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SUPPORTING INFORMATION

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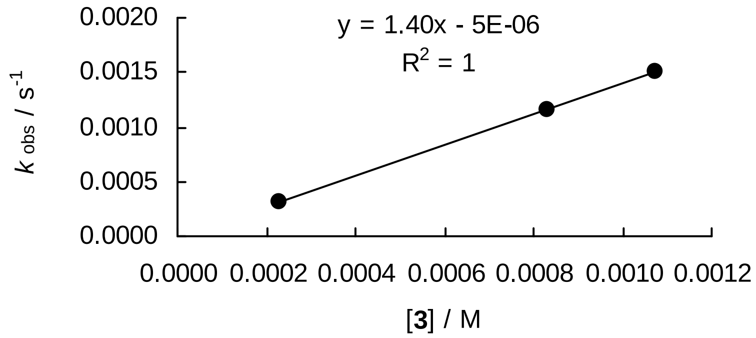
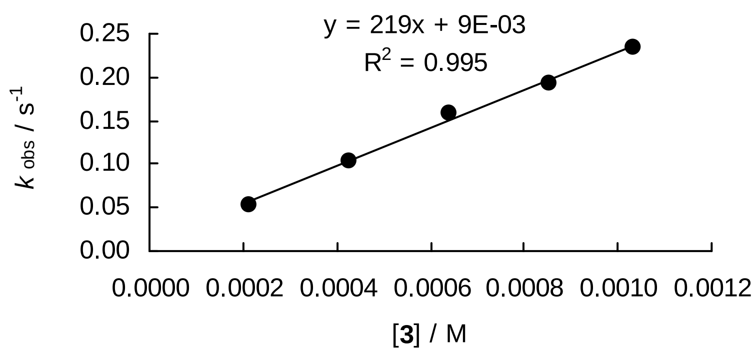
[**8d**]$_0$ / M	[**3**]$_0$ / M	[**3**]$_0$/[**8d**]$_0$	conv. / %	k_{obs} /s^{-1}
1.09×10^{-5}	2.28×10^{-4}	21	89	3.17×10^{-4}
1.04×10^{-5}	8.31×10^{-4}	78	90	1.15×10^{-3}
1.05×10^{-5}	1.07×10^{-3}	102	86	1.50×10^{-3}



$k_2 = 1.40$ M^{-1} s^{-1}

Rate constants for the reactions of 2,5-dimethylpyrrole (**3**) with $(mpa)_2CH^+BF_4^-$ (**8f**) in CH_3CN (20 °C, stopped-flow, λ = 622 nm)

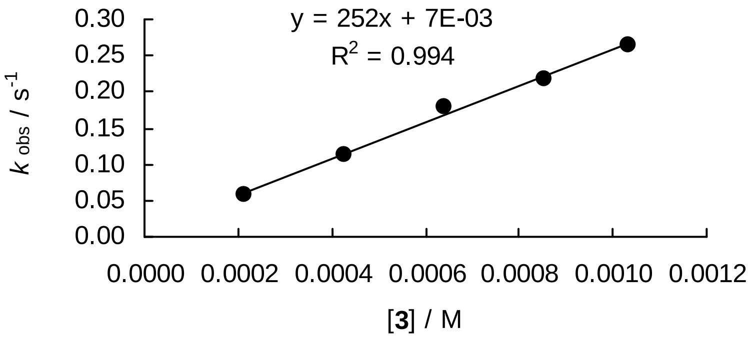
[**8f**]$_0$ / M	[**3**]$_0$ / M	[**3**]$_0$/[**8f**]$_0$	k_{obs} /s^{-1}
1.32×10^{-5}	2.13×10^{-4}	16	5.33×10^{-2}
1.32×10^{-5}	4.27×10^{-4}	32	1.03×10^{-1}
1.32×10^{-5}	6.40×10^{-4}	49	1.58×10^{-1}
1.32×10^{-5}	8.54×10^{-4}	65	1.92×10^{-1}
1.32×10^{-5}	1.03×10^{-3}	78	2.35×10^{-1}



$k_2 = 2.19 \times 10^2$ M^{-1} s^{-1}

Rate constants for the reactions of 2,5-dimethylpyrrole (**3**) with $(mor)_2CH^+BF_4^-$ (**8g**) in CH_3CN (20 °C, stopped-flow, λ = 620 nm)

[**8g**]$_0$ / M	[**3**]$_0$ / M	[**3**]$_0$/[**8g**]$_0$	k_{obs} /s^{-1}
1.51×10^{-5}	2.13×10^{-4}	14	5.69×10^{-2}
1.51×10^{-5}	4.27×10^{-4}	28	1.14×10^{-1}
1.51×10^{-5}	6.40×10^{-4}	42	1.80×10^{-1}
1.51×10^{-5}	8.54×10^{-4}	56	2.18×10^{-1}
1.51×10^{-5}	1.03×10^{-3}	68	2.65×10^{-1}

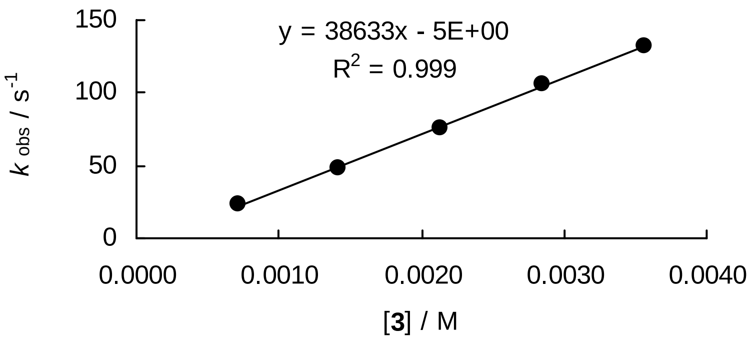


$k_2 = 2.52 \times 10^2$ M^{-1} s^{-1}

Rate constants for the reactions of 2,5-dimethylpyrrole (**3**) with $(dpa)_2CH^+BF_4^-$ (**8h**) in CH_3CN (20 °C, stopped-flow, λ = 672 nm)

[**8h**]$_0$ / M	[**3**]$_0$ / M	[**3**]$_0$/[**8h**]$_0$	k_{obs} /s^{-1}
3.54×10^{-5}	7.12×10^{-4}	20	2.30×10^{1} [a]
3.54×10^{-5}	1.42×10^{-3}	40	4.87×10^{1} [a]
3.54×10^{-5}	2.14×10^{-3}	60	7.60×10^{1}
3.54×10^{-5}	2.85×10^{-3}	81	1.06×10^{2}
3.54×10^{-5}	3.56×10^{-3}	101	1.32×10^{2}

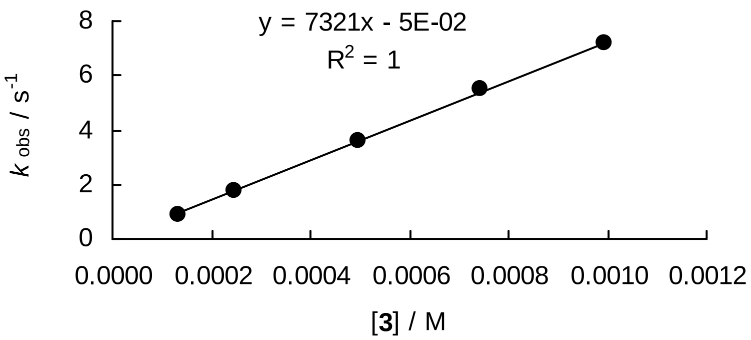
[a] Exponential decay only during the first half-life.



$k_2 = 3.87 \times 10^4$ M^{-1} s^{-1}

Rate constants for the reactions of 2,5-dimethylpyrrole (**3**) with $(mfa)_2CH^+BF_4^-$ (**8i**) in CH_3CN (20 °C, stopped-flow, λ = 593 nm)

[**8i**]$_0$ / M	[**3**]$_0$ / M	[**3**]$_0$/[**8i**]$_0$	k_{obs} /s^{-1}
1.25×10^{-5}	1.32×10^{-4}	11	9.05×10^{-1}
1.25×10^{-5}	2.48×10^{-4}	20	1.76
1.25×10^{-5}	4.97×10^{-4}	40	3.59
1.25×10^{-5}	7.45×10^{-4}	60	5.50
1.25×10^{-5}	9.93×10^{-4}	80	7.16

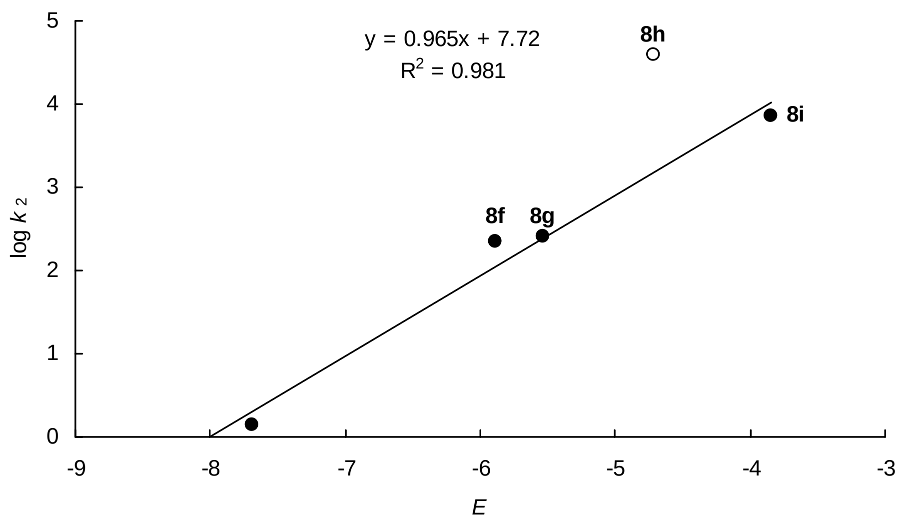


$k_2 = 7.32 \times 10^3$ M^{-1} s^{-1}

Nucleophilicity parameters of 2,5-dimethylpyrrole (**3**) in CH_3CN: N = 8.01, s = 0.96

Reference electrophile	E parameter	k_2(20 °C) / M^{-1} s^{-1}
$(pyr)_2CH^+BF_4^-$ (**8d**)	–7.69	1.40
$(mpa)_2CH^+BF_4^-$ (**8f**)	–5.89	2.19×10^2
$(mor)_2CH^+BF_4^-$ (**8g**)	–5.53	2.52×10^2
$(dpa)_2CH^+BF_4^-$ (**8h**)	–4.72	3.87×10^4 [a]
$(mfa)_2CH^+BF_4^-$ (**8i**)	–3.85	7.32×10^3

[a] The k_2 values for **8h** deviates significantly from the linear correlations of lg k_2 with E and has not been used for the determination of N and s.

