– Electronic Supplementary Information (ESI) –

Characterization of the nucleophilic reactivities of thiocarboxylate, dithiocarbonate and dithiocarbamate anions

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1. General

Materials.

Commercially available acetonitrile (VWR, Prolabo, HPLC-gradient grade) was used. The benzhydrylium tetrafluoroborates $Ar_2CH^+BF_4^-$ were prepared as described before.[S1] The phosphonium salts of benzhydrylium tetrafluoroborates (P-salt) and benzhydryl chlorides were synthesized according to literature procedures.[S2,S3] Potassium thioacetate (**1a**, Aldrich, >98%), potassium *O*-ethyl dithiocarbonate (**1b**, Aldrich, >98%) and 18-crown-6 (Aldrich, 98%) were purchased and used directly without further purification. The other thioester salts **1c**-**h** were prepared according to the literature procedure.[S4]

Analytics.

^{1}H- and ^{13}C-NMR spectra were recorded on *Varian* NMR-systems (400 MHz) in CD_3CN or d_6-DMSO and the chemical shifts in ppm refer to the solvent residual signal as internal standard ($\delta_H(CDCl_3)$ = 7.24, $\delta_C(CDCl_3)$ = 77.2, or δ_H(DMSO) = 2.50, δ_C(DMSO) = 39.5). For reasons of simplicity, the ^{1}H-NMR signals of AA'BB'-spin systems of *p*-disubstituted aromatic rings are treated as doublets.

2. Product Studies

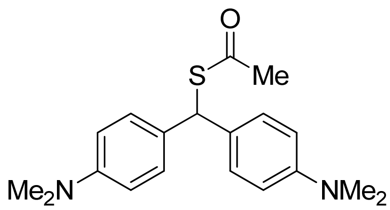
2.1 Product studies for the reactions of the 1–3 with the benzhydrylium ions

The reactions of **1–3** with the reference electrophiles (Ar_2CH^+) were performed under exclusion of moisture in an atmosphere of dry nitrogen in carefully dried Schlenk glassware.

General procedure (GP):

At room temperature a solution of benzhydrylium ion ($Ar_2CH^+BF_4^-$) (31 mg, 0.091 mmol) in MeCN (1.5 mL) was added to a solution of **1a** (10 mg, 0.088 mmol) in DMSO (0.5 mL) under the nitrogen. The resulting mixture was stirred for 1h. The crude product was washed with water, extracted in EtOAc, dried over Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography to afford the products.

S-(Bis(4-(dimethylamino)phenyl)methyl) ethanethioate was obtained from **1** (10 mg, 0.088 mmol) and $(dma)_2CHBF_4$ (31 mg, 0.091 mmol) in dry MeCN/DMSO (2 mL); purification was achieved by column chromatography on silica gel; 25 mg (0.076 mmol, 85%).



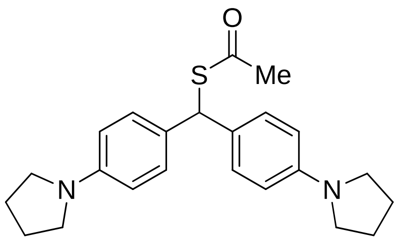
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24 (d, J = 6.7 Hz, 4 H, Ar), 6.70 (d, J = 6.8 Hz, 4 H, Ar), 5.89 (s, 1 H, Ar_2CH-S), 2.95 (s, 12 H, $N(CH_3)_2$), 2.35 (s, 3 H, CH_3) ppm.

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 194.8 (s, C=O), 149.7 (s, Ar), 129.5 (s, Ar), 129.2 (d, Ar), 112.6 (d, Ar), 51.4 (d, Ar_2CH-S), 40.8 (q, $N(CH_3)_2$), 30.5 (q, CH_3) ppm.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2885, 2800, 1685, 1611, 1519, 1480, 1444, 1350, 1164, 1131, 1105, 948, 819, 802, 759.

HRMS (ESI, positive): Calculated for $C_{19}H_{25}O_1N_2{}^{32}S_1$ [M + H^+] is 329.1682: Found 329.1682. Calculated for $C_{17}H_{21}N_2$ [M – CH_3COS^-] is 253.1699; found 253.1698.

S-(Bis(4-(pyrrolidin-1-yl)phenyl)methyl) ethanethioate was obtained from the thioester salt **1** (10 mg, 0.088 mmol) and $(pyr)_2CHBF_4$ (35 mg, 0.089 mmol) in dry MeCN/DMSO (2 mL); purification was achieved by column chromatography on silica gel; 23 mg (0.060 mmol, 68%).



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18 (d, J = 8.7 Hz, 4 H, Ar), 6.47 (d, J = 8.7 Hz, 4 H, Ar), 5.84 (s, 1 H, Ar_2CH-S), 3.32-3.26 (m, 8 H, NCH_2CH_2), 2.29 (s, 3 H, CH_3), 1.98-1.94 (m, 8 H, NCH_2CH_2) ppm.

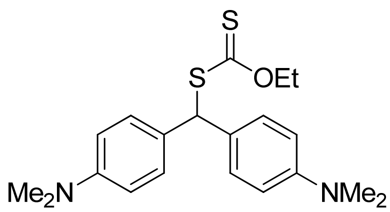
^{13}C NMR (75.5 MHz, $CDCl_3$): δ 194.9 (s, C=O), 147.1 (s, Ar), 129.3 (d, Ar), 128.4 (s, Ar), 111.6 (d, Ar), 51.7 (d, Ar_2CH-S), 47.8 (t, NCH_2CH_2), 30.6 (q, CH_3), 25.7 (t, NCH_2CH_2) ppm.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2966, 2833, 2360, 2341, 1683, 1610, 1518, 1486, 1370, 1180, 1133, 1104, 964, 798, 769.

HRMS (ESI, positive): Calculated for $C_{17}H_{21}N_2$ [M – CH_3COS^-] is 253.1699; found 253.1698.

Reaction of potassium *O*-ethyl dithiocarbonate (2a) with $(dma)_2CH^+BF_4^-$:

2a (13 mg, 0.081 mmol) and $(dma)_2CHBF_4$ (28 mg, 0.081 mmol) were mixed in an NMR tube in d_6-DMSO, and the mixture was analyzed by NMR spectroscopy.



^{1}H NMR (400 MHz, d_6-DMSO): δ 7.18 (d, J = 8.7 Hz, 4 H, Ar), 6.67 (d, J = 8.7 Hz, 4

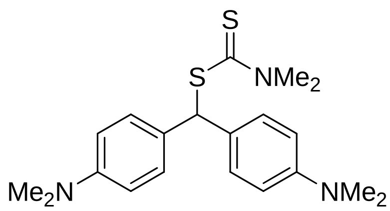
H, Ar), 5.92 (s, 1 H, Ar_2CH-S), 4.49 (q, J = 7.1 Hz, 2 H, CH_2), 2.86 (s, 12 H, $N(CH_3)_2$), 1.21 (t, J = 7.1 Hz, 3 H, CH_3) ppm.

^{13}C NMR (100 MHz, d_6-DMSO): δ 212.3 (s, C=S), 149.4 (s, Ar), 128.7 (d, Ar), 127.4 (s, Ar), 112.2 (d, Ar), 69.9 (t, CH_2), 56.9 (d, Ar_2CH-S), 40.1 (q, $N(CH_3)_2$), 13.3 (q, CH_3) ppm.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2922, 2852, 2360, 2341, 1612, 1520, 1444, 1352, 1224, 1164, 1046, 948, 801.

Reaction of potassium *N,N*-dimethyldithiocarbamate (2a) with $(dma)_2CH^+BF_4^-$:

2a (13 mg, 0.081 mmol) and $(dma)_2CHBF_4$ (28 mg, 0.081 mmol) were mixed in an NMR tube in d_6-DMSO and the mixture was analyzed by NMR spectroscopy.



^{1}H NMR (400 MHz, d_6-DMSO): δ 7.15 (d, J = 8.8 Hz, 4 H, Ar), 6.67 (d, J = 8.8 Hz, 4 H, Ar), 6.18 (s, 1 H, Ar_2CH-S), 3.41 (s, 3 H, $C(S)N(CH_3)_2$) 3.33 (s, 3 H, $C(S)N(CH_3)_2$) 2.86 (s, 12 H, $ArN(CH_3)_2$) ppm.

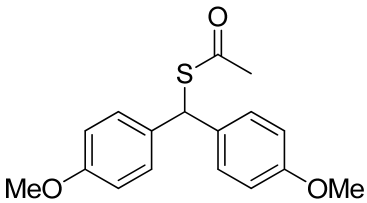
^{13}C NMR (100 MHz, d_6-DMSO): δ 194.1 (s, C=S), 149.1 (s, Ar), 129.0 (d, Ar), 114.6 (s, Ar), 112.3 (d, Ar), 59.3 (d, Ar_2CH-S), 44.7 (q, $C(S)N(CH_3)_2$) 41.1 (q, $C(S)N(CH_3)_2$) , 40.2 (q, $ArN(CH_3)_2$) ppm.

2.2 Reaction of 1–3 with $(ani)_2CHCl$ or $(ani)_2CHBr$

General procedure (GP):

At room temperature a solution of $(ani)_2CHCl$ or $(ani)_2CHBr$ in MeCN (1.5 mL) was added to a solution of **1–3** in DMSO or MeCN (0.5 mL) under the nitrogen. The resulting mixture was stirred for 1 h. The crude product was washed with water, extracted in EtOAc, dried over Na_2SO_4, concentrated under reduced pressure, and purified by chromatography to afford the products.

Thioacetic acid *S*-[bis-(4-methoxy-phenyl)-methyl] ester[S5] was obtained from **1a** (14 mg, 0.12 mmol) and the $(ani)_2CHCl$ (32 mg, 0.12 mmol) in dry MeCN/DMSO (2 mL); purification was achieved by column chromatography on silica gel; 29 mg (0.096 mmol, 80%).



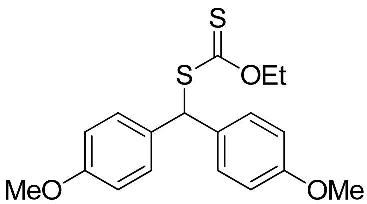
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (d, J = 8.4 Hz, 4 H, Ar), 6.86 (d, J = 8.7 Hz, 4 H, Ar), 5.90 (s, 1 H, Ar_2CH-S), 3.80 (s, 6 H, OCH_3), 2.35 (s, 3 H, CH_3) ppm.

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 194.3 (s, C=O), 158.9 (s, Ar), 133.5 (s, Ar), 129.5 (d, Ar), 114.1 (d, Ar), 55.5 (q, OCH_3), 51.0 (d, Ar_2CH-S), 30.5 (q, CH_3) ppm.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2955, 2930, 2836, 2361, 2340, 1689, 1509, 1463, 1302, 1248, 1176, 1134, 1109, 1033, 956, 817, 768.

HRMS (EI): Calculated for $C_{15}H_{15}O_2^+$ [M – CH_3COS^-] is 227.1067; found 227.1058.

S-(Bis(4-methoxyphenyl)methyl) O-ethyl carbonodithioate was obtained from **2a** (16 mg, 0.10 mmol) and the $(ani)_2CHBr$ (31 mg, 0.090 mmol) in dry MeCN/DMSO (2 mL); purification was achieved by column chromatography on silica gel; 16 mg (0.041 mmol, 46%).

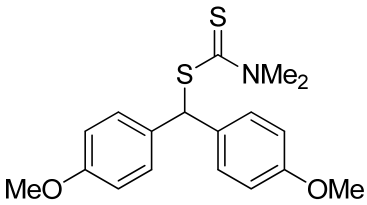


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.23 (m, 4 H, Ar), 6.84-6.80 (m, 4 H, Ar), 6.00 (s, 1 H, Ar_2CH-S), 4.53 (q, J = 7.1 Hz, 2 H, CH_2), 3.76 (s, 6 H, OCH_3), 1.27 (t, J = 7.1 Hz, 3 H, CH_3) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.9 (s, C=S), 159.0 (s, Ar), 132.2 (s, Ar), 129.8 (d, Ar), 114.1 (d, Ar), 70.0 (t, CH_2), 57.5 (d, Ar_2CH-S), 55.5 (q, OCH_3), 13.8 (q, CH_3) ppm.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2932, 2836, 1738, 1610, 1510, 1462, 2366, 1302, 1249, 1175, 1111, 1044, 816.

Bis(4-methoxyphenyl)methyl dimethylcarbamodithioate was obtained from **2a** (21 mg, 0.13 mmol) and the $(ani)_2CHBr$ (41 mg, 0.13 mmol) in dry MeCN/DMSO (2 mL); purification was achieved by column chromatography on neutral Al_2O_3; 35 mg (0.10 mmol, 78%).

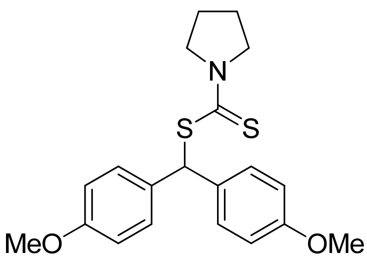


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.6 Hz, 4 H, Ar), 6.82 (d, J = 8.8 Hz, 4 H, Ar), 6.43 (s, 1 H, Ar_2CH-S), 3.76 (s, 6 H, OCH_3), 3.49 (s, 3 H, NCH_3), 3.34 (s, 3 H, NCH_3) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8 (s, C=S), 158.8 (s, Ar), 133.1 (s, Ar), 130.1 (d, Ar), 113.9 (d, Ar), 59.7 (d, Ar_2CH-S), 55.4 (q, OCH_3), 45.5 (q, NCH_3), 41.6 (q, NCH_3) ppm.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2932, 1608, 1508, 1374, 1301, 1246, 1174, 1146, 1110, 1032, 983, 907, 833, 816, 726, 647.

Bis(4-methoxyphenyl)methyl pyrrolidine-1-carbodithioate was obtained from the **3b** (22 mg, 0.12 mmol) and the $(ani)_2CHCl$ (32 mg, 0.12 mmol) in dry MeCN/DMSO (2 mL); purification was achieved by column chromatography on neutral Al_2O_3; 35 mg (0.094 mmol, 78%).

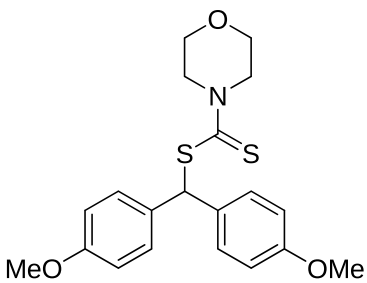


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 4 H, Ar), 6.84-6.80 (m, 4 H, Ar), 6.53 (s, 1 H, Ar_2CH-S), 3.93-3.87 (m, 2 H, NCH_2CH_2), 3.76 (2 × s, 6 H, OCH_3), 3.65-3.61 (m, 2 H, NCH_2CH_2), 2.06-1.99 (m, 2 H, NCH_2CH_2), 1.96-1.89 (m, 2 H, NCH_2CH_2) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5 (s, C=S), 158.8 (s, Ar), 133.4 (s, Ar), 130.1 (d, Ar), 114.0 (d, Ar), 58.3 (d, Ar_2CH-S), 55.4 (q, OCH_3), 55.2 (t, NCH_2CH_2), 50.7 (t, NCH_2CH_2), 26.2 (t, NCH_2CH_2), 24.4 (t, NCH_2CH_2) ppm.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2953, 2835, 1606, 1582, 1508, 1461, 1431, 1329, 1302, 1247, 1174, 1110, 1032, 1006, 956, 816, 770.

Bis(4-methoxyphenyl)methyl morpholine-4-carbodithioate was obtained from **3e** (20 mg, 0.10 mmol) and the $(ani)_2CHBr$ (31 mg, 0.10 mmol) in dry MeCN/DMSO (2 mL); purification was achieved by column chromatography on neutral Al_2O_3; 29 mg (0.074 mmol, 74%).

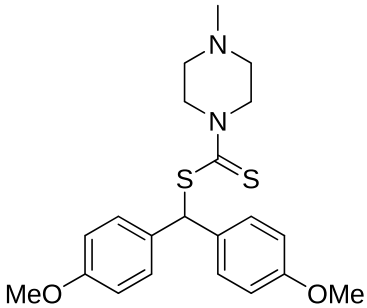


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 4 H, Ar), 6.84-6.81 (m, 4 H, Ar), 6.49 (s, 1 H, Ar_2CH-S), 4.33-3.97 (br. m, 4 H, CH_2), 3.76 (s, 6 H, OCH_3), 3.72-3.70 (m, 4 H, CH_2) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4 (s, C=S), 159.1 (s, Ar), 133.1 (s, Ar), 130.2 (d, Ar), 114.1 (d, Ar), 66.5 (t, CH_2), 59.0 (d, Ar_2CH-S), 55.5 (q, OCH_3), 51.1 (t, CH_2) ppm.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2960, 2928, 2836, 1607, 1582, 1509, 1462, 1419, 1301, 1248, 1229, 1175, 1113, 1030, 996, 834, 816, 770.

Bis(4-methoxyphenyl)methyl 4-methylpiperazine-1-carbodithioate was obtained from **3d** (21 mg, 0.10 mmol) and the $(ani)_2CHBr$ (31 mg, 0.10 mmol) in dry MeCN/DMSO (2 mL); purification was achieved by column chromatography on neutral Al_2O_3; 34 mg (0.084 mmol, 84%).



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, J = 8.4 Hz, 4 H, Ar), 6.82 (d, J = 8.8 Hz, 4 H, Ar), 6.48 (s, 1 H, Ar_2CH-S), 4.25-3.99 (m, 4 H, $CH_3NCH_2C\mathit{H}_2$), 3.75 (s, 6 H, OCH_3), 2.46-2.43 (m, 4 H, $CH_3NC\mathit{H}_2CH_2$) 2.29 (s, 3 H, NCH_3) ppm.

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 195.6 (s, C=S), 158.8 (s, Ar) , 133.0 (s, Ar), 130.1 (d, Ar), 114.0 (d, Ar), 59.2 (d, Ar_2CH-S), 55.4 (q, OCH_3), 54.6 (t, $CH_3N\mathit{C}H_2CH_2$), 50.8 (br. t, $CH_3NCH_2\mathit{C}H_2$), 45.8 (q, NCH_3) ppm.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2936, 2835, 2794, 1607, 1582, 1508, 1462, 1421, 1290, 1246, 1174, 1143, 1032, 994, 920, 833, 816, 778, 632.

3. Kinetics

Kinetics for the reactions of 1–3 with benzhydrylium ions Ar_2CH^+ in CH_3CN at 20 °C

All rate constants were measured by using the laser-flash photolysis technique. The benzhydrylium ions (Ar_2CH^+) were generated from suitable precursors, phosphonium salts ($Ar_2CH–PR_3^+BF_4^–$, P-salt, Table 1 in the main text) in CH_3CN. A solution of known concentration of P-salt in CH_3CN (≈ $10^{–5}$ mol $L^{–1}$) was mixed with a solution of known concentration of **1–3** (≈ $10^{–4}$ to $10^{–3}$ mol $L^{–1}$) and 18-crown-6 (18-C-6, ≈ $10^{–4}$ to $10^{–3}$ mol $L^{–1}$) in CH_3CN. The resulting colorless solution was then irradiated with 6.5-ns laser pulses (266 nm) to generate the benzhydrylium ions Ar_2CH^+. The decay of the absorbance of Ar_2CH^+ was monitored by UV/Vis spectroscopy at the corresponding absorption maxima. The resulting pseudo-first-order rate constants k_{obs} ($s^{–1}$) were obtained from at least five runs (typically 5–7 runs) at each nucleophile concentration. The absorbance-time curves were fitted to the single exponential function $A = A_0 \exp(–k_{obs}t) + C$ to yield the rate constants k_{obs} ($s^{–1}$).

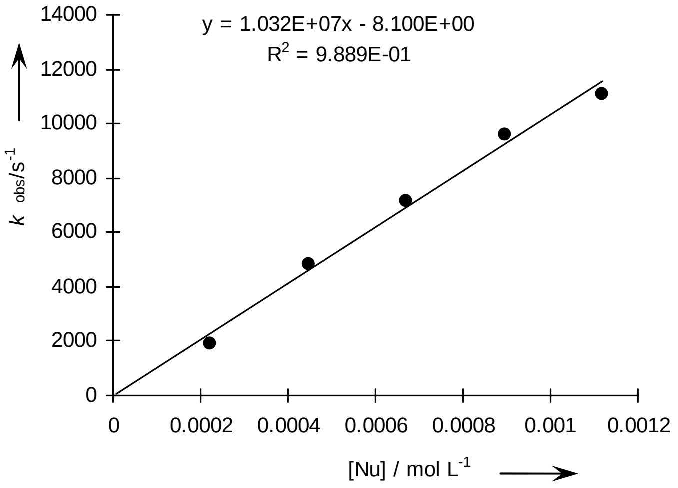
Laser-flash photolysis techniques photolysis setup

The laser pulse (6.5 ns pulse width, 266 nm, 40-60 mJ/pulse) originates from a Nd-YAG laser (Innolas SpitLight 600) with second (532 nm) and fourth (266 nm) harmonic generators. The UV-visible detection unit comprises a Xe-light source (Osram XBO 150 W/CR OFR in a Hamamatsu E7536 housing with Hamamatsu C8849 power supplier), a shutter to prevent unnecessary exposure of the sample to the light of the Xe-lamp, a spectrograph (Acton Spectra Pro 2300i from Princeton Instruments), a photomultiplier (Hamamatsu H-7332-10 with C7169 power supply) with amplifier (Stanford Research Systems SR445A), and a pulse generator (Berkeley Nucleonics Corp. BNC 565). For the data acquisition a 350 MHz oscilloscope (Tektronix DPO 4032) was used. The sample was kept in a temperature controlled fluorescence cell, the temperature of which was maintained at 20 °C.

Kinetics of the reaction of 1 with Ar_2CH^+

Rate constants for the reactions of potassium thioacetate (**1**) with $(lil)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 632 nm).

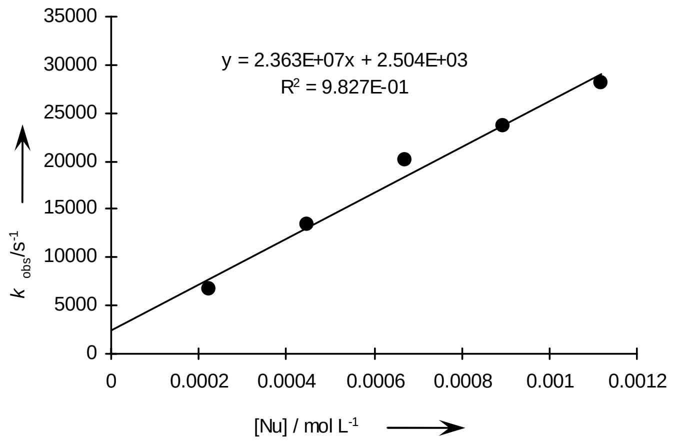
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.72×10^{-5}	2.24×10^{-4}	4.57×10^{-4}	1.91×10^{3}
2.72×10^{-5}	4.48×10^{-4}	9.14×10^{-4}	4.85×10^{3}
2.72×10^{-5}	6.72×10^{-4}	1.37×10^{-3}	7.16×10^{3}
2.72×10^{-5}	8.96×10^{-4}	1.83×10^{-3}	9.59×10^{3}
2.72×10^{-5}	1.12×10^{-3}	2.29×10^{-3}	1.11×10^{4}



$k = 1.03 \times 10^{7}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium thioacetate (**1**) with $(jul)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 640 nm).

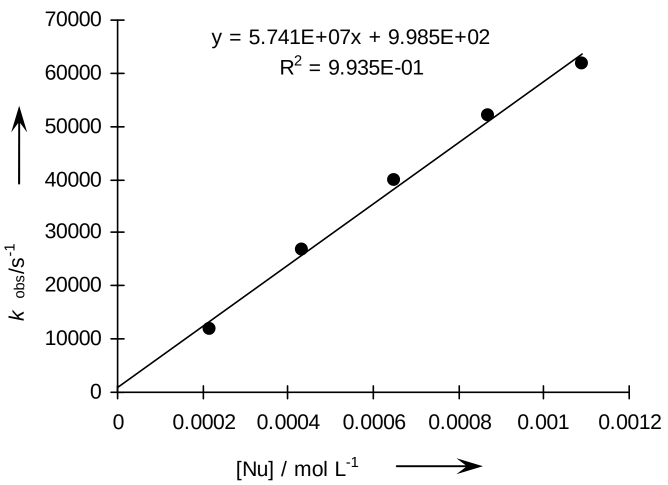
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.60×10^{-5}	2.24×10^{-4}	5.84×10^{-4}	6.73×10^{3}
2.60×10^{-5}	4.48×10^{-4}	1.17×10^{-3}	1.34×10^{4}
2.60×10^{-5}	6.72×10^{-4}	1.75×10^{-3}	2.01×10^{4}
2.60×10^{-5}	8.96×10^{-4}	2.34×10^{-3}	2.36×10^{4}
2.60×10^{-5}	1.12×10^{-3}	2.92×10^{-3}	2.81×10^{4}



$k = 2.36 \times 10^7$ M^{-1} s^{-1}

Rate constants for the reactions of potassium thioacetate (**1**) with $(ind)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 616 nm).

