-ELECTRONIC SUPPORTING INFORMATION (ESI)-

Nucleophilic reactivities of benzenesulfonyl-substituted carbanions

*Florian Seeliger and Herbert Mayr**

Department Chemie und Biochemie, Ludwig-Maximilians-Universität München,

Butenandtstr. 5-13, 81377 München, Germany

herbert.mayr@cup.uni-muenchen.de

Table of contents

Kinetic experiments ____ *2*

Reactions of **1a**$^-$ ____ 2

Reactions of **1b**$^-$ ____ 7

Reactions of **1c**$^-$ ____ 12

Reactions of **1d**$^-$ ____ 17

NMR spectra ____ *21*

7 ____ 21

8 ____ 22

9 ____ 23

10 ____ 24

11 ____ 25

12 ____ 26

13 ____ 27

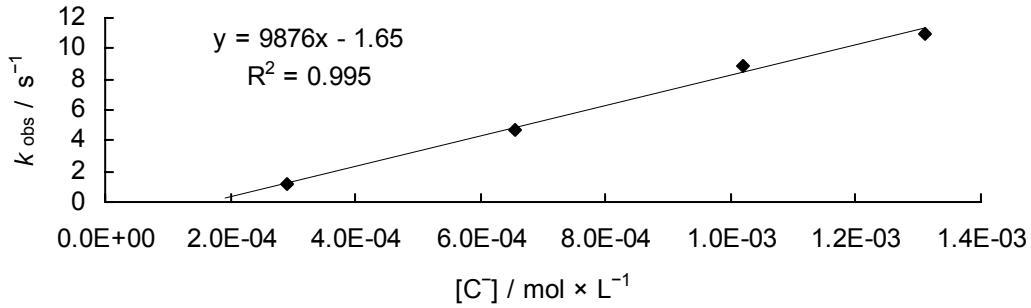
Kinetic experiments

The temperature of the solutions during all kinetic studies was kept constant (20 ± 0.1°C) by using a circulating bath thermostat. Dry DMSO for kinetics was purchased (< 50 ppm H_2O). For the evaluation of kinetics the stopped-flow spectrophotometer systems Hi-Tech SF-61DX2 or Applied Photophysics SX.18MV-R stopped-flow reaction analyzer were used. Rate constants k_{obs} (s^{-1}) were obtained by fitting the single exponential $A_t = A_0\exp(-k_{obs}t) + C$ to the observed time-dependent electrophile absorbance (averaged from at least 3 kinetic runs for each nucleophile concentration). For the stopped-flow experiments 2 stock solutions were used: A solution of the electrophile in DMSO and a solution of the carbanion, which was either used as potassium salt or generated by the deprotonation of the CH acid with 1.05 equivalents of base.

Reactions of 1a⁻ (X = m-Cl)

Reaction of **1a**$^-$ with **2a** (DMSO, P_4-^{t}Bu, 20 °C, stopped-flow, 524 nm)

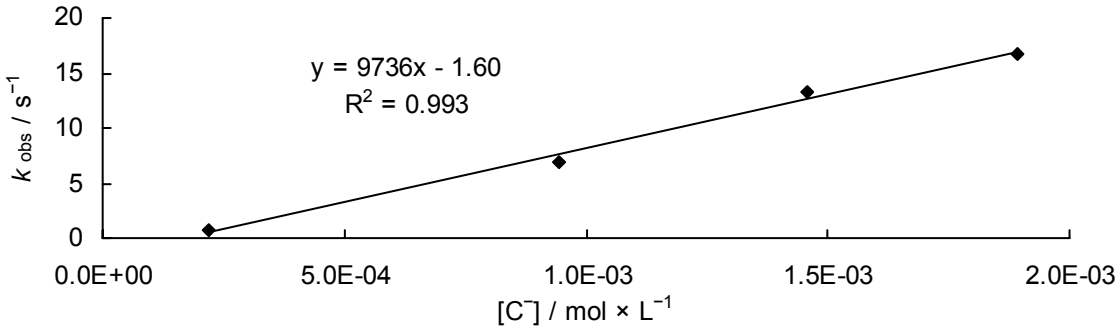
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.28×10^{-5}	2.91×10^{-4}	1.16
1.28×10^{-5}	6.55×10^{-4}	4.71
1.28×10^{-5}	1.02×10^{-3}	8.87
1.28×10^{-5}	1.31×10^{-3}	1.10×10^{1}



$k_2 = (9.88 \pm 0.50) \times 10^3$ $M^{-1}s^{-1}$

Reaction of **1a**$^-$ with **2a** (DMSO, KO^{t}Bu / 18-crown-6, 20 °C, stopped-flow, 524 nm)

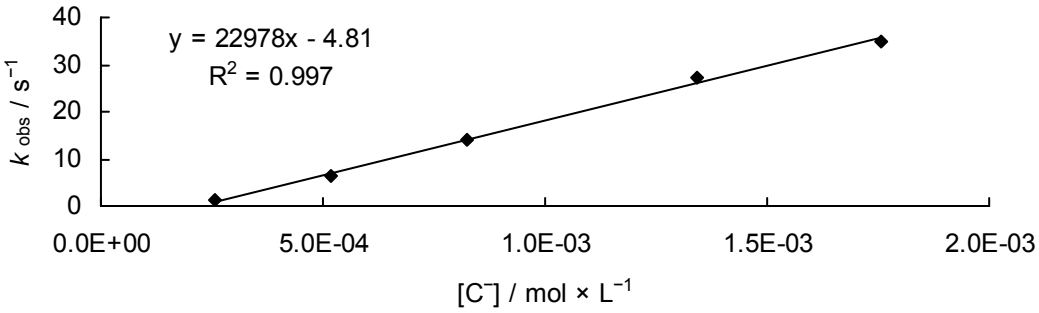
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.93×10^{-5}	2.18×10^{-4}	8.03×10^{-1}
1.93×10^{-5}	9.46×10^{-4}	6.85
1.93×10^{-5}	1.46×10^{-3}	1.32×10^{1}
1.93×10^{-5}	1.89×10^{-3}	1.67×10^{1}



$k_2 = (9.74 \pm 0.57) \times 10^3$ $M^{-1}s^{-1}$

Reaction of **1a**$^-$ with **2b** (DMSO, P_4-^{t}Bu, 20 °C, stopped-flow, 500 nm)

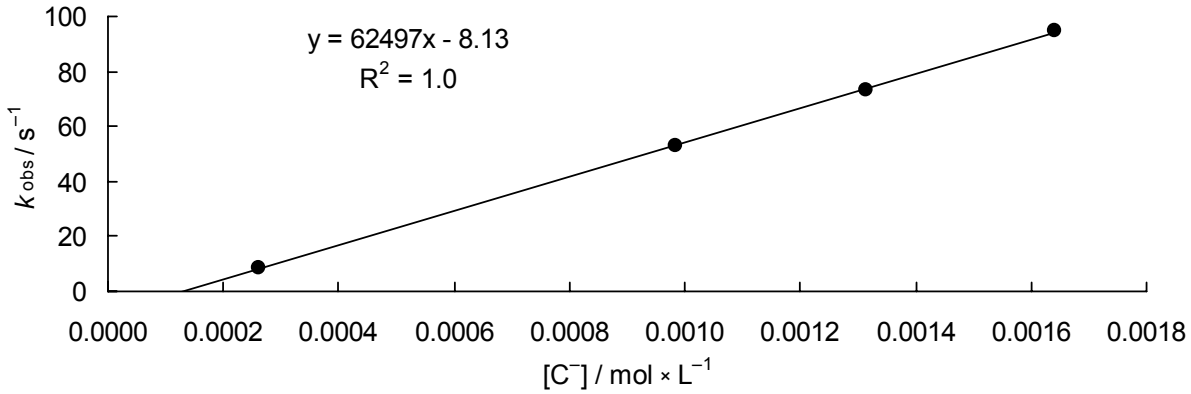
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.76×10^{-5}	2.58×10^{-4}	1.42
1.76×10^{-5}	5.17×10^{-4}	6.47
1.76×10^{-5}	8.27×10^{-4}	1.40×10^{1}
1.76×10^{-5}	1.34×10^{-3}	2.71×10^{1}
1.76×10^{-5}	1.76×10^{-3}	3.50×10^{1}



$k_2 = (2.30 \pm 0.07) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1a**$^-$ with **6a** (DMSO, KO^{t}Bu, 20 °C, stopped-flow, 500 nm)

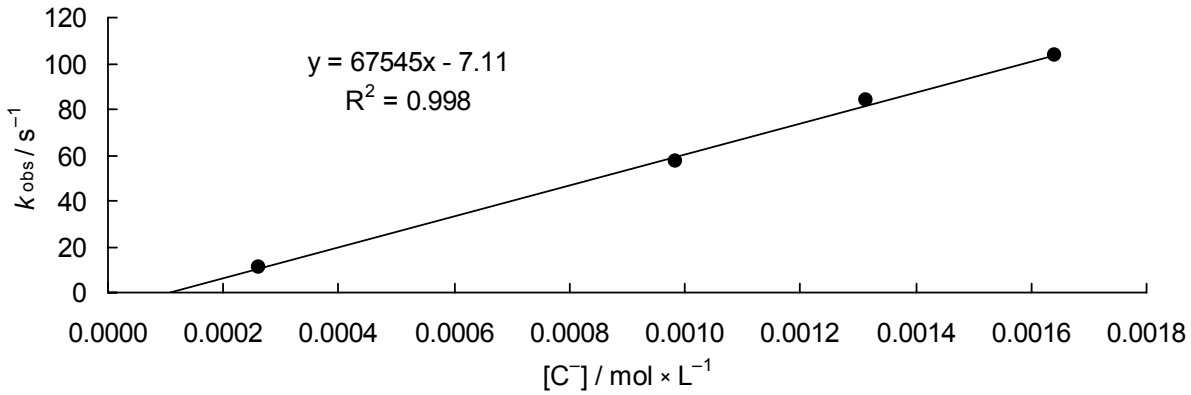
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.77×10^{-5}	2.63×10^{-4}	8.64
1.77×10^{-5}	9.85×10^{-4}	5.30×10^{1}
1.77×10^{-5}	1.31×10^{-3}	7.32×10^{1}
1.77×10^{-5}	1.64×10^{-3}	9.50×10^{1}



$k_2 = (6.25 \pm 0.07) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1a**$^-$ with **4a** (DMSO, KO^{t}Bu, 20 °C, stopped-flow, 500 nm)

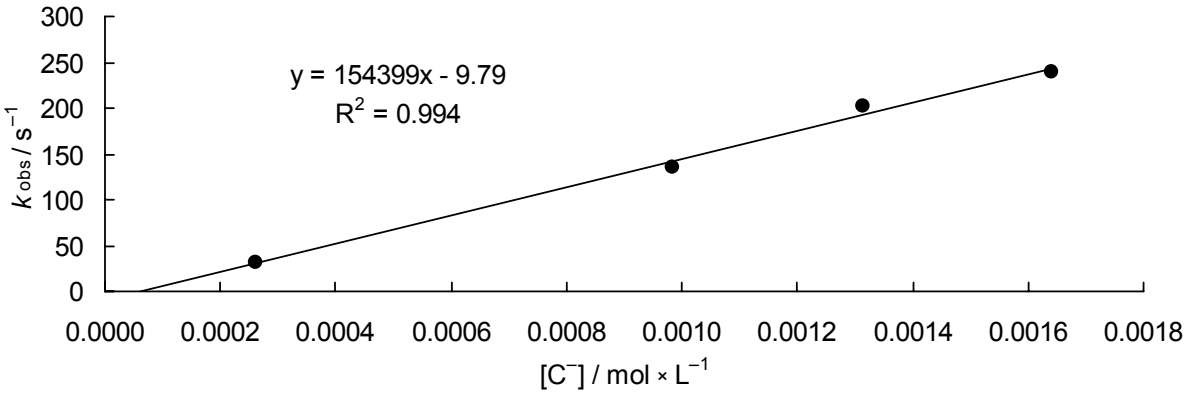
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.66×10^{-5}	2.63×10^{-4}	1.11×10^{1}
1.66×10^{-5}	9.85×10^{-4}	5.73×10^{1}
1.66×10^{-5}	1.31×10^{-3}	8.37×10^{1}
1.66×10^{-5}	1.64×10^{-3}	1.03×10^{2}



$k_2 = (6.75 \pm 0.23) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1a**$^-$ with **5a** (DMSO, KO^{t}Bu, 18-crown-6, 20 °C, stopped-flow, 500 nm)

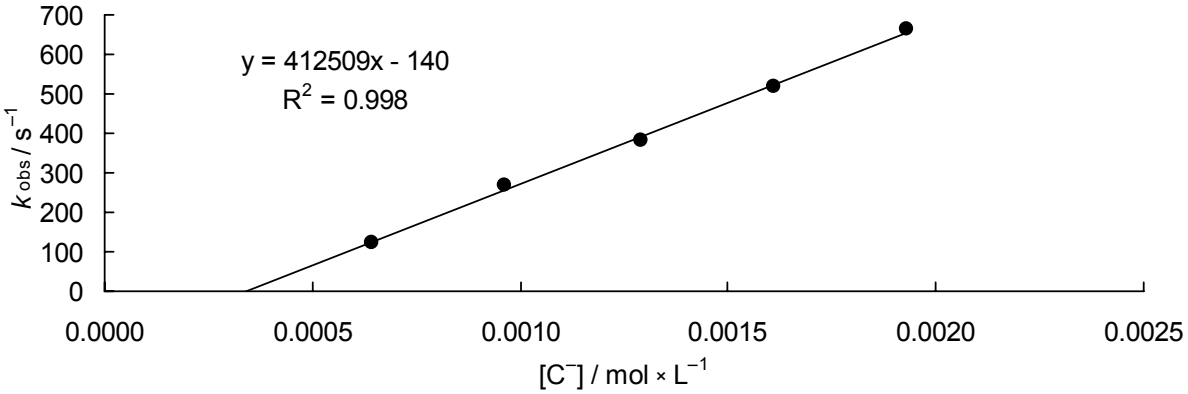
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.58×10^{-5}	2.63×10^{-4}	3.20×10^{1}
1.58×10^{-5}	9.85×10^{-4}	1.35×10^{2}
1.58×10^{-5}	1.31×10^{-3}	2.02×10^{2}
1.58×10^{-5}	1.64×10^{-3}	2.40×10^{2}



$k_2 = (1.54 \pm 0.09) \times 10^5$ $M^{-1}s^{-1}$

Reaction of **1a**$^-$ with **6b** (DMSO, KO^{t}Bu, 20 °C, stopped-flow, 500 nm)

$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
2.89×10^{-5}	6.43×10^{-4}	1.25×10^{2}
2.89×10^{-5}	9.65×10^{-4}	2.68×10^{2}
2.89×10^{-5}	1.29×10^{-3}	3.84×10^{2}
2.89×10^{-5}	1.61×10^{-3}	5.16×10^{2}
2.89×10^{-5}	1.93×10^{-3}	6.65×10^{2}