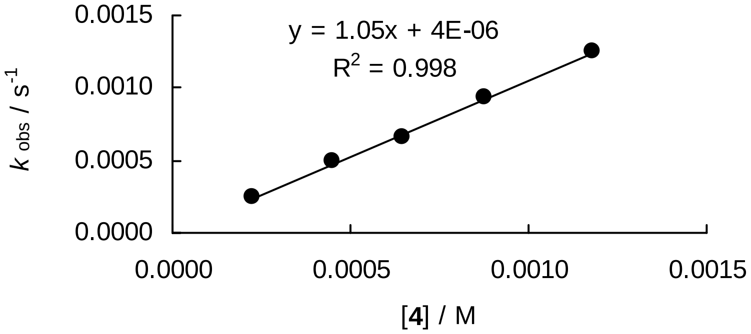


N = 8.01
s = 0.96

1.2 Determination of the Nucleophilicity Parameters of 1,2,5-Trimethylpyrrole (4)

Rate constants for the reactions of 1,2,5-trimethylpyrrole (**4**) with $(ind)_2CH^+BF_4^-$ (**8c**) in CH_3CN (20 °C, J&M, λ = 625 nm)

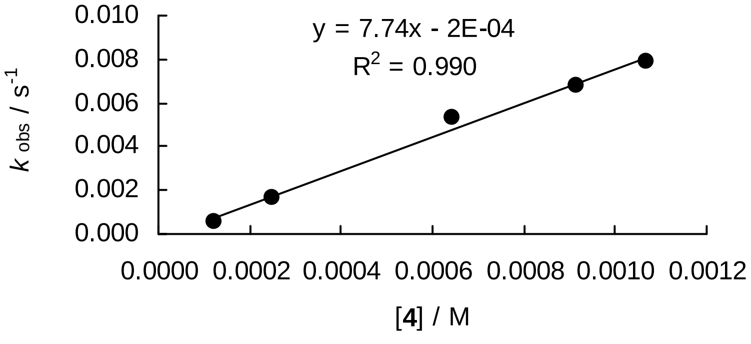
[**8c**]$_0$ / M	[**4**]$_0$ / M	[**4**]$_0$/[**8c**]$_0$	conv. / %	k_{obs} /s^{-1}
1.08×10^{-5}	2.23×10^{-4}	21	91	2.41×10^{-4}
1.10×10^{-5}	4.51×10^{-4}	41	92	4.92×10^{-4}
1.05×10^{-5}	6.48×10^{-4}	62	91	6.55×10^{-4}
1.11×10^{-5}	8.79×10^{-4}	79	82	9.30×10^{-4}
1.15×10^{-5}	1.18×10^{-3}	103	89	1.25×10^{-3}



k_2 = 1.05 M^{-1} s^{-1}

Rate constants for the reactions of 1,2,5-trimethylpyrrole (**4**) with $(pyr)_2CH^+BF_4^-$ (**8d**) in CH_3CN (20 °C, J&M, λ = 620 nm)

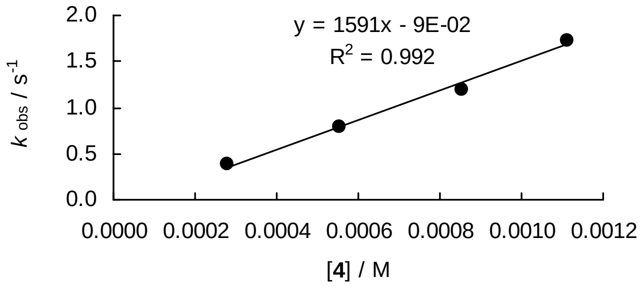
[**8d**]$_0$ / M	[**4**]$_0$ / M	[**4**]$_0$/[**8d**]$_0$	conv. / %	k_{obs} /s^{-1}
1.14×10^{-5}	1.22×10^{-4}	11	66	5.89×10^{-4}
1.17×10^{-5}	2.48×10^{-4}	21	81	1.65×10^{-3}
1.08×10^{-5}	6.44×10^{-4}	60	80	5.35×10^{-3}
1.13×10^{-5}	9.14×10^{-4}	81	92	6.82×10^{-3}
1.05×10^{-5}	1.07×10^{-3}	102	83	7.86×10^{-3}



k_2 = 7.74 M^{-1} s^{-1}

Rate constants for the reactions of 1,2,5-trimethylpyrrole (**4**) with $(mpa)_2CH^+BF_4^-$ (**8f**) in CH_3CN 20 °C, stopped-flow, λ = 622 nm)

[**8f**]$_0$ / M	[**4**]$_0$ / M	[**4**]$_0$/[**8f**]$_0$	k_{obs} /s^{-1}
1.39×10^{-5}	2.78×10^{-4}	20	3.77×10^{-1}
1.39×10^{-5}	5.56×10^{-4}	40	7.98×10^{-1}
1.39×10^{-5}	8.52×10^{-4}	61	1.20
1.39×10^{-5}	1.11×10^{-3}	80	1.73

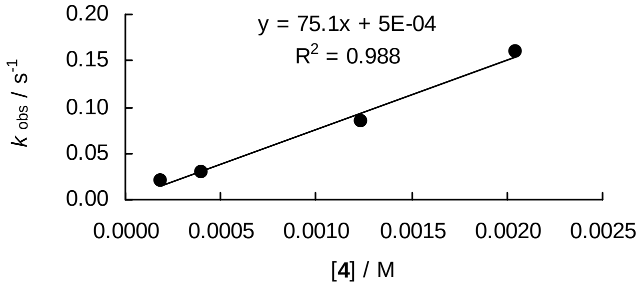


$k_2 = 1.59 \times 10^3$ M^{-1} s^{-1}

Rate constants for the reactions of 1,2,5-trimethylpyrrole (**4**) with $(mpa)_2CH^+BF_4^-$ (**8f**) in CH_2Cl_2 in presence of *N*-methyl morpholine (NMM) (20 °C, J&M, λ = 622 nm)

[**8f**]$_0$ / M	[**4**]$_0$ / M	[**4**]$_0$/[**8f**]$_0$	[NMM]$_0$ / M	k_{obs} /s^{-1}
1.88×10^{-5}	1.88×10^{-4}	10	2.23×10^{-5}	2.03×10^{-2} [a]
1.99×10^{-5}	3.98×10^{-4}	20	2.35×10^{-5}	2.86×10^{-2} [a]
2.06×10^{-5}	1.23×10^{-3}	60	2.43×10^{-5}	8.40×10^{-2} [a]
2.51×10^{-5}	2.01×10^{-3}	80	2.98×10^{-5}	1.71×10^{-1} [a]

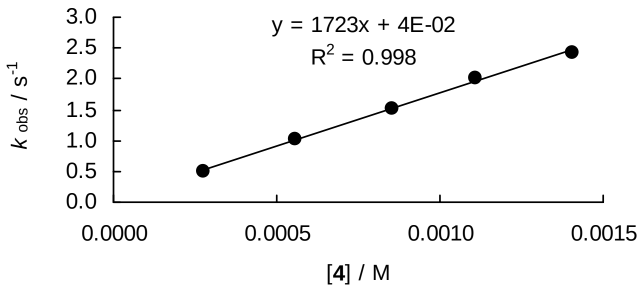
[a] Evaluation of the first half-life time



$k_2 = 1 \times 10^2$ M^{-1} s^{-1}

Rate constants for the reactions of 1,2,5-trimethylpyrrole (**4**) with $(mor)_2CH^+BF_4^-$ (**8g**) in CH_3CN (20 °C, stopped-flow, λ = 620 nm)

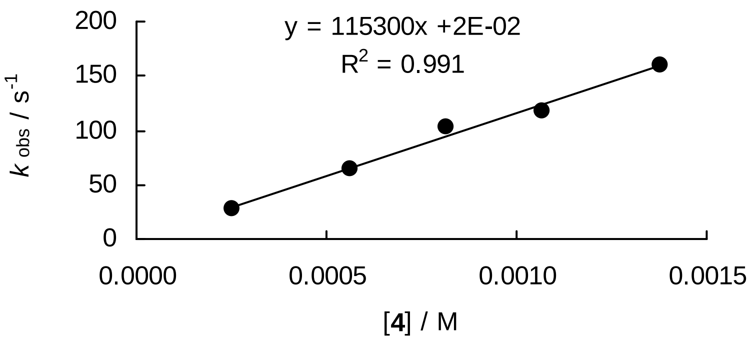
[**8g**]$_0$ / M	[**4**]$_0$ / M	[**4**]$_0$/[**8g**]$_0$	k_{obs} /s^{-1}
1.41×10^{-5}	2.78×10^{-4}	20	4.97×10^{-1}
1.41×10^{-5}	5.56×10^{-4}	39	1.02
1.41×10^{-5}	8.52×10^{-4}	60	1.51
1.41×10^{-5}	1.11×10^{-3}	79	2.01
1.41×10^{-5}	1.41×10^{-3}	100	2.43



$k_2 = 1.72 \times 10^3$ M^{-1} s^{-1}

Rate constants for the reactions of 1,2,5-trimethylpyrrole (**4**) with $(dpa)_2CH^+BF_4^-$ (**8h**) in CH_3CN (20 °C, stopped-flow, λ = 672 nm)

[**8h**]$_0$ / M	[**4**]$_0$ / M	[**4**]$_0$/[**8h**]$_0$	k_{obs} /s^{-1}
2.69×10^{-5}	2.51×10^{-4}	9	2.73×10^{1}
2.69×10^{-5}	5.64×10^{-4}	21	6.37×10^{1}
2.69×10^{-5}	8.15×10^{-4}	30	1.02×10^{2}
2.69×10^{-5}	1.07×10^{-3}	40	1.18×10^{2}
2.69×10^{-5}	1.38×10^{-3}	51	1.59×10^{2}

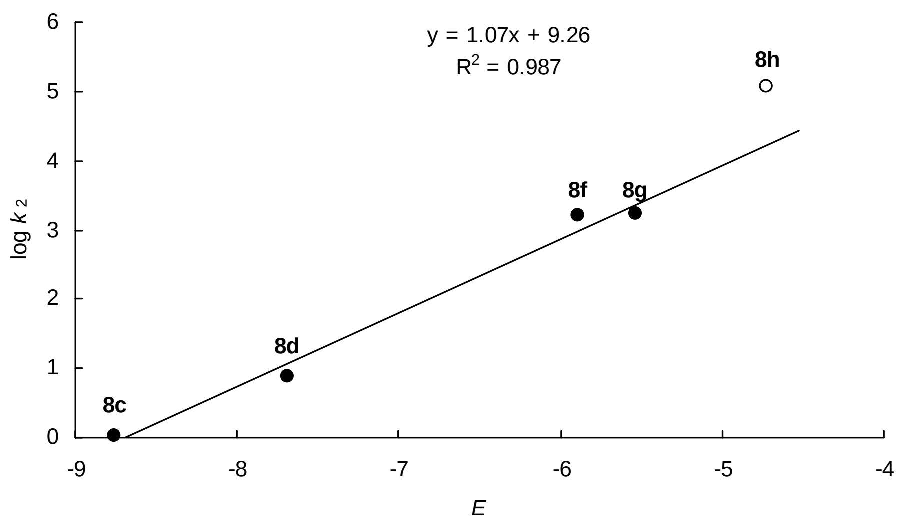


$k_2 = 1.15 \times 10^5$ M^{-1} s^{-1}

Nucleophilicity parameters of 1,2,5-trimethylpyrrole (**4**) in CH_3CN: N = 8.69, s = 1.07

Reference electrophile	E parameter	k_2(20 °C) / M^{-1} s^{-1}
$(ind)_2CH^+BF_4^-$ (**8c**)	–8.76	1.05
$(pyr)_2CH^+BF_4^-$ (**8d**)	–7.69	7.74
$(mpa)_2CH^+BF_4^-$ (**8f**)	–5.89	1.59×10^3
$(mor)_2CH^+BF_4^-$ (**8g**)	–5.53	1.72×10^3
$(dpa)_2CH^+BF_4^-$ (**8h**)	–4.72	1.15×10^5 [a]

[a] The k_2 values for **8h** deviates significantly from the linear correlations of lg k_2 with E and has not been used for the determination of N and s.