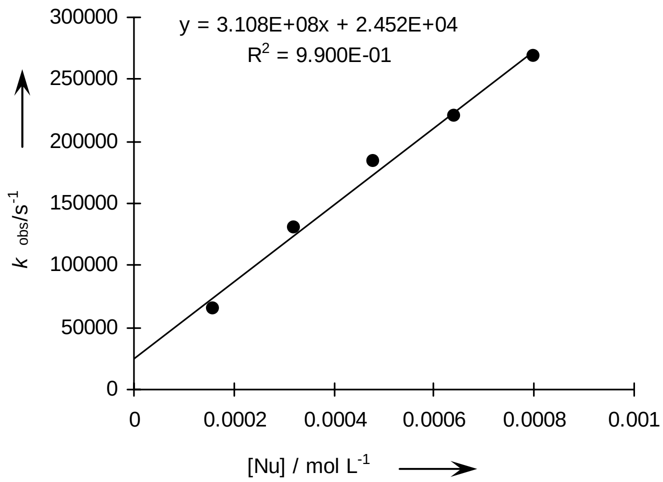
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.12×10^{-5}	2.17×10^{-4}	4.45×10^{-4}	1.18×10^{4}
2.12×10^{-5}	4.34×10^{-4}	8.90×10^{-4}	2.68×10^{4}
2.12×10^{-5}	6.51×10^{-4}	1.34×10^{-3}	3.99×10^{4}
2.12×10^{-5}	8.68×10^{-4}	1.78×10^{-3}	5.20×10^{4}
2.12×10^{-5}	1.09×10^{-3}	2.23×10^{-3}	6.18×10^{4}



$k = 5.74 \times 10^7$ M^{-1} s^{-1}

Rate constants for the reactions of potassium thioacetate (**1**) with $(pyr)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 612 nm).

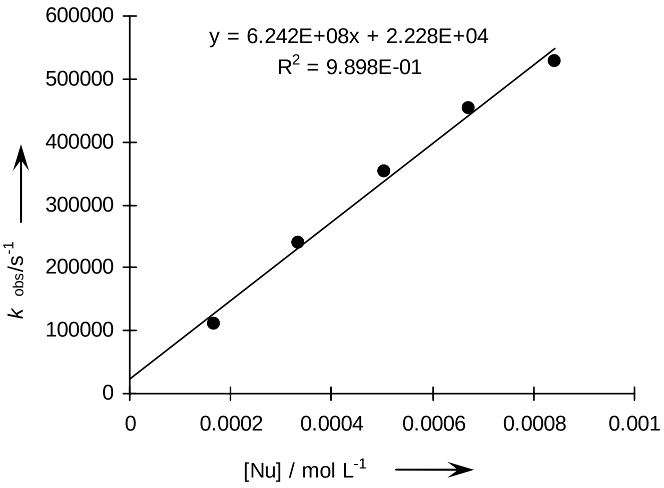
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.06×10^{-5}	1.60×10^{-4}	1.92×10^{-4}	6.54×10^{4}
3.06×10^{-5}	3.20×10^{-4}	3.84×10^{-4}	1.30×10^{5}
3.06×10^{-5}	4.80×10^{-4}	5.76×10^{-4}	1.84×10^{5}
3.06×10^{-5}	6.40×10^{-4}	7.68×10^{-4}	2.20×10^{5}
3.06×10^{-5}	8.00×10^{-4}	9.60×10^{-4}	2.69×10^{5}



$k = 3.11 \times 10^{8}\ M^{-1}\ s^{-1}$

Rate constants for the reactions of potassium thioacetate (**1**) with $(dma)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 607 nm).

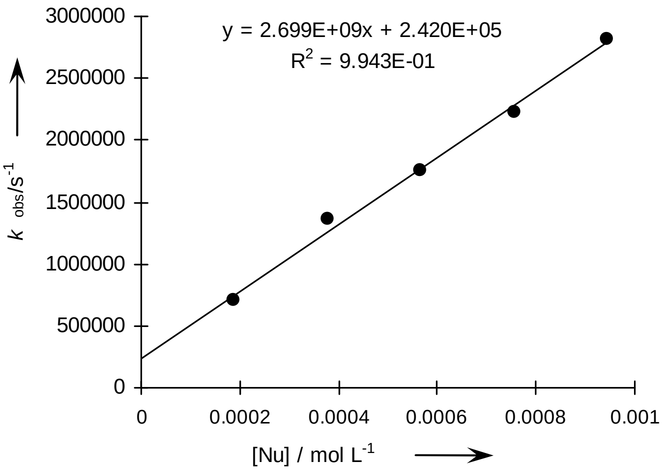
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.73×10^{-5}	1.68×10^{-4}	2.63×10^{-4}	1.10×10^{5}
1.73×10^{-5}	3.36×10^{-4}	5.26×10^{-4}	2.40×10^{5}
1.73×10^{-5}	5.04×10^{-4}	7.89×10^{-4}	3.54×10^{5}
1.73×10^{-5}	6.72×10^{-4}	1.05×10^{-3}	4.54×10^{5}
1.73×10^{-5}	8.41×10^{-4}	1.32×10^{-3}	5.28×10^{5}



$k = 6.24 \times 10^8$ M^{-1} s^{-1}

Rate constants for the reactions of potassium thioacetate (**1**) with $(mor)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 618 nm).

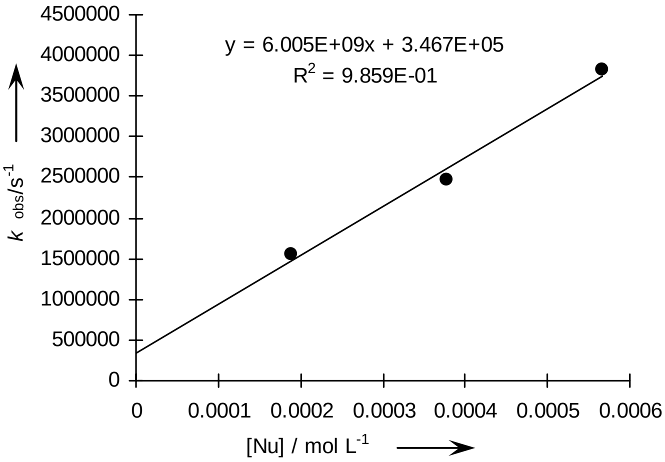
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.65×10^{-5}	1.89×10^{-4}	2.84×10^{-4}	7.04×10^{5}
1.65×10^{-5}	3.78×10^{-4}	5.67×10^{-4}	1.36×10^{6}
1.65×10^{-5}	5.67×10^{-4}	8.51×10^{-4}	1.75×10^{6}
1.65×10^{-5}	7.56×10^{-4}	1.13×10^{-3}	2.23×10^{6}
1.65×10^{-5}	9.45×10^{-4}	1.42×10^{-3}	2.82×10^{6}



$k = 2.70 \times 10^9$ M^{-1} s^{-1}

Rate constants for the reactions of potassium thioacetate (**1**) with $(dpa)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 644 nm).

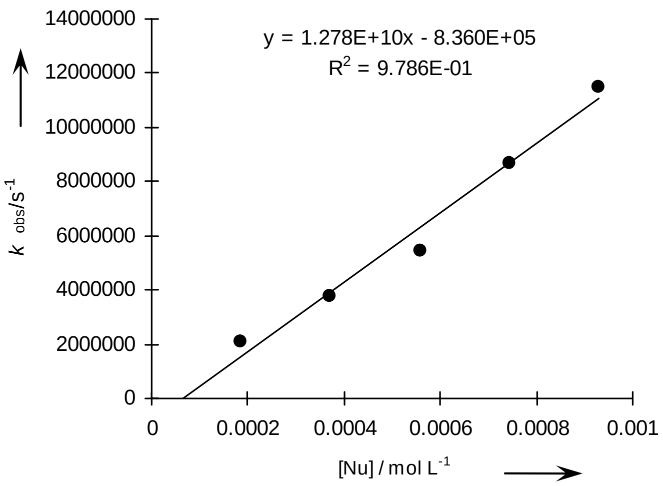
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.83×10^{-5}	1.89×10^{-4}	3.02×10^{-4}	1.56×10^{6}
1.83×10^{-5}	3.78×10^{-4}	6.05×10^{-4}	2.46×10^{6}
1.83×10^{-5}	5.67×10^{-4}	9.07×10^{-4}	3.83×10^{6}



$k = 6.01 \times 10^{9}\ M^{-1}\ s^{-1}$

Rate constants for the reactions of potassium thioacetate (**1**) with $(mfa)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 586 nm).

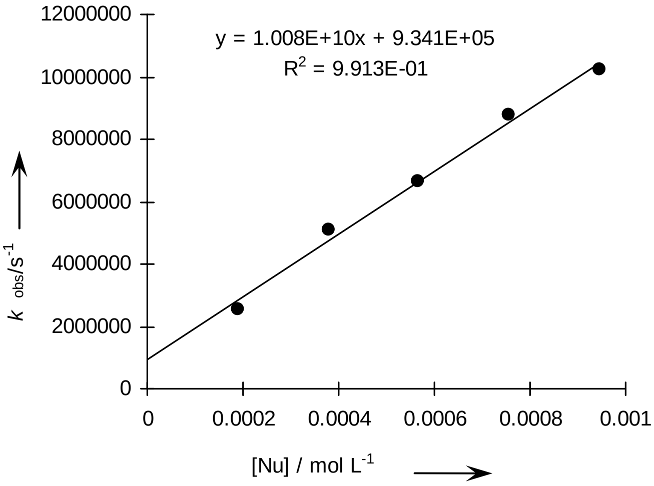
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.11×10^{-5}	1.86×10^{-4}	2.90×10^{-4}	2.09×10^{6}
2.11×10^{-5}	3.72×10^{-4}	5.80×10^{-4}	3.74×10^{6}
2.11×10^{-5}	5.58×10^{-4}	8.70×10^{-4}	5.46×10^{6}
2.11×10^{-5}	7.44×10^{-4}	1.16×10^{-3}	8.70×10^{6}
2.11×10^{-5}	9.30×10^{-4}	1.45×10^{-3}	1.15×10^{7}



$k = 1.28 \times 10^{10}\ M^{-1}\ s^{-1}$

Rate constants for the reactions of potassium thioacetate (**1**) with $(pfa)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 599 nm).

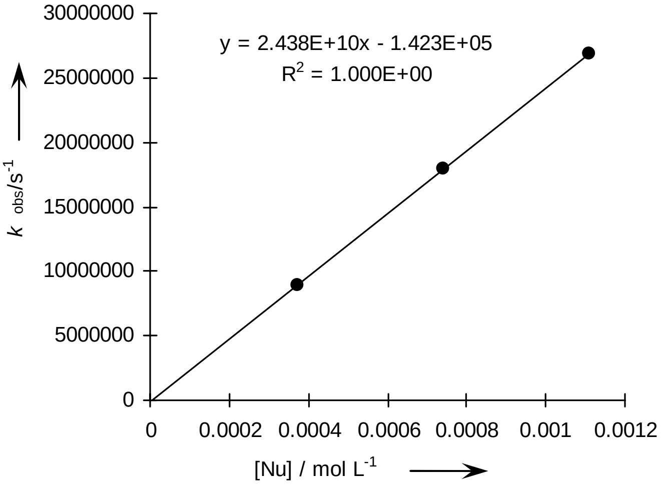
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.81×10^{-5}	1.89×10^{-4}	3.02×10^{-4}	2.53×10^{6}
1.81×10^{-5}	3.78×10^{-4}	6.05×10^{-4}	5.09×10^{6}
1.81×10^{-5}	5.67×10^{-4}	9.07×10^{-4}	6.63×10^{6}
1.81×10^{-5}	7.56×10^{-4}	1.21×10^{-5}	8.77×10^{6}
1.81×10^{-5}	9.45×10^{-4}	1.51×10^{-5}	1.02×10^{7}



$k = 1.01 \times 10^{10}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium thioacetate (**1**) with $(fur)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 523 nm).

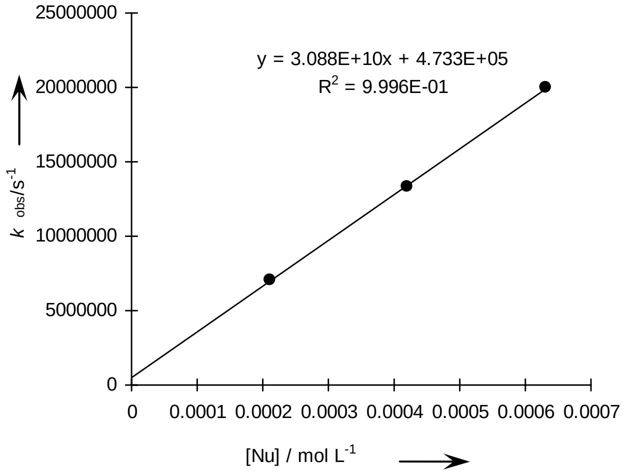
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.80×10^{-5}	3.71×10^{-4}	5.57×10^{-4}	8.88×10^{6}
3.80×10^{-5}	7.42×10^{-4}	1.11×10^{-5}	1.80×10^{7}
3.80×10^{-5}	1.11×10^{-3}	1.67×10^{-5}	2.69×10^{7}



$k = 2.44 \times 10^{10}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium thioacetate (**1**) with $(ani)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 500 nm).

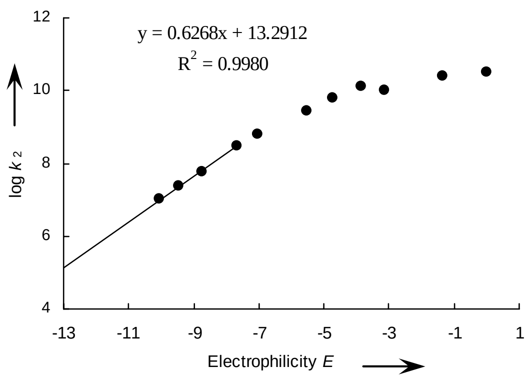
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.50×10^{-5}	2.10×10^{-4}	4.75×10^{-4}	7.03×10^{6}
2.50×10^{-5}	4.20×10^{-4}	9.50×10^{-4}	1.33×10^{7}
2.50×10^{-5}	6.30×10^{-4}	1.43×10^{-3}	2.00×10^{7}



$k = 3.10 \times 10^{10}$ M^{-1} s^{-1}

Determination of the parameters N and s_N for **1**

Electrophiles	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	1.03×10^{7}
$(jul)_2CH^+$	–9.45	2.36×10^{7}
$(ind)_2CH^+$	–8.76	5.74×10^{7}
$(pyr)_2CH^+$	–7.69	3.11×10^{8}
$(dma)_2CH^+$	–7.02	6.24×10^{8} [a]
$(mor)_2CH^+$	–5.89	2.70×10^{9} [a]
$(dpa)_2CH^+$	–4.72	6.01×10^{9} [a]
$(mfa)_2CH^+$	–3.85	1.28×10^{10} [a]
$(pfa)_2CH^+$	–3.14	1.01×10^{10} [a]
$(fur)_2CH^+$	–1.36	2.44×10^{10} [a]
$(ani)_2CH^+$	0	3.10×10^{10} [a]



***N* = 21.21**

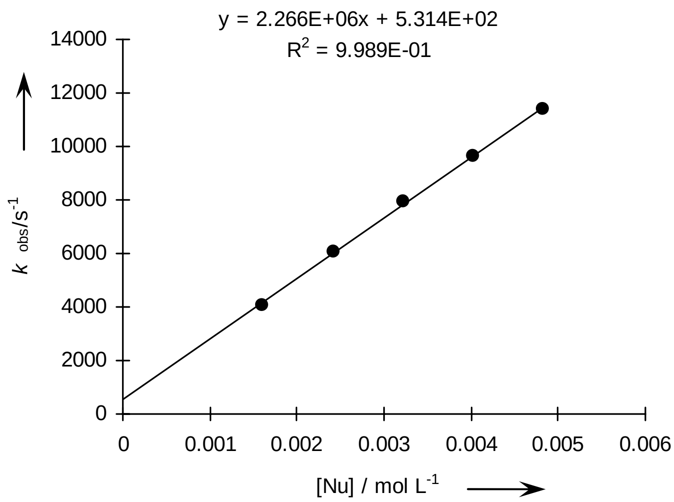
s_N = 0.63

[a] Because of the proximity of the diffusion limit, not used for the calculation of N and s_N.

Kinetics of the reaction of the thioester salts 2a with Ar_2CH^+.

Rate constants for the reactions of potassium *O*-ethyl dithiocarbonate (**2a**) with $(lil)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 632 nm).

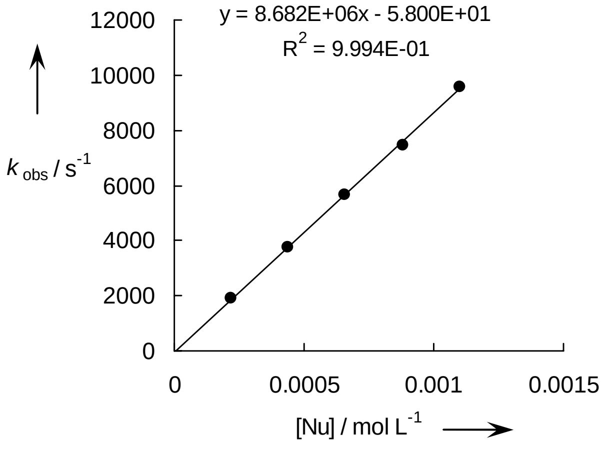
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
6.40×10^{-5}	1.61×10^{-3}	1.74×10^{-3}	4.08×10^{3}
6.40×10^{-5}	2.42×10^{-3}	3.63×10^{-3}	6.06×10^{3}
6.40×10^{-5}	3.22×10^{-3}	4.83×10^{-3}	7.96×10^{3}
6.40×10^{-5}	4.03×10^{-3}	6.05×10^{-3}	9.66×10^{3}
6.40×10^{-5}	4.83×10^{-3}	7.25×10^{-3}	1.14×10^{4}



$k = 2.27 \times 10^{6}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-ethyl dithiocarbonate (**2a**) with $(jul)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 640 nm).

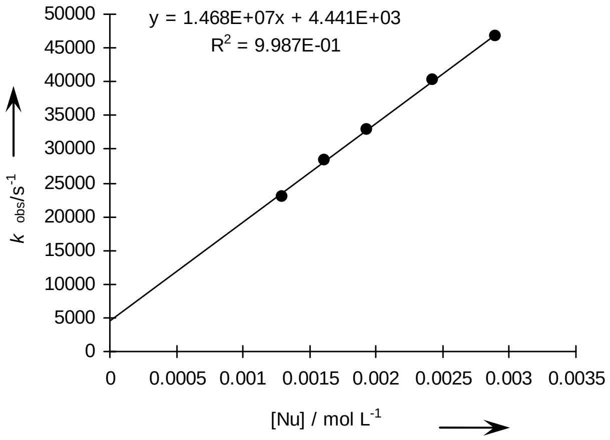
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.60×10^{-5}	2.20×10^{-4}	6.48×10^{-4}	1.88×10^{3}
2.60×10^{-5}	4.40×10^{-4}	1.30×10^{-3}	3.77×10^{3}
2.60×10^{-5}	6.60×10^{-4}	1.94×10^{-3}	5.66×10^{3}
2.60×10^{-5}	8.80×10^{-4}	2.59×10^{-3}	7.47×10^{3}
2.60×10^{-5}	1.10×10^{-3}	3.24×10^{-3}	9.58×10^{3}



$k = 8.68 \times 10^6$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-ethyl dithiocarbonate (**2a**) with $(ind)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 616 nm).

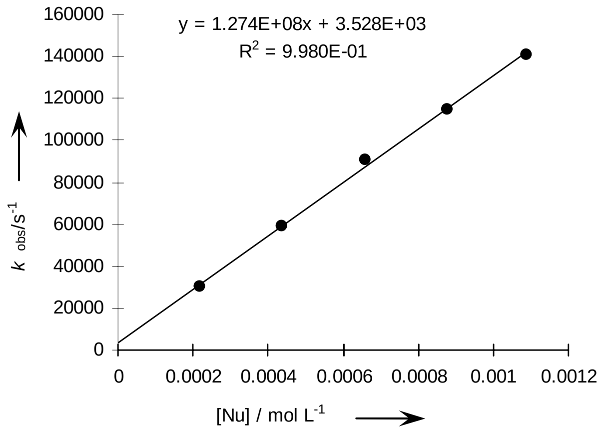
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.18×10^{-5}	1.29×10^{-3}	1.68×10^{-3}	2.30×10^{4}
3.18×10^{-5}	1.61×10^{-3}	2.09×10^{-3}	2.84×10^{4}
3.18×10^{-5}	1.93×10^{-3}	2.51×10^{-3}	3.28×10^{4}
3.18×10^{-5}	2.42×10^{-3}	3.15×10^{-3}	4.03×10^{4}
3.18×10^{-5}	2.90×10^{-3}	3.77×10^{-3}	4.67×10^{4}



$k = 1.47 \times 10^7$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-ethyl dithiocarbonate (**2a**) with $(pyr)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 612 nm).

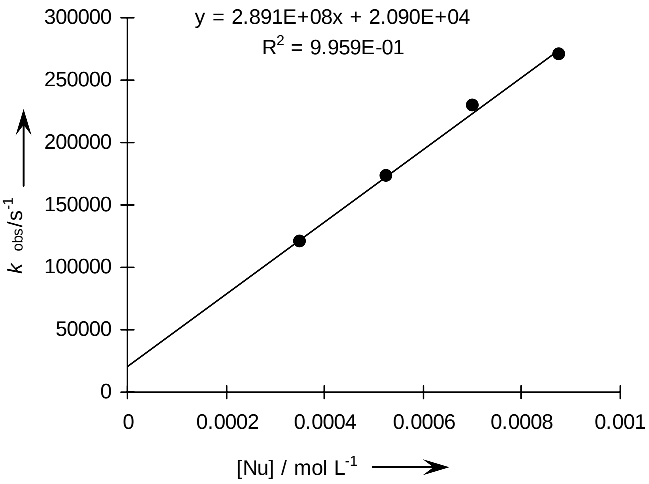
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.15×10^{-5}	2.19×10^{-4}	3.50×10^{-4}	2.99×10^{4}
2.15×10^{-5}	4.38×10^{-4}	7.00×10^{-4}	5.93×10^{4}
2.15×10^{-5}	6.58×10^{-4}	1.05×10^{-3}	9.07×10^{4}
2.15×10^{-5}	8.77×10^{-4}	1.40×10^{-3}	1.15×10^{5}
2.15×10^{-5}	1.09×10^{-3}	1.75×10^{-3}	1.41×10^{5}



$k = 1.27 \times 10^{8}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-ethyl dithiocarbonate (**2a**) with $(dma)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 607 nm).

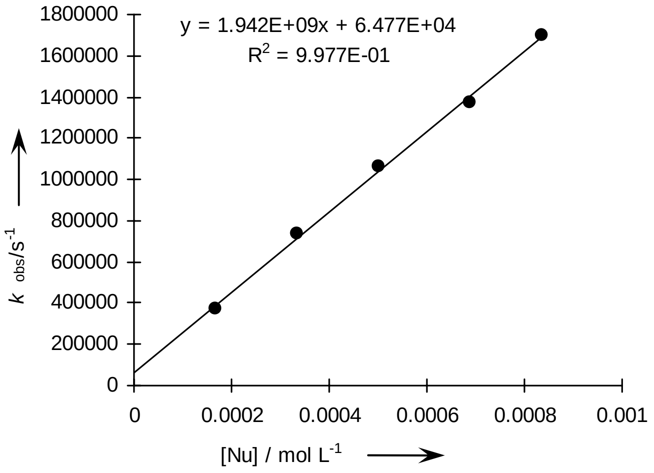
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.73×10^{-5}	3.50×10^{-4}	3.72×10^{-4}	1.20×10^{5}
1.73×10^{-5}	5.25×10^{-4}	7.45×10^{-4}	1.73×10^{5}
1.73×10^{-5}	7.00×10^{-4}	1.12×10^{-3}	2.29×10^{5}
1.73×10^{-5}	8.75×10^{-4}	1.49×10^{-3}	2.70×10^{5}



$k = 2.89 \times 10^{8}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-ethyl dithiocarbonate (**2a**) with $(mor)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 618 nm).