$k_2 = (4.13 \pm 0.10) \times 10^5$ $M^{-1}s^{-1}$

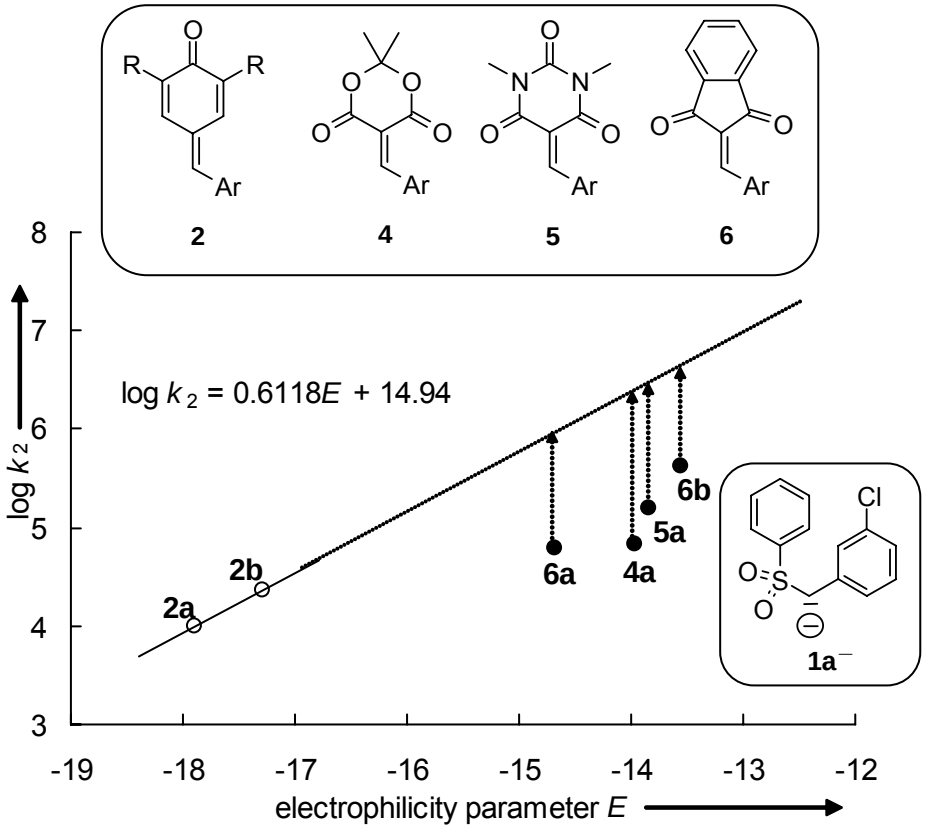
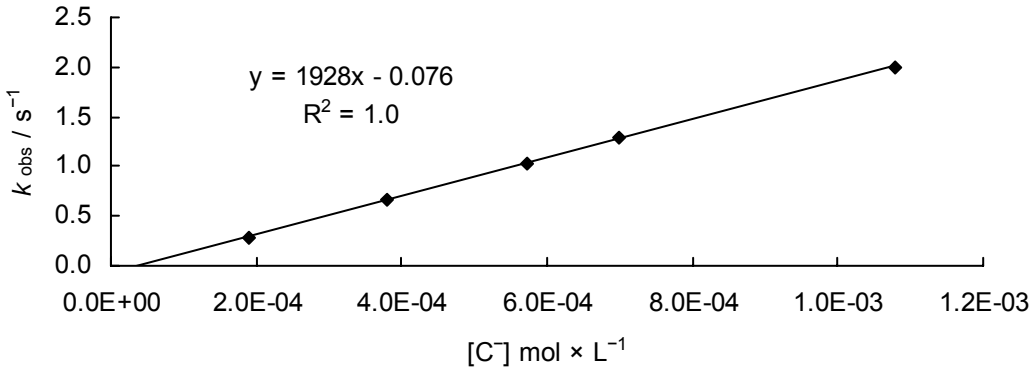


Fig. S1 Plot of log k_2 (DMSO) versus electrophilicity parameters E for the reactions of carbanion **1a**$^-$ with the quinone methides **2** and Michael acceptors **4**-**6**.

Reactions of 1b⁻ (X = p-CF₃)

Reaction of **1b**$^-$ with **2a** (DMSO, P_2-^{t}Bu, 20 °C, stopped-flow, 524 nm)

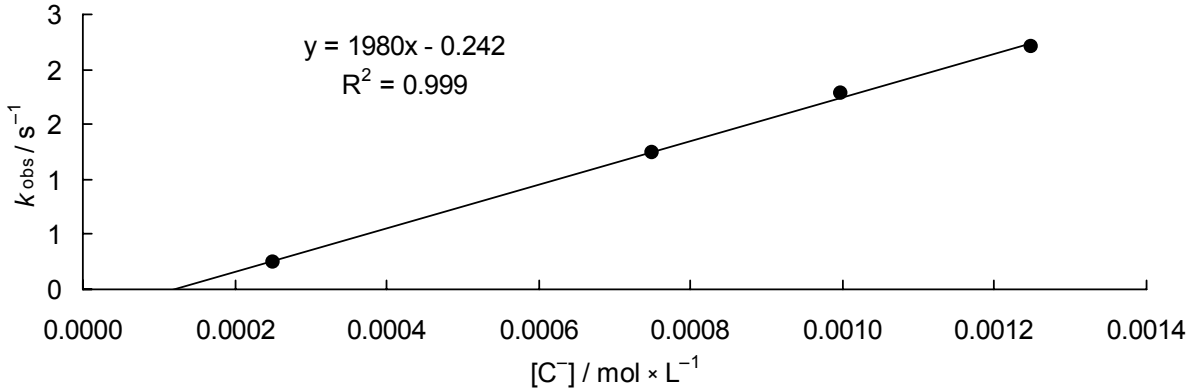
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.29×10^{-5}	1.91×10^{-4}	2.89×10^{-1}
1.29×10^{-5}	3.81×10^{-4}	6.55×10^{-1}
1.29×10^{-5}	5.72×10^{-4}	1.03
1.29×10^{-5}	6.99×10^{-4}	1.28
1.29×10^{-5}	1.08×10^{-3}	2.00



$k_2 = (1.93 \pm 0.01) \times 10^3$ $M^{-1}s^{-1}$

Reaction of **1b**$^-$ with **2a** (DMSO, KO^{t}Bu, 20 °C, stopped-flow, 510 nm)

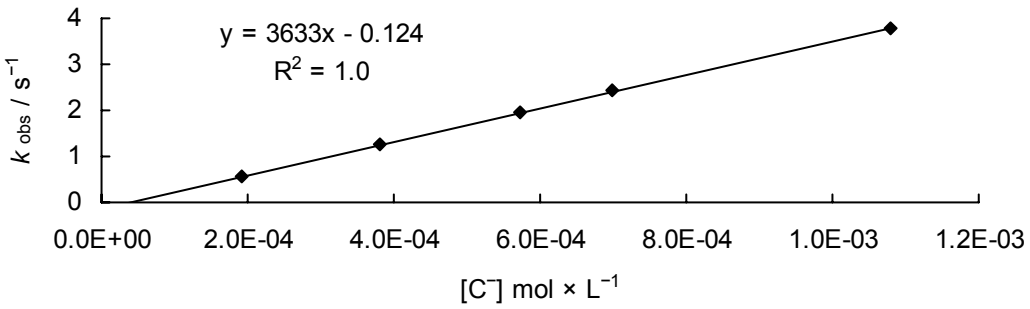
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.31×10^{-5}	2.50×10^{-4}	2.42×10^{-1}
1.31×10^{-5}	7.49×10^{-4}	1.24
1.31×10^{-5}	9.99×10^{-4}	1.78
1.31×10^{-5}	1.25×10^{-3}	2.20



$k_2 = (1.98 \pm 0.05) \times 10^3$ $M^{-1}s^{-1}$

Reaction of **1b**$^-$ with **2b** (DMSO, P_2-^{t}Bu, 20 °C, stopped-flow, 500 nm)

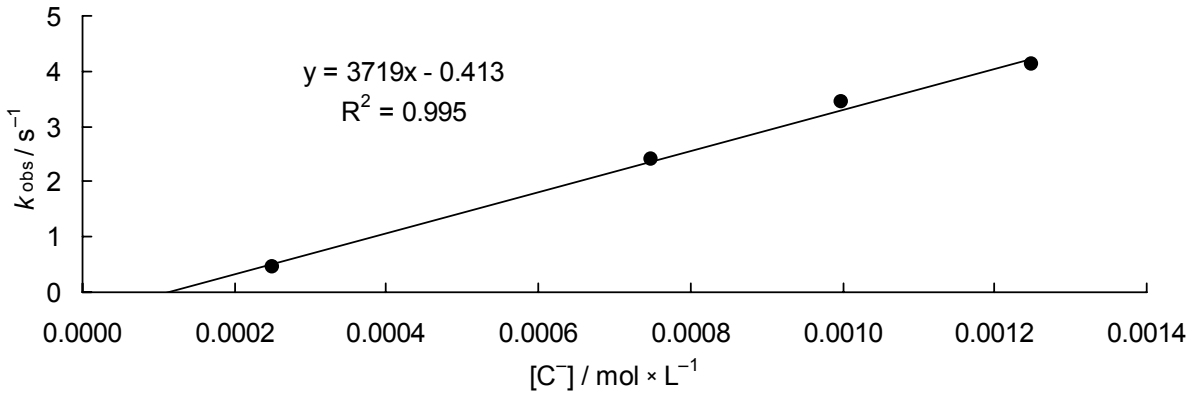
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.35×10^{-5}	1.91×10^{-4}	5.60×10^{-1}
1.35×10^{-5}	3.81×10^{-4}	1.27
1.35×10^{-5}	5.72×10^{-4}	1.94
1.35×10^{-5}	6.99×10^{-4}	2.44
1.35×10^{-5}	1.08×10^{-3}	3.79



$k_2 = (3.63 \pm 0.03) \times 10^3$ $M^{-1}s^{-1}$

Reaction of **1b**$^-$ with **2b** (DMSO, KO^{t}Bu, 20 °C, stopped-flow, 510 nm)

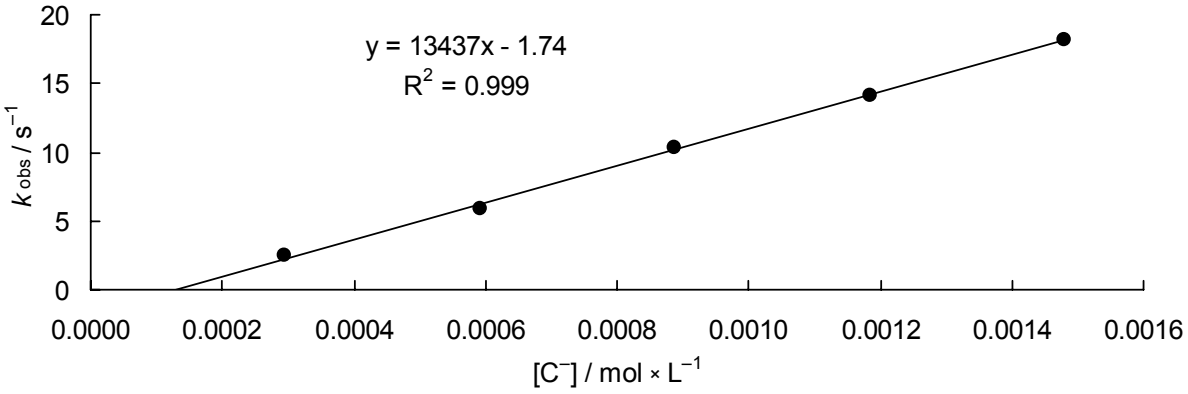
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.35×10^{-5}	2.50×10^{-4}	4.65×10^{-1}
1.35×10^{-5}	7.49×10^{-4}	2.40
1.35×10^{-5}	9.99×10^{-4}	3.45
1.35×10^{-5}	1.25×10^{-3}	4.11



$k_2 = (3.72 \pm 0.19) \times 10^3$ $M^{-1}s^{-1}$

Reaction of **1b**$^-$ with **6a** (DMSO, Verkade's base, 20 °C, stopped-flow, 500 nm)

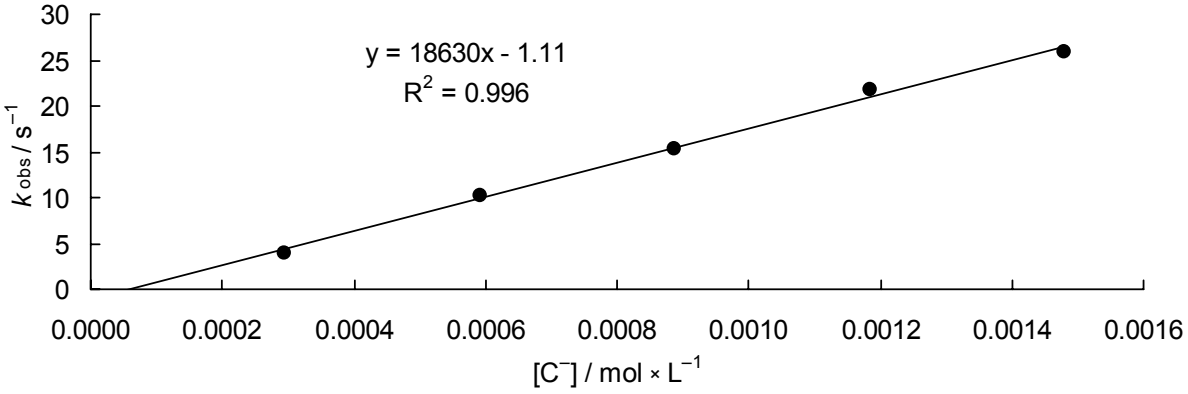
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.36×10^{-5}	2.96×10^{-4}	2.48
1.36×10^{-5}	5.92×10^{-4}	5.82
1.36×10^{-5}	8.88×10^{-4}	1.03×10^{1}
1.36×10^{-5}	1.18×10^{-3}	1.41×10^{1}
1.36×10^{-5}	1.48×10^{-3}	1.82×10^{1}



$k_2 = (1.34 \pm 0.03) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1b**$^-$ with **4a** (DMSO, Verkade's base, 20 °C, stopped-flow, 500 nm)