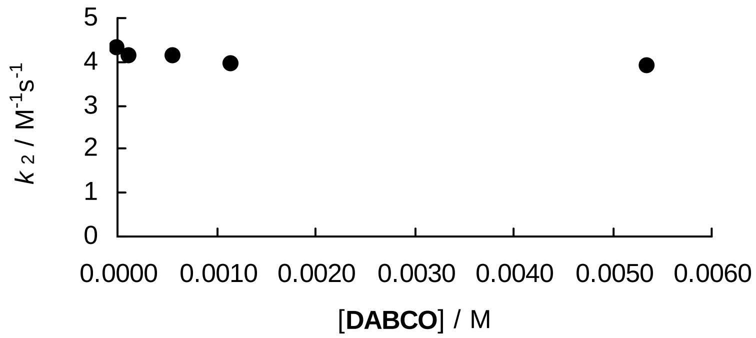


N = 8.69
s = 1.07

1.3 Determination of the Nucleophilicity Parameters of 2,4-Dimethylpyrrole (5)

Rate constants for the reactions of 2,4-dimethylpyrrole (**5**) with $(lil)_2CH^+BF_4^-$ (**8a**) in the presence of DABCO in CH_3CN (20 °C, J&M, λ = 639 nm)

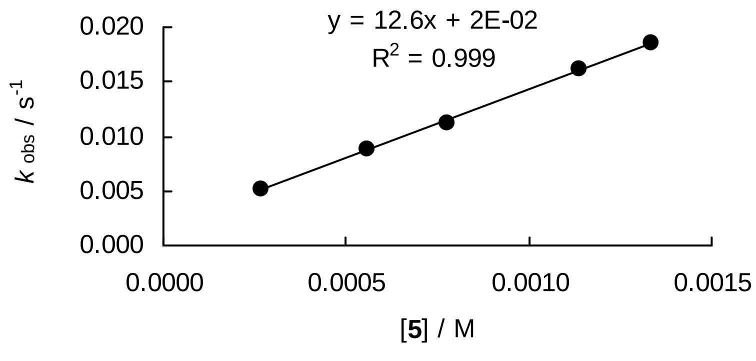
$[\mathbf{8a}]_0$ / M	$[\mathbf{5}]_0$ / M	$[DABCO]_0$ / M	$[DABCO]_0/[\mathbf{8a}]_0$	conv. / %	k_{obs} / s^{-1}	k_2 / $M^{-1}s^{-1}$
1.11×10^{-5}	7.72×10^{-4}	5.35×10^{-3}	483	89	3.01×10^{-2}	3.90
1.19×10^{-5}	8.30×10^{-4}	1.15×10^{-3}	97	88	3.28×10^{-2}	3.95
1.17×10^{-5}	8.14×10^{-4}	5.65×10^{-4}	48	89	3.35×10^{-2}	4.11
1.17×10^{-5}	8.16×10^{-4}	1.13×10^{-4}	10	84	3.38×10^{-2}	4.14
1.19×10^{-5}	8.26×10^{-4}	0	0	84	3.54×10^{-2}	4.29



k_2 = 4.29 M^{-1} s^{-1}

Rate constants for the reactions of 2,4-dimethylpyrrole (**5**) with $(jul)_2CH^+BF_4^-$ (**8b**) in CH_3CN (20 °C, J&M, λ = 642 nm)

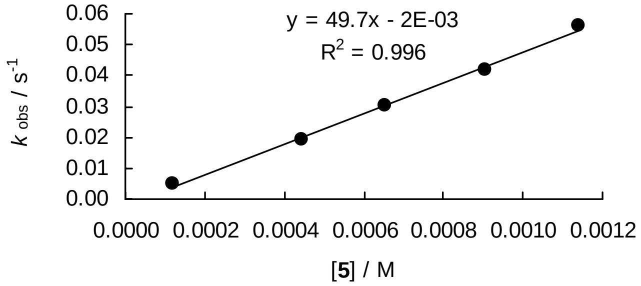
$[\mathbf{8b}]_0$ / M	$[\mathbf{5}]_0$ / M	$[\mathbf{5}]_0/[\mathbf{8b}]_0$	conv. / %	k_{obs} /s^{-1}
1.34×10^{-5}	2.68×10^{-4}	20	66	5.07×10^{-3}
1.40×10^{-5}	5.60×10^{-4}	40	76	8.85×10^{-3}
1.29×10^{-5}	7.77×10^{-4}	60	78	1.13×10^{-2}
1.42×10^{-5}	1.14×10^{-3}	80	82	1.62×10^{-2}
1.34×10^{-5}	1.34×10^{-3}	100	82	1.85×10^{-2}



$k_2 = 1.26 \times 10^1$ M^{-1} s^{-1}

Rate constants for the reactions of 2,4-dimethylpyrrole (**5**) with $(ind)_2CH^+BF_4^-$ (**8c**) in CH_3CN (20 °C, J&M, λ = 625 nm)

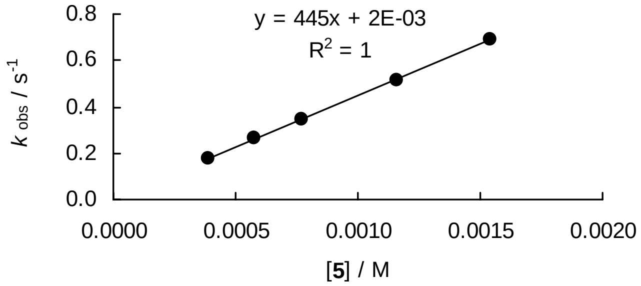
[**8c**]$_0$ / M	[**5**]$_0$ / M	[**5**]$_0$/[**8c**]$_0$	conv. / %	k_{obs} /s^{-1}
1.28×10^{-5}	1.20×10^{-4}	9	89	5.05×10^{-3}
1.36×10^{-5}	4.42×10^{-4}	33	90	1.91×10^{-2}
1.28×10^{-5}	6.55×10^{-4}	51	92	3.01×10^{-2}
1.30×10^{-5}	9.06×10^{-4}	70	91	4.18×10^{-2}
1.22×10^{-5}	1.14×10^{-3}	93	87	5.62×10^{-2}



$k_2 = 4.97 \times 10^1$ M^{-1} s^{-1}

Rate constants for the reactions of 2,4-dimethylpyrrole (**5**) with $(pyr)_2CH^+BF_4^-$ (**8d**) in CH_3CN (20 °C, stopped-flow, λ = 620 nm)

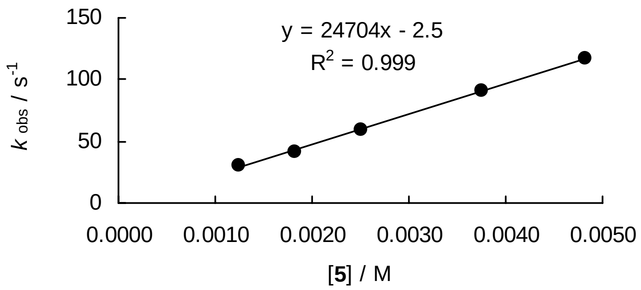
[**8d**]$_0$ / M	[**5**]$_0$ / M	[**5**]$_0$/[**8d**]$_0$	conv. / %	k_{obs} /s^{-1}
1.55×10^{-5}	3.86×10^{-4}	25	85	1.73×10^{-1}
1.55×10^{-5}	5.79×10^{-4}	38	72	2.63×10^{-1}
1.55×10^{-5}	7.72×10^{-4}	50	86	3.43×10^{-1}
1.55×10^{-5}	1.16×10^{-3}	75	87	5.15×10^{-1}
1.55×10^{-5}	1.54×10^{-3}	100	87	6.89×10^{-1}



$k_2 = 4.45 \times 10^2$ M^{-1} s^{-1}

Rate constants for the reactions of 2,4-dimethylpyrrole (**5**) with $(mpa)_2CH^+BF_4^-$ (**8f**) in CH_3CN (20 °C, stopped-flow, λ = 622 nm)

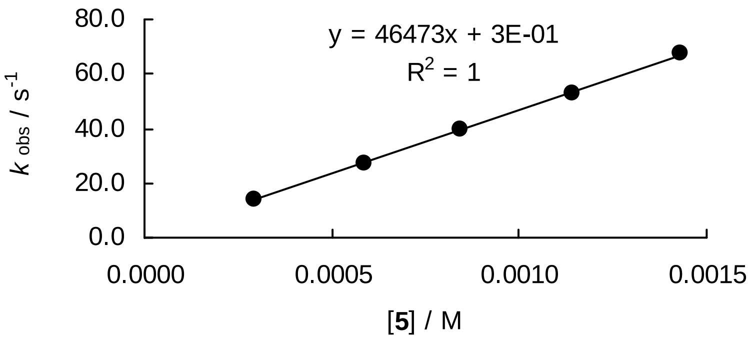
[**8f**]$_0$ / M	[**5**]$_0$ / M	[**5**]$_0$/[**8f**]$_0$	k_{obs} /s^{-1}
2.50×10^{-5}	1.25×10^{-3}	50	2.97×10^1
2.50×10^{-5}	1.83×10^{-3}	73	4.14×10^1
2.50×10^{-5}	2.51×10^{-3}	100	5.92×10^1
2.50×10^{-5}	3.76×10^{-3}	150	9.02×10^1
2.50×10^{-5}	4.82×10^{-3}	193	1.17×10^2



$k_2 = 2.47 \times 10^4$ M^{-1} s^{-1}

Rate constants for the reactions of 2,4-dimethylpyrrole (**5**) with $(mor)_2CH^+BF_4^-$ (**8g**) in CH_3CN (20 °C, stopped-flow, λ = 620 nm)

