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Supporting information for: The Quest for Determining One-Electron Redox Potentials of Azulene-1-Carbonitriles by Calculation

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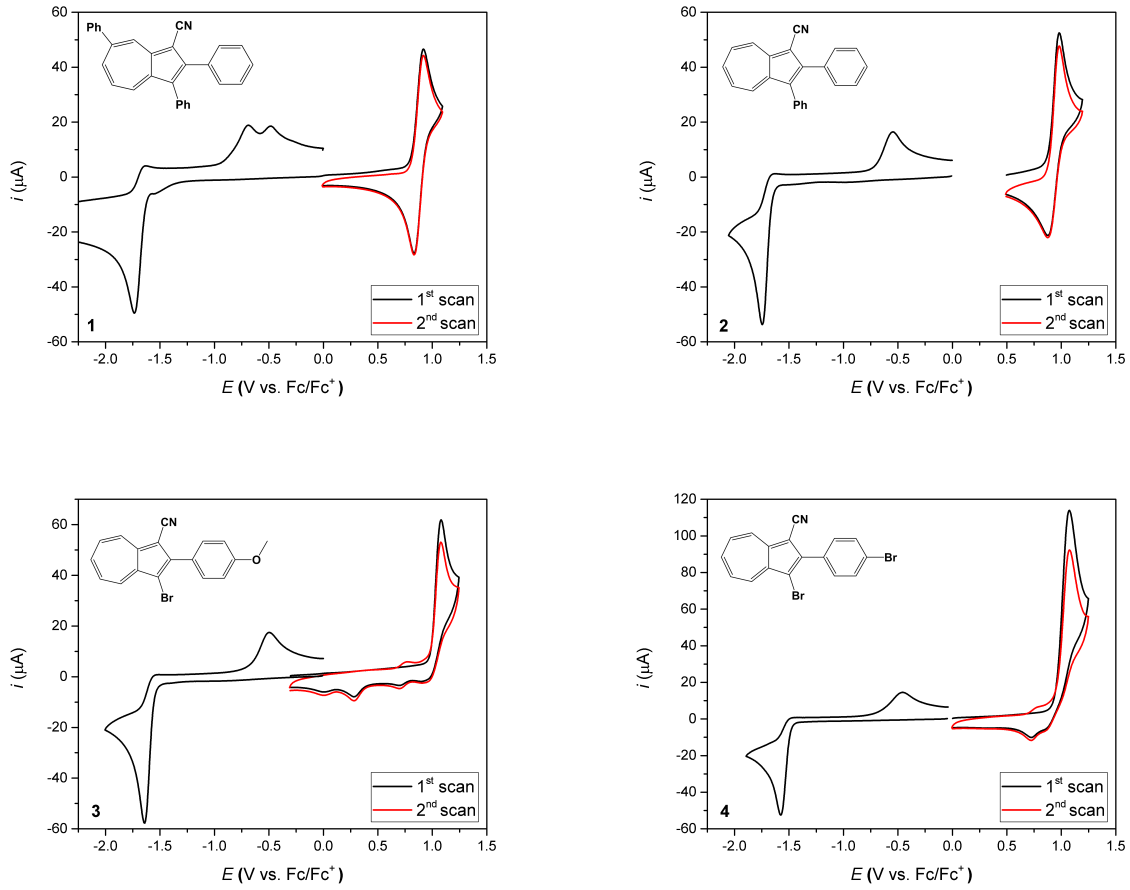
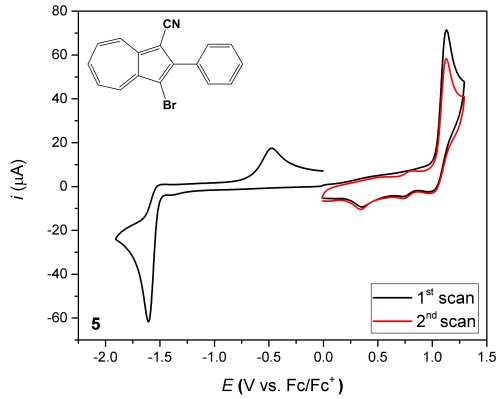
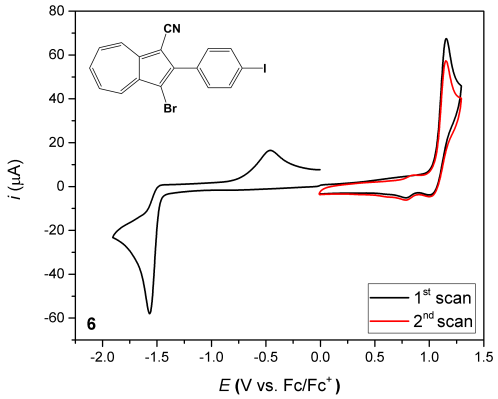
1.1 Slow Scans

Cyclic voltammograms of compounds **1-10** recorded at 0.5 Vs^{-1} using a glassy carbon working electrode ($d = 3$ mm) in CH_2Cl_2 (0.1 M Bu_4NPF_6). The substrate concentrations were 1 mM.