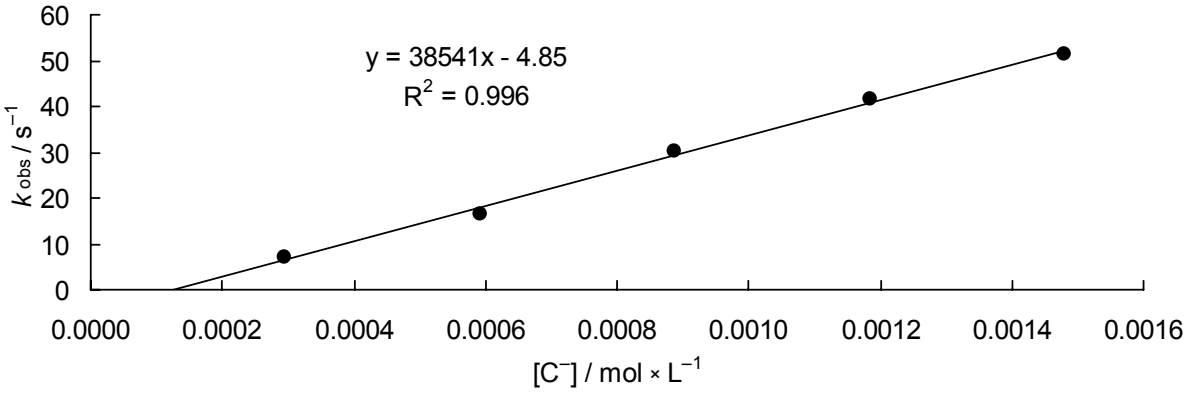
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.47×10^{-5}	2.96×10^{-4}	4.01
1.47×10^{-5}	5.92×10^{-4}	1.02×10^{1}
1.47×10^{-5}	8.88×10^{-4}	1.54×10^{1}
1.47×10^{-5}	1.18×10^{-3}	2.17×10^{1}
1.47×10^{-5}	1.48×10^{-3}	2.58×10^{1}



$k_2 = (1.86 \pm 0.07) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1b**$^-$ with **5a** (DMSO, Verkade's base, 20 °C, stopped-flow, 500 nm)

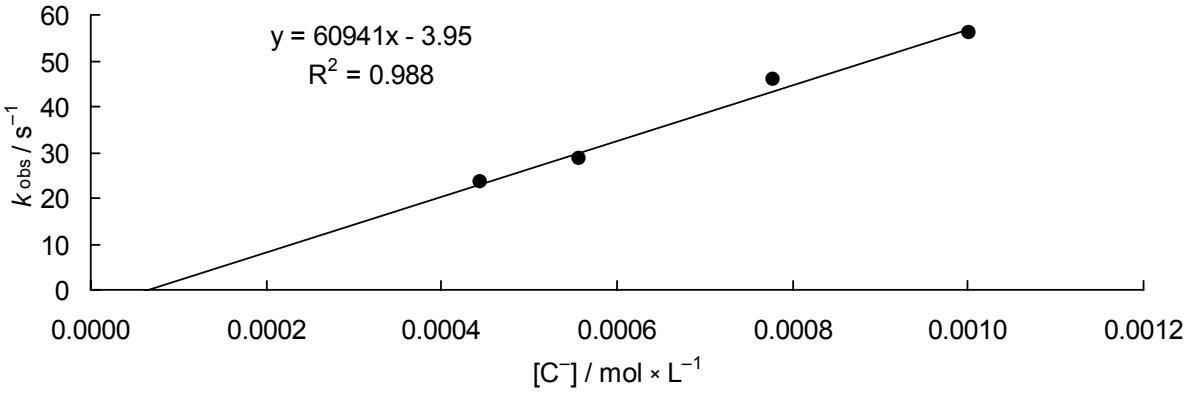
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
2.45×10^{-5}	2.96×10^{-4}	7.13
2.45×10^{-5}	5.92×10^{-4}	1.64×10^{1}
2.45×10^{-5}	8.88×10^{-4}	3.01×10^{1}
2.45×10^{-5}	1.18×10^{-3}	4.16×10^{1}
2.45×10^{-5}	1.48×10^{-3}	5.15×10^{1}



$k_2 = (3.85 \pm 0.13) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1b**$^-$ with **6b** (DMSO, Verkade's base, 20 °C, stopped-flow, 500 nm)

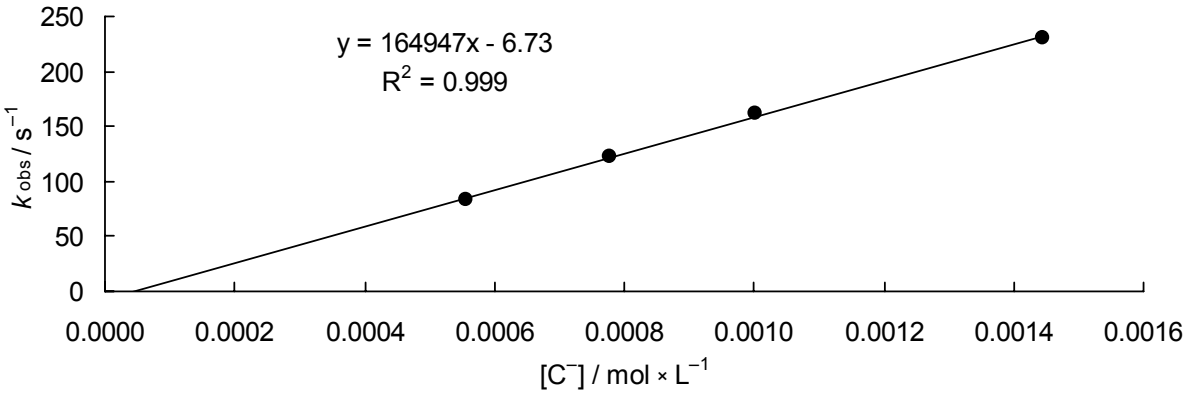
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
2.81×10^{-5}	4.45×10^{-4}	2.34×10^{1}
2.81×10^{-5}	5.56×10^{-4}	2.85×10^{1}
2.81×10^{-5}	7.79×10^{-4}	4.58×10^{1}
2.81×10^{-5}	1.00×10^{-3}	5.59×10^{1}



$k_2 = (6.09 \pm 0.48) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1b**$^-$ with **5b** (DMSO, Verkade's base, 20 °C, stopped-flow, 500 nm)

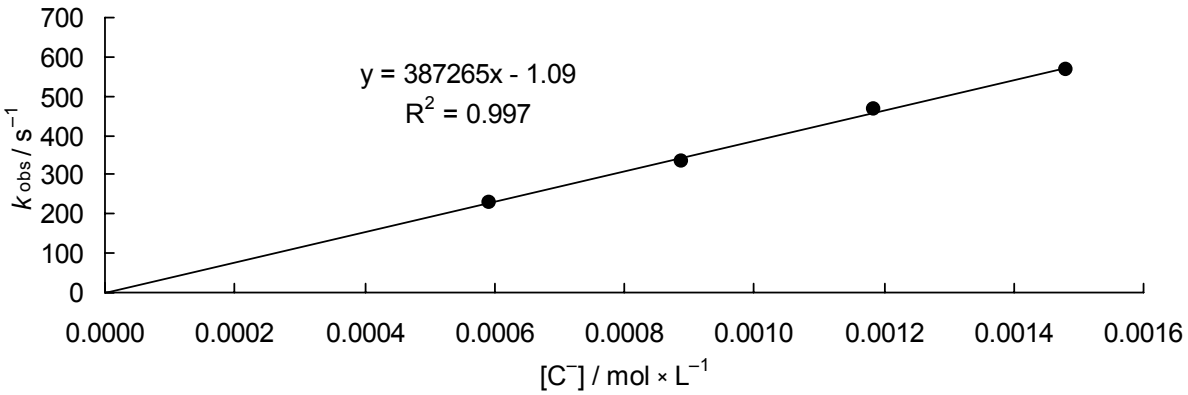
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
5.85×10^{-5}	5.56×10^{-4}	8.34×10^{1}
5.85×10^{-5}	7.79×10^{-4}	1.22×10^{2}
5.85×10^{-5}	1.00×10^{-3}	1.61×10^{2}
5.85×10^{-5}	1.45×10^{-3}	2.31×10^{2}



$k_2 = (1.65 \pm 0.04) \times 10^5$ $M^{-1}s^{-1}$

Reaction of **1b**$^-$ with **2e** (DMSO, Verkade's base, 20 °C, stopped-flow, 500 nm)

$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.47×10^{-5}	5.92×10^{-4}	2.31×10^{2}
1.47×10^{-5}	8.88×10^{-4}	3.34×10^{2}
1.47×10^{-5}	1.18×10^{-3}	4.65×10^{2}
1.47×10^{-5}	1.48×10^{-3}	5.69×10^{2}

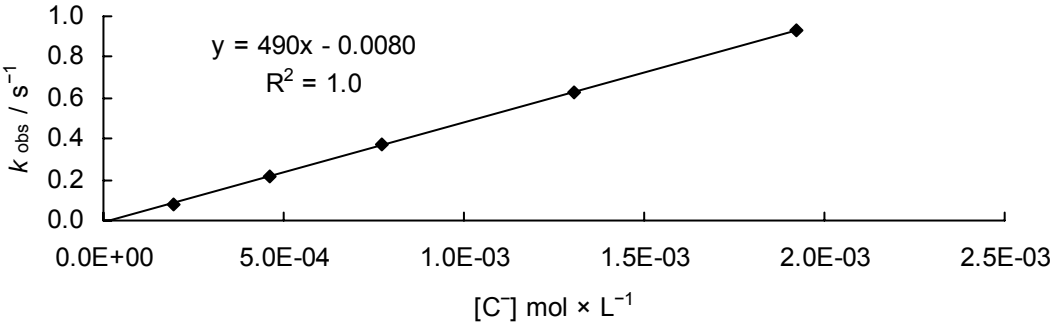


$k_2 = (3.87 \pm 0.14) \times 10^5$ $M^{-1}s^{-1}$

Reactions of 1c⁻ (X = p-CN)

Reaction of **1c**⁻ with **2a** (DMSO, P_2-^{t}Bu, 20 °C, stopped-flow, 524 nm)

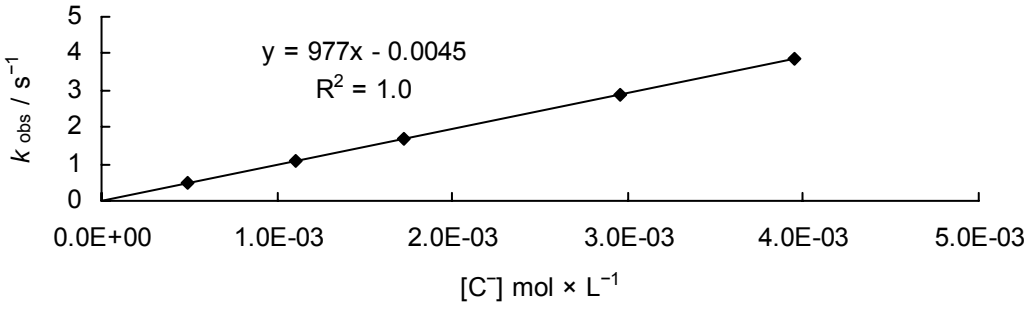
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.93×10^{-5}	1.92×10^{-4}	8.29×10^{-2}
1.93×10^{-5}	4.62×10^{-4}	2.20×10^{-1}
1.93×10^{-5}	7.70×10^{-4}	3.70×10^{-1}
1.93×10^{-5}	1.31×10^{-3}	6.31×10^{-1}
1.93×10^{-5}	1.92×10^{-3}	9.32×10^{-1}



$k_2 = (4.90 \pm 0.02) \times 10^2$ $M^{-1}s^{-1}$

Reaction of **1c**⁻ with **2b** (DMSO, P_2-^{t}Bu, 20 °C, stopped-flow, 500 nm)

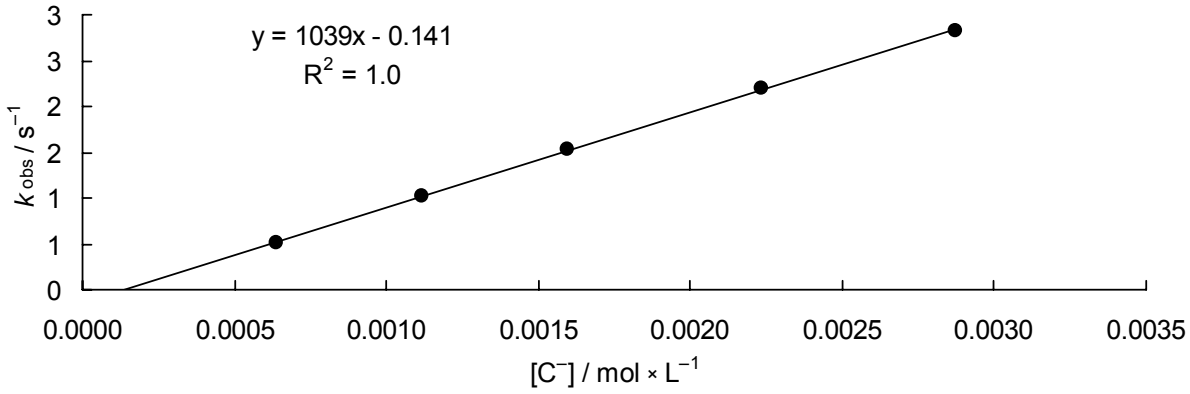
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
3.53×10^{-5}	4.94×10^{-4}	4.74×10^{-1}
3.53×10^{-5}	1.11×10^{-3}	1.08
3.53×10^{-5}	1.73×10^{-3}	1.69
3.53×10^{-5}	2.96×10^{-3}	2.89
3.53×10^{-5}	3.95×10^{-3}	3.85



$k_2 = (9.77 \pm 0.02) \times 10^2$ $M^{-1}s^{-1}$

Reaction of **1c**$^-$ with **2b** (DMSO, KO^{t}Bu, 20 °C, stopped-flow, 500 nm)

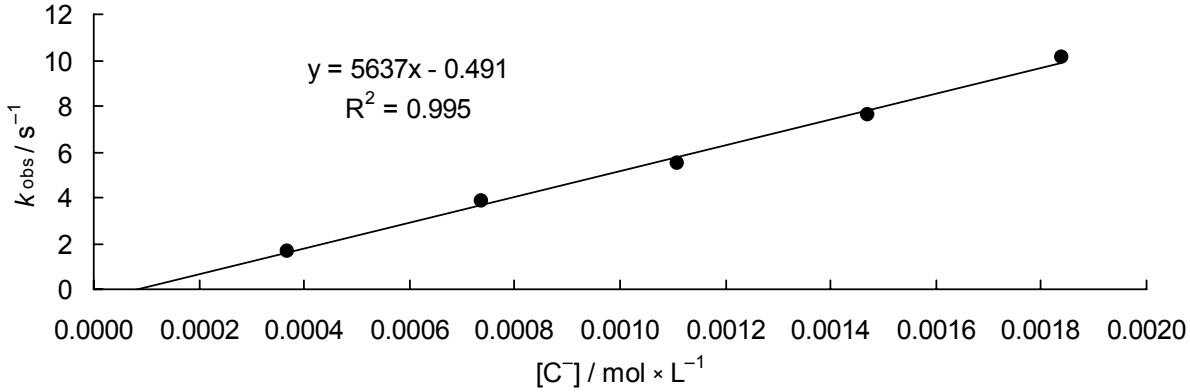
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
2.84×10^{-5}	6.39×10^{-4}	5.18×10^{-1}
2.84×10^{-5}	1.12×10^{-3}	1.02
2.84×10^{-5}	1.60×10^{-3}	1.53
2.84×10^{-5}	2.24×10^{-3}	2.20
2.84×10^{-5}	2.87×10^{-3}	2.83



