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Electronic Supporting Information

Metal-free synthesis of quinoline-2,4-dicarboxylate derivatives using aryl amines and acetylenedicarboxylates through pseudo three-component reaction

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Figure: S1. ORTEP Diagram of compound 3k with 40% ellipsoid probabilit

Table S1. Crystal data and structure refinement for compound 3k

Entry	Identification code	Compound 3k
01	Empirical formula	C ₁₅ H ₁₅ NO ₄
02	Formula weight	273.1001
03	Temperature	296 (2)K
04	Wavelength	0.71073
05	Radiation type	MoK\a
06	Radiation source	'fine-focus sealed tube'
07	Crystal system	Monoclinic
08	Space group	P 21/n
09	Cell length	a=3.9964(3)b=38.647(3)c=8.7063(5)
10	Cell Angle	α 90(9)β 97.942(3)γ90
11	Cell Volume	1331.77(3)
12	Density	1.363
13	Completeness to theta	0.998-28.293
14	Absorption correction	multi-scan
15	Refinement method	Full
16	Index ranges	$-5 \le h \le 5, -55 \le k \le 55, -11 \le l \le 11$
17	Reflection number	3314
18	Theta range	2.108-28.293
19	Cell formula units Z	4
20	CCDC no	2053801

¹H NMR spectrum of compound: 3a







HRMS spectrum of compound: 3a



¹H NMR spectrum of compound: 3b



4.5

4.0

3.5

3.0

2.5

2.0

1.5

1.0

0.5

0.0

5.0 f1 (ppm)

5.5

7.5

7.0

6.5

6.0

8.0

10.0

9.5

9.0

8.5

¹³C NMR spectrum of compound: 3b





HRMS spectrum of compound: 3b



¹³C NMR spectrum of compound: 3c



HRMS spectrum of compound: 3c



¹H NMR spectrum of compound: 3d

10	91 91 88	36 36 34
4.4	5 5 5 5	
\mathbf{Y}		

ATK-SA-4Et-DMDE	66	63	63	29	26	73	72	71	70	
	<u>ي</u>	8	σ.	ő	% /	2.	7	~	7.	





¹³C NMR spectrum of compound: 3d





HRMS spectrum of compound: 3d



ATK-SA-4Me-DMDE	3.62 3.58 3.23 3.21 3.21 7.66 7.66 7.64 7.64	1.04	2.59





¹³C NMR spectrum of compound: 3e





HRMS spectrum of compound: 3e

¹H NMR spectrum of compound: 3f







¹³C NMR spectrum of compound: 3f





HRMS spectrum of compound: 3f











HRMS spectrum of compound: 3g



¹H NMR spectrum of compound: 3h



6.87 6.86 6.63 6.42 6.41









S25

HRMS spectrum of compound: 3h



¹H NMR spectrum of compound: 3h'







HRMS spectrum of compound: 3h'







S31



HRMS spectrum of compound: 3i



¹³C NMR spectrum of compound: 3j

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	ATK-SA-35Me-DMDE	— 170.00 — 165.49	\sim 149.46 - 146.69 \sim 139.98 \sim 133.50 \sim 128.97 \sim 122.55 \sim 119.24	77.55 77.23 76.91	53.47 53.32	21.71 21.02
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HRMS spectrum of compound: 3j



ATK-SA-2-4-ME-DMDE-1H 1H	8.60 8.40	7.53	4.07	2.87	2.55
	1 1		\searrow		




¹³C NMR spectrum of compound: 3k





HRMS spectrum of compound: 3k



¹H NMR spectrum of compound: 31



¹³C NMR spectrum of compound: 31





HRMS spectrum of compound: 31

Counts vs. Mass-to-Charge (m/z)









¹³C NMR spectrum of compound: 3m



HRMS spectrum of compound: 3m

Sample Name	ATK-SA-5-IND-DMDE-A	Position	P1-A6	Instrument Name	Instrument 1	User Name	
Inj Vol Data Filename	20 ATK-SA-5-IND-DMDE-A.	InjPosition ACQ Method	ESI ALS 100-1000.m	SampleType Comment	Sample	IRM Calibration Status Acquired Time	Success 2/3/2021 11:43:18 AM



¹H NMR spectrum of compound: 3m'



¹³C NMR spectrum of compound: 3m'



HRMS spectrum of compound: 3m'

Sample Name	ATK-SA-5IND-DMDE-B3	Position	P1-A3	Instrument Name	Instrument 1	User Name	
Inj Vol Data Filename	20 ATK-SA-5IND-DMDE-B3.	InjPosition ACQ Method	ESI ALS 100-1000.m	SampleType Comment	Sample	IRM Calibration Status Acquired Time	Success 2/3/2021 11:11:55 AM













HRMS spectrum of compound: 3n

Sample Name	ATK-SA-SES-DMDE-A	Position	P1-A5	Instrument Name	Instrument 1	User Name	
Inj Vol Data Filename	20 ATK-SA-SES-DMDE-A.d	InjPosition ACQ Method	ESI ALS 100-1000.m	SampleType Comment	Sample	IRM Calibration Status Acquired Time	Success 2/3/2021 11:32:03 AM



¹H NMR spectrum of compound: 30



¹³C NMR spectrum of compound: 30



HRMS spectrum of compound: 30



¹H NMR spectrum of compound: 3p







¹³C NMR spectrum of compound: 3p







HRMS spectrum of compound: 3p



¹H NMR spectrum of compound: 3q





¹³C NMR spectrum of compound: 3q

ATK-SA-2CI-DMDE-13C	165.84 165.30	148.26 145.18 136.96 135.74 130.95 130.95 123.20 124.80 123.23	77.48 77.23 76.98	53.56 53.22
	\searrow			\checkmark





HRMS spectrum of compound: 3q





¹³C NMR spectrum of compound: 3r



HRMS spectrum of compound: 3r

Sample Name Inj Vol	SA-4SME-DMDE 20	Position InjPosition	P1-A5	Instrument Name SampleType	Instrument 1 Sample	User Name IRM Calibration Status	Success
Data Filename	SA-4SME-DMDE.d	ACQ Method	ESI ALS 100-550.m	Comment		Acquired Time	3/31/2021 12:12:22 PM
x10 6 + 5	Scan (0.395 mir	1) SA-4SME-E	DMDE.d				
2.4-			292	2.06555			
2.3-							
2.2-							
2.1-		CO ₂ N	Ле				
2-	MeS						
1.9-							
1.8-		N N	CO ₂ Me				
1.7-		3r	-				
1.6-							
1.5-							
1.4-							
1.3-							
1.2-							
1.1-							
1-							
0.9-							
0.8-							
0.7-							
0.6-							
0.5-							
0.4-							
0.3-							
0.2-							
0.1-							
o—							202 0 202

¹H NMR spectrum of compound: 4a

ATK-SA-4OMe-DEDE-1H	8.69 8.28 8.25 8.25 8.23	- 7.48 - 7.46	4.55 4.55 4.50 4.00	1.51 - 1.50 - 1.49
	$\overline{)}$	\searrow		







S64

HRMS spectrum of compound: 4a



¹H NMR spectrum of compound: 4b





¹³C NMR spectrum of compound: 4b

HRMS spectrum of compound: 4b



¹H NMR spectrum of compound: 4c

8.559 8.559 8.27 8.255 8.255 8.255 7.66 8.255 7.66	4.55 4.55 4.55 4.55 4.55 4.51 4.51	-2.61	$1.52 \\ 1.51 \\ 1.51 \\ 1.50 \\ 1.49 \\ 1.48 \\ $
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¹³C NMR spectrum of compound: 4c



HRMS spectrum of compound: 4c



¹H NMR spectrum of compound: 4d




¹³C NMR spectrum of compound: 5d



HRMS spectrum of compound: 4d









S76

HRMS spectrum of compound: 4e



¹H NMR spectrum of compound: 4f

ATK-SA-24Me-DEDE-1H	3.56 3.38	7.52	4.55 4.54 4.51 4.51 4.50	2.87	2.55	1.51 1.50 1.50 1.48 1.48 1.47
	$\frac{1}{\sqrt{2}}$	Î		Ì	Ì	



 $0.95_{
m H}$ 1.00H 3.00₌ 3.00₌ 4.04∃ $1.03_{ op}$ 6.02∃ 4.5 1.5 0.0 Т 5.5 5.0 f1 (ppm) 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 4.0 3.5 3.0 2.5 2.0 1.0 0.5

¹³C NMR spectrum of compound: 4f



HRMS spectrum of compound: 4f



¹H NMR spectrum of compound: 4h

ATK-SA-SES-DEDE	22	61	19	48 52 52 52 58 48 52 51 52 52 58	51 51 44 46 47 46 47 50 51
00	80		9	4444444	ने ने ने ने ने ने
1	1	1	I	indu indu	







S82

HRMS spectrum of compound: 4h



¹H NMR spectrum of compound: 4i

5225228	5 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
4 4 4 4 4 4 4	4
The first state of the state of	





¹³C NMR spectrum of compound: 4i



HRMS spectrum of compound: 4i



¹H NMR spectrum of compound: 4j

SA-1NAP-DEDE 944	74 66 95 93 81 77 75 75	62 55 53 53	55 53 51
	8.8.8.8.7.7.7.7.7.7.7.7.7.7.7.7.7.7.7.7	4 4 4 4 4	ਜ ਜ ਜ ਜ
\checkmark			





¹³C NMR spectrum of compound: 4j $\overbrace{}^{166.28}$ $\overbrace{}^{165.42}$ 147.64
146.37
146.37
136.40
133.54
131.95
131.72
131.72
129.45
129.45 127.92 125.87 125.67 125.67 122.87 122.26 ATK-SA-1NAP-DEDE $\stackrel{62.42}{< 62.40}$ $\stackrel{14.60}{<}_{14.53}$ 77.55 × 76.91 h ÇO₂Et CO₂Et 'N 4j 100 f1 (ppm) 80 40 10 190 180 170 160 150 140 130 120 110 90 70 60 50 30 20

0

HRMS spectrum of compound: 4j



¹H NMR spectrum of compound: 4k

ATK-SA-4CI-DEDE へへの H のののへらの	7 M U A A H	800122
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8888877777	44444	





¹³C NMR spectrum of compound: 4k



HRMS spectrum of compound: 4k



¹H NMR spectrum of compound: 41

atk-sa-2CI-DEDE C C C C 8 8 8 6 6 6 6 9 9 9 9 9 9 9 9 9 9 9 9 9	5 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
лии 8 8 8 8 8 7 7 7 7 7 7 7 7 8 8 8 8 8 8	4 4 4 4 4 4 4	ㅋㅋㅋㅋㅋ





¹³C NMR spectrum of compound: 41



HRMS spectrum of compound: 41



¹H NMR spectrum of compound: 4m







¹³C spectrum of compound: 4m





HRMS spectrum of compound: 4m

¹H NMR spectrum of compound: A

SA-40Me-DMDE-IMD ഗ്ര റ	6.86 6.85 6.78 6.78	5.27	3.74 3.69 3.63
			\sim





¹³C NMR spectrum of compound: A



HRMS spectrum of compound: A





¹³C NMR spectrum of compound: 5a





HRMS spectrum of compound: 5a

¹H NMR spectrum of crude mixture of compound: 3a





HRMS spectrum of mixture