CN
Br
5
1st scan
2nd scan
i (μA)
E (V vs. Fc/Fc+)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I
Br
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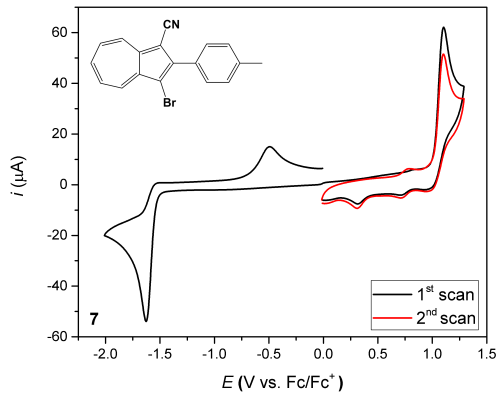
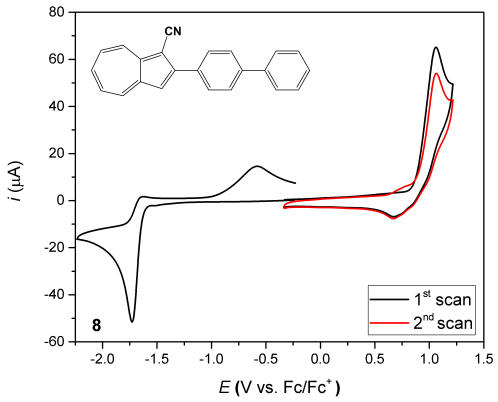
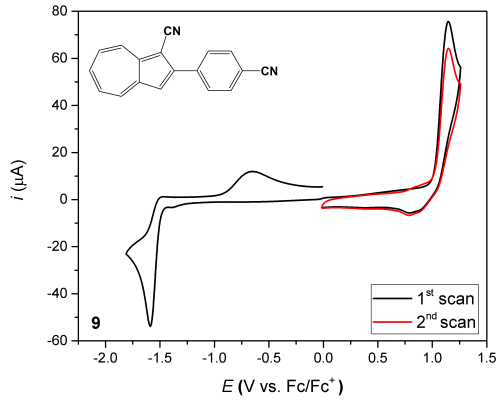
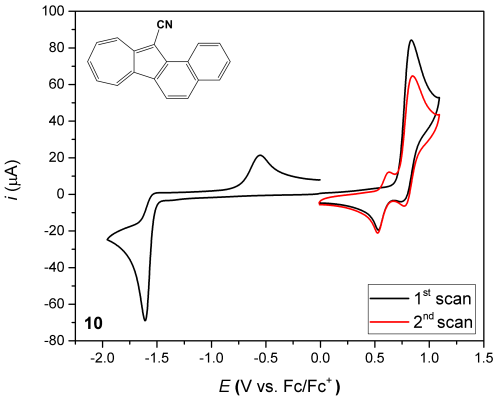
1st scan
2nd scan
i (μA)
E (V vs. Fc/Fc+)


CN
Br
7
1st scan
2nd scan
i (μA)
E (V vs. Fc/Fc+)