$k_2 = (1.04 \pm 0.01) \times 10^3$ $M^{-1}s^{-1}$

Reaction of **1c**$^-$ with **6a** (DMSO, KO^{t}Bu, 18-K-6, 20 °C, stopped-flow, 500 nm)

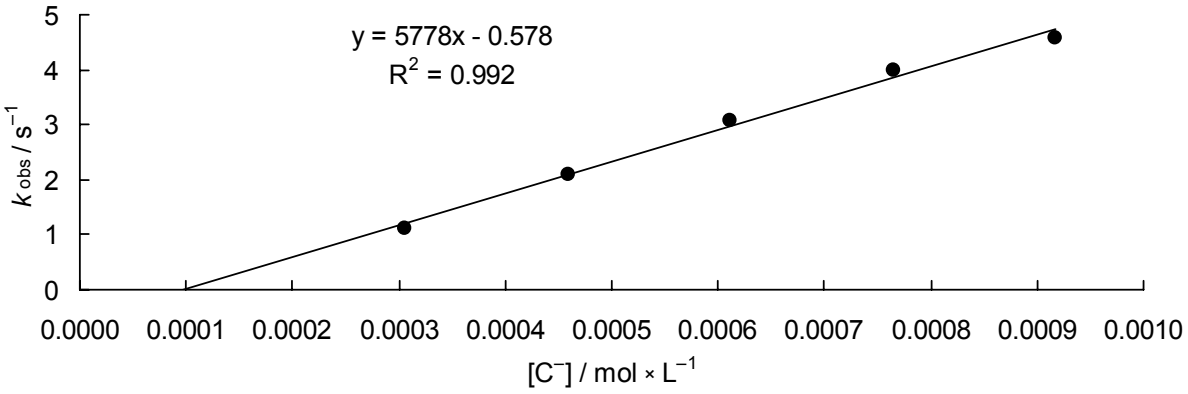
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.77×10^{-5}	3.68×10^{-4}	1.62
1.77×10^{-5}	7.37×10^{-4}	3.87
1.77×10^{-5}	1.11×10^{-3}	5.46
1.77×10^{-5}	1.47×10^{-3}	7.64
1.77×10^{-5}	1.84×10^{-3}	1.01×10^1



$k_2 = (5.64 \pm 0.23) \times 10^3$ $M^{-1}s^{-1}$

Reaction of **1c**$^-$ with **6a** (DMSO, KO^{t}Bu, 20 °C, stopped-flow, 525 nm)

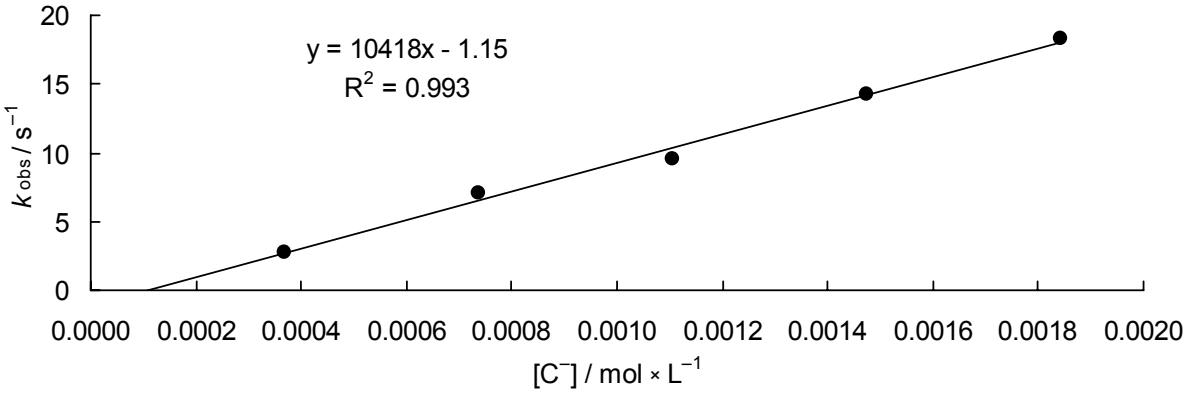
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.86×10^{-5}	3.06×10^{-4}	1.10
1.86×10^{-5}	4.59×10^{-4}	2.08
1.86×10^{-5}	6.12×10^{-4}	3.06
1.86×10^{-5}	7.65×10^{-4}	3.98
1.86×10^{-5}	9.18×10^{-4}	4.57



$k_2 = (5.78 \pm 0.30) \times 10^3$ $M^{-1}s^{-1}$

Reaction of **1c**$^-$ with **4a** (DMSO, KO^{t}Bu, 20 °C, stopped-flow, 500 nm)

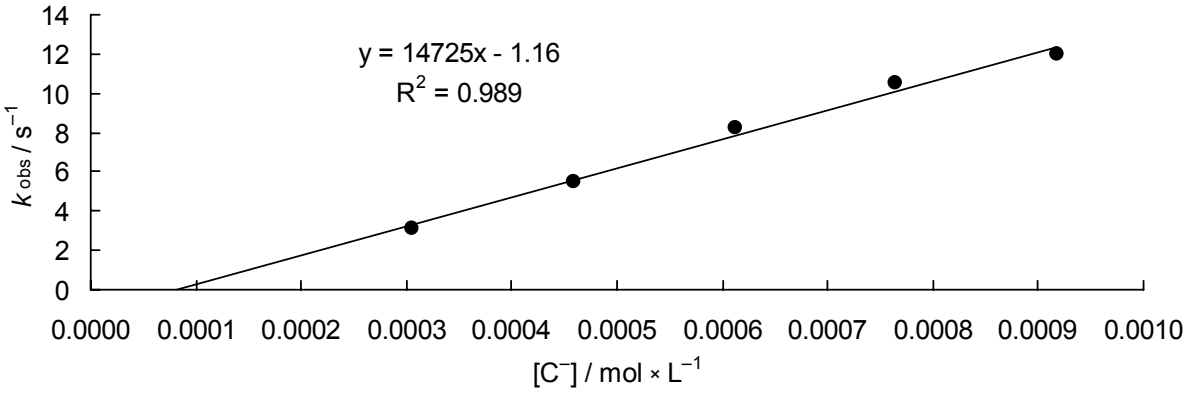
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.66×10^{-5}	3.68×10^{-4}	2.73
1.66×10^{-5}	7.37×10^{-4}	7.02
1.66×10^{-5}	1.11×10^{-3}	9.58
1.66×10^{-5}	1.47×10^{-3}	1.42×10^{1}
1.66×10^{-5}	1.84×10^{-3}	1.83×10^{1}



$k_2 = (1.04 \pm 0.05) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1c**$^-$ with **5a** (DMSO, Verkade's base, 20 °C, stopped-flow, 495 nm)

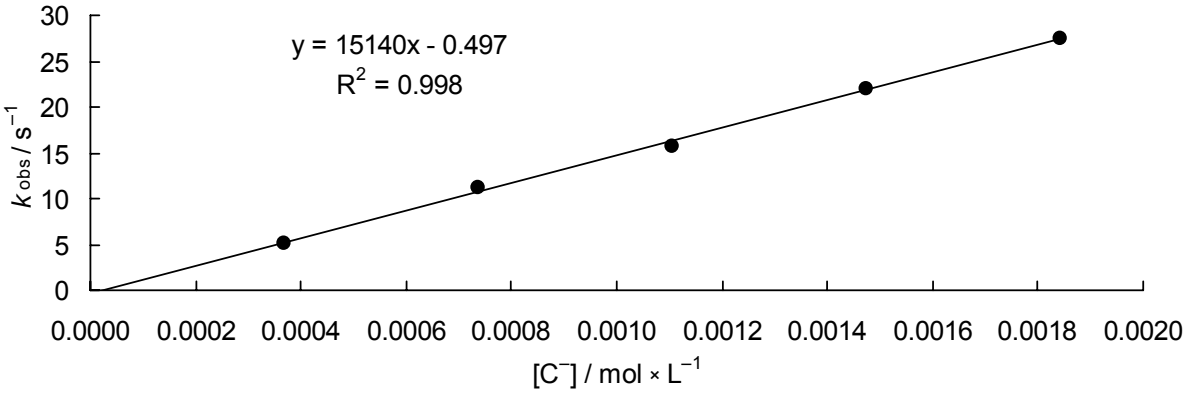
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.84×10^{-5}	3.06×10^{-4}	3.14
1.84×10^{-5}	4.59×10^{-4}	5.49
1.84×10^{-5}	6.12×10^{-4}	8.25
1.84×10^{-5}	7.65×10^{-4}	1.05×10^{1}
1.84×10^{-5}	9.18×10^{-4}	1.19×10^{1}



$k_2 = (1.47 \pm 0.09) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1c**$^-$ with **5a** (DMSO, KO^{t}Bu, 20 °C, stopped-flow, 500 nm)

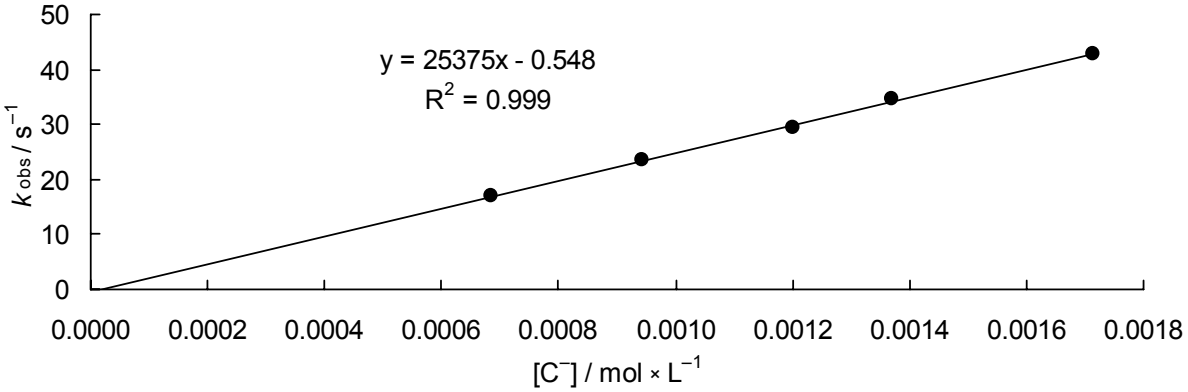
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.58×10^{-5}	3.68×10^{-4}	5.06
1.58×10^{-5}	7.37×10^{-4}	1.11×10^{1}
1.58×10^{-5}	1.11×10^{-3}	1.56×10^{1}
1.58×10^{-5}	1.47×10^{-3}	2.19×10^{1}
1.58×10^{-5}	1.84×10^{-3}	2.75×10^{1}



$k_2 = (1.51 \pm 0.04) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1c**$^-$ with **6b** (DMSO, Verkade's base, 20 °C, stopped-flow, 500 nm)

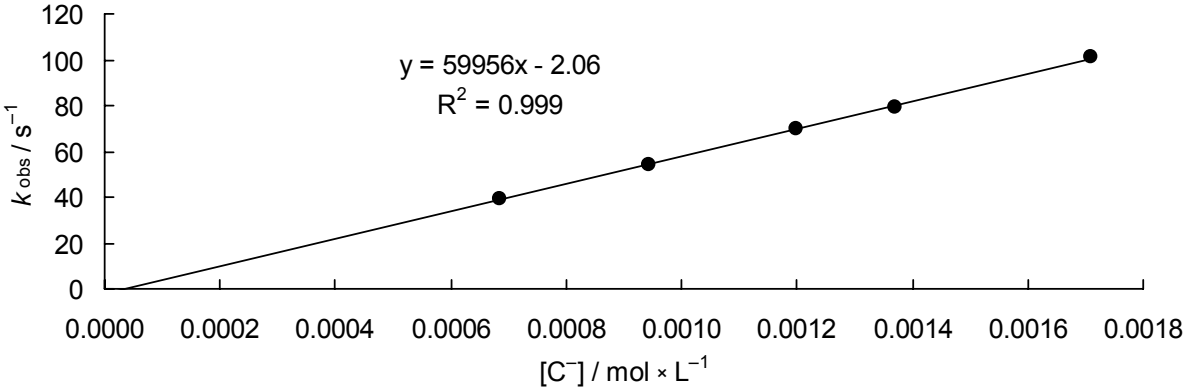
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
2.81×10^{-5}	6.86×10^{-4}	1.69×10^{1}
2.81×10^{-5}	9.43×10^{-4}	2.36×10^{1}
2.81×10^{-5}	1.20×10^{-3}	2.93×10^{1}
2.81×10^{-5}	1.37×10^{-3}	3.45×10^{1}
2.81×10^{-5}	1.71×10^{-3}	4.29×10^{1}



$k_2 = (2.54 \pm 0.05) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1c**$^-$ with **5b** (DMSO, Verkade's base, 20 °C, stopped-flow, 500 nm)

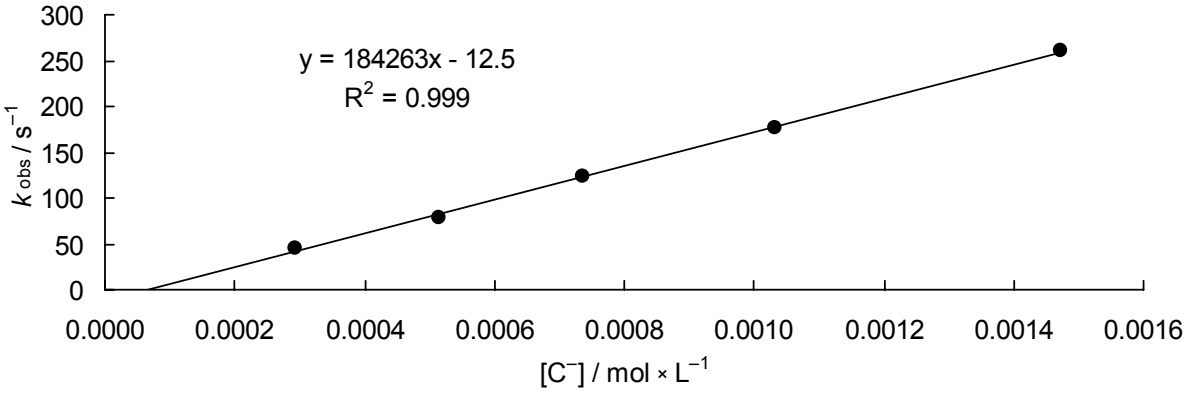
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
5.85×10^{-5}	6.86×10^{-4}	3.94×10^{1}
5.85×10^{-5}	9.43×10^{-4}	5.43×10^{1}
5.85×10^{-5}	1.20×10^{-3}	7.01×10^{1}
5.85×10^{-5}	1.37×10^{-3}	7.92×10^{1}
5.85×10^{-5}	1.71×10^{-3}	1.01×10^{2}



$k_2 = (6.00 \pm 0.08) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1c**$^-$ with **2e** (DMSO, KO^{t}Bu, 20 °C, stopped-flow, 533 nm)