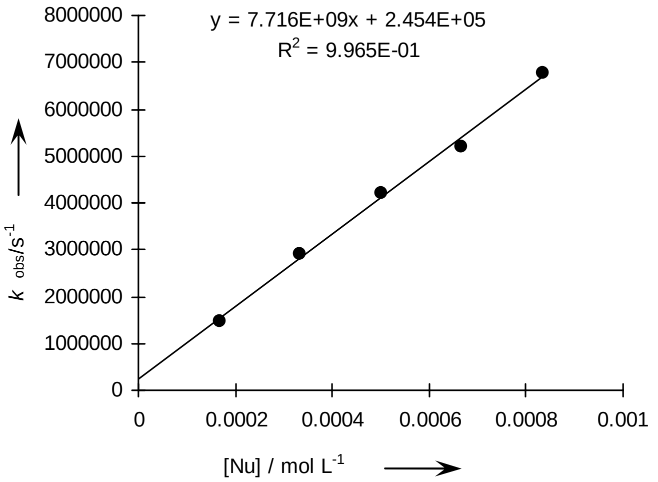
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.65×10^{-5}	1.67×10^{-4}	2.84×10^{-4}	3.71×10^{5}
1.65×10^{-5}	3.34×10^{-4}	5.68×10^{-4}	7.34×10^{5}
1.65×10^{-5}	5.02×10^{-4}	8.52×10^{-4}	1.06×10^{6}
1.65×10^{-5}	6.90×10^{-4}	1.14×10^{-3}	1.37×10^{6}
1.65×10^{-5}	8.36×10^{-4}	1.42×10^{-3}	1.70×10^{6}



$k = 1.94 \times 10^9$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-ethyl dithiocarbonate (**2a**) with $(dpa)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 644 nm).

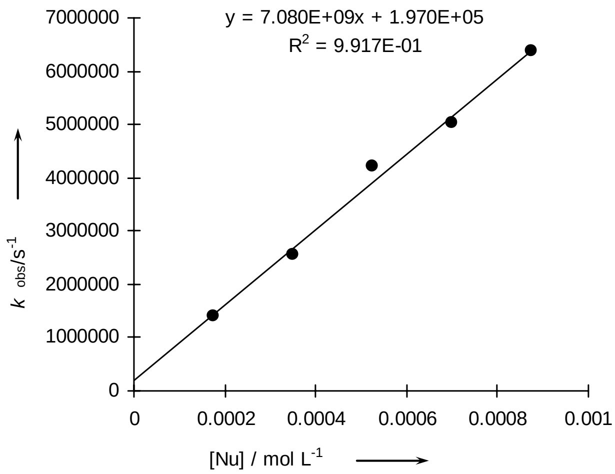
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.83×10^{-5}	1.67×10^{-4}	2.84×10^{-4}	1.48×10^{6}
1.83×10^{-5}	3.33×10^{-4}	5.68×10^{-4}	2.90×10^{6}
1.83×10^{-5}	5.01×10^{-4}	8.52×10^{-4}	4.19×10^{6}
1.83×10^{-5}	6.68×10^{-4}	1.14×10^{-3}	5.21×10^{6}
1.83×10^{-5}	8.35×10^{-4}	1.42×10^{-3}	6.77×10^{6}



$k = 7.72 \times 10^9$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-ethyl dithiocarbonate (**2a**) with $(mfa)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 586 nm).

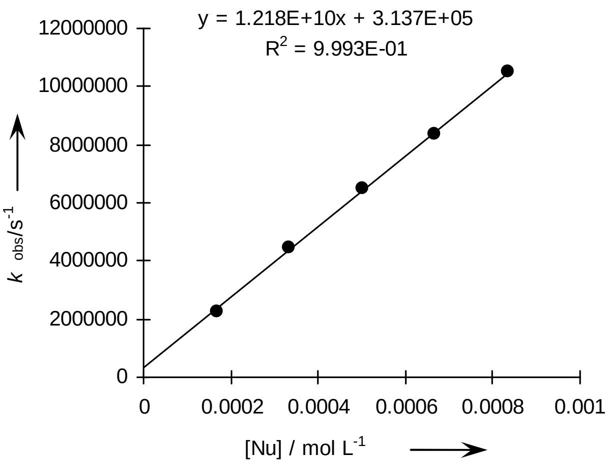
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.46×10^{-5}	1.75×10^{-4}	2.80×10^{-4}	1.41×10^{6}
1.46×10^{-5}	3.50×10^{-4}	5.60×10^{-4}	2.55×10^{6}
1.46×10^{-5}	5.25×10^{-4}	8.40×10^{-4}	4.22×10^{6}
1.46×10^{-5}	7.00×10^{-4}	1.12×10^{-3}	5.02×10^{6}
1.46×10^{-5}	8.75×10^{-4}	1.40×10^{-3}	6.37×10^{6}



$k = 7.08 \times 10^{9}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-ethyl dithiocarbonate (**2a**) with $(pfa)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 599 nm).

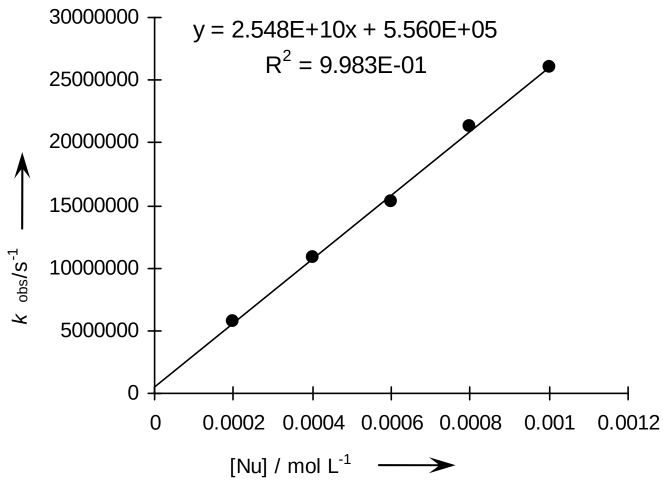
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.81×10^{-5}	1.67×10^{-4}	2.51×10^{-4}	2.27×10^{6}
1.81×10^{-5}	3.34×10^{-4}	5.01×10^{-4}	4.47×10^{6}
1.81×10^{-5}	5.01×10^{-4}	7.52×10^{-4}	6.49×10^{6}
1.81×10^{-5}	6.68×10^{-4}	1.00×10^{-4}	8.35×10^{6}
1.81×10^{-5}	8.35×10^{-4}	1.25×10^{-4}	1.05×10^{7}



$k = 1.22 \times 10^{10}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-ethyl dithiocarbonate (**2a**) with $(ani)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 500 nm).

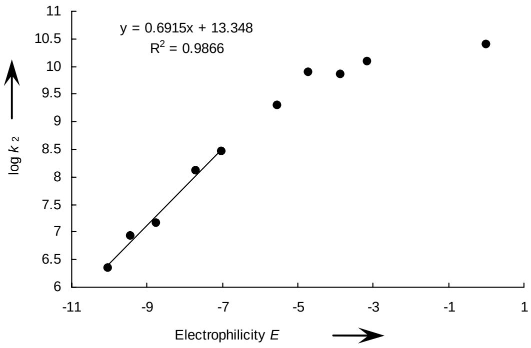
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.50×10^{-5}	2.00×10^{-4}	4.78×10^{-4}	5.72×10^{6}
2.50×10^{-5}	4.00×10^{-4}	9.56×10^{-4}	1.09×10^{7}
2.50×10^{-5}	6.00×10^{-4}	1.43×10^{-3}	1.53×10^{7}
2.50×10^{-5}	8.00×10^{-4}	1.91×10^{-3}	2.13×10^{7}
2.50×10^{-5}	1.00×10^{-3}	2.39×10^{-3}	2.60×10^{7}



$k = 2.55 \times 10^{10}$ M^{-1} s^{-1}

Determination of the parameters N and s_N for **2a**

Electrophiles	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	2.27×10^{6}
$(jul)_2CH^+$	–9.45	8.68×10^{6}
$(ind)_2CH^+$	–8.76	1.47×10^{7}
$(pyr)_2CH^+$	–7.69	1.27×10^{8}
$(dma)_2CH^+$	–7.02	2.89×10^{8}
$(mor)_2CH^+$	–5.89	1.94×10^{9} [a]
$(dpa)_2CH^+$	–4.72	7.72×10^{9} [a]
$(mfa)_2CH^+$	–3.85	7.08×10^{9} [a]
$(pfa)_2CH^+$	–3.14	1.22×10^{10} [a]
$(ani)_2CH^+$	0	2.55×10^{10} [a]



N = 19.30

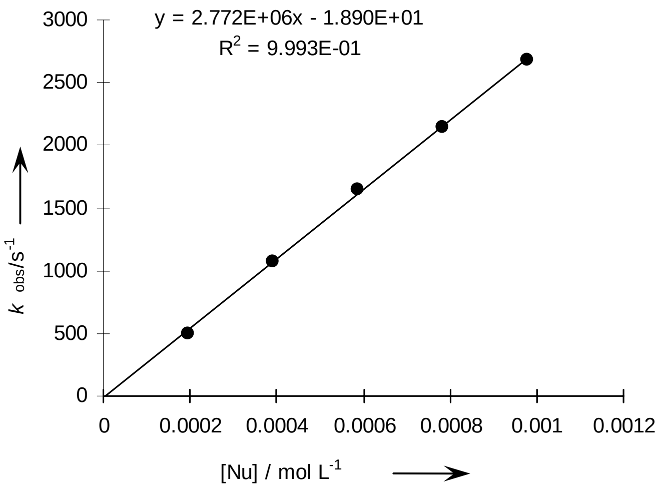
s_N = 0.69

[a] Because of the proximity of the diffusion limit, not used for the calculation of N and s_N.

Kinetics of the reaction of 2b with Ar_2CH^+.

Rate constants for the reactions of potassium *O*-isopropyl dithiocarbonate (**2b**) with $(lil)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 632 nm).

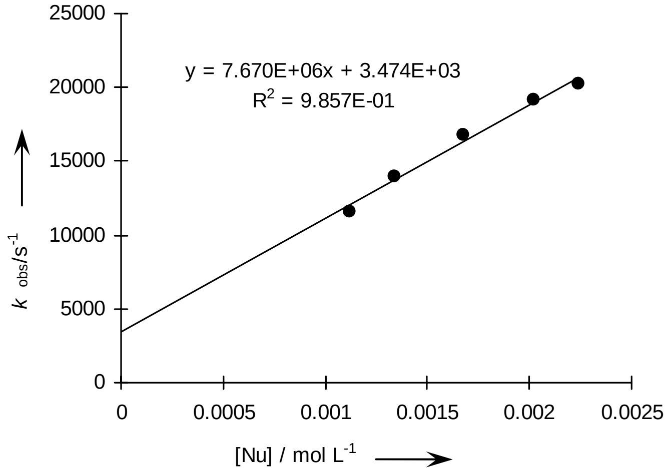
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.91×10^{-5}	1.96×10^{-4}	3.14×10^{-4}	5.04×10^{2}
2.91×10^{-5}	3.92×10^{-4}	6.27×10^{-4}	1.07×10^{3}
2.91×10^{-5}	5.88×10^{-4}	9.41×10^{-4}	1.65×10^{3}
2.91×10^{-5}	7.84×10^{-4}	1.25×10^{-3}	2.15×10^{3}
2.91×10^{-5}	9.80×10^{-4}	1.57×10^{-3}	2.68×10^{3}



$k = 2.77 \times 10^{6}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-isopropyl dithiocarbonate (**2b**) with $(jul)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 640 nm).

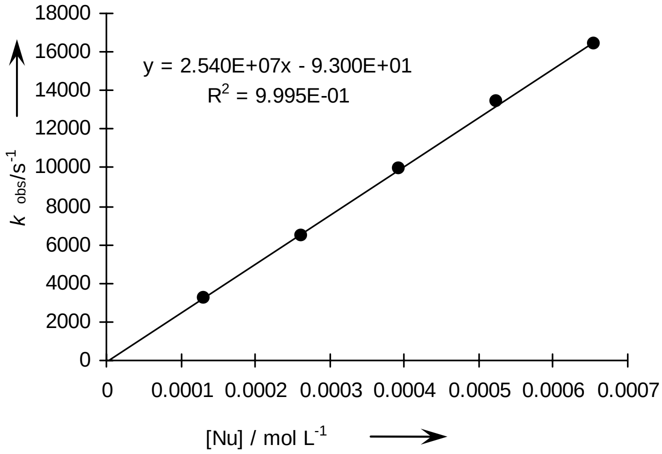
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.34×10^{-5}	1.12×10^{-3}	1.68×10^{-4}	1.16×10^{4}
3.34×10^{-5}	1.34×10^{-3}	2.01×10^{-4}	1.40×10^{4}
3.34×10^{-5}	1.68×10^{-3}	2.52×10^{-4}	1.68×10^{4}
3.34×10^{-5}	2.02×10^{-3}	3.03×10^{-3}	1.92×10^{4}
3.34×10^{-5}	2.24×10^{-3}	3.36×10^{-3}	2.02×10^{4}



$k = 7.67 \times 10^6$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-isopropyl dithiocarbonate (**2b**) with $(ind)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 616 nm).

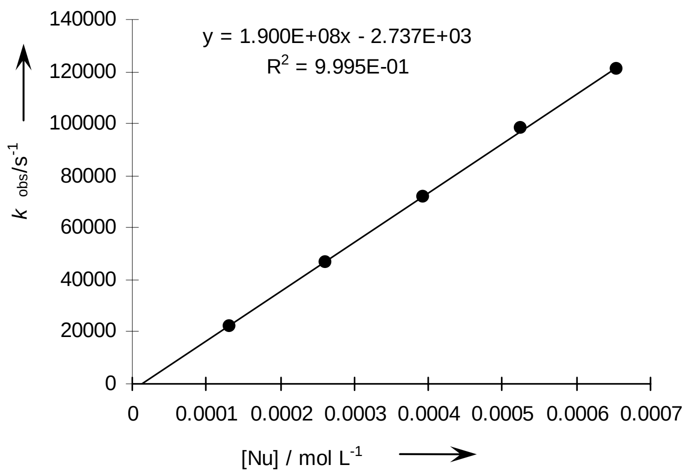
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.33×10^{-5}	1.31×10^{-4}	2.17×10^{-4}	3.21×10^{3}
2.33×10^{-5}	2.62×10^{-4}	4.35×10^{-4}	6.51×10^{3}
2.33×10^{-5}	3.93×10^{-4}	6.52×10^{-4}	9.92×10^{3}
2.33×10^{-5}	5.24×10^{-4}	8.70×10^{-4}	1.34×10^{4}
2.33×10^{-5}	6.55×10^{-4}	1.09×10^{-3}	1.64×10^{4}



$k = 2.54 \times 10^7$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-isopropyl dithiocarbonate (**2b**) with $(pyr)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 612 nm).

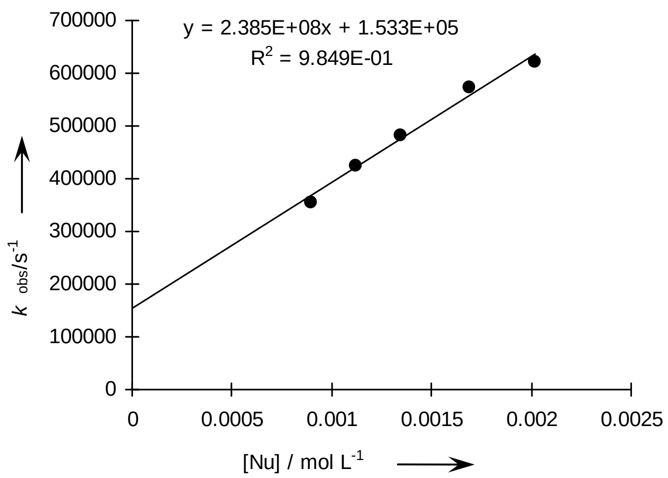
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.58×10^{-5}	1.31×10^{-4}	2.33×10^{-4}	2.21×10^{4}
2.58×10^{-5}	2.62×10^{-4}	4.66×10^{-4}	4.66×10^{4}
2.58×10^{-5}	3.93×10^{-4}	7.00×10^{-4}	7.19×10^{4}
2.58×10^{-5}	5.24×10^{-4}	9.33×10^{-4}	9.82×10^{4}
2.58×10^{-5}	6.55×10^{-4}	1.17×10^{-3}	1.21×10^{5}



$k = 1.90 \times 10^{8}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *O*-isopropyl dithiocarbonate (**2b**) with $(dma)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 607 nm).

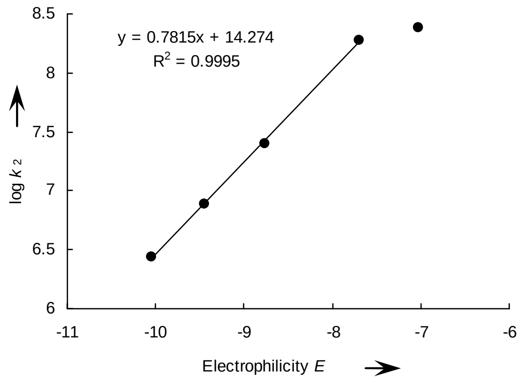
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.34×10^{-5}	8.99×10^{-4}	1.17×10^{-3}	3.56×10^{5}
3.34×10^{-5}	1.12×10^{-3}	1.46×10^{-3}	4.24×10^{5}
3.34×10^{-5}	1.35×10^{-3}	1.76×10^{-3}	4.81×10^{5}
3.34×10^{-5}	1.69×10^{-3}	2.20×10^{-3}	5.73×10^{5}
3.34×10^{-5}	2.02×10^{-3}	2.63×10^{-3}	6.20×10^{5}



$k = 2.39 \times 10^{8}$ M^{-1} s^{-1}

Determination of the parameters *N* and s_N for **2b**

Electrophiles	*E*	*k* ($M^{-1} s^{-1}$)
$(lil)_2CH^+$	–10.04	2.77×10^6
$(jul)_2CH^+$	–9.45	7.67×10^6
$(ind)_2CH^+$	–8.76	2.54×10^7
$(pyr)_2CH^+$	–7.69	1.90×10^8
$(dma)_2CH^+$	–7.02	2.39×10^{8} [a]



***N* = 18.27**

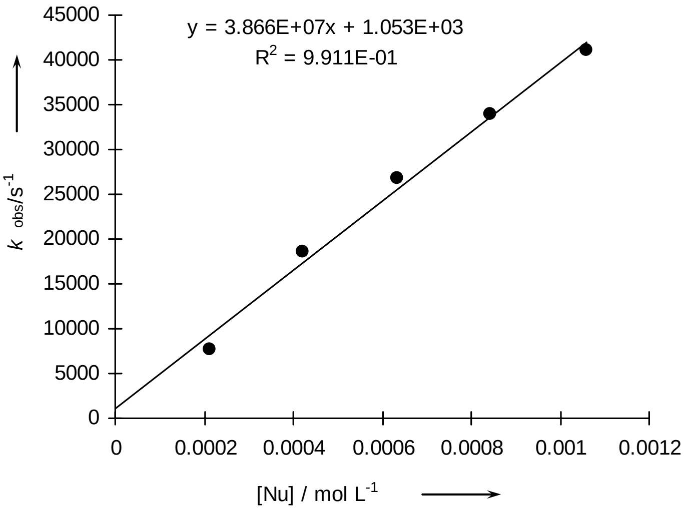
s_N = 0.78

[a] Because of the proximity of the diffusion limit, not used for the calculation of *N* and s_N.

Kinetics of the reaction of the 3a with Ar_2CH^+.

Rate constants for the reactions of potassium *N*,*N*-dimethyldithiocarbamate (**3a**) with $(lil)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 632 nm).

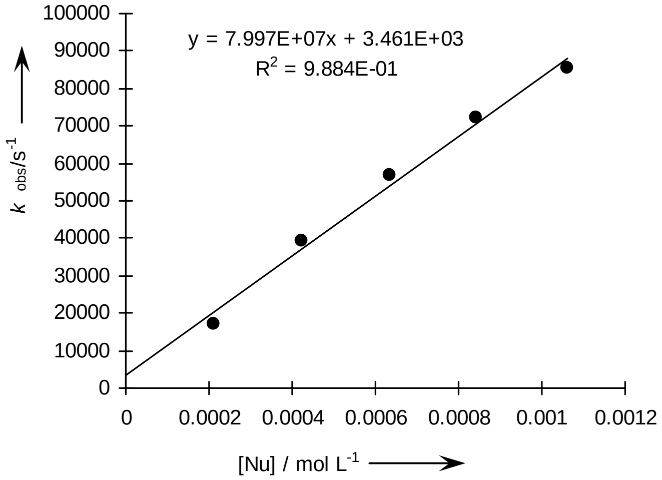
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.91×10^{-5}	2.11×10^{-4}	3.80×10^{-4}	7.71×10^{3}
2.91×10^{-5}	4.22×10^{-4}	7.60×10^{-4}	1.85×10^{4}
2.91×10^{-5}	6.33×10^{-4}	1.14×10^{-3}	2.67×10^{4}
2.91×10^{-5}	8.44×10^{-4}	1.52×10^{-3}	3.39×10^{4}
2.91×10^{-5}	1.06×10^{-3}	1.90×10^{-3}	4.10×10^{4}



$k = 3.87 \times 10^{7}\ M^{-1}\ s^{-1}$

Rate constants for the reactions of potassium *N*,*N*-dimethyldithiocarbamate (**3a**) with $(jul)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 640 nm).

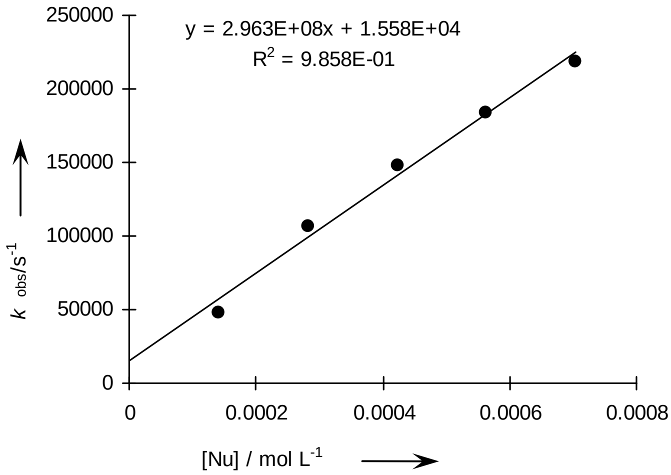
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.15×10^{-5}	2.11×10^{-4}	3.80×10^{-4}	1.70×10^{4}
3.15×10^{-5}	4.22×10^{-4}	7.60×10^{-4}	3.93×10^{4}
3.15×10^{-5}	6.33×10^{-4}	1.14×10^{-3}	5.69×10^{4}
3.15×10^{-5}	8.44×10^{-4}	1.52×10^{-3}	7.23×10^{4}
3.15×10^{-5}	1.06×10^{-4}	1.90×10^{-3}	8.53×10^{4}



$k = 8.00 \times 10^{7}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$

Rate constants for the reactions of potassium *N*,*N*-dimethyldithiocarbamate (**3a**) with $(ind)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 616 nm).

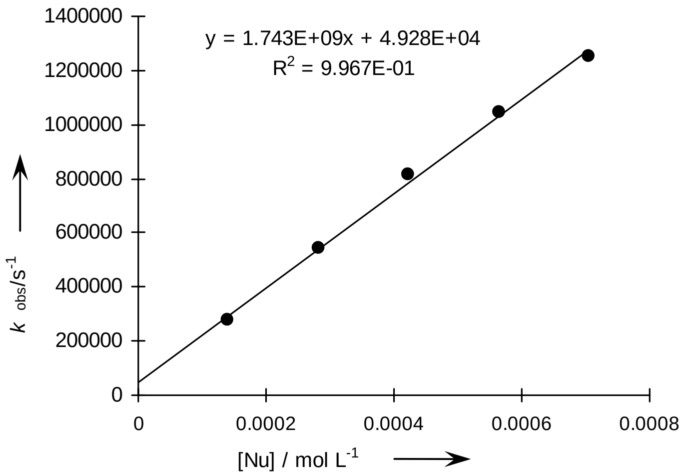
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.33×10^{-5}	1.41×10^{-4}	2.65×10^{-4}	4.76×10^{4}
2.33×10^{-5}	2.82×10^{-4}	5.30×10^{-4}	1.07×10^{5}
2.33×10^{-5}	4.23×10^{-4}	7.94×10^{-4}	1.48×10^{5}
2.33×10^{-5}	5.64×10^{-4}	1.06×10^{-4}	1.84×10^{5}
2.33×10^{-5}	7.05×10^{-4}	1.32×10^{-3}	2.18×10^{5}



$k = 2.96 \times 10^{8}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$

Rate constants for the reactions of potassium *N*,*N*-dimethyldithiocarbamate (**3a**) with $(pyr)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 612 nm).

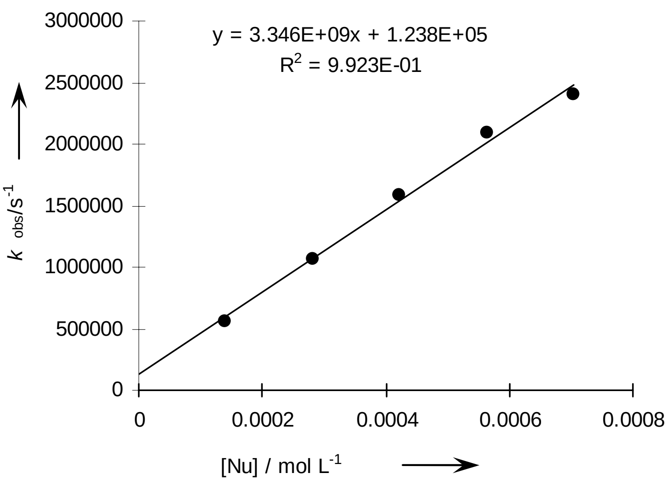
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.58×10^{-5}	1.41×10^{-4}	2.65×10^{-4}	2.75×10^{5}
2.58×10^{-5}	2.82×10^{-4}	5.30×10^{-4}	5.45×10^{5}
2.58×10^{-5}	4.23×10^{-4}	7.94×10^{-4}	8.15×10^{5}
2.58×10^{-5}	5.64×10^{-4}	1.06×10^{-4}	1.05×10^{6}
2.58×10^{-5}	7.05×10^{-4}	1.32×10^{-3}	1.25×10^{6}



$k = 1.74 \times 10^{9}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium *N*,*N*-dimethyldithiocarbamate (**3a**) with $(dma)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 607 nm).

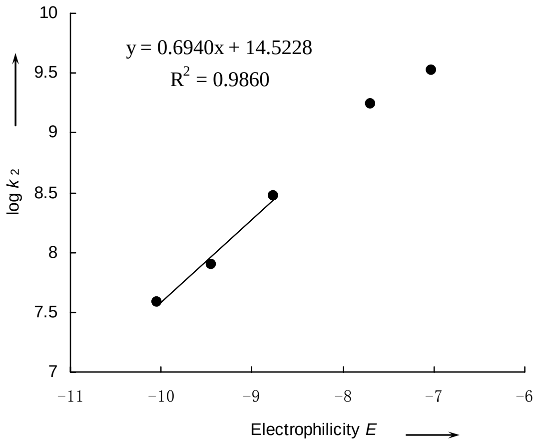
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.91×10^{-5}	1.41×10^{-4}	2.46×10^{-4}	5.56×10^{5}
1.91×10^{-5}	2.82×10^{-4}	4.92×10^{-4}	1.06×10^{6}
1.91×10^{-5}	4.23×10^{-4}	7.38×10^{-4}	1.59×10^{6}
1.91×10^{-5}	5.64×10^{-4}	9.84×10^{-4}	2.09×10^{6}
1.91×10^{-5}	7.05×10^{-4}	1.23×10^{-3}	2.40×10^{6}



$k = 3.35 \times 10^{9}$ M^{-1} s^{-1}

Determination of the parameters N and s_N for **3a**

Electrophiles	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	3.87×10^7
$(jul)_2CH^+$	–9.45	8.00×10^7
$(ind)_2CH^+$	–8.76	2.96×10^8
$(pyr)_2CH^+$	–7.69	1.74×10^9 [a]
$(dma)_2CH^+$	–7.02	3.35×10^9 [a]



***N* = 20.93**

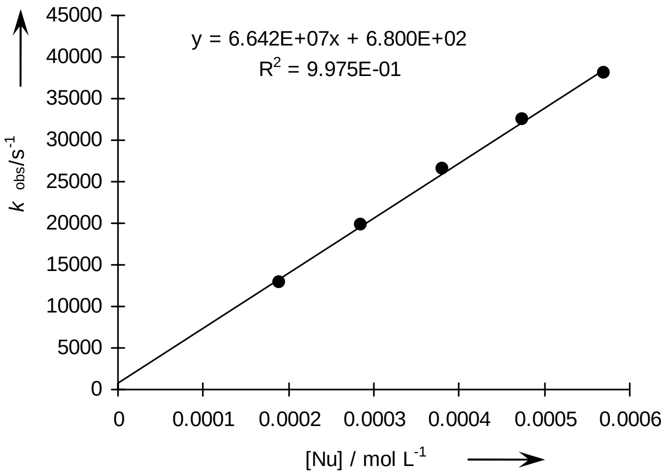
***s*$_N$ = 0.69**

[a] Because of the proximity of the diffusion limit, not used for the calculation of N and s_N.

Kinetics of the reaction of 3b with Ar_2CH^+.

Rate constants for the reactions of potassium pyrrolidinedithiocarbamate (**3b)** with $(lil)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 632 nm).

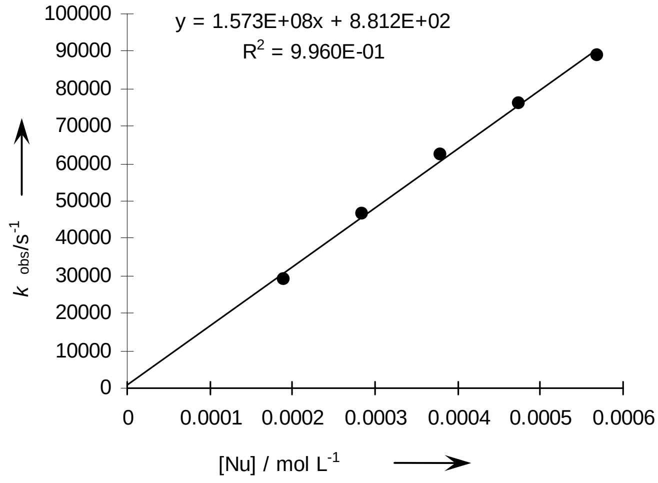
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.21×10^{-5}	1.90×10^{-4}	3.93×10^{-4}	1.28×10^{4}
3.21×10^{-5}	2.85×10^{-4}	5.90×10^{-4}	1.98×10^{4}
3.21×10^{-5}	3.80×10^{-4}	7.86×10^{-4}	2.65×10^{4}
3.21×10^{-5}	4.75×10^{-4}	9.83×10^{-4}	3.25×10^{4}
3.21×10^{-5}	5.70×10^{-4}	1.18×10^{-3}	3.80×10^{4}



$k = 6.64 \times 10^{7}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium pyrrolidinedithiocarbamate (**3b**) with $(jul)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 640 nm).

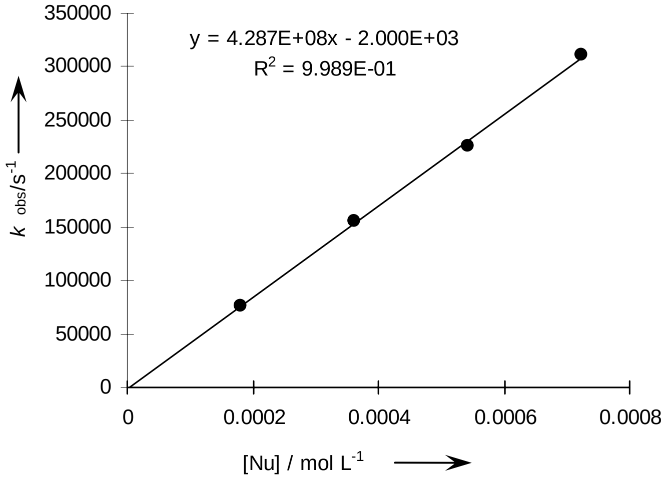
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.15×10^{-5}	1.90×10^{-4}	3.93×10^{-4}	2.92×10^{4}
3.15×10^{-5}	2.85×10^{-4}	5.90×10^{-4}	4.65×10^{4}
3.15×10^{-5}	3.80×10^{-4}	7.86×10^{-4}	6.25×10^{4}
3.15×10^{-5}	4.75×10^{-4}	9.83×10^{-4}	7.61×10^{4}
3.15×10^{-5}	5.70×10^{-4}	1.18×10^{-3}	8.91×10^{4}



$k = 1.57 \times 10^{8}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium pyrrolidinedithiocarbamate (**3b**) with $(ind)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 616 nm).

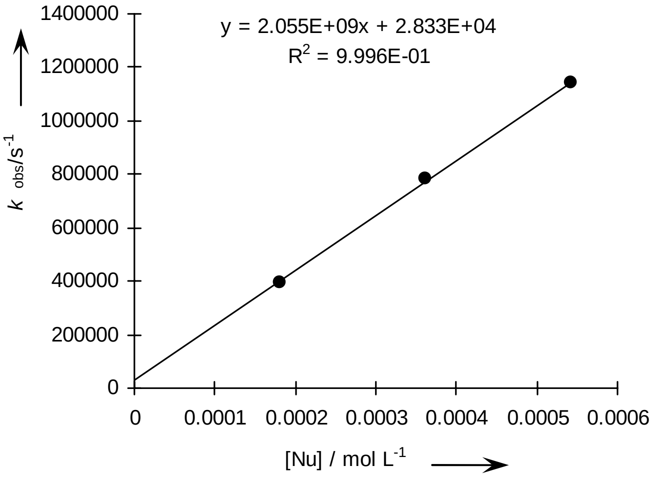
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.54×10^{-5}	1.81×10^{-4}	3.78×10^{-4}	7.60×10^{4}
2.54×10^{-5}	3.62×10^{-4}	7.57×10^{-4}	1.55×10^{5}
2.54×10^{-5}	5.43×10^{-4}	1.13×10^{-3}	2.26×10^{5}
2.54×10^{-5}	7.24×10^{-4}	1.51×10^{-3}	3.11×10^{5}



$k = 4.29 \times 10^{8}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium pyrrolidinedithiocarbamate (**3b**) with $(pyr)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 612 nm).

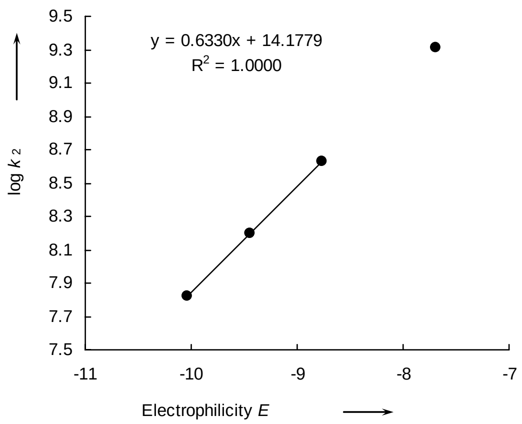
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.58×10^{-5}	1.81×10^{-4}	3.78×10^{-4}	3.96×10^{5}
2.58×10^{-5}	3.62×10^{-4}	7.57×10^{-4}	7.81×10^{5}
2.58×10^{-5}	5.43×10^{-4}	1.13×10^{-3}	1.14×10^{6}



$k = 2.06 \times 10^9$ M^{-1} s^{-1}

Determination of the parameters N and s_N for **3b**

Electrophiles	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	6.64×10^7
$(jul)_2CH^+$	–9.45	1.57×10^8
$(ind)_2CH^+$	–8.76	4.29×10^8
$(pyr)_2CH^+$	–7.69	$2.06 \times 10^{9\,a}$



***N* = 22.40**

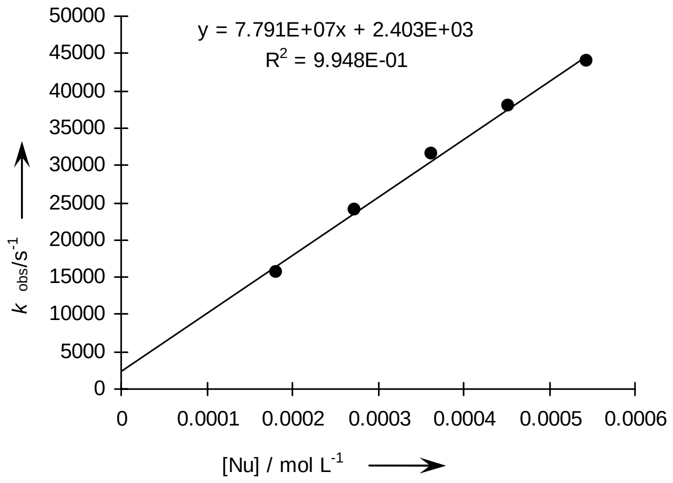
s_N = 0.63

[a] Because of the proximity of the diffusion limit, not used for the calculation of N and s_N.

Kinetics of the reaction of 3c with Ar_2CH^+.

Rate constants for the reactions of potassium piperidine-1-carbodithioate (**3c**) with $(lil)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 632 nm).

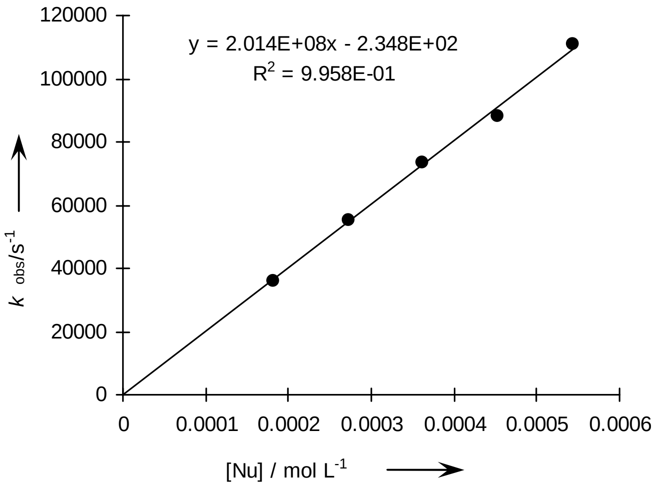
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.21×10^{-5}	1.81×10^{-4}	3.93×10^{-4}	1.56×10^{4}
3.21×10^{-5}	2.72×10^{-4}	5.90×10^{-4}	2.41×10^{4}
3.21×10^{-5}	3.62×10^{-4}	7.87×10^{-4}	3.15×10^{4}
3.21×10^{-5}	4.53×10^{-4}	9.84×10^{-4}	3.80×10^{4}
3.21×10^{-5}	5.43×10^{-4}	1.18×10^{-3}	4.39×10^{4}



$k = 7.79 \times 10^{7}\ M^{-1}\ s^{-1}$

Rate constants for the reactions of potassium piperidine-1-carbodithioate (**3c**) with $(jul)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 640 nm).

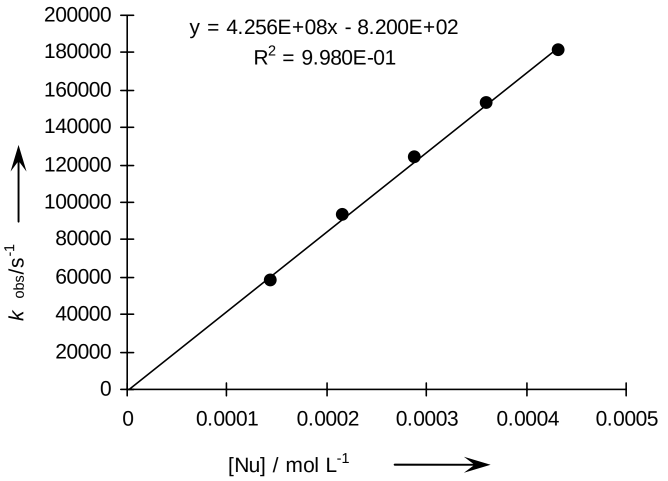
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.15×10^{-5}	1.81×10^{-4}	3.93×10^{-4}	3.62×10^{4}
3.15×10^{-5}	2.72×10^{-4}	5.90×10^{-4}	5.52×10^{4}
3.15×10^{-5}	3.62×10^{-4}	7.87×10^{-4}	7.33×10^{4}
3.15×10^{-5}	4.53×10^{-4}	9.84×10^{-4}	8.79×10^{4}
3.15×10^{-5}	5.43×10^{-4}	1.18×10^{-3}	1.11×10^{5}



$k = 2.01 \times 10^{8}\ M^{-1}\ s^{-1}$

Rate constants for the reactions of potassium piperidine-1-carbodithioate (**3c**) with $(ind)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 616 nm).

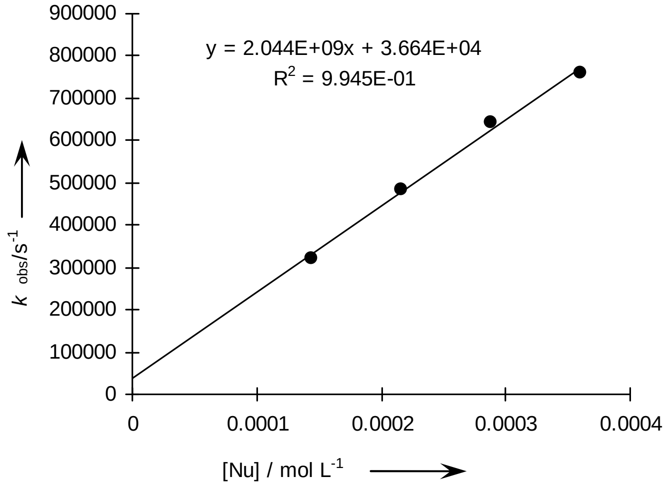
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.75×10^{-5}	1.44×10^{-4}	3.33×10^{-4}	5.79×10^{4}
2.75×10^{-5}	2.16×10^{-4}	4.99×10^{-4}	9.28×10^{4}
2.75×10^{-5}	2.88×10^{-4}	6.66×10^{-4}	1.24×10^{5}
2.75×10^{-5}	3.60×10^{-4}	8.32×10^{-4}	1.53×10^{5}
2.75×10^{-5}	4.32×10^{-4}	1.04×10^{-3}	1.81×10^{5}



$k = 4.26 \times 10^{8}\ M^{-1}\ s^{-1}$

Rate constants for the reactions of potassium piperidine-1-carbodithioate (**3c**) with $(pyr)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 612 nm).

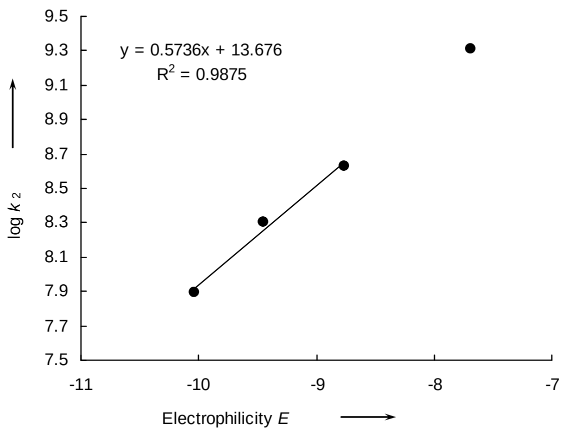
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.74×10^{-5}	1.44×10^{-4}	3.33×10^{-4}	3.21×10^{5}
2.74×10^{-5}	2.16×10^{-4}	4.99×10^{-4}	4.84×10^{5}
2.74×10^{-5}	2.88×10^{-4}	6.66×10^{-4}	6.42×10^{5}
2.74×10^{-5}	3.60×10^{-4}	8.32×10^{-4}	7.59×10^{5}



$k = 2.04 \times 10^{9}$ M^{-1} s^{-1}

Determination of the parameters N and s_N for **3c**

Electrophiles	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	7.79×10^{7}
$(jul)_2CH^+$	–9.45	2.01×10^{8}
$(ind)_2CH^+$	–8.76	4.26×10^{8}
$(pyr)_2CH^+$	–7.69	2.04×10^{9} [a]



***N* = 23.84**

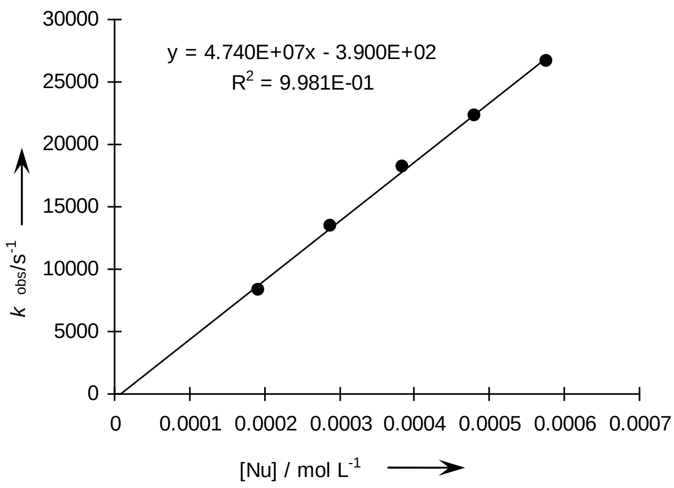
***s*$_N$ = 0.57**

[a] Because of the proximity of the diffusion limit, not used for the calculation of N and s_N.

Kinetics of the reaction of 3d with Ar_2CH^+.

Rate constants for the reactions of potassium 4-methyl-1-piperazinecarbodithioate (**3d**) with $(lil)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 632 nm).

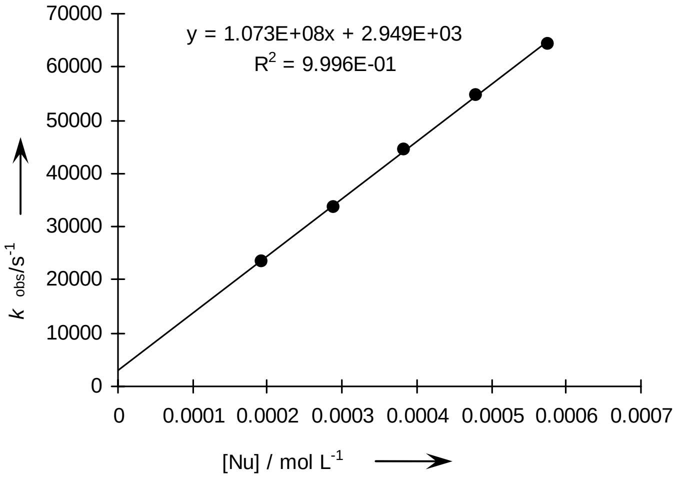
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.21×10^{-5}	1.92×10^{-4}	3.93×10^{-4}	8.35×10^{3}
3.21×10^{-5}	2.88×10^{-4}	5.90×10^{-4}	1.35×10^{4}
3.21×10^{-5}	3.84×10^{-4}	7.87×10^{-4}	1.82×10^{4}
3.21×10^{-5}	4.80×10^{-4}	9.84×10^{-4}	2.23×10^{4}
3.21×10^{-5}	5.76×10^{-4}	1.18×10^{-3}	2.67×10^{4}



$k = 4.74 \times 10^{7}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium 4-methyl-1-piperazinecarbodithioate (**3d**) with $(jul)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 640 nm).

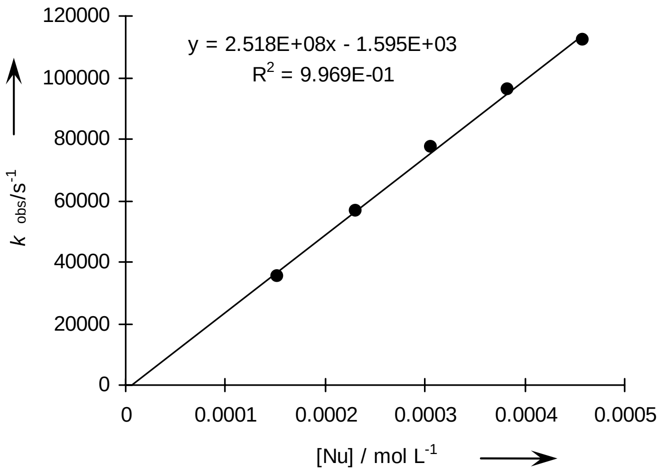
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.15×10^{-5}	1.92×10^{-4}	3.93×10^{-4}	2.34×10^{4}
3.15×10^{-5}	2.88×10^{-4}	5.90×10^{-4}	3.37×10^{4}
3.15×10^{-5}	3.84×10^{-4}	7.87×10^{-4}	4.46×10^{4}
3.15×10^{-5}	4.80×10^{-4}	9.84×10^{-4}	5.47×10^{4}
3.15×10^{-5}	5.76×10^{-4}	1.18×10^{-3}	6.44×10^{4}



$k = 1.07 \times 10^8$ M^{-1} s^{-1}

Rate constants for the reactions of potassium 4-methyl-1-piperazinecarbodithioate (**3d**) with $(ind)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 616 nm).