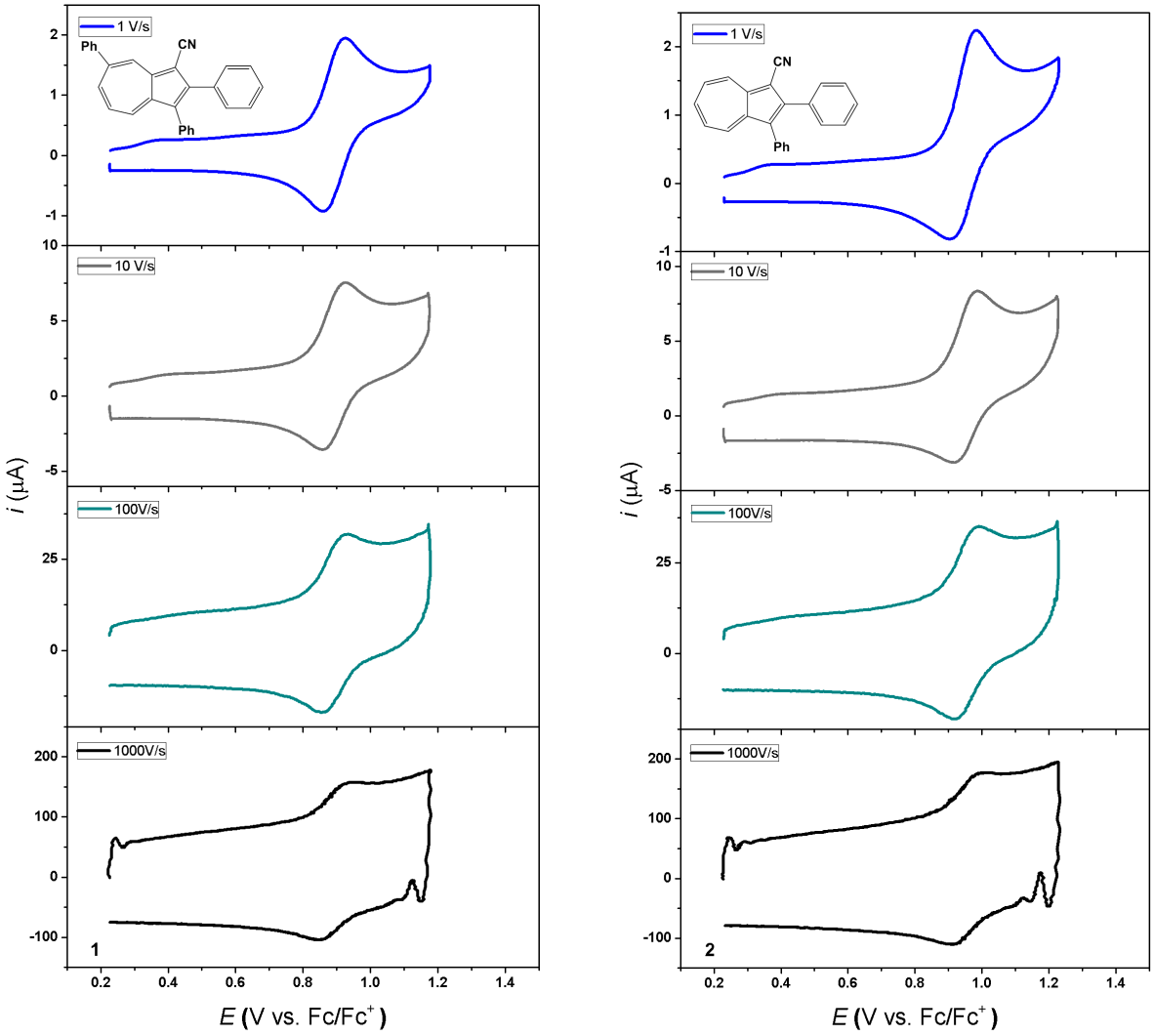

CN
8
1st scan
2nd scan
i (μA)
E (V vs. Fc/Fc+)

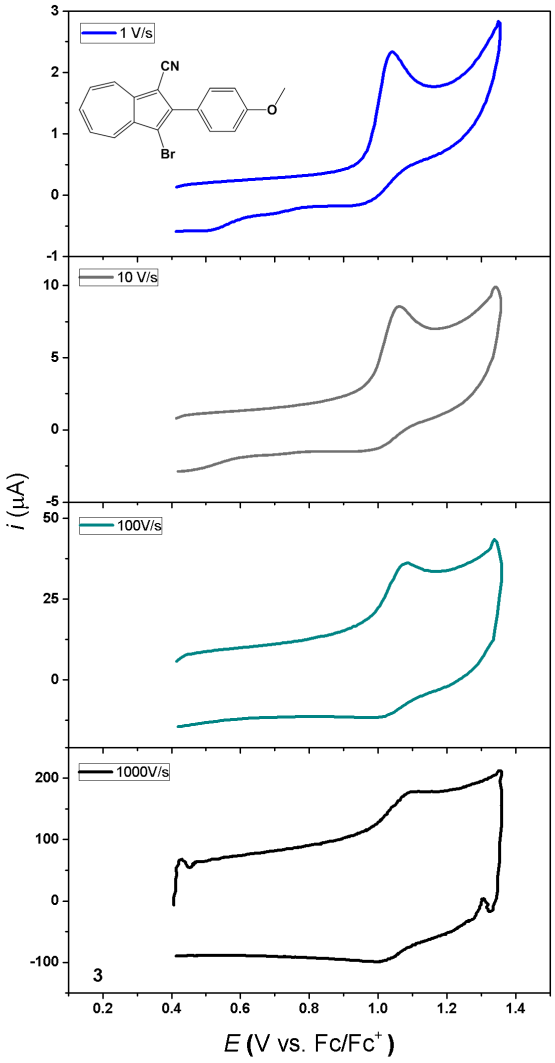

CN
CN
9
1st scan
2nd scan
i (μA)
E (V vs. Fc/Fc+)


CN
10
1st scan
2nd scan
i (μA)
E (V vs. Fc/Fc+)

1.2 Fast Scans

Cyclic voltammograms of compounds **1-10** recorded at 1, 10, 100 and 1000 Vs^{-1} using a platinum working electrode (d = 0.6 mm) in 1:1 CH_2Cl_2:CH_3CN (0.2 M Bu_4NPF_6). The substrate concentrations were 0.5 mM.