$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
2.51×10^{-5}	2.95×10^{-4}	4.56×10^{1}
2.51×10^{-5}	5.16×10^{-4}	7.88×10^{1}
2.51×10^{-5}	7.37×10^{-4}	1.23×10^{2}
2.51×10^{-5}	1.03×10^{-3}	1.76×10^{2}
2.51×10^{-5}	1.47×10^{-3}	2.60×10^{2}

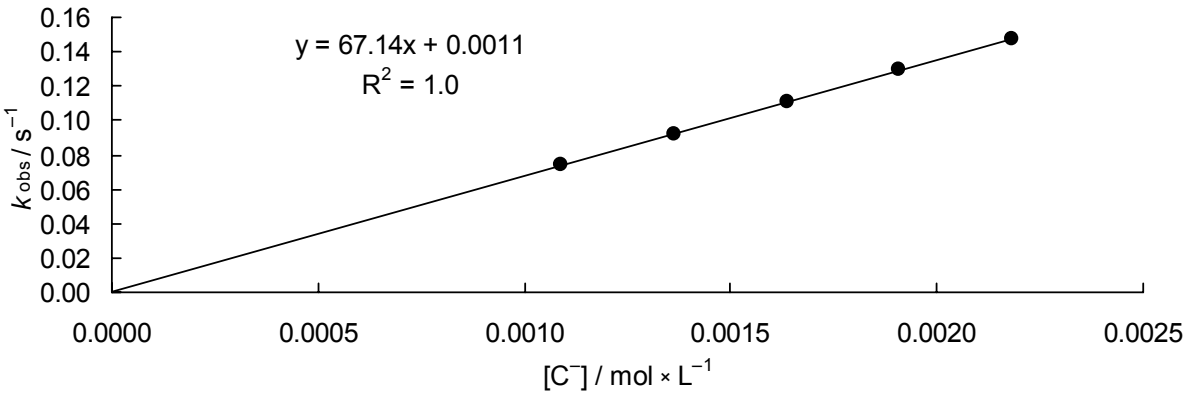


$k_2 = (1.84 \pm 0.04) \times 10^5$ $M^{-1}s^{-1}$

Reactions of 1d$^-$ (X = p-NO$_2$)

Reaction of **1d**$^-$ with **2c** (DMSO, Verkade's base, 20 °C, stopped-flow, 400 nm)

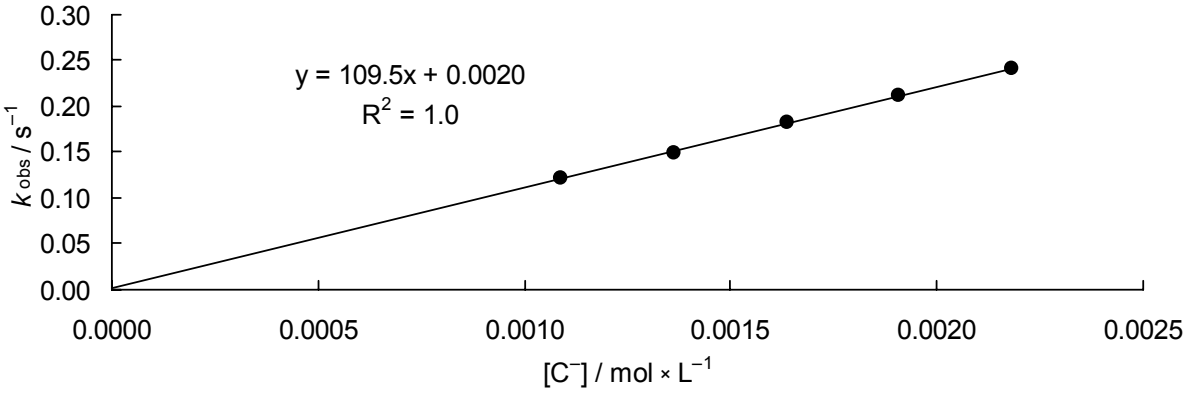
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
4.85×10^{-5}	1.09×10^{-3}	7.42×10^{-2}
4.85×10^{-5}	1.36×10^{-3}	9.23×10^{-2}
4.85×10^{-5}	1.64×10^{-3}	1.11×10^{-1}
4.85×10^{-5}	1.91×10^{-3}	1.30×10^{-1}
4.85×10^{-5}	2.18×10^{-3}	1.47×10^{-1}



$k_2 = (6.71 \pm 0.06) \times 10^1$ $M^{-1}s^{-1}$

Reaction of **1d**$^-$ with **2d** (DMSO, Verkade's base, 20 °C, stopped-flow, 400 nm)

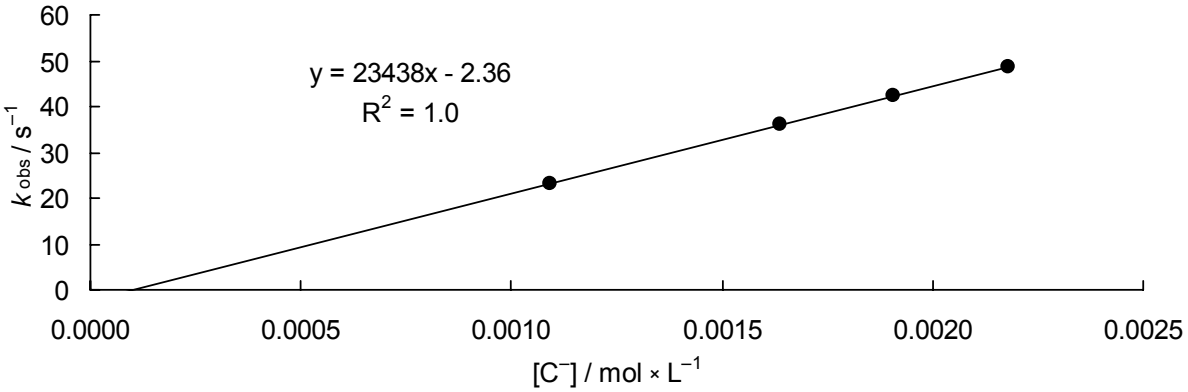
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
4.64×10^{-5}	1.09×10^{-3}	1.22×10^{-1}
4.64×10^{-5}	1.36×10^{-3}	1.50×10^{-1}
4.64×10^{-5}	1.64×10^{-3}	1.82×10^{-1}
4.64×10^{-5}	1.91×10^{-3}	2.11×10^{-1}
4.64×10^{-5}	2.18×10^{-3}	2.41×10^{-1}



$k_2 = (1.10 \pm 0.01) \times 10^2$ $M^{-1}s^{-1}$

Reaction of **1d**$^-$ with **6c** (DMSO, Verkade's base, 20 °C, stopped-flow, 400 nm)

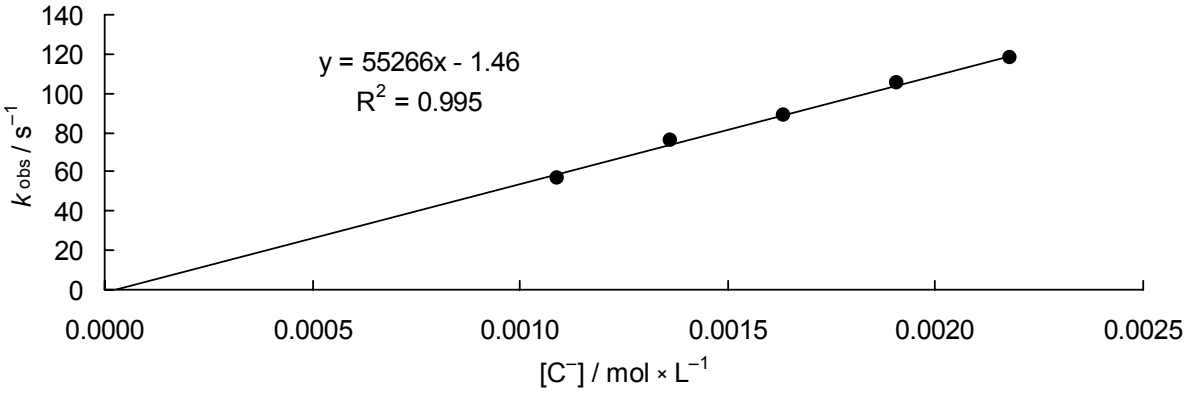
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
4.77×10^{-5}	1.09×10^{-3}	2.32×10^{1}
4.77×10^{-5}	1.64×10^{-3}	3.60×10^{1}
4.77×10^{-5}	1.91×10^{-3}	4.25×10^{1}
4.77×10^{-5}	2.18×10^{-3}	4.87×10^{1}



$k_2 = (2.34 \pm 0.01) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1d**$^-$ with **5c** (DMSO, Verkade's base, 20 °C, stopped-flow, 400 nm)

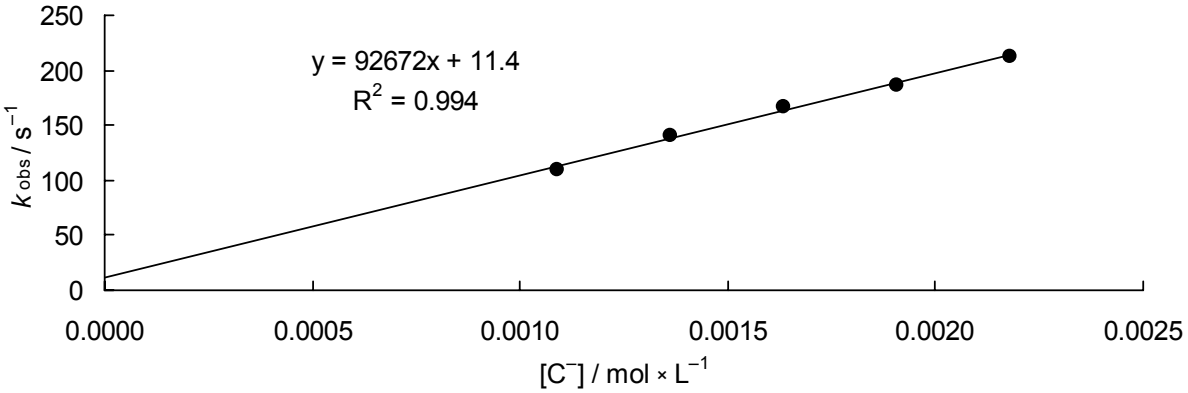
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
5.08×10^{-5}	1.09×10^{-3}	5.70×10^{1}
5.08×10^{-5}	1.36×10^{-3}	7.61×10^{1}
5.08×10^{-5}	1.64×10^{-3}	8.87×10^{1}
5.08×10^{-5}	1.91×10^{-3}	1.05×10^{2}
5.08×10^{-5}	2.18×10^{-3}	1.18×10^{2}



$k_2 = (5.53 \pm 0.22) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1d**$^-$ with **6d** (DMSO, Verkade's base, 20 °C, stopped-flow, 350 nm)

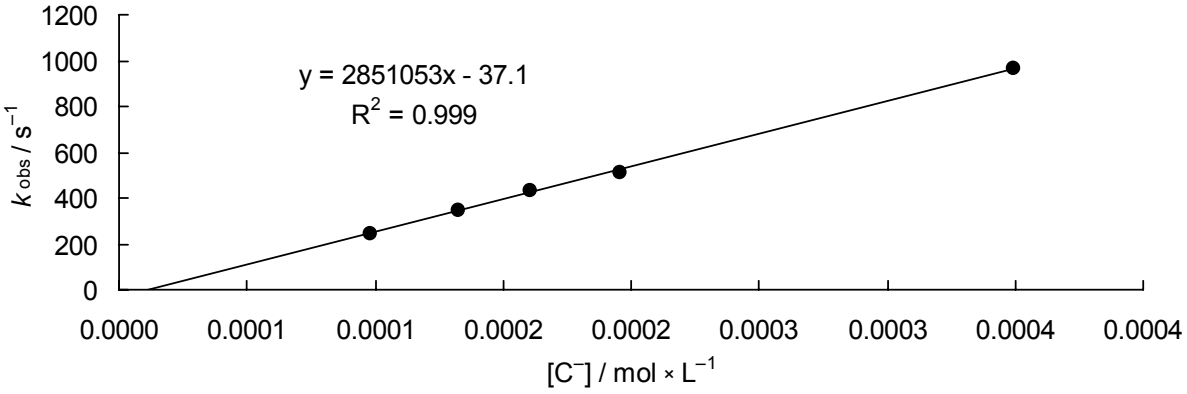
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
4.93×10^{-5}	1.09×10^{-3}	1.09×10^{2}
4.93×10^{-5}	1.36×10^{-3}	1.41×10^{2}
4.93×10^{-5}	1.64×10^{-3}	1.66×10^{2}
4.93×10^{-5}	1.91×10^{-3}	1.86×10^{2}
4.93×10^{-5}	2.18×10^{-3}	2.13×10^{2}



$k_2 = (9.27 \pm 0.41) \times 10^4$ $M^{-1}s^{-1}$

Reaction of **1d**$^-$ with **3b** (DMSO, Verkade's base, 20 °C, stopped-flow, 640 nm)

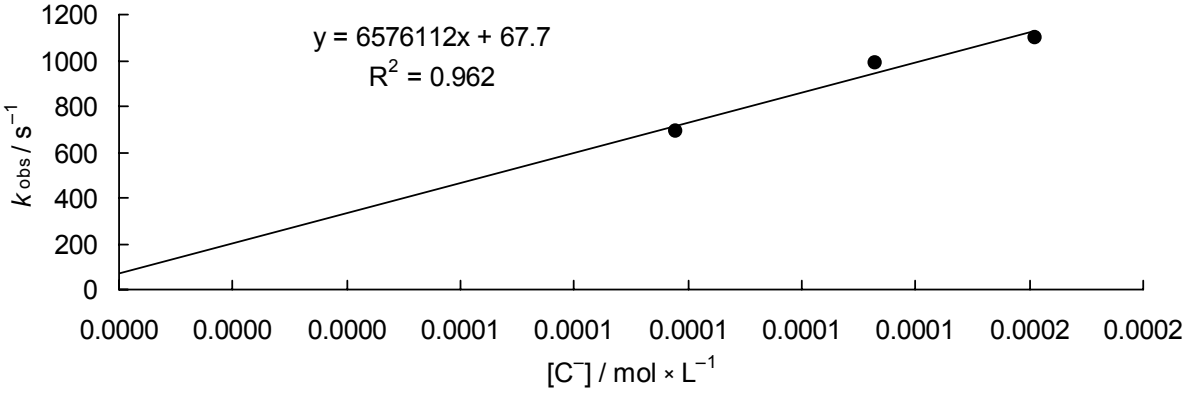
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.01×10^{-5}	9.80×10^{-5}	2.44×10^{2}
1.01×10^{-5}	1.33×10^{-4}	3.44×10^{2}
1.01×10^{-5}	1.61×10^{-4}	4.28×10^{2}
1.01×10^{-5}	1.96×10^{-4}	5.09×10^{2}
1.01×10^{-5}	3.50×10^{-4}	9.64×10^{2}



$k_2 = (2.85 \pm 0.04) \times 10^6$ $M^{-1}s^{-1}$

Reaction of **1d**$^-$ with **3a** (DMSO, Verkade's base, 20 °C, stopped-flow, 640 nm)