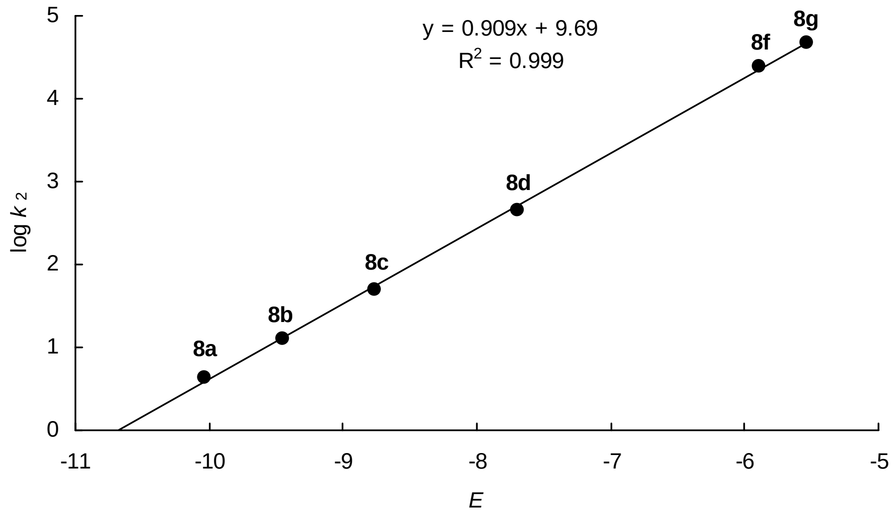
$[\mathbf{8g}]_0$ / M	$[\mathbf{5}]_0$ / M	$[\mathbf{5}]_0/[\mathbf{8g}]_0$	k_{obs} /s^{-1}
1.41×10^{-5}	2.94×10^{-4}	21	1.42×10^{1}
1.41×10^{-5}	5.89×10^{-4}	42	2.74×10^{1}
1.41×10^{-5}	8.41×10^{-4}	59	3.95×10^{1}
1.41×10^{-5}	1.14×10^{-3}	80	5.26×10^{1}
1.41×10^{-5}	1.43×10^{-3}	101	6.72×10^{1}



$k_2 = 4.65 \times 10^4$ M^{-1} s^{-1}

Nucleophilicity parameters of 2,4-dimethylpyrrole (**5**) in CH_3CN: N = 10.67, s = 0.91

Reference electrophile	E parameter	k_2(20 °C) / M^{-1} s^{-1}
$(lil)_2CH^+BF_4^-$ (**8a**)	–10.04	4.29
$(jul)_2CH^+BF_4^-$ (**8b**)	–9.45	1.26×10^{1}
$(ind)_2CH^+BF_4^-$ (**8c**)	–8.76	4.97×10^{1}
$(pyr)_2CH^+BF_4^-$ (**8d**)	–7.69	4.45×10^{2}
$(mpa)_2CH^+BF_4^-$ (**8f**)	–5.89	2.47×10^{4}
$(mor)_2CH^+BF_4^-$ (**8g**)	–5.53	4.65×10^{4}

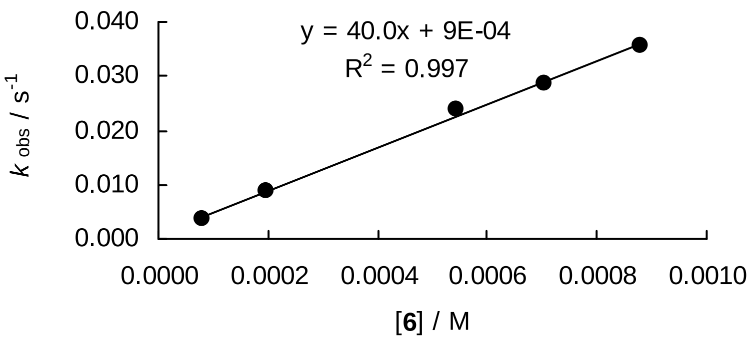


N = 10.67
s = 0.91

1.4 Determination of the Nucleophilicity Parameters of 3-Ethyl-2,4-dimethylpyrrole (6)

Rate constants for the reactions of 3-ethyl-2,4-dimethylpyrrole (**6**) with $(lil)_2CH^+BF_4^-$ (**8a**) in CH_3CN (20 °C, J&M, λ = 639 nm)

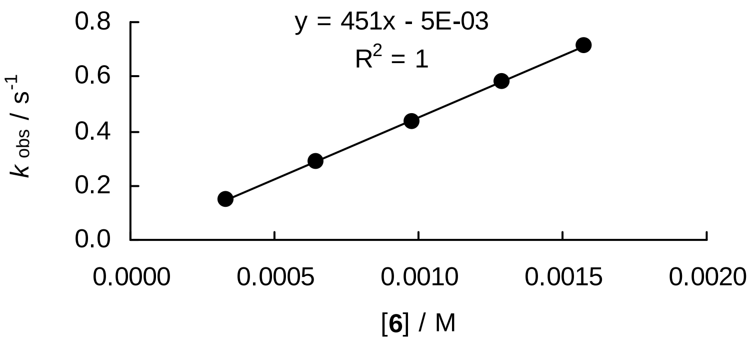
[**8a**]$_0$ / M	[**6**]$_0$ / M	[**6**]$_0$/[**8a**]$_0$	conv. / %	k_{obs} /s^{-1}
9.29×10^{-6}	8.03×10^{-5}	9	77	3.64×10^{-3}
9.18×10^{-6}	1.98×10^{-4}	22	88	8.90×10^{-3}
8.96×10^{-6}	5.42×10^{-4}	61	87	2.38×10^{-2}
9.04×10^{-6}	7.03×10^{-4}	78	92	2.88×10^{-2}
8.84×10^{-6}	8.79×10^{-4}	100	91	3.56×10^{-2}



$k_2 = 4.00 \times 10^1$ M^{-1} s^{-1}

Rate constants for the reactions of 3-ethyl-2,4-dimethylpyrrole (**6**) with $(ind)_2CH^+BF_4^-$ (**8c**) in CH_3CN (20 °C, stopped-flow, λ = 625 nm)

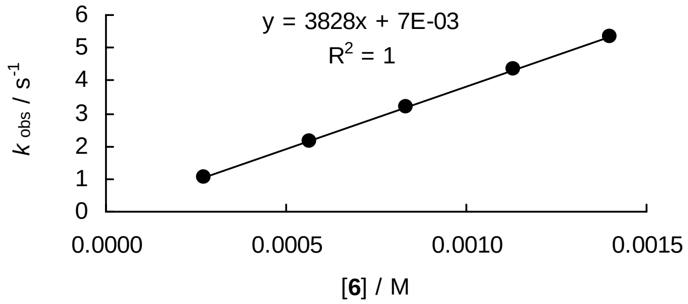
[**8c**]$_0$ / M	[**6**]$_0$ / M	[**6**]$_0$/[**8c**]$_0$	k_{obs} /s^{-1}
1.62×10^{-5}	3.32×10^{-4}	20	1.48×10^{-1}
1.62×10^{-5}	6.47×10^{-4}	40	2.85×10^{-1}
1.62×10^{-5}	9.79×10^{-4}	60	4.35×10^{-1}
1.62×10^{-5}	1.30×10^{-3}	80	5.81×10^{-1}
1.62×10^{-5}	1.58×10^{-3}	97	7.11×10^{-1}



$k_2 = 4.51 \times 10^2$ M^{-1} s^{-1}

Rate constants for the reactions of 3-ethyl-2,4-dimethylpyrrole (**6**) with $(pyr)_2CH^+BF_4^-$ (**8d**) in CH_3CN (20 °C, stopped-flow, λ = 620 nm)

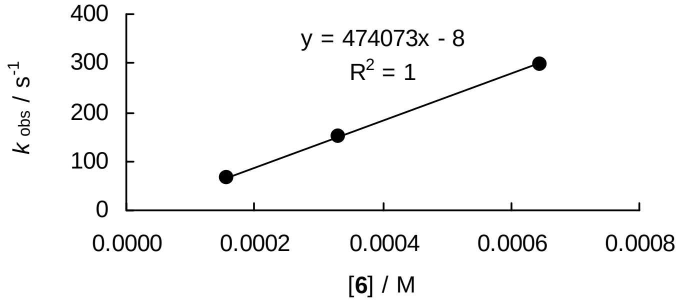
[**8d**]$_0$ / M	[**6**]$_0$ / M	[**6**]$_0$/[**8d**]$_0$	k_{obs} /s^{-1}
1.51×10^{-5}	2.71×10^{-4}	18	1.05
1.51×10^{-5}	5.64×10^{-4}	37	2.15
1.51×10^{-5}	8.35×10^{-4}	55	3.21
1.51×10^{-5}	1.13×10^{-3}	75	4.34
1.51×10^{-5}	1.40×10^{-3}	92	5.36



$k_2 = 3.83 \times 10^3$ M^{-1} s^{-1}

Rate constants for the reactions of 3-ethyl-2,4-dimethylpyrrole (**6**) with $(mpa)_2CH^+BF_4^-$ (**8f**) in CH_3CN (20 °C, stopped-flow, λ = 625 nm)

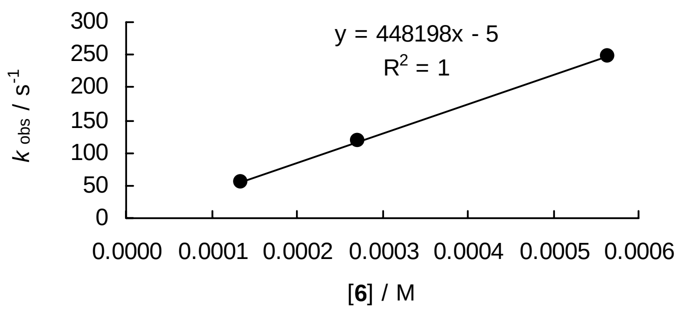
[**8f**]$_0$ / M	[**6**]$_0$ / M	[**6**]$_0$/[**8f**]$_0$	k_{obs} /s^{-1}
1.63×10^{-5}	1.58×10^{-4}	10	6.70×10^1
1.63×10^{-5}	3.32×10^{-4}	20	1.50×10^2
1.63×10^{-5}	6.47×10^{-4}	40	2.99×10^2



$k_2 = 4.74 \times 10^5$ M^{-1} s^{-1}

Rate constants for the reactions of 3-ethyl-2,4-dimethylpyrrole (**6**) with $(mor)_2CH^+BF_4^-$ (**8g**) in CH_3CN (20 °C, stopped-flow, λ = 620 nm)