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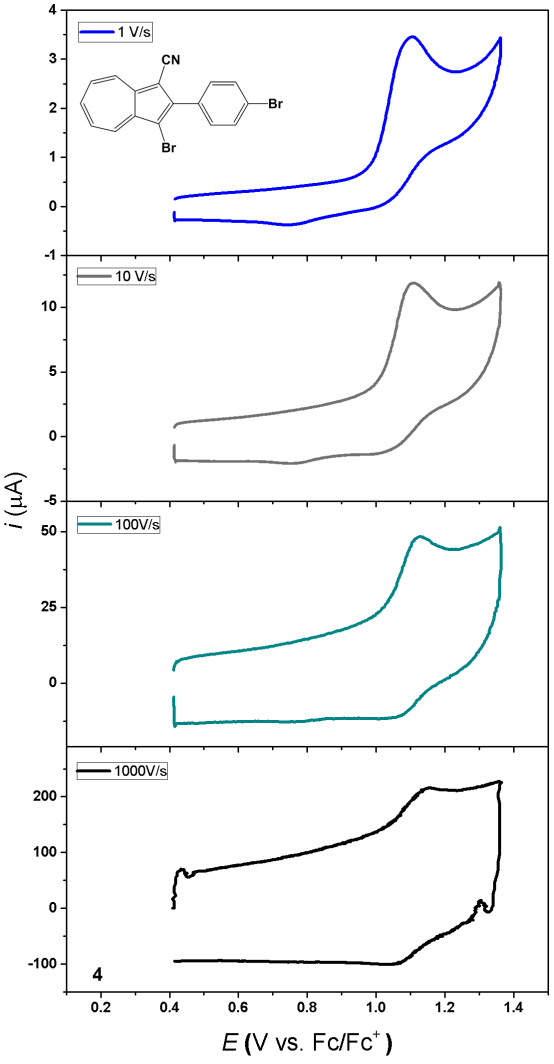
CN
O
Br
10 V/s
100V/s
1000V/s
3
i (μA)
E (V vs. Fc/Fc+)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