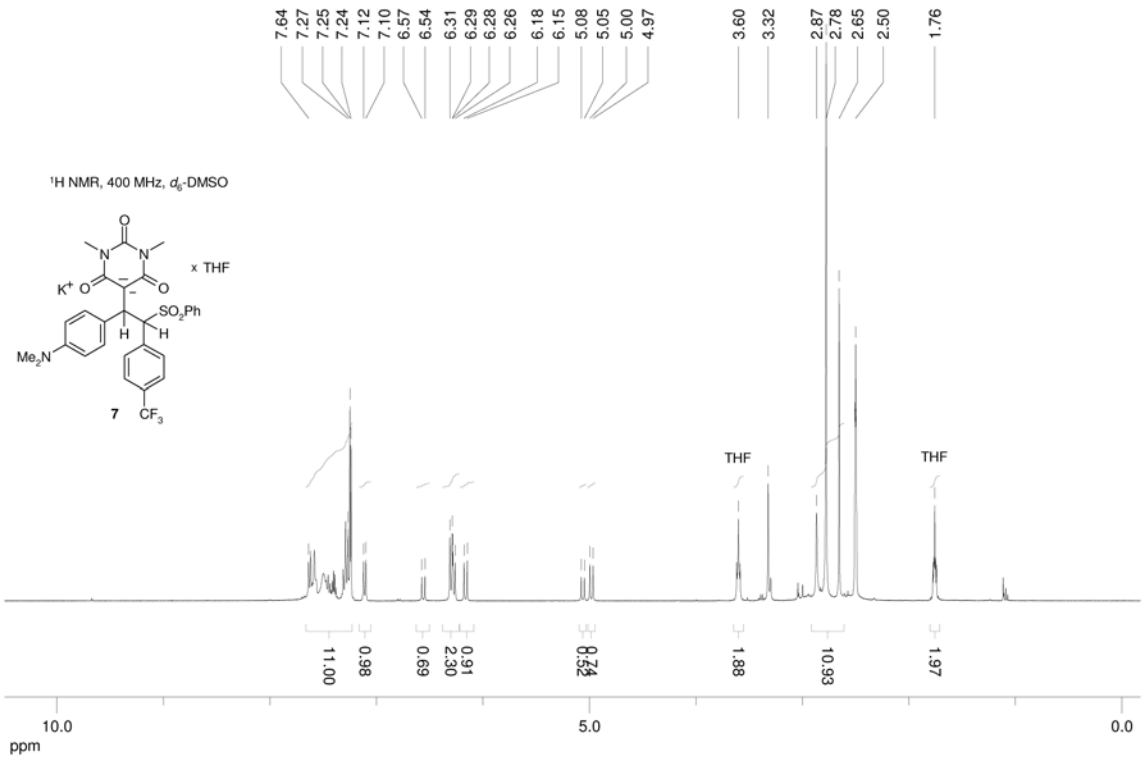
$[E]_0$ / M	$[C^-]_0$ / M	k_{obs} / s^{-1}
1.01×10^{-5}	9.80×10^{-5}	6.91×10^{2}
1.01×10^{-5}	1.33×10^{-4}	9.90×10^{2}
1.01×10^{-5}	1.61×10^{-4}	1.10×10^{3}