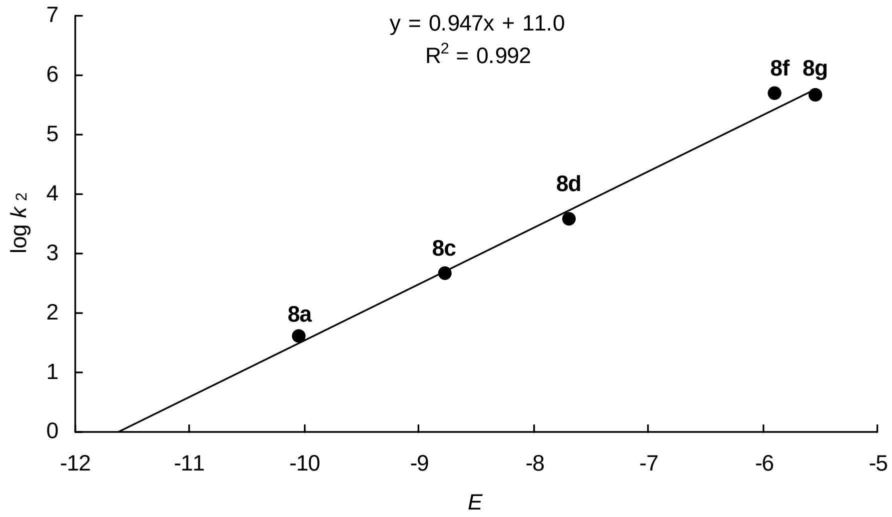
[**8g**]$_0$ / M	[**3**]$_0$ / M	[**3**]$_0$/[**8g**]$_0$	k_{obs} /s^{-1}
1.34×10^{-5}	1.35×10^{-4}	10	5.38×10^1
1.34×10^{-5}	2.71×10^{-4}	20	1.19×10^2
1.34×10^{-5}	5.64×10^{-4}	42	2.47×10^2



$k_2 = 4.48 \times 10^5$ M^{-1} s^{-1}

Nucleophilicity parameters of 3-ethyl-2,4-dimethylpyrrole (**6**) in CH_3CN: $N = 11.63$, $s = 0.95$

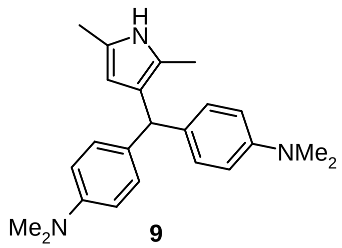
Reference electrophile	*E* parameter	k_2(20 °C) / M^{-1} s^{-1}
$(lil)_2CH^+BF_4^-$ (**8a**)	–10.04	4.00×10^1
$(ind)_2CH^+BF_4^-$ (**8c**)	–8.76	4.51×10^2
$(pyr)_2CH^+BF_4^-$ (**8d**)	–7.69	3.83×10^3
$(mpa)_2CH^+BF_4^-$ (**8f**)	–5.89	4.74×10^5
$(mor)_2CH^+BF_4^-$ (**8g**)	–5.53	4.48×10^5



$N = 11.63$
$s = 0.95$

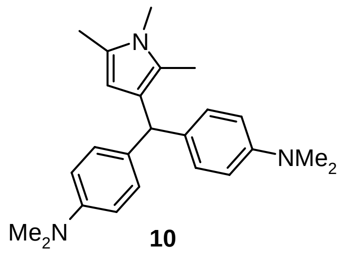
2 PRODUCT STUDIES

2,5-Dimethyl-3-[bis-(4-dimethylaminophenyl)methyl]-1H-pyrrole (**9**). 2,5-Dimethylpyrrole (**3**, 83 μL, 0.82 mmol) was dissolved in CH_3CN (20 mL) and cooled to –15 °C. The benzhydrylium tetrafluoroborate **8e**-BF_4 (0.14 g, 0.40 mmol) dissolved in CH_3CN (100 mL) was dropped to the vigorously stirred solution over 3 h, allowing the reaction mixture to decolorize after each drop. The brownish solution was then washed with ice water (50 mL) containing saturated NaCl solution (1 mL) and the phases were separated at low temperature (homogenization upon warm-up). The organic phase was dried (Na_2SO_4), filtered and the volatile components were evaporated in the vacuum (60 °C, 1 mbar for 1 h): **9** (90 mg, 0.26 mmol, 65%), light brown solid which turned within minutes into a pink oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 3 H, 2-Me), 2.14 (s, 3 H, 5-Me), 2.93 (s, 12 H, 2 × NMe_2), 5.13 (s, 1 H, 3-$CHAr_2$), 5.45 (s, 1 H, 4-H), 6.84 (d, J = 8 Hz, 4 H, Ar), 7.09 (d, J = 8 Hz, 4 H, Ar), 7.58 ppm (br. s, 1 H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 9.5 (q), 11.2 (q), 40.2 (q), 45.1 (d), 105.2 (d), 112.4 (d), 120.0 (s), 120.1 (s), 122.8 (s), 127.9 (d), 135.3 (s), 145.2 ppm (s). MS (EI, 70 eV), *m/z* (%): 348 (21), 347 (100) [M$^+$], 346 (39), 333 (17), 332 (52), 253 (17), 228 (16), 227 (71), 225 (43), 211 (15); HR-MS (EI): calcd. for $C_{23}H_{29}N_3$: 347.2361, found 347.2352.



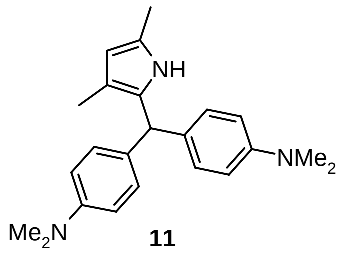
9

1,2,5-Trimethyl-3-[bis-(4-dimethylaminophenyl)methyl]-1H-pyrrole (**10**). 1,2,5-Trimethylpyrrole (**4**, 95 μL, 0.80 mmol) was dissolved in CH_3CN (20 mL) and cooled to –15 °C. The benzhydrylium tetrafluoroborate **8e**-BF_4 (0.14 g, 0.40 mmol) dissolved in CH_3CN (100 mL) was dropped to the vigorously stirred solution over 1 h, allowing the reaction mixture to decolorize after each drop. The solution was then washed with ice-water (50 mL) containing saturated NaCl solution (1 mL) and the phases were separated at low temperature. The organic phase was dried (Na_2SO_4), filtered and the volatile components were evaporated in the vacuum (60 °C, 1 mbar for 1 h): **10** (98 mg, 0.27 mmol, 68%), light ochre solid which turned within minutes into a pink oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.03 (s, 3 H, 2-Me), 2.13 (s, 3 H, 5-Me), 2.95 (s, 12 H, 2 × NMe_2), 3.34 (s, 3 H, NMe), 5.16 (s, 1 H, 3-$CHAr_2$), 5.44 (s, 1 H, 4-H), 6.79 (d, J = 7 Hz, 4 H, Ar), 7.08 ppm (d, J = 7 Hz, 4 H, Ar). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 8.5 (q), 10.7 (q), 28.3 (q), 40.2 (q), 45.3 (d), 104.3 (d), 112.1 (d), 119.2 (s), 121.9 (s), 124.4 (s), 127.9 (d), 135.2 (s), 145.3 ppm (s). MS (EI, *m/z* (%) = 361 (42) [M$^+$], 360 (15), 346 (39), 255 (20), 254 (100), 253 (85), 241 (48), 240 (19), 239 (33), 237 (22), 210 (34), 134 (56), 127 (20), 126 (32), 118 (22), 109 (34), 108 (50); HR-MS (EI): calcd. for $C_{24}H_{31}N_3$: 361.2518, found 361.2516.



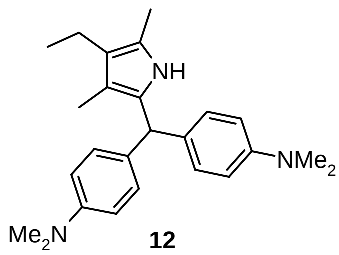
10

3,5-Dimethyl-2-[bis-(4-dimethylaminophenyl)methyl]-1H-pyrrole (**11**). 2,4-Dimethylpyrrole (**5**, 82 μL, 0.80 mmol) was dissolved in CH_3CN (20 mL) and cooled to –15 °C. The benzhydrylium tetrafluoroborate **8e**-BF_4 (0.14 g, 0.40 mmol) dissolved in CH_3CN (100 mL) was added in small portions to the vigorously stirred solution within 15 min, allowing the reaction mixture to decolorize after each drop. The solution was then washed with ice-water (50 mL) containing saturated NaCl solution (1 mL) and the phases were separated at low temperature. The organic phase was dried (Na_2SO_4), filtered and the volatile components were evaporated in the vacuum (60 °C, 1 mbar for 1 h): **11** (104 mg, 0.30 mmol, 75%) almost colourless residue which turned within minutes into a pink oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.85 (s, 3 H, 3-Me), 2.13 (s, 3 H, 5-Me), 2.94 (s, 12 H, 2 × NMe_2), 5.33 (s, 1 H, 3-$CHAr_2$), 5.70 (s, 1 H, 4-H), 6.73 (d, J = 8 Hz, 4 H, Ar), 7.00 (d, J = 8 Hz, 4 H, Ar), 7.11 ppm (br. s, 1 H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 11.1 (q), 13.0 (q), 41.2 (q), 46.5 (d), 108.2 (d), 113.2 (d), 114.5 (s), 124.9 (s), 128.1 (s), 129.5 (d), 132.9 (s), 148.4 ppm (s). MS (EI, 70 eV), *m/z* (%) = 347 (9) [M^+], 255 (20), 254 (100), 253 (92), 240 (17), 239 (19), 237 (24), 211 (13), 210 (39), 134 (38), 126 (16), 120 (18), 118 (23); HR-MS (EI): calcd. for $C_{23}H_{29}N_3$: 347.2361, found 347.2347.



