiles 1b,c with the electrophiles 3h–j

General. Compounds (**1b**,**c**)-H were mixed with KO*t*Bu in dry DMSO. After the addition of the electrophiles **3h-j** the reaction mixture was stirred for 1 h at ambient temperature. After the consecutive addition of water and concentrated aqueous HCl the products were isolated and purified as described separately for each reaction. The products were characterized by MS and NMR spectroscopy. Signal assignments are based on additional DEPT, COSY, gHMBC and gHSQC experiments. Diastereomeric ratios (*dr*) were determined on the basis of the integrals in the ^{1}H NMR spectra. The signals of the ^{13}C NMR spectra are given in higher precision because some of the signals of the corresponding diastereomers have very similar chemical shifts.

4-(1-Cyano-2-(4-(dimethylamino)phenyl)-2-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)ethyl)-benzonitrile (4bi). From **1b**-H (100 mg, 703 µmol), KO*t*Bu (95.0 mg, 847 µmol), and **3i** (195 mg, 703 µmol) in DMSO (6 mL). After the addition of water and hydrochloric acid, the resulting suspension was extracted with dichloromethane. The combined organic layers were washed with H_2O and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure yielded the crude product, which was purified by chromatography (SiO_2, $CHCl_3$/MeOH): 206 mg (491 µmol, 70 %); yellow solid (*dr* 1:1.9). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.75-2.83 (m, 6.41 H, 11-H, 5-H), 3.87 (dd, ^{3}J = 12.1 Hz, ^{3}J = 3.9 Hz, 1 H, 6-H, both diastereomers), 3.93 (d, ^{3}J = 4.0 Hz, 0.35 H, 5-H), 5.01 (d, ^{3}J = 11.8 Hz, 0.35 H, 13-H), 5.17 (d, ^{3}J = 12.1 Hz, 0.65 H, 13-H), 6.26-6.30, 6.49-6.53 (2m, 2 H, 9-H), 6.71-6.75, 7.08-7.12 (2m, 2 H, 8-H), 7.24-7.27 (m, 0.92 H, 15-H), 7.47-7.50 (m, 0.70 H, 16-H), 7.69-7.87 (m, 6.10 H, 1-H, 1-H′, s 2-H or 2-H′, 15-H, 16-H), 7.96-7.99 ppm (m, 0.36 H, 2-H or 2-H′). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 39.98, 40.12 (2q, C-11), 40.20, 40.38 (2d, C-13), 48.69, 49.02 (2d, C-6), 53.65, 56.60 (2d, C-5), 111.96 (d, C-9), 112.10 (s, C-17), 112.37 (d, C-9), 112.93 (s, C-17), 117.97, 118.17 (2s, C-18), 119.15, 119.61 (s, C-12), 120.99, 122.71 (s, C-7), 122.97, 123.17, 123.34 (3d, C-2 und C-2′, one signal superimposed), 129.16 (d, C-16), 129.27, 129.45 (2d, C-8), 129.79 (d, C-16), 132.38, 133.05 (2d, C-15), 135.69, 135.75, 135.80, 135.85 (4d, C-1 und C-1′), 139.84, 140.04 (2s, C-14), 142.34, 142.35, 142.46 (3s, C-3 und C-3′, one signal superimposed), 149.72, 150.15 (2s, C-10), 197.66, 197.90, 199.69, 200.00 ppm (4s, C-4 and C-4′). HR-MS (ESI) [M + H^+]: calcd 420.1707 ($C_{27}H_{22}N_3O_2^+$); found 420.1696. R_f ($CHCl_3$/MeOH 25:1) = 0.81.

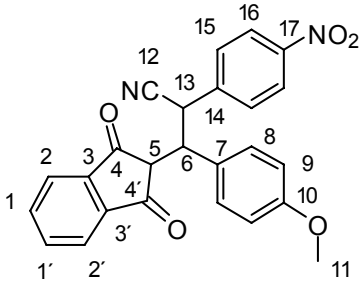


4-(1-Cyano-2-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)-2-(1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin)-9-yl)ethyl)benzonitrile (4bj). From **1b**-H (50.1 mg, 352 µmol), KO*t*Bu (43.4 mg, 387 µmol), and **3j** (117 mg, 355 µmol) in DMSO (10 mL). After the addition of water and conc. hydrochloric acid, the resulting suspension was extracted with ethyl acetate. The combined organic layers were twashed with H_2O and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure yielded the crude product. Attempts to purify the product by chromatography (SiO_2, *i*hex/EtOAc) failed because of partial decomposition. Nevertheless, the characteristic ^{1}H NMR signals for 1-H and HR-MS gave evidence for the formation of **4bj**: red solid (*dr* 1:1.3). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 4.91 (d, ^3J = 11.8 Hz, 0.43 H, 1-H), 5.07 ppm (d, ^3J = 12.1 Hz, 0.58 H, 1-H). HR-MS (ESI) [M + H$^+$]: calcd 472.2019 ($C_{31}H_{26}N_3O_2^+$); found 472.2012.



3-(1,3-Dioxo-2,3-dihydro-1*H*-inden-2-yl)-3-(4-methoxyphenyl)-2-(4-nitrophenyl)propionitrile (4ch). From **1c**-H (50.0 mg, 308 µmol), KO*t*Bu (41.5 mg, 370 µmol), and **3h** (81.5 mg, 308 µmol) in DMSO (6 mL). After the addition of water and conc. hydrochloric acid, a green solid precipitated which was isolated by filtration and washed with H_2O. The purified product precipitated from a chloroform/n-pentane mixture: 93.3 mg (219 µmol, 71 %); pale yellow solid (*dr* 1:1.9). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 2.84 (d, ^3J = 4.0 Hz, 0.62 H, 5-H), 3.59, 3.69 (2s, 3 H, 11-H), 3.92-3.98 (m, 1.35 H, 6-H, 5-H), 5.09 (d, ^3J = 11.8 Hz, 0.35 H, 13-H), 5.25 (d, ^3J = 12.0 Hz, 0.65 H, 13-H), 6.50-6.52, 6.72-6.74 (2m, 2 H, 9-H), 6.83-6.85, 7.18-7.20 (2m, 2 H, 8-H), 7.32-7.33 (m, 0.70 H, 15-H.), 7.70-7.88 (m, 4.90 H, 1-H, 1-H′, 2-H oder 2-H′, 15-H), 7.98 (d, ^3J = 7.5 Hz, 0.36 H, 2-H oder 2-H′) 8.05-8.07, 8.28-8.29 (2m, 2 H, 16-H). ^{13}C NMR ($CDCl_3$, 151

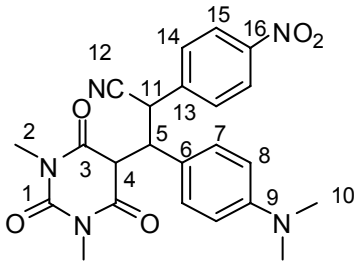
MHz): δ = 39.83, 39.89 (2d, C-13), 48.69, 49.03 (2d, C-6), 53.44 (d, C-5), 54.96, 55.09 (2q, C-11), 56.41 (d, C-5), 114.05, 114.33 (2d, C-9), 118.83, 119.26 (2s, C-12), 123.07, 123.23, 123.30, 123.39 (4d, C-2 und C-2′), 123.92, 124.54 (2d, C-16), 125.89, 127.40 (2s, C-7), 129.37 (d, C-15), 129.75, 129.90 (2d, C-8), 130.07 (d, C-15), 135.89, 135.96, 136.01, 136.07 (4d, C-1 und C-1′), 141.38, 141.51 (2s, C-14), 142.23, 142.24, 142.26, 142.35 (4s, C-3, C-3′), 147.62, 148.18 (2s, C-17), 159.10, 159.49 (2s, C-10), 197.38, 197.59, 199.39, 199.72 (4s, C-4, C-4′). HR-MS (ESI) [M – H^+]: calcd 425.1132 ($C_{25}H_{17}N_2O_5^-$); found 425.1149.



Products 4 from the reactions of the nucleophiles 1c with the electrophiles 3l

3-(1,3-Dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)-3-(4-(dimethylamino)phenyl)-2-(4-nitrophenyl)propionitrile (4cl). After mixing **1c**-H (30.0 mg, 185 µmol) with KO*t*Bu (25.0 mg, 223 µmol) in dry DMSO (5 mL) and subsequent addition of the electrophile **3l** (64.0 mg, 223 µmol), the reaction mixture was stirred for 1.5 h at ambient temperature. Subsequently water and conc. hydrochloric acid were added. The resulting mixture was extracted with ethylacetate, and the combined organic layers were washed with H_2O and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure yielded the crude product, which was purified by chromatography (SiO_2, $CHCl_3$/MeOH). The product was characterized by MS and NMR spectroscopy. Signal assignments are based on additional DEPT, COSY, gHMBC and gHSQC experiments. Diastereomeric ratios (*dr*) were determined on the basis of the integrals in the ^{1}H NMR spectra. The signals of the ^{13}C NMR spectra are given in higher precision because some of the signals of the corresponding diastereomers have very similar chemical shifts: 71.0 mg (158 µmol, 85 %); orange solid (*dr* 1:1). ^{1}H NMR ($CDCl_3$, 600 MHz,): δ = 2.85, 2.95 (2s, 6 H, 10-H), 3.06, 3.08 (2s, 3 H, 2-H), 3.13 (d, ^3J = 3.1 Hz 0.52 H, 4-H), 3.14, 3.26 (2s, 3 H, 2-H), 3.96, 3.98 (2t, ^3J = 3.1 Hz, 1 H, 5-H), 4.31 (d, ^3J = 3.6 Hz, 0.50 H, 4-H), 4.93 (d, ^3J = 12.1 Hz, 0.52 H, 11-H), 5.09 (d, ^3J = 12.3 Hz, 0.52 H, 11-H), 6.37-6.40, 6.60-6.62 (2m, 2 H, 8-H), 6.64-6.70, 6.95-6.98 (2m, 2 H, 7-

H), 7.33-7.35, 7.92-7.94 (2m, 2 H, 14-H), 8.04-8.06, 8.32-3.35 ppm (2m, 2 H, 15-H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 28.20, 28.35 (2q, C-2), 28.47, 28.53 (2q, C-2), 39.48 (d, C-11), 39.94, 40.11 (2q, C-10), 40.18 (d, C-11), 49.45 (d, C-4), 52.31, 52.39 (2d, C-5), 53.01 (d, C-4), 111.93, 112.29 (2d, C-8), 118.45 (s, C-6), 118.70, 119.34 (2s, C-12), 120.20 (s, C-6), 123.90, 124.62 (2d, C-15), 128.16, 128.54 (2d, C-7), 129.48, 130.21 (2d, C-14), 141.28, 141.41 (2s, C-13), 147.58, 148.25 (2s, C-16), 150.35, 150.36 (2s, C-9), 150.59, 150.85 (2s, C-1), 166.93, 167.04, 167.19 ppm (3s, C-3, C-3′, signal for the other diastereomer superimposed). HR-MS (ESI) [M + H^+]: calcd 450.1772 ($C_{23}H_{24}N_5O_5^+$); found 450.1758. R_f ($CHCl_3$/MeOH 10:1): 0.17.

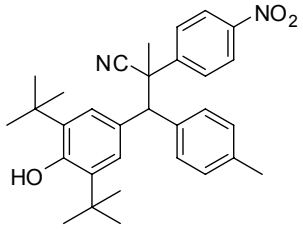


Products 5 from the reactions of the nucleophile 2c

3-(3,5-Di-*tert*.butyl-4-hydroxyphenyl)-2-methyl-2-(4-nitrophenyl)-3-*p*-tolylpropionitrile (5cc). After mixing **2c**-H (63.0 mg, 0.36 mmol) with KO*t*Bu (42.0 mg, 0.37 mmol) in DMSO (5 mL) and subsequent addition of **3c** (122 mg, 0.40 mmol), the reaction mixture was stirred for 30 min at ambient temperature. Then the reaction mixture was poured into cold aqueous acetic acid (1 %) and extracted with CH_2Cl_2. The combined organic layers were washed with water and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure yielded the crude product, which was purified by chromatography (SiO_2, hexane/EtOAc 15:1, R_f = 0.5): 75 mg (0.15 mmol, 42 %; colorless solid (dr 1:1.1).

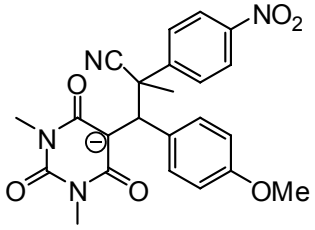
Major diastereomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.45 (s, 18 H, *t*butyl), 1.72 (s, 3 H, CH_3), 2.02 (s, 3 H, CH_3), 4.04 (s, 1 H, CH), 5.20 (s, 1 H, OH), 6.85 (s, 2 H, CH_{ar}), 6.93 (d, ^3J = 8.0 H, 2 H, CH_{ar}), 7.10 (d, ^3J = 8.0 H, 2 H, CH_{ar}), 7.55 (d, ^3J = 8.8 H, 2 H, CH_{ar}), 8.10 ppm (d, ^3J = 8.8 H, 2 H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.9 (q, CH_3), 26.8 (q, CH_3), 30.3 (s, $C(CH_3)_3$), 34.5 (s, $C(CH_3)_3$), 47.7 (s, CR_4), 61.9 (d, CH), 122.5 (s, CN), 123.6 (d, CH_{ar}), 125.6 (d, CH_{ar}), 127.5 (d, CH_{ar}), 128.5 (d, CH_{ar}), 129.1 (d, CH_{ar}), 135.9 (s, CH_{ar}), 136.4 (s), 136.7 (s), 147.0 (s), 147.6 (s), 152.8 ppm (s).

Minor diastereomer: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.26 (s, 18 H, *t*butyl), 1.75 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 3.95 (s, 1 H, CH), 5.04 (s, 1 H, OH), 7.21 (d, ^3J = 8.0 H, 2 H, CH_{ar}), 7.40 (s, 2 H, CH_{ar}),7.43 (d, ^3J = 8.8 H, 2 H, CH_{ar}), 7.58 (d, ^3J = 8.0 H, 2 H, CH_{ar}), 8.11 ppm (d, ^3J = 8.8 H, 2 H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.0 (q, CH_3), 28.1 (q, CH_3), 30.1 (s, $C(CH_3)_3$), 34.2 (s, $C(CH_3)_3$), 47.9 (s, CR_4), 62.6 (d, CH), 122.4 (s, CN), 123.3 (d, CH_{ar}), 125.9 (d, CH_{ar}), 127.4 (d, CH_{ar}), 128.5 (d, CH_{ar}), 129.6 (d, CH_{ar}), 136.3 (s, CH_{ar}), 137.4 (s), 137.4 (s), 147.0 (s), 147.9 (s), 153.3 ppm (s). HR-MS (EI): calcd 484.2798 ($C_{31}H_{37}N_2O_3$); found 485.2928.



3-(1,3-Dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)-3-(4-methoxyphenyl)-2-methyl-2-(4-nitrophenyl)propionitrile anion (5ck). In an NMR tube **2c**-K (10.0 mg, 46.7 μmol) was dissolved in d_6-DMSO (0.7 mL). After the addition of **3k** (10.6 mg, 38.6 μmol) the products were analyzed by NMR spectroscopy without further work up: **5ck** as a mixture of diastereomers (7:4). ^{1}H NMR ($CDCl_3$, 200 MHz), major diastereomer: δ = 1.63 (s, 3 H, CH_3), 2.87 (s, 6 H, NCH_3), 3.72 (s, 3 H, OCH_3), 4.59 (s, 1 H, CH), 6.79 (d, ^3J = 8.8 Hz, 2 H, Ar-H), 7.64 (d, ^3J = 8.8 Hz, 2 H, Ar-H), 7.73 (d, ^3J = 8.8 Hz, 2 H, Ar-H) 8.09 ppm (d, ^3J = 8.8 Hz, 2 H, Ar-H).

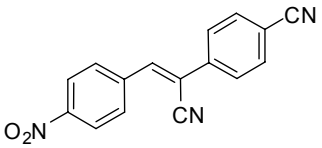
Minor diastereomer: δ = 1.70 (s, 3 H, CH_3), 3.02 (s , br., 3 H, NCH_3), 3.08 (s, br., 3 H, NCH_3), 3.64 (s, 3 H, OCH_3), 4.64 (s, 1 H, CH), 6.60 (d, ^3J = 8.8 Hz, 2 H, Ar-H), 7.20 (d, ^3J = 8.8 Hz, 2 H, Ar-H), 7.57 (d, ^3J = 8.8 Hz, 2 H, Ar-H) 8.17 ppm (d, ^3J = 8.8 Hz, 2 H, Ar-H).



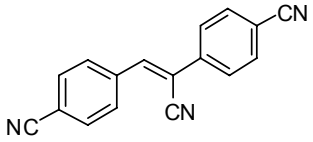
Products 6 from reactions of nucleophiles 1b,c with electrophile 3m–u

General. Equimolar amounts of NaOMe and CH-acids (**1b**,**c**)-H were dissolved in dry MeOH (5 mL). Subsequently electrophiles **3** (1 equiv.) were added. After stirring for 5–10 min at ambient temperature the resulting precipitates were isolated by filtration, washed with MeOH, and dried under reduced pressure to yield the products **6**. NMR signal assignments were based on additional DEPT, gHMBC and gHSQC experiments.

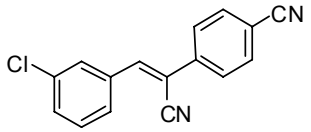
4-(1-Cyano-2-(4-nitrophenyl)-vinyl)benzonitrile (6bm). From **1b**-H (114 mg, 0.80 mmol) and **3m** (234 mg, 0.80 mmol): 91 mg (0.33 mmol, 41 %); colorless solid; mp 212.9-213.7 °C (ref.[S2]: mp 212 °C). ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 7.99-8.05 (m, 4 H, CH_{ar}), 8.17 (d, ^{3}J = 8.8 Hz, 2 H, CH_{ar}), 8.39-8.42 ppm (m, 3 H, CH_{ar} and C=CH). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 112.1 (s), 112.6 (s), 116.5 (s), 118.2 (s), 124.0 (d, CH_{ar}), 126.9 (d, CH_{ar}), 130.4 (d, CH_{ar}), 132.1 (d, CH_{ar}), 133.1 (d, CH_{ar}), 137.4 (s), 139.4 (s), 143.3 (d, C=CH), 148.1 ppm (s). MS (EI) m/z (%) = 276 (16), 275 (100) [M^+], 229 (28), 228 (26), 202 (14), 190 (20), 175 (10). HR-MS: calcd 275.0689 ($C_{16}H_9N_3O_2$); found 275.0692.



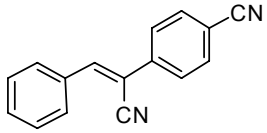
4, 4´-(1-Cyanoethene-1,2-diyl)dibenzonitrile (6bn). From **1b**-H (81 mg, 0.57 mmol) and **3n** **(**170 mg, 0.62 mmol): 109 mg (0.43 mmol, 75 %); colorless solid; mp 303–304 °C (dec.) (ref.[S3]: mp 302-303 °C). ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 7.98-8.06 (m, 6 H, CH_{ar}), 8.09-8.12 (m, 2 H, CH_{ar}), 8.35 ppm (s, 1 H, C=CH). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 112.0 (s), 112.8 (s), 116.6 (s), 118.2 (s), 126.8 (d, CH_{ar}), 129.8 (d, CH_{ar}), 132.8 (d, CH_{ar}), 133.0 (d, CH_{ar}), 137.6 (s), 143.8 ppm (d, C=CH). MS (EI) m/z (%) = 256 (33), 255 (100) [M^+], 254 (82), 228 (39), 215 (63), 200 (14). HR-MS: calcd 255.0796 ($C_{17}H_9N_3$); found 255.0791.



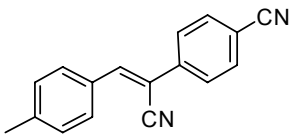
4-(2-(3-Chloro-phenyl)-1-cyanovinyl)benzonitrile (6bo). From **1b**-H (146 mg, 1.03 mmol) and **3o** (291 mg, 1.03 mmol): 121 mg (0.46 mmol, 45 %); colorless solid; mp 196.9-197.5 °C (Lit. ref.[S2]: mp 195-195.5 °C). ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 7.60-7.62 (m, 2 H, CH_{ar}), 7.95-8.02 (m, 6 H, CH_{ar}), 8.25 ppm (s, C=CH). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 110.2 (s), 111.5 (s), 116.6 (s), 118.0 (s), 126.4 (d, CH_{ar}), 127.5 (d CH_{ar}), 128.8 (d, CH_{ar}), 130.6 (d, 2 × CH_{ar}), 132.8 (d, CH_{ar}), 133.3 (s), 135.0 (s), 137.5 (s), 143.8 ppm (d, C=CH). MS (EI), *m*/*z* (%): 266 (24), 264 (73) [M^+], 229 (100), 202 (18), 201 (18), 100 (15). HR-MS: calcd 264.0448 ($C_{16}H_9{}^{35}ClN_2$); found 264.0436.



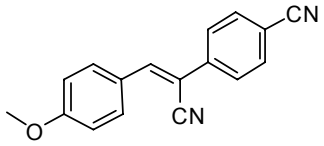
4-(1-Cyano-2-phenylvinyl)benzonitrile (6bp). From **1b**-H (99 mg, 0.70 mmol) and **3p** (172 mg, 0.69 mmol): 61 mg (0.26 mmol, 38 %); colorless solid; mp 146.0-146.5 °C (ref.[S2]: mp 144.5-145.5 °C). ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 7.56-7.58 (m, 3 H, CH_{ar}), 7.96-8.01 (m, 6 H, CH_{ar}), 8.26 ppm (s, 1 H, C=CH). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 108.7 (s), 111.4 (s), 117.2 (s), 118.3 (s), 126.5 (d, CH_{ar}), 129.0 (d, CH_{ar}), 129.4 (d, CH_{ar}), 131.2 (s), 133.0 (d, CH_{ar}), 133.2 (d, CH_{ar}), 138.1 (s), 145.8 ppm (s, C=CH). MS (EI), *m*/*z* (%): 231 (15), 230 (100) [M^+], 229 (55) [M - H^+], 215 (18), 202 (11), 190 (16).



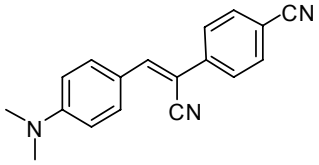
4-(1-Cyano-2-*p*-tolylvinyl)benzonitrile (6bq). From **1b**-H (98 mg, 0.69 mmol) and **3q** (182 mg, 0.69 mmol): 105 mg (0.43 mmol, 62 %); colorless solid; mp 172.8-173.8 °C. ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 2.39 (s, CH_3), 7.38 (d, ^{3}J = 8.2 Hz, 2 H, CH_{ar}), 7.89 (d, ^{3}J = 8.2 Hz, 2 H, CH_{ar}), 7.93-7.99 (m, 4 H, CH_{ar}), 8.20 ppm (s, C=CH). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 21.1 (q, CH_3), 107.4 (s), 111.1 (s), 117.4 (s), 118.3 (s), 126.3 (d, 2 × CH_{ar}), 129.5 (d, 2 × CH_{ar}), 130.5 (s), 132.9 (d, CH_{ar}), 138.3 (s), 141.7 (s), 145.7 ppm (d, C=CH). MS (EI), *m*/*z* (%): 245 (15), 244 (100) [M^+], 229 (69). HR-MS: calcd 244.0995 ($C_{17}H_{12}N_2$), found 244.0999.



4-(1-Cyano-2-(4-methoxyphenyl)vinyl)benzonitrile (6br). From **1b**-H (72 mg, 0.51 mmol) and **3r** (141 mg, 0.51 mmol): 60 mg (0.23 mmol, 45 %); yellow solid; mp 161.8-162.6 C (ref.[S4]: 161-162 °C). ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 3.86 (OCH_3), 7.14 (d, ^{3}J = 8.9 Hz, 2 H, CH_{ar}), 7.91-8.01 (m, 6 H, CH_{ar}), 8.17 ppm (s, C=CH). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 55.4 (q, OCH_3), 105.2 (s), 110.6 (s), 114.6 (d, CH_{ar}), 117.7 (s), 118.4 (s), 125.7 (s), 126.1 (d, CH_{ar}), 131.6 (d, CH_{ar}), 132.9 (d, CH_{ar}), 138.6 (s), 145.2 (d, C=CH), 161.7 ppm (s). MS (EI), *m*/*z* (%): 261 (24), 260 (100) [M^+], 215 (12), 190 (41). HR-MS: calcd 260.0945 ($C_{17}H_{12}N_2O$); found 260.0937.

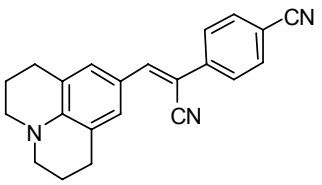


4-(1-Cyano-2-(4-(dimethylamino)phenyl)vinyl)benzonitrile (6bs). From **1b**-H (142 mg, 1.00 mmol) and **3s** (253 mg, 0.87 mmol): 191 mg (0.70 mmol, 80 %); yellow solid; mp 208.5-209.1 °C (ref.[S5] 205 °C). ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 3.05 (s, 6 H, $N(CH_3)_2$), 6.83 (d, ^{3}J = 9.2 Hz, 2 H,), 7.84-7.94 (m, 6 H, C-H_{ar}), 8.02 ppm (s, HC=C). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 40.0 (t, $N(\mathbf{C}H_3)_2$), 100.5 (s), 110.1 (s), 112.1 (d, CH_{ar}), 119.1 (s), 119.2 (s), 120.8 (s), 125.9 (d, CH_{ar}), 132.3 (d, CH_{ar}), 133.3 (d, CH_{ar}), 140.0 (s), 145.9 (d, CH_{ar}, H**C**=C), 152.7 ppm (s). MS (EI), *m*/*z* (%): 274 (15), 273 (100) [M^+], 272 (61), 229 (9). HR-MS: calcd 273.1261 ($C_{18}H_{15}N_3$); found 273.1254.

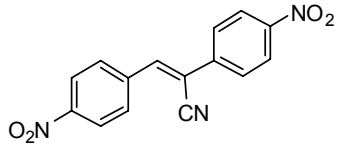


4-(1-Cyano-2-(1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinolin-9-yl)vinyl)benzonitrile (6bu). From **1b**-H (123 mg, 0.87 mmol) and **3u** (343 mg, 1.00 mmol): 255 mg (0.78 mmol, 90 %); orange solid; mp 164.0-164.5 °C. ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 1.88 (quint, ^{3}J = 6.0 Hz, 4 H, $NCH_2C\mathbf{H_2}CH_2$), 2.69 (t, ^{3}J = 6.0 Hz, 4 H, $NCH_2CH_2C\mathbf{H_2}$), 3.29 (t, ^{3}J = 6.0 Hz, 4 H, $NC\mathbf{H_2}CH_2CH_2$), 7.50 (s, 2 H, $C_{ar(jul)}$), 7.79-7.90 ppm (m, 5 H, C_{ar}). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 20.7 (t, $NCH_2\mathbf{C}H_2CH_2$), 27.1 (t, $NCH_2CH_2\mathbf{C}H_2$), 49.2 (t, $N\mathbf{C}H_2CH_2CH_2$), 98.0 (s), 109.1 (s), 119.1 (s), 120.2. (s), 125.0 (d, CH_{ar}), 129.4 (d, CH_{ar}), 132.7 (d, CH_{ar}), 139.8 (s), 145.2

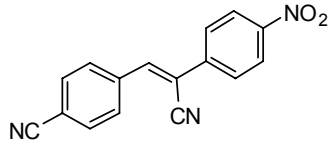
(d, H**C**=C), 145.6 ppm (s). MS (EI), *m*/*z* (%): 326 (22), 325 (100) [M^+], 322 (10). HR-MS: calcd 325.1574 ($C_{22}H_{19}N_3$); found 325.1561.



2,3-Bis-(4-nitrophenyl)acrylonitrile (6cm). From **1c**-H (144 mg, 0.89 mmol) and **3m** (260 mg, 0.89 mmol): 80 mg (0.27 mmol, 30 %); brown solid; mp 214.2-214.9 °C (ref.[S2]: 214-215 °C). ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 8.09 (d, ^3J = 9.0 Hz, 2 H, CH_{ar}), 8.19 (d, ^3J = 8.8 Hz, 2 H, CH_{ar}), 8.38 (d, ^3J = 9.0 Hz, 2 H, CH_{ar}), 8.41 (d, ^3J = 8.8 Hz, 2 H, CH_{ar}), 8.46 (s, 1 H, C=CH). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 112.2 (s), 116.6 (s), 124.0 (d, 2 × CH_{ar}), 124.3 d, 2 × CH_{ar}), 127.4 (d, 2 × CH_{ar}), 130.5 (d, 2 × CH_{ar}), 139.2, 139.3 (2 × s), 144.0 (d, C=CH), 147.8 (s), 148.2 (s). MS (EI), *m*/*z* (%): 296 (18), 295 (100) [M^+], 203 (26), 190 (25); HR-MS: calcd 295.0588 ($C_{15}H_9N_3O_4$); found 295.0580.

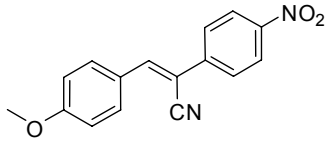


4-(2-Cyano-2-(4-nitrophenyl)vinyl)benzonitrile (6cn). From **1c**-H (124 mg, 0.76 mmol) and **3n** (204 mg, 0.75 mmol): 120 mg (0.44 mmol, 59 %); green solid; mp 134.0-135.1 °C. ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 8.04-8.13 (m, 6 H, CH_{ar}), 8.37-8.40 ppm (m, 3 H, CH_{ar}, C=CH). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 111.6 (s), 112.9 (s), 116.6 (s), 118.2 (s), 124.3 (d, CH_{ar}), 127.3 (d, CH_{ar}), 129.9 (d, CH_{ar}), 132.8 (d, CH_{ar}), 137.5 (s), 139.3 (s), 144.4 (d, C=CH), 147.7 ppm (s). MS (EI), *m*/*z* (%): 276 (15), 275 (100) [M^+], 228 (27), 201 (15). HR-MS: calcd 275.0689 ($C_{16}H_9N_3O_2$); found 275.0675.

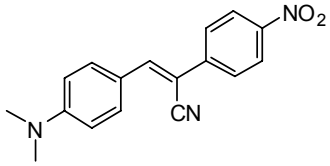


3-(4-Methyoxyphenyl)-2-(4-nitrophenyl)acrylonitrile (6cr). From **1c**-H (150 mg, 0.93 mmol) and **3r** (257 mg, 0.92 mmol): 116 mg (0.41 mmol, 45 %); yellow solid; mp 160.8-161.4 C (ref.[S2]: 162-163 °C). ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 3.86 (s, 3 H, OCH_3); 7.14 (d, ^3J = 9.0 Hz, 2 H, CH_{ar}), 7.98-8.03 (m, 3 H, CH_{ar}), 8.22 (s, 1 H, HC=C), 8.33 ppm (d, ^3J = 9.0 Hz, 2 H, CH_{ar}). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 55.5 (q, OCH_3), 104.8 (s), 114.6 (d, CH_{ar}), 117.7 (s), 124.2 (d,

CH_{ar}), 125.7 (s), 126.4 (d, CH_{ar}), 131.8 (d, CH_{ar}), 140.5 (s), 145.9 (s), 146.9 (d, H**C**=C), 161.8 ppm (s). MS (EI), *m*/*z* (%): 281 (17), 280 (100) [M^+], 189 (24). HR-MS: calcd 280.0843 ($C_{16}H_{12}N_2O_3$); found 280.0848.

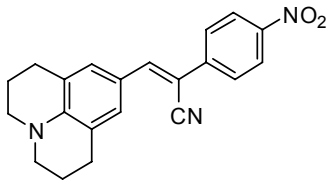


3-(4-(Dimethylamino)phenyl)-2-(4-nitrophenyl)acrylonitrile (6cs). From **1c**-H (162 mg, 1.00 mmol) and **3s** (291 mg, 1.00 mmol): 200 mg (0.68 mmol, 68 %); dark red solid; mp 250.7-251.5 °C (ref.[S6]: 245-246 °C). ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 3.06 (s, 6 H, NMe_2), 6.85 (d, ^3J = 9.0 Hz, 2 H, CH_{ar}), 7.94 (d, ^3J = 7.2 Hz, 2 H, CH_{ar}), 7.96 (d, ^3J = 7.2 Hz, 2 H, CH_{ar}), 8.09 (s, HC=C), 8.30 (d, ^3J = 8.9 Hz, 2 H, CH_{ar}) (in agreement with ref. [S7]). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 39.8 (q, $N(CH_3)_2$), 99.5 (s), 111.6 (d, CH_{ar}), 118.7 (s), 120.2 (s), 124.2 (d, CH_{ar}), 125.6 (d, CH_{ar}), 132.0 (d, CH_{ar}), 141.6 (s), 146.1 (s), 146.1 (d, CH_{ar}, H**C**=C), 152.3 (s). HR-MS (EI): calcd 293.1159 ($C_{17}H_{15}N_3O_2$); found 293.1157.



3-(1,2,3,5,6,7-Hexahydropyrido[3,2,1-*ij*]quinolin-9-yl)-2-(4-nitrophenyl)acrylonitrile (6cu). From **1c**-H (108 mg, 0.67 mmol) and **3u** (228 mg, 0.66 mmol): 108 mg (0.41 mmol, 62 %); purple solid; mp 235.3 °C (dec).