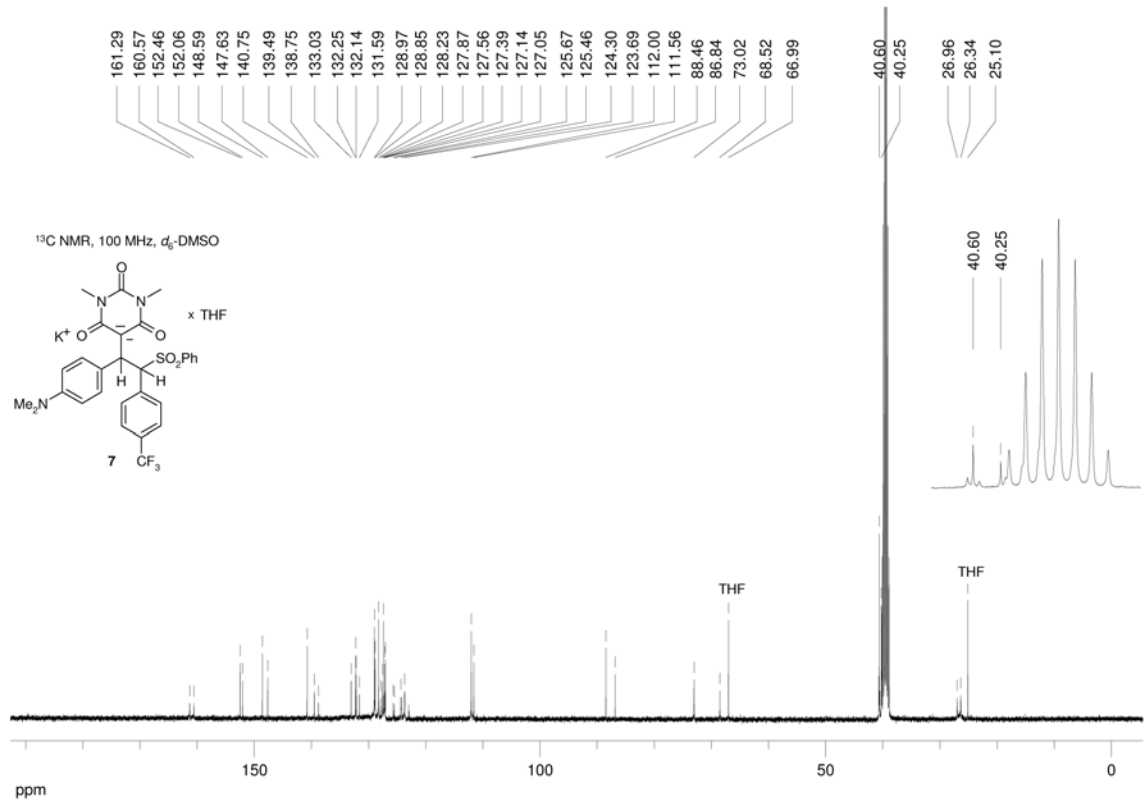


$k_2 = (6.58 \pm 1.31) \times 10^6$ $M^{-1}s^{-1}$

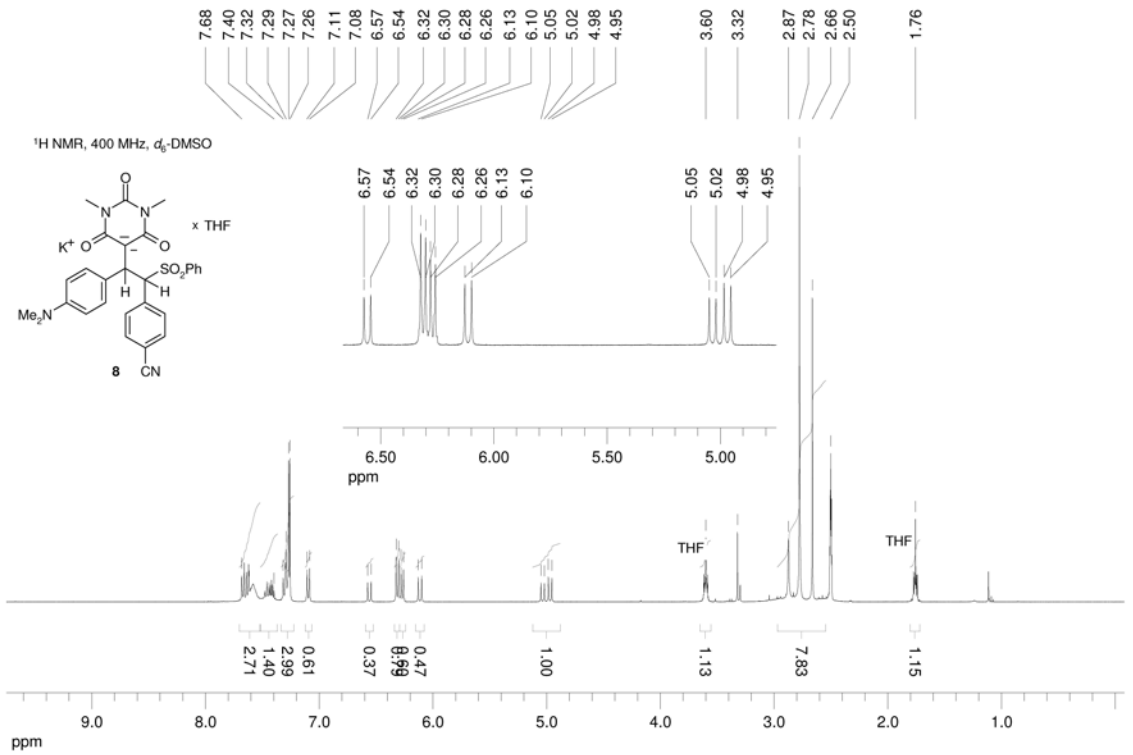
NMR spectra

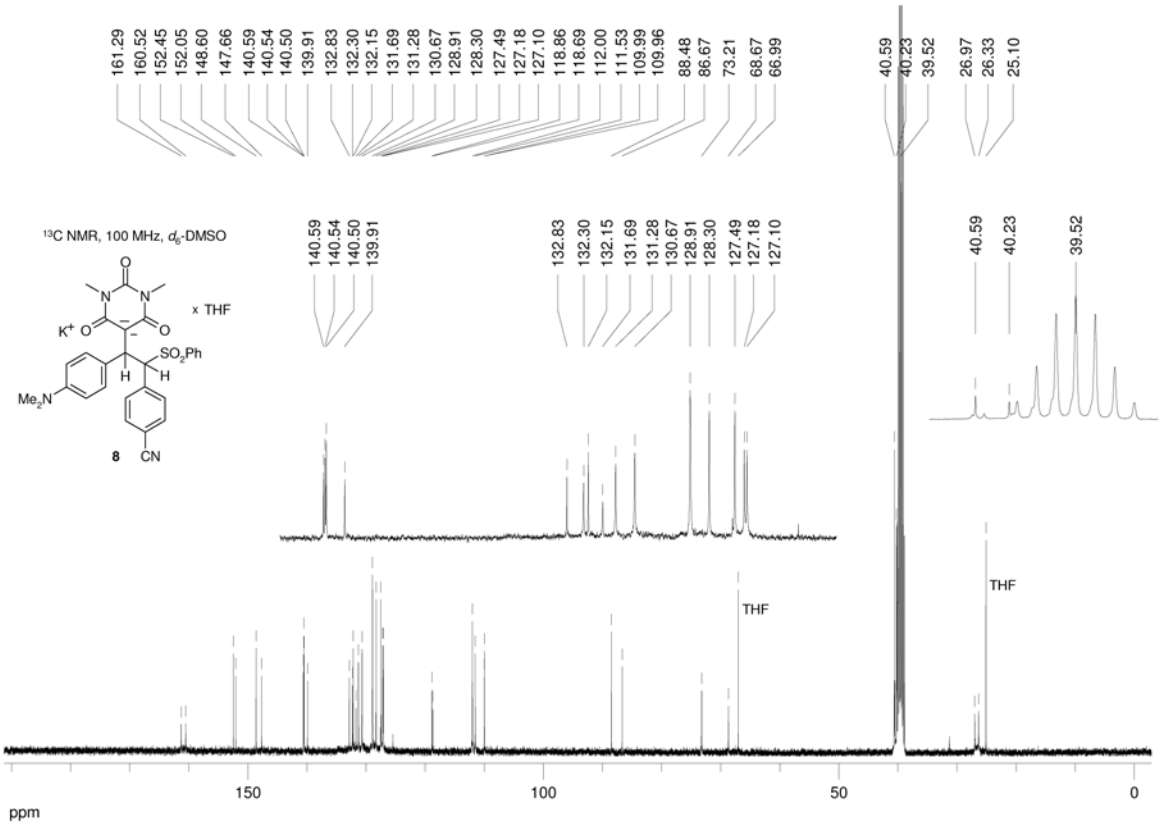
7



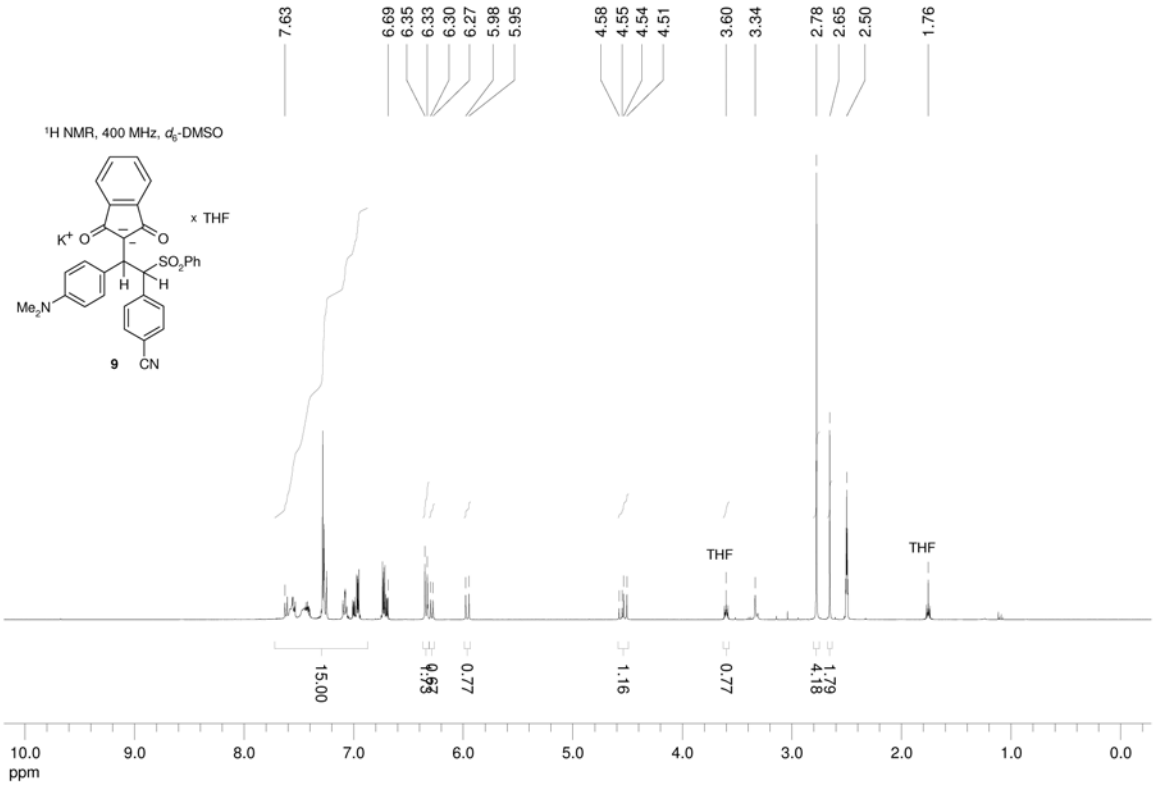


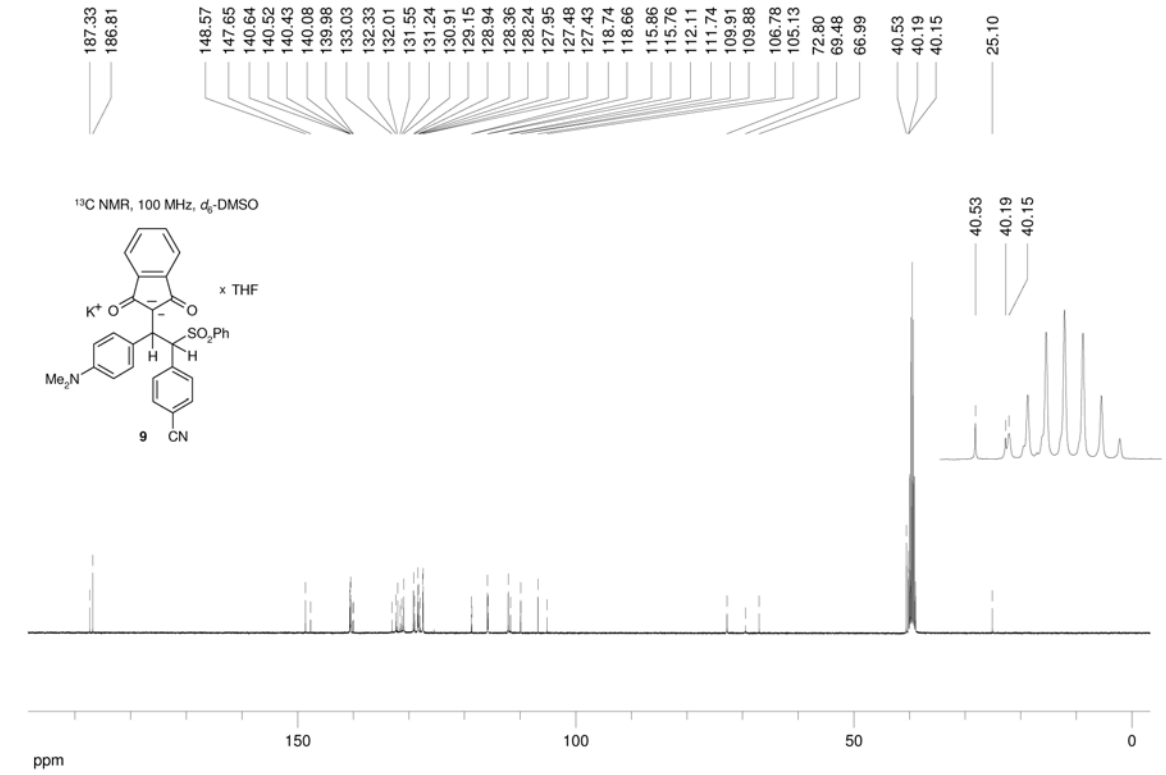
8


7.68 7.40 7.32 7.29 7.27 7.26 7.11 7.08 6.57 6.54 6.32 6.30 6.28 6.26 6.13 6.10 5.05 5.02 4.98 4.95 3.60 3.32 2.87 2.78 2.66 2.50 1.76
¹H NMR, 400 MHz, d6-DMSO
x THF
SO2Ph
Me2N
8
CN
THF
THF
ppm

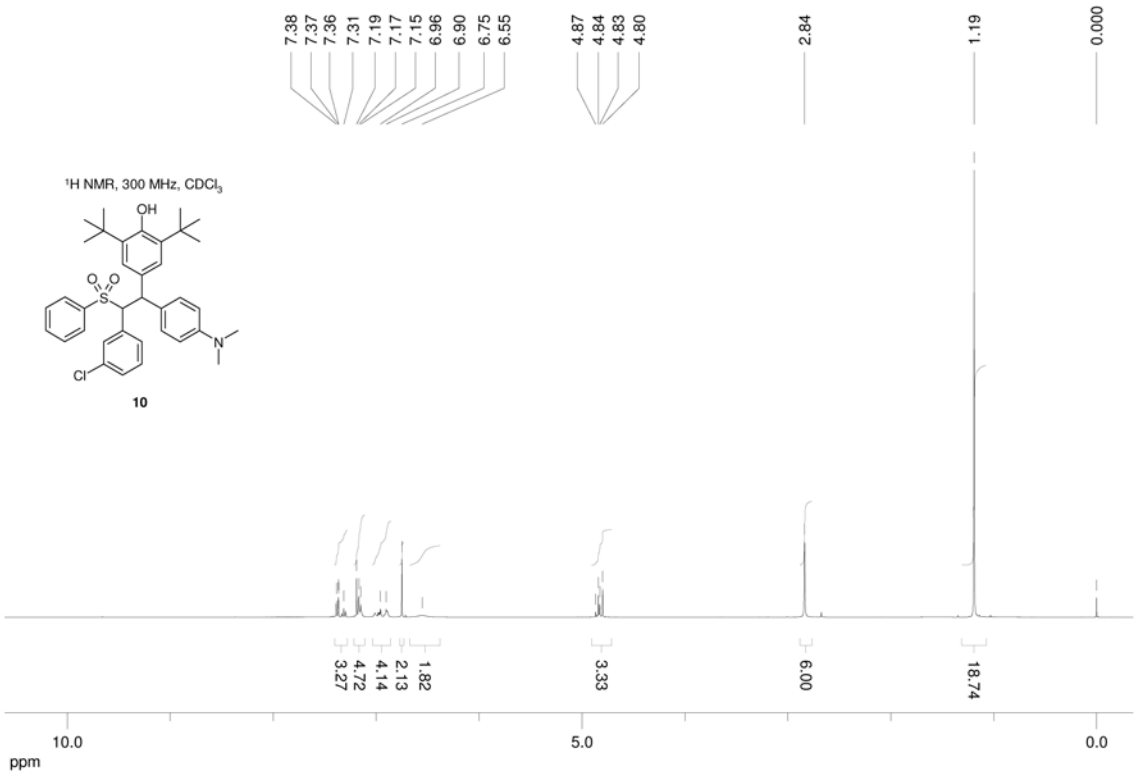

161.29 160.52 152.45 152.05 148.60 147.66 140.59 140.54 140.50 139.91 132.83 132.30 132.15 131.69 131.28 130.67 128.91 128.30 127.49 127.18 127.10 118.86 118.69 112.00 111.53 109.99 109.96 88.48 86.67 73.21 68.67 66.99 40.59 40.23 39.52 26.97 26.33 25.10
¹³C NMR, 100 MHz, d6-DMSO
x THF
SO2Ph
Me2N
8
CN
THF
THF
ppm

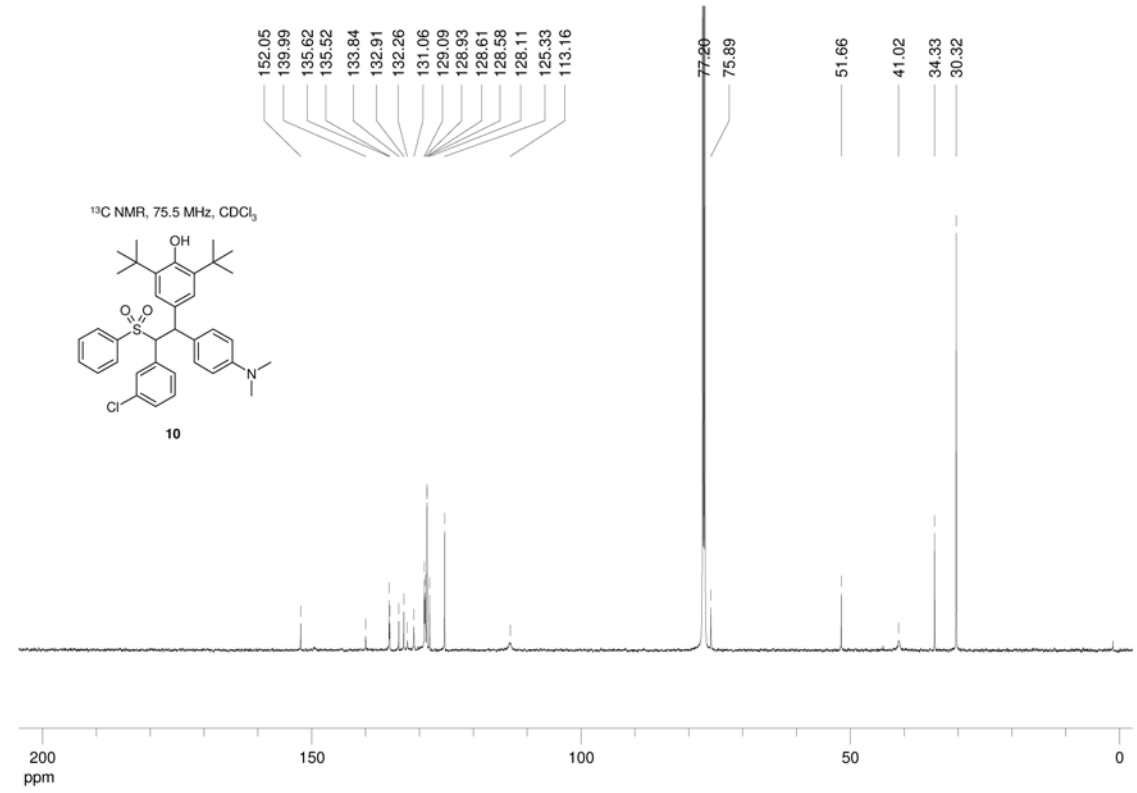
9


7.63
6.69
6.35
6.33
6.30
6.27
5.98
5.95
4.58
4.55
4.54
4.51
3.60
3.34
2.78
2.65
2.50
1.76
¹H NMR, 400 MHz, d6-DMSO
x THF
9
THF
THF
15.00
0.77
1.16
0.77
4.18
1.79
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

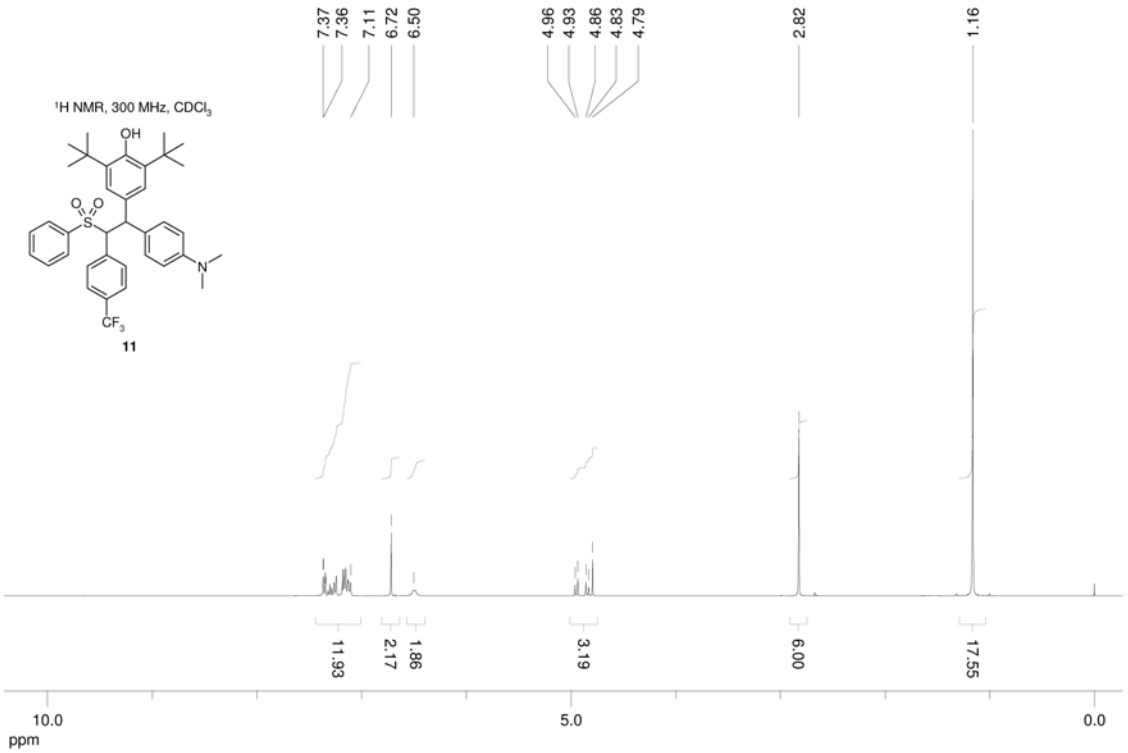

187.33
186.81
148.57
147.65
140.64
140.52
140.43
140.08
139.98
133.03
132.33
132.01
131.55
131.24
130.91
129.15
128.94
128.36
128.24
127.95
127.48
127.43
118.74
118.66
115.86
115.76
112.11
111.74
109.91
109.88
106.78
105.13
72.80
69.48
66.99
40.53
40.19
40.15
25.10
¹³C NMR, 100 MHz, d6-DMSO
x THF
9
150
100
50
0
ppm

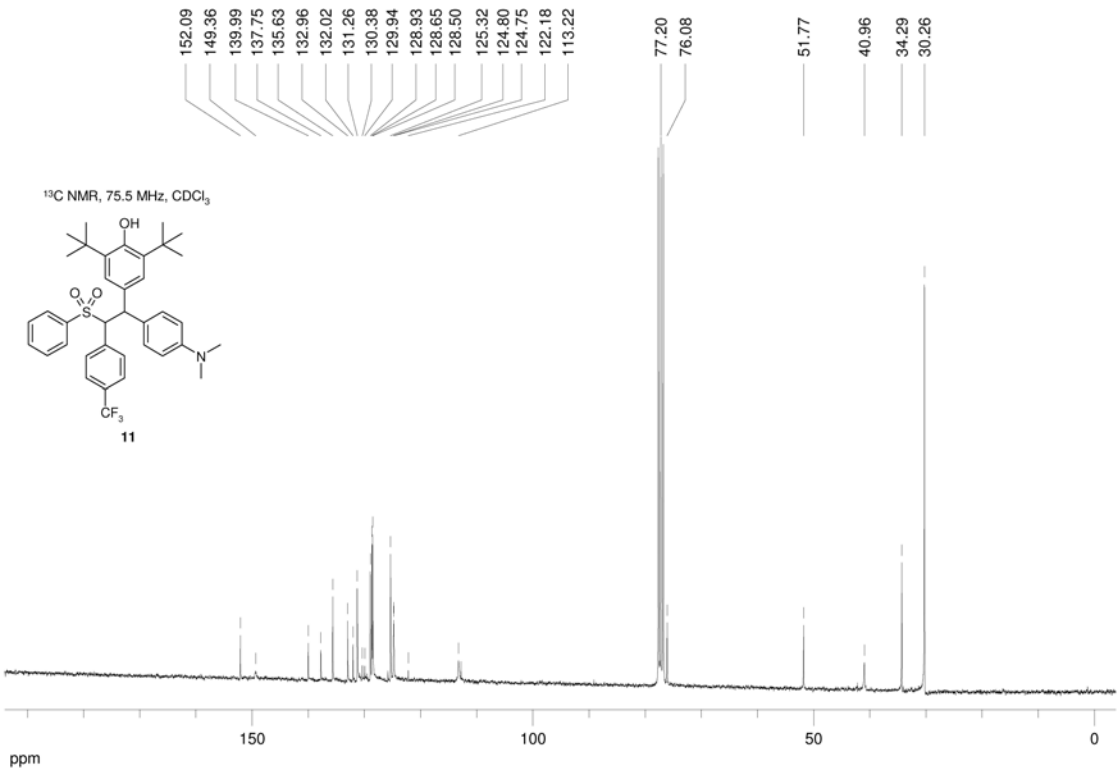
10


7.38
7.37
7.36
7.31
7.19
7.17
7.15
6.96
6.90
6.75
6.55
4.87
4.84
4.83
4.80
2.84
1.19
0.000
¹H NMR, 300 MHz, CDCl₃
OH
O
O
S
N
Cl
10
3.27
4.72
4.14
2.13
1.82
3.33
6.00
18.74
10.0
5.0
0.0
ppm