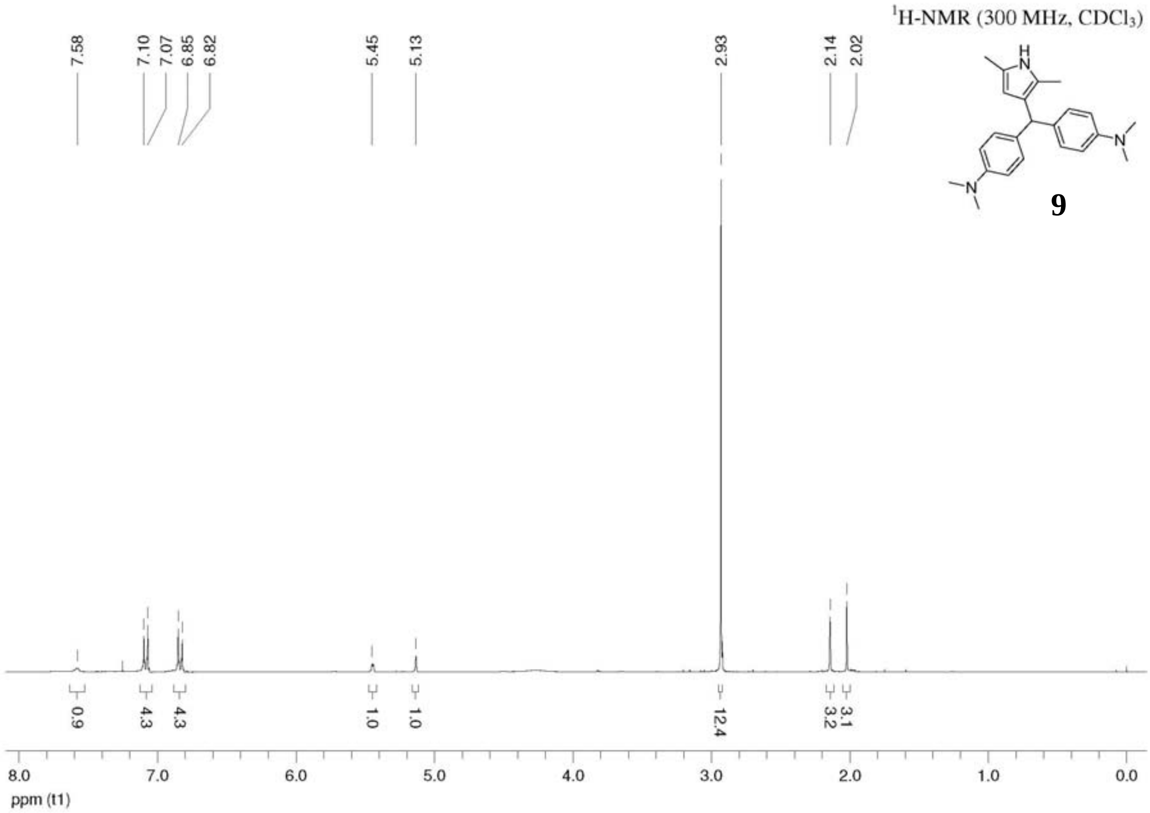
11

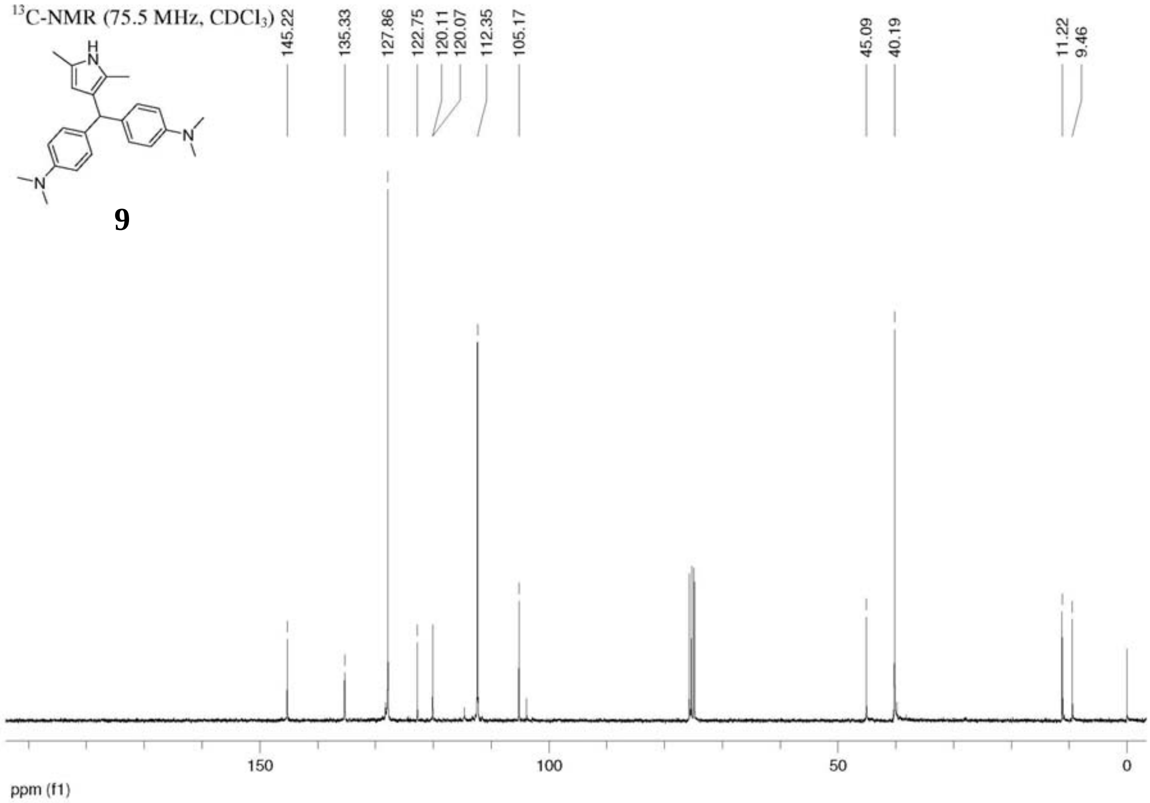
2,5-Dimethyl-3-[bis-(4-dimethylaminophenyl)methyl]-4-ethyl-1H-pyrrole (**12**). The benzhydrylium tetrafluoroborate **8e**-BF_4 (0.14 g, 0.40 mmol) was dissolved in CH_3CN (50 mL), cooled down to –15 °C and a solution of 3-ethyl-2,4-dimethylpyrrole (**6**, 0.10 mL, 0.74 mmol) in CH_3CN (20 mL) was allowed to drop to the blue reaction mixture. After the addition of 11.4 mL, the blue color faded and a slightly brown clear solution was obtained (0.42 mmol of **6** have been used). The solution was then washed with ice water (50 mL) containing saturated NaCl solution (1 mL) and the phases were separated at low temperature. The organic phase was dried (Na_2SO_4), filtered and the volatile components were evaporated in the vacuum: **12** (0.12 g, 0.31 mmol, 78%), colourless oil which turned within minutes into a pink oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.05 (t, J = 9 Hz, 3 H, CH_2CH_3), 1.79 (s, 3 H, 3-Me), 2.07 (s, 3 H, 5-Me), 2.36 (q, J = 9 Hz, 2 H, CH_2CH_3), 2.99 (s, 12 H, 2 × NMe_2), 5.20 (br. s, 1 H, NH), 5.36 (s, 1 H, 3-$CHAr_2$), 6.93 (d, J = 8 Hz, 4 H, Ar), 7.04 ppm (d, J = 8 Hz, 4 H, Ar). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 7.5 (q), 9.3 (q), 13.9 (q), 15.9 (t), 40.5 (q), 45.2 (d), 111.8 (s), 113.1 (d), 119.0 (s), 119.2 (s), 124.1 (s), 128.0 (d), 133.8 (s), 144.9 ppm (s). MS (EI, 70 eV), *m/z* (%) = 375 (26) [M^+], 360 (20), 256 (16), 255 (42), 253 (100), 252 (93), 241 (27), 240 (21), 239 (30), 237 (21), 212 (18), 210 (34), 164 (25), 150 (17), 136 (17), 134 (33), 126 (17), 120 (17), 118 (16), 108 (27); HR-MS (EI): calcd. for $C_{25}H_{33}N_3$: 375.2674, found 375.2669.



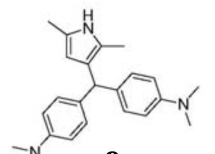
12

3 ^{1}H AND ^{13}C NMR SPECTRA OF 9–12

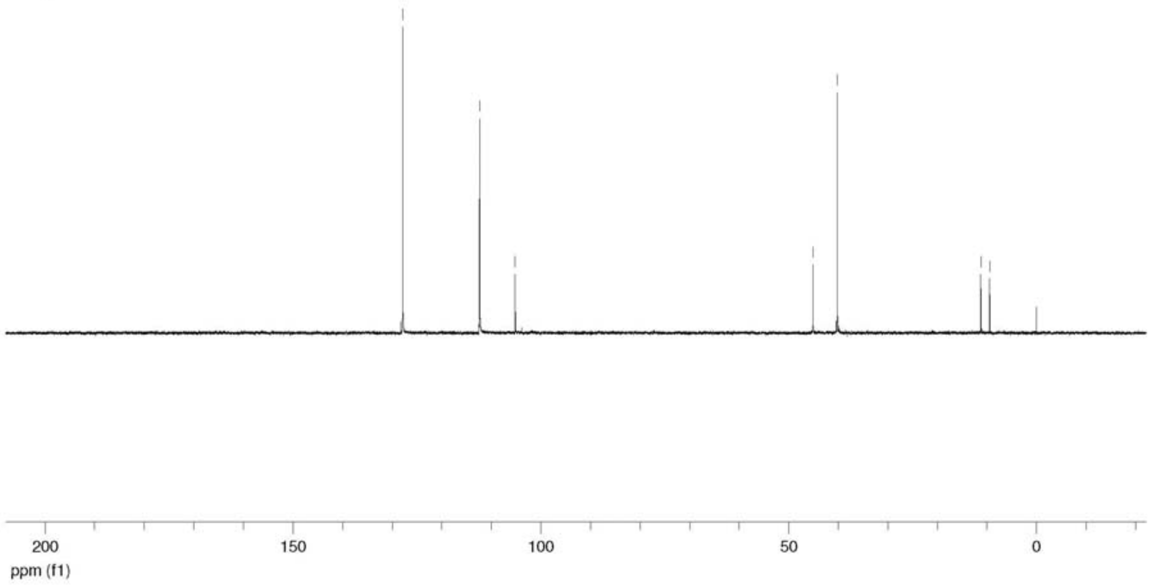




DEPT (75.5 MHz, $CDCl_3$)