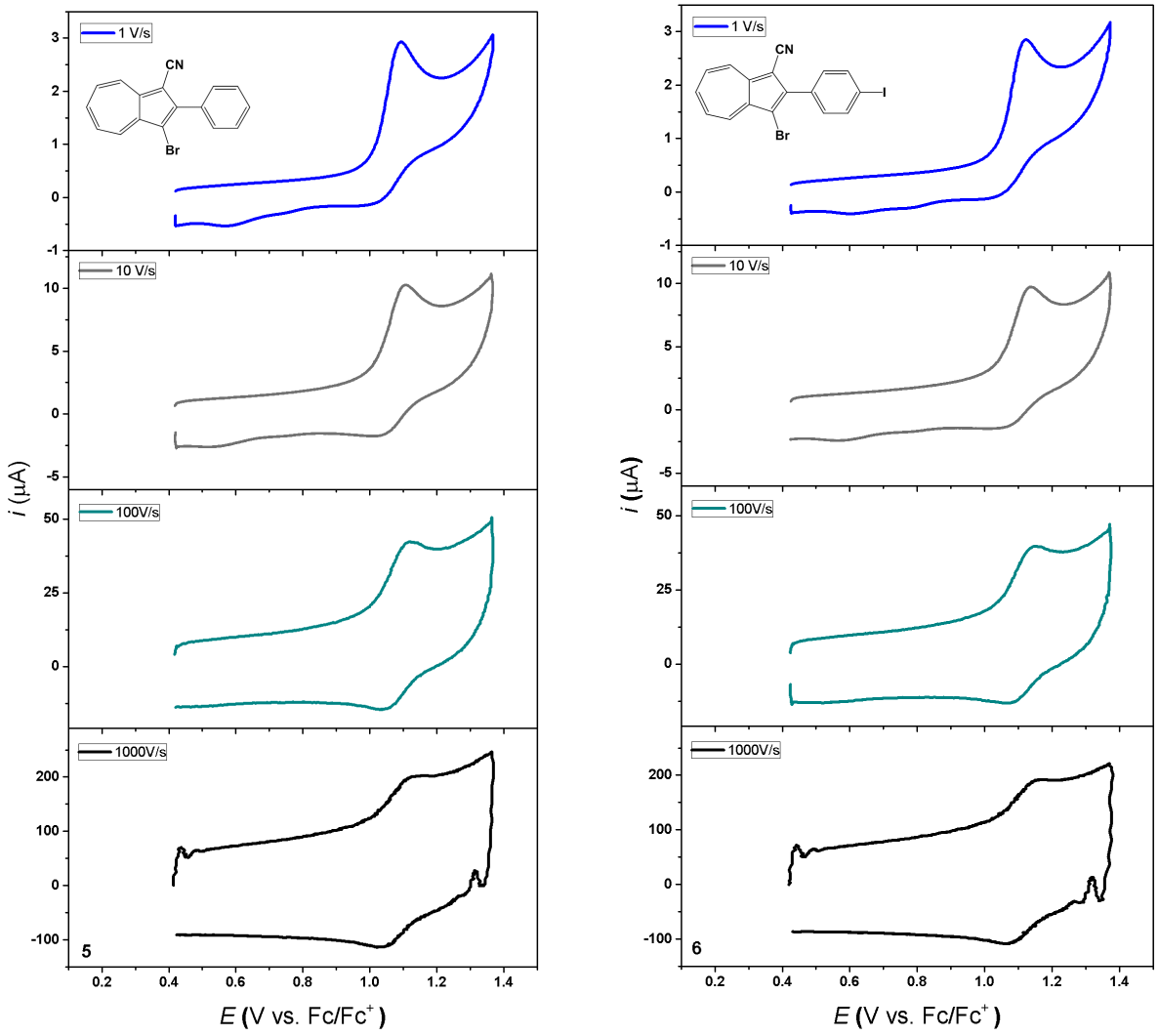
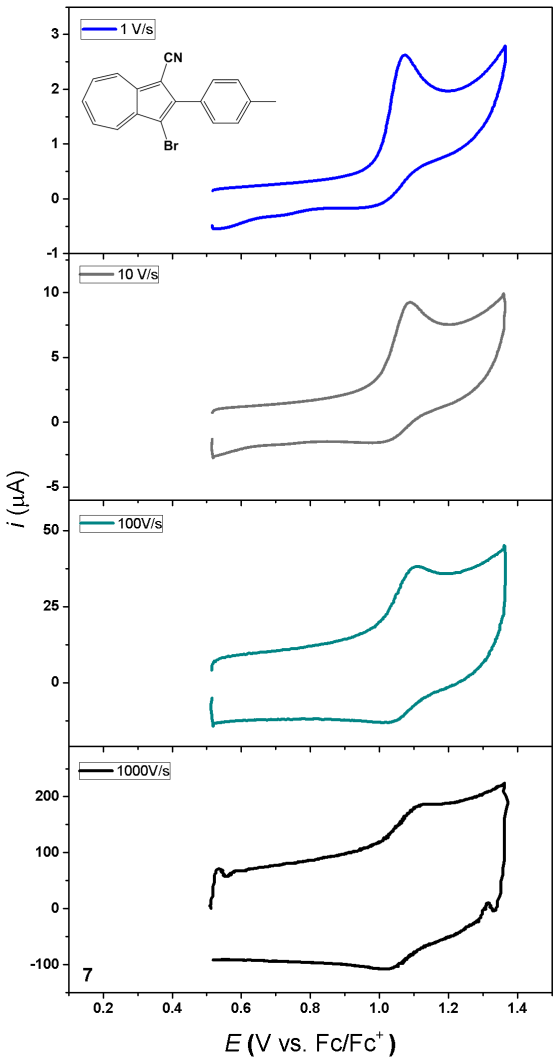
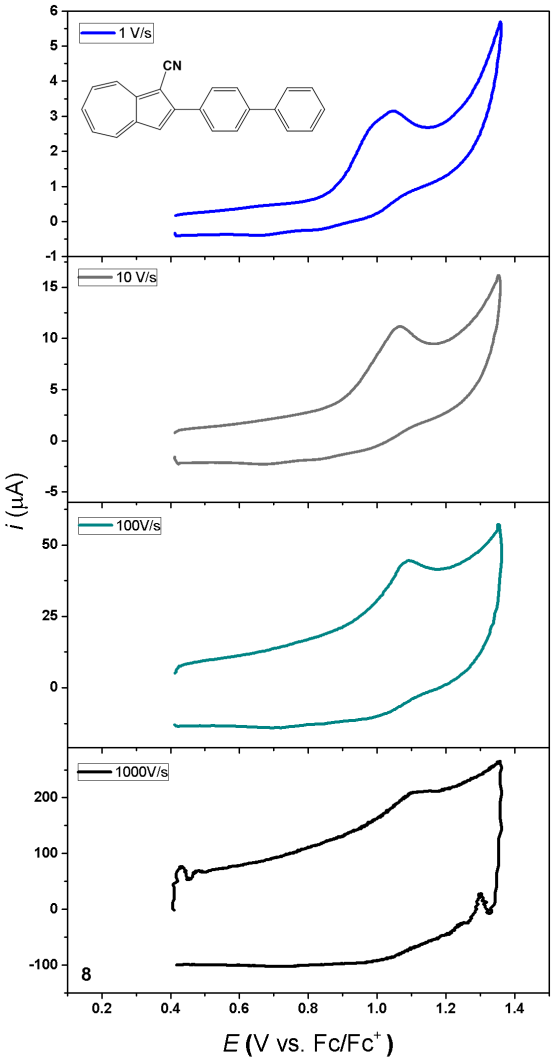
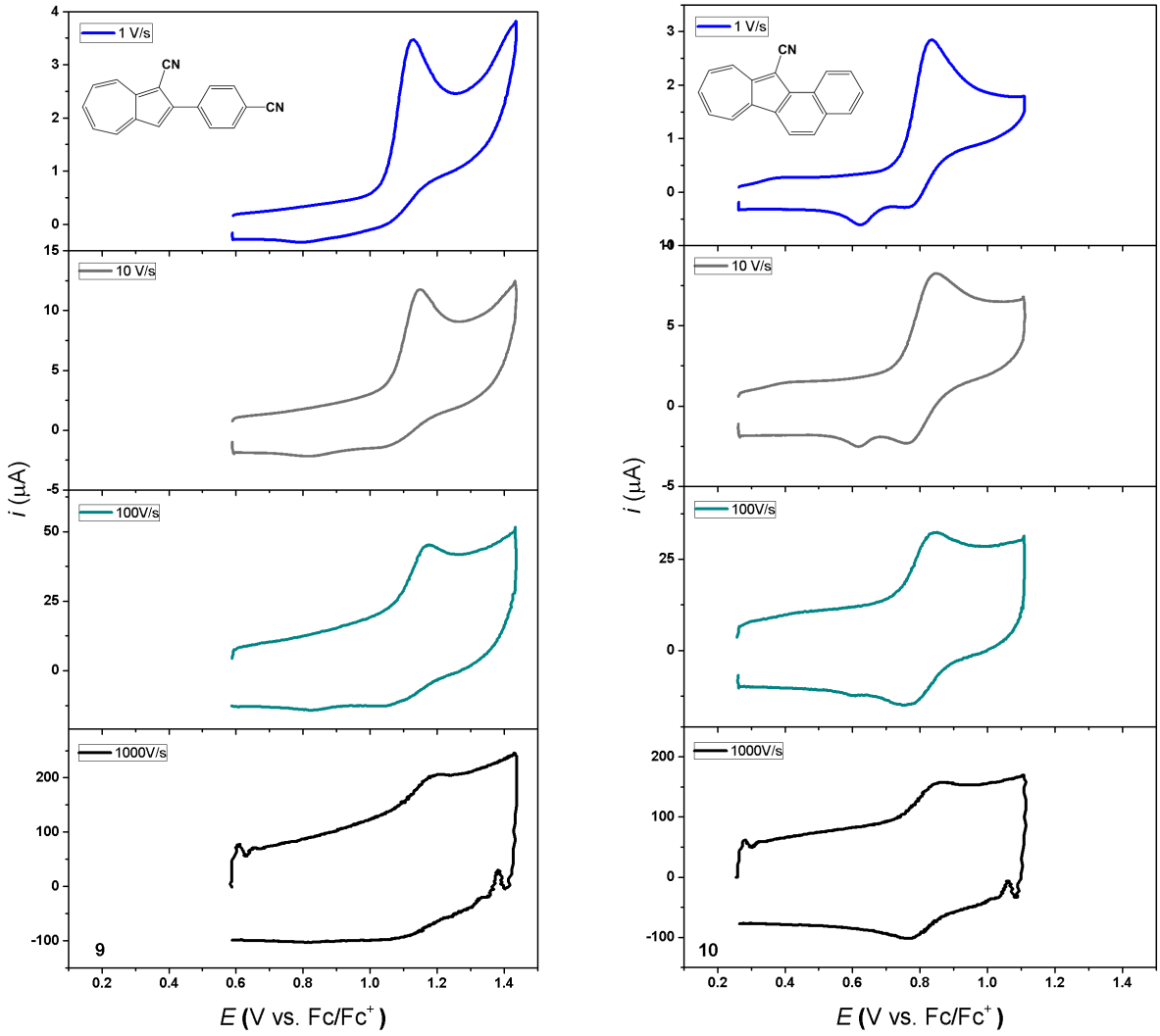
Br
Br
10 V/s
100V/s
1000V/s
4
i (μA)
E (V vs. Fc/Fc+)