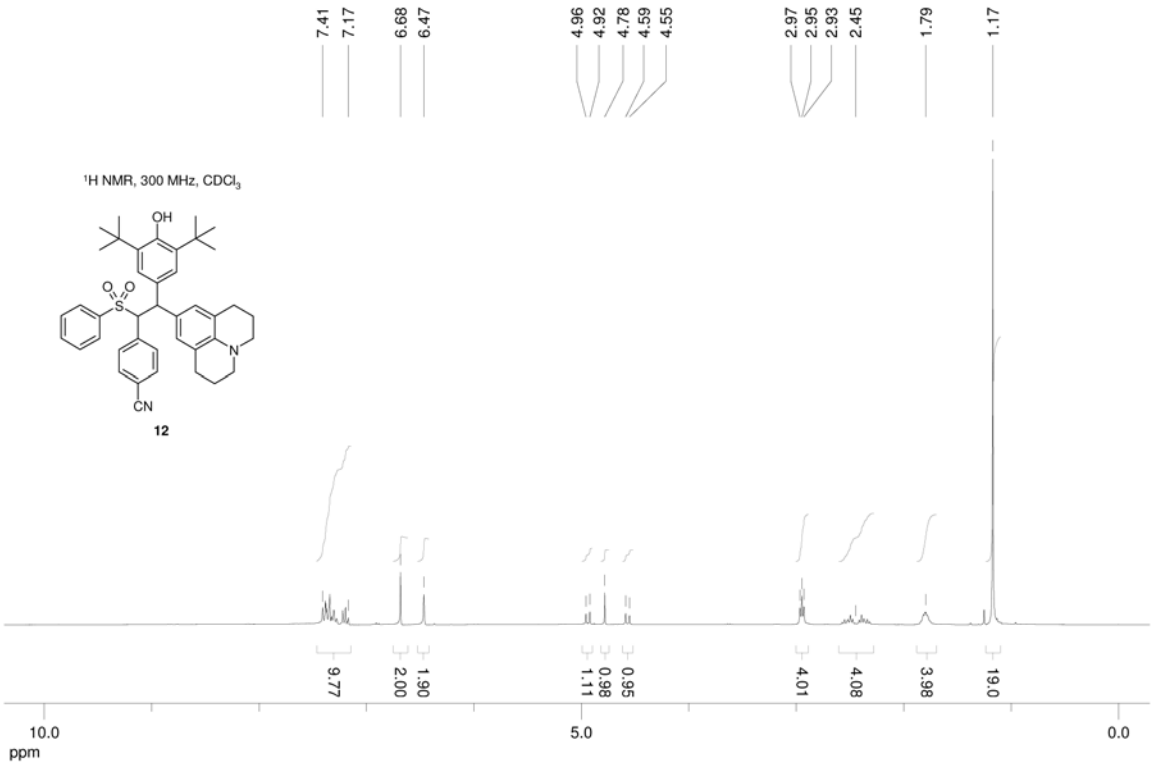

152.05
139.99
135.62
135.52
133.84
132.91
132.26
131.06
129.09
128.93
128.61
128.58
128.11
125.33
113.16
77.20
75.89
51.66
41.02
34.33
30.32
¹³C NMR, 75.5 MHz, CDCl₃
OH
O
O
S
N
Cl
10
200
150
100
50
0
ppm

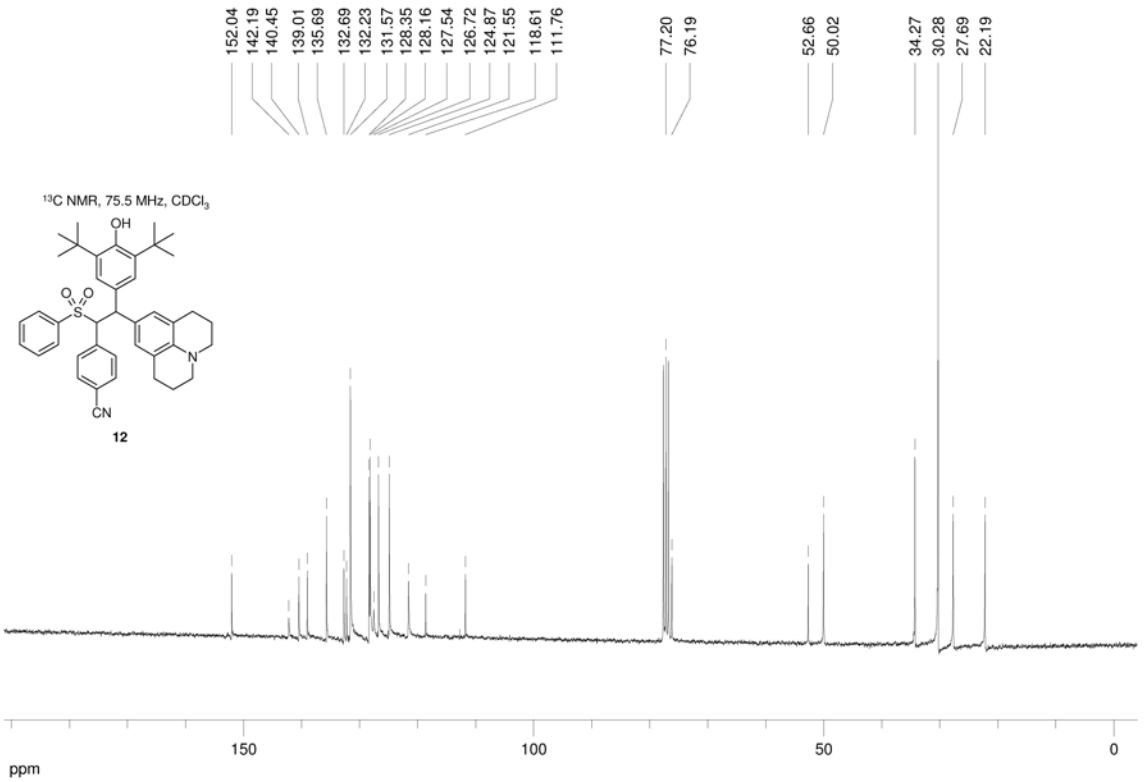
11


7.37
7.36
7.11
6.72
6.50
4.96
4.93
4.86
4.83
4.79
2.82
1.16
^{1}H NMR, 300 MHz, CDCl$_3$
OH
O
O
S
N
CF$_3$
11
11.93
2.17
1.86
3.19
6.00
17.55
10.0
5.0
0.0
ppm

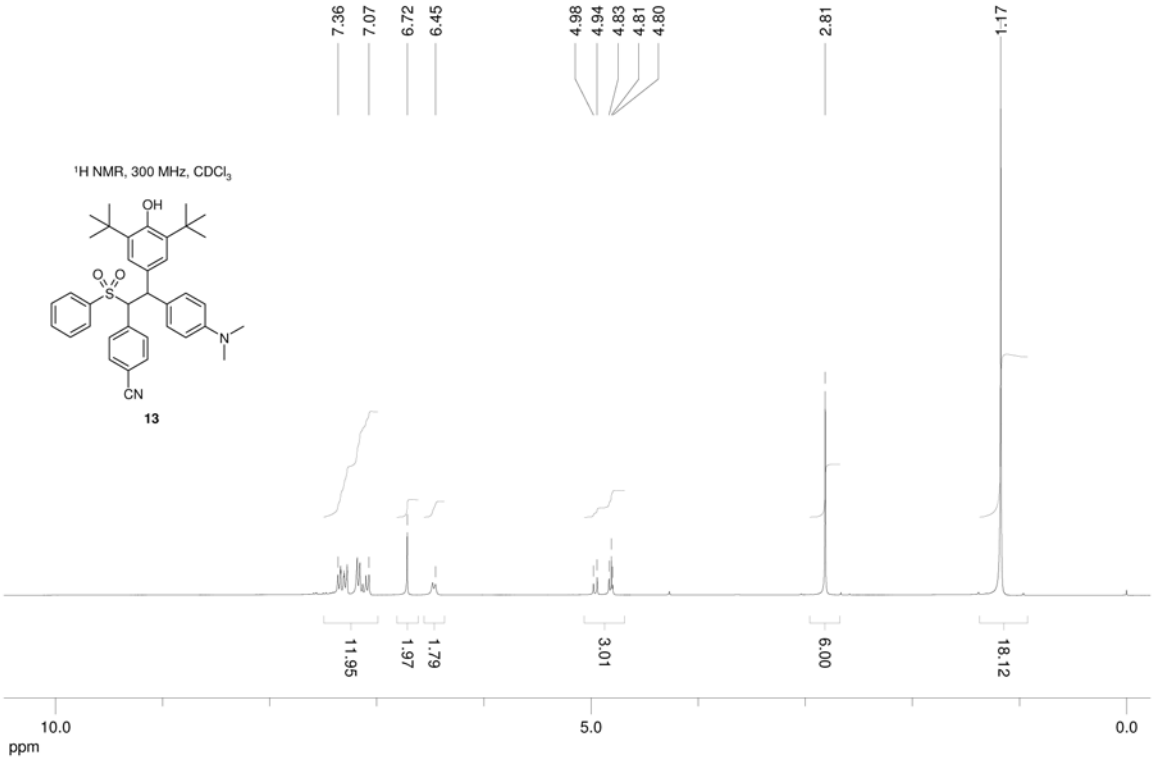

152.09
149.36
139.99
137.75
135.63
132.96
132.02
131.26
130.38
129.94
128.93
128.65
128.50
125.32
124.80
124.75
122.18
113.22
77.20
76.08
51.77
40.96
34.29
30.26
^{13}C NMR, 75.5 MHz, CDCl$_3$
OH
O
O
S
N
CF$_3$
11
150
100
50
0
ppm

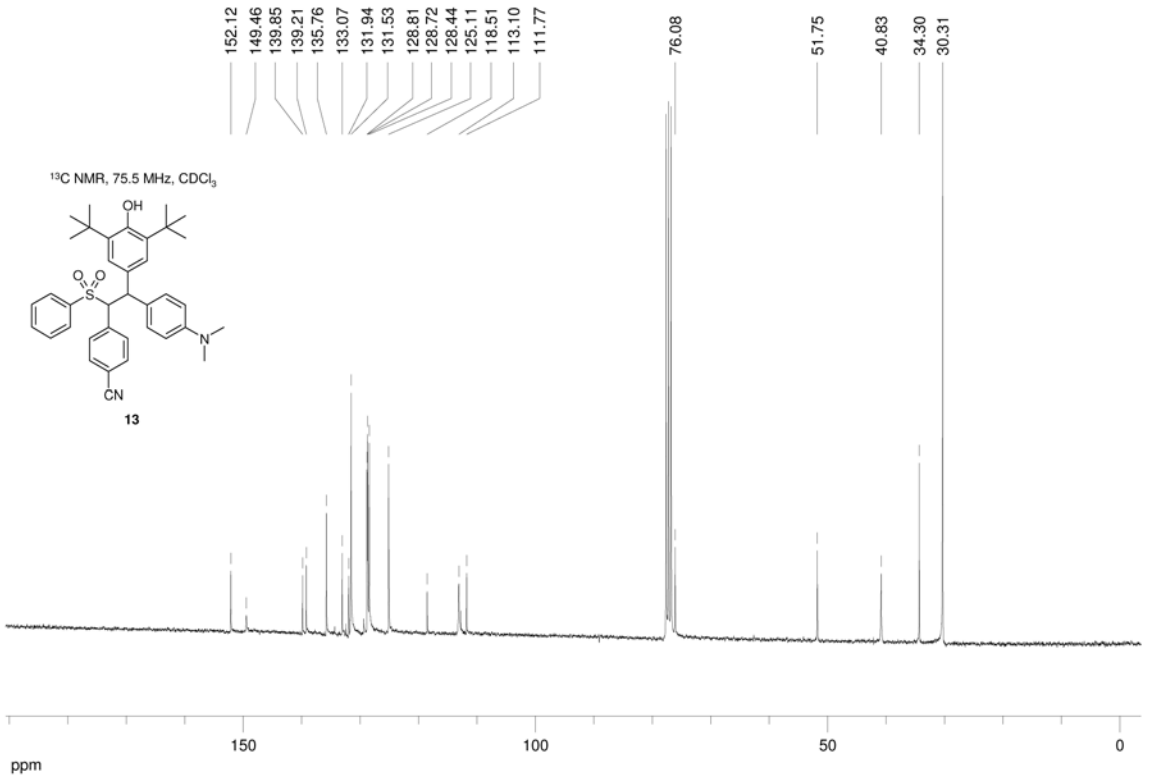
12


7.41
7.17
6.68
6.47
4.96
4.92
4.78
4.59
4.55
2.97
2.95
2.93
2.45
1.79
1.17
^{1}H NMR, 300 MHz, CDCl$_3$
OH
O
O
S
N
CN
12
9.77
2.00
1.90
1.11
0.98
0.95
4.01
4.08
3.98
19.0
10.0
5.0
0.0
ppm


152.04
142.19
140.45
139.01
135.69
132.69
132.23
131.57
128.35
128.16
127.54
126.72
124.87
121.55
118.61
111.76
77.20
76.19
52.66
50.02
34.27
30.28
27.69
22.19
^{13}C NMR, 75.5 MHz, CDCl$_3$
OH
O
O
S
N
CN
12
150
100
50
0
ppm

13


7.36
7.07
6.72
6.45
4.98
4.94
4.83
4.81
4.80
2.81
1.17
^{1}H NMR, 300 MHz, CDCl$_3$
OH
O
O
S
N
CN
13
11.95
1.97
1.79
3.01
6.00
18.12
10.0
5.0
0.0
ppm


152.12
149.46
139.85
139.21
135.76
133.07
131.94
131.53
128.81
128.72
128.44
125.11
118.51
113.10
111.77
76.08
51.75
40.83
34.30
30.31
^{13}C NMR, 75.5 MHz, CDCl$_3$
OH
O
O
S
N
CN
13
150
100
50
0
ppm