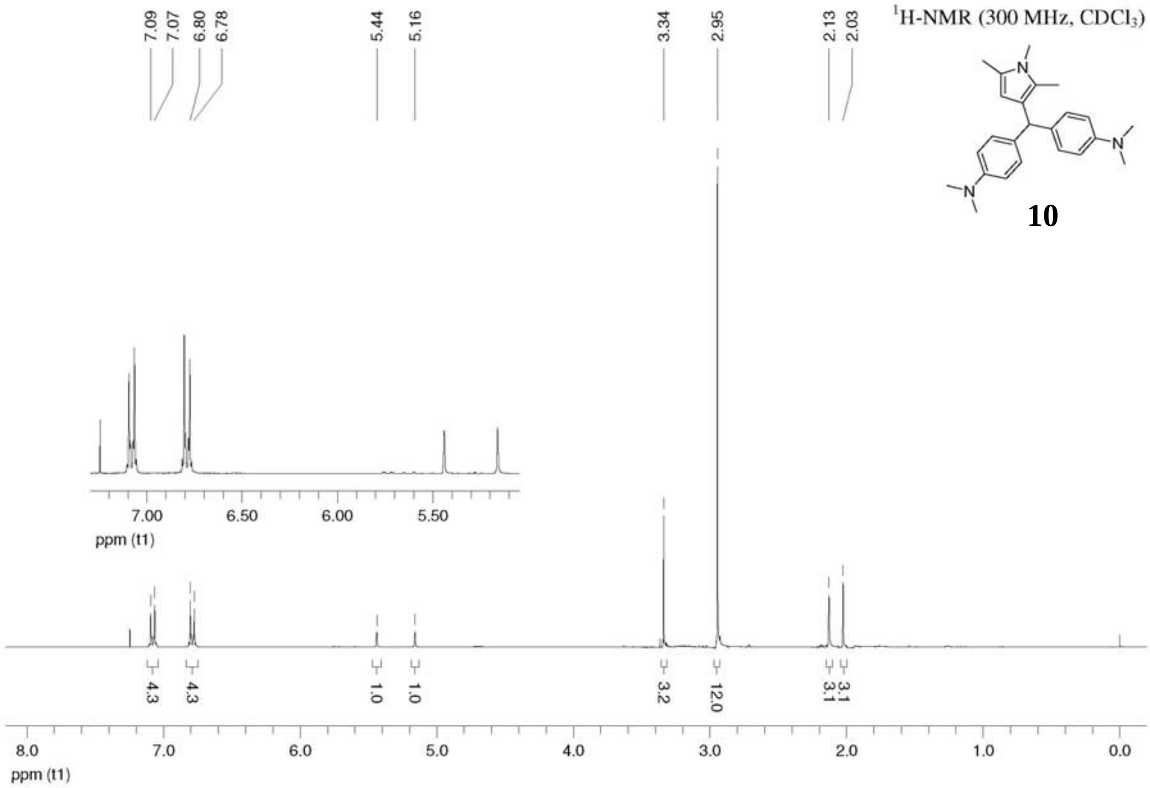


9



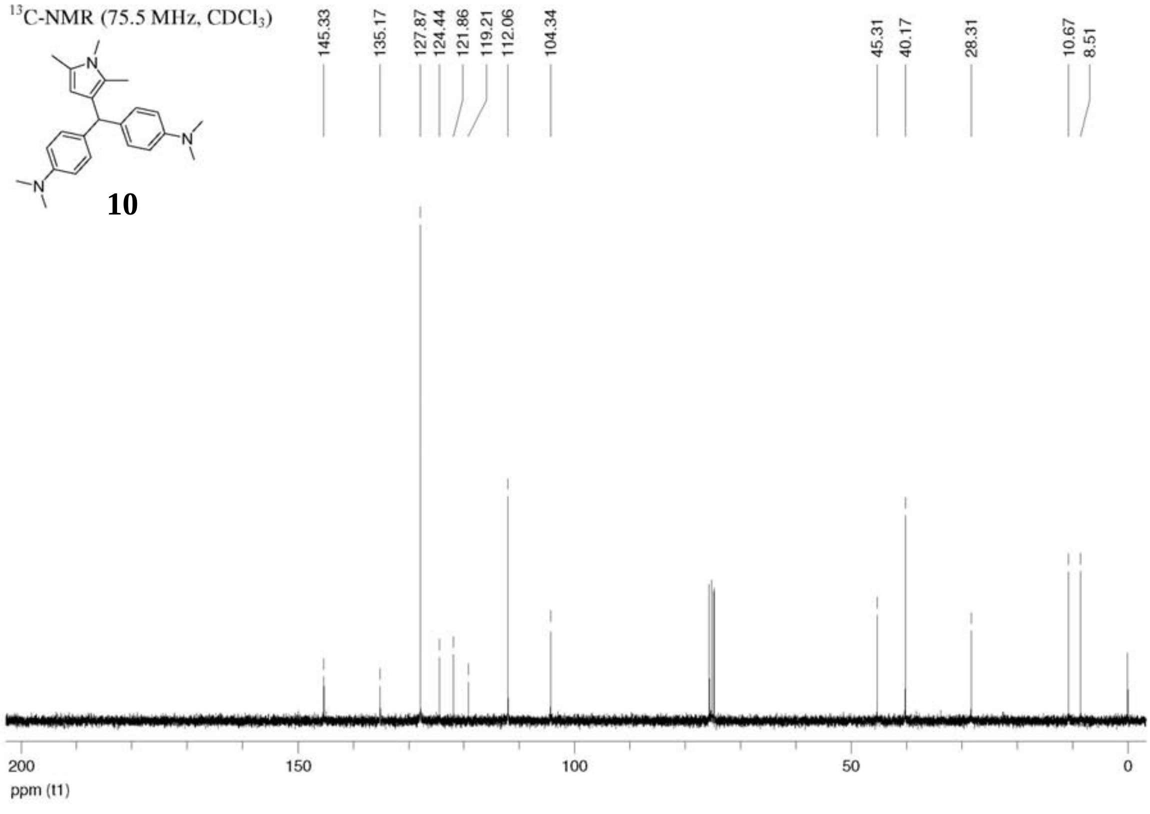
[1]H-NMR (300 MHz, $CDCl_3$)

10

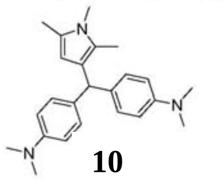


[13]C-NMR (75.5 MHz, $CDCl_3$)

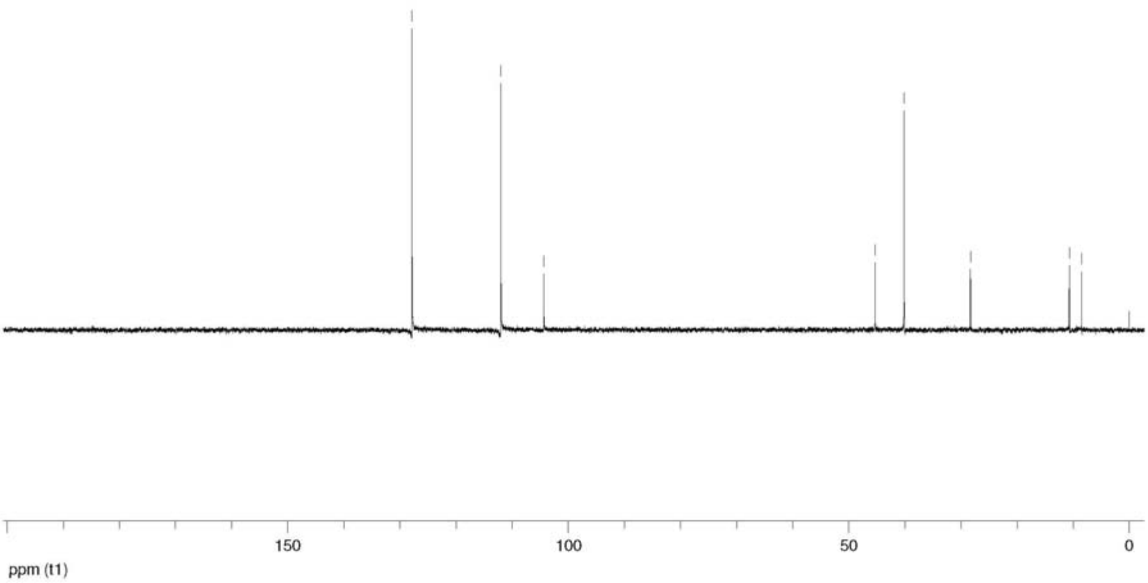
10



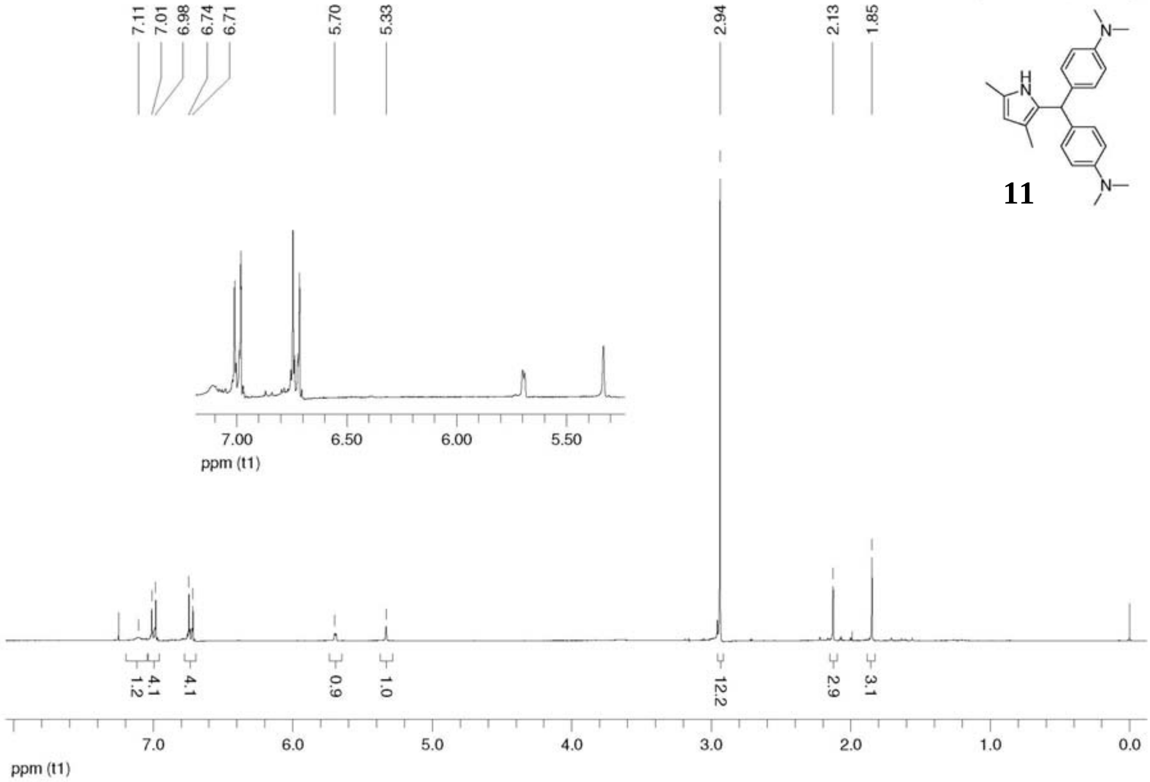
DEPT (75.5 MHz, $CDCl_3$)