1 V/s
CN
Br
10 V/s
100V/s
1000V/s
5
6
i (μA)
E (V vs. Fc/Fc+)


1 V/s
CN
Br
10 V/s
100V/s
1000V/s
7
i (μA)
E (V vs. Fc/Fc+)


1 V/s
CN
10 V/s
100V/s
1000V/s
8
i (μA)
E (V vs. Fc/Fc+)


1 V/s
10 V/s
100V/s
1000V/s
CN
CN
9
10
i (μA)
E (V vs. Fc/Fc+)

2 Absolute Standard Redox Potentials

The absolute standard redox potentials of the investigated azulene derivatives are presented in the following. The calculations include different basis-sets and functionals in vacuum, dichloromethane, and a 1:1 dichloromethane:acetonitrile mixture. It should be noted that all data not denoted SMD are calculated with the IEF-PCM solvation model.

Table S1: The calculated absolute standard redox potentials in vacuum using the M06-2X functional in conjunction with different basis sets.

Vacuum - M06-2X (Units: Volt [V])

	Def2-TZVP		**DZ:AVTZ-PP**[a]		**TZ:AVTZ-PP**[b]	
No.	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}
1	7.08	1.77	7.09	1.76	7.12	1.81
2	7.30	1.68	7.30	1.67	7.34	1.72
3	7.48	1.77	7.45	1.77	7.50	1.81
4	7.71	1.98	7.67	1.96	7.71	2.01
5	7.62	1.83	7.59	1.82	7.63	1.86
6	7.70	1.98	7.66	1.97	7.70	2.02
7	7.56	1.80	7.54	1.76	7.57	1.83
8	7.52	1.70	7.53	1.70	7.58	1.73
9	7.94	2.04	7.92	2.03	7.97	2.07
10	7.18	1.79	7.16	1.78	7.21	1.83

[a] 6-31+G(d):aug-cc-pVTZ-PP, [b] 6-311+G(d):aug-cc-pVTZ-PP

Table S2: The calculated absolute standard redox potentials in vacuum using the CAM-B3LYP functional in conjunction with different basis sets.

Vacuum - CAM-B3LYP (Units: Volt [V])

	Def2-TZVP		**DZ:AVTZ-PP**[a]		**TZ:AVTZ-PP**[b]		**TZ:AVTZ-PP**[b] **(GD3**[c]**)**	
No.	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}
1	6.92	1.73	6.90	1.72	6.95	1.76	6.94	1.76
2	7.15	1.66	7.12	1.65	7.17	1.69	7.16	1.69
3	7.32	1.76	7.28	1.75	7.33	1.79	7.33	1.79
4	7.53	1.96	7.48	1.94	7.53	1.97	7.53	1.98
5	7.44	1.82	7.39	1.81	7.44	1.84	7.44	1.84
6	7.51	1.96	7.47	1.96	7.52	1.98	7.52	1.99
7	7.38	1.78	7.33	1.77	7.38	1.80	7.38	1.80
8	7.38	1.69	7.35	1.68	7.41	1.71	7.41	1.71
9	7.75	2.04	7.71	2.03	7.76	2.06	7.77	2.06
10	7.00	1.78	6.96	1.76	7.02	1.81	7.02	1.81

[a] 6-31+G(d):aug-cc-pVTZ-PP, [b] 6-311+G(d):aug-cc-pVTZ-PP, [c] Grimme's dispersion correction (GD3)

Table S3: The calculated absolute standard redox potentials in dichloromethane using the M06-2X functional in conjunction with different basis sets and solvation models.