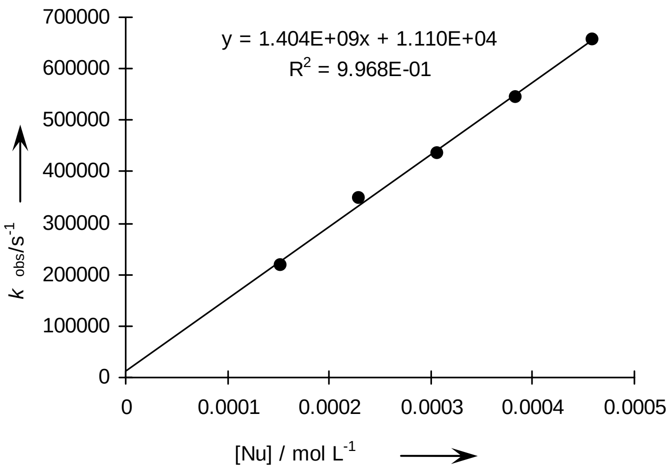
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.75×10^{-5}	1.53×10^{-4}	3.78×10^{-4}	3.54×10^{4}
2.75×10^{-5}	2.30×10^{-4}	5.68×10^{-4}	5.67×10^{4}
2.75×10^{-5}	3.06×10^{-4}	7.57×10^{-4}	7.73×10^{4}
2.75×10^{-5}	3.83×10^{-4}	9.46×10^{-4}	9.61×10^{4}
2.75×10^{-5}	4.59×10^{-4}	1.13×10^{-3}	1.12×10^{5}



$k = 2.52 \times 10^8$ M^{-1} s^{-1}

Rate constants for the reactions of potassium 4-methyl-1-piperazinecarbodithioate (**3d**) with $(pyr)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 612 nm).

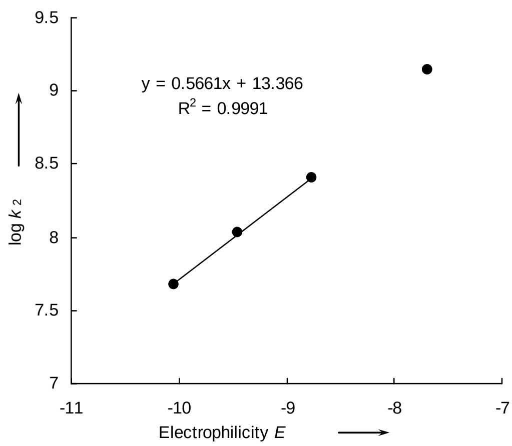
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.74×10^{-5}	1.53×10^{-4}	3.78×10^{-4}	2.18×10^{5}
2.74×10^{-5}	2.30×10^{-4}	5.68×10^{-4}	3.50×10^{5}
2.74×10^{-5}	3.06×10^{-4}	7.57×10^{-4}	4.35×10^{5}
2.74×10^{-5}	3.83×10^{-4}	9.46×10^{-4}	5.44×10^{5}
2.74×10^{-5}	4.59×10^{-4}	1.13×10^{-3}	6.58×10^{5}



$k = 1.40 \times 10^{9}$ M^{-1} s^{-1}

Determination of the parameters N and s_N for **3d**

Electrophiles	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	4.74×10^{7}
$(jul)_2CH^+$	–9.45	1.07×10^{8}
$(ind)_2CH^+$	–8.76	2.52×10^{8}
$(pyr)_2CH^+$	–7.69	1.40×10^{9} [a]



***N* = 23.61**

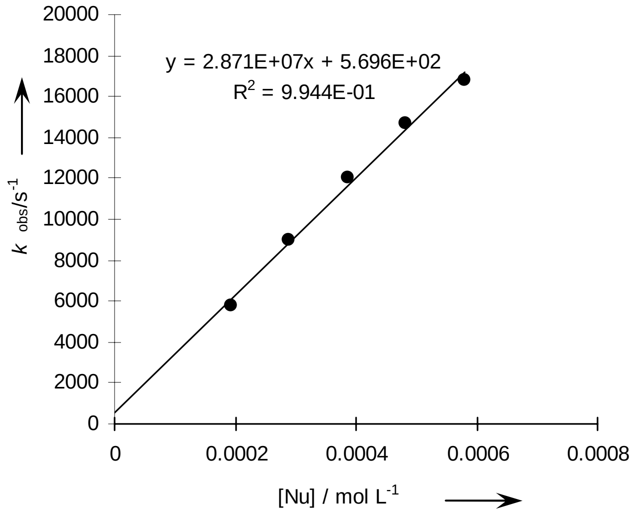
s_N = 0.57

[a] Because of the proximity of the diffusion limit, not used for the calculation of N and s_N.

Kinetics of the reaction of 3e with Ar_2CH^+.

Rate constants for the reactions of potassium morpholino-4-dithiocarboxylate (**3e**) with $(lil)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 632 nm).

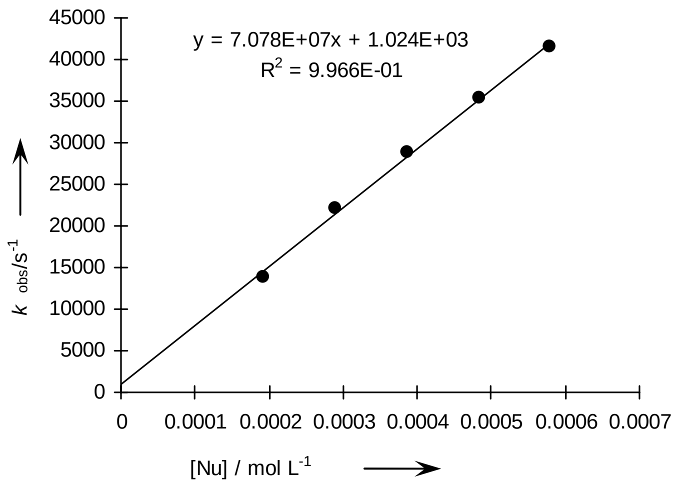
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.21×10^{-5}	1.93×10^{-4}	4.39×10^{-4}	5.82×10^{3}
3.21×10^{-5}	2.90×10^{-4}	6.59×10^{-4}	8.96×10^{3}
3.21×10^{-5}	3.86×10^{-4}	8.78×10^{-4}	1.20×10^{4}
3.21×10^{-5}	4.83×10^{-4}	1.10×10^{-3}	1.47×10^{4}
3.21×10^{-5}	5.79×10^{-4}	1.32×10^{-3}	1.68×10^{4}



$k = 2.87 \times 10^{7}\ M^{-1}\ s^{-1}$

Rate constants for the reactions of potassium morpholino-4-dithiocarboxylate (**3e**) with $(jul)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 640 nm).

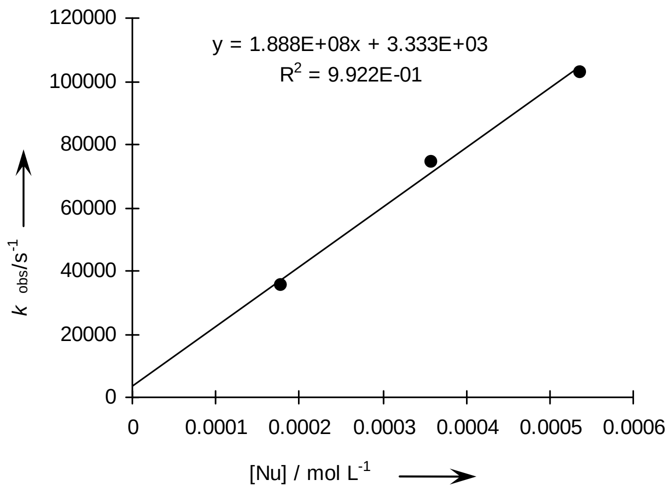
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.15×10^{-5}	1.93×10^{-4}	4.39×10^{-4}	1.39×10^{4}
3.15×10^{-5}	2.90×10^{-4}	6.59×10^{-4}	2.22×10^{4}
3.15×10^{-5}	3.86×10^{-4}	8.78×10^{-4}	2.89×10^{4}
3.15×10^{-5}	4.83×10^{-4}	1.10×10^{-3}	3.53×10^{4}
3.15×10^{-5}	5.79×10^{-4}	1.32×10^{-3}	4.15×10^{4}



$k = 7.08 \times 10^7$ M^{-1} s^{-1}

Rate constants for the reactions of potassium morpholino-4-dithiocarboxylate (**3e**) with $(ind)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 616 nm).

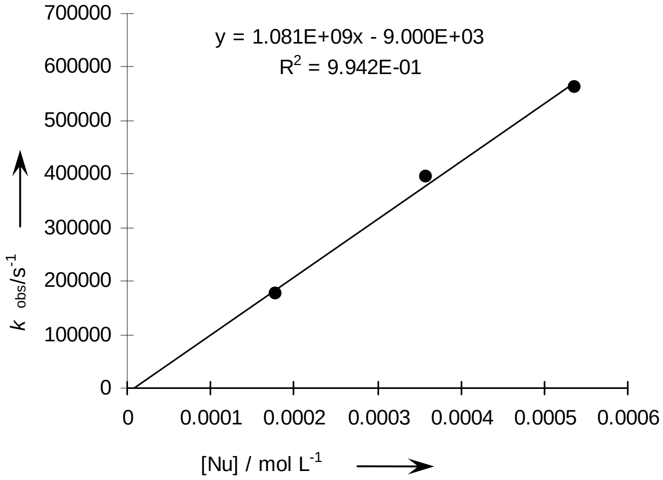
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
2.54×10^{-5}	1.79×10^{-4}	3.75×10^{-4}	3.54×10^{4}
2.54×10^{-5}	3.58×10^{-4}	7.52×10^{-4}	7.44×10^{4}
2.54×10^{-5}	5.37×10^{-4}	1.13×10^{-3}	1.03×10^{5}



$k = 1.89 \times 10^8$ M^{-1} s^{-1}

Rate constants for the reactions of potassium morpholino-4-dithiocarboxylate (**3e**) with $(pyr)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 612 nm).

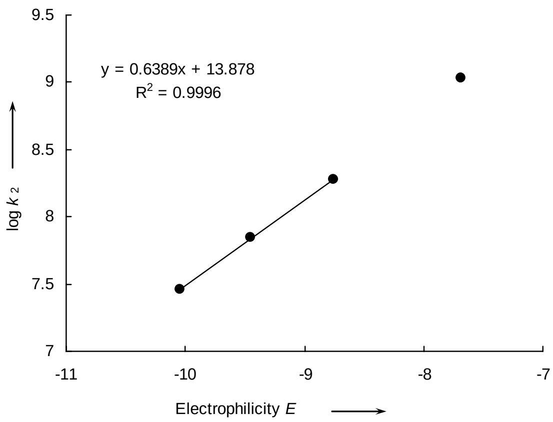
[P-salt] / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
3.44×10^{-5}	1.79×10^{-4}	3.75×10^{-4}	1.76×10^{5}
3.44×10^{-5}	3.58×10^{-4}	7.52×10^{-4}	3.95×10^{5}
3.44×10^{-5}	5.37×10^{-4}	1.13×10^{-3}	5.63×10^{5}



$k = 1.08 \times 10^9$ M^{-1} s^{-1}

Determination of the parameters N and s_N for **3e**

Electrophiles	E	k (M^{-1} s^{-1})
$(lil)_2CH^+$	–10.04	2.87×10^7
$(jul)_2CH^+$	–9.45	7.08×10^7
$(ind)_2CH^+$	–8.76	1.89×10^8
$(pyr)_2CH^+$	–7.69	$1.08 \times 10^{9\ a}$



***N* = 21.72**

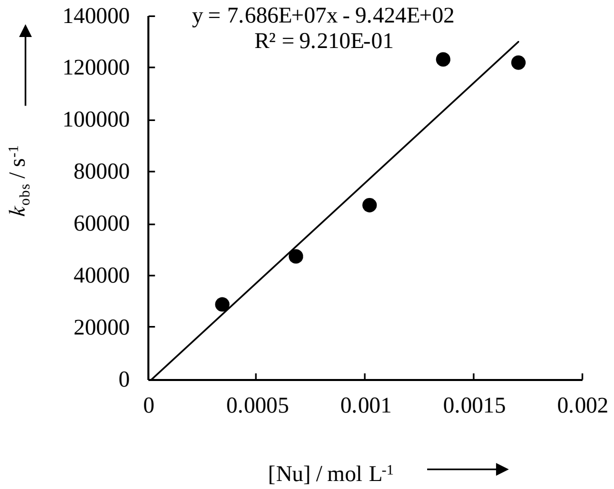
***s*$_N$ = 0.64**

[a] Because of the proximity of the diffusion limit, not used for the calculation of N and s_N.

Kinetics of the reaction of 4 with Ar_2CH^+.

Rate constants for the reactions of potassium potassium hexane-1-thiolate (**4**) with $(lil)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 632 nm).

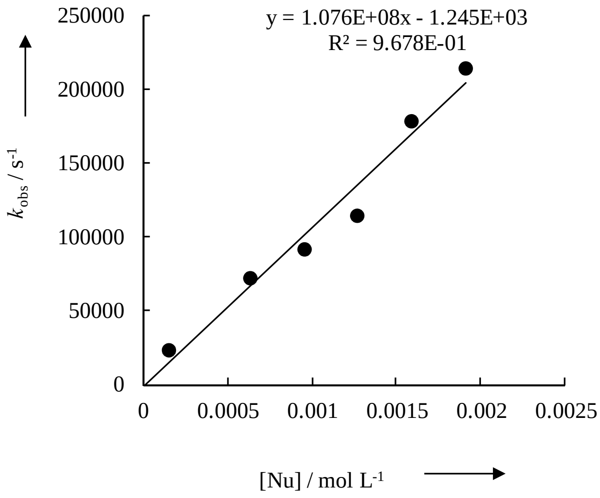
$[Ar_2CH^+]$ / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.25×10^{-5}	3.41×10^{-4}	3.41×10^{-4}	2.87×10^{4}
1.25×10^{-5}	6.82×10^{-4}	6.82×10^{-4}	4.76×10^{4}
1.25×10^{-5}	1.02×10^{-3}	1.02×10^{-3}	6.68×10^{4}
1.25×10^{-5}	1.36×10^{-3}	1.36×10^{-3}	1.23×10^{5}
1.25×10^{-5}	1.71×10^{-3}	1.71×10^{-3}	1.22×10^{5}



$k = 7.87 \times 10^{7}$ M^{-1} s^{-1}

Rate constants for the reactions of potassium potassium hexane-1-thiolate (**4**) with $(jul)_2CH^+$ in CH_3CN (20 °C, laser-flash photolysis techniques, λ = 640 nm).

$[Ar_2CH^+]$ / mol L^{-1}	[Nu] / mol L^{-1}	[18-C-6] / mol L^{-1}	k_{obs} / s^{-1}
1.26×10^{-5}	1.59×10^{-4}	1.63×10^{-4}	2.37×10^{4}
1.26×10^{-5}	6.36×10^{-4}	6.51×10^{-4}	7.20×10^{4}
1.26×10^{-5}	9.54×10^{-4}	9.76×10^{-4}	9.22×10^{4}
1.26×10^{-5}	1.27×10^{-3}	1.30×10^{-3}	1.14×10^{5}
1.26×10^{-5}	1.59×10^{-3}	1.63×10^{-3}	1.78×10^{5}
1.26×10^{-5}	1.91×10^{-3}	1.95×10^{-3}	2.14×10^{5}



$k = 1.08 \times 10^8\ M^{-1}\ s^{-1}$

4. References

S1. H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov and H. Schimmel, *J. Am. Chem. Soc.*, 2001, **123**, 9500–9512.

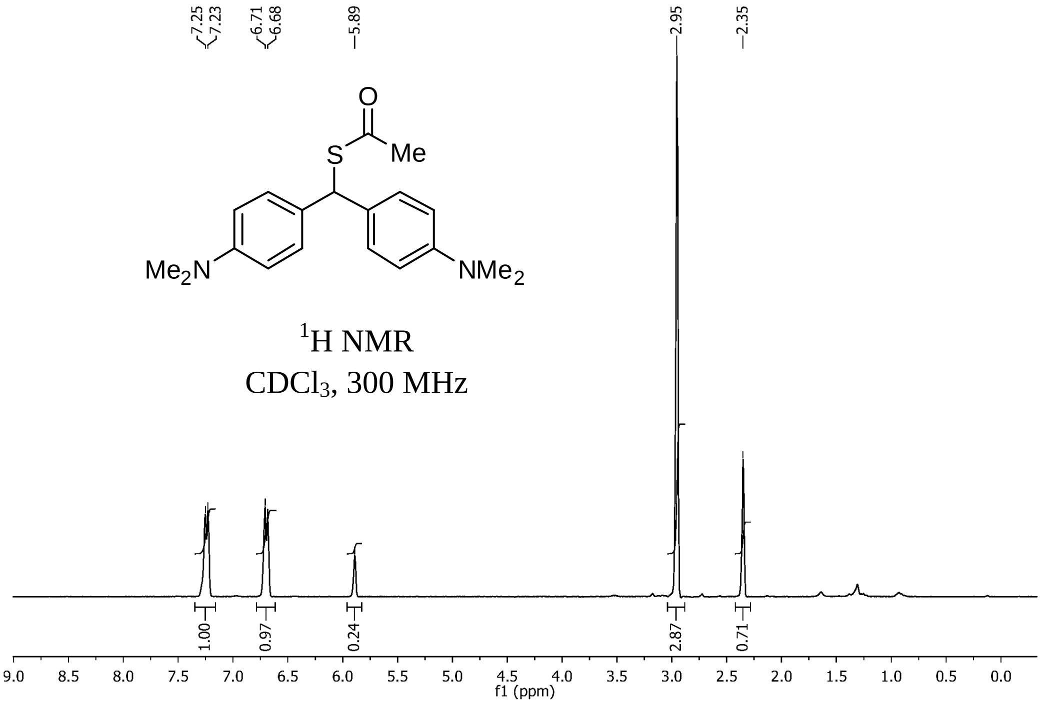
S2. B. Kempf and H. Mayr, *Chem. Eur. J.,* 2005, **11**, 917–927.

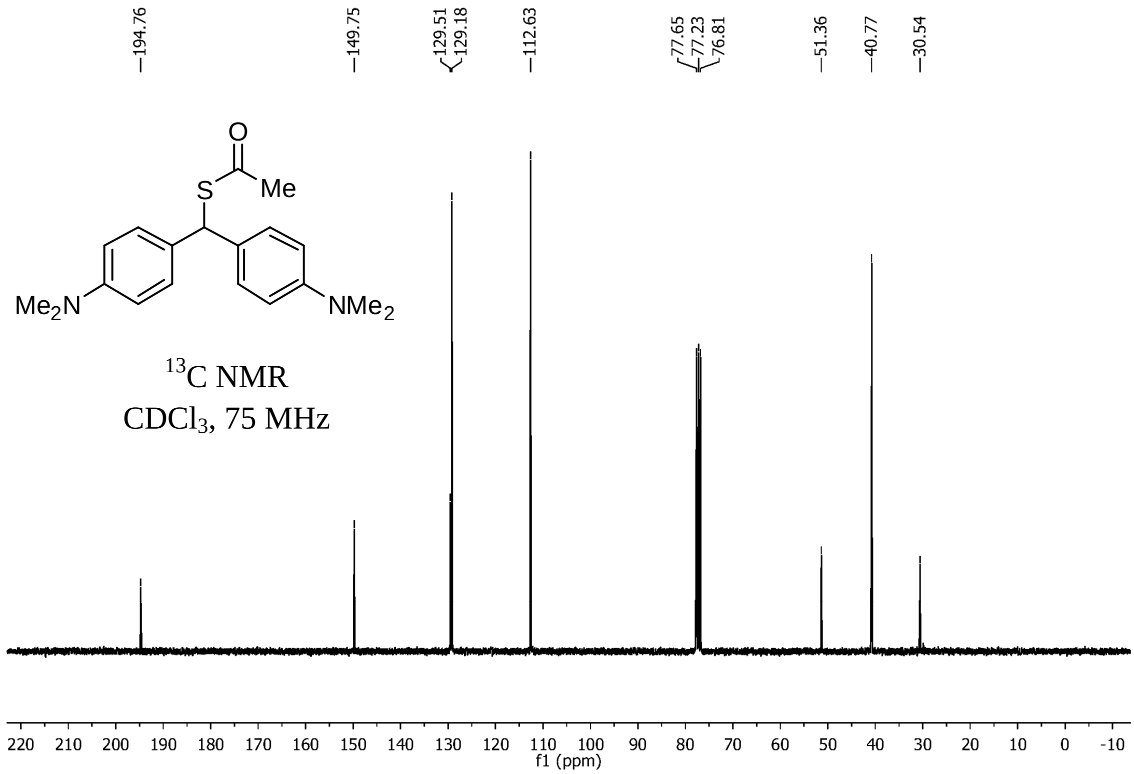
S3. (a) B. Denegri, A. Streiter, S. Juric, A. R. Ofial, O. Kronja and H. Mayr, *Chem.–Eur. J.*, 2006, **12**, 1648–1656. (b) M. Baidya, S. Kobayashi, F. Brotzel, U. Schmidhammer, E. Riedle and H. Mayr, *Angew. Chem. Int. Ed.*, 2006, **46**, 6176–6179.

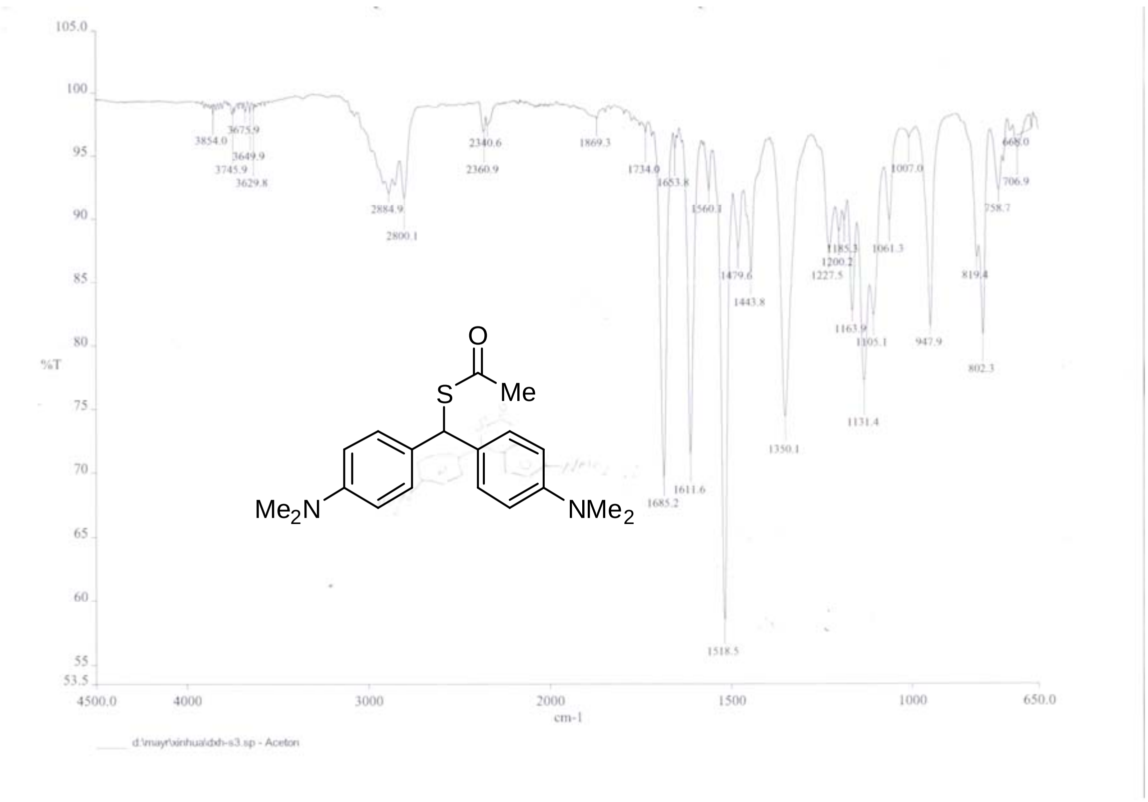
S4. Ö. Güzel and A. Salman, *Bioorg. Med. Chem*., 2006, **14**, 7804–7815.

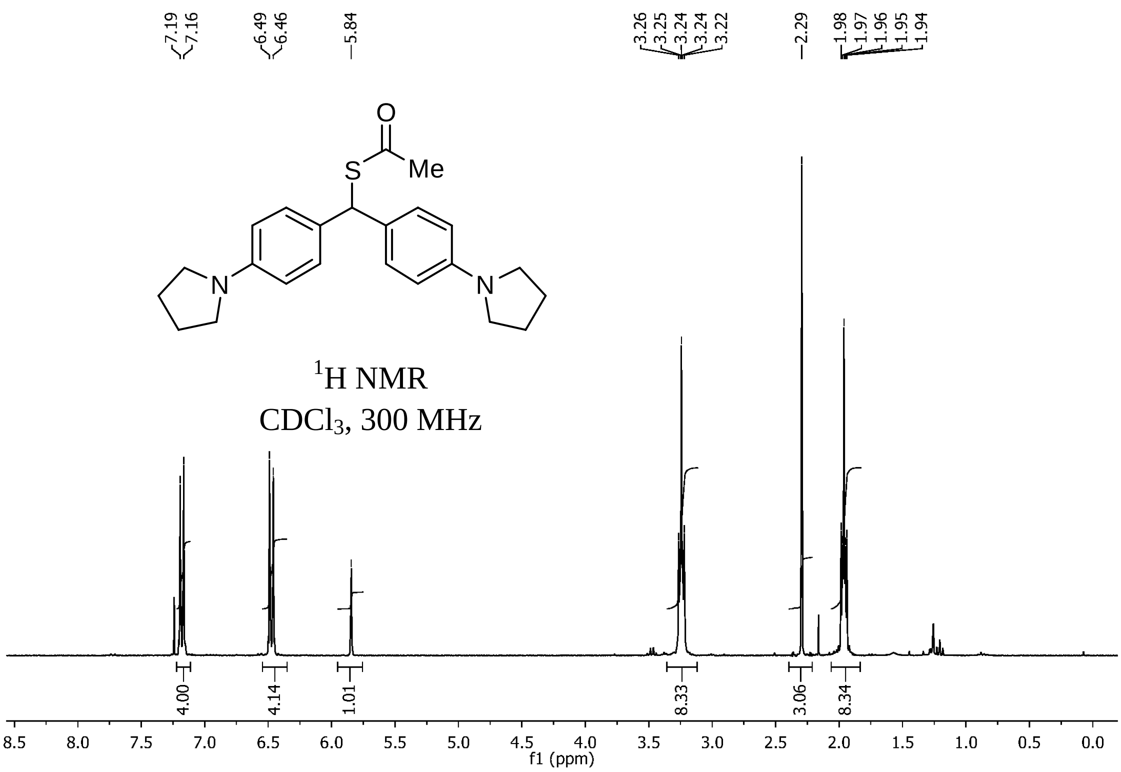
S5. D. E. Laycock and H. Alper, *J. Org. Chem.*, 1981, **46**, 289–293.

5. Copies of NMR and IR spectra

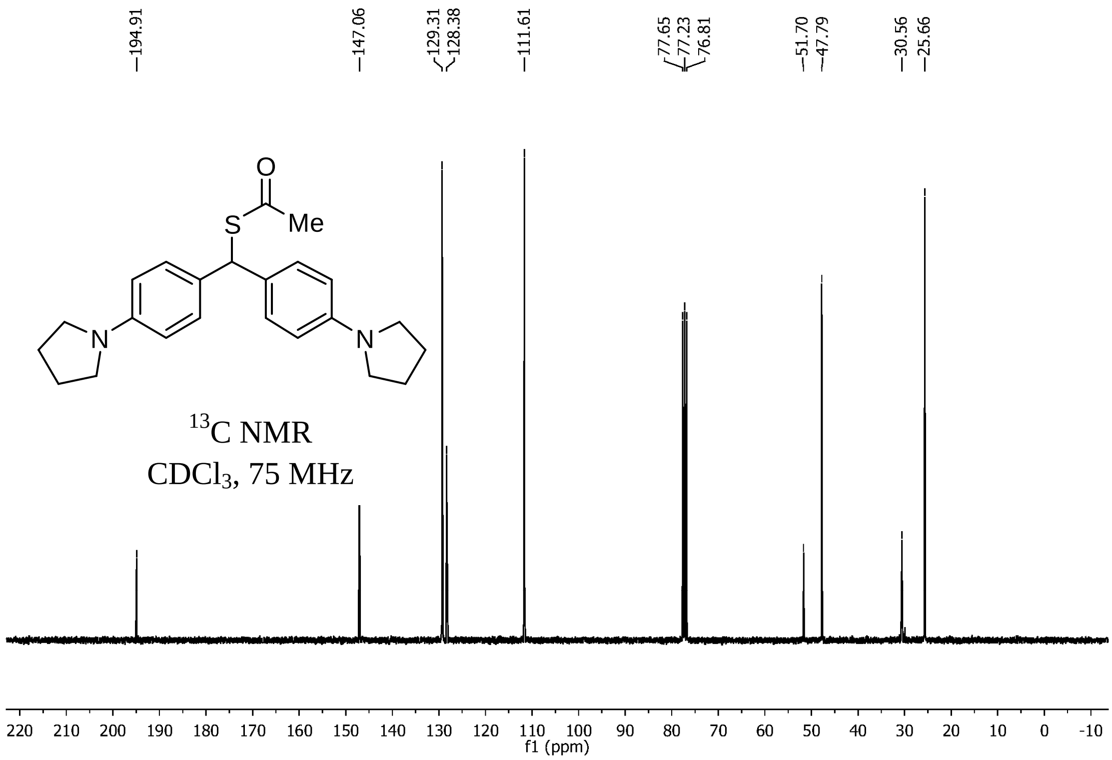


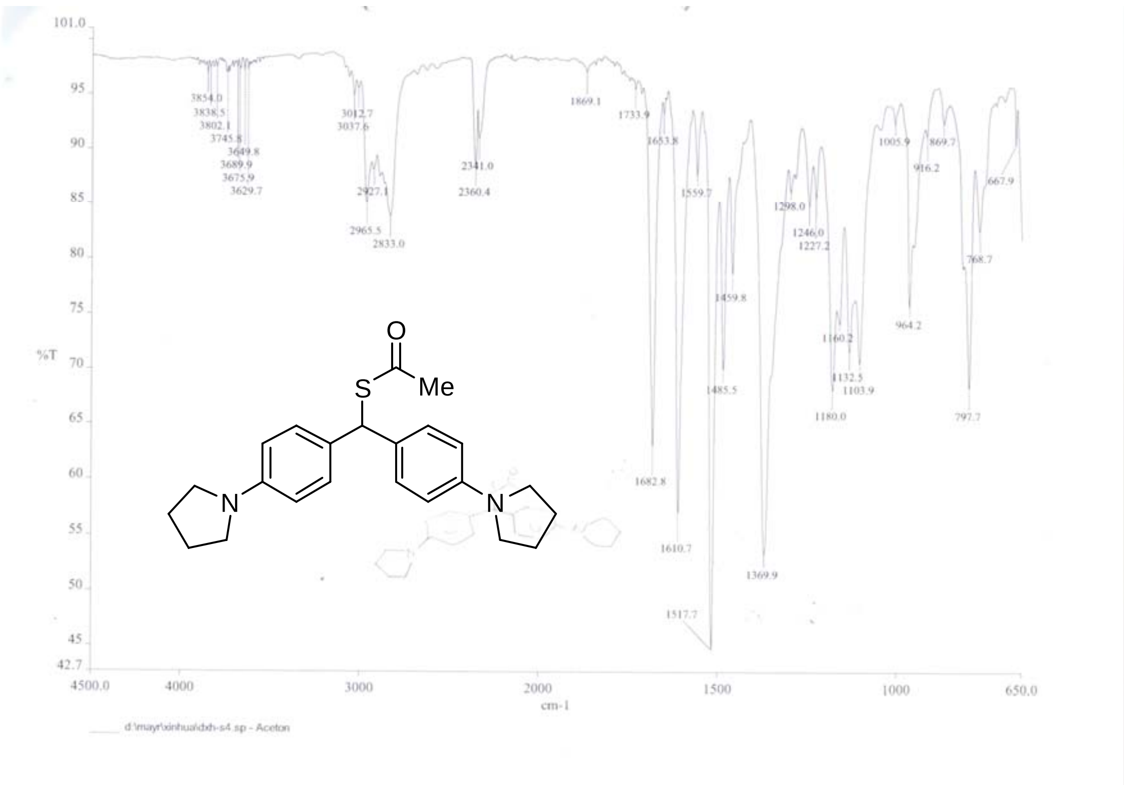


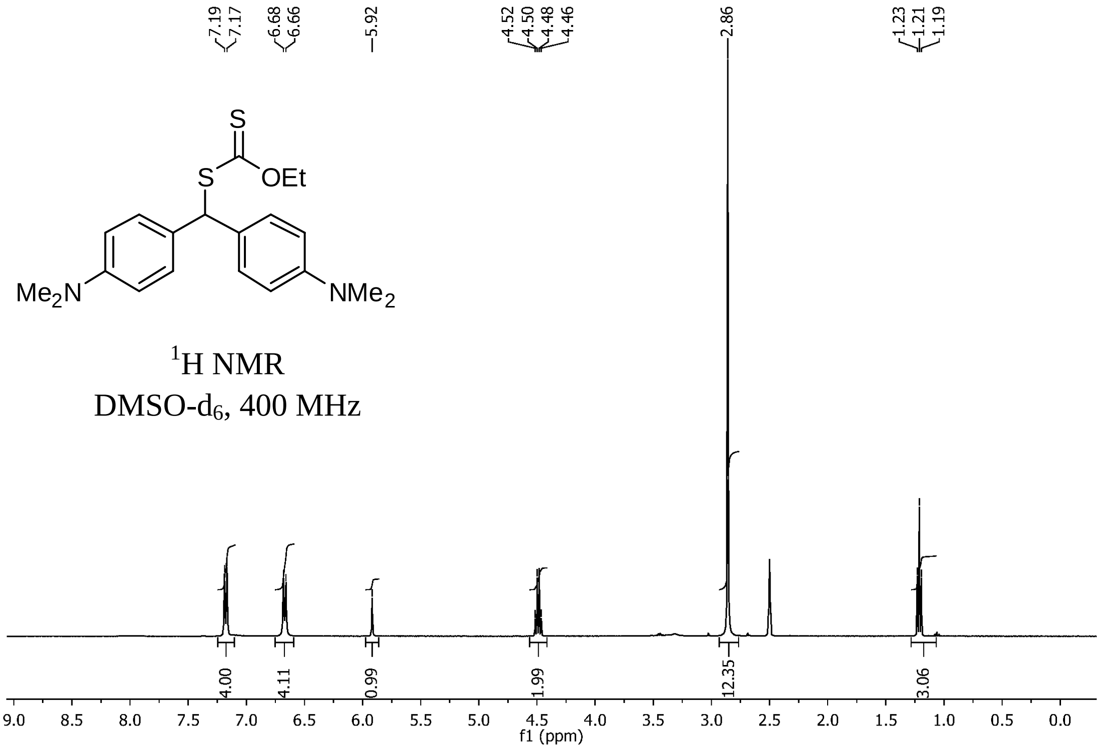


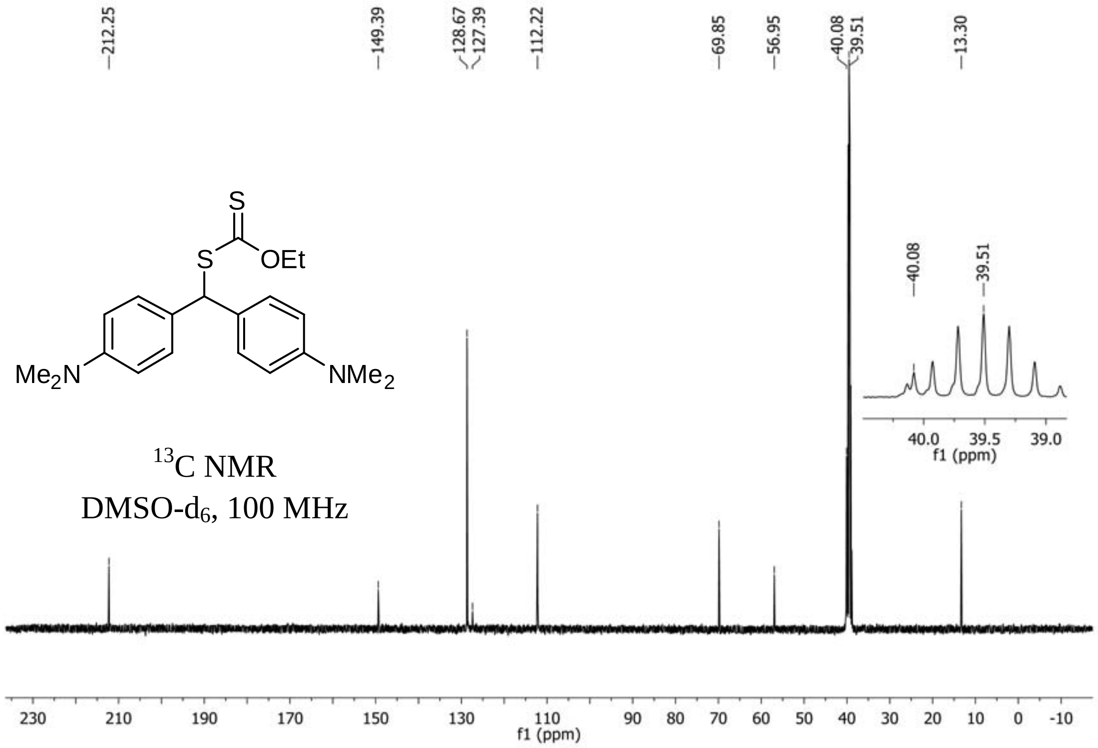


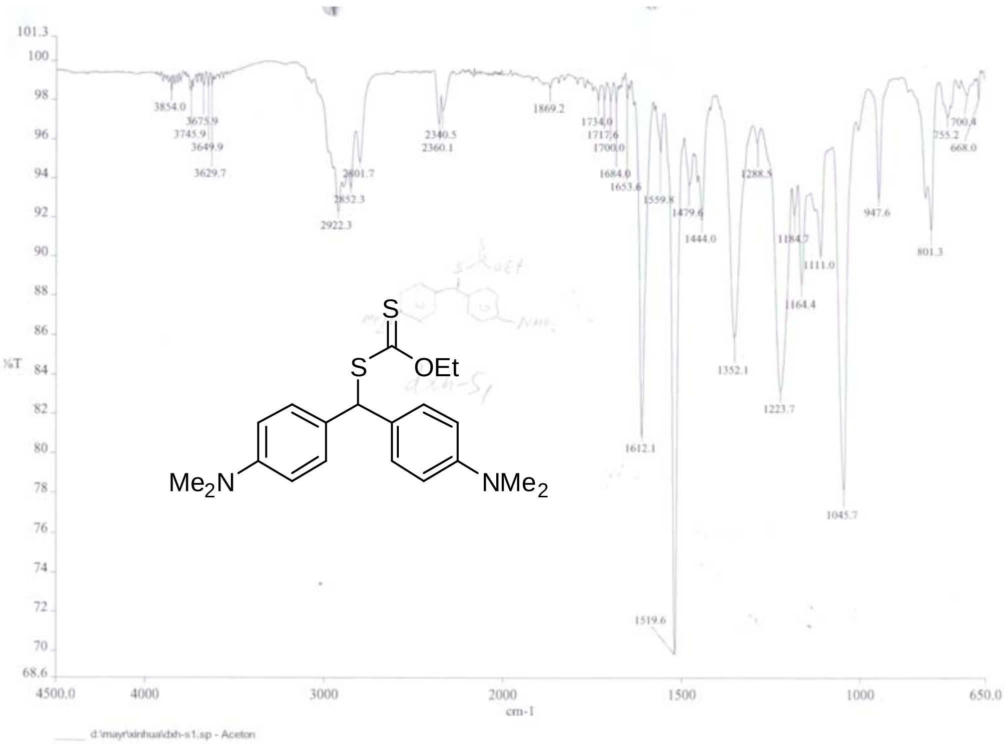
[1]H NMR
CDCl3, 300 MHz

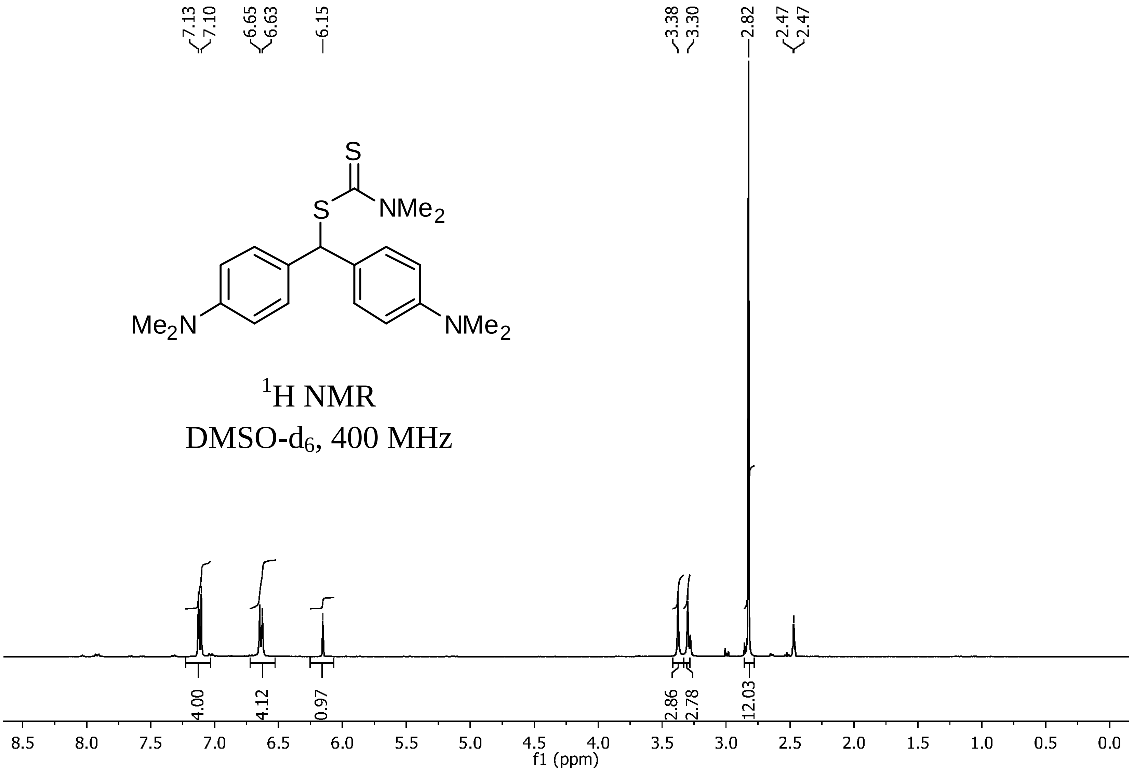

194.91
147.06
129.31
128.38
111.61
77.65
77.23
76.81
51.70
47.79
30.56
25.66
O
S
Me
N
N
13C NMR
CDCl3, 75 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

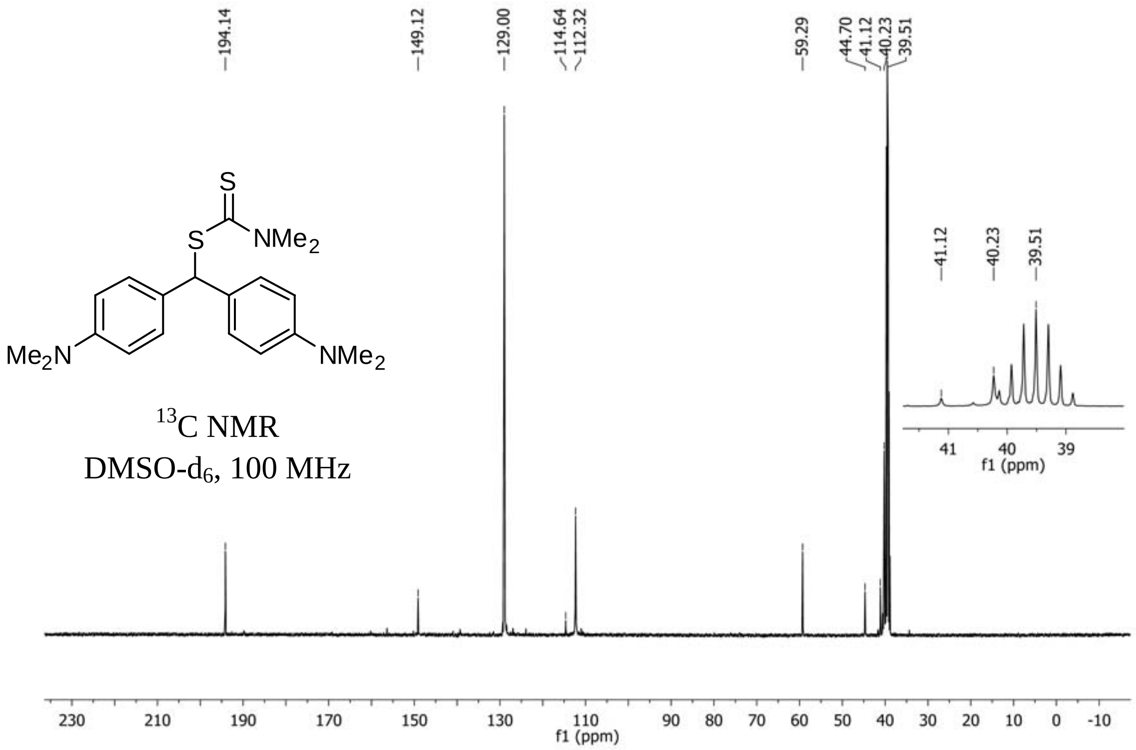

%T
cm-1
O
S
Me
N
N

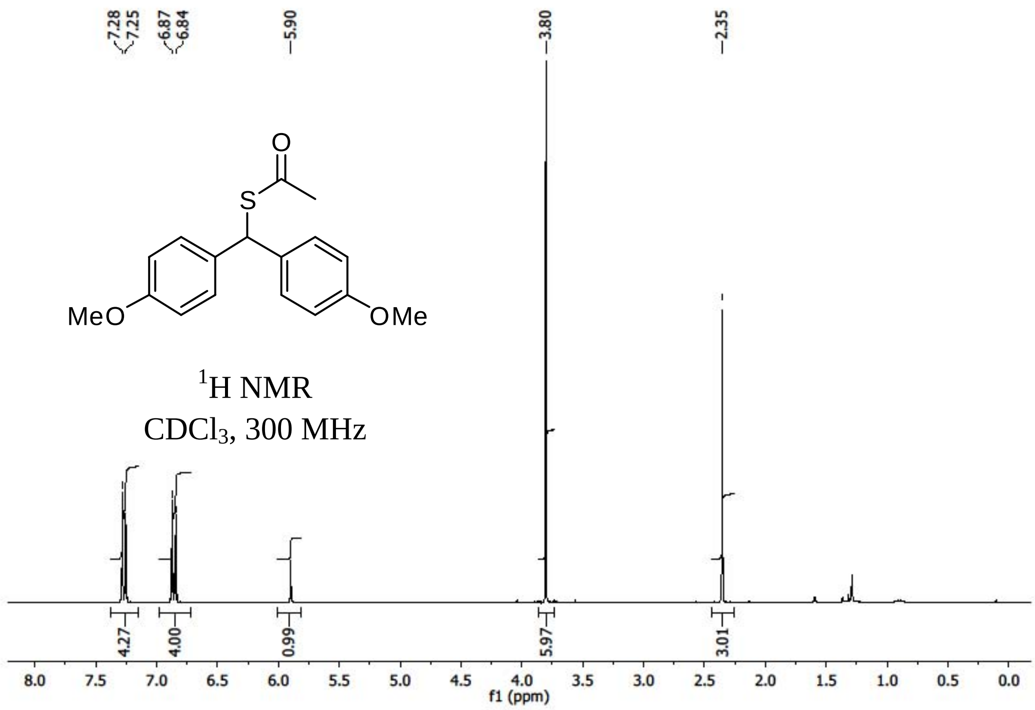

7.19
7.17
6.68
6.66
5.92
4.52
4.50
4.48
4.46
2.86
1.23
1.21
1.19
S
S
OEt
Me2N
NMe2
1H NMR
DMSO-d6, 400 MHz
4.00
4.11
0.99
1.99
12.35
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

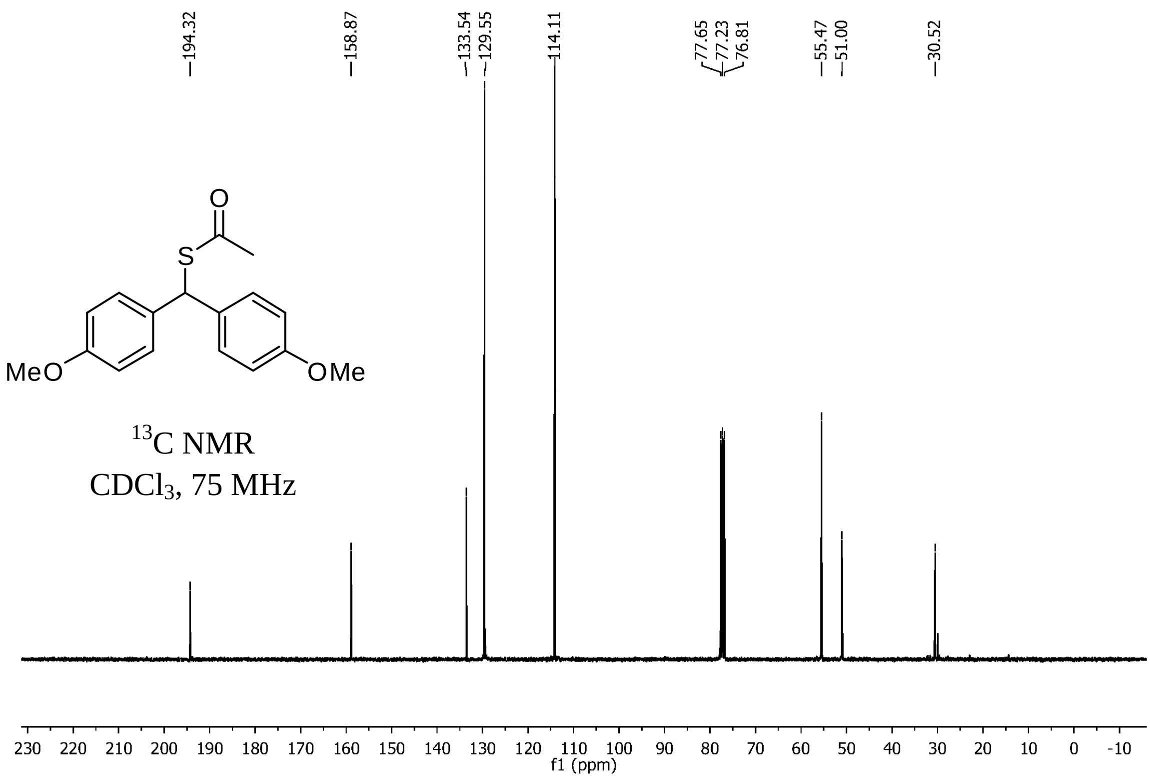

212.25
149.39
128.67
127.39
112.22
69.85
56.95
40.08
39.51
13.30
S
S
OEt
Me2N
NMe2
13C NMR
DMSO-d6, 100 MHz
40.08
39.51
40.0
39.5
39.0
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


S
S
OEt
Me2N
NMe2
%T
cm-1
4500.0
4000
3000
2000
1500
1000
650.0
d:\mayr\xinhua\dxh-s1.sp - Aceton


7.13
7.10
6.65
6.63
6.15
3.38
3.30
2.82
2.47
2.47
S
S
NMe2
Me2N
NMe2
1H NMR
DMSO-d6, 400 MHz
4.00
4.12
0.97
2.86
2.78
12.03
f1 (ppm)


194.14
149.12
129.00
114.64
112.32
59.29
44.70
41.12
40.23
39.51
S
S
NMe2
Me2N
NMe2
^{13}C NMR
DMSO-d$_6$, 100 MHz
41.12
40.23
39.51
41
40
39
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.28
7.25
6.87
6.84
5.90
3.80
2.35
MeO
OMe
S
O
^{1}H NMR
$CDCl_3$, 300 MHz
4.27
4.00
0.99
5.97
3.01
f1 (ppm)


194.32
158.87
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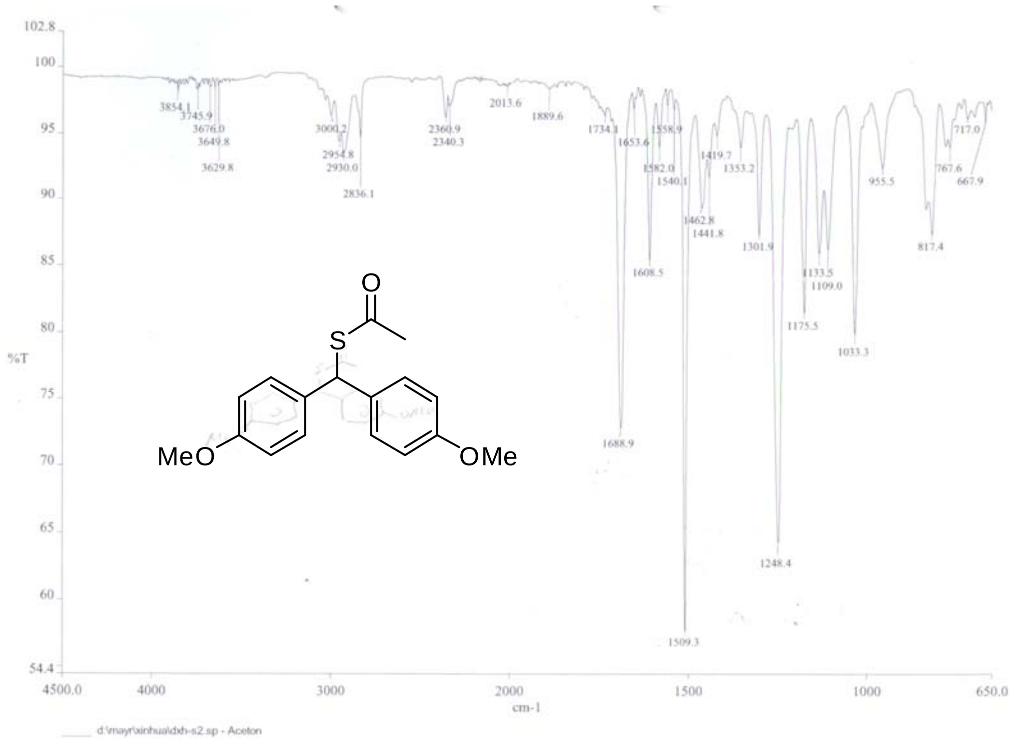
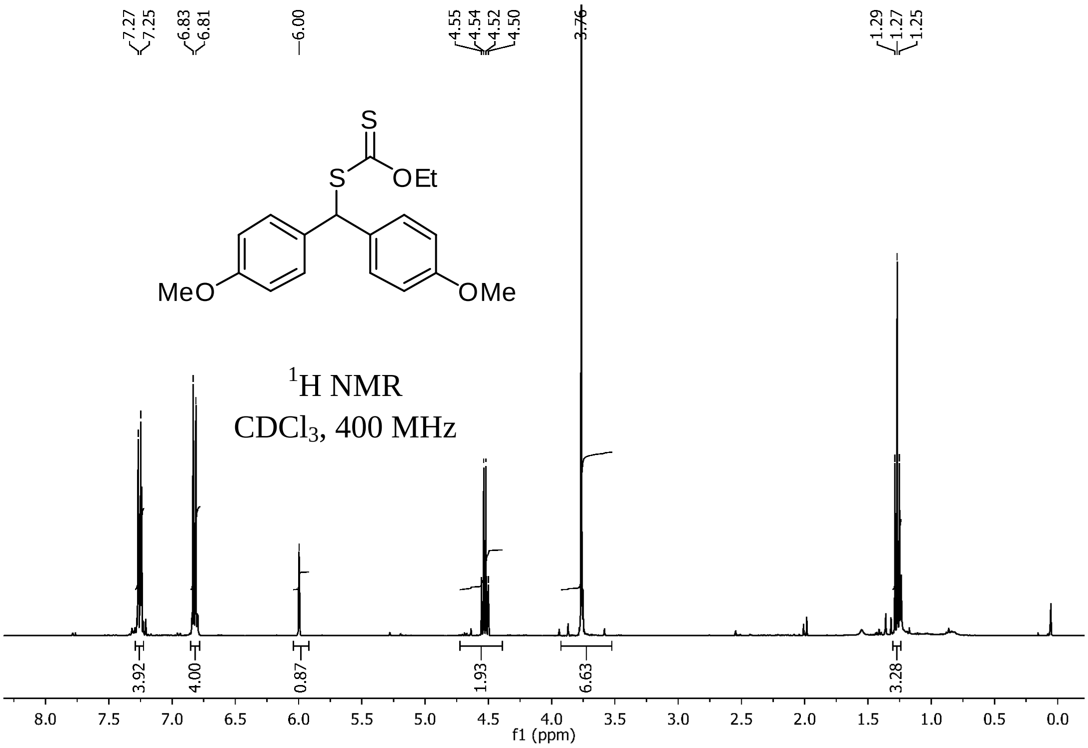
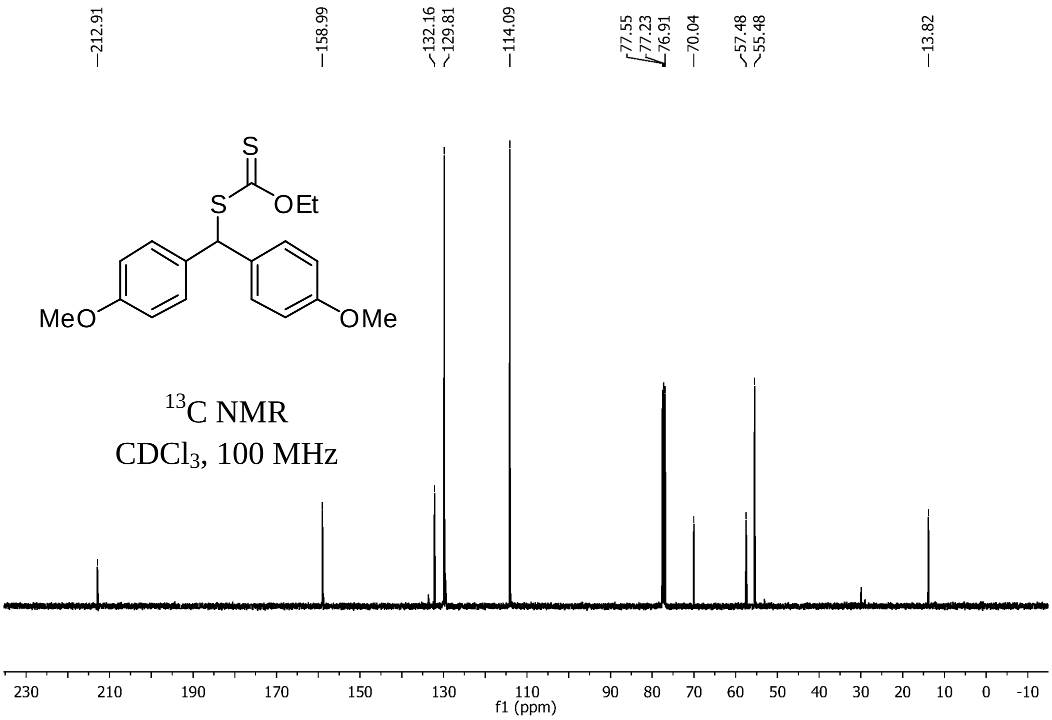
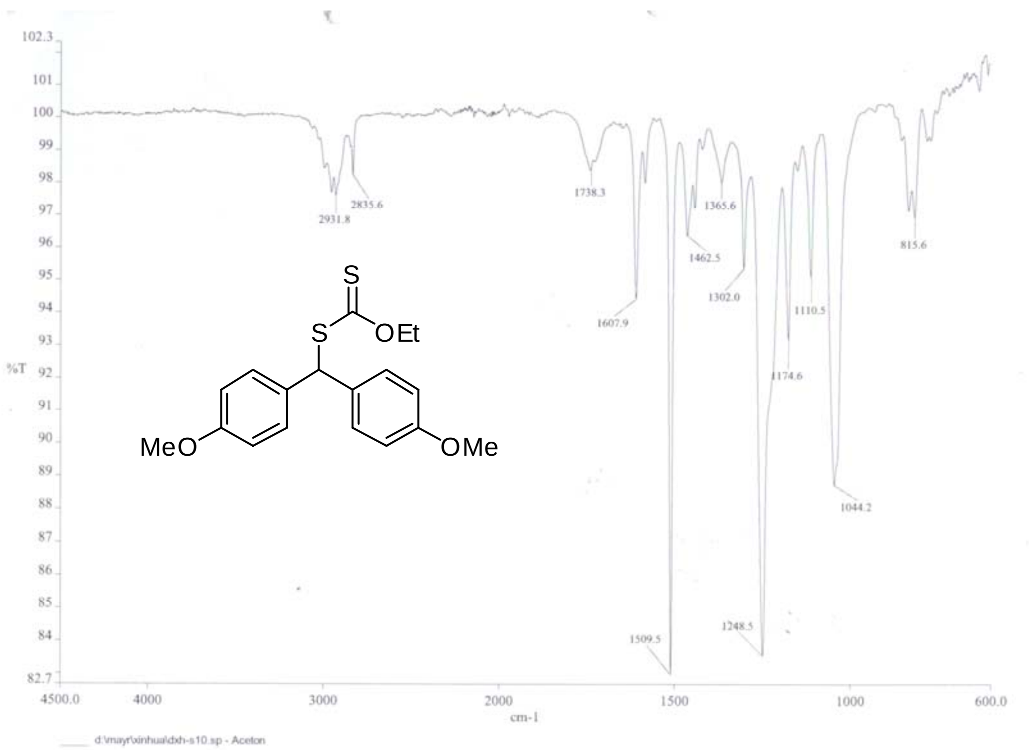
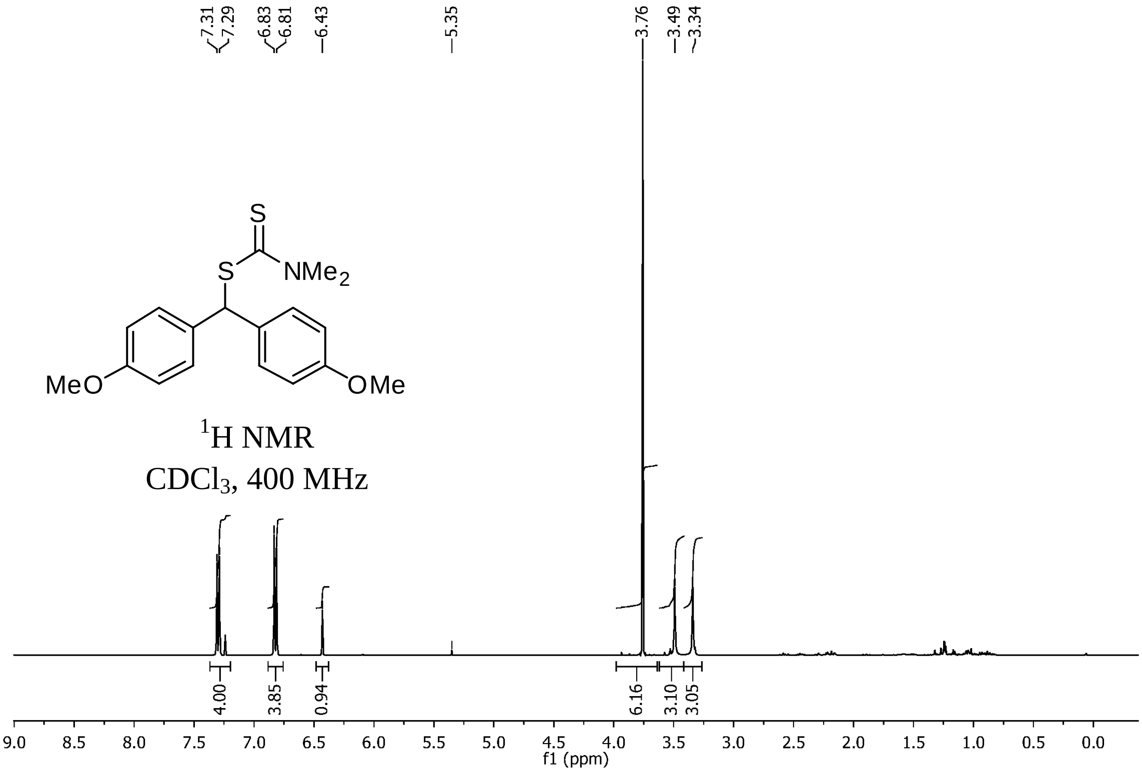
129.55
114.11
77.65
77.23
76.81
55.47
51.00
30.52
MeO
OMe
S
O
^{13}C NMR
$CDCl_3$, 75 MHz
f1 (ppm)

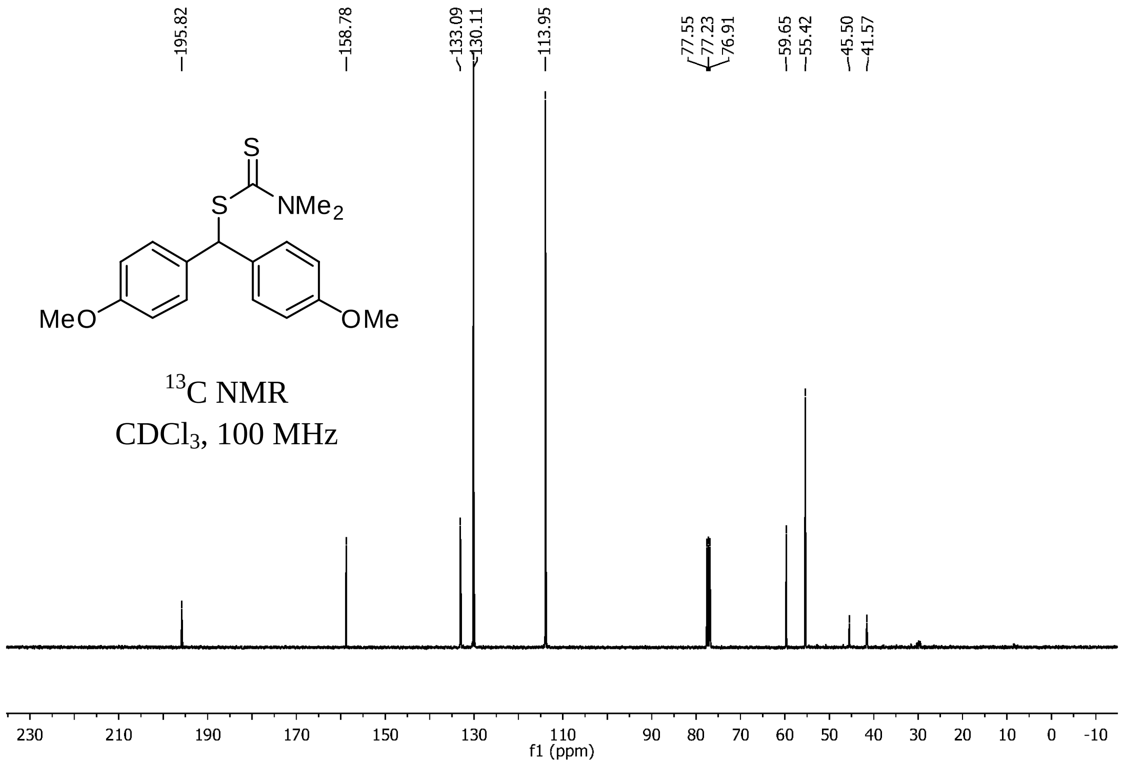

MeO
OMe
S
O
%T
cm-1
d:\mayr\xinhua\dxh-s2.sp - Aceton

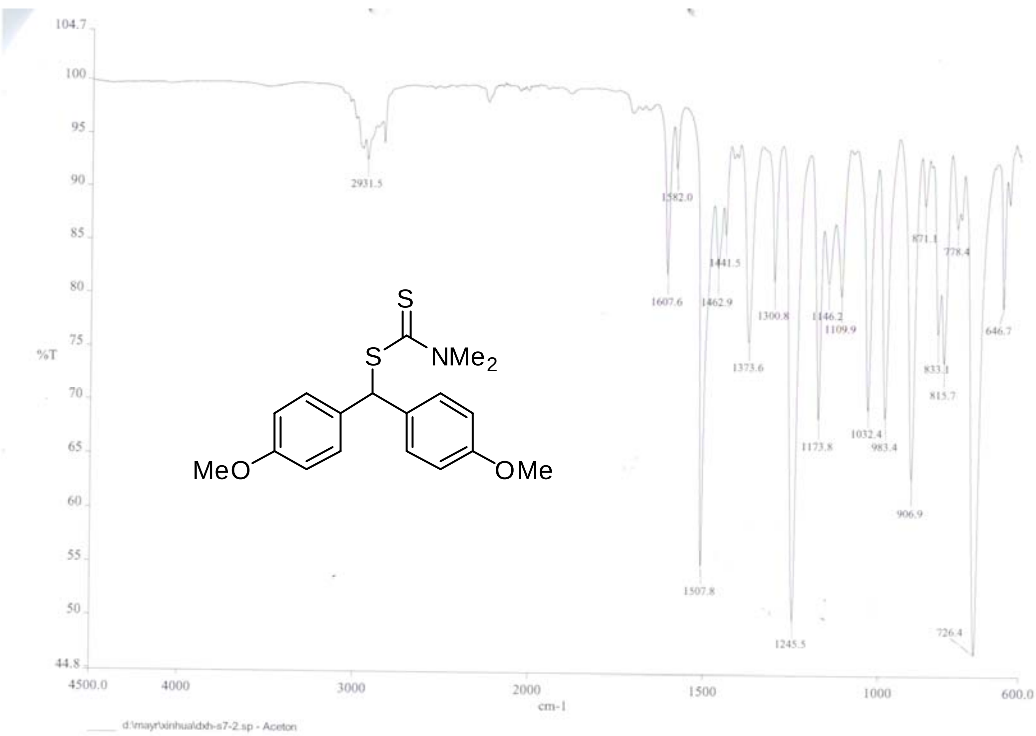

S
S
OEt
MeO
OMe
1H NMR
CDCl3, 400 MHz
f1 (ppm)


212.91
158.99
132.16
129.81
114.09
77.55
77.23
76.91
70.04
57.48
55.48
13.82
S
S
OEt
MeO
OMe
13C NMR
CDCl3, 100 MHz
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


%T
cm-1
2931.8
2835.6
1738.3
1607.9
1509.5
1462.5
1365.6
1302.0
1248.5
1174.6
1110.5
1044.2
815.6
S
S
OEt
MeO
OMe


7.31
7.29
6.83
6.81
6.43
5.35
3.76
3.49
3.34
S
S
NMe2
MeO
OMe
1H NMR
CDCl3, 400 MHz
4.00
3.85
0.94
6.16
3.10
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


195.82
158.78
133.09
130.11
113.95
77.55
77.23
76.91
59.65
55.42
45.50
41.57
S
S
NMe2
MeO
OMe
13C NMR
CDCl3, 100 MHz
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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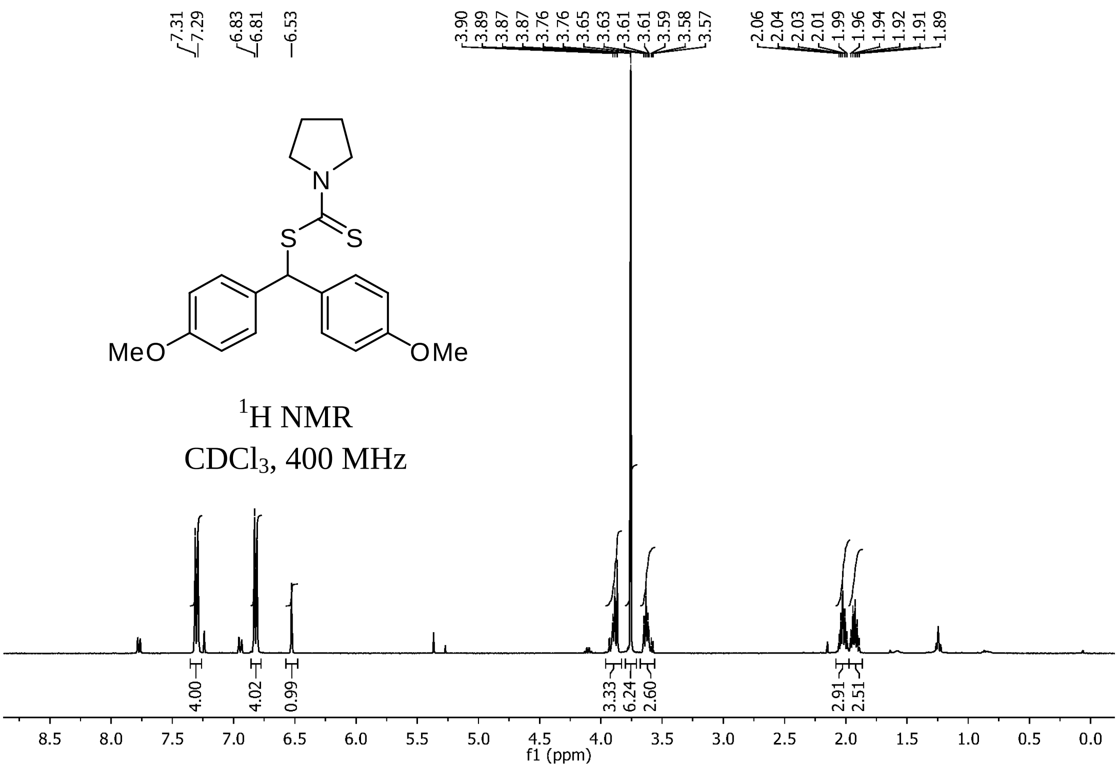
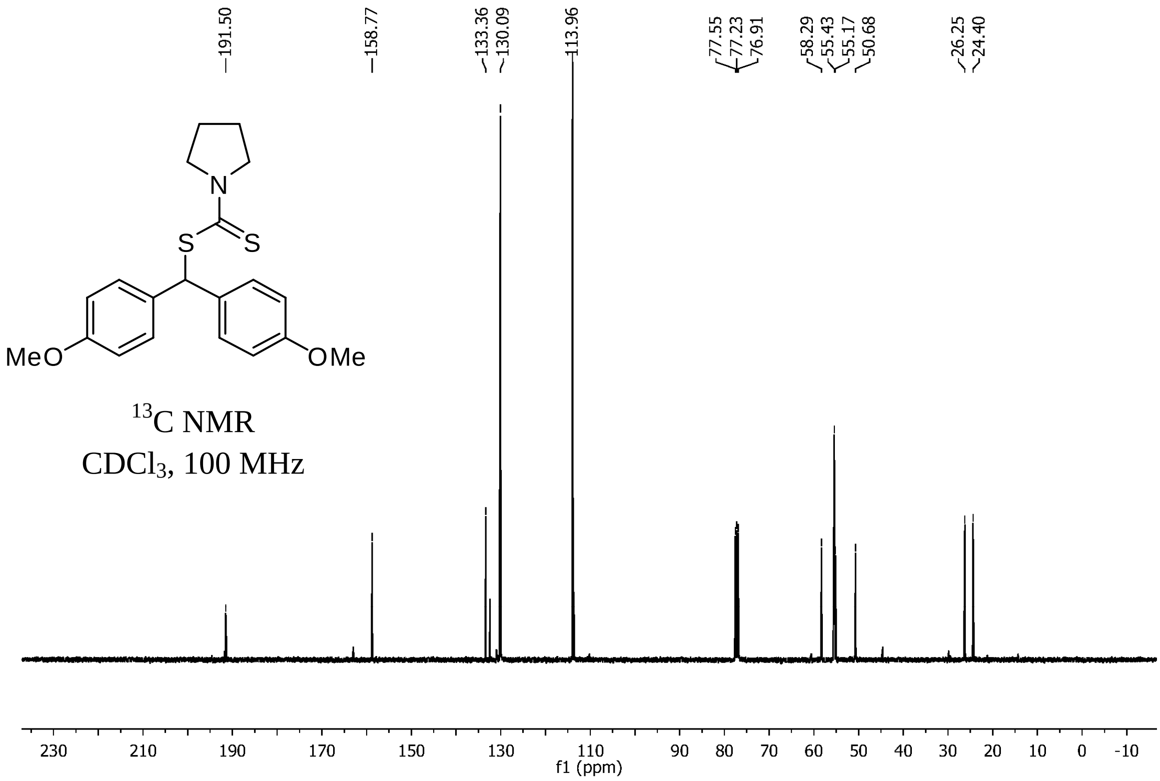
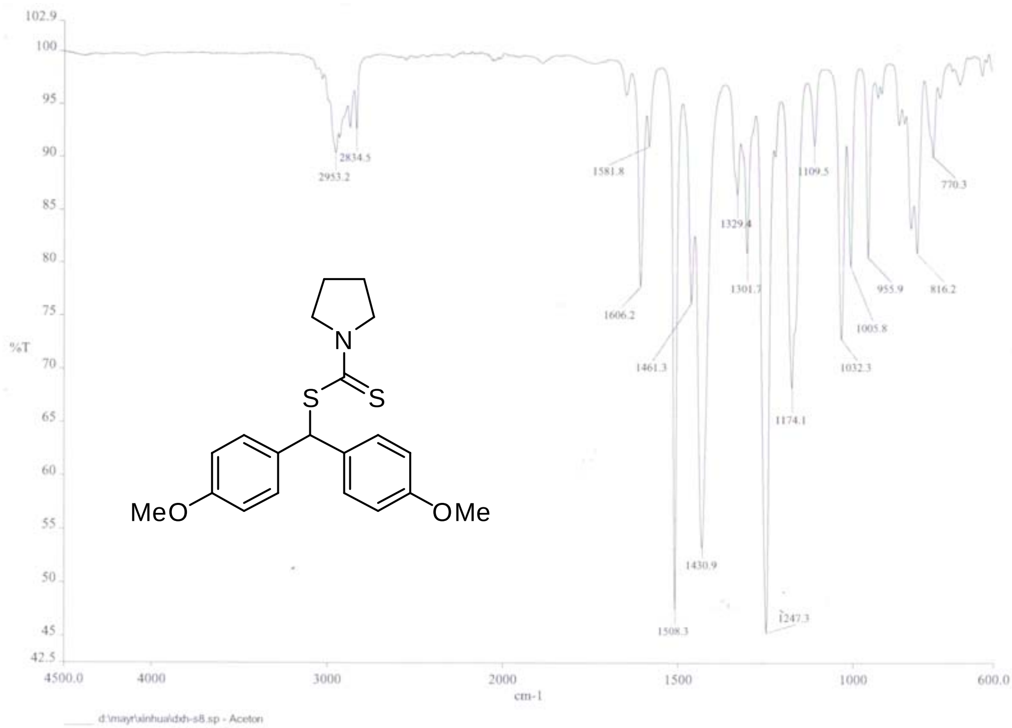
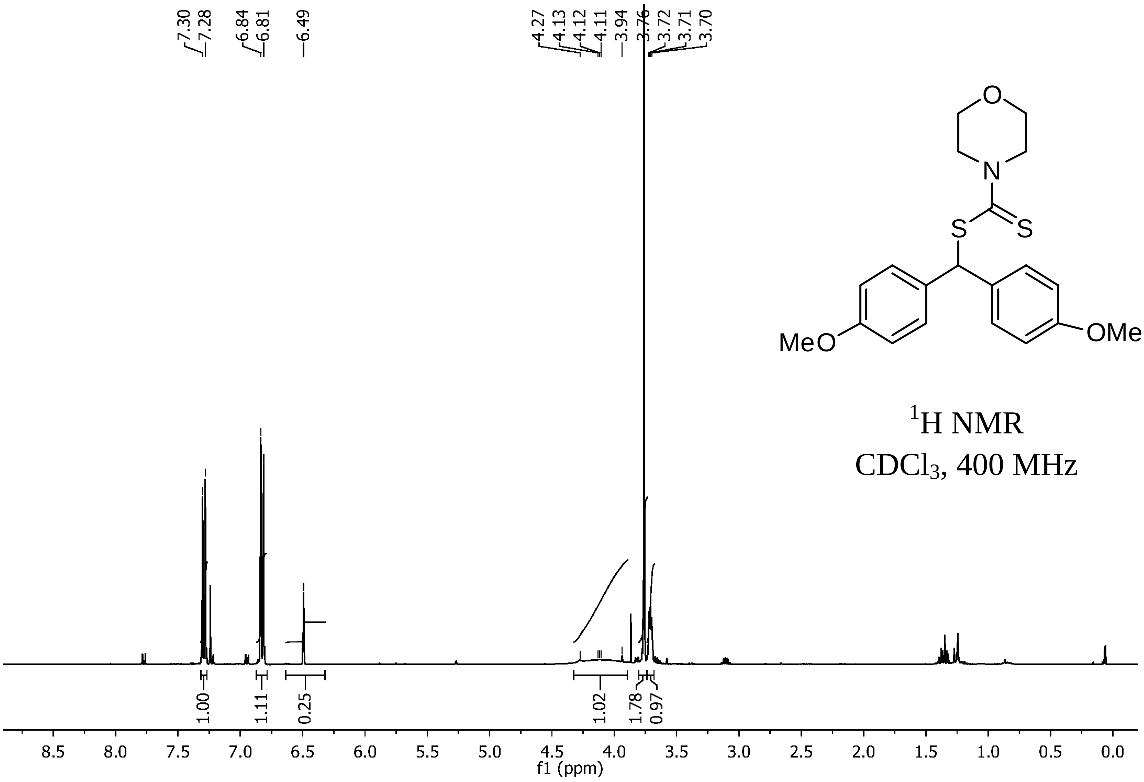
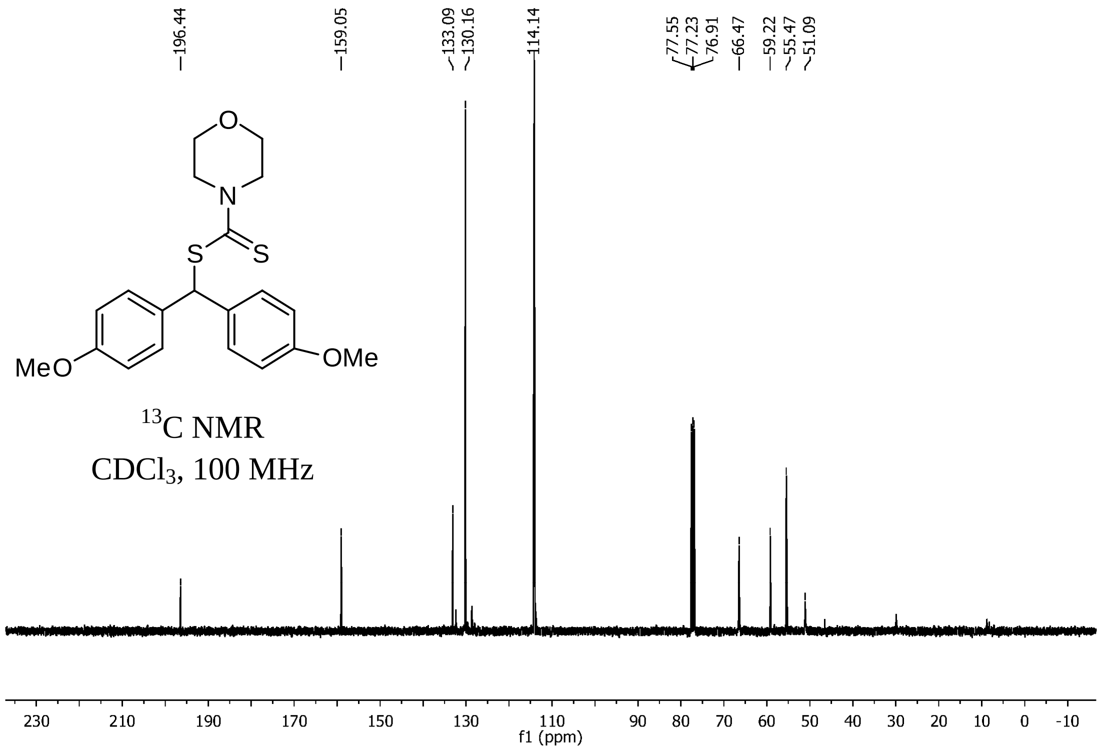
cm-1
2931.5
1582.0
1607.6
1462.9
1441.5
1373.6
1300.8
1146.2
1109.9
1173.8
1245.5
1507.8
1032.4
983.4
906.9
871.1
833.1
815.7
778.4
726.4
646.7
S
S
NMe2
MeO
OMe
d:\mayr\xinhua\dxh-s7-2.sp - Aceton

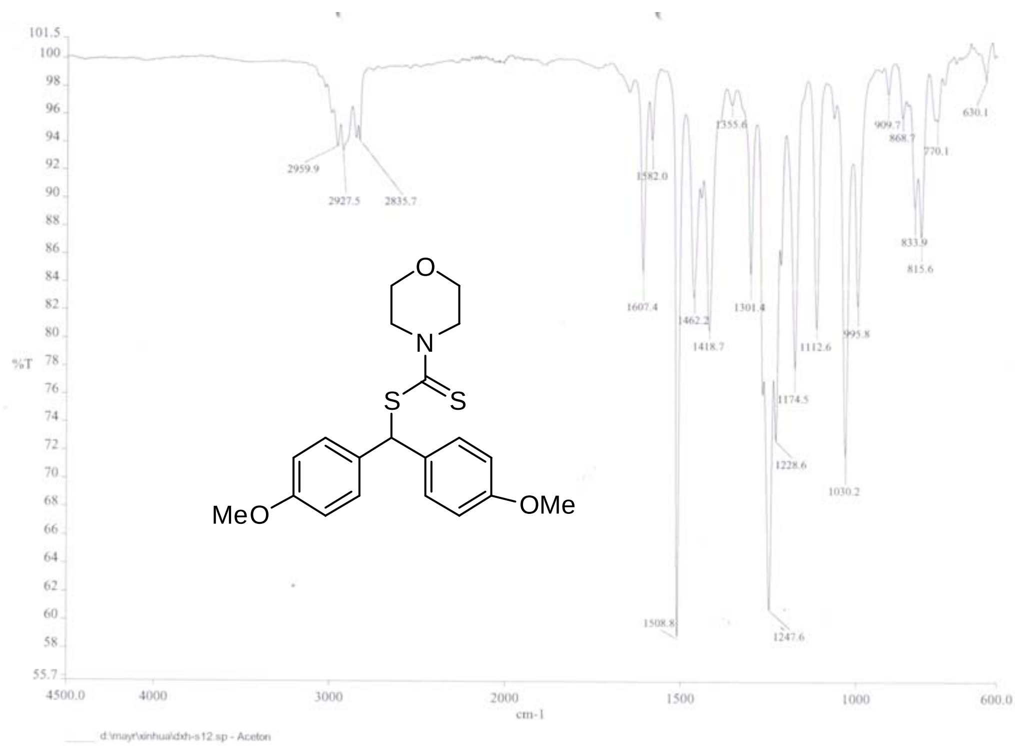

7.31
7.29
6.83
6.81
6.53
3.90
3.89
3.87
3.87
3.76
3.65
3.63
3.61
3.61
3.59
3.58
3.57
2.06
2.04
2.03
2.01
1.99
1.96
1.94
1.92
1.91
1.89
N
S
S
MeO
OMe
^{1}H NMR
CDCl$_3$, 400 MHz
4.00
4.02
0.99
3.33
6.24
2.60
2.91
2.51
f1 (ppm)


191.50
158.77
133.36
130.09
113.96
77.55
77.23
76.91
58.29
55.43
55.17
50.68
26.25
24.40
N
S
S
MeO
OMe
13C NMR
CDCl3, 100 MHz
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


%T
cm-1
2953.2
2834.5
1606.2
1581.8
1508.3
1461.3
1430.9
1329.4
1301.7
1247.3
1174.1
1109.5
1032.3
1005.8
955.9
816.2
770.3
N
S
S
MeO
OMe


7.30
7.28
6.84
6.81
6.49
4.27
4.13
4.12
4.11
3.94
3.76
3.72
3.71
3.70
O
N
S
S
MeO
OMe
1H NMR
CDCl3, 400 MHz
1.00
1.11
0.25
1.02
1.78
0.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


196.44
159.05
133.09
130.16
114.14
77.55
77.23
76.91
66.47
59.22
55.47
51.09
O
N
S
S
MeO
OMe
13C NMR
CDCl3, 100 MHz
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


%T
cm-1
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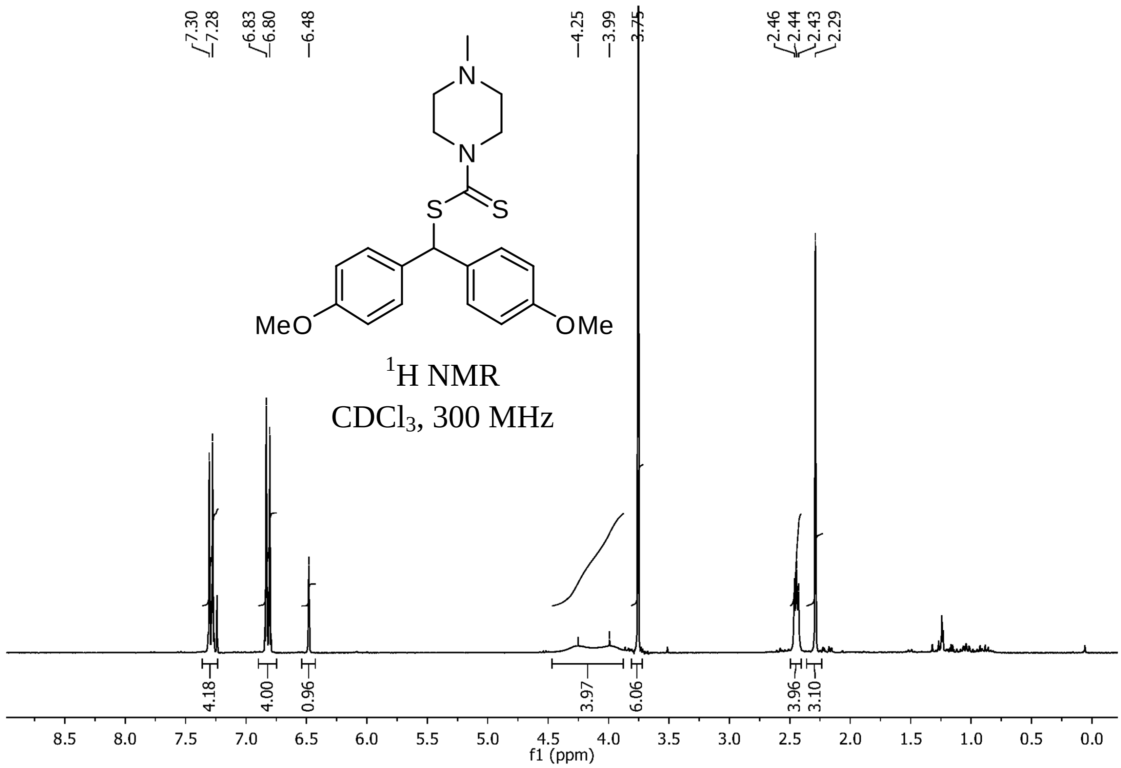
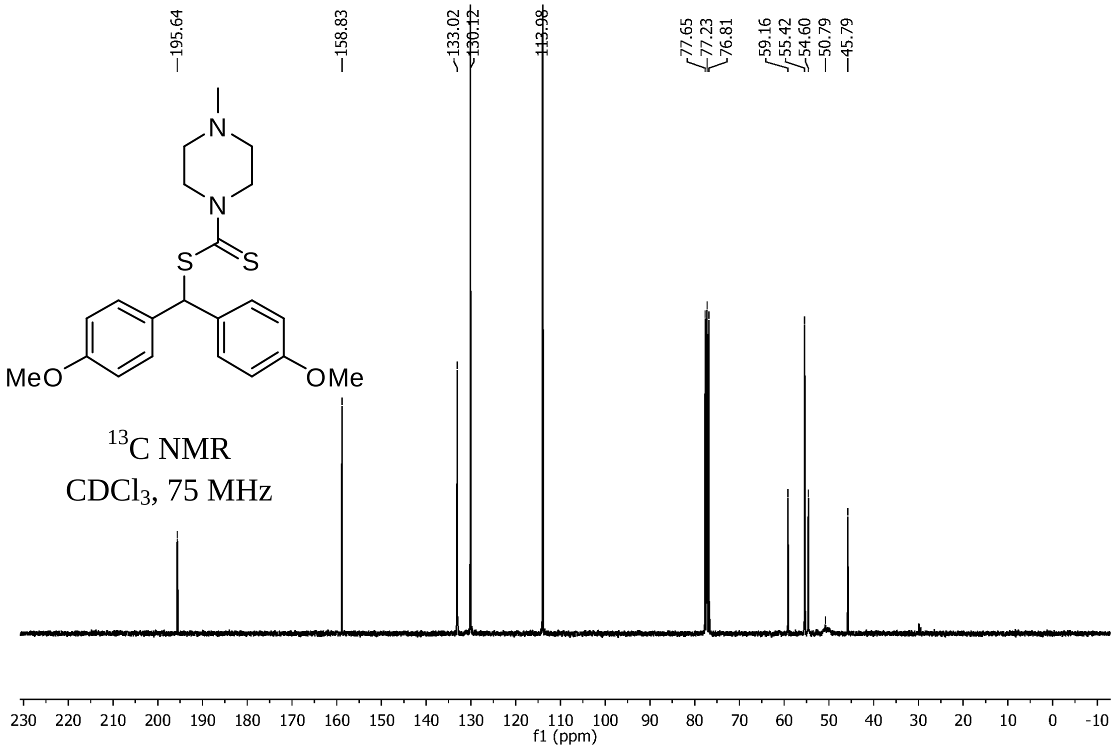
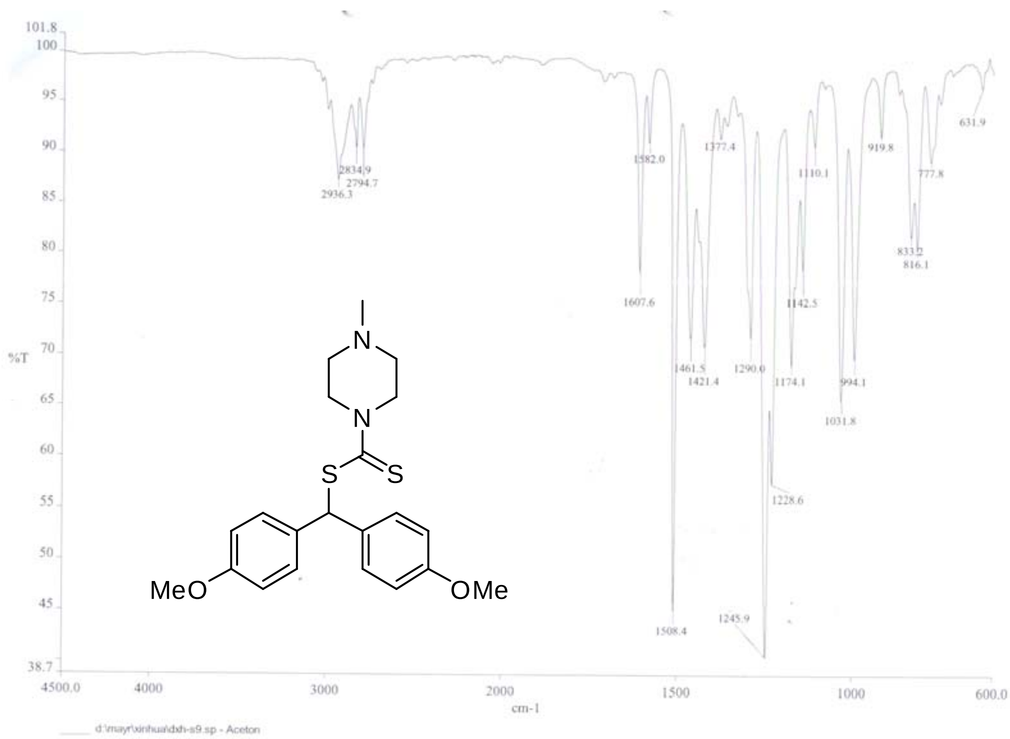
2927.5
2835.7
1607.4
1582.0
1508.8
1462.2
1418.7
1355.6
1301.4
1247.6
1228.6
1174.5
1112.6
1030.2
995.8
909.7
868.7
833.9
815.6
770.1
630.1
MeO
OMe
O
N
S
S
d:\mayr\xinhua\dxh-s12.sp - Aceton


7.30
7.28
6.83
6.80
6.48
4.25
3.99
3.75
2.46
2.44
2.43
2.29
N
N
S
S
MeO
OMe
1H NMR
CDCl3, 300 MHz
4.18
4.00
0.96
3.97
6.06
3.96
3.10
f1 (ppm)


195.64
158.83
133.02
130.12
113.98
77.65
77.23
76.81
59.16
55.42
54.60
50.79
45.79
N
N
S
S
MeO
OMe
13C NMR
CDCl3, 75 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


%T
cm-1
2936.3
2834.9
2794.7
1607.6
1582.0
1508.4
1461.5
1421.4
1377.4
1290.0
1245.9
1228.6
1174.1
1142.5
1110.1
1031.8
994.1
919.8
833.2
816.1
777.8
631.9
N
N
S
S
MeO
OMe