^{1}H NMR (d_6-DMSO, 400 MHz): δ = 1.89 (quint, ^3J = 6.2 Hz, 4 H, $NCH_2C\mathbf{H_2}CH_2$), 2.70 (t, ^3J = 6.2 Hz, 4 H, $NCH_2CH_2C\mathbf{H_2}$), 3.31 (t, ^3J = 6.2 Hz, 4 H, $NC\mathbf{H_2}CH_2CH_2$), 7.54 (s, 2 H, $CH_{ar(jul)}$), 7.87-7.92 (m, 3 H, HC=C, 17-H, 21-H), 8.26 (d, ^3J = 9.1 Hz, 2 H, 18-H, 20-H). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 20.7 (t, $NCH_2\mathbf{C}H_2CH_2$), 27.1 (t, $NCH_2CH_2\mathbf{C}H_2$), 49.2 (t, $N\mathbf{C}H_2CH_2CH_2$), 97.4 (s), 119.1 (s), 120.3 (d, $C_{ar(Jul)}$), 124.2 (d, CH_{ar}), 125.1 (d, CH_{ar}), 129.6 (s), 142.0 (s), 145.6 (s), 145.9 (d, H**C**=C). HR-MS: calcd 345.1477 ($C_{21}H_{19}N_3O_2$); found 345.1472.



5. Deprotonation experiments

The formation of the carbanions **1a**–**c** and **2a** from their conjugate CH acids (**1a**–**c**)-H and **2a**-H, respectively, were recorded by using diode array UV-Vis spectrometers. The temperature during all experiments was kept constant by using a circulating bath (20.0 ± 0.02 °C). The CH acids (**1a**–**c**)-H and **2a**-H were dissolved in DMSO and subsequently treated with various amounts of KO*t*Bu or phosphazene base P_4-*t*Bu (dissolved in DMSO).

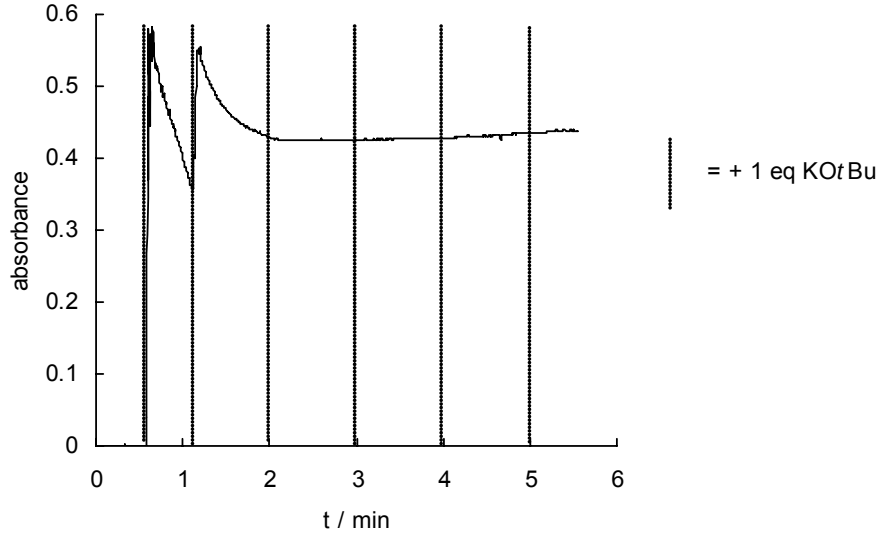


Figure S1: Deprotonation experiment with *p*-(trifluoromethyl)-phenyl-acetonitrile **1a**-H (n = 1.35×10^{-6} mol) in DMSO at 20°C (deprotonated with KO*t*Bu, λ = 360 nm).

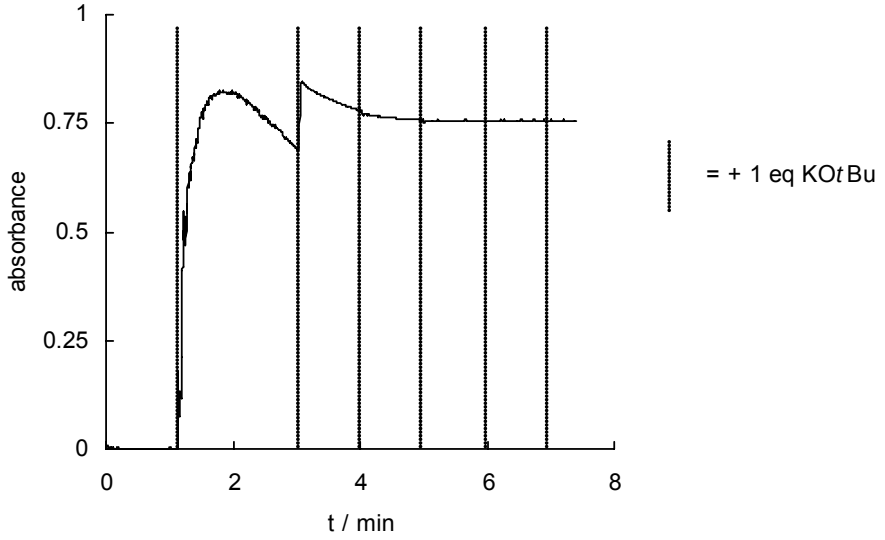


Figure S2: Deprotonation experiment with *p*-cyano-phenyl-acetonitrile **1b**-H (n = 1.31×10^{-6} mol) in DMSO at 20°C (deprotonated with KO*t*Bu, λ = 390 nm).

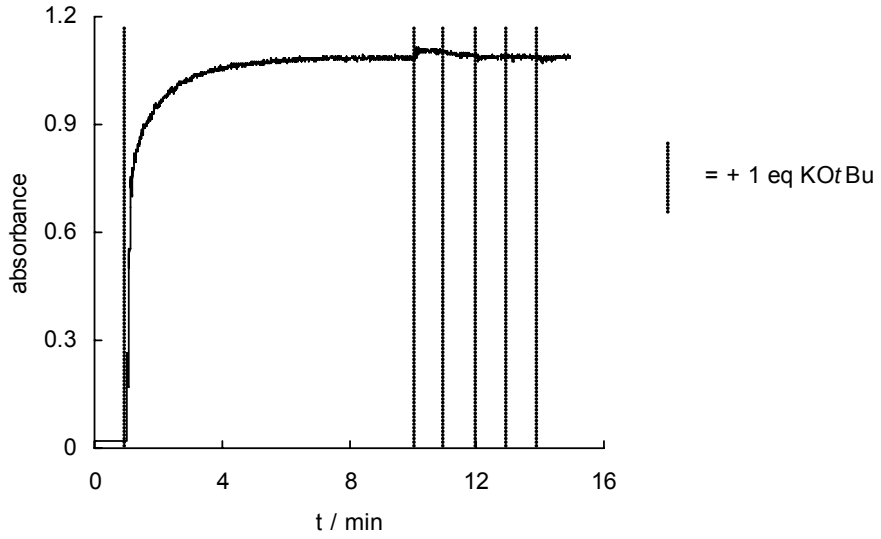


Figure S3: Deprotonation experiment with *p*-nitro-phenyl-acetonitrile **1c**-H n = 1.52 × 10^{-6} mol) in DMSO at 20°C (deprotonated with KO*t*Bu, λ = 540 nm).

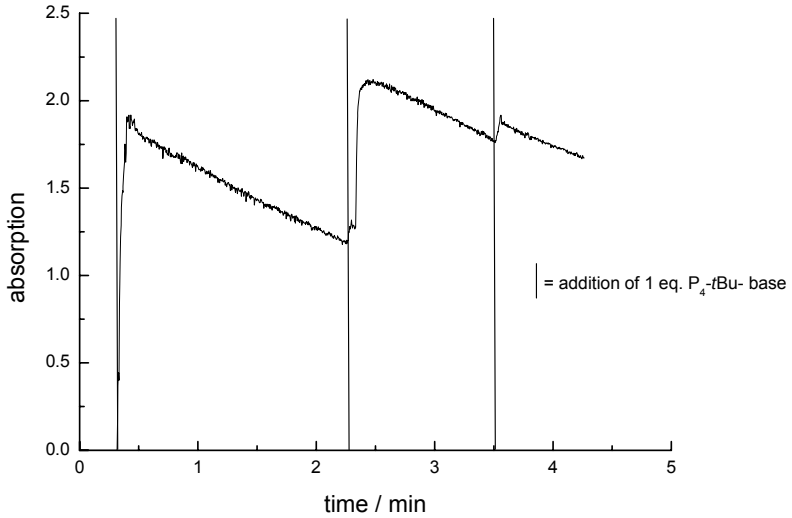


Figure S4: Deprotonation experiment of phenyl propionitrile **2a**-H in DMSO (with phosphazene base P_4-*t*Bu, λ = 354 nm, c_0 (**2a**-H) = 5.3 × 10^{-5} mol L^{-1}).

The influence of KO*t*Bu on the first order rate constanst k_{obs} for the reactions of electrophiles **3e** with carbanion **2b** and of **3s** with **2a** was investigated in DMSO at 20 °C. The concentrations for the electrophiles **3e**, **3s**, and for the CH acids **2b**-H and **2a**-H were kept constant throughout the reactions. The influence of KO*t*Bu was investigated by changing the concentration of base, which is necessary for the generation of the carbanions **2a** and **2b**.

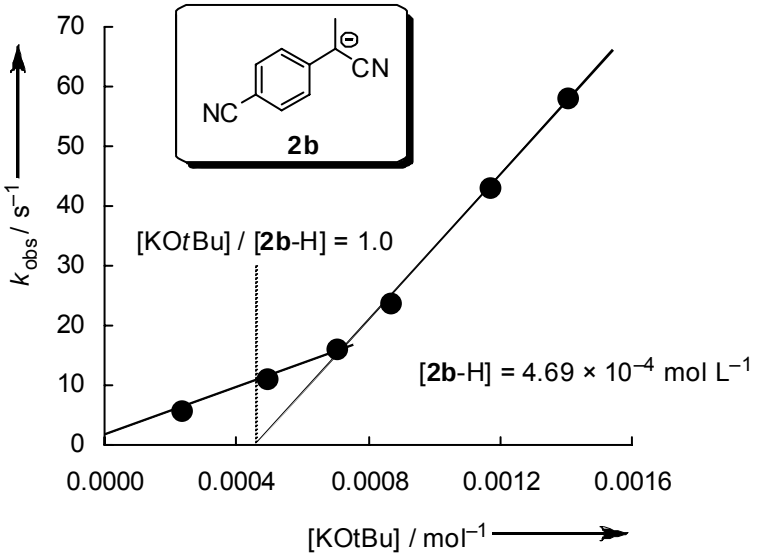


Figure S5: Plot of the first-order rate constants k_{obs} for the reactions of electrophile **3e** (c_0 = 2.00 × 10^{-5} mol L^{-1}) with the nucleophile **2b** against the concentration of KO*t*Bu used for the deprotonation of **2b**–H (c_0 = 4.69 × 10^{-3} mol L^{-1}).

Table S2: First Order Rate Constants for the Reaction of the Electrophile **3s** (c_0 = 2.00 × 10^{-5} mol L^{-1}) with Carbanion **2b**, Generated from **2b**–H (c_0 = 4.69 × 10^{-3} mol L^{-1}) with Various Amounts of KO*t*Bu in DMSO at 20 °C.

Entry	[KO*t*Bu] / mol L^{-1}	Equivalents [KO*t*Bu]/[**2b**–H]	k_{obs} / s^{-1}
1	2.35 × 10^{-4}	0.50	5.78
2	4.93 × 10^{-4}	1.05	11.00
3	7.04 × 10^{-4}	1.50	15.97
4	8.68 × 10^{-4}	1.85	23.70
5	1.17 × 10^{-3}	2.50	42.93
6	1.41 × 10^{-3}	3.00	58.10

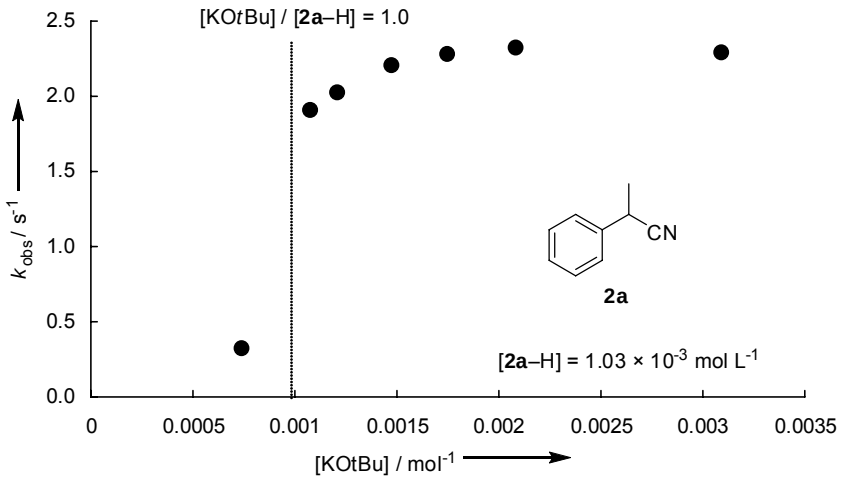


Figure S6: Plot of the first order rate constant k_{obs} for the reactions of electrophile **3s** (c_0 = 3.23 × 10^{-5} mol L^{-1}) with carbanion **2a** versus the concentration of KO*t*Bu which has been used to generate **2a** from its corresponding CH acid **2a**–H (c_0 = 1.03 × 10^{-3} mol L^{-1}) in DMSO at 20°C.

Table S3: First Order Rate Constants for the Reaction of the Electrophile **3s** (c_0 = 3.23 × 10^{-5} mol L^{-1}) with Carbanion **2a**, Generated from **2a**-H (c_0 = 1.03 × 10^{-3} mol L^{-1}) with Various Amounts of KO*t*Bu in DMSO at 20 °C.

Entry	[KOtBu] / mol L^{-1}	Equivalents [KO*t*Bu]/[**2a**–H]	k_{obs} / s^{-1}
1	7.39 × 10^{-4}	0.72	0.32
2	1.08 × 10^{-3}	1.05	1.90
3	1.21 × 10^{-3}	1.17	2.02
4	1.48 × 10^{-3}	1.43	2.02
5	1.75 × 10^{-3}	1.69	2.28
6	2.08 × 10^{-3}	2.02	2.32
7	3.09 × 10^{-3}	3.00	2.29

6. KINETICS

Kinetics for the anion of (p-trifluoromethyl-phenyl)acetonitrile (1a)

Table S4: Kinetics of the reaction of electrophile **3d** with the anion of (p-trifluoromethyl-phenyl)acetonitrile (**1a**) in DMSO at 20°C (deprotonated with 1.00 – 1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 440 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
RAK 3.10-2	2.96×10^{-5}	3.59×10^{-4}	1.42×10^{2}
RAK 3.10-1	2.96×10^{-5}	4.06×10^{-4}	1.60×10^{2}
RAK 3.10-3	2.96×10^{-5}	4.54×10^{-4}	1.84×10^{2}
RAK 3.11-1	2.96×10^{-5}	4.95×10^{-4}	2.00×10^{2}
RAK 3.11-2	2.96×10^{-5}	5.54×10^{-4}	2.19×10^{2}

$k_2 = 4.04 \times 10^5$ L mol^{-1} s^{-1}

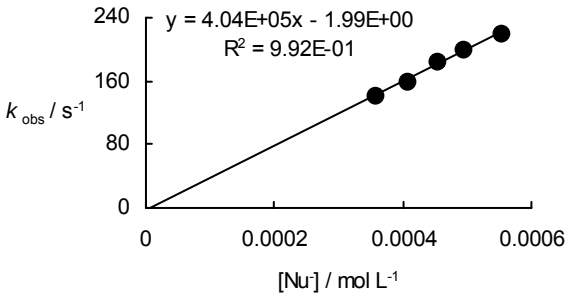


Table S5: Kinetics of the reaction of electrophile **3e** with the anion of (p-trifluoromethyl-phenyl)acetonitrile (**1a**) in DMSO at 20°C (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 486 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
RAK 3.dma-1	1.26×10^{-5}	3.11×10^{-4}	2.72×10^{1}
RAK 3.dma-2	1.26×10^{-5}	4.04×10^{-4}	3.50×10^{1}
RAK 3.dma-3	1.26×10^{-5}	5.02×10^{-4}	3.98×10^{1}
RAK 3.dma-4	1.26×10^{-5}	6.37×10^{-4}	5.20×10^{1}
RAK 3.dma-5	1.26×10^{-5}	7.53×10^{-4}	6.06×10^{1}
RAK 3.dma-6	1.26×10^{-5}	1.01×10^{-3}	8.54×10^{1}

$k_2 = 8.24 \times 10^4$ L mol^{-1} s^{-1}

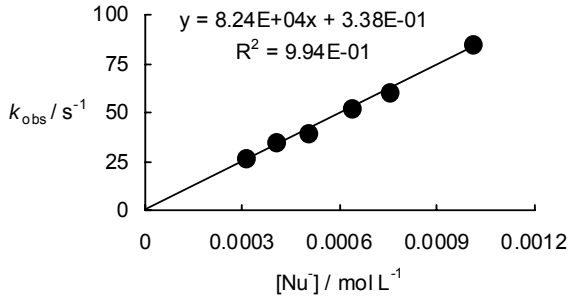
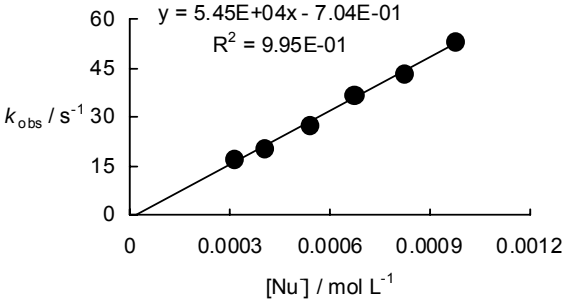


Table S6: Kinetics of the reaction of electrophile **3f** with the anion of (p-trifluoromethyl-phenyl)acetonitrile (**1a**) in DMSO at 20°C (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 521 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
RAK 3.9-1	1.29×10^{-5}	3.11×10^{-4}	1.73×10^{1}
RAK 3.4-1	1.27×10^{-5}	4.03×10^{-4}	2.06×10^{1}
RAK 3.4-2	1.27×10^{-5}	5.38×10^{-4}	2.75×10^{1}
RAK 3.4-3	1.27×10^{-5}	6.72×10^{-4}	3.68×10^{1}
RAK 3.4-4	1.27×10^{-5}	8.22×10^{-4}	4.33×10^{1}
RAK 3.4-5	1.27×10^{-5}	9.77×10^{-4}	5.31×10^{1}

$k_2 = 5.45 \times 10^4$ L mol^{-1} s^{-1}



Kinetics for the anion of(p-cyano-phenyl)acetonitrile (1b)

Table S7: Kinetics of the reaction of electrophile **3e** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) in DMSO at 20°C (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 486 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
RAK 4.3Z-1	1.27×10^{-5}	1.59×10^{-4}	1.74
RAK 4.3Z-2	1.27×10^{-5}	1.98×10^{-4}	2.08
RAK 4.3Z-3	1.27×10^{-5}	2.38×10^{-4}	2.49
RAK 4.3Z-4	1.27×10^{-5}	3.96×10^{-4}	4.29
RAK 4.3Z-5	1.51×10^{-5}	5.98×10^{-4}	6.50

$k_2 = 1.10 \times 10^4$ L mol^{-1} s^{-1}

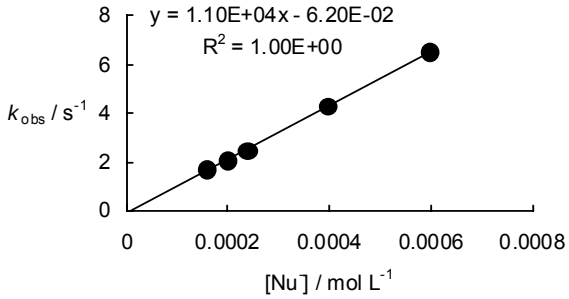


Table S8: Kinetics of the reaction of electrophile **3f** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) in DMSO at 20°C (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 521 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
RAK 4.1-1	1.03×10^{-5}	1.13×10^{-4}	7.27×10^{-1}
RAK 4.2-1	1.23×10^{-5}	1.33×10^{-4}	9.03×10^{-1}
RAK 4.1-6	1.03×10^{-5}	1.51×10^{-4}	9.35×10^{-1}
RAK 4.1-2	1.03×10^{-5}	1.88×10^{-4}	1.24
RAK 4.1-3	1.03×10^{-5}	2.64×10^{-4}	1.79
RAK 4.1-4	1.03×10^{-5}	3.39×10^{-4}	2.21
RAK 4.2-2	1.23×10^{-5}	4.43×10^{-4}	2.90
RAK 4.2-3	1.23×10^{-5}	5.40×10^{-4}	3.64
RAK 4.2-4	1.23×10^{-5}	7.76×10^{-4}	5.07

$k_2 = 6.59 \times 10^3$ L mol^{-1} s^{-1}

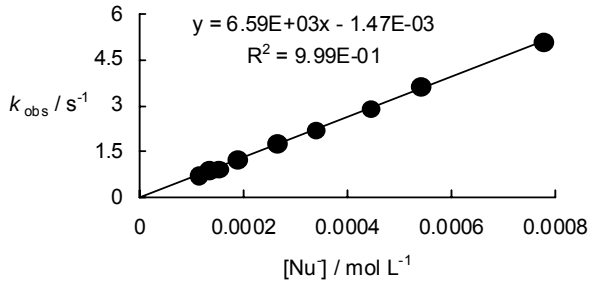


Table S9: Kinetics of the reaction of electrophile **3i** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) in DMSO at 20°C (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 490 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
RAK 4.10-1	8.09×10^{-6}	8.18×10^{-5}	1.30×10^{2}
RAK 4.10-4	8.09×10^{-6}	1.06×10^{-4}	1.69×10^{2}
RAK 4.10-3	8.09×10^{-6}	1.23×10^{-4}	1.96×10^{2}
RAK 4.10-2	8.09×10^{-6}	1.47×10^{-4}	2.38×10^{2}
RAK 4.3-1	8.09×10^{-6}	2.38×10^{-4}	3.81×10^{2}

$k_2 = 1.61 \times 10^{6}$ L mol^{-1} s^{-1}

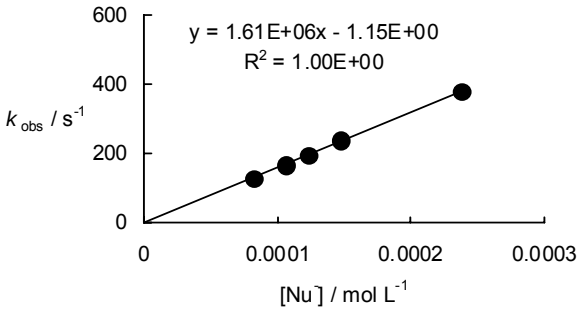


Table S10: Kinetics of the reaction of electrophile **3j** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) at 20°C (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 523 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
RAK 4.5Z-1	8.50×10^{-6}	1.23×10^{-4}	4.88×10^{1}
RAK 4.5Z-2	8.21×10^{-6}	2.86×10^{-4}	1.10×10^{2}
RAK 4.5Z-3	8.21×10^{-6}	4.29×10^{-4}	1.70×10^{2}
RAK 4.5Z-4	8.21×10^{-6}	4.84×10^{-4}	1.90×10^{2}

$k_2 = 3.94 \times 10^{5}$ L mol^{-1} s^{-1}

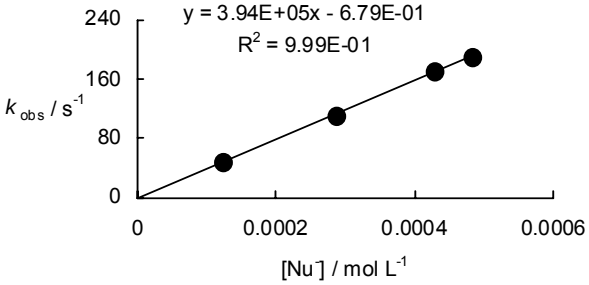


Table S11: Kinetics of the reaction of electrophile **3j** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) in DMSO at 20°C in the presence of 18-crown-6 (deprotonated with 1.00-1.12 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 523 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	[18-crown-6] / M	k_{obs} / s^{-1}
RAK 4.11-1	8.96×10^{-6}	1.16×10^{-4}	-	4.63×10^{1}
RAK 4.11-2	8.96×10^{-6}	2.32×10^{-4}	1.27×10^{-3}	9.23×10^{1}
RAK 4.11-3	8.96×10^{-6}	4.64×10^{-4}	-	1.87×10^{2}
RAK 4.11-4	8.96×10^{-6}	6.96×10^{-4}	2.54×10^{-3}	2.83×10^{2}

$k_2 = 4.09 \times 10^5$ L mol^{-1} s^{-1}

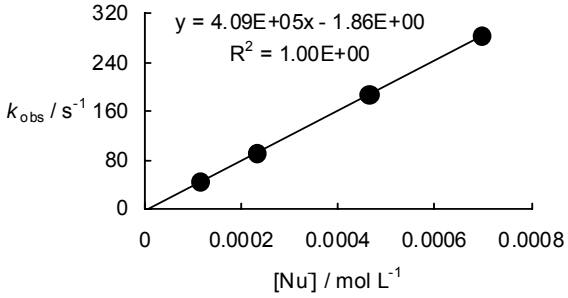


Table S12: Kinetics of the reaction of electrophile **3m** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) in DMSO at 20 °C (deprotonated with 2 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 394 nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
a313-1	4.08×10^{-5}	5.00×10^{-4}	7.60
a313-2	4.08×10^{-5}	1.00×10^{-3}	1.61×10^{1}
a313-3	4.08×10^{-5}	1.50×10^{-3}	2.53×10^{1}
a313-4	4.08×10^{-5}	2.00×10^{-3}	3.36×10^{1}
a313-5	4.08×10^{-5}	2.50×10^{-3}	4.13×10^{1}

$k_2 = 1.70 \times 10^4$ L mol^{-1} s^{-1}

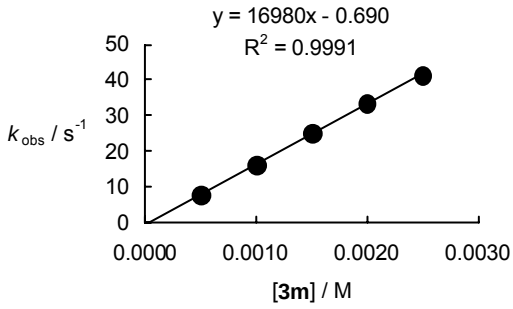


Table S13: Kinetics of the reaction of electrophile **3m** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) in DMSO at 20 °C (deprotonated with 2 equiv. KO*t*Bu, in the presence of 18-crown-6, stopped-flow UV-Vis spectrometer, λ = 398 nm).

Nr.	$[Nu^-]_0$ / M	[18-crown-6] / M	$[E]_0$ / M	k_{obs} / s^{-1}
a325-1	4.18×10^{-5}	4.39×10^{-5}	7.21×10^{-4}	1.22×10^{1}
a325-2	4.18×10^{-5}	4.39×10^{-5}	1.44×10^{-3}	2.51×10^{1}
a325-3	4.18×10^{-5}	4.39×10^{-5}	2.16×10^{-3}	3.79×10^{1}
a325-4	4.18×10^{-5}	4.39×10^{-5}	2.88×10^{-3}	4.83×10^{1}
a325-5	4.18×10^{-5}	4.39×10^{-5}	3.60×10^{-3}	5.97×10^{1}

$k_2 = 1.64 \times 10^4$ L mol^{-1} s^{-1}

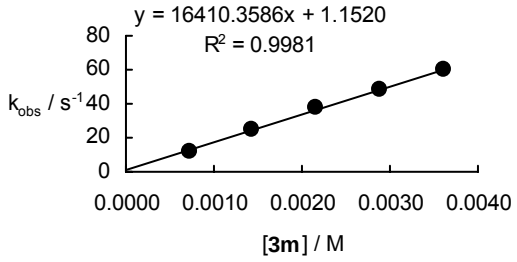


Table S14: Kinetics of the reaction of electrophile **3m** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) in DMSO at 20 °C (deprotonated with 2 equiv. KO*t*Bu, addition 18-crown-6, addition of CH acid, stopped-flow UV-Vis spectrometer, λ = 398 nm).

Nr.	$[Nu]_0$ / M	[18-crown-6] / M	[**1b**-H] / M	$[E]_0$ / M	k_{obs} / s^{-1}
a325b-1	4.18×10^{-5}	4.39×10^{-5}	1.25×10^{-4}	7.21×10^{-4}	1.37×10^{1}
a325b-2	4.18×10^{-5}	4.39×10^{-5}	1.25×10^{-4}	1.44×10^{-3}	2.50×10^{1}
a325b-3	4.18×10^{-5}	4.39×10^{-5}	1.25×10^{-4}	2.16×10^{-3}	3.59×10^{1}
a325b-5	4.18×10^{-5}	4.39×10^{-5}	1.25×10^{-4}	2.88×10^{-3}	4.84×10^{1}

$k_2 = 1.60 \times 10^4$ L mol^{-1} s^{-1}

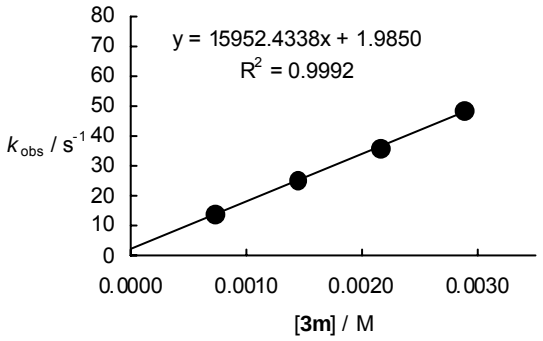


Table S15: Kinetics of the reaction of electrophile **3m** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) in DMSO at 25 °C (deprotonated with 2 equiv. KO*t*Bu, addition of 18-crown-6, stopped-flow UV-Vis spectrometer, λ = 398 nm).

Nr.	$[Nu^-]_0$ / M	[18-crown-6] / M	$[E]_0$ / M	k_{obs} / s^{-1}
a324-5	4.43×10^{-5}	4.65×10^{-5}	7.11×10^{-4}	1.72×10^{1}
a324-2	4.43×10^{-5}	4.65×10^{-5}	1.42×10^{-3}	3.03×10^{1}
a324-3	4.43×10^{-5}	4.65×10^{-5}	2.13×10^{-3}	4.35×10^{1}
a324-4	4.43×10^{-5}	4.65×10^{-5}	2.84×10^{-3}	5.75×10^{1}
a324-6	4.43×10^{-5}	4.65×10^{-5}	3.56×10^{-3}	6.97×10^{1}

$k_2 = 1.86 \times 10^4$ L mol^{-1} s^{-1}

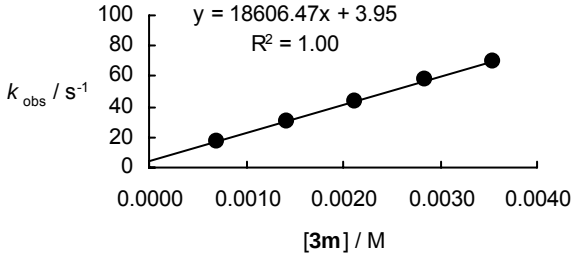


Table S16: Kinetics of the reaction of electrophile **3n** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) in DMSO at 20 °C (deprotonated with 2 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 394$ nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
a312-5	4.08×10^{-5}	9.35×10^{-4}	7.89
a312-1	4.08×10^{-5}	1.40×10^{-3}	1.18×10^{1}
a312-2	4.08×10^{-5}	1.87×10^{-3}	1.61×10^{1}
a312-3	4.08×10^{-5}	2.34×10^{-3}	2.04×10^{1}
a312-4	4.08×10^{-5}	3.27×10^{-3}	2.85×10^{1}

$k_2 = 8.87 \times 10^3$ L mol^{-1} s^{-1}

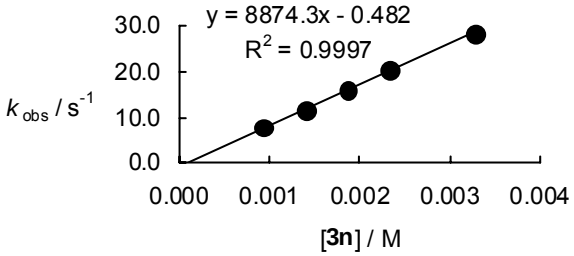


Table S17: Kinetics of the reaction of electrophile **3o** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) in DMSO at 20 °C (deprotonated with KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 397$ nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
a309-1	3.10×10^{-5}	6.59×10^{-4}	1.84
a309-3	3.10×10^{-5}	1.32×10^{-3}	3.55
a309-4	3.10×10^{-5}	1.98×10^{-3}	5.33
a309-4	3.10×10^{-5}	2.64×10^{-3}	7.24
a309-5	3.10×10^{-5}	3.30×10^{-3}	9.26

$k_2 = 2.81 \times 10^3$ L mol^{-1} s^{-1}

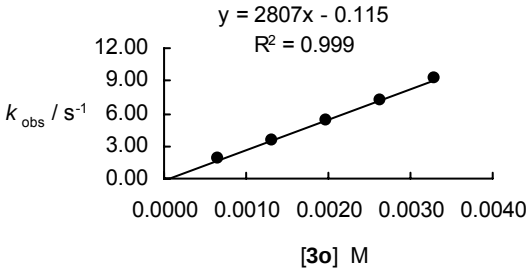


Table S18: Kinetics of the reaction of electrophile **3p** with the anion of (p-cyanophenyl)acetonitrile (**1b**) in DMSO at 20 °C (deprotonated with KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 397 nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
a307b-1	2.12×10^{-5}	4.08×10^{-4}	1.07×10^{-1}
a307b-2	2.12×10^{-5}	8.16×10^{-4}	2.36×10^{-1}
a307b-3	2.12×10^{-5}	1.22×10^{-3}	3.42×10^{-1}
a307b-4	2.12×10^{-5}	1.63×10^{-3}	4.57×10^{-1}
a307b-5	2.12×10^{-5}	2.04×10^{-3}	5.68×10^{-1}

$k_2 = 2.80 \times 10^2$ L mol^{-1} s^{-1}

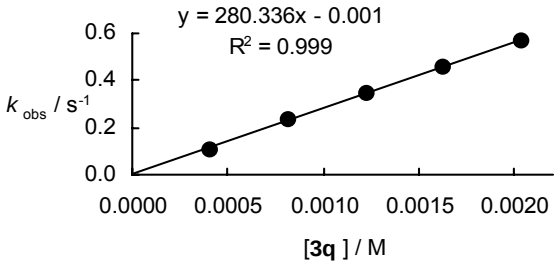


Table S19: Kinetics of the reaction of electrophile **3q** with the anion of (p-cyanophenyl)acetonitrile (**1b**) in DMSO at 20 °C (deprotonated with KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 394 nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
a311-2	8.27×10^{-5}	1.43×10^{-3}	2.58×10^{-1}
a311-1	8.27×10^{-5}	2.86×10^{-3}	4.99×10^{-1}
a311-4	8.27×10^{-5}	4.29×10^{-3}	7.12×10^{-1}
a311-5	8.27×10^{-5}	5.72×10^{-3}	9.23×10^{-1}

$k_2 = 1.54 \times 10^2$ L mol^{-1} s^{-1}

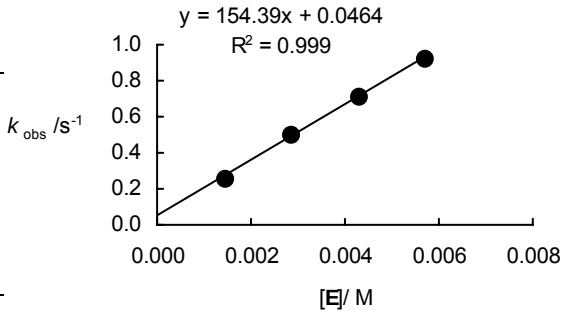
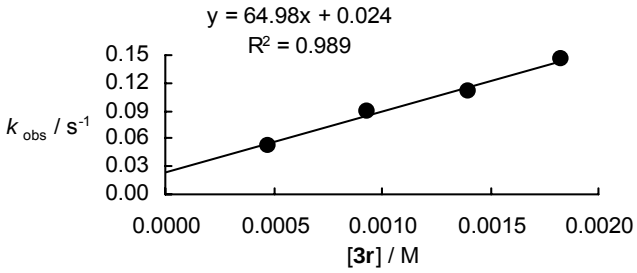


Table S20: Kinetics of the reaction of electrophile **3r** with the anion of (p-cyano-phenyl)acetonitrile (**1b**) in DMSO at 20 °C (deprotonated with KO*t*Bu, J&M UV-Vis spectrometer, $\lambda = 394$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
c310-1	4.33×10^{-5}	4.72×10^{-4}	5.26×10^{-2}
c310-2	4.33×10^{-5}	9.31×10^{-4}	8.83×10^{-2}
c310-3	4.33×10^{-5}	1.40×10^{-3}	1.10×10^{-1}
c310-4	4.33×10^{-5}	1.83×10^{-3}	1.45×10^{-1}

$k_2 = 6.50 \times 10^{1}$ L mol^{-1} s^{-1}



Kinetics for the anion of (p-nitro-phenyl)acetonitrile (1c)

Table S21: Kinetics of the reaction of **3a** with the anion of (p-nitro-phenyl)acetonitrile (**1c**) in DMSO at 20°C in the presence of 18-crown-6 (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 400 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	[18-crown-6] / M	k_{obs} / s^{-1}
RAK 1.17-1	5.37×10^{-5}	5.99×10^{-4}	-	7.20×10^{1}
RAK 1.17-2	5.37×10^{-5}	7.98×10^{-4}	1.12×10^{-3}	9.74×10^{1}
RAK 1.17-3	5.37×10^{-5}	9.98×10^{-4}	-	1.24×10^{2}
RAK 1.17-4	5.37×10^{-5}	1.20×10^{-3}	1.60×10^{-3}	1.49×10^{2}

$k_2 = 1.29 \times 10^5$ L mol^{-1} s^{-1}

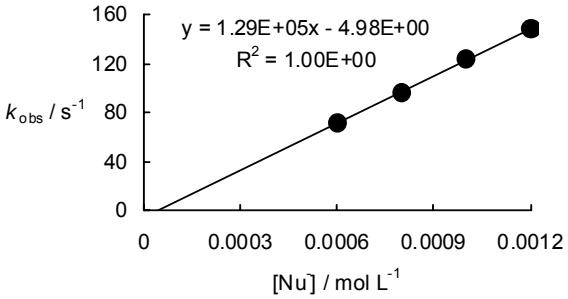


Table S22: Kinetics of the reaction of electrophile **3c** with the anion of (p-nitro-phenyl)acetonitrile (**1c**) in DMSO at 20°C (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 380 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
RAK 1.8-1	6.03×10^{-5}	5.99×10^{-4}	2.63×10^{-1}
RAK 1.8-2	6.03×10^{-5}	7.50×10^{-4}	3.05×10^{-1}
RAK 1.8-3	6.03×10^{-5}	9.00×10^{-4}	3.95×10^{-1}
RAK 1.8-4	6.03×10^{-5}	1.01×10^{-3}	4.38×10^{-1}
RAK 1.8-5	6.03×10^{-5}	1.87×10^{-3}	7.90×10^{-1}

$k_2 = 4.19 \times 10^2$ L mol^{-1} s^{-1}

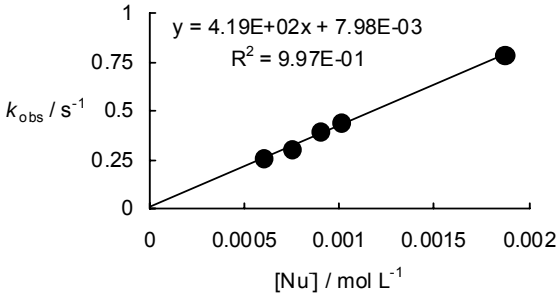


Table S23: Kinetics of the reaction of electrophile **3c** with the anion of (p-nitro-phenyl)-acetonitrile (**1c**) in DMSO at 20°C in the presence of 18-crown-6 (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 400$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	[18-crown-6] / M	k_{obs} / s^{-1}
RAK 1.13-1	3.08×10^{-5}	5.13×10^{-4}	7.69×10^{-4}	2.27×10^{-1}
RAK 1.13-2	3.08×10^{-5}	7.06×10^{-4}	1.68×10^{-3}	3.25×10^{-1}
RAK 1.13-3	3.08×10^{-5}	8.98×10^{-4}	1.88×10^{-3}	4.10×10^{-1}
RAK 1.13-4	3.08×10^{-5}	1.09×10^{-3}	2.18×10^{-3}	4.89×10^{-1}
RAK 1.13-5	3.08×10^{-5}	1.60×10^{-3}	3.80×10^{-3}	7.14×10^{-1}

$k_2 = 4.43 \times 10^2$ L mol^{-1} s^{-1}

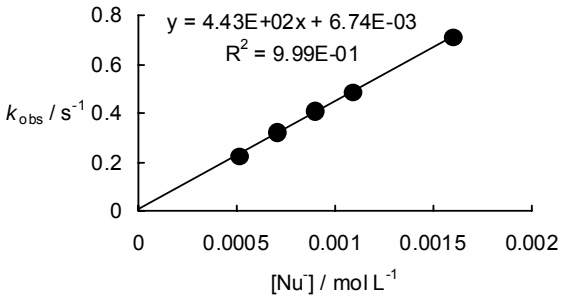


Table S24: Kinetics of the reaction of electrophile **3d** with the anion of (p-nitro-phenyl)acetonitrile (**1c**) in DMSO at 20°C (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 400$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
RAK 1.7-1	5.03×10^{-5}	5.45×10^{-4}	2.51×10^{-1}
RAK 1.7-2	5.03×10^{-5}	6.82×10^{-4}	2.88×10^{-1}
RAK 1.7-3	5.03×10^{-5}	8.18×10^{-4}	3.35×10^{-1}
RAK 1.7-4	5.03×10^{-5}	9.54×10^{-4}	3.87×10^{-1}
RAK 1.7-5	5.03×10^{-5}	1.09×10^{-3}	4.35×10^{-1}

$k_2 = 3.43 \times 10^2$ L mol^{-1} s^{-1}

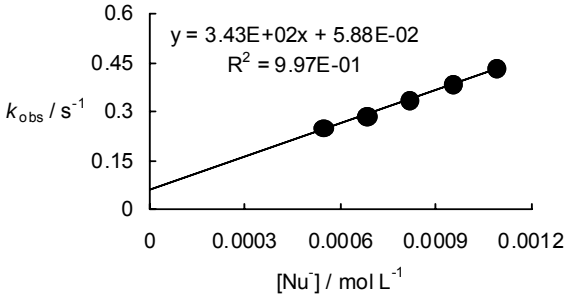


Table S25: Kinetics of the reaction of electrophile **3d** with the anion of (p-nitro-phenyl)-acetonitrile (**1c**) in DMSO at 20°C in the presence of 18-crown-6 (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 400$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	[18-crown-6] / M	k_{obs} / s^{-1}
RAK 1.16-1	4.33×10^{-5}	4.98×10^{-4}	-	2.32×10^{-1}
RAK 1.16-2	4.33×10^{-5}	6.09×10^{-4}	1.24×10^{-3}	2.68×10^{-1}
RAK 1.16-3	4.33×10^{-5}	7.93×10^{-4}	-	3.18×10^{-1}
RAK 1.16-4	4.33×10^{-5}	1.29×10^{-3}	1.31×10^{-3}	4.86×10^{-1}
RAK 1.16-5	4.33×10^{-5}	1.57×10^{-3}		5.85×10^{-1}
RAK 1.16-6	4.33×10^{-5}	1.75×10^{-3}	2.06×10^{-3}	6.35×10^{-1}

$k_2 = 3.26 \times 10^2$ L mol^{-1} s^{-1}

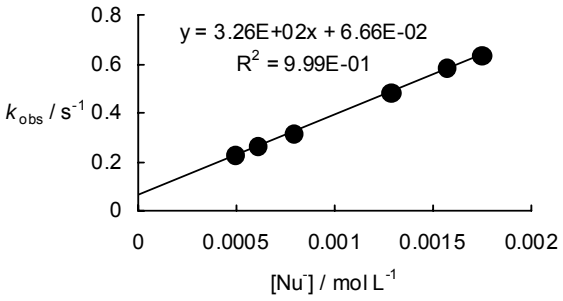


Table S26: Kinetics of the reaction of electrophile **3h** with the anion of (p-nitro-phenyl)acetonitrile (**1c**) in DMSO at 20°C (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 388$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
RAK 1.9-1	7.72×10^{-5}	7.77×10^{-4}	3.94×10^2
RAK 1.9-4	7.72×10^{-5}	9.33×10^{-4}	4.85×10^2
RAK 1.9-2	7.72×10^{-5}	1.04×10^{-3}	5.48×10^2
RAK 1.9-5	7.72×10^{-5}	1.14×10^{-3}	5.82×10^2
RAK 1.9-3	7.72×10^{-5}	1.30×10^{-3}	6.78×10^2
RAK 1.9-6	7.72×10^{-5}	1.40×10^{-3}	7.21×10^2

$k_2 = 5.23 \times 10^5$ L mol^{-1} s^{-1}

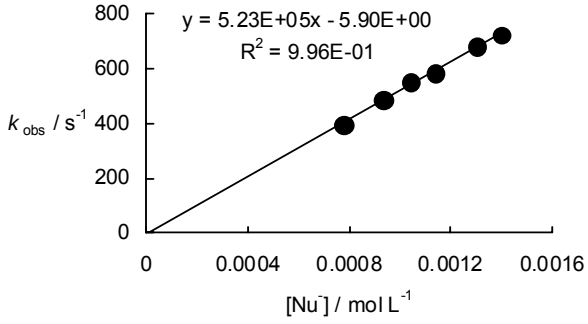


Table S27: Kinetics of the reaction of electrophile **3l** with the anion of (p-nitrophenyl)acetonitrile (**1c**) in DMSO at 20°C (deprotonated with 1.00-1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, λ = 560 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
RAK 1.12-1	4.72×10^{-4}	4.63×10^{-5}	2.02×10^{1}
RAK 1.12-6	5.90×10^{-4}	4.63×10^{-5}	2.51×10^{1}
RAK 1.12-2	7.08×10^{-4}	4.63×10^{-5}	3.03×10^{1}
RAK 1.12-7	8.26×10^{-4}	4.63×10^{-5}	3.50×10^{1}
RAK 1.12-3	9.44×10^{-4}	4.63×10^{-5}	4.02×10^{1}
RAK 1.12-4	1.18×10^{-3}	4.63×10^{-5}	5.00×10^{1}
RAK 1.12-5	1.42×10^{-3}	4.63×10^{-5}	5.96×10^{1}

$k_2 = 4.17 \times 10^4$ L mol^{-1} s^{-1}

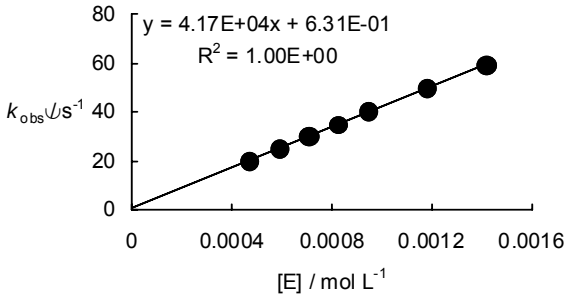


Table S28: Kinetics of the reaction of electrophile **3m** with the anion of (p-nitrophenyl)acetonitrile (**1c**) in DMSO at 20 °C (deprotonated with 1.05 equiv. KO*t*Bu, J&M UV-Vis spectrometer, λ = 537 nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
c305-2	2.66×10^{-5}	5.57×10^{-4}	2.82×10^{-2}
c305-3	2.66×10^{-5}	8.44×10^{-4}	3.50×10^{-2}
c305-4	2.66×10^{-5}	1.12×10^{-3}	4.26×10^{-2}
c305-5	2.66×10^{-5}	1.42×10^{-3}	4.96×10^{-2}

$k_2 = 2.51 \times 10^1$ L mol^{-1} s^{-1}

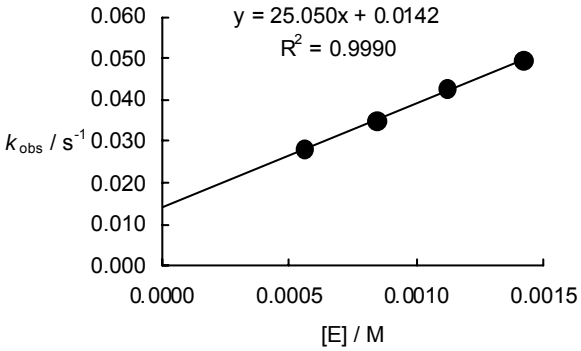
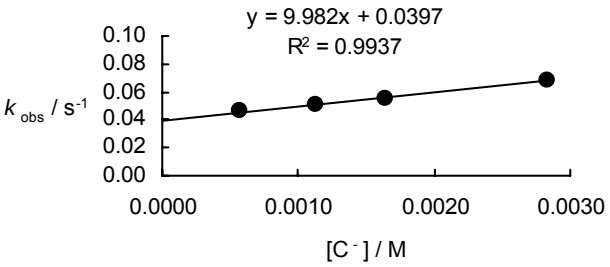


Table S29: Kinetics of the reaction of electrophile **3n** with the anion of (p-nitrophenyl)acetonitrile (**1c**) in DMSO at 20 °C (deprotonated with KO*t*Bu, J&M UV-Vis spectrometer, $\lambda = 537$ nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
c306-1	4.69×10^{-5}	5.70×10^{-4}	4.62×10^{-2}
c306-2	4.69×10^{-5}	1.13×10^{-3}	5.03×10^{-2}
c306-6	4.69×10^{-5}	1.65×10^{-3}	5.55×10^{-2}
c306-4	4.69×10^{-5}	2.83×10^{-3}	6.84×10^{-2}

$k_2 = 9.98$ L mol^{-1} s^{-1}



Kinetics for the anion of 2-phenyl-propionitrile (2a)

Table S30: Kinetics of the reaction of **3f** with the anion of 2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with 1.05 eq. phosphazene base P_4-*t*Bu, stopped-flow UV-Vis spectrometer, λ = 524 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
265-1	2.01×10^{-5}	3.62×10^{-4}	5.79×10^{2}
265-2	2.01×10^{-5}	5.07×10^{-4}	9.40×10^{2}
265-3	2.01×10^{-5}	6.52×10^{-4}	1.49×10^{3}
265-4	2.01×10^{-5}	7.97×10^{-4}	2.54×10^{3}

$k_2 = 2.50 \times 10^{6}$ L mol^{-1} s^{-1}

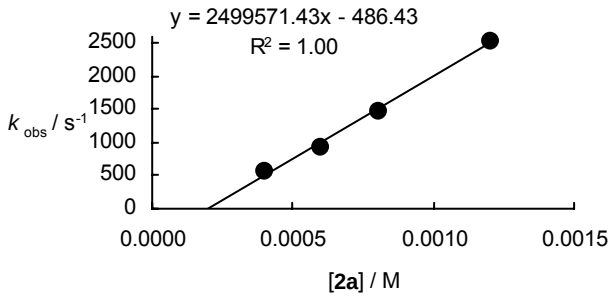


Table S31: Kinetics of the reaction of electrophile **3s** with the anion of 2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with phosphazene base P_4-*t*Bu, stopped-flow UV-Vis spectrometer, λ = 405 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a369-1	1.92×10^{-5}	3.62×10^{-4}	3.85×10^{-1}
a369-2	1.92×10^{-5}	5.07×10^{-4}	7.72
a369-3	1.92×10^{-5}	6.52×10^{-4}	1.28
a369-4	1.92×10^{-5}	7.97×10^{-4}	1.66

$k_2 = 3.05 \times 10^{3}$ L mol^{-1} s^{-1}

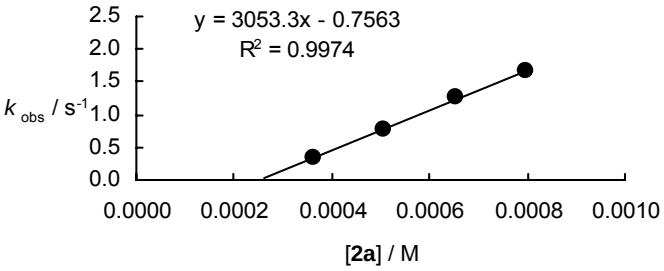


Table S32: Kinetics of the reaction of electrophile **3s** with the anion of 2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with 1.05 eq. phosphazene base P_4-*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 410$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a373-2	1.85×10^{-5}	5.25×10^{-4}	4.34×10^{-1}
a373-3	1.85×10^{-5}	6.75×10^{-4}	8.81×10^{-1}
a373-4	1.85×10^{-5}	8.25×10^{-4}	1.31
a373-5	1.85×10^{-5}	9.75×10^{-4}	1.73

$k_2 = 2.87 \times 10^3$ L mol^{-1} s^{-1}

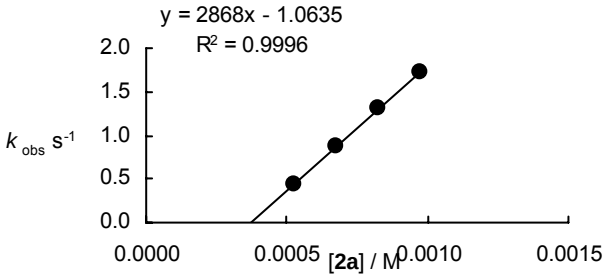


Table S33: Kinetics of the reaction of electrophile **3s** with the anion of2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with 1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 400$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a368c-2	1.92×10^{-5}	5.75×10^{-4}	3.93×10^{-1}
a368c-3	1.92×10^{-5}	7.67×10^{-4}	9.47×10^{-1}
a368c-4	1.92×10^{-5}	9.58×10^{-4}	1.55
a368c-5	1.92×10^{-5}	1.12×10^{-3}	2.11

$k_2 = 3.12 \times 10^3$ L mol^{-1} s^{-1}

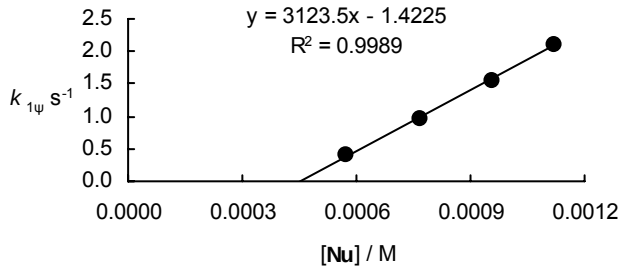


Table S34: Kinetics of the reaction of electrophile **3s** with the anion of 2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with 2.00 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 400$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a368b-2	1.92×10^{-5}	4.38×10^{-4}	4.22×10^{-1}
a368b-3	1.92×10^{-5}	5.75×10^{-4}	7.72×10^{-1}
a368b-4	1.92×10^{-5}	7.67×10^{-4}	1.43
a368b-5	1.92×10^{-5}	9.31×10^{-3}	1.92

$k_2 = 3.09 \times 10^3$ L mol^{-1} s^{-1}

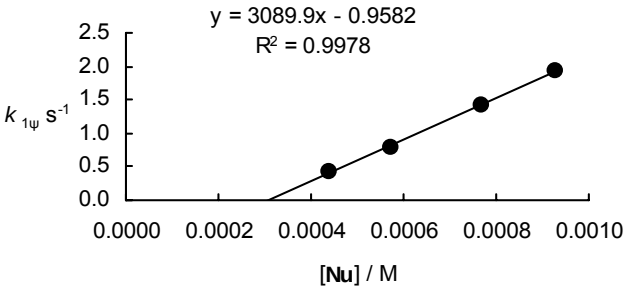


Table S35: Kinetics of the reaction of electrophile **3s** with the anion of 2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with 3.00 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 400$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a368a-2	1.92×10^{-5}	4.38×10^{-4}	5.01×10^{-1}
a368a-3	1.92×10^{-5}	5.75×10^{-4}	9.29×10^{-1}
a368a-4	1.92×10^{-5}	7.67×10^{-4}	1.54
a368a-5	1.92×10^{-5}	9.58×10^{-3}	2.14

$k_2 = 3.15 \times 10^3$ L mol^{-1} s^{-1}

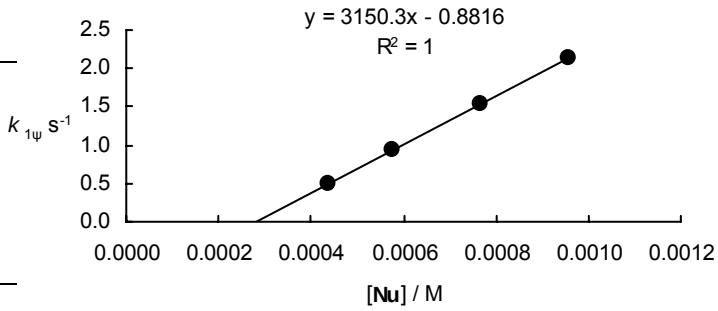


Table S36: Kinetics of the reaction of electrophile **3t** with the anion of 2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with P_4-*t*Bu phosphazene base, stopped-flow UV-Vis spectrometer, $\lambda = 405$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a369b-1	1.66×10^{-5}	3.62×10^{-4}	3.50×10^{-1}
a369b-2	1.66×10^{-5}	5.07×10^{-4}	5.95×10^{-1}
a369b-3	1.66×10^{-5}	6.52×10^{-4}	8.86×10^{-1}
a369b-4	1.66×10^{-5}	7.97×10^{-4}	1.15

$k_2 = 1.86 \times 10^3$ L mol^{-1} s^{-1}

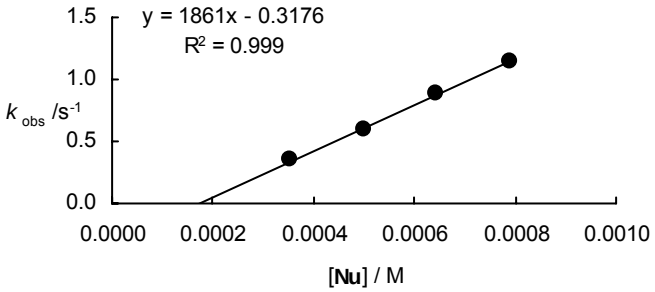


Table S37: Kinetics of the reaction of electrophile **3t** with the anion of 2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with 2.00 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 405$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a366-1	2.02×10^{-5}	3.18×10^{-4}	3.00×10^{-1}
a366-5	2.02×10^{-5}	3.98×10^{-4}	4.24×10^{-1}
a366-2	2.02×10^{-5}	6.36×10^{-4}	8.22×10^{-1}
a366-3	2.02×10^{-5}	8.35×10^{-4}	1.17
a366-4	2.02×10^{-5}	9.94×10^{-4}	1.44

$k_2 = 1.69 \times 10^3$ L mol^{-1} s^{-1}

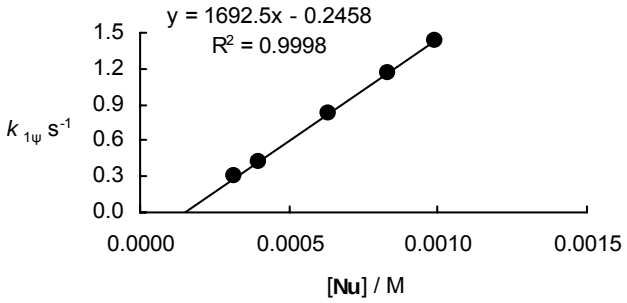


Table S38: Kinetics of the reaction of electrophile **3t** with the anion of 2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with 1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 405$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a354-1	3.27×10^{-5}	6.04×10^{-4}	2.98×10^{-1}
a354-2	3.27×10^{-5}	9.05×10^{-4}	7.58×10^{-1}
a354-4	3.27×10^{-5}	1.21×10^{-3}	1.19
a354-5	3.27×10^{-5}	1.51×10^{-3}	1.67

$k_2 = 1.50 \times 10^3$ L mol^{-1} s^{-1}

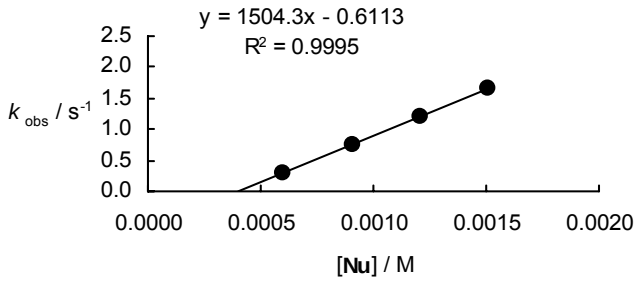


Table S39: Kinetics of the reaction of electrophile **3u** with the anion of 2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with P_4-*t*Bu phosphazene base, stopped-flow UV-Vis spectrometer, $\lambda = 405$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a369c-1	1.63×10^{-5}	3.82×10^{-4}	2.86×10^{-1}
a369c-2	1.63×10^{-5}	5.35×10^{-4}	4.34×10^{-1}
a369c-3	1.63×10^{-5}	6.88×10^{-4}	5.88×10^{-1}
a369c-4	1.63×10^{-5}	8.41×10^{-3}	7.34×10^{-1}

$k_2 = 9.90 \times 10^2$ L mol^{-1} s^{-1}

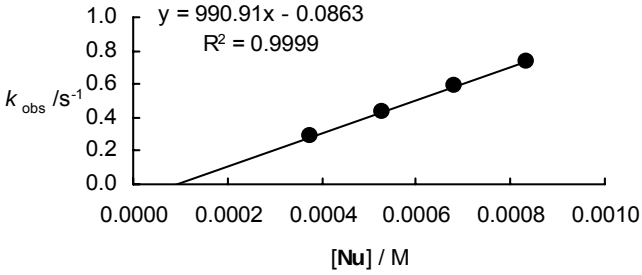


Table S40: Kinetics of the reaction of electrophile **3u** with the anion of 2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with 1.05 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 405$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a352-2	2.88×10^{-5}	5.53×10^{-4}	1.58×10^{-1}
a352-3	2.88×10^{-5}	8.30×10^{-4}	4.29×10^{-1}
a352-4	2.88×10^{-5}	1.11×10^{-3}	6.37×10^{-1}
a352-5	2.88×10^{-5}	1.38×10^{-3}	8.77×10^{-1}

$k_2 = 8.54 \times 10^2$ L mol^{-1} s^{-1}

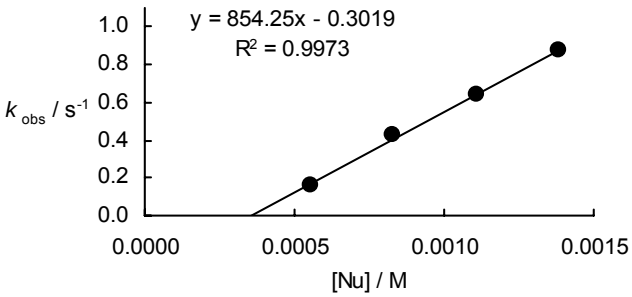
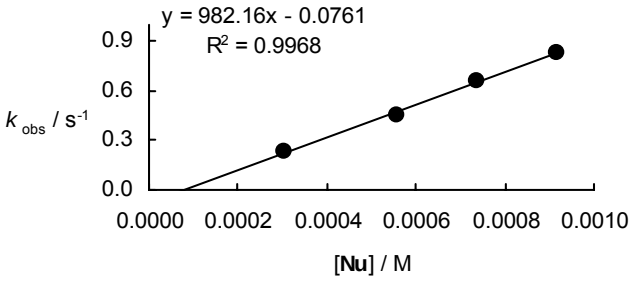


Table S41: Kinetics of the reaction of electrophile **3u** with the anion of 2-phenyl-propionitrile (**2a**) in DMSO at 20 °C (deprotonated with 2.00 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 405$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
a365-1	1.96×10^{-5}	3.06×10^{-4}	2.34×10^{-1}
a365-6	1.96×10^{-5}	5.57×10^{-4}	4.50×10^{-1}
a365-5	1.96×10^{-5}	7.37×10^{-4}	6.57×10^{-1}
a365-3	1.96×10^{-5}	9.17×10^{-4}	8.27×10^{-1}

$k_2 = 9.82 \times 10^2$ L mol^{-1} s^{-1}



Kinetics for the anion of 2-(p-cyanophenyl)-propionitrile (2b)

Table S42: Kinetics of the reaction of **3b** with the anion of 2-(p-cyanophenyl)-propionitrile (**2b**) in DMSO at 20 °C (deprotonated with phosphazene base P_2-*t*Bu, UV-Vis spectrometer, λ = 533 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
270-1	8.00×10^{-6}	5.72×10^{-5}	4.04×10^{2}
270-2	8.00×10^{-6}	1.24×10^{-4}	9.22×10^{2}
270-3	8.00×10^{-6}	1.86×10^{-4}	1.42×10^{3}
270-4	8.00×10^{-6}	2.49×10^{-4}	1.87×10^{3}
270-5	8.00×10^{-6}	3.11×10^{-4}	2.37×10^{3}

$k_2 = 7.73 \times 10^6$ L mol^{-1} s^{-1}

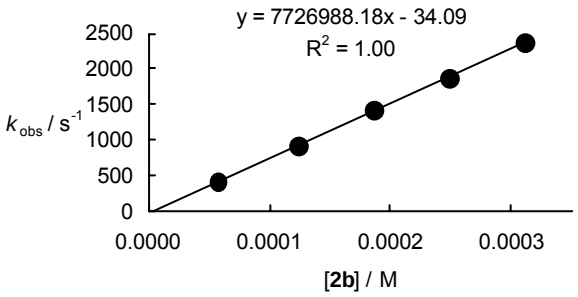


Table S43: Kinetics of the reaction of **3e** with the anion of 2-(p-cyanophenyl)-propionitrile (**2b**) in DMSO at 20 °C (deprotonated with phosphazene base P_2-*t*Bu, stopped-flow UV-Vis spectrometer, λ = 488 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
T-271-1	3.78×10^{-5}	2.49×10^{-4}	1.04×10^{1}
T-271-2	3.78×10^{-5}	3.73×10^{-4}	1.60×10^{1}
T-271-3	3.78×10^{-5}	4.97×10^{-4}	2.12×10^{1}
T-271-4	3.78×10^{-5}	7.46×10^{-4}	3.22×10^{1}
T-271-5	3.78×10^{-5}	9.94×10^{-4}	4.39×10^{1}
T-271-6	3.78×10^{-5}	1.24×10^{-3}	5.55×10^{1}

$k_2 = 4.54 \times 10^4$ L mol^{-1} s^{-1}

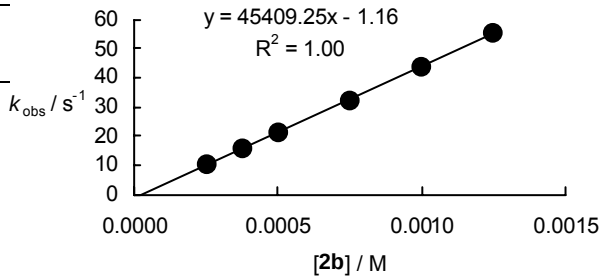


Table S44: Kinetics of the reaction of **3e** with the anion of 2-(p-cyanophenyl)-propionitrile (**2b**) in DMSO at 20 °C (deprotonated with 1.00 equiv. KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 488$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
T-141-1	2.02×10^{-5}	2.61×10^{-4}	4.93
T-141-2	2.02×10^{-5}	5.00×10^{-4}	1.28×10^{1}
T-141-3	2.02×10^{-5}	7.51×10^{-4}	1.96×10^{1}
T-141-4	2.02×10^{-5}	1.00×10^{-3}	2.64×10^{1}
T-141-5	2.02×10^{-5}	1.25×10^{-3}	3.65×10^{1}
T-141-6	2.02×10^{-5}	1.50×10^{-3}	4.49×10^{1}

$k_2 = 3.20 \times 10^4$ L mol^{-1} s^{-1}

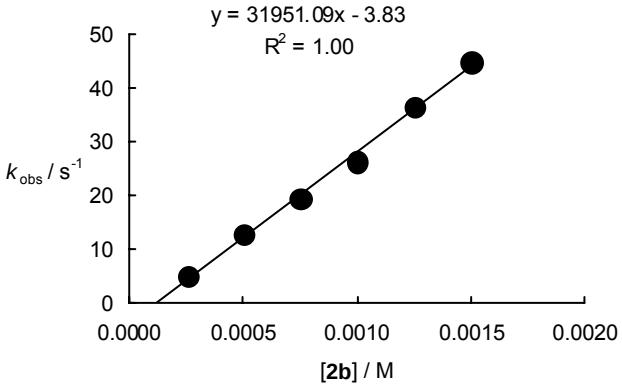


Table S45: Kinetics of the reaction of electrophile **3f** with the anion of 2-(p-cyanophenyl)-propionitrile (**2b**) in DMSO at 20 °C (deprotonated with phosphazene base P_2-*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 524$ nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
272-1	2.48×10^{-5}	2.49×10^{-4}	9.71
272-2	2.48×10^{-5}	4.97×10^{-4}	1.51×10^{1}
272-3	2.48×10^{-5}	7.46×10^{-4}	2.15×10^{1}
272-4	2.48×10^{-5}	1.24×10^{-3}	3.30×10^{1}
272-5	2.48×10^{-5}	1.74×10^{-3}	4.72×10^{1}

$k_2 = 2.51 \times 10^4$ L mol^{-1} s^{-1}

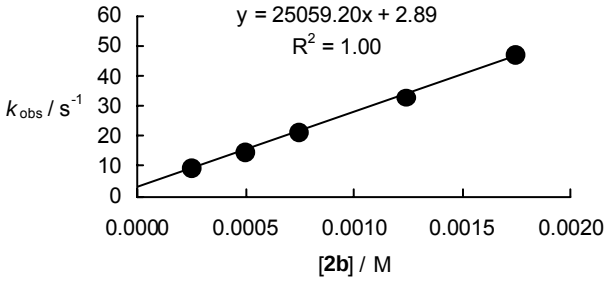


Table S46: Kinetics of the reaction of electrophile **3m** with the anion of 2-(p-cyanophenyl)-propionitrile (**2b**) in DMSO at 20 °C (deprotonated with 2 eq. of KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 403$ nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
a357-1	5.54×10^{-5}	5.29×10^{-4}	9.63
a357-2	5.54×10^{-5}	1.06×10^{-3}	1.52×10^{1}
a357-3	5.54×10^{-5}	1.59×10^{-3}	2.06×10^{1}
a357-4	5.54×10^{-5}	2.12×10^{-3}	2.65×10^{1}
a357-5	5.54×10^{-5}	2.29×10^{-3}	2.85×10^{1}
a357-6	5.54×10^{-5}	2.64×10^{-3}	3.26×10^{1}

$k_2 = 1.08 \times 10^4$ L mol^{-1} s^{-1}

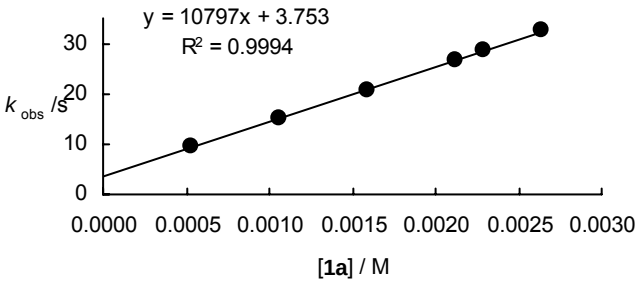


Table S47: Kinetics of the reaction of electrophile **3m** with the anion of 2-(p-cyanophenyl)-propionitrile (**2b**) in DMSO at 20 °C under Ar atmosphere (deprotonated with 2 eq. of KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 403$ nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
a357b-1	5.91×10^{-5}	4.06×10^{-4}	7.09
a357b-2	5.91×10^{-5}	8.12×10^{-4}	1.14×10^{1}
a357b-3	5.91×10^{-5}	1.22×10^{-3}	1.72×10^{1}
a357b-4	5.91×10^{-5}	1.62×10^{-3}	2.13×10^{1}
a357b-5	5.91×10^{-5}	2.03×10^{-3}	2.55×10^{1}

$k_2 = 1.15 \times 10^4$ L mol^{-1} s^{-1}

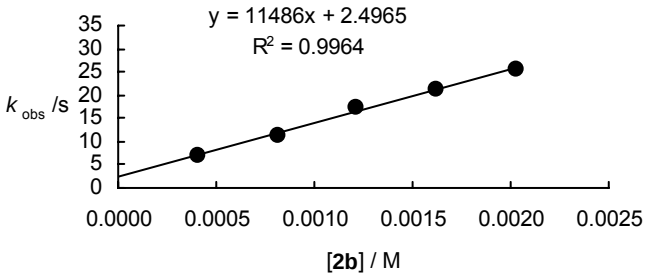


Table S48: Kinetics of the reaction of electrophile **3n** with the anion of 2-(p-cyanophenyl)-propionitrile (**2b**) in DMSO at 20 °C (deprotonated with KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 403$ nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
a355d-1	5.54×10^{-5}	1.95×10^{-3}	1.37×10^{1}
a355d-2	5.54×10^{-5}	3.89×10^{-3}	2.43×10^{1}
a355d-3	5.54×10^{-5}	5.84×10^{-3}	3.53×10^{1}
a355d-5	5.54×10^{-5}	9.73×10^{-3}	5.78×10^{1}

$k_2 = 5.68 \times 10^3$ L mol^{-1} s^{-1}

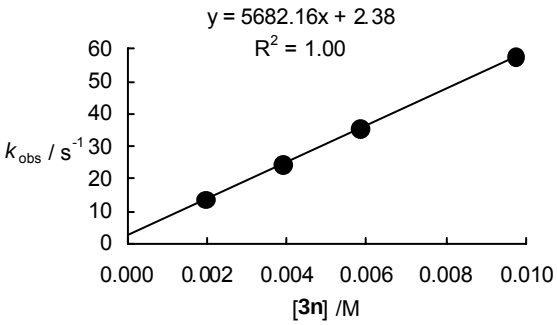


Table S49: Kinetics of the reaction of electrophile **3o** with the anion of 2-(p-cyanophenyl)-propionitrile (**2b**) in DMSO at 20 °C (deprotonated with 2 eq. of KO*t*Bu, stopped-flow UV-Vis spectrometer, $\lambda = 403$ nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
a356-1	8.31×10^{-5}	8.30×10^{-4}	3.80
a356-2	8.31×10^{-5}	1.66×10^{-3}	5.59
a356-3	8.31×10^{-5}	2.49×10^{-3}	7.49
a356-4	8.31×10^{-5}	3.32×10^{-3}	9.34
a356-5	8.31×10^{-5}	4.98×10^{-3}	1.39×10^{1}

$k_2 = 2.44 \times 10^3$ L mol^{-1} s^{-1}

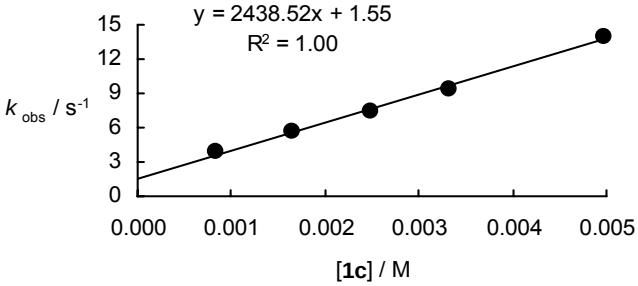
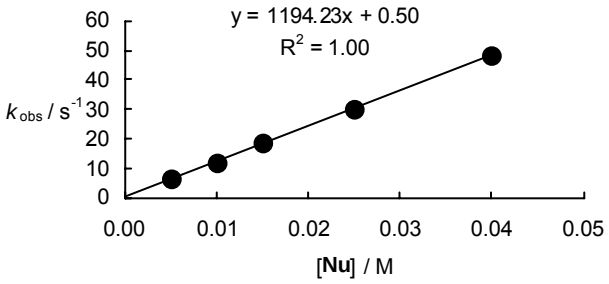


Table S50: Kinetics of the reaction of electrophile **3p** with the anion of 2-(p-cyanophenyl)-propionitrile (**2b**) in DMSO at 20 °C (stopped-flow UV-Vis spectrometer, λ = 403 nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
148-1	1.00×10^{-4}	5.00×10^{-3}	6.86
148-2	1.00×10^{-4}	1.00×10^{-2}	1.20×10^{1}
148-3	1.00×10^{-4}	1.50×10^{-2}	1.85×10^{1}
148-4	1.00×10^{-4}	2.50×10^{-2}	3.05×10^{1}
148-5	1.00×10^{-4}	4.00×10^{-2}	4.84×10^{1}

$k_2 = 1.19 \times 10^3$ L mol^{-1} s^{-1}



Kinetics for the anion of 2-(p-nitrophenyl)-propionitrile (2c)

Table S51: Kinetics of the reaction of electrophile **3a** with the anion of 2-(p-nitrophenyl)-propionitrile (**2c**) in DMSO at 20 °C (employed as potassium salt **2c**–K, in the presence of **2c**-H (c_o = 1.07 × 10^{-4} M^{-1}), stopped-flow UV-Vis spectrometer, λ = 410 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
122-1	1.00 × 10^{-4}	5.11 × 10^{-4}	4.05 × 10^{1}
122-2	1.00 × 10^{-4}	1.02 × 10^{-3}	8.08 × 10^{1}
122-3	1.00 × 10^{-4}	2.04 × 10^{-3}	1.62 × 10^{2}

k_2 = 7.95 × 10^4 L mol^{-1} s^{-1}

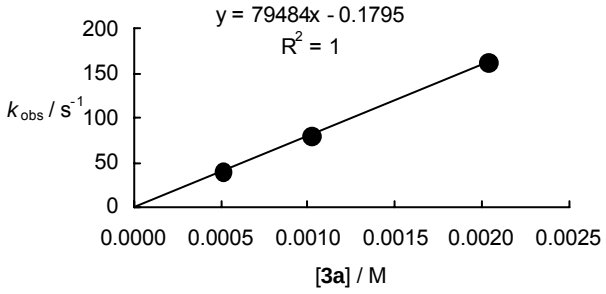


Table S52: Kinetics of the reaction of electrophile **3c** with the anion of 2-(p-nitrophenyl)-propionitrile (**2c**) in DMSO at 20 °C employed as potassium salt **2c**-K, in the presence of **2c**-H (c_o = 5.36 × 10^{-5} M^{-1}), stopped-flow UV-Vis spectrometer, λ = 375 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
119-1	3.01 × 10^{-5}	1.32 × 10^{-4}	1.78 × 10^{-2}
119-2	3.01 × 10^{-5}	2.64 × 10^{-4}	3.48 × 10^{-2}
119-3	3.01 × 10^{-5}	5.27 × 10^{-4}	9.46 × 10^{-2}
119-4	3.01 × 10^{-5}	1.05 × 10^{-3}	2.00 × 10^{-1}
119-5	3.01 × 10^{-5}	1.58 × 10^{-3}	3.15 × 10^{-1}
119-6	3.01 × 10^{-5}	2.64 × 10^{-3}	5.24 × 10^{-1}

k_2 = 2.04 × 10^2 L mol^{-1} s^{-1}

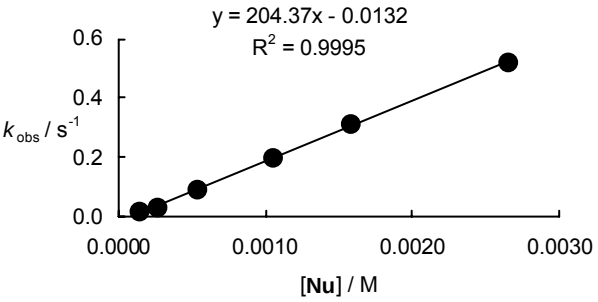


Table S53: Kinetics of the reaction of electrophile **3d** with the anion of 2-(p-nitrophenyl)-propionitrile (**2c**) in DMSO at 20 °C (employed as potassium salt **2c**-K, in the presence of **2c**-H (c_o = 1.41 × 10^{-4} M^{-1}), stopped-flow UV-Vis spectrometer, λ = 393 nm).

Nr.	$[E]_0$ / M	$[Nu^-]_0$ / M	k_{obs} / s^{-1}
90-1	7.71 × 10^{-5}	6.38 × 10^{-4}	3.60 × 10^2
90-2	9.54 × 10^{-5}	5.32 × 10^{-4}	3.10 × 10^2
90-3	7.69 × 10^{-5}	2.66 × 10^{-4}	1.66 × 10^2

k_2 = 9.61 × 10^1 L mol^{-1} s^{-1}

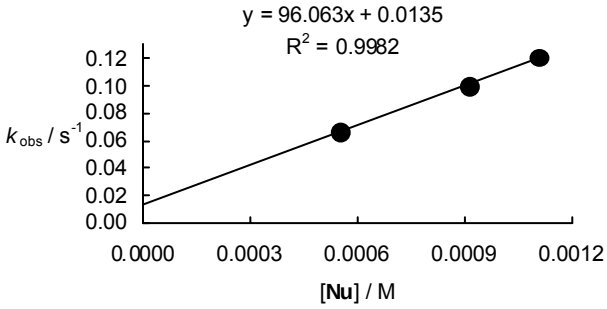


Table S54: Kinetics of the reaction of electrophile **3g** with the anion of 2-(p-nitrophenyl)-propionitrile (**2c**) (employed as potassium salt **2c**-K) in DMSO at 20 °C (stopped-flow UV-Vis spectrometer (1:10), λ = 590 nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
07-1	2.21 × 10^{-5}	2.66 × 10^{-4}	1.66 × 10^2
07-2	2.21 × 10^{-5}	3.30 × 10^{-4}	2.03 × 10^2
07-3	2.21 × 10^{-5}	4.36 × 10^{-4}	2.67 × 10^2
07-4	2.21 × 10^{-5}	5.32 × 10^{-4}	3.10 × 10^2
07-5	2.21 × 10^{-5}	6.38 × 10^{-4}	3.60 × 10^2

k_2 = 5.22 × 10^5 L mol^{-1} s^{-1}

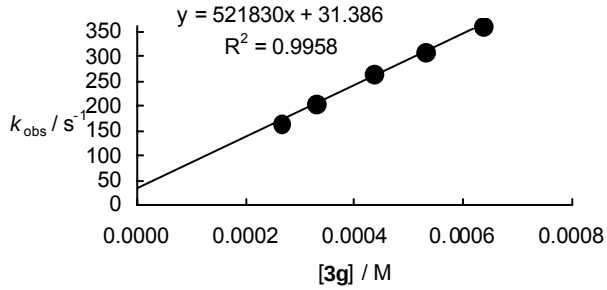


Table S55: Kinetics of the reaction of electrophile **3h** with the anion of 2-(p-nitrophenyl)-propionitrile (**2c**) (employed as potassium salt **2c**-K) in DMSO at 20 °C (stopped-flow UV-Vis spectrometer (1:10), λ = 590 nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
05-1	2.50×10^{-5}	8.92×10^{-4}	1.02×10^{2}
05-2	2.50×10^{-5}	7.43×10^{-4}	8.53×10^{1}
05-3	2.50×10^{-5}	6.13×10^{-4}	7.14×10^{1}
05-4	2.50×10^{-5}	5.02×10^{-4}	5.87×10^{1}
05-5	2.50×10^{-5}	3.72×10^{-4}	4.25×10^{1}

$k_2 = 1.15 \times 10^5$ L mol^{-1} s^{-1}

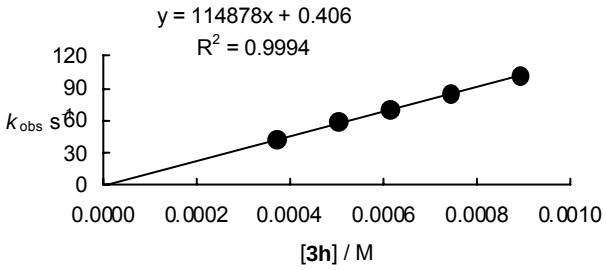


Table S56: Kinetics of the reaction of electrophile **3k** with the anion of 2-(p-nitrophenyl)-propionitrile (**2c**) (employed as potassium salt **2c**-K) in DMSO at 20 °C (stopped-flow UV-Vis spectrometer (1:10), λ = 590 nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
06-1	2.50×10^{-5}	9.86×10^{-4}	1.92×10^{2}
06-2	2.50×10^{-5}	7.49×10^{-4}	1.49×10^{2}
06-3	2.50×10^{-5}	6.31×10^{-4}	1.27×10^{2}
06-4	2.50×10^{-5}	4.73×10^{-4}	9.66×10^{1}
06-5	2.50×10^{-5}	3.55×10^{-4}	7.32×10^{1}

$k_2 = 1.88 \times 10^5$ L mol^{-1} s^{-1}

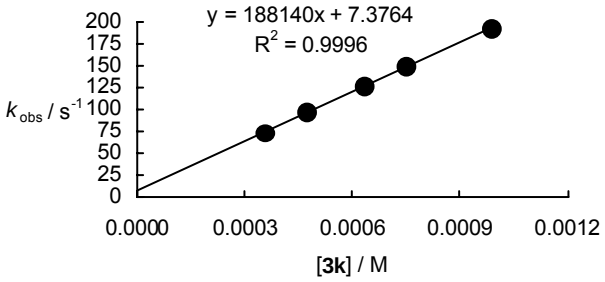
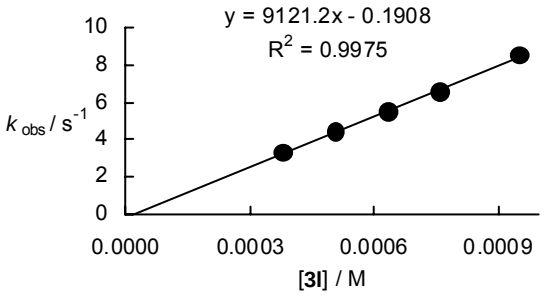


Table S57: Kinetics of the reaction of electrophile **3l** with the anion of 2-(p-nitrophenyl)-propionitrile (**2c**) (employed as potassium salt **2c**-K) in DMSO at 20 °C (stopped-flow UV-Vis spectrometer (1:10), λ = 590 nm).

Nr.	$[Nu^-]_0$ / M	$[E]_0$ / M	k_{obs} / s^{-1}
04-1	2.50×10^{-5}	9.49×10^{-4}	8.58
04-2	2.50×10^{-5}	7.59×10^{-4}	6.60
04-3	2.50×10^{-5}	6.33×10^{-4}	5.51
04-4	2.50×10^{-5}	5.06×10^{-4}	4.45
04-5	2.50×10^{-5}	3.80×10^{-4}	3.34

$k_2 = 9.12 \times 10^3$ L mol^{-1} s^{-1}



7. Copies of NMR spectra

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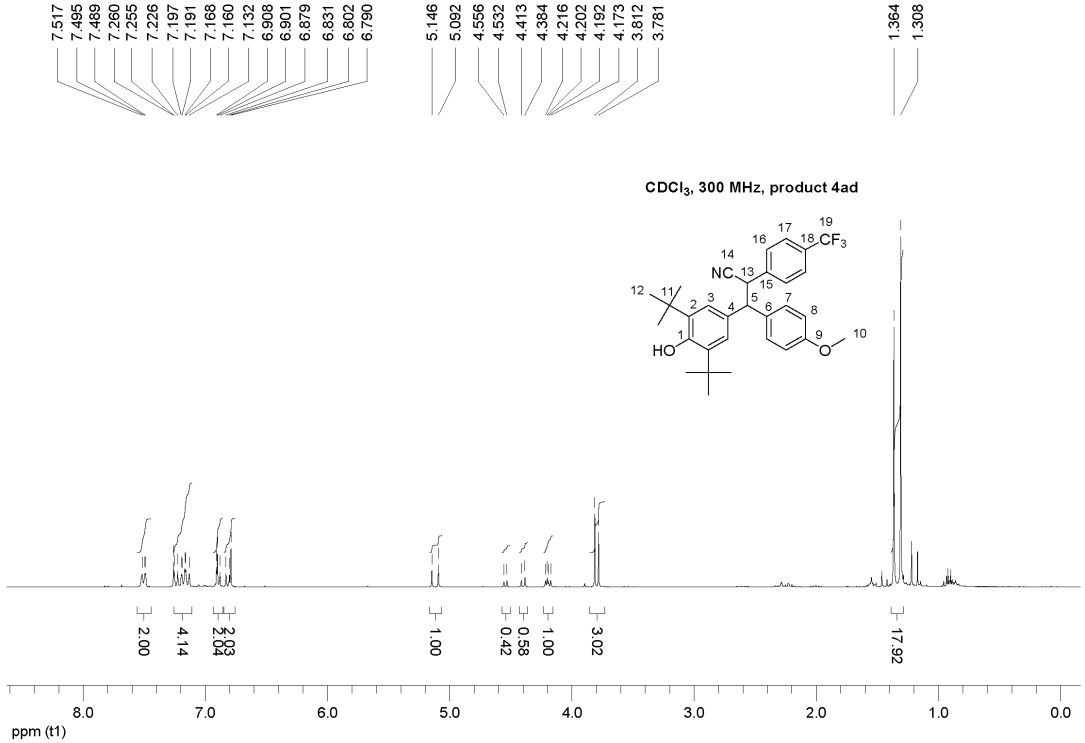
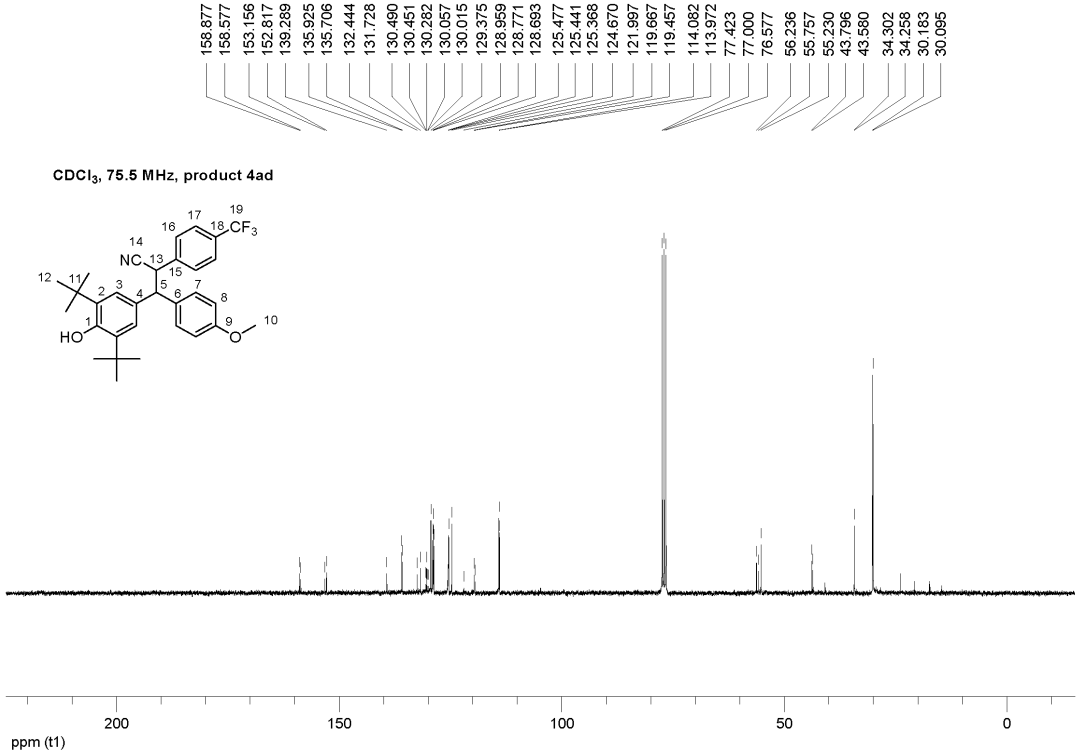


^{13}C-NMR



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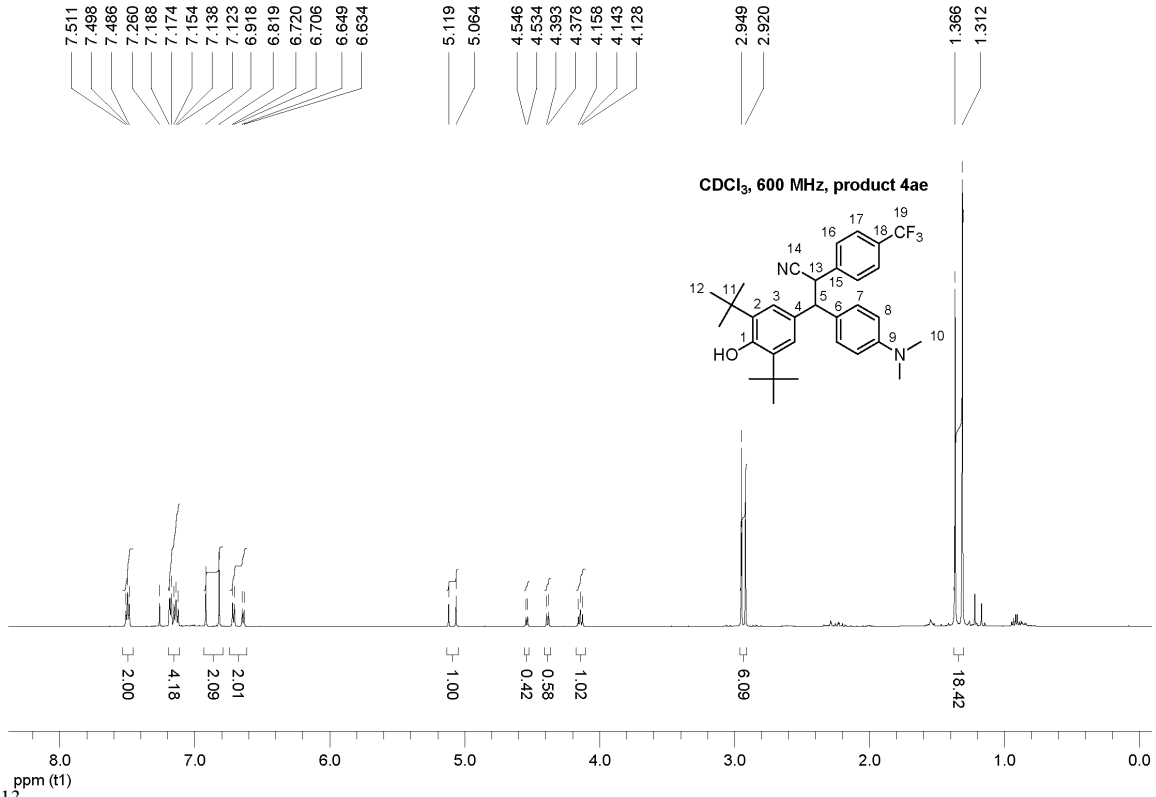

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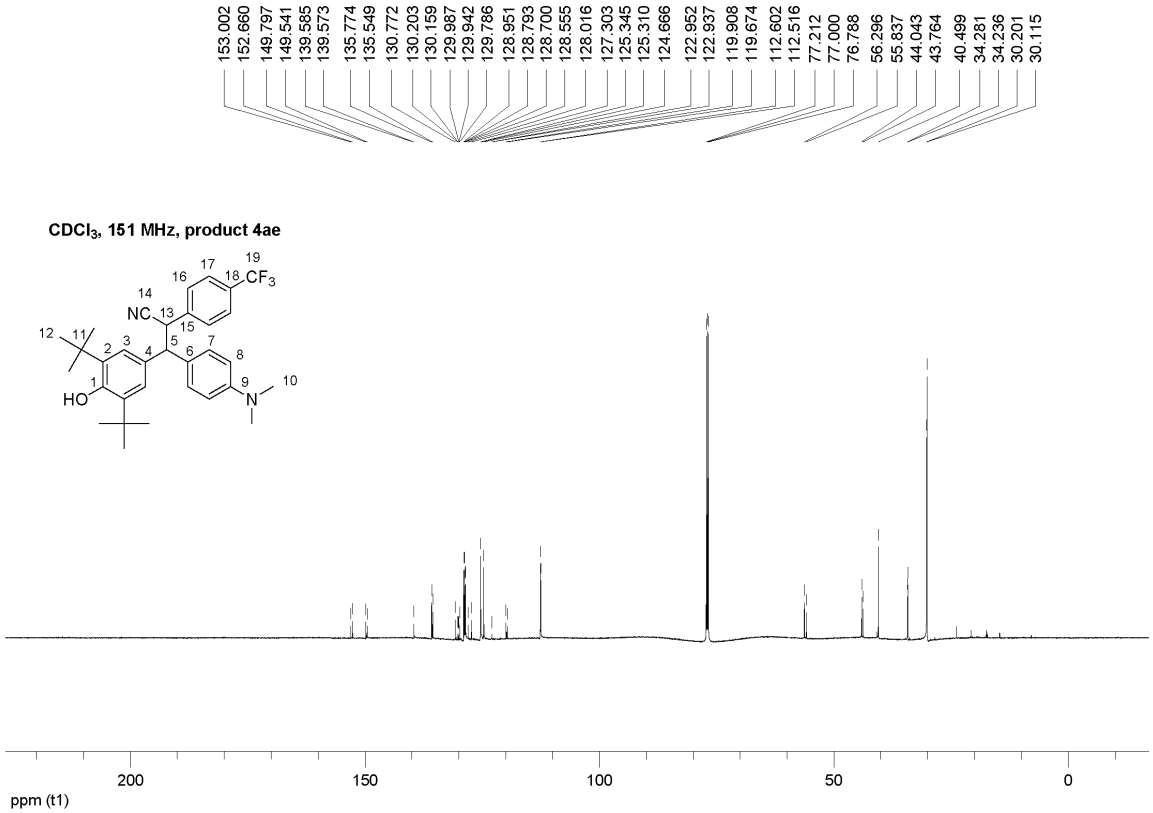

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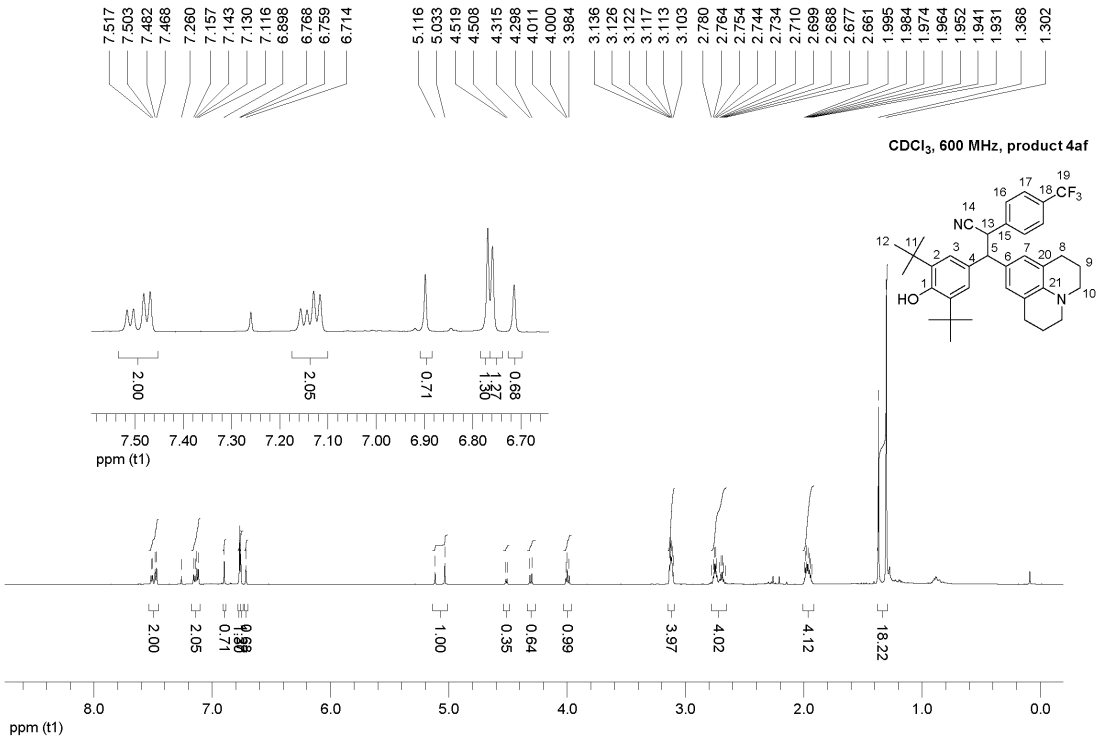

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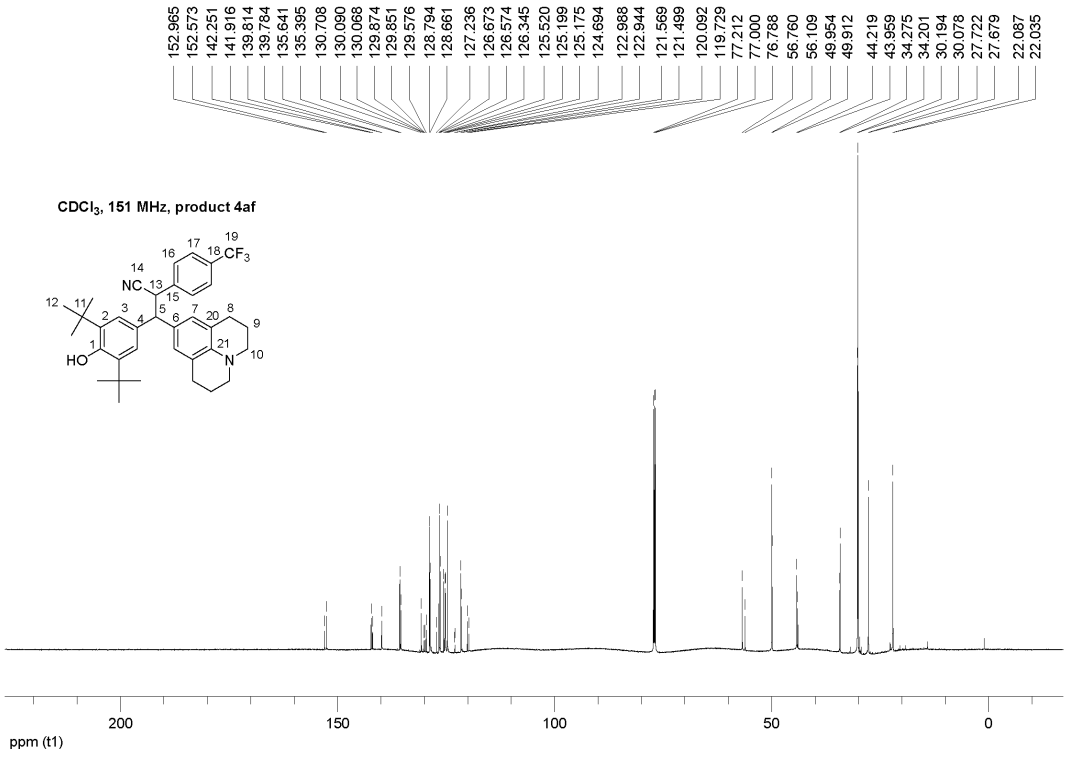

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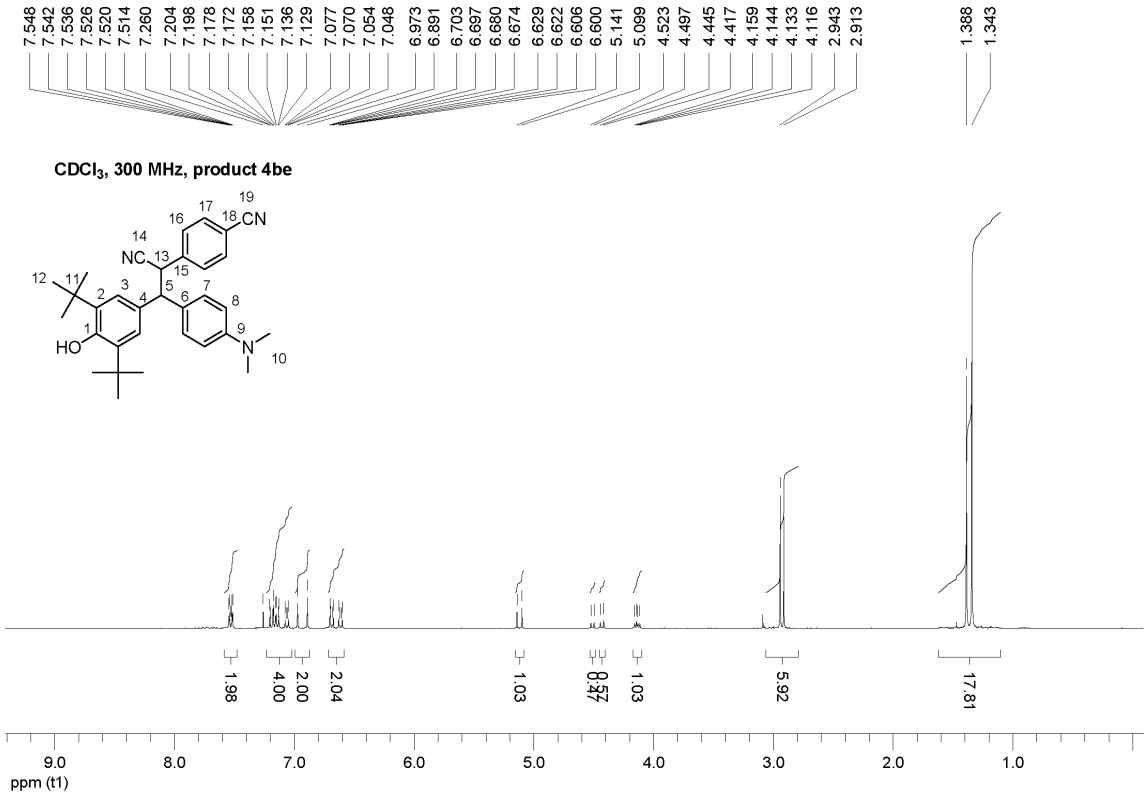

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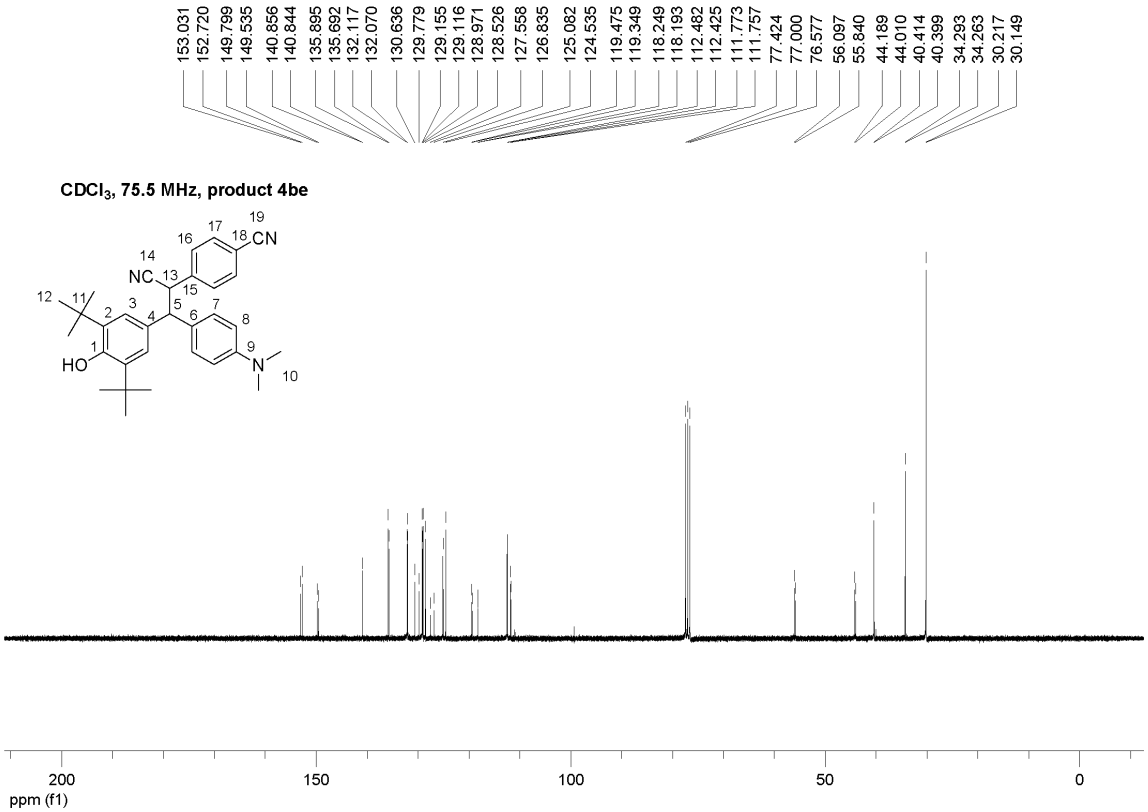

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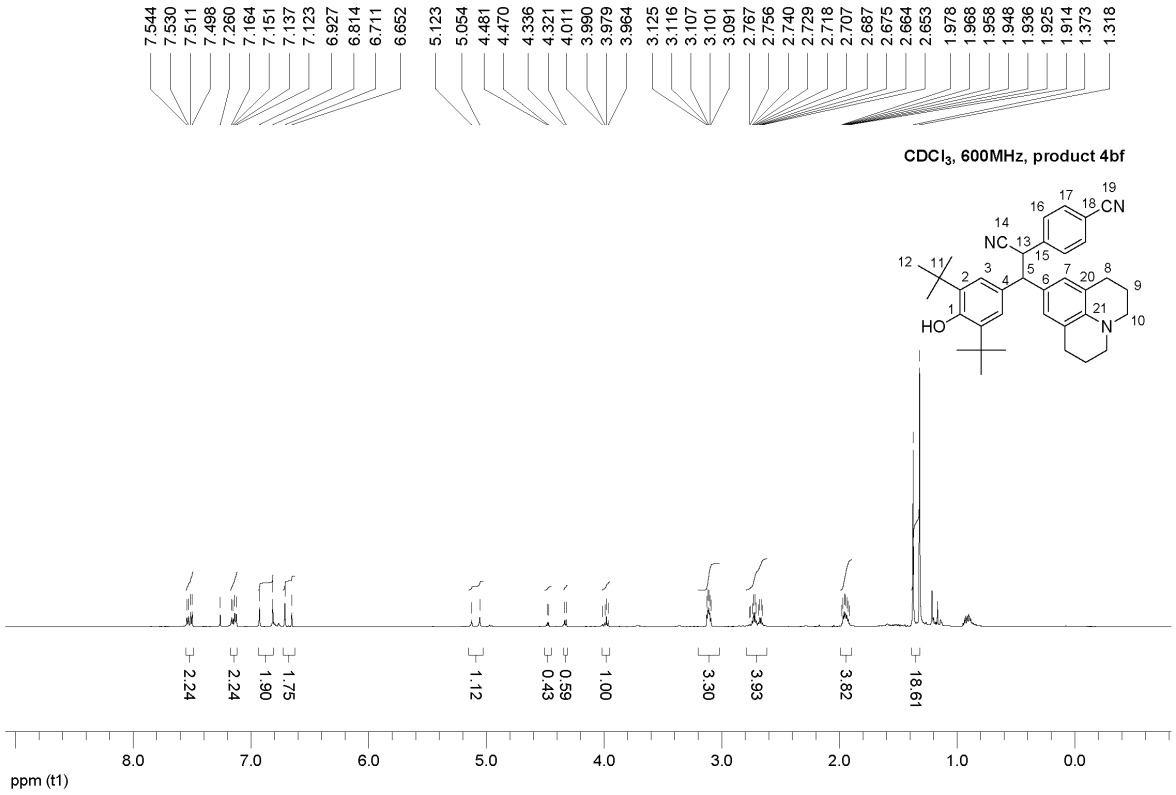

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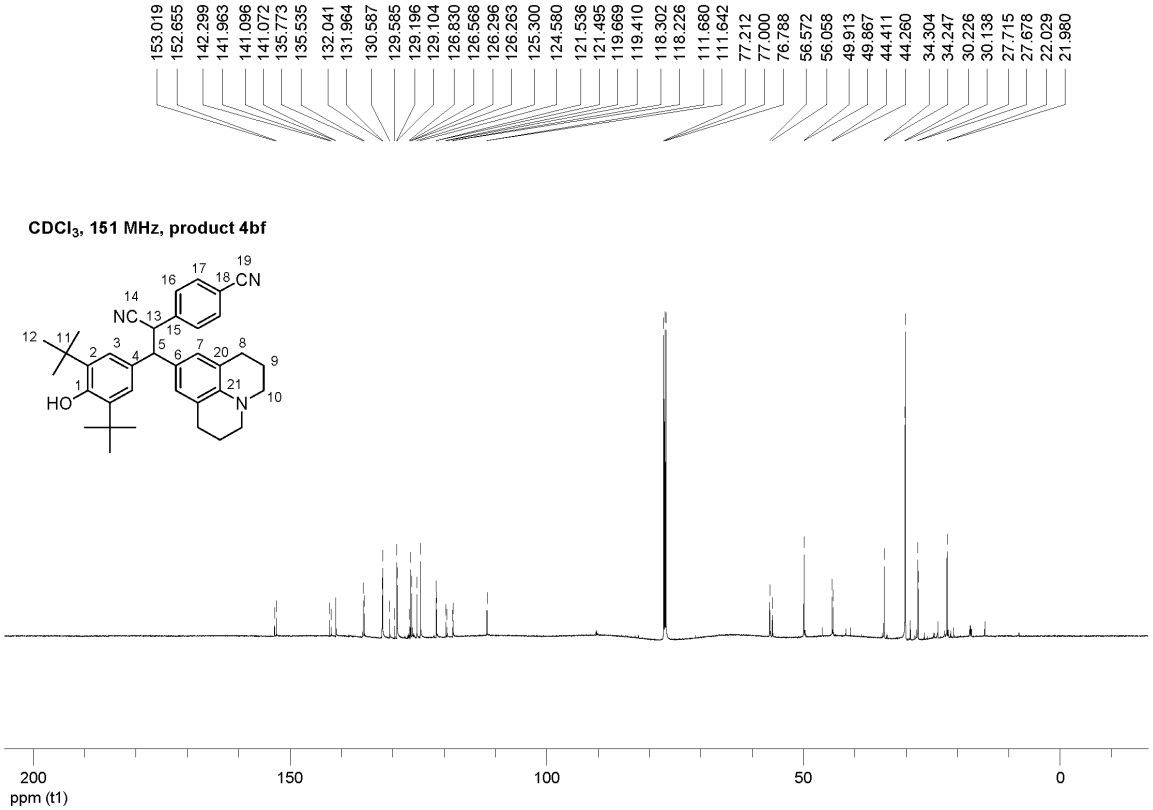

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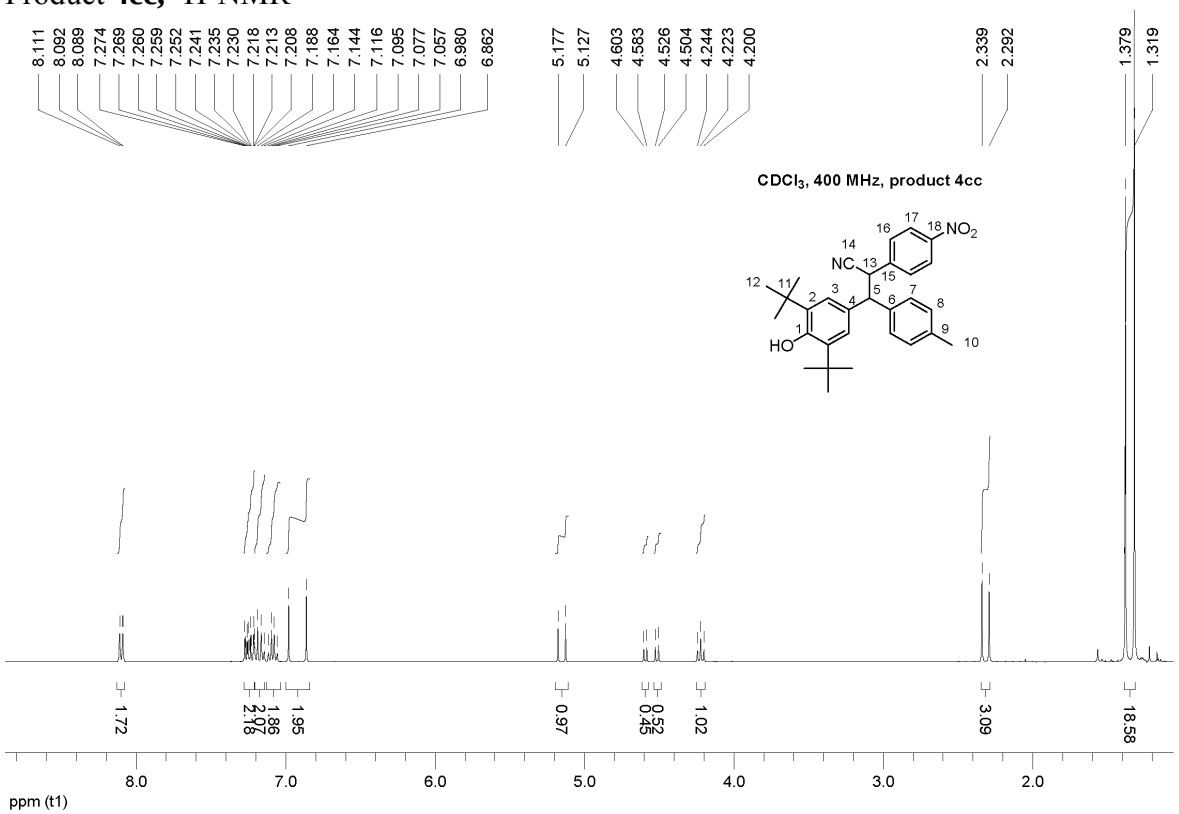

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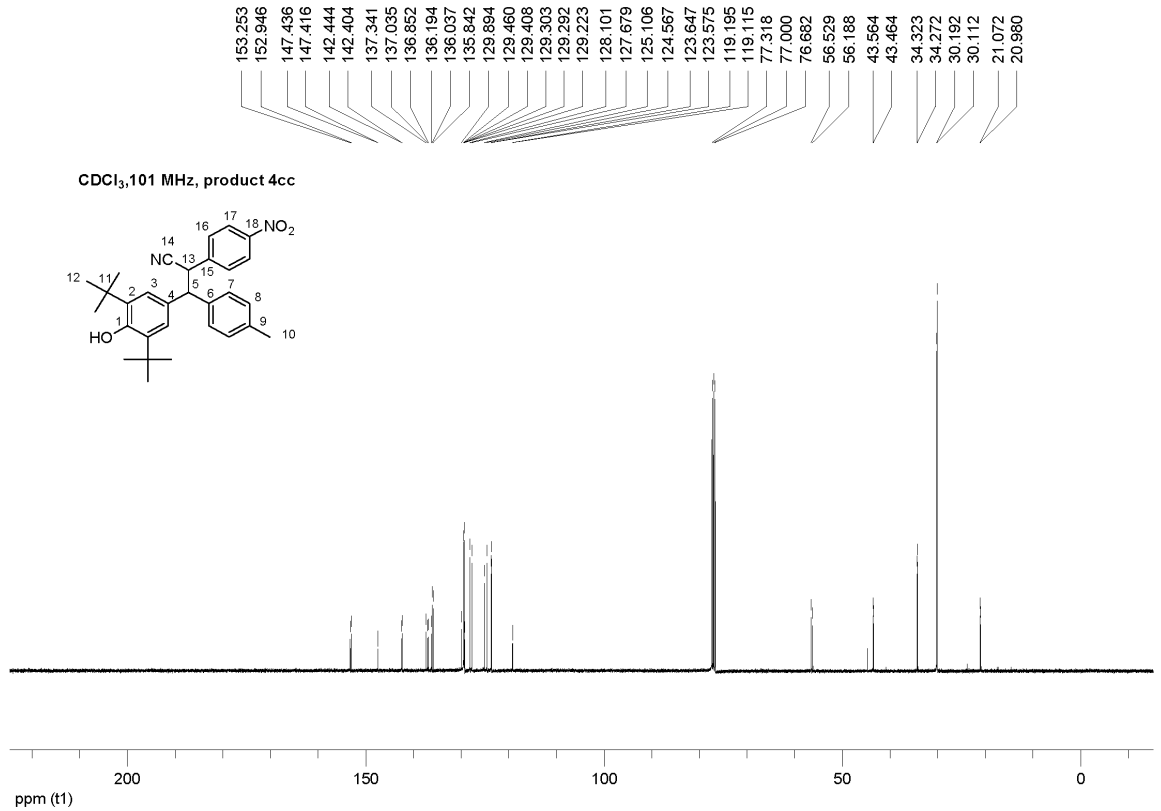

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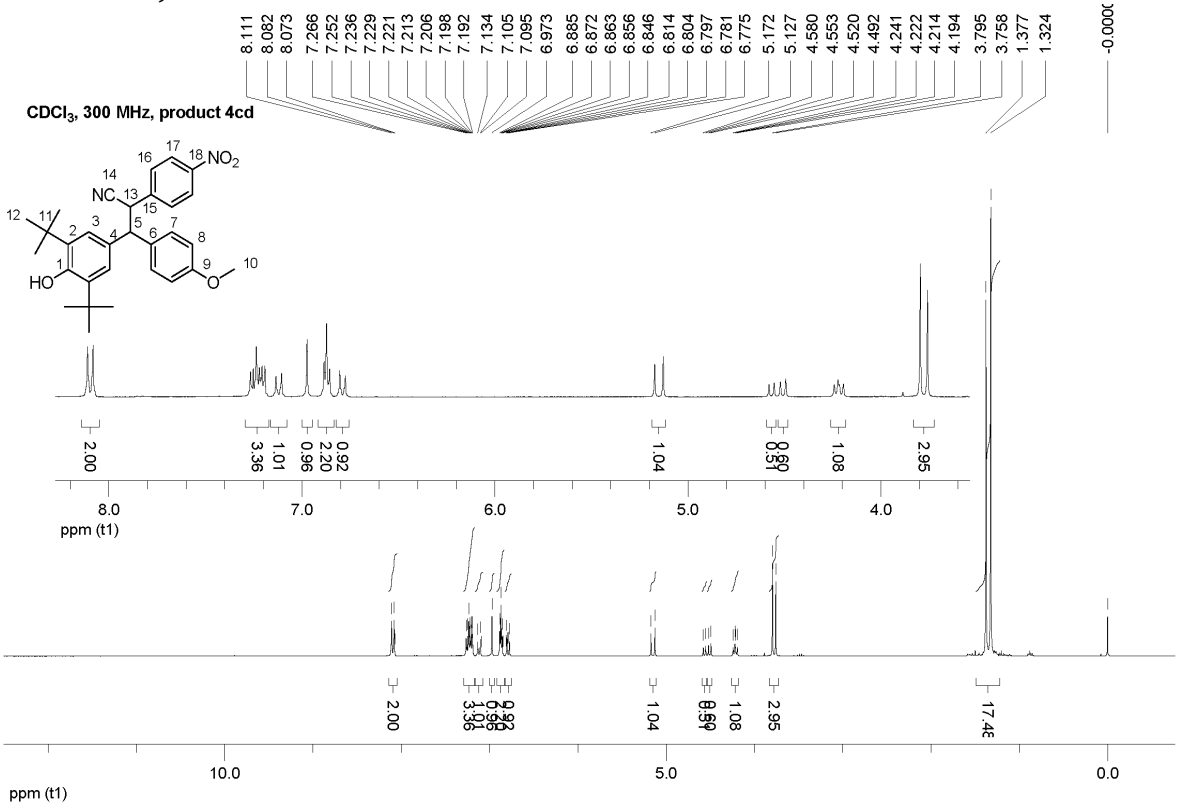

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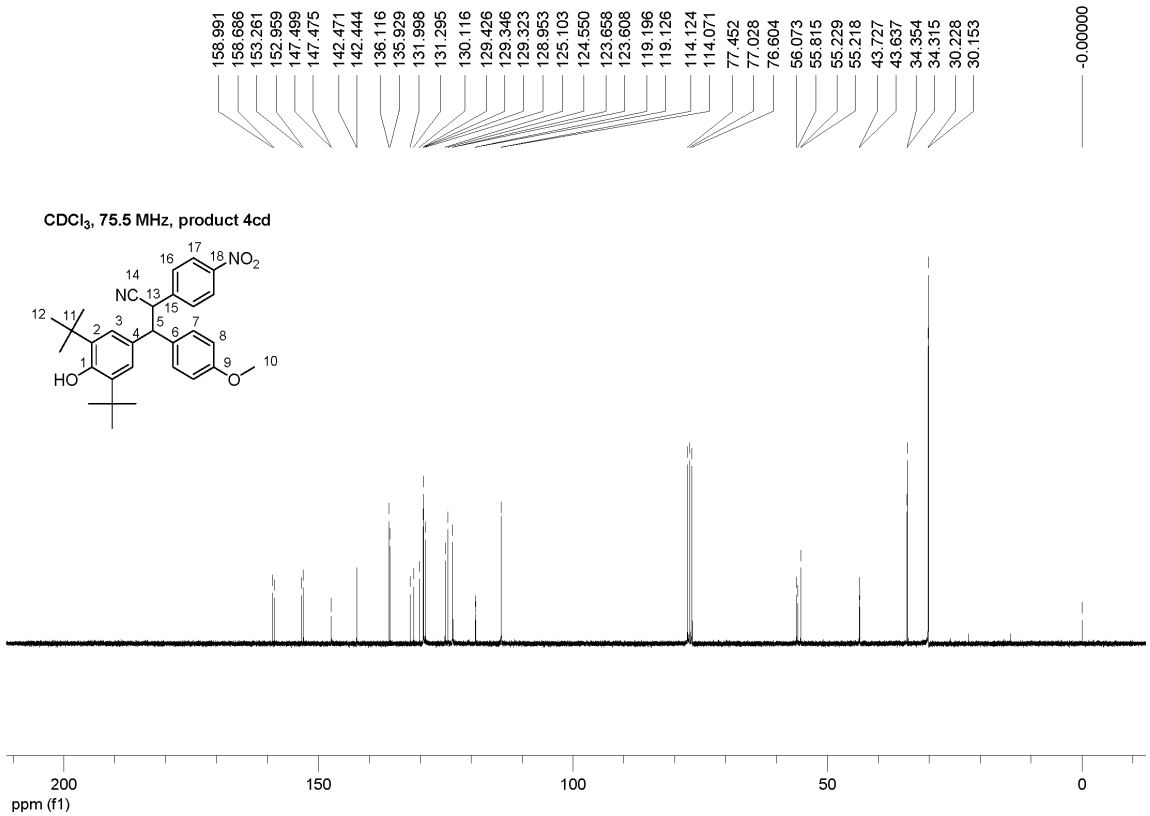

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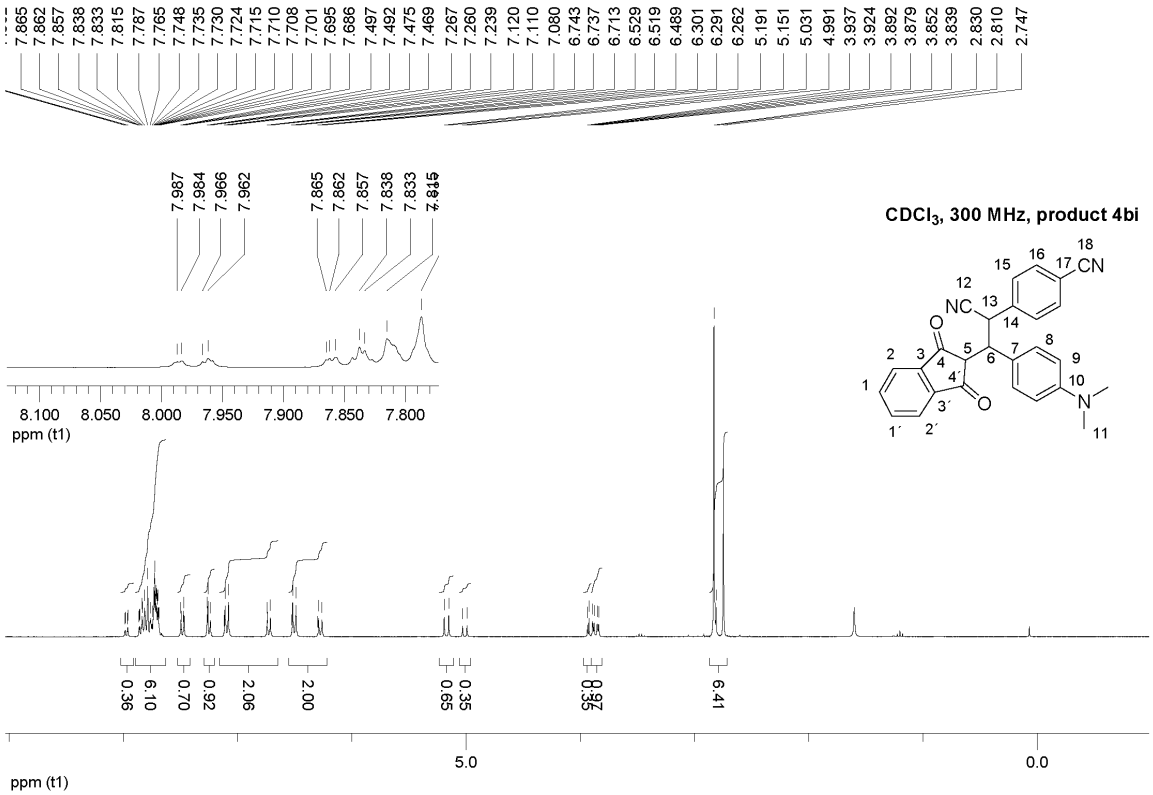

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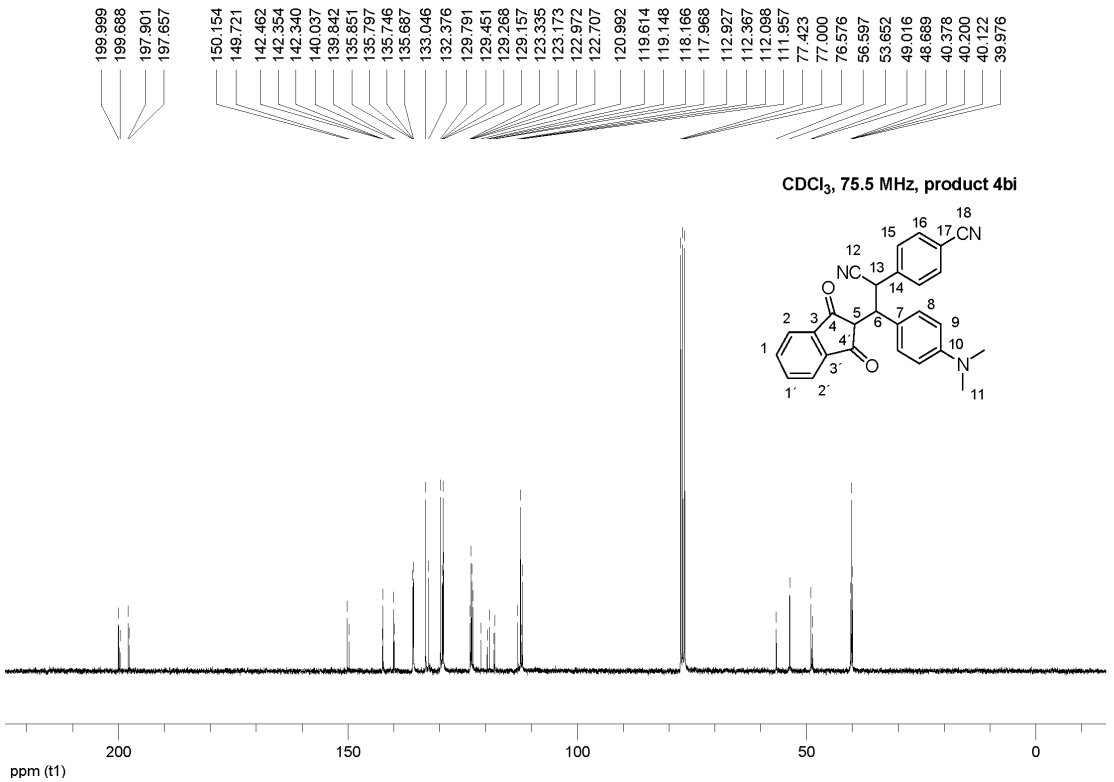

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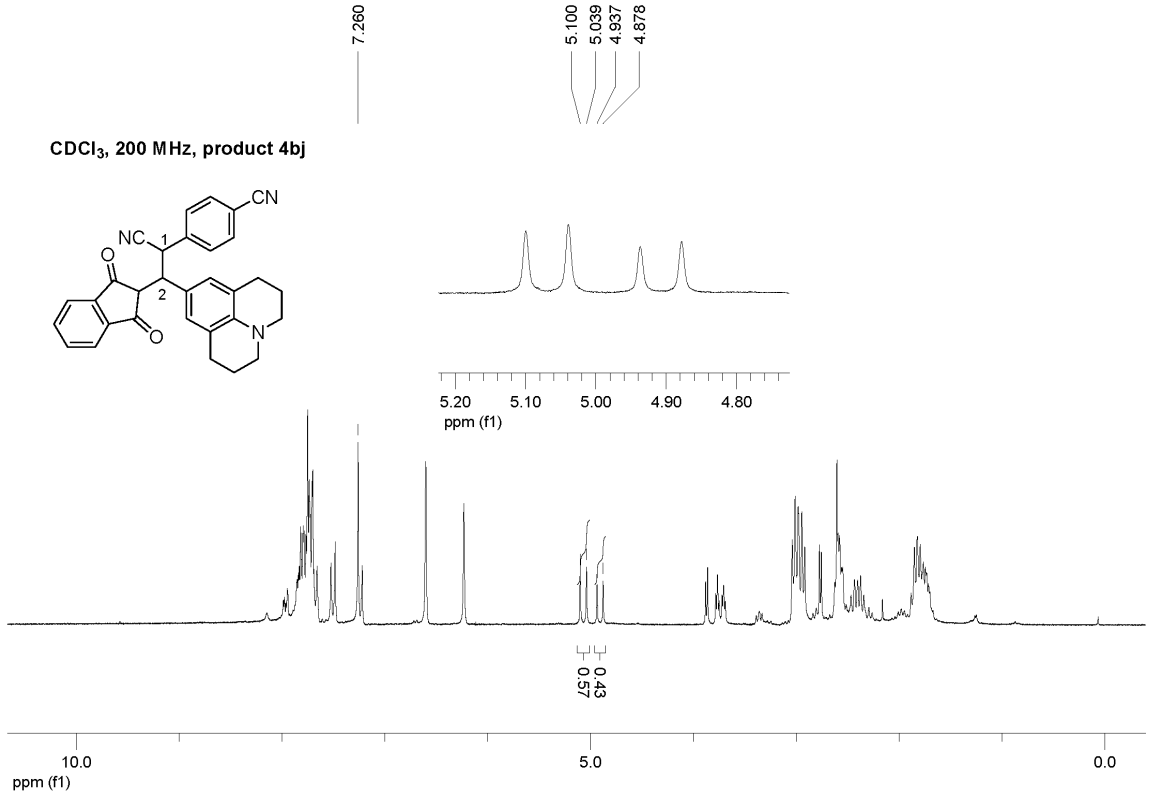

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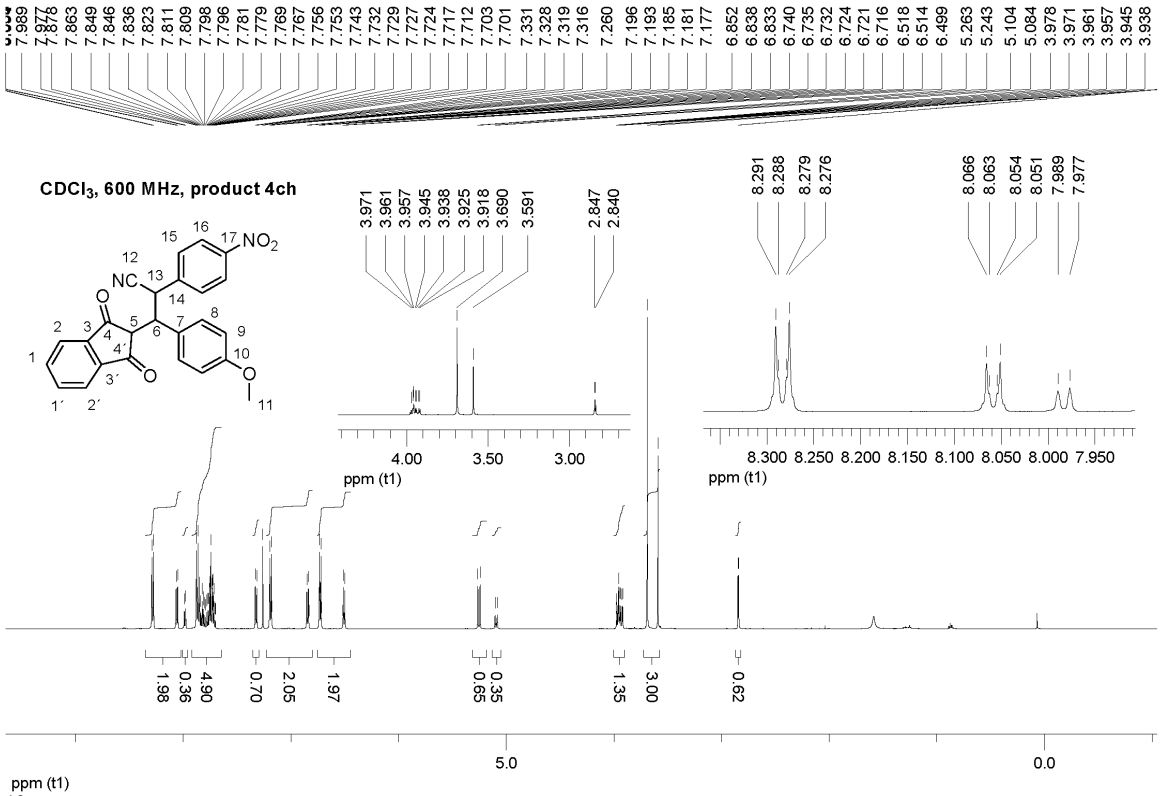

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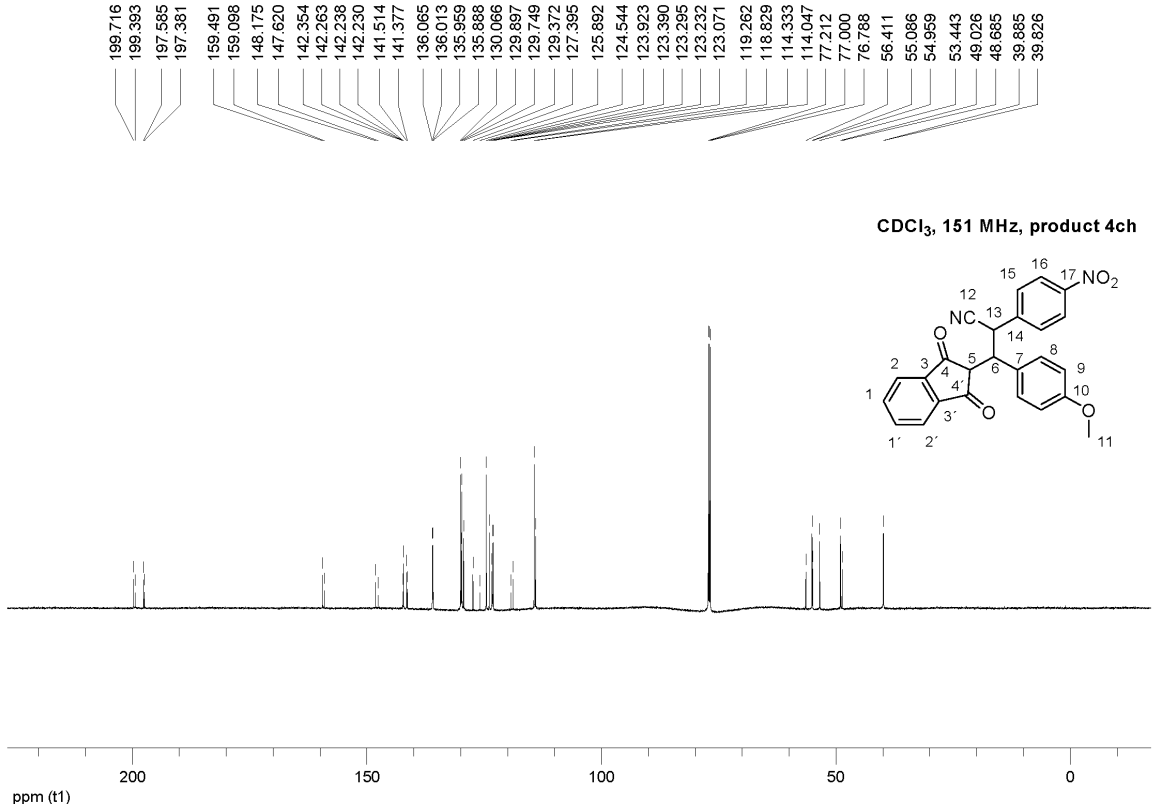

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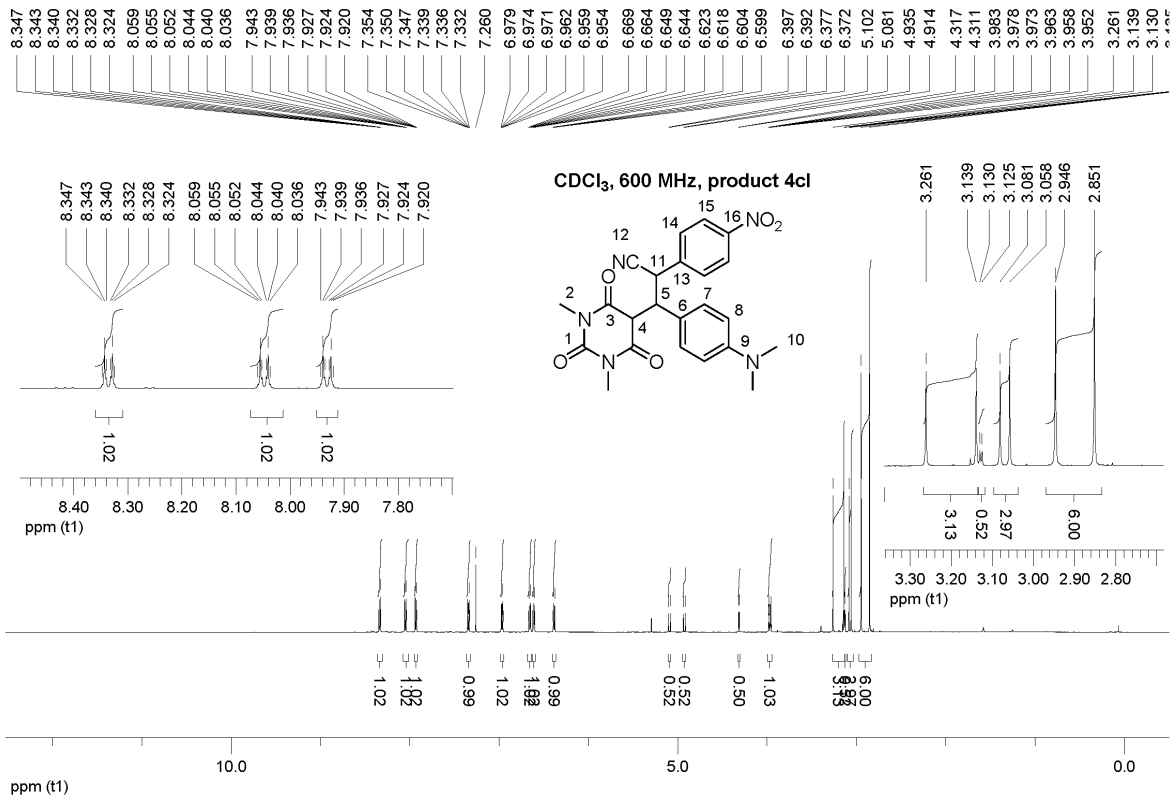

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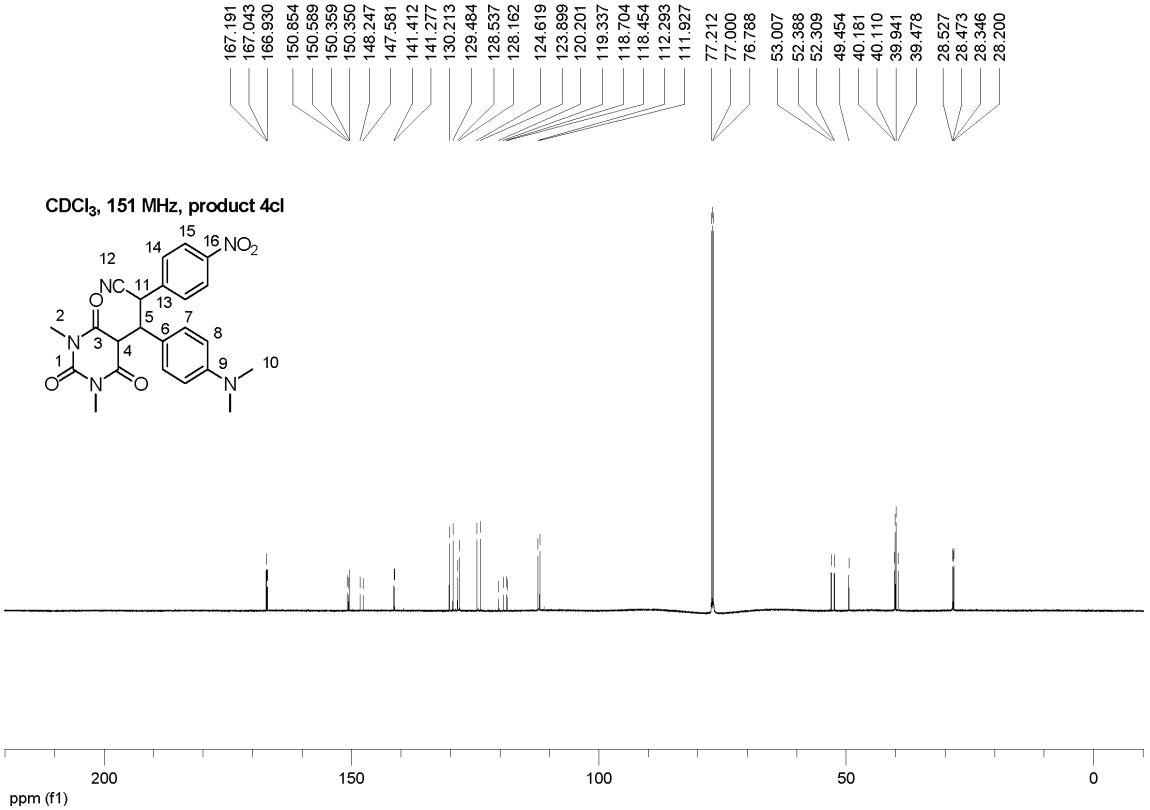

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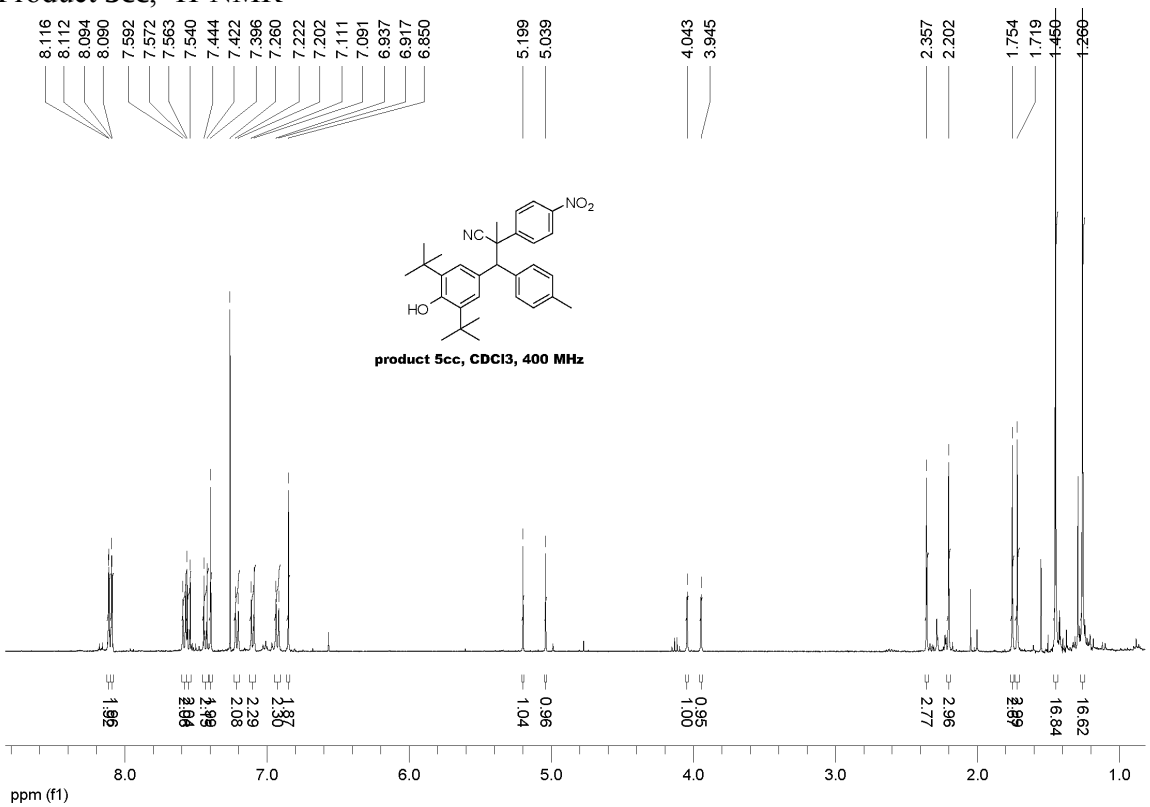

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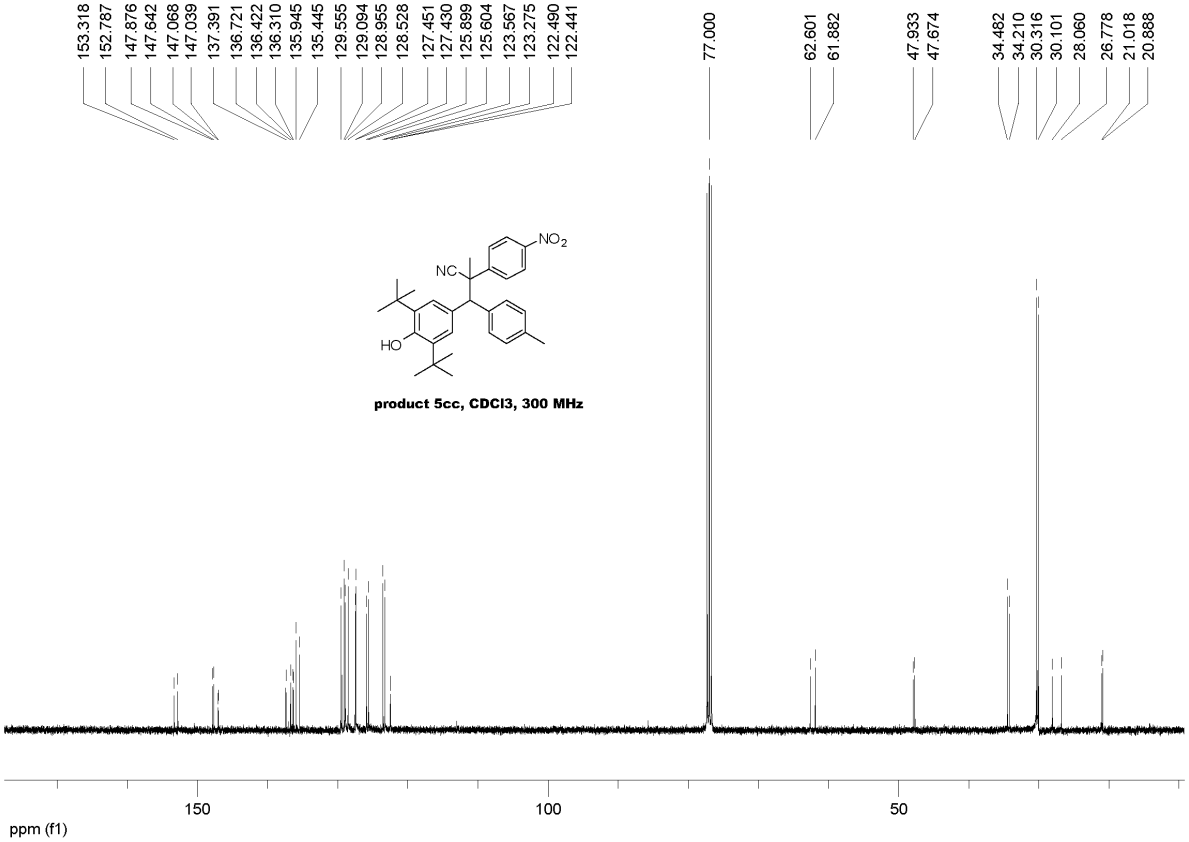

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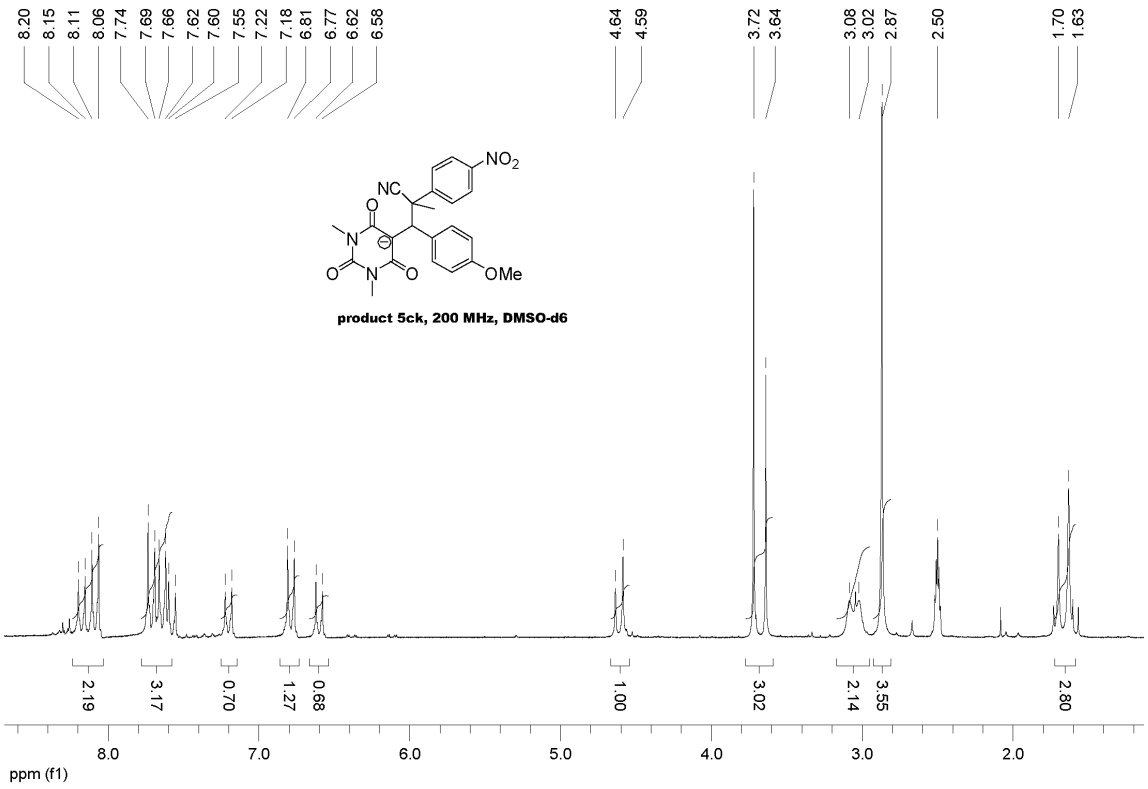

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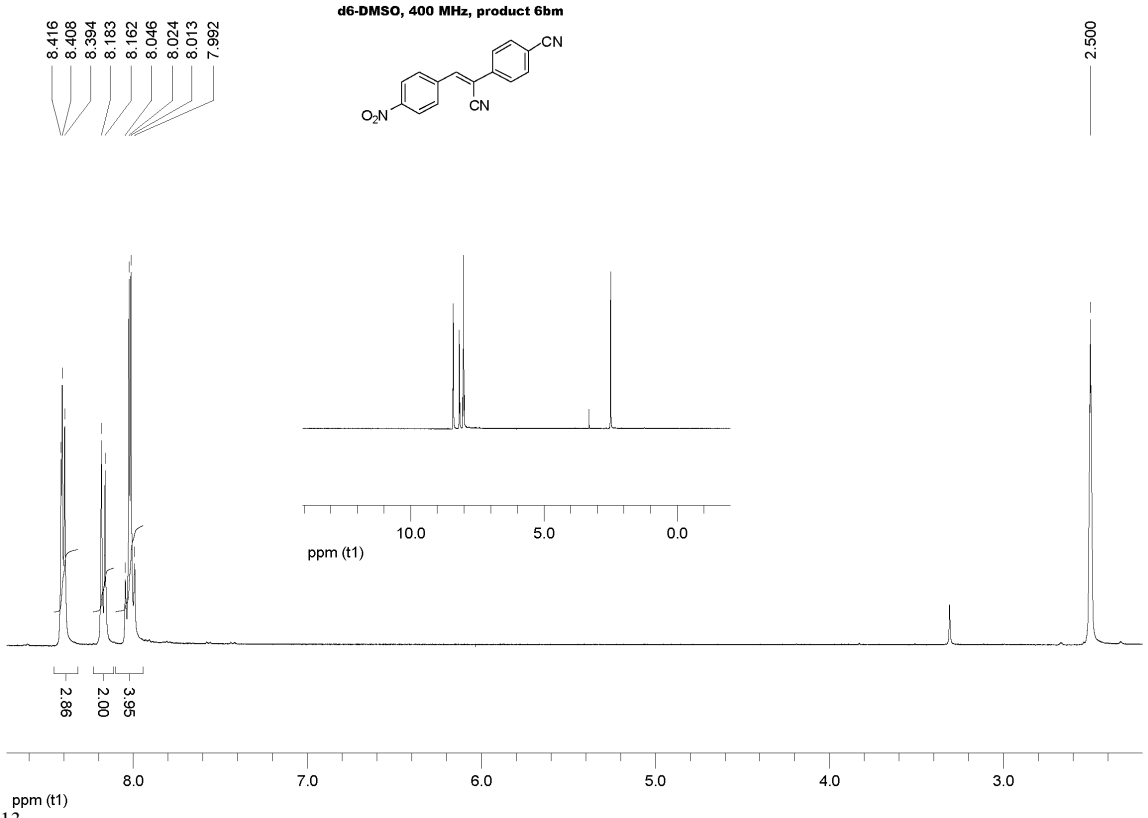

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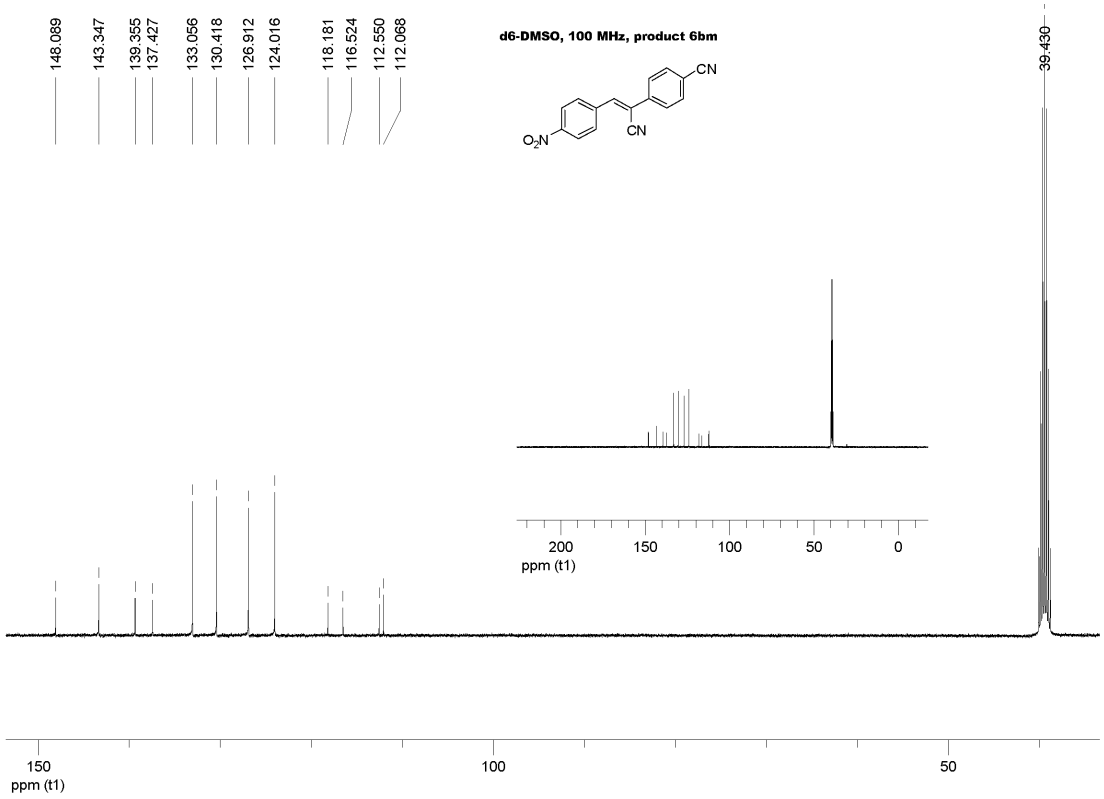

Product **6bn**

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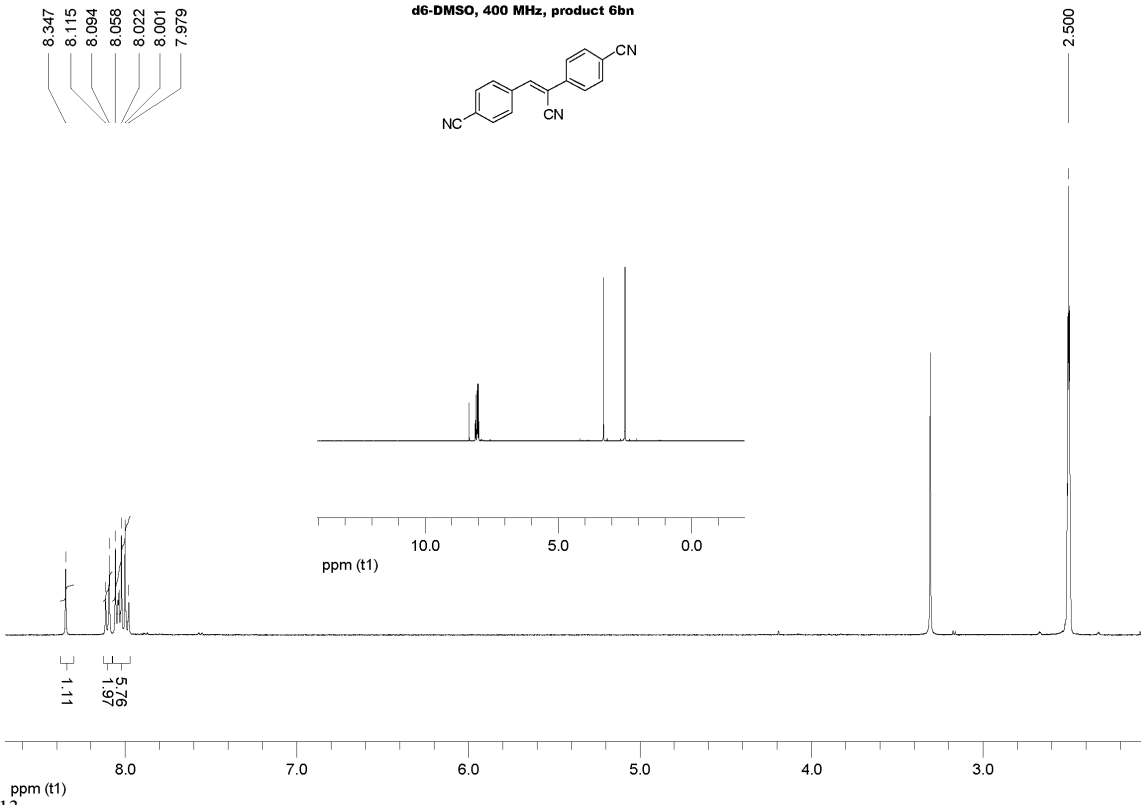

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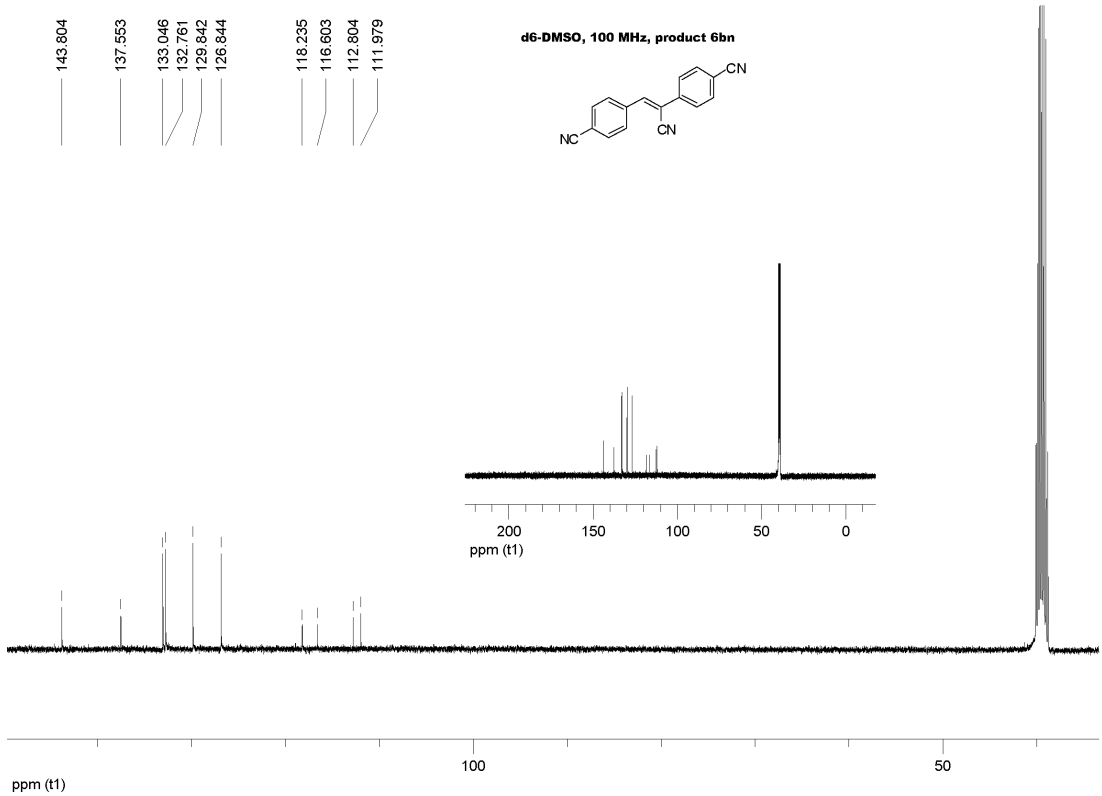
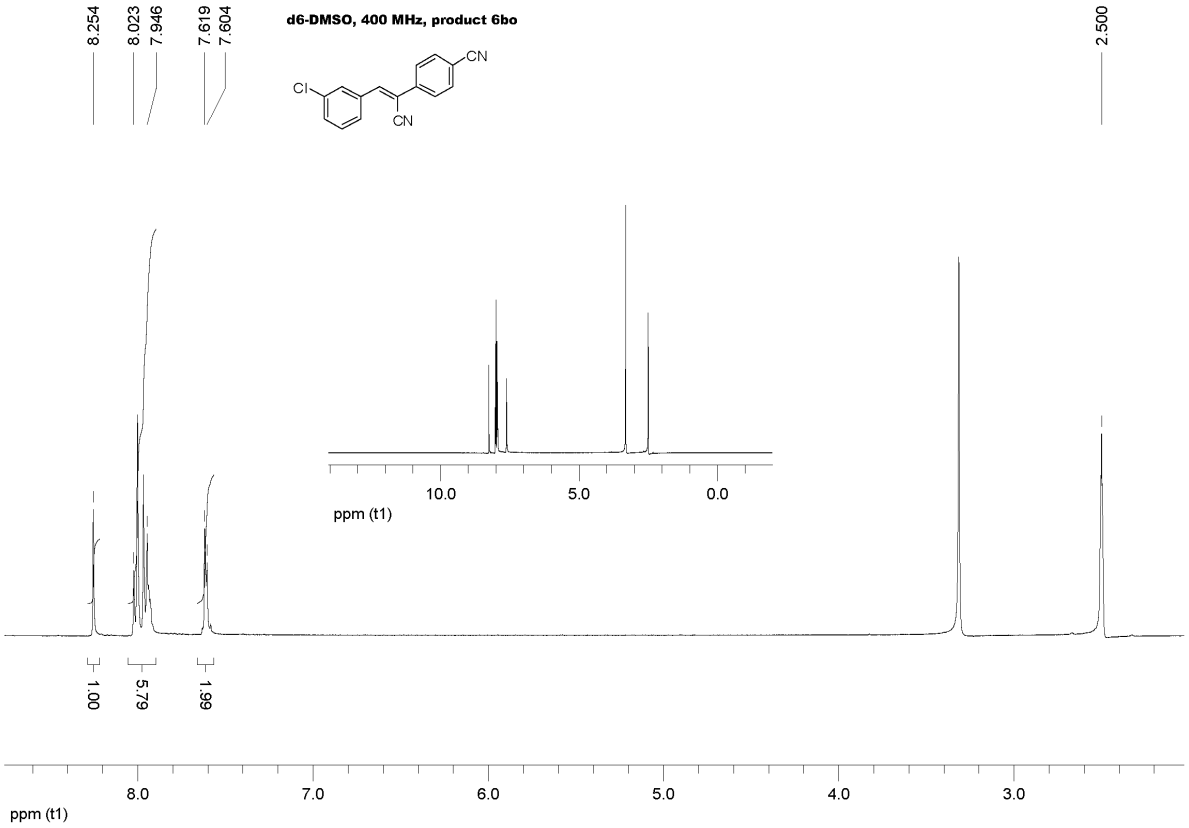


Product **6bo**

^{1}H-NMR



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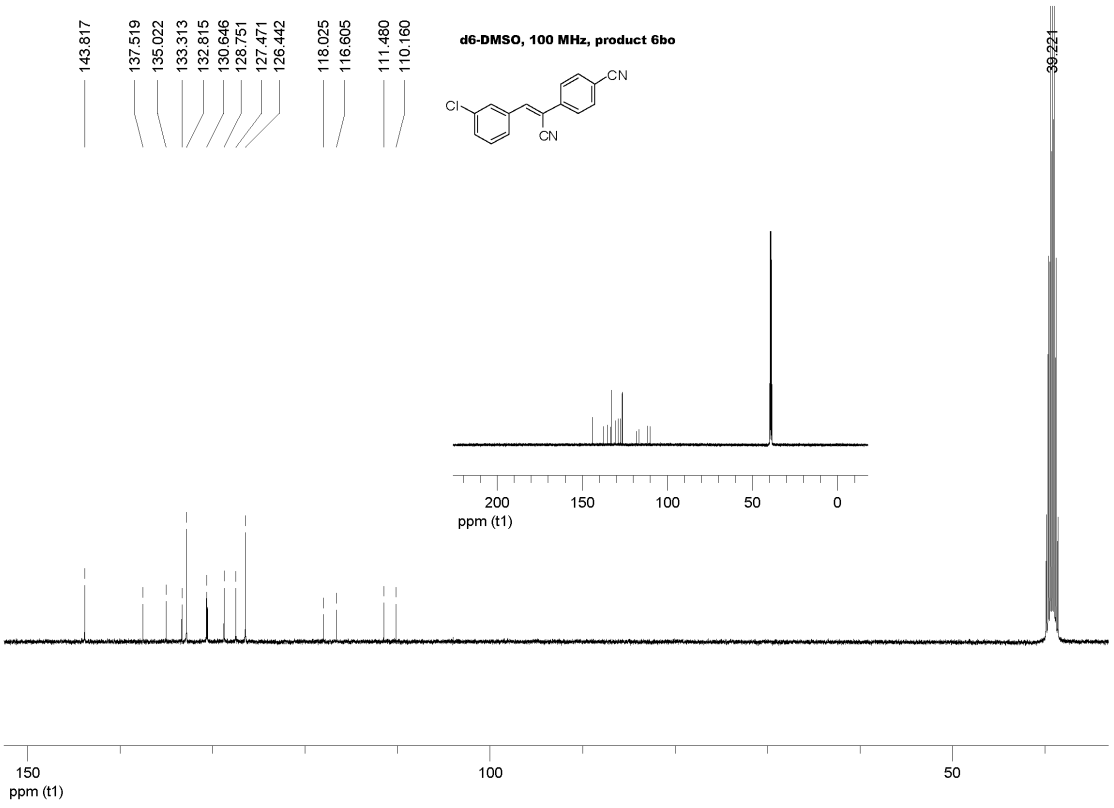

Product **6bp**

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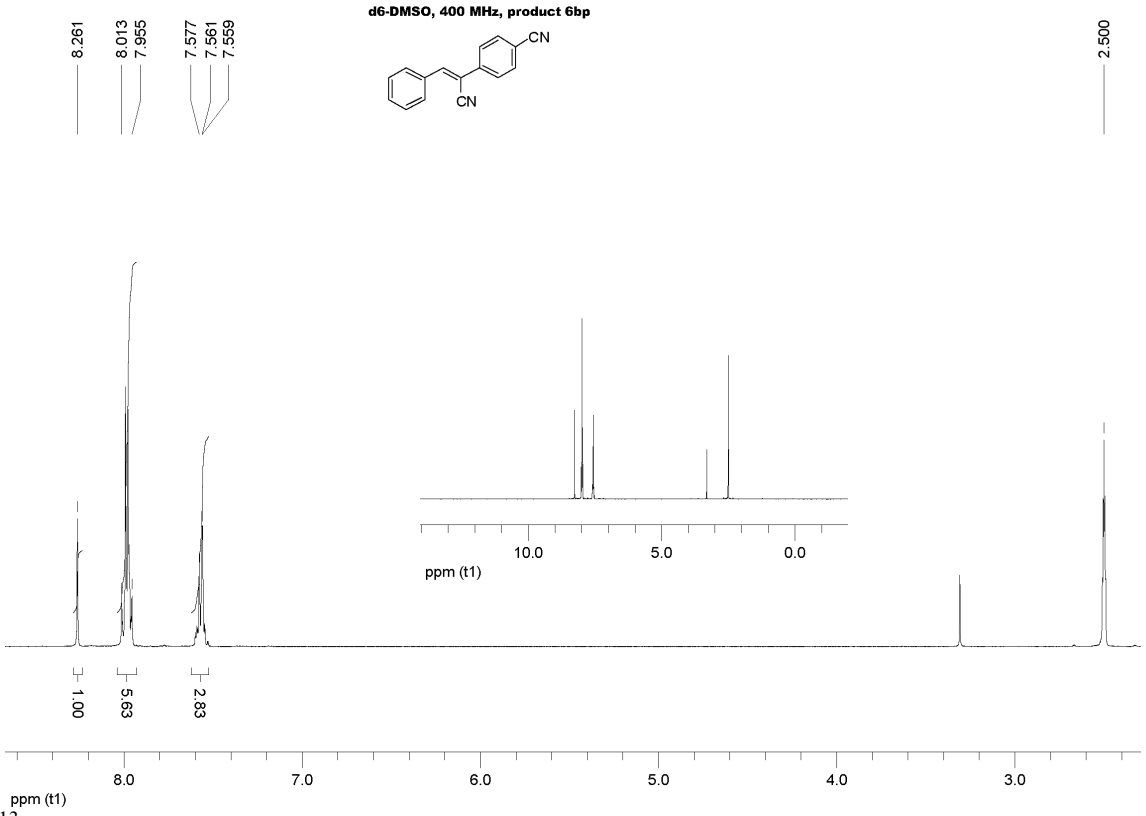

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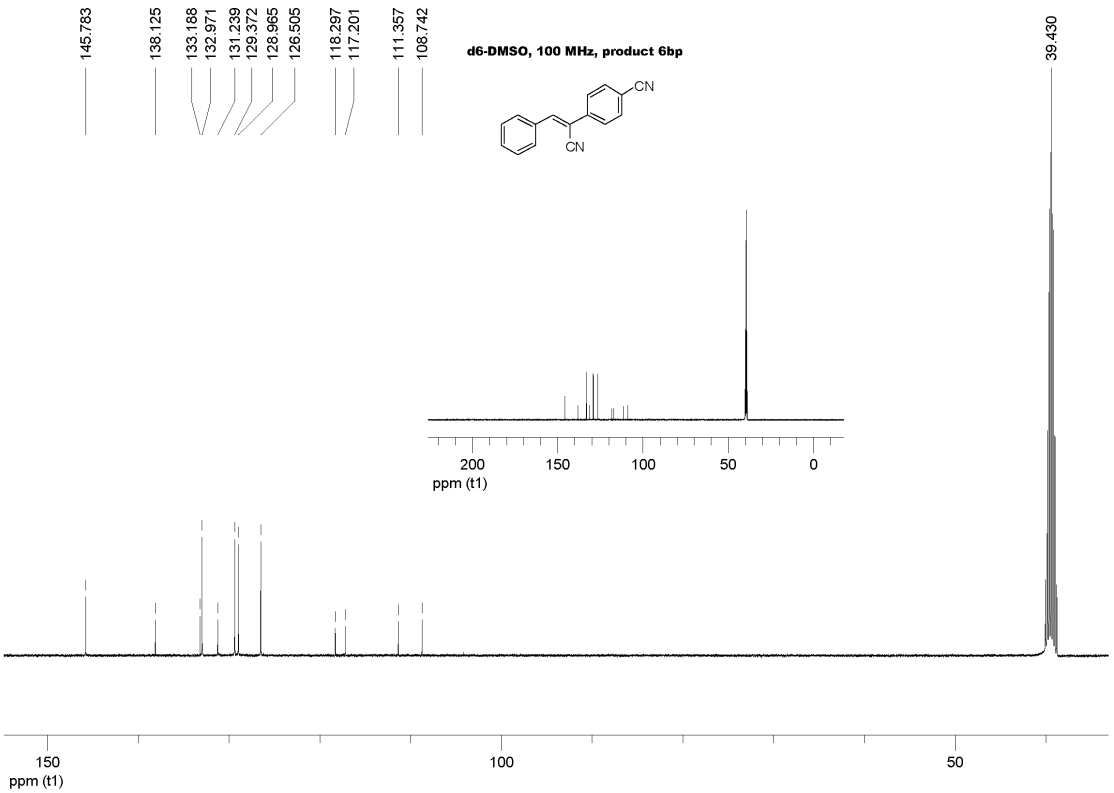
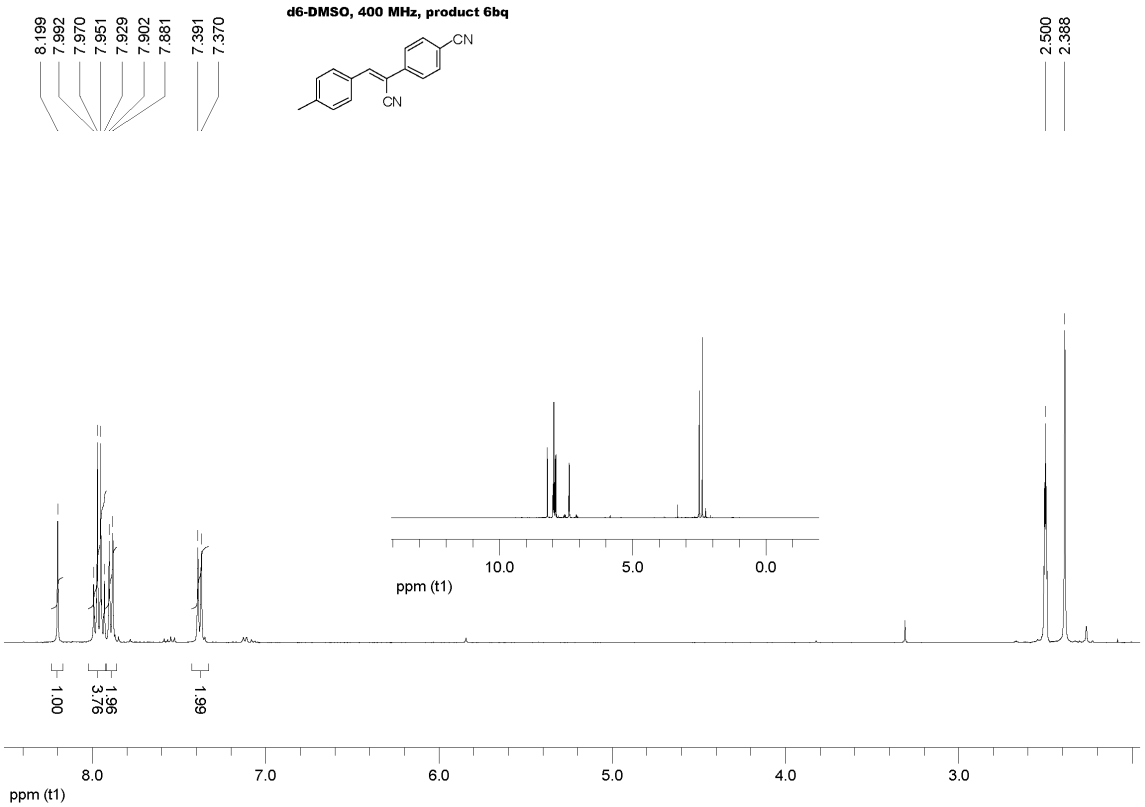
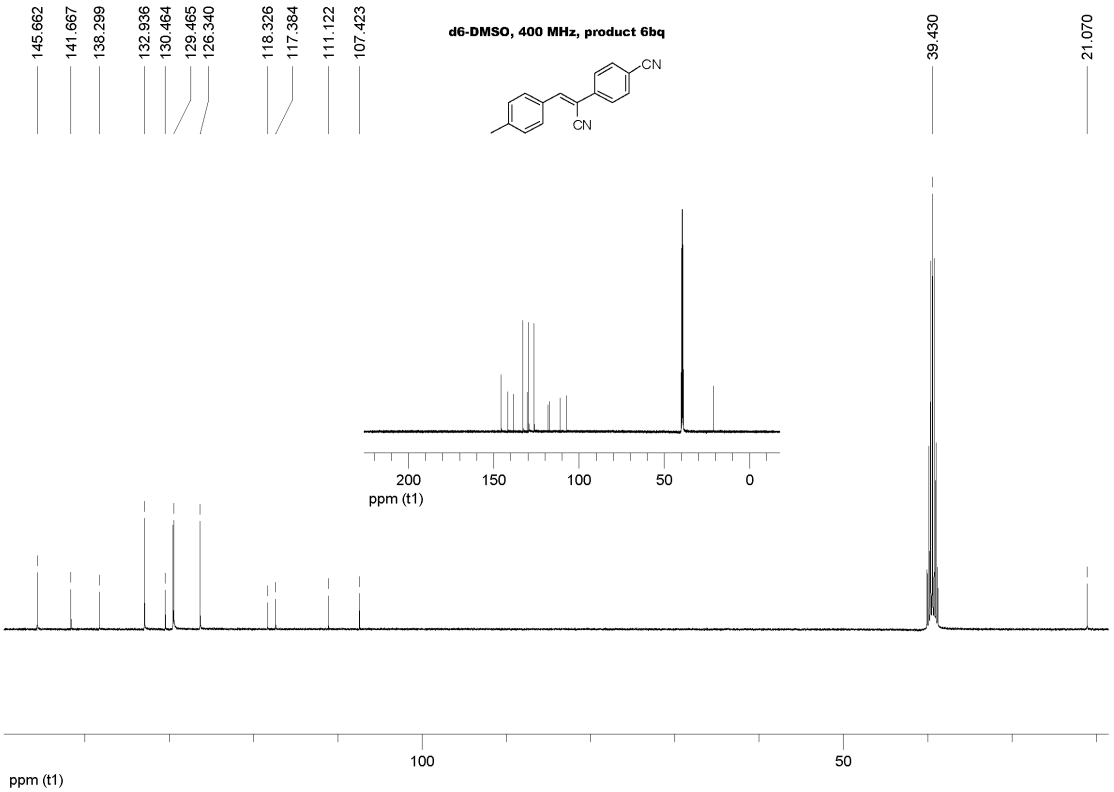


Product **6bq**

^{1}H-NMR

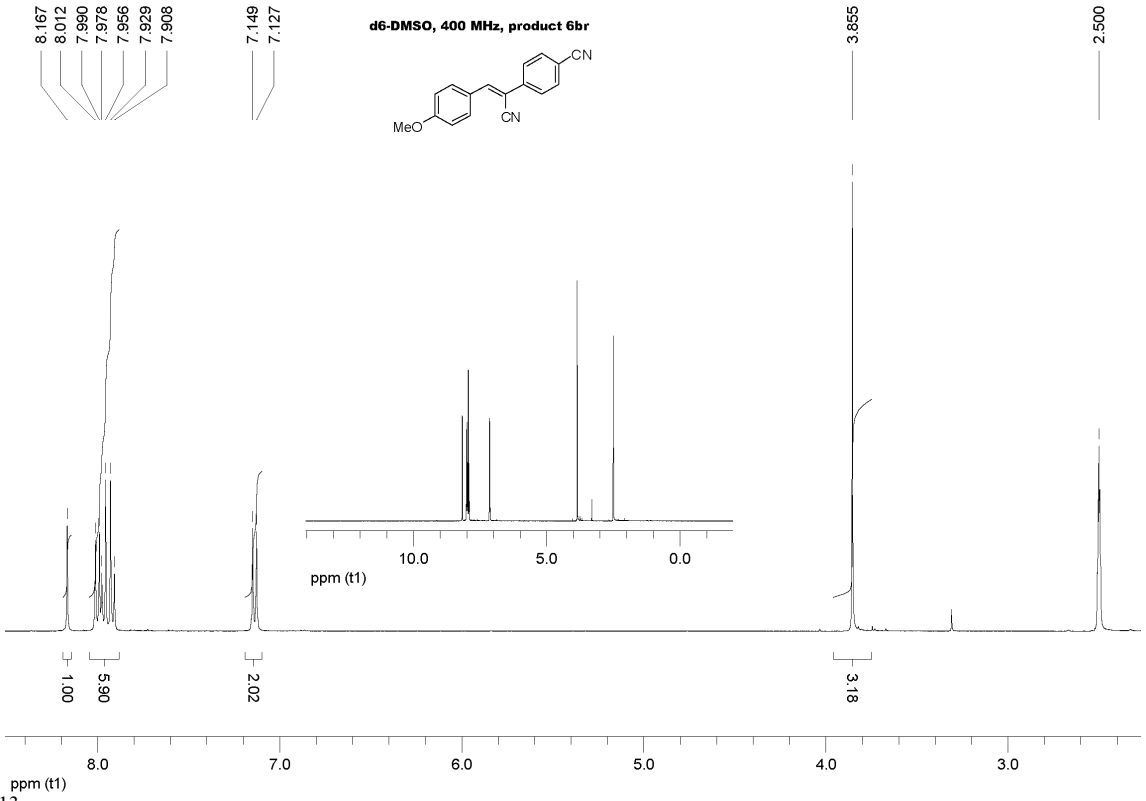


^{13}C-NMR



Product **6br**

^{1}H-NMR



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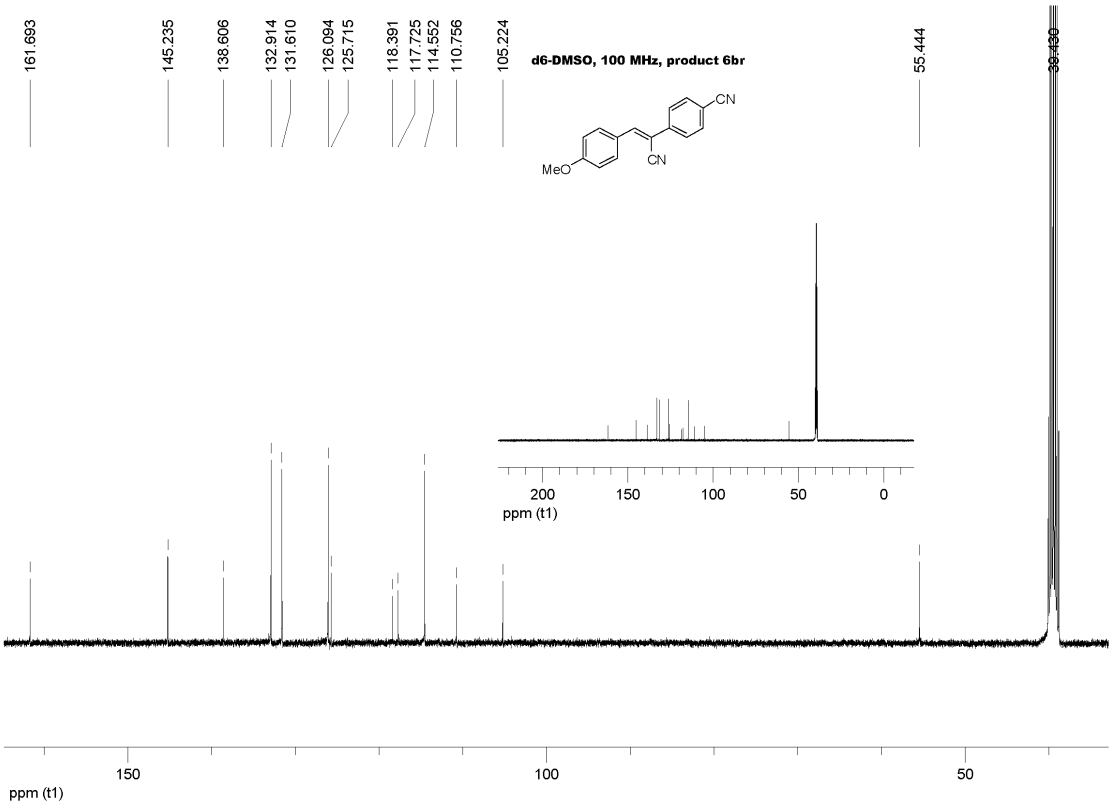
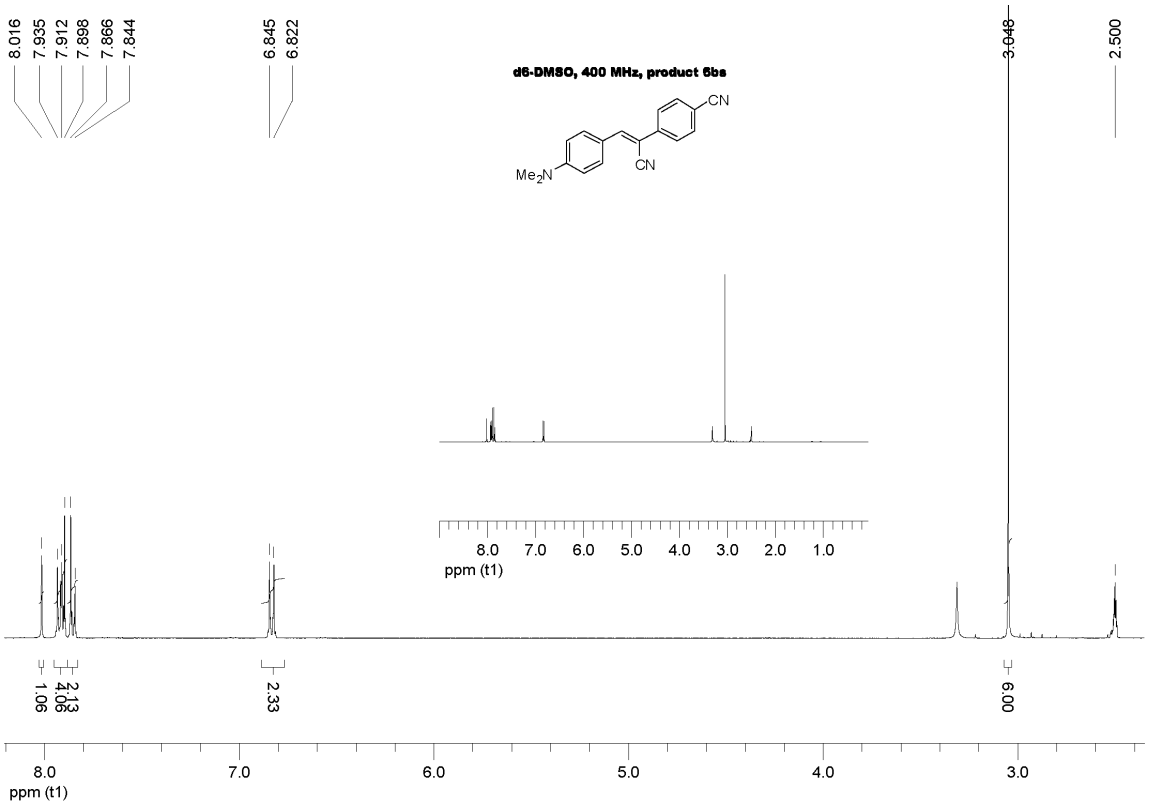


Product **6bs**

^{1}H-NMR



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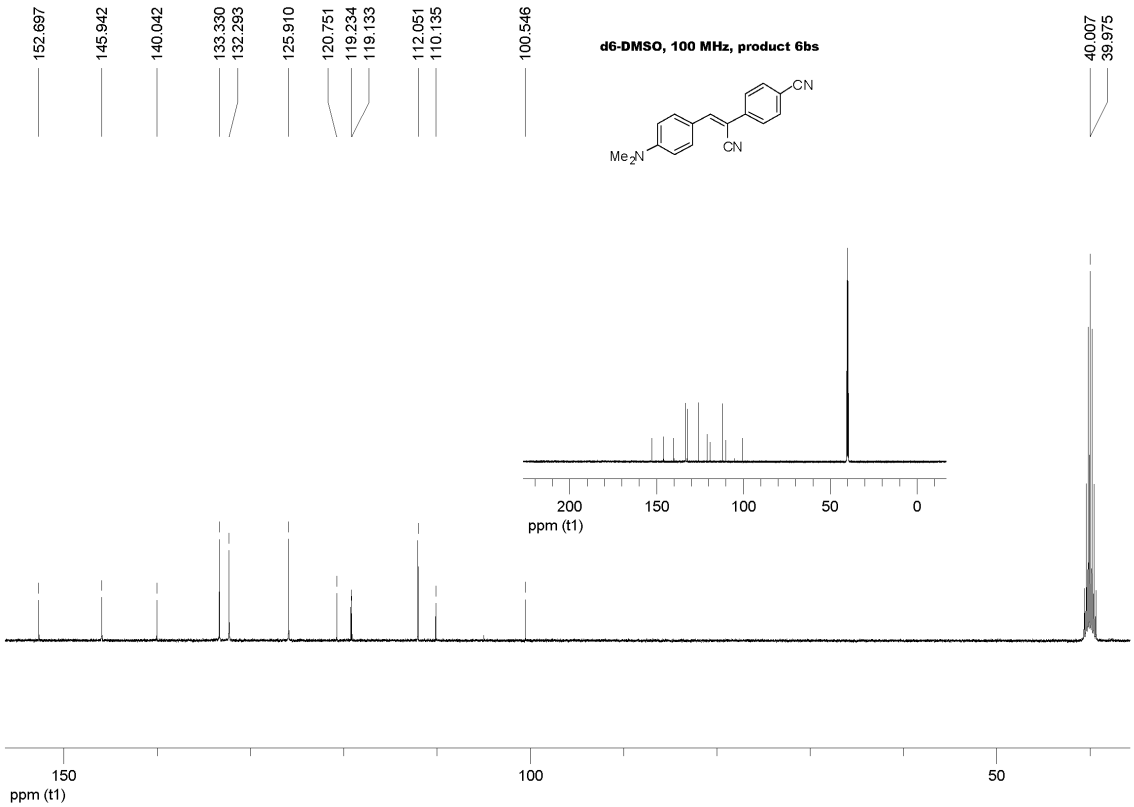

Product **6bu**

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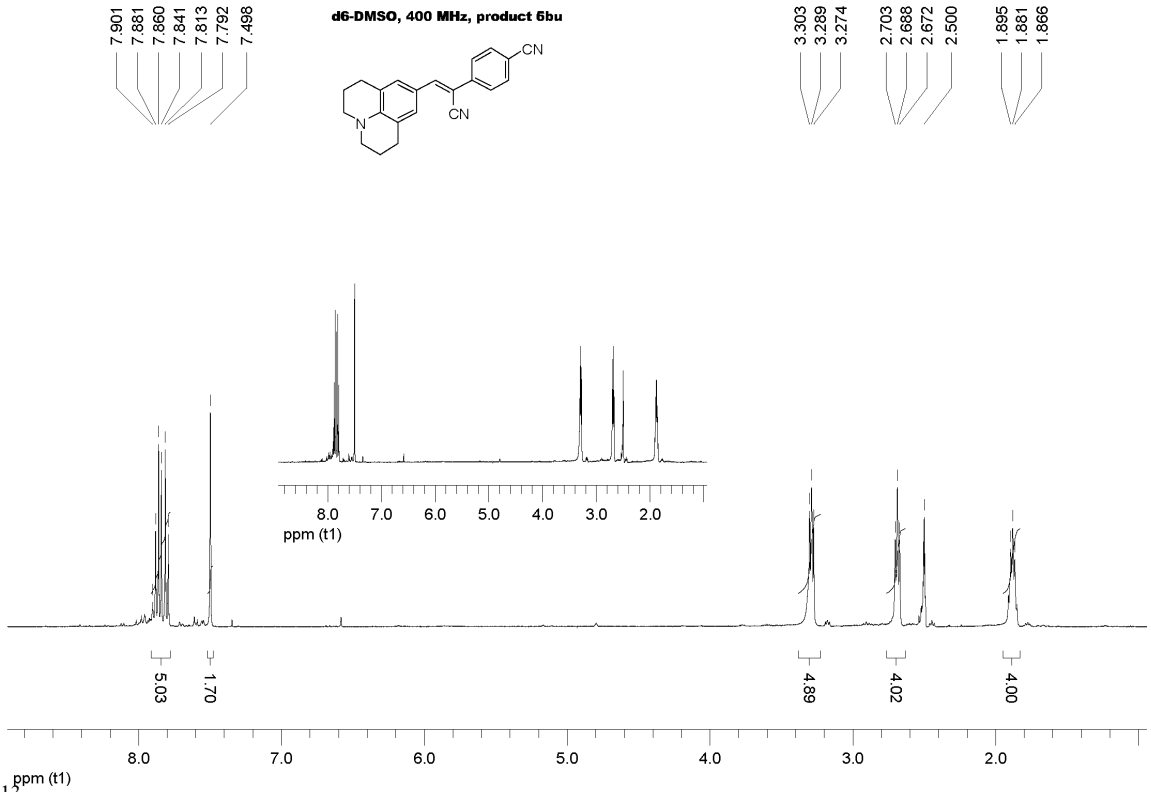

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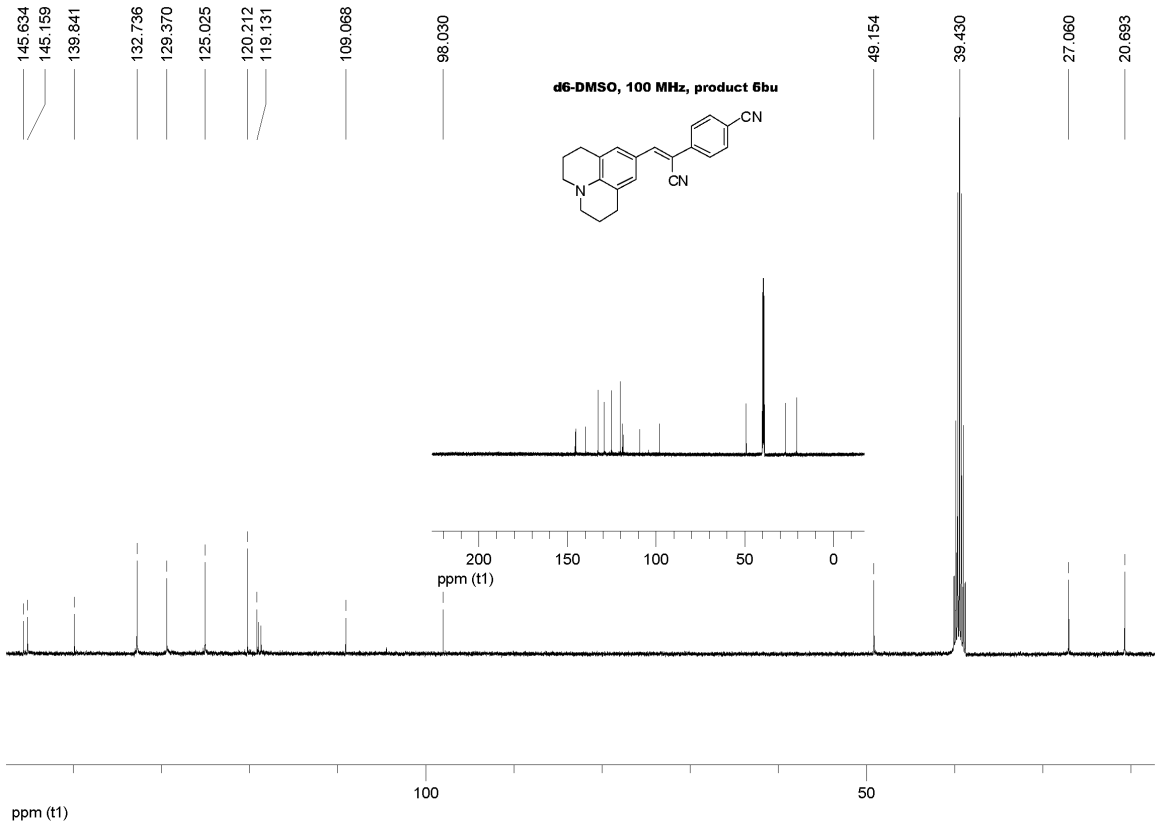

Product **6cm**

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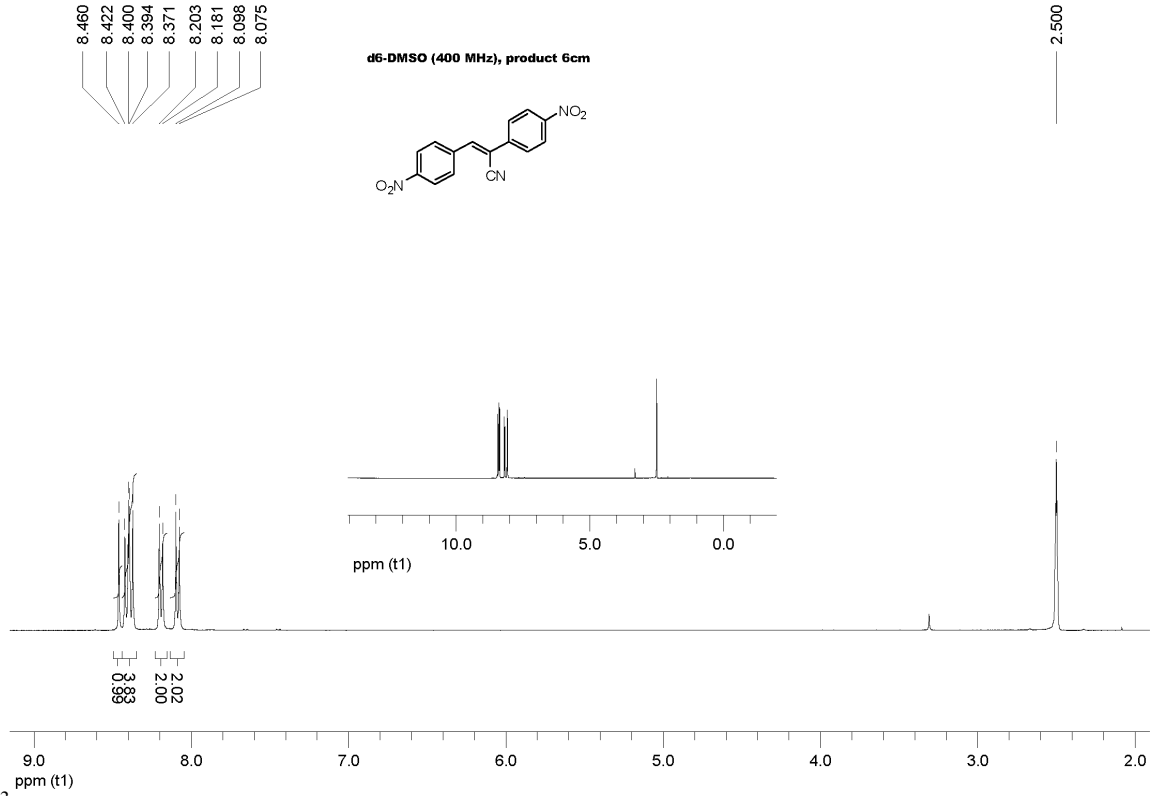

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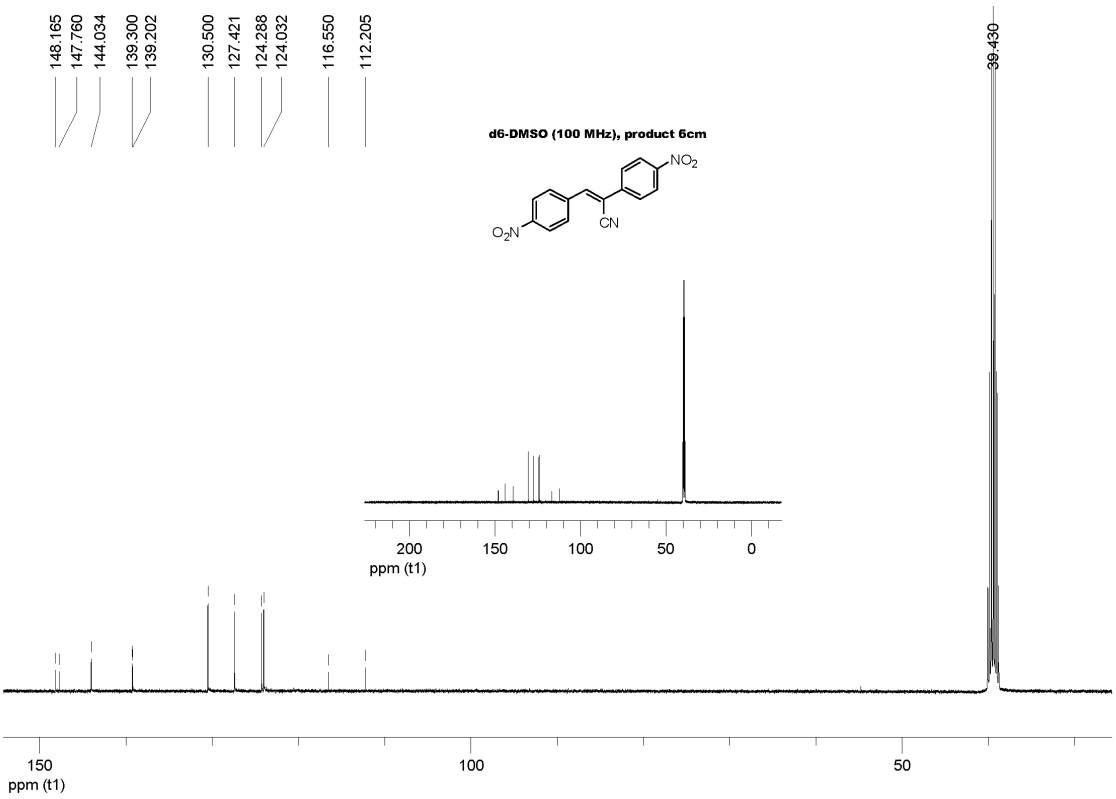

Product **6cn**

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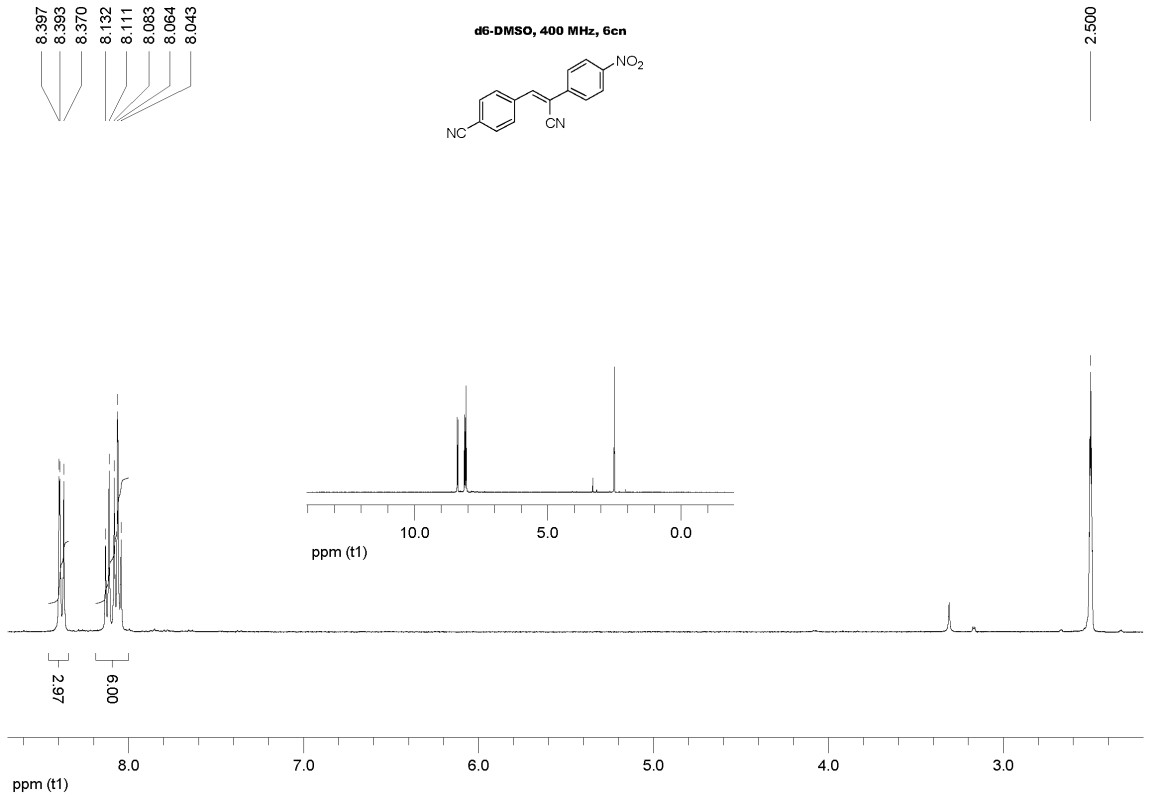

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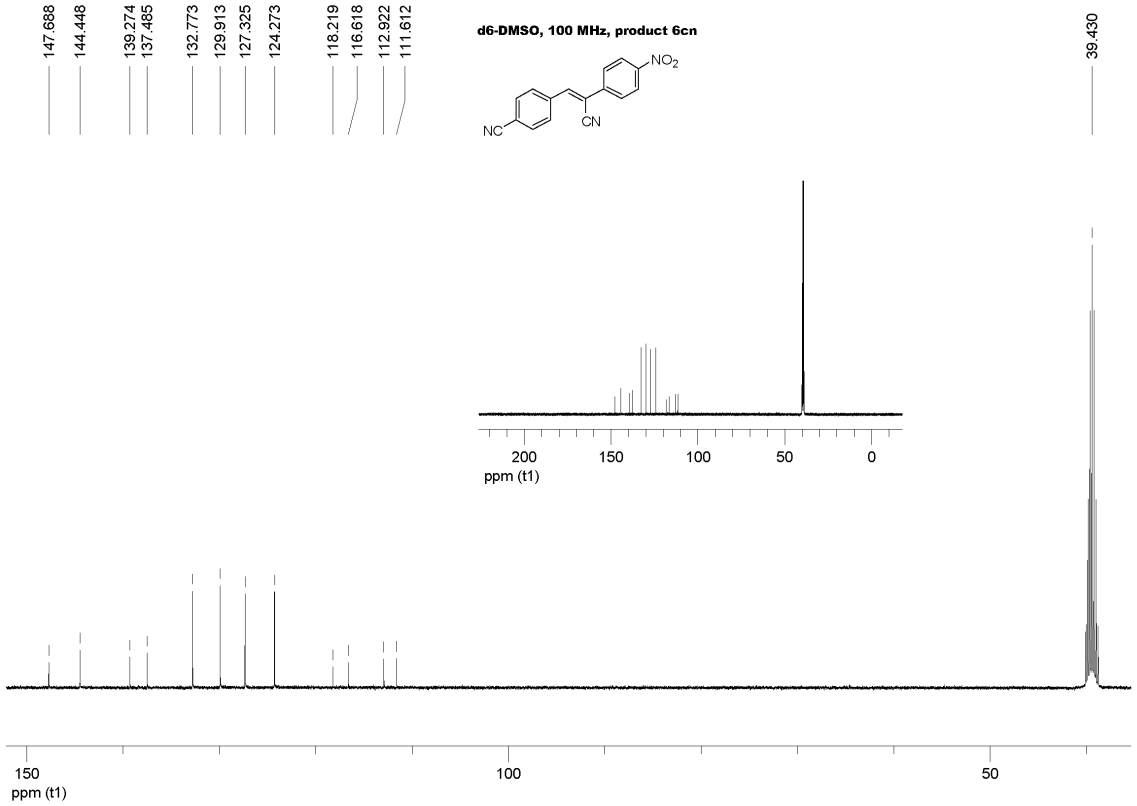
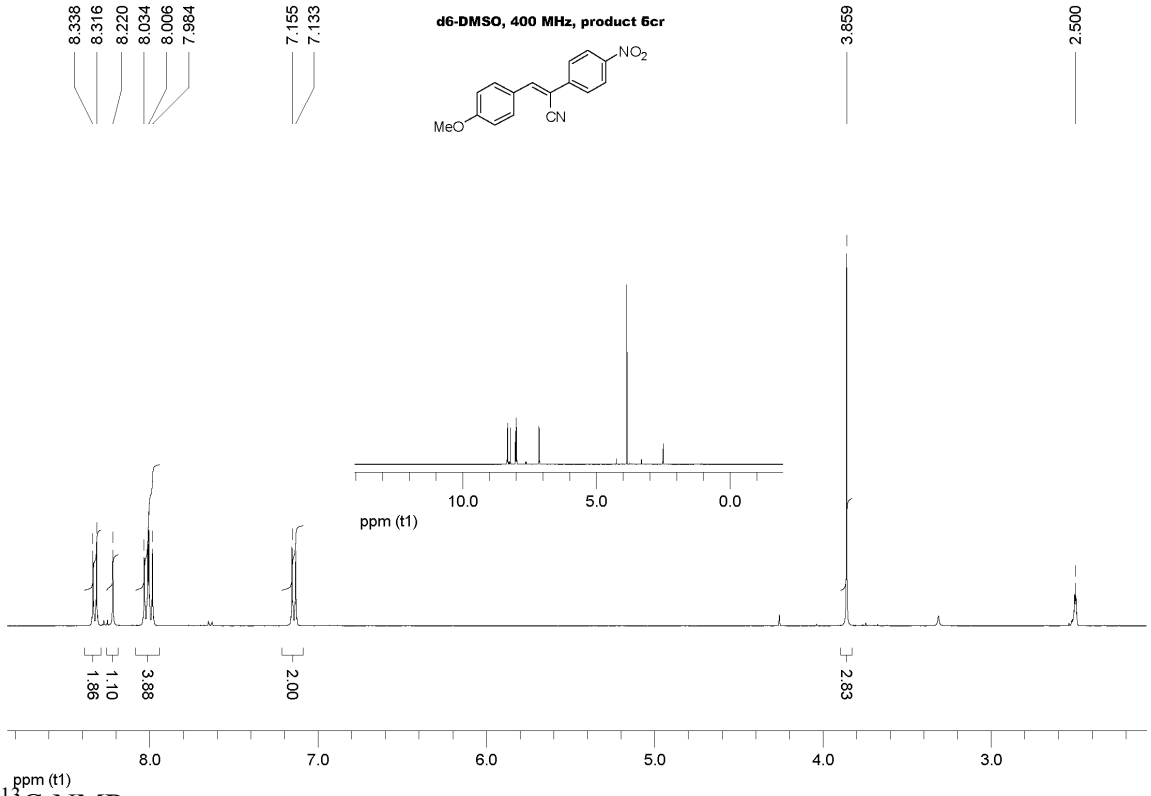
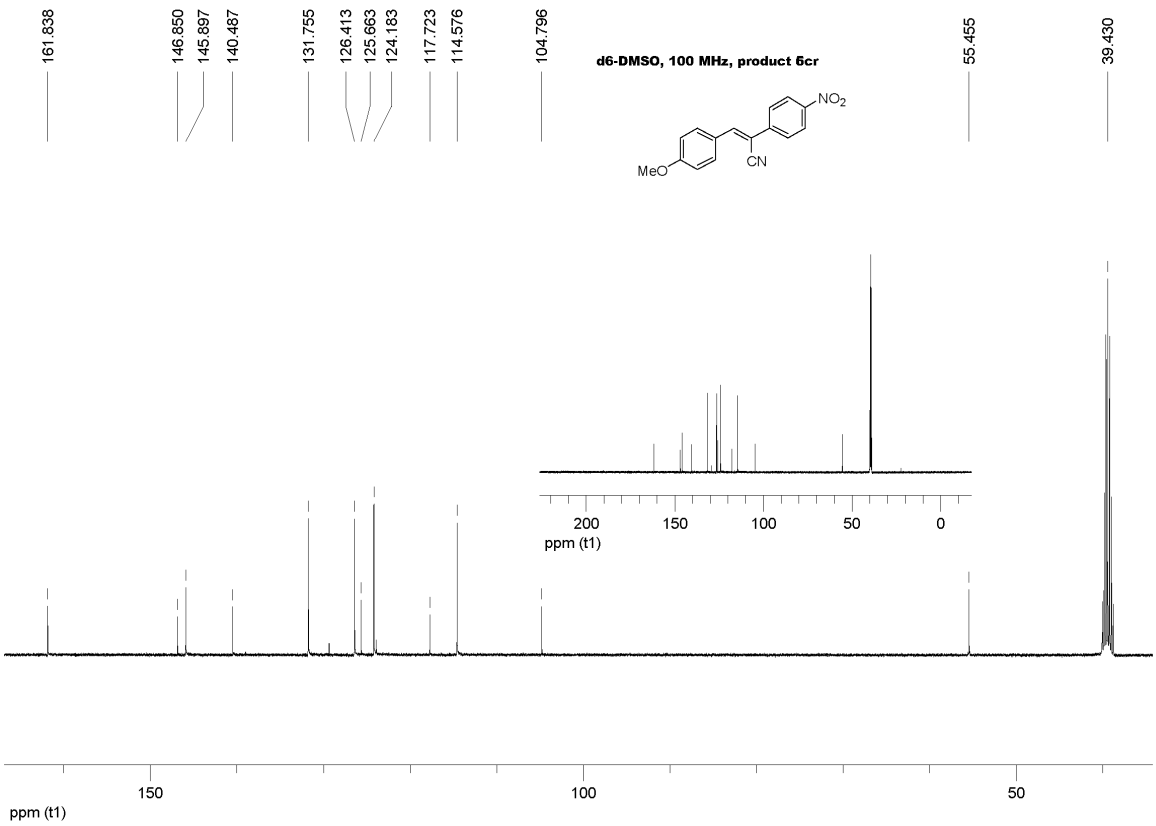


Product **6cr**

^{1}H-NMR

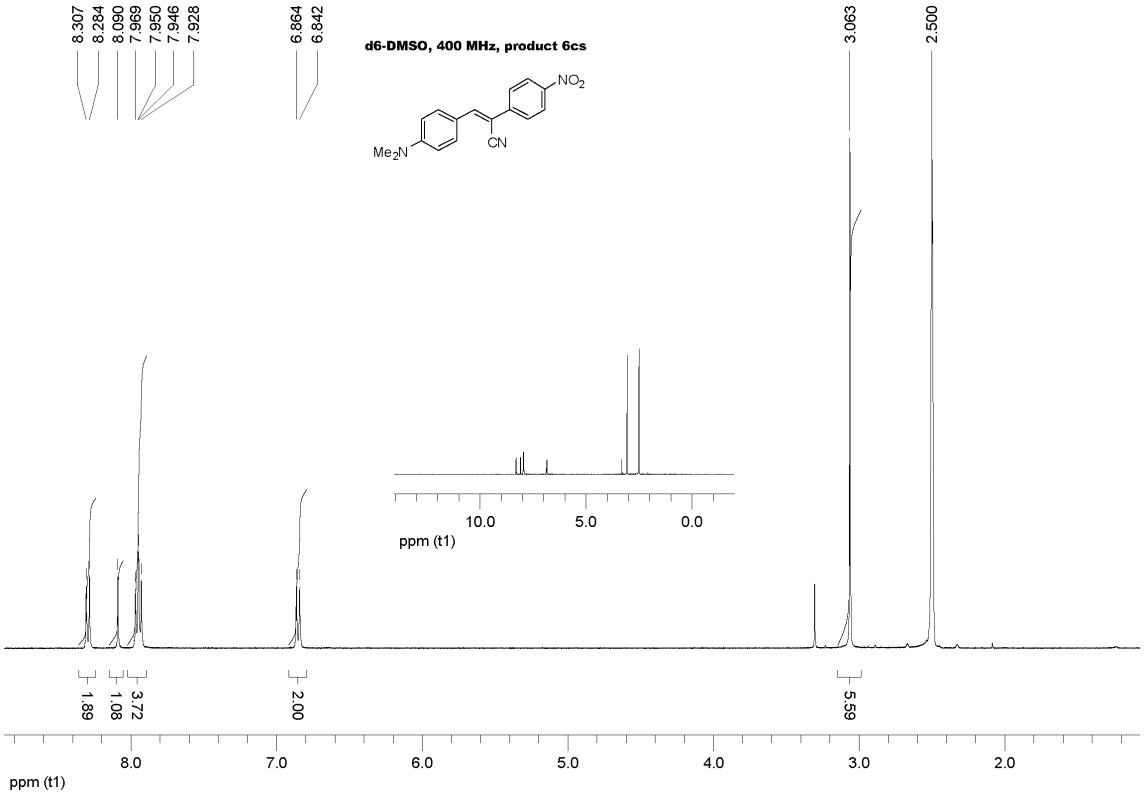


^{13}C-NMR

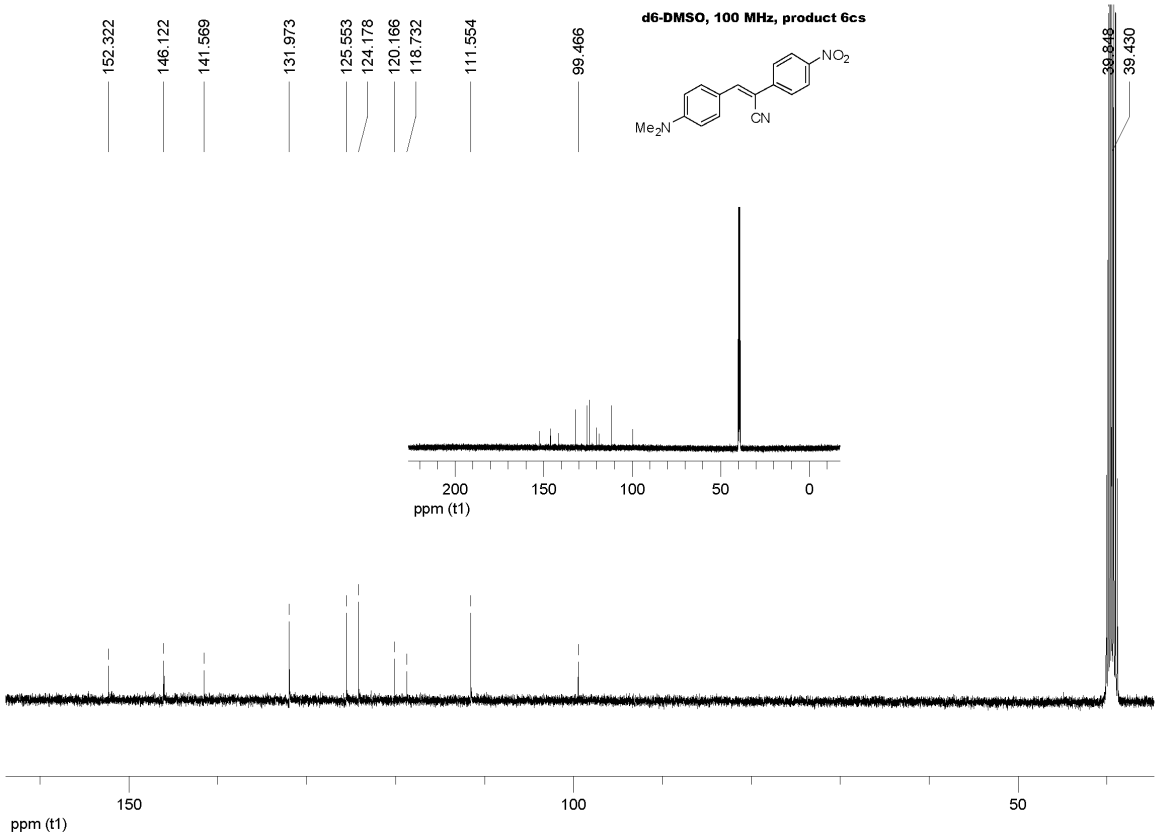


Product **6cs**

^{1}H-NMR

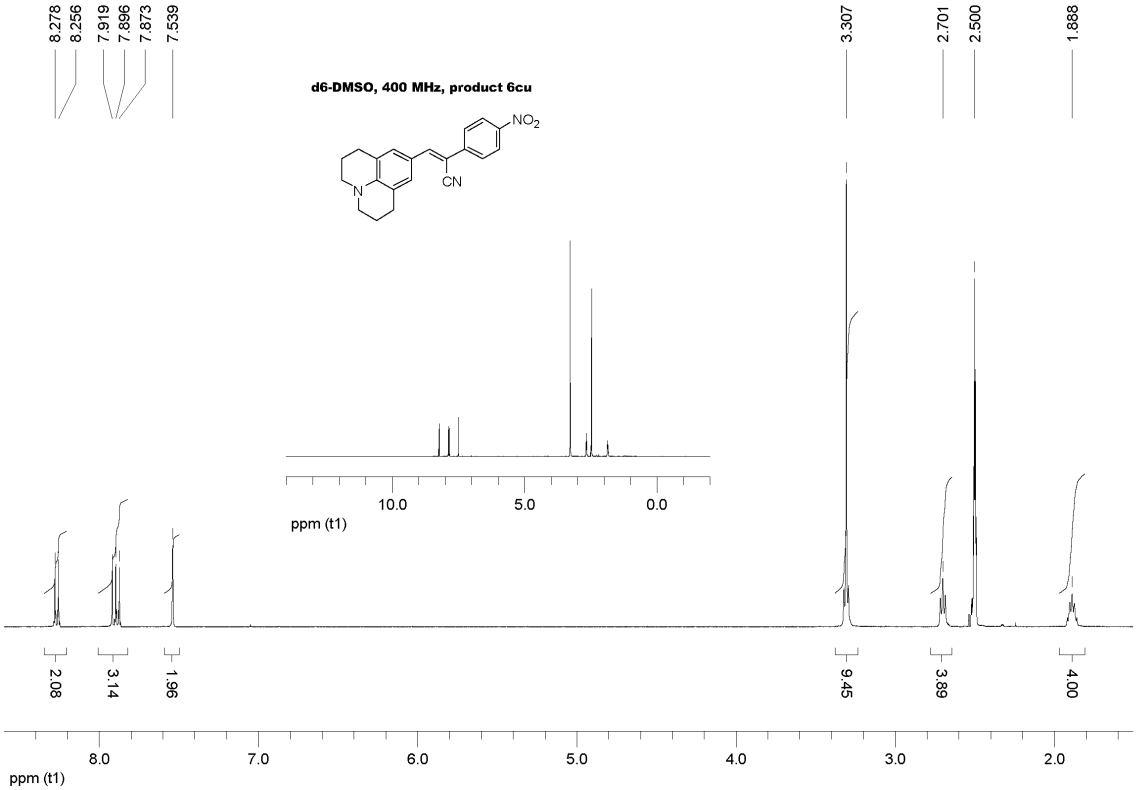


^{13}C-NMR



Prodduct **6cu**

^{1}H-NMR



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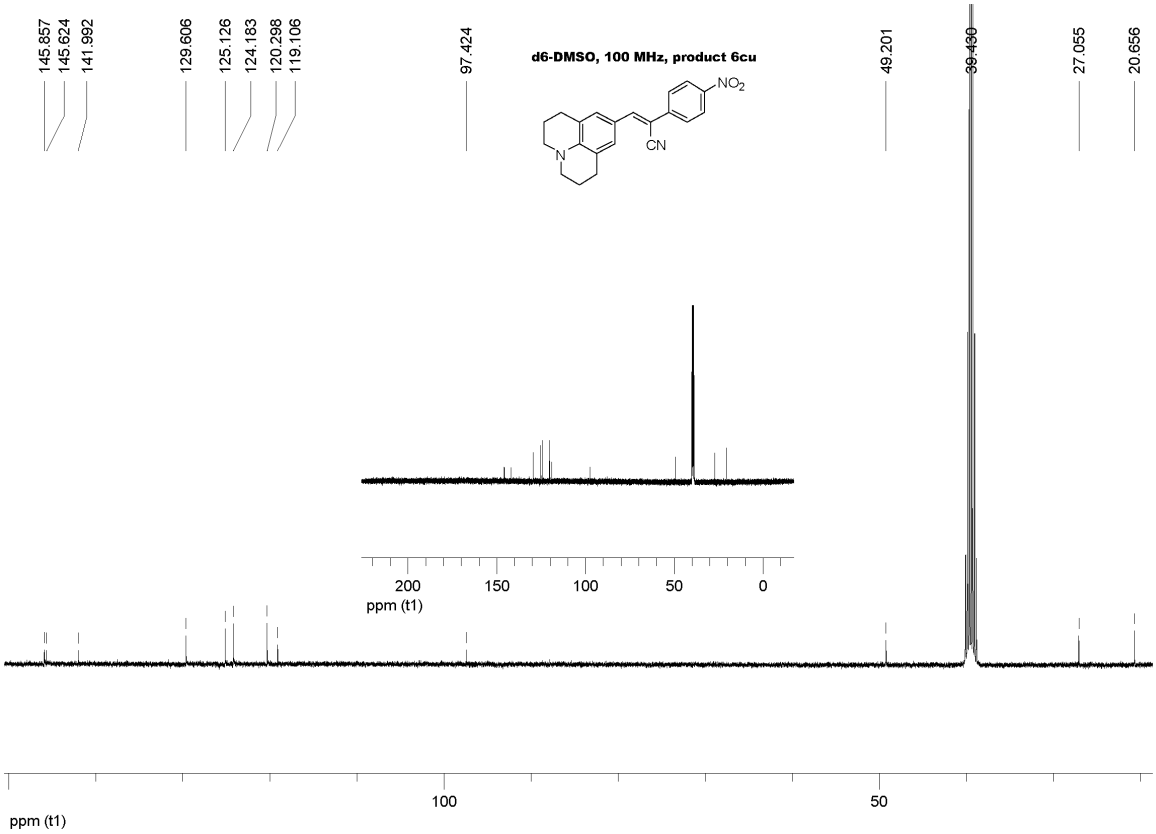

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