Dichloromethane - M06-2X (Units: Volt [V])

	Def2-TZVP		**DZ:AVTZ-PP**[a]		**TZ:AVTZ-PP**[b]		**TZ:AVTZ-PP**[b] **(SMD)**	
No.	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}
1	5.90	3.13	5.90	3.12	5.94	3.18	5.71	3.10
2	5.98	3.07	5.99	3.06	6.04	3.12	5.80	3.07
3	6.11	3.18	6.09	3.16	6.15	3.21	5.98	3.14
4	6.18	3.26	6.15	3.24	6.20	3.30	6.04	3.22
5	6.14	3.21	6.10	3.20	6.16	3.26	6.00	3.18
6	6.17	3.26	6.15	3.24	6.19	3.30	6.04	3.21
7	-	3.20	6.10	3.20	6.14	3.31	5.99	3.17
8	6.16	3.10	6.16	3.08	6.22	3.13	5.95	3.06
9	6.26	3.24	6.25	3.23	6.30	3.30	6.02	3.21
10	5.78	3.18	5.77	3.17	5.82	3.24	5.60	3.15

[a] 6-31+G(d):aug-cc-pVTZ-PP, [b] 6-311+G(d):aug-cc-pVTZ-PP

Table S4: The calculated absolute standard redox potentials in dichloromethane using the CAM-B3LYP functional in conjunction with different basis sets and solvation models.

Dichloromethane - CAM-B3LYP (Units: Volt [V])

	Def2-TZVP		**DZ:AVTZ-PP**[a]		**TZ:AVTZ-PP**[b]		**TZ:AVTZ-PP**[b] **(GD3**[c]**)**		**TZ:AVTZ-PP**[b] **(SMD)**	
No.	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}
1	5.69	3.06	5.68	3.05	5.74	3.10	5.73	3.11	5.51	3.01
2	5.78	3.04	5.76	3.02	5.82	3.08	5.81	3.08	5.58	3.00
3	5.90	3.15	5.86	3.13	5.91	3.18	5.92	3.18	5.75	3.10
4	5.97	3.22	5.93	3.20	5.99	3.25	5.98	3.25	5.81	3.15
5	5.94	3.18	5.90	3.16	5.96	3.21	5.96	3.21	5.78	3.12
6	5.96	3.22	5.93	3.20	5.99	3.25	5.98	3.26	5.80	3.14
7	5.91	3.16	5.87	3.13	5.93	3.19	5.93	3.19	5.77	3.09
8	5.94	3.05	5.91	3.03	5.97	3.09	5.97	3.10	5.69	3.01
9	6.04	3.22	5.99	3.19	6.07	3.25	6.06	3.24	5.78	3.14
10	5.57	3.14	5.54	3.12	5.61	3.19	5.61	3.19	5.37	3.09

[a] 6-31+G(d):aug-cc-pVTZ-PP, [b] 6-311+G(d):aug-cc-pVTZ-PP, [c] Grimme's dispersion correction (GD3)

Table S5: The calculated absolute standard redox potentials in a 1:1 dichloromethane:acetonitrile mixture using the M06-2X functional in conjunction with different basis sets and solvation models.

Mixture - M06-2X (Units: Volt [V])

	Def2-TZVP		**DZ:AVTZ-PP**[a]		**TZ:AVTZ-PP**[b]		**TZ:AVTZ-PP**[b] **(SMD)**	
No.	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}
1	5.80	3.25	5.81	3.25	5.85	3.30	5.60	3.22
2	5.88	3.19	5.88	3.20	5.94	3.25	5.68	3.20
3	6.00	3.30	5.99	3.28	6.03	3.35	5.85	3.26
4	6.06	3.36	6.03	3.35	6.08	3.41	5.89	3.33
5	6.03	3.33	6.00	3.32	6.06	3.38	5.87	3.31
6	6.05	3.36	6.03	3.35	6.07	3.41	5.90	3.32
7	6.03	3.30	6.00	3.29	6.03	3.36	5.87	3.28
8	6.04	3.22	6.04	3.20	6.10	3.25	5.81	3.19
9	6.12	3.33	6.11	3.32	6.16	3.40	5.86	3.31
10	5.68	3.29	5.67	3.28	5.73	3.36	5.49	3.27

[a] 6-31+G(d):aug-cc-pVTZ-PP, [b] 6-311+G(d):aug-cc-pVTZ-PP

Table S6: The calculated absolute standard redox potentials in a 1:1 dichloromethane:acetonitrile mixture using the CAM-B3LYP functional in conjunction with different basis sets and solvation models.

Mixture - CAM-B3LYP (Units: Volt [V])

	Def2-TZVP		**DZ:AVTZ-PP**[a]		**TZ:AVTZ-PP**[b]		**TZ:AVTZ-PP**[b] **(GD3**[c]**)**		**TZ:AVTZ-PP**[b] **(SMD)**	
No.	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}	E°_{ox}	E°_{red}
1	5.59	3.18	5.58	3.17	5.64	3.22	5.63	3.22	5.40	3.13
2	5.67	3.15	5.65	3.14	5.71	3.19	5.71	3.20	5.45	3.11
3	5.78	3.26	5.75	3.25	5.80	3.30	5.81	3.30	5.61	3.21
4	5.84	3.33	5.81	3.31	5.86	3.36	5.86	3.36	5.67	3.24
5	5.82	3.29	5.78	3.27	5.84	3.32	5.84	3.33	5.64	3.23
6	5.84	3.32	5.80	3.31	5.86	3.36	5.86	3.36	5.65	3.24
7	5.80	3.27	5.77	3.24	5.81	3.31	5.82	3.31	5.60	3.22
8	5.82	3.17	5.79	3.15	5.85	3.21	5.85	3.21	5.56	3.13
9	5.89	3.31	5.86	3.28	5.93	3.34	5.92	3.34	5.62	3.23
10	5.47	3.26	5.44	3.24	5.51	3.30	5.51	3.30	5.26	3.21

[a] 6-31+G(d):aug-cc-pVTZ-PP, [b] 6-311+G(d):aug-cc-pVTZ-PP, [c] Grimme's dispersion correction (GD3)

3 Reference Potentials

The Gibbs free energies and absolute redox potentials of the ferrocene/ferrocenium (Fc/Fc^+) redox couple in dichloromethane and a 1:1 dichloromethane:acetonitrile mixture are presented at the M06-2X/6-311+G(d):aug-cc-pVTZ-PP and CAM-B3LYP/6-311+G(d):aug-cc-pVTZ-PP level of theory using the IEF-PCM solvation model.

Table S7: The Gibbs free energies and absolute redox potential of the Fc/Fc^+ redox couple in dichloromethane and a 1:1 dichloromethane:acetonitrile mixture using the 6-311+G(d):aug-cc-pVTZ-PP basis set and the IEF-PCM solvation model.

Dichloromethane

	M06-2X			**CAM-B3LYP**		
	Fc	**Fc^+**	**Fc/Fc^+**	**Fc**	**Fc^+**	**Fc/Fc^+**
ΔG° [eV]	-13897.4	-13892.6		-13895.5	-13889.9	
E°_{abs} [V]			4.78			5.53

Mixture

ΔG° [eV]	-13897.4	-13892.1		-13895.5	-13890.0	
E°_{abs} [V]			5.23			5.40

4 LCP Regression Parameters

The linear least squares regressions through E°_{red} and E°_{ox} separately are presented in the following. The regressions are performed using the statistical function module within the SciPy library designed for scientific computing in Python.

Table S8: The LCP regression parameters and mean absolute error (MAE) between the experimental and calculated reduction potentials in dichloromethane.

	Def2-TZVP	**DZ:AVTZ-PP**[a]	**TZ:AVTZ-PP**[b]	**TZ:AVTZ-PP**[b] **(SMD)**
M06-2X				
Slope	0.966	0.966	0.829	1.070
y-intercept [V]	-4.677	-4.665	-4.286	-4.975
x-intercept [V]	4.843	4.830	5.168	4.649
r^2	0.9047	0.8903	0.8092	0.8772
MAE	0.0280	0.0273	0.1112	0.0580
CAM-B3LYP				
Slope	0.903	0.934	0.972	1.119
y-intercept [V]	-4.443	-4.518	-4.694	-5.055
x-intercept [V]	4.919	4.840	4.828	4.518
r^2	0.9351	0.9283	0.9566	0.9515
MAE	0.0663	0.0467	0.0216	0.0983

[a] 6-31+G(d):aug-cc-pVTZ-PP, [b] 6-311+G(d):aug-cc-pVTZ-PP

Table S9: The LCP regression parameters and mean absolute error (MAE) between the experimental and calculated oxidation potentials in a 1:1 dichloromethane:acetonitrile mixture.

	Def2-TZVP	DZ:AVTZ-PP[a]	TZ:AVTZ-PP[b]	TZ:AVTZ-PP[b] (SMD)
M06-2X				
Slope	0.783	0.814	0.823	0.742
y-intercept [V]	-3.642	-3.819	-3.912	-3.261
x-intercept [V]	4.653	4.691	4.753	4.394
r^2	0.9868	0.9712	0.9632	0.9406
MAE	0.7918	0.6714	0.6426	0.9243
CAM-B3LYP				
Slope	0.813	0.837	0.855	0.784
y-intercept [V]	-3.644	-3.758	-3.916	-3.316
x-intercept [V]	4.485	4.492	4.577	4.231
r^2	0.9909	0.9808	0.9820	0.9252
MAE	0.6576	0.5680	0.5047	0.7425

[a] 6-31+G(d):aug-cc-pVTZ-PP, [b] 6-311+G(d):aug-cc-pVTZ-PP