10

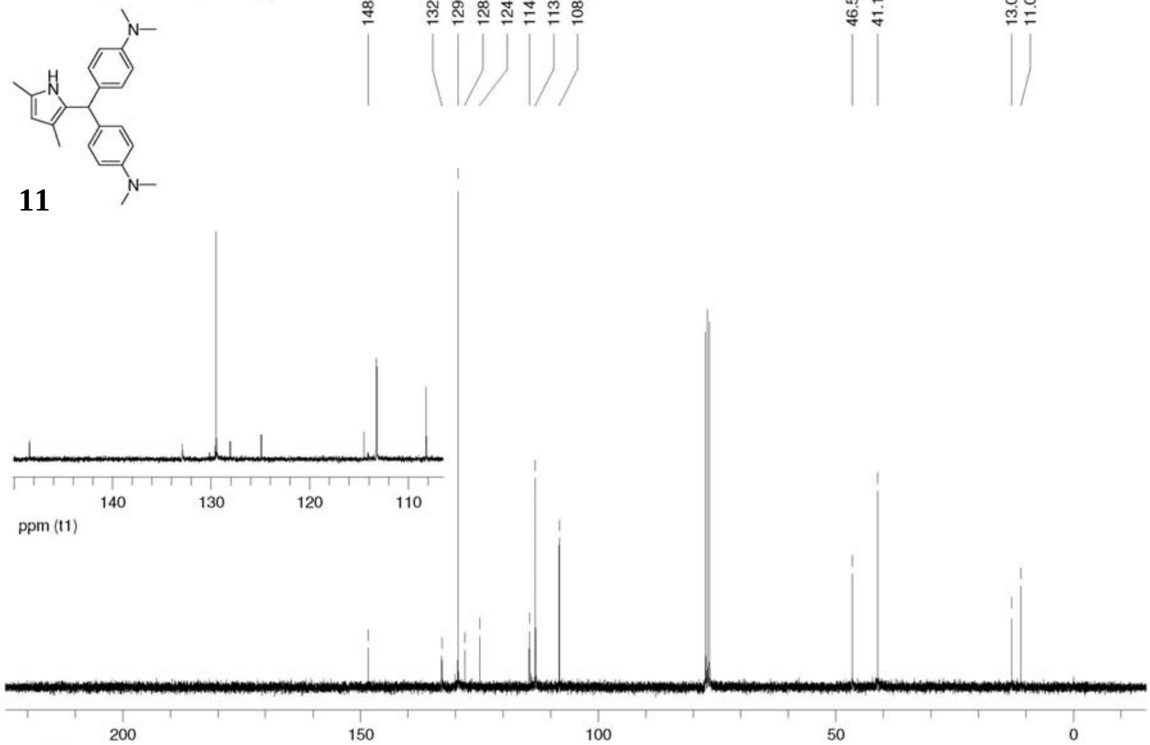


[1]H-NMR (300 MHz, $CDCl_3$)



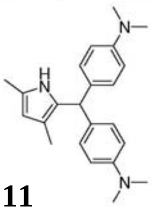
11

[13]C-NMR (75.5 MHz, $CDCl_3$)

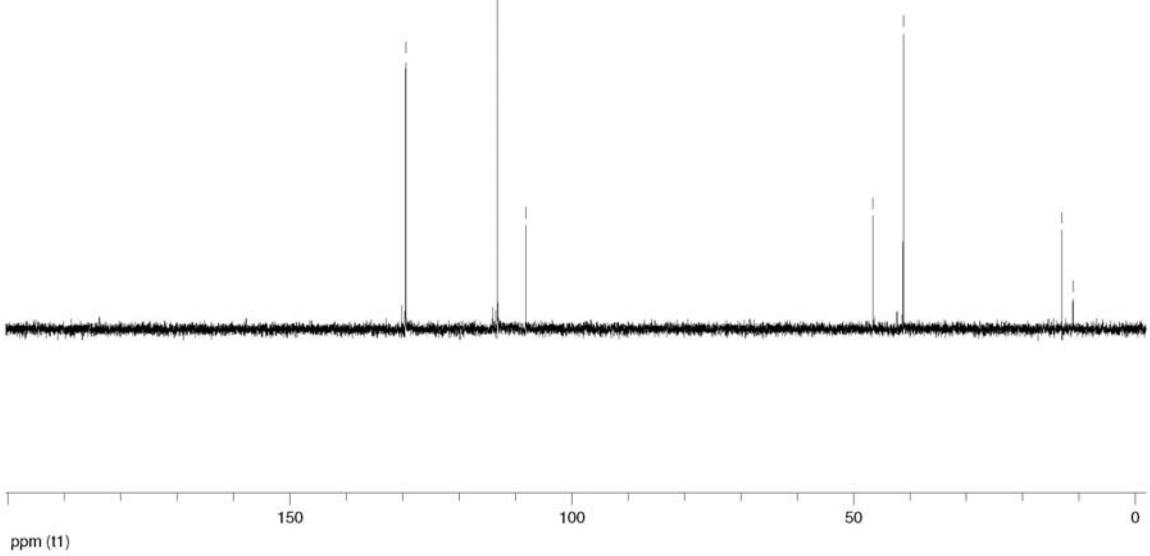


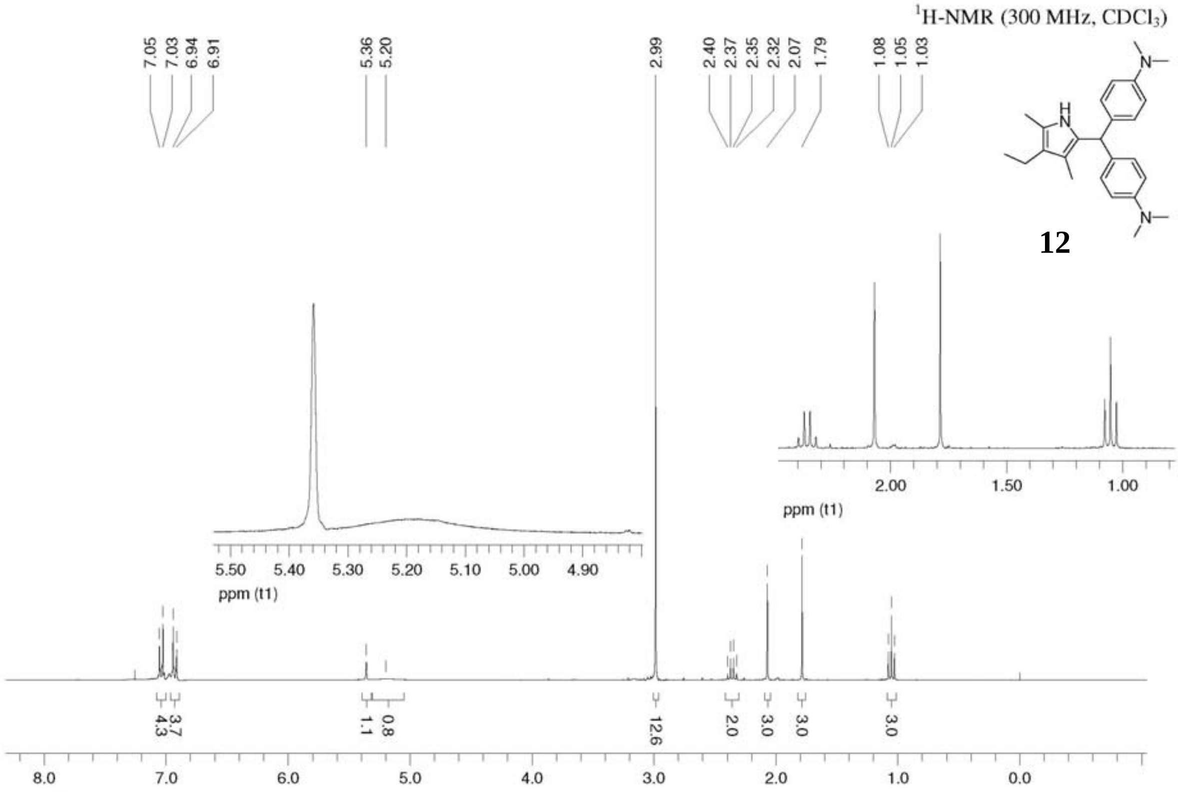
11

DEPT (75.5 MHz, $CDCl_3$)

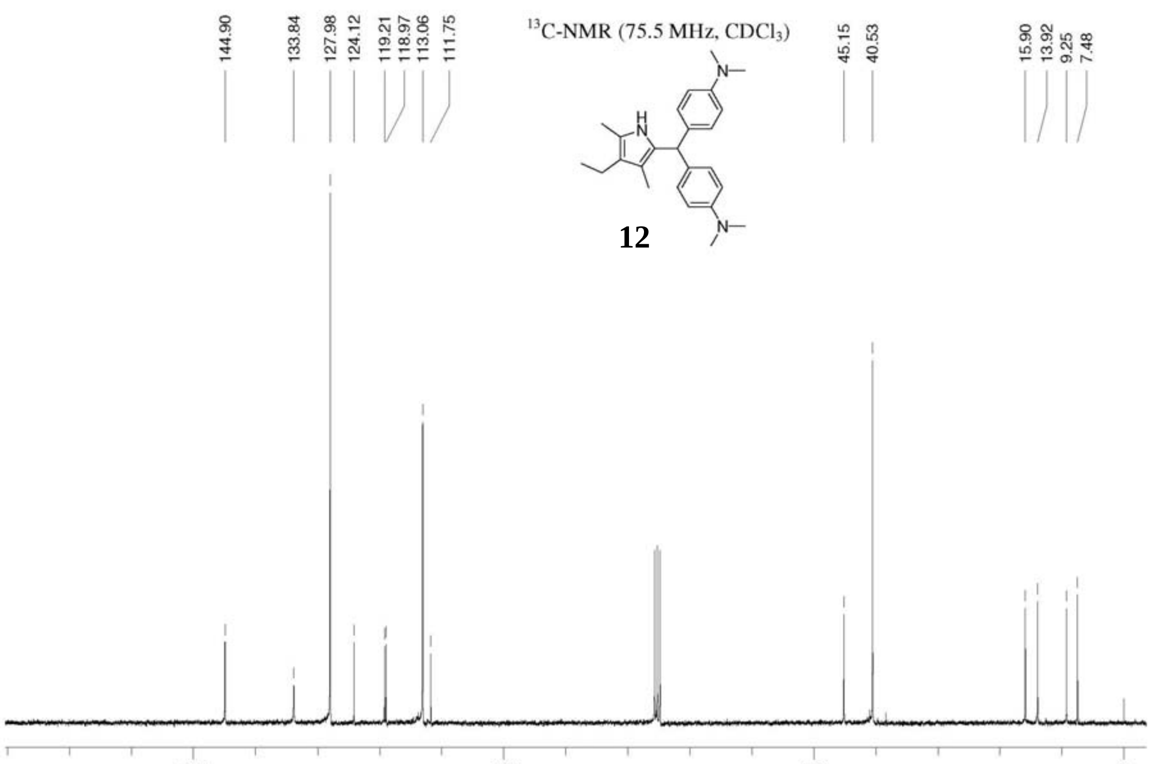


11



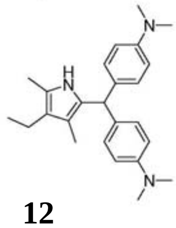


1H-NMR (300 MHz, CDCl3)
7.05
7.03
6.94
6.91
5.36
5.20
2.99
2.40
2.37
2.35
2.32
2.07
1.79
1.08
1.05
1.03
12
5.50 5.40 5.30 5.20 5.10 5.00 4.90
ppm (t1)
2.00 1.50 1.00
ppm (t1)
4.3 3.7 1.1 0.8 12.6 2.0 3.0 3.0 3.0
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)



13C-NMR (75.5 MHz, CDCl3)
144.90
133.84
127.98
124.12
119.21
118.97
113.06
111.75
45.15
40.53
15.90
13.92
9.25
7.48
12
150 100 50 0
ppm (f1)

DEPT (75.5 MHz, $CDCl